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DETERMINATION OF THE MOLAR MASS OF PETROLEUM DISTILLATION RESIDUES USING GEL PERMEATION CHROMATOGRAPHY

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SUMMARY

A gel permeation chromatographic technique has been developed for the determination of the molar mass of petroleum distillation residues. Ultraviolet and infrared detectors are used to identify aromatic or paraffinic components, respectively, and a system of three gel columns allows the wide range of component molar masses from 100 to 10,000 g/mol to be identified. Absolute measurements of molar mass are not available for these residues, but the new technique is shown to have much improved repeatability and efficiency over customary cryoscopic measurements. In addition to average molar mass measurements, the technique allows fingerprint analyses of both residues and lighter petroleum products.

INTRODUCTION

Petroleum distillation residues are complex mixtures containing normal, branched and cyclic alkanes, aromatics, asphaltenes, mercaptan sulphides and other components in a wide molar mass range (100–10,000 g/mol). Their complexity is such that separation techniques are difficult to apply and impossible to use for routine measurements.

Average molar mass measurements on petroleum distillation residues are mainly carried out by cryoscopic or vapour pressure osmometric methods based on the application of Raoult's law; non-volatile non-electrolytes when dissolved in a definite mass of a given solvent under the same conditions lower the solvent's freezing point, elevate its boiling point and reduce its vapour pressure by an amount proportional to the molar mass. The main problem with this type of measurement is the reproducibility of the results, especially due to the low concentration used, as Raoult's law applies to limiting dilution. For the most popular method, cryoscopy (difference in freezing point), the apparatus (cryoscope) is difficult to operate owing to the small amount of heat involved and, even if measurement relative to a standard is used, the reproducibility between measurements is poor. It is also difficult to appreciate the real influence of the wide molar mass range on the results. Some workers[1] have demonstrated the effect of the solvent (dielectric constant) on the apparent molar mass of asphaltenes due to the formation of asphaltene–asphaltene grouped

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molecules of various molecular sizes (from 4000 to 7000 g/mol) in the same sample. In addition, the time needed for such a measurement is about 3 h (preparation of samples and standard solutions and measurements), which is very important for a single measurement of average molar mass, which shows poor reproducibility.

This paper describes the results of an investigation to develop a technique with improved efficiency and at least an equivalent accuracy compared with cryoscopy.

PRELIMINARY DEVELOPMENT

The main problem when using the gel permeation chromatographic (GPC) technique selected is to discriminate between the different hydrocarbon families that are eluting at different rates owing to their varying geometrical molecular sizes. Early use of GPC for molar mass measurements on petroleum products concentrated on use of refractive index detectors with tetrahydrofuran (THF) as the solvent (and mobile phase). The wide refractive index range of the components in our mixtures means that the response factor will be very variable (some components with the same refractive index as the solvent will not be detected at all). Our trials with this type of detector confirmed the above and showed that its use was unacceptable for our requirements. GPC calibrations are frequently made using polymers (*e.g.*, polystyrenes) even if other types of molecules are to be analysed. Trials here showed that it was far better to use some real components from the families present in our mixtures for calibration, even if extrapolation was necessary for high molar masses. It was found that considering hydrocarbon molecules to consist mainly of alkyl chains and/or aromatic rings, it is possible to have a selective response: for paraffinic C–H bonds using an infrared (IR) detector set at a wavelength of 3470 nm and for unsaturated bonds an ultraviolet (UV) detector set at a wavelength of 280 nm. The solvent selected was carbon tetrachloride, which is transparent at both these IR and UV wavelengths.

EXPERIMENTAL

Apparatus

The chromatographic system consisted of a Waters M45 solvent pump, a Waters U6K sample injector, three Waters Ultra-Styragel columns in series (1 × 500 Å + 2 × 100 Å), a Waters M440 UV detector (filter at 280 nm), a Foxboro Miran 1A IR detector and a Spectra-Physics SP4200 computing integrator with floppy disc storage device. For cryoscopy measurements, a Knauer Type 24.00 cryoscope was used.

Method

The optimum flow-rate for the best resolution was found to be 0.8 cm^3/min using a multi-component *n*-alkane mixture. The best IR wavelength was found to be 3470 nm, which is selective for C–H bonds (stretching), and the UV detector was set at 280 nm owing to the UV cut-off of carbon tetrachloride at the normal wavelength used for unsaturated bonds (254 nm). The columns are used at ambient temperature and the solvent is deoxygenated by bubbling helium through it to prevent sensitivity problems with the UV response. The ambient temperature must be stabilized to prevent any change in viscosity of the solvent. For this work the laboratory was air-conditioned.

Calibration

The system is calibrated for molar mass *versus* retention time using a qualitative mixture of *n*-alkanes ($C_{40}H_{82}$, $C_{30}H_{62}$, $C_{20}H_{42}$, $C_{10}H_{22}$ and C_4H_{10}) dissolved in carbon tetrachloride. From this run the *n*-alkane calibration curve is obtained as in Fig. 1. This curve can be fitted using a cubic equation of the type

$$\text{Log } M_a = a_1 t_R^3 + a_2 t_R^2 + a_3 t_R + a_4$$

where M_a = molar mass of *n*-alkane, a_1, a_2, a_3 and a_4 = calibration parameters and t_R = retention time.

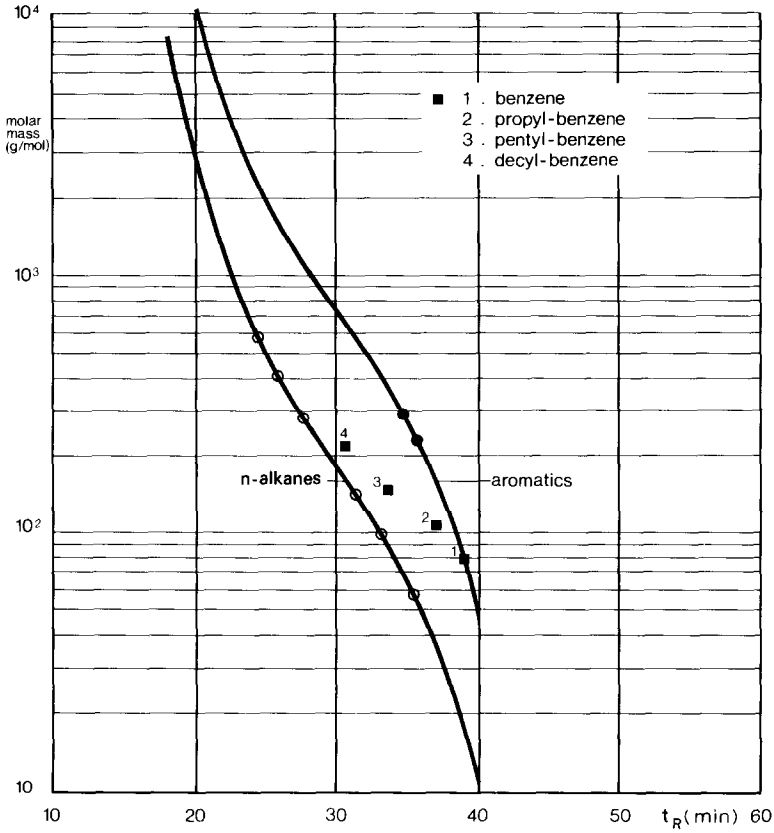

Fig. 1. GPC calibration graphs.

By injecting under the same operating conditions pure aromatic compounds (benzene, naphthalene, anthracene) and some compounds of a mixed type containing both aromatic rings and alkyl groups, it is possible to calculate a coefficient based on the detector response ratio (IR/UV). This is used to adjust the molar mass from the pure *n*-alkane calibration curve (see Fig. 1). A further adjustment of the global response of each detector is calculated using GPC and cryoscopic measurements (on at least 50 different residues in this instance), as it is impossible to prepare standard

mixtures containing all the hydrocarbon families in the molar mass range of interest. The evaluation of this coefficient is made once only and further calibrations to allow for column ageing are carried out with the standard *n*-alkane mixture only. The time difference between the two detectors for the same component, due to the length of the tubing used to connect the two detectors, was previously determined by injecting a mixed-type molecule (*e.g.*, xylene) under the same conditions.

Sample preparation

The optimum dilution of the sample in carbon tetrachloride was found to be 1:20 by volume. A more concentrated sample produces unrepeatable tailing phenomena (see Fig. 2). The amount injected into the system is around 100 μl (this corresponds to the maximum sensitivity of the detectors in terms of the best signal-to-noise ratio). A check showed that the analyses are independent of the amount injected quantity (in the input range of the integrator), as illustrated in Table I.

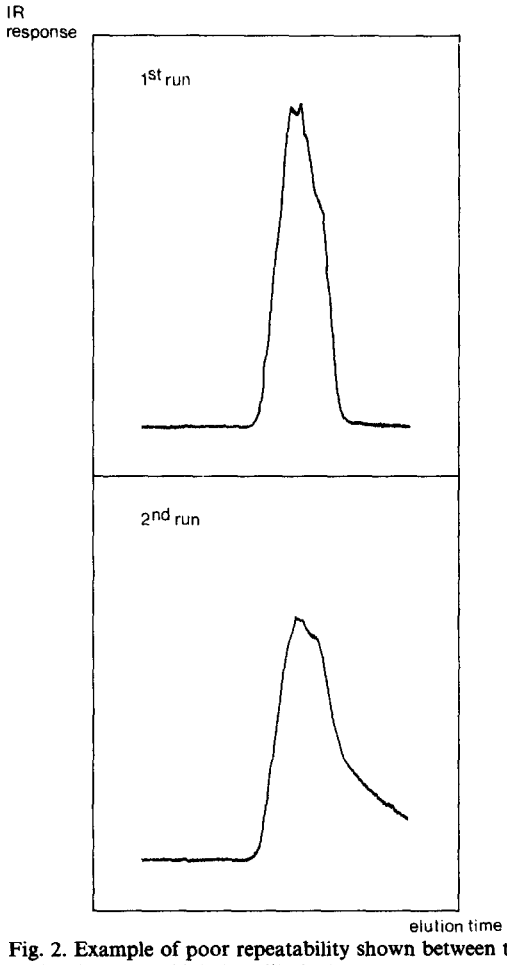

Fig. 2. Example of poor repeatability shown between two runs with the same sample due to the concentration being too high (1:5 dilution).

TABLE I

CHECK SHOWING THE INDEPENDENCE OF THE INJECTED VOLUME OF A DILUTED SAMPLE (1:20) FROM THE NUMBER-AVERAGE MOLAR MASS

Injected volume (μl)	M_n*(GPC) (g/mol)*
100	359
50	360
25	360

RESULTS

The results obtained during the analysis are acquired using the time slicing method. A file containing 100 time values (average of each slice) and 100 areas for each detector is stored in the computer memory. The number of 100 time slices was selected after several trials as giving sufficient resolution for the memory available in the computer. As the *n*-alkane calibration was made on the IR detector, all the slice areas are linked to the IR detector time slices. Then, for each slice, and *n*-alkane molar mass is calculated from the calibration equation and is corrected with the non-alkyl correction factor from the IR area/UV area ratio. In this way data are reduced to 100 average slice molar masses and 100 slice areas (proportional to the mass of sample passing through the detector), and it is now possible to calculate the following properties:

number-average molar mass:

$$M_n = \frac{\sum_{1}^{100} A_i}{\sum_{1}^{100} \frac{A_i}{M_i}}$$

mass-average molar mass:

$$M_n = \frac{\sum_{1}^{100} A_i M_i}{\sum_{1}^{100} A_i}$$

polydispersity index:

$$I_p = \frac{M_m}{M_n}$$

lower and higher slice molar masses at 10% of maximum slice area;

mean alkyl relative response:

$$R_{al} = 100 \frac{\sum_{1}^{100} A_i(\mathrm{IR})}{\sum_{1}^{100} A_i}$$

where A_i = total area of the ith slice [A_i(IR) + A_i(UV)]; M_i = average molar mass of the ith slice.

Lower and higher molar masses were chosen at 10% of the maximum slice area to avoid inaccurate values in the lower part of the curve, which is asymptotic to the axis, and the slice area becomes much less sensitive to molar mass.

DISCUSSION

Because it is not possible to make absolute measurements or to prepare standard mixtures of sufficient complexity (few of the necessary components are available from suppliers), cross-checking of results was only possible against other established techniques and by internal consistency checks as detailed below.

To quantify and compare the repeatibility, the same cryoscope and operating conditions were used by nine different operators on each of two distillation residues. The results given in Table II show relative standard deviations of 5.1% and 5.0%. For the GPC technique one residue was analysed seven times over a 3-month period by at least three operators and the results (Table III) showed a relative standard deviation of 1.1%.

A comparison between the average molar mass obtained by both GPC and cryoscopy was made for twenty petroleum distillation residue samples from widely different sources to check the validity of the method (see Table IV). Comparison here shows that the relative difference is always less than the maximum relative difference shown in the cryoscopy reproducibility test in Table II (16%).

TABLE II

CHECK OF REPEATIBILITY OF RESULTS FROM THE CRYOSCOPIC TECHNIQUE

Cryoscope operator	*Average molar mass (g/mol)*	
	Sample 1	*Sample 2*
1	322	307
2	300	278
3	349	300
4	332	291
5	324	278
6	355	323
7	314	276
8	326	285
9	310	293
GPC	331	280

TABLE III

CHECK OF REPRODUCIBILITY OF GPC MEASUREMENTS

Analysis date	M_n *(GPC) (g/mol)*
5.12.83	331
5.12.83	338
8.12.83	335
8.12.83	339
16.12.83	331
10.1.84	339
9.2.84	329

TABLE IV

COMPARISON OF MEASUREMENTS PERFORMED BY GPC AND CRYOSCOPY

Sample No.	M_n *(g/mol)*		*Polydispersity index*	*Alkyl relative response (%)*	*Relative difference (%)*
	Cryoscopy	*GPC*			
1	307	280	2.2	78.3	−8.8
2	322	331	2.3	70.0	+2.8
3	281	284	2.0	74.8	+1.1
4	275	280	2.0	75.2	+1.8
5	233	247	1.9	78.8	+6.0
6	234	234	1.7	80.0	0
7	320	359	2.5	65.3	+12.2
8	303	340	2.9	67.6	+12.2
9	333	317	2.4	73.4	−4.8
10	510	435	1.1	79.2	−14.7
11	291	323	2.8	69.7	+11.0
12	218	243	1.9	78.3	+11.5
13	333	285	1.3	91.4	−14.7
14	283	276	2.7	73.3	−2.5
15	299	278	2.1	75.8	−7.0
16	258	248	2.6	73.8	−3.9
17	265	286	1.7	76.1	+7.9
18	226	238	1.8	80.0	+5.3
19	306	314	2.7	72.2	+2.6
20	506	492	1.4	75.6	−2.8

Hence the accuracy of the GPC results was shown to be at least better than those of cryoscopy. In addition, the technique is simpler and more efficient; the operator time is 10 min and the apparatus analysis time is 60 min for analysis or calibration. Thus the primary aim of the technique development was achieved.

Additionally, some analyses were run on distillation cuts to check the effect of polydispersity on the results. For these cuts it was also possible to analyse by combined gas chromatography–mass spectrometry (GC–MS) in order to obtain an accurate measurement of the average molar mass by identifying all families. These results are shown in Table V and Fig. 3. The average molar mass differences are in the same range as the cryoscopic repeatability and in addition the series of GPC

TABLE V

MEASUREMENTS PERFORMED ON A VARIETY OF DISTILLATION CUTS AND RESIDUES FROM A CRUDE OIL SAMPLE

Cut boiling range (°C)	M_n *(g/mol)*			*Polydispersity index*	*Alkyl relative response (%)*
	GC–MS	*Cryoscopy*	*GPC*		
T_i*–112	86		82	1.1	99.7
112–226	124		115	1.1	99.9
226–343**	216		186	1.1	99.0
343–401**	321		274	1.1	90.6
Residue > 112		265	286	1.7	76.1
Residue > 401		506	492	1.4	75.6
Initial mixture	(205)***		215	2.0	79.4

* T_i = Initial boiling point (= 30°C).
** These cuts were taken under vacuum to avoid thermal cracking.
*** This value was calculated from cut yields, M_n from GC–MS and cryoscopy.

measurements are internally consistent. The efficiency of the gel columns decreases for low molar masses, and cycloalkanes (mainly with C_5 and C_6 rings), which are present in the low molar mass range, cannot be discriminated by the detectors used from alkanes eluting at the same time. This explains the systematic difference between molar masses obtained by GPC and GC–MS. Note, however, that the goal of this GPC technique is not to replace GC, which is still the best routine technique for low-boiling mixtures (alkanes up to C_{30}), but is to be used for residues that cannot be analysed by GC.

A good consistency check is revealed by the comparison of the measured GPC value with that calculated from all distillation cuts for the initial mixture, which agrees to within 5%.

Some comparison was attempted between our alkyl relative response factor and the Watson characterization factor[2] and Jacoby aromaticity factor[3]. The results of these comparisons showed equally poor agreement between all the three factors. This is not unreasonable, because the Watson and Jacoby factors are calculated using the following different equations based on the same two measured properties:

$$K = 4.557 M_n^{0.15178\gamma - 0.84573}$$

$$Ja = (\gamma - 0.8468 + 15/M_n)/(0.2456 - 1.77/M_n)$$

where K is Watson factor [range: 13 (paraffinic)–10 (aromatic)], Ja is the Jacoby aromaticity factor [range: 0 (paraffinic)–1 (aromatic)], M_n is the number-average molar mass and γ is average specific gravity (60/60°F), whereas our alkyl relative response was calculated from two measurements on each of 100 molar mass slices. Our own preliminary comparison between the densities and molar masses of residues showed good agreement with our alkyl relative response factor. A more detailed comparison will be possible when more measurements are available. Whitson[4] investigated the characterization of hydrocarbon plus fractions using a probabilistic

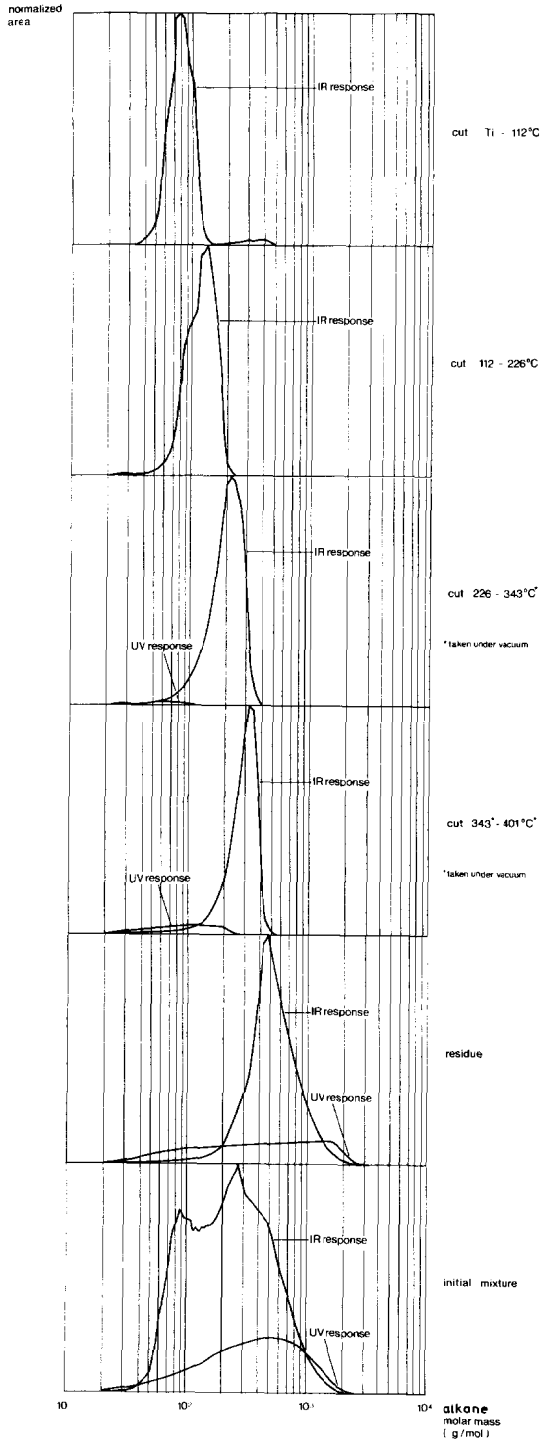

Fig. 3. Example of fingerprints run on the products of a distillation. Note: all fingerprints are normalized to 100% for the maximum of the curve.

model, in which many pseudo-components have different Watson or Jacoby factors, for use in equations of state. Our GPC technique gives experimental data that can be used for pseudo-component characterization.

An additional result of this GPC analysis is the "fingerprint" of the residue (or any hydrocarbon system), which can help to classify and compare crude oils. We give one example (Fig. 4), which shows almost identical fingerprints for samples from different wells in the same oil field. Fingerprints can also show that two very different mixtures can have the same average molar mass and possibly even density. This agrees with our observations above concerning the limitations of characterization factors calculated from average data. A second example of two fingerprints (of clearly

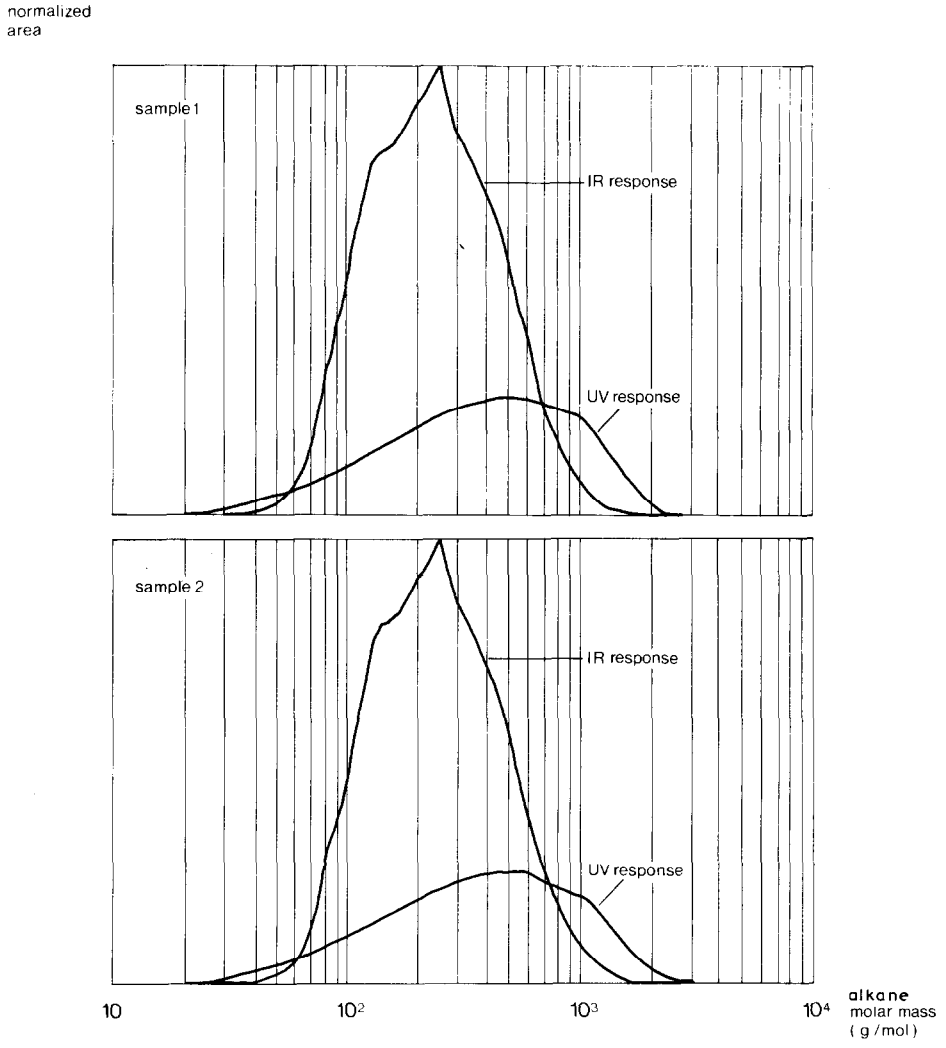

Fig. 4. Example showing almost identical fingerprints for two samples from different wells in the same oil field.

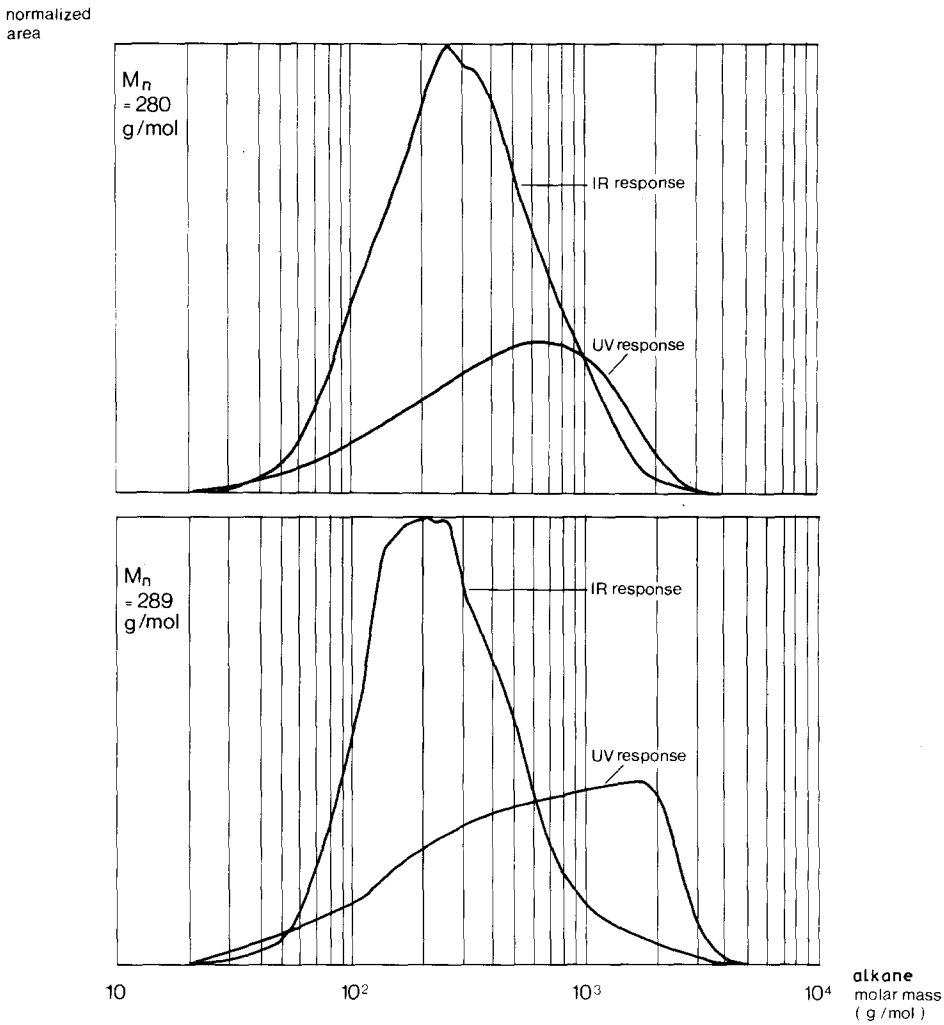

Fig. 5. Example of differences in distribution for two samples giving similar average molar mass.

different samples) having similar average molar masses is given in Fig. 5. Note that the fingerprint is the plot of detector responses *versus* alkane molar mass before any calculations are made on the acquired data, and is thus qualitative. The alkane molar mass calibrations are used in this instance to relate fingerprint analyses performed on different apparatus to the same basis.

CONCLUSION

Methods giving global measurements of molar mass on complex mixtures cannot be as accurate as absolute measurements and are partly empirical (in this instance with the assumption of only two types of bond, alkyl and aryl, and a non-specific

linear response for the UV detector), but they are suitable for routine measurements where a maximum number of results must be obtained in a minimum time. Here, the GPC technique has been shown to be capable of replacing cryoscopy as it is a simpler and more time-efficient method. It gives at least as good an accuracy and a far better reproducibility. It is better to use GPC only for residues owing to the efficiency of gel columns and the presence of cycloalkanes in lighter liquids. Hence GC alone or GC–MS remain the best methods for the determination and characterization of light hydrocarbons.

In addition to the number-average molar mass given by cryoscopy, more information can be obtained from GPC, and in the next development it will be possible to define a certain number of "molar mass cuts" for each of which the relative abundance (mole-%), the alkyl relative response and the average molar mass will be given. This type of residue composition will assist in the development of reservoir computer models giving more detailed information on what is sometimes 95% of the reservoir fluid.

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