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COMPARISON OF DETECTORS FOR SIZE EXCLUSION CHROMATOGRAPHY OF HEAVY OIL RELATED SAMPLES

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by

S. Coulombe

ABSTRACT

A differential refractive index detector, a flame ionization detector for liquid chromatography and an evaporative detector were compared in terms of linearity, response factors and detection limits. Operating conditions were also optimized in order to ensure adequate detector response. Pitch samples were analyzed by size exclusion chromatography using the three detectors. Optimization, performances and analytical results are discussed.

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COMPARAISON DE DETECTEURS POUR LA CHROMATOGRAPHIE D'EXCLUSION D'ECHANTILLONS D'HUILES LOURDES

par

S. Coulombe

RÉSUMÉ

Un réfractomètre différentiel, un détecteur à ionisation de flamme pour chromatographie liquide et un détecteur évaporatif ont été comparés en terms de linéarité, de facteurs de réponse et de limites de détection. Les conditions d'opération ont également été otpimisées de manière à assurer un fonctionnement adéquat. Des échantillons de brai ont été analysés par chromatographie d'exclusion en utilisant ces trois détecteurs. L'optimisation, les performances et les résultats chromatographiques sont discutés.

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INTRODUCTION

Size exclusion chromatography (SEC) is commonly used for determining average molecular weight of polymers. This technique is capable of providing the distribution of the material as well as the average molecular weight. Although this technique is mainly used for polymers, it is often used in the petroleum industry to characterize heavy oils, residues, and pitches before and after upgrading.

Results are often approximative and cannot be treated as absolute values because of the complexity of the samples. This is due to three different phenomena. First, the exclusion process does not separate the molecules by mass but rather as a function of size and shape of the molecules. Second, the sample is composed of hundreds of molecules having widely different properties which implies that secondary interactions will add to the size exclusion process itself (1-4). Thus, the retention time will not be a function of the molecular size only. These two aspects are intrinsic to the size exclusion chromatography process. However, for homopolymers, these phenomena are not very important since polymers are long chains of identical units where the difference in length does not imply large changes in chemical properties.

The third problem encountered in SEC of petroleum related fractions concerns liquid chromatography detectors. The most widely used detector is the differential refractometer. As opposed to polymers, refractive indices in oil samples can differ widely among compounds and negative response can occur with some solvents. Thus, molecular weight calculations are significantly affected. Detectors are required that can provide a response that is identical for all

components and is proportional to the quantity of compounds present. The evaporative detector (or mass detector) (5-8) and the flame ionization detector for liquid chromatography (3,9,10) have both been introduced for this reason. They are said to be mass responsive and applicable to a wide variety of samples.

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

EXPERIMENTAL

The refractive index detector is a Waters 401 differential refractometer whose reference cell was always filled with solvent. A temperature controlled bath was used in order to keep the detector in isothermal conditions.

The flame ionization detector is a Tracor 945 LC-FID specially designed for liquid chromatography (9). It consists of a heated block containing a wheel on which a belt is fixed. The eluant is deposited on the belt and solvent is evaporated before introduction to the detector flame (H_2 and air) which will only detect the solute. After the detector flame, a hotter cleaning flame is used to burn all unreacted residues remaining on the belt. The belt is then ready to accept more eluant.

The evaporative detector (or light scattering detector) is an Applied Chromatography System (ACS) 750/14 "Mass Detector" (6-8). In this device, the eluant is nebulized at the entrance of a heated tunnel by a nitrogen-operated nebulizer. The solvent is evaporated in this tunnel, thus leaving solute particles in a gas

stream. A light source is directed at right angles to this stream and a portion of the light scattered by the non-gaseous particles is detected by a photomultiplier which will measure a signal proportional to the concentration of particles.

When in use, the detector is connected to a Varian 401 Data Station for data treatment. Experiments were performed on a Varian 5000 liquid chromatograph using two types of columns: a Techsphere 5µm amino column (HPLC Technology Ltd) for light standards and three Ultrastyragel® (10^3, 500 and 100 Å) styrene/divinylbenzene GPC columns (Waters) for polymer standards. All solvents (Caledon, BDH, HPLC grade) were degassed before use. Table 1 gives the source of the standards used in this study.

Pitch samples are high boiling material (>525°C) that were available from vacuum bottoms. Analysis was performed using THF at a flowrate of 1.2 mL/min.

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) was 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 limits to solubility limits at room temperature.

Differential refractometer

This detector was evaluated because it is widely used in size exclusion chromatography. Its response is a function of the difference of refractive indices of the pure solvent (reference) and the eluant (solvent with or without solute).

Table 2 shows that response factors can vary widely among compounds. This can obviously cause errors in quantitation unless comparing samples with standards containing the same component or knowing the actual response factor for that component. Detection limits were calculated for two extreme compounds avoiding cases where solubility problems were suspected. Finally, Figure 1 shows the excellent linearity over three orders of magnitude for phenanthrene.

Flame ionization detector

Whereas the refractometer was very easy to use, the flame ionization and evaporative detectors had to be carefully optimized and detector performance was also evaluated in terms of operating conditions in order to ensure proper response. Thus, all measurements with the LC-FID were made after proper optimization of detector gas flow rates.

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 injections were all done early in the day to obtain the best detection limits.

The belt is a rather fragile device that can deteriorate at weak spots after extensive use. This would cause the response to vary widely because of non-uniform depositing of eluant. Figure 3 is an example of variations that can be observed upon deterioration of the belt surface. The positions (1 to 4) are defined at 90° on the belt-supporting wheel. Injections are synchronized with the passage of these points over a reference point on the heating block. Component responses are different because of different retention times. Differences of up to 50% can be noted between two injections.

Table 3 shows how response factors can vary greatly among compounds. Linearity (Fig. 4) 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 exponentional as shown by the slope different than 1. For large concentration ranges, a log-log calibration is thus necessary while a linear calibration could be used on short concentration intervals.

Evaporative detector

This detector had to be optimized for several parameters such

as solvent flowrate, nitrogen pressure (nebulizer) and temperature of the evaporation tunnel. Flowrate and pressure were expected to have an effect on the response because they affect the quality of the aerosol. This was confirmed by experiments which also showed that a stabilization time was needed after pressure or flowrate variations. Upon adequate stabilization, the response was more uniform and did not vary significantly for flowrates between 1 and 2 mL/min and for pressure higher than 35 psi.

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). As shown in Figure 5, a high temperature setting can seriously affect the response. Also, different compounds are affected to different degrees. Heavier components have a more uniform response than lighter molecules. 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°C. Even then, some of the components lost over 95% response upon increasing temperature setting from 0 to 15. This was also found by Bartle (6) who 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 4). At higher temperature settings, 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°C). Of course, detection limits vary to the same extent (Table 5). Again, the less volatile compounds have more uniform detection limits throughout the variation of temperature.

Linearity plot (Fig. 6) shows obvious 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 and eluant 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 for polymer analysis, response factors and linearity were investigated for selected polymers. Table 6 shows that the response factors for the selected polymers seem to be more uniform than for the refractometer, and also more uniform than for the individual standards analyzed in previous sections. Linearity (Fig. 7) appears to improve slightly with polymers but again it is preferable to avoid concentrations approaching detection limits.

DISCUSSION

Performance

The three performance criteria (linearity, response factor and detection limit) were assessed for the three detectors and are compared in this section. Linearity (Fig. 1, 4, 6 and 7) 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 7 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 8). However, minimum and maximum values give an overview of the detection limit 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. 8). Finally, it can be seen that heating can be detrimental to the detection limits of the evaporative detector.

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 a different solvent. This detector needs to be thermostated to ensure signal stability. 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 needs some time to stabilize (nebulization and temperature) but it 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 and it needs time for stabilization of the flames. However, once good conditions are found, they do not have to be changed. One could question the completeness of detection (see discussion below) and of combustion by the cleaning flame when heavy compounds are analyzed.

Analysis of pitch samples

Table 9 shows the results obtained for the SEC analysis of three pitch samples while comparative chromatograms for sample 1 are given in Fig. 8. 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 ($\overline{M_w}$) values since more importance is given to heavier species in the calculation of $\overline{M_w}$. Conversely, the LC-FID does not detect high molecular weight species very well as shown by the low $\overline{M_w}$ values. This detector also displayed severe spiking and high systematic noise that were responsible for the poor detection limits. This can be troublesome for quantitation and calculation of average molecular weight.

As shown in Table 9, average molecular weght values can differ widely and moreover the trends between samples are not always the same (see $\overline{M_n}$ for samples 2 and 3). Figure 8 shows that the refractometer detects 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 but there is no definite characteristic that would favour either the refractometer or the evaporative detector. The only procedure that would aid the selection of a detector would be to collect and weigh narrow fractions of the chromatographic effluents and to calculate the molecular weight of these less complex fractions. Thus the results obtained with each detector could be verified and calibrated. 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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FIGURE CAPTIONS

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

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

Fig.3 - Variation of signal with the position of the LC-FID belt (□ dibenzofuran, + dibenzothiophene, o benzophenone, X 3-methyl cholanthrene)

Fig.4 - Linearity of LC-FID for thianthrene (--- : slope=1.447, r=0.9946; ——— : slope=1.594, r=0.9999)

Fig.5 - Relative variation of signal with temperature setting of evaporative detector: □ dibenzofuran (MW=168), + benzophenone (MW=182), O o-terphenyl (MW=230), X 3-methyl cholanthrene (MW=268)

Fig.6 - Linearity of evaporative detector for pyrene (--- slope= 1.537, r=0.9839; —— slope=1.161, r=0.9892)

Fig.7 - Linearity of evaporative detector for polystyrene of M_w=6200 (--- slope=1.286, r=0.9888; —— slope=1.011, r=0.9969)

Fig.8 - 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)

Table 1 - List of standard compounds

Compound	Boiling point (°C)	Molecular weight (g/mol)	Source
$n\text{-}C_{40}$	520	563	PolyScience
$n\text{-}C_{30}$	446	423	PolyScience
$n\text{-}C_{21}$	355	297	PolyScience
Carbazole	355	297	Aldrich
Diphenylamine	302	169	Aldrich
Dibenzofuran	285	168	Aldrich
Benzophenone	305	182	Aldrich
5,6-Benzoquinoline	350	179	ICN
Dibenzothiophene	332	184	Aldrich
Thianthrene	366	218	Aldrich
Xanthene	311	182	Aldrich
Triphenyl methyl mercaptan	?	276	K+K Labs
Phenanthrene	340	178	BDH
Pyrene	393	202	Aldrich
o-Terphenyl	332	230	Eastman
Eicosanol	369	299	Eastman
3-Methyl cholanthrene	?	268	Eastman

Table 2 - 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 3 - 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		
$n\text{-}C_{21}$	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 4 - 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
$n\text{-}C_{21}$			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 5 - 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 6 - 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
$n\text{-}C_{36}$	0.18	0.61

Table 7 - Summary of response factors

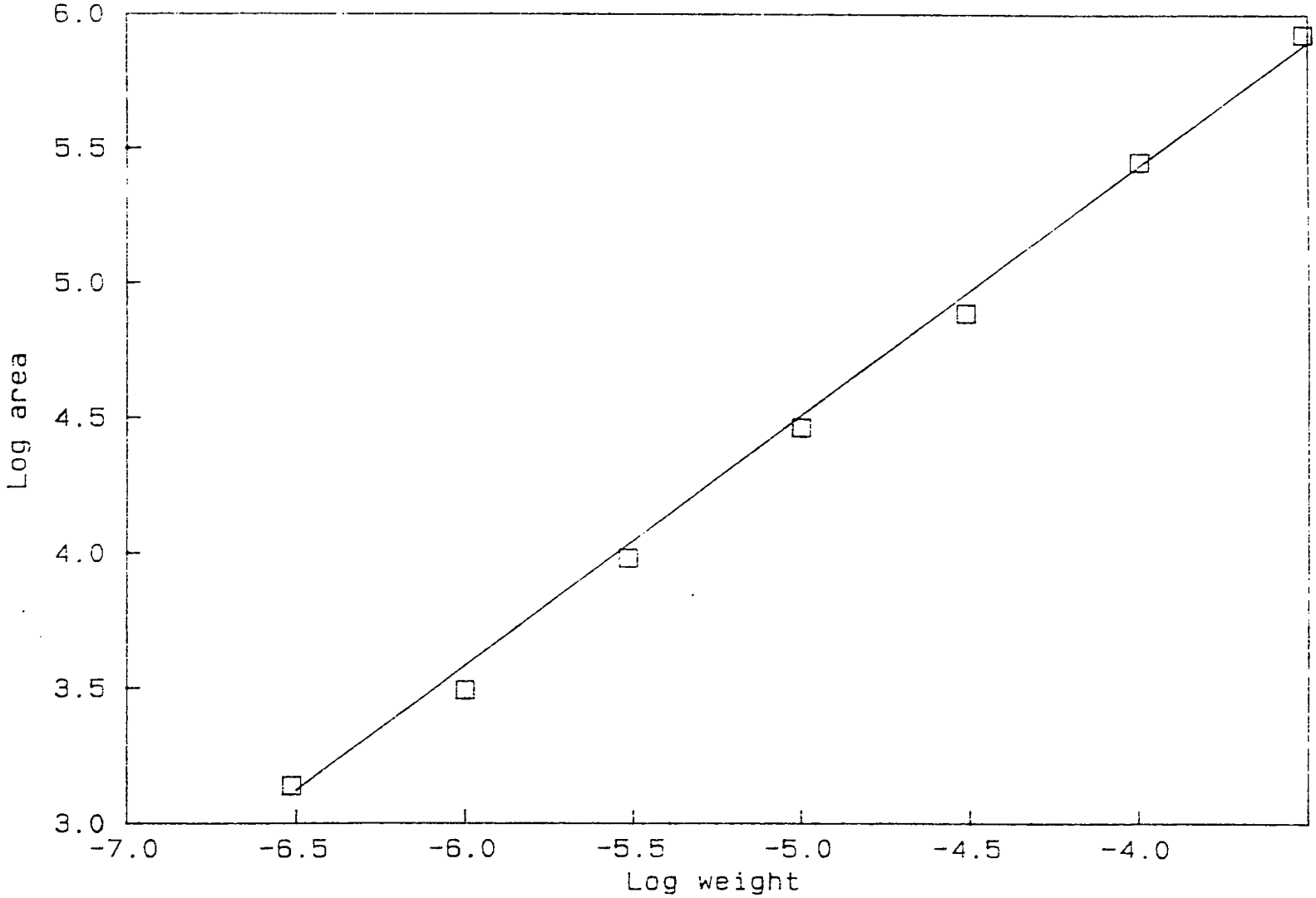
Detector	Min	Max	n	$\bar{X}$	σ	RSD
Standard compounds						
Refractometer	0.25	1.0	14	0.72	0.22	31%
Flame ionization	0.12	1.58	15	0.64	0.39	61%
Evaporative (T=0)	0.027	1.57	6	0.45	0.40	89%
detector (T=10)	0.011	1.43	15	0.50	0.43	86%
Polymers						
Refractometer	0.18	1.0	6	0.49	0.37	76%
Evaporative det.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

Table 8 - 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 9 - Average molecular weight of pitch samples

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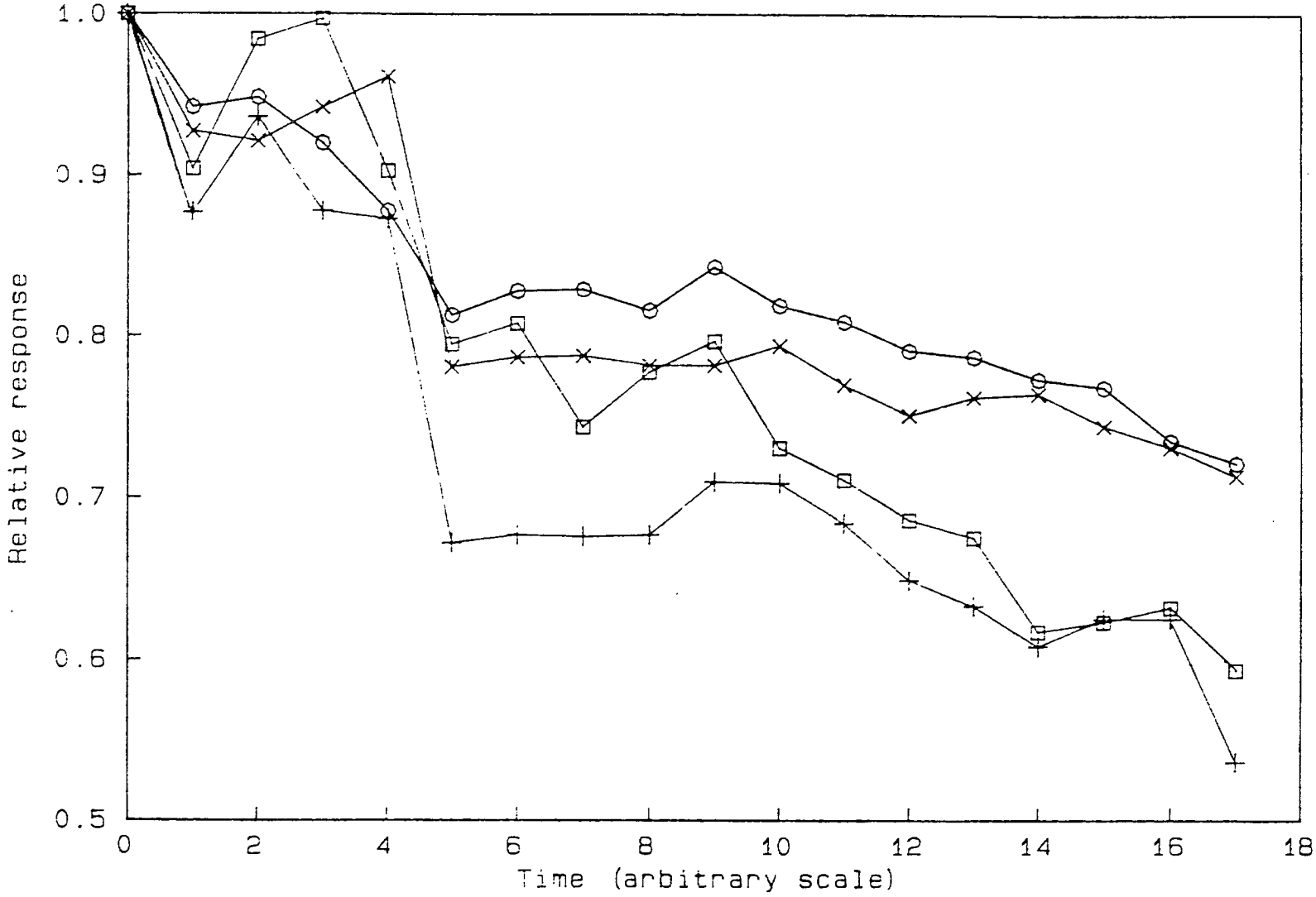
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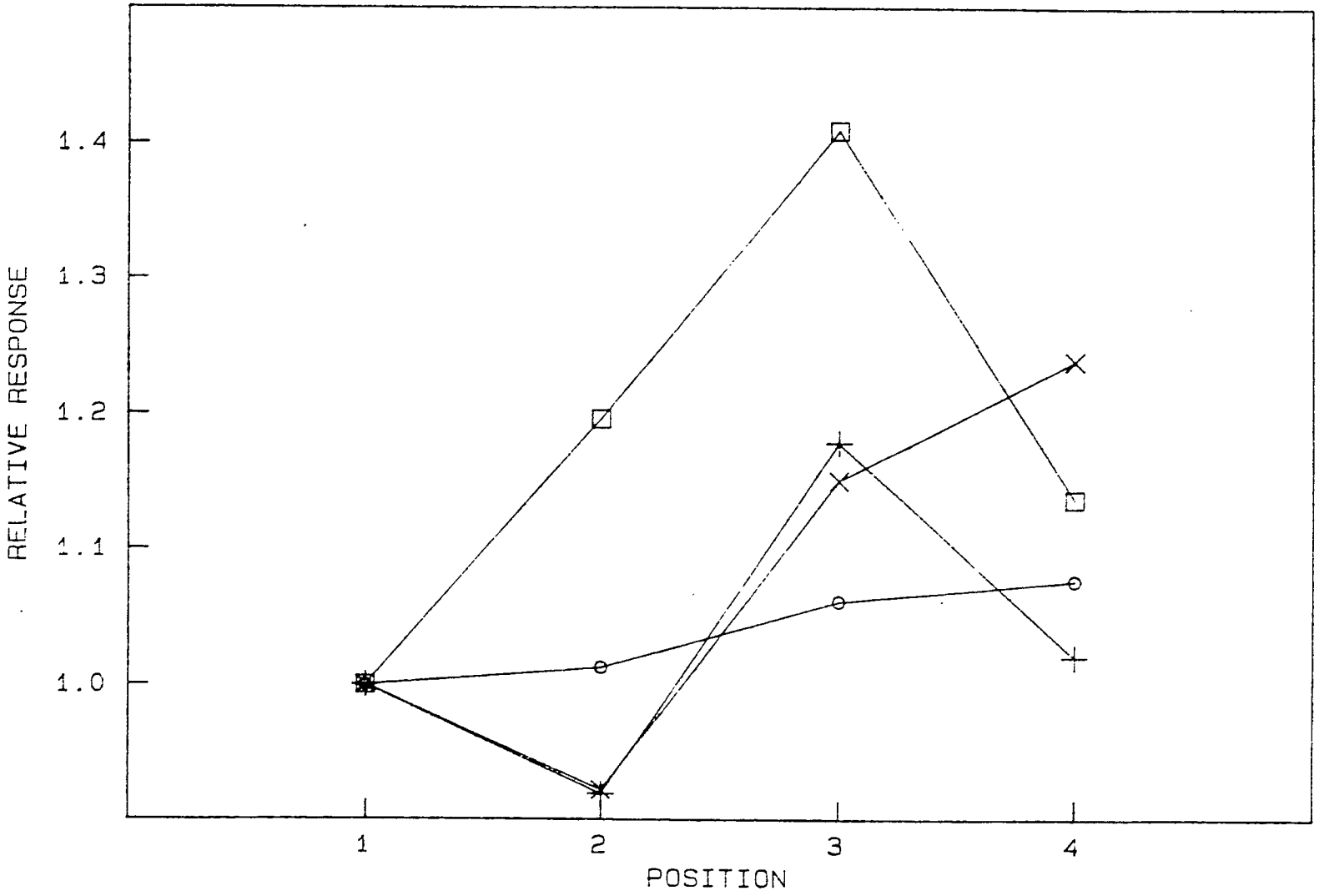
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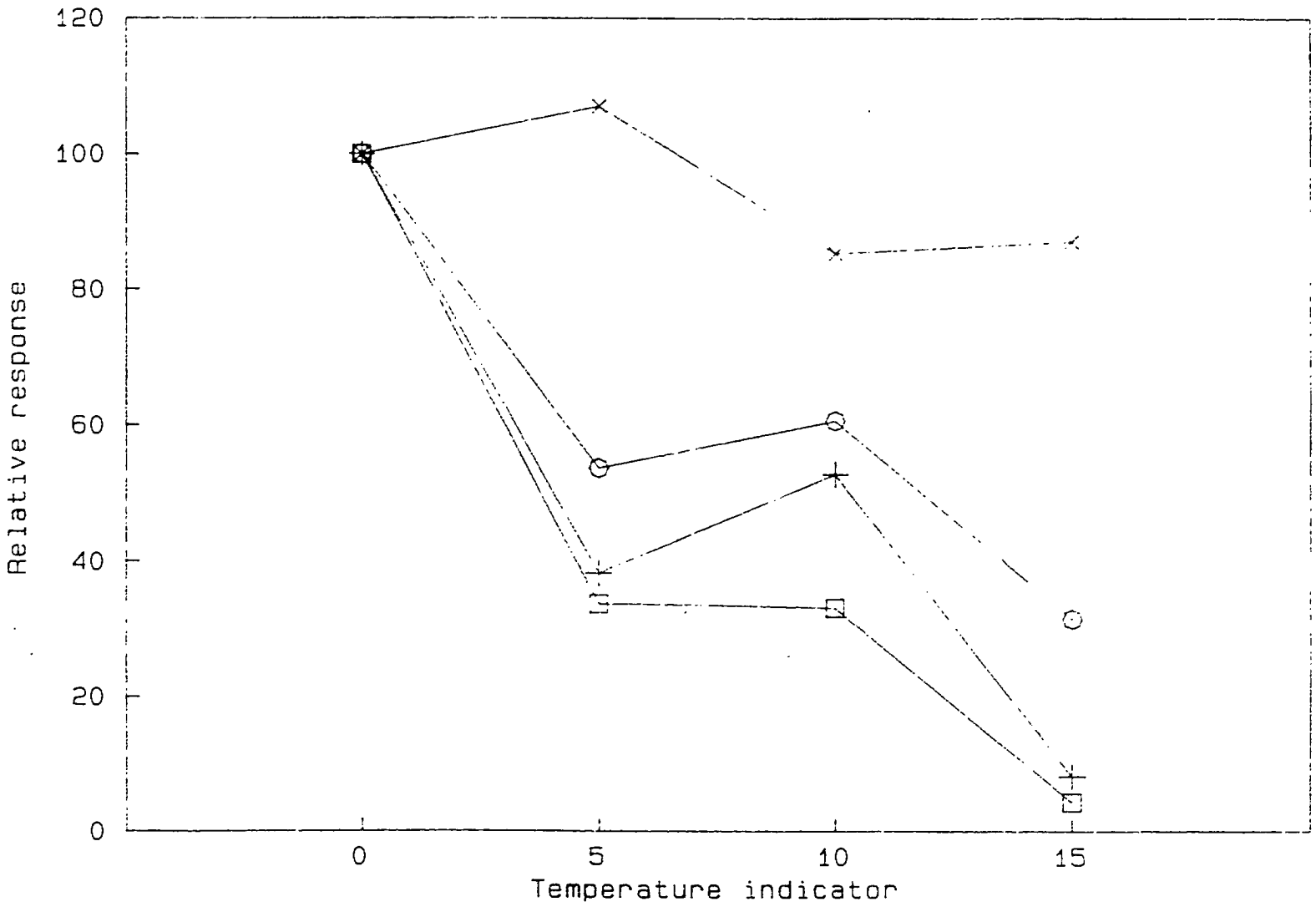
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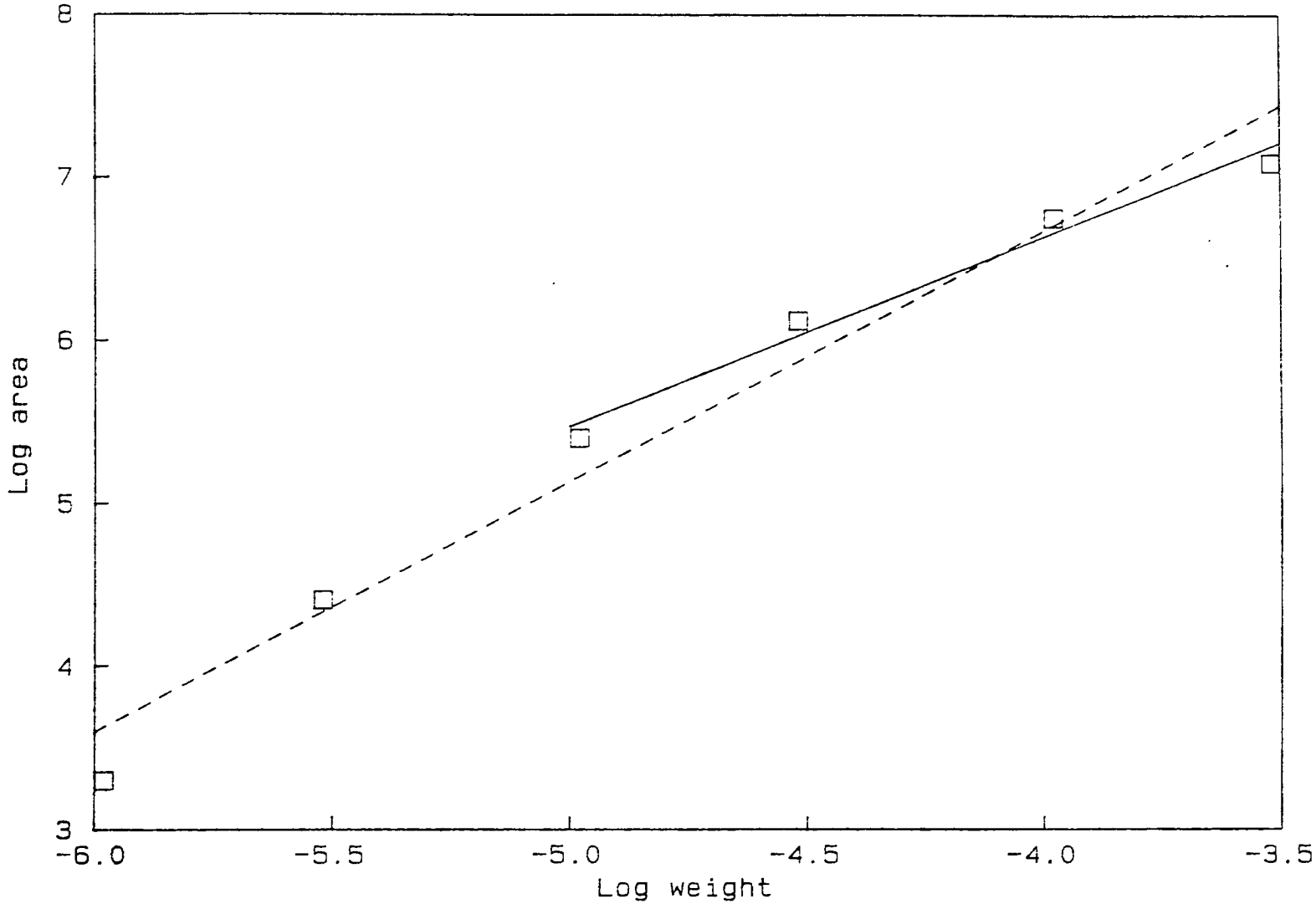
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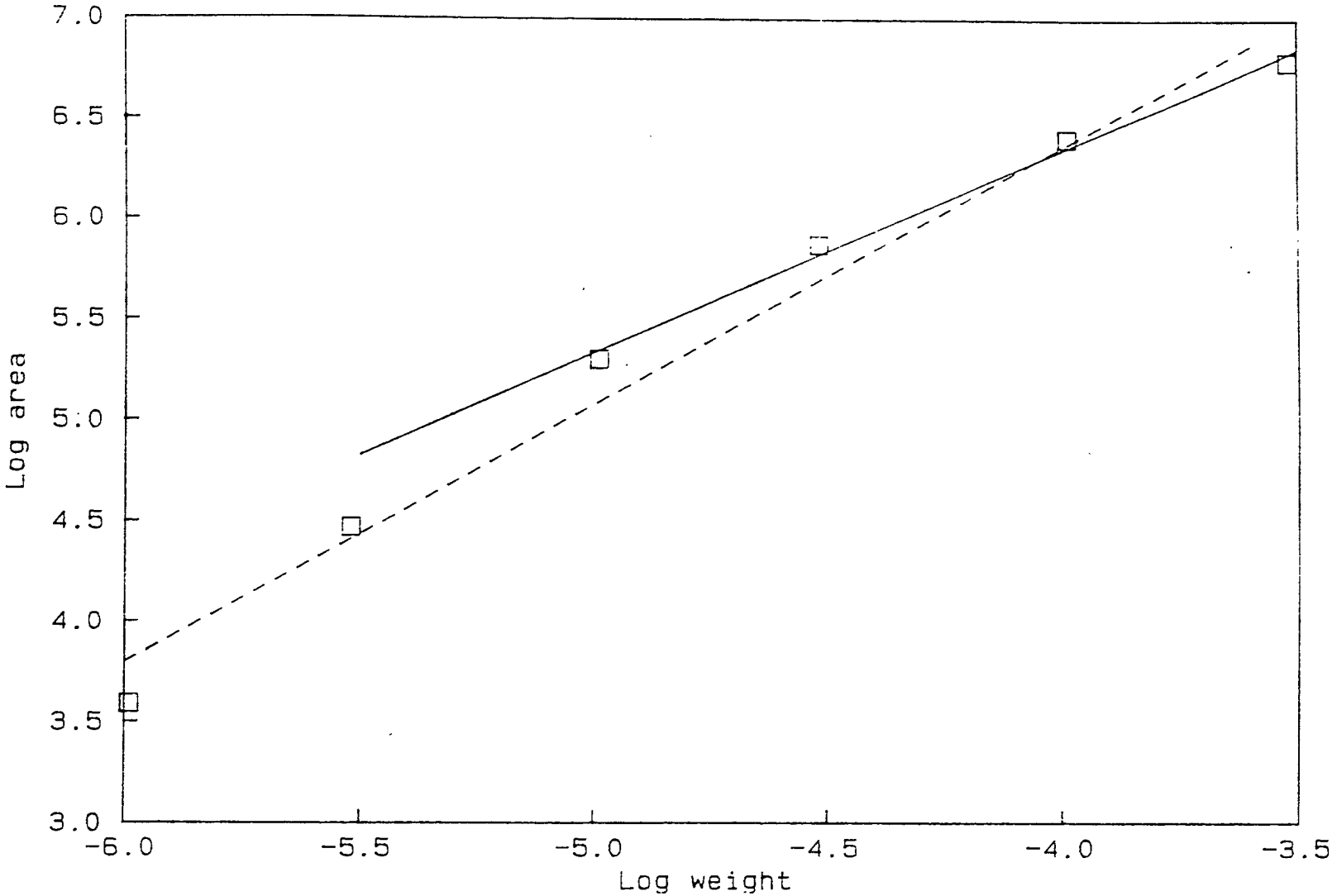
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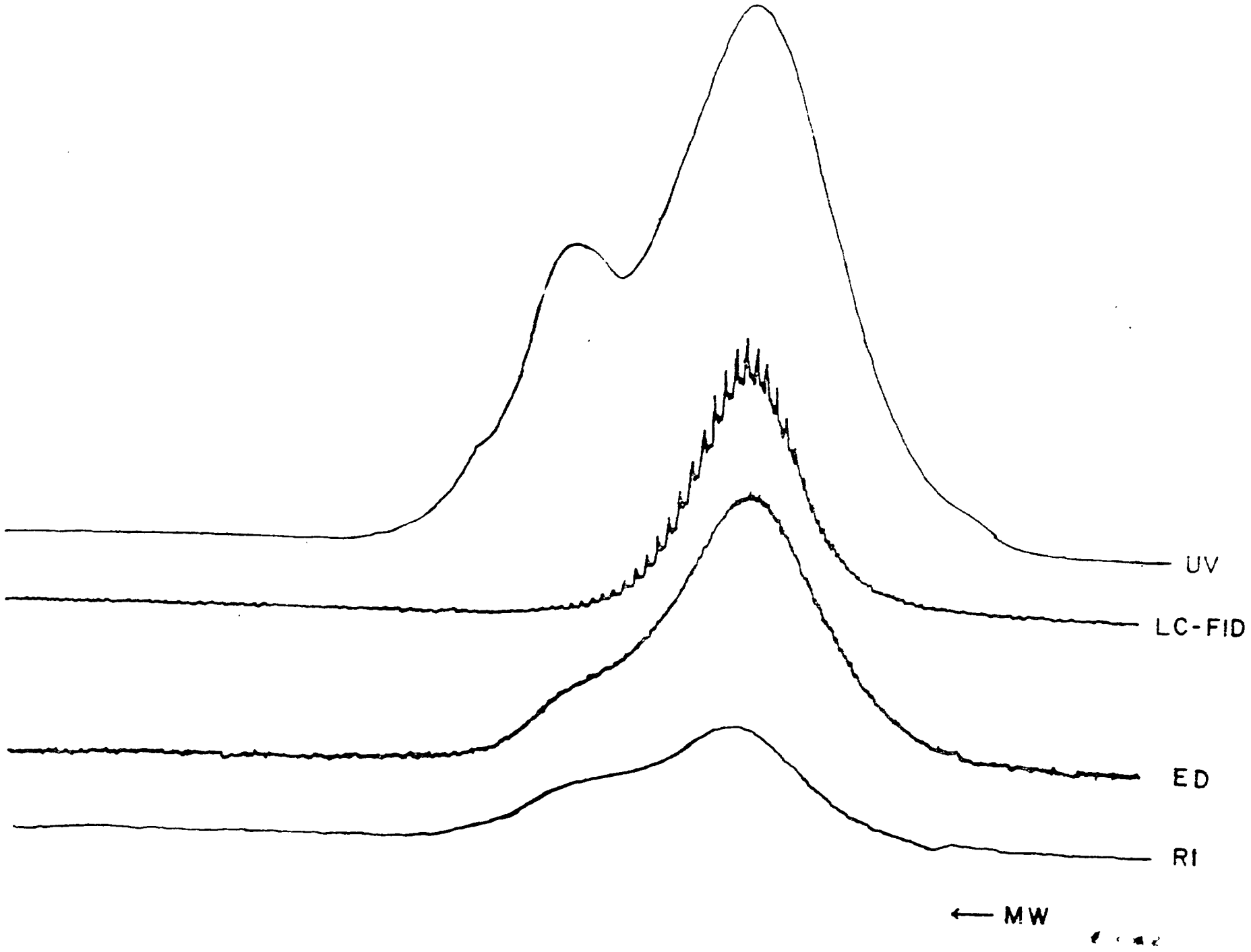
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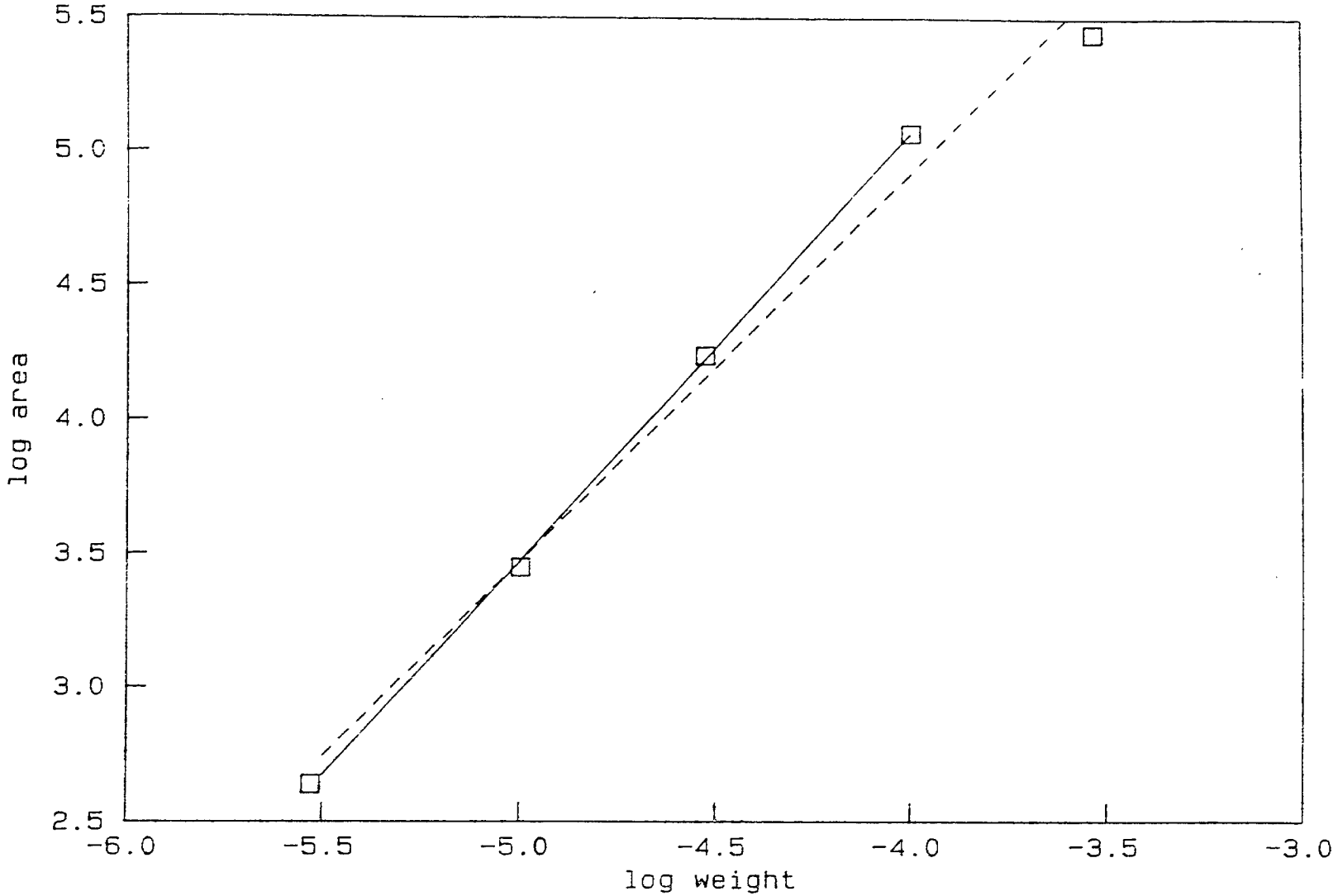
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