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EDITED BY

VINCENT J. COATES

The Perkin-Elmer Corporation
Norwalk, Connecticut

HENRY J. NOEBELS

Beckman Instruments, Inc.
Fullerton, California

IRVING S. FAGERSON

University of Massachusetts
Amherst, Massachusetts

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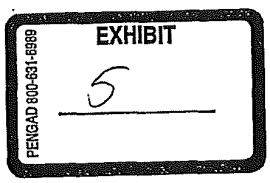

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LIST OF CONTRIBUTORS

B. O. AYERS, *Phillips Petroleum Company, Research and Development Department, Process Development Division, Bartlesville, Oklahoma*

W. J. BAKER, *Monsanto Chemical Company, Plastics Division, Texas City, Texas*

PAUL BENEDEK, *Hungarian Petroleum and Gas Research Institute, Veszprém, Hungary*

C. EUGENE BENNETT, *Polychemicals Department, E. I. du Pont de Nemours & Co., Inc., Du Pont Experimental Station, Wilmington, Delaware*

D. W. CARLE, *Scientific Instrument Division, Beckman Instruments, Inc., Fullerton, California*

H. NEWELL CLAUDY, *The Perkin-Elmer Corporation, Norwalk, Connecticut*

C. B. COWAN, *Central Research Laboratory, Canadian Industries Limited, McMasterville, Quebec, Canada*

W. A. DIETZ, *Esso Research and Engineering Co., Linden, New Jersey*

A. S. DUNLOP, *Polymer Corporation Limited, Sarnia, Ontario, Canada*

HERMAN R. FELTON, *Organic Chemicals Department, Jackson Laboratory, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware*

MARCEL J. E. GOLAY, *The Perkin-Elmer Corporation, Norwalk, Connecticut*

J. C. HARDEN, *Polychemicals Department, E. I. du Pont de Nemours & Co., Inc., Du Pont Experimental Station, Wilmington, Delaware*

LEWIS F. HATCH, *Department of Chemistry, The University of Texas, Austin, Texas*

CHARLES C. HELMS, *The Perkin-Elmer Corporation, Norwalk, Connecticut*

E. A. HINKLE, *Monsanto Chemical Co., Texas City, Texas*

THERON JOHNS, *Beckman Instruments, Inc., Fullerton, California*

S. E. J. JOHNSEN, *Monsanto Chemical Co., Texas City, Texas*

J. J. KIRKLAND, *Grasselli Chemicals Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware*

STANLEY H. LANGER, *U. S. Bureau of Mines, Pittsburgh, Pennsylvania*

J. S. LEWIS, *Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee*

A. J. P. MARTIN, *Abbotsbury, Barnet Lane Elstree, Herts., England*

R. A. MEYER, *Consolidated Electrodynamics Corp., Pasadena, California*[1]

J. L. MONKMAN, *Department of National Health and Welfare, Occupational Health Division, Ottawa, Ontario, Canada*

[1] Present Address: Atomics International Division of North American Aviation, Canoga Park, California

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S. DAL NOGARE, *Polychemicals Department, E. I. du Pont de Nemours & Co., Inc., Du Pont Experimental Station, Wilmington, Delaware*

STANLEY D. NOREM, *The Perkin-Elmer Corporation, Norwalk, Connecticut*

H. L. NORLIN, *Monsanto Chemical Company, Plastics Division, Texas City, Texas*

STEPHEN S. OBER, *Abbot Laboratories, North Chicago, Illinois*

H. W. PATTON, Research Laboratories, *Tennessee Eastman Company, Division of Eastman Kodak, Company, Kingsport, Tennessee*

C. PHILLIPS, *Merton College, Oxford, England*

RUSSEL D. RING, *Wyandotte Chemicals Corporation, Wyandotte, Michigan*

RALPH E. RIPPERE, *General Engineering Laboratory, General Electric Company, Schenectady, N. Y.*

M. J. ROOT, *G. Barr & Co., Chicago, Illinois*

P. H. STIRLING, *Central Research Laboratory, Canadian Industries Limited, McMasterville, Quebec, Canada*

STEPHEN SZÉPE, *Hungarian Petroleum and Gas Research Institute, Veszprém, Hungary*[2]

LESLIE SZEPESY, *Hungarian Petroleum and Gas Research Institute, Veszprém, Hungary*

B. W. TAYLOR, *Fisher Scientific Company, Pittsburgh, Pennsylvania*

G. W. TAYLOR, *Polymer Corporation Limited, Sarnia, Ontario, Canada*

R. F. WALL, *Monsanto Chemical Company, Plastics Division, Texas City, Texas*

J. F. YOUNG, *Douglas Aircraft Co., Santa Monica, California*

CHARLES ZAHN, *U. S. Bureau of Mines, Pittsburgh, Pennsylvania*

T. L. ZINN, *Monsanto Chemical Company, Plastics Division, Texas City, Texas*

[2] Present address: Sinclair Research Laboratories, Inc., Harvey, Illinois

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CHAPTER VI

Gas Chromatography Instrumentation for the Laboratory

C. PHILLIPS

Merton College, Oxford, England

INTRODUCTION

Gas chromatography consists of a process in which at one end of a column you push in very rapidly a whole collection of substances and then at the other end you sit back and watch each substance emerge in its own characteristic time. Most of the instrumentation of gas chromatography has been connected with the ingenious vapor detectors which have been constructed for watching the substances emerge, and to a lesser extent with devices for the virtually instantaneous introduction of small samples. I propose to say very little about these, and to concentrate rather on the processes which are taking place inside the column. By so doing I hope to illustrate some of the many ways in which gas chromatography can be used for the solution of laboratory problems.

The emergence of each substance is normally recorded as a peak in a chromatogram. Each peak possesses two important characteristics (*9*)

(1) The retention time of the peak maximum.

(2) The spread of the peak. This is generally measured in terms of the number of theoretical plates, to which the column is approximating in its behavior, a good and soundly operated column being equivalent to a large number of plates.

Separation of two substances is assisted by a large retention time ratio, or separation factor, and by using a column with many plates. The relations between the two characteristics have been formulated most clearly in a diagram due to Glueckauf (*2*) which is reproduced in Fig. 1. From this diagram one may deduce the degree of separation (i.e., η the fractional impurity left in each substance if a cut is made at such a point that the fractional impurity will be the same for both substances) in terms of the separation factor α, the number of theoretical plates n, and the mol fractions m_1 and m_2 of the substances to be separated. For simplicity we may restrict our attention to the case of a 1:1 molar ratio (for which incidentally the impurity is at a maximum) i.e., $\eta_{1:1}$. Then it will be seen from the figure that the two substances will be separated to 99% purity ($\eta = 10^{-2}$) on a column equivalent to 1000 plates if the separation factor is 1.16, or on

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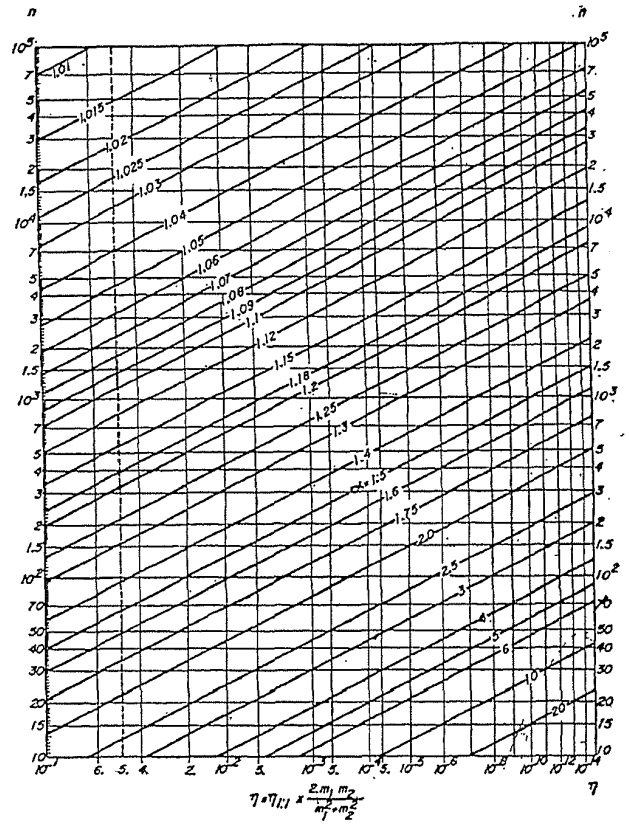

FIG. 1. Relation between number of plates (n), separation factor (α), and fractional band impurity (η). (After E. Glueckauf, courtesy Reinhold Publishing Corp.)

a column equivalent to 10,000 plates if the separation factor is 1.05. Much poorer separations than this will still appear as two peaks, and even worse cases can usually be unravelled into two peaks by noting the abnormally low theoretical plate number of the composite peak.

THEORETICAL PLATES

The consideration of theoretical plate efficiency is a sort of chemical engineering. It has been well summarized by Keulemans (*6*). Reduction of efficiency and consequent increase in the HETP results in the main from four factors.

(*a*) Non-instantaneous introduction of sample. This is reduced by using a small sample size, and hence creates problems of sampling and detector sensitivity.

(*b*) Irregularities and channelling of flow in the column. These can generally be reduced by efficient packing techniques.

(*c*) Longitudinal diffusion in the gas stream. This can be reduced by using a carrier gas of low diffusivity (e.g., nitrogen instead of hydrogen), a carrier gas at high pressure, and by an increase in flow rate until an optimum is set by the operation of the fourth factor.

(*d*) Slow diffusion into and out of the liquid phase. This effect is less marked with substances of large retention time (high solubility in the liquid phase), so that theoretical plate values tend to rise along any chromatogram, and to rise (for any particular substance) with a lowering of

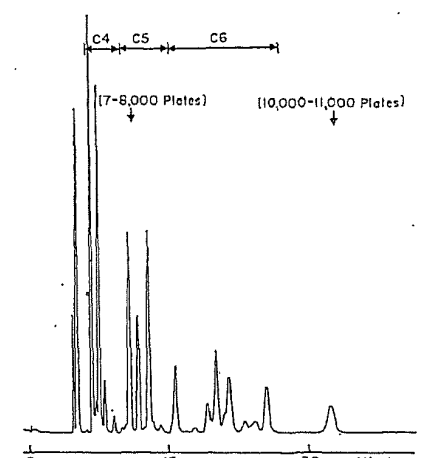

FIG. 2. Use of a column with large theoretical plate number. Petroleum fraction, 0°–75°C; 5% apiezon oil on C22 brick (100-200 mesh); 75% hydrogen, 25% nitrogen; column length = 25 feet; internal diameter = 3.6 mm; flow rate = 37 ml/min; 78°C. (Courtesy of Benzole Producers, Ltd., Watford, England.)

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column temperature and hence increase of solubility. The slow diffusion can also be reduced by using a very thin liquid film. This effect is shown in Fig. 2, which has been kindly provided by Mr. Scott and Mr. Cheshire of Benzole Producers, Limited.

Retention Times

The retention time of the peak maximum can, by very simple corrections be made a physicochemical constant, characteristic of the vapor substance, the fixed liquid phase of the column and the temperature of operation. A retention time can thus be used directly for the identification of an unknown substance, just as the more familiar constants such as boiling point, melting points, or refractive index. Unlike these however, it is almost completely insensitive to the purity of the sample used, and for each substance one may use a variety of column liquids, each of which will provide a new characteristic time. These most valuable properties would seem to suggest that tables of retention times should be drawn up on some standard and commonly accepted basis. In Europe we have recently started on such a project in the "Gas Chromatography Discussion Group" (associated with the Hydrocarbon Research Group of the Institute of Petroleum). At a coming A. C. S. meeting,* we are presenting a paper, which has been written by Ambrose, Keulemans, and Purnell (*1*), containing some suggestions on how this compilation of data should be made. Briefly we consider that there are two kinds of data which are of importance:

(1) Relative Retention Times, i.e., retention times relative to certain internal standard vapor substances. These are obtainable with high precision and reliability with relatively little trouble, and they will serve for nearly all analytical purposes. The relative times should be corrected for the dead volume of the column, should be extrapolated to zero size of sample, and should if possible, be quoted at at least two temperatures; better still a graph of (the logarithm of the) relative retention times may be plotted against $1/T$.

The compilation of such times will obviously be greatly simplified if, at least at first, data is presented for a certain relatively small range of standard and reproducible column liquids. We have made some suggestions of suitable liquids (up to about 150° column temperature) and have succeeded in persuading some of the chemical firms to produce these liquids for us.

(2) Absolute Retention Volumes or Partition Coefficients. For a number of purposes, in particular the prediction of exact column performance, and for thermodynamic studies, it is desirable that absolute values of retention data should be published. The simplest manner of doing this is probably as V_g values (or specific retention volumes) as Littlewood, Price, and myself suggested (*7*) and as illustrated in Fig. 3. Specific retention volumes require accurate flow (and temperature) measurements, and a knowledge

* *Editor's Note*: Held in New York City, September, 1957.

of the weight of column liquid. It should, however, be noted that conversion of relative retention times to absolute values only requires the determination of the absolute value(s) for the internal standard substance(s).

An alternative absolute value is provided by the partition coefficient, K, which requires in addition a knowledge of the density of the column liquid at the column temperatures. As V°_g and K are simply related by the equation.

$$V^\circ_g = \frac{273K}{T_c \rho_c}$$

(where T_c is the column temperature, and ρ_c the column liquid density at this temperature), it does not matter greatly which is given.

I hope very much that soon there will be discussion of this matter of the publication of standardized retention data in some detail, and perhaps some decisions which will enable all workers in the field to publish their results in such a manner as to be of the greatest assistance to others.

Separation

Data plotted as in Fig. 3, (or relative retention times), can be used to decide the degree of separation which will be achieved with a particular

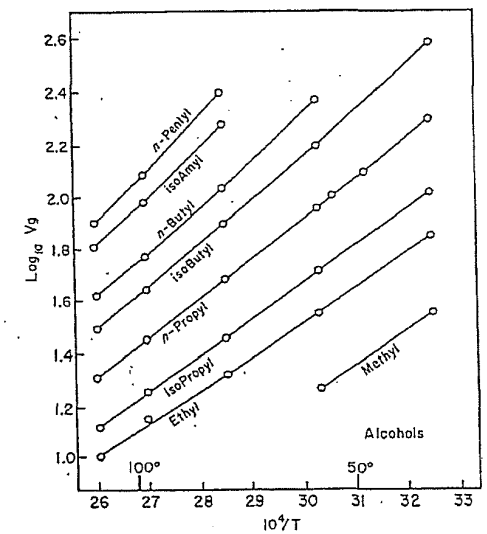

Fig. 3. Specific retention volumes for alcohols on Silicone 702 fluid. (Courtesy The Chemical Society, London.)

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column liquid. Thus if we build and operate our column under conditions to give say 1,000 plates we shall require a separation factor of 1.16 for 99% separation, i.e., we shall separate two substances to this extent if they are $\log_{10}$ 1.16 or 0.065 apart on the $\log_{10} V^\circ_g$ (or RRT) scale. Within an homologous series, the separation factor may vary from about 3.4 per CH_2 group at 20° to about 1.5 at 200° (e.g., with liquid paraffin as column liquid), but between e.g., positional isomers such as 2-Me-heptane and 4-Me-heptane, separation factor 1.04 on paraffin at 80°, this may be much lower (*5*). We then have to decide whether to construct a more efficient column so as to obtain more plates, or to change the column liquid so as to achieve a better separation factor. Commonly one adopts some compromise procedure.

Variation of Column Liquid

The variation of column liquid is of particular value for the separation of substances of different chemical type. One of the clearest examples is provided by an early paper of James (*4*), in which the oxygen atoms of polyethylene oxide (column liquid) were used to retard those amines which were able to form H-bonds with them. The marked retardation of primary amines, the lessor retardation of secondary amines, and the negligible retardation of tertiary (no active H-atoms) amines is shown up most clearly by a comparison of the retention times using polyethylene oxide as column liquid, with the retention times using paraffin as column liquid. This is shown in Fig. 4.

Now it is to be noted that the different active groups cause the retention times of the molecules containing them to fall on straight lines. This would seem to suggest that we are observing in each case a fairly constant free energy change of transfer from one column liquid to the other, which can be directly attributed to the active grouping. Gas chromatography thus provides a new way of testing for such groups. Instead of searching, as has become traditional organic practice, for a reagent to give a color reaction or characteristic smell (e.g., carbylamine test for primary amines) or, as more recently, for a suitable region of the spectrum for specific group absorption, we can now look instead for a suitable pair of differentiating column liquids.

The selective retardation of aromatics, napthenes, and unsaturated hydrocarbons on passing e.g., from paraffin to benzyl-diphenyl as column liquid is now also well known. It is however, I think not always so generally recognized that this change of column liquid also produces a useful relative retardation of straight chain aliphatic hydrocarbons with respect to branched chain aliphatic hydrocarbons. Thus the separation factor

n-heptane/2:2:4 trimethylpentane

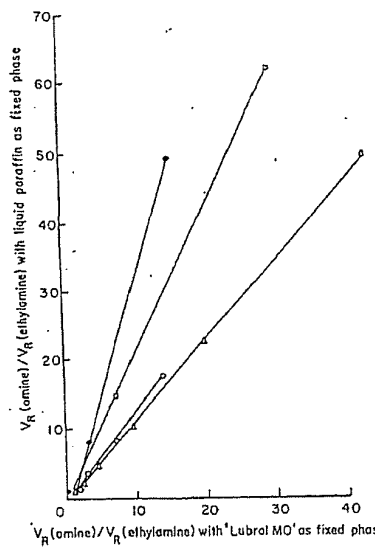

Fig. 4. The relationship between relative retention volumes (retention vol. of amine/retention vol. of ethylamine) for aliphatic amines on columns having stationary liquid phases of (a) liquid paraffin and (b) Lubrol MO, showing the relative speeding up of secondary and tertiary amines on changing from a solvent not allowing, to one allowing, hydrogen bonding. △-△, primary straight-chain amines; ○-○, primary isoalkylamines; □-□, secondary straight chain amines; ⊙-⊙, secondary isoalkylamines; ●-●, tertiary straight-chain amines. (After A. T. James, courtesy Cambridge University Press.)

at 80° is 1.08 with a liquid paraffin column, but 1.23 with a column of benzyl-diphenyl (*5*). The use of selective adsorbents may well prove useful for separations where structural rather than chemical differences are involved, for highly specific separations of this kind are well known in classical liquid-adsorbent chromatography. Molecular sieves provide a case in point.

More marked retardation of aromatics can be achieved by use of specific complexing with metal salts, for here the forces which can be used are considerably greater in magnitude than those encountered in mere solution. Thus while the separation factor

benzene/*n*-hexane

changes from about 1.6 on paraffin liquid to between 4 and 5 on an aromatic

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liquid such as benzyl-diphenyl or tetralin, we have found that it rises to 40 when a column of silver perchlorate (1.7 gm) dissolved in tetralin (4 gm) is employed.

Use of Metal Salts as Column Liquids

More recently we have studied in my laboratory (*12*) the use of fused salts as column liquids. Our prime purpose in this work has been the study of inorganic complexing equilibria, as I shall describe later. We have used for the most part very short (and therefore, inefficient columns) because of the large retardations observed. However, the results are sufficient to show how these specific retardations can be used for analytical work, and the studies we have made may also be of interest as a model for work at really high column temperatures (above 500°C) where purely inorganic metal salts suggest themselves as satisfactory column liquids.

We have worked in particular with zinc stearate (M.P. 121–122°), copper stearate (M.P. 101°) and nickel oleate (M.P. 25–30°). These materials

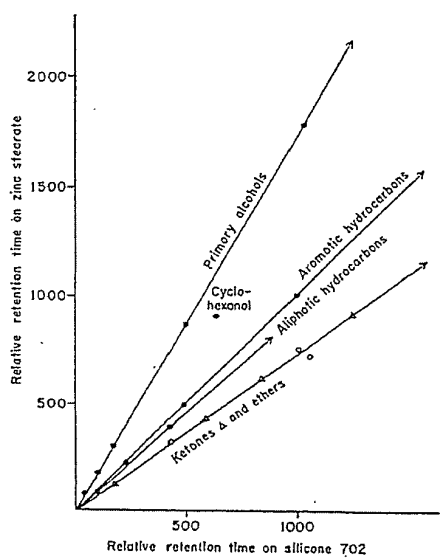

Fig. 5. Retention times on Silicone 702 and on zinc stearate columns at 150°C. (Relative to mesitylene as 1000.)

have proved to be quite stable over a six month period (e.g., zinc stearate at 157°). They are mixed with Celite in benzene solution and the benzene then evaporated off. As so prepared they have efficiency of about 3 to 4 plate per cm while a similar column of Silicone (702) fluid which we have used for comparison had an efficiency of 5 plates per cm. It is probable that this efficiency could be materially increased by a better mixing procedure. The columns have been run at temperatures above the melting points, although it is of interest to note that on one occasion due to an accident when the zinc stearate column was run 25° below its melting point it functioned as a separating column though with only about half the normal number of theoretical plates.

The selective retardations which can be achieved with such columns can be illustrated by the results in Fig. 5, where I have plotted the retention times on zinc stearate against retention times on silicone. All values have been referred to mesitylene as standard (retention time equal to 1000) a

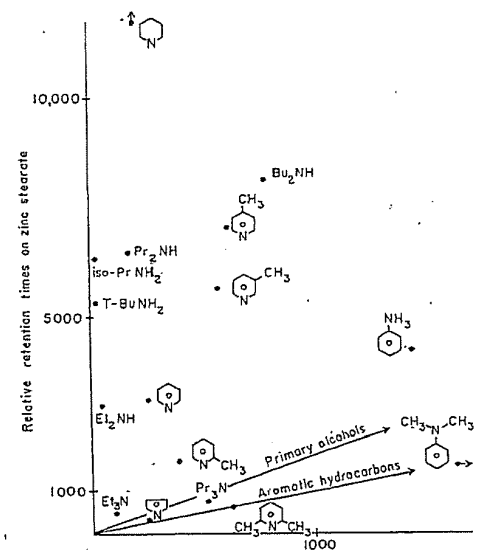

Fig. 6. Retention times on Silicone 702 and on zinc stearate columns at 150°C. (Relative to mesitylene as 1000.)

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procedure which finds some justification in the fact that the heat of transfer of mesitylene from silicone to zinc stearate is only −0.1 kcal, a result which we obtained from absolute retention volume data made at two temperatures. It will be seen that relative to aromatic hydrocarbons, primary alcohols are retarded on the zinc stearate by a factor of 1.8, while ketones and ethers are accelerated by a factor of 1.4. On changing to copper stearate the primary alcohol retardation factor (again relative to aromatic hydrocarbons) is however, less than one (0.8), while for nickel oleate it is 3.1.

The largest retardation effects have been observed with amines. The results for zinc stearate are shown in Fig. 6. It will be seen that the retardation factors are now much more specific, but in general tertiary amines (e.g., tripropylamine 1.6) are less retarded than secondary (e.g., dipropylamine 38), which are less retarded than primary amines (e.g., isopropylamine 4,000). Some amines are so heavily retarded that they do not appear to move at all. Thus ethanolamine and ethylene diamine would seem to have retardation factors well in excess of 30,000. With copper stearate the retardation of amines is somewhat greater than with zinc stearate (e.g., pyridine has a retardation factor on zinc stearate of 12.5, and on copper stearate one of 17.5), except for the case of tertiary amines where the effect is the other way.

The manner in which these column materials may be used for separative purposes is illustrated in Fig. 7, which shows a separation of the picolines and 2:6 lutidine which is possible on a very inefficient (50 cm) zinc stearate column, but impossible on a silicone column with more than twice the plate efficiency. The most extreme case in this example is provided by

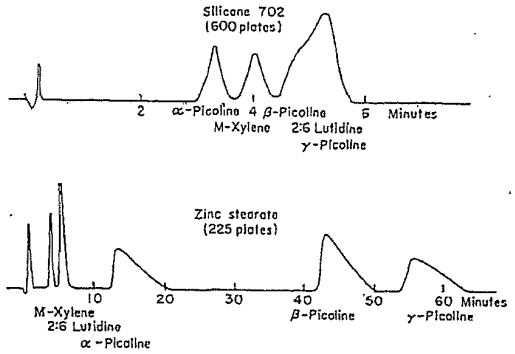

FIG. 7. Separation of picolines at 156°C.

γ-picoline and 2:6 lutidine, which would require for 99% separation a Silicone column of 250,000 plates (i.e., about ¼ mile long) but a zinc stearate column of only 4 plates (i.e., about 1 cm long). In the chromatogram of Fig. 7, the column has been deliberately overloaded to demonstrate the marked asymmetry which can then result, as a consequence of the competition by picoline molecules for the specific sites around the metal atom. With low sample sizes these peaks return to the more normal symmetrical shape. The assymetric peaks suggest however, that the system might well form a useful one for the application of displacement analysis (*12*) and might have the marked advantage over adsorbent columns in this connection that the active sites were much more uniform.

PHYSICOCHEMICAL EQUILIBRIA

Gas chromatography makes use of processes of solution and adsorption to effect separations and analyses, but it is also a very valuable tool for the reverse process, namely the evaluation of physicochemical data connected with solution and adsorption (e.g., heats and entropies, and perhaps even diffusion rates) from analytical type experiments. As a technique it should have particular attraction to the physical chemist if the old story be true that while a physicist spends his time making very accurate measurements on impure substances, and the chemist spends his time making inaccurate measurements on very pure substances, the physical chemist only makes inaccurate measurements on impure substances. Even living down to this reputation he can do valuable work if he uses gas chromatography.

I would like to illustrate this type of application, by referring again to our work with metal salt columns, for this provides us with a new way of studying metal-complex equilibria. From measurements of absolute retention volumes it is a relatively simple matter to work out the free energies of solution of say an amine in the liquid metal salt. From relative retention times only, free energies of solution may be compared along a series. These free energies of solution are found to parallel very closely the (logarithm of the) basic dissociation constants of the aliphatic amines, but there are much greater free energies of solution in the case of amines like pyridine and the picolines which are capable of forming π complexes with the metal atoms than would be expected from this direct comparison of bonding strength to hydrogen. A similar situation has been found in the study of aqueous complexes by more traditional methods.

The effect of varying the metal is illustrated in Fig. 8. Here again we have a similar situation to aqueous complexing studies, where it has been found e.g., for ethylene diamine (R.H.S. of Fig. 8) that up to four active groups are accommodated more strongly around copper than around either nickel or zinc, but the fifth and sixth groups (K_5) less strongly owing

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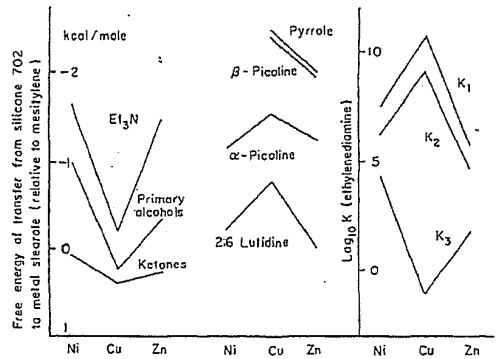

FIG. 8. Free energy of transfer from Silicone 702 to metal stearate. (Relative to mesitylene.)

to the Jahn-Teller effect. The L.H.S. of Fig. 8 shows how in our studies some substances follow the K_1, K_2 pattern and are presumably able to replace the CO group (of the stearate) from its coordination to the metal, while others are less strongly attached and follow the K_3 pattern.

INSTRUMENTATION

As I said at the beginning I have spent most of my time considering column processes, and that I do so is meant as a tribute to the excellence of the instrumentation which is now available commercially. While of course it is always very difficult to find a laboratory worker who would not wish to have an even better instrument than he has already, the available instruments do seem to provide all that is commonly required in the way of accurate flow control, precise and rapid injection systems, good column temperature control over a wide temperature range, and high sensitivity low-noise vapor detectors. It is, however, true that there still remain some problems where extremely high detector sensitivity is required. The most difficult separations require very small sample sizes and low operation temperatures and with thermolabile substances one may wish to work at temperatures so low that only very high sensitivity detectors can persuade them that they still are slightly volatile after all. High sensitivity ionization and discharge detectors have already been described by Ryce and Bryce (*11*), and by Harley and Pretorious (*3*). I would like here to

draw attention to two recent British developments in the same direction. Dr. J. E. Lovelock (*8*) (National Institute for Medical Research, Mill Hill, London) has shown how a considerable (× 100) increase in sensitivity of the ionization type detector may be achieved by using argon as carrier gas. Argon atoms are easily raised to an excited, but non-ionized and hence non-conducting, state of about 11.5 volts. These excited atoms store up ionization energy and pass it on to the vapor molecules in collisions. Dr. R. C. Pitkethly (*10*) (British Petroleum Co., Sunbury-on-Thames) has develped a simple and improved discharge detector, in which the discharge tubes are made from ordinary neon indicator tubes. The instrument as at present developed has a noise level which corresponds to as little as one part of vapor in 50 million parts of nitrogen, which in other terms means that recognizable peaks are produced for example, with a sample containing 25% propane, 25% iso-butane, and 50% *n*-butane having a total gas volume of 10^{-6} ml. Using such a detector the maximum sample size is of the order 10–20 micrograms.

Commercial instrumentation has also provided satisfactory means for rapid quantitative analysis. The importance of this in applied chemistry is obvious, but to the academic it is of peculiar significance in the opportunity which it provides for the transformation of organic chemistry into an exact science. No longer shall we need to be satisfied with yields in an organic reaction quoted for one substance, and one particular set of operating conditions, but we shall hope for something of a mass balance with details of all the other products and the way in which the relative quantities of these may be changed with change of conditions. Perhaps a whole new field of organic chemistry may be found hidden away among the side reactions of organic chemistry, in the same way as a whole chemical industry was founded on the tar materials rejected in the manufacture of coal-gas.

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Discussion

Jones (*E. I. du Pont de Nemours & Co., Inc., Delaware*): I would like to ask you, Dr. Phillips, if you would care to comment a little more on your discharge detector. We have had a little bit of experience with this ourselves, and have found it to be nonlinear. In fact, it was approximately logarithmic, with an order of magnitude higher noise level than reported in the literature. In addition, it had the annoying property of reducing hydrocarbons to carbon.

Phillips: Perhaps Mr. Desty can offer some information on this point.

Jones: I was commenting, Mr. Desty, that we have been rather discouraged with our results on the electrical discharge detectors, having observed them to be logarithmic more than linear, and have not been as successful as you have been in achieving good signal-to-noise ratios. Our results have been about an order of magnitude poorer. We have also observed that with practically anything higher than C_2 the hydrocarbons are broken down to carbon, which deposits on the electrodes.

Desty (*British Petroleum Co., Ltd., England*): I brought along some specimen tubes from England. One of these has been used for about six months. You can see that though the tubes have large electrodes, the discharge occupies only about 25 per cent of the area. We have had no trouble at all with contamination of the electrodes, since they are being continually cleaned by the discharge. With regard to noise level, the presence of a positive column could be the source of the noise you have noted. Upon introducing hydrocarbon vapor into the discharge, the number of striations changes, and, as there is a small voltage drop across each striation, this can cause some trouble. Pitkethly has developed the use of the small indicator bulbs, which have the large electrodes separated by a very short distance (approximately 2 mm). In these tubes the positive column with the striations is completely eliminated. I remember that tubes of the type originally described by Pretorius did have a rather large noise level; larger than that he reported. In fact, that was one reason that Pitkethly abandoned this design and went to the small indicator bulbs.

Jones: I was working with helium. Perhaps this had some effect. Your work was with argon, was it not, Mr. Desty?

Desty: No, with both nitrogen and hydrogen.

Hinkle (*Monsanto Chemical Co., Texas*): With regard to your comment, Dr. Phillips, of the retardation of aromatics as compared to the naphthenes and paraffins, have you, in your experience, had occasion to try dinitrile-type compound in addition to your fused salts; for instance, adiponitrile?

Phillips: No, we have only used metal salts so far.

Hinkle: The reason I suggest this is that it is extremely selective for the aromatics and the data that you present on the tailing of the peaks is almost analogous in the dinitriles.

Lewis (*Tennessee Eastman Co., Tennessee*): With regard to your slide showing the plot of the retention times for the columns having different characteristics, if you plot logarithmically instead of linearly you avoid a crowding of points near the origin, and the lines are straight. The separation between the various homologous series, then, is fairly constant and the points representing homologs of each series are equally spaced.

Phillips: This has been done. Usually you obtain a series of lines cutting across one of the axes. There was no specific reason for the presentation used here.

Desty: Two further thoughts have occurred to me about the discharge detector. With regard to linearity, the design developed by Pitkethly was linear over a sample size range of from 10^{-9} to 10^{-6} grams. Secondly, the formation of carbon may have been confused with sputtering of the electrodes. Using platinum, as Harley and Pretorius described, the electrodes quickly sputter a dark film onto the inside of the glass envelope, which leads to electrical leakage and additional noise. This may be an alternative explanation of the results that were obtained by the du Pont group.

Jones: On further reflection, I believe it is quite possible the nonlinearities that we have observed are due to the difference in carrier gas. We have an effect with helium that is not present with hydrogen or nitrogen. It may be that Mr. Desty has had this good result because of a fortunate choice of carrier gases. Regarding the formation of carbon (it is carbon—we have been able to grow carbon in filaments up to 2 mm in length), if any carbon does collect on the electrode, it forms a surface which can produce a discharge at a lower voltage; hence, the current tends to concentrate at these points. Thus, the nodules tend to build up into filaments. We have used platinum working surfaces, and have also used tungsten, with similar results. Perhaps there are other surfaces that have a lower firing potential and, hence, do not concentrate the current in this manner.

Mackay (*Evans Research & Development Co., New York*): I was interested, Dr. Phillips, in your comments on the identification of compounds by their behavior in a column. My interest has been in the identification of compounds by using them as the substrate of a column. Have you had any experience in this direction?*

Phillips: Yes, it's a perfectly feasible procedure. It means, of course, that you're restricted to some extent to things that are not particularly volatile, and of course, you have a mixture of substances—and you can't really distinguish between two mixtures. It also takes much longer to make a column than to run something through it. It is a nice technique to use to provide additional information on high molecular weight materials. Perhaps it might be important for the identification of polymers and similar materials.

* Later communication: My reference to the identification of compounds by using them as the substrate of a column should have been amplified to state that the method involves characterizing an unknown by its ability to separate a standard mixture of volatiles under standard chromatographic conditions. For example the polyoxyethylene derivatives of sorbitan and related compounds (The Atlas Company's "Spans" & "Tweens") are very difficult to characterize as Span 20, 40, 60 etc. by chemical or spectroscopic methods, once beyond the stage of placing the unknown in the polyoxyethylene derivative class. If the possible knowns are made into substrates under standard conditions (this does not take long), and used to separate a standard mixture of esters or alcohols under standard conditions, a characteristic separation pattern may be obtained for each known and compared with that given by the unknown. I believe that this kind of chromatography can be a valuable adjunct to other kinds of analysis, especially where the unknown is a mixture or commercial product rather than a pure compound.

In fact, it is in just those cases where the unknown is a mixture that I believe best use can be made of this technique and accordingly I disagree with Phillips' views on this point.

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CHAPTER XVII

An Instrument Designed for High Temperature Gas Chromatographic Analysis

B. W. TAYLOR

Fisher Scientific Company, Pittsburgh, Pennsylvania

Gas chromatography has proven to be a very important and powerful technique in the analytical field with most of the work concentrated at temperatures below 150°C. There is still much work to be done at these lower temperatures and it is only a matter of time before some of the more difficult problems will be solved.

Since the technique is expanding at a very fast rate, it is a natural step into higher temperatures for higher boiling materials. This interest has brought about the development of an instrument to handle a much wider variety of components. If the problem of higher temperatures only involved increasing the heat input our job would have been relatively simple. However, this was not so.

With the desire to employ gas chromatography for the analysis of higher boiling materials a completely new instrument had to be designed.

In order to satisfactorily analyze the very high boiling materials, it is important that the sample be vaporized quickly. This permits the column and cell to be operated at a somewhat lower temperature and still give resolution. With this fact in mind, we have attempted to design an instrument that will cover a wide temperature range and maintain high sensitivity over the entire temperature range.

The following features are incorporated in this instrument:

1. Temperature range
   - A. Cell bath thermistor regulated up to 200°C.
   - B. Column bath regulated from below room temperature to 300°C.
   - C. Flash evaporator controlled up to about 425°C.
2. Sensitivity
   - A. Newly designed thermistor thermal conductivity cell.
   - B. 0–2 mv recorder.
   - C. Stepwise sensitivity control.
   - D. Coarse and fine balance control.
3. Transistor regulated power supply delivering up to 100 ma.
4. New readout trace for integrator.
5. Reproducible sample introduction system for high temperature work.

The above features are shown in detail on a block diagram of the chroma-

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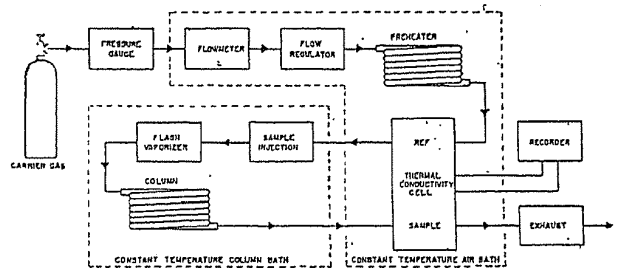

FIG. 1. Block diagram.

tographic system in Fig. 1. This system is very much like some other chromatographic systems in that the cell is in one temperature controlled air bath and the chromatographic column is in another. The carrier gas first passes through a flowmeter which is calibrated for helium at approximately 20 psi at 25°C. It passes on through a flow regulator into a preheater coil and into the reference side of the thermal conductivity cell. From the cell the gas passes through 1/16" O.D. tubing, out of the cell bath and into the sample introduction system which is in the column bath. Then out through an orifice of the introduction system into the "flash evaporator" and on into the chromatographic column. The exhaust of the column passes through 1/16" O.D. tubing into the cell bath, and into the sample side of the thermal conductivity cell it is then exhausted to the atmosphere or a sample collecting device.

The chromatographic system is housed in two separate baths and each, of course, is temperature regulated. This makes it possible to change columns without affecting the thermal equilibrium of the conductivity cell.

Let us discuss the cell compartment temperature control. Experimental evidence has shown that the temperature of this compartment must be controlled within very narrow limits. This has been accomplished by employing a thermistor sensing element, and a magnetic amplifier to operate a relay, which cycles a heater. A temperature range switch having four positions, (50, 100, 150, and 200°C), allows one to operate this chamber at a temperature which gives maximum sensitivity in line with minimizing the possibility of the accumulation of condensate in the cell itself. This bath is attached to the front panel. Such arrangement allows the whole drawer assembly to be withdrawn to exchange columns without affecting the cell compartment temperature equilibrium.

The column bath, on the other hand, is designed with five sides that are

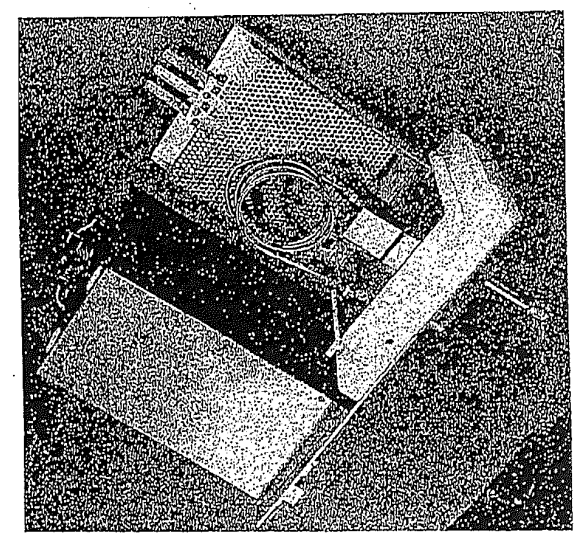

FIG. 2. Drawer assembly.

an integral part of the main cabinet; but, the column, heaters, and thermostats are part of the drawer assembly as shown in Fig. 2.

The temperature of the column bath is controlled by a series of preset bimetallic thermoregulators from 50 to 300°C in intervals of 25°. There are two wire-wound heaters, one being controlled by a Powerstat as a constant heater, and a smaller one cycled by the thermoregulators. A cooling coil is attached to the column bath by which the chamber can be cooled below the ambient temperature by passing a coolant through this coil. This is desirable for the analysis of low boilers or when it is desired to reduce the bath temperature quickly.

The sample introduction system is similar to that developed by the Esso Research Laboratories, Baton Rouge, Louisiana. It differs in that we have incorporated the orifice into a "flash evaporator" (Fig. 3). When the sample is introduced into the system it comes in contact with a heated section, whose temperature can be considerably above the column temperature, before it enters the column. This contributes to rapid sample

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vaporization, which has two virtues. The sample may enter the column in the vapor phase, and, the possibility of slow vaporization which results in broad or multiple peaks is reduced.

In order to heat the "flash evaporator", it is surrounded by a metal block of large mass in which a 100 watt cartridge heater is located. The temperature of the block is read with a dial thermometer which can be slid in or out, permitting the thermometer to indicate block or bath temperature. Since close temperature control of the column is not required as much as of the cell, a Powerstat is used to control the heat input to the block, which can be heated up to about 425°C, or 125°C above the maximum column temperature.

The high sensitivity is obtained by a combination of conditions. First, we have incorporated a 0–2 mv recorder into the instrument. The thermal conductivity cell has been redisigned, the sample thermistor being located directly in the stream and the cell cavity volume has been reduced to approximately 0.1 ml. The current input to the cell is controlled to give high sensitivity at all bath temperatures.

A new transistor power supply has been developed which can deliver up to 100 ma, making it possible to introduce more current to the thermistors at the higher temperatures, thereby maintaining high sensitivity.

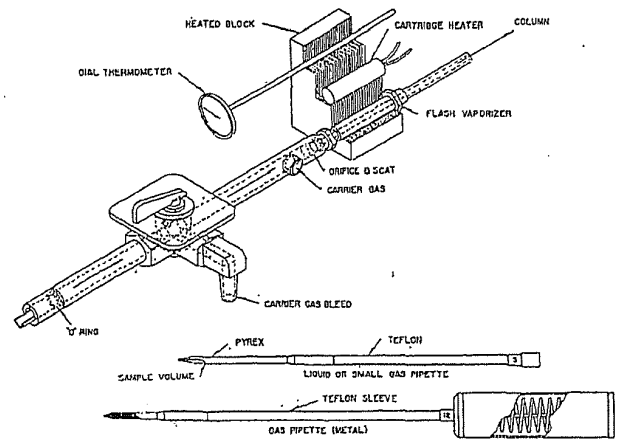

Fig. 3. Flash evaporator.

As the ambient cell temperature is increased the current input to the thermistors is increased to give nearly constant sensitivity.

While operating any except very special thermistors at high temperatures, the sensitivity is reduced because the resistance decreases. With an input of about 20 ma into the thermistors there is a very sharp decrease in sensitivity above 150°C.

We have not experienced a significant shortening of thermistor life as a result of exceeding the thermistor current rating for extended periods.

In working with high boiling materials there is a tendency for condensate or liquid phase to form in the cell when the cell temperature is much lower

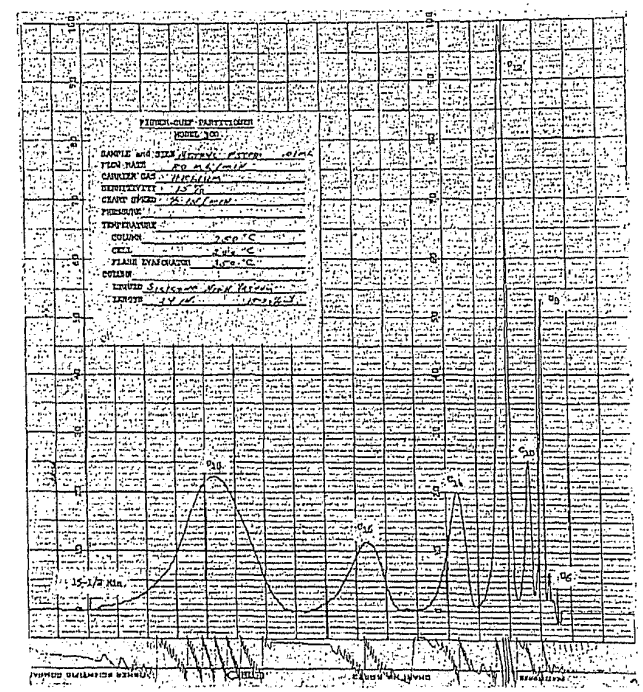

Fig. 4. Methyl esters.

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than the column temperature. The cell is mounted in such a way that any liquid tends to drain out of the cavity housing the thermistor. Components with boiling temperatures of 400°C have not been a problem.

Actually, if the thermistor does pick up a small droplet of condensate

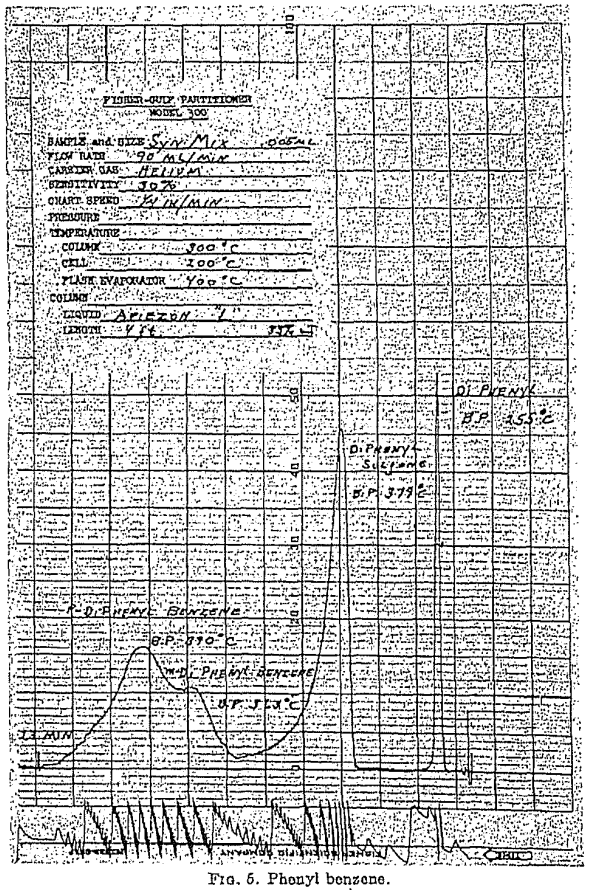

Fig. 5. Phenyl benzene.

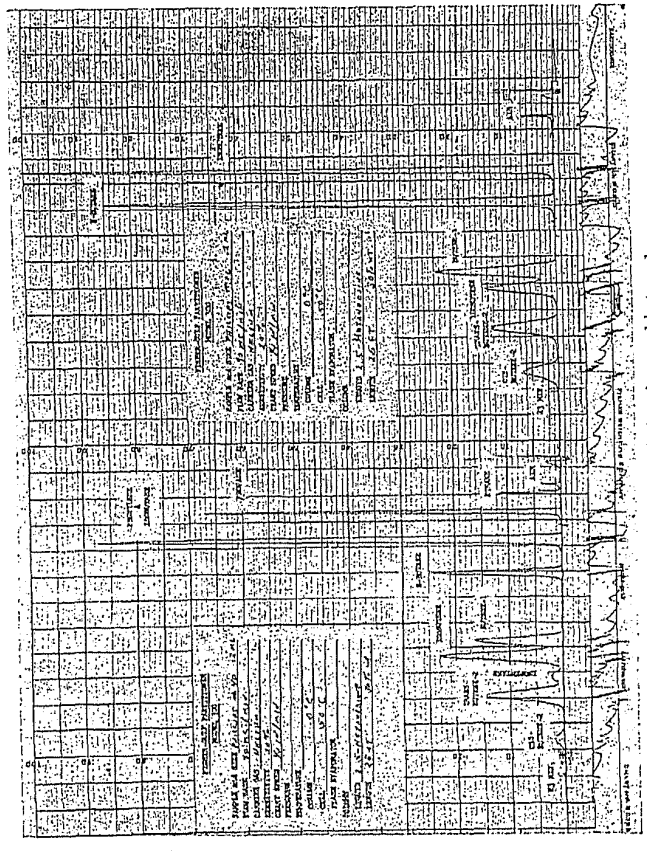

Fig. 6. Analysis of isobutylene and butene-1.

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(evidenced by very erratic recorder behavior), it can most often be dislodged by a solvent.

Automatic integration of the area under the curve has been widely accepted. However, with the pip type trace which we employ, it is difficult

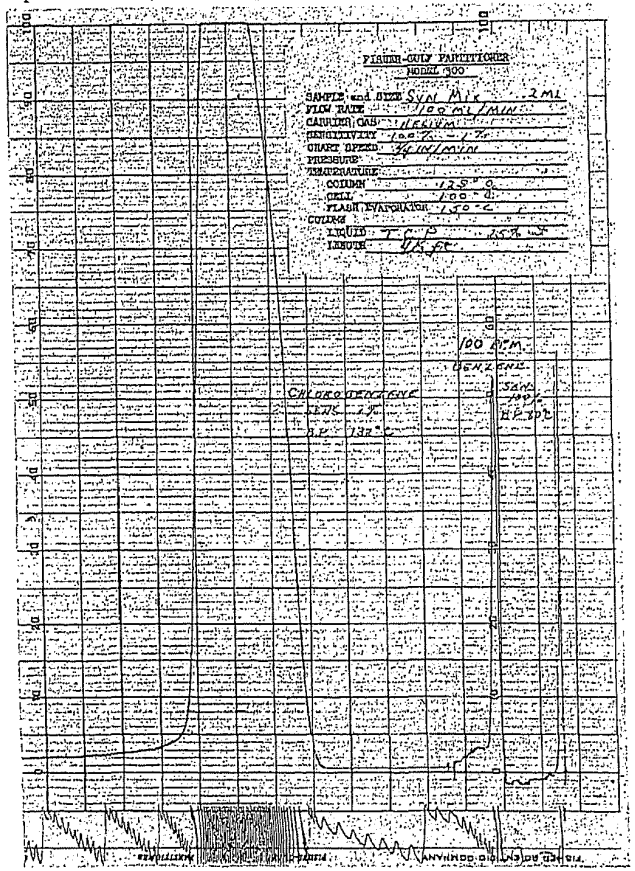

FIG. 7. Separation of benzene (100 ppm) from chlorobenzene.

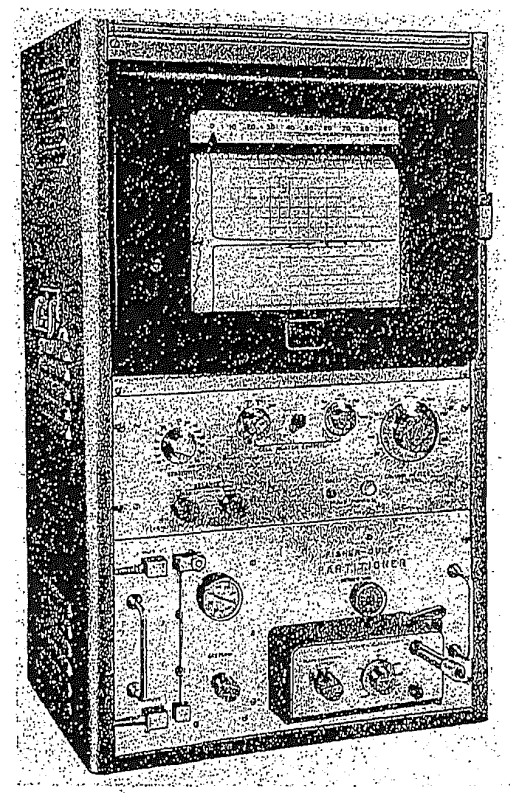

FIG. 8. Instrument.

to count the pips accurately at full scale deflection. A method of making a novel trace has been developed making it possible to count the pips more accurately. With the new trace it is possible to increase the integrator disc drive speed, thus increasing the number of pips per unit time.

There are many difficulties encountered in high temperature gas chromatography. Getting the sample into the system and vaporized quickly, and maintaining good sensitivity, are certainly real problems.

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Probably the most difficult one, however, is to find a liquid phase which will separate the sample into its various components and, in addition, "stay put" on the column. Here is a list of materials we have uncovered or heard about, which have proven moderately satisfactory.

1. Apiezon Grease "L"
2. D.C. Silicone High Vacuum Grease (Extracted with ethyl acetate)
3. Stearone
4. Polyethylene
5. Aromatic Extracts

Employing a few of the above liquid phases as packing we have carried out some separations of high boilers that indicate the type of results obtained at different temperature conditions. These are shown in Figs. 4 and 5.

The analysis of isobutylene and butene-1 has always been somewhat of a problem. Figure 6 shows this separation operating the instrument at 0°C. Analysis has also been carried out by changing the column temperature during an analysis.

Figure 7 is an example of the sensitivity that can be expected with this instrument in separating benzene from chlorobenzene.

A formal picture of the instrument is shown in Fig. 8.

Designing an instrument to overcome some of the mechanical and thermal problems has been a real challenge. The application of a high temperature unit to the analysis of high boilers surely presents an equal one.

The satisfactory routine analysis of such things as fatty acids, high molecular weight hydrocarbons, ketones, alcohols, etc., is sure to come in time with the introduction of high temperature gas chromatography apparatus. Great possibilities are evident in the clinical field. The use of reduced pressures in combination with high temperature certainly broadens the scope of application even more.

Discussion

Knoblauch (*Minneapolis-Honeywell Regulator Co., Pennsylvania*): What is the maximum pipping rate of your integrator?

Taylor: We have an input motor giving us an input of 8 rpm on a mechanical integrator with an output at full scale deflection of about 200 pips per minute.

Knoblauch: Based on previous questions in earlier sessions, 200 pips per minute seems to be on the slow side. I am wondering about your experience.

Taylor: I would definitely state that the more counts per minute that one can get, the more accurate the results will be.

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CHAPTER XXVII

Exploratory Process Gas Chromatography

T. L. ZINN, W. J. BAKER, H. L. NORLIN, AND R. F. WALL

Monsanto Chemical Company, Plastics Division, Texas City, Texas

INTRODUCTION

Interest in process gas chromatography at Monsanto led to the determination of several design parameters and operating conditions that were considered best and/or necessary for process instruments. These proved to be a guide for process applications of chromatographs, and are discussed below.

INSTRUMENT

The instrument consists of a thermistor type thermal conductivity cell, a thermostated air bath for detector and column, a rotary 6-way valve, and normally a ¼ in. diameter column. Design was kept as simple as possible, as shown in Fig. 1. For process applications a programing unit was found necessary to adjust to several ranges of sensitivity for ease of calibration to the several components in the stream. Experience has indicated that an automatic zero is usually essential, particularly in applications requiring high sensitivity. Almost every process stream has a minor component of interest which requires high sensitivity.

Thermistors

Thermistors have been used exclusively because of the sensitivities required. They made possible high sensitivity without voltage amplification or microvolt recorders. Average life has been from 6–12 months with cause of failures generally unknown. The replacement was not considered overly troublesome.

Air Bath

The air bath employs a conventional blower and heater usually with a bi-metal thermostat. A precision ±0.1°C thermostat is used for high sensitivity applications. Some insulation of the column and detector and addition of thermal mass makes the bi-metal thermostat adequate except for the most sensitive applications. Direct heating of the detector and column block appears to be simple but time was not found to explore this approach. A continuously adjustable thermostat has been found very desirable

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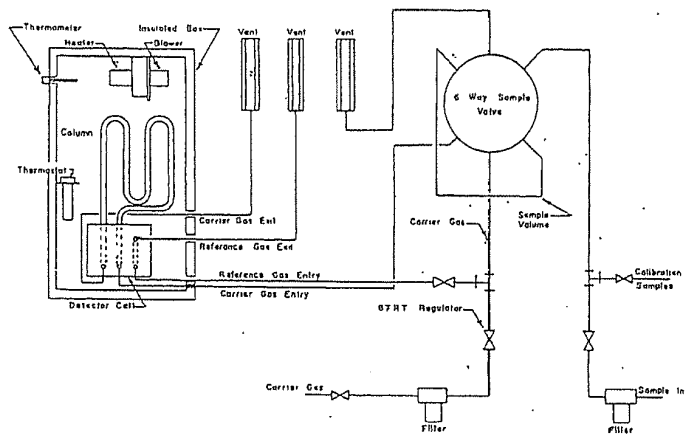

FIG. 1. Schematic of gas chromatograph.

to allow elution time adjustment to compensate for column aging. Thermostating the column and detector together was the simplest procedure, and well suited to process chromatographs.

Sample Valve

The sample valve is a conventional 6-way plug valve as shown in Fig. 2. This type was chosen because it requires less precision of construction.

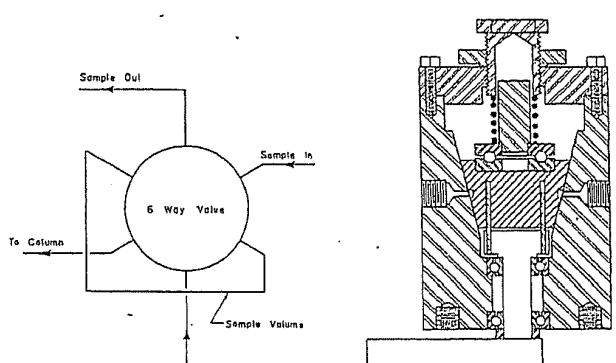

FIG. 2. Six-way sample valve.

The floating plug allows self alignment and the ball bearings were found necessary for long life.

Columns

Columns of $\frac{1}{4}$ in. tubing were used following general practice. Later exploration indicated that $\frac{3}{8}$ in. tubing gave almost equal resolution, was easier to pack and had less pressure drop so that the sample valve could be operated under lower pressure with less likelihood of leaking. No significant differences were observed between straight, spiral, or hair pin columns. The hair pin column is compact and is preferred because it is easy to form. Stainless steel columns were used when the sample stream was corrosive. The use of copper or aluminum is preferred where possible because stainless steel is difficult to form.

Flow System

The flow system employed is indicated in Fig. 1. The bypass to the reference thermistor results in less signal noise with valve actuation than when the reference thermistor is located at the elevated pressure in the carrier stream ahead of the valve. Experiment has shown that long tubes between column and detector, bends, right angles, and tee's have little effect on resolution. The conclusion was that close streamlined coupling is not necessary. Reasonable care with standard fittings is adequate.

Thermistor Location

Figure 3 presents the results of a study of thermistor position in a $\frac{3}{16}$ in. diameter carrier stream. With regard to peak symmetry and sensitivities the position of the thermistor is not critical. A 50% increase in resolution is obtained in moving from the edge to the center of the flow path. It is concluded that reasonable care should be taken to locate the detector in the center of the flow path.

Recording

Recording of the peak height in a process chromatograph appears to be the practical method of measurement. If the instrument stability is not adequate to allow use of peak height, then on a long term basis, with presently available equipment, the application is not considered practical. Nonlinearities resulting from peak height calibration have not warranted area calibration. While bar graphs offer advantages in data presentation they are not justified on the basis of chart paper saving alone. They offer complication in programing and fail to record seldom occuring new components that might be detected by the conventional chromatogram.

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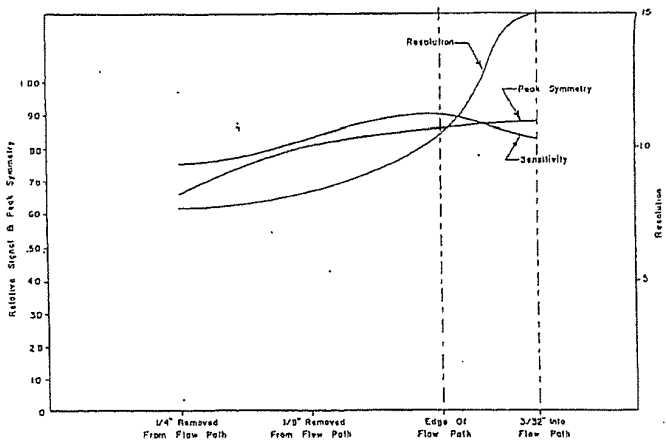

FIG. 3. Thermistor position study.

PROCESS EXPERIENCE

Experience in applying chromatographs to streams indicated some general desired design and operational characteristics. Specific column development will not be discussed, for each stream requires a column adopted to that particular problem. Adsorption columns are used for light hydrocarbons. However, pure adsorption columns tend to load with heavier materials often found in a process stream and the resultant change of elution time causes calibration and programing problems. The use of 1 to 3 % heavy oil pre-loading of these column has eliminated most of these difficulties while retaining most of their adsorption characteristics.

Columns requiring operation below 110°F are at the present time impractical for field applications in the Gulf Coast Area since this is the minimum practical thermostating temperature. Particular attention must be given to the volatility of the liquid phase of columns used in process instruments. Some that are quite usable in the laboratory will tend to drift in plant use.

Attention must be given to the change of elution time of peaks with change of relative concentration of major stream components due to the change in the nature of the column at equilibrium with these components. The effects of water are particularly bad, and even though apparently eluted in the program period, a considerable effect on elution time and hence on calibration and programing may occur. Adsorbed polar compounds can be expected to change the nature of the packing surface.

APPLICATION TECHNIQUES

The following techniques are advisable to obtain maximum reliability.

Sample

Overall analytical instrument performance cannot be better than the sample system; therefore, consider the requirements carefully and do the job thoroughly. The sample system should employ adequate filtering, i.e., 0.1 micron filters, and removal of condensables or drying, as required. It may be necessary to heat sample lines to avoid condensation. If condensables are present, care must be taken to have instrument vents which will not become loaded with liquid and apply back pressure on the detector and sampler.

Reference Checks

In the event of doubtful analysis the use of reference standards has proved to be the best possible way to isolate the source of trouble. If the instrument checks the reference as it has previously then the sample system or process is upset. A retained master reference standard against which routine reference standards can be checked is very valuable.

Installation

The instrument should be properly installed and sheltered from the weather to avoid extreme temperature changes such as direct sun light, rain, or hail. The shelter also makes maintenance possible during extreme weather conditions and reduces instrument down time.

These are standard procedures for any analytical instrument and have evolved through experience.

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