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E. W. Albaugh[a]; P. C. Talarico[a]; B. E. Davis[a]; R. A. Wirkkala[a]
[a] GULP RESEARCH & DEVELOPMENT COMPANY, PITTSBURGH, PENNSYLVANIA

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Fractionation of Residuals by Gel Permeation Chromatography*

E. W. ALBAUGH, P. C. TALARICO, B. E. DAVIS,
and R. A. WIRKKALA
GULF RESEARCH & DEVELOPMENT COMPANY
PITTSBURGH, PENNSYLVANIA 15230

Summary

Gel permeation chromatography has been effectively used for the fractionation of residuals. The preparative-scale gel permeation chromatograph employed for these studies is described along with selected operating parameters. The instrument has been used to fractionate a shale oil residue, 50% reduced crude, and 25% reduced crude, into fairly narrow molecular weight fractions. The individual cuts from each residual have been analyzed and the elemental distribution established. The trends of heteroatom distribution, i.e., nitrogen, sulfur, nickel, and vanadium, as a function of molecular weight for the various residuals are discussed.

The heavy ends of petroleum are a complex mixture of hydrocarbons that vary widely in molecular weight and composition. A serious problem in characterizing these heavy ends has been the lack of a good and simple method for separating the molecules according to molecular weight. Gel permeation chromatography (GPC) has been shown to produce a molecular weight separation for many materials. The mechanism of the separation appears to be primarily a function of the size of the molecules in solution. However, with certain types of compounds, such as highly condensed aromatics, secondary effects become important and produce anomalous behavior. This work was undertaken to determine if GPC could separate residuals into mo-

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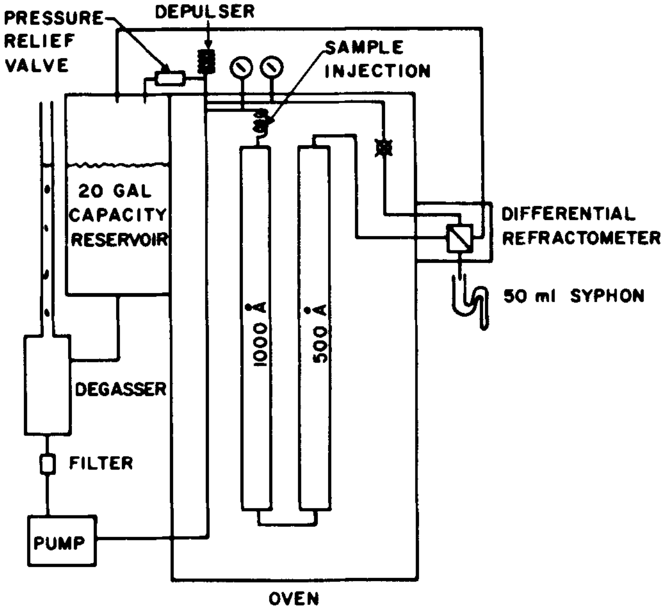

FIG. 1. Preparative scale gel permeation chromatograph.

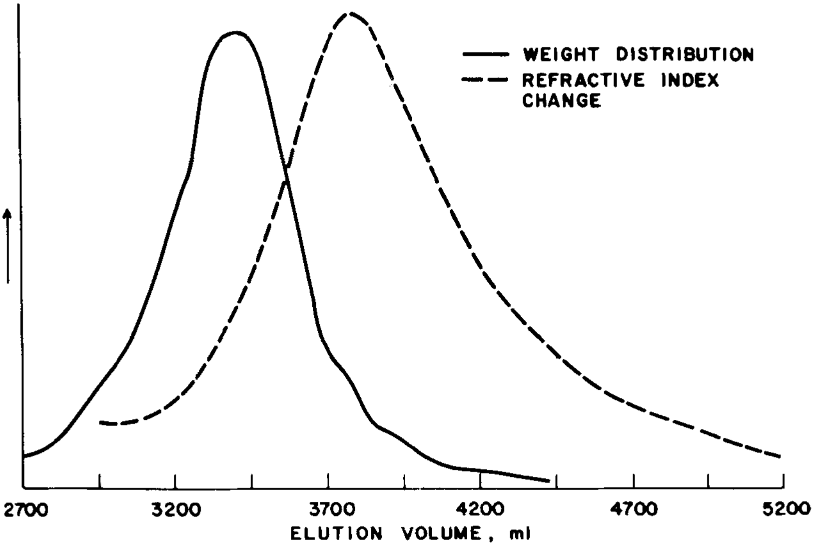

FIG. 2. Chromatogram of 25% reduced Kuwait VTB.

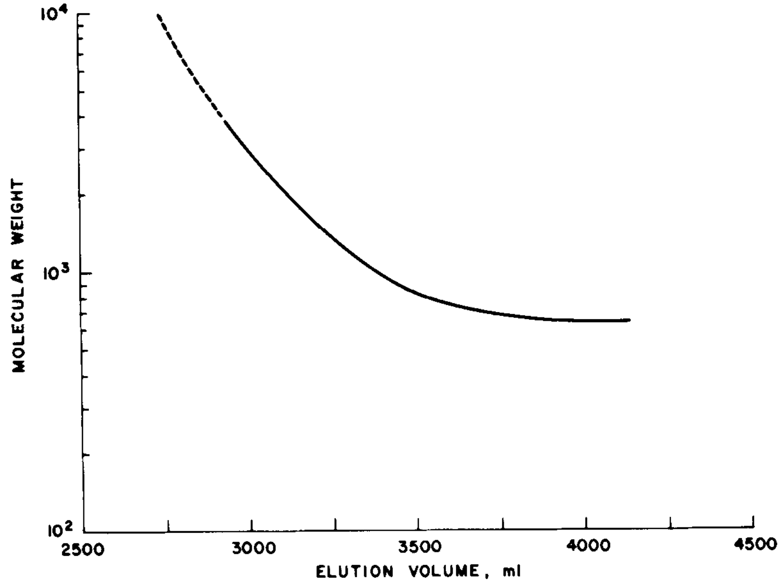

FIG. 3. Calibration curve for 25% reduced Kuwait VTB.

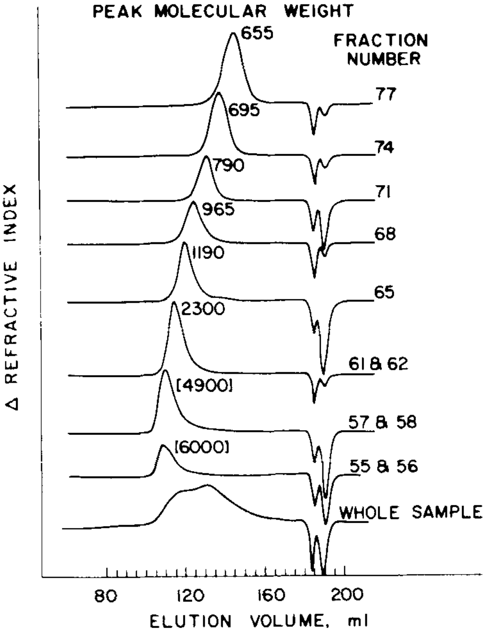

FIG. 4. Preparative scale separation of 25% reduced Kuwait VTB.

lecular weight fractions that could be used to determine the heteroatomic distribution as a function of molecular weight.

Preliminary separations were applied to a 25% reduced Kuwait vacuum tower bottom (VTB) on an analytical scale using a unit of our design with four Waters Associates Styragel columns. A satisfactory molecular weight separation was achieved with approximately 99% recovery.

In order to obtain sufficient material for characterization, a preparative-scale gel permeation chromatograph was built. A schematic diagram of the instrument is shown in Fig. 1. Benzene was used as solvent and was stored in a 20-gal reservoir. The degasser consisted of a 2-liter stainless steel cylinder wound with resistance heating wire and fitted with a glass standpipe. A 10-μ porous metal filter was placed between the degasser and pump. A piston-type pump with a capacity of 80 ml/min was used. For reducing the pump surges, a stainless steel bellows was placed in the line ahead of the columns. A pressure relief valve was also incorporated ahead of the columns. The sample valve was air-actuated and contained a 50-cc sample loop. The columns, 4 ft × 2-½ in., were purchased from Waters Associates and contain Styragel with the designation of 1000 and 500 Å. Both the sample valve and columns were housed in an oven maintained at 40°C. A Waters R-4 differential refractometer was used for detection. The volume of eluant was measured with a 50-cc siphon. When the siphon empties, the effluent flows over a thermistor that is part of a relay circuit. The heating of the thermistor by the eluant actuates the relay, placing a mark on the recorder chart and activating the fraction collector.

The chromatogram of a 1-g charge is shown in Fig. 2. The dashed curve represents the change in refractive index during elution and the solid line the weight distribution. The refractive index curve is displaced toward lower molecular weights. The molecular weight calibration curve is shown in Fig. 3. The molecular weights were determined by vapor pressure osmometry on selected fractions. The slope of the curve shows a molecular weight separation up to an elution volume of approximately 3750 ml. Over 90% of the sample falls in the size separation range.

To determine the effectiveness of the separation, selected fractions were analyzed using five analytical columns (10^5, 10^3, 250, 100, and 60 Å). The results are shown in Fig. 4. The bottom curve is the whole sample, and the curves above represent selected fractions from the

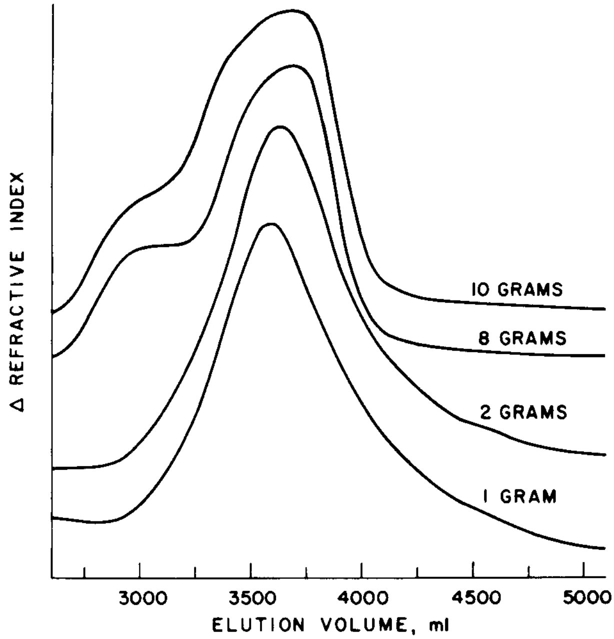

FIG. 5. Effect of sample size on separation.

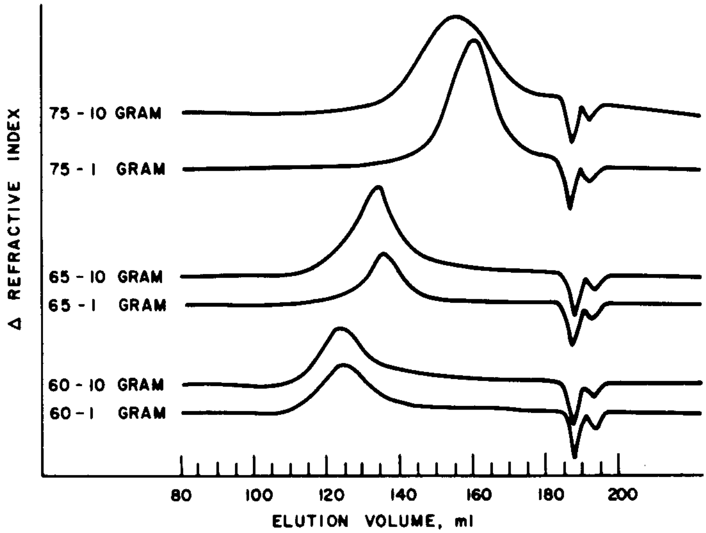

FIG. 6. Comparison of fractions from 1 and 10 g charges.

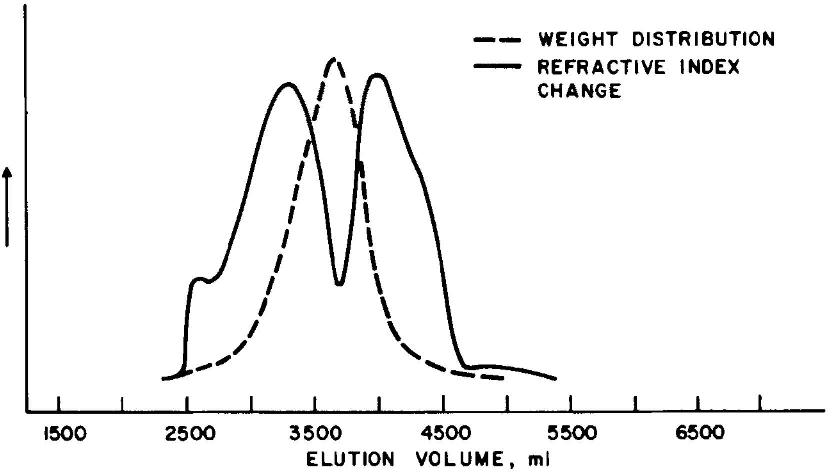

FIG. 7. Chromatogram of 50% Kuwait VTB.

preparative-scale separation. The molecular weight at the peak was obtained from the calibration curve. The numbers in brackets are extrapolated values. For the purposes of our study, these fractions were sufficiently narrow. If more narrow fractions are desired, the

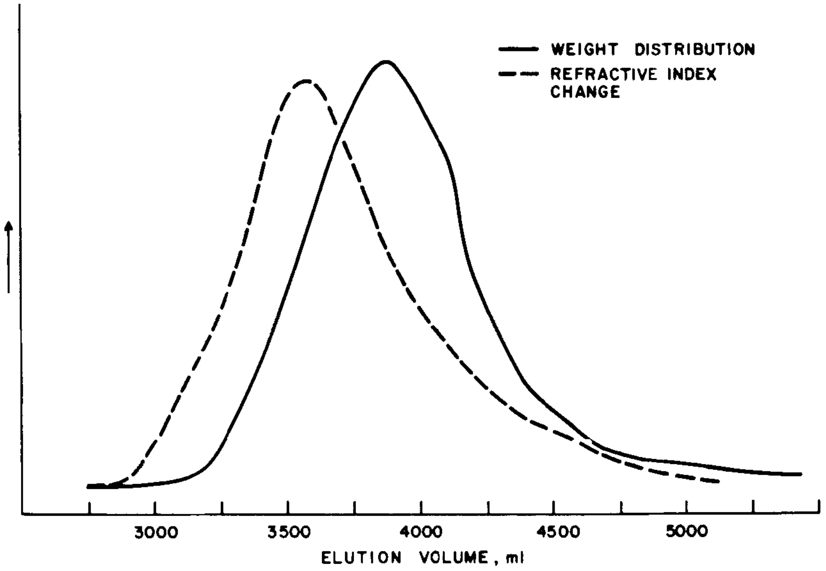

FIG. 8. Chromatogram of shale oil residue.

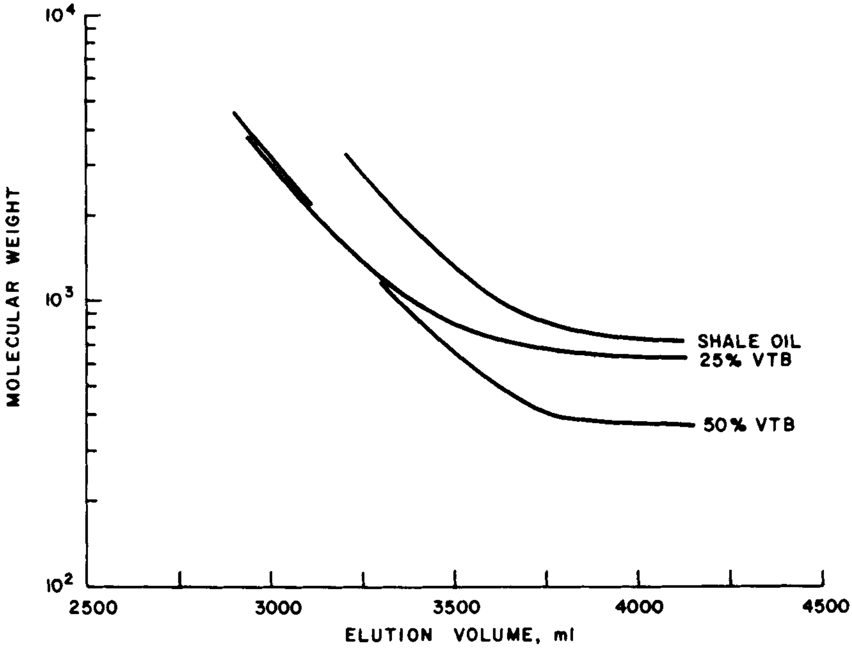

FIG. 9. Calibration curves for three residuals.

individual fractions can be rechromatographed and only the center cuts retained.

To determine the optimum size sample, a series of runs was made in which the sample size was varied from 1 to 10 g. In Fig. 5 are shown the curves from these runs. They are displaced vertically for clarity. The 1- and 2-g samples have nearly identical contours, while the 8- and 10-g samples show some distortion, possibly due to overloading. Several of the fractions from the 1- and 10-g runs were analyzed using the 5-analytical column set. The chromatograms of these fractions are shown in Fig. 6. In all cases, the 10-g fractions are nearly as narrow as the 1-g. The effects of overloading should be most noticeable in Cut 60. However, no appreciable difference is seen.

Two other residues were also fractionated: a 50% Kuwait VTB and a shale oil residue. The chromatogram of the 50% reduced material is shown in Fig. 7. The solid curve is the change in refractive index during elution, while the dashed curve represents the actual weight distribution. This is a very good example of how a refractive index curve can be misleading for complex materials. In Fig. 8 is shown

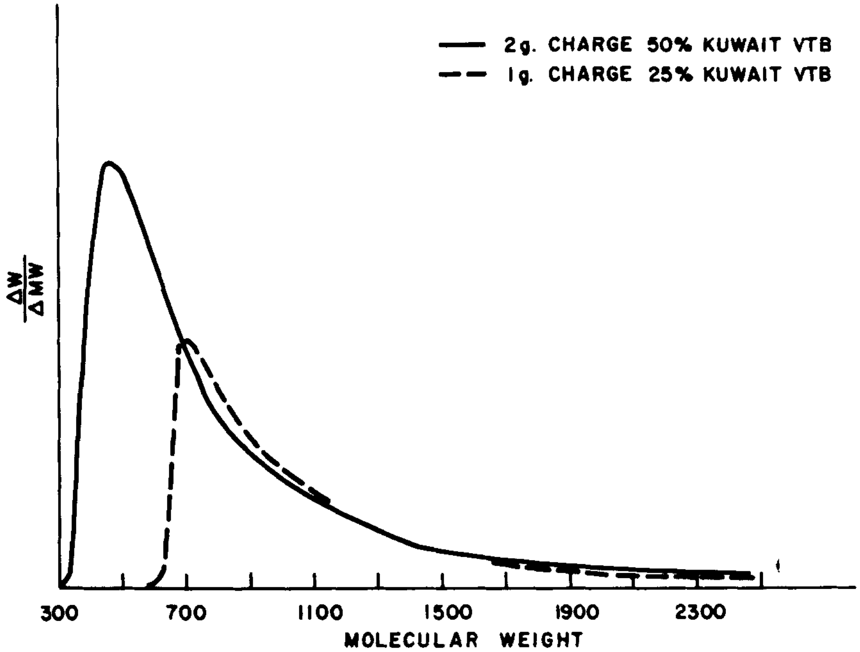

FIG. 10. Differential weight distribution.

the chromatogram for the shale oil. Here, the contours of the curves are similar, but the refractive index curve is displaced toward higher molecular weights, the converse of the 25% reduced material shown earlier. The differences between the weight and refractive index curves for the three materials are due to the variation in compositions. Figure 9 shows the comparison of the calibration curves for the three residues. The slopes of the curves show that a nearly-equivalent separation has been achieved for all three materials. The differential weight distribution of the 25 and 50% Kuwait VTB is shown in Fig. 10. These curves clearly show the weight change during distillation and demonstrate the usefulness of GPC in monitoring the distillation of petroleum.

The fractions from the 25 and 50% reduced Kuwait VTB were analyzed for nitrogen, sulfur, vanadium, and nickel. The differential weight distribution for the 50% reduced Kuwait VTB is shown in Fig. 11. The curves show that the heteroatom distribution is not uniform and the heaviest concentration is in the 350–450 molecular weight

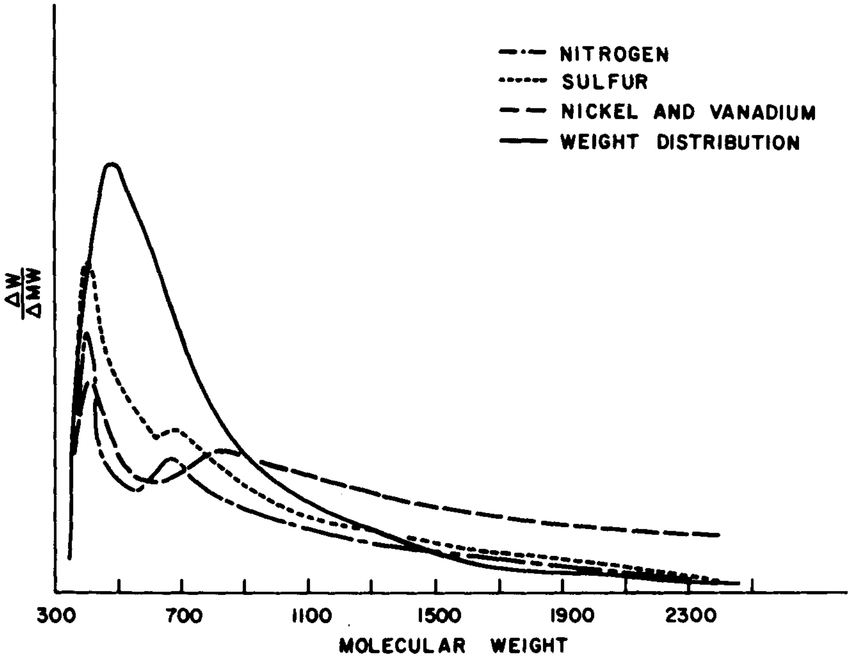

FIG. 11. Heteroatom distribution for 50% Kuwait VTB.

range. While the sample differential weight distribution decreases uniformly with increasing molecular weight, the heteroatom differential weight curve shows a second maximum at 600–700 molecular weight for nitrogen and sulfur and 750–850 for nickel and vanadium.

The heteroatom differential weight distribution curves for the 25% reduced Kuwait VTB are shown in Fig. 12. The sulfur differential distribution shows a maximum in the 700–800 molecular weight range and decreases uniformly with increasing molecular weight. This is the same distribution shown by the VTB differential weight curve, indicating the sulfur is fairly uniformly distributed throughout the sample. The nitrogen shows a similar maximum in the 700–800 molecular weight range and, in addition, a second maximum in the 1000–1100 molecular weight range. The nickel and vanadium distribution curves likewise have a maximum in the 700–800 molecular weight range with a second maximum centered around 1800 molecular weight.

Elemental analyses were obtained on the shale oil. The oxygen contents of the individual fractions were all higher than the original

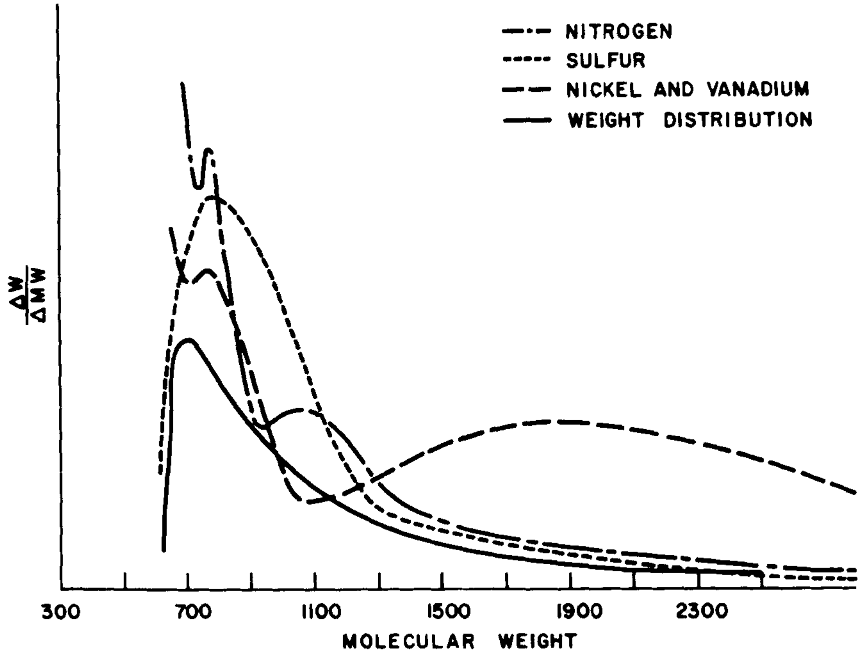

FIG. 12. Heteroatom distribution for 25% Kuwait VTB.

sample. This suggests oxidation during solvent removal, although precautions were taken to minimize this. The elemental data do indicate, however, that the heteroatom distribution is uniform throughout the entire molecular weight range.

In conclusion, we have found that large-scale separations of residuals into narrow molecular weight fractions can be accomplished by gel permeation chromatography. As a result of these separations, the study of heteroatom distribution as a function of molecular weight can be more easily accomplished.

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