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QUARTERLY PROGRESS REPORT

ON

CONFIGURATIONAL DIFFUSION OF ASPHALTENES IN FRESH AND AGED CATALYST EXTRUDATES

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Statement of Work

Configurational Diffusion of Asphaltenes in Fresh and Aged Porous Catalyst Extrudates

Objective: The objective of this research is to determine the relationship between the size and shape of coal and petroleum macromolecules and their diffusion rates i.e., effective diffusivities, in catalyst pore structures. That is, how do the effective intrapore diffusivities depend on molecule configuration and pore geometry.

Task 1. Relationship Between Effective Intrapore Diffusion Coefficients, Molecular Size and Pore Geometry.

Finite bath-type diffusion experiments will be performed using both coal and petroleum-derived macromolecular species, e.g. asphaltenes, as well as model compounds, e.g. porphyrins, polymers, of known molecular size. By monitoring the concentration of solute macromolecules in the bath, the effective intrapore diffusion coefficients will be determined through application of the appropriate diffusion equations. Macromolecular species concentrations will be monitored by size exclusion chromatography (SEC). Relationships will be sought between the size, and shape, e.g. planar, coil, of the diffusing solutes and the pore geometry (pore size distribution) of the catalyst support. The effects of molecule configuration and catalyst pore size distribution on the effective intrapore diffusivity will be examined. Specially prepared laboratory catalysts with very narrow pore size distributions and other model porous media, e.g. porous Vycor glass, will be utilized in the experiments. Pore structures of all catalysts and other porous media will be characterized by mercury porosimetry and surface area (BET) analysis.

Task 2. Effects of Solvent Composition, Solute Concentration, and Temperature on the Molecular Configuration and Diffusion Rate of Coal and Petroleum Asphaltenes in Catalyst Pores.

Diffusion experiments such as in Task 1 will be performed with varying solvent compositions, i.e., paraffinic-aromatic mixtures, to examine the effects of the state of molecular aggregation (self-assemblies) on the rates of diffusion of coal and petroleum asphaltenes in the catalyst pores. Similar experiments will be performed to study the effect of *temperature* and solute (macromolecule) *concentration* on the state of molecular configuration and aggregation on the resulting pore diffusivity.

Task 3. Assessment of Diffusional Limitations in Aged Catalysts

Diffusivity measurements such as conducted in Task 1 will be performed with both model compound and coal-derived macromolecular species using extrudate-type aged catalysts from laboratory experiments as well as aged catalysts obtained from actual coal liquefaction pilot plants such as the Wilsonville, AL Advanced Coal Liquefaction R & D Facility. From the experimental diffusivities so obtained, an evaluation of effects of changes in catalyst pore structure, e.g. tortuosity, pore plugging, shall be made. The changes in pore diffusivities associated with the pore structural changes caused by coke and metals deposition will be investigated, as compared with the fresh catalysts. As assessment of the relationship of increased diffusional limitations to coke and metals deposition in the catalyst pores will be made based on the results of the diffusivity measurements. The degree to which pore diffusivities can be restored to their original values by carefully controlled oxidation and/or extractive catalyst regeneration techniques also will be explored. The practical importance of these findings to coal liquefaction technology will be evaluated.

Summary

This quarter, GPC column efficiency and resolution were tested. Better resolution and separation of petroleum asphaltenes were obtained in GPC by connecting four columns (1000A°, 1000A°, 500A°, 500A° pore sizes, respectively) in series. A good linear column calibration curve was obtained using several polystyrene standards with molecular weights ranging from 500 to $5*10^4$. The molecular weight distribution of a petroleum asphaltenes was approximated by the polystyrene calibration curve.

Planned Work

Next quarter, more detailed adsorptive diffusion experiments of asphaltenes on porous catalysts will be performed. Asphaltenes from coal liquid residua will also be employed as solutes in the study. The asphaltenes will be treated as several fractions. The molecular weight of each fraction will be obtained by the calibration curve of polystyrene standards. The adsorption-diffusion parameters of each asphaltene fraction will be ascertained by simulating experimental data with a simplified adsorption-diffusion model.

CALIBRATION OF GPC COLUMNS

Experimental

1. Materials: Polystyrene standards (purchased from Aldrich Co.) with weight average molecular weights ranging from 500 to $5*10^4$ were used to obtain column performance. An asphaltene sample extracted from a petroleum asphalt, AAD-1, was used as solute in the diffusion experiment. THF was employed as solvent in this experiment.

2. Equipment: A GPC (gel permeation chromatograph) device was used to analyze samples. The GPC consists of a solvent delivery system (Waters Associates, Model 590), a sample injector (Waters, Model U6K), a variable wavelength UV detector (Waters, Model 484), a bank of GPC columns (each of tube size 300 x 7.8 mm) with column temperature control module (Waters), and a computer data acquisition system. The temperature of the column heater was controlled at 30 °C. HPLC grade tetrahydrofuran (THF) was used as a mobile phase with a flow rate of 1.0 ml/min. Before use in GPC analysis, THF was filtered through a filter paper with 0.1 μm nominal pore size and was degassed for ten minutes by using a sonicator. The THF reservoir was purged with He gas to keep THF from forming peroxides. Each sample for analysis was filtered before injection through a 0.1 μm syringe filter.

Results and Discussion

1. Column Efficiency

This quarter we ordered three new columns of 1000, 500 and 100 A° pore sizes, respectively, from American Polymer Standards Corporation. In GPC studies, column efficiency is one of the important factors. Thus, the efficiencies of the new and old columns were tested using pure acetone as a marker. In practice, column efficiency can be expressed in terms of number of theoretical plates by the following equation

$$N = 16\left(\frac{V_R}{W}\right)^2 \tag{1}$$

where V_R is the peak elution volume, and W is the chromatogram peak width formed by intersection of the tangents to the curve inflection points with the baseline. Table 1 shows numbers of theoretical plates for different columns. It can be seen that, compared to the new columns, the old columns have smaller theoretical plate counts.

2. Column Resolution

In separation of mixtures such as asphaltenes, the column performance is usually expressed in terms of column resolution R_s, or

$$R_s = \frac{2(V_{R2}-V_{R1})}{W_1+W_2} \tag{2}$$

The subscripts in the above equation refer to solutes 1 and 2, respectively. It has been shown that in GPC for a linear region of the calibration curve by polymer, the column resolution can be normalized as expressed in the following equation, which is independent of molecular weight,

$$R_{sp} = \frac{2(V_{R2}-V_{R1})}{W_1+W_2}\,\frac{1}{\log_{10}(MW1/MW2)} \tag{3}$$

To optimize the separation, different combinations of columns were tested. The column resolution for each combination was obtained using two polystyrene standards of weight average molecular weights of 47950 and 13502, respectively, dissolved in THF with concentration of 1 mg/cc. Testing results were verified by analyzing the petroleum asphaltenes.

Table 2 shows values of column resolution calculated from equation (3) for different column combinations. It can be seen that the column combination of 1000A°-1000A°-500A°-500A° gives the best resolution. This was verified by analyzing the petroleum asphaltenes separation on GPC, as shown in Figure 1. Thus, we will use this column combination to analyze petroleum asphaltenes in our work.

3. Column Calibration

GPC analysis of asphaltenes requires the use of calibration standards to determine the average molecular weights of its fractions from elution volume. Studies have shown that a linear calibration curve obtained from the polystyrene standards gives a reasonable approximate value of the molecular weights of asphaltene fractions. Thus a calibration curve was first obtained by the use of some narrow molecular weight distribution polystyrenes as calibration standards, and a sample of petroleum asphaltene solution was analyzed.

Polystyrene standards with weight average molecular weights ranging from 500 to $5*10^4$ were first dissolved in THF, each with concentration of 1 mg/cc. This solution of polystyrene/THF was analyzed via GPC. Figure 2 shows GPC chromatograms of the polystyrene standards, and Table 3 gives physical properties of these polystyrene standards and the corresponding GPC elution volumes. The logarithm of polystyrene molecular weight vs. elution volume is plotted in Figure 3. It can be seen that a good linear fit of log(MW) vs. elution volume is obtained as:

$$\log(MW) = -0.152V_R+8.015 \tag{4}$$

Figure 4 shows a GPC chromatogram for a dilute solution of asphaltene in THF (1 mg/cc). The abscissa is expressed as polystyrene-equivalent molecular weight, calculated from equation (4). The polystyrene equivalent molecular weights of asphaltenes are equal to those of polystyrenes with same elution volumes. It should be pointed out that this is not the exact asphaltene true molecular weight due to the complexity of asphaltene molecules, however, it is a reasonable approximation.

In the next quarter, adsorptive diffusion of asphaltenes in THF with commercial catalysts will be studied in finite bath experiments. The asphaltenes will be treated as several fractions, each with average molecular weight obtained from the corresponded polystyrenes of same GPC elution volumes. The concentration change of each asphaltene fraction during the adsorptive-diffusion process in the surrounding bath will be obtained by the change in the chromatographic area of that fraction, and the adsorption-diffusion parameters will be ascertained.

Table 1. Column Efficiency using Acetone as a Marker(a)

pore size A°	gel type	particle size µm	manufacturer	plates/column
1000	ultrastyragel	5	American Polymer Standards Corporation (new)	9300
500	ultrastyragel	5		11200
100	ultrastyragel	5		9810
1000	ultrastyragel	7	Phenomenex (old)	6400
500	ultrastyragel	7		5860
500	phenogel	5		8600
100	phenogel	5		9000

(a). GPC Conditions: 1 µl injection, 254 nm UV wavelength.

Table 2. Column Resolution using Polystyrenes of 47950 and 13502 Molecular Weight(a)

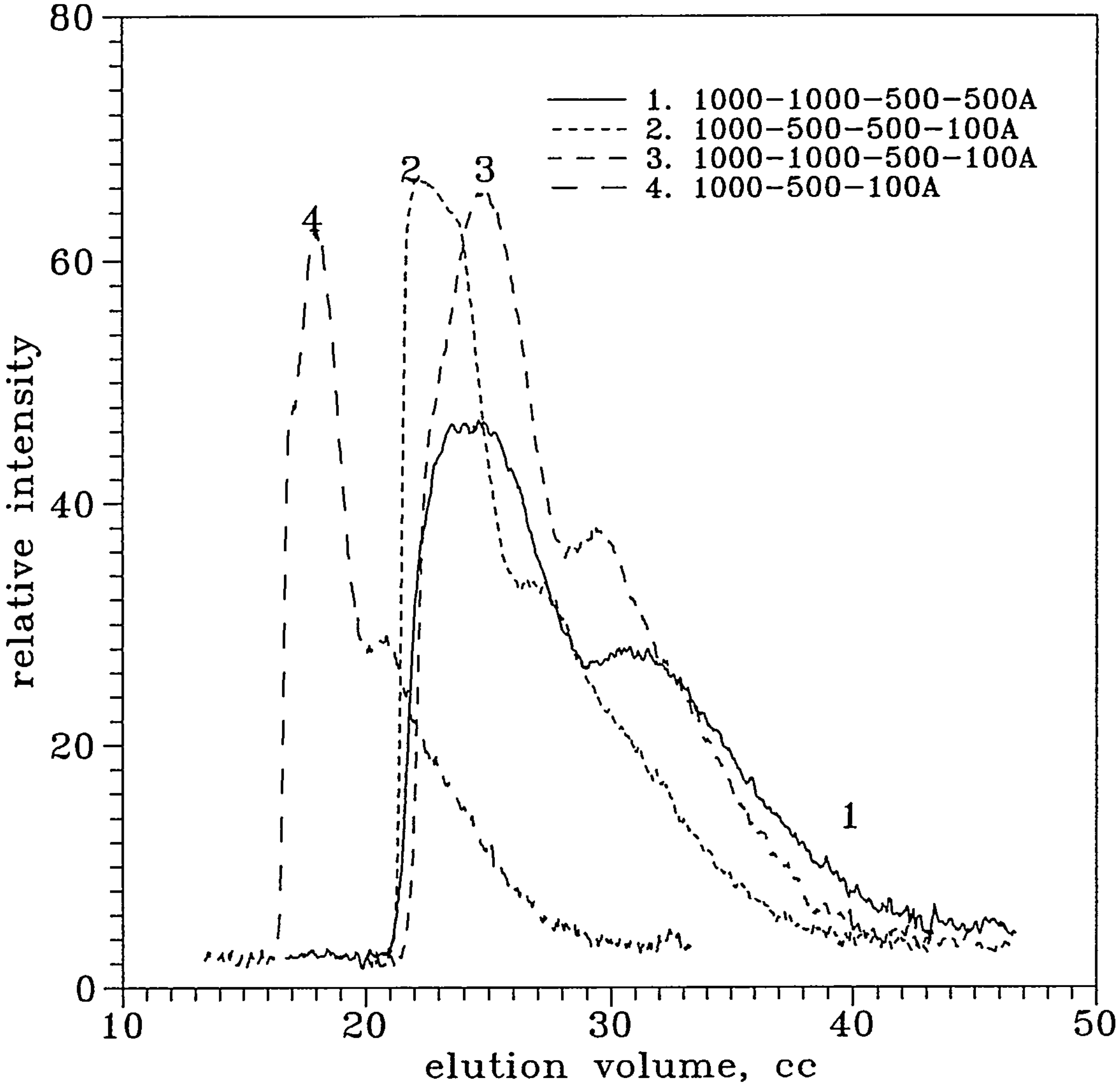
column combination	resolution R_{sp}
1000A°-500A°-100A°	2.19
1000A°-500A°-500A°-100A°	3.07
1000A°-1000A°-500A°-100A°	3.31
1000A°-1000A°-500A°-500A°	3.37

(a). GPC Conditions: 5 µl injection, 262 nm UV wavelength.

Table 3. Molecular Weights of Polystyrene Standards and GPC Elution Volumes

M_w	M_n	M_v	M_w/M_n	V_R, cc
568	503	/	1.13	35.0
794	700	687	1.13	34.0
1306	1221	/	1.07	32.3
2514	2300	2727	1.09	30.2
4136	3967	4075	1.04	28.5
13502	12910	12860	1.05	25.4
24670	23750	24150	1.04	24.0
47950	45550	45730	1.05	22.6

(a). GPC Conditions: 262 nm wavelength, 5 μl sample injection.



Figire 1. Comparison of HPLC Performance of Different Column Series using Aphaltenes/THF

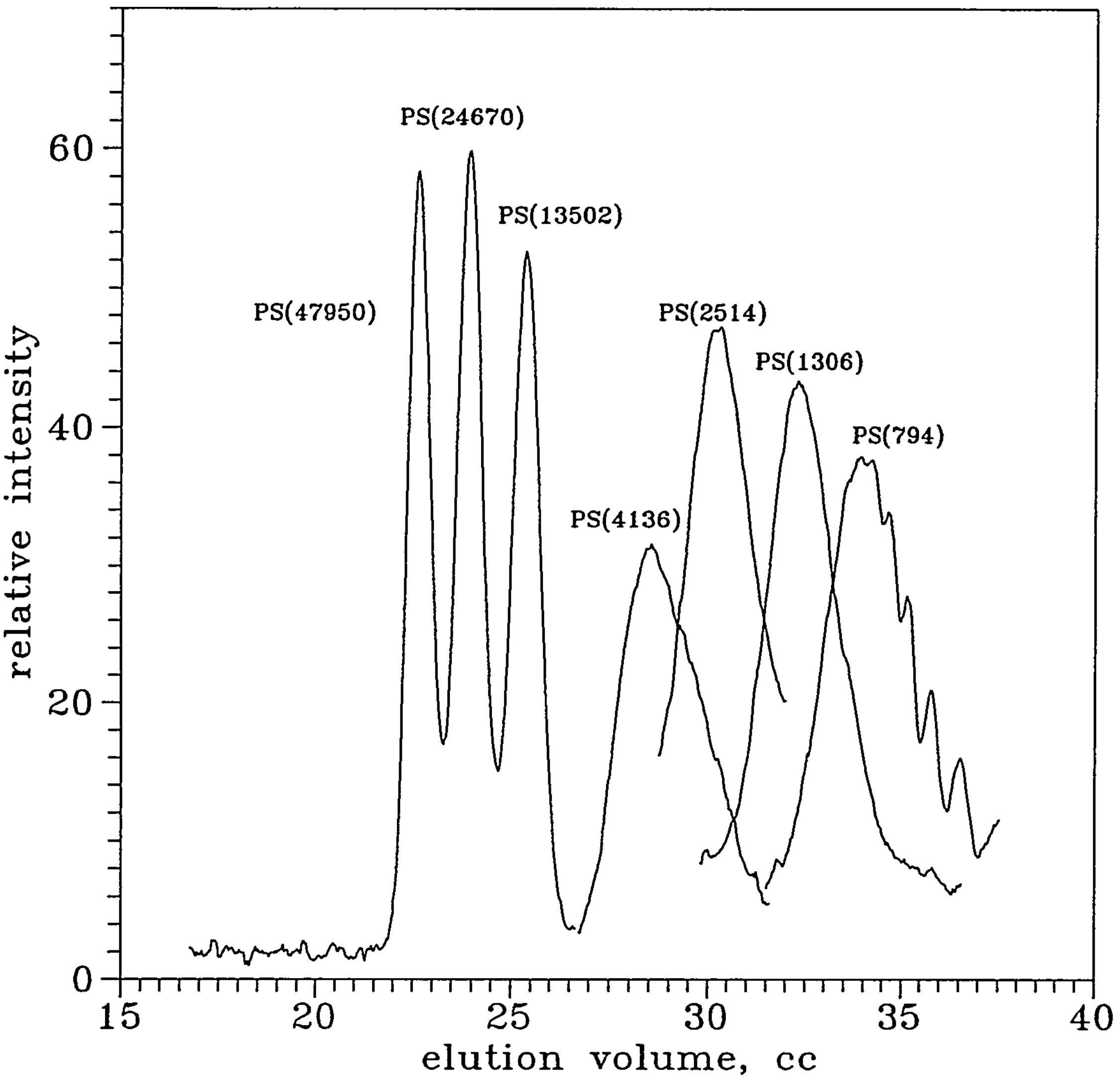


Fig.2. Elution Time for Different Polystyrene Standards

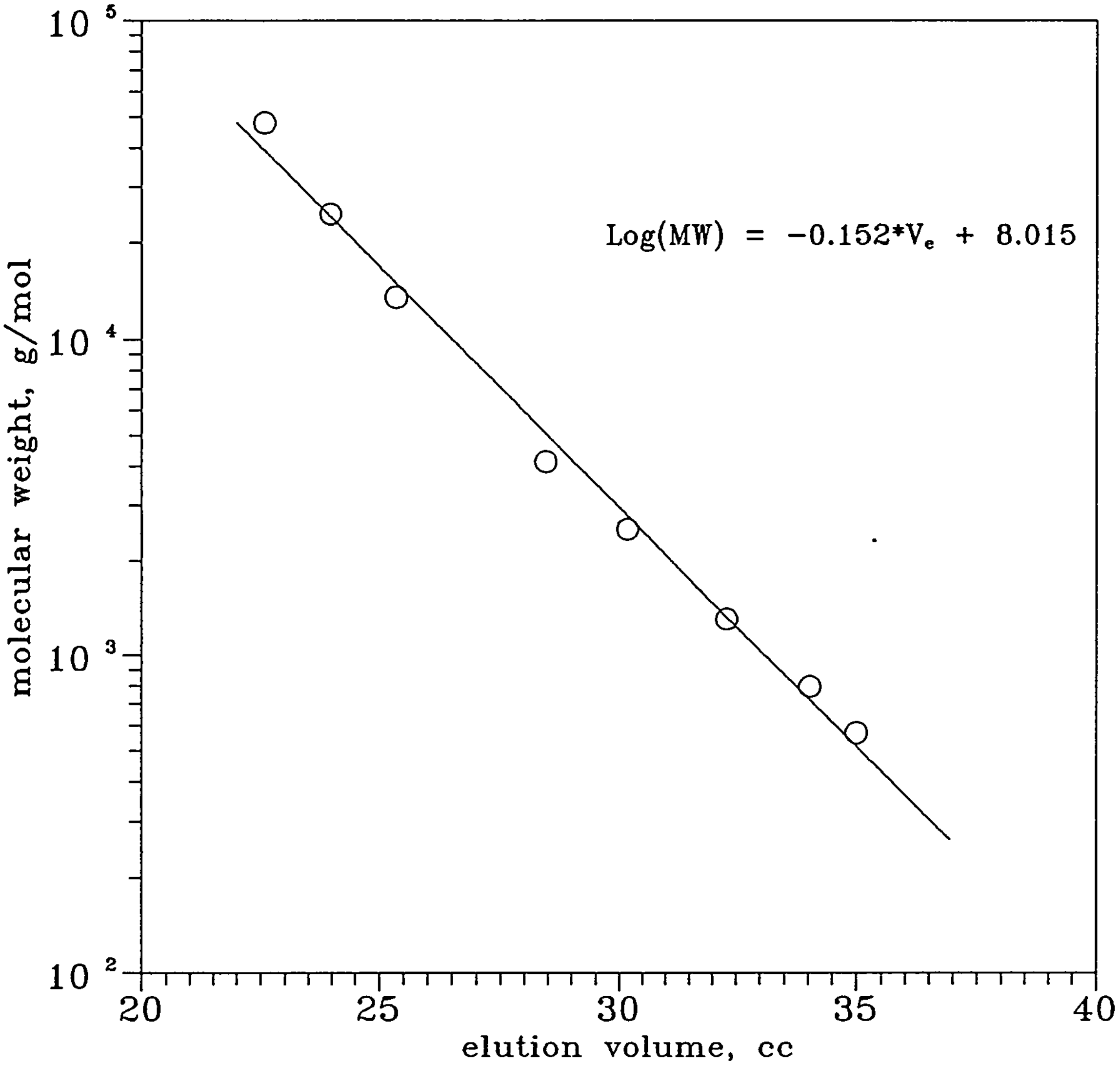
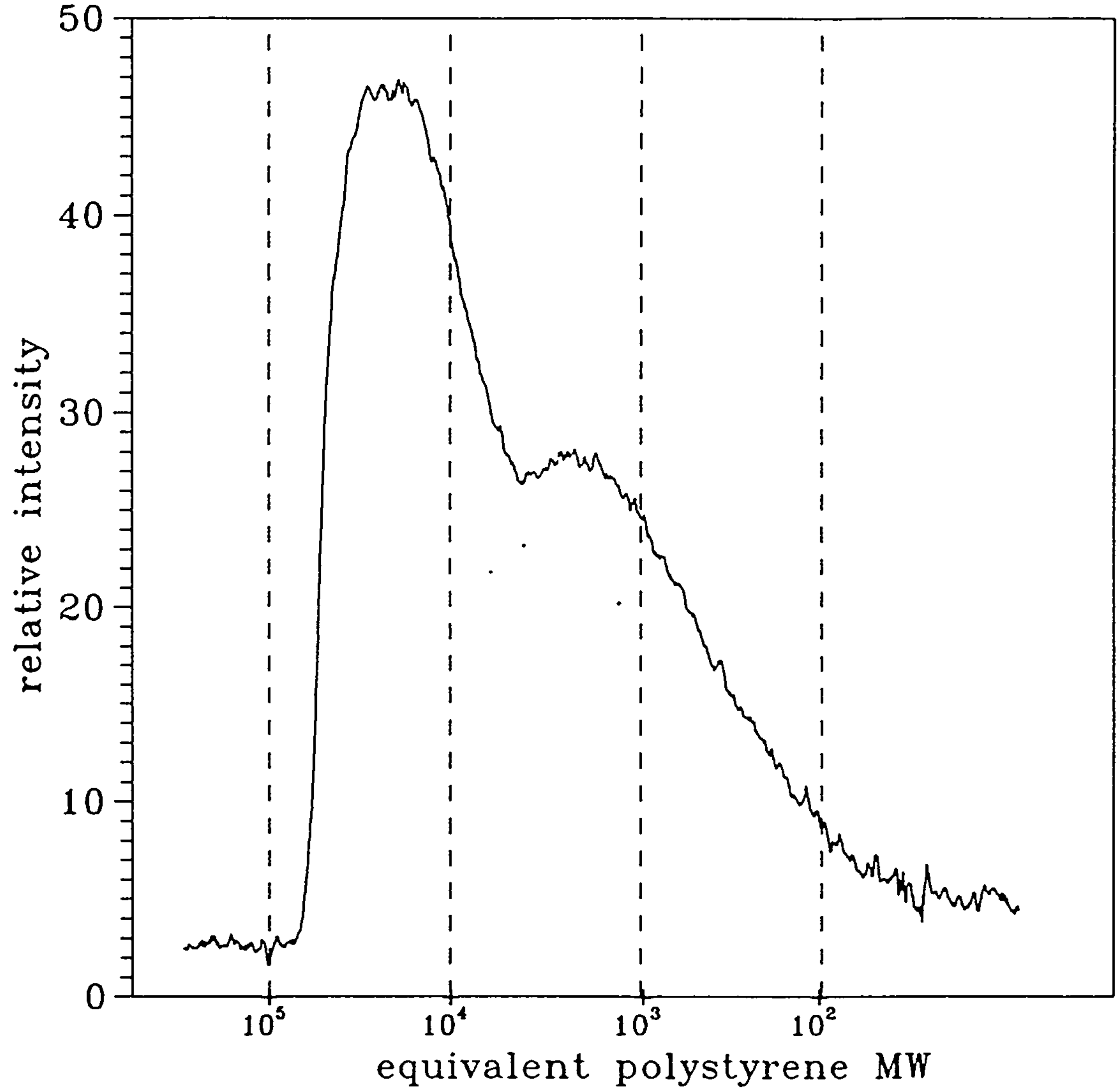


Figure 3. Calibration of HPLC Columns by Polystyrene Standards



Figire 4. GPC elution curve for asphaltene solution. Equivalent polystyrene molecular weight is plotted in place of elution volume using equation (4)