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Technical Progress Report
on
FUNDAMENTAL STUDIES OF SEPARATION PROCESSES

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ABSTRACT

Three technical reports have been prepared which deal with the subjects of optimization in supercritical fluid chromatography, the gas chromatographic fractionations of the isotopes of carbon and oxygen in carbon monoxide, and a method for measuring the information content of a complex chromatogram. A fourth report, in preparation, compares different liquid chromatographic column packings with respect to the fractionation of a mixture of oligomers of polystyrene.

Two other studies are relatively far along. One is a study of the recycle mode of operation as applied to gas chromatography. The second one deals with the fractionation of vanadium compounds in Boscan petroleum crudes.

Finally, there are three other studies that are just getting started. The first involves an examination of pattern recognition as applied to coal tars and petroleum pitches. The second is exploring the possibility of using high-pressure gas chromatography to characterize carbon blacks and charcoals. The third is the long-delayed study of column-switching techniques that do not involve recycle.

INTRODUCTION

This research program covers a number of areas in the field of separations most of which relate either directly or indirectly to optimization. One direction that the optimization takes is to study relatively uncommon methods that are of potential importance to the field of separations, e.g., the recycle mode in gas chromatography, column-switching techniques, and supercritical fluid chromatography. A second aspect of optimization involves the use of samples that are very complex mixtures and, at the same time, are of practical importance. Coal tars and commercial polymers fall into that category. In a third category there are some cases, such as those represented by isotopic fractionations, which represent relatively simple mixtures in which the difficulty arises because the behavior of the species is only slightly different.

With an eye toward developing methods for evaluating the results obtained with very complex mixtures, a study has been made (and is continuing) on the application of information theory. The goal is to find a simple quantitative way in which the results of a very complex chromatogram can be expressed. Another goal directed toward separations of complex mixtures involves an evaluation of pattern recognition techniques as applied to coal tars and petroleum pitches. Finally, there are the separations, themselves. There is a continuing study of the fractionation (and later identification) of vanadium compounds in Venezuelan petroleum. There is also an exploration

of the possible use of high-pressure gas chromatography for the characterization of carbon blacks and charcoals.

This report will take up the studies in the same order as they were in last year's proposal so as to facilitate a comparison between our goals of last year and our accomplishments at this time. Before discussing the results, however, it is important to note that this research program derived a significant fraction of its financial support from the University. First, two graduate students received most of their financial support in the form of University fellowships. Second, there was direct financial support from the Chemistry Department for payment of the very large computer-repair bill that resulted from several months of part-time effort by the manufacturer of the computer.

RESULTS

Information Content of a Chromatogram

The information content of analytical results is a subject that has been considered for a number of years, especially by chemists in Europe (1). When applied to chromatograms, information content should be useful as a measure of the separation when one is trying to optimize. It should also be useful as a basis for comparing the results from chromatograms of quite different systems. Like other methods of optimization, information content requires that specific criteria be defined as a basis for determining whether or not information is con-

tained in a given data point. Likewise, constraints can be imposed on the system, such as a maximum time in which to complete the separation or a maximum oven temperature.

In brief, the method developed in this study followed the original work of Shannon (2) in that it determined the amount of information contained in a single data point and then summed up the information from each of the points in order to determine the total information content of the "message" (chromatogram).

The first part of the study was devoted to simulations in which the effects of peak shape, retention time, and noise were evaluated. Then, real gas chromatographic analyses were performed using mixtures of n-alkanes and also a sample of regular gasoline. Especially in the latter case, the intention was not to obtain the best possible resolution but merely to observe how changes in experimental variables, together with the resulting chromatograms, related to an experienced chromatographer's evaluation of the "goodness" of the chromatogram.

The present algorithm clearly proved to be easy to use and quite versatile. Although there are obvious ways in which it can be improved, such as including weighting factors for selected variables, it has considerable promise. The detailed results are presented in a report no. DOE/ER/00854-25. Further studies are currently in progress.

Multiple Columns

High-speed, high-precision column switching. As indicated in the proposal, the goal of this study is to push this technique, which is not new, toward faster gas-chromatographic separations under isothermal conditions by taking advantage of the fact that two or more columns can be used in parallel or in series. Isothermal operation could be a disadvantage with respect to the limited range of boiling points that can be handled by a given column in a reasonable time. However, isothermal operation has an advantage over a programmed-temperature operation in that successive samples can be injected without an intermediate delay for cooling the column to the starting temperature.

This program was dropped when the repair period for the computer system proved to be unexpectedly long. As a result, it is just now being reactivated. The goal is to test the principle using packed columns together with a series of simple solutes, such as some of the homologous n-alkanes.

Recycle gas chromatography. As indicated in the proposal, the ability to pass a sample from one column to another and then back again into the first provides, in principle, the equivalent of a very long column that has only a moderate pressure drop. The fact that the number of plates that can be obtained by a pair of packed columns in a recycling system approaches that attained by the best capillaries makes the technique of great interest, especially as a preparative tool.

The key to its successful operation for a large number of cycles has been shown independently by a Russian group (3) and by our laboratory (4) to depend on having the pressure at the exit above atmospheric. In addition, our earlier experiments indicated that it might be advantageous to use column packings of larger particles than had previously been reported.

During the past year, important findings have been made with respect to both particle size and maximum exit pressure. First, a 1/4" column has been successfully packed with 20/30 mesh Chromosorb to yield a higher plate efficiency than the best reported for a 1/8", 45/60. In an effort to determine whether one can gain further efficiency by eliminating diffusion within the particles, solid glass beads, 1 mm in diameter (approximately 20 mesh), are now being studied.

The second finding relates to the optimum level of the operating pressure. Our previous study (4) was limited to 90 psi by the precision pressure transducer that was available. However, a new transducer permits pressures up to 200 psi (and higher) to be measured if desired. To date, it appears that, although there are small differences between different column packings, the column efficiency appears to reach a flat minimum in the region between 90 and 135 psi--when using porous particles. It remains to be seen whether use of the solid beads will alter that finding significantly.

Multiple Detectors in Liquid Chromatography

This study was designed to evaluate the effects on peak shape of having two or more liquid chromatographic detectors in series. A year ago, this study was in its final stages when the computer, which was being used to control the experiment as well as to acquire data, broke down. By the time the computer had been repaired, the postdoctoral research associate who was doing the study, had already left for a teaching position. This experiment will be set up again and the few remaining runs completed.

Phase Composition/Density

As pointed out in the proposal, conventional gas chromatography derives almost all of its selectivity from the stationary phase. In high-pressure gas chromatography, including supercritical fluid chromatography, both the density and the composition of the mobile phase affect the chromatographic mobility of the species. Hence, high-pressure gas chromatography closely resembles liquid chromatography. In the section of the report that follows, studies using high pressure gas chromatography as well as gradient elution liquid chromatography will be discussed.

Supercritical chromatography, as its name implies, is carried out above the critical temperature and critical pressure of the mobile phase. In the present study, n-pentane that contained 5% isopropanol was used as the mobile phase.

The pressure was programmed linearly to increase the density of the mobile phase, a property that governed its ability to "dissolve" the components of the sample.

In order to evaluate the effects of operating variables on column efficiency, a commercial preparation of polystyrene was used that consisted of a large number of oligomers. Variables studied were the flow rate of the mobile phase, the particle size of the column packing, the column length, and the rate of programming the pressure. As pointed out in the enclosed report, DOE/ER/00854-23, the key factor was the ratio of the programming rate to the flow rate of the mobile phase. It was interesting to find that resolution improved with flow rate up to the limit of our particular apparatus. Perhaps, in part, because the conditions giving optimum resolution could not be attained, the fractionations that were observed did not approach the degree of separation reported below using reverse-phase liquid chromatography.

Another brief study involving supercritical pentane has been carried out at the suggestion of James Petty and David Stallings of the Columbia National Fisheries Research Laboratory. In brief, they have found a preparation of carbon black to be very efficient for the collection of trace concentrations of a wide variety of aromatic species, such as those found in insecticides, pesticides, and polyhalogenated aromatics. While our scouting experiments clearly demonstrated that some of the more tightly adsorbed species could, indeed, be desorbed using

high-pressure pentane, that mobile phase also attacked the carbon black. The result was a high and continuously varying background, especially at supercritical pressures. Hence, even if the sought-for compounds could be removed in this way, there would be large variable concentrations of background material present on which further separations would have to be performed.

Returning to the fractionation of mixtures of polystyrene oligomers, the results from gradient elution liquid chromatography were much more promising than those from programmed pressure supercritical fluid chromatography. To date, the best resolution by supercritical fluid chromatography of 2200 molecular weight polystyrene produced 40-plus peaks in a 20-hour experiment using an apparatus that maintained the flow rate constant while the pressure was programmed upward (5). In our liquid chromatographic study, silica and four different surface-derivatized silicas were used. The nitro derivative, which resolved 43 components, and silica, which resolved 41 components--each in a run taking less than two hours--were clearly superior to the rest. The amino, octadecyl, and cyano derivatives produced 25, 19, and 10 peaks, respectively, under similar conditions. By adjusting the operating conditions on going from one column packing to another, some improvements would undoubtedly have resulted for the last three columns.

A universally important variable proved to be the composition of the solvent used for the sample. Use of too good a

solvent greatly decreased the resolution that was attainable. In addition, it greatly extended the pretreatment period required for the silica column. The detailed results of this study are currently being written up for publication.

Another liquid chromatographic study involved a different type of complex sample, Venezuelan crude oil, which contains a large number of vanadium compounds. These are usually porphyrins of different types. As reported in last year's proposal, a paper had just been published (6) in which promising separations were reported using a column packing of silica. Although we were able to improve somewhat the overall fractionation, no major gain was made. As a result, because a variety of derivatized silica packings are now available in our laboratory, the present plan is to extend that study to include those packings. The derivatized silicas are easier to recondition following a gradient-solvent elution, and they offer the possibility of greater selectivity. Meanwhile, other fractions of the crude are being explored for vanadium-containing species.

The final study in this section of last year's proposal should really have been in the following section ("Other Studies"). It deals with the isotopic fractionations of carbon and oxygen in carbon monoxide. In brief, on chromatographic columns packed with silica, the carbon isotopes fractionated to approximately the same extent as in carbon dioxide. However, the separation of the oxygen isotopes was much smaller in carbon

monoxide, suggesting that hydrogen bonding had contributed substantially to the larger fractionation observed when using carbon dioxide.

On a column of elemental nickel, formation of nickel carbonyl increased the fractionation of the carbon isotopes by roughly an order of magnitude. However, the difference between the oxygen isotopes was also increased to a noticeable extent. The enhanced fractionations undoubtedly reflected the strong chemical interaction involved between the nickel and carbon atoms. These results are discussed in more detail in DOE/ER/00854-24.

Other Studies

None of these studies were started. However, there is a strong possibility that a new graduate student may elect to work on the effect of the chelate/anion moiety on the sensitivity of the atomic absorption procedure for determining vanadium (7).

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