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IDENTIFICATION AND CHARACTERIZATION OF PETROLEUM AND PETROLEUM PRODUCTS BY GEL PERMEATION CHROMATOGRAPHY WITH MULTIPLE DETECTORS

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SUMMARY

The usefulness of the gel permeation chromatographic technique has been extended through the incorporation of multiple detectors to monitor the effluent for additional characterization information. This approach can: (1) detect differences in crude oils; (2) match source and spill samples in oil pollution studies; (3) distinguish blended bunker fuels from total crudes; and (4) show comparative changes in molecular weight and aromaticity during petroleum processing.

INTRODUCTION

Petroleum and petroleum products are identified and characterized by techniques that range from simple physical tests to complex separations and detailed structural analysis. The extent and complexity of the testing depend upon the information required. There is a need, especially in the higher boiling fractions, for a rapid and relatively inexpensive method to obtain this type of information. This paper describes a preliminary application of gel permeation chromatography (GPC) with multiple detectors to the identification of crude oils, fuel oils, oil spills and the monitoring of changes that occur during petroleum processing.

EXPERIMENTAL

The gel permeation chromatographs used were of conventional design and consisted of a solvent reservoir, degasser, pumping system, sample injection valve, 4 ft. \times 3/8 in., styragel columns, an oven, and detectors. A flow-rate of 1.7 ml/min was maintained for most experiments.

Three detectors were used either singly or in series: (1) a differential refractive index monitor (Waters Associates, Inc., Model R-4); (2) a differential ultraviolet

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absorbance monitor set at 313 nm and/or 365 nm (Isco, Model UA2); and (3) a flame ionization detector (Pye Ltd., System 2, and Packard Model 7101).

Three solvents were used: reagent grade tetrahydrofuran, commercial grade benzene with less than 0.01% residue, and trichlorobenzene that had been distilled in glass.

RESULTS AND DISCUSSION

GPC is a technique that separates primarily by size. In practice, the columns are packed with particles of gel that contain pores of different sizes. As a sample traverses the columns, the molecules that are larger than the pores are excluded and elute at the void volume of the column while the smaller molecules pass into the pores and are retarded. The exact elution volume of a given species depends upon the interstitial gel volume that is available to it. With certain types of compounds, such as condensed aromatics, secondary effects (primarily adsorption) become important and cause these compounds to elute later than would be predicted from their size. It has been found that GPC produces a size separation (mainly as judged by molecular weight) for crude oils as well as the asphaltene, oil, resin, and saturate fractions¹⁻⁵.

If the effluent from the GPC separation is monitored with the appropriate continuous detectors, the change of various sample properties with size can be determined rapidly and simultaneously.

Information available from the differential refractometer

The refractive index is a fundamental property of organic compounds and is related to the overall composition of the molecule or mixture. DONE AND REID⁶ have calculated refractive indices of saturates and single-ring aromatic compounds and have shown that their refractive indices asymptotically approach a value of approximately 1.47 with increasing molecular weight. Condensed polynuclear aromatic systems often exhibit refractive index exaltation and have refractive indices greater than 1.47 (ref. 7). Commercial refractive index detectors (RID) are differential instruments that measure the difference in refractive index between a reference stream of the solvent and a sample stream. The signal from the detector is a function of the algebraic sum of the refractive indices of the compounds present and their concentrations. The chromatograms of six crude oils using benzene as solvent are presented in Fig. 1. The areas above the baseline represent mixtures of compounds with total refractive indices greater than benzene (1.5011, 20°C), and the areas below the baseline represent mixtures of compounds with refractive indices less than benzene.

Information available from the flame ionization detector

The profiles from the RID are often misleading with respect to determining the weight distribution of complex samples⁸. The only commercial detector presently available that will approximate a mass response is the flame ionization detector (FID). In operation, the effluent from the column is deposited on a moving wire (or belt, chain, etc.) and is transported through a chamber where the solvent is evaporated. After the solvent is removed, the sample enters the pyrolysis or oxidation chamber and is decomposed or volatilized. The volatile material is then swept into the FID. The main drawback to the FID has been the high noise level. Several workers have

DETECTOR RESPONSE:

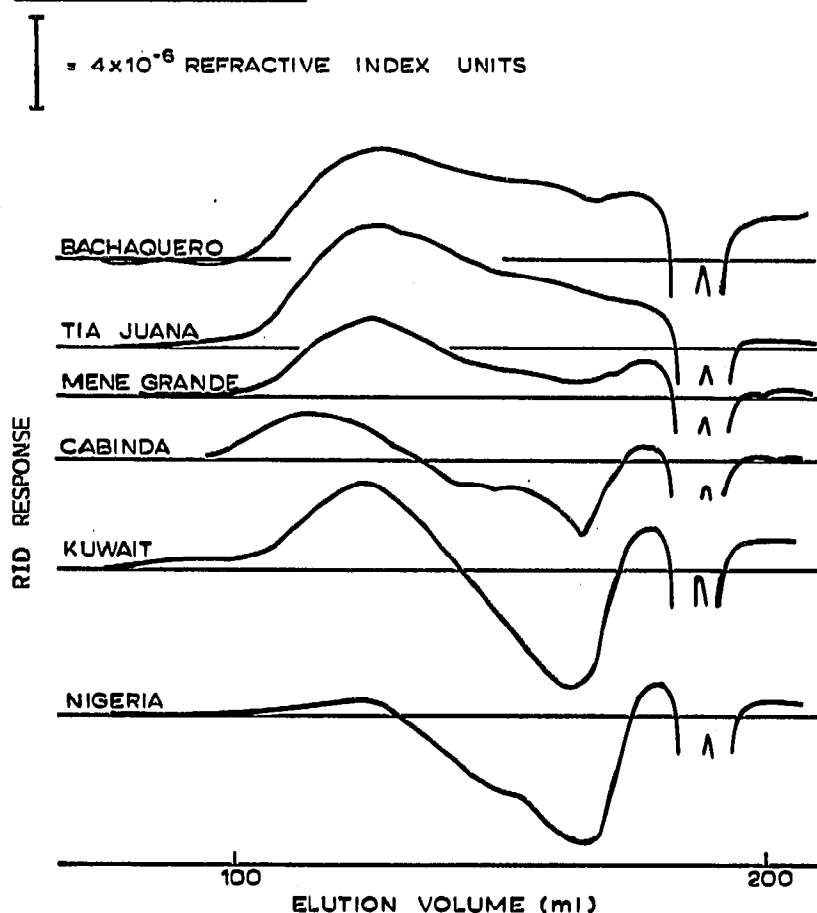


Fig. 1. RID chromatograms of crude oils. Columns, $1 \times 10^4 \text{ \AA}$, $1 \times 10^3 \text{ \AA}$, 250 \AA , 100 \AA , 60 \AA ; solvent, benzene; temperature, $50 \text{ }^\circ\text{C}$; flow-rate, 1.7 ml/min ; sample size, 5 mg .

attempted to overcome this problem by modification of the sample application mechanism and the transport system⁹. In our initial attempts to overcome this problem with the Packard FID, the type of transport, *i.e.*, wire, belt, or chain, was studied as well as the method of application of the sample to the transport. Some noise reduction was achieved, but the results for polymer and heavy petroleum fractions were far from satisfactory. It was observed during these studies that the amount of noise was more dependent upon the type of compound being determined than the mode of application or transport. For fairly low-molecular-weight compounds, such as hexadecane, a nearly noise-free symmetrical peak was obtained. However, with polyolefins and polystyrenes the noise level was undesirably high. (With polymethacrylate, which is more easily pyrolyzed than polystyrene or polyolefins, the noise level was much lower than with other polymers.) From this it was concluded that the noise in FID was mainly due to high-molecular-weight fragments entering the flame. Wires of several different metals were placed in the pyrolysis chamber of the Packard instrument in an attempt to catalyze the decomposition to smaller fragments. Copper wire with an oxide coating was found to be the most effective.

The work reported in this paper was carried out with the Pye instrument. As

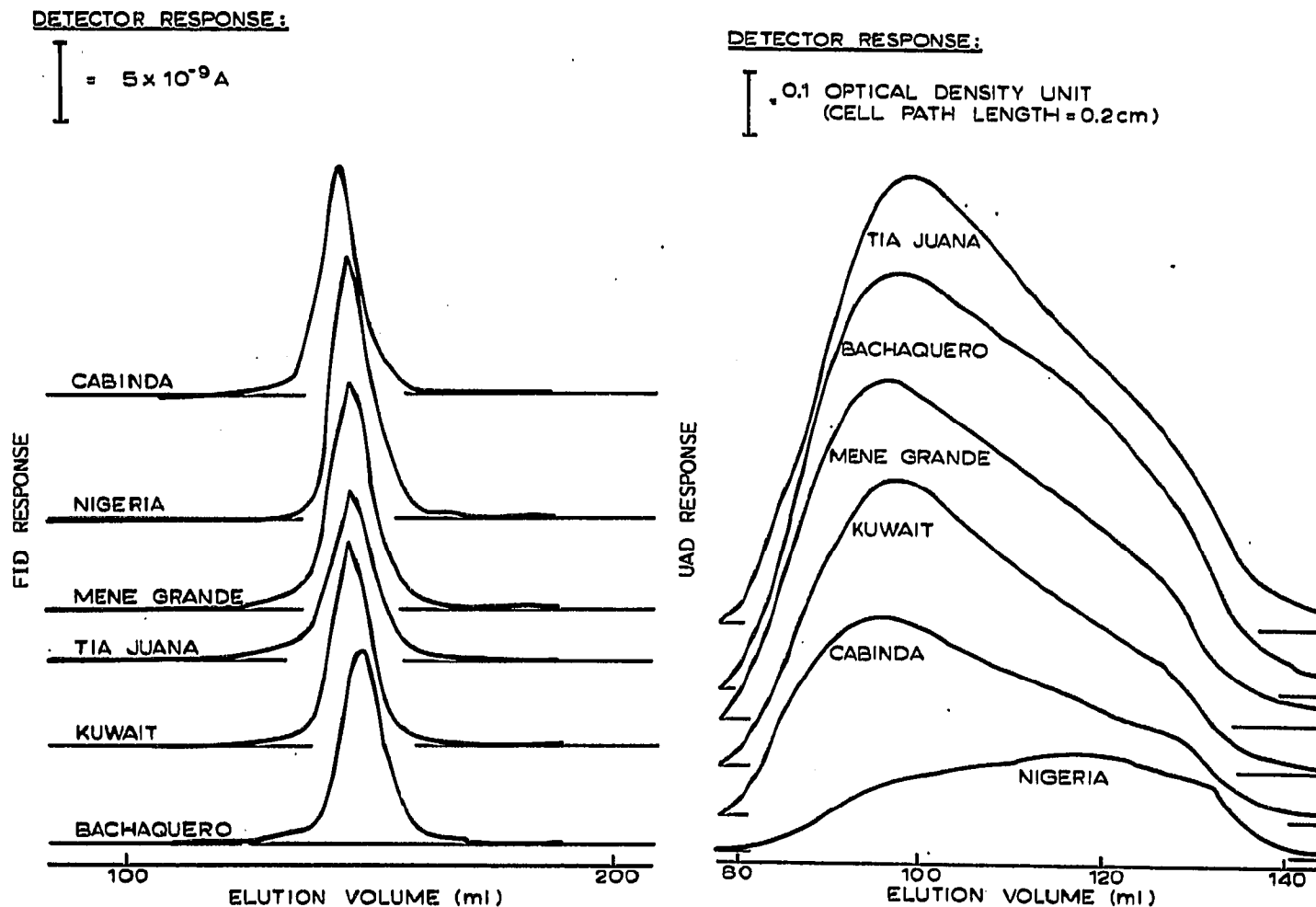


Fig. 2. FID chromatograms of crude oils. Columns, 1×10^4 Å, 1×10^3 Å, 250 Å, 100 Å, 60 Å; solvent, benzene; temperature, 50 °C; flow-rate, 1.7 ml/min; sample size, 5 mg.

Fig. 3. UAD chromatograms of crude oils. Columns, 1×10^4 Å, 1×10^3 Å, 250 Å, 100 Å, 60 Å; solvent, benzene; temperature, 50 °C; flow-rate, 1.7 ml/min; sample size, 5 mg.

received, this instrument exhibited the same noise pattern. The noise was reduced by placing copper wire with an oxide coating in the exit tube from the pyrolysis chamber. However, the same effect and more reproducible performance were obtained by using air in the cleaner chamber instead of nitrogen. This places an oxide coating on the wire and accomplishes the same purpose as the copper oxide. Though this modification does not completely solve the noise problem, it does point to a major source of the noise and much useful information can be obtained with the modified detector that would be difficult to obtain otherwise. In Fig. 2 the chromatograms of six crude oils using the Pye FID are shown. These are the same crudes as shown in Fig. 1. It has been found that saturates produce a greater response than aromatics. For thirteen crude oils the total response varied approximately 20%; however, the curves approximated the weight distributions of the samples. Recently SCOTT AND LAWRENCE¹⁰ have reported a modification of the Pye instrument that has overcome these deficiencies. In this modification the sample is oxidized to carbon dioxide and then converted to methane which is determined with the FID.

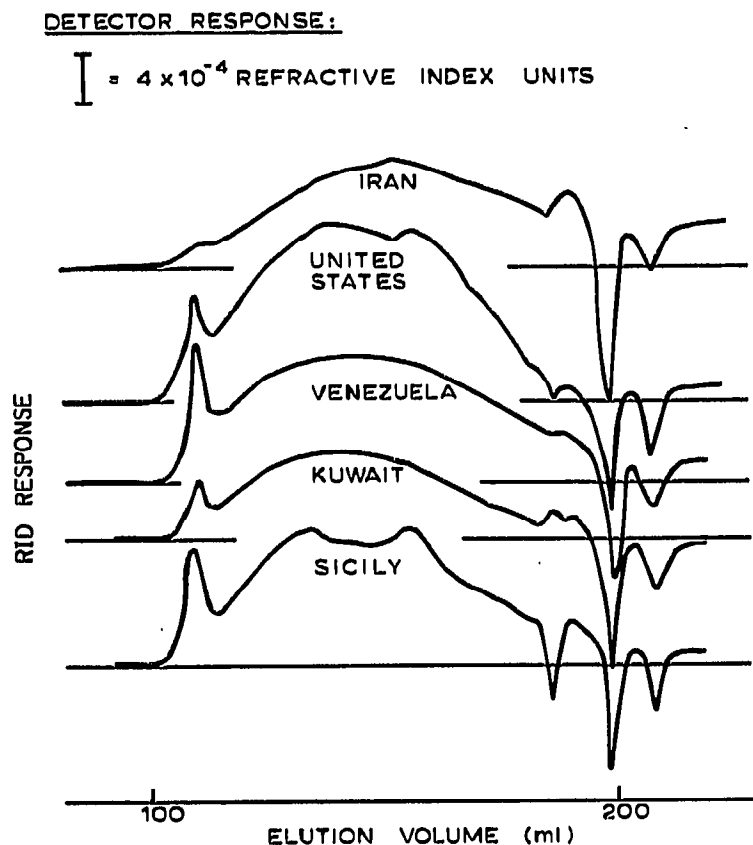


Fig. 4. RID chromatograms of crude oils in tetrahydrofuran. Columns, five of 500 Å; solvent, tetrahydrofuran; temperature, 30 °C; flow-rate, 1 ml/min; sample size, 8 mg.

Information available from ultraviolet absorbance detector

The ultraviolet absorbance detector (UAD) used in this work is capable of monitoring two wavelengths simultaneously. The wavelengths chosen were 313 nm and 365 nm. These wavelengths approximate the absorption region of many two- and three-ring condensed aromatics found in petroleum as well as a number of higher condensed systems. In Fig. 3 the chromatograms of six crude oils that were obtained by measuring the absorbance at 313 nm are presented. Except for the Nigerian crude, the absorbance increases to a maximum at lower elution volumes (higher molecular weights) and then gradually decreases as elution continues. The total absorbance of the Nigerian crude is less than that of the other crudes and gradually increases with elution volume reaching its maximum value at the higher elution volumes (lower molecular weights).

Identification of crude oils

Inspection of the chromatograms in Fig. 1 readily demonstrates that GPC does portray differences between crude oils. However, the details of the profiles will be dependent upon the experimental conditions (mainly columns and solvent) used to obtain them as well as upon the composition of the crude oils. In our initial studies, a series of crude oils was also analyzed by Waters Associates in a cooperative study. Five Styragel columns (500 Å) were used with tetrahydrofuran as solvent and a

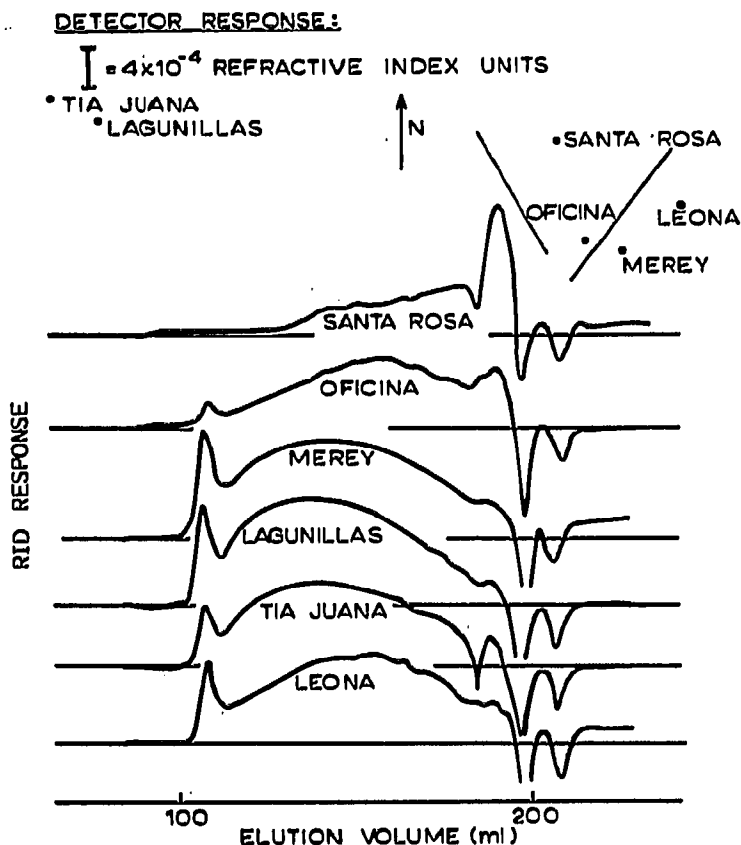


Fig. 5. RID chromatograms of Venezuelan crude oils in tetrahydrofuran. Columns, five of 500 Å; solvent, tetrahydrofuran; temperature, 30 °C; flow-rate, 1 ml/min; sample size, 8 mg.

differential refractometer detector. The chromatograms of crude oils from five countries are shown in Fig. 4. The initial rapid rise of the chromatograms (lowest elution volume region) indicates the presence of material that is completely excluded from the columns. The two negative peaks in the highest elution volume region are due to solvent impurities. Though there are similarities among the chromatograms, the total profiles exhibit marked differences. The chromatograms of six crude oils (using the same conditions) from Venezuela are shown in Fig. 5 and the total profiles likewise show differences. Lagunillas and Tia Juana crudes are produced in Western Venezuela. The Leona and Merrey are from Eastern Venezuela and their profiles are quite similar to those of the Western Venezuela crudes. The Oficina and Santa Rosa profiles are quite different from those of the other four Venezuela crudes as well as from each other. The Oficina and Santa Rosa crude sources are located northwest of the Leona and Merrey productions in Eastern Venezuela, with the Santa Rosa being the most northerly and showing the greatest difference (see map, Fig. 5). Though the data are very limited, it does show that the crudes from the Oficina-Santa Rosa area are different from the crudes east and west of it.

In order to obtain maximum information from the GPC separation, it is necessary to use a set of columns that will provide resolution over the full range of the crude. In Fig. 6 the chromatograms of the same crude oil run on two different column sets are shown. One set consisted of five columns with designations of 1×10^4 Å,

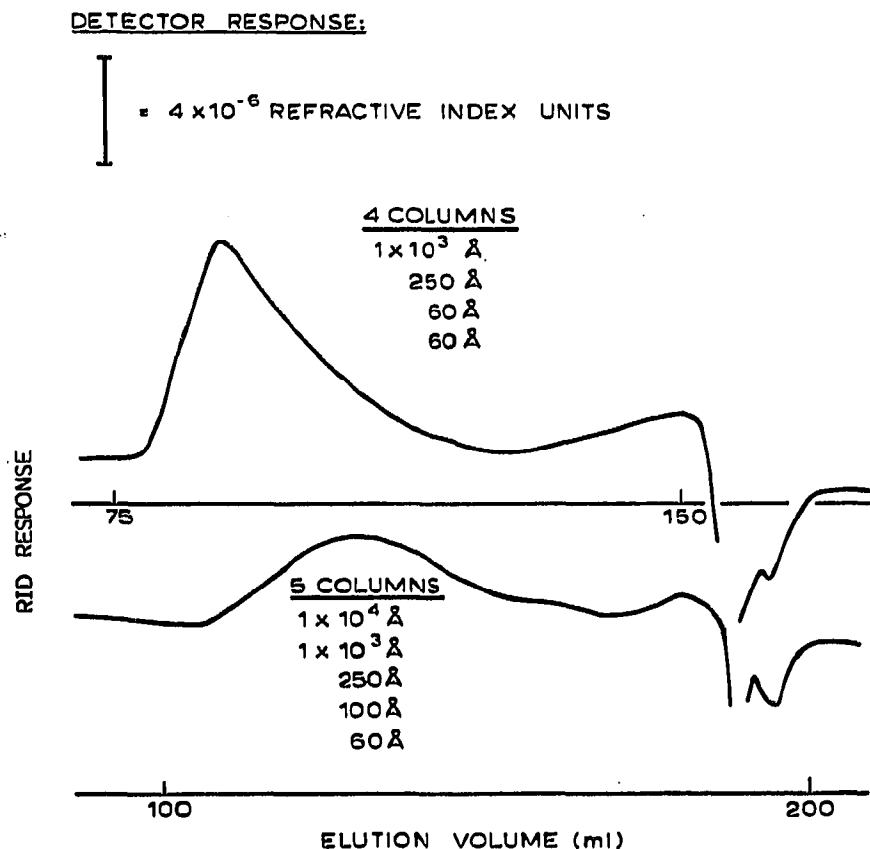


Fig. 6. Comparison of RID chromatograms from two-column sets using the same crude oil. Solvent, benzene; temperature, 50°C ; flow-rate, 1.7 ml/min ; sample size, 5 mg .

$1 \times 10^3 \text{ \AA}$, 250 \AA , 100 \AA , and 60 \AA . The other column set, consisted of four columns with designations of $1 \times 10^3 \text{ \AA}$, 250 \AA , 60 \AA and 60 \AA . With the second set, the exclusion limit was lowered and the resolution increased in the smaller exclusion limit area. The rapid initial rise of the chromatogram with the four-column set suggests that a 10^4 \AA column will provide more information for residues and similar heavy fractions. Comparison of the two chromatograms also suggests that equal resolution over the full range rather than the lower exclusion limit area would be more useful. It has been found that chromatograms similar to that obtained with the five-column set can be obtained with a three-column set consisting of columns with designations of 10^4 \AA , 10^3 \AA and 250 \AA or three linear 10^4 \AA columns. It appears from this study that a three-column set of 10^4 \AA linear columns should be satisfactory for crude oil studies.

Many workers have been aware of the anomalous GPC behavior of aromatic compounds. It has been found that condensed aromatic compounds elute later than would be predicted from their molar volumes or molecular weights^{5,11}. In an effort to reduce this effect, some workers have added methanol to the eluting solvent². Perhaps the most significant contribution in this area was the observation by BERGMAN AND DUFFY⁵ that alkanes, cata-condensed aromatics, and peri-condensed aromatics have different elution volume/molar volume relationships in tetrahydrofuran. Toluene produced essentially the same results. However, when trichlorobenzene was used as

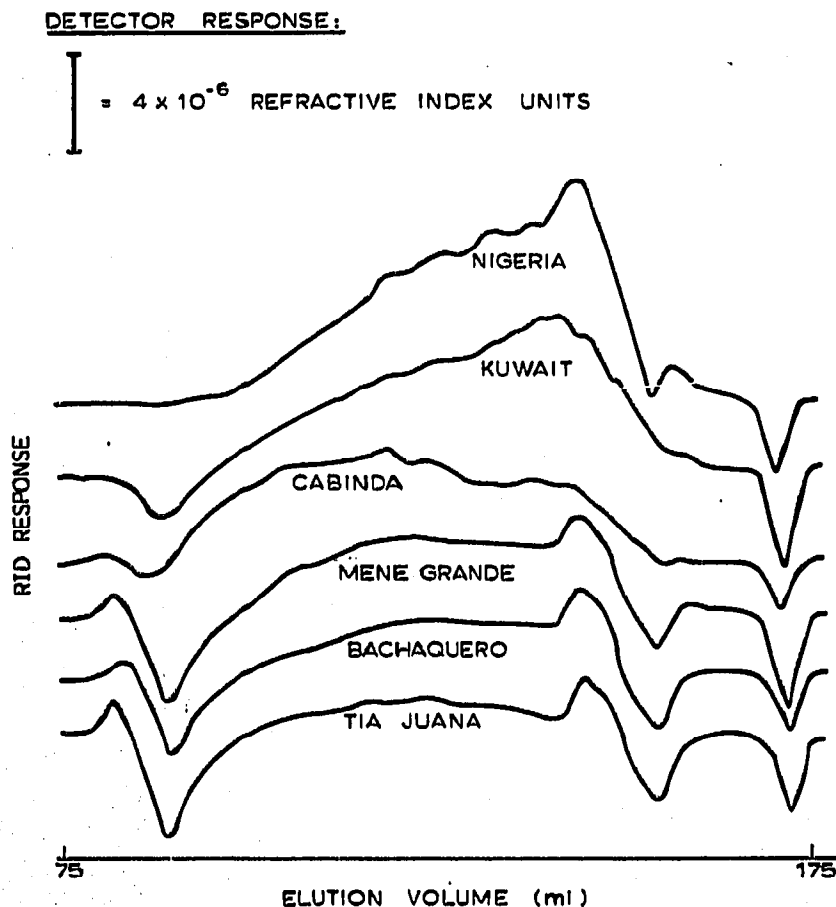


Fig. 7. RID chromatograms of crude oils in trichlorobenzene. Columns, $1 \times 10^3 \text{ \AA}$, 250 \AA , 60 \AA , 60 \AA ; solvent, trichlorobenzene; temperature, 125°C ; flow-rate, 1.5 ml/min ; sample size, 5 mg .

the eluting solvent, the three classes of compounds fell on the same elution volume/molar volume curve. A series of crude oils was run in trichlorobenzene at 125° with the four-column set to determine if these conditions would produce more definitive profiles. The profiles (Fig. 7) are characteristic for each crude but are not appreciably more definitive than those obtained in benzene. Tetrahydrofuran also produces characteristic chromatograms, but they are not more definitive than those run in other solvents (Fig. 4).

From these studies it was concluded that benzene at 50° would be a satisfactory solvent. It is readily available in high purity, stable, has good solvent properties for crude oil and crude oil fractions, and is sufficiently volatile to permit use of the FID for most samples. The main disadvantages are its toxicity and absorbance in the lower wavelength ultraviolet.

The aromatic, saturate, oil (saturate + aromatic fractions) and polar non-hydrocarbon fractions¹² from two typical gas oils with very different histories were chromatographed with benzene as solvent to demonstrate the behavior of each class in this system. The chromatograms from the three detectors are shown in Fig. 8. The differences between the saturate and aromatic RID chromatograms demonstrate very well the effect of structure on the refractive index response. The RID chromato-

DETECTOR RESPONSES

$I = 8 \times 10^{-6}$ REFRACTIVE INDEX UNITS
 $I = 1 \times 10^{-9} A$
 $I = 0.1$ OPTICAL DENSITY UNITS
 (CELL PATH LENGTH = 0.2 cm)

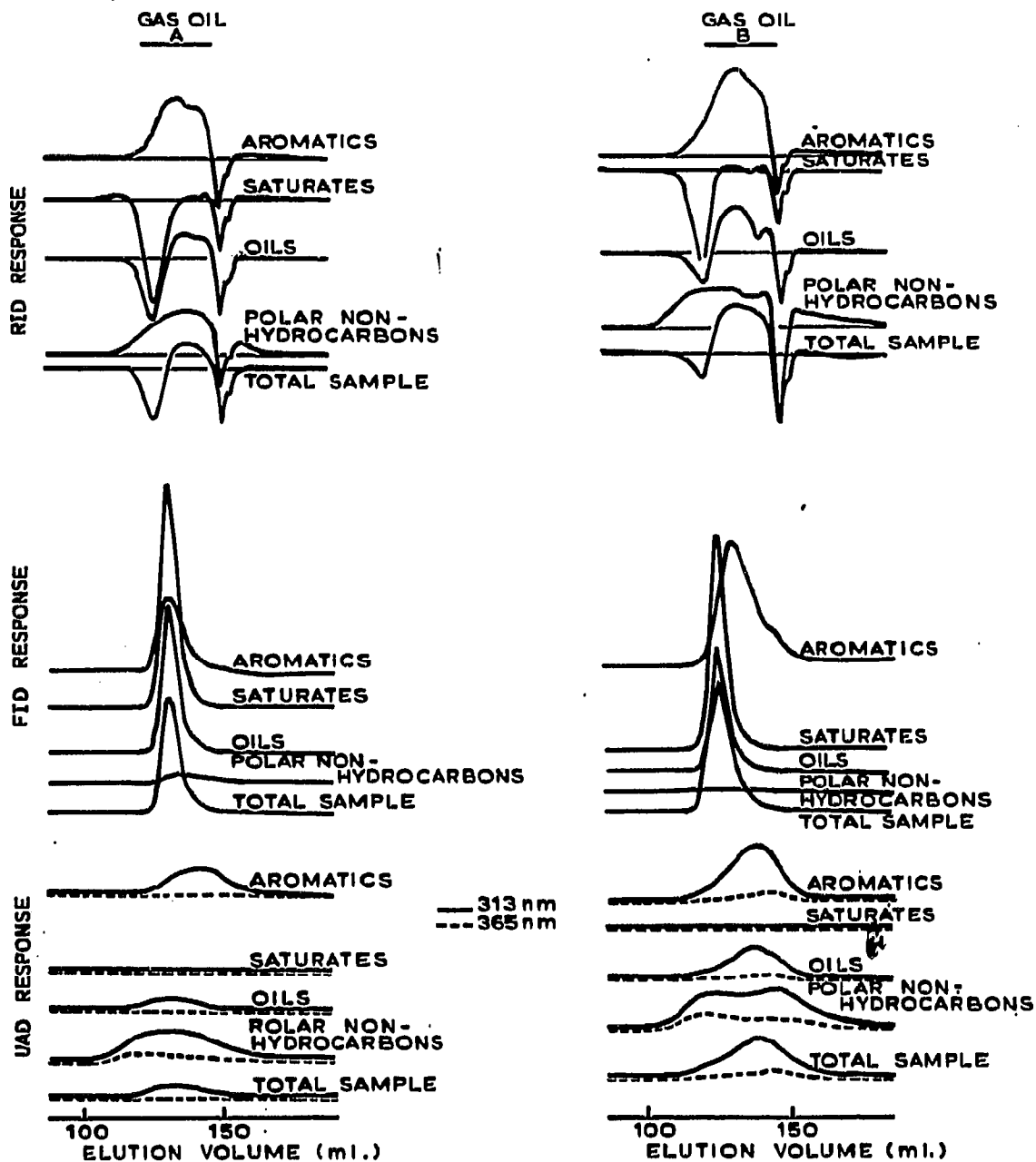


Fig. 8. RID, FID and UAD chromatograms of gas oils and gas oil fractions. Columns, $1 \times 10^4 \text{ \AA}$, $1 \times 10^3 \text{ \AA}$, 250 \AA ; solvent, benzene; temperature, $50 \text{ }^\circ\text{C}$; flow-rate, 1.7 ml/min ; sample size, 5 mg .

grams of the oils show the additive effect of blending the aromatics and saturates on the total profile. The RID chromatograms of the feedstock show the same effect for all three classes. The FID chromatograms approximate the sample distributions for the aromatic and saturate fractions as well as the feedstock, but the response for the polar non-hydrocarbons is too low to be definitive. The UAD chromatograms show the distribution of the compounds absorbing at 313 nm and 365 nm in each of the fractions and total samples.

Classification of profiles

When an attempt is made to classify the profiles and to compare them quantitatively, a decision must be made as to what are the distinguishing features and how can they be measured. As stated earlier, GPC separates by size and produces a molecular weight separation for crude oils and crude oil fractions, although different molecular weight components are often obtained at the same elution volume for different crudes. Thus, the amounts and kinds of components eluting at a given volume are characteristic. With the differential refractometer, the response is a function of both the amount present and the cumulative refractive index of the individual components present. At any given elution volume, then, that fraction has been size-classified by the GPC columns and the refractometer gives information as to the composition of the fraction. The profile is the summation of this information. In the GPC analysis of polymers, the refractive index response represents the amount of the polymer present and the elution volume represents the molecular weight. After proper calibration, the profile is used to calculate the number average molecular weight and the weight average molecular weight of the polymer¹³. Both of these values are functions of the total profile and are sensitive to changes in it. Using this scheme and a calibration curve based on the calculated Ångstrom size of several narrow molecular weight polystyrenes and other aromatic compounds, number average values and weight average values were calculated for the six crudes shown in Fig. 1. The RID response values above the baseline were taken as positive and those below as negative. The results are shown in Table I.

TABLE I

MATHEMATICAL TREATMENT OF GPC CRUDE OIL DATA

<i>Crude oil</i>	<i>Number average^a</i>	<i>Weight average^a</i>
Tia Juana	5	11
Bachaquero	5	13
Mene Grande	4	7
Cabinda	-21	71
Kuwait	-3	80
Nigerian	-3	1

^a Based on calculated Å size of aromatic calibration standards.

The numbers reflect the visual differences in the profiles. The values for the Tia Juana and Bachaquero are very close and the profiles are nearly identical. These two crudes are from the same reservoir. The Mene Grande crude, from the same area, has a similar profile and the calculated values reflect this similarity. The numbers for the

other three crudes have very different values, demonstrating the sensitivity of this type of calculation to the differences in overall composition as reflected by the GPC profiles.

TABLE II

MATHEMATICAL TREATMENT OF GPC CRUDE OIL DATA

Crude No.	RID		FID	
	M_n^a	M_w^a	M_n^a	M_w^a
1	314	519	298	342
2	234	306	228	253
3	238	-342	305	331
4	193	183	269	283
5	238	295	249	299
6	215	410	315	341
7	250	641	326	369
8	289	295	270	286
9	215	216	260	277
10	230	245	296	309
11	260	241	278	292
12	73	-111	219	237
13	202	213	269	285

^a Based on molecular weights of normal hydrocarbon calibration standards.

Table II shows the same type of data, based on normal hydrocarbon molecular weights, for thirteen other crude oils. The chromatographic conditions used included a three-column set ($2 \times 10^4 \text{ \AA}$, $1 \times 10^3 \text{ \AA}$ and 250 \AA), benzene as solvent, a flow-rate of 1.7 ml/min, a temperature of 50°C , and both the RID and FID were used. Chromatograms from the series are shown in Fig. 9 and represent the extremes of the crudes examined. Crude No. 1 contained 2% saturates, 58% aromatics and 40% non-hydrocarbons while Crude No. 10 contained 83% saturates, 15% aromatics and less than 1% non-hydrocarbons¹³.

Examination of the data in Table II shows that the four numbers listed for each crude are different. Two more numbers based on another property can be generated in the same manner using the ultraviolet absorbance at 313 nm or some other appropriate wavelength.

These numbers do not give compositional information about the percentage of aromatics, etc., but they do reflect absolute differences in composition and, with a standardized set of GPC conditions, can be used to identify a crude oil. With data from an adequate number of reference crudes, it should be possible to make tentative identifications of unknown ones.

While the number and weight average concepts show differences among profiles, chromatograms can be more accurately described if a larger number of data points are compared. If 50 or 100 data points are taken across a chromatogram and matched with the same points on another chromatogram, a much more definitive comparison can be made. This approach is similar to the one used in the treatment of infrared and mass spectrometry data. Once sample and GPC conditions are standardized so that the profile of a reference material can be reproduced over a long

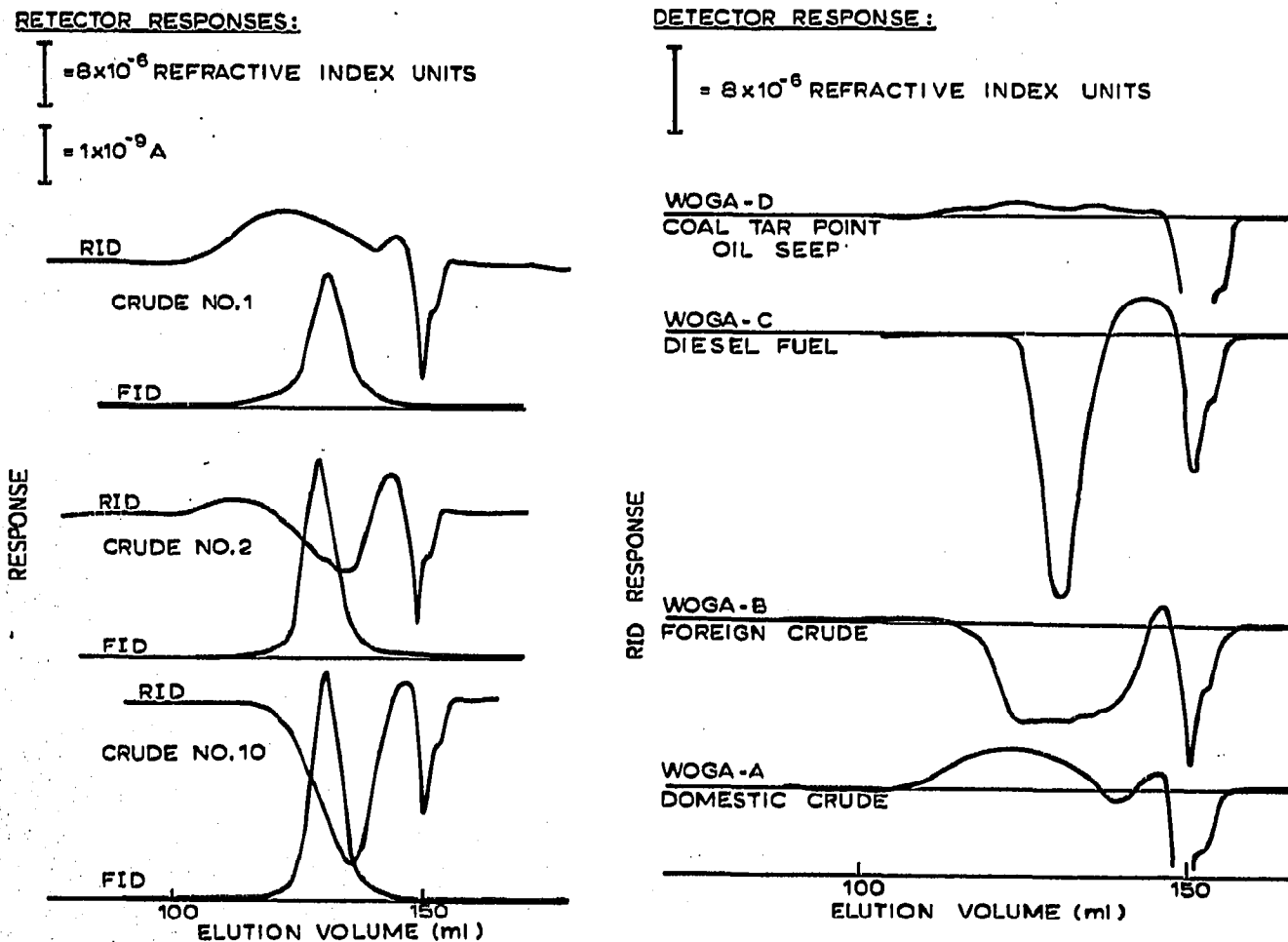


Fig. 9. RID and FID chromatograms of different crude types. Columns, 1×10^4 Å, 1×10^3 Å, 250 Å; solvent, benzene; temperature, 50 °C; flow-rate, 1.7 ml/min; sample size, 5 mg.

Fig. 10. RID chromatograms of WOGA samples A, B, C, and D. Columns, 1×10^4 Å, 1×10^3 Å, 250 Å; solvent, benzene; temperature, 50 °C; flow-rate, 1.7 ml/min; sample size, 5 mg.

period of time and by other laboratories, a computerized system of identification could be developed.

Application to oil spill identification

The Western Oil and Gas Association (WOGA) has sponsored a program to develop techniques for oil spill identification¹⁴. Samples from this cooperative program were analyzed by GPC with multiple detectors to determine the applicability of this technique to oil spill identification. For the separation, a three-column set with designations of 2×10^4 Å, 1.8×10^3 Å, and 300 Å was used with benzene as solvent. For a part of the samples the RID and FID were used and for the rest the UAD was also included.

The first series of samples (A, B, C and D) consisted of a coal tar point seep, a diesel fuel, a foreign crude oil, and a domestic crude oil. The chromatograms based on refractive index (Fig. 10) readily show differences between the samples. The positive

refractive index of the domestic crude and the negative refractive index of the foreign crude are good examples of the extremes noted in the crude oil studies (Figs. 1 and 9). The narrow distribution expected in a distillate fraction is seen in the diesel fuel with the absence of heavy materials being clearly shown. The low response for the coal tar point seep indicates a loss of sample in the GPC system. This had been found previously with coal hydrogenation products. The chromatograms from the FID (Fig. 11) approximate the weight distribution of the samples and indicate that the diesel fuel is lighter than the other samples. The loss of the coal tar sample in the GPC system is also shown by the FID.

One of the important problems in oil spill identification is distinguishing between crude oils and bunker fuels. Bunker fuels are normally produced by two processes: topping of a crude oil and blending a residue and cutter stock(s). Two samples of a blended fuel and one of a topped crude fuel oil were included in this study for reference purposes. The chromatograms based on refractive index are shown in Fig. 12. The profile of the topped crude fuel oil (Mene Grande "C") is typical of a crude oil, while the blended fuels show a pronounced peak in the lighter molecular

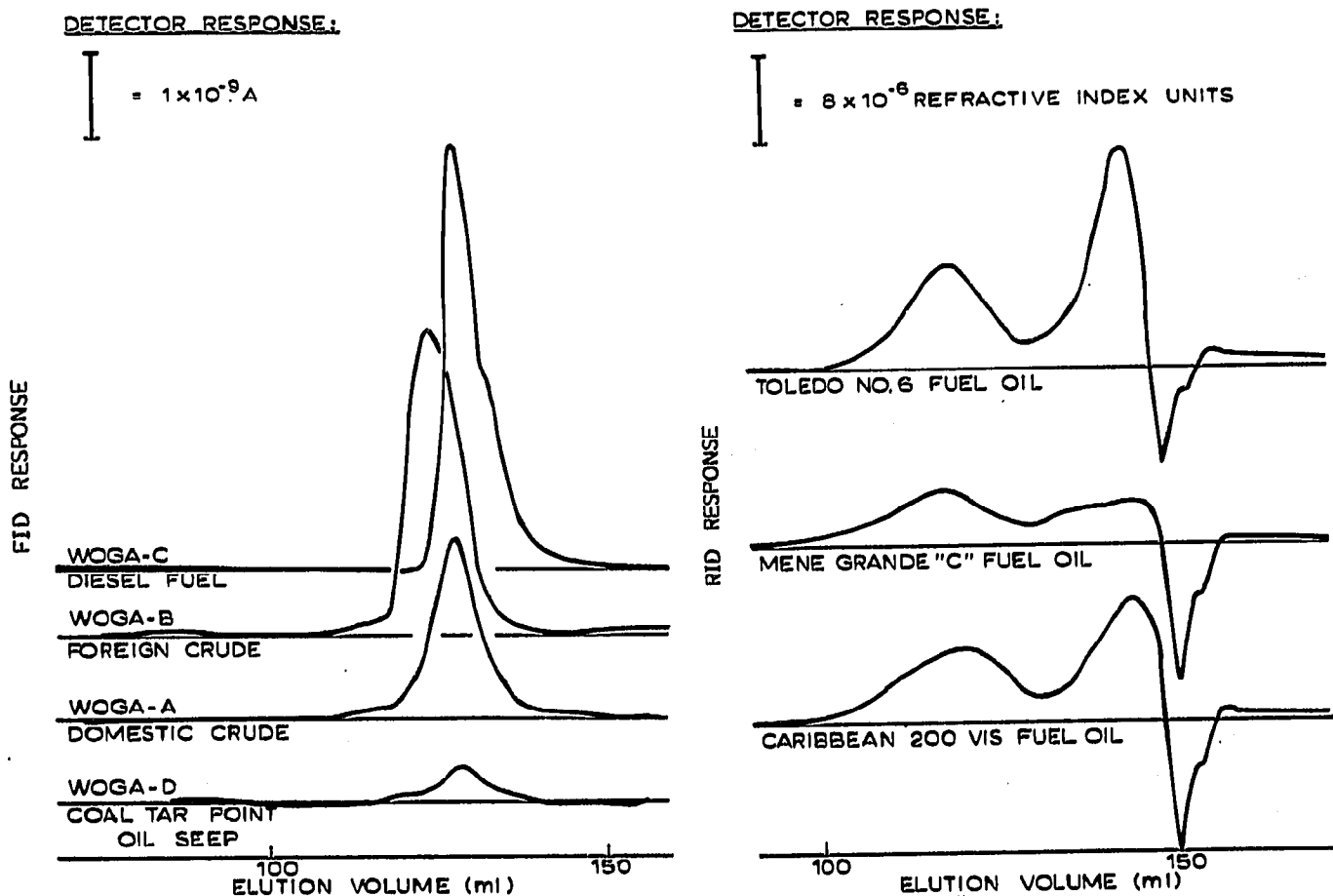


Fig. 11. FID chromatograms of WOGA samples A, B, C, and D. Columns, $1 \times 10^4 \text{ \AA}$, $1 \times 10^3 \text{ \AA}$, 250 \AA ; solvent, benzene; temperature, $50 \text{ }^\circ\text{C}$; flow-rate, 1.7 ml/min ; sample size, 5 mg .

Fig. 12. RID chromatograms of bunker fuel oil samples. Columns, $1 \times 10^4 \text{ \AA}$, $1 \times 10^3 \text{ \AA}$, 250 \AA ; solvent, benzene; temperature, $50 \text{ }^\circ\text{C}$; flow-rate, 1.7 ml/min ; sample size, 5 mg .

DETECTOR RESPONSE:

$$I = 0.1 \text{ OPTICAL DENSITY UNITS} \\ (\text{CELL PATH LENGTH} = 0.2 \text{ cm})$$

— 313 nm
 - - - 365 nm

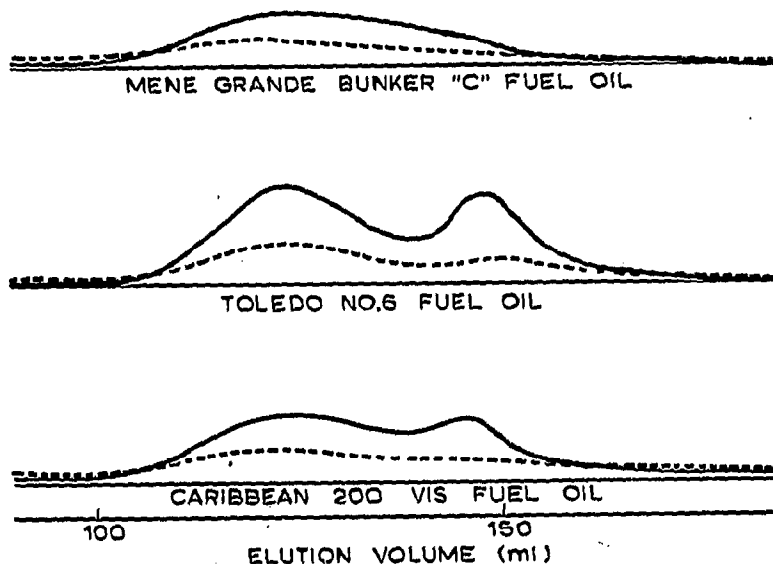


Fig. 14

DETECTOR RESPONSE:

$$I = 1 \times 10^{-9} \text{ A}$$

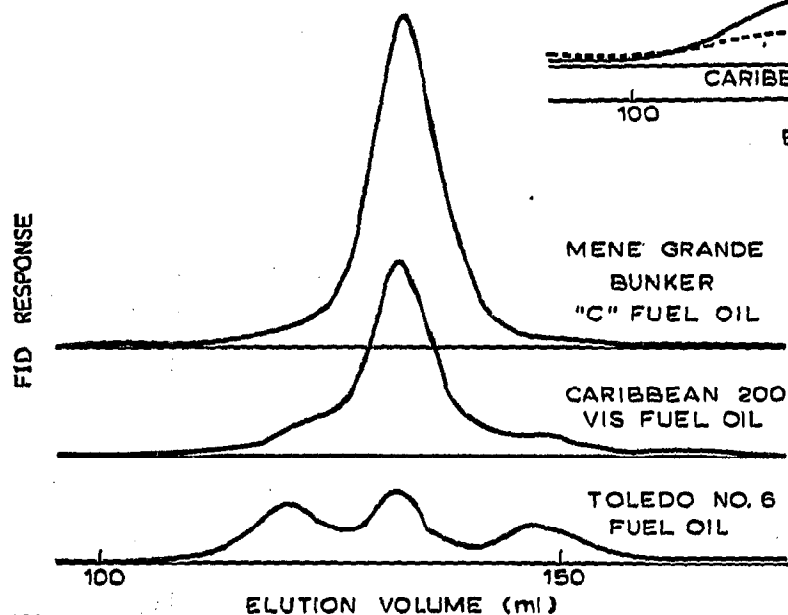


Fig. 13

Fig. 13. FID chromatograms of bunker fuel oil samples. Columns, $1 \times 10^4 \text{ \AA}$, $1 \times 10^3 \text{ \AA}$, 250 \AA ; solvent, benzene; temperature, $50 \text{ }^\circ\text{C}$; flow-rate, 1.7 ml/min ; sample size, 5 mg .

Fig. 14. UAD chromatograms of bunker fuel oil samples. Columns, $1 \times 10^4 \text{ \AA}$, $1 \times 10^3 \text{ \AA}$, 250 \AA ; solvent, benzene; temperature, $50 \text{ }^\circ\text{C}$; flow-rate, 1.7 ml/min ; sample size, 5 mg .

weight regions (immediately preceding the negative solvent impurity peaks). In Fig. 13 the chromatograms from the FID are shown. The topped crude fuel oil profile shows a symmetrical monomodal distribution typical of a crude oil, while the blended fuel oil profiles are non-symmetrical and polymodal. The chromatograms of the ultraviolet absorption at 313 nm and 365 nm are shown in Fig. 14. The profiles

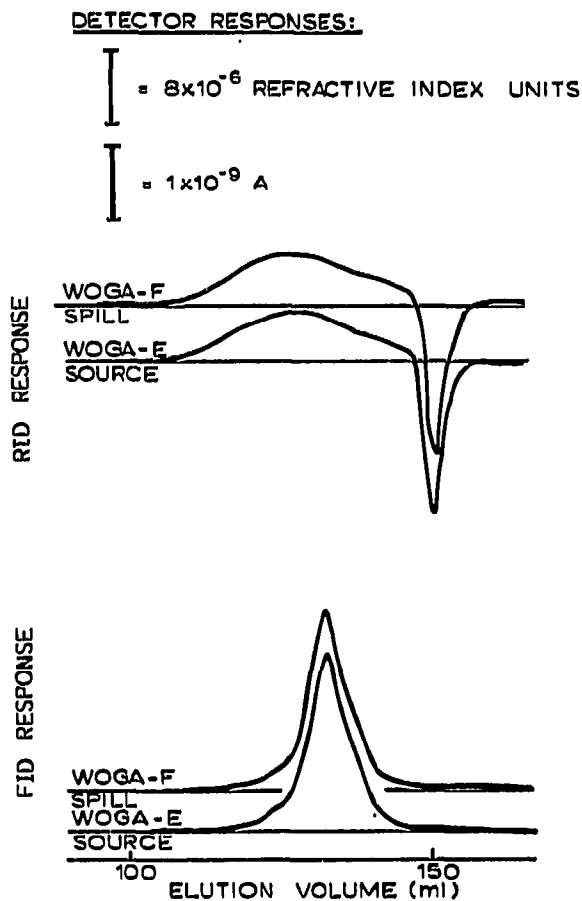


Fig. 15

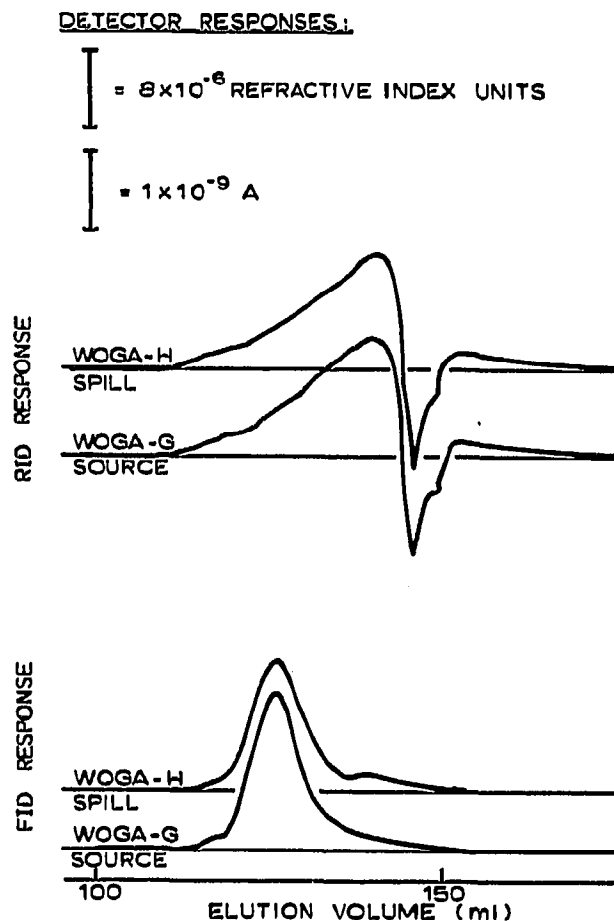


Fig. 16

Fig. 15. Chromatograms of Huntington beach crude oil source and spill samples. Columns, 1×10^4 Å, 1×10^3 Å, 250 Å; solvent, benzene; temperature, 50 °C; flow-rate, 1.7 ml/min; sample size, 5 mg.

Fig. 16. Chromatograms of bunker fuel source and spill samples. Columns, 1×10^4 Å, 1×10^3 Å, 250 Å; solvent, benzene; temperature, 50 °C; flow-rate, 1.7 ml/min; sample size, 5 mg.

from both wavelengths for the topped crude fuel oil show a monomodal distribution of the compounds absorbing at these wavelengths, while the profiles from the blended fuels are bimodal. This technique, then, will distinguish blended fuel oils from topped crude fuel oils, but will not always distinguish between a topped crude fuel oil and a total crude from the same source.

The second set of samples in the WOGA program was source and spill samples from a Huntington Beach crude oil and a bunker fuel. The chromatograms from the RID and the FID for the Huntington Beach crude are shown in Fig. 15 and for the bunker fuel in Fig. 16. These samples had been topped to 540 °F under a stream of nitrogen before analysis. The chromatograms clearly indicate that the source and spill samples are identical for both materials. The FID profiles in Fig. 16 are bimodal indicating it is a bunker fuel, while the FID profiles in Fig. 15 are monomodal and typical of a crude oil.

The third set of WOGA samples consisted of a Navy Special Fuel (M), and the same material after artificial weathering (N); a raw Midway special crude (J), and a

naturally weathered raw Midway special crude from a pipeline break (L); and two crude oils, San Joaquin, 29.3° API (K), and San Ardo, 11.0° API (P), which came from the same region of California between Fresno and the coast. These samples were chromatographed as received using the three detectors in series (Figs. 17-19).

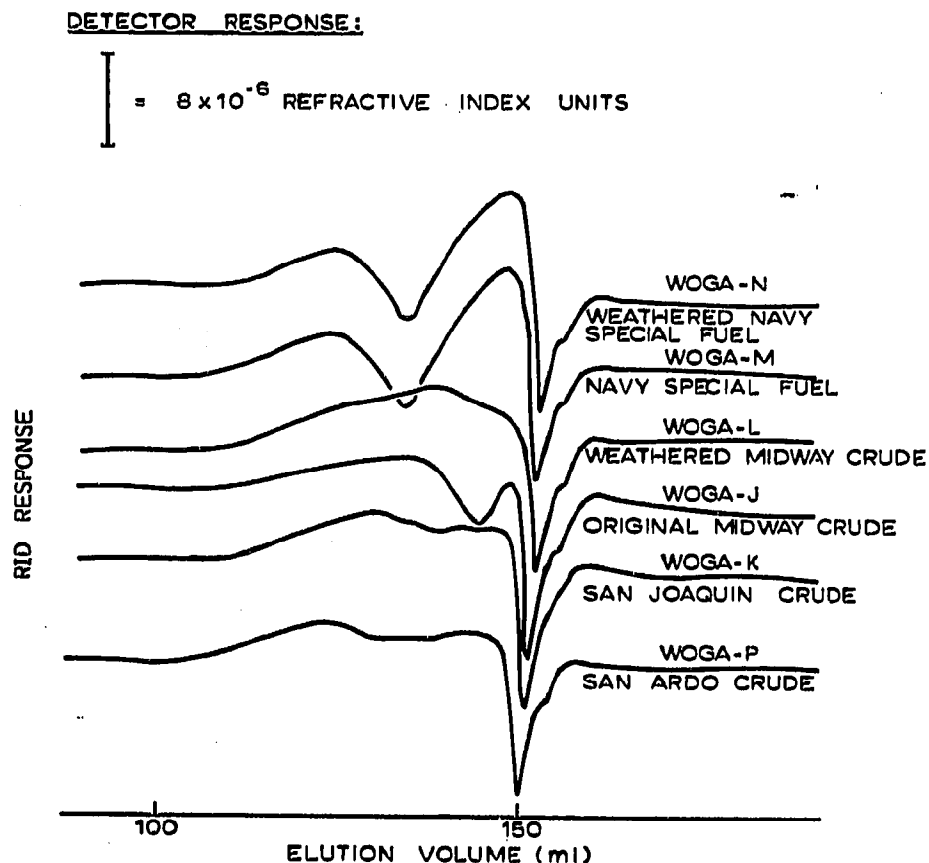


Fig. 17. RID chromatograms of WOGA samples J, K, L, M, N, and P as received. Columns, 1×10^4 Å, 1×10^3 Å, 250 Å; solvent, benzene; temperature, 50 °C; flow-rate, 1.7 ml/min; sample size, 5 mg.

The effect of weathering on the Midway special crude is very evident from comparison of the RID chromatograms of the original (WOGA-J) and the weathered sample (WOGA-L) in Fig. 17. With topping (Fig. 20) the RID chromatograms become more similar but there is still a distinct difference indicating, at least for this crude, that topping and weathering do not produce identical samples.

The chromatograms from the three detectors of the San Joaquin and San Ardo crudes are typical of crude oils with the refractive index profiles showing the greatest differences (Fig. 17). With topping, the RID chromatogram of the San Joaquin, a light oil (29.3° API), changes, while the San Ardo, a heavier oil (11.0° API), remains essentially the same (Fig. 20).

Application to monitoring changes during processing

In petroleum processing, two parameters that are often important are the changes in molecular weight distribution and in the aromaticity as a function of

DETECTOR RESPONSE:

$I = 0.1$ OPTICAL DENSITY UNITS
(CELL PATH LENGTH = 0.2 cm)

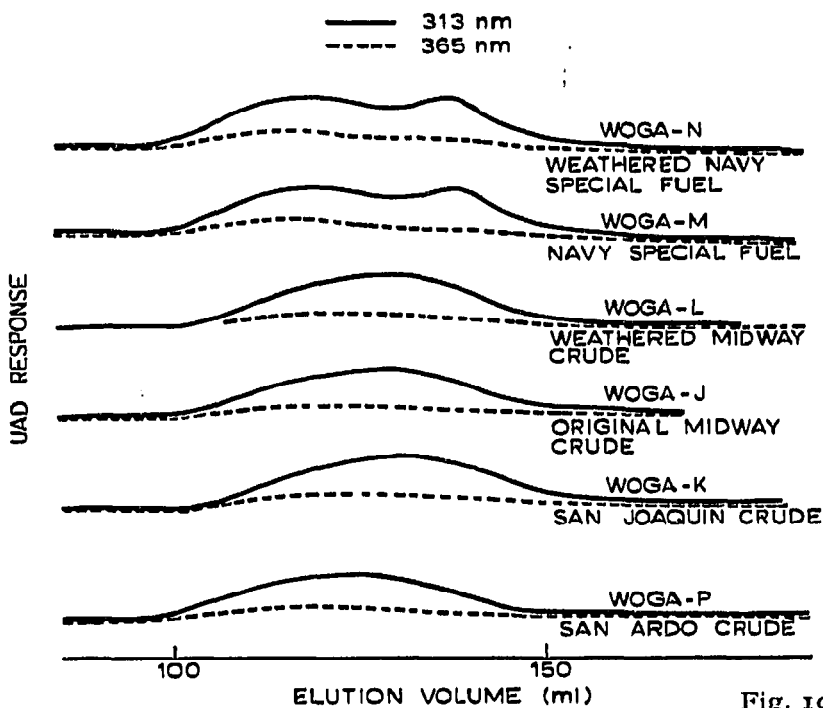


Fig. 19

DETECTOR RESPONSE:

$I = 1 \times 10^{-9}$ A

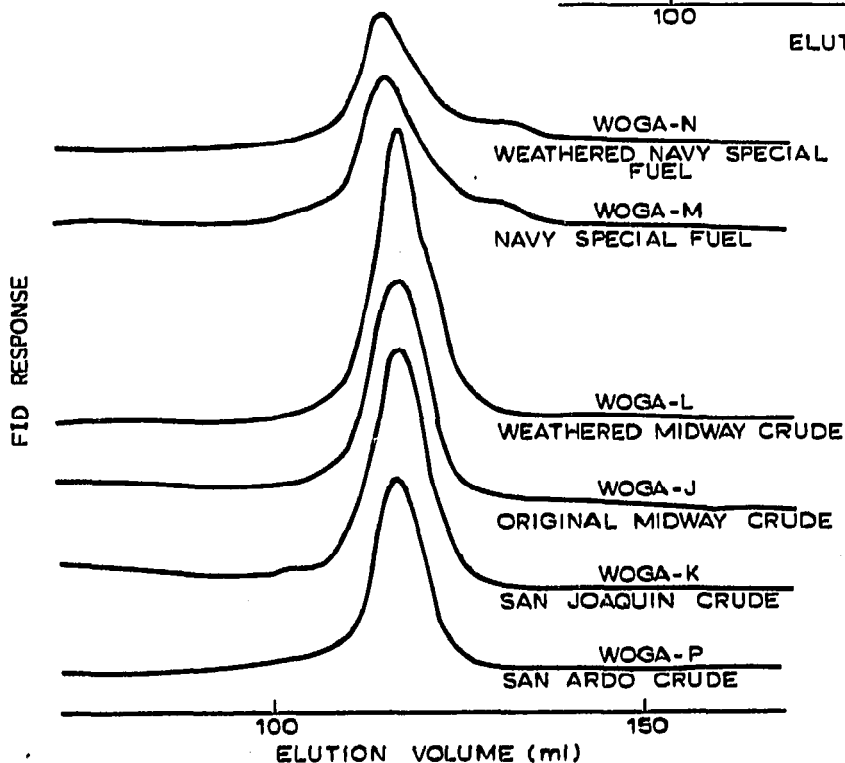


Fig. 18. FID chromatograms of WOGA samples J, K, L, M, N, and P as received. Columns, $1 \times 10^4 \text{ \AA}$, $1 \times 10^5 \text{ \AA}$, 250 \AA ; solvent, benzene; temperature, $50 \text{ }^\circ\text{C}$; flow-rate, 1.7 ml/min ; sample size, 5 mg .

Fig. 19. UAD chromatograms of WOGA samples J, K, L, M, N, and P as received. Columns, $1 \times 10^4 \text{ \AA}$, $1 \times 10^5 \text{ \AA}$, 250 \AA ; solvent, benzene; temperature, $50 \text{ }^\circ\text{C}$, flow-rate, 1.7 ml/min ; sample size, 5 mg .

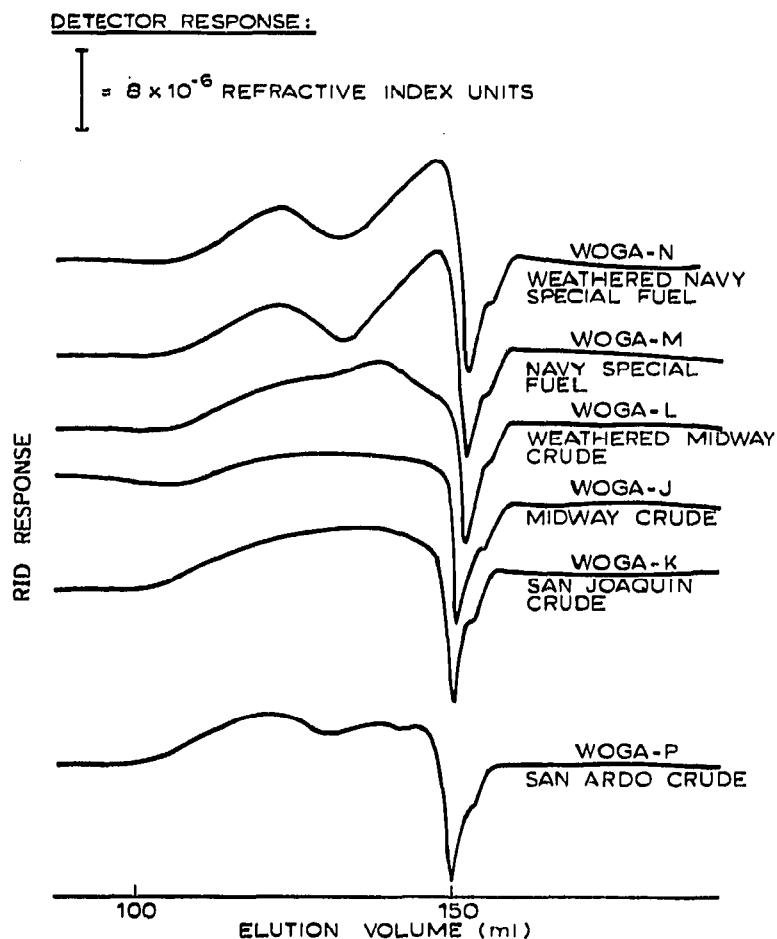


Fig. 20. RID chromatograms of WOGA samples topped at 540 °F. Columns, $1 \times 10^4 \text{ \AA}$, $1 \times 10^3 \text{ \AA}$, 250 Å; solvent, benzene; temperature, 50 °C; flow-rate, 1.7 ml/min; sample size, 5 mg.

molecular weight. If samples are taken at different processing conditions and analyzed by GPC with the RID, FID, and UAD in series, an estimation of this type of information can be obtained in a comparatively short time. In Figs. 21–23 chromatograms of residue samples taken from various reactor conditions in a desulfurization study are shown. The same sample weight and chromatographic conditions were used for all samples so a relative comparison of detector responses could be made. In Fig. 21 are shown the RID chromatograms of a residue and samples taken after 74% and 85% of the sulfur had been removed. The large positive refractive index response of the original residue is primarily due to condensed ring aromatic systems. As the residue was processed, the relative response decreased (indicating a change in aromaticity) and the profile became bimodal and shifted toward the lower molecular weight region. In Fig. 22 the FID chromatograms are shown. The low response of the residue has been found typical of this type of material but the normalized profile is an indication of the weight distribution. Comparison of the profiles of the three samples shows an initial decrease in molecular weight distribution and then no significant further change. This is in agreement with the vapor pressure osmometer molecular weight data which showed the number average molecular weights go from 1080 for the residue

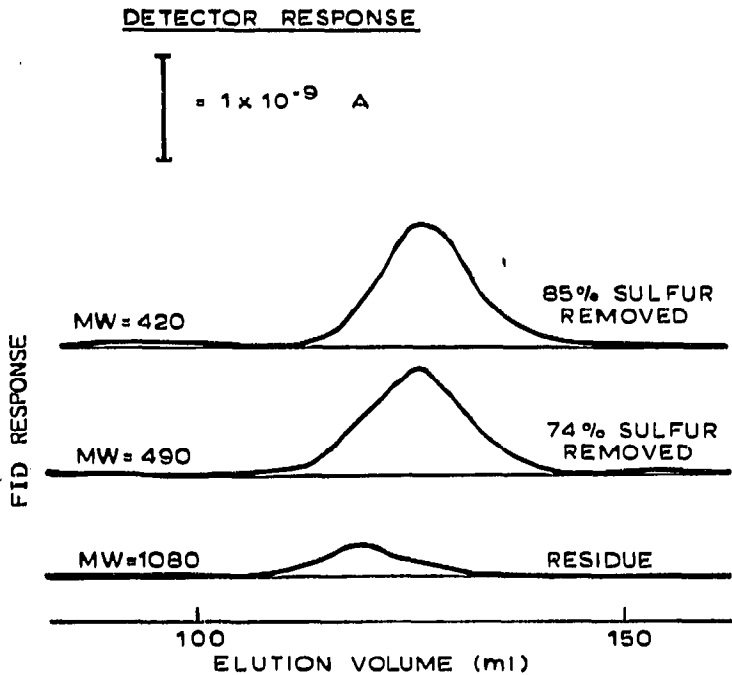


Fig. 21. RID chromatograms of changes occurring during desulfurization of a residue. Columns; $1 \times 10^4 \text{ \AA}$, $1 \times 10^3 \text{ \AA}$, 250 \AA ; solvent, benzene; temperature, $50 \text{ }^\circ\text{C}$; flow-rate, 1.7 ml/min ; sample size, 5 mg .

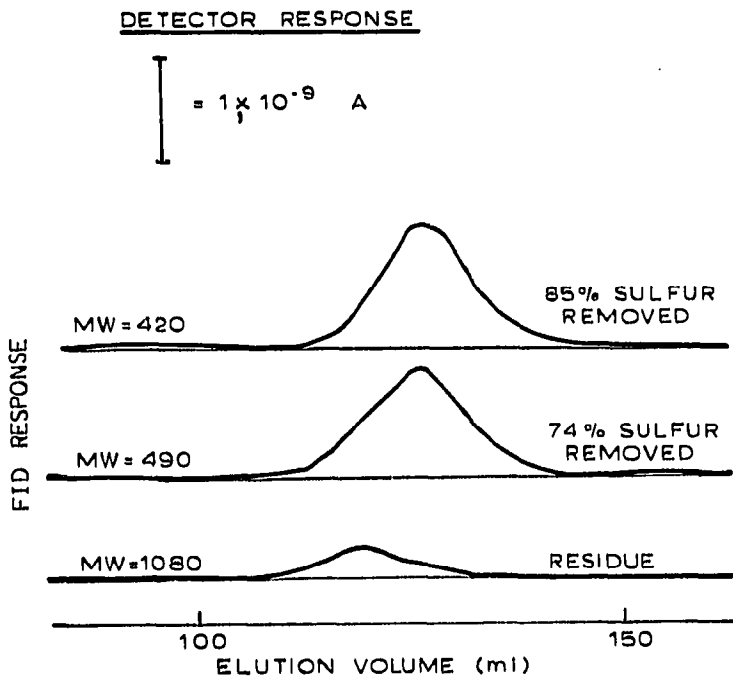


Fig. 22. FID chromatograms of changes occurring during desulfurization of a residue. Columns, $1 \times 10^4 \text{ \AA}$, $1 \times 10^3 \text{ \AA}$, 250 \AA ; solvent, benzene; temperature, $50 \text{ }^\circ\text{C}$; flow-rate, 1.7 ml/min ; sample size, 5 mg .

to 490 for the 75% sulfur removed sample and to 420 for the 85% sulfur removed sample. Examination of the UAD profiles (Fig. 23) shows that compounds absorbing at 313 nm and 365 nm (presumably dinuclear, trinuclear and higher condensed systems) are being converted during processing. Comparison of the areas under the curves shows that during the initial processing conditions (74% desulfurization) there

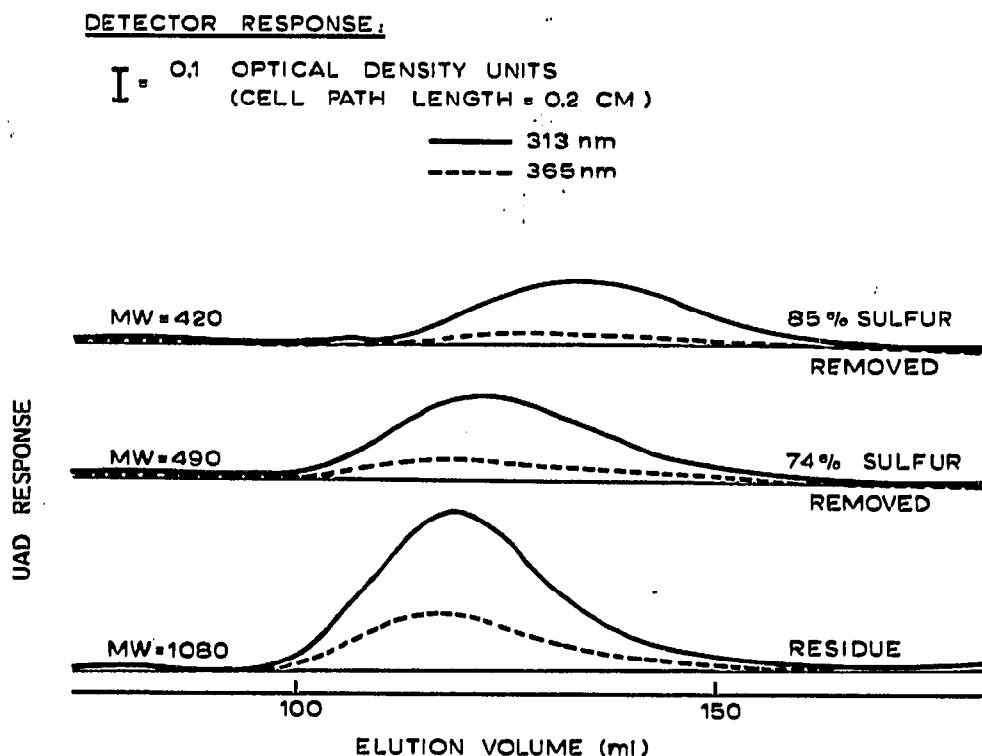


Fig. 23. UAD chromatograms of changes occurring during desulfurization of a residue. Columns $1 \times 10^4 \text{ \AA}$, $1 \times 10^3 \text{ \AA}$, 250 \AA ; solvent, benzene; temperature, 50°C ; flow-rate, 1.7 ml/min; sample size, 5 mg.

was an approximately 65% decrease in area at 365 nm and approximately 50% reduction in area at 313 nm. Also both profiles shifted toward lower molecular weights. With conditions that removed 85% of the sulfur, there was almost a 90% reduction in the 365 nm area and 65% reduction in the 313 nm area. In addition to the increased reduction in areas with the more severe conditions, there was a greater shift of the profiles to lower molecular weights.

While this is a very limited and cursory application of the technique to follow changes occurring during processing, it does illustrate its potential. If there is an interest in the mononuclear aromatics range, a different solvent could be used and the 254 nm absorption area monitored.

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