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SOLVENT TAILORING IN COAL LIQUEFACTION

Quarterly Report for the Period April-June 1984

By
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Work Performed Under Contract No. FG22-80PC30209

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United States Department of Energy

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SOLVENT TAILORING IN COAL LIQUEFACTION

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PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY
Under Contract No. DEFG2280PC30209

Acknowledgements

The following personnel contributed to the work performed in the Auburn Coal Conversion Laboratory. Their contributions are gratefully acknowledged:

Sharon Nulon

Frankie Cassell

Frank Bowers

Lynn Perry

Objective. This project addresses the physical and chemical role played by the process solvent during coal liquefaction and focuses upon the interaction of the solvent with the dissolving coal matrix. The aim of this project is to identify mechanisms whereby the solvent functions so as to allow tailoring of the process solvent composition for improved coal liquefaction and product selectivity.

Summary of Work. Although the numerous functions of the solvent during liquefaction are not completely understood, the provision for and the maintenance of an effective process solvent is necessary for effective coal liquefaction. In this project, the function of the process solvent regarding vapor-liquid equilibrium, hydrogen donation, and catalyst activity has been explored.

In previously reported work, a number of donor compounds were evaluated for their relative efficiency in converting coal to cresol solubles. Attempts to correlate the relative efficiency of the various donor compounds were made on the basis of thermodynamic stability and structural features of the molecules. Currently, work is underway with selected model donor compounds to determine if the chemical nature of the model compound influences the product distribution obtained from coal during coal liquefaction as well as affecting the amount of conversion obtained. The product distribution which is being used to evaluate the liquefaction products is based upon extraction of the products into different solvents. The products are divided into oil, pentane soluble material; asphaltenes, pentane insoluble, benzene soluble material; preasphaltenes, benzene insoluble, methylene chloride/methanol soluble material; and insoluble organic matter, methylene chloride/methanol insoluble material. The effectiveness of the hydrogen donor solvent will be measured by

the amount of higher quality material, oil and asphaltenes, obtained from coal as well as by the amount of coal converted.

As with any analysis method involving coal and coal-derived products, the solvent extraction method has inherent difficulties. These difficulties are described herein. In an attempt to monitor the effects of different process parameters and the effect of solvent composition on products obtained from coal liquefaction in a different manner, the use of size exclusion chromatography (SEC) is being explored. Initially, a literature survey investigating the technique and its application to coal liquids analysis has been performed. This literature study is attached.

Experimental work has begun in evaluating SEC columns and in developing a calibration curve for coal liquids analysis. A number of problems have been encountered, with the primary problem being the difficulty in obtaining constant flowrates. Constant flowrates are necessary to achieve accurate molecular weight analysis of the coal product materials, since the molecular weights will be based on elution volumes and compared to the calibration curve for actual molecular weight determinations. A description of the necessity of achieving a constant flowrate for accurate analysis in SEC is attached along with some practical methods of obtaining such flowrates.

SIZE EXCLUSION CHROMATOGRAPHY

Application to Analysis of Coal Liquids

Introduction

Size exclusion chromatography (SEC) is a method of separating molecules according to size. It may be subdivided according to the type of solvent used. It is called gel filtration chromatography for aqueous solvents and gel permeation chromatography for organic solvents. It is also known as molecular sieving and steric exclusion chromatography.

The order of elution of compounds in SEC is determined by the size of the molecule, with the molecules eluting in order of decreasing molecular size. Some molecules are small enough to pass into all of the pores of the packing while others will be larger than all of the pores. Still others will pass into some of the pores and be excluded from some. The large molecules that cannot diffuse into any of the pores will elute in the void volume of the column, that is the volume occupied by the mobile phase. The small molecules that diffuse into all of the pores are eluted at some maximum elution volume characteristic of the system. All other molecules elute somewhere between the two extremes. Therefore, the distribution coefficient, k , will always have a value between zero and one. This is one of the inherent problems in SEC. All work is limited by the small difference in elution volumes of the largest and smallest molecules. Generally, about a 10% difference in molecular weights is required for separation.

To determine an unknown molecular weight, a calibration curve of $\log MW$ versus elution volume is used. Dark and McFadden (1978) have shown that each homologous series of compounds has its own size - molecular weight relationship. Therefore, a suitable calibration standard may be a problem in

some applications. A universal calibration curve may be prepared based on the logarithm of the hydrodynamic volume, number average molecular weight times the hydrogen content versus the elution volume. The viscosity or the H:C ratio may also be used instead of the hydrogen content. Baltisberger and Jones (1984) have shown that polystyrenes, asphaltenes, and preasphaltenes will occur on the same curve using this method.

The selection of a column for use with SEC is determined by consideration of several factors. Work with SEC may be considered to be analytical or preparative. With analytical work the SEC chromatogram is the final result. With preparative work the eluent is collected by an arbitrary division of elution times for further analysis. Preparative work requires a larger diameter column for sufficient sample sizes. The pressure, flow rate, and temperature desired will also effect the column choice. Two other considerations, the choice of the stationary phase and the mobile phase, will be considered in greater detail.

There are three major types of stationary phase or packing available for use in size exclusion chromatography. They are soft gels, semi-rigid gels, and rigid packings. The soft gel packings are cross-linked dextrans. They swell when immersed in the solvent and must be soaked in the solvent overnight to avoid a change in volume. They are useful for separation of water soluble substances and are commonly used in work with proteins and enzymes. The soft gels have the highest sample capacity of the three types of packing. The gel column is very susceptible to fluctuations in flow rate and cannot withstand pressures greater than approximately 150 psi. If it must be used, a pre-column filled with rigid support should be used to moderate fluctuations from the pump. It is also subject to bacterial degradation. Chloroform, cresol, formalin, or sodium azide can be used to reduce the chances of

degradation occurring. Semi-rigid packings are based on polystyrene crosslinked with various percentages of divinyl benzene. They are capable of operating at high pressures and high flow rates. They are compatible with most organic solvents except the lower alcohols. Tetrahydrofuran (THF) and chloroform are commonly used. The semi-rigid packings are capable of separating complex polymer samples and are frequently used in the rubber and plastics industries. The rigid packings are small inorganic particles such as silica. They are capable of high flow rates with modest pressures. They are compatible with more solvents than the first two types of packings but do exhibit problems with adsorption, particularly with polar compounds. pH's greater than 7.5 should be avoided as high pH's may dissolve the packing.

When selecting a mobile phase for the system there are several considerations. It must be a good solvent for the samples of interest. It must be inert toward the column packing, yet capable of wetting the packing surface. It must be of high purity, low viscosity, and it must be compatible with the detectors. Common solvents used in SEC include THF, toluene, and halogenated aromatics. Of these only THF is potentially usable with UV detection at 254 nm. Specially purified THF is available with a UV cutoff of 215 nm. The temperature of the system is sometimes elevated to decrease solvent viscosity therefore increasing the efficiency of diffusion.

Although the detector chosen for SEC work is frequently restricted to what is available with the LC, it is still important to have some knowledge of the detectors available for LC work. Parris (1976) lists seven requirements of what he considers the ideal detector. It should: '(1) be of such a design that the separated components are not re-mixed while passing through the detector, (2) have a low drift and noise level so that small quantities of eluting components may be observed, (3) have a fast response time so as to

faithfully record fast eluting peaks, (4) have a wide linear dynamic range so that quantitative analysis may be accomplished in a straightforward manner, (5) be relatively insensitive to changes in mobile phase flow-rate, temperature and composition - within the limits described earlier, (6) respond either to all substances in an equivalent manner, or alternatively, if selective, be readily tunable so that its response to different species may be optimized, and (7) be easy to operate and reliable.'

Detectors can generally be divided into two types, specific and non-specific. Specific detectors are selective in their response, being highly sensitive to some chemical substances and showing little or no response to others. Detectors such as the UV detector are sensitive only to the sample components. Non-specific or universal detectors respond to a wide range of substances with approximately the same sensitivity. These general detectors measure a change in some overall physical property of the solvent due to the presence of the sample. A universal detector that is commonly used is the refractive index (RI) detector.

The RI detector is probably the most commonly used in SEC. Components may appear as positive or negative peaks with reference to the mobile phase. The major weakness of this detector is its modest sensitivity, making it unsuitable for detecting very low concentrations. Its extreme sensitivity to temperature fluctuations is also a disadvantage. Advantages include the fact that it is a nondestructive method and is convenient and reliable.

The ultraviolet (UV) detector has limited use in SEC due to a restricted choice of solvents with an acceptable UV cut-off. UV detectors have high sensitivity but only for samples with some UV absorptivity. They also display good linearity of response with changing concentrations. They are relatively

insensitive to changes in flow rate and temperature. They are also reliable and easy to operate.

There are also several other types of detectors which are less commonly used. Low-angle laser light-scattering (LALLS) photometry is sensitive to both molecular weight and sample concentration. Infrared (IR) detection has the sensitivity of an RI detector and can be used to monitor an organic solute by monitoring the C-H stretching frequency. Viscometer detectors have been used in conjunction with RI detectors to produce universal calibration plots for molecular weight determination. These are not presently available commercially.

Because of the capabilities of SEC it has been considered for use for analyzing products obtained from coal liquefaction. A commonly held mechanism of coal liquefaction consists of breaking the large coal molecules; producing free radicals; and capping the free radicals with a small molecule; preferably hydrogen, thus producing smaller molecules with a higher H:C ratio. The products of this reaction may then be used to produce products similar to those obtained from petroleum. Since the molecular size is a key factor in the coal liquefaction process and SEC separates according to size, SEC shows promise as an analytical tool for coal liquefaction.

Application of Size Exclusion Chromatography to Coal-Derived Products

A literature survey of the work done concerning coal liquefaction in conjunction with SEC since 1975 has been done. Table 1 shows the solvents and columns used and standards used for calibration in this work.

Wong and Gladstone (1983) compared the separation of coal liquids using three different types of packing. The three types of packing used were controlled pore glass or inorganic silica particles (CPG), soft polyvinyl

Table 1

Reference	Column	Solvent	Standards
Baltisberger (1984)	m-Styrigel	THF	
Baltisberger (1984)	Bio-Beads m-Styrigel	THF	polystyrene Oligo (phenyl ethers) Oligo (phenyl methylenes)
Bartle (1983)	'PL Gel'	THF	
Bly (1975)	m-Styrigel		
Bly (1976)	m-Styrigel		
Bockrath (1979)	m-Styrigel	THF	
Bockrath (1978)	m-Styrigel	THF	
Coleman (1977)	Bio-Beads Sephadex Enzacryl	THF CHCl ₃	
Curtis (1980)	m-Styrigel	THF	Polyethylene glycol Polynuclear aromatics
Drake (1983)	Sephadex Poragel Styrigel	THF	
Hathaway (1978)	m-Styrigel	THF	Polyethylene glycol Polynuclear aromatics
Ignasiak (1978)	Poragel	Toluene	Normal alkanes Polystyrenes Perfluoralkanes
Ignasiak (1983)	Bio-Beads	CHCl ₃	
Khan (1982)	Polyvinyl- acetate Toyo Soda		Hexane-soluble fractions

Table 1 (Continued)

Reference	Column	Solvent	Standards
Lynch (1983)	m-Styrigel	THF	Preasphaltenes Asphaltenes Oils
Martin (1981)	'PL gel'	THF	Polystyrene
Philip (1982)	m-Styrigel	THF Toluene	Straight-chain alkanes
Reerink (1975)	Styrigel	THF	Asphaltenes Bitumens
Richards (1983)	'PL gel'	THF	Polynuclear aromatics Polymer fractions
Schwager (1979)	Bio-Beads m-Styrigel	THF	Variety of compounds
Wong (1983)	Glycophase Fractogel	Chloroform/MeOH	Polystyrene
	TSK	Chloroform	
Wootton (1976)	m-Styrigel	THF	

acetate gel (PVA), and polystyrene-divinylbenzene gel (PSB). The coal liquids were characterized by FT-nmr methods, vapor pressure osmometry (VPO), and SEC to fractionate and derive molecular weight information. Based on their data, they concluded that the PVA column was the best choice for both analytical and preparative work. They discounted the PSB column due to its smaller sample capacity and increased cost. However, it had 20,000 theoretical plates compared to less than 2,000 for the PVA column. They achieved 'a multitude of well-resolved peaks compared to the broad peaks obtained from the PVA column'. Also, only the hexane-soluble portions were analyzed to avoid contamination of the column with polar compounds. However, although rigid packings are susceptible to this problem, the column packing used is classified as a semi-rigid gel, not a rigid packing. There are also other problems associated with a soft gel column that were not mentioned, such as its susceptibility to fluctuations in pressure and bacterial degradation.

In SEC work, the researcher is restricted in his choice of solvent or mobile phase by the relative insolubility of coal and coal products. Martin et al (1981) have attempted to increase the solubility. It has been shown that the solubilities of benzene-insoluble fractions of coal extracts in common solvents can be increased by silylation of the phenolic hydroxyl groups. However, this has not been successfully used because of a tendency for the coal liquids to hydrolyze during the separation procedure. An alternative to this procedure may be methylation. The coal may then be extracted with toluene or tetralin. The toluene soluble portion may be subdivided to give asphaltene and benzene-insoluble portions. With an increased solubility a greater percentage of the coal can be analyzed with SEC and the choice of solvents may increase.

Some studies concentrate on the molecular weight distributions of the initial stages of liquefaction, the solubilization, and rely heavily on SEC and VPO. Ignasiak et al (1978) caution the researcher about a possibly incorrect assumption commonly used in this type of work. They claim that reductive alkylation, a method commonly used to make the coal more soluble, does not necessarily leave the molecular core configurations of the coal intact. Ignasiak et al also issue a warning about the choice of calibration standards. They state that molecular weights of alkylated coal products obtained by means of calibration with normal alkanes will be 50-65% lower than those derived from a calibration with polystyrene or perfluoroalkanes. Although they do not suggest a more suitable calibration standard, it is important to be aware of the fact that if, for example, polystyrene is used for a calibration standard, the molecular weight obtained will be a 'polystyrene-equivalent' molecular weight and not a true molecular weight.

The choice of a detector is a key consideration in the SEC system. Bartle et al (1983) considered the requirements of a detector for coal work and compared the choices. The detector must respond equally to a given concentration of solute throughout the entire molecular weight range. Large differences of up to 50% have been observed in the average molecular mass (MM) with UV detection because coal molecules absorb more strongly at longer wavelengths as MM increases. Drawbacks of the differential refractive index detector (DRI) include poor linearity for higher MM material and a change of sign of response with increasing MM. Bartle et al made an investigation of the evaporative analyser as an alternative to the conventional choices. It is a mass responsive detector, i.e. responding equally to a given quantity of material regardless of chemical composition and MM. The solvent stream is nebulized and the solvent is removed while the stream passes through a heated

chamber. A photodetector produces a signal which is dependent on the factors affecting the rate of solvent evaporation, such as the temperature of the column, the flow rate of the gas, and the size of the droplets leaving the nebulizer. The evaporation of the solute may interfere with detection of lower MM coal materials. Therefore, the method is particularly applicable for MM greater than 300, where the response is almost uniform, and limited for lower MM molecules.

Work by Curtis et al (1980) used SEC in the comparison of untreated coal and Solvent Refined Coal (SRC). The basic chemical characteristics of SRC were investigated in hopes of applying it to an understanding of the parent coal. SEC was used on both an analytical and preparative scale. It was attempted to characterize the nature of each of six arbitrary fractions from the SEC separation. SEC proved to be quite adequate for this purpose, particularly as the SRC is almost totally soluble in the SEC solvent allowing analysis of the total substance. The molecular weights present in the SRC range from about 60 to 650. The general chemical compounds present in the SRC were identified for each of the six fractions although the particular chemicals are dependent on the feed coal and the processing conditions in the liquefaction process.

Hathaway et al (1978) used SEC for characterization of several SRC's and their parent coals. As expected, there was a large difference between the solubility of the two. The molecular weight distributions of the coals were noted by observing the initial and final elution times. An elution time greater than what was expected for some of the coals may be attributed to adsorption of the components on the micro-styragel columns. When the SEC was used for fractionation of the sample the fractions were arbitrarily divided by elution time. Each SEC fraction was then analyzed by electron impact mass

spectroscopy. It was found that the increasing elution times corresponded to an increase in aromaticity.

Wooton et al (1976) used SEC to study the SRC coal produced at the Wilsonville plant. They were interested in eventually determining what proportion of the product could be attributed to the original coal and what fraction was due to the solvent used in the process. Presently, several generalizations may be made about the structure of SRC as a whole. They found the THF-soluble portion of the coal to be composed of three to four major constituents based on a molecular size separation. The hexamethylphosphoramide (HMPA) -soluble portion was predominantly low molecular weight aromatic molecules with a small amount of aliphatic components.

Due to an interest in finding a good calibration standard for use with coal liquids, Baltisberger et al (1984) investigated the use of oligomeric models of coal asphaltenes and preasphaltenes as standards. The initial goal was to synthesize a series of model oligomers in agreement with the average structural formulas of selected coal-derived asphaltenes and preasphaltene samples. The second goal was to test the model compounds and polystyrene; a commonly used standard, as calibration standards for SEC. A linear relationship for the log of the molecular weight and the retention volume was observed on the micro-Styrigel column. VPO was used to determine number average molecular weights of asphaltene and preasphaltene solvent refined lignite (SRL) fractions. A deviation from linearity may be observed in the response curve if condensed aromatic nuclei are present. The study concludes that the most suitable standards for derivatized SRL asphaltenes and preasphaltenes are polystyrene, phenyl ethers, and oligo (phenyl methylenes). More condensed aromatic oligomers may be required for accurate SEC determination of molecular weights of SRL samples with highly condensed

aromatics. Last, the SRL groups must be derivatized to block free OH groups and prevent interaction with the SEC solvent, THF.

Currently, a common method of analysis for coal liquids is that of solvent extraction, dividing the products into oils, asphaltenes, preasphaltenes, and insoluble organic matter. Lynch and Thomas (1983) investigated the possibility of replacing this method with SEC. The solvent extraction method is derived from similar tests in the petroleum industry. However, there are two inherent problems in this procedure. The length of the procedure is prohibitive requiring up to 20 hours and it is highly susceptible to operator dependence. There are several factors that produce discrepancies. These include extraction time, drying and weighing techniques, and the order in which the solvents are used. Because of these problems the possibility of correlating the results of the solubility analysis with the SEC analysis was considered. A sample of the product was prepared using THF as the solvent. The amounts of asphaltenes and preasphaltenes were determined from measured intensities (peak heights) and the peak height to weight ratio for known standards. The oil concentration was determined by difference. The oil concentration was not attained directly from the chromatograph since there was a large variation in UV response due to the H-content of the oil. Again, the problem with calibration standards surfaced. There were not enough standards to cover the wide range of parameters such as temperature, time, catalyst, etc. The standards currently used were prepared using components made from coal and solvent under similar conditions. The molecular weights were then determined by an alternate method. To check for adsorption on the packing the recovery was measured. Recovery was greater than 98% showing minimum adsorption. The major advantage of this method is the analysis time. Six samples can easily be analyzed in a single eight-hour day.

An application of this work could be the on-line monitoring of a stream flowing through a coal liquefaction reactor with SEC maintaining a continuous analysis of product quality.

Bockrath et al (1979) compared three asphaltenes produced under varying conditions. They were separated into acid/base fractions. SEC and molecular weight data indicate that the molecules in the base fraction are predominantly larger than those in the acid fraction. They also found that the fractions from solvent analysis have broad distributions of molecular size with considerable overlap of the fractions. However, it was still possible to distinguish between fractions such as oils and asphaltenes.

Richards et al (1979) showed a variation of coal extract structure with molecular mass. With an increase of molecular mass, conclusions indicate a decrease in aromaticity and phenolic hydroxyl contents, a decrease in the C:H ratio, an increase in the amount of oxygen, and an increase in the size of aliphatic substituents.

Khan (1982) used vapor phase osmometry to check the accuracy of SEC in the determination of molecular weights. Calibration standards of similar size and known molecular weight were used. They were fractionated using the SEC column and the molecular weight of the resulting fraction was determined using VPO. A UV detector was used with the wavelength set at 254 nm for the analytical work. However, the setting had to be increased to 313 nm for the preparative work to maintain a linear response at higher concentration levels due to lower extinction coefficients. VPO was found to be in close agreement with the molecular weights found from SEC for the hexane-soluble fractions of the atmospheric still overhead (ASO) and the vacuum still overhead (VSO). However, there was a significant difference in the values for VPO and the atmospheric still bottoms (ASB) and the vacuum still bottoms (VSB). Conclusions are that the hexane-soluble fractions of ASO and VSO are chemically

similar, while ASB and VSB are unlike ASO and VSO. This indicates that coal liquids may have limited use as calibration standards for SEC and may not be used to predict MW of other coal liquids.

Philip and Anthony (1982) discussed the use of SEC in conjunction with gas chromatography and mass spectrometry (GC/MS) as an analytical tool. Using SEC on a preparative scale followed by GC/MS, they were able to identify many of the compounds found in coal. They have shown that the SEC separations are based on the length of the molecule more than any other parameter. Therefore, rigid aromatics will elute later than straight chain hydrocarbons of comparable molecular weight. Drake and Jones (1983) suggest that the SEC separation is a function of the size, shape, and polarity of the molecule. Philip and Anthony used both toluene and THF as solvents in their work. One disadvantage of THF is that it may have a tendency to form H-bonds with certain species, resulting in a smaller elution volume for a particular molecule. Toluene does not appear to affect molecular size. However, its use is limited due to its inability to dissolve coal as well as THF.

Coleman et al (1977) evaluated three packing materials for preparative scale SEC based on the extent and size of separation and cost of material. VPO was used to check the results of the separation. It was noted that separation according to molecular weight appears to have occurred. A short tapered glass column was used for preparative work to obtain gram quantities of material. A glass column was used because of easier column fabrication, readily observed separation, and fewer contamination problems. Solid SRC products were examined using an RI detector. The SRC products exhibited a 97-98% solubility in THF. Because of the problem with partial decomposition in THF, it was attempted to find another solvent for use with SEC and coal liquids. A 95% recovery was achieved using trichloromethane. Although less

SRC dissolves in it than in THF, the distribution by weight in each soluble portion is the same for the two. However, the molecular composition is not the same. Considerably higher molecular weights were obtained with the trichloromethane. The results were not surprising considering that the exclusion limit of certain SEC materials is known to change drastically with different solvents.

The three columns investigated were Bio-Beads S-X4 (a styrene-divinyl benzene packing), Enzacryl Gel K-1 (a cross-linked polymer), and Sephadex LH-20 (an alkylated dextran). Bio-Beads was determined to be the packing of choice. The Enzacryl separation was found to be faster but not as effective as the Bio-Beads. The Sephadex appears to retain polar compounds longer than anticipated based on their molecular weight. Also, the analysis time is twice that of the Bio-Beads, sixty minutes instead of thirty.

Reerink and Lijzenga (1975) investigated developing a calibration curve for asphaltenes and bituminous resins. A standard curve relating molecular weight and elution volume is needed for the analysis of unknown compounds in SEC work. Ideally, the molecules are separated according to hydrodynamic volume. This depends on both size and shape. If the molecules are truly separated by size a negative slope must result. The rate of transport of a molecule through the column depends on the unknown hydrodynamic volume and the unknown pore-size distribution of the packing. Although polystyrene is commonly used as a calibration standard, this paper warns against it due to its small hydrodynamic volume. For a particular elution volume, one would obtain a smaller molecular weight using the polystyrene curve rather than the following. Reerink and Lijzenga constructed a calibration curve using asphaltenes of known molecular weight. The curve was constructed in two parts. The higher molecular weight portion used the ultracentrifuge to

determine the molecular of the SEC fractions. This method could not be used for the lower molecular weights because the sedimentation of the small molecules is counteracted by rapid diffusion. Vapor phase osmometry was used as an alternative for the small molecules. The curve can be calculated if the curve of a polymer is known and the viscosity data of both types of macromolecules is known.

Although SEC has been used for many years in the polymer industry, it is relatively new to the coal industry. Its full potential in this field may be yet to be realized.

The Importance of Constant Flowrates in Size Exclusion Chromatography

Flowrate consistency is crucial in the reproducibility of results in SEC. Bly et al (1975) divide flowrate variations into four categories. The least serious is a random variation about a fixed level. This is to be expected from a reciprocating pump due to its design. Typically, a one to four percent variation of this type can be tolerated for all but the most critical applications. The second type of variation is a uniform increase or decrease in flowrate after injection of the sample. This may be caused by a large difference in viscosity between the sample and the mobile phase or by the practice of staggered injections in which a new sample is injected while the previous sample is emerging at the outlet. The elution times are measured with reference to a specific component, typically a large molecule which elutes in the void volume of the column, which is included with each sample rather than with reference to the injection time. This type of variation is not too serious with a one percent change in flowrate causing only a one or two percent error in the molecular weights obtained. The third type of flowrate variation is a uniformly increasing or decreasing flowrate. This may be due to dirty or clogged check valves or to temperature drifts in the column. Dirty check valves can be easily cleaned by running a polar solvent, such as methanol, through the pump, for ten to fifteen minutes at a rate of four or five ml/minute. The columns should be bypassed to prevent any damage. Temperature drifts can be controlled by obtaining a constant temperature column jacket. A one percent drift over a period of twenty minutes would result in about a six percent error in the molecular weights calculated.

The last and most serious of the four types of flowrate variations is poor flowrate repeatability. Flowrate repeatability is defined as 'the ability of the pump to deliver exactly a specified volume per unit time on a day-to-day basis under the same set of operating conditions'. For a one percent change in flowrate between the time when the calibration curve was prepared and when the sample is injected an error of approximately twenty percent can result. Flowrate repeatability must be better than 0.3 percent for errors of about six percent in molecular weight.

Abnormal variations in flowrate may be due to leaks or malfunctions in the pump. The pressure, which is related to the flowrate, can easily be monitored on the Waters 6000 LC. The LC is connected to a strip-chart recorder with banana plugs to check variations in pressure. If a variation in pressure is detected, a faulty check valve is often at fault. The Waters' ramp test (Appendix A) can be used to isolate the check valves and determine which is malfunctioning. During the test, the pressure is monitored as discussed previously.

Since Bly et al state that the average LC is only capable of pumping stabilities of one-half to one percent, a method is needed for accurately determining the flowrate during a SEC run. Parris (1976) discussed the three methods used for measuring flowrate in general LC work. These are volumetric, gravimetric, and flow meters. The volumetric work is typically done with a siphon counter. Each time a specific volume (one, five, or ten milliliters) passes through the column the siphon empties. By using a photocell that marks the chromatograph each time the siphon is dumped, a record of volumetric flow is obtained. Gravimetric measurements weigh the eluent at specified intervals of time. Flow meters are 'calibrated tapered glass tubes in which a float or ball of known mass is suspended by the upward flow of the moving

liquid'. The latter two methods depend on the density of the fluid which is subject to any fluctuations in temperature and will change as the composition changes.

Bly et al (1976) investigated the possibility of using the siphon counter technique with SEC. Due to the small total volume used in an experiment (approximately thirty milliliters or less) a small siphon (one to two milliliters) must be used to obtain an adequate number of data points. Problems with using a small siphon may cause significant error in the flow measurements. The solution suggested by Bly et al is to measure only the total number of dumps made by the siphon-counter and calculate an average flowrate based on the total elapsed time and the total volume. The flowrate was deliberately varied about plus or minus five percent around a base value. The elution volumes are calculated with and without using the siphon compensation. The percent variation in the elution volume (standard deviation divided by the mean) is 0.33 percent with the siphon compensation compared to 4.03 percent without the siphon compensation. Uncompensated variations of five to ten percent can result in errors in molecular weight of up to several hundred percent.

Patel et al (1974) suggests another method of compensation for irregular flowrate. The elution volume of an internal standard is determined. This standard is then injected with each sample. A corrected elution volume can then be calculated for each sample using the equation:

$$V(\text{corr}) = V(\text{ob}) * S(\text{calib}) / S(\text{ob})$$

where

$V(\text{corr})$ = corrected elution volume of the sample

$S(\text{calib})$ = elution volume of the internal standard

$S(\text{ob})$ = elution volume of the internal standard during the sample run

Even by varying the flowrate more than fifty percent, the variations in $V(\text{corr})$ for each of nine polymers was less than a tenth of a percent.

By using even a very simple method to calculate the flowrate of the mobile phase, errors in elution volume can be greatly minimized. In this case a stopwatch was used to record the time it took to catch ten ml of eluent in a volumetric flask. Table 2 shows the comparison of elution volume with elution time for repeated injections of triacontane. This data was taken on a pump with a faulty check valve, with a flowrate variation up to four percent. In using a pump with no malfunctions, elution volume again proves to be a more reproducible quantity than elution time. See Table 3.

Table 2
Comparison of Elution Times and Volumes
with a Defective Pump

Column: 100 Å m- Styragel Mobile Phase: THF		
	Elution Time (min.)	Elution Volume (ml)
	6.72	6.16
	6.68	6.18
	6.67	6.21
	6.70	6.23
	6.86	6.20
	6.82	6.18
	6.61	6.14
	6.62	6.16
	6.64	6.21
(S.D./Mean)*100	1.29%	0.48%

Table 3
Comparison of Elution Times and Volumes

Column: 500A Ultra-Styrigel Mobile Phase: THF				
	2Cyclohexyl Phenol Elution Time (min.)	Elution Volume (ml)	Xylene Elution Time (min.)	Elution Volume (ml)
	9.22	9.42	10.26	10.48
	9.26	9.41	10.30	10.47
	9.22	9.37	10.27	10.44
	9.18	9.38	10.23	10.45
(S.D./Mean)*100	0.35%	0.25%	0.28%	0.17%

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APPENDIX A

M6000A Tests and Calibrations

Pump Check Valve and Plunger Seal Check

Tools Required: 5/16" Open End Wrench
2 Compression Plug Fittings (PN 25566)

1. Shut off pump power.
2. Disconnect the outlet line from the heat NOT being checked at its terminus at the reference valve.
3. Place a 1/16" compression plug into the port the outlet line was removed from.
4. Plug pump outlet at the outlet of the transducer.
5. Set pressure limit switch to 6000 psi.
6. Connect PSI recording cable between 10 mv recorder and pressure monitor terminal jacks on pump.
7. Open reference valve.
8. Turn on pump power and set flow rate between .5 and 1.0 ml/min.
9. Close reference valve tightly.
10. Compare trace obtained on recorder with Figure 2-8.
11. There should be approximately three strokes of the pump required to drive the pressure reading to 6000 psi.
12. If the pump does not generate pressure at all, the problem will be a dirty inlet check valve or broken plunger. To clean the valve, pump a polar solvent through the head or purge head with H₂O, then chase the water with 6M HNO₃. (Use 10 ml. syringe and hypo needle supplied with pump to force solvent into pump head.) If plunger is broken, refer to the Plunger Replacement Procedure.
13. If pressure is generated as the plunger comes forward and then falls back precipitately as the plunger moves back into the head, the problem will be found in the outlet check valve. See replacement of the outlet check valve to correct this failure.
14. If the pressure rises a given amount on the 1st stroke and then to a noticeably lesser degree on each successive stroke, the problem will be a leaking plunger seal or a partially failing check valve. If the plunger seal is leaking, there will be solvent evident either around the indicator rod or leaking from the bottom hole in the support head.

15. If the problem is a slight leak in the plunger seal, attempt to close the seal by tightening the two Allen cap screws on the front of the pump head. Then, rerun the ramp check. If unable to seal the old plunger seal, the plunger seal must be replaced.
16. If the problem in Step 14 is not a plunger seal problem, then the problem may be in the inlet check valve.
17. If, after the pump reaches 6000 psi and shuts off, the pressure falls back faster than 15% in 10 minutes, there is a leak in the pump compression fittings or the outlet check valve. Look for the leaking fitting and tighten, replace, or clean the outlet check valve.
18. Check the 2nd head in a like manner.

Independent Ramp Check-off Head

Figure 1
Ramp Test Pressure Trace of One Pump Head

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