the Restek Advantage

2006.01

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Erratum
The transfer line used in the methyl tert-butyl ether / tert-butyl alcohol analysis reported in Advantage 2005v4 (Figure 1, page 4) was the factory-installed Eclipse transfer line.

We thank Laura Chambers at O.I. Analytical, College Station, Texas, for reviewing the analysis with us, and we are very grateful to O.I. Analytical for their generous loan of the O.I. 4660 Eclipse purge and trap system.

By Professor Walter Jennings ("Walt")

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For the past few years, the aging process has been catching up with the Jennings family. While I still enjoy participating in seminars and lectures, I now find seven to ten events on a two week trip is more tiring than it was just a few years ago. In addition, my wife has been successfully battling Parkinson's disease for almost twenty years, but we realize that it is now inexorably advancing. Hence, she needs more of my time, and I must limit myself to shorter absences. Because of these developments, I permitted my Agilent contract to expire when it ran out on June 30, 2005. Agilent was sympathetic and understanding, our parting was amicable, and I still value my contacts with them. But after two months in my home office, I sometimes feel a need for the challenge of discussion and argument, and when friends at Restek asked if I would be interested in writing a short paper that was purely educational and pushing no particular product line, it sounded appealing. Here it is.

The "Replacement" Column, A Recurring Problem in Gas Chromatography

One of the problems that gas chromatographers frequently ask concerns the behavior of a "replacement" column. Even skilled practitioners have been known to protest when they install a replacement column, use the same operational parameters, and find that not only have solute retention times shifted, but peak 15 now elutes prior to peak 13. In most such cases, they blame the column manufacturer. There are programs available to correct this problem, but some of those solutions have been so simplified that the user still has no comprehension of the causative factors, a state of blissful ignorance which should be corrected.

Columns are produced, bought, and sold using nominal measurements, e.g., "30 meters x 0.25mm, film thickness 0.25µm". As a specification, this is not equivalent to "30.0 meters x 250µm". Depending on the manufacturer's specifications, the actual column dimensions may be "30 +/- 1 meter x 250 +/- 6µm". Some manufacturers now give better attention to the length tolerance, but the diametric variation will continue to be a problem. Fused silica draw towers are often computer controlled, with the feed rate of the silica blank, the draw rate of the capillary tube, and the temperature of the softening oven controlled by a computer whose input comes from a laser micrometer that monitors the tubing diameter during the drawing process. In our hands, a blank could be drawn to approximately 14 kilometers of 0.25mm capillary tubing. The two ends of that tube may show a significant variation in diameter, but those changes occur so slowly that over lengths of a few hundred meters the diameter is reasonably constant. It is rare to find a column where the diameters at the two ends are significantly different, but it is not unusual to find that columns from the two ends of that draw, or from different draws, do exhibit significant differences in diameter, e.g., 244µm vs. 256µm[i].

An analyst whose original 29.9m x 256µm column is replaced by one measuring 30.1m x 244µm will likely experience difficulties if he or she uses the same operational parameters, i.e., same temperature program, same carrier gas, same inlet and outlet pressures. Because of the geometric differences, the columns possess different pressure drops and under the same operational parameters, the carrier gas velocities would be different in the two columns. This will affect solute retention times, and this introduces the major problem.

Gas chromatography is a volatility phenomenon, and solutes elute in a sequence mandated by what I prefer to call their "net vapor pressures". The net vapor pressure is a function of the intrinsic vapor pressure of that solute, increased by the temperature at that point in the program, and *further decreased by the sum of all interactions between that solute and that stationary phase*.[ii] The strengths of these various interactive forces usually vary inversely with temperature in a non-linear manner, and for a given increase in temperature both the rate of change and the degree of change are unique functions of that solute in that stationary phase under these particular conditions. As a result, the molecules of a chromatographing solute experience a specific temperature-sensitive "selectivity profile" in their passage through the column. These interactions are rendered moot while those molecules are in the mobile phase, and endure only while they are in contact with the stationary phase. Hence we are interested in keeping retention times, and particularly t'_R (time in stationary phase) constant from column to column and run to run. From the two relationships of $K_c = ßk$ and $µ = L/t_M$ we can establish that $t'_R = c_S/c_M \times d_f/d_c \times L/u$. The three terms of course are the distribution constant, the reciprocal of the phase ratio, ß, and column length divided by the average linear gas velocity. K_c is a function of the solute, the stationary phase, and the temperature. While, by definition, the temperature changes in program mode, the rate of change is constant, run to run and column to column, under the same program parameters, and one can usually ignore this term if the two stationary phases are indeed identical[iii]. The second term can also be ignored, provided the ratio of d_f/d_c is constant. Column diameter, d_c and column length are both nominal values and usually differ from column to column. We can compensate for either or both of these by varying the gas velocity, u. This is most easily accomplished in constant pressure mode. In constant flow mode it is more complicated and beyond the scope of this paper.

In constant pressure mode, the solution is quite simple, assuming that the replacement column has the same stationary phase and the same phase ratio as the original column. 1) Using the original operational parameters (initial temperature and program parameters, column inlet and outlet pressures, same carrier) install the new column and inject the same mixture. 2) Determine the retention time of an easily identifiable peak, and compare this to the retention time of that peak on the original column. 3) Adjust the column inlet pressure to make the retention time of the target peak the same as it was on the original column. Retention times on the replacement column should now agree closely with the values observed on the original column, each solute will now experience its original temperature-sensitive "selectivity profile", and chromatograms generated on the replacement column should essentially duplicate those from the original column.

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i Fortunately, the column phase ratio (ß) is usually unaffected by these changes in diameter because almost all manufacturers currently employ static coating methods. Provided the concentration of the stationary phase in the coating solution remains constant, the ratio of the film thickness (d_f) to column diameter (d_c) will remain constant.

ii These interactions include (but are not limited to) dispersive interactions, hydrogen bonding and other proton forms of proton sharing, dipole interactions, and in some cases, molecular size and shape.

iii In some cases, surface preparation and deactivation treatments can also affect retentions. These treatments are generally proprietary and vary from manufacturer to manufacturer. With complex mixtures, the separations achieved on columns coated with the same stationary phase but from different suppliers may yield slightly different results.