GAS AND LIQUID CHROMATOGRAPHY

ON POROUS GRAPHITIC CARBON

H. Dias B.Sc. M.Sc.

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SUMMARY

A new hydrophobic support material, Porous Graphitic (or Graphitised) Carbon (PGC) has been studied using both Liquid (LC) and Gas Chromatography (GC).

The heat of adsorption (ΔH) of typical LC solvents determined on PGC, using GC, showed that ΔH increased with the molecular area (Ax) of solvents for well graphitised carbons, but that $\Delta H/Ax$ values were similar for all solvents studied. By definition, $\Delta H/Ax$ is a measure of eluotropic strength. The results reveal that a strong eluotropic series does not exist on carbon.

A strong eluotropic series does exist on silica. In this case, $\Delta H/Ax$ values of solvents were dependant upon their eluotropic strengths (Eo), determined by LC.

GC work was carried out using alcohols, ketones and aliphatic hydrocarbons on PGC, modified with different amounts of Carbowax 1500. Symmetrical peaks were obtained with coated materials. The column efficiency (N), first increased and then dropped with increasing Carbowax content on the PGC surface. The retention of ketones and hydrocarbons decreased with increasing amount of Carbowax on PGC. In the case of alcohols, the retention decreased with the initial introduction of Carbowax on to PGC. Some alcohols displayed enhanced retention at 0.10 % of Carbowax. All alcohols

showed increased retention at the monolayer coverage of Carbowax.

In the quest for a perfect material for adsorption GC, PGC samples were hydrogen treated at elevated temperatures (230-1030°C). All hydrogen treated samples failed to display significantly improved chromatographic properties.

PGC was then treated with toluene in a stream of either hydrogen (at 630°C) or nitrogen (at 630°C or 300°C) to eliminate any active sites present on the surface. Hexane was used as an alternative to toluene at 630°C in a stream of hydrogen. Such surface treatments yielded improved materials for adsorption GC. On heating the columns (beyond 230°C), containing these materials, with carrier gas running through the columns, the chromatography deteriorated in the cases of toluene-treated PGC whilst the chromatography of the hexane-treated PGC remained unaffected.

LC work on some aromatic compounds using PGC, coated with surfactants such as Tween 80 or Span 80 showed that, analyte retention decreased with increasing surfactant concentration (up to 0.03% of Tween and 0.02% of Span) in the eluent. N dropped with the introduction of Tween to the PGC. Increasing the ratio of water to methanol in the eluent, at a constant eluent concentration of surfactant, resulted in diminishing N, increasing eluent polarity and analyte retention values.

Ion pairing was carried out on PGC using cetyltrimethylammonium bromide (CTAB) as the ion pairing agent, at an eluent pH of 12.5. The retention of solutes, that ionise under these conditions, increased whereas the retention of analytes, that do not ionise, decreased with increasing eluent concentration of CTAB.

The coated or chemically modified PGC surfaces are useful in GC whilst the dynamically coated PGC surfaces are important in LC. Such surface treatments can alter the following properties of PGC; (a) Retention characteristics, (b) the selectivity and (c) chromatographic efficiency.

CONTENTS

"I often say that when you can measure what you are speaking about, and express it in numbers, you know something about it. When you cannot express it in numbers, then your knowledge is of a meagre and unsatisfactory kind; it may be the beginning of knowledge but you have scarcely, in your thoughts, advanced to that stage of science whatever the matter may be."

Lord Kelvin

Postgraduate Lecture Courses Attended (1985-88)

East of Scotland HPLC meetings (1985-88).

Twelth International Symposium on Column Chromatography (1988).
Washington DC, U.S.A.

Scottish Chromatography Group meetings (1986, 1988).
Ninewells Hospital, Dundee.

Mass Spectrometry
by Prof. K.R. Jennings (University of Warwick).

Industrial Catalysis
by Dr. D.A. Whan et al (ICI Ltd.).

The elements of Cell Biology
by Dr. J. Phillips (Dept. of Biochem., Edinburgh University).

Signal Processing
by Dr. M.A.D. Fluendy et al (Chem. Dept., Edinburgh University).

Solving and Refining Crystal Structures
by Dr. R.O. Gould and Dr. A. Blake
(Chem. Dept., Edinburgh University).

Advances in Physical Chemistry
by Dr. K. McKendrick et al (Chem. Dept., Edinburgh University).

Medicinal Chemistry
by Prof. P.G. Samms (Smith, Kline and French).

DECLARATION

This thesis has been compiled by myself. The thesis contains my own research work. This research is not submitted for any other degree or professional qualification.

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CHAPTER 1

INTRODUCTION

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PART I

General History

(1903 - 1988)

First use of Chromatography to the

Development of Porous Graphitic (Graphitised) Carbon

CHAPTER 1

INTRODUCTION

Gas and Liquid Chromatography on Porous Graphitic Carbon

1.1 A BRIEF INTRODUCTION TO COLUMN CHROMATOGRAPHY

Column chromatography is an important analytical tool and its popularity is attributed to its simplicity and reproducibility [1]. The technique is employed to separate mixtures of chemical substances by introducing a sample mixture at one end of a bed containing tightly packed partitioning material known as the stationary (or solid) phase (silica, carbon or alumina). A mobile phase or the eluent (either a liquid or a gas) transports the mixture along the column. Different components of the mixture have different affinities for the stationary phase and hence the constituents of the sample mixture migrate at different rates through the column. Thus a separation is achieved [2]. The basic theories of chromatography will be discussed in detail in Section 1.4.

1.1.1 General History

Column chromatography was invented and first used by Tswett [3] in 1903 to separate coloured leaf pigments. He passed a solution of the pigments through a column containing chalk particles. At the time, the scientists failed to recognise the enormous potential of this method, and it was largely forgotten until the 1930's when

Lederer [4] used chromatography to separate carotine isomers.

Wilson [5] in 1940 proposed the first mathematical theory of chromatography. He described the non-equilibrium in chromatography and related it to band dispersion. Wilson also suggested that the peak tailing was the result of low rates of adsorption and desorption, and such undesirable effects could be diminished by reducing the velocity of the mobile phase through the column [5].

In 1941, Martin and Synge invented plate theory of chromatography [6]. This describes the formation of a zone profile due to successive equilibration of a solute between a mobile and stationary phase contained in a series of plates under condition of a linear partition isotherm. They predicted that the plate thickness or height H, was proportional to the flow velocity and square of the particle diameter. They also deduced that the use of very small particles in a column and a higher pressure gradient across the length of the column would enable fast liquid chromatography to be performed. They also suggested that a gas could advantageously be used as the mobile phase.

The Martin and Synge theory was not directly applicable to the adsorption chromatography of the 1940's. Some adsorbents at that time gave severely non-linear adsorption isotherms, which resulted in distorted (non-Gaussian) peaks, where the major cause of peak spreading arose from thermodynamic rather than kinetic effects.

During this period, the theoretical treatment of adsorption chromatography was based on the assumed non-linearity of adsorption isotherms [2].

Thomas's first mathematical treatment of non-equilibrium in chromatography appeared in 1944 [7]. He mathematically expressed effluent concentration as a function of time. Thomas considered close to equilibrium conditions by reducing the flow rate to prevent large deviations from equilibrium. He derived equations to calculate the adsorption and desorption rates from experimentally established solute concentration-time curves.

In 1952 James and Martin described the first use of a gas-liquid partition chromatography [8], in which they determined the analysis of fatty acids. The solutes were distributed between a carrier gas, nitrogen and a stationary phase which was silicone oil coated on a diatomaceous earth support.

Throughout the 1950's gas chromatography (GC) developed rapidly and the popular view was that, to obtain narrow and well separated zones, the chromatographic operations required sufficient running times. This would allow adequate time for the sorption-desorption to occur with only a small deviation from equilibrium.

Giddings and Eyring [9] in 1955 introduced probability concepts into the molecular migration in chromatography which were the basis

for the later random walk theory (Section 1.4.7).

The most crucial development in the theory of GC at the time was made by Van Deemter el al [10] in 1956. They described the zone spreading in terms of three dispersive processes each of which contributed independently to the height equivalent to a theoretical plate (HETP). Thus the HETP was the sum of three terms, each had a different velocity dependence. The application of this equation was to a large extent responsible for the rapid progress of GC in the late 1950's and early 1960's, and this equation is still the foundation of our understanding of band spreading in not only GC but also in LC.

In 1958, Golay [11] assumed that a large number of equilibrations took place and time for equilibration is small as a solute migrates through a capillary GC column whose walls were evenly coated with a stationary phase. He then derived an equation for the plate height which contained an axial diffusion term and two mass transfer terms. The two mass transfer terms described the equilibration of solute in gas and stationary phases.

A generalised non-equilibrium theory was developed by Giddings [12] in 1959 which for the first time provided regional mathematical expressions for the contribution to HETP for slow equilibration steps in chromatography. Then these were applicable to adsorption-desorption processes, diffusion limited processes etc. when

operated on packed beds [13].

1.1.2 GC Materials

The particle size range used in GC is from 100μ to 300μ in diameter. The actual range used in a GC column is usually within ±100μ. The size range, 100-300μ, is the optimum size range which would offer the best column efficiency and at the same time allow the mobile phase to pass through the packed bed.

1.1.2.1 Molecular sieves

The molecular sieves used in the 1950's were calcium aluminium silicates [13a]. Such compounds are commonly called zeolites. These materials have only been used to separate mixtures of n-paraffins, kerosenes and permanent gases [13a]. Liquid stationary phases and other adsorbents which display a much wider range of analytical applications have been developed.

The structures of zeolite supports have well defined molecular dimensions and are able to trap solutes that can enter such structures.

The zeolite columns should be heated above 300°C before use in order to remove any chemisorbed water in the material. Purnell [13a] stated that the selectivity of a number of gaseous solutes

are influenced by the amount of water occluded in the zeolite lattice structure. When using molecular sieves, the chromatographic system must be free of water and carbon dioxide, which may otherwise react with the support to alter its chromatographic properties [13a].

1.1.2.2 Alumina

Alumina has been used for the separation of paraffin wax and C_1-C_5 hydrocarbon mixtures [13a]. The activity of the adsorbent and hence the quality of the separation is dependant upon the amount of water present in the adsorbent surface.

1.1.2.3 Silica

Silica is the most widely used adsorbent. The uses of this material include the analysis of permanent gases, low boiling hydrocarbons and the oxides of sulphur and nitrogen [13a]. The water content of this material just as in alumina, should be carefully controlled to achieve the best separation [13a].

1.1.2.4 Liquid phases

A liquid stationary phase may be coated on diatomaceous earth support to carry out gas-liquid chromatography. The technique has widened the field of applications. Polar compounds can generally

be separated by coating the support with a polar stationary phase. Examples of such a phase include polyethylene glycols (PEG), esters and silicone oils. A coating of hydrocarbon on this support would present with a surface for the separation of non-polar solute mixtures.

1.1.2.5 Bonded phases in GC

A range of bonded solid phases for GC were marketed in the early 1970's by Waters Associates [13b]. The entire range of these supports were called 'Durapak materials'. These were originally prepared by Halasz and Sebestian. The use of such materials fell due to the development of capillary GC which offered considerably higher column efficiencies.

1.1.2.6 Carbon

Graphitised carbon black (GCB) (also see Section 1.3), and Porous graphitized carbon (PGC) have been available of late. GCB is composed of colloidal units which are bound together by Van der Waals forces. Whereas PGC has a sponge-like two dimensional structure. The structure of PGC is explained in detail in Section 1.6.1.

Both the carbon materials possess hydrophobic surfaces and are suitable for the separation of non polar compounds. The non polar

character of these surfaces can be altered by adsorbing a stationary phase such as Carbowax (PEG) which introduces a certain degree of polarity to these supports. The chromatography carried out by the research teams of Kiselev, Bruner and Di Corcia on coated GCB surfaces are described in Chapter 3. The author's results obtained on Carbowax coated PGC are described in Section 3.3.

The adsorption gas chromatography carried out by the above mentioned research teams on GCB are mentioned in the introductions of Chapters 2 and 4. These two chapters also describe the author's experience with adsorption gas chromatography on PGC.

1.2 DEVELOPMENT OF HPLC

After the invention of GC, chromatographers realised that smaller particles can be used as the stationary phase with a pressure gradient across the length of the column to perform high performance liquid chromatography (HPLC).

In the early days, before the late 1960's, gravity was used to pass the liquid eluent through a packed bed of particles. The diffusivity in a gas is much more (about 10^4 times) than that in a liquid. Therefore the particles used in LC are about 50 times smaller than those used in GC [14]. A bed of smaller particles ($<10\mu$) would not readily allow a liquid eluent to permeate under

the influence of gravity. If such a LC technique is to be employed it would eventually lead to unsatisfactory plate heights and long retention times. Therefore it was necessary to apply pressure to the mobile phase to assist its passage through the packed column.

The volumes of detectors, tubing in the system, injector valves and dead volumes of columns must be minimised to avoid serious peak dispersions. The manufacture of HPLC equipment therefore demands a great deal of precision and micro-engineering. Proper technology has not been available until the late 1960's to carry out HPLC.

Horvath [15], Huber [16] and Kirkland [17] developed the first HPLC systems to be used for practical separations. Giddings [13] contributed largely towards the theoretical developments of this new technique.

HPLC could separate substances that have:-

(i) been classified as highly non volatile

(ii) high polarity

(iii) large molecular weights

(iv) low thermal stability

(v) the tendency to ionize in solution [18].

1.2.1 HPLC Packing Materials

1.2.1.1 Pellicular supports

The early HPLC packing materials were large (approximately 30μ) porous adsorbents. Such particles displayed poor mass transfer properties as a result of large diffusion distances. Kirkland [19] in 1968 used pellicular porous supports. These were superficially porous materials, which were non-porous spherical glass particles covered wih a layer (1-2μ) of porous silica or alumina. Such pellicular materials had low sample capacity.

1.2.1.2 Micro adsorbent particles

The efficiency could be enhanced by using porous materials of approximately 5μ. These solids would have higher sample capacity and shorter diffusion distances. Silica and alumina are commonly used in LC. The pores of such stationary phases should ideally be about 5nm to prevent the solutes trapping inside the particles and giving rise to tailed peaks.

Kirkland [20] in 1972 used packing materials which were 10μ and he compared their performance with pellicular supports (approximately 29μ). He discovered that the efficiencies obtained with 10μ particles were less than those observed with pellicular supports. Kirkland attributed this to difficulties encountered in

packing such micro particles into a column. He also stated that non-spherical irregular particles would contribute towards the lowering of efficiency. He discovered that for solutes with smaller k^1 values, 5-6μ silica particles displayed higher column efficiencies than 37μ pellicular material. He also mentioned that the efficiency of a column packed with micro particles can be improved by improving the packing procedure. Kirkland achieved good separations for the mixtures of urea, carbonates and chlorinated insecticides with 5μ silica particles.

1.2.1.3 Polymer coated stationary phases

Cohen et al [21], Volkin et al [22] and Anderson and co-workers [23] used cross linked polymers as ion exchangers for the separation of bases, neucleotide and neucleosides. Early ion exchange resins were prone to changes in their volumes under different pH and ionic strength conditions. Such materials deformed under pressure and hence displayed poor mass transfer properties. Recently developed gels are rigid due to the existence of tightly polymerised regions which would not allow the solvent and analyte to penetrate.

In 1967, Horvath [24] developed a pellicular ion exchange resin. Glass beads were coated with a polystyrene/divinyl benzene polymer. Sulphonation of this polymer yielded cation exchange terminals on the surface. Chloromethylation of the polymer

followed by the reaction with tertiary amine produced anion exchange sites on the surface. Such materials possessed low swelling characteristics and favourable physical properties.

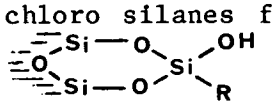
1.2.1.4 Reversed phase materials in LC

Majors [25] stated that, in the late 1970's vast majority of HPLC users have favoured the use of reverse phase materials. Such materials are non-polar stationary phases and were invented in the 1950's for the separation of polar molecules [26]. Whereas, normal phase materials are polar and adsorbents such as silica gel fall into such a category.

Silanol groups (SiOH) of silica gel can be derivatised to prepare a variety of bonded hydrophobic stationary phases.

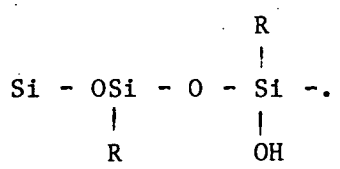
(a) Reaction with alcohol [27] to produce Si-OR groups on the silica surface. The reaction of silica with an amine would yield Si-NR terminals.

(b) Majors has described the reaction of silnol with alkyl chloro silanes followed by hydrolysis to obtain Si-OSi(OH)$_2$R and



[28,29] on the surface.

(c) Organochloro silane can be hydrolysed to form silane triols. These triols may be polymerised and reacted with silica to form



Such materials offer good hydrolytic stability [30-31].

(d) In the mid 1970's Grignard reactions have offered a route to the preparation of Si-R bonds on the surface. Such materials offer good hydrolytic stability and non polar character.

Silica as a stationary phase is highly polar. Even derivatisation of surface silanol groups of silica cannot sufficiently decrease the polarity. Also, silica is very unstable at high pH values. Due to these disadvantages, there is a need to develop a stable, robust and non-polar stationary phase for LC. Graphite could fill such a role.

1.3 THE HISTORY OF CARBON AS A STATIONARY PHASE IN CHROMATOGRAPHY

Before 1955, charcoal was used as an adsorbent in chromatography [32,33]. Tiselius and co-workers [34,35] carried out early LC work using activated carbon as the stationary phase. These carbons were used in early LC for the separation of hydrocarbons [33,36-40]. The demand for carbon as a stationary phase fell in the early 1960's as a result of the poor peak shape obtained due to the non linearity of the adsorption isotherms. The decreasing popularity of carbon as an adsorbent at that time is also attributed to the

competition from thin layer chromatography (TLC) which used silica gel. This material is white and therefore the spots could easily be detected.

Graphitized carbon black (GCB) was first developed in the early 1960's by Supelco Inc., Belfonte, PA, U.S.A. This material consists of loosely aggregated colloidal units having only Van der Waals bonding between them. Until 1988, this was the only commercially available two dimensional graphite material that was suitable for chromatography.

Kiselev in the early 1960's was the first to study the adsorption properties of GCB [41]. He considered heat of adsorption (ΔH) values of solutes, adsorption isotherms and Adsorbate-Adsorbent interaction on GCB. Kiselev realised that GC is a versatile, simple and accurate technique that he could use in his work [42]. He compared the heats of adsorption values of hydrocarbons and alcohols obtained from the GC and calorimetric methods with those predicted by calculations [42]. He discovered that the ΔH values determined via the GC technique agreed well with the predicted results.

Kiselev did extensive work on carbon [41-43] and wrote a review on GCB as a GC packing material [44].

Liberti, Dicorcia and Kiselev successfully used GCB to carry out a

vast number of GC separations in the 1970's and 80's. Detailed accounts of their work are given in Chapters 2-4.

GCB is fragile and therefore incapable of withstanding high pressures, (a) applied whilst packing of HPLC columns, (b) experienced during HPLC. GCB therefore cannot be used as an LC stationary phase for routine analytical work.

Liberti et al [45] in 1981 used GCB in Liquid Chromatography. They purchased 80-100μ mesh from Supelco and crushed the granules to obtain smaller particles. Liberti and co-workers discovered that the particles with diameters less than 20u were irregularly shaped micro particles and thus were unsuitable for LC. They used 25-33μ granules in their analytical work.

They packed HPLC columns using a dry packing technique. The conventional slurry packing technique was not employed as this would have given a column full of crushed particles.

They successfully separated triazine isomers, degradation products of triazine, components in a pharmaceutical preparation, mixtures of phthalates, uv absorbing amino acids, chlorinated pesticides and aromatic hydrocarbons. By and large, the peaks were symmetrical, analysis times were favourable and the reduced plate heights were less than 4. Their research [45] indicated that carbon has shown a great deal of promise as a LC stationary phase.

The drawbacks of this material are that (i) smaller particles were unsuitable for LC, (ii) Liberti et al [45] reported high back pressures (approximately 2000 psi) during chromatography, (iii) only dry packing technique may be employed due to the fragility of the particles, and (iv) only solvents with lower viscosities such as pentane or methanol may be used as eluents.

In the 1970's chromatographers recognised the potential of using carbon in LC while appreciating the problems encountered in packing and during chromatography. Several attempts were made to strengthen the material and hence to develop a suitable stationary phase for LC.

The first attempt to do this was made by Guichon and co-workers [46]. The pyrolytic carbons prepared, by pyrolysing benzene and other hydrocarbons [47-49], could be deposited on GCB particles to enhance the mechanical strength of GCB. Barmakova et al [47] applied this idea to obtain carbons for GC. Guichon et al [46] used this technique to prepare a suitable material for LC. The mechanical strength of this prepared material was greater than that of GCB but still lacked mechanical hardness required for an LC stationary phase. Guichon [46] therefore pyrolysed benzene on silica gels. The amount of hydrocarbon deposited was about 20% (w/w) to obtain a graphite material that can be used in LC. Guichon found that the surface of this stationary phase was hetrogeneous and as a result, displayed undesirable chromatographic

properties.

Plazk and co-workers [50] prepared a carbon for LC by the reduction of polytetrafluoroethylene (PTFE) with alkali metal amalgams in vacuo at 100°C. This procedure yielded a carbon with a high surface area (approximately 2000 m^2g^{-1}). The surface area was reduced by various treatments, including high temperature treatment. The resulting low surface area carbon powder possessed excellent mechanical properties but displayed poor chromatography.

Unger et al [51] used purified calcinated active charcoals and cokes in LC. These particles were mechanically hard but had rather low surface areas (a few m^2g^{-1}); and hetrogeneous surfaces which gave unfavourable chromatograhic properties.

Knox, Gilbert and Kaur [2,52-55] in the late 1970's and early 80's developed a new kind of porous graphite (PGC) that could withstand high pressure experienced during column packing and chromatography. Also, PGC displayed favourable chromatographic properties, and possessed sufficiently large surface area with good mass transfer properties. This material was marketed in 1988 by Shandon Scientific (Runcorn, Cheshire) under the trade name of Hypercarb. The following section describes the preparation of this material.

1.3.1 Preparation of PGC

Graphitization to the Warren Structure (see Section 1.6.1) occurs when amorphous and glassy carbons are heated in excess of 2000°C [2,52-56].

PGC is made by polymerising a mixture of phenol and hexamine deposited in the pores of a silica gel and then pyrolising the polymer in the mixture by heating to 1000°C. Then the silica template was dissolved in alkali and the porous carbon obtained was graphitized by heating in a stream of argon to above 2300°C. Carbons produced this way are moderately robust [2,55].

Above the temperature of 2300°C, the randomly arranged sheets of graphite tend to form within the material [2, 52-56]. They gradually extend and organise into an ordered two dimensional crystalline structure as temperature increases [54]. Most synthetic carbons when heated above 2000°C tend to arrange themselves such that they assume the 2-dimensional structure described in Section 1.6.1 and Figure 1.16, where the sheets are randomly orientated relative to one another [54].

Silica gels of lower surface area (approximately 50 m^2g^{-1}) are used as templates for the preparation of GC particles (100-300μ) of PGC. Silica gels of higher surface area (approximately 60 m^2g^{-1}) are suitable to be used as templates in the preparation of PGC

particles (3-10μ) for LC.

PART II

Principles and Theories of Chromatography

and

Principles of Adsorption

1.4 CHROMATOGRAPHY - PRINCIPLES AND THEORIES

1.4.1 GC and HPLC Systems - Block Diagrams

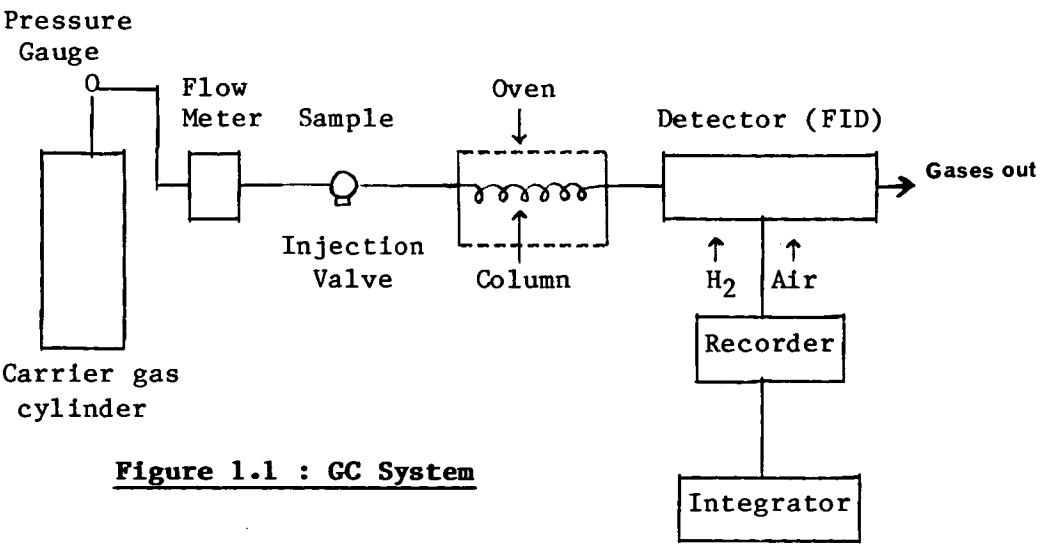


Figure 1.1 : GC System

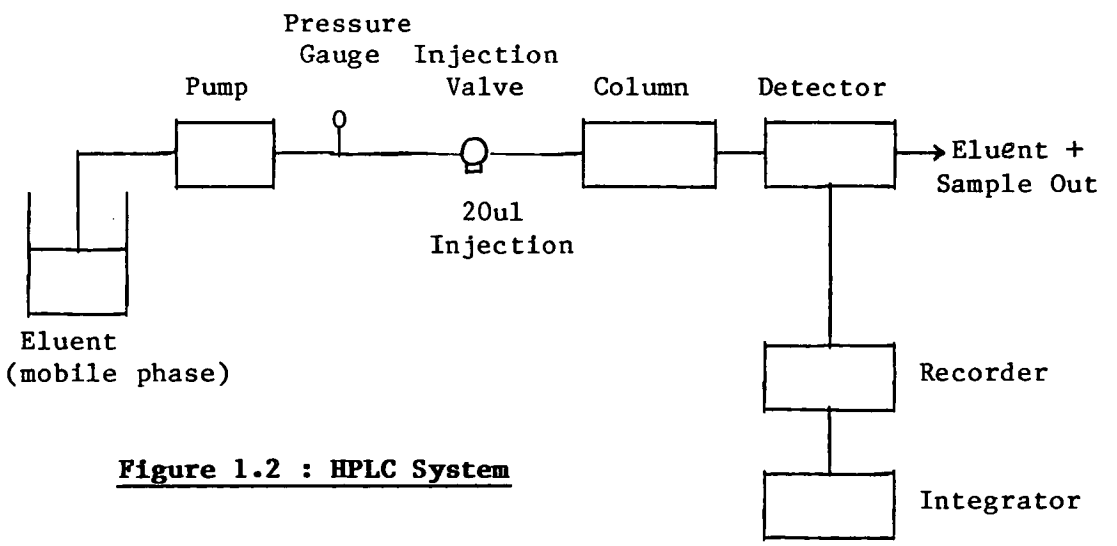


Figure 1.2 : HPLC System

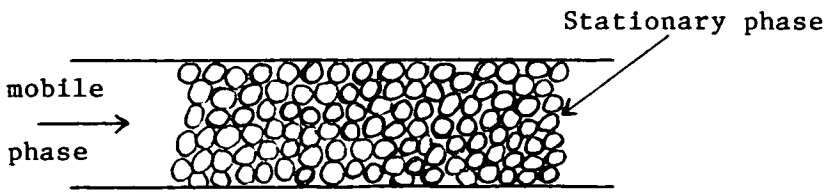


Figure 1.3 : A Magnified Portion of the Chromatographic Column

Figures 1.1 and 1.2 show block diagrams of GC and HPLC systems respectively.

GC is the forerunner of HPLC. The LC system is modelled closely on the GC outfit. In LC as in GC, the mobile phase (m) is driven through the column by a pressure gradient. In both HPLC and GC, the column temperature, inlet pressure and flow rate can be carefully controlled in order to achieve the optimum separation of a sample (analyte, solute or eluate) mixture. The analyte mixture is introduced at the inlet end of the chromatographic column via an injection valve in the case of HPLC. Whereas, an enclosed septum injection system is used in GC.

Individual solutes emerge from the column at different times and a property of the compound is detected. (In GC : Thermal conductivity, ionization in a flame and ability to capture electrons. In HPLC : Ultraviolet (UV) absorption fluorescence, refractive index and electrochemical properties).

The signal from the detector is amplified and normally recorded by a potentiometric chart recorder on chart paper. The response for any eluted solute is recorded as a peak. The area under the peak is proportional to the quantity of solute. Qualitative identification of a compound is by its retention time (t_r). This is the time the solute spends inside the column (Figure 1.4).

The magnified portion of a chromatographic column is shown in Figure 1.3. This consists of particles of a solid stationary phase (an adsorbent) or a support material coated with a liquid stationary phase (s).

When a sample mixture enters a column, the migration of sample components through the column is governed by their respective solubilities in the stationary phase or the strength of their adsorption by the adsorbent [57,58]. While an analyte is inside the column, the analyte molecules in the mobile phase are in equilibrium with the analyte molecules in the stationary phase.

The equilibration of the solute depends upon the diffusion of solute within the particles of the packing. The time (t) for diffusion or equilibration depends on diffusion coefficient (D) of a solute and the variance (σ_{diff}^2) due to diffusion.

$$\text{Therefore} \qquad \sigma_{diff}^2 = 2Dt \qquad \text{——— 1.1 [59]}$$

σ_{diff}^2 is generally proportional to the particle diameter (dp) which is the distance diffused by a solute molecule in the stationary phase [58].

The diffusion coefficient of a small molecule in a gas (eluent in GC) is approximately 10^4 times greater than that in a liquid (eluent in LC). Therefore the packing material is chosen such that

in GC, the particles (100-300μ) are much larger than in LC (5-10μ) [14].

At the same time the viscosity of a liquid is about 100 times larger than that of a gas and therefore the pressure drop across the LC column is correspondingly greater than the pressure drop across a GC column [14], for the same overall elution time.

When a sample mixture enters a chromatographic column, equal times are spent by each sample component in the mobile phase but the analytes have different retention times. This means that the solutes spend different times on the adsorbent surface or in the liquid stationary phase. This phenomenon leads to the separation of the sample mixture.

1.4.2 Retention : Capacity Ratio and Band Speed

A chromatogram is a record of the detected property of the solute versus time, as it emerges from the column (Figure 1.4).

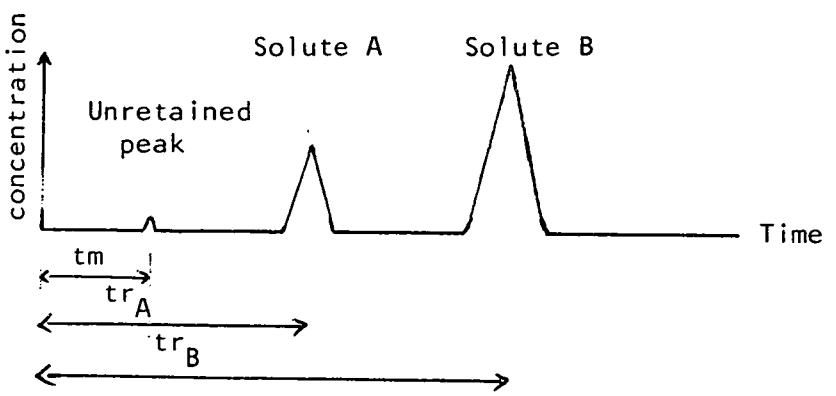


Figure 1.4

A number of basic chromatographic quantities emerge from this simple picture. The degree of retention is measured by the capacity ratio k^1, for solute A, for example, is given by:-

$$k^1_A = (tr_A - tm)/tm \quad \text{——— 1.2}$$

where tr_A is the retention time of solute A and tm is the dead volume of column. In GC, tm is measured by injecting a dose of methane into the column. Methane is unretained and therefore the retention time of methane is taken as tm. In LC, tm is the time taken by the solvent front to pass through the column.

$$\text{Now } tr_A = tm(1+ k^1_A) \quad \text{——— 1.3}$$

The flowrate through the column is given by,

$$f = Vr_A / tr_A \quad \text{——— 1.4}$$

(where Vr_A = retention volume at tr_A). The flowrate is the same for all the solutes. We can equally well write

$$Vr_A = Vm(1 + k^1_A) \quad \text{——— 1.5}$$

$$\text{Therefore } k^1_A = \frac{Vr_A - Vm}{Vm} \quad \text{——— 1.6}$$

In thin layer chromatography (TLC), retention is usually expressed in terms of relative band speed R_f. R_f can be expressed in several alternative ways.

$$R_f = \frac{U}{\frac{\text{solute band}}{\text{solvent front}}} = \frac{tm}{tr} = \frac{Vm}{V_r} = \frac{1}{1+k^1} \quad \text{——— 1.7}$$

k' can alternatively be expressed in terms of R_f whence,

$$k^1 = \frac{1}{R_f} - 1 = \frac{1 - R_f}{R_f} \quad \text{——— 1.8}$$

U = velocity of the sample band or solvent front.

1.4.3 Relationship between Retention and Partition Coefficients of Solute X between Mobile and Stationary Phases

When a solute X is added to the eluent and moves down the column, X is distributed between the mobile (m) and the stationary phases (s) and we can write:-

$$\frac{\text{quantity of X in s}}{\text{quantity of X in m}} = \frac{qs}{qm} = \frac{Cs}{Cm} \cdot \frac{Vs}{Vm} \quad \text{——— 1.9}$$

$$= K\Phi \quad \text{——— 1.10}$$

Cs and Cm are concentrations of X in stationary and mobile phases respectively.

Vs and Vm are volumes of stationary and mobile phases respectively (in the column).

$$K = \text{distribution ratio} = Cs/Cm \quad \text{——— 1.10(a)}$$

$$\Phi = \text{Phase ratio} = Vs/Vm$$

If a molecule X spends a total of (ts) seconds in the stationary phase, and (tm) seconds in the eluent. Then at equilibrium

$$\frac{qs}{qm} = \frac{ts}{tm} \quad \text{———1.11}$$

In well behaved chromatography, K is independant of solute concentration. Non-homogeneity of the solid phase due to the presence of active sites will make K dependent upon the concentration.

If the eluent is flowing at velocity U, the solute velocity is U, while in the eluent and the distance it moves is (tm)(U). The solute molecule has a velocity of zero while in the stationary phase. The total time spent by the molecule in both phases is (tm+ts)sec. The Velocity of solute band = U_{band}

$$U_{band} = \frac{tmU}{ts+tm} = U\left[\frac{1}{(1 + ts/tm)}\right] \quad \text{——— 1.12}$$

From equation 1.3,

$$t_r = tm(1 + k^1)$$

and

$$\frac{U_{band}}{U} = \frac{1}{1 + k^1} \quad \text{——— 1.7}$$

Now we can identify k^1 as

$$k^1 = ts/tm \quad \text{——— 1.13}$$

$$= qs/qm = K\Phi \quad \text{——— 1.14}$$

and $\Phi = Vs/Vm$ applies to two bulk phases of gas-liquid chromatography.

Retention volume, $V_r = Vm\ (1 + k^1)$,

for two bulk phases, $V_r = Vm\ (1 + (Cs/Cm)(Vs/Vm))$ ——— 1.15

$$= Vm + (Cs/Cm)Vs \quad \text{——— 1.16}$$

$$= Vm + K\ Vs \quad \text{——— 1.17}$$

1.4.3.1 Adsorption isotherm

For an adsorbent, the distribution of solute between the adsorbent and the eluent can be represented by an adsorption isotherm (Figure 1.5). However, assuming for the time being that at low concentrations Cs^1/Cm is constant, and is independent of concentration, (isotherm 1, Figure 1.5),

$$k^1 = qs^1/qm = \frac{Cs^1}{Cm} \cdot \frac{As}{Vm} = k_{ads}\ \Phi^1 \quad \text{——— 1.18}$$

k_{ads} = Adsorption coefficient = Cs^1/Cm ——— 1.18(a)

Φ^1 = Phase ratio = As/Vm

Cs^1 = concentration of solute on the adsorbent (moles/unit surface area)

Cm = concentration of solute in the eluent (moles/unit volume)

As = area of adsorbent.

For an adsorbent,

$$V_r = Vm\ [1 + (Cs^1/Cm)(As/Vm)] \quad \text{——— 1.19}$$

$$= Vm + k_{ads}\ As \quad \text{——— 1.20}$$

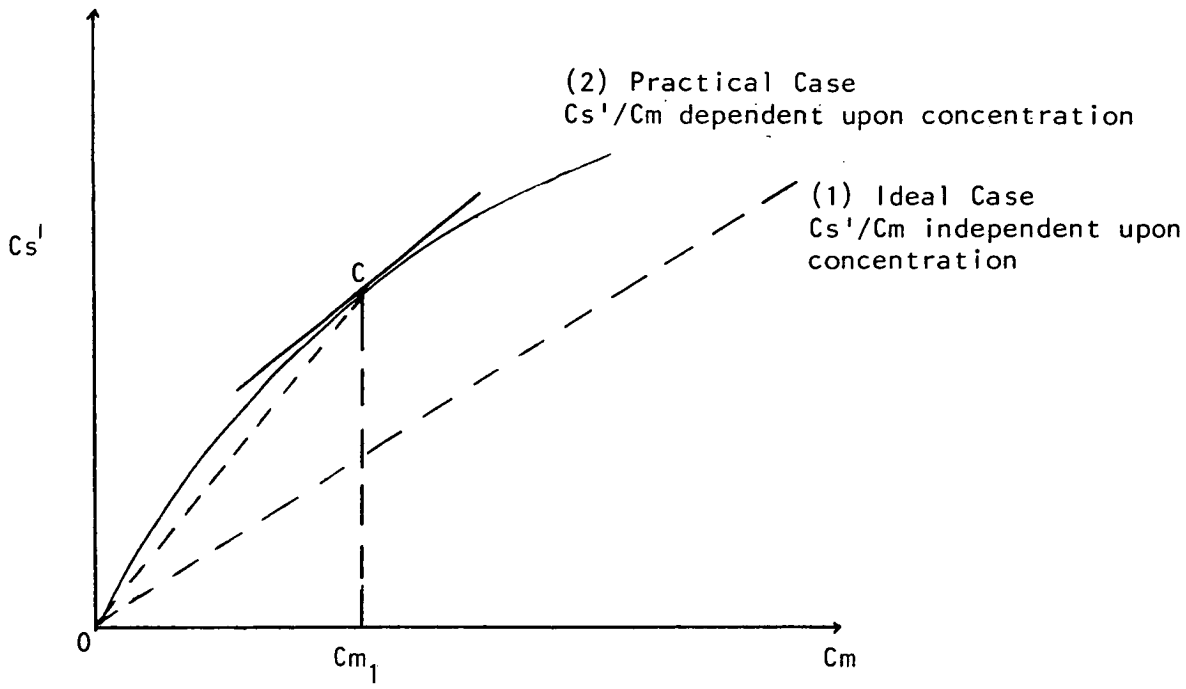


Figure 1.5

Very often, the adsorption isotherm is curved and convex towards the ordinate. Under such conditions, Cs^1/Cm is dependent upon the concentration (Figure 1.5, isotherm 2).

A step change in concentration of a solute in the eluent (0 to a value Cm) can be created by including the solute in the eluent reservoir. The k^1 of the front is given by equation 1.21.

$$k^1_{front} = \Phi (Cs^1/Cm) \quad \text{——} \quad 1.21$$

K^1_{front} can be measured, Φ and Cm are known. Therefore, Cs^1 may be calculated.

The concentration of solute in the eluent is then changed back to zero. Then the solute profile would leave a tail.

$$k^1_{tail} = \Phi \left(\frac{dCs^1}{dCm}\right) \quad \text{——— 1.22}$$

Different concentrations of a solute can be used in the eluent to obtain a series of k^1_{front} values. The corresponding Cs^1 values can be deduced using equation 1.21. Such information is useful for plotting the adsorption isotherm of a solute on a chromatographic support.

After the measurement of each k^1_{front}, the concentration of solute in the eluent is changed back to zero to flush the solute off the column.

For example, Cs^1/Cm_1 is the gradient of a chord joining O and a point C on the isotherm 2 (Figure 1.5). Cs^1/Cm_1 and Φ enable the calculation of k^1 of a step front (Figure 1.5a) of concentration Cm_1 using equation 1.21.

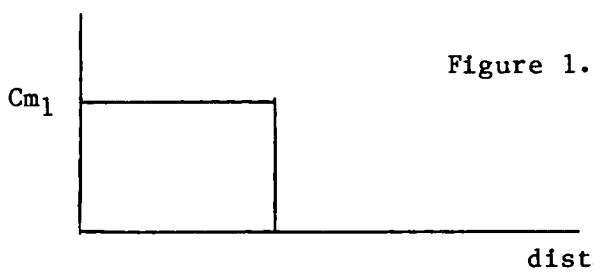


Figure 1.5a - Step front

The gradient (dCs^1/dCm_1) of tangent at point C (Figure 1.5) and equation 1.22 would be useful in the calculation of k^1_{tail} of the step front. The tail is shown in Figure 1.5b.

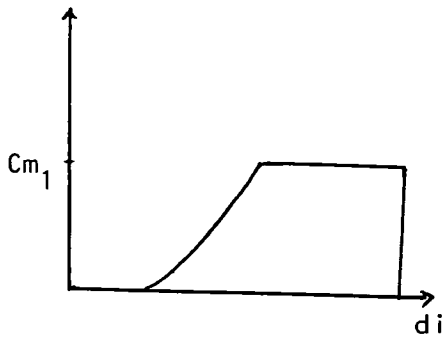


Figure 1.5b - Tail of step front

The velocity of front of step change (of concentration Cm_1, for example) is less than that of its tail. Consequently, k^1_{front} is greater than k^1_{tail}. Therefore the gradient of tangent at C (Figure 1.5, isotherm 2) is less than the gradient of chord OC.

A solute dose can be introduced on to the column, in the absence of analyte in the eluent. If causes of peak spreading other than due to concentration are absent, the peak migrates along the column as shown in Figure 1.6. As the solute moves down the column the peak width increases and the peak height decreases due to the increased number of interactions with the solid phase.

When a solute dose is introduced on to a column, the solute molecules would interact with hetrogenities on the adsorbent, and as a result the higher concentrations of the concentration profile (peak) overides the lower concentrations and so producing a vertical step in the profile. Such a phenomenon would give rise to peak tailing. The k^1 of any concentration Cm in the tail is given

by equation 1.22.

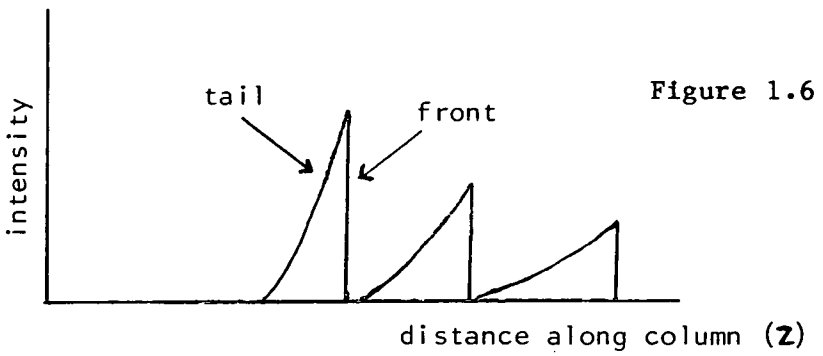


Figure 1.6

When a solute dose is introduced on to a column, the tail and the front of peak separated out, then

$$k_{tail} = \Phi(dCs^1/dCm) \quad \text{——} \quad 1.22$$

The k_{tail} is the measured k^1 of a solute dose. The gradient of isotherm at the corresponding value of Cm (i.e. concentration of solute introduced on to the column) and equation 1.22 enables the calculation of k^1 of solute dose.

At lower concentrations of Cm, the chord gets steeper and k^1_{front} gets larger. The gradient of isotherm 2 in Figure 1.5, display a steeper gradient than the ideal case (isotherm 1) due to almost all the solute molecules in the dose occupying the sites on the adsorbent. The greater the steepness of the isotherm 2, the greater the uptake of the adsorbate and hence the greater the heterogenity of the adsorbent surface.

1.4.4 Measurement of True Retention Volume in Gas Chromatography

[References 8, 60]

The true retention time in GC depends upon the nature of the stationary phase or adsorbent, column temperature, carrier gas flow rate and the volume of free space inside the column. The compressibility of the gaseous eluent adds another variable to the above list. This is clearly seen with the diminishing cross sectional area whilst the amount of stationary phase remained constant. The narrower the column, the greater the pressure gradient across its length, and hence the smaller the velocity of mobile phase passing through the column. This would result in an increase in analysis time. If the retention is therefore to mean anything in GC, a correction must be applied to overcome the consequences of the pressure gradient.

The pressure correction factor may be derived by considering the Darcy's Law which states that the velocity (Ua) of flow through a packed column is proportional to the pressure drop (dP/dl) causing it.

$$Ua = B \frac{dP}{dl} \qquad \text{——— 1.24}$$

where B = permeability coefficient.

After making allowances for the eluent viscosity (n),

$$Ua = \frac{-Bo}{n} \cdot \frac{dP}{dl} \quad \text{——— 1.25}$$

where Bo = specific permeability coefficient.

Ua is calculated by dividing the volumetric flow rate by the cross sectional area of the column. This treatment does not consider the actual area available for the flow, which is only a fraction of the total area. The fraction of free space available inside the column per unit column volume is the porosity E. Therefore the true velocity (u^1) of eluent passing through the column is Ua/E.

Therefore $$u^1 = \frac{-Bo}{nE} \cdot \frac{dP}{dl} \quad \text{——— 1.26}$$

Applying Boyle's Law [60] for the flow through a packed column,

$$Pu^1O = PoUoO \quad \text{——— 1.27}$$

where O = cross sectional area of the column.

Uo = velocity of eluent at the outlet.

P and Po = Pressure of eluent at a given point inside the column and at the outlet respectively.

Therefore $$u^1 = \frac{PoUo}{P} \quad \text{——— 1.28}$$

By substituting equation 1.28 to the Darcy's equation,

$$Uo = \frac{-BoP}{PoEn} \cdot \frac{dP}{dl} \quad \text{——— 1.29}$$

$$dl = \frac{-Bo.P}{PoEnUo} \cdot dP \quad \text{——— 1.30}$$

and by multiplying through by P,

$$Pdl = \frac{-Bo}{PoEnUo} p^2 \, dP \quad \text{——— 1.31}$$

The average pressure $\bar{P}$ is given by

$$\bar{P} = \frac{\int Pdl}{\int dl} \quad \text{——— 1.32}$$

Dividing equations 1.31 by 1.30

$$\bar{P} = \frac{\int Pdl}{\int dl} = \frac{\int_{Po}^{Pi} p^2 dP}{\int_{Po}^{Pi} PdP} \quad \text{——— 1.33}$$

which gives $$\bar{P} = \frac{2}{3}\left[\frac{(Pi^3 - Po^3)}{(Pi^2 - Po^2)}\right] \quad \text{——— 1.34}$$

after rearrangement

$$j = \frac{Po}{\bar{P}} = \frac{3}{2}\frac{[(Pi/Po)^2 - 1]}{[(Pi/Po)^3 - 1]} \quad \text{——— 1.35}$$

where Pi = inlet pressure.

$$\frac{\bar{P}}{Po} = \frac{Vr}{\bar{V}} \quad \text{——— 1.36} \quad [63]$$

where Vr = measured retention volume

$\bar{V}$ = true retention volume.

$$Vr = \bar{V}j \quad \text{——— 1.37}$$

The compressibility factor is important when determining true retention volumes under different flow conditions. j cancels out when determining k^1.

$$\frac{(Vr - Vm)j}{Vmj} = k^1 \quad \text{——— 1.38}$$

Therefore $$\frac{Vr - Vm}{Vm} = k^1 \quad \text{——— 1.6}$$

1.4.5 Temperature Effects on Solute Retention [58] in GC

During chromatography, a solute X is transferred between the mobile and the stationary phase (either a solid coated with a liquid stationary phase or an adsorbent).

$$Xm \rightleftharpoons Xs \quad \text{——— 1.39}$$

The standard free energy change for this reaction is

$$\Delta G^\circ = -RT\ln K \quad \text{——— 1.40}$$

where $$K = Cs/Cm \quad \text{——— 1.41}$$

T = Temperature of reaction, R = Gas constant.

ΔG° is the free energy change when a reaction proceeds (i) with the products and reactants are in their standard state, (ii) with each product and reactant at a partial pressure of one atmosphere (If products and reactants are solutions, each product and reactant would have unit concentrations), and (iii) at a specified temperature.

Now $$k^1 = K\Phi \quad \text{——— 1.14}$$

Therefore $$\Delta G^\circ = -RT\ln k^1 + RT\ln\Phi \quad \text{——— 1.42}$$

Gibbs-Helmholtz equation states that

$$\frac{d(\Delta G^\circ/T)}{dT} = \frac{-\Delta H^\circ}{T^2} \quad \text{——— 1.43}$$

whence $$\Delta H^\circ = RT^2 \frac{d\ln k^1}{dT} - RT^2 \frac{d\ln\Phi}{dT} \quad \text{——— 1.44}$$

The free energy change of a reaction is concentration dependent. The standard conditions must therefore be stated when defining ΔG. The standard enthalpy change (ΔH°) of a reaction is concentration independent, and therefore the symbol ΔH could be used to describe the heat of transfer of a solute from the mobile phase to the stationary phase.

$$RT^2 \frac{d\ln\Phi}{dT} = 0 \quad \text{——— 1.45}$$

The left hand side of equation 1.45 is equal to zero since the volume of column, mobile and stationary phases inside the column do not significantly vary with column temperature. The value of Φ therefore does not significantly vary with temperature.

Therefore $$ {}_{m}\Delta H_{s} = -RT^2 \frac{d\ln k^1}{dT} \quad \text{——— 1.46}$$

$$\int d\ln k^1 = \int \frac{-{}_{m}\Delta H_{s}}{RT^2} dT \quad \text{——— 1.47}$$

$$\ln k^1 = -\frac{\Delta H}{RT} + C \quad \text{——— 1.48}$$

Footnote: ΔH is the Heat of transfer of a solute from the eluent to the solid phase. In adsorption GC, the symbol ΔH represents the heat of adsorption (ΔH_{ads}).

Since, on the subject of adsorption, it is useful to describe the heat of transfer of a solute from the gaseous eluent to a surface covered with a liquid stationary phase. This is known as the heat of partition (ΔH_{par}).

In Chapter 3, the term ΔH is used to describe the heat of transfer from the gaseous mobile phase to the solid phase (bare PGC surface or PGC surface, partially/fully covered with Carbowax), i.e. ΔH refers to (a) ΔH_{ads}, (b) ΔH resulting from a combination of adsorption and partition, and (c) ΔH_{par}.

ΔH is the heat of transfer of a solute from the eluent to the adsorbent or the liquid stationary phase. Equation 1.48 shows, the dependence of k^1 on temperature. The gradient of the graph of k^1 vs 1/T thus enables the calculation of heat of transfer (also see Chapter 2).

ΔH values in GC (i.e. heats of transfer of solutes from gaseous eluent in the solid phase) are much greater than the ΔH values in LC. In LC, the variation of column temperature has only a modest effect on retention and ΔH. In this case, ΔH approximately equals 0 $kJmol^{-1}$. This involves the migration of solutes from one condensed phase to another. The retention in LC is varied by altering the polarity of the eluent. The retention in GC can be controlled by varying the column temperature.

Retention of analytes also depends upon (i) the homogeneity of the adsorbent (in adsorption chromatography) and (ii) the stationary phase on the adsorbent (in the case of partition chromatography). Chapters 2-6 deal with these subjects in detail.

The quality of chromatography can be generally improved by (i) controlling the analyte retentions, (ii) decreasing the width of analyte peaks, and (iii) increasing the efficiency (N) of column (plates per column) or decreasing the plate height (H) (see later).

Retention was introduced and discussed in Sections 1.4.3 to 1.4.5. The Sections 1.4.6 and 1.4.7 will discuss the parameters that can be varied to achieve the best peak shape and the overall plate height.

1.4.6 Peak Shape and Peak Height [58]

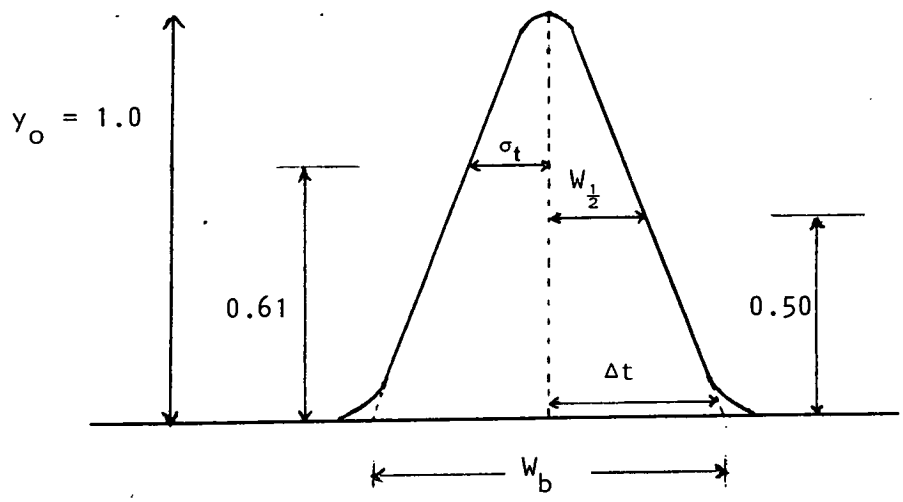


Figure 1.7

The peak shape shown in Figure 1.7 is described by

$$y = y_o \exp[-\Delta t^2 / \sigma_t^2] \quad \text{——— 1.49}$$

y = height on peak, y_o = maximum height of peak, σ_t = peak width at 0.61 of height, Δt = half width of peak.

The peak width at half height $W_{\frac{1}{2}} = \sqrt{5.54}\ \sigma_t$ ——— 1.50

This enables the calculation of the number of theoretical plates to which a column is equivalent (usually stated as the plate number).

Height equivalent to a theoretical plate

$$H = L/N \quad \text{——— 1.51}$$

L = length of column and N = efficiency of column (plates).

$N = \frac{L}{H}$ and H is defined as $\frac{d\ \sigma_z^2}{dz}$ ——— 1.52

Therefore, the peak width, $W_b = 4\sigma_z = 4\sqrt{HL}$ ——— 1.53

Therefore $\sigma_z^2 = HL$ ——— 1.54

or $H = \frac{\sigma_z^2}{L}$ ——— 1.55

$$N = \frac{L}{\sigma_z^2/L} = \frac{L^2}{\sigma_z^2} \quad \text{——— 1.56}$$

Since the record of solute concentration in the eluent as a function of time is exact parallel of the record of solute concentration within the column as a function of distance along the column, we can write,

$$N = \frac{(tr)^2}{(\sigma_t)^2} \quad \text{——— 1.57}$$

Therefore $H = \frac{L}{N} = L\left(\frac{\sigma_t}{(tr)^2}\right)^2$ ——— 1.58

By substituting the value of σ_t (into equation 1.57), the equation 1.50, where $\sigma_t = \frac{W}{\sqrt{5.54}}$ ——— 1.59

that gives $N = 5.54\left(\frac{tr}{W}\right)^2$ ——— 1.60

The area under the curve (Figure 1.7) is,

$$A = \sqrt{2\pi}\, y_o\, \sigma_t = 2.51\, y_o\, \sigma_t \quad \text{——— 1.61}$$

$$\sigma_t = \frac{A}{y_o\sqrt{2\pi}} \quad \text{——— 1.62}$$

$$A^2 = \sigma_t^2\, y_o^2 . 2\pi \quad \text{——— 1.63}$$

$$\sigma_t^2 = L^2/N \quad \text{———1.64 (from 1.56)}$$

Therefore $A^2 = \frac{L^2}{N} y_o^2\, 2\pi$ ——— 1.65

$$N = \left(\frac{Ly_o}{A}\right)^2 . 2\pi \quad \text{——— 1.66}$$

From equation 1.53,

$$W_b = 4\,\sigma_t \quad \text{——— 1.53}$$

Therefore

$$\sigma_t^2 = (W_b)^2/16 \quad \text{——— 1.67}$$

$$N = \frac{tr^2}{W_b^2/16} = \frac{16tr^2}{W_b^2} \quad \text{——— 1.68}$$

$$H = L/N,$$

Therefore

$$H = \frac{L}{16} \cdot \frac{(W_b)^2}{(tr)^2} \quad \text{——— 1.69}$$

The ratio (W_b/tr) can be reduced in order to decrease H and hence increase the efficiency of column. In GC, this effect is apparent, when solutes are chromatographed on PGC that has been coated with a certain amount of a liquid stationary phase (Chapter 3). Column efficiencies similar to the coated surfaces are observed when solutes are chromatographed on a 'Grade A' adsorbent (Table 2i) such as PGC 219 CEN (Figure 3.24). Narrow, sharp analytical peaks and favourable analysis times are observed (Figure 2.6) on PGC 219 CEN.

The column length can be increased to increase N, an increase in column length would result in increased analysis time. A compromise should be reached between L and N to obtain favourable retention values.

1.4.7 Band (or Peak) Spreading : Van Deemter Equation [10,58]

The equation determines the factors which contribute towards the overall plate height. Total plate height arise from A, B and C

terms of the equation

$$H = A + \frac{B}{u} + Cu \quad \text{——— 1.70}$$

u = velocity of mobile phase through the column.

(i) Flow Tortuosity : Peak spreading due to tortuous nature of the flow through a packed bed. The A term of the above equation can be derived from Giddings' random Walk treatment [13].

Flow tortuosity may be explained by considering two solute molecules of a solute front starting at one position and commence moving with the eluent. After some time the two molecules will be in two places. Each molecule has taken several steps to arrive at these positions.

$$\sigma_z^2 = nl^2 \quad \text{——— 1.71}$$

where l = overall step length of the solute front

n = number of steps taken by both molecules

σ_z^2 = variance of the steps (or variance due to tortuous flow).

Also $$l = dp\,\lambda \quad \text{——— 1.72}$$

and $$n = Lw/\lambda(dp) \quad \text{——— 1.73}$$

where dp = particle diameter

λ = Geometrical parameter

L = length of column

and w = constant.

Therefore $$\sigma_z^2 = (w\,\lambda)(dp)L \quad \text{——— 1.74}$$

$$H = \frac{\sigma_z^2}{L} = \lambda\, w(dp) \quad \text{——— 1.75}$$

The A term is $(w\,\lambda\,dp)$.

This indicates that the larger the particles diameter, the greater the H value and hence the smaller the magnitude of N.

(ii) Axial Diffusion : The magnitude of this term depends on the time spent by the solute band inside the column. This term is significant at lower flow velocities. The diminished flow velocities are accompanied by enhanced residence times.

If two solute molecules start at one position and start to move with the eluent, and then after a short while one molecule may reside on the stationary phase while the other remains in the eluent.

Now $$(\sigma_{diff})^2 = 2\,Dt \quad \text{——— 1.1}$$

For the two molecules in stationary and mobile phases, the variance due to diffusion is

$$(\sigma_{diff})^2 = 2[(\gamma_m)(Dm)(tm) + (\gamma_s)(Ds)(ts)] \quad \text{——— 1.76}$$

$$k^1 = ts/tm \quad \text{——— 1.13}$$

γ_m and γ_s = obstructive factors of mobile and stationary phases respectively.

Dm and Ds = Diffusion coeffients of a solute in the mobile and stationary phases respectively.

in LC.

$$H_{diffusion} = \frac{(\sigma_{diff})^2}{L} = 2\,\frac{tm}{L}[(\gamma_m)(Dm) + (\gamma_s)(Ds)k^1] \quad \text{— 1.77}$$

$(u = L/tm)$

$$H = \frac{2}{u}[(\gamma_m)(Dm) + (\gamma_s)(Ds)k^1] = \frac{B}{u} \quad \text{——— 1.78}$$

In GC, Dm » Ds

Therefore B term = $2(\gamma_m)(Dm)$ ——— 1.79

Therefore $H_{diffusion} = [2(\gamma_m)(Dm)]/u$ ——— 1.80

$(\sigma_{diff})^2$ is proportional to the square of the distance migrated by a molecule. Decreasing dp would therefore reduce H and in turn would enhance N.

u can be increased to decrease H and hence improve N.

(iii) Mass transfer term : This is the non-equilibrium term (C term) of the van Deemter equation. Considering two molecules, starting together just inside the column, one molecule remains in the eluent and runs ahead whilst the other penetrates into the stationary phase. Then the latter re-enters the mobile phase.

Velocity of the sample band = $u/(1+k^1)$ ——— 1.81.

Velocity of molecules on the stationary phase = 0.

Velocity of molecules in the eluent = u.

The time spent by a molecule in the eluent when it jumps from the stationary phase to the eluent and then back into the stationary phase = Tm.

Time taken by a molecule to diffuse through a particle of the stationary phase = Ts.

The overall step length of the solute profile is,

$$l^1 = \left[\left(\frac{u}{(1+k^1)}\right) - 0\right] Ts \quad \text{——— 1.82}$$

Now $k^1 = Ts/Tm$ ——— 1.13(a)

Therefore the overall step length of the solute front inside the column is,

$$1^1 = \left[\frac{uk^1}{1+k^1}\right] Tm \quad \text{——— 1.84}$$

$$n^1 = 2\,\frac{tm}{Tm} \quad \text{——— 1.85}$$

where n^1 = Total number of steps taken by the two molecules.

$$\sigma_E^2 = n^1 1^{1^2} \quad \text{——— 1.71}$$

where $(\sigma_E)^2$ = varience due to slow equilibration of the system.

Therefore $(\sigma_E)^2 = 2\,\frac{tm}{Tm}\left[\frac{k^1}{1+k^1}\right]^2 u^2\, Tm^2$ ——— 1.86

$$H = (\sigma_E)^2/L = 2\,\frac{tm}{L}\left[\frac{k^1}{1+k^1}\right]^2 u^2\, Tm \quad \text{——— 1.87}$$

$$= \frac{2k^1}{(1+k^1)^2} \cdot Ts \cdot u \quad \text{——— 1.88}$$

For LC, $Ts = (q^1{}_1)\,(dp)^2/Ds$ ——— 1.89

For GC, $Ts = (q^1{}_g)\,(d_p)^2/Ds$ ——— 1.90

Therefore C term can be written as

$$H = \frac{(q^1{}_{g,1})k^1}{(1+k^1)^2} \cdot \frac{(dp)^2 u}{Ds} \quad \text{——— 1.91}$$

i.e. $H = Cu$ ——— 1.92

For GC and LC, q^1_g and q^1_l apply respectively. This quantity is a geometrical parameter, dependent upon the geometry of particles.

The C term is dependent upon k^1 of analyte, particle diameter, diffusivity in the stationary phase and u.

The thickness of any liquid stationary phase on the solid support will dictate the magnitude of the C term and hence the efficiency. Greater the thickness, the deeper the penetration of the solute into the stationary phase, and hence the longer the analyte takes to get back into the mobile phase. By the time the deeply penetrated molecules come out of the stationary phase, the solute profile in the eluent has already moved forward. This effect is shown in Figure 1.8 by the concentration profile (B). The dotted lines in Figure 1.8 display the ideal situation where rapid equilibrium takes place between the solute in the stationary phase and mobile phases (profile A).

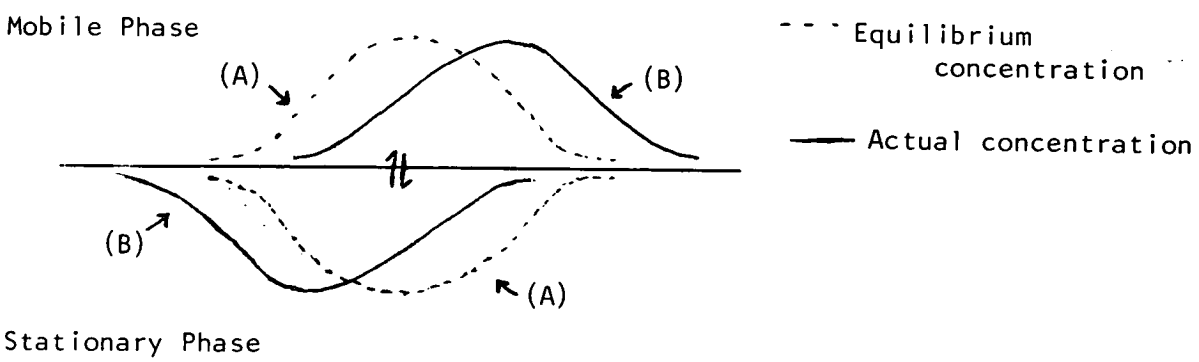


Figure 1.8 : Concentration Profiles

The thickness of the stationary phase should be optimised to achieve the desired separation and, at the same time, avoid peak spreading.

The Van Deemter equation can be written as,

$$H = A + \frac{B}{u} + Cu \quad \text{——— 1.70}$$

For LC,

$$H = \frac{L}{N} = w\lambda(dp) + \frac{2}{u}[(Dm)(\gamma m)+(\gamma s)(Ds)k^1] + \frac{(q^1_1)(k^1)}{(1+k^1)^2} \cdot \frac{(dp)^2u}{Ds}$$

——— 1.93

For GC,

$$H = \frac{L}{N} = w\lambda(dp) + \frac{2}{u}(Dm)(\gamma m) + \frac{(q^1_g)k^1}{(1+k^1)^2} \cdot \frac{(dp)^2u}{Ds} \quad \text{——— 1.94}$$

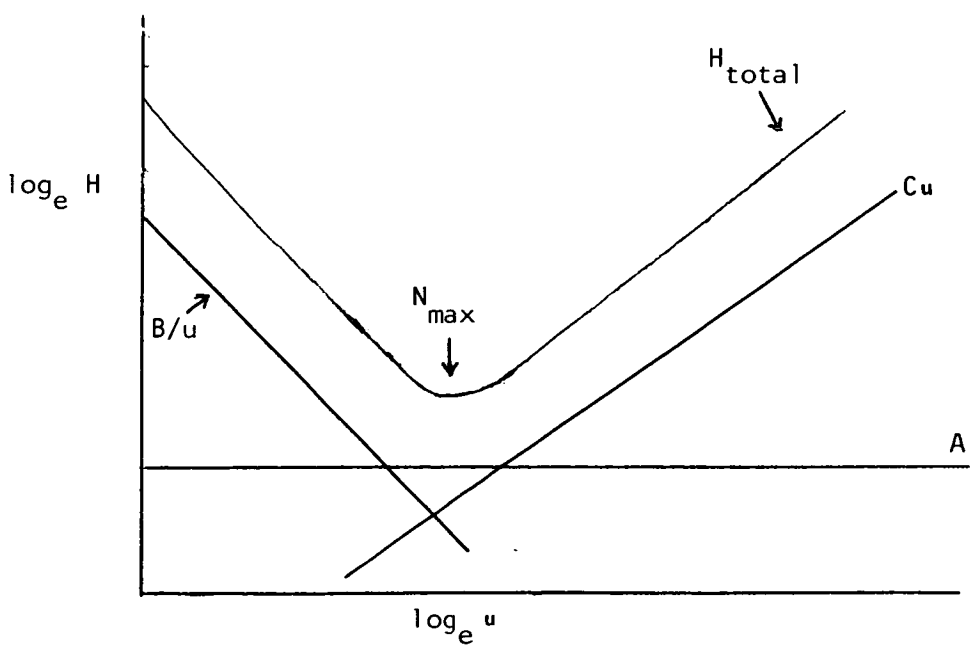


Figure 1.9

Figure 1.9 shows the van Deemter plot. The velocity of the eluent (u) should be adjusted such that the system is operated at H min for maximum efficiency.

The plate height of a column can be written in terms of reduced plate height (h).

where $h = H/dp$ ——— 1.95

h expresses the number of particles corresponding to H and also, the degree of band spreading by the packing in relation to dp.

$$h = \frac{H}{dp} = w \cdot \lambda + \frac{2}{\nu}\left[\gamma_m + k^1(\gamma_s)\frac{Ds}{Dm}\right] + (q^1_{g,1})\frac{k^1 \nu}{(1+k^1)^2}\frac{D_m}{D_s} \quad \text{——— 1.96}$$

where $\nu = \frac{u(dp)}{Dm}$ = reduced velocity of eluent ——— 1.97

$k^1 \gamma_s Ds/Dm$ is neglegible in GC.

The particle size (dp) should be selected such that the maximum efficiency may be achieved. If dp is too large, A, B and C terms of equation 1.70 would increase and therefore N would decrease. The optimum dp [14] can be calculated by

$$dp = \left[\frac{Nh\,\bar{\Phi}\,\nu_{opt}{}^n\,Dm}{\Delta p}\right]^{\frac{1}{2}} \quad \text{——— 1.98}$$

N = efficiency of column

h = reduced plate height (minimum value)

n = viscosity of the eluent

$\bar{\Phi}$ = pressure resistance factor

Δp = pressure drop across the length of column

ν_{opt} = optimum reduced velocity

In theory, the smaller the particle size, the higher the value of N. With smaller particles, higher pressures are required to pump the eluent. In GC, (i) high pressures can be dangerous to be used in the laboratory, and (ii) gaseous eluent finds it difficult to pass through a packed bed of smaller particles. Capillary GC therefore may be used for higher efficiences.

1.5 PRINCIPLES OF ADSORPTION

Adsorption is the basis for understanding (a) the chromatography on different solid surfaces, and (b) the determination of surface areas of solids.

The first part of this sub-section gives a brief introduction on Physical and Chemical Adsorption which leads to the discussion on the thermodynamics of adsorption chromatography. This is the foundation for understanding the nature of the eluotropic relationships on graphite (see Chapter 2).

The latter half of this section describes the Langmuir and Brunauer, Emmett and Teller (B.E.T.) isotherms, and the principles behind the determination of surface area of solids.

1.5.1 Adsorption and the Physical Chemistry that takes place on the Carbon Surface

In order to understand chromatography it is vital to fully appreciate the processes that are taking place as chromatography proceeds.

1.5.1.1 Physical adsorption (physisorption)

In physisorption (commonly called "adsorption") there are Van der Waals interactions (e.g. dispersion) between the surface and the adsorbed molecules. Such interactions can cause the formation of monolayers and multilayers on solids. These are weak interactions and the molecules are not permanently attached to the surface.

The energy released as a result of adsorption is in the order of enthalphy of condensation (about 20 kJ mol^{-1}) [61]. As adsorption occurs, a general decrease in the free energy of the system takes place. The energy evolved in the form of heat is insufficient to break any bonds and therefore in physisorption, the molecules do not undergo any chemical change. The physically adsorbed species may be stretched or bent in the close proximity of the surface.

1.5.1.2 Chemical adsorption (chemisorption)

The adsorption process occuring as a result of bonding due to

electron transfer is known as chemisorption [61,62]. The bonded layer is only one molecule thick. This phenomenon tends to proceed with increasing temperature and it involves rather large activation energies (approximately 100-400 kJ mol^{-1}). Chemisorption is normally irreversible and cannot be used as a basis for chromatographic retention.

1.5.1.3 Gas-solid interface [62]

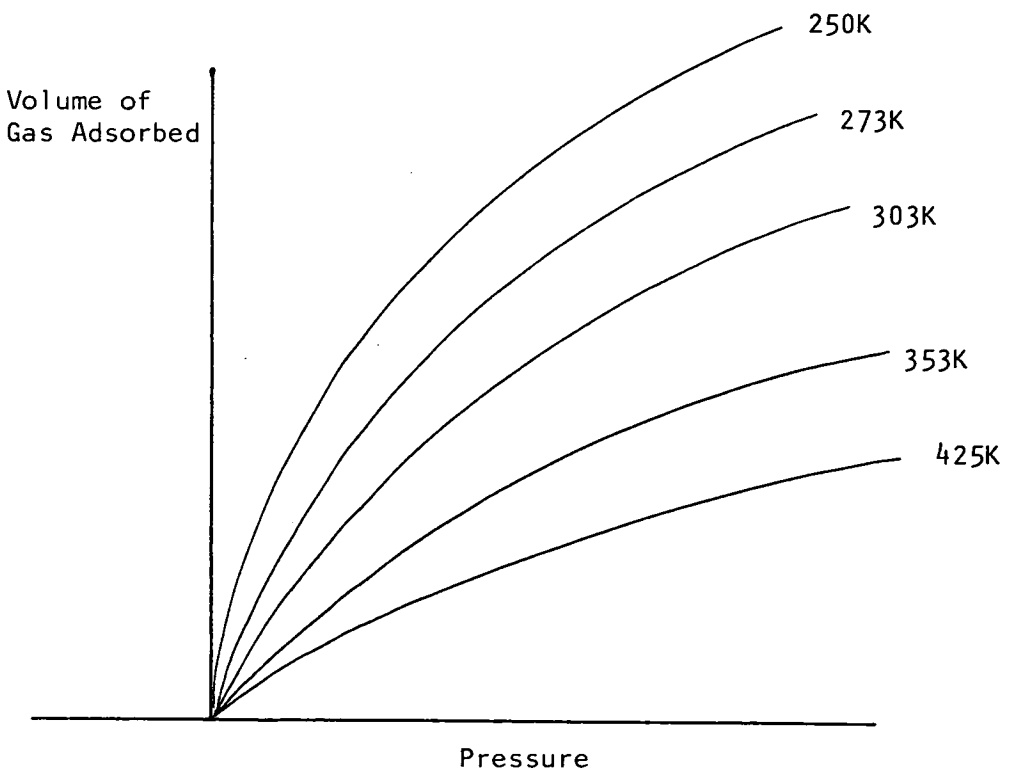


Figure 1.10

Figure 1.10 shows a series of adsorption isotherms at different

temperatures where the higher the temperature, the lower the adsorption at a given concentration. Adsorption depends on pressure, temperature and effective surface area of solids [62]. Adsorption isotherms of importance are discussed in detail in Sections 1.5.4-1.5.5. Highly porous materials (>70%) of large surface area (approximately 80-150 m^2g^{-1}) are most useful as chromatographic adsorbents.

Adsorption reduces the imbalance of attractive forces which exist on the surface, this enables the reduction of the free energy of the surface of a hetrogeneous system.

Figure 1.11 shows the processes that are taking place when a molecule approaches a surface. In Figure 1.11, Curve P represents physical interaction energy between surface and X_2. This includes attraction from Van der Waals forces and repulsion due to overlapping of electron clouds. An additional contribution from dipole interactions may be included if permanent dipoles are involved.

Curve W represents chemisorption, in which an atom X is adsorbed by the system. The curve is displaced vertically by ½ D(X-X) to relate it properly to curve P for the diatomic molecule. The heat of chemisorption is represented by the deep minimum. A species involved in chemisorption is closer to the surface than a species involved in physisorption.

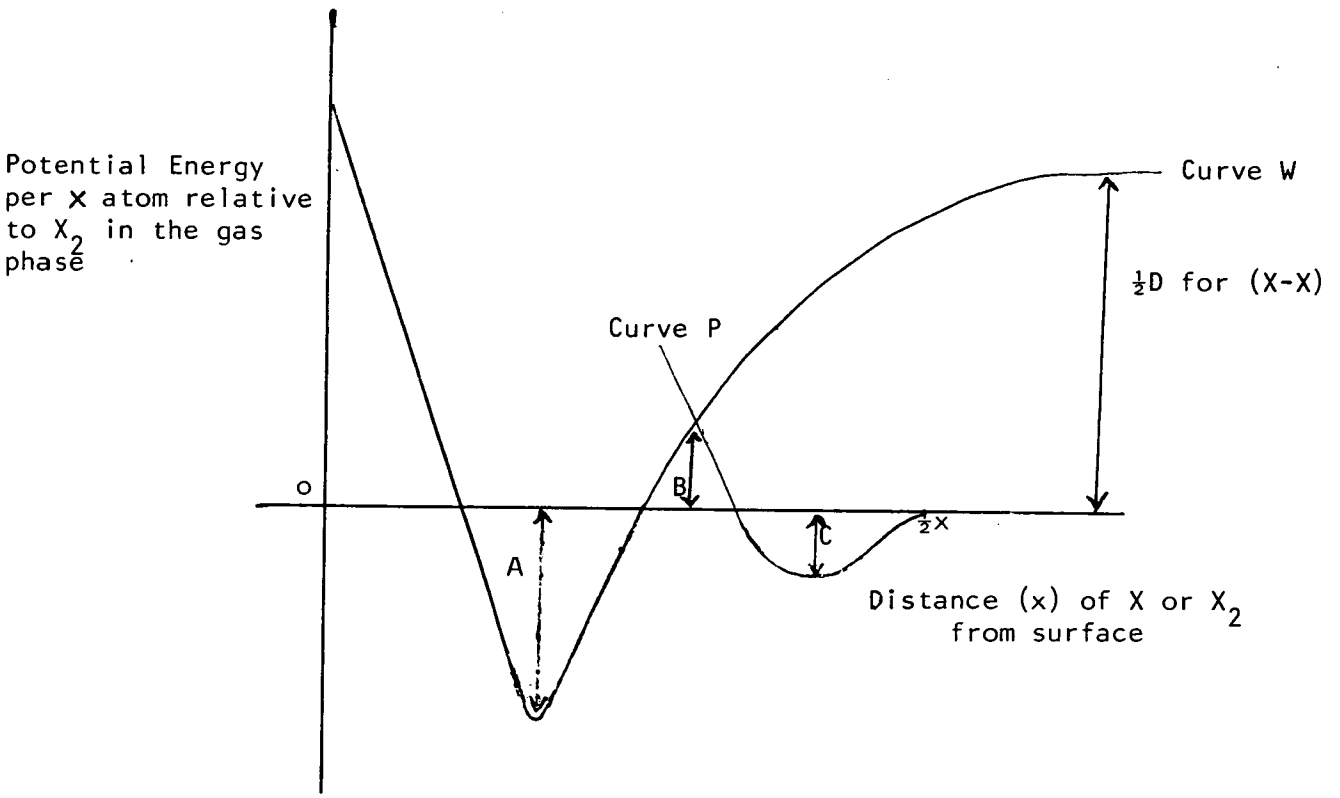


Figure 1.11 [62]

X_2 = A diatomic gas molecule, X is a single atom.

A = Heat of chemisorption for X.

B = Activation energy for chemisorption of $\frac{1}{2}X_2$.

C = ½ (heat of physisorption of X_2).

D = ½ (Dissociation energy of X_2).

Before a molecule is chemically adsorbed, it is physically adsorbed. This means that the molecule approaches the solid surface along a low energy path. If physical adsorption is non-existent, then the activation energy for chemisorption would be equal to dissociation energy of X_2 molecule. Transition from physical adsorption to chemical adsorption takes places at the point where the curves P and W intercept. Energy at this point is the activation energy for chemisorption. The activation energy depends on the shapes of the curves P and W.

1.5.2 Thermodynamics of Adsorption from the Gas Phase

1.5.2.1 Heat of adsorption (ΔH)

The technique of GC can be used to establish the ΔH values of solutes and hence the nature of the eluotropic series on an adsorbent. Therefore it is necessary to appreciate the thermodynamics associated with the determination of ΔH values.

The process of distribution in adsorption chromatography can be represented by equations 1.39 and 1.18(a).

$$Xm \rightleftharpoons Xs \qquad 1.39$$

where Xs = solute on the adsorbent

Xm = solute in the mobile phase.

$$k_{ads} = \frac{Cs^1}{Cm} \quad \text{——— 1.18(a)}$$

For any chemical or physical equilibrium, the standard thermodynamic relationships may be applied. These are,

$$\Delta G^\circ = -RT\ln(k_{ads}) \quad \text{——— 1.40}$$

and

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{——— 1.99}$$

Therefore

$$\ln k_{ads} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad \text{——— 1.100}$$

ΔG° = Change in free energy for the reaction under standard conditions (J mol^{-1})

ΔS° = Entropy change for the reaction under standard conditions (J/mol). K^{-1}

R = Gas constant = 8.314 J mol^{-1} K^{-1}.

T = Temperature at which the reaction occurs (Kelvin).

ΔH° = Enthalpy change for the reaction under standard conditions. In the case of adsorption, this is the heat of adsorption (kJ mol^{-1}).

Now from equation 1.18,

$$k^1 = q_s^{\,|} / q_m \quad \text{——— 1.18}$$

$q_s^{\,|}$ = quantitiy of solute on the adsorbent surface

$$q_s^{\,|} = Cs^1 As \quad \text{——— 1.18(b)}$$

and

$$q_m = Cm\ Vm \quad \text{——— 1.18(c)}$$

From equations 1.18(b), 1.18(c) and 1.21

$$k^1 = \frac{qs^1}{qm} = \frac{Cs^1}{Cm} \cdot \frac{As}{Vm} = k_{ads} \frac{As}{Vm} \quad \text{——— 1.101}$$

$$\ln k^1 = \ln k_{ads} + \ln \frac{(As)}{(Vm)} \quad \text{——— 1.102}$$

$$\ln k^1 = \frac{-\Delta H}{RT} + \left[\frac{\Delta S}{R} + \ln \frac{(As)}{(Vm)}\right] \quad \text{——— 1.103}$$

If ΔH is constant, then a linear relationship is obtained between $\ln k^1$ and $1/T$. ΔH is calculated from the gradient of such a plot.

$$\Delta H = \text{(gradient)} \times 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \quad \text{——— 1.104}$$

1.5.3 Nature of the Eluotropic Series of Solvents on Carbon and Silica

The nature of the eluotropic series was established on carbon using GC. Silica was also used in this study for comparison. The ΔH values of some HPLC solvents were determined on carbon and silica.

The quantity $\Delta H/Ax$ of these samples were calculated from the ΔH results obtained on each adsorbent. Ax is the area occupied by a solvent molecule on the adsorbent surface. The Ax values were found in reference 63. Snyder [63] has determined the eluotropic strengths (Eo) of solvents on silica gel. Eo is defined as the free energy of adsorption of a solvent molecule per area of that molecule (also see next section). $\Delta H/Ax$ is a measure of eluotropic strength. $\Delta H/Ax$ of solvents determined on each adsorbent are plotted against their Eo values that were determined

on silica gel (found in Ref.63). Such graphs would display the differences between the eluotropic series of carbons and that of silica. Chapter 2 deals with this subject in detail.

1.5.3.1 Thermodynamics of adsorption from solution - Snyder theory (applied to LC)

Snyder used the displacement model (equation 1.105) to describe the adsorption process in a normal phase liquid-solid system. He assumed that the solvent on the surface is replaced by the solute molecules.

$$n\ S_{ads} + X \rightleftharpoons X_{ads} + nS \quad \text{——— 1.105}$$

where n = a number, S = an eluent molecule, X = a solute molecule, and S_{ads} and X_{ads} = an adsorbed eluent and solute molecule respectively.

The equation 1.105, shows the adsorption of a solute molecule by displacing a number of eluent molecules. This is the basis for understanding the solvent strength on an adsorbent surface. Eluotropic strength is the ability of a solvent in an LC system to occupy the sites on the surface and disallow the solute to interact with the adsorbent. The strength adsorption of a solvent on an adsorbent would determine the k^1 of a given solute in an LC system. The greater the interaction between the eluent and the solid phase, the smaller the retention of the analyte. The strongly adsorbing eluents may not be easily replaced by the

solute. Consequently, the greater the adsorption of a solvent on a solid phase, the larger the eluotropic strength of that solvent would be on that adsorbent.

Solvents can be arranged according to their ability to elute a given solute on an adsorbent. Such an arrangement is termed an eluotropic series.

Eo values can be determined by an LC technique which will be described later in this section.

$$\text{Now} \quad Eo = E_{sa}/Ax \quad \text{——} \quad 1.106$$

Eo is the adsorption displacement free energy of solvent (E_{sa}) per solvent molecular area (Ax) of the standard activity surface with relative to the standard solvent. Pentane was considered as the standard solvent as Snyder found that all solutes in a normal-phase liquid-solid system displayed highest retention when chromatographed using pentane as the eluent. He stated that pentane is the least polar and therefore the weakest solvent when using a normal phase liquid-solid system. Snyder fixed the Eo value of pentane to be zero and measured the Eo of other solvents relative to pentane.

The concept of eluotropic strength was developed by Snyder for the above mentioned system. The theory assumes that,

(a) As adsorption occurs, the solute molecules displace the liquid eluent molecules that are already adsorbed on to the surface.

(b) The number of mobile phase molecules displaced is dependant upon the area occupied by the solute molecule.

(c) The balance between the free energy of adsorption of a solute and mobile phase determines the strength of adsorption from a standard reference solvent (pentane).

(d) Specific molecular interactions between solute and mobile phase are neglected.

The theory leads to the equation 1.107,

$$\log_{10} k^1 = \log_{10}(\bar{V}s/V_M) + \beta(Sx^\circ - Eo\ Ax) \quad \text{——— 1.107}$$

$\bar{V}s$ = Volume of a monolayer of eluent adsorbed on the stationary phase.

V_M = Volume of eluent in the column (excluding the volume $\bar{V}s$).

β = Surface activity factor taken as 1 for fully activated surfaces (which includes PGC),

$Sx^\circ = \Delta Gx^\circ/2.303RT$ (sample adsorption energy), where ΔGx° is the standard free energy of adsorption for solute x on to the surface from the reference solvent [64].

Ax = Area occupied by a solute molecule in units of $8.5\mathring{A}^2$ (sum of the area of all the groups in the solute molecule).

$$Ax = \Sigma Ai \quad \text{——— 1.108}$$

where Ai = area of a group or an atom in a molecule.

This unit of 8.5Å is, 1/6 of area occupied by an adsorbed molecule of benzene which is 51 $Å^2/6 = 8.5\ Å^2$. This is the area occupied by one aromatic carbon atom [64]. Snyder gives a table of (Ai) values for different atoms and groups in reference 63.

Eo = $\Delta G°m/2.303RT$ where $\Delta G°m$ is the standard free energy of adsorption of eluent sufficient to cover an area of $8.5Å^2$ x (6.02×10^{23}) [64]. The units of Eo can be written as $(8.5Å^2)^{-1}$.

Since $$Eo = \Delta G°m/2.303RT \quad \text{——— 1.109}$$

also $$\Delta G°m = \Delta H° - T\Delta S° \quad \text{——— 1.110}$$

by substituting equation 1.110 into equation 1.111

$$Eo = \frac{\Delta H°}{2.303RT} - \frac{\Delta S°}{2.303R} \quad \text{——— 1.112}$$

Therefore $$\frac{\Delta S°}{2.303R} + Eo = \frac{\Delta H°}{2.303RT} \quad \text{——— 1.113}$$

$$\Delta S°T + Eo\ 2.303RT = \Delta H° \quad \text{——— 1.114}$$

where $\Delta H°$ is the heat of adsorption in KJ mol^{-1}.

Equation 1.114 shows that ΔH should be a linear function of Eo .

Heat of adsorption per carbon atom may be plotted against Eo to establish the nature of the eluotropic series on silica.

The theoretical gradient of such a plot would be

$$= 2.303RT = 5.74\ kJ\ mol^{-1}\ (8.5Å^2)^{-1} \quad \text{——— 1.115}$$

The eluotropic strength of a solvent may be determined by using equation 1.107.

A solute may be chromatographed on a polar adsorbent such as silica using the solvent of interest as the eluent. The same solute is chromatographed on the same column under the identical conditions, except that pentane is used as the eluent.

For the solvent of interest whose eluotropic strength is Eo_1. Now the equation 1.107 becomes

$$\log_{10} k_1^1 = \log_{10} (\bar{V}s/V_M) + \beta(Sx^\circ - Ax\ Eo_1) \quad \text{——— 1.116}$$

where k_1^1 is the capacity factor of the chromatographed solute when using the solvent of interest as the eluent.

The same solute is chromatographed on the same column with pentane as the mobile phase. Then the capacity ratio of the solute is k_2^1. Then,

$$\log_{10} k_2^1 = \log_{10} (\bar{V}s/V_M) + \beta(S_x^\circ - Ax0) \quad \text{——— 1.117}$$

By subtracting equation 1.117 from 1.116,

$$\log_{10} (k_1^1/k_2^1) = -Ax\ Eo_1 \quad \text{——— 1.118}$$

$$Eo_1 = \frac{\log_{10} (k_2^1/k_1^1)}{Ax} \quad \text{——— 1.119}$$

The equation 1.119 can be used to calculate the eluotropic strength of the unknown solvent.

Figure 1.12 shows the relationship, predicted by Snyder, between $\Delta H/Ax$ and Eo for solvents on silica gel.

A strong additive present in small quantities in a weak eluent, can localise with the active sites of the silica gel. This would

increase the eluotropic strength of the eluent. The strong additive occupies the sites on the adsorbent and prevents the solutes from interacting with the active sites. The increased elutropic strength of eluent is given the symbol Eo'.

The concept of localisation [65] and other interactions occurring on the silica surface may be explained further with reference to Figure 1.13.

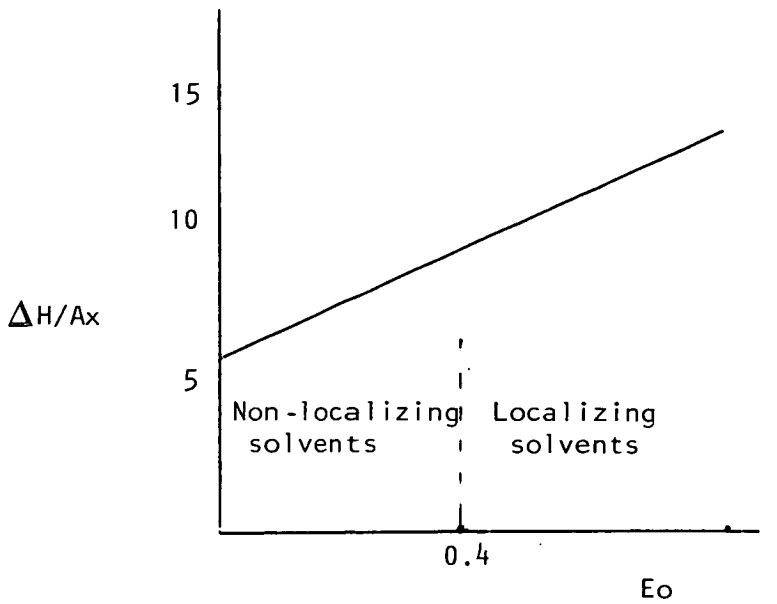


Figure 1.12

In Figure 1.13(a), molecule A is non-localised and the molecule B is localised. In Figure 1.13(b), the molecules A and B are non-localised.

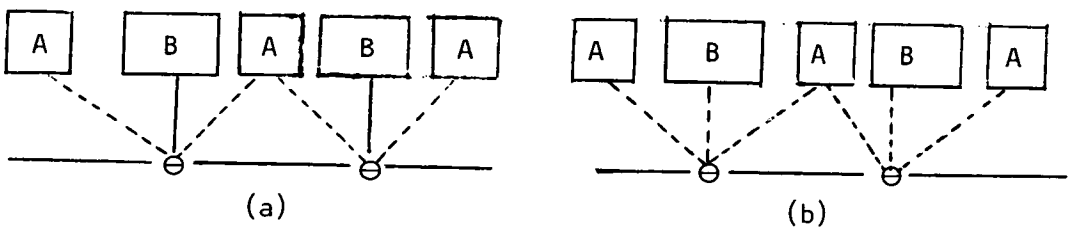


Figure 1.13

⊖ denote active sites (surface groups).

---- denote weak interactions.

—— denote hydrogen bonds.

Localising solvents are those which form hydrogen bonds with silanol groups of silica gel [65]. Such solvents display higher eluotropic strengths than the non-localising solvents.

Snyder's theory gets complicated for strong solvents and does not give easily predictable results. But this theory may be applied quite successfully for weak solvents [56], since interactions between molecules are less in weak solvents.

Snyder's theory described the adsorption of a solute in a normal phase system. The following considers the adsorption of an analyte in a reversed phase system. Carbon may be taken as the adsorbent.

A given solute may be adsorbed on to graphite from different solvents. These solvents would have different molecular areas. In each case, the solute is adsorbed by replacing the already adsorbed solvent molecules on the carbon surface.

The degree of disorder (due to translational motion) and hence the entropy of component in a solution is larger than that of the same component on the surface, so the entropy (ΔS) of displacement of solvent by the solute becomes more negative the more molecules of solvent are displaced by the solute. If the heat of adsorption (ΔH) of solute on to carbon is constant, then the thermodynamics indicate that the free energy (ΔG) of adsorption and hence the equilibrium constant (k) for the adsorption process of solute would be most favourable for the adsorption of solute from the solvent with the smallest molecules. This means that, the smaller the molecular area of eluent, the larger the ΔS, ΔG and k would be for the adsorption of eluate.

The interactions between solute and eluent would also influence adsorption of solute. The solute retention on carbon would decrease with increasing molecular size of solvent used in the eluent. Therefore the solvents with larger molecules can be used

to elute substances that display unfavourably high retention times on carbon.

1.5.4 Surface Coverage, with reference to the Determination of Surface Areas

Physisorption is not only the basis of adsorption chromatography (Sections 1.52, 1.53 and Chapter 2) but also the basis for understanding the determination of surface areas of solid stationary phases. This would give an indication of the areas available for chromatography.

1.5.5 The Langmuir Adsorption Isotherm [61]

As adsorption takes place, the surface is gradually covered with the molecules. Before a monolayer is achieved, if the total area is regarded as made up of a number N of adsorption sites, the fractional coverage θ , is defined as,

$$\theta = \frac{\text{number of adsorption sites filled}}{\text{number of sites available}} \qquad \text{——— 1.120}$$

The Langmuir isotherm arises when, (a) ability of a molecule to occupy a site does not depend on whether the neighbouring sites are occupied, (b) every adsorption site is equivalent, and (c) adsorbed and free molecules are in equilibrium.

A molecule of gas (a) hitting the surface (S) may be physically

adsorbed and then may return to the gas phase.

$$a(g) + S \underset{kd}{\overset{ka}{\rightleftharpoons}} aS \quad \text{——— 1.121}$$

The equilibrium summarises the reaction, ka and kd are the rate coefficients of adsorption and desorption respectively.

The rate of adsorption is proportional to the pressure of the gas (a). This pressure is Pa. The rate of adsorption is also proportional to the number of vacant sites on the surface, $N(1-\theta)$, where N = total number of sites.

$$\text{Rate of adsorption} = (ka)PaN(1-\theta) \quad \text{——— 1.122}$$

$$\text{Rate of desorption} \propto N\theta .$$

$$\text{Rate of desorption} = (kd)N\theta \quad \text{——— 1.123}$$

At equilibrium, the two rates are equal.

$$(kd)N\theta = (ka)(Pa)N(1-\theta) \quad \text{——— 1.124}$$

$$\theta = \frac{(K')Pa}{1+(K')Pa} \quad \text{——— 1.125}$$

$K' = ka/kd$ = equilibrium constant at zero coverage ——— 1.126

$$\theta = V/Va \quad \text{——— 1.127}$$

where V = uptake volume and Va = monolayer capacity.

Equation 1.125 is the Langmuir adsorption isotherm.

Now,

$$\theta + \theta(K')(Pa) = K.Pa \quad \text{——— 1.128}$$

$$\frac{V}{Va} + \frac{V}{Va} . K' . Pa = K.Pa \quad \text{——— 1.129}$$

$$\frac{1}{K'Va} + \frac{Pa}{Va} = \frac{Pa}{V} \quad \text{——— 1.130}$$

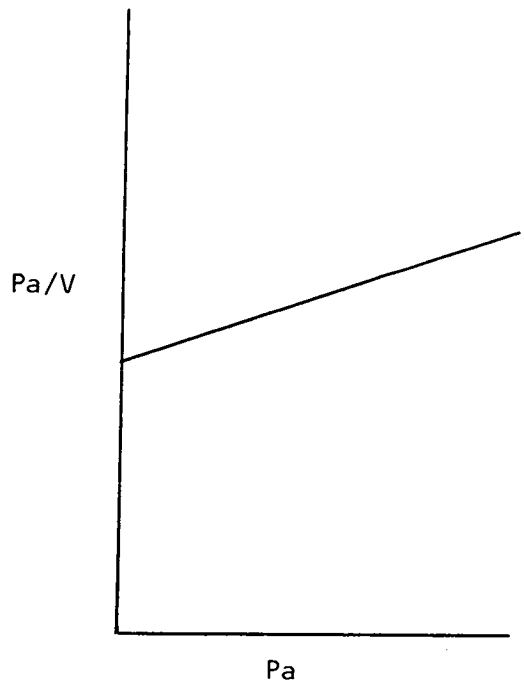


Figure 1.14(a)

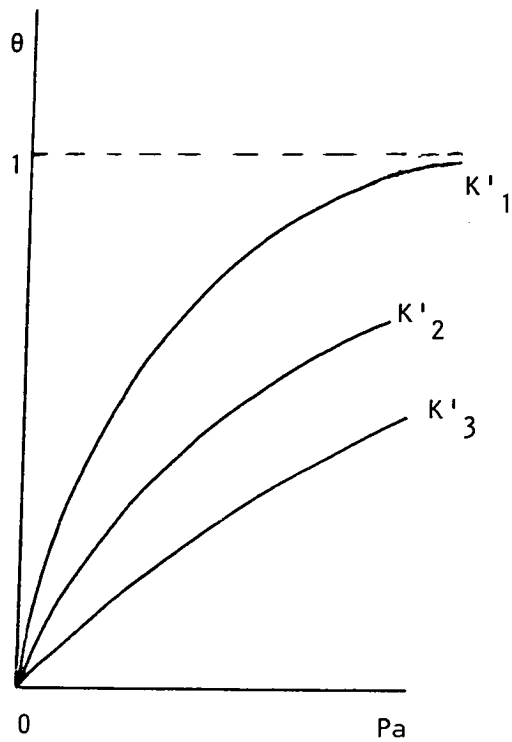


Figure 1.14(b)

From equation 1.130 and Figure 1.14(a), it can be seen that Pa/V versus Pa yields a straight line of gradient 1/Va and an intercept 1/K'Va. Hence the monolayer capacity and then the surface area of a solid may be calculated [61,62].

Figure 1.14(b) shows three values of K' at three temperatures. K'_3 was established at the highest temperature whilst K'_1 was determined at the lowest. K'_2 was observed at an intermediate temperature. The lower the temperature, the greater the number of molecules sticking to the surface and hence the faster the surface would approach the monolayer coverage.

K' is the equilibrium constant for distribution of adsorbate between the gas phase and the surface at zero coverage. The dependance of Pa on temperature can be used to determine the ΔH value of the adsorbate [61].

From the Van't Hoff equation,

$$\left[\frac{d(\ln Pa)}{dT}\right]_{\text{const }\theta} = \frac{-\Delta H_{\text{adsorption}}}{RT^2} = \frac{\Delta H_{\text{desorption}}}{RT^2} \quad \text{——— 1.131}$$

$$\ln Pa = \frac{-\Delta H_{\text{adsorption}}}{RT} + C \quad \text{——— 1.132}$$

A plot of lnPa versus 1/T yield a straight line where the gradient $= -\Delta H_{\text{adsorption}}/R$.

1.5.6 Brunauer, Emmett and Teller (BET) Equation for Multilayer Adsorption [61,62]

Forces acting in physical adsorption are Van der Waals forces. Physisorption can continue until a layer of liquid covers the adsorbent surface.

The BET equation derived from balancing the rates of evaporation and condensation for various adsorbed layers of molecules [62]. BET theory allows for multilayer adsorption. ΔH_1 arises as a

result of the formation of a monolayer on to the bare surface and ΔH_2, ΔH_3 ... arise due to the formation of subsequent layers. $\Delta H_1 \gg \Delta H_2$ (Figure 1.15).

Shaw [62] believes that the heat of liquification (ΔH_L) of the vapour in question applies to second molecular layer and to subsequent molecular layers. But the heat of adsorption of the second layer (ΔH_2) need not be ΔH_L [56]. If it was the case, a second layer is not expected until P = Po (P and Po are defined on the next page). Evidently, $\Delta H_2 > \Delta H_L$ if a second layer is formed at low pressure. Figure 1.15 shows the drop in heat of adsorption as molecular layers are formed. Eventually, ΔH_L is reached.

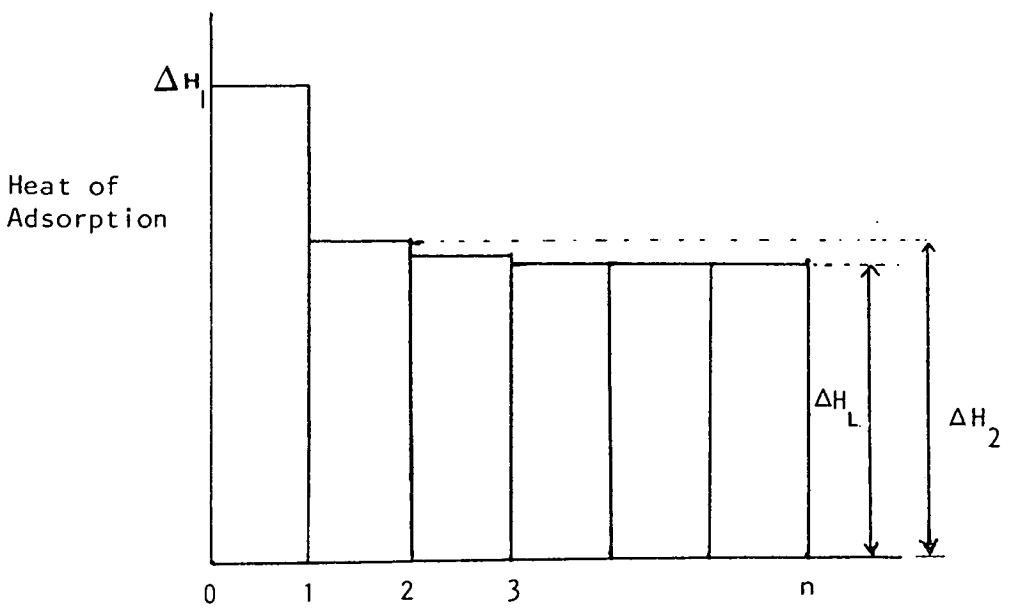


Figure 1.15

The BET equation has the form,

$$\frac{P}{V(Po-P)} = \frac{1}{VaC} + \frac{(C-1)}{VaC}\frac{P}{Po} \qquad 1.133$$

Va = monolayer coverage

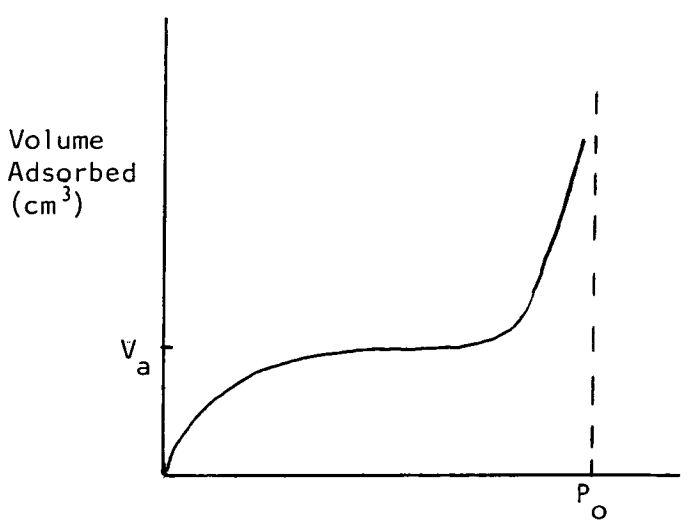
Po = saturated vapour pressure of adsorbate

V = volume of gas adsorbed on to the surface

P = equilibrium pressure as molecules are adsorbed on to the surface

$$C = \exp([\Delta H_L - \Delta H_1]/RT) \qquad 1.134$$

Figure 1.16 shows the form of the BET isotherm. A 'knee' bend is observed and is followed by a flattish portion. Then the curve rises to infinite V_{ads} where P=Po. At this point, liquification has taken place.



Pores are filled with the liquid (adsorbate) as Po is approached.

Figure 1.16

At low pressures, the BET equation reduces to the Langmuir equation. If adsorption is limited to n molecular layers, as can occur in porous solids,

$$V = \frac{Va\ Cx}{(1-x)} \cdot \frac{1 - (n+1)x^n + nx^{n+1}}{1 + (C-1)x - Cx^{n+1}} \quad \text{——— 1.135}$$

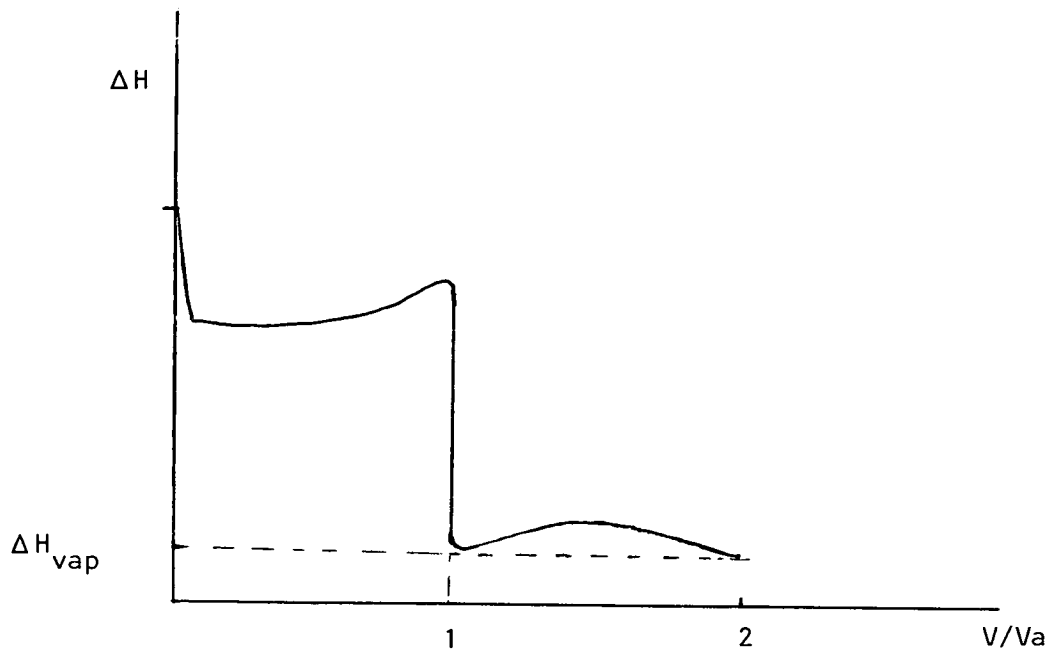
n is related to the pore size and x = P/Po.

This equation reduces to the Langmuir equation when n=1 and to the BET equation when $n = \infty$ [62].

1.5.7 Adsorption Energies

On hetrogeneous solids, the adsorption at active sites is favoured at low coverage. Heat of physical adsorption then becomes less as surface coverage increases.

When a gas molecule is adsorbed on a solid surface which is partially covered with a monolayer, lateral interactions with the adsorbed gas molecule will be involved in addition to interaction with the solid. In this respect, the heat of adsorption, of adsorbate increases with increasing surface coverage, as shown in Figure 1.17 [41].



1 = Va (formation of monolayer)

2 = Va_2 (formation of second monomolecular layer)

Figure 1.17

Multilayer physical adsorption depends on tendency of each adsorbed monomolecular layer (especially the first layer) to be completed before adsorption of further layers. This arrangement is favoured if adsorption energy for the layer being completed is greater than that for commencing further adsorbed layers [62].

1.5.8 Surface Areas

Va can be used to calculate the surface area of an adsorbent, if area occupied by each adsorbate molecule is known.

A plot of P/V (Po-P) versus P/Po (from equation 1.133) gives a straight line. Slope = (C-1)/VaC and intercept = 1/VaC.

$$Va = \frac{1}{\text{slope} + \text{intercept}} \qquad \text{——— 1.136}$$

Monolayer capacity is reached when P = 0.05 - 0.35.

Nitrogen at 77K is used as the adsorbate. The area occupied by each nitrogen molecule at monolayer capacity is calculated from density of nitrogen, on the basis of a model of closely packed spheres.

High value of C is (i.e. $\Delta H_1 \gg \Delta H_L$) required for a well defined Va (Figure 1.16). Nitrogen has a high C value to give a well defined Va and not too high to give excessive localisation of adsorption [62].

PART III

Properties of a Chromatographic

Stationary Phase (with reference to carbon)

1.6 DESIRABLE CHARACTERISTICS OF A COLUMN PACKING MATERIAL FOR HPLC (WITH REFERENCE TO CARBON)

Ideally, a HPLC stationary phase should have (a) hardness, (b) adequate surface area, (c) uniform surface energy to give linear adsorption isotherms, and (d) mean pore diameter of not less than 10nm and absence of micropores to ensure rapid mass transfer of solutes in an out of particles.

Any HPLC material should be sufficiently hard to withstand high pressures and high eluent flow rates during chromatography.

The hardness of carbon is directly related to its molecular and pore structures. The graphitised glassy carbons have high mechanical strength due to their microcrystalline mosaic structure.

Particle porosity also plays a major role in determining the mechanical strength of a material. Generally, when the particle porosity exceeds 70%, the particles become too fragile for HPLC.

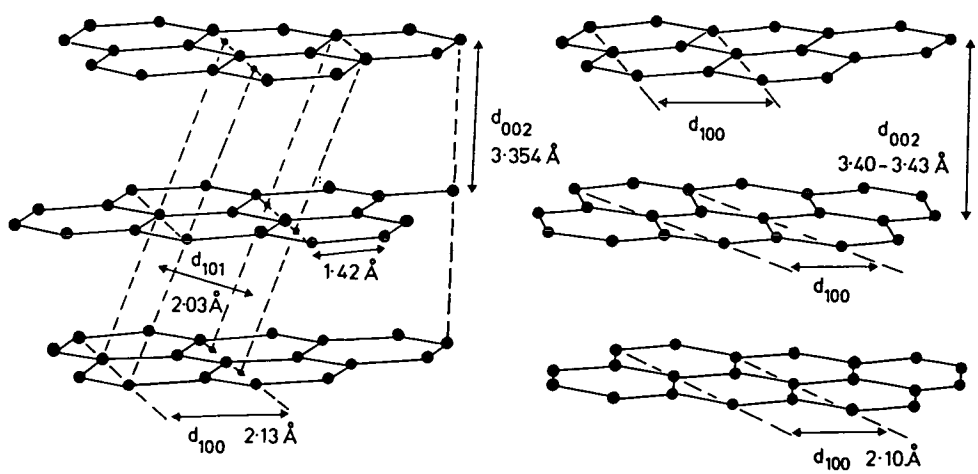
Active carbons in general have higher surface areas, than graphitised materials. Carbons with high surface areas ($>1000\ m^2\ g^{-1}$) display heterogeneous energies of adsorption due to micropores and surface groups present on the surface. This may lead to peak tailing. Solutes are unretained on carbons with low surface areas (a few m^2g^{-1}). Therefore a compromise (100-150 m^2g^{-1}) should be

reached to ensure good chromatography.

1.6.1 Structure of Porous Graphitised Carbon (PGC)

PGC can be used as a stationary phase in both high performance liquid and in gas chromatography (HPLC and GC). It was first developed at Wolfson Liquid Chromatography Unit (WLCU) of Edinburgh University [2,52-55]. This material is a meso-porous two dimensional crystalline graphite which has a surface area of about 100 m^2g^{-1} and a pore volume of 2 cm^3g^{-1} [59]. The PGC particles are spherical and hard. 3-10μ particles are used in HPLC and 100-300μ particles are used in GC.

Graphitised carbons can exist in two- or three-dimensional crystalline forms [54]. Figure 1.18 shows the two forms.



Atomic structures of graphites. Left: Bernal structure of perfect 3-dimensional graphite with ABAB.. layer registration. Right: Warren structure of two-dimensional turbostratic graphite with no layer registration.

Figure 1.18

The Bernal structure [66] of perfect three-dimensional graphite (Figure 1.18) consists of layers of carbon atoms which are organised in a hexagonal array and shows an AB AB AB ... layer arrangement. This is called hexagonal graphite [2,54]. A second rare form of three-dimensional graphite described by Lipson and Stokes [67] has layers ordered ABC ABC ... . This form is named rhombohedral graphite [54,67].

Many synthetic carbons show only two-dimensional order. The Warren structure [68] (Figure 1.18) is a two-dimensional graphite where the sheets of graphite are randomly orientated relative to one another [54]. The layer spacing of two-dimensional graphite is slightly greater than that of three-dimensional graphite [2,54], and the atomic spacing within layers is slightly less. This two-dimensional graphite has a turbostratic structure, a term first used by Warren [54,68], when referring to graphitised carbon black (GCB).

In general, graphites consist of layers of carbon atoms where the bonding within the graphite planes is strong and the interlayer bonding is rather weak [2,54].

1.6.2 Pore Diameter

The pores of PGC contribute towards the surface area of the material. Adsorption takes place on the walls of these pores. The

pore diameter (d) is related to the surface area (A) and pore volume (Vp) by,

$$d = \lambda Vp/A \quad \text{_____} \quad 1.137$$

where λ is the configurational constant. If the pores are cylindrical, then $\lambda = 4$.

Pores may be divided into three categories [2].

(i) Micropores with diameters $<40\text{Å}$.

(ii) Transitional pores with diameters 40-200Å.

(iii) Meso-pores with diameters $>200\text{Å}$.

In general, effective chromatographic adsorbents have no micropores. The micropores are to be found in active carbons, and play a major role in adsorption [69]. Such materials show a heterogeneous spectrum of adsorption energies and consequently display poor chromatographic properties.

PGC contains mainly meso-pores with a few transitional pores. The pores present on PGC are $>100\text{Å}$.

1.7 SURFACE ACTIVITY DURING CHROMATOGRAPHY

Surface chemistry determines the nature and energy of interaction between adsorbent and adsorbate. Measurement of heats of adsorption (Chapter 2), study of molecular interactions and

adsorption isotherms give an indication of the quality of the material as a chromatographic adsorbent (Ref.4, Chapter 4) [46]. Adsorption studies on PGC, GCB and silica are discussed in Chapter 2.

When a molecule approaches the carbon surface, the interaction potential is the sum of dispersion interactions and repulsion forces. Chemical and polar interactions could also exist if any groups are present on the adsorbent surface.

There is attraction between adsorbent and adsorbate. Lateral interactions can also exist between the adsorbed molecules on the surface. In GC, the carbon material does not distinguish between functional groups. The retention depends upon the polarisability of each solute which in turn is governed by the number of contact points displayed by each analyte on the carbon surface.

Additionally, in an LC system there will be attraction forces between adsorbed solute and the eluent molecules in the bulk of the mobile phase. These include the interactions between any polar groups of analytes and the polar constituents of the mobile phase. Electrostatic interactions can also be important in an LC system where the species are charged as in ion pair chromatography (Chapter 6).

In chromatography dispersion forces (London or Van der Waals) exist

between non-bonded similar or dissimilar atoms. It is generally accepted that on graphite, the adsorption is due exclusively to such interactions whether adsorbates are non polar or polar [50,51]. On such an adsorbent, the contribution of dispersion interactions to the adsorption energy (E_1) of an atom is proportional to polarisability (α) of that atom.

$$E_1 = C\alpha \qquad \text{——— } 1.138$$

C is a constant.

Adsorption energies of a wide range of compounds (hydrocarbons, ethers, pyridine, acetone) on graphite are proportional to the polarisabilities of adsorbates [50].

Carbon interacts non specifically with adsorbates. Functional groups can be introduced on to graphite by coating the carbon surface with modifiers. Then the specific interactions taking place on a carbon surface are due to any functional groups introduced on to the adsorbent.

On a coated surface, a monofunctional adsorbate molecule may interact with one active site. A polyfunctional molecule may require several sites. Gas chromatography on coated PGC is described in Chapter 3 whilst liquid chromatography on modified PGC is described in Chapters 5 and 6.

The surface of graphite is crystalline and should be totally

homogeneous. Materials suitable for chromatography are crystalline. However, there are physical defects such as cracks and cleavages on carbon. Also there are chemical heterogeneities occurring at the edges of the microcrystals and these will generally be functional groups of various types [70]. The existence of such groups is undesirable but has long been known and specifically studied by Kiselev [70].

The above mentioned heterogeneities may be removed by the pre adsorption of a liquid stationary phase or by chemical reactions on the PGC surface. The surface treatment of GC materials via these methods are discussed in Chapters 3 and 4.

The GCB surfaces obtained after hydrogen treatment are described in reference 71. These surfaces were found to be homogeneous and such materials interact non specifically with analytes. The GC separations on these materials show little selectivities to different functional groups.

1.8 SIGNIFICANCE OF SAMPLE STRUCTURE AND PLANARITY OF SURFACE WITH REFERENCE TO ADSORPTION ON GRAPHITE

1.8.1 Effect of Sample Structure on Adsorption

The sample adsorption energy S°_{x}, on graphite is mainly determined by total number of groups in the sample molecule, group composition of

the molecule and their arrangement.

Adsorption of a group of a molecule takes place when it approaches a particular site on the surface. A bulky constituent in the molecule can interfere with this process by steric hindrance. This results in a decrease in adsorption energy of that group.

Heat of adsorption values (Δ H) gives an indication of how molecules interact on the surface. ΔH values on GCB are similar for pyridine (has a large peripheral dipole moment, non-bonding electron pair and π bonds) and benzene (has π bonds). ΔH values of cyclohexane, cyclohexene, pyridine and benzene are less than that of n-Hexane, although molecular weights are similar and boiling point of n-Hexane is lower. The effect of molecular weight is masked by molecular geometry which has a great effect on adsorption energy. The above sequence of Δ H values are due to non-specific interactions [70]. Retention values of six membered compounds depend on their structure which determine how they rest on the surface. The number of non-specific interactions between the adsorbent and the adsorbates and hence the adsorbate ΔH values are dependant upon the number of contact points displayed by each solute on the adsorbent surface [70].

Carbon surface is planar [2]. This arrangement favours planar or near planar solute molecules for adsorption rather than non-planar molecules of similar size [2,46]. The closer the atoms of a

molecule, to the carbon surface, the greater the adsorption of molecule on to carbon.

1.9 SURFACE REACTIONS ON CARBON

Graphitised carbon layers are well ordered and are parallel to one another. On heating carbons in a vacuum or in an unreactive gas to graphitisation temperatures, microcrystals of graphite grow from smaller nuclei and eventually link up. At the joints of these microcrystals, there will exist exposed defects and dislocations. These are called active sites. These are associated with unpaired electrons and therefore these sites are open to chemisorption with gases.

PGC has a continuous porous sponge like structure while carbon blacks are composed of weakly bound colloidal particles and both have large internal areas. On exposure to reactive atmospheres such as air, hydrogen and water the active sites will react by chemisorption. Typical surface groups formed on eventual exporsure to the ambient atmospheres will be OH, CO, COOH, C-O-C, CH, etc. As a result, surface complexes are formed. Surface reactions on carbon take place either because of their ability to chemisorb other elements or due to the existence of a layer of chemically bonded elements. Almost all types of carbon have oxygen complexes formed on their surfaces, unless special precautions are taken to eliminate them.

Pure carbon is hydrophobic, but whenever oxygen is present on the surface giving rise to oxygen containing functional groups a degree of hydrophilicity is introduced and water, for example, may be adsorbed by hydrogen bonding. In ungraphitised carbon the surface may be more or less completely covered by oxygen groups, giving a hydrophilic active carbon. Oxygens provide sites at which the sorption of water proceeds in the form of isolated clusters through hydrogen bonds [72-74]. These clusters increase in size with the adsorption of water molecules. At a higher vapour pressure these clusters form a continuous layer and block the pores of the porous carbon [72-74].

1.10 ISOMER SEPARATION ON CARBON

Interaction energy of a molecule depends on the number of contact points with the graphite surface. The planar graphite structure can be used to separate substances that are different only in their geometrical structure. Separation is determined by both orientation and geometry. Thus if a compound has more points of contact with the surface, it takes longer to elute.

The surface of adsorbent may be treated as planar. Therefore a planar molecule or those which can adopt a planar structure will be adsorbed strongly on the surface. Aromatics may be adsorbed on a flat or parallel configuration on the surface. Generally, the retention of ortho and para isomers are greater than that of meta

isomers on graphite. The separation observed on graphite is due to the planarity of the isomers. The ortho and para isomers have two CH groups touching the surface; so these have similar retention times. The ortho and para isomers can be separated on a specific adsorbent since they have different electron density distributions [70].

Cis and trans isomers can also be separated on graphite [70]. The separations depend upon the geometry and hence the number of contact points displayed by each isomer on the carbon surface. The greater the number of contact points, the greater the adsorption and hence the greater the retention of compound on carbon.

A particularly important aspect of isomeric separation is that of diasterioisomers, and is the basis for the unique property of PGC in separation of enantiomers.

1.11 RESEARCH CARRIED OUT IN THIS PROJECT

1.11.1 Investigation of the Eluotropic Series of HPLC Solvents on PGC

ΔH values of some typical organic HPLC solvents were determined on carbon and silica using GC.

The relationship between ΔH and the area occupied by a molecule (Ax) on the adsorbent surface was established for carbon.

The eluotropic strength parameter (Eo) of a solvent is its ability to occupy adsorption sites on a surface and disallow solutes to interact with the solid phase, in a liquid-solid chromatographic system. Eo is also the power of a solvent to elute substances from a LC column and is the free energy of adsorption per Ax.

GC can be used to obtain some idea of the eluotropic strengths of substances on an adsorbent. $\Delta H/Ax$ is a measure of eluotropic strength. Snyder has established the Eo values of solvents on silica using an LC technique [63]. In Chapter 2, $\Delta H/Ax$ values of the solvents were determined on carbon and silica, and plotted against Eo values that are found in reference 63.

$\Delta H/Ax$ versus Eo graphs on carbon and silica enabled the contrast between the two surfaces to be established.

1.11.2 The Study of Chromatographic Properties of Carbowax Coated PGC, using GC

The effect on retention characteristics of alcohols, ketones and aliphatic hydrocarbons (C_1-C_5) was observed with varying amounts of Carbowax on the surface.

Also, the analyte peak shapes, efficiency of column and the surface area of PGC were studied as the amount of modifier on the surface was varied.

1.11.3 The Study of Chromatographic Properties of Chemically Modified PGC, using GC

The surfaces of PGC were hydrogen treated at elevated temperatures, in order to improve the GC characteristics of PGC. The retention and the peak shapes of alcohols, aliphatic hydrocarbons (C_1-C_5) and ketones were studied. The variation in surface areas was also recorded.

In another attempt to improve the GC properties of PGC, the surfaces were toluene-treated in a stream of nitrogen or hydrogen at elevated temperatures. Hexane was used as an alternative to toluene in a stream of hydrogen. The peak shapes, retention characteristics of the above mentioned solutes were noted.

1.11.4 The Study of Chromatographic Properties of Surfactant Coated PGC, using HPLC

The carbon surface was modified by including surfactants such as Tween and Span in the eluent.

The effect on the variation of some aromatic solutes by varying the surfactant concentration while the polarity of the eluent remained constant, and the result of altering the polarity of the eluent while the surfactant concentration remained constant, were examined. The dependence of the efficiency of the column with increasing amounts of water in the mobile phase was observed.

1.11.5 Ion Pairing on PGC at Alkaline pH Values

The change in retention of certain aromatic compounds was studied by dynamically coating the PGC surface with different amounts of CTAB. The eluent pH was maintained at 12.5 throughout. After the experiment, dioxan was passed through the column with the intention of removing the ion pairing agent from the PGC surface. Retention of the solutes was recorded afterwards to compare with the values obtained on the PGC before the introduction of CTAB.

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CHAPTER 2

Nature of the Eluotropic Series of HPLC Solvents on Carbon and Adsorption Studies on PGC

CHAPTER 2

Nature of the Eluotropic Series of HPLC Solvents on Carbon and Adsorption Studies on PGC

2.1 INTRODUCTION

As explained in the previous chapter, ΔH values of HPLC solvents are relevant in establishing the eluotropic series on carbon.

In this work, heats of adsorption of HPLC solvents from the gas phase have been determined using GC. The solutes used in the experimental work are the HPLC solvents. The support materials used were carbon and silica where the atomic/molecular structures are vastly different. The eluotropic series on Graphite is compared with that obtained on silica.

Later in the Chapter, the results are treated further to understand more about the adsorption on PGC.

First, the eluotropic relationships on carbon and silica may be investigated.

2.1.1 Surfaces of Carbon and Silica

Since the ΔH values of adsorbates are dependent upon the nature of the adsorbents used, the structures of carbon and silica may be

considered.

2.1.1.1 Carbon

The structure of PGC is given in Figure 1.18 and 2.1.

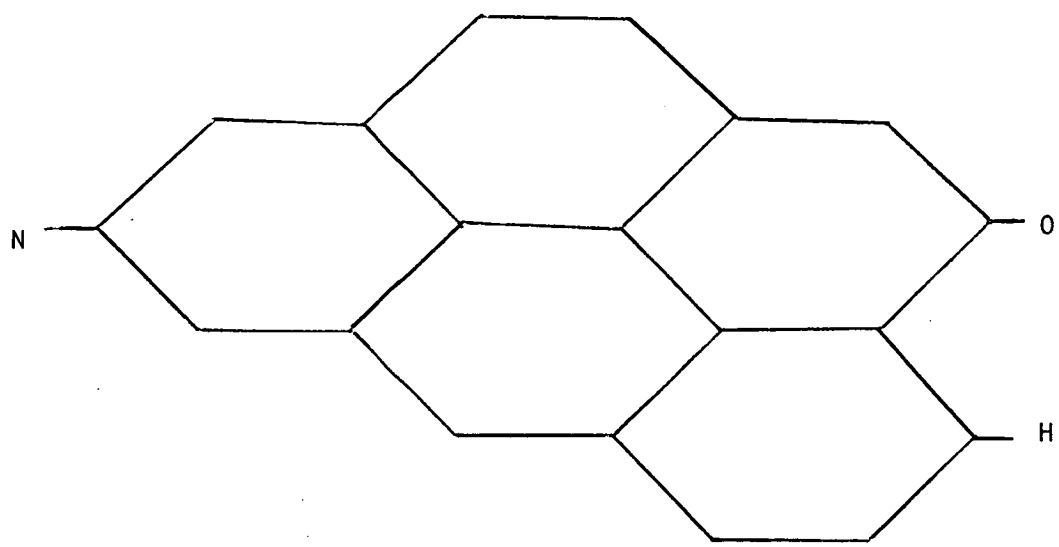


Figure 2.1 - Surface Structure of PGC

Pure graphite is a non-polar adsorbent composed of aromatic sheets of carbon. There are no surface groups for specific interactions. However, any microcrystalline graphite may contain impurity sites and defect sites. These can alter the adsorptive character of the adsorbent especially at low surface coverage. Figure 2.1 indicates that the carbon atoms are arranged hexagonally and possible impurities are attached to the edges of the structure. These

groups can interact with the sample molecules to give peak tailing and their presence may affect retention. As a result of all defects the adsorption isotherms, of solutes, on PGC, may be concave to the C_S axis.

Carbon has step-like defects which also contribute towards tailed peaks, enhanced retention and ΔH values. This is in comparison with graphite materials without such heterogeneities, where more symmetrical peaks, favourable retention times, straighter adsorption isotherms and diminished ΔH values are commonplace.

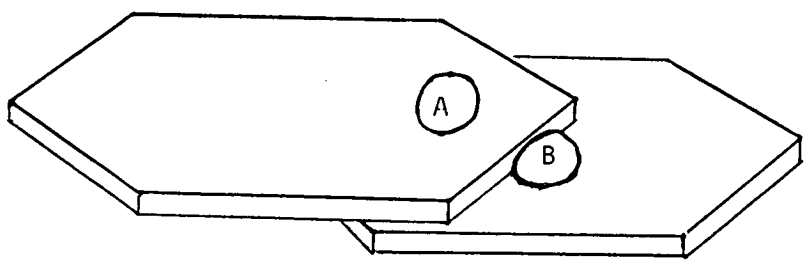


Figure 2.2

The step-like defects may be responsible for enhanced retention of a molecule such as 'B' (Figure 2.2). As 'B' rest on the 'step' it may be in contact with more than one plane of the surface. The molecule 'A' of similar size rests on the flat surface. In this case, the retention of 'A' is smaller than that of 'B'. Also, any cracks and clevages (physical defects) present on the surface may increase the retention and cause peak tailing, since the solutes may enter these cracks and interact with more than one plane of the

adsorbent. In developing an adsorbent it is important to avoid as far as possible such defect sites or at least if they are present to deactivate them.

2.1.1.2 Silica

The surface of silica is amorphous and therefore heterogeneous. Silanol groups and possible hydrogen bonding that could take place are shown in Figure 2.3 [1]. An oxygen containing compound may interact with the Si-OH groups to give rise to H-bonds. As a result, oxygen and some nitrogen-containing compounds display higher retention times and tailed peaks compared with non-hydrogen bonding substances of same molecular weight. Accordingly, polar solutes show higher ΔH values than non-polar compounds.

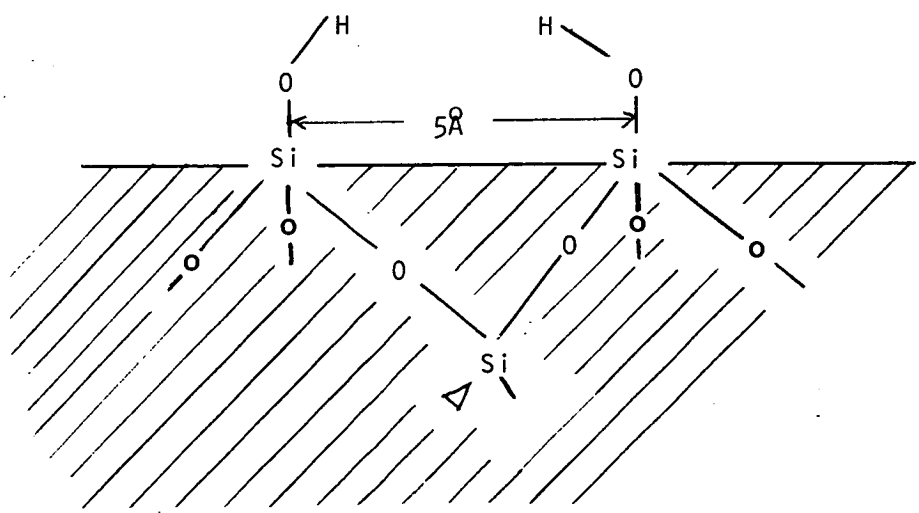
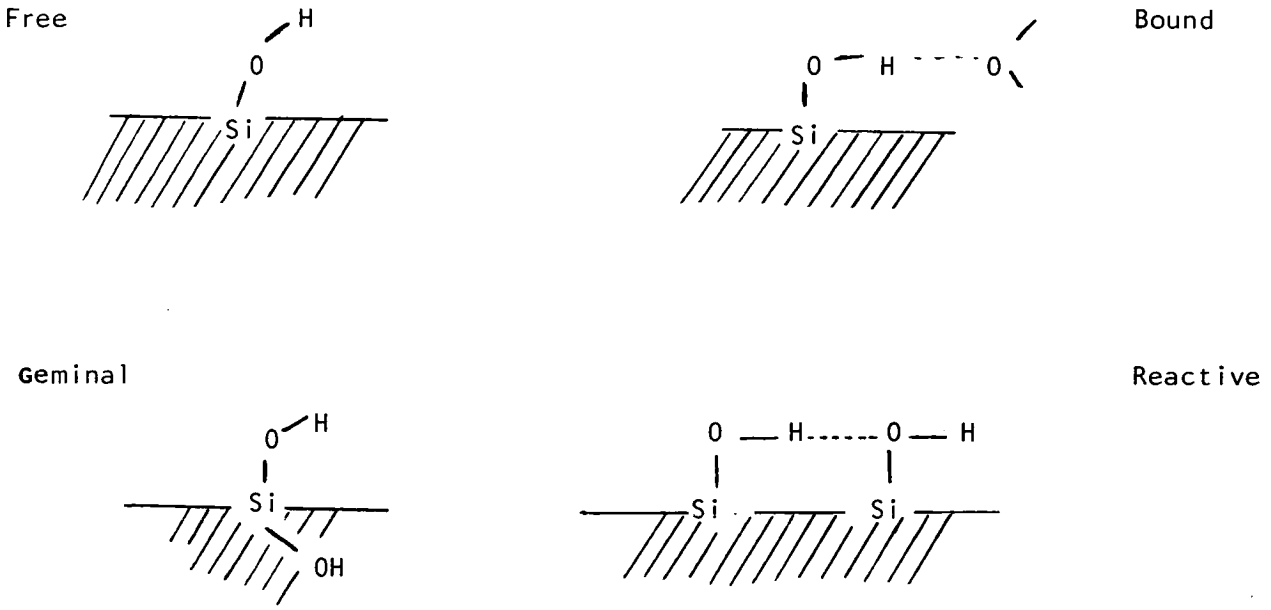


Figure 2.3



The Structure of the Silica Surface [1] Figure 2.3 (Cont.)

2.1.2 Adsorption Studies on Graphitized Carbon Black (GCB)

Adsorption studies by Kiselev describe how molecules interact with the GCB surface and gives some idea about the nature of the material. Such background information on adsorption is important in forming a complete picture about the eluotropic series on graphite.

In 1962 Kiselev [2] carried out adsorption studies on several GCB samples using a calorimetric method. He investigated the change in ΔH of hexane and benzene with sample coverage. The graph he obtained for hexane was shown in Figure 1.17. In this case, ΔH displayed an initial decrease with surface coverage due to the masking of physical and chemical heterogeneities on the GCB

surface. After reaching a minimum, ΔH increased and reached a maximum value at the monolayer coverage. Such an increase in ΔH is due to the adsorbate-adsorbate energy of cohesion, observed just before the formation of the monolayer [2]. The maximum is followed by a sharp fall in ΔH as a result of multilayer adsorption. Beyond the monolayer, the ΔH of hexane was governed by the adsorption on to the adsorbed layer of hexane rather than on to graphite.

Kiselev later used the GC technique (Chapter 1) for the measurement of the heat of adsorption of many unsaturated and saturated hydrocarbons on GCB. He discovered that ΔH increased with (a) the carbon number and (b) the polarisability of solute [3].

In the case of olefins Kiselev found that cis isomers emerged before the trans isomer in all but one of the cases [4]. The elution order was reversed for 1,2-bis(trimethylsilyl)ethylenes and their germanium analogues. Kiselev claimed that the elution order depended upon the number of points of contact displayed by the solute on the GCB surface [4]. He suggested that the greater the points of contact, the greater the elution volume of solute. Kiselev concluded that in all but the above mentioned case, the trans form is the more favourable orientation on graphite [4].

Kiselev [5] found that the ΔH of benzene is higher than 1,3-cyclohexadiene and the ΔH of cyclohexadiene to be greater than that of

cyclohexane. He argued that the flat molecule benzene, had all six of its carbon atoms touching the GCB surface. Whereas only three carbons of cyclohexane would rest on the adsorbent. The solute 1,3-cyclohexadiene is slightly flatter than cyclohexane and subsequently could contact the surface at four or five atoms. These experiments of Kiselev confirmed that, the greater the number of contacts on the surface the higher the ΔH of solute.

Alkanes displayed lower ΔH values than the corresponding halogen substituted alkanes [5]. The ΔH is greatest for an alkane substituted with an iodine and smallest for the same alkane substituted with fluorine. That is, an increase in the radius of halogen enhances ΔH. This is caused by the increase in polarisability with increasing atomic radius of halogen which in turn increases dispersion interactions [5], between solute and the solid phase.

Kiselev [4] found that the contributions of different functional groups to ΔH of solutes, varied linearly with the covalent radii of the functional groups. The covalent radii of C-I $>$ C-Br $>$ C-N $>$ C-OH. Oxygen has the smallest radius and therefore ΔH values are lowest for ethers and alcohols [4]. Increase in atomic radii of the groups combined with the increase in polarisability of the corresponding units, would increase the strength of dispersion interactions between solute and the adsorbent.

Adsorption studies on GCB indicated that the presence of π bonds, and quadrupole moment in a molecule increased the ΔH value [6]. The ΔH value provide the information on homogeneity and non specific nature of GCB. The ΔH values are governed by non specific intermolecular interactions and are not directly related to boiling points of the solutes [6].

The adsorption studies on GCB [2-6] are the foundation for understanding the extent of interaction of analytes with a graphite surface. Such information is useful in understanding how solutes interact with PGC, and hence establishing the order of elution of solutes on PGC.

2.1.3 Study of Solvent Strengths on PGC

The importance of ΔH values in the study of the eluotropic series on graphite and the method of determining Eo values were described in Chapter 1. This section outlines the differences between the eluotropic series of carbon and silica and also, the relevant recent research on carbon (PGC).

The eluotropic strengths of HPLC solvents have been determined using LC systems [1,7,8]. On polar adsorbents, the greater the polarity of the solvent, the greater the Eo .

Snyder used alumina and silica as adsorbents [1,8]. He believed

that the liquid mobile phase molecules are first adsorbed on to the adsorbent and a certain number of these are displayed by each solute molecule. Snyder assumed that the energy of interaction when a solute combined with the mobile phase molecules are negligible relative to $\Delta H_{displacement}$.

On PGC however, $\Delta H_{displacement}$ values are so small that the solute-eluent interactions are much more important [7]. This leads to different scale of eluotropic strengths being obtained depending upon the solutes used or the methods used to determine them.

The retention of eluates on a non polar surface such as graphite is based upon the balance between non-specific intermolecular interactions. It is generally believed that on carbon, the weakest solvent will be the most polar and thus is the opposite of the trend observed on silica gel]7]. Water is the weakest solvent on graphite and benzene and xylene are the strongest. Methanol is of intermediate strength [7].

Kaur's experimental data [7] on the determination of Eo values on carbon show, (a) the range of Eo values for PGC is rather small compared with the results of the previous workers [9], (b) Eo for a solvent is dependant upon the solute or solute groups used to determine them, and (c) there is no evidence for a strong eluotropic series [7].

2.1.4 Research Performed

(a) The ΔH values of certain HPLC solvents were determined to establish the nature of the eluotropic series on graphite. Eluotropic series on an adsorbent depends upon how the solvents interact with the adsorbent surface. The homogeneity of a material determines the type of interactions taking place on its surface. This first section is concerned with establishing the quality of the carbons as chromatographic adsorbents. The magnitude of the ΔH values on a material would be useful in assessing the quality of that material as a chromatographic adsorbent. Therefore, the ΔH values determined on PGC 219 CEN are compared with those obtained on other carbons. PGC 219 CEN was found to possess the most homogeneous surface for chromatography. Therefore ΔH values on other carbons were plotted against those obtained on PGC 219 CEN for comparison.

(b) The dependence of ΔH of HPLC solvents on their molecular areas was investigated on each carbon adsorbent. Such graphs would be useful in the direct determination of the eluotropic series on graphite.

(c) The $\Delta H/A_x$ values on each adsorbent may be plotted against the Eo values determined on silica, found in Reference [1]. Such graphs would point out the difference between eluotropic series of carbon and silica.

(d) The experimental results may be treated further to understand more about the adsorption on to PGC.

(e) The ΔH_{vap} is the energy required to break the dispersion forces that exist between molecules in the liquid phase. Now ΔH is the energy released when dispersion forces are formed between a molecule and the graphite surface. Therefore ΔH is plotted against ΔH_{vap} to discover whether there is any relationship between these two quantities. Also, the dependance of ΔH_{vap} on A_x was investigated to compare with the plots of ΔH vs A_x.

(f) The ΔH values on PGC 219 CEN may be plotted against the molecular polarisabilities (α) of those HPLC solvents to investigate any relationship between these two quantities. This plot may show whether the π electron cloud on the PGC surface would influence adsorption.

The molecular polarisability may be defined in the following way. When a molecule is exposed to an electric field, the electronic structure of the molecule is distorted. Also, the equilibrium positions of the molecule's nuclei are changed. This in turn would give rise to a dipole moment of a size dependent upon the strength of the electric field and the responsiveness of the molecule. This responsiveness is known as the molecular polarisability (α).

Also, α is called the ratio of induced dipole moment to the electric field strength.

2.2 EXPERIMENTAL

2.1.1 Materials and Equipment

Heat of adsorption values were determined using the technique of gas chromatography.

The F11 Perkin-Elmer Gas Chromatograph with Flame Ionization detector (FID), was used in this work. This chromatograph was obtained from Perkin-Elmer of Beaconsfield, Bucks.

The packing materials were PGC 218 CEN (105-420μ), PGC 219 CEN (105-250μ), PGC 219/220 SIG (105-250μ) and Silica (177-210μ).

These adsorbents were prepared at Wolfson Liquid Chromatography Unit, Edinburgh University, Edinburgh.

The adsorbent Carbopack B (GCB) 297-420μ was obtained from Supelco Inc., Belfonte, PA, USA.

The GC columns were prepared with stainless steel tubing. The columns were 100cm long. ID = 2.3mm and OD = 1/8". These tubing obtained from Phase Sep., Queensferry, Clwyd.

Parker-Hanifin nuts and ferrules were used to connect the packed columns to the GC.

A $25cm^3$ funnel was used to pour the material into the GC column. A piece of rubber tubing (30mm long and ID less than 1/8") was used to connect the funnel to the top end of column.

The ends of columns were plugged with glass wool.

Analytes were introduced on to the column with a 10ul syringe. This syringe was purchased from Hamilton, Switzerland.

Nitrogen was used as the carrier gas (at 17 psi). Hydrogen (at 11 psi) and air (at 50 $cm^3\ min^{-1}$) were used to operate the FID. These gases were purchased from British Oxygen, Brentford, Middlesex.

All solutes (HPLC solvents) were obtained from Rathburn Chemical Company, Walkerburn, Peebleshire.

The peaks were noted on chart paper using a BBC SE-120 chart recorder obtained from Belmont Instruments, Glasgow.

The Hewlett-Packard 3390A integrator is useful in measuring peak areas in chromatography. This integrator has the added advantage of recording retention times of peaks ($\pm$0.02min) which is useful in the determination of ΔH values of analytes.

The temperature of the GC oven was recorded (±1°C) using a Cormack digital thermometer.

2.2.2 Packing of GC Columns

One end of a stainless steel tube (100cm long) was blocked with glass wool and the tube held vertically so that the end with the glass wool plug was at the bottom. The top end of the column was fitted with a piece of plastic tubing connected to the $25cm^3$ funnel. The connections were tightly fitted to avoid any spillages during packing. The granules of the material were poured into the funnel and the bottom end of the column was frequently tapped on the floor to achieve an even packing. The material was added to the column until 3-4mm were left from the top. The tapping was continued for 10 minutes, to make certain that there was no further settling. More adsorbent granules were added if the level inside the column decreased during tapping. Further additions of the solid phase followed by tapping continued until no further settling took place. Then a piece of glass wool was inserted into the space (3-4mm) left at the top of the column. The column was coiled and then connected to the GC using swage-locks.

The gas chromatograph was switched on and left at 300°C for 2-3 hours with carrier gas running (at 11 PSI). This is the usual procedure for cleaning the surface of the packing material (i.e. conditioning the column). When the surface was free of adsorbed

substances, the chart recorder pen came down to the base line. Usually, a clean chromatographic surface was achieved after 2-3 hours. At this stage, the column was ready for the determination of heats of adsorption of the solvents.

The above procedure was adopted for cleaning the adsorbent surface of every packed column. In the case of coated materials (see Chapter 3), the columns were conditioned at 150°C as the liquid stationary phase was unstable beyond this temperature.

2.2.3 Procedure for the Determination of Heats of Adsorption

Precise and rapid results were obtained with the GC technique. Retention values of the solvents were recorded at different temperatures on each adsorbent. $\ln k^1$ was plotted against $1/T$ (equation 1.48) for each compound with the results obtained on each adsorbent in order to calculate the ΔH values (see Figures 2.4, 2.7-2.9 and 2.16).

2.3 RESULTS AND DISCUSSION

2.3.1 Quality of Graphites as GC Adsorbents

The quality of a material as a chromatographic adsorbent is important in the study of the eluotropic relations on that material since the nature of the surface in question determines the types of

interactions taking place on the material during chromatography. The integrity of each graphite adsorbent is explained in terms of experimental results.

Linear $\ln k^1$ vs 1/T curves wre obtained on a more homogeneous surface such as that of PGC 219 CEN. Such graphs (Figure 2.4) and the corresponding results in the tables of Appendix II enables the calculation of ΔH values of eluates on each adsorbent using the least squares method.

Figure 2.6 shows that favourable retention times and symmetrical peak shapes were observed for ketones when chromatographed on PGC 219 CEN. Such a material is thus classified as a grade 'A' adsorbent (Table 2I). On the surface of such a carbon it may be assumed that there are only a fewer number of impurity groups or physical defects to interact with the analyte molecules, in comparison with the surfaces of other carbons considered in this work. The main interactions taking place on PGC 219 CEN would be between the sample molecules and the graphite surface. As a result, the retention values for a given temperature range, and hence the ΔH values of the solvents observed on PGC 219 CEN would

Footnote: $\ln k^1$ vs 1/T graphs are shown in Figures 2.4, 2.8, 2.7, 2.9 and 2.16. Only Figures 2.4 and 2.16 show the points on the graphs. These two figures wre taken as examples, to display the difficulties in immediately locating the different lines if all points are included. Therefore the points of graphs in Figures 2.7, 2.8 and 2.9 are not shown. All points of Figures 2.7-2.9 are stated in Appendix II.

be lower than those obtained on other carbons. This is shown by the line (a) of Figure 2.5. Line 'a' is the result of plotting the ΔH values on PGC 219 CEN vs the values determined on PGC 219 CEN. The ΔH values determined on other carbons are plotted against the values obtained on PGC 219 CEN.

The solutes chromatographed on PGC 218 CEN displayed higher ΔH values relative to those obtained on PGC 219 CEN [10]. This is shown by the higher position of line (b) in Figure 2.5. The PGC 218 CEN material is termed as grade 'B' adsorbent (Table 2I). The surface of this adsorbent could be slightly less homogeneous than that of PGC 219 CEN. This may be the reason for observing enhanced retention values and hence increased ΔH values on PGC 218 CEN.

The position of line 'c' in Figure 2.5 indicates that the ΔH values on Carbopack B were much greater than those obtained on PGC 218 CEN. Figure 2.6 shows the peak shapes of ketones on Carbopack B. There is a certain degree of tailing in comparison with the peaks observed on PGC 219 CEN. Such results may be attributed to Physical and Chemical heterogeneities present on the GCB surface. Carbopack is thus termed a Grade 'C' material.

Highest retention and hence ΔH values were displayed on PGC 219/200 SIG. This is shown by the position of line 'd' in Figure 2.5. The $\ln k^1$ vs 1/T graph (Figure 2.8) of methanol on this adsorbent was convex to the $\ln k^1$ axis. This may be due to

reaction of analyte with this hetrogeneous adsorbent. Consequently, the retention properties of this adsorbent would be altered. In the case of methanol on PGC 218 CEN, $\ln k^1$ vs 1/T (Figure 2.7) was concave to the $\ln k^1$ axis. This is attributed to the formation of hydrogen bonds with oxide groups that may be present on the surface. This may be the case when obtaining k^1 measurements at lower temperatures ($<$ 60°C).Such undesirable interactions would deviate $\ln k^1$ vs 1/T for methanol from linearity. In such cases, the average ΔH values were considered.

The chromatograms of ketones on PGC 219/220 SIG. are shown in Figure 2.6. The peak tailing is much greater than that observed on Carbopack. PGC 219/220 SIG. is therefore called a grade 'D' carbon (Table 2I). The surface of PGC 219/220 SIG. is believed to have the highest concentrations of surface groups, oxygen complexes and physical heterogeneities compared to other carbons mentioned in this Chapter. Solute molecules would interact with such defects and as a result, the molecules spend more time on the adsorbent. This in turn would enhance the ΔH values of eluates.

The preceeding study on the quality of graphites as chromatographic adsorbents would explain the possible relationships that exist between A_x (Table 2iii) and ΔH values on each carbon. A_x values are calculated using equation 1.108 and the data from Ref.1 (Table 2ii).

Figure 2.11 shows the graph of A_x vs ΔH on PGC 218 CEN and PGC 219 CEN. Clear linear relationships are seen on these two graphite materials (Figure 2.11). Carbopack results are displayed in Figure 2.13. In this case, molecular area (A_x) has a dependance on ΔH. The linearity is not as clear as in the cases displayed in Figure 2.11.

The above results show that the adsorption on more homogeneous carbon surfaces depends upon how molecules rest on the surface. Carbon is a non-specific adsorbent. The larger the size of molecule, the greater the number of points of contact on the adsorbent surface and hence the larger the ΔH of solute.

The magnitude of ΔH values on a grade 'D' adsorbent such as PGC 219/220 SIG. are influenced to a certain extent by the defects present on its surface. In this case, the ΔH has no clear dependence upon the size of molecules (Figure 2.14).

Interactions between the molecules and different carbon surfaces are explained above. Such a study would form the basis for understanding any differences that may exist between the eluotropic relationships determined on different carbons.

2.3.2 Eluotropic Relationships on Carbon

Tables 2iii-2iv show the results of $\Delta H/A_x$ of solvents on PGC 218

CEN, 219 CEN, 219/220 SIG. and Carbopack. The $\Delta H/A_x$ values of the solvents determined on each carbon surface are plotted against the eluotropic strengths of solvents that were determined on silica (from Ref.1.) (Figures 2.10, 2.12 and 2.15 display the results.)

The graphs in Figures 2.10, 2.12 and 2.15 are parallel to the abscissa $\Delta H/A_x$ vary only within a small range (Tables 2iii-2v). This property is shown by all carbons considered in this chapter.

The individually calculated $\Delta H/A_x$ values on PGC 219/220 SIG were not vastly different to one another and therefore gave a graph parallel to the Eo axis (Figure 2.15).

These trends on carbon are due to the dependence of ΔH values on how molecules rest on the adsorbent surface [2-6]. The larger the size of molecule, the greater the number of contact points, the solute would have on the surface and therefore the greater the ΔH value of eluate. The ratio $\Delta H/A_x$ values of the analytes are similar on a given graphite adsorbent. Consequently graphs in Figures 2.10, 2.12 and 2.15 display zero gradients.

Now, by definition, the quantity, $\Delta H/A_x$, is a measure of eluotropic strength. The conclusion which can be drawn from these figures (2.10, 2.12 and 2.15) is that there is no evidence for a strong eluotropic series on graphite. A more homogeneous surface such as that of PGC 219 CEN produced (Figure 2.10) similar results

to those produced by a hetrogeneous surface such as that of PGC 219/220 SIG. (Figure 2.15).

The x-axis of the graphs (Figures 2.10, 2.12 and 2.15) represent the Eo values of the solvents determined on silica [1]. This indicates that there is a range of eluotropic strengths on silica.

Table 2.VI indicates the ΔH results of the solvents determined on silica (Surface Area : approximately 35 m^2g^{-1}). Figure 2.16 show $\ln k^1$ vs 1/T graphs. Some of the graphs in Figure 2.16 show curvature due to the localisation of solutes with the surface groups.

Non polar adsorbents such as hexane, cyclohexane and cyclopentane have lower ΔH values (Table 2VI) since these molecules do not interact with the surface silanol groups.

Molecules such as benzene and acetonitrile display higher ΔH values on silica (Table 2.vi) compared with the values seen on carbon (Tables 2iii-2v). This may be due to the π electrons of these molecules interacting with the surface groups [11]. Benzene however has sufficiently small $\Delta H/Ax$ to be classified as non localising (Figure 2.17). Acetonitrile has a small area (Ax), therefore the ratio $\Delta H/Ax$ is large and this compound can be categorised as localising.

Adsorbates such as N-butyl chloride have a higher dipole moment compared with dichloromethane. The ratios $\Delta H/Ax$ are similar, for these two compounds (Figure 2.17) and these two solutes are classified as non localising on silica, since these do not appear to form strong interactions with the surface groups.

The molecules with oxygen atoms have higher ΔH values due to the localisation with the surface groups, of silica. These interactions could include hydrogen bonds between surface groups and the oxygens of the molecules. Also in certain cases chemisorption [12] may take place between molecules of the sample and the surface groups. These inferences are made since peak tailing is observed for almost all the solutes. Surface area of this adsorbent is lower than those of the carbons, and therefore this has a lesser loading ability [1,12,13]. This could be another reason for observing unfavourable chromatography on the silica surface.

Figure 2.17 shows that $\Delta H/Ax$ values are strongly dependent upon the Eo values. This leads to the conclusion that a strong eluotropic series does exist on silica. The higher the eluotropic strength, the higher the localisation and the greater the $\Delta H/Ax$ of the solute.

Snyder [1,8] and later Kaur [7] carried out adsorption studies on stationary phases using HPLC systems. In such a system, the

inclusion of a contaminant in the eluent would increase the eluotropic strength of the mobile phase. Any contaminant present in the eluent tends to occupy the adsorption sites and prevents the solutes from interacting with the solid phase.

In a chromatographic system where carbon is used as the solid phase, the addition of an additive such as benzene to a liquid mobile phase may prevent the solutes from interacting with the carbon surface. In this case the contaminant is planar, and have many points of contact on the surface. Therefore its molecules could occupy the surface and hence reduce the solute retention values.

2.3.3 Further Adsorption Studies on PGC

The experimental results may be treated further to extend the understanding of general adsorption on carbon.

A molecule in its liquid phase and held on all sides by other molecules. Dispersion interactions hold the molecule in the liquid. It may be therefore deduced that the greater the value of ΔH_{vap} of a compound, the larger the number of such dispersion interactions required to be broken in order to take a molecule to the vapour phase.

When a solute molecule is adsorbed on to a solid surface, that

molecule is held by dispersion interactions. The greater the ΔH value of a compound, the larger the number of dispersion interactions with the adsorbent and consequently, the greater the energy required to remove the molecule from the adsorbent surface. Therefore there should be a relationship between ΔH and ΔH_{vap}.

Figure 2.18 shows that this is not the case. In the liquid phase, a solute molecule is held on all sides by other molecules. If that molecule is adsorbed on carbon, only one side of the molecule is in touch with the graphite surface. ΔH value of a solute is dependent upon how the molecules rest on the carbon surface. Whereas ΔH_{vap} does not depend on how the molecules land on the adsorbent.

In certain cases, the ΔH of an analyte may be influenced by the interactions with the neighbouring solute molecules on the adsorbent surface. Also, the ΔH values of analytes are dependent upon the interactions of solutes with any heterogeneities present on the carbon surface. The electrical field on the PGC surface (described later in this section) would influence ΔH of solutes. Due to all these factors, a relationship between ΔH_{vap} and ΔH is not observed.

Table 2iii displays that the ΔH values of benzene, dimethyl-formamide, butyl chloride and methyl, t-butyl ether are greater than their ΔH_{vap} values. In such cases, the strengths of the interactions of these analyte molecules with the graphite surface

are much greater than the strengths of interactions that exist when these solute molecules are in their liquid phases.

Table 2iii also shows that the ΔH values of ethanol, methanol, dichloromethane and acetonitrile are much less than their ΔH_{vap} values. Methanol and ethanol form hydrogen bonds with their neighbours in the liquid phase. Such interactions would not exist on a more homogeneous graphite adsorbent. Therefore the ΔH_{vap} values of these analytes would be much higher than their ΔH values determined on a surface such as that of PGC 218 CEN. The heat of adsorption of methanol determined on a less homogeneous surface such as that of PGC 219/220 SIG, would be much closer to methanol's ΔH_{vap} value (Table 2iv).

The molecules of methanol, ethanol, dichloromethane and acetonitrile in their liquid phases are held on all sides by other neighbouring molecules. When these solutes are adsorbed on carbon, only one side of each molecule is in contact with the graphite surface. Therefore the number of interactions, between solute and the solid phase after adsorption are much less than the number of interactions present when the molecules are in their liquid phases. Consequently, the ΔH measurements of these solutes would be lower than their ΔH_{vap} values. Also, these solute molecules which are smaller in size compared to other analytes in Table 2iii. On carbon, the smaller the size of molecule, the lower the ΔH of compound.

The ΔH_{vap} values of other solutes, considered in this work (Table 2iii) are in the same order of magnitude as their ΔH measurements. In these cases, the dispersion interactions of each solute in the liquid phase (which governs their ΔH_{vap} values) are similar to the interactions of the analytes with (a) the graphite adsorbent, and (b) any defects present on the adsorbent surface (which determine their ΔH values).

Figure 2.14 shows that there is no relationship between ΔH_{vap} and Ax. Figure 2.14 indicates that ΔH_{vap} does not depend upon Ax. The larger molecules do not necessarily form stronger interactions with their neighbours in the liquid phase.

The above part of this section compares and contrasts between analyte interactions that exist on a carbon surface and those that are present in the liquid phase. The following part of this section describes the adsorbent (PGC)-adsorbate interactions in terms of the analyte molecular polarisabilities (α).

The results may be treated further to extend the understanding of general adsorption on carbon. The graphite surface has a π cloud of electrons which generates an electric field. A dipole moment may be induced in certain molecules when exposed to such a field. When polarised the molecules may be attracted to the adsorbent surface. The ΔH values of analytes on PGC 219 CEN are plotted against their molecular polarisabilities (α) [14] to conclude

whether the adsorption of molecules is influenced by the electrical field on the PGC surface.

Figure 2.19 indicates that there is a dependence of ΔH on α . A clear linear relationship is not observed. Also, the graph (Figure 2.19) does not pass through the origin. Such observations may be attributed to several factors. (a) The surface of PGC 219 CEN is much more homogeneous than the surfaces of other carbons used in this work. However, there may be a certain number of physical and chemical heterogeneities which could increase the ΔH of solutes. (b) The non-uniformity of the electrical field. Any defects present on the surface could distort the uniform distribution of electrons in the cloud. (c) The α values recorded in reference [14] were calculated assuming that all atoms of each solute molecule experience the identical field strength. The extent of the field's influence on the atoms of an adsorbed molecule and hence on the overall molecule depends upon the distance between those atoms and the graphite surface. The shape and the centre of gravity of a molecule determines how it rests on the adsorbent and hence the position of its atoms relative to the graphite surface. The closer an atom of a solute to the PGC surface, the greater the electric field experienced by that atom. Therefore the field on PGC would have a larger influence on molecules with a greater number of contact points on the carbon surface in comparison to molecules with fewer atoms touching the adsorbent.

Benzene and hexane display the highest ΔH and α values in comparison to other analytes (Figure 2.19). These two solutes have a higher number of contact points on the carbon surface than the other eluates. These non polar molecules would be induced with a higher dipole moment than the more polar analytes and consequently the non polar compounds would have greater α values.

The molecules such as chloroform and dichloromethane have molecular polarisabilities of 9.5 and 7.2 10^{-24} cm^3 respectively. Such fairly high α values are not matched in magnitude by their ΔH values. The reasoning for this may be two fold; (i) the size of the chlorine atoms are such that the centre of gravity of each compound would be elevated well above the graphite surface, (ii) each of these solutes have only three contact points on the adsorbent surface. These two factors may combine to lower the ΔH values of these two analytes. The ΔH values are 25.8 and 25.2 $kJmol^{-1}$ for chloroform and dichloromethane respectively.

Figure 2.19 shows that dimethylformamide and ethyl acetate have similar ΔH values. The polarities of these molecules are different therefore the induced dipole moments in these molecules would be different. Consequently, these two eluates would have dissimiliar α values.

In Figure 2.19, methanol and acetonitrile display the lowest α and ΔH values. Such analytes are polar, and therefore the induced

dipole moments when exposed to an electrical field are much less than those induced in non-polar molecules when subjected to the same field. Also, these two solutes have the least numbers of contact points on the adsorbent surface. Consequently, low ΔH values are observed for these two compounds. The ΔH values of acetonitrile and methanol are 22.8 and 20 $kJmol^{-1}$ respectively.

Figure 2.19 displays that the α values of cyclohexane and cyclopentane are large (11 and 9.1 10^{-24} cm^3 respectively). The points of these two solutes, shown in Figure 2.19, are below the straight line to indicate that the α values are not matched in magnitude by their ΔH values. These are non-polar molecules and therefore the induced dipole moments are larger than those induced in polar molecules. Consequently, α values of cyclopentane and cyclohexane tend to be rather large.

The ΔH values of these two analytes are governed by their number of contact points on the adsorbent surface. Their puckered structures would only allow certain atoms in each molecule to rest on the adsorbent whilst the other atoms in their structures would be elevated above the graphite surface. Therefore low ΔH values are observed for these two compounds. ΔH of cyclohexane and cyclopentane and 32.4 and 28 $kJmol^{-1}$ respectively.

Table 2i

The Quality of Graphite Materials as Chromatographic Adsorbents

Batch of PGC	Surface Area m^2/g	Quality as a Chromatogrpahic Adsorbent	Firing or High Temperature (2500°C) treatment during the preparation of the PGC was carried out at	Particle Size Range used (μm)
PGC 219 CEN	73	Excellent (Grade A)	Centorr Associates Inc., U.S.A.	105–250
PGC 218 CEN	73	Good (Grade B)	Centorr Associates Inc., U.S.A.	105–420
Carbopack B	69	Moderate (Grade C)	Prepared at Supelco Inc., U.S.A.	297–420
PGC 219/220 SIG	64	Poor (Grade D)	Sigri, FRG.	105–250

Table 2ii

Solvent Molecular Areas (Ax)/8.5 $Å^2$

Solvent	Quoted Value	Calculated Value	Accepted Value	No. of Heavy Atoms
Hexane	6.8	6.8	6.8	6
n-Butyl Chloride	4.2	5.8	5.8	5
Chloroform	5.0	5.4	5.0	4
Dichloro Methane (methylene chloride)	4.1	3.9	3.9	3
me, t-bu ether		6.4 (5.3)*	5.3	6
Ethyl Acetate	5.7	5.7	5.7	6
Dioxane	6.0	5.6	5.6	6
Acetonitrile		3.1	3.1	3
Tetrahydrofuran	5.0	4.6	4.6	5
Dimethyl Formamide		6.3	6.3	5
Methanol		2.9	2.9	2
Benzene		6.0	6.0	6
Cyclohexane	6.0	5.2	5.4	6
Cyclopentane	5.0	4.5	4.5	5
Ethanol	3.8	3.8	3.8	3
Iso Octane	7.6	9 (8)*	7.6	8

* 5.3 - calculated by formula assuming only 2 of 3 methyl groups in contact with the surface.

Table 2(ii) shows solvent molecular areas and these values calculated by using the equation 2.1.

The Ax values were found in Ref.1.

Table 2iii

Graphite Results - Heats of Adsorption on PGC 218 CEN and PGC 219 CEN

Solute	Symbol	Eo / $(8.5Å^2)^{-1}$	Ax/ $/8.5Å^2$	$-\Delta H$ /kJmol^{-1}		ΔH_{vap} kJ/mol	$\lvert\Delta H/Ax\rvert$		$\lvert\Delta H_{vap}/Ax\rvert$
				PGC218	PGC219		PGC218	PGC219	
Hexane	HEX	0.00	6.8	42.9±1.1	40.6±0.4	31.9	6.3	6.0	4.7
Butyl Chloride	BCL	0.27	5.8	38.7±0.6	35.4±0.5	34.1	6.7	6.1	5.9
Chloroform	CHL	0.26	5.4	32.6±0.3	25.9±1.8	31.4	6.0	4.8	5.8
Dichloromethane	DCM	0.30	3.9	26.3±0.2	25.2±0.2	31.7	6.7	6.5	8.1
Methyl,t-Butyl ether	MBE	0.48	5.3	36.1±0.5	33.2±0.6	29.7	6.8	6.3	4.6 6.1
Ethyl Acetate	EAC	0.48	5.7	37.3±0.4	34.3±0.5	34.7	6.5	6.0	6.1
Dioxane	DOX	0.51	5.6	35.3±0.4	32.1±0.3	35.8	6.3	5.7	6.4
Acetonitrile	ACN	0.52	3.1	23.4±1.2	22.9±0.2	34.2	7.5	7.4	11.0
Tetrahydrofuran	THF	0.53	4.6	33.5±0.6	28.3±0.5	29.6	7.3	6.2	6.4
Dimethyl Formamide	DMF	NV	6.3	41.9±0.6	34.8±0.6	36.8	6.7	5.5	5.8
Methanol	MOL	0.95	2.9	23.1±1.3	20.0±0.6	39.2	8.0	6.9	13.5
Benzene	BEN	0.25	6.0	40.7±0.5	37.6±0.6	34.1	6.8	6.3	5.7
Cyclohexane	CYH	0.03	5.4	36.2±0.5	32.4±0.5	32.8	6.7	6.0	6.1
Cyclopentane	CYP	0.01	4.5	31.9±0.2	28.0±0.6	31.7	7.1	6.2	6.9
Ethanol	EOL	0.95	3.8	21.3±2.0		40.2	5.6		10.6
						Mean	6.73	6.14	7.2, 6.04*
						S.D.	0.59	0.61	2.6, 0.92*

NV = no value
SD = Standard Deviation

* Omiting values of $\Delta H_{vap}/Ax$ which are >10

Eo = Eluotropic Strength/$(8.5Å^2)^{-1}$ [1] (determined on silica)
Ax = Area occupied by each solute molecule on the PGC surface [1]

Table 2iv

Graphite Results - Heats of Adsorption on PGC 219/220 SIG

Solute	Symbol	Eo/ $(8.5Å^2)^{-1}$	Ax/ $(8.5Å^2)$	$-\Delta H$ on PGC219/220SIG	ΔH_{vap}/ $kJmol^{-1}$	$\lvert\Delta H/Ax\rvert$ $kJmol^{-1}$ $(8.5Å^2)^{-1}$
Hexane	HEX	0.00	6.8	47.3 ± 0.6	31.9	6.94
Butyl Chloride	BCL	0.27	5.8	41.7 ± 1.0	34.9	7.19
Chloroform	CHL	0.26	5.4	35.5 ± 0.4	31.4	6.57
Dichloromethane	DCM	0.30	3.9	28.8 ± 0.6	31.7	7.37
Methyl,t-Butyl ether	MBE	0.48	5.3	40.2 ± 0.7	24.7	7.59
Ethyl Acetate	EAC	0.48	5.7	41.1 ± 0.9	34.7	7.22
Dioxane	DOX	0.51	5.6	38.5 ± 0.5	35.8	6.88
Acetonitrile	ACN	0.52	3.1	32.4 ± 1.4	34.2	10.5
Tetrahydrofuran	THF	0.53	4.6	37.1 ± 0.8	29.6	8.08
Dimethyl Formamide	DMF	NV	6.3	53.6 ± 2.6	36.8	8.51
Methanol	MOL	0.95	2.9	35.5 ± 4.0	39.2	12.2
Benzene	BEN	0.25	6.0	44.6 ± 0.7	34.1	7.43
Cyclohexane	CYH	0.03	5.4	40.7 ± 0.6	32.8	7.53
Cyclopentane	CYP	0.04	4.5	35.1 ± 0.4	31.7	7.80
Ethanol	EOL	0.95	3.8		40.2	
					Mean	8.0
					S.D.	1.5

ΔH_{vap} = Heat of vapourisation [14]

Eo = Eluotropic strength of solutes determined on silica [1]

Ax = Molecular Area [1]

S.D. = Standard Deviation

Table 2v

Graphite Results - Heats of Adsorption (ΔH) on Carbopack B

Solute	Eo/ $(8.5\text{Å}^2)^{-1}$	Ax /8.5Å^2	$-\Delta H$/kJmol^{-1}	$\lvert\Delta H/Ax\rvert$ kJmol^{-1} (8.5Å^2)
Hexane	0.00	6.8	45.0 ± 0.9	6.6
Butyl Chloride	0.27	5.8	40.3 ± 1.5	6.9
Chloroform	0.26	5.4	36.0 ± 1.2	6.7
Dichloromethane	0.30	3.9	29.1 ± 0.9	7.5
Methyl,t-Butyl ether	0.48	5.3	37.9 ± 1.6	7.2
Ethyl Acetate	0.48	5.7	43.6 ± 1.4	7.6
Dioxane	0.51	5.6	34.9 ± 2.2	6.2
Acetonitrile	0.52	3.1	33.7 ± 1.3	10.9
Tetrahydrofuran	0.53	4.6	34.8 ± 1.3	7.6
Dimethyl Formamide	NV	6.3	42.9 ± 3.0	6.8
Methanol	0.95	2.9	23.1 ± 0.35	8.0
Benzene	0.25	6.0	43.6 ± 0.7	7.3
Cyclohexane	0.03	5.4	38.9 ± 0.8	7.2
Cyclopentane	0.04	4.5	32.0 ± 0.7	7.1
Ethanol	0.95	3.8	39.0 ± 1.8	10.3

For symbols see Table 2iii

Table 2vi

Silica Gel Results

Solute	Eo $(8.5\text{Å}^2)^{-1}$	Ax 8.5Å^2	$-\Delta H$ $kJmol^{-1}$	$\lvert\Delta H/Ax\rvert$
Hexane	0.00	6.8	34.7 ± 0.9	5.1
Butyl Chloride	0.27	5.8	47.6 ± 1.4	8.2
Chloroform	0.26	5.0	32.2 ± 1.9	6.44
Dichloromethane	0.30	3.9	29.9 ± 1.7	7.7
Methyl,t-Butyl ether	0.48	5.3	71.0 ± 3.8	13.4
Ethyl Acetate	0.48	5.7	51.9 ± 6.5	9.1
Dioxane	0.51	5.6	60.6 ± 4.0	10.8
Acetonitrile	0.52	3.1	49.9 ± 1.3	16.1
Tetrahydrofuran	0.53	4.6	49.2 ± 6.0	10.7
Dimethyl Formamide	NV	6.3	63.7 ± 3.0	10.1
Methanol	(0.95)	2.9	53.3 ± 3.0	18.4
Benzene	0.25	6.0	49.6 ± 1.8	8.3
Cyclohexane	0.03	5.4	32.0 ± 1.2	5.9
Cyclopentane	0.04	4.5	28.4 ± 1.4	6.3
Ethanol	0.95	3.8	51.6 ± 2.0	13.6
Iso Octane (IOC)	0.01	8.0	49.3 ± 5.0	6.2

For symbols see Tables 2iii and 2iv.

lnk' Vs 1/T PGC 219 CEN (105 - 250µ) FIGURE 2.4

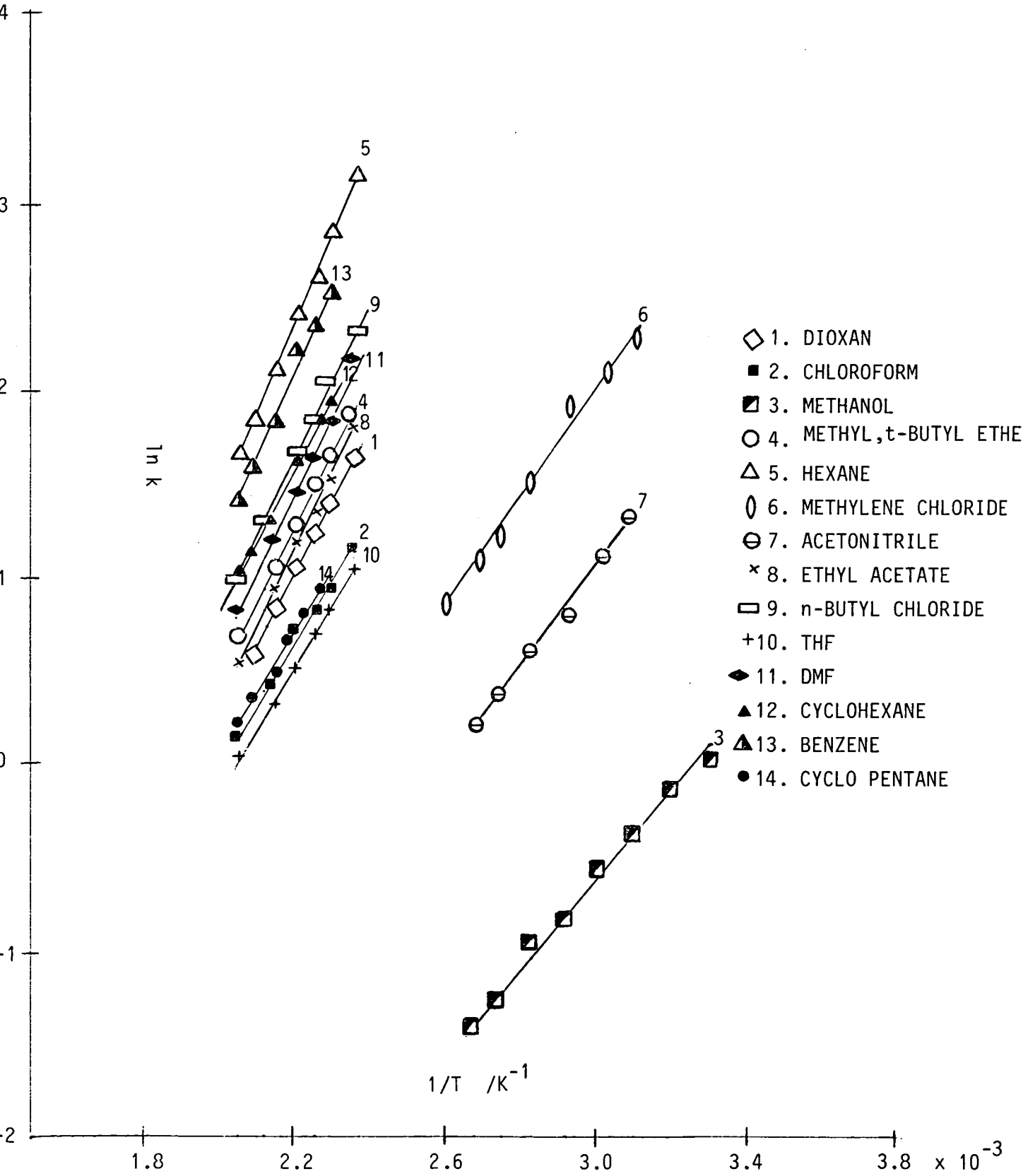
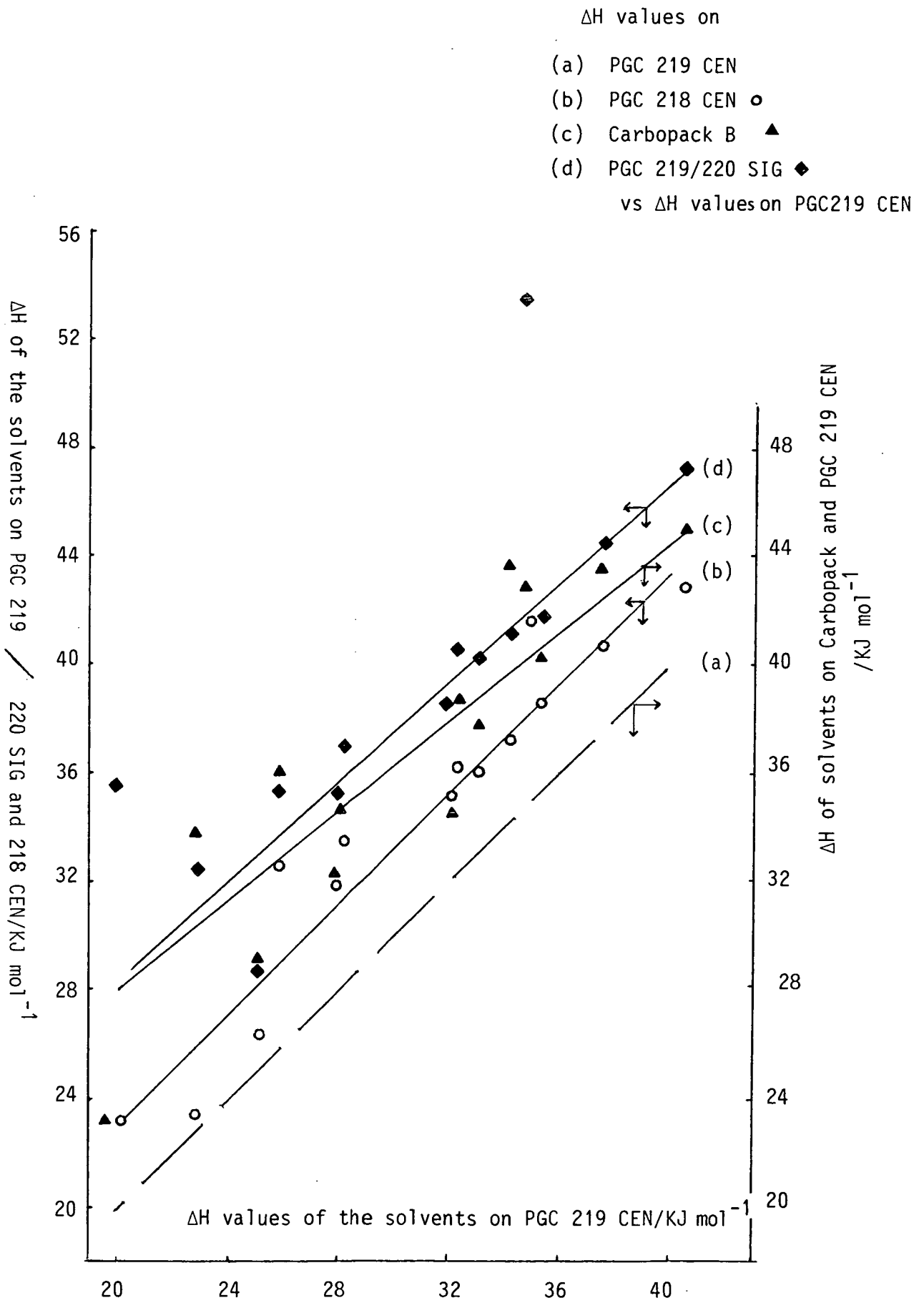


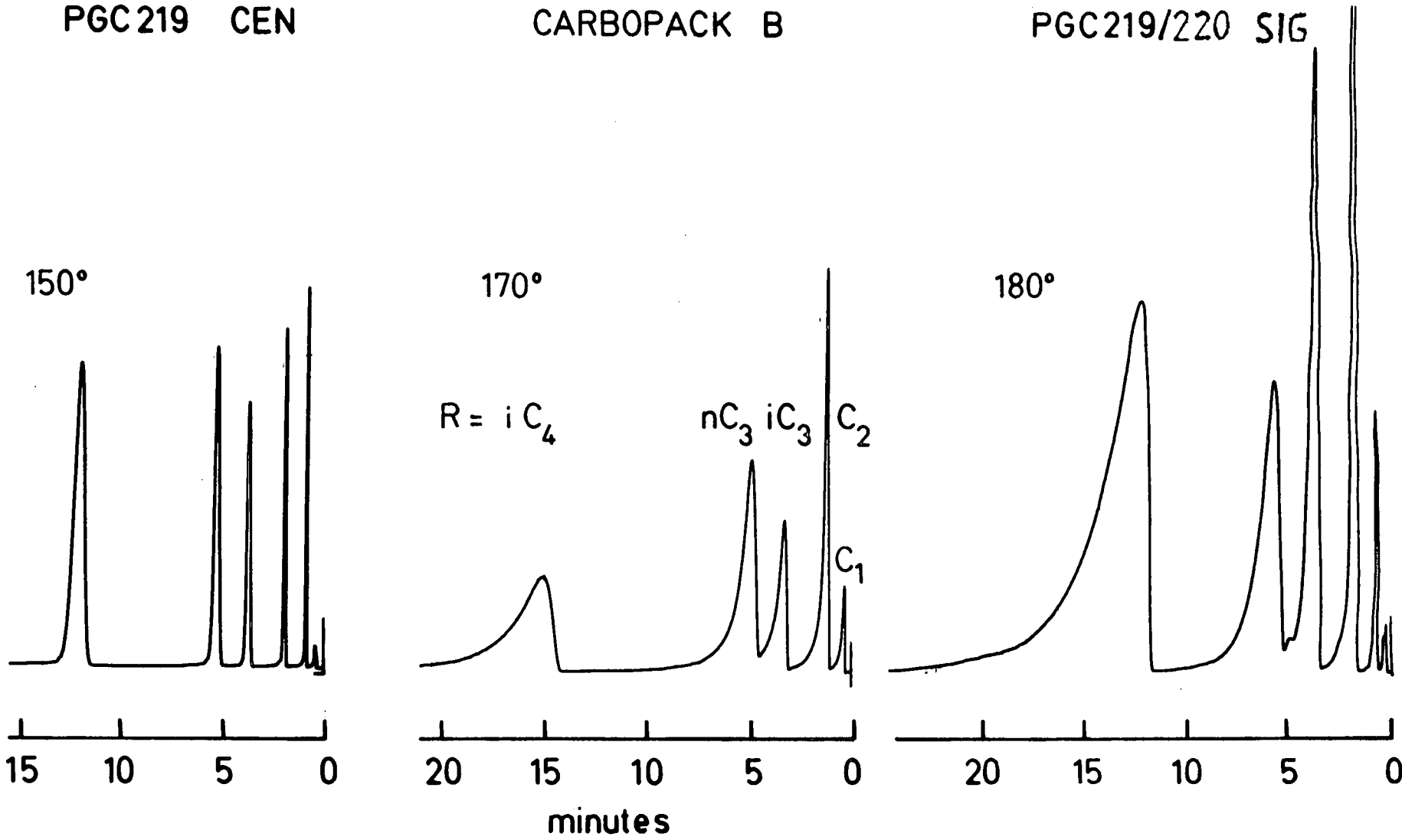
FIGURE 2.5

ΔH values on each carbon vs ΔH values on PGC 219 CEN for the HPLC solvents



KETONES $CH_3.CO.R$

FIGURE 2.6



ln k' Vs 1/T PGC 218 CEN (105 - 420μ)

FIGURE 2.7

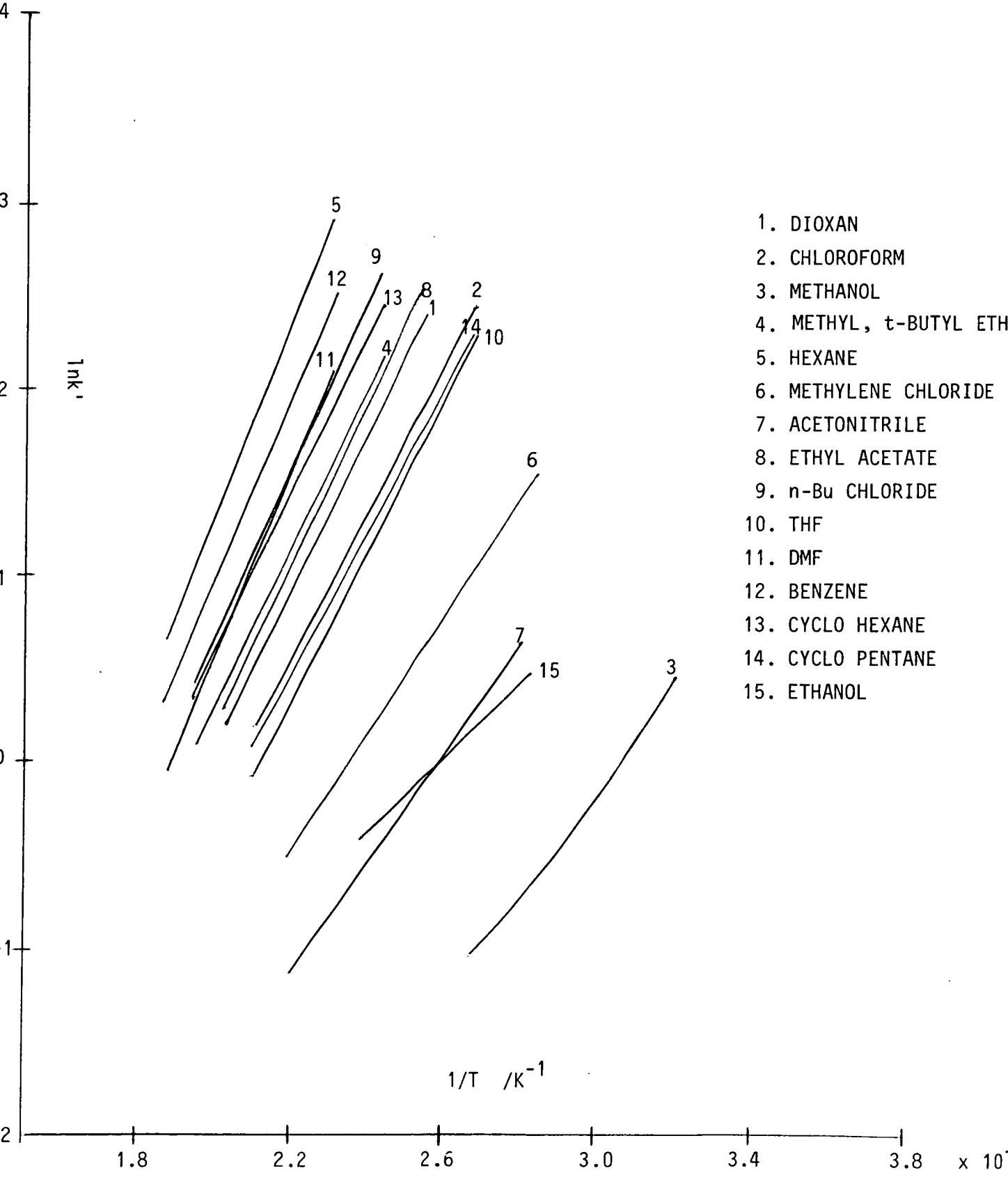


FIGURE 2.8

ln k' Vs 1/T PGC 219/220 SIGIRI

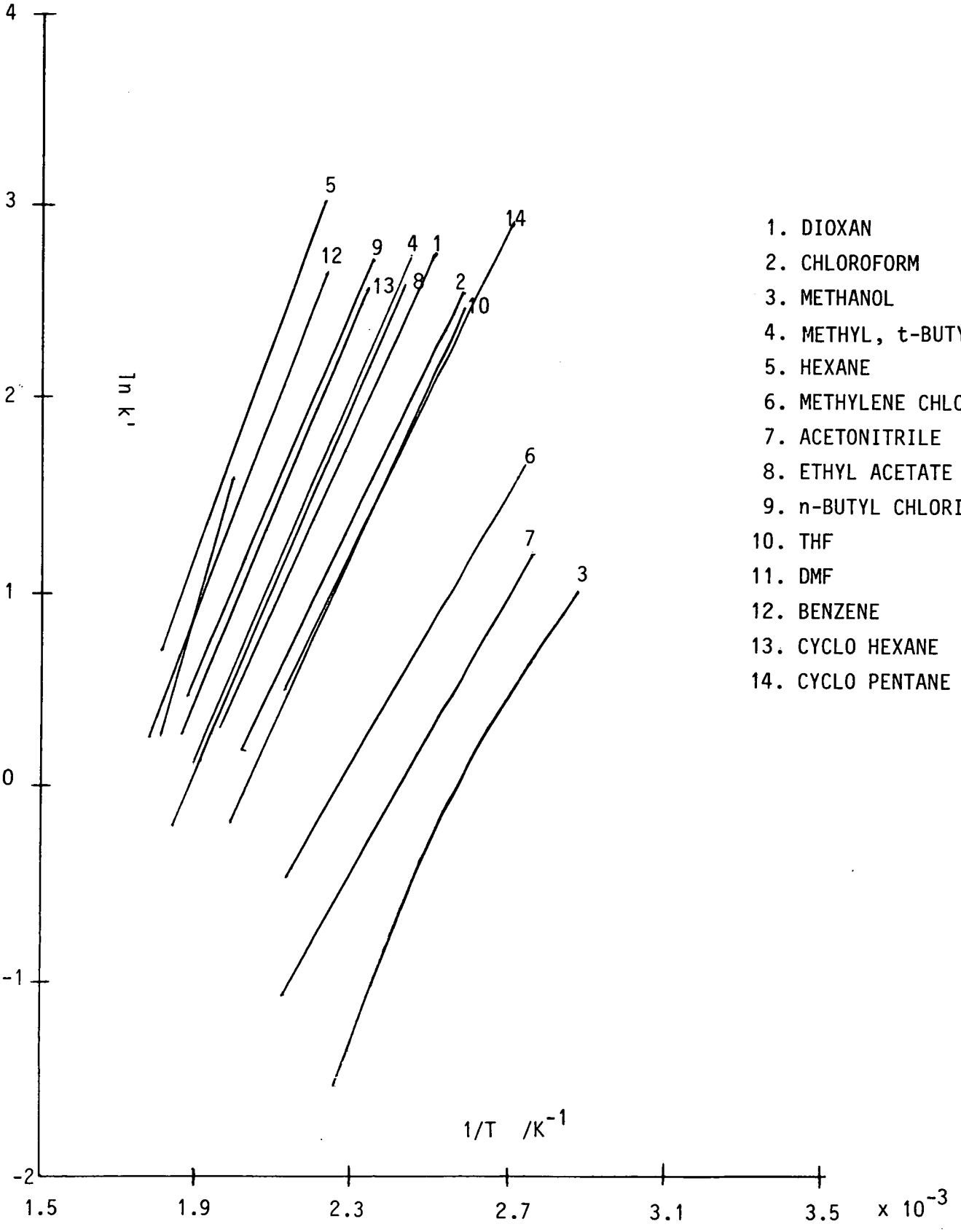


FIGURE 2.9

CARBOPAC. lnk' Vs 1/T (297 - 420μ)

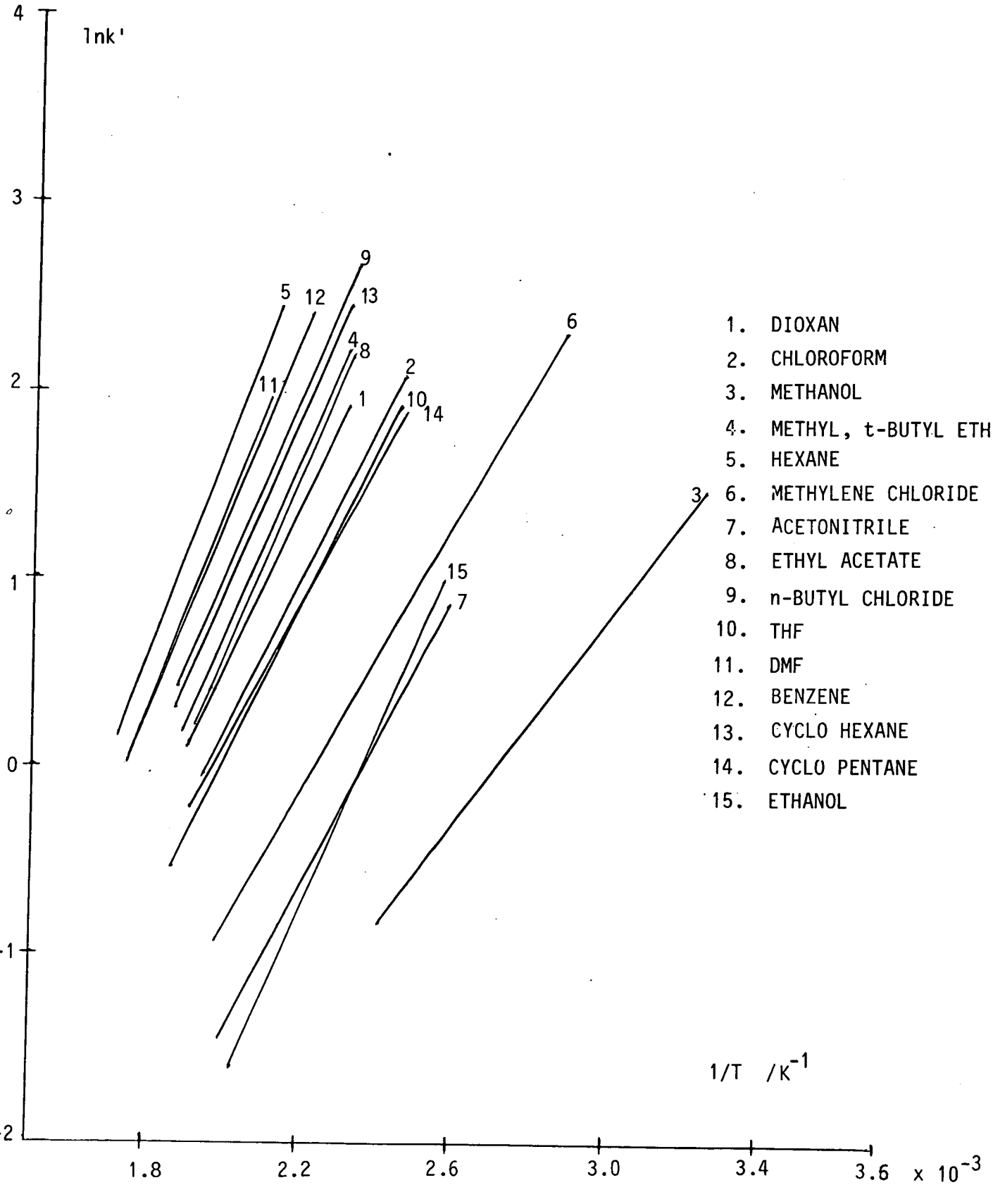


FIGURE 2.10

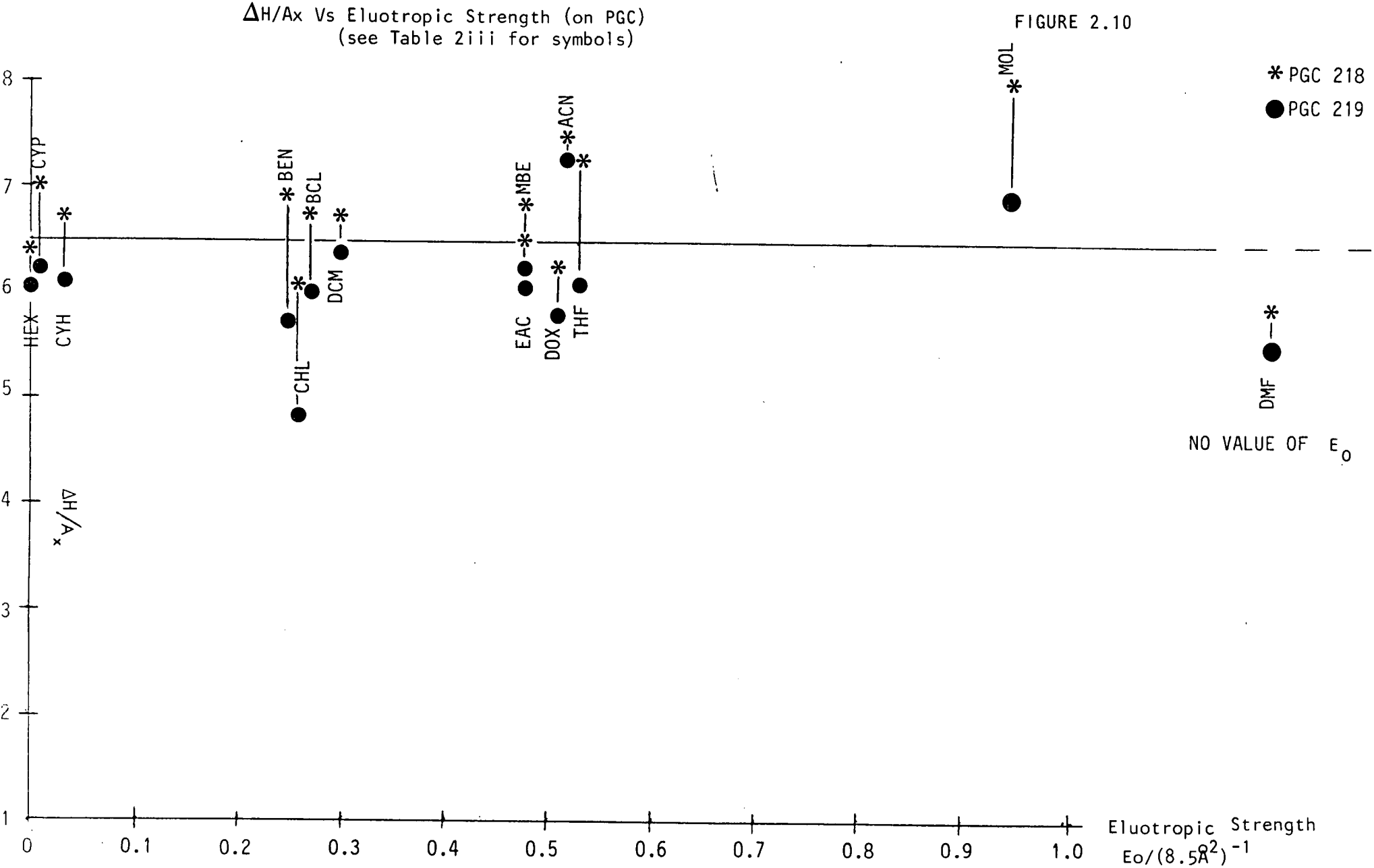

ΔH/Ax Vs Eluotropic Strength (on PGC)
(see Table 2iii for symbols)
* PGC 218
● PGC 219
CYP
HEX
CYH
BEN
CHL
BCL
DCM
MBE
EAC
ACN
DOX
THF
MOL
DMF
NO VALUE OF E_0
$\Delta H/A_x$
Eluotropic Strength
$Eo/(8.5\mathring{A}^2)^{-1}$
8
7
6
5
4
3
2
1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

FIGURE 2.11

See Table 2iii for Symbols

Ax Vs ΔH, ON GRAPHITE

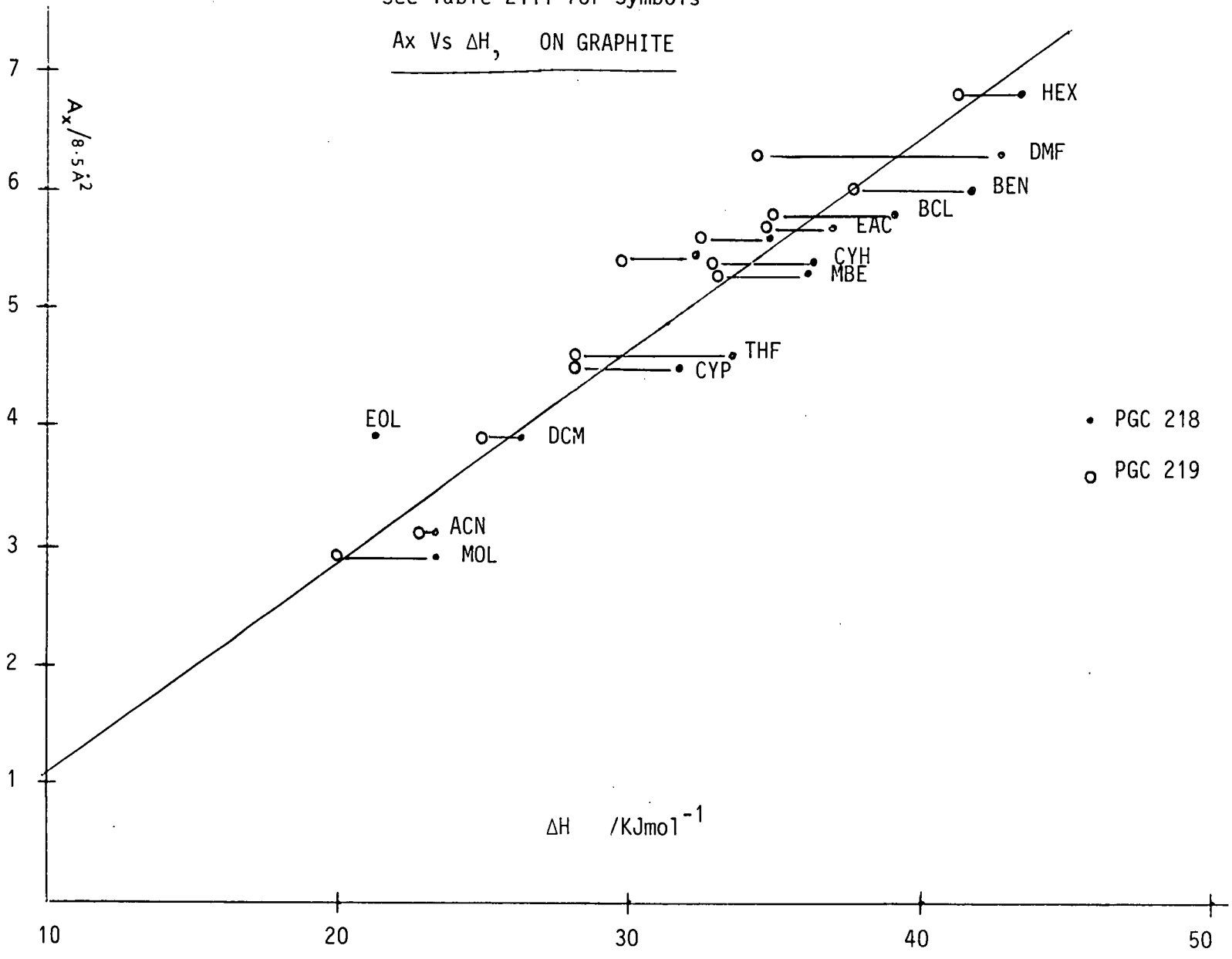


FIGURE 2.12

ΔH/Ax Vs Eluotropic Strength (on Carbopack)

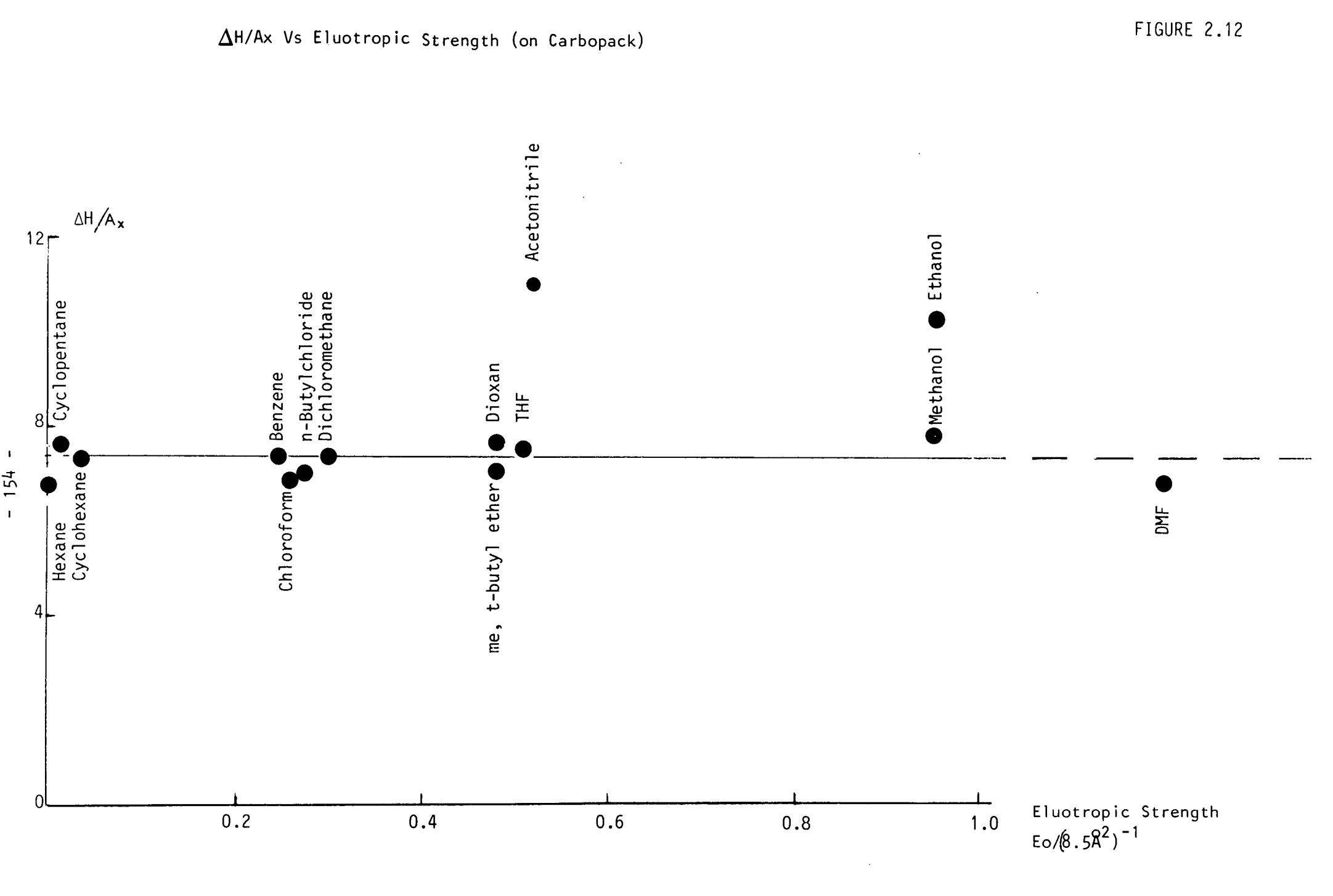
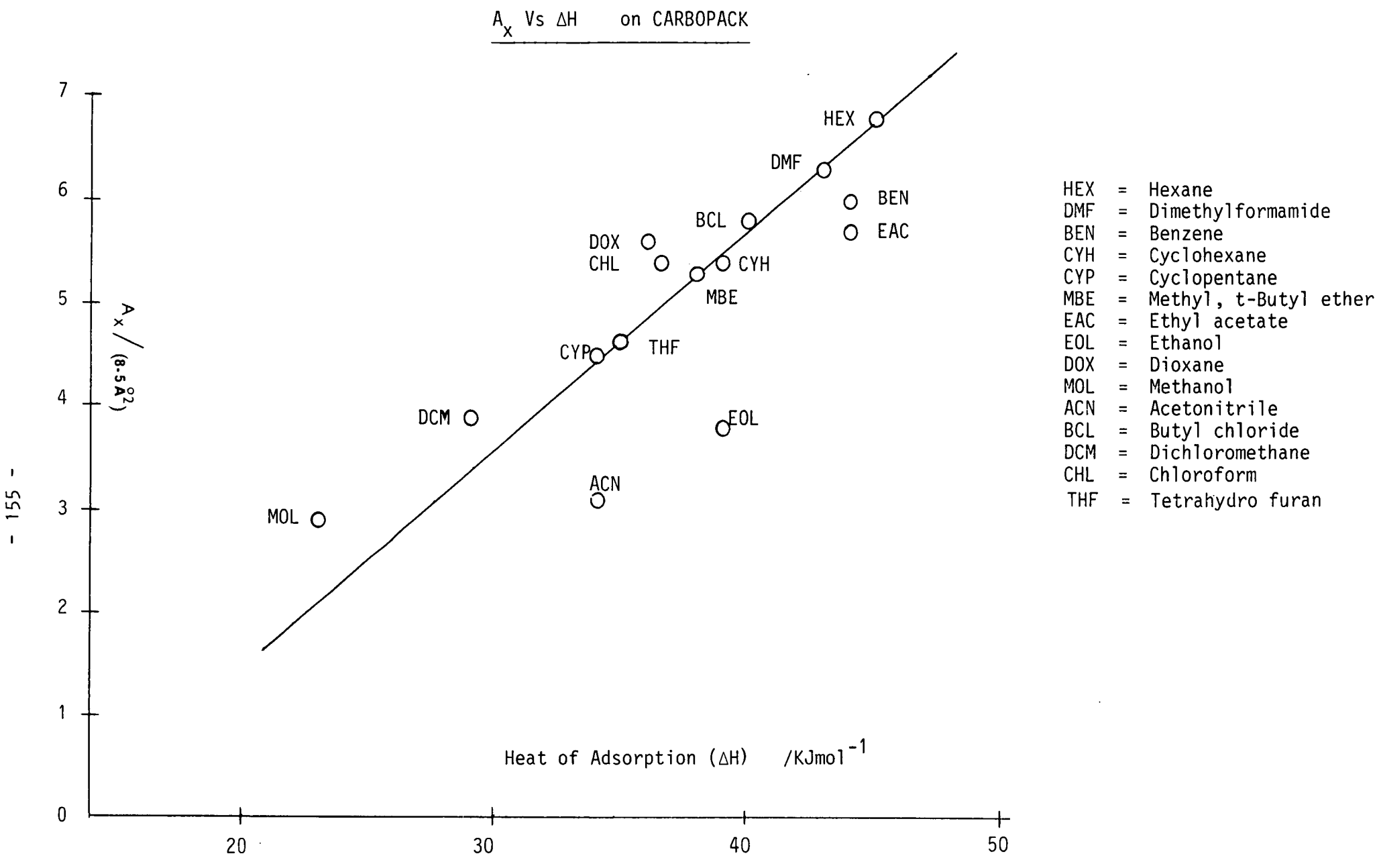


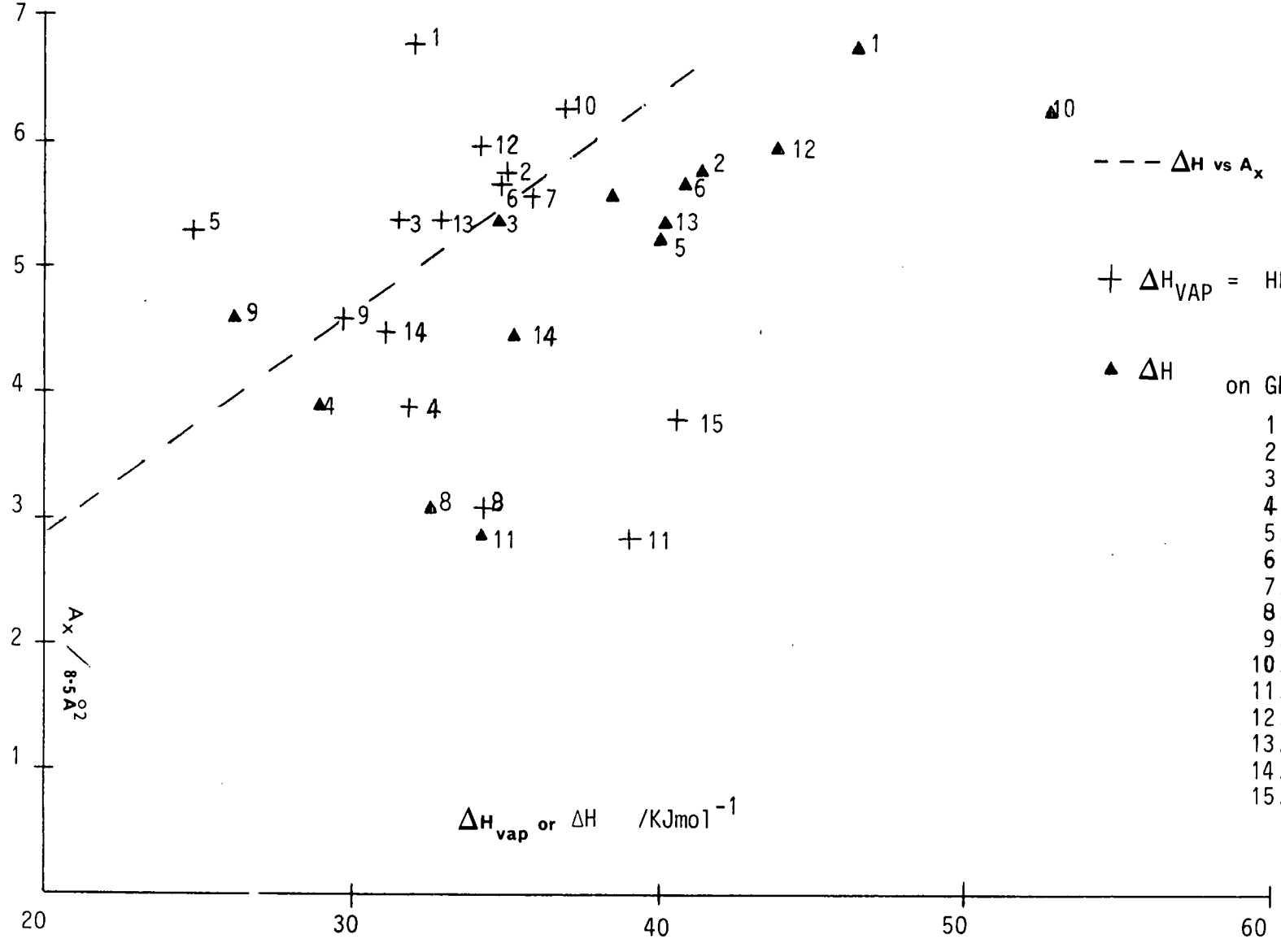
FIGURE 2.13



HEX = Hexane
DMF = Dimethylformamide
BEN = Benzene
CYH = Cyclohexane
CYP = Cyclopentane
MBE = Methyl, t-Butyl ether
EAC = Ethyl acetate
EOL = Ethanol
DOX = Dioxane
MOL = Methanol
ACN = Acetonitrile
BCL = Butyl chloride
DCM = Dichloromethane
CHL = Chloroform
THF = Tetrahydro furan

Ax Vs ΔH and Ax Vs ΔH_{vap}; on PGC 219/220 SIGRI

FIGURE 2.14



– – – ΔH vs A_x for PGC 219 CEN,

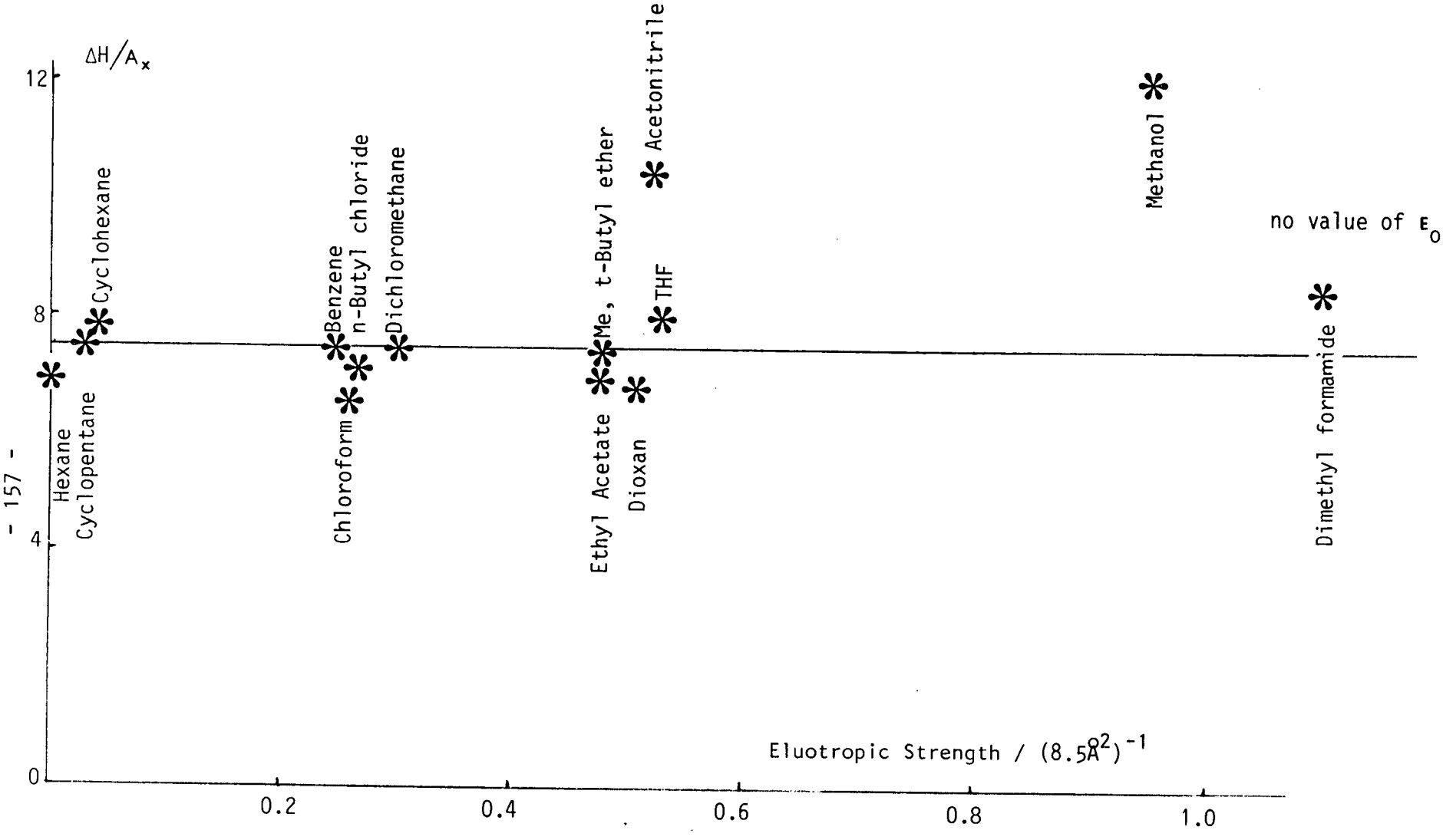
\+ ΔH_{VAP} = HEAT OF VAPORIZATION

▲ ΔH on GRAPHITE (SIGRI)

1. Hexane
2. n-Butyl Chloride
3. Chloroform
4. Dichloro methane
5. Methyl, t-butyl ethe
6. Ethyl acetate
7. Dioxane
8. Acetonitrile
9. Tetrahydrofuran
10. Dimethylformamide
11. Methanol
12. Benzene
13. Cyclohexane
14. Cyclopentane
15. Ethanol

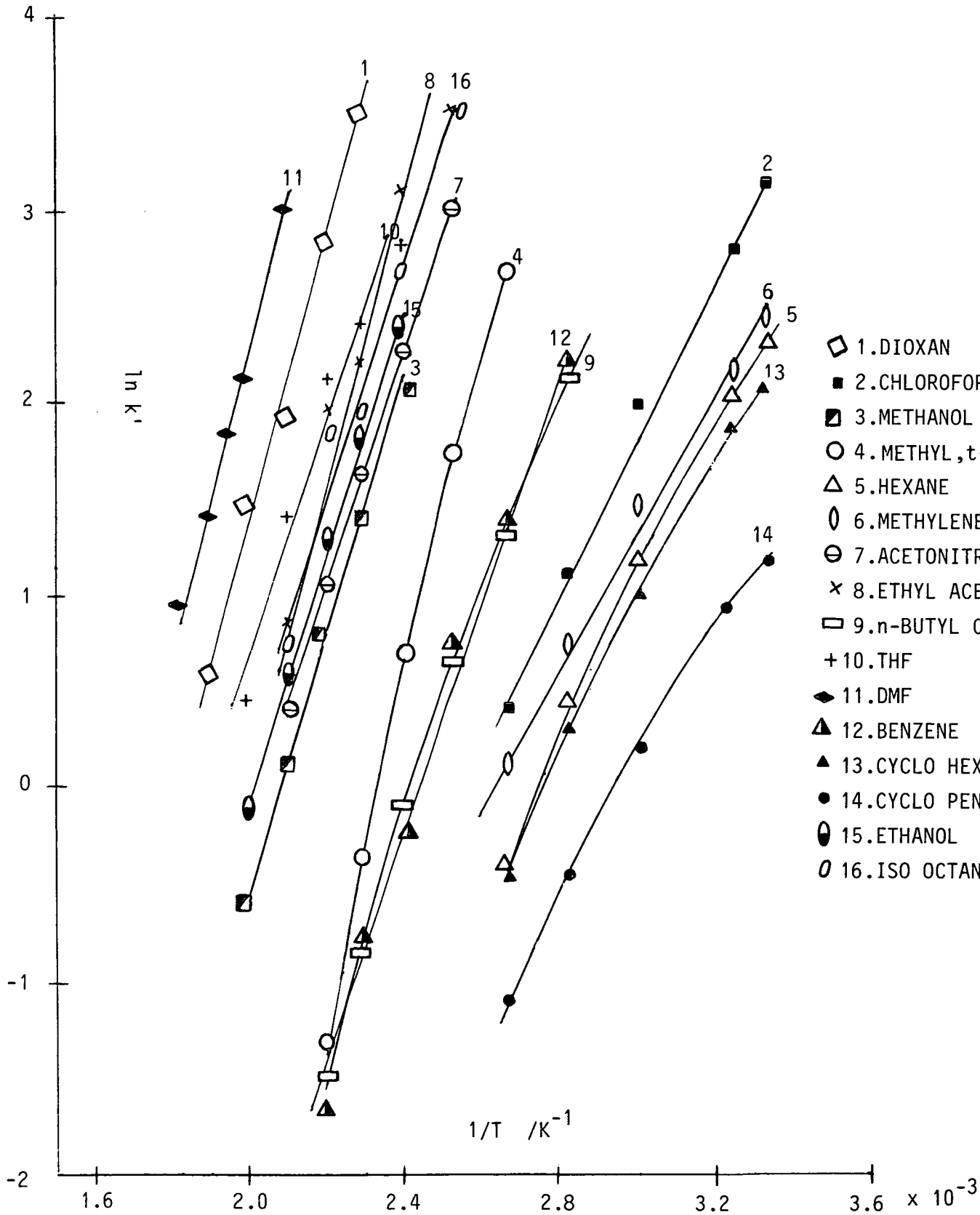
$\Delta H/Ax$ Vs Eluotropic Strength (on PGC 219/220 SIGRI)

FIGURE 2.15



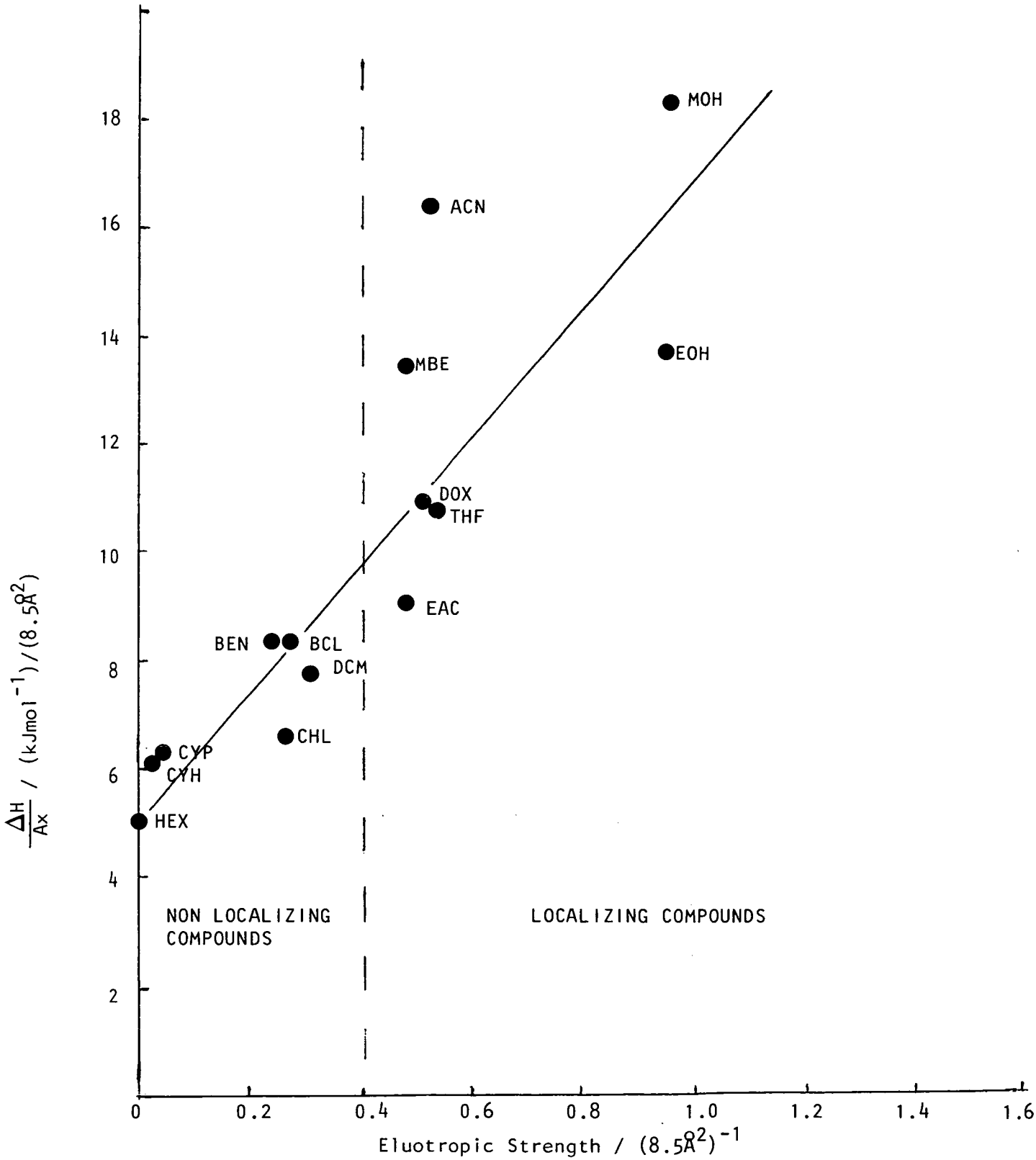
Silica. lnk' Vs 1/T (177 - 210µ)

FIGURE 2.16



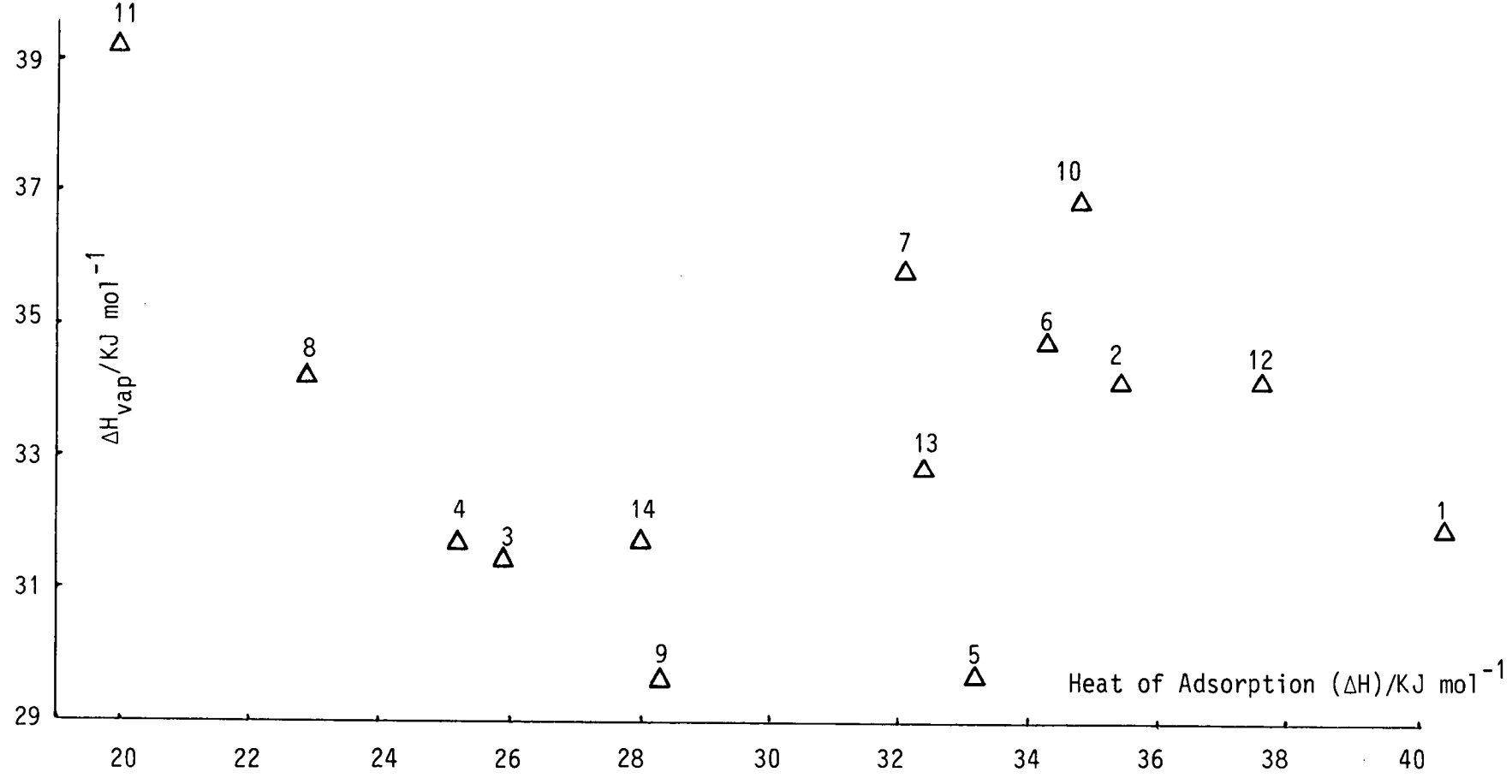
$\Delta H/Ax$ Vs Eluotropic Strength (for Silica)
(see Table 2iii for Symbols)

FIGURE 2.17



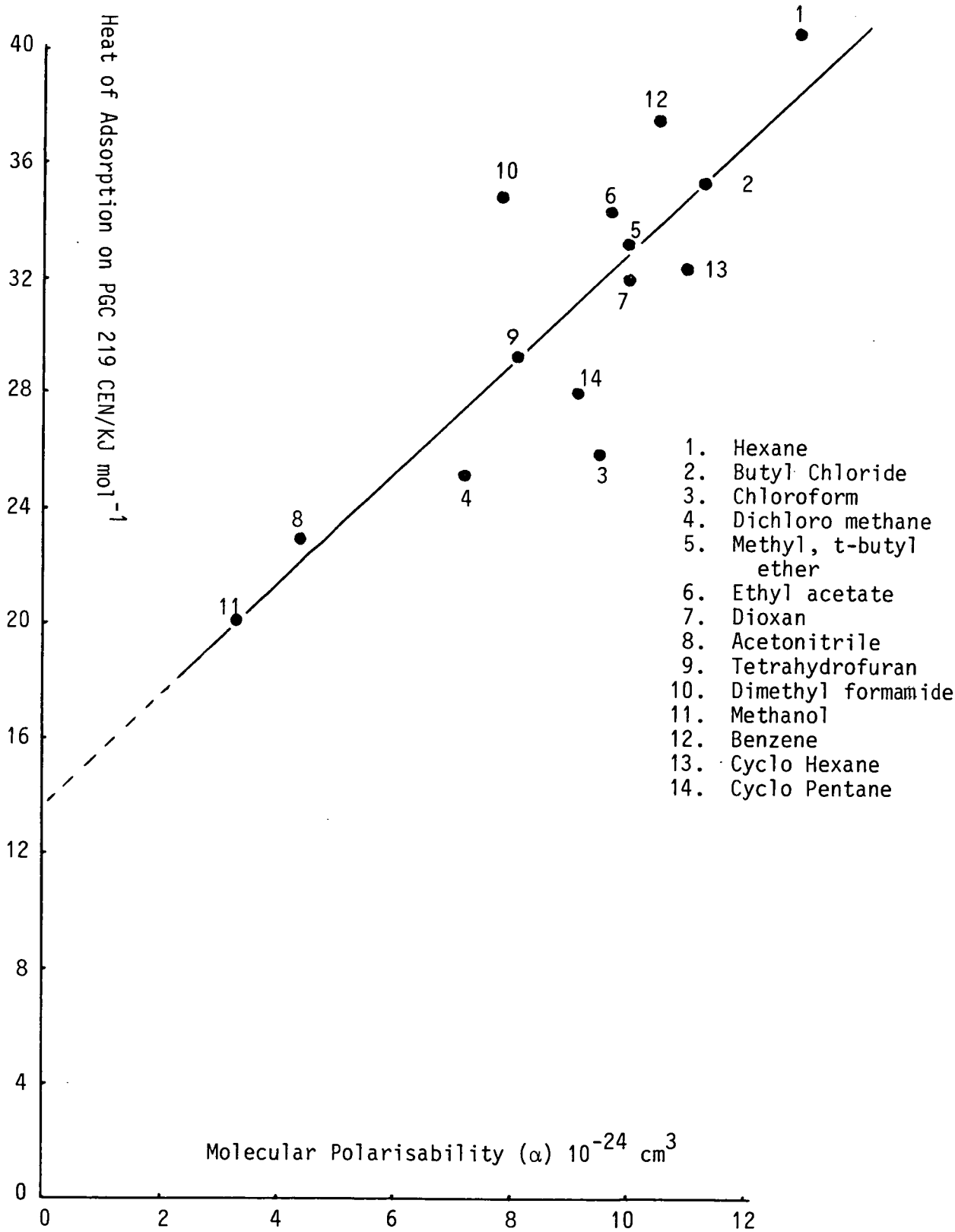
Heat of Vaporization vs Heat of Adsorption (on PGC219 CEN)
for HPLC Solvents

(see Fig. 2.19 for Compounds)



Heat of Adsorption vs Molecular Polarisability of HPLC Solvents

FIGURE 2.19



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CHAPTER 3

The Effect on GC Properties of PGC, After Modification of the Graphite Surface by the Adsorption of a Liquid Stationary Phase

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The Effect on GC Properties of PGC, after the Modification of the Graphite Surface by the Adsorption of a Liquid Stationary Phase

3.1 INTRODUCTION

The chromatographic properties of a graphite adsorbent can be changed considerably by coating the adsorbent surface with a liquid stationary phase. This chapter describes the changes that occur in PGC as its surface is modified with Carbowax 1500 (Polyethylene glycol or PEG).

Kiselev et al [1-4], Di Corcia and co-workers [5-8] and Bruner and his research team [9-11] have successfully carried out a number of separations after coating the GCB with the appropriate liquid stationary phase. The characteristics of the coated GCB have therefore been used as guidelines for understanding the chromatography on coated PGC.

The following section describes the reasons for the application of a liquid stationary phase on carbon.

3.1.1 The need for the preparation of coated carbon materials

Carbon (GCB or PGC) is a non-specific chromatographic support material. That is, the separation on carbon does not depend upon

the functional groups present in the eluates. The graphite surface is non-polar; and quite suitable for the separation of non-polar analytes.

Carbon may be converted to a specific material by coating its surface with a liquid stationary phase. Polarity can be introduced on to this substrate by the adsorption of the appropriate liquid stationary phase. The amount of liquid phase on the adsorbent and hence the polarity of the chromatographic surface, can be controlled to achieve the desired separation.

As described in the preceeding chapter, the graphite surface may have chemical and physical heterogeneities that influence the retention and peak shapes of analytes. Such defects could be covered by coating the carbon surface with a liquid stationary phase. The quality of the carbon materials as chromatographic adsorbents can thus be improved.

The next section describes the properties of the coated carbon surfaces and this would lead to an understanding of the chromatography on such modified surfaces.

3.1.2 Properties of the coated graphite materials

When the graphite surface is coated with a liquid stationary phase, the solid phase would have functional groups which show selectivity

towards certain analytes. Consequently, such solutes would display enhanced retention values. For example, Carbowax shows selectivity towards hydrogen bonding analytes such as alcohols. The hydroxyl groups of PEG can interact with those of the alcohols.

At monolayer coverage, the liquid stationary phase behaves like a liquid film where the functional groups in this film would have vibrational and translational energy. The active sites (i.e. the functional groups) may be mobile in the liquid film. The solutes would interact with these moving groups.

During gas-liquid chromatography, the solutes may be soluble in the liquid stationary phase. Due to the thermal motion of the liquid stationary phase molecules, the distances between the analyte and the liquid phase would be greater in comparison to the distances between those solutes and the carbon surface in the case of adsorption chromatography. As a result, the energy of interaction and hence the retention times of the solutes that have interacted with the liquid stationary phase would be lower than those when the analytes were adsorbed on to a bare carbon adsorbent. This property of coated materials can be exploited to decrease retention of analytes that display unfavourably high elution times on the bare carbon surface.

The next section describes the uses of the coated GCB in chromatography. This may give some idea of the possible

applications on coated PGC surfaces.

3.1.3 Applications of coated GCB

This section describes the literature survey compiled to describe the research carried out on GCB surfaces that were modified with different liquid stationary phases.

The separation of polar analytes are first described. This is followed by the separation of sulphur compounds and the chromatography of π acceptors.

Dicorcia et al [5] modified the GCB surface with trimesic acid (1,3,5-tricarboxybenzene) followed by Carbowax 20m for the separation of phenols in drinking water. The treatment with trimesic acid was necessary to eliminate any basic sites on the GCB surface, which would otherwise react with the phenols. The Carbowax was not only selective towards the compounds of interest but also covered the heterogeneities on GCB that could have given rise to peak tailing.

Kiselev et al [2] observed that benzoic and toluic acids gave fronted peaks, when chromatographed on the bare GCB. They also found that the adsorption isotherms of these compounds on GCB (moles adsorbed or uptake vs corresponding partial pressure of solute) were convex to the pressure axis. Such results, they

believed, were due to the molecular association of each solute on the graphite surface.

Kiselev and co-workers modified the GCB surface with orthophosphoric acid and successfully separated a mixture containing benzoic acid and stereo isomers of toluic acid. They observed that the analyte peaks were symmetrical and the adsorption isotherms were straight lines. They attributed this to the decrease in mutual association of solute molecules on the absorbent after the introduction of this stationary phase and also, the hydroxyl groups of orthophosphoric acid forming specific interactions with the functional groups of the above named solutes.

Kiselev and his team also chromatographed other oxygen-containing compounds on orthophosphoric acid coated GCB. They found that the hydroxyl groups of this liquid stationary phase forming interactions with oxygen containing compounds such as acetone, methanol and diethylether.

Di Corcia et al [8] modified the GCB surface with trimesic acid followed by Carbowax 20M, for the separation of the components in an alcoholic drink. At higher concentrations ($> 2.4\%$), of the trimesic acid, the alcohols present in the beverage tend to give slightly tailed peaks. The authors attributed this to the anomalous interactions of the alcohols with the trimesic acid. The Carbowax concentration was adjusted for the best separation, since

the amount of this stationary phase on the adsorbent governs the number of interactions between the solutes and Carbowax, which in turn determines the order of elution.

Micropacked columns were constructed using GCB as a support for gas-liquid-solid chromatography by Bruner and coworkers [10]. They prepared such supports by coating the GCB with polymetaphenoxylene (PMP). Bruner et al obtained tailed peaks and diminished detector signals for polar compounds on these supports. Such unsatisfactory results were due to the adsorption of water that is used to dissolve or suspend the analytes. This water is adsorbed by the material and then eluted as a tailed peak.

Bruner et al hydrogen treated GCB and then coated the solid material with PMP. Such a support adsorbed only negligible amounts of water at low column temperatures (approximately 50°C). They introduced each mixture into the column and chromatographed each mixture for 10 minutes at 50°C before using temperature programming to achieve the desired separations. They successfully separated (a) different functional groups, (b) organic pollutants in air, and (c) a mixture of hydrocarbons from cracking naphtha (C_3-C_{11}); on PMP coated, hydrogen treated GCB (HTGCB).

The columns of PMP coated HTGCB gave satisfactory efficiencies, column capacities, peak shapes and detector signals.

The separation of hydrocarbons is another application of modified GCB.

Kiselev et al [4] modified GCB with sodium salts of sulphonated cobalt phthalocyanines ($CoPth(SO_3Na)_n$). The components in the mixtures of unsaturated, saturated, aromatic and cyclic hydrocarbons were separated using such a material.

Kiselev and his team discovered that $CoPth(SO_3Na)_n$ salt coated GCB columns offered higher efficiencies and more symmetrical analyte peaks than the uncoated GCB columns. They also reported that the use of such a salt-coated surface would give faster analysis times than a squalane-coated capillary column in the separation of a hydrocarbon mixture.

Kiselev and coworkers noted that the retention of hydrocarbons were much greater on the salt-coated GCB than on Apiezon L or hydrozone, coated GCB. These increased retention values were attributed to the salt on the GCB surface interacting with the adsorbates, as a result of the induction of an electrostatic field in the solutes by the highly polarized atoms in the ($CoPth(SO_3Na)_n$) salt.

Unsaturated and aromatic hydrocarbon solutes interact specifically with the positive charges on the salt-coated GCB surface. Kiselev et al found that greater the unsaturation, larger the retention of the analyte on such a modified material. Aromatic molecules

displayed the highest retention on the salt-coated GCB support.

Kiselev and coworkers also reported that, the greater the value of n in $CoPth(NaSO_3)_n$, the larger the retention of unsaturated and aromatic hydrocarbons due to the increased number of interactions between the π electrons of analytes and the Na^+ ions of the stationary phase.

Di Corcia and Samperi [6] separated the components in light hydrocarbon mixtures between 46-50°C. Each mixture contained unsaturated and saturated components. They compared the chromatography of the light hydrocarbons on PEG 1500 coated GCB with Picric acid coated GCB.

At sub-monolayer coverages, the retention of compounds depends upon their geometrical structures and polarisabilities [6]. Unsaturated hydrocarbons can be polarised by the functional groups of PEG. At higher concentrations of PEG (2.8% w/w), Di Corcia and Samperi achieved no separation between acetylene and ethane. These two analytes were separated by decreasing the concentration of PEG on the adsorbent surface. At lower concentrations of PEG (around 1.5% w/w), the overlap of cis-2-butene and butane occurred. Di Corcia and Samperi used picric acid coated GCB column to separate the latter pair of compounds. On this stationary phase, the mechanism of separation is due to the transfer of π electrons between the unsaturated hydrocarbons and the picric acid. The

authors found that the acid-coated GCB was better able to separate the pairs of saturated and unsaturated compounds (for example, propane and propene or ethane and ethylene) than the PEG coated GCB material, but the acid coated support was unsuitable for the routine analysis as such a material was found to be chemically and thermally unstable.

Di Corcia and Samperi [7] found that, C_5 hydrocarbons (saturated and unsaturated) were not well separated from one another on Picric acid coated GCB surfaces. They decreased the picric acid concentration and achieved the optimum separation at 50°C. Picric acid is a strong π acid and therefore Dicorcia and Samperi found that the small variations in the amount of acid on GCB produced considerable alterations in the retention times of analytes. They then used 1,3,5-trinitrobenzene (TNB) on GCB since TNB is a weaker π acid than picric acid. They discovered that small variation in the amount of TNB on GCB did not significantly alter the retention of the C_5 hydrocarbon analytes.

The authors used hydrogen as carrier gas in the analysis since u^-_{opt} (carrier gas velocity which gives minimum H) with hydrogen was twice as much as that obtained with nitrogen. Hydrogen was therefore used to decrease the analysis time.

Another important application of coated GCB is the separation of sulphur compounds in air [9]. The HTGCB may be treated with H_3PO_3

to eliminate any remaining basic sites which may otherwise react with the analytes. The graphite surface is then coated with XE60 (cyanosilicon) to perform the analysis.

The stationary phase is selective towards sulphur-containing compounds. Bruner et al [9] reported that such a column could separate H_2S, SO_2, CH_3SH, C_2H_5SH and CH_3SCH_3.

The above literature survey on modified GCB would be useful in understanding the chromatography on coated PGC (Section 3.1.4). the information in Section 3.1.3 on GCB has indicated the potentials of coated PGC in the field of gas chromatrography.

The next section gives a summary of the research on PGC coated with Carbowax 1500. The work in this chapter aims to compare the chromatography on modified and bare PGC surfaces.

3.1.4 Chromatography on PGC, coated and uncoated

The change in heat of transfer of certain solutes, the surface area of solid stationary phase, analyte peak shapes, column efficiencies and the retention properties of ketones, alcohols and light hydrocarbons (C_1-C_5) were investigated by varying the amount of Carbowax 1500 on PGC 210 CL.

The results are explained in terms of what may be happening on the

surface as its 'personality' is changed. These results would enable one to understand the chromatography on modified PGC.

Retention values of above mentioned analytes are recorded for other PGC samples (PGC 219 CL, 220 CEN and 222 CEN) before and after coating the PGC surface with a monolayer of Carbowax 1500. The k^1 values obtained on bare and modified PGC are compared between different PGC batches. The column efficiencies are also compared between bare and coated PGC 222 CEN. PGC 219 CEN is classified as a grade 'A' adsorbent (Chapter 2). Retention values of solutes and the efficiency of a column are determined on PGC 219 CEN to see how well these results agree with the coated materials.

Heat of transfer values (ΔH) give an indication of the processes that may be taking place as the surface polarity is altered. ΔH values and efficiencies on PGC 210 CL were determined up to the monolayer coverage of Carbowax 1500. Analytically important results are obtained before the unimolecular layer. Beyond the monolayer the particles may not be uniformly covered with the liquid stationary phase and the PGC is fully converted to a polar material. In the course of this research programme, the changing polarity of the surface is studied. Therefore research into ΔH and column efficiencies beyond the monolayer coverage of Carbowax is not pursued.

Carbowax coated PGC 210 CL was used to chromatograph two whisky

samples. Same support material was useful in the separation of the components in an artificial mixture of blood alcohols and their metabolites.

3.2 EXPERIMENTAL

3.2.1 Materials and Equipment

The liquid stationary phase was Carbowax 1500. This is also called polyethylene glycol (PEG 1500) purchased from Phase Separations, Queensferry, Clwyd.

The Analar grade methanol was from Fisons Chemicals, Loughborough, Leics.

The solid phases were PGC 210 CL, 219 CL, 220 CEN and 222 CEN. These were obtained from Wolfson Liquid Chromatography Unit, Chemistry Department, Edinburgh University. These materials were prepared by Dr. Y. Ghaemi. In these experiments, the particle range of 100-200μ mesh was used.

The solutes such as pentane and acetaldehyde were purchased from Fisons Chemical Company, Loughborough, Leics. The ketones were obtained from Rathburn Chemical Company, Walkerburn, Peebleshire and hydrocarbons (except pentane) from Matheson Company (Subsidiary of Union Carbide), Oevel, Belgium.

The vacuum oven (model no. 790458) from Townson and Mercer, Croydon.

The rest of the equipment used was identical to those mentioned in Chapter 2.

3.2.2 Amount of Carbowax per monolayer

Four 2g portions of PGC 210 CL were taken and each added to a methanolic solution (approximately $30cm^3$) of Carbowax 1500. Each solution contained different amounts of the liquid stationary phase (2, 4, 6 and 8% (w/w) of the weight of carbon).

The carbon samples in these solutions were swirled for 2 minutes and separated from the liquid by vacuum filtration. Each carbon sample was washed with three $10cm^3$ aliquots of Analar grade methanol. The carbon samples were dried (3-4 hours at 120°C) in a vacuum oven and the amount of Carbowax on each PGC sample was determined by Thermogravimetric analysis (TGA).

The results revealed that all but one of the carbon samples had 2.5-2.7% Carbowax on their surfaces. The carbon sample added to the methanolic solution containing 2% of Carbowax showed that 2.0% of the stationary phase was on the carbon surface.

These results show that the monolayer coverage of Carbowax is about

2.6% (w/w) on PGC 210 CL. This is confirmed by the points of inflection in Figures 3.1, 3.2 and the maximum of Figure 3.3. Such observations are explained in Section 3.3.

The area of PGC 210 CL is 91 m^2g^{-1}. The amount of Carbowax 1500 needed for a monolayer was 2.6%.

3.2.3 Procedure for coating Carbowax on PGC

2 grams of carbon were weighed into a cylindrical glass dish (diameter approximately 17cm and depth approximately 7cm). Carbowax 1500 was melted and the quantity of Carbowax taken as a percentage of the weight of PGC. Hence the amount of Carbowax was expressed as a percentage (w/w) of carbon. This stationary phase is a wax-like solid, and therefore it is rather inconvenient to weigh in its solid state. The molten Carbowax was much easier to handle.

The molten Carbowax was weighed into a $20cm^3$ sample bottle and dissolved in $5cm^3$ of Analar grade methanol. The methanolic solution of Carbowax was poured into the dish containing the carbon. The sample bottle was washed with four or five small aliquots ($5cm^3$) of methanol in order to transfer any traces of the stationary phase to ensure quantitative transfer. If required, further methanol could be added to the dish in order to fully immerse the carbon granules in the methanolic solution.

After swirling for 2 minutes, the methanol was evaporated by placing the dish inside the oven at 120°C. The dry, Carbowax coated carbon was then ready to be packed into a GC Column.

PGC 210 CL (91 m^2g^{-1}) required 2.6% (w/w) of Carbowax for a monolayer. By knowing the surface areas of PGC 219 CL, 220 CEN and 222 CEN, the percentage of the liquid stationary phase required for a monolayer can be calculated using proportionality. The amounts coated on PGC 219 CL, 220 CEN and 222 CEN are given in Table 3(i). These are the amounts predicted for a monolayer coverage.

3.2.4 Preparation of Columns

The GC columns were packed as described in Chapter 2. The GC conditions were as in Chapter 2. The columns were conditioned at 145°C since Carbowax is thermally unstable beyond this temperature. The carrier gas (nitrogen) flowrate during conditioning was about 50 cm^3/min (11 PSI).

Table 3(i)

Carbowax Coated PGC Materials

Solid Phase	Surface Area m^2/g	Quality of material as an absorbent (Grade)	%(w/w) of Carbowax 1500 on the surface	High Temperature Treatment (2500°C) at.
PGC 210 CL	91	D	0.05,0.1, 0.2,0.4,0.8, 1.5,2.6,4&6	Carbon Lorraine, France
PGC 219 CL	91	B	2.5	Carbon Lorraine, France
PGC 220 CEN	101	C	2.8	Centorr Ass. Inc., U.S.A.
PGC 222 CEN	76	D	2.1	Centorr Ass. Inc., U.S.A.
PGC 219 CEN	73	A	0.00	Centorr Ass. Inc., U.S.A.

Also see Table 2(i) of Chapter 2 for the quality of carbon materials as chromatographic adsorbents.

3.3 RESULTS AND DISCUSSION

Figures 3.1-3.6, 3.8-3.11, 3.13-3.15 and 3.17 show the effect of Carbowax 1500 on PGC 210 CL. The chromatography on uncoated material (Figures 3.7, 3.12 and 3.16) are included for comparison.

Retention values of ketones (Figures 3.1), alcohols (Figure 3.3) and alkanes (Figure 3.2) sharply decreased at low Carbowax coverages. This effect is due to the decrease in dispersion interactions between the solutes and the PGC surface and the deactivation of chemical and physical heterogeneities by the liquid stationary phase [11,12] which otherwise contribute towards unfavourably long retention and unsymmetrical peaks [10].

The k^1 values of ketones and hydrocarbons show little change between 0.2% Carbowax and the monolayer coverage (2.7%) (Figures 3.1 and 3.2). This could be the result of the analytes interacting with the available carbon surface rather than with the sub monolayer of the liquid stationary phase.

Beyond the monolayer, sudden reductions in the retention values of ketones and hydrocarbons were observed. This may be due to two reasons. Firstly, the polarity of the Carbowax layer on the PGC surface. The hydrophobic analytes (ketones and hydrocarbons) interact to a lesser extent with this stationary phase than with the non-polar PGC surface that was available before the formation

of the monolayer. Secondly, the behaviour of the multimolecular layer of Carbowax on a liquid film. Hydrocarbons and ketones may interact with the hydrophobic parts of PEG. The PEG units in the film may be mobile due to Brownian motion. As a result, the distances between any interacting analytes (ketones or hydrocarbons) and the non-polar parts of the Carbowax would be much greater than those when these analytes were adsorbed on PGC. Consequently, any interactions of ketones and hydrocarbons with the hydrophobic parts of this stationary phase would be much weaker than the association of these solutes with the solid PGC surface.

The peak shape improved (Figures 3.8-3.11, 3.13-3.15 and 3.17) and efficiency of column increased (Figure 3.6) with the introduction of Carbowax on to PGC. This liquid stationary phase eliminated any heterogeneities that can cause peak tailing [3]. Figures 3.6 shows that the efficiency (N) of column initially increased with the increasing Carbowax content on the PGC surface. The column efficiency decreased beyond 0.4% of Carbowax due to the increasing thickness of the liquid stationary phase on PGC. The increasing thickness of the Carbowax layer would have led to an increase in the resistance to mass transfer.

The column containing PGC with 0.2-0.4% Carbowax 1500 should be used in analytical applications since such columns would offer sharper peaks, favourable analysis time and maximum efficiencies. All the heterogeneities on the surfaces of such materials were

covered by the liquid stationary phase. As a result, these solid phases displayed favourable chromatographic properties.

Between 0.4% and monolayer of Carbowax, the efficiency decreased (Figure 3.6), since the surface area was gradually being covered with a liquid film, and at this stage, the solute peaks were beginning to broaden out.

Figure 3.5 shows the variation in ΔH for certain compounds with increasing Carbowax content on PGC. The increase in ΔH at 0.2% of Carbowax 1500 (ln 0.2 = -1.6 in Figure 3.5) was the result of maximum lateral interactions [11] and the evolution of adsorbate-adsorbate energy of cohesion. That is, the solute molecules on PGC interacting with each other to enhance the heat of transfer values. Such an effect can be observed with certain alcohols (Figure 3.3) at a Carbowax coverage of 0.1% (ln 0.1 = -2.3). This effect then diminishes with further additions of Carbowax on to PGC (see Figures 3.3 and 3.5).

The coated PGC displayed the maximum ΔH (Figure 3.5) and retention (Figure 3.3) values of alcohols at the monolayer coverage of Carbowax. This is the result of having the maximum number of OH groups on the PGC surface, at the monolayer coverage. The retention of alcohols tend to diminish beyond this point. Further additions of the liquid stationary phase on to the PGC, fills the pores on the PGC surface, which leads to a reduction in surface

area (Figure 3.4) of PGC, As a result, the concentration of terminal OH groups on the surface diminishes. This in turn would lead to a reduction in the k^1 values of alcohols.

The selectivity of PGC towards some compounds vary with the content of Carbowax 1500 on the PGC surface, and this is indicated by the 'crossing' of the graphs shown in Figure 3.3. The degree of interactions between OH groups on the stationary phase and those of the analytes depends on the arrangement of the groups in the solute molecule. On bare PGC, larger molecules such as 2-methyl, 2-butanol display greater retention values in comparison to other compounds (see Figure 3.3) due to the larger molecules having greater number of contact points on the graphite surface.

The introduction of Carbowax introduces polar character (OH groups) on to the surface. The larger molecules continue to display greater retention times (Figure 3.3) in comparison to other solutes since there may be interactions between the hydrophobic part of the solute and that of the Carbowax. The hydroxyl of the analytes may combine with the OH groups on the surface. Also, the solutes may continue to interact with the bare part of the PGC surface before the monolayer coverage of Carbowax is reached.

The 'crossing over' of 2-methyl, 2-butanol and 2,2-dimethyl, 1-propanol is seen between 0.4 and 0.8% Carbowax (-0.2 and -0.9 on Carbowax scale of Figure 3.3). This may be due to the arrangement

of the groups in the molecule. 2,2-dimethyl, 1-propanol is a primary alcohol, and therefore the OH terminal of molecule can be easily attached to an OH group on the surface. The tertiary alcohol (2-methyl, 2-butanol), may find it rather difficult to attach its hydroxyl to an OH on the surface. Therefore the retention of the primary alcohol would be greater than that of the tertiary alcohol.

A similar explanation can be offered for crossing over between Butanol (a primary alcohol) and 2 me, 2-butanol. Up to the monolayer, the retention of 2 me, 2-butanol is governed by, (a) the adsorption on to PGC, (b) any interactions between hydrophobic parts of the liquid stationary phase and analyte, and (c) the interactions between hydroxyl groups on the surface and those of the analyte molecule. 2-methyl, 2- butanol is a larger molecule than butanol. Therefore this would explain the smaller retention of the latter before the monolayer coverage. The larger the molecule, the greater the interactions with the bare part of the PGC surface, and hence the greater the overall retention.

At the monolayer, the retention values of butanol and 2-methyl, 2-butanol are quite similar. Just after the monolayer coverage of Carbowax, it may be easier for the OH group of primary alcohol to attach itself to an OH group on the surface. Therefore the strength of interaction between the primary alcohol's hydroxyl group and a hydroxyl on the PGC surface is greater than the

association between the OH group of the tertiary alcohol and an OH group on the surface.

These interactions between butanol and the Carbowax coated surface can be much stronger than any association between the Carbowax and the 2-methyl, 2-butanol. As a result, butanol displays an enhanced k^1 value whereas 2,methyl, 2-butanol shows a diminished retention just beyond the monolayer coverage of Carbowax (Figure 3.3).

Figure 3.11 shows the influence of temperature on k^1. Higher temperatures encourage solutes to spend less time on the stationary phase. This effect is therefore indicated by the decrease in k^1 values.

Chromatograms of PGC 219 CEN in Figure 3.18, 3.19 and 3.24(a) show symmetrical peaks, clear separations, low k^1 values and enhanced efficiencies (2570 plates in Figure 3.24(a)) in comparison to other solid phases considered in this work. The efficiency of PGC 219 CEN is similar to those obtained with coated materials. This chromatographic information indicates that the surface of PGC 219 CEN is uniform and homogeneous in comparison to other PGCs mentioned in this chapter. Therefore PGC 219 CEN is ideal for adsorption chromatography.

Uncoated PGC 219 CL (Figure 3.20 and 3.27), PGC 220 CEN (Figure 3.22(b and 3.25) and PGC 222 CEN (Figure 3.23 and 3.28) displayed

unsymmetrical analyte peaks. The retention of solutes on bare PGCs are recorded in Tables 3(ii), 3 (iv) and 3(vi). When PGC 219 CL was coated with a monolayer of Carbowax, the retention of solutes decreased (Tables 3(iii), 3(v) and 3(vii)), the eluate peak shapes improved (Figure 3.21 and 3.29(b)) and efficiency of column increased from 1222 to 1630 plates. Similar results were obtained for PGC 220 CEN (Figures 3.26 and 3.22(a) and Tables 3(iii), 3(v) and 3(vii)) and PGC 222 CEN (Figure 3.24(b) and 3.29(a) and Tables 3(iii), 3(v) and 3(vii)).

Before coating, each PGC displayed different retention characteristics due to the different numbers of heterogeneities on each PGC surface. On coating, the Carbowax covered such defects. Even though the PGCs have been fired (exposed to temperatures in excess of 2500°C) at two different establishments during preparation and the three materials were not prepared at the same time, the batch to batch agreement in solute retention has been achieved after coating each PGC with a monolayer of Carbowax 1500 (Tables 3(iii), 3(v) and 3(vii). These findings lead to the conclusion that PGC materials with identical chromatographic properties can be prepared by coating the bare PGCs with a liquid stationary phase. The separation of 2-methyl,2-buol & butanol (Figure 3.24(b)) can be improved by decreasing the amount of Carbowax on the PGC surface; since the amount of the liquid stationary phase control the number of weak interactions between the solutes and the solid phase. In turn, the amount of liquid phase on PGC would

control the analyte retention. Also, temperature of column may be controlled to obtain improved separations.

Figures 3.30 and 3.31 display two applications of Carbowax coated PGC. Figure 3.30 shows the components found when analysing blood alcohol. An artificial mixture was prepared for this experiment. Favourable analysis times and symmetrical peak shapes were obtained on coated PGC.

Two whisky samples (0.8µl of each) were analysed via gas chromatography using Carbowax coated PGC as the packing material (Figure 3.31). The striking difference between the two brands is that one brand has higher concentrations of certain alcohols than the other.

The components 1 and 2 of the whisky samples (Figure 3.31) may be separated by lowering the amount of Carbowax on the surface. A temperature programmer may be used to improve the overall separation of components. Then the peak 4 would appear to be much sharper and more separated from its neighbours.

3.4 FUTURE WORK

PGC may be coated with the appropriate stationary phase to carry out the following analyses.

(a) Organic pollutants in water [5,10,13] and in air [13,14].

(b) Unsaturated [13], saturated [6,7] and aromatic [15] hydrocarbons.

(c) Glycols and ethylene oxide [13].

(d) Complex mixtures of industrial solvents [13].

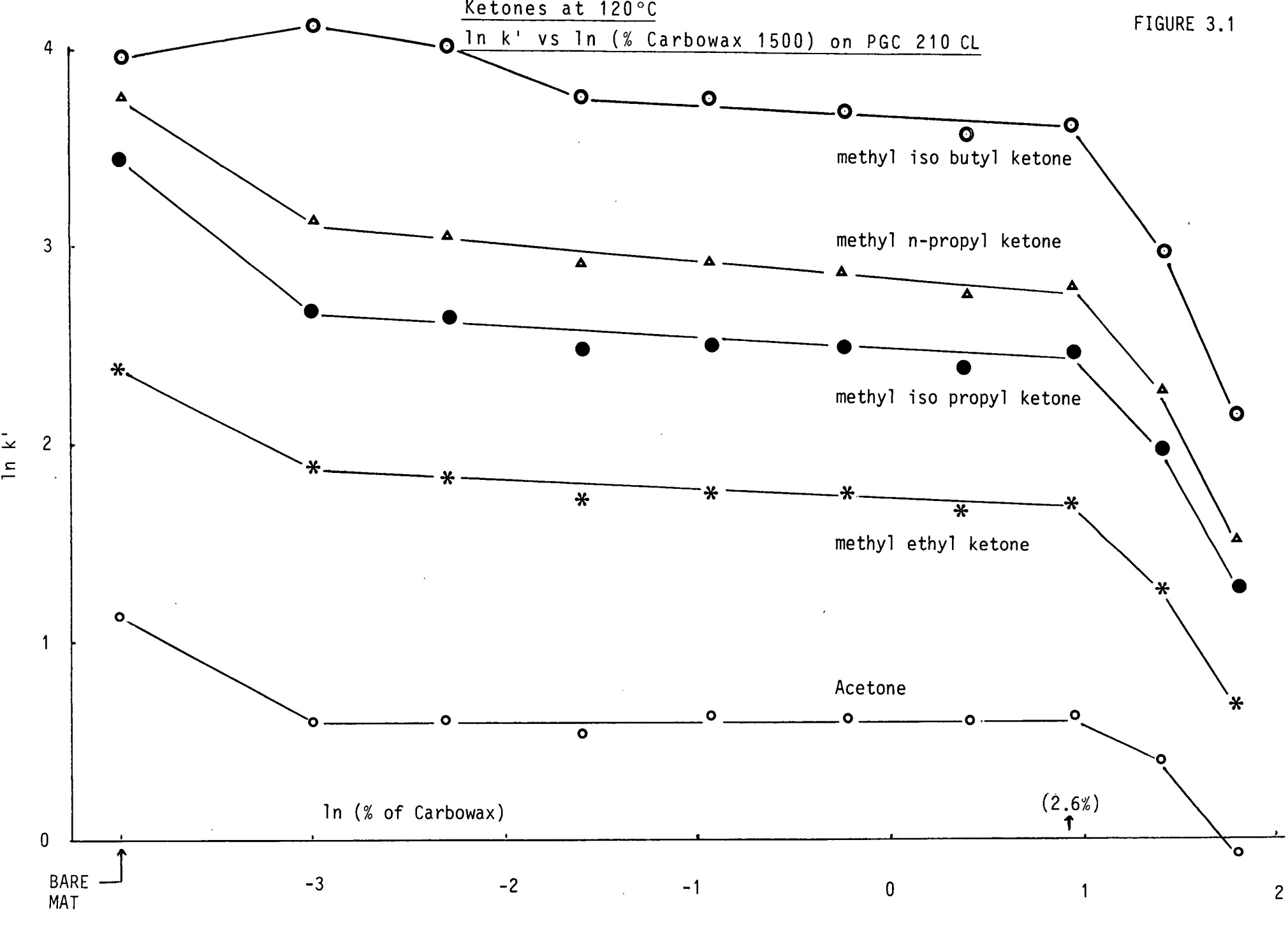
(e) Trace analysis of sulphur gases [9].

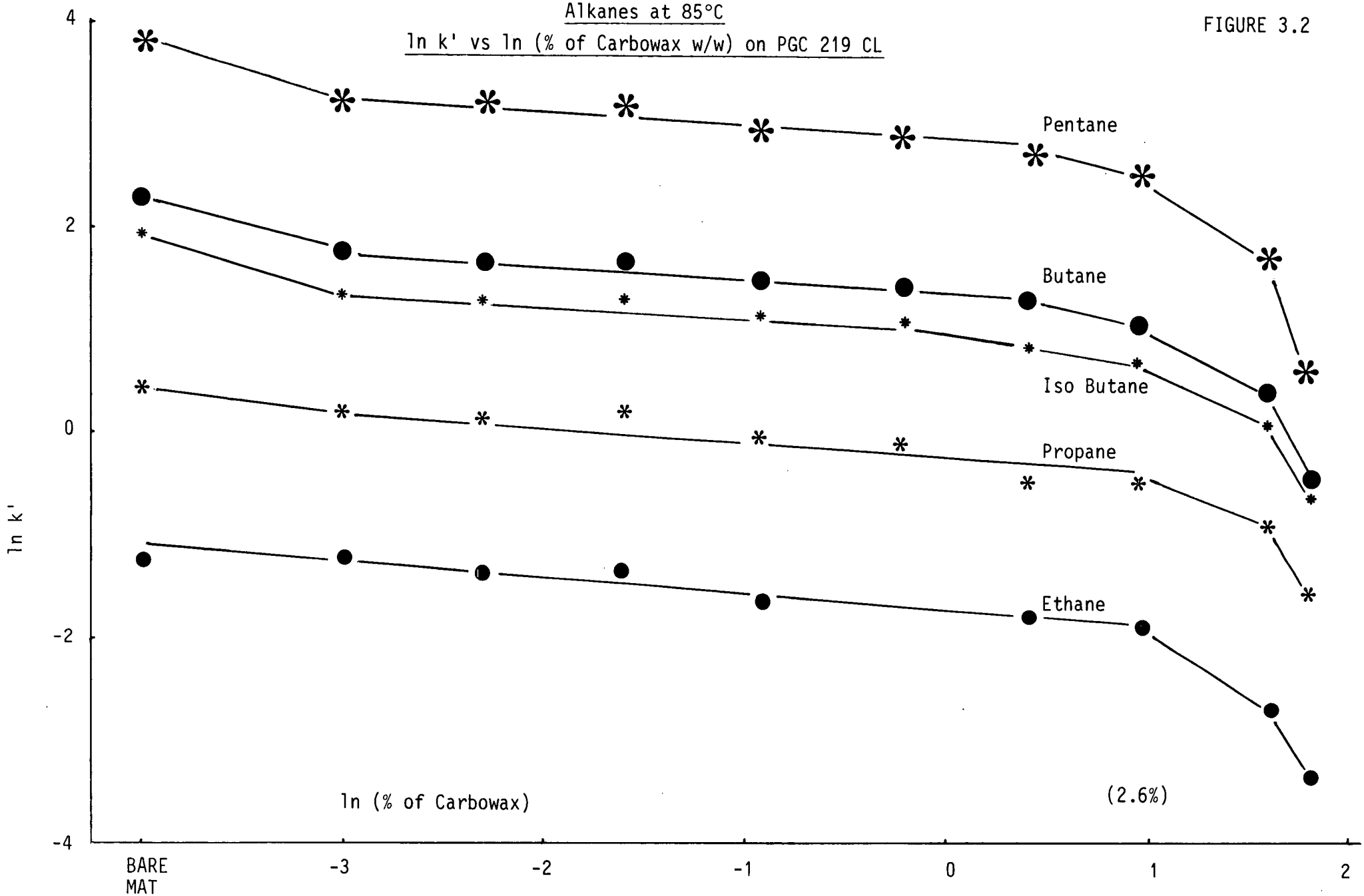
(f) Constituents in alcoholic beverages [8].

The research on PGC may be extended further by obtaining Van Deemter plots, with different particle size ranges, after coating the PGC samples with a constant percentage of a liquid stationary phase. This would give a view to the optimum operating plate heights for coated PGC. Also, the variation in the optimum plate height with particle size can be observed. It may be worth investigating the effect on the optimum mobile phase velocity by varying the mean particle diameter of PGC at a constant optimum value of H. In this case, the amount of liquid stationary phase on PGC, must be kept constant.

The above mentioned research has been carried out on GCB [5, 6-10, 13-15]. Comparisons may be possible between the two packing materials on efficiencies, analysis times and shape of peaks.

FIGURE 3.1


Ketones at 120°C
ln k' vs ln (% Carbowax 1500) on PGC 210 CL
methyl iso butyl ketone
methyl n-propyl ketone
methyl iso propyl ketone
methyl ethyl ketone
Acetone
ln k'
ln (% of Carbowax)
(2.6%)
BARE MAT
4
3
2
1
0
-3
-2
-1
0
1
2


Alkanes at 85°C
ln k' vs ln (% of Carbowax w/w) on PGC 219 CL
FIGURE 3.2
Pentane
Butane
Iso Butane
Propane
Ethane
ln k'
ln (% of Carbowax)
(2.6%)
4
2
0
-2
-4
BARE MAT
-3
-2
-1
0
1
2

Alcohols at 100°C

FIGURE 3.3

ln k' vs ln (% of Carbowax) on Surface of PGC 210 CL

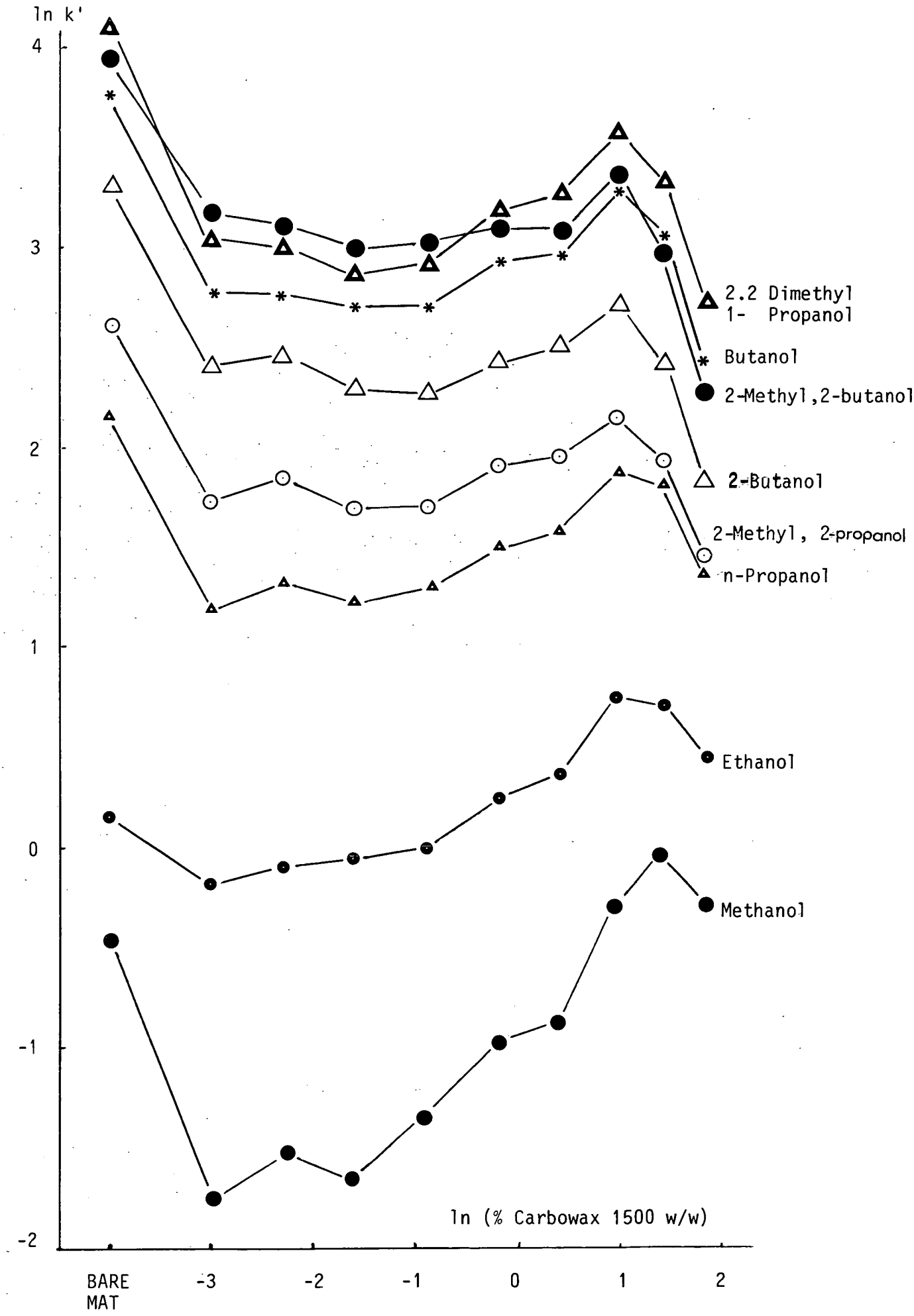


FIGURE 3.4

Variation of Surface Area of PGC 210 CL with different amounts of Carbowax on the PGC Surface

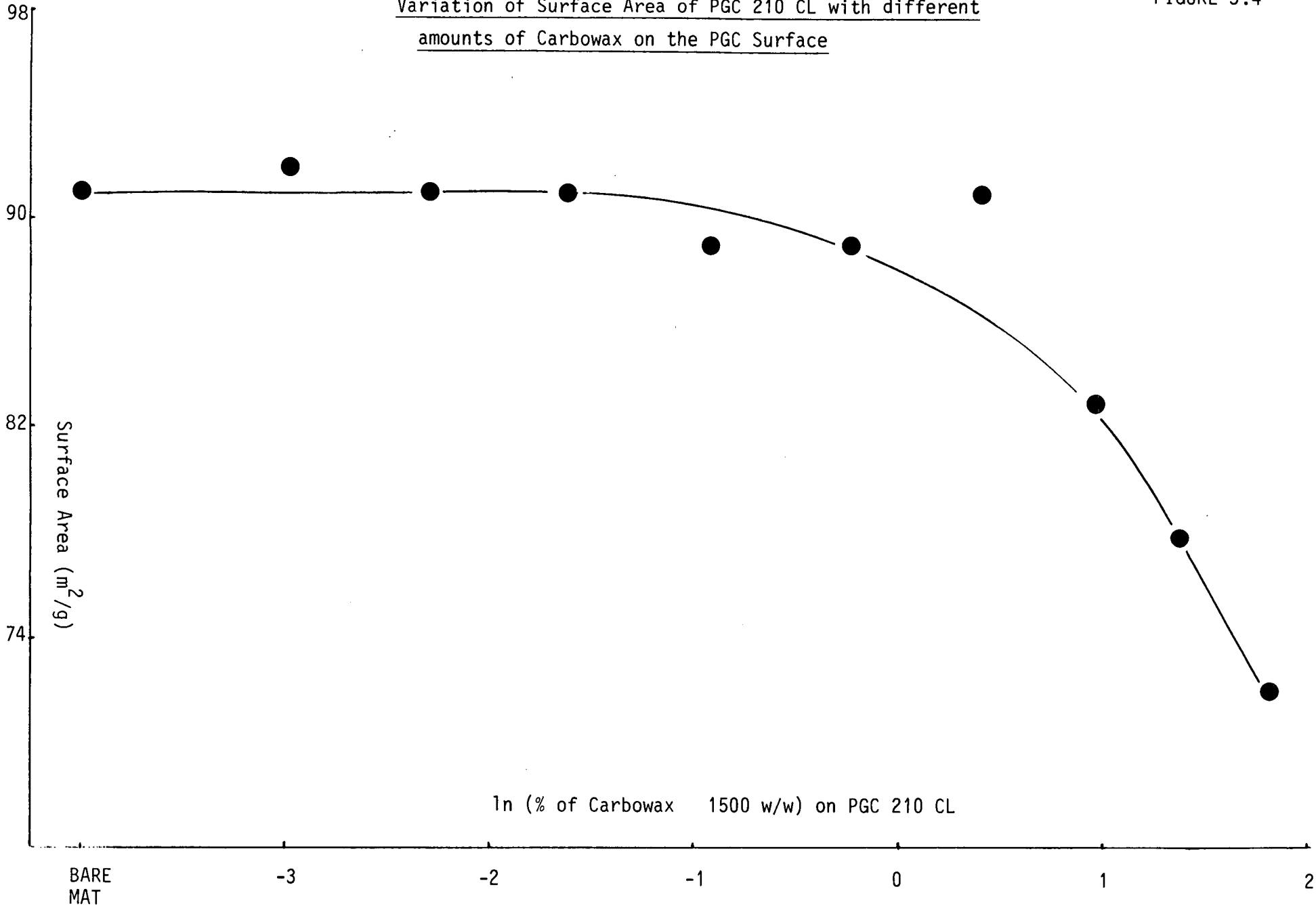


FIGURE 3.5

ΔH vs % of Carbowax on PGC 210 CL

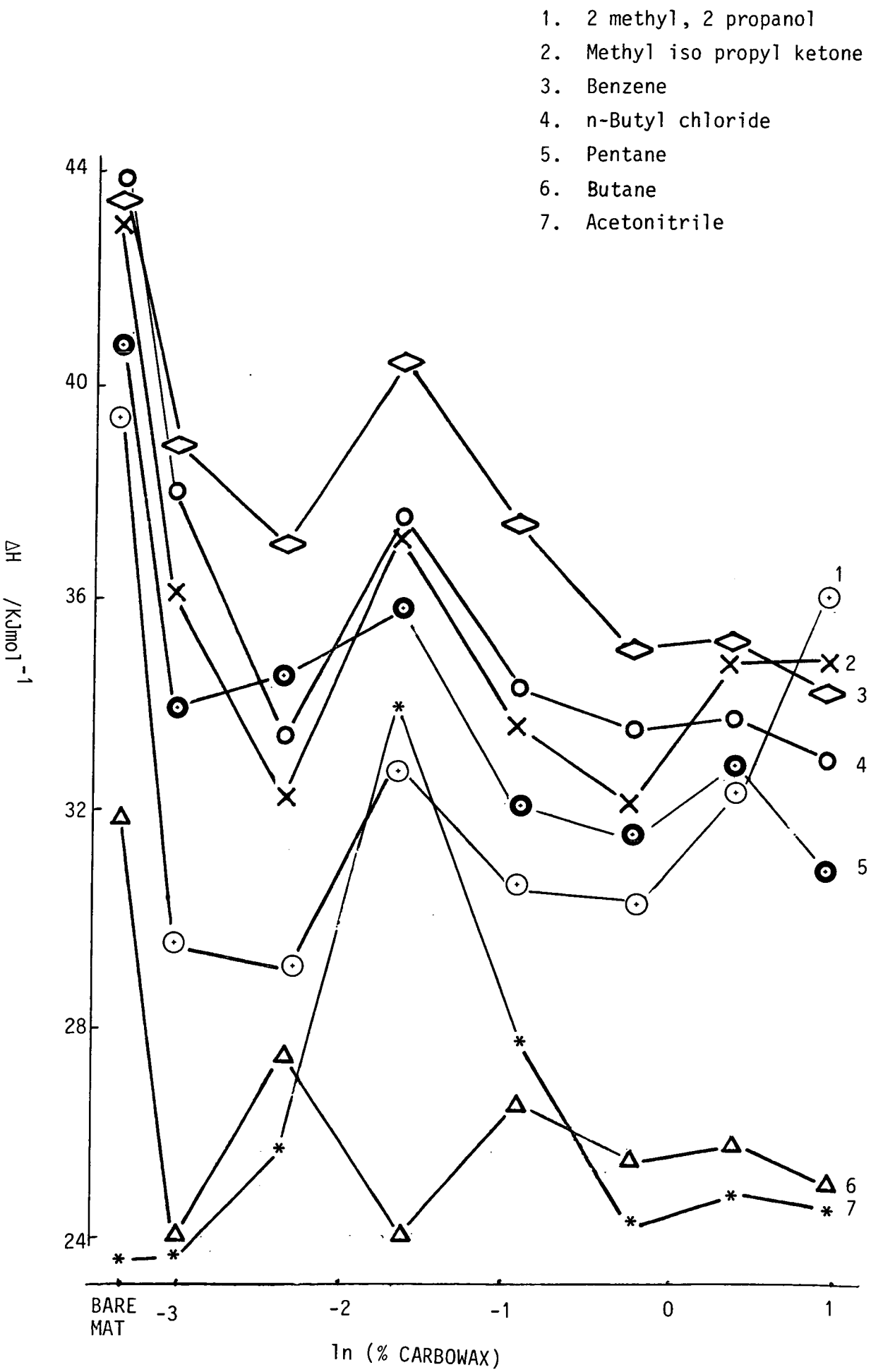
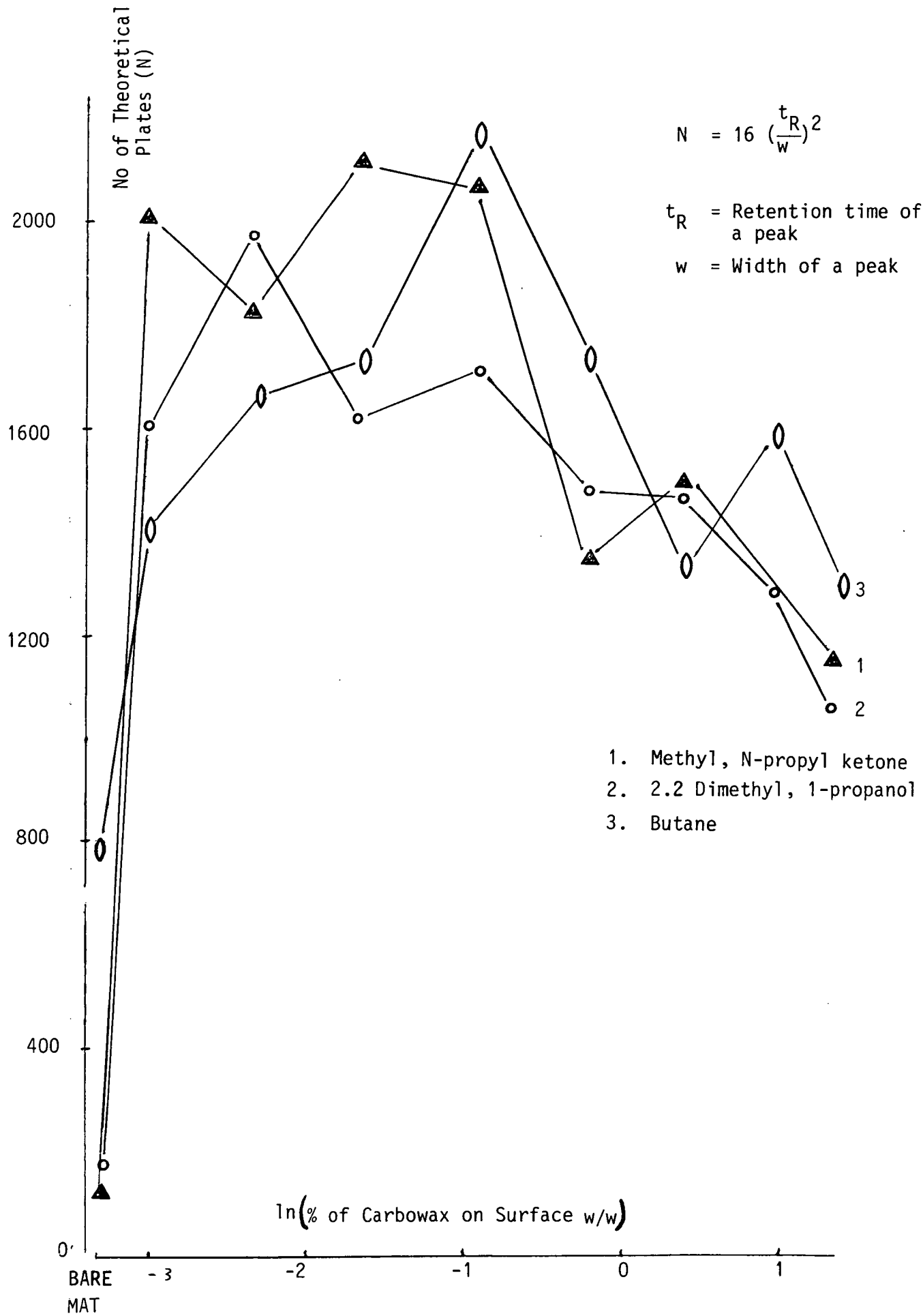


FIGURE 3.6

Number of Theoretical plates of Columns

vs

% of Carbowax on PGC 210 CL



Ketones at 120C on PGC 210 CL

FIGURE 3.7

1. Acetone
2. Methyl Ethyl Ketone
3. Methyl Iso-propyl Ketone
4. Methyl n-propyl Ketone
5. Methyl Iso-butyl Ketone (permantly retained)

Carrier gas pressure= 11 psi

Chart speed= 0.5 cm/min

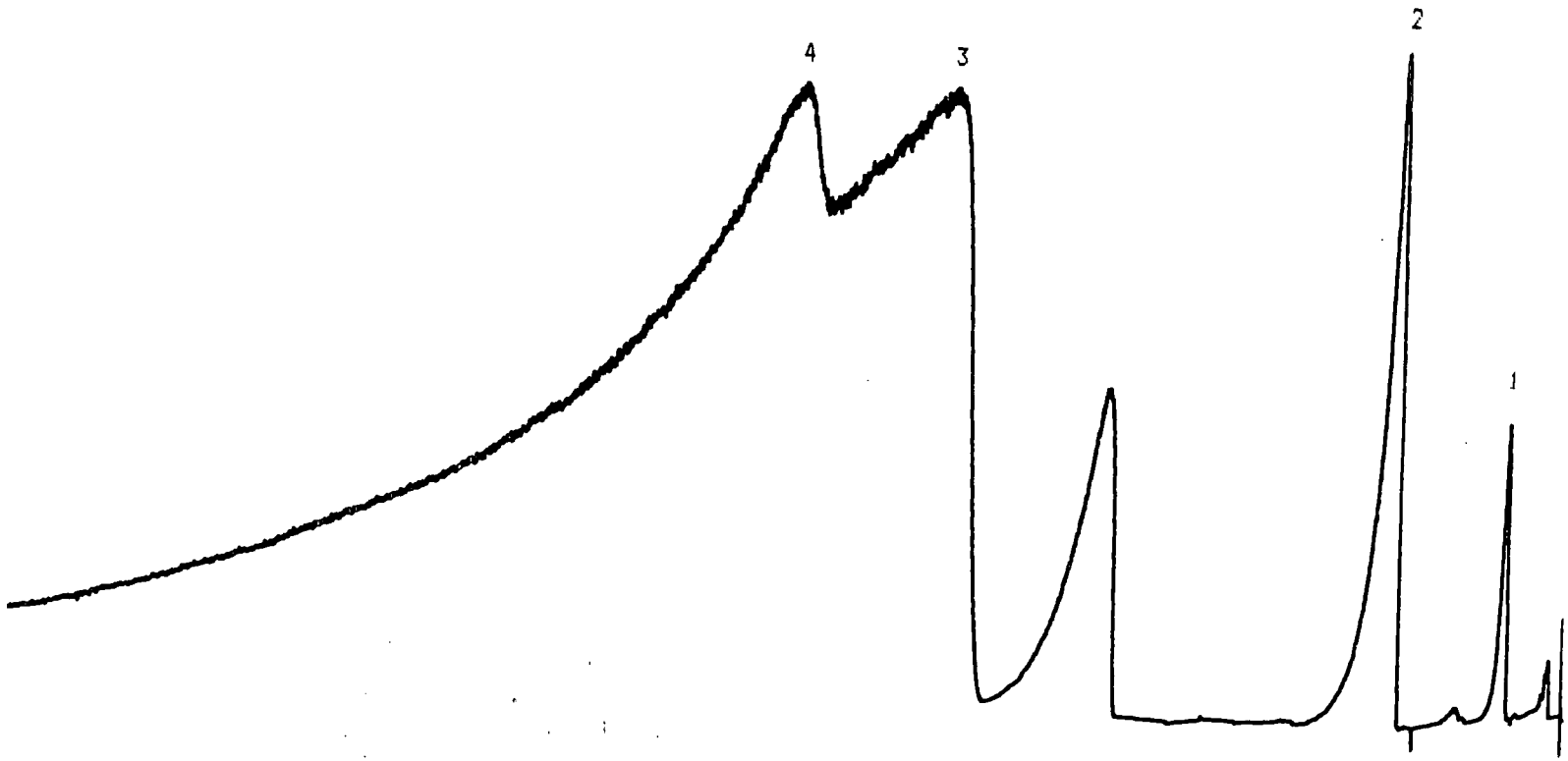


FIGURE 3.8

Ketones at 120C on PGC 210 CL with 0.4% w/w Carbowax 1500.

1. Acetone
2. Methyl Ethyl Ketone
3. Methyl Iso-propyl Ketone
4. Methyl n-proply Ketone
5. Methyl Iso-butyl Ketone

Carrier gas pressure= 11 psi.

Chart speed= 0.5 cm/min.

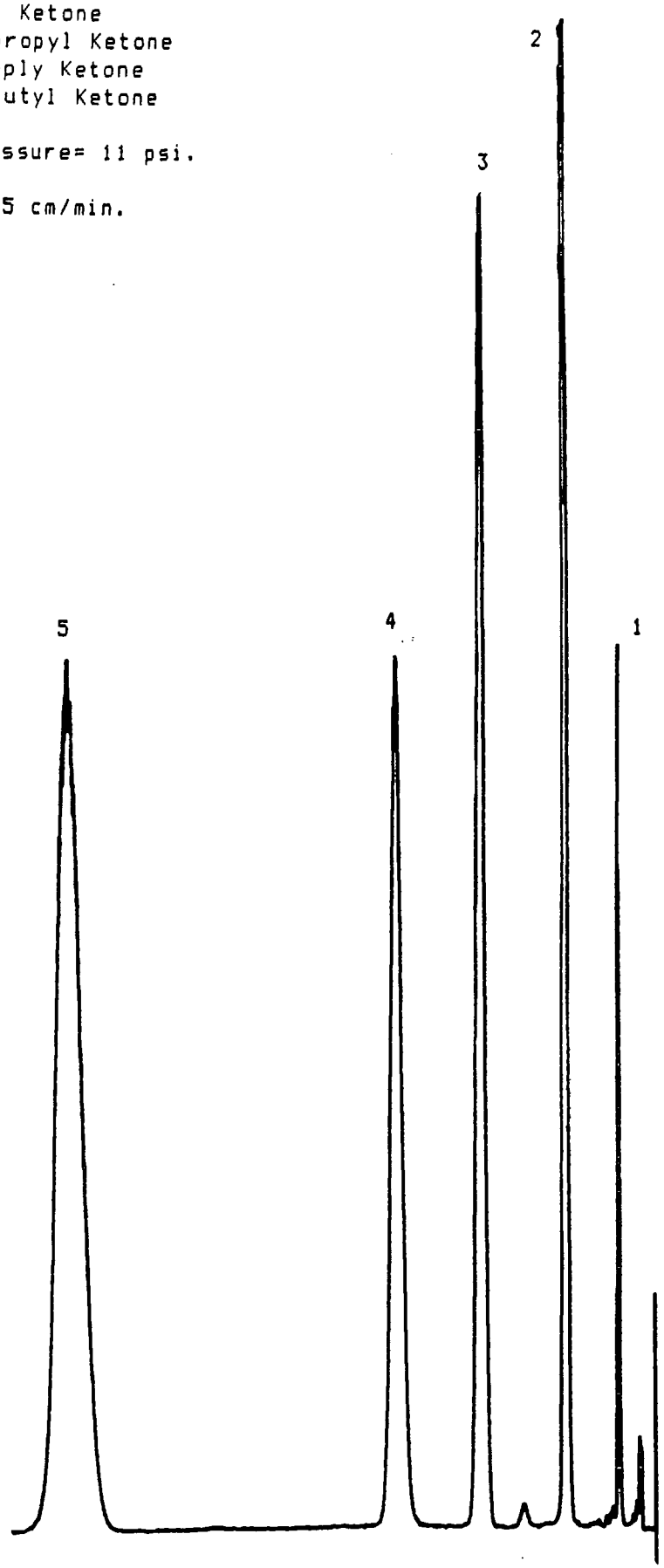


FIGURE 3.9

Ketones at 100C on PGC 210 CL with 0.8% w/w Carbowax 1500

1. Acetone
2. Methyl Ethyl Ketone
3. Methyl Iso-propyl Ketone
4. Methyl n-propyl Ketone
5. Methyl Iso-butyl Ketone

Carrier gas pressure= 11 psi

Chart speed= 0.5 cm/min

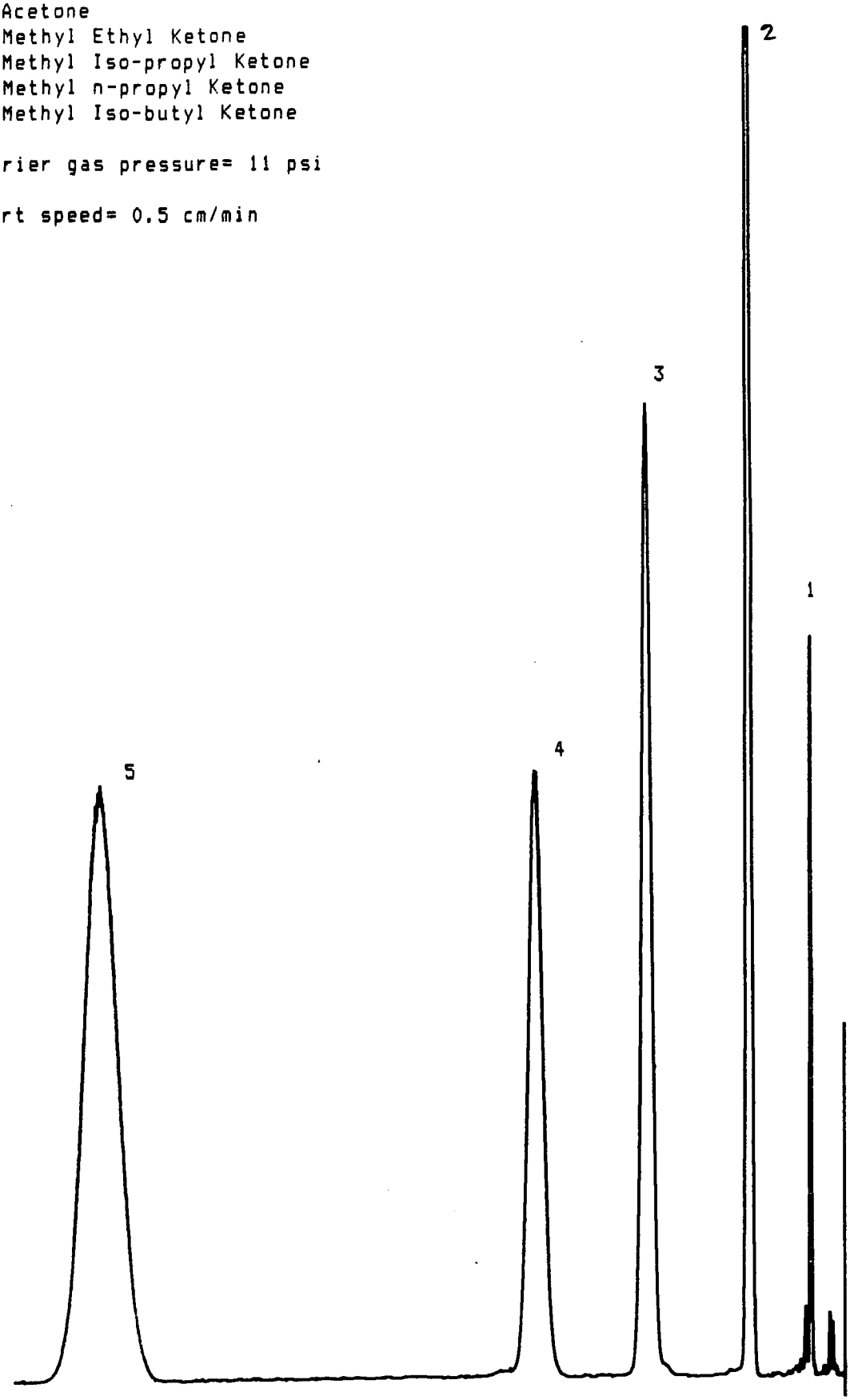


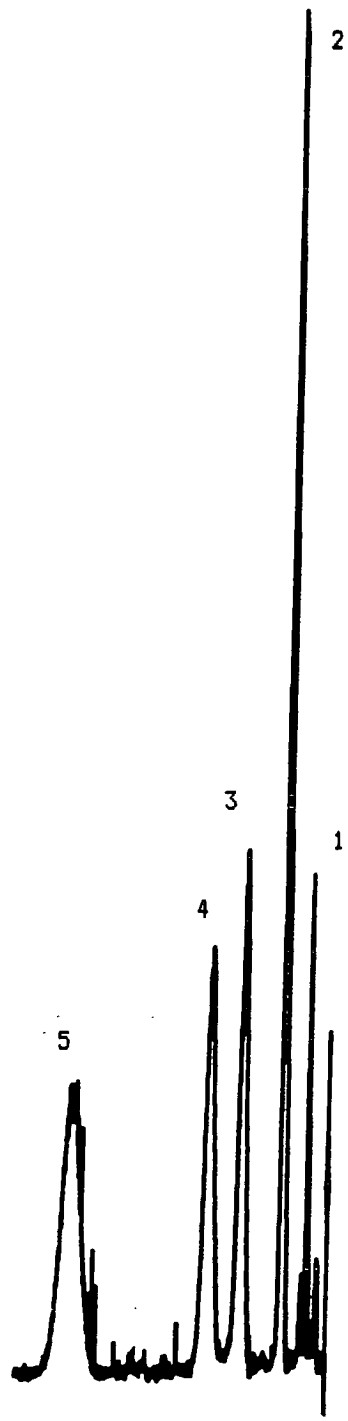
FIGURE 3.10

Ketones at 120C on PGC 220 CEN with 2.8% w/w Carbowax 1500

1. Acetone
2. Methyl Ethyl Ketone
3. Methyl Iso-propyl Ketone
4. Methyl n-proply Ketone
5. Methyl Iso-butyl Ketone

Carrier gas pressure= 11 psi.

Chart speed= 0.5 cm/min.



Ketones at 120C and 100C on PGC 210 CL with 6% w/w Carbowax 1500.

FIGURE 3.11

1. Acetone
2. Methyl Ethyl Ketone
3. Methyl Iso-propyl Ketone
4. Methyl n-proply Ketone
5. Methyl Iso-butyl Ketone

Carrier gas pressure= 11 psi.

Chart speed= 0.5 cm/min.

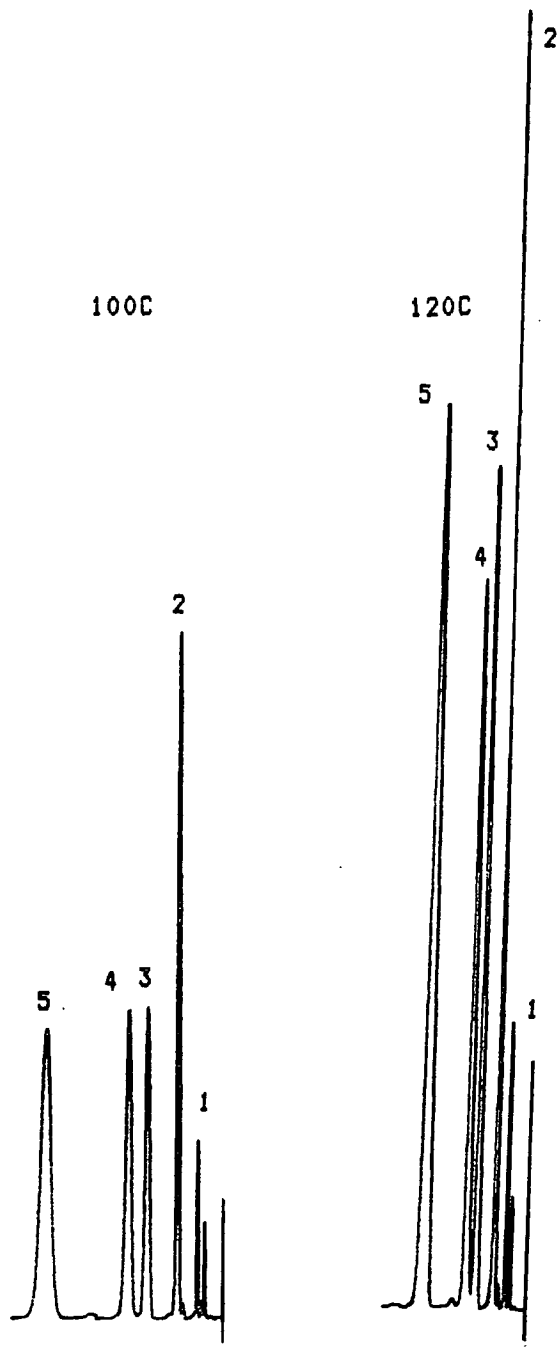


FIGURE 3.12

Alcohols at 100C PGC 210 CL.

1. Methanol
2. Ethanol
3. n-Propanol
4. 2- Methyl, 2- propanol
5. 2- Butanol
6. Butanol
7. 2-Methyl, 2- Butanol
8. 2,2- Dimethyl, 1- propanol

Carrier gas (Nitrogen) Pressure= 11 psi

Chart speed= 0.5 cm/min.

1ul of mixture, 1/8"x1m column, 105-210u mesh.

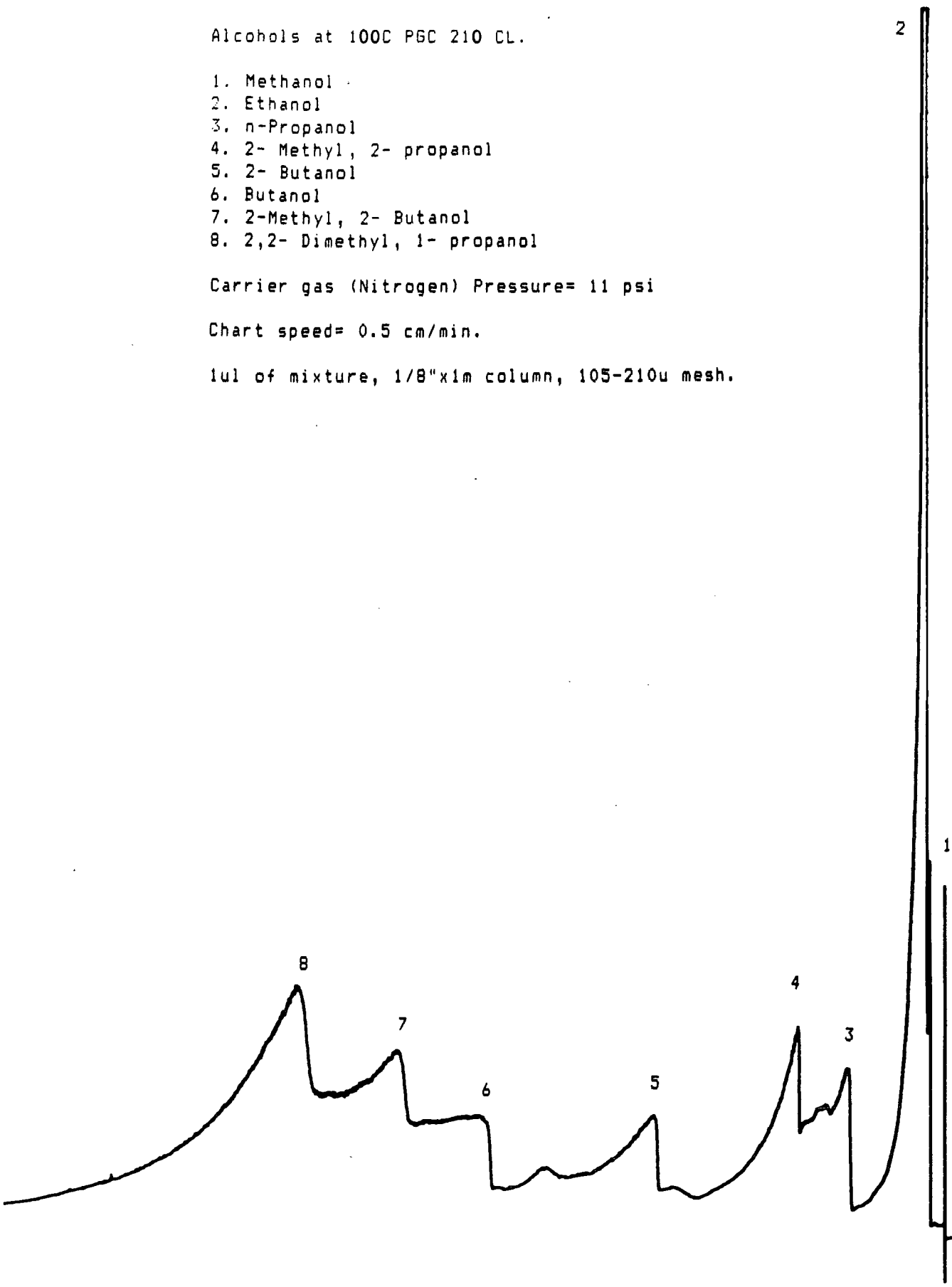


FIGURE 3.13

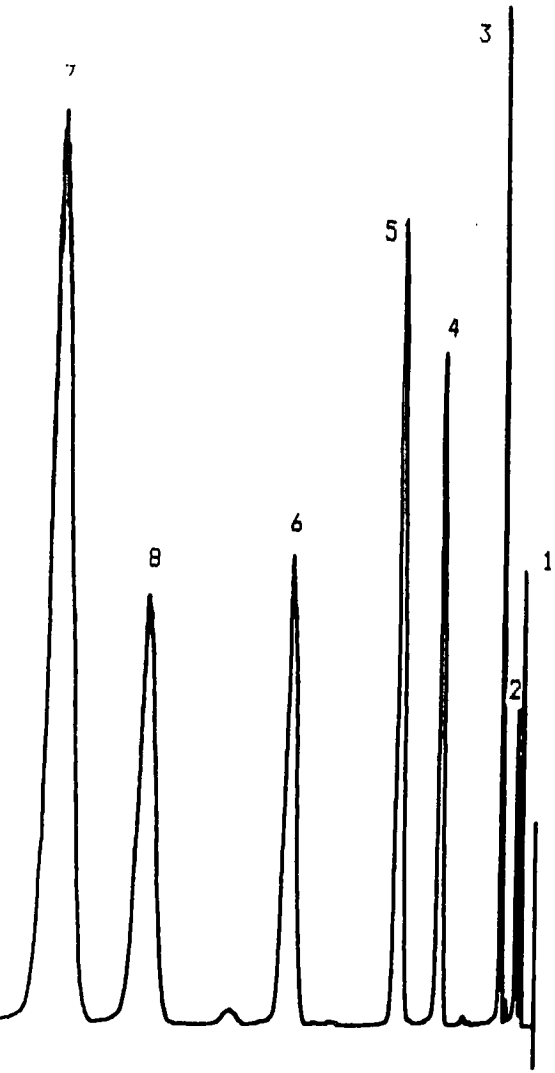
Alcohols at 85C on PGC 210 CL.

1. Methanol
2. Ethanol
3. n-Propanol
4. 2- Methyl, 2-propanol
5. 2- Butanol
6. Butanol
7. 2- Methyl, 2- butanol
8. 2,2- Dimethyl, 1- propanol.

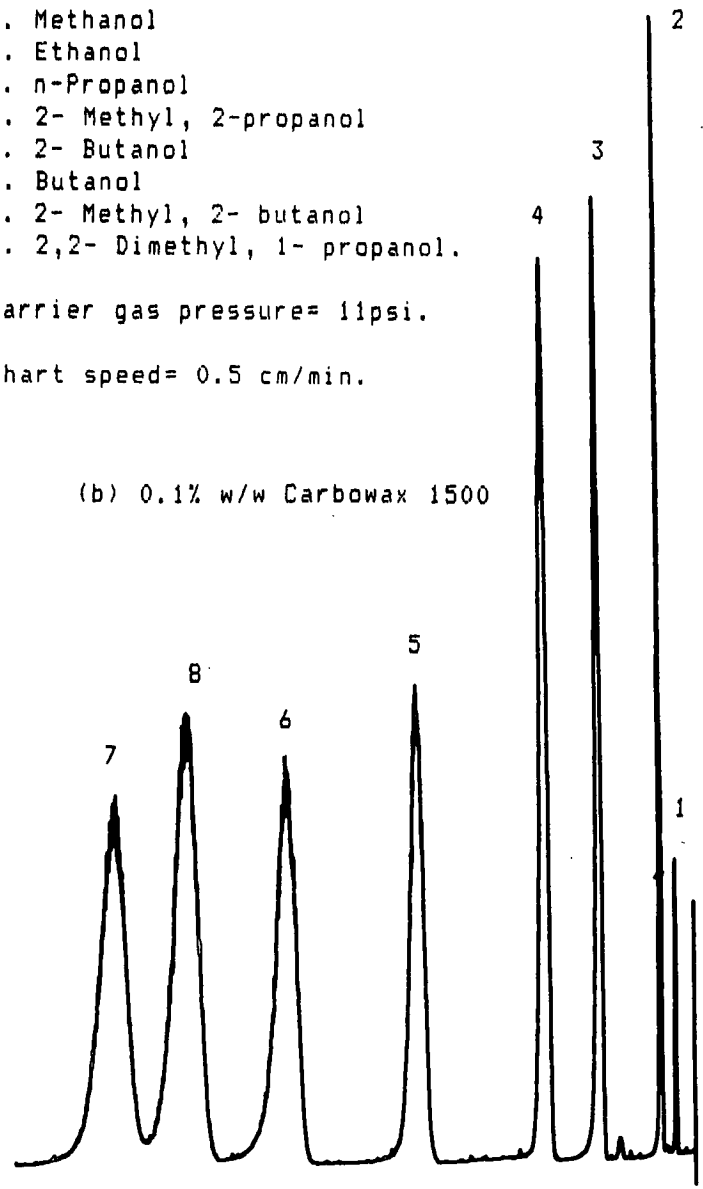
Carrier gas pressure= 11psi.

Chart speed= 0.5 cm/min.

(a) 0.4% w/w Carbowax 1500,



(b) 0.1% w/w Carbowax 1500



(c) 0.05% w/w Carbowax 1500

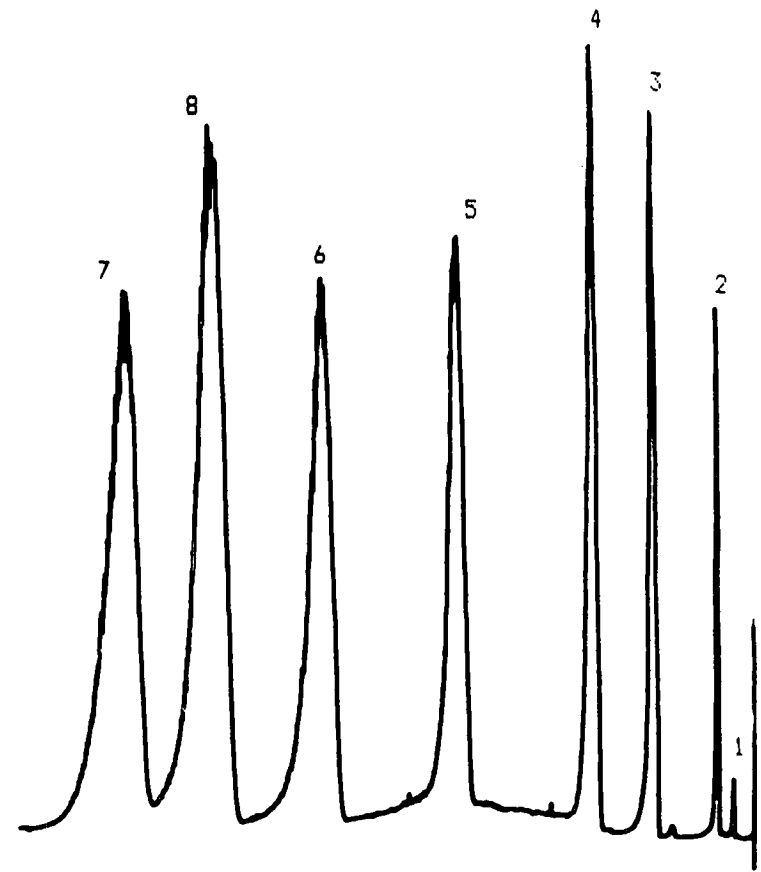


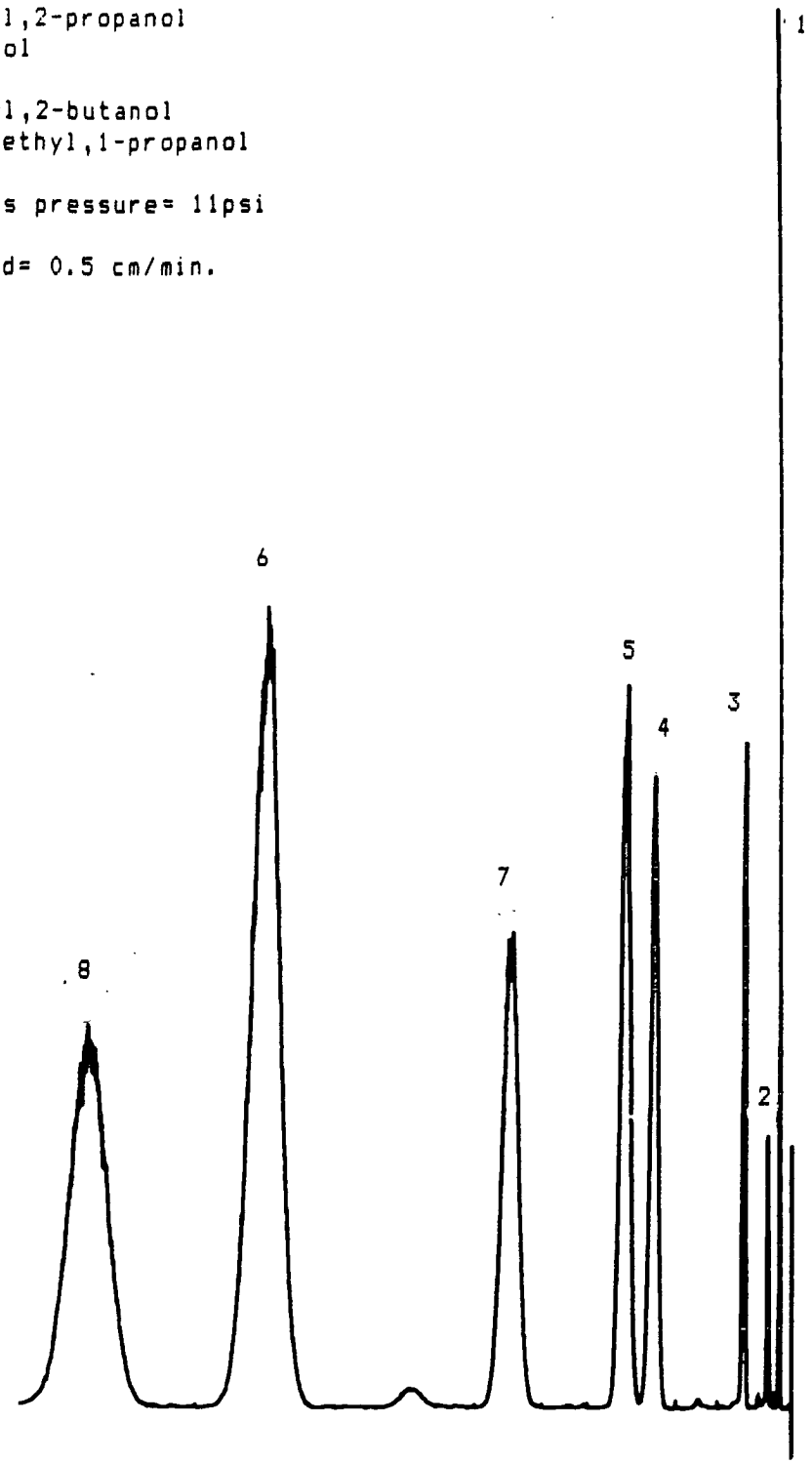
FIGURE 3.14

Alcohols at 85C on PGC 210 CL with 2.7% w/w Carbowax 1500.

1. Methanol
2. Ethanol
3. n-Propanol
4. 2-Methyl,2-propanol
5. 2-Butanol
6. Butanol
7. 2-Methyl,2-butanol
8. 2,2-Dimethyl,1-propanol

Carrier gas pressure= 11psi

Chart speed= 0.5 cm/min.



Alcohols at 100C. PGC 210 CL.

FIGURE 3.15

1. Methanol
2. Ethanol
3. n-Propanol
4. 2- Methyl, 2- propanol
5. 2- Butanol
6. Butanol
7. 2- Methyl 2- butanol
8. 2,2- Dimethyl 1- propanol
9. Pentanol

Carrier gas pressure= 11 psi

Chart speed= 0.5 cm/min.

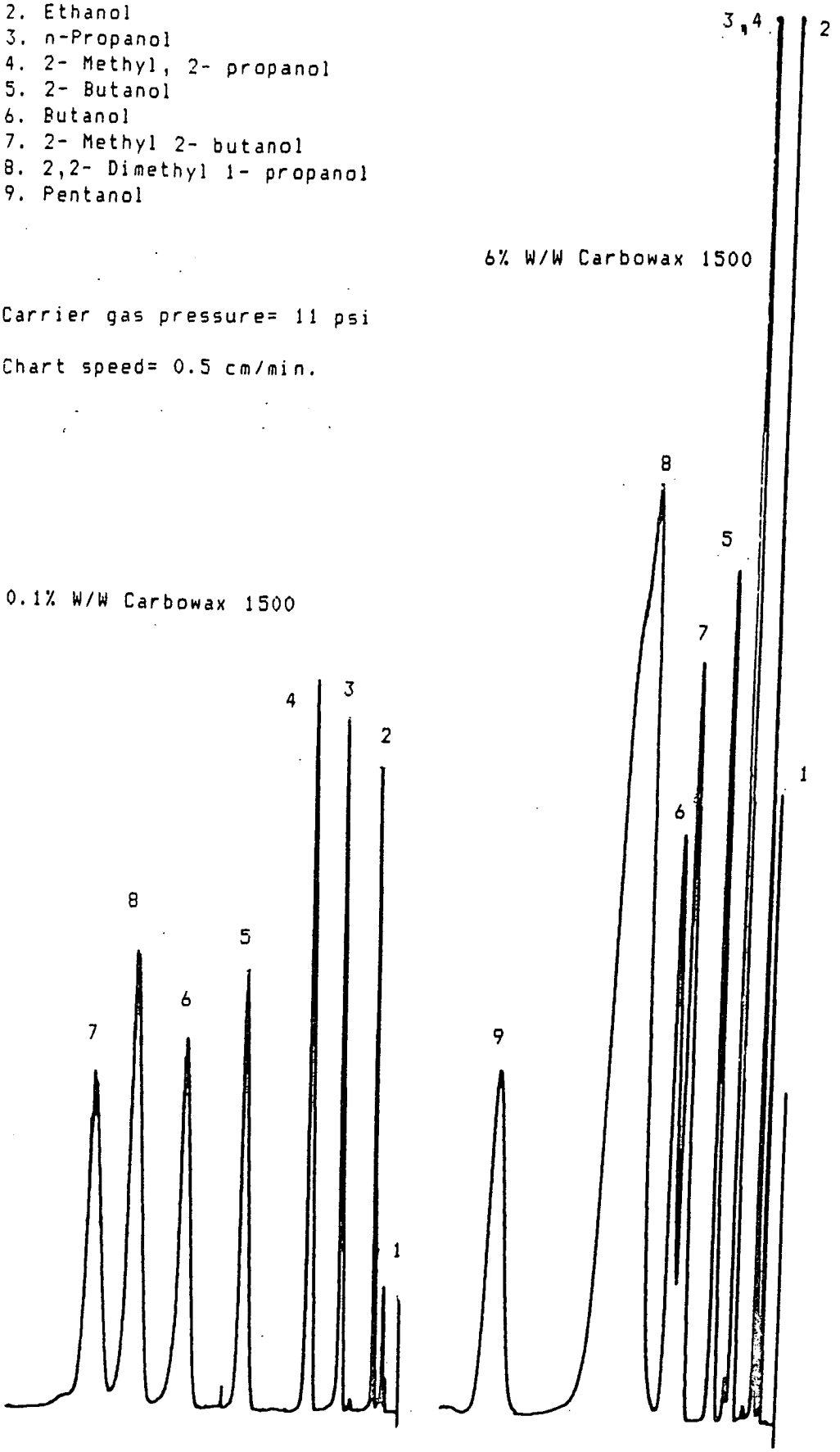


FIGURE 3.16

Hydrocarbons at 85C on PGC 210 CL.

1. Methane
2. Ethane
3. Propane
4. Iso butane
5. Butane
6. Pentane

Carrier gas pressure= 11 psi

Chart speed= 0.5 cm/min

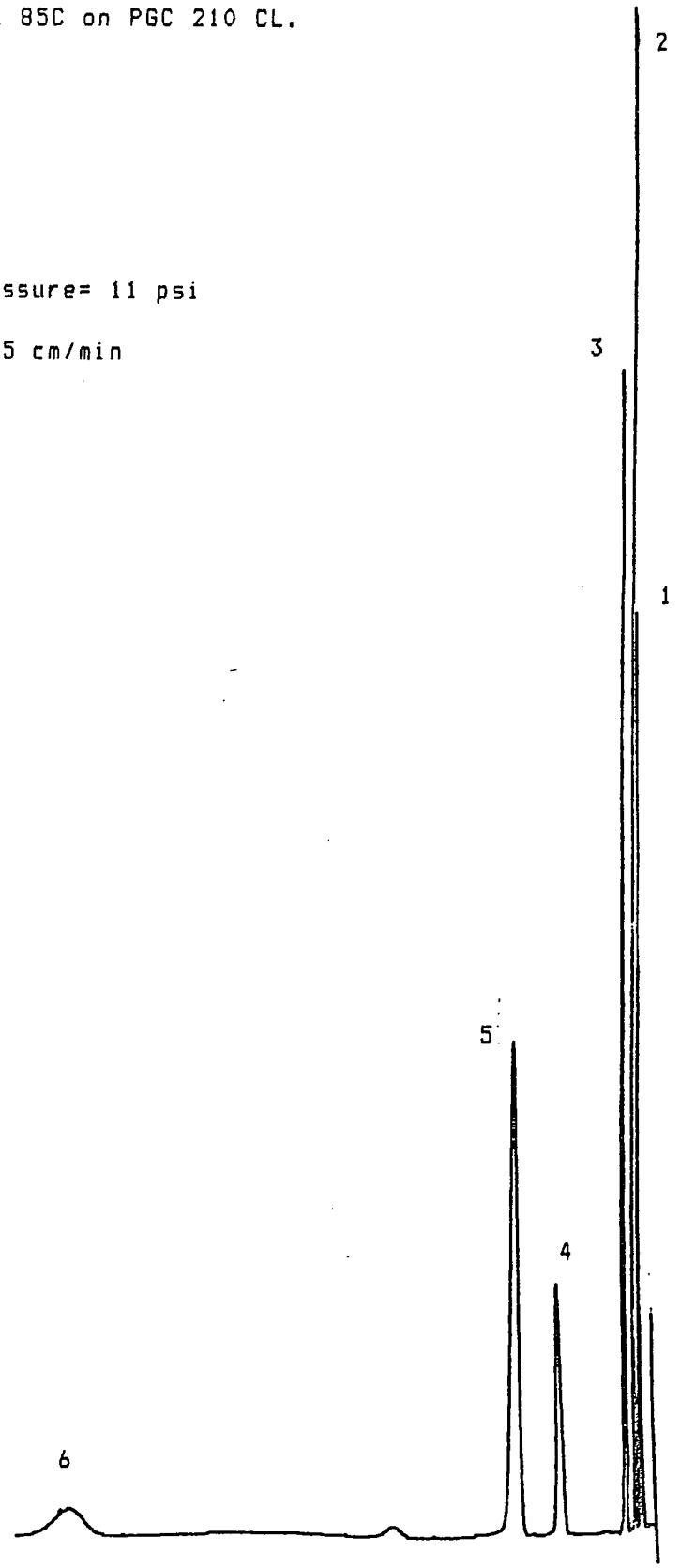


FIGURE 3.17

Hydrocarbons at 85C on PGC 210 CL with 2.7% w/w Carbowax 1500

1. Methane
2. Ethane
3. Propane
4. Iso butane
5. Butane
6. Pentane

Carrier gas pressure= 11 psi

Chart speed= 0.5 cm/min

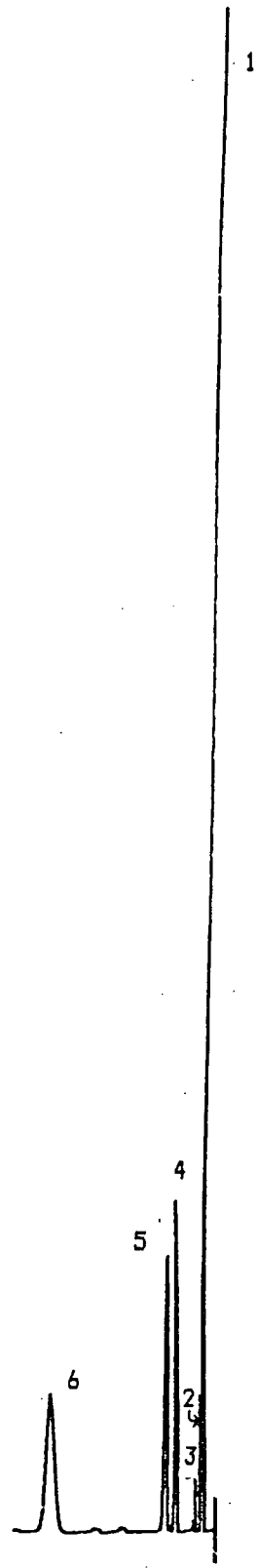


FIGURE 3.18

Ketones at 120C on PGC 219 CEN.

1. Acetone
2. Methyl Ethyl Ketone
3. Methyl Iso-propyl Ketone
4. Methyl n-proply Ketone
5. Methyl Iso-butyl Ketone

Carrier gas pressure= 11 psi.

Chart speed= 0.5 cm/min.

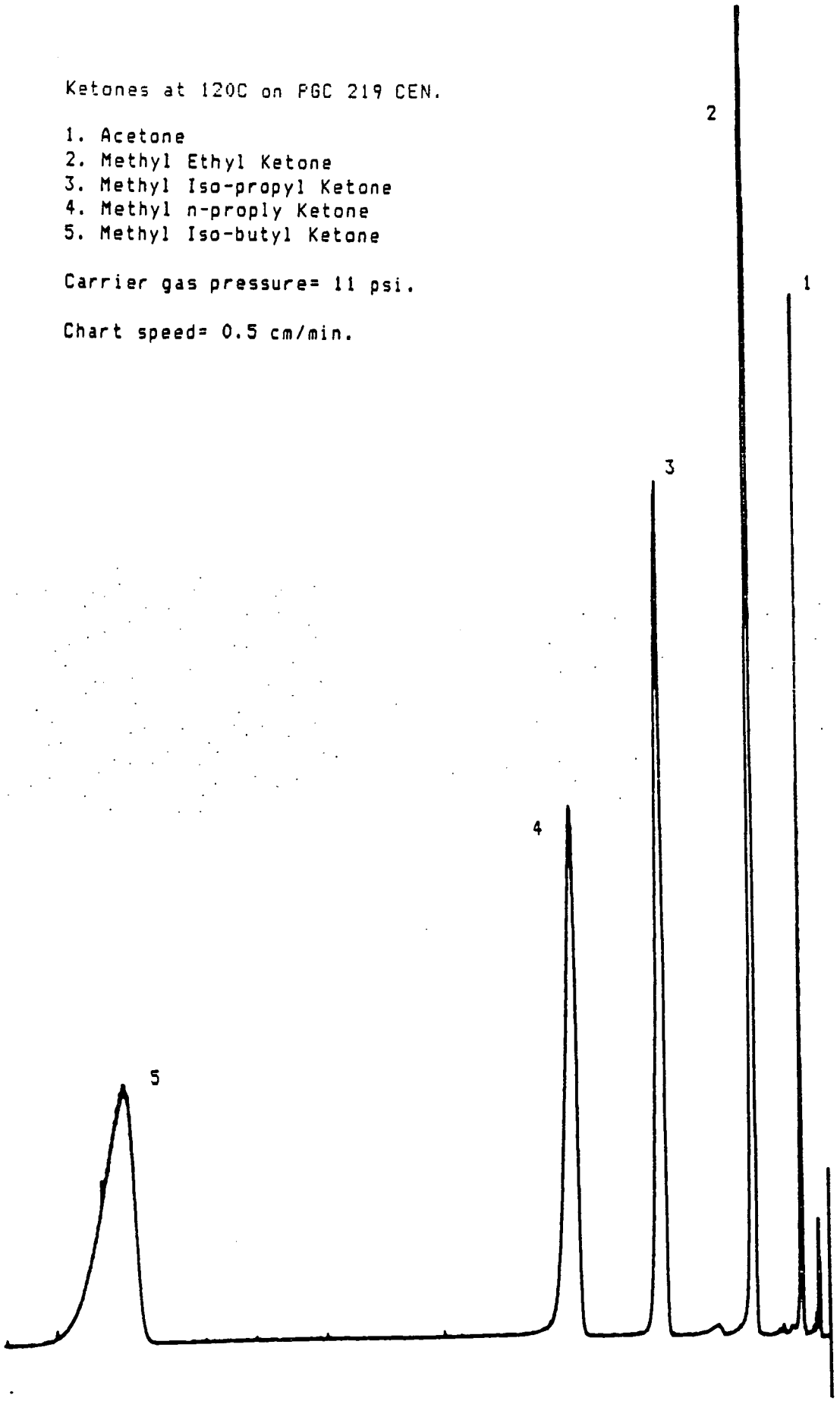


FIGURE 3.19

Hydrocarbons at 85C on PGC 219 CEN

1. Methane
2. Ethane
3. Propane
4. Iso butane
5. Butane
6. Pentane

Carrier gas pressure= 11 psi

Chart speed= 0.5 cm/min

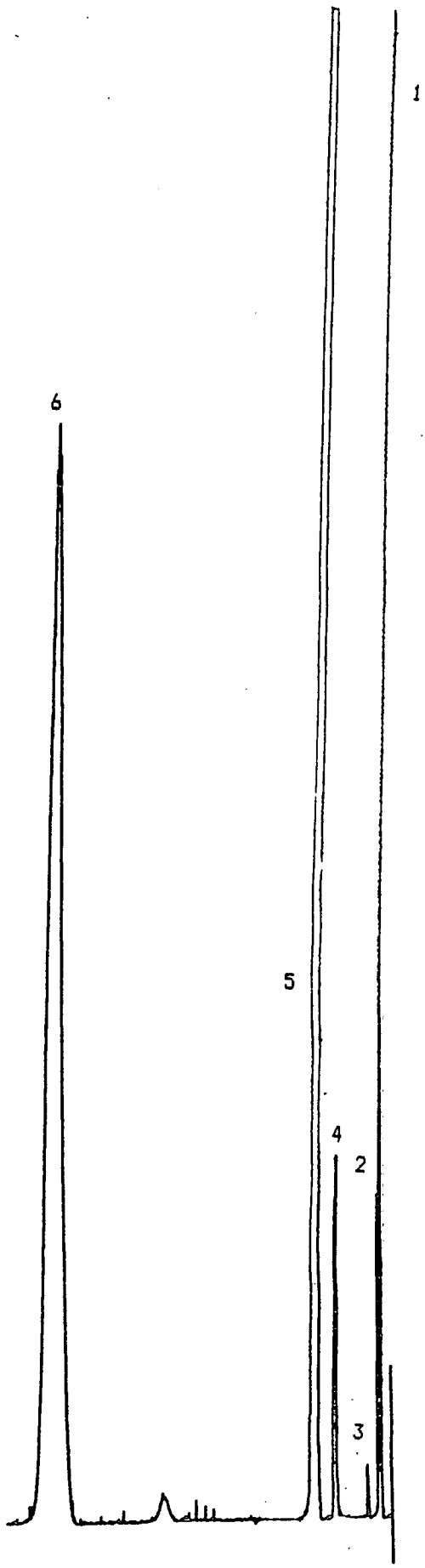


FIGURE 3.20

Alcohols at 100C on PGC 219 CL.

1. Methanol
2. Ethanol
3. n-Propanol
4. 2- Methyl, 2-propanol
5. 2- Butanol
6. Butanol
7. 2- Methyl, 2- butanol
8. 2,2- Dimethyl, 1- propanol.

Carrier gas pressure= 11psi.

Chart speed= 0.5 cm/min.

Efficiency of column= 1222 plates.

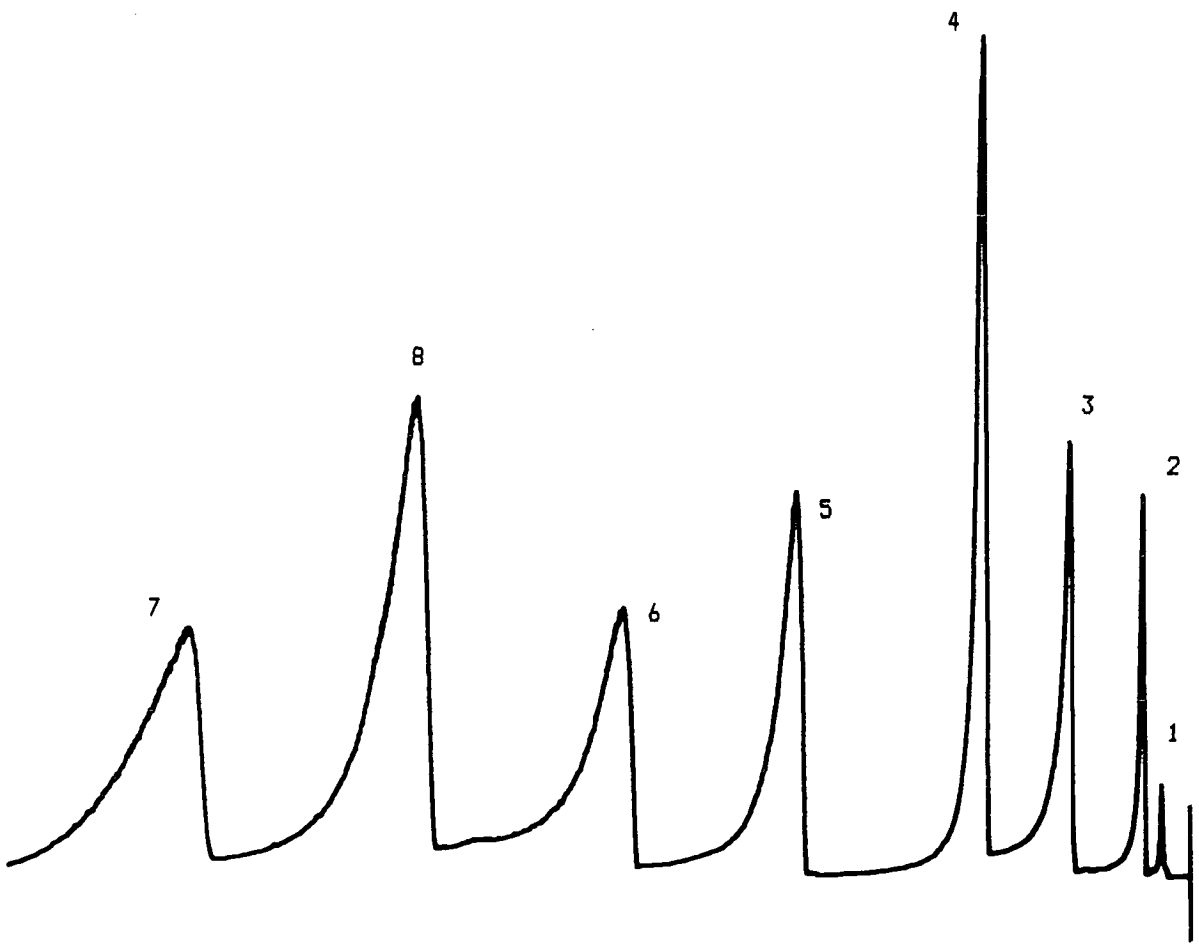


FIGURE 3.21

Alcohols at 100C. PGC 219 CL with 2.5% w/w of Carbowax 1500.

1. Methanol
2. Ethanol
3. n-Propanol
4. 2- Methyl, 2- propanol
5. 2- Butanol
6. Butanol
7. 2- Methyl, 2- butanol
8. 2,2- Dimethyl, 1- propanol

Carrier gas pressure= 11psi

Chart speed= 0.5 cm/min.

Efficiency of column= 1630 plates.

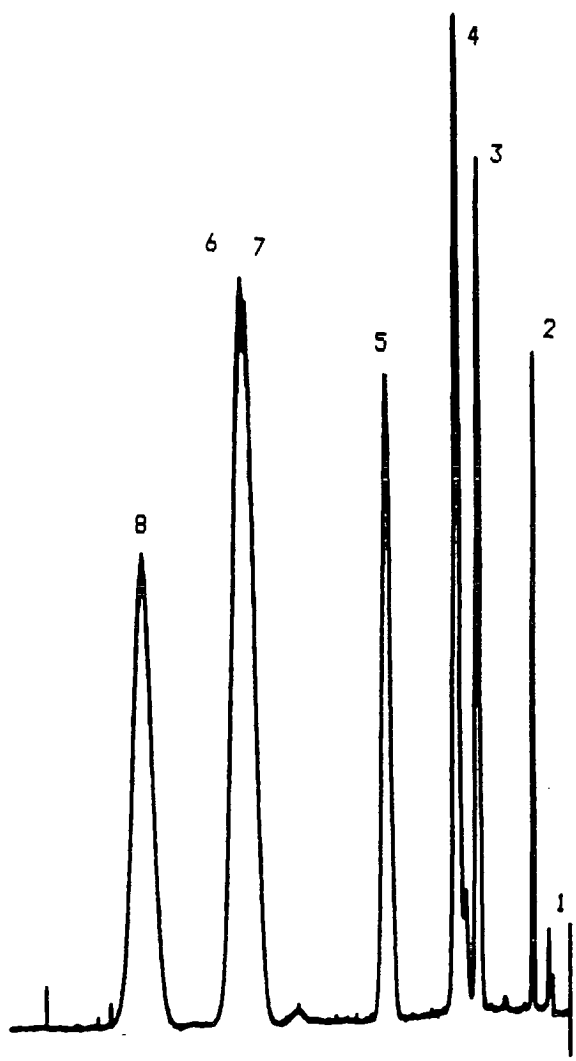


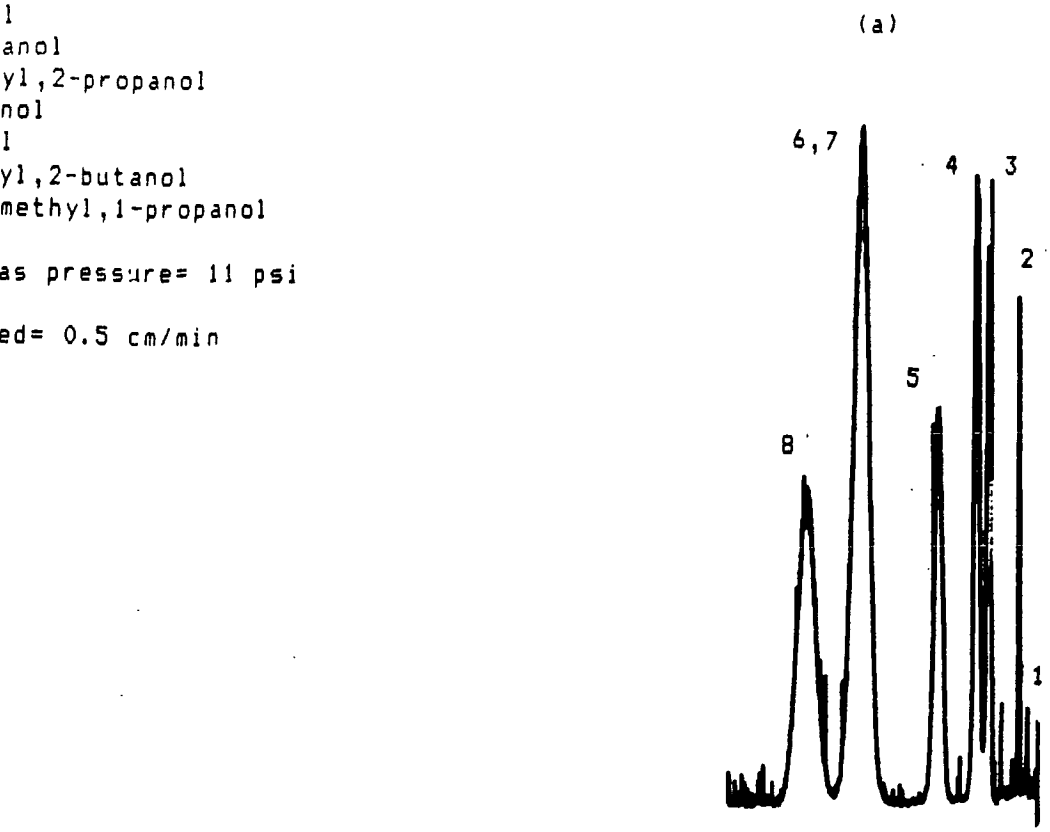
FIGURE 3.22

Alcohols at 100C on (a) PGC 220 CEN with 2.8% w/w Carbowax 1500 (b) PGC 220 CEN.

1. Methanol
2. Ethanol
3. n-Propanol
4. 2-Methyl,2-propanol
5. 2-Butanol
6. Butanol
7. 2-Methyl,2-butanol
8. 2,2-Dimethyl,1-propanol

Carrier gas pressure= 11 psi

Chart speed= 0.5 cm/min



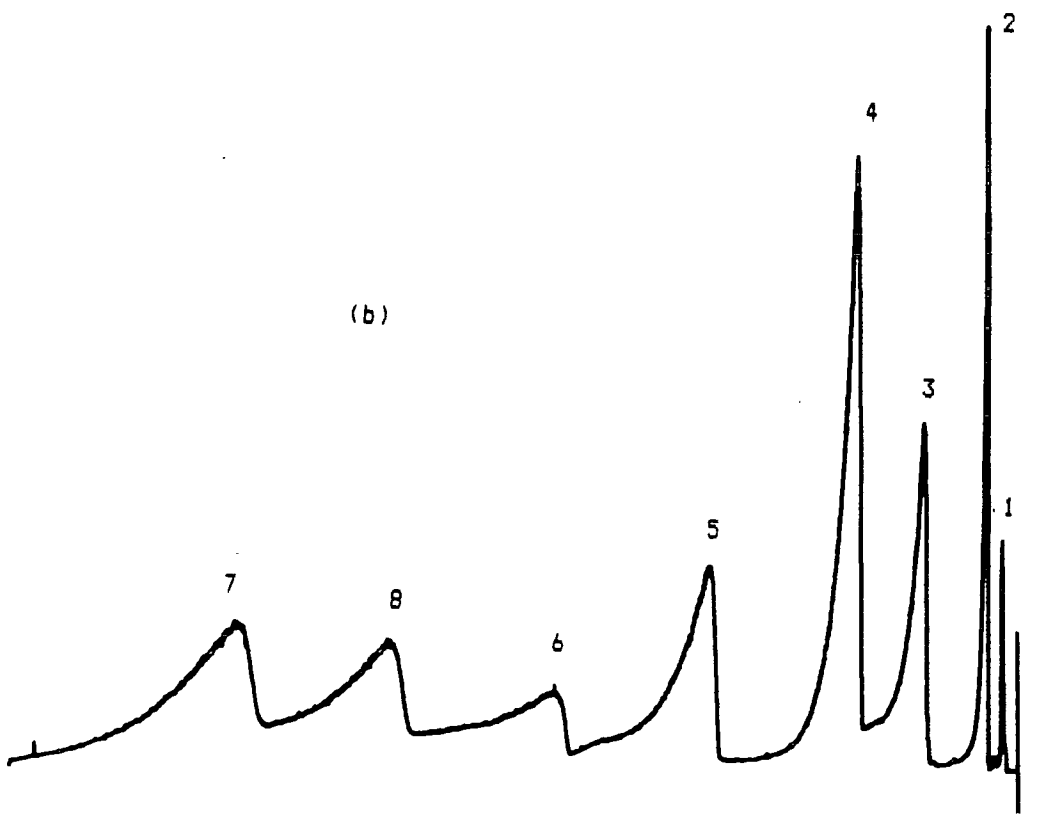


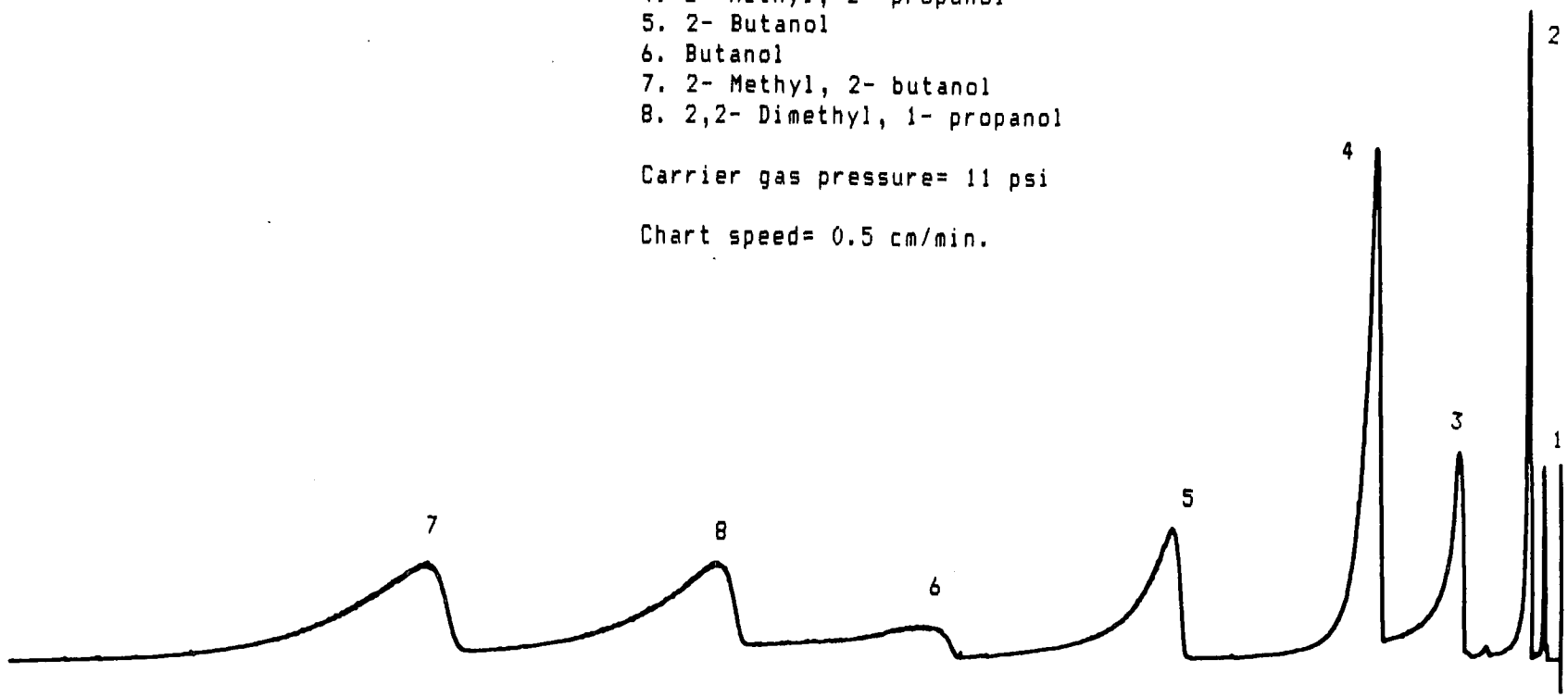
FIGURE 3.23

Alcohols at 100C on PGC 222 CEN.

1. Methanol
2. Ethanol
3. n-Propanol
4. 2- Methyl, 2- propanol
5. 2- Butanol
6. Butanol
7. 2- Methyl, 2- butanol
8. 2,2- Dimethyl, 1- propanol

Carrier gas pressure= 11 psi

Chart speed= 0.5 cm/min.



Alcohols at 100C. (a) on PGC 219 CEN. (b) on PGC 222 CEN with 2.1% (w/w) Carbowax 1500.

FIGURE 3.24

1. Methanol
2. Ethanol
3. N-propanol
4. 2-Methyl,2-propanol
5. 2-Butanol
6. Butanol
7. 2-Methyl,2-butanol
8. 2,2-Dimethyl,1-propanol

Carrier gas pressure= 11 psi

Chart speed= 0.5 cm/min.

Efficiency= 2570 plates

Efficiency= 1156 plates

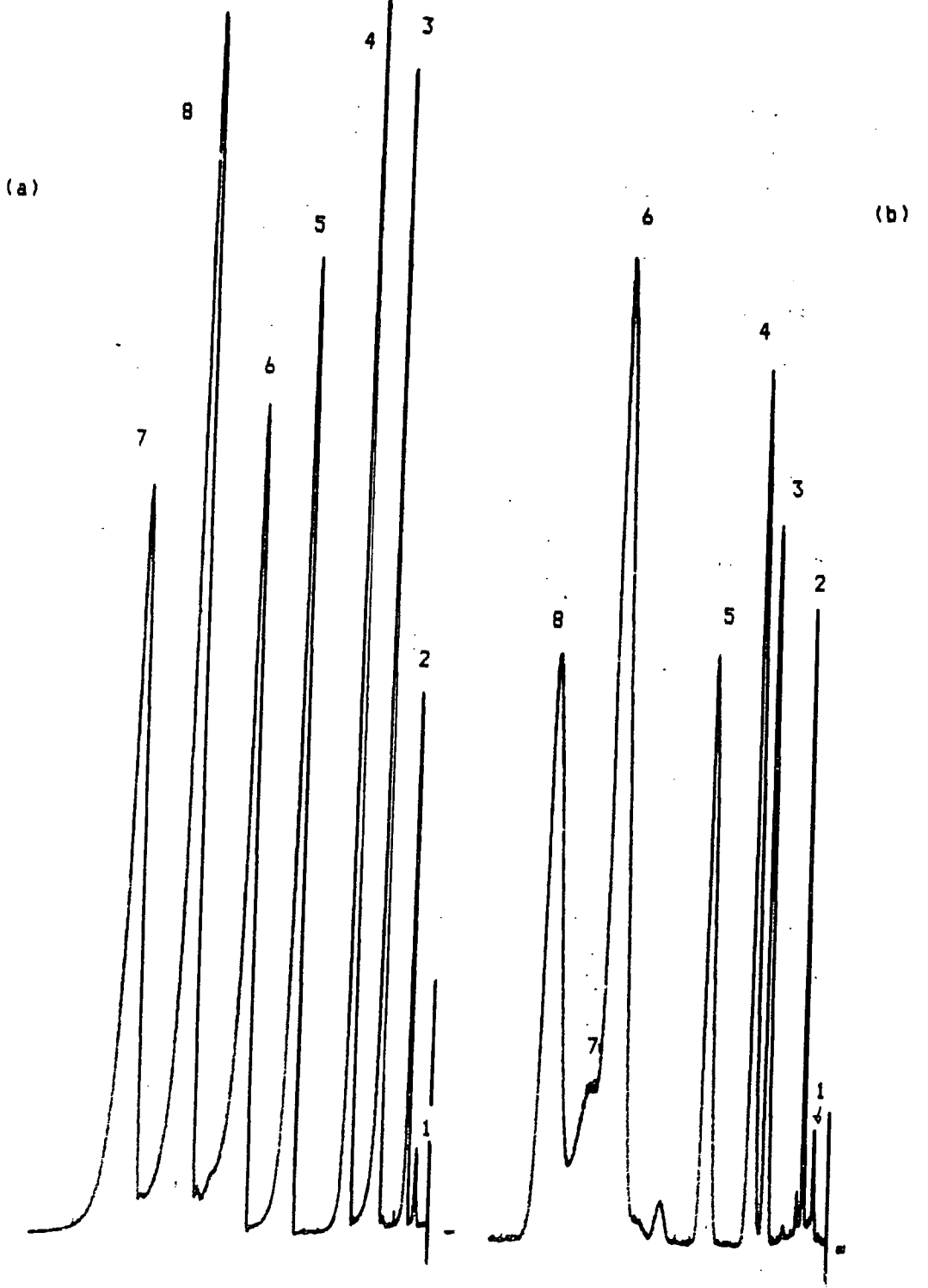


FIGURE 3.25

Ketones at 120C on PGC 220 CEN.

1. Acetone
2. Methyl Ethyl Ketone
3. Methyl Iso-propyl Ketone
4. Methyl n-proply Ketone
5. Methyl Iso-butyl Ketone

Carrier gas pressure= 11 psi.

Chart speed= 0.5 cm/min.

(Original chromatogram reduced to 70%).

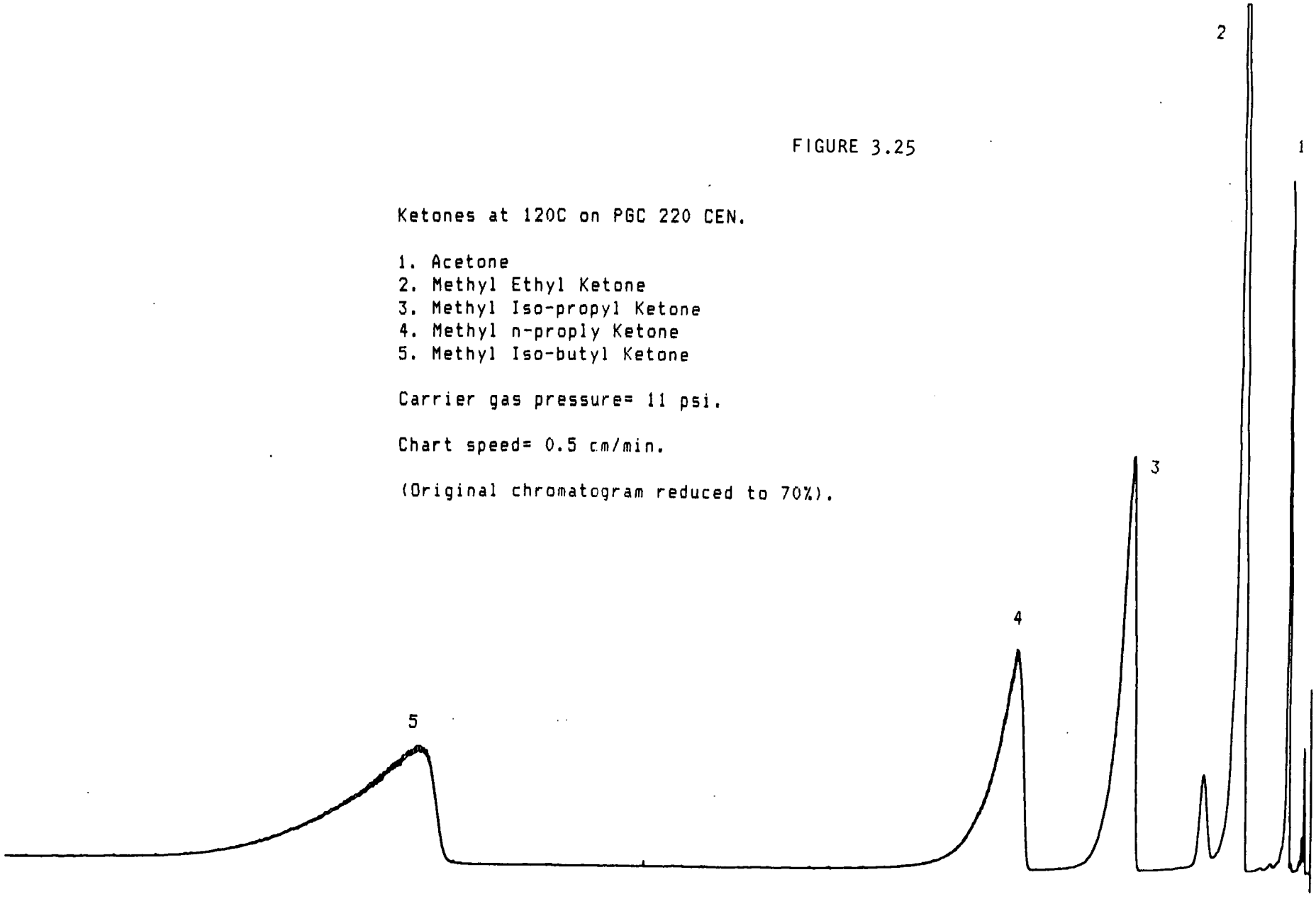


FIGURE 3.26

Ketones at 120C.

2.8% w/w Carbowax 1500 on PGC 220 CEN.

Carrier gas pressure= 11 psi.

Chart speed= 0.5 cm/min.

1. Acetone
2. Methyl Ethyl Ketone
3. Methyl Iso-propyl Ketone
4. Methyl n-propyl Ketone
5. Methyl Iso-butyl Ketone.

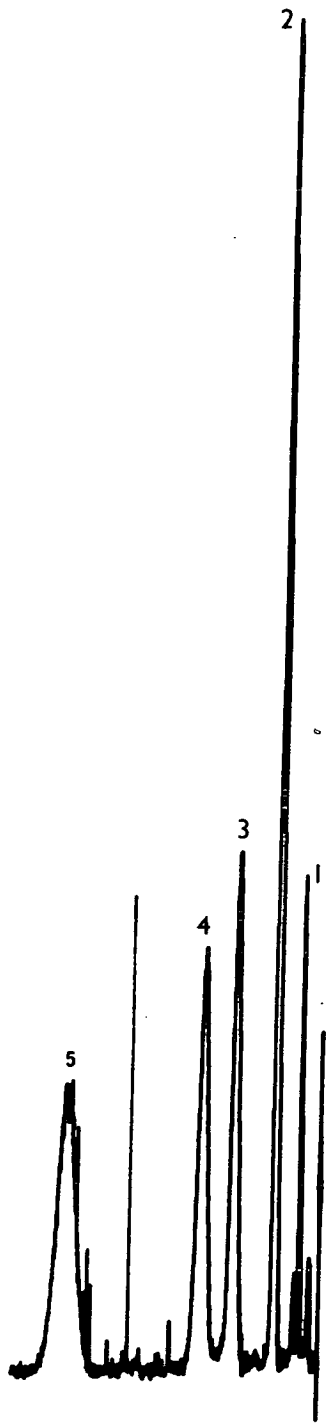


FIGURE 3.27

Hydrocarbons at 85C on PGC 219 CL.

1. Methane
2. Ethane
3. Propane
4. Iso butane
5. Butane
6. Pentane

Carrier gas pressure= 11 psi.

Chart speed= 0.5 cm/min.

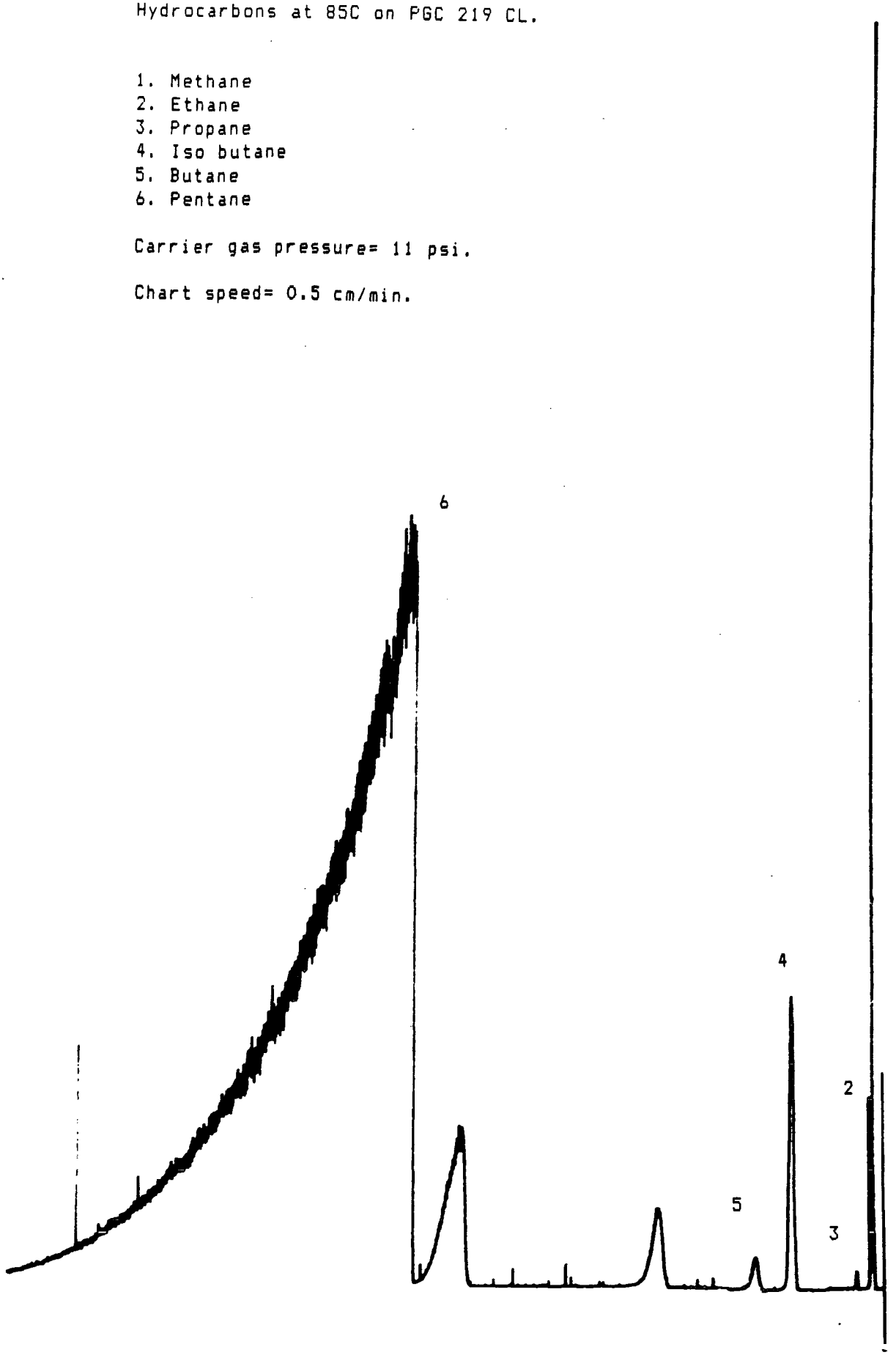


FIGURE 3.28

Hydrocarbons at 85C on PGC 222 CEN. 2

1. Methane
2. Ethane
3. Propane
4. Iso butane
5. Butane
6. Pentane

Carrier gas pressure= 11 psi.

Chart speed= 0.5 cm/min.

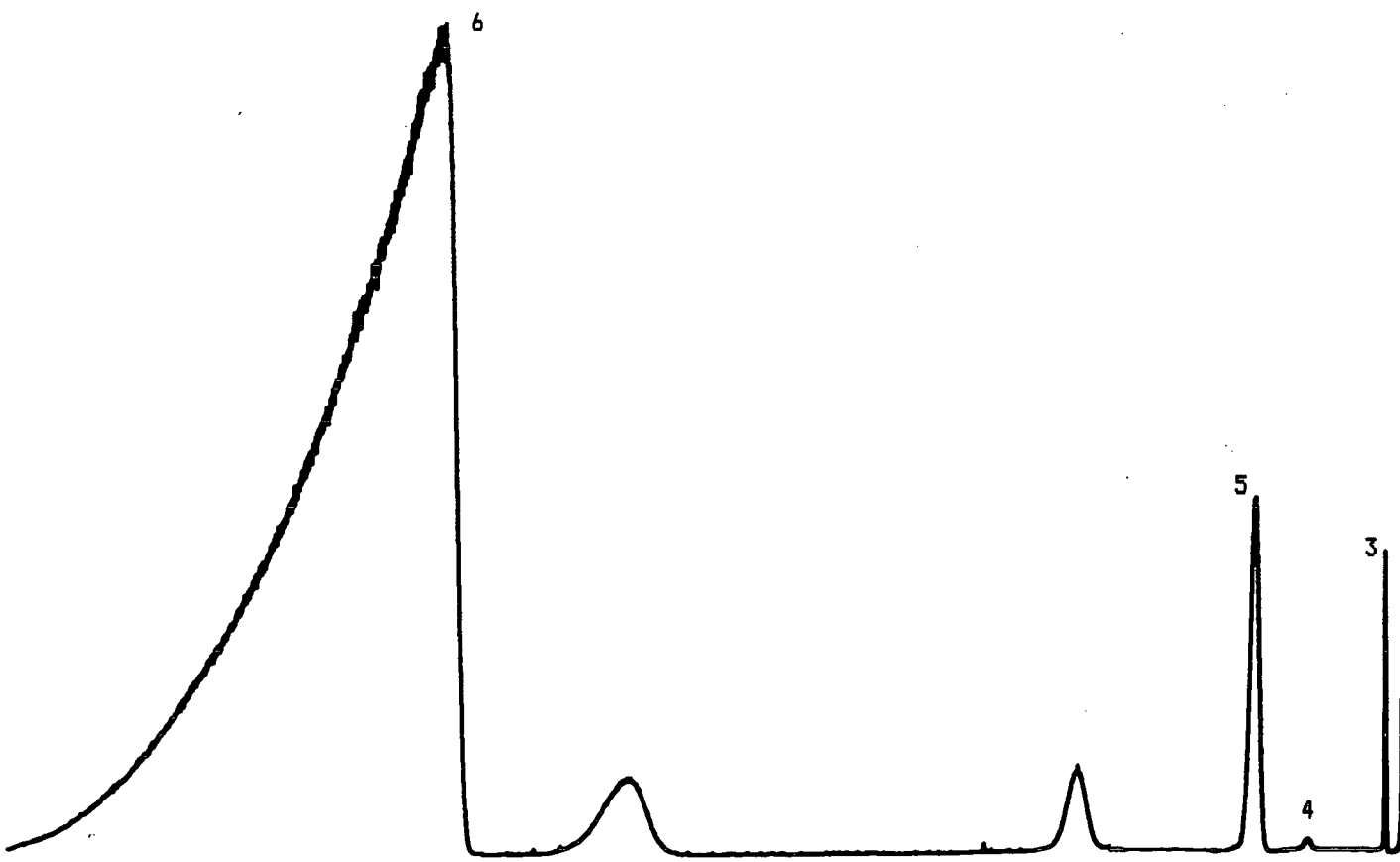


FIGURE 3.29

Hydrocarbons at 85C on (a) PGC 222 CEN with 2.1% w/w Carbowax 1500 and (b) PGC 219 CL with 2.5% w/w Carbowax 1500.

1. Methane
2. Ethane
3. Propane
4. Iso butane
5. Butane
6. Pentane

Carrier gas pressure= 11 psi.

Chart speed= 0.5 cm/min.

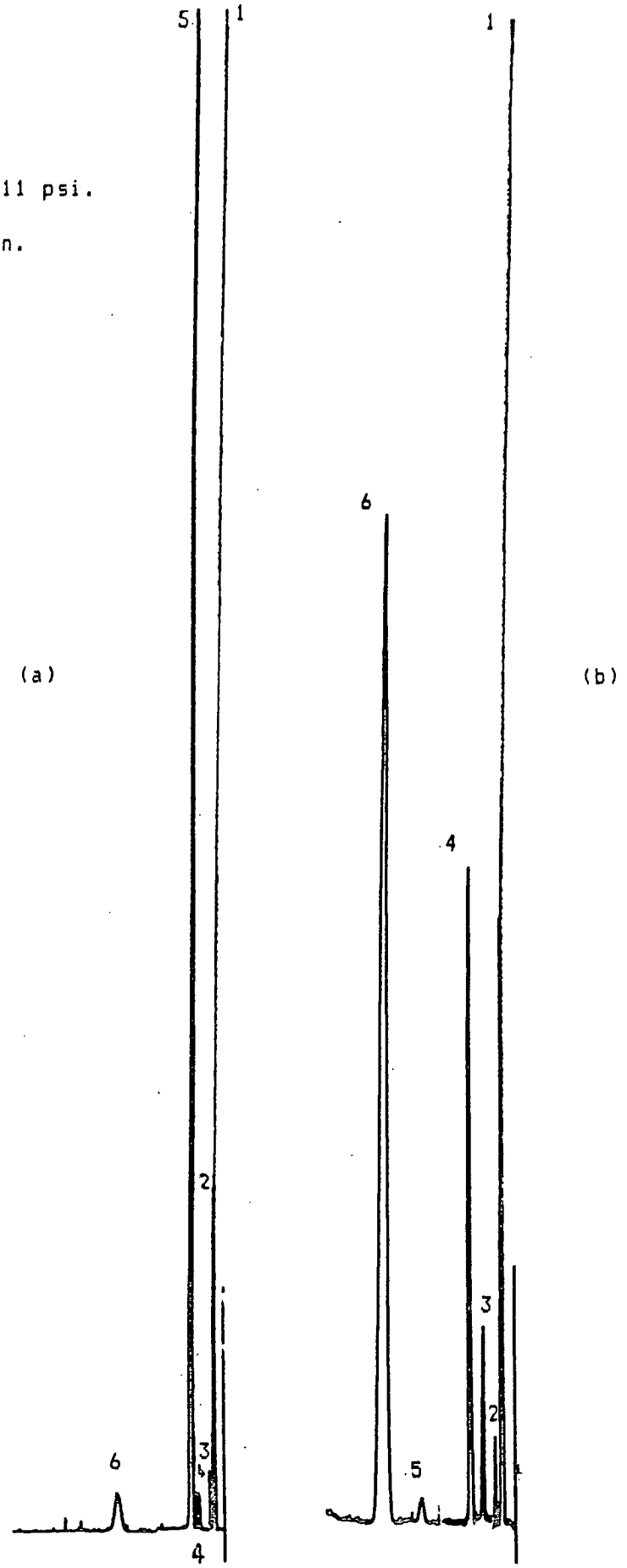


FIGURE 3.30

A clinical mixture at 60C on PGC 210 CL (a) 0.2% w/w Carbowax 1500 and (b) 6% w/w Carbowax 1500.

1. Acetaldehyde
2. Methanol
3. Acetone
4. Ethanol
5. 2- Propanol
6. n- Propanol

Carrier gas pressure= 11 psi.

Chart speed= 0.5 cm/min.

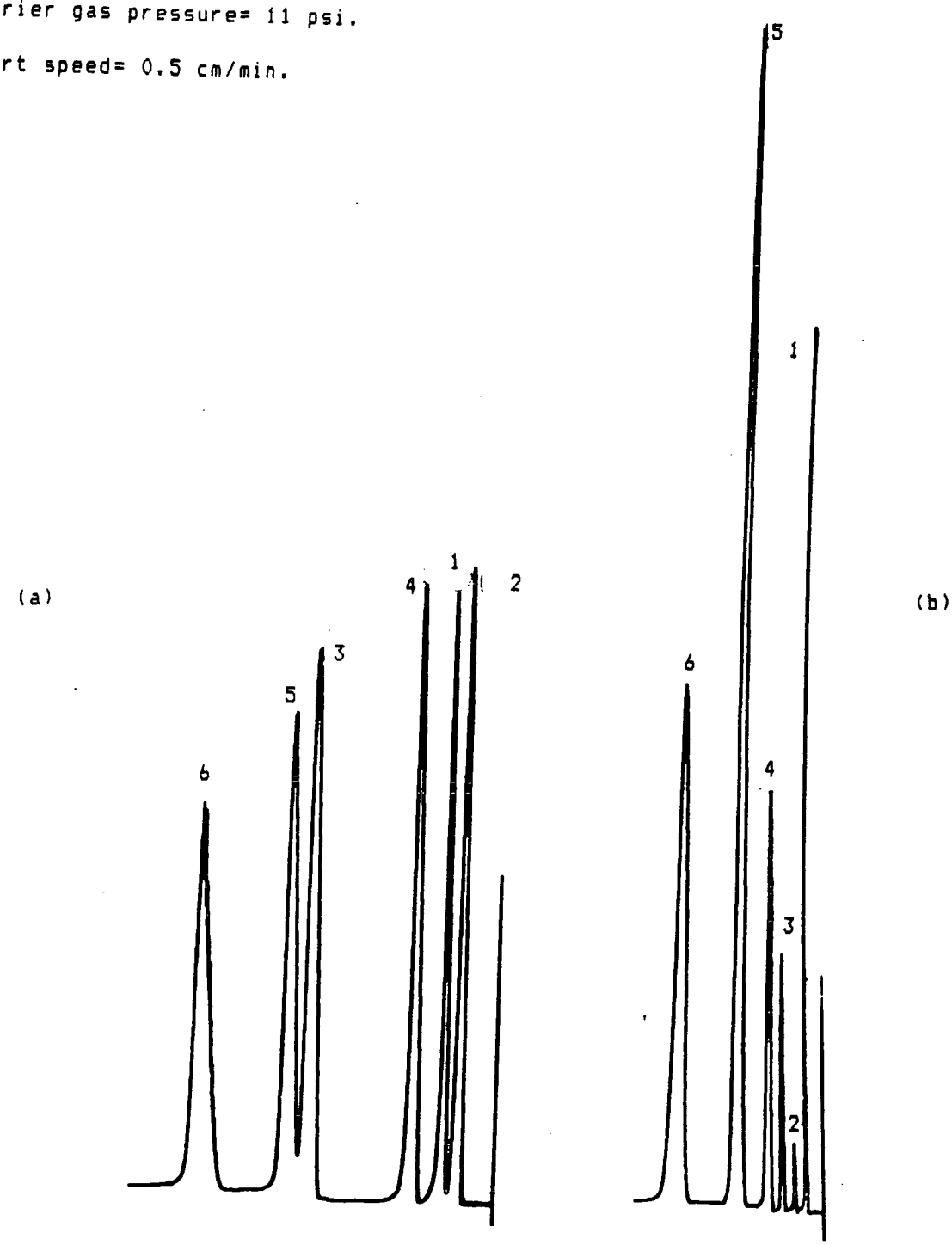


FIGURE 3.31

Whisky samples (a) Glenlivert (b) Dimple. on PGC 210 CL with 1.5% w/w Carbowax 1500.

1. Acetaldehyde
2. Methanol
3. Ethanol
4. Ethyl Acetate
5. n-Propanol
6. 2- Methyl, 1- propanol
7. S-(-)- 2- Methyl,1- butanol
8. 3- Methyl,1- butanol
9. Acetic acid

Carrier gas pressure= 11 psi.

Chart speed= 0.5 cm/min.

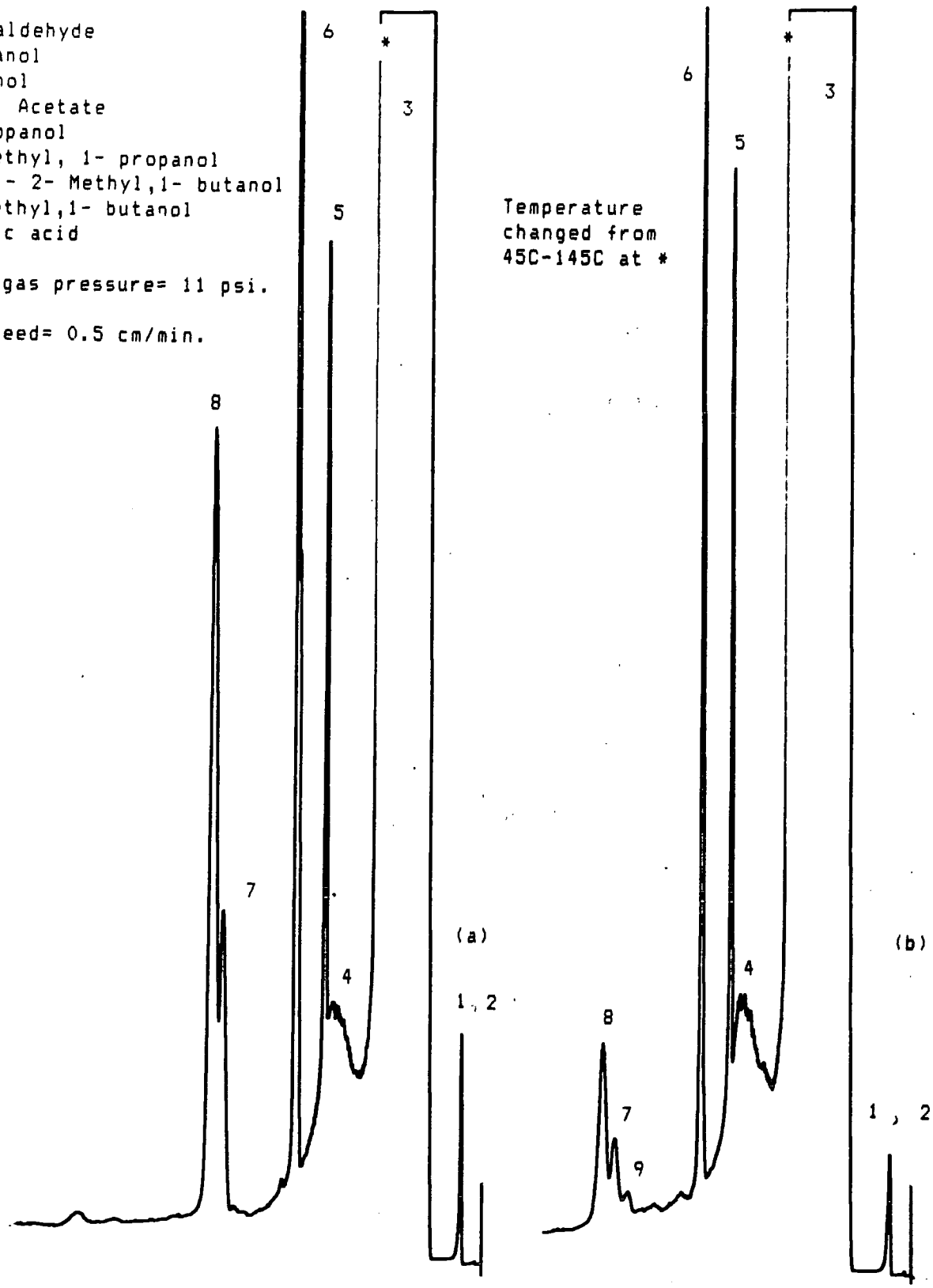


Table 3(ii)

Ketones at 120°C

Bare Surfaces

	PGC 219 CL k^1	PGC 220 CEN k^1	PGC 222 CEN k^1
Methyl ethyl ketone	2.23	1.98	2.45
Methyl isopropyl ketone	7.53	6.83	9.52
Methyl n propyl ketone	12.76	11.70	16.75
Methyl isobutyl ketone	39.8	37.8	59.40

Table 3(iii)

Ketones at 120°C

k^1 Values when coated with Carbowax (monolayer

	PGC 219 CL	PGC 220 CEN	PGC 222 CEN
Methyl ethyl ketone	1.18	1.21	1.19
Methyl isopropyl ketone	3.25	3.25	3.24
Methyl n propyl ketone	4.85	4.83	4.84
Methyl isobutyl ketone	11.67	11.50	11.74

Table 3(iv)

Alcohols at 100°C

k^1 Values on Bare Surface

	PGC 219 CL	PGC 220 CEN	PGC 222 CEN
Methanol	0.138	0.24	0.170
Ethanol	0.862	1.41	1.12
N-Propanol	3.78	6.12	5.88
2-Methyl, 2-Propanol	7.18	11.2	11.5
2-Butanol	14.77	22.4	25.4
Butanol	21.51	34.4	42.4
2-Methyl 2-Butanol	38.40	58.9	76.0
2,2-Dimethyl, 1-propanol	29.69	46.9	56.1

Table 3(v)

Alcohols at 100°C

k^1 Values when Surface is Coated with a Monolayer of Carbowax

	PGC 219 CL	PGC 220 CEN	PGC 222 CEN
Methanol	0.58	0.53	0.54
Ethanol	1.75	1.68	1.71
N-Propanol	5.83	5.79	5.75
2-Methyl, 2-Propanol	7.39	7.37	7.25
2-Butanol	12.44	12.42	12.25
Butanol	22.92	22.94	22.25
2-Methyl 2-Butanol	23.61	22.47	23.5
2,2-Dimethyl, 1-propanol	30.10	30.21	30.04

Table 3(vi)

Alkanes (C_2-C_5) at 85°C

k^1 Values on the Bare Surface

	PGC 219 CL	PGC 220 CEN	PGC 222 CEN
Ethane	0.25	0.25	0.19
Propane	1.40	1.44	1.36
Iso Butane	6.76	2.00	6.14
Butane	9.83	8.00	9.43
Pentane	39.1	50.30	59.8

Table 3(vii)

Alkanes (C_2-C_5) at 85°C

k^1 Values when Coated the Surface with a Monolayer of Carbowax

	PGC 219 CL	PGC 220 CEN	PGC 222 CEN
Ethane	0.43	0.40	0.50
Propane	0.63	0.67	0.57
Iso Butane	1.94	1.95	2.07
Butane	2.78	2.76	2.86
Pentane	10.89	11.76	11.5

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CHAPTER 4

Adsorption Gas Chromatography on Chemically Modified PGC

CHAPTER 4

Adsorption Gas Chromatography on Chemically Modified PGC

4.1 INTRODUCTION

Certain batches of PGC yielded tailed peaks and long retention values during chromatography. The cause of such poor chromatography was due to heterogeneities such as oxygen complexes, cracks and cleavages on the carbon surface [1,2]. Bruner [3], Di Corcia [2,4] and Kiselev [1,5,6] have successfully eliminated such undesirable characteristics of GCB, by the hydrogen treatment of the material at elevated temperatures (1000-1050°C). Their work is described in Section 4.1.1.

First part of this chapter (Section 4.1.2-4.3) is concerned with the hydrogen treatment of PGC. The second part (Section 4.4-4.6) descibes the toluene and the hexane treatments of PGC. These were attempts to improve the gas chromatographic properties of this adsorbent.

Before the details of hydrogen treatment of PGC are described, it is necessary to review the work of Kiselev, Di Corcia and Bruner to fully appreciate the advantages and the chromatographic properties of hydrogen-treated GCB (HTGCB).

4.1.1 Hydrogen-Treated GCB (HTGCB)

Bruner, Di Corcia and Kiselev [1-6] studied the GC properties of HTGCBs. Heat of adsorption of substances were determined on these hydrogen-treated materials to assess the quality of each support as a chromatographic adsorbent [1,2,4-6]. Heats of adsorption values were determined by the GC technique (see Chapter 2). Bruner, Di Corcia and Kiselev deduced that the lower the ΔH, the greater the uniformity of the adsorbent surface [2-4,6] and hence the greater the suitability of the material as a chromatographic adsorbent. The properties of HTGCB are described further in the rest of this section.

Di Corcia et al [3] hydrogen-treated GCB at 1000°C. Analysis of alcohols, carboxylic acids and aliphatic amines were successfully performed. After hydrogen treatment, the heterogeneities such as chemisorbed oxygen on the surface were eliminated, and as a result, Di Corcia et al observed symmetrical peaks. Also the analytical signals, and the column efficiencies were increased. The retention and ΔH values of solutes were decreased. The analyses were carried out in a shorter time. The reproducibility of results improved and the separations were possible at higher temperatures than with polymer-coated materials. Consequently, faster analyses were possible with HTGCB, than with polymer-coated phases.

Kiselev et al [1] also treated GCB with hydrogen at elevated

temperatures (approximately 1000°C) to remove any heterogeneities present on the carbon surface. They discovered that, HTGCB was stable at elevated temperatures (› 200°C) in comparison with the coated materials and the operation of a HTGCB column above 200°C decreased the analysis time. Enhanced, symmetrical solute peaks were obtained when using HTGCB. This shows that the solutes are not chemisorbed on the material.

Geometrical isomers with similar boiling points were successfully separated on HTGCB, whereas coated materials failed to perform such a separation [1]. Kiselev et al used amines and nitriles as samples. As expected the retention values on HTGCB increased with increasing carbon number of the analyte.

The retention and ΔH values of amines with the same number of carbon atoms decreased from primary to secondary and then to tertiary. This behaviour is attributed to (a) the loss of a hydrogen atom from the amino group, (b) decrease in polarisability of N-containing groups of the molecule, and (c) modification of the molecular structure [1].

They studied the dependence of ΔH on the structures and the constituents of sample molecules. The structures of the molecules would determine how they rest on the HTGCB surface, which in turn would dictate the ΔH values.

Kiselev et al [1] also discovered that the distance between HTGCB surface and nitrogen-containing group of the amines or nitriles would have an effect on ΔH values. The closer the nitrogen to the surface, the greater the retention and ΔH of compound.

Di Corcia et al [4] found that on untreated GCB, ΔH of samples decreased with sample coverage, ΔH values were large, reproducibility was poor and adsorption isotherms were convex to the uptake axis. This behaviour was due to the surface heterogeneities which interact with samples.

After hydrogen treatment, (a) the peak shapes of analytes improved, (b) the adsorption isotherms tend to be straighter lines, and (c) the ΔH value diminished and were independent of solute concentrations [4].

Di Corcia et al found that the ΔH value of acetic acid increased after the hydrogen treatment, since hydrogen bonds were formed between the adsorbed molecules on the surface. These hydrogen bonds are much stronger than the interactions between the acetic acid molecules and the surface. Before hydrogen treatment, the acid molecules were prevented from forming hydrogen bonds with one another by the groups present on the GCB surface [4].

Di Corcia and Samperi [4] hydrogen treated GCB to eliminate cracks, steps and cavities, on the surface so that the non-polar molecules

such as alkanes can be successfully chromatographed. Before hydrogen treatment, the alkanes on Carbopack (Graphitised Carbon Black) gave high retention and tailed chromatographic peaks. The sample molecules interact with more than one plane of the adsorbing surface when these geometric heterogeneities are present. Also, enhanced ΔH values were observed for alkanes.

At the boundaries of the surface irregularities it is assumed that the carbon atoms are not arranged in any sort of graphitic structure [2]. If this is the case, these carbon atoms are more reactive than the graphitic ones. Hydrogen reacts with these active carbon atoms around the cavities and this leads to the formation of hydrocarbons. As a result, this reaction causes widening of these cavities until a flat surface is obtained. After the hydrogen treatment, the ΔH values of alkanes established on such carbons have diminished and are equal to the values determined on another carbon which has a flat homogeneous surface. The treatment has eliminated chemical as well as geometric heterogeneities. On HTGCB, the sample molecules interact with only one plane of the adsorbing surface.

Kalashnikova [5,6] and co-workers hydrogen treated GCB to eliminate adsorbed oxygen complexes and investigated the retention properties of oxygenated and halogenated compounds.

They found that the retention of aldehydes and ketones of the same

carbon number are similar. Primary alcohols, aldehydes and ketones displayed higher retention compared with ethers. The oxygen of the alcohols, aldehydes and ketones are arranged such that, those are more accessible to the surface. Therefore their interaction energy with the adsorbent surface is greater [6]. The ethers show lower retention and ΔH values since the oxygen is elevated as the molecules rest on the adsorbent surface.

Of the alcohols, the primary alcohols displayed highest retention values. Next highest retention data were shown by secondary alcohols, while the tertiary alcohols gave the lowest values. This trend is due to the lowering of the number of points of contact of the solutes with the adsorbent surface. Iso alcohols and secondary alcohols have similar retention and ΔH values. Their adsorption energies tend to be similar, and are governed by polarisability and geometry of the molecules [6].

The retention of oxygenated hydrocarbons (alcohols, aldehydes and ketones) were enhanced due to their oxygens interacting with the chemisorbed oxygen complexes on the GCB surface. On HTGCB however, the retention of smaller ($< C_5$) oxygenated hydrocarbons displayed diminished values [6].

This effect is not very apparent for oxygenated hydrocarbons with longer hydrocarbon chains. These larger molecules display similar retention values on HTGCB and GCB. In this case, the oxygens of

these analytes have very little effect on retention. Their retention is primarily governed by the hydrocarbon parts of the molecules [6] interacting with the GCB surface.

The authors [5] also observed that the retention of halogenated alkanes increased with increasing atomic radius of halogen atom. Also, the higher the number of halogens, the larger the retention of the molecule. But $CHCl_3$ and CCl_4 have similar retention data since only three chlorine atoms of CCl_4 rest on the graphite surface, whereas all three chlorines of $CHCl_3$ lie on the adsorbent. The ΔH and retention of molecules on carbon depends on how they rest on the adsorbent [5].

The above literature survey shows that HTGCB has been used in studying (a) the effect of hydrogen treatment on several GCB surfaces [2-4], and (b) how different molecules interact with the resulting homogeneous surface [1,5,6].

The next section describes the research performed on chemically modified PGC. Such a research programme would allow the comparison between the chromatographic properties of HTPGC and HTGCB.

4.1.2 Research Carried Out

The previous section described the advantages of using HTGCB in GC. Hydrogen treatment has clearly improved the chromatographic

properties of GCB. The following sections give details of the hydrogen treatment of PGC and the chromatography on hydrogen treated PGC (HTPGC).

PGC samples from the same batch were hydrogen treated to study the chromatographic properties of the material before and after the exposure to hydrogen. Any variation in surface area of the samples were also noted. The data are explained in terms of the likely processes occurring on the adsorbent surface.

4.2 EXPERIMENTAL

4.2.1 Materials and Equipment

PGC 221 B1 CEN was the packing material (105-210μ). This was a 'grade C' (see Table 2i) adsorbent. This support was developed at the Wolfson Liquid Chromatrography Unit (Chemistry Department, Edinburgh University). This batch of PGC was fired (high temperature treatment during preparation) at Centorr Associated Inc., Suncook, NH, U.S.A.

The hydrogen and nitrogen (oxygen free) used in the preparation of HTPGC was obtained from British Oxygen, Brentford, Middlesex.

The retention of analytes on the hydrogen treated materials were determined using F11 Perkin-Elmer Gas Chromatograph (Perkin-Elmer,

Beaconsfield, Bucks.).

A hydrogen diffusion unit (hydrogen purifier) was used to produce pure hydrogen in the treatment of PGC. The operation of the purifier is explained in Appendix III. The diffusion unit (model no. H140/5) was obtained from Johnson Matthey Metals Ltd., London.

The flow rates of hydrogen (20-250 $ml.min^{-1}$) and nitrogen (60-600 $ml.min^{-1}$) were monitored using 'GAP' flowmeters.

Stainless steel boats (approximately 2.5cm cross sectional diameter and approximately 5cm long) were prepared at the workshop of the Chemistry Department, Edinburgh University, for containing the PGC during hydrogen treatment.

The boats containing PGC, were placed inside a stainless steel tube (100cm long, 2.8cm OD and 2.5cm ID and air tight). This tube was also built in the workshop of the Chemistry Department, Edinburgh University.

This stainless steel tube was placed inside a furnace (Figure 4.1) for the hydrogen treatment of PGC at elevated temperatures (400-1000°C). The furnace (CFMI-1400 PID) was obtained from Carbolite, Bamford, Sheffield, Yorks.

The system in Figure 4.1 was connected using stainless steel tubing

(1/8"). The GC columns were prepared using 1/8" stainless steel tubing. These were purchased from Phase Separations, Queensferry, Clywd.

The analytes used were alcohols, ketones and alkanes. These were purchased from the organisations mentioned in Section 2.2.

4.2.2 Hydrogen Treatment of PGC

The boats containing the PGC were placed inside the stainless steel tube so that they lay in the middle of the tube. The tube was then placed inside the furnace so that the boats were in the middle section of the furnace for optimum temperature (Figure 4.1) using swagelok couplings, and the connections were made air tight to avoid any oxygen or water vapour entering this set up.

The operation of the hydrogen purifier unit is described in Appendix III. The supply of hydrogen to the purifier was adjusted to a pressure of 20 atm., and the temperature of the diffusion cell of the unit was raised to 200°C. These conditions gave an output flowrate of 200-250 $cm^3.min^{-1}$ of pure hydrogen. This flowrate was maintained for 2 hours and pure hydrogen was allowed to pass through the tube containing the PGC at ambient temperature in order to flush out the oxygen and water vapour from the entire system.

Afterwards, the temperature of the furnace was gradually raised to

1030°C. This final temperature was maintained for 4 hours with pure hydrogen (240-250 $cm^3.min^{-1}$) passing through the tube. After 4 hours, the furnace was switched off and the system was allowed to cool to ambient temperature. The pure hydrogen flowrate was maintained throughout the cooling period.

PGC 221 B1 CEN samples were hydrogen treated at 1030°C, 830°C, 630°C, 430°C and 230°C using the above procedure.

4.2.3 Column Packing

The GC column packing procedure is described in Chapter 2. The columns were 60cm long x 1/8".

4.2.4 Chromatography on Hydrogen Treated PGC (HTPGC)

Ketones (0.5µl, 120°C) and alcohols (0.1µl) and alkanes (C_1-C_5) (1-2µl) were chromatographed on each hydrogen-treated PGC sample. Chromatography was carried out at 120°C. The carrier gas pressure (N_2) was maintained at 25 psi, The retention properties of the above analytes were recorded on untreated PGC 221 B1 for comparison (Figure 4.5 and 4.9).

The surface areas of the PGC 221 B1 CEN samples hydrogen treated at different temperatures were also monitored. The surface areas were determined by the B.E.T. method (Chapter 1 and Appendix I). The

B.E.T. system was constructed at the Chemistry Department of Edinburgh University.

4.3 RESULTS AND DISCUSSION

Figures 4.2-4.4 show the variation of k^1 of analytes with hydrogen treatment temperature. Results indicate that the retention of ketones have not significantly decreased (Figure 4.2); to give faster analysis times. In Figure 4.3, 2-methyl, 2 Butanol and 1 butanol display considerable decreases in k^1 when chromatographed on the PGC which has been hydrogen treated at 1030°C (Figure 4.3). In the case of alkanes (Figure 4.4), the retention of pentane decreased when hydrogen treated at 1030°C whilst the k^1 of others remained unchanged (Figure 4.4).

Pentane, 2 methyl 2 butanol, 1 butanol and methyl iso propyl ketone displayed enhanced retention values at intermediate temperatures (Figures 4.2-4.4). The retention versus hydrogen treatment temperature graphs of the above solutes reached maxima. An attempt will be made later in this section to explain the results.

In comparison to the analyte peak shapes observed on untreated PGC (Figures 4.5 and 4.9), significantly improved peak shapes were not observed on HTPGC (Figures 4.6-4.8 and 4.10). Unsymmetrical peaks were common place (Figures 4.6-4.8 and 4.10).

The reasons for the above observations may be explained by comparing the structures of PGC and GCB. Mechanically, PGC is much stronger than GCB]7]. Also, the latter may have a larger number of heterogeneities on its surface. Groszek's method [8] has shown that the chemical heterogeneities on the PGC 218 CEN surface is about 0.3% of the total area of sample [9]. This may be much lower than the concentration of chemical defects present on GCB. The reasons will be soon made clear.

Bruner et al [3], Di Corcia and co-workers [2,4] and Kiselev and his team [5,6] reduced the concentration of heterogeneities of GCB by the hydrogen treatment of the material at 1000°C. Such a treatment led to a considerable improvement in the chromatographic properties of GCB.

In the case of PGC, the unsymmetrical peak shapes and unfavourable retention values were not improved after such a treatment. This may be attributed to three factors.

(a) A certain amount of corrosion is taking place on the PGC surface during hydrogen treatment at 1030°C. The surface of PGC may be cleaner than that of GCB. The hydrogen could be reacting with the carbons on PGC to create methane. In the case of GCB, the hydrogen reacted with the surface impurity groups to give a cleaner surface for adsorption GC.The difference between the concentrations of surface heterogeneities on GCB and PGC may explain

the differences in the chromatographic properties of HTGCB and HTPGC.

The thermodynamic data enabled the calculation of the amount of methane produced (Appendix IV) during the hydrogen treatment of PGC at 1030°C. The formation of the theoretically predicted amounts of methane at temperatures below 1000°C is unlikely since it is thermodynamically unfavourable to produce a significant amount during the time allocated for the reaction. The estimated partial pressure of methane produced during the hydrogen treatment at 1030°C was 0.06 atm. The corrosion of the PGC surface during hydrogen treatment occurs only at temperatures above 1000°C.

(b) The elevated temperatures (> 400°C) would assist in the removal of any chemisorbed oxygen complexes present on the PGC and that would lead to the exposure of reactive carbon atoms on the graphite surface. Such sites could react with oxygen and water vapour in the system during hydrogen treatment and in turn such chemisorbed oxides could associate with the analytes to give unfavourable chromatography. This is shown by the enhanced k^1 values in Figures 4.2 and 4.3 and the peak shapes in Figures 4.6-4.8 and 4.10.

There is considerable difficulty in excluding the undesirable substances such as oxygen and water vapour and reproducing exact conditions at all hydrogen treatment temperatures.

(c) The third factor is a physical change, where the defects such as any cracks on the PGC surface could have widened to create deeper holes to allow the analytes to enter and interact with more than one surface of the adsorbent. Such interactions would lead to enhanced retention and unsymmetrical peaks. This does not seem to be happening to an extent that it is large enough to alter the surface area of the PGCs (Table 4.i). However, this process may be occurring to an extent that is sufficient to create surfaces to give unfavourable chromatography. Figure 4.4 shows that retention of pentane reaches a maximum at 830°C. Such a result could be due to the above mentioned physical change.

Except for the following solutes, the retention of other analytes on HTPGC show little change in comparison to the values observed on the untreated PGC surface. Greatly diminished retention values are seen for 2 methyl 2 Butanol, 1-Butanol and Pentane; after the hydrogen treatment of PGC at 1030°C (Figures 4.3 and 4.4). The above mentioned decrease could be due to the introduction of solute doses that are too large. The sample size governs the retention on a 'grade C' adsorbent.

The overall chromatography of PGC was unimproved after the hydrogen treatment. This fact was shown by the unsymmetrical peaks (Figures 4.6-4.8 and 4.10) and the undiminished retention times displayed by the majority of solutes.

All the above findings lead to the conclusion that the chromatography of PGC cannot be improved by hydrogen treating the material at elevated temperatures.

4.4 TOLUENE OR HEXANE TREATED PGC

4.4.1 Introduction

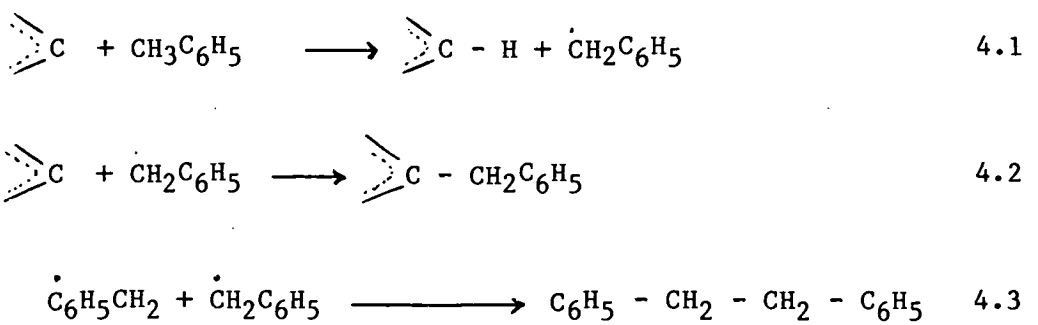
The hydrogen treatment failed to introduce favourable chromatographic properties to PGC. As explained in the previous section, such treatment appears to have led to the erosion of the surface. To obtain a suitable chromatographic material, it was necessary to eliminate the surface heterogeneities such as cracks, oxygen complexes and reactive carbon atoms without introducing other undesirable features. THe next stage was to carry out chemical reactions on the surface, so that the number of such defects present on PGC may be diminished.

Swarc [11] used toluene as a radical trap to monitor unimolecular homolytic decomposition of unstable organics. Swarc [11] suggested and Steacie et al [12] who did similar work, confirmed that toluene reacts with the free radicals that are created by the decomposition of unstable organics, at elevated temperatures to produce benzyl radicals.

Benzyl radicals may also be created as a result of the reaction of

toluene with the carbon free radical sites that are created on the PGC surface at moderately high temperatures (300-630°C). These benzyl radicals may also react with carbon free radical sites on the PGC surface. Such reactions would lead to the production of an adsorbent surface with few or no heterogeneous sites. Such a surface is considered to be highly suitable for adsorption GC.

The reactions between PGC and toluene can be shown by the following reaction scheme.



$$\text{C} + CH_3C_6H_5 \longrightarrow \text{C} - H + \dot{C}H_2C_6H_5 \qquad 4.1$$

$$\text{C} + \dot{C}H_2C_6H_5 \longrightarrow \text{C} - CH_2C_6H_5 \qquad 4.2$$

$$\dot{C}_6H_5CH_2 + \dot{C}H_2C_6H_5 \longrightarrow C_6H_5 - CH_2 - CH_2 - C_6H_5 \qquad 4.3$$

The $C_6H_5CH_2$ species may react with the reactive carbon atoms of PGC as shown in equation 4.2 or may dimerise as in equation 4.3. This toluene treatment was performed at 630°C. At this temperature, any chemisorbed oxygen complexes are likely to be removed from the PGC or at least be highly reactive, creating reactive sites. Then these reactive sites could interact with $C_6H_5\dot{C}H_2$ radicals or toluene.

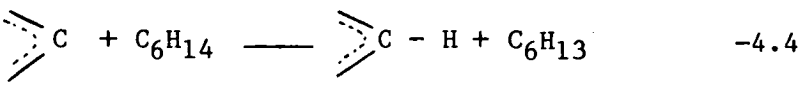
The toluene molecules or a part of the molecules may get inside any cracks on the PGC, and hence prevent the analytes from entering

such defects.

The experiment V shows that there was a considerable amount of toluene absorbed on to the PGC surface during this treatment (see later).

Hexane was considered as an alternative to toluene to see whether similar results could be obtained with another hydrocarbon.

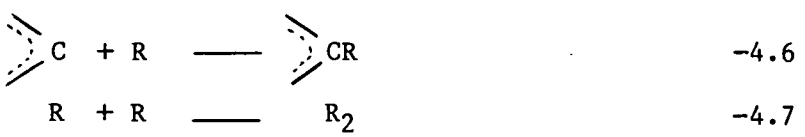
The reaction of hexane with PGC may be explained by the following reaction scheme.



$$\gg C + C_6H_{14} \longrightarrow \gg C - H + C_6H_{13} \qquad -4.4$$

$$C_6H_{13} \xrightarrow{600^\circ C} \text{Olefins} + \dot{C}H_3 \text{ and } \dot{C}_2H_5 \qquad -4.5$$

$$R = \dot{C}H_3 \text{ or } \dot{C}_2H_5$$



$$\gg C + R \longrightarrow \gg CR \qquad -4.6$$

$$R + R \longrightarrow R_2 \qquad -4.7$$

Hydrogen was used as the 'carrier gas' to carry the toluene (or hexane) vapour into stainless steel tube containing the carbon sample (Figure 4.1). One experiment was performed using toluene with nitrogen as the 'carrier gas', since this is a much safer alternative to hydrogen.

Another PGC 221 B1 sample was toluene treated at 300°C. Hydrogen was used as the carrier gas on this occasion. Such an experiment was performed to discover whether the decrease in temperature of reaction (between PGC and $C_6H_5\dot{C}H_2$) makes any difference to the retention characteristics of the PGC. The details of experiments and their results are fully described in Section 4.6.

4.5 EXPERIMENTAL

Analar grade toluene was used in the treatment of PGC at elevated temperatures (300°C or 600°C). This reagent was obtained from May and Baker Chemical Company, Dagenham, Essex.

Analar grade hexane, used in the treatment of PGC, was purchased from Rathburn Chemical Company, Walkerburn, Peebleshire. Hexane is the alternative to toluene.

All other reagents and equipment were as in Section 4.2.

A bubbler constructed in the Chemistry Department of Edinburgh University was used in this series of experiments. The bubbler is the device to contain $50cm^3$ of toluene or hexane. The pure 'carrier gas' (i.e. hydrogen from the purifier or oxygen free nitrogen from the cylinder) may be directed into the solvent inside the bubbler. The emerging stream of carrier gas/solvent vapour mixture may be connected to the stainless steel tube containing the

carbon sample (Figure 4.1).

4.5.1 Procedures

The GC conditions were as in 4.2.4. The column dimensions and the packing procedure were as in Section 4.2.3 and Chapter 2 respectively.

4.5.2 Experiment I

The basic system in Figure 4.1 was used in this series of experiments. This system was slightly modified to accommodate the bubbler containing the toluene. This device was placed in between the hydrogen purifier (C) and the stainless steel tube (E) of Figure 4.1.

1.5g of PGC 221 B1 CEN were placed inside the tube (E) and the pure hydrogen flow was adjusted to 240 cm^3/minute by adjusting the eurotherm temperature controller of the hydrogen purifier to 200°C (Appendix III). The hydrogen and the toluene vapour were allowed to pass through the tube containing the PGC at ambient temperature for 2 hours in order to flush out any water vapour and oxygen that might have been present in the system. Then the temperature of the furnace (O) was raised to 630°C. The furnace was maintained at this temperature to 4 hours with toluene/hydrogen mixture running through at 240 cm^3/minute. At the end of this period, the furnace

was switched off and the tube containing the PGC allowed to cool whilst the flow of toluene/hydrogen (240 cm^3/minute) was maintained.

After the stainless steel tube had reached ambient temperature (approximately 12 hours), the purifier was turned off to terminate the flow of pure hydrogen. The shut down procedure of purifier is described in Appendix III.

A packed GC column was prepared with 0.6-0.7g of the toluene treated PGC and connected into the gas chromatograph. The oven temperature was raised to 150°C and the GC carrier gas pressure was maintained at 25 psi for 90 minutes in order to condition the column. The conditioning was necessary to remove any excess solvent on the PGC surface and hence obtain a steady base line. The alcohols, ketones and light hydrocarbons were chromatographed at 120°C.

Afterwards, the temperature of the GC oven was raised to 300°C and the column temperature maintained at 300°C for 100 minutes with nitrogen running through the column at a pressure of 25 psi.

After this period the column was cooled to 120°C whilst maintaining the carrier gas flow. The retention values of ketones, alcohols and hydrocarbons were again recorded at this temperature. These results enabled the comparison of data between, before and after

exposure of column to elevated GC oven temperatures.

The surface area of toluene treated PGC sample was determined using the B.E.T. method (Chapter 1).

4.5.2.1 Results and Discussion (Experiment I)

In comparison to the untreated PGC, the toluene treated material yielded improved peak shapes (Figures 4.11, 4.13 and 4.14), shorter retention times and enhanced column efficiencies (for example, n-propyl ketone displayed 3.5 fold increase in column efficiency).

The duplicate retention values of most solutes (Table 4.II) are in good agreement (within 95%). The worst case was n-propanol which showed only 86% agreement between duplicate retention values.

The duplicate samples from the same batch of PGC may chemically interact with different amounts of toluene during treatment. The chemical reaction between the toluene and the carbon is dependent upon the number of heterogeneities present on each PGC sample. Also, during conditioning, of the GC columns containing the treated PGC, different amounts of toluene may be desorbed from the two surfaces. As a result, the two surfaces would display different retention properties. The results in Table 4.II show that these differences between the two surfaces are not vast enough to give large variations in duplicate k^1 values.

The quality of a material as a chromatographic adsorbent is reflected in the heats of adsorption values determined on that material (Chapter 2). Table 4.III displays ΔH values of certain compounds determined on PGC 221 B1 CEN before and after the toluene treatment. The diminished ΔH of solutes on the treated PGC suggest that the toluene treatment has considerably improved the material as a GC adsorbent. The treated material may display straighter adsorption isotherms (Cs versus Cm).

The experimental results may be explained further by considering the likely processes occurring on the PGC surface. The toluene treatment temperature (630°C) may assist in the removal of any chemisorbed oxygen from the PGC surface. This would expose reactive sites. In addition, there may be reactive carbon atoms on the surface. The toluene would react with PGC according to equations 4.6 and 4.7. The possibility of $C_6H_5\dot{C}H_2$ radicals directly reacting with any chemisorbed oxygen complexes cannot be ruled out. This may lead to the deactivation of such sites.

Any physical defects present on the adsorbent surface may be covered with toluene molecules or parts of molecules depending on the dimensions of these defects. Such a phenomenon would contribute towards the decrease in the surface area of PGC during the treatment. There may be a sufficient amount of toluene physically adsorbed on the PGC surface to alter the retention characteristics of PGC (Experiment V). It is likely that this

physically adsorbed toluene is present in the form of a unimolecular layer since the conditioning stage of the GC column would have removed any multilayers.

The likely processes taking place on the PGC surface are (a) the reaction of toluene with chemical defects/carbon, (b) the interaction of toluene with physical defects, and (c) physical adsorption of toluene on PGC. These three factors have improved the GC properties of PGC.

Table 4.II and Figure 4.12 display the results after the exposure of toluene treated PGC surfaces to 300°C for 110 minutes. This resulted in enhanced analyte retention and asymmetrical peak shapes. That may be attributed to the removal of a considerable amount of reacted and adsorbed toluene from the PGC surface. As a consequence, the surface heterogeneities would have been re-exposed and this would have led to the re-introduction of undesirable chromatographic properties to the PGC surface. These results point to the conclusion that the toluene treated carbon surfaces are unable to withstand temperatures in excess of 300°C.

4.5.3 Experiment II

A sample of PTC 221 B1 CEN was toluene treated using nitrogen as the carrier gas during treatment (Figure 4.1). The stream of oxygen free nitrogen from the cylinder was directly connected to

the bubbler containing the toluene. The toluene vapour/nitrogen mixture was directed into the stainless steel tube containing the PGC sample. The experiment was performed at 630°C. The rest of the procedure is as described in Experiment I.

The aim of experiment II was to discover whether the use of hydrogen could be discontinued as hydrogen may be explosive at elevated temperatures. Nitrogen is inert and safe to use. These qualities make nitrogen a suitable carrier gas for toluene treatment.

Alcohols, ketones and hydrocarbons were chromatographed on toluene and nitrogen treated PGC, at 120°C, so that comparisons may be made with the results of other experiments (Experiments I, III and IV). The surface area of this PGC sample was determined via the B.E.T. method.

The column with toluene and nitrogen treated PGC 221 B1 CEN was exposed to 300°C for 100 minutes as described in section 4.5.2. The chromatography of the above mentioned analytes were noted afterwards.

4.5.3.1 Results and Discussion (Experiment II)

PGC 221 B1 CEN was toluene treated using nitrogen as the 'carrier gas'. This treatment also resulted in an improved surface for

adsorption GC (Figures 4.15, 4.17 and 4.19). The peak tailing and analyte retention sharply decreased as a consequence of this treatment. Except acetone, the k^1 values determined on this surface are slightly lower than those obtained on toluene/hydrogen treated PGC (Tables 4.II and 4.IV). Results of experiments I and II are comparable and of the same order of magnitude (Tables 4.II and 4.IV). The selectivities of analytes on the two surfaces described in Experiments I and II are identical.

The carrier gas used during the toluene treatment did very little to influence the chromatographic properties of PGC. Therefore nitrogen could be used as an alternative to hydrogen.

The exposure of the toluene/hydrogen treated surface to 300°C for 110 minutes resulted in asymmetrical peak shapes for ketones and alcohols (Figures 4.16 and 4.18), and enhanced retention times for all solutes (Table 4.IV). The analyte 2,2 dimethyl 1-propanol, for example, displayed a 53% reduction in efficiency of column after the exposure of the treated adsorbent to 300°C. The comparison between Figures 4.19 and 4.20 reveal that the peak shapes of alkanes undergo very little or no change after the exposure of the treated PGC surface to a temperature of 300°C. This is attributed to the alkanes associating with the surface and hence any re-exposed heterogeneities to a far lesser extent than other analytes.

4.5.4 Experiment III

The above mentioned (Experiment II) toluene treatment was carried out after setting the temperature of the furnace (in Figure 4.1) to 300°C. All other details were exactly as in Experiment I.

This was an attempt to see whether the toluene treatment at a lower temperature would yield similar results to those obtained in Experiments I and II.

The GC properties of ketones, alcohols and hydrocarbons were recorded at 120°C using the toluene and nitrogen treated (at 300°C) PGC 221 B1 CEN as the stationary phase. Afterwards this GC column was exposed to 300°C for 100 minutes with nitrogen running through the column. Then the chromatography of the above mentioned solutes were determined at 120°C.

The surface area of this toluene/(nitrogen) treated (at 300°C) PGC sample was determined using the B.E.T. method.

4.5.4.1 Results and Discussion (Experiment III)

In this experiment, the toluene treatment was carried out at 300°C with nitrogen as the 'carrier gas'. Results can be compared with those of Experiments II and III (Table 4.IV). The retention values of each solute determined in these two experiments agreed within

90% of one another. Figures 4.21-4.23 show the improved peak shapes and analysis times.

It may be noteworthy to mention that the retention values determined in this experiment are slightly higher than the results of the preceeding experiment. This slight difference may be due to the amount of toluene interacted with the PGC surface during the two experiments. The amount of toluene combined with the surface at 630°C may be slightly higher than the amount interacted at 300°C. The experimental results determined on the two surfaces (in Experiments II and III) can be considered as in good agreement (tables 4.II and 4.IV). The general conclusion which can be drawn is that the toluene treatment at 630°C and 300°C yielded similar results.

Exposure of the toluene treated surface to 300°C for 110 minutes resulted in enhanced retention times (Table 4.IV) and a general deterioration in the quality of the material as an adsorbent. This is consistent with the observations of Experments I and II.

4.5.5 Experiment IV

Experiment I described toluene treatment of PGC at 630°C, using pure hydrogen as the carrier gas.

In this experiment, the toluene was replaced with hexane to see

whether the latter could fill the role of toluene. The procedure was as described in Experiment I.

Hexane is much more volatile than toluene. Therefore the bulb of the bubbler containing the solvent was immersed in a mixture of ice and dry ice throughout the experiment.

The hexane and hydrogen treated PGC (0.6-0.79g) was packed into a column, and the chromatography of alcohols, ketones and light hydrocarbons was determined at 120°C.

Afterwards, the column was exposed to 300°C for 100 minutes and then the chromatography of the above mentioned solutes was again recorded at 120°C.

The surface area of the hexane treated PGC 221 B1 CEN sample was determined via the B.E.T. method (see Appendix I).

4.5.5.1 Results and Discussion (Experiment IV)

The hexane treatment also produced an improved chromatographic surface (Figures 4.24 and 4.26). The retention of analytes on PGC decreased after the hexane treatment. The likely interactions of hexane with carbon are given in equations 4.9-4.11. The surface area of PGC displayed a remarkable decrease as a result of this treatment to indicate that the long chain-like hexane molecules

could have entered any cracks and other geometrical defects. This phenomenon contributed towards the improvement in the chromatographic properties of PGC.

Retention values determined on hexane treated PGC (Experiment IV) are comparable to those determined on toluene treated PGC (Experiment I).

Table 4.VI shows the ratio of analyte k^1 values determined on toluene treated PGC and hexane treated PGC. For most analytes, k^1 values obtained on the two surfaces are not vastly different (1 ± 0.2).

Toluene and hexane would interact differently with PGC. Toluene would provide $C_6H_5CH_2$ radicals whilst hexane would give $\dot{C}H_3$ and $\dot{C}_2H_5$ species for reaction with PGC. There may also be a difference between the number of heterogeneities present on the surface of the two PGC samples used in the hexane/hydrogen/ and toluene/hydrogen treatments. Consequently, there are some differences between the analyte retention values determined on these two surfaces (Table 4.VI).

Enhanced retention times and non-symmetrical peak shapes did not result after the exposure of the hexane treated PGC to 300°C for 110 minutes (Tables 4.V, Figures 4.25, 4.27 and 4.28). The comparison of bond strengths would reveal the reason for this

observation.

The bond between carbon (PGC) and R (CH_3 or C_2H_5) is stronger than the bond between PGC and $C_6H_5CH_2$ species (Section 4.4.1). The exposure temperature of 300°C was unsuccessful in removing a considerable number of R groups to expose reactive carbon atoms and hence diminish the integrity of the hexane treated PGC as a GC material.

4.5.6 Experiment V

The change in chromatographic properties of PGC after the introduction of a large dose (1µl) of toluene on to the PGC surface was studied. This toluene covered surface was then exposed to different temperatures to understand the likely processes occuring and the interactions between toluene and the PGC.

A GC column (60cm) was packed with untreated PGC 221 B1 CEN (approximately 0.6g) and conditioned at 200°C inside the GC oven for 90 minutes. The GC carrier gas pressure was maintained at 25 psi throughout the entire experiment. The oven temperature was reduced to 120°C with the carrier gas running through the GC system. Then 0.1µl of toluene (dose 1) was injected into the column. The retention of the toluene dose was noted. The peak was recorded on chart paper. The chart paper enclosing the peak was cut out and weighed. This 'weight of peak' is a measure of the

area under that peak.

A 1µl sample of toluene (dose 2) was introduced on to the column whilst maintaining the GC oven temperature at 120°C. Then the chart recorder pen was allowed to settle at the base line. A 0.1µl injection of toluene (dose 3) was introduced on to the column at 120°C. The retention time and the 'weight of peak' were recorded.

Afterwards, the GC oven temperature was raised to 150°C and the column inside was exposed to this temperature for 90 minutes. Then the oven temperature was reduced to 120°C and a 0.1µl of toluene (dose 4) was introduced on to the column. The retention and 'weight of peak' were recorded.

The procedure mentioned in the preceeding paragraph was repeated after exposing the column for 90 minutes to each of the following temperatures, 180, 210, 240, 270 and 300°C. The relevant chromatographic information of doses 5-9 (0.1µl aliquots of toluene) were noted at 120°C. The experimental procedure is illustrated in Figure 4.29. The results are shown in Figures 4.29-4.31.

4.5.6.1 Results and Discussion (Experiment V)

The diminished k^1 of the 0.1µl toluene injection after the introduction of the lul toluene sample (dose 2) on to the column is

shown in Figures 4.29 and 4.30 (compare k^1 of dose 1 and dose 3).

The diagrams also display the effect of column temperature of k^1 of the toluene samples (doses 3-9), after the PGC was treated with 1ul of toluene (dose 2). Figure 4.31 shows the variation of peak areas (i.e. weight of peak) with column temperature. The trace in Figure 4.31 is the opposite of that in Figure 4.30.

These observations may be explained by considering the likely processes occurring on PGC. The enhanced retention (Figure 4.29) and the diminished peak area (Figure 4.31) of the first dose of toluene are due to the strong adsorption of toluene molecules (from dose 1) on to the PGC. Dose 1 was chromatographed at 120°C. This temperature was insufficient to desorb all toluene molecules from the adsorbent surface. Any heterogeneities present on the PGC may have contributed towards the enhanced retention and diminished peak area of dose 1.

Then, a 1ul of toluene was introduced on to the column (dose 2) at 120°C. This dose changed the chromatographic properties of PGC. The retention and the peak area of the following 0.1µl toluene injection (dose 3) displayed a considerable change in comparison with the chromatography of dose 1. Dose 3 was chromatographed at 120°C. The retention displayed a decrease and the peak area showed an increase in comparison to the retentin and peak area of dose 1. The next paragraph gives the reasons for observing this change in

the chromatographic properties of PGC.

The adsorption of toluene on a bare carbon surface is governed by dispersion interactions and the association with any heterogeneities present on the surface. On a toluene covered surface, the toluene acts as a liquid film, and this film covers any surface heterogeneities. The toluene in dose 3 interacts with this layer of toluene. Such interactions are weaker than the associations between toluene of the initial dose and the bare PGC surface containing heterogeneities. The lowering of analyte retention, due to the adsorbed liquid films on PGC, are described elsewhere in this thesis (Chapter 3).

The column was then exposed to 150°C for 90 minutes. The retention and peak area ('weight of peak') were then recorded for another 0.1µl sample of toluene (dose 4) at 120°C. The retention displayed a diminished value (Figure 4.30) whilst peak area displayed an increase (Figure 4.31) in comparison with the retention and peak area of dose 3.

When dose 3 was chromatographed (at 120°C) it was likely that the PGC surface was unevenly covered with the toluene of dose 2. There may have been uncovered particles towards the end of the column whilst the PGC particles at the beginning of the column may have had multilayers of toluene covering any heterogeneous sites.

The exposure of column to 150°C for 90 minutes, may have resulted in the removal of the multilayers and the adsorption of these extra molecules on the bare parts of the PGC surface to give a more even layer of toluene on PGC. This adsorption of toluene on the bare parts on the PGC may have resulted in covering more heterogeneous sites present on the PGC surface.

The two preceeding paragraphs could explain why dose 4 displayed diminished retention and increased peak area in comparison with retention and peak area of dose 3.

The exposure of column to 180°C for 90 minutes may have caused the desorption of toluene from the PGC surface. This would re-expose the surface heterogeneities and the bare surface for interaction with toluene in dose 5. The increase in k^1 (Figure 4.29) and the reduction in peak area (Figure 4.31) of dose 5, may be the result of the above mentioned desorption process.

Further desorption of toluene from the PGC surface may have occurred when the column was exposed to 210°C for 90 minutes. Dose 6 which displayed enhanced retention (Figure 4.29) and diminished peak area (Figure 4.31) was chromatographed at 120°C. The exposure of column to 240°C for 90 minutes may have resulted in the chemisorption of toluene (any remaining toluene from dose 6) on the PGC surface. As a result this toluene may have deactivated any heterogeneities on the PGC. This may have led to the decrease in

retention (Figure 4.29) and an increase in the peak area (Figure 4.31) of the following toluene dose (dose 7).

Further reaction between PGC and toluene (of dose 7) may have occurred on exposure of column to 270°C (for 90 minutes). This is reflected in the diminished retention (Figure 4.30) and increased peak area (Figure 4.31) of dose 8.

Finally, the column was heated at 300°C for 90 minutes. Any chemisorbed toluene from the previous injections may have been removed from the PGC to re-expose heterogeneities on the adsorbent surface. Dose 9 was introduced on to the column at 120°C. The re-exposed heterogeneities may have interacted with toluene of dose 9 to increase the retention (Figure 4.30) and decrease the peak area (Figure 4.31) of that toluene dose.

Experiment V has shown that the chromatographic properties of PGC are drastically altered when the adsorbent surface was covered with toluene. This toluene covered surface was exposed to different temperatures to study different processes occurring on the PGC. The processes that could be taking place on the surface were explained in terms of retention and peak areas of toluene doses injected on to the column at different stages.

It may be concluded that adsorbed or chemisorbed toluene on PGC, diminishes analyte retention and increases the analytical signals.

This is due to the toluene molecules covering the heterogeneities present on the PGC surface.

Adsorbed toluene can be removed from the PGC surface at 150°C whereas chemisorbed toluene would remain on PGC up to 270°C. As a guideline, it may be stated that the toluene treated PGC surfaces would not be stable beyond 270°C.

4.6 FUTURE WORK

A study of the defects present on the PGC surface. Electron microscopy may be used for this purpose.

Hexane or toluene treated PGC can be used in analytical work. For example, the analysis of fatty acids, alcohols and amines may be performed on such a material.

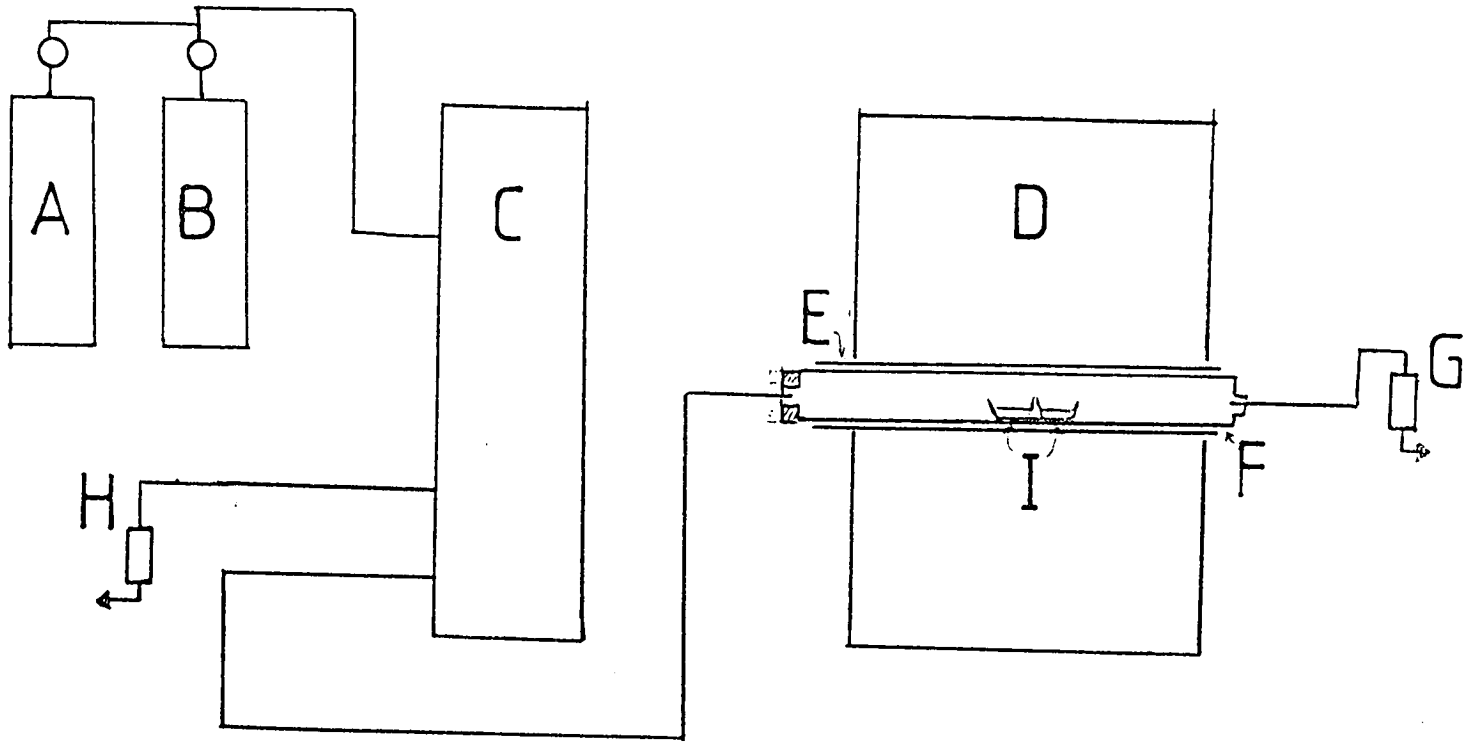
Adsorption isotherms may be established on chemically treated PGCs to determine the quality of the materials as chromatographic adsorbents [3].

The quality of the hexane or toluene treated material may be studied further by determining the dependance of retention and ΔH values on the surface coverage of solute.

These experimental data may be compared with those obtained on

HTGCB, to see whether chemically treated PGC would yield better chromatographic properties.

FIGURE 4.1

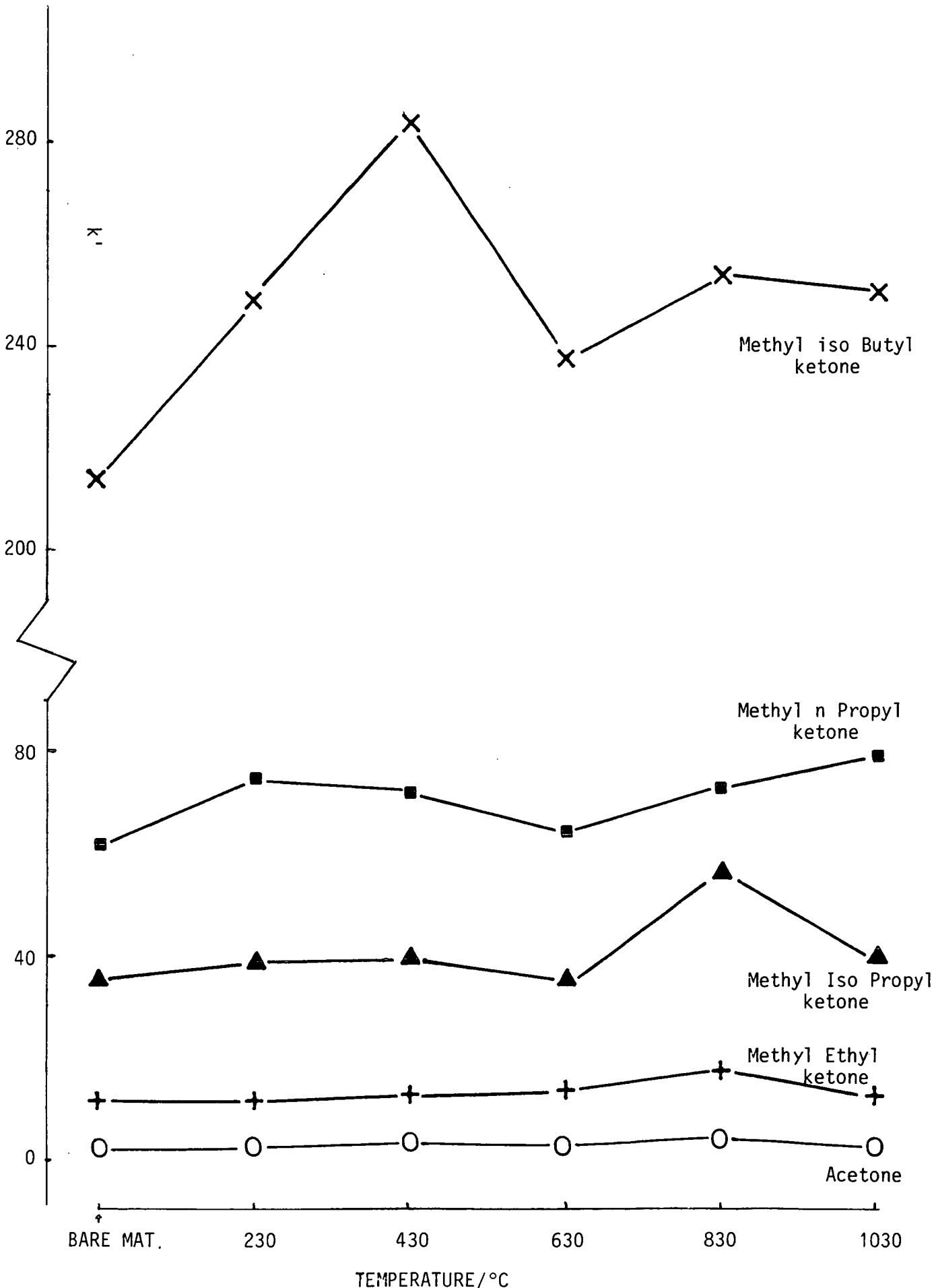


A = Nitrogen Cylinder
B = Hydrogen Cylinder
C = Hydrogen Purifier
D = Furnace
E = Ceramic Tube
F = Stainless Steel Tube
G & H = Flow Meters
I = Stainless Steel Boats containing PGC

FIGURE 4.2

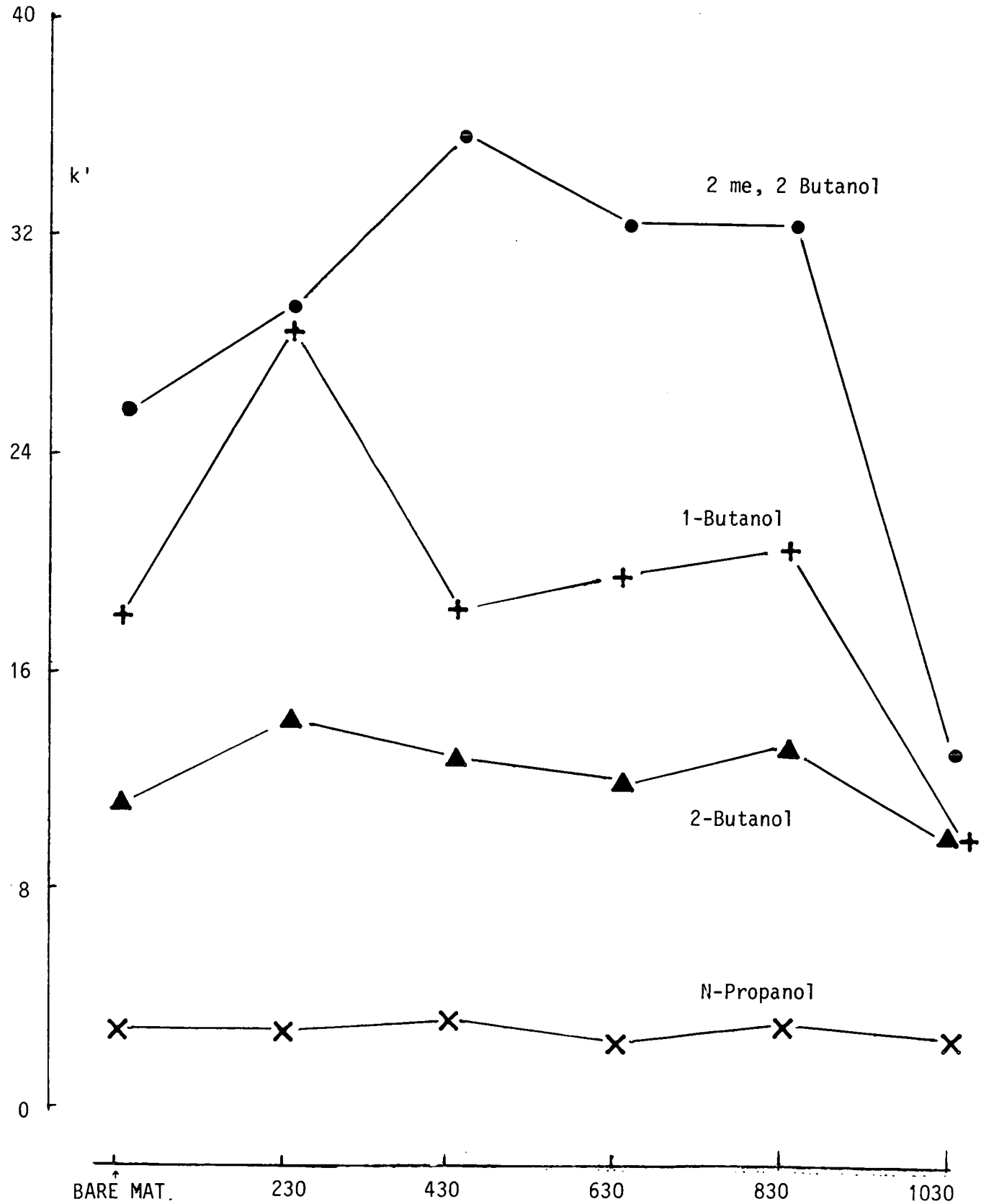
k' of Ketones Vs Hydrogen Treatment Temperature

(Chromatography carried out at 120°C) PGC 221 BI CEN



k' of Alcohols (at 120°C) Vs Temperature of Hydrogen Treatment

FIGURE 4.3



k' of Alkanes (at 120°C) Vs Hydrogen treatment temperature

FIGURE 4.4

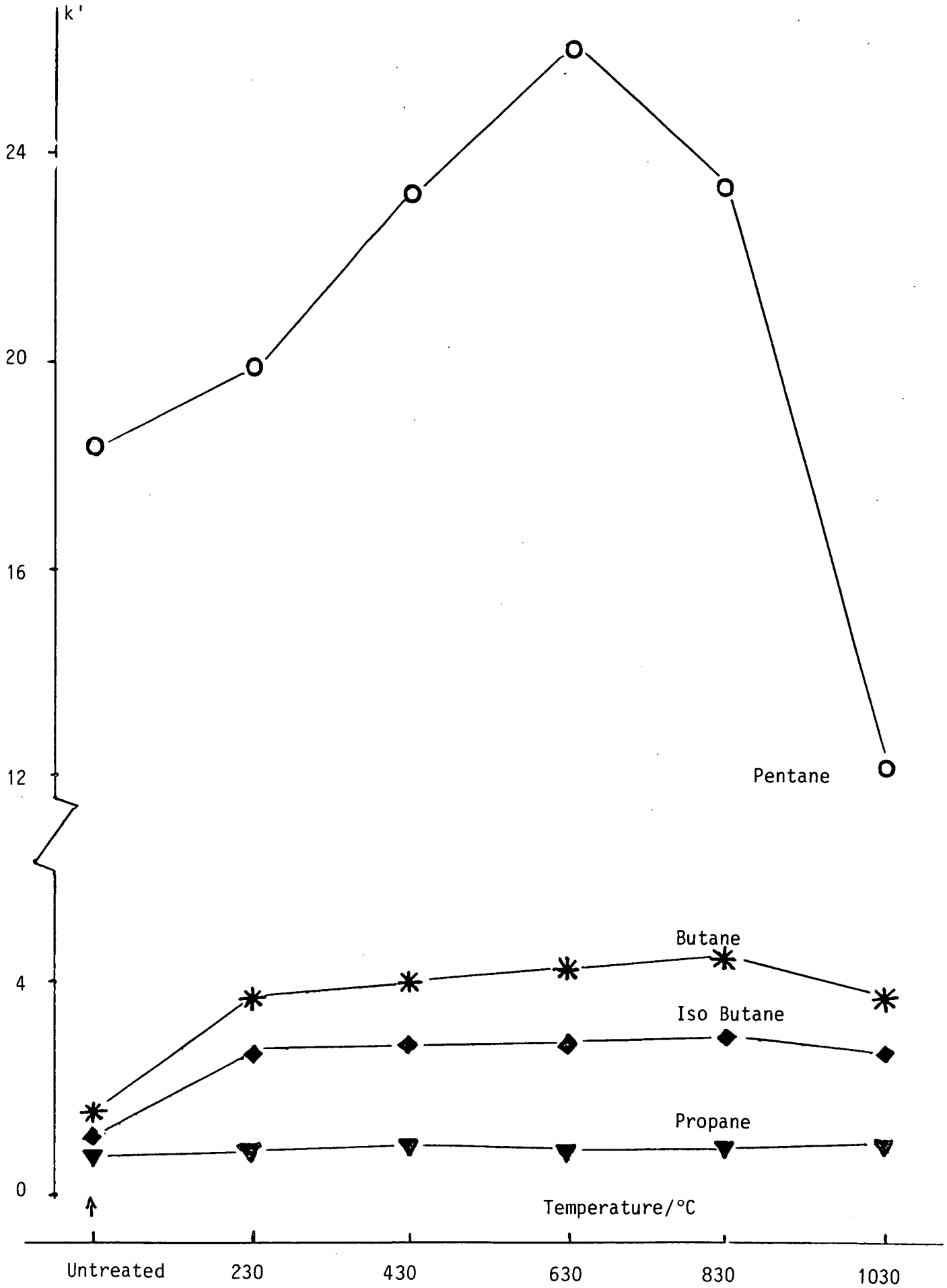


FIGURE 4.5

KETONES at 120C.

PGC 221 B1 CEN.

1. Acetone.
2. Methyl Ethyl Ketone.
3. Methyl Iso-Propyl Ketone.
4. Methyl n-Propyl Ketone.
5. Methyl Iso-Butyl Ketone.

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

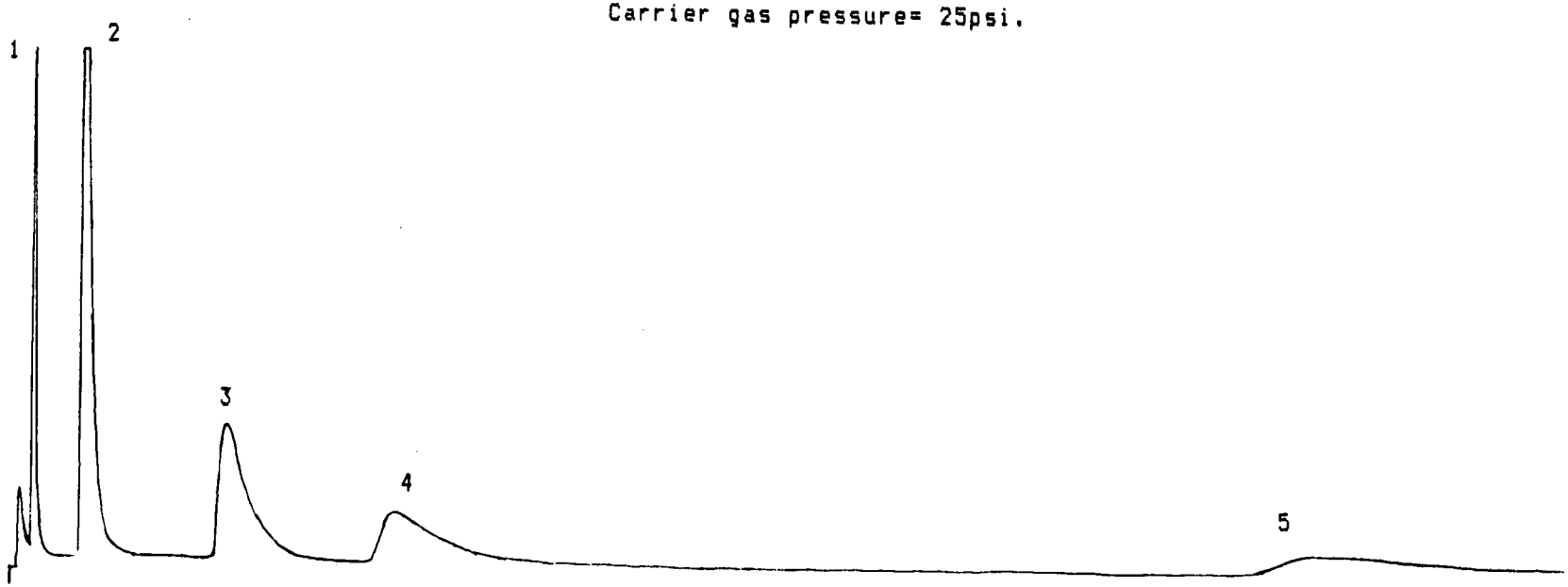


FIGURE 4.6

Ketones at 120C.

Hydrogen treated PGC 221 B1 CEN (1030C).

1. Acetone.
2. Methyl Ethyl Ketone.
3. Methyl Iso- Propyl Ketone.
4. Methyl n- Propyl Ketone.
5. Methyl Iso- Butyl Ketone.

Chart Speed= 0.5 cm/min.

Carrier gas pressure= 25 psi.

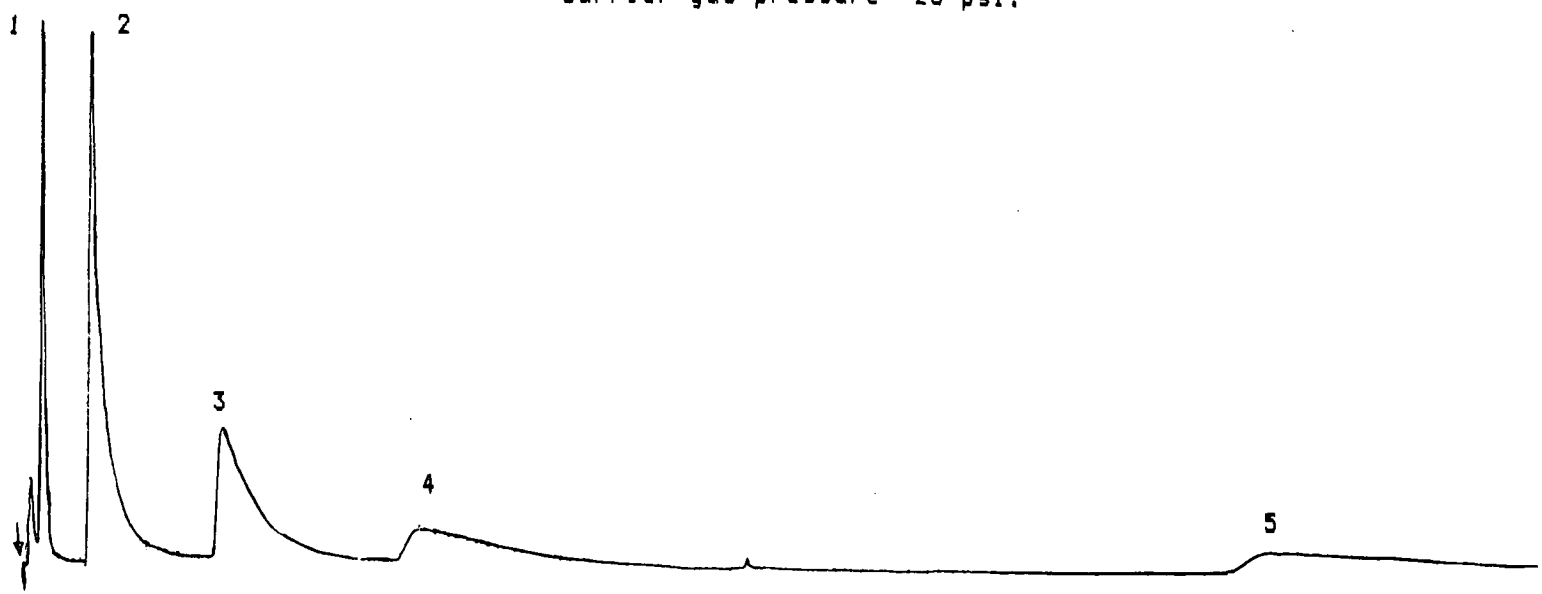


FIGURE 4.7

KETONES at 120C.

Hydrogen treated PGC 221 B1 CEN (830C).

1. Acetone
2. Methyl Ethyl Ketone.
3. Methyl Iso-Propyl Ketone.
4. Methyl n-Propyl Ketone.
5. Methyl Iso-Butyl Ketone.

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

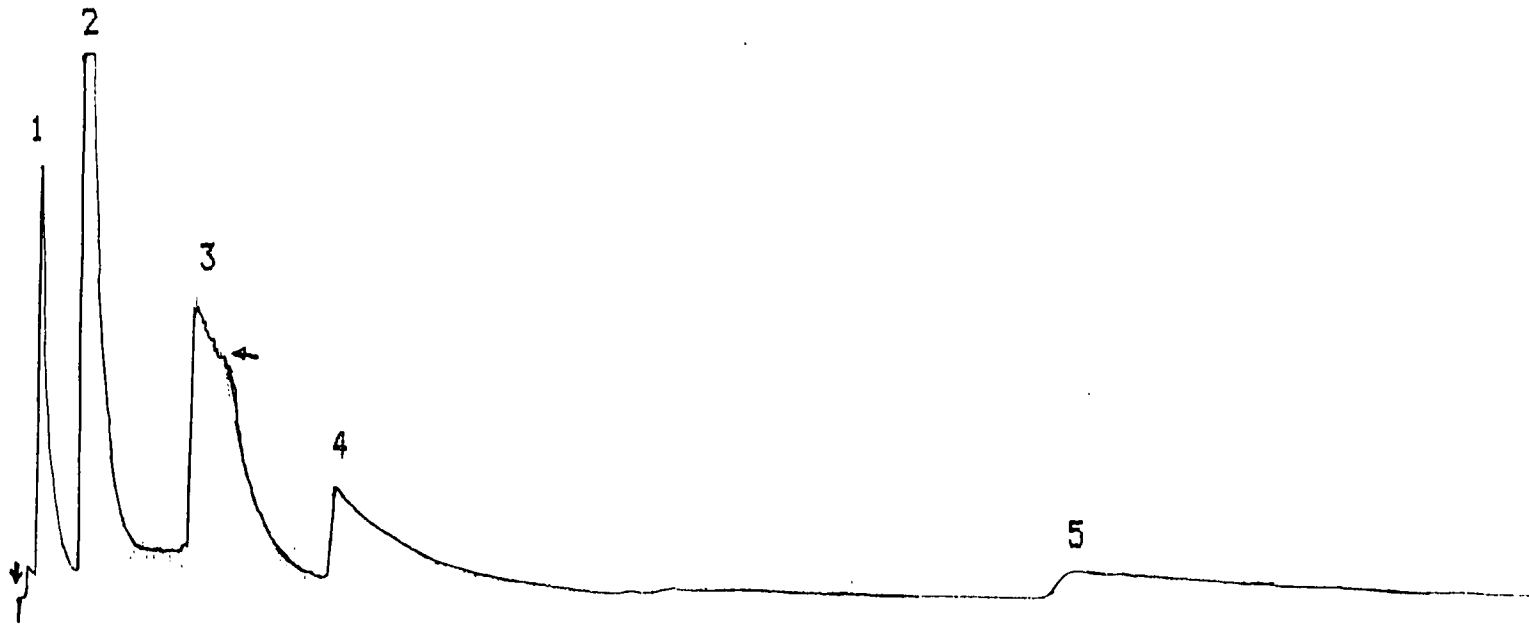


FIGURE 4.8

KETONES at 120C.

Hydrogen treated PGC 221 B1 CEN (630C).

1. Acetone
2. Methyl Ethyl Ketone.
3. Methyl Iso-Propyl Ketone.
4. Methyl n-Propyl Ketone.
5. Methyl Iso-Butyl Ketone.

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

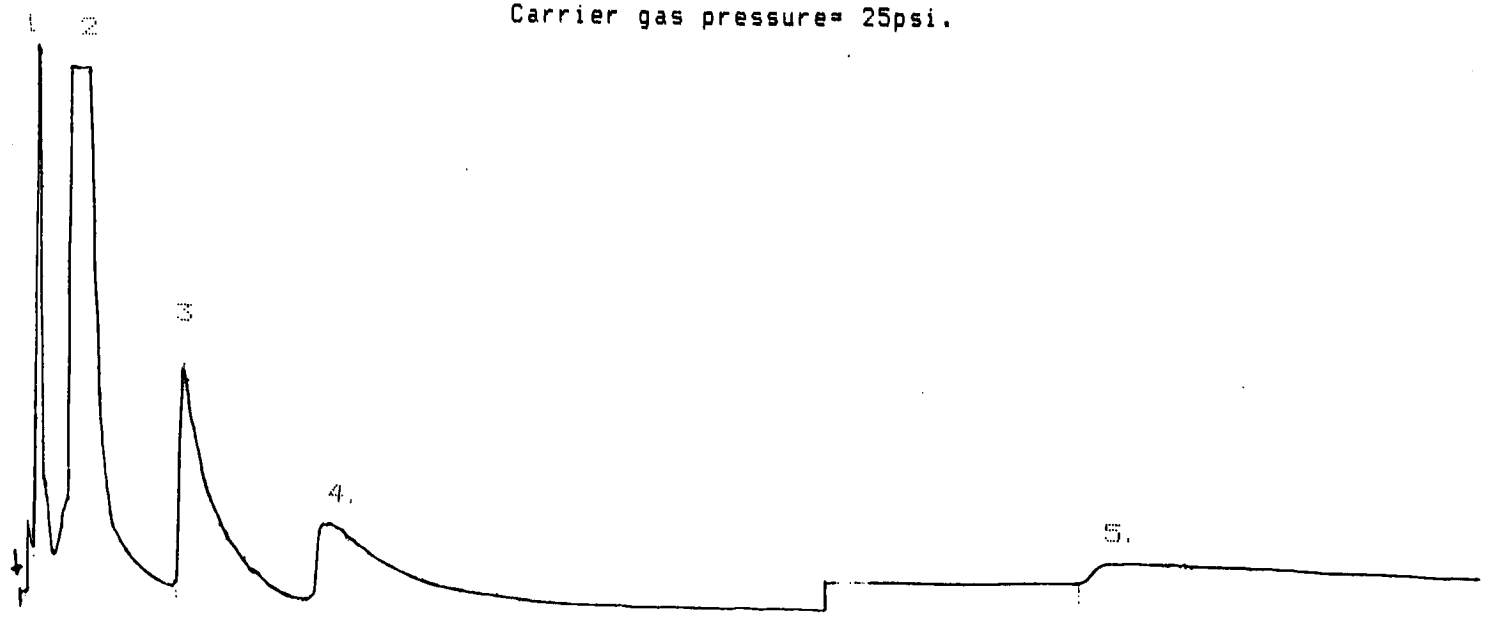


FIGURE 4.9

Alcohols at 120C.

PGC 221 B1 CEN.

Chart Speed= 0.5 cm/min.

Carrier Gas Pressure= 25psi.

1. n-Propanol.
2. Butanol.
3. 2,2-Dimethyl,1-Propanol.
4. 2-Methyl, 2-Butanol.
5. 2-Butanol.

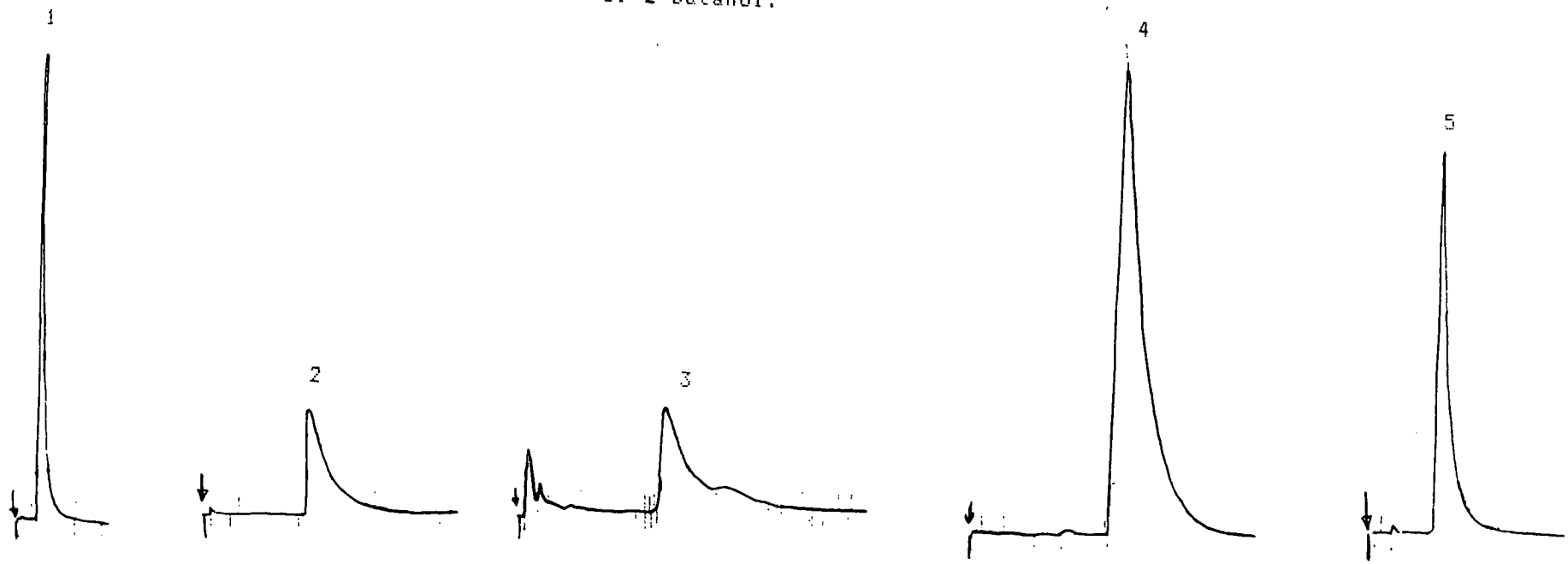


Table 4.I

Temperature of hydrogen treatment / °C	Surface Area of PGC 221 B1 CEN /m^2g^{-1}
Untreated material	78
430	77
630	77
830	77
1030	80

FIGURE 4.10

Alcohols at 120C.

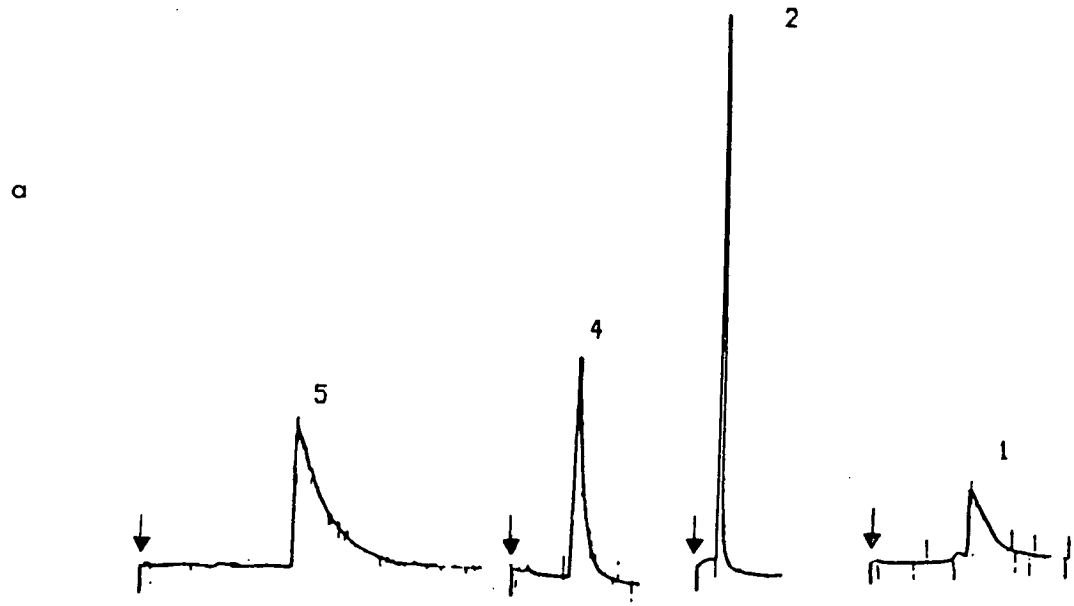
(a). Hydrogen treated PGC 221 B1 CEN at 630C.

(b). Hydrogen treated PGC 221 B1 CEN at 1030C.

1. Butanol.
2. n-Propyl Alcohol.
3. 2,2-Dimethyl,1-propanol.
4. 2-Butanol.
5. 2-Methyl,2-Butanol.

Chart Speed= 0.5cm/min.

Carrier Gas Pressure= 25psi.



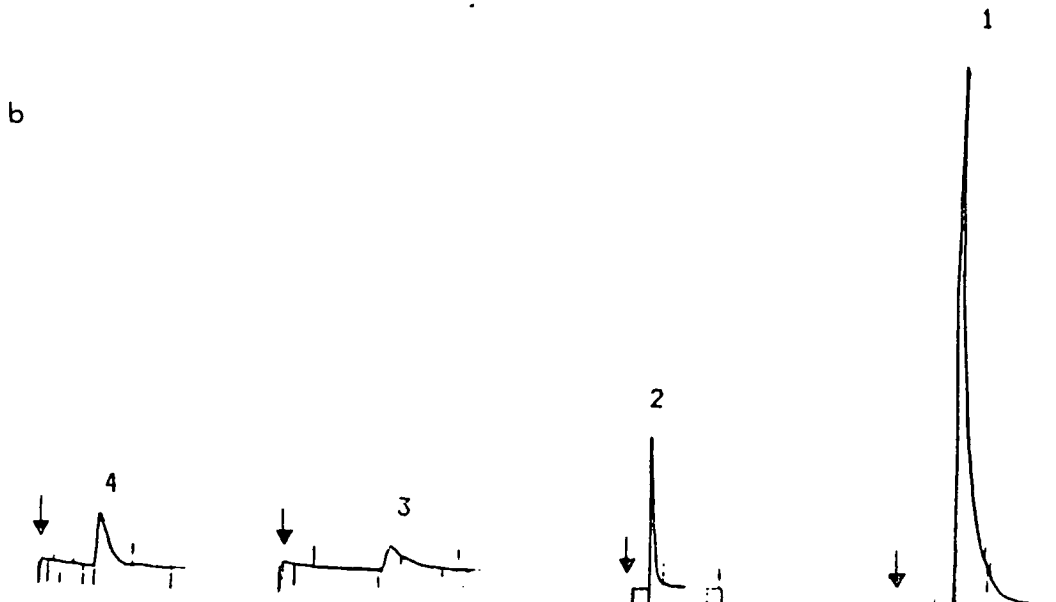


FIGURE 4.11

KETONES at 120C.

The column containing Hydrogen and Toluene treated PGC 221 B1 CEN (630C),

1. Acetone
2. Methyl Ethyl Ketone.
3. Methyl Iso-Propyl Ketone.
4. Methyl n-Propyl Ketone.
5. Methyl Iso-Butyl Ketone.

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

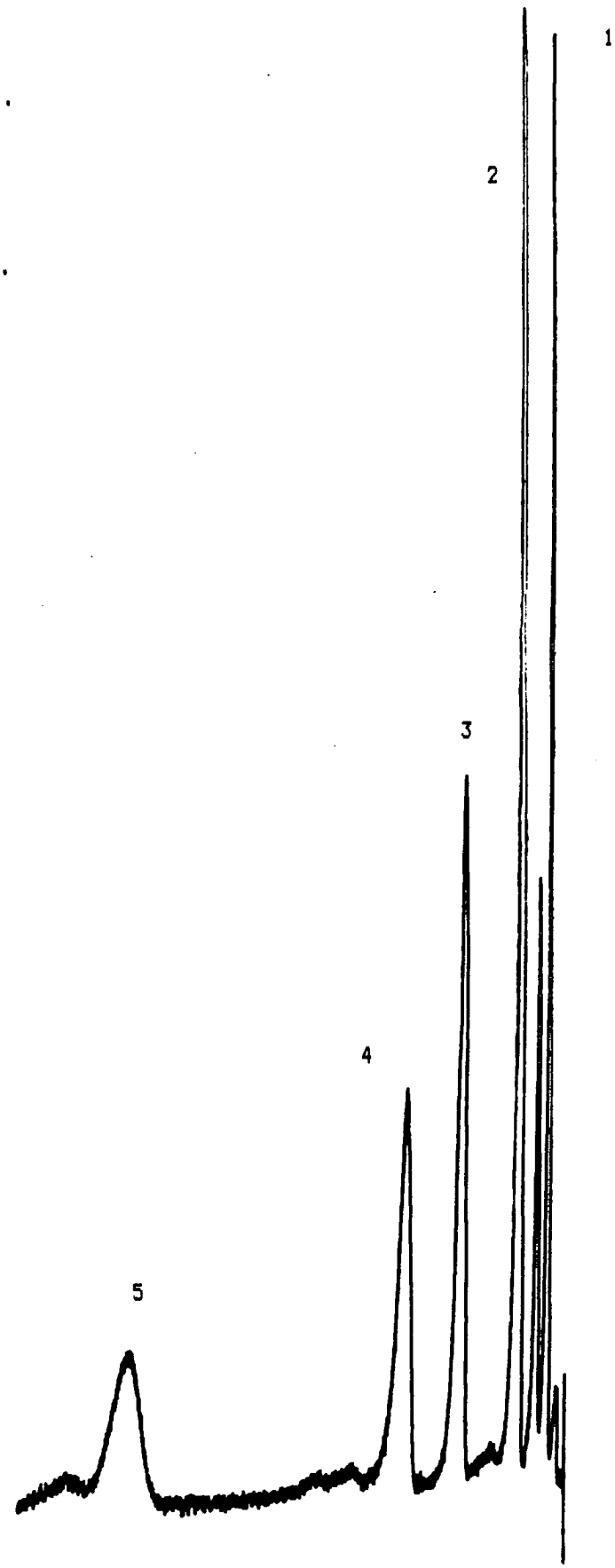


FIGURE 2.12

Ketones at 120C.

Hydrogen and Toluene treated PGC 221 B1 CEN (630C), left for 90min. at 300C with carrier gas running through the column.

1. Acetone
2. Methyl Ethyl Ketone
3. Methyl Iso-Propyl Ketone
4. Methyl n-Propyl Ketone
5. Methyl Iso-Butyl Ketone.

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

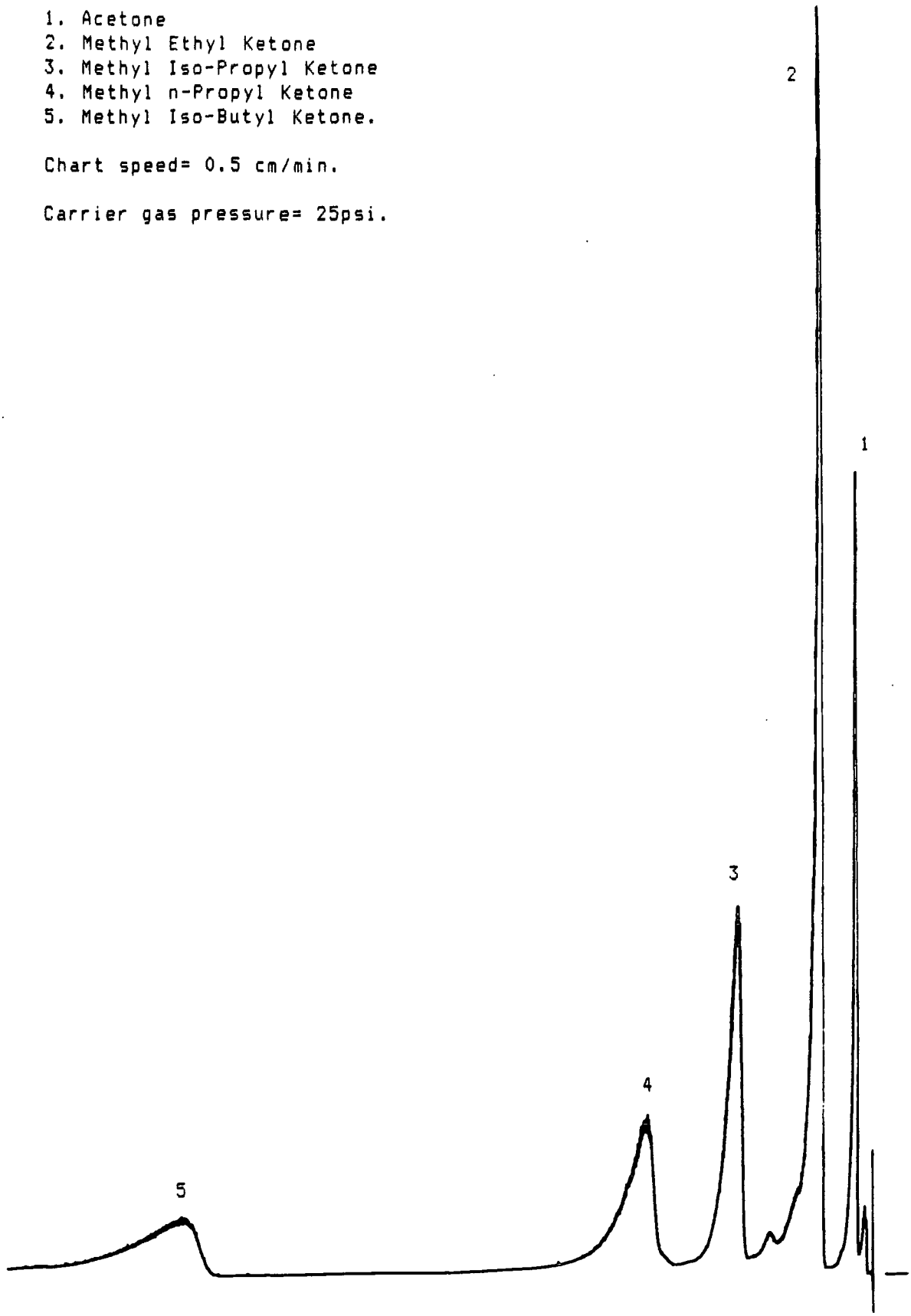


FIGURE 4.13

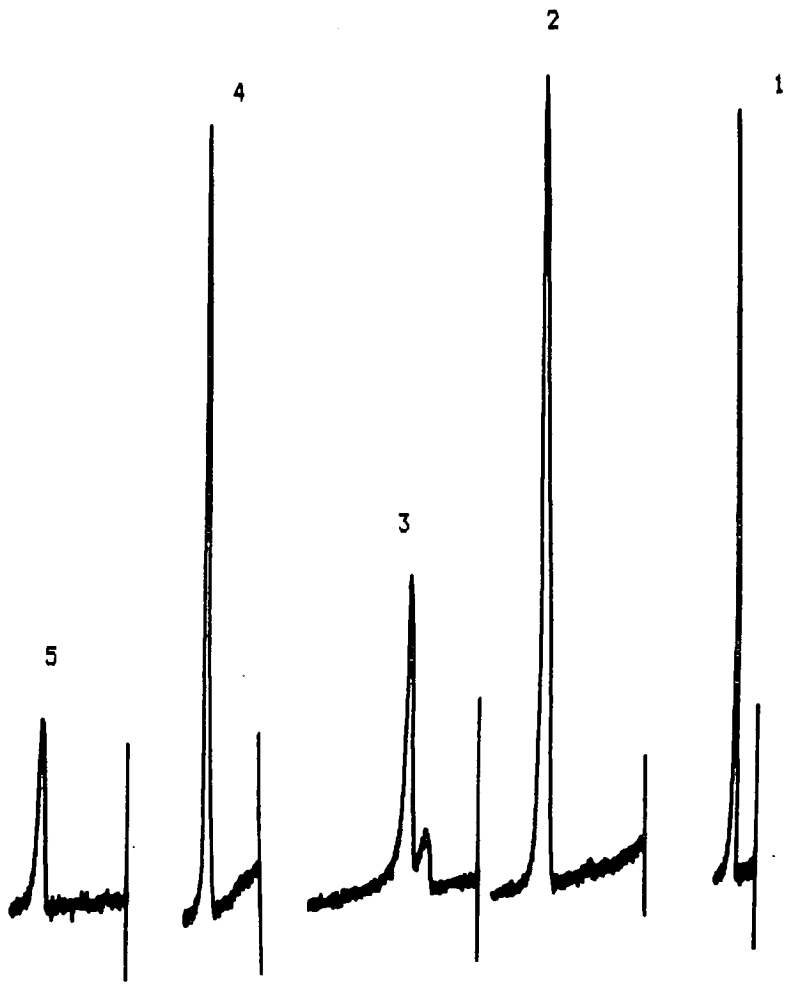
ALCOHOLS at 120C.

Hydrogen and Toluene treated PGC 221 B1 CEN (630C).

1. n-Propanol.
2. 2-Methyl 2-Butanol.
3. 1-Butanol.
4. 2-Butanol.
5. 2,2-Dimethyl 1-Propanol.

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.



ALKANES at 120C.

FIGURE 4.14

Hydrogen and Toluene treated PGC 221 B1 CEN (630C).

1. Methane
2. Propane
3. Iso Butane
4. Butane
5. Pentane

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

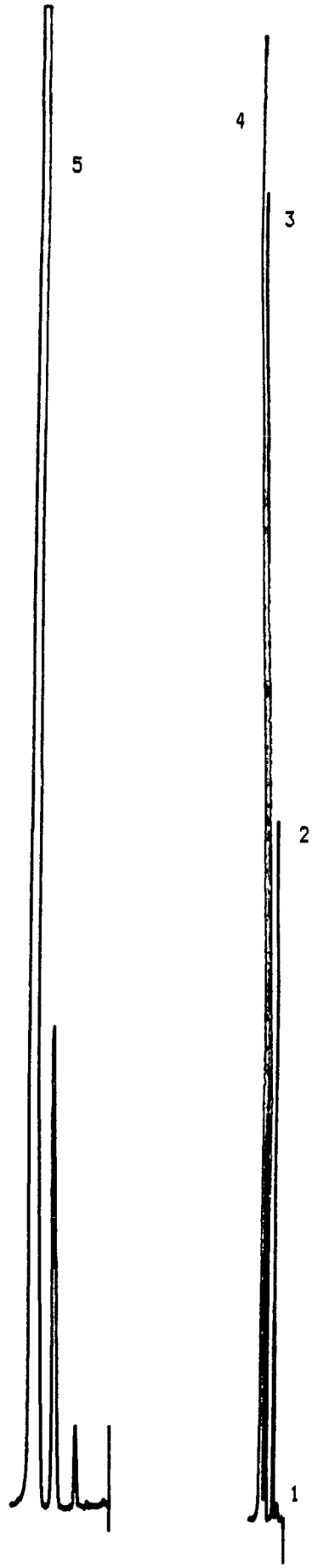


Table 4.II

k^1 Values on Hydrogen and Toluene treated PGC 221 B1 CEN (at 630°C)

Column dimensions approx 1/8" x 60cm, amount injected = 0.1-0.4µl H_2 used as the carrier gas during treatment (corresponds to Figures 4.11-4.14).

Compound	Untreated Material	Treated at 630°C (GC Column 1)	After GC Column 1 was exposed to 300°C for 100 min	Treated at 630°C (GC Column 2) (duplicate)
Acetone	2.41	1.73	2.36	1.83
Methyl ethyl ketone	10.8	6.45	10.5	6.61
Methyl iso propyl ketone	34.5	15.7	34.6	16.1
Methyl n-propyl ketone	61.8	24.7	59.0	25.4
Methyl iso butyl ketone	214	70.9	216	70.2
Butanol	18.1	8.10	15.8	8.83
2-Butanol	11.3	6.09	10.6	6.44
n-Propanol	2.94	1.82	2.73	2.11
2 me,2-butanol	25.8	14.1	27.7	13.8
2,2 dimethyl, 1-propanol	25.2	11.5	-	11.5
Propane	0.65	0.55	0.82	0.57
Butane	3.00	2.27	3.63	2.38
Iso Butane	2.00	1.64	2.55	1.76
Pentane	18.3	9.73	20.8	9.90
Surface Area				$75 m^2 g^{-1}$

Table 4.III

Heat of adsorption (ΔH) values of certain analytes on hydrogen/ toluene (H&T) treated and untreated PGC 221 B1 CEN

Solute	$-\Delta H$ on untreated mat./kJmol^{-1} ($-\Delta H_1$)	$-\Delta H$ on H&T treated mat./kJmol^{-1} ($-\Delta H_2$)	Decrease in ΔH after H&T treatment $\lvert\Delta H_1 - \Delta H_2\rvert$/ kJmol^{-1}
Methyl iso-propyl ketone	45.7 ± 0.5	38.7 ± 1.3	7.0
Pentane	43.4 ± 0.6	36.8 ± 0.6	6.6
Benzene	44.9 ± 1.3	42.3 ± 0.7	2.6
t-butyl alcohol	43.3 ± 0.7	32.6 ± 0.9	10.7
n-Butyl chloride	45.0 ± 1.0	38.0 ± 0.3	7.0
Acetonitrile	26.1 ± 0.9	21.0 ± 0.8	4.9

Table 4.IV

k^1 of solutes and toluene and nitrogen (T&N) treated PGC 221 B1 CEN (at 630°C and 300°C) (Also see Figures 4.15-4.23)

GC conditions: Column dimensions = 1/8" x 60cm, Amount injected = 0.1-0.4ul, 105-210u mesh used.

Compound	Untreated material	N&T treated material (at 630°C) Column 1	N&T treated material (at 300°C) Column 2	After columns exposed to 300°C for 100 minutes with carrier gas running Col.1	Col. 2
Acetone	2.41	1.78	1.81	2.26	2.00
Methyl Ethyl Ketone	10.8	6.00	6.06	8.84	8.65
Methyl Iso Propyl Ketone	34.5	13.9	14.3	24.3	26.5
Methyl n-Propyl Ketone	61.8	22.1	23.0	42.0	44.9
Methyl iso butyl ketone	214	58.4	64.6	129	155
Butanol	18.1	7.78	7.94	12.0	13.5
2 Butanol	11.3	5.67	5.88	8.68	11.7
n-propanol	2.94	1.94	1.94	2.42	2.76
2-methyl, 2-Butanol	25.8	12.0	13.3	19.9	25.7
2,2-dimethyl 1-propanol	25.2	9.94	11.3	16.1	21.4
Propane	0.65	0.56	0.56	0.63	0.53
Butane	3.00	2.17	2.19	2.79	2.24
Iso Butane	2.00	1.67	1.81	2.05	-
Pentane	18.3	8.72	9.31	13.4	13.0
Surface Area		$75 m^2 g^{-1}$	$78 m^2 g^{-1}$		

FIGURE 4.15

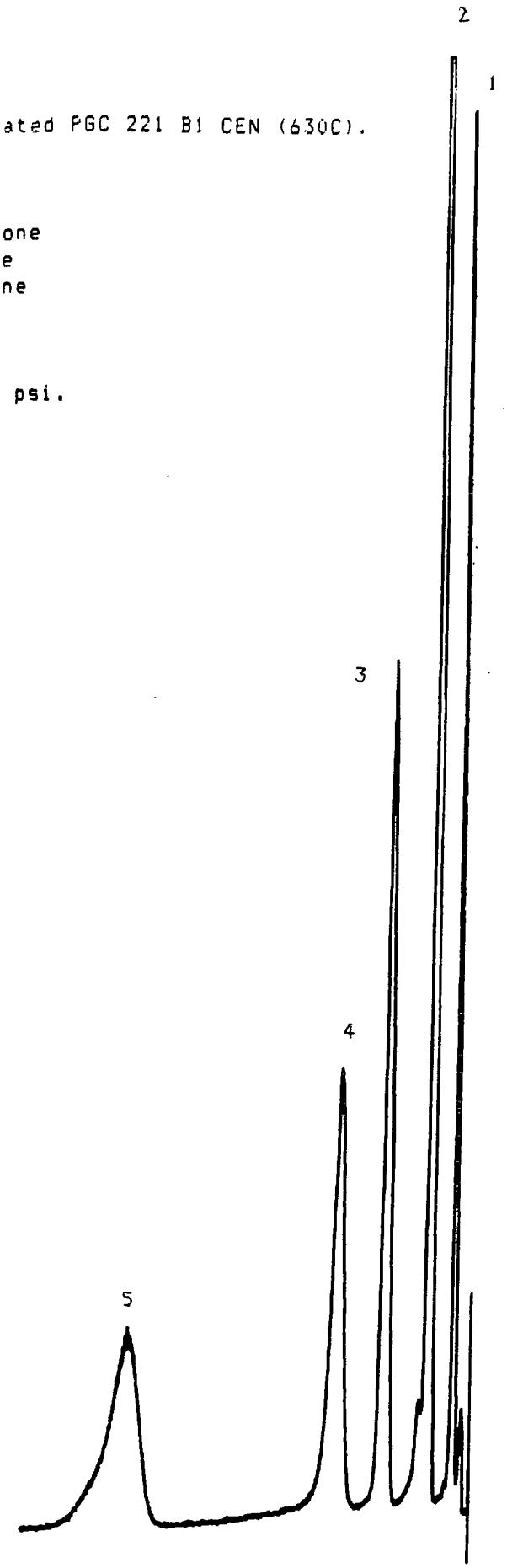
Ketones at 120C.

Toluene and Nitrogen treated PGC 221 B1 CEN (630C).

1. Acetone
2. Methyl Ethyl Ketone
3. Methyl Iso-Propyl Ketone
4. Methyl n-Propyl Ketone
5. Methyl Iso-Butyl Ketone

Chart speed= 0.5cm/min.

Carrier gas pressure= 25 psi.



Ketones at 120C.

FIGURE 4.16

Nitrogen and Toluene treated PGC 221 B1 CEN (630C), left for 90min. at 300C with carrier gas running through the column.

1. Acetone
2. Methyl Ethyl Ketone
3. Methyl Iso-Propyl Ketone
4. Methyl n-Propyl Ketone
5. Methyl Iso-Butyl Ketone.

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

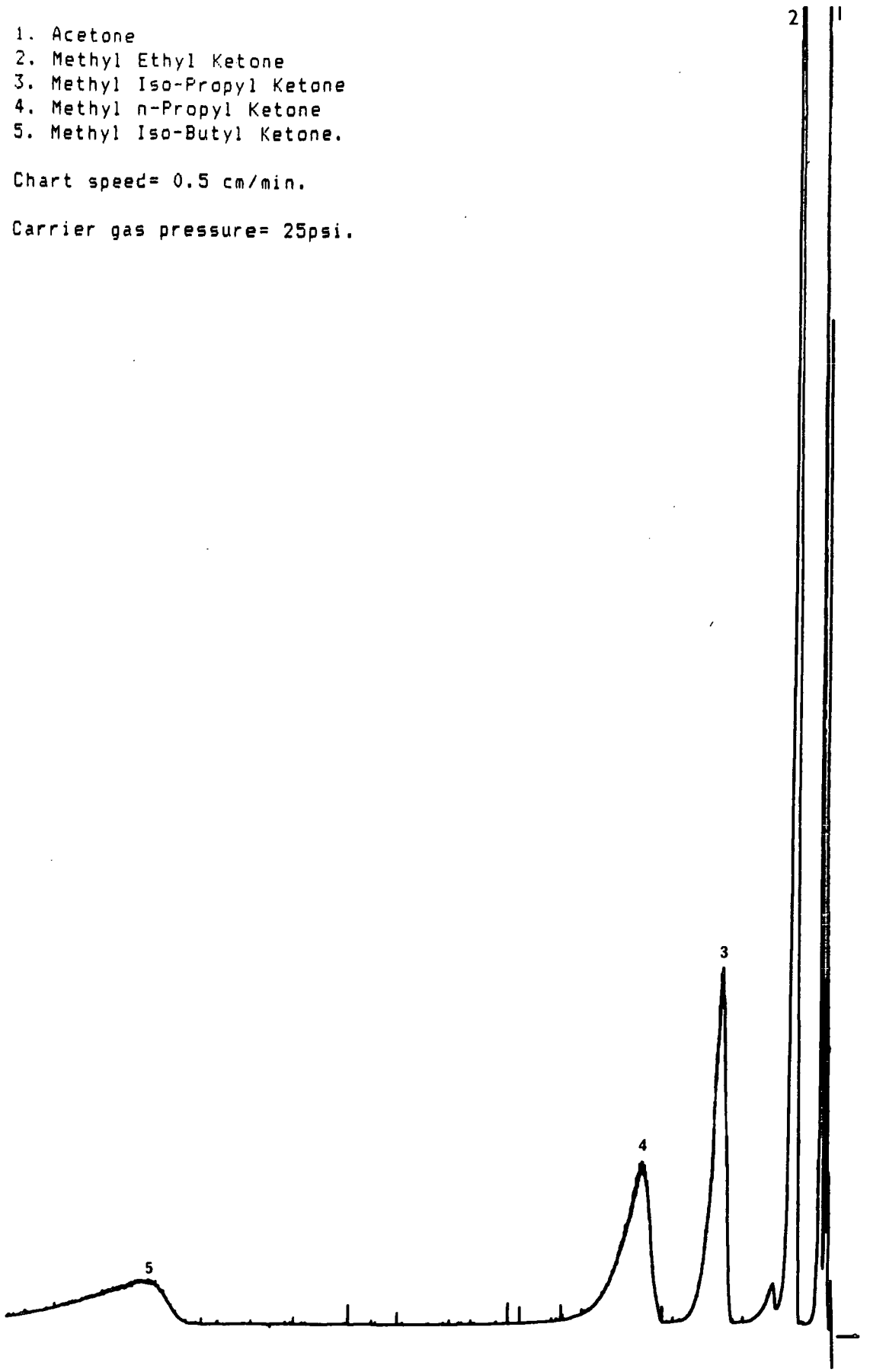


FIGURE 4.17

Alcohols at 120C.

Nitrogen and Toluene treated PGC 221 B1 CEN (630C).

1. 1-Butanol
2. 2-Butanol
3. 2-Methyl, 2-butanol
4. n-Propanol
5. 2,2-Dimethyl,1-propanol

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

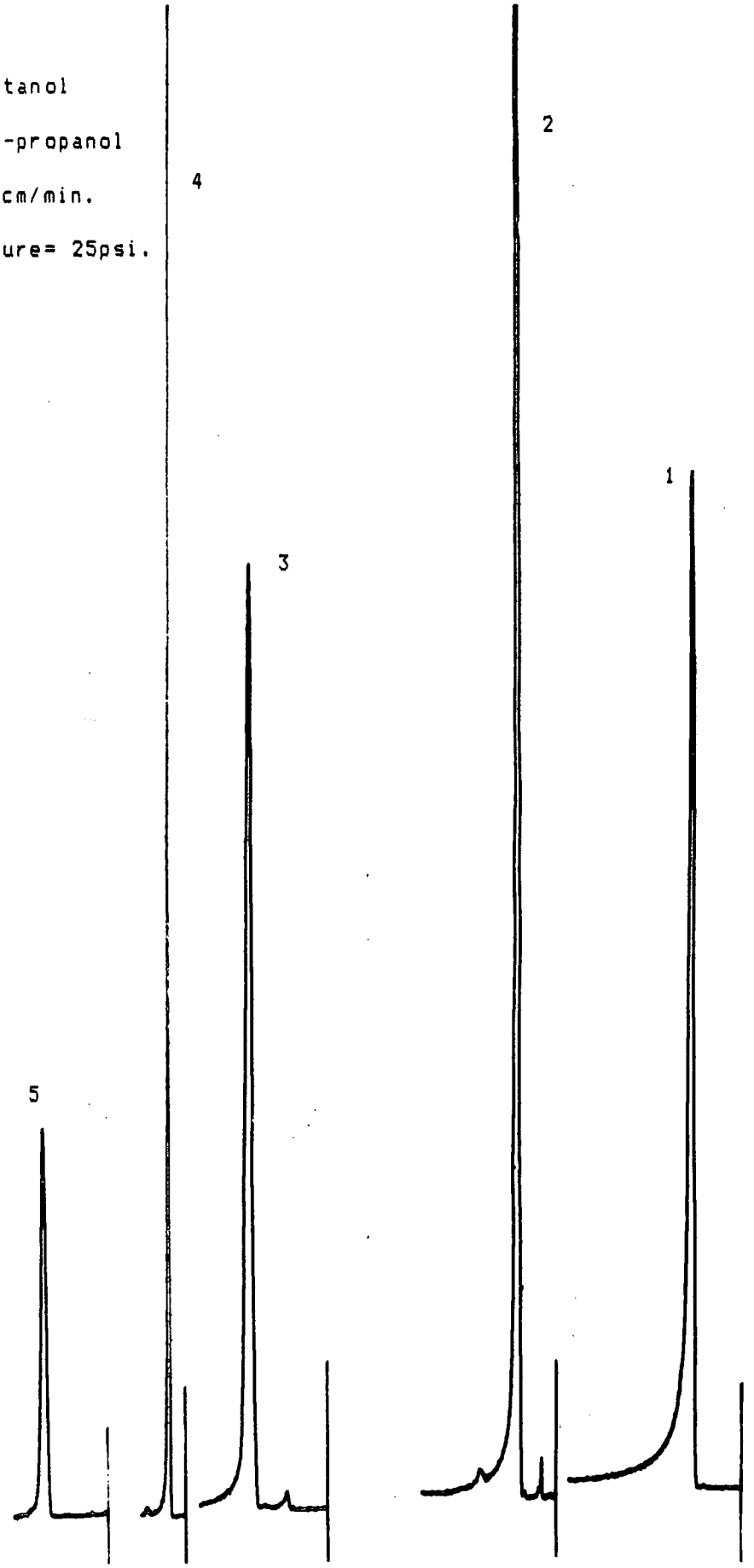


FIGURE 4.18

Alcohols at 120C.

The column containig Nitrogen and Toluene treated PGC 221 B1 CEN (630C), left for 90min, at 300C with carrier gas running through the column.

1. 2-Methyl,2-butanol
2. n-Propanol
3. 1-Butanol
4. 2-Butanol
5. 2,2-Dimethyl,1-propanol.

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

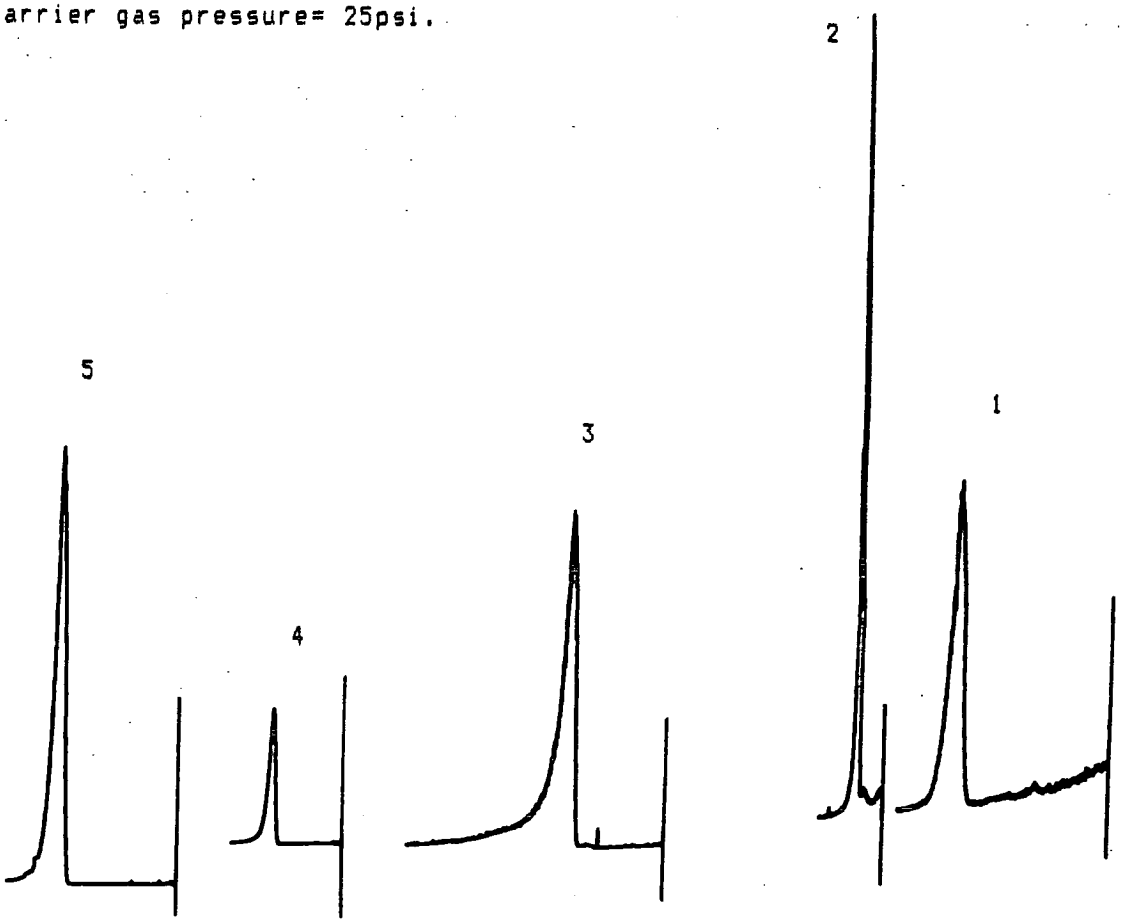


FIGURE 4.19

Alkanes at 120C

Nitrogen and Toluene treated PGC 221 B1 CEN (630C).

1. Propane
2. Iso-Butane
3. Butane
4. Pentane

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

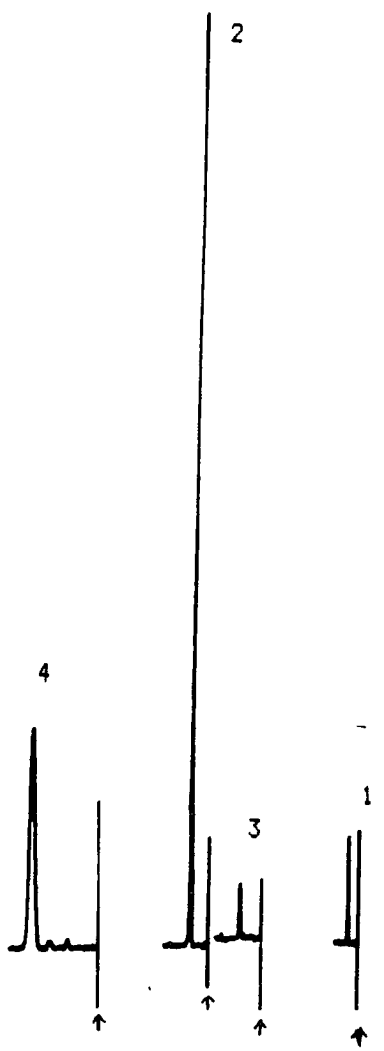


Table 4.V

k^1 Values on Hydrogen and Hexane (H&H) treated PGC 221 B1 CEN (at 630°C)

GC conditions as in Table IV.
Also see Figures 4.24-4.28.

Compound	k^1 at 120°C		
	Untreated material	H&H treated material	After column exposed to 300°C for 100 min.
Acetone	2.41	2.00	2.00
Methyl ethyl ketone	10.8	7.76	7.63
Methyl iso propyl ketone	34.5	19.8	19.0
Methyl, n-propyl ketone	61.8	34.2	32.2
Methyl, iso butyl ketone	214	101	89.3
Butanol	18.1	11.1	11.1
2-Butanol	11.3	7.47	7.45
n-Propanol	2.94	2.29	2.36
2-methyl, 2-Butanol	25.8	16.9	16.5
2,2-dimethyl 1-propanol	25.2	14.3	14.0
Propane	0.65	0.53	0.55
Butane	3.00	2.29	2.41
Iso Butane	2.00	1.65	1.73
Pentane	18.3	10.5	10.4

Surface Area = $69 m^2 g^{-1}$

FIGURE 4.20

ALKANES at 120C.

Nitrogen and Toluene treated PGC 221 B1 CEN (630C), left for 90min. at 300C with carrier gas running through the column.

1. Propane
2. Iso Butane
3. Butane
4. Pentane

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

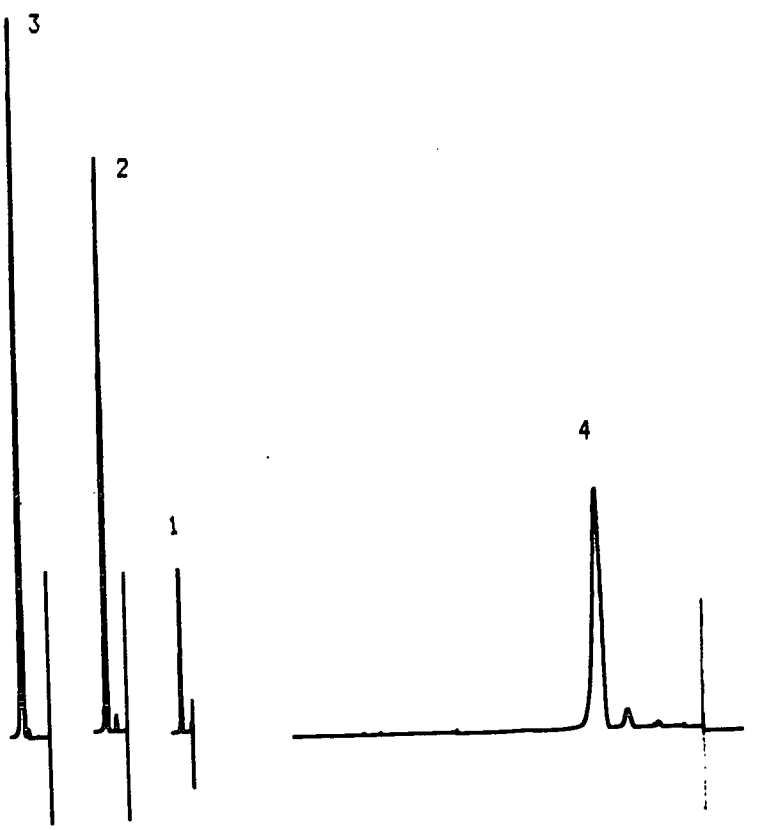


FIGURE 4.21

Ketones at 120C

Nitrogen and Toluene treated PGC 221 B1 CEN (300C).

1. Acetone
2. Methyl Ethyl Ketone
3. Methyl Iso-Propyl Ketone
4. Methyl n-Propyl Ketone
5. Methyl Iso-Butyl Ketone

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

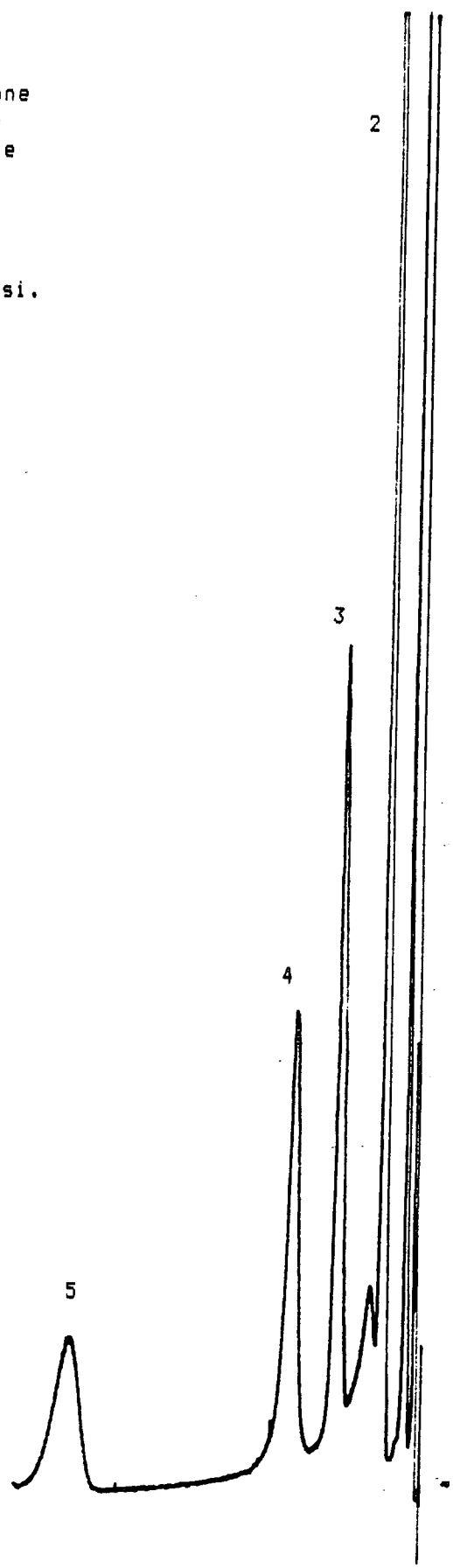


Table 4.VI

The ratios of k^1 on toluene and hydrogen (T&H) treated PGC to k^1 on hexane and hydrogen (H&H) treated PGC

k^1 values were recorded at 120°C.
(T&H) and (H&H) treatments carried out at 630°C. PGC 221 B1 CEN used.

Analyte	k^1 on T&H treated PGC 221 B1 CEN k^1 (T&H)	k^1 retention on H&H treated PGC 221 B1 CEN k^1 (H&H)	k^1(T&H)/ k^1(H&H)
Acetone	1.83	2.0	0.92
Methyl ethyl ketone	6.61	7.76	0.85
Methyl iso propyl ketone	16.1	19.8	0.81
Methyl, n-propyl ketone	25.4	34.2	0.74
Methyl, iso butyl ketone	70.2	101	0.70
Butanol	8.83	11.1	0.80
2-Butanol	6.44	7.47	0.86
n-Propanol	2.11	2.29	0.92
2-methyl, 2-Butanol	13.8	16.9	0.82
2,2-dimethyl 1-propanol	11.5	14.3	0.81
Propane	0.57	0.53	1.08
Butane	2.38	2.29	1.04
Iso Butane	1.76	1.65	1.06
Pentane	9.90	10.5	0.94

FIGURE 4.22

Alcohols at 120C.

Nitrogen and Toluene treated PGC 221 B1 CEN (300C).

1. n-Propanol
2. 1-Butanol
3. 2-Methyl, 2-butanol
4. 2-Butanol
5. 2,2-Dimethyl, 1-propanol

Chart Speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

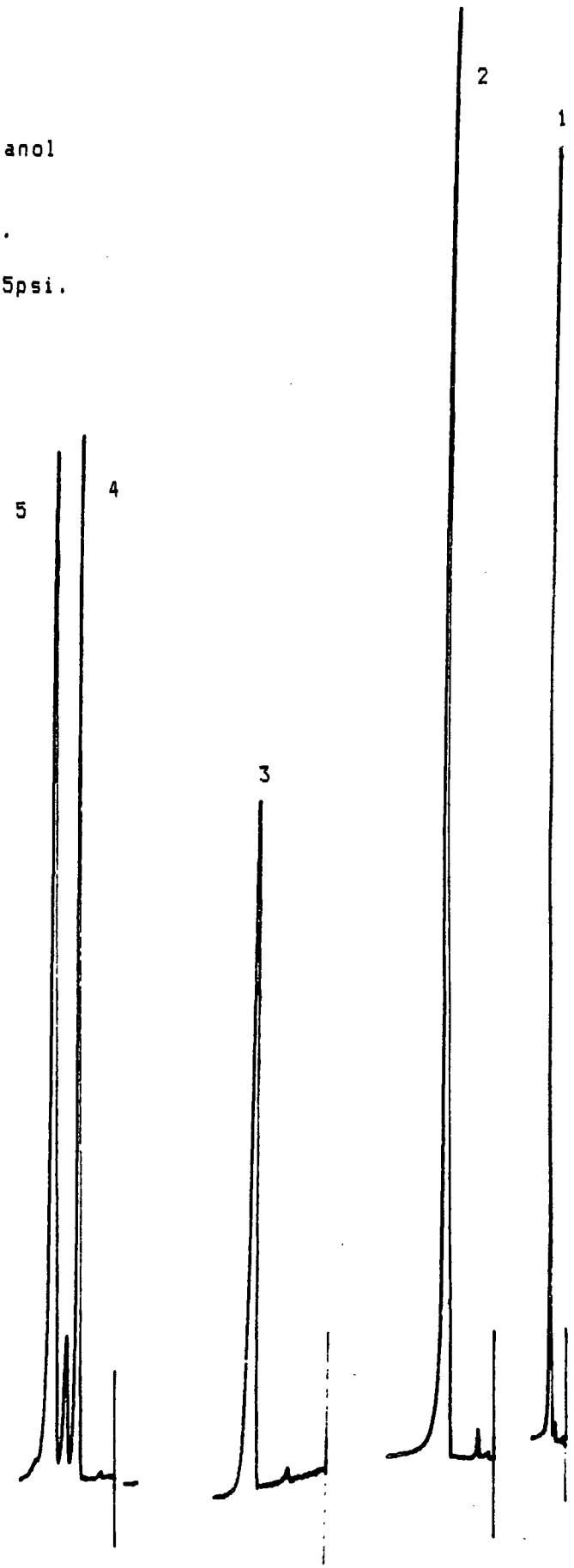


FIGURE 4.23

Alkanes at 120C.

Nitrogen and Toluene treated PGC 221 B1 CEN (300C).

1. Methane
2. Propane
3. Iso-Butane
4. Butane
5. Pentane

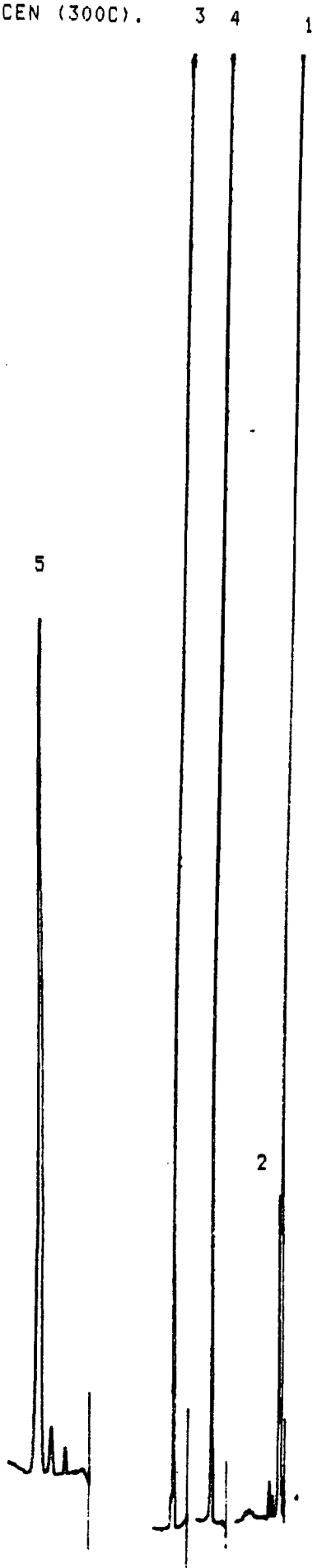


FIGURE 4.24

Ketones at 120C.

Hexane and Hydrogen treated PGC 221 B1 CEN (630C).

1. Acetone
2. Methyl Ethyl Ketone
3. Methyl Iso-Propyl Ketone
4. Methyl n-Propyl Ketone
5. Methyl Iso-Butyl Ketone

Chart speed= 0.5cm/min.

Carrier gas pressure= 25 psi.

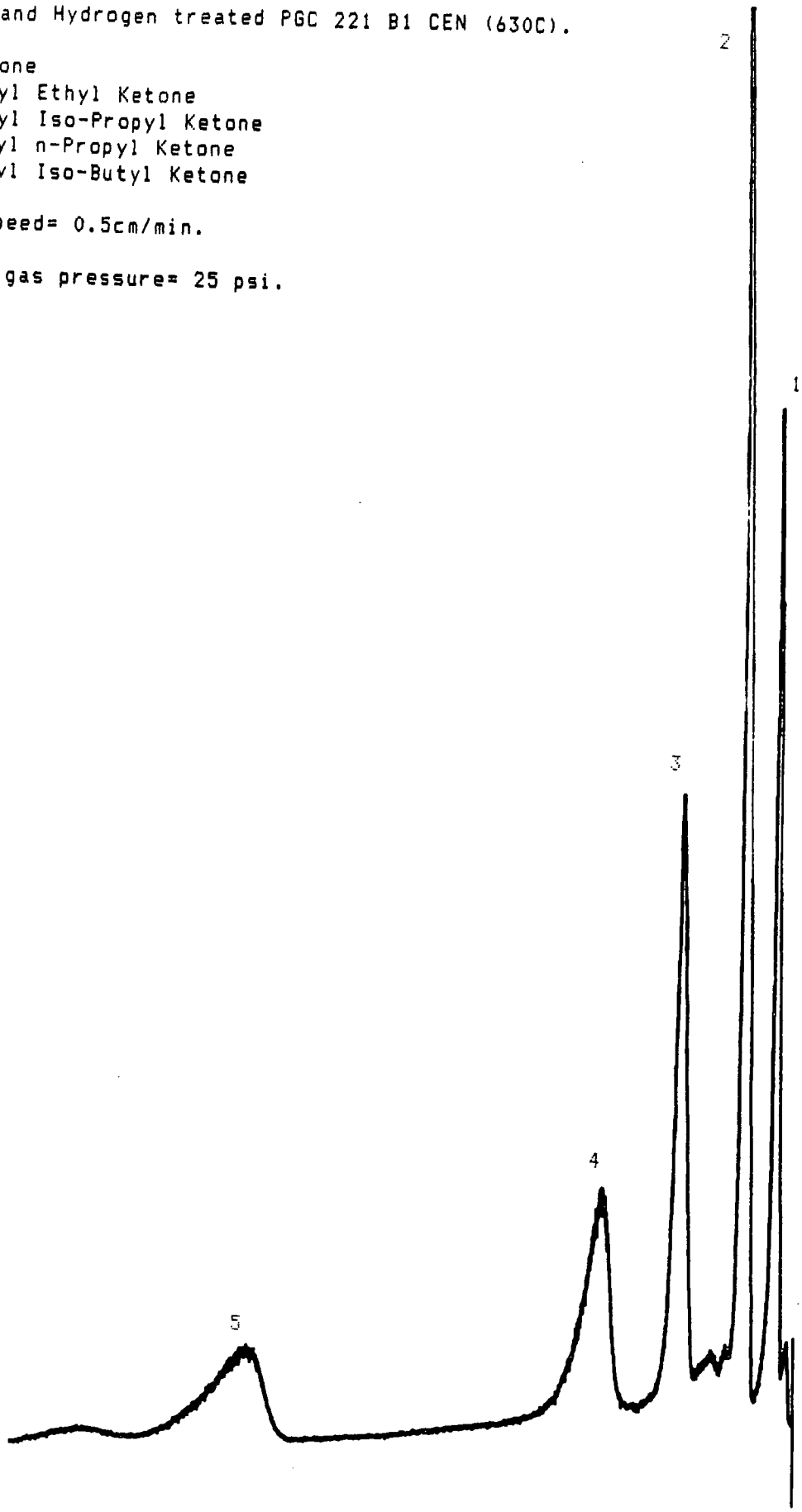


FIGURE 4.25

KETONES at 120C.

The column containing Hydrogen and Hexane treated PGC 221 B1 CEN (630C), left for 90min. at 300C with the carrier gas running through the column.

1. Acetone
2. Methyl Ethyl Ketone.
3. Methyl Iso-Propyl Ketone.
4. Methyl n-Propyl Ketone.
5. Methyl Iso-Butyl Ketone.

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

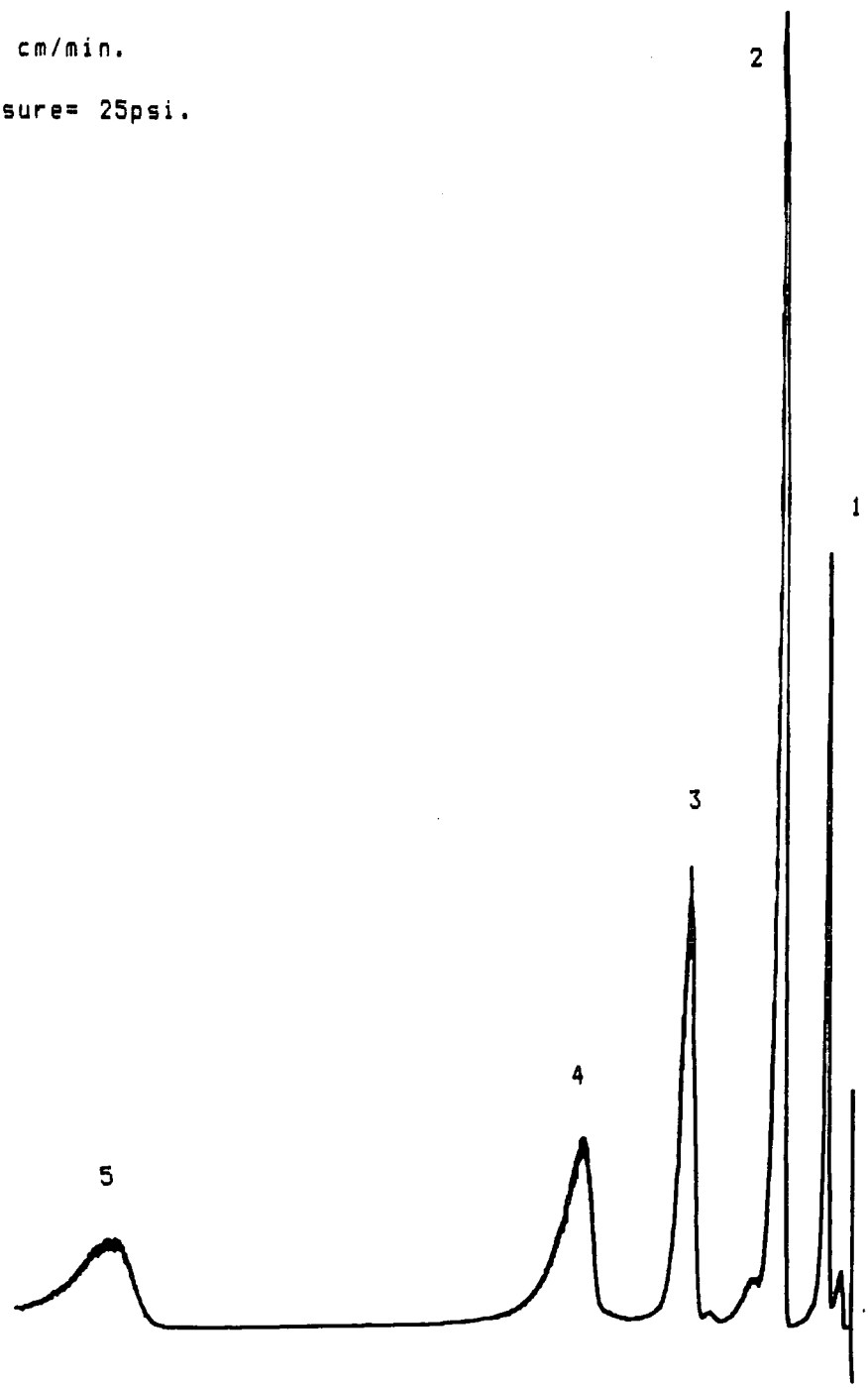


FIGURE 4.26

Alcohols at 120C.

Hydrogen and Hexane treated PGC 221 B1 CEN (630C).

1. 2-Butanol
2. 1-Butanol
3. 2-Methyl,2-butanol
4. 2,2-Dimethyl,1-propanol
5. n-Propanol

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

FIGURE 4.27

Alcohols at 120C.

The column containing Hydrogen and Hexane treated PGC 221 B1 CEN (630C), left for 90min at 300C with carrier gas running through the column.

1. n-Propanol
2. 2-Butanol
3. 2-Methyl,2-butanol
4. 1-Butanol
5. 2,2-Dimethyl,1-propanol

Chart speed= 0.5 cm/min.

Carrier gas pressure= 25psi.

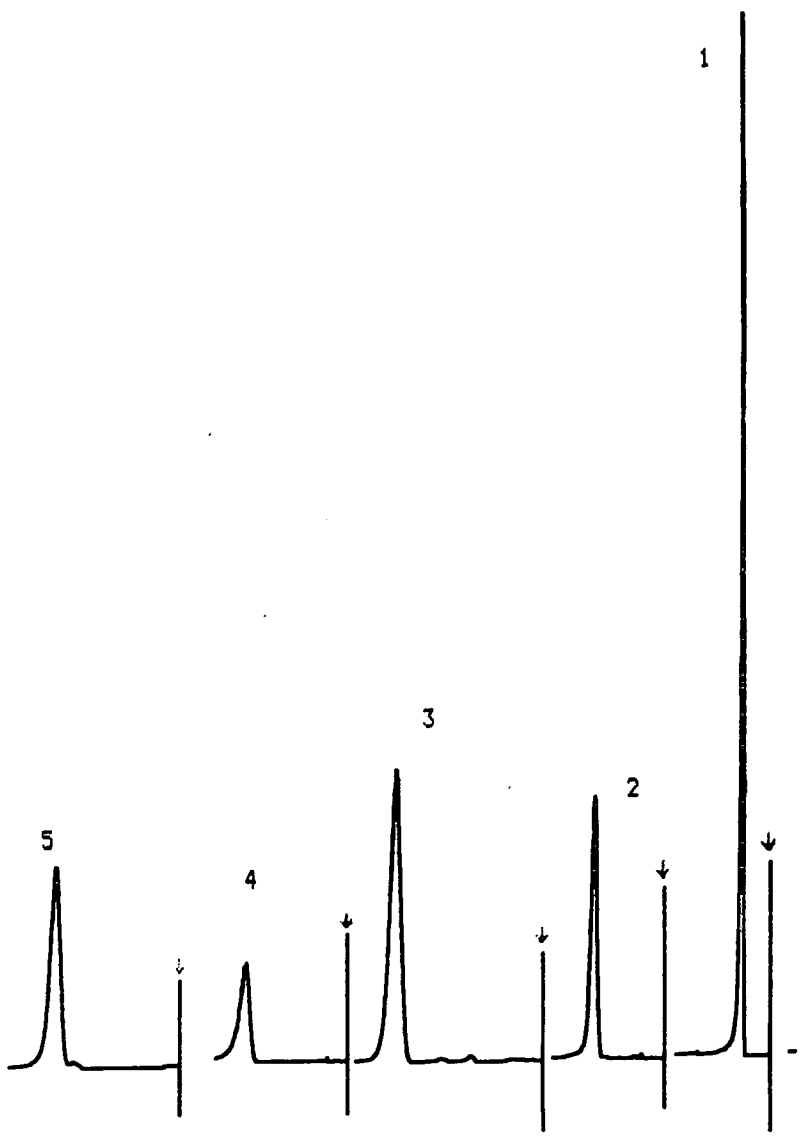


FIGURE 4.28

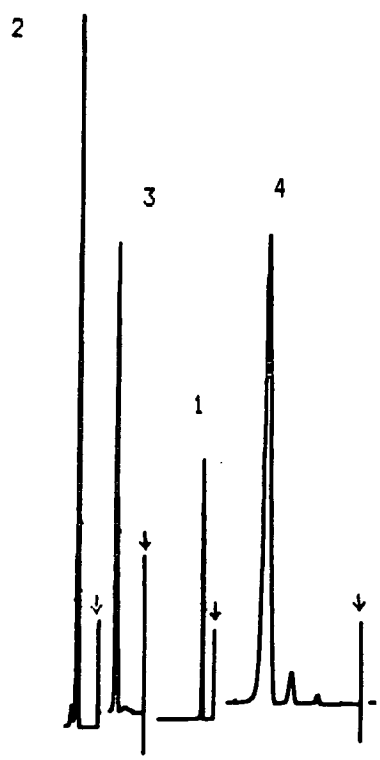
Alkanes at 120C.

Hydrogen and Hexane treated PGC 221 B1 CEN (630C), left for 90min. at 300C with carrier gas running through the column.

1. Propane
2. Iso-Butane
3. Butane
4. Pentane

Chart speed= 0.5cm/min.

Carrier gas pressure= 25psi.



EXPERIMENT V - Method and Results (see Section 4.6.5)

FIGURE 4.29

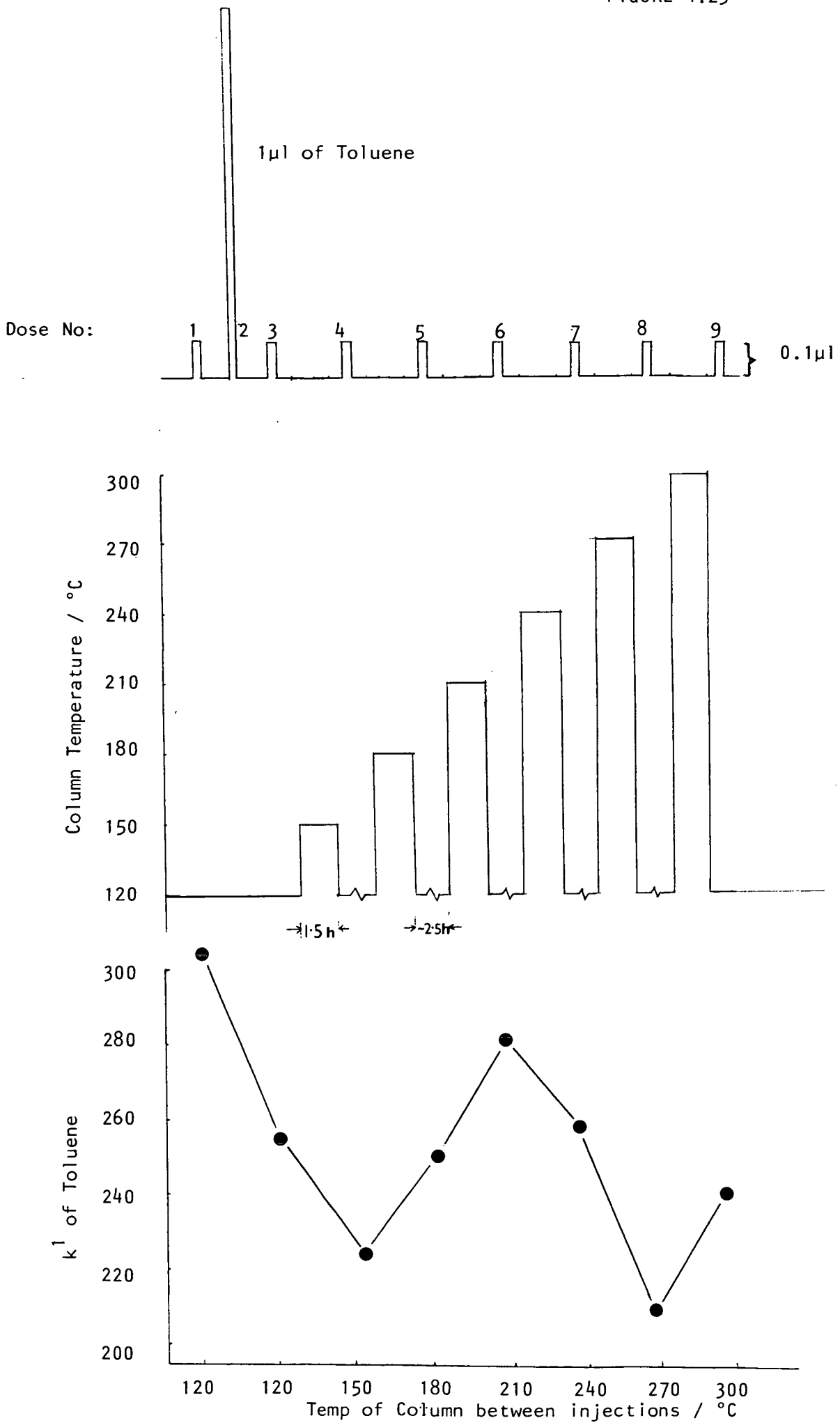
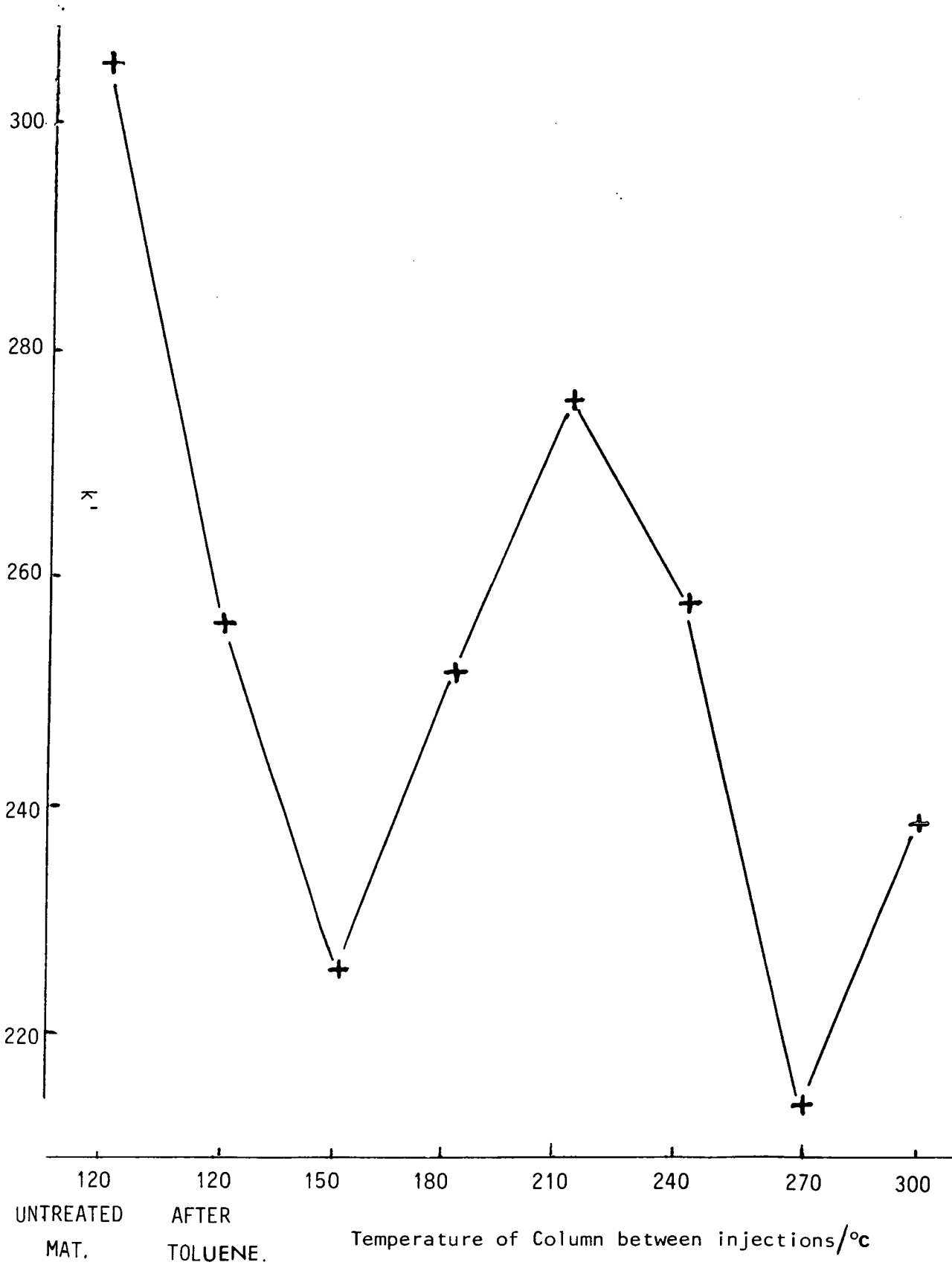


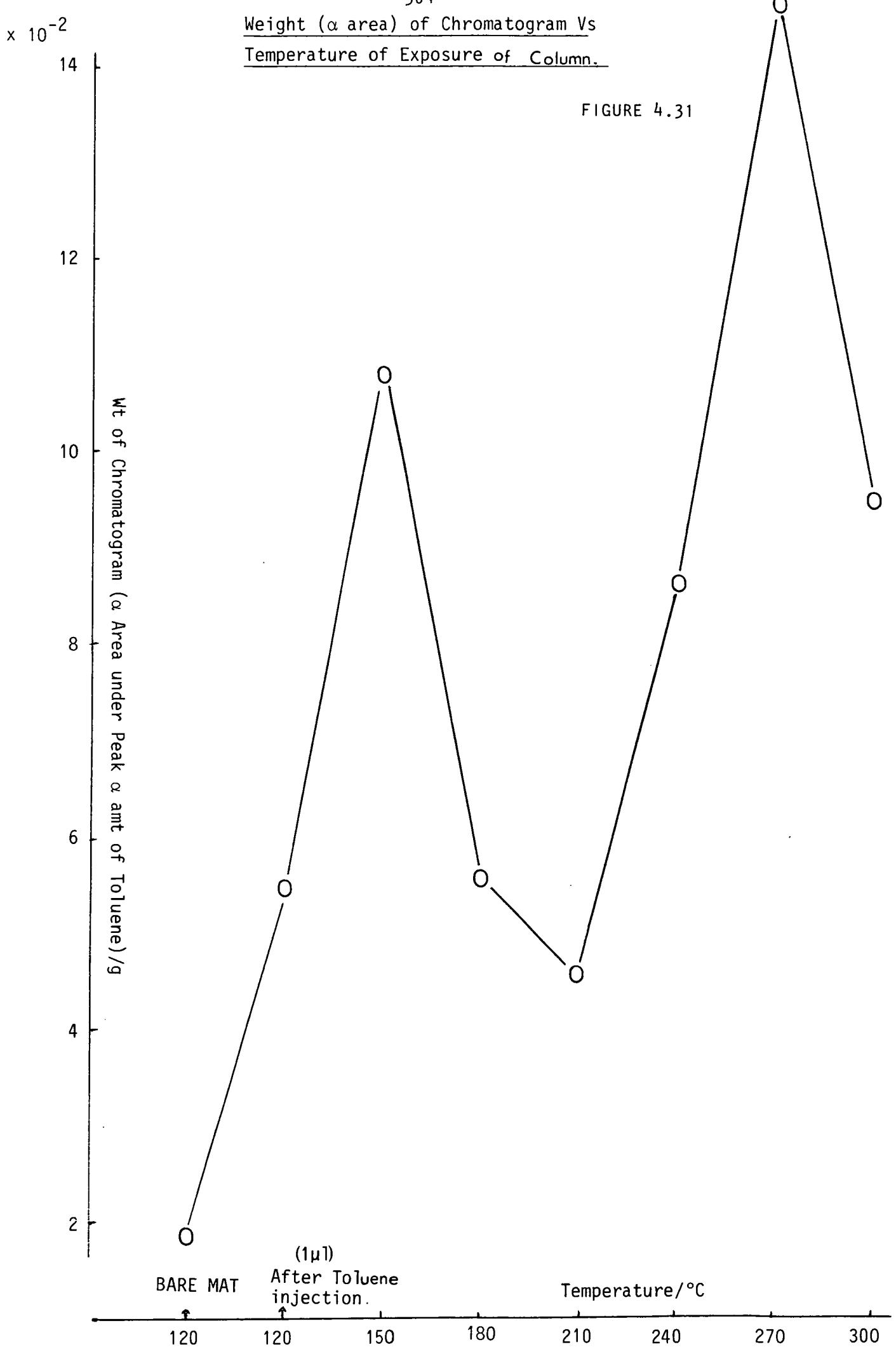
FIGURE 4.30

k^1 of toluene Vs Temperature of Exposure of Column between injections (PGC 221 B1 CEN)



Weight (α area) of Chromatogram Vs
Temperature of Exposure of Column.

FIGURE 4.31



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CHAPTER 5

The Study of the Chromatographic Properties of the Coated PGC Surfaces with Non Ionic Surfactants using HPLC

CHAPTER 5

The Study of the Chromatographic Properties of the Coated PGC Surfaces with Non Ionic Surfactants Using HPLC

5.1 INTRODUCTION

The surface of an adsorbent inside a HPLC column can be dynamically coated with a surfactant by including the surfactant (also called the additive) in the eluent. This would drastically alter the chromatographic properties of the packing material. The concentration of additive and the amount of organic solvent in the mobile phase can be adjusted to achieve the optimum separation of components in a sample mixture.

In this work, hydrophilic character is introduced on to the hydrophobic PGC by including a non-ionic surfactant such as Tween 80 or Span 80 in the eluent.

Tween 80 is Polyethylene oxide (20) Sorbitan mono-oleate ($C_{17}H_{33}C^{O}$ - $OCH_2(CHOH)_4CH_2O(C_2H_2O)_{20}H$). Span 80 is Sorbitan mono-oleate ($C_{17}H_{33}C^{O}$ - $CH_2(CHOH)_4CH_2OH$).

Separations due to the ionic nature of surfactants are described elsewhere in this thesis (Chapter 6).

The work mentioned in the literature describes the non-ionic

chromatography on dynamically coated silica [1-3] and reverse phase silica [4] surfaces. Ghaemi and Wall [1] used silica as well as zirconia and ceria in their work.

In this chapter, non-ionic chromatography on dynamically coated PGC surfaces are described. Where possible, the chromatographic properties of coated PGC and those of coated silica surfaces are compared.

At this stage, it is appropriate to review the research carried out in the field of "non-ionic chromatography on dynamically modified surfaces".

5.1.1 Literature Survey Related to the Separations (Non-Ionic) on Dynamically Coated Adsorbents

Ghaemi and Wall [1] dynamically interacted the silanol groups ($Si\text{-}O^{-}H^{+}$) of silica with a quaternary ammonium cation (R_4N^{+}) to produce a reverse phase material.

The analytes used by Ghaemi and Wall were multi nuclear aromatics. Polar or non-polar groups were attached to the aromatic nuclei of the analytes. By and large these analytes were regarded as hydrophobic. The hydrophobicity of the molecules relative to one another depended upon the groups attached to their structures.

They [1] discovered that analyte retention increased with increasing concentration of R_4N^+ species on the eluent. The greater the R_4N^+ concentration in the mobile phase, the larger the number of reverse phase terminals created on the silica surface for analyte retention. The solute retention increased with R_4N^+ concentration in eluent up to the critical micelle concentration (CMC). Beyond CMC, the analyte retention dropped due to the R_4N^+ species forming micelle in the eluent.

Ghaemi and Wall [1] reported that the solute retention also increased with the carbon number of the additive (R_4N^+ species) due to the increased hydrophobicity of the coated solid phase.

They [1] found that the selectivities observed on these solvent generated hydrophobic packing are quite similar to those displayed by ODS-TMS (Octadecylsilica-trimethylsilane) bonded phases.

Ceria and zirconia adsorbents were less polar in comparison with silica. Such materials can be dynamically modified with certain additives to control the retention of certain compounds and hence achieve the best separation of a solute mixture.

The separation of compounds could also be controlled by varying the polarity of the mobile phase at a constant concentration of additive in the eluent. The change in polarity of eluent is achieved by altering the ratio of organic solvent to water, in the

mobile phase [1].

Similar researches to those of Chaemi and Wall [1] were carried out by Hansen et al [2,3]. They too produced a reverse phase material by dynamically interacting a quatenary ammonium salt [R_4N^+] with $Si\text{-}O^-H^+$ groups of silica gel, in the pH range of 5-8.

Hansen et al discovered that the analyte retention (i) increased with pH of eluent (5-8) due to the formation of more $Si\text{-}O^-$ terminals for the interaction wtih R_4N^+ species; (ii) increased with the concentration of R_4N^+ species in the eluent up to CMC and then decreased due to the micelle formation in the eluent; (iii) decreased with increasing content of organic solvent in the mobile phase; and (iv) decreased with increasing concentration of cations in the eluent, since these extra cations compete with R_4N^+ species for $Si\text{-}O^-$ terminals on the silica surface.

Hansen and co-workers stated that the surface polarity and hence the analyte retention can be controlled by varying the carbon chain length of R_4N^+ species. They also found that the retention of hydrogen bonding compounds decreasing with increasing coverage of the silica surface with R_4N^+ groups due to the unavailability of the Si-OH terminals.

This dynamically prepared reverse phase material described by Hansen et al is useful in the separation of analytes such as

phenols and cresols found in body fluids [2]. Such a solid phase could also be used to analyse mixtures of amines [3].

Hansen and co-workers [2,3] reported that the main mechanism of separation is by partition of analytes between the mobile phase and the dynamically prepared reverse phase material. In addition to this partition, any solutes present in their ionic forms could display other retention mechanisms. The cationic analytes may compete with R_4N^+ species for the $Si\text{-}O^-$ sites. They suggested that the anionic analytes may interact with R_4N^+ units in the eluent and then this neutral species may interact with the reverse phase material. Such a view on the retention of anionic solutes is different to the one held by Knox, Van de Veen and Pietrzyk. Their work is described in Chapter 6.

Ghaemi and Wall [4] did further chromatographic work on dynamically prepared surfaces. They produced a reverse phase material by dynamically coating a Tween on silica gel. The polar groups of the surfactant interacted with those on the silica surface. Ghaemi and Wall found that the chromatographic properties of Tween coated silica gels are similar to those of C-18 reverse phase silica materials.

They used multi-nuclear aromatic compounds as solutes. The analyte retention initially increased with the concentration of Tween in the eluent. The analyte retention then reached a maximum and then

dropped with the increasing surfactant concentration in the mobile phase.

The initial increase in analyte retention was due to the creation of hydrophobic sites for the interaction with the analytes. The decrease in the retention, that was observed afterwards, was due to the increase in the hydrophilic character of the solid phase. This hydrophilic character is introduced on to the solid phase when a second layer of Tween is created due to the interactions between the hydrophobic parts of the first layer of Tween on the silica gel and those of the Tween molecules in the eluent. The hydroxyl groups of this second Tween layer were 'sticking out' into the mobile phase. Therefore, these OH groups would introduce hydrophilic character to the solid phase.

Ghaemi and Wall [4] discovered that the greater the chain length of the Tween used, the greater the hydrophobicity of the additive and hence the smaller the concentration of Tween required to achieve the same degree of retention for a solute.

They [4] concluded that the greater the polarity of the eluent used, the larger the analyte retention at the concentration of Tween where maximum surface hydrophobicity is seen. A similar effect was also observed by Rupprecht [5]. He suggested that the adsorption of surfactants on materials such as silica gel is influenced by a combination of three factors. (a) The interactions

between the functional groups present on the adsorbent surface and the surfactant, (b) the strength of adsorption of solvent on to the solid phase and (c) the solvation of the surfactant.

A polar solvent such as an alcohol present in an eluent, reduces the adsorption of a surfactant by competing with the additive for the adsorption sites on the solid phase. Where as, in a less polar solvent such as chloroform, the solvation of the additive leads to a reduction in the number of interactions between the surfactant and the solid phase.

An additive such as Tween can combine (solvate) with any hydrophobic constituents in a non-polar eluent. This would reduce the adsorption of Tween on to silica gel. This in turn would diminish analyte retention values. Such an observation was made by Ghaemi and Wall [4] when using eluents prepared with less polar solvents. This reduction in the number of interactions between the surfactant and the adsorbent due to the solvation effects in non polar eluents is more prominent than the competition effects found in polar eluents. This competition effect is due to the other constituents in the eluent competing with Tween for the silica surface. Since the competition effect is less than the solvation effect, Ghaemi and Wall [4] noticed that the analyte retention values increasing with increasing polar nature of the mobile phase.

Surfaces that are dynamically modified with Tween 80 can be useful

in the field of analytical chemistry. Chang [6] successfully separated proteins using Tween 80 coated diphenylsilica solumns. He achieved high recoveries (› 75%) of proteins from these columns.

Polar character was introduced on to diphenyl silica when the material was dynamically coated with Tween. This led to a reduction in the number of interactions between the solutes and the solid phase. Chang [6] reported that the elution volumes of analytes fell below the void volume of column. The retention of the proteins was apparently controlled by size exclusion. The results showed that the retention values of the proteins is a linear function of log (molecular weight) in a certain molecular weight range.

Favourable peak shapes and analyte retention values were achieved with this Tween coated diphenyl silica surface in comparison with Triton X-100 (1-[1,1-dimethyl-3,3-dimethylbutane]-4-polyethylene oxy (9.5) benzene) coated diphenyl silica materials.

Borgerding and Hinze [7] used micellar solutions of a non-ionic surfactant as mobile phases in reversed phase HPLC to chromatograph mixtures of certain aromatics. Brij 35 (polyoxyethlene (23) dodecanol), a polar additive, was considered as the non-ionic surfactant. Reverse phase C-18 silica was used as the packing material.

Brij 35 was being deposited on the solid phase during chromatography. This led to the introduction of polarity on to the C-18 silica phase. Borgerding and Hinze then observed diminished analyte retention values and a change in the selectivity of the solid phase. The column efficiencies diminished with increasing thickness of Brij 35 on the packing material due to the increasing resistance to mass transfer [7].

The deposition of Brij 35 on the solid phase continued beyond the CMC. Borgerding and Hinze claimed that this was in contrast to the behaviour of the ionic additives.

5.1.2 Chromatography on PGC - Before and After the Dynamic Modification with Tween 80 or Span 80

The preceeding section described the research on coated silica based materials. The rest of this chapter will discuss the work on Tween 80, as well as Span 80 coated PGC surfaces. Where possible the observed experimental results on modified PGC are explained with reference to the research mentioned in the literature survey.

In this work, the change in the retention of certain aromatic compounds were studied on PGC by altering the (i) concentration of surfactant at constant concentration of organic solvent, and (ii) ratio of water:organic solvent at constant concentration of surfactant, in the eluent.

The column efficiency is studied with and without Tween on the PGC surface.

At the end, an attempt was made to rejuvenate the PGC by dynamically washing the Tween 80 coated PGC with Dioxan.

5.2 EXPERIMENTAL

5.2.1 Materials and Equipment

The packing material, PGC 84/85B CEN (7μ) was kindly supplied by Dr. B. Kaur of Wolfson Liquid Chromatography Unit at the Chemistry Department, University of Edinburgh.

The eluent was prepared using methanol of HPLC grade. The columns were packed using methanol and acetone of HPLC grade. These solvents were purchased from BDH Chemical Company of Poole, Dorset.

The solutes were Aniline, Toluene, Benzyl alcohol, Acetophenone, Phenol, Anisol, Nitrobenzene and Benzoic acid. The non-ionic surfactants were Span 80 and Tween 80. All these chemicals were purchased from Sigma Chemical Company of Poole, Dorset.

The water used in all aspects of experimental work was double distilled in the laboratory.

The ultraviolet (UV) detector, the pumps used for column packing and pumping the eluent through the HPLC system were supplied by Shandon scientific Limited of Runcorn, Cheshire. The HPLC columns (HETP pattern, 10cm long and 0.5cm wide) were leased from Shandon Scientific Limited. A Rheodyne 7125 injector valve (20µl) was used to introduce the analytes on to the column.

5.2.2 Preparation of HPLC Columns

A known weight of PGC (1.5g) was slurried in acetone and ultrasonicated for 10 minutes. The columns were packed downwards at 2000 PSI using acetone as the follower. After 100cm^3 of solvent was collected, the column was inverted so that the packing continued downwards. At this point, the solvent was changed to HPLC grade methanol and 200cm^3 was collected.

5.2.3 Experiments Performed

All the analytes were chromatographed on the bare PGC surface. The columns were operated at a flowrate of 0.4$cm^3.min^{-1}$ and a back pressure of 80 BAR. The eluent was an aqueous methanol solution (95% (v/v)).

Tween 80 solutions (600-700cm^3 of each) were prepared using the 95% methanol solution. The concentrations of Tween 80 in these solutions were 0.01, 0.02, 0.03, 0.05, 0.1 and 0.2% (w/v).

The eluent in the HPLC system was replaced with the least concentrated Tween 80 solution. The analyte retentions were monitored until steady values were reached (Figure 5.1).

The procedure mentioned in the preceeding paragraph was repeated with other Tween 80 solutions, taking care to use the solutions in the ascending order of Tween 80 concentration (Figures 5.2-5.5).

The steady solute retention values obtained, using the Tween solutions as the eluents, were plotted against the concentrations of surfactant in those solutions (Figure 5.6).

It was soon discovered that the analyte retention did not considerably change beyond the Tween 80 concentration of 0.03% in the eluent (Figure 5.6). Therefore a freshly packed column of PGC 84/85B CEN was equilibrated using the 0.03% Tween 80 solution (Tween in 95% methanol). The ratio of water to methanol in the eluent was varied whilst maintaining the eluent Tween concentration at 0.03%. The effects on column efficiency and analyte retention are displayed in Figures 5.7 and 5.8 respectively. The water to methanol ratios used in the eluents were 5:95, 70:30, 50:50 and 30:70.

Afterwards, the 30:70 methanol-water solution, which contained 0.03% Tween 80 was replaced with a 95:5 methanol-water solution which also contained 0.03% (w/v) of Tween 80. The solutes were

chromatographed, then the eluent was replaced with pure methanol in an attempt to wash off the Tween 80 from the PGC surface. After 10 hours, the pure methanol was replaced with 95% methanol and the analyte retention times were recorded. The retention of solutes did not show any change in comparison with the results obtained when using the 0.03% Tween 80 (in 95% methonol) solution as the eluent.

The pure Dioxan was used in an attempt to remove the adsorbed Tween from the PGC surface. After 25 hours of Dioxan treatment, the solutes were chromatographed using 95% methanol as the eluent. The results are displayed in Table 5.I.

A third PGC column was packed and the analytes were chromatographed on the bare PGC, as described at the beginning of this section. The eluent was replaced with 0.01% (w/v) Span 80 (in 95% methanol) solution, and solute retentions were noted until steady values were reached (Figure 5.11). The eluent was then replaced with 0.02% (w/v) Span 80 (in 95% v/v methanol) solution and analyte retention values were again recorded until steady values were reached (Figure 5.12). These stable retention values are displayed in Table 5II. It was impossible to further increase the Span 80 concentration in the eluent as this surfactant is far less soluble than Tween 80, in 95% (v/v) methanol.

The steady analyte k^1 values were recorded on a freshly packed PGC

84/85B CEN column using 0.1% Span 80 (in 95% v/v acetonitrile) solution (Table 5III).

A 0.1% (w/v) Span 80 solution was prepared using 80% (v/v) acetonitrile. At this concentration of acetonitrile, a small amount of Span 80 came out of solution. This solution was therefore filtered to remove any matter that could block the HPLC system. The 0.1% Span 80 (in 95% acetonitrile) solution was then replaced with the filtered Span 80 solution as the mobile phase. The analyte retention values were recorded (Table 5.III).

The effect on analyte retention, as a result of adding water to the eluent at constant concentration of Span 80, is shown in Table 5III.

5.3 RESULTS AND DISCUSSION

5.3.1 The Introduction of Surfactant on to PGC

Initially, PGC was a hydrophobic packing material. The aromatic solutes could rest on the adsorbent with most of the heavy atoms in each analyte touching the adsorbent surface. Consequently enhanced analyte retention values resulted (Figure 5.6 and Table 5I) when solutes were chromatographed on the bare PGC.

The introduction of Tween 80 or Span 80 on to PGC resulted in the

physical adsorption of the surfactant on the adsorbent surface. The hydrophobic parts of the additive interacted with the PGC whilst the OH groups of the surfactant were 'sticking out' into the mobile phase. The dynamic modification of PGC with Span 80 or Tween 80 would therefore yield a polar solid phase for chromatography.

Now only the polar groups present on the analyte molecules could interact with the OH groups on Tween or Span 80 coated PGC. The greater the surfactant concentration in the eluent, the greater the adsorption of additive on to PGC and hence the greater the polarity of solid phase. The adsorption of surfactant and the subsequent increase in the polarity of the PGC continued up to a concentration of 0.03% of Tween in the eluent (Figure 5.6) and up to 0.02% in the case of Span (Table 5II). The change in polarity of PGC surface is reflected in the observed analyte retention values.

The introduction of those surfactants on to PGC resulted in decreasing the number of hydrophobic interactions that originally existed between the solutes and the solid phase. This is reflected in the diminished analyte retention values (Figure 5.6 and Table 5I). (Retention of solutes in Figure 5.9 can be compared with those in Figure 5.10.) The reduction in analyte retention continued up to the mobile phase concentrations of 0.03% Tween 80 (Figure 5.6). The solute retention values did not display significant changes beyond this mobile phase concentration of Tween

80 (i.e. 0.03%). It may be deduced that no further adsorption of surfactant on to PGC occurred above that surfactant concentration.

In the case of Span, the concentration of additive in the eluent (95% methanol) was increased only up to 0.02%, as it was impossible to dissolve more Span in the mobile phase.

The results in this chapter have indicated that the dynamic modification of PGC with Tween 80 or Span 80 resulted in decreasing the retention of analytes. Such observations can be compared with those of other research teams [4,7] who also discovered that the introduction of a polar additive on to a non polar adsorbent resulted in the reduction of the k^1 values of aromatic analytes.

The efficiency of column decreased after the introduction of Tween on to PGC (see Figures 5.9 and 5.10). This could be due to the non-linearity of the adsorption isotherm (uptake of solute vs amount of sample in eluent) and/or unsatisfactory mass transfer from solid phase to the mobile phase. More experiments are needed to confirm the real cause behind the observed reduction in efficiency. The dependence of analyte peak width on sample size would confirm the non-linearity of the adsorption isotherm. The dependence of peak width on eluent velocity would lead to the conclusion that the diminished efficiency is due to unsatisfactory mass transfer.

If sample size and eluent velocity have no effect on peak width,

the reduction in column efficiency is the result of uneven distribution of material inside the column, due to uneven fractionation of packing.

The selectivity of PGC changed at lower eluent concentrations (< 0.05%) of Tween due to the changing polarity of the PGC. This effect is displayed by the crossing of graphs in Figure 5.6. Borgerding and Hinze [7] also noticed that the dynamic modification of a hydrophobic solid phase with a surfactant such as Brij 35 resulted in changing the polarity and hence the selectivity of that solid phase.

5.3.2 The Consequences of Increasing the Water to Methanol Ratio in the Eluent, at a Constant Mobile Phase Concentration of Surfactant

The effects on analyte retention values and column efficiencies were noted by varying the ratio of water to methanol in the eluent (Figures 5.8 and 5.7). The mobile phase concentration of Tween was maintained at 0.03% throughout the entire experiment.

The selectivity of PGC changed with increasing water to methanol ratio in the mobile phase. This change in selectivity is shown by the crossing of graphs in Figure 5.8. The solute retention values increased with increasing water to methanol ratio in the eluent. Figure 5.8 and Table 5III display the results on Tween coated and

Span coated PGC respectively.

Increasing the water to methanol ratio would increase the polarity of eluent. Consequently, the solid phase would become less polar in comparison to the mobile phase. The greater the polarity of eluent, the greater the time spent by the aromatic solutes on the solid phase. Consequently, the analyte k^1 values would increase. Such observations can be compared with those of Hansen et al [2] and Ghaemi and Wall [4] who altered the analyte retention by varying the polarity of the mobile phase whilst maintaining the polarity of the solid phase constant. Ghaemi and Wall changed the polarity of eluent in two ways, (i) by changing the solvent used to prepare the mobile phase whilst keeping the other eluent parameters (contents of water and surfactant) constant, (ii) by altering the ratio of water to organic solvent in the eluent whilst keeping the surfactant concentration constant. Hansen et al [2] used method (ii) to alter the polarity of eluent. Both the above methods yielded similar results. This means that an increase in eluent polarity resulted in enhanced analyte retention values.

The amount of surfactant and the solvent to water ratio in an eluent can be controlled to achieve the optimum separation of a sample mixture.

At a constant mobile phase concentration of Tween, the column efficiency decreased with increasing water to methanol ratio in the

eluent (Figure 5.7). The reasons for observing diminished column efficiencies were discussed in the previous section.

5.3.3 Rejuvenation of PGC

Table 5I shows that analyte retention increased after the passage of Dioxan through the column containing Tween 80 coated PGC. The results indicate that Dioxan was able to remove a considerable amount of surfactant from the PGC surface. Pure methanol, however, failed to remove a significant amount of Tween from the PGC. It may be deduced that, when using methanolic eluents, Tween coated PGCs would behave as stable, normal phase chromatographic materials.

5.4 FUTURE WORK

Figure 5.6 shows that the lowest analyte k^1 values were first observed at a mobile phase concentration of 0.03% Tween 80. The breakthrough method [8] can be employed to discover the amount of surfactant adsorbed on to PGC at a Tween concentration of 0.03% (in 95% methanol). The ratio of water to organic solvent in the eluent can be altered, whilst maintaining the mobile phase concentration of Tween 80 at 0.03%, to establish the relationship between the mobile phase composition and the amount of Tween adsorbed on to PGC. A freshly packed PGC column should be used at each mobile phase composition. This is an experiment to discover whether the

water to methanol ratio in the eluent affects the adsorption of additive on to the adsorbent.

PGC can be modified with other Tweens to establish the minimum eluent concentration of each Tween required to reach the lowest retention values for a set of analytes. That is, similar graphs to those in Figure 5.6, can be drawn using the results obtained on each Tween coated PGC surface. Then the dependence of the minimum retention values obtained for each solute upon the carbon number of additive can be established.

The results of experiments mentioned in the preceeding paragraph can be treated further. The minimum eluent concentration of each Tween required to obtain the lowest retention values can be noted. These are the minimum concentrations of the additives required to obtain maximum adsorption of Tween on to the PGC surface. The dependence of these concentrations upon the carbon numbers of the Tweens can be established. These experiments would be useful in understanding more about the adsorption of Tweens on to PGC.

The ratio of water to organic solvent in the eluent must be kept constant throughout the experiment.

A reverse phase material such as ODS (octadecylsilica) Hypersil can be used in a similar series of experiments to those described in section 5.2.3 to see whether such a material behaves in a similar

way to PGC.

Other additives such as Carbowax and Steric acids can be dynamically coated on PGC to investigate whether the chromatographic properties of such surfaces are similar to those of Tween 80 coated PGC.

FIG. 5.1 k' vs VOLUME OF ELUENT.

0.01 % Tween 80 in 95 % methanol as eluent.

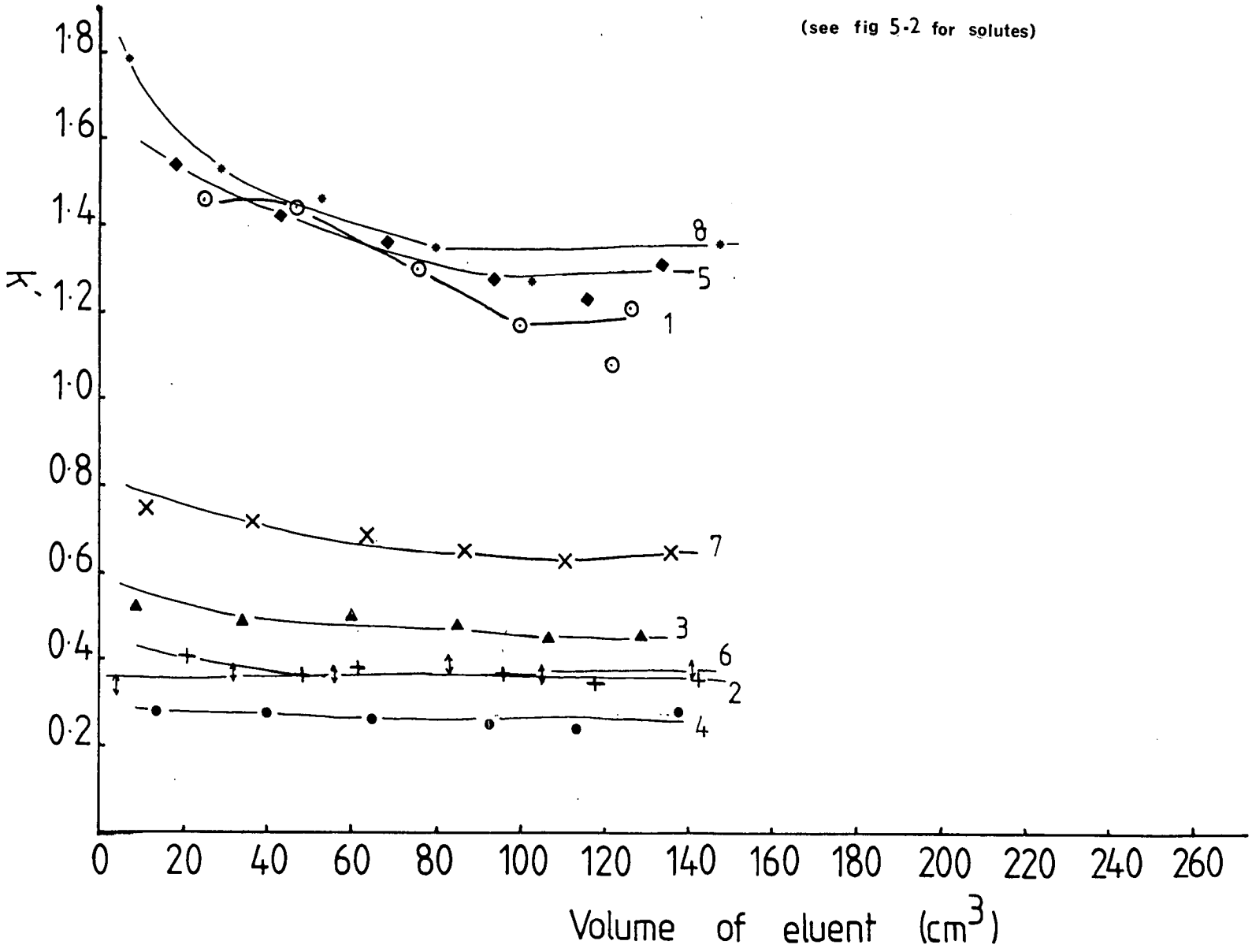


FIG. 5-2 k vs VOLUME OF ELUENT.

0.02 % Tween 80 in 95 % methanol as eluent.

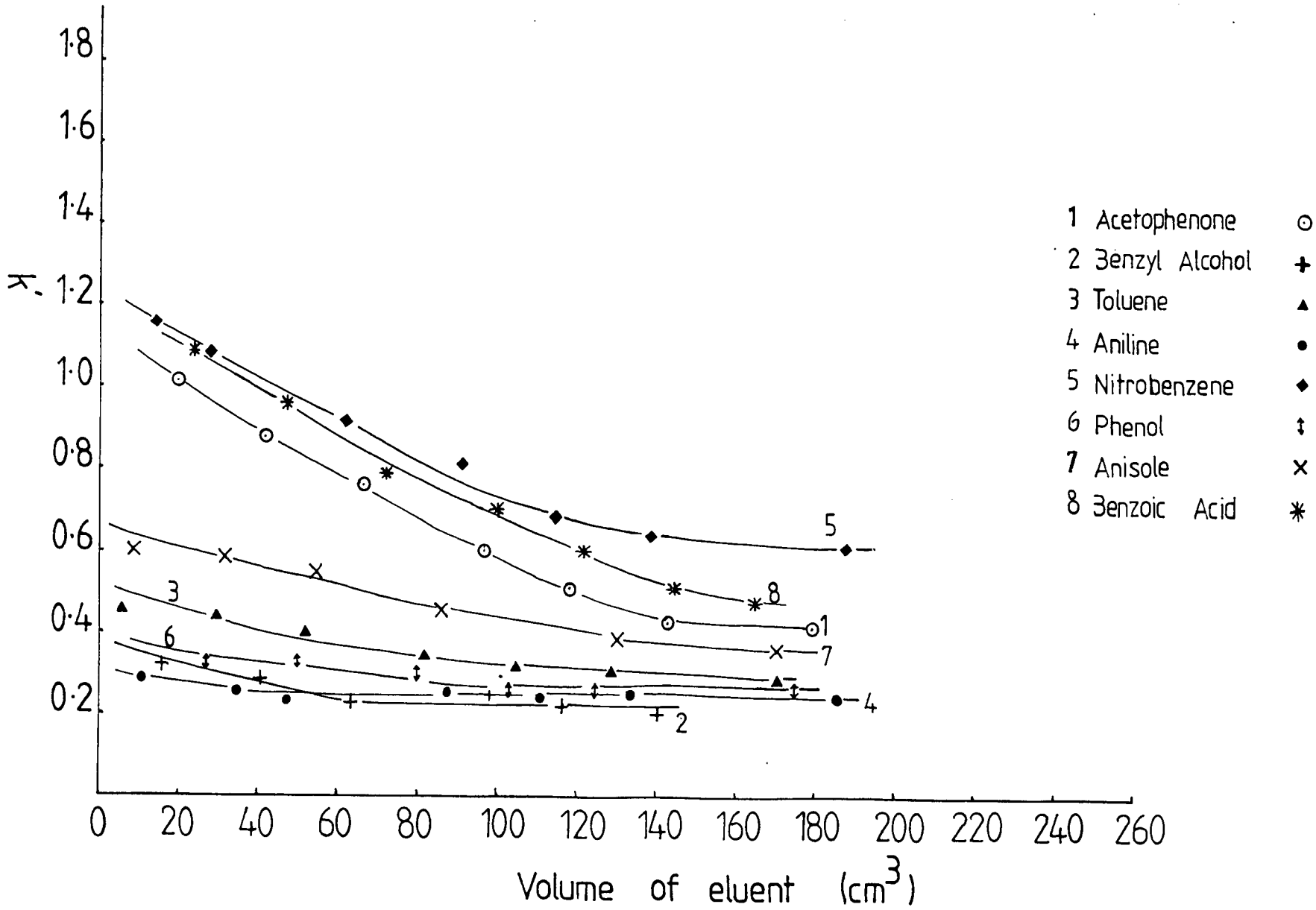


FIG. 5.3 k vs VOLUME OF ELUENT.

0.03 % Tween 80 in 95 % methanol as eluent.

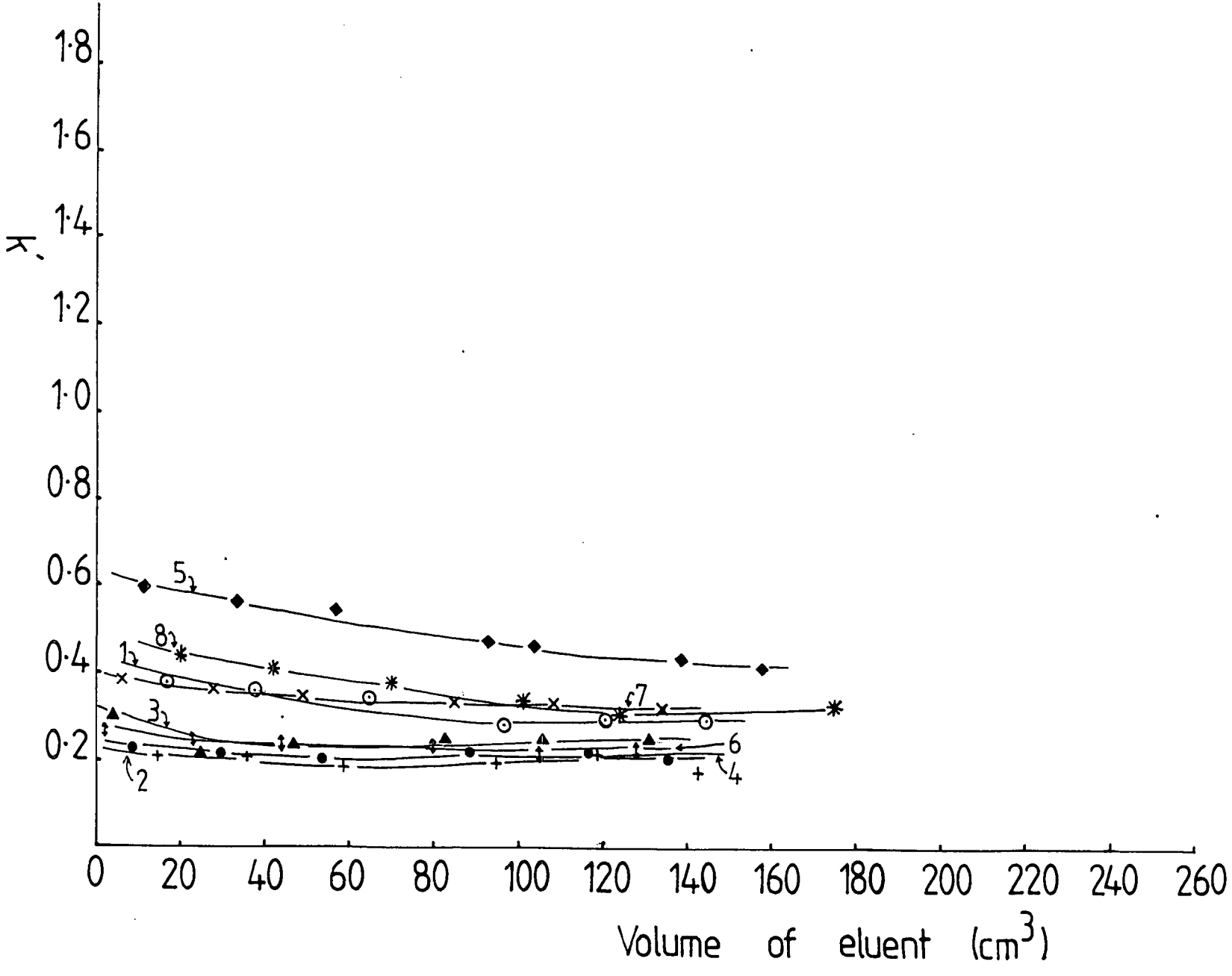


FIG. 5.4 k' vs VOLUME OF ELUENT

0.1 % Tween 80 in 95 % methanol as eluent.

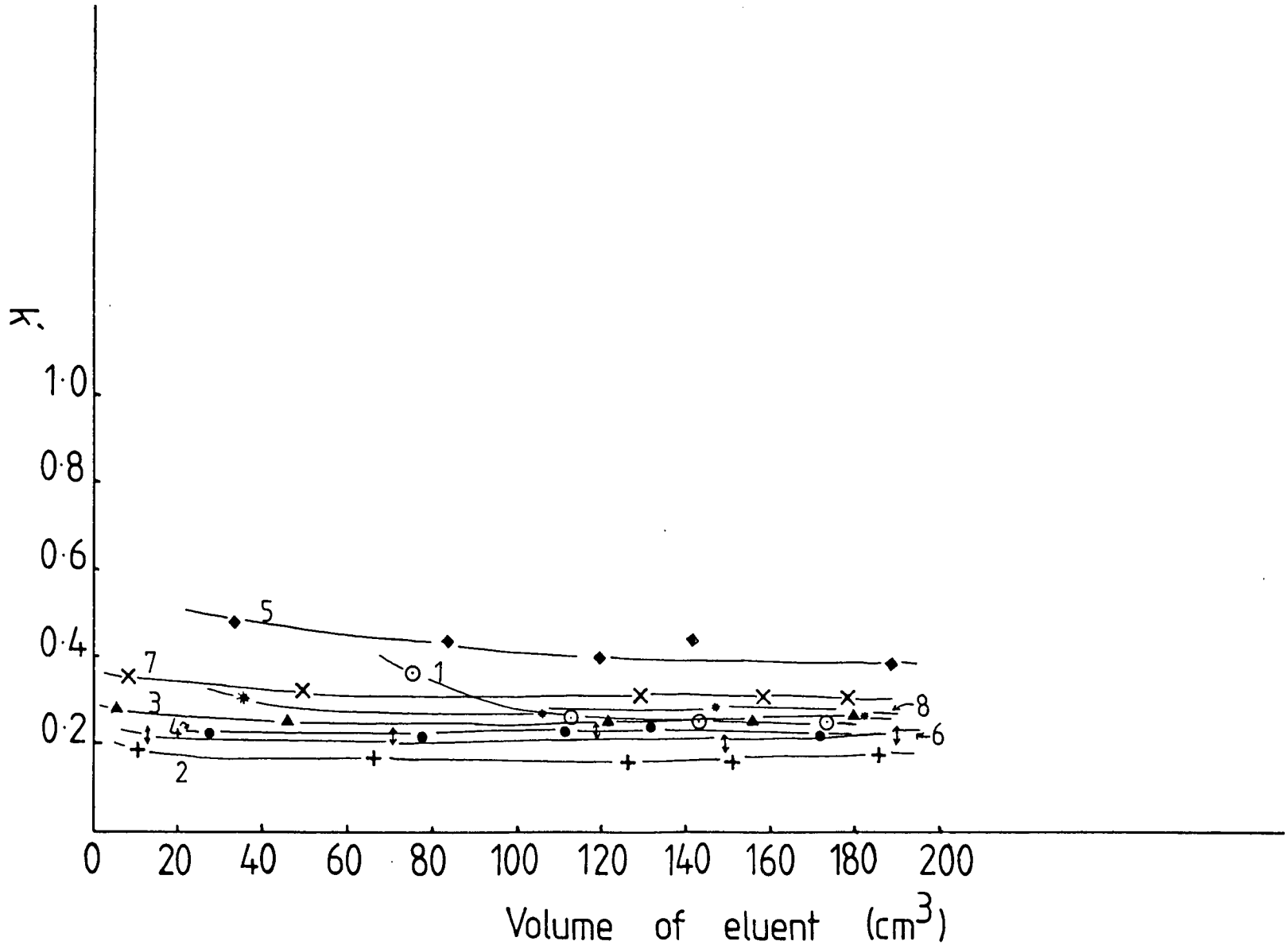


FIG. 5.5 k' vs VOLUME OF ELUENT.

0.2 % Tween 80 in 95 % methanol as eluent.

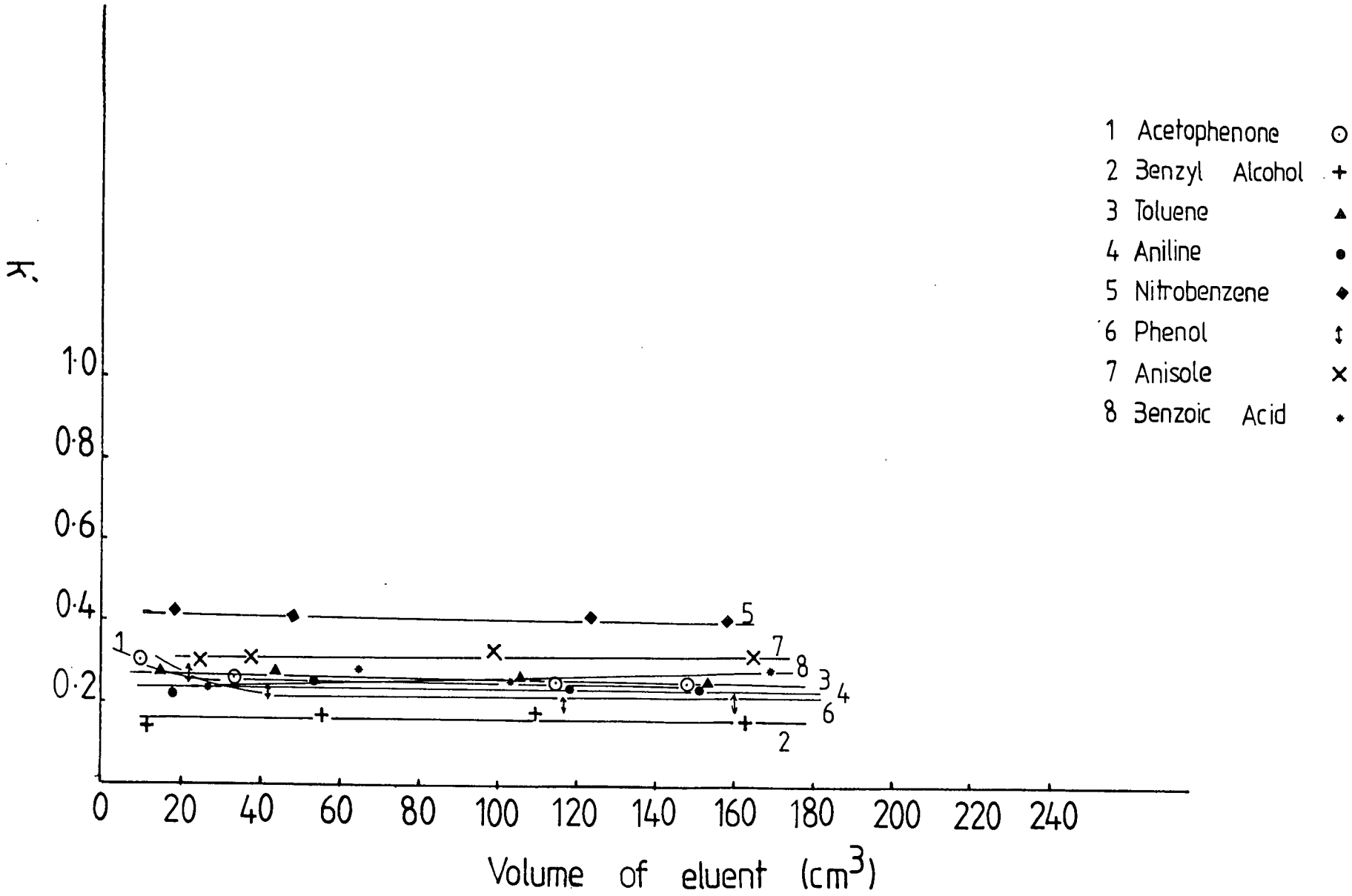


FIG. 5-6 k' vs CONCENTRATION OF TWEEN 80.

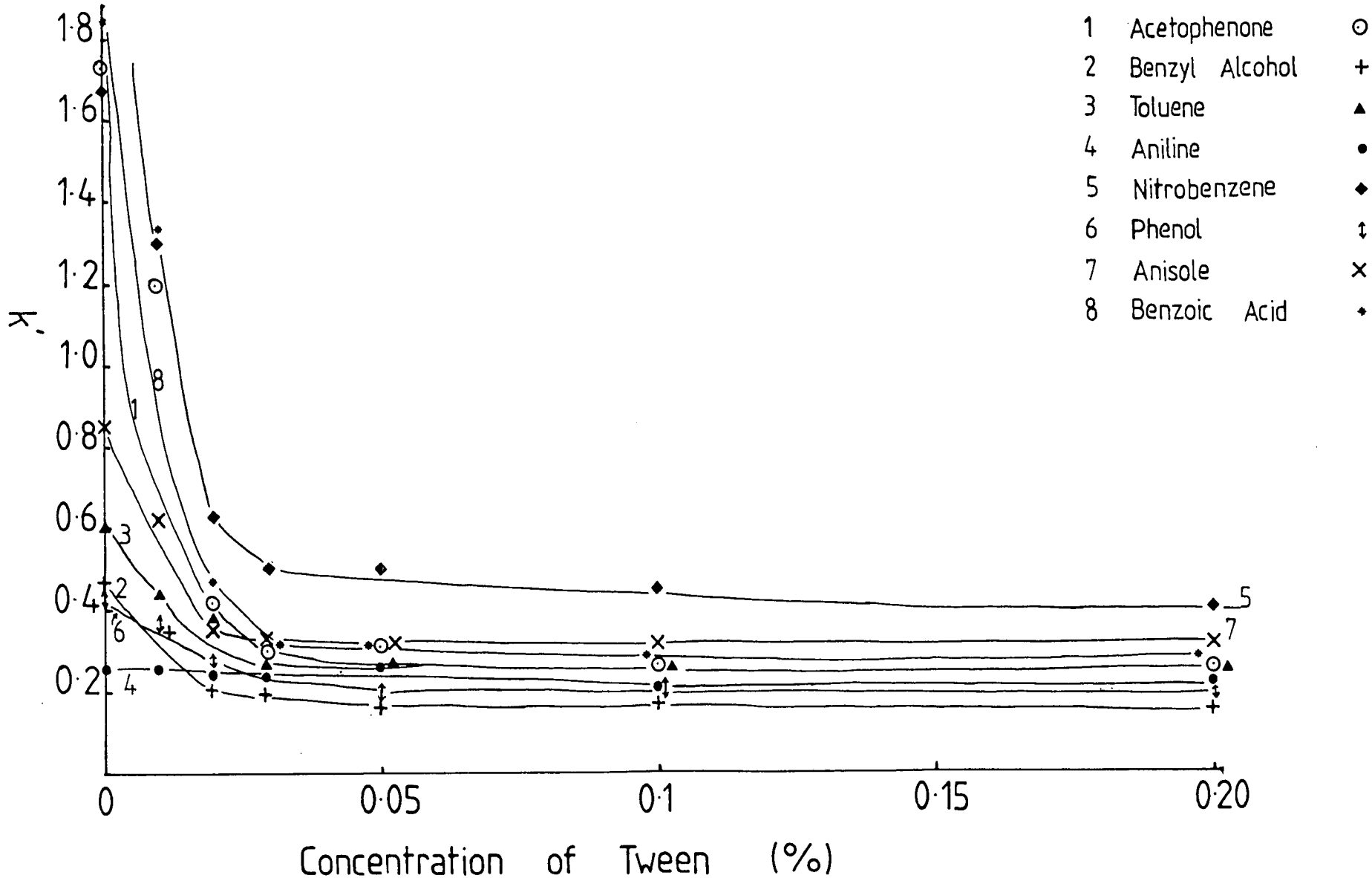


FIG. 5.7 EFFICIENCY vs AMOUNT OF WATER IN ELUENT.

0·03 % Tween 80 solutions used. $N = 16(t_r / t_w)^2$

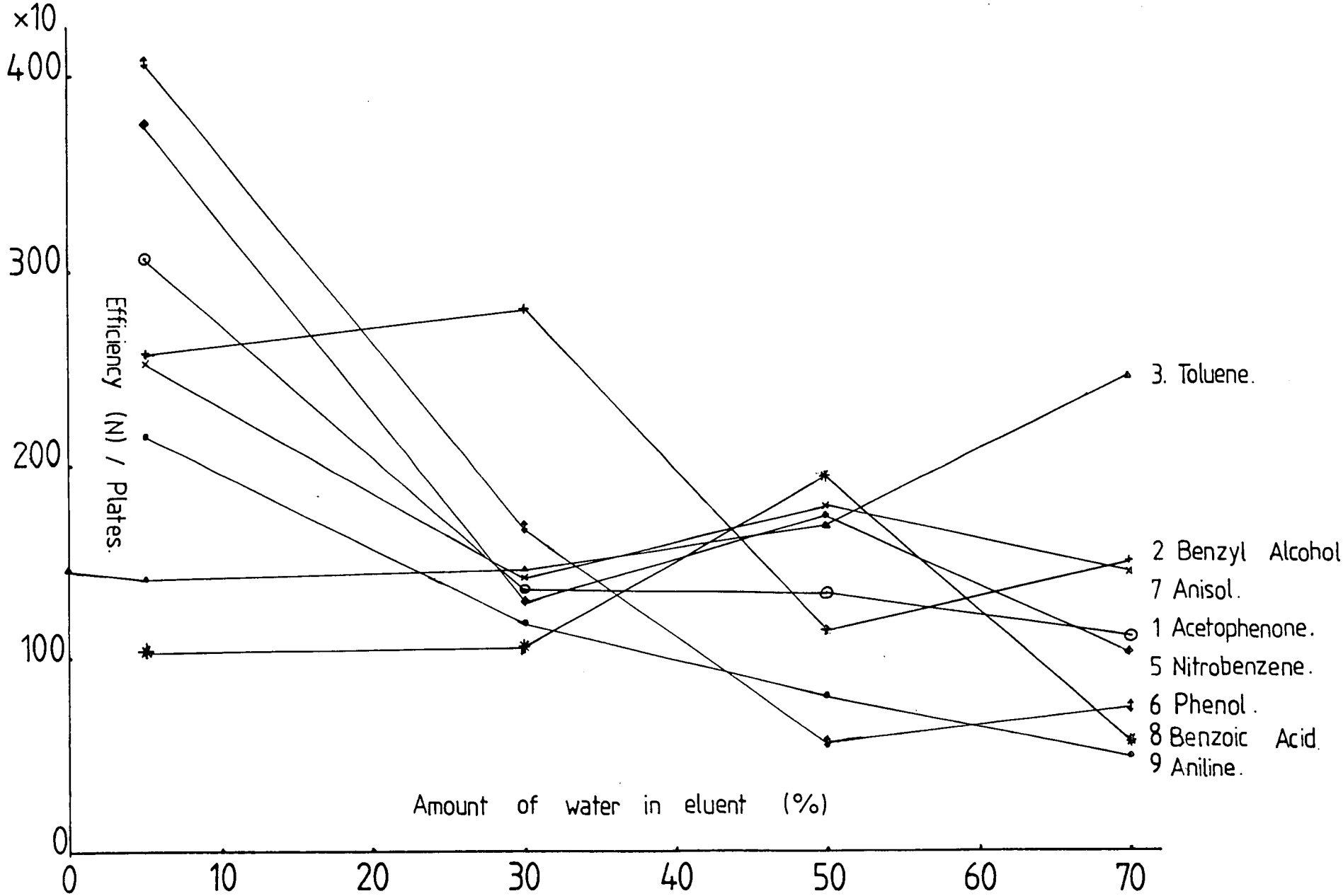


FIGURE 5.8

k' vs Amount of Water in Eluent

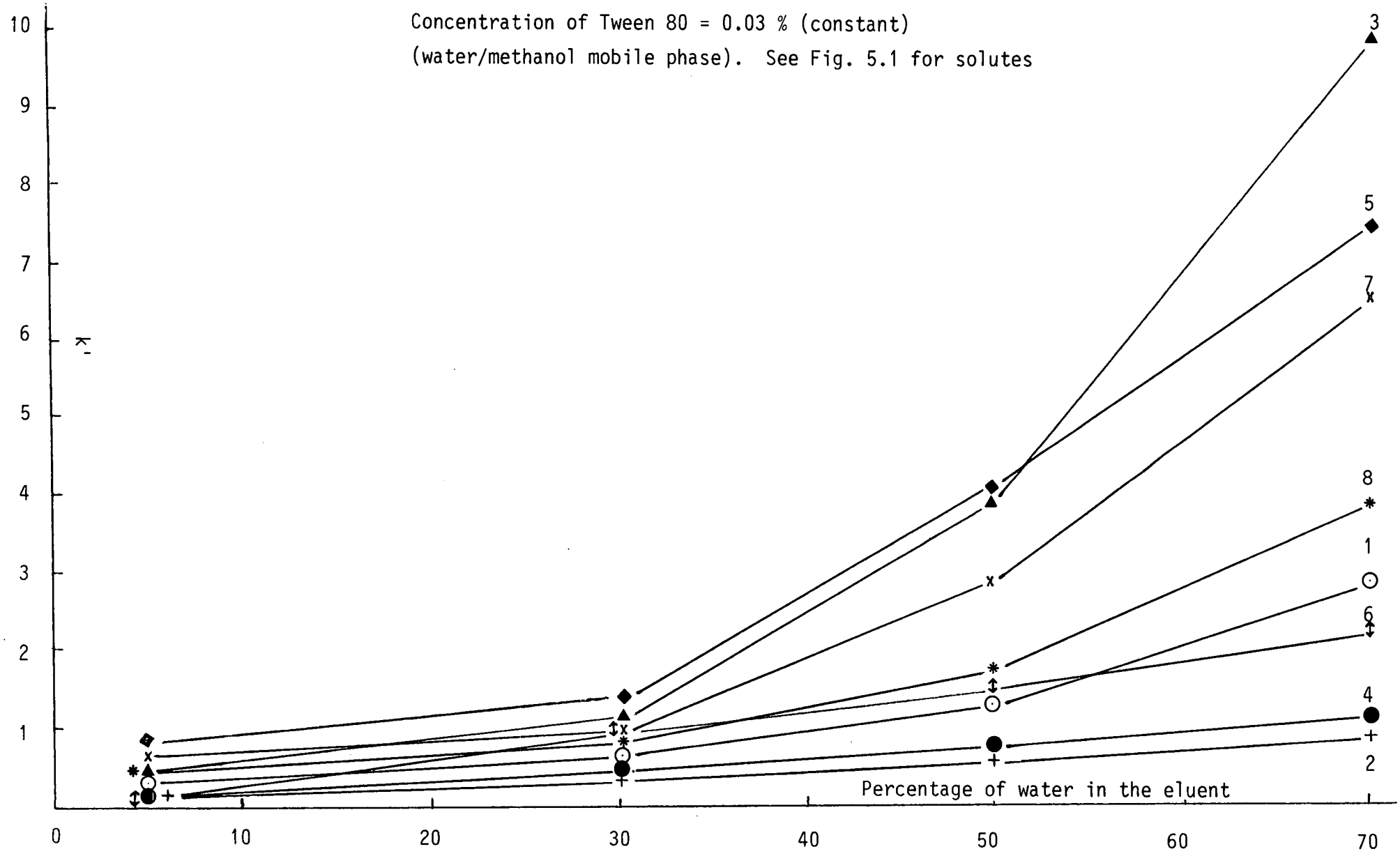


FIGURE 5.9

Slow rate = 0.4cm^3/min

Chart speed = 0.2mm/sec

95% CH^{3}OH as eluent

Back pressure 0 80 BAR

Without Tween 80

		k'
(i)	Aniline	0.40
(ii)	Benzyl Alcohol	0.46
(iii)	Toluene	0.63
(iv)	Acetophenone	1.77

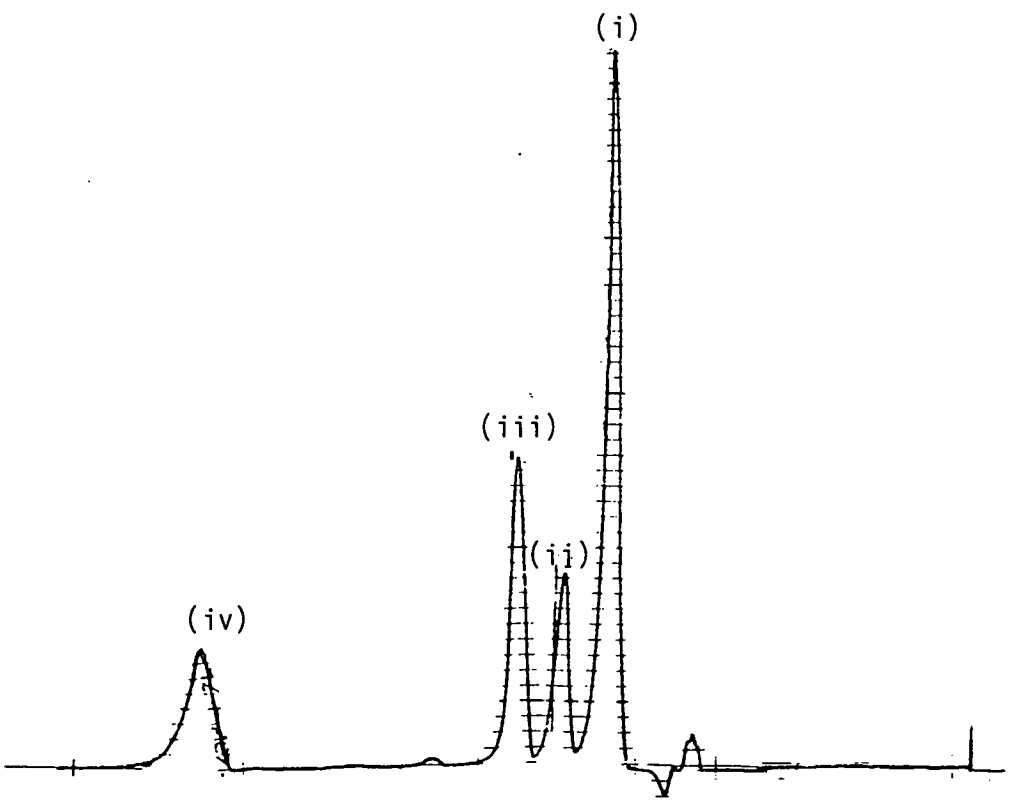


FIGURE 5.9 (contd.)

Flow rate = 0.4cm^3/min

Chart speed = 0.2mm/sec

95% methanol as eluent

Back pressure = 80 BAR

Without Tween 80

		k'
(i)	Phenol	0.44
(ii)	Anisol	0.88
(iii)	Nitrobenzene	1.77
(iv)	Benzoic Acid	1.88

N = 5689

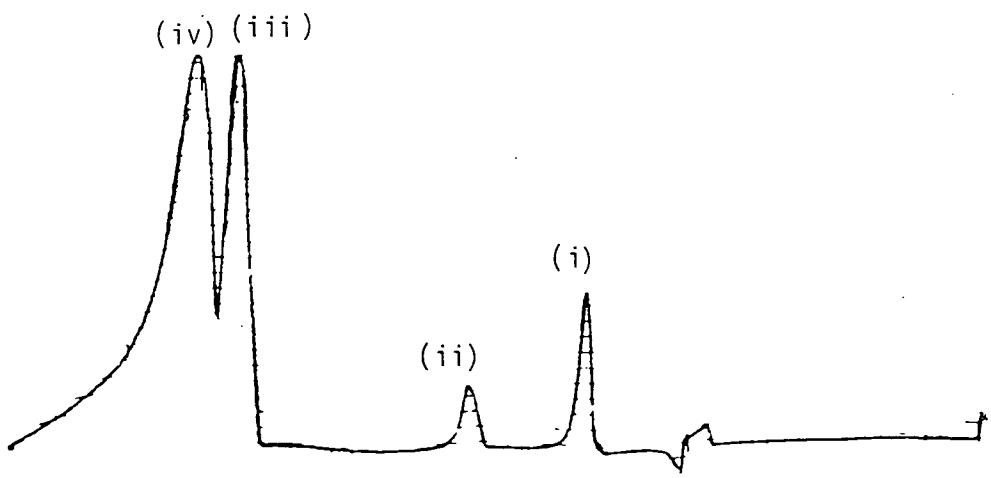


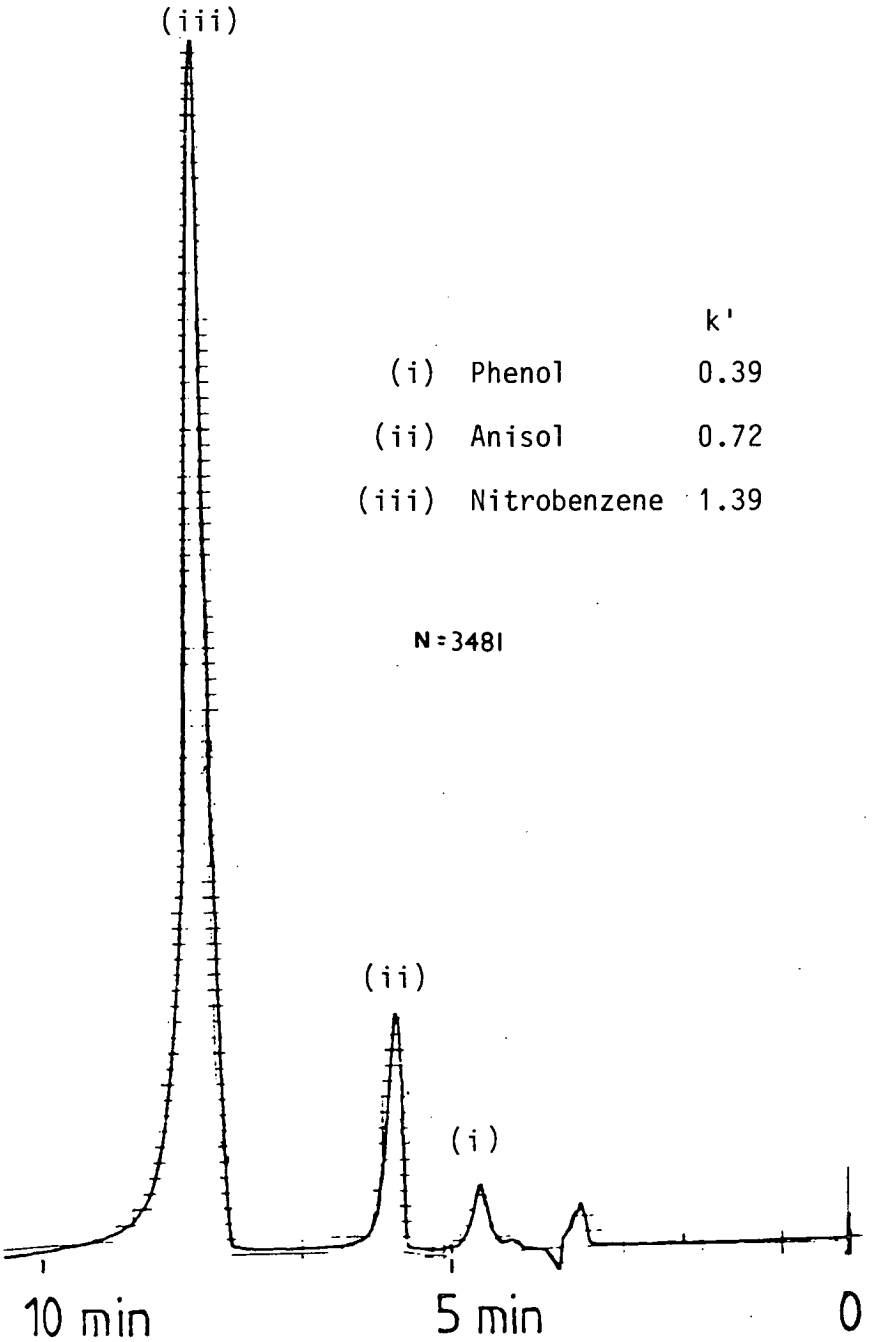
FIGURE 5.10

Chart Speed = 0.2mm/sec

Flow rate = 0.4cm^3/min

0.05% Tween 80 in 95% methanol as eluent

		k'
(i)	Phenol	0.39
(ii)	Anisol	0.72
(iii)	Nitrobenzene	1.39

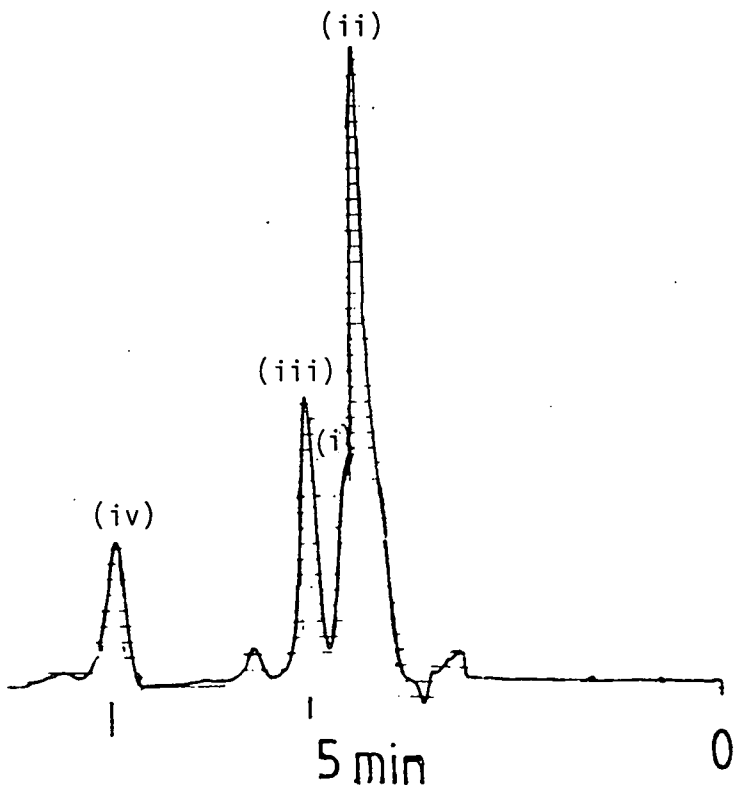


Amount of eluent passed 40 cm^3

k' and retention times decrease when Tween 80 has passed through the column

FIGURE 5.10 (contd)

		k'
(i)	Benzyl Alcohol	
(ii)	Aniline	0.34
(iii)	Toluene	0.71
(iv)	Acetophenone	1.31



Volume of eluent passed $52\ cm^3$

Table 5.1

k' values before and after Dioxan treatment

Solute	k' before Tween	k' after 0.03% Tween 80	k' after Dioxan
Toluene	0.59	0.25	0.46
Aniline	0.30	0.22	0.34
Acetophenone	1.80	0.30	1.12
Nitrobenzene	1.74	0.44	1.35
Benzyl Alcohol	0.42	0.19	0.39
Benzoic Acid	1.80	0.33	1.45
Phenol	0.40	0.23	0.35
Anisol	0.83	0.34	0.68

FIG. 5.11 k' vs VOLUME OF ELUENT.

0.01 % Span 80 in 95 % methanol as eluent.

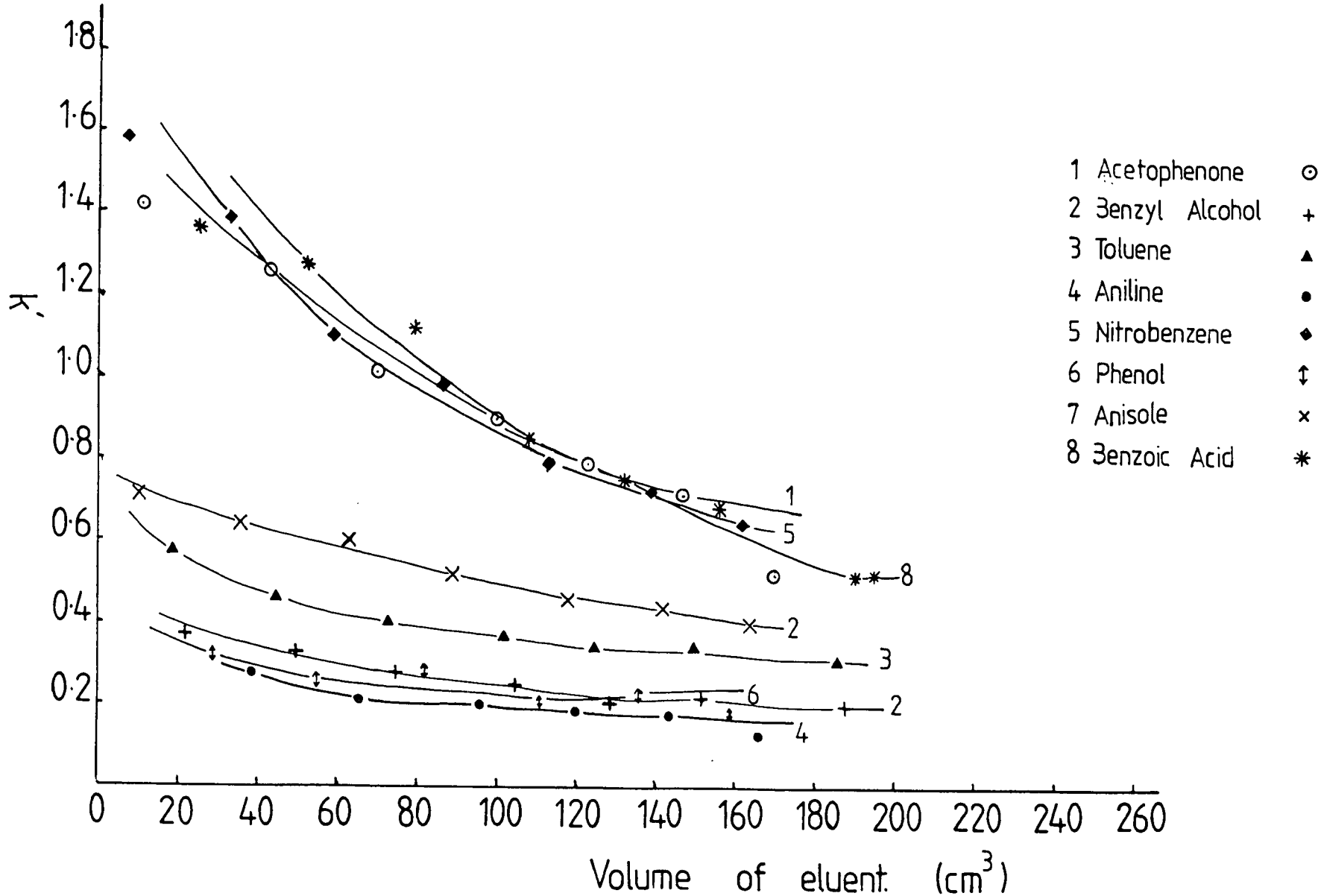


FIG. 5-12 k vs VOLUME OF ELUENT.

0·02 % Span 80 in 95 % methanol as eluent.

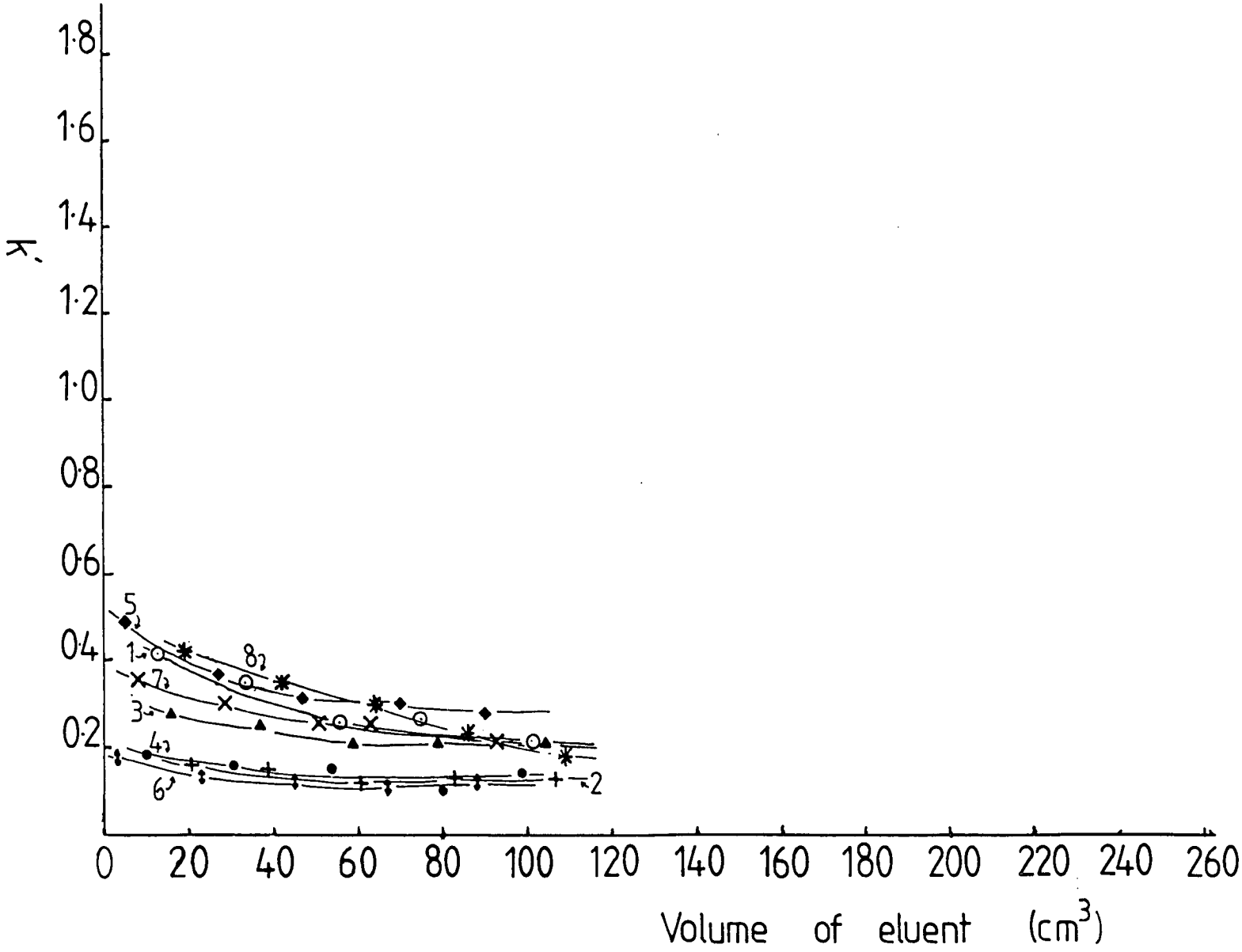


Table 5.11

k' values at different concentrations of Span 80

[Span 80] as a % w/v	0.0	0.01	0.02
Phenol	0.37	0.22	0.14
Nitrobenzene	1.74	0.64	0.34
Anisol	0.81	0.40	0.22
Aniline	0.25	0.16	0.17
Acetophenone	1.64	0.53	0.22
Toluene	0.66	0.31	0.21
Benzyl Alcohol	0.40	0.20	0.17
Benzoic Acid	1.61	0.52	0.19

Table 5.III

Effect of variation in water content of eluent

Span 80. 0.01% solutions

Solute	0.01% Span 80 95% Acetonitrile as eluent	* 0.01% Span 80 (filtered) 80% CH_3CN as eluent	% increase in k'
	k'	k'	
Phenol	0.12	0.17	42
Toluene	0.11	0.31	180
Acetophenone	0.12	0.25	108
Anisol	0.11	0.28	155
Nitrobenzene	0.12	0.27	125
Aniline	0.10	0.22	120
Benzoic Acid	0.13	0.22	69
Benzyl Alcohol	0.10	0.23	130

* Filtered (0.01% Span 80 in 80% CH_3CN) to obtain a clear solution.
Span 80 comes out of solution below 80% of CH_3CN.

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CHAPTER 6

Liquid Chromatographic Separation of Certain Aromatic Compounds via Ion Pairing on PGC

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6.1 INTRODUCTION

Poor separations and unsatisfactorily low retention times are observed for certain mixtures of aromatic compounds when chromatographed on an adsorbent. The solutes may be converted to their ionic form under extreme pH conditions. An ion pairing agent (salt, additive) may be dynamically adsorbed on to a solid phase to introduce ion exchange characteristics to the substrate. Such conditions may be exploited to obtain higher retention times and hence good separations for these compounds. This is known as ion pair chromatography (IPC). Such a technique is useful in the analysis of pharmaceutical products [1-3].

The work described in this chapter involves the study of retention characteristics of certain aromatic compounds in their anionic form on coated PGC. The effect on the capacity ratios of these solutes were studied by varying the concentration of ion pairing agent in the eluent. Cetyl trimethylammonium bromide (CTAB) was used as the ion pairing agent.

6.1.1 Retention Models

6.1.1.1 Model I

In the late 1970's two possible mechanisms were suggested for IPC. Horvath et al[4] argued that the solute in its ionic form, forms an ion pair with the hydrophobic part of the ion pairing additive (hetaeron) and this neutral species is adsorbed on to the solid phase. This view was supported by Schill and coworkers[5]. Both these research teams derived mathematical expressions in support of this theory. Their retention model could be shown thus.

The dissociation of analyte in eluent,

$$X^-A^+ \rightleftharpoons X^- + A^+ \quad \text{—— } 6.1$$

where X^- = hydrophobic anion and A^+ = accompanying cation.

The combination of X^- with an ion pairing additive such as CTAB can be shown thus,

$$X^- + Q^+B^- \rightleftharpoons Q^+X^- + B^- \quad \text{—— } 6.2$$

where QB is the ion pairing additive, Q^+ = hetaeron and B^- = accompanying ion.

In this model, the neutral species QX is adsorbed on to the solid phase. This theory has excluded the possibility of the ion pairing agent interacting with the substrate.

6.1.1.2 Model II

An alternative to the above model was proposed by Knox and coworkers [2,3,6]. This view was shared by Van de Venne et al [7]. They suggested that the ion pairing additive (Q^+B^-) is first adsorbed on to the solid phase. The hetaeron (Q^+) which is fixed to the adsorbent surface, occupies the primary layer, whilst the co-ion (B^-) occupies the secondary layer. The solute molecules in their ionic form (X^-) combine with Q^+ by replacing the ions (B^-) from the secondary layer. This retention model can be shown by the following scheme.

First, the adsorption of the ion pairing additive on the adsorbent takes place.

$$Q^+B^- + S \overset{K_1}{\rightleftharpoons} SQ^+B^- \quad \text{—— 6.3}$$

where S is the adsorbent surface and K_1 is the equilibrium constant for this process.

Then the hetraeon interacts with the ionized solute by an ion exchange mechanism.

$$SQ^+B^- + X^- \overset{K_2}{\rightleftharpoons} SQ^+X^- + B^- \quad \text{—— 6.4}$$

where K_2 is the equilibrium constant for this process.

Knox and Hartwick [6] plotted the uptake of hetaeron (C_s) on to the solid phase (reversed phase silica) versus the analyte retention (k^1) and found that a proportionality exists between the two

quantities up to the critical micelle concentration (CMC). Micelle formation occurs at this concentration of the ion pairing agent in the eluent.

The linear relationship between C_s and k^1 led Knox and Hartwick to believe that the latter retention model best described the sequence of events.

Van de Venne et al [7] devised an experiment to check this second retention model. An eluent containing Octyl sulphate and 0.01M Na^+ (pH=3) was passed through a newly packed Column of Lichrosorb (RP-18). The system was allowed to equilibrate and a known amount of adrenaline was added to the solvent reservoir. Before recycling they measured the amounts of Na^+, $(Octylsulphate)^-$ and adrenaline in the eluent by isotachophoresis [8]. They recycled the eluent and equilibrated the column. Again they measured the above mentioned quantities.

They discovered that the quantity of (a) Na^+ has increased, (b) adrenaline had decreased and (c) Octylsulphate has remained constant in the eluent. The increase in the amount of Na^+ is equal to the decrease in the quantity of adrenaline. The results (a), (b) and (c) indicated that a certain amount of Octylsulphate had adsorbed on to the solid phase. The adrenaline has interacted with the adsorbed Octylsulphate by replacing sodium ions bound to the hetaerons.

Iskandarani and Pietrzyk [9] also found that the retention of hetaerons on the solid phase governs the analyte retention. They stated that the ion pairing additives are highly dissociated when present in the eluent under their experimental conditions. Such evidence led them also to conclude that the second retention model described the ion pairing scenario.

The research in this chapter is described with reference to Model II.

6.1.1.2.1 The effects of Model II on Analyte Retention

The equilibrium constant for equation 6.4 can be written as

$$K_2 = \frac{[SQ^+X^-][B^-]}{[SQ^+B^-][X^-]} \quad \text{—— 6.5}$$

The partition coefficient (D) for this retention process is

$$D = \frac{[SQ^+X^-]}{[X^-]} \quad \text{—— 6.6}$$

$$= \frac{K_2[SQ^+B^-]}{[B^-]} \quad \text{—— 6.7}$$

The capacity ratio k^1 of a solute can be defined as

$$k^1 = \Phi\, K_2\frac{[SQ^+B^-]}{[B^-]} \quad \text{—— 6.8}$$

The equation 6.8 shows that, the analyte k^1 is directly proportional to the concentration of the ion pairing additive on the adsorbent surface.

The process described in equation 6.3 would be driven to the right hand side by increasing the concentration of Q^+B^- in the eluent.

The larger the concentration of ion pairing additive in the mobile phase, the greater the amount of additive adsorbed and hence greater the number of ion pairing terminals (SQ^+B^-) created on the adsorbent surface. As a consequence, the analyte retention would increase [9]. This was the case upto a certain concentration of additive in the eluent. Beyond this concentration, the analyte retention fell due to micella formation in the mobile phase [6].

This fall in solute retention could also be due to the increased concentration of additive co-ions. These co-ions of additive (B^-) compete with the ionized analytes for ion pairing terminals on the solid phase [9]. Equation 6.8 shows this effect. The solute retention is inversely proportional to concentration of B^-. Analyte retention could be controlled by varying the concentrations of B^- and Q^+B^- in the mobile phase.

6.1.2 Background and Literature Survey Related to Ion Pair Chromatography on Polymer Based Columns and Comparison of those Phases with Reversed Phase Silica Materials

Pietrzyk and co-workers [9-20] have carried out a considerable amount of IPC of late. They managed the successful separation of cationic and anionic species via this technique.

Pietrzyk et al have chosen polymer based solid phases for IPC. Their work also included comparisons between the popular silica

based phases and this polymer solid phase. It may be noteworthy to mention that their work could be carried out on PGC in the future for comparison with the above mentioned materials.

The research of Pietrzyk and his team has been chosen to describe the applications and details of IPC.

They separated amino acids (AA) and peptides on a poly(styrene-divinyl(benzene)) (PRP-1) column using tetraalkyl ammonium salts (R_4N^+) and alkyl sulphonates salts (RSO_3^-) as ion pairing agents in the eluent [10].

Pietrzyk and coworkers suggested that the ion pairing agent is first adsorbed on the substrate and then the ionized solute interacts with the adsorbed additive via an ion exchange mechanism. The strength and the extent of interactions determine the retention and hence the separation of analytes.

R_4N^+ salts were added to an aqueous eluent and the pH adjusted to 10. Under such conditions, the acidic side chains and the carboxyl terminus of AA and peptides were converted to their cationic form.

When RSO_3^- salts were used, the eluent was made acidic in order to protonate any basic side chains and amine terminus of AA and the peptides.

R_4N^+ Salts:

Pietrzyk and his team observed that the retention of solutes increased with the increasing chain length of additive [10]. They maintained an additive concentration of 1 m molar in the eluent. Longer the chain length of R_4N^+ salt, the easier it was to be adsorbed on to the polymer solid phase. This would have presented with more sites for ion pairing. After a certain carbon number, the analyte retention decreased. This could be the result of decreasing the concentration of ion pairing terminals on the solid phase. The larger additive molecules occupy greater area of the surface which decreases the space available for further ion pairing sites.

The initial introduction of R_4N^+ additives to the eluent, resulted in a marked increase in solute retention. Greatly diminished analyte retentions ($k' < 1$ in most cases) were observed in the absence of R_4N^+ salts. Such a trend was also seen by Knox and Jurand [3] in their research.

Pietrzyk et al [10] discovered that the addition of anions to the eluent decreased the solute retention since the analytes in their anionic form compete with the added anions in the eluent for the ion pairing terminals on the solid phase.

The strength of the anion accompanying the additive salt could have an effect on the solute retention. Strong anions such as Br^- do not readily go into solution and therefore the ionized solute

cannot readily interact with the adsorbed additive. A weak accompanying anion such as F^- could easily be replaced by the ionized solute. Therefore the greater the strength of the counter anion of additive, the smaller the retention of solute.

Additional anionic charges on the side chains of the solutes would increase retention due to the existence of larger number of ion pairing terminals.

The greater the alkyl chain length of the R_4N^+ salt, the larger the increase in retention of acidic AA in comparison to AA without acidic side chains. This property could be exploited to separate acidic or hydrophobic AA from a mixture of AAs.

The hydrophobicity of the mobile phase can be increased by the inclusion of an organic modifier such as acetonitrile. The retention of analytes decreased with the increasing concentration of the modifier in the eluent. As the hydrophobicity of the mobile phase is increased, the amount of additive on the stationary phase is decreased. A fewer number of sites are therefore available on the surface for ion pairing [10]. Also, the solutes with hydrophobic side chains would display decreasing retention with increasing acetonitrile content in the eluent.

The retention of peptides increases as any anionic side chain such as tyrosine moves further away from the COO^- terminus. This may be

due to the ease of attachment to the R_4N^+ terminals on the stationary phase, as two separate ion pairing groups are available in the solute for interaction with R_4N^+ terminals. When the Tyrosine Group is near the COO^-, only one Group may be able to interact with the surface R_4N^+ terminals.

RSO_3^- M^+ Salts:

The chromatographic system was operated at a pH value of 2, in order to obtain the cationic forms of the solutes. Then the adsorbed RSO_3^- salts on the stationary phase interact with the solutes. The amine terminus and the basic side chains of the AA were converted to the cationic form at this pH.

Pietrzyk et al investigated the effect on retention of AA and peptides with increasing chain length of salt. They went up to C_8 and found that the retention increased with increasing chain length of additive. The larger molecules tend to stick more easily on the stationary phase and create more ion pairing sites. Knox and Hartwick[6] also found that,at a given concentration of additive,in eluent, analyte retention depended upon the additive chain length.

In Pietrzyk's work additives with hydrogen as the counter cation gave highest solute retention values [10]. This could be due to the ease of ionization of additive in the acidic solution. Salts with Na^+ as the counter cation displayed shorter retention times in comparison to salts with H^+, since the ionic bond between Na^+ and RSO_3^- is much stronger than H^+-SO_3R bond.

Pietrzyk's data indicate that RSO_3^- salts are more selective towards polar AA and polar peptides than R_4N^+ salts. Also, solutes with ionized side chains in position 1 or in the same unit as the terminal NH_3^+ showed the highest retention, when RSO_3^- salts were used as the ion pairing agent. This is in contrast to the RSO_3^- system. The reason could be that the negative charge of RSO_3^- is carried by the three oxygens and therefore allowing larger area of charge for more than one ion pairing terminal to interact.

Pietrzyk and Iskandarani [11] considered an application of ion pair chromatography. They analysed for NO_3^- and NO_2^- in baby food, water, beer and oven cleaner samples. They used the PRP-1 copolymer stationary phase, and tetraalkyl ammonium bromide as the ion pairing agent. Solute retention was dependent on the length of the organic part of the ion pairing agent, the additive concentration, the amount of organic modifier in the eluent, the strength of the co-anion of the additive and the concentration of sodium fluoride in the mobile phase.

They also separated several mono and divalent anions via ion pairing [12]. Retention of divalent ions are larger than monovalent ions since the former could occupy two sites on the surface to give additional protonic equilibria.

Retention of solutes decreased with (a) increasing acetonitrile content in the eluent, (b) increasing analyte concentration due to

the saturation of the column, (c) decreasing chain length of the ion pairing agent (R_4N^+), since the hydrophobicity of smaller additives is not great enough for adsorption to take place between the PRP-1 stationary phase and the additive ($R_4N^+F^-$), and (d) decreasing concentration of NaF in the eluent.

Solute retention first increased with the concentration of the additive and then it began to drop. Initial increase in retention is due to the adsorption of the additive on to the stationary phase, and creation of more ion pairing sites. Then the decrease in retention is the result of the increase in the concentration of F^- accompanying the additive. These F^- ions would compete for the ion pairing sites (R_4N^+) on the surface of the stationary phase. As a result, a decrease in solute retention is observed.

Pietrzyk and Iskandarani [9] investigated the retention properties of R_4N^+ salts on PRP-1 columns. They discovered that the retention of these compounds increased with the carbon number of the R groups of the R_4N^+ salt. Higher the carbon number greater the hydrophobicity and hence easier for the salt stick to the polymer surface, up to a certain carbon number. Afterwards, the analyte retention dropped as a result of (a) the decrease in ion pairing terminals on the surface, and (b) micelle formation in the eluent. This is in contrast to the observation by Knox and Hartwick [6]. They found that at a given surface concentration of hetaeron (between 0-2μmol m^{-2}) analyte retention was independent of additive

chain length. It may be believed that the solid phase used by Pietrzyk et al [9] would have had a larger concentration of ion pairing terminals than that used by Knox and Hardwick [6].

Pietrzyk et al [9] also stated that the anionic solute retention depended upon the counter anion of the additive, and its ability to be replaced by the solute. Salts with F^- as the counter anion displayed largest solute retention while the additives with Br^- gave the smallest. The counter anion series may be arranged thus,

$$F^- > Cl^- > \text{formate} > NO_3^- > Br^-$$

This means that the salts with F^- are the easiest to ionize and the salts with Br^- being the most difficult.

Pietrzyk et al found that the analyte retention increased with, (a) decreasing concentration of acetonitrile which governed the hydrophobicity of the eluent, and (b) the increasing ionic strength of the eluent since this could decrease the hydrophobicity of the mobile phase.

Pietrzyk et al [13] chemically bonded tetraalkyl ammonium groups (R_4N^+) to PRP-1 stationary phase. The mechanism of separation on this bonded phase were by ion exchange/pairing and adsorption. Only a fraction of the surface was covered by the R_4N^+ groups. Benzoic acids (BA), amino acids (AA) and peptides were used as solutes.

They defined the column's anion exchange capacity as the "number of anion exchange sites per column". As the anion exchange capacity increased, k^1 of solutes due to adsorption on stationary phase decreased, but more anion exchange sites were created, hence the retention of solutes due to anion exchange increased.

Hydrophobic analytes are highly retained on the 'polymer part' of the column. The retention may be decreased by increasing the amount of organic modifier in the eluent.

The retention of benzoic acid (BA) showed a maximum with increasing column exchange capacity at acidic pH values. After passing through the maximum, the retention of BA reached a lower value than the original starting value. This may be explained thus; the starting retention value was due to the adsorption of BA on the polymer surface. With increasing number of charged sites, the area available for adsorption was decreasing. The maximum could be due to the lateral interactions (Chapter 3) between BA molecules. As more additive was adsorbed, the BA retention decreased since the solute molecules remain unionized at this acidic pH. Therefore no interactions existed between BA molecules and the adsorbed additive.

At high pH values however, ion pairing can take place between ionized benzoic acid molecules and the ion pairing agent which is on the stationary phase.

At an alkaline pH value, the retention of BA can be increased by, (a) decreasing the amount of organic modifier in the eluent (this was also the case for amino acids and peptides), (b) increasing the carbon number of the additive, or (c) decreasing the ionic strength of the eluent. For example, SO_4^{2-} ions are strongly attached to an additive such as R_4N^+ than Cl^- ions. If SO_4^{2-} are present in the mobile phase, these would be strongly attached to the ion pairing sites. The solutes therefore cannot interact with the additive on the stationary phase. If a weaker anion such as Cl^- is present in the eluent, these may be weakly attached to the ion pairing terminals. Such Cl^- ions could easily be replaced by the solute anions. Therefore the solute retention could be enhanced by decreasing the strength of counter anion in the eluent.

When peptides were chromatographed, k^1 of these solutes increased with (a) the column capacity, (b) the length of carbon side chain of peptide (ion pairing as well as adsorption of the hydrophobic part of the solute contribute towards retention) (c) the distance of the carbon side chain from the anionic charge centre, as this would facilitate the adsorption of the solute to the stationary phase (same trend is observed in the case of amino acids), (d) the increasing ionic strength of the eluent, and (e) the increasing valency of the anionic side chain.

For amino acids, selectivity, resolution and retention increased with the size of the amino acid molecule. Retention was also

dependent upon the hydrophobicity of the eluent which was governed by the amount of acetonitrile present. Amino acids with hydrophobic side chains show a marked decrease in retention with increasing concentration of organic modifier in the eluent.

Walker and Pietrzyk [14] used $RSO_3^-H^+$ salts to study the separation of amino acids. Retention of analytes depended upon the adsorption of the salt and then ion pairing between solute and the salt.

They used PRP-1 and alkyl bonded silica (RSi) as stationary phases. Following general inferences were made about the retention of solutes. The k^1 of AA increased with the following. (a) The chain length of the additive. (b) The concentration of salt and then the k^1 values decreased since the increasing additive concentration increased H^+ ion concentration in the eluent (these extra H^+ ions compete for the ion pairing sites on the stationary phase). (c) Decreasing pH of eluent (at high pH the basic side groups of the terminal NH_2 cannot exist as cations, and therefore does not interact with the charged additive). (d) The decreasing concentration of the organic modifier in the eluent, (the smaller the concentration of the modifier, the greater the amount of additive found on the stationary phase and this would create more ion pairing sites for solutes to interact). (e) Decreasing ionic strength of the eluent. (f) Decreasing valency of the ion

accompanying the salt. Additives with divalent co-ions are more difficult than salts with monovalent ions to ionize. As a result, when divalent salts are used as mobile phase additives, the retention of solutes are greatly reduced.

Sharper peaks and enhanced efficiencies were observed with silica columns, due to smaller size of silica particles. PRP-1 columns were able to operate below pH=2 with RSO_3^- salts, but chromatography was not improved due to the increase in $[H^+]$ concentration. Walker and Pietrzyk [14] discovered that the additive is reversibly retained on PRP-1 columns compared with RSi columns.

Walker and Pietrzyk did further work on amino acids [15]. They compared the chromatographic performance of ODS and PRP-1 columns with the amino acids after including an ion pairing agent in the eluent.

They found that the ODS columns used gave higher efficiencies and better resolution than the PRP-1 polymer columns. This is due to more RSO_3^- being adsorbed on the ODS surface than on PRP-1.

Pietrzyk et al [16] did further work on ion pairing and separated inorganic anionic and cationic analytes using silica and PRP-1 columns.

C_{18}, C_8 and C_1 silica columns were used in their work. They found that on silica and PRP-1 columns, the retention of R_4N^+ and RSO_3^- salts (a) increased with the hydrophobicity of R groups, (b) increased as the amount of organic modifier in eluent is decreased, (c) increased with the ionic strength (μ) of eluent, (d) decreased with the solvent strength of organic solvent used in the mobile phase, (e) were dependant upon the type of accompanying counter ion. The retention of additives $R_4N^+C^-$ and $RSO_3^-C^+$, for the counter ion C, followed the order:-

$$M^{2+} > Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$

and

$$I^- > NO_3^- > Br^- > NO_2^- > Cl^- > F^-$$

M^{2+} and I^- are the strongest and Li^+ and F^- being the weakest counter ions.

The retention of RSO_3^- salts increased with the ionic strength of the mobile phase. This indicates that the hydrophobic ion occupies a layer on the stationary phase (PRP-1 or silica (RSi)), then the counter ions occupies the next layer giving an electrical double layer [16]. The counter anion of the salt is replaced by the analyte ion.

Pietrzyk et al found that, the R_4N^+ species interacting with free SiO^-H^+ groups on the RSi surface. SiO^--N^+R_4 bond seems to be quite strong since acetonitrile was unable to elute R_4N^+.

Each adsorbent takes up different amounts of the ion pairing agent. Thus, the electrostatic interactions between the retained hydrophobic ion and the analyte ion will differ between stationary phases. The amount of salt retained on the column can be varied by varying the salt concentration and the amount of organic modifier in the eluent. These factors may be used to control the number of ion pairing sites on stationary phase and hence solute retention [16].

Analyte retention is proportional to the concentration of the ion pairing agent (R_4N^+) and inversely proportional to (a) concentration of analyte and (b) counter anion concentration. These relationships are valid on both PRP-1 and R-Si columns [16].

On RSi and PRP-1 columns, the retention of anionic analytes (NO_2^-, Br^-, NO_3^- and I^-) increases and then falls with increasing concentration of an ion pairing agent such as tetrapentyl ammonium fluoride. The increase in solute retention is the result of the creation of increasing number of ion pairing sites and the decrease in retention is due to the competition from F^- ions accompanying the salt.

An identical trend is observed for cations on PRP-1 columns when using a RSO_3^- salt in the eluent. This is not the case for RSi columns. Appreciably larger k^1 values were observed for cations at zero or lower eluent concentrations of the additive. As the RSO_3^-

concentration is increased, the retention of the analyte cation tend to fall. This leads to the explanation that, the higher retention of the analytes at lower eluent concentrations of the additive is due to SiO^-H^+ groups on the silica surface. The solutes interact with SiO^- groups by replacing the H^+. The retention differs between cations and thus a mixture can be separated. As the concentration of RSO_3^- in the eluent is increased, the concentration of ion pairing terminals on the surface is also increased, and this would make the SiO^-H^+ sites less accesible for the cationic solutes. The main interactions therefore are between the analytes and the RSO_3^- terminals on the surface. These interactions are much weaker than the interactions observed when the analytes combined with the $Si-O^-$ species. This explains the reduction in k^1 of the solutes as the eluent concentration of the additive is increased [16]. The retention of analytes settled down at a lower value after a certain eluent concentration (C_A) of additive indicating that no more additive is adsorbed on to the solid phase.

By fixing the eluent concentration of the ion pairing agent at an intermediate value (between 0 and C_A), the retention of cations could be increased by increasing the pH of eluent, to about 8. These conditions would favour the creation of more SiO^- sites for cation exchange.

Divalent cations are strongly retained due to the extra charge.

The retention of solutes is decreased by (a) increasing the amount of methanol in the eluent which reduces the number of ion pairing sites on the stationary phase, (b) increasing the concentration of a ligand in the eluent. The greater the ligand - Analyte complexation, the smaller the retention of analyte. The increasing concentration of methanol would favour the ligand - Analyte complexation and hence would reduce the retention of solute, and (c) increasing the ionic strength of the mobile phase. This would enhance competition for ion pairing sites and hence redue retention.

The alkyl groups of R-Si are not relevant for the separation of cations in the absence of RSO_3^- salts. The removal of such groups may increase retention, cation exchange capacity and column efficiency [16]. The details of the separation of alkali metal cations and alkali earth metal cations on ordinary silica columns are reported in reference [17].

When using R_4N^+ salts, Pietrzyk found that a certain amount of this additive ion pairing with the free SiOH groups on the silica surface. As a result, the retention of this salt was enhanced on silica. Due to the partial consumption of the R_4N^+ salt by the silnol groups, the number of sites available for ion pairing on silica was much less than the number of terminals that would be available on PRP-1. As a result, higher solute retention values have been achieved on the latter stationary phase [16].

Pietrzyk et al [16] carried out the separation of certain anions using R-Si and PRP-1 columns with tetrapentylammoniumfluoride salt in the eluent. The eluent ionic strength, the additive concentration and the water to acetonitrile ratio were adjusted to give favourable retention times. Column efficiencies obtained with RSi columns were greater than those obtained with PRP-1 columns. This is attributed to the smaller size of RSi particles and the narrower peaks obtained with such materials. Pietrzyk et al also claimed that the efficiency of column increased with the increasing length of R group of RSi. The retention and resolution displayed by the anions on PRP-1 columns were greater than those displayed on RSi columns. Also, the polymer based columns were capable of withstanding basic pH values.

Rigas and Pietrzyk [17] used $Fe(Phen)_3^{2+}$ as the in pairing agent to separate mixtures of inorganic anions on PRP-1 columns. Favourable detection limits, resolutions, retention times and column efficiencies were obtained.

They did further work in this field and separated simple organic acids [18]. The pH of mobile phase was adjusted to 6.2 in order to dissociate all the acids, and obtain their anionic form for the separation. The divalency of $Fe(Phen)_3^{2+}$ would enable the formation of stronger interaction with solutes. This would enhance their retention values. The peak shapes, resolution and

efficiencies were favourable [19].

The amount of additive retained on the surface PRP-1 increased with its concentration. This led to an increase in analyte retention. The concentration of the anion accompanying the additive also increased with the amount of additive in the eluent. After a certain concentration of the additive, the retention of solutes decreased since the extra counter anions compete for the sites on the stationary phase. The increase in $Fe(Phen)_3^{2+}$ concentration in the eluent would reduce the radiation reaching the detector and consequently diminish the intensity of the analyte signals [20].

The retention of the organic acids decrease with (a) the strength of the counter anion of the salt, (b) the ionic strength of mobile phase, and (c) the concentration of methanol in the eluent.

The selectivity of the acids remain constant as long as they are ionized. The retention of the analytes remain constant over the pH range 4.7-7.0. At low pH values the acids are unionized. These species compete against $Fe(Phen)_3^{2+}$ for the PRP-1 surface. At lower pH, the retention of acids is due to the adsorption of the unionized acids. The hydrophobic side chains present in an acid molecule may enhance this effect, and as a result certain organic acids display elevated retention times at lower pH values.

More complex aromatic and hydrophobic acids may be retained via adsorption on the stationary phase even though these may be ionized. This property may be exploited to achieve satisfactory separations.

Increasing the number of chlorine atoms in an acid would enhance its retention. This would increase the polarity of the analyte and hence increase retention and also the -I (inductive) effect of the Cl atoms would increase the acidity of the molecule. It may therefore be easier for acids with increasing number of Cl to give up the H^+ sites and ionize. The ionized species could easily combine with the ion pairing agent present on the surface of the stationary phase.

The retention values of sulphonic acids increased with their carbon number. These carbon chains could be interacting with (a) the adjacent solute molecules that have combined with the additive on the solid phase, (b) any bare parts of the PRP-1 surface, and (c) the hydrophobic parts of the additive on the solid phase.

Retention of the organic acids and dianions can be decreased by (a) increasing the concentration of the organic modifier in the eluent, (b) increasing the ionic strength of eluent, and (c) decreasing the column length (to reduce the number of ion pairing sites).

The next section (6.2) describes the experiments performed on PGC. Results and discussion follows in Section 6.3. An attempt is made to describe the retention of analytes in terms of what may be taking place on the surface of PGC.

6.2 EXPERIMENTAL

6.2.1 Preparation of the Mobile Phase

A methanol-water (95:5 w/w) solution (approximately 3000g) was prepared and 1.7g of potassium hydroxide dissolved per 1000g of this solution, in order to adjust its pH to 12.6. Different quantities of cetyltrimethylammonium bromide (CTAB) were dissolved in 500cm^3 aliquots of this alkaline methanol solution. The strengths of these CTAB solutions were 0.5, 1, 2, 3, 5 and 10 milli Molar. These solutions were degassed and used as eluents in the experiments.

6.2.2 Equipment and Reagents

Methanol was obtained from Rathburn Chemical Company, Wakersburn, Peebleshire.

The water was double distilled in the laboratory.

Solutes were: Phenol, Benzoic acid, p-nitro aniline and isophthalic acid from BDH Chemical Company, Poole, Dorset.

p-Cresol from Fisons Chemical Company, Loughborough, Leics.

Phenetole and 2,3 xylenol from Aldridge Chemical Company, Gillingham, Dorset.

UV detector - Spectroflow 773 from Kratos Urmston, Manchester.

Chart recorder - BBC Goerz Metrawatt SE120 from Belmont Instruments, Glasgow.

Chromatographic pump - 6000A from Waters Associates Inc., Milford, U.S.A.

Rheodyne loop injector valve was used (20ul).

Tubing - PTFE and stainless steel (for the HPLC system) from Phase Sep., Queensferry, Clwyd.

The solid phase PGC 86 CEN (7u) from Wolfson Liquid Chromatography Unit, Edinburgh University, Edinburgh.

HPLC columns (10cm x 4.7mm (ID)) from Shandon Scientific Limited, Runcorn, Cheshire.

CTAB from BDH Chemical Company, Poole, Dorset.

6.2.3 Procedure

The HPLC columns were packed with PGC 86 CEN according to the procedure described in Chapter 5.

The solutes were chromatographed on the bare PGC surface. 95% (w/w) methanol at pH 12.6 was used as the eluent. The chart speed was adjusted to 0.5 cm min^{-1} and the eluent flow rate, through the HPLC system, kept at 1 cm^3 min^{-1}. These conditions were kept unaltered throughout this series of experiments.

The following stage was to replace the methanol eluent with the most dilute CTAB solution (0.5mM) and record the k^1 of analytes until steady values were reached. Analyte retentions were noted in this manner using all the CTAB solutions (Figures 6.1-6.6), taking care to use the solutions in the ascending order of CTAB concentration. Most dilute solute was used first and the most concentrated last. Figures 6.1-6.6 display how analyte retention changes with volume of eluent. The solutes were detected at 254nm.

How analyte retentions vary with the CTAB concentration was studied. At the end, an attempt was made to wash off the adsorbed CTAB from the PGC surface by the passage of dioxan through the column for about 7 hours at a flowrate of $1cm^3$ min-1.

Afterwards, 95% (w/w) methanol was used to wash off the dioxan from the adsorbent surface. Finally, the retention of analytes were noted on this column using 95% methanol as the eluent.

6.3 RESULTS AND DISCUSSION

The evidence [7,6,9] suggests that the analyte retention in IPC follows model II (Section 6.1.1.2).

The CTAB is first adsorbed on to the PGC surface. The organic cationic parts of this additive occupies the primary layer whilst the bromine ions occupy the secondary layer. Then the Br^- ions are replaced by the analytes in their anionic form. The high pH of eluent (12.6) facilitates the conversion of all but two solutes into their anionic form.

Figure 6.7 shows the variation of analyte retention with the concentration of CTAB in the eluent. The iso-phthalic acid shows a large increase in k^1 with increasing amounts of CTAB in the mobile phase. This is attributed to the formation of a dianion. The two-COOH groups of the molecule ionizes to give two ion pairing terminals. These two anionic sites would interact with two adsorbed hetaerons to increase the retention of isophalic acid.

Figure 6.7 shows that the retentions tend to reach a 'plateau' for all the analytes that are capable of ion pairing with the adsorbed

CTAB. This may be due to (a) the PGC surface becoming saturated with the additive, (b) micellar formation beginning to occur in the eluent, and (c) the Br^- ions beginning to compete for the ion pairing terminals ont he PGC surface. The factors (a), (b) and (c) may decrease the retention of the ionized solutes if the concentration of CTAB in the eluent is increased beyond the 'plateau' concentration.

As the concentration of CTAB in the eluent was increased, the number of ion pairing terminals on the PGC also increased. An increase in retention (Figure 6.7) is therefore seen for the solutes which are in their anionic form (Section 6.1.1.2.1). This is the result of increased number of interactions between the 'anionic' solutes and the adsorbed additive (CTAB).

Phenetole and p-nitroaniline are unionized at high pH. These molecules do not exist as anions under these conditions. Therefore these two solutes do not ion pair with the adsorbed CTAB. Phenetole and p-nitroaniline are relatively flat molecules. The retention on bare PGC depends on the molecular area of the solute. Before CTAB is introduced into the eluent, the retention of these analytes were attributed to their adsorption on the PGC surface. Also, these analytes are quite hydrophobic in comparison with the eluent. Therefore these solutes prefer to spend more time on the bare stationary phase. As a result, larger k^1 values were observed for these two compounds in the absence of the ion pairing agent

(Figure 6.7).

As the column anion exchange capacity increases [13] the space available for solute adsorption decreases. As a result, the retention of Phenetole and p-nitroaniline displayed diminished values.

All other solutes had poor resolution and low retention in the absence of CTAB. These analytes existed as anions in the alkaline solution. There may be solvation between these ions and methanol/water. These species may be classified as polar in comparison with the hydrophobic PGC. All these analytes would therefore display diminished retention values in the absence of the ion pairing agent.

The introduction of CTAB did (a) improve the resolution (Figures 6.8 and 6.9) and hence the solute separation, (b) increase the analyte retention values. The strength of ionic interaction between the ion pairing agent and the ionic forms of the solutes were greater than the strength of any interactions that existed between the solutes and the bare PGC before the introduction of CTAB.

Table 6.1 shows the retention of solutes before and after ion pairing. The k^1 values after dioxan treatment (approximately 7 hours) are also displayed. By and large the dioxan has been

successful in rejuvenating the PGC surface.

6.4 FUTURE WORK

(1) ICP may be performed on PGC to separate mixtures of (a) amino acids, (b) peptides, (c) anions and (d) cations. The retention of solutes, column capacities and efficiencies may be determined on PGC. The results could be compared with those obtained on other solid phases (RSi and PRP-1).

(2) The dependence of (a) additive retention and (b) solute retention (at constant eluent concentrations of the ion pairing agents), on carbon number of additive can be determined, using PGC as the solid phase.

The ratio of organic solvent to water, in the eluent, is kept constant.

Such experiments would be useful in understanding the adsorption of additives on to PGC.

(3) The dependence of (a) solute retention (at a constant eluent concentration of additive) and (b) additive retention, upon eluent polarity can be established.

The eluent polarity could be changed by (i) using different solvents to prepare the eluent (the ratio of water to organic solvent is kept constant), or (ii) altering the ratio of water to organic solvent. In (ii), only one organic solvent is used.

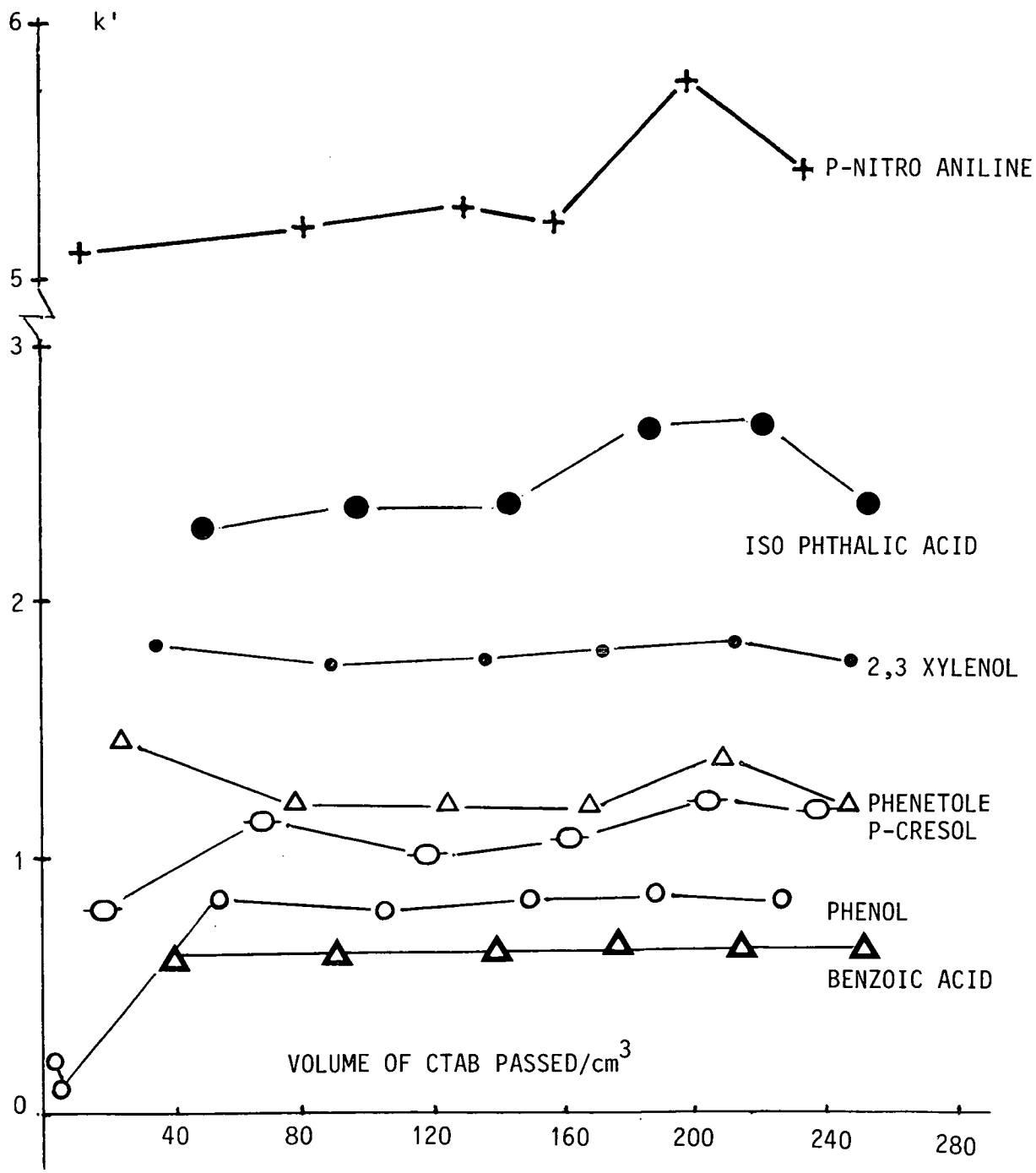
Table 6.1

k^1 of Solutes on PGC 86 CEN

Analyte	On Bare PGC	With 10mM CTAB (in eluent)	After Dioxan treatment (approximately 7 hours) (1 cm^3 min^{-1})
Phenol	0.153	2.10	0.154
P-nitro aniline	5.46	3.2	6.24
P-cresol	0.30	2.6	0.29
Phenetole	1.42	0.63	1.42
2,3-xylenol	1.23	3.0	1.32
Benzoic acid	0.21	1.46	0.12
Isophalic acid	0.06	20	0.08
2-t-Butyl-1,5-methyl Phenol	-	0.63	0.68

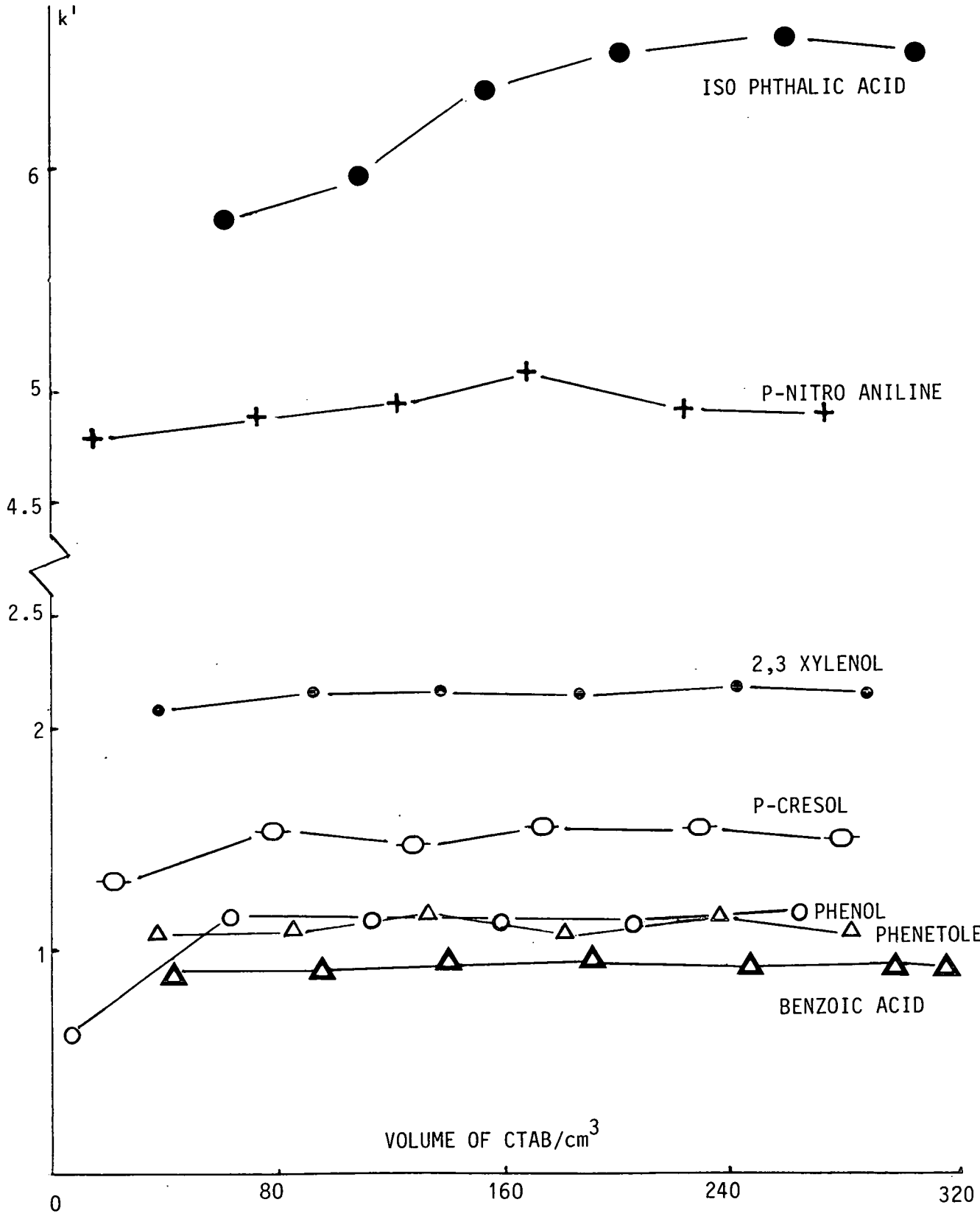
k' Vs VOLUME OF CTAB PASSED
0.5 m MOLAR

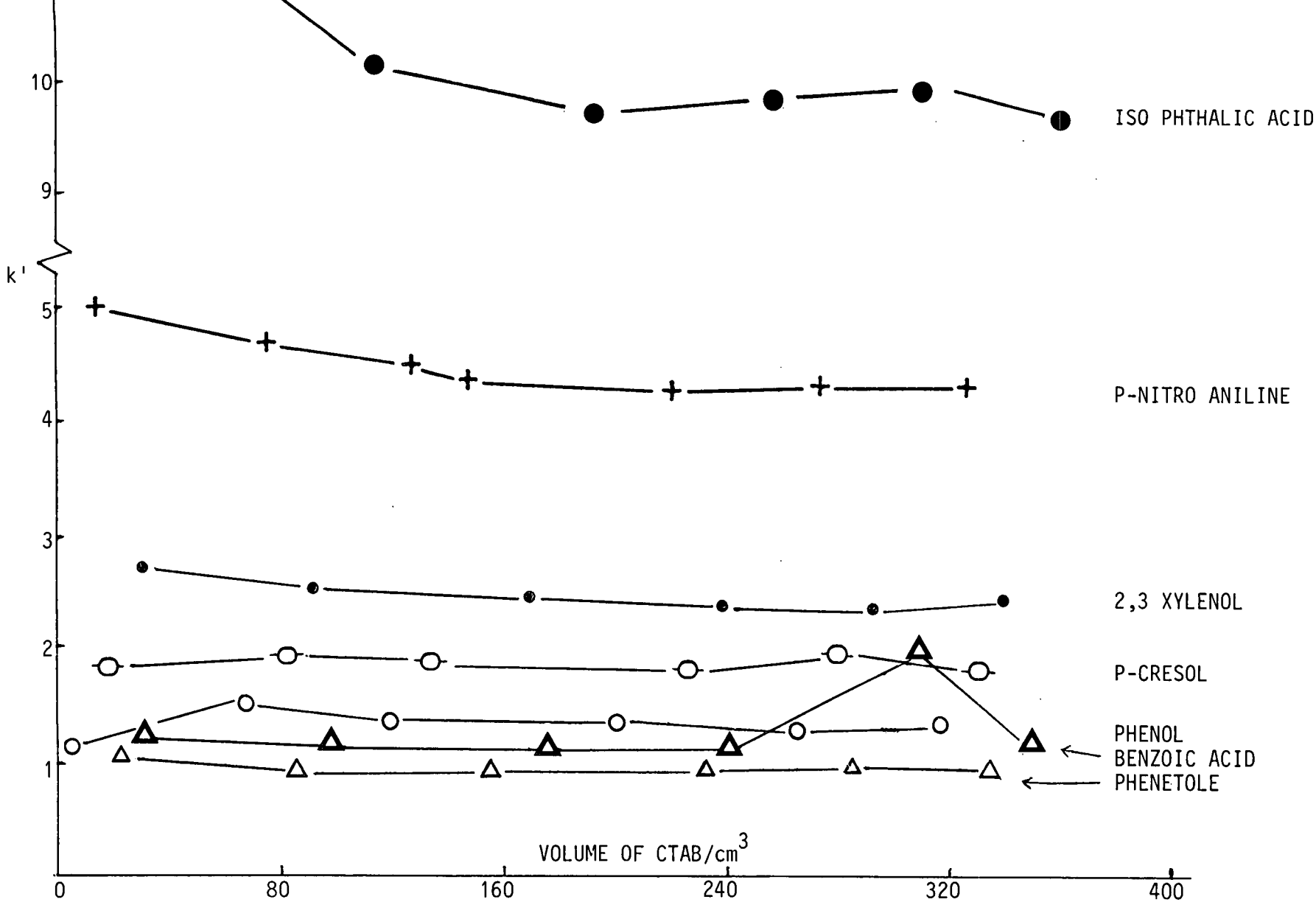
FIGURE 6.1

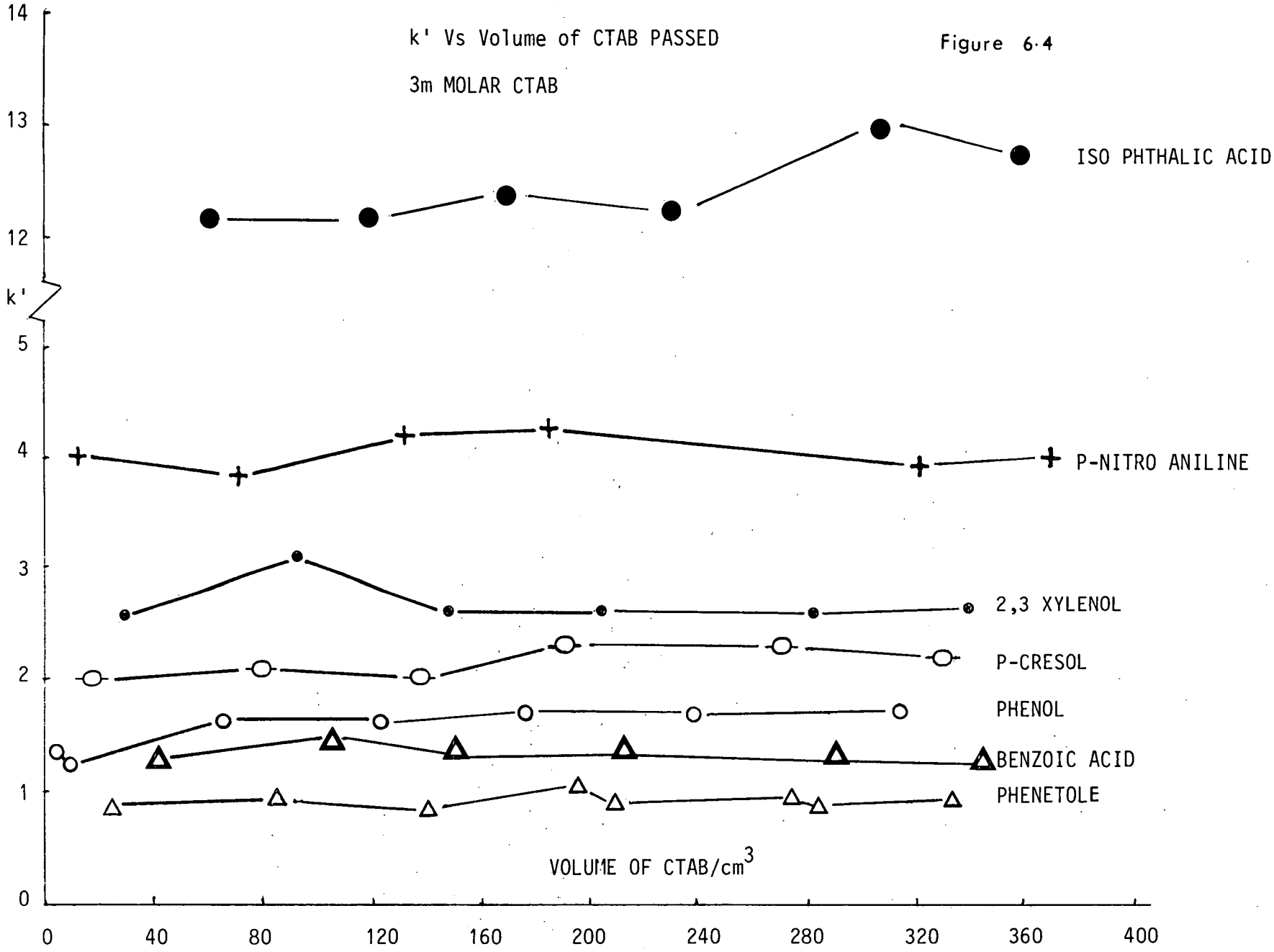


k' Vs VOLUME OF CTAB PASSED
1m MOLAR CTAB

FIGURE 6.2



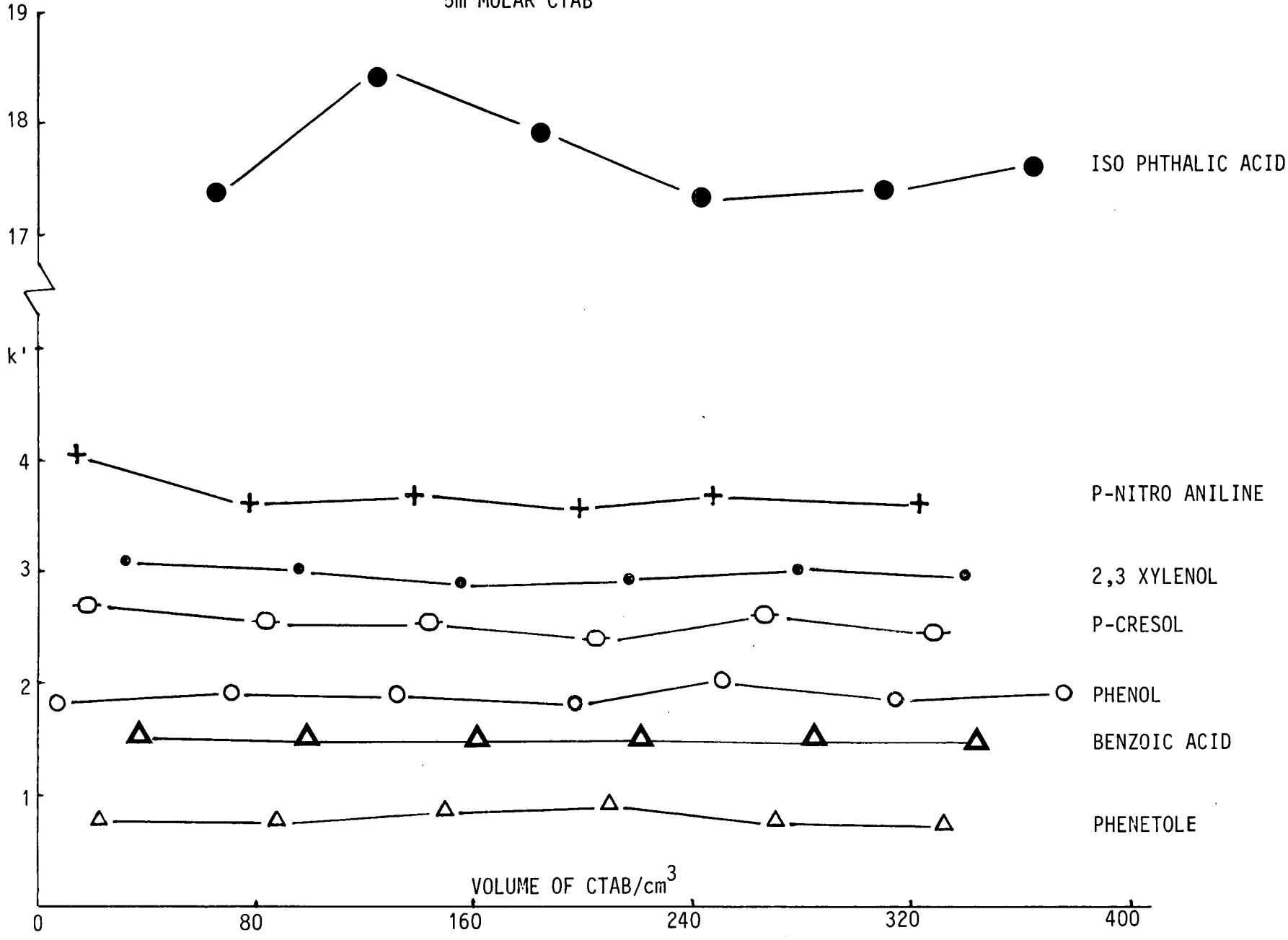

k'
10
9
5
4
3
2
1
ISO PHTHALIC ACID
P-NITRO ANILINE
2,3 XYLENOL
P-CRESOL
PHENOL
BENZOIC ACID
PHENETOLE
VOLUME OF CTAB/cm3
0
80
160
240
320
400


k' Vs Volume of CTAB PASSED
3m MOLAR CTAB
Figure 6·4
ISO PHTHALIC ACID
P-NITRO ANILINE
2,3 XYLENOL
P-CRESOL
PHENOL
BENZOIC ACID
PHENETOLE
k'
VOLUME OF CTAB/cm3
0
1
2
3
4
5
12
13
14
0
40
80
120
160
200
240
280
320
360
400

k' Vs VOLUME OF CTAB PASSED

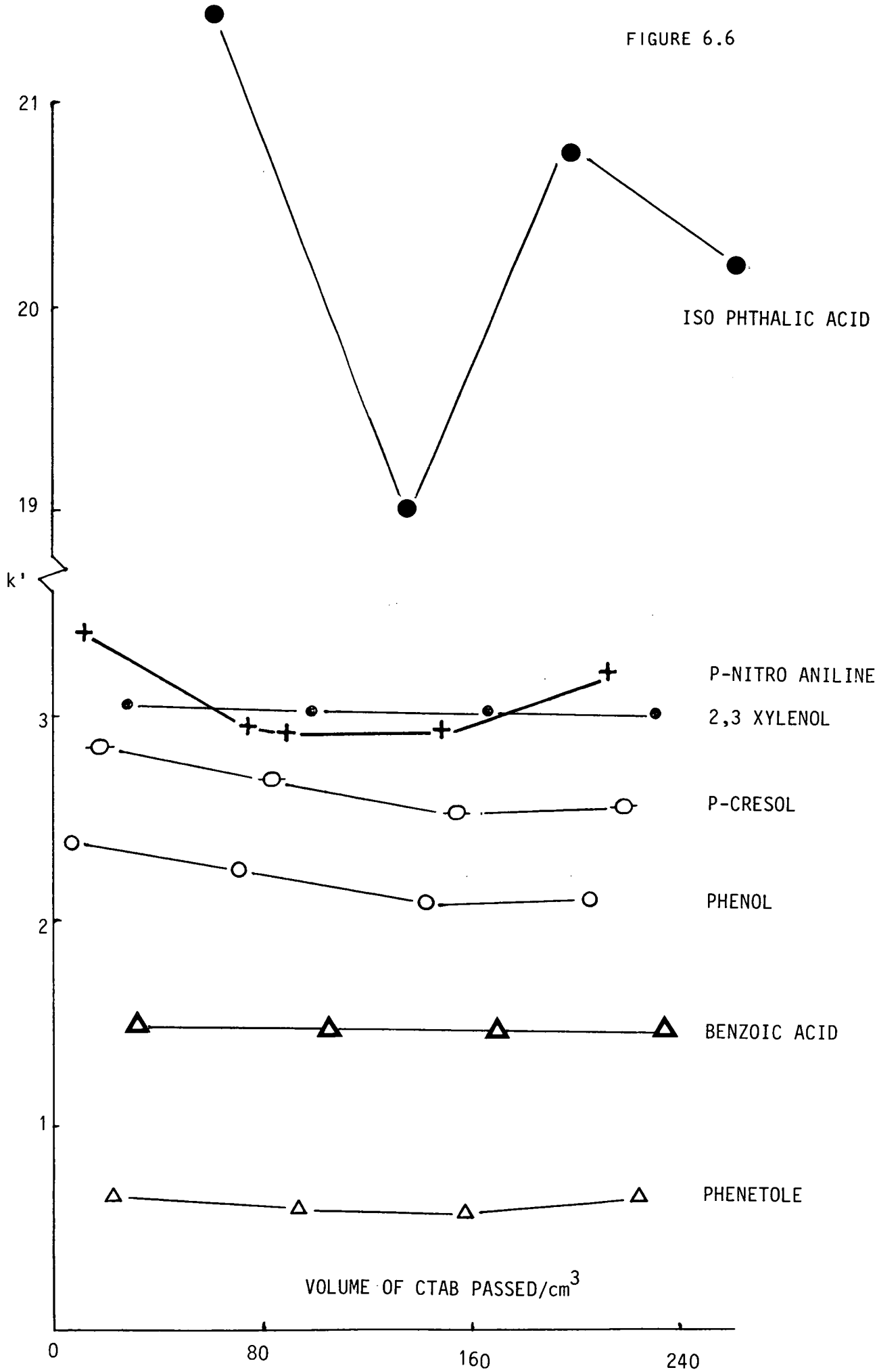
5m MOLAR CTAB

Figure 6·5

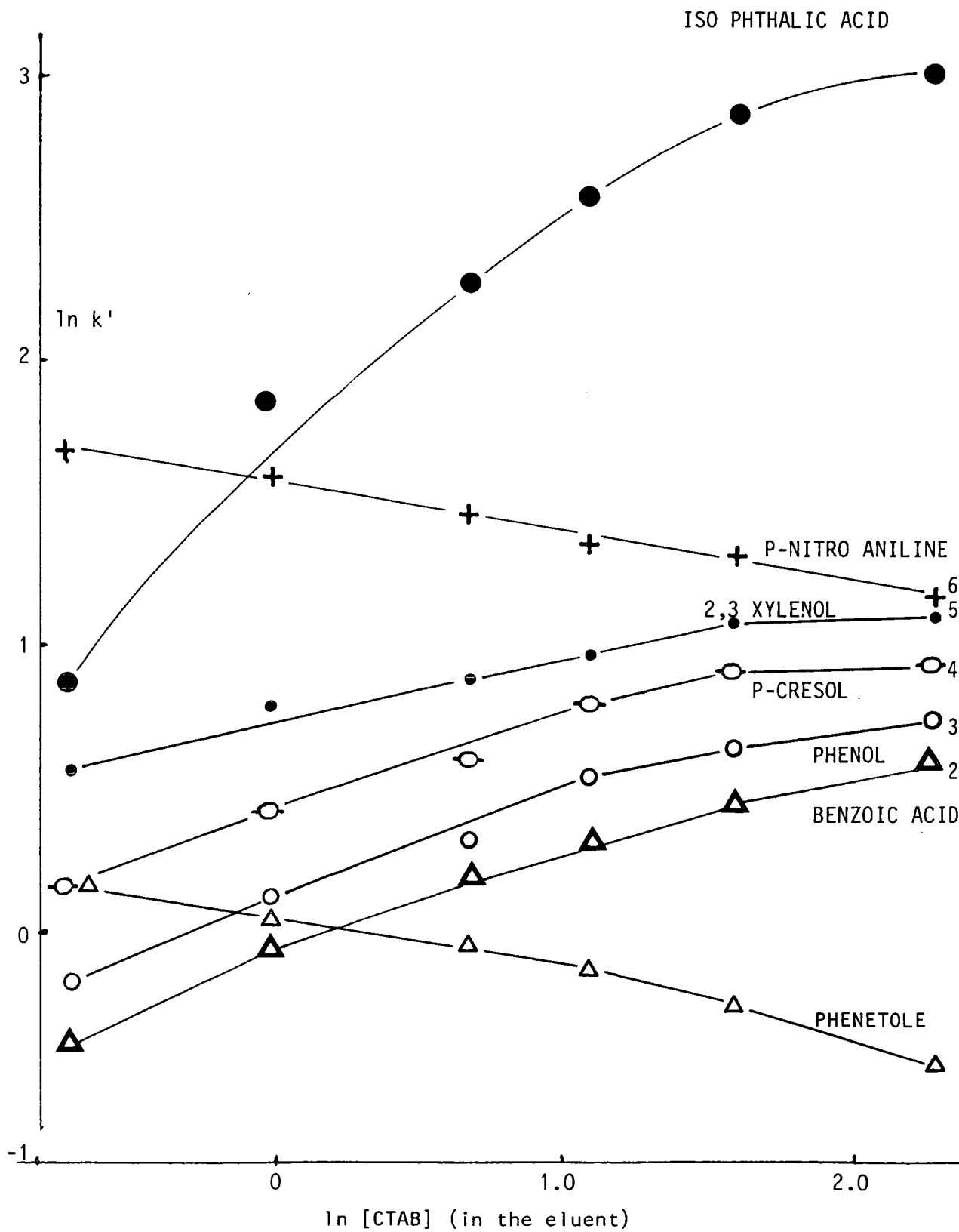


k' Vs Volume of CTAB 10 m MOLAR

FIGURE 6.6



$\ln k^1$ Vs ln (CTAB Concentration) FIGURE 6.7



Ion pairing on PGC FIGURE 6.8

10 mMolar Cetyltrimethylammonium bromide (pH= 12.6) in 95% w/w methanol as eluent.

1. Phenetole
2. Phenol
3. p-Cresol
4. 2,3 Xylenol

Chart speed= 1 cm/min

Flow rate of eluent= 1 ml/min.

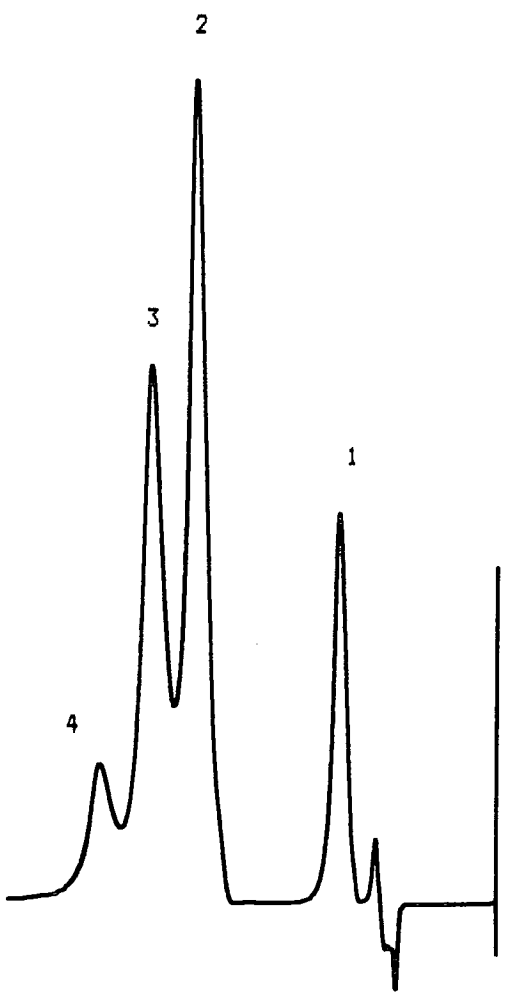


FIGURE 6.9

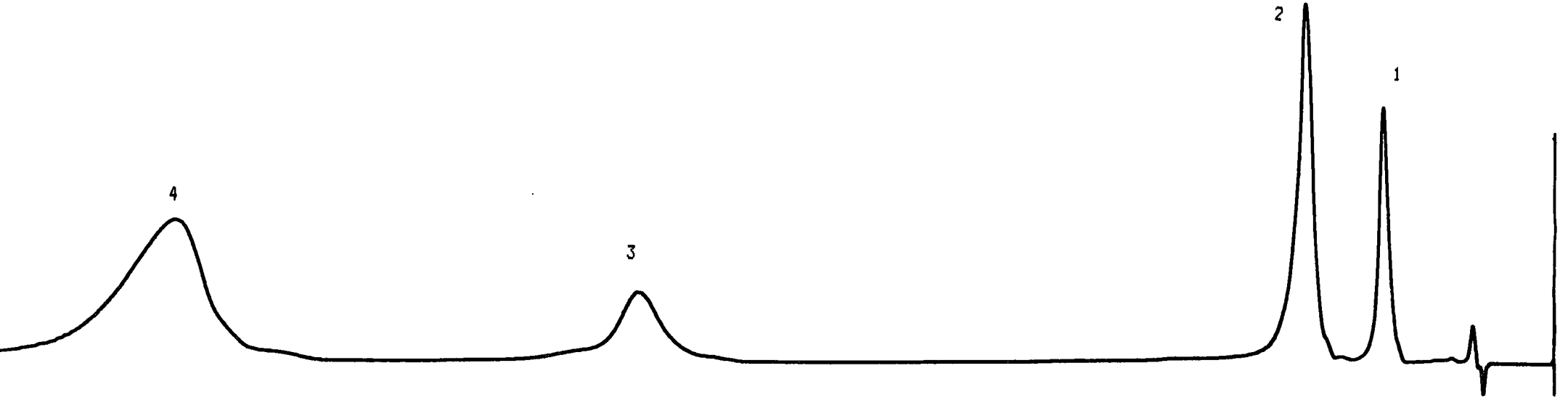
Ion pairing on PGC

10 mMolar Cetyltrimethylamonium bromide (pH= 12.6) in 95% w/w methanol as eluent.

1. Benzoic acid
2. p-Nitro aniline
3. unknown
4. Iso phthalic acid

Chart speed= 1 cm/min

Flow rate of eluent= 1 ml/min



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APPENDIX I

Determination of Surface Areas of Solids

The surface area of PGC samples were determined using the B.E.T. method. The theory is explained in Chapter 1. This appendix briefly describes the operation of the system in the laboratory.

A known quantity of sample (approximately 0.15g) is placed inside a sample tube (approximately $10cm^3$) and the tube degased until the pressure inside the system falls below 0.01 atm. The sample tube is surrounded with a furnace (temperature (150-300°C) depending on the sample) to aid the degassing process. The samples are sufficiently degassed and ready for the surface area determination after about four hours.

Then the furnace was replaced with a thermos flask filled with liquid nitrogen, to assist the adsorption of gaseous nitrogen doses on to the sample surface. Known nitrogen doses were introduced and the equilibrium pressure (P) of each dose was recorded as an output mV value from a pressure transducer and fed into the surface area calculation.

The volume of gas adsorbed per gram of adsorbate at standard temperature (273K) and pressure (atmospheric pressure) can be calculated.

The uptake volume of nitrogen, per gram of solid, after the introduction of the first dose is,

$$V_1 = [(Va_1)(Pd-P_1) - (V_{tube})P_1] \frac{273}{TRm} \times \frac{1}{W \times P_{atm}} \quad \text{——— AI.1}$$

where Va_1 = The volume of gaseous nitrogen in the initial dose.

Pd = Initial dose pressure (atmospheric pressure + pressure of gaseous nitrogen in the system).

TRm = Room temperature.

P_1 = Equilibrium pressure of nitrogen after the introduction of the first dose.

P_{atm} = Atmospheric pressure.

V_{tube} = Volume of sample tube.

W = Weight of material in the sample tube.

The uptake volume of nitrogen, per gram of adsorbent, after the introduction of the second dose is,

$$V_2 = V_1 + [Va_2(Pd-P_2) - V_{tube}\ (P_2-P_1)] \frac{273}{TRm \times W \times P_{atm}} \quad \text{——— AI.1}$$

where Va_2 = Volume of nitrogen in the second dose.

P_2 = Equilibrium pressure of nitrogen, after the introduction of the second dose.

After n doses, the volume of nitrogen adsorbed per gram of adsorbent is,

$$V_n = \left\{ \left[\sum_{i=1}^{i=n} Va_n\ (Pd-Pi) \right] - V_{tube}\ Pn \right\} \frac{273}{TRm \times W \times P_{atm}} \quad \text{——— AI.3}$$

where i = dose number.

Several doses of nitrogen can be introduced on to the adsorbent and the reslting uptake volumes (V) of adsorbate per gram of adsorbent can be calculated. Also the corresponding equilibrium pressures (P) may be noted [1,2[.

The pressure of a fixed mass of nitrogen at 77K enabled the determination of saturated vapour pressure (Po) of nitrogen.

The values of pressures (Pd, P_{atm}, Po) were measured in mm Hg and then converted to their equivalent mV values before feeding into the surface area calculation. This is because the equilibrium pressure values were recorded as output mV signals from a pressure transducer. The conversion factor of the transducer is 38.55mm Hg = 1mV.

A computer program may be used to calculate [2] the values of V and treat the data (V and P) pf each dose according to the B.E.T. equation, to calculate x (=P/Po) and y (= P/V(Po-P). The B.E.T. equation is in the form of y = mx + C. This treatment of results would enable the calculation of sample surface area (also see Chapter 1).

A typical surface area calculation is given on the next page.

References

[1] Third year undergraduate Physical Chemistry practical (Surface Area Determination) notes (Edinburgh University).

[2] Private Comm. with H.J. Ritchie.

SAMPLE NUMBER PGC 221 B1 CEN

Atmospheric Pressure	19.72mV
Initial Doser Pressure	22.75mV
Vapour Pressure of Nitrogen	18.52mV
Sample Weight (g)	0.1147
Room Temperature (K)	291
Sample Volume (ml)	10.55
Number of Doses	12
Intercept	-0.16814516

Dose Vol. (cm^2)	Eq. Pressure (mV)	X x 10^{-2}	Y x 10^{-3} (cm^{-3})	Vol.Ads. per gram (cm^3)
1.797	0.044	0.238	0.142	16.735
0.285	0.172	0.929	0.497	18.845
0.285	0.274	1.479	0.713	21.056
0.285	0.952	5.140	2.622	20.666
0.285	1.462	7.894	4.091	20.951
0.285	1.958	10.572	5.567	21.238
0.285	2.436	13.153	7.029	21.548
0.285	2.896	15.637	8.471	21.882
0.285	3.340	18.035	9.896	22.234
0.285	3.752	20.259	11.204	22.677
0.285	4.138	22.343	12.408	23.188
0.285	4.524	24.428	13.666	23.653
Surface Area	78 sq. metres per gram			

APPENDIX II

Tables of $\ln k^1$ vs 1/T

for

(a) PGC 219 CEN

(b) PGC 218 CEN

(c) CARBOPACK B

(d) PGC 219/220 SIG

(e) SILICA

The final column (i.e. 1/T) of the tables are headed 1E3 (1/T). This means, the table heading is 1/T and the figures in the column are to be multiplied by 10^{-3}.

PGC 219 CEN

Adsorbate : Hexane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
10.42	0.41	422	24.41	3.20	2.37
7.69	0.42	434	17.31	2.85	2.30
5.96	0.41	443	13.70	2.62	2.26
5.05	0.43	454	10.76	2.38	2.20
5.59	0.51	477	9.85	1.86	2.10
3.26	0.44	486	6.41	1.66	2.06

Gradient = 4878.84K
Intercept = -8.38

Heat of adsorption = -40.56 kJ/mol
Uncertainty in delta H = 0.41 kJ/mol

Adsorbate : N-Butyl Chloride

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
4.64	0.41	422	10.33	2.33	2.37
3.81	0.43	434	7.86	2.06	2.30
3.01	0.41	443	6.34	1.85	2.26
3.63	0.43	467	7.43	1.34	2.14
2.51	0.52	487	3.83	1.00	2.05

Gradient = 4262.52K
Intercept = -7.76

Heat of adsorption = -35.44 kJ/mol
Uncertainty in delta H = 0.47 kJ/mol

Adsorbate : Chloroform

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.85	0.41	423	3.52	1.26	2.36
1.69	0.44	433	2.85	1.05	2.31
1.39	0.41	443	2.38	0.87	2.26
1.29	0.43	454	1.99	0.69	2.20
1.37	0.53	467	1.58	0.46	2.20
1.06	0.44	486	1.39	0.33	2.06

Gradient = 3112.41K
Intercept = -6.14

Heat of adsorption = -25.88 kJ/mol
Uncertainty in delta H = 1.78 kJ/mol

PGC 219 CEN

Adsorbate : Dichloromethane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
4.59	0.41	323	10.20	2.32	3.09
3.58	0.41	333	7.73	2.05	3.00
2.82	0.41	343	5.88	1.77	2.91
2.31	0.41	353	4.63	1.53	2.83
1.95	0.42	363	3.64	1.29	2.75
1.50	0.39	373	2.85	1.05	2.68
1.46	0.43	383	2.38	0.87	2.61

Gradient = 3028.46K
Intercept = -7.05

Heat of adsorption = -25.18 kJ/mol
Uncertainty in delta H = 0.23 kJ/mol

Adsorbate : Me T-Butyl Ether

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
3.21	0.41	423	6.82	1.92	2.36
2.73	0.43	433	5.35	1.68	2.31
2.17	0.41	443	4.30	1.46	2.26
1.94	0.43	454	3.51	1.26	2.20
1.96	0.53	467	2.70	0.99	2.14
1.25	0.42	487	1.98	0.68	2.05

Gradient = 3989.28K
Intercept = -7.53

Heat of adsorption = -33.17 kJ/mol
Uncertainty in delta H = 0.61 kJ/mol

Adsorbate : Ethyl Acetate

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
2.96	0.41	423	6.21	1.83	2.36
2.48	0.42	433	4.90	1.59	2.31
2.01	0.41	443	3.90	1.36	2.26
1.79	0.43	454	3.17	1.16	2.20
1.79	0.52	467	2.41	0.88	2.14
1.16	0.42	486	1.76	0.57	2.06

Gradient = 4124.11K
Intercept = -7.93

Heat of adsorption = -34.29 kJ/mol
Uncertainty in delta H = 0.48 kJ/mol

PGC 219 CEN

Adsorbate : Dioxan

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
2.61	0.41	422	15.35	1.68	2.37
2.19	0.42	433	4.21	1.44	2.31
1.85	0.41	443	3.52	1.26	2.26
1.65	0.43	454	2.83	1.04	2.20
1.34	0.41	466	2.27	0.82	2.15
1.20	0.42	477	1.86	0.62	2.10

Gradient = 3858.74K
Intercept = -7.46

Heat of adsorption = -32.08 kJ/mol
Uncertainty in delta H = 0.31 kJ/mol

Adsorbate : Acetonitrile

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.99	0.41	323	3.84	1.35	3.09
1.62	0.42	333	2.90	1.07	3.00
1.36	0.41	343	2.32	0.84	2.91
1.17	0.41	353	1.84	0.61	2.83
1.02	0.41	363	1.49	0.40	2.75
0.86	0.39	373	1.22	0.20	2.68

Gradient = 2752.69K
Intercept = -7.18

Heat of adsorption = -22.89 kJ/mol
Uncertainty in delta H = 0.21 kJ/mol

Adsorbate : Tetrahydrofuran

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.60	0.41	423	2.95	1.08	2.36
1.43	0.42	433	2.39	0.87	2.31
1.23	0.41	443	2.01	0.70	2.26
1.15	0.43	454	1.66	0.51	2.20
1.29	0.55	467	1.35	0.30	2.14
0.85	0.42	487	1.02	0.02	2.05

Gradient = 3405.92K
Intercept = -6.98

Heat of adsorption = -28.32 kJ/mol
Uncertainty in delta H = 0.45 kJ/mol

PGC 219 CEN

Adsorbate : Dimethyl Formamide

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
3.86	0.41	422	18.41	2.13	2.37
3.17	0.42	433	6.55	1.88	2.31
2.51	0.41	443	5.13	1.64	2.26
2.18	0.43	454	4.07	1.40	2.20
2.16	0.52	467	3.15	1.15	2.14
1.37	0.42	487	2.26	0.82	2.05

Gradient = 4190.78K
Intercept = -7.81

Heat of adsorption = -34.84 kJ/mol
Uncertainty in delta H = 0.60 kJ/mol

Adsorbate : Methanol

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
0.86	0.42	303	1.06	0.06	3.30
0.76	0.41	313	0.87	-0.14	3.19
0.69	0.41	323	0.70	-0.36	3.09
0.64	0.41	333	0.56	-0.58	3.00
0.60	0.42	343	0.44	-0.82	2.91
0.56	0.41	353	0.38	-0.97	2.83
0.54	0.42	363	0.29	-1.25	2.75
0.48	0.39	373	0.24	-1.41	2.68

Gradient = 2409.58K
Intercept = -7.84

Heat of adsorption = -20.03 kJ/mol
Uncertainty in delta H = 0.56 kJ/mol

Adsorbate : Benzene

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
5.33	0.38	435	13.03	2.57	2.30
4.39	0.39	445	10.27	2.33	2.25
3.62	0.39	456	8.27	2.11	2.19
2.97	0.40	466	6.42	1.86	2.15
2.53	0.40	476	5.34	1.67	2.10
2.16	0.40	486	4.40	1.48	2.06

Gradient = 4517.62K
Intercept = -7.81

Heat of adsorption = -37.56 kJ/mol
Uncertainty in delta H = 0.60 kJ/mol

PGC 219 CEN

Adsorbate : Cyclohexane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
3.09	0.38	435	17.14	1.97	2.30
2.61	0.39	446	5.69	1.74	2.24
2.25	0.39	456	4.78	1.56	2.19
1.94	0.40	466	3.86	1.35	2.15
1.72	0.40	476	3.30	1.19	2.10
1.52	0.40	486	2.80	1.03	2.06

Gradient = 3898.75K
Intercept = -7.00

Heat of adsorption = -32.41 kJ/mol
Uncertainty in delta H = 0.47 kJ/mol

Adsorbate : Cyclopentane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.42	0.38	435	2.75	1.01	2.30
1.27	0.39	446	2.24	0.81	2.24
1.15	0.39	456	1.95	0.67	2.19
1.04	0.40	466	1.60	0.47	2.15
0.97	0.40	476	1.41	0.35	2.10
0.89	0.40	486	1.22	0.20	2.06

Gradient = 3360.22K
Intercept = -6.72

Heat of adsorption = -27.94 kJ/mol
Uncertainty in delta H = 0.63 kJ/mol

PGC 218 CEN

Adsorbate : Hexane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.84	0.61	533	1.99	0.69	1.88
2.31	0.61	514	2.79	1.02	1.94
3.08	0.60	494	4.13	1.42	2.02
4.44	0.56	473	6.92	1.93	2.11
6.39	0.58	453	10.02	2.30	2.21
11.07	0.56	434	18.60	2.92	2.30

Gradient = 5155.80K
Intercept = -9.00

Heat of adsorption = -42.87 kJ/mol
Uncertainty in delta H = 1.13 kJ/mol

Adsorbate : N-Butyl Chloride

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.53	0.61	514	1.51	0.41	1.94
1.88	0.60	494	2.13	0.76	2.02
2.43	0.59	473	3.13	1.14	2.11
3.36	0.58	454	4.75	1.56	2.20
4.96	0.57	434	7.70	2.04	2.30
8.16	0.55	413	13.84	2.63	2.42

Gradient = 4653.95K
Intercept = -8.67

Heat of adsorption = -38.69 kJ/mol
Uncertainty in delta H = 0.58 kJ/mol

Adsorbate : Chloroform

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.33	0.59	473	1.24	0.22	2.11
1.51	0.53	453	1.85	0.61	2.21
2.04	0.56	434	2.61	0.96	2.30
2.87	0.55	413	4.22	1.44	2.42
4.15	0.54	394	6.69	1.90	2.54
6.87	0.55	373	11.49	2.44	2.68

Gradient = 3920.30K
Intercept = -8.06

Heat of adsorption = -32.59 kJ/mol
Uncertainty in delta H = 0.27 kJ/mol

PGC 218 CEN

Adsorbate : Dichloromethane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
0.95	0.58	454	0.62	-0.49	2.20
1.05	0.56	434	0.86	-0.15	2.30
1.24	0.55	413	1.25	0.23	2.42
1.54	0.55	394	1.79	0.58	2.54
2.08	0.55	373	2.78	1.02	2.68
3.07	0.55	353	4.57	1.52	2.83

Gradient = 3164.50K
Intercept = -7.45

Heat of adsorption = -26.31 kJ/mol
Uncertainty in delta H = 0.16 kJ/mol

Adsorbate : Me T-Butyl Ether

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.29	0.61	513	1.11	0.11	1.95
1.51	0.60	494	1.52	0.42	2.02
1.88	0.59	473	2.19	0.78	2.11
2.30	0.54	453	3.26	1.18	2.21
3.45	0.56	434	5.15	1.64	2.30
5.37	0.56	413	8.60	2.15	2.42

Gradient = 4345.77K
Intercept = -8.38

Heat of adsorption = -36.13 kJ/mol
Uncertainty in delta H = 0.47 kJ/mol

Adsorbate : Ethyl Acetate

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
7.48	0.55	395	12.60	2.53	2.53
5.00	0.56	413	7.93	2.07	2.42
3.19	0.56	434	4.65	1.54	2.30
2.25	0.58	454	2.85	1.05	2.20
1.73	0.59	473	1.93	0.66	2.11
1.42	0.60	494	1.34	0.29	2.02

Gradient = 4480.21K
Intercept = -8.79

Heat of adsorption = -37.25 kJ/mol
Uncertainty in delta H = 0.41 kJ/mol

PGC 218 CEN

Adsorbate : Dioxan

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.35	0.60	494	1.25	0.22	2.02
1.64	0.59	473	1.78	0.58	2.11
2.12	0.59	453	2.60	0.96	2.21
2.92	0.58	433	4.03	1.39	2.31
4.21	0.55	413	6.65	1.89	2.42
6.43	0.54	394	10.91	2.39	2.54

Gradient = 4244.46K
Intercept = -8.39

Heat of adsorption = -35.29 kJ/mol
Uncertainty in delta H = 0.36 kJ/mol

Adsorbate : Acetonitrile

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
0.78	0.59	454	0.32	-1.13	2.20
0.80	0.56	434	0.44	-0.83	2.30
0.89	0.55	413	0.62	-0.48	2.42
1.00	0.55	394	0.81	-0.21	2.54
1.33	0.55	373	1.42	0.35	2.68
1.54	0.55	353	1.79	0.58	2.83

Gradient = 2809.04K
Intercept = -7.30

Heat of adsorption = -23.35 kJ/mol
Uncertainty in delta H = 1.17 kJ/mol

Adsorbate : Tetrahydrofuran

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.27	0.66	477	0.94	-0.06	2.10
1.44	0.59	454	1.43	0.36	2.20
1.81	0.57	434	2.18	0.78	2.30
2.46	0.58	413	3.21	1.17	2.42
3.58	0.54	394	5.57	1.72	2.54
5.96	0.54	373	9.94	2.30	2.68

Gradient = 4024.93K
Intercept = -8.51

Heat of adsorption = -33.46 kJ/mol
Uncertainty in delta H = 0.62 kJ/mol

PGC 218 CEN

Adsorbate : Dimethyl Formamide

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.23	0.63	533	0.95	-0.05	1.88
1.43	0.61	514	1.33	0.28	1.94
1.76	0.60	494	1.91	0.65	2.02
2.47	0.60	473	3.12	1.14	2.11
3.44	0.60	454	4.73	1.55	2.20
5.60	0.60	434	8.26	2.11	2.30

Gradient = 5044.87K
Intercept = -9.53

Heat of adsorption = -41.94 kJ/mol
Uncertainty in delta H = 0.57 kJ/mol

Adsorbate : Methanol

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.33	0.53	313	1.51	0.41	3.19
1.12	0.53	323	1.10	0.10	3.09
0.96	0.54	332	0.78	-0.25	3.01
0.90	0.55	344	0.63	-0.47	2.91
0.84	0.55	353	0.52	-0.65	2.83
0.76	0.56	373	0.36	-1.03	2.68

Gradient = 2778.23K
Intercept = -8.52

Heat of adsorption = -23.10 kJ/mol
Uncertainty in delta H = 1.25 kJ/mol

Adsorbate : Benzene

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.54	0.62	533	1.48	0.39	1.88
1.87	0.61	514	2.07	0.73	1.94
2.38	0.60	494	2.97	1.09	2.02
3.27	0.59	473	4.54	1.51	2.11
4.81	0.59	454	7.14	1.97	2.20
7.22	0.55	434	12.13	2.50	2.30

Gradient = 4895.19K
Intercept = -8.80

Heat of adsorption = -40.70 kJ/mol
Uncertainty in delta H = 0.50 kJ/mol

PGC 218 CEN

Adsorbate : Cyclohexane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.48	0.61	513	1.43	0.36	1.95
1.77	0.60	494	1.95	0.67	2.02
2.25	0.59	473	2.81	1.03	2.11
3.04	0.59	454	4.16	1.43	2.20
4.19	0.55	434	6.55	1.88	2.30
6.73	0.56	414	10.91	2.39	2.41

Gradient = 4358.86K
Intercept = -8.16

Heat of adsorption = -36.24 kJ/mol
Uncertainty in delta H = 0.46 kJ/mol

Adsorbate : Cyclopentane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.27	0.59	473	1.15	0.14	2.11
1.53	0.59	454	1.57	0.45	2.20
1.90	0.56	434	2.35	0.86	2.30
2.56	0.55	413	3.65	1.30	2.42
3.71	0.55	394	5.75	1.75	2.54
5.96	0.54	373	10.04	2.31	2.68

Gradient = 3833.77K
Intercept = -7.98

Heat of adsorption = -31.87 kJ/mol
Uncertainty in delta H = 0.21 kJ/mol

Adsorbate : Ethanol

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
0.78	0.59	454	0.32	-1.13	2.20
0.85	0.60	434	0.42	-0.88	2.30
0.98	0.57	413	0.72	-0.33	2.42
1.10	0.56	394	0.97	-0.03	2.54
1.19	0.55	373	1.15	0.14	2.68
1.46	0.56	353	1.61	0.47	2.83

Gradient = 2561.74K
Intercept = -6.68

Heat of adsorption = -21.30 kJ/mol
Uncertainty in delta H = 2.17 kJ/mol

CARBOPAC B

Adsorbate : Hexane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.60	0.67	574	1.39	0.33	1.74
1.99	0.67	554	1.97	0.68	1.80
2.52	0.69	533	2.65	0.98	1.88
3.53	0.70	514	4.04	1.40	1.94
5.34	0.70	492	6.63	1.89	2.03
8.29	0.70	471	10.84	2.38	2.12

Gradient = 5408.94K
Intercept = -9.11

Heat of adsorption = -44.97 kJ/mol
Uncertainty in delta H = 0.93 kJ/mol

Adsorbate : N-Butyl Chloride

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
10.31	0.71	432	13.52	2.60	2.31
6.20	0.72	452	7.61	2.03	2.21
4.14	0.70	472	4.91	1.59	2.12
2.95	0.70	492	3.21	0.71	1.95
2.18	0.72	513	2.03	0.71	1.95
1.75	0.66	534	1.65	0.50	1.87

Gradient = 4846.48K
Intercept = -8.66

Heat of adsorption = -40.29 kJ/mol
Uncertainty in delta H = 1.50 kJ/mol

Adsorbate : Chloroform

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
6.24	0.69	411	8.04	2.08	2.43
3.71	0.71	432	4.23	1.44	2.31
2.66	0.71	452	2.75	1.01	2.21
2.02	0.70	472	1.89	0.63	2.12
1.62	0.70	492	1.32	0.28	2.03
1.36	0.70	514	0.94	-0.06	1.94

Gradient = 4334.88K
Intercept = -8.53

Heat of adsorption = -36.04 kJ/mol
Uncertainty in delta H = 1.16 kJ/mol

CARBOPAC B

Adsorbate : Dichloromethane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
3.00	0.72	392	3.17	1.15	2.55
2.05	0.72	411	1.85	0.61	2.43
4.33	0.73	372	4.93	1.60	2.69
7.40	0.74	352	9.00	2.20	2.84
1.34	0.71	452	0.89	-0.12	2.21
1.04	0.71	493	0.46	-0.77	2.03
0.98	0.69	514	0.42	-0.87	1.94

Gradient = 3501.79K
Intercept = -7.81

Heat of adsorption = -29.11 kJ/mol
Uncertainty in delta H = 0.87 kJ/mol

Adsorbate : Me T-Butyl Ether

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.51	0.66	534	1.29	0.25	1.87
1.80	0.70	512	1.57	0.45	1.95
2.35	0.70	492	2.35	0.85	2.03
3.19	0.70	471	3.56	1.27	2.12
4.61	0.72	452	5.40	1.69	2.21
7.29	0.71	432	9.27	2.23	2.31

Gradient = 4558.24K
Intercept = -8.38

Heat of adsorption = -37.90 kJ/mol
Uncertainty in delta H = 1.58 kJ/mol

Adsorbate : Ethyl Acetate

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
7.19	0.71	432	9.13	2.21	2.31
4.86	0.70	452	5.94	1.78	2.21
2.99	0.69	472	3.33	1.20	2.12
1.65	0.69	513	1.39	0.33	1.95
1.06	0.66	492	0.61	0.77	2.03

Gradient = 5240.18K
Intercept = -9.88

Heat of adsorption = -43.57 kJ/mol
Uncertainty in delta H = 1.35 kJ/mol

CARBOPAC B

Adsorbate :Dioxan

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
5.36	0.71	432	6.55	1.88	2.31
3.97	0.72	452	4.51	1.51	2.21
2.79	0.70	471	2.99	1.09	2.12
2.06	0.76	492	1.72	0.54	2.03
1.64	0.70	514	1.34	0.29	1.94
1.42	0.66	533	1.15	0.14	1.88

Gradient = 4195.97K
Intercept = -7.83

Heat of adsorption = -34.89 kJ/mol
Uncertainty in delta H = 2.23 kJ/mol

Adsorbate : Acetonitrile

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
2.20	0.69	391	2.19	0.78	2.56
1.74	0.71	411	1.45	0.37	2.43
1.25	0.71	432	0.77	-0.26	2.31
1.11	0.70	452	0.59	-0.53	2.21
0.99	0.71	472	0.39	-0.93	2.12
0.88	0.70	492	0.26	-1.36	2.03

Gradient = 4053.94K
Intercept = -9.55

Heat of adsorption = -33.70 kJ/mol
Uncertainty in delta H = 1.32 kJ/mol

Adsorbate : Tetrahydrofuran

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
5.47	0.70	410	6.81	1.92	2.44
3.49	0.71	432	3.91	1.36	2.31
2.34	0.72	452	2.25	0.81	2.21
1.89	0.70	471	1.70	0.53	2.12
1.52	0.69	492	1.20	0.18	2.03
1.32	0.71	514	0.86	-0.15	1.94

Gradient = 4183.28K
Intercept = -8.33

Heat of adsorption = -34.78 kJ/mol
Uncertainty in delta H = 1.34 kJ/mol

CARBOPAC B

Adsorbate : Dimethyl Formamide

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.37	0.66	574	1.08	0.07	1.74
1.82	0.70	554	1.60	0.47	1.80
1.96	0.68	533	1.88	0.63	1.88
2.55	0.70	514	2.64	0.97	1.94
4.30	0.69	493	5.23	1.65	2.03
5.99	0.72	472	7.32	1.99	2.12

Gradient = 5161.65K
Intercept = -8.94

Heat of adsorption = -42.91 kJ/mol
Uncertainty in delta H = 3.08 kJ/mol

Adsorbate : Methanol

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.02	0.70	411	0.46	-0.78	2.43
1.15	0.70	391	0.64	-0.44	2.56
1.40	0.72	371	0.94	-0.06	2.69
1.82	0.72	351	1.53	0.42	2.85
2.54	0.75	331	2.39	0.87	3.02
3.84	0.76	310	4.05	1.40	3.22

Gradient = 2779.75K
Intercept = -7.54

Heat of adsorption = -23.11 kJ/mol
Uncertainty in delta H = 0.35 kJ/mol

Adsorbate : Benzene

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.64	0.68	554	1.41	0.34	1.80
1.97	0.69	535	1.86	0.62	1.87
2.68	0.69	514	2.88	1.06	1.94
3.79	0.70	492	4.41	1.48	2.03
5.62	0.70	472	7.03	1.95	2.12
9.07	0.71	452	11.77	2.47	2.21

Gradient = 5241.63K
Intercept = -9.15

Heat of adsorption = -43.58 kJ/mol
Uncertainty in delta H = 0.65 kJ/mol

CARBOPAC B

Adsorbate : Cyclohexane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
9.17	0.71	432	11.92	2.48	2.31
5.68	0.71	452	7.00	1.95	2.21
3.88	0.70	471	4.54	1.51	2.12
2.82	0.71	492	2.97	1.09	2.03
2.11	0.70	514	2.01	0.70	1.94
1.71	0.68	534	1.51	0.42	1.87

Gradient = 4678.36K
Intercept = -8.39

Heat of adsorption = -38.90 kJ/mol
Uncertainty in delta H = 0.83 kJ/mol

Adsorbate : Cyclopentane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
5.20	0.74	411	6.03	1.80	2.43
3.42	0.72	432	3.75	1.32	2.31
2.46	0.72	453	2.42	0.88	2.21
1.91	0.71	472	1.69	0.52	2.12
1.53	0.69	493	1.22	0.20	2.03
1.38	0.71	514	0.94	-0.06	1.94

Gradient = 3852.71K
Intercept = -7.60

Heat of adsorption = -32.03 kJ/mol
Uncertainty in delta H = 0.72 kJ/mol

Adsorbate : Ethanol

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
2.51	0.69	391	2.64	0.97	2.56
1.61	0.71	410	1.27	0.24	2.44
1.23	0.70	432	0.76	-0.28	2.31
1.07	0.70	452	0.53	-0.64	2.21
0.89	0.74	493	0.20	-1.60	2.03

Gradient = 4689.49K
Intercept = -11.09

Heat of adsorption = -38.99 kJ/mol
Uncertainty in delta H = 1.85 kJ/mol

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Adsorbate : Hexane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.42	0.47	551	2.03	0.71	1.81
1.79	0.46	531	2.90	1.07	1.88
2.42	0.45	510	4.39	1.48	1.96
3.81	0.48	490	6.95	1.94	2.04
6.27	0.49	470	11.80	2.47	2.13
10.59	0.48	449	20.84	3.04	2.23

Gradient = 5682.61K
Intercept = -9.63

Heat of adsorption = -47.25 kJ/mol
Uncertainty in delta H = 0.63 kJ/mol

Adsorbate : N-Butyl Chloride

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.20	0.46	531	1.61	0.48	1.88
1.48	0.44	510	2.33	0.84	1.96
1.94	0.44	490	3.42	1.23	2.04
2.96	0.50	470	4.93	1.60	2.13
4.78	0.49	449	8.76	2.17	2.23
7.69	0.47	429	15.36	2.73	2.33

Gradient = 5016.21K
Intercept = -9.00

Heat of adsorption = -41.70 kJ/mol
Uncertainty in delta H = 1.02 kJ/mol

Adsorbate : Chloroform

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.19	0.52	491	1.29	0.25	2.04
1.42	0.49	470	1.89	0.64	2.13
1.84	0.48	449	2.83	1.04	2.23
2.47	0.46	429	4.38	1.48	2.33
3.67	0.47	411	6.81	1.92	2.43
6.18	0.47	391	12.00	2.48	2.56

Gradient = 4266.73K
Intercept = -8.45

Heat of adsorption = -35.47 kJ/mol
Uncertainty in delta H = 0.36 kJ/mol

PGC 219/220 SIGIRI

Adsorbate : Dichloromethane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
0.82	0.49	470	0.66	-0.42	2.13
0.91	0.48	449	0.88	-0.13	2.23
1.04	0.46	429	1.26	0.23	2.33
1.16	0.42	411	1.76	0.57	2.43
1.81	0.48	391	2.76	1.02	2.56
2.71	0.47	370	4.76	1.56	2.70

Gradient = 3457.94K
Intercept = -7.81

Heat of adsorption = -28.75 kJ/mol
Uncertainty in delta H = 0.55 kJ/mol

Adsorbate : Me T-Butyl Ether

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.15	0.54	531	1.13	0.12	1.88
1.37	0.53	510	1.58	0.45	1.96
1.69	0.52	490	2.25	0.81	2.04
2.18	0.49	470	3.46	1.24	2.13
3.11	0.49	449	5.35	1.68	2.23
4.79	0.46	429	9.41	2.24	2.33
7.22	0.42	411	16.19	2.78	2.43

Gradient = 4837.39K
Intercept = -9.03

Heat of adsorption = -40.22 kJ/mol
Uncertainty in delta H = 0.74 kJ/mol

Adsorbate : Ethylacetate

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
0.95	0.46	531	1.05	0.05	1.88
1.12	0.45	510	1.49	0.40	1.96
1.39	0.44	490	2.16	0.77	2.04
2.14	0.50	470	3.29	1.19	2.13
3.14	0.49	449	5.41	1.69	2.23
5.05	0.47	429	9.74	2.28	2.33

Gradient = 4946.66K
Intercept = -9.30

Heat of adsorption = -41.13 kJ/mol
Uncertainty in delta H = 0.87 kJ/mol

PGC 219/220 SIGIRI

Adsorbate : Dioxan

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.24	0.52	510	1.36	0.31	1.96
1.50	0.52	490	1.88	0.63	2.04
1.88	0.49	470	2.84	1.04	2.13
2.67	0.47	449	4.67	1.54	2.23
3.85	0.47	429	7.19	1.97	2.33
5.62	0.42	410	12.37	2.52	2.44

Gradient = 4631.85K
Intercept = -8.79

Heat of adsorption = -38.51 kJ/mol
Uncertainty in delta H = 0.54 kJ/mol

Adsorbate : Acetonitrile

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
0.68	0.50	470	0.35	-1.05	2.13
0.71	0.49	449	0.44	-0.82	2.23
0.79	0.46	430	0.73	-0.32	2.32
0.86	0.42	411	1.05	0.05	2.43
1.25	0.48	391	1.59	0.47	2.56
2.05	0.48	370	3.28	1.19	2.70

Gradient = 3898.48K
Intercept = -9.42

Heat of adsorption = -32.41 kJ/mol
Uncertainty in delta H = 1.44 kJ/mol

Adsorbate : Tetrahydrofuran

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.10	0.52	491	1.11	0.10	2.04
1.29	0.50	470	1.57	0.45	2.13
1.66	0.49	449	2.39	0.87	2.23
2.33	0.46	430	4.07	1.40	2.32
2.96	0.42	412	6.06	1.80	2.43
5.77	0.48	391	11.02	2.40	2.56

Gradient = 4469.95K
Intercept = -9.03

Heat of adsorption = -37.16 kJ/mol
Uncertainty in delta H = 0.75 kJ/mol

PGC 219/220 SIGIRI

Adsorbate : Dimethyl Formamide

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.16	0.47	551	1.47	0.38	1.81
1.29	0.47	541	1.76	0.56	1.85
1.54	0.46	531	2.35	0.85	1.88
1.69	0.46	521	2.66	0.98	1.92
2.12	0.46	510	3.60	1.28	1.96
2.62	0.45	501	4.83	1.58	2.00

Gradient = 6448.11K
Intercept = -11.33

Heat of adsorption = -53.61 kJ/mol
Uncertainty in delta H = 2.58 kJ/mol

Adsorbate : Methanol

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
0.57	0.49	449	0.16	-1.81	2.23
0.61	0.47	429	0.31	-1.18	2.33
0.81	0.47	411	0.72	-0.32	2.43
0.98	0.48	391	1.05	0.05	2.56
1.25	0.48	369	1.59	0.47	2.71
1.79	0.48	349	2.73	1.00	2.86

Gradient = 4270.32K
Intercept = -11.06

Heat of adsorption = -35.50 kJ/mol
Uncertainty in delta H = 3.98 kJ/mol

Adsorbate : Benzene

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.21	0.47	551	1.56	0.45	1.81
1.48	0.45	531	2.24	0.81	1.88
1.92	0.45	511	3.27	1.18	1.96
2.88	0.48	490	4.94	1.60	2.04
4.55	0.48	470	8.48	2.14	2.13
7.55	0.50	449	14.10	2.65	2.23

Gradient = 5357.84K
Intercept = -9.29

Heat of adsorption = -44.55 kJ/mol
Uncertainty in delta H = 0.70 kJ/mol

PGC 219/220 SIGIRI

Adsorbate : Cyclohexane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.15	0.46	531	1.49	0.40	1.88
1.40	0.45	510	2.10	0.74	1.96
1.78	0.44	489	3.05	1.11	2.04
2.76	0.48	470	4.75	1.56	2.13
4.14	0.47	449	7.72	2.04	2.23
6.36	0.45	429	13.13	2.58	2.33

Gradient = 4890.80K
Intercept = -8.84

Heat of adsorption = -40.66 kJ/mol
Uncertainty in delta H = 0.64 kJ/mol

Adsorbate : Cyclopentane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.31	0.49	469	1.67	0.51	2.13
1.69	0.50	450	2.39	1.30	2.22
2.19	0.47	430	3.66	1.30	2.32
2.80	0.42	411	5.67	1.73	2.43
5.24	0.48	391	9.93	2.30	2.56
8.95	0.46	370	18.46	2.92	2.70

Gradient = 4222.98K
Intercept = -8.51

Heat of adsorption = -35.11 kJ/mol
Uncertainty in delta H = 0.36 kJ/mol

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Adsorbate : Hexane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
4.29	0.40	301	9.72	2.27	3.32
2.93	0.41	313	6.15	1.82	3.19
1.65	0.43	333	2.84	1.04	3.00
1.05	0.45	354	1.33	0.29	2.82
0.79	0.48	374	0.65	-0.44	2.67

Gradient = 4176.14K
Intercept = -11.54

Heat of adsorption = -34.72 kJ/mol
Uncertainty in delta H = 0.92 kJ/mol

Adsorbate : N-Butyl Chloride

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
0.67	0.55	455	0.22	-1.52	2.20
0.73	0.50	435	0.46	-0.78	2.30
0.93	0.49	414	0.90	-0.11	2.41
1.40	0.48	393	1.93	0.66	2.54
2.21	0.46	374	3.80	1.34	2.67
4.21	0.44	353	8.57	2.15	2.83

Gradient = 5728.05K
Intercept = -13.99

Heat of adsorption = -47.62 kJ/mol
Uncertainty in delta H = 1.40 kJ/mol

Adsorbate : Chloroform

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
7.86	0.40	300	18.65	2.93	3.33
5.54	0.41	313	12.51	2.53	3.19
3.30	0.43	333	6.67	1.90	3.00
1.77	0.45	354	2.93	1.08	2.82
1.16	0.47	374	1.47	0.38	2.67

Gradient = 3873.91K
Intercept = -9.88

Heat of adsorption = -32.31 kJ/mol
Uncertainty in delta H = 1.85 kJ/mol

SILICA

Adsorbate : Dichloromethane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
5.34	0.40	300	12.35	2.51	3.33
3.24	0.41	313	6.90	1.93	3.19
2.32	0.43	333	4.40	1.48	3.00
1.36	0.45	354	2.02	0.70	2.82
0.98	0.47	374	1.09	0.08	2.67

Gradient = 3599.96K
Intercept = -9.47

Heat of adsorption = -29.93 kJ/mol
Uncertainty in delta H = 1.68 kJ/mol

Adsorbate : Me T-Butyl Ether

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
0.71	0.57	455	0.25	-1.40	2.20
0.95	0.57	436	0.67	-0.41	2.29
1.53	0.49	414	2.12	0.75	2.41
3.42	0.47	393	6.28	1.84	2.54
7.29	0.46	373	14.85	2.70	2.68

Gradient = 8542.84K
Intercept = -20.03

Heat of adsorption = -71.03 kJ/mol
Uncertainty in delta H = 3.79 kJ/mol

Adsorbate : Ethyl Acetate

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.64	0.52	477	2.15	0.77	2.10
3.96	0.52	455	6.62	1.89	2.20
5.34	0.50	435	9.68	2.27	2.30
12.72	0.48	414	25.50	3.24	2.41
16.82	0.47	394	34.79	3.55	2.54

Gradient = 6243.24K
Intercept = -12.07

Heat of adsorption = -51.91 kJ/mol
Uncertainty in delta H = 6.51 kJ/mol

SILICA

Adsorbate : Dioxan

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.51	0.57	530	1.65	0.50	1.89
2.94	0.53	500	4.55	1.51	2.00
4.02	0.53	476	6.58	1.88	2.10
8.47	0.51	456	15.61	2.75	2.19
18.52	0.50	435	36.04	3.58	2.30

Gradient = 7283.04K
Intercept = -13.21

Heat of adsorption = -60.55 kJ/mol
Uncertainty in delta H = 3.98 kJ/mol

Adsorbate : Acetonitrile

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.32	0.53	477	1.49	0.40	2.10
2.12	0.56	455	2.79	1.02	2.20
3.22	0.50	435	5.44	1.69	2.30
5.82	0.49	414	10.88	2.39	2.41
10.52	0.47	393	21.38	3.06	2.54

Gradient = 5995.40K
Intercept = -12.14

Heat of adsorption = -49.85 kJ/mol
Uncertainty in delta H = 1.25 kJ/mol

Adsorbate : Tetrahydrofuran

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.37	0.55	500	1.49	0.40	2.00
2.57	0.52	477	3.94	1.37	2.10
4.84	0.56	456	7.64	2.03	2.19
6.48	0.50	435	11.96	2.48	2.30
9.44	0.48	414	18.67	2.93	2.41

Gradient = 5919.70K
Intercept = -11.18

Heat of adsorption = -49.22 kJ/mol
Uncertainty in delta H = 6.25 kJ/mol

SILICA

Adsorbate : Dimethyl Formamide

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
2.01	0.58	548	2.47	0.90	1.82
2.61	0.57	531	3.58	1.28	1.88
3.94	0.56	516	6.04	1.80	1.94
5.11	0.55	500	8.30	2.12	2.00
12.11	0.56	476	20.62	3.03	2.10

Gradient = 7655.93K
Intercept = -13.10

Heat of adsorption = -63.65 kJ/mol
Uncertainty in delta H = 2.98 kJ/mol

Adsorbate : Methanol

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
0.86	0.54	499	0.58	-0.54	2.00
1.12	0.53	476	1.11	0.11	2.10
1.79	0.51	455	2.51	0.92	2.20
2.99	0.56	435	4.34	1.47	2.30
4.34	0.49	414	7.86	2.06	2.41

Gradient = 6408.91K
Intercept = -13.31

Heat of adsorption = -53.28 kJ/mol
Uncertainty in delta H = 3.04 kJ/mol

Adsorbate : Benzene

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
0.66	0.55	455	0.20	-1.61	2.20
0.74	0.50	435	0.48	-0.73	2.30
0.88	0.48	414	0.83	-0.18	2.41
1.44	0.48	393	2.00	0.69	2.54
2.25	0.46	374	3.89	1.36	2.67
4.65	0.44	353	9.57	2.26	2.83

Gradient = 5964.95K
Intercept = -14.57

Heat of adsorption = -49.59 kJ/mol
Uncertainty in delta H = 1.75 kJ/mol

SILICA

Adsorbate : Cyclohexane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
3.59	0.40	300	7.97	2.08	3.33
2.58	0.41	313	5.29	1.67	3.19
1.59	0.44	333	2.61	0.96	3.00
1.03	0.45	353	1.29	0.25	2.83
0.77	0.47	374	0.64	-0.45	2.67

Gradient = 3851.31K
Intercept = -10.68

Heat of adsorption = -32.02 kJ/mol
Uncertainty in delta H = 1.24 kJ/mol

Adsorbate : Cyclopentane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.65	0.40	300	3.12	1.14	3.33
1.30	0.41	313	2.17	0.78	3.19
0.94	0.43	333	1.19	0.17	3.00
0.73	0.45	354	0.62	-0.47	2.82
0.61	0.46	374	0.33	-1.12	2.67

Gradient = 3419.19K
Intercept = -10.18

Heat of adsorption = -28.43 kJ/mol
Uncertainty in delta H = 1.36 kJ/mol

Adsorbate : Ethanol

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.00	0.53	499	0.89	-0.12	2.00
1.61	0.58	476	1.78	0.57	2.10
2.19	0.52	455	3.21	1.17	2.20
3.69	0.50	435	6.38	1.85	2.30
5.98	0.49	414	11.20	2.42	2.41

Gradient = 6210.12K
Intercept = -12.50

Heat of adsorption = -51.63 kJ/mol
Uncertainty in delta H = 2.01 kJ/mol

SILICA

Adsorbate : Iso Octane

tr	tm	Temp/K	k^1	$\ln(k^1)$	1E3(1/T)
1.78	0.54	476	2.30	0.83	2.10
3.95	0.55	455	6.18	1.82	2.20
4.35	0.56	435	6.77	1.91	2.30
8.65	0.49	414	16.65	2.81	2.41
17.11	0.47	394	35.40	3.57	2.54

Gradient = 5926.10K
Intercept = -11.50

Heat of adsorption = -49.27 kJ/mol
Uncertainty in delta H = 5.34 kJ/mol

APPENDIX III

Operation of the Hydrogen Purifier

Principle

The purifier consists of a diffusion cell made of Pd/Ag alloy. Hydrogen molecules are first absorbed, into the alloy lattice, and then dissociates to give two protons. These protons diffuse through the lattice under the influence of the pressure/concentration gradient. The electrons from the hydrogen molecule joins the electron cloud around the alloy's lattice.

Each pair of protons emerging from the other side of the Pd/Ag membrane combine with two electrons from the electron cloud of the metal lattice to form hydrogen molecules. These molecules are desorbed as more hydrogen passes through the membrane.

The greater the surrounding temperature of the diffusion cell, the greater the absorption of hydrogen on to the metal lattice. The greater the input pressure of impure hydrogen, the larger the pressure/ concentration gradient across the Pd/Ag membrane. Therefore the temperature of the diffusion cell and the input pressure of hydrogen must be adjusted to achieve the desired output flowrate.

A temperature of 200°C and an input pressure of 20 atm (output was

240-250 cm^3 min^{-1}) were found to be adequate for the purposes mentioned in Chapter 4.

Shut Down Procedure for the Hydrogen Purifier

After the use of the purifier, the temperature of the Pd/Ag diffusion cell was reduced to ambient temperature by switching off the heat supply to the cell. This would decrease the absorption of hydrogen in the alloy which in turn would reduce and finally terminate the flow of pure hydrogen. The input hydrogen supply was maintained (at 20 atm) during the cooling period of the diffusion cell to avoid irrepairable damage to the metal lattice.

References

"EP Series Hydrogen Purifiers"
Johnson Matthey Catalytic Systems Division, Engineered Products.

Appendix IV

Calculation of the Amount of Methane produced during Hydrogen Treatment of PGC

The Standard Enthalpy Change ($\Delta Hf°$) for the formation of methane is -74.776 KJ mol^{-1} [1].

The formation reaction of methane is

$$C_{(s)} + 2H_{2(g)} \text{ ——— } CH_{4(g)} \text{ ——— AIV.1}$$

The data from reference [1] enabled the calculation of the standard entropy change ($\Delta S°$) of this reaction

$S°_{CH_4} = 186$ J mol^{-1}, $S°_{c} = 5.68$ J mol^{-1} and $S°_{H_2} = 130.41$ J mol^{-1}

now $\Delta S° = S°_{CH_4} - (S°_{c} + S°_{H_2})$ ——— AIV.2

$\Delta S° = 186 - 5.68 - (2 \times 130.41) = -80.5$ J mol^{-1}

For the above reaction, the standard free energy charge ($\Delta G°$) is given by,

$\Delta G° = \Delta H° - T\Delta S°$ ——— AIV.3 [2]

$= -74776 + 1303\ (80.5)$ at 1030°C

therefore $\Delta G° = +30116$ J mol^{-1}

Also, $\Delta G° = -RT\ln K$ ——— AIV.4 [2]

K is the equilibrium constant of the reaction in equation AIV.1.

R is the gas constant = 8.314 J mol^{-1} K^{-1}.

T is the temperature of reaction.

The equilibrium constant of the reaction and hence the concentration of methane produced at 1030°C can be calculated thus,

$$\ln K = \frac{-30116}{8.314 \times 1303} = -2.78$$

now $K = \frac{[CH_4]}{[H_2]^2}$, since $[H_2] = 1$ atm

$K = [CH_4] = 0.062$ atm at 1030°C

therefore $[CH_4] = 0.062$ atm.

The VantHoff isochore,

$$\ln K_1 - \ln K_2 = \frac{-\Delta Hf^\circ}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad \text{——— AIV.5 [2]}$$

would enable the calculation of the equilibrium constant and hence the theoretical amount of methane produced at 830°C (1103K).

K_1 = equilibrium constant of reaction (equation AIV.1) at 1030°C = 0.062 atm.

K_2 = equilibrium constant of reaction (equation AIV.1) at 830°C.

T_1 = 1030°C and T_2 = 830°C.

therefore $K_2 = 0.21$ atm at 830°C

therefore $[CH_4] = 0.21$ atm.

This calculation shows that in theory, the amount of methane produced increases with decreasing temperature. In practice however, the rate of reaction does not reach thermodynamic equilibrium, at temperatures below 1000°C to produce the theoretically predicted amount of methane, during the time allowed for the reaction (equation AIV.1) [3].

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