

SIZE EXCLUSION CHROMATOGRAPHY IN THE ANALYSIS OF PITCH

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Abstract

Size exclusion chromatography (SEC) has been investigated as a tool to analyze pitch. SEC is a high pressure liquid chromatography (HPLC) method where the components are separated by hydrodynamic volume. The method is well known from polymer science where it is used to obtain molecular weight distributions. Several mobile phases were investigated. It was found that when the column was used at elevated temperature and N-methyl-2-pyrrolidinone (NMP) was used as the mobile phase, the chromatographic system could be operated without interference from effects not related to molecular size. The chromatographic system also allowed analysis of the entire quinoline soluble fraction. The method was applied to pitch that, as part of the preparation procedure, had received mild thermal treatment of the feedstock tar. The study followed the formation of large molecular species by analyzing the toluene insoluble fraction of pitch dissolved in NMP. Chromatographic fractions were collected for further analysis by fluorescence spectroscopy.

Introduction

High quality binder pitch is essential for the production of successful carbon anodes, cathodes and sidewall blocks for the aluminium smelting industry. Pitch producers and users possess only modest information on what happens at a molecular level when either feedstock tar or product pitch is held for an extended period at, or just above, the maximum process temperature required to produce industrial pitches. Fundamental work on pitch is handicapped by a distinct lack of information about the heaviest

compounds that are present just prior to forming either mesophase or green coke. SEC is one of the few analytical tools that could unlock knowledge in this area. There is a strong prospect that reliable fundamental knowledge about the behavior of the heaviest molecules found in tar and pitch will indicate the preferred route to advances in pitch production and improvements to carbon-carbon artifacts such as anodes. This study has focused in particular on the heavy, high MW, 'difficult' compounds present in pitch. These compounds are 'difficult' because they have low solubility in common solvents, which excludes less sophisticated chromatographic techniques. The basic method applied in this work has been size exclusion chromatography, which is also known as gel permeation chromatography.

Size exclusion chromatography (SEC) has shown to be a very powerful tool to obtain molecular weight distribution data in polymer science [1]. It has also been applied to characterization of coal tar pitches [2, 3, 4], other coal derived material [5, 6] and aromatic petroleum products [7].

SEC is based on a column with a rigid polymer gel as packing and an organic solvent as mobile phase. In a perfect SEC analysis the compounds are not adsorbed onto the stationary phase, the components of the sample are separated by their ability to enter pores in the gel particles. Larger compounds that cannot enter the pores will travel with a high linear speed in the space between the gel particles and therefore exit the column first. Smaller components will enter pores that are larger than they are (or more precisely larger than their hydrodynamic volume) and thereby be delayed. This elution range is the size exclusion zone.

Components of the same or smaller hydrodynamic volumes than the mobile phase will enter all pores and suffer the longest delays. They will elute with the original sample solvent. In perfect SEC no components will elute after this total permeation limit of the system. In SEC, many mobile phases will cause some compounds known to be present in pitch not only to elute after the permeation limit but also to have the elution order affected by the chemical functionality of the molecules. These effects are caused by absorption to the column packing. The phenomenon is referred to as non-size retention or non-size effects.

When choosing the chromatographic system and operating conditions there are two major concerns that have to be taken into account.

1. Solubility of the sample in the mobile phase
2. Non-size effects

The sample is transported into the column dissolved in the liquid mobile phase. For this reason only the part of the sample which is soluble in the mobile phase can be analyzed. Ideally the mobile phase should be a very good solvent for the sample. If the sample is only partially soluble this can introduce non-size effects which might be multiplied because of high column pressure. These unwanted effects can be reduced by 1) choosing another solvent and 2) raising the column temperature [1].

An important question when applying SEC to petroleum or coal derived samples is whether the output is a reliable molecular weight distribution curve uncompromised by the other effects mentioned above. One approach has been to test this with pure compounds which are known to appear in coal or petroleum derived samples [2, 6]. It has been found that most chromatographic SEC systems depend on group functionalities. An additional drawback is that only the lightest components in the samples can be obtained in pure form so the heaviest components are then not covered by the calibration. Another approach is to fractionate a sample of the material that is of interest and determine the molecular weight of the fractions [4, 7]. This approach has reassuringly shown that the fractions are eluted by a size exclusion based mechanism.

Even though a true molecular mass distribution is not always easily determined by SEC the main strength of the method is comparison between similar samples. As previously stated, choosing a good solvent for the pitch as mobile phase can reduce the non-size effects. Good results have been obtained using the solvent N-methyl-2-pyrrolidinone at column temperature of 80°C [3, 5, 6].

Experimental

The SEC system consisted of a Gynkotek, High Precision Pump, model 300 delivering a mobile phase flow of 0.5 ml/min. Sample injection was performed via a Rheodyne 7725 valve fitted with a 20 µl sample loop. Separation was achieved through a 30 cm PL-Gel Mixed D column with a 5 µm guard column. Two different mobile phases were applied. When using THF (tetrahydrofuran) as the mobile phase, the columns were operating at ambient temperature with detection through a RI detector (differential refractive index detector). In the measurements with NMP as the mobile phase the column was operating at 90°C. Detection was through a DA (Diode Array) Detector, PE, model 235C, with collection of UV absorption data at 300nm and 350nm. Samples were prepared as 2 g/L solutions which were treated in ultrasonic

bath for at least 30 minutes, left to equilibrate overnight and centrifuged before use.

Fluorescence spectrometry was used to further analyze chromatographic fractions. The equipment was a Fluorescence Spectrophotometer (MFP-3, PE). It was operated in synchronous mode with a constant difference between the excitation and emission wavelength of 20nm.

Samples

All tar and pitch samples were supplied from Koppers Denmark. CTP A was used as received (properties in Table I). This pitch was solvent fractionated by extracting 10 grams of pitch with solvent followed by suction filtration to obtain the solution. This procedure was repeated until the solvent washings ran clear and colorless. The insoluble fraction was then washed with a stronger solvent. The soluble fraction was reduced in a rotary evaporator and dried in a vacuum oven. Vapor pressure osmometry was used to determine the molecular weight of the fractions by measuring four concentrations in pyridine at 60°C and extrapolating the readings to infinite dilution.

The TI fraction of the treated pitches was derived from samples obtained from Koppers Denmark. The preparation included a six hour tar thermal treatment step. The procedure has been described elsewhere [8, 9, 10].

Table I: Properties of the coal tar pitch (CTP A)

	Unit			
SP (ASTM D-3104)	°C	115.5		
QI (ISO 6791)	%(w/w)	7.4		
TI (ISO 6376)	%(w/w)	26.8		
CV (ISO 6998)	%(w/w)	59.1		
Solvent fractionation of pitch				
Fraction	Code	Unit	Yield	Mol. wt.
HS	F-hep	%(w/w)	7.5	265 g/mol
HI, TS	F-tol	%(w/w)	68.8	413 g/mol
TS, THFS	F-thf	%(w/w)	10.8	1044 g/mol
THFI, NMPS	F-nmp	%(w/w)	(10.0) ^a	-
NMPI	F-res	%(w/w)	(18.9) ^a	-

^a Might still contain NMP

Calibrating the Chromatographic System

Two different solvents were tested as the mobile phase for the chromatographic system, tetrahydrofuran (THF) and N-methyl-2-pyrrolidinone (NMP).

Initially THF was used as a solvent. THF is a slightly better solvent for coal tar pitch than toluene [11] and it would therefore be expected that all of the toluene soluble part of the pitch and part of the toluene insolubles could be made soluble and analyzed with this solvent. Figure 1 is a calibration curve made with polystyrene standards. Some selected PAH components are included in the figure as individual plot points (Naphthalene, Phenanthrene, Fluorene, Fluoranthene, Benz(a)anthracene, benzo(b)fluorene, Coronene). The graph shows that the components cannot be represented by the polystyrene calibration curve and that the elution volumes are actually beyond the

permeation limit of the system. One of the PAH's was separated from the cohort of PAH plot points. This was Coronene, which is a highly compact aromatic molecule.

Figure 2 shows a similar calibration with NMP as the mobile phase and a column temperature of 90°C. The PAH compounds are now eluting closer to the calibration line and Coronene is grouped with the other PAH's. This might be attributed to the better solvent power of NMP and or because it is possible to run the column at a higher temperature due to the higher boiling point ($B_p(\text{THF})=65^\circ\text{C}$, $B_p(\text{NMP})=202^\circ\text{C}$).

The position of the calibration line has shifted to lower elution volumes. The gel particles are in suspension in the mobile phase and swell when a better solvent is used. In other words, elution volumes can only be compared when the chromatographic system and solvent are the same. The calibration curves appear to show that the size exclusion mechanism is better when NMP is the mobile phase.

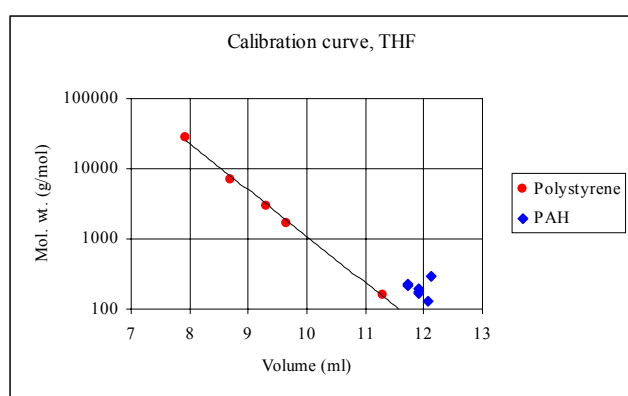


Figure 1: SEC calibration curve with THF as mobile phase

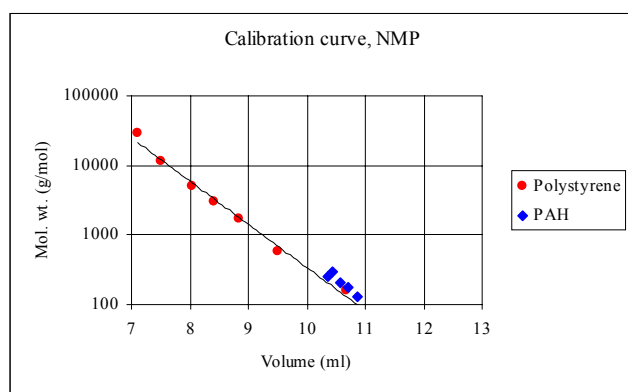


Figure 2: SEC calibration curve with NMP as mobile phase

The SEC chromatograms for pitch CTP A, obtained with the two mobile phases, are shown in Figure 3. There are two improvements to observe; 1) the elution of the pitch is moved within the size exclusion zone and 2) a new heavy material peak is appearing.

When THF was used as the mobile phase the peak maximum for CTP A occurred after the permeation limit. This further indicated

that the separation is not only due to size exclusion mechanisms but that some adsorption onto the column packing is taking place. When NMP is used as the mobile phase the entire sample is eluting within the size exclusion zone.

The chromatogram obtained with NMP shows a new, early eluting peak in the heavy end of the chromatogram. The greater solvent power of NMP means that a larger part of the pitch is soluble in the mobile phase and that this heavy material may therefore be analyzed with the new system. This notion is in accordance with the results of Johnson et al. [5].

In the first chromatogram with THF an RI detector is used. This type of detector cannot be used when NMP is used as the mobile phase, so for this system a DA detector is applied. This means the peak heights in the two chromatograms are not directly comparable.

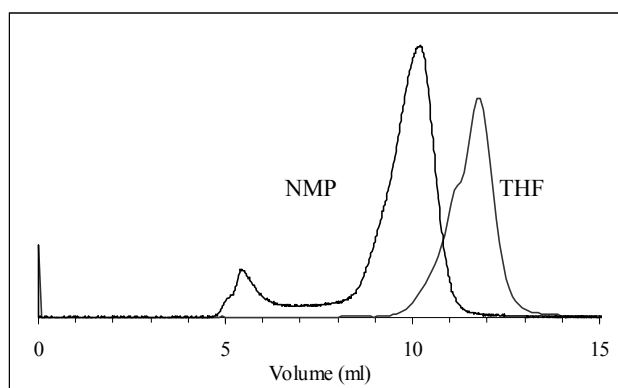


Figure 3: The sample CTP A analyzed using different mobile phases. Conditions: THF: ambient temperature, RI detector, NMP: $t=90^\circ\text{C}$, DA detector.

SEC of Pitch Fractions

Pitch CTP A was fractionated with heptane, toluene, THF and NMP. The yields are given in Table I. Fractions that had either been dissolved in NMP or washed with it could not be completely dried in the vacuum oven, so the yields do not add up to 100%. The fractions were given a code, which is also displayed in the table.

The average molecular weight of the lightest fractions F-hep, F-tol and F-thf was determined by VPO and is listed in Table I. The heptane soluble part of the pitch (F-hep) has an average molecular weight of 265 g/mol. This is comparable to the weight of the pure PAH's which was analyzed earlier (Figure 2) and the SEC chromatogram of this fraction (Figure 4) is eluting in the same range as a sharp peak right before the permeation limit. The largest fraction of the pitch is the toluene soluble, heptane insoluble fraction (F-tol) that has an average molecular weight of 413 g/mol. This material is apparently responsible for the light material peak in the chromatogram. There is an indication of a peak in the heavy end in the chromatogram.

The THF soluble, toluene insoluble fraction (F-thf) has an average molecular weight of 1044 g/mol and the fraction is divided between the two peaks. The THF insoluble, NMP soluble peak elutes mainly as part of the first peak close to the exclusion limit.

The peak elutes prior to the polystyrene sample with a molecular weight of 28500 g/mol so this range of material is not covered by the calibration curve. This example confirms that the calibration curve cannot be used directly for the heavy end of coal tar pitch. Unfortunately it was not possible to determine the molecular weight of the F-nmp fraction because it contained some NMP and was not completely soluble in pyridine.

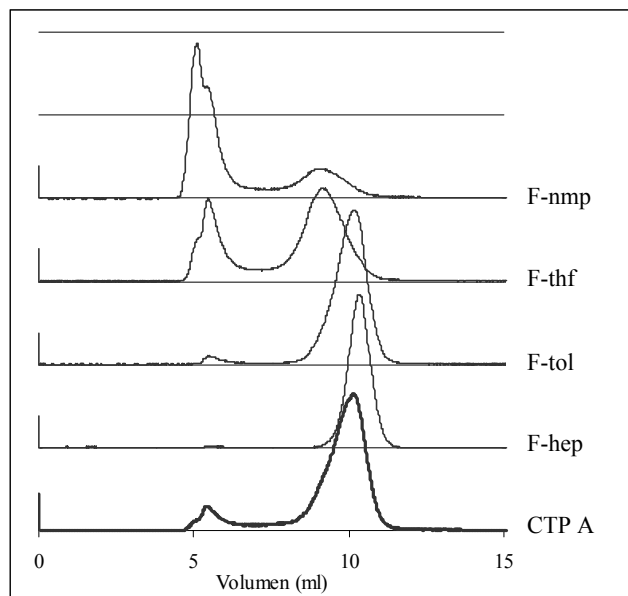


Figure 4: Size exclusion chromatograms of solvent fractions

Solvent fractions derived from the ISO 6791 and ISO 6376 standard methods were collected for SEC analysis (Figure 5). The toluene soluble fraction (TS) obtained by this method mainly consists of light material. There is however, a clear indication of a peak representing heavy material. All components, which elute at the permeation limit, are contained in this fraction. The toluene insoluble fraction was not completely soluble in NMP. The part of the fraction which is eluted is divided in the two peaks. The quinoline insoluble (QI) part of the pitch is almost completely insoluble in NMP. The part of the material that can be analyzed mainly consists of very heavy material with the possible inclusion of some light compounds. The heavy material is interesting because these molecules are the nearest to mesophase (or green coke) that can be analysed.

Analysis of Thermally Treated Pitch

The chromatographic method was used to analyze petroleum pitch samples that had received a thermal treatment for 6 hours at different temperatures prior to vacuum distillation [9]. The developments in the heaviest components were the main interest. When the whole pitch were analyzed, the small modifications in the pitch was hardly visible on the SEC chromatograms. The toluene soluble fraction was still the major part of the pitch and it mainly eluted as part of the late light material peak, blurring the development of heavier species (Figure 5). We therefore attempted only to analyze the TI fraction of the pitch.

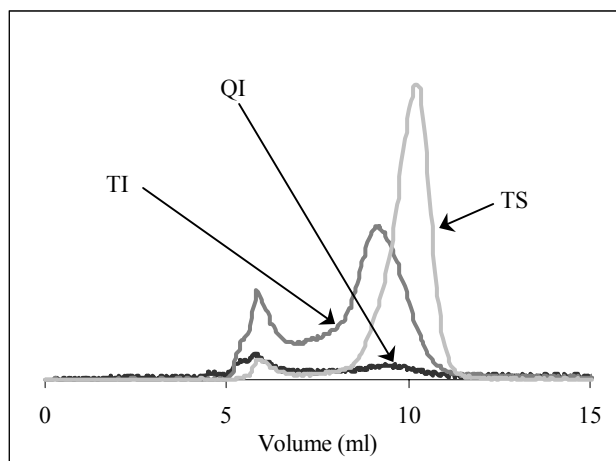


Figure 5: Size exclusion chromatogram of QI, TI and TS obtained from ISO 6791 and ISO 6376 methods

ISO method 6376 was used to obtain TI material. Figure 6 shows SEC chromatograms for five samples which have received a thermal tar treatment at temperatures between 307°C and 415°C. In Figure 6 the sample concentration of TI material was kept constant at 2 g/L, consequently the chromatograms do not represent the development in the pitch but in the TI fraction of the pitch.

As the tar thermal treatment temperature is increased, the peak eluting at 5.4 ml is growing. At the same time, the peak that elutes last is shifting towards longer eluting times. As the severity of the thermal treatment is increased a new early eluting peak is formed. This high molecular weight peak is a key finding from this study and it illustrates the complex, consecutive and sometimes competing processes likely to take place when pitch is produced and used.

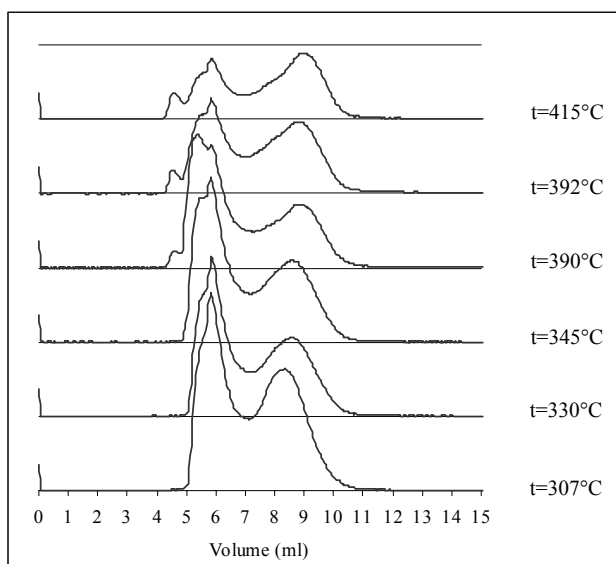


Figure 6: SEC chromatograms of TI fraction from tar treated pitch samples [9].

The chromatograms of the pitches treated at 390°C and 392°C do look very different. The main difference between the two samples is that the pitch, which was produced with tar thermal treatment at 392°C, contains visible mesophase (0.4%(v/v) by counting) while the other shows no visible mesophase. The formation of this liquid crystalline phase might account for the difference, which may represent molecules that have progressed to form the mesophase bodies. In the chromatogram for pitch made from tar heated to 415°C further material seems to have disappeared from the middle peaks. Intermediate molecular weight components appear to be polymerizing to form very large molecules together with some “light ends”. This observation gives some new insight into the fundamental process taking place in a part of the pitch that is not accessible by most commonly used analysis tools.

The amount of TI material is increased as a result of the treatment. If the output level of the chromatograms is scaled to represent the whole pitch, it is noted that raising the severity of thermal treatment increases the content of material covering the entire molecular weight range. The pattern is broken when the treatment temperature is raised to 392°C and 415°C, where optically visible mesophase is found in the pitch. At these temperatures the amount of material in the new, early peak and the light material peak continue to increase whereas the middle peak is reduced.

Figure 6 reveals that material appearing in the high molecular weight end of the chromatogram is being formed as a result of the thermal treatment. The nature of these peaks is the subject of an ongoing discussion. If the chromatographic system is working ideally, the peaks should represent high molecular weight species. There have however, been suggestions that it might also be non-chemically bonded aggregates of smaller polar molecules (see [3] for further discussion). The fact that the early peaks are reduced in size by the formation of mesophase could be interpreted as formation of larger molecules that subsequently become mesophase.

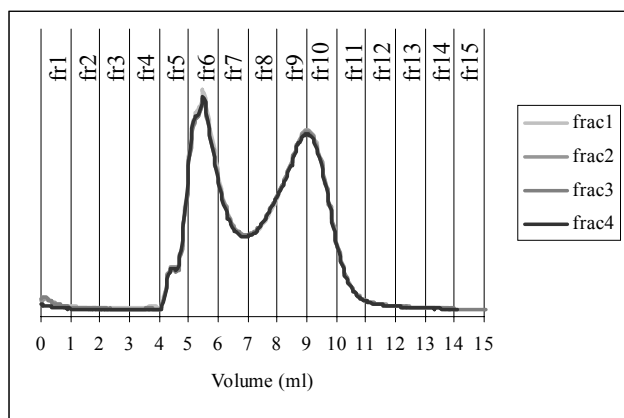


Figure 7: SEC fractionation of a petroleum pitch sample (Thermally tar treated at 410°C)

Fluorescence Spectrometry of SEC Fractions

In order to obtain more information about the molecular structure, chromatographic fractions were collected and further analyzed by fluorescence spectrometry. Each fraction was a 1ml cut of the chromatogram. The fractions were named fr1-fr15 (i.e. fr1: mobile phase eluted between 0 ml and 1 ml). This column was not

a preparative column and it was necessary to run four samples to obtain sufficient material (Figure 7). The fractions were transferred to the sample cuvette in the fluorescence spectrometer without further treatment.

Figure 8 displays the spectra for all the fractions from fr3 to fr12. The fractions collected between 9ml and 12 ml gave the strongest fluorescence signals. This means that if a fluorescence detector had been used for the SEC, the chromatograms of the TI fractions had appeared as a single peak right at the permeation limit. The fraction that shows the largest fluorescence is the fraction fr11 that was collected between 10 and 11 ml.

The fluorescence spectra of the fractions fr10 – fr12 shows clear peaks at discrete emission wavelengths (Figure 8). If the intensity of the peaks is viewed as percentage of maximum intensity, a shift towards higher wavelengths with lower elution volume is observed. This can be interpreted as an increase in molecular weight and is well in line with the SEC results.

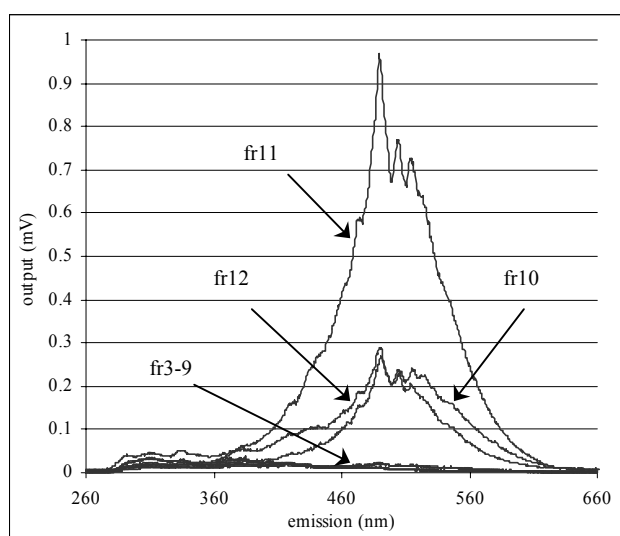


Figure 8: Fluorescence spectra of SEC fractions. Collected directly on the sec fractions with $\Delta\lambda=20\text{nm}$, slit widths=5 nm, sensitivity= 30 %.

In order to record spectra of the fractions that show low fluorescence, the slit width was increased to allow more light through the sample. Figure 9 shows four selected spectra for SEC fractions collected between 2 to 9 ml. For the fractions fr6-fr9 the maximum fluorescence intensity is lower than for pure NMP. In the wavelength range 280-400 nm the intensity of the fluorescence from fraction fr6-fr9 is lower than the fluorescence of pure NMP. At the higher wavelengths the intensity of the fluorescence is higher. The presence of very large molecules can manifest itself as absorption of fluorescence caused by internal energy quenching within the molecule [12]. Large molecular species are also known to have lower fluorescence intensity than smaller molecules. This supports the theory of large molecules in these fractions and represents new knowledge on pitch constitution and behavior.

The fraction fr5 is almost identical with the fraction fr3, which was collected prior to the exclusion limit. The fluorescence

spectra do not give any indication of the nature of this fraction. Both of the spectra differ somewhat from the spectra of pure NMP. This could be attributed to absorbed material in the column slowly eluting over the entire range of the chromatogram.

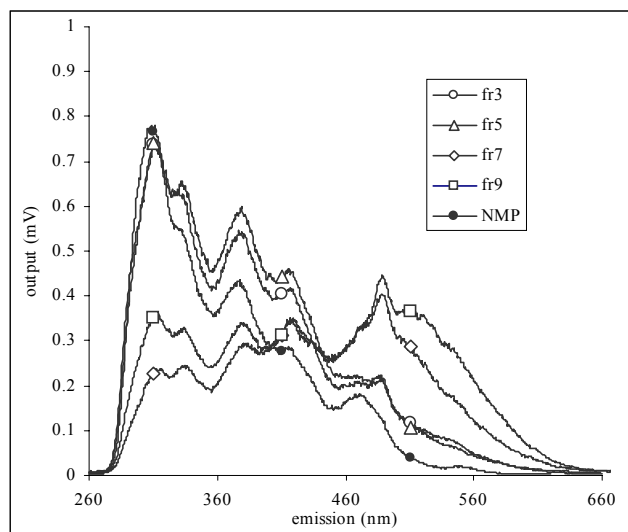


Figure 9: Fluorescence spectra of SEC fractions (see Figure 7). Collected directly on the SEC fractions with $\Delta\lambda=20\text{nm}$, slit widths=10 nm, sensitivity=30 %.

Conclusions

Size exclusion chromatography has been presented as a method to gain information about the toluene insoluble material in pitch. The method has offered new understanding of the heavy molecular weight compounds that participate in mesophase and coke formation. Pitch carbonisation behavior is central to anode carbon technology

The analysis results are better when N-methyl-2-pyrrolidinone (NMP) is the solvent (mobile phase) than when tetrahydrofuran (THF) is used. Using NMP as the mobile phase also allowed analysis of larger compounds that were insoluble in toluene and THF.

Analysis of solvent fractions confirmed that a true size exclusion mechanism had been obtained. Determination of average molecular weights of the fractions did, however, confirm that the polystyrene calibration used in polymer industries did not apply to pitch.

Solvent fractions containing heavy molecular weight components elute earlier than lighter fractions. Successful fractionation was re-confirmed by applying fluorescence spectrometry to SEC fractions. This enabled us to make direct conclusions about the formation and disappearance of molecular weight classes based on peaks growing and shrinking in the chromatograms.

Size exclusion chromatography may help in the understanding of the role of different molecular weight classes during the early stages of carbonization.

We believe this new knowledge can lead to a better overall understanding of carbonization mechanisms as well as providing a new tool for the helping direct the development of new binder pitches for anodes and cathodes in the aluminum industry.

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