

USE OF CARBON MOLECULAR SIEVES FOR CHROMATOGRAPHIC SEPARATIONS OF PERMANENT AND OTHER GASES

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Introduction

Carbon molecular sieves have been prepared for use in gas-solid chromatographic (GSC) separations of permanent gases and light hydrocarbons. Optimization of the porous carbons involved preparing a range of sieves which possesses monoporous properties as well as combinations of macropores, mesopores, and micropores. GSC techniques were used to study the kinetic properties of the sieves. The data obtained have led to the development of packed bed and wall coated open tubular chromatographic columns for use in separating small molecular sized analytes.

Experimental

Three experiments were performed for this study. For the first experiment, packed bed chromatographic columns were prepared using standard column packing techniques (1). Inerted (i.e., silanized) glass columns (2 m x 0.25 in. O.D.) of both 2.0 and 0.75 mm I.D., were chosen. Both columns were packed with the same carbon molecular sieve, Carboxen-1000 (Supelco) with 20/45, 45/60, 60/80, and 80/100 mesh particle size distributions. The columns were installed in a Varian Model 3700 gas chromatograph with a thermal conductivity detector. Kinetic information was obtained from the van Deemter plots for carbon dioxide at 125 oC and ethane at 225 oC (2). Helium was used as the carrier gas.

Experiment two involved the evaluation of 2 m x 0.25 in. x 0.75 mm I.D. columns packed with three different carbon molecular sieves. The first column was packed with a sieve which possessed only micropores, the second was packed with a sieve possessing both micropores and mesopores, and the third was packed with a

sieve possessing macropores, mesopores, and micropores. Kinetic data were generated for CO₂ and ethane using the approach chosen for the first experiment.

Experiment three involved preparing a carbon molecular sieve possessing an optimum porosity based on the data obtained from experiment two. These particles were adhered to the side walls of a narrow bore glass capillary column, 30 m x 0.53 mm I.D. resulting in a 25 uM film thickness. Separations data were obtained for this column using a Hewlett Packard Model 5880 gas chromatograph with a thermal conductivity detector.

Results and Discussion

The data obtained from experiment one, which focused on different particle size distributions of Carboxen-1000 packed in columns of 2.0 and 0.75 mm I.D. columns are presented in Table I.

Table I
Carbon molecular sieve kinetic data

parameter	values					
col. dia. (mm)	2.0	2.0	2.0	2.0	0.75	0.75
part. dia. (mesh)	80/100	60/80	45/60	20/45	80/100	60/80
pd/cd	0.08	0.11	0.15	0.30	0.22	0.28
HETP(mm),CO ₂	0.80	1.21	1.41	3.80	0.76	1.93
HETP(mm),C ₂	0.80	1.23	1.42	4.04	0.72	1.77
slope(x10 ⁻⁴)CO ₂	5.34	16.5	32.5	295	5.90	18.9
slope(x10 ⁻⁴)C ₂	7.80	16.0	23.5	270	4.80	15.5

The data presented in Table I, extracted from the van Deemter plots (3), represent an improvement in performance over previously prepared molecular sieves in this laboratory,

hence this data was chosen for discussion here. Figure 1 illustrates the van Deemter plots for carbon dioxide.

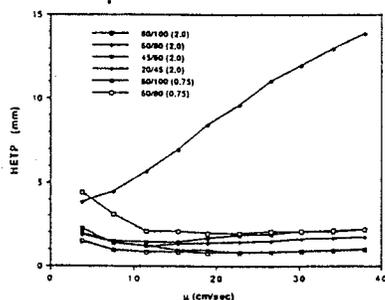


Figure 1. Van Deemter plots for carbon dioxide using Carboxen-1000.

The HETP (i.e., height equivalent to a theoretical plate) value of 0.76 for the 80/100 mesh (0.150 - 0.175 mm) sieve packed in the 0.75 mm I.D. column indicates optimum efficiency for this study. The slope of the plot also indicates that higher velocities can be used without a loss in separation efficiency, hence faster analyses times can be obtained without loss of analyte separation. A decrease in efficiency is obtained with larger particle sizes as noted by the slope for the 20/45 mesh particles and a larger HETP value (i.e., HETP = 1/column efficiency). Similar plots were obtained for ethane.

Figure 2 illustrates a chromatographic profile of the optimum column I.D./particle size distribution determined in experiment 1.

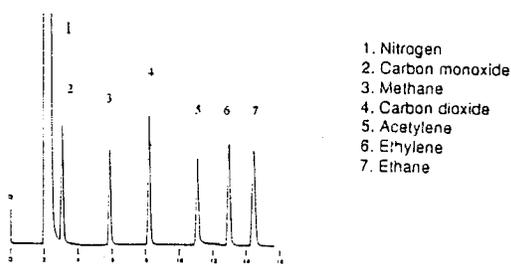


Figure 2. Chromatographic profile of permanent gases and light hydrocarbons using a packed bed column.

The data obtained from the second experiment are illustrated in Figure 3.

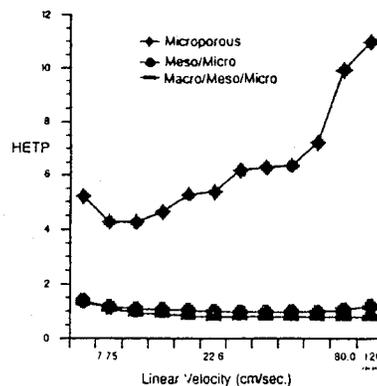


Figure 3. Van Deemter plots for monoporous and multiporous carbon molecular sieves.

These data indicate that a carbon molecular sieve possessing macropores, mesopores, and micropores provide an optimum efficiency for chromatographic analyses.

The data obtained from experiment three indicate a carbon molecular sieve prepared in a sub-micron particle size and adhered to the side walls of a capillary column provide similar chromatographic performance characteristics to the packed bed columns, with improved efficiency due to the decrease in column diameter. Figure 4 illustrates a chromatographic profile similar to Figure 2.

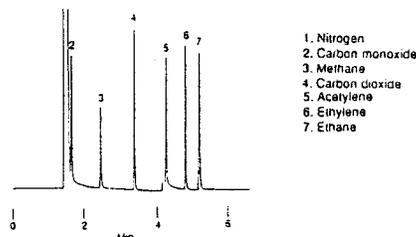


Figure 4. Chromatographic profile of permanent gases and light hydrocarbons.

Conclusion

GSC has been used as a dynamic technique for understanding the kinetic characteristics of several carbon molecular sieves. Pore distributions, particle size distributions, and column diameters have been optimized.

References

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