

COMPARISON OF DETECTORS FOR SIZE EXCLUSION CHROMATOGRAPHY OF HEAVY OIL FRACTIONS

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INTRODUCTION

Size exclusion chromatography (SEC) is often used for the molecular weight determination of heavy oils, residues, pitches and asphaltenes because it is capable of providing the molecular weight distribution in addition to the average molecular weights. However, since these samples are very complex, results are often approximative because of three factors. First, the exclusion process separates molecules by size and shape instead of weight. Second, the sample is composed of hundreds of molecules having widely different properties which implies that additional interactions will add to the size exclusion process (1-4). Finally, the quantitation itself is approximative since usual LC detectors do not provide a signal that is independant of the molecular structure.

In this paper, the performance of a differential refractometer, an evaporative detector and a flame ionization detector for liquid chromatography is compared in terms of linearity, response factors and detection limits.

EXPERIMENTAL

The refractive index detector is a Waters 401 differential refractometer used in conjunction with a thermostated bath to keep the detector in isothermal conditions.

The flame ionization detector is a Tracor 945 LC-FID specially designed for liquid chromatography. The eluant is deposited on the belt and the solvent is evaporated before the belt enters the detector flame which will detect only the solute.

The evaporative detector is an Applied Chromatography System (ACS) 750/14 "Mass Detector" in which the eluant is nebulized at the entrance of a heated tunnel. The solvent is evaporated in this tunnel, thus leaving solute particles in a gas stream. Light scattered by the non-gaseous particles is detected by a photomultiplier.

Experiments were performed on a Varian 5000 liquid chromatograph using two types of columns: a Techsphere 5um amino column (HPLC Technology Ltd) for light standards and three Ultrastyrigel styrene/divinylbenzene GPC columns (Waters) for polymer standards. All solvents were degassed before use.

RESULTS

Results are presented in terms of response factors, detection limits and linearity. Response factors are calculated according to the following equation:

$$RF = \frac{\text{area under peak X}}{\text{amount of compound X}} * \frac{\text{amount of standard}}{\text{area under standard peak}}$$

Detection limit (DL) is calculated as the amount of compound equivalent to twice the noise level. In order to take account of different retention times and peak shapes, a time corrected detection limit (DLT) was defined as the detection limit (DL) divided by the peak width at half-height.

Finally, the linearity range was evaluated using log-log graphs of peak area vs injected amount for concentrations ranging from detection limit to solubility limit at room temperature.

Differential refractometer

This detector is the most widely used in size exclusion chromatography. Table 1 shows how response factors can vary from compound to compound. This can obviously cause errors in quantitation. Detection limits were calculated for two extreme compounds avoiding cases where solubility problems were suspected. Finally, Figure 1 shows excellent linearity over three orders of magnitude for phenanthrene.

Flame ionization detector

Figure 2 shows the signal decrease observed with time for a series of injections of a four-component mixture. Note that the time scale is not linear nor proportional. The numbers only indicate the order of injection. Pearson and Gharfeh (10) found that this decrease was caused by a gradual overheating of the block supporting the belt, thus causing evaporation of the solute before it gets to the flame. They proposed to use a fan to keep a good ventilation. In our experiments, an internal standard was used to calculate the response factors and calculations of detection limits were done on early injections.

Table 2 shows how response factors can vary between compounds. Linearity (Fig. 3) is good if one avoids high concentrations where low response was probably due to detector saturation. However, it must be noted that the relation is exponential as shown by the slope different than 1.

Evaporative detector

Temperature is the most important operating parameter of this detector. Ideally, the evaporation tunnel is maintained at a temperature which will ensure complete evaporation of the solvent while the solute is not affected by the process. This temperature

setting is not in degrees but in arbitrary units, 0 meaning no heating. Figure 4 shows that a high temperature setting can seriously affect the response and how the variation is closely related to the molecular weight (or boiling point) of the compound. One must note here that standards selected for this study are not particularly volatile since their molecular weight is higher than 165 g/mol and their boiling point $>285^{\circ}\text{C}$. Bartle (6) also stated that the analysis of samples having a molecular weight lower than 300 g/mol is questionable.

Response factors were calculated for several temperature settings (Table 3). At higher temperatures, response factors are extremely different. When no heating is applied, differences are less severe but still very significant. It can be observed that even without heating the response factors are still correlated with boiling points although these are relatively high ($>285^{\circ}\text{C}$). Of course, detection limits vary to the same extent (Table 4).

Linearity plot (Fig. 5) shows some curvature. However, if one avoids a lower concentration range, the curve could be approximated to an acceptable straight line whose slope is closer to 1, which facilitates calibration. Oppenheimer and Mourey (8) already indicated that operating conditions must be carefully chosen in order to ensure linear relationship. Along with Charlesworth (5,7), they also indicated that aerosol formation influences detection. Hence, surface tension and viscosity of the solvent are important since the droplet size will influence the size of the particles that cross the light beam. It is also possible that the refractive index (7,8) and opacity of these particles have a significant influence on the output signal.

Polymers

Since the evaporative detector is mainly used in polymer analysis, response factors and linearity were investigated for selected polymers. Response factors for these polymers seem to be more uniform than for the refractometer, and also more uniform than for the individual standards analyzed in previous sections (Table 5). Linearity (Fig. 6) appears to improve slightly with polymers but again it is preferable to avoid concentrations approaching detection limits.

DISCUSSION

Performance

Linearity (Fig. 1, 3, 5 and 6) is definitely better for the refractometer than for the other detectors. Both LC-FID and evaporative detector linearity plots show curvature that could be avoided if not working with too high or too low concentrations. In the case of LC-FID, the response is clearly exponential and one must be careful in using a calibration curve.

Table 6 shows a summary of the variation of response factors for a series of components. For individual standards of molecular weight

between 165 and 300 g/mol, the refractometer showed the least scatter of data as the relative standard deviation (RSD) indicates. The evaporative detector gave the worst results because the evaporation of solute was a limiting factor. When polymers are considered, this detector seems to be slightly superior to the refractometer since evaporation of solute is minimal.

The variety of response factors obviously influences detection limits (Table 7). However, minimum and maximum values give an overview of the range that can be expected for a given detector. One can see that the LC-FID has detection limits one order of magnitude higher than the other detectors due to high noise levels and spiking problems (see Fig. 7).

Other characteristics

The refractometer cannot be operated in a solvent gradient mode. This is not really a problem in SEC since gradients are seldom used with this type of chromatography. The nature of the detection process also implies that response factors thus quantification might be different when using different solvents. On the other hand, the refractometer is a very simple and easy-to-use detector showing good reproducibility. A definite advantage over the two other detectors is that it is suitable for both light and heavy compounds.

The evaporative detector response is partly related to the quality of the aerosol thus to physical properties of the eluant. These properties are affected by operating temperature, pressure, flow rate and solvent. For this reason, one must be careful in using gradients. As mentioned previously, volatile compounds cannot be analyzed using this detector. Finally, the evaporative detector is solid and relatively easy to use.

In comparison, the LC-FID is a fragile detector, especially the belt. It is more complicated to operate. However, once good conditions are found, they do not have to be changed. One could question the completeness of detection and of combustion by the cleaning flame when heavy compounds are analyzed.

Analysis of pitch samples

Table 8 shows the results obtained for the SEC analysis of three pitch samples while comparative chromatograms for sample 1 are given in Fig. 7. A ultraviolet detector trace was added for comparison. Obviously, a UV detector is not recommended since the extinction coefficient can be widely different between components. It can be seen here that it overestimates the contribution of the high molecular weight portion of the sample. This is indicated by very high weight average molecular weight (M_w) values since more importance is given to heavier species in the calculation of M_w . Conversely, the LC-FID does not detect high molecular weight species very well as shown by the lower M_w values. This detector also displayed severe spiking and high systematic noise that were responsible for the poor detection limits.

As shown in Table 8, average molecular weight values can differ widely and moreover the trends between samples are not always the same (see M_n for samples 2 and 3). Figure 7 shows that the refractometer detectsⁿ a larger quantity of heavy material than other detectors (except UV) and that detection of the light material with the refractometer can be disturbed by the solvent front. On the other hand, the lighter components might not be detected properly by the evaporative detector. Finally, the noise level is slightly lower for the refractometer than for the evaporative detector.

SUMMARY

When considering all factors, it is very difficult to select a specific detector as the best for size exclusion chromatography of heavy oil related samples. The LC-FID was found to be unsatisfactory. The only procedure that would aid the selection between the refractometer or the evaporative detector would be to collect and weigh narrow fractions of the chromatographic effluents and to calculate the molecular weight of these less complex fractions. However, this time consuming procedure would have to be repeated for different types of samples. Current practice in our laboratory is to analyze samples with both detectors in series in order to get a better idea of the nature of the sample.

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Table 1 - Response factors and detection limits
for differential refractometer

Compound	RF	DL (10 ⁻⁷ g)	DLT (10 ⁻⁸ g/s)
Pyrene	1.0		
Phenanthrene	0.94	2.8	3.3
o-Terphenyl	0.74		
3-Methyl cholanthrene	0.95		
Dibenzofuran	0.74		
Benzophenone	0.65		
Xanthene	0.75		
Eicosanol	0.25		
Diphenyl amine	0.78		
5,6-Benzoquinoline	0.85		
Carbazole	0.34		
Dibenzothiophene	0.84		
Thianthrene	0.72		
Triphenyl methyl mercaptan	0.52	11.3	18.9

Table 2 - Response factors and detection limits
for flame ionization detector

Compound	RF	DL (10 ⁻⁶ g)	DLT (10 ⁻⁷ g/s)
Pyrene	1.0		
Phenathrene	0.21		
o-Terphenyl	0.86		
3-Methyl cholanthrene	0.78		
n-C ₂₁	1.58		
Dibenzofuran	0.26	4.2	3.5
Benzophenone	0.54		
Xanthene	0.54		
Eicosanol	0.87		
Diphenyl amine	0.30		
5,6-Benzoquinoline	0.59		
Carbazole	0.12		
Dibenzothiophene	0.69		
Thianthrene	0.99	2.6	2.2
Triphenyl methyl mercaptan	0.26		

Table 3 - Response factors for evaporative detector

Compound	Temperature setting			
	0	5	10	15
Pyrene	1.0	1.0	1.0	1.0
Phenanthrene			0.26	0.21
o-Terphenyl	0.53	0.46	0.31	0.62
3-Methyl cholanthrene	0.85	1.57	1.43	5.21
n-C ₂₁			0.69	1.69
Dibenzofuran	0.027	0.014	0.011	0.004
Benzophenone	0.13	0.073	0.083	0.040
Xanthene			0.060	0.047
Eicosanol			0.80	2.75
Diphenyl amine			0.11	0.064
5,6-Benzoquinoline			0.60	0.34
Carbazole			0.76	2.45
Dibenzothiophene	0.19	0.12	0.15	0.12
Thianthrene			0.25	0.32
Triphenyl methyl mercaptan			1.04	1.94

Table 4 - Detection limits for evaporative detector

Compound	DL (10^{-6} g)				DLT (10^{-7} g/s)				
	Temperature:	0	5	10	15	0	5	10	15
Dibenzofuran	2.11	37.3				3.51	62.2		
Benzophenone	1.55	14.6	9.84	34.8	1.04	9.76	8.2	29.1	
Pyrene	0.741	2.24	1.73	3.45	0.617	1.87	1.44	2.88	
3-Methyl cholanthrene	0.575	1.01	1.06	1.06	0.319	0.564	0.588	0.588	

Table 5 - Response factors for polymers

Compound	Refractometer	Evaporative detector
Polystyrene	1.0	1.0
Polyvinyl acetate	0.19	0.44
Polysulfone	0.92	0.71
Polyethylene glycol	0.31	0.67
Polyamide	0.34	0.35
n-C ₃₆	0.18	0.61

Table 6 - Summary of response factors

Detector	Min	Max	n	X		RSD
Standard compounds						
Refractometer	0.25	1.0	14	0.72	0.22	31%
Flame ionization	0.12	1.58	15	0.64	0.39	61%
Evaporative (T=0)	0.027	1.57	6	0.45	0.40	89%
detector (T=10)	0.011	1.43	15	0.50	0.43	86%
Polymers						
Refractometer	0.18	1.0	6	0.49	0.37	76%
Evaporative det. (T=0)	0.35	1.0	6	0.63	0.23	36%

Table 7 - Summary of detection limits

Detector	DL (ug/g)		DLT (ng/s)	
	Min	Max	Min	Max
Refractometer	0.28	1.13	33	189
Flame ionization	2.6	4.2	220	350
Evaporative det. (T=0)	0.58	2.1	32	35
(T=5)	1.0	37	56	6200

Table 8 - Average molecular weight of pitch samples

Sample	Refractometer	Evaporative det.	LC-FID	UV
Number average molecular weight, M_n				
1	780	590	560	580
2	500	380	470	290
3	290	340	330	250
Weight average molecular weight, M_w				
1	2730	1960	1050	3410
2	2250	1520	880	2540
3	2170	1380	630	2240

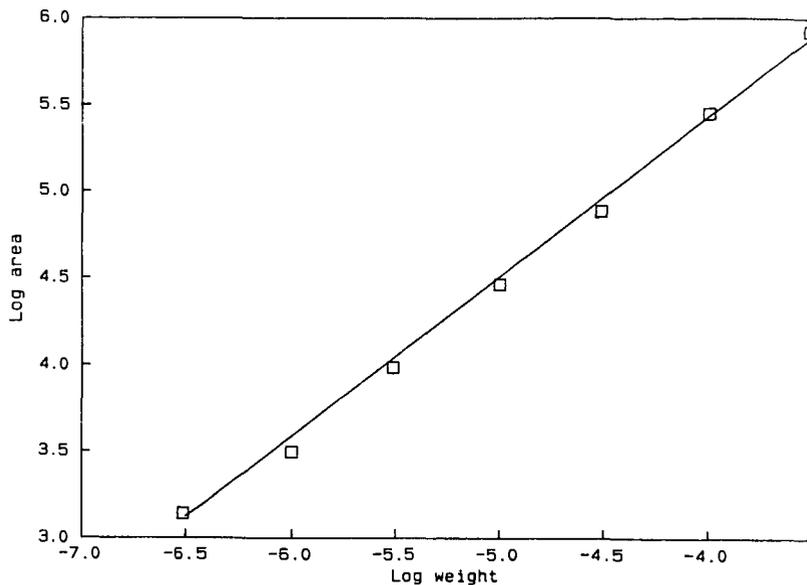


Fig.1 - Linearity of refractometer for phenanthrene (Slope=0.941, r=0.9988)

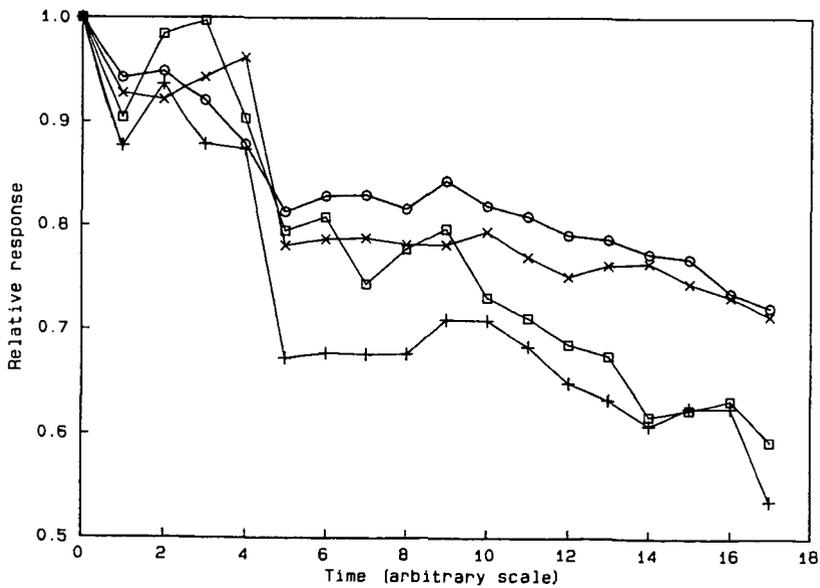


Fig.2 - Variation of signal with time for LC-FID (□ dibenzofuran, + dibenzothiophene, ○ pyrene, × benzophenone)

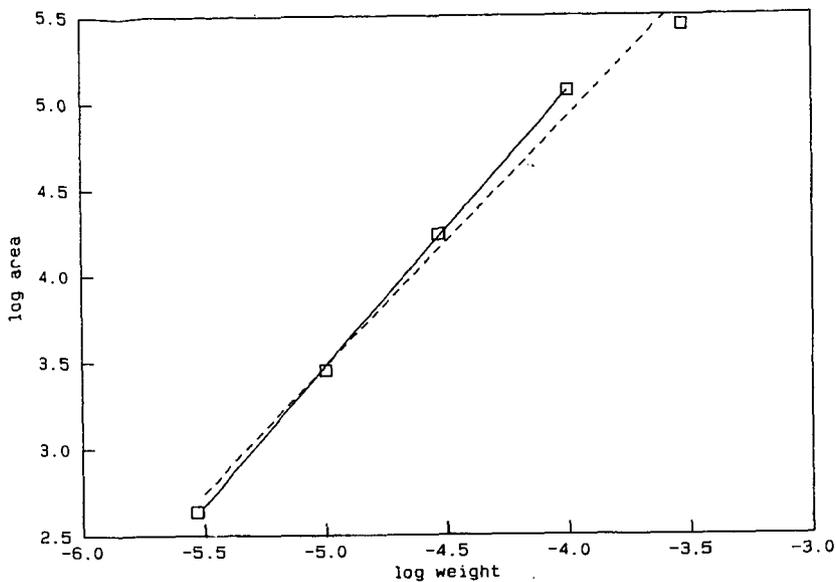


Fig.3 - Linearity of LC-FID for thianthrene (--- : slope=1.447, $r=0.9946$; — : slope=1.594, $r=0.9999$)

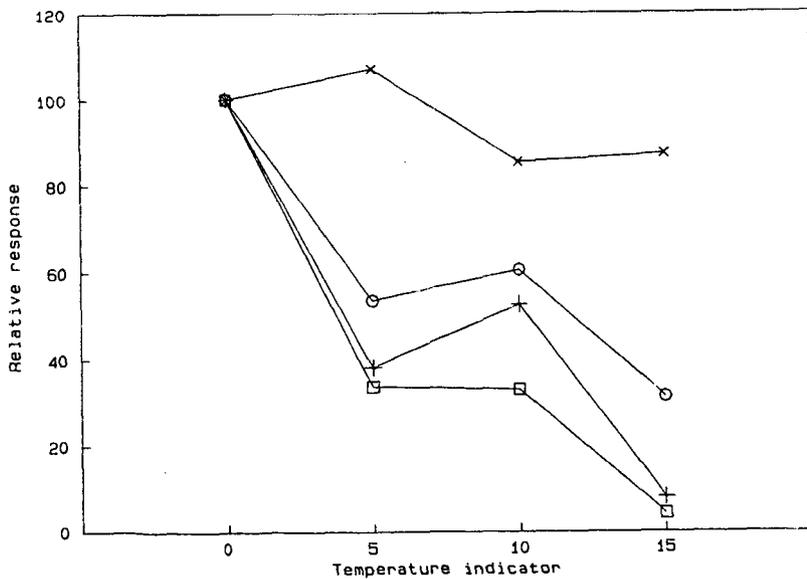


Fig.4 - Relative variation of signal with temperature setting of evaporative detector: \square dibenzofuran (MW=168), $+$ benzophenone (MW=182), \circ o-terphenyl (MW=230), \times 3-methyl cholanthrene (MW=268)

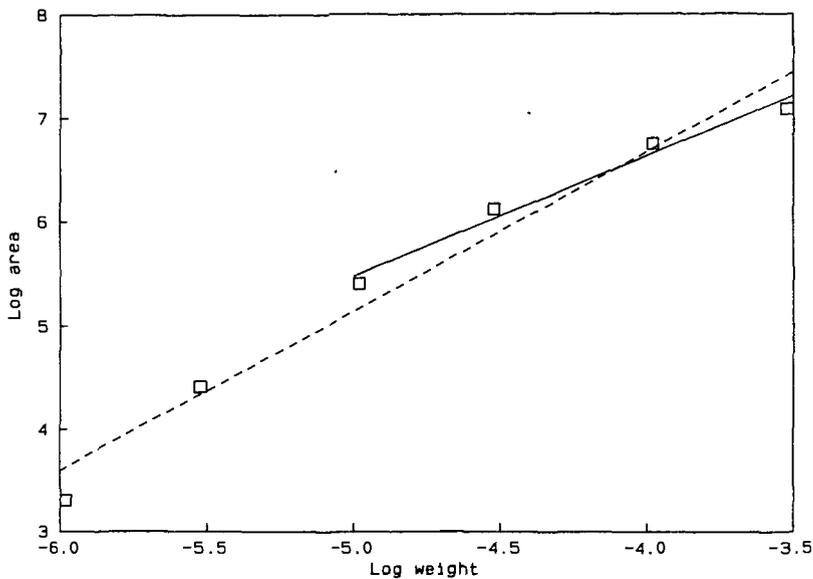


Fig.5 - Linearity of evaporative detector for pyrene (--- slope=1.537, $r=0.9839$; — slope=1.161, $r=0.9892$)

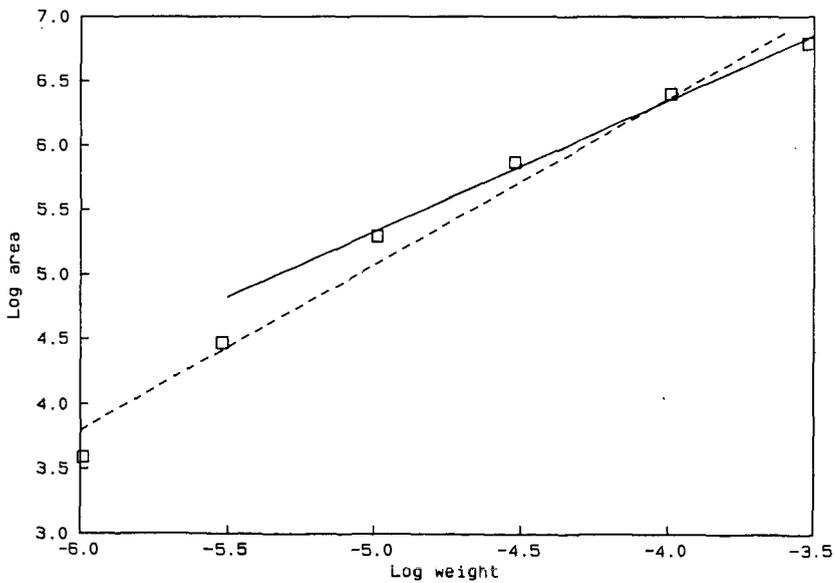


Fig.6 - Linearity of evaporative detector for polystyrene of $M_w=6200$ (--- slope=1.286, $r=0.9888$; — slope=1.011, $r=0.9969$)

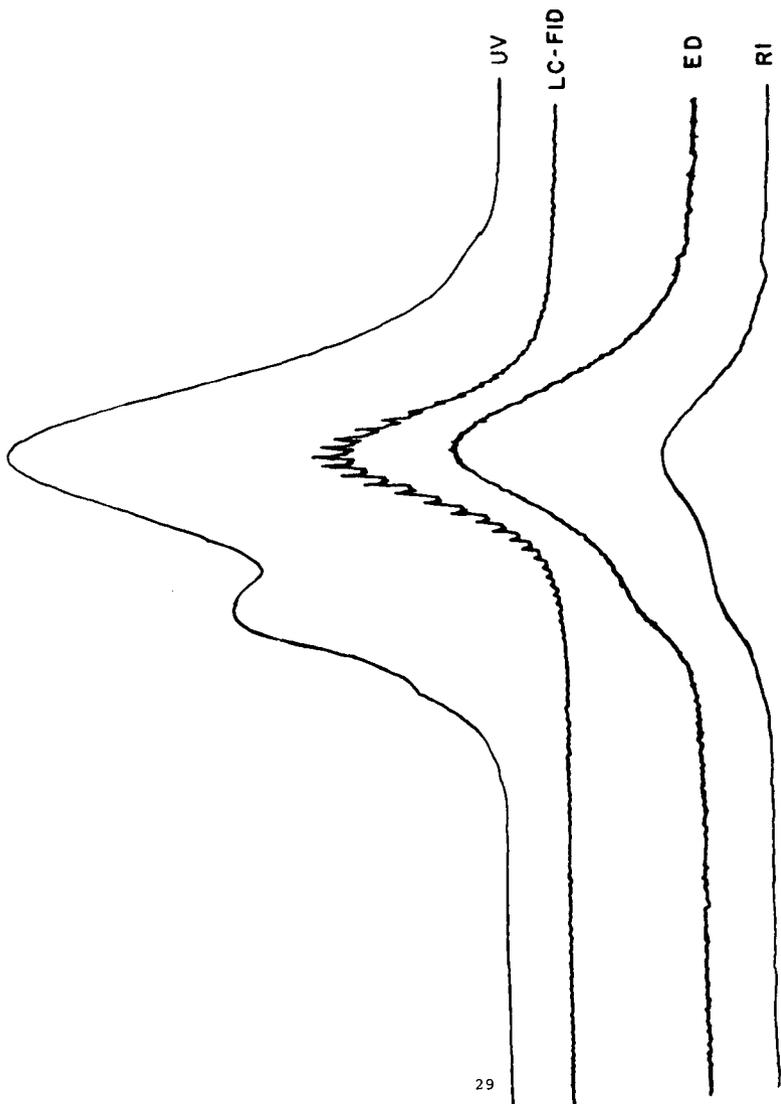


Fig. 7 - SEC chromatogram of a pitch sample as detected by different detectors (UV = ultraviolet, LC-FID = flame ionization detector for liquid chromatography, ED = evaporative detector, RI = refractometer)