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FUNDAMENTAL STUDIES OF SEPARATION PROCESSES

by

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ABSTRACT

During the past year, four technical reports have been issued. These have dealt with relative retentions in gas chromatography of the sulfur isotopes in COS, CS₂ and SO₂, fractionations of oligomers in commercial polystyrene, identifications of classes of compounds removed from different types of carbonaceous materials by

supercritical pentane, and a comparison of the speed of a system of multiple isothermal columns with that of a programmed-temperature column for the fractionation of a mixture of compounds covering a wide range of boiling points.

Other studies have involved optimization of the recycle mode in gas chromatography, selective weighting of peaks in the measurement of information conveyed by a chromatogram, development of procedures for the isolations of various vanadium compounds from Venezuelan crude oil, and evaluation of the effect of organic ligand on the sensitivity of the flame emission signal observed for vanadium.

INTRODUCTION

In general, the goal of each of these studies is directed toward optimization of separation processes. Sometimes this is done by using samples consisting of only one or two components so as to understand better the effects of variables. In other cases, complex samples are employed in the hope of deriving general principles on which to base future approaches to those types of situations. Complex samples are also selected because the specific results themselves will be of practical value.

Before discussing the chemistry, it is appropriate to state that the Department of Chemistry provided substantial financial support, largely in the form of supplies. In addition, the University provided fellowships to two of the graduate students.

The topics will be discussed below in the order in which they appeared in the proposal. In that way, it will be easier for the reader to compare the actual accomplishments with the earlier plans.

RESULTS

Information Content of a Chromatogram

The goal of this study is to explore ways in which one might compare complex chromatograms on the basis of the information they provide. Obviously, the simplest approach would be to count the number of components one can detect and then report the total. Having a single value for each chromatogram greatly facilitates a comparison, though there are obviously many subtleties, such as extents of overlap of different pairs of peaks, that will be lost in the process.

Our first efforts to use the approach of Shannon (1) have recently been published (2). In that paper, the amount of information contributed by each digitized point in a chromatogram was summed so as to calculate the total amount of information provided. Although the algorithm

was in a primitive state, it did have the advantage that it could easily be calculated automatically using a on-line digital computer.

Presently, our work is directed toward testing some modifications of that algorithm using simulated data. In one case, the weighting of specific information, for example, the relative importance of a single peak, is being examined using the criteria of minimum retention time and minimal overlap with other peaks. In other simulations, the contribution of tailing to the information is being evaluated in terms of a τ/δ ratio, where τ is the exponential that is superimposed on a Gaussian distribution that has a standard deviation of δ (3). In the latter case, the tailing that is normally encountered in chromatography was found to contribute 10% or less to the total amount of information produced by a peak.

Work is continuing on both of the above aspects. Once those ideas have been developed, it should be easy to extend them to the case of multiple peaks.

Multi-column Chromatographic Techniques

Recycle gas chromatography. Optimization of this technique using packed columns is being explored because it offers the possibility of obtaining large numbers of plates, comparable to those obtained using open tubular capillaries. The chief advantage to be gained is that larger sample sizes can be used with the packed columns

thereby affording preparative capability.

In the past, we have found that the key to a large number of cycles is having a relatively high outlet pressure (rather than atmospheric) and a low pressure-drop in the system (4). Although it is immediately clear that the use of larger particles of column packings will lead to lower pressure drops, such an approach results in larger plate heights (lower efficiencies). The goal, therefore, is to find the cross-over point, and to determine how that point is affected by column length and outlet pressure.

n-Hexane alone is being used for the column-efficiency studies. One of the most interesting and important findings has been the fact that, although a 20-30 mesh porous packing (Chromosorb A coated with SE-30) gave very poor efficiencies, etched glassed beads of the same size (approximately 1 mm diameter) gave excellent efficiencies. The plate heights for the SE-30 coated beads reached a minimum of approximately 1 mm, a value almost identical to that obtained using somewhat finer porous packings. Although, such a value is very poor in terms of values ordinarily obtained for single-column chromatography using 100 mesh packings, the latter mesh has shown to be quite unsatisfactory for the recycle mode (4). Using two 1.5 meter columns packed with glass beads, more than 70,000 plates have been obtained. As soon as the present studies of efficiency versus outlet pressure have been completed, two 7.5 meter columns will

be characterized. It is expected that the characterization phase will be completed by the end of the calendar year. Then, separations of positional isomers (5) and, possibly, isotopic species will be examined.

Column Switching (Other Than the Recycle Mode).

In order to obtain an improved separation of a complex mixture in a shorter time than would be required to elute the sample through a column of suitable length, various switching techniques have been employed (6). One option that has been exercised by others is to switch a portion of the effluent into a column having a different packing so as to fractionate faster one or more difficult pairs of species. Another option has sometimes been employed in which the second column, having the same or different packing than the first one, was held at a different temperature. Finally, if there was no interest in the most strongly retained species, the time for an analysis was shortened by back-flushing so as to remove those species.

In our study, the possible benefits of using three isothermal columns, each at a different temperature, was explored. Although the same packing material was employed in each column, the fact that three columns can efficiently cover a temperature range of close to 150°C greatly expanded the system capability over that of a comparable 2-column system.

As shown in the accompanying report (7) it was possible to separate 15 n-alkanes more quickly using the

3-column system than by using a single column in a programmed-temperature mode. One aspect that was explored was the effect of the time selected for switching; a second was the effect of the uncertainty in that time on the reproducibility of the areas for a sample species that was itself split.

Time was gained by using the 3-column system primarily from the need for the programmed-temperature mode to include a cooling period for the oven before another sample was injected. As a result, the multi-column approach should be useful for analyzing routine samples in large numbers.

At the present time, the 3-column isothermal system is being studied using more complex mixtures involving two or more homologous series. Those samples should provide a more stringent test of the 3-column approach.

Difficult Analyses

Complex Mixtures. The fractionation of the vanadium species in Venezuelan crude oil is technically a very challenging one. At the same time, it is of interest not only to the petroleum industry but also to those interested in the origin of oil. During the past year, familiarity has been gained with existing procedures for the separation of a "clean" fraction of vanadium porphyrins (8). In addition, new procedures for isolating a vanadium non-porphyrin fraction have been tested which appeared to represent an improvement over the existing procedures.

By means of pyrolysis gas chromatography, relatively large amounts of several components containing sulfur have

been found. This not only tends to confirm that sulfur was present in that fraction but provides an interesting problem with respect to determining more precisely the form in which the sulfur occurs. Future work will be directed toward isolation and identification of some of the ligands after first removing the vanadium.

An implied feature in the above study is the ability to be able to detect, preferably determine, vanadium in the chromatographic eluate. A convenient way to do that was to use flame spectroscopy, either emission or absorption, but the sensitivity is not especially high using either method. Furthermore, there is a literature report (9) to the effect that the organic ligand attached to vanadium exerts a major effect on the sensitivity. The same has also been shown for common chelates of nickel, such as those involving cupferron and 8-quinolinol (10). Because both of those studies were performed using atomic absorption whereas atomic emission was the method available to us, the effect of the ligand on vanadium sensitivity has been explored using cupferron and 8-quinolinol. Significant differences in sensitivity were found for the vanadium species indicating that one could use the vanadium signals from unknown compounds in a chromatographic eluate only in a qualitative way.

Another type of complex mixture that has been examined is one that results from the treatment of carbonaceous materials with high-temperature solvents, including supercritical

fluids. The study that has just been completed (11) showed quite clearly that different types of carbonaceous materials could be distinguished readily by the relative amounts of different classes of compounds that were "extracted". In addition, the relative amount of total extracted material decreased noticeably on going from graphite, to active carbon, and then to charcoal. For example, high purity graphite yielded large polycyclic aromatic compounds; technical grade graphite yielded alkanes plus alkyl-substituted benzenes and naphthalenes; active carbons yielded alkanes, dienes, and small amounts of alkyl-substituted benzenes; while charcoals yielded almost entirely small amounts of alkanes. The fact that the compounds could be removed for long periods of time suggested that the supercritical fluid was not simply removing adsorbed material but was attacking the carbonaceous material. Such a suggestion has already been proposed in relation to supercritical extractions of coals (12).

A third set of studies has been concerned with the fractionations of oligomers found in commercial samples of polystyrene. Excellent progress has been made during the past year as indicated in the accompanying report (13). Several important conclusions were drawn from this study. First, using a solvent gradient in liquid chromatography permitted the resolution of more than 40 oligomers from polystyrene 2200 in approximately 80 min. The best prior

separation had been obtained using supercritical fluid chromatography and consumed nearly 20 hours. Second, even though the sample was dissolved in only a few microliters of solvent, the use of too good a solvent seriously degraded the attainable resolution. Third, although it was not surprising, there were significant differences between silica packings that had been derivatized with different groups. The nitro-derivative was the best for our application and was closely followed by plain silica; amino and octadecyl derivatives were intermediate; while cyano and phenyl were virtually useless. The column packings judged to be the worst not only failed to resolve as many individual peaks but they usually produced a sizable hump of overlapped oligomers at the high-molecular-weight end of the chromatogram. It is quite possible that two effects were occurring: (a) poor differentiation based upon the differences in physical chemical interactions and (b) superposition of a second separation process, steric exclusion. The latter process has been shown to be important when using an octadecyl-derivatized silica (14) as well as in an ion exchange fractionation of polyglycines (15). During the forthcoming year, an attempt will be made to sort out the factors that contribute to the formation of the hump.

Isotopic species. Fractionations of isotopic species, unlike the systems of complex mixtures that have already been described, derive their difficulty from the very small

differences in the behaviors of the isotopes. In the past, fractionations on silica of carbon and oxygen isotopes in carbon monoxide (16) and in carbon dioxide (17) have demonstrated that silanol groups on the surface made a major contribution to the fractionation of oxygen through the mechanism of hydrogen bonding. Because the corresponding hydrogen bond formed by sulfur is much weaker, it was of interest to examine carbon disulfide, carbonyl sulfide, and sulfur dioxide with respect to the fractionation of $^{32}\text{S}/^{34}\text{S}$. In all three separations, the fractionation was small (1.0008 in the temperature range of approximately 25°C to 110°C. In addition, the temperature effect was so small as to be of questionable significance. The interesting difference was that in SO_2 , the ^{32}S was held more strongly than the ^{34}S , whereas the opposite was true for the COS and CS_2 . Hence, direct hydrogen bonding with sulfur, rather than to an adjacent atom, produced a normal isotope effect in which ^{32}S eluted first.

Other Efforts

Multiple detectors. This project was not pursued because of a man-power shortage. However, it is important to note that a quantitative theoretical treatment of band-spreading in detectors has just appeared (18). As a result, it will now be possible to complete the studies in a less empirical fashion.

Supporting studies. Considerable effort has been devoted to hardware improvements and software changes

related to the implementation of a multi-user real-time FORTRAN. Although software handlers for hardware, such as the A/D, need to be modified as do some individual operating programs, a major fraction of the conversion has been completed.

Another project, conversion of a combined gas chromatograph/quadrupole mass spectrometer for identification of volatile organic species of less than mass 300 has nearly been completed. An elevated temperature interface between the two instruments has been finished so that the only remaining step is to calibrate the relative sensitivities of the different mass-to-charge ratios so that one can identify species using standardized mass spectra.

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Inst.

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