SHRP-A-663

## Topical Report on:

# Size Exclusion Chromatography and Ion Exchange Chromatography Separations of Asphalts

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# Abstract

In this topical report, experimental procedures used in the separation of asphalts by size exclusion chromatography and ion exchange chromatography are described. These experimental procedures were developed during the course of the Binder Characterization and Evaluation Program (Contract A-002A) of the Strategic Highway Research Program. A brief background section on chromatographic separations of asphalts is included.

# Introduction

Preparative chromatographic separations of asphalts are beset with a number of difficulties, mostly caused by the complexity of asphalt components. Most asphalts of commerce are petroleum distillation residua, and therefore contain those constituents of petroleum that are the most polar and/or of highest molecular weight. One model of asphalt structure holds that asphalts are dispersions of polar, aromatic molecules in relatively aliphatic, non-polar molecules that serve as a solvent (Pfeiffer and Saal 1940). The polar, aromatic moiety engages in associative behavior (by means of hydrogen bonding, $\pi$-$\pi$ interactions, dipolar interactions, etc.) that is a function of concentration and external influences such as temperature and shear. Thus asphalts consist of molecules which are of very different chemical properties. Long-chain alkanes and steranes are present, as are aromatic species containing acidic and basic functional groups. Also present are metalloporphyrins, carbazoles, phenols having long alkyl side chains, and polynuclear aromatic species. These compound types are comprised of methylene homologues ranging over many carbon numbers.

Most chromatographic separations are designed to process less diverse mixtures of lower molecular weight, and asphalts have the additional complication of polar associations which persist in solution at the temperatures at which most chromatographic separations of asphalts are performed. The most commonly used procedure is the Corbett method (Corbett 1969). In this separation, asphaltenes are precipitated from asphalts and only the maltenes are separated into three fractions of increasing polarity on alumina. Asphaltenes, which can comprise over 20% of tank asphalts, consist of highly polar and high molecular weight molecules and tend to adsorb irreversibly on alumina. Therefore they must be separated first in order to obtain satisfactory recoveries from alumina. Unfortunately, in many ways asphaltenes are the most interesting components of asphalts, but are not amenable to preparative column chromatographic separation. The problem of irreversible adsorption has been partly resolved in the separation of specific compound types from asphalts using silica gels activated with potassium salts to isolate carboxylic acids (Ramljak et al. 1977) and quinolones (Preece et al. 1992).

Another familiar chromatographic separation of asphalts is size exclusion chromatography (SEC). In most studies, molecular weight ranges of milligram size samples of asphalts are determined using styragel columns (Altgelt and Hirsch 1970; Bynum and Traxler 1970; Haley 1975; Reerink and Lijzenga 1975; Huynh et al. 1978; Brule et al. 1986; Beazley et al. 1987; Donaldson et al. 1988; Jennings et al. 1988.) Detectors employed accurately measure some asphalt components, but not others. Consequently some researchers have chosen a gravimetric finish (Bishara et al. 1991). Use of SEC as a preparative separation technique has been limited. The SEC method has the advantage that it is not based on adsorption properties of the stationary phase, but on relative residence time of molecules in gel pores, and so recoveries may be expected to be nearly quantitative.

The ion exchange chromatography (IEC) technique has long been used to separate high-boiling bituminous materials into chemically meaningful fractions. The anion and cation macroreticular resins generally have been used to isolate fractions of acids, bases, and neutral compounds although in some cases subfractions such as solvent-defined weak acids and strong acids have been generated. Among the materials separated are petroleum high-boiling distillates (Jewell et al. 1972, Haines et al. 1975, Green et al. 1984), petroleum residues (McKay et al. 1981), shale oil bitumens (Chong 1976), tar sand bitumens (Bunger et al. 1979), asphalt (Boduszynski 1977), and asphaltenes (McKay 1978).

The following experimental descriptions are the result of four years experimentation with preparative separations of asphalts in the Strategic Highway Research Program (SHRP) Binder Characterization and Evaluation Program using SEC and IEC. These lines of experimentation follow from the original proposal. The objective of the SEC work was to separate molecules engaging in associations from solvent moieties of asphalts. To accomplish this, concentrated solutions of asphalts in solvents that are of similar solubility parameter to asphalt solvent moieties were separated. Furthermore, it was observed many years ago in American Petroleum Project 60 that when crude oils are subjected to SEC separation, the initial eluates are non-fluorescent when irradiated with 350 nm light. Later eluates are strongly fluorescent. This phenomenon cannot be observed by refractive index or ultraviolet radiation detectors. It is interpreted that the non-fluorescent eluates (which by the nature of SEC are those molecules of largest apparent size) consist of strong associations of polar, aromatic species (verified by analyses) in which fluorescence is quenched. Thus SEC is a method by which asphalts can be separated into their most fundamental components, and the point in an SEC chromatogram at which this separation has been accomplished can be determined.

At the outset of the SHRP Binder Characterization and Evaluation Program, preparative SEC separations of samples of tank and aged asphalts large enough (16 g) to provide fractions sufficient for rheological and other measurements were performed. This procedure takes two or three days to complete and uses large amounts of solvent. If rheological measurements are not necessary, smaller amounts of sample may be separated and the procedure is scaled down such that it may be completed in a few hours and still yield fractions sufficient for analyses such as number-average molecular weight and infrared functional group. Both the preparative SEC separation (PSEC) using large amounts of sample and the preparative SEC separation using smaller amounts of sample (SPSEC) were developed during the Binder Characterization and Evaluation Program. Mass fraction data from each method are comparable and are used in a number of composition-property relationships.

To complement the SEC separations, a separation of asphalts by chemical type by IEC was performed. Initially, asphalts were separated into a neutral and four polar fractions by a method virtually identical to that of Green et al. (1984). This was done to compare results with those obtained by other workers separating various petroleum fractions. After adaptation of the procedure for asphalts, it was then decided to isolate all amphoteric materials in asphalts in one fraction in order to study their properties. In the IEC procedure initially used, amphoteric materials are collected in three of the polar fractions, so a different IEC separation method was designed to accomplish this goal. This modified procedure is described in the experimental section.

A great deal of trial-and-error experimentation went into the development of the methods described below. The IEC procedure is particularly rigorous, and depends on proper activation of the resins, a point which cannot be overemphasized. Highly trained personnel also are required. The IEC procedure is purely a research tool, as it takes two weeks to activate resins, fill columns, perform separations, and dry samples. Material and labor costs are high. Nevertheless, IEC provides chemically defined fractions unobtainable by any other method. There is some question whether it is possible to shorten the procedure (particularly if nonpolar solvents are used) and still obtain results that are of real value (Selucky et al. 1981), due to the necessity of breaking up associations of acidic and basic species in asphalts. In short-time, low temperature IEC separations, such associations may not be sufficiently disrupted.

In the procedures described below, chemicals and equipment used in SEC and IEC separations during the SHRP program were obtained from suppliers that are specifically mentioned. Mention of these suppliers does not constitute an endorsement by SHRP or WRI. Most of the chemicals and supplies may be obtained from other vendors, but inferior grades of chemicals should not be substituted. Some of the chromatographic equipment used is no longer stocked by the vendors mentioned, and so other suppliers must be found.

# Size Exclusion Chromatography Separations

Size exclusion chromatography (SEC) is a method used to separate solutions of mixtures according to the molecular size of the components. Solutions to be analyzed are percolated through columns filled with gel particles swollen in organic solvents. The gel particles are porous, and the pore diameters vary in size. Different gels are characterized by different pore size distributions. When gels of appropriate pore size distributions have been properly matched with molecular weight ranges of materials to be separated, large molecules or extensive associations of molecules do not enter gel pores, but pass through gel columns between particles. Unlike most chromatographic methods, larger entities elute first. Somewhat smaller molecules, depending on their size, spend varying amounts of time within the gel particles during an SEC separation. The smallest molecules enter all pores in gel particles and are not separated from each other. If the chemical properties of a mixture vary along with molecular size, an SEC separation effects a chemical separation, otherwise not.

The method has seen wide application in fossil fuel science particularly in the separation of heavy crude oils and derived materials. One model of the structure of heavy crude oils holds that these materials are composed of associations of polar molecules dispersed in a relatively non-polar solvent phase. The same model has been proposed for asphalts. Any extensive associations of polar molecules must be of fairly large size, and so it should be possible to separate associated from non-associated components by preparative SEC (and analyze differences between the components by analytical SEC) if associations are stable in solvents used for SEC separations. The SEC separation methods do not suffer from irreversible absorption, as are ion exchange chromatographic and liquid chromatographic procedures. In SEC, recoveries of charged materials usually are quantitative. Therefore SEC can be used to separate highly aged asphalts, containing many highly polar functional groups, for which other chromatographic separations and analyses are unsuitable. The method inherently is not capable of the resolution characteristic of other chromatographic methods, but is one of the only effective tools for the fingerprinting of the larger components of fossil fuels.

A variety of gels of widely different pore sizes are commercially available. Most are categorized according to average pore diameters. A gel having a large average pore diameter will not efficiently separate mixtures of small molecules, and vice versa.

The SEC method can be adapted as an analytical technique separating minute amounts of sample or as a preparative separation of samples weighing several grams.

## PSEC Experimental Procedure

Preparative size exclusion chromatography (PSEC) is used to provide fractions of asphalts large enough in size so that rheological analyses can be performed. In addition, gram quantities of asphalt PSEC fractions are needed to perform blending experiments. The procedure developed in the SHRP A-002A program is described below.

The equipment required for the PSEC separation consists of the following. An Andrews Glass Company Lab Crest (5.08 cm ID by 100 cm long) water jacketed column, connected to end fittings with stopcocks, is packed with Bio-Rad Bio-Beads S-X1 (200-400 mesh) gel swelled in toluene (EM Sciences, HPLC grade). The end fittings contain fritted glass discs to contain the gel and add 2.4 cm to the total length of the column. A water circulation bath connected to the column water jacket by Tygon® tubing provides 40°C (104°F) temperature control for the column. The column is vertically mounted in a well-ventilated space. The pump used is an FMI model RPG-50 (1/4 inch piston), and an FMI model PD-60-LF pulse dampener is placed in the solvent stream between the pump and the column. Teflon® tubing is used to conduct solvent from one piece of equipment to another. Graduated cylinders are used as receivers and Erlenmeyer flasks are used as sample and solvent reservoirs. Similar pumps, pulse dampeners, and columns are available from other manufacturers. A diagram of the preparative SEC apparatus is shown in Figure 1.

The column is packed by making a slurry of most of the required amount of gel with toluene. The amount of gel needed can be calculated from the volume of the column (about 2000 mL), estimating that the gel swells in toluene to about 7.9 mL/g and also compresses under the pressure of solvent pumping to about 75% of its unconfined swelled volume. For the column used in most experiments, about 330 to 340 g of dry gel is needed. A few grams of dry gel is reserved for the final packing step after all of the slurry has been poured into the column. To fill the column, toluene is poured into the top of the column to about one half the column height. Then the gel slurry is added in increments while draining solvent by gravity out of the bottom of the column. After all the slurry has been added the column appears to be thoroughly packed. However, pumping solvent through the top of the column will pack the gel further so that a gap between the top of the gel bed and the glass frit develops. For best results, this gap must be filled with gel. Therefore, it is necessary to pump a few mLs of methanol into the top of the column, which shrinks the gel so that the reserved dry gel can be added to the top of the column. Toluene is then pumped into the bottom of the column, which flushes out the methanol and swells the shrunken gel and the added dry gel.

Before a sample is introduced into the column, toluene is pumped into the bottom of the column at 3.5 mL/min for about an hour to allow the gel bed to settle. The toluene is contained in an Erlenmeyer flask, and one end of a tube connected to the pump inlet is placed in the flask below the liquid level. The sample, 16 ± 0.5 g of either unaged or aged asphalt, is dissolved in 150 mL toluene in an Erlenmeyer flask and is introduced into the bottom of the column through the pump. The delivery tube is placed inside a 500 mL graduated cylinder. During sample injection, the pulse dampener is removed from the sample stream and the pump setting is not changed even if the flow rate slows down, as increasing pressure may break the glass frit. After sample injection has been completed, the pulse dampener is replaced in the sample stream. The removal of the pulse dampener may be accomplished either directly or be setting up an alternate stream and switching between the two. The reason for removal of the pulse dampener is that portions of the charges are retained in it.

When color is detected at the outlet of the column (this occurs after about 450 - 530 mL of eluate has been collected after sample introduction; the amount varies with the column because no two columns are packed exactly alike and there is also variation among asphalts), the delivery tube is put into a second 500 mL graduated cylinder and placed so that eluates flow down the side of the collecting cylinder. The first material emerging from the column is a black solution and does not vividly fluoresce when exposed to light of 350 nm wavelength. After about 240 - 275 mL additional eluate is collected, stronger fluorescence begins to be detected. When an additional 25 - 60 mL (making a total of about 300 - 325 mL; this total, again, can vary among asphalts) has been collected, the transition between relative nonfluorescence and uniformly bright fluorescence is complete and the delivery tube is transferred to a third graduated cylinder. This is the cutpoint between SEC Fraction-I and subsequent fractions. The exact determination of the cutpoint depends on the judgement of the operator. In the separations described herein, a Gelman-Camag Universal UV lamp was used. Other lamps generating light in the 350-360 nm range may be used. The lamp is normally held 10 cm from the material irradiated, and white paper is placed behind it. The nonfluorescent material contains the associated molecular species. The transition zone is the result of material flowing up the outside of the column of gel faster than the inside. If the eluate is allowed to stand about one hour in the graduated cylinder, layers will form of gradually increasing brightness until uniform brightness occurs. This allows the operator to make the judgement between transition and uniformly bright eluate, or in other words, between the associated species and the nonassociated species. Also at this point the operator must decide (if such a decision has not already been made) whether to perform a two fraction run or a multi-fraction run. If a two fraction run is required, then all of the remaining eluate collected will be SEC Fraction-II. If a multi-fraction run is required, then the size of each fraction must be decided on and the run will proceed accordingly. After SEC Fraction-I has been eluted, the separation can be interrupted and the remainder of the asphalt sample can be eluted at a later time. In the multi-fraction runs performed in the SHRP A-002A program, the SEC Fraction-II was divided into eight subfractions consisting of successive 200 mL volumes of eluates.

The fractions collected are then divested of solvent by pouring eluates from the collecting cylinders into round bottom flasks. Most of the solvent is removed by attaching the flasks to a rotary evaporator with a hot water bath. To remove toluene, a vacuum is required. After most solvent is removed, the eluates are transferred to weighed vials and the residual solvent is removed. The mass of each fraction is determined. The mass % of each fraction is then calculated using the following equation:

$$\text{mass } \% = (\text{mass of fraction} \times 100) / \text{wt asphalt}$$

About one and one-half days are required to perform one preparative SEC separation for a 16.0 g sample of asphalt. This estimate assumes that the column has been packed and calibrated and that all solid material has been removed from the asphalt solution by filtration.

The duration of solvent removal step depends on the number of fractions collected and the number of rotary evaporators available. Customarily, in multi-fraction runs, masses of each of the fractions are plotted versus cumulative column bed volumes after which each of the fractions has been collected, in order to construct chromatograms. The first point in such a chromatogram corresponds to breakthrough of colored materials which is zero mass.

## SPSEC Experimental Procedure

The streamlined preparative size exclusion chromatography (SPSEC) procedure was devised to shorten the time necessary to obtain results comparable to those obtained from the large scale preparative size exclusion chromatography (PSEC) procedure. The techniques are basically the same except for time and scale. The PSEC procedure takes about two working days from sample introduction to final weighing of fractions. The SPSEC procedure takes about three hours. In both cases toluene (EM Sciences HPLC grade) is used as the eluant and Bio-Rad Bio-Beads S-X1 are used as the column packing.

The equipment required for the SPSEC separation consists of the following. A Lab-Crest 0.9 cm ID by 50 cm long water jacketed column fitted with stopcocks at both ends is packed with Bio-Rad Bio-Beads S-X1 (200-400 mesh) gel beads. The end fittings contain fritted glass discs that hold the resin in place and add about 2 cm to the length of the column. The columns presently in use were purchased from Andrews Glass Company, but similar columns are available elsewhere. A water circulation bath connected to the column water jacket by Tygon® tubing provides 40°C (104°F) temperature control. The pump used is an FMI model RPG-50 (1/8 inch piston) with a FMI-PD-60-LF pulse dampener in the solvent stream between the pump and the column. Teflon® tubing is used in the sample stream. Small (10 and 25 mL) graduate cylinders are used as receivers. Erlenmeyer flasks are used as solvent reservoirs. Graduated test tubes are used as sample reservoirs.

The gel swells about 7.9 mL/g in toluene, but compresses in the column under the influence of the pressure from solvent pumping to about 75% of that volume. A calculation of the volume of the column, including end fittings, yields a volume of about 33 mL. Therefore, it takes approximately 5.6 g of the gel to fill a column. The column can be packed in either of two ways. The first involves swelling the gel with toluene before putting it into the column, pouring some of the slurry into the column, allowing the gel to settle, and then adding more gel slurry as the gel settles. However, the gel compresses as solvent is pumped through the column, and so a small amount of dry gel must be added at the very end of the column filling process to compensate for not being able to fill the column completely with swelled gel. The second way to pack the column is to partially fill the column from the top with dry resin and then pump toluene in from the bottom and alternate addition of gel with toluene finishing, again, with dry resin.

After filling, solvent is pumped through the column from the bottom, whereupon a gap between the surface of the gel bed and the glass frit occasionally develops at the bottom of the column. For best results, this gap must be filled with gel. Therefore, pumping is reversed so that the gap forms at the top of the column, and shrinks when pumping is discontinued and the gel swells. It thus will be impossible to add the right amount of gel for proper operation without shrinking the gel. This is accomplished by pumping in a few mL of methanol at the top of the column. The calculated amount of dry gel can then be added by removing the fitting at the top of the column. The amount of gel to be added is calculated from the volume of the gap and assuming the known swelling ratio of the gel of 7.9 mL/g and the 75% compression of the gel under pressure. Occasionally, another gap may develop after prolonged use of the column and this can be corrected in the same way. It should also be mentioned that if the column is overpacked, one or both of the frits at the ends of the column may break and need to be replaced.

The columns are mounted vertically in a well-ventilated space and solvent is pumped into the bottom. The pulse dampener is taken out of the solvent stream when sample is being pumped into the column, after which it is put back into the solvent stream. The eluate is piped to a graduated cylinder collector immediately after the column. The toluene flow rate is 0.26 ± 0.04 mL/min.

The sample, 0.15 ± 0.0025 g, is dissolved in enough toluene to make 3.0 mL of solution in a graduated test tube. The sample solution is introduced through the pump into the bottom of the column. The delivery tube is put into a 25 mL graduated cylinder at that point and the tip of the delivery tube is placed so that as liquid level rises the tip is immersed in the liquid. The receiver is placed on a white piece of paper to allow easy detection of color when the first of the sample starts to emerge. When the first color is observed in the receiver the delivery tube is transferred to a 10 mL graduated cylinder. The next 5.5 to 6.0 mL of eluate contains SEC Fraction-I, which corresponds to the associated or the dispersed part of the asphalt. The next 25 mL of eluates are collected in a second 25 mL graduated cylinder and contain SEC Fraction-II of the asphalt. The fractions are then transferred to weighed 30 mL vials.

The fractions are divested of solvent overnight using a static solvent evaporator, such as an Organomation N-Evap with an inert gas flow and a hot water bath, or, if results are needed sooner, a rotary evaporator can be used. The vials are then weighed and the results are calculated using the following formula:

$$\text{mass } \% = (\text{mass of fraction} \times 100) / \text{wt asphalt}$$

The important datum to be obtained is the mass % of SEC Fraction-I. That means that the determination of the cutpoint between Fraction-I and Fraction-II is critical. There are two ways that this cutpoint can be ascertained during a run. Initially the onset of fluorescence to 350 nm light was used to determine the cutpoint. Then it was found that for small samples all asphalts gave essentially the same cutpoint, so the use of the volume of 5.5 mL collected as the cutpoint was established. This gave reproducible and accurate results, when compared to results from the PSEC. However, as we continued to use the columns, it was discovered that results deviated slightly from the PSEC results and so the volume of SEC Fraction-I was increased to 6.0 mL. This cutpoint gives good results but suggests that a "standard" asphalt be run weekly to ensure that results are staying within acceptable bounds.

## Fast SEC Procedure

The preparative SEC procedure described previously has been developed to give samples that are large enough to analyze and to use in other experiments. For an analysis that gives numbers only, a faster procedure was desired that could give results in minutes instead of the hours required by the preparative SEC procedure. This procedure uses high performance liquid chromatography (HPLC) equipment with its associated software and hardware.

The equipment used here is a Hewlett-Packard (HP) 1090A equipped with a UV/visible diode array detector (DAD), a DR5 solvent delivery system, and an auto-injector. The system operates from an HP-85B personal computer equipped with an HP 9121B dual disc drive and uses the HP 1090 B-2517 version software. The system is also equipped with an HP 7470A plotter and an HP thinkjet printer.

The sample is injected into the system, passes through a guard column into a Phenomenex Phenogel 10,000 Å (5 micron particle size) column followed by a Phenomenex Phenogel 1,000 Å (10 micron particle size) column. The sample loop is then lead outside the HPLC mainframe to an HP 1046A fluorescence detector (FD), thence back to the mainframe to the DAD, and then outside again to a Waters R401 differential refractive index detector (DRID). The order of the detectors is dictated by the pressures each is able to operate under.

The FD and the DRID are each equipped with an HP 3393A integrator and each integrator is equipped with an HP 9114B disc drive. The disc drives allow storage of the raw data on 3.5" double-sided double-density floppy discs for further analysis if necessary. The DAD puts out enough raw data that only two runs can be stored on one 3.5" disc. However, data from hundreds of runs from the other detectors can be stored on one disc. Each integrator is programmed to report data as 30 second data slices. Evaluation routines allow preparation of either 2D or 3D plots of the DAD data.

Column conditions include a flow rate of 2.0 mL/min toluene at a temperature of 30°C (86°F). Samples (1.25 mg) are injected in 50 µL of a solution prepared by dissolving 50 mg sample in 2.0 mL toluene. A run is complete in 18 min and it takes about another 2 min to run the BASIC programs on the FD and DRID integrators. The program for the DAD is run automatically. Some examples of the 30-second slice data are available in the SHRP data base.

Results of SEC separations of SHRP asphalts are presented and discussed in Volume II, Chapter 2 of the Final Report for Contract A-002A, Binder Characterization and Evaluation.

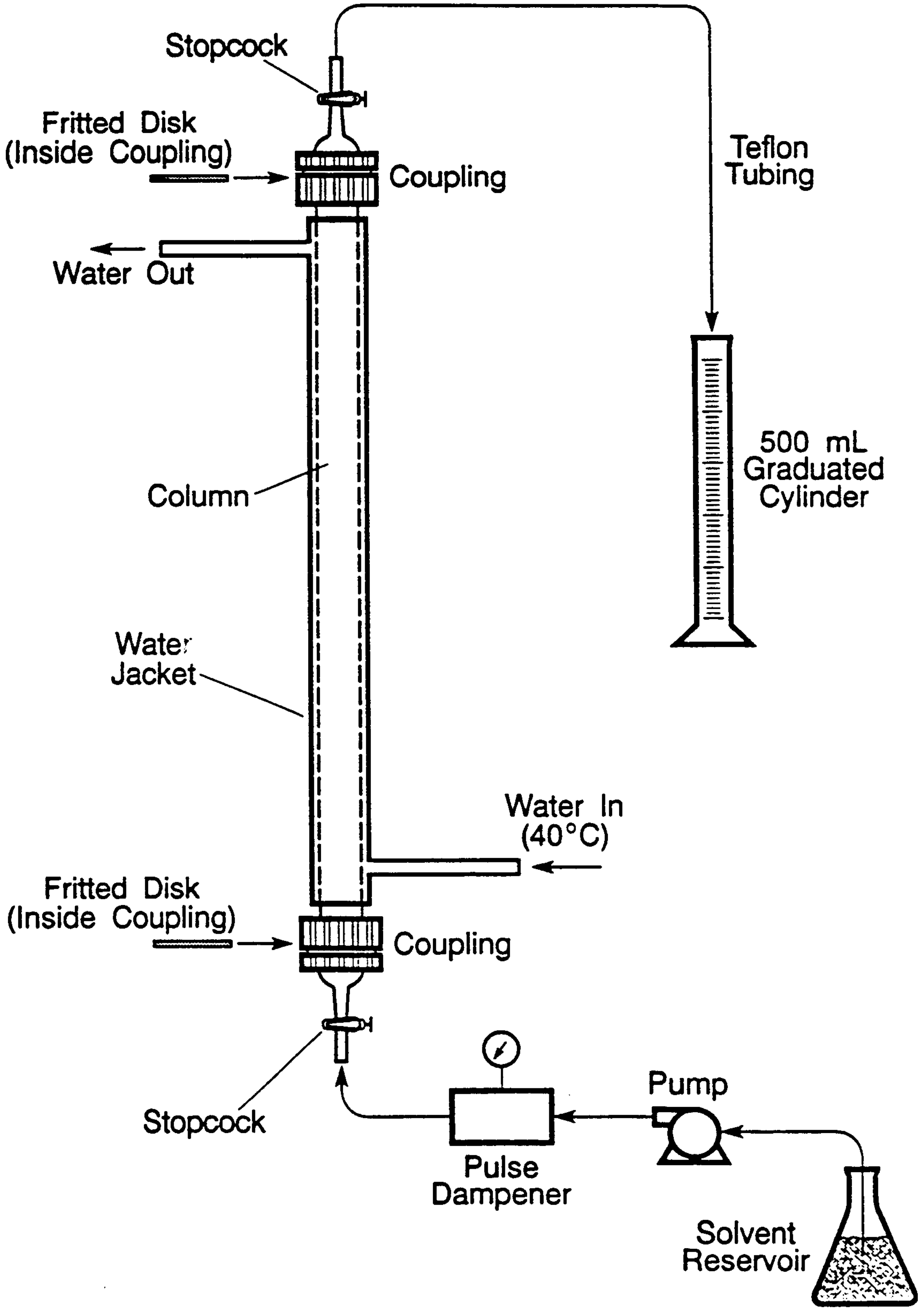

Figure 1 Diagram of Apparatus Used for Preparative Size Exclusion Chromatography Separations

# Ion Exchange Chromatography Separations

One of the principal objectives of the SHRP Binder Characterization and Evaluation Program is to attempt to correlate asphalt chemical and physical properties. In order to accomplish this objective, it is necessary to divide asphalts into defined chemical fractions and determine the influence of the fractions on selected physical properties for a number of asphalts. Asphalts are known to consist of relatively non-polar hydrocarbons and acidic and basic heteroatom-containing molecules of varying polarity. These components cannot be completely separated by solvent precipitation methods or techniques that separate molecules according to molecular size. Ion exchange chromatography (IEC) can be used to separate solutions of asphalts into defined neutral, acidic, and basic fractions. Amounts of samples may be processed in one experiment so that fractions are obtained of sufficient size that various physical property measurements can be performed. The IEC separation can be varied to isolate specific fractions of interest.

The procedure consists of pumping solutions of asphalts through columns filled with activated anion or cation resins. The procedure is exacting and time-consuming and depends for success on proper resin activation. One week (assuming eight hour work days) is required to activate substantial amounts of resins as described below. Another week is required to separate asphalt solutions into four fractions and remove solvents. Highly trained personnel are essential.

## Activation of the Resins

Activation of the cation and anion resins is the first step in IEC. This procedure requires four days to complete. The day before the experiment is started, glassware and chemicals are collected. The solutions to be used are prepared as needed prior to the beginning of the activation process.

Five hundred grams of analytical grade macroporous cation resin AG MP-50, 100-200 mesh, hydrogen form (Bio Rad Laboratories), stored in an amber bottle, is poured into a 3L Buchner funnel with a coarse porosity sintered glass plate. The Buchner funnel rests on a 4L filter flask. The resin is washed successively with the solutions listed below. The washing of the resin proceeds rapidly enough without the use of suction.

The first wash solution is 11.7L of 1.5N NaOH, prepared by adding sodium hydroxide pellets (700 grams, Baker analyzed reagent) to distilled water. The amber resin bottle is rinsed with some of the NaOH solution to remove residual resin. The NaOH wash solution then is poured over the resin bed portionwise. The resin bed is stirred occasionally with a stainless steel spatula throughout the activation to allow all the resin particles to contact the solutions evenly. Any resin particles adhering to the spatula are transferred to the resin bed by rinsing with distilled water. After the last portion of each of the different wash solutions has been added to the Buchner funnel, the resin bed is allowed to drain to near dryness and then a portion of the next wash solution is added.

The second wash solution is approximately 1.3L of distilled water. After the resin has been washed with the distilled water, 11.7L of 1.5N hydrochloric acid (1,727 mL of 36.5-38.0% Baker analyzed reagent) is added to the resin in portions. When half of the HCl solution has been added, filtration is interrupted and the resin is allowed to soak in the HCl solution for 1 hour to neutralize residual NaOH. This is accomplished by inserting a nalgene stopper in the stem of the Buchner funnel. After washing of the resin with HCl is completed, the resin bed is washed with 4.0 liters of distilled water, followed by 8.3L of a 1-propanol-water solution (1:1 by volume). The 1-propanol can be obtained from redistillation of 1-propanol used in previous activations.

When the 1-propanol-water wash is completed, the resin should not contact water for the remainder of the activation or else the resin will not be properly activated. The filter flask is rinsed with a small amount of the 1-propanol-water solution.

The resin then is washed with 8.3L of 1-propanol (Burdick & Jackson, HPLC Grade). The 1-propanol is allowed to filter slowly and is stoppered for 1 hour after 4L has filtered through. It has been determined that both the HCl and 1-propanol soak are essential to proper activation. When the contact time was too short and the resin was not allowed to soak for a time in the solvents, the resin was not fully activated. When there is approximately 2L of 1-propanol remaining to be filtered, the Buchner funnel is stoppered and the activation may be suspended until the following day. The 1-propanol that passes through the resin bed is collected in the filter flask and is redistilled for use in the 1-propanol-water solutions in future activations.

The next day, preparations are made for the Soxhlet extraction of the resin with diethyl ether (Baker analyzed reagent). A complete diagram of the Soxhlet extraction apparatus is shown in Figure 2. Before the remaining 2L of 1-propanol is filtered the ether is cooled in ice for 15 minutes. Then, the 1-propanol filtration is begun, and when there is approximately 1L remaining to be filtered in the Buchner funnel, the ether is transferred to a 3L round bottom two-neck flask and is degassed by bubbling argon into the ether. Enough ether is added to allow for convenient flushing during extraction, approximately 2L. When the 1-propanol filtration is complete, the resin is spooned into a glass extraction thimble having a coarse porosity sintered glass disc (8.5 cm I.D. and 19.5 cm height above the disc), and a glass frit is placed on top of resin bed to reduce resin loss during flushing. The thimble is placed into a large Soxhlet extraction apparatus 17.5 cm in height and 9.0 cm I.D. (Rocky Mountain Scientific Glassblowing Co.). The extraction apparatus is set-up in a walk-in fume hood.

The Soxhlet extractor rests on the 3L round bottom flask nested in a heating mantle, which rests on a laboratory jack, and a Friedrichs condenser is connected to the top of the extractor using an adaptor. A stream of nitrogen or argon is added to the top condenser to prevent oxygen from contacting the resin. Teflon® boiling chips are added to the flask through a side neck and the ether is heated to reflux for 24 hours.

After 24 hours reflux, the extraction ether is allowed to cool approximately 30 minutes by turning off the heating mantle, removing the mantle by lowering the lab jack, and immersing the round bottom flask in ice. Concurrently, n-pentane (EM Sciences) is cooled in ice and degassed with argon. The thimble is then carefully removed from the Soxhlet extractor and rinsed five times with portions of n-pentane to remove ether. The round bottom flask is emptied of ether, rinsed with pentane, and then filled with n-pentane to a level that allows convenient flushing, approximately 2L. Nitrogen (or argon) is used to further degas the n-pentane. Teflon® boiling chips are added and heating is begun and the n-pentane is allowed to reflux for 24 hours.

The next day, after the reflux period has elapsed, the n-pentane is cooled for 30 minutes and the thimble is removed from the Soxhlet extractor. The resin is transferred by means of a spoon into a plastic funnel, the neck of which is inserted into the mouth of an amber bottle. Degassed cyclohexane (EM Sciences) in a wash bottle is used to assist the transfer of the resin into the amber bottle. The amber bottle is filled with cyclohexane and blanketed with argon. The lid is closed and taped to prevent any leakage of argon. The date of resin preparation should be noted on the bottle. The activated resins should be used within a period of six months. After this period of time, the resins should be tested for activity as discussed subsequently, using Wilmington distillate (370-535°C; 698-995°F) or other materials previously separated.

Activation of the analytical grade macroporous anion resin AG MP-1, 100-200 mesh, chloride form (500 grams) is similar to the cation resin, with a few changes in procedure. The HCl and NaOH washes are reversed in order. The activation is performed in a fume hood. The resin is first washed with a HCl mixture, 8.3L of 1.5N HCl (1,233 mL conc. HCl diluted in water to 8.3L = 1.5N). Distilled water, 1.3L, is added to the resin followed by 8.3L 1.5N NaOH (500 grams in 8.3L aqueous solution = 1.5N). The NaOH solution is prepared during the HCl wash and is degassed with argon to assure adequate removal of dissolved carbon dioxide and oxygen. For the remainder of the activation the solvents should be rigorously degassed to minimize contact of the resin with air. During the introduction of the NaOH, the resin bed is also blanketed with argon to protect it from the air. After the NaOH wash, the succession is the same as for the cation resin. Argon is continuously bubbled into the solvent above the resin bed when filtration is interrupted. The ether and n-pentane Soxhlet extractions are the same as for the cation resin. The anion resin turns a pinkish color during the ether extraction, which seems to be an indication of proper activation. Occasionally, batches of resin cannot be properly activated. These resins never develop proper color after activation. If they are used to separate asphalts, excessive irreversible adsorption is encountered, resulting in virtual cessation of flow through columns packed with the resins. The reason why some batches of resin do not become properly activated is not known. For this reason, batch numbers of resins from the supplier should be monitored.

## Column Packing

Activated resins are packed into columns using helium pressure. Reasonable safety considerations dictate that the packing operation must be performed behind a protective shield. The procedure can be completed in about 30 minutes.

A packing reservoir (Rainin) is attached to the top of a 25 mm I.D. by 500 mm Altex Prep column fitted with end caps. A filter disc, size 30-60 µ (Rainin) and Teflon® screen (Rainin) are placed on the flat end of a bed support (Rainin) fitted with two Viton® o-rings, size 2-116 (Rocket Seals Corp). This assembly is held together with a Teflon® sleeve (Rainin), and the entire assembly is inserted into the bottom of the column (Figure 3). The packing reservoir is connected to the column with a column extender and then the whole assembly is mounted vertically. Degassed cyclohexane is poured into the top of the packing reservoir until the solvent level reaches the neck of the reservoir. A bed support connected to a helium tank by Teflon® tubing is inserted into the top of the reservoir. Pressure of up to 50 psi helium in 10 psi increments is applied, and any leakage or loose connection is identified and corrected.

About 240 mL activated anion or cation resin slurried in cyclohexane is poured into a graduated cylinder. Helium pressure is relieved from the column, and more degassed cyclohexane is added to fill the packing reservoir halfway. The resin-cyclohexane slurry is poured into the top of the packing reservoir, followed by cyclohexane rinses until the reservoir is filled. The bed support connected to the helium tank is reinserted into the top of the packing reservoir, and a pressure of no more than 50 psi is applied. Cyclohexane flows out of the column by means of Teflon® tubing connected to the bed support at the bottom of the column. When the solvent level is reduced to about 10 mm above the resin bed level in the column, the packing reservoir is detached from the column and replaced with a plunger. The components of the plunger also are illustrated in Figure 3.

Filled columns are allowed to stand 24 hours before use. Gas bubbles that form are maneuvered to the top of the columns by gently tapping the sides of the columns. Gas is released by opening the tube that runs through the plunger and lowering the plunger until it makes contact with the liquid in the column.

## Testing of Activated Resin

Portions of some batches of the activated anion and cation resins were occasionally tested with a Wilmington distillate (370-535°C; 698-995°F) to determine if the resins were activated completely. The procedure used is the same as described by Green et al. (1984) for the separation of asphalts into acidic, basic, and neutral fractions using cyclohexane as eluant. Green et al. (1984) report normalized recoveries of 10.1 mass % acids, 8.0 mass % bases, and 81.8 mass % neutrals for this material. Using columns of different dimensions, when the Wilmington distillate was separated on batches of resins activated during the SHRP A-002A program, normalized recoveries of 10.7% acids, 7.1% bases, and 82.2% neutrals were observed. The two values of the neutral fractions vary by only 0.5%. The two determinations of the polar fractions are reasonably close considering that columns of different dimensions were used. In the separation of the Wilmington distillate, small (~ 2%) losses during workup are encountered, but only negligible amounts of irreversible absorption on resins is observed. Separation of non-distilled materials results in some irreversible absorption. If yields of neutral and polar fractions differ from these results by over 5%, the resins may not have been properly activated, or for unknown reasons are unsuitable.

Testing of the resins also may be carried out using MRL asphalts available from the Federal Highway Administration Long Term Pavement Performance Program materials library.

## Separation of Asphalts into Neutral, Acid, Base, and Amphoteric Fractions

The IEC separation of asphalts into neutral, acid, base, and amphoteric fractions differs from the procedure of Green et al. (1984). Solutions of asphalts contact cation resins first instead of anion resins, as in the Green et al. (1984) procedure. A flow sheet for this separation is illustrated in Figure 4.

Chromatographic separation of asphalts into neutrals, acids, bases, and amphoterics is performed with cyclohexane as the solvent at 37°C (98.6°F). Use of cyclohexane allows basic and amphoteric functionalities to adsorb on a cation resin while acids adsorb on an anion resin and the neutrals are eluted. Amphoteric fractions are then separated from bases with an anion column in a separate operation. The use of cyclohexane for IEC separation is reported by Boduszynski et al. (1977). The IEC separation can be performed in approximately five hours.

Sixteen grams of asphalt is dissolved in 64 mL of degassed cyclohexane. Two columns, one filled with activated cation resin and the other filled with activated anion resin are used. The plungers are adjusted to remove any voids. A 1/4 inch gap is left between the resin bed and the plunger in each column to prevent pressure build-up. Two FMI Lab Pumps, model RP-SY are connected to two FMI Pulse Dampeners, model PD-60-LF which are then connected to the bottom of the columns. Approximately 250 mL of degassed cyclohexane is pumped through each column individually at a flowrate of five milliliters per minute. Water jackets (not illustrated in the schematic diagram of the column, plunger assembly, and bed support assembly in Figure 3) are fitted onto the columns, and the water jackets are connected to a constant temperature bath maintained at 37°C (98.6°F). The columns are arranged in series, with the top of the cation column connected to the bottom of the anion column, and 50 mL of degassed cyclohexane then is pumped through them. Removal of the pulse dampener from the system, to prevent damage to it, is necessary before the asphalt solution is introduced. The dissolved asphalt is introduced into the system via Teflon® tubing, followed by rinsing of the flask that contained the asphalt solution with approximately 30 mL of degassed cyclohexane. The pulse dampener is reconnected to the system and 750 mL of degassed cyclohexane is pumped through both columns. Another 200 mL of degassed cyclohexane is pumped through the anion column alone. All eluates are collected as the neutral fraction. These eluates are filtered through a 350 mL Buchner funnel with a medium porosity sintered glass plate to remove resin particles. The filtrate then is divested of solvent on a rotary evaporator (Buchi). After most cyclohexane has been removed, the neutral fraction is transferred to a 100 mL round bottom flask with methylene chloride (EM Sciences) and again is divested of the solvent on the rotary evaporator. The flask and contents are then rotated in a boiling water bath under reduced pressure until a constant weight is reached, approximately 2 hours. The water bath is replaced by an oil bath, which is heated to 125°C (257°F). During heating, reduced pressure (2 torr) is applied for 2 hours. After this treatment, the flask then is removed from the rotary evaporator. The neutral fraction is blanketed with nitrogen and the flask is stoppered. The flask and contents are stored in a cool, dark cabinet.

## Extraction of Asphalt Fractions Adsorbed on Resins

The combination of amphoteric and basic fractions are adsorbed on the cation resin, and these materials must be desorbed. This is done as follows. The plunger on the top of the column is removed and rinsed with benzene (EM Sciences) in a 1 L beaker. This and subsequent operations must be performed in a good fume hood to avoid exposure to vapors. The plunger is removed from the beaker and the column is inverted over the beaker. Approximately 30 mL benzene is pumped into the column. The pump is then detached from the column and a syringe containing about 25 mL benzene is inserted into the Teflon® tube which leads into the top of the column. Hand pressure on the syringe should be sufficient to dislodge the resin into the beaker. Several rinses are required to fully remove the resin from the column. Pumping the syringe with air may speed up the process. The end cap at the top of the column is unscrewed and the bed support assembly is removed and rinsed into the beaker. Fifteen mL of a mixture of 1-propylamine (Aldrich Chemical Co., 98%) and benzene then is added to the beaker. This mixture, which desorbs asphaltic materials from the cation resin, had previously been prepared and consists of 50 mL 1-propylamine and 100 mL benzene. After adding the 15 mL of the mixture to the beaker, the remainder is reserved.

The cation resin in the beaker is poured into a Soxhlet thimble resting in another beaker. After the solvent has drained from the thimble, a glass frit is placed on top of the resin bed. The liquids drained from the resin are poured into a 2 L round bottom, two-necked flask with a vertical side arm containing a magnetic stirring bar. More benzene is added to the flask to allow for convenient flushing. A Soxhlet extraction apparatus is set-up similar to the one used in the resin activation only on a smaller scale. A stirring plate (Sargent-Welch Scientific Co.) is set under the heating mantle in place of the laboratory jack. A drip funnel with a pressure by-pass is placed in the second neck of the flask to allow the remainder of the 1-propylamine-benzene mixture to be slowly added to the system, approximately 5 mL every 15 minutes. The amine-benzene mixture must be added cautiously, or "bumping" of the resin will result, causing resin to be ejected from the extractor. The solvent is allowed to reflux for approximately 12 hours (which need not be continuous), after which the resin should be clean of most adsorbed material. During the addition of the 1-propylamine and the extraction, dry argon is introduced into the mouth of the condenser. This is to minimize contact of water and oxygen with the contents of the extractor.

When the extraction is finished the thimble is carefully removed from the Soxhlet and the resin is removed as a slurry into a beaker. The solution of desorbed IEC fraction in the round bottom flask is then filtered through a 350 mL medium porosity Buchner funnel by gravity filtration. The resin in the flask, if any (some usually escapes from the thimble as a result of bumping), is washed with benzene until the filtrate is clean. The resin from the thimble is then poured into the Buchner funnel and rinsed with benzene until a clean filtrate appears.

After desorption is complete the solution containing the desorbed amphoteric and basic fractions is transferred to a pear-shaped flask and is carefully divested of solvent using a rotary evaporator. These fractions are highly surface active and tend to form rigid foams which enter the rotary evaporator from the flasks. After almost all solvent has been removed, the residue concentrated in the flask is rinsed three times with benzene to remove 1-propylamine. The desorbed materials are then transferred to a 100 mL round bottom flask and dried to a constant weight, as for the neutral fraction. These desorbed materials comprise the base and amphoteric fractions. They are stored under a blanket of inert gas in the dark.

The desorption of the anion resin is similar to the procedure above with a few changes. The column is emptied of resin as described above and the anion resin is desorbed with 50 mL of formic acid (Aldrich Chemical Co., Inc., 96% A.C.S. reagent). Approximately 15 mL of formic acid is mixed with the anion resin slurry before the resin is transferred to the Soxhlet thimble and the remaining 35 mL is added to a 1L round bottom, single-necked flask. Enough benzene is then added to allow for convenient refluxing. The anion resin is placed in an extraction thimble. The thimble and contents are placed in a Soxhlet extractor, which is mounted on the round bottom flask. A condenser is mounted on top of the Soxhlet extractor. The benzene-formic acid mixture will reflux for approximately 12 hours or until the resin is cleaned of adsorbed material. Dry argon is introduced into the mouth of the condenser during addition of formic acid and refluxing. The filtration procedures after the extraction are the same.

In order to separate the base from the amphoteric fraction, a second separation is required. The mixture of the two fractions is dissolved in cyclohexane (4 mL cyclohexane for each 1.0 g mixture) and the solution is pumped through a column of activated anion resin, as described above. The base fraction is eluted, and the amphoteric fraction is adsorbed on the resin. Isolation of each fraction is the same as described above for the anion resin.

## Separation of Asphalts into Strong Acid, Strong Base, Weak Acid, Weak Base, and Neutral Fractions

Ion exchange chromatography separation of the asphalts into strong acid, strong base, weak acid, weak base, and neutral fractions is based on the method reported by Green et al. (1984). A flow sheet for this separation is illustrated in Figure 5. This separation uses a mixed solvent consisting of 810 mL benzene, 810 mL tetrahydrofuran (Burdick and Jackson), and 180 mL ethanol (Aldrich Chemical Co.). In this separation, 64 g of this mixed solvent are used to dissolve 16 g asphalt for each experiment. One column filled with activated anion resin and one column filled with activated cation resin are connected in series. The asphalt solution is pumped into the column filled with anion resin first. Use of the mixed solvent allows strong acids to adsorb on an anion resin while strong bases adsorb on a cation column, and the neutrals, weak acids, and weak bases are eluted. The eluates are divested of solvent, redissolved in cyclohexane (four volumes/g substrate) and the solution is pumped through two different columns of activated anion and cation resins, the solution contacting the anion resin first. Weak acids, adsorbing on an anion column, and weak bases, adsorbing on a cation column, are then separated from the eluted neutrals. The details of this separation and subsequent operations are essentially the same as those that are explained more fully in the previous two sections.

Results of IEC of SHRP asphalts are presented and discussed in Volume II, Chapter 1 of the Final Report for Contract A-002A, Binder Characterization and Evaluation.

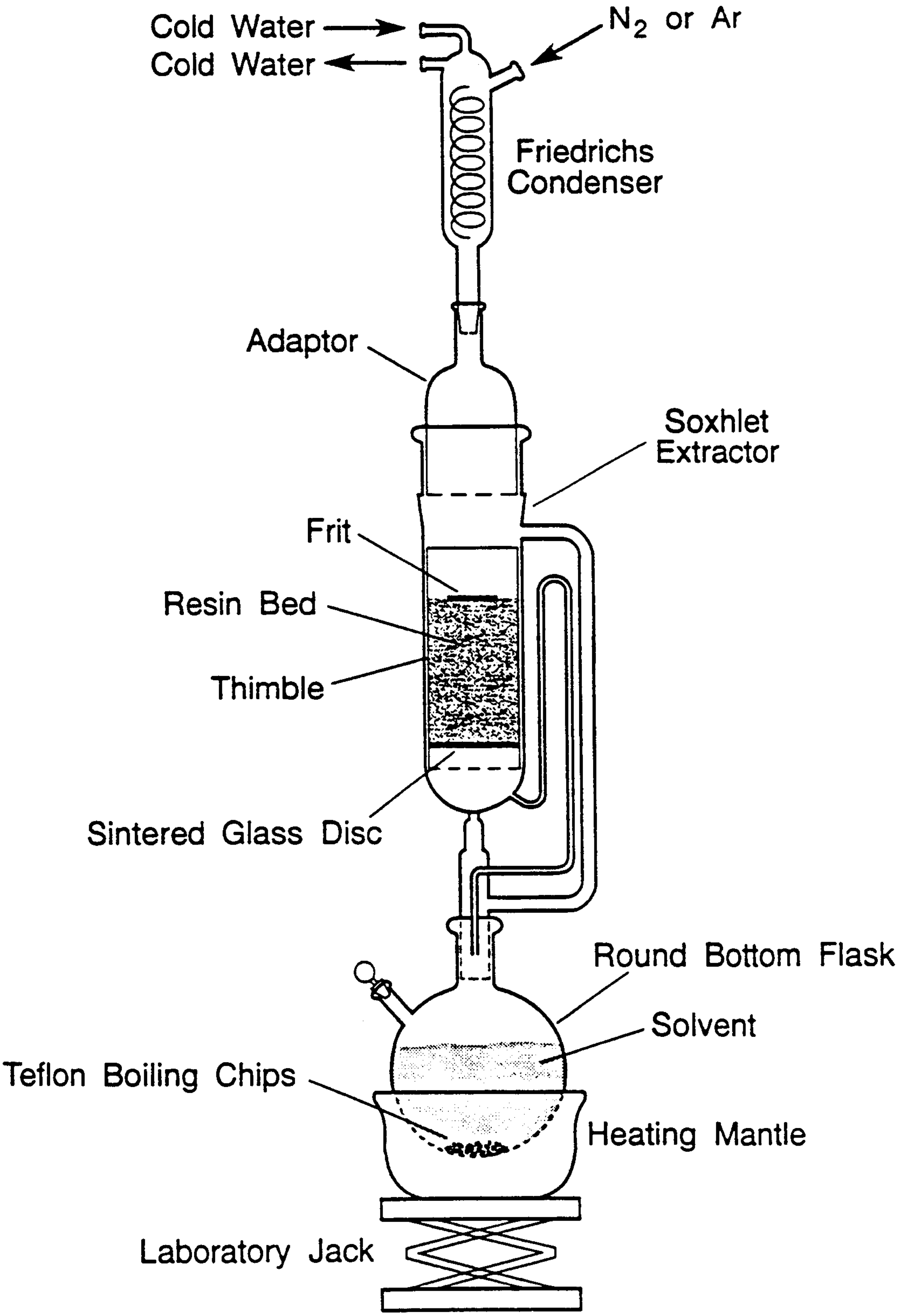

**Figure 2** Apparatus for Extraction of Activated Resins

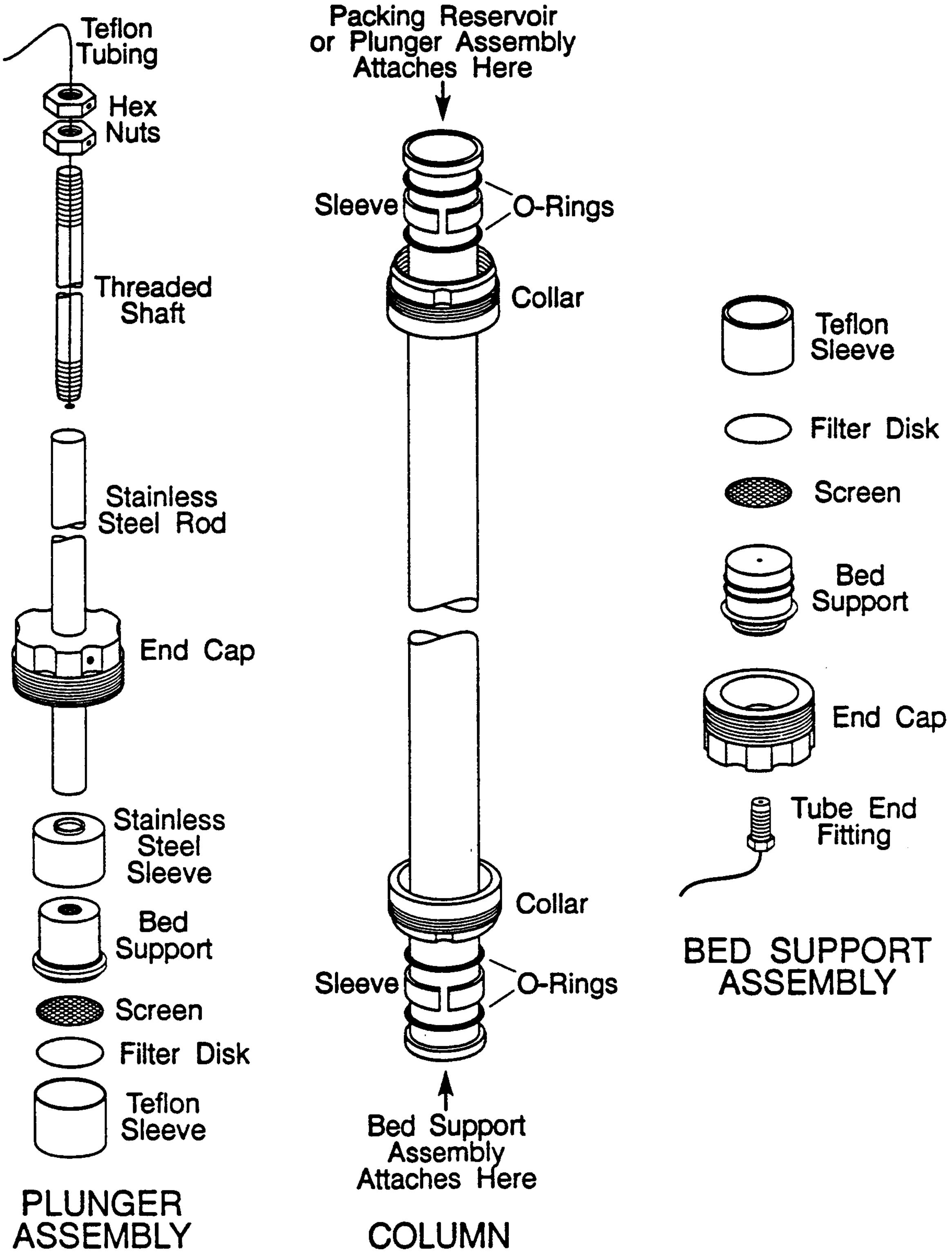

Figure 3 Schematic Diagram of Column, Plunger Assembly, and Bed Support Assembly for Columns Used in Ion Exchange Chromatography Separations

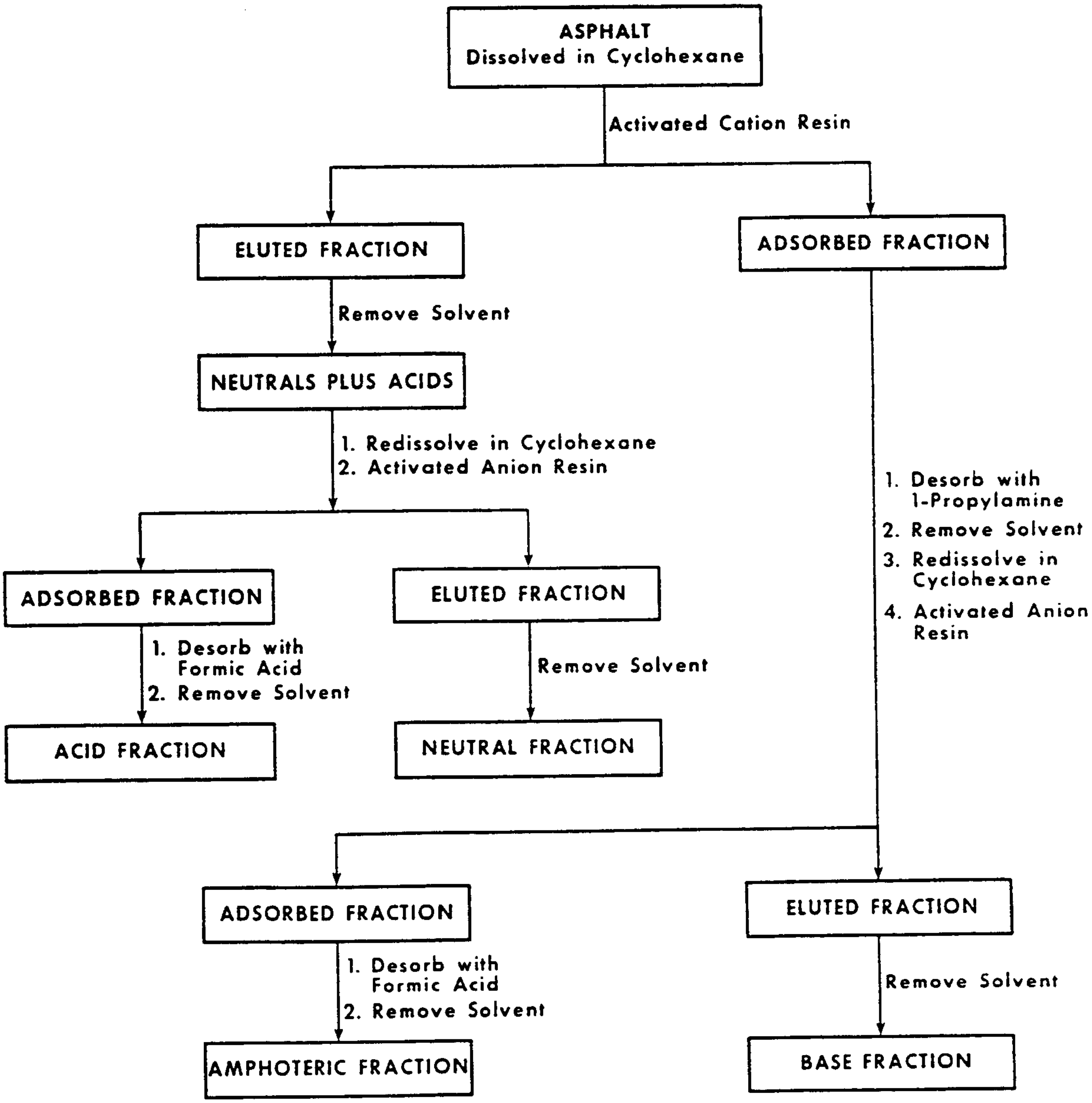

Figure 4 Flow Sheet for Isolation of Amphoterics by IEC

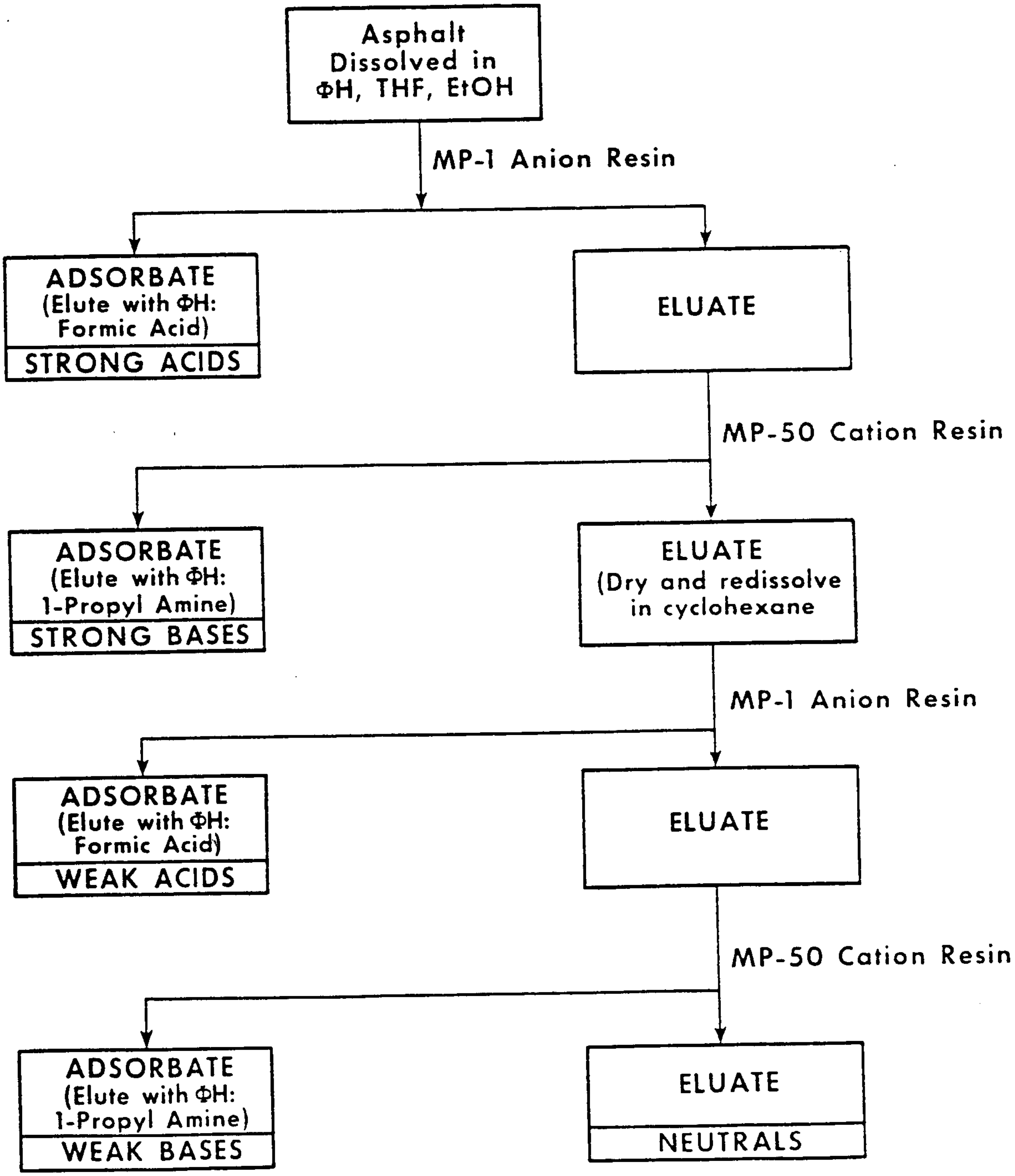

Figure 5 Flow Sheet for Separation of Asphalts into Five Fractions by IEC

# References

Altgelt, K.H. and E. Hirsch (1970). GPC Separation and Integrated Structural Analysis of Petroleum Heavy Ends. Separation Sci., 5, 855-862.

Beazley, P.M., L.E. Hawsey, and M.A. Plummer (1987). Size Exclusion Chromatography and Nuclear Magnetic Resonance Techniques for Predicting Asphalt Yields and Viscosities from Crude Oil Analyses. Trans. Res. Rec., 1115, 46-50.

Bishara, W.W., R.L. McReynolds, and E.R. Lewis (1991). The Interrelationship Between Performance-Related Properties of Asphalt Cement and Their Correlation with Molecular Size Distribution (MSD). Trans. Res. Rec., 1323, 1-9.

Boduszynski, M.M., B.R. Chadha, and T.S. Pochopien (1977). Investigations on Romaskino Asphaltic Bitumen. 3. Fractionation of Asphaltenes Using Ion Exchange Chromatography. FUEL, 56, 432-436.

Brule, B., G. Raymond, and C. Such (1986). Relationships Between Composition, Structure, and Properties of Road Asphalts: State of Research at the French Public Works Central Laboratory. Trans. Res. Rec., 1096, 22-34.

Bunger, J.W., K.P. Thomas, and S.M. Dorrence (1979). Compound Types and Properties of Utah and Athabasca Tar Sand Bitumens. FUEL, 58, 183-195.

Bynum, D. and R.N. Traxler (1970). Gel Permeation Chromatography Data on Asphalts Before and After Service in Pavements. Proc. Assoc. Asph. Pav. Technol., 39, 683-702.

Chong, S.-L., J.J. Cummins, and W.E. Robinson (1976). Fractionation of Soluble Extracts Obtained from Kerogen Thermal Degradation with CO and $H_2O$. Am. Chem. Soc. Preprints, Div. Fuel Chem., 21, 265-277.

Corbett, L.W. (1969). Composition of Asphalt Based on Generic Fractionation Using Solvent Deasphaltening, Elution-Adsorption Chromatography, and Densimetric Characterization. Anal. Chem., 41, 576-579.

Donaldson, G.R., M.W. Hlalinka, J.A. Bullin, C.J. Glover, and R.R. Davison (1988). The Use of Toluene as a Carrier Solvent for Gel Permeation Chromatography Analyses of Asphalt. Liq. Chrom., 11, 749-765.

Green, J.B., R.J. Hoff, P.W. Woodward, and L.L. Stevens (1984). Separation of Liquid Fossil Fuels into Acid, Base, and Neutral Concentrates. 1. An Improved Nonaqueous Ion Exchange Method. FUEL, 63, 1290-1301.

Haines, W.E. and C.J. Thompson (1975). Separating and Characterizing High-Boiling Petroleum Distillates: The USBM-API Procedure. Rept. of Inv. LERC/RI-75/5, BERC/RI-75/2, July.

Haley, G.M. (1975). Changes in Chemical Composition of a Kuwait Short Residue During Air Blowing. Anal. Chem., 47, 2432-2438.

Huynh, H.K., T.D. Khong, S.L. Malhotra, and L.P. Blanchard (1978). Effect of Molecular Weight and Composition on the Glass Transition Temperatures of Asphalts. Anal. Chem., 50, 976-979.

Jennings, P.W., J.A.S. Pribanic, J. Smith, and T.M. Mendes (1988). Predicting the Performance of Montana Test Sections by Physical and Chemical Testing. Trans. Res. Rec., 1171, 59-65.

Jewell, D.M., J.H. Weber, H. Plancher, and D.R. Latham (1972). Ion-Exchange, Coordination, and Adsorption Chromatographic Separation of Heavy-End Petroleum Distillates. Anal. Chem., 44, 1391.

McKay, J.F., P.J. Amend, T.E. Cogswell, P.M. Harnsberger, R.E. Erickson, and D.R. Latham (1978). Petroleum Asphaltenes--Chemistry and Composition. In "Analytical Chemistry of Liquid Fuel Sources: Tar Sands, Oil Shale, Coal, and Petroleum," P.C. Uden, S. Siggia, and H.B. Jensen, Eds. Adv. Chem. Ser., 170, ACS, Washington, D.C., Chapter 9, 128-142.

McKay, J.F., P.J. Amend, P.M. Harnsberger, T.E. Cogswell, and D.R. Latham (1981). Composition of Petroleum Heavy Ends. Part I: Separation of Petroleum Above 675°C Residues. FUEL, 60, 14-16.

Pfeiffer, J.P. and R.J.N. Saal (1940). Asphaltic Bitumen as a Colloidal System. Phys. Chem., 44, 139-149.

Preece, S.C., J.F. Branthaver, and S.S. Kim (1992). Separation of a Quinolone-Enriched Fraction from SHRP Asphalts. Am. Chem. Soc., Div. Fuel Chem., 37, 1342-1349.

Ramljak, Z., A. Solc, P. Arpino, J.M. Schmitter, and G. Guichon (1977). Separation of Acids from Asphalts. Anal. Chem., 49, 1222-1225.

Reerink, H., and J. Lijzenga (1975). Gel Permeation Chromatography Calibration Curve for Asphaltenes and Bituminous Resins. Anal. Chem., 47, 2160-2167.

Selucky, M.L., S.S. Kim, F. Skinner, and O.P. Strausz (1981). Structure-Related Properties of Athabaska Asphaltenes and Resins as Indicated by Chromatographic Separation. In "Chemistry of Asphaltenes," Bunger, J.W., and Li, N.C., Eds., Adv. Chem. Ser. 195, ACS, Washington, DC, Chapter 6.

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