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NATHANIEL BRENNER

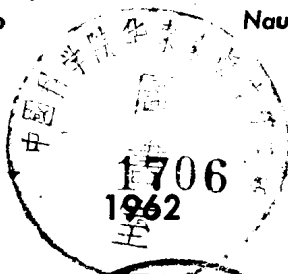
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FOREWORD

The following compilation of papers and discussions constitutes the proceedings of the Instrument Society of America's Third International Symposium on Gas Chromatography. The Symposium was held at the Kellogg Center for Continuing Education, Michigan State University, June 13-16, 1961.

The meeting was organized into a series of morning and evening sessions, each of which contained several papers relating to a particular area of instrumentation or application of gas chromatography. The afternoons were devoted to informal meetings for questions and discussion pertinent to each group of papers or on any subject of common interest to the participants.

This volume contains the final completed text of each paper presented at the Symposium, and appendices which include the edited transcripts of the informal discussions on these papers as well as the edited transcripts of discussions on Preparative Chromatography and Food and Flavor Analysis. A Bibliography of Gas Chromatography is also appended which is a continuation of the reference list contained in the proceedings of the previous Symposia.^{1,2} We trust that this volume will further contribute to the efforts to advance the gas chromatography technique made under the auspices of the Instrument Society's Analysis Instrumentation Division.

The success of the Symposium was largely a result of the cooperation and efforts of the session chairmen, discussion leaders, and the authors and participants. We also wish to express our thanks to Mr. Thomas Collins and the staff of the Kellogg Center for their efficient and considerate management of arrangements, and to Mrs. Jane Lahey for her competent handling of the myriad secretarial problems involved in organizing a symposium of this magnitude.

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INTRODUCTION

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The subject chosen for this introduction is "Gas Chromatography and Invention." Since the inventions that have made chromatography what it is today are well known, I would like to speculate about the yet unmade inventions.

I should like to recall first Professor Keulemans' remark that chromatography has just completed the cycle. Chromatography started with biochemistry. There was liquid chromatography at first. Later in 1940, Dr. Martin invented gas-liquid chromatography. Then, physical chemistry took a hand to guide the choice of more favorable partitioning agents. Physics played the crucial role of furnishing the various detectors, various forms of bolometers or catharometers, the density balance of Dr. Martin, the flame ionization detector of Dr. McWilliam, the Argon detector of Dr. Lovelock. Communication engineering contributed the formalism of the Telegrapher's Equation to bring a fresh viewpoint on the partition process. This, together with the concept of the performance index (P.I.) led to the realization that the pneumatic resistance of a column is equally as important as the plate height, and this realization led in turn to the idea of using an open tube in order to minimize the pneumatic resistance. And now the cycle completes itself with a return to biochemistry, for the art has been so dramatically advanced with the several inventions of the last few years that we may set as our eventual goal the partitioning of compounds with more than 50 carbon atoms. Much smaller molecules are of interest to the petroleum engineer, the perfume and food flavor industrialists, but with molecules containing 42 carbon atoms today, as you have heard reported, and the prospect of larger molecules tomorrow, we shall go back to the biochemists who gave us chromatography, and we shall present them with a real tool.

Let us begin with the small bore tubular columns, some of which have a P.I. inching toward the less-than-one poise region, but most of which have a P.I. of a few poises. The contribution of the oil diffusion term to the HETP is mostly responsible for this departure from the optimum column, and in order to reduce it, several possibilities are open, two of which are particularly attractive. The first, which I mentioned in Amsterdam three years ago, is to use porous wall tubes in which the in-

creased surface permits the use of a thinner oil layer, and these porous wall tubes can be formed either by adding something to the internal surface of a smooth tube, or, perhaps more elegantly, by leaching out the inner surface of a smooth tube so as to obtain a porous inner surface. The difficulties of forming such porous wall tubes must be very great, since very few results have been reported during the last three years.

A second approach is to use suitable fixed phases in which the oil diffusion term is not reduced at the expense of the capacity ratio k . Now, I am using here a new name for an important quantity which, as far as I could determine, has been nameless until now. The partition coefficient has been used in the past to describe the ratio of the densities of a component in the oil phase and in the gas phase. It is a scientific concept, and when you multiply that coefficient by the ratio of the oil volume over the gas volume you obtain what I propose to call the capacity ratio, k , which is one of the most important engineering concepts in a gas chromatographic column.

To come back to our subject, Dr. Averill has found that a class of chemicals, essentially long carbon chains with one very polar end, have the property of inactivating the active sites on the solid surfaces in chromatographic columns, thereby reducing absorption which is responsible for tailing of polar materials. As Dr. Averill has indicated, it is as if these long carbon chains hook themselves on adsorption sites with their polar end and form a kind of submicroscopic velvety wall on the inner surface of the tube.

Another possibility, now shown to be quite practical by the elegant work of Mr. Desty, is the use of very thin oil coatings in tubular columns used below room temperature, utilizing the circumstance that, at reduced temperatures, the partition coefficient increases more rapidly than the diffusion time. This is only one of the several advances in the practical use of tubular columns which Mr. Desty has reported, and which I find personally most gratifying.

All of these techniques are aimed at lowering the P.I. until the theoretical limit of around one-tenth poise is approached. But, in order to be fair, I should include a few words about possibilities of, shall I say, fooling the P.I.; that is, of devising arrangements in which the P.I. concept is no longer a limitation. I have two such possibilities in mind.

The first, which was devised by Saunders of Yale University, is essentially applicable to the separation of two or more components with nearly the same partition coefficients, and it goes like this. There are two columns in series, and injection takes place at the beginning of the first column. After the components have passed the first column and are in the second column, the source of carrier gas is switched to the be-

ginning of the second column, the end of the second column is connected to the beginning of the first column, and the end of the first column becomes the outlet of the system. When the components have flowed back into the first column, the original switching arrangement is restored, and the components are thus kept circulating in the loop until, hopefully, they become separated before they have spread across the entire column. If we can switch a hundred times, we obtain the separating effect of a single column a hundred times as long as the columns actually used, but the pressure required is only that required for two columns, and the theoretical P.I. of the system is one-fiftieth that for a single column. A spectroscopist would be tempted to say that this arrangement bears to the conventional one-column system the same relationship which exists between an interferometer or an echelon and a grating spectrometer.

The other arrangement which escapes the limitations imposed by the P.I. has been, I believe, conceived by Dr. Martin. In this arrangement, several columns, which may as well be tubular columns, are connected in series. Each connection consists of a flexible tube which is given a peristaltic motion with a roller, so that it acts as a booster pump. This has two advantages: first, you do not need an excessively high inlet pressure, and second, the optimum velocity is higher at lower pressures. Enormously large numbers of plates will be achievable in this manner, but, there is a "but": this arrangement will work well only if the oil diffusion time can be made small, and this should act as an extra incentive for the development of nearly ideal tubular columns.

So far, I have talked only about open tubular columns, which are essentially analytical columns, not only for qualitative analysis, but also for quantitative analysis, as indicated by the good results which Dr. Halász has obtained. Now, I would like to do some speculating about packed columns, which, as preparative columns, may never be displaced by the tubular columns. Last year, at Edinburgh, I suggested that packing grains with hard centers may serve to reduce the mass transfer terms in packed columns. I cannot report that such packing material has been actually produced, but interesting progress in this direction has been made by Professor Keulemans who has utilized, in a Dutch candy factory, the very equipment in which magic balls are produced, those round candies with ten to fifty layers of different colors. These candies are made in large, slowly rotating tumblers; and by using about 80% crushed brick and 20% waterglass, Keulemans has produced packing grains of unusual sphericity, about ten thousandths of an inch in diameter. As is often the case in new developments, these packing grains turned out to have advantages which were other than those hoped for.

The advantage of these spherical particles turned out to be great uni-

formity from column to column. On the other hand, their performance index was poor, uniformly poor. In retrospect, this is easily explained. Spherical particles tend to pack closely, so as to occupy theoretically 76% of the available space, while only 24% is left for the gas passages. They cannot be packed more closely without crushing. Therefore, a column is formed, which it would be difficult to make worse, and uniformity of performance can be equated with uniformity of worseness. Where do we go from here? Perhaps we should add to the requirement of hard center particles the further requirement that these particles should be as jagged as possible, so as to elbow each away from the other, in order to provide more air passage. But other possibilities may be worth trying. Why not uniform flat particles which are given a hard helicoidal twist, or particles in the form of doughnuts, or very short elbow macaroni, or gnocchi? Why not go to the spaghetti manufacturers or even the puzzle makers, who are used to thinking in terms of unusual three-dimensional configurations, and give them our requirements which are: uniform particles which pack uniformly in the statistical sense, and which have a thickness which is smaller than the average dimension of the open spaces in between.

Before leaving the subject of columns, I would like to include just a few words about temperature programming, merely to indicate what I believe to be a likely rigorous approach to an intriguing problem. I should like to start by saying that if a column is temperature programmed, the temperature of the entire column should be raised uniformly, because any attempt to make a temperature front travel along the column is roughly equivalent to reducing the effective length of the column to the length of the front. Now if the temperature of the column is raised uniformly and linearly from, say, room temperature to a terminal temperature at which it is kept for the end of the run, it can be shown that the following three problems can be treated by a rigorous nomographic method.

First, knowing the capacity ratio of a given component as a function of temperature, the rate of temperature rise, and the terminal temperature, determine the elution time of this component.

Second, the reverse: knowing the capacity ratio as a function of temperature, determine the rate of temperature rise to obtain a given elution time.

And third, given the activation energy of a component relative to the fixed phase, determine, from its elution time and from the elution time of an inert component for a given temperature program, what its capacity ratio would have been at room temperature.

All three of these important problems appear to be solvable neatly

and rigorously by a nomographic method, and the solution of the last problem should lead to a procedure for comparing the partition coefficients of high boilers on a standardized basis.

So much about the columns. What about the detectors? It is quite obvious that the greatest demand on detectors has been for increased sensitivity, and will continue to be so, until we can count individually every heavy molecule of an organic high boiler heated to just below its temperature of decomposition. Detectors based on the catharometer principle fall far short of the mark. By pushing a catharometer to the theoretical limit, we calculate that the smallest fraction which can be detected in a stream of helium is of the order of the square root of kT over the energy dissipated in the catharometer during the time of a single measurement, and this falls more than ten orders of magnitude short of detecting single molecules. There seems to be little doubt that the most sensitive detector will be based on some ionization phenomenon. So far the flame ionization detector of Dr. McWilliam and the argon detector of Dr. Lovelock have had a close race, with the argon detector somewhat ahead. Yet, both are still some six to eight orders of magnitude short of the goal of individual molecule detection. It can be speculated that increased knowledge of the pertinent ionization phenomena, and especially of the ionization of large organic molecules caused by the metastable states of certain gases, perhaps coupled with the principle of the Geiger counter, will lead to the invention of detectors with ultimate sensitivity. Perhaps, also, the new understanding of the energy transfers which are utilized in gas lasers will help spark the invention of these new detectors. And, of course, these new detectors will bring new problems, such as the background noise due to elution of the liquid phase, or to impurities in the carrier gas. This should, in turn, spark a revival of interest in the adsorption column, which may well take the form of an open tubular column with an adsorptive coating. Such columns could turn out to be very attractive, because they would be utilized in the linear region of the isotherm for the extremely small vapor pressure of large organic substances.

This concludes what I wanted to say on gas chromatography and invention. It is always good fun to try and chart a likely path of development, and I must prepare myself to take it in good fun also, when future developments will make clear how far off the mark my guesses will have been.

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