The Predictive Modelling of the Performance of a Crude Oil Fractionator in terms of Gas Chromatographic Characterization

by

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Submitted in partial fulfilment of the
requirements for the degree of Doctor
of Philosophy, in the Department of
Chemical Engineering, University of Natal
Durban

December 1973

All the work reported in this thesis, except where indicated to the contrary in the text, is my own original work, assistance being rendered by staff of the department in running the pilot fractionator.

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ACKNOWLEDGEMENTS

The work reported in this thesis was carried out in the Department of Chemical Engineering, University of Natal, Durban.

I would like to express my sincere gratitude towards dr. Robin Judd, my supervisor, for his continual interest and guidance during the course of the investigation and also towards prof. E.T. Woodburn and dr. P. King for the many fruitful discussions.

To mr. H. Kropholler my thanks for his assistance in the formulation of the basic problem and to mr. W. Pferdekämper of Siemens (Pty) Ltd. for his interest and help in the writing of the thesis.

I also want to acknowledge the work done by mr. D. Penn and his workshop staff in the construction of the pilot fractionator.

The CSIR and the University of Natal provided the financial backing which made this work possible.

Finally, I want to thank my wife, parents and parents-in-law for their interest and encouragement.

CONTENTS

ACKNOWLEDGEMENTS iii

SUMMARY vii

1. INTRODUCTION AND OBJECTIVES 1

2. BACKGROUND 5

2.1. Crude Oil and Fractionator Products 5

2.2. Fractionation 7

2.3. Fractionator Control 9

2.4. Present Analysis Procedures 10

2.4.1. True-Boiling-Point (TBP) Analysis 11

2.4.2. ASTM Distillation 13

2.4.3. Simulated Distillation 14

3. GAS-CHROMATOGRAPHIC PROCEDURES 15

3.1. General 15

3.1.1. Ideal Solution Theory 15

3.1.2. Non-ideal Solution Theory 25

3.1.3. Isothermal and Programmed Temperature Operation 29

3.2. Simulated Distillation 30

3.3. Further Development of Existing Procedures 34

4. GAS CHROMATOGRAPHIC BOILING POINT CHARACTERIZATION PROCEDURE 37
4.1. Data Handling 38
4.2. Vapour-Liquid Equilibrium Correlation 51
4.3. Generalized Chromatographic Identification Procedure 58
4.4. Fractionator Model 75
4.5. Application of GC Characterization Procedure 91

5. INDUSTRIAL DEBUTANIZER/GASOLINE SPLITTER TEST USING CHARACTERIZATION PROCEDURE 93

6. PILOT PLANT FRACTIONATOR STUDIES 104
6.1. Introduction 104
6.2. Basic Plant Hardware 104
6.3. Instrumentation 111
6.4. Computer System 115
6.5. Feedstock 117

7. PILOT FRACTIONATOR CHARACTERIZATION TESTS 120
7.1. General 120
7.2. Test Procedure 120
7.3. Results 122

7.3.1. Column efficiency 129

7.3.2. Vaporization efficiency 131

7.3.3. GC Characterization Procedure 131

7.3.4. Reflux ratio 133

7.3.5. Thermal conditions of feed and reflux 135

7.3.6. Column Pressure and Tray Differential Pressure 137

7.4. Conclusion 138

8. CONCLUSIONS AND RECOMMENDATION 139

8.1. General Conclusion 139

8.2. Recommendation for further work 140

9. APPENDIX 142

9.1. Derivation of equation 4.19. 142

9.2. Parameters for Correlations used in Distillation Calculations 143

9.2.1. Molecular weight - boiling point 144

9.2.2. Vapour and liquid heat content 144

9.3. Details of plant hardware 146

9.4. GC Analysis-series 149

9.5. Computer programs 171

NOMENCLATURE 172

REFERENCES 176

SUMMARY

The performance of a crude oil fractionator is governed by a large number of factors, but since the refining of oil is basically an economic process, the main operational objective can be readily defined: controlling the yields of products as a function of their relative economic importance, while maintaining product quality, in spite of composition changes, are in the feed and variations in product demands.

To take corrective action against the primary disturbance acting on a fractionator, namely composition variation in the feed, it is necessary to measure the change and to predict its influence on the system. Finding solutions for these two aspects: the measurement of the feed composition and the prediction of the steady-state response of the system to composition changes, the major objectives of this investigation.

In order to employ a standard gas chromatograph, while at the same time meeting the exacting requirements imposed by the industrial environment with respect to response time, reproducibility and ease of handling, it was necessary to adopt a new gas chromatographic approach. This approach is based on a study of the thermodynamic relationships of gas chromatography, which are briefly outlined in the thesis. Whereas existing techniques for handling wide boiling range petroleum fractions are based on a temperature dependent calibration of boiling point versus retention time, a more basic relationship could be developed which employs the systematic vapour pressure-retention time behaviour of the constituents of petroleum in a GC column with a non-polar stationary phase. This relationship is temperature independent and since temperature is the main factor affecting separation in a gas chromatographic column, it is also the main source of error in any analysis and the new procedure for characterizing the components in a mixture thus achieves a significant improvement in the reproducibility of high-speed chromatography.

The characterization procedure requires a vapour pressure-temperature correlation which will permit a substance to be identified from a set of vapour pressures (obtained from vapour pressure-retention time relationship)and a set of temperatures (measured directly in GC). A suitable correlation, using boiling point as identification parameter, was developed for this purpose.

The qualitative GC identification described above is supplemented by a quantitative peak evaluation procedure. A thorough study of existing mathematical overlapping peak resolution methods lead to the development of a new technique which meets the requirements imposed on an on-line real-time system.

The qualitative and quantitative characterization procedures outlined were individually tested, also on an industrial plant, and the results are reported in the thesis. In order to apply these methods for predicting the performance of a fractionator, the GC characterization procedure was used in conjunction with two well-known distillation calculation procedures (or models): the plate-to-plate Thiele-Geddes method with θ-convergence using equal-molal overflow; and the tridiagonal matrix method using enthalpy data for internal flow correction. Using the characterization technique, it was possible to compare these calculation procedures with each other and with the experimental results obtained from a pilot fractionator.

The overall procedure offers a unique feature: the accurate comparison of a method of analysis and a predictive model with actual plant performance. This

feature was used extensively to determine the significance of the various factors affecting fractionator performance and full details are reported in the thesis. One of the most important conclusions that could be drawn, is that the accuracy of the procedure is such that it provides a valuable insight into the separating efficiency of a fractionator. By adjusting the number of theoretical trays, a very good agreement with plant data could be achieved. A bypass model representing tray efficiency is also proposed and tested. The applicability of the procedure for predicting the performance of a fractionator is confirmed by the experimental results obtained from the semi-industrial pilot fractionator constructed for the investigation.

CHAPTER 1

1. INTRODUCTION AND OBJECTIVES

The introduction of computers into industrial plants, either at operating level for controlling the process or at management level for controlling business activities, has lead to a reappraisal of existing techniques, which has in itself produced noteworthy results. This is due to the fact that the installation of a computer is preceded by a detailed analysis of the system to be controlled. The knowledge about the system is expressed in the form of a mathematical model which represents the interrelations between the variables of the system. These variables have to be determined either by direct measurement or by estimation. Here again the computer not only opened new avenues but has necessitated a reassessment of existing methods.

The investigation reported here is concerned with the first stage in the development of a control strategy for a particular industrial process, that of distillation, and hence covers the phases of analysis of the process, evaluation of existing measuring techniques and the development of a more meaningful performance assessment procedure.

The separation of liquid mixtures by distillation is probably one of the most widely used chemical engineering processes, and vast experience, as well as a good understanding of the mechanisms involved, makes it possible to design and operate increasingly large plants. However, in collecting and organizing this existing knowledge into a process model, a basic problem is immediately encountered, namely that of determining the composition of material streams entering and leaving the fractionator. Composition is the most important variable, since the principal control objective is that of satisfying individual product specifications in spite of composition changes in the feed and variations in the product demand.

In the case of a binary mixture, the concentrations of the two components are determined unambiguously by a temperature and pressure measurement. Although this does not hold exactly for mixtures containing more than two components, temperature and pressure can still be used as an approximate measure of the concentrations of the components contained in the mixture. The composition as such cannot be calculated from a temperature and pressure measurement.

The composition of material streams to and from the fractionator can be described in terms of physical properties; the most generally used one being normal boiling point distribution. For design purposes, as well as for steady-state analysis, various equipments have been devised for determining the distribution of different boiling point fractions in the fractionator streams, the so-called true boiling point (TBP) curve. On-stream analyzers for determining individual points on these curves also exist. A detailed high-speed composition analysis can, however, not be obtained on this basis. One possible alternative method is afforded by the gas chromatograph which has found successful application as on-line composition analyzer for light hydrocarbons (up to C6) in a large number of fractionator applications. Being basically similar to fractional distillation, gas chromatography can also under certain circumstances provide a separation of components on the basis of their boiling points. The integral representation of the GC data then yields, in essence another version of the TBP curve. To facilitate the analysis of components covering a wide boiling range, a GC method must be employed in which the temperature is raised during the test. This is necessary to achieve a partial compensation of the exponential increase in retention time with carbon number. This method of boiling point characterization could be directly used for on-stream analysis, but since it is based on a temperature dependent calibration curve of retention time versus boiling point, good reproducibility can only be achieved at low rates of temperature rise and correspondingly long analysis times. This method of integration furthermore neglects the additional information afforded by the inherently discrete form of the GC.

This then is the status quo: the assessment of the performance of a wide boiling-range fractionator on an on-line, real time basis is not possible and our principal objective of composition measurement and control cannot be fulfilled.

This investigation is concerned with the analysis of this problem, the development of a characterization procedure and the testing of this proposed model on both industrial plants and a specially constructed semi-industrial pilot fractionator.

CHAPTER 2

2. BACKGROUND

The first major processing unit through which crude oil passes in a refinery is the crude tower, where it is fractionated into various cuts, which undergo further processing in other refining units. The performance of the crude fractionator is consequently of decisive importance for the efficiency of downstream operations. Tangible financial benefits can be derived from an increase in the throughput, controlling the yields of products as a function of their relative economic importance and maintaining product quality specifications within narrow limits. In view of the wide differences in crude oils and product requirements, many different processing schemes have to be used. A short preamble on the composition and properties of feedstocks and products will illustrate the complexity of crude oil fractionation.

2.1. Crude Oil and Fractionator Products

The most important compounds present in petroleum are the different series of hydrocarbons. The best known of these are: the paraffin series (typical formula C_nH_{2n+2}, also called alkanes) including isoparaffins, the naphthene series (typical formula C_nH_{2n}, also called cycloparaffins) and the aromatic series (typical formula C_nH_{2n-6}, also called benzenes). Unsaturates, or olefins, are not present in substantial quantities in petroleum and are therefore neglected. Since a detailed analysis of the compounds contained in an oil constitutes a formidable, if not impossible task, such methods are at present not of major engineering importance in the petrochemical industry. The properties of the finished product are, however, directly affected by the constituents and the development of composition analysis procedures will be accompanied by improved product quality estimation and testing techniques. In the gas chromatographic procedure developed later, the significance of the different hydrocarbon series will be discussed in more detail.

As crude oils vary in their properties, so do the products yielded by them. The following is a listing of the more important products of a main fractionator, given in terms of boiling range, for a typical crude (Nelson, 1958).

TABLE 1 CRUDE OIL PRODUCTS

PRODUCT	BP RANGE
RAW GASOLINE	40 - 220 °C
NAPHTHA	40 - 160 °C
RAW KEROSENE	220 - 280 °C
JET FUEL	50 - 300 °C
GAS OIL	280 - 400 °C
RESIDUAL FUEL OIL	> 400 °C

The performance of the product is the ultimate measure of the efficiency of the refining operation. Because of the difficulties encountered in controlling product characteristics, product specifications have been compiled, which detail product requirements. These are of no direct consequence to the present investigation, but it is important to note that wide ranges of physical properties (such as boiling range) can be tolerated, whereas a knowledge of the chemical composition (e.g. hydrocarbon series) might enable more direct product quality analysis and control procedures to be used (Walsh and Mortimer, 1971; Anderson, Sharkey and Walsh, 1972; De Bruine and Ellison, 1973; Petrović and Vitorović, 1973). Composition analysis methods can therefore be expected to gain in importance and will gradually replace the more empirical physical property tests (IP Mathematical Analysis Panel, 1972).

2.2. Fractionation

The pilot fractionator shown in Fig. 6.1. serves to illustrate the general arrangement of a typical petroleum fractionator. The preheated feed enters the fractionator in the lower half of the column. The lowest boiling product is withdrawn from the top as a vapour, and the heavier distilled products are withdrawn from the side and bottom of the column. At the sidestream withdrawal plates, the products contain some of the low-boiling overhead vapour passing that plate, and such products are usually stripped in auxiliary stripping columns. In the present work, only straight-run products will be considered.

When applying the Gibb's phase rule, relating the number of degrees of freedom (F) to the number of components (C) and of phases (P)

$$F = C - P + 2 \qquad 2.1.$$

to a two-phase binary mixture, two degrees of freedom remain. This implies that when the system is in equilibrium, the specification of temperature and pressure is sufficient to define completely the state of the system. It is common practice, therefore, to say that at constant pressure, temperature is a measure (unambiguous in the case of a binary mixture) for the composition of the mixture. The word "composition" in this sense actually refers to the relative amounts of the components in the mixture and does not imply an identification of the components in the mixture.

The accuracy in using temperature as a measure of concentration in a pressure-controlled multicomponent system depends on the type of mixture being fractionated. For the mixtures encountered in the present investigation the near-ideal behaviour of hydrocarbon components permits narrow boiling fractions to be treated as pseudo-components. Since their behaviour in a fractionator is governed by a systematic difference in volatility, temperature may be used for general composition control purposes. Changes in feed composition, however, can only be corrected in a feedback control system. This is where feedforward has a strong advantage, an advantage which can only be fully utilized if a fast composition analysis procedure is available.

2.3. Fractionator Control

In designing a fractionator control system, one is faced with a multivariable interacting situation, with the result that conventional control schemes usually fix one of the two major independent variables and adjust the other from a plant observation. The two independent variables normally employed are the reboil rate and the reflux ratio. Since the criterion for good distillation control is usually product purity, which is determined by inferential temperature measurement, it is not possible to maintain all streams exactly on specification at all times in a multicomponent mixture. Since the effects of a change in reflux tends to move down a column much slower than the effect of a change in reboil rises up the column, it is usual to use the latter for fast column control. These main control loops are augmented by mass balance control systems for maintaining flow rates and levels.

This short discussion of fractionator control serves to illustrate that there is substantial merit in investigating direct composition measurement by on-line analyzers. In conjunction with feedword control schemes, there is a definite incentive for testing the extent of interaction between variables when attempting quality control at more than one point in the column.

2.4. Present Analysis Procedures

The refining of oil is, basically, an economic process and the particular market requirements therefore have a significant influence on the operation of every plant. In order to exploit these possibilities in the operation of the fractionator, data is required on the properties of the feed stock, which will allow the economy of various cuts of the feed to be explored. Once these have been established, a plant operational strategy can be drawn up. During operation of the plant, checking of product properties is necessary to ensure that product specifications are met.

Of particular significance in the evaluation of feed stock or finished products, is the range of boiling point fractions contained in the mixture. Various techniques have been developed for deriving this information.

2.4.1. True-Boiling-Point (TBP) Analysis

The true-boiling-point distillation curve is obtained by means of any equipment accomplishing a good degree of fractionation and numerous designs of TBP equipment have been developed (Nelson, 1958). A typical TBP curve for a crude is shown in Fig. 2.1., with the approximate boiling ranges of products indicated.

A TBP still usually separates the isomers of a compound only with difficulty but distinguishes between groups of like compounds. The temperature measured at the top of the still is the dew point of the vapour mixture, but since the still gives sharp separation between groups of components, this temperature differs only slightly from the boiling point of a liquid of the same composition (Sawistowski, 1963).

Although the feed is a mixture of very many components, it is possible to divide it into a finite number of cuts and to ascribe average physical properties to each cut. This rather arbitrary procedure is facilitated, in cases where the TBP distillation is conducted at a variable

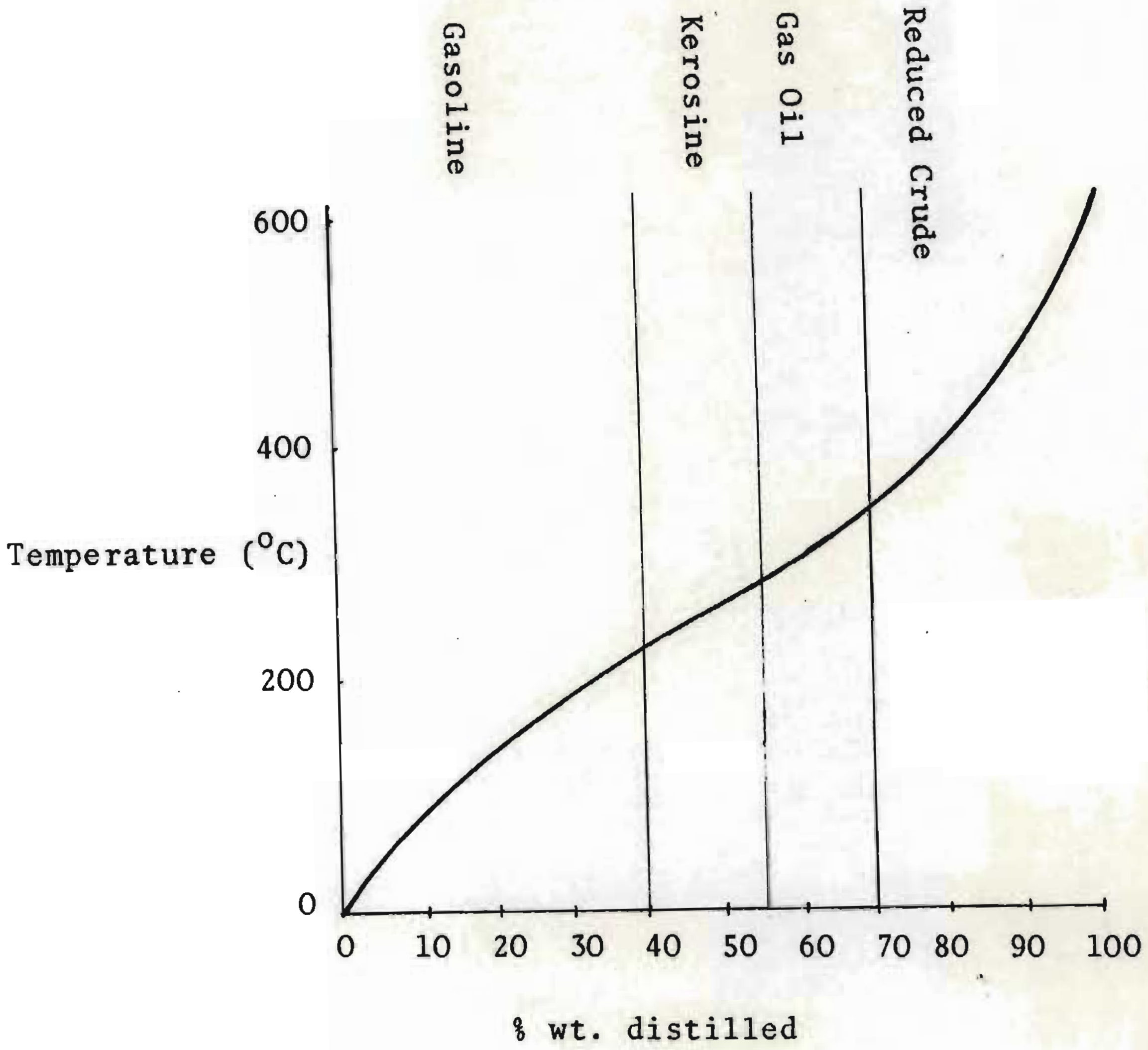


Fig. 2.1. Typical TBP curve for a wide boiling range oil

rate of distillation, i.e. when the rate is governed by the amount of material distilled, by observing the shape of the TBP curve. A plateau or nearly horizontal section indicates that a considerable volume of the sample must have distilled over in a small temperature interval, representing the presence of a large amount of a single compound, or a group of similar components, within this division. In this way the complex mixture is broken down into a limited number of cuts with assigned average physical properties for further calculations.

Because of the different designs of TBP apparatus, the time required for a complete analysis on a wide boiling range sample varies, but typical values range from 3 hours to 120 hours. This limits the application of this important procedure to design and performance calculations of an off-line nature.

2.4.2. ASTM Distillation

The distillation characteristics of a wide range of petroleum products can be determined by means of a faster procedure generally known as ASTM distillation. Whereas TBP analysis is based on fractionation of the sample, no deliberate attempt to fractionate is made in ASTM distillation. The latter is a batch vaporization procedure operating on a differential principle, since vapour is removed as it is formed and is not kept in physical contact with the remaining liquid. Consequently the hydrocarbons in the oil are not distilled one by one in the order of their boiling points, but as successively higher and higher boiling mixtures. The results obtained by ASTM distillation are to a large extent only of significance when compared with similar results from other ASTM distillations, although some correlations with TBP data have been developed (Nelson, 1958).

2.4.3. Simulated Distillation

A gas chromatographic technique of obtaining the equivalent of boiling-point data has been developed, and the name "simulated distillation" has been proposed (Green, Schmauch and Worman, 1964). Because of the wide experience that has been accumulated in the petrochemical industry in the use of distillation curves, gas chromatographs were initially employed to provide the same information as conventional TBP or ASTM methods. Gas chromatography however, offers the important advantages of high speed of analysis and high resolution. These characteristics are described in detail in paragraph 3.2.

CHAPTER 3

3. GAS - CHROMATOGRAPHIC PROCEDURES

3.1. General

Gas chromatography has become one of the most widely used tools in all branches of chemistry. Since the original paper by James and Martin in 1952, phenomenal growth has been reported in this field.

The theory of gas chromatography is exhaustively treated in a large number of standard books (Purnell, 1962; Harris and Habgood, 1966; Ettre and Zlatkis, 1967; ASTM Special Technical Publication, 1967; Schupp, 1968; Leathard and Shurlock, 1970; Littlewood, 1970) and only aspects which are of importance for this investigation will be discussed here.

When using a liquid stationary phase absorbed on an inert solid support in a gas chromatograph, the procedure is known as gas-liquid chromatography. Since gas-liquid chromatography is almost completely independent of other chromatographic techniques, no possibility of confusion exists and the method will be referred to as gas chromatography.

3.1.1. Ideal Solution Theory

As in the case of fractional distillation, gas chromatography is based on the distribution of a substance, the solute, between two phases. The one phase is a liquid stationary phase (the solvent) and the other a moving gas phase (the solute). To describe the behaviour of this system, comprising the vapour of the solute in equilibrium with the solution of the solute in the stationary liquid, it is necessary to consider a fundamental law of solution, Raoult's law.

This law states that for ideal solutions, the partial vapour pressure p_i of each component is proportional to its vapour pressure in the pure state p_i^o, with the proportionality constant x_i being the mole fraction:

$$p_i = x_i p_i^o \qquad 3.1.$$

For the present discussion it will be sufficient to assume that an ideal solution is defined as one obeying 3.1. In ideal gas chromatography, we consider the individual components of the solute independent of each other, and since the vapour pressure of the stationary liquid phase is very nearly zero, we have the special case of a binary mixture, comprising solute (subscript 1) and solvent (subscript 2) in which $p_2^o = 0$, and can write (refer to Fig. 3.1.)

$$p_1 = x_1 p_1^o \qquad 3.2.$$

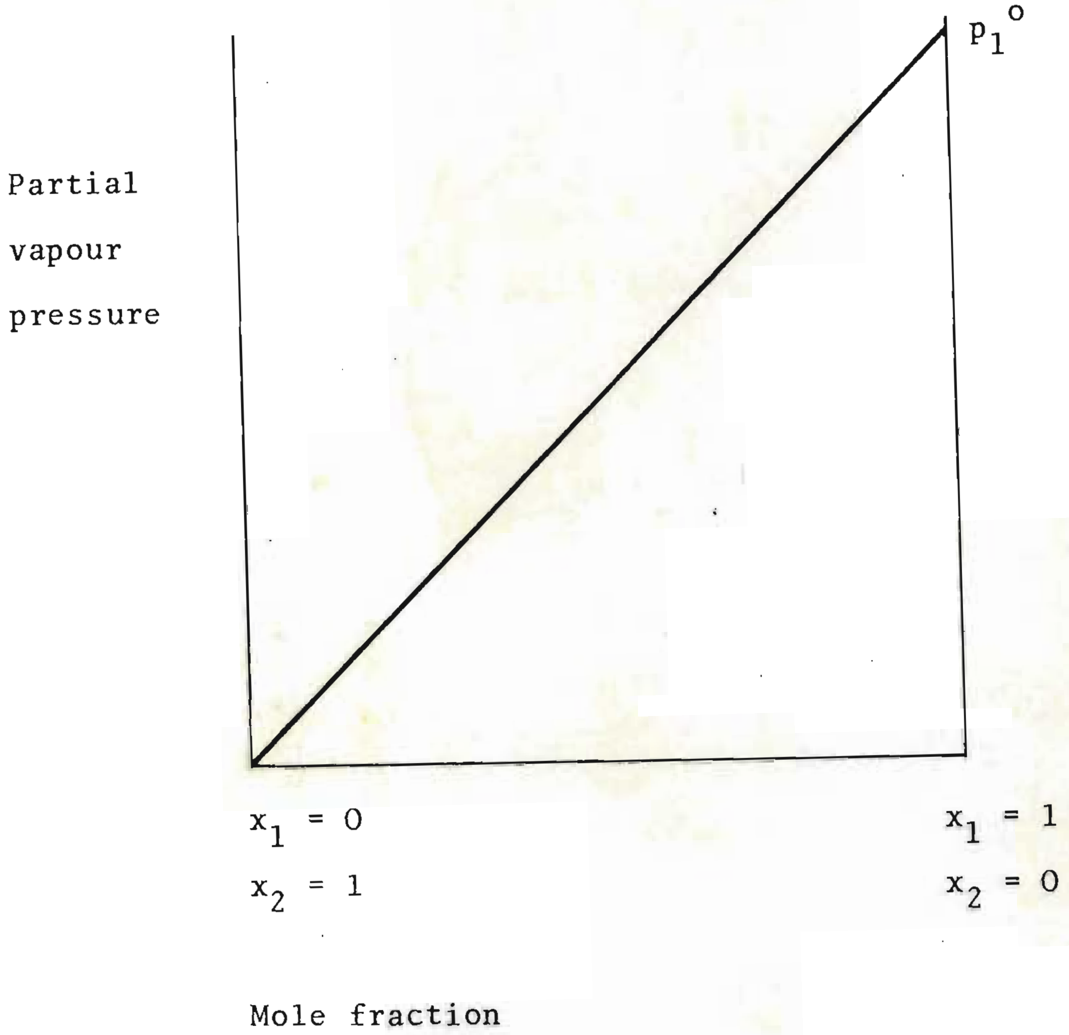


Fig. 3.1. Partial vapour pressure as a function of mole fraction for ideal gas chromatography (binary mixture with vapour pressure of stationary phase equal to zero)

Since the concentration of the solute is small for all general GC applications, only the lower end of the line plotted in Fig. 3.1. is relevant.

The movement of a solute band in a chromatographic column can be described quantitatively in the following simplified form (Marshall and Pigford, 1947; Mickley, Sherwood and Reed, 1957)

Let h - solute hold-up in gas phase per unit column volume (moles/cm^3)
H - solute hold-up in liquid phase per unit column volume (moles/cm^3)
ρ - gas phase density (moles/cm^3)
t - time since start of process (sec)
V - superficial gas velocity (cm/sec)
x - mole fraction of solute in stationary phase
y - mole fraction of solute in gas phase
z - distance from column inlet (cm)
m - equilibrium relation (= K when ideal)
L - total column length

A material balance across a small element of unit cross section gives

$$- V\rho \frac{\partial y}{\partial z} = h \frac{\partial y}{\partial t} + H \frac{\partial x}{\partial t}$$

The equilibrium relation, i.e. the relationship between y and x, must be specified. Assume a relation y = mx

Then

$$- V\rho \frac{\partial y}{\partial z} = (h + \frac{H}{m}) \frac{\partial y}{\partial t}$$

The quantity $\frac{h}{V\rho} \Delta z$ is the time required to displace the gas held up in the column distance Δz. Consequently the column dead time may be written

$$t_d = \frac{hL}{V\rho}$$

Then

$$- \frac{\partial y}{\partial z} = \frac{t_d}{L} (1 + \frac{H}{hm}) \frac{\partial y}{\partial t} \qquad 3.3.$$

Introduce

$$\Theta = - \frac{t_d}{L} (1 + \frac{H}{hm})$$

If a delta-function solute input distribution is assumed and the effect of band broadening is neglected, the boundary conditions are

$$y = 0 \text{ at } z = 0, \; t < 0$$

$$y = y_o \, \delta \, (t) \text{ at } z = 0, \; t = 0$$

Using the Laplace transformation and substituting Θ, equation 3.3. becomes

$$\frac{\partial Y}{\partial z} = \Theta s Y - \Theta y \; (t = 0)$$

$$= \Theta s Y$$

$$Y = A e^{\Theta s z}$$

The inverse transformation gives

$$y = y_o \delta \; (t - \Theta z)$$

At $z = L$

$$y = y_o \delta \; (t + t_d \; (1 + \frac{H}{hm}))$$

The impulse function entering the column thus leaves the column as impulse and the retention time is

$$t_R = t_d \; (1 + \frac{H}{hm}) \qquad 3.4.$$

or $t_R = t_d + t_R{}'$

where $t_R{}'$ - net retention time 3.4a

Equation 3.4. is a basic chromatographic relationship, which is normally expressed in terms of the distribution of the solute between the gas and liquid phases as (Littlewood, 1970) :

$$t_R = t_d\ (1 + k) \qquad 3.5.$$

where k is the capacity or partition ratio, and

$$k = \frac{\text{weight of solute in liquid phase}}{\text{weight of solute in gas phase}}$$

This equation can also be written in terms of the partition coefficient

$$\alpha = \frac{\text{weight of solute per cc stationary phase}}{\text{weight of solute per cc gas phase}}$$

or in the more readily accessible form

$$\beta = \frac{\text{weight of solute per gram stationary phase}}{\text{weight of solute per cc gas phase}}$$

These different forms are related as follows

$$\alpha = \frac{V_G}{V_s}\ k \qquad 3.6.$$

where V_G - volume of mobile phase in column

V_s - volume of stationary phase in column and $$\beta = \frac{\alpha}{\rho s} \qquad 3.7.$$

where ρ_s - density of stationary phase

The equivalence of equations 3.4. and 3.5. can be shown as follows:

In equation 3.2., x_1 is a measure of the concentration of the solute in the liquid phase, and p_1 is a measure of the concentration of the solute in the gas phase. These two values are therefore related to the numerator and denominator respectively of the partition coefficients described above (α or β).

If n_1 and n_2 are the number of moles of solute and solvent in a solution

$$x_1 = \frac{n_1}{n_1+n_2} = \frac{n_1}{n_2}$$

(since we are considering dilute solutions with $n_2 > n_1$)

Converting to weight units, w, by using the molecular weight of the stationary phase, M_2:

$$x_1 = \frac{n_1 M_2}{w_2}$$

The concentration of the solute in the stationary phase is

$$q = \frac{n_1}{w_2}$$

therefore

$$x_1 = q\, M_2 \qquad 3.8.$$

The general form of the gas law is

$$PV = nRT$$

from which the concentration of the solute in the gas phase can be written as

$$c = \frac{p_1}{RT}$$

Where p_1 is the partial vapour pressure. By expressing Dalton's law in the form

$$p_1 = Py_1$$

where P - total pressure

y_1 - mole fraction in the gas phase

then

$$c = \frac{Py_1}{RT}$$

The equilibrium constant in 3.4. then becomes

$$m_1 = \frac{y_1}{x_1} = \frac{RTc}{PM_2q} \qquad 3.9.$$

However, from the definition of the partition coefficient

$$\beta = \frac{q}{c}$$

therefore $m_1 = \dfrac{RT}{PM_2\beta}$ 3.10.

or $\beta = \dfrac{RT}{PM_2m_1}$ 3.11.

An expression for the ratio of liquid to gas hold-up (H/h) in 3.4. can then also be found. From 3.4. and 3.5.:

$$k = \frac{H}{hm}$$

but

$$k = \frac{\beta\rho_2V_2}{V_1}$$

and using 3.11.

$$k = \frac{RT}{PM_2m_1}\,\frac{\rho_2V_2}{V_1}$$

thus $$\frac{H}{h} = \frac{RT\rho_2 V_2}{PM_2 V_1} \qquad 3.12.$$

3.1.2. Non-ideal Solution Theory

In paragraph 3.1.1. it was stated that ideality in the present context is defined in terms of the validity of Raoult's law. In the non-ideal case, the relationship of equation 3.2. becomes non-linear with respect to x.

In the dilute solute case considered in gas chromatography, the lower end of the line representing equation 3.2. (refer to Fig. 3.1.) can still be considered straight, but the proportionality constant is not the vapour pressure of the pure solute. The relationship between vapour pressure and mole fraction is then given by Henry's law

$$p_1 = H\, x_1 \qquad 3.13.$$

The departure from ideality in 3.13. can be expressed quantitatively as the ratio of the actual vapour pressure of the solute to the ideal vapour pressure. This ratio is the activity coefficient, γ, of the solute. In terms of this definition, equation 3.2. becomes

$$p_1 = \gamma p_1^{o} x_1 \qquad 3.14.$$

This is consistent with the fundamental thermodynamic approach (Hála, 1967) where the condition for equilibrium can be expressed as

$$\phi_i \, y_i \, P = \gamma_i \, x_i \, f_i^o$$

where ϕ_i - fugacity coefficient of component i

γ_i - activity coefficient of component i

f_i - fugacity of component i

f_i^o - standard fugacity of component i

with $$\phi_i = \frac{f_i}{p_i}$$

and $$\gamma_i = \frac{f_i}{f_i^o x_i}$$

In the derivation of equation 3.5. the equilibrium relationship between x and y was given as $m = \frac{y}{x}$. Using Dalton's law and equation 3.14, the constant m can be approximated as

$$m_1 = \frac{y_1}{x_1} = \frac{p_1}{P} \; \frac{\gamma p_1^o}{p_1} = \frac{\gamma p_1^o}{P} \qquad 3.15.$$

The effect of the activity coefficient on GC retention time can be derived qualitatively as follows:

For $\gamma < 1$

p_1 actual $< p_1$ ideal

therefore the partition coefficient

β actual $> \beta$ ideal

with the result

t_R actual $> t_{ideal}$

The retention time of a solute as given by 3.4. can be written by substitution of equation 3.15 as:

$$t_R = t_d \left(1 + \frac{HP}{h\gamma p_1{}^o}\right) \qquad 3.16.$$

From 3.16 and 3.4a, the net retention time can be written

$$t_R' = t_d\, HP/h\gamma p_1{}^o$$

If the solutes and the stationary phase are such that the activity coefficients for different solutes are the same (not necessarily unity), separation of solutes occurs solely on the basis of differences in their vapour pressures, in accordance with 3.16.

The effect of temperature on vapour pressure can be described by Clausius-Clapeyron equation which can be expressed as:

$$\ln p^{o} = -\frac{\Delta H_v}{RT} + A \qquad 3.17.$$

where ΔH_v - heat of vaporization of the pure solute

A - constant

Heat of vaporization can be related to boiling point by Trouton's rule.

Hence $$\ln p^{o} = -\frac{A_1 T_B}{RT} + A$$

where T_B - boiling point

A_1 - Trouton's constant

Thus, when separation is based on differences in vapour pressure only, components will be eluted in the order of increasing boiling point. In the gas chromatographic analyses used in this investigation, separation is required on the basis of boiling point and the stationary phase is selected so as not to enhance the effect of differences in activity coefficients. Any non-polar stationary phase meets this requirement, since separation takes place mainly on the basis of vapour pressure and elution of components from a non-polar liquid is generally in order of increasing boiling point. In view of this, the effect on the retention time of differences in activity coefficients between the components contained in petroleum samples is neglected.

3.1.3. Isothermal and Programmed Temperature Operation

The vapour pressure of a solute is a non-linear function of temperature as can be seen from equations 3.17 and 3.18 with the result that retention time as expressed by equation 3.16 is also very much dependent on temperature. The logarithmic relationship indicates that only a relatively limited range of column temperatures would result in a suitable retention time for a particular solute-solvent pair. In a wide boiling range mixture the selection of an intermediate column temperature results in the first peaks overlapping to a large degree whereas higher boiling point solutes will be eluted with excessively long retention times. By raising the temperature of the column during analysis, this effect can be counter-acted resulting in a more linear relationship between retention time and boiling point.

The theory of programmed temperature gas chromatography has been treated in detail by Harris and Habgood (1966) for both linear and step-wise linear temperature programming rates. Non-linear programs, which are the result of non-uniform heating rates at high rates of temperature change are treated in a first approximation as a series of successive discrete heating rates. Since most commercially available GC's are of the low heat capacity type permitting high heating rates to be achieved as well as short column cooling times, programmed temperature rates are not always linear and furthermore depend on the time allowed for equalization at the initial temperature. Under carefully controlled conditions and a relatively low range of boiling points, reproducibilities of better than 2 % have been reported (Dal Nogare and Harden, 1959). However, detailed studies on sources of error in retention time measurements, especially under programmed temperature conditions have brought some investigators to the conclusion that this technique is not ideally suited for process chromatographs and that equipment more advanced than most available commercial GC's is required to handle wide boiling-range mixtures successfully (McWilliam, 1968; Ebing, 1969; Scott, 1969; Goedert and Guiochon, 1970; French, 1972).

3.2. Simulated Distillation

The distribution of various compounds in petroleum fractions, as given by a standard boiling point curve, can also be obtained by gas chromatographic analysis. Analytical distillation by GC was first described by Eggertsen, Groennings and Holst (1960) and subsequently by Green, Schmauch and Worman (1964); Gaylor, Jones, Landerl and Hughes (1964); Gouw, Hinkins and Jentoft (1967); Philyaw, Krc and O'Neal (1971) and Adlard et al. (1971). The term Simulated Distillation was proposed by Green et al. (1964) for this boiling point characterization procedure.

Simulated distillation is based on the elution of solutes in the order of increasing boiling point as described in 3.1.2., i.e. a non-polar stationary phase is used with the result that separation takes place mainly as a result of differences in vapour pressure. Using linear programmed temperature conditions, an approximately linear relationship exists between boiling point and net retention time. This can be seen by combining equations 3.12, 3.16a and 3.18:

$$T_B = \frac{-RT}{A_1} \ln \frac{t_d RTW_2}{V_1 M_2 \gamma t_R'} + \frac{ART}{A_1} \qquad 3.19.$$

Assuming a linear temperature programming rate

$$T = a + bt \qquad 3.20.$$

and introducing the constants C_A, C_B, C_C, equation 3.19 becomes

$$T_B = - C_A \,(a + bt) \ln \left[\frac{C_B}{t_R'} + \frac{C_C t}{t_R'}\right] + AC_A \,(a+bt) \qquad 3.21.$$

The logarithmic term in 3.21 is small relative to the other terms and is only significant at small values of t, since it contains the molecular weight in the denominator in both C_B and C_C which has a value in the order of 10^4

for the non-polar stationary phase normally used for simulated distillation.

It is important to consider the effect of chemical type on this systematic boiling point-retention time relationship. Whereas the frequently reported approximately linear relationship between retention time and carbon number depends on the particular homologous series (Harris and Habgood, 1966; Schupp, 1968; Littlewood, 1970) it follows from the discussion in paragraph 3.1.2. that the use of a non-selective column liquid tends to produce a more nearly linear relationship between boiling point and retention time (Green, Schmauch, Worman, 1964). Such a stationary phase suppresses the effect of differences in activity coefficient and vapour pressure is the predominant separating characteristic. The success of this technique for hydrocarbon mixtures is, however, also due to the fact that the differences in activity coefficients between the non-polar constituents can be expected to be small. Mixtures containing strongly polar substances will exhibit larger deviations from this ideal behaviour. The importance of the type of stationary phase can also be seen from the use of selective (polar) liquids to enhance the separation of components of almost identical boiling point, on the basis of differences in activity coefficients (Littlewood, 1962).

To relate the retention times of the peaks of an unknown sample to boiling points, use is made of a calibration curve. Calibration takes place under carefully controlled temperature programmed conditions, using a calibration sample containing a wide range of compounds with known boiling points. To obtain the equivalent of a TBP curve, the area under the curve of the sample to be tested is integrated and using the calibration curve, a plot of boiling point versus weight percent is drawn. The weight-proportional detection can be obtained by two methods. In the original procedures use was made of a combustion attachment for converting the hydrocarbons to carbon dioxide prior to detection in a thermal conductivity detector. Similar results can be obtained directly by using a flame ionization detector (FID). Despite the fact that deviations have been reported (Desty, Goldup and Geach, 1960; Deans, 1968) simulated distillation is based on the assumption that an FID response factor of unity applies to all substances encountered in the hydrocarbon mixture, i.e. the area under the peak detected by the FID is directly proportional to the mass of the eluted component. The accuracy obtained by chromatographic procedures compares well with the tedious precision distillation and is superior to the routine ASTM distillation. Furthermore better initial and final boiling point accuracy can be claimed (Green, Schmauch and Worman, 1964).

3.3 . Further Development of Existing Procedures

Two important points arise from the above discussion: First, repeatability of retention times determine the accuracy of analysis and secondly, the representation of GC data is in integral form to correspond to the well established TBP procedure. These points require further investigation.

The difficulties encountered with respect to repeatability in programmed temperature gas chromatography have already been emphasized in paragraph 3.1.3. The requirements for good repeatability and high speed of analysis are not readily compatible and all simulated distillation equipment is designed with this in mind. To obtain an accurate and repeatable temperature program, a high heat capacity oven would be preferable but since the associated cooling times and equalizing times at the initial temperature are excessively long, specially constructed low heat capacity column configurations are used (e.g. Adlard et al., 1971). If the simulated distillation equipment is basically a single-purpose instrument this is acceptable. In most industrial laboratories, however, standard gas chromatographs are available for other routine analyses and the cost of additional single-purpose chromatographs hardly justifiable. Especially at the present state of development of chromatographic procedures, with the vast field of product specification tests still to be further explored, there is merit in finding a more versatile approach to boiling point characterization by GC.

The second point, namely that of integral representation of GC data is a direct result of the conventional TBP approach in the petro-chemical industry. This approach is based on the traditional testing procedure, and the dividing of TBP curves into a finite number of cuts has become an accepted procedure (refer also to 2.4.1.). That the integration of discrete GC information and subsequent cutting of the integral curve is illogical, has already been pointed out by others (Adlard et al. 1971) and the grouping of peaks to pseudo-components has also been considered (Walsh and Mortimer, 1971; Anderson, Sharkey and Walsh, 1972).

The discrete method of data handling poses data processing problems. Since a wide boiling range petroleum mixture contains an almost infinite number of components, the number of peaks obtained in a GC analysis is mainly a function of the performance of the equipment. On capillary columns, using low temperature programming rates, up to

300 components have been identified in the range from C_8 to C_{23} (Kemmner, Kolb and Pauschmann, 1963). Since this number of components (or pseudo-components) cannot be handled even by computer processing systems, it is necessary to group peaks, either after separation on a column with a large number of theoretical plates, or by employing a lower efficiency column. The latter technique is simpler to use, since the grouping of a large number of peaks and the matching of different chromatograms is an inherently subjective procedure. Since the availability of a computer for handling the processing of the GC data is a prerequisite for short analysis times, use can be made of mathematical procedures to offset the loss in information caused by an instrumental technique of lower resolution.

The boiling point characterization procedure described in the next section, was developed against this background, with the stress on the on-line nature of the application, where the main considerations are the speed of analysis and data processing, the suitability of the results for use in a computer control strategy and the insensitivity of the procedure to environment and handling.

CHAPTER 4

4. GAS CHROMATOGRAPHIC BOILING POINT CHARACTERIZATION PROCEDURE

The development of the gas chromatographic fractionator boiling point characterization procedure can be considered as four practically independent problems:

1. Development of the gas chromatograph-computer data handling system
2. Development of a boiling-point/vapour-liquid equilibrium correlation
3. Development of an accurate non-linear temperature programmed GC analysis technique.
4. Development of a fast fractionator calculation procedure (model) permitting the prediction of fractionator performance.

The combination of the solutions to these problems provides a powerful analysis tool which permits:

a. Rapid analysis of wide boiling range oils, without GC temperature rate-of-change restrictions.
b. The use of the results directly in a fractionator model or plate-to-plate distillation calculation procedure.
c. The prediction of the performance of the fractionator in terms of composition distribution.
d. The possible development of combined feedforward-

feedback control strategies in terms of the most meaningful fractionator variable, composition.

4.1. Data Handling

Except for the extreme case of very slow high resolution capillary analyses, one is faced with the problem of allocating areas to peaks which are not baseline resolved. This problem is not new, and a large number of suitable techniques have been developed. However, if peak separation is required to form part of an on-line computer control strategy, where both instrumental analysis time and data processing time are of prime importance, it is necessary to re-evaluate both computer processing strategies and deconvolution techniques. It is necessary to examine both hardware and software considerations in designing a suitable system for the application outlined before.

In order to improve the separation of wide boiling-range mixtures, programmed temperature operation was recommended in 3.1.3. On a complex mixture such as crude oil or its fractions, this does not, however, mean that all peaks are baseline resolved, especially in the case of high speed operation of the GC.

The practical separation of such fused peaks is only feasible by the use of computer systems (Smith, 1969;

Gill, 1969; Perone, 1971; Anderson, 1972; Gill, 1972). These may be either off-line systems for acquiring and processing chromatographic and, if necessary, other analytical data on a time-sharing basis (Raymond, Lawrey and Mayer, 1970; Schomburg et al, 1971; Jackson, 1971; Guichard and Sicard, 1972) or dedicated computers for real-time control of the gas chromatograph, including high-precision data processing (Burke and Thurman, 1970; Swingle and Rogers, 1971; Hettinger, 1971; Frazer and Guran, 1971; Price, 1971). It is to be expected that, as the prices of both hardware and software of small computer systems become more competitive, the trend will be for on-line machines to replace off-line systems (Oberholtzer, 1969).

In view of these different computer configurations, a large variety of peak separation techniques have been developed. It is generally accepted today that graphical techniques (dropping perpendiculars, tangential method for shoulders or peaks riding on the skewed peak tail) introduce errors in the allocation of areas between unresolved chromatographic peaks which are unacceptable in many applications (Westerberg, 1969; Hancock, Dahm and Muldoon, 1970).

An alternative approach is to use least square procedures (Fraser and Suzuki, 1966; Roberts, Wilkinson and Walker, 1970). In this method the original data set is replaced by a synthetic data array, based on a model of a gas chromatographic peak described by a finite set of parameters (Anderson, Gibb and Littlewood, 1970). The most generally used model for describing a peak, is the skewed Gaussian shape (Fraser and Suzuki, 1969; Hock, 1969; Scott et al.,1970). Since quantitative analysis is sensitive to models which do not describe the actual data accurately, various attempts have been made to improve the skewed Gaussian model. Extracolumn contributions to chromatographic band broadening can be expressed in the form of a first order lag (Schmauch, 1959; Johnson, 1959; Sternberg,1966) and an exponential-Gaussian convolute can therefore be used to describe the GC peak (Gladney, Dowden and Swalen, 1969; Anderson, Gibb and Littlewood, 1970). A more empirical approach is to describe the shape by a data array recorded for a pure component (Rudenko, 1968; Rudenko et al. 1970; Anderson et al. 1969 and 1970; Westerberg, 1969; and Mori, 1972).

The use of most of the methods outlined above is restricted to applications of off-line nature. Despite their obvious advantages, multi-dimensional search procedures are not suitable for the analysis of complex chromatograms in a real-time environment. For these applications, a compromise is desired between time and accuracy, while at the same time excluding the possibility of large non-convergence errors. This necessitates the use of the original data instead of synthetic data arrays. If sufficient care is taken with noise suppression, the original fused peaks as described by their apparent peak heights and retention times may be used to calculate approximations to true peak heights and retention times. Such a procedure again uses a model for describing a GC peak and deconvolutes fused peak data by a simple process of calculation and subtraction of the effect of every peak on all neighbouring ones in a recursive mode (Metzger, 1970; Mori, 1972).

In the present investigation, a real-time process computer was hooked up to a single gas chromatograph while at the same time handling fractionator modelling calculations and data logging on a pilot distillation plant. These activities can be divided into two categories: "Foreground" tasks with a fixed time requirement and "background" tasks which can be processed in an off-line mode. The former includes GC data acquisition and plant data logging, whereas the latter is associated with fused peak deconvolution techniques, compound identification and fractionator model calculations. In order to make full use of the computer's capabilities, it was decided to separate GC data acquisition and processing, by acquiring and storing the information in foreground, while processing it in background. By assigning different priorities, it is possible to run activities of an off-line nature in background at a low priority, while simultaneously carrying out GC data acquisition of a higher priority nature.

The computer deconvolution program developed for this purpose, can therefore be divided into three parts

1. Acquisition of real-time GC data and storage in foreground

   The data acquisition program is initiated by injection of the sample into the gas chromatograph. The syringe plunger is used to provide contact closure to a digital input of the computer. This was done to ensure good reproducibility of retention times and this system was preferred to an automatic sampling valve with air actuator which was found to be unreliable. The millivolt output signals from the detector amplifier and a GC oven temperature monitoring thermocouple are scanned at a rate of 6 times per second, which was found to be a favourable compromise between faithful representation of data and excessive storage requirements.

2. Deconvolution of fused peaks, in background at high priority

   The high priority background program carries out peak deconvolution according to the arithmetic procedure described above (Metzger, 1970; Mori, 1972). Since care was taken to keep the noise level in the GC analog signals low, the only software precaution taken was single-exponent smoothing (Koppel, 1968):

$$\bar{c}_n = \alpha c_n + (1 - \alpha)\,\bar{c}_{n-1}$$

Where $\bar{c}_n$ - smoothed value

c_n - present unsmoothed value

$\bar{c}_{n-1}$ - previous smoothed value

α - smoothing constant $0 \leq \alpha \leq 1$

A low value of α is used when large random fluctuations are suspected in the signal, but since the smoothed signal lags the actual signal, too low value of α will cause the smoothed signal to be unrepresentative of the actual signal. When $\alpha = 1$, no smoothing takes place. The lag introduced by single-exponent smoothing was neglected in the calculation of retention times, since true retention times were used, i.e. relative to an unabsorbed GC component. The peak data is baseline corrected. Since the temperature drift in the dual column configuration employed was negligible, a constant offset baseline, based on the signal value before peak detection, was used. The onset of a peak is detected by the signal exceeding a preselected threshold, while a peak maximum is based on the first derivative becoming zero. Shoulder peaks at which the first derivative does not become zero are thus not detected, but higher order derivatives with slightly noisy data do not give satisfactory results and higher order smoothing techniques were not deemed necessary or justifiable in a real time procedure. Peaks not exceeding a preselected amplitude are rejected.

The retention times at peak maximum are determined and stored. Having processed all peaks in this manner, the peak having the largest influence on adjacent peaks is determined, assuming a skewed-Gaussian peak model. The effect of this peak is subtracted from all adjacent peaks to which it contributes. This procedure is continued until all peaks have been treated. Depending on the degree of overlapping and the accuracy required, a second and further iterations may be necessary. Having separated all fused peaks in this fashion, the areas can be calculated by integrating the individual peaks using the corrected peak heights. Corrections may also be effected to retention times in a similar way, although this was not found necessary for the present applications.

3. Improvement of GC peak model, in background at low priority

It is obvious that one of the main factors affecting the efficiency of this method is the accuracy by means of which the skewed-Gaussian model describes the actual peaks. The program employs two methods for limiting errors due to an incorrect model:

a. The ratio of peak widths of adjacent peaks is used in the calculation instead of the actual widths;
b. The peak model parameters are improved by the low-priority search procedure described below

The advantage of using a peak width ratio rather than actual widths lies in the fact that the ratio remains almost constant over a wide range of retention times, whereas the absolute widths cover a wide range of values for the wide boiling range samples analysed.

The low priority background program improves the model used for calculating GC peak shapes. A skewed-Gaussian peak shape can be described by three parameters, the height H, the width of the first half of the peak B_s and the width of the second half of the skewed peak B_f:

$$x(t) = H\,e^{-\left(\frac{t}{B_s}\right)^2} \qquad t < 0$$

$$x(t) = H\,e^{-\left(\frac{t}{B_f}\right)^2} \qquad t > 0 \qquad 4.1.$$

Assuming that H is given by the corrected observed chromatogram height, two parameters are necessary, per peak, to describe the skewed-Gaussian shape, resulting in 2 x n parameters for n peaks. In order to simplify the search procedure, use can be made of the fact that peak width is a function of retention time (v.d. Vlies and Caron, 1963; Blaustein and Feldman, 1964; Habgood and Harris, 1966). Under isothermal and linear temperature programmed conditions, the relationship is approximately linear and even under the non-linear temperature conditions resulting from high temperature programming rates this approximation holds to a sufficient degree of accuracy. The degree of skewness is also a function of retention time and temperature, but to a lesser extent than the peak width. The model parameter search procedure can then be simplified by introducing the parameters a, b and c, where

$$B_f = a + b \cdot t_R \qquad 4.2.\ (a)$$

(describing the change in width with retention time)

$$B_s = c \cdot B_f \qquad 4.2.\ (b)$$

(describing the degree of skewness)

The low priority search routine thus carries out a least squares fit on the deconvoluted peaks, finding the best set of parameters in equation 4.2. for describing the original enveloping curve.

The complete data handling procedure was tested under both isothermal and programmed temperature conditions and compared with graphical area calculation procedures. The computer flow diagram is shown in Fig. 4.1. and the results of the isothermal and programmed temperature test runs in Fig. 4.2. and Fig. 4.3. The deconvolution procedure is clearly superior to the graphical techniques and a substantial saving in analysis time is possible when using the chromatograph in conjunction with the computer deconvolution procedure.

When using this data handling system on fractionator streams, there are other considerations of importance, such as the complexity of the mixture (which determines the degree of overlapping) and the identification of the same pseudo-components in different sample streams.

The first consideration determines the degree of success of the deconvolution procedure. It is clear that wide boiling range mixtures, such as crude oil, will produce a set of peaks when analysed by a fast GC procedure which do not represent pure components, i.e. every pseudo-component will represent a large number of actual constituents, as pointed out before. This implies that the simplification introduced into the deconvolution procedure of a linear relationship between peak width

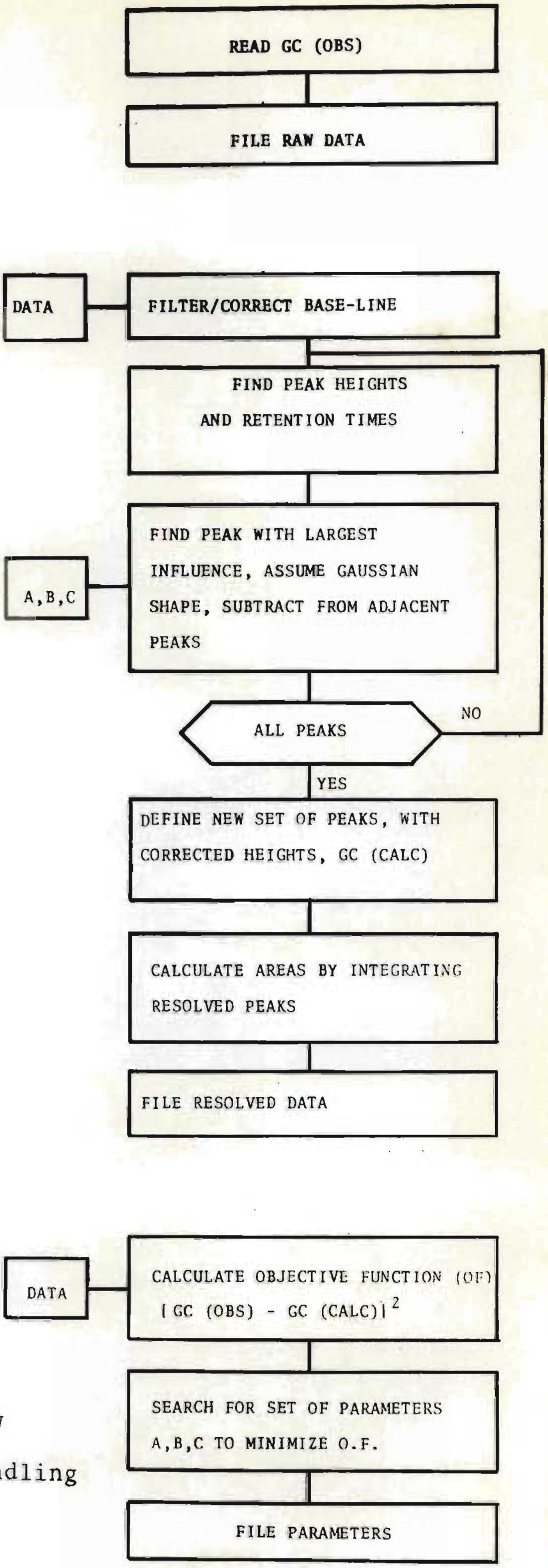


Fig. 4.1. Computer flow diagram for GC data handling procedure

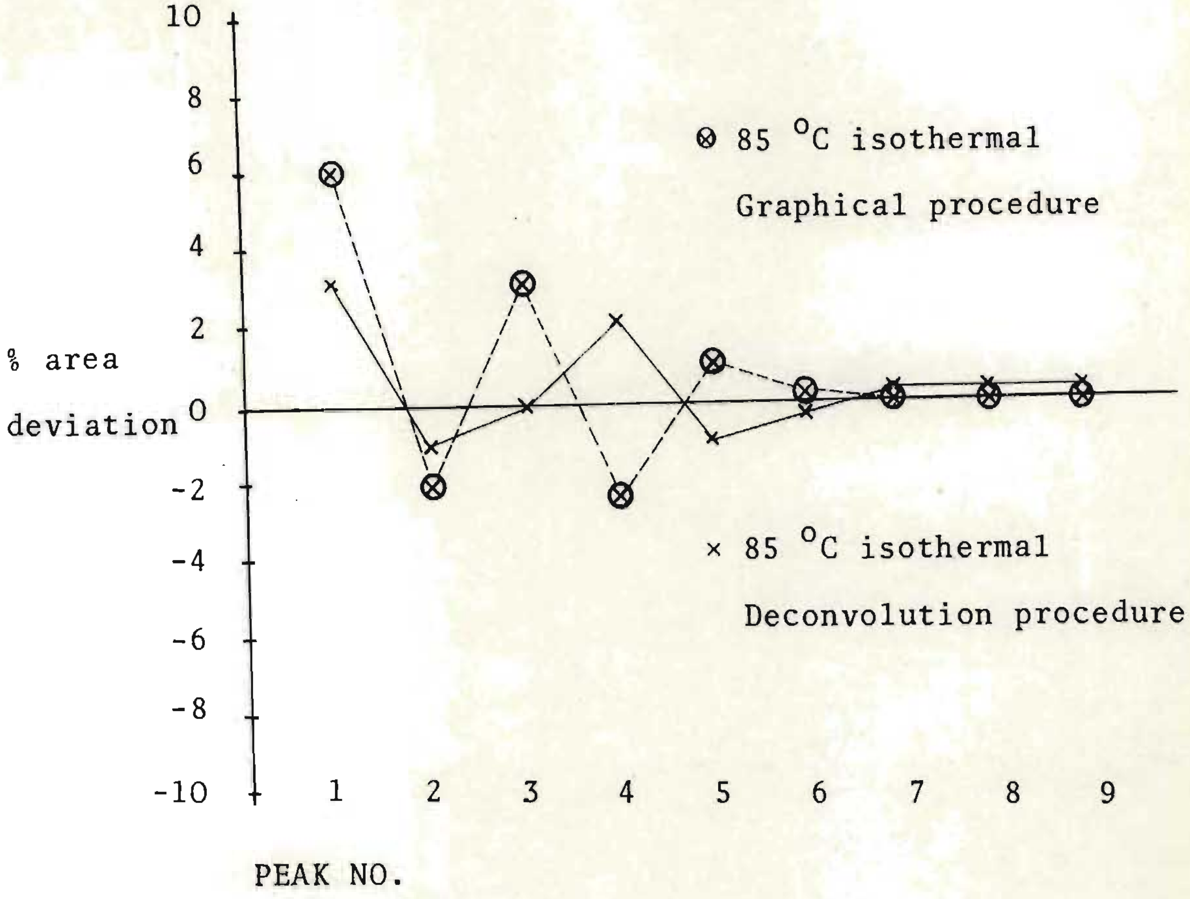


Fig. 4.2. Results of one of the isothermal test runs for comparing graphical and curve fitting procedures. The deviation calculation is based on the areas assigned to the peaks by the two methods, as compared with the actual areas obtained from base-line resolved chromatograms of the same sample under programmed temperature conditions (10 °C/min).

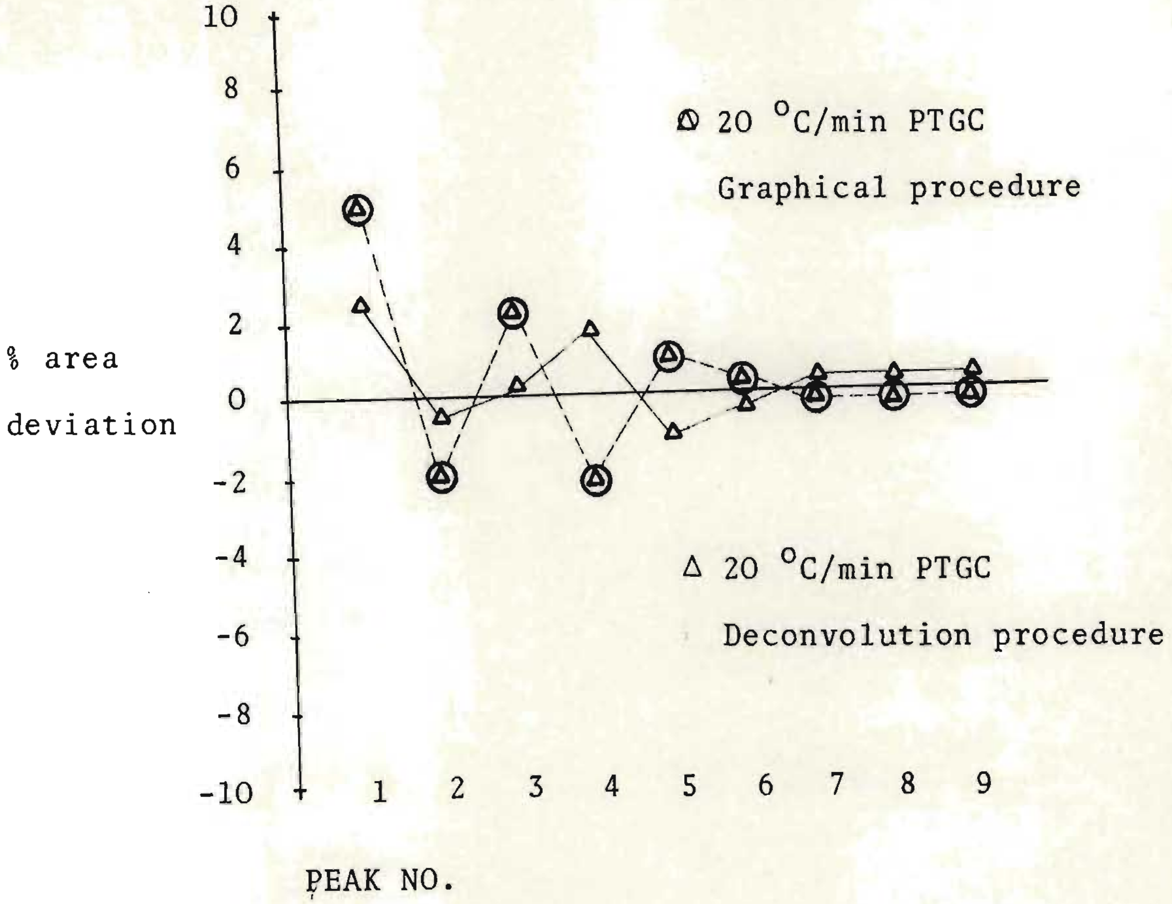


Fig. 4.3. Results of one of the programmed temperature test runs for comparing graphical and curve fitting procedures. The deviation calculation is based on the areas assigned to the peaks by the two methods, as compared with the actual areas obtained from base-line resolved chromatograms of the same sample under programmed temperature conditions (10 °C/min).

and retention time does not hold. In such cases graphical techniques have to be used, since all other multi-parameter techniques would be unsuitable for an on-line analysis procedure. In this respect it is however important to note that a fast GC analysis on petroleum mixtures frequently reveals a definite pattern, in which a particular homologous series is dominant (refer to Fig. 4.4. and Fig. 7.1.) The convolution procedure is then particularly useful in assigning correct areas to these dominant peaks.

The second aspect mentioned above is that of pseudo-component identification in different streams. This aspect will be considered in more detail in chapter 5, but in the present context it suffices to point out that for a material balance calculation, the same pseudo-components as identified in the feed stream have to be detected in the product streams. A detailed analysis of the smaller number of pseudo-components in the product streams, using the complete deconvolution program, then affords useful information on the component distribution in the feed.

4.2. Vapour-Liquid Equilibrium Correlation

The distribution of compounds in petroleum fractions, whether obtained from conventional boiling point curves or from gas chromatographic procedures, is expressed in

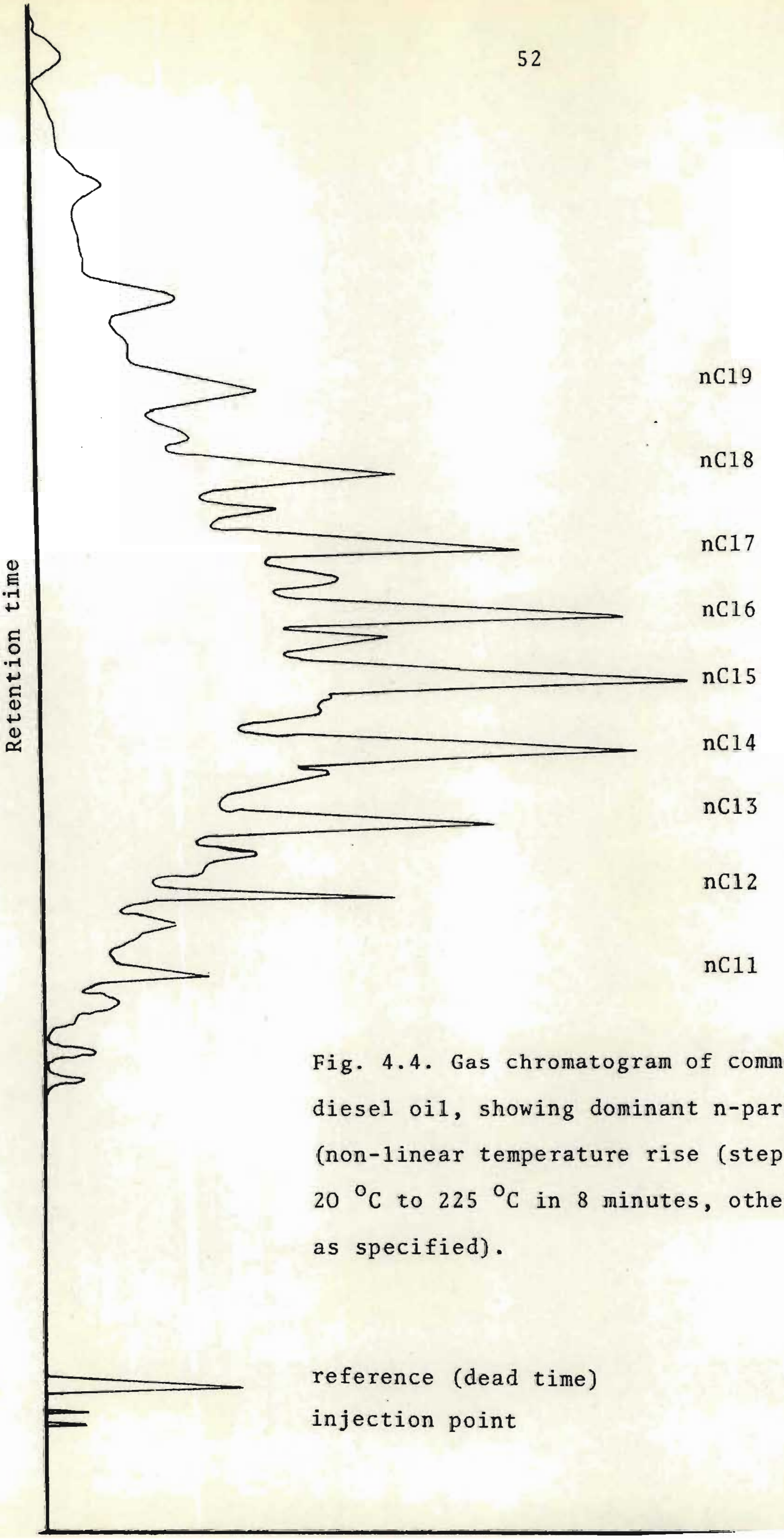


Fig. 4.4. Gas chromatogram of commercial diesel oil, showing dominant n-paraffin peaks (non-linear temperature rise (step change), 20 °C to 225 °C in 8 minutes, other GC conditions as specified).

terms of boiling points. In distillation calculation procedures use is made of vapour-liquid equilibria data to describe the equilibrium conditions of the individual components. Since hydrocarbon mixtures behave in a near-ideal fashion, it can be assumed that the Henry's law constant ,

$$H_i = \frac{p_i}{x_i} \qquad 4.3.$$

where p_i - partial vapour pressure of component i

and x_i - mole fraction of component i in the liquid phase

equals the vapour pressure in the pure state (Raoult's law) p_i^o, i.e.

$$x_i = \frac{p_i}{p_i^o} \qquad 4.4.$$

Writing Dalton's law in the form

$$p_i = y_i \ P \qquad 4.5.$$

where y_i - mole fraction of component i in the gas phase

P - total pressure

and substituting into the definition of the vapour-liquid equilibrium constant

$$K_i = \frac{y_i}{x_i} \qquad 4.6.$$

one obtains

$$K_i = \frac{p_i^o}{P} \qquad 4.7.$$

which is the ideal form of equation 3.15 (with $\gamma = 1$). This relationship is based on the assumption that the laws for ideal mixtures apply and neglects the effect of composition on the K-value. More accurate correlations have been developed (Chao and Seader, 1961; for general treatment refer to Holland, 1963). For practical hydrocarbon calculations, general use is made of equation 4.7. The form of this equation is also of particular interest in the gas chromatographic context, where it has been shown (in Chapter 3) that component separation can be based on differences in vapour pressure. It is therefore necessary to investigate different vapour pressure correlations.

Existing vapour pressure correlations fall into two broad categories: those in which use is made of a reference substance in order to obtain a linear relationship between functions of vapour pressure and temperature; and those using compound specific parameters for expressing vapour pressure as a function of temperature. The first category encompasses methods such as the Cox and Othmer relationships which have been the basis of a large number of correlations (Cox, 1923; Othmer, 1942; Driesbach and Spencer, 1949; Riedel, 1954; Maxwell and Bonnell, 1957). The second category includes the Antoine equation and extensions of similar form, with characteristic parameters for each individual compound (Thodos, 1950; Prausnitz et al. 1967).

These methods have been used to develop generalized vapour pressure correlations and monographs which are widely used (Maxwell and Bonnel, 1957; Nelson, 1958).

In order to utilize these correlations for distillation calculation procedures involving equation 4.7., a distinction must be made between fractionators handling process streams containing a large number of hydrocarbons, none of which is separated into pure products and fractionators separating low boiling point components into nearly pure products. In the latter case pure component characteristics are available and the second category of vapour pressure equations or accurate vapour-liquid equilibria data can be employed. In the first case, however, use must be made of the near ideal behaviour of hydrocarbon mixtures, in order to treat the narrow boiling fractions as pseudo-components. Ideally, a correlation is required which uses one parameter only, namely boiling point. Further incentive for the development of a single parameter correlation is the fact that the generalized gas-chromatographic boiling point characterization procedure described in paragraph 4.3. requires the identification of substances eluted by the GC of which the vapour pressure at column temperature is known. This inverse problem can not be solved in the case of a multi-parameter correlation.

The simple correlation developed in paragraph 3.1.2. and given by equation 3.18 is not suitable for quantitative use, since the accuracy is not very high (Littlewood, 1962). The Maxwell and Bonnell correlation which relates vapour pressure and temperature using boiling point as parameter, accounts for the effect of chemical type by using as second parameter the Characterization Factor of Watson, Nelson and Murphy (1935). Since the effect of this factor is relatively small, a general correlation was developed on the basis of the Maxwell and Bonnell procedure, but in a form directly suitable for computer calculations.

This general reference substance correlation relates vapour pressure to temperature to obtain a family of curves intersecting at a common point, with boiling point as parameter. The abscissa scale is a reciprocal temperature scale, the ordinate scale, representing pressure, is equivalent to the reciprocal temperature of the reference substance (here n-Hexane). The reciprocal temperature scale is converted into a pressure scale by using the Antoine equation for n-Hexane:

$$\log_{10} p = A - \frac{B}{C+T} \qquad 4.8.$$

with $A = 6.893$ p in mm Hg

$B = 2124.0$ T in ^{o}R

$C = -85.98$

These parameters were obtained by fitting the API table 20 (Research Project 44, 1969) data for n-Hexane to the above equation for the range 10 mm Hg to 1500 mm Hg, using a non-linear regression program based on the standard Law and Bailey (1963) technique. The normalized individual 95 % confidence limits for these parameters were

for A 1.84×10^{-3}
B 6.25×10^{-3}
C 4.01×10^{-3}

To obtain the generalized form of the vapour pressure-temperature correlation, use is made of the fact that the family of curves have a common point of intersection. Knowing this point, only one parameter, boiling point, is required. The equation is then

$$\log_{10} p = A - \frac{B}{C+Q}$$

$$Q = \frac{Tbp \, \frac{Trc}{Tnc} - Trc}{\left[1 - \frac{Trc}{Trbp} \right] \frac{Tbp}{Tn} + \frac{Trc}{Tnc \; Trbp} \, Tbp - 1} \qquad 4.9.$$

Using API data for a wide range of n-paraffins and the Law and Bailey program, the parameters obtained were:

$Trc = 3652.$ p in mm Hg
$Tnc = 3612.$ T in ^{o}R

The normalized individual 95 % confidence limits for these parameters were

for Trc 3.44×10^{-2}
Tnc 2.09×10^{-2}

The correlation was tested on a large number of substances, including n-paraffins, aromatics, iso-paraffins and cycloparaffins, using API data. The predicted vapour pressures for given boiling points, covering the range expected in a crude oil sample, corresponds closely to the actual API data as shown in Fig. 4.5. and Fig. 4.6.

Despite the errors introduced by neglecting chemical type, the correlation has the advantages of generality, availability of data and speed of calculation. As can be seen from Fig. 4.6. the average error for a complex mixture containing different homologous series may be reduced by using data from all these chemical types when carrying out the regression analysis for obtaining the correlation parameters Trc and Tnc. In order to have a more standard equation, the parameter values for equation 4.9. were based on n-paraffins only.

4.3. Generalized Chromatographic Identification Procedure

The background for the development of a general GC identification procedure was outlined in paragraph 3.3. and the difficulties of reproducibility and discrete data handling pointed out. The latter problem is treated in detail in paragraph 4.1., whereas a solution to the problems of high-speed chromatography will be proposed in this section.

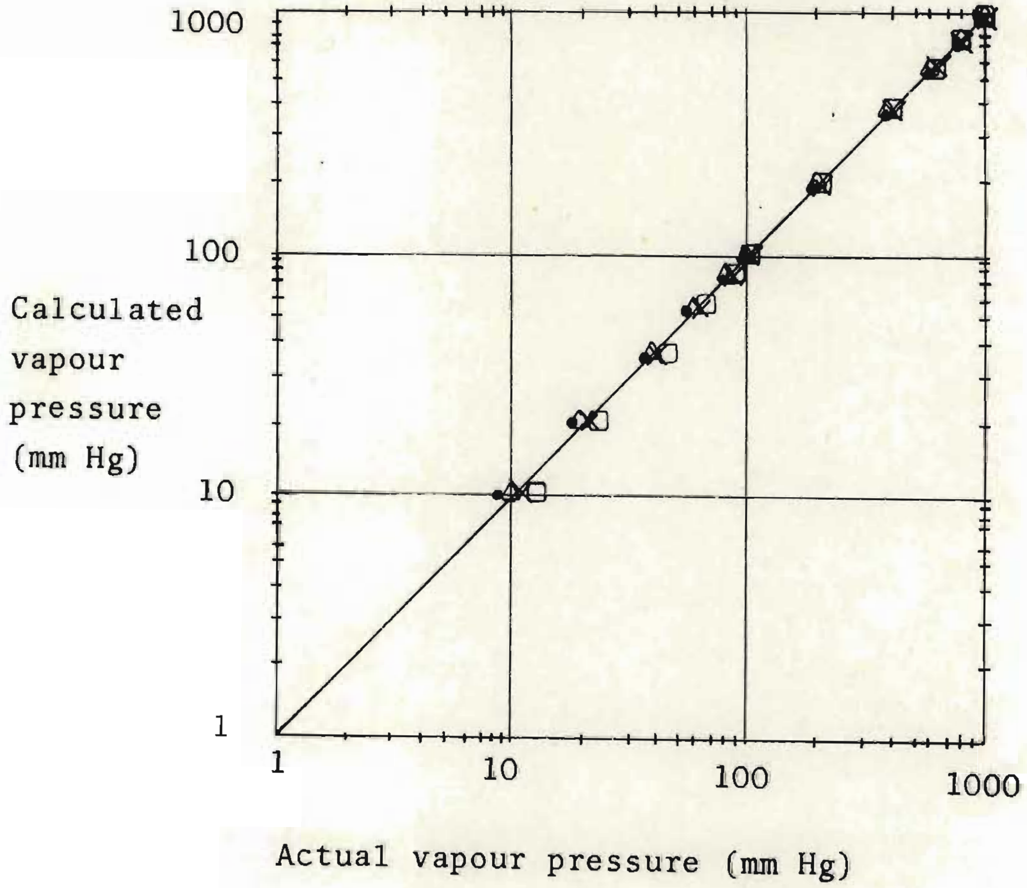


Fig. 4.5. Single parameter vapour pressure correlation

● n-paraffin

x aromatic

Δ iso-paraffin

□ cyclo-paraffin

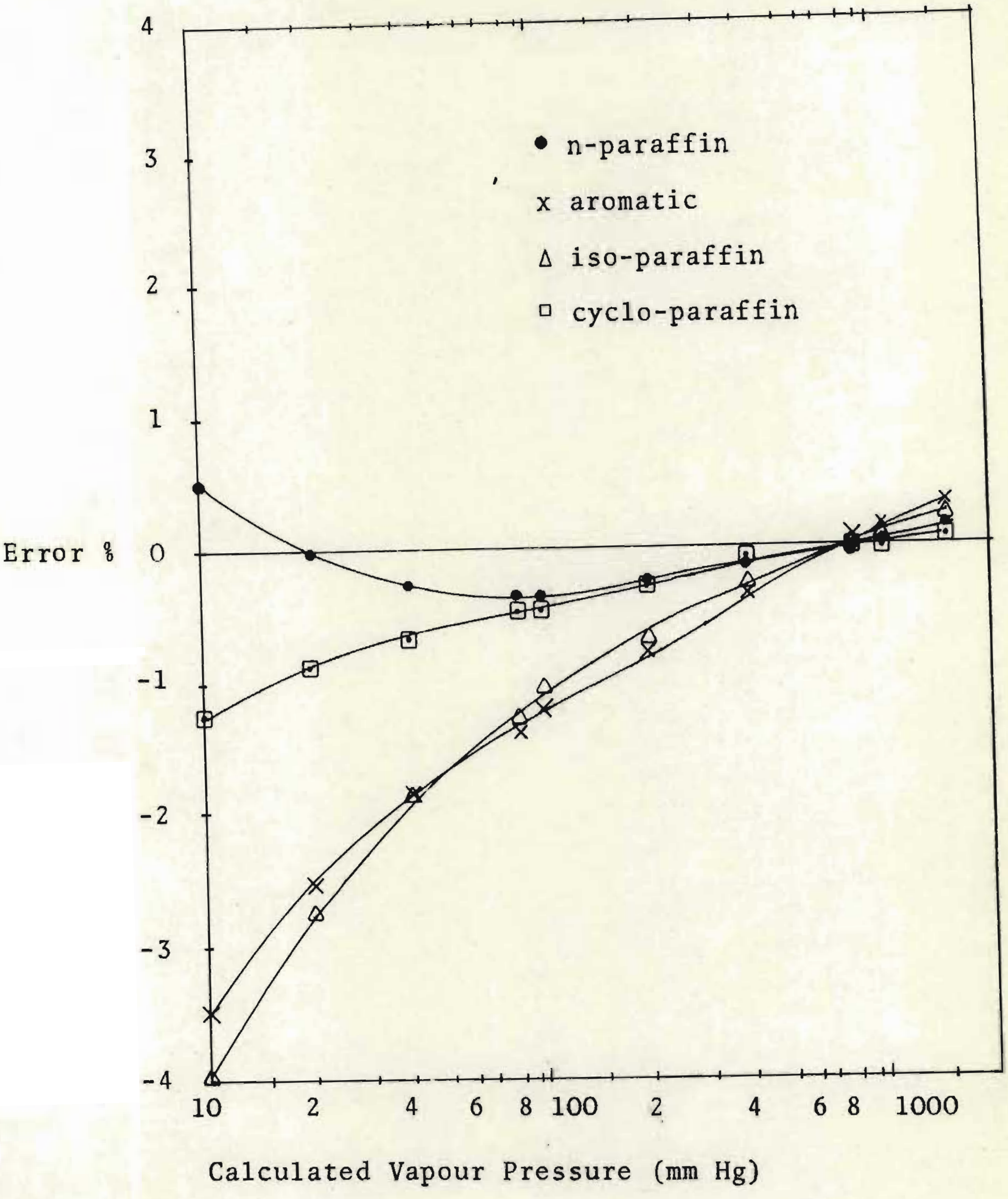


Fig. 4.6. Vapour pressure correlation error curve ($\log p_{true} - \log p_{calc}$)

When investigating rapid analysis by programmed temperature gas chromatography, it is necessary to consider the quality of separation obtained, as assessed by the resolution of recorded peaks (Littlewood, 1970). Resolution of a peak pair under isothermal conditions is defined as the ratio of peak separation to average peak width, i.e.

$$R = \frac{t_2 - t_1}{0.5\ (W_2 + W_1)} \qquad 4.10.$$

where t_1 - retention time of peak 1

t_2 - retention time of peak 2

W_1 - width of peak 1

W_2 - width of peak 2

The numerator, giving peak separation, depends on the difference in retention times of the two substances, whereas the denominator, describing peak width, is mainly a function of the column efficiency, or number of theoretical plates. The number of theoretical plates in isothermal chromatography is defined as (Littlewood, 1970):

$$n = 16\left(\frac{t}{W}\right)^2 \qquad 4.11.$$

where t - retention time of peak

W - width of peak

Assuming that the number of theoretical plates for two adjacent peaks does not differ much, an average n_{av}

may be assigned and substituting 4.11 into 4.10 the relationship obtained is

$$R = \left[\frac{t_2 - t_1}{t_2 + t_1}\right] \frac{\sqrt{n}_{av}}{2} \qquad 4.11.$$

By noting that the number of theoretical plates n equals the column length L divided by the height equivalent to a theoretical plate H and by expressing the average number of plates as well as the average retention time in terms of the more retained peak,(peak 2), i.e.

$$n_{av} = \left[\frac{L}{H_1} + \frac{L}{H_2}\right] 0.5 \simeq \frac{L}{H_2} \qquad 4.12.$$

and $t_{av} = (t_1 + t_2)\ 0.5 \simeq t_2$

equation 4.11 can be written in terms of the capacity or partition ratio of equation 3.5. as

$$R = \frac{(k_2 - k_1)}{4\ (1 + k_2)} \sqrt{\frac{L}{H_2}} \qquad 4.13.$$

where k_2 = capacity ratio of peak 2

k_1 - capacity ratio of peak 1

The first term in equation 4.13 depends only on the solute-solvent interaction; the second depends on the column efficiency. In high-speed chromatography, it is important to achieve reasonably good resolution at the shortest possible analysis time, i.e. to search for a possible set of optimum parameters to make 4.13 a maximum. This has been dealt with by a number of investigators

(Karger and Cooke, 1964; Guiochon, 1966; Grushka, 1971; Sibley, Eon and Karger, 1973) for isothermal and for programmed temperature conditions.

Since only programmed temperature operation is of importance for the present investigation, it is necessary to write equation 4.13 in the equivalent programmed temperature form, by introducing the quantity t_T, which is the isothermal retention time at the retention temperature at which a band is eluted under programmed temperature conditions. The corresponding equation is then (Harris and Habgood, 1966)

$$R_T = \left[\frac{t_2 - t_1}{4t_{Tav}}\right] \sqrt{\frac{L}{H_2}} \qquad 4.14.$$

The two terms of 4.14 can now be considered separately. The first term can be determined from a plot of retention time against temperature, as given in Fig. 4.7. Two qualitative observations may be made with respect to the effect of the first term of 4.11 and 4.14: firstly, resolution is improved in both isothermal and programmed temperature chromatography by a decrease in temperature, secondly, temperature programming improves the resolution for a range of wide boiling point compounds. From the second term of equation 4.14 it can be seen that resolution can be increased by increasing the length. This is, however, in direct confluct with the minimum time requirement, since retention time is directly proportional to column

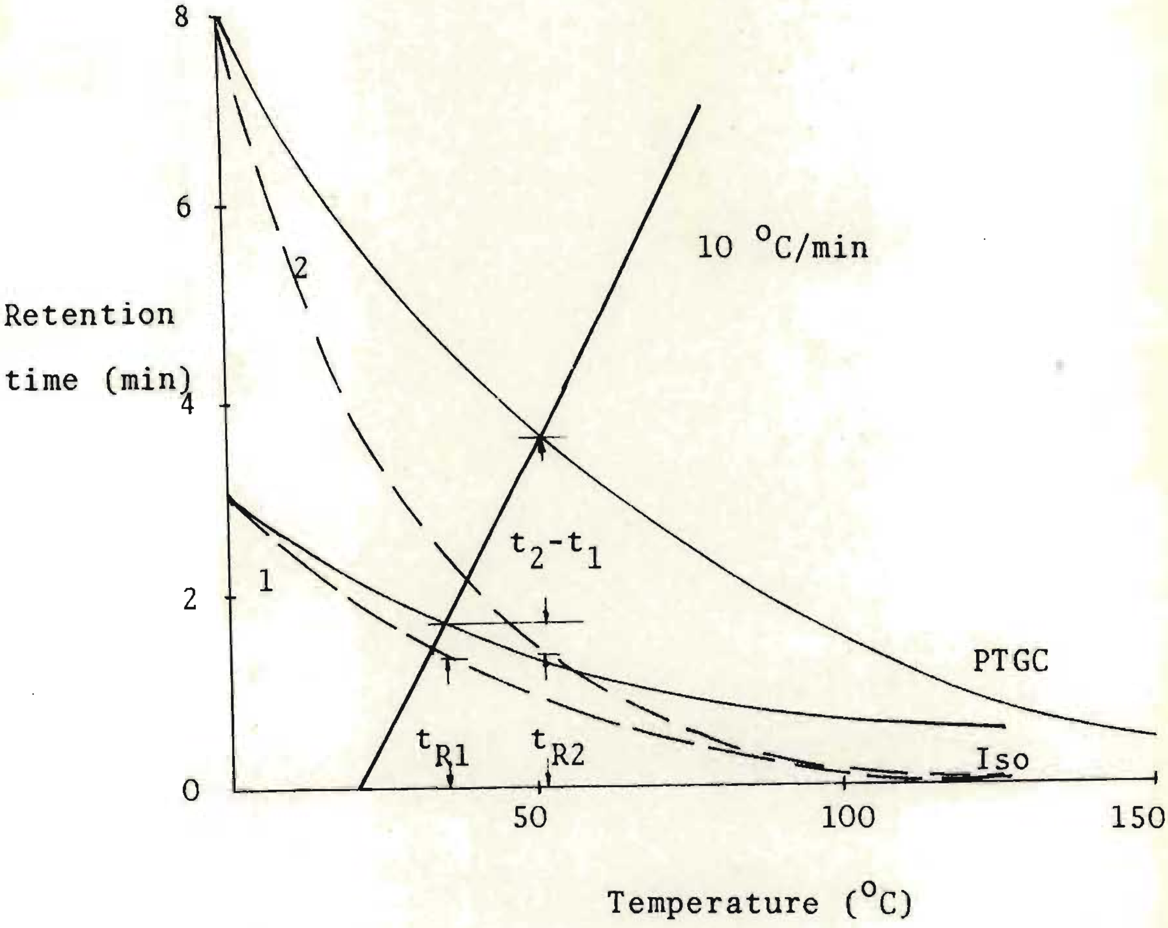


Fig. 4.7. Curves for illustrating the effect of temperature on resolution in isothermal (broken lines) and programmed temperature (solid lines) gas chromatography for two components, 1 and 2.

length. The second factor, that of the height equivalent to a theoretical plate H is a complex function of various column parameters in a programmed temperature chromatograph but an increase in the number of plates (decrease in H) has been reported for an increase in temperature. (Harris and Habgood, 1966).

These points indicate that optimizing resolution in a minimum time chromatographic procedure is only possible if the temperature dependence of the individual terms of equation 4.14 are known quantitatively. This is beyond the scope of this investigation. However, in selecting a column for rapid analysis, these considerations lead to the selection of a medium resolution packed column with a length of 5 ft. The number of theoretical plates measured isothermally is 2000. The loss in resolution for any peak pair under high temperature programming rates was found to be small, which suited the requirements for rapid analysis.

In using high temperature programming rates, not only the column performance is important, but also the experimental problems associated with rapid heating and cooling, which seem forbidding in commercial chromatographs with low heat capacity heating systems. In order to overcome this problem, it is necessary to derive a calibration procedure which does not incorporate the temperature dependence associated with simulated distillation methods (refer to paragraph 3.2.).

Characterization Procedure

The solution to the general elution equation for programmed gas chromatography has been variously reported by Dal Nogare and Langlois (1960) and Harris and Habgood (1966). These equations can be extended to include the effect of a non-linear temperature program. According to the basic relationship of gas chromatography developed in paragraph 3.1.1. the retention time of a solute (t_{Rj}) can be expressed in terms of the retention time of an unabsorbed compound (dead-space time t_{dj}) and a solute-solvent specific characteristic (k_j) (refer to equation 3.5.) as:

$$t_{Rj} = t_{dj} \quad (1 + k_j) \qquad 4.15$$

where the subscript j refers to the temperature of evaluation, Tj.

The partition ratio k_j can be related to the vapour-liquid equilibrium constant K_j by

$$k_j = \frac{H}{hK_j} = \frac{c}{K_j}$$

Observing that

$$t_{dj} \quad (1 + \frac{c}{K_j}) = t_{dj} + t'_{Rj} = t_{Rj} \qquad 4.16.$$

and approximating K_j as the ratio between the product of the activity coefficient γ and the vapour pressure p_j^o and total pressure P (equation 3.15), the net retention time (t'_{Rj}) may be written

$$t'_{Rj} = \frac{P\ c\ t_{dj}}{\gamma\ p_j^o}$$

or in logarithmic form

$$\ln t'_{Rj} = -\ln p_j^o + \ln c\ P\ t_{dj} - \ln \gamma \qquad 4.17.$$

Using the relationship developed by Guggenheim (1957) for the activity coefficient:

$$\ln \gamma = \frac{\Delta H_v - \Delta H_s}{RT} \qquad 4.18.$$

where ΔH_v - heat of vaporization of pure solute

ΔH_s - heat of vaporization of solute from a solvent

and the Clausius-Clapeyron relationship given in 3.17:

$$\ln p^o = -\frac{\Delta H_v}{RT} + \text{constant}$$

equation 4.17. may be written in the form given by Hoare and Purnell (1955 and 1956) and Knox (1957):

$$\ln t'_{Rj} = b \ln p_j^o + \text{constant} \qquad 4.19.$$

where

$$b = -\frac{\Delta H_s}{\Delta H_v}$$

is a measure of the non-ideality, since for $\Delta H_s = \Delta H_v$, the activity coefficient γ equals unity.

For solute-solvent pairs forming near-ideal solutions, equation 4.19 suggests a linear $\ln t'_R$ versus $\ln p^o$ plot. This is confirmed by experimental results plotted in Fig. 4.8. The slope of the line is approximately -0.75 for all petrochemical samples tested. The value of the constant in equation 4.19 is a function mainly of the flow rate and the form of the equation in terms of retention time applies only in the case of a constant flow rate gas chromatograph, otherwise use must be made of the retention volume which incorporates flow rate.

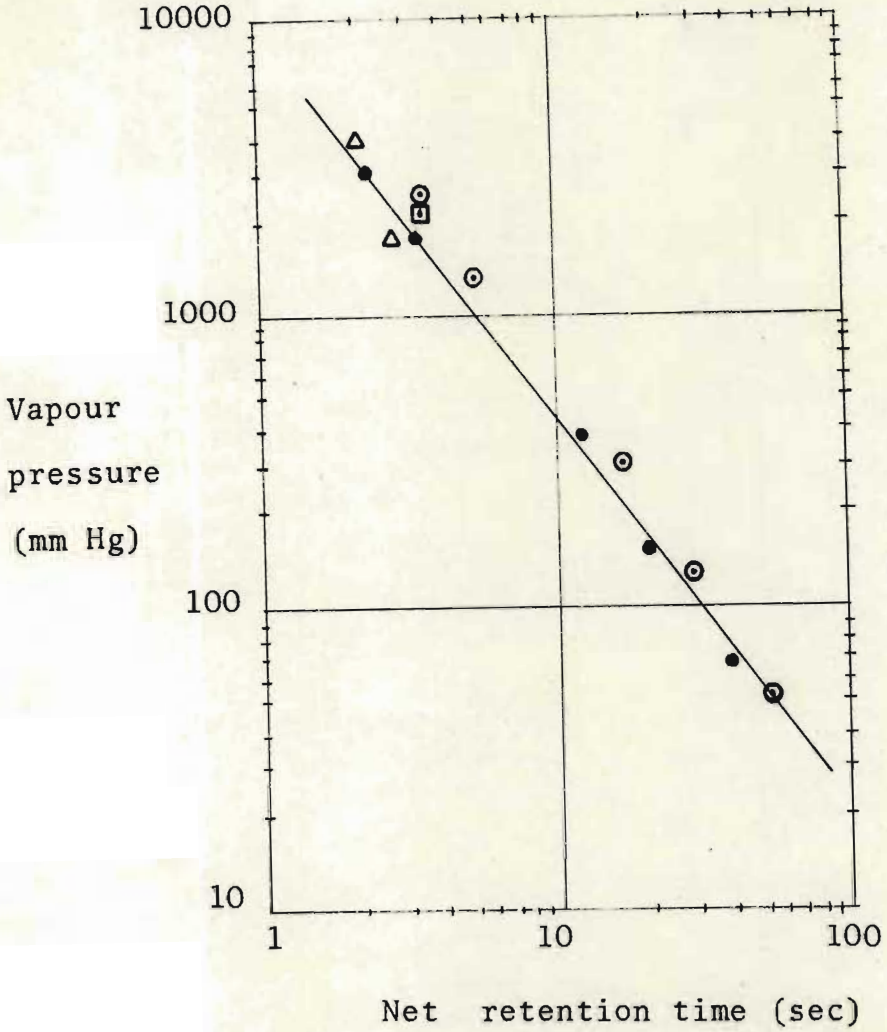


Fig. 4.8. Retention time - vapour pressure dependence of members of different homologous series

- ● n-paraffin
- ○ aromatic
- △ iso-paraffin
- □ cyclo-paraffin

The importance of equation 4.19 lies in the fact that it describes a substance under all temperature conditions, whereas the boiling point versus retention time relationships described before, only apply for a particular temperature program.

Equation 4.19 can now be written in the form:

$$t'_{Rj} = ap_j^{\,b} \qquad 4.20.$$

Equations 4.19. and 4.20. are derived for the isothermal case. In order to expand the relationship for the non-isothermal case, it is necessary to consider the movement of the solute bands in a column of length L in which the temperature is raised in a series of n isothermal steps (referred to by subscript j). A uniform temperature distribution is assumed, and no temperature gradient down the column exists.

The total retention time of any substance is then

$$t_R = \sum_{j=1}^{n} \frac{\Delta x}{\left[\frac{\Delta x}{\Delta t_R}\right]_j} \qquad 4.21.$$

where Δx - incremental distance moved by band in time Δt.

The similar expression for net retention time is

$$t'_R = \sum_{j=1}^{n} \left[\frac{\Delta x}{\left[\frac{\Delta x}{\Delta t_R}\right]_j} - \frac{\Delta x}{\left[\frac{\Delta x}{\Delta t_d}\right]_j} \right] \qquad 4.22.$$

Noting that

$$\left[\frac{\Delta x}{\Delta t_R}\right]_j = \frac{L}{t_{Rj}}$$

$$\left[\frac{\Delta x}{\Delta t_d}\right]_j = \frac{L}{t_{dj}}$$

and $\Delta x = \frac{L}{n}$

then

$$t'_R = \sum_{j=1}^{n} \frac{t_{Rj} - t_{dj}}{n} \qquad 4.23.$$

Substituting from equation 4.20.

$$t'_R = \sum_{j=1}^{n} \frac{a(p_j^{\,o})^b}{n} \qquad 4.24.$$

The criterion for characterizing a solute in the gas chromatograph is reduced by equation 4.24 to finding that set of values of p_j^o which satisfy the equality

$$1 = \frac{t_R' \text{ observed}}{\sum_{j=1}^{n} \frac{a(p_j^o)^b}{n}} \qquad 4.25.$$

for each band eluted.

It is at this point important to note that net retention times are used in equation 4.25 for two reasons:

1. By using a reference substance which is not delayed in the stationary phase but gives the true dead time of the column, difficulties encountered in accurate triggering of the data processor (or any other retention time measuring device) are bypassed.
2. The use of total retention times would necessitate the use of an expression for the dead time, in order to incorporate the dependence of this time on various column parameters.

Equation 4.25 thus permits the characterization of any GC solute as a set of vapour pressures. By monitoring the temperature in the gas chromatograph, it is now possible to identify the substances by a parameter which describes the behaviour of the vapour pressure of the substance as a function of the temperature in the column. The correlation necessary for this procedure was already developed in paragraph 4.2., with the final form given in equations 4.9.

By using equation 4.9. in conjunction with equation 4.25 and the actual GC temperature, an algorithm is established which permits the calculation of the boiling point of the pseudo-component associated with every net retention time observed, independent of the temperature conditions in the chromatograph.

The boiling point characterization procedure was tested under various temperature conditions, including isothermal runs, programming rates of up to 20 °C/min and step changes causing temperature rates in excess of 20 °C/min (40 to 200 °C in approx. 4 min) and cooling and heating cycles without allowing temperature stabilization. Substances from different homologous series were tested to verify the use of this procedure on complex petroleum mixtures. The results of these tests are plotted in Fig. 4.9. with true boiling point data (API, 1969) plotted against boiling points calculated by computer from equations 4.9. and 4.25.

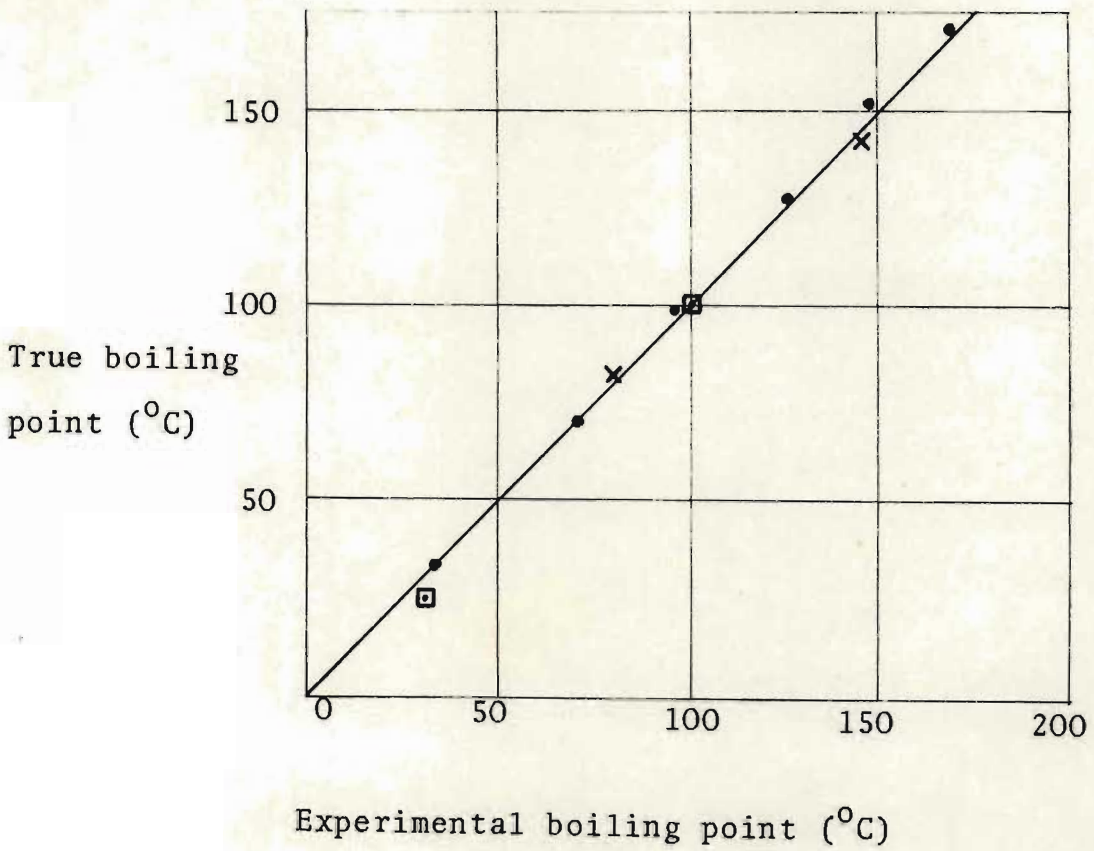


Fig. 4.9. Boiling points obtained by gas chromatograph and characterization algorithm

- ● n-paraffin
- X aromatic
- □ iso-paraffin

4.4. Fractionator Model

In developing the gas chromatographic identification procedure in the previous sections, the main consideration was the suitability of any technique used for incorporation into a fractionator control strategy. The last element of this procedure is the actual fractionator model, which uses the material identification data made available by a rapid GC analysis and the data processing routine.

In the present investigation, only steady state fractionator conditions are considered. In view of the speed of analysis and the feedforward nature of the overall procedure, as discussed in paragraph 4.5. and Chapter 8, this does not place serious limitations on the development of basic concentration control strategies which is now made possible by the characterization procedure, and offers the advantage of the availability of vast experience in steady-state plate-to-plate distillation calculation procedures.

Before describing the actual calculation procedures used, it is necessary to formulate the exact requirements:

1. The development of a completely rigorous distillation model is an impossible task. The real requirement, however, is that the model must provide a sufficiently

adequate description of the real process to produce results to a desired degree of accuracy.

2. In order to use a model for predictive feed-forward control, the time requirement becomes important. The results must be available within a period of time which has to be much smaller than the typical plant time constant for the variable to be controlled.
3. Based on requirements 1. and 2. certain simplifying assumptions are made, which have to be justified either because of their negligible effect or because of their necessity to simplify the problem to a level where it can be handled in the time permitted on the hardware available.
4. The ultimate test of any model is a comparison with the real system for which it provides an analogy.

It is against this background that existing techniques have to be studied.

The solution of the basic multi-component fractionator equations has been the subject of a very large number of publications. In a rigorous equilibrium stage calculation, there are four sets of equations which must be satisfied (refer to Fig. 4.10).

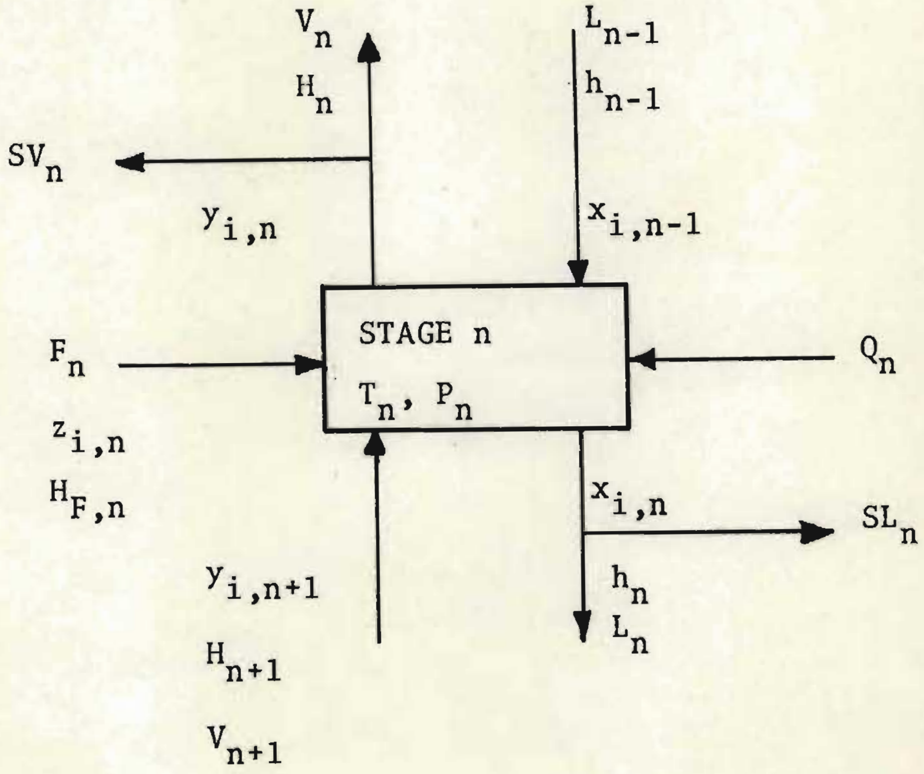


Fig. 4.10. General model for an equilibrium stage

1. Material balance for component i on stage n

$$L_{n-1}\, x_{n-1} + V_{n+1}\, y_{n+1} + F_n z_{i,n} -$$

$$(V_n + SV_n)\, y_{i,n} - (L_n + SL_n)\, x_{i,n} = 0 \qquad 4.26.$$

2. Equilibrium equation for component i, stage n

$$y_{i,n} = K_{i,n}\, x_{i,n} \qquad 4.27.$$

3. Composition restrictions on mole fractions on stage n

$$\sum_{i=1}^{NC} x_{i,n} = 1.0 \; ; \qquad \sum_{i=1}^{NC} y_{i,n} = 1.0 \qquad 4.28.$$

4. Energy balance equation on stage n

$$E_n = - Q_n - F\, H_{F,n} - L_{n-1}\, h_{n-1} + (L_n + SL_n)\, h_n$$

$$+ (V_n + SV_n)\, H_n - V_{n+1}\, H_{n+1} = 0 \qquad 4.29.$$

The independent variables which can be specified in advance are a function of the particular application, but having fixed these, the remaining variables are determined so as to satisfy the model equations 4.26. to 4.29. Of the vast number of proposed fractionator calculation procedures, two methods have gained wide acceptance.

These methods, which differ in their approach to the solution of the model equations, are:

1. The Thiele-Geddes procedure with Θ convergence and
2. The Tridiagonal matrix procedure.

These two procedures are compared in the simplified flow diagrams shown in Fig. 4.11.

The Thiele-Geddes method with Θ convergence follows the following general procedure:

Step 1: Using the principle of equal molal overflow (discussed in more detail further below) and known terminal values, an initial set of vapour and liquid flows are calculated. An initial temperature profile is estimated.

Step 2: Equilibrium constants are calculated for every component on every plate, using the temperature on the plate and suitable K-value data

Step 3: The Thiele-Geddes method (Holland, 1963) is used to solve equations 4.26 and 4.27 for phase compositions throughout the column. Absorption and stripping factors are employed.

In the rectifying section (above the feed plate) each material balance is written around a given plate and the condenser; in the stripping section (feed plate and below) each balance includes the given plate and the reboiler. Although the direction

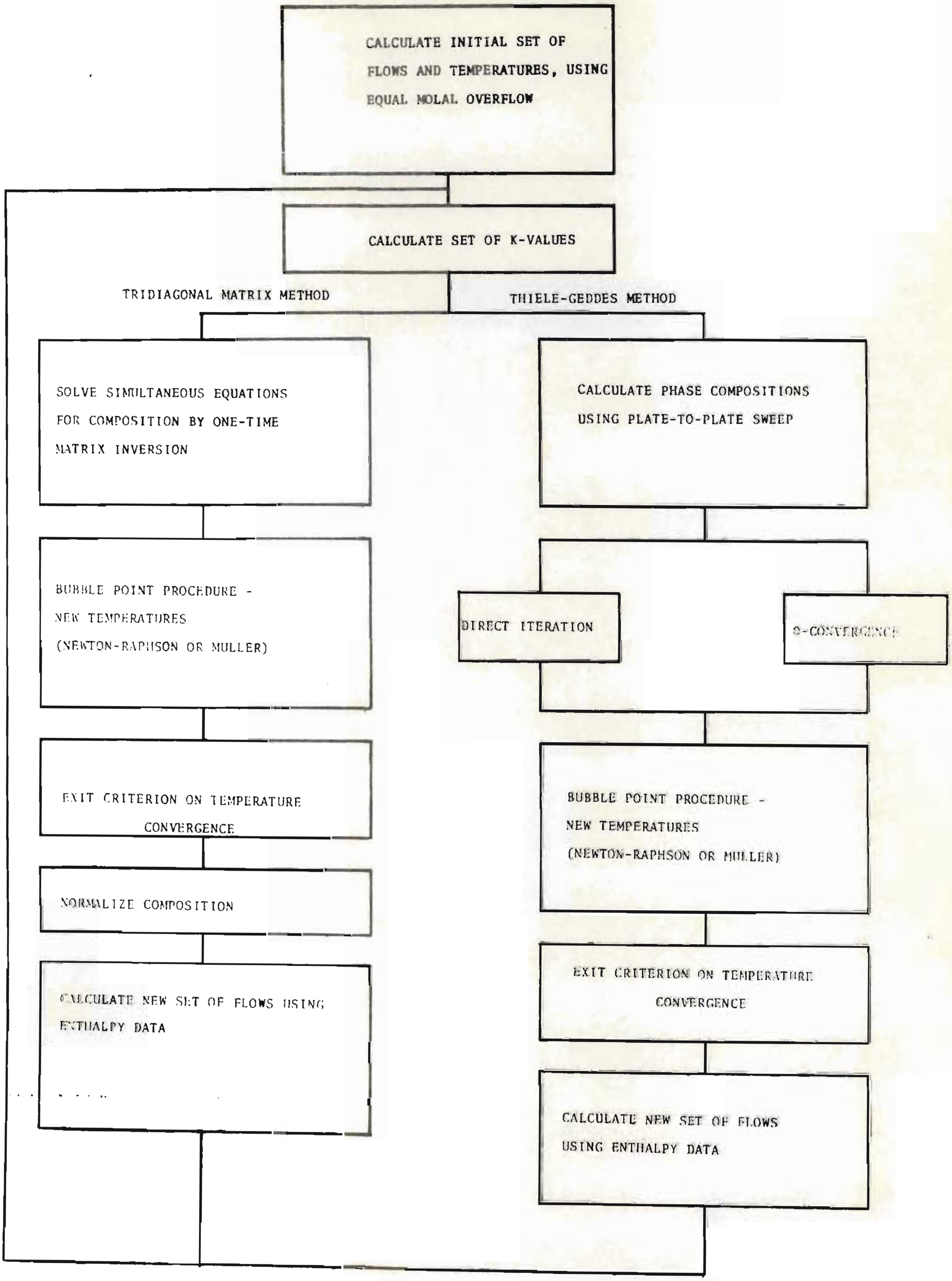


Fig. 2.11. Simplified flow diagrams for comparing the distillation models used. Left: tridiagonal method; right: Thiele-Geddes

of calculation is not significant, it is normal to carry out these calculations from each end of the column up to the feed plate where the equation for the ratio of bottoms to tops (b/d) can be solved for every component. From these values, the new estimates of a set of phase compositions can be calculated.

Step 4: If using direct iteration, these new phase composition values are used in a bubble point calculation for obtaining a new set of plate temperature values. In the Θ convergence method, convergence is speeded up by using a corrected value of b/d for calculating the phase compositions used in the bubble point procedure.

Step 5: The liquid and vapour rates can now be corrected by using enthalpy balances (equation 4.29) to remove the limitations imposed by equal molal overflow as initially assumed.

The iterative procedure is then repeated from step 2. The convergence exit criterion is usually based on the difference between a new temperature profile as calculated in step 4 and the previous estimate.

The tridiagonal matrix procedure as proposed by Admundson and Pontinen (1958) and Wang and Henke (1966) uses a rigorous computational procedure for the simultaneous solution of the model equations 4.26 and 4.27. This procedure is then basically as follows (refer to Fig. 4.11):

Step 1: Vapour and liquid flows and initial temperature estimated as at Thiele-Geddes procedure

Step 2: Equilibrium constants calculated as at Thiele-Geddes procedure

Step 3: Solve equations 4.26 and 4.27 for phase composition, using matrix methods.

Equations 4.26 and 4.27 can be combined to give

$$L_{n-1}\, x_{i,\, n-1} - (V_n K_{i,n} + L_n + SL_n)\, x_{i,n}$$

$$+ V_{n+1}\, K_{i,\, n+1}\, x_{i,\, n+1} = - F_n Z_{i,n} \qquad 4.30.$$

or

$$A_n\, x_{i,\, n-1} + B_n\, x_{i,n} + C_n\, x_{i,n+1} = D_n \qquad 4.31.$$

This can be rearranged to give a matrix equation for each component

$$\begin{vmatrix} B_1 & C_1 & & & \\ A_2 & B_2 & C_2 & & \\ & A_n & B_n & C_n & \\ & & A_{n-1} & B_{n-1} & C_{n-1} \\ & & & A_n & B_n \end{vmatrix} \begin{vmatrix} x_{i,1} \\ x_{i,2} \\ x_{i,n} \\ x_{i,n-1} \\ x_{i,n} \end{vmatrix} = \begin{vmatrix} D_1 \\ D_2 \\ D_n \\ D_{n-1} \\ D_n \end{vmatrix} \qquad 4.32.$$

The coefficient matrix is tridiagonal and the matrix equation can be solved for compositions.

Step 4: A bubble point procedure is again used to calculate a new temperature profile, using normalized compositions

Step 5: Liquid and vapour rate correction by energy balance as at Thiele-Geddes procedure

The iterative procedure is then again repeated from Step 2.

A number of important general comments have to be made:

1. Convergence

Since the equations used at various stages of both procedures described above cannot be solved explicitly for the unknowns, iteration procedures have to be used. This applies to the temperature profile calculations using the bubble point equation in Step 4 of both procedures and to the calculation of Θ values in the Θ convergence procedure used with the Thiele-Geddes calculation method. The most widely used method is that proposed by Newton, known as the Newton-Raphson method when applied to functions of several variables. Because of the fact that there is generally no assurance that this method will converge, alternative methods having a greater likelihood of success have been proposed, such as Muller's method (Wang and Henke, 1966).

In the case of the tridiagonal matrix procedure, it is normal that the sum of the mole fractions (after Step 3) on a particular plate does not equal unity. The compositions on every plate are then normalized by dividing each composition by the composition sum on the plate. Although rapid convergence is claimed for this procedure (Admundson & Pontinen, 1958), convergence was found to be slower at systems comprised of a large number of components (up to 30) than the Thiele-Geddes procedure with Θ convergence. A further difficulty, which was treated in detail for the Thiele-Geddes procedure by Holland (1963) is the introduction of enthalpy balances for correcting liquid and vapour rates before a certain degree of convergence of the temperature profile has been attained. In all calculations made using the tridiagonal matrix procedure, it was found necessary to introduce flow correction only after a number of constant molal overflow iterations. If this is not done, the procedure frequently diverges.

Both the Newton-Raphson method (at Thiele-Geddes procedure with Θ convergence) and Muller's method (at the tridiagonal matrix procedure) have been employed in this investigation. The latter method never failed to converge for the systems tested, whereas the Newton-Raphson procedure converged under certain conditions, but frequently had to be terminated because of continuous cycling between two values. This effect is due to the point of inflection exhibited by the bubble-point curve (at the solution of $\Sigma K_i x_i -1$ on every plate). Non-convergence could be avoided in all systems tested by the introduction of an upper constraint on the temperature calculated by the Newton-Raphson procedure for the next iteration.

2. Data Sources

If possible, accurate equilibrium data is used, in which the equilibrium ratio K is expressed as a function of temperature, pressure and composition, such as the generalized correlation of Chao and Seader (1961). As described in paragraph 4.2. this is not always possible. Data sources which are less complex than Chao-Seader give greatly reduced computational times (Burmingham and Otto, 1967) but different answers are obtained. In all calculation procedures used in this investigation, the correlation described in paragraph 4.2. was used.

3. Equal molal overflow

The initial vapour and liquid rates are calculated on the assumption of equal molal overflow. The approximations on which equal molal overflow is based (Mc Cabe and Smith, 1956) are:

a. In a heat balance on any plate (except feed plate, top plate and bottom plate) the following factors may be omitted (refer also to general model, Fig. 4.10):

(sensible heat in vapour V_{n+1}) + (heat of mixing) - (sensible heat in liquid L_{n-1}) - (radiation loss) and only latent heats need to be considered.

b. Chemically similar materials of nearly the same boiling point have nearly equal latent heats, as expressed by Trouton's rule:

$$\Delta H = A_1 \cdot T_B = A \qquad 4.33.$$

The resulting equal molal overflow equations are

$$V_n = V_{n+1} \qquad 4.34.$$

$$L_n = L_{n+1}$$

These approximations usually are acceptable assumptions for multi-component hydrocarbon systems, but care must be taken to ensure that the thermal condition of the feed and reflux streams is taken into account.

Introduction of the feed or the reflux at a temperature differing from the corresponding plate temperature affects the flow rates of vapour and liquid from that plate. Only in the case of a saturated liquid or a saturated vapour feed and a reflux at the top temperature may the flow rates be calculated simply by adding to the corresponding equal molal overflow rates

If these assumptions are not permissible and enthalpy data is used, it is acceptable in a hydrocarbon system to express the enthalpy of a liquid or vapour stream as a function of temperature alone, neglecting composition. (Refer to Appendix)

In order to test the effect of enthalpy balance on the internal flow rates, flow corrections are included in the program using the tridiagonal matrix procedure. The influence of these corrections on composition profiles were found to be very small, as can be seen from a comparison of the results given in chapter 7.

4. Column efficiency

Column and plate efficiencies have to be considered when carrying out plate-to-plate distillation calculations for use with industrial columns. A detailed discussion of efficiency is beyond the scope of this investigation, but since the gas chromatographic characterization procedure developed here makes it possible to carry out process stream analyses to a higher degree of accuracy than previously possible and since the data thus obtained is in a form suitable for detailed plate-to-plate procedures, it is possible to provide quantitative data on the overall efficiency of a fractionator.

Two approaches will be considered here. Firstly, a theoretical plate efficiency approach is described, and secondly the effect of overall column efficiency is considered.

(i) The efficiency of mass transfer is customarily described by the Murphee plate efficiency. Because of its simplicity, it has been preferred to employ the modified vaporization efficiency (Holland, 1963) in this investigation.

For any component i this efficiency is defined by

$$E_i = \frac{y_i}{K_i\, x_i} \qquad 4.36.$$

or alternatively

$$K_i = E_i\, \frac{y_i}{x_i} \qquad 4.37.$$

Holland proposes the use of a plate and composition dependent vaporization efficiency of the form:

$$E_{ji} = \beta_j\, E_i$$

where - β_j depends only on the plate number j

- E_i depends only on the component i

(Values of β_j approximately 0.9 to 1 and values of E_i from 0.75 to 2.00 in the examples given in Holland).

It is at this stage instructive to compare equation 4.37 with equation 3.15 which indicates that the activity coefficient, which is a measure of the non-ideality of the system as described in paragraph 3 can be used qualitatively to describe the vaporization efficiency. From equation

4.18, the ratio $\frac{\Delta H_s}{\Delta H_v} = -b$ from equation 4.19 and Trouton's rule, the activity coefficient can be written as

$$\ln \gamma \approx (1 - b) \frac{22 T_B}{R T}$$

$$= \text{const} \frac{T_B}{T} \qquad 4.38.$$

Since it is known from GC analysis that $b < 1$, equation 4.38 would suggest the use of vaporization efficiencies in excess of unity, in agreement with Holland.

(ii) The overall plate efficiency is defined as the ratio of theoretical plates to actual plates required for a particular separation. Although apparent efficiencies in excess of 100 per cent can theoretically be attained (Nelson, 1958), typical fractionator efficiencies in the order of 80 % are more usual. The effect of reduced overall plate efficiency is introduced in the fractionator calculation procedures by reducing the number of theoretical plates relative to the actual plates in the column. The effect of overall plate efficiency is shown in the experimental results.

In the present investigation the emphasis is placed on the development of a gas chromatographic procedure and the fractionator calculation procedures used therefore mainly serve to compare predicted results, based on a single feed analysis and a plate-to-plate calculation procedure, with actual composition profiles again determined by GC analysis, on every plate in the case of the pilot plant studies or at the terminal points in the case of industrial plant studies.

5. Programming

The computer programs for the two distillation calculation procedures described in this chapter are based on the following programs:

5.1. Thiele-Geddes procedure, basic program by Clark (1972), with modifications to ensure convergence and using vapour-liquid equilibrium correlation developed above.

5.2. Tridiagonal matrix procedure, based on Wang and Henke (1966), basic program from Kropholler, with modifications to use vapour-liquid equilibrium correlation developed here and enthalpy data as outlined in the appendix.

4.5. Application of GC Characterization Procedure

The most important feature of the characterization procedure developed above is the fact that it provides rapid and accurate identification of the components in a process stream in a form directly suitable for further processing. This can be illustrated by the two main applications to be described in detail:

1. Industrial plant test on an industrial debutanizer/ gasoline splitter (Chapter 5)
2. Pilot plant studies on a semi-industrial wide boiling range fractionator (Chapters 6 and 7)

In the industrial plant test, the GC boiling point characterization procedure provided the composition analysis required for a material balance smoothing procedure. Direct comparison with the TBP curves from the industrial laboratories was possible, which provided valuable insight into the pseudo-component grouping of GC peaks. The GC data was used directly in the weight fraction form provided by the GC detector and data processing procedure.

In the pilot plant studies, the GC boiling point characterization procedure was used to generate data providing an insight into the performance of the fractionator. Every experiment of the investigation covered a single feed stream analysis which provided the composition data for two plate-to-plate calculation methods. The methods provided predictions of the expected composition profiles in the fractionator using, in addition to the feed composition input, also conventional plant measurements.

The predicted profiles are compared with actual profiles as determined by plate-to-plate sampling and GC analysis. The effects of the different distillation parameters can then be tested and full details are given in Chapter 7.

CHAPTER 5

5. INDUSTRIAL DEBUTANIZER/GASOLINE SPLITTER TEST USING CHARACTERIZATION PROCEDURE

In carrying out performance test runs on an industrial debutanizer/gasoline splitter system, the very common problem had to be solved of a material balance that did not close. This is clearly occasioned by errors in flow measurement, and one of the best ways of adjusting the raw data to achieve closure is to measure component concentration in addition to the flow rates, and to use this extra information to set up an overdetermined set of material balance equations which can be solved to yield the best (least square) estimates of the flow rates (Judd, 1973).

However, characterization of the streams to and from the system in terms of component analysis is not a simple matter for a gasoline splitter; a TBP analysis is not really satisfactory since the cut between gases and the lighter ends is difficult to achieve reproduceably with gasolines, and a detailed laboratory GC analysis is also undesirable owing to the excessively large number of chemical compounds that are detected and the associated identification difficulties. The boiling point characterization procedure was therefore used to generate a smaller number of pseudo-components.

The flow sheet for the plant is shown in Fig. 5.1. The problem is to determine from the measured set of flow rates (b_j) the set of flows (x_j) that will best close the material balance equations:

$$x_1 - x_3 - x_4 - x_5 = 0 \qquad 5.1.$$

and

$$x_5 - x_6 - x_7 = 0 \qquad 5.2.$$

By determining component analysis (a_{ij}) the best estimate (y_{ij}) of the analysis is further desired, to satisfy the component material balance equations:

$$y_{i1}\, x_1 - y_{i3}\, x_3 - y_{i4}\, x_4 - y_{i5}\, x_5 = 0, \; i = 1,n \qquad 5.3.$$

and

$$y_{i5}\, x_5 - y_{i6}\, x_6 - y_{i7}\, x_7 = 0, \; i = 1,n \qquad 5.4.$$

where the subscript ij refers to the analysis of component i in stream j for the n components.

Furthermore it is known that the sum of the component analyses in any stream must total unity and hence we have the equation

$$\sum_{i=1}^{n} y_{ij} = 1 \qquad j = 1,7 \text{ excluding } 2 \qquad 5.5.$$

The equations 5.1. through 5.5. are the required set of equations, in x and y.

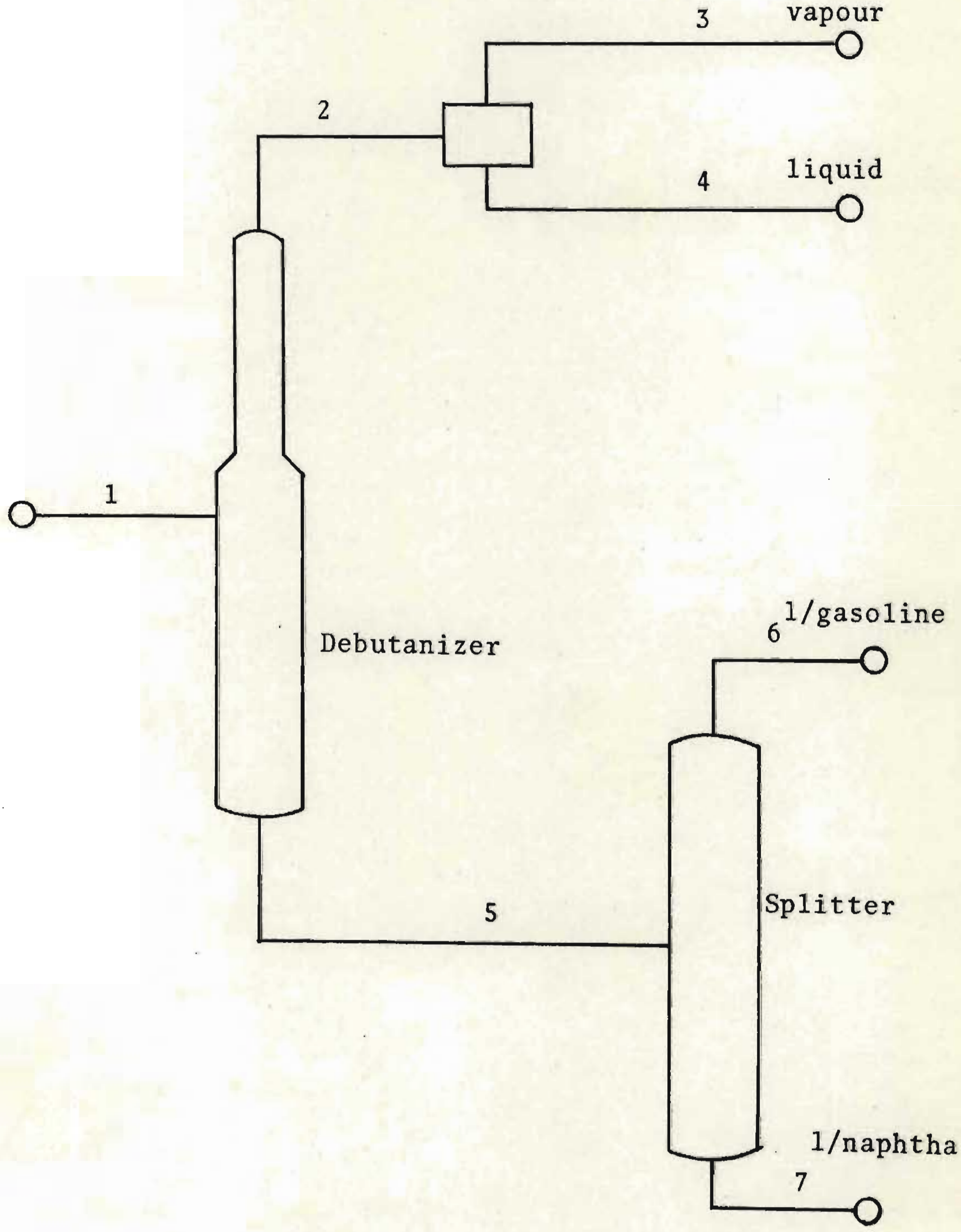


Fig. 5.1. Debutanizer/gasoline splitter flow diagram

If it is assumed that the observed and true values of the flows and analyses can be related by the equations

$$x_j = b_j + z_j \sigma_j \qquad 5.6.$$

and $y_{ij} = a_{ij} + w_{ij} \eta_{ij}$

where σ and η are related to the standard deviations of the measurements b and a, then the equations 5.1. through 5.5. can be solved by seeking that set of x and y to minimize

$$\sum_j z_j^2 + \sum_i \sum_j w_{ij}^2 \qquad 5.7.$$

subject to the constraints of equation 5.5.

The component analyses a_{ij} required above were obtained in two alternative ways. First, use was made of TBP analyses* for streams 1, 5, 6 and 7 and laboratory GC analyses of streams 3 and 4. The TBP curves were "cut" in the conventional way into 9 pseudo-components, as shown in Figs. 5.2, 5.3 and 5.4. The boiling point characterization procedure was used in the second alternative to provide TBP information in the form of discrete pseudo-components. This method yielded about 20 peaks on the samples analysed, with peaks representing a number of real components.

* TBP analyses were carried out at the plant laboratories by plant personnel

Six chromatograms were generated, one for each stream in the system (with the exception of stream 2 which is not needed in the data smoothing procedure). The results are plotted in Figs. 5.2. to 5.4. The average boiling points of the set of pseudo-components in the feed, tops and bottoms streams of each column as well as the qualitative analysis are shown in Table 5.1.

Many of the pseudo-components were common to certain streams (for example components 8a to 8j in Table 5.1. are common to both feed, debutanizer bottom and gasoline splitter bottom); these were therefore further lumped together since a detailed knowledge of such common components would not yield any further independent information for the material balance problem. Similarly the gas analyses from the debutanizer were grouped. A total of 9 lumped pseudo-components (similar to number of TBP "cuts") was thus generated.

The results of the material smoothing using the GC characterization procedure are shown in Table 5.2. The adjusted data agrees well with the results which were expected by the plant personnel. One of the completely undefined streams (x_3) was awarded a reasonable flow by the method, and one of the suspect flow meters (on stream x_6) was shown to be reading too high. When using the TBP data instead of the data generated by the GC characterization procedure, the overall least squares error after smoothing was larger. If the times required for the two methods are also taken into consideration (± 4 hours for TBP, excluding subjective cutting; ± 0.3 hours for GC procedure, affording data in the required form) it is clear that the GC characterization approach offers a practical compromise between the unsuitable TBP method and detailed component GC method in problems where a simple but characteristic analysis of petroleum fractions is required.

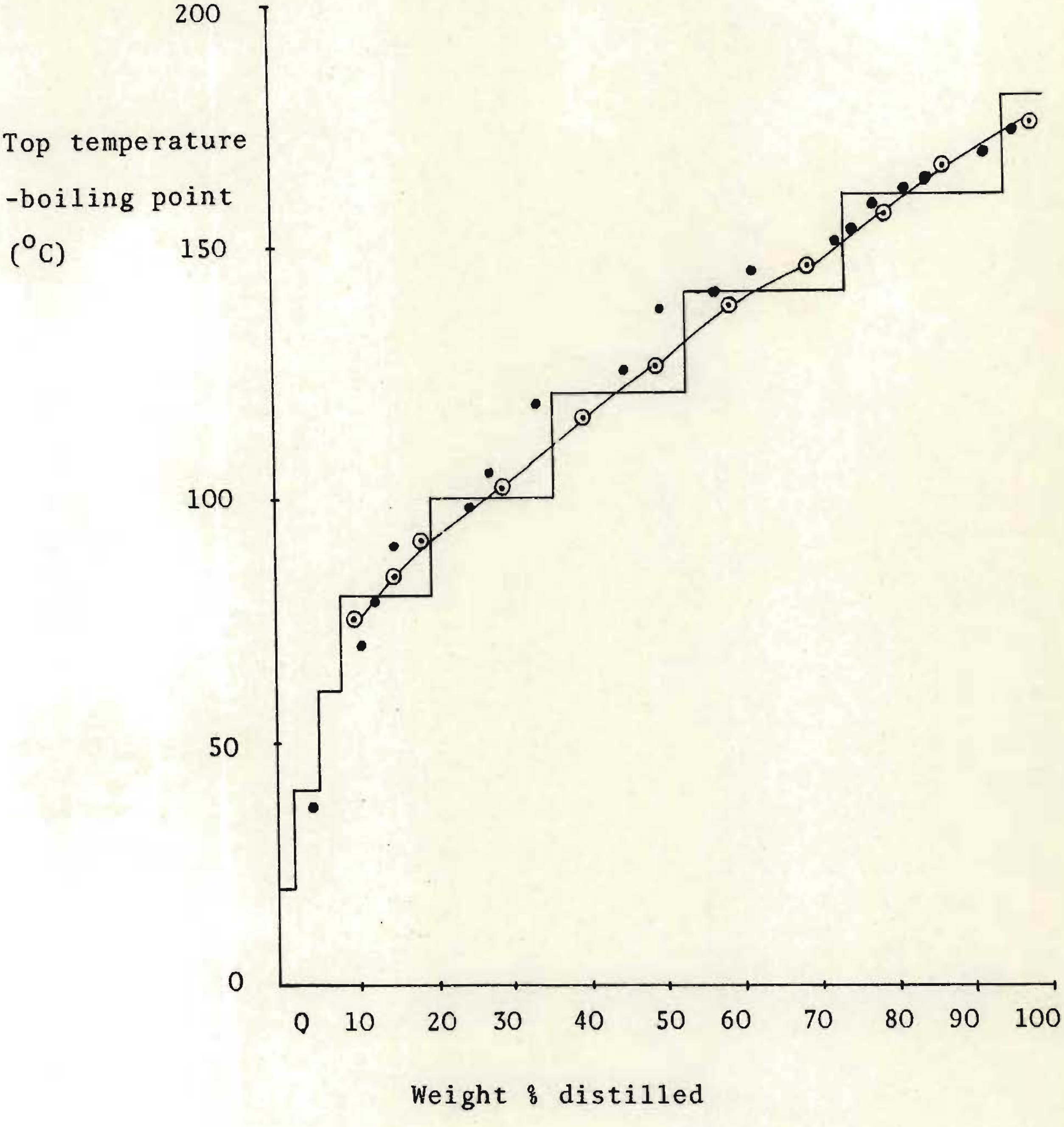


Fig. 5.2. Feed to gasoline splitter (stream 5), comparing TBP and gas chromatographic boiling point analyses

○ TBP analysis

● GC analysis

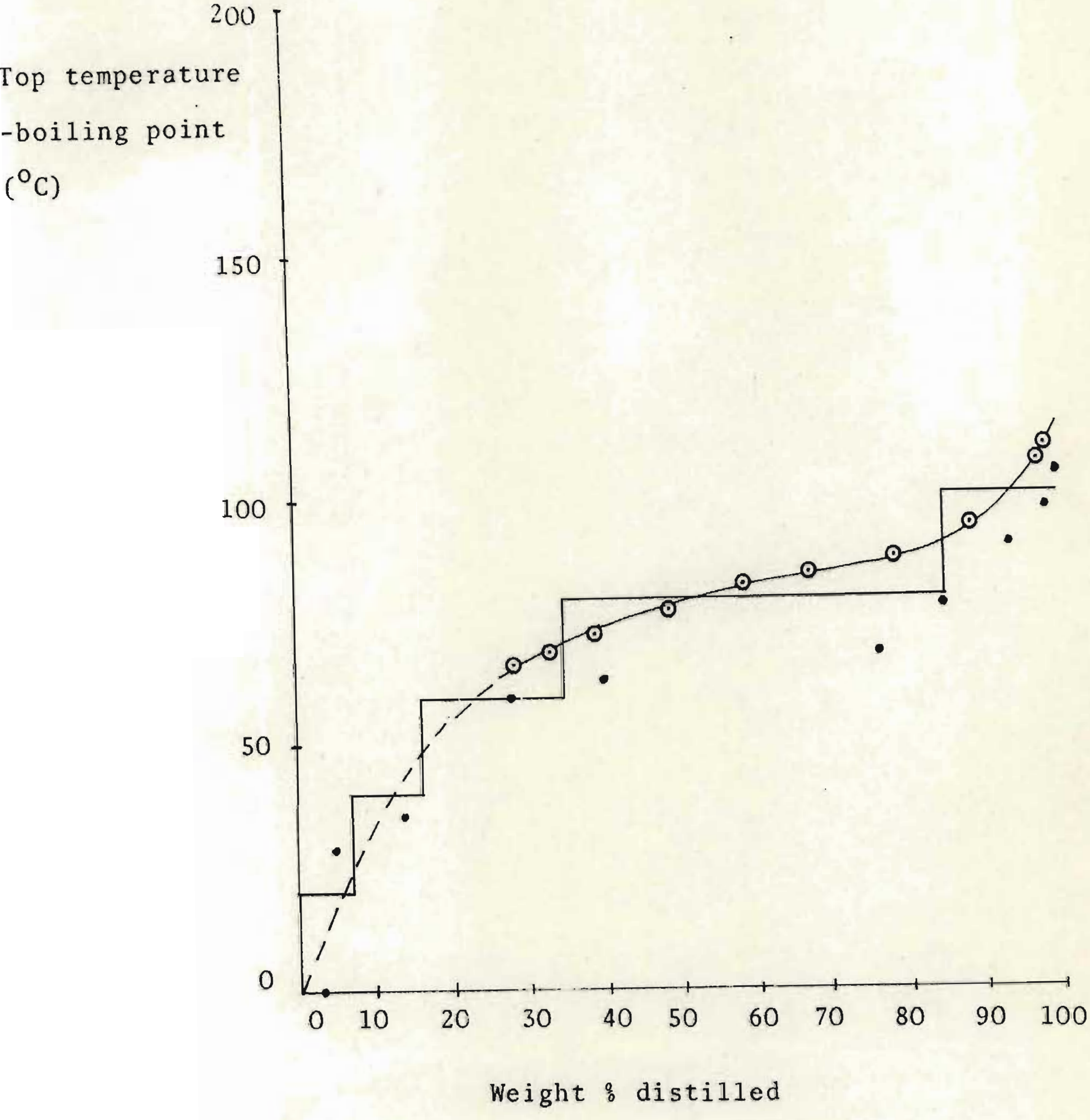


Fig. 5.3. Light gasoline from splitter (stream 6), comparing TBP and gas-chromatographic analyses

○ TBP analysis

● GC analysis

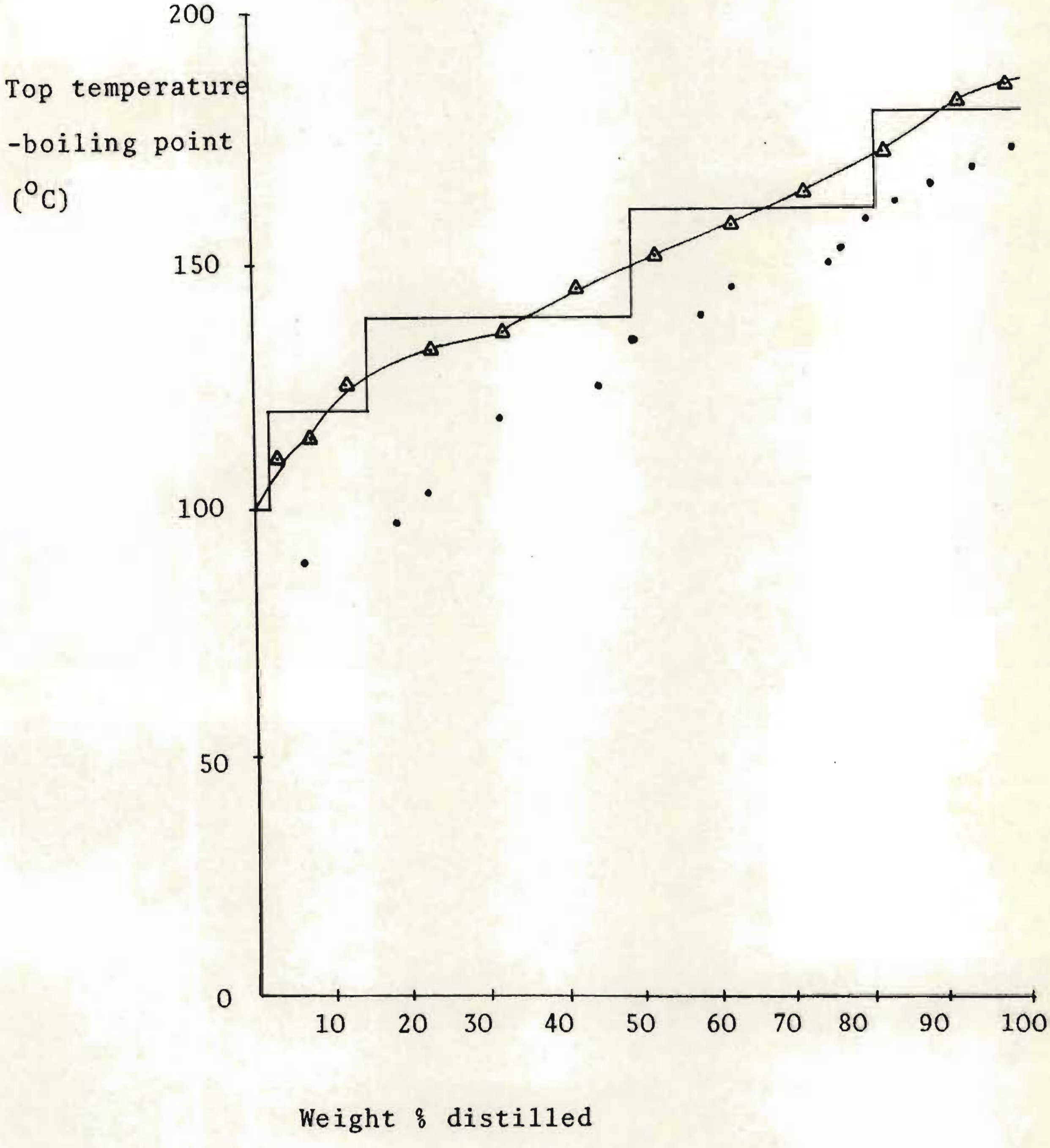


Fig. 5.4. Light naphtha from splitter (stream 7) comparing TBP and gas-chromatographic analyses

Δ TBP analysis

● GC analysis

TABLE 5.1. Component Analysis of Principle Streams (wt %)

COMPONENT		BOILING POINT °C	FEED TO DEBUTANIZER (wt %)		VAPOUR EX OVERHEAD ACCUMULATOR (wt %)	LIQUID PRODUCT EX OVERHEAD ACCUMULATOR (wt %)	BOTTOM OF DEBUTANIZER (wt %)		LIGHT GASOLINE (wt %)		LIGHT NAPHTHA (wt %)	
C_1)					0.049	0.003	)					
)					0.147	0.048	)					
C_2)	9				0.470	0.432	)					
C_3)					0.093	0.142	)	0.0				
)					0.200	0.368	)					
iC_4)						0.002	)					
nC_4)							)					
)												
	1	5.7	2.9				0.9		6.1			
	2	38.0	6.5				5.3		36.4			
	3	59.5	5.2				5.4		21.1			
	4	67.2	9.5				10.1		28.7		3.8	
5a)	5	75.1	2.4)	8.1			2.4)	8.8	5.2)	7.7	1.5)	9.1
5b)		85.4	5.7)				6.4)		2.5)		7.6)	
	6	94.2	9.7				10.0				13.0	
7a)		100.4	3.3)				3.5)				4.3)	
7b)	7	111.5	5.4)	17.3			5.7)	18.0			6.9)	22.3
7c)		119.6	8.6				8.8)				11.1	
8a)		128.0	3.1)				3.1)				3.7)	
8b)		134.6	5.3)				5.6)				6.4)	
8c)		139.5	2.4)				2.5)				3.0)	
8d)		143.8	7.4)				7.3)				9.0)	
8e)	8	150.	3.3)	41.6			2.8)	39.2			3.4)	49.6
8f)		153.	2.3)				2.4)				5.4)	
8g)		157.	3.5)				3.4)				4.1)	
8h)		160.	3.0)				2.0)				3.3)	
8i)		165.	6.3)				6.0)				7.3)	
8j)		176.	4.2)				3.3)				4.0)	

Table 5.2. Results of Material Balance Smoothing

Stream flow number j	Measured flow rate (mt/d)	Smoothed flow rate (mt/d)
1	3634	3627
3	5?	17.6
4	232	384
5	3226	3233
6	798?	601
7	2625	2629

CHAPTER 6

6. PILOT PLANT FRACTIONATOR STUDIES

6.1. Introduction

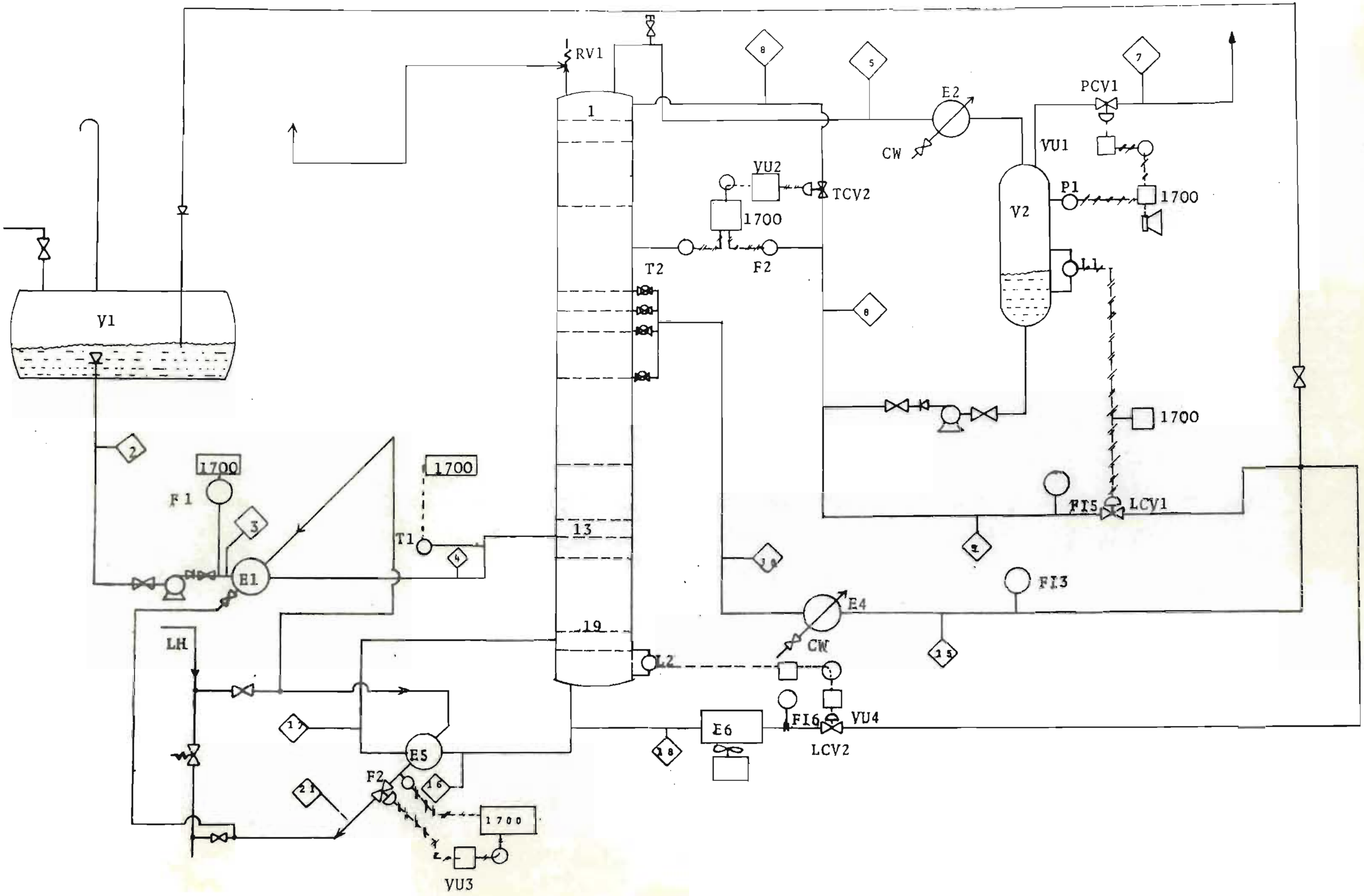
Since the fractionator control project of which the present investigation forms part requires complete freedom from the production limitations inherent to any industrial plant, it was decided to construct a pilot fractionator. Since the plant is to serve as a vehicle for testing practical control schemes, the system has a definite industrial bias and no attempt was made to bypass the difficulties experienced in running a laboratory scale experiment in a near-industrial environment.

6.2. Basic Plant Hardware

The complete fractionator lay-out is shown schematically in Fig. 6.1. The distillation column is constructed from flanged sections, using 6" mild steel pipe with table H (to BSS) flanges. Each section is 12 in. long and a total of 22 sections are bolted together to form the column. The sections are provided with 1 in. side flanges to provide access for temperature measurement and sampling probes. Details of the sieve trays used are given in Fig. 6.2. The 19 trays are inserted between the flanged sections as shown in Fig. 6.3.

	Feed				Overheads					Sidestream		Reboiler		Bottoms		Hot Oil	
STREAM NUMBER	1	2	3	4	5	6	7	8	9	10	15	16	17	18	19	20	21
Flow (kg/hr)		249	249	249	227	227	10	80	139	17	17	206	206	84	84		1210
Temperature (°C)		30	30	154	159	37	37	37	37	227	35	252	283	252	40		
Pressure (Bar Gauge)		0	1.5	1.3	1.0	0.9	0	1.5	1.5	1.0	0.3	1.1	1.1	1.1	0.3		

Fig. 6.1. Plant lay-out - see next page


RV1
1
8
5
E2
CW
7
PCV1
VU1
VU2
TCV2
1700
P1
1700
V2
F2
L1
T2
8
V1
2
1700
F1
3
1700
T1
4
E1
13
10
9
FI5
LCV1
1700
FI3
E4
CW
15
19
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LH
17
E5
F2
16
21
1700
VU3
18
E6
FI6
VU4
LCV2

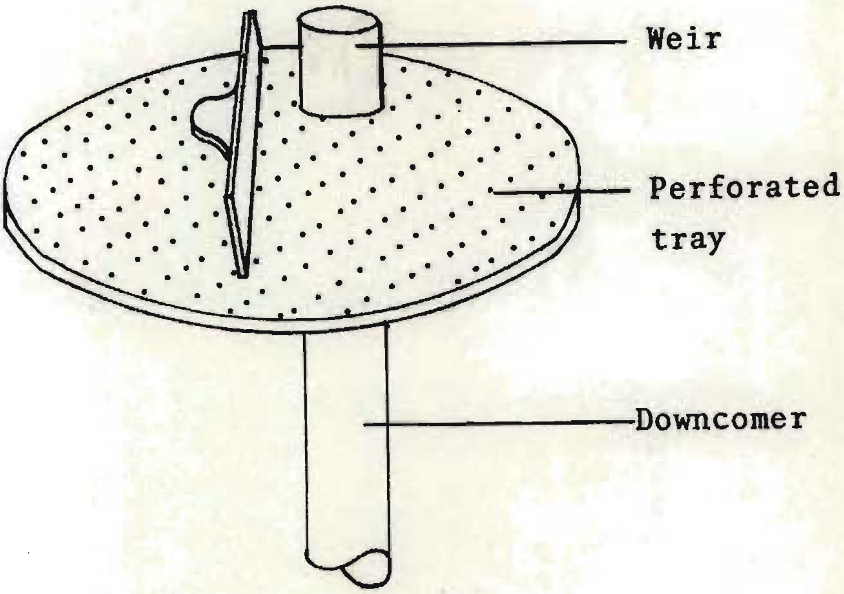

Fig. 6.2. Typical tray configuration for pilot fractionator

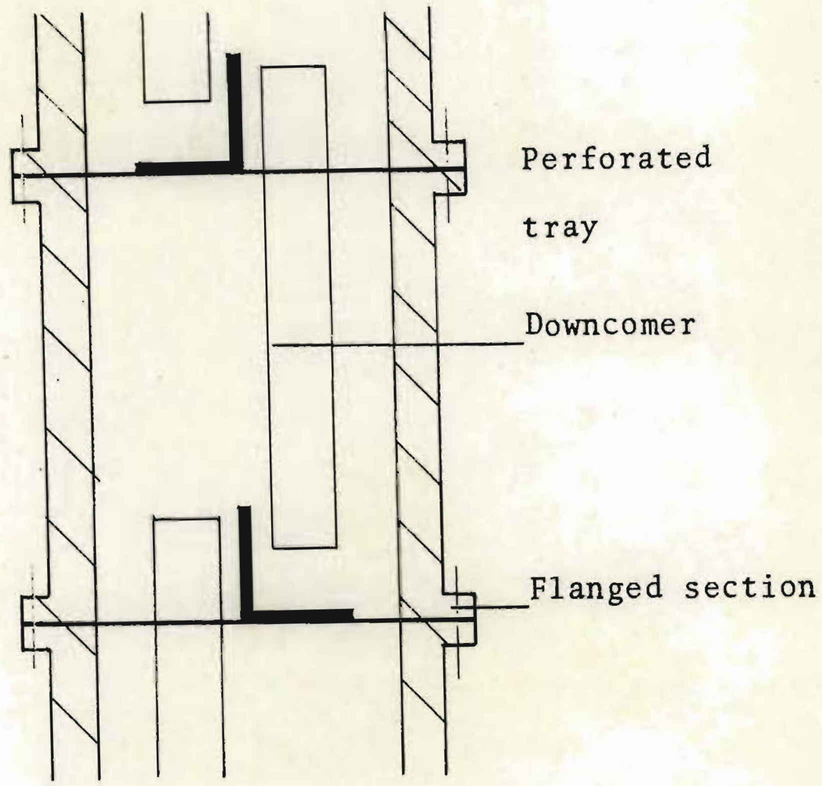

Fig. 6.3. Schematic diagram showing arrangement of sieve trays between flanged sections

The wide boiling range feedstock used (for details refer to paragraph 6.4.) is housed in a 2000 litre outside storage vessel (V1 Fig. 6.1.). The run down lines from overhead vessel, sidestream heat exchanger and bottoms cooler are combined in a return manifold where the feedstock is reconstituted and returned to the main storage vessel.

The heat supply to the bottom reboiler and feed preheater is provided by a liquid phase heater (LH Fig. 6.1.) rated at 400 000 Btu/hr. The radiant heater is gasoil fired and the unit circulates hot oil (Mobiltherm 603) at a flow rate of approximately 190 litres/min through the closed-loop system. The maximum hot oil temperature is 316 ^{o}C.

Pressure tests on the fractionator and the hot-oil loop were conducted using mains water pressure. This practice cannot be recommended for closed liquid-phase systems because of the almost insurmountable difficulty encountered in removing water from the system. In the particular case, this could only be achieved by running the heater under full load for many days.

The following heat exchangers are used in the fractionator plant:

1. Reboiler (E5 Fig. 6.1.) (Alfa-Laval type VR 125/43).

A lamella type thermosyphon heat exchanger is used to vaporize oil from the bottoms, using the hot oil supply described above. The total heating surface of 6.6 m^2 is capable of transferring 52 000 kilocalories per hour.

2. Feed Preheater (E1 Fig. 6.1.) (Alfa-Laval type VVAT)

The feed preheater also uses hot oil from the liquid-phase heater. A torell-type heat exchanger is used and provides for feed temperatures up to 150 ^{o}C.

3. Sidestream Rundown Cooler (E4 Fig. 6.1.) (Alfa-Laval type VVAG)

The torell-type sidestream cooler uses mains water for cooling the rundown to 50 ^{o}C before it is passed back to storage.

4. Overheads Condenser (E2 Fig. 6.1.) (Foster Wheeler)

A shell and tube type heat exchanger cools the overhead vapour, using mains water, before it is passed to the overhead accumulator from which the top product and the reflux are obtained.

5. Bottoms Rundown Cooler (E6 Fig. 6.1.) (Foster Wheeler)

The bottom product heat exchanger is a forced air draught finned tube unit which cools the bottom rundown to approximately 60 °C before it is passed back to main storage.

Heat exchangers were selected not only on a basis of suitability for the particular application but an attempt was made to select a wide range of exchanger types for general educational purposes and to acquaint students in the department, at undergraduate level, with different designs.

The first series of test runs (refer to Chapter 7) indicated the necessity of lagging both the column and the hot oil system. The individual sections of the column were consequently lagged by means of 1" asbestos lagging rope and the complete hot oil loop by means of fibre-glass lagging sections. This brought the temperature gradient achieved in subsequent runs to within the desired operating range.

The complete fractionator system, with the exception of the main storage vessel is housed within an enclosed laboratory, thus limiting the adverse effect of sudden ambient temperature changes. The construction was under-taken by the departmental workshop and the time required for design, purchasing of plant hardware and instrumentation, construction and testing was less than eighteen months.

6.3. Instrumentation

The instrumentation is shown on the main fractionator lay-out plan in Fig. 6.1. The basic philosophy on which the instrumentation design is based, is that it must be possible to run the plant on manual in order to test individual computer control loop strategies and no provision is therefore made for back-up control. To facilitate the changeover from manual to computer, commercially available computer-manual stations are used. These stations (Honeywell, Vutronik) are designed for use with D.D.C. (direct digital control) systems. In the manual position the station permits the output of a 4 to 20 mA dc output signal to regulate the final control element. In the computer mode, the station accepts address and update signals and contains a hold circuit for the output variable. Update signals can therefore be incremental. The interfacing difficulties experienced are described in paragraph 6.4.

Electric transmitters (4 to 20 mA) (Honeywell, Vutronik) are used for all flow, pressure and temperature measurements. Orifice plates are used with DP-cells for flow and NiCr-Ni thermocouples for temperature. Reference junction temperature compensation is provided by the transmitter. Since a two-wire 24 V system was selected, no further precautions such as zener barriers were deemed necessary for use in the explosion hazardous area. Air actuators are used on the control valves. Electro-pneumatic positioners provide conversion of the 4 to 20 mA signal into a 3 to 15 psig actuating signal. All process variable signal lines (4 to 20 mA) are hooked up to the terminals of the computer I/O interface via indicators in a control panel in the control room.

The control room also houses the gas chromatographic analysis equipment. The gas chromatograph used is a standard Varian model 2740 gas chromatograph with dual flame ionization detectors and linear temperature programmer. By using two identical columns and operating the detector amplifiers in differential mode, the signal from column bleed is cancelled and temperature programming can be accomplished with a minimum of baseline drift. In view of the requirements of the algorithm developed in paragraph 4.3., temperature in the GC oven is monitored directly by means of a NiCr-Ni thermocouple which is hooked up to the process computer.

The columns used are 1/8" x 5' stainless steel with 3 % SE 30 on 100/120 Var-A-Port 30. The stationary phase SE 30 is a non-polar liquid, methyl silicone gum, with a maximum temperature limit of approximately 300 °C. This stationary phase was selected, since it is one of the most widely used non-polar stationary phases. As discussed in paragraph 3.2., non-polar stationary phases exhibit the general characteristic of separating solutes in order of boiling point. This is true for several classes of hydrocarbons, and even though exceptions have been reported (Littlewood, 1970), no deviations were found in this investigation.

Unless specifically stated, the following standard conditions apply to all GC analyses reported

Carrier gas: N_2

Supply pressure	4.5 bar
Column flow rate (regulated by automatic column inlet pressure control)	20 ml/min

Combustion gas for FID: H_2

Supply pressure	0.7 bar
Flow rate	20 ml/min

Combustion air for FID	
Supply pressure	2.0 bar
Flow rate	300 ml/min
Column temperature	Programmed temperature from ambient (± 30 °C) to 200 °C by step change. Monitored by additional thermocouple
Injector temperatures (A & B)	215 °C
Detector block temperature	230 °C
Sample size	0.2 μl
Injection: Syringe, on column via septum	
Attenuation of electrometer	2 x
Range of electrometer	10^{-10}
Reference peak for t_{dead}	Methane, added to liquid sample before injection
Electrometer output signal range	0 to 50 mV, recorded on potentiometric recorder and hooked up to I/O interface of 1700 system.

The on-line liquid sampling system on the fractionator was originally intended for automatic sample injection into the gas chromatograph. Due to difficulties encountered with respect to the repeatability obtained from the automatic sampling valve, comprised of an on-column valve with air operated actuator, syringe techniques had to be reverted to. By using the plunger and fixed needle of a Hamilton 10 μl syringe as contact, a digital input to the computer can be used for initiating reading of the GC. The use of a reference (dead time) peak eliminated all analog reading difficulties. The liquid sampling system on the fractionator is comprised of 20 proboscises made of 1/8" OD copper tubing which enter through the side flanges on the column and withdraw liquid from the tray surfaces. After passing through a cooling bath, the sample tubes are terminated in hand valves. During a run, continuous samples are drawn, in order to reduce the response time of the sampling system and to minimize dynamic withdrawal disturbances.

6.4. Computer System

All data processing for this investigation were carried out on a CDC 1700 process computer. This processor is hooked up directly to the instrumentation described above, including the gas chromatograph. The system affords

real-time processing on a multi-program basis, which provides simultaneous access to various users, but limits the available core size. As in the industrial environment, the process computer used is required to perform more than execute the fractionator pilot plant algorithms. It is linked to various other pilot plants in the department. Limitations on core size and processing time therefore have the same significance as would be experienced in industry. For the fractionator pilot plant, use is made of both the foreground and background facilities afforded by the executive routine.
The foreground systems are:

GC data acquisition, comprising detector amplifier output signal (0 - 50 mV) and column temperature (thermocouple, mV);
Plant data logging, transmitter signals (4 - 20 mA);
GC peak deconvolution.

The background systems are:

GC peak model calculations;
Fractionator model calculations.

Interfacing problems were encountered both with respect to the GC (automatic liquid sampling valve as described before) and the DDC stations. The difficulties experienced with the latter were due to the incompatibility of the control equipment and the computer as far as signal timing is concerned. The short station updating signals required cannot be generated by the available computer hardware and additional interfacing has to be developed. This would consist of simple monostable flip-flop circuits which would provide the necessary pulse shaping for the contact-closure output of the computer. Since DDC operation of the plant is not an integral part of the present project, the three-term PID algorithm written for this purpose was not tested.

6.5. Feedstock

Despite the fact that it was desireable to operate the pilot plant under near-industrial conditions, which would indicate the use of a full-boiling range desulphurized crude as feedstock, practical limitations had to be taken into account, and the feedstock selected is therefore a "topped" and "tailed" crude. In order to provide flexibility in the selection of the boiling range, the feedstock was blended from material obtained from refinery main fractionator straight-run product streams. To distinguish between their boiling ranges, the constituents blended can be referred to as: 1. Naphtha, 2. Kerosene, 3. Gas oil.

Standard ASTM distillation experiments (API) were conducted on all three constituents and on the blend selected on the basis of required boiling range. Details of the ASTM distillations are given in Fig. 6.4 . The ASTM distillation for the feedstock is compared with the gas chromatographic equivalent in Fig. 6.5.

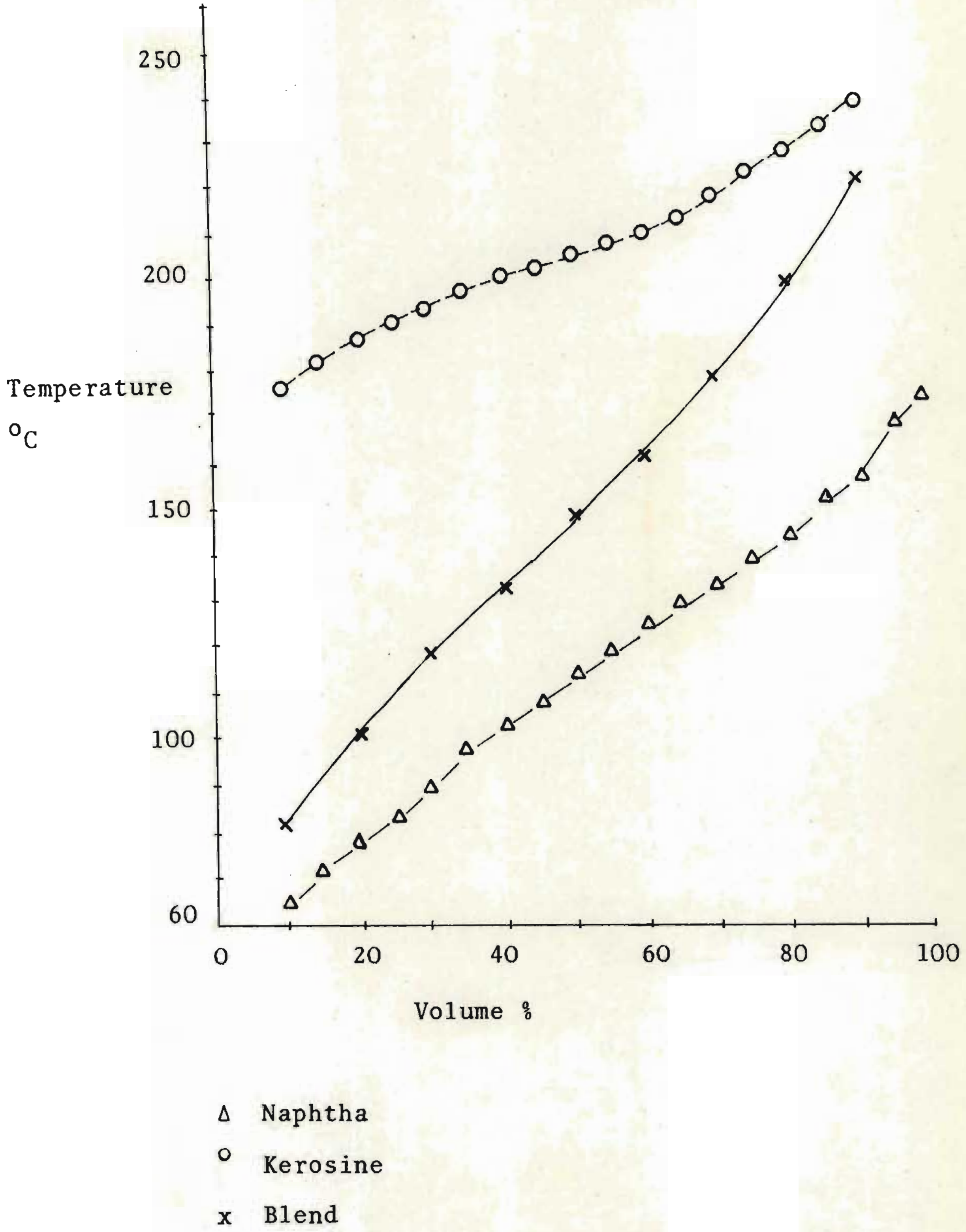

Fig. 6.4. Details of ASTM distillation analyses on feedstock

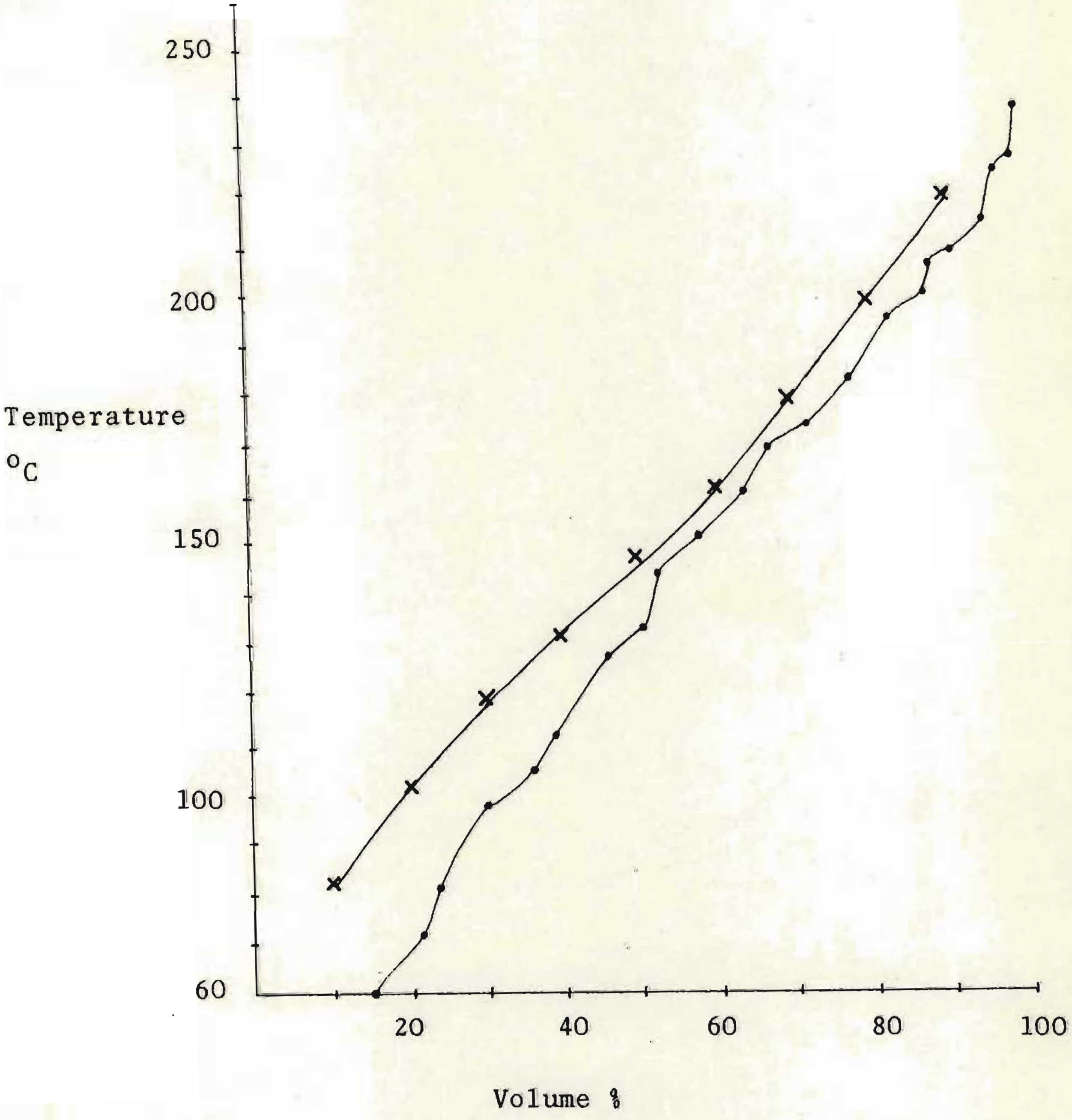

Fig. 6.5. Comparison of ASTM distillation and GC analysis of feedstock. The ASTM analysis exhibits a shift to the left due to loss of light ends

CHAPTER 7

7. PILOT FRACTIONATOR CHARACTERIZATION TESTS

7.1. General

The pilot fractionator described in Chapter 6 was used for testing all the procedures developed in this investigation. It permits the direct comparison of predicted and actual composition distribution on a plate-to-plate basis, and every attempt has been made to consider all variables which may influence the results. Care was taken to ensure reproducibility of experimental results: GC analyses were repeated where necessary, steady-state plant conditions were ensured by integrating measurements over a period of time, flow rates are checked by means of a material balance, the latter being assisted by a knowledge of the distillate-to-bottoms ratio from the corresponding GC analyses.

7.2. Test Procedure

In order to predict the performance of a fractionator, it is necessary to have a model which describes the fractionator to a suitable degree of accuracy. The steady state distillation models used in this investigation require data input from the plant in the form of temperatures, flow rates and feed composition, the latter being the main disturbance variable acting on the plant.

There remains one further important parameter, column efficiency, which forms the indispensible link between the ideal model and the true fractionator. Despite its importance and comprehensive theoretical treatment (Holland, 1963), fractionator efficiency has remained a subject treated with utmost care when comparing the theoretical and actual results of performance assessment procedures (Gilbert, Wanless and Wilsdon, 1969; Distillation, 1969). The main reason for this approach has been the lack of reliable component analysis data and the difficulties consequently encountered in attempting to "calibrate" a model using this one dominant parameter. The pilot fractionator characterization tests demonstrated that the GC procedure developed in this investigation is so accurate that it permits quantitative evaluation of overall column efficiency.

In accordance with the original aim of developing a high-speed GC characterization procedure for use as part of a predictive control strategy in an industrial environment, the GC method presented in Chapter 4 was tested by comparing the results predicted by two distillation models (using a high-speed GC analysis of the feed composition and conventional plant data) with those obtained by direct GC analysis of samples taken on the column, running under steady state conditions, on a plate-to-plate basis.

The feed analysis affords weight fraction and boiling point data as outlined in chapter 4. Weight fractions are converted to mole fractions by using average molecular weights based on n-paraffins. The feed mole fraction data, together with other plant data serve as input to the two models (Thiele-Geddes with Θ convergence, using equal molal overflow; and tridiagonal matrix using enthalpy balances for flow correction). The composition distribution profiles obtained from the models are then compared with the actual composition profiles. The influence of the different factors affecting fractionator performance (such as material balances, heat balances, column efficiencies) can then be checked in order to establish a best fit.

7.3. Results

Details of a complete plate-to-plate GC analysis series of one of the lagged test runs are shown in Fig. 7.1.* The GC traces plotted illustrate the shift of the dominant peak (or pseudo-component) from the light end

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* see Appendix

of the range (top vapour analysis) towards the heavy end (bottoms analysis). Based on the analysis of the feed also shown in Fig. 7.1. a total of 29 pseudo-components are selected for further processing. The first peak represents the undetained or dead-time component on which net retention times are based. In addition to illustrating qualitatively the performance of the fractionator, the GC traces also indicate the difficulties that could be experienced in processing the GC data obtained from wide boiling range substances, both with respect to peak identification and the assignment of areas to individual peaks, unless suitable procedures (as developed in chapter 4) are used. It is important also to note that the analysis (up to nC15) is completed in just over 3 minutes.

Details of the component distribution at the two ends of the column are given in Fig. 7.2. The first two plots contain details of the predicted profiles obtained with the two models after column efficiencies have been adjusted for the best fit. These predicted values compare well with the actual analysis on the plate. The second pair of plots in Fig. 7.2. illustrate the effect of column efficiency on the fit. The best fit was obtained for a fractionator configuration comprised of 4 theoretical plates, and the effect of both an increase and a decrease

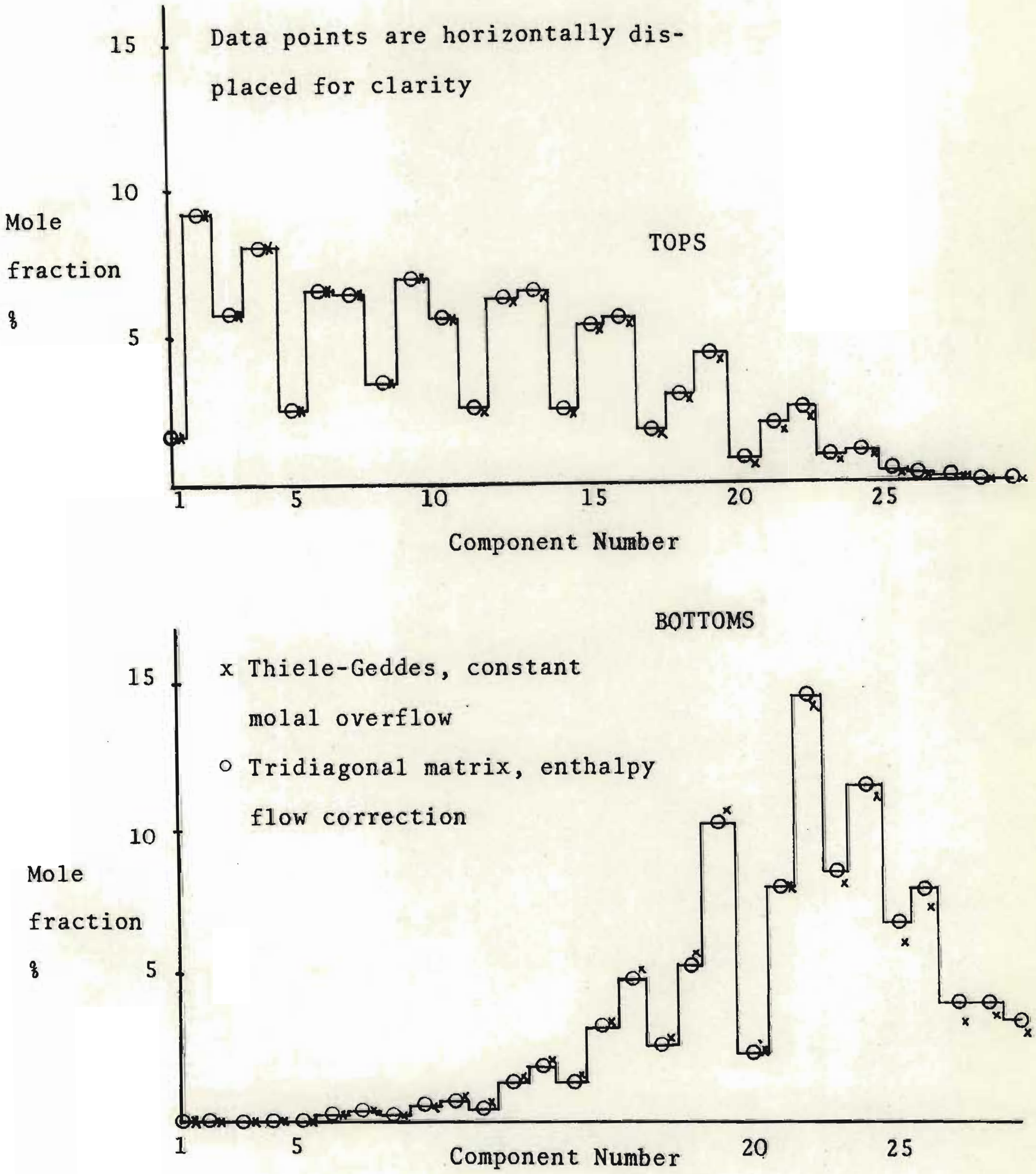


Fig. 7.2a.Composition distribution in tops and bottoms for comparing two distillation calculation procedures

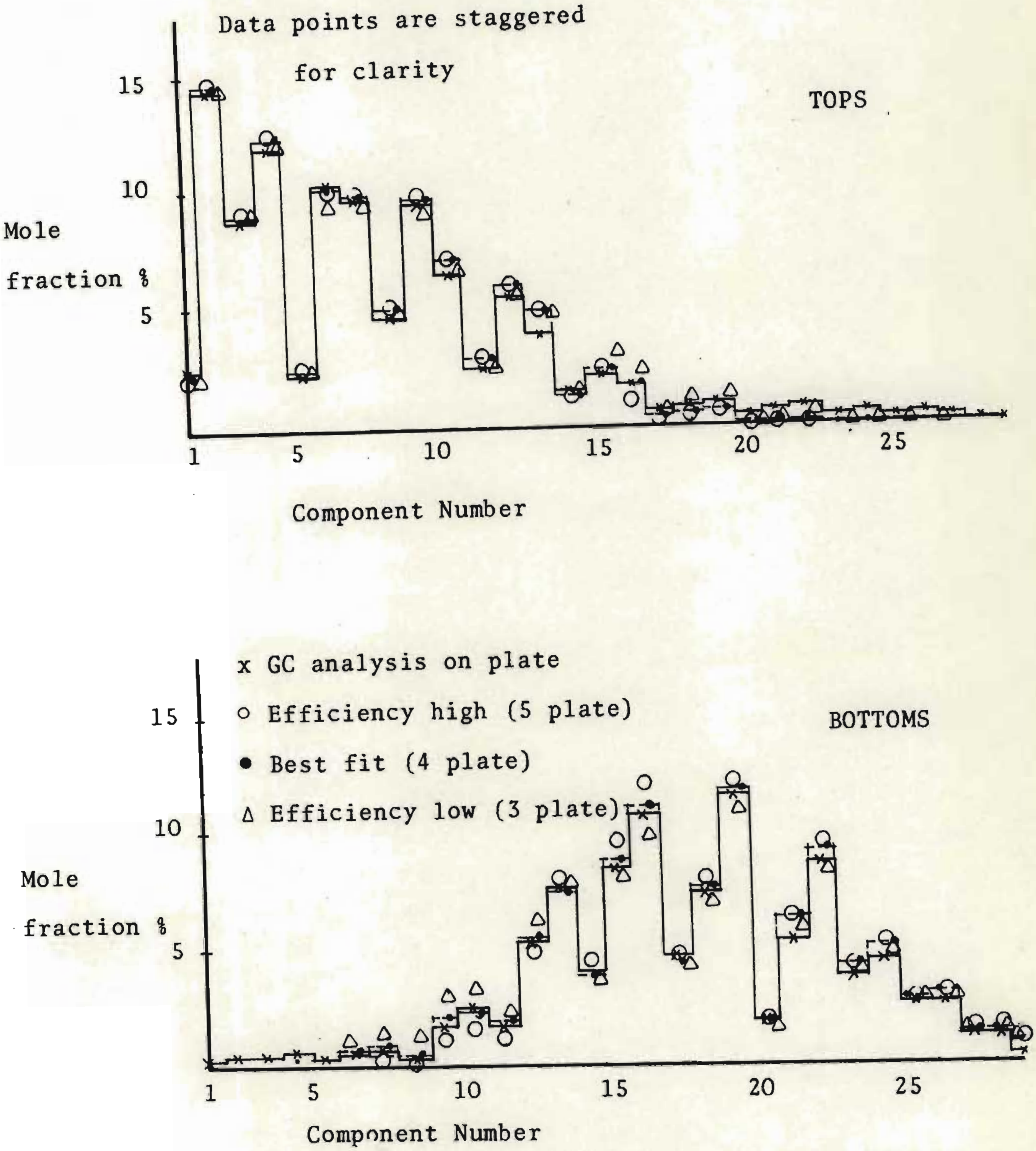


Fig. 7.2b. Effect of column efficiency (number of theoretical plates) on component distribution in tops and bottoms

in the number of theoretical plates are shown. The low plate efficiency obtained in this test run may be attributed to insufficient vapour and liquid loading of the column, and this has been confirmed by the following testing procedures:

1) Too low liquid and vapour flow rates causes insufficient contact between phases on a tray. To simulate this effect a bypass term was incorporated in the plate-to-plate distillation calculation procedure. This bypass term is obtained by withdrawing a fraction of the internal flow rate of both vapour and liquid as sidestream on every plate. This sidestream is then routed back to the column so that it, in effect, bypasses the following tray (one tray down from the withdrawal point in the case of liquid, one tray up in the case of vapour), thus not taking part in the vapour-liquid contacting on that tray. Sets of liquid and vapour bypassing coefficients can be selected for the column to describe the influence of internal flow rates on tray efficiency. Using a number of theoretical plates equal to the number of actual plates, suitable bypass coefficients could be found to achieve results similar to those shown in Fig. 7.2..

2) The influence of vapour and liquid loading on the plate efficiency could not be tested exhaustively

because of the limitations of the given plant internal hardware, the reboiler capacity and the attainable reflux flow rate. An increase in the vapour rate (at least in the rectifying section) can be achieved by increasing the feed temperature. The introduction of such a change to the distillation model produces a change in internal flow rates, but no change in efficiency (as measured by the component distribution) is predicted. In the experimental run at which a higher feed temperature was used, a small improvement in the overall column efficiency was recorded, which may be attributed to better plate flow conditions.

The accuracy of prediction of composition profiles for a complete test run are illustrated by the set of plots of Fig. 7.3. These plots are based only on the one model (tridiagonal matrix) because of the insignificantly small differences between the models.

The distillation model used for predicting composition distribution is based on plant parameters determined from the plant instrumentation. Because of the errors (especially in flow measurements) that can normally be expected, it is standard practice to carry out data smoothing before using this information in a distillation calculation procedure (Chapter 5). In the pilot plant runs this was not found necessary, but it is important to

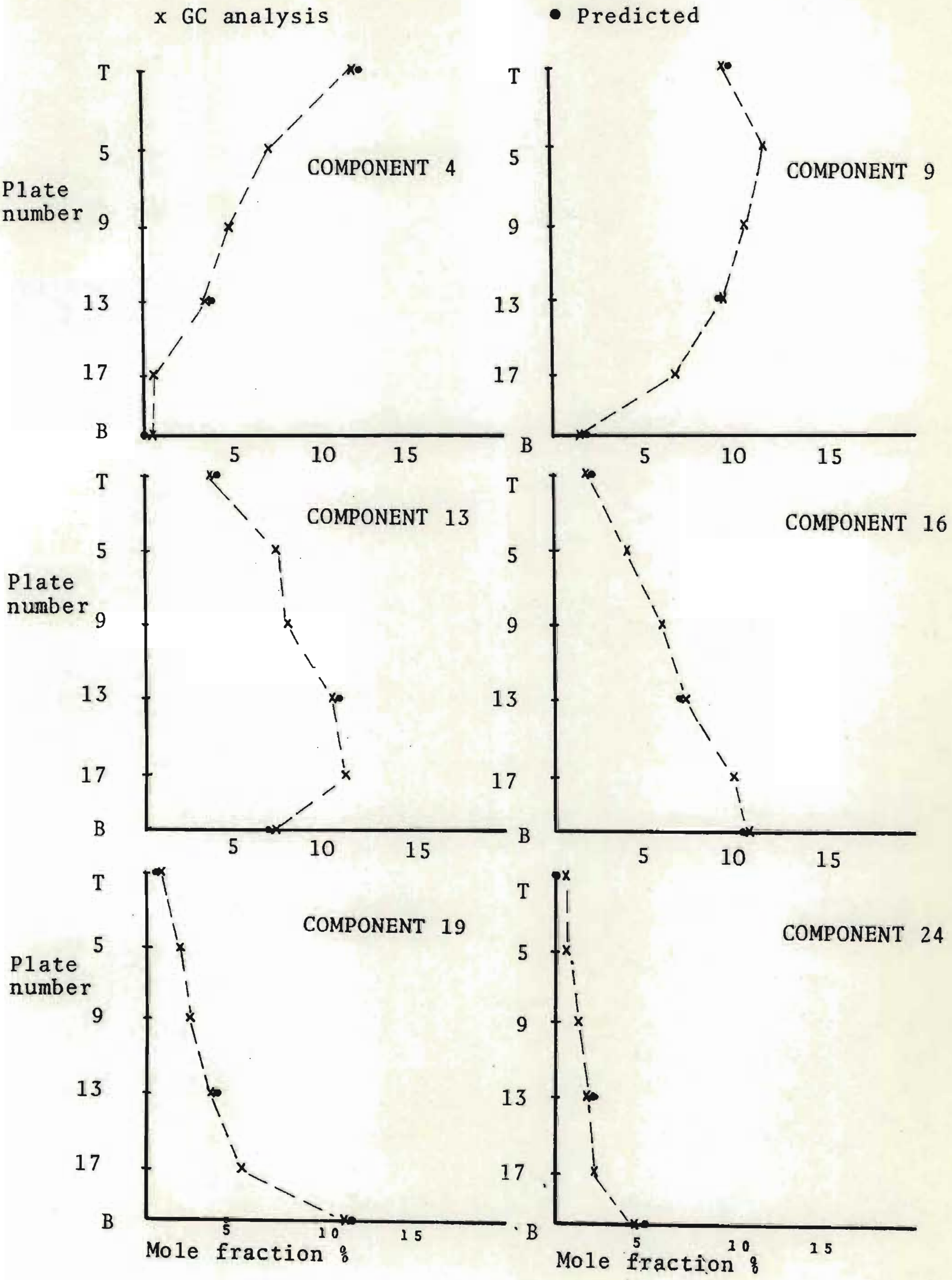


Fig. 7.3. Composition profiles for six selected components

determine the sensitivity of the results to changes in plant observations. The effect of plant parameters on a number of components is shown in Fig. 7.4. These tests clearly indicate that the two most significant parameters in the fractionator characterization procedure are material balance (i.e. distillate-to-bottoms ratio) and column efficiency (i.e. number of theoretical plates compared with number of actual plates). These and other parameters will now be discussed in more detail.

7.3.1. Column efficiency

When comparing the plate-to-plate GC analysis results with predicted values by plotting mole fraction versus component number for the top and bottom plates of the fractionator (Fig. 7.2.) it is found that a column of 100 % efficiency (number of theoretical plates = number of actual plates) exhibits a sharper cut-off characteristic, i.e. a narrower distribution profile with less overlapping between components in the top product and components in the bottom product. All further parameter tests (as described below) did not produce the required broadening effect to fit the experimental data whereas good correlation could be established by correct choice of column efficiency.

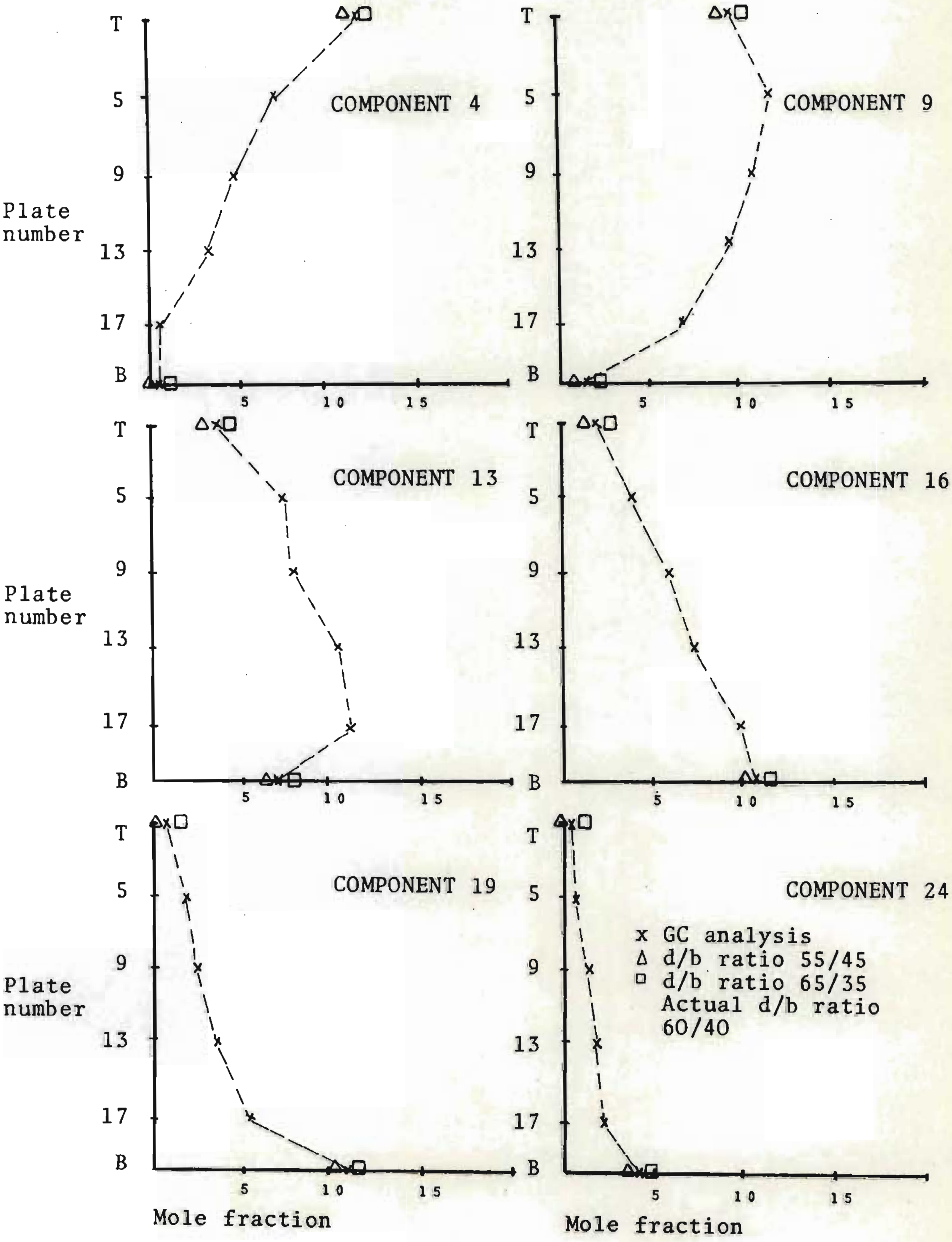


Fig. 7.4. Effect of d/b ratio on composition profiles

7.3.2. Vaporization efficiency

The use of a vaporization efficiency term in the calculation of equilibrium constants as outlined in paragraph 4.4. is appropriate, since

a) it caters for a certain degree of non-ideality in the substances handled and
b) comparison of the predicted temperature profile (assuming number of theoretical plates = number of actual plates) with the temperatures measured at two points in the column indicated that the predicted values are high. A vaporization efficiency term greater than unity causes a reduction in the predicted temperatures (Fig. 7.5.).

Since the vaporization efficiency factor described above is assumed to be approximately constant for all substances encountered in a crude oil, the influence of vaporization efficiency on component distribution on a plate is very small; in effect it corresponds to an increase in the volatility of every component without changing volatilities relative to each other.

7.3.3. GC Characterization Procedure

In order to confirm the validity of the GC boiling point characterization procedure, a detailed GC identification

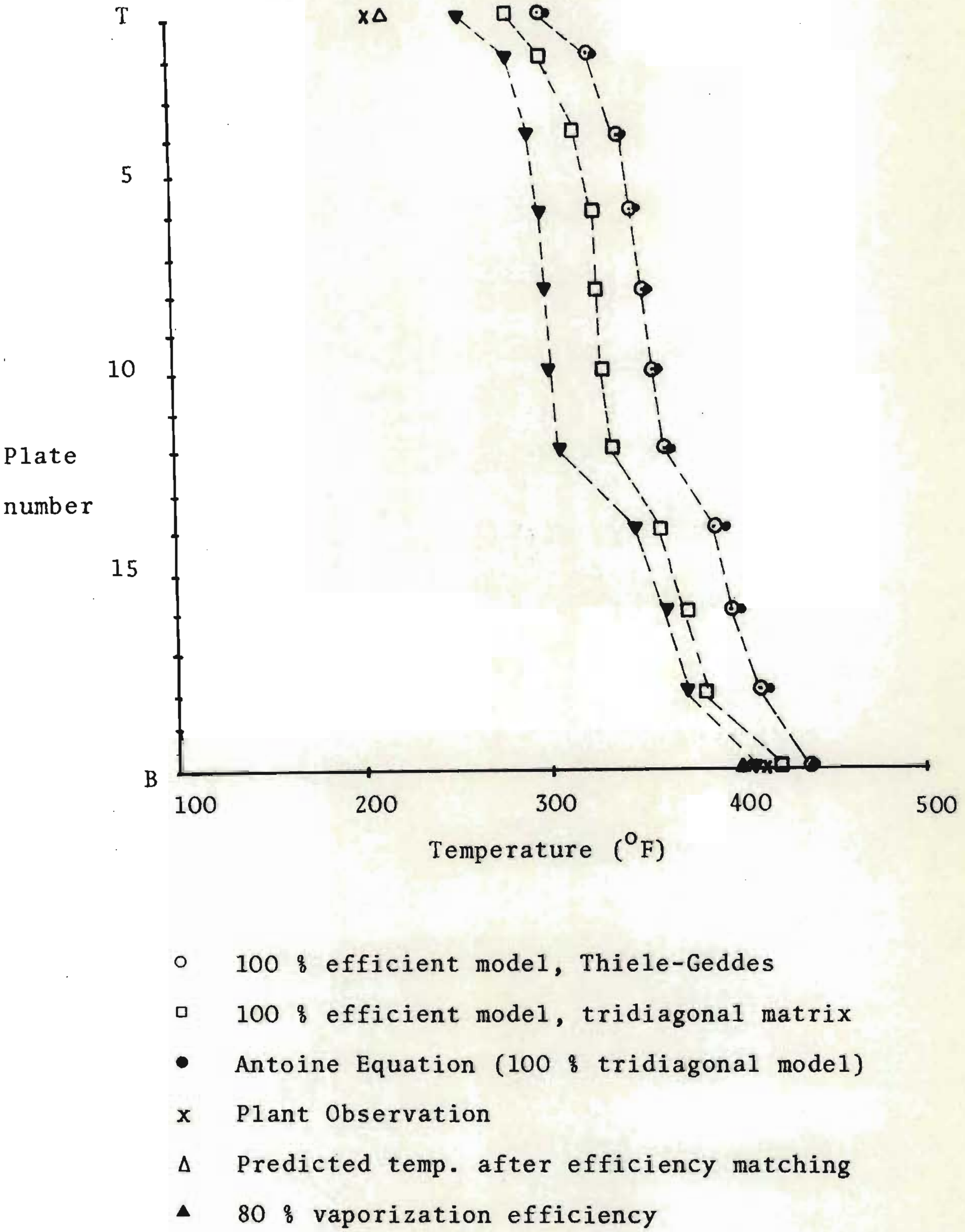


Fig. 7.5. Effect of different factors on temperature profile

test was carried out on the feed sample to establish the identity of the major constituents, using a set of standard reference components. These tests indicated that the error in the boiling point identification procedure is small (refer to Table 7.1.). The use of the actual boiling points (and not the GC identification values) in the fractionator models had no significant effect on the composition distribution results obtained.

The applicability of the vapour pressure correlation developed for this investigation was established in paragraph 4.2. To test the sensitivity of the distillation calculation procedure to the errors introduced by this correlation, the Antoine equation with parameters given by API (Research project 44, 1969), was used for the substances identified in the feed and the resulting profiles compared with those from the boiling point correlation. Again the differences were negligible and no broadening of the composition distribution was noticeable (Fig. 7.5.).

7.3.4. Reflux ratio

On a wide boiling range mixture, reflux ratio has only a small influence on the composition distribution once a certain minimum value is exceeded (Nelson, 1966) and this has been confirmed by a large number of distillation

Table 7.1. Comparison of actual boiling points with boiling points determined by GC

COMP. No.	GC BOILING POINT	ACTUAL BOILING POINT
1	15.	± 15.
2	36.	36.1
3	60.6	62.
4	72.2	68.7
5	81.	77.
6	96.	92.
7	101.	98.
8	105.	106.
9	113.	117.
10	125.4	125.6
11	134.3	135.
12	143.9	141.
13	151.7	150.8
14	160.2	160.
15	169.	165.
16	174.	174.1
17	181.4	182.
18	189.5	189.
19	194.1	195.8
20	199.7	206.
21	208.4	209.
22	214.2	216.2
23	225.7	228.
24	233.1	234.
25	242.3	245.
26	252.4	252.5
27	260.9	263.
28	266.4	270.5
29	282.3	285.

model calculations. However, since the reflux ratio affects the internal liquid and vapour flow rates, it can be expected that the overall column efficiency will be modified with a resulting change in the composition distribution. This qualitative observation was verified by experiment (Fig. 7.6.). A decrease in reflux ratio is accompanied by lower liquid loading of the rectification section. The expected decrease in column efficiency is reflected by the lower component selectivity in both top and bottom products.

7.3.5. Thermal conditions of feed and reflux

It was pointed out in the discussion of equal molal overflow in paragraph 4.4. that the introduction of feed or reflux at a temperature differing from the corresponding plate temperature affects the vapour and liquid flow rates from that plate. The influence of internal flow rates on the composition profile in a multicomponent fractionator is of the same order of magnitude as the experimental error of the investigation. This is illustrated by the results obtained from the two models (one with equal molal overflow and one with enthalpy balance flow correction) shown in Fig. 7.2. The flow corrections effected by the enthalpy balance can be seen from table 7.2., which is typical of the deviations from equal molal overflow observed at all test runs. It is clear

Table 7.2. Internal flow rates, comparison of two models, using 10 theoretical plates, run F3

Plate No.	Model with equimolal overflow Moles/hr		Model with enthalpy balance flow correction Moles/hr	
	Vapour	Liquid	Vapour	Liquid
T	0.	30.0	0.	30.
2	85.0	30.0	85.0	29.06
3	85.0	30.0	84.06	30.15
4	85.0	30.0	85.15	31.09
5	85.0	30.0	86.09	30.38
6	85.0	30.0	85.38	20.94
7	85.0	112.97	75.94	103.28
8	67.97	112.97	58.28	111.88
9	67.97	112.97	66.88	114.43
B	67.97	45.0	69.43	45.0

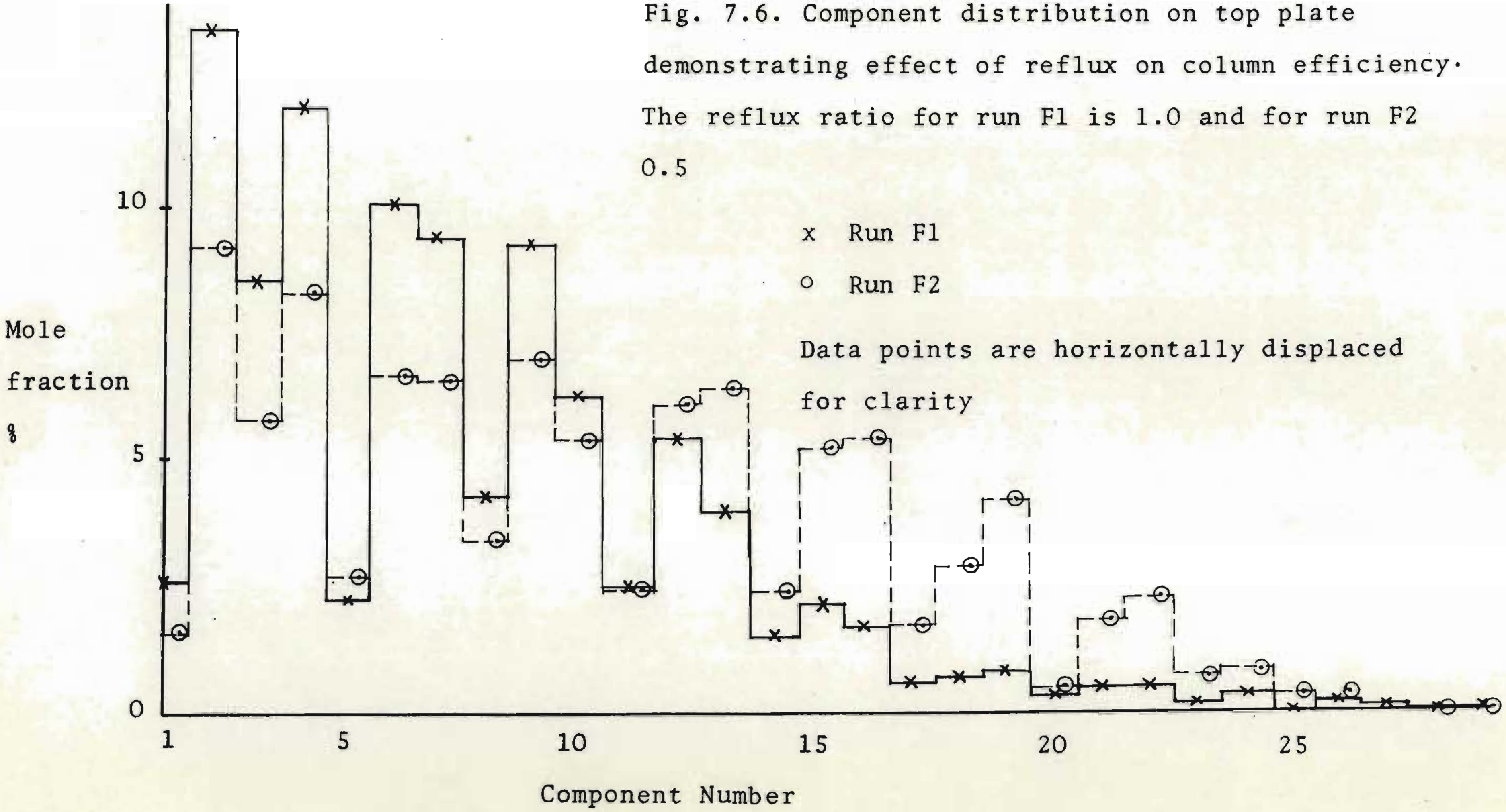


Fig. 7.6. Component distribution on top plate demonstrating effect of reflux on column efficiency. The reflux ratio for run F1 is 1.0 and for run F2 0.5

that the internal flow rates are a function of the thermal condition of both feed and reflux. The feed temperature determines the fraction of the feed in the liquid and the vapour state and the temperature of the reflux determines the fraction of the vapour on the top plate which is condensed by a cold reflux or evaporated by a superheated reflux. These conditions were investigated by using the tridiagonal matrix model with enthalpy balance feed correction. The actual plant conditions (reflux temperature, approximate thermal load of heat exchanger) were used in the model, but the influence of the different internal flow conditions thus obtained had no significant effect on the predicted composition distribution on any plate. As pointed out before, these conditions have a definite influence on the composition profile of the actual column only due to the change in plate loading and efficiency.

7.3.6. Column Pressure and Tray Differential Pressure

The sensitivity of the predicted profiles to column pressure and tray differential pressure was also determined. Changes in both these parameters had only a small effect on the composition distribution over the range tested. Values for tray differential pressure were based on published values (Nelson, 1958).

7.4. Conclusion

The comprehensive experimental analyses and detailed model calculation procedures verify the applicability of the gas chromatographic procedures for the assessment of fractionator performance.

It could be shown that sources of possible errors in the GC characterization method had an insignificant influence on predicted component distributions. By testing the effect of the main distillation variables it could also be established that the accuracy of the GC procedure is such that the overall column efficiency can be directly determined. The importance of column loading on the plate efficiency was verified by a plate by-pass model.

The semi-industrial pilot fractionator proved to be an indispensible aid in the present investigation, and the GC characterization procedure provided valuable insight into the performance of this unit.

CHAPTER 8

8. CONCLUSIONS AND RECOMMENDATIONS

8.1. General Conclusion

By deriving a simple model describing a component property, boiling point, in terms of retention time and the temperature history in the chromatograph, it has been possible to develop a high-speed characterization procedure which uses standard equipment under programmed temperature conditions for analysing wide boiling range hydrocarbons. The procedure solves the problems which have in the past precluded the use of standard equipment and which have necessitated analysis times which were not compatible with the requirements of industrial control. This GC method forms part of and immediately provides data in the discrete form required by the fractionator performance assessment procedure developed in the investigation.

The parts constituting the assessment procedure were individually tested and the applicability of the overall scheme verified by two different experimental applications, the industrial plant test (chapter 5) and the pilot fractionator tests (chapter 7). In addition to the possibility of providing conventional composition data, it could be demonstrated that the accuracy of the method is sufficient to permit the quantitative evaluation of fractionator efficiency.

One of the main factors attributing to column efficiency, namely effectiveness of phase contact on a tray, was shown to be accurately described by a bypass model.

In order to justify the significance attached to the overall efficiencies found by this procedure comprehensive experimental and computational results are provided.

8.2. Recommendation for further work

Since the GC fractionator performance assessment procedure is the first of a series of investigations on fractionator control by process computer, it is clear that a vast and difficult, but rewarding, field still has to be covered. It is, therefore, necessary to limit the present discussion to the direct application of the procedures developed here to fractionator control.

Since it has been possible to achieve the aim of a rapid feed composition analysis coupled to a predictive feed-forward model for describing the performance of the fractionator, the possibility now exists of implementing a composition control scheme where the main disturbance variable, feed composition, can be corrected for.
Used in conjunction with existing or, where necessary, new gas chromatographic product specification and testing methods, the following column control scheme can be visualised:

1. Fractionator feed composition feedforward control, specifying sidestream withdrawal locations where the composition is such that prescribed product specifications of the sidestreams can be met.

2. Feedback control loops on sidestreams, controlling withdrawal quantity as a function of the product specification.

Although this represents a dynamic situation, the fractionator model calculations can be repeated to suit the new set of conditions without re-running the feed analysis. The advantages of such a sidestream withdrawal policy would result from the possibility of maintaining the main controlled variables (reflux ratio and reboil rate) as steady as possible (close to maximum design values) and controlling product quality by withdrawal location and withdrawal quantity only. In view of the growing economic pressure to maximize the yield of certain products (eg. gasoline) there is a definite incentive for considering this avenue of research.

APPENDIX

9. APPENDIX

9.1. Derivation of equation 4.19.

From equation 4.17.

$$\ln t'_{Rj} = -\ln p_j^{o} + \ln c\,P\,t_{dj} - \ln \gamma \qquad 9.1.$$

Consider the term $c\,P\,t_{dj}$ in 9.1.

Define $A = c\,P\,t_{dj}$

$$= \frac{H}{h}\,P\,t_{dj} \qquad 9.2.$$

Noting that

$$t_{dj} = \frac{V_G}{\dot{V}}$$

where V_G - volume of mobile phase in column

$\dot{V}$ - flow rate of mobile phase in column

and from 3.12., equation 9.2. may be written

$$A = \frac{RTW_s}{PM_sV_G} \quad P\,\frac{V_G}{\dot{V}}$$

$$= \frac{RW_s\ T}{M_s\ \dot{V}}$$

In the case of a constant flow chromatograph, the value of A as described by 9.3. is largely temperature independent. This has been confirmed by experiment.

Equation 9.1. may then be written

$$\ln t'_{Rj} = -\ln p_j^o + \ln A - \ln \gamma$$

Using 3.17. and 4.18. this becomes

$$\ln t'_{Rj} = \frac{\Delta H_v}{RT} - \frac{\Delta H_v}{RT} + \frac{\Delta H_s}{RT} + \text{const.}$$

$$= \frac{\Delta H_s}{RT} + \text{const.}$$

$$= -\frac{\Delta H_s}{\Delta H_v} \ln p_j^o + \text{const.} \qquad 9.4.$$

which is the form given in equation 4.19.

9.2. Parameters for Correlations used in Distillation Calculations

A program (POLY) was used to fit a polynomial to experimental data in order to obtain parameters for the following correlations.

9.2.1. Molecular weight - boiling point

Based on the known molecular weights and boiling points (in $^{\circ}C$) of n-paraffins the correlation found is :

$$\text{Mol. wt.} = 61.1435 + 0.2966\,(\text{boiling pt.}) + 0.00098\,(\text{boiling pt.})^2$$

Using the assumption that the FID response is governed by weight, this correlation is used for the conversion from weight fractions (provided by GC analysis) to mole fractions (required by distillation calculations).

9.2.2. Vapour heat content and liquid heat content as a function of temperature

Enthalpy data is required for correcting internal vapour and liquid flow rates in accordance with the energy balance equation 4.29.

Vapour enthalpy can be calculated from

$$H = \lambda + T\,c_p$$

where λ - latent heat

c_p - heat capacity

T - temperature

The relationship for liquid enthalpy is

$$h = T\ c_p$$

For the present investigation, total heat content was calculated from published data (Nelson, 1958), which is plotted against temperature with API gravity as parameter. A value for the latter was calculated from the SG's measured on the plant. Using this data, the polynomials fitted for total heat content were:

$$H = 162.9199 + 0.3259\ T + 0.0003\ T^2$$

$$h = 0.4678\ T + 0.0003\ T^2$$

with H and h in Btu/lb
and T in ^{o}F

These values are converted to Btu/mole, as required by the program, by using average molecular weights.

9.3. Details of plant hardware

The lay-out of the pilot fractionator is shown in Figs. 9.1. and 9.2.

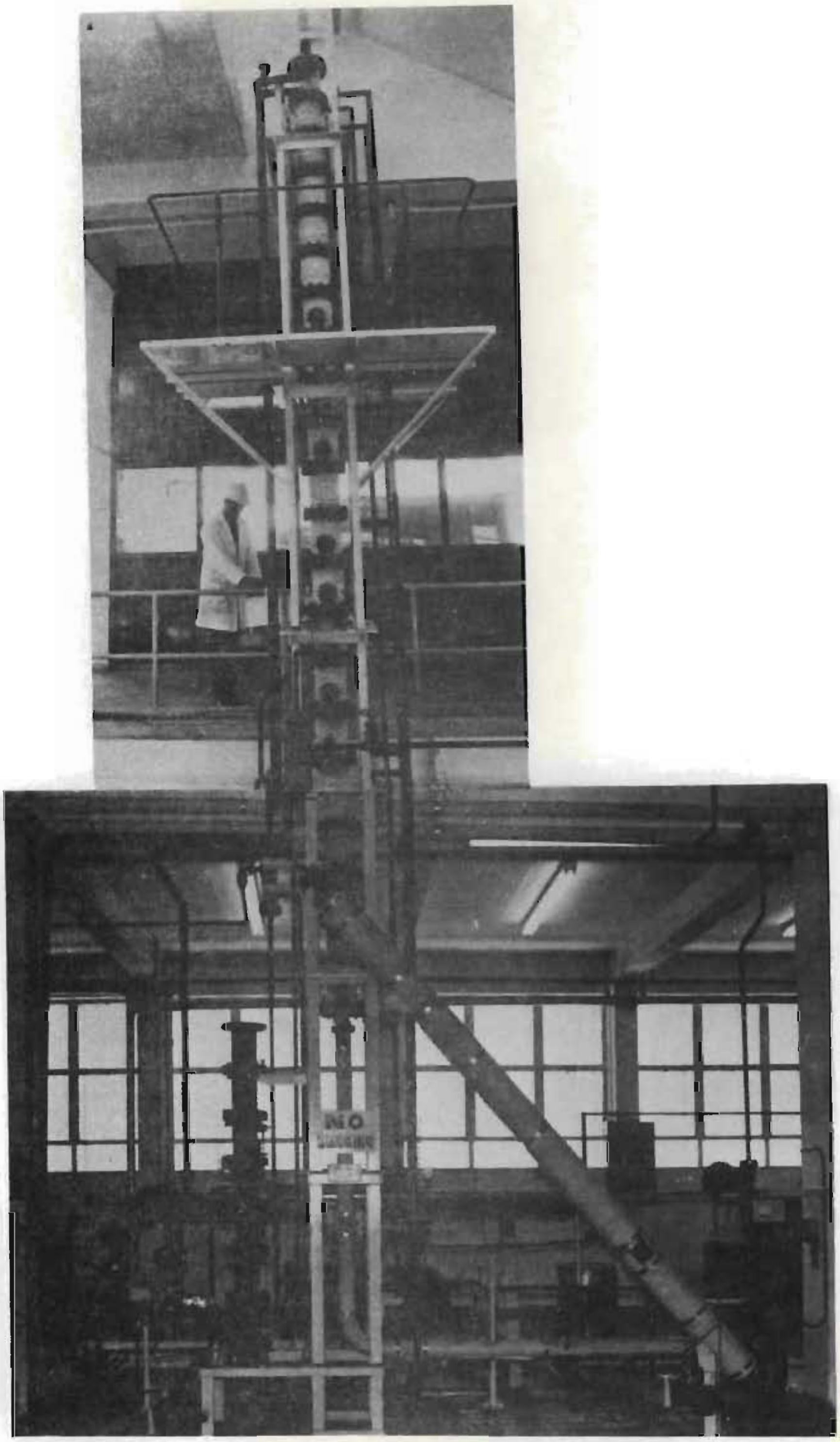


Fig. 9.1. Pilot fractionator, composite photograph showing complete plant

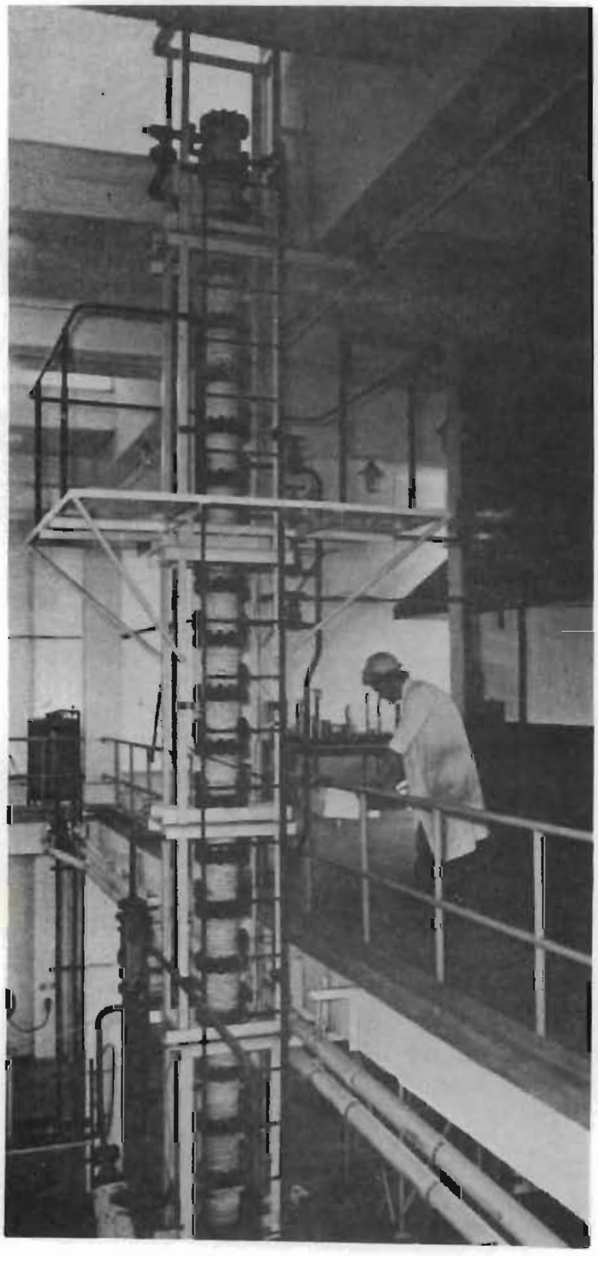


Fig. 9.2. Pilot fractionator

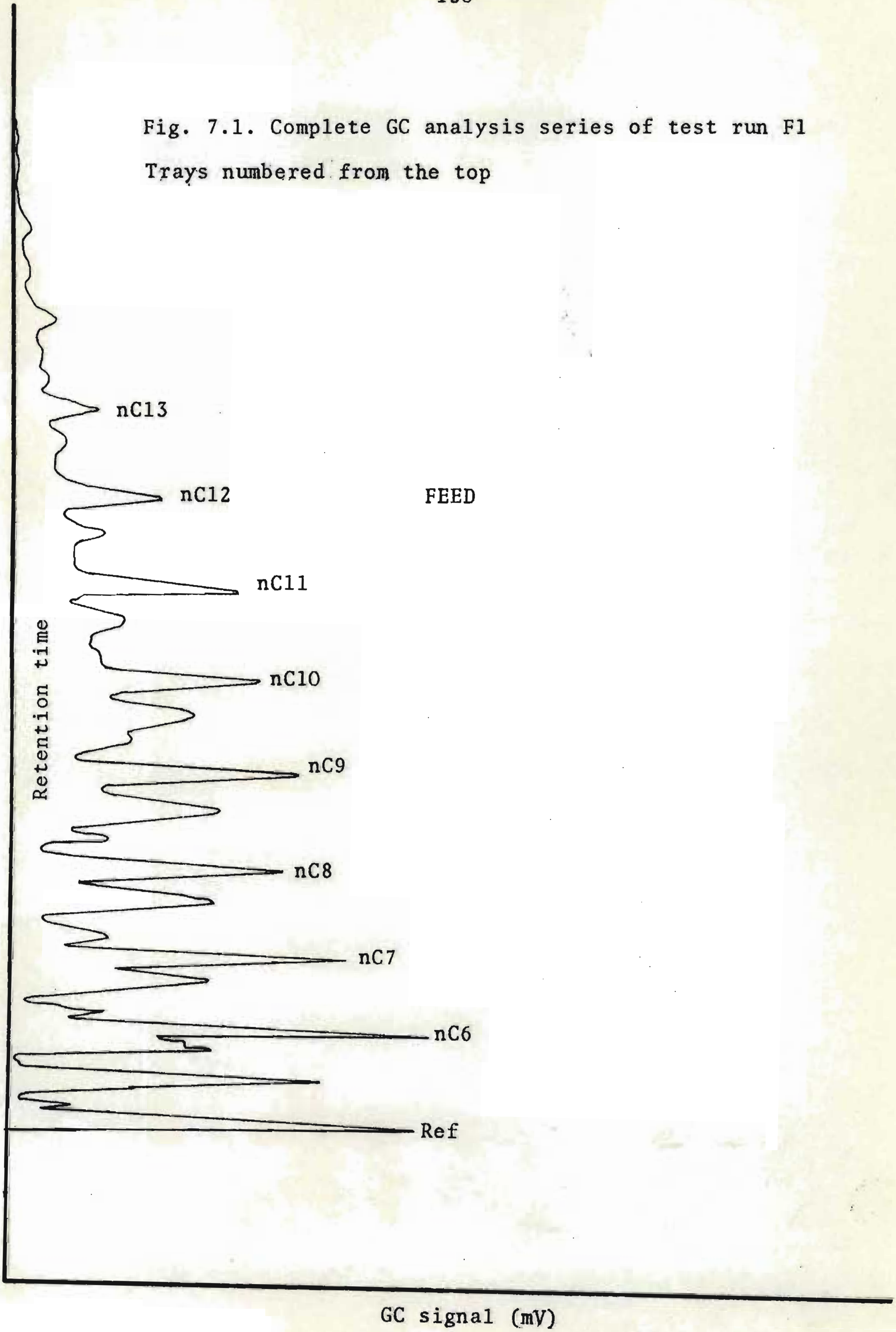
9.4. GC Analysis-series on pilot fractionator

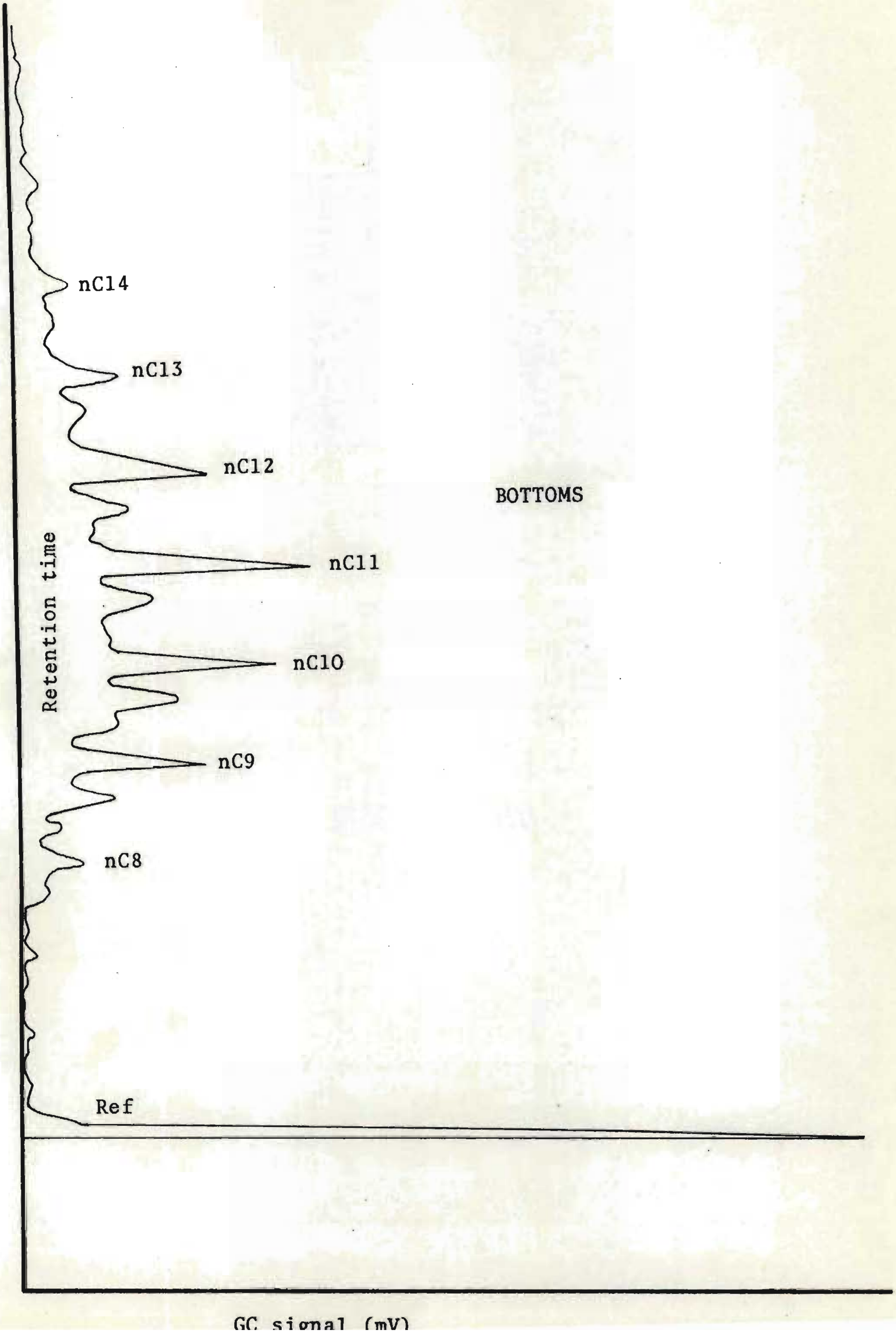
Details of a complete series of plate-to-plate GC analysis are shown in Fig. 7.1. Note the shift in the major peak on every plate from the light end of the column to the heavy end.

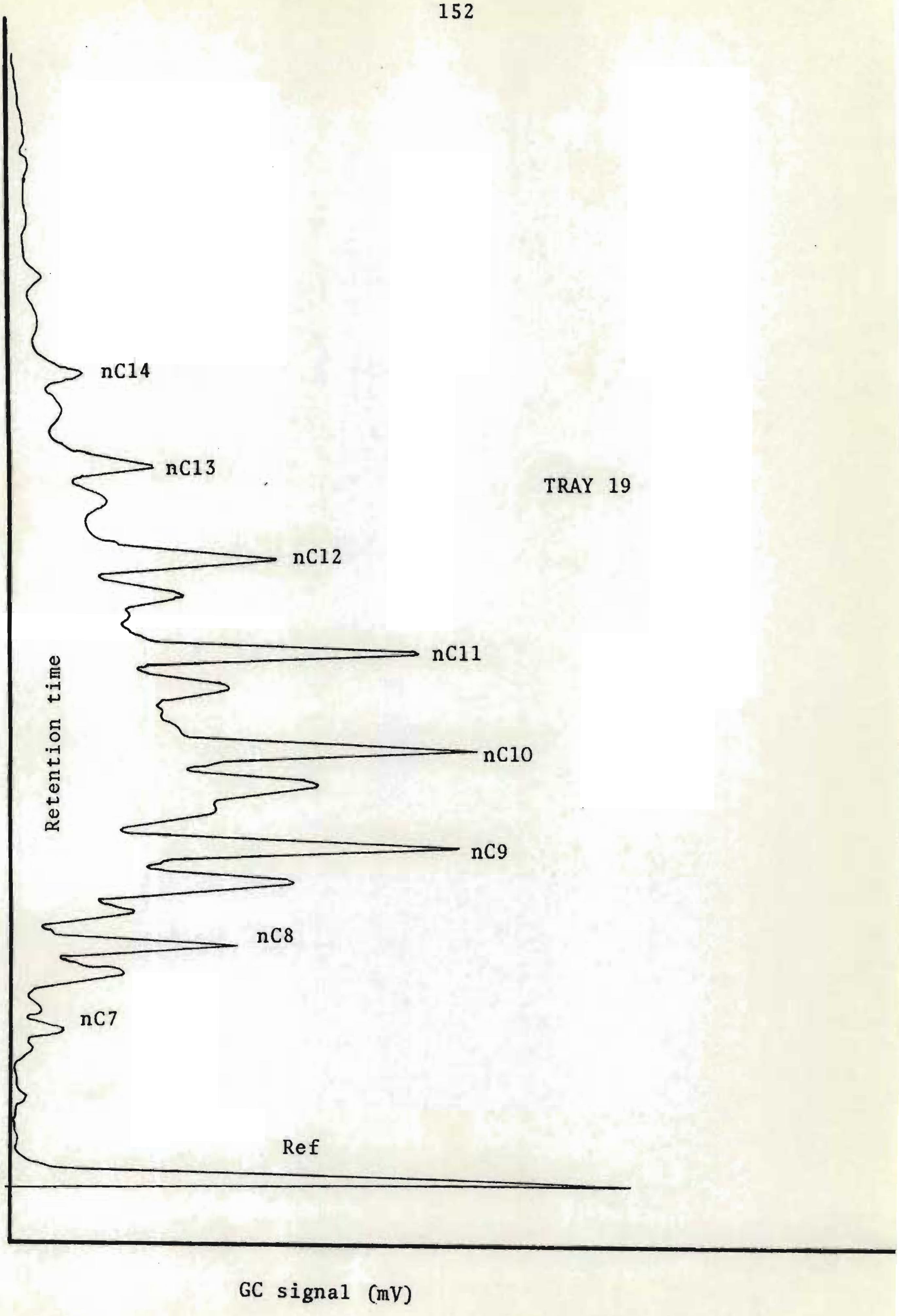
149

Fig. 7.1. Complete GC analysis series of test run F1

Trays numbered from the top




nC14
nC13
nC12
BOTTOMS
nC11
Retention time
nC10
nC9
nC8
Ref
GC signal (mV)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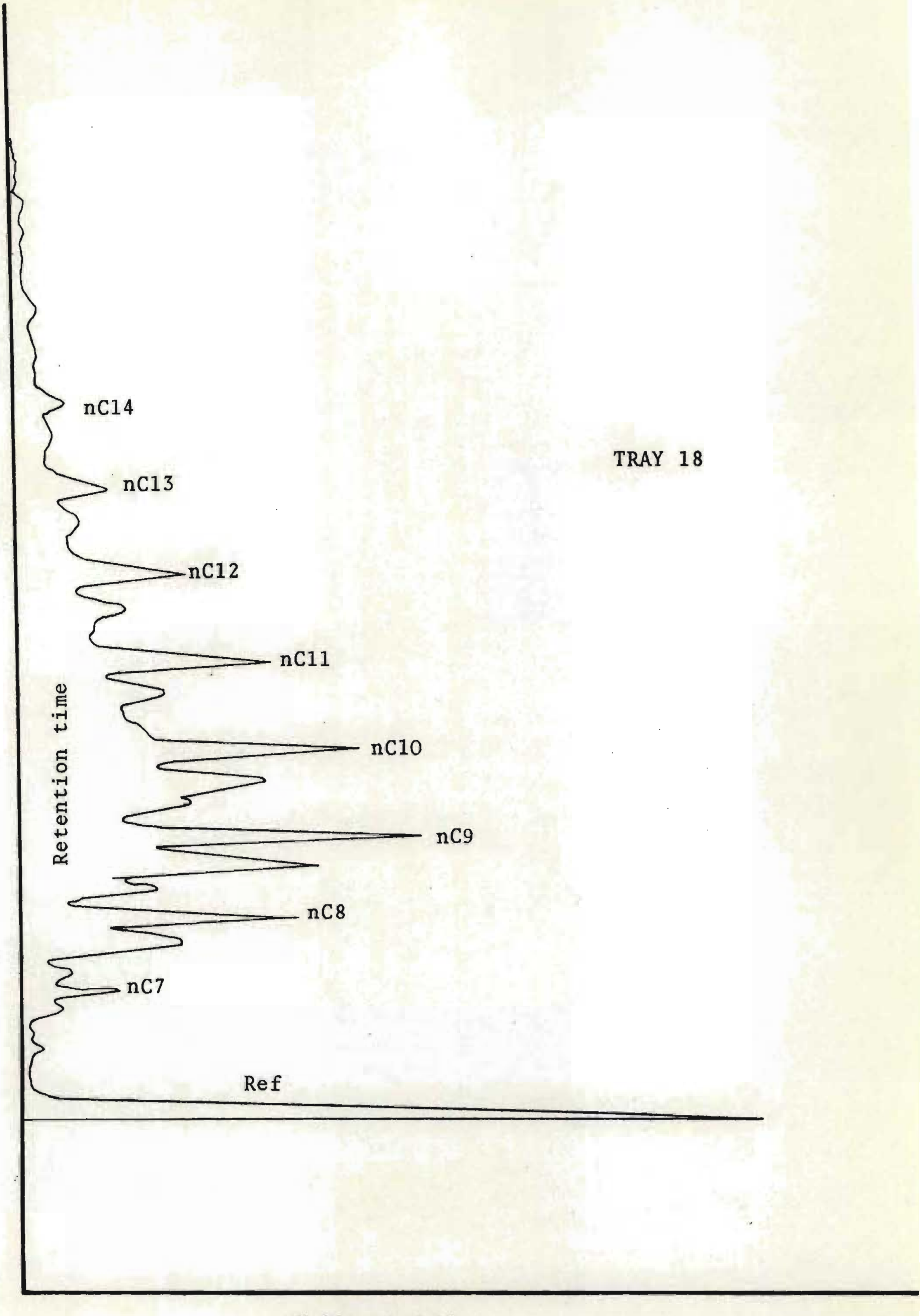
nC13
TRAY 19
nC12
nC11
Retention time
nC10
nC9
nC8
nC7
Ref
GC signal (mV)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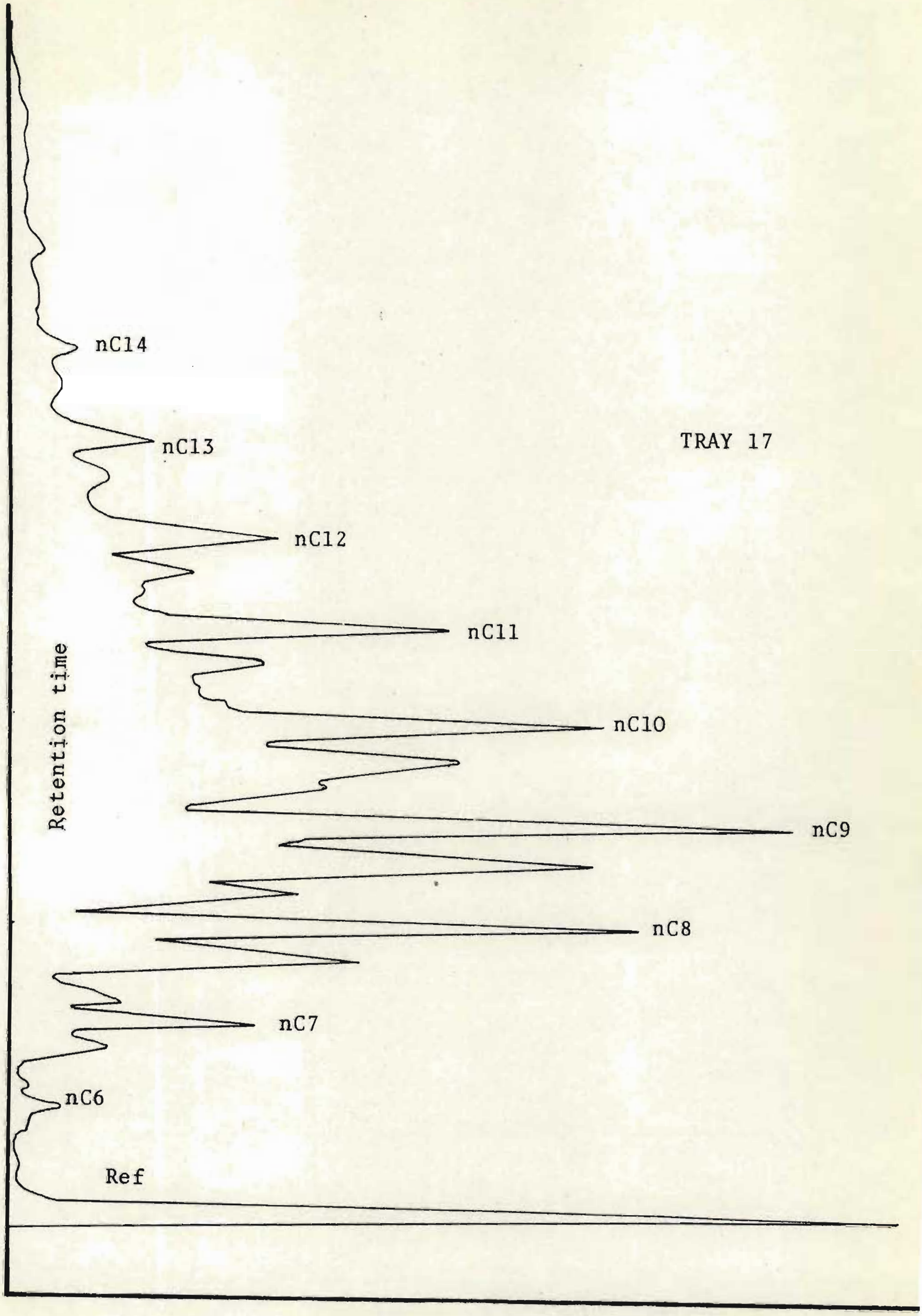
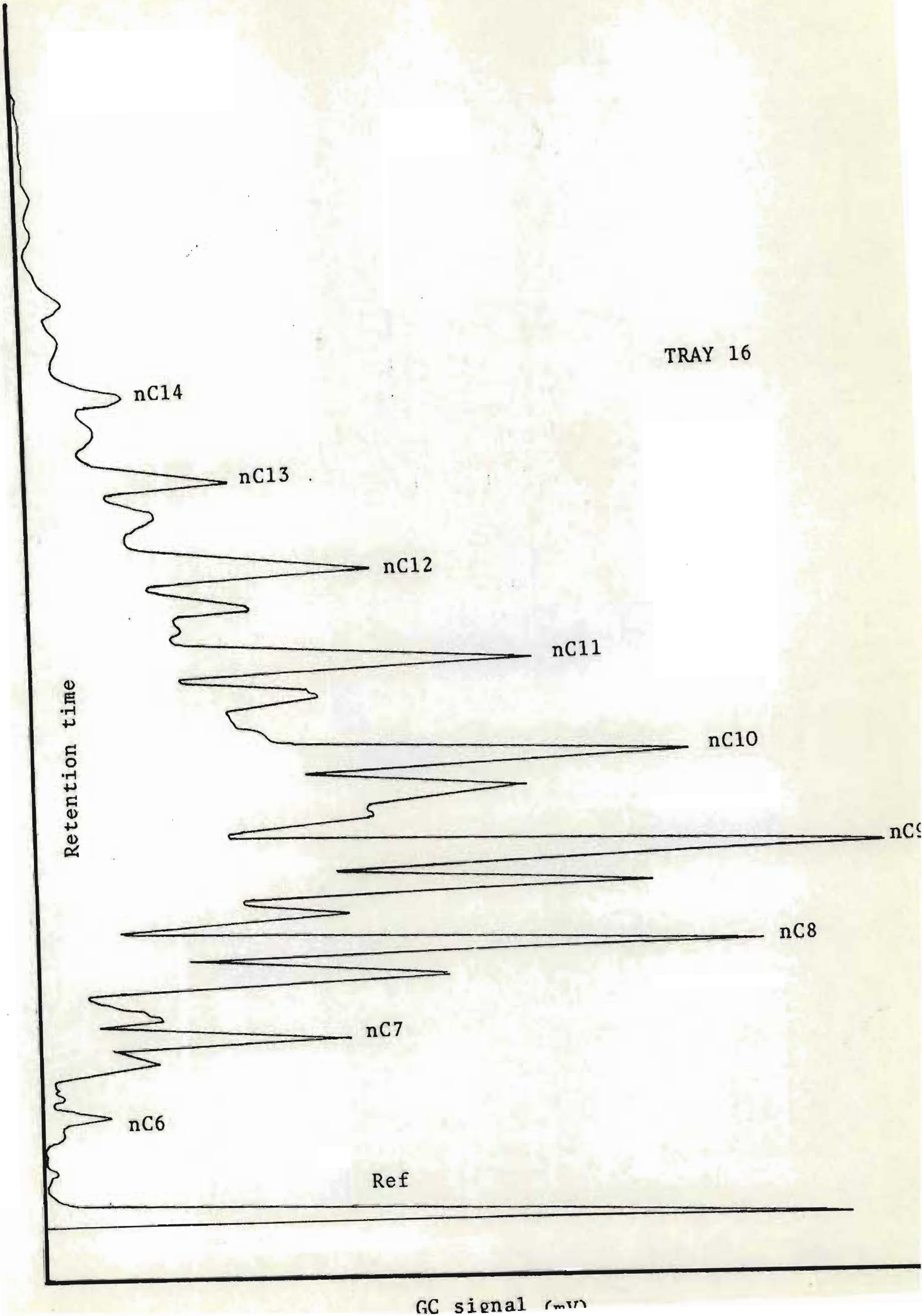
nC12
nC11
nC10
nC9
nC8
nC7
Ref
TRAY 18
Retention time
GC Signal (mV)


nC14
nC13
TRAY 17
nC12
nC11
nC10
Retention time
nC9
nC8
nC7
nC6
Ref
GC signal (mV)


TRAY 16
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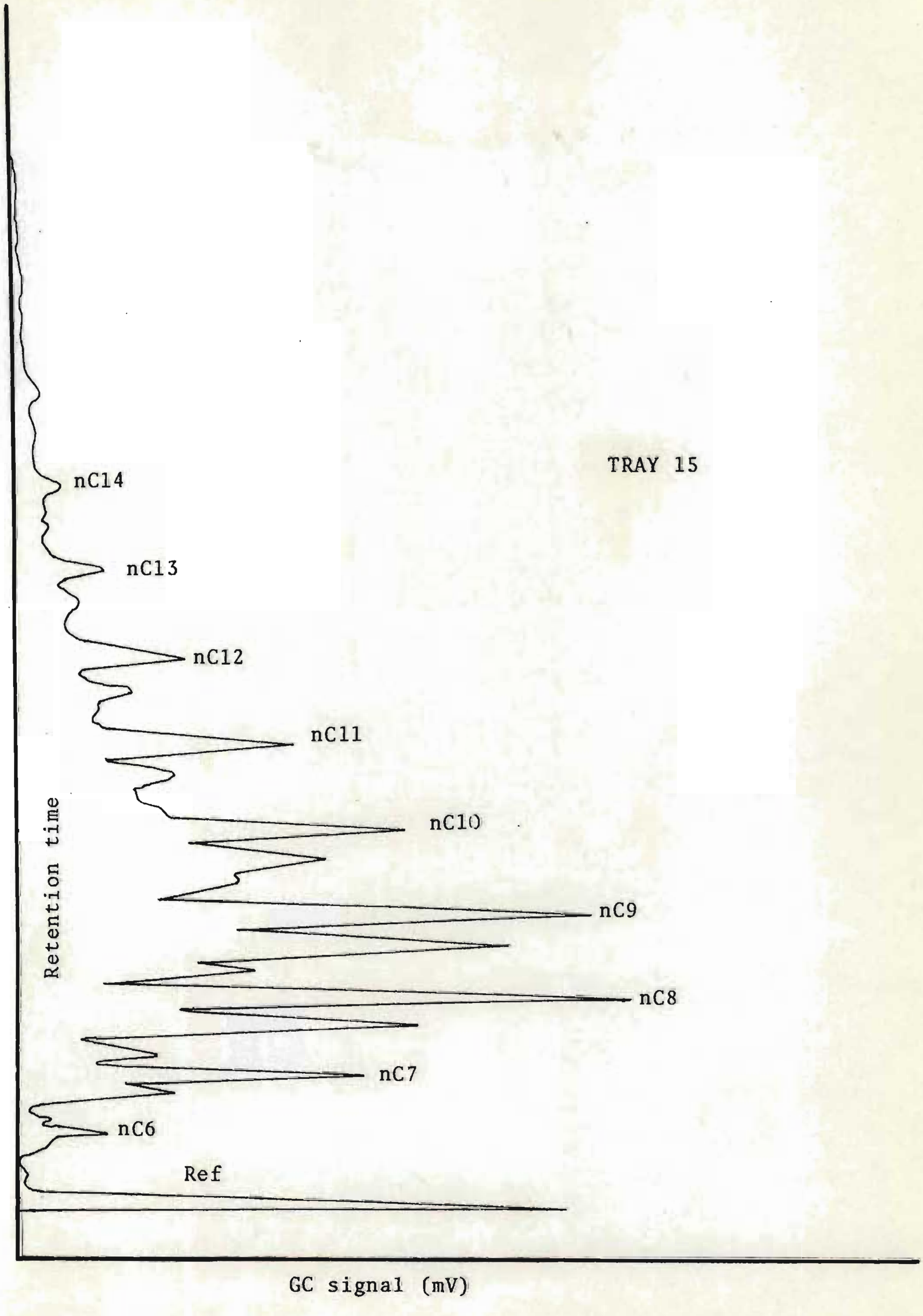
nC12
nC11
nC10
nC9
nC8
nC7
nC6
Ref
Retention time
GC signal (mV)


TRAY 15
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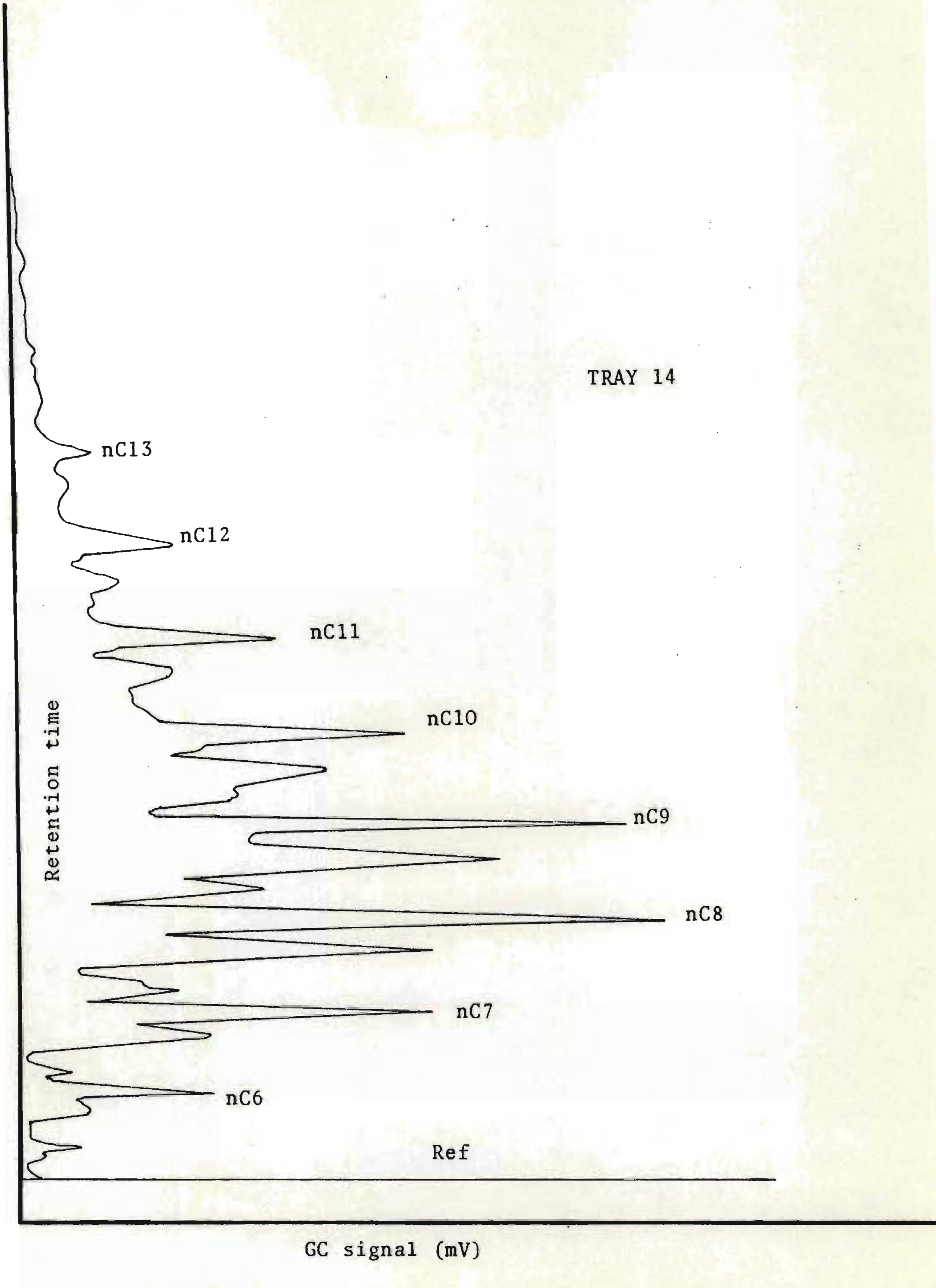
nC13
nC12
nC11
nC10
nC9
nC8
nC7
nC6
Ref
Retention time
GC signal (mV)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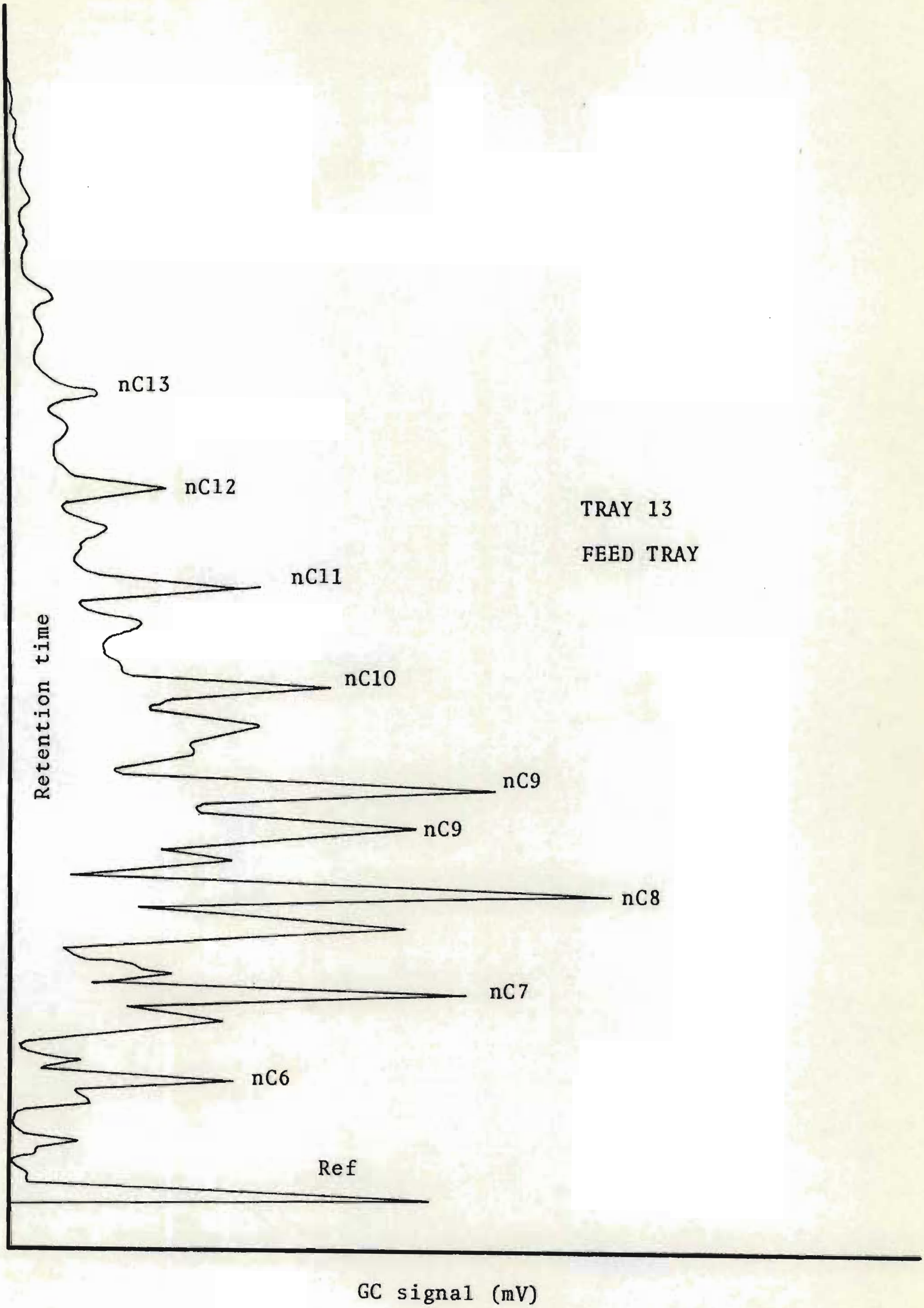
nC12
nC11
nC10
nC9
nC8
nC7
nC6
Ref
Retention time
GC signal (mV)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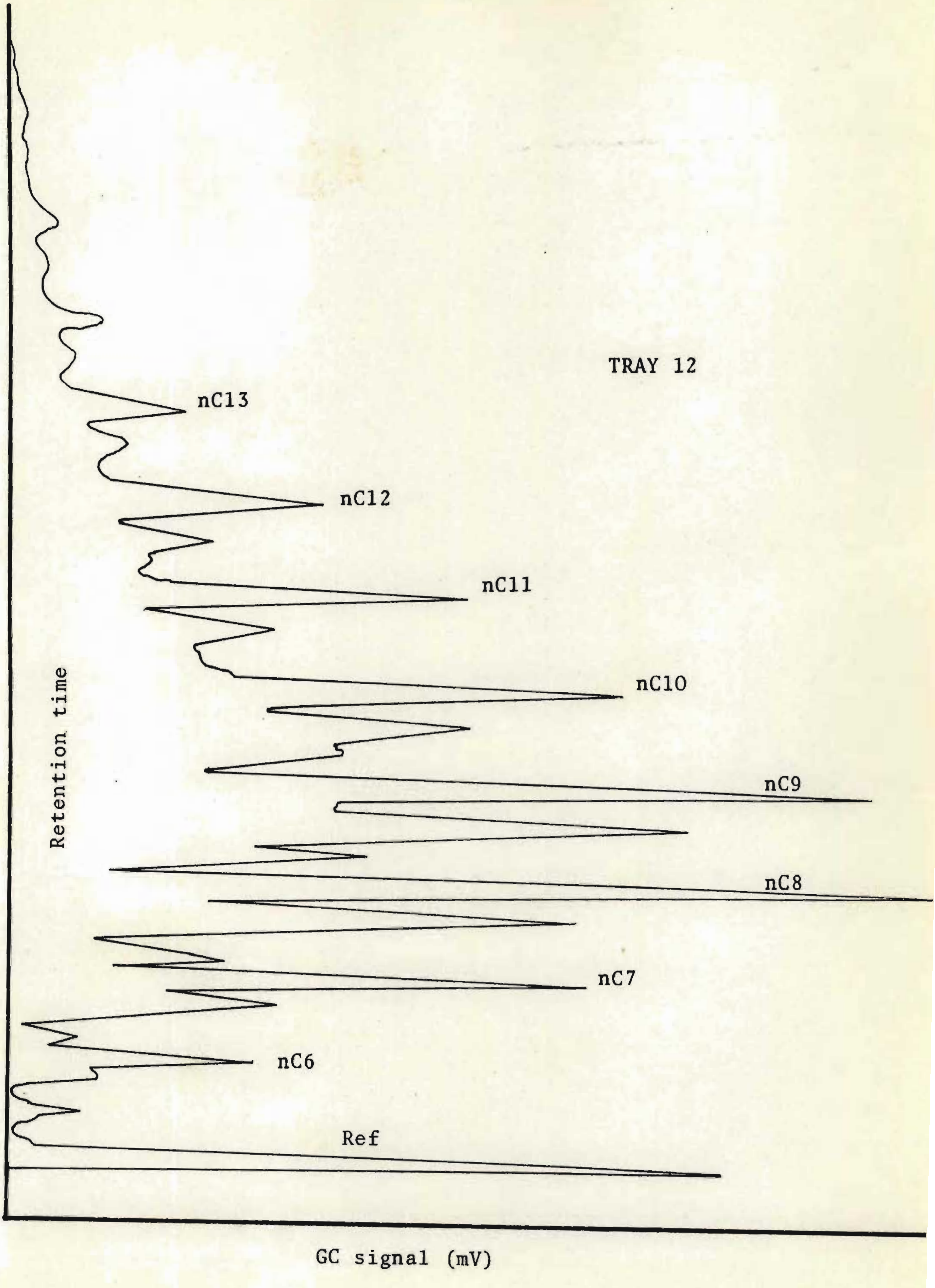
nC12
TRAY 13
FEED TRAY
nC11
nC10
nC9
nC9
nC8
nC7
nC6
Ref
Retention time
GC signal (mV)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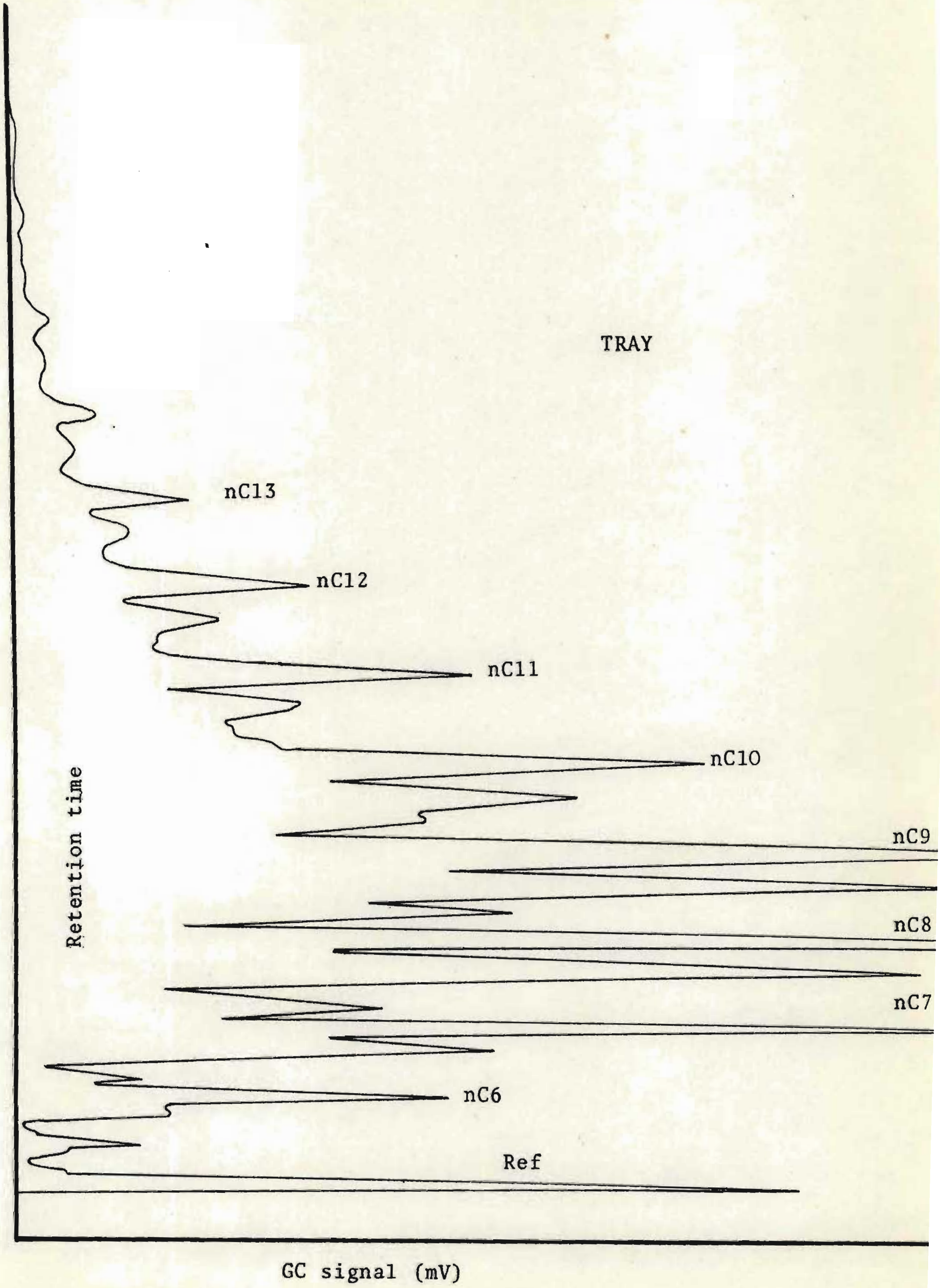
nC12
nC11
nC10
nC9
nC8
nC7
nC6
Ref
Retention time
GC signal (mV)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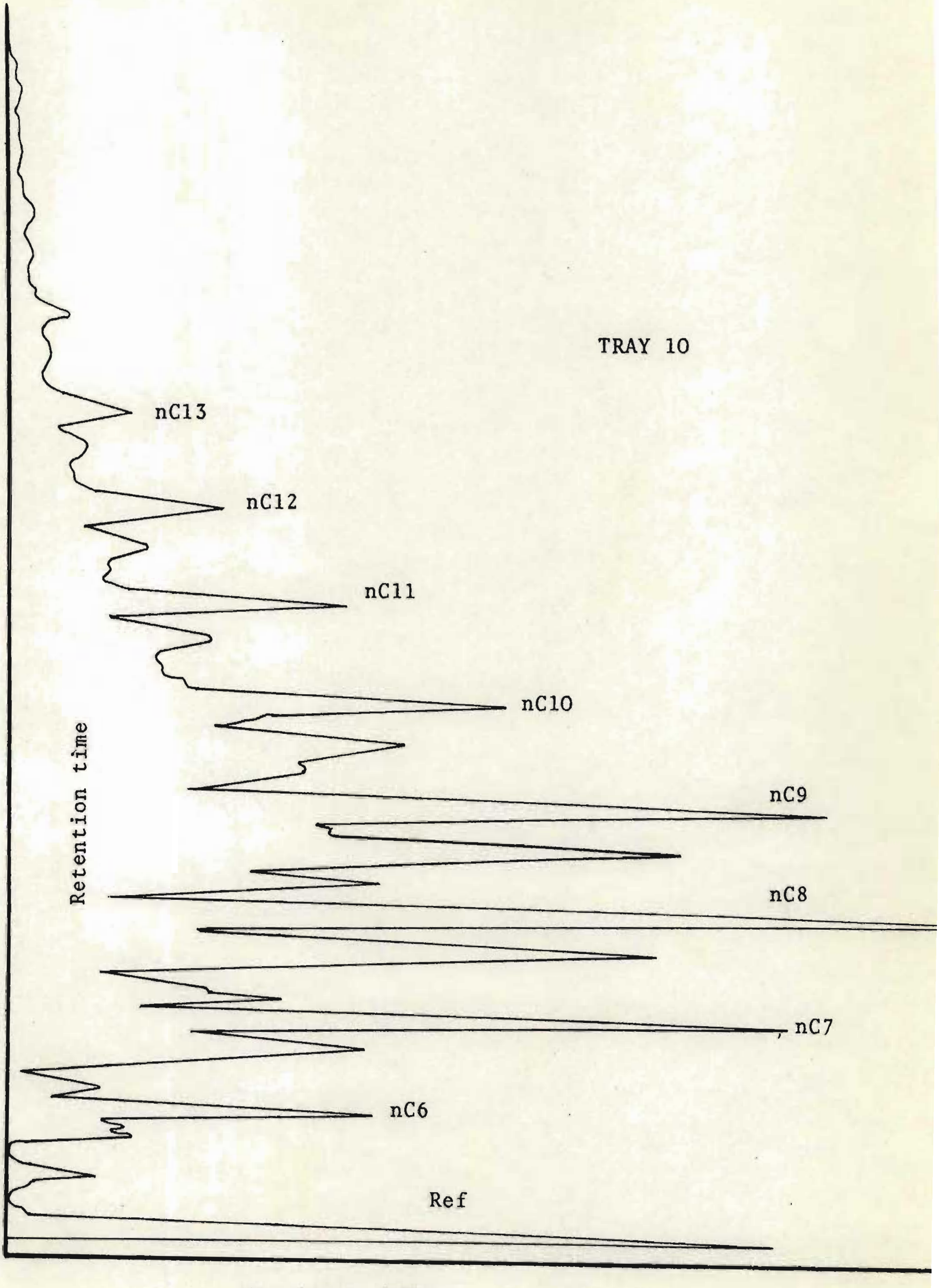
nC11
nC10
nC9
nC8
nC7
nC6
Ref
Retention time
GC signal (mV)


TRAY 10
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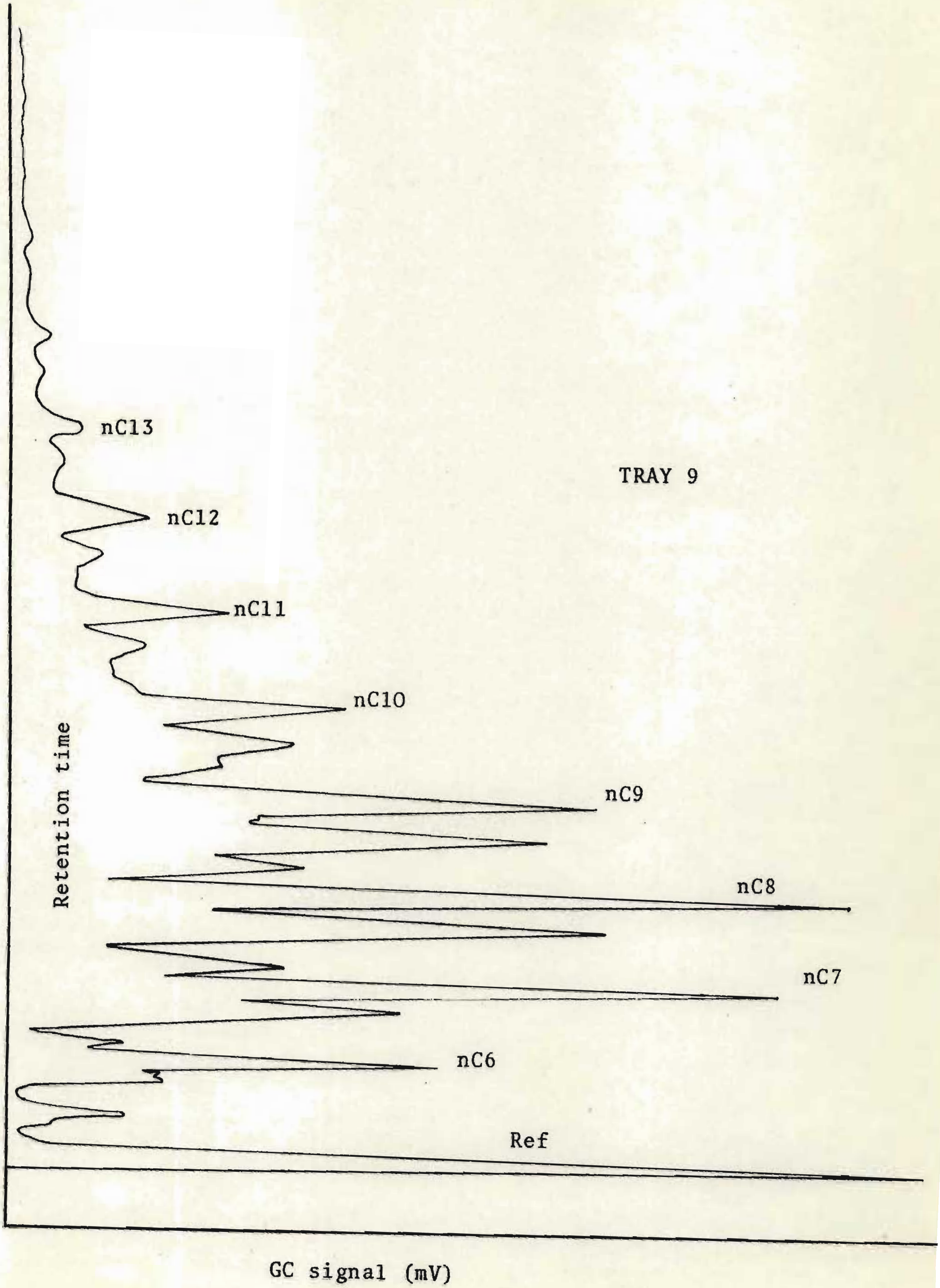
nC12
nC11
nC10
nC9
nC8
nC7
nC6
Ref
Retention time
GC signal (mV)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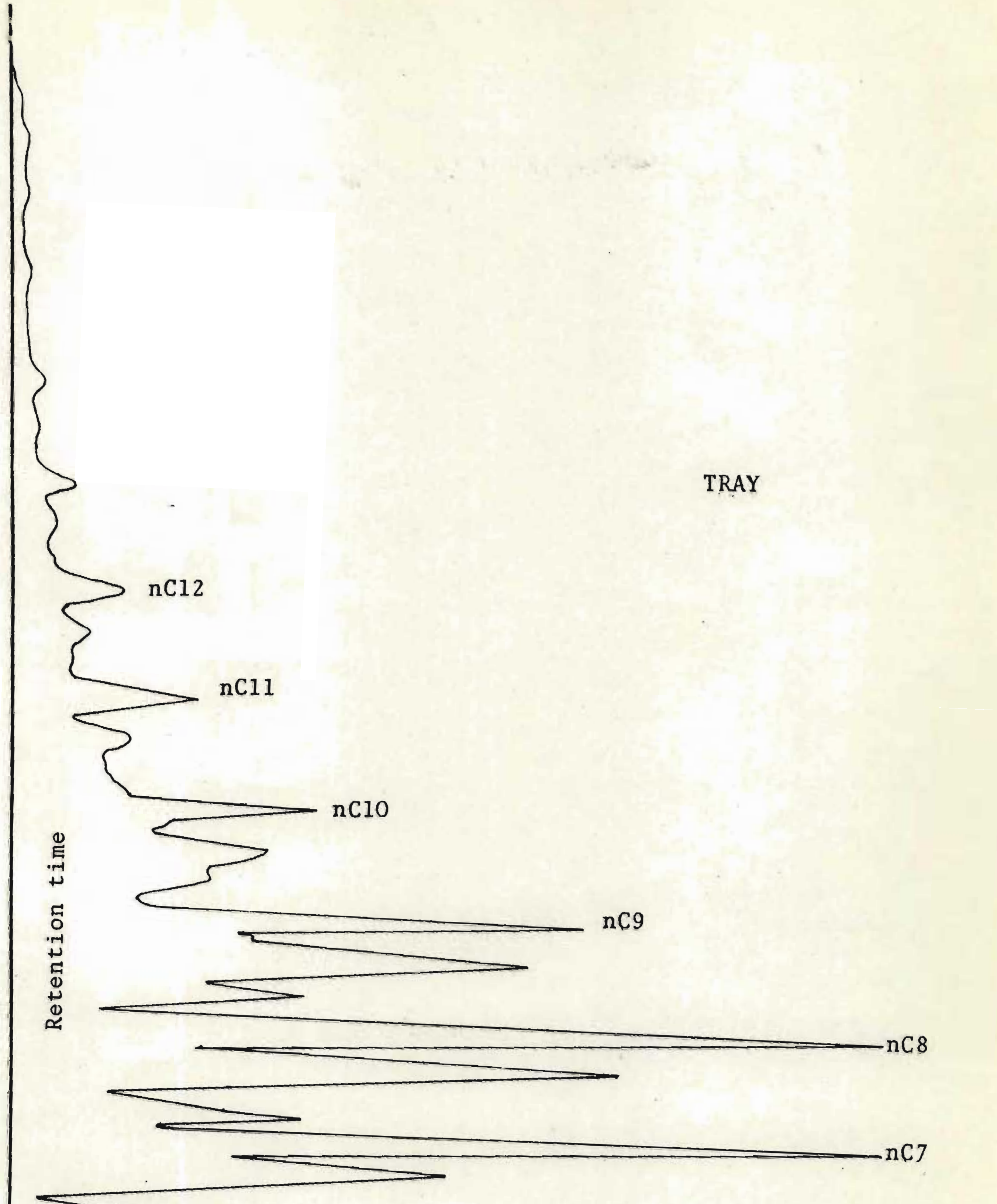
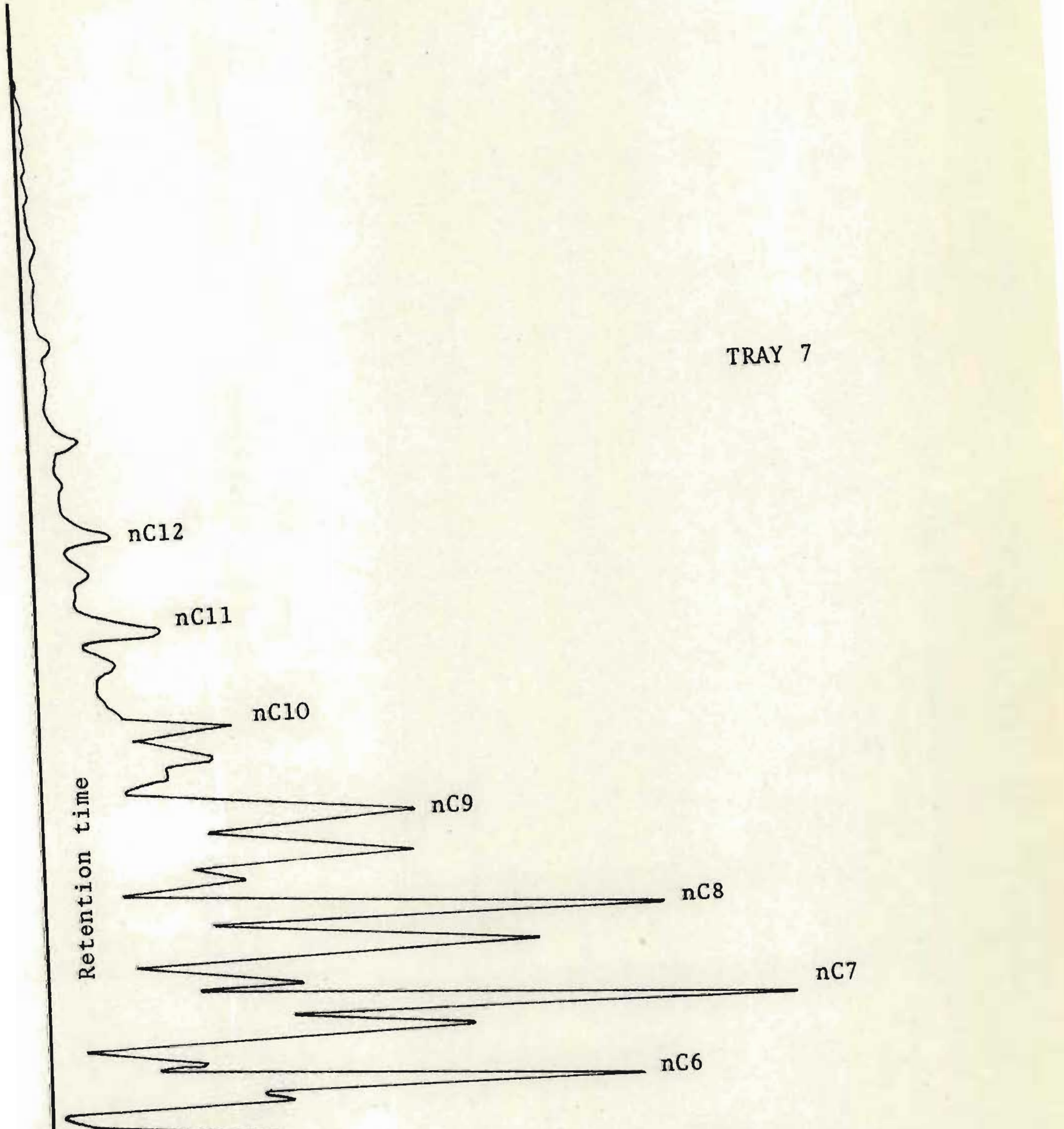
nC12
nC11
nC10
nC9
nC8
nC7
nC6
Ref
TRAY 9
Retention time
GC signal (mV)


TRAY
nC12
nC11
nC10
nC9
nC8
nC7
nC6
Ref
Retention time
GC signal (mV)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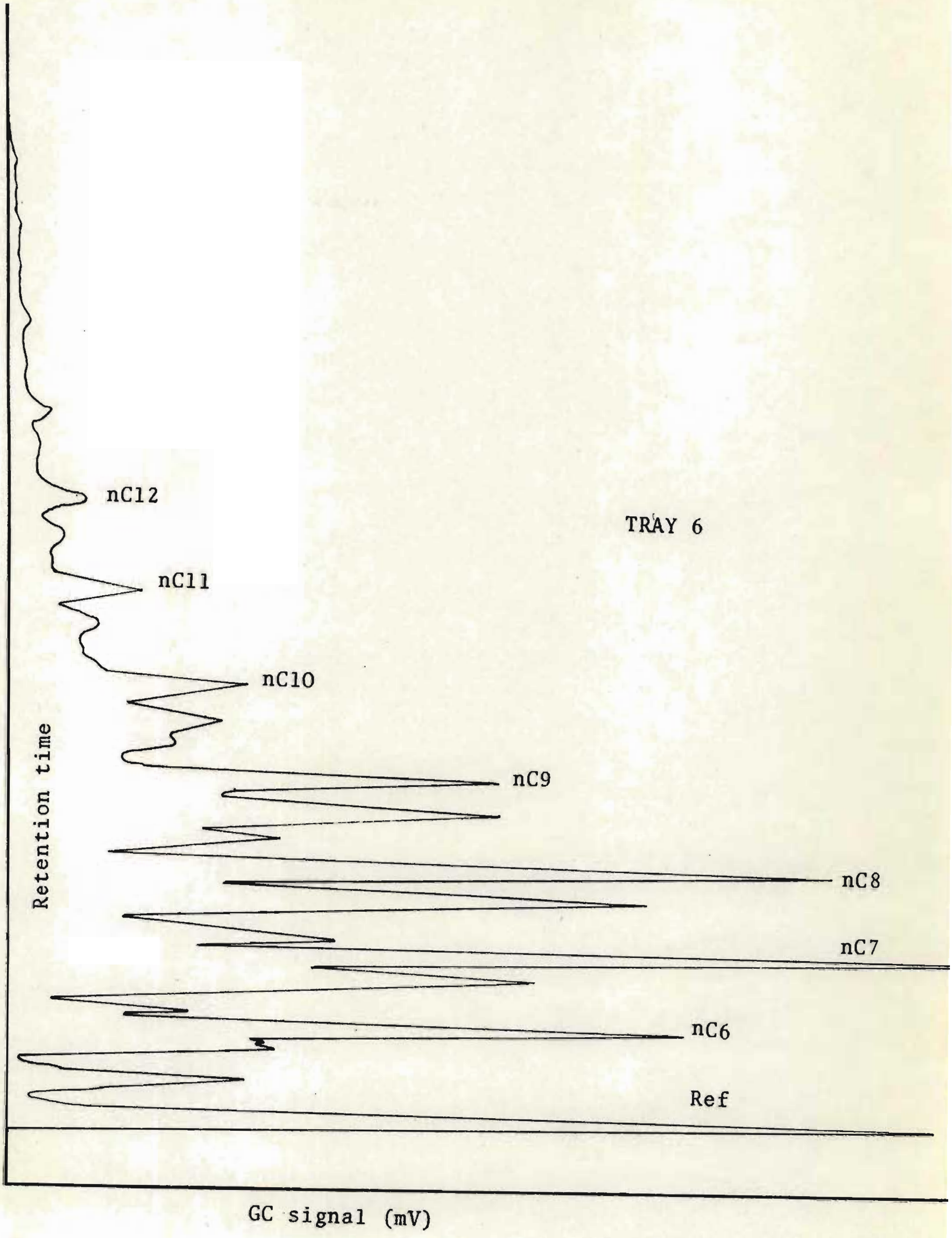
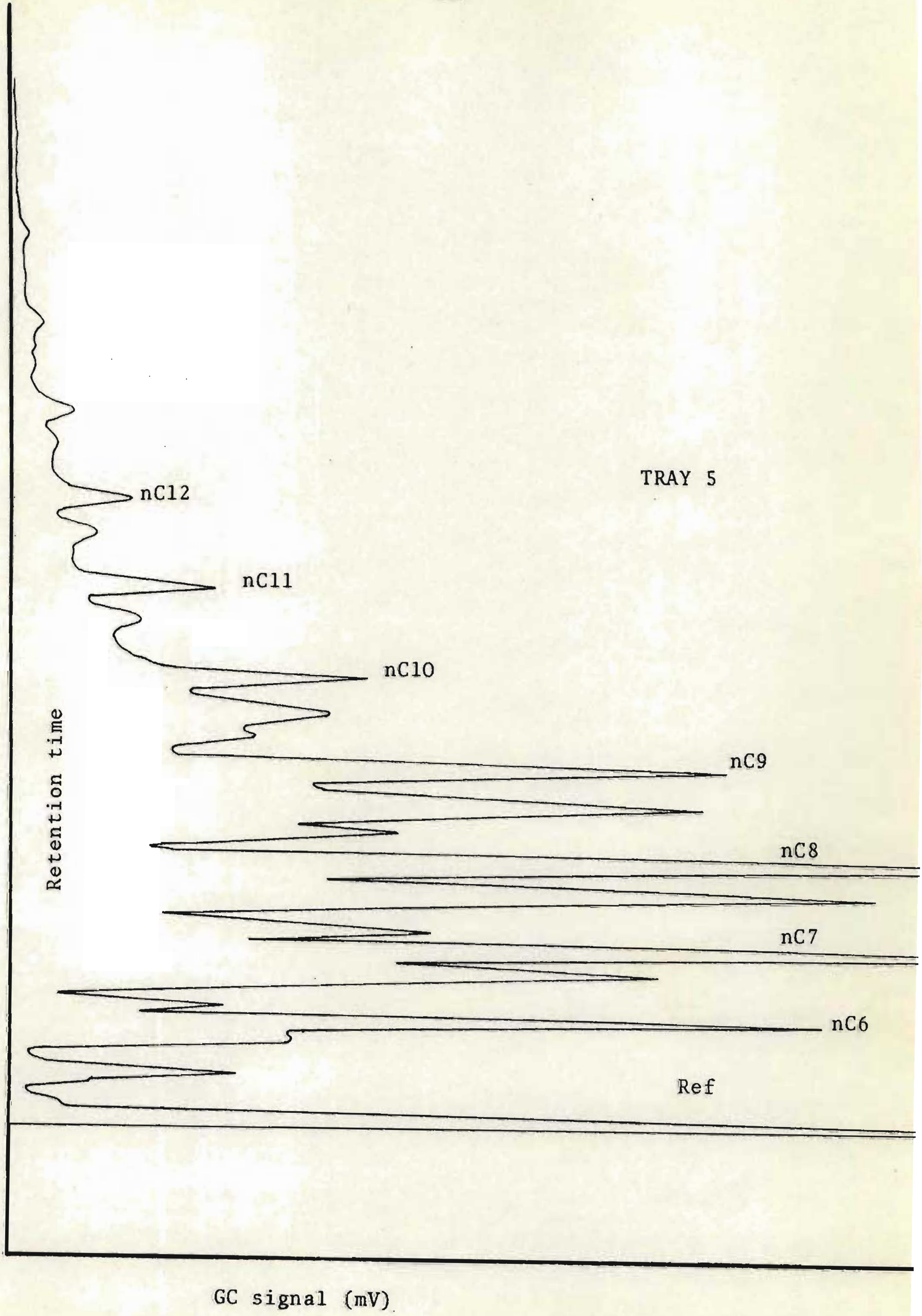
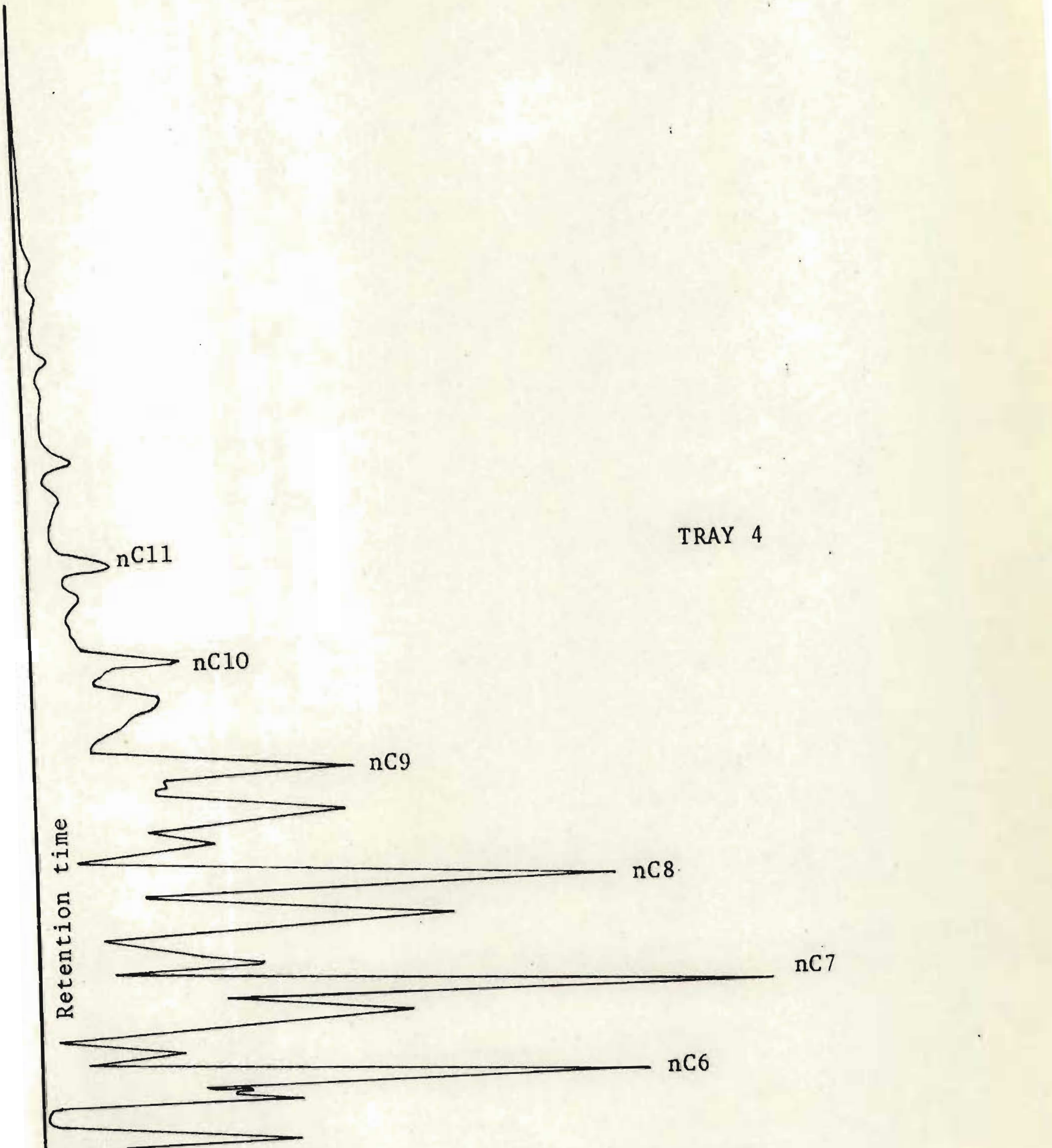
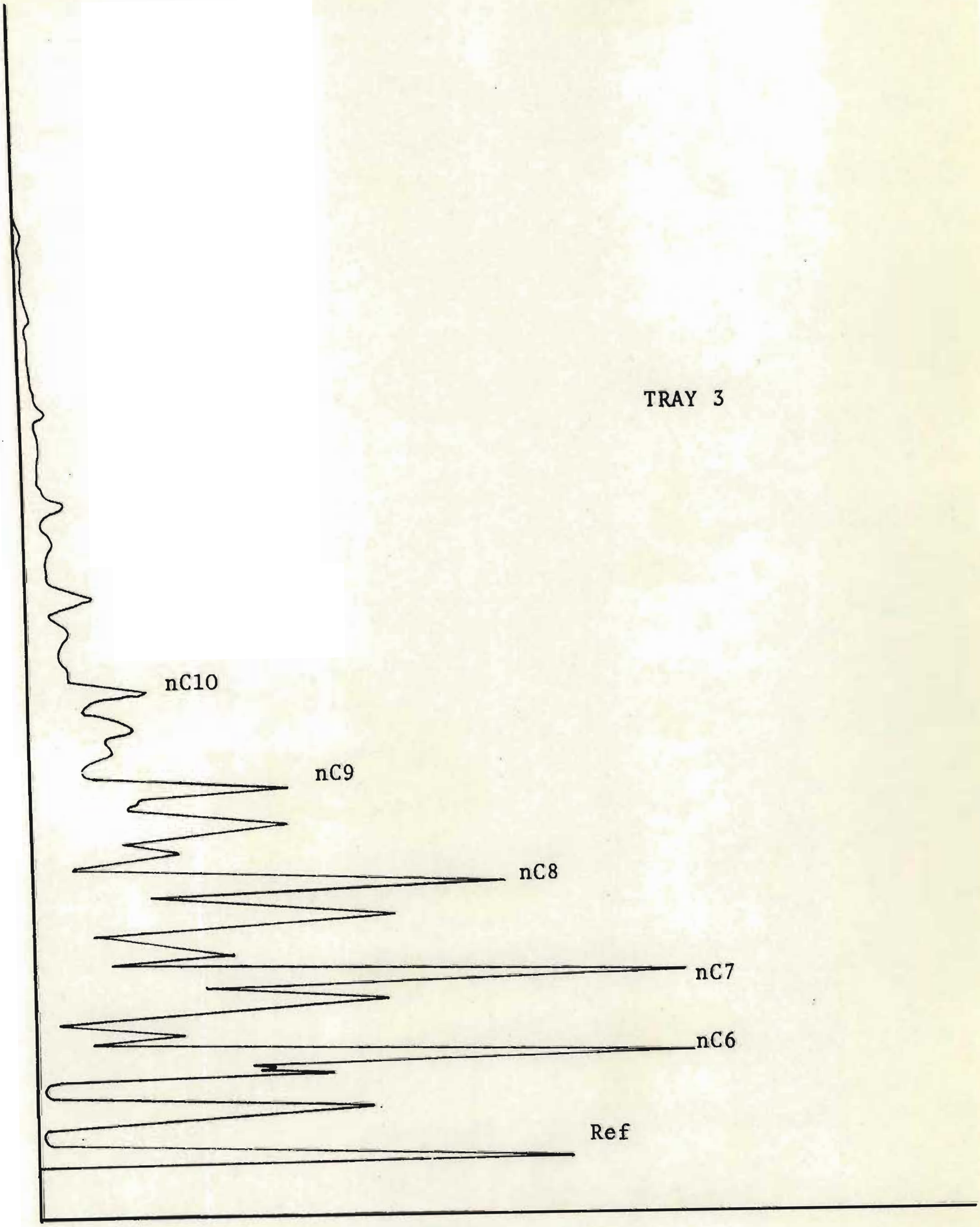
nC11
nC10
nC9
nC8
nC7
nC6
Ref
Retention time
GC signal (mV)

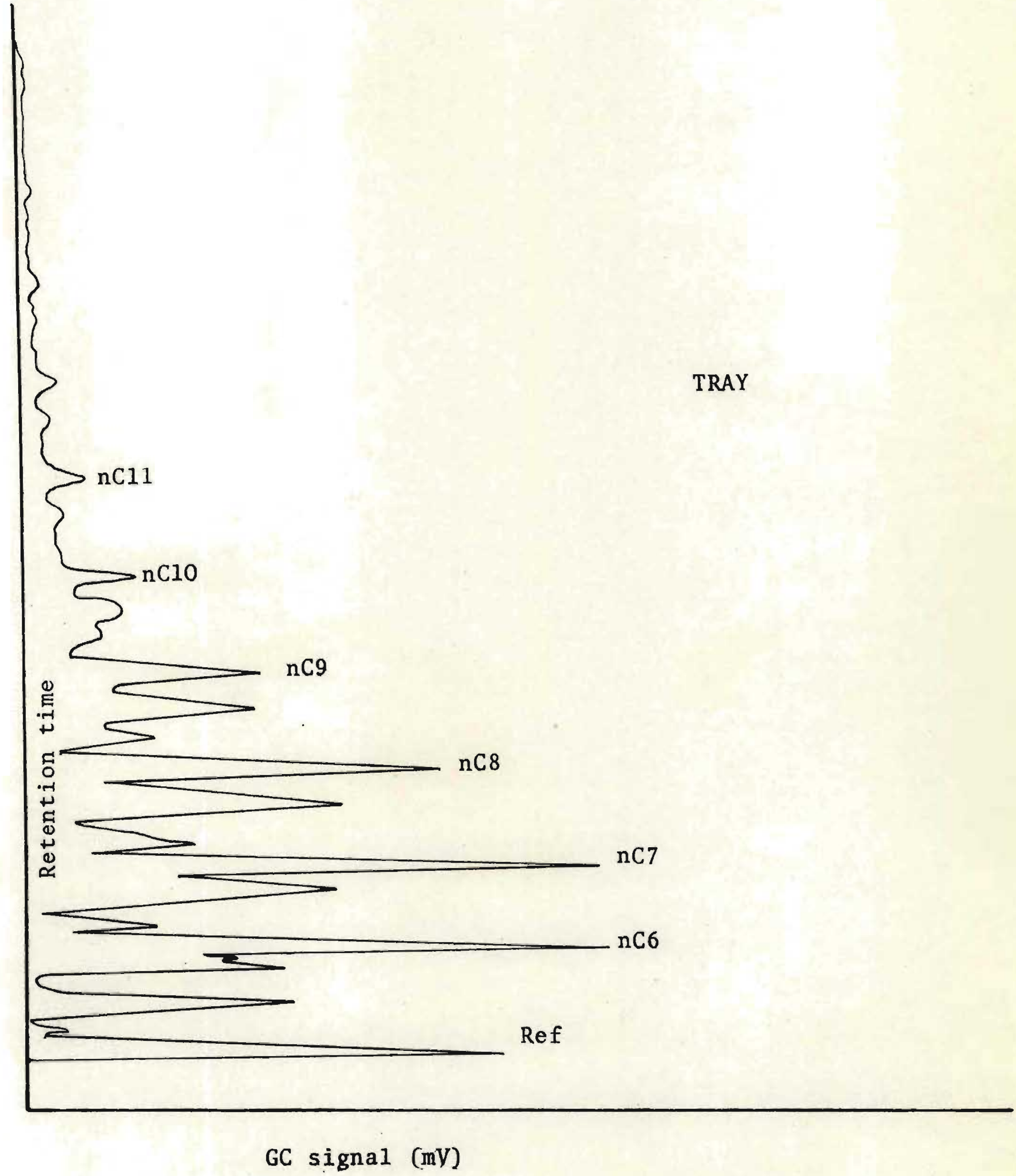

nC12
TRAY 6
nC11
nC10
nC9
nC8
nC7
nC6
Ref
Retention time
GC signal (mV)

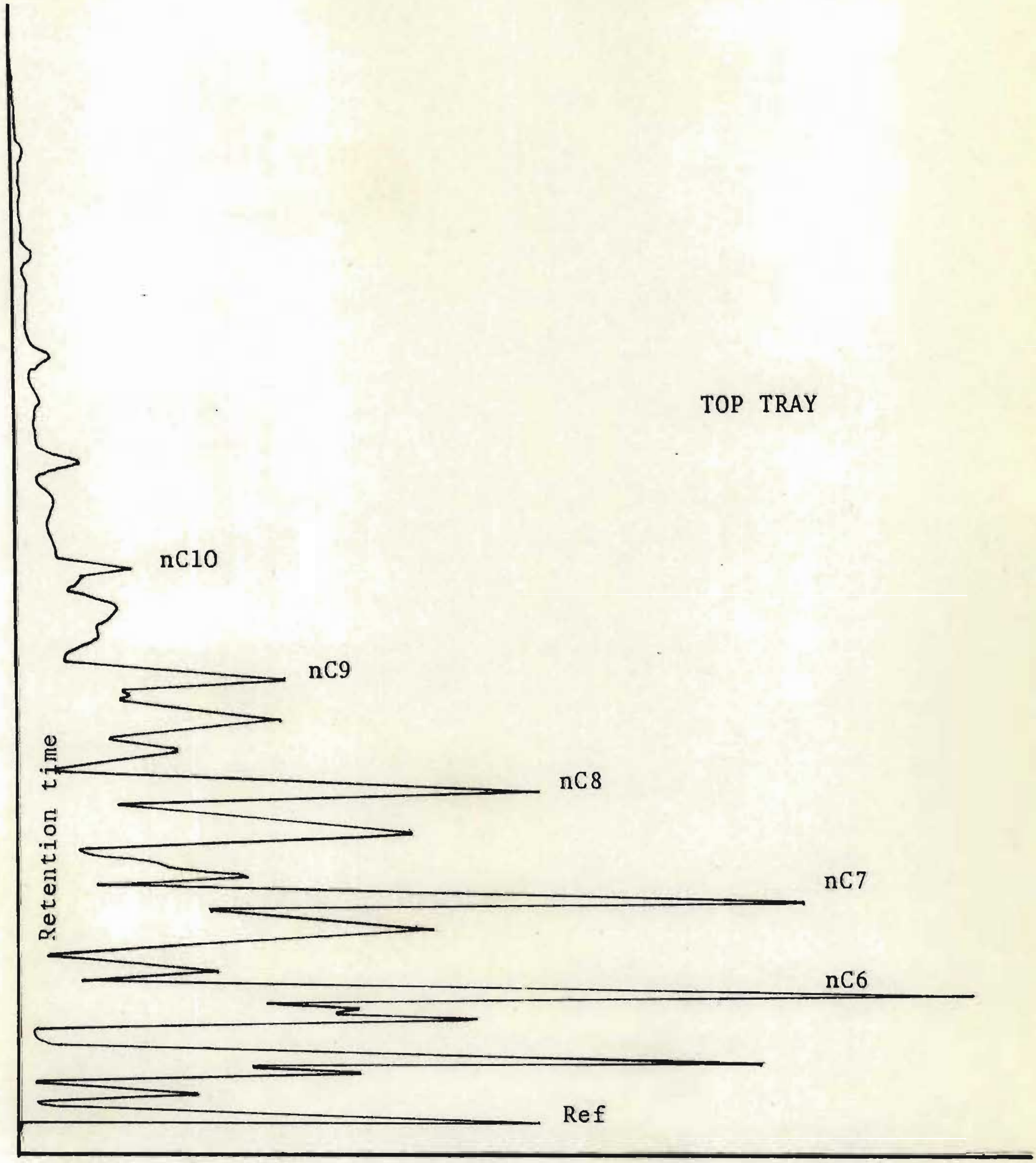

nC12
TRAY 5
nC11
nC10
nC9
nC8
nC7
nC6
Ref
Retention time
GC signal (mV)


nC11
nC10
nC9
nC8
nC7
nC6
Ref
TRAY 4
Retention time
GC signal (mV)


TRAY 3
nC10
nC9
nC8
nC7
nC6
Ref
GC signal (mV)

TRAY




TOP TRAY
nC10
nC9
nC8
nC7
nC6
Ref
Retention time
GC signal (mV)

9.5. Computer programs

A complete set of the computer programs used in this investigation is filed at the Department of Chemical Engineering, University of Natal, Durban.

The individual programs are

GCREAD	(GC acquisition)
FILE HANDLING ROUTINE	
GCVZ	(Resolving overlapping peaks with Rosenbrock (1961) off-line search to improve peak model)
GCTEST	(Calibrates GC, parameters a & b, eq. 4.25.)
PTGC	(Uses eq. 4.25 & 4.9. to assign BP's to components, using Nelder & Mead (1965) search)
MCDIS	(Multi-component distillation program, based on Clark (1972), using Thiele-Geddes + Θ-convergence and equal molal overflow)
DISTIL	(Multi-component distillation program, based on Wang and Henke (Kropholler, 1973) using tridiagonal matrix, and enthalpy data for flow correction

NOMENCLATURE

Arbitrary constants used in equations are not specified

Units are given in the text where required

a - component analysis
b - measured flow rate
c - concentration of solute in gas phase
  - unsmoothed data value
$\bar{c}$ - smoothed data value
c_p - heat capacity
E - vaporization efficiency
F - feed flow rate to distillation tray
h - solute hold-up in gas phase per unit column volume
  - liquid enthalpy
H - solute hold-up in liquid phase per unit column volume
  - vapour enthalpy
  - height of Gaussian peak
  - height equivalent to a theoretical peak
ΔH_v heat of vaporization of pure solute
ΔH_s heat of vaporization of solute from solvent
K - vapour-liquid equilibrium constant
k - capacity or partition ratio
L - total column length
  - liquid flow rate from distillation tray

m - equilibrium relation

M - molecular weight

n - number of moles

- number of theoretical plates of GC column

p - partial vapour pressure

P - total pressure

q - concentration of solute in stationary phase

R - gas law constant

- resolution of peak pair

R_T - resolution equivalent at PTGC

SV - sidestream vapour flow rate

SL - sidestream liquid flow rate

t - time

t_d - dead time

t_R - retention time

T - temperature

T_B - boiling point

V - superficial gas velocity

- vapour flow rate from distillation tray

V_G - volume of mobile phase

V_s - volume of stationary phase

w - mass

- weighting factor for standard deviation of component analysis

W - width of peak

x - mole fraction of solute in stationary phase

x - best estimate of flow rates

$x(t)$ time function describing Gaussian peak

y - mole fraction of solute in gas phase

- best estimate of analysis

z - distance from column inlet

- composition of feed to distillation column
- weighting factor for standard deviation of measured flow rate

SUBSCRIPTS

i - component number

j - stream number

- GC scan point number

s - stationary phase

1 - solute

- peak no.

2 - solvent

- peak no.

SYMBOLS

ρ - gas phase density

α - partition coefficient

- single-exponent smoothing constant

γ - activity coefficient

β - partition coefficient

ϕ - fugacity coefficient

f - fugacity

σ - standard deviation of measured flow rate

η - standard deviation of component analysis

λ - latent heat

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