

**THE SEMIPERMEABLE SURFACE (SPS): NATURE AND RETENTION CHARACTERISTICS, THEORY AND EXPERIMENT**

**SPS Literature to Date:** The first paper to be devoted exclusively to the Semipermeable Surface appeared late in 1992:

**THE SEMIPERMEABLE SURFACE, A NEW RESTRICTED ACCESS MEDIUM**, Glunz, L. J.; Perry, J. A.; Invergo, B.; Wagner, H.; Szczerba, T. J.; Rateike, J. D.; Glunz, P. W. *J. Liq. Chromatogr.* **1992**, *15*, 1361-1380.

The SPS is further described within a forthcoming chapter:

**APPLICATION OF RESTRICTED-ACCESS MEDIA TO THE DIRECT ANALYSIS OF BIOLOGICAL SAMPLES**, Perry, J. A., in *Pharmaceutical and Biomedical Applications of Liquid Chromatography*, Wainer, I., Lough, J., Riley, C., Eds., Pergamon, New York, in press.

The aspects of SPS to be sketched out in this Application Note have been described in considerably more detail in the papers just cited.

The Nature and Retention Mechanisms of the SemiPermeable Surface:

As Figure 1 suggests, porous chromatographic particles that have been coated with a SemiPermeable Surface (SPS) have an outer phase and an inner phase. The outer phase, a polyethylene polymer, is hydrophilic; the inner, usually but not necessarily some common reversed phase such as the octadecylsilyl, correspondingly is usually hydrophobic. The hydrophilic outer phase restricts proteins or other biopolymers from gaining access to the hydrophobic inner phase. Smaller molecules interact with both the outer surface, by hydrogen bonding, and the inner, by partition (1,2).

HYDROPHILIC  
OUTER PHASE/SURFACE  
[-O-CH<sub>2</sub>-CH<sub>2</sub>-O-]

HYDROPHOBIC  
INNER PHASE  
[CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>]

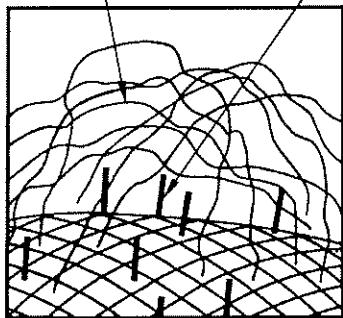


Figure 1. SemiPermeable Surface (SPS) media consist of particles that bear two phases: an outer semipermeable surface that is also a hydrophilic phase, and an inner hydrophobic phase. The outer semipermeable surface prevents large molecules such as proteins from reaching the inner phase. Small molecules interact with the outer phase/surface, particularly if they are hydrophilic; small molecules also can and do penetrate the outer surface, reach the inner phase, and interact with it, particularly if they are hydrophobic. The chemical nature of both the outer SPS phase/surface and the SPS inner phase can be varied independently.

If hydrogen bonding of solutes to the SPS stationary phase is not involved, as, with hydrocarbon solutes it is not, the, as might be expected, retention increases with size--either solute size or stationary phase length. This effect can be seen in Table I. On the other hand, hydrophilic solutes interact primarily by hydrogen bonding to the outer phase.

Retention of such solutes therefore does not increase with stationary phase chain length, may indeed decrease. See Table II.

We should not neglect to point out here that SPS materials show not only excellent chromatographic efficiency but also roughly twice the retentivity of comparable restricted access media.

**Table I**  
Aromatic Hydrocarbons on 15 cm SPS Columns  
Retention Times (min.)\*

	C1	C4	C8	C18
Benzene	2.51	2.60	2.93	3.24
Naphthalene	3.56	3.94	4.76	6.32
Phenanthrene	5.56	6.71	8.85	14.38
Chrysene	9.45	12.24	17.98	37.76

\* Mobile Phase, at 1.0 mL/min: 75/25 methanol/water

**Table II**  
Selected Compounds on 15 cm SPS Columns  
Retention Times (min.)

	C1	C4	C8	C18
Tartaric acid	2.40	2.50	2.29	1.93
Citric acid	3.19	3.61	3.83	2.73
Barbital	2.11	2.08	2.03	1.89
Secobarbital	3.66	4.33	4.56	4.65
Methyl Paraben	2.57	2.65	2.67	2.83
Propyl Paraben	3.18	3.56	3.91	4.51

**Table III**  
Comparing Retention Times (min) of Selected Drugs

	Conventional	SPS 5PM				
	C8	C18	C8	C18	CN	Phenyl
Toluic acid	2.6	3.0	2.2	1.8	2.3	2.2
Caffeine	2.6	2.4	1.8	1.6	1.8	1.8
Trimethoprin	4.9	4.6	3.9	3.2	4.2	3.9
Phenobarbital	11.7	10.9	10.0	9.9	10.1	9.8
Sulfinpyrazone	26.0	27.7	15.1	13.4	15.4	15.2
Carbamazepine	36.7	41.8	15.1	13.6	15.2	14.9
Methyl Salicylate	62.6	92.9	29.4	32.6	20.5	20.9

**References:** (1) Desilets, C. P.; Rounds, M. A.; Regnier, F. E. *J. Chromatogr.* **1991**, 554, 25-39.

(2) Wang, H.; Desilets, C. P.; Regnier, F. E. *Anal. Chem.* **1992**, 64, 2821-2825.