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APPLICATIONS
OF
GAS-SOLID CHROMATOGRAPHY

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A - Introduction

Gas-solid chromatography is now an important analytical tool for the separation and identification of various mixtures, from hydrogen isotopes and isomers to high boiling point substances. The interest in gas-solid chromatography has grown rapidly, since Scott[1] demonstrated that elution chromatograms can be obtained which are entirely comparable to those obtainable in gas-liquid chromatography.

About ten years ago, gas-solid chromatography was restricted mainly to gas analysis. Owing to the high activity and the chemical and geometrical heterogeneity of the adsorbents used at that time, the chromatographic elution peaks of higher molecular weight compounds exhibited severe tailing effects : non-linear adsorption isotherms are sources of very important peak asymmetry[2, 3] in addition Giddings[4] has shown that tailing may also occur when the adsorption isotherm is linear, originating as a kinetic phenomenon due to the long average desorption time of the adsorbate from the "active" sites of the adsorbent.

The development of gas-solid chromatography is related to a greater control on the homogeneity and specificity of molecular adsorbents. This has been achieved through advances in the synthesis of adsorbents of high chemical purity whose nature, specific surface area and degree of porosity can be controlled and by the chemical modification of their surface[5, 6]. Moreover the advantages of gas-solid chromatography over gas-liquid chromatography are obvious : one of the most important is the fact that most adsorbents are non-volatile and have a high thermal and chemical stability which enables one to use this technique in programmed temperature analysis, without experiencing base-line drift up to high temperature. In many cases the temperature limit is set by the thermal stability of the compounds to be analyzed, and not by the stationary phase. Another important advantage is the large specificity observed for geometrical isomers. Scott[7] has written a review in which the potentialities of gas-solid chromatography are described.

The work of Giddings[8] laid the basis for a theoretical treatment of efficiency and resolution in gas-solid chromatography. Peak broadening at large carrier gas flowrate is controlled by the kinetics of mass-transfers. Usually the kinetics of adsorption-desorption is much faster than diffusion in the liquid phase, so gas-solid chromatography allows in many cases to obtain much shorter HETP than gas-liquid chromatography. The theory of non-equilibrium chromatography has been reviewed by Giddings[9] and the statistical moments theory of gas-solid chromatography has been discussed by Grubner[10] who gave relationships between the centered peak moments and various parameters of the adsorbent.

In addition to the more usual analytical applications of gas adsorption chromatography, this technique is now an important tool in physicochemical investigations of the surface chemistry of solids, in studies of isotherms, of heats and entropies of adsorption[5].

Huber and Gerritse[11] have recently discussed the use of gas chromatography for the determination of adsorption isotherms and Choudhary and Doraiswamy[12] have written a review covering the use of gas chromatography as applied to catalysis : experimental methods in catalysis, determination of the physicochemical properties of solid catalysts and adsorbents, catalyst evaluation and kinetics of catalytic reactions, and study of catalytic reactions under chromatographic conditions.

In this work, the analytical aspects of gas-solid chromatography are reviewed. The adsorbents used are described from the point of view of their analytical applications : graphitized carbon, black and activated charcoal, silica gel, zeolites, alumina, inorganic salts and organic adsorbents. Various practical aspects of their applications are differentiated, including their use as packing material in conventional or capillary columns, as porous adsorbent layers on different supports and as chemically modified adsorbents. This last field is going to become more and more important in the near future, as the various methods of blocking the active centers or changing the chemical nature of the surface by reactions[6] or by deposition of a monomolecular layer[5], anchored or not on the surface are developing fast and becoming more sophisticated and flexible.

In addition, at the beginning of each section a short survey of the more fundamental studies made on these adsorbents, mainly using gas-solid chromatography, are given. The physicochemical investigations of the adsorption properties of the solid are important for a better understanding of the retention process and of the physical and structural factors which determine the relative retention of two compounds. Such a basic knowledge is a major help in the choice of an adsorbent to solve a given analytical problem, in the choice of the experimental conditions in which the adsorbent should be used and eventually in the selection of surface modifications.

B - Graphitized Carbon Black and other Carbon Adsorbents

Thermal treatment of carbon blacks around 3000°C or above, particularly thermal blacks with a small specific surface area (from 6 to 30 m^2/g) converts the small carbon black particles into polyhedra having homogeneous basal graphite faces[1-3], a crystalline structure similar to graphite and a very homogeneous surface. Because of this last property and also because its properties are reproducible easily from laboratory to laboratory throughout the world, this adsorbent has been the first one used to analyze high boiling organic compounds and is still one of the most widely used.

1 - ADSORPTION STUDIES

Graphitized carbon blacks are non-specific adsorbents, as their surface carries practically no unsaturated bonds, functional groups or ions although a few paramagnetic sites are sometimes found; most if not all the interaction energy results from dispersion forces[4, 5]. Unsaturated and aromatic hydrocarbons are retained on columns packed with graphitized carbon black almost as much as alcohols, ethers, ketones, nitriles and amines of similar structure and having the same number of heavy atoms (C, O and N). However the energy of adsorption due to these non-specific interactions, which depends only on the geometry of the adsorbate, is very high, because of the large concentration of carbon atoms on the basal face of graphite and therefore high temperatures are required when the adsorbent is used as column packing in gas chromatography.

Ross, Saelens and Olivier[6] have, by gas-solid chromatography, measured the heat of adsorption for various adsorbates (Xenon, methane, krypton, Freon 11, chloroform and benzene). A theoretical basis for comparison of the results obtained by static and dynamic methods is developed. Heats of adsorption measured by gas chromatography show closer agreement than has yet been reported with the limiting isosteric heat of adsorption at zero coverage measured by static methods. This result was made possible by using as an adsorbent highly graphitized carbon black for which a quantity of precisely determined adsorption data has been reported.

Gale and Beebe[7] have derived the isosteric heats of adsorption from gas-solid chromatography data and compared the results with those determined by calorimetric measurements at low coverage. Chromatographic heats were obtained for various systems using N_2, O_2, Ar, CH_3Cl, C_2H_5Cl, NH_3, H_2O, CO_2, CH_4, SF_6, C_2F_6, C_3F_8 as adsorbates and as adsorbents, bovine bone mineral and a series of carbon blacks and graphitized carbon blacks. The agreement between data of chromatographic and calorimetric origin is generally good. Beebe and coworkers[8] have measured the adsorption isotherms down to low coverage by frontal analysis chromatography for systems containing the carrier gas, one of the gases N_2, Ar, O_2, CO or C_2F_6 and either carbon black or bone mineral. Isosteric heats of adsorption have been calculated from these isotherms.

Chirnside and Pope[9] have measured by gas-solid chromatography the isosteric heats of adsorption of n-butane, n-pentane and n-hexane. These results were compared with previous chromatographic data and also with heats of adsorption determined by equilibrium measurement showing again a good agreement between the data of various origin.

Using gas-solid chromatography, Kiselev and coworkers[10], and Curthoys and Elkington[11] have shown the nonspecificity of adsorption on the surface of graphitized carbon blacks. The result is derived from a comparison of the adsorption coefficient (retention volume per unit of surface area of the adsorbent) and of the heats of adsorption of molecules capable of specific interaction (i.e. alcohols, ketones, esters...) with that of "reference molecules" similar in size and polarizability, which are only capable of non-specific interaction (for example, n-alkanes, noble gases).

Belyakova, Kiselev and Kovaleva[12] have shown that the heats of adsorption determined by gas chromatography, correspond to much smaller surface coverage ratio than the data obtained by static methods; therefore, the energy of adsorbate-adsorbate association is not included. Correspondingly, the heats of adsorption of hydrocarbons determined by either gas chromatography or by static methods are in excellent agreement and are close to the values of the adsorption energies derived from theoretical calculations, whereas for alcohols, the heats of adsorption determined by gas chromatography are still close to the theoretical values of the adsorption energies but are 5 Kcal. per mole less than the heats of adsorption measured in a calorimeter. This difference represents the energy of hydrogen bonding between alcohol molecules.

In a study of the adsorption properties of graphitized carbon black, Belyakova, Kiselev and Kovaleva[13] have measured by gas chromatography the adsorption isotherm of water and benzene in the temperature range from 30°C to 100°C. The first isotherm has no inflection point whereas the second isotherm has one.

As shown above the retention on graphitized carbon black is determined by the dispersion forces. These forces are well known and can be accounted for simply by using a model similar to the one used in the theory of gases, to account for the Van Der Waals forces, using a Lennard-Jones potential[14-17]. Since the surface of graphitized carbon black is very homogeneous, flat and chemically inert, and since the polyhedral particles are practically for that purpose equivalent to semi-infinite lattices of ideal graphite crystals, it is possible to calculate the potential energies of adsorption of molecules of various structure and composition. The values obtained from approximate numerical calculation are in satisfactory agreement with experimental data[15, 16], and in the simplest cases other thermodynamic properties of adsorption systems, in particular the absolute retention volumes, could be derived[14, 17, 18].

Kiselev and coworkers[10] have reported a systematic determination of the absolute retention volumes at various temperatures of molecules of different geometric and electronic structure, on graphitized carbon black. The equilibrium constants, the differential heats of adsorption and other physicochemical properties of these adsorption systems were derived from these data.

Belyakova, Kiselev and Kovaleva[19] have used gas chromatography to study the adsorption properties of several straight-chain, aromatic and cyclic hydrocarbons with 1 to 7 carbon atoms and of some of their derivatives. The differential heats of adsorption determined by gas chromatography and by static methods, using both calorimetric data and isosteres are very near for all compounds whose molecules cannot associate in the adsorbed layer. Kiselev, Migunova and Yashin[20] have continued this investigation by measuring the absolute retention volumes of 68 adsorbates.

Boukova and Shcherbakova[21] have studied the adsorption and separation of several geometric isomers of alkanes and alkenes. Petov, Shcherbakova and Kiselev[22, 23] have measured the retention volumes and the heats of adsorption of various terpenes and terpene derivatives on graphitized thermal carbon black. These values depend only upon the structure of the molecules of terpenes and their probable orientation when adsorbed on the surface.

Kouznetsov and Guiochon[24] have calculated the adsorption potential of terpenes and aromatic hydrocarbons on graphite. The results obtained agree well with the experimental heats of adsorption at zero coverage measured by Kiselev and coworkers[23] using gas chromatography. Kiselev and coworkers[25] have calculated the potential adsorption energies of different classes of compounds and compared the results with the heats of adsorption of these substances obtained by gas chromatography on graphitized carbon black. The results obtained show, in agreement with experimental facts, that the main factors in the chromatographic separation of molecules on graphitized carbon black are their geometry (shape, steric configuration, dimensions of the atoms, bond length, and favorite orientation on the basal plane of graphite) and the polarisability of the atoms or groups of atoms, in particular those in contact with the surface.

Kiselev and coworkers[26] have measured the retention volumes and the heats of adsorption at low surface coverage on graphitized carbon black for C_1 - C_6 alkanes, alkenes, alkadienes, alkynes, cyclanes, cyclenes and benzene. The dependence of the heats of adsorption of these molecules on their polarisability, carbon number, and shape ("isomeric structure"), on the presence of double bonds and conjugated double bonds were investigated. The same measurements were carried out for n-alkenes C_6 - C_{10}[27]. The retention of n-alkenes is determined mainly by their cis-trans isomerism but is dependent on the position of the double bond too.

From a rather rigorous statistical calculation, Poshkus[14] has derived the absolute retention volumes per unit surface, at zero surface coverage (small sample size) and high temperature of very simple molecules. Kiselev and Poshkus have calculated the retention volumes and the thermodynamic function of adsorption of inert gases[14, 28-30], benzene[14, 31, 32], nitrogen[33], hydrogen and deuterium[34], on graphitized carbon black. Then Poshkus, Kiselev and Afreimovitch[18, 35-37], have made similar calculations for light alkanes (CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}), taking into account the internal rotation of molecules. Poshkus[38] has calculated the ratios of the retention volumes for isotopic pairs: CH_4-CD_4, C_2H_6-C_2D_6, C_2H_4-C_2D_4, C_2H_6-C_2D_6, C_6H_{12}-C_6D_{12}. The values obtained agree well with experimental results on graphitized carbon black. In all these calculations many approximations had to be made in order to allow numerical results to be obtained by conventional methods. These simplifications introduced either semi-empirical constants or discrepancies between calculated and measured data.

Vidal-Madjar and Guiochon[39], using the molecular theory of adsorption, have calculated the retention volumes of aromatic hydrocarbons (benzene, naphthalene, phenanthrene and anthracene). The use of modern computer calculations[40] allowed them to reduce drastically the approximations made and to discuss the most appropriate model of the molecule sorbed on the surface to account for the easy separation of phenanthrene and anthracene on graphitized carbon black.

The enthalpy and entropy of adsorption calculated for the molecules studied agree with the experimental data within the accuracy of these last data, c.a. 0.5% which shows that physical adsorption on a simple surface like graphitized carbon black is quantitatively understood.

2 - APPLICATIONS

Thermal blacks which have been graphitized near 3000°C are thermally stable, inert, non-specific and non porous adsorbents, having a very homogeneous surface. The high surface uniformity of graphitized blacks and the non-specifity of adsorption enable the elution with symmetrical peaks of many high boiling point, polar substances.

Graphitized carbon black was first used in gas chromatography by Halasz and Horvath[41] as a thin, porous layer on the walls of capillary columns. Figure 1 shows the quick and unusual separation of the xylene isomers obtained on graphitized carbon black: m-xylene and p-xylene are perfectly resolved in 70 sec. on a 15 meter long capillary column, while o-xylene and p-xylene remain unresolved, a situation which is opposite to the one observed in gas liquid chromatography. Since that time, many analytical applications of graphitized carbon black have been reported for the separation of geometrical isomers and isotopic pairs. The selectivities obtained on this adsorbent are quite different from those observed with liquid stationary phases. Graphitized carbon black has been used directly to pack conventional gas chromatographic columns. It has also been used as a fine powder deposited on different kinds of support and as an adsorbent layer on the walls of capillary columns. Interesting analytical applications of graphitized carbon black modified with thin layers of various liquid phases have also been reported. The use of graphitized carbon black as a support for organic adsorbents will be discussed in section G - organic adsorbents.

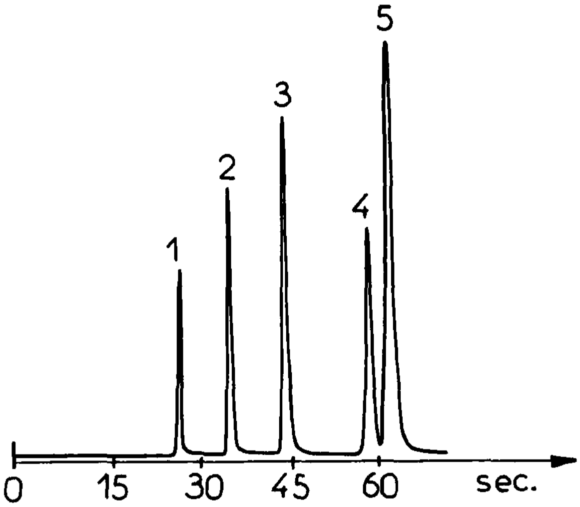

FIGURE 1

Separation of aromatic hydrocarbons on graphitized carbon black.

(1) benzene, (2) toluene, (3) ethylbenzene, (4) m-xylene, (5) o- and p-xylene.
Porous layer open tube capillary column; 15 m x 0.25 mm i.d. copper; 5.4 mg graphitized carbon black/meter (surface area 72.8 m^2/g); temperature 245° C; hydrogen flow rate: 2 ml/min. inlet pressure: 2.7 atm.

After Halasz and Horvath[41]: Figure 2.

a) - Packed conventional column

Conventional columns packed with graphitized thermal carbon black, were first used for the gas chromatographic investigation of the adsorption properties of these blacks[6-13]. The interesting potentialities for analytical applications were not realized before 1963[41]. As results from the previous discussion and as demonstrated by Kiselev and Yashin[42] using conventional columns packed with graphitized carbon black, the retention volumes are determined by the energy of non-specific dispersion interactions, and therefore depend to a greater extent on the molecular weight and the geometrical structure of the molecules, but not on the boiling point or the dipole moment. Graphitized carbon blacks can thus be used to separate geometrical isomers, for example substituted aromatic hydrocarbons, isomeric butylbenzenes, cis and trans decahydronaphthalenes, cis and trans olefines, terpene isomers.

Shcherbakova and coworkers[22, 43-45] have shown that gas chromatography on graphitized carbon black can be used not only for analytical purposes, but can also be used in conjunction with other methods for the investigation of the geometrical structure of the molecules. Retention of terpene derivatives[22], cyclic hydrocarbons and cis-trans configuration of 3-methylpentene-2 and 3,4 dimethyl pentene-2 have been studied in relation with their spatial configuration[44]. Graphitized carbon black has been successfully used for the separation of endo and exo-isomers of bicyclo (2,2,1) heptane derivatives[45]. The endo-isomers are eluted first from the column. The preferential orientation of the studied molecules on the surface of graphitized carbon blacks is determined from the comparison of the experimental adsorption enthalpy and the calculated adsorption potential. Kiselev and coworkers[46] have described the separation on graphitized carbon black of the organometallic compounds of group IV B containing bonds between two heteroatoms, silicon, germanium and tin chalcogenides as well as heterocyclic compounds with silicon atoms in the ring. Gas adsorption chromatography on a graphitized thermal carbon black has been found to provide higher selectivity in comparison with gas-liquid chromatography in the separation of the organometallic compounds of group IV B, especially of the sterically hindered silicon-containing (o-,p-) isomers of phenol derivatives.

Zane[47] has separated a mixture of phenanthrene and anthracene on a column (70 cm long x 2.3 mm i.d) packed with graphitized carbon black, at 415°C. Onuska and coworkers[48] have compared the separation of biphenyl and the three terphenyl isomers on columns packed with graphitized carbon black and chromosorb coated with caesium chloride.

Di Corcia and Bruner[49] have greatly extended the possibilities of application of graphitized carbon black for the analysis of polar compounds by treating the adsorbent under a flow of hydrogen at 1000°C. The comparison of the adsorption isotherms measured on samples of treated and untreated graphitized carbon black shows that chemisorbed oxygen, always present on the surface of untreated blacks, is removed during the treatment. Peak tailing is eliminated or strongly reduced and the elution of alcohols, aliphatic amines, and free carboxylic acids as symmetrical peaks can be performed on columns, packed with this material. Figure 2 shows the separation of aliphatic and aromatic amines at several temperatures on hydrogen treated graphitized carbon black, Sterling M.T (specific surface area 8 m^2/g).

Jequier and Robin[50] have studied the gas-solid chromatographic behavior of various samples of graphite and have compared the retentions of hydrocarbons and of the corresponding perfluorinated hydrocarbons with those observed on silanized Chromosorb and on polytrifluoro ethylene.

Other forms of carbon have been used as packing materials in gas-solid chromatography. Synthetic diamonds have been used by Hirschmann and Mariani[51] as an adsorbent for the separation of corrosive gases (HF and F_2).

Kaiser[52] has prepared a porous carbon black (carbon molecular sieve) by thermal degradation of a polymer like polyvinylidene chloride. The specific area of this material is very large, the pore distribution is narrow and the surface is very homogeneous. Water is eluted before methane on carbon molecular sieves and this adsorbent seems to be especially usefull for inorganic gas analysis and for the analysis of highly polar compounds with less than five to six carbon atoms per molecule.

b) - Porous layer beads

Pope[53] has reported the analytical applications of columns in which carbon black has been fused as an uniform layer into the

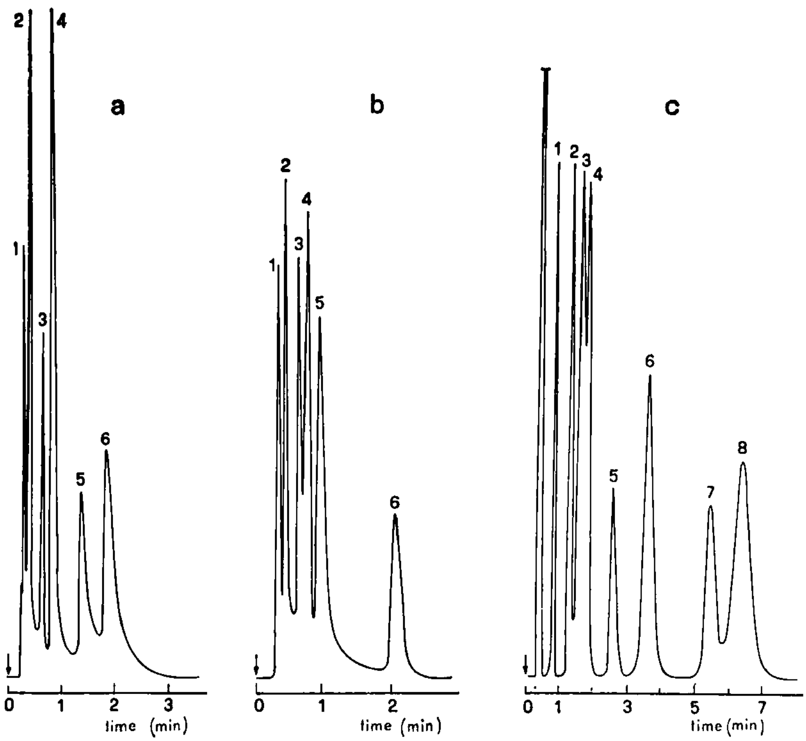

FIGURE 2

Separation of aliphatic and aromatic amines at different temperatures on Sterling MT, hydrogen treated (8 m^2/g).

Column: 0.8 m x 2.5 mm i.d.

a) temperature: 94° C; nitrogen flow rate: 25 ml/min.
(1) methylamine, (2) ethylamine, (3) trimethylamine, (4) tert-butylamine, (5) isobutylamine, (6) n-butylamine.

b) temperature: 133° C; nitrogen flow rate: 20 ml/min.
(1) dimethylamine, (2) n-propylamine, (3) pyrrolidine, (4) diethylamine, (5) piperidine, (6) di-n-propylamine.

c) temperature: 243° C; nitrogen flow rate; 15 ml/min.
(1) aniline, (2) n-heptylamine, (3) di-n-butylamine, (4) N-methylaniline, (5) n-nonylamine, (6) N, N dimethylaniline, (7) n-nonylamine, (8) N, N diethylaniline.

Reproduced from : A. Di Corcia and F. Bruner, "Gas Solid Chromatography of Hydrogen bonding compounds", Anal. Chem. 43, 1634 (1971): Figure 5.

outer surface of polyethylene beads. High resolution was obtained for the separation of hexane isomers. Halasz and Horvath[54] have used columns packed with glass beads on which a layer of graphitized carbon black has been deposited for the analysis of alcohols, low boiling point hydrocarbons and normal paraffins from n-heptane to n-tridecane.

Kiselev and coworkers[55] have examined the gas chromatographic behavior of graphitized carbon black, when introduced into the pores of macroporous silica gel. The retention volumes of several adsorbates have been determined; the heats of adsorption at low surface coverage derived from these results are in good agreement with direct calorimetric measurements.

Frycka[56] has resolved benzo [e] pyrene, benzo [a] pyrene, dibenz [a,c] anthracene and dibenz [a,h] anthracene, on a column packed with 15% graphitized carbon black deposited on chromosorb W. Frycka[57] has compared the chromatograms obtained for mixtures of phenanthrene, anthracene and carbazole on graphitized carbon black, Bentone 34 and calcium chloride deposited on chromosorb W.

c) - Capillary columns

As explained above Halasz and Horvath[41] have used first graphitized carbon black as a thin, porous layer on the walls of capillary columns. Halasz and coworkers[58] have analyzed the products resulting from the catalytic reforming of n-heptane in 11 minutes with a 30 meter long porous layer graphitized carbon black column and an alumina packed capillary precolumn of 1.2 meters long. Methane, ethane and propane, as well as all the isomers of heptane together with benzene and toluene have been completely resolved.

Halasz and coworkers[59] have analyzed C_1 to C_8 hydrocarbons by carbon number, using capillary columns packed with graphitized carbon black and impregnated with about 0.4% squalane.

Goretti, Liberti and Nota[60, 61] have prepared porous layer capillary columns by coating the walls of glass capillary columns with a thick layer of graphitized carbon black during the drawing of the glass tube. These columns give large resolution of geometrical and structural isomers such as o, m, p cresols, xylenes, polar compounds like amines and alcohols and also of isotopic compounds. The same authors have also prepared another type of capillary columns by introducing a graphitized carbon black thread into a capillary column by a similar procedure[62] and obtained the separation of o, m, p xylene.

Vidal-Madjer, Ganansia and Guiochon[63] have reported the application of highly efficient open tube capillary columns coated with a thin layer of graphitized carbon black for the analysis of high boiling point compounds. Polynuclear aromatic hydrocarbons are separated with a selectivity not achieved in gas-liquid chromatography; compounds with 22 carbon atoms and five rings are analyzed at 585°C in 12 minutes (cf. Figure 3). The fatty acid methyl esters, methyloleate and methylelaidate, due to their different geometrical configuration are completely resolved in less than 10 minutes. Polar compounds such as phenols and menthols are eluted with symmetrical peaks; their retention order depends mainly on their geometrical structure and may be predicted in most cases.

d) - Modified carbon blacks

The active sites still remaining on the surface of graphitized carbon black may be eliminated by coating the adsorbents with small amounts of a liquid stationary phase, which has also the advantage to reduce the density of atoms on the surface of the adsorbent and the adsorption energy. This method has been called by Halasz and Horvath[64], gas-adsorption layer chromatography.

Brodasky[65] has described the use of graphitized carbon black as a support for liquid stationary phases. Graphitized carbon black, when compared to other packings, allows to obtain the greatest reduction in peak assymmetry for alcohols, ketones and amines.

Bruner and Di Corcia[66] have deactivated a partially graphitized thermal carbon black (surface area: 100 m^2/g) by coating it with a

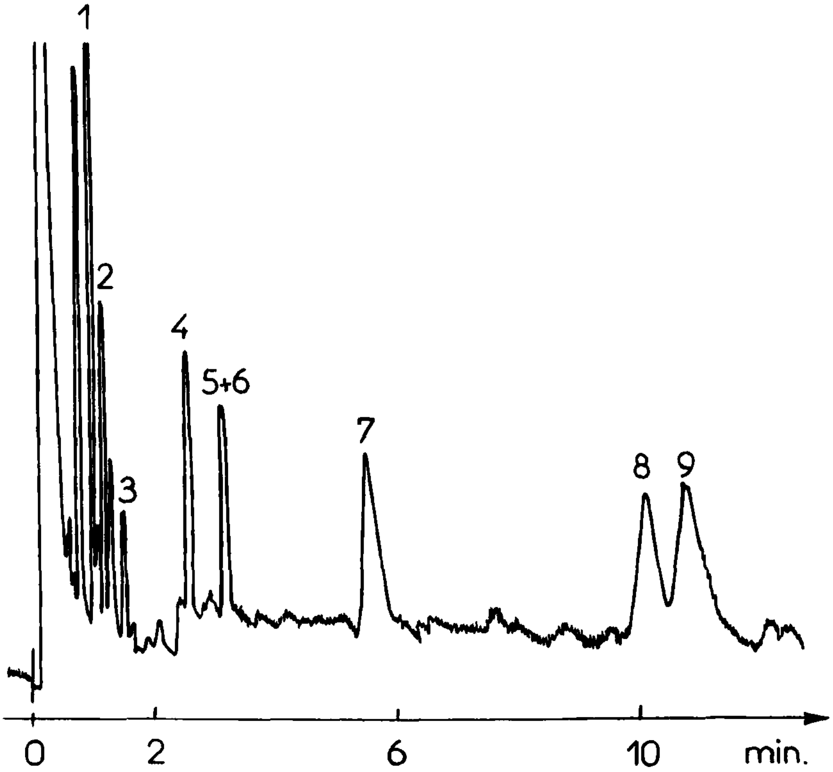

FIGURE 3

Analysis of polynuclear aromatic hydrocarbons.

(1) chrysene, (2) benzo (a) anthracene, (3) naphthacene, (4) perylene, (5) benzo (a) pyrene, (6) benzo (k) fluoranthene, (7) 3 methylcholanthene, (8) benzo (g,h,i) perylene, (9) dibenzo (a,h) anthracene.
Porous layer open tube capillary column; 8.5 m x 0.5 mm i.d. glass; 6 mg/meter graphitized carbon black Sterling F.T (13 m^2/g). Temperature: 585°C; inlet pressure: 2 atm; helium carrier gas.

After Vidal-Madjar, Ganansia and Guiochon.[63]

small amount of squalane. A conventional column (60m x 4mm i.d) packed with the adsorbent would achieve the complete resolution of $^{14}N_2$ and $^{15}N_2$ at 77°K. With similar columns the semi preparative separation of the isotopic pair CH_4-CH_3D was reported[67] on graphitized carbon black modified with small amounts of various stationary phases. Di Corcia and coworkers have analyzed sulfur dioxide and water, ammonia, aliphatic amines, carboxylic acids[68], nitrogen heterocyclic compounds and amphetamines[69]. In all cases the peaks obtained were symmetrical.

On a hydrogen treated Graphon, deactivated with a mixture of polyfluoroether and benzophenone, Di Corcia, Ciccioli and Bruner[70] have analyzed successfully: HCl, HF, Cl_2 and BF_3, obtaining for all these compounds sharp, symmetrical peaks.

Bruner and coworkers[71] have analyzed the isotopic mixtures obtained as reaction products of propene and HT in the presence of catalysts, on highly efficient columns, about 100 m long, packed with graphitized carbon black (Sterling FT surface area: 12 m^2/g) deactivated with 0.2% squalane.

Kiselev and coworkers[72, 73] have deposited a continuous monolayer of polyethylene glycol on the surface of various samples of channel black, heat treated at 3000°C (surface area: 80 m^2/g). Because of residual inhomogeneity of the unmodified adsorbent, in contrast to what happens with graphitized thermal carbon blacks, the retention times of all the substances decrease markedly and the peaks become much more symmetrical after deposition of the liquid stationary phase.

The graphite surface is replaced by a surface consisting mainly of the ether and methylene groups of polyethylene glycol which is capable of specific adsorption. It was shown[72] that the contribution of the specific interaction forces to the total heat of adsorption for benzene, ethyl ether and n-alcohols, increases with the decreasing molecular weight of polyethylene glycol. Dense monolayers of lower molecular weight compounds like molecules of

2, 4 dinitrophenylhydrazone deposited on the surface of channel carbon black are even more selective for alcohols than a polyethylene glycol monolayer.

e) - Conclusion

The use of graphitized thermal carbon black allows to obtain very efficient columns and so fast analysis of complex mixtures of closely related isomers. The columns are very stable and can be used at very high temperature. Even the most polar compounds can be analyzed on hydrogen treated graphitized carbon blacks if care is taken to deactivate the column walls too.

3 - ACTIVATED CHARCOALS

Activated charcoals are essentially strongly specific adsorbents with a large surface area (400-900 m^2/g). The activated charcoal network is made of irregularly packed and fused hexagonal aromatic rings. Hydrogen, hydroxyls, oxygenated groups like carboxylic groups are chemically bonded to this carbon skeleton[74]. Activated charcoals are mainly used in gas chromatography for the analysis of permanent gases or low boiling point hydrocarbons.

Greene and coworkers[75] have shown the analysis of low boiling gases and hydrocarbons on a column containing activated charcoal at 170°C.

Greene and Roy[76] have investigated the effect of five different carrier gases, on the retention times of methane on an activated charcoal column. Madison[77] has analyzed a mixture of H_2, O_2, N_2, CO, CH_4, C_2H_6 and n-C_4H_{10} using a two-stage gas chromatograph. The permanent gases unresolved on a first partition column are trapped in a liquid nitrogen cooled charcoal trap. After desorption, they are resolved on a charcoal column.

Habgood and Hanlan[78] have measured the retention volumes of nitrogen and low boiling points hydrocarbons on a series of steam-activated coconut charcoal. From these measurements the initial slopes of the adsorption isotherms and the heats of adsorption have been derived.

Both values decrease with increasing degree of activation of the charcoal (i.e. with increasing specific surface area). A greater resistance to mass transfer is observed for charcoal of greatest activation.

Hanlan and Freeman[79] have shown, using the experimental data given by Habgood and Hanlan[78] that the concept of excess retention volume in gas chromatography relates in a simple way to the concept of excess apparent volume introduced in the theory of Van der Waals interaction of gas and surface. Hansen and coworkers[80] have studied the temperature dependence of retention volumes over the temperature range 300-700°K for A, N_2, CO, CH_4, C_2H_4, C_2H_6, C_3H_6 on activated carbon.

Data are adequately represented in each case by a 3:9 gas solid interaction potential.

Retention volumes and adsorption enthalpies were determined by Boucher and Everett[81] for Ne, Ar, Kr, Xe, CH_4 and N_2 on an active carbon. Retention volumes were used to compute potential energies of adsorption and surface areas according to the approximate procedure of Hansen and coworkers[80].

Gant and Yang[82] have measured the retention times of isotopic methane using a charcoal column. The data are given for a wide temperature range (-35°C to 250°C). Retention times are shown to decrease progressively with increasing D or T substitution.

Smith and Clark[83] have tested a variety of column materials and found that only acid washed charcoal effectively resolves CO_2 and N_2O.

Stevenson and Harrison[84] have used a single column consisting of acid washed coconut charcoal to resolve H_2, N_2, CO, CO_2, N_2O and NO (or O_2). The sensitivity of the method for NO and CO was improved considerably by previously purging the column with these gases in order to block the active sorption sites responsible for their irreversible retention.

Gvozdovich, Kiselev and Yashin[85] have separated a mixture of low boiling point inorganic gases and hydrocarbons using only one

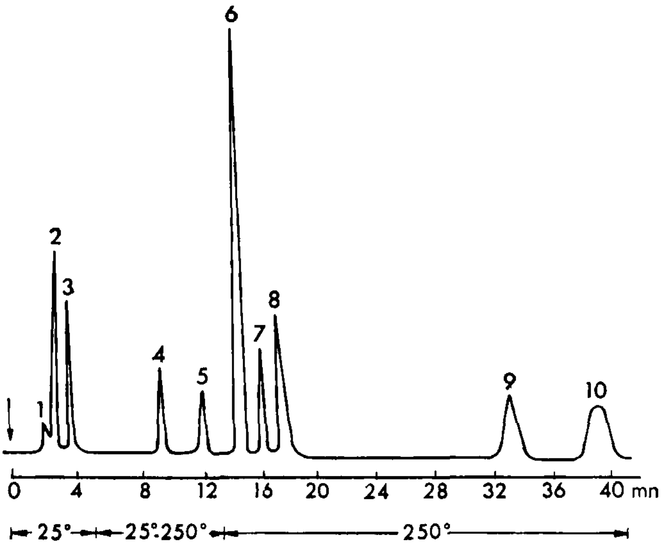

FIGURE 4

Separation of low boiling point hydrocarbons on activated carbon black (Saran type).

(1) oxygen, (2) nitrogen, (3) carbon monoxide, (4) methane, (5) acethylene, (6) carbon dioxide, (7) ethylene, (8) ethane, (9) propylene, (10) propane.
Column: 3 m x 3 mm i.d; helium flow rate: 30 ml/min.

Reproduced from : T.N. Gvozdovich, A.V. Kiselev and Y.I. Yashin, "Use of Saran type activated charcoal in Gas Chromatography", Neftekhimiya, 8, 476 (1968): figure 5. By courtesy of Neftekhimiya.

column packed with Saran carbon and temperature programming (Figure 4).

C - Silica Adsorbents

Continuing interest in silica as a chromatographic adsorbent is apparent from a survey of the recent literature. The analysis of light gases and of various complex mixtures of relatively high molecular weight compounds on this adsorbent has been described and will be discussed later. The study of these adsorbents has also been the topic of studies of a more fundamental nature and gas chromatography has helped to improve our knowledge of the chemistry of silica surfaces.

1 - STRUCTURE OF SILICA GEL AND CHROMATOGRAPHIC PROPERTIES

Kiselev[1-6] has investigated the type of surface interactions that occur in gas solid chromatography on silica adsorbents. He was especially concerned with the specificity of adsorbate-adsorbent interactions, the effect of surface modification and the nature of the adsorbed phase.

The high concentration of free hydroxyl groups with partly protonized hydrogen on the hydroxylated surface of silica causes specific adsorption of molecules with high electron concentration density[4]. These include both polar molecules containing for example atoms of oxygen or nitrogen with lone electron pairs (water, alcohols, ethers, ketones, etc..., ammonia, amines, pyridine, etc...) and non-polar molecules with π bonds (aromatic and unsaturated hydrocarbons, nitrogen) which are polarisable. The molecule possessing spherical symmetrical electron shells (inert gases) or only σ bonds (saturated hydrocarbons) are adsorbed non-specifically: then the adsorbate-adsorbent interaction originates only from the dispersion forces.

The effect of the geometrical structure of silica gels upon their adsorption properties has been investigated by Kiselev and coworkers[8, 9]. To reduce the nonlinearity of the adsorption isotherm, the necessity of using wide pore silica gel has been shown. Silica gels with an average pore diameter not exceeding 20 Å, should be used for the separation of low boiling gases. Silica gels with a pore diameter from 50 to 200 Å could be used to separate hydrocarbons with boiling temperatures not exceeding 100°C. To separate and analyze higher boiling substances only silica gels with larger pore diameters (higher than 500 Å) are suitable[9, 10].

Eberly[11] has studied the kinetics of adsorption of n-butane on silica gel using the technique of gas-solid chromatography. The adsorbed molecules spend a finite time in the adsorbent particle, time which is proportional to the power 3/2 of the particles' size. From the temperature variation of this change a heat of adsorption of 8 kcal/mole was derived.

Kiselev[1] has shown that the presence on the silica surface of impurities such as atoms of aluminum and boron can create strong Lewis acid adsorption centers and cause an increase in the interaction energy with electron-donor molecules. For analytical gas solid chromatography of organic compounds, wide pore silica gels with homogeneous surfaces of high chemical purity are necessary. The presence of admixtures of Al_2O_3, Fe_2O_3 and other oxides in geometrically modified silica gels[12-14] results in unsymmetrical peaks, increase of the retention time and poor separation of specifically adsorbed substances. Kiselev and coworkers have developed a method for the preparation of high purity, wide pore silica gel[13, 14].

Kiselev[4] has measured retention volumes on hydroxylated and dehydroxylated, wide pore silica gels for n-dodecane (non specific interaction) and for mesitylene and ether (weak and strong specific interaction respectively). The non-specifically adsorbed hydrocarbon produces a symmetrical peak which remains unaffected by dehydroxylation of the surface. For mesitylene and ether surface dehydroxylation reduces retention times and narrows the chromatographic bands. It is shown by comparing with infra-red and calorimetric data that an increase in the strength of specific interactions leads to an increase in the ratio of the retention volumes on hydroxylated and dehydroxylated surfaces[4, 15].

Kiselev and coworkers[16] have also investigated, using gas chromatography, the adsorption of molecules of various geometrical and electronic structures on samples of macroporous silica gels and alumina-silica gels. When the silica gel and alumina-silica gel surfaces are dehydroxylated, the retention volumes of straight-chain alkanes increase while that of benzene falls sharply.

The retention volumes of diethyl ether and acetone also decrease sharply when the silica gel surface is dehydroxylated, but increase with the dehydroxylation of the alumina silica gel. This phenomenon may be explained by the formation of alumino-silicate complexes during the heat treatment.

Rogers and coworkers[17-19] have measured line widths and chemical shifts in nuclear magnetic resonance spectra for molecules of cyclohexane, p-xylene, mesitylene, acetone and methylacetate, adsorbed on silica, both before and after silanization. The samples of silica used were of two types, pyrogenic and precipitated.

The N.M.R data suggest that the silanized surface is much less active than the hydroxylated surface. However, the elution order and the heat of the adsorption measured by gas chromatography on the silanized silica, as well as the infra-red data indicates a still significant population of hydroxyl sites on the surface. Rogers and coworkers[18] have concluded then, that adsorption could have occurred on the residual hydroxyl groups of the silanized surface.

In order to clarify the nature of gas-solid adsorptive interactions on silica, Cadogan and Sawyer[20] have measured retention volumes on salt-modified silica gel and porous silica beads subjected previously to varying amounts of thermal pretreatment (250 - 700°C). The enthalpies and entropies of adsorption are then evaluated for various molecules with functional group substituted on the aromatic ring. The variation of the various functional group contributions with heat treatment is studied and the data provide insight into the nature of the active sites. The surface of the silica gel is covered initially by considerable amounts of molecular water bonded to surface silicon atoms; some free hydroxyl groups also are present. On raising the temperature of activation to 200°C most of the hydrogen-bonded water appears to be removed with hydrogen bonds forming between favorably placed hydroxyls. Further heating to 500°C removes most of the coordinated water molecules and increases hydrogen bonding between hydroxyls. At 600°C the hydrogen-bonded hydroxyls appear to condense to form surface siloxane linkages with few single hydroxyls still present.

2 - APPLICATIONS

a) - Silica gel adsorbent particles:

Silica gel has found wide applications in analytical practice of gas chromatography[2, 21]. Greene and Pust[22] have analyzed a mixture of some low boiling gases on a silica gel column with temperature programming from 5°C to 155°C (Figure 5). The same mixture is analyzed on a silica column (Figure 5a) and on an alumina column (Figure 5b) and the separations obtained are compared. Carbon dioxide is eluted just after ethane on silica gel and is irreversibly adsorbed on alumina. Greene and Pust[23] have measured by gas-solid chromatography the heat of adsorption of some hydrocarbons (CH_4, C_2H_6, CO_2, C_2H_4, C_3H_8) on silica gel and alumina. The results are found to agree well with those obtained calorimetrically.

Szulczewski and Higuchi[24] have analyzed mixtures of permanent gases (O_2, N_2, NO, CO, N_2O, CO_2) on silica gel at the temperature of dry ice. After the emergence of CO the temperature is raised to room temperature for the elution of N_2O and CO_2.

Smith and coworkers[25] have used a column packed with two layers of silica gel separated by an intermediate layer of iodine pentoxide for the separation of CO from CO_2, and N_2O, the last two gases appearing as a single peak.

The iodine pentoxide is used to oxidize carbon monoxide to carbon dioxide and nitric oxide to nitrogen dioxide. Brenner and Ettre[26] have used a silica gel column cooled in dry ice to adsorb trace impurities. The condensing system is connected to a gas

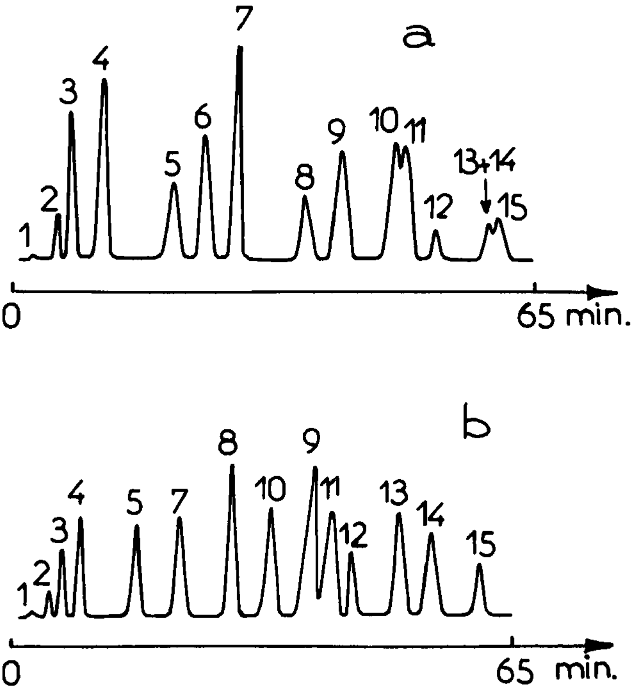

FIGURE 5

Separation of gases on a silica gel column (a), and on an alumina column (b).

(1) hydrogen, (2) air, (3) carbon monoxide, (4) methane, (5) ethane, (6) carbon dioxide, (7) ethylene, (8) propane, (9) acetylene, (10) propylene, (11) isobutane, (12) n-butane, (13) isobutylene, (14) cis-2-butene, (15) butadiene. Column: 20 feet; particle size: 20-40 mesh. helium flow rate: 70 ml/min; temperature programmed from 5 to 155° C.

After Greene and Pust[22]: Figure 1.

chromatography and after desorption the impurities are analyzed at 50°C.

Marvillet and Tranchant[27] have reported on the use of gas chromatography in the analysis of decomposition products of propellants. They have analyzed mixtures of N_2, NO, N_2O, CO_2, CO, at

- 20°C on a carefully sieved silica gel. Sakaida and coworkers[28] using silica gel as adsorbent developed a procedure to determine nitric oxide present at low concentrations in nitrogen.

Gregory[29] has analyzed a mixture of O_2, SF_6, CCl_2F_2, on a silica gel column and Greene and Wachi [30] some low molecular weight fluorocarbons with temperature programmed from room temperature to 180°C. The cis and trans isomers of C_4F_8 - 2 were not resolved, but n- and cyclic C_3F_6 could be resolved.

Manka[31] has used in series a silica gel and a molecular sieve 13 X column to analyze a mixture of H_2, O_2, N_2, CO, CO_2, CH_4. Pannetier and Djega-Mariadassou[32] have separated a mixture of H_2, N_2, CO, CO_2 on silica gel at 35°C.

De Grazio[33] has resolved a mixture of CO_2 and N_2O using a two column system at 180°C: a 10cm long precolumn of molecular sieve 13 X, coupled to a column packed with silica gel adsorbent. Lo Chang[34] has developed five gas chromatographic methods to analyze gas mixtures containing H_2, A(or O_2), N_2, CO, CO_2, CH_4 and C_2H_6. He used combination of three kinds of gas-solid columns of various lengths packed with either silica gel, molecular sieve 5 A or activated charcoal.

Hodges and Matson[35] have separated a mixture of sulphur compounds on silica gel at 100°C. Then more recently, in the same laboratory, Thornsberry[36] has tried to reproduce these results and failed. He succeeded however to separate the sulphur gases on Deactigel, a treated silica gel, Figure 6 shows the separation obtained using a 2 foot x 1/4 inch column of acid washed Deactigel at a temperature of 122°C and a helium carrier gas flow rate of 55 cc/min.

Yee[37] has used a column packed with silica gel to analyze O_2, OF_2 and CF_4 at - 78°C.

Bellar and Sigsby[38] have reported gas-solid chromatographic data for the separation of several hydrocarbons on silica gels of varying water content. These data were predicted by Snyder[39] using

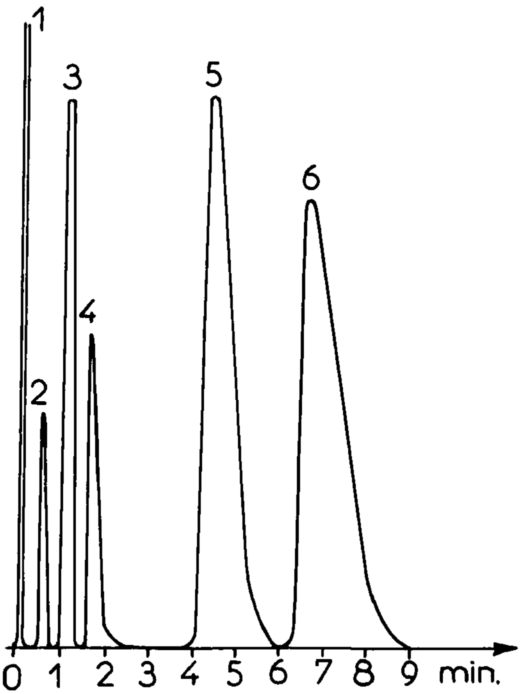

FIGURE 6

Separation of sulphur gases on
a column of acid washed Deactigel.

(1) air, (2) carbon dioxide, (3) carbon oxysulfide, (4) hydrogen sulfide, (5) carbon disulphide, (6) sulfur dioxide.
Column: 2 feet x 1/4 inch i.d; helium flow rate: 55 ml/min.
temperature: 122° C.

After Thornsberry[36]: Figure 1.

a semi-empirical equation for gas-solid chromatography similar to the one he has developed for liquid-solid chromatography.

Sokolov and coworkers[40] have obtained good separation of zinc from cadmium upon injection of a zinc-cadmium alloy (1 : 1) into columns containing diatomite clinkers, crushed quarts or silica gel at 850°C. The best results for Zn, Cd (and Hg) separation were obtained with graphite of spectral purity[41]. Sulphur and selenium vapors have different retention values on silica gel and graphite at 450 - 600°C and give symmetrical peaks. Separation of mixtures of these elements were unsuccessful however as a result of the formation of selenium sulphide vapor, masking the separation[41].

Kiselev and coworkers[12] have developed a new macroporous aero silogel of high purity, Silochrom C80, with a specific surface area of about 80 m^2/g and pore diameter about 550 Å, to analyze[42] with symmetrical peaks saturated, unsaturated and aromatic hydrocarbons, ethers, esters, alcohols, acetophenone, nitrobenzene and aniline. Figure 7 shows that alcohols emerge from a 1 m x 0,3 cm column of Silochrom C80 at 140°C, with narrow peaks. Nitrogen is the carrier gas.

Kiselev and coworkers[43] have measured accurately the retention volumes for n-hexane and n-heptane on macroporous aerosilogel with a fairly homogeneous surface. From the data, the differential heats of adsorption as well as the difference in heat capacities of n-hexane and n-heptane in the adsorbed and gaseous state were calculated.

Other silica gels of high chemical purity called porous silica beads allow effective separation in gas-solid chromatography of permanent gases and complex mixtures of various chemical compounds.

This adsorbent (Porasil or Spherosil) has been first prepared and used in gas-solid chromatography by Guillemin and coworkers[44] and is availabe in a wide range of surface areas and particle diameters.

Good separations have been achieved for light hydrocarbons: C_4 alkanes and alkenes, aromatics.

In some cases, it is advantageous to add slight amounts of modifier (Carbowax 20 M) to suppress tailing of polar compounds. A systematic gas chromatographic study of this support illustrates the mechanism of separation on silica beads[45].

Feltl and Smolkova[46] have measured adsorption isotherms of benzene, n-hexane and cyclohexane by frontal chromatography, using

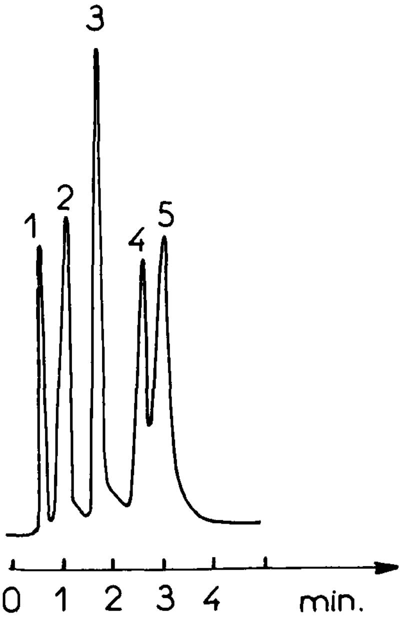

FIGURE 7

Analysis of a mixture of
alcohols on Silochrom C 80.

(1) methanol, (2) ethanol, (3) isopropanol, (4) isobutanol,
(5) n-butanol.
Column: 1 m x 3 mm i.d; nitrogen flow rate: 40 ml/min.
temperature: 140° C.

After: Bebris, Kiselev, Mokeev, Nikitin, Yashin and
Zaizeva[42]: Figure 5b.

porous silica beads of different surface area. It is concluded that a change in the geometrical surface area and in porosity plays a predominant role in adsorption and that the concentration of hydroxyl groups on the surface is independent of the surface area.

b) - Highly dispersed silica:

Highly dispersed silicas with particle diameters less than 1µ form colloidal solution with water. They have generally been used as porous layers on glass beads or on the walls of capillary columns.

Halasz and Gerlach[47], however have produced capillary columns by drawing out glass tubes with highly dispersed silica having a particle size of about 1 micrometer.

Fast analysis of C_1 to C_6 paraffins and olefins, within seconds, were carried out on these "aerogel columns".

Kirkland[48, 49] has coated glass beads with thin layers of finely divided silica or diatomaceous earth anchored to the surface by means of fibrillar Boehmite. These columns show better efficiencies when compared with columns of untreated beads. Schwartz and coworkers[50] were able to prepare capillary columns by wetting the walls of the capillary with colloidal silica sols. A stainless steel capillary column containing hydrophobic silica (Nalco CD 100) prepared in the same way[51], provides high resolution separations of complex hydrocarbon mixtures. Figure 8 shows the separation of C_6 - C_8 aromatic hydrocarbons at room temperature.

Kiselev and coworkers[52] have studied the chromatographic properties of a highly dispersed, pure, non porous silica deposited on Chromosorb and compared its properties with those of a macroporous silica gel of high purity.

The use of a surface layer adsorbent increases the column efficiency and reduces the time of analysis.

c) - Etched glass capillary columns:

Glass capillary columns, after treatment of their internal surface with an alkaline solution may be used as adsorption columns. The porous layer coating the inner wall of the glass tube is practically a layer of pure silica with a large specific surface area. Mohnke and Saffert[53] employed glass capillaries in which an internal layer of corroded silica behaves as an adsorption medium for the separation of hydrogen isotopes. The inside wall of the capillary is coated with a SiO_2 film, approximately 20µ thick, after treatment with an ammonia solution for 170 hours. With a 80 m long capillary column, isotopes and isomers of hydrogen are completely separated at 77.6°K (Figure 9). More recently, Mohnke

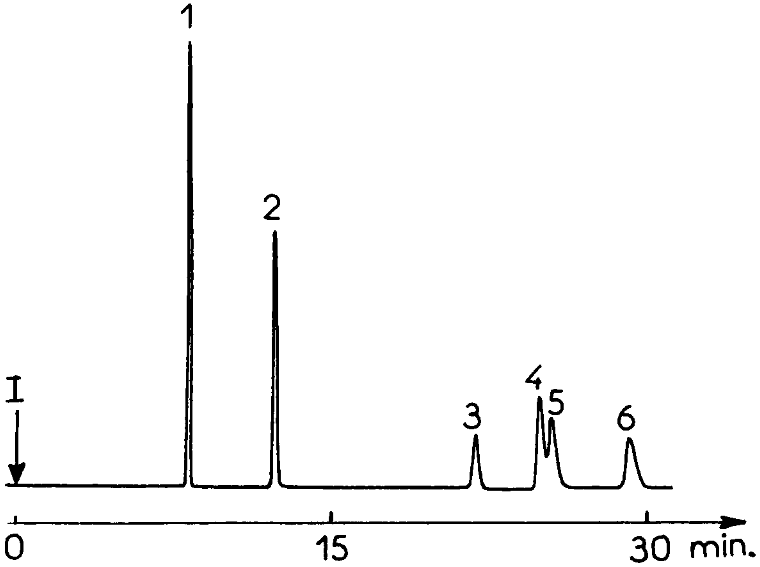

FIGURE 8

Analysis of C_6 to C_8 aromatic hydrocarbons on silica capillary adsorption column.

(1) benzene, (2) toluene, (3) ethylbenzene, (4) m-xylene, (5) p-xylene, (6) o-xylene.
Silica capillary adsorption column; 200 feet x 0.01 inch i.d. stainless steel; colloidal hydrophobic silica Nalco CD-100; room temperature; inlet pressure 20 p.s.i; argon carrier gas.

After Schwarz, Brasseaux and Matthews[51]: Figure 3.

and coworkers[54] used capillary columns prepared in the same way to separate isotopic hydrogen molecules in extreme concentration ratios. This is accomplished with the capillary column and a highly sensitive electrolytic conductivity detector.

Purer and Kaplan[55] have achieved the complete separation of helium, para hydrogen, orthohydrogen, paradeuterium and orthodeuterium on a 82 m long glass capillary column with an etched internal surface. This investigation covers the temperature range of 29° to 60°K. The same column has been previously used to separate neon isotopes[56].

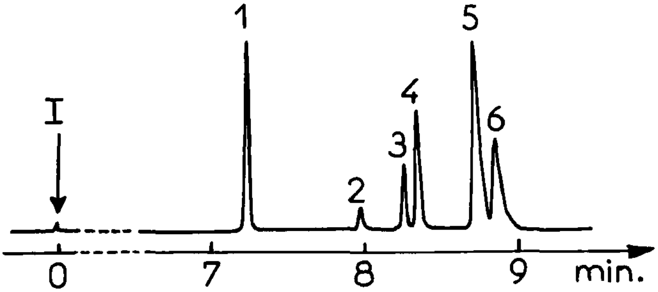

FIGURE 9

Separation of hydrogen isotopes and their nuclear Spin isomers on etched glass capillary column.

(1) He, (2) p-H_2, (3) o-H_2, (4) HD, (5) o-D_2, (6) p-D_2. ammonia treated glass capillary column 80 meter long. temperature: 77.6°K; neon flow rate: 2 ml/min.

After Mohnke and Saffert[53]: Figure 3.

Bruner and Cartoni[57] have shown that glass capillaries with inner walls etched with an alkaline solution are useful for the analysis of low boiling hydrocarbons at room temperature. By coating these capillaries with different amounts of liquid phase, modified silica adsorbents are obtained. Bocola and coworkers[58] have used the same etched internal surface capillary column to separate the isotopic molecules of oxygen. Bruner and coworkers[59] have established optimum working conditions for columns of this type in terms of peak resolution and analysis time. The following systems have been studied at temperatures up to 77°K: CH_4 - CD_4, C_2H_6 - C_2D_6, C_2H_4 - C_2D_4, C_7H_8 - C_7D_8, and O_2^{16} - O_2^{18}.

Bruner and coworkers[60] have separated a mixture of all the isotopic methanes with an etched internal surface capillary column, 47 meters long, at 77°K. The radio-active compounds are detected by an ionization chamber and the stable isotopes by a flame ionization detector (Figure 10).

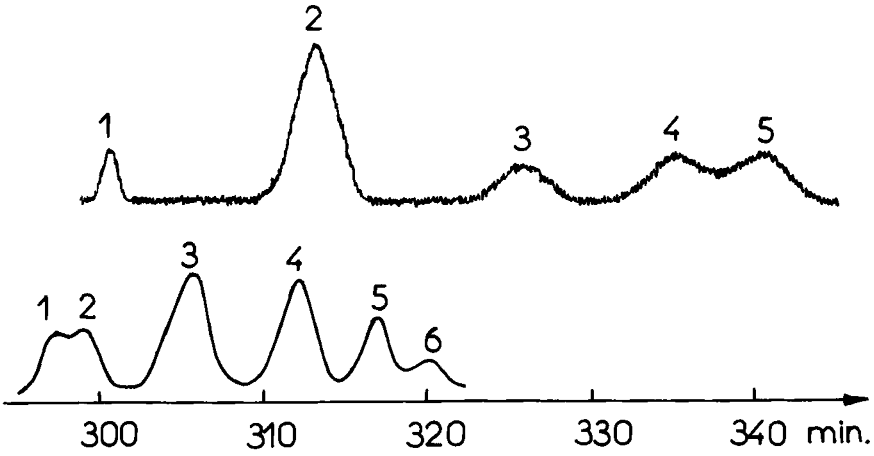

FIGURE 10

Separation of a mixture of deuterated and tritiated methanes on etched glass capillary column.

(1) $C^{12}H_4$, (2) $C^{13}H_4$, (3) CH_3D, (4) CH_2D_2, (5) CHD_3, (6) CD_4.
flame ionisation detector, lower chromatogram.
(1) $C^{14}H_4$, (2) CH_3T, (3) CH_2T_2, (4) CHT_3, (5) CT_4. ion chamber detector, upper chromatogram.
NaOH treated glass capillary column 47 meter long.
temperature 77° K; 70% nitrogen + 30% helium flow rate:
1 ml/min;
pressure drop: 21 cm Hg.

After Bruner, Cartoni and Possanzini[60]: Figure 1.

Cartoni and Possanzini[61] have reported the separation at 77°K of a mixture of $^{14}N_2$ and $^{15}N_2$ on an etched glass capillary column, 175 m long.

d) - Porous glasses:

Porous glasses can be considered as polar sorbents with a surface formed mainly of hydrated silica[2]. The advantages of porous glasses in gas chromatography were first pointed out by Zhdanov and coworkers[2, 8, 62].

Dobychin and coworkers[63] have developed methods for production of porous glasses with pores in the range between 15 and 15,000 Å and showed that the very uniform pore size distribution make them effective adsorbents in gas chromatography. Zhdanov and coworkers[64] have shown the considerable advantages of surface porous glass beads in gas chromatography, by comparison with bulk porous glass beads. These adsorbents were prepared by controlled attack by an HCl solution.

Alberini and coworkers[65] have compared the physical adsorption properties of glasses etched with hot alkaline solutions and its gas chromatographic behavior. They could achieve the separation of CH_4 and CH_3D with an etched glass bead packed conventional column, 8 meters long, 2 mm i.d.

3 - MODIFIED SILICA ADSORBENTS

a) - With organic compounds:

Modification of wide pore silica gel by means of adsorbed dense monolayers offers the possibility of obtaining homogeneous surfaces of different composition, with low adsorption energies[2, 8, 66].

In order to eliminate the asymmetry of chromatographic peaks, Kiselev and coworkers[67] have deposited a small amount of polyethylene glycol on silica gel. The specific interactions of molecules of different types with the acidic hydroxyl groups on the surface of silica gel are then replaced by specific interactions with the ether groups of polyethylene glycol. These authors[67] have also modified a macroporous silica gel with a polymer ("polyarylate Ph-1") of average molecular weight 30000, carrying on its surface negative charges concentrated mainly on the oxygen atoms of carbonyl and ether groups.

The use of "polyarylate Ph-1" as a thin adsorption layer on silica gel permits a sharp reduction of the strong retention of n-alkanes and aromatic hydrocarbons. Spreading of the chromatographic peak is reduced.

The adsorptive properties of silica gels treated with several aromatic hydrocarbons (benzene, toluene, ethylbenzene, diphenylmethane, o-xylene, m-xylene, naphthalene) have been studied by Rogers and coworkers[68]. Benzene, toluene, ethylbenzene are eluted sooner and with narrower peaks on the pretreated silica gels. The surface area of these gels were measured by frontal analysis[69].

The surface areas measured with benzene show a change in the adsorption mechanism which was not apparent when nitrogen surface areas were used.

Guillemin and coworkers[70] have coated porous silica beads with various amounts of liquid stationary phases. Polar compounds like alcohols are eluted with symmetrical peaks on modified porous silica beads (Figure 11).

b) - With inorganic compounds:

Karger and coworkers[71, 72] have used water to deactivate porous silica beads and presaturate the carrier gas with water.

Brookman and Sawyer[73] have coated porous silica beads with an inorganic salt, Na_2SO_4, in order to provide symmetrical peaks. They have evaluated the enthalpy and the entropy of adsorption for compounds with various functional groups, on salt modified porous silica beads[74, 75]. Isbell and Sawyer[76] have measured the functional group contribution to adsorption on porous silica beads modified with Na_2SO_4, NaCl, LiBr, Na_3PO_4, Na_2MoO_4, $NiSO_4$, $CoSO_4$, $Al_2(SO_4)_3$ and $Cr_2(SO_4)_3$. The adsorption properties of salt modified aluminas and magnesium silicates are compared with those of porous silica beads in reference 77. Cadogan and Sawyer[78] have studied the gas chromatographic properties of lanthanum chloride on Silica gel and Graphon. Okamura and Sawyer[79] have measured differential enthalpies, entropies and free energies of adsorption of sorbate molecules on Graphon, salt modified alumina, and salt modified porous silica beads. The contribution of molar refraction dipole moments to adsorption are determined and retention volumes of other compounds are predicted.

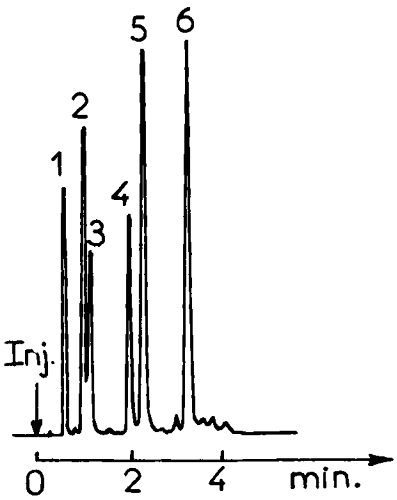

FIGURE 11

Separation of thiols and alcohols on porous silica beads.

(1) tertiobutanethiol, (2) n-butane thiol, (3) tertiobutanol, (4) n-pentane thiol, (5) n-butanol, (6) n-pentanol.
Column 2 m x 1/8 inch. i.d; Spherosil XOC 005 (7m^2/g) plus 2% LAC 446 (Applied Science Laboratories);
temperature programmed from 50° C to 150° C; nitrogen flow rate: 60 ml/min.

After Guillemin, Deleuil, Cirendini and Vermont[70]:Figure 22.

c) - By chemical reactions:

Effort has been made to prepare more uniform surfaces by substitution of more inert groups for the surface hydroxyls. The reactions with either chlorosilanes or alcohols result in the elimination of HCl or H_2O respectively.

Modified silica gels treated with trimethyl chlorosilane have been used in gas solid chromatography by Kiselev and co-workers[8, 80, 81].

Halasz and Sebastian[82] have esterified the surface of porous silica beads with 3 - hydroxypropionitrile. They obtained a material highly efficient and more thermally stable than chromatographic materials using either this nitrile or 3 - 3' oxypropionitrile as liquid phase.

Little and coworkers[83] have grafted new stationary phases to porous silica. The elution behavior of several types of compounds and the thermal stability of these packings are studied in detail.

Aue and Hastings[84] have prepared layers of substituted polysiloxane silica surface. They were synthesized from a variety of pure and mixed monomers.

Sorrell and Rowan[85] have studied silica gels modified by chemical reaction of an alcohol or a chlorosilane with the surface hydroxyls of the gel. They correlate the physical properties of these adsorbents with their behavior in gas solid chromatography. The concentration of high energy adsorption sites was generally reduced after the reaction, and this resulted in a more uniform surface, superior for chromatography. In most cases, the chemical modification improved column efficiency.

Resolution was also increased and peak tailing was often reduced markedly[86].

This new field of chemical modifications of silica surfaces by reacting various molecules to the silanole groups[82] seems extremely promising and will certainly arouse much interest in the near future.

D - Zeolites

The structure of synthetic zeolites (molecular sieves) consists of a three dimensional framework of SiO_4, and AlO_4 tetrahedra[1, 2]. The aluminum ion is small enough to occupy the central position in the tetrahedron made by four oxygen atoms. As each silicon shares the oxygen atoms of its tetrahedron with its neighbour there are twice as many oxygen atoms as silicon atoms and the silica is neutral. Each substitution of Al^{3+} for Si^{4+} requires the additional presence of one alkaline ion or half an alkaline - earth ion such as Na^+, K^+, or Ca^{2+}, Sr^{2+} in order to maintain electrical neutrality. Many different species have been prepared in the Linde research Laboratory[1]. Although some of these are analogs to zeolite minerals, many were new varieties not found in nature. Two of these, used in gas chromatography, are designated as zeolite type A and type X.

In each crystallographic unit cell of zeolite type A, there are 12 AlO_4 and 12 SiO_4 tetrahedra and 12 monovalent cations. These tetrahedra form truncated octahedra solids with 8 regular hexagon faces and 6 square faces (cf. Figure 12) which are linked in a cubic array (cf. Figure 13). The framework of the synthetic zeolites type X and Y is basically the same, except that the basic truncated octahedra are linked through their hexagon faces

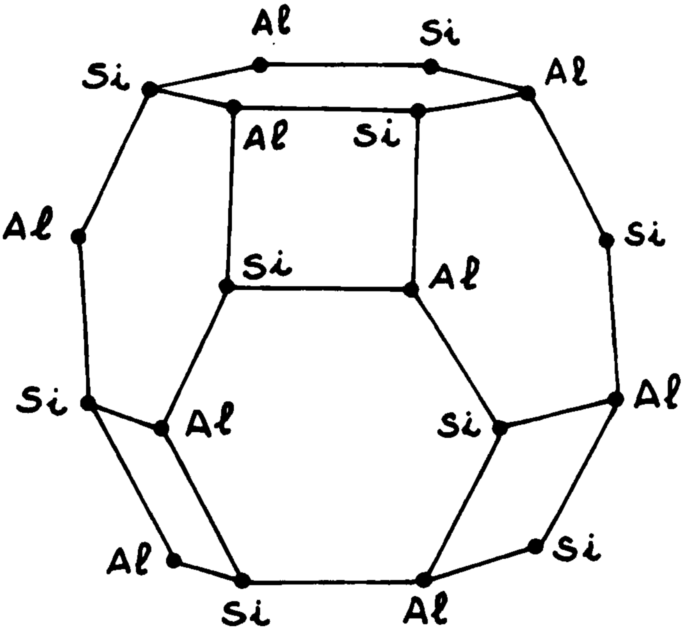

FIGURE 12

Position of the silicon and aluminum atoms in the basic truncated octahedron cell of the molecular sieves.

instead of their square faces as in zeolites A and so are more loosely packed.

The sodium form of the A-type zeolite, NaA, has a nominal pore opening of 4 Å, but when potassium ions replace the sodium ions, a pore opening of 3 Å results. Replacement of the sodium ions with calcium (CaNaA) gives a nominal pore size of 5 Å. Zeolite 13 X (NaX) and zeolite 10 X (CaNaX) have respectively a

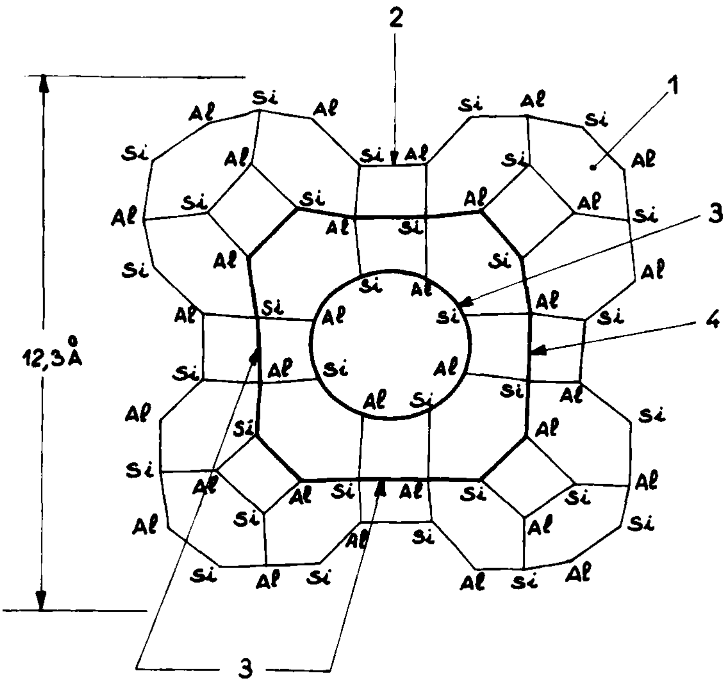

FIGURE 13

Position of the silicon and aluminum atoms in type A molecular sieves.

1 - Basic truncated octahedron cell.
2 - Cube junction between basic cells.
3 - Inlet of pores.
4 - Contour line of a pore.

nominal pore size of 10 Å and 8 Å [3]. Synthetic zeolites have large surface areas[4, 5], on the order of 700-800 m^2/g.

It should also be pointed out that molecular sieve pellets which is the main commercial product, are made of microcrystals of zeolite (≈ 1μ in diameter) embedded in a dried clay matrix. Some side effects may arise from adsorption on this clay.

1 - ADSORPTION STUDIES ON ZEOLITES:

The inner surface of the cavity of porous crystals of cationated zeolites carries positive charges concentrated on the exchanged cations. Consequently, zeolites are adsorbents which interact specifically with molecules of high electron density (class IV of Kiselev's classification[6]). Although Benson and King[7, 8] have suggested that separations on molecular sieves occur only because of electrostatic interactions between the adsorbate and the external surface of the zeolite crystal, others[9, 10] have presented strong evidence that diffusion within the crystal is important enough for compounds that can enter the apertures of the pores.

Gas chromatographic technique has been used for studying the low pressure adsorption behavior of zeolites. Kiselev and co-workers[11] have determined the heats of adsorption of the lower hydrocarbons on zeolite 5 A. They have also studied the specific interaction of acetylene, ethylene and ethane with zeolite 10 X.[12]. Eberly[13, 14] has examined the adsorptive properties of various cationic forms of zeolite X and A towards n-hexane, hexene and benzene. Habgood[15] has measured retention volumes for O_2, N_2, CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_2H_4 and C_3H_6 over a range of temperature between 25 and 400°C on the following ion-exchanged forms of zeolite X : Li^+, Na^+, K^+, Mg^{++}, Ca^{++}, Ba^{++}, Ag^+. He observed that the cationic field increases with decreasing ionic radius; divalent cations while having greater fields are only half the number of monovalent cations and tend to be found on less exposed sites; the polarizing power of silver ion, which also occpuies all types of exposed sites is very strong. The significance of molecular quadrupole interactions on these surfaces is shown by the much weaker cationic effects observed with O_2 (which has negligible quadrupole moment) than with N_2.

Kiselev and coworkers[16] have compared the differential heats of adsorption, measured by gas chromatography, of various straight chain alkanes on macroporous silica gel, graphitized carbon black, NaA zeolite and NaX zeolite (Figure 14). The heats of non-specific adsorption of straight chain hydrocarbons on the external surface of NaA zeolite (for geometrical reasons, the molecules of straight chain hydrocarbons cannot be adsorbed within the pores of this zeolite) are higher than the heats of adsorption on graphitized carbon black. This is associated with a high density of the distribution of oxygen atoms. The highest heats of adsorption were obtained on NaX zeolite: straight chain alkanes penetrate into the large cavities of these porous crystals, where they are surrounded by atoms of the adsorbents.

Berezkin and Nikitina[17] have measured by gas chromatography the heats of adsorption of C_5-C_{12} straight chain alkanes on NaX zeolite crystals deposited on Chromosorb G. The results agree with the previous data[16] obtained on bulk phase NaX zeolites.

Tsitsishvili and coworkers[18] have determined the heats of adsorption of CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_4H_{10} and CO on type X zeolites containing the following cations: Li^+, K^+, Rb^+, Cs^+, Ag^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+} and Cd^{2+}. Type X zeolites containing Ag^+ and Cd^{2+} give a specific retention of ethylene, propylene and carbon monoxide. Similarly the elution order of methane and carbon monoxide depends on the nature of the zeolite[19, 20] cation. Matsumoto and coworkers[21] have studied the adsorptive properties of partly decationated zeolite Y for simple aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylenes by means of gas chromatography at 270-330°C. The specific retention of these alkylbenzenes increases with the sodium ion content and with the pretreatment of zeolite.

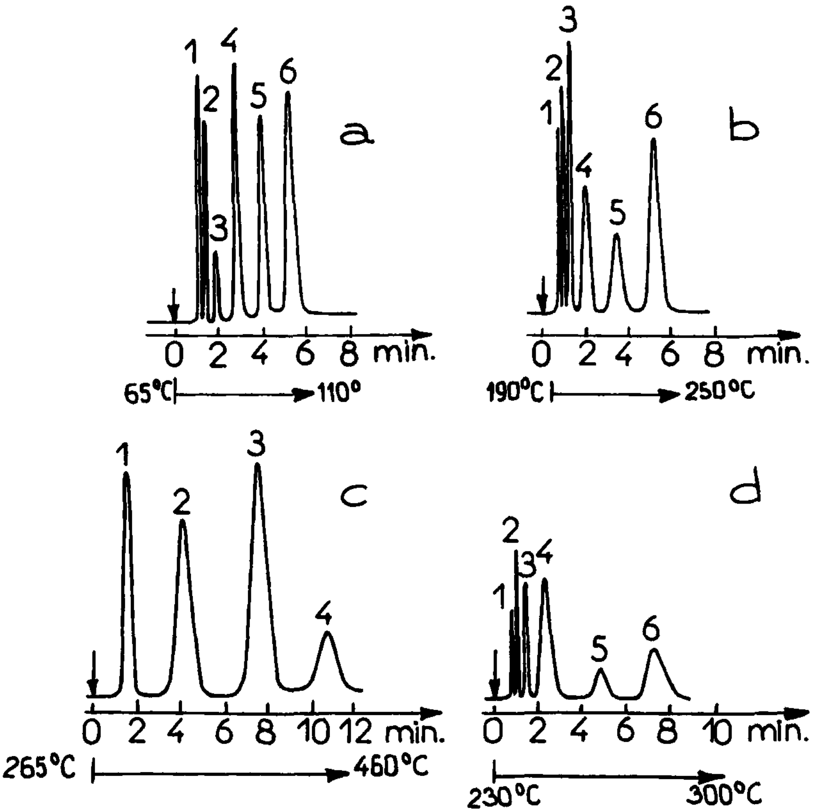

FIGURE 14

Chromatograms of normal hydrocarbons obtained in temperature programming.

(1) n-pentane, (2) n-hexane, (3) n-heptane, (4) n-octane, (5) n-nonane, (6) n-decane.
a) Silica gel; b) graphitized carbon black 1 m x 4 mm.i.d. column; carrier gas helium. c) NaX zeolite; d) NaA zeolite. 16 cm x 4 mm.i.d. column; carrier gas helium.

After Keibal, Kiselev, Savinov, Khudyakov, Shcherbakova and Yashin[16]: Figure 4.

Patselova[22] has studied by gas chromatography the effect of water presorption on the adsorption of oxygen, nitrogen, krypton and carbon monoxide on NaX zeolite. Navalikhina and coworkers[23] have investigated the acidic properties of decationated zeolites by measuring the chromatographic heats of adsorption of benzene and toluene (weak bases) at high temperature after poisoning of the zeolite by pyridine (a strong base).

Kiselev[24] has discussed the framework of a general theory of molecular adsorption for the equilibrium between the zeolite and adsorbate molecules.

Kiselev and coworkers have calculated using methods of statistical thermodynamics, the chemical potential, the differential entropy and the enthalpy of adsorption of neon, argon[25] and neopentane[26] on NaA zeolite at low coverages. Bräuer and coworkers[27] have carried out the same calculations for the systems Ar-NaA zeolite and CH_4-CaA zeolite. The results agree well with experimental data[28].

Mayorga and Peterson[29] have presented the adsorption potential contour maps for a series of six non-polar molecules of varying size within the H zeolite mordenite lattice. A comparison between calculated adsorption potentials and heats of adsorption derived from gas chromatographic measurements agree satisfactorily[30], when the interaction parameters are evaluated by the London formula, in the case of atomic adsorbates (Argon, krypton). The poor agreement found with alkanes (methane, ethane, propane, n-butane) reflects an inadequacy of treating the molecules as spherical, even in the case of methane.

Gant and coworkers[31] have employed gas adsorption chromatographic techniques to study the adsorption at low surface coverage of the six isomers of hydrogen (H_2, D_2, T_2, HD, HT, DT) on molecular sieve 4 A in the temperature range from 169 to 219°K. The separation factors for o-H_2/p-H_2 were also determined in the range from 135 to 160°K. An adsorption model based on a hybrid partition function which takes full account of molecular rotation and vibration fits the experimental data of the symmetric weight isomers. The observed $o\text{-}H_2/p\text{-}H_2$ separation factors are accounted for, demonstrating that the effects of hindered rotation are of great importance in this temperature region.

Oberholtzer and Rogers[32] using a high precision chromatograph have studied the porosity effects of zeolites by comparing the elution behavior of methane, ethane and isobutane on 4 A and 5 A molecular sieves. A pronounced decrease in column efficiency with increasing temperature was observed for methane and ethane peaks, in the region where resistance to mass transfer controls the efficiency. These effects were attributed to slow diffusion within the zeolite because isobutane which was excluded from the zeolite pores did not exhibit those effects. Moreland and Rogers[33] have studied the elution behavior of CH_4, C_2H_6, n-C_3H_8, iso-C_4H_{10}, Ar, O_2, N_2 and SF_6 on type A zeolite containing K^+, Na^+, Li^+, Sr^{2+}, Ca^{2+} and Mg^{2+} and on a 10 X zeolite. Temperature and flow rate dependence of peak tailing and changes in the retention volumes with flow-rate were observed for those adsorbates, able only to partially penetrate the pores.

Zikanova[34] has studied the internal diffusion of pentane in granulated zeolite 5 A by a gas chromatographic method in the temperature range between 144 and 285°C. The results obtained give evidence that the transport rate of the molecules from the surface to the adsorption site is limited by activated diffusion within zeolite crystallites.

2 - APPLICATIONS:

Synthetic zeolites have been used as adsorbents in gas solid chromatography, to solve a wide variety of analytical problems. Because of the well defined pore size and structure of zeolites, many separations are possible on this adsorbent, which are due to exclusion of larger molecules from the large internal surface area[33]. Thus straight-chain and branched-chain hydrocarbons are separated, as also are aromatic and cyclic hydrocarbons from aliphatic species. In addition to such molecular effects, the activity of the zeolite surface allows separations based on pure adsorption[33]: separations of hydrogen isotopes, permanent gases and low molecular weight hydrocarbons on the large internal surface and separation of heavier bulkier molecules on the smaller external surface of zeolites.

a) - Analysis of hydrogen isotopes:

The first reported success[35] in resolving a mixture of protium, protium deuteride and deuterium came from Ohkoshi, Fugita and Kwan[36]. The resolution was obtained on a column of molecular sieve 5 A of 80 cm at -196°C and hydrogen was used as carrier gas. Ohkoshi and coworkers[37] have used this method to study the amounts of D_2, HD and H_2 before and after equilibrium on platinum at 300°C. Ohkoshi and coworkers[38] have described the enrichment in deuterium by flowing a mixture of hydrogen isotopes through a molecular sieve column in a liquid nitrogen bath which is a frontal analysis. Gant and Yang[39] have reported the separation of protide-protium tritide-tritium mixtures on a 6 m long molecular sieve column, with helium as carrier gas.

Bachmann, Bechtold and Cremer[40] have achieved the complete separation of para and ortho-hydrogen on an iron-free molecular sieve 13 X column, 3 meter long at 77°K (the origin of iron is most probably to be found in the clay used to bind zeolite particles). It is noted that the total time of analysis is reduced if the molecular sieve is previously heated in a stream of CO_2. The complete separation could not be obtained on Linde molecular sieve 13 X: a small conversion takes place because of the iron content. Cercy and Botter[41] have compared the separations of the hydrogen isotopes obtained with conventional packed columns and packed capillary columns prepared with molecular sieves. They used molecular sieves 5 A for the separation of isotopic hydrogen and molecular sieve 13 X for the analysis of a mixture of ortho and para hydrogen.

Liebenberg[42] has reported the quantitative analysis of He^3 isotope on Linde molecular sieve 5 A at 100°C, and that of H_2 and He^3 at 40°C. Conti and Lesimple[43] have shown that it is possible to resolve completely the six isotopic species of hydrogen on molecular sieve 4 A in the temperature range -140° to -150°C in the order H_2, HD, HT, D_2, DT, T_2. A partial resolution of ortho and para hydrogen is observed on this adsorbent.

Sato and coworkers[44] have studied the influence of the carrier gas on the separation of hydrogen isotopes using various samples of ammonia-treated molecular sieve 13 X.

Krejci and coworkers[45] have reported the separation of helium, neon and hydrogen on molecular sieve 5 A using argon as carrier gas. Neon and helium are completely resolved at -78°C. Baum[46] has analyzed hydrogen and helium at room temperature using a molecular sieve 5 A column.

b) - Analysis of low boiling gases:

Zeolites are generally used in gas-solid chromatography for the separation of low boiling point gases[47]. The analysis of H_2, O_2, N_2, CH_4, and CO (eluted in this order) can be conveniently achieved by gas chromatography using molecular sieve columns at ambiant or higher temperature. Kyriacos and Boord[48] have analyzed this mixture on a molecular sieve type 5 A column at 100°C.

Aubeau and coworkers[49] have reported the analysis of krypton and xenon in the presence of H_2, O_2, N_2, CH_4 and CO on molecular sieve 5 A at 40°C.

Farre-Rius and Guiochon[50,51] have achieved the separation of O_2, N_2, CH_4 and CO in 25 Sec. at 100°C on molecular sieve 5 A, using hydrogen as carrier gas. Brenner and Ettre[52] have shown that it is possible to detect O_2, N_2, CH_4, and CO as impurities between 0.1 to 0.5 ppm in a 10 liter sample of electrolytic hydrogen. The impurities were trapped at -80°C in a silica gel column and analyzed on a 2 meter long molecular sieve 5 A chromatographic column at 50°C.

Kiselev and coworkers[53] have studied the ability of several zeolite types to separate the above mixture. CO is easily separated from O_2, N_2 and CH_4 on all zeolites. When alumina, silica gel or carbon black are used, CO is eluted before CH_4. Carbon dioxide is highly retained on zeolites but is easily eluted on a silica gel column[54]. Blanc and coworkers[55] have described the enrichment of carbon monoxide in $^{13}C^{16}O$ and the separation of ^{20}Ne and ^{22}Ne on a molecular sieve column.

Graven[56] has shown that when using temperature programming from room temperature to 400°C with a molecular sieve 5 A column, it is possible to separate the low boiling point gases from carbon dioxide. The analysis of a mixture of low boiling point gases (H_2, O_2, N_2, CH_4, CO) together with higher molecular weight compounds like CO_2, C_2H_4, C_2H_6, C_2H_2 is a very complicated problem: the conditions which favour the separation of the lighter compounds on molecular sieve are totally unsuitable for the elution of the heavier compounds. The simplest solution to this analytical problem is either to run two or more analysis on different columns or to use two or more columns in series and switch them during the analysis. One of these columns is a molecular sieve 5 A column[57-61].

Marukami[62] has analyzed a mixture of gases containing O_2, N_2, CH_4, CO and CO_2, using two columns in series. The gases passed first through a silica gel column to the reference cell of a thermal detector, then through a molecular sieve 5 A column and finally through the measuring cell of the detector. Manka[63] has used a similar technique for the separation of H_2 in addition to the other gases.

Deans and coworkers[64] have described a column switching system for the isothermal analysis of H_2, O_2, N_2, CO, CH_4, CO_2, C_2H_4, C_2H_6 and C_2H_2. Higher hydrocarbons and water are backflushed from the system. The use of 13 X molecular sieve in a relatively deactivated state shortens the elution times of light components and improves peak shapes.

The separation of O_2, N_2, CO, C_2H_6, N_2O and CO_2 is possible on molecular sieve 5 A by temperature programming[56]. Bennett[65] has shown that this mixture can be successfully separated using both sides of a thermal conductivity detector. The first column is filled with Porapak Q and the second with molecular sieve 5 A. Both columns are operated at ambiant temperature. Solomon[66] using a 6 port column switching valve and peak parking technique has avoided the irreversible adsorption of CO_2 and N_2O on the molecular sieve. The separation of O_2, N_2, CH_4, CO_2, N_2O can be achieved within 5 minutes. McAllister and Southerland[67] have discussed the separation of N_2O and CO_2 at 250°C on molecular sieve 5 A.

Greene and Pust[68] have described a method for determining nitrogen dioxide by gas-solid chromatography. The method employs a molecular sieve 5 A column, the first part of which is wetted with water. NO_2 will not be eluted through the column, but reacts with water and gives NO, separated from genuine nitrogen oxide.

Trowell[69] has been able to separate a mixture of H_2, O_2, N_2, NO, CO, N_2O, CO_2, C_2H_6, C_2H_4, C_2H_2 and (NO_2- N_2O_4),using three columns in series. The third column which is packed with zeolite 13 X, deactivated only for 5 minutes at 250°C is used for the analysis at 25°C, of H_2, O_2, N_2, NO, CO.

To eliminate the tailing of the nitric oxide peak, Dietz[70] has specially treated the molecular sieve 5 A and obtained a permanently bound layer of nitrogen dioxide. A resulting chromatogram obtained with this treated sieve shows no tailing of the NO peak (Figure 15a) and no loss in resolution of the components of a sample containing 1% each of H_2, O_2, N_2, CH_4, and CO in CO_2 (Figure 15b).

Using molecular sieve 5 A, Vizard and Wynne[71] have shown that argon can be determined quantitatively in the presence of oxygen, using a 10 meter long column at 18°C. Lard and Horn[72] have analyzed the argon-oxygen fraction on molecular sieve 5 A at -72°C.

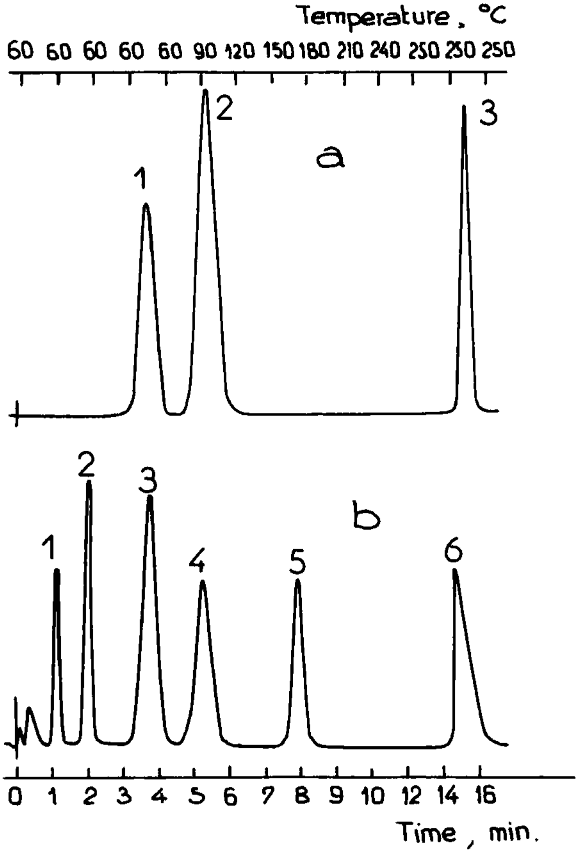

FIGURE 15

Separation of inorganic gases
and methane on molecular sieve 5A.

a) (1) nitrogen, (2) nitric oxide, (3) nitrogen dioxide
b) (1) hydrogen, (2) oxygen, (3) nitrogen, (4) carbon monoxide, (5) carbon dioxide.
Treated molecular sieve 5A with NO and O_2.
Column 6 feet x 1/4 inch.i.d, helium flow rate: 20 ml/min.

After Dietz[70]: Figure 1 and 2.

Heylmun[73] has repeated both experiments and analyzed traces of oxygen at -72°C in a gas containing over 99% of argon. Obermiller and Freedman[74] have determined argon, oxygen and nitrogen in air. Argon and oxygen are separated at -40°C on molecular sieve 5 A and nitrogen is then eluted out of the column at 50°C. Gunter and Musgrave[75] have separated A - O_2 - N_2 at -9°C on molecular sieve 5 A. Walker[76] has shown that the separation of argon and oxygen is possible if the molecular sieve 5 A was heated at 400°C for 24 hrs. under a steady flow of pure helium. Karlsson[77] has been able to resolve completely argon and oxygen on molecular sieve 5 A, heated at 450°C with argon.

The separation is nearly as good on molecular sieve 13 X treated in the same way.

Root and coworkers[78] have used molecular sieve 5 A columns greatly extended in length by the use of paired 15 m columns in a recycling apparatus, to separate butane (n-C_4H_{10}) from perdeuterated butane (n-C_4D_{10}) and methane from perdeuterated methane.

c) - Separations of high molecular weight hydrocarbons:

Methods involving a subtractive technique using molecular sieve 5 A have been developed for the analysis of normal paraffins in gasoline[79, 80]: the sample is eluted through a column to obtain a total chromatogram and then eluted again through the same column used this time in series with a short precolumn packed with 5 A molecular sieve. The sieves adsorb the normal paraffins in the gas stream and the second chromatogram represents only the branched hydrocarbons. Eggersten and Groennings[81] have released the normal paraffins by heating and backflushing. Only one sample was needed and the chromatogram areas for the normal and non-normal (iso- and cyclo-) hydrocarbons were observed independently, which resulted in improved sensitivity.

Blytas and Peterson[82] were able to extend the method to the kerosine range.

Barrall and Baumann[83] have used a 10 foot long gas liquid chromatographic column in series with a 15 foot molecular sieve 5 A column, to separate normal and branched chain hydrocarbons in the range C_7 to C_{20}. Thermal detectors are placed after each column.

Brunnock and Luke[84] have reported the discovery of a new hydrocarbon-type separation based on the use of molecular sieve 13 X in gas chromatography.

This method[85] permits a quantitative separation of the saturated hydrocarbons of petroleum distillates boiling up to 185°C by carbon number and by bulk hydrocarbon type within each carbon number. Naphthenes and paraffins were determined in a saturated petroleum distillate at each carbon number up to and including C_{10} (cf. Figure 16). The caustic soda treatment of the molecular sieves decreases the overall interaction energies of the sieves. It is possible by adjusting the chemical treatment and by careful control of temperature to trap and concentrate a particular isomer[85]. The technique however, because of interference from aromatics is not directly applicable to the analysis of a straight-run distillate of wide boiling range. The authors[86] have developed a new approach where the separation of the aromatics from the saturated hydrocarbons is achieved on 10 X molecular sieves in a short precolumn.

McTaggart, Luke and Wood[87] have discussed the gas-solid chromatographic methods previously described, based upon the use of 13 X, 10 X and 5 A molecular sieves. The use of type 13 X molecular sieve as an accurate "pre-cutting" column and the rapid determination of normal paraffins in a narrow boiling range, using 5 A molecular sieves are also covered. Some aspects of the preparation and the ion-exchange of molecular sieves for particular analysis have been studied in detail[87].

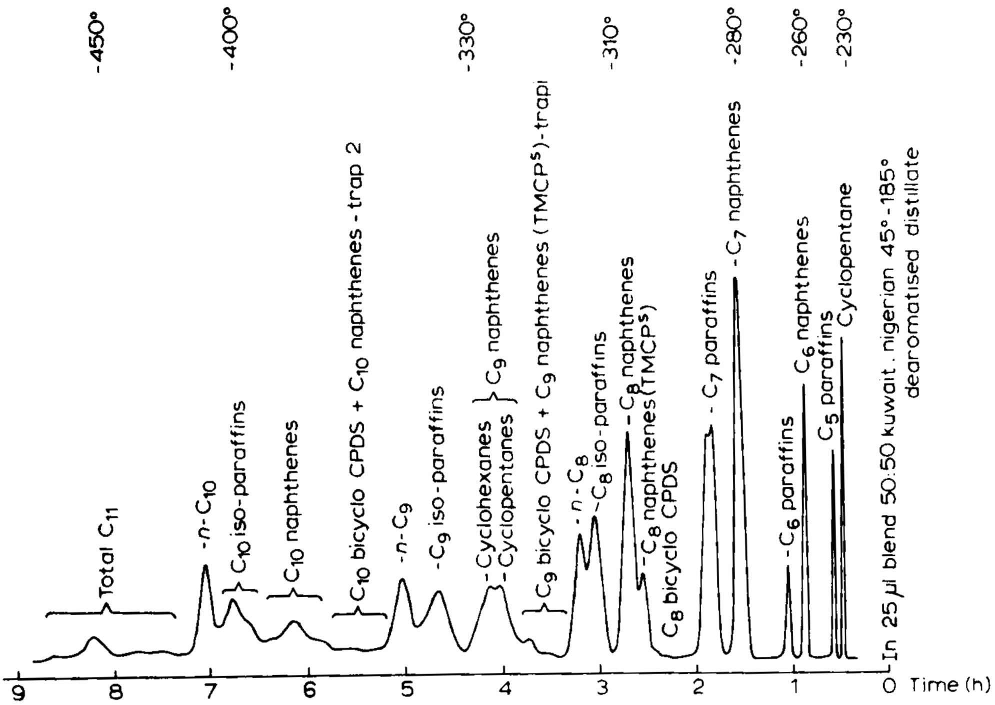

FIGURE 16

Typical Gas solid Chromatogram obtained with 13 X molecular sieve when used for collection and identification of fractions from a 45-185° dearomatized petroleum distillate.
Column: 3 feet x 5/32 inch.i.d; helium flow rate: 80 ml/min.

Reproduced from: J.V. Brunnock and L.A. Luke, "Separation of naphthenes and paraffins on an alkali-treated molecular sieve", J. Chromatogr., 39, 502 (1969): Figure 1.

By courtesy of Journal of Chromatography.

E - Alumina

Activated alumina has been used for many years as an adsorbent in liquid-solid adsorption chromatography[1]. Its use as an adsorbent in gas-solid chromatography has not been so widespread, however, because the resulting chromatographic peaks are most often asymmetrical due to the non-linear isotherms for solutes. Much of the asymmetry of the chromatographic peak is eliminated if the adsorbent is partially deactivated with silicone oil or water[2] or with inorganic salts[3, 4].

Silica gel and alumina have been used very early for the analysis of gases and low boiling point organic compounds, mainly unsaturated hydrocarbons. But whereas much work has been devoted to the preparation of various silica adsorbents suitable for the analysis of heavy compounds, similar studies have been much less numerous for alumina.

1 - ADSORPTION STUDIES ON ALUMINA

Most commercial aluminas used in chromatography are of the low temperature variety, generally impure γ-alumina with surface areas of 100-200 m^2/g[1]. The active sites on alumina are[5]:

(a) three, or five, types of hydroxyl group, the type being determined as for silica by the number of nearest oxygen neighbors, (three of these types can be distinguished by spectroscopic analysis and they show slightly different reactivities);

(b) the Lewis acid (electron accepting) sites which are due to aluminum ions attached to three oxygen atoms;

(c) the oxide ions.

From catalytic studies, it is generally agreed that the Lewis acid sites are the most active sites on alumina[5]. These acid sites are thought to arise when the hydroxyl groups condense with elimination of water, at temperatures above 400°C, leaving oxide ions and vacancies on the surface. When two vacancies are adjacent, an aluminum ion is exposed; this makes a Lewis acid site.

King and Benson[6] by calculating the field intensity over the (100) plane of an idealized Al_2O_3 surface, have shown that adsorbents like Al_2O_3 do create strong electric fields, in the vicinity of the surface. These strong fields are attributed to the existence of normal structural vacancies in the lattice of the adsorbent. King and Benson[6, 7] have postulated that electrostatic forces are mainly responsible for the adsorption of molecules on alumina. The authors[6] were able to calculate the gas chromatographic separation factors and heats of adsorption for hydrogen isotopes on alumina. The results are in good agreement with experimental values. The electrostatic theory[7] when applied to the separation of the rare gases and methane on a γ-Al_2O_3 column, gives the correct elution order. It gives also a qualitative explanation of the inability of chromatography to separate argon and oxygen at room temperature.

Katorski, White and Lassettre[8], in a complete treatment using quantum mechanics, have considered not only the separation of the ortho and para species, but the separation of the isotopes themselves. In this theory adsorption is considered as being caused by non-polar Van der Waals forces between the isotopes and the surface. It does not postulate, as King and Benson have done[6, 7], that adsorption on alumina is mainly caused by electrostatic forces. Haubach and coworkers[9] have investigated the chromatographic separation of the molecular species, H_2, D_2 and HT as well as that of ortho and para-hydrogen and deuterium at 27 and 55°K. At this low temperature, it is found that the retention times on γ-alumina are strongly dependent on the volume of sample. At low surface coverage, the separation factors are in fair agreement with the theory of Katorski, White and Lassettre who assumed that the adsorbent is a homogeneous plane surface.

Klemm and Airee[10], using gas-solid chromatography, have measured on alumina, either plain or pre-treated with quinuclidine, the retention times and heats of adsorption for benzene, eight monoalkylbenzens, m-xylene, naphthalene and 2,6-lutidine. In general, both values decreased when impregnating alumina with quinuclidine. For plain alumina various pyridine and quinolines were very strongly retained.

Brookman and Sawyer[11] have shown that physical adsorption at the interface between a gas and a salt-modified alumina adsorbent, can be expressed as the summation of non-specific and specific interactions. Gas chromatographic studies[11] of selected model compounds have allowed isolation of the specific and the non-specific group contributions to adsorption in such a way that prediction of retention volumes is possible[12]. Hargrove and Sawyer[13] have studied the thermodynamics and separation efficiencies of gas-solid chromatography for Na_3PO_4 and Na_2SO_4 modified alumina adsorbents. The energy of interaction and the adsorption entropy are much greater for molecules having π-electron systems. The adsorption of a series of cyclic C_8, C_7, C_6 and C_5 alkenes, polyalkenes and alkanes on salt-modified aluminas and porous silica beads have been determined by Brookman and Sawyer[14] using gas-solid chromatography on salt-modified silica beads and aluminas. The results established that the degree of specific interaction with the π-electron systems is highly dependent on geometric and steric factors.

McCreery and Sawyer[15] have measured the differential enthalpies, entropies and free energies of adsorption for the functional groups of substituted hydrocarbons on salt-modified aluminas and on activated magnesium silicate (Florisil). The contribution to the adsorption of molar refractions directly proportional to polarizabilities[16] on columns of Graphon, salt-modified alumina and salt-modified silica beads are determined. Then, the authors were able to predict retention volumes for other compounds on these adsorbents.

Neuman and Hertl[5] have undertaken a parallel infra-red spectroscopic-gas-chromatographic study in which three representative compounds, n-butanol, pyridine and acetic anhydride, were used to partially deactivate an alumina supported material. The most active sites on an alumina surface, which lead to severe tailing and excessive retention times are the electron-accepting aluminum atoms. These sites can be effectively removed by treating the alumina with pyridine or an acid anhydride, which results in greatly improved resolution in hydrocarbon analyses.

2 - APPLICATIONS

Moore and Ward[17] have separated ortho and parahydrogen using activated alumina at 17°K with helium as carrier gas.

The chief difficulty for the separation of H_2, HD and D_2 is due to the fact that at low temperatures alumina columns also resolve para from ortho hydrogen and that the separation factor of $O\text{-}H_2$ from HD is close to unity[18]. Smith and Hunt[19, 20] have supressed the resolution of the spin isomers by coating alumina with chromia, a paramagnetic substance which prevents the resolution of para and ortho hydrogen by catalyzing their interconversion. These authors[19] have realized the first complete analysis of H_2, HD and D_2. Subsequently, Moore and Ward[21] accomplished the same separation by coating alumina with ferric hydroxide. These authors have also observed that strongly activated aluminas lead to ortho - para equilibration. Venugoplan and Kutschke[22] have confirmed this observation and have successfully analyzed H_2, HD and D_2 on pure alumina.

Van Hook and Emmett[23] have published a graphical method for estimating the amounts of H_2, HD and D_2 from a chromatogram obtained with alumina columns. Furuyama and Kwan[24] have reported a method for obtaining separate peaks corresponding to $p\text{-}H_2$, $o\text{-}H_2$, HD and D_2. Two columns were employed in series, the first one containing alumina and the second one alumina coated with ferric oxide.

Analyses of mixtures of H_2, D_2, T_2, HD and HT have been reported independently by King[25] and Carter and Smith[26]. The most efficient resolution is realized on columns of alumina coated with ferric hydroxide[25] at 77°K. Haubach and White[27] have determined the relative separation factors of the isotopic and nuclear species of hydrogens on γ-alumina free from paramagnetic impurities at 55°K.

Gersh[28] has found that addition of a small amount of hydrogen to the helium carrier gas obviates the problem of tailing and improves the separation factor. The method was applied to the separation of HT and DT.

Cercy and Botter[29] have compared the separation of isomers and isotopes of hydrogen on packed capillary column and conventional columns of alumina. The quantitative separation of H_2, HD, HT, D_2, DT and T_2 (Cf. Figure 17) was carried out by Genty and Schott[30] using a 3 meters long column packed with alumina coated with ferric oxide.

Van Cauwelaert and Hall[31] have determined separation factors for ortho and para hydrogen and hydrogen isotopes over pseudo-boehmite, alumina and fluorided alumina columns. Separation factors increased with retention times for pretreatment temperatures up to about 350°C where the ortho-para separation collapsed as the conversion reaction became faster than the separation.

Greene, Moberg and Wilson[32] have separated low boiling point hydrocarbons from methane to butenes on an alumina column at 150°C. Then, Greene and Pust[33] have made a comparison, of the separation of some low-boiling gases and their elution order on silica gel and alumina columns (Cf. Figure 5). In fact, this elution order depends in part on the degree of activation of the adsorbent.

Halasz and Heine[34] were the first to succeed in making packed capillary columns. Figure 18 shows the analysis of a mixture of 15 saturated and unsaturated low boiling point hydrocarbons in 6 minutes on a capillary column packed with alumina. Presaturation of the carrier gas with water at a given temperature is suitable for setting the polarity at a chosen level. Landault and Guiochon[35] using the same technique have analyzed in a very short time mixtures of low boiling point hydrocarbons.

Kirkland[36] has described the use of a new fine alumina, fibrillar colloidal boehmite, in packed columns for separating low boiling materials such as hydrocarbons, fluorocarbons and fixed gases. Separation of Freon fluorocarbons mixtures has been achieved on fibrillar boehmite deposited on firebrick. The same mixture has been analyzed with a capillary column coated with fibrillar boehmite. Kirkland[37, 38] has prepared glass beads coated with a thin layer of finely divided diatomaceous earth or silica. The particles are tightly anchored to the glass bead surface by means of a fibrillar boehmite. HETP of 0.8 mm have been obtained with silica-sol-modified 60 to 80 mesh glass beads coated with a silicone oil.

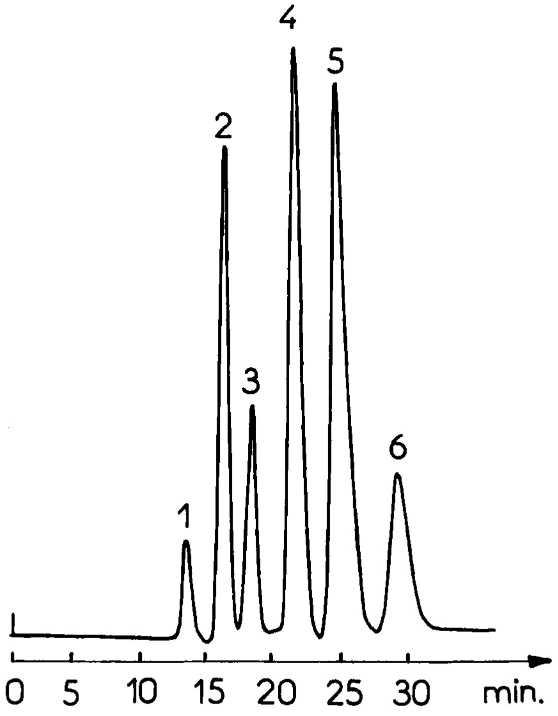

FIGURE 17

Separation of hydrogen isotopes on alumina.

(1) H_2, (2) HD, (3) HT, (4) D_2, (5) DT, (6) T_2.
Column: 3 meter long x 4 mm.i.d, packed with activated alumina.
temperature: 77° K, neon flow rate: 200 ml/min.

After Genty and Schott[30]: Figure 2.

Philippe and coworkers[39] have analyzed on alumina the liquid air condensible fraction of cigarette smoke and have shown the presence of some 37 compounds. Philippe and Honeycutt[40] have studied the effect of deactivation process on the elution order of several low boiling point hydrocarbons.

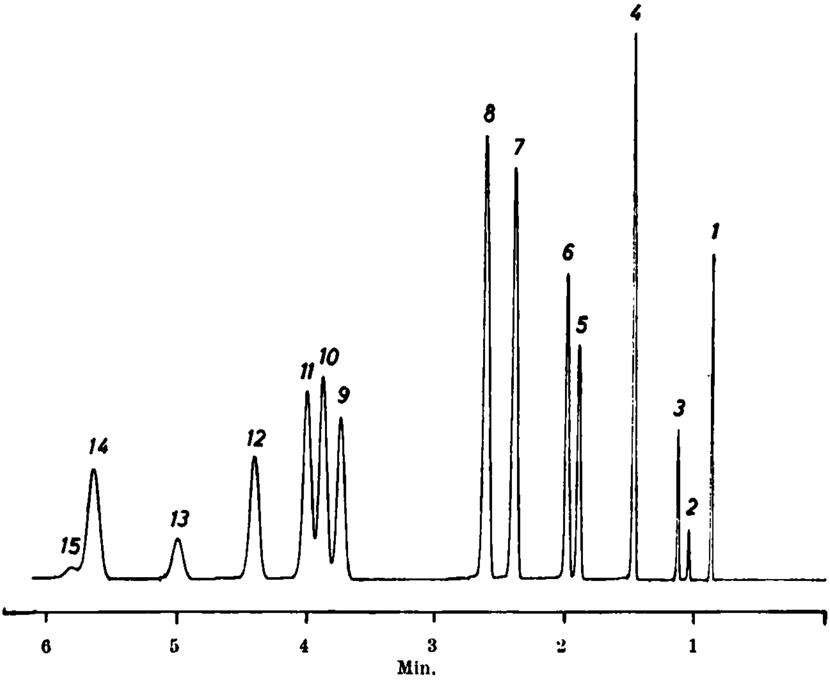

FIGURE 18

Separation of low molecular weight hydrocarbons on alumina packed capillary column.

(1) methane, (2) ethane, (3) ethylene, (4) propane,
(5) propylene, (6) acetylene, (7) isobutane, (8) n-butane,
(9) butene-1, (10) trans-butene-2, (11) isobutene,
(12) cis-butene-2, (13) isopentane, (14) n-pentane,
(15) butadiene.

Alumina packed capillary column 10 meter long.
temperature: 80° C, water presaturated hydrogen flow rate: 2.5 ml/min.

Reproduced from: I. Halasz and E. Heine, "Separation of low boiling hydrocarbons by Gas Chromatography using packed capillary columns", Nature, 194, 971 (1972): Figure 2.

By courtesy of Nature.

List, Hoffman and Evans[41, 42] have reported the separation of C_1 to C_8 hydrocarbons on activated alumina. Hoffman and Evans[43] have investigated the use of several carrier gases for analyses on activated alumina. Brookman and coworkers[44] have shown that the change of retention time observed in[43] was due only to the different viscosities of the carrier gases: the retention volume of n-butane is constant from gas to gas.

Scott and Rowell[45] have deactivated alumina by treating it with 40% sodium hydroxide, for the separation of high molecular weight hydrocarbons (from C_{15} to C_{36}). Scott[3] has obtained symmetrical elution peaks at low temperature for C_6 and C_7 hydrocarbons with aluminas modified with sodium hydroxide. Scott and Phillips[4] have shown that hydrocarbons are eluted with symmetrical peaks on alumina modified with a variety of inorganic salts.

Vernon[46] described the use of a sodium chloride-impregnated and sodium hydroxide modified alumina stationary phase for the separation of polycyclic aromatic hydrocarbons. The possibility of using gas-solid chromatography for the analysis of heavy oil and anthracene oil fractions from coal for distillation is indicated.

Pitak[47] has found that aluminum oxide modified with a fluorinated polymer is an efficient packing for adsorption column. This was demonstrated by the complete separation of F_2, MoF_6, UF_6 and SbF_6.

Myers and Giddings[48] have developed a new chromatographic system which combines the advantages of high pressures, small particles and small columns diameters. NaOH modified alumina packings, with particle size ranging from 2.7 to 26.2 microns have been used. Plate height as low as 0.082 mm (using 13 micron particles) have been obtained with an optimum inlet pressure of 157 atm. The efficiencies of the alumina columns are compared with those of columns packed with various materials (Baymal alumina, silica gel, molecular sieve 13 X and 5 A, activated carbon). Partly because of the development of high pressure liquid chromatography, the analytical applications of this work has been limited.

F - Inorganic Salts and Other Inorganic Adsorbents

Various inorganic salts are used in gas-solid chromatography, mainly for the analysis of saturated, unsaturated and aromatic hydrocarbons. Very seldom, these adsorbents are packed directly in the chromatographic column, due to their low specific surface area, which would result in very low efficiency. They are generally deposited on different supports like alumina, silica gels, chromosorb or other diatomaceous earths supports, since the early work of Scott[1] who has shown that symmetrical elution peaks are obtained with alumina coated with different sodium halides.

In the first part of this chapter are reported the more fundamental studies of the adsorption on inorganic salts by gas chromatography, leading however to some very interesting analytical analysis. The second part is devoted to the analytical applications of inorganic salt adsorbents in gas chromatography.

1 - ADSORPTION STUDIES

Scott[1] has investigated the gas-solid chromatographic behavior of sodium halides supported on alumina. The interaction with unsaturated hydrocarbons is higher with the larger halide ion. Scott and Phillips[2] have compared the selectivities for some aromatics of samples of alumina coated with NaOH, CdI_2 and NaI. Figure 19 shows the retardation of benzene relative to saturated hydrocarbons on changing from sodium chloride to sodium iodide deposited on alumina.

Guran and Rogers[3] have studied the influence of crystal phase transition (at 79 °C) of thallium (I) nitrate on the adsorption of some representative organic compounds. Large changes in capacity ratios were observed in the temperature regions of a solid-solid transition for hydrocarbons containing isolated ethylenic bonds. However, these changes are not associated with changes in geometry of the salt but rather with indirect effects such as desorption of water. At the same time, the authors have compared the gas chromatographic behavior of a pure thallium nitrate column, and of

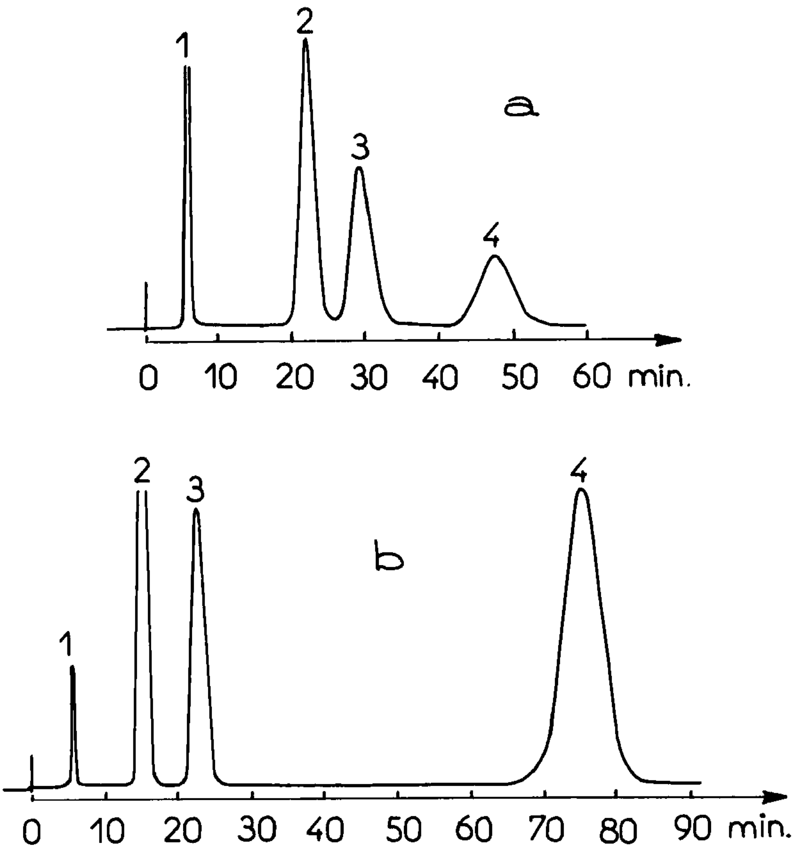

FIGURE 19

Elution of hydrocarbons on columns packed with halide modified aluminas.

(1) cyclohexane, (2) n-heptane, (3) iso-octane, (4) benzene.
a- NaCl modified alumina column, 45 cm x 3 mm i.d.
b- NaI modified alumina column, 80 cm x 3 mm i.d.
temperature: 100° C.

After Scott and Phillips[2]: Figure 3.

a column packed with 3% of the salt on Chromosorb W. Oxygenated compounds were retained disproportionately longer than hydrocarbons on supported thallium column and no appreciable change for hydrocarbons was observed at the transition temperature. Next, two thermochromic solids Ag_2HgI and Cu_2HgI_4 were investigated[4] to determine their adsorption behavior in the temperature regions of their solid-solid crystal phase transition. The elution orders and heats of adsorption on the high temperature forms of both solids were very similar, alkenes being eluted before alkanes and cyclanes before straight chain hydrocarbons; the elution order on Cu_2HgI_4 was the same on both sides of the transition temperature. On the contrary, on the high temperature form of Ag_2HgI_4, the heat of adsorption for unsaturated hydrocarbons was higher than on the low temperature form, so that at 45°C their elution order was reversed.

Guran and Rogers[5] have used six unsupported alkaline metal halides as adsorbents in gas-solid chromatography (NaCl, NaBr, NaI, KCl, KBr, KI). Changes in capacity ratios with conditioning of a given salt, as well as differences between salts were attributed largely to differences in the amount of adsorbed water.

Grob and coworkers[6] have studied the adsorption of non-polar, polar and aromatic compounds on the following salts: LiCl, NaCl, KCl, RbCl, CsCl and $LiNO_3$, KNO_3, $RbNO_3$ and $CsNO_3$. Alkaline nitrates give larger retention times than alkaline chlorides.

Grob and McGronigle[7] have studied the anhydrous chlorides of vanadium (II), manganese (II) and cobalt (II) as possible packings in gas-solid chromatography. Various saturated and unsaturated organic compounds were investigated as adsorbates to observe the influence of varying π electron densities. The heats of sorption were calculated and found to increase with increasing π-electron density of the adsorbate and with decreasing number of 3d electrons of the adsorbent. The data indicates that chemisorption plays a major role in the interaction between adsorbent and adsorbate.

The halide salts (chloride, bromide, iodide) of strontium and barium have been investigated next[8]. Adjusted retention volumes increase with the size of the anion. In both publications[7, 8] it has been noticed that retention volumes generally follow boiling points, that chain branching reduces retention volume and that the more polar compound has, the greater retention volume.

Using gas-solid chromatography Versino and Geiss[9] have compared the selectivities of different adsorbents, mainly CsCl and $CdSO_4$, either as pure crystals or crystallized or fused on Chromosorb P, Chromosorb G, graphitized carbon black, porous polymers and porous silica beads. These inorganic salts exhibit poor selectivity for light molecules with π-bonds. The elution order on $CdSO_4$ crystallized on Chromosorb P is different from that on CsCl crystallized on the same support.

Brookman and Sawyer[10] have determined the retention volumes on 10% NaCl, Na_2SO_4, Na_2MoO_4, Na_3PO_4 or NaOH coated on alumina. Minimum retention volumes are found for the sodium phosphate and the sodium hydroxide modified adsorbents: both materials are known to react with alumina and cause a large decrease in surface area. The adsorbents studied show specific interaction towards molecules with π-electrons. The sodium molybdate modified adsorbent is the most selective for alkanes and methyl benzenes. The sodium chloride modified alumina is as specific as the sodium molybdate adsorbent.

Hargrove and Sawyer[11] have compared Na_3PO_4 and Na_2SO_4 modified alumina adsorbents as packings in gas-solid chromatography. Specificity towards molecules with π-electrons is observed and Na_2SO_4 gives larger retention for all the sorbate studied. The specific interaction of several substituted aromatic compounds with 10% Na_2SO_4 on porous silica beads was investigated by gas chromatography[12].

A retention index system has been developed for alumina coated with 10% NaCl or 10% Na_2SO_4 and for porous silica beads impregnated with 10% Na_2SO_4[13]. The calculation is based on the evaluation of the enthalpies and entropies of adsorption for a series of hydrocarbons and substituted aromatic hydrocarbons. The differential enthalpies, entropies and free energies of adsorption for a series of cyclic C_8, C_7, C_6 and C_5 alkenes, polyalkenes and alkanes on adsorbents made by coating alumina with 10% NaCl, 10% NaBr or 10% Na_2SO_4 and porous silica beads with 10% Na_2SO_4 have been determined[14]. The Na_2SO_4 modified adsorbents interact with the olefin compounds to a greater degree than the NaCl and NaBr modified aluminas.

Isbell and Sawyer[15] have compared the retention volumes of various substituted hydrocarbons on porous silica beads modified with Na_2SO_4, NaCl, LiBr, Na_3PO_4, Na_2MoO_4, $NiSO_4$, $CoSO_4$, $Al_2(SO_4)_3$ and $Cr_2(SO_4)_3$. Surface treatment with hexamethyldisilazane eliminates the specific interactions with olefinic and aromatic π-electron systems. This provides a basis for evaluation of substituent contributions to aromatic π-electron density. Examples of optimized separation of difficult mixtures are presented (low molecular weight hydrocarbons, mixtures of substituted methyl and chloro - benzenes).

McCreery and Sawyer[16] have determined the optimum conditions for selective separation on alumina modified with 10% Na_2SO_4, Na_2MoO_4, NaCl or $Al_2(SO_4)_3$ and on Florisil (activated magnesium silica) modified with 10% NaCl, Na_2SO_4 or Na_2MoO_4. The properties of these adsorbents are compared with those of modified porous silica beads (Porasil).

Cadogan and Sawyer[17] have studied the adsorption properties of silica gels and graphitized carbon black (Graphon) coated with 10% of NaCl or $LaCl_3$. Coating active solids with salts of metals like lanthanum which contain partly filled d or f shells adds another parameter which may be varied to achieve more selective analytical separations. The heat of adsorption for benzene on $LaCl_3$ coated silica gel is increased 5 kcal over its value on NaCl coated silica gel. The enhancement of the benzene interaction by $LaCl_3$ relative to NaCl is much less on Graphon than on silica gel.

Belyakova, Kiselev and Soloyan[18] have studied the adsorption properties of two different samples of $BaSO_4$ with specific surface areas of 8.1 and 2.5 m^2/g. The contribution of the specific interaction with Ba^{2+} ions on the surface of the crystal. It is shown that $BaSO_4$ is a useful adsorbent for the separation of cyclic unsaturated and aromatic hydrocarbons (meta, para and ortho xylenes are completely resolved).

Kiselev and coworkers[19] have calculated the adsorption potential of argon on the surface of a potassium chloride crystal. The configurational integrals were determined[20] using the molecular theory of adsorption and the adsorption energy and entropy were derived. The thermodynamic adsorption functions calculated for argon at low surface coverage and their dependance on the surface coverage agree satisfactorily with the experimental results.

Curthoys and Elkington[21] have calculated the potential adsorption energy of hydrocarbons on boron nitride. The heats of adsorption derived from gas chromatographic measurements agree fairly well with the interaction energy of hydrocarbons on boron nitride. The lamellar structure of BN crystals is analogous to that of graphite, except that there are alternate B and N atoms instead of C atoms. When the crystal lattice is practically free of defects, the basal plane BN exhibits the properties of a non-specific adsorbent.

Cvetanovic and coworkers[22] using gas chromatography have studied the interactions of olefins and saturated hydrocarbons with molecular iodine deposited either on firebrick, on silanized firebrick or on silanized celite. Olefins are retained considerably longer on the iodine-coated columns than the corresponding paraffins. The interaction of deuterated olefins with iodine is higher than that of the normal compounds.

Levy and Steinberg[23] using a gas chromatographic technique have determined the heats of adsorption of carbon dioxide on zinc oxide and zinc oxide doped with lithium and gallium. Carbon dioxide, being an electron acceptor, is more strongly adsorbed on the n-type, galliated zinc oxide than on the p-type, lithiated zinc oxide. The heat of chemisorption of carbon dioxide on oxygen-deficient zinc oxide[24] has also been measured.

Wydeven and Leban[25] have measured the heats of adsorption of carbon dioxide on silver (I) oxide and copper (II) oxide. Carbon dioxide was found to be more weakly adsorbed by CuO than by Ag_2O.

Moro-Oka[26] has determined the heats of adsorption and the relative adsorption constants for C_4, C_5 and C_6 hydrocarbons on cobalt oxide by gas-solid chromatography. The heats of adsorption are about 1.5 to 4.0 kcal/mole larger for olefins than for the corresponding paraffins. These energy differences result from the interaction of the double bond with the surface. The head of adsorption of isomeric olefins increases with the number of alkyl substituents on the double bonded carbon atoms. Thus the higher the electron density of the double bond, the stronger the adsorption. The heat of adsorption of isomeric olefins having the same number of alkyl substituents decrease with increasing steric hindrance, especially in C_6 olefins. The heat of adsorption and the retention volumes of cis olefins are slightly larger than those of the corresponding trans isomers.

The heats of adsorption of some saturated and unsaturated hydrocarbons have been measured on γ-Al_2O_3 and MgO[27] and on ZrO_2[28] by Sanesi and coworker. It was concluded that with saturated hydrocarbons, dispersion forces only are responsible for the adsorption interaction, whereas the contribution of specific interactions, mainly of electrostatic nature, are important in the adsorption of unsaturated or aromatic compounds.

2 - APPLICATIONS

Duffield and Rogers[29] have shown that silver nitrate and silver sulfate coated on Chromosorb are useful adsorbents in gas chromatography for the analysis of very small samples of unsaturated hydrocarbons. These columns however should be operated at high temperature (190°C).

Halasz and Horvath[30] have prepared open tube capillary columns whose walls are covered with a thin layer of ferric oxide impregnated with a small amount of Carbowax 1500. These columns are superior to conventional capillary columns as they show higher resolution in a shorter analysis time but the stationary phase gives a non-specific retention pattern much similar to the one of squalane. Columns packed with glass beads coated with a thin layer of highly dispersed ferric oxide or zirconium oxide and impregnated with triethylene glycol have been used[31] for the separation of aliphatic and aromatic hydrocarbons and of aliphatic derivatives with oxygen or halogens. The higher permeability and lower capacity ratio of these columns packed with "porous layer glass beads" result in shorter analysis time, when compared to conventional packed columns. Halasz and Holdinghausen[32] have shown the applicability of porous layer glass beads coated with a layer of ferric oxide impregnated with 1% Carbowax and 0.1% potassium hydroxide in programmed pressure chromatography.

As a continuation of the work of Hanneman, Spencer and Johnson[33] who used an inorganic salt eutectic on firebrick for the separation of polyphenyls, Favre and Kallenbach[34] have tried 25% solid phase inorganic salts on Chromosorb P to improve resolution and decrease tailing. Resolution of a mixture of the terphenyl isomers has been measured for 44 solid phase inorganic salts including antimonates, borates, carbonates, hydroxides, metal halides, nitrates, oxides and phosphates. The best results were obtained with potassium carbonate, borate, antimonate and phosphate. Column temperature was programmed over the range 250° to 400°C and helium was used as carrier gas.

Solomon[35] has analyzed polyphenyls in the temperature range 200° to 500°C using gas-solid chromatography. Columns packed with Chromosorb coated with LiCl, CsCl and $CaCl_2$ were suitable for this analysis. Good qualitative separations of isomeric quaterphenyls and hexaphenyls were obtained.

Sauerland[36] has been able to separate phenanthrene, anthracene and carbazole on 30% $CaCl_2$ deposited on Chromosorb W (the temperature was programmed from 250°C to 300°C).

Versino and coworkers[37] have compared the separation of aromatic hydrocarbons, and especially of polyphenyls on modified Bentone columns and on solid cesium chloride, a phase which guarantees an unlimited life.

Chortyk and coworkers[38] have used 20% lithium chloride on Chromosorb P to separate a mixture of aromatic hydrocarbons having from two to seven rings and boiling points ranging from 182°C (indene) to about 600°C (coronene). The temperature was programmed from 80°C to 320°C, at 2°C per minute.

Sauerland and Zander[39] using gas-solid chromatography on inorganic salts like LiCl or $CaCl_2$ deposited on Chromosorb P, have been able to identify acenaphthylene as a constituent of coal tar. Figure 20 shows the analysis of naphthalene and methylsubstituted naphthalenes on 40% $CaCl_2$ deposited on Chromosorb P.

Onuska and Janak[40] have studied the separation of biphenyl, terphenyls and several polyphenyls on cesium chloride deposited on Chromosorb. Zane[41] has shown the application of potassium antimonate and potassium carbonate plus potassium hydroxide as solid substrates deposited on Chromosorb P in G.C. separations of polynuclear aromatic hydrocarbons. The separation of anthracene and phenanthrene has been achieved under isothermal conditions.

Geiss and Versino[42] have studied the chromatographic behavior of LiCl, CsCl, NaCl, KCl, $CdSO_4$ and of the eutectic mixture $LiNO_3$, $NaNO_3$, KNO_3. The best separations are achieved when the salts are deposited on common gas chromatographic supports. The retention characteristics measured for alkaline halides are much related to

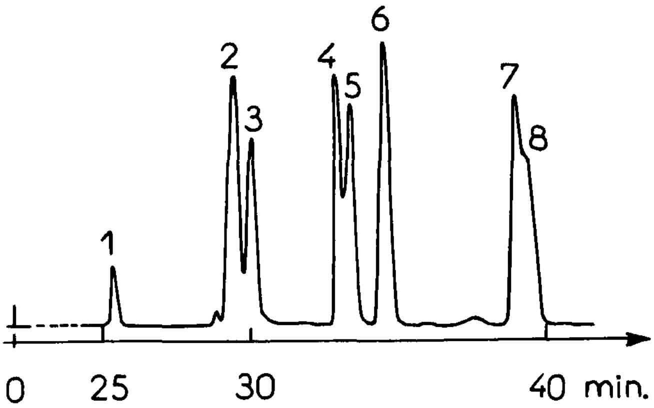

FIGURE 20

Separation of methyl substituted naphthalenes on calcium chloride.

(1) naphthalene, (2) 1-methylnaphthalene, (3) 2-methylnaphthalene, (4) 1, 4 dimethylnaphthalene, (5) 1, 5 dimethylnaphthalene, (6) 2,3 dimethylnaphthalene, (7) 2,3,5 trimethylnaphthalene, (8) 2,3,6 trimethylnaphthalene. Column 4 meter long packed with 40% $CaCl_2$ on Chromosorb P. Temperature programmed from 90° C, 4.8° C /min.

After Sauerland and Zander[39]: Figure 3.

the way they are deposited on the support (simply recrystallized from solution or melted). The elution temperature of biphenyl is 140°C lower on solid CsCl previously melted on the support. Gump[43] has employed gas-solid chromatography with inorganic salts to resolve benzpyrene fractions. The performance of these salt packings (LiCl, NaCl, KCl, RbCl, CsCl, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$) is affected by the solid support. Pink diatomaceous earth supports produced longer retention times but better resolution of polycyclic hydrocarbons than does either the Chromosorb W or G support.

Hawton and Campbell[44] have shown that there is a linear relationship between the degree of hydrogenation and the retention temperature on a column packed with Chromosorb coated with 10%

potassium tetraborate. In each series from benzene to p-terphenyl a 0 per cent hydrogenation is affected to the aromatic compound and 100 per cent hydrogenation to the saturated hydrocarbon (cyclohexane, bicyclohexyl, tercyclohexyl). This helps in the identification of the components of complex mixtures.

Hirshman and coworkers[45] have analyzed on a column packed with metal fluoride (10% CsF-90% CaF_2) a mixture of oxyfluorides ($F_2C = O$, CF_3CFO and $(CF_3)_2C = O$).

Tadmor[46] has described an isotopic exchange procedure in gas-solid chromatography. $GeCl_4$, $SnCl_4$, $AsCl_3$ and $FeCl_3$ were labelled and separated on Cl^{36} labelled Sil-O-Cell insulating firebrick. The uncoated solid phase was labelled using hydrochloric acid labelled Cl^{36} solution. Even after coating and radioisotope labelled solid adsorbent with a thin layer of liquid, isotopic exchange still occurs between the Cl^{36} sorbed on the solid phase and the gaseous inorganic sample, indicating that the solid support is not always as inert as one could expect. Labelling of $FeCl_3$ with radioactive Fe^{59} was investigated by gas-solid chromatography using a similar technique. No activity was detected in the carrier gas when $Fe^{59}S$ was used as the adsorbent. When irradiated Sil-o-Cell firebrick containing 0.78% Fe was used as the solid packing, $Fe^{59}Cl_3$ of low specific activity was eluted as a well defined peak.

G - Organic Adsorbents

The organic adsorbents used in gas-solid chromatography are of four different types and will be reviewed separately in each of the following sections: crystals of organic compounds of high melting point and low vapour pressure; liquid stationary phases below their melting point; organic clay derivaties; porous polymers.

Between the two recognized extremes distinguished in gas chromatography, according to whether the stationary phase is a liquid or a solid (crystalline or amorphous), there exist also liquid crystals, porous layer adsorbents[1], dense monomolecular layers[2], organic groups chemically graphted on conventional adsorbents[3].

The use of liquid crystals in gas chromatography has already been reviewed by Kelker and Von Schivizhoffen[4] and is not discussed here. The other products have been covered in the section corresponding to the modified adsorbent.

1. ORGANIC CRYSTAL COMPOUNDS

The first reported use of a solid organic stationary phase in gas chromatography was due to Scott[5] who obtained symmetrical elution peaks for cyclohexane, benzene, n-heptane and iso-octane, at 20°C on 10% benzophenone deposited on firebrick. This work has shown that it is possible to work in the linear range of the isotherm, at low temperature, with molecules of higher molecular weight than the permanent gases and the low boiling point hydrocarbons.

Vidal-Madjar and Guiochon[6] have compared the gas chromatographic properties of benzophenone deposited on graphitized carbon black (Sterling M.T. 9 m^2/g) and on Chromosorb. The best results were obtained with the first packing. The surface of this adsorbent has a high density of π-electrons, so it belongs to type III of Kiselev's classification[7]. This adsorbent has a non-specific retention and columns packed with it have a good efficiency for molecules with π bonds and unshared electron pairs (benzene, ether, acetone). The surface of the adsorbent obtained by coating benzophenone on Chromosorb is heterogeneous as shown by the large tailing of either peak due to the non-linearity of the adsorption isotherm. Vidal-Madjar and Guiochon[8] have determined experimentally the average desorption time of cyclohexane and benzene on the non-uniform support (benzophenone on firebrick) from the value of the kinetic mass transfer term of the plate height equation. This time is less than 10^{-4} seconds for cyclohexane, while for benzene it depends on the temperature and varies between 10^{-4} and 10^{-3} seconds.

Anthraquinone when deposited on the homogeneous surface of graphitized carbon black (5% anthraquinone on Sterling MT)[9] has the same adsorption properties as benzophenone on graphitized carbon black. Non specific retention is observed for ketones, esters, alkyl chlorides and aromatic hydrocarbons. The thermal stability is higher (160°C) than with benzophenone (melting point : 49°C).

Altenau and Rogers[10, 11] have used some copper amine complexes, directly as column packings. A column of the pyridine derivative, $Cu(PY)_2(NO_3)_2$ gave very good separations of numerous aliphatic and aromatic hydrocarbons, alcohols, esters, ethers and ketones with minimal tailing of peaks. The major disadvantage of these adsorbents is their low thermal stability, as they begin to decompose around 100°C. Altenau and Merritt[12] have coated Chromosorb W with copper amine complexes, but the elution zone of polar compounds tails badly on these adsorbents because of the presence of high energy adsorption sites on the surface of Chromosorbs.

Cvetanovic and coworkers[13] have studied the chromatographic behavior of 1,3,5-trinitrobenzene (TNB) on Chromosorb in order to study the complex formation between TNB and olefins. Retention times generally increase with increasing substitution at the double bond, indicating that for the formation of TNB complexes, the increase in basicity due to double-bond substitution outweighs the opposite effect of steric hindrance which frequently predominates.

Heveran and Rogers[14] have investigated by gas chromatography the adsorption on phthalic anhydride, the isomeric phthalic acids, potassium acid ortho-phthalate and dipotassium ortho-phthalate and dipotassium ortho-phthalate. Burke and Rogers[15] have studied the chromatographic behavior of isomeric dimethylbenzenes and dichlorobenzenes on the solid isomeric phthalic acids. Each acid, except paraphthalic acid was studied by itself and as a coating on Chromosorb G. The dipole-dipole interaction of the adsorbate with the surface of the unsupported phthalic acid is the predominant factor affecting the chromatographic behavior.

Vidal-Madjar and Guiochon[16-19] have prepared a full range of adsorbents suitable for gas chromatography by using metallic phthalocyanines as organic adsorbents, coated on graphitized carbon black. These compounds are thermally very stable and columns can work as high as 300°C. Pecsok and Vary[20] have also used some metallic phthalocyanines, as a suspension in a silicone oil coated on Chromosorb T; they have shown that each metallic phthalocyanine has its own specificity towards some of the main organic functions. These results are in agreement with those obtained by gas-solid chromatography on metallic phthalocyanines coated on graphitized carbon black.

Vidal-Madjar and Guiochon[16] have shown that the efficiency of the columns packed with these adsorbents is large and that the elution zones are symmetrical, even for example with polar compounds like phenols on copper phthalocyanine deposited on graphitized carbon black. New specificities have been found[17] as examplified by the separation of phenanthrene and anthracene at 260°C, in 9 minutes, on a one meter long column, packed with the same adsorbent. The adsorption properties of the surfaces obtained by coating 5% of various phthalocyanines (metal-free, copper, nickel, cobalt and zinc) on graphitized carbon black, Sterling M.T., have been studied[18]. The use of graphitized carbon black allows to obtain highly efficient columns because of its large surface area (9 m^2/g) and of its non selective adsorption properties. It also allows the adsorptive behavior of each phthalocyanine to be determined since the effect of the support is kept very small.

The adsorptive properties of all the phthalocyanines studied are different and this makes possible to understand better the conditions leading to separations in gas solid chromatography[19]. The phthalocyanines which have a weak specificity towards polar compounds like dimethyl ether, acetone, methyl propionate, are suitable adsorbents for the separation of alcohols, phenols, aromatic bases (pyridine, picolines, aniline, ...).

As is observed with pure graphitized carbon black[21], the retention depends to large extent on the geometrical structure of the molecule[19]. Figure 21 shows the separation of a terpene mixture on metal free phthalocyanine deposited on graphitized carbon black (Sterling M.T.). The specificity of the adsorbent is relatively low, because Sterling M.T. is coated with only 1% of phthalocyanine. Nevertheless, the relative retentions of polar terpene compounds are larger on this adsorbent than on pure graphitized carbon black[21] (see for example, the migration of camphor and fenchone peaks). The reduction in the adsorption enthalpy generally observed when organic solids are coated on graphitized carbon black[7, 9] allows the separation to be achieved at a much lower temperature: carvone is eluted here in 25 minutes at 157°C with a four meter long column, instead of 40 minutes at 180°C with a 1.2 meter long column packed with pure graphitized carbon black[21].

Cobalt phthalocyanine is very interesting in practice for it is a specific adsorbent towards the aromatic rings and a non-specific adsorbent towards OH or NH_2 groups. The separation of phenols and aromatic amines on this adsorbent depends on the position of the methyl substituent on the aromatic ring; the elution peaks are symmetrical[19]. Franken, Vidal-Madjar and Guiochon[22] have separated aromatic amines, pyridine, picolines and lutidines in a very short time (150 seconds) with a 10 m long porous open tube capillary column coated with a porous layer of cobalt phthalocyanine on graphitized carbon black (Cf. Figure 22).

Kouznetsov, Vidal-Madjar and Guiochon[23] have calculated the adsorption potential on metal-free phthalocyanine for alkanes and aromatic hydrocarbons. The values for alkanes agree fairly well with the experimental adsorption enthalpies measured by gas chromatography. The calculated adsorption potential is lower for benzene, toluene and ethylbenzene and the difference is qualitatively explained by a contribution of an inductive effect of the dipole and quadrupole moments. The authors have shown in this work that the adsorption enthalpies measured on the adsorbent made by coating 5% phthalocyanine on graphitized carbon black do correspond to the adsorption on the phthalocyanine surface, with only negligible contribution for the carbon black support.

Pflaum and Cook[24] have measured retention volumes of various organic compounds on nickel complexes deposited on gas Chromosorb P.

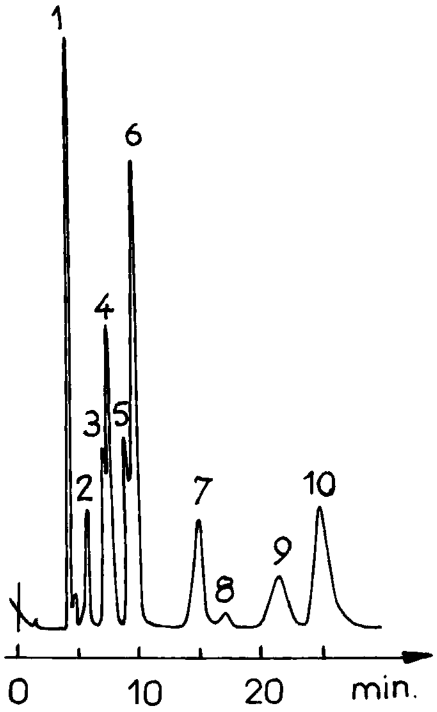

FIGURE 21

Analysis of a terpene mixture on metal-free phthalocyanine.

(1) α pinene and camphene, (2) sabinene, (3) Δ^3 carene, (4) fenchone, (5) camphor, (6) p-cymene and limonene, (7) n-decane, (8) isomenthone, (9) menthone, (10) carvone. Column 4 m x 2 mm i.d., packed with 1% metal-free phthalocyanine on Sterling M.T. (8.7 m^2/g); Temperature: 157° C; carrier gas: hydrogen; inlet pressure: 4 atm.

After Vidal-Madjar and Guiochon[19]: Figure 5a

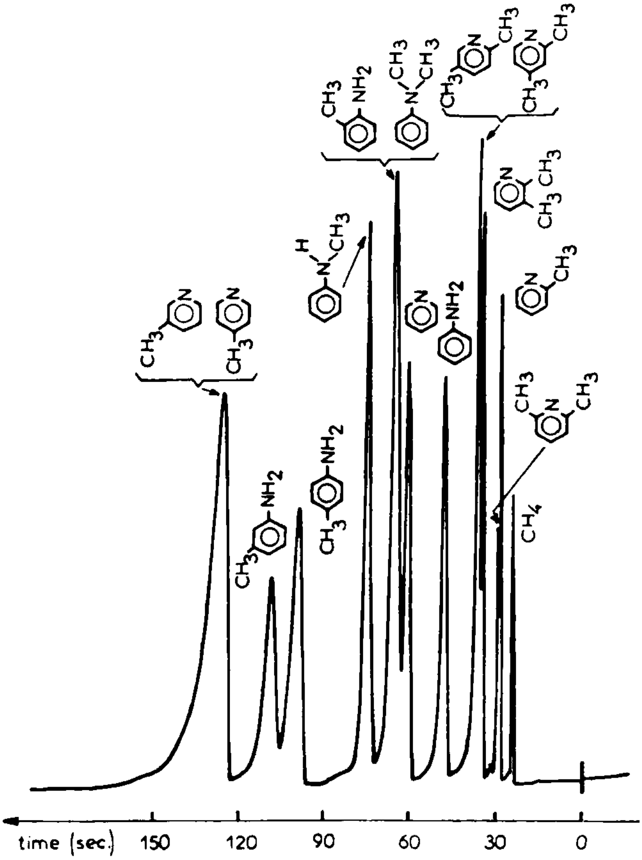

FIGURE 22

Analysis of nitrogen compounds on a cobalt phthalocyanine porous layer open tube capillary column.

methan, 2-picoline, 2, 6-lutidine, 2,3-lutidine, 2,4-lutidine + 2,5-lutidine, aniline, pyridine, ortho-toluidine + N,N-dimethylaniline, N-methylaniline, paratoluidine, meta-toluidine, 3-picoline + 4-picoline. capillary column 10 m x 0.5 mmi.d., glass. porous layer of 5% cobalt phthalocyanine on Sterling FT (13 m^2/g). Temperature: 178°C, carrier gas hydrogen, pressure drop: 0.35 atm.

Reproduced from: J.J. Franken, C. Vidal-Madjar and G. Guiochon, "Gas-Solid Chromatographic Analysis of Aromatic Amines, Pyridine, Picolines and Lutidines on cobalt phthalocyanine with porous layer open-tube columns", Anal. Chem. 43, 2034 (1971): Figure 2.

The complexes studied were bis (dimethylglyoximato) nickel II, bis (1,2 cyclohexane dionedioximato) nickel II, bis (salicyladimino) nickel II and nickel perchlorate. These adsorbents are stable up to 220°C in a nitrogen atmosphere. Cook and Givand[25] have studied by gas solid chromatography the interaction between olefins and complexes of $AgNO_3$ with various heterocyclic amines. The complex was coated on Chromosorb W acid washed and dimethylchlorosilane treated.

2. CONVENTIONAL LIQUID STATIONARY PHASES UNDER THEIR MELTING POINT

Scott has observed[5], when employing benzophenone as the stationary phase, a marked decrease in the retention time of alkanes and benzene when the column temperature was reduced below the melting point of benzophenone (49°C). The column efficiency, however, remained very good.

Merritt and his coworkers[26] have obtained the separation of light hydrocarbons at very low temperatures, on liquid stationary phases which should have been either glasses or crystalline solids. Temperature was programmed from - 170°C to 0°C to obtain a complete resolution of a mixture of the light hydrocarbons.

Dal Nogare[27] and Fiddler and Doerr[28] have studied in detail the behavior of Carbowax 20 M deposited on Chromosorb, above and below its melting point. Above 60°C, it is gas-liquid chromatography and below 50°C it is gas-solid chromatography. In the 50°C to 60°C interval the retention times increase with increasing temperature.

Altenau and coworkers[29] have shown that gas solid adsorption processes were responsible for the separation of solutes at temperatures below the freezing point of the stationary phase. The phases studied were Carbowax 20 M, squalane and SE 30 coated on Chromosorb W.

In this study, the behavior of several solutes on the three stationary phases as well as the mechanism of separation were investigated over a temperature range from + 100°C to - 180°C.

Claeys and Freund[30] have investigated the effect of decreasing temperature below the freezing point of the stationary phase with several polymeric and one pure stationary phase. Carbowax 1540 and 20 M, polyethylene glycol succinate and cetyl alcohol show sharp discontinuities of the plot Log V_R vs $1/T$, where V_R is the retention volume and T, the absolute temperature. Column efficiencies decrease abruptly at the temperature for which large discontinuities of the plot are observed and generally improve again at temperatures below the freezing point of the stationary phase.

Corbin and Rogers[31] have described the gas chromatographic behavior of three optically active stationary phases at temperature below the melting point. Open tubular glass columns were used in this work. The high temperature form of the solid ureide of l-valine isopropyl ester gave excellent separations of enantiomers while the low temperature form gave no detectable separation. The separation of enantiomers is not possible on the solid form of N-TFA-l-phenylalanine cyclohexyl ester.

3. ORGANIC CLAY DERIVATIVES

An organo clay, namely the Bentone 34 (dimethyldioctadecylammonium montmorillonite) is widely used as stationary phase deposited on usual gas chromatographic supports because of its high selectivity for aromatic hydrocarbons. The use of organo-montmorillonite in gas-solid chromatography was first described by White[32] in 1957. The cations in the naturally occuring clay had been replaced by alkyl quaternary ammonium ions and the resulting compound exhibits a selective retention of aromatics relative to paraffins and naphtenes. In 1958, White and Cowan[33] have investigated the performances of dimethyldioctadecyl bentonite as stationary phase for the separation of mixtures of paraffins and obtained symmetrical elution peaks. The separation of aromatic hydrocarbons on this adsorbent[34] however is not so good (peak tailing and change of retention volume with amount of sample injected are observed).

Hughes, White and Roberts[35] have shown that a complete separation of meta and para xylenes is possible on Bentone 34 in the absence of ortho xylene. It is shown also that the isomers of the cresols and toluidines can be separated, but the asymmetry of the elution peaks observed with aromatic hydrocarbons is even more marked with the phenols and bases. The disadvantage of asymmetrical elution curves was overcome to a large extent by Cowan and Hartwell[36] and again by Van Rysselberge and Van der Stricht[37] when separating the dichlorobenzenes and the xylenes, respectively. Both groups of workers used very small sample sizes (0.025 µl) together with ionization detectors.

A more satisfactory separation of the xylenes has been achieved by Mortimer and Gent[38] using Bentone 34 modified with silicone oil. A chromatogram illustrating the separation of the C_8 aromatics and other hydrocarbons is shown in Figure 23. The separation of the xylenes was completed in less than 30 minutes and symmetrical peaks were obtained. The elution order of these compounds is para, meta, ortho, in contrast to the order: para, ortho, meta observed on an unmodified Bentone 34 column. Blake[39] has separated the diethyl benzene isomers on Bentone 34 modified with silicone oil. Spencer[40] has used the Bentone 34 impregnated with 5% diisodecylphthalate and coated on Chromosorb, to reduce the time of analysis of the xylene isomers from 60 to 12 minutes. Bentone 34 modified with Apiezon L have been reported by Van der Stricht and Van Rysselberge[41] to separate difficult mixtures: naphthalene, methylnaphthalenes, ethylnaphthalenes and dimethylnaphthalenes; the dimethoxybenzene isomers; the chloroacetophenone isomers; the cynene isomers; the xylene isomers; some amino aromatic isomers.

Mortimer and Gent[42] have investigated the performances of organo clay columns modified with different liquid stationary phases (silicone oil, dinonylphthalate, tolylphosphate). The effect of varying the operating temperature, the quantity and the

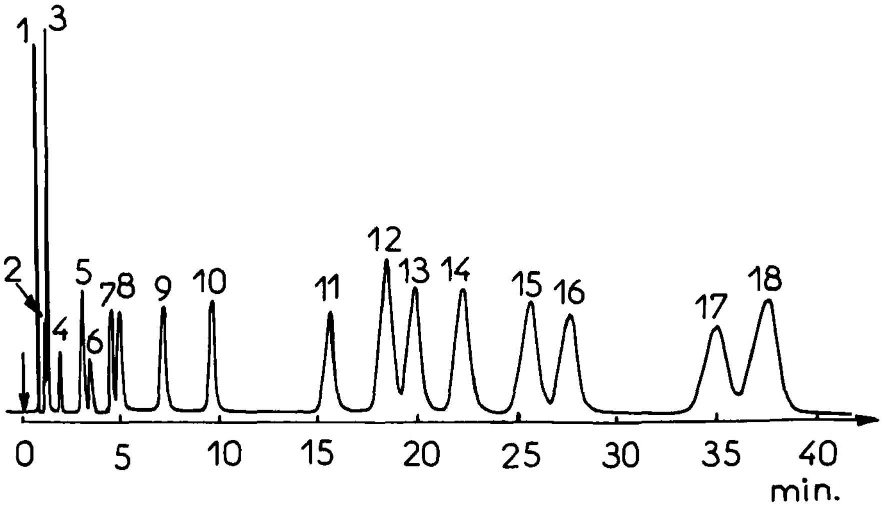

FIGURE 23

Separation of hydrocarbons including xylenes on modified Bentone 34.

(1) air, (2) isopentane, (3) n-pentane, (4) n-hexane, (5) cyclohexane, (6) n-heptane, (7) methylcyclohexane, (8) benzene, (9) n-octane, (10) toluene, (11) n-nonane, (12) ethylbenzene, (13) p-xylene, (14) m-xylene, (15) o-xylene, (16) isopropylbenzene, (17) styrene, (18) n-propylbenzene.
Column 12 feet x 8/16 inch.i.d., packed with 1: 1: 10 silicone oil/Bentone 34/Celite;
Temperature: 70° C; helium flow rate: 120 ml/min.

After Mortimer and Gent[38]: Figure 1.

nature of the modifying solvent is discussed and the conditions allowing the separation of C_6 to C_9 alkylbenzenes, dichlorobenzenes, cresols and xylenols are described. The effect of the amount of Apiezon L[43] and of dinonylphthalate[44] used as modifying agent of Bentone 34 has been investigated for the separation of aromatic hydrocarbons. Bentone 34 modified with didecyl phthalate has been used for the quantitative analysis of cynene isomers[45]. Vergnaud[46] has found that in addition to the isomers of xylenes, dichlorobenzenes or diethylbenzenes, terphyenyl isomers and a mixture of naphthalene, decahydronaphthalene cis and trans, and tetrahydronaphthalene could be analyzed on Bentone 34 modified with silicone grease. Wiley and coworkers[47] have separated p-divinylbenzene from impurities and purified the commercial compound (99 + %) in gram quantities by gas chromatography using a column packed with Bentone 34/Ucon, coated on Chromosorb W. Klemm and coworkers[48] have compared retention ratios on Bentone-Silicone DC 170 on Chromosorb and Silicone DC 710 on Chromosorb. The 49 substances studied are alkyl substituted and halo substituted compounds in the thiophene, benzo(b)thiophene, pyridine, quinoline, isoquinoline and thienopyridine ring system.

Fuchs[49] has shown that the dimethyldioctadecylammonium derivatives of Hungarian bentonites containing 40-90% of montmorillonite have superior selectivity and efficiency compared with those of the well known stationary phase Bentone 34 in the gas chromatography of aromatic hydrocarbons.

Kwa and Boelhouwer[50] have satisfactorily related, using statistical mechanics, the contribution of rotational energy to the differences in the logarithm of the relative retention on a liquid stationary phase (Apiezon L) and on an adsorbent (Bentone 34) for each methyl substituted aromatic isomers (xylenes, trimethylbenzenes, tetramethylbenzenes). They have derived the relative retentions on the pure Bentone 34 adsorbent from experimental data obtained on different mixed columns of Apiezon L and Bentone 34.

Taramasso and Fuchs[51] have discussed the physical properties and the preparation of organic derivatives of clay minerals as well as their application in gas chromatography. These minerals, called 2 : 1 mica-type phyllosilicates, have a lamellar structure built up from two planar layers of silica tetrahedrons and alumina octahedrons. A single unit consists of two tetrahedral sheets connected by an octahedral one. The well known Bentone 34 is the dimethyldioctadecylammonium complex of montmorillonite, a clay mineral. In montmorillonite charge deficits are located in the octahedral sheet, far from the basal surface. With clay minerals belonging to the beidellite-vermiculite family, charge deficits are located in the tetrahedral sheet, nearer the basal surface than in the case of montmorillonites. To render the structure electrically neutral, the negative charges within the lattice are compensated by inorganic cations held on the basal surface. Using a suitable procedure, these inorganic cations can be replaced by long-chain alkylammonium ions.

The beidellite-vermiculite type clay minerals are more effective adsorbents for gas chromatography. This may be due to the fact that these minerals have a greater charge density near the basal surface, which, in turn, may ensure a more regular arrangement of the alkyl chains and more homogeneous external surface.

The organic derivatives of clay mineral are deposited on the surface of a convenient support, 10 to 15% by weight. These complexes can be used between the temperature limits of 50 and 150°C and do not require the addition of modifying liquid.

Taramasso and Veniale[52] have investigated the gas chromatographic performance of dimethyldioctadecyl ammonium derivatives of "beidellite-type" clay minerals. Results are noticeably better with nontronite complexes deposited on Chromosorb P than with the commonly used Bentone 34. The xylene isomers are completely resolved and the elution order is para, ortho and meta-xylene. This adsorbent does not require the addition of a coating liquid phase. Due to the more homogeneous structure of the "beidellite type" complexes (nontronite and vermiculite), these adsorbents are more effective for the separation of some olefin, diolefin or alicyclic isomers[53]. Between 30 and 50°C there is a structural transition for the interlamellar complexes and below this point both the efficiency and the separating power drop down.

Taramasso and Timidei[54] have shown that the selectivity of the adsorbents towards meta and para isomers is directly related to the area available for a single cation. Best results are obtained when this area reaches about 37 Å^2 as in the case of vermiculite materials.

Taramasso[55] has given examples of the epitaxial modification of mica-type layered silicas (for example montmorillonite) with pyridinium ions, N,n-alkylpyridinium ion and n-alkylammonium ion. Bulky cations as trimethylhexadecylammonium or dimethyldioctadecylammonium are convenient, owing to both their basic character and their good surface covering power.

3 - POROUS POLYMERS

In recent years, macroporous copolymers have been used frequently as packings in gas chromatographic columns, especially copolymer of styrene and ethylvinylbenzene with divinylbenzene as crosslinker. Hollis[56] using for the first time porous copolymers of the ethylvinylbenzene-divinylbenzene type in gas chromatography has demonstrated that these beds are superior to any known conventional column packing for the separation and trace analysis of glycols, polyols, amines, acids, mixtures of organic and inorganic compounds. As the mechanism of retention is not quite elucidated, we shall mention first their analytical applications. Their adsorption properties have been studied about two years after Hollis[56] has demonstrated their ability for the analysis of highly polar compounds.

a) - Applications of porous polystyrene beads

The porous polymers of the polystyrene divinylbenzene crosslinked type are manufactured under various trade names: Porapak P and Q (Waters Associates), Chromosorb 101 and 102 (Johns-Manville), Par 1 and Par 2 (Hewlett-Packard), Synachrom, Polysorb 1 and 6 ...

Further development was pursued and other types of porous polymers are available which again are copolymers based on styrene and divinylbenzene with a certain quantity of a polar monomer containing different functional groups: Porapak R, S, T, N; Chromosorb 103-105; Polysorbate-2 (methylacrylate and para-divinylbenzene copolymer).

Hollis was the first to describe analyses on porous polymer bead columns. The synthesis of the porous polymer was designed to give material in bead form with large surface area (100 to 700 m^2/g) and strong physical structure. Notably sharp, symmetrical peaks were found for water, alcohol and glycols and it is remarkable that methanol is eluted at the same time as propane. Some examples of the application of this support in gas chromatography are also given ranging from the analysis of the nitrogen oxides to the determination of diethylene glycol in dipropylene glycol[56].

The components of air (N_2, O_2 and A) can be separated in 5 minutes at -78°K. The elution order N_2, O_2, A is the reverse of that achieved in gas-solid chromatography on molecular sieve and silica gel. N_2O and CO_2 which are difficult to analyze on conventional gas-solid chromatographic adsorbents are easily resolved at 27°C in 10 minutes. The analysis of trace quantities of water has been greatly facilitated because water is eluted very rapidly, with good peak shape from these columns. Trace amounts of water have been determined in hydrocarbons, alcohols, oxides, glycols, chlorinated hydrocarbons, ammonia and hydrogen chloride on porous polymer beads[57]. Hollis and Hayes[58] have shown that reactive gases such as the oxides of nitrogen (NO and NO_2) are eluted with symmetrical peaks.

Previously Hollis[56] has described the separation of C_1 to C_3 hydrocarbons (alkanes, alkenes and alkynes) on gels of styrene-ethylvinylbenzene-divinylbenzene copolymer (Porapak Q). Then, Hollis and Hayes[58] have shown that the separation is much easier on the more polar polymers (Porapak R, S and T), the relative retention times of acetylenic compounds increasing with the polarity of the gel polymers. The retention times of "polar gases" such as the oxides of nitrogen and carbon, gaseous compounds of sulphur, chlorine or nitrogen, and water vapor are greatly affected by the polarity of the polymer. H_2S, COS and SO_2 as well as HCN have excellent elution characteristics on Porapak Q. Figure 24 shows

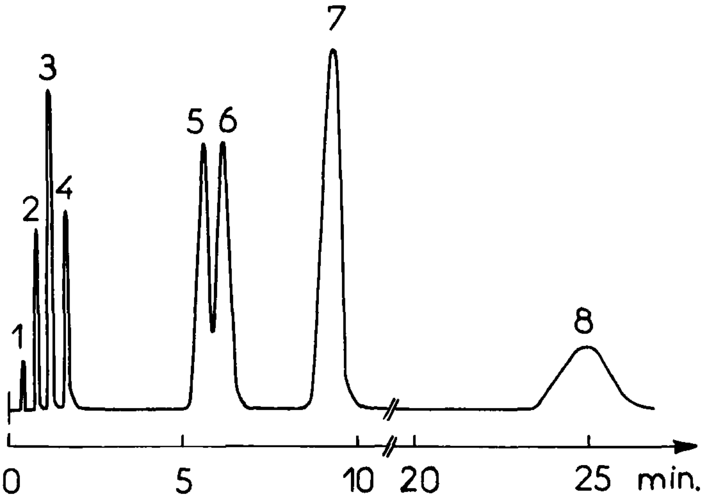

FIGURE 24

Separation of polar compounds on Porapak Q.

(1) air, (2) carbon dioxide, (3) ethylene, (4) water, (5) acetaldehyde, (6) ethylene oxide, (7) ethanol, (8) acetic acid.
Column 6 feet x 1/10 inch i.d., packed with Porapak Q, temperature 105° C, helium flow rate: 28.6 ml/min.

After Hollis and Hayes[58]: Figure 9.

the analysis on Porapak Q of a mixture of substances of widely different physical and chemical properties. Water is eluted quantitatively from the porous gel column and peak shapes for acetic acid and other acid components are also very good.

Wilhite and Hollis[59] have proved that porous polymer beads are an excellent gas chromatographic material separating the following possible Martian atmosphere components in 14 minutes on one column (temperature programmed from 25 to 150°C): H_2, N_2, O_2, A, CO, CO_2, CH_4, H_2O, NO, N_2O, NO_2, NH_3, CH_3F, CH_3Cl, H_2S and SO_2.

All components were resolved, except for O_2, A and CO, on an 8 foot Porapak Q column, in series with an 8 foot Porapak R column.

In this work the temperature stability of Porapak Q, R, S and T was investigated. They can be used up to 220°C.

Obermiller and Charlier[60] have analyzed a gas mixture on Porapak Q, using two columns in series, one at a high temperature (90°C), the other at a low temperature (-70°C). The hot column separates first CO_2, H_2S and SO_2, detected on one side of a thermistor detector, while the cold column separates A, O_2, N_2 and CO, detected on the other side of the detector. They have later improved the sensitivity of the detection and reduced the analysis time to 10 minutes[61].

Rabbani, Rusek and Janak[62] have shown that the retention volumes of different gases (Kr, CO_2, N_2O, C_2H_6, C_3H_8) decrease considerably when carbon dioxide or gaseous hydrocarbons are used as carrier gases on Porapak Q columns. The retention sequence of ethane, ethylene and acetylene is changed with CO_2 as carrier gas, when the temperature is decreased from room temperature to about -40°C.

Weems and coworkers[63] have separated helium-3, neon and hydrogen on Porapak Q using helium-4 as carrier gas at 194°K. The capacity ratio for neon increases from 0.08 at 194°K to 2.3 at 76°K.

Czubryt and Gesser[64] have resolved CH_4 and CD_4 on Porapak Q at -85°C. The separation is compared with that obtained on other adsorbents in gas-solid chromatography: molecular sieves, modified glass capillary (i.e. silica) and activated charcoal. Besides allowing a relatively short analysis time, the porous polymer column can be packed very easily, without any previous treatment of the packing, and the support is unaffected by water or by impurities in the carrier gas. Possanzini and coworkers[65] have separated on Porapak Q various isotopic molecules with deuterium substitution: CH_4-CD_4, C_2H_6-C_2D_6, CH_3COCH_3-CD_3COCD_3, C_6H_{12}-C_6D_{12}.

Zlatkis and Kaufman[66] have determined trace impurities in ethylene by gas chromatography on Porapak Q. Porapak Q deactivated with small amounts of a non polar liquid phase was used to determine trace amounts of water in iso-octane[67].

Palframan and Walker[68] have used porous polymers for the separation of glycols and glycol ethers. Porapak Q has been successfully used for the determination of ethanol in blood[69, 70]. Batier and coworkers[71] have described the simultaneous quantitative microdetermination of ethanol, methanol, isopropanol, acetaldehyde and acetone in blood by gas chromatography on Porapak Q. Gas chromatography at 120°C, on Porapak N, can be used to analyze trace amounts of formaldehyde and methanol in water[72].

Foris and Lehman[73] have separated C_1 and C_2 halocarbons on Porapak Q. The Kovats retention indexes increase with chlorine content more than with fluorine content and is directly proportional to molecular weight and boiling point.

Gvosdovich and Jashin[74] have eluted fluorinated compounds on Chromosorb 101 and 102. The contribution of non-specific interactions to the total adsorption energy of the molecules on these unsaturated surfaces predominates. As a result organic compounds elute after their fluorinated analogs. On a specific adsorbent like Porapak T, the reverse order is observed. The pairs of compounds studied are: C_3H_7OH-$C_3H_2F_5OH$, CH_3COOCH_3-CF_3COOCH_3, $C_5H_{11}OH$-$C_5H_2F_9OH$, $CH_3COC_6H_5$-p-$CH_3COC_6H_4F$.

Dufka and coworkers[75] have developed for gas chromatography a porous polymer bead, Synachrom, based on styrene divinylbenzene copolymer. The properties of this adsorbent(specific surface area: 520 m^2/g; pore diameter: 45Å) correspond to those of analogous porous polymer beads. The elution order follows the increasing value of the polarity of substances. Bartonicek and Lukac[76] have analyzed water, free fatty acids C_1-C_6 and free fatty succinic acid on Synachrom. Dimethylformamide used as a solvent is eluted after propionic acid. At the maximum temperature of the column (185°C) oxalic, malonic, succinic and glutaric acids could not be analyzed. Only succinic acid which is thermally decomposed elutes from the column in three individual peaks: water, succinic anhydride and succinic acid.

Lindsay-Smith and Waddington[77] have used Porapak Q and Par-1 to separate a wide range of simple aliphatic amines. To reduce peak tailing, polyethylene imine (PEI), tetraethylene pentamine (TEPA) or potassium hydroxide have been used as coating materials. It appears that the peak tailing arises because of two types of active sites on the polymer: simple acidic sites which can be neutralized by treatment with a base, and metal ions which can be neutralized by addition of an involatile complexing agent, for example the polyamines. A difference in the behavior of the two polymers used arises from their different structural properties. In general, however, by varying the amount of PEI, TEPA or potassium hydroxide, it is possible to resolve the same mixtures on both polymers. If an excess of the polyamine is used, separation of the amines appears to be a combination of gas-solid and gas-liquid chromatography.

Lindsay-Smith and Waddington[78] have shown that the gas-solid separations of alcohols and ethers on porous polymers (Par-1 and Porapak Q) are essentially the same as those on Celite-Apiezon L, although the retention times on the latter column are much shorter. Within a class of compounds there is a linear relationship between the logarithm of the retention time and the boiling point of the eluent. Modifying Par-1 with polyethylene glycol, up to a loading of 10%, has little effect on the separation which is still principally due to the polymer. On Porapak Q and S there is some tailing of the elution peak of the diols. Better separations occur on Par-1, the peaks being symmetrical with no evidence of decomposition.

Burger[79] has determined the retention time of 90 organic compounds on Porapak Q. The logarithm of the adjusted retention time is an approximately linear function of the logarithm of the molecular weight of the compound. Supina and Rose[80] have compared the gas chromatographic behavior on Porapak N, P, R, S, T and Chromosorb 101, 102, 103 for various classes of compounds: alkanes, alcohols, acids, ketones, nitriles, glycols, nitrogen aromatic compounds. Except Chromosorb 103, all the polymers studied appear to be suitable for the analysis of the compounds studied. Dave[81] has evaluated all the porous polymers commercially available. Data and chromatograms are presented for many classes of compounds to aid gas chromatographers in selecting the appropriate packing for specific separations.

Because of their relatively low thermal stability, porous organic polymers have been used so far for the separation of compounds with molecular weight not exceeding 150.

Cough and Simpson[82] have studied the variation of performances of different batches and types of porous polymer bead columns (Porapak Q and Chromosorb 102), for the analysis of water-alcohol mixtures.

The quantitative analysis was found to be satisfactory using all but one of several different batches and types of polymer beads. Column efficiencies and peaks resolutions varied with the packing material and are not much affected by conditioning up to 220°C. Deterioration is observed after prolonged conditioning at 275°C.

Dressler and coworkers[83] have compared retention data published by different authors and have carried out measurements on different batches of Porapak Q and Porapak Q conditioned in various ways. The differences in retention data are so large that the tabulated retention data taken from the literature and those measured on a certain batch of Porapak subjected or not to a certain conditioning cannot be used in practice for the qualitative identification of compounds on other batches.

b) - Adsorption studies on porous polystyrene type polymers

Owing to their low specific adsorption properties, porous polymers are used for the separation of mixtures of polar compounds or of aqueous solutions as well as of mixtures of highly reactive compounds or deuterium containing compounds. Porous polymers containing no polar functional groups are low specific adsorbents of the third type, according to the classification of Kiselev[84]. As a result of the predominant contribution of the dispersion interactions, the logarithm of the retention times increases with increasing electronic polarizability of molecules[85].

Johnson and Barrell[86] have measured the pore size distribution and the specific surface area of Porapak P, Q, R and S. There appears to be no significant difference in separations that depend on either the total micropore volume or the average micropore size. The controlling factor for separations is a function of the polarity of the adsorbate.

Sakodinski[87] has investigated the gas chromatographic behavior of porous polymers obtained by the polymerization of styrene and divinylbenzene in the presence of isooctane (Polysorb) and of some other polymers produced by Waters and Johns Manville. Separations on the non-polar porous polymers are mainly due to dispersion forces, which determine the sequence of elution of permanent gases in contrast to the separation on molecular sieves, silica gels and other adsorbents. The most polar polymer is Porapak T; on this adsorbent the elution of unsaturated hydrocarbons depends on the nature of the unsaturated bonds.

Sakodinski and Panina[88] have made a comparative study of the retention of various classes of molecules on Polysorb-6 (styrene and p-divinylbenzene copolymer), corresponding to Porapak Q, on Chromosorb 102, Polysorb-1, and Polysorbate-2 which is a polymer containing ether groups. The retention of compounds with similar boiling points on Polysorbate-2 differs from that on Polysorb-6 and depends both on the dipole moment and on the ability of the adsorbate to form hydrogen bonds with the active sites of the sorbent surface.

Gvosdovich, Kiselev and Yashin[85] have studied the adsorption properties of Chromosorb 102 by gas chromatography. Porous polymers containing no polar functional groups as Chromosorb 102 are low specificity adsorbents of the third type according to Kiselev's classification[84]. Molecules containing hydroxyl groups are more retained than those of the same molecular weight which have only σ and π bonds. Relationships between the logarithm of the corrected retention time and the number of carbon atoms have been plotted for nine classes of organic substances. Adsorption isotherms of water, diethylether and n-butanol have been calculated from the chromatograms obtained at different temperature.

Zado and Fabecic[89] have investigated by gas chromatography, the adsorption properties of Porapak Q and T. Attempt has been made to derive characteristic functional group incremental energies for the non-polar Porapak Q and the very polar Porapak T. It has been demonstrated that Porapak T exhibits a characteristic, strong interaction with the oxygen atom of alcohols, ethers and ketones. Porapak Q on the other hand, shows repulsion or weak interaction with oxygen atoms, but strongly interact with the hydroxylic hydrogen.

Czubryt and Gesser[90] have measured by gas chromatography and by conventional methods, the distribution coefficients of A, CH_4, CO_2, O_2 and N_2 on Porapak S, at various temperatures. The enthalpies of adsorption measured by gas chromatography in the 273°K - 351°K range, are lower than those obtained by static methods in the 155 - 240°K range for CH_4 and CO_2.

Eeck and Galceran[91] have shown that the retention time of water, ethanol, isopropanol, ethylacetate and n-heptane on Porapak Q, Chromosorb 101 and 102, decreases when sample size increases from 0.1 µl to 10 µl.

Gassiot-Matas and Monrabal-Bas[92] have derived the adsorption isotherm of water and alcohols on Porapak Q from their retention volumes. The water isotherm has an inflexion point below 100°C (Langmuir type III isotherm), while for alcohols whose retention volume decreases with increasing sample size, the isotherms are concave towards the pressure axis. The decrease of the retention volume observed with increasing sample size, for small amounts of water, is due to the heterogeneity of the adsorbent; the reverse phenomenon observed for water under 100°C, i.e. decrease in retention volume with increasing sample size, is explained by adsorbate-adsorbate interactions coming into play.

Patzelova and Volkova[93] have studied the interaction of Porapak R with water and methanol at temperatures above and below their boiling points, using frontal and elution techniques. At temperatures below the boiling points of the two compounds adsorbate-adsorbate interaction occurs at very low partial pressures for both and the heats of adsorption are higher, owing to hydrogen bonding. The adsorbate-adsorbate interaction decreases with increasing temperature at any given partial pressure of the adsorbate.

Dressler, Guha and Janak[94] have measured the standard deviations of the gas chromatographic peaks of different types of organic compounds, on different varieties of Porapak. They observed an abnormally large peak widths for the branched alkanes and for cycloalkanes on Porapak P. The higher the degree of branching of the compound, the lower its retention time and the greater the HETP. Silylation of the Porapak (Porapak PS) has no effect. The anomalous behavior with Porapak P is due to phenomena that occur within the pores of the polymer. As the pores are gradually filled with a stationary liquid, the effect decreases.

c) - Other porous polymers

We shall mention here the work of Urbach[95] who has shown that it is possible to separate by gas-solid chromatography C_6 to C_9 fatty acids on modified ion exchangers (Dowex 50-8 X in the H^+ form modified with 1.5% squalane).

The range of porous polymer packings has been extended by Van Wijk[96] with poly 2,6 diphenyl paraphenylene oxide (Tenax) which exhibits attractive chromatographic properties. In the normal temperature range (50-250°C), separations are comparable with those obtained on the crosslinked polystyrene porous polymers (separation of 5 alkyl amines, of benzoic and hydrobenzoic acids, of adipic and sebacic acids) but this temperature range can be extended up to 400-450°C (separation of ethylene glycol oligomers in Carbowax 400, determination of the dimethylester of naphthalene-2,6-dicarboxylic acid).

Bebris, Kiselev and Nikitin[97] have described the use of porous polyacrylonitrile as an adsorbent for gas chromatography, with a specific surface area of 30 and 49 m^2/g. Treatment at 250°C decreases the specific surface area to 11 m^2/g.

In the past few years there has been a great deal of research on non-diatomite supports for gas chromatography. Ottenstein[98] has reviewed most of this research up to 1965. The most widely used products up to now have been the fluorine containing polymers. We shall only briefly mention three recent works in this field.

Jequier and Robin[99] have compared the adsorption properties of porous polytrifluorethylene (Chromosorb T) and graphite. The adsorption of linear perfluorocarbons on Chromosorb T seems to be followed by dissolution in the polymer network, hence a larger retention of these compounds occurs.

Brazhnikov and coworkers[100] have described a method of preparing a sufficiently strong and efficient Teflon support possessing a particularly high degree of inertness to corrosive samples.

Bender and Meloan[101] have studied the chromatographic properties of polyolefin molding powders. Uncoated polypropylene columns are very good for trace water analysis in organic compounds.

H - Conclusion

This survey of the literature on gas-solid chromatography shows how intensive research efforts have been devoted to this field during the last few years. The main developments have been made essentially to solve the most important drawback of gas-solid chromatography at the origin: the lack of adsorbents suitable for the analysis of complex organic molecules.

Until recently only graphitized carbon black could be used to analyze compounds which are not gaseous at ambiant temperature. A better control of the purity and homogeneity of the conventional adsorbents, the synthesis of macroporous adsorbents, modifications of the chemical nature of the surface by grafting various molecules, the synthesis of new adsorbents (porous polymers) give now to the chemist a broad spectrum of adsorbents and the possibility to adjust the relative contributions of specific and non-specific forces to the adsorption and allow to obtain fast, easy separations of closely related isomers, including optical isomers in some instances. This however has often been achieved at the expense of the thermal stability of the stationary phase. Nevertheless practical applications are developing rapidly. Still, more are to come in the next years, especially in the field of chemical modifications of the surface of conventional adsorbents, so it has seemed worthwhile to underline these trends by a few typical examples.

A good deal of the interesting analytical results discussed above have been obtained by using pure, chemically well-defined adsorbents, with homogeneous surfaces of known chemical structure, for impurities, which can easily segregate on the surface, and geometrical defects are usually responsible of peak tailing gas-solid chromatography.

For example, macroporous silica gels of high chemical purity and controlled porosity have been especially prepared to analyze several classes of organic compounds with symmetrical peaks.

Zeolites with different nominal pore diameters are used depending on the analysis to be achieved: low boiling point gases or classes of hydrocarbons in petroleum fractions. Many inorganic salts have been used as adsorbents, one of them, $BaSO_4$, prepared in samples of high specific surface area (8.1 m^2/g) separates with symmetrical peaks the xylene isomers. Many others show promise in specific applications. A new porous polymer of high thermal stability has been recently developed.

To remove functional oxygenated groups which remain on its surface, graphitized carbon black has been treated at 1000°C under an hydrogen stream.

Modification of adsorbents by means of adsorbed dense monolayers offers the possibility of obtaining more homogeneous surfaces than the naturally occuring ones, to change their selectivities and to decrease the adsorption energies. Metallic phthalocyanines deposited on graphitized carbon black are a good example, since selectivity depends on the metal ion. A much broader field of application will probably be found for silica gels modified by substitution of more inert groups for the surface hydroxyls, which offer unlimited opportunities to the ingenuity of chemists. Similarly, the selectivity of porous polymers can be changed by the use of comonomers of different chemical functionality.

Obviously, organic adsorbents or inorganic adsorbents modified with organic compounds are less thermally stable than inorganic adsorbents, which partly reduce the advantage of gas-solid chromatography, the high thermal stability of the adsorbent and the possibility to work at high temperature, as exemplified by the analysis of polynuclear aromatic hydrocarbons on graphitized carbon black at 600°C or the separation of zinc-cadmium alloy at 850°C on silica gel. It should be observed however that inorganic adsorbents have a compact surface with a high density of atoms, give strong interaction energies with the adsorbed molecules and generally have large surface areas, so that the temperature needed to elute most compounds in a reasonable amount of time is at least 100°C higher than what is necessary in gas-liquid chromatography. For high molecular weight compounds, the thermal stability is then a problem. So, except if they have a very large specific surface area as porous polymers of the polystyrene type (T. max. ≈ 250°C), the modified adsorbents, which have smaller adsorption energies, may be used at lower temperature and their reduced thermal stability solid organic crystals like phthalocyanines (300°C), chemically modified adsorbents (250°C), is less constraining that it would seem at first.

The three main fields of application of gas solid chromatography are:

- the analysis of gases and low-boiling point hydrocarbons (zeolites, silica gels, alumina porous polymers),
- the analysis of types and groups of compounds that cannot be obtained by gas-liquid chromatography which is less specific, for example for geometrical isomers (graphitized carbon black, modified silica gels, various organic and inorganic adsorbents),
- the analysis of very polar compounds which interact too strongly with supports used in gas-liquid chromatography, whose surface is heterogeneous (porous polymers, graphitized carbon black).

Hydrogen isotopes and their nuclear spin isomers have been separated on silica gel, alumina and zeolite at -196°K. Permanent gases and low boiling point hydrocarbons are conveniently analyzed at room temperature on conventional adsorbents.

Many isotopic molecular pairs have been resolved on graphitized carbon black, some on silica gel and porous polymers.

Several phases have been used for the separation of geometrical isomers of organic compounds. Organo clay derivatives deposited on a chromatographic support and modified or not with a liquid stationary phase, have been used for the separation of xylene isomers only, because of their low thermal stability.

Phthalocyanines deposited on graphitized carbon black show selectivities that could not be achieved in gas-liquid chromatography: separation of xylene isomers, of phenanthrene and anthracene, of phenol and methyl substituted phenols (up to pentamethylphenol), of alcohols and terpene mixtures. The retention order on graphitized carbon black and on phthalocyanine depends mainly on the geometrical structure of the molecule which determines the number of atoms of the molecule which are near the surface in the most favorable orientation of the molecule on the surface, i.e. the one in which the dispersion forces are maximized.

Highly polar organic compounds of low molecular weight (alcohols, glycols, free acids) are analyzed with summetrical peaks on porous polymers; water itself is eluted very rapidly with symmetrical peak.

Alcohols of high molecular weight have been separated on silica gel modified with a liquid stationary phase. Alcohols, phenols and nitrogen aromatic compounds are eluted with symmetrical peaks on phthalocyanines deposited on graphitized carbon black and on chemically grafted silica gels.

To achieve difficult separations it has been necessary to use types of columns different from the conventional packed columns. These columns are usually easier to prepare and more stable than in gas-liquid chromatography. Porous layer beads columns have better efficiency, and resolution and give faster analysis. High efficiencies and high speed of analysis have also been obtained with porous layer open tube columns. These techniques are especially valuable when the packing does not have enough mechanical stability or is only available in fine powder (graphitized carbon black, highly dispersed silica gel and alumina).

Finally, we want to point out that one of the basic reasons of the very fast development of gas-solid chromatography is the availability of many studies on adsorption which provide a deep understanding of the phenomenon of adsorption and especially of the separation mechanism. In favorable cases it is even possible to predict the retention volumes, using data derived from collisions in gas phase (coefficient of Lennard-Jones potential, Van der Waals radii, ...) and methods of statistical thermodynamics.

Because theory can provide quantitative predictions of absolute retention data in some cases, of relative retention data in many cases and offers a good understanding of the physical adsorption phenomena both static and dynamic, allowing an accurate description of the necessary adsorbents, because the preparation of solids with the required porosity, pore distribution, specific surface area and surface chemical composition has now become possible, gas-solid chromatography has become a very sophisticated tool in separation and analytical chemistry, whose possibilities are now well beyond those of gas liquid chromatography.

I- References

(The references are numbered beginning with (1) in each section, and are grouped together according to section.)

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