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MASTER

PROGRESS
REPORT

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FUNDAMENTAL STUDIES OF SEPARATION PROCESSES

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TECHNICAL PROGRESS REPORT
ON
FUNDAMENTAL STUDIES OF SEPARATION PROCESSES

L. B. Rogers

ABSTRACT

During the past year, studies have been initiated in the following areas: information content as a means of describing chromatographic separations, effects of operating pressure and particle size on the efficiency of recycle gas chromatography, comparison of new liquid chromatographic column packings (and solvent combinations) for difficult fractionations as represented by oligomeric polystyrenes, fractionations of the isotopic species of carbon monoxide, and complex mixtures of vanadium porphyrin complexes found in Venezuelan crude oils. In addition, a study of the fractionation of oligomers of polystyrene using supercritical fluid chromatography was completed and another on the effects of multiple (in series) liquid chromatographic detectors on chromatographic peak shapes is nearing completion. Finally, the effects of flow rate and dead volume on peak shapes obtained in steric-exclusion chromatography have been examined using two different methods for data analysis.

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INTRODUCTION

Each of the studies in this report has been discussed in the order in which it was found in the Proposal. In that way, the reader should be able to follow more readily the agreement between the plans of one year ago and the accomplishments to date. As indicated in the abstract, studies have been started in several new areas.

An otherwise hidden aspect that deserves mention among the accomplishments of the past year has been the reconditioning, and in several cases upgrading, of our equipment. For example, our quadrupole mass spectrometer, which has been used to follow chromatographic separations of isotopes, is now being used to study isotopic species of carbon monoxide. The fact that carbon monoxide has a mass of 28 meant that extensive reworking of the vacuum system was required so as to minimize the amount of nitrogen, also mass 28, in the system as a result of tiny air leaks. To cite a second example, the performance of the sampling valve and also the thermal conductivity detector had to be upgraded so that the gas chromatographic recycling system could be operated at higher pressures. Finally, the continuing goal of computer-automating more of our equipment has steadily progressed. New capabilities for computer control of our chromatographic systems as well as for data acquisition have been added. As a result, we are able not only to obtain better data but to manipulate it in ways that were not possible before.

Finally, it is worth noting that one of the graduate students who will be completing the work for his Ph.D. in September 1978 was supported during the past academic year by a University fellowship. Fortunately, two other students will be supported in the same way during the coming academic year, while working on studies in the proposed extension of this Contract.

RESULTS

Problems Related to Energy Sources

Vanadium in Venezuelan crudes. The poisoning of catalysts used in petroleum refining by volatile vanadium complexes of the porphyrins has long been known. Recent evidence has indicated that there are not only different types of porphyrin complexes but also members of different homologous series (1, 2, 3). Our interest in this problem arises in two different ways. First, it is a challenging separation because of the complexity of the mixture. Second, if individual compounds can be isolated, characterized, and quantitated, it may be possible to understand better the formation of the petroleum itself as well as the probable source of these compounds.

During the past year, extensive modifications have been made to an old flame emission spectrometer so as to make it suitable for both atomic emission and atomic absorption measurements. For example, a feedback circuit has been incorporated into the power supply for the hollow-cathode lamp so as to give better current regulation; an adjustable frequency modulation (square-wave) unit (4) and a suitable lock-in amplifier (5) plus a logarithmic amplifier have been assembled for atomic absorption measurements. All of these modifications have recently been shown to be operating quite satisfactorily. As a result, it is now possible to pass the eluent from a liquid chromatographic column directly into an on-line flame spectrometer for detection of vanadium.

In principle, there should be no interference from hydrocarbons from which the vanadium compounds may have been incompletely separated. However, such measurements will, at best, be semi-quantitative for two reasons. First, if elution is accomplished by using a solvent gradient, it would

be surprising if the sensitivity for vanadium did not change with solvent composition. Second, it has been shown recently that the nature of the vanadium porphyrin complex itself can influence the sensitivity when dissolved in a given solvent (6). As a result, accurate quantitative results for vanadium cannot be expected when it is measured on-line. Instead, if accurate results are required, individual fractions will probably have to be converted chemically to the same inorganic salt--recognizing the possibility of volatility losses of vanadium during both the digestion and ashing steps.

Over the years, a variety of procedures have been reported for the separation of vanadium-rich fractions from crude oil. Ordinarily, the asphaltene fraction is isolated first and then the vanadium compounds are separated from it by liquid extraction. When samples of such an extract were spotted on thin-layer plates coated with activated silica, four distinct red-pink porphyrin bands were formed as well as several other darker bands. While this separation was being scaled up for use with packed columns, a paper was published (3), confirming the idea that silica columns were capable of fractionating the vanadium porphyrins. Since that time, we have been able to show that those separations can be improved by using a non-linear solvent gradient. At the present time, work is being continued not only with the silica and the octadecyl columns (3) but also with other column packings.

A brief exploratory study has also been made using supercritical fluid chromatography. Such an approach should be useful not only because the vanadium complexes are generally considered to be volatile but also because in an early study using supercritical fluids, nickel porphyrins were found to be mobile (7). A preliminary study has shown that, using supercritical pentane, a broad non-retained peak was quickly eluted. While this may

have been due in part to solvent, there is a good chance that some vanadium species may also have been present. Unfortunately, the vanadium-specific detector had not yet been brought into operating condition at the time this experiment was done, but the experiment will be repeated now that the detector is available.

A new student has recently started to make capillary columns and is testing his coatings using standard procedures. We plan to check the applicability of those columns to the separations of vanadium complexes.

Silica scaling by geothermal brines. The proposed study of the solubility of silica as a function of temperature, pressure, and partial pressure of carbon dioxide (pH) has not been started. The P.I. has since heard that "someone" was already doing such a study. Our work will not be started until that point can be clarified so as to minimize duplication.

Unusual Chromatographic Techniques

In general, we have been interested over the years in exploring the basic aspects of little-used chromatographic techniques, especially those that appear to be valuable for carrying out otherwise difficult separations. For example, large molecules, especially mixtures of oligomers, represent one type of difficult separation. In addition, isotopic species and enantiomers represent difficult mixtures. The two techniques with which this report is concerned are supercritical fluid chromatography and recycle chromatography. In the former, a dense fluid is used above its critical temperature to "dissolve" otherwise non-volatile species. In the latter, two columns are used in series. As soon as the volatile species have passed from the first column into the second, the inlets and exits are changed so that the species eventually pass

from the second column back to the first. In effect, one has a long column of adjustable length which, however, has a relatively low pressure-drop. Surprisingly little has been done until quite recently on the basic aspects of these techniques.

Supercritical fluid chromatography. Our laboratory has recently published results of a study involving the fractionation of a mixture of oligomers found in a monodisperse sample of polystyrene (8). In that publication it was pointed out that pressure-drop was an important variable, and that the heavier polystyrene oligomers appeared to be serving as a partitioning phase for other fractions. As a result, studies of the influence of particle size and column length were carried out. Unfortunately, Klesper and Hartmann (9) had many of the same ideas and reported them in an elegant study. It is important to note, however, that a typical separation lasted 20 hours. We believe that it may be possible to obtain the same type of information in a shorter time, but that remains to be demonstrated.

Recycle Gas Chromatography. The recycling mode has been extensively used in liquid chromatography but has been used relatively little in gas chromatography. Only recently has it been studied with the goal of optimizing its performance in gas chromatography using elevated pressures (10, 11). As a result, it now appears that the total number of plates available may be of the same order as those found for capillary columns, thereby making possible the performance of very difficult separations. However, because recycle chromatography makes use of packed columns, much larger samples can be handled. As a result, a "preparative-scale" separation of the isotopically substituted species, 1, 3, 5-trideuterobenzene, from normal benzene has been demonstrated (12).

Earlier work in our laboratory indicated that there might be advantages to be gained by working at higher operating pressures and by using larger particles of packing materials (11). Special arrangements have been made to obtain from the manufacturer fractions of material containing particles as large as 20 mesh. After showing that some of the earlier data could be duplicated, the studies have been extended to the next larger cut of mesh size with encouraging results. On the other hand, the use of pressures above 100 psi did not have any effect on the column efficiency because of the low pressure drop. Hence, attention is currently focused on longer columns where the pressure drop is larger for a given rate of flow.

High-precision, high-speed column switching. As indicated in last year's Proposal, much work is now being directed toward faster separations. While the idea of using two or more columns for an analysis is not new, the applications have been rather limited. We believe that this is due, in part, to a failure to examine carefully the potentialities of this technique.

A graduate student has recently elected to start this project and has designed a simple system involving only two different columns. Work will first be done isothermally using a small number of compounds from each of two homologous series.

Difficult Separations

Oligomers of polystyrene. As indicated earlier, mixtures of oligomers represent a very difficult type of separation. Supercritical fluid chromatography has been used very successfully, especially in the molecular-weight range below 5,000. However, during the past two years, there has been increasing attention paid to oligomeric separations in the liquid chromatographic literature.

The latter approach is clearly more appealing because the operation of the equipment is simpler and because chemists are more familiar with liquid chromatography. Most important, however, is the availability of new column packings.

The advertising literature has shown examples of separations involving not only different column materials but also different solvents. In order to compare better the capabilities of the different packings, a study has been begun in which "polar" packings are compared under the same or very similar conditions. Non-polar packings are also treated in an analogous fashion using a different combination of solvents. In that way, the behavior of the packing itself is more clearly defined relative to other similar materials.

Our initial studies employed a monodisperse polystyrene having a nominal molecular weight of 2200, a sample which much experience had already been obtained using supercritical fluid chromatography. Using a linear gradient of tetrahydrofuran in hexane, pure silica resolved 30 oligomers (out of a total of approximately 46) while an amino-bonded silica resolved 24 oligomers. Hence, from the standpoint of resolution using those particular solvents, pure silica was clearly the best. On the other hand, if one's interest was primarily in the lighter oligomers, the amino column was best because it could be reconditioned rapidly between runs. For the C_{18} -bonded silica a tetrahydrofuran-water eluent had to be used, and it resolved the fewest oligomers, 19. However, it required virtually no reconditioning between runs. Examination of an 800 molecular-weight sample of polystyrene is being run so as to check the above trends. In addition, non-linear gradients will be explored so as to extend the upper limit of the fractionation.

Isotopic species of carbon monoxide. An earlier study from our laboratory (13) reported on the fractionation of both the carbon and oxygen isotopes in carbon dioxide as a result of adsorption by silica and by Porapak Q. A computer-controlled quadrupole mass spectrometer followed the chromatograms of the species in terms of masses 44, 45, and 46. Relatively short chromatographic columns could be used since the different species did not have to be chromatographically resolved in order to measure their relative retentions.

The goal of the present study is two-fold. First, carbon monoxide will be examined under as close to the same conditions as possible so as to determine the effect on physical adsorption of the loss of the oxygen from carbon dioxide. Second, fractionations obtained using nickel metal as an adsorbant should produce even greater differences due to the chemisorption of carbon monoxide on nickel.

Preliminary experiments have shown that carbon monoxide is sufficiently strongly adsorbed on silica to permit accurate measurements of relative retentions to be made, especially when the chromatographic column was cooled 20-50°C^o below room temperature. Under the same conditions, a column of Porapak Q retained carbon monoxide much less, so comparisons with the behavior of carbon dioxide will be difficult to obtain. On the other hand, alumina has been found to retain the carbon monoxide somewhat stronger than silica so comparisons of two adsorbants will be possible.

Preliminary experiments have also been run using nickel metal, and the results are quite promising. Carbon monoxide is strongly adsorbed at temperatures less than 80°C. However, it appears that carbon monoxide is mobile at a temperature close to 100°C where nickel carbonyl is known to be approximately 6% decomposed. If the temperature is higher than 180°C,

any traces of oxygen on the surface of the nickel tend to form carbon dioxide. Hence, it should be possible to use that reaction to monitor the presence of oxygen in the system.

As soon as the finishing touches have been put on the computer software, the isotopic studies of carbon monoxide will be ready to go. Only a recent extended breakdown of the computer system has prevented the reporting of preliminary fractionation data at this time.

Broad Aspects of Chromatography

Peak shapes. The chief goal of this study has been to examine different ways of analyzing chromatographic peak shapes and to relate changes in peak shapes to experimental parameters. For many years, it has been recognized that chromatographic peaks are not symmetrical, but, instead, may be considered to be made up of a symmetrical component that arises from the separation process in the column and an unsymmetrical (tailing) component contributed by dead volume in the system, including the detector, and the sample injection into the column.

A study of steric-exclusion chromatography has been made using three different monodisperse polystyrenes and toluene as solutes (SRO-854-21). By studying a series of different flow rates, by using detectors having different dead volumes, and by inserting dead volume in the form of short pieces of empty tubing either before or after the chromatographic column, three very interesting results were obtained. First, a new mathematical approach for evaluating the tailing component in a chromatographic peak (14, 15) was found to give information complementary to that provided by the second moment. Second, for the first time, experimental confirmation was obtained for the interaction between flow rate and molecular weight of the solute with

respect to peak spreading. Prior to this time, simulations (16) had suggested that such an effect should be found but there had been no experimental evidence. Third, an unexpected effect of dead volume was found in that, occasionally, peaks were found to be somewhat narrower when dead volume in the form of empty tubing was placed before the column. While this result seems hard to believe, it occurred several times and did not appear to be the result of another experimental error. Further work needs to be done to confirm (or correct) this observation.

Another study has also been done in which two detectors were placed in series at the end of a chromatographic column. A practical reason for doing the study was to determine whether or not peak-spreading became too great to be tolerated. The second goal was to compare different methods for analyzing the additional peak spreading.

Results to date are easy to rationalize. For example, when the detector that had the largest dead volume (broadest peak) followed a detector that gave a narrower peak, there was a noticeable (and measureable) difference in the Gaussian and exponential tailing values for those peaks. However, when the order was reversed, the two peaks were not significantly different. In other words, the small contribution from the second detector could not be distinguished either visually or mathematically from the first one. The point that remains to be tested is whether two detectors that give broad peaks will result in a significantly wider second peak when they are put in series.

Recently, simulations have been carried out using noise-free peaks for which two different tailing functions were convoluted with a Gaussian function. The goal is to find a relatively simple mathematical approach that can be used to deconvolute those functions. Up to the present study, all

of the tailing has been assumed to arise from one source. However, the simulations have provided convincing evidence that misleading data result from such an assumption.

Information content of a chromatogram. As indicated in last year's Proposal, there has been interest growing in this topic (17). At the same time, the advent of digital computers has increased the capability for making such measurements and also the closely related optimization studies. For example, temperature flow rates of the carrier gas and time have been the constraints reported in one study (18) while in another, the composition of the stationary phase (i.e., the use of mixtures) has been examined (19). Actually, all three types of studies shared the same goal since the maximum information (best separation) under a given set of constraints was being sought. In essence, the use of information content attempts to express quantitatively in a single number the different aspects of separations, such as resolution and detectability.

In our studies, the information content of a chromatogram is measured simply as the sum of the information obtained from each sampling point rather than from overall relationships between neighboring peaks. However, the amount of information still depends on the resolution and other factors that are more explicitly expressed in optimization studies. In simulation studies, the effects of plate numbers, dead time, and other variables are being examined. Then, the same approach will be explored for the use of mixed phases. Finally, the approach will be applied to real samples.

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