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16. Abstract

The principal objectives of this study were to use supercritical fractionation of asphalt and a study of fraction properties to gain a deeper understanding of what determines asphalt properties and how the asphalt composition can be manipulated to improve properties. This report describes the first attempts to fractionate asphalt, characterize the fractions and recombine them to produce superior asphalts. A large part of the project involved design and construction of a supercritical extraction unit capable of producing kilogram quantities.

Three asphalts were fractionated into eight fractions each. The fractions were characterized by a variety of methods. Surprisingly, nickel and vanadium were distributed essentially uniformly throughout all sizes of asphaltenes. The log of the viscosity of the asphaltene-free fractions varied nearly linearly with the fraction "heaviness"; the presence of asphaltenes caused a large jump in viscosity.

A total of thirteen asphalt blends of AC-10 or AC-20 grade were produced by removing various amounts of the heaviest and lightest materials. Nearly all blends had improved aging indexes and most had equal or better temperature susceptibility. Several showed a 25% improvement in toughness.

The results from the first fractionation and reblending work demonstrate significant improvement and excellent potential for further major improvements in asphalt quality. The fractionation methods used in the present work to produce superior asphalts can be readily implemented in refineries.

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DESIGN AND MANUFACTURE OF SUPERIOR ASPHALT BINDERS

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METRIC (SI*) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

LENGTH

Symbol	When You Know	Multiply By	To Find	Symbol
in	inches	2.54	centimetres	cm
ft	feet	0.3048	metres	m
yd	yards	0.914	metres	m
mi	miles	1.61	kilometres	km

AREA

Symbol	When You Know	Multiply By	To Find	Symbol
in²	square inches	645.2	centimetres squared	cm ²
ft²	square feet	0.0929	metres squared	m²
yd²	square yards	0.836	metres squared	m²
mi²	square miles	2.59	kilometres squared	km²
ac	acres	0.395	hectares	ha

MASS (weight)

Symbol	When You Know	Multiply By	To Find	Symbol
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams	Mg

VOLUME

Symbol	When You Know	Multiply By	To Find	Symbol
fl oz	fluid ounces	29.57	millilitres	mL
gal	gallons	3.785	litres	L
ft³	cubic feet	0.0328	metres cubed	m³
yd³	cubic yards	0.0765	metres cubed	m³

NOTE: Volumes greater than 1000 L shall be shown in m³.

TEMPERATURE (exact)

Symbol	When You Know	Multiply By	To Find	Symbol
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

APPROXIMATE CONVERSIONS TO SI UNITS

LENGTH

Symbol	When You Know	Multiply By	To Find	Symbol
mm	millimetres	0.039	inches	in
m	metres	3.28	feet	ft
m	metres	1.09	yards	yd
km	kilometres	0.621	miles	mi

AREA

Symbol	When You Know	Multiply By	To Find	Symbol
mm²	millimetres squared	0.0016	square inches	in²
m²	metres squared	10.764	square feet	ft²
km²	kilometres squared	0.39	square miles	mi²
ha	hectores (10 000 m²)	2.53	acres	ac

MASS (weight)

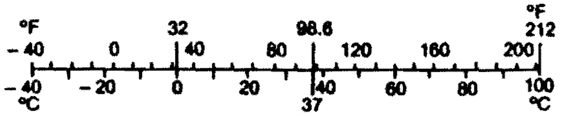
Symbol	When You Know	Multiply By	To Find	Symbol
g	grams	0.0353	ounces	oz
kg	kilograms	2.205	pounds	lb
Mg	megagrams (1 000 kg)	1.103	short tons	T

VOLUME

Symbol	When You Know	Multiply By	To Find	Symbol
mL	millilitres	0.034	fluid ounces	fl oz
L	litres	0.264	gallons	gal
m³	metres cubed	35.315	cubic feet	ft³
m³	metres cubed	1.308	cubic yards	yd³

TEMPERATURE (exact)

Symbol	When You Know	Multiply By	To Find	Symbol
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



These factors conform to the requirement of FHWA Order 5190.1A.

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* SI is the symbol for the International System of Measurements

SUMMARY

The principal objectives of this study were to use supercritical fractionation of asphalt and a study of fraction properties to gain a deeper understanding of what determines asphalt properties and how the asphalt composition can be manipulated to improve properties. This report describes the first attempts to fractionate asphalt, characterize the fractions and recombine them to obtain asphalts possessing improved properties.

A large part of the project involved design and construction of a supercritical extraction unit. It is capable of producing four fractions per run in quantities of several kilograms of total feed per day. Because of tightened safety requirements during construction, considerable time was spent modifying the unit to meet these more stringent specifications, but once operations began, good progress was made.

Three asphalts were fractionated into eight fractions each. First the asphalts were split into a light and heavy fraction. The light portion was then separated into four fractions in the supercritical unit and the bottom material, being too hard to melt, was fractionated using solvents at room temperature. The fractions were characterized by Gel Permeation Chromatography (GPC), Infrared spectrophotometry (IR), metal analysis, Corbett fractionation, and viscosity where possible. GPC analyses were then made of the Corbett fractions.

There were a number of interesting findings. First, nickel and vanadium were distributed essentially identically, and uniformly, throughout the asphaltene material. Second, the log of the viscosity of the asphaltene-free fractions varied nearly linearly with the "fraction mean," a number representing the size and location within the whole asphalt (i.e., "heaviness") of the fraction relative to the other fractions; the presence of asphaltenes caused a large jump in viscosity away from this linear trend. Third, supercritical fractionation tended to separate asphalt components with respect to both molecular size and polarity while Corbett fractionation separates primarily on the basis of polarity. The Corbett fractionation showed that processing the materials caused an increase in asphaltenes and a decrease in polar aromatics.

A total of thirteen asphalt blends were produced which in general met all specifications for either AC-10 or AC-20 asphalts. Three of these were attempts to reproduce the original asphalt. The other ten were obtained by removing various amounts of the heaviest and lightest materials. This would be expected to increase compatibility by reducing the saturate and asphaltene content. Several of the blends suffered from incomplete solvent removal, but of the remainder, nearly all had improved aging indexes and most had equal or better temperature susceptibility. Several showed marked improvement. One blend and the original asphalt were formed into cores and tested with the Marshall apparatus. The blend showed a 25% improvement in toughness. Both this blend and whole asphalt had very similar viscosity and penetration.

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IMPLEMENTATION

The results from the first attempts to fractionate and reblend asphalts have demonstrated significant improvement in asphalt binder quality and show excellent potential for further major improvements. This work is being continued under Study 1249 and is not ready for implementation at this time. The fractionation methods used in the present work are of the type such that they will be readily implementable in refineries.

DISCLAIMER

The contents of this report reflect the views of the authors who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Federal Highway Administration or the Texas Department of Transportation. This report does not constitute a standard, specification, or regulation.

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CHAPTER 1

LITERATURE SURVEY

Asphalt Fractionation

It has long been known that asphalt can be separated into a number of fractions having quite disparate properties. Over the years many schemes employing solvent precipitation and extraction, chemical reactions and solvent chromatography have been developed. Each gives a somewhat different separation, but many do give quite similar results. Perhaps the two most used are that of Corbett and Swarbrick (1960) and Corbett (1969) ASTM D4124 and that of Rostler and Sternberg (1949) ASTM D2006. The former precipitates asphaltenes with n-heptane and separates three other fractions on an alumina column using several solvents. The latter uses sulfuric acid of various strengths following pentane precipitation of asphaltenes to yield four additional fractions. Rostler (1979) claims his test based on reactivity is more fundamental, but this is highly debatable. Chemical similarity can still be accompanied by differences in structure and physical properties as surely as chromatographic similarity does not guarantee similar chemical reactivity.

Actually, Pavlovich, et al. (1986) have shown that there is a good degree of correlation between the Rostler analysis and a clay gel absorption procedure, and Dunkel, et al., (1954) have shown the similarity between the Rostler analysis and a silica gel separation procedure. Rostler's pentane precipitate includes all of Corbett's heptane asphaltenes plus some of his polar aromatics which also may include some of Rostler's first acidaffins. Most of the first acidaffin fraction and all of the second acidaffin fraction of Rostler's will be included in Corbett's naphthene aromatics. The paraffins of Rostler are essentially the same as Corbett's saturates.

Methods of Separation

In addition to the ASTM standard procedures discussed above, a variety of techniques have been used to fractionate asphalt.

Solvent Separation. The first attempt to fractionate asphalt by its solubility in different solvents was made by Richardson (1914). In this method, asphalt is first separated from inorganic material by its solubility in carbon disulfide. This fraction he defined as native bitumens. Next, the native bitumens are further divided into low boiling petrolenes and residual asphalt. Finally, the residual asphalt is separated into asphaltenes and maltenes by its solubility in 88° Baumé naphtha.

Hoiberg and Garris (1944) devised a scheme to give five fractions instead of three using four different solvents and solvent mixes. Their procedure is as follows: 1) asphaltenes are precipitated with hexane; 2) hard resins are precipitated with 80:20 (vol/vol) isobutyl alcohol:cyclohexane; 3) waxes with 1:2 (vol/vol) acetone:methylene chloride; 4) soft resins with isobutyl alcohol; and 5) oils as the remaining soluble fraction. Hoiberg and Garris conclude that asphalt composition could be selectively controlled by blending "stocks relatively rich in needed fractions."

A similar method is that of Knowles, et al. (1958). This method consists of: 1) separation of asphaltenes with n-pentane; 2) separation of resins with propane with further precipitation into hard and soft resins using aniline; 3) waxes precipitated with methylisobutyl ketone; and 4) oils as the remaining fraction which is further separated into paraffinic and naphthenic oils with acetone.

At present the best means of fractionating asphaltenes into <u>recoverable</u> fractions seems to be with the use of various organic solvents. Mitchell and Speight (1973) tabulate the performance of different solvents. In general, they have shown that cycloparaffins will precipitate 1% to 2% (by weight) of the n-heptane asphaltenes (ASTM D 4124, Corbett procedure). Paraffins, however, precipitate between approximately 8% to 17% of the total. Varying proportions of benzene in n-pentane can selectively precipitate between 0.9% and 14.9% of the n-heptane asphaltenes.

Chromatographic Separations. Numerous investigators employ chromatography in their analytical research of asphalt fractions. The common bond between all of their methods is the use of an adsorbent material in conjunction with various solvents. The Corbett procedure mentioned above is the most-used chromatographic method. The clear advantage in using chromatography as a separation technique is that it separates quite cleanly on the basis of chemical functionality. In general, the more saturated hydrocarbons will have less tendency to adsorb.

A procedure similar to the Corbett method is that of Kleinschmidt (1955). Kleinschmidt defines asphaltenes as the n-pentane insoluble fraction of asphalt with the remaining maltene divided into asphaltic resins, dark oils, and white water oils. A fifth fraction of residue, which is present in small amounts, he defines as "black solids slightly harder than asphaltic resins." This is generally lumped in with the asphaltic resins.

One of the more complex methods is that of O'Donnell (1951). Asphalt is separated into asphaltenes and maltenes using isopentane solvent precipitation. Next, molecular distillation is employed as a means of separating the asphaltenes and maltenes into ten fractions of varying molecular size. The next step then utilizes chromatography to separate these fractions into saturates, aromatics, and resins. The saturates undergo solvent dewaxing to yield waxes and oils. The waxes are then mixed with urea to separate wax from long chain paraffins. Alumina chromatography is used with the remaining aromatic fractions to further divide these into monocyclic and dicyclic aromatics.

Other well-known methods which employ chromatography exist in addition to those listed above. These include: Watson, (1952); Eby, (1953); Dunkel, et. al (1954); Glasgow-Termini, (1953); and Hubbard and Stanfield, (1948).

Properties of Asphalt Fractions

There have been many attempts to correlate physical properties and performance in terms of these fractions such as those by Rostler and White (1959, 1962), Skog et al. (1966), Halstead et al. (1966), Gotolski, et al. (1968), Lamb and Couper (1968), Peters (1975), Anderson and Dukatz (1980), and Rostler and Rostler (1981). Many of these involved groupings of fractions such as the Rostler parameter, calculated as the sum of the nitrogen bases plus the first acidaffins divided by the sum of the second acidaffins and the paraffins, in which all of these were fractions defined by the Rostler and Sternberg separation procedure. None of these studies, however, was successful at achieving particularly outstanding correlation between physical and chemical properties.

The problem is not that the approach is wrong so much as it is simplistic. In the first place, the asphaltenes have a very important effect on performance and show the most variation in properties from asphalt to asphalt, but this factor is ignored by the Rostler parameter. Secondly, the Rostler parameter does not distinguish between the second acidaffins and the paraffins though they are quite different in their effect. The same complaint could be made against the groupings found in other parameters. Finally, as we shall see later, any of the fractions from one asphalt can have different properties from the same fraction from another asphalt.

Anderson, et al. (1976) attempted to correlate road performance in a Utah test with some Rostler fractions as well as with physical properties and load. The test involved twenty test sections over a period of seven years. They found that accumulated 18 KIP loads, pavement age, percent asphalt, percent voids, temperature susceptibility and ductility all correlated with various aging problems. Significantly, they found a good correlation between high paraffins and high temperature susceptibility and low ductility.

It has been assumed by many that the paraffins are necessary to have a good asphalt. The paraffins are called plasticizers, or are said to be necessary for a gelling effect (Rostler and White, 1959), or are beneficial in small amounts (Gotolski, et al., 1968, Rostler, 1979), and are said to contribute to durability (Rostler and Rostler, 1981). On the other hand, Corbett (1979), says that the saturates, or paraffins make no contribution to good test quality.

It is true that paraffins are the least reactive asphalt component, but there is no evidence that they improve properties and considerable evidence that they harm properties. It is well known that paraffins plus asphaltenes contribute to incompatibility (White, et al., 1970, Altgelt and Harle, 1975, Skog, et al., 1966). It may be that small amounts of paraffins are not harmful, but the main benefit would seem to be viscosity control.

Asphalt properties are extremely dependent on both the amount and characteristics of the asphaltene fraction. It has been shown by many that this is the most variable fraction and that the molecular weight varies over the greatest range. Indeed there is quite a lot of disagreement over what constitutes the molecular weight, Glover, et al. (1987). Part of the variability is that unlike other fractions, asphaltenes are separated purely by solubility in n-alkanes with differing n-alkanes used. The asphaltenes obtained by n-pentane precipitation contain much material that would probably be in the polar aromatics fraction of the Corbett separation scheme.

The asphaltenes contribute much more to viscosity than do other fractions and they may also improve temperature susceptibility. Altgelt and Harle (1975) have shown a decided effect of asphaltene molecular weight on viscosity. They separated asphaltenes into a range of apparent molecular weights and studied the effect of molecular weight, concentration, and solvency on viscosity. The effect of concentration was approximately linear at lower asphaltene molecular weights, but at higher molecular weights the viscosity increased dramatically with concentration. This was much more apparent in poor solvents and was found to vary quite significantly when different maltenes were used with a given asphaltene.

A large number of studies have shown that the principal change that occurs as an asphalt ages is an increase in the asphaltene content. This also is the principal change in the hot-mix step and in air blowing of asphalt. Corbett and Swarbrick (1960) showed that essentially all of this increase came from their heavy multi-ring aromatic fraction, which is essentially what they later called polar aromatics. Corbett and Merz (1975), examining the Michigan test roads after 18 years, found that the main factor was a change in naphthene aromatics to polar aromatics and a change of polar aromatics to asphaltenes. This was accompanied by an increase in viscosity and a decrease in ductility. Rostler and White (1962) showed that their nitrogen bases, which are largely equivalent to polar aromatics, and their first acidaffin fraction, which is the most reactive part of the naphthene aromatics, were most reactive with the nitrogen bases going to asphaltenes and the first acidaffins to nitrogen bases. Very interestingly, the first acidaffins that converted to nitrogen bases did not, in turn, convert to asphaltenes. GPC data from Glover et al. (1987) show that while the quantity of the Corbett fractions changed on road aging, their molecular size distribution changed little.

Having discussed the effects of paraffins and asphaltenes on asphalt quality, let us consider briefly the contribution of the other fractions of Corbett and Rostler. Rostler (1979) says that only the nitrogen base fraction is a solvent for the asphaltenes. Certainly the asphaltenes are most soluble in this fraction, but the formulation by Corbett (1979) of an asphalt composed only of asphaltenes and naphthene aromatics indicates that Rostler's statement has exceptions. There are orders of magnitude difference in the viscosity of individual fractions with paraffins having much the lowest viscosity and the lowest temperature susceptibility (Corbett and Schweyer, 1981), but as noted earlier, paraffins can increase the viscosity contribution of asphaltenes and actually increase temperature susceptibility. The viscosity of each fraction increases with molecular weight. The paraffins from different asphalts roughly follow the same viscosity molecular weight function, but the other fractions can differ in viscosity by orders of magnitude at the same molecular weight (Griffin, et al., 1959). The polar aromatics seem to contribute most to ductility but may have a bad effect on temperature susceptibility (Corbett, 1970). Peters (1975) says the Rostler second acidaffin factor contributes most to durability.

Studies of Recombined Fractions. The idea of studying asphalts by not only separating asphalts into fractions, but also recombining these fractions has long interested researchers. Hoiberg and Garris (1944) separated asphalts into fractions and aged the individual fractions with essentially the same results as obtained by others, a large increase in asphaltenes and a decrease in the resin fraction. They also analyzed the fractions removed by degrees of distillation and by propane extraction. They reported an increased loss of resins as lower pen numbers are reached. They suggested, "The propane precipitate contains large contents of resins, and could therefore be added to residue to raise their penetration-temperature susceptibility and increase ductility; while the extracted aromatic oils of high viscosity could be substituted for paraffin oils removable by distillation or solvent treatment--."

Rostler and White (1962) reported a rather extensive study of recombining fractions separated by the Rostler procedure, and they reported that based on the Rostler parameter, they could produce a variety of recombinations that behave as predicted on their abrasion test. White, et al. (1970) combined fractions from four asphalts based on the Rostler analysis. They found, as have others, that asphaltenes of higher molecular weight resulted in higher asphalt viscosity. Substitution of a higher molecular weight fraction obtained from a normally lower molecular weight asphaltene into an asphalt normally having a high molecular weight asphaltene produced an asphalt of similar viscosity at 275°F. This trend was not confirmed at lower temperatures, and between 140 and 275°F, the lower molecular weight asphaltenes produced higher temperature susceptibility and the asphaltenes had more effect on the temperature susceptibility than did the maltenes, except for maltenes of very high viscosity. From 77 to 140°F the lower molecular weight asphaltenes still produced the highest temperature susceptibility, but the effect of the maltenes dominate. On the abrasion test, asphaltenes could be interchanged as long as the amount was adjusted to keep the viscosity the same. They concluded that maltene fractions can be interchanged as far as the abrasion test is concerned if the asphaltenes are adjusted to maintain the same viscosity.

Rostler and Rostler (1981) discuss a synthetic asphalt blend in which the asphaltenes were replaced with a polymer. They also made the following suggestion: "The chemical steps that are used in addition to selective refining and blending are hydrogenation to reduce unsaturation and mild oxidation such as air blowing to pre-age the asphalt and by this means reduce the amount of highly reactive components."

Peters (1975) did some work with blends and aging with Rostler fractions and concluded the following: "Asphalts can be blended together to achieve practically any desirable viscosity or aging index or combination of both; the second acidaffin fraction of an asphalt is the most important fraction in the improvement of durability--."

Corbett (1970, 1979) has done some fascinating work on the contribution of fractions to asphalt quality and the properties of synthetic asphalts made from two fractions only. Four two-component 90 pen asphalts were made and compared with a typical 90 pen product. A saturates/polar aromatics blend showed poor temperature susceptibility and poor low temperature ductility. A saturates/asphaltenes blend displayed a good temperature susceptibility in spite of inhomogeneity and almost no ductility. The naphthene aromatics/polar aromatics blend provided overall good properties and very high low-temperature ductility. The naphthene aromatics plus asphaltenes also had overall good properties. He concludes the following: "Naphthene aromatics contribute much to good temperature susceptibility. Polar aromatics contribute the most to ductility. Asphaltenes give the highest values of viscosity. The saturates which are always present in all asphalts make no contribution to good test quality."

Corbett noted that some asphalts tend to be of higher molecular weights and thus are low in asphaltenes and have poor temperature susceptibility. By combining a pentane precipitate with vacuum gas oil, a superior asphalt is produced that is low in polar aromatics and essentially free of paraffins. This kind of improvement could also be achieved, in some cases, by recombining fractions recovered by the ROSE process (Gearheart and Garwin, 1976, Garrick and Wood, 1986, Newcomer and Soltau, 1982).

In the ROSE process pentane at different temperatures near the critical region is used to separate asphalts into three fractions, asphaltenes, resins, and oils. Newcomer and Soltau (1982) stated, "The resins and asphaltene pitches are blended into finished asphalt cements and cut-back asphalts. Adjusting the percentages of each in a blend yields a wide variety of premium asphalts from any type of crude oil."

Compatibility of Asphalt Fractions. The compatibility of an asphalt refers to the mutual solubility of its components. Because the paraffin and asphaltene components are immiscible, the increase of either of these tends toward immiscibility. The composition of the other fractions is also very important, and it is known that the polar aromatic fraction, or nitrogen base fraction, adds greatly to the ability of the whole maltene fraction to dissolve asphaltenes. Altgelt and Harle (1975) showed that the increase in viscosity with increasing asphaltenes was highly sensitive to the compatibility of the fractions.

A number of tests have been devised to test this mutual compatibility of the asphalt components, the oldest are the spot tests such as that of Oliensis (1957). The flocculation procedure of Heithaus (1960) and Van Kerkvoort, et al. (1952) has been frequently used to measure compatibility. In this procedure, various ratios of a good and a poor solvent that cause precipitation are determined. The settling rate of precipitated asphaltenes has also been found to correlate with compatibility (Plancher, et al., 1979).

Mertens (1960) showed a good correlation between endurance of roofing asphalts in the weather-ometer test and the dispersibility of the asphaltenes as defined by the Heithaus test. He also showed that this related to the solubility parameter of Hildebrand and Scott (1949) of the solvent from which the asphaltenes would just precipitate. The lower this value (poorer solvent for asphalts) the higher the durability. Hagen, et al. (1984) determined solubility parameter profiles for asphalts. The data were presented as solubility profiles on a two-dimensional solubility parameter plot. A tighter contour profile was identified with greater compatibility and superior performance.

Plancher, et al. (1979) reported several studies in which there seems to be a correlation between asphaltene settling time and performance, with each showing poorer performance with a shorter settling time.

Skog, et al. (1966) tried a number of correlations using the Heithaus factors with laboratory-aged asphalts. Some correlation was found between solubility of the asphaltenes and viscosity of the aged asphalt and some correlation between the "state of peptization" and the shear susceptibility. Newcomb, et al. (1984) indicated that asphalt modifiers that gave the best Heithaus compatibility also gave the best aging index. Glover, et al. (1987) showed a strong correlation between the flocculation ratio and asphalt tenderness, but they also showed a strong correlation with asphaltene content and large molecular size. They also found a fair correlation between the asphaltene content and the flocculation ratio.

Industrial Fractionation and Processing Techniques

Petroleum refineries have a large number of refining unit operations which they can use to extract desired products from crude oil. The goal, of course, in the refinery is to maximize profit. Therefore, the real test of an asphalt fractionation technique is economics. The following list, taken from Hydrocarbon Processing, 1984, 1986 and 1988 Refining Process Handbooks, summarizes some of the schemes being used today to separate asphalt from crude and being used to produce by-products from asphalts.

Solvent Deasphalting. Solvent deasphalting is used primarily as a means of producing deasphalted oil (DAO) which is low in asphaltenes and metals. This reduces catalyst poisoning and coking as compared to treating the vacuum resid alone. However, nitrogen and sulfur levels remain relatively constant (Ditman, 1973). Vacuum resid is sent to an extractor where it is mixed with solvent at a pressure of 600 psig and a temperature of 300-360°F. Propane or pentane are used as solvents. Pentane has been found to be more advantageous in that it produces two to three times more DAO and will in fact reduce nitrogen levels (Billon et al., 1977). Asphalt is sent off for further processing whereas the DAO is used as feedstock for catalytic cracking and hydrotreating. The process described above is licensed by Institut Francais du Petrole. Similar processes using hydrocarbon solvents from C_2 to C_7 are described in the Hydrocarbon Processing Handbooks.

Low-Energy Deasphalting. This process is similar to solvent deasphalting. However, energy consumption is reduced by using lower solvent-to-feed ratios along with multiple effect evaporators. The operating conditions can be adjusted to select a range of selectivities and solubilities. This allows for a wider range of products including lube oil refining, catalytic cracking and hydrocarbon feedstocks, and asphalt which is at specifications without further processing.

Asphalt Residual Treatment (ART). The ART process, developed by Engelhard and licensed by M. W. Kellogg, is used to remove undesirable materials from full crude, atmospheric residuum, and vacuum residuum. The feed stream enters a column resembling a riser cracker where it comes into contact with a solid sorbent material which has an affinity for asphaltenes and metals. The manufacturer claims that 100% of the asphaltenes can be removed, along with 95% of metals, 70% of carbon residue, and 35-50% of sulfur and nitrogen.

The process in its current state of operation is not applicable toward improving asphalts as its product is mainly an enhanced feed for catalytic cracking. However, the demetalizing and asphaltene removal capabilities of the ARTCAT contact material warrant further investigation as a possible unit operation in asphalt enhancement.

Adsorption. The use of adsorbents is in commercial use today in the removal of paraffins from petroleum fractions. Adsorbents work on the molecular sieve principle as discovered by McBain (1926). Synthetic zeolite sorbents of this type are commercially available under the trade names of Linde Molecular Sieves and Xerogels.

Work in this area shows promise where straight chain paraffinic material, at higher commercial value when isolated from other species, could be removed and processed. Corbett (1979) claims that saturates (paraffins) provide no contribution to road asphalt quality. This claim is further supported by the work done by Altgelt and Harle, (1975), and Skog et al., (1966). Thus, the optimum asphalt treatment facility would include a unit operation to remove as much paraffinic material as possible.

Supercritical Extraction. Supercritical fluid extraction was first observed in London in 1879 by Hannay and Hogarth (1879). By varying the pressure of a solution of inorganic salts in ethanol above its critical temperature, they found that different degrees of solubility could be achieved. Perhaps the most intriguing aspect of supercritical extraction is that it can separate a mixture based on both the mechanisms of distillation and molecular interactions as is the case in liquid extraction. Therefore, a complex mixture such as asphalt can be separated based on its solubility in one solvent. As a result, the fractions will be separated based on their adjacent compatibilities with other fractions. This is perhaps the most important consideration in the performance of an asphalt.

In addition to creating more compatible asphalts, supercritical extraction also offers the advantage of being a very economical refinery process. One such process which is in use today is Kerr McGee's ROSE (Residuum Oil Supercritical Extraction) process, capable of processing 5600 barrels of crude feed per day. This process is used to fractionate asphalt into three fractions; high asphaltene pitch, resins, and deasphalted oil (DAO). The high asphaltene pitch can be burned as solid or liquid fuel or can be partially oxidized for synthetic fuel gas. The resins can be burned as a liquid fuel or blended back with the high asphaltene pitch to produce "premium asphalt." The lightest product, DAO, has a wide range of applications including catalytic cracking, hydrocracking, or hydrotreating for gasoline, or lubricating oils (Newcomer and Soltau, 1982).

The Demex process, licensed by UOP, also produces DAO and asphalt by supercritical extraction in a manner similar to the ROSE process.

CHAPTER 2

DESCRIPTION AND OPERATION OF THE SUPERCRITICAL APPARATUS

The design and construction of the supercritical unit was a major task in Study 1155. The unit was designed to process kilogram quantities of asphalt, residuum or other heavy fractions dividing the material into up to four fractions per pass.

The system is simply described in both Figures 2-1 and 2-2. Figure 2-1 shows the process on a pressure-enthalpy diagram in which enthalpy is a measure of heat content and generally increases with temperature. The envelope is the two-phase region with liquid to the left and gas to the right. This diagram represents the solvent properties, and in the neighborhood of the critical region the properties are between those of normal liquids and gases.

Asphalt and solvent are each pumped by a metering pump to supercritical pressure (600-1000 psi) mixed and heated to a temperature at which the desired amount of asphalt will be dissolved. These conditions are shown as point A in Figures 2-1 and 2-2. This temperature may be subcritical but not greatly so. In this region solubility decreases with increasing temperature because of the very high coefficient of expansion of the fluid.

After undissolved material is separated in the extractor A, solvent with the remaining asphalt is removed, further heated to the conditions shown as point B in Figure 2-1 and 2-2 and the precipitated material removed in the second extractor or separator B. This is repeated in the vessel C (Point C in both figures). Following the separation C, the fluid is heated to a higher temperature and the pressure reduced below the critical level (point D in both figures). At these conditions the remaining extracted material has essentially no solubility in the now gaseous phase. The pure solvent is removed, condensed (point S in both figures) and recirculated. The precipitated materials are removed from each separator and subsequently stripped of solvent. These fractions may be further fractionated by recycling through the system at a different set of conditions.

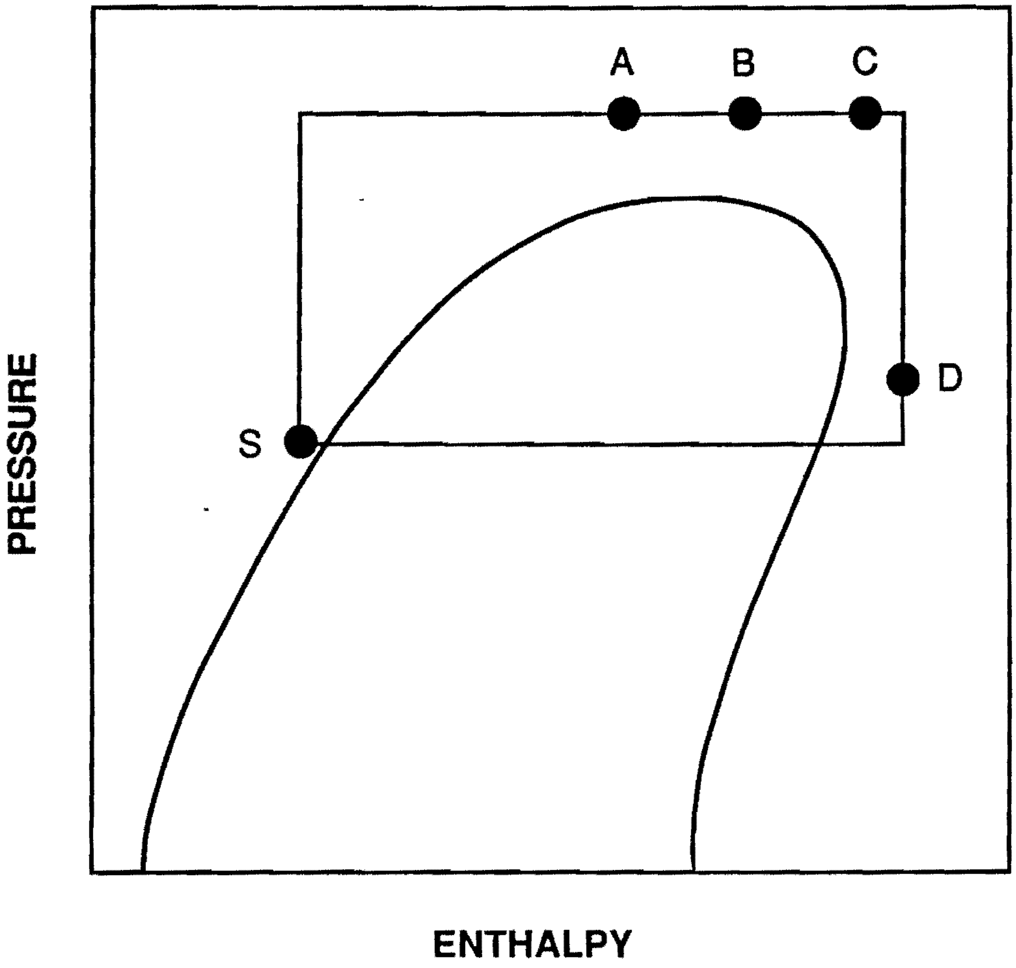

Figure 2-1
Typical Supercritical Cycle for Asphalt

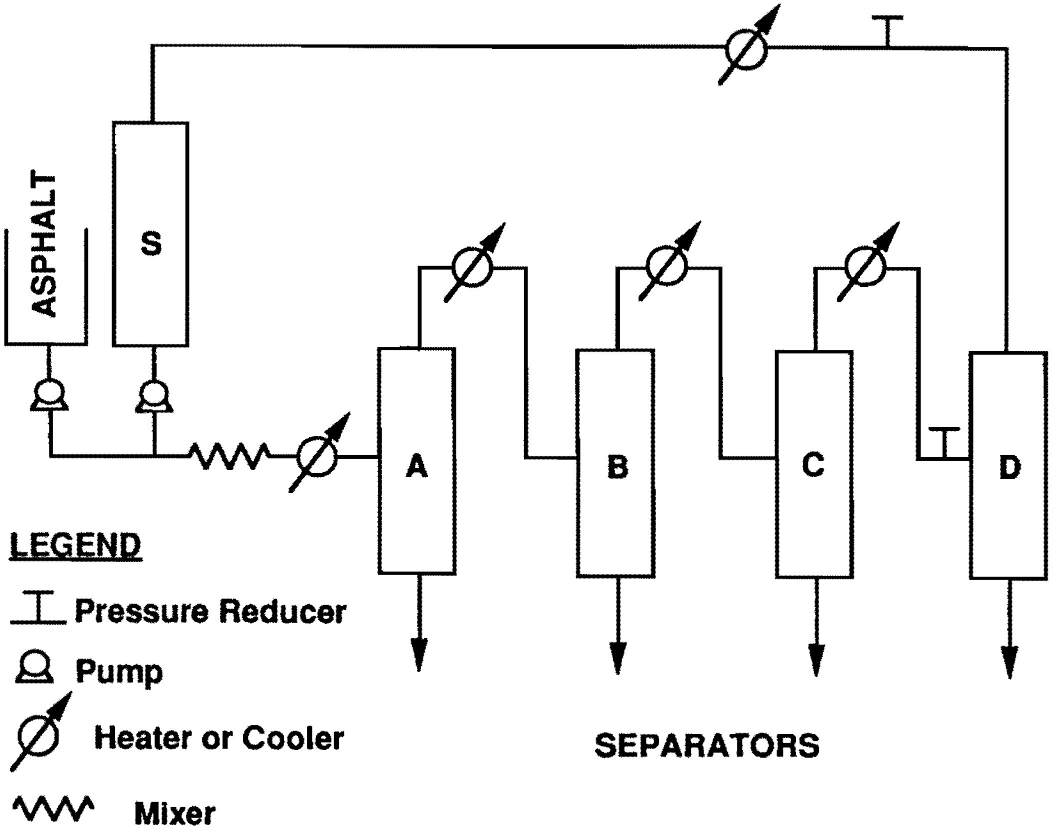

Figure 2-2
Simplified Flow Diagram for
Asphalt Supercritical Extraction Unit

In the neighborhood of the critical region, fluid density changes a rapidly with temperature. Thus over a relatively narrow temperature range, solvent power can be altered quite dramatically providing considerable versatility in the selection of the desired cuts.

Description of the Supercritical Unit

A detailed drawing is shown in Figure 2-3. The principal vessels (upper from left to right) are the asphalt and solvent feed tanks and separators A through D, and below the separators are sample collection vessels A through D. Safety features are shown in Figure 2-4. A key to Figures 2-3 and 2-4, showing other process controls and equipment, is given in Figure 2-5. A complete description of the apparatus with all safety features is given in Appendix A.

Operation of the Unit

When the system is operating with all four separators, the following order of events occurs.

Asphalt or an asphalt fraction is pumped by a metering pump at a temperature from 150 to 350 degrees F. Solvent, either n-pentane, cyclohexane or a mixture of the two is pumped by another metering pump. At this point, both streams are at a pressure of 700 to 1000 psia. In this work, a solvent flow of about 250 g/min was used. The two streams come together in a 10:1 (wt:wt) solvent:asphalt ratio where they pass through a heated mixer consisting of a 440 micron mesh filter. By passing through this filter, the undissolved (but molten) asphalt is dispersed, thereby increasing the asphalt/solvent contact area and hastening solution of the asphalt.

After leaving the mixer, the mixture passes through heater 1 where it is heated to a subcritical, but near-critical, temperature. Heater 2 further heats the mixture to supercritical conditions where it is passed into separator A which is held at the same temperature as the second heater. At this point a heavy fraction of asphalt will

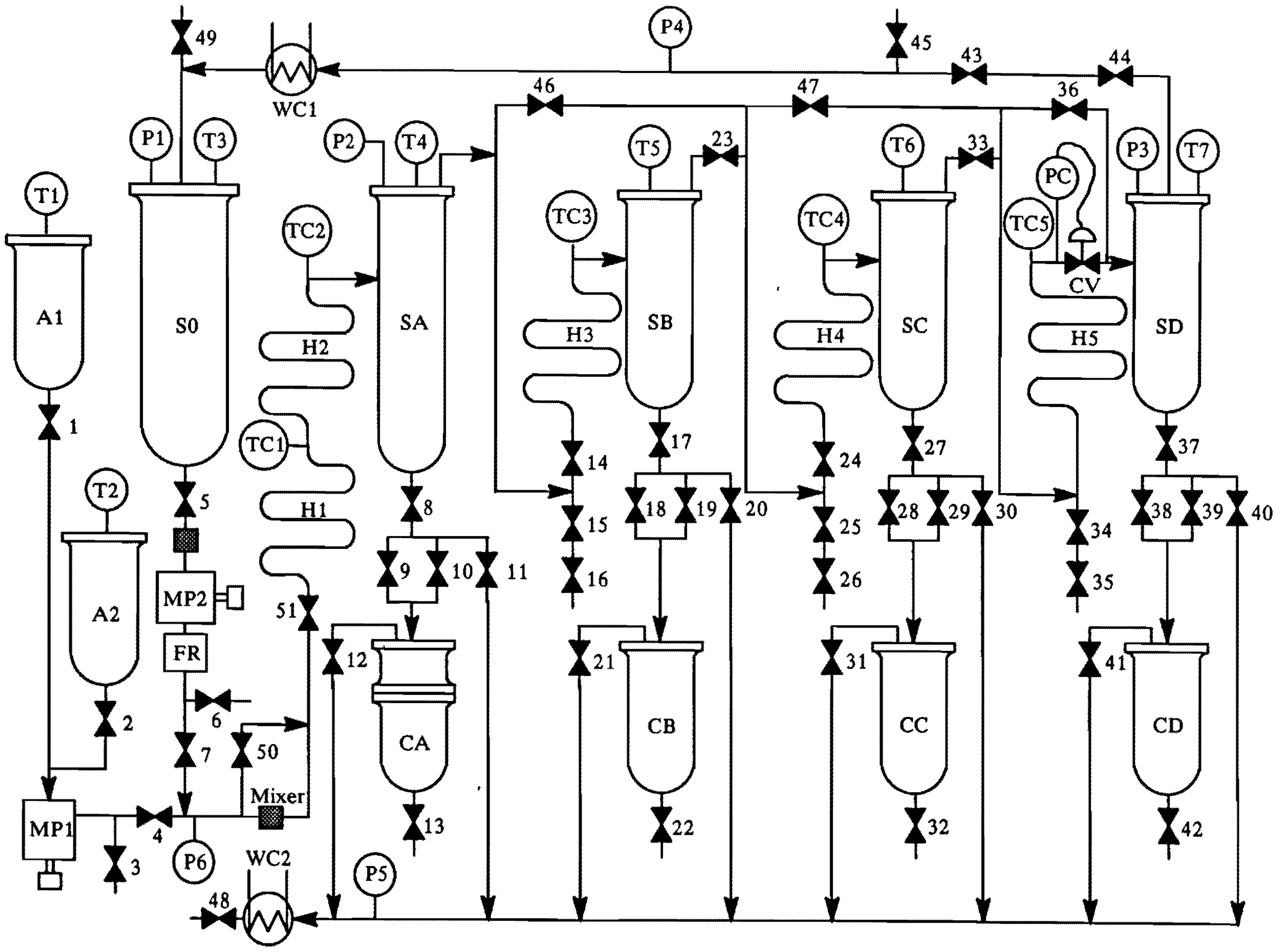

Figure 2-3
Flow Diagram of Supercritical Extraction Unit

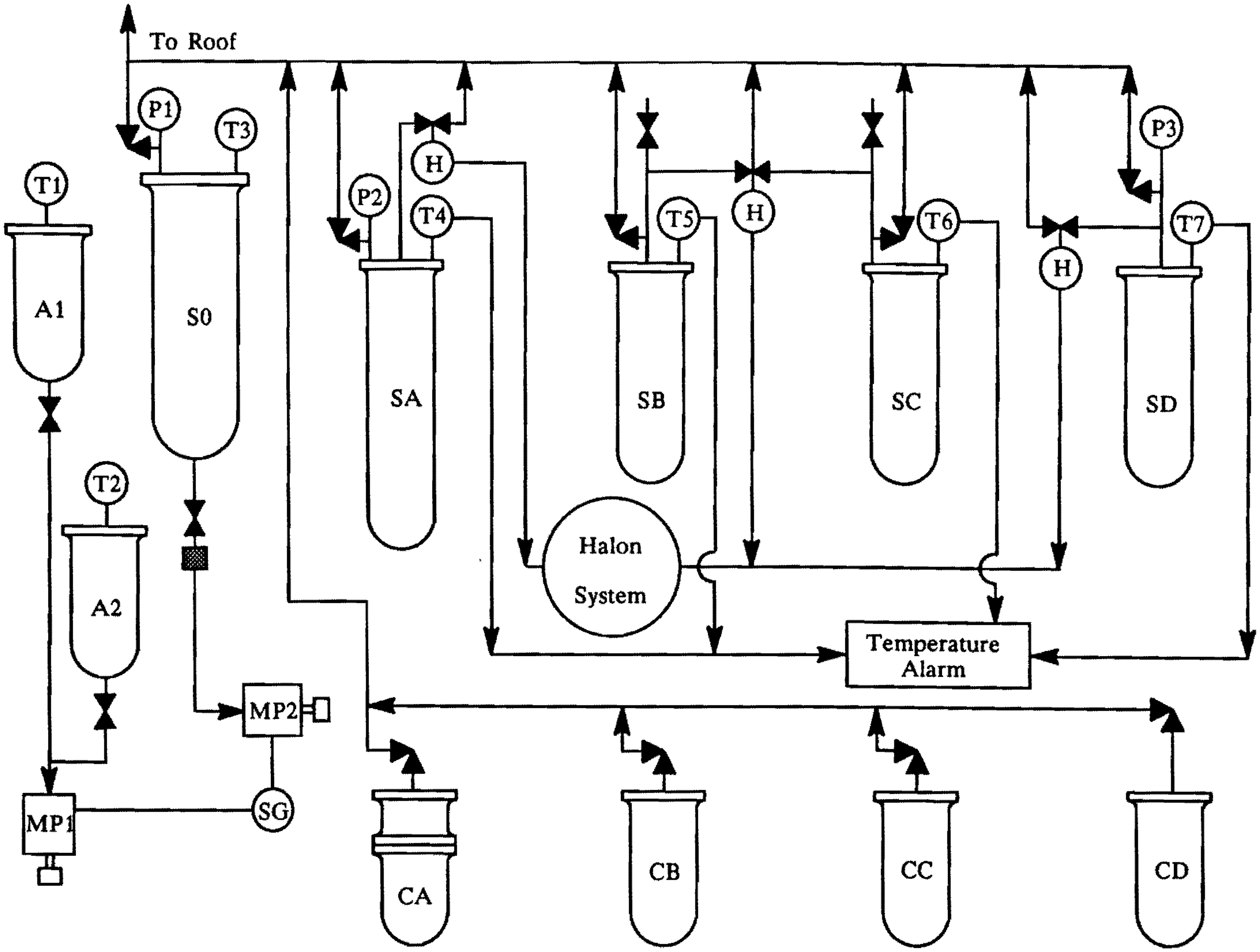

Figure 2-4
Flow Diagram of Halon and Alarm Systems
of Supercritical Extraction Unit

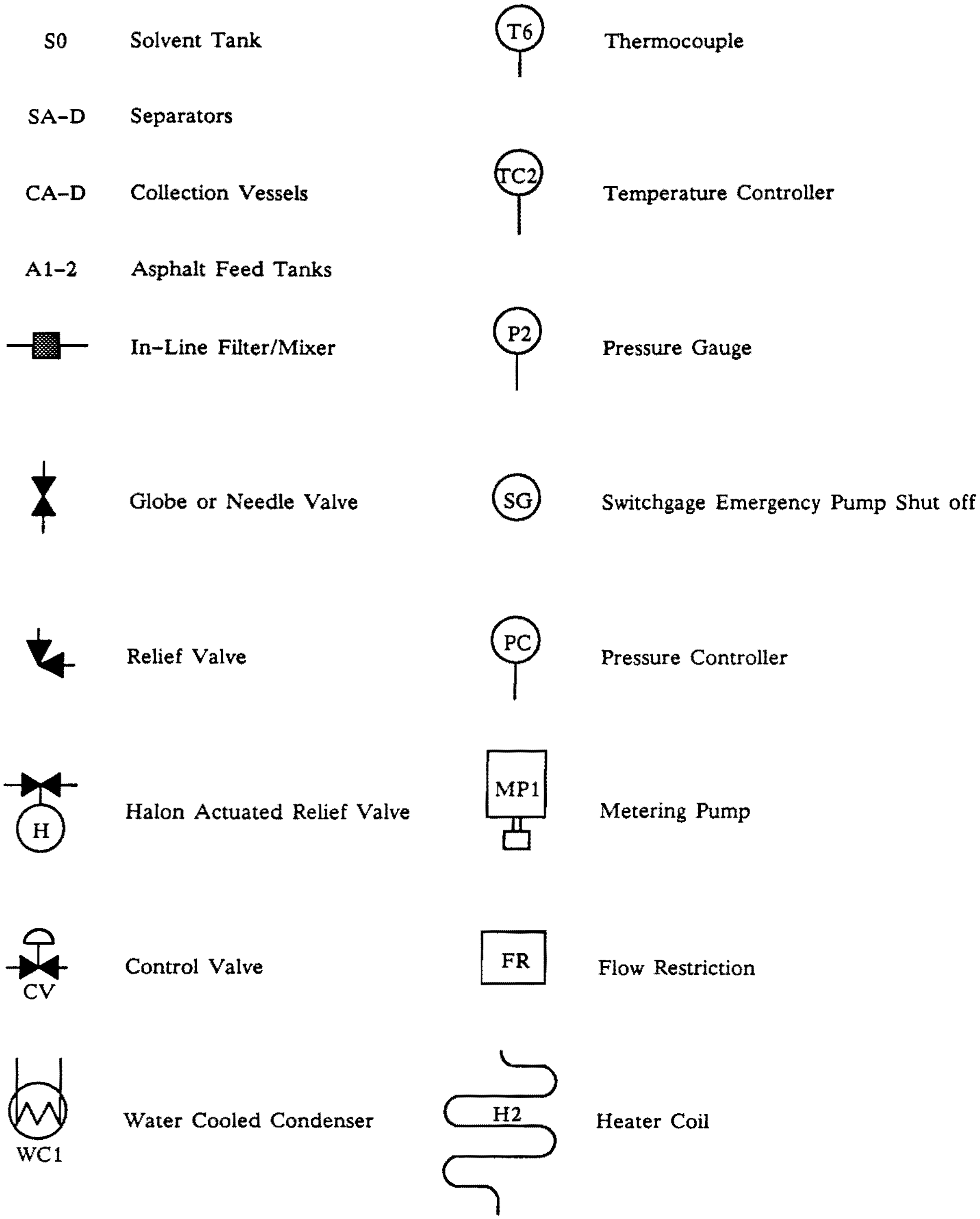

Figure 2-5
Key to Schematic of Figure 2-3 and 2-4

precipitate (Any precipitate which is found within heater 2 is carried into the separator by the fluid flow.). The top fraction will then pass through heater 3 and then into separator B where the temperature is increased, thus precipitating an additional fraction. This will be the case in separator C as well. The solution leaving separator B will pass through heater 4 and into separator C where the temperature is once again raised. A precipitate will form on the bottom of separator C consisting of material which is lighter than the material precipitated in separator B. The solution leaving separator C will pass through heater 5 and then into separator D.

At separator D, the pressure is suddenly decreased as the mixture passes through the pressure control valve. The final fraction will precipitate here and the remaining solvent will flash and condense where it is returned to the solvent feed tank. The lightest of the asphalt fractions will be found here.

It is not necessary, however, to use all four separators. Separators B, C, or both can be bypassed so that two, three, or four fractions can be made. Furthermore, the overhead from separators A, B, or C can be monitored by sampling valves 16, 26, and 35, respectively. The sampling valves consist of stainless steel syringe needles mounted at the end of a needle valve. Pre-evacuated test tubes with a rubber septum are used to collect samples from these. By knowing the weight of the test tube, the weight of the solution can be determined. The solvent can be driven off by lightly heating it. The weight of the remaining precipitate can then be used to determine the concentrations of the asphalt fractions in the overhead streams.

After all of the asphalt has been fed to the unit, some time is allowed for equilibrium to be achieved in each separator. When this is achieved, the precipitated fractions are blown down into collection vessels located beneath the separators where the solvent is flashed, condensed, and collected. The fraction is then removed from the collector into any suitable storage container. These containers are then placed in a vacuum oven overnight for further solvent removal.

Supercritical Operating Parameters Determination

The operating conditions for the supercritical extraction were determined by trial and error. Since n-pentane was used as the extracting solvent, the operating conditions had to be at least above the critical temperature and pressure of n-pentane which are 470.4 K (387°F) and 3.34 MPa (485 psia) respectively.

A period of three months was spent in determining good cut points for American PetroFina AC-20 asphalt. American PetroFina is also referred to as Ampet in this report and is now known as Final Oil and Chemical-Port Arthur. Initially a binary cut using only separators A and D was made which split the whole asphalt into approximately a 40:60 (wt/wt) heavy fraction (bottom):light fraction (top) ratio. The hard fraction was precipitated in separator A and the light fraction was obtained from separator D. The same conditions were used to make a binary split of the Coastal and Texaco whole asphalts as well and are listed in Table 4-1. The Texaco asphalt is now known as Star Enterprise.

The lighter 60% material was then split into four fractions by using all four separators of the supercritical extraction apparatus. These fractions were labelled as fractions 1 through 4 with fraction 1 (obtained from separator D) being the lightest (least viscous) and fraction 4 (obtained from separator A) the heaviest. The weight fractions of each were determined by dividing the amount of material in each fraction by the total amount of material recovered. The amount of material recovered was used in the denominator as opposed to the amount of material fed, to eliminate the effects of any material which may have stuck to walls of the separators or collectors.

Finally, the unit was washed between runs to remove any of the excess material by circulating four to five gallons of trichloroethylene (TCE) at a modest temperature and pressure (not exceeding 75°C and 150 psia). The separators and collectors were then emptied to remove all of the dissolved asphalt in TCE. This was placed in a five gallon metal can and removed for waste disposal. The unit was then dried by turning on all of the heaters to 20% of capacity as nitrogen at 50 psi was allowed to blow through the unit for a period of one-half hour.

Heavy Material Fractionation

The heavier 40% material obtained from the initial binary cut for each asphalt was divided into four additional fractions using room-temperature solvent precipitation. The first cut was made by adding 400 grams of the heavy material to a 4000 mL beaker. To this was added 3500 mL of n-pentane at room temperature and pressure. The mixture was stirred using an air-driven impeller for a period of one-half hour. The beaker was then covered with aluminum foil and allowed to sit overnight.

A thick layer of solid precipitate formed on the bottom of the beaker. This was separated from the material in solution by decantation of the solution from the precipitate to a 1000 mL round-bottomed flask for immediate solvent recovery. Then, the precipitate was washed twice with an additional 3500 ml of n-pentane.

The solvent was evaporated from the decanted solution by heating with an electric heating mantle. The round-bottomed flask was attached to a water-cooled condensing column. This was heated until most of the solvent was removed and a concentrated solution remained. This solution was then transferred to a 250 mL distillation flask for further solvent recovery.

Further solvent recovery was achieved by following the modifications of Burr et al. (1990) to the solvent recovery section of "Recovery of Asphalt From Solution by Abson Method," (ASTM D 2856). Additional cuts were made by adding cyclohexane-pentane mixtures in various ratios to the unextracted residue from the previous extraction. Otherwise the successive extractions and recoveries were conducted in the same manner as the pentane extraction.

CHAPTER 3

TESTING METHODS AND DERIVED PROPERTIES

Whole asphalts, fractions and blends were subjected to a variety of chemical and physical tests. These included standard or slightly modified ASTM procedures as well as methods developed in this laboratory. The procedures are listed and described below.

Viscosity. Viscosities at 60°C were determined using the ASTM standard procedure "Viscosity of Asphalts by Vacuum Capillary Viscometer" (ASTM D 2171).

Viscosities at 135°C were determined using the ASTM method "Standard Test for Kinematic Viscosity of Asphalts (Bitumen)" (ASTM D 2170).

Temperature Susceptibility. The viscosity temperature susceptibilities were determined as suggested by Puzinauskas (1979) as follows:

$$\mathrm{VTS} = \frac{\log\log(\text{viscosity at } T_2) - \log\log(\text{viscosity at } T_1)}{\log T_1 - \log T_2}$$

with viscosity in centipoises.

The penetration-viscosity number was calculated as suggested by McLeod (1979) and Button et al. (1983).

$$\mathrm{PVN} = -1.5\left[\frac{6.489 - 1.59\log(\text{penetration at } 25^\circ\mathrm{C}) - \log(\text{viscosity at } 60^\circ\mathrm{C})}{1.050 - 0.2234\log(\text{penetration at } 25^\circ\mathrm{C})}\right]$$

Aging Index. The aging index was defined as the ratio of the viscosity at 60°C of the asphalt following aging to the viscosity of the original or virgin asphalt. The aging was done according to the ASTM procedure "Effect of Heat and Air on a Moving Film of Asphalt" (Rolling Thin Film Oven Test) (ASTM D 2872).

Penetration. Penetrations were run at 25°C according to ASTM D 5, "Penetration of Bituminous Materials."

Ductility. Ductilities were run at 25°C according to the procedure "Standard Test Method for Ductility of Bituminous Materials" (ASTM D 113). However, the equipment used had been modified so that force ductilities could also be run. In so doing, the scale was shortened from 150 cm to 119 cm so the maximum ductility that could be measured was 119 cm.

Corbett Fractionation. Corbett analyses were run in accordance with the procedure, "Standard Test Method for Separation of Asphalt into Four Fractions" (ASTM D 4124).

Gel Permeation Chromatography (GPC). GPC analyses were run as described previously (Donaldson et al., 1988), with an IBM 9533 liquid chromatograph, an IBM 9505 automatic sampler, and a Waters R401 differential refractometer detector with a 500Å/50Å column combination using 60 cm PL Gel columns. The solvent was redistilled Tetrahydrofuran (THF) at a flow rate of 1 ml per minute. The samples were 5 wt% asphaltic material in THF.

Fourier Transform Infrared (FT-IR) Spectroscopy. The Attenuated Total Reflectance (ATR) Method for sample preparation as described by Davison, et al., (1989) was used for asphalt analysis using FT-IR. In this method, a small asphalt sample (less than 1 gram) was melted onto a single-reflection ATR prism obtained from Harrick Scientific. The prism itself is constructed of zinc selenide so as to have a high refractive index.

The whole assembly was then placed in a Nicolet 60SXB FT-IR in such a way as to have the infrared source beam bounce off a mirror, into the prism and then into the sample. The beam penetrates the sample, reflects into a mirror and then into a detector.

The advantage of this method is that no normalization or baseline manipulation is required. However, a slight rise in the baseline at lower wavenumbers will occur due to the increasing pathlength with increasing wavelength.

Metal Analysis With Atomic Absorption. Samples for atomic absorption were prepared according to the procedure used in Davison, et al. (1989). Due to the strong interferences in the the absorption spectra inherent with the metal-asphalt bonds, the samples were digested in acid followed by ashing at high temperature rather than with simple dissolution in organic solvents.

The procedure entails addition of a slight excess by weight of sulfuric acid to 2 to 3 gram samples of asphalt. These were heated at low heat on a hot plate to allow for complete digestion. The acid was driven off as the temperature was slowly increased over a period of one and one-half days. Eventually, the temperature reached 540°C at which time the samples began to ash. This temperature was maintained overnight.

Finally, hydrochloric acid was added to each of the ashed samples and was heated lightly on hot-plate samples until the ash was dissolved. This solution was then filtered and diluted to 25 ml using distilled, deionized water.

Analysis for nickel and vanadium was then performed using a Varian AA-30 atomic absorption spectrophotometer analyzer.

Preparation of Asphalt/Aggregate Test Specimens. Test specimens were prepared following the ASTM "Standard Practice for Preparation of Test Specimens of Bituminous Mixtures by Means of Gyratory Shear Compactor, (ASTM D 4013)."

The procedure consisted of screening limestone rock, river sand, and silt to yield the distribution shown in Table 3-1. The total amount of aggregate in each sample was 1000 grams with 52 grams of asphalt or asphalt blend added as the binder. Thus, each test specimen consisted of 4.9 wt% asphalt binder and 95.1 wt% aggregate.

Table 3-1: Relative Aggregate Amounts in Gyratory Prepared Test Samples[a]

Mesh #	% Limestone	% River Sand	% Silt
> ⅜ inch	4.9		
⅜ inch - 4	34.1		
4 - 8	15.6		
8 - 10	3.9		
10 - 16	1.4		
16 - 30		2.0	
30 - 40		1.4	
40 - 50		3.3	
50 - 100		11.7	
100 - 200			13.6
< 200			2.9

[a] Percents are of the total sample, including asphalt, by weight.

Indirect Tensile Strength Test

Cylindrical specimens (4" diameter x 2.5" long) were created using the Gyratory Shear Compactor and tested using a Material Testing System (MTS) 810 machine. The samples were held at a temperature of $4.4^{o}C \pm 1.2^{o}C$ by first refrigerating the samples, and then injecting liquid carbon dioxide into the testing chamber with the use of an automatic temperature controller attached to the MTS.

The test is based upon the indirect tensile strength determination of the AASHTO Method T 283-85, Resistance of Compacted Bituminous Mixture to Moisture Induced Damage, and ASTM C 496-86, Standard Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens. The test consisted of placing the cylindrical sample along its rounded surface between two axially aligned loading strips measuring 0.5 inches (12.7 mm) across and exceeding the sample length. The upper loading strip moved downward at a rate of 0.02 inches per minute (0.051 cm/min). This slow rate is used to reduce dynamic effects on the measurement. This caused an indirect tension to build up, thus causing a deformation or elongation in the horizontal direction. The elongation was measured by use of a strain gauge. The resulting elongation was then plotted versus the force by use of an automatic strip chart recorder. The test was stopped about one minute after the sample failed (indicated by a vertical crack in the sample and a decrease in the loading with increasing strain). The mix design and test conditions were selected to accent the binder properties.

Marshall "Toughness"

Similar to the indirect tension test is the Marshall "Toughness" test. In this test the compressive strength was measured by placing two of each of the samples prepared with the Gyratory Shear Compactor between two curved plates (ASTM D 1559-82) which matched the curvature of the test samples. The samples were first refrigerated at 4.4°C ± 1.2°C. The temperature was maintained by use of liquid carbon dioxide injected into the system's testing chamber with a temperature controller.

The upper plate was lowered at a rate of 0.02 inches per minute (0.051 cm/min) and stopped at a point after failure of the sample occurred. As was the case for the Indirect Tensile Test, this slow loading rate was used so that near-equilibrium values were determined; dynamic effects associated with the measurement were minimized. The vertical compressive force was plotted against the vertical compressive deformation using a strip chart recorder. The resulting area under the curve was then calculated in Newton-centimeters as a measure of the "toughness" or work load that the sample could maintain before failure. The mix design and test conditions were selected to accent the binder properties.

CHAPTER 4

ASPHALT FRACTIONS AND THEIR PROPERTIES

Asphalt Fractionation

This study addresses, primarily, the properties of the fractions produced from three virgin asphalts and of the designed asphalts produced by the reblending of these fractions. The asphalts were fractionated following the general procedures described in Chapter 2. The original asphalts, the fractions obtained, and the blends obtained from the fractions were characterized by the wide variety of chemical and physical tests described in Chapter 3. Many runs were made to determine the desired operating conditions for fractionation, but the bulk of this study is concerned with the fractions produced at the conditions shown in Table 4-1.

The asphalts studied were all AC-20 grade and the separating conditions were very nearly the same in each case, yet the relative amounts of the fractions recovered at these conditions vary considerably. This fact is emphasized in the bar graph Figure 4-1. It would appear that the Ampet asphalt is more balanced in the sense of having more material in the middle fractions. This should indicate greater compatibility. The data that follow on the whole asphalt and fraction properties indicate that this may be so.

Fraction Viscosities

The viscosity of the fractions 1 through 5 for each asphalt were measured at 60°C. Table 4-2 tabulates the values measured. As was expected, the viscosity for each fraction increases with increasing fraction number.

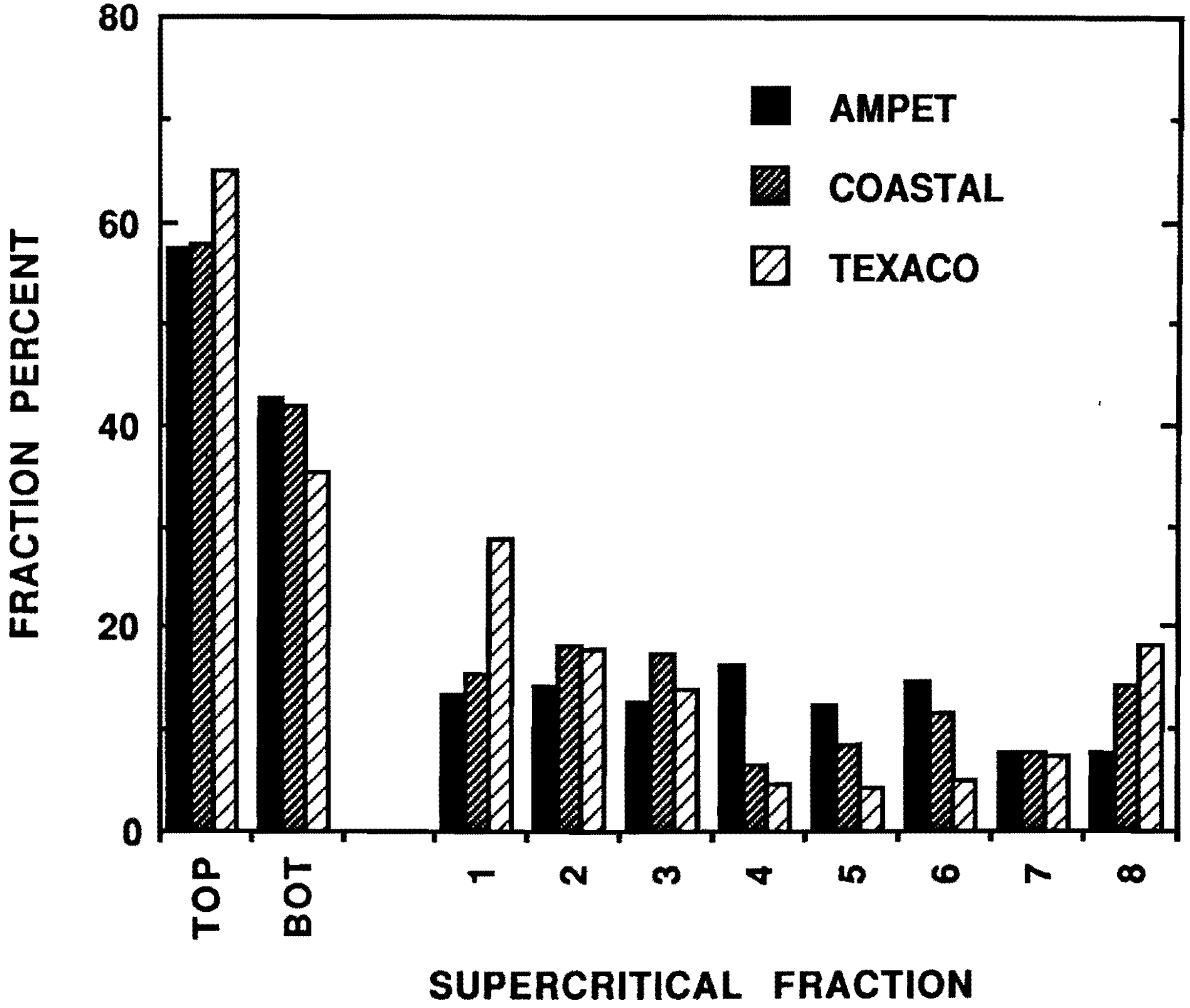

Figure 4-1
Supercritical Fraction Yield Comparison

Table 4-1
Supercritical and Solvent Fractionation Data

Asphalt	Fraction	Solvent	Temperature (°F)	Pressure (psig)	Weight Percent
Ampet (run 4)	Bottom	n-pentane	395	700	42.6
	Top	n-pentane	---	---	57.4
	1	n-pentane	>435	700	13.5
	2	n-pentane	435	700	14.4
	3	n-pentane	427	700	13.0
	4	n-pentane	415	---	16.5
	5	n-pentane	room	room	12.5
	6	mixture 1	room	room	14.6
	7	mixture 2	room	room	7.7
	8	---	room	room	7.8
Coastal					
	Bottom	n-pentane	395	700	42.0
	Top	n-pentane	---	---	58.0
	1	n-pentane	>435	700	15.7
	2	n-pentane	435	700	18.3
	3	n-pentane	427	700	17.6
	4	n-pentane	413	---	6.5
	5	n-pentane	room	room	8.4
	6	mixture 1	room	room	11.6
	7	mixture 2	room	room	7.7
	8	---	room	room	14.2
Texaco	Bottom	n-pentane	395	700	35.2
	Top	n-pentane	---	---	64.8
	1	n-pentane	>435	700	28.6
	2	n-pentane	435	700	18.0
	3	n-pentane	427	700	13.8
	4	n-pentane	415	---	4.6
	5	n-pentane	room	room	4.3
	6	mixture 1	room	room	5.0
	7	mixture 2	room	room	7.3
	8	---	room	room	18.4

Note: Mixture 1 consists of 35:65 (vol:vol) cyclohexane:n-pentane
Mixture 2 consists of 50:50 (vol:vol) cyclohexane:n-pentane

Table 4-2
Viscosities of Asphalt Fractions

	Fraction	Viscosity at 60°C (poise)
Ampet (run 4)	Whole	2350
	1	2.5
	2	12.2
	3	45.9
	4	1019
	5	1206
Coastal	Whole	2013
	1	6.4
	2	27.3
	3	60.9
	4	184
	5	1778
Texaco	Whole	1891
	1	7.7
	2	30.4
	3	75.9
	4	348
	5	1763

As can be seen from the values listed above, there is some deviation in the viscosity of a given fraction from one source of asphalt to another. The most striking is that of fraction 4 which has a viscosity difference of over half an order of magnitude between Ampet and Coastal. This clearly demonstrates that whole asphalts of a given viscosity can produce fractions having greatly different properties.

Figures 4-2 to 4-4 are plots of the log viscosity versus the mean of the fraction composition. To further explain the abscissa of these graphs, note that the Ampet fraction 1, run 4 in Figure 4-2, would be plotted at 93.25 as it covers the range from 86.5 (100 - 13.5) (see Table 4-1) to 100. Fraction 2 is plotted at 79.3 as it covers the range from 72.1 to 86.5. The whole asphalt, on the other hand, covers the entire range from zero to 100% and is plotted at 50%. In Figure 4-2 we have plotted some

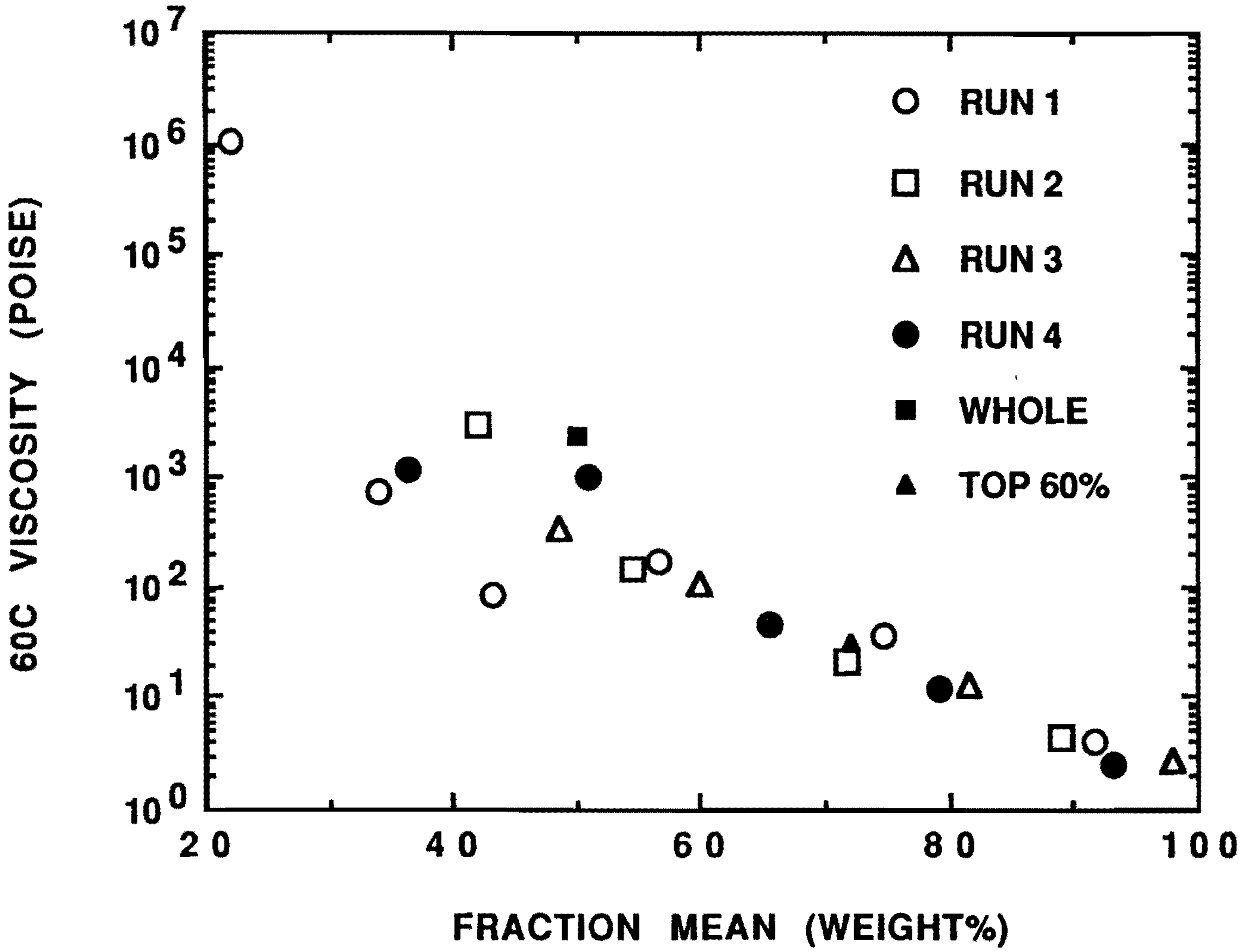

Figure 4-2
Viscosities of Ampet Fractions

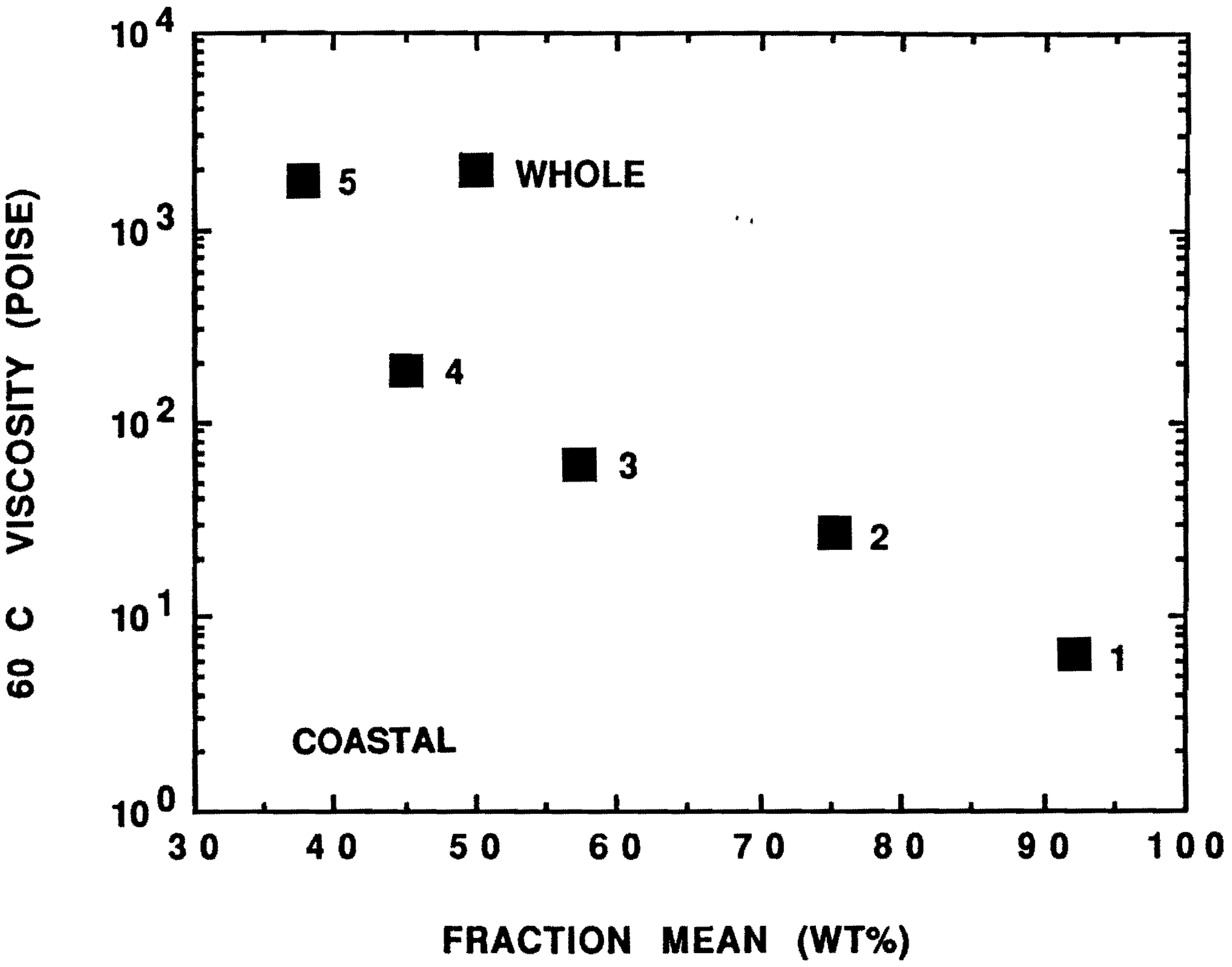

Figure 4-3
Viscosities of Coastal Fractions

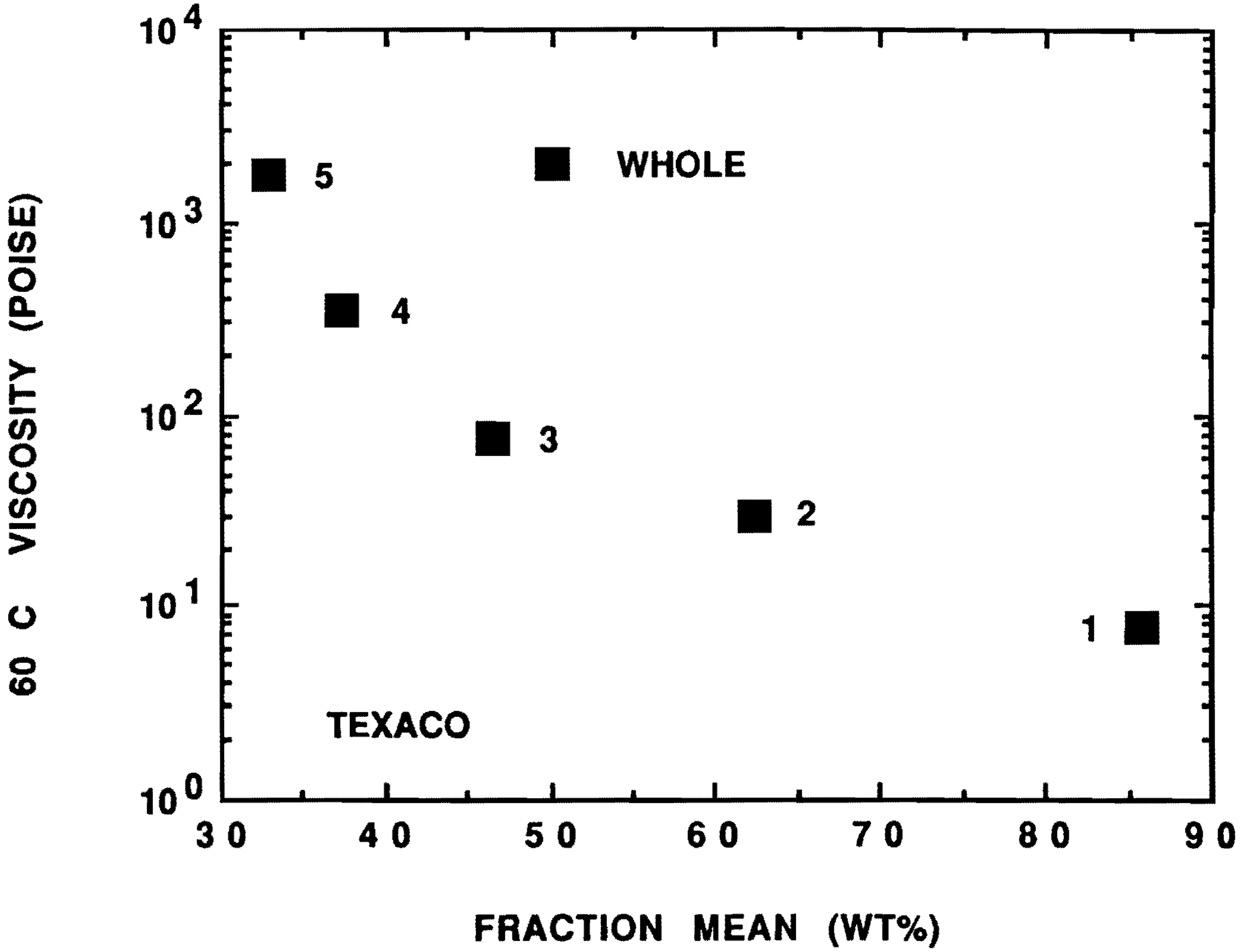

Figure 4-4
Viscosities of Texaco Fractions

data obtained from earlier runs, runs 1-3, with the Ampet asphalt and also the entire top cut which for that particular run was about 60% of the total, and so covers the range from about 40 to 100% and is plotted at approximately 70%. We see that for the top three fractions the plot is linear in all cases (to within experimental error) and for Ampet, fraction 5 and the top fraction also fall on the curves. These fractions are all nearly asphaltene free. The large jump in viscosity for the whole asphalt (Figures 4-2 through 4-4) and for fraction 6 of run 1 (Figure 4-2), show the large effect on viscosity of asphaltenes. Fraction 4 is also generally above the curve, and as we shall see, it is anomalously high in asphaltenes.

Corbett Analysis

Corbett analyses were performed on the whole asphalts and on all fractions, and these are shown in Table 4-3 and Figures 4-5 to 4-8. In these figures the Corbett frctions are denoted by: Sat. = saturates, N.A. = naphthene aromatics, P.A. = polar aromatics, and Asph. = asphaltenes. The surprising thing, perhaps, is that each Corbett fraction is so widely distributed among the supercritical and solvent fractions. However, the distribution is not uniform from one asphalt to the next; the ratio of the amount of a given Corbett fraction in the top 60% supercritical fraction to that in the bottom 40% fraction may vary considerably from asphalt to asphalt. For instance, the ratio of the amount of saturates in the top fraction divided by the amount in the bottom fraction is 3.5 for Ampet, 5.9 for Texaco and 14 for Coastal which, incidently, is in reverse order to the quantity of saturates originally present in each of these asphalts. Asphaltenes, on the other hand are very nearly all in fractions 5 through 8 and what did go in solution in the top 60% cut wound up almost entirely in fraction 4. The naphthene aromatic content is widely distributed among the fractions and seems to maximize between fractions 2 and 5. Polar aromatics are also widely distributed but are skewed more to the heavy fractions and maximize at fractions 4 to 6. This is more clearly seen in Figure 4-6 which is the same data as Figure 4-5.

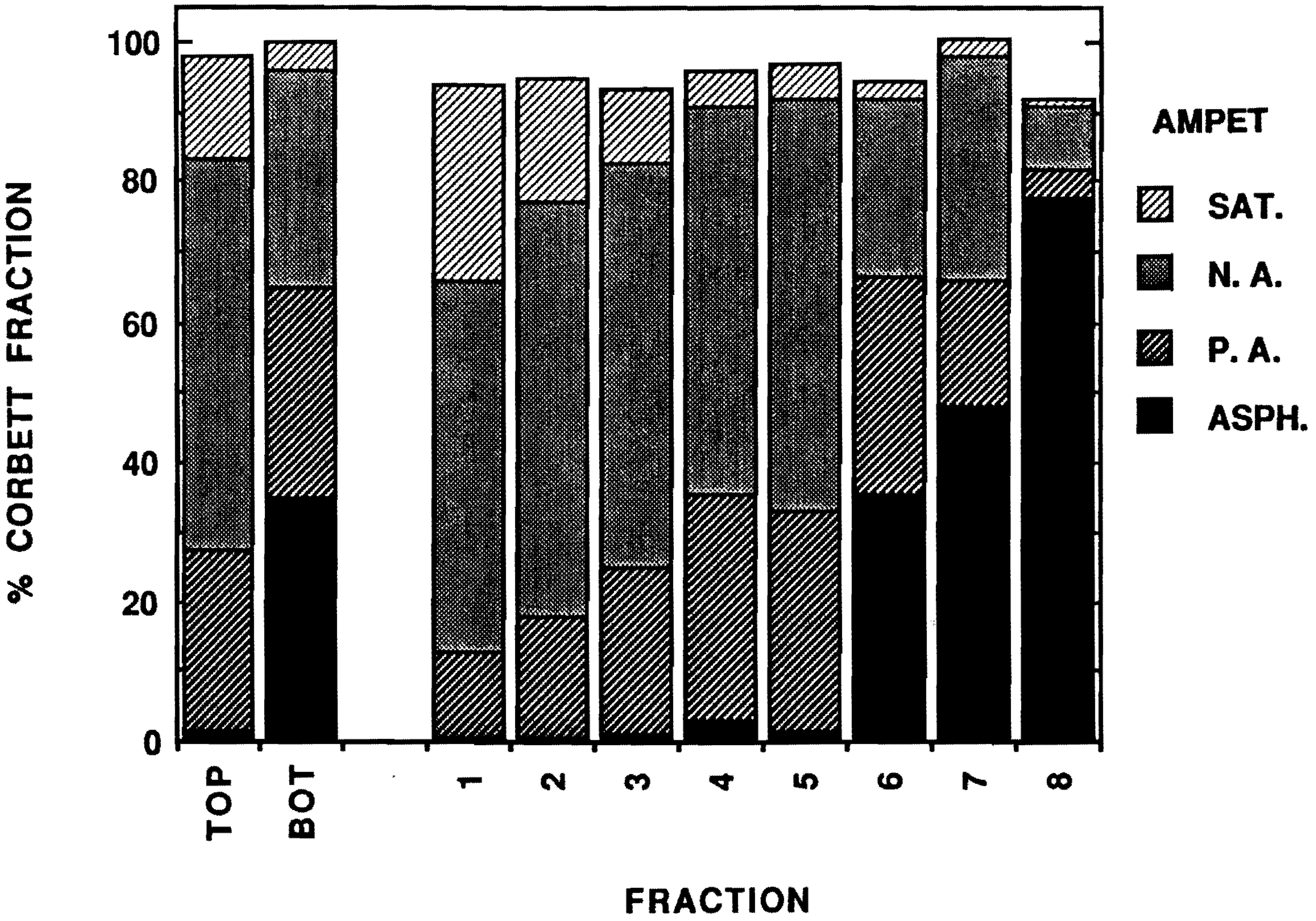

Figure 4-5
Corbett Analysis of Ampet Fractions

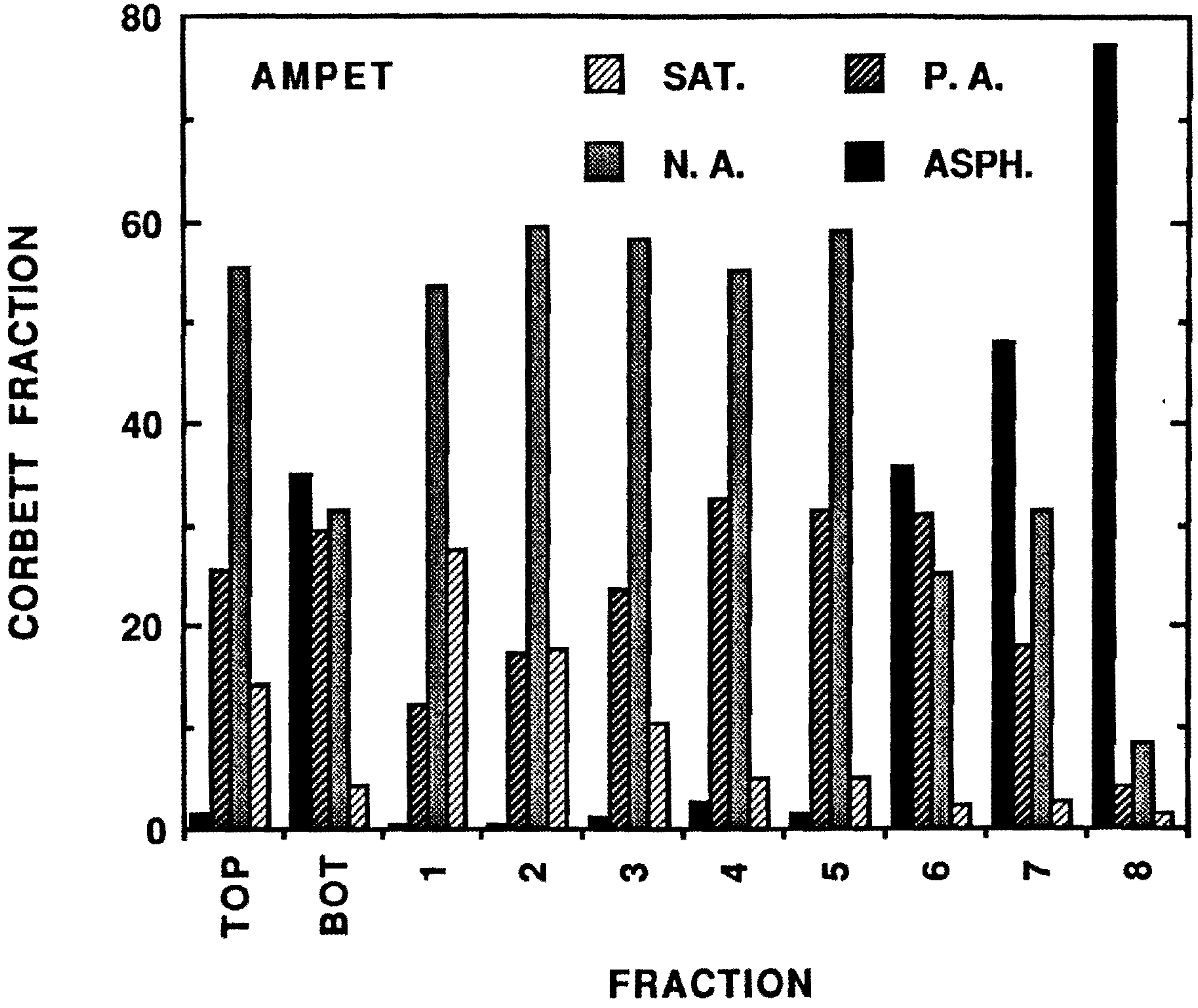

Figure 4-6
Corbett Analysis of Ampet Fractions

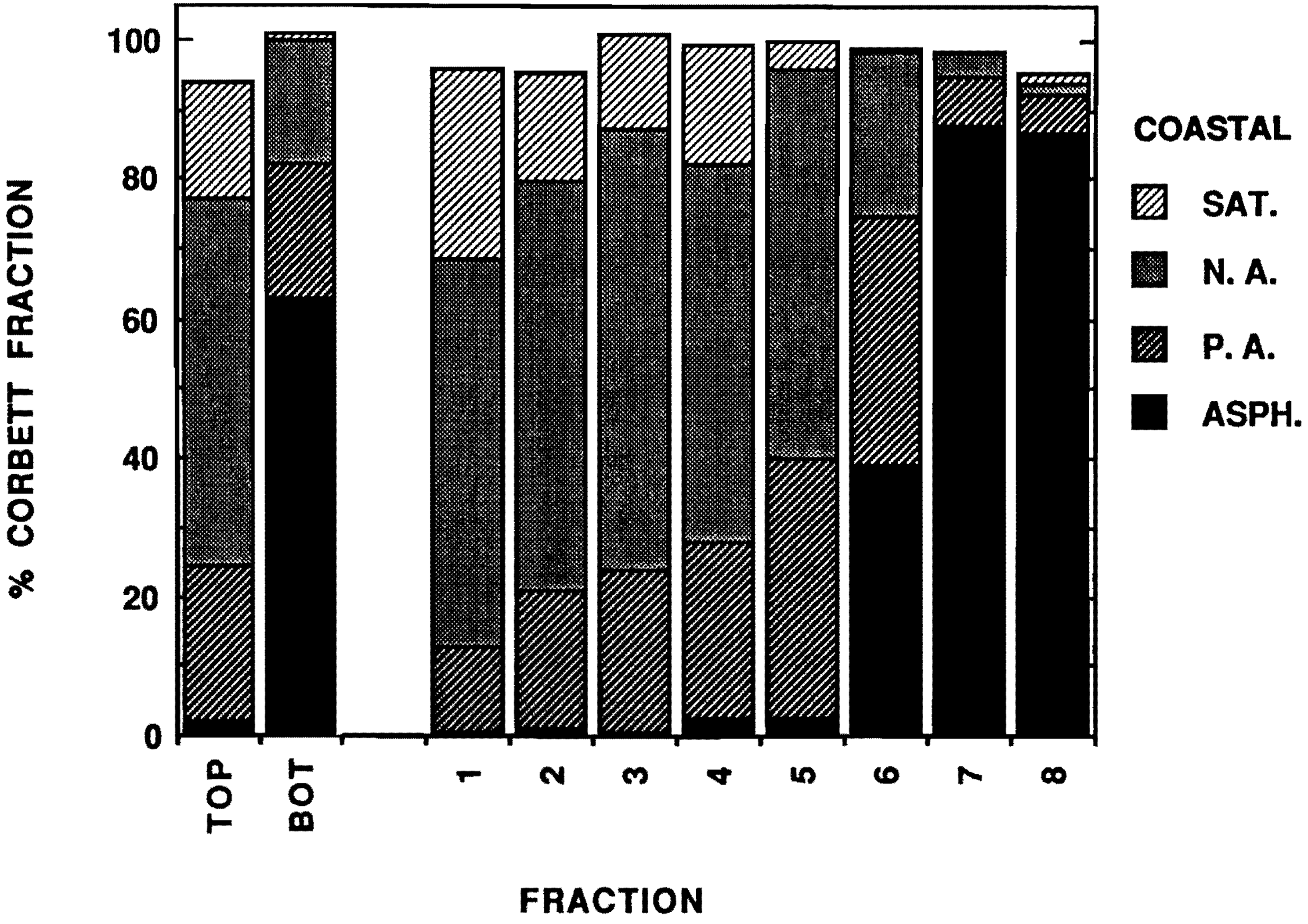

Figure 4-7
Corbett Analysis of Coastal Fractions

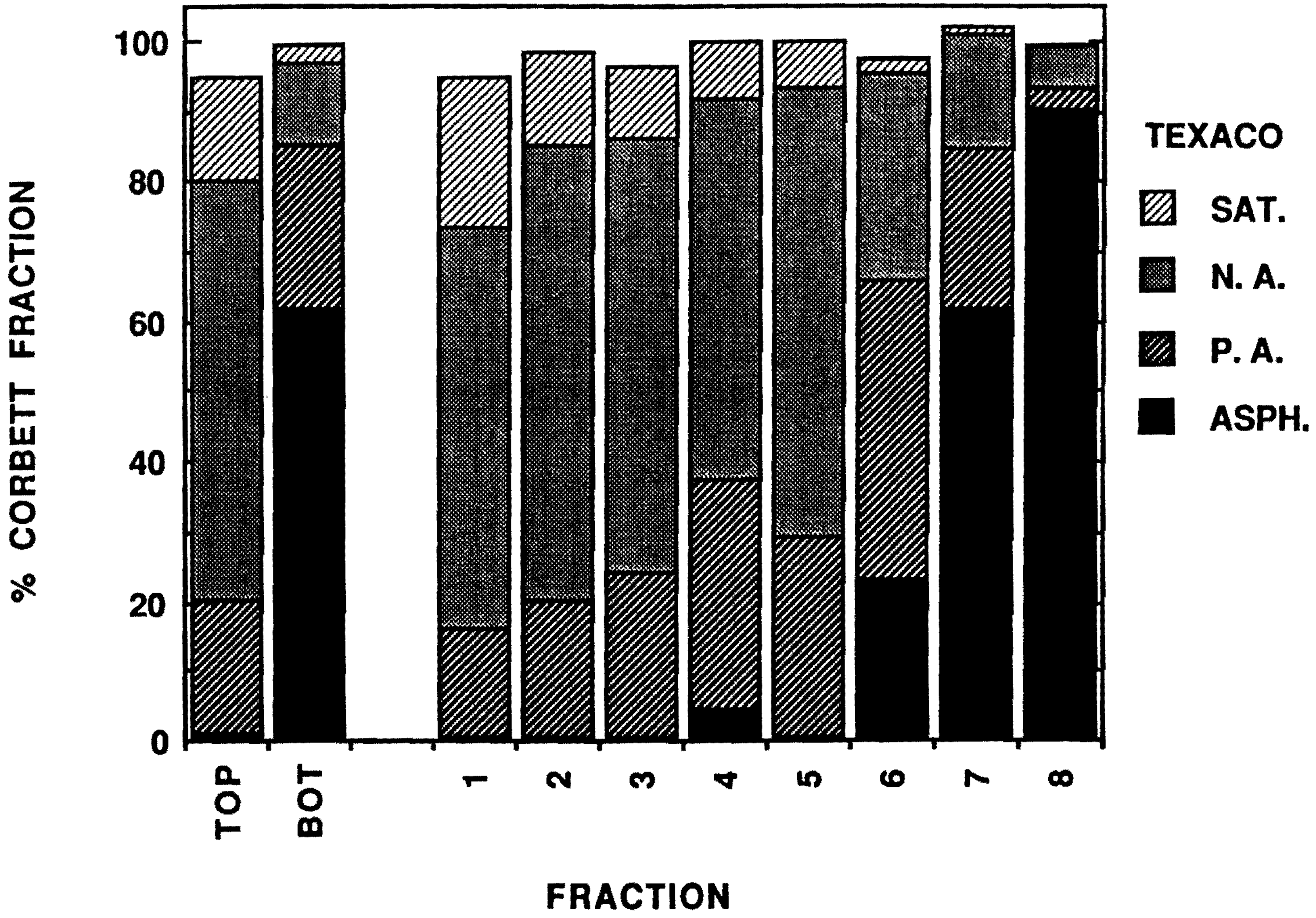

Figure 4-8
Corbett Analysis of Texaco Fractions

Table 4-3
Percent of Corbett Fractions Produced

		Saturates	Naphthene Aromatics	Polar Aromatics	Asphaltenes
Ampet					
	Top	14.54	55.66	25.78	1.69
	Bottom	4.15	31.31	29.55	35.14
	1	27.71	53.45	12.33	0.31
	2	17.95	59.38	17.31	0.40
	3	10.57	58.08	23.62	1.15
	4	5.12	55.04	32.69	2.83
	5	5.14	58.99	31.52	1.38
	6	2.25	25.39	30.96	35.55
	7	2.75	31.65	18.07	48.07
	8	1.38	8.72	4.40	77.43
	Whole	9.34	45.45	32.91	12.37
Coastal					
	Top	16.80	52.79	22.19	1.95
	Bottom	1.20	17.35	19.34	63.00
	1	27.27	55.63	12.11	0.63
	2	15.59	58.93	20.02	0.87
	3	13.50	63.34	23.62	0.41
	4	17.15	54.39	25.22	2.61
	5	4.02	55.50	37.47	2.70
	6	0.72	23.47	35.61	39.12
	7	0.29	3.58	6.66	88.00
	8	1.29	1.54	5.66	86.74
	Whole	12.38	39.47	26.60	18.07
Texaco					
	Top	14.50	60.03	19.14	1.18
	Bottom	2.45	11.62	23.24	61.97
	1	21.39	57.07	15.75	0.53
	2	13.01	64.65	20.21	0.33
	3	10.34	61.65	24.15	0.38
	4	8.37	54.46	32.79	4.56
	5	6.82	63.55	28.99	0.63
	6	1.93	29.88	42.18	23.55
	7	0.99	16.23	23.00	61.73
	8	0.30	6.25	2.69	90.41
	Whole	12.30	43.63	21.99	17.80

Marked differences can be observed between the asphalts which are perhaps best seen in Table 4-3. Ampet and Coastal fraction 1 contains about the same percent of saturates despite a considerably higher level in the Coastal whole asphalt. Also Ampet fraction 2 is slightly higher in saturates. Not surprisingly, this resulted in larger Coastal fractions 1 and 2. Texaco showed about the same saturates content as Coastal in the whole asphalt but a considerably lower percent in fraction 1. This was due to a larger amount of naphthene and polar aromatics and a correspondingly larger total amount for this fraction. With Ampet, there is a much sharper drop in saturates between fractions 3 and 4 than with the other asphalts. Ampet whole asphalt has the lowest asphaltene content and also the smallest fraction 8 with a lower per cent asphaltenes. Coastal fraction 7 is as high in asphaltenes as fraction 8, while the other two asphalts show considerable increase in asphaltenes in going from fraction 7 to 8. The distribution ratio of naphthene aromatics between the top and bottom cuts is 1.8 for Ampet, 3.0 for Coastal and 5.2 for Texaco. Yet the distribution of polar aromatics is near one for all those asphalts.

Obviously, the Corbett fractionation and the supercritical-solvent fractionation are two very different processes, producing fractions with only rough correspondence. This result enhances their use, in combination, to study asphalt properties. It also supports the work of Altgelt and Harle (1975) who showed that corresponding Corbett fractions from different asphalts could have markedly different properties.

One of the most interesting phenomena shown in these data is the non-zero level of asphaltenes in fractions 4 and 5. One would expect both to be zero, as asphaltenes by definition do not dissolve in pentane at room temperature, corresponding to fraction 5, and, it would be reasonable to suppose, should be even less soluble at the supercritical condition of fraction 4. The non-zero amount in fraction 5 can be accounted for by the lower solvent/asphalt ratio used in this fractionation than is used in the Corbett analysis. The even larger amount in fraction 4 for Ampet and Texaco, however, seems anomalous. It was at first feared that the asphalt content of fraction 4 might be the result of entrainment, but as will be shown later, the asphaltenes in fraction 4 are much lower in molecular size than that in the other fractions. The most likely answer is that while supercritical pentane is a poorer solvent than room-temperature pentane, the asphaltenes, and especially the lower molecular size asphaltenes become much more soluble at high temperature and therefore are, in fact soluble in the first-pass (supercritical) top cut but are subsequently precipitated in the (room temperature) Corbett asphaltenes determination of fraction 4.

Metal Analysis

Table 4-4 summarizes the concentration of nickel and vanadium, in each whole asphalt, asphalt fraction, and asphalt blends. (The blends are discussed more fully in Chapter 5.) Figures 4-9 and 4-10 show content in each fraction. It is interesting to note that in these figures, the nickel and vanadium concentrations, for the most part, rise with increasing fraction number. Thus, nickel and vanadium concentrations increase with increasingly heavier fractions.

Table 4-5 shows the results of material balance calculations performed on the metals. The weight percent of each fraction was multiplied by the concentration of metal in each corresponding fraction. These values were then summed for each metal in each type of asphalt. A perfect material balance would yield a sum which is equal to the metal content for each whole asphalt. Instead, there was a high degree of scatter in the nickel and vanadium sums. For example, the material balance for nickel for the Texaco fractions had a margin of error of only 0.5% whereas the vanadium balance for Texaco had a margin of error of 12.3%. Similarly, the Ampet nickel balance had a margin of error of 12.9% with a vanadium material balance margin of error of 20.2%. It would seem that for a given asphalt, the material balance error should be quite similar between two types of metals. That is, if the nickel balance were in error by 10%, the vanadium balance should have an error of 10% as well if the error were in the percent of each fraction. Since this is not the case, it can only be concluded, the errors in the nickel and vanadium balances are due to summation of errors in experimental procedure, both with

Table 4-4
Atomic Absorption Data for Whole Asphalts, Fractions, and Asphalt Blends

Sample	Nickel Content in ppm	Vanadium Content in ppm
Ampet Fraction 1	5.5	6.5
Ampet Fraction 2	10.9	14.1
Ampet Fraction 3	8.6	33.4
Ampet Fraction 4	32.8	89.4
Ampet Fraction 5	23.0	62.2
Ampet Fraction 6	74.3	231.8
Ampet Fraction 7	96.0	285.6
Ampet Fraction 8	138.7	417.2
Ampet Whole	46.8	148.6
Ampet Blend 1	42.4	122.5
Ampet Blend 2	34.9	101.1
Ampet Blend 3	33.1	94.6
Ampet Blend 4	27.8	73.4
Coastal Fraction 1	5.7	33.4
Coastal Fraction 2	17.0	59.8
Coastal Fraction 3	18.7	74.0
Coastal Fraction 4	36.4	131.7
Coastal Fraction 5	47.3	176.6
Coastal Fraction 6	133.8	555.1
Coastal Fraction 7	173.4	710.1
Coastal Fraction 8	231.4	997.8
Coastal Whole	68.6	280.9
Coastal Blend 1	63.9	259.0
Coastal Blend 2	66.5	285.9
Coastal Blend 3	55.7	226.5
Coastal Blend 4	66.1	240.1
Coastal Blend 5	69.8	265.6

Table 4-4
Atomic Absorption Data for Whole Asphalts, Fractions, and Asphalt Blends
(Cont'd)

Sample	Nickel Content in ppm	Vanadium Content in ppm
Texaco Fraction 1	9.4	13.8
Texaco Fraction 2	8.5	29.9
Texaco Fraction 3	12.5	42.0
Texaco Fraction 4	26.7	103.8
Texaco Fraction 5	22.7	63.8
Texaco Fraction 6	75.8	239.6
Texaco Fraction 7	115.6	361.8
Texaco Fraction 8	155.0	472.7
Texaco Whole	48.7	168.8
Texaco Blend 1	42.2	170.8
Texaco Blend 2	33.5	113.2
Texaco Blend 3	30.6	102.1
Texaco Blend 4	33.5	101.0

Table 4-5
Atomic Absorption Data for Whole Asphalts, Results of Material Balance on Each Metal

Sample	Nickel Content in ppm	Calculated	% Error
Ampet Whole	46.8	40.78	-12.9
Coastal Whole	68.6	75.51	10.1
Texaco Whole	48.7	48.9	0.5

Sample	Vanadium Content in ppm	Calculated	% Error
Ampet Whole	148.6	118.6	-20.2
Coastal Whole	280.9	313.9	11.8
Texaco Whole	168.8	148.0	-12.3

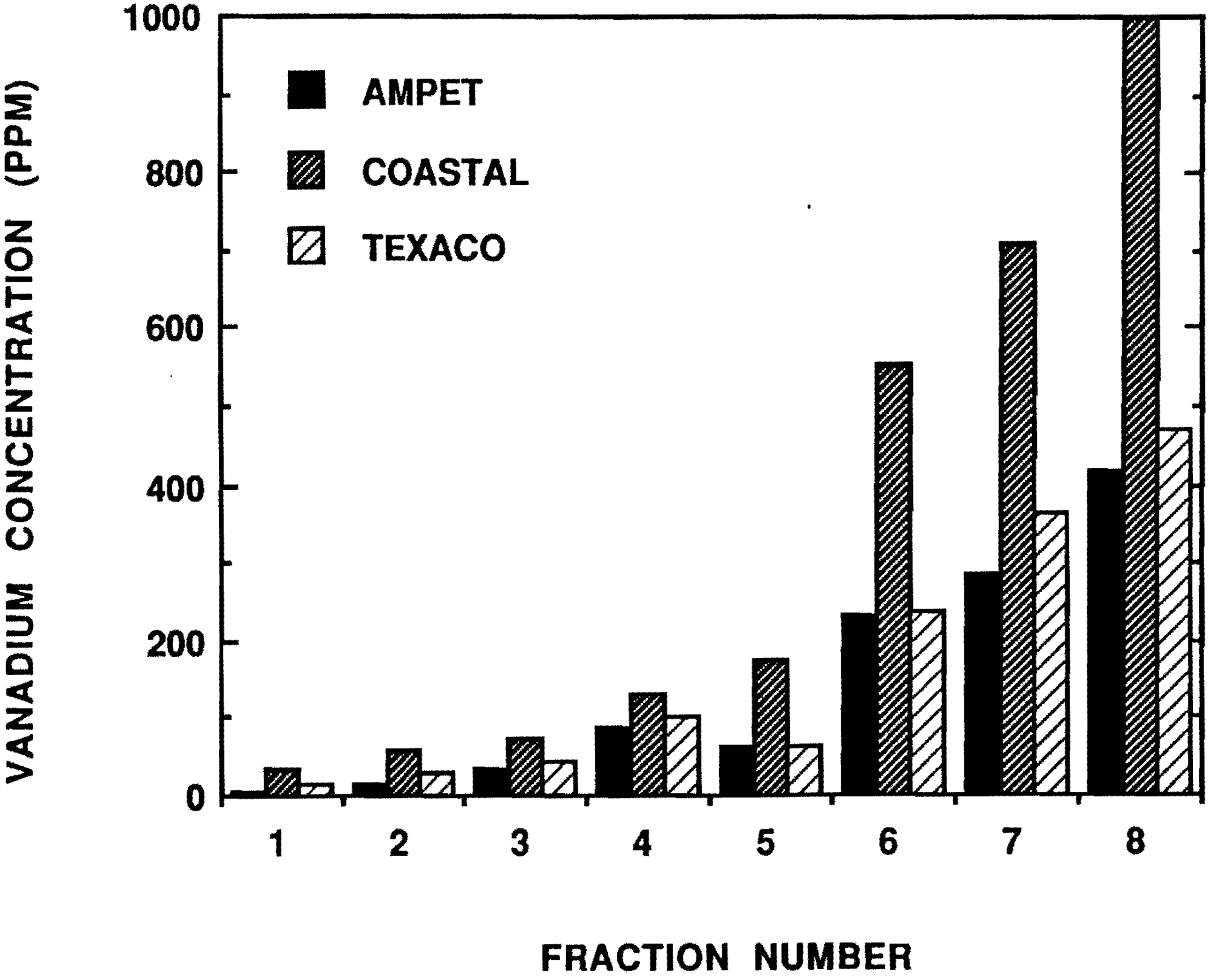

Figure 4-9
Vanadium Content of Asphalt Fractions

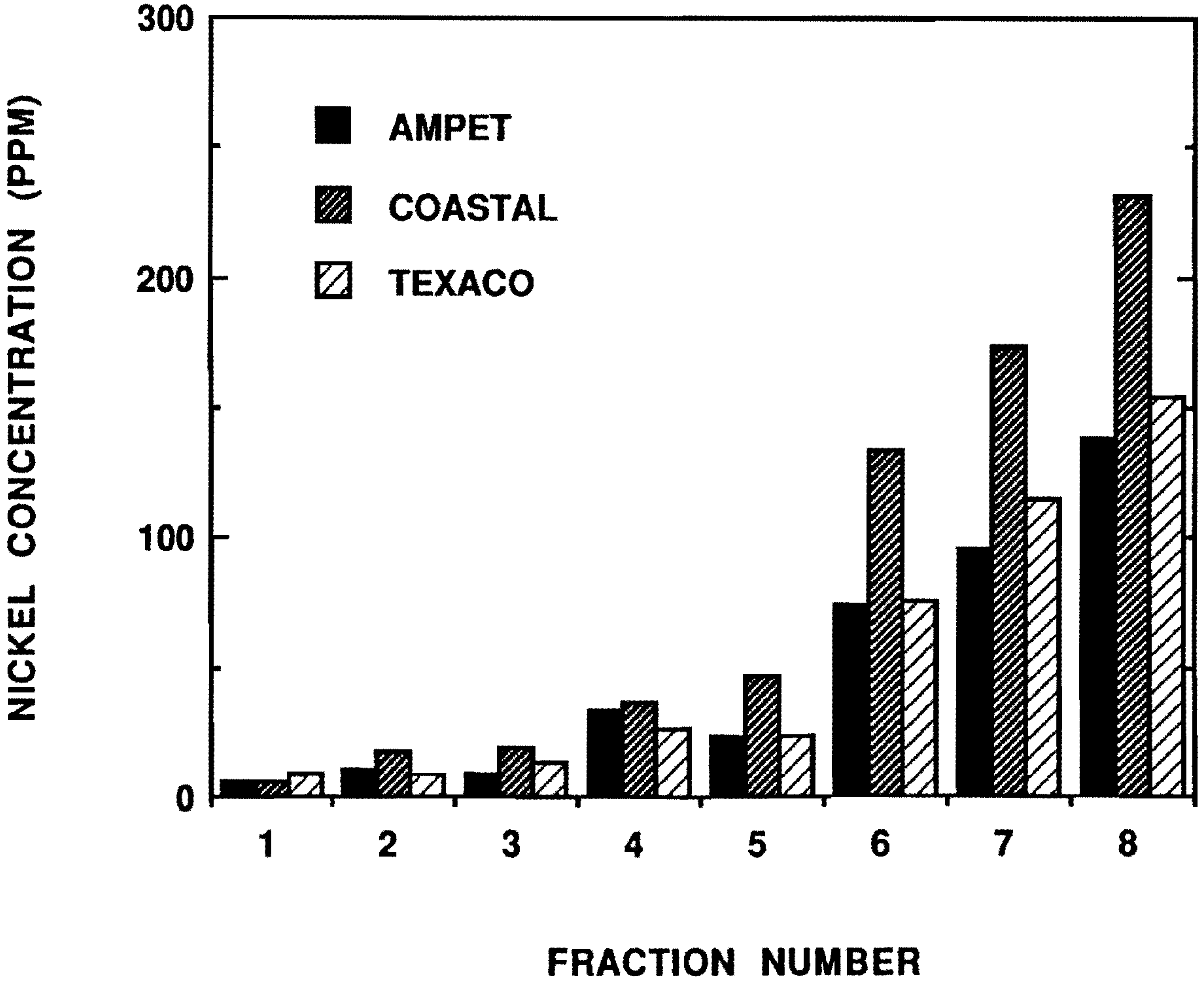

Figure 4-10
Nickel Content of Asphalt Fractions

determining the fractional weight percents and in measuring metal concentrations. The blend metal concentrations are included here rather than later when blends are discussed because the data don't vary enough for correlation. The blend concentrations are all quite uniform because the blends were produced largely by omitting the fractions with very high metal content.

The results shown in Figure 4-11 to 4-13 are very significant. Nickel is plotted vs. vanadium for the fractions and blends. For each asphalt, the ratio of nickel to vanadium is constant in all fractions. This indicates that the two metals are essentially interchangeable in the molecular structures in which they are found.

In Figures 4-14 to 4-19 similar plots are shown for metals vs. asphaltenes. The results are generally linear except for fractions with very low metal and asphaltene content. Also the intercept is not zero. In Figures 4-20 to 4-25 the metal content is plotted vs. asphaltenes, but only for fractions 1 to 4. There is scatter because of inherent error in analysis at these low levels, but it appears that a strong relation again exists and it could be linear and pass through the origin. What is surprising, however, is that because the metal to asphaltene ratio is higher in the light fractions near the origin, either the asphaltenes in the light fractions are richer in metals or some of the metal is associated with another fraction or fractions (naphthene or polar aromatics, e.g.). One thing is clear. For the most part, the metals go with the asphaltenes and they are not concentrated in the asphaltenes of the heavier fractions.

GPC Analysis of Fractions

Chromatograms for the whole asphalt, the top and bottom fractions and the final eight fractions, as described in Table 4-1, are shown in Figures 4-26 to 4-37. Figures 4-26 to 4-28 compare the whole asphalt and the top and bottom fractions for all three asphalts. All are similar and there is a large molecular size difference between the top and bottom fractions. The chief difference is a small peak of very high molecular size material in the bottom fraction and a slight shoulder on the top fraction for the Ampet material.

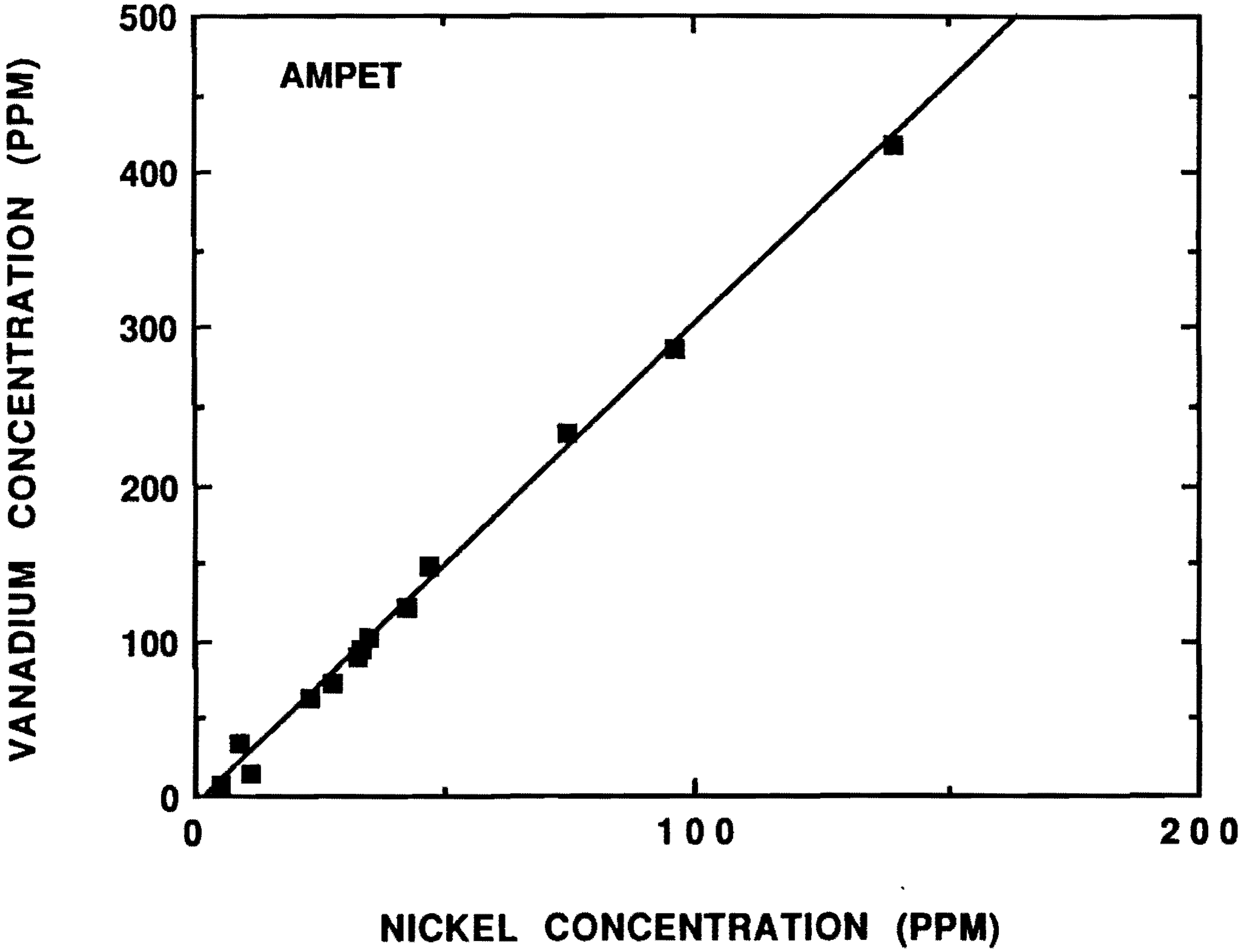

Figure 4-11
Vanadium Versus Nickel - Ampet

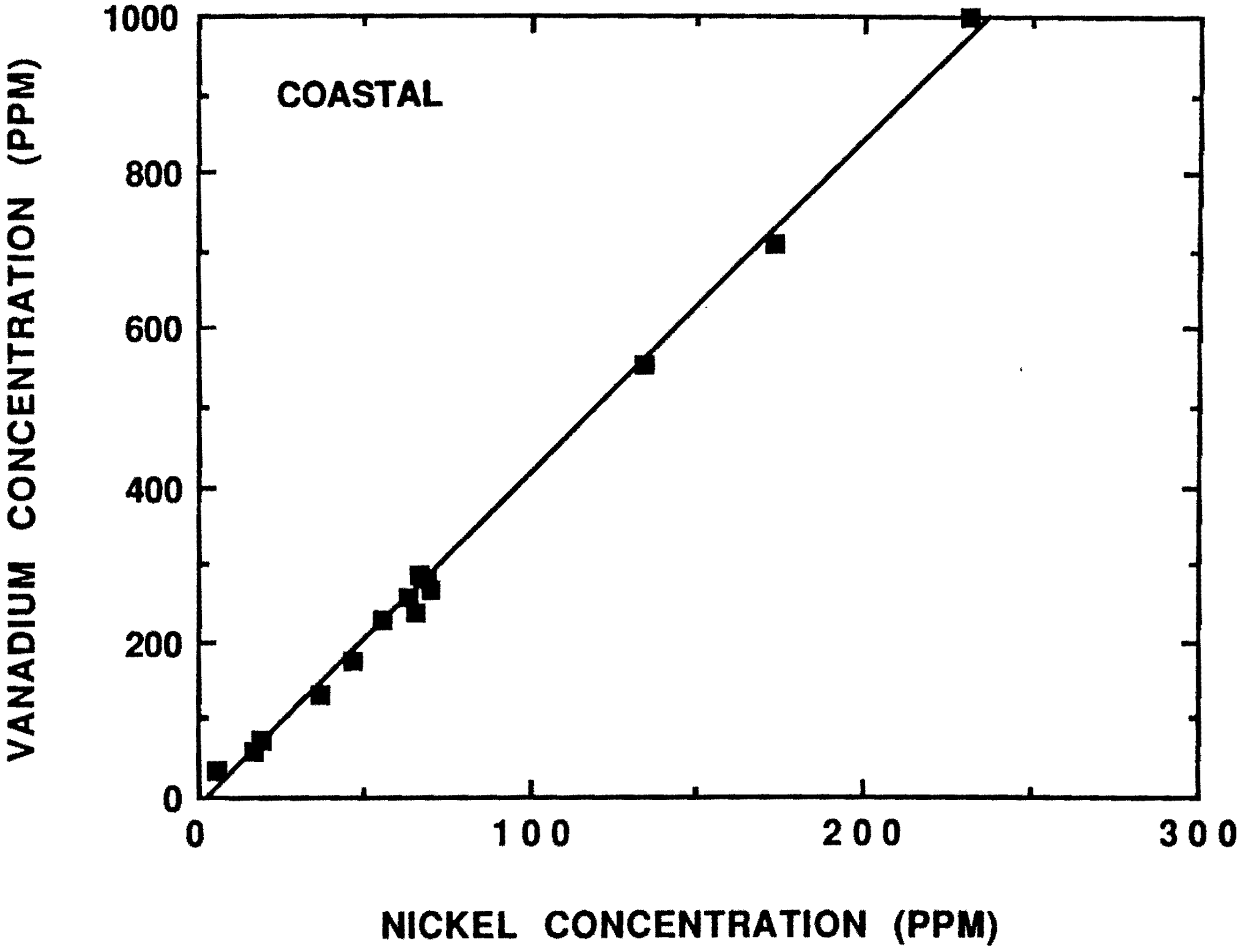

Figure 4-12
Vanadium Versus Nickel - Coastal

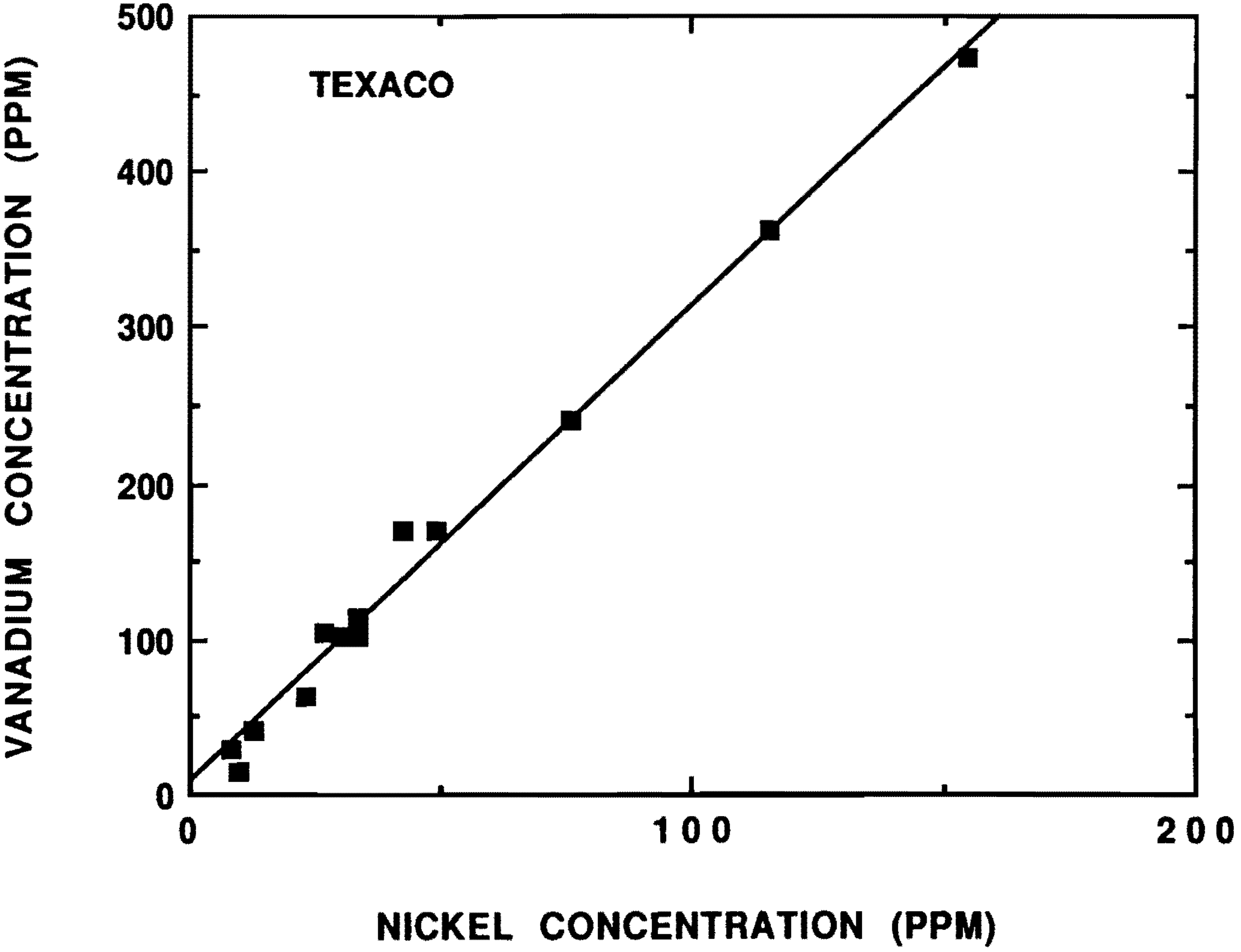

Figure 4-13
Vanadium Versus Nickel - Texaco

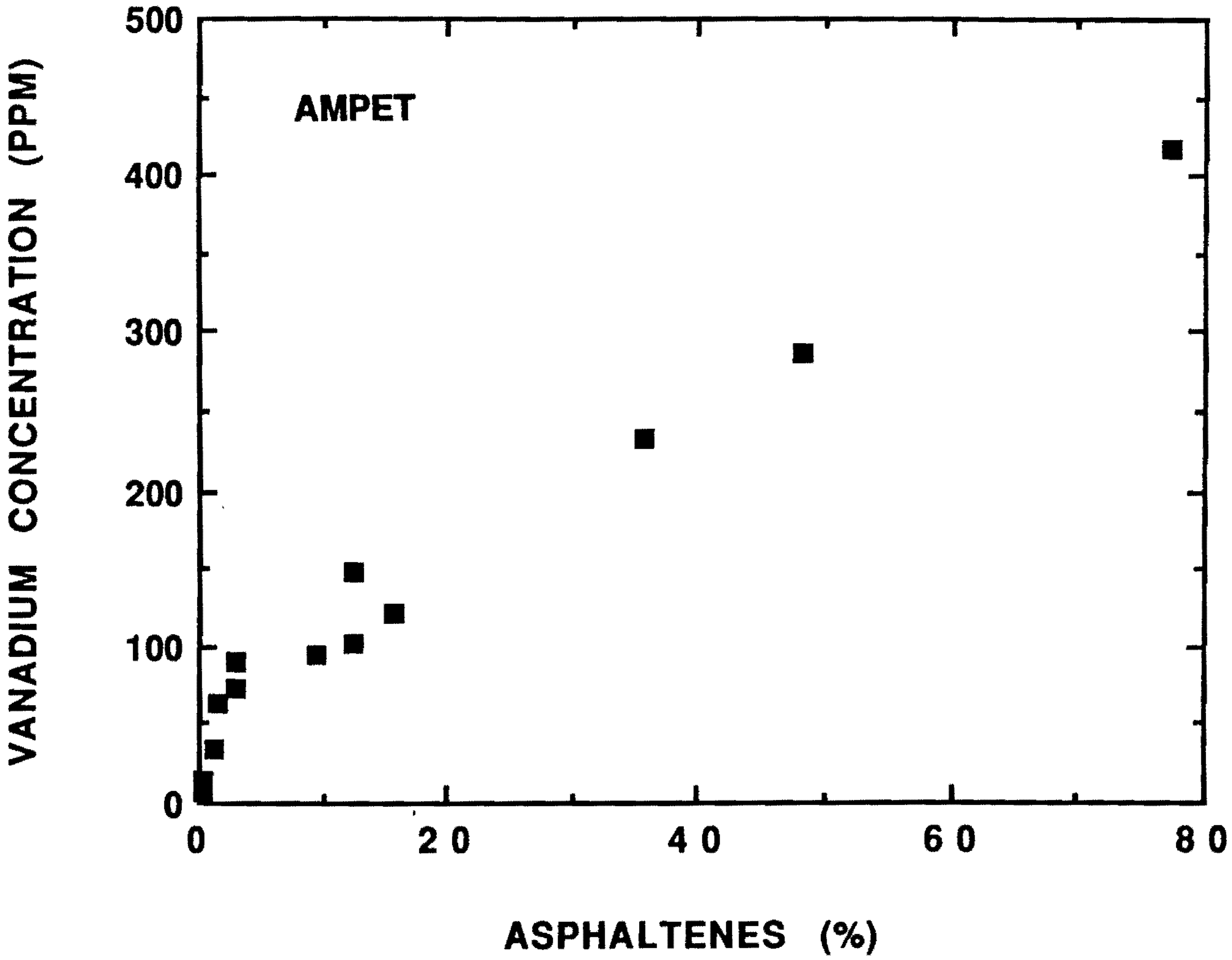

Figure 4-14
Vanadium Versus Asphaltenes - Ampet

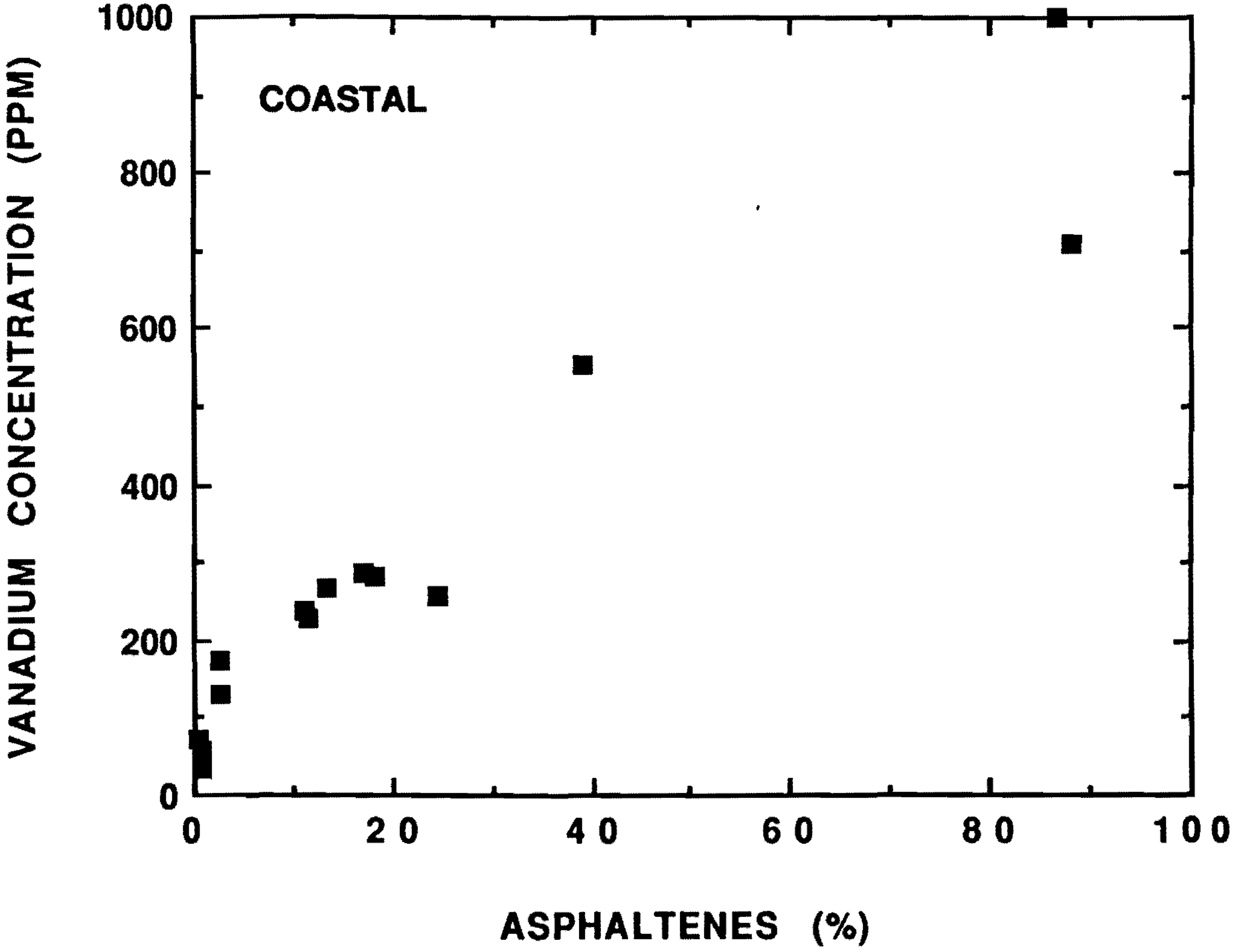

Figure 4-15
Vanadium Versus Asphaltenes - Coastal

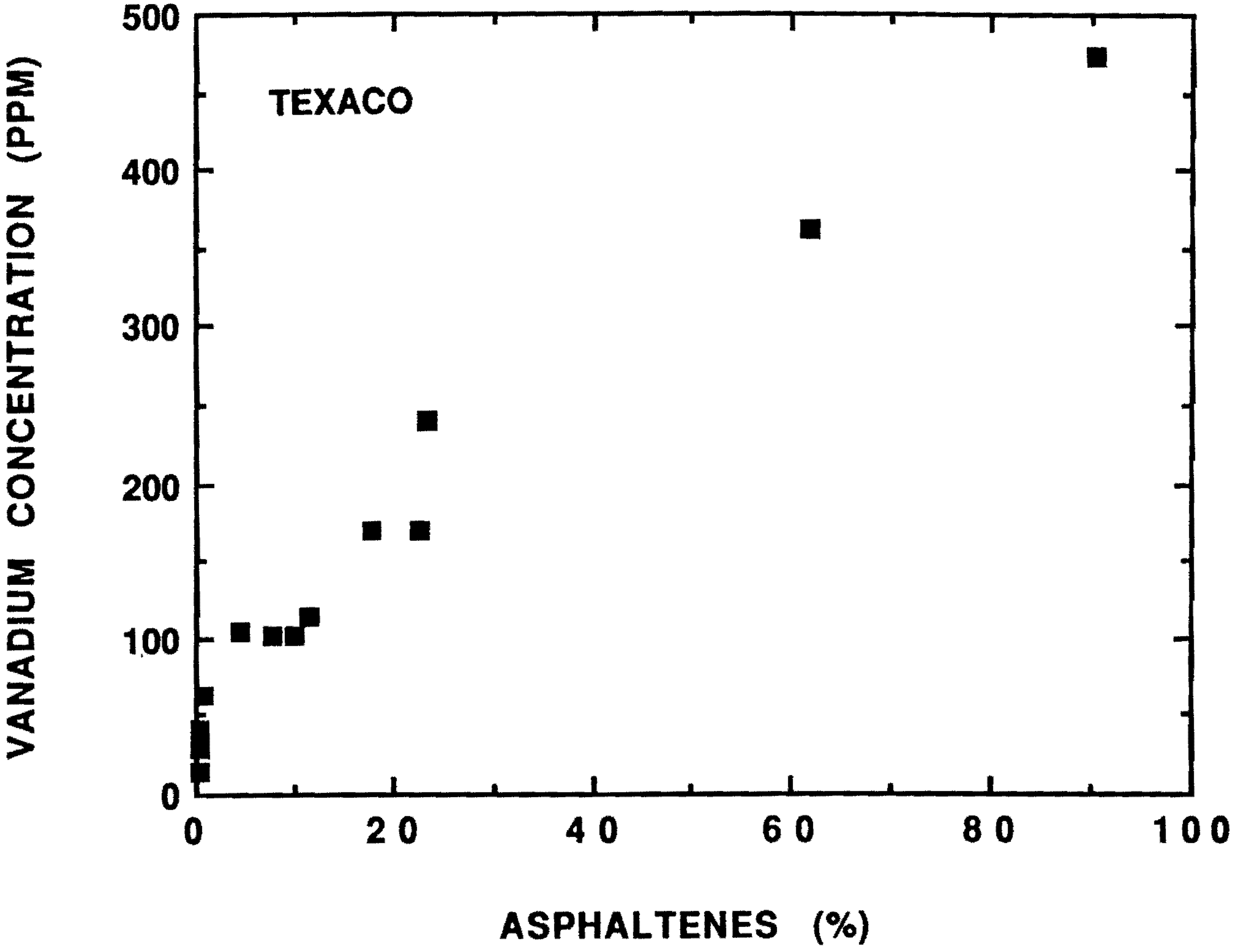

Figure 4-16
Vanadium Versus Asphaltenes - Texaco

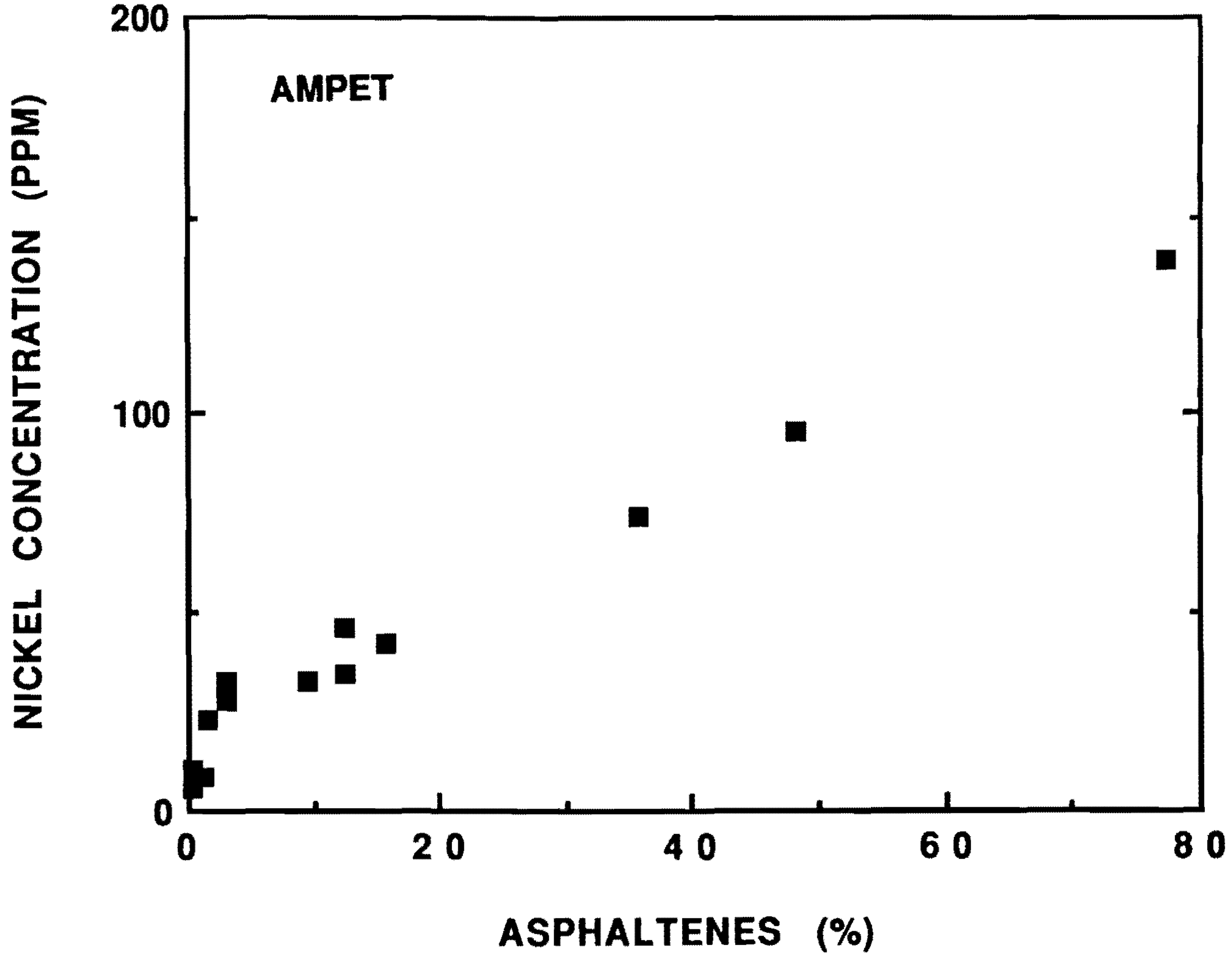

Figure 4-17
Nickel Versus Asphaltenes - Ampet

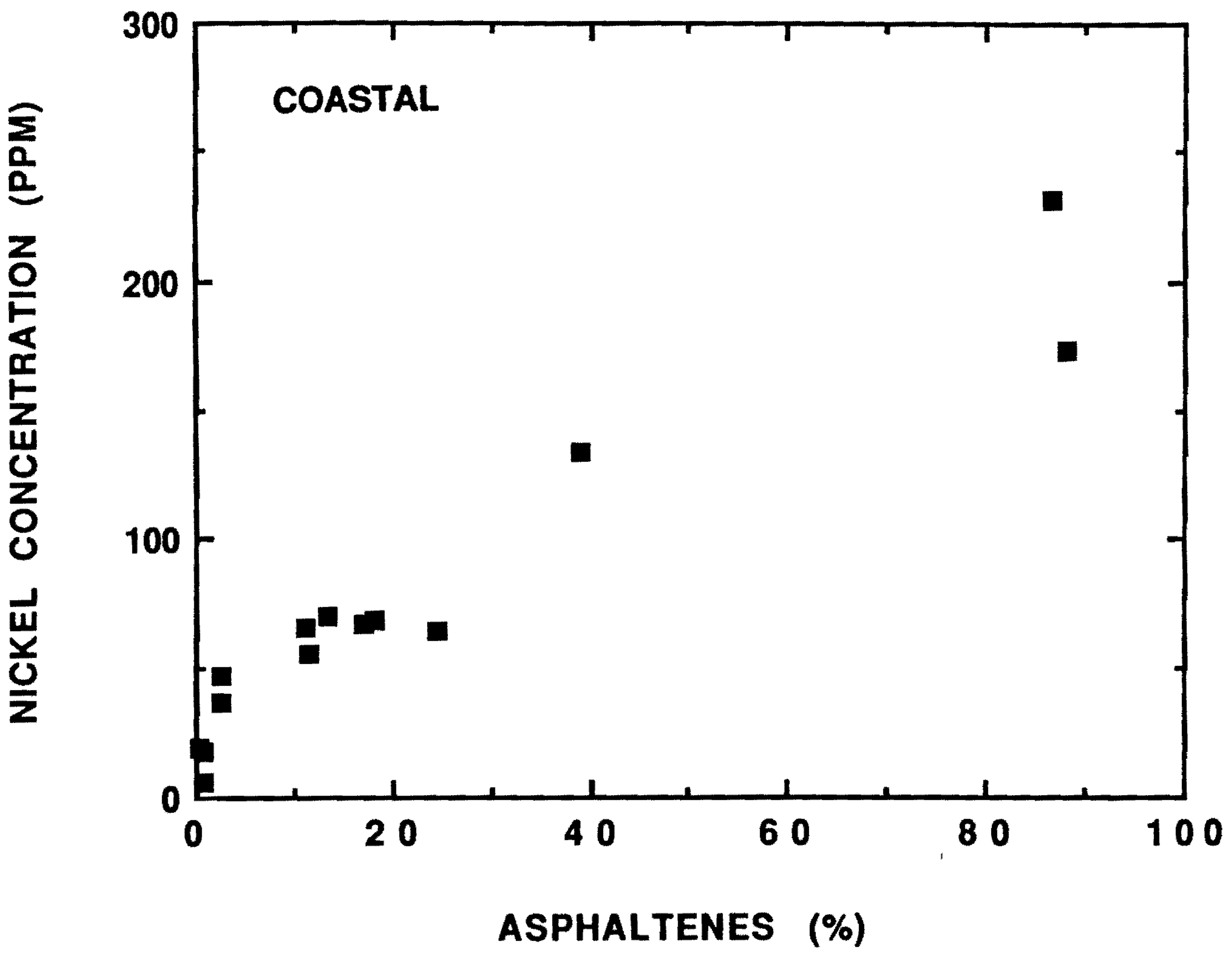

Figure 4-18
Nickel Versus Asphaltenes - Coastal

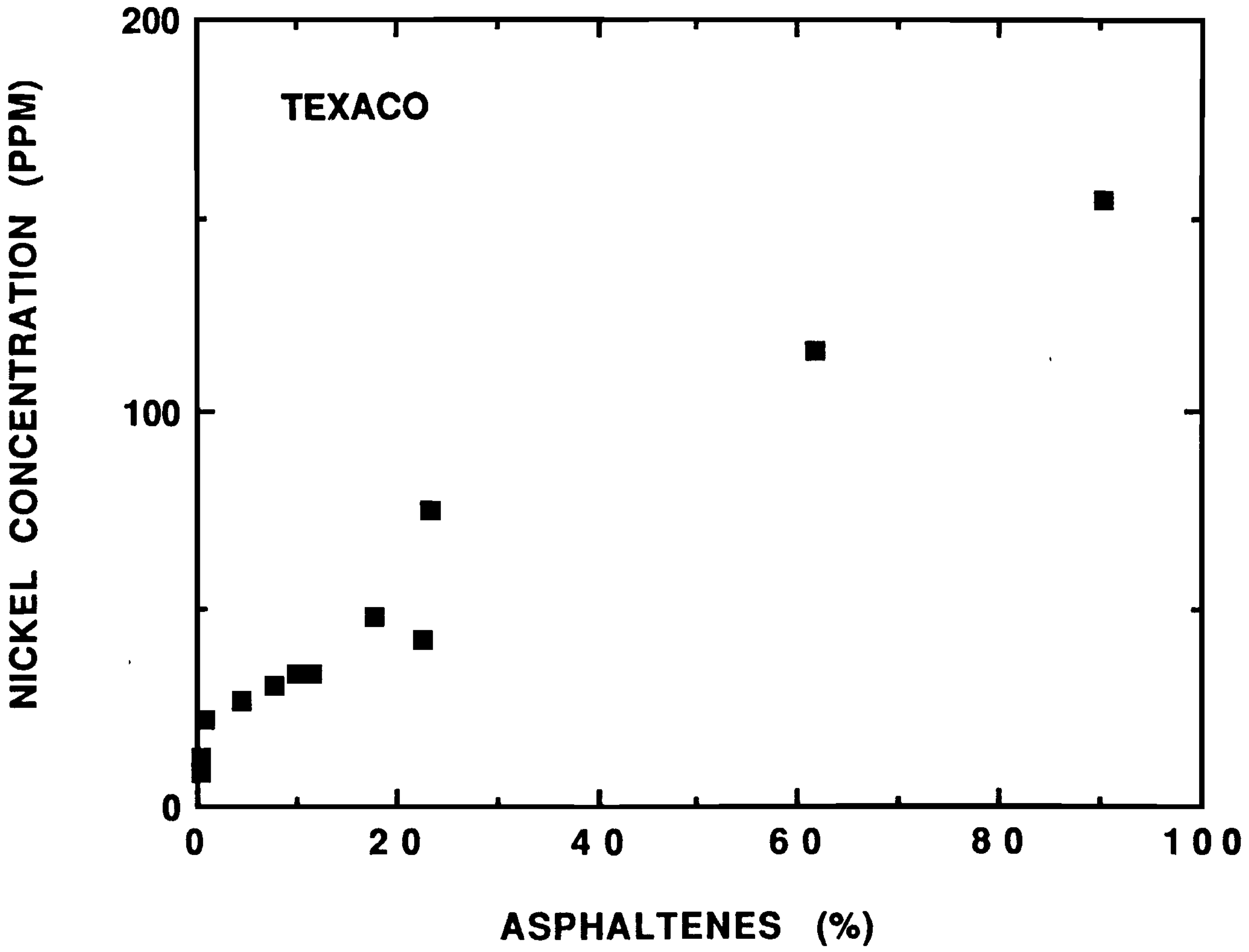

Figure 4-19
Nickel Versus Asphaltenes - Texaco

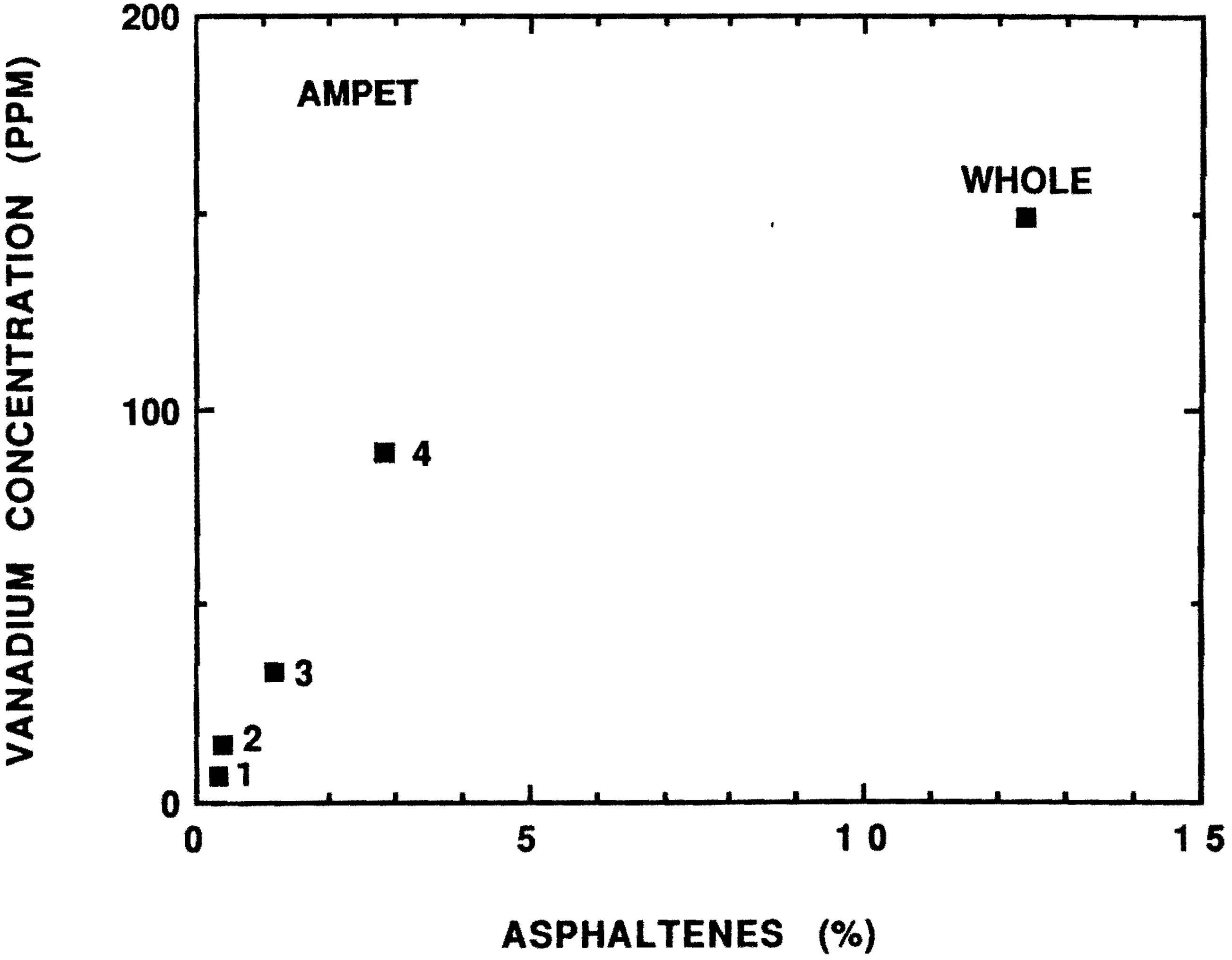

Figure 4-20
Vanadium Versus Asphaltenes -
Ampet Fractions 1-4 and Whole Asphalt

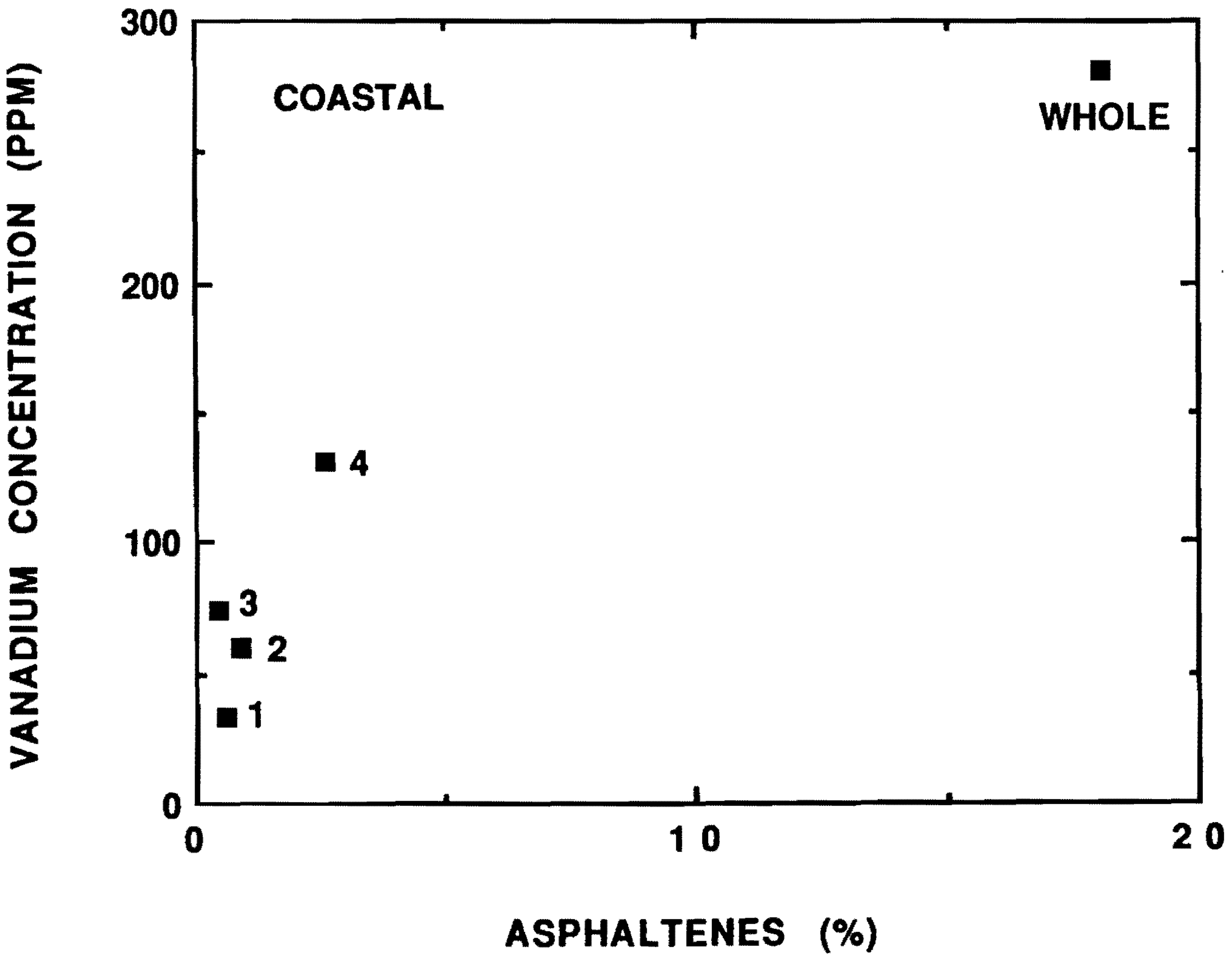

Figure 4-21
Vanadium Versus Asphaltenes -
Coastal Fractions 1-4 and Whole Asphalt

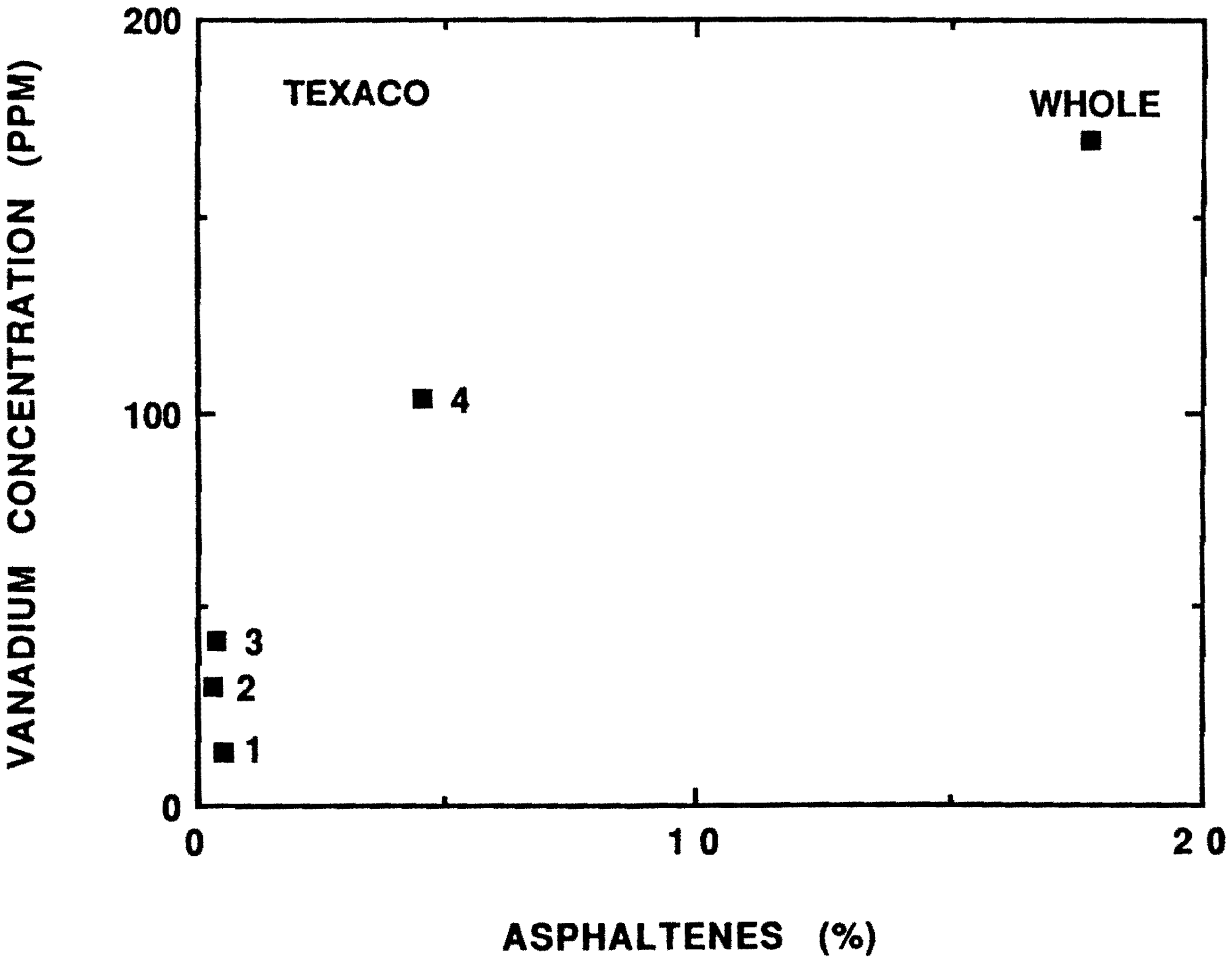

Figure 4-22
Vanadium Versus Asphaltenes -
Texaco Fractions 1-4 and Whole Asphalt

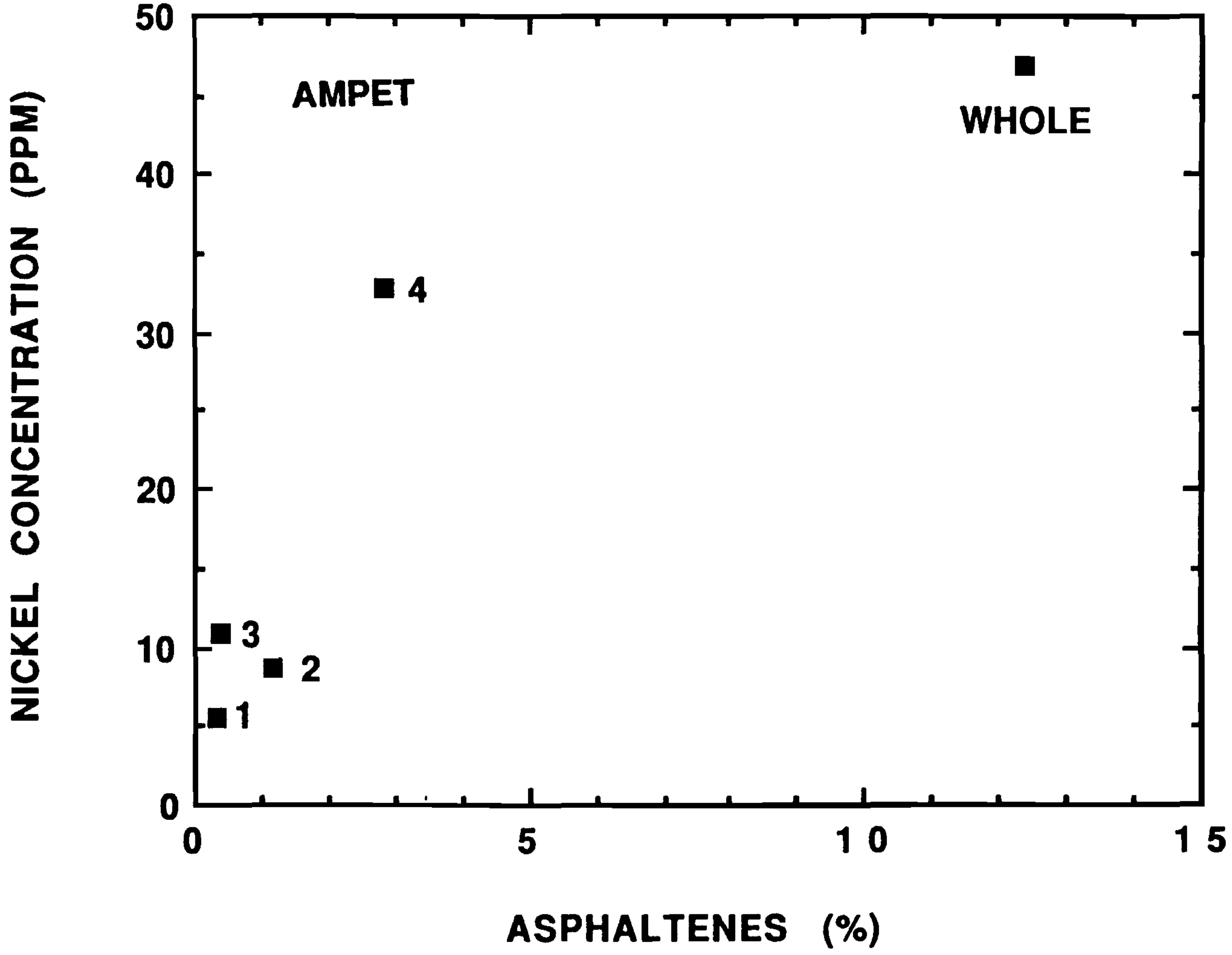

Figure 4-23
Nickel Versus Asphaltenes -
Ampet Fractions 1-4 and Whole Asphalt

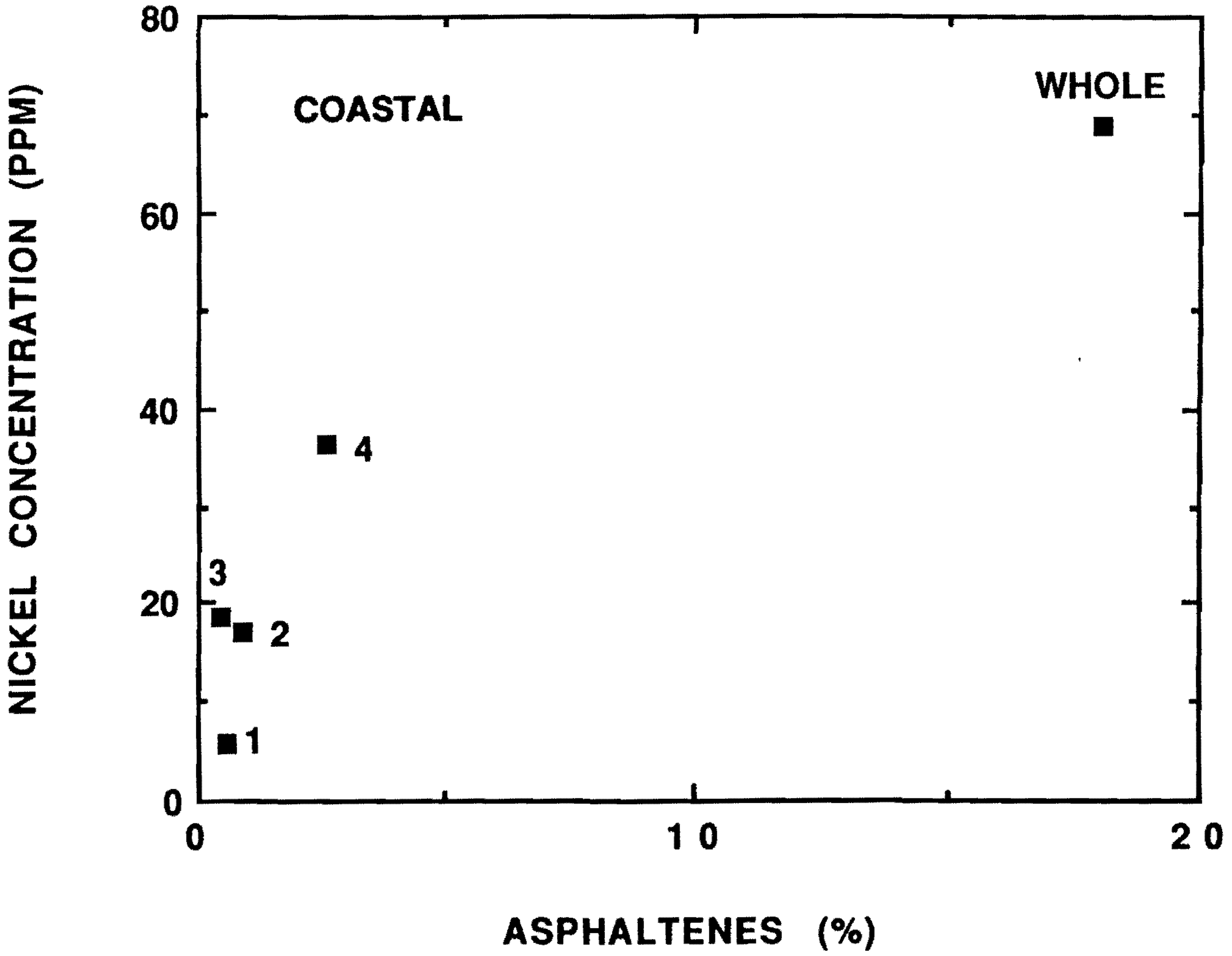

Figure 4-24
Nickel Versus Asphaltenes -
Coastal Fractions 1-4 and Whole Asphalt

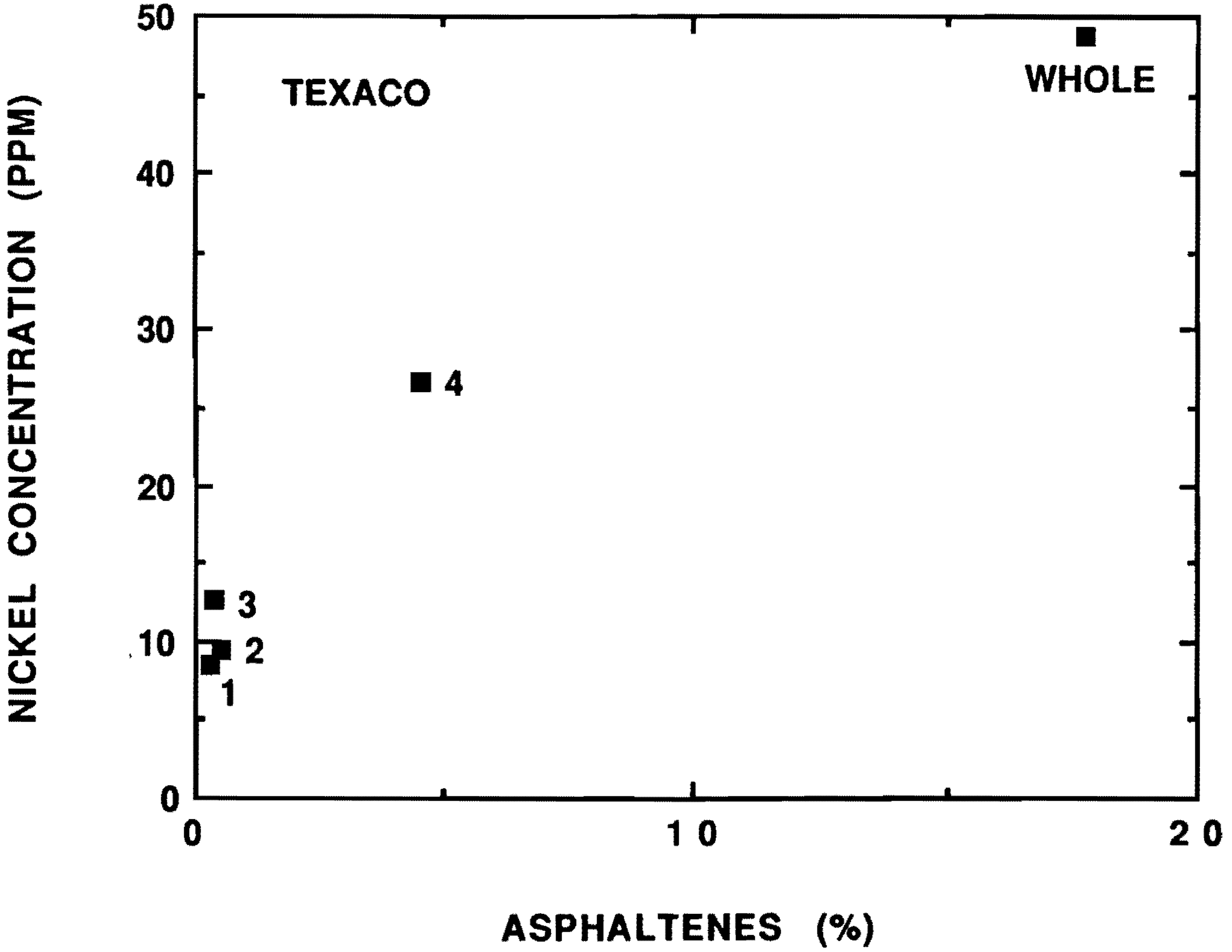

Figure 4-25
Nickel Versus Asphaltenes -
Texaco Fractions 1-4 and Whole Asphalt

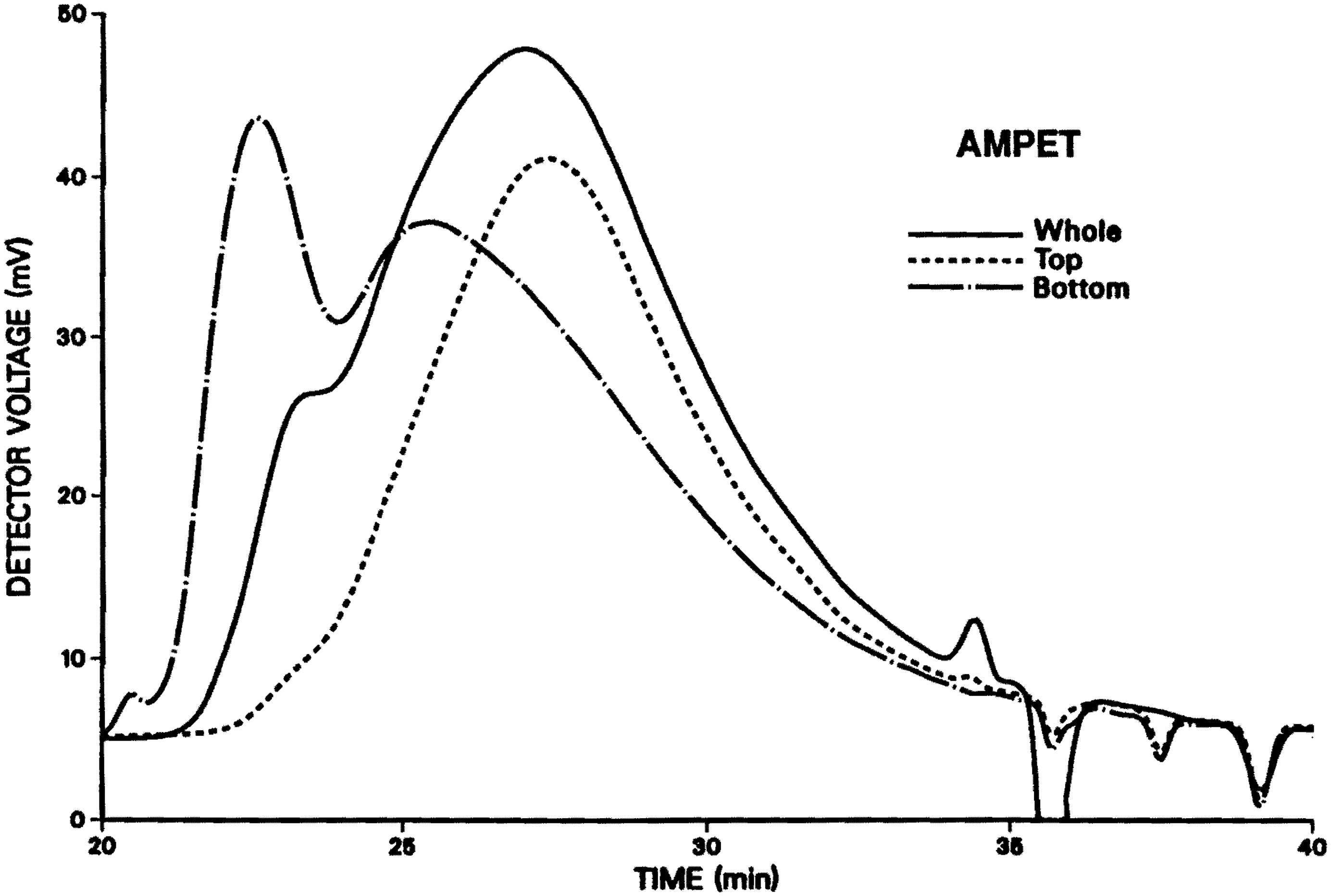

Figure 4-26
GPC Chromatograms of Ampet Whole
and Top and Bottom Fractions

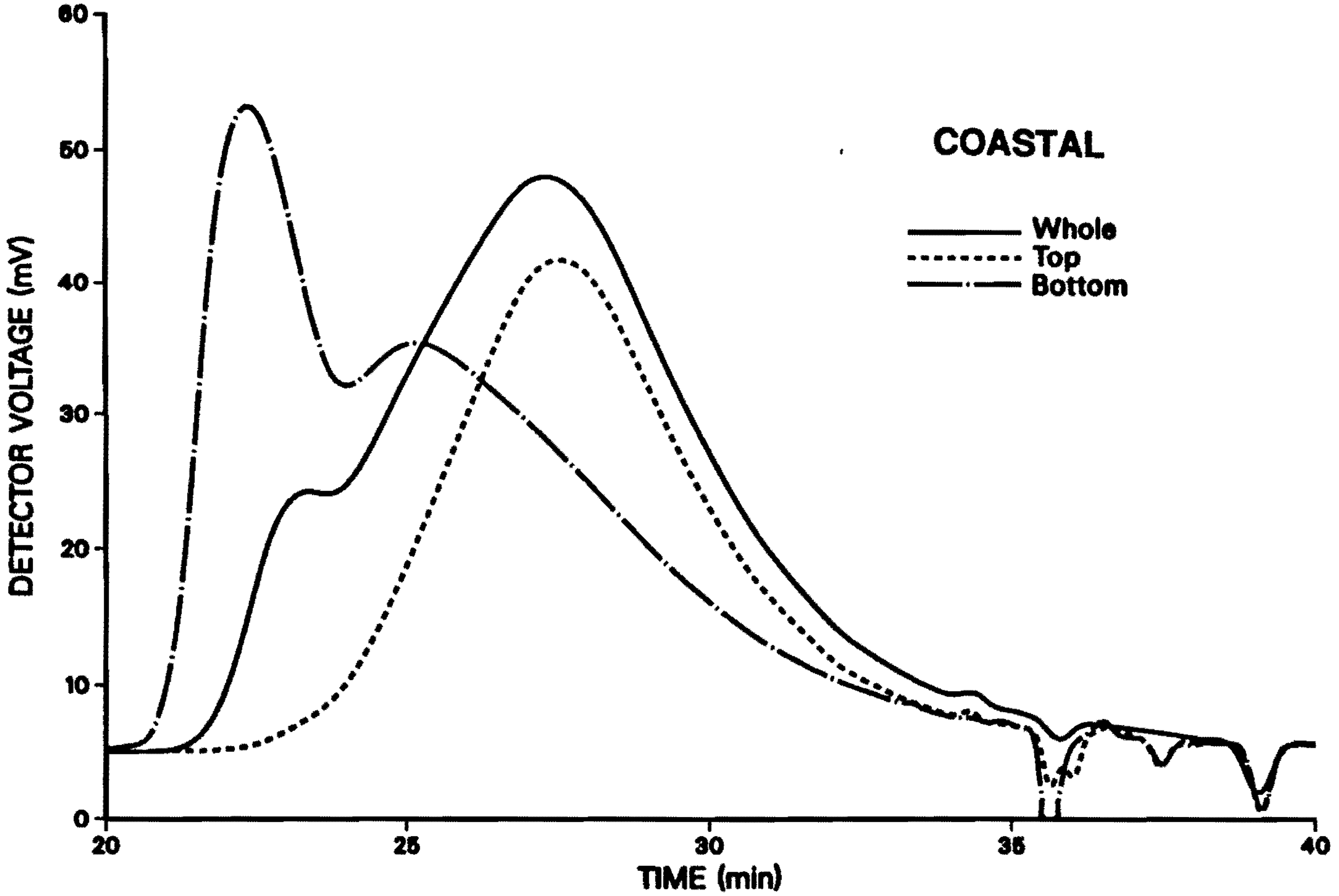

Figure 4-27
GPC Chromatograms of Coastal Whole
and Top and Bottom Fractions

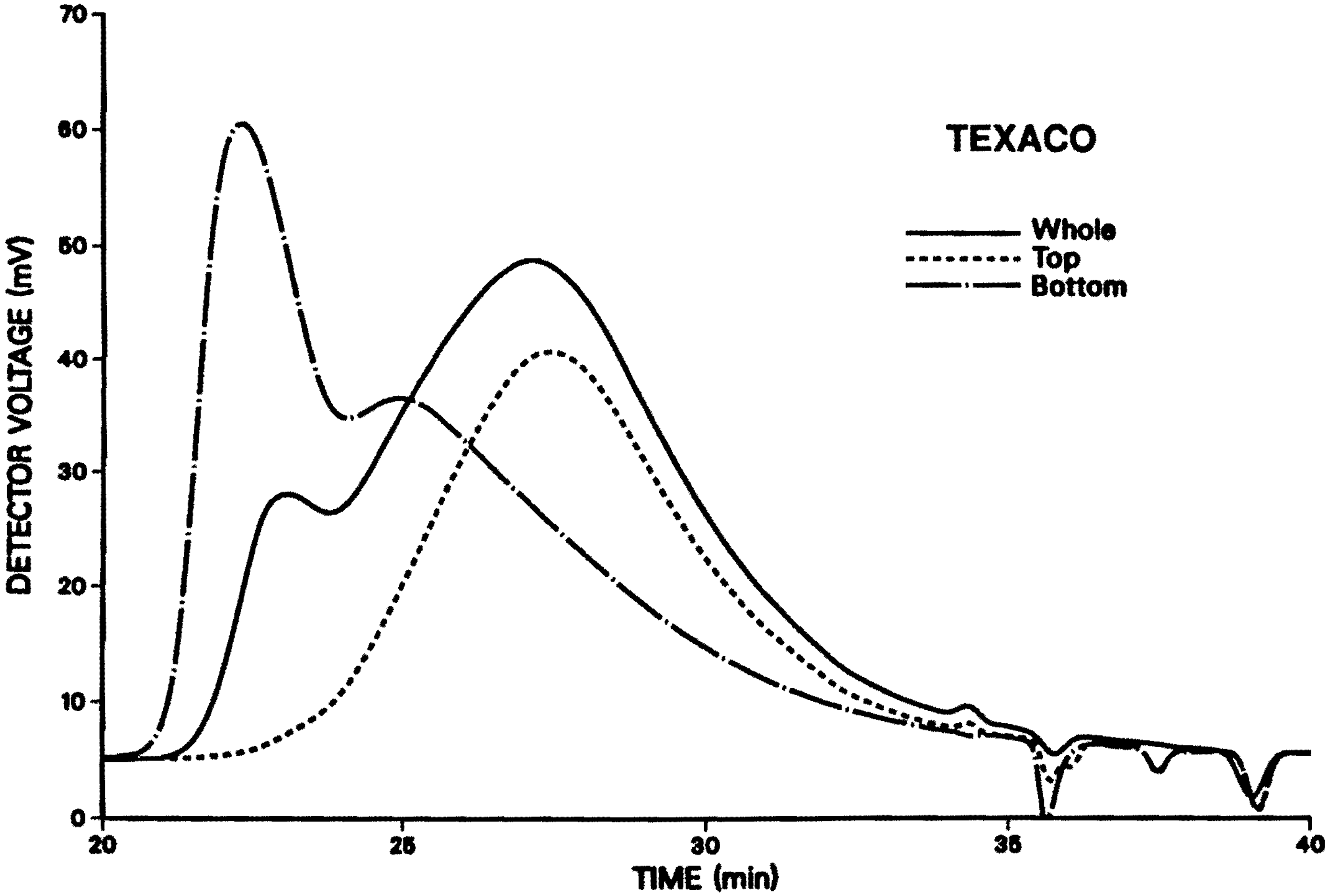

Figure 4-28
GPC Chromatograms of Texaco Whole
and Top and Bottom Fractions

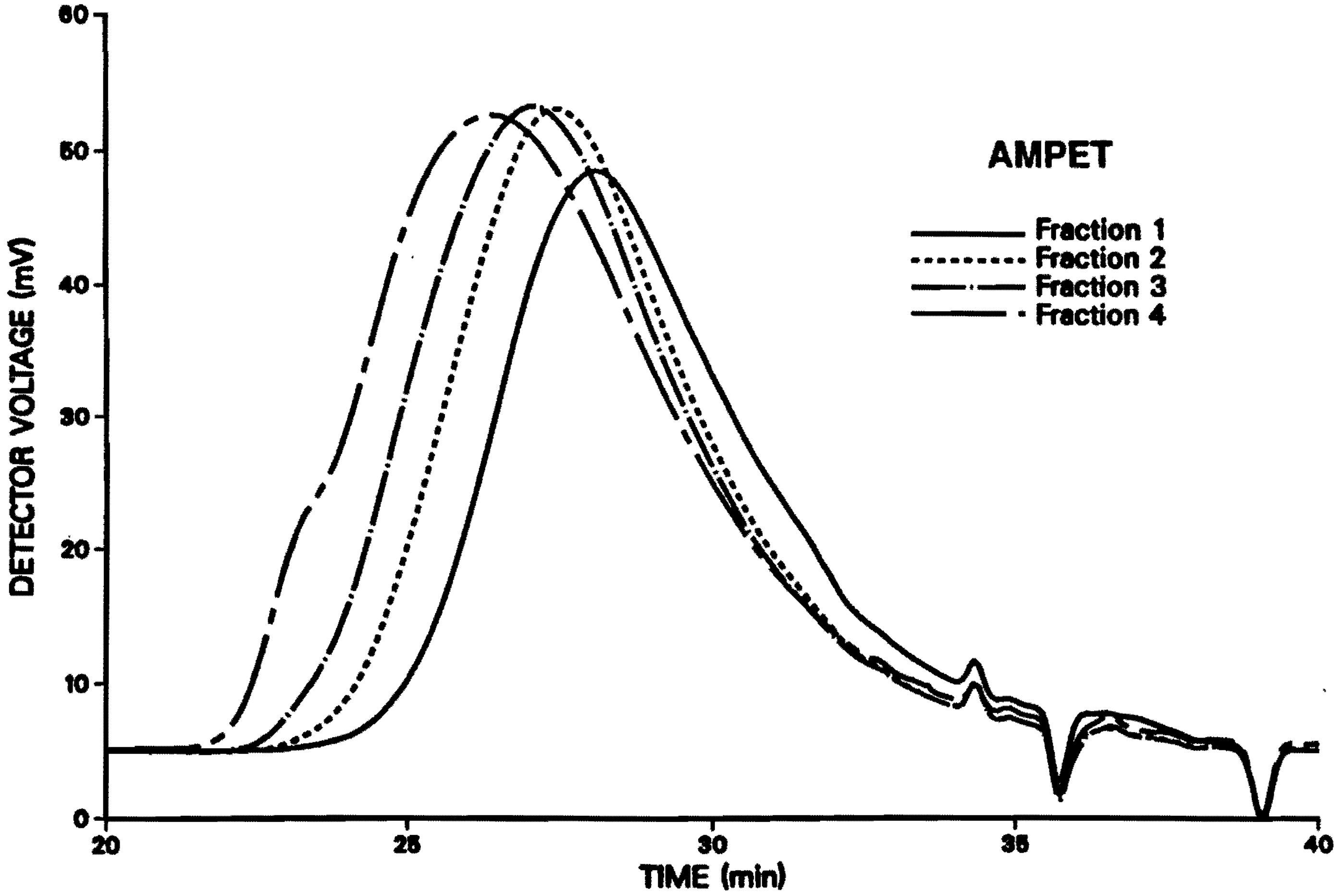

Figure 4-29
GPC Chromatograms of Ampet Fractions 1-4

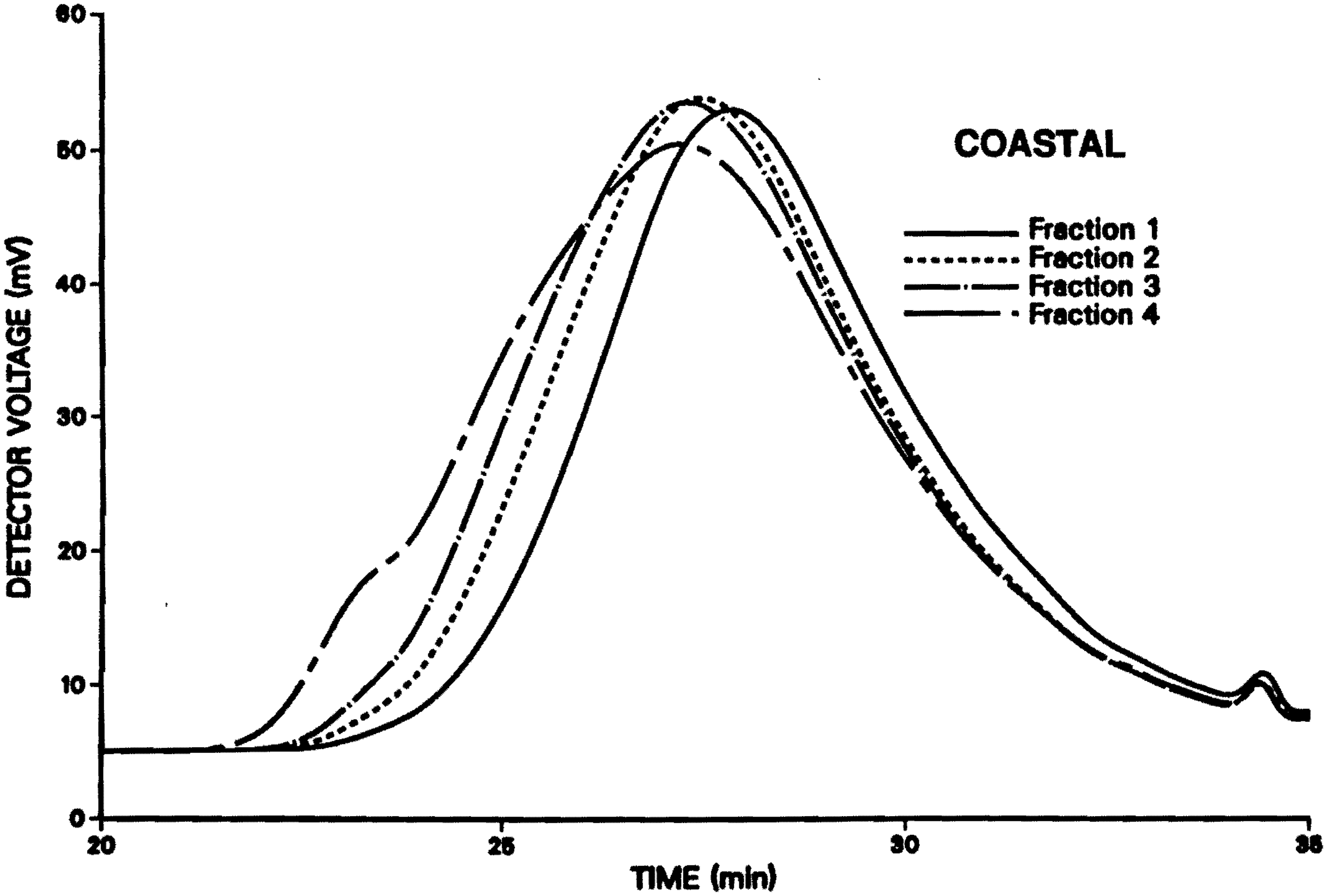

Figure 4-30
GPC Chromatograms of Coastal Fractions 1-4

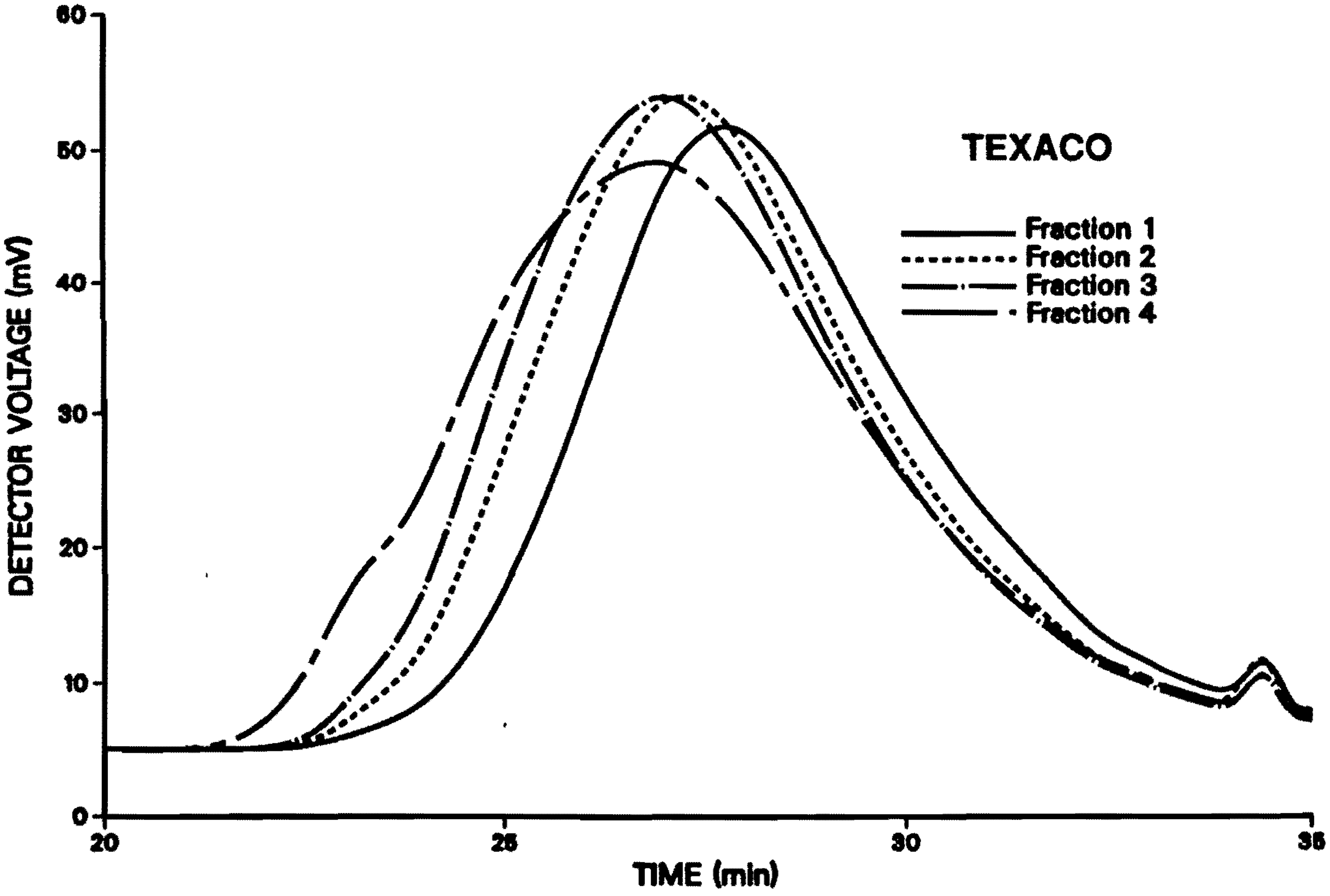

Figure 4-31
GPC Chromatograms of Texaco Fractions 1-4

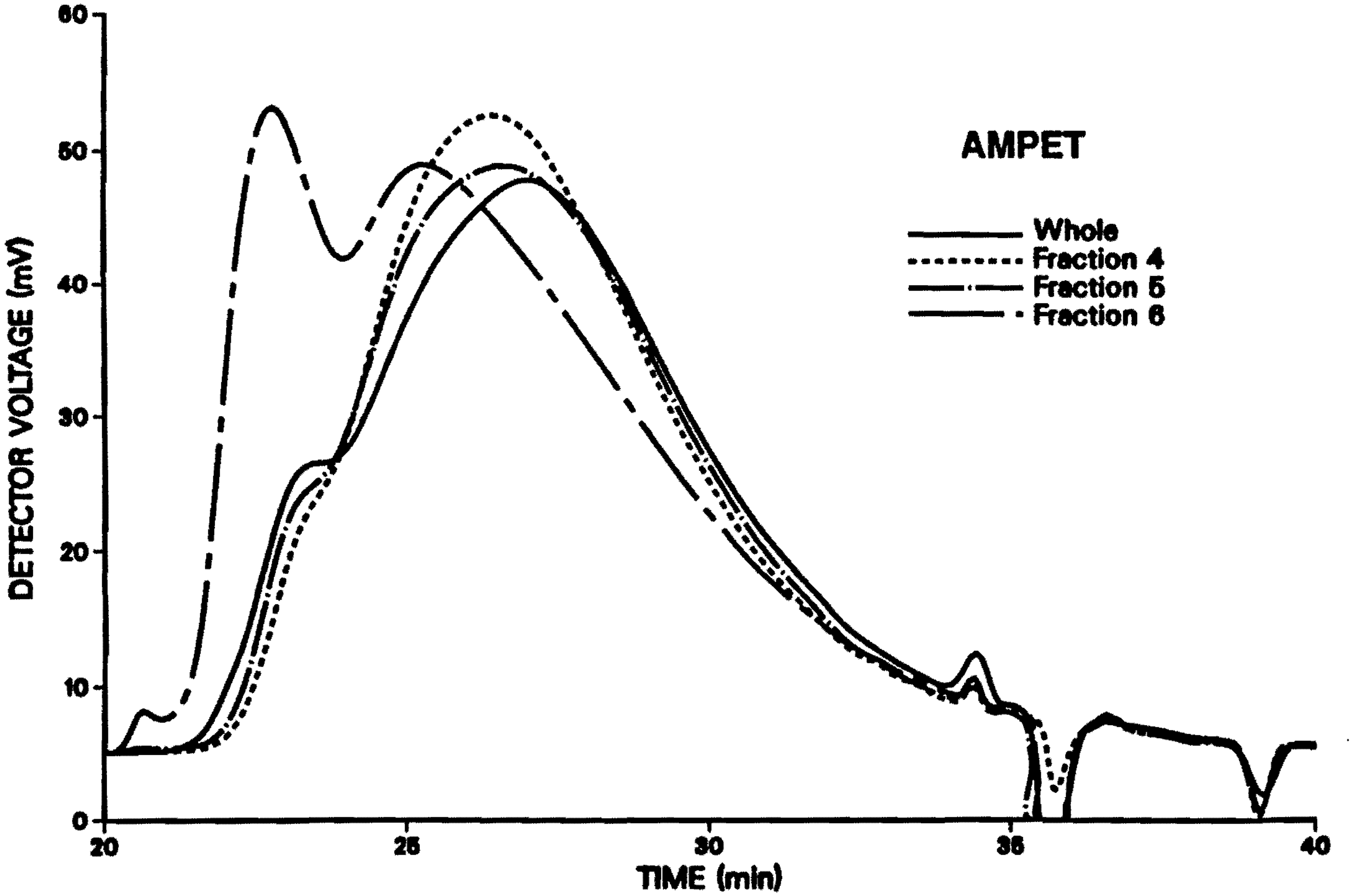

Figure 4-32
GPC Chromatograms of Ampet Whole and Fractions 4-6

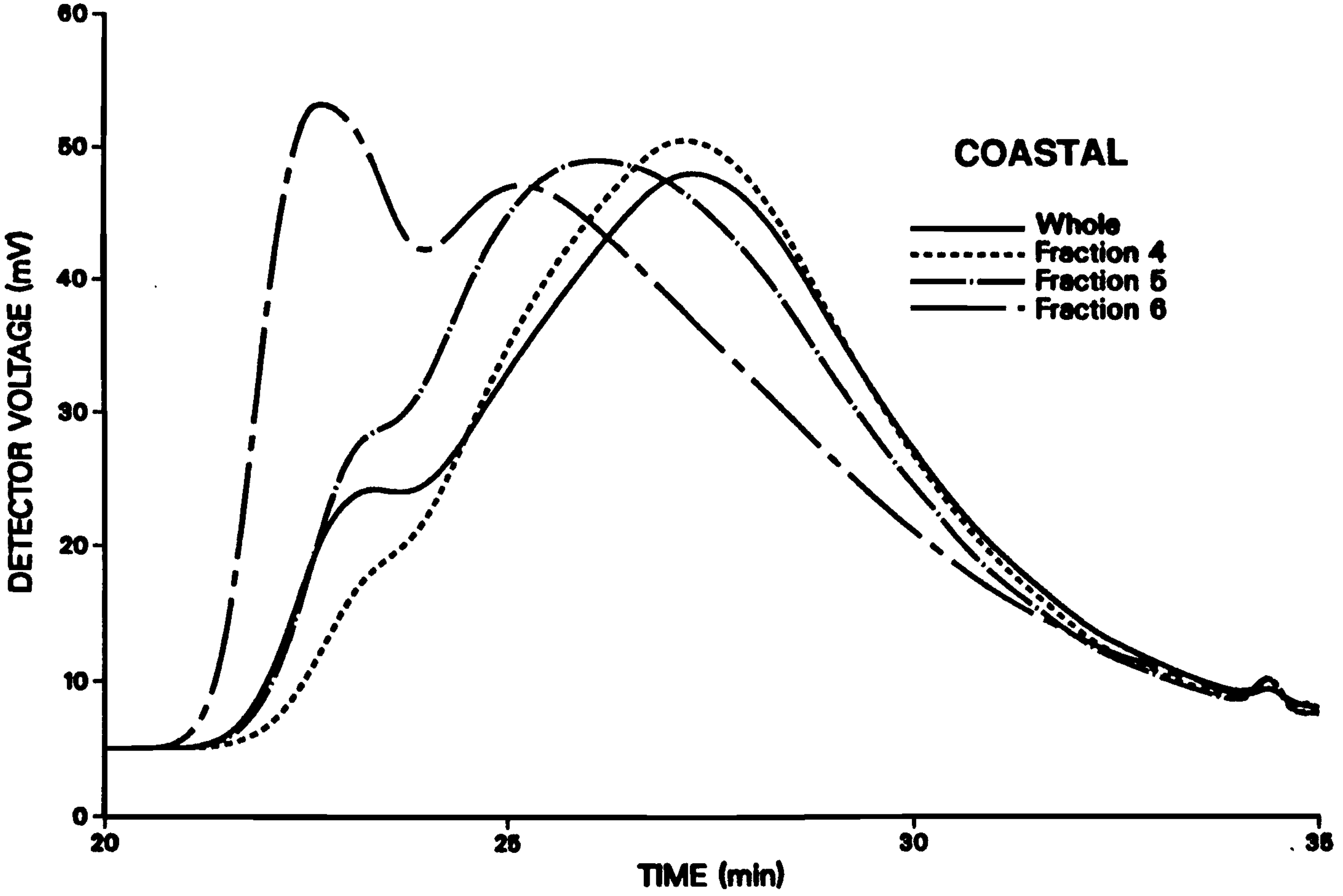

Figure 4-33
GPC Chromatograms of Coastal Whole and Fractions 4-6

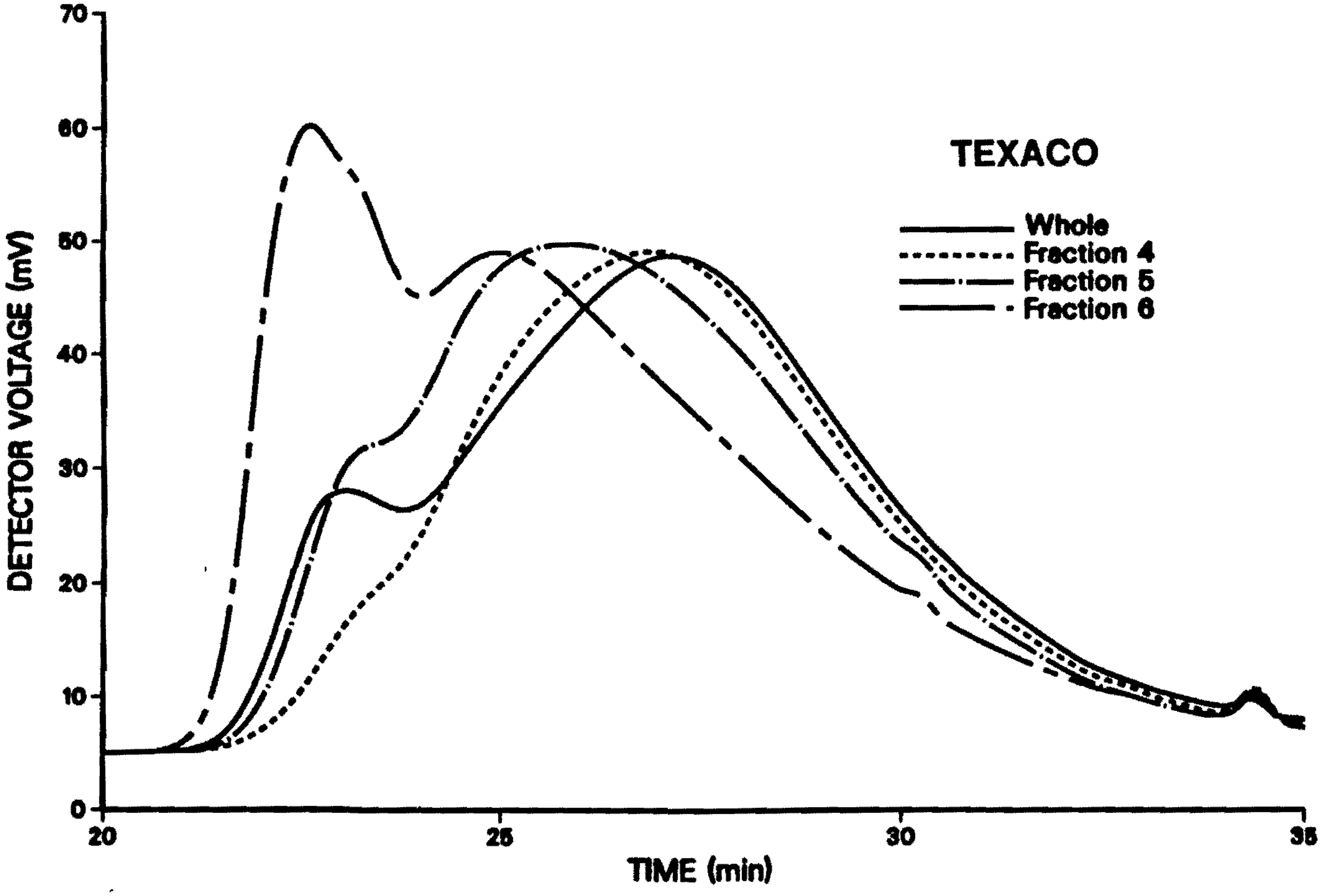

Figure 4-34
GPC Chromatograms of Texaco Whole and Fractions 4-6

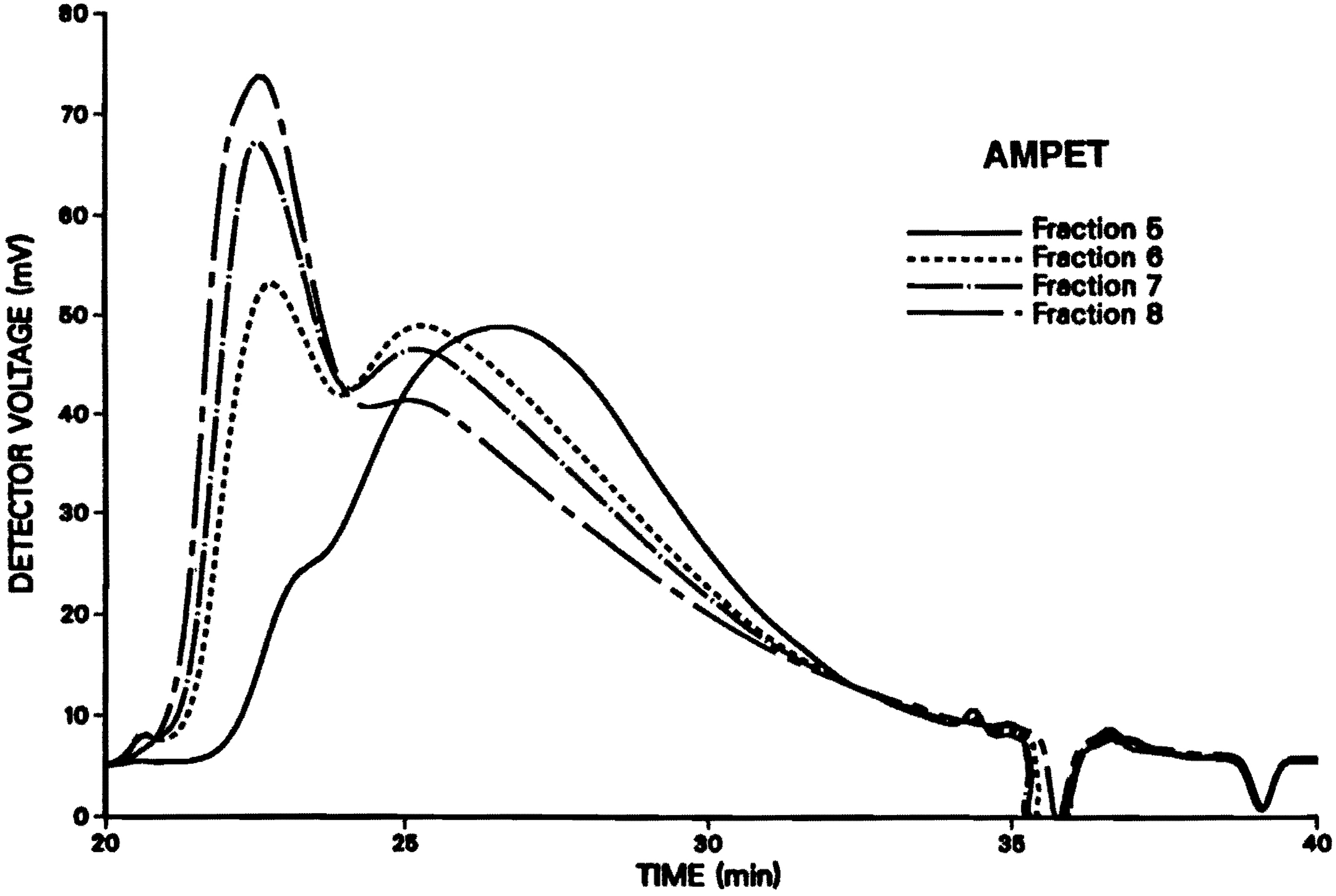

Figure 4-35
GPC Chromatograms of Ampet Fractions 5-8

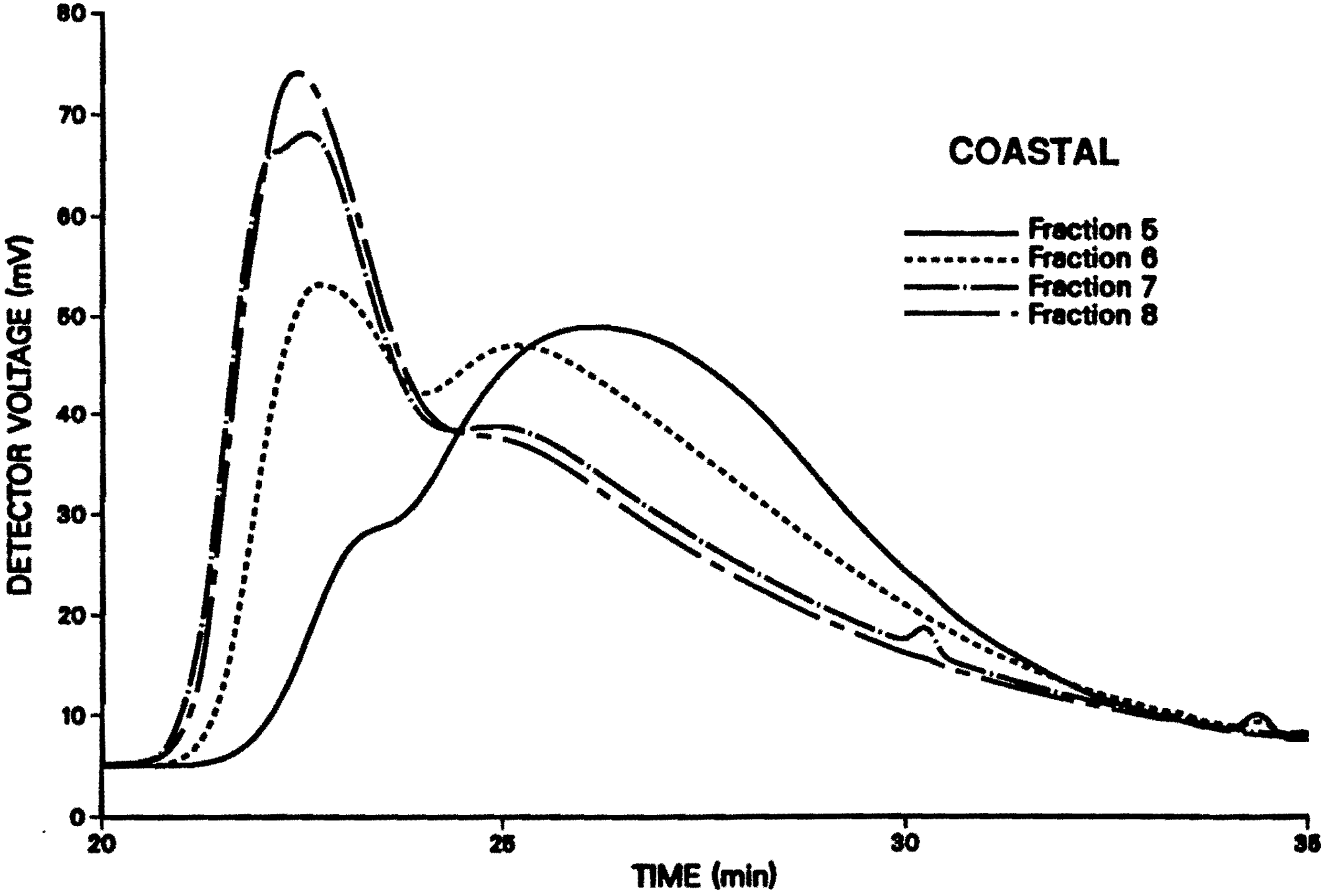

Figure 4-36
GPC Chromatograms of Coastal Fractions 5-8

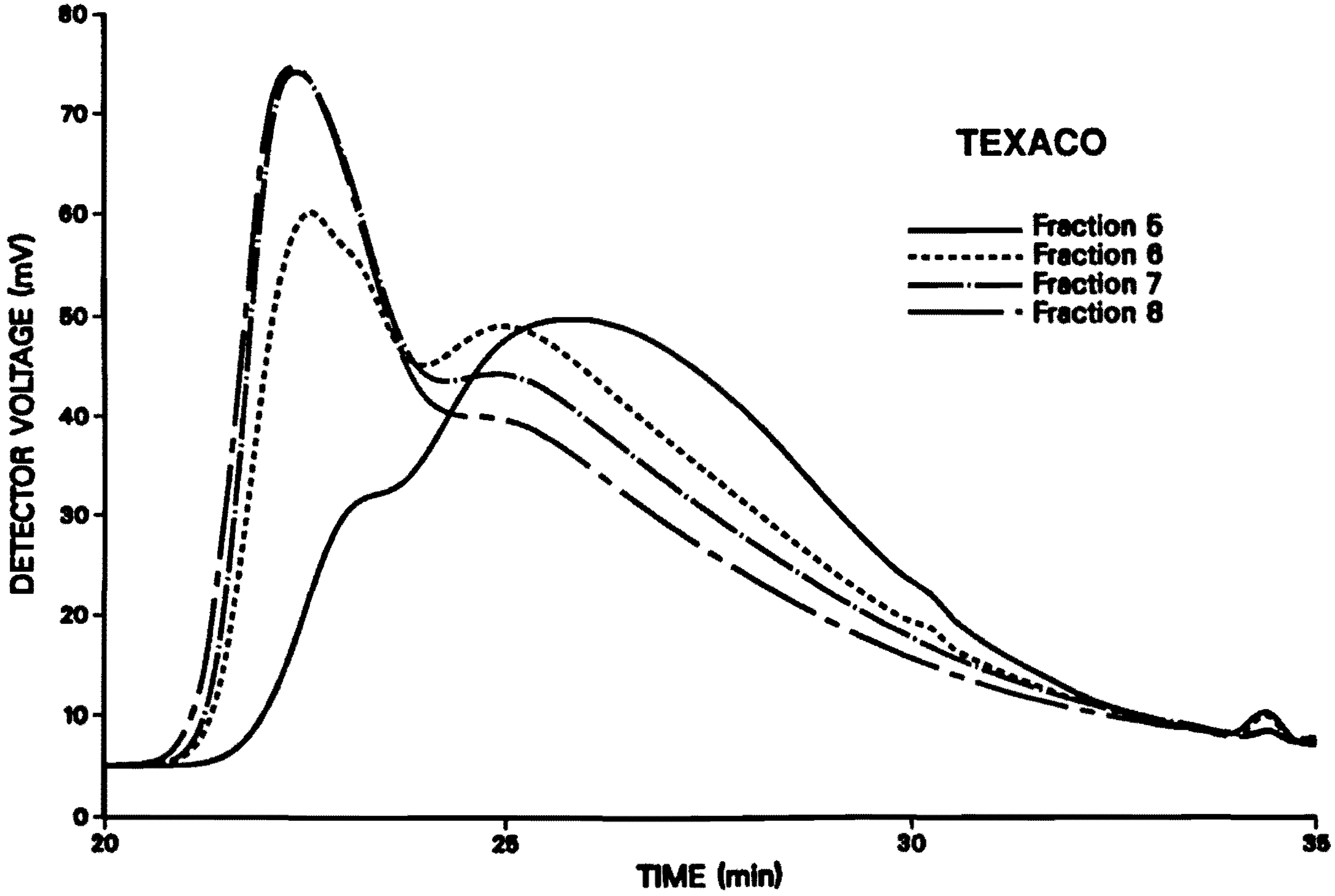

Figure 4-37
GPC Chromatograms of Texaco Fractions 5-8

Figures 4-29 to 4-31 show a steady increase in molecular size for fractions 1 to 4 which were obtained by fractionating the top material. Ampet differs again from the other two having a higher molecular size fraction 4 that likely accounts for the previously noted shoulder in the top material chromatograms and also for its much higher viscosity.

Figure 4-32 to 4-34 compare the whole asphalt to fractions 4, 5, and 6. Again Ampet differs from Coastal and Texaco. Coastal and Texaco show maxima for the whole asphalt and fraction 4 near 27 minutes, though the fraction 4s lack the prominent LMS peak (node) of the whole asphalts, having only a gentle shoulder. Fraction 5 begins in a manner similar to fraction 4 for these two asphalts but the maxima for fraction 5 are clearly of higher molecular size than fraction 4, occurring at about 26 minutes. With Ampet, on the other hand, fractions 4, 5, and the whole asphalt are rather close in molecular size distribution. Interestingly, Ampet fractions 4 and 5 have nearly the same viscosity while the viscosity of 4 is significantly lower than the whole asphalt and fraction 5 for the other two. Fraction 5 for Texaco and Coastal have almost identical viscosities but the chromatograms do not suggest that the fraction 5 viscosity would actually be lower than the AC-20 grade whole asphalts. This is no doubt the result of the near absence of asphaltenes in fraction 5.

Fraction 6 contains markedly higher molecular size material than fraction 5 for all the asphalts. This is not surprising since fraction 5 is the pentane solubles and, therefore, contains little asphaltenes. Figure 4-35 to 4-37 show fractions 5 through 8. These sets of chromatograms are quite similar. Fraction 6 is the most evenly binodal and, as expected, is shifted to the lower molecular size material, especially for Texaco.

GPC Analysis of the Corbett Fractions of the Solvent-Separated Fractions

Where possible, GPC analyses were made of all the Corbett fractions on the whole asphalts and their fractions. For a few samples, insufficient material was available. When only a very small Corbett fraction exists, considerable error can occur from the cut-point determination, and this probably accounts for some anomalies that will be noted. Because there are a rather large number of these chromatograms, only a sample will be found here and the rest are in Appendix B.

Figures 4-38 and 4-39 show chromatograms for the saturates in fractions 1 to 5 and the whole asphalt for the Coastal asphalt. There is remarkably little variation, indicating that pentane may have shown poor selectivity for saturates. Texaco and Ampet saturates do show significant deviation of fraction 1 from the others (Figures B-7 and B-42). Also, Texaco shows a large deviation in fraction 4 in the LMS region that is almost surely contamination; saturates do not have such LMS material.

The Texaco naphthene aromatics are shown for all eight fractions and the whole asphalt in Figures 4-40 through 4-42. Fractions 1 to 4 are in a smooth progression in Figure 4-40 with the heavier fractions (higher fraction number) being shifted to larger molecular size. This progression is typical of the other asphalts as well although the Ampet naphthene aromatics from fractions 1 to 4 (Figure B-10) show an even greater separation whereas those from the Coastal fractions 2 and 3 (Figure B-28) are close to each other though well separated from fractions 1 and 4.

The naphthene aromatics for the upper fractions, 5 through 8, do not show this monotonic trend to larger molecular size, however. Naphthene aromatics for Texaco fractions 5 to 8 are shown in Figure 4-42. The results are quite anomalous with the naphthene aromatics from fraction 6 showing a larger molecular size than those from fraction 7 and about the same as those from fraction 8. Ampet (Figure B-12) showed a peak in the amount of large molecular size naphthene aromatic material at fraction 7 with the fraction 8 naphthene aromatics having considerably less large molecular size material than 7 and even 6. There was not enough Coastal material to run, but there was considerable fraction 6 and 7 material for the other two. These results should be viewed with some skepticism, but in view of the polar aromatics results (discussed below) a peak in the amount of large molecular size naphthene aromatics at about fraction 7 may be real.

The polar aromatics analyses of the fractions parallel those of the naphthene aromatics. Results for Ampet are shown in Figures 4-43 through 4-45. The polar

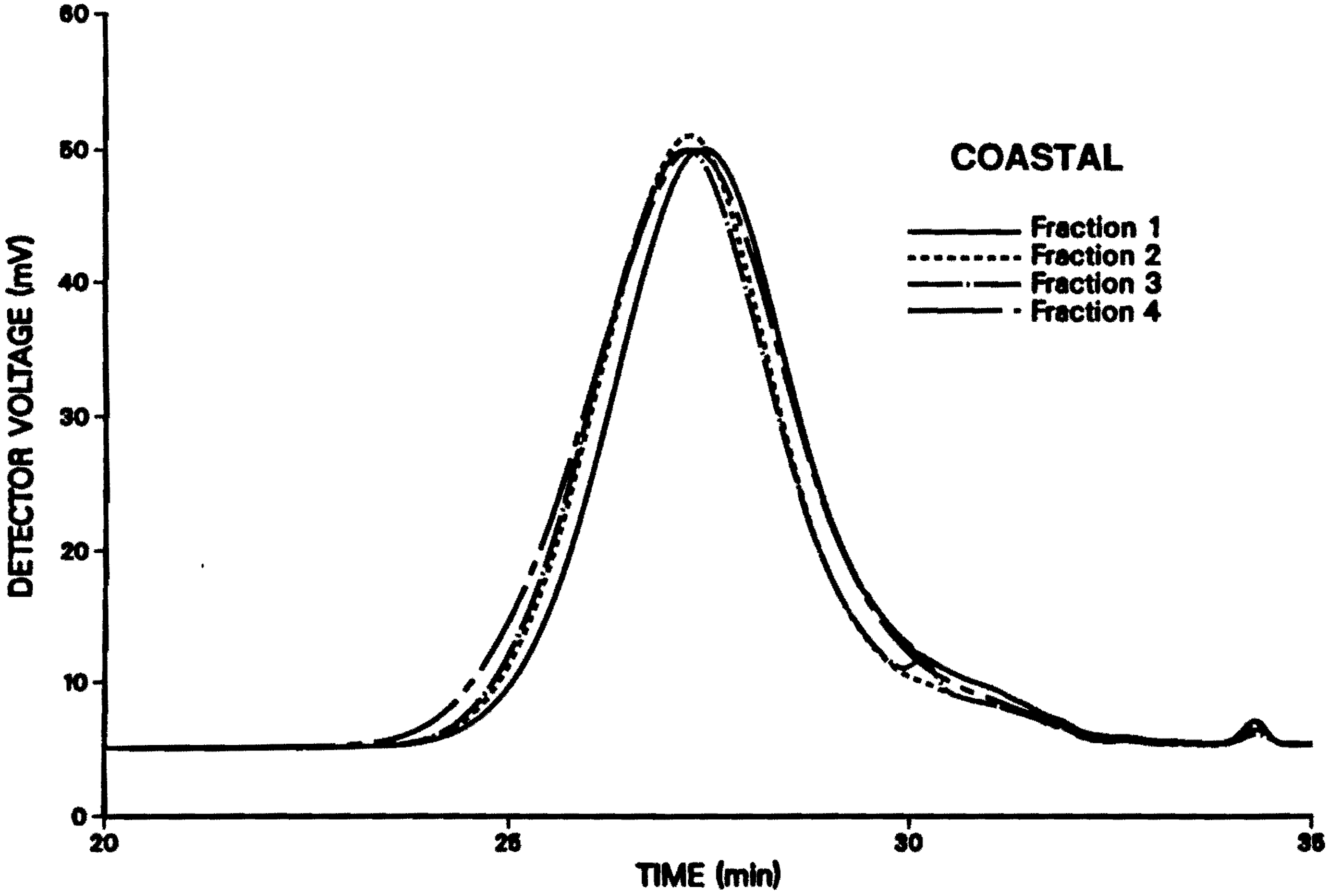

Figure 4-38
GPC Chromatograms of Saturates from Coastal Fractions 1-4

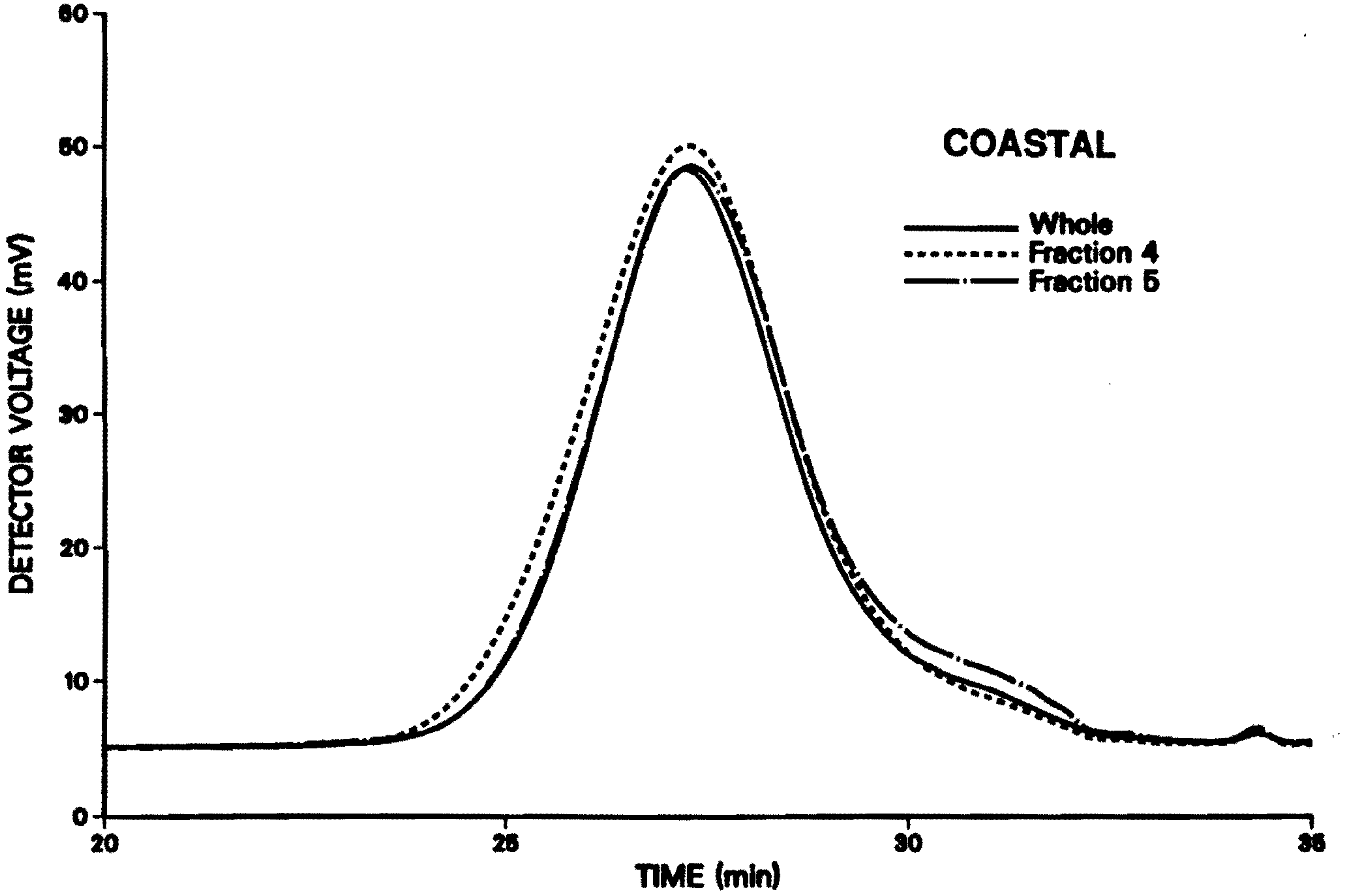

Figure 4-39
GPC Chromatograms of Saturates from
Coastal Whole and Fractions 4 and 5

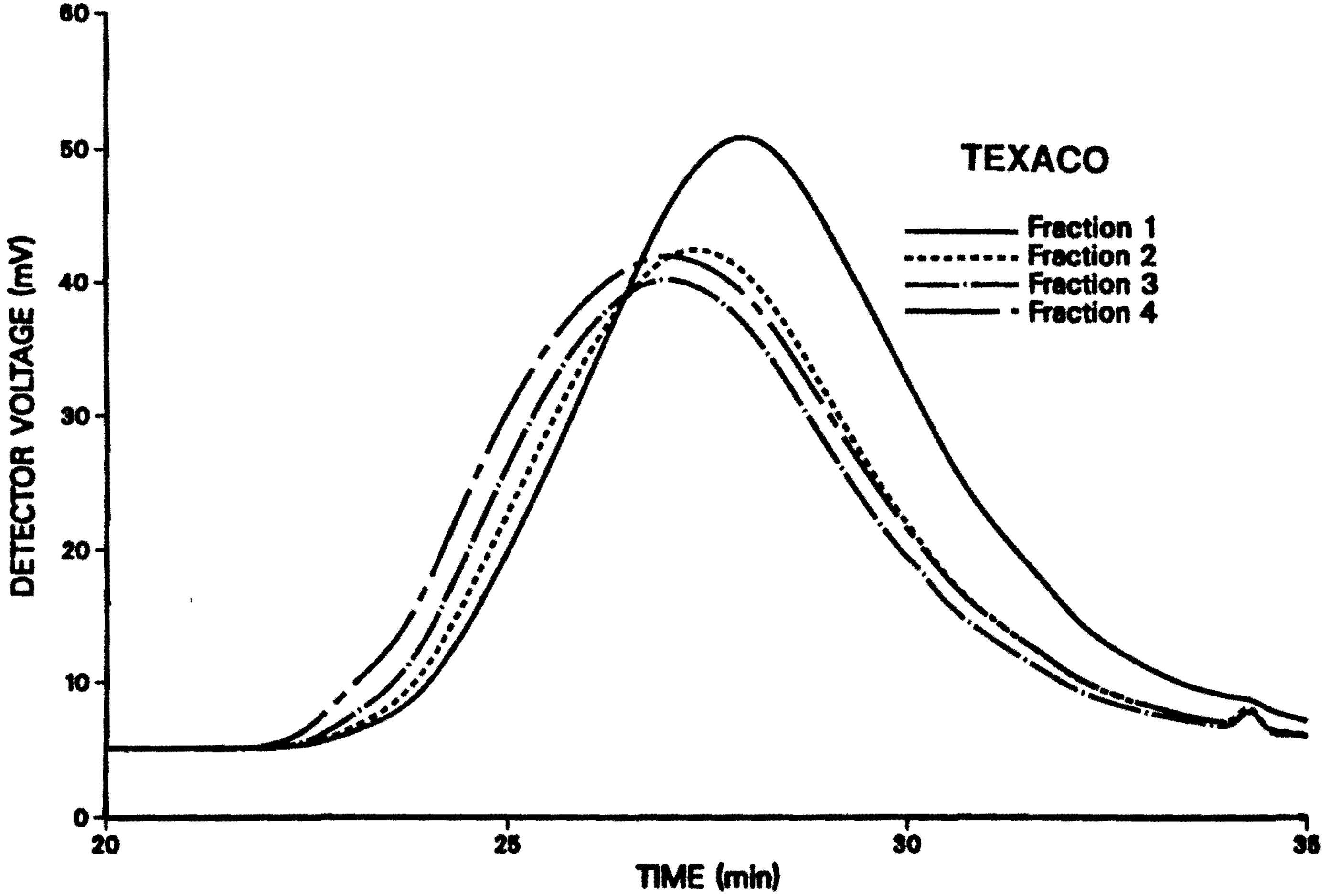

Figure 4-40
GPC Chromatograms of Naphthene Aromatics
from Texaco Fractions 1-4

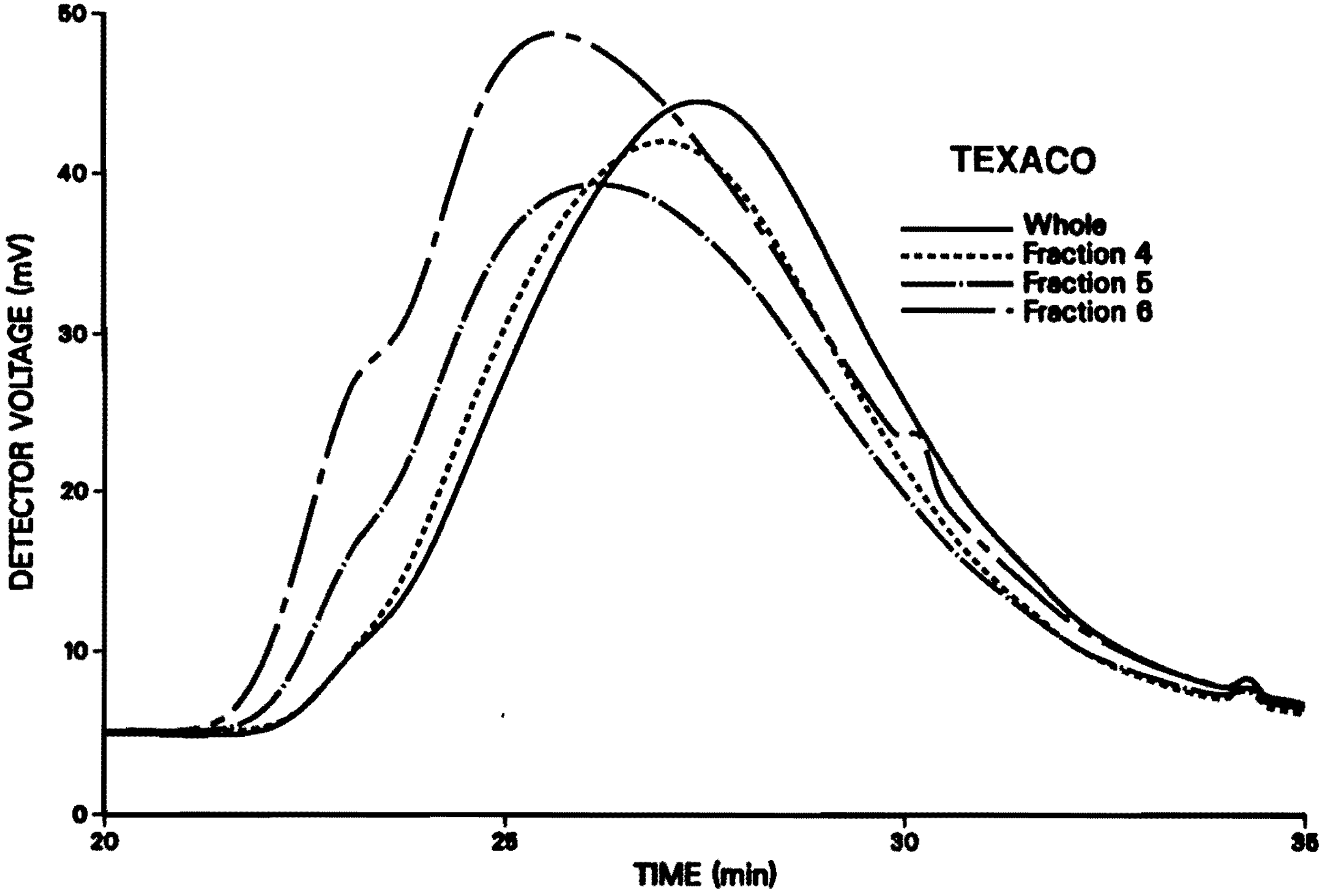

Figure 4-41
GPC Chromatograms of Naphthene Aromatics
from Texaco Whole and Fractions 4-6

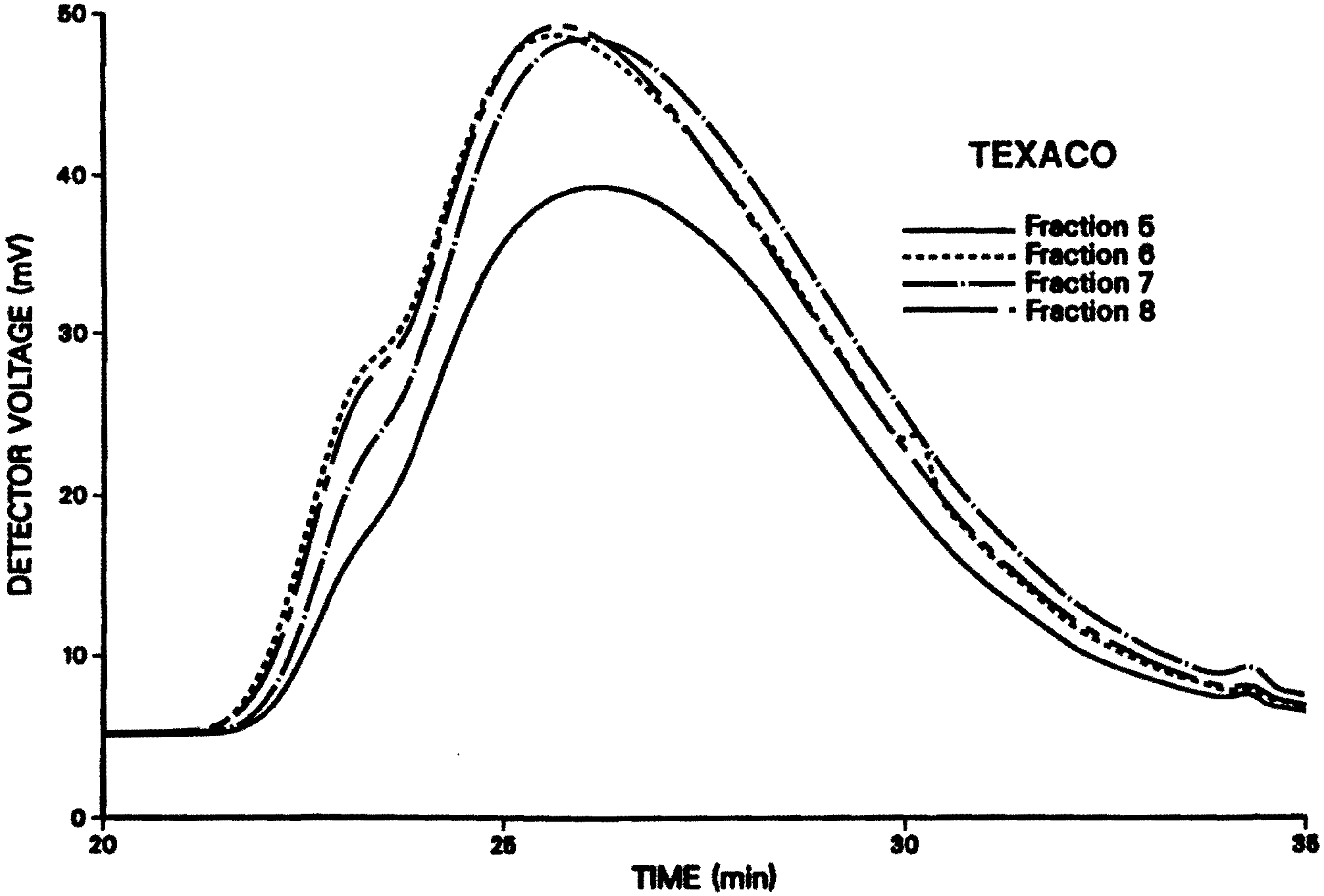

Figure 4-42
GPC Chromatograms of Naphthene Aromatics
from Texaco Fractions 5-8

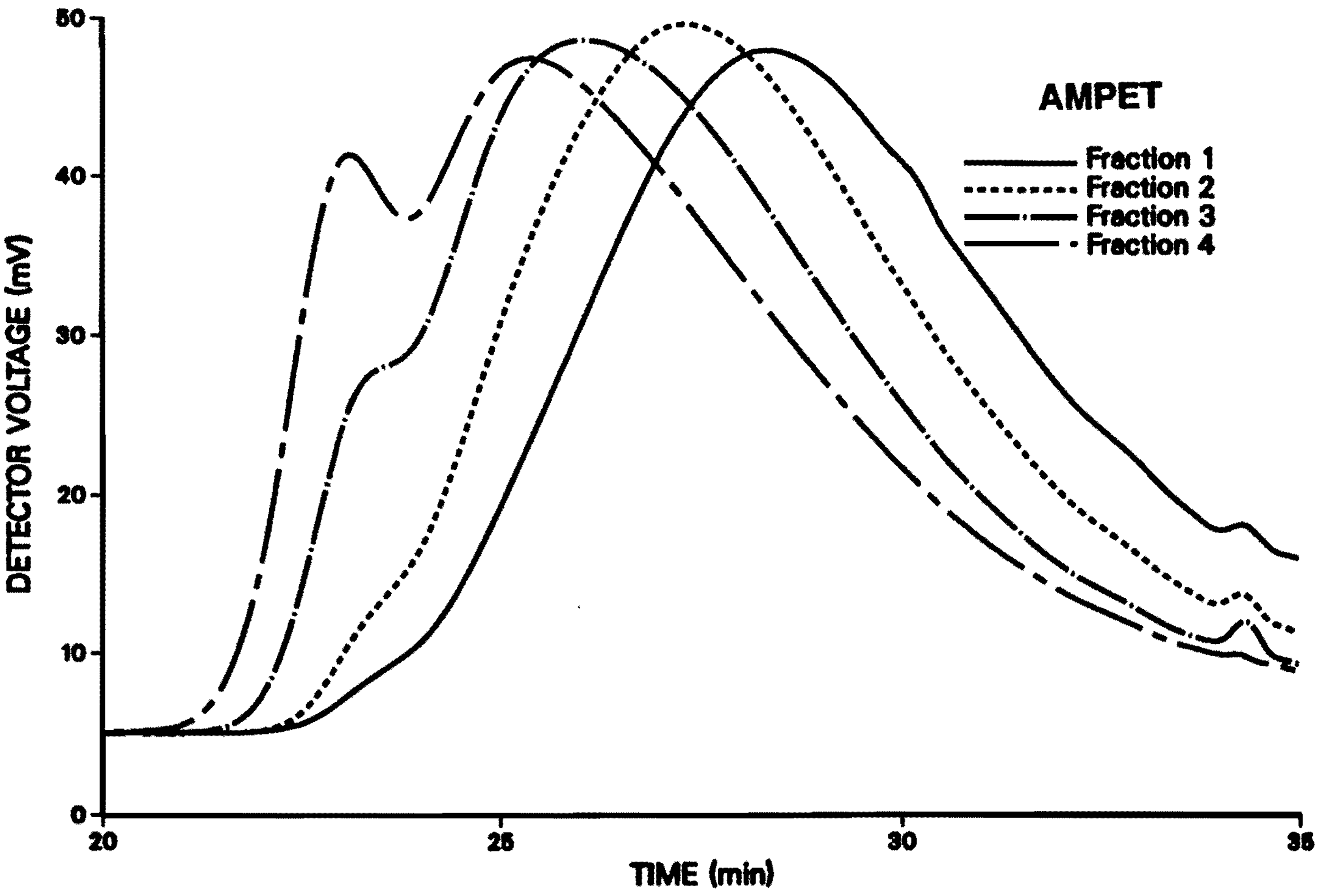

Figure 4-43
GPC Chromatograms of Polar Aromatics
from Ampet Fractions 1-4

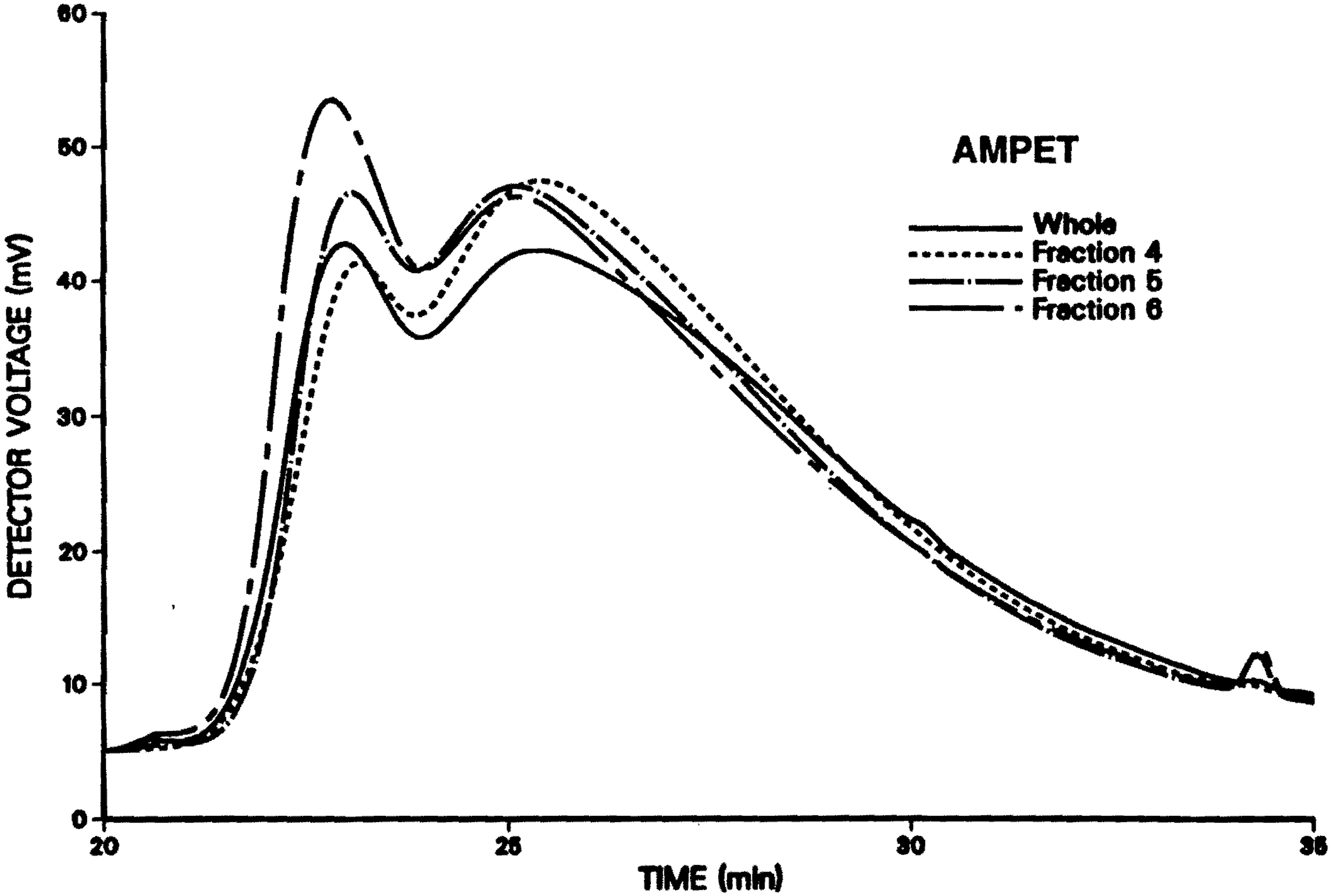

Figure 4-44
GPC Chromatograms of Polar Aromatics
from Ampet Whole and Fractions 4-6

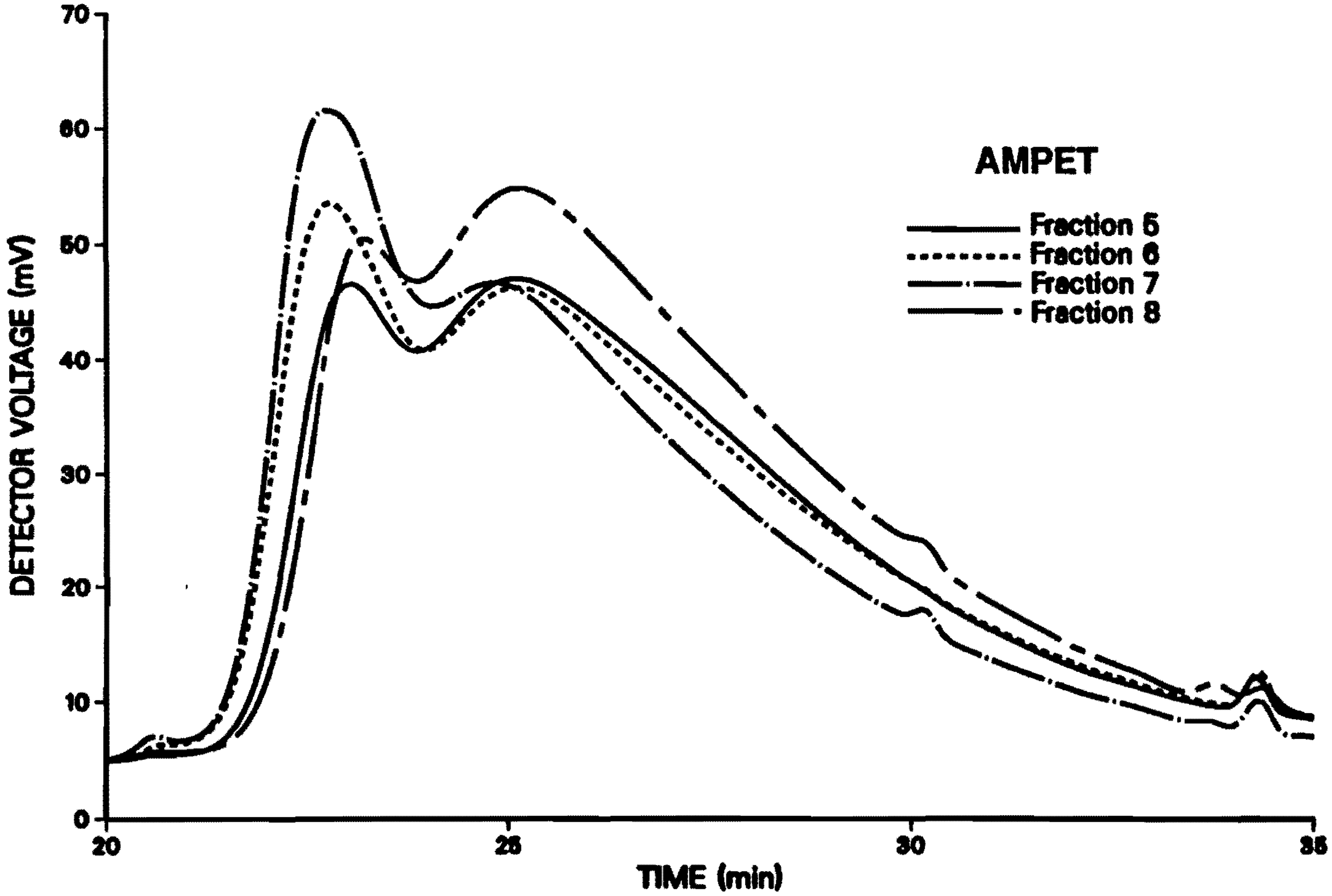

Figure 4-45
GPC Chromatograms of Polar Aromatics
from Ampet Fractions 5-8

aromatics from fractions 1 to 4 are well separated in a smooth progression toward higher molecular size and these results are representative of the Coastal and Texaco as well. Fractions 4 to 6 (Figure 4-44) are binodal and well separated for all the asphalts, though fraction 4 for Texaco (Figure B-50) contains relatively less higher molecular size material.

The higher numbered fractions show a peak in the amount of large molecular size polar aromatics at about fraction 6. For the Ampet fractions (Figure 4-45) the maximum occurs at fraction 7 with fraction 8 falling well below and to the right of 7 and even of fraction 6. For the Coastal and Texaco fractions (Figures B-33 and B-51, respectively) fraction 6 has the greatest amount of large size material and fraction 8 falls even below 7.

Figure 4-46 shows Ampet asphaltenes for fractions 4 and 6 to 8. The results are quite similar for all asphalts with fraction 4 asphaltenes of much lower molecular size than those of the other fractions. It is interesting that this is the material that was soluble in pentane at the supercritical conditions. Little fractionation seems to be occurring in the asphaltenes of fractions 6 to 8.

In summary, several observations can be made about the lighter four fractions. Saturates, although appearing in all four fractions, seem not to be distributed among the fractions by molecular size; while their weight fraction tend to decrease from fractions 1 to 4, there is no discernible difference in molecular size distribution. For naphthene aromatics, however, the separation is primarily on the basis of molecular size. This is most pronounced for the Ampet material. The polar aromatic fractions show a monotonic increase in weight fraction from fractions 1 to 4 but also show a very marked increase in molecular size. Lighter-fraction asphaltenes appear almost exclusively in fraction 4 and these are of low (for asphaltenes) molecular size with a smaller size range than most fractions.

For the heavier four fractions things are less clear. Saturates are largely absent from these fractions. Asphaltenes are largely absent from fraction 5, the pentane soluble fraction. Naphthene aromatics also markedly decreased in quantity in fraction 6 while polar aromatics are slightly less in fraction 6 for Ampet and

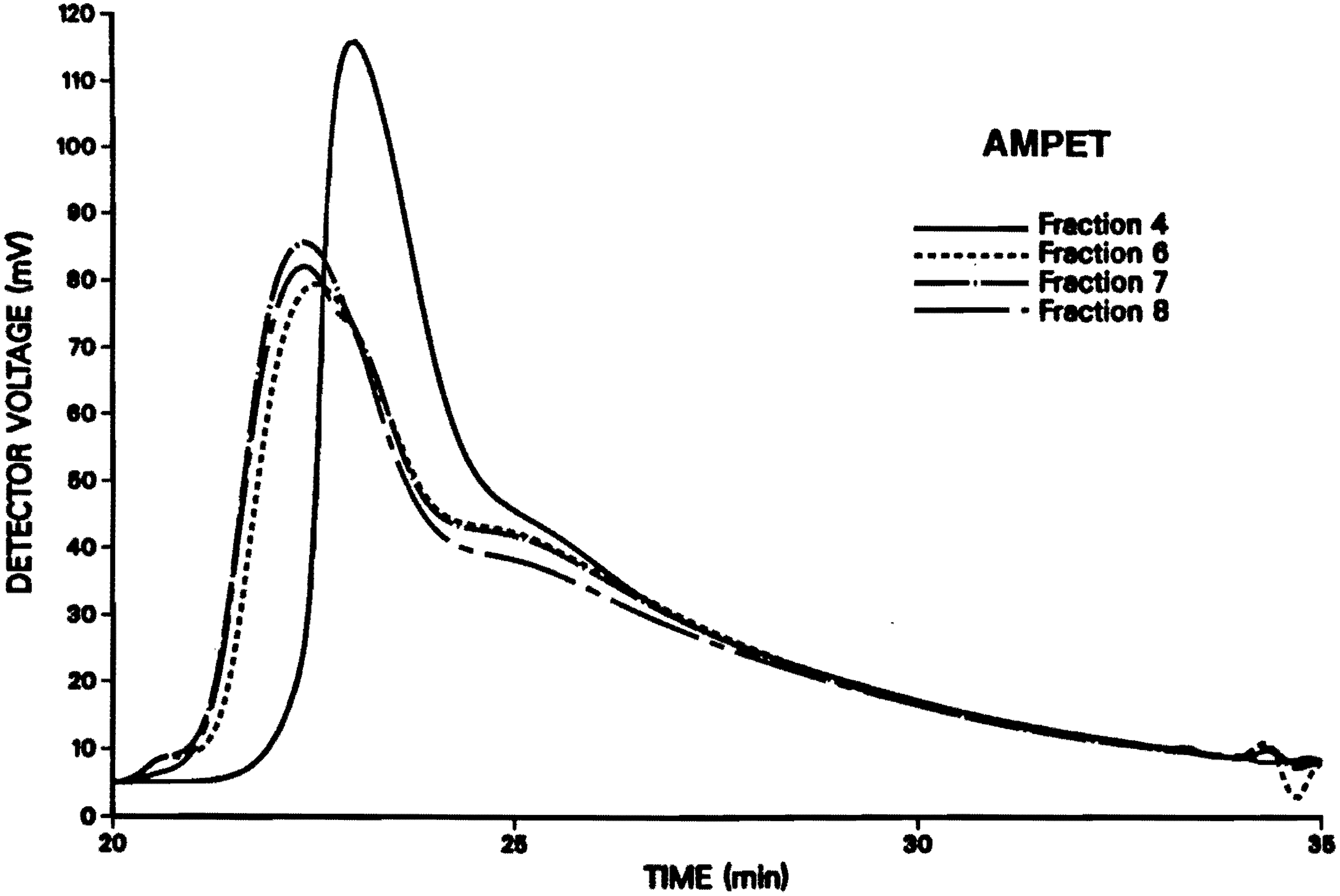

Figure 4-46
GPC Chromatograms of Asphaltenes
from Ampet Fractions 4 and 6-8

Coastal but show a large increase in Texaco fraction 6. This is based on one set of data and should be further confirmed. With respect to effective molecular size, both the naphthene and polar aromatic average sizes maximize at fraction 6 or 7.

Asphaltenes in fractions 6 to 8 are not much separated relative to size though the weight fraction rapidly increases with increasing fraction numbers.

Infrared Spectra of Fractions

Figures 4-47 to 4-55 show infrared spectra (over a wavenumber range of 900 to 1800 cm^{-1}) for the asphalt fractions and the whole asphalts. The striking feature of these spectra is their qualitative similarity, with respect to the functionalities which are present, as well as their distribution. Even though the fractions obtained for each asphalt exhibit widely different solubility characteristics, in accordance with their conditions of separation, they still all have essentially the same features to their spectra. Furthermore, the similarity of corresponding fractions from one asphalt to the next is very evident.

Superimposed upon this general similarity is a progression in the IR spectra of the fractions, for each asphalt, in moving from fraction 1 to 8. The lower the fraction number, the lower the absorbance in the range from 900 to 1350 cm^{-1} and again from about 1500 to 1700 cm^{-1}; as the fraction number increases, these bands increase in absorbance. This is especially noticeable in the heavier fractions, 6 through 8. Also, the bands at 1380 and 1450 cm-1, which are characteristic of saturated hydrocarbon chains, undergo some changes in peak absorbance, although not as great as the rest of the spectrum. The peak at 1600 cm^{-1} is associated with aromaticity and that at 1030 cm^{-1} with sulfoxide; the adjacent region to 1300 cm-1 is contributed to by a number of functional groups, generally having heteroatom content. Consequently, the spectra indicate that in going from fraction 1 to 8, there is an increase in aromaticity and in heterocontent which exceeds that of saturated chains. Of course, this conclusion also is consistent with the Corbett analyses, Table 4-3.

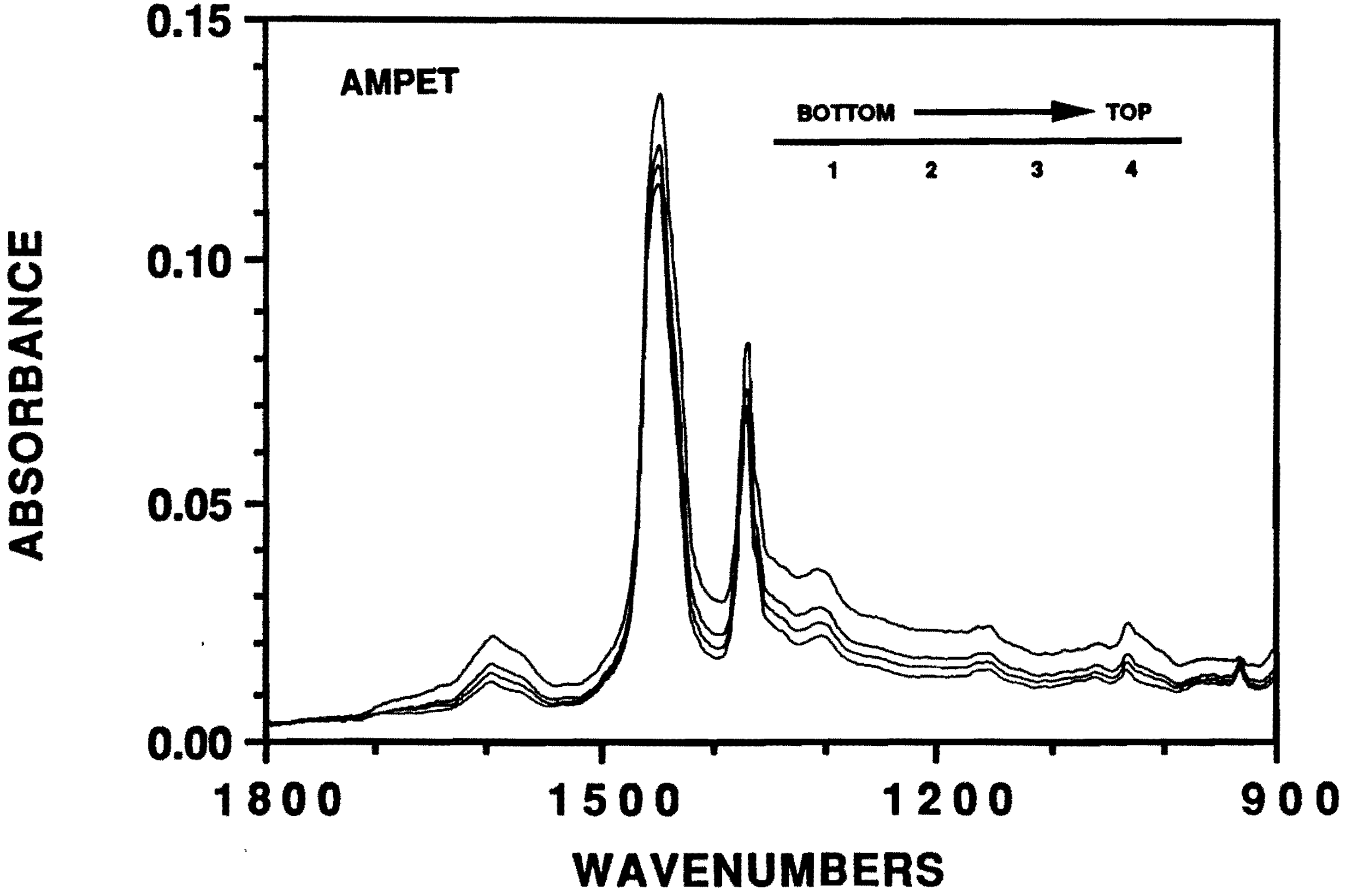

Figure 4-47
IR Spectra for Ampet Fractions 1-4

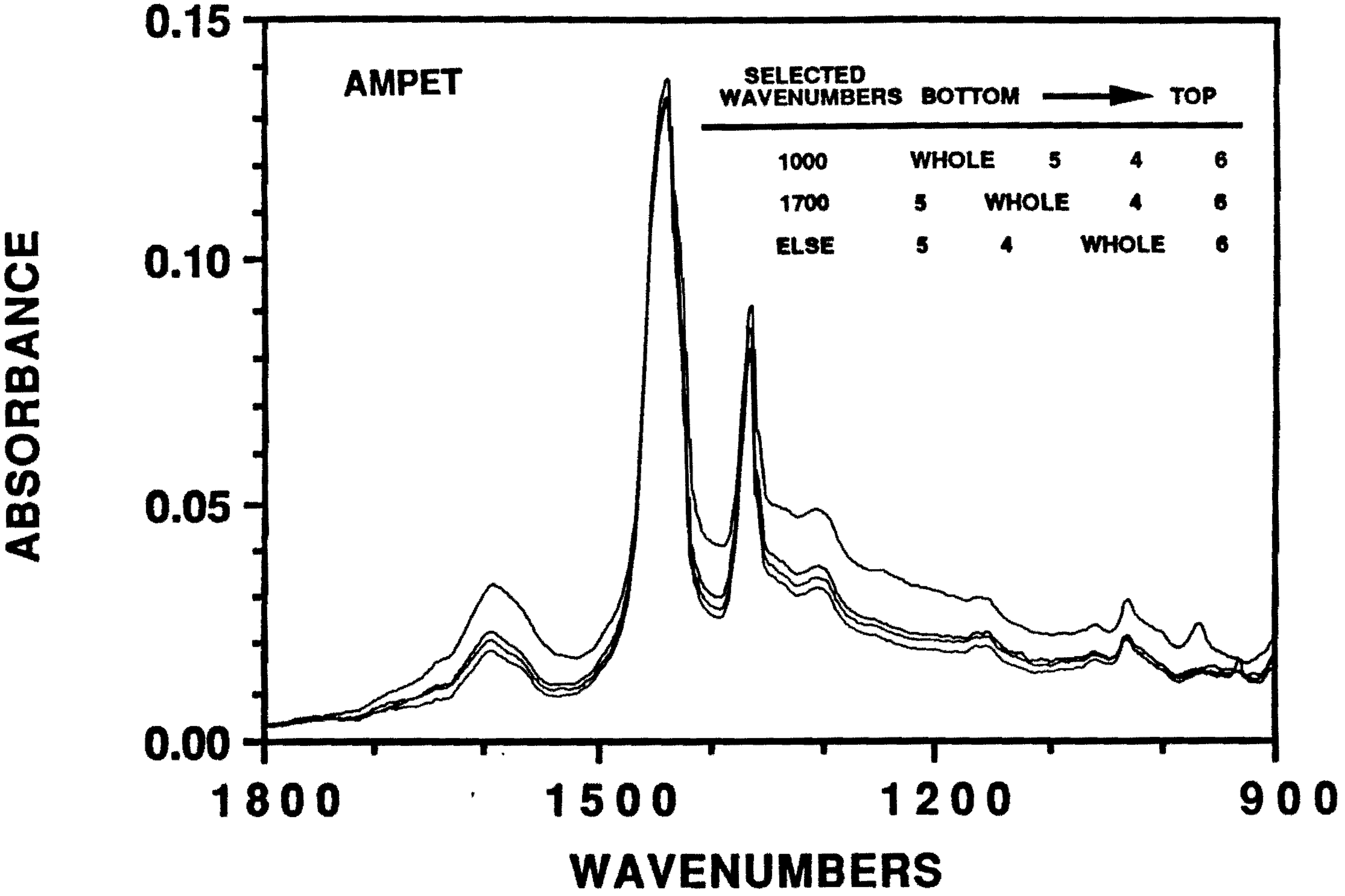

Figure 4-48
IR Spectra for Ampet Whole and Fractions 4-6

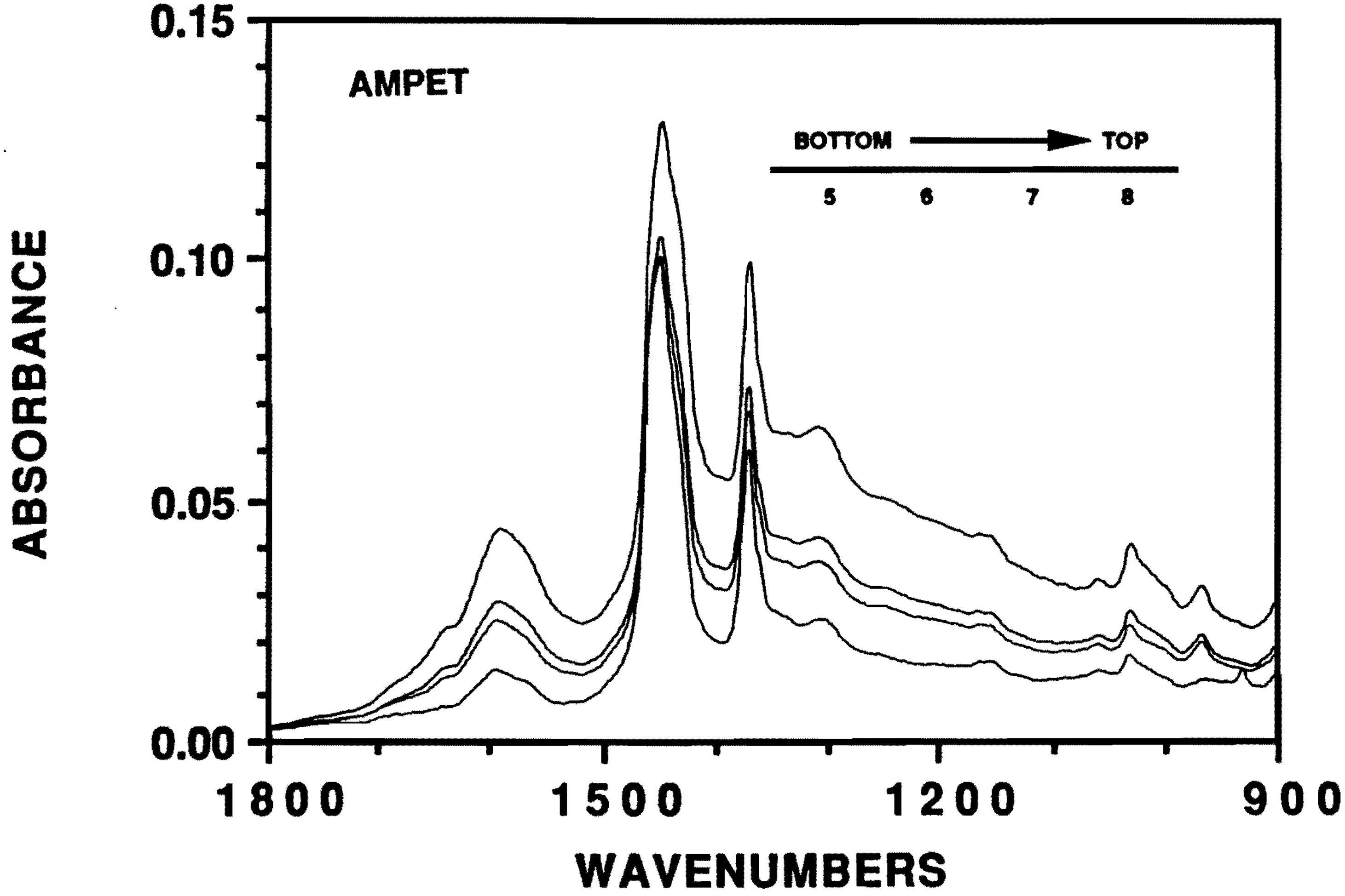

Figure 4-49
IR Spectra for Ampet Fractions 5-8

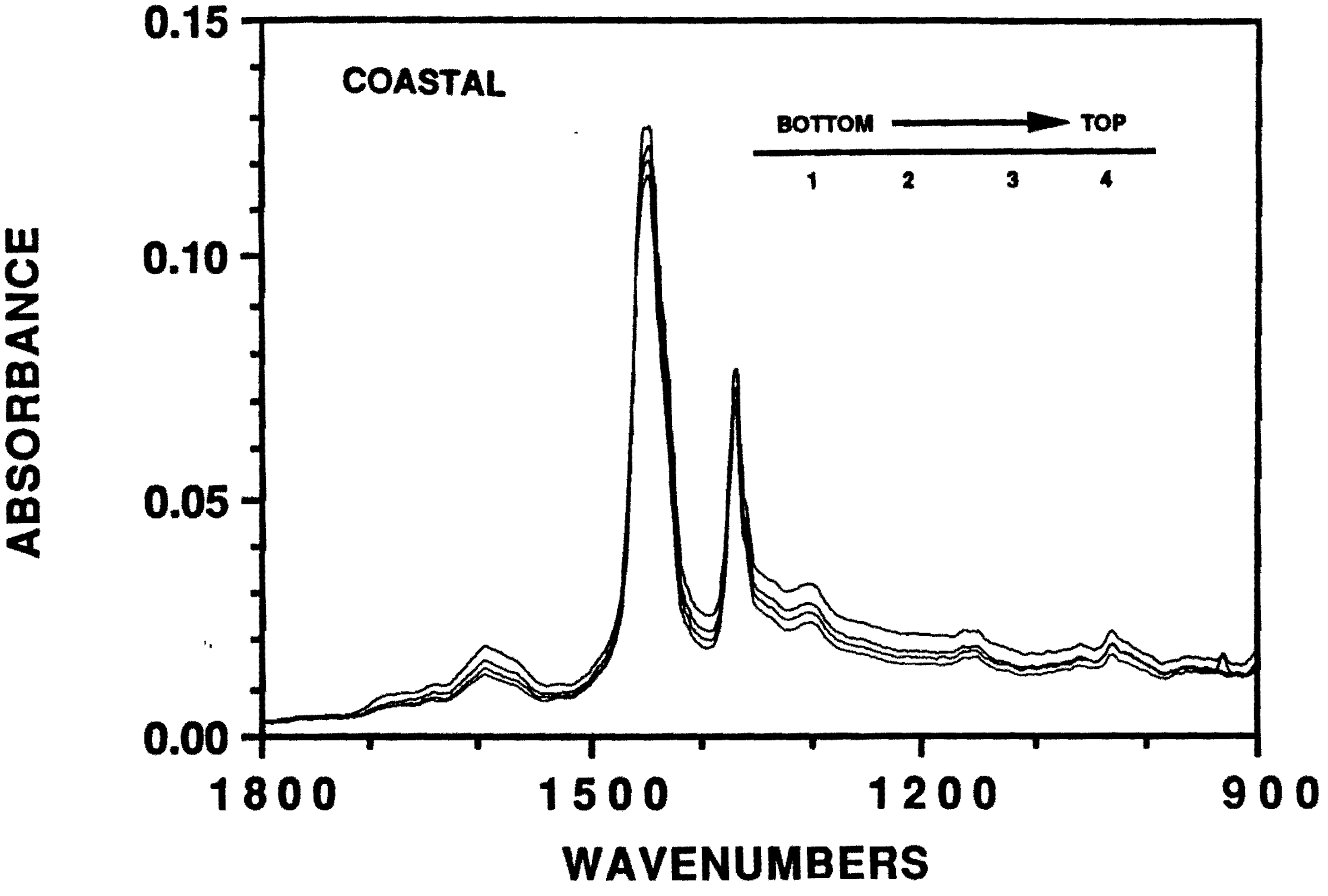

Figure 4-50
IR Spectra for Coastal Fractions 1-4

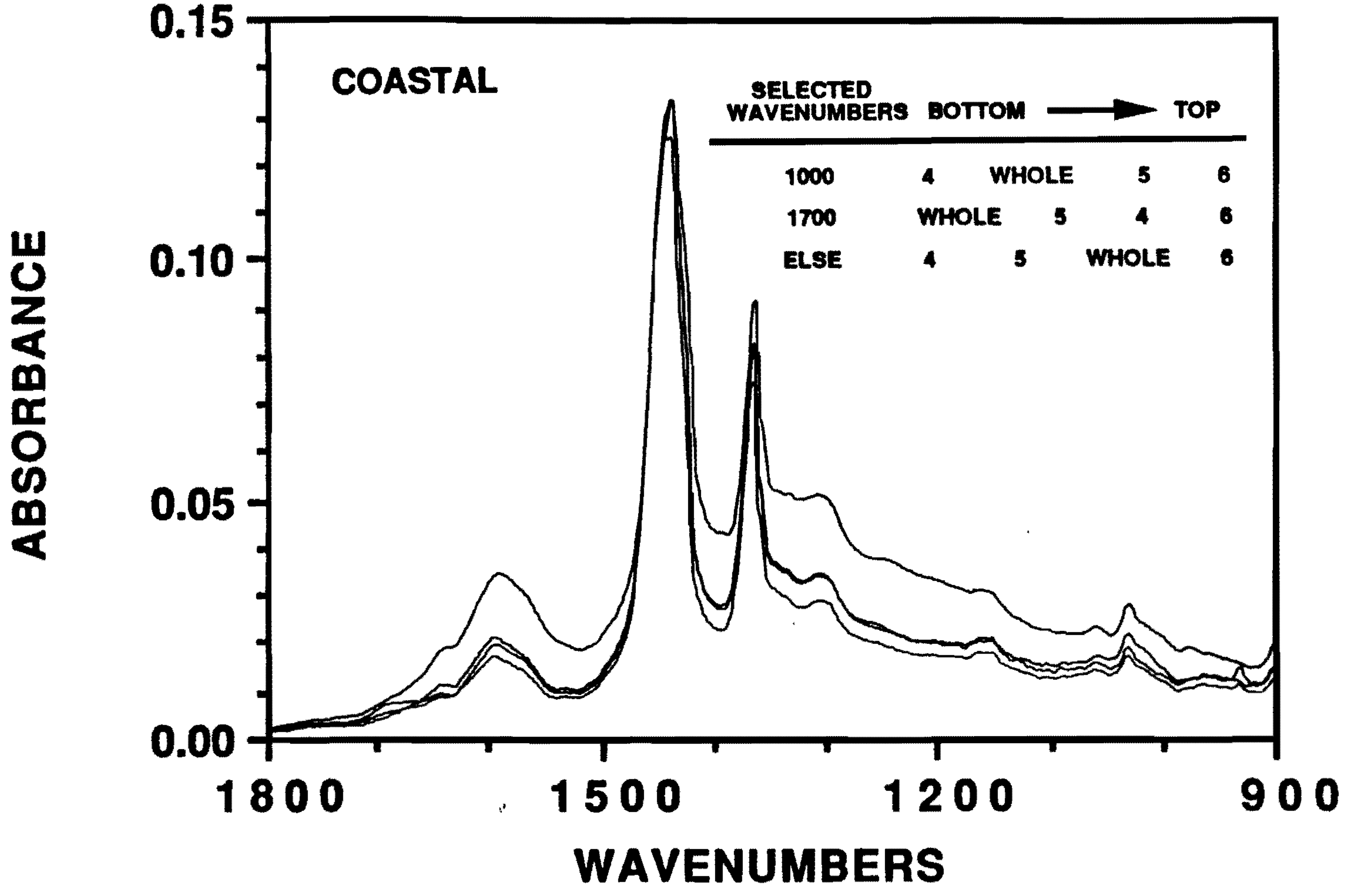

Figure 4-51
IR Spectra for Coastal Whole and Fractions 4-6

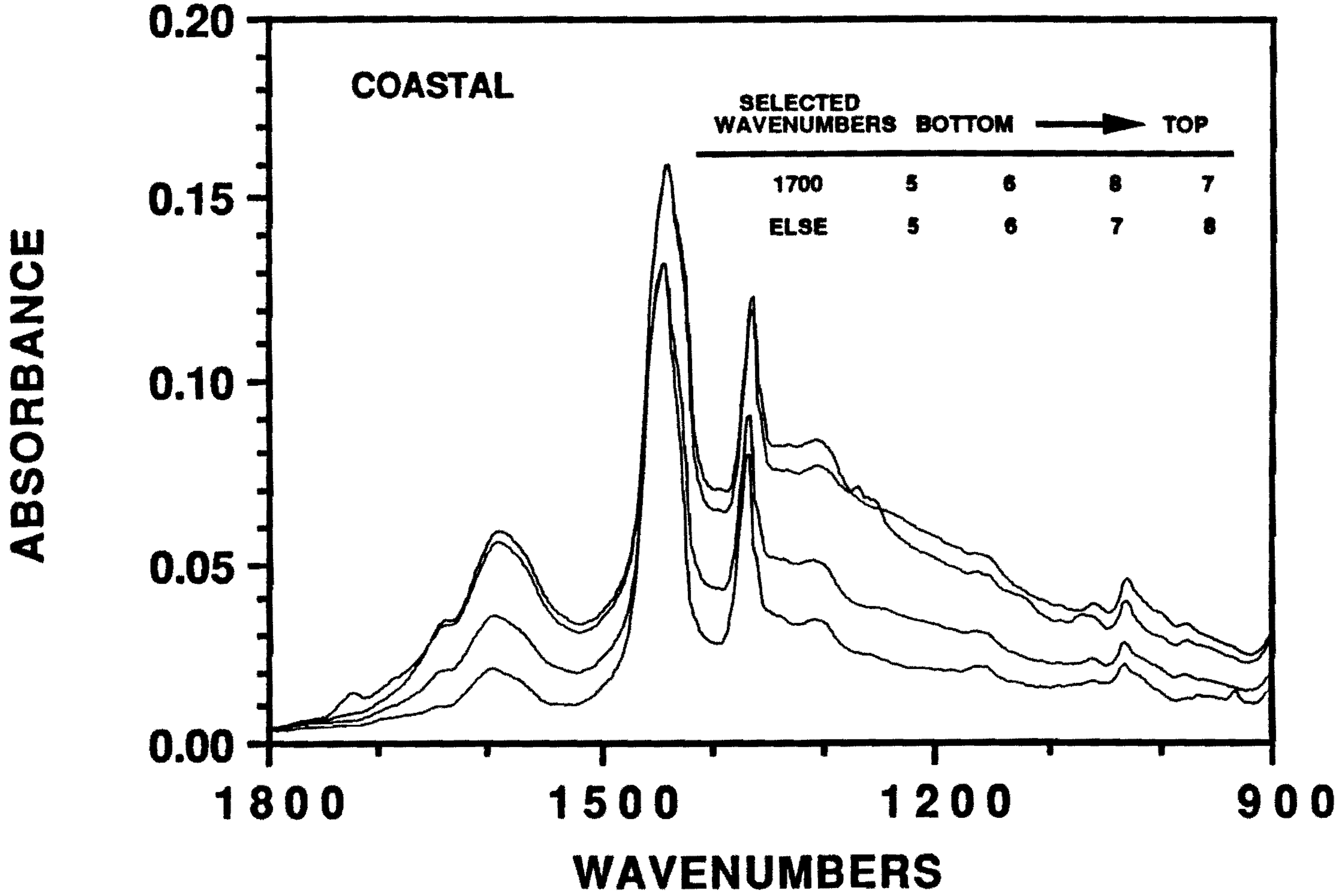

Figure 4-52
IR Spectra for Coastal Fractions 5-8

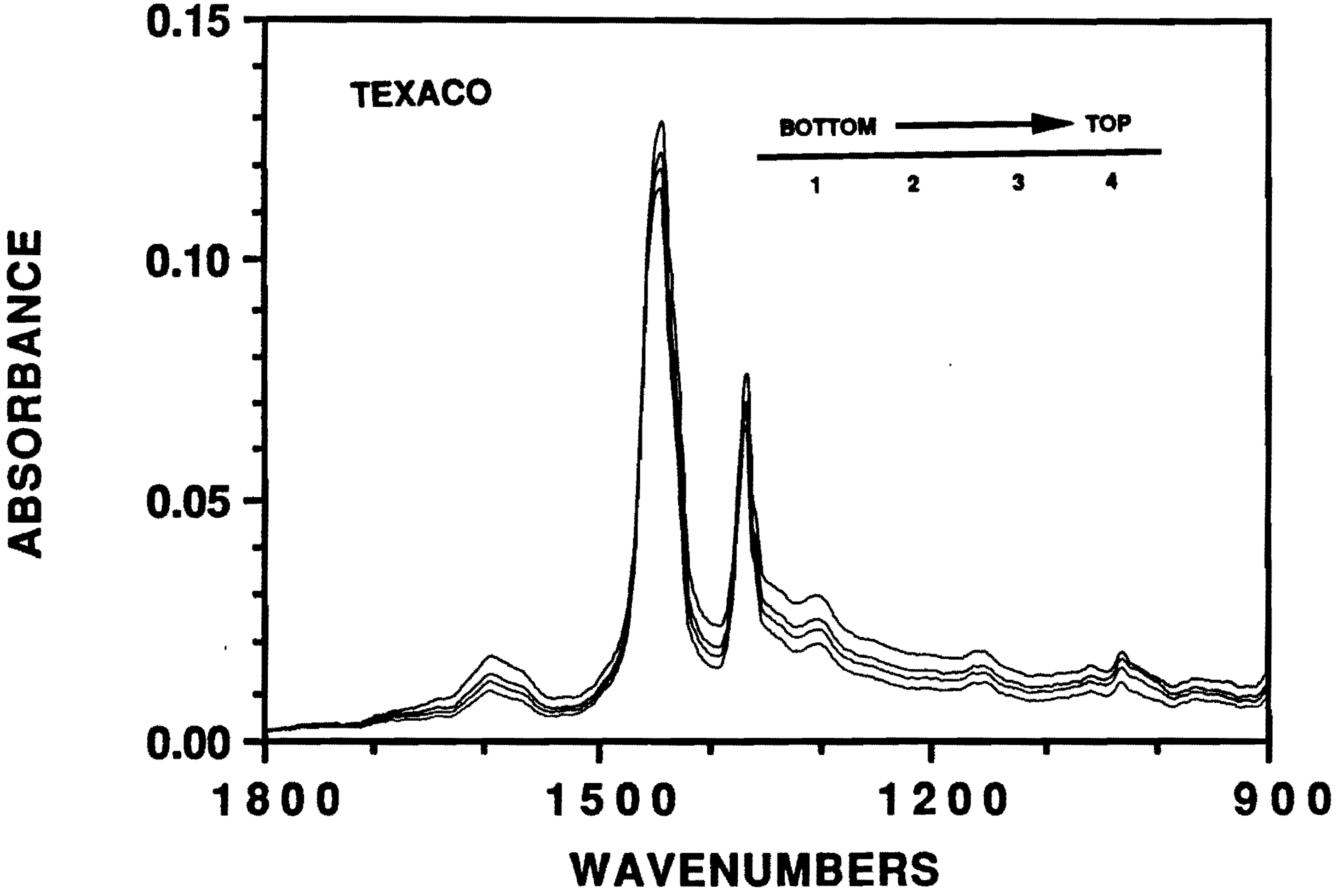

Figure 4-53
IR Spectra for Texaco Fractions 1-4

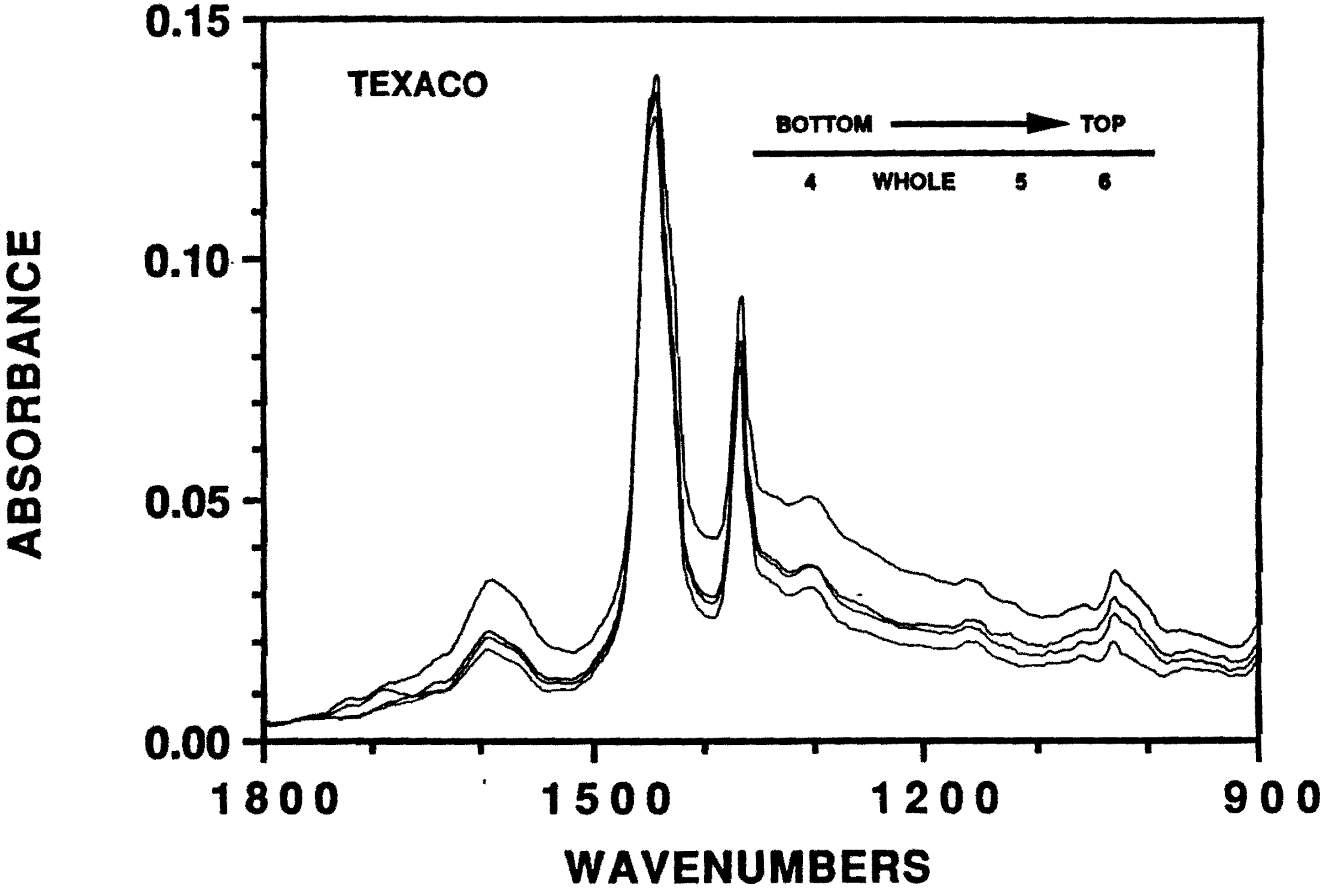

Figure 4-54
IR Spectra for Texaco Whole and Fractions 4-6

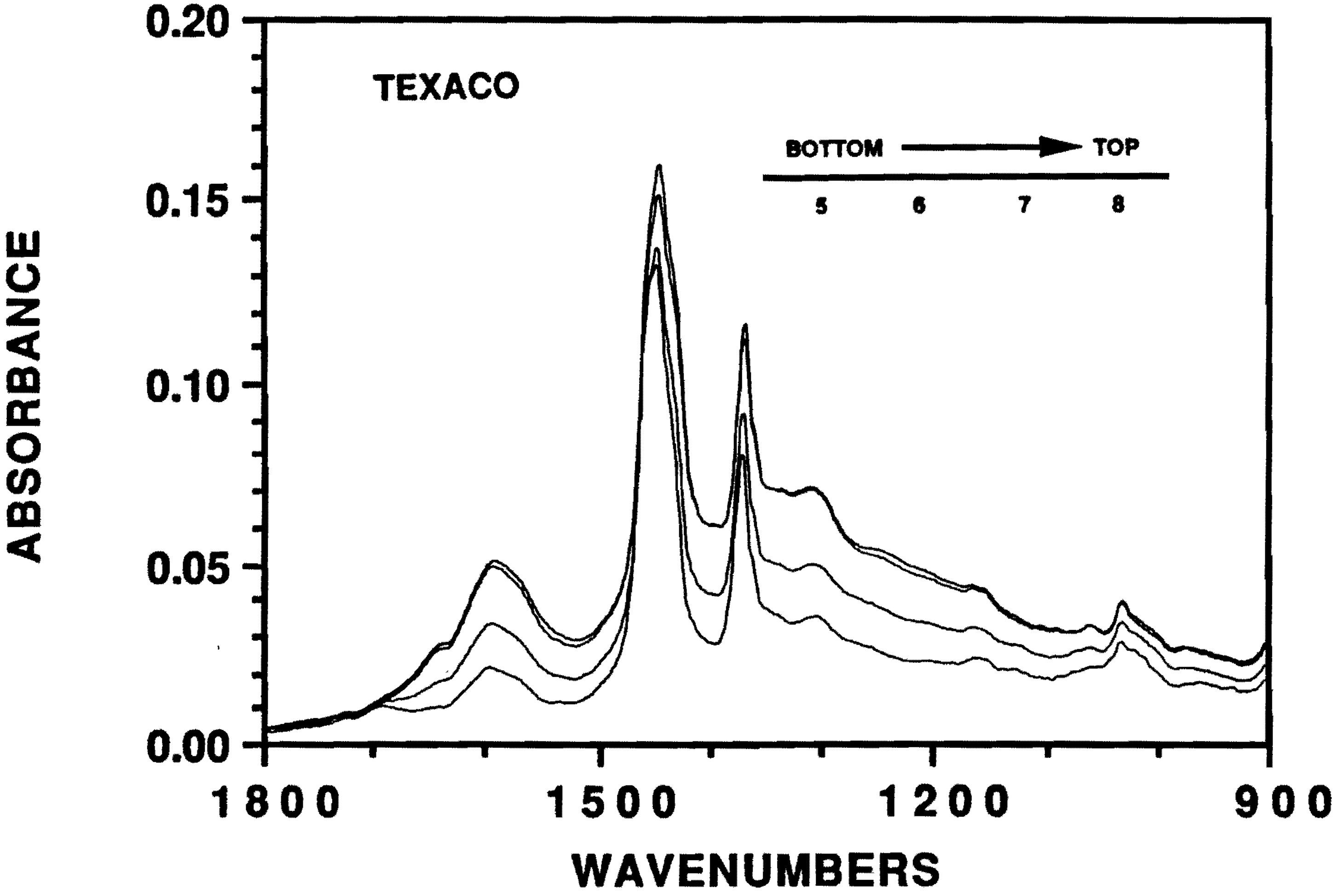

Figure 4-55
IR Spectra for Texaco Fractions 5-8

CHAPTER 5

ASPHALT REBLENDING AND BLEND PROPERTIES

The principal goal of this study was the fractionation of asphalt not only to study fraction properties, but also to reblend the fractions to study the contributions of various fractionated asphalt properties, and to design superior asphalts. Although this part of the work is still in its early stages, a number of blends have been formulated that have properties that are superior to those of the original asphalt. In this study, blends were made from fractions obtained from three AC-20 asphalts designated as Ampet, Coastal, and Texaco.

Solvent Aging of Asphalts

Before discussing in detail the blends and their properties, a few comments on the phenomenon of solvent aging are appropriate. As has been reported in the literature (Davison et al., 1989, Burr et al., 1991), asphalts undergo aging in dilute solvent solutions. This aging is usually manifested by a growth in the carbonyl region of the infrared spectrum and by increases in the viscosity of the material (hardening) and also by changes in the Corbett analyses; solvent aging results in a growth of the asphaltene fraction at the expense of primarily polar aromatics. These effects, although small at room temperature over reasonably short periods of incubation time (a few hours), can be appreciable at elevated temperatures and/or for longer contact times. For example, in the ASTM D 2172, Method B extraction procedure hardening of the asphalt material can easily be 50% (this process occurs with the asphalt in dilute solution at solvent reflux temperatures of approximately 90°C for several hours.) This aging of asphalt in solution occurs in the absence of oxygen and in the presence of relatively inert solvents such as cyclohexane.

Obviously, with solvent aging occurring to this extent at these conditions, it would be expected that significant aging of some of the asphalt components would occur during processing in the supercritical unit. Although the residence time in dilute solution is not necessarily that great (of the order of 1 to 2 hours, total during all processing) and oxygen is excluded, the process temperature is quite high (400 to 450°F; 200 to 230°C).

Direct evidence of solvent aging in the supercritical unit is seen in the Corbett analyses of the whole asphalts compared to those of the supercritical first-pass top and bottom fractions. Using the top and bottom weight fractions (Table 4-1) and the Corbett analyses (Table 4-3) gives:

Asphalt	Whole (Before Processing)	Top + Bottom (After Processing)
Ampet		
Saturates	9.34	10.11
Naphthene Aromatics	45.45	45.29
Polar Aromatics	32.91	27.39
Asphaltenes	12.37	15.94
Total	100.07	98.73
Coastal		
Saturates	12.38	10.25
Naphthene Aromatics	39.47	37.91
Polar Aromatics	26.60	20.99
Asphaltenes	18.07	27.59
Total	96.52	96.74
Texaco		
Saturates	12.30	10.26
Naphthene Aromatics	43.63	42.99
Polar Aromatics	21.99	20.58
Asphaltenes	17.80	22.58
Total	95.72	96.41

Note the generally lower polar aromatics fraction and higher asphaltenes, with saturates and naphthene aromatics staying the same, to within experimental error.

With these compositional changes occurring during processing, we would expect blends of the supercritical unit fractions to be harder than if the aging had not occurred. For example, a blend which is designed to reconstitute the original whole asphalt, based on the supercritical unit weight fractions, would be expected to be more viscous than the original material. In fact, as is discussed in later sections of this chapter, this usually is the case. (The less than 100% recovery with the Corbett procedure is normal when all solvent is removed from the recovered fractions, although values as low as 96% are somewhat low. Probably this is due to a combination of volatiles loss from the asphalt or blends and incomplete recovery of the polar aromatics. The discrepancies are not enough, however, to change the conclusions about solvent aging.)

This hardening of asphalt in solution is not yet understood, but is most certainly of little consequence with respect to the objectives of 1) understanding asphalt composition-physical property relations and 2) designing asphalt processing units to produce premium asphalts. It is the compositional and physical properties of the *blends,* not the original asphalt, that will be used to unravel the property interrelations. Then, with a good understanding of the compositional changes which are needed for a given application, the solvent aging that is known to occur can be taken into account to produce the proper blend from the original asphalt.

Nevertheless, in the discussions which follow the solvent-aging phenomenon must be remembered. Otherwise, comparisons between the original asphalts and the blends will lead to confusion.

Asphalt Reblending

Asphalts were reblended from the eight fractions corresponding to their original source whole asphalt. For each asphalt, fractions 1 through 5 were easily melted in a 149°C oven. Fractions 6 through 9, however, would not melt easily and were, therefore, ground into a powder using a mortar and pestle. These were then dissolved using a 5:1 volume-to-weight ratio of trichloroethylene to powder. This solution was added to the molten fractions 1 through 5 as needed. After the mixture became homogeneous, the trichloroethylene was removed (Abson Method, ASTM D 1856, as modified by Burr et al., 1990). Although done with no effort to exclude air, the temperatures (oven and room) and time (the oven and dilute solution) were low enough that additional aging of the asphalt components was minimal.

Blend 1 in each case was an attempt to reconstruct the original whole asphalt by adding all eight fractions in their original proportions. All other blends were designed to leave out varying proportions of the heaviest and lightest fractions; for example, blend 2 consisted of fractions 2, 3, 4, 5, 6, and 7. The target viscosity was in the AC-10 to AC-20 range and often additional light or heavy fraction had to be added in order to achieve the desired viscosity. Each successive addition of these fractions was facilitated by additional melting and dissolution in trichloroethylene, with subsequent solvent removal. In order to minimize these steps and, therefore, to minimize the amount of solvent aging produced by the blending, any blend satisfying either AC-10 or AC-20 specifications was accepted for testing even though the source asphalts were always AC-20's. Table 5-1 and Figures 5-1 to 5-13 summarize the content of each asphalt blend.

Ampet blend 2 corresponds to the original asphalt with fractions 1 and 8 removed and with fractions 2 to 7 in the same ratio as in the original asphalt. Ampet blend 3 has fractions 1, 2, 7, and 8 removed; fractions 4, 5, and 6 are in the original ratio but fraction 3 is increased to 32.4% rather than the 23% that would result from only removing the four fractions. Ampet blend 4 is 100% Ampet fraction 4. It had a viscosity of about 1000 poise, considerably higher than the fraction 4 of the other two asphalts (Table 4-2). Its properties were not atypical of an AC-10 asphalt.

Coastal blend 2 has very nearly the composition that would result from the complete removal of fractions 1 and 8, the only changes being slight increases in fraction 5 and 6. Coastal blend 3 resulted from complete removal of fractions 1, 2, 7, and 8 with the other fractions in their original ratios. Coastal blend 4 contains only fractions 4, 5, and 6 but the proportion of fraction 4 is considerably increased and that of 6 equally decreased as compared to the original. Blend 5 has fractions 1, 7, and 8 completely removed; fractions 3, 4, and 5 remain in the same relative ratio as in the original asphalt but fraction 2 is increased to 29.9% from 26.6% that would result if it had remained in its original ratio, and fraction 6 is 32.4% rather

Table 5-1
Fractional Content of Each Blend
(Percentages are Indicated)

Asphalt Blend	Fraction Numbers 1	2	3	4	5	6	7	8
Ampet								
1	13.5	14.4	13.0	16.5	12.5	14.6	7.7	7.8
2	--	18.3	16.5	20.9	15.9	18.6	9.8	--
3	--	--	32.4	25.4	19.4	22.8	--	--
4	--	--	--	100.0	--	--	--	--
Coastal								
1	15.7	18.3	17.6	6.5	8.4	11.7	7.7	14.2
2	--	26.1	25.1	9.2	12.2	16.6	11.0	--
3	--	--	39.8	14.7	19.0	26.5	--	--
4	--	--	--	42.2	34.0	23.8	--	--
5	--	29.9	20.3	7.5	9.7	32.4	--	--
Texaco								
1	28.6	18.0	13.8	4.6	4.3	5.0	7.3	18.4
2	--	34.0	26.0	8.7	8.1	9.4	13.8	--
3	--	--	43.3	14.6	13.4	28.7	--	--
4	--	--	48.1	16.0	15.1	9.6	11.2	--

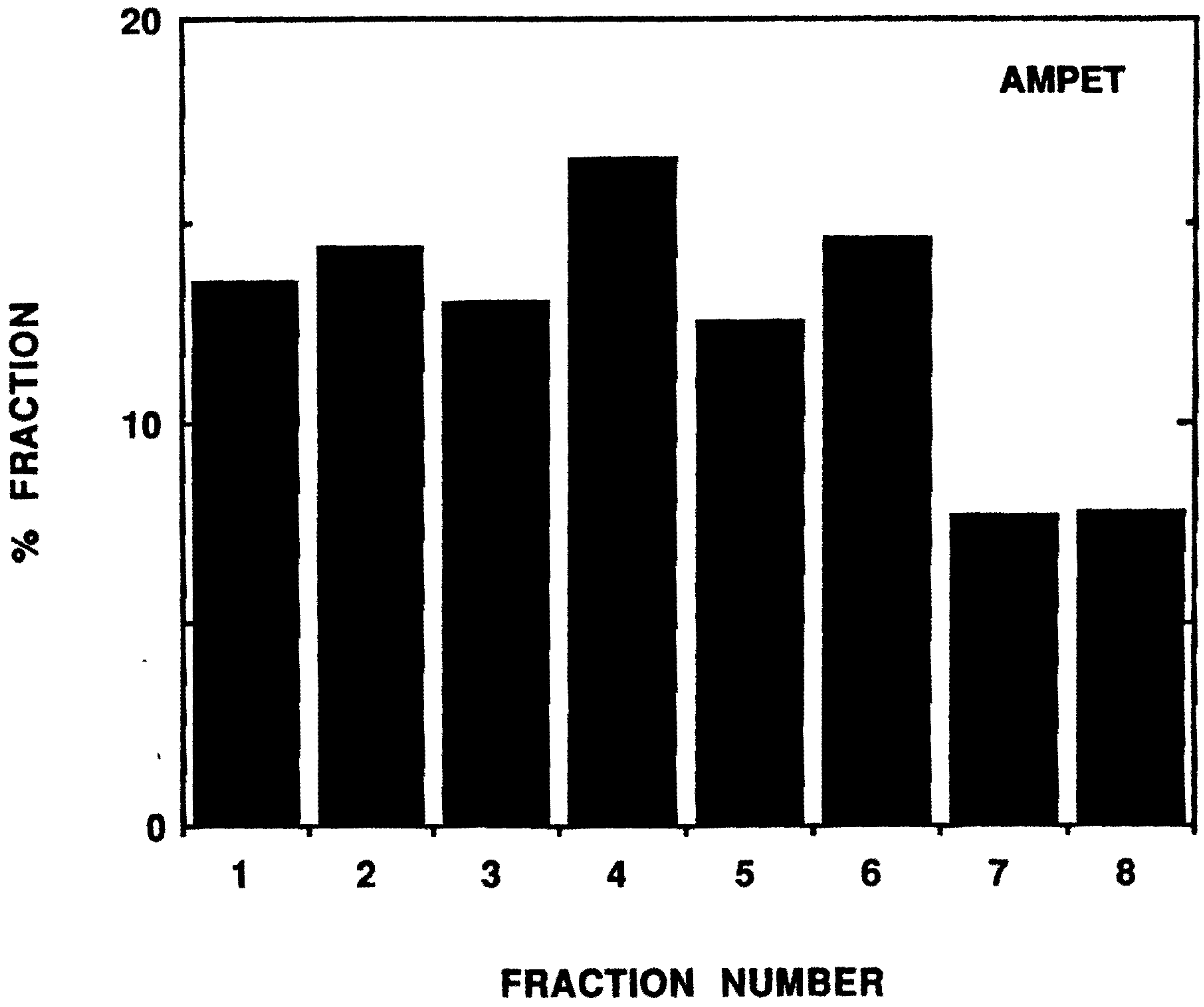

Figure 5-1
Fractional Content of Ampet Blend 1

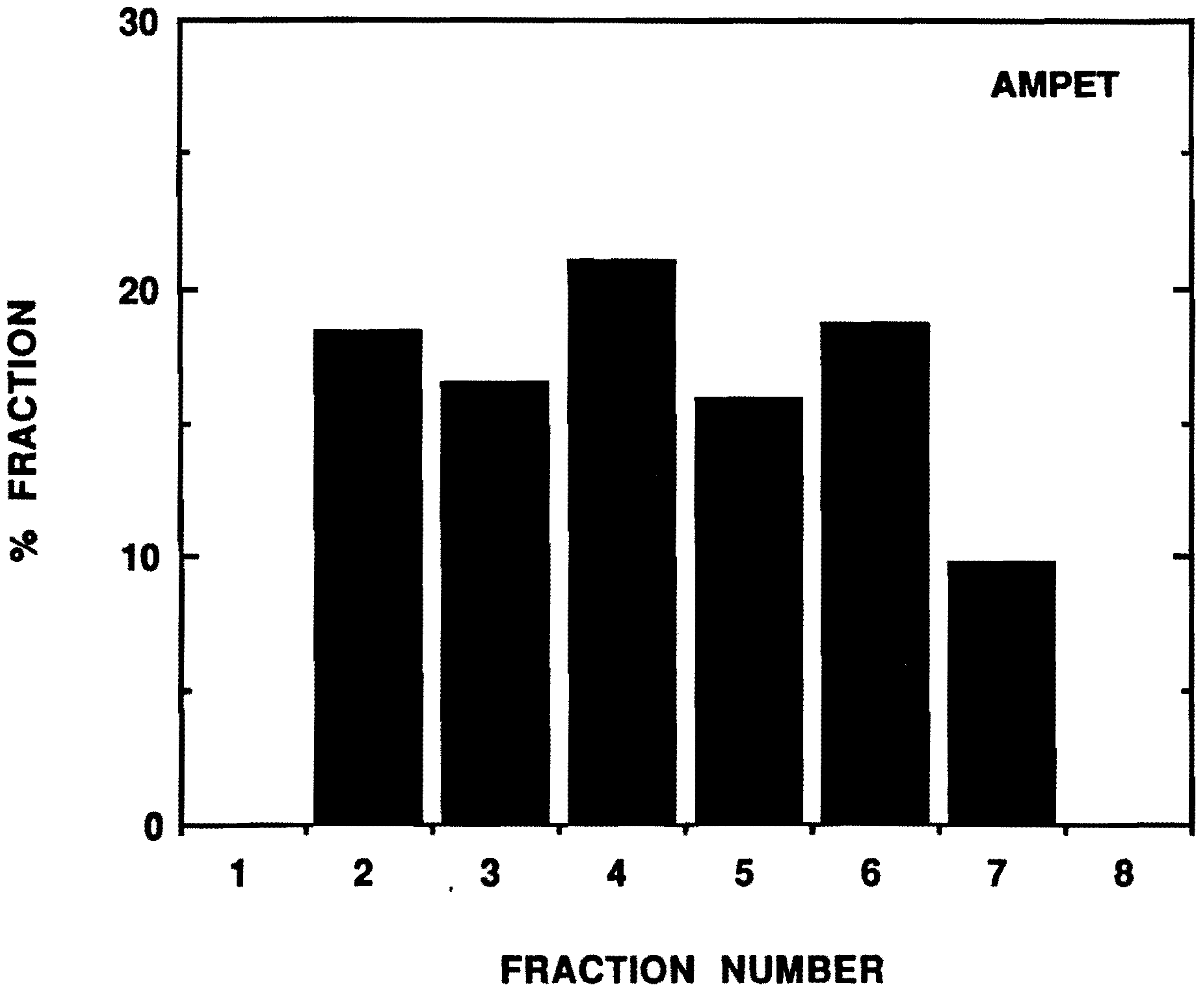

Figure 5-2
Fractional Content of Ampet Blend 2

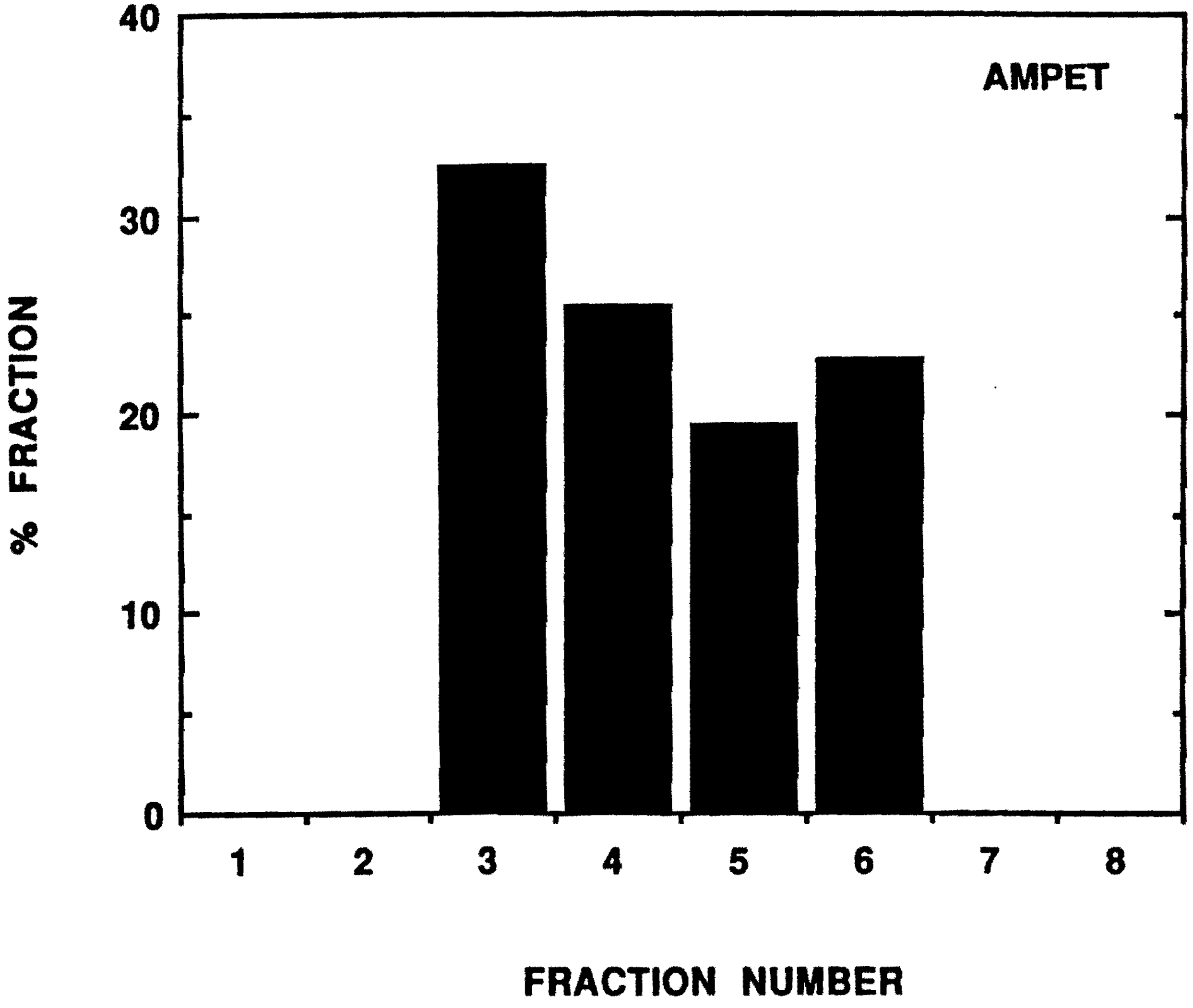

Figure 5-3
Fractional Content of Ampet Blend 3

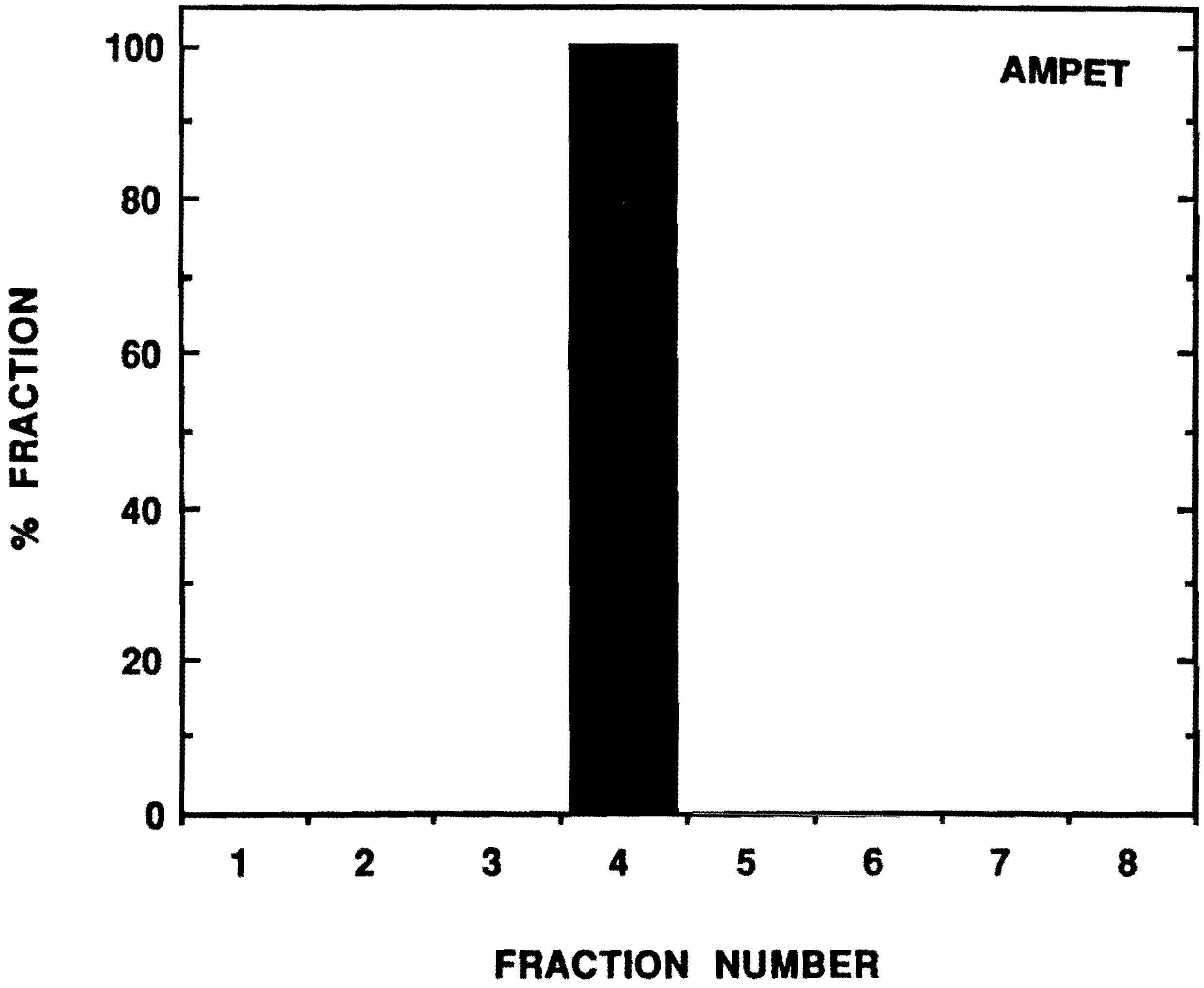

Figure 5-4
Fractional Content of Ampet Blend 4

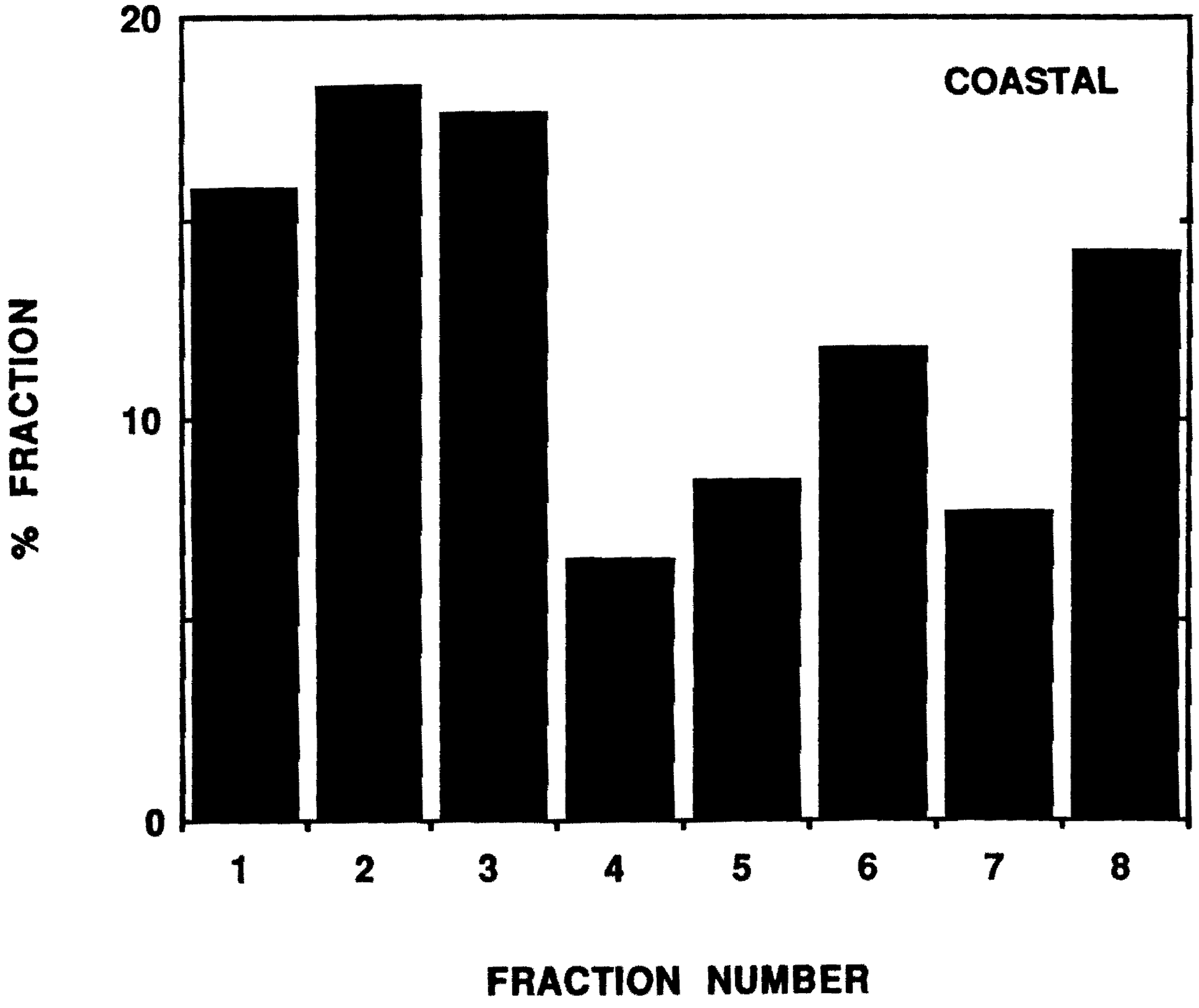

Figure 5-5
Fractional Content of Coastal Blend 1

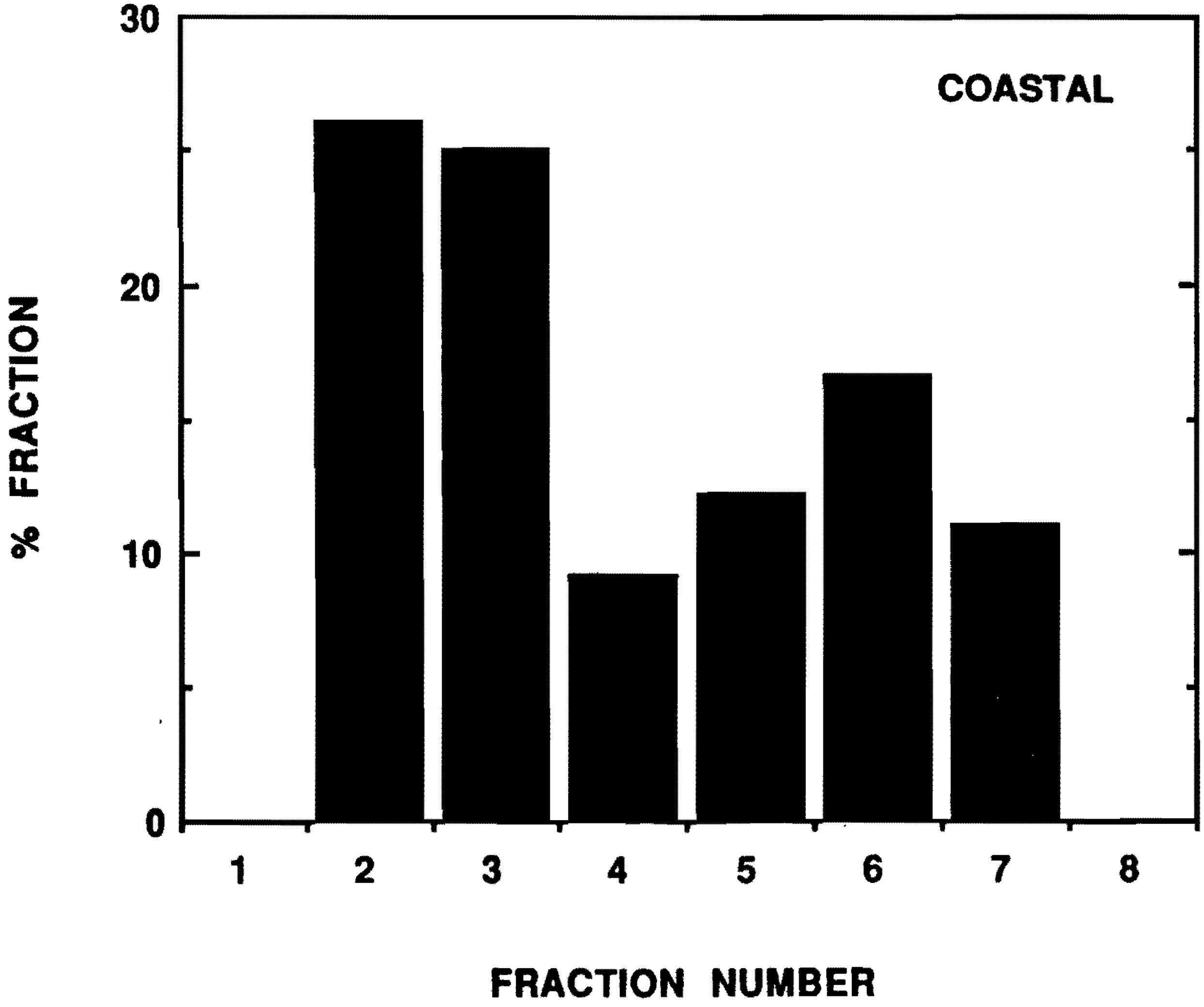

Figure 5-6
Fractional Content of Coastal Blend 2

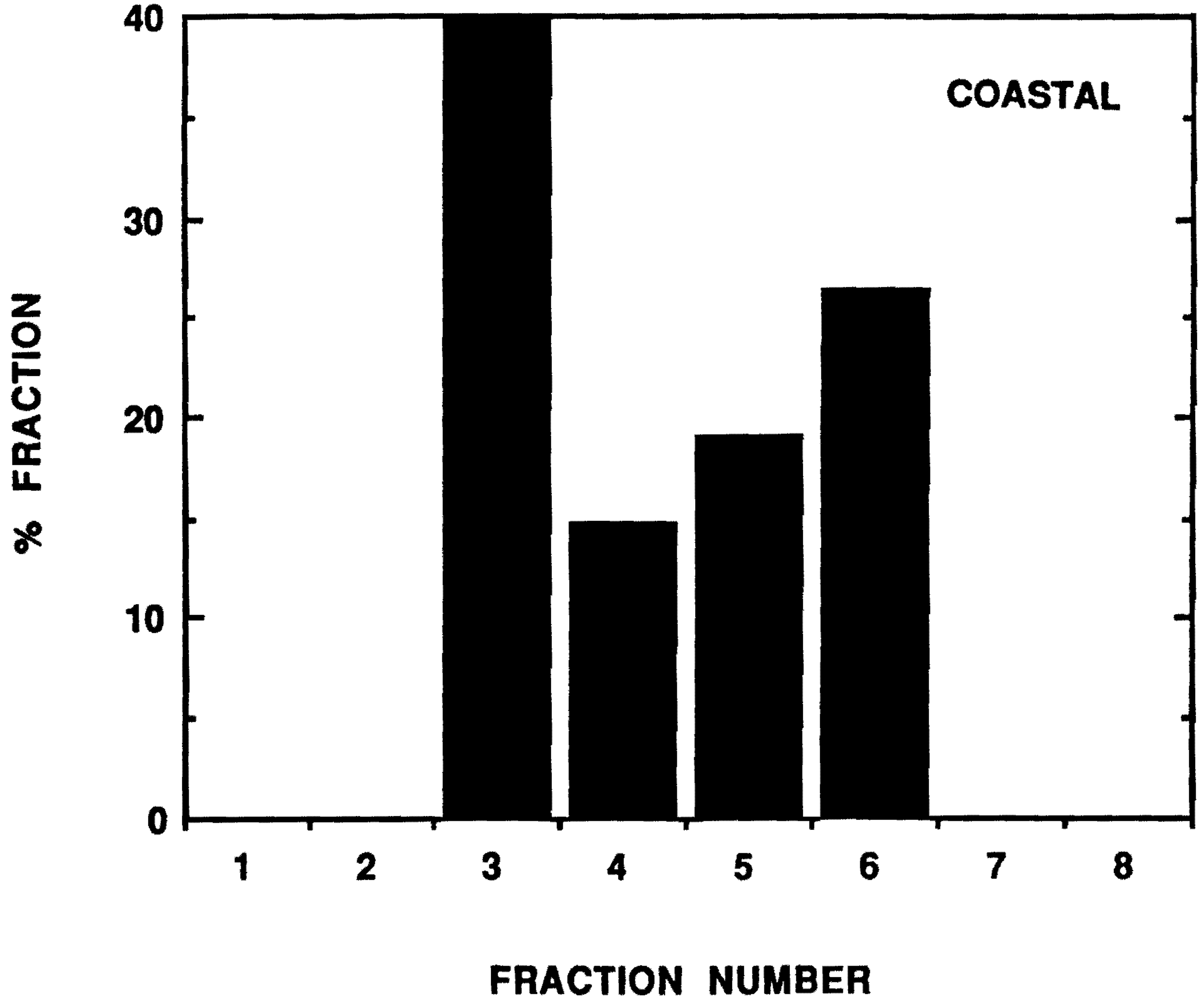

Figure 5-7
Fractional Content of Coastal Blend 3

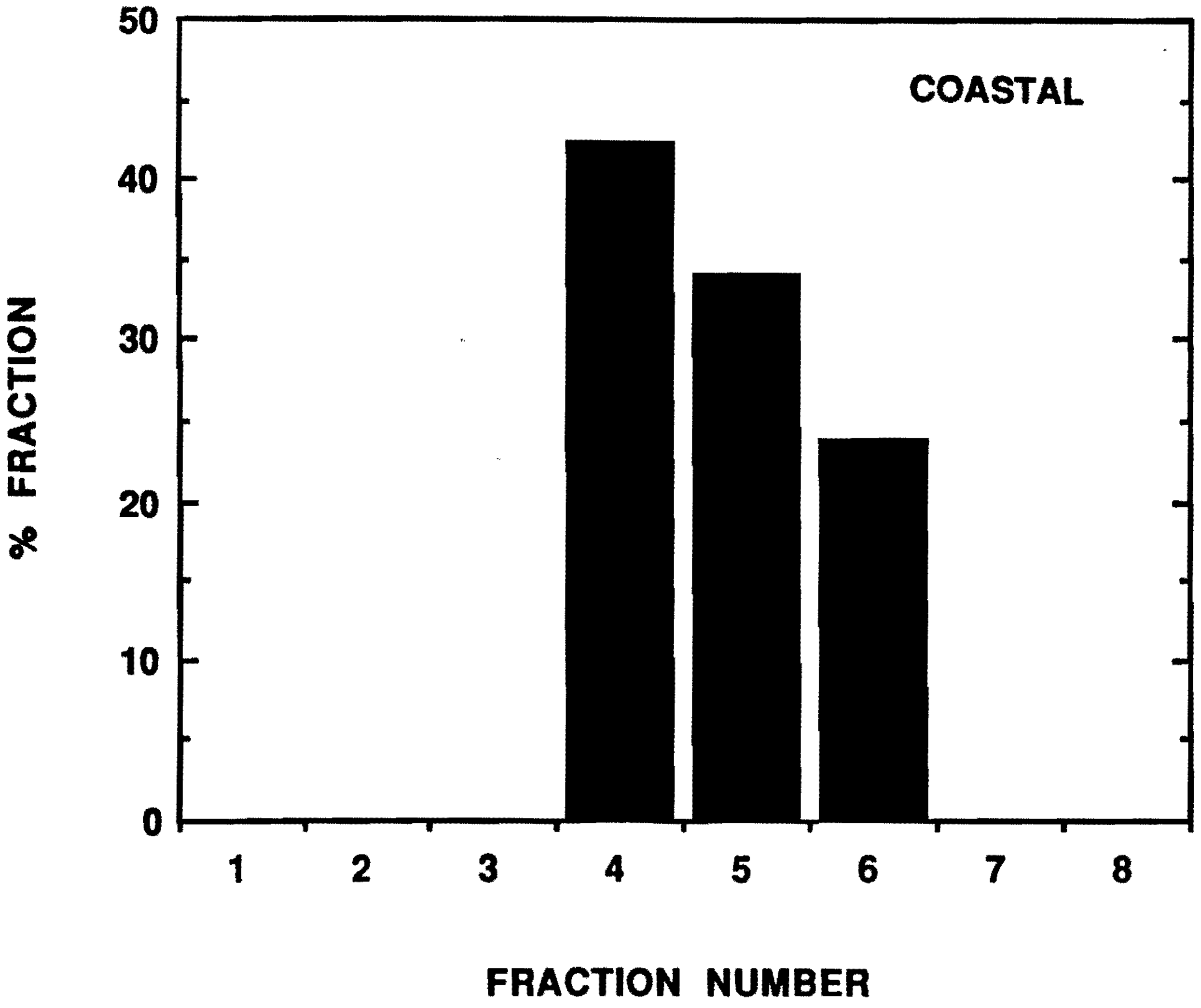

Figure 5-8
Fractional Content of Coastal Blend 4

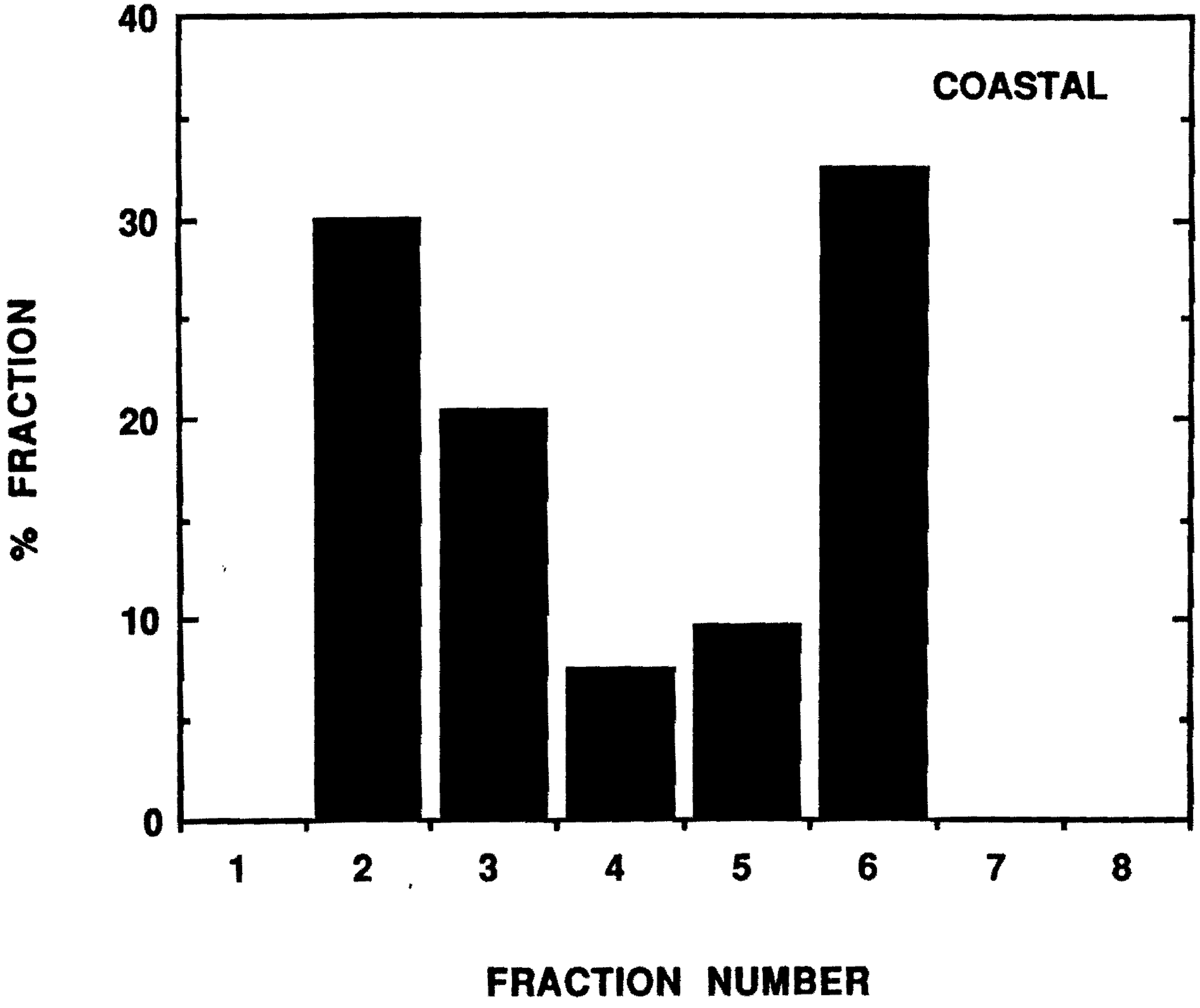

Figure 5-9
Fractional Content of Coastal Blend 5

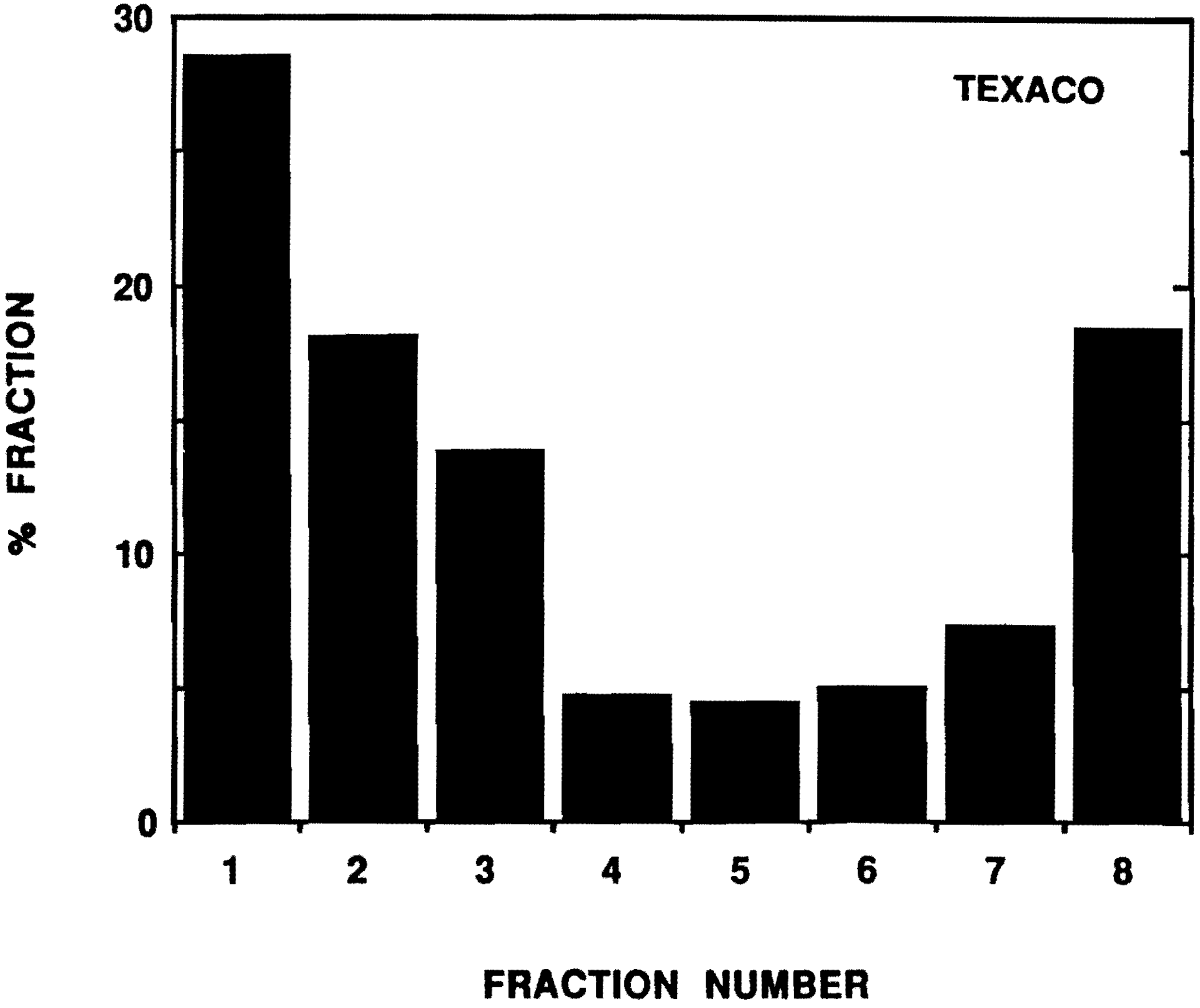

Figure 5-10
Fractional Content of Texaco Blend 1

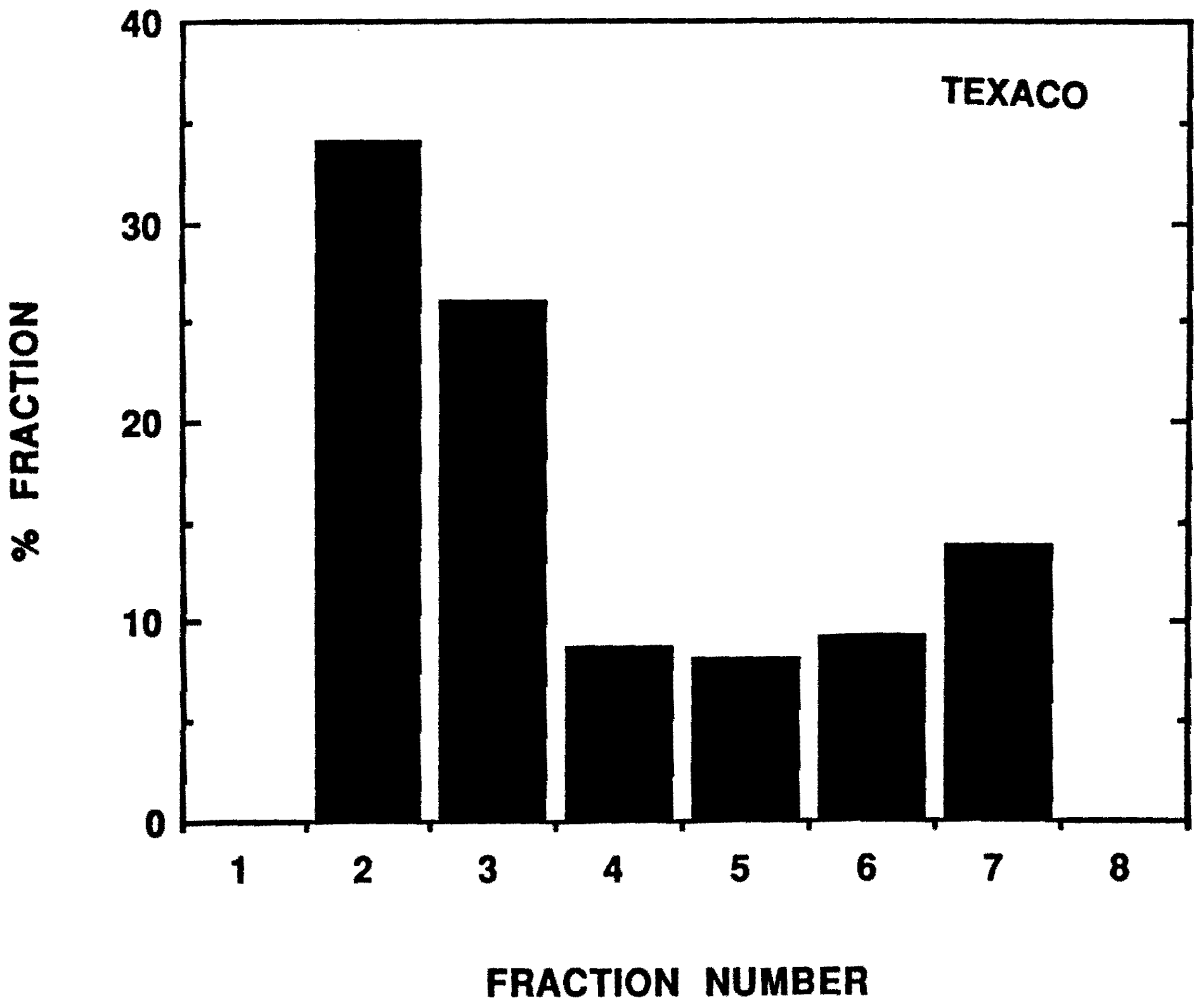

Figure 5-11
Fractional Content of Texaco Blend 2

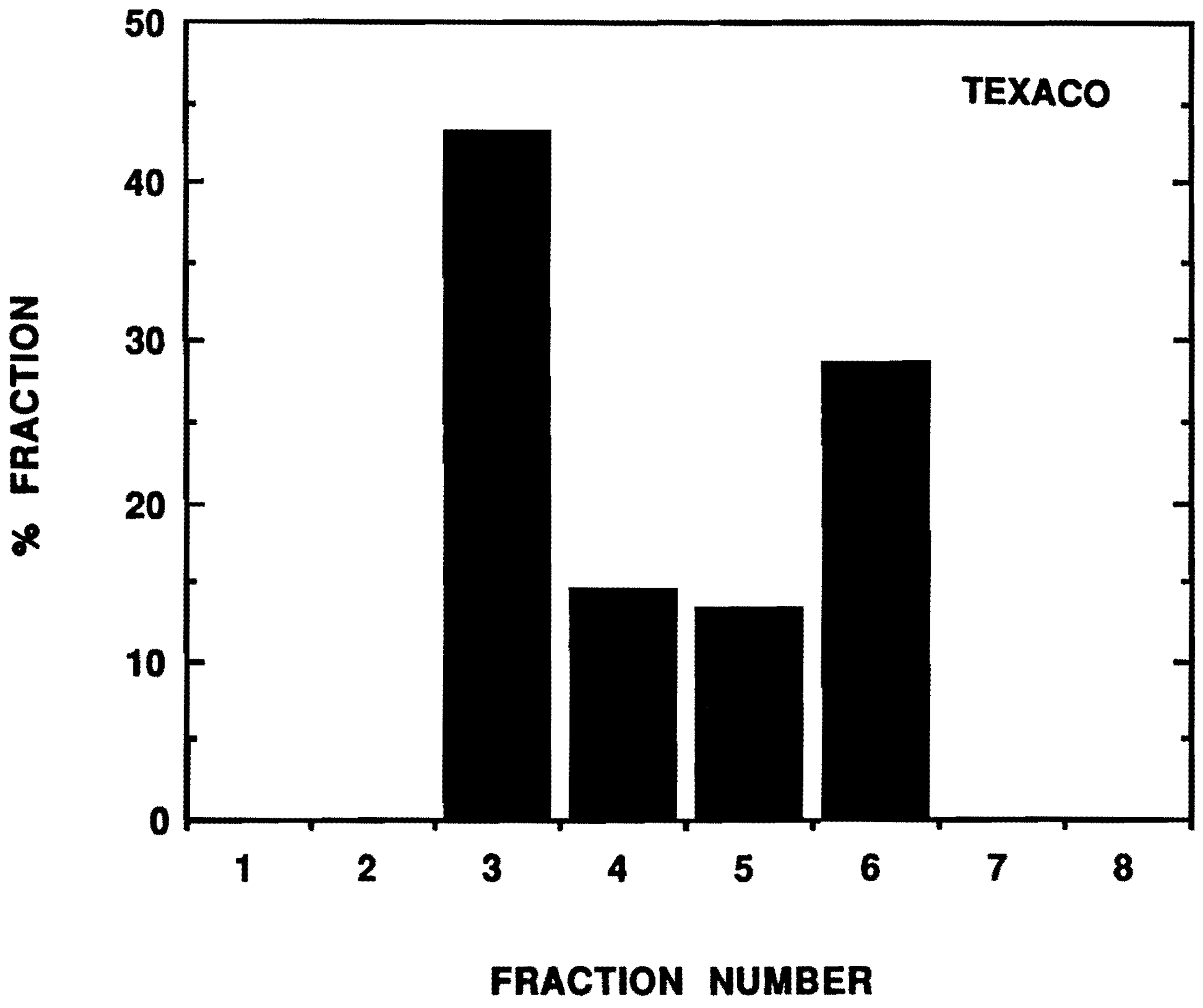

Figure 5-12
Fractional Content of Texaco Blend 3

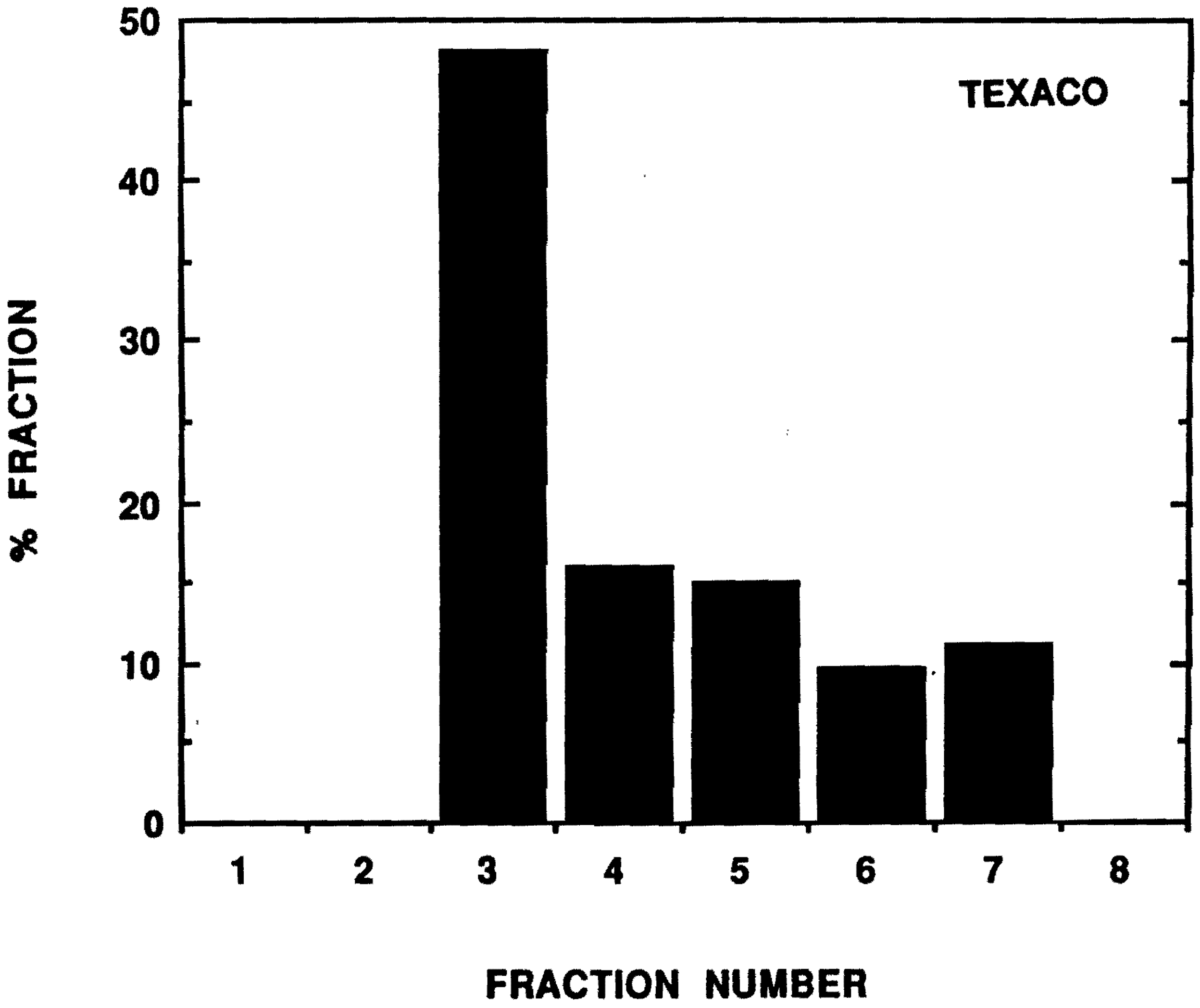

Figure 5-13
Fractional Content of Texaco Blend 4

than 17% that would result from an unchanged ratio of the remaining fractions. Fractions 3, 4, and 5 thus comprise 37.5% of blend 5 rather than the 47.2% that would result if the original ratios of the included fractions had been maintained.

Texaco blend 2 is the result of removing fractions 1 and 8 with the other fractions remaining in their original ratio. In blend 3, fractions 1, 2, 7, and 8 are completely removed; fractions 4 and 5 have the same ratio to each other as in the original; fraction 3 is reduced to 43.3% rather than 49.8% that would result from an unchanged ratio, and fraction 6 is increased similarly from 18% to 28.7%. Fractions 4 and 5 combined are thus reduced from 32% that would result from a fixed ratio of all remaining fractions to 28%. Blend 4 has fractions 1, 2, and 8 completely removed with the other fractions in unchanged ratio.

Corbett Analysis

Corbett analyses were run on only two blends, and the rest were calculated by material balances using the fraction Corbett analyses (Table 4-3) and fractional compositions (Table 5-1). The exceptions were the Ampet blend 2, used in the Marshall toughness and indirect tensile strength tests, and Texaco blend 4 which exhibited a very low aging index. The results along with whole asphalt analyses are shown in Table 5-2 and Figures 5-14 to 5-16. Blend 1 and the whole asphalt are approximately identical for each asphalt except for the solvent hardening which occurs during the supercritical processing and which converts some polar aromatics to asphaltenes.

While there seems to be little visual difference between the whole asphalt and blends, compositional differences are reflected in the Corbett analyses. In general, both asphaltenes and saturates are decreased in all blends except blend 1, with corresponding increases in naphthene and polar aromatics. Ampet blend 2 would seem to be an exception, having the same asphaltene content as the whole asphalt, but these are, however, on average, lower molecular size asphaltenes than in the whole asphalt. Otherwise, there is a progressive increase in naphthene and polar

Table 5-2
Percent of Corbett Fractions in Whole Asphalts and Blends[a]

		Saturates	Naphthene Aromatics	Polar Aromatics	Asphaltenes
Ampet					
	Whole	9.34	45.45	32.91	12.37
	Blend 1	9.83	46.60	22.82	15.82
	Blend 2	7.60	49.16	26.44	12.40
	Blend 3	6.24	50.03	29.13	9.46
	Blend 4	5.12	55.04	32.69	2.83
Coastal					
	Whole	12.38	39.47	26.60	18.07
	Blend 1	11.25	42.10	19.99	24.40
	Blend 2	9.68	47.34	24.69	17.07
	Blend 3	8.85	49.97	29.66	11.43
	Blend 4	8.78	47.41	31.86	11.33
	Blend 5	9.31	47.55	27.84	13.48
Texaco					
	Whole	12.30	43.63	21.99	17.80
	Blend 1	10.79	45.53	18.51	22.82
	Blend 2	8.71	52.94	25.49	11.39
	Blend 3	7.17	51.74	31.23	7.67
	Blend 4	7.64	52.65	27.87	10.18

[a] The values for the blends are calculated from the Corbett analyses of fractions 1 through 8 (Table 4-3) and the blend compositions (Table 5-1).

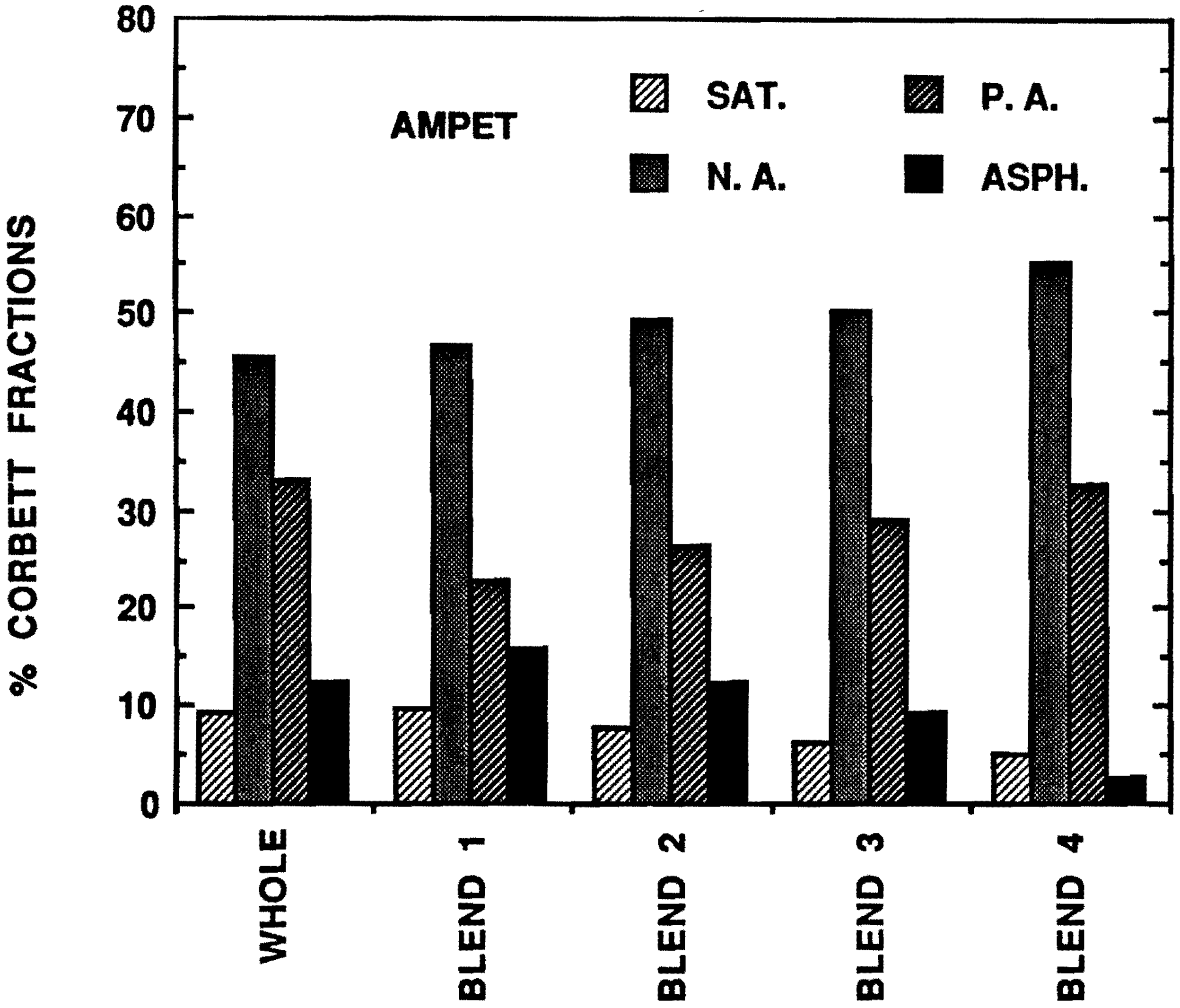

Figure 5-14
Corbett Analyses of Ampet Blends

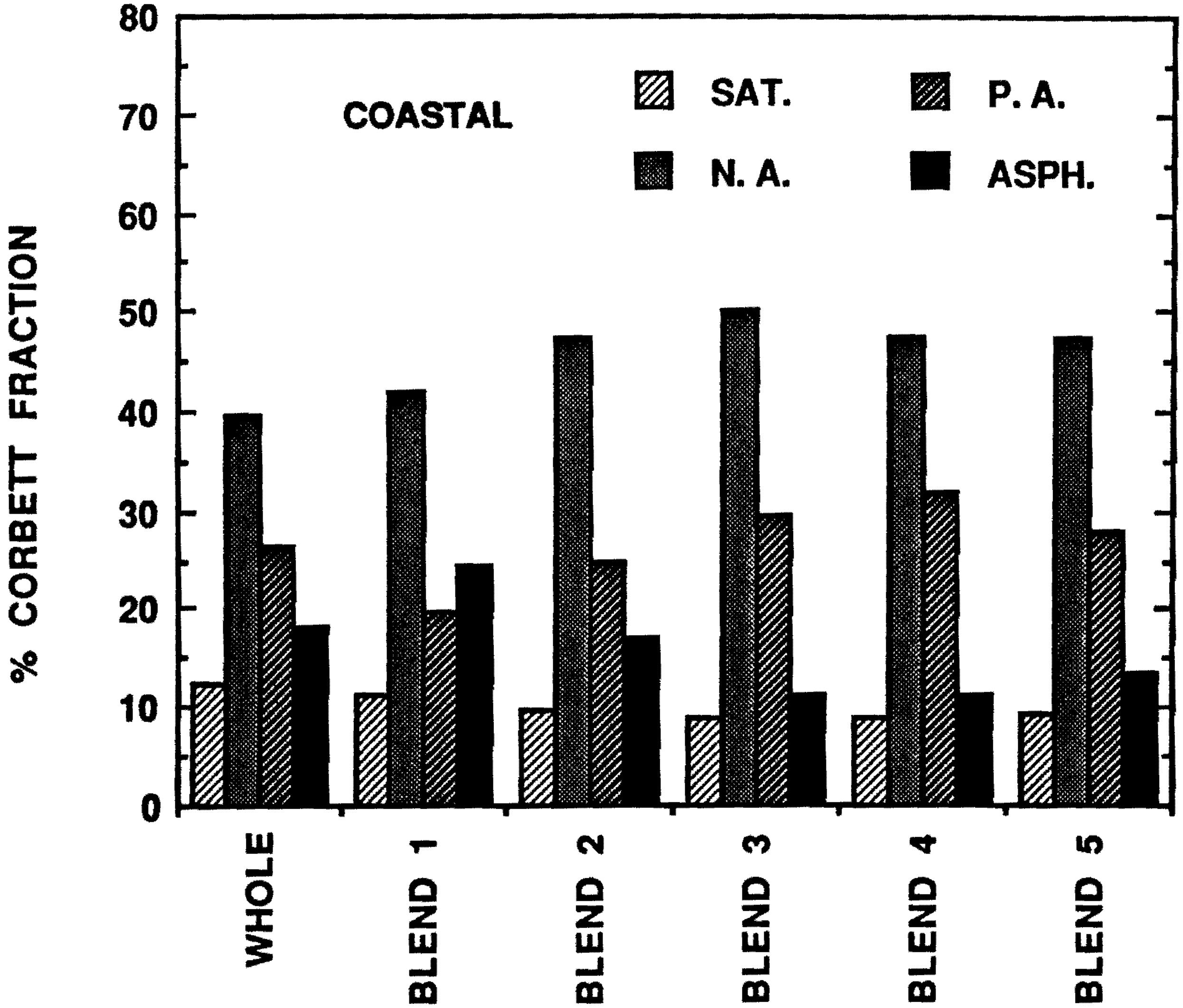

Figure 5-15
Corbett Analyses of Coastal Blends

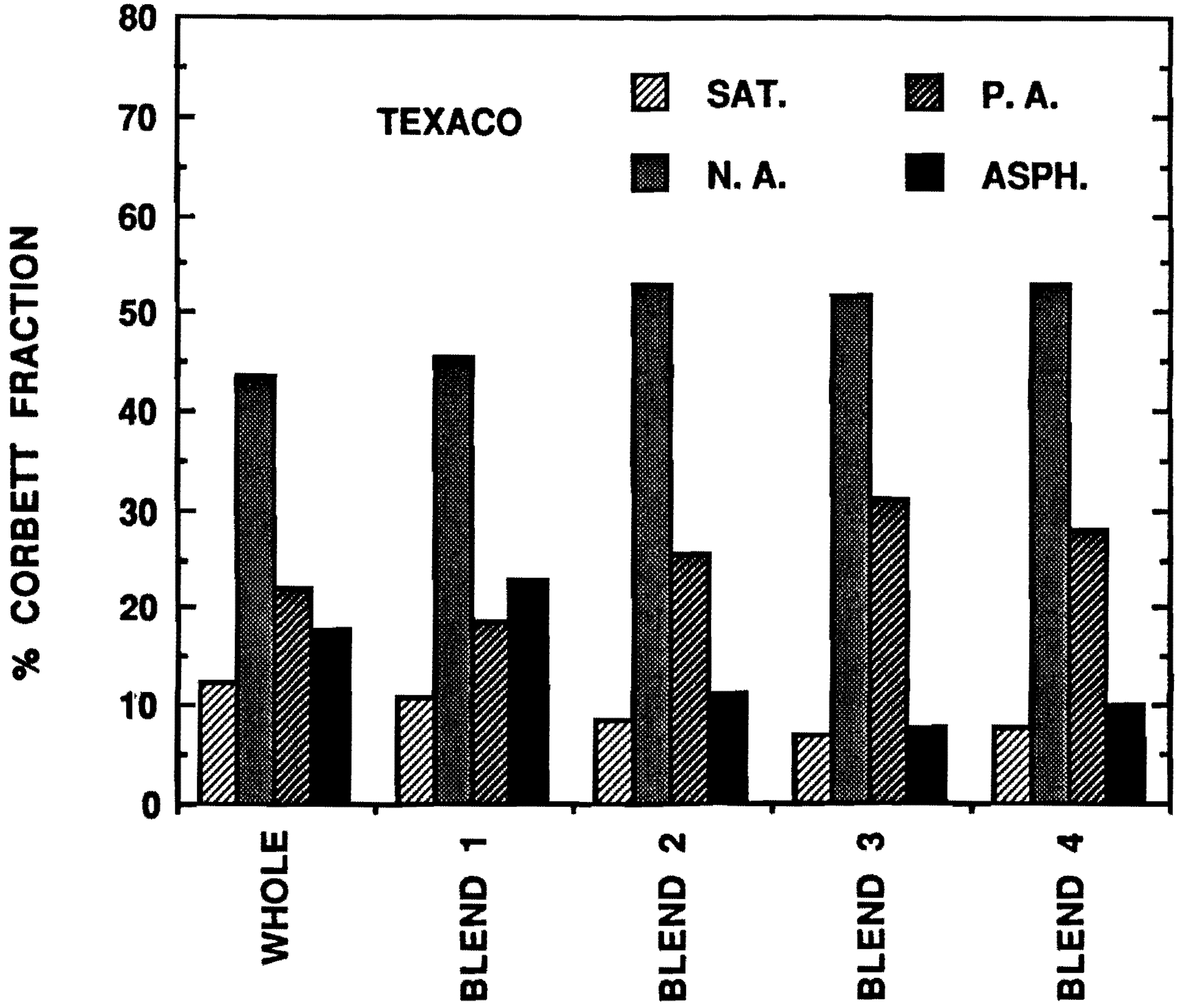

Figure 5-16
Corbett Analyses of Texaco Blends

aromatics with a decrease in saturates and asphaltenes in progressing from Ampet blend 2 to blend 4.

For the Coastal blends, asphaltenes decreased in progressing from whole asphalt, to blends 2, 4, and 5. Blends 2 to 5 have roughly the same saturate content but all are lower in saturates than the whole asphalt. Saturates and naphthene aromatics are nearly the same in blends 2 and 5 but asphaltenes are lower and polar aromatics higher in blend 5. Blends 3 and 4 are very similar in Corbett analysis even though two fractions present in blend 3 (3 and 7) are absent in blend 4.

Because Texaco has higher amounts of saturates and asphaltenes which are largely concentrated in the light and heavy fractions respectively, the blends show considerable decrease in these Corbett fractions. Blend 3 is lowest in saturates and asphaltenes and has a considerably elevated polar aromatic content. Actually, the differences in the amount of naphthene aromatics and polar aromatics between blends is not very great, in general, but this ignores the fact that although these Corbett fractions are widely distributed in the supercritical-solvent extracted fractions, the nature of this material is considerably different in going from fractions 1 to 8.

GPC Analysis of Blends

The GPC chromatograms of the whole asphalts and blends 1 and 2 for all three source asphalts are shown in Figures 5-17 to 5-19. Blend 1 is an attempt to restore the original asphalt, but in each case blend 1 has more (or larger) large molecular size material than the whole asphalt. We believe this is caused primarily by the solvent hardening that has been shown to occur whenever an asphalt is dissolved in a solvent, and this effect is greatly accelerated by high temperature (Davison, et al. 1989). These results are also consistent with the higher asphaltene content calculated for all blend 1s from the fractional analyses. This calculated excess is smallest for the Ampet blend 1, and this is consistent with its Corbett analysis.

Blend 2 for the three asphalts is the result of removing fractions 1 and 8

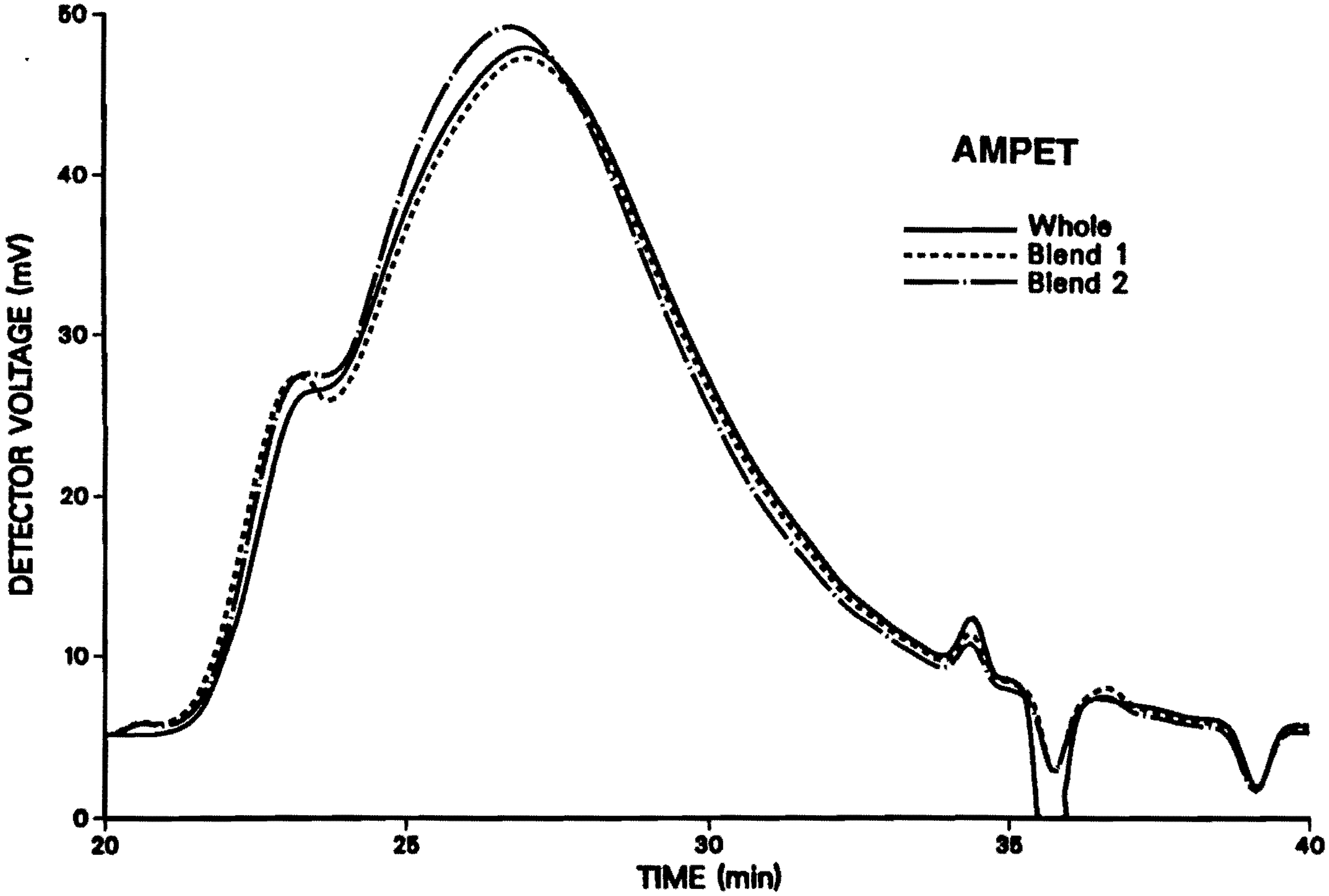

Figure 5-17
GPC Chromatograms of Ampet Whole
and Blends 1 and 2

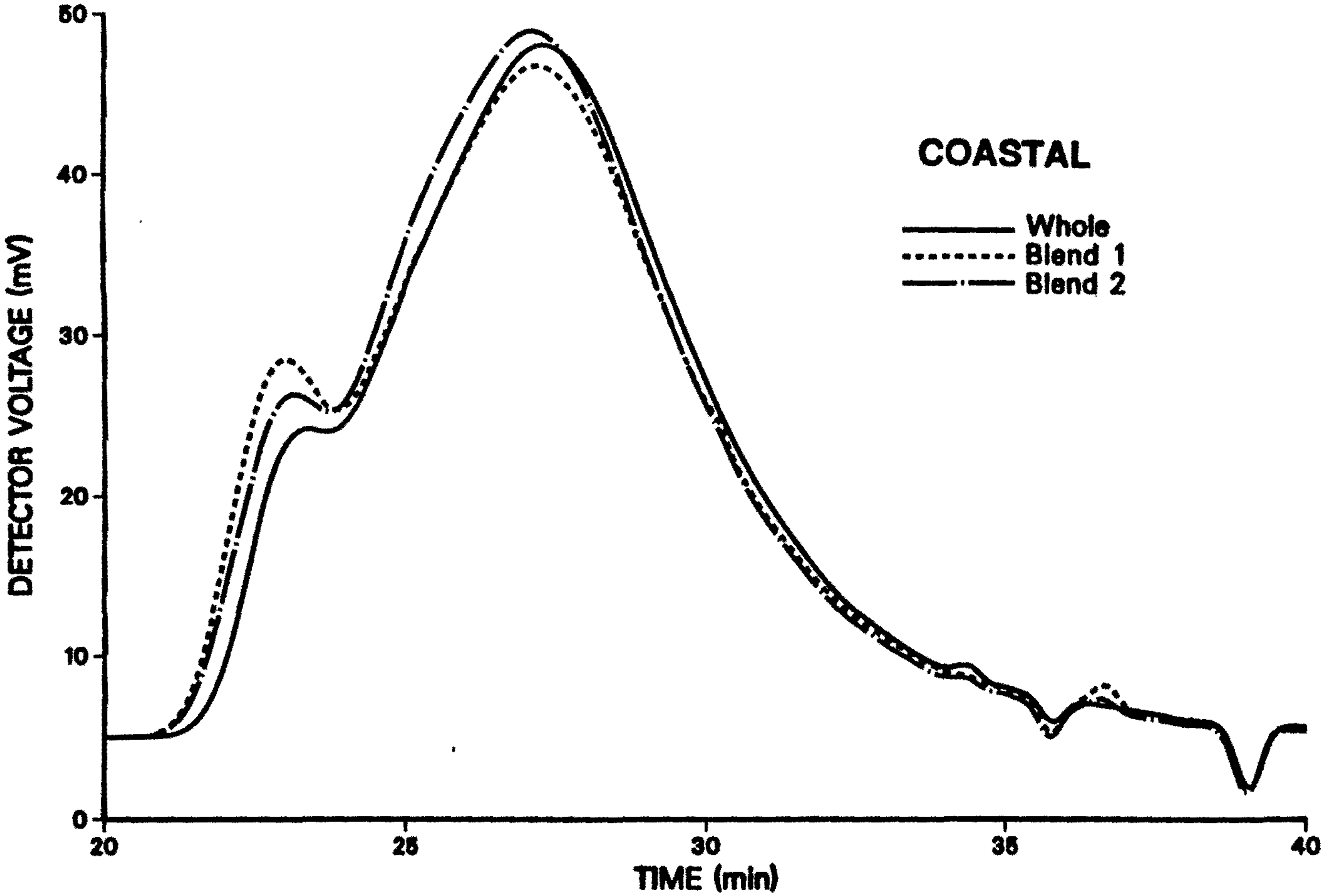

Figure 5-18
GPC Chromatograms of Coastal Whole
and Blends 1 and 2

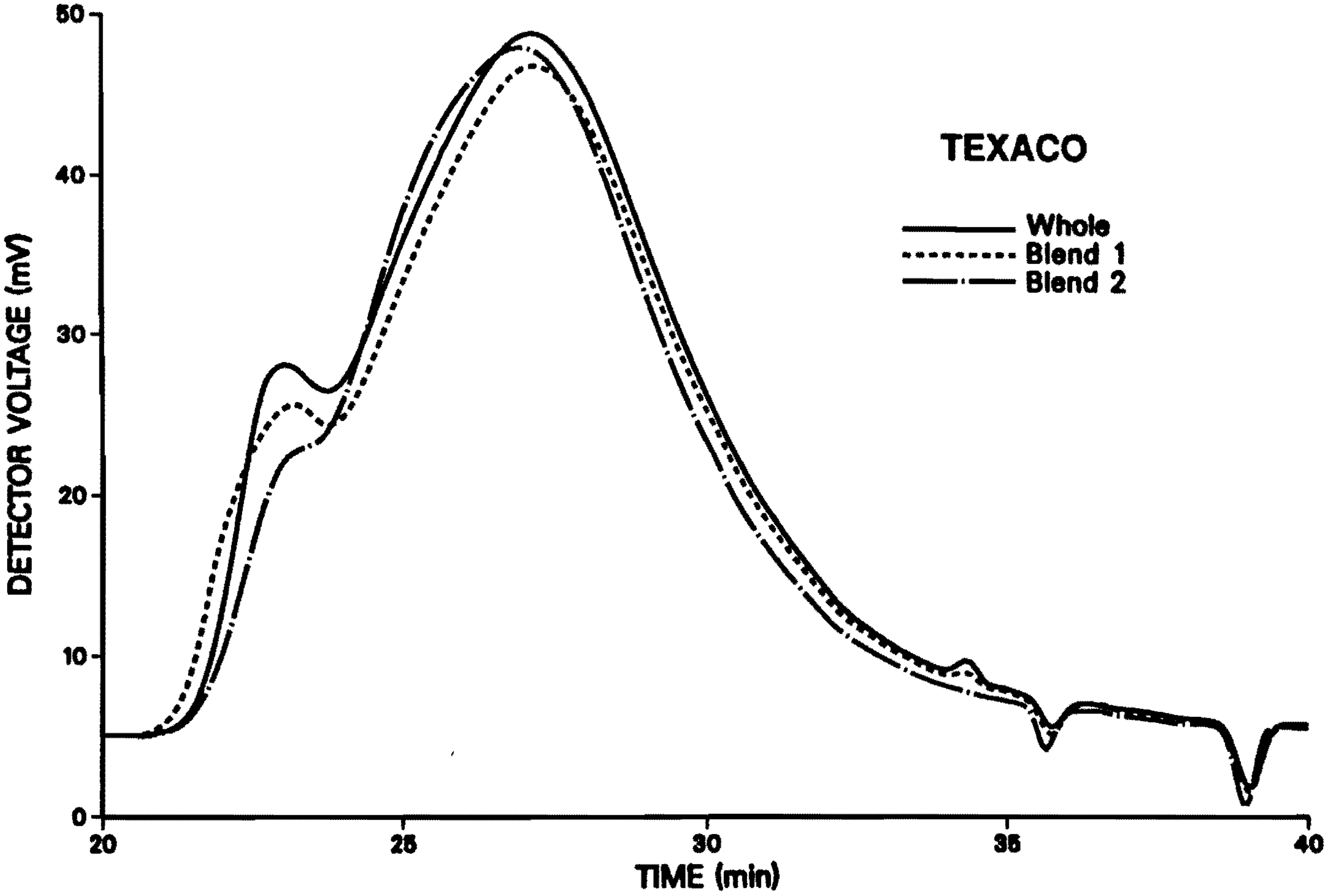

Figure 5-19
GPC Chromatograms of Texaco Whole
and Blends 1 and 2

except for the Coastal material which also had slight manipulation of other fractions to achieve the desired viscosities. The Texaco whole asphalt has the largest fraction 8, and the lower quantity of large-size material in blend 2 is consistent with this. However, both Coastal and Ampet blend 2 show more large-size material than the whole asphalt, and at this point, this can only be explained by the production of larger-size material by the supercritical processing.

All three blend 3s, however, are inconsistent in this respect, Figures 5-20 to 5-22. With both fraction 7 and 8 gone and fraction 6 as the only remaining fraction having very large-size material (and this at a lower percentage than of the removed material) it is difficult to explain the close agreement between these blends and the whole asphalt.

Ampet and Texaco blend 4 show much less large-size material, as expected. Coastal blend 4, on the other hand is close to blend 3. Coastal blend 4 differs from Texaco and Ampet in the absence of fraction 3 and a great increase in fraction 4. GPC analysis of the fractions used to make Coastal blend 4 does not indicate that it should contain as much material eluting at 22 min as there is. Coastal blend 5 has a large fraction 6 offset by increased fraction 2 and 3.

Figures 5-23 to 5-30 are chromatograms of the Corbett fractions of the two blends for which Corbett analyses were actually run, the Ampet blend 2 and the Texaco blend 4. These are compared to fractions from the whole asphalt and from the initial top and bottom separation made of each asphalt. For the saturate fractions there was not sufficient material in the bottom of the Ampet cut. The wide size distribution in the Texaco bottom saturates (Figure 5-24) indicates probable contamination with naphthene aromatics due to an error in the cut point. Also the slightly overall wider chromatograms shown by the Ampet top saturates as compared to the whole asphalt saturates (Figure 5-23) could be caused by slight contamination. However, the higher molecular size shown by both blend 2 and blend 4 saturates compared to their whole asphalt saturates is reasonalbe, as each has the low-sized saturates of fraction 1 removed (See Figures B-7 and B-42). Furthermore, the general similarity of the chromatograms at the small-sized material end indicates a

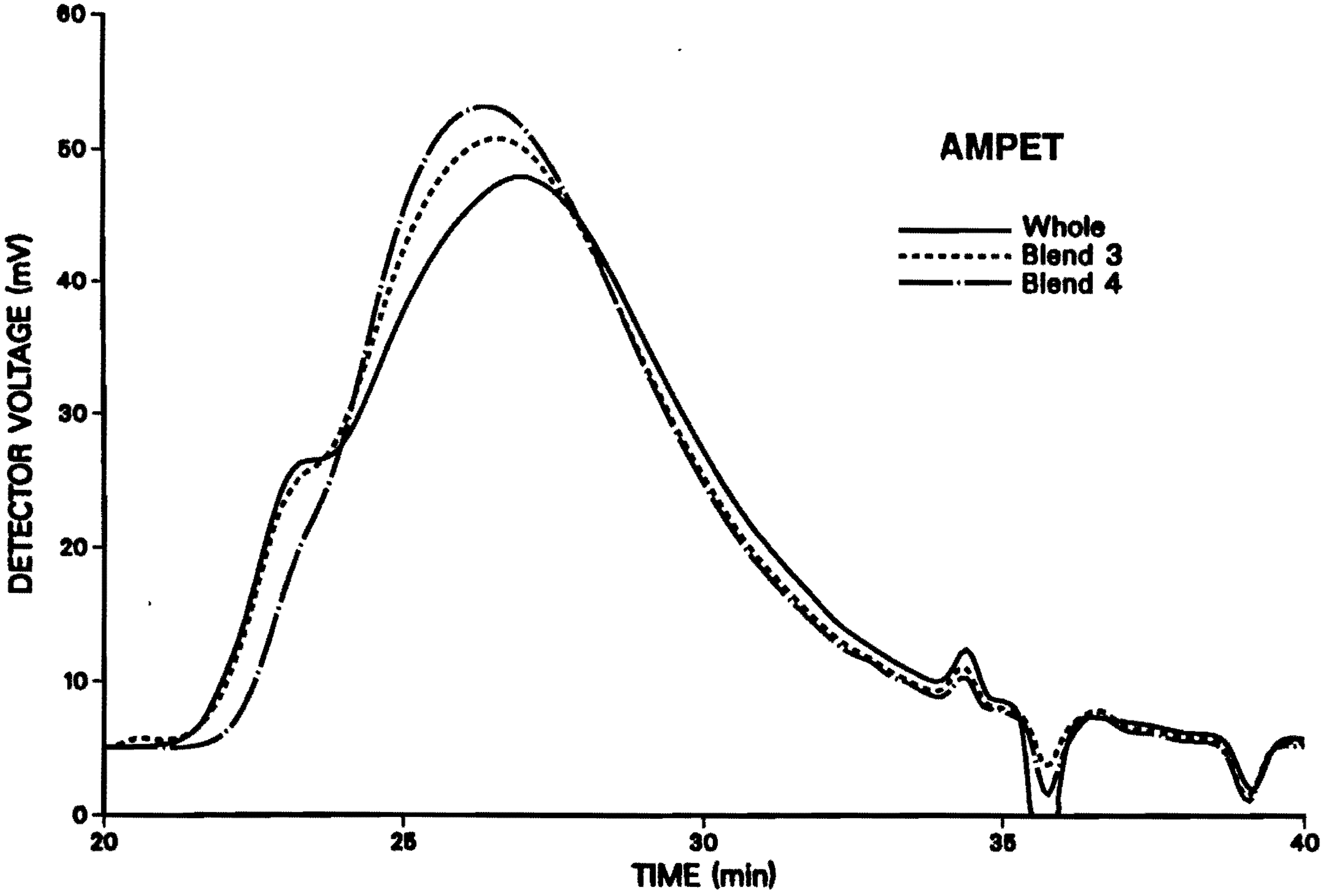

Figure 5-20
GPC Chromatograms of Ampet Whole
and Blends 3 and 4

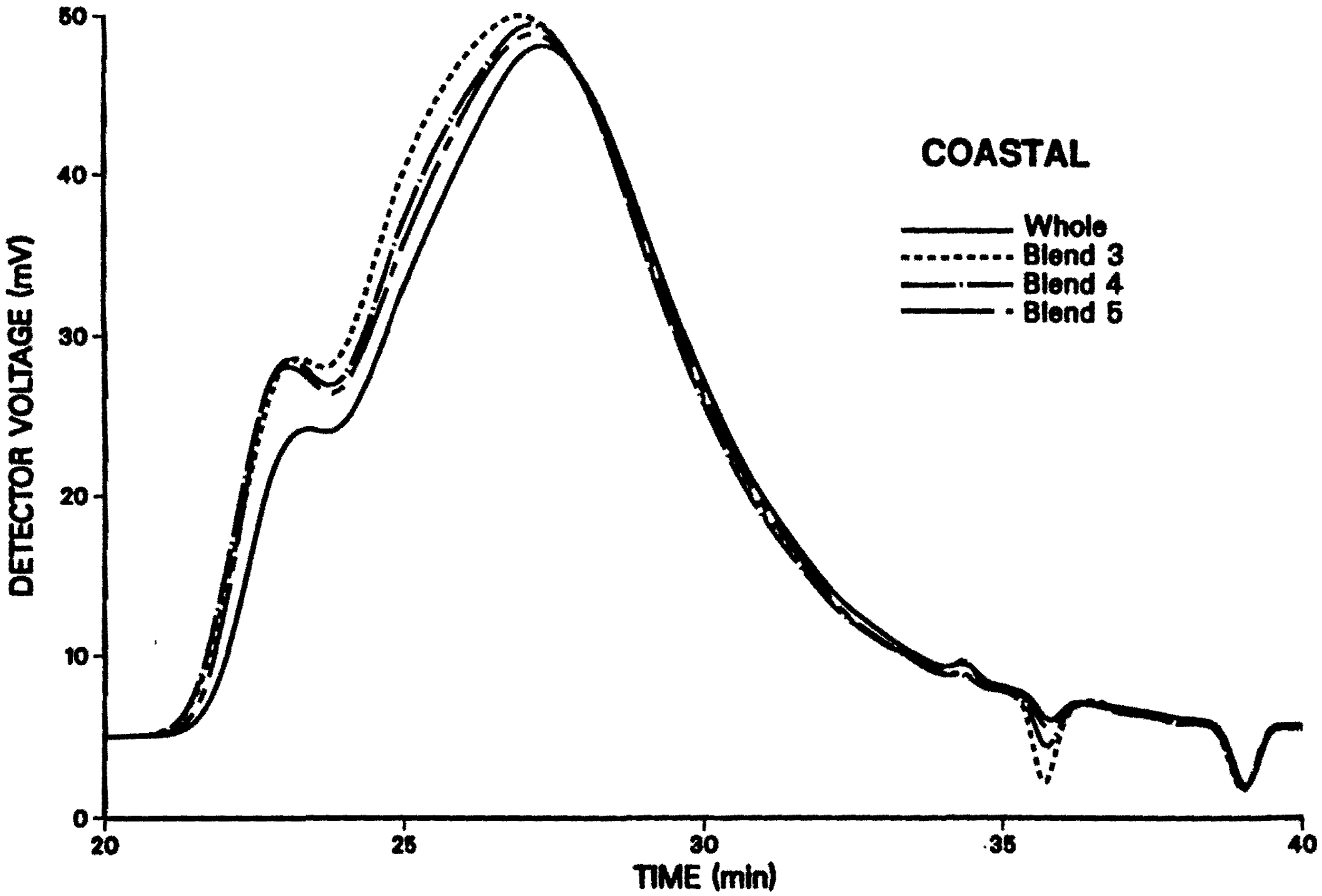

Figure 5-21
GPC Chromatograms of Coastal Whole
and Blends 3-5

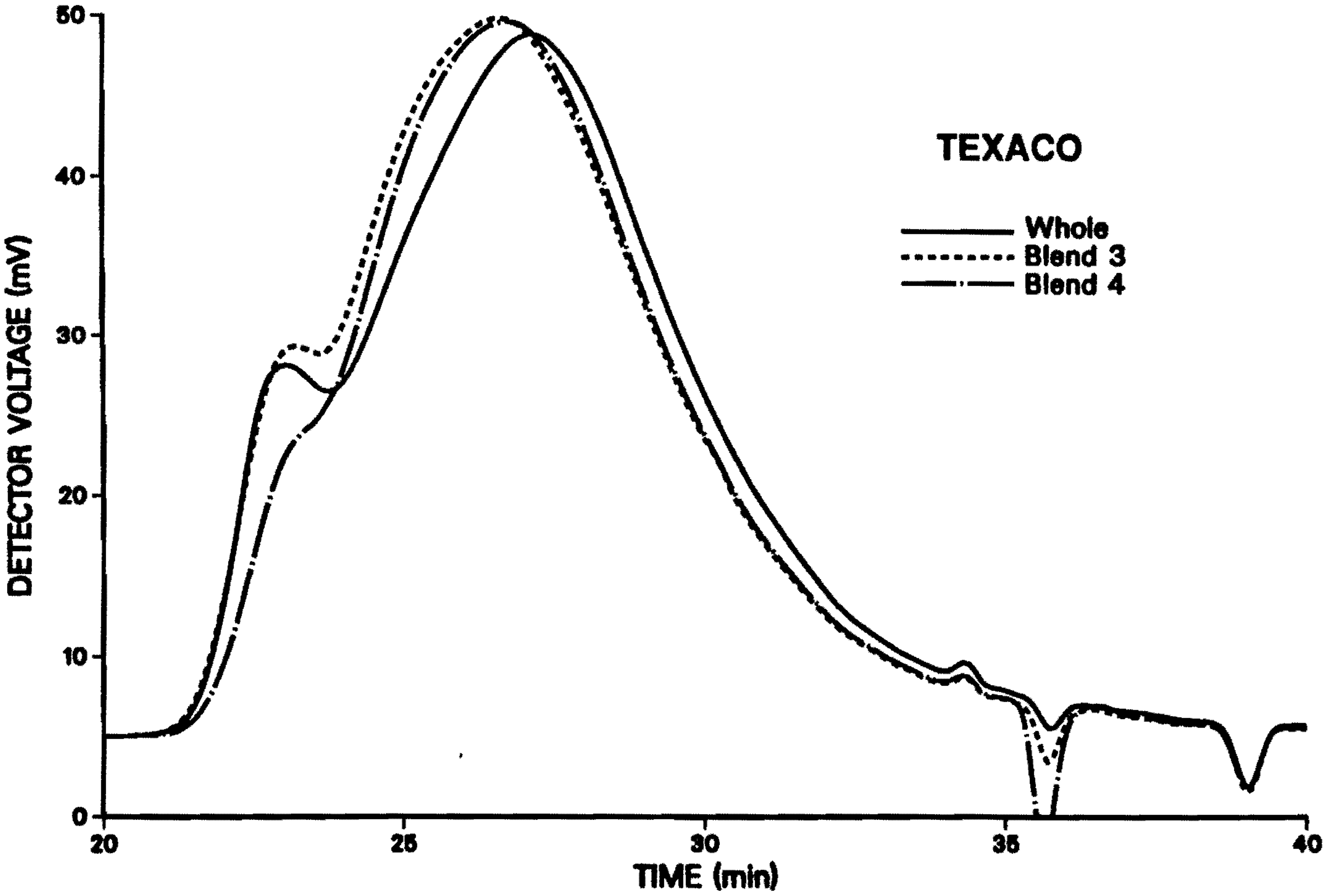

Figure 5-22
GPC Chromatograms of Texaco Whole
and Blends 3 and 4

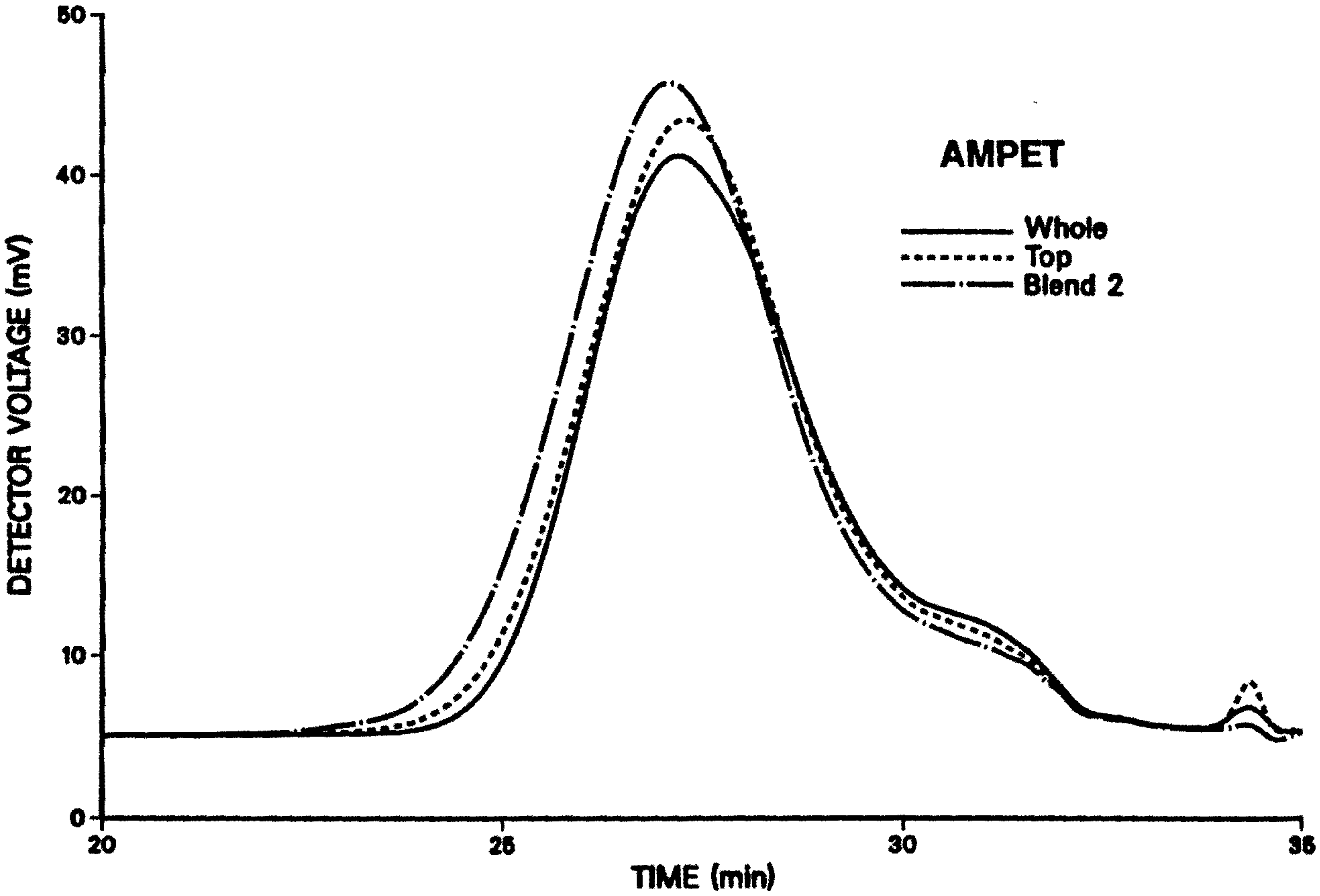

Figure 5-23
GPC Chromatograms of Saturates from
Ampet Whole, Top Fraction, and Blend 2

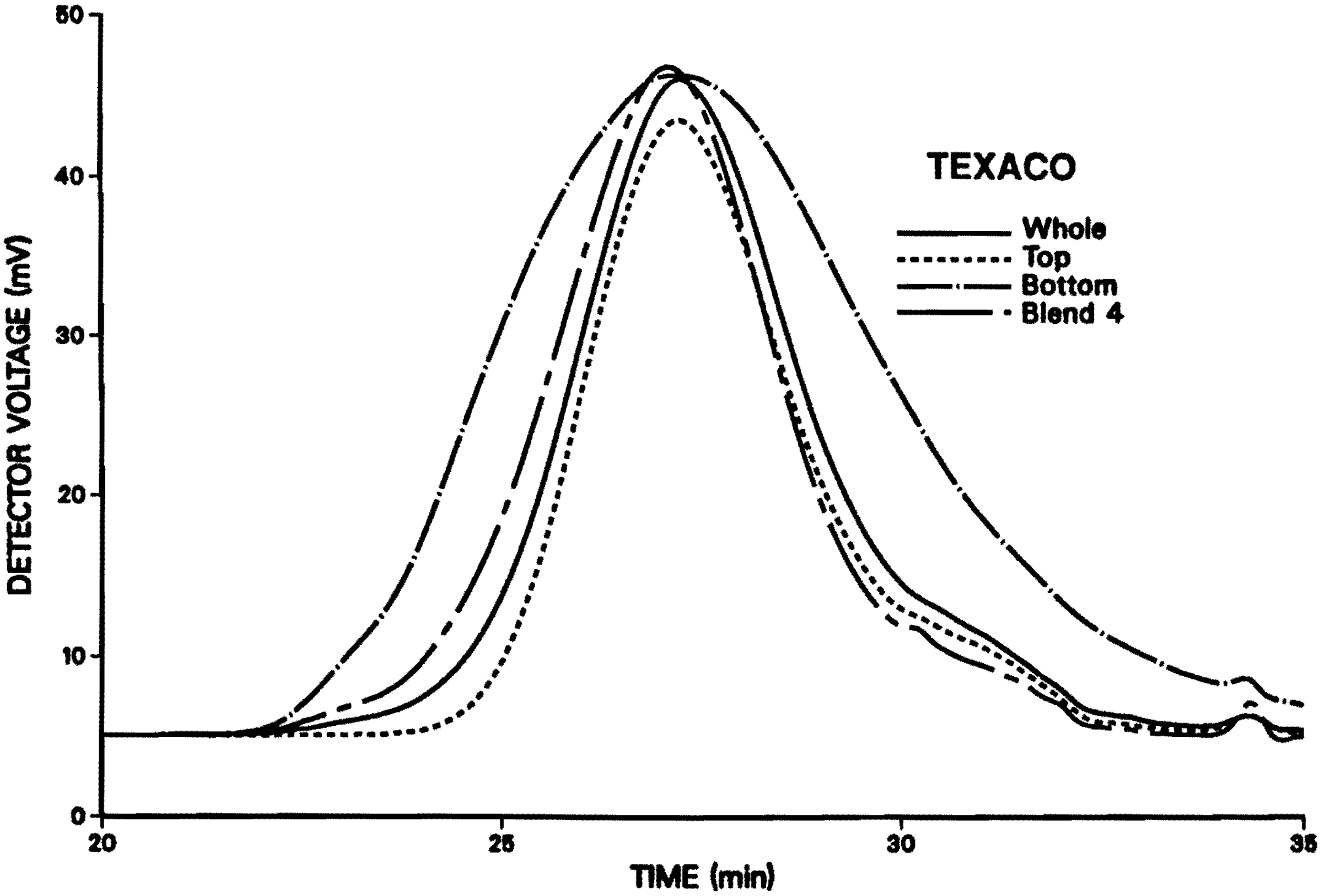

Figure 5-24
GPC Chromatograms of Saturates from Texaco Whole,
Top and Bottom Fractions, and Blend 4

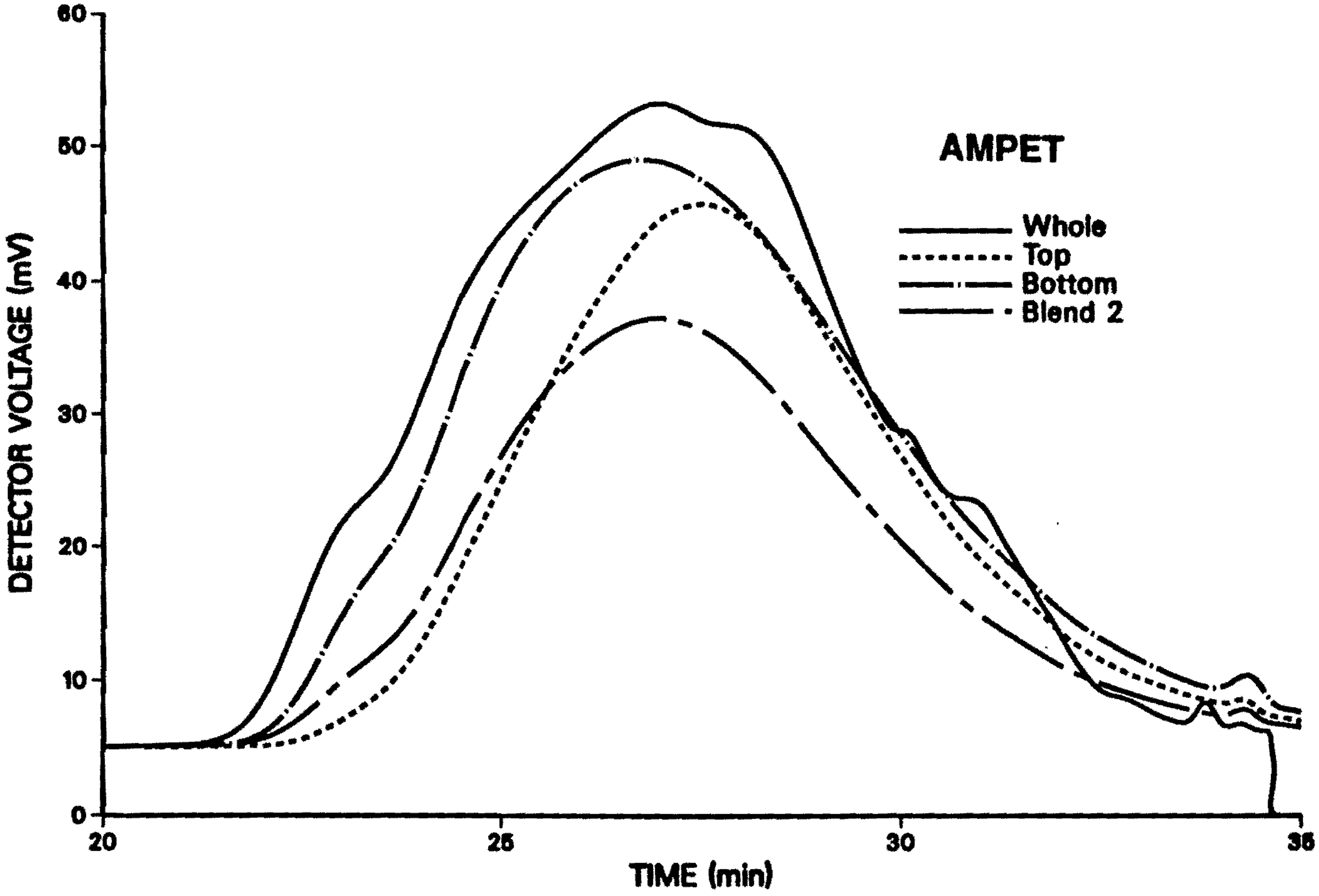

Figure 5-25
GPC Chromatograms of Naphthene Aromatics from
Ampet Whole, Top and Bottom Fractions, and Blend 2

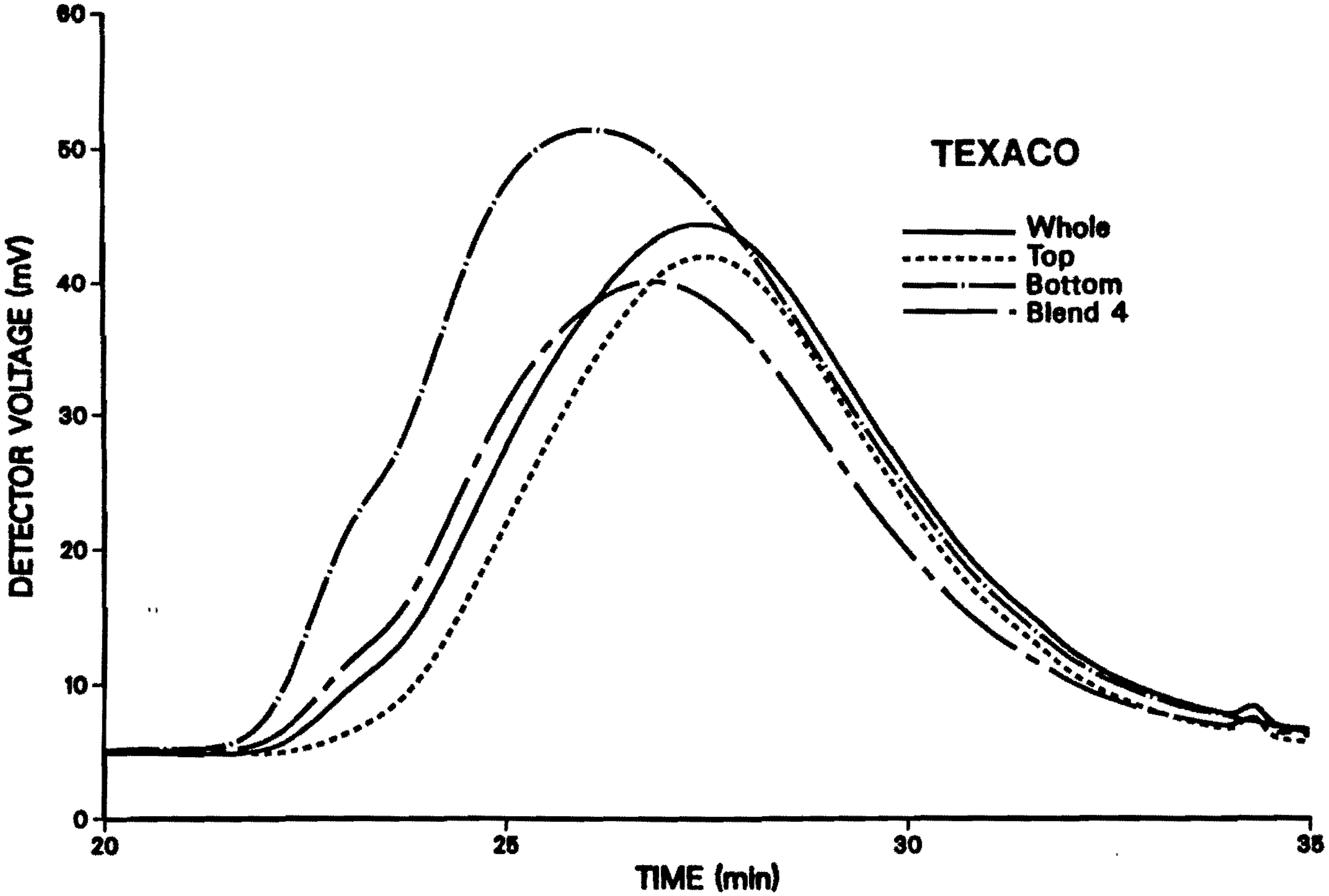

Figure 5-26
GPC Chromatograms of Naphthene Aromatics from
Texaco Whole, Top and Bottom Fractions, and Blend 4

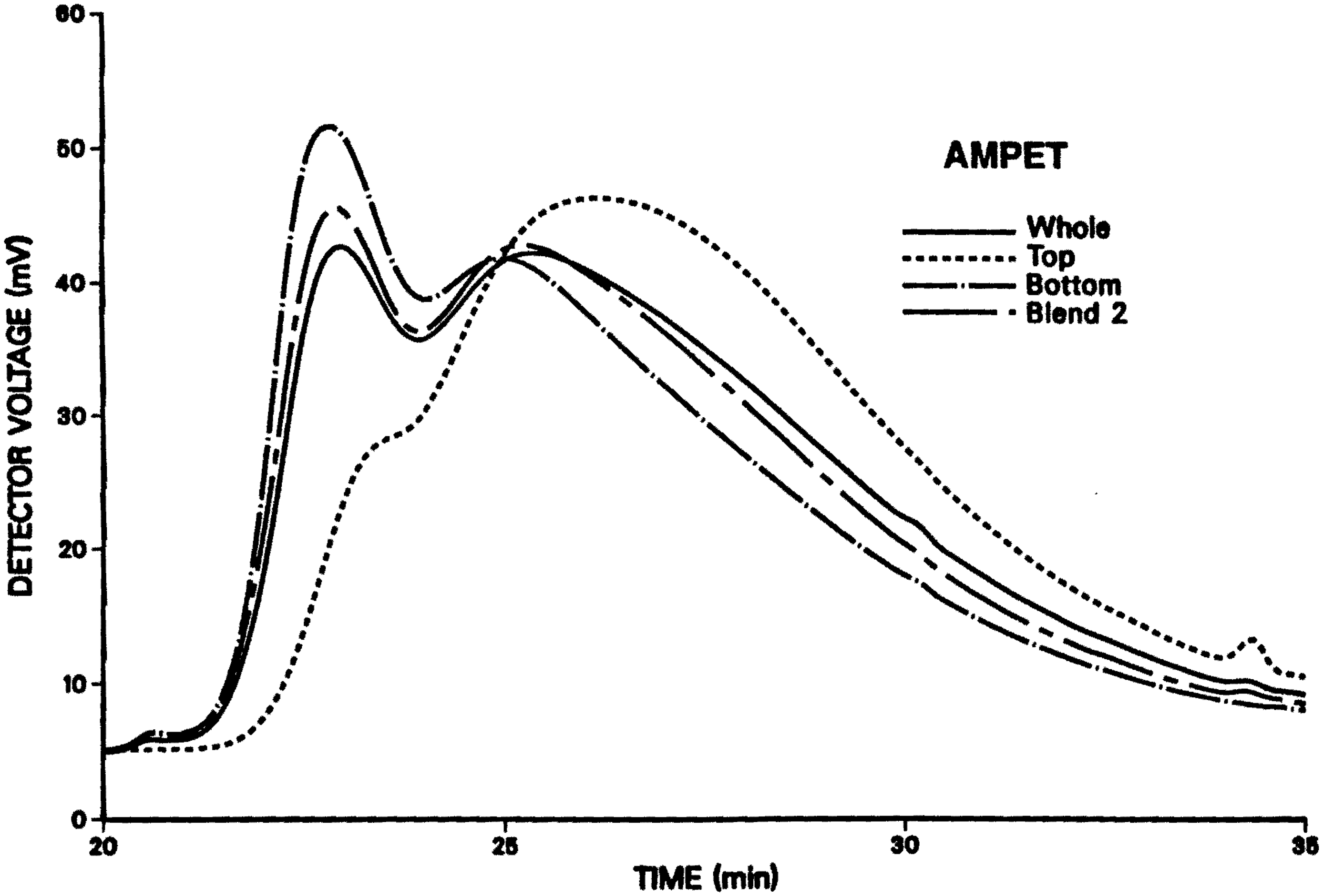

Figure 5-27
GPC Chromatograms of Polar Aromatics from
Ampet Whole, Top and Bottom Fractions, and Blend 2

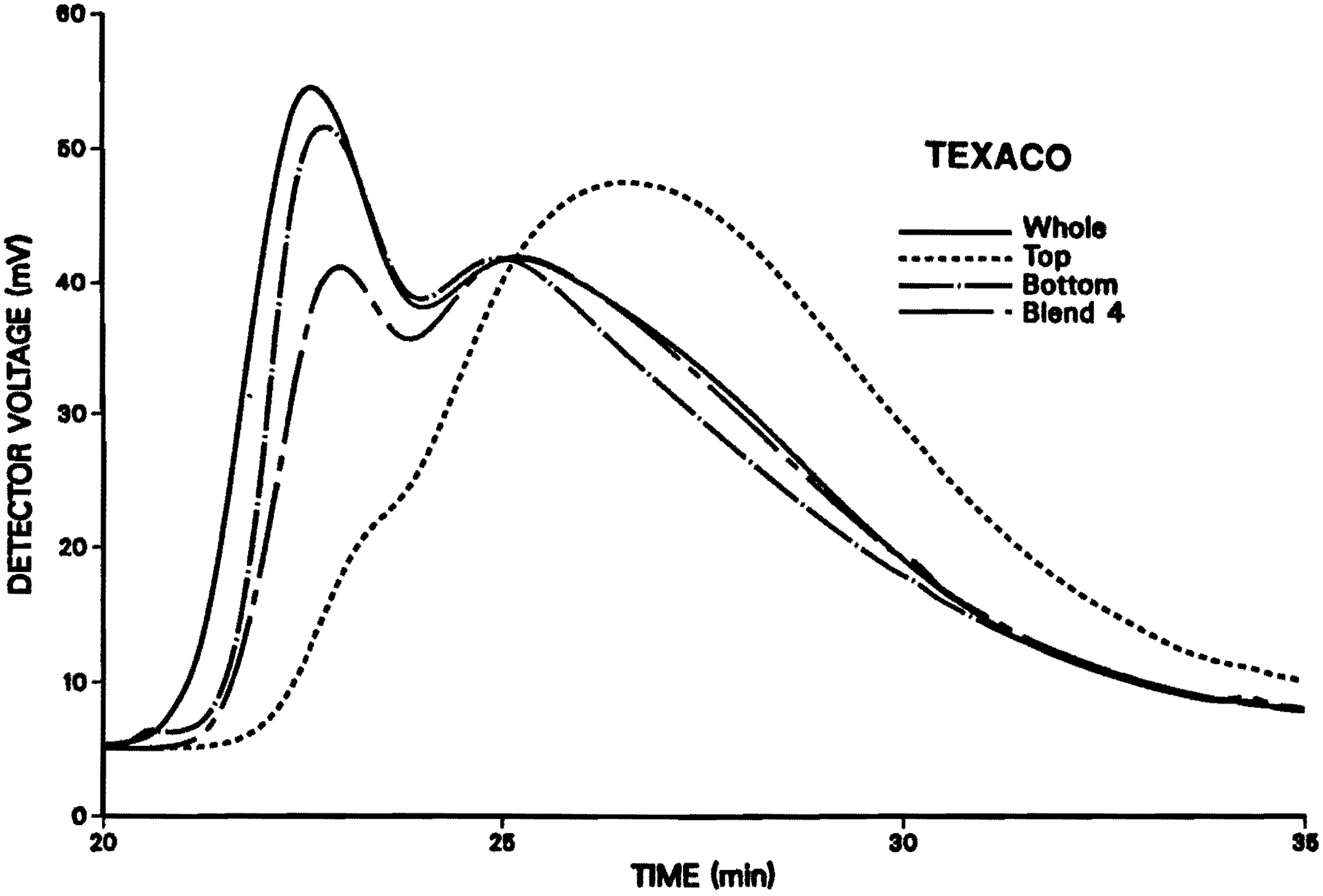

Figure 5-28
GPC Chromatograms of Polar Aromatics from
Texaco Whole, Top and Bottom Fractions, and Blend 4

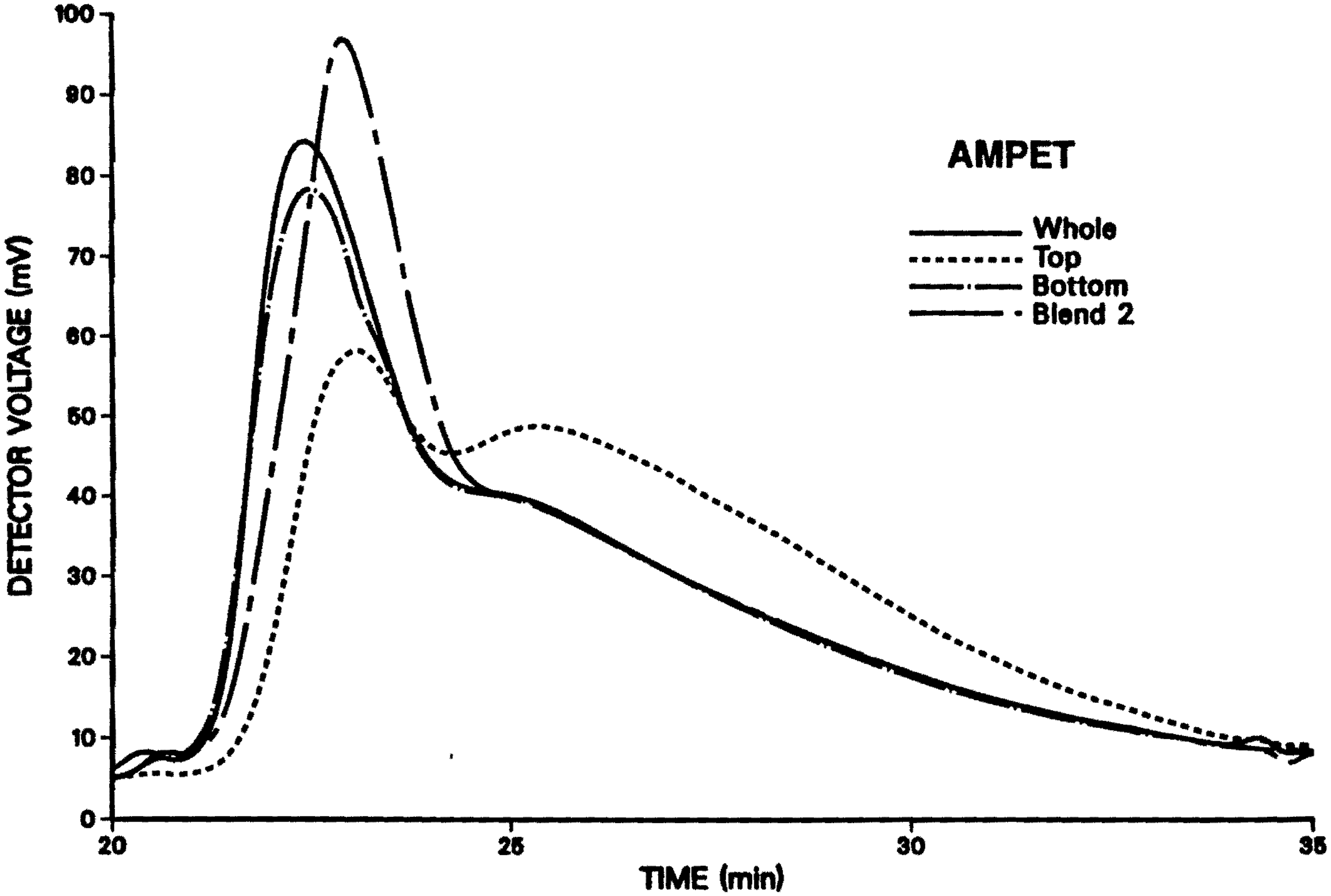

Figure 5-29
GPC Chromatograms of Asphaltenes from
Ampet Whole, Top and Bottom Fractions, and Blend 2

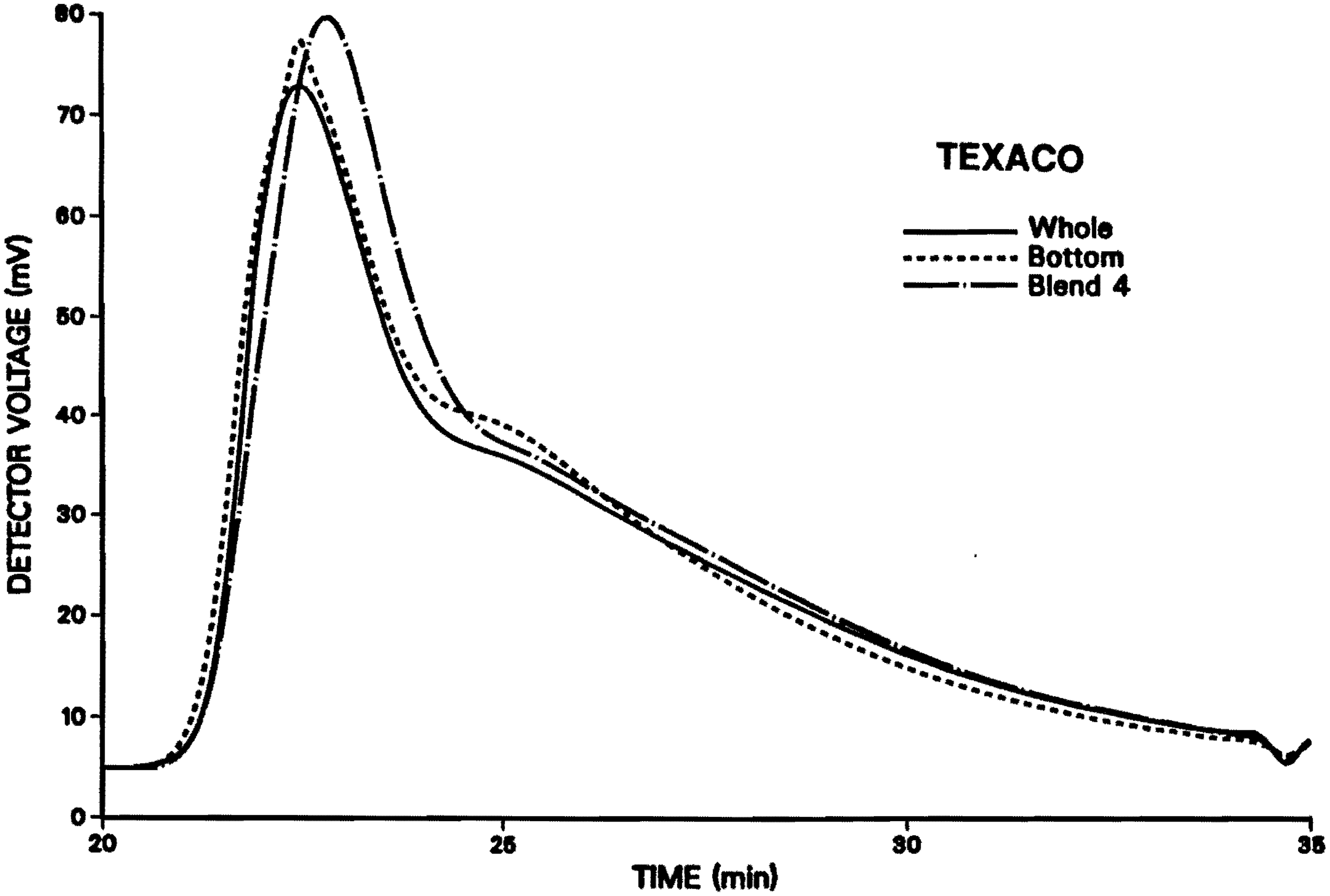

Figure 5-30
GPC Chromatograms of Asphaltenes from
Texaco Whole, Bottom Fraction, and Blend 4

lack of contamination.

The naphthene aromatic fractions of these blends and their source whole asphalts (Figures 5-25 and 5-26) are distributed about as expected except for the obviously contaminated Ampet whole asphalt naphthene aromatics. In the blends, there is more large-size material because of increased fraction 5 and 6 ratios but less small-size material because of the removal of fraction 1. The Texaco whole asphalt polar aromatics (Figure 5-28) also indicate contamination as they show more large-size material than the bottom fraction polar aromatics. The blend polar aromatics, however, are related to the top and bottom polar aromatics, as would be expected, falling between the top and bottom material at both the large and small ends of the chromatogram (Figures 5-27 and 5-28).

The blend asphaltenes show the effect of removing fraction 8 asphaltenes and increasing the lower-sized fraction 4 asphaltenes (Figures 5-29 and 5-30). Even here, the Ampet whole asphalt asphaltenes seem to contain more larger sized material than the bottom fraction asphaltenes which seems unlikely unless some of the bottom material were not recovered from the supercritical unit. This is a possibility as it was very difficult to recover all of the hard bottom fraction and it might be that some of the hardest material was not completely recovered.

Blend Physical Properties

Table 5-3 contains results of viscosity and penetration measurements for the whole asphalts and blends. In addition, values of the aging index (ratio of 60 °C viscosity after aging to that before) and temperature susceptibility are given. Blend 1 in each case is an attempt to reproduce the original asphalt. As already reported, the Corbett and GPC data indicate an increase in asphaltenes and large-sized material during processing. The increased viscosities for the Coastal and Texaco blends are consistent with this, but the Ampet blend 1 does not show this and, in fact, shows lower viscosities and higher penetration. The cause of this is unknown. Results for Coastal blends 1, 2, and 4 are marred by incomplete solvent removal

Table 5-3: Viscosity, Penetration, VTS, PVN, and Aging Index For Asphalts and Asphalt Blends

Sample	Visc 60°C (poise)	Visc 135°C (stokes)	Pen 25°C	RTFOT Visc 60°C (poise)	VTS	PVN	Viscosity Aging Index
Ampet							
Whole	2350	4.19	60	5462	3.53	-0.67	2.32
Blend 1	1447	3.83	101	3723	3.41	-0.35	2.57
Blend 2	2250	4.57	65	4834	3.44	-0.59	2.15
Blend 3	1688	3.94	81	4132	3.45	-0.55	2.45
Blend 4	1019	2.85	129	2898	3.51	-0.32	2.84
Coastal							
Whole	2013	4.14	72	5639	3.48	-0.55	2.80
Blend 1	4875	11.55	57	54427	3.05	-0.02	11.16
Blend 2	1828	4.19	84	5327	3.43	-0.41	2.91
Blend 3	2484	5.01	60	4914	3.41	-0.61	1.98
Blend 4	1598	4.26	91	7129	3.36	-0.42	4.46
Blend 5	2303	4.32	66	4650	3.50	-0.54	2.02
Texaco							
Whole	1891	4.09	93	4822	3.46	-0.33	2.55
Blend 1	2500	6.09	94	6357	3.26	0.11	2.54
Blend 2	804	2.70	180	1418	3.46	0.01	1.76
Blend 3	2222	4.63	74	3814	3.43	-0.39	1.72
Blend 4	1192	3.25	126	1665	3.47	-0.19	1.40

which resulted in a higher apparent aging index and no doubt affected other properties. (The solvent was detected in the original GPC chromatograms of the blends. The chromatograms of this report were made significantly after the blends were made, long enough that solvent had evaporated to considerably lower levels. The original chromatograms appear in the Master of Science Thesis of J. R. Stegeman, 1991. New data were obtained for this report so that a consistent set of results, obtained on the same chromatographic columns, could be given. Solvent can also be detected in infrared spectra by the presence of a peak at about 930 cm^{-1}. However, because the spectra are obtained by depositing a thin film of asphalt on the ATR prism, much of the residual solvent is lost before the measurement can be made. Consequently, such measurements are not quantitative indicators of the blend solvent concentrations.)

Blends other than blend 1s were produced, as described previously, by removing progressively more material from the light and heavy fractions, and the properties of these blends were of particular interest. Excluding from these the solvent-contaminated blends (Coastal blends 2 and 4), six of the remaining eight blends show significantly better aging indexes than the original asphalts and a number show considerably better PVN but not VTS. For instance, Texaco blend 4 has an extremely good aging index and a very good PVN.

While these results are very encouraging as this was the first attempt at blending fractions, correlations between the chemical and physical properties remain elusive. Attempts to correlate VTS or PVN with Corbett analyses or to correlate the aging index with Corbett results and metal analysis failed. VTS, being essentially unchanged by the blending, provides no differences to correlate with the composition differences; PVN, although exhibiting changes with composition, still has not yielded a correlation. The only obvious trend in the results would appear to be the rapidly improving aging index in the Texaco blends from blend 2 to blend 4. With Ampet, only blend 2 is significantly improved. With Coastal, two blends have an improved aging index without much change in VTS or PVN.

The problem of course, is that we only have 13 blends, the materials were changed during processing, and some of the heaviest material may have been lost. In addition there were, doubtless, some material balance errors and perhaps also some errors in Corbett analysis. But more importantly, the normal variety to asphalt composition has been increased by the blending, and it will require much more, very systematic data to untangle the resulting complications. To be successful, we believe that measures of blend compatibility must be incorporated in addition to chemical composition. Even so, the results are very encouraging. The aging index for three Texaco blends is better than that of all three whole asphalts as well as for the 14 SHRP asphalts for which we have data.

Indirect Tensile Strength Test

The indirect tensile strength tests were run at 4.4°C using an MTS 810 testing apparatus. Table 5-4 and Figures 5-31 and 5-32 show the results. A test specimen made with Ampet AC-20 whole asphalt was compared with a test specimen made with Ampet blend number 2. The blended asphalt specimen sustained a significantly higher maximum load than the source asphalt. The elongation at the point of maximum force in the blended asphalt test specimen, however, was less than that of the whole asphalt. Essentially, the blended asphalt could handle more load with less deformation at that temperature.

Both the whole asphalt and blend 2 had similar properties of aging index, VTS, PVN, and penetration. Furthermore, they had nearly the same quantity of asphaltenes. The saturate content in the blend was 1.7 percentage points smaller (Table 5-2). The GPC data (Figure 5-29), however, indicate that although the percentage of asphaltenes is identical, the average size of the asphaltene molecules in blend 2 is smaller. We hypothesize that this reduction in asphaltene species size and saturate content yielded a more compatible asphalt which may have had the effect of increasing the adhesive and cohesive properties of the asphalt as a cement for the aggregate.

Table 5-4
Indirect Tensile Strength Test

Elongation (cm)	Force (Newtons)			
	Ampet AC-20 Whole		Ampet Blend 2	
	Run 1	Run 2	Run 1	Run 2
0	0	0	0	0
0.000424	4003	4003	5671	4671
0.000848	4671	4671	6672	6606
0.001697	6005	6005	8340	9241
0.002545	7006	6839	9341	10142
0.003393	7840	7673	10342	11009
0.004242	8507	8240	11009	11677
0.005090	9008	8674	11677	12344
0.005939	9508	9174	12110	12844
0.006787	9842	9508	12511	13278
0.007635	10275	9908	12844	13678
0.008484	10509	10142	13278	14012
0.010605	11176	10843	14012	14679
0.012725	11677	11343	14512	15079
0.014846	12010	11710	14913	15580
0.016967	12344	12010	15113	15813
0.019088	12511	12310	15280	16014
0.021209	12677	12511	15446	16080
0.023330	12844	12677	15446	16180
0.025451	12844	12677	15446	16247
0.027572	12944	12711	15380	16180
0.029693	12844	12711	15346	16114
0.031814	12844	12778	15313	16014
0.033934	12778	12778	15180	15980
0.036055	12677	12711	15013	15780

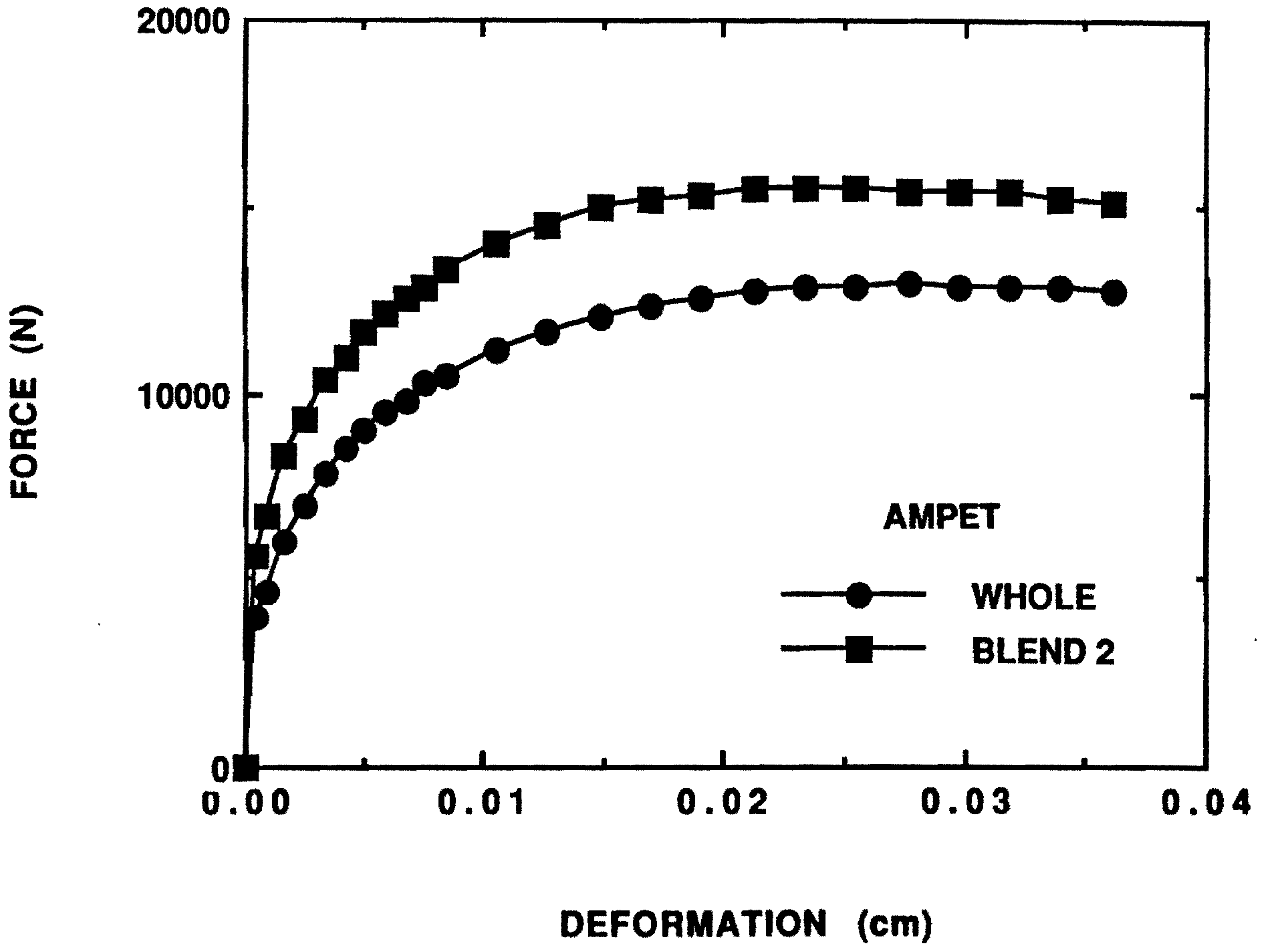

Figure 5-31
Indirect Tensile Strength Tests on
Ampet Whole Asphalt and Blend 2 - Run 1

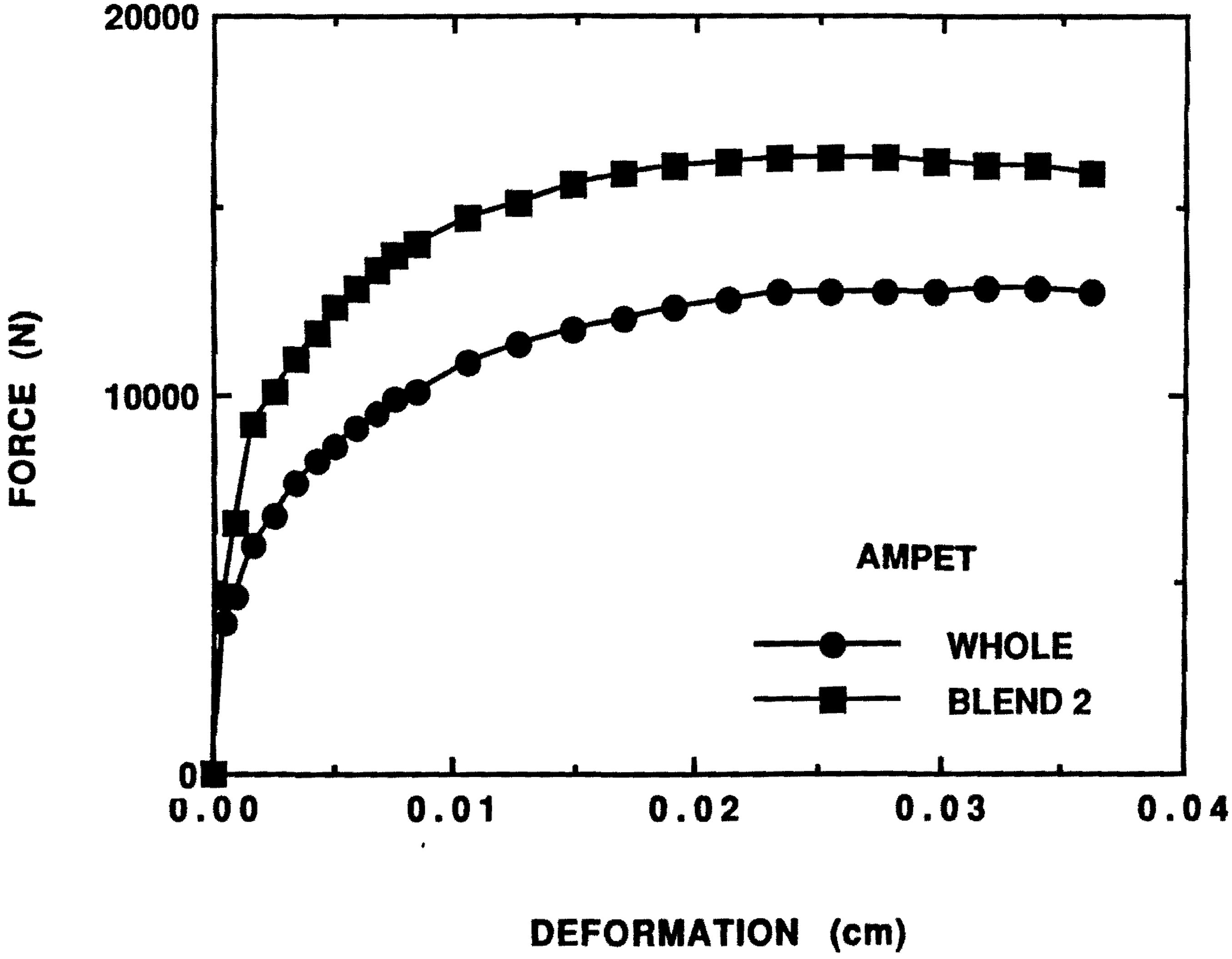

Figure 5-32
Indirect Tensile Strength Tests on
Ampet Whole Asphalt and Blend 2 - Run 2

Marshall "Toughness" Test

The Marshall "Toughness" test was run under the same temperature conditions as was the indirect tensile strength test. The ultimate goal of this test is to determine the area under the curve from zero loading until failure of the sample. The units of this area will be in N-cm which are the same units for work or energy. A larger area under the curve is an indication of how much work a road can handle, thus giving it the name toughness. Note that the force exerted for this Marshall toughness test is considerably greater than for the Indirect Tension Test. This is a consequence of the different loading heads. The Indirect Tension Test loading strips essentially act as diametral point loads whereas the much larger, curved heads of the Marshall apparatus serve to clamp and hold the sample, to some degree.

Table 5-5 and Figures 5-33 and 5-34 show the results of an Ampet whole asphalt test specimen compared to an Ampet blend 2 specimen. The area under the curve was calculated using a spread-sheet with trapezoidal areas between abscissa intervals. The average "Toughness" for the Ampet whole asphalt test specimen was 6935 Newton-cm, whereas the average "Toughness" for the Ampet blend 2 test specimen was 8691 Newton-cm. This represents a 25% work-load increase from the whole asphalt to the blend.

Infrared Analysis of the Blends

Infrared spectra (from 900 to 1800 cm^{-1}) of the whole asphalts and their blends are shown in Figures 5-35 to 5-40. As was the case for the individual fractions, the striking feature of the spectra of these blends is their general similarity to the spectrum of the whole asphalts.

In some blends this similarity is remarkably close. Examples are the Coastal whole asphalt and its blend 2, 3, and 4 and the Texaco whole and blends 3 and 4 (except in the sulfoxide band), and the Ampet whole and its blend 1. In spite of these small differences between the spectra however, the viscosities vary considerably (see Table 5-3).

Table 5-5
Marshall "Toughness" Test

	Force (Newtons)			
Elongation (cm)	Ampet AC-20 Whole		Ampet Blend 2	
	Run 1	Run 2	Run 1	Run 2
0	0	0	0	0
0.042333	534	445	667	445
0.084667	1668	1557	2002	1334
0.127000	4003	3559	4671	3114
0.169333	12010	8229	10676	6672
0.186267	15680	13345	18015	9119
0.203200	18683	19350	24020	13567
0.220133	21351	23131	29358	21129
0.237067	24020	27579	34029	27134
0.254000	26356	31138	38032	32027
0.270933	28491	33362	41035	35808
0.287867	30025	35586	43370	39144
0.304800	31493	37810	45372	41591
0.321733	32694	39500	47040	43815
0.338667	33428	40701	48108	45817
0.355600	34029	41457	48708	46706
0.372533	34563	42036	48908	47329
0.389467	34696	42258	49042	47863
0.406400	34563	42258	48708	48041
0.423333	34363	41902	48174	48041
0.440267	33895	41368	47440	47774
0.457200	33362	40835	46373	47240
0.474133	32828	39856	45372	46617
0.491067	32027	39144	44037	45817
0.508000	31360	37899	42703	44838

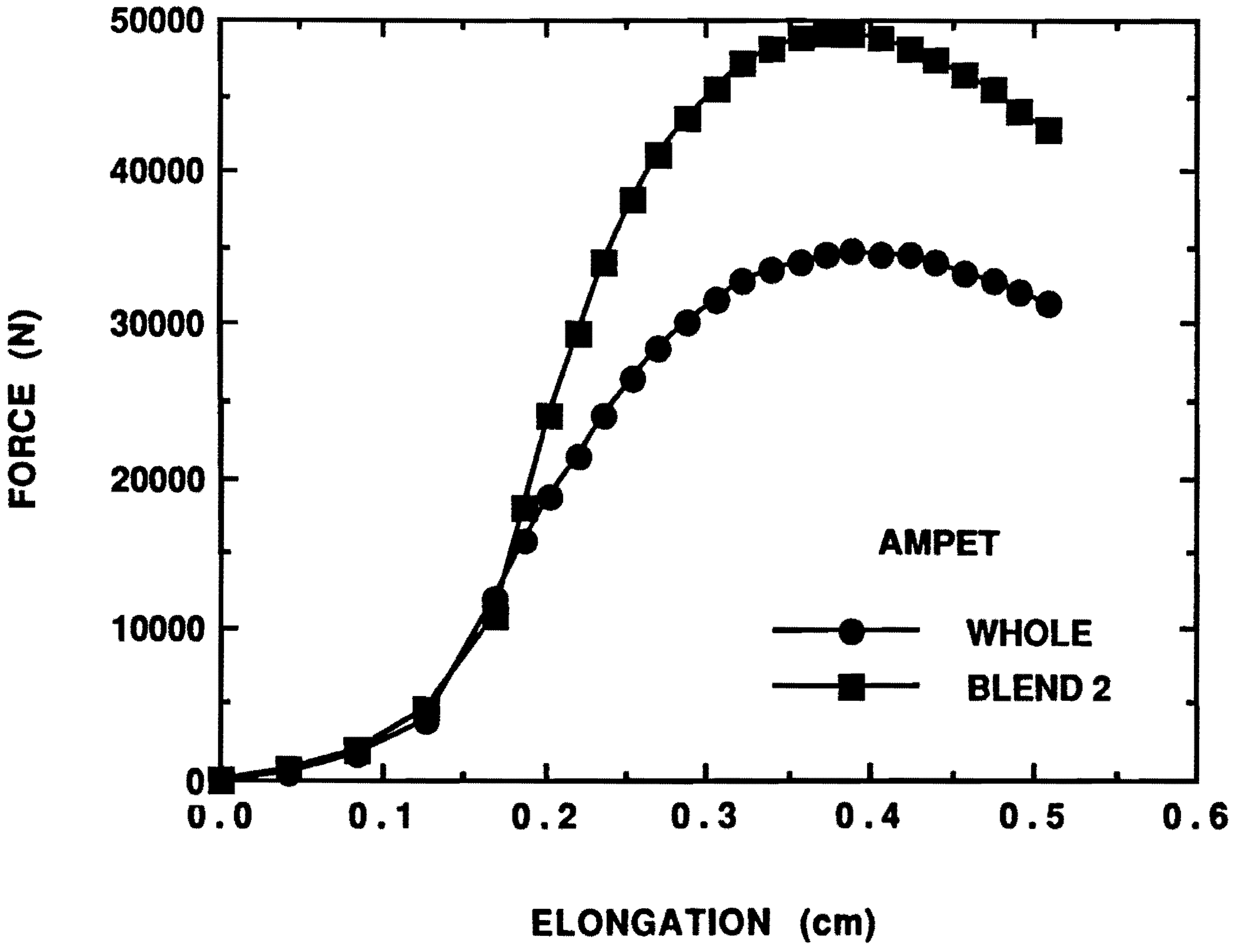

Figure 5-33
Marshall Toughness Tests on Ampet
Whole Asphalt and Blend 2 - Run 1

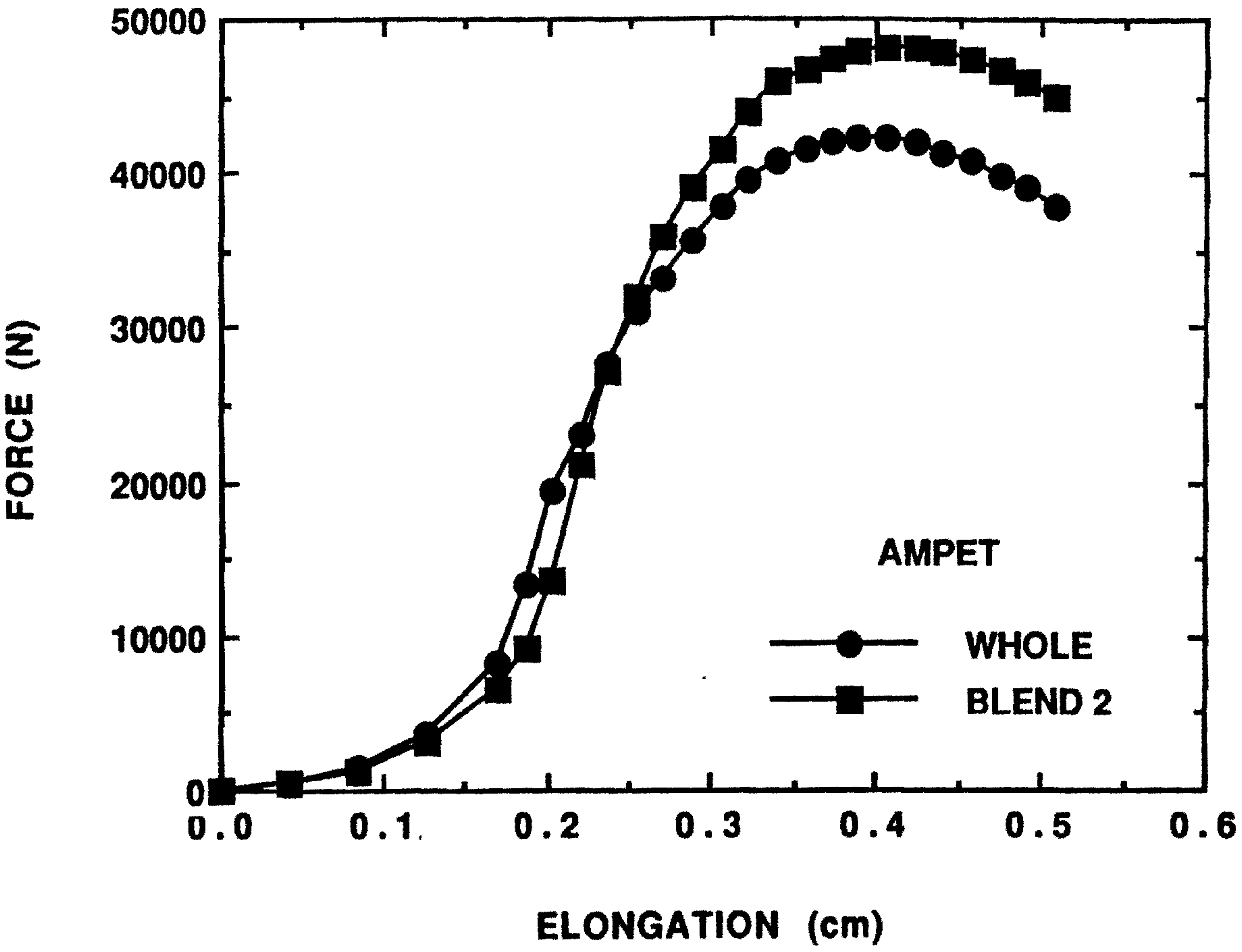

Figure 5-34
Marshall Toughness Tests on Ampet
Whole Asphalt and Blend 2 - Run 2

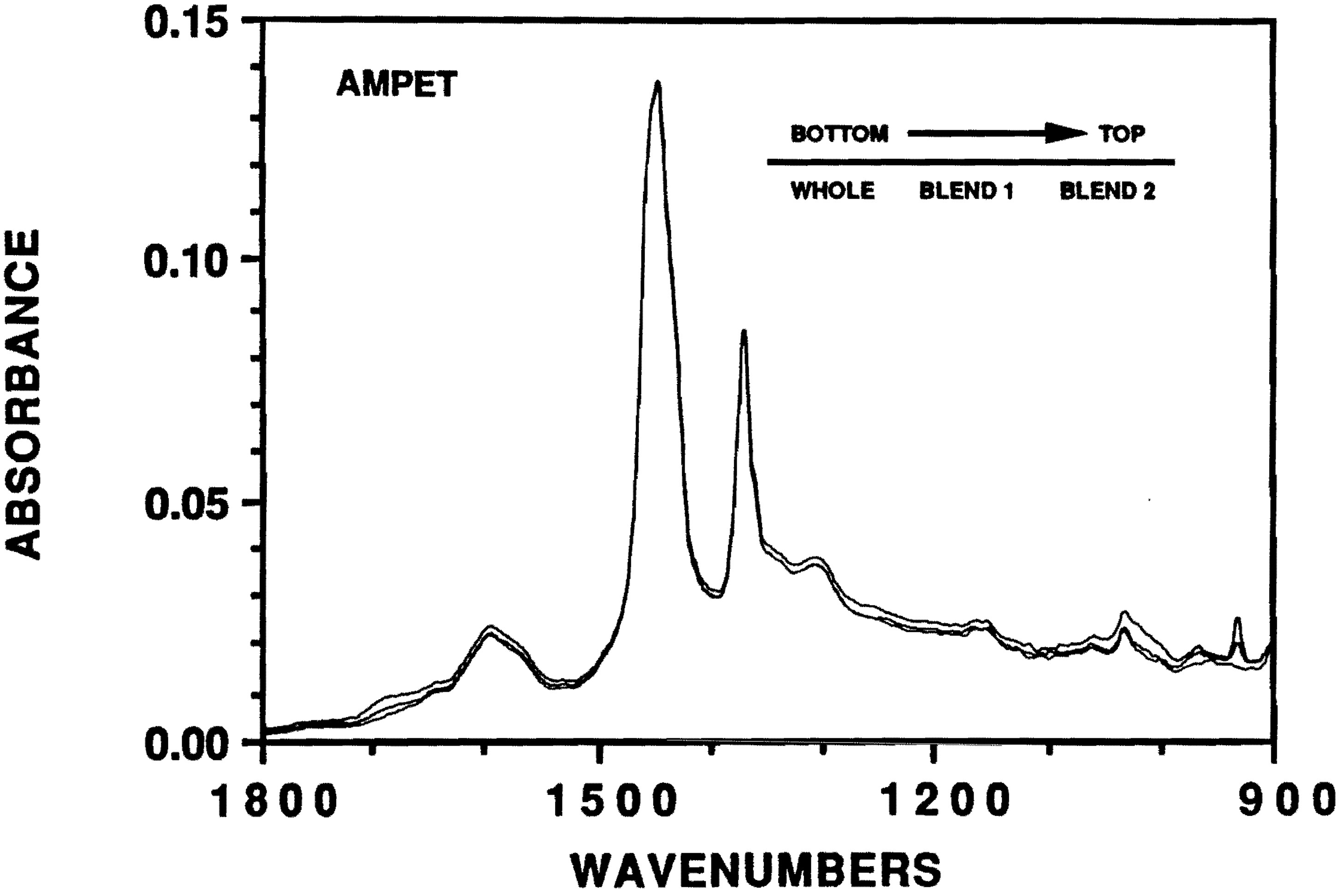

Figure 5-35
IR Spectra for Ampet Whole and Blend 1 and 2

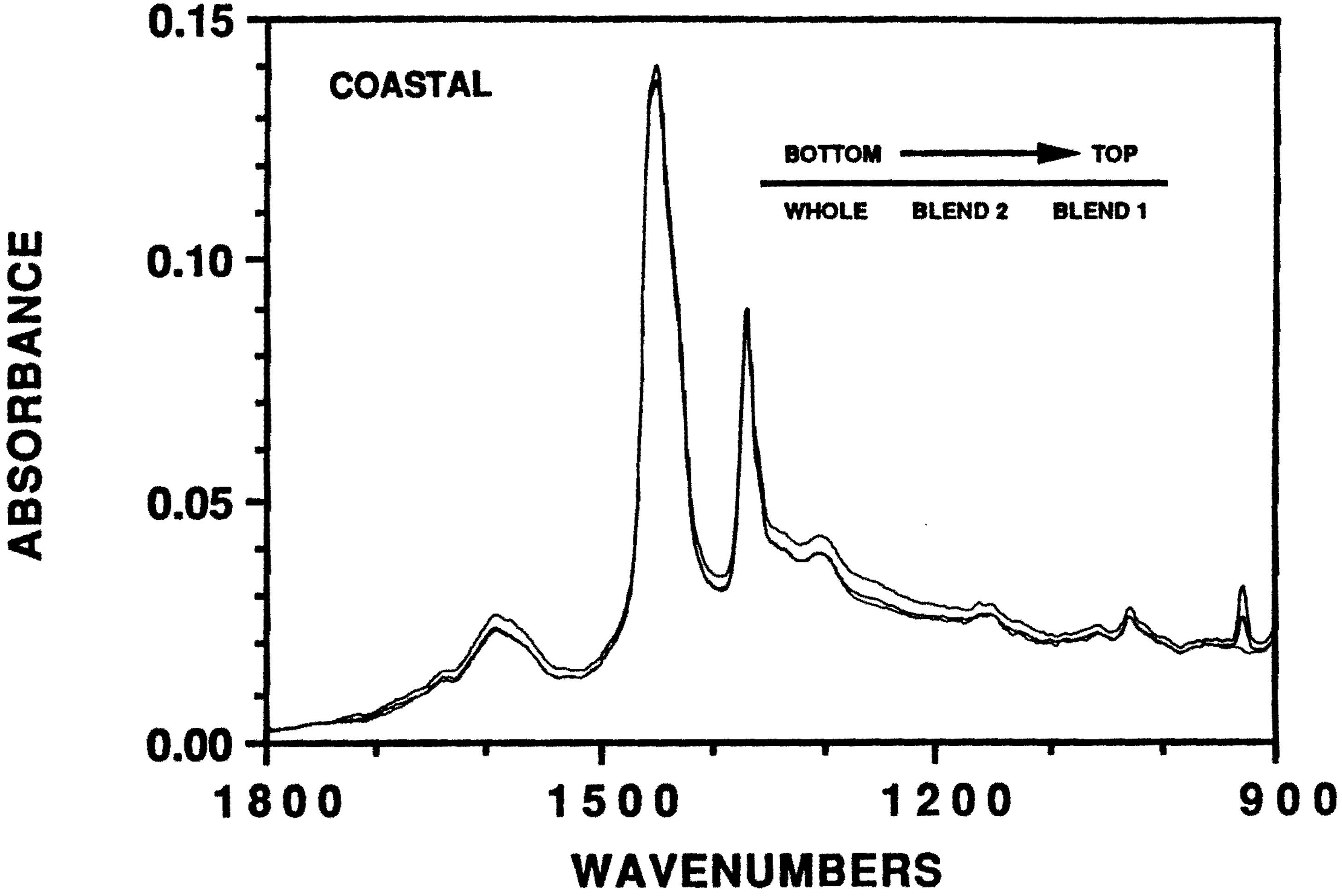

Figure 5-36
IR Spectra for Coastal Whole and Blends 1 and 2

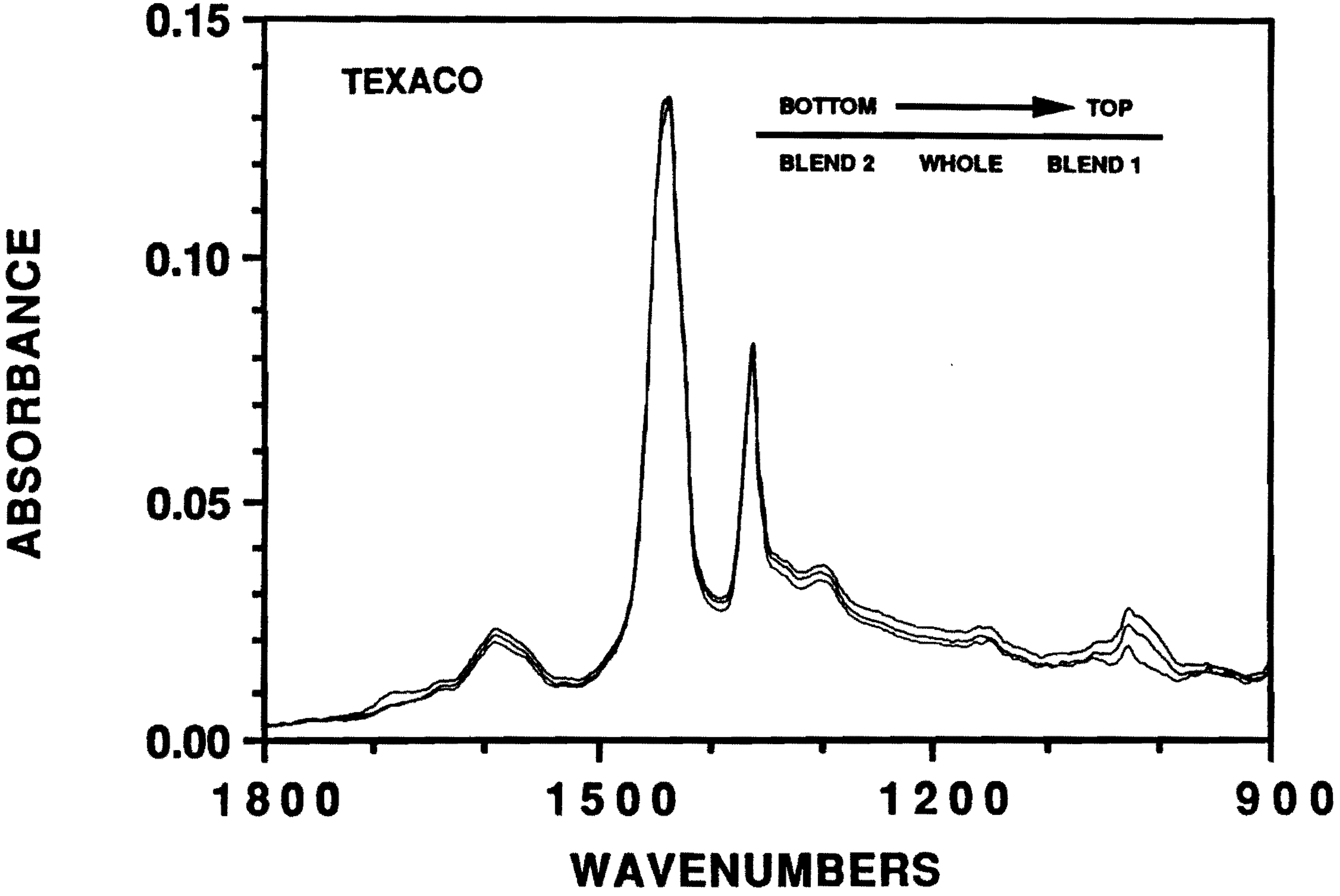

Figure 5-37
IR Spectra for Texaco Whole and Blends 1 and 2

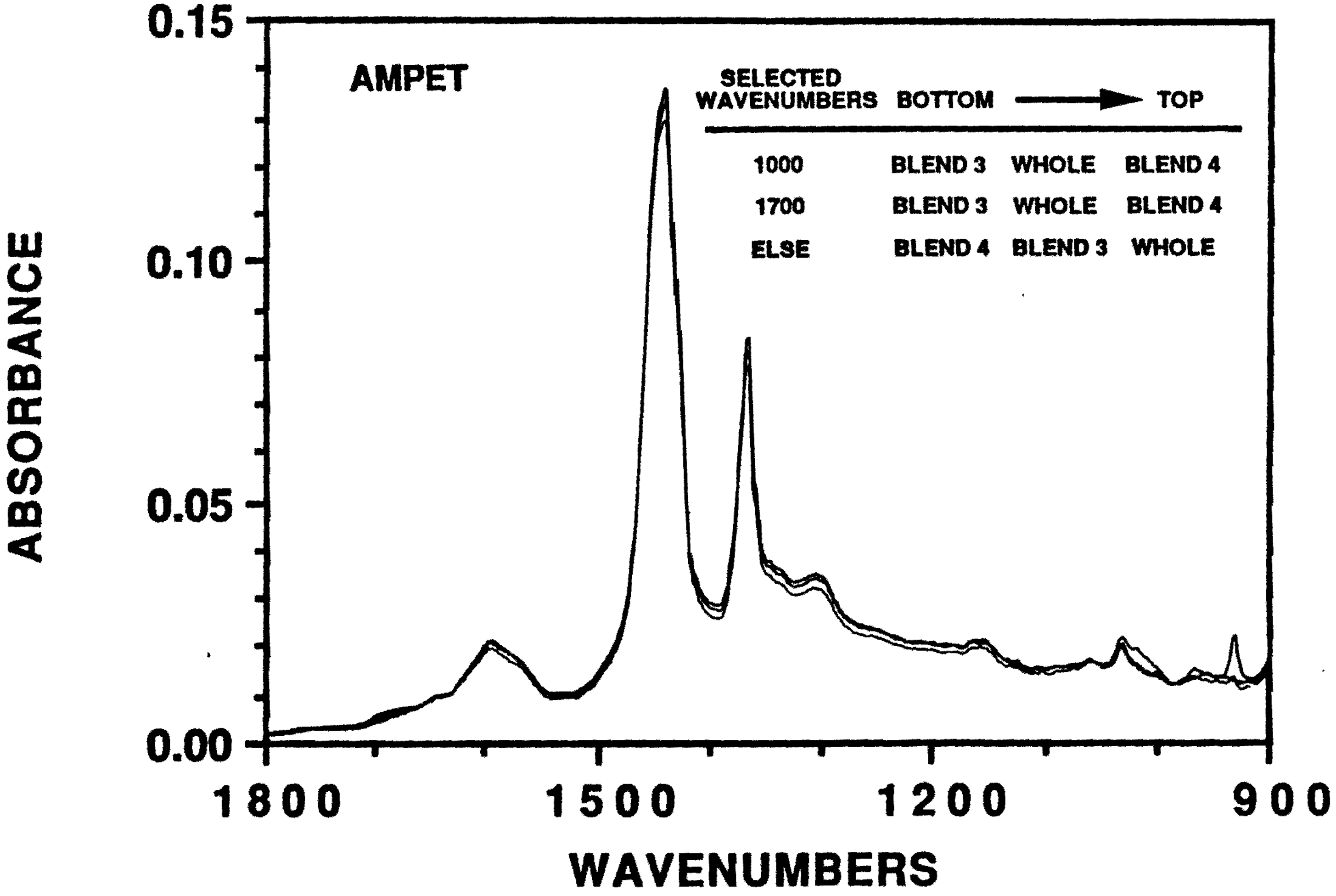

Figure 5-38
IR Spectra for Ampet whole and Blends 3 and 4

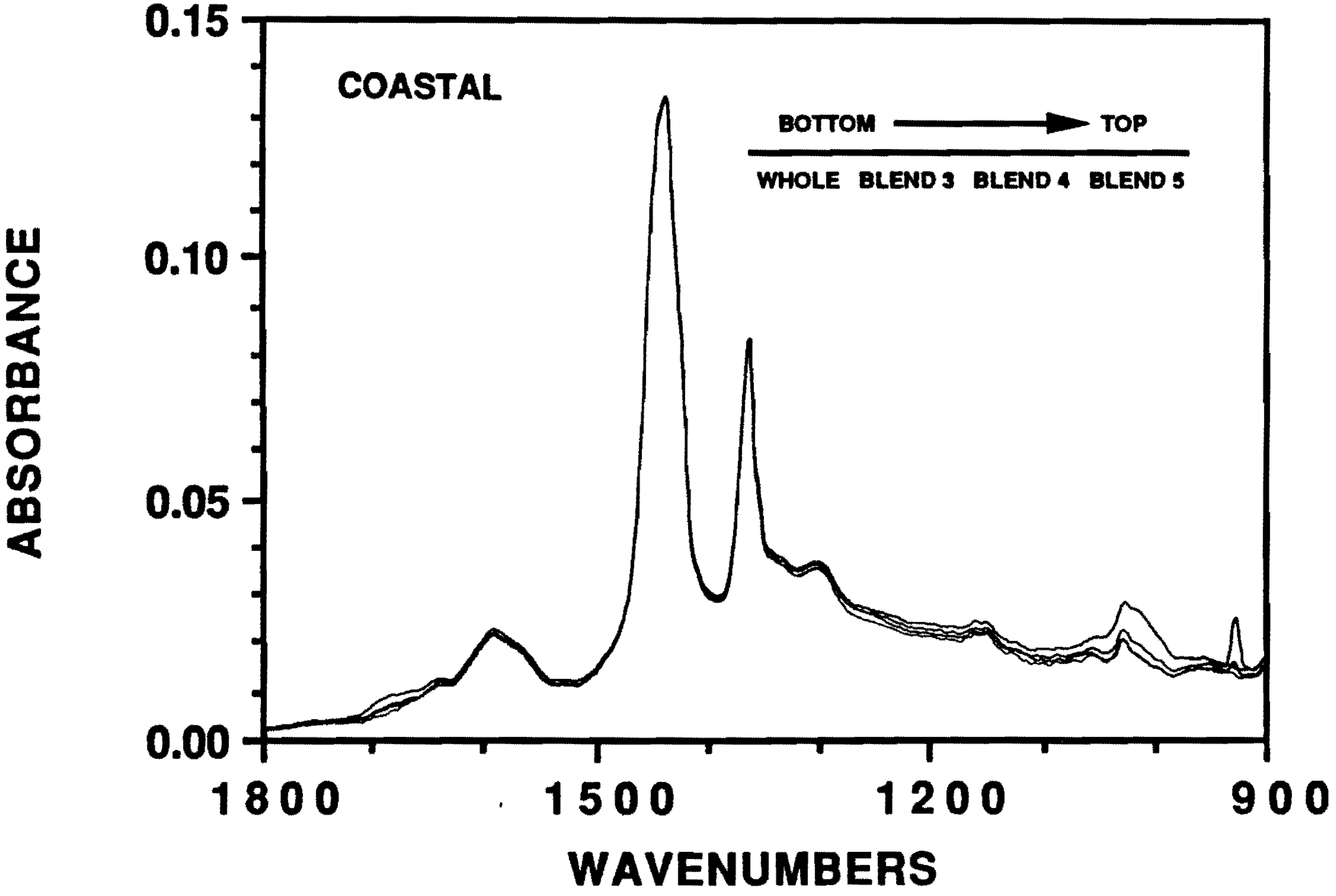

Figure 5-39
IR Spectra for Coastal Whole and Blends 3-5

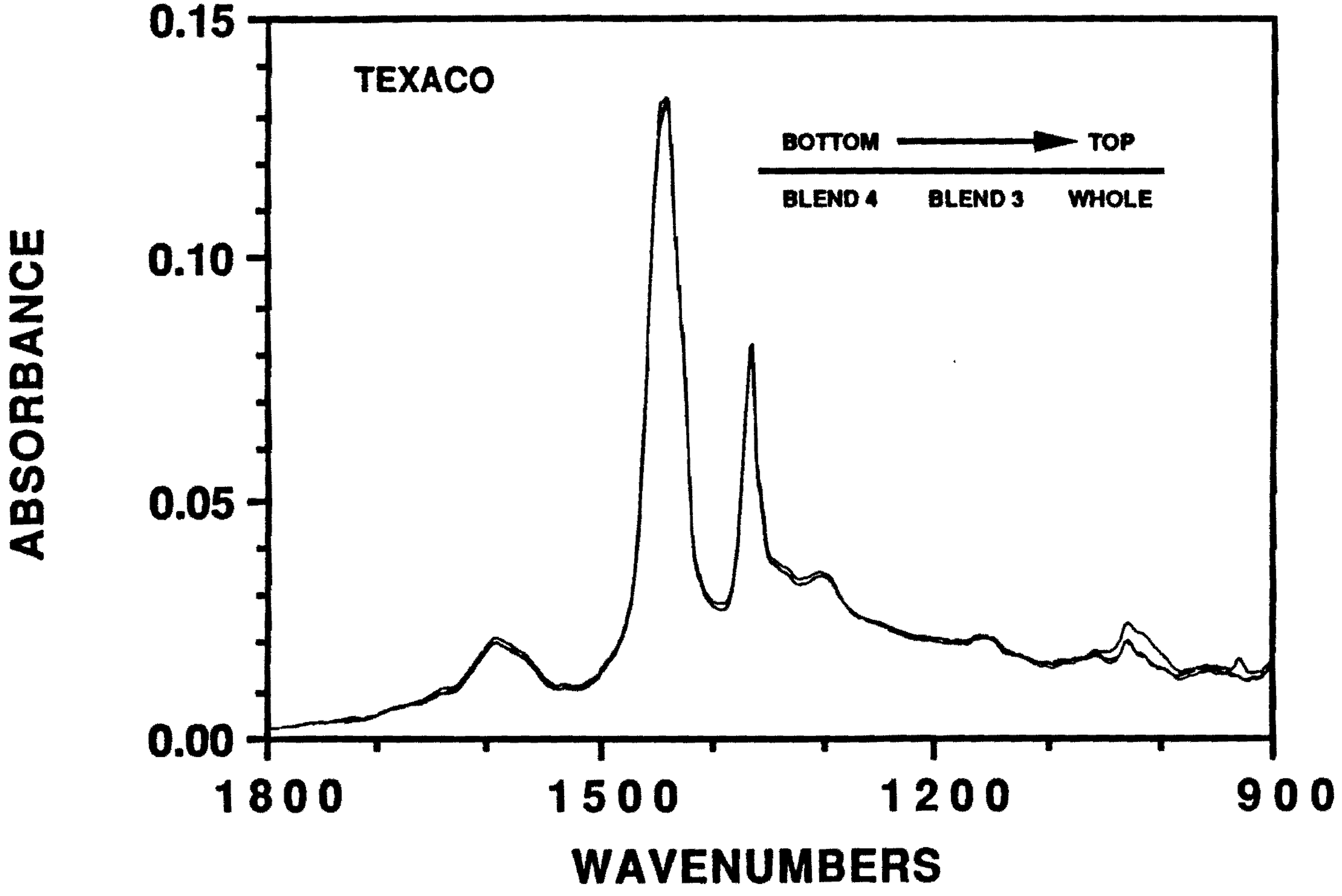

Figure 5-40
IR Spectra for Texaco Whole and Blends 3 and 4

In the other blends, however, there are more noticeable differences between the whole asphalts and their blends. Mostly, these consist of a larger difference in the carbonyl band in the region of 1700 cm^{-1} and the sulfoxide band at about 1030 cm^{-1}. Additionally, there may be a complete lifting (with respect to absorbance) of the spectrum in the range from about 1030 to 1350 cm^{-1}. These differences are seen between the Ampet whole asphalt and its blend 2, the Coastal whole asphalt and its blend 1, the Texaco whole asphalt and its blend 1, and the Coastal whole asphalt and its blend 5. One anomaly that appears is the Texaco blend 2 which lies underneath the whole asphalt over a good portion of the spectrum.

Increases in absorbance in the carbonyl and sulfoxide regions, with respect to the whole asphalt, are typical of aged asphalts and probably occurred in these samples as a result of solvent aging in the supercritical unit, as discussed previously. The small differences observed in the Texaco blends are unusual, but is a feature that we have observed previously in solvent aging i.e., that solvent aging can produce significant hardening in asphalts with very little change in the IR spectrum. Obviously there is more to be understood with respect to changes to the infrared spectra and their relationship to physical properties.

Another way to approach comparisons of asphalt materials is to subject them to oven aging and compare the physical and chemical properties before and after. In Figures 5-41 through 5-46 we compare the infrared spectra of oven-aged whole asphalts to their derived blends. Then in Figures 5-47 through 5-62 we compare the spectrum for each whole asphalt or blend before rolling thin film oven aging to that after aging. It is from these latter comparisons that we have the best chance of correlating changes in physical properties to changes in chemical properties because these samples have no gross change in chemical composition; no major components are added or removed and there is no blending. The composition is changing only as a result of a relatively small degree of oxidation.

Previous work at developing such aging correlations (Davison, et al. 1989) suggests that for any given asphalt the viscosity following either oven or road aging shows a very good correlation with the carbonyl peak; log (viscosity) is linearly

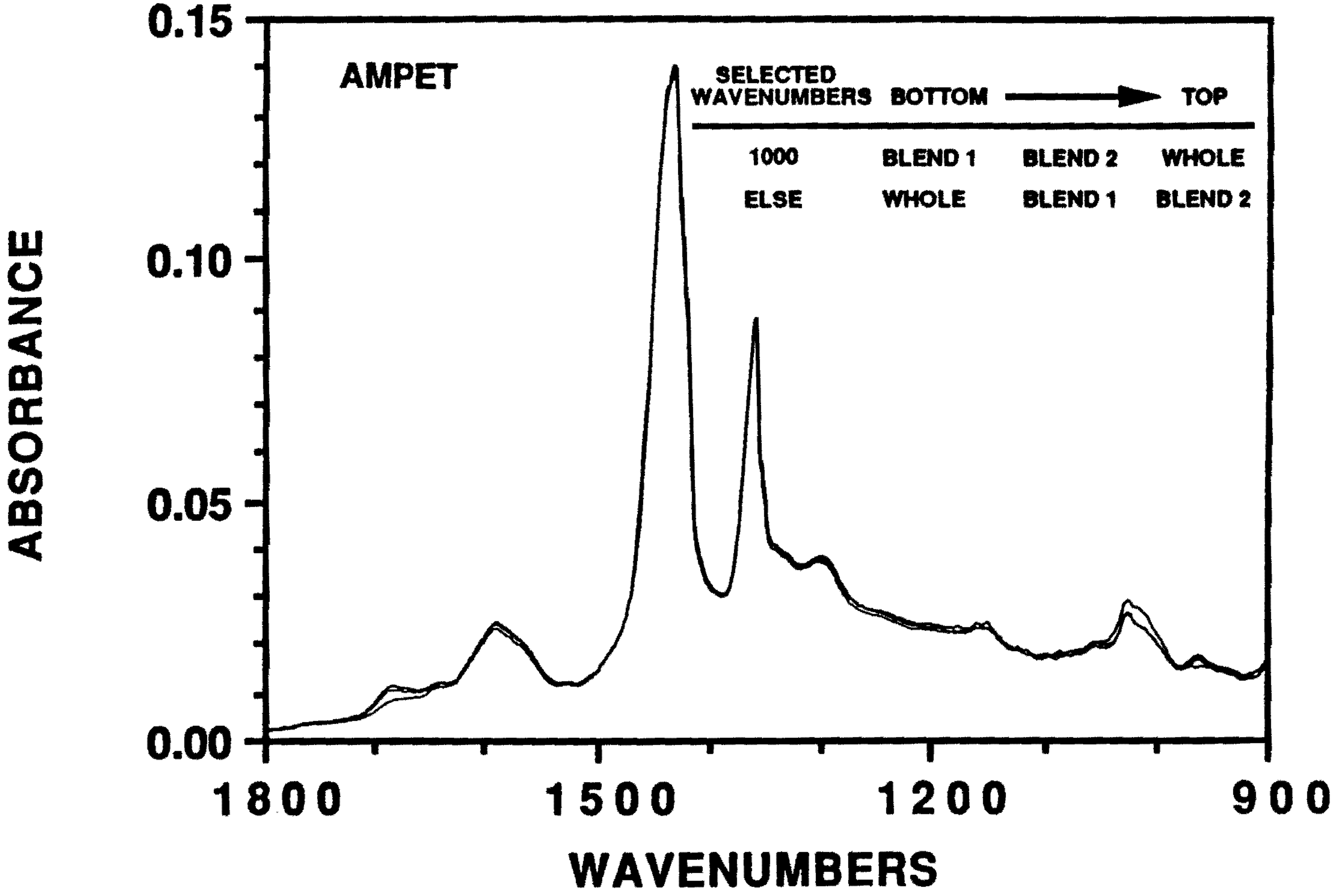

Figure 5-41
IR Spectra of Oven-Aged Ampet
Whole and Blends 1 and 2

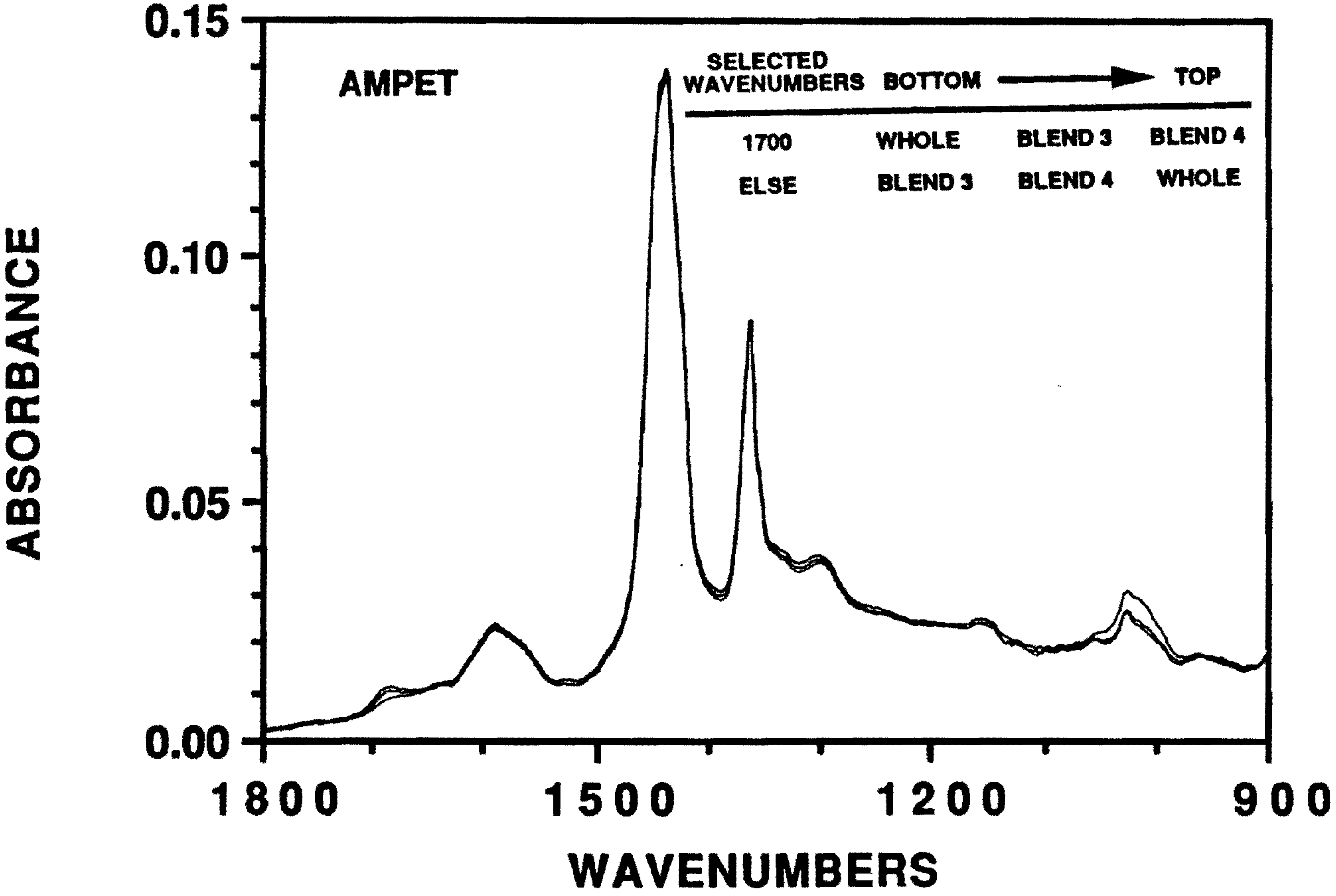

Figure 5-42
IR Spectra of Oven-Aged Ampet
Whole and Blends 3 and 4

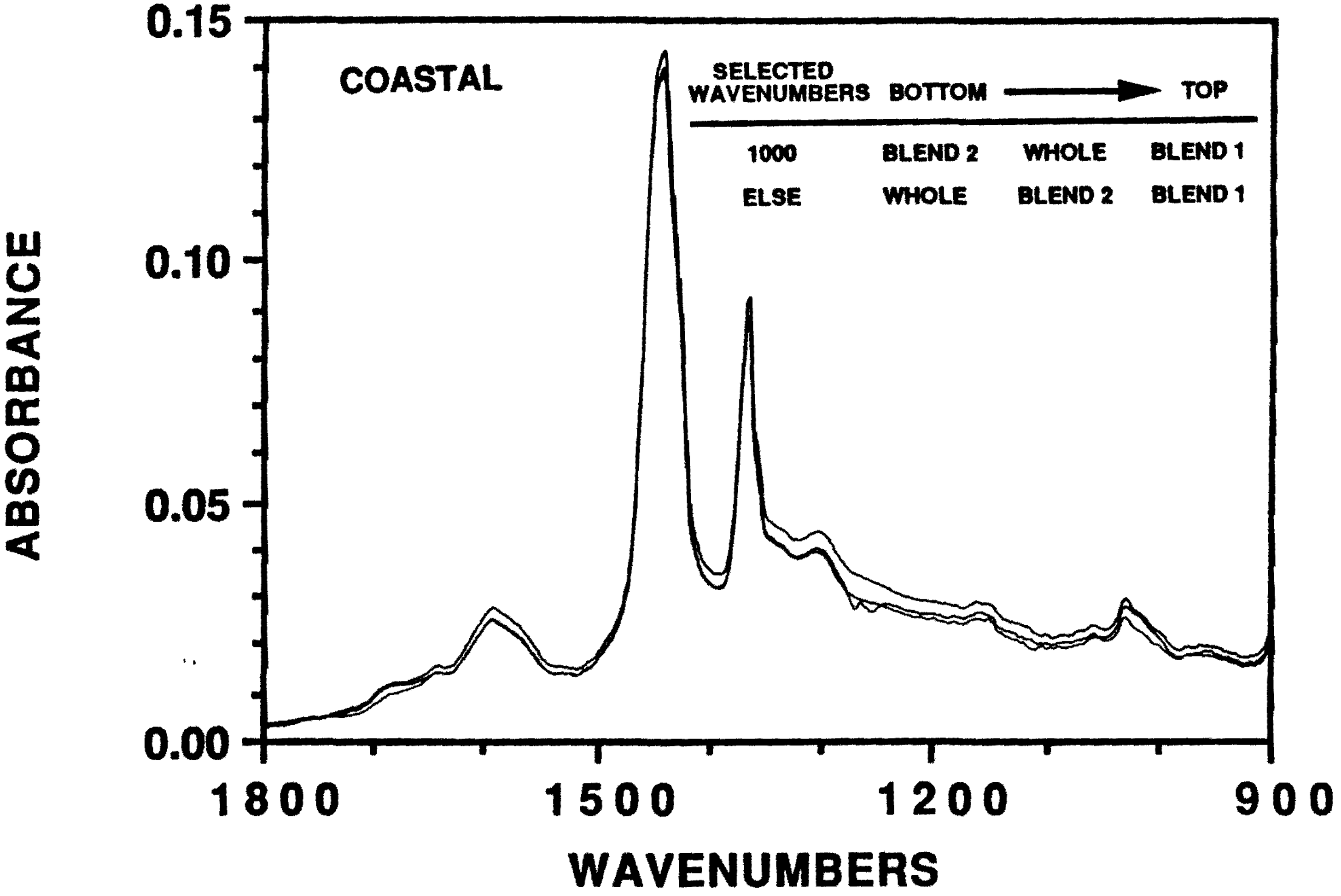

Figure 5-43
IR Spectra of Oven-Aged Coastal
Whole and Blends 1 and 2

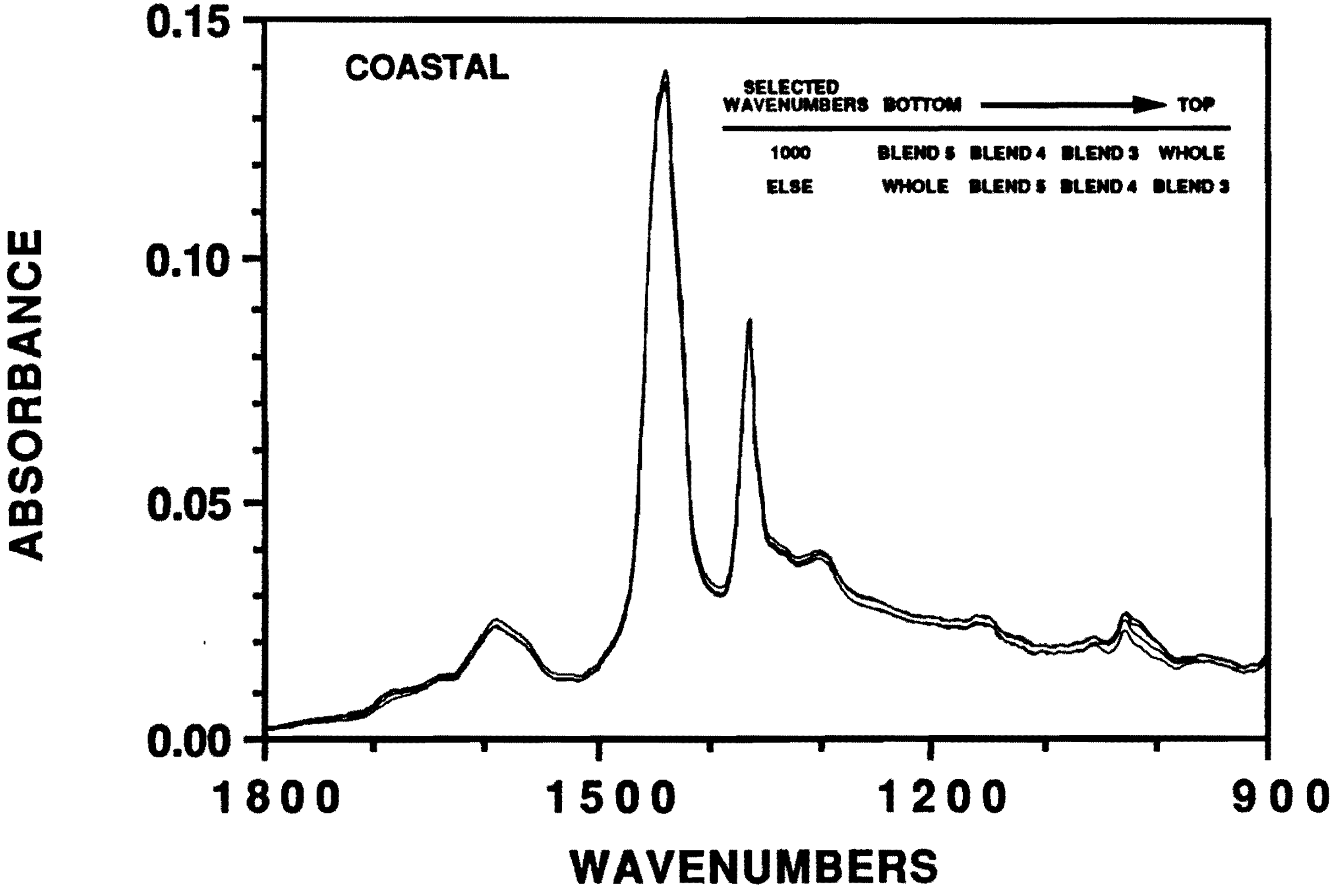

Figure 5-44
IR Spectra of Oven-Aged Coastal
Whole and Blends 3-5

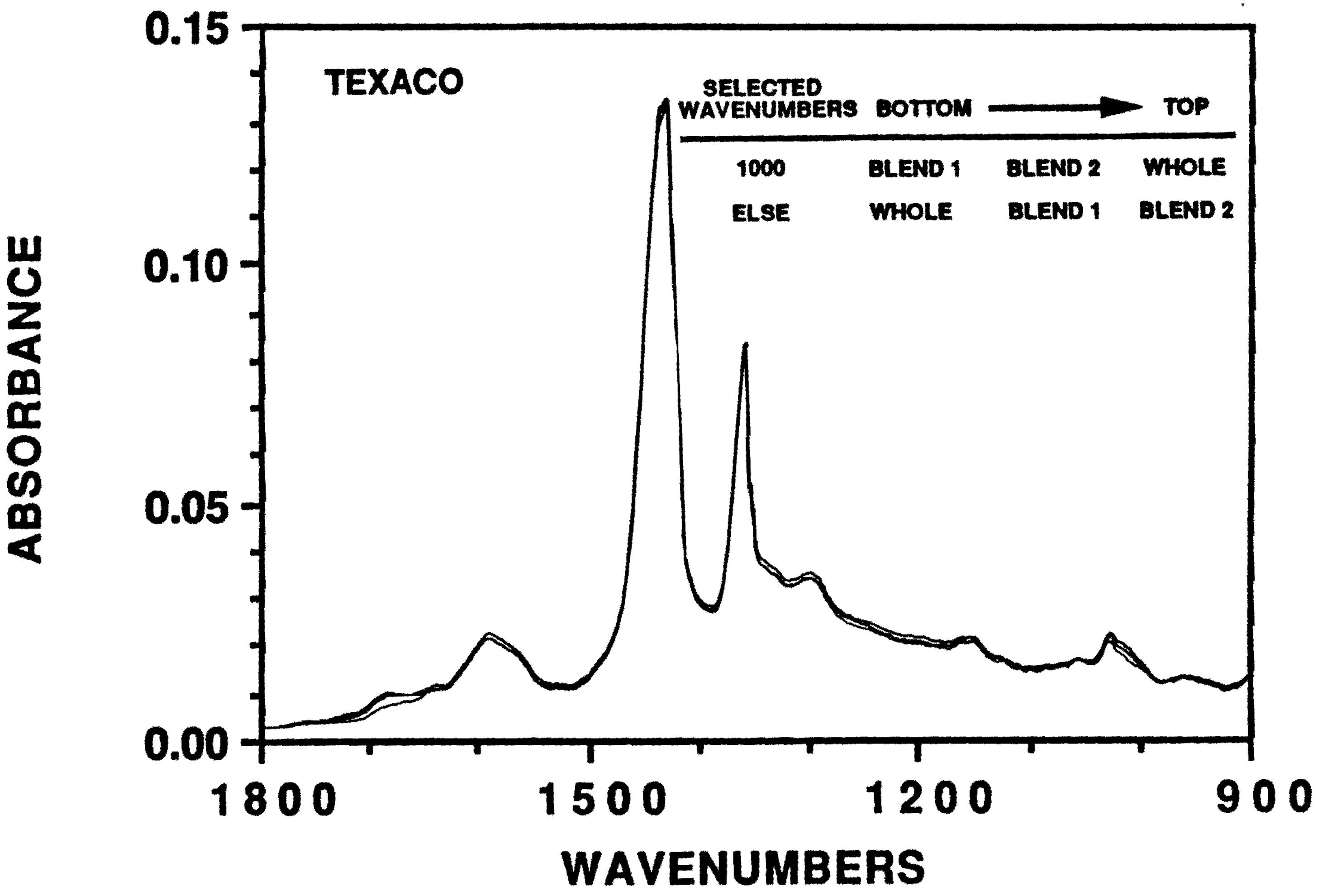

Figure 5-45
IR Spectra of Oven-Aged Texaco
Whole and Blends 1 and 2

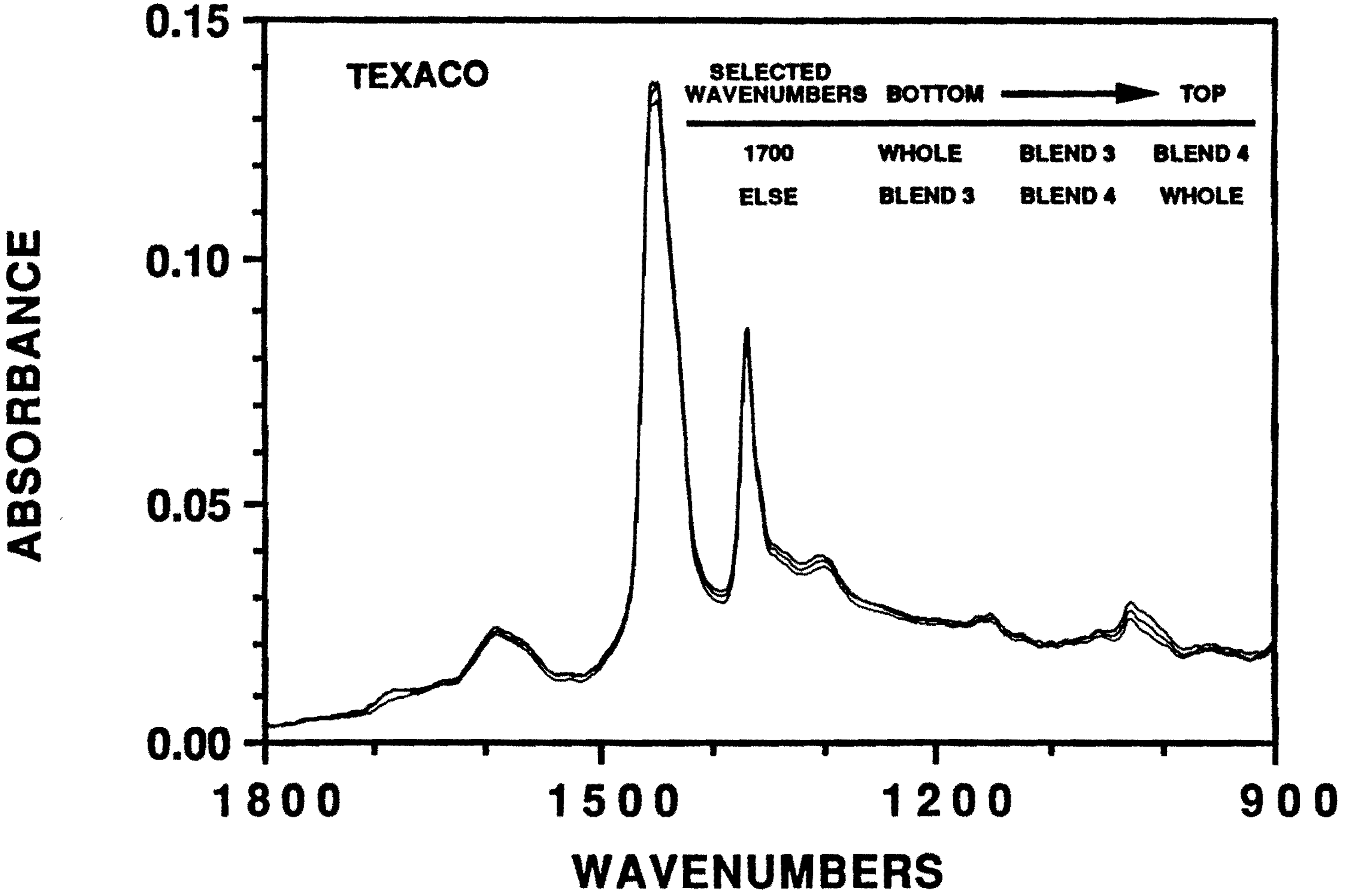

Figure 5-46
IR Spectra of Oven-Aged Texaco
Whole and Blends 3 and 4

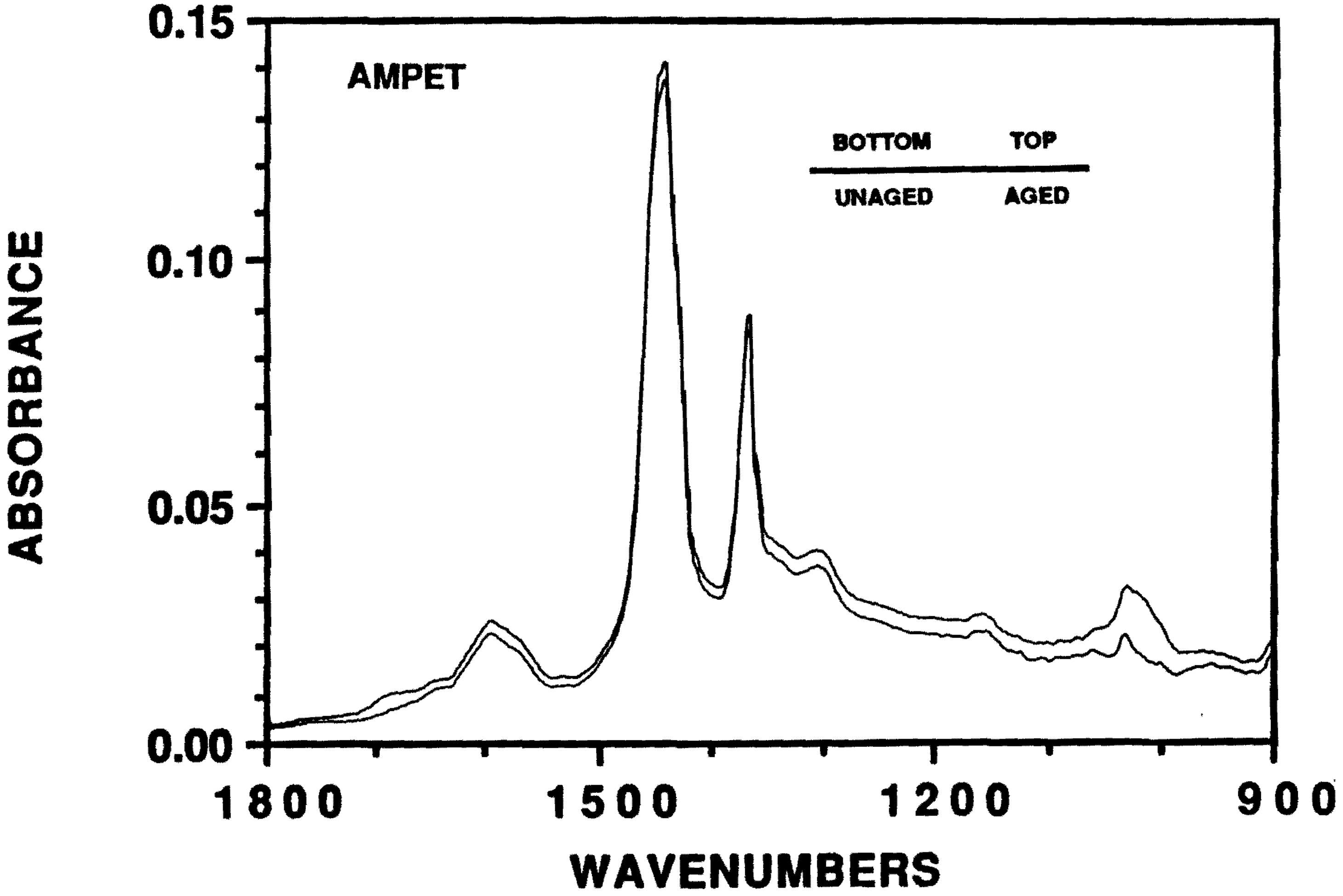

Figure 5-47
IR Spectra for Ampet Whole Asphalt
Before and After Aging

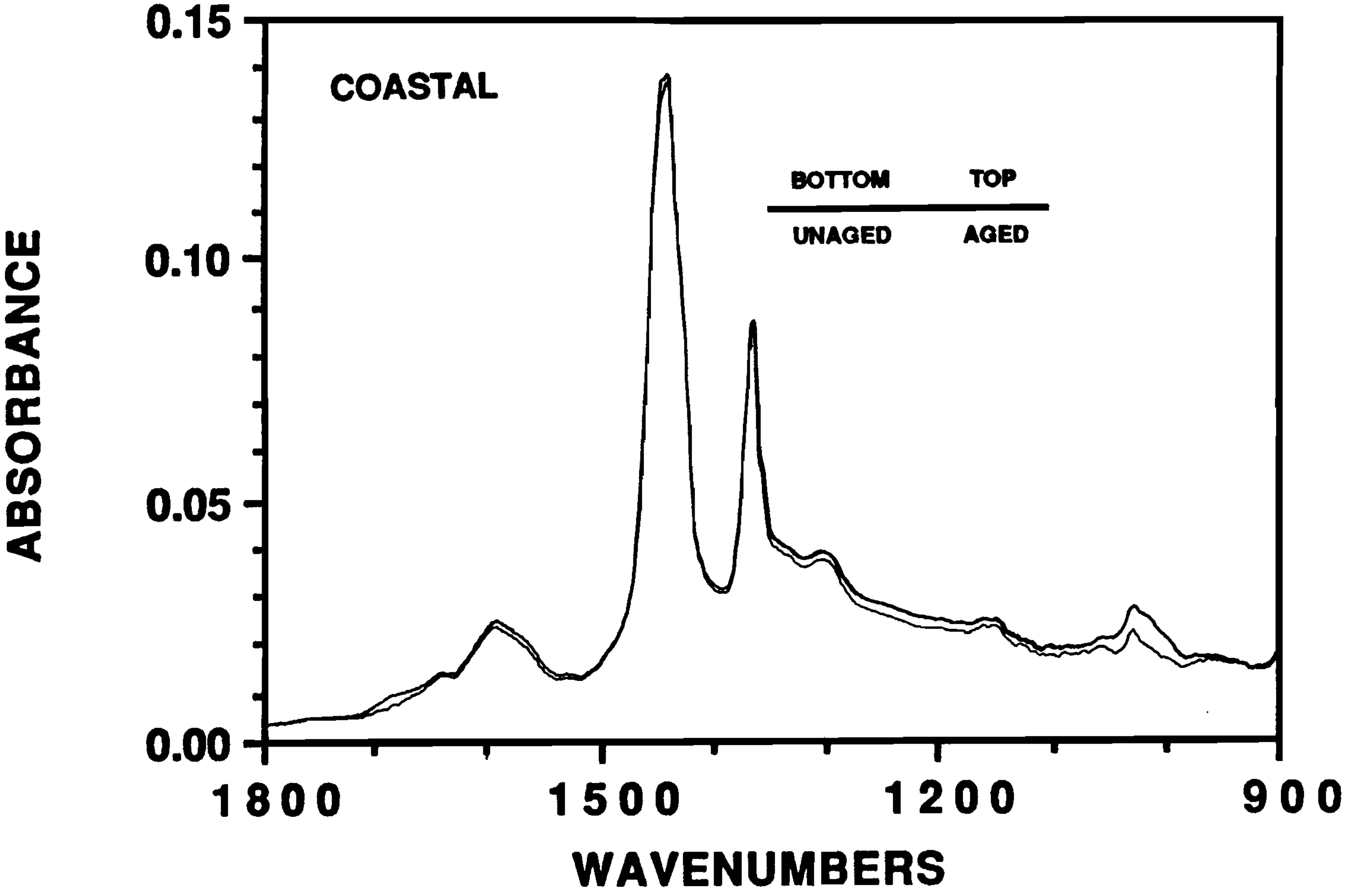

Figure 5-48
IR Spectra for Coastal Whole Asphalt
Before and After Aging

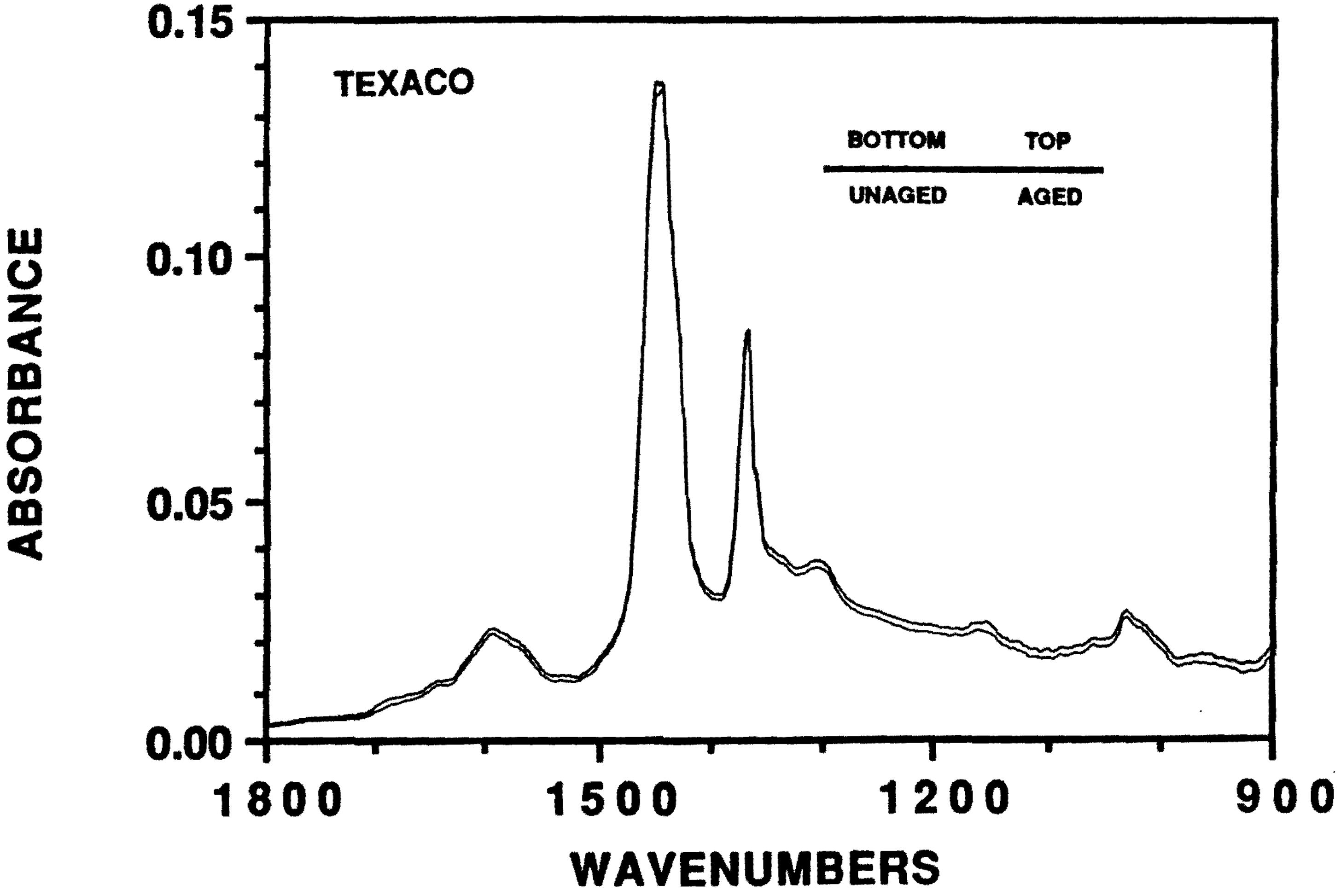

Figure 5-49
IR Spectra for Texaco Whole Asphalt
Before and After Aging

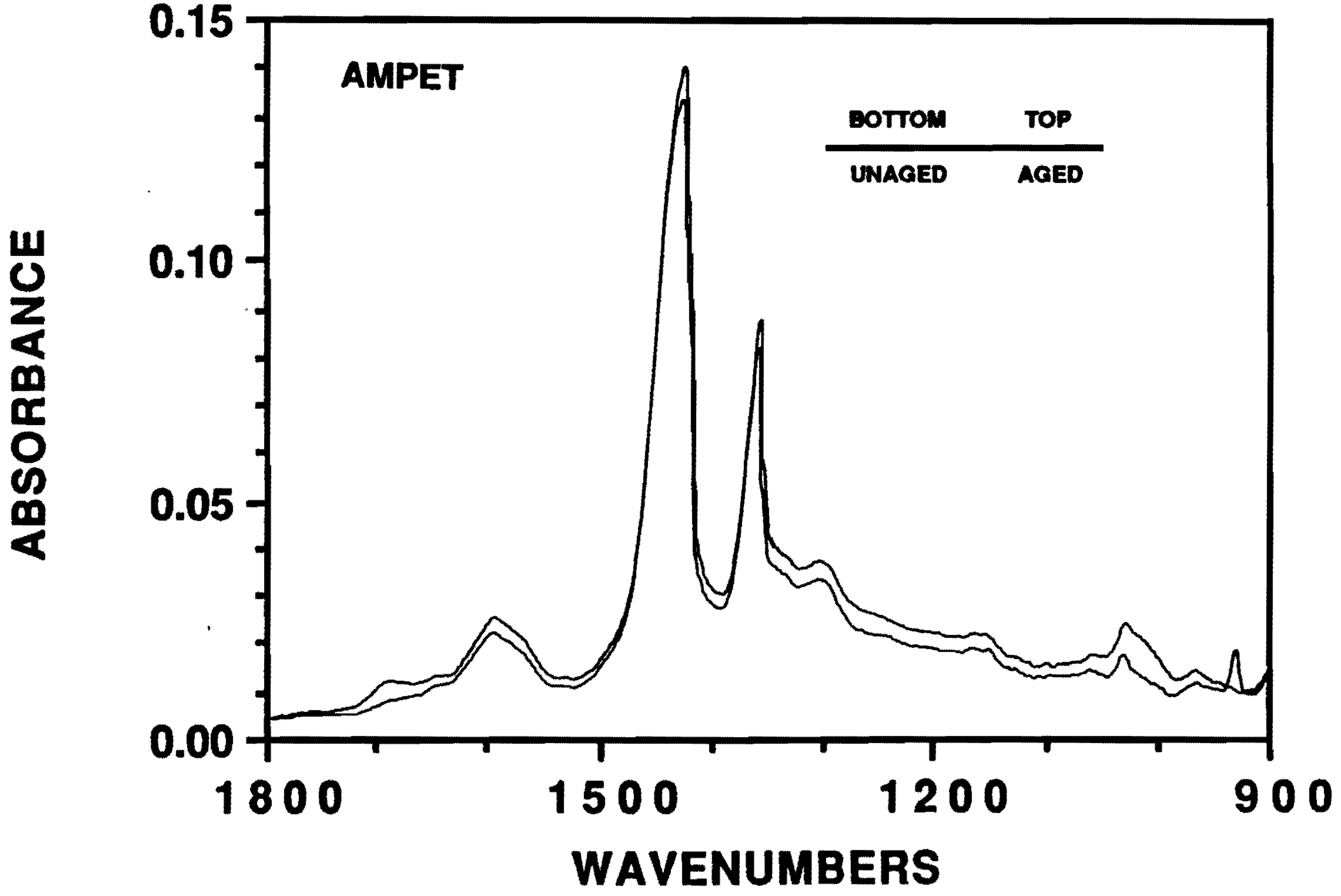

Figure 5-50
IR Spectra for Ampet Blend 1 Before and After Aging

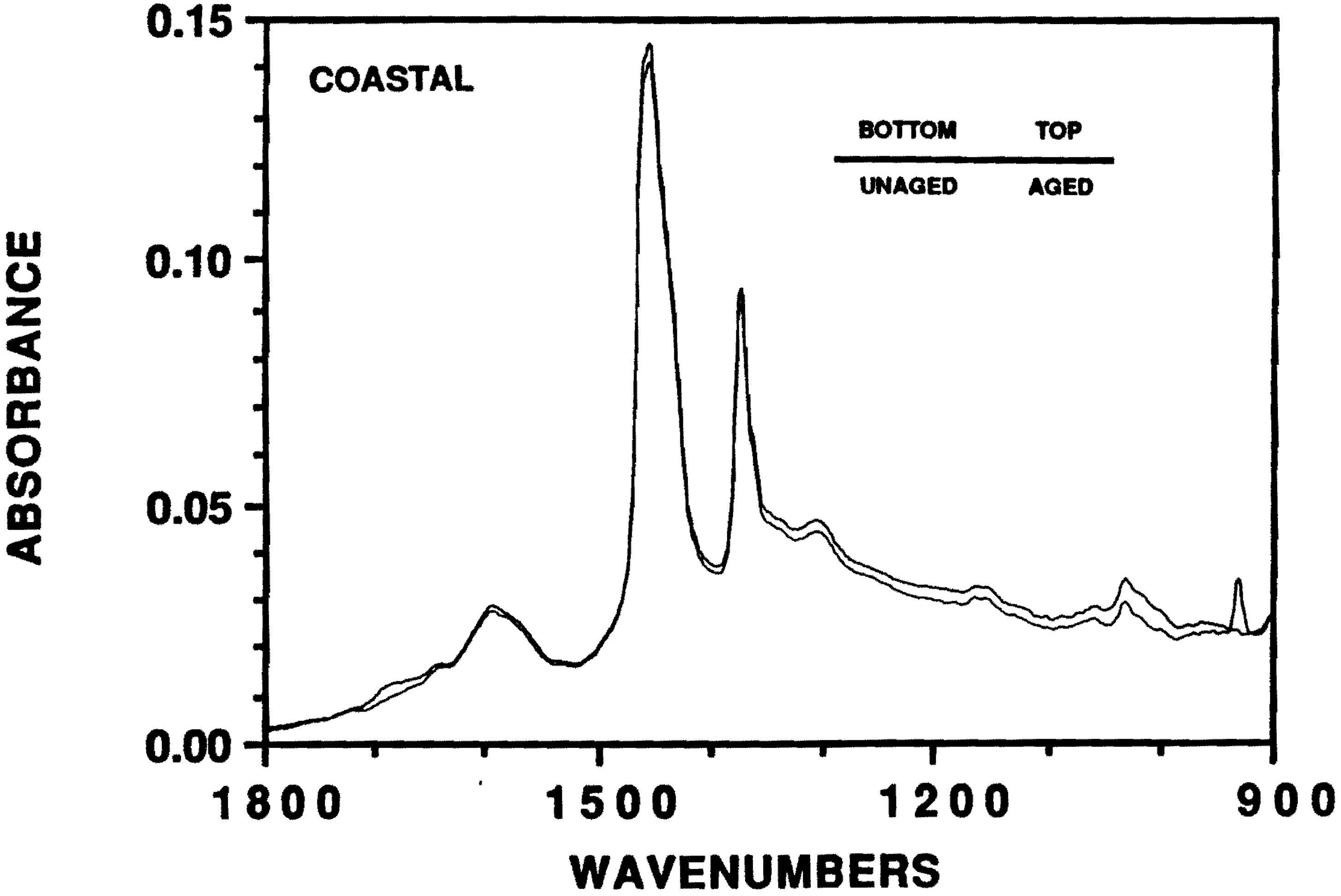

Figure 5-51
IR Spectra for Coastal Blend 1 Before and After Aging

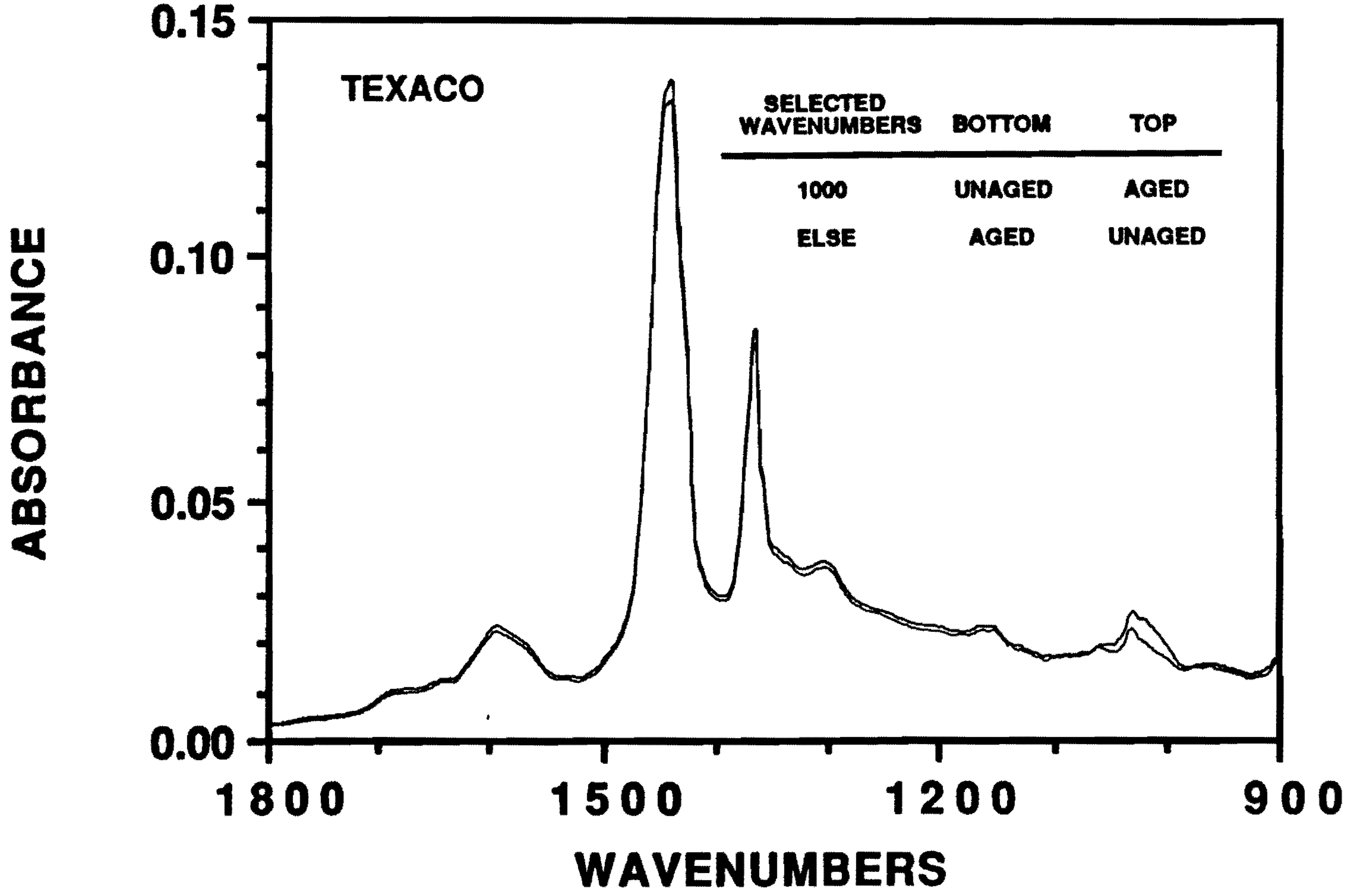

Figure 5-52
IR Spectra for Texaco Blend 1 Before and After Aging

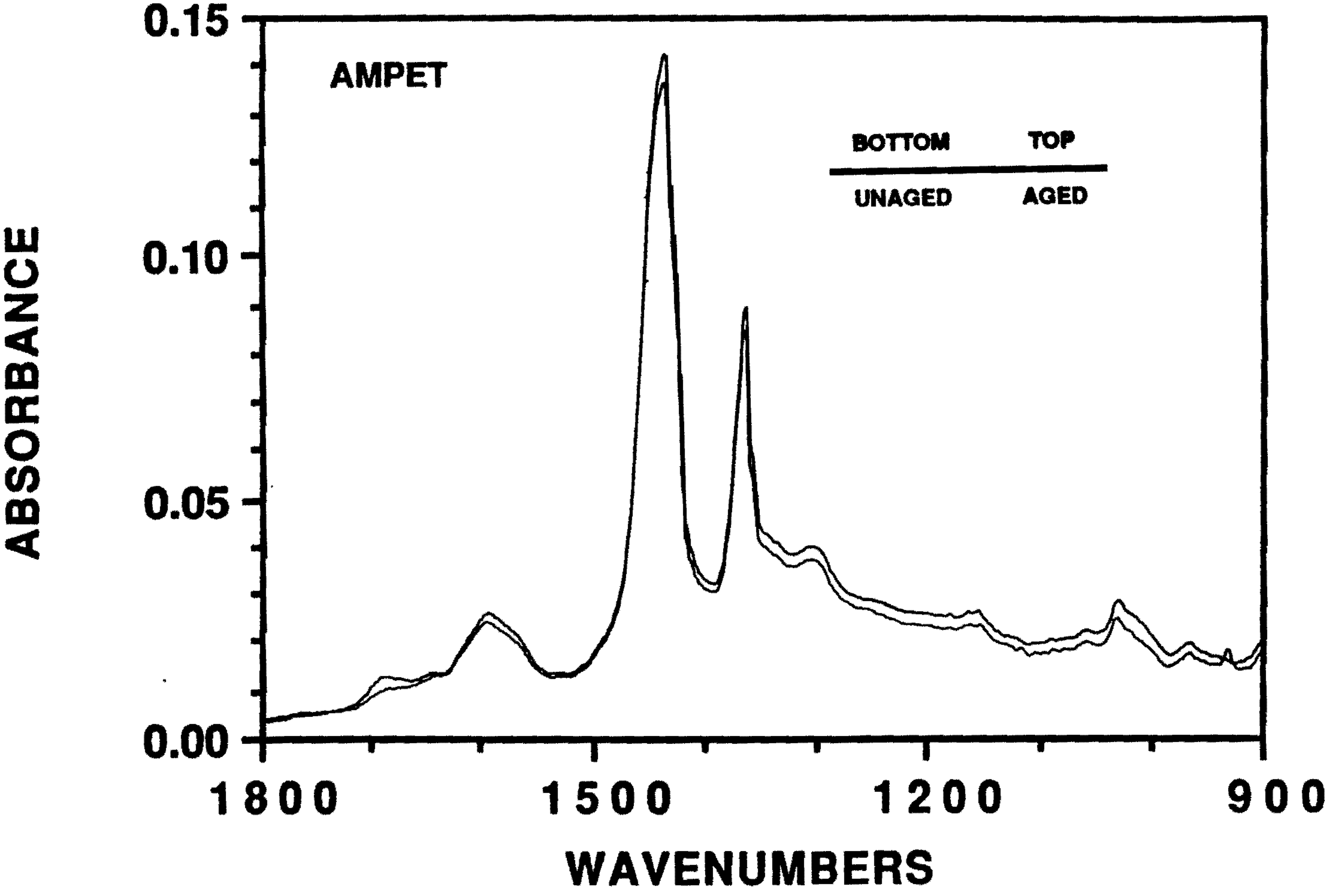

Figure 5-53
IR Spectra for Ampet Blend 2 Before and After Aging

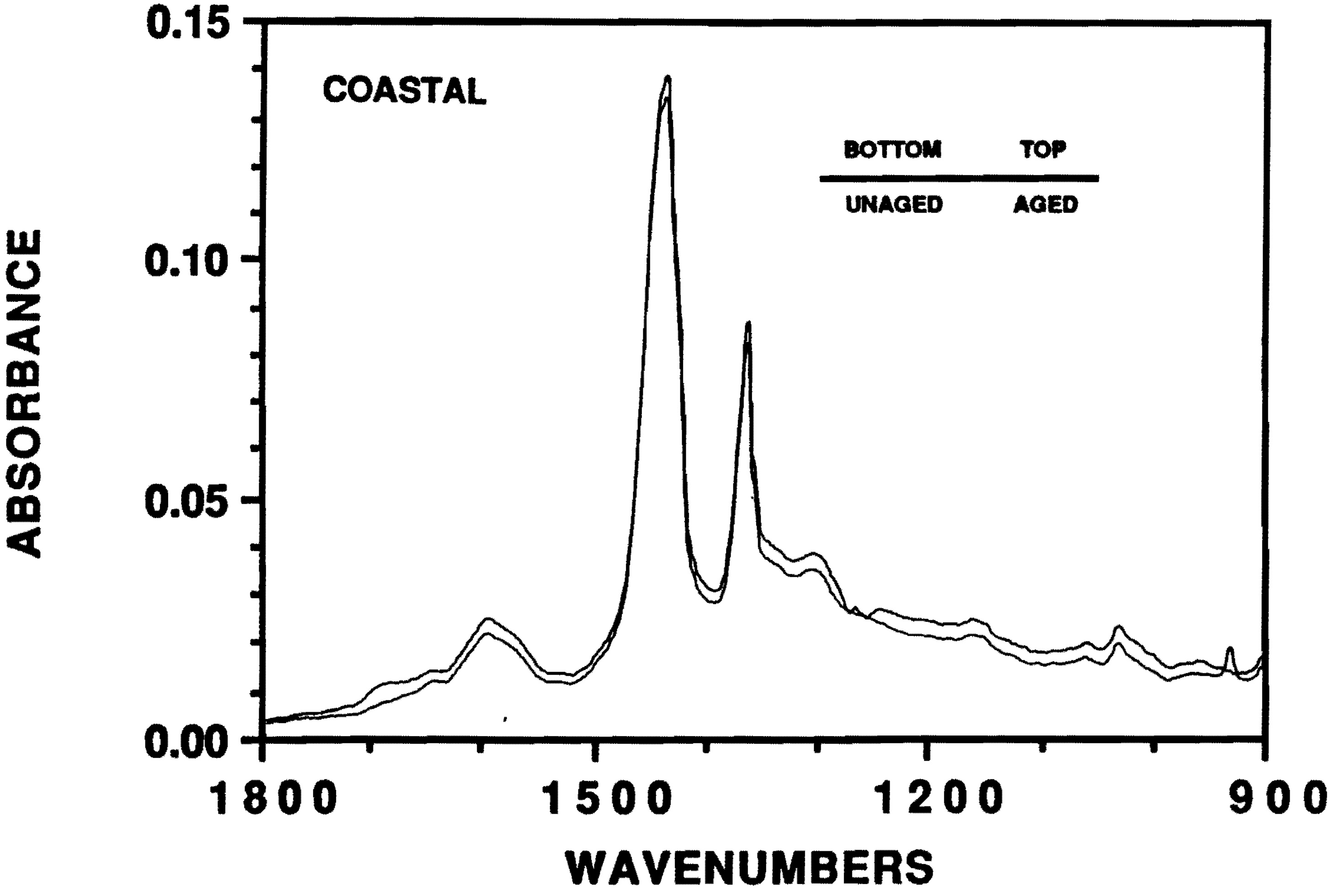

Figure 5-54
IR Spectra for Coastal Blend 2 Before and After Aging

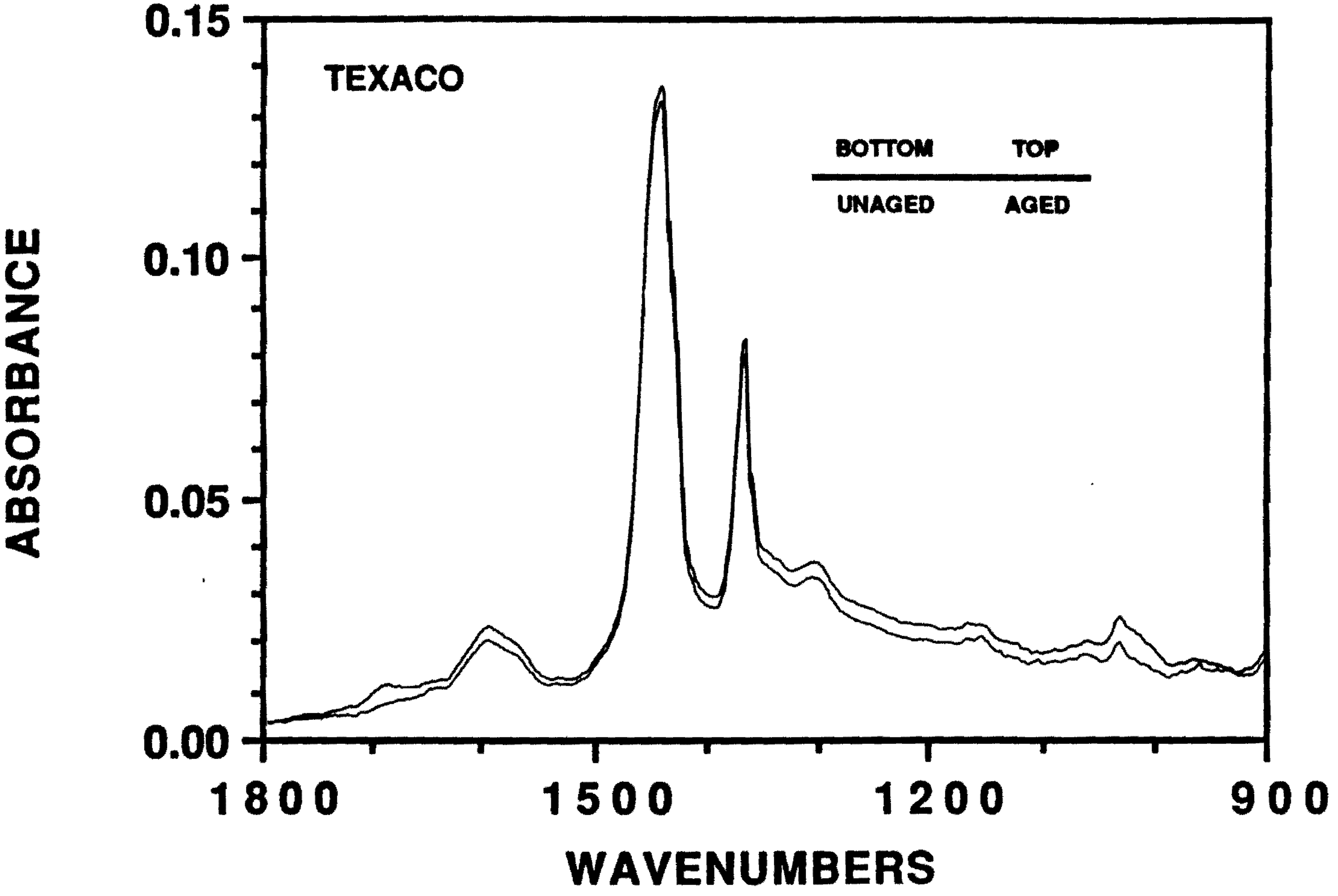

Figure 5-55
IR Spectra for Texaco Blend 2 Before and After Aging

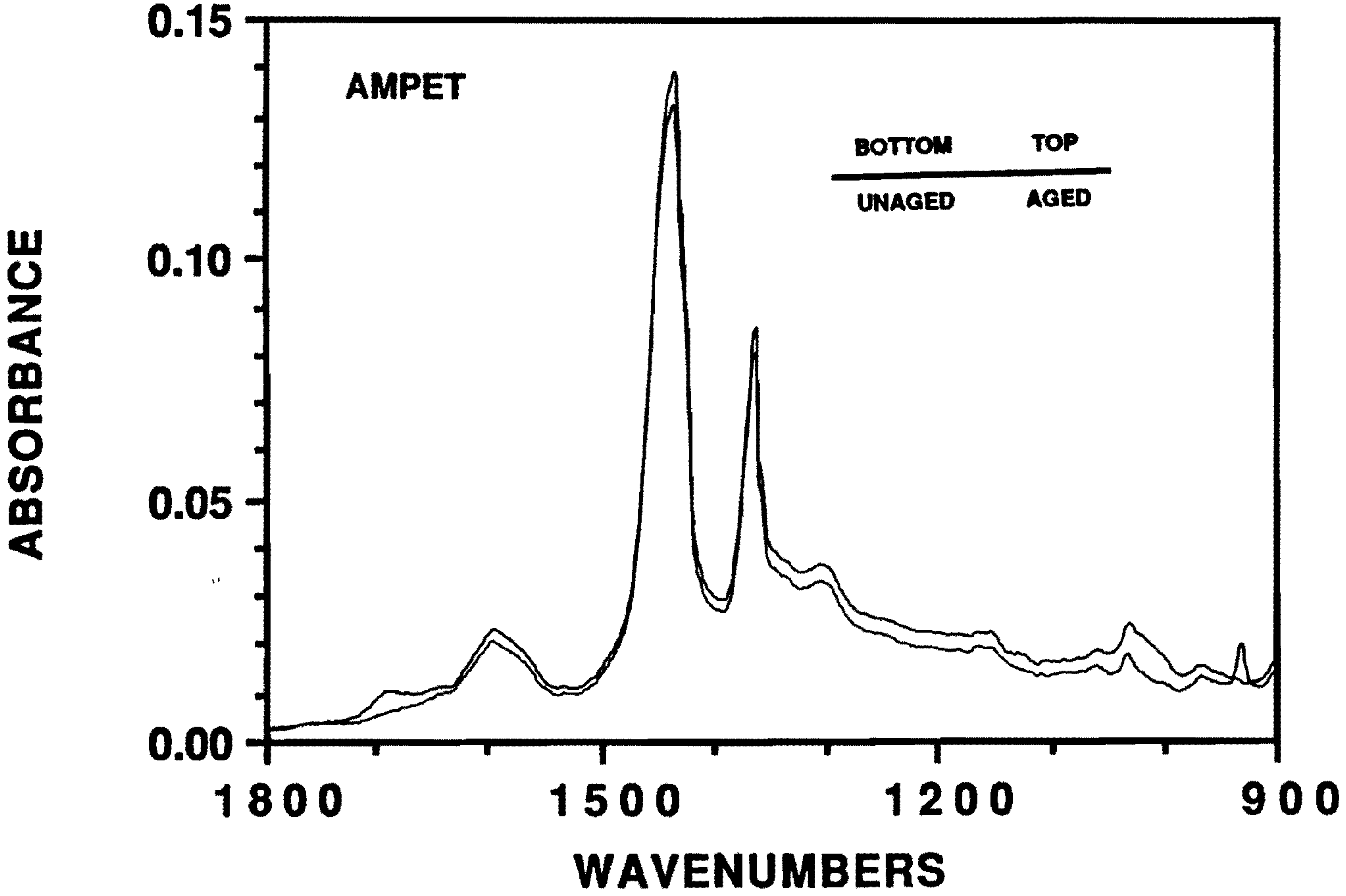

Figure 5-56
IR Spectra for Ampet Blend 3 Before and After Aging

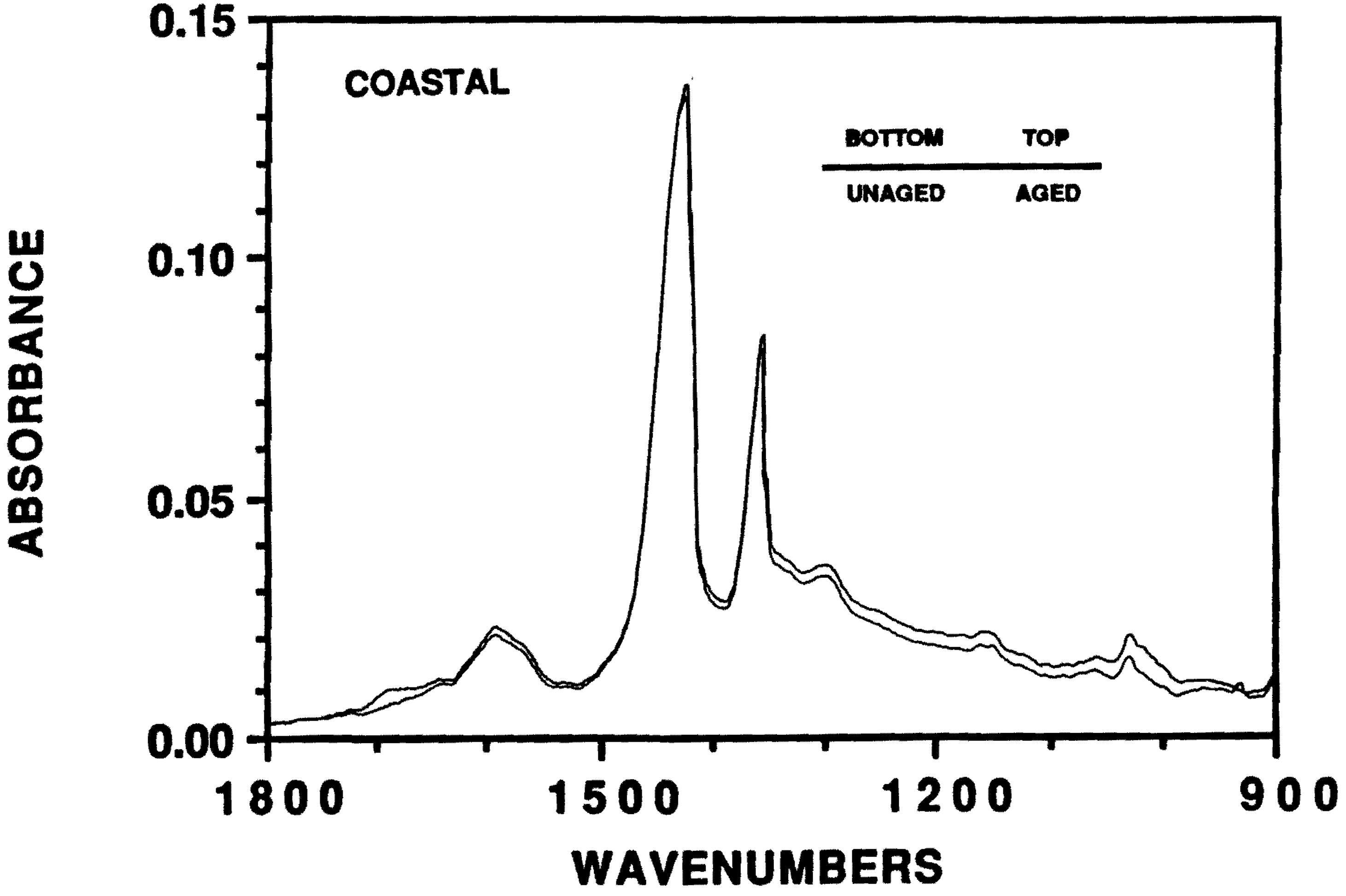

Figure 5-57
IR Spectra for Coastal Blend 3 Before and After Aging

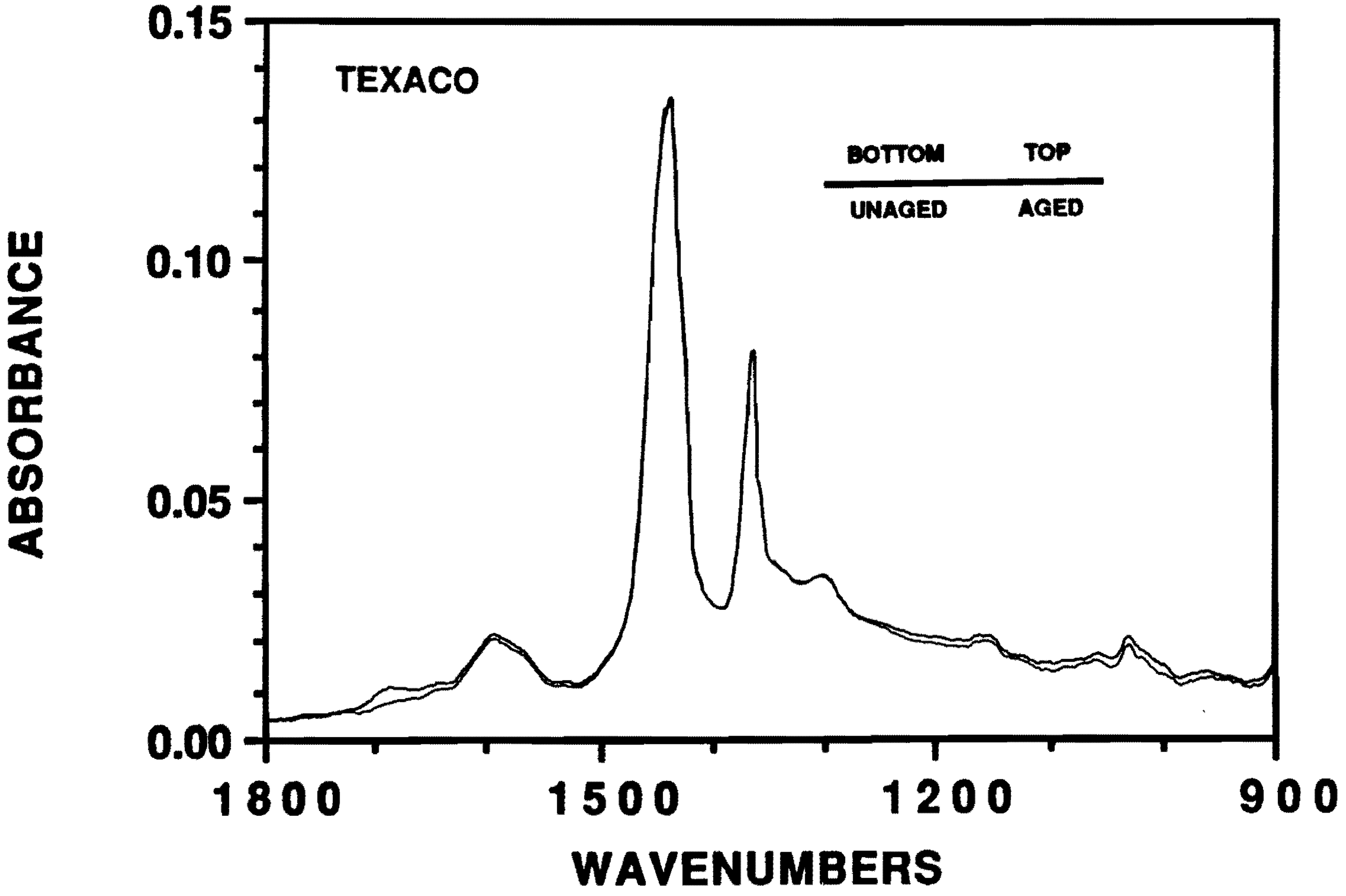

Figure 5-58
IR Spectra for Texaco Blend 3 Before and After Aging

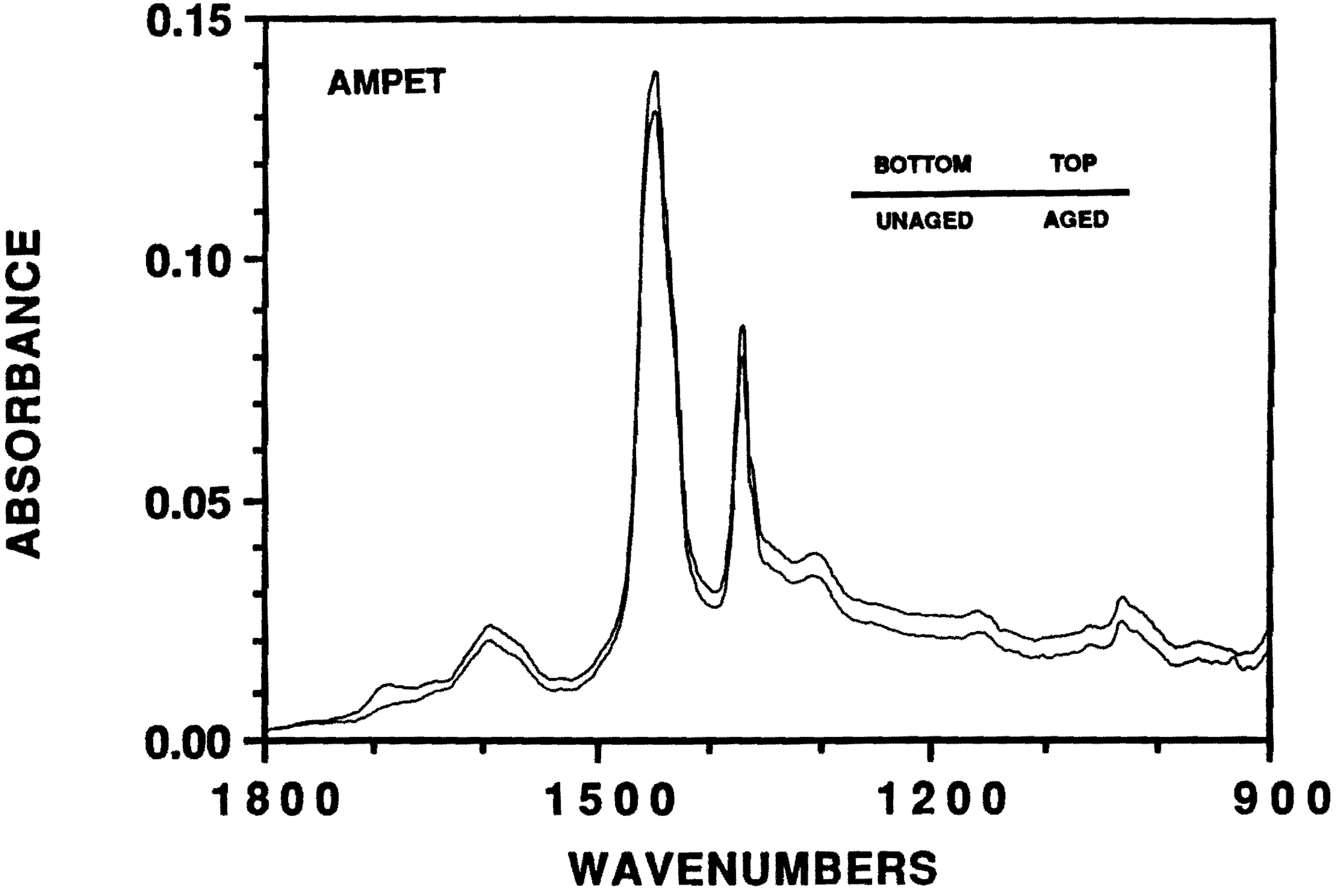

Figure 5-59
IR Spectra for Ampet Blend 4 Before and After Aging

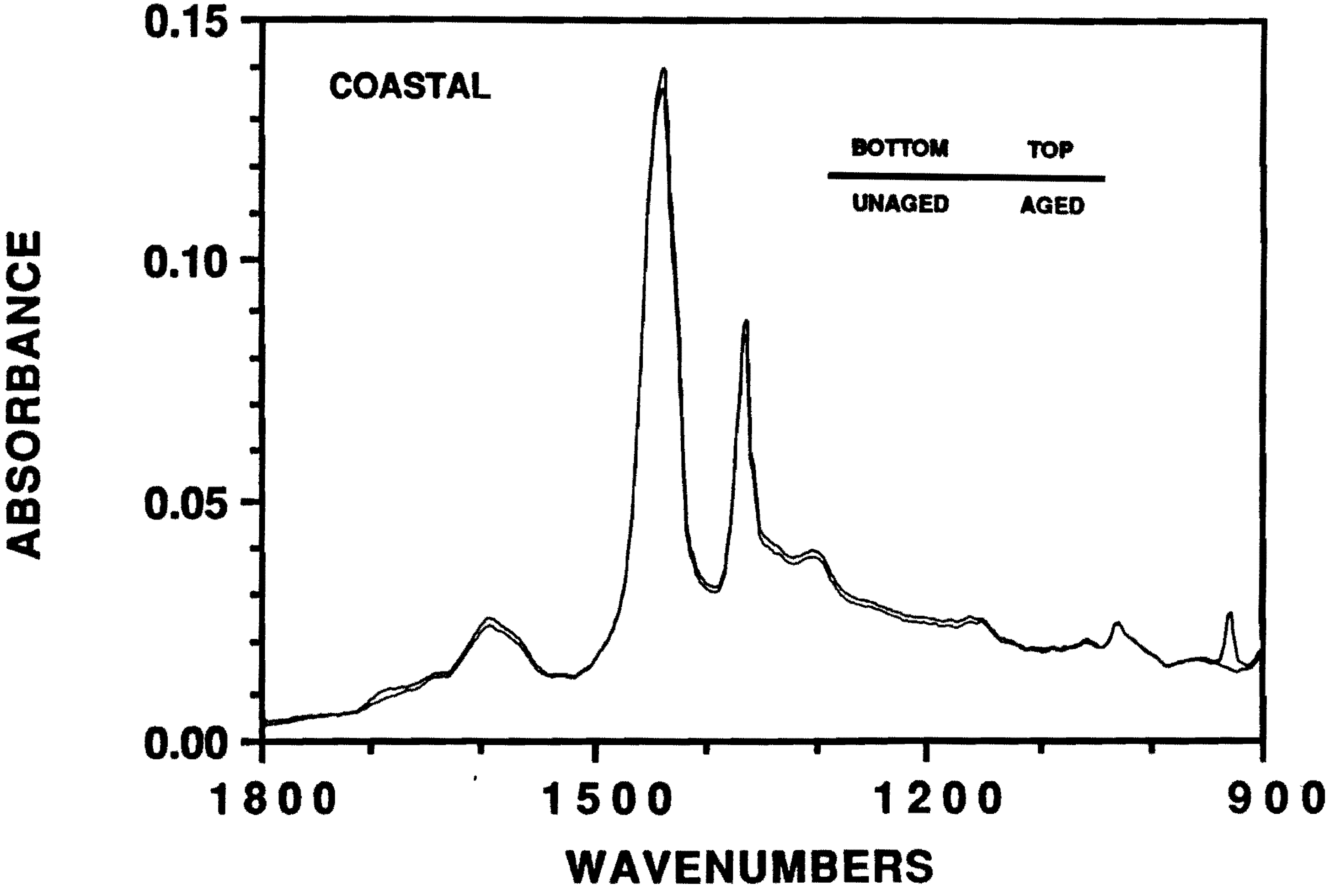

Figure 5-60
IR Spectra for Coastal Blend 4 Before and After Aging

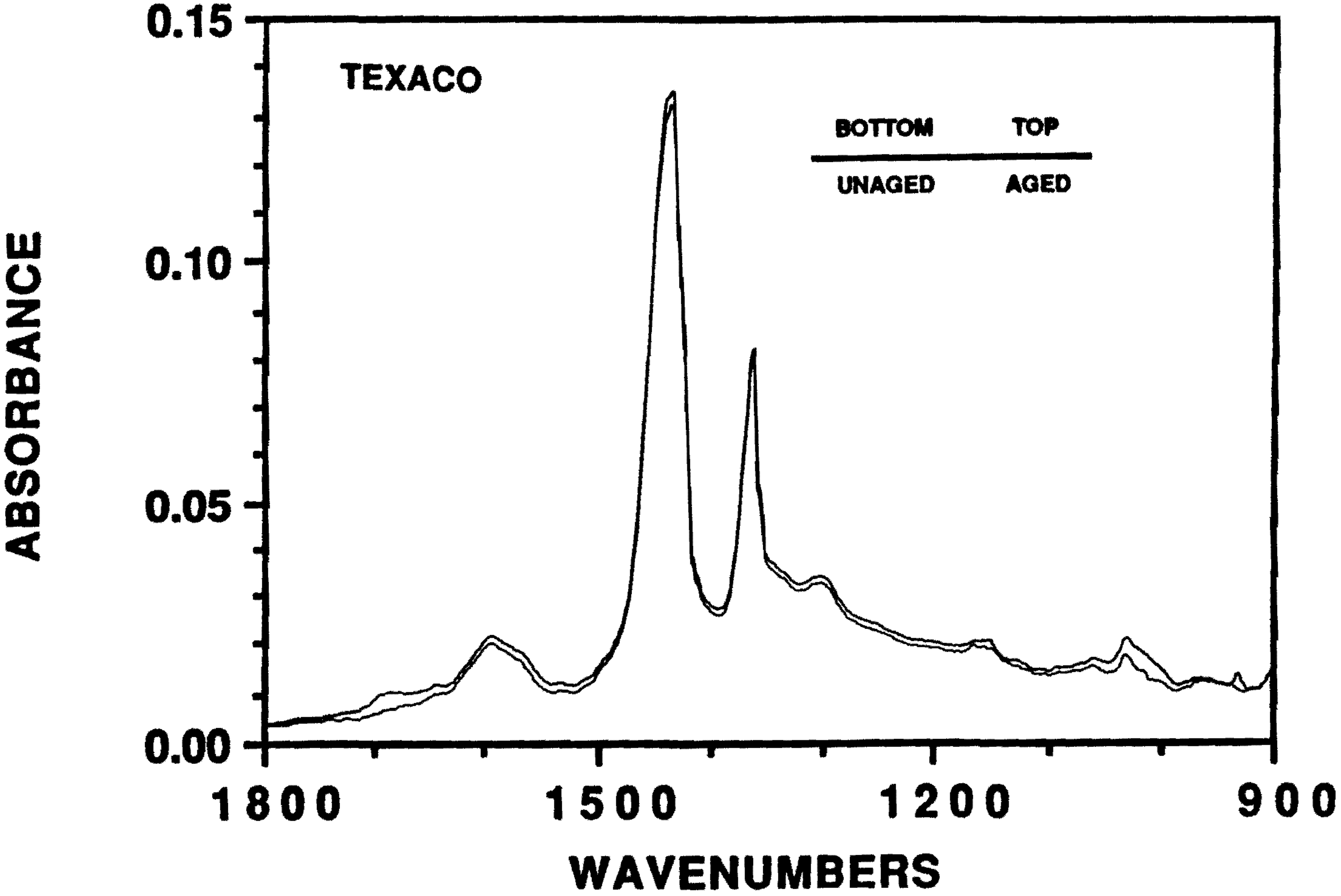

Figure 5-61
IR Spectra for Texaco Blend 4 Before and After Aging

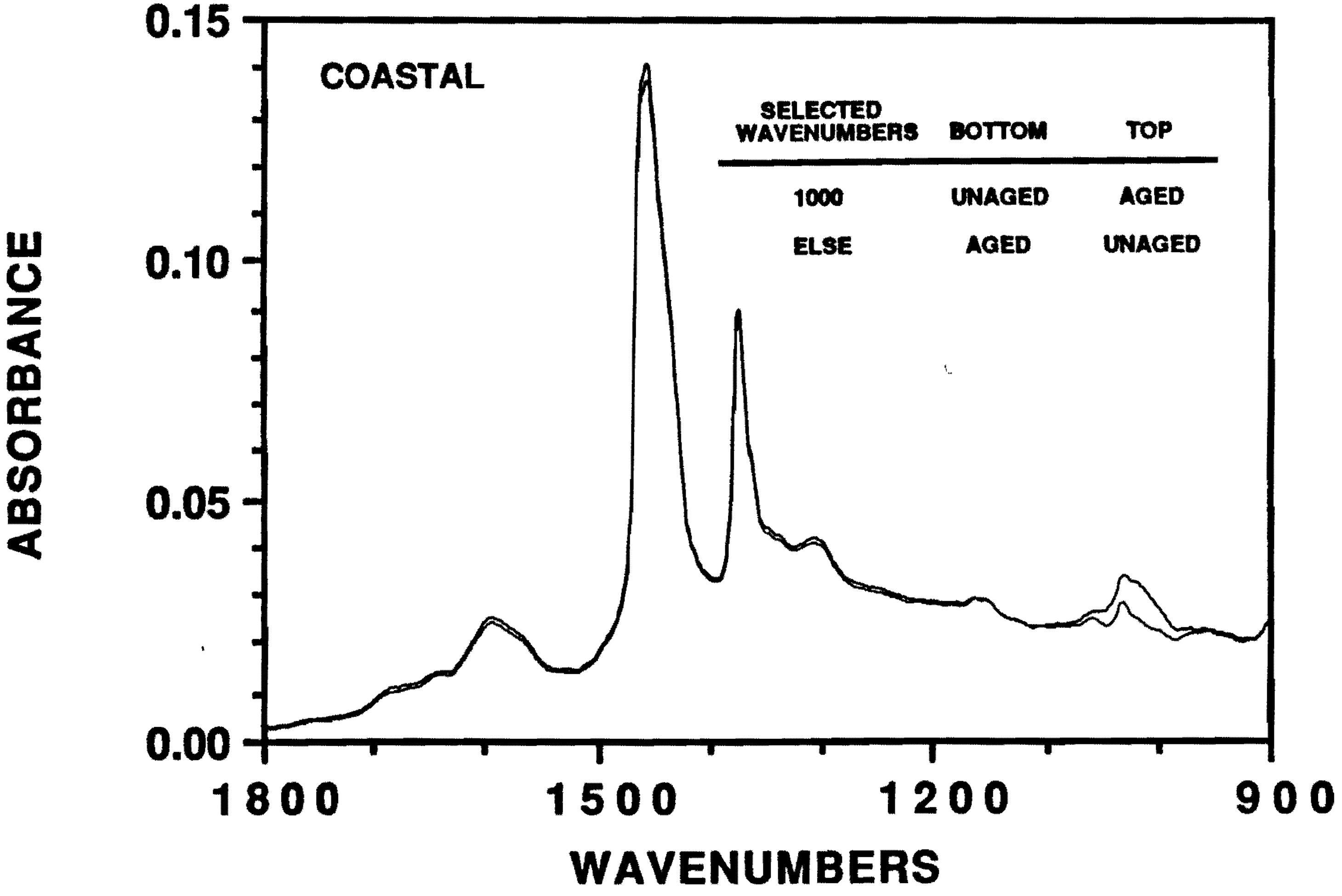

Figure 5-62
IR Spectra for Coastal Blend 5 Before and After Aging

related to growth of the carbonyl peak. The correlation slope is different for different asphalts and appears to depend on the aging mechanism; i.e., hot-mix aging produces less viscosity change for a given carbonyl peak than does oven aging. This slope we term the ***hardening susceptibility;*** it is an indication of how much an asphalt hardens as the result of a given amount of chemical aging. (In general, the growth of the sulfoxide peaks did not correlate with viscosity.) In producing improved asphalts, one would like to reduce this hardening susceptibility so that asphalts are more tolerant (with respect to physical properties) of chemical aging.

In Table 5-6 we give the carbonyl areas, aging indices, and hardening susceptibilities for the whole asphalts used in this study and the blends which were made from the supercritical and room-temperature fractions. The carbonyl areas are defined as bounded by the IR spectrum and a horizontal baseline between 1650 cm^{-1} and 1820 cm^{-1}.

As discussed previously in the section on Blend Physical Properties, Coastal blends 1 and 4 inadvertently contained a significant amount of residual solvent. This led to increased hardening upon aging; hardening due to volatiles loss occurred in addition to that due to oxidation. Consequently, these blends' hardening susceptibilities should be discounted in any attempt to correlate the chemical changes due to aging to the resulting physical changes (viscosity aging index). Coastal blend 2 also contained more residual solvent than desirable and its results may be questionable also. Note that Coastal blend 5 and Texaco blend 1 have very high hardening susceptibility (25.4 and 28.9 respectively) due to the very small degree of carbonyl growth accompanying the "normal" aging indices (2.02 and 2.54, respectively).

Of interest, then are 1) the aging index, 2) the carbonyl growth, and 3) the hardening susceptibility (not independent from (1) and (2)). For Ampet whole asphalt and blends the aging indices are all about the same while the hardening susceptibility shows improvement in the blends. The Coastal blends 3 and 5 (omitting the solvent-contaminated blends 1, 2, and 4) show reduced aging indices (compared to the whole asphalt) while only blend 3 shows an improved hardening

Table 5-6: Hardening Susceptibility of the Blends and Their Whole Asphalts

	Carbonyl Area			Aging Index	Hardening Susceptibility[a]
	Unaged	Aged	Increase		
Ampet					
Whole	0.454	0.624	0.170	2.32	2.15
Blend 1	0.491	0.745	0.254	2.57	1.61
Blend 2	0.624	0.799	0.175	2.15	1.90
Blend 3	0.434	0.724	0.290	2.45	1.34
Blend 4	0.478	0.744	0.266	2.84	1.70
Coastal					
Whole	0.457	0.612	0.155	2.80	2.88
Blend 1	0.643	0.851	0.208	11.16	5.04
Blend 2	0.531	0.752	0.221	2.91	2.10
Blend 3	0.534	0.751	0.217	1.98	1.37
Blend 4	0.538	0.705	0.167	4.46	3.89
Blend 5	0.654	0.666	0.012	2.02	25.4
Texaco					
Whole	0.451	0.527	0.076	2.55	5.35
Blend 1	0.620	0.634	0.014	2.54	28.9
Blend 2	0.473	0.661	0.188	1.76	1.31
Blend 3	0.472	0.616	0.144	1.72	1.64
Blend 4	0.457	0.653	0.196	1.40	0.75

[a] Hardening Susceptibility = $\log_{10}$(Viscosity Aging Index)/($\text{carb}_{\text{aged}}$-$\text{carb}_{\text{unaged}}$)

susceptibility. Texaco shows much improved aging index and hardening susceptibility in blends 2, 3, and 4 while blend 1 has about the same aging index and a much greater hardening susceptibility.

Obviously, the relation between chemical changes, as reflected in infrared spectra changes, and changes in physical properties, such as viscosity, are complex. As mentioned above, our experience is that as long as a single asphalt is subjected to a given aging environment the changes correlate well. If the aging method or asphalt is changed, however, the relation can change drastically. In this study, the aging was complicated by the fact that each blend is really a new asphalt.

But it is exactly these complications which are introduced by blends which *must* be studied if we are to truly understand and to be able to design improved asphalts. Understanding the changes which occur to a single asphalt are important, but it is equally important, if not more so, to understand the differences which exist between different asphalts.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Work described in this report leads to the following conclusions:

1. It is possible using the methods described in this report to produce asphalts with considerably improved properties.
2. The most obvious way to improve the properties of many asphalts is to reduce the saturate and asphaltene content, thereby making the asphalt more compatible.
3. Supercritical extraction is a powerful tool for studying the effect of composition on properties.
4. Supercritical extraction, being a variation of the commercial ROSE process and having the capability of producing improved asphalts, appears to be an economic way of improving asphalt properties as well as refinery profitability.

This is the first set of runs made with this equipment. As noted in the text there is doubtless error in some analyses and there is probably some error in fraction material balances because of the difficulty in completely recovering material. More seriously, the properties of several blends were adversely affected by small amounts of unremoved solvent. Almost certainly solvent hardening occurred during processing. While this is not of serious consequence as far as obtaining good blends is concerned, it is not understood and needs further study as to its mechanism and ultimate effect on properties.

In spite of the fact that at this point more questions have been raised than answers obtained, it is highly significant that with only rudimentary understanding of the complex changes involved, several blends with significantly improved properties were obtained. It appears that if corrections are made for solvent contamination, several more blends can also be included. We believe strongly that the results reported here are but an introduction to an extremely promising research venture.

Recommendations

Based on the results of this study the following recommendations are made:

1. Make some minor piping changes and use cyclohexane as solvent to supercritically fractionate the harder material.
2. Conduct a systematic test plan relating physical properties to incremental changes in composition.
3. Use a more complete viscoelastic property evaluation.
4. Do a systematic study of the effect of fractional composition on properties after aging.

Supercritical fractionation will give the refiner greater versatility in processing residuum both to improve asphalt quality and refinery profitability. Valuable asphalt components now going to the coker could be recovered while undesirable asphalt components could be sent to the coker or to more profitable processing such as catalytic cracking.

5. Obtain composition distribution ratios to permit process design.
6. Further define operating parameters so that economic calculations can be made.

The results obtained in this study certainly are not adequate to prove relations between chemical and physical properties or hypotheses about how to produce premium blends. However, they are supportive of the belief that blending can produce improved asphalt performance. What remains to be done, of course, is to carry out expanded, systematic studies designed to unravel further the connections (which must exist) between physical and chemical (including compatibility) properties.

Only by studying asphalt properties — chemical (IR, GPC, aging), physical (rheological and cracking), and compatibility — can we learn about the fundamental reasons for asphalt behavior. The supercritical fractionation unit is an extremely valuable tool for understanding these relationships by providing the means to obtain significant quantities of asphalt blends of different compositional, compatibility, and physical properties, as well as information on refinery implementation. We recommend that these capabilities be fully exploited.

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APPENDIX A

SUPERCRITICAL FRACTIONATION UNIT PROCESS SAFETY ANALYSIS

APPENDIX A
SUPERCRITICAL FRACTIONATION UNIT
PROCESS SAFETY ANALYSIS

General Description and Objective

The supercritical extraction unit fractionates asphalts or other heavy petroleum products into multiple fractions according to solubility in supercritical solvents. The unit operates at a constant pressure that is higher than the critical pressure of the extracting solvent. Increasing the temperature of the mixture causes density changes that produce different fractions. An increase in temperature in the supercritical region results in a decrease in density and a corresponding decrease in solvent power, so that as the temperature increases, a fraction precipitates. This precipitated fraction is collected in tanks where residual solvent is flashed by decreasing the pressure. The vaporized solvent is then cooled and collected. By dropping the pressure in the last tank, the solvent is flashed. The solvent vapors are then condensed and recycled. The extracting solvents are either n-pentane or cyclohexane.

Equipment Details

The maximum pressure used is 800 to 1000 psi and the maximum temperature is 600 to 800°F. The apparatus consists of:

five tanks	that are 1 ft long, 4 in. Sch 80 stainless steel (S.S.) pipe with a S.S. cap welded on one end and a 300 lb. S.S. Slip-on flange welded on the other. (A1, A2, C2 - C4)
one tank	that is 1 ft long, 4 in. Sch 80 S.S. pipe with a S.S. cap welded on one end, two 300 lb S.S. slip-on flanges welded in the middle and one at the other end (C1).

These six tanks will not be subjected to more than 10 to 30 psi. They were pressure tested with water up to 500 psi to check the

	welding.
three tanks	that are 2 ft long, 4 in. Sch 80 S.S. pipe with a S.S. cap welded on one end and a 1500 lb S.S. necking flange welded on the other end. (SB-SD)
one tank	that is 2.3 ft. long, 4 in. Sch 80 S.S. pipe with a S.S. cap welded on one end and a 1500 lb S.S. necking flange welded on the other end. (SA)
	These four tanks will be operated at up to 1000 psi. They were pressure tested with water up to 2500 psi to check the welding.
one tank	that is 3 ft. 3 in. long, 6 in. Sch 40 carbon steel (C.S.) pipe with a C.S. cap welded on one end and a 300 lb C.S. slip-on flange welded on the other end. (S0) This tank is operated at approximately 100 psi and 200°F. It was pressure tested with water up to 500 psi to check the welding. A gauge glass is connected to the tank and is rated 165 psi at 300°F.

All fittings are S.S. 316 Swagelok which can handle up to 10,000 psi. The pressure gauges are thermally isolated from the hot solvent by placing them at the end of a tubing loop of cold solvent. Global and Needle valves have grafoil inside to withstand temperatures up to 900°F. They are rated 6000 psi at 100°F.

Process Description

Asphalt from tank 1 (or 2) is pumped by a metering pump, P1 (see Figure A-1). The solvent, n-pentane or cyclohexane, is pumped to a supercritical pressure by a metering pump, P2. The two streams are combined and mixed by passing through a screen filter and then heated in H1. H2 further heats the mixture to a supercritical temperature. The density of the solvent decreases in the supercritical region forcing some parts of the mixture to fall out in Separator A (SA). The overhead of the separator is heated further and subsequent fractions are precipitated in the other separators.

Pure solvent is recovered from the overhead of the separator C by expansion through the control valve. This flashes the solvent and precipitates the remaining solute. The overhead of the last separator (D), pure solvent, is cooled by a water cooler and the pressure is dropped again through two globe valves in series before returning to the solvent tank. Collection tanks below each of the separators receive and store each of the fractions (CA - CD).

The apparatus is capable of bypassing either the second or the third separator or both. Samples of the first, second, or third overhead streams are analyzed to determine when equilibrium has been reached.

Utilities. Tap water for WC 1 and WC 2 cools the solvent vapors. Air lines (with filter, regulator, and gauge) operate the pressure control valve at about 20 psi.

Chemicals. Chemicals used include n-pentane, cyclohexane, and asphalt.

Hazard Analysis

Physical Hazards. Maximum temperature is 600 to 800°F inside the apparatus. The tanks and the flow lines are insulated. The handles of the valves are around 270 to 300°F so thermal protection gloves are needed. The entire apparatus is enclosed in a vented Lexan™ box.

Chemical Hazards. N-pentane is a Class 1A, and cyclohexane is a Class 1B solvent. Both solvents are highly flammable and incompatible with oxidizers and they must be kept away from sources of ignition. Therefore, all pumps used are explosion proof.

Biological Hazards. There are no biological hazards associated with the apparatus or experiments.

Electrical Hazards. All electrical wiring is insulated, and the control panel is grounded, to minimize electrical hazards.

Glass Hazards. The gauge glass is the only glass on the apparatus. This is rated sufficiently high, but is enclosed in plexiglass in case of breakage. The Lexan™

shields provide additional protection for the operators.

Design Precautions (refer to FIgure 1). The apparatus is enclosed in a 1/4" thick Lexan™ box that functions essentially as a large fume hood. Two separate fans on the roof provide the necessary ventilation. Other functions of the Lexan™ include protection from personal burns from heat sources, from leaks due to failure of any part of the equipment, and from shattering of the gauge glass (additionally protected with an outer plexiglass sleeve).

The system is monitored continuously during operation. Catch pans underneath each section of the apparatus and around the pump catch any spills. A pressure activated switch (Murphy Switchgage) shuts down <u>both</u> pumps in the event of extreme high or low pressure. An audible alarm system monitors the separator temperatures. A hydrocarbon detector detects concentrations at or above 0.05 volume percent.

Relief valves are set to relieve the separators A-C (SA-SC) at 1175 psi and separator D (SD) at 550 psi. These valves are rated for 400°F and are located above the separator outlets. Enough tubing is between the valves and the top of the tanks to ensure that these valves will never exceed a temperature of 400°F. This has been determined by bringing the system up to operating temperature with water. The solvent tank pop-off valve relieves pressure at or above 150 psi. This value is 25% below that of which the gauge glass has been tested.

Simulations and experiments performed verified the venting time for the limiting case of tanks SB and SC venting together through the same dump valve. The computer simulation was for pentane in its worst case of passing through the phase envelope such that most of the material will tend to stay as a liquid and gave a vent time (for 10 lb of pentane) of 75 s. Furthermore, an experiment was performed using freon at similar conditions. In this test, 28.5 lb of freon was brought up to a temperature and pressure at the top of the phase envelope. The valve to the cylinder was then suddenly opened and the venting time was recorded. In evaluating this experiment, we should consider that we were passing through a globe valve adding further friction effects. The results show that it requires 12 minutes to exhaust 85% of the freon to a pressure of 20 psig, which compares with a simulated time of 16 minutes, verifying the calculational procedure used for pentane and that the bleed time (75 s) is well within the Halon system design.

The halon system performs the following functions:

1. Automatically detects a fire by detecting both ultraviolet light in fires and sudden steep temperature rises.
2. Turns off power to the extraction unit
3. Opens relief valves to relieve the pressure in all four separators.
4. Turns off the exhaust fans and air conditioning.
5. Discharges enough halon inside and outside the Lexan™ enclosure to extinguish a fire and prevent reignition for 7 to 8 minutes.
6. Can be manually activated.

Material Compatibility. Both solvents are stable and nonreactive. All parts of the apparatus are stainless steel either 304 L or 316 which are compatible with asphalt, n-pentane, and cyclohexane. The interior of the valves, grafoil, is compatible with the solvents and asphalt. The gaskets on the tank flanges and other areas are completely compatible with n-pentane and cyclohexane.

Limits of Safe Operation. The equipment was designed for 1500 psi and 900°F.

Relief Valve Testing. The relief valves will be regularly tested and inspected during shut-down of the system. This is easily performed by removing the aluminum manifold, attaching each valve to a nitrogen tank with appropriate regulator, and adjusting the valve to open at the proper pressure.

Response to Unsafe Conditions. If one of the pressure relief valves opens, due to either failure in the pressure controller or asphalt blockage, the pump breaker and variacs should immediately be turned off. If one of the temperatures continues to increase without being able to control it with the corresponding variac or the pressure of any tank starts rising, the system must be shut-down by turning off the pump breaker and shutting the main electrical switch in the breaker box.

In case of fire the pump breaker must be shut off immediately and the main electrical switch in the breaker box turned off. The ultraviolet flame detectors will sense a fire and initiate the discharge of halon into the room. If the halon is not automatically discharged, manual activation may be necessary, or a fire extinguisher may be used.

If any leaks form that can be heard or seen, the emergency pentane relief switch should be thrown. It is located on the control panel. The emergency damper open switch should then be thrown to re-open the fume hood dampers. The pump breaker and the variacs should be turned off. The fume hoods that ventilate the apparatus should not be turned off.

If the gauge glass shatters, when it is safe, shut-off the bottom valve leading to the gauge glass.

In case of hood failure, the pump breaker and main electrical switch should be turned off. The pressure in the system should then be relieved by opening valve 36 to bypass the pressure control valve.

Reagent Storage. Both solvents are stored in the chemical storage room outside Zachry Engineering Center for permanent storage. For temporary storage, the flammable safety cabinet is used. Opened containers are stored in the walk-in hood.

Waste Hazards. The solvent is recycled, so there is little waste.

Waste Disposal. The recycled solvent yields little waste, and the solid wastes are disposed of normally.

Personal Protection. Safety glasses are, of course, always worn. When taking samples, face shield and safety glasses should be worn. When opening/closing valves while the equipment is running thermal protection gloves are recommended. Since the cement floor can be slippery, shoes with good traction are desirable. Skin should be covered when dealing with these solvents. This includes long-sleeve shirts, long pants, and gloves.

Availability of Emergency Response Equipment. A safety shower, eye-wash station, and fire extinguisher are located in the corner of the room.

Check Lists

Preliminary.

1. Take the intermediate tank outside to the staff parking lot area on the side of the Zachry building.
2. Take all bottles of solvent one at a time to the same location.
3. Fill the intermediate tank by directly pouring the solvent through the upper opening.
4. Close the upper opening to the intermediate tank.
5. The tank can now be moved to the apparatus.

Charging the System (see Figure 1).

1. Open all valves on the apparatus except for those which are directly open to the air. (3, 6, 13, 16, 22, 26, 32, 35, 42, 45, 48, 49)
2. Attach the vacuum pump to the nozzle at the end of valve 42.
3. Open valve 42 and turn on the pump to evacuate the system. Allow 3 hours time to pull as much vacuum as possible. Close the valve and disconnect the vacuum pump.
4. Attach a pure nitrogen supply to valve 45.
5. Turn on the fans to the hoods.
6. Open valve 45 and pressure the system up to 5 psig. Bleed down to 1 psig using valve 49. Repeat several times.
7. Move the movable solvent tank with a carrier into position to valve 45. Connect the movable solvent tank to the quick connect at the end of valve 48.
8. Attach a nitrogen supply to the movable solvent tank.
9. Pressurize the tank with 25 psi. (The solvent tank has been pressure tested to 100 psi).
10. Open valve B on the solvent tank and valve 45 on the apparatus.
11. Open valve 49 slightly.
12. Continue to allow flow of solvent from the movable solvent tank into

the fixed solvent tank S0 until the movable tank is empty. Repressurize the movable solvent tank as necessary.

13. Close valves B and C on the solvent tank and valve 45 on the apparatus.
14. Disconnect movable solvent tank and place it in the hood.

Start-up.

1. All the variacs should be set on zero. The switches should be in the <u>OFF</u> position.
2. Turn on the apparatus hoods (if not already on).
3. Check if the batteries for the hand-held hydrocarbon leak detector need to be replaced.
5. Close all valves.
6. Open valves 5, 7, 36, 43, 44, and 51, and according to the number of desired fractions: 2 fractions - open valves 46 and 47
   3 fractions - open valves 24, 33, and 46
   4 fractions - open valves 14, 23, 24, and 33.
7. Place asphalt in either A1 (or A2).
8. Turn on the solvent pump and let the solvent circulate cold.
9. Open water to WC 1.
10. Turn on the switches in breaker box (close to the lab door).
11. Turn on the variacs for the heaters on the separators (SA-SD) and asphalt tank (A1 or A2).
12. Through the Lexan™ doors check with the detector if there are any leaks. If a leak is detected, shut-off the pump and isolate the leak.
13. Put the power output of the variacs on 10 to 15%.
14. Adjust the variac for A1 (or A2) so that the temperature is around 300°F
15. Close valve 36 slowly and watch the pressure gauges. Increase the system pressures only by 100 psi at a time and wait for 5 to 10 min.
16. Repeat step 10 until the desired pressure is reached.

17. Watch the temperatures and adjust the variac so that the maximum temperature of the system does not exceed 100 to 200^{o}F
18. Adjust the variacs of S0 and SA-SD so that the temperatures of these tanks stay constant.
19. After the desired pressure is reached for 30 minutes, increase the temperatures slowly by changing the setting on the temperature controllers.
20. Repeat step 18 to 19 until the desired temperature is reached.

Experimental Operation.

1. Open valve 1 (or 2).
2. Turn on asphalt pump.
3. Check if the temperatures need adjustment after the asphalt is introduced into the system.
4. Once steady-state is reached, record the setting of the various variacs and the temperature readings of the tanks and the controllers.

Inline sampling - Purging

1. Wait for the system to reach steady-state.
2. Compute the maximum ratio of n-pentane to asphalt. This number will be used to determine the maximum amount of n-pentane which will be purged at any one time.
3. Place a 100 ml plastic beaker which has been placed inside a 400 ml plastic beaker full of an ice water bath under valve 16 (26 or 35).
4. Bleed off 0.2 cubic inches of asphalt. (This assumes that 2:1 asphalt is in the longest length of stagnant line thus always ensuring a sufficient purge. If this volume were to be at the highest possible ratio of pentane to asphalt, 20:1, then approximately 4 cubic inches of liquid pentane will escape. If all of this pentane were to vaporize, the concentration would still be below the explosive limit).

Inline Sampling - Sampling

1. Tare a vacutainer pre-evacuated test-tube.

2. Place the pre-evacuated test tube inside the plexiglass test-tube holder.
3. Make sure that valves 16, 26, and 35 are closed.
4. Open valve 15 (25 or 34) slightly to allow the mixture to flow into the bottom section of tubing between the valves 15 and 16 (25 and 26, or 34 and 35).
5. Close the upper valve. (15, 25, or 34).
6. Allow ample time for the mixture in this section to cool to a temperature at or close to room temperature (at least 10 minutes).
7. Place tared vacutainer test tube and plexiglass holder assembly under valve 16 (26 or 35) and insert the needle underneath the valve through the septum of the vacutainer.
8. Open valve 16 (26 or 35) a quarter turn.
9. Collect until the vacutainer pulls out the trapped volume of sample.
10. Close valve 16 (26 or 35).
11. If the needle becomes clogged due to asphalt precipitation, close valve 16 (26 or 35), remove holder assembly, remove needle and soak the needle in a solution of TCE until it is no longer occluded. Replace the needle and proceed with step 1.
12. Pull the vacutainer and plexiglass holder assembly from the needle and move it into the hood.
13. Pull the septum from the top of the vacutainer.
14. Remove vacutainer from plexiglass holder.
15. Heat vacutainer gradually on the explosion proof heating plate.
16. After solvent evaporates, weigh the vacutainer with asphalt residue.

<u>Filling Collection Vessels</u> (one at a time)

1. Open the water supply to WC2.
2. Connect movable solvent tank to valve 48.
3. Open valve 48 (slowly).
4. Open slowly 12 (21, 31, or 41). This will allow pentane vapors to flash from the asphalt mixture and then return to the movable solvent tank

as a condensed liquid.

5. Slowly open valve 8 (17, 27, or 37).
6. Slowly open valve 10 (19, 29, or 39).
7. Wait until the flow rate of the flash off line increases dramatically (a dramatic change in sound). This indicates that the bottom of the separator is empty. Close valve 8 (17, 27, or 37).
8. If the flow is stopped (no sound) the valves are blocked; open valve 9 (18, 28, or 38). Turn off asphalt pump and let solvent dissolve through the lines.

Collecting Fractions

1. Empty one tank at a time.
2. Turn on the variac for CA-CD so that their temperatures are between 100 to 200°F to remove most of the remaining pentane and to keep the asphalt fractions melted.
3. Place a permanent container under valve 13 (22, 32, or 42).
4. Open valve 13 (22, 32, or 42).
5. Empty CA (CB, CC, or CD).
6. Close valve 13 (22, 32, or 42) immediately after the asphalt has emptied out of the system. This will ensure that only a minimal amount of remaining pentane vapor escapes. It is possible that some flammable liquid or vapor could escape. Therefore, all possible precautions should be taken.
7. Close the permanent container and place it in a freezer which is rated for flammables.

Shut-down.

1. Turn off the asphalt pump.
2. Close valves 1 (or 2) and 4.
3. Turn off the solvent pump.
4. Close valves 5 and 7.
5. Turn off all the variacs.

6. Turn off the switches in the breaker box.
7. Turn off the pump breaker.
8. After 30 minutes shut off the water supply to WC1 & WC2.
9. Turn pressure controller to 0.
10. Shut off air supply to the pressure controller.

Emergency Shut-down.

1. Turn off the pump breaker.
2. Turn off the main switch in the breaker box (near the exit).
3. Throw the switch on the control panel marked <u>Pressure Relief Switch</u>. This will open all of the relief valves installed with the halon system and thus instantly relieve all of the pressure in <u>each</u> separator down to atmospheric pressure.
4. Relieve the pressure in the solvent tank by opening valve 49. This will vent all pressurized solvent to the roof.

Emptying the System.

1. After shut down, close all valves.
2. Open water supply to WC2.
3. Connect moveable solvent tank to valves 5, 7, and 48.
4. Open valve C on the moveable solvent tank to release any excess vapors into the hood.
5. Turn on the solvent pump.
6. Open valves 11, 14, 20, 23, 24, 30, 33, 36, 40, 46, 47.
7. When solvent level in gauge glass has disappeared, turn off the solvent pump.
8. Wait until there is no flow into the moveable solvent tank.
9. Close valve on that tank.
10. Close valve 48.
11. Close water supply to WC2.
12. Close all valves.

Cleaning the System. All procedures will be the same as for a normal run using cyclohexane or pentane except for the following:

1. The temperature will remain at room temperature.
2. Lower pressures will be used.
3. No asphalt will be used.

Potential Accidents and Responses

Utility Failure. In the case of a power failure the emergency shut-down procedure should be used. Water failure would prevent cooling of the recycled solvent and vapor, and the pumps and variacs should be turned off. An air failure would shut down the pressure controller, and the pumps and variacs should be turned off and the pressure relieved through valve 36.

Leaks. The total amount of solvent in the equipment is 7 gal. Not all the tanks will leak or break at the same time. The largest tank holds a maximum of 6 gallons (the solvent tank). As mentioned before, if there are any small leaks, the process is shut-down and the hoods will evaporate the solvent. If suddenly a large leak occurs use emergency shut down and turn on the walk-in hood. If leaks are in-line (due to fittings) isolate the leak by shutting off the appropriate valves. The apparatus is ventilated at a rate 3943 ft^3/min (measured in the hood duct) by two fans. The bottom face air flow of the apparatus is approximately 2000 ft^3/min (measured at the bottom of the apparatus). The difference (around 2000 ft^3/min) enters the apparatus between the Lexan™ side panels.

Worst Possible Case:

If the 7 gallons spill and there is no ventilation, the concentration of n-pentane is 2.1%. For cyclohexane the concentration is 2.3%. With ventilation working, all the solvent will be removed from the room. Any solvent released at our conditions into room-conditions will be vapor. However, the solvent from the solvent tank will be in the two phase region. Two-thirds of this solvent will be in the liquid phase, but with the constant air flow it will quickly vaporize.

Spills. If a spill occurs while filling the moveable solvent tank, it will be outside the building and the solvent will quickly evaporate. A spill while collecting samples from CA-CD will yield only traces of solvent that will evaporate quickly.

Equipment Failure. Failure of the pressure relief valves requires that the system be shut down. Pump failure will result in insufficient pressure to the system, shutting the system down automatically. Ventilation failure will require emergency shut-down.

Fire. The halon system will be automatically activated when the ultraviolet flame detector senses a fire. The system also will be emptied automatically through halon activated relief valves to the roof. The ducts to the hood will be closed automatically to keep the halon in the room. The operator should stay in the room and perform the emergency shut down procedures.

If the halon system fails to discharge, it may be activated manually or a fire extinguisher may be used.

Building Evacuation. The emergency shut down procedure should be performed and the hoods left on in the case of a building evacuation.

Documentation and Maintenance Records. Equipment and instrument manuals for the two pumps, the pressure controller and control valve, temperature controllers, and temperature indicators are available in the laboratory. MSDS sheets were read and signed. The hydrocarbon leak detector is tested before every run.

Equipment Labels. All utility shut-offs and emergency shut down and relief switches are labelled.

Noncompliance with Department Safety Policy. Pentane and cyclohexane are purchased in one-gallon quantities. They may be temporarily stored in large metal pressure vessels as described in the preliminary procedures. This is against the department safety policy of storing Class 1A solvents in one-quart containers. The pentane and cyclohexane will only be stored in large quantities in the chemical storage room (Zachry Room 99) or in the apparatus. Waste solvents will be stored in the one-gallon containers and tagged for immediate disposal by University Safety Office.

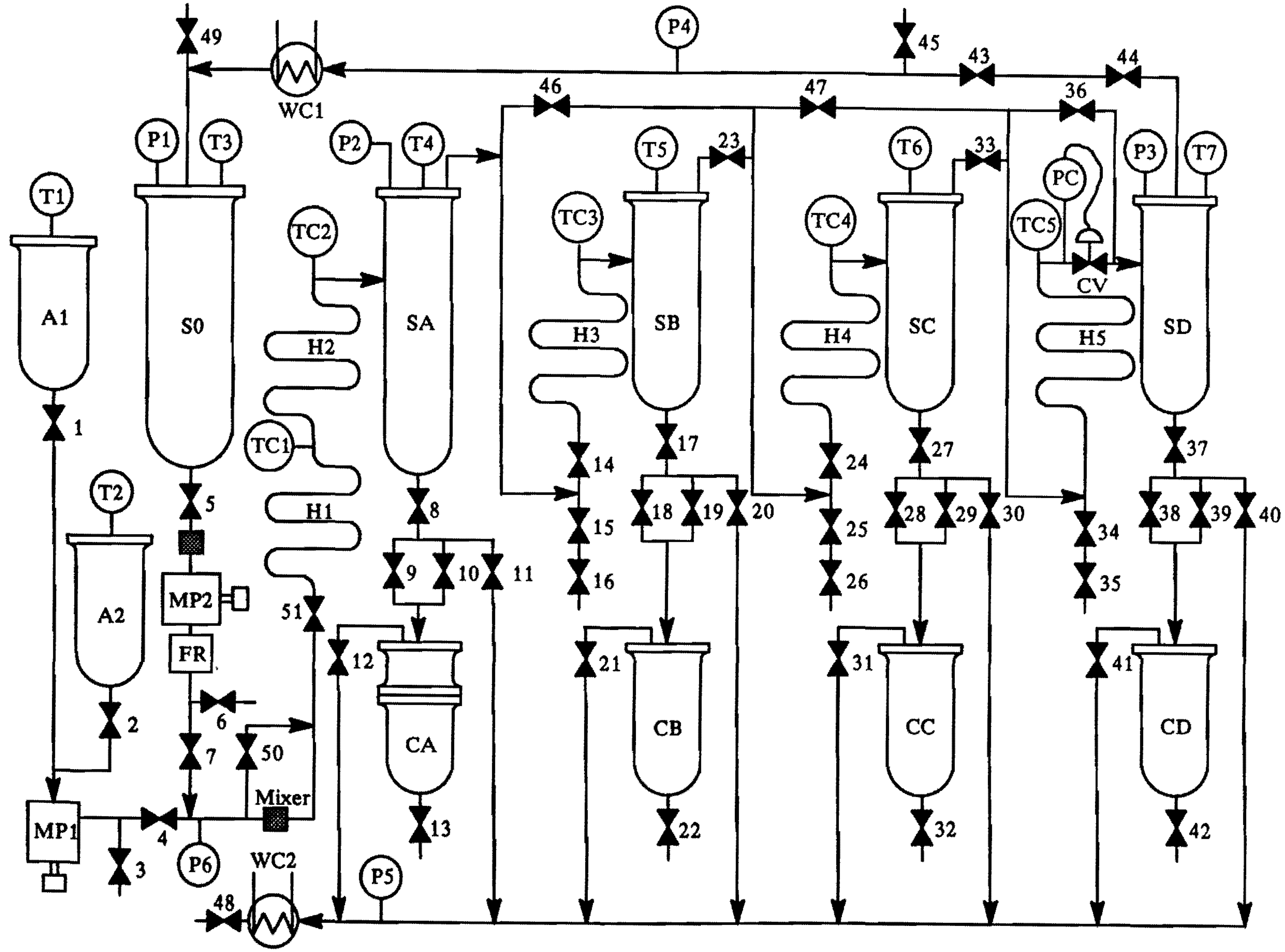

Figure A-1
Flow Diagram of Supercritical Extraction Unit

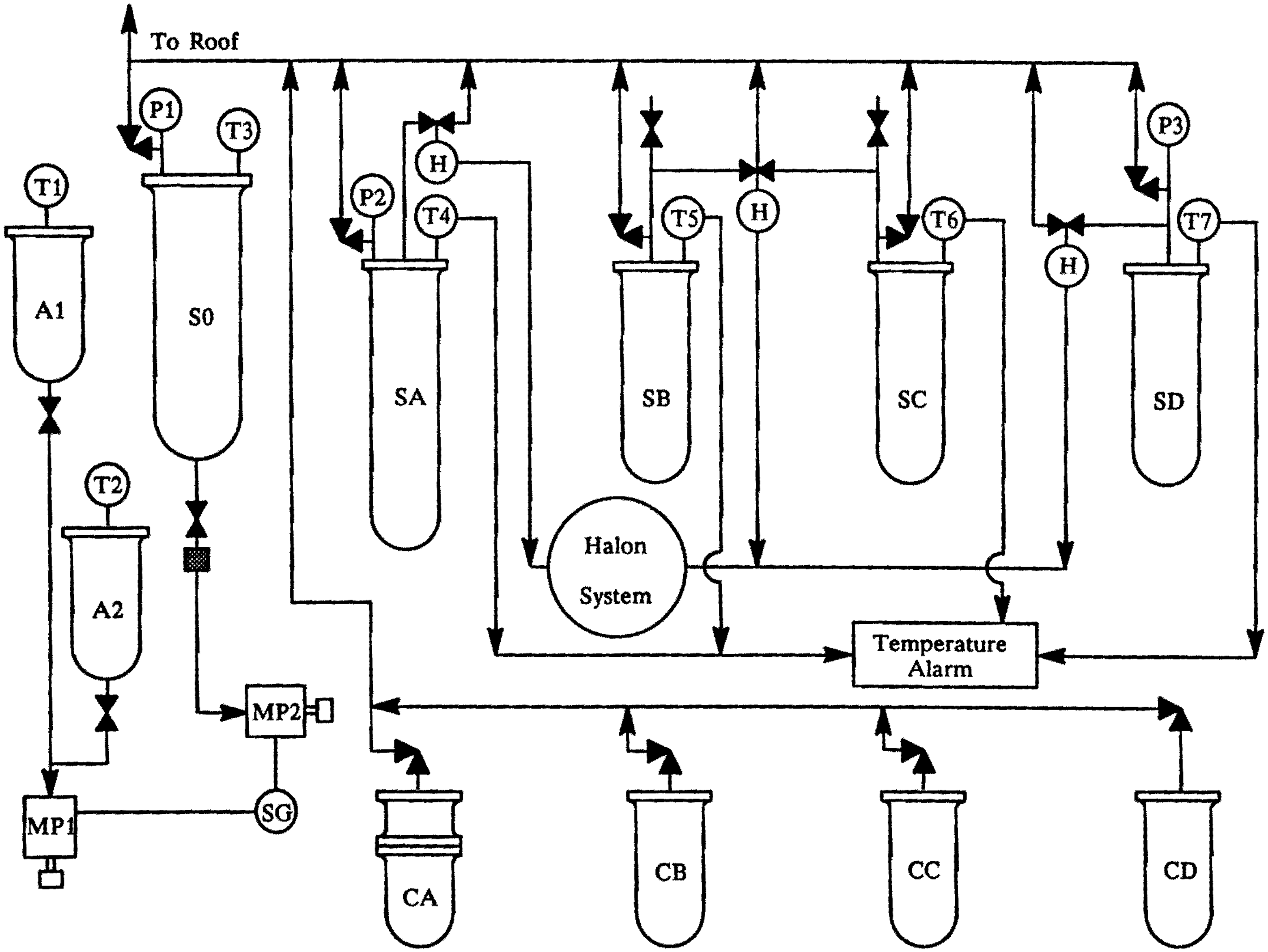

Figure A-2
Flow Diagram of Halon and Alarm Systems
of Supercritical Extraction Unit

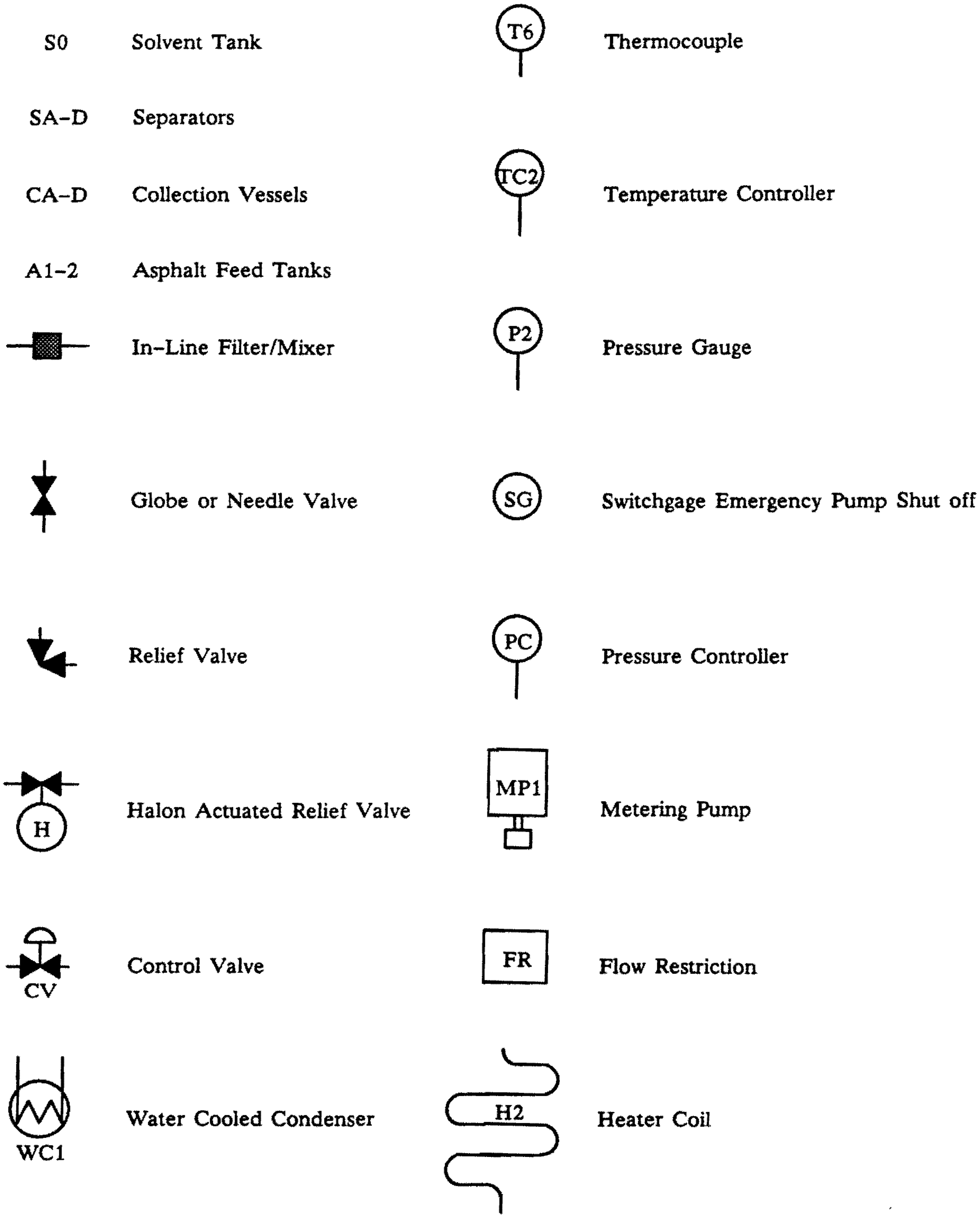

Figure A-3
Key to Schematic of Figure A-1 and A-2

APPENDIX B

ADDITIONAL GPC CHROMATOGRAMS

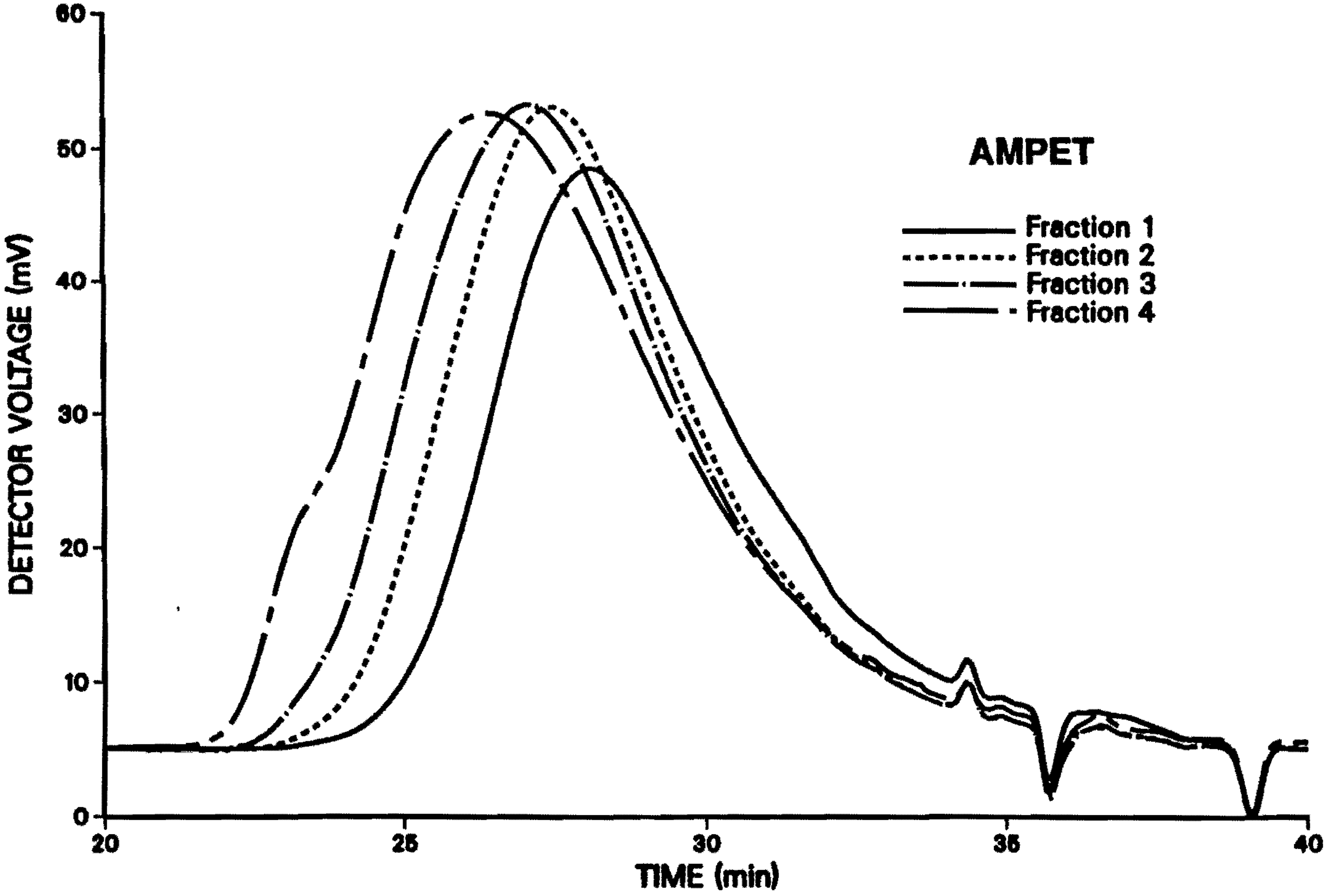

Figure B-1
GPC Chromatograms of Ampet Fractions 1-4

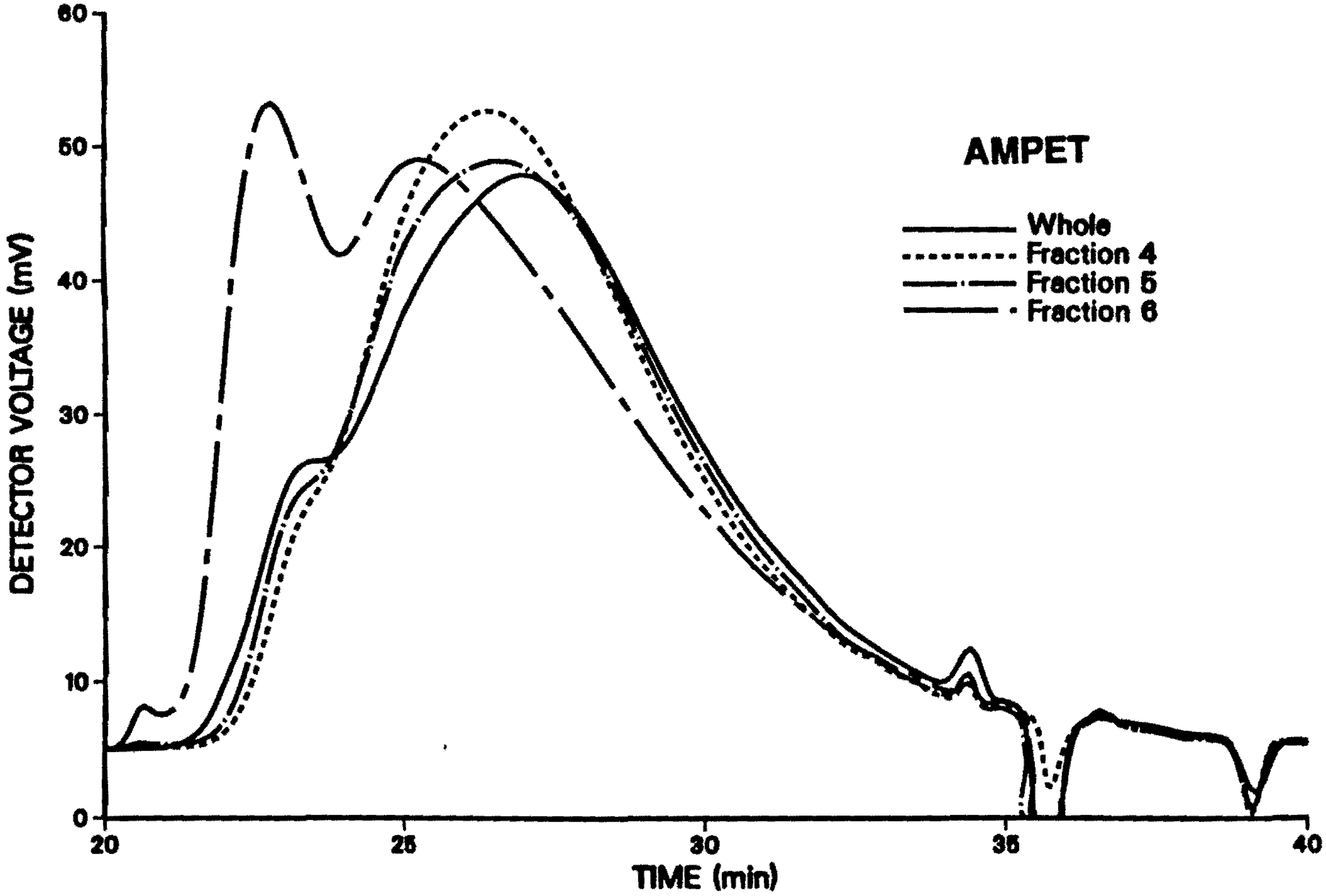

Figure B-2
GPC Chromatograms of Ampet Whole and Fractions 4-6

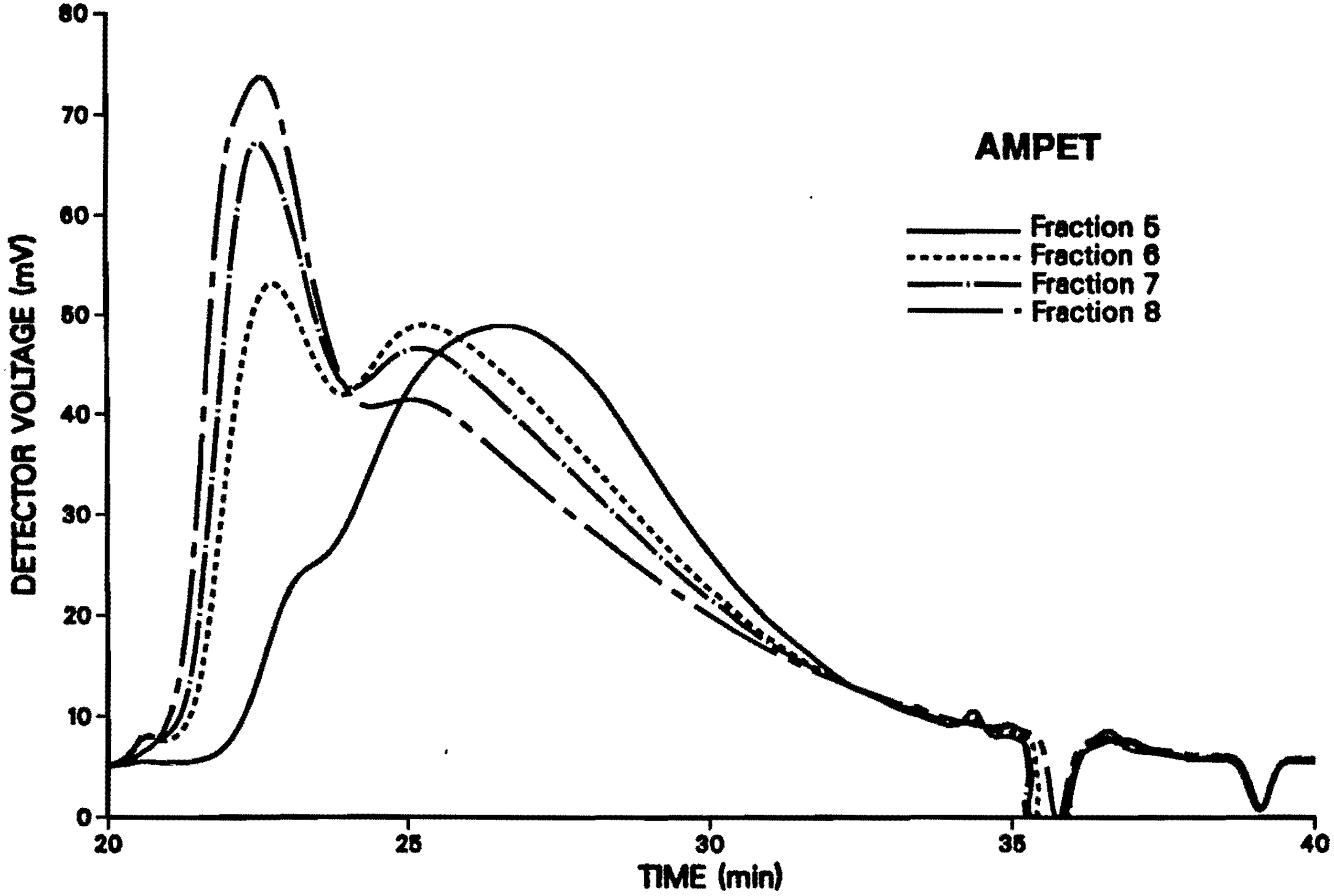

Figure B-3
GPC Chromatograms of Ampet Fractions 5-8

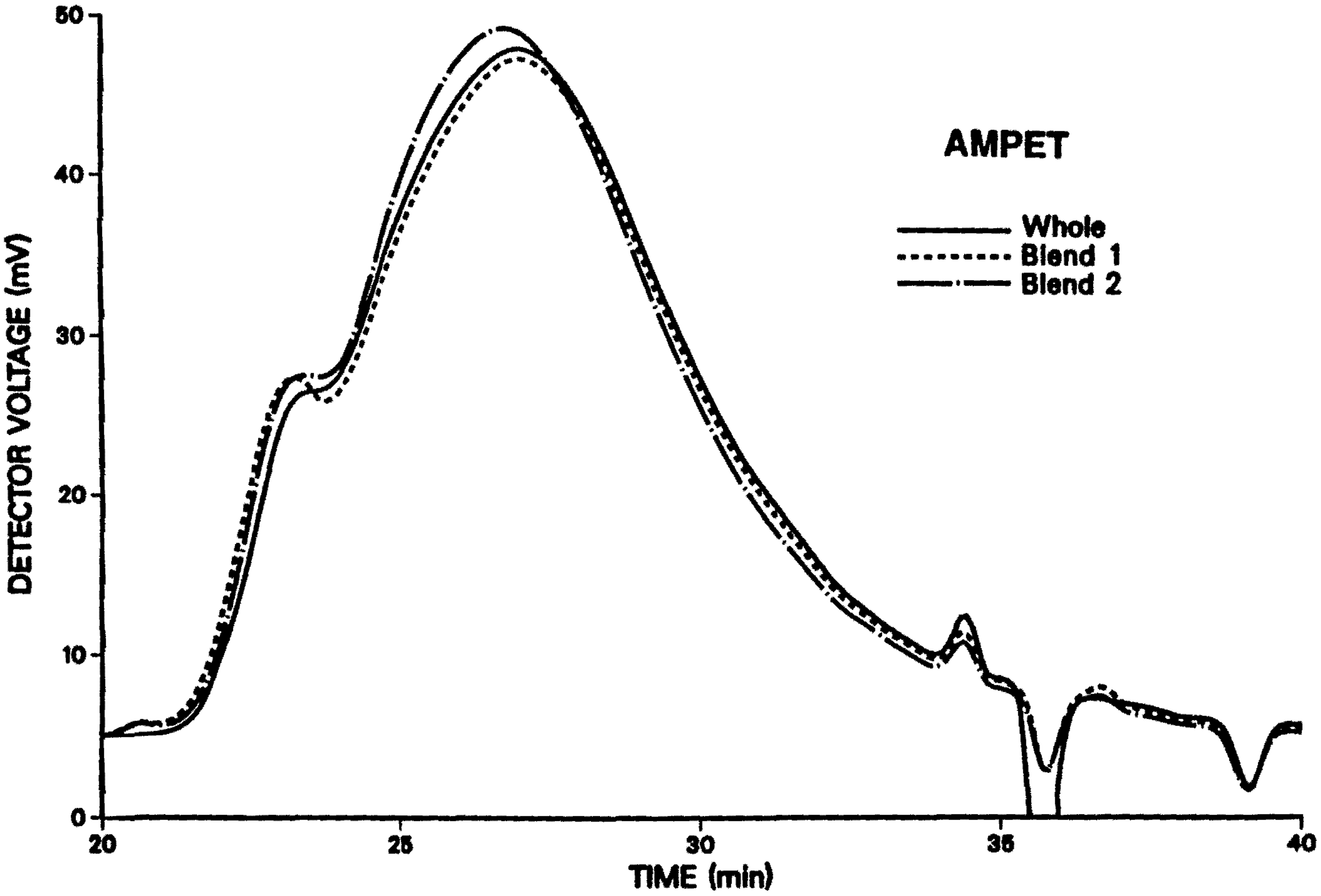

Figure B-4
GPC Chromatograms of Ampet Whole and Blends 1 and 2

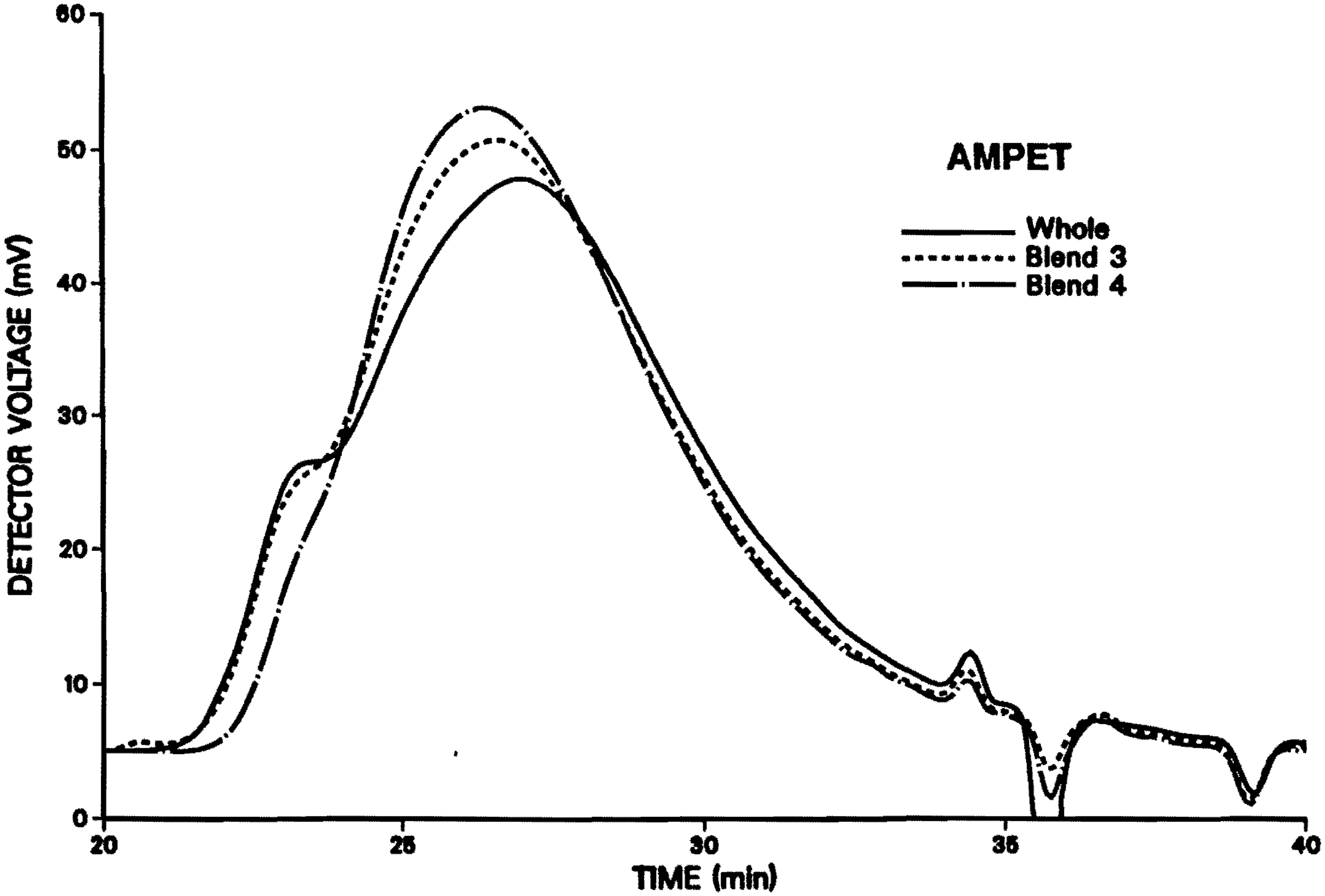

Figure B-5
GPC Chromatograms of Ampet Whole and Blends 3 and 4

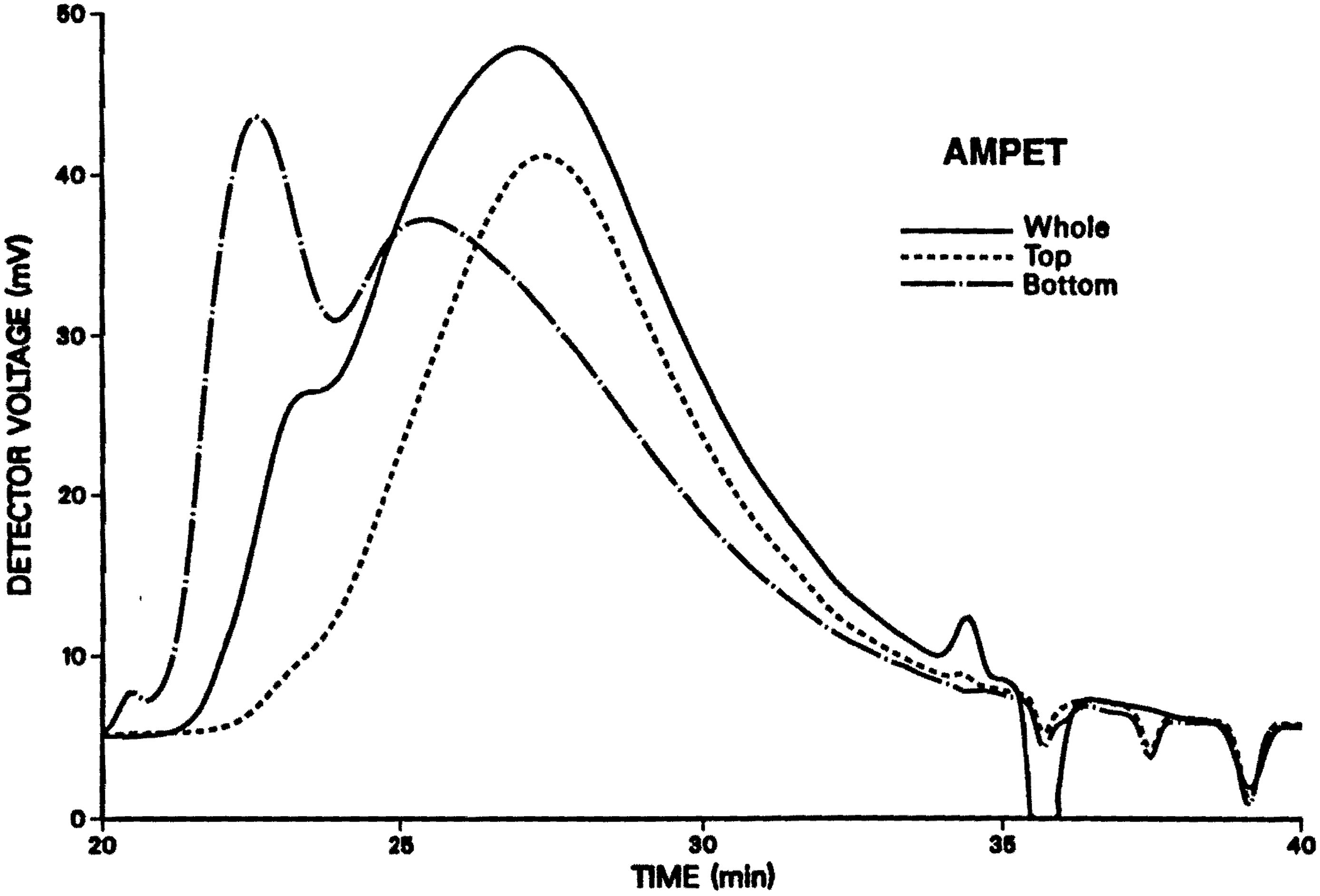

Figure B-6
GPC Chromatograms of Ampet Whole, Top, and Bottom

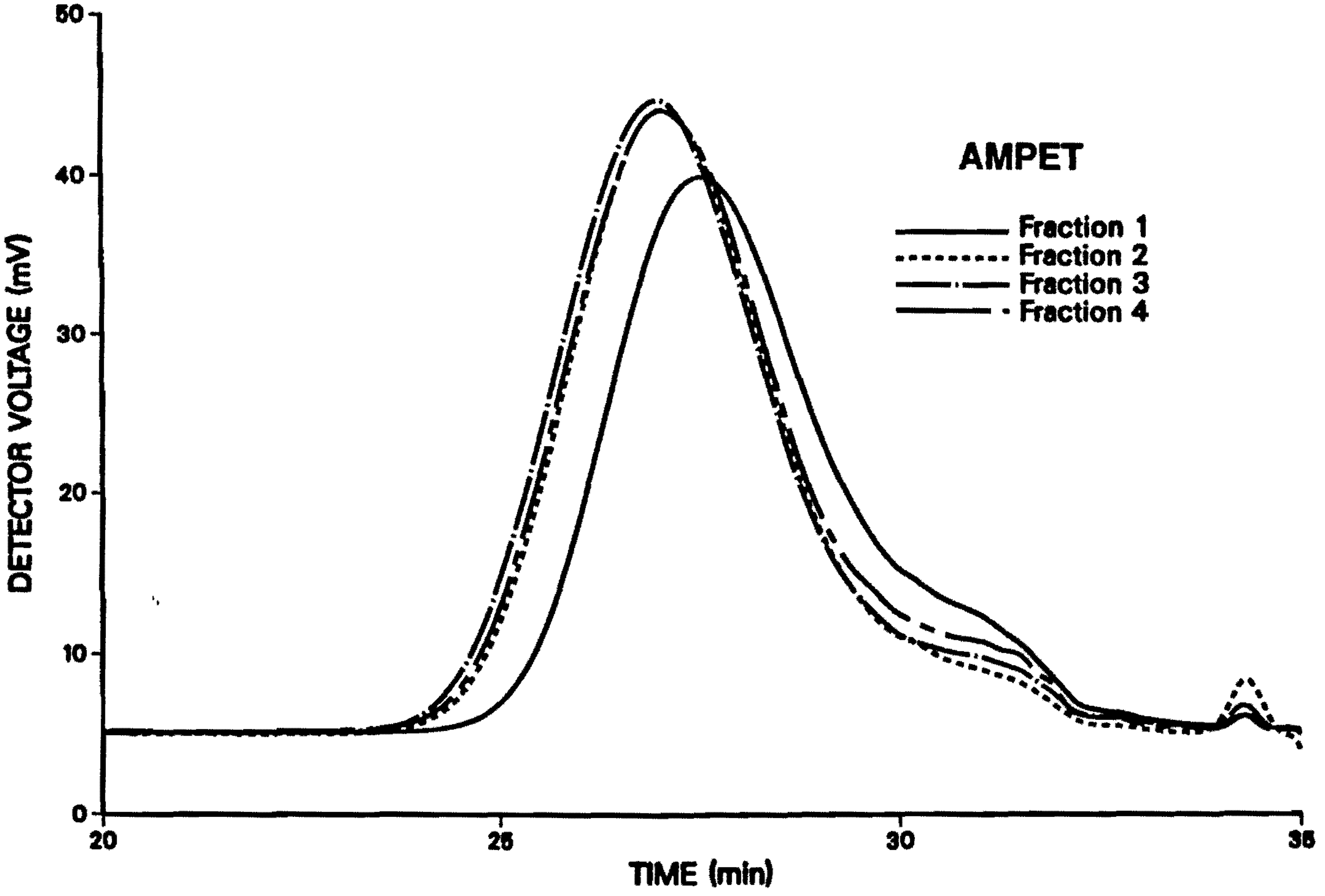

Figure B-7
GPC Chromatograms of Ampet Saturate Fractions 1-4

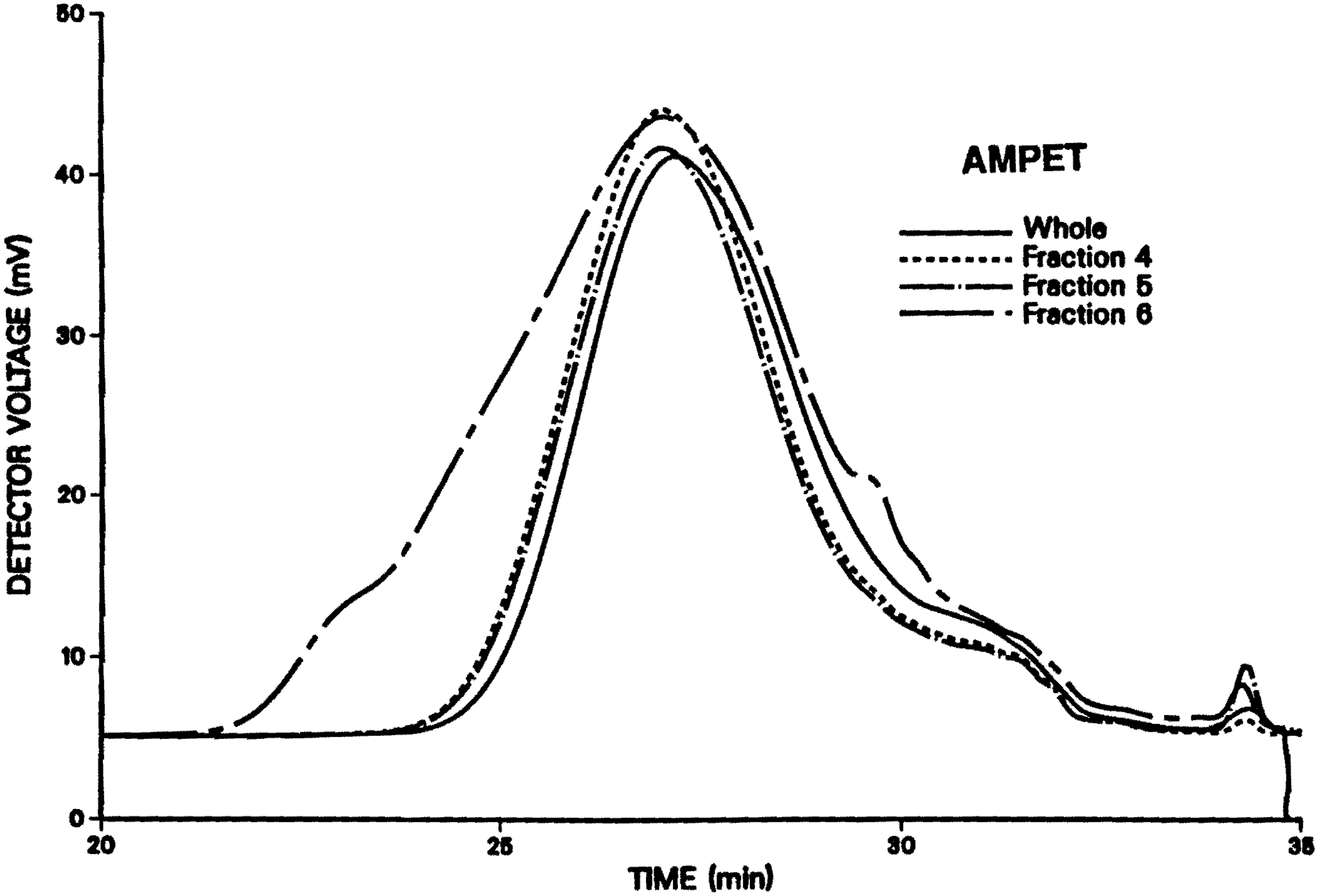

Figure B-8
GPC Chromatograms of Ampet Saturate
Whole and Fractions 4-6

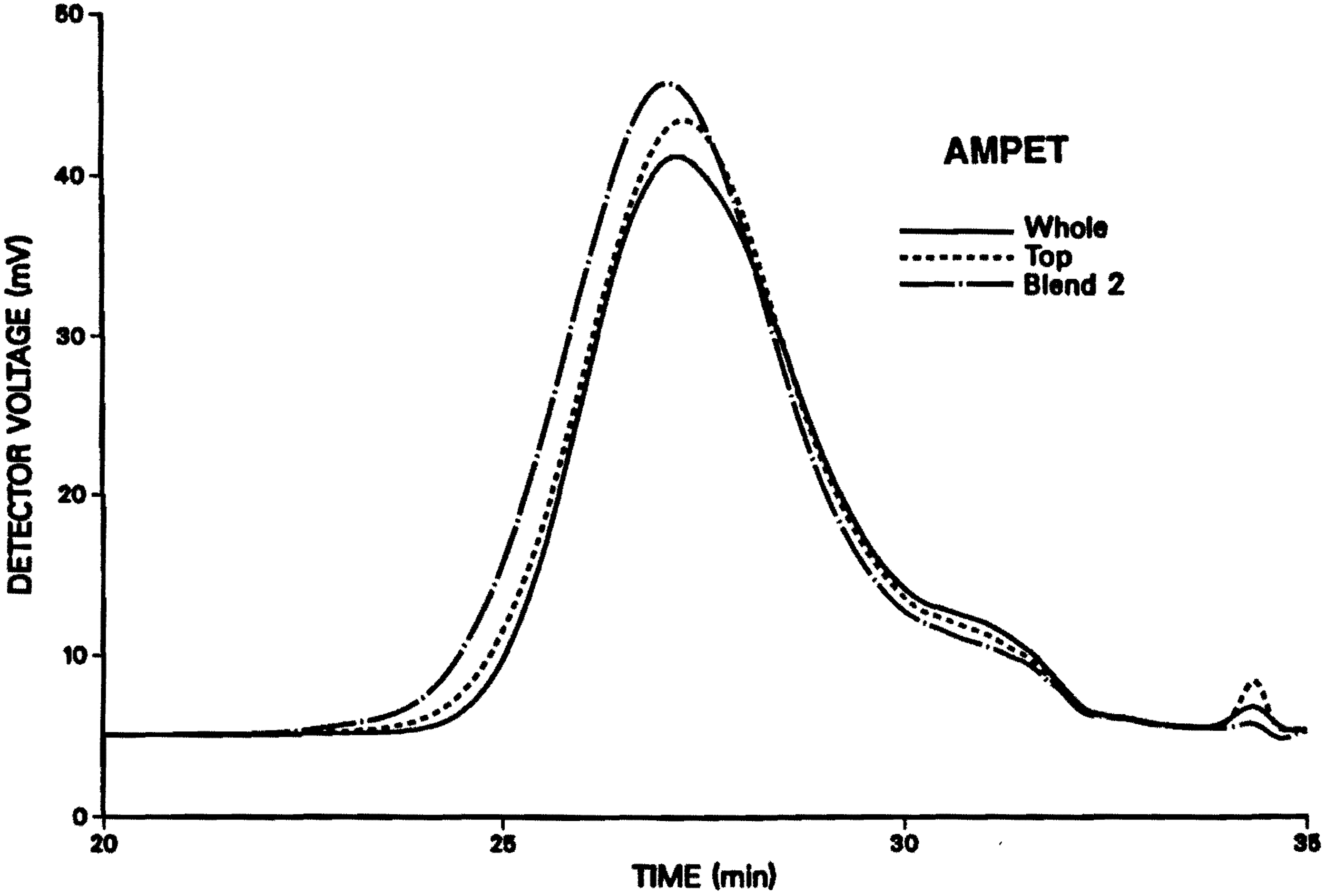

Figure B-9
GPC Chromatograms of Ampet Saturate Whole,
Top, and Blend 2

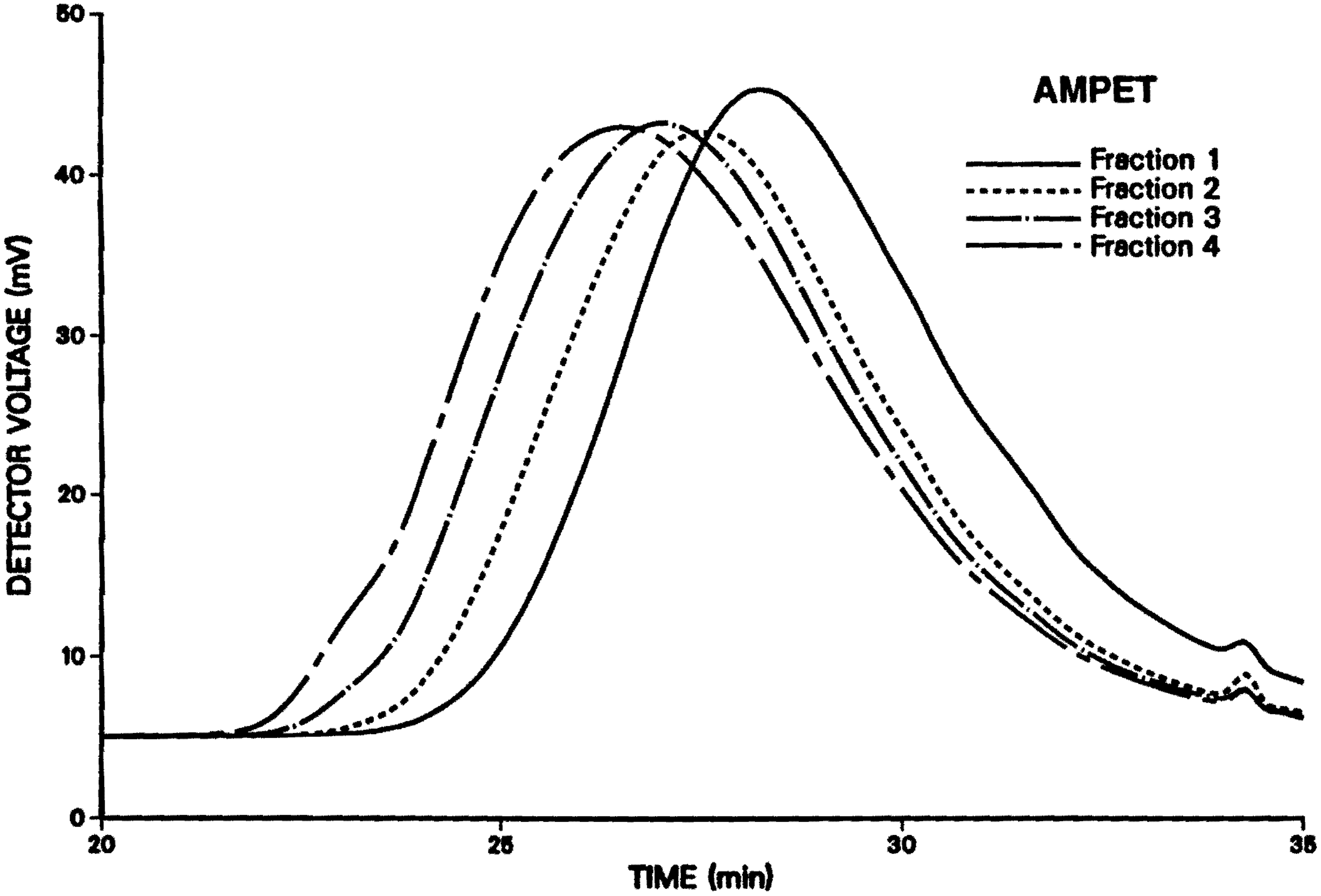

Figure B-10
GPC Chromatograms of Ampet
Naphthene Aromatic Fractions 1-4

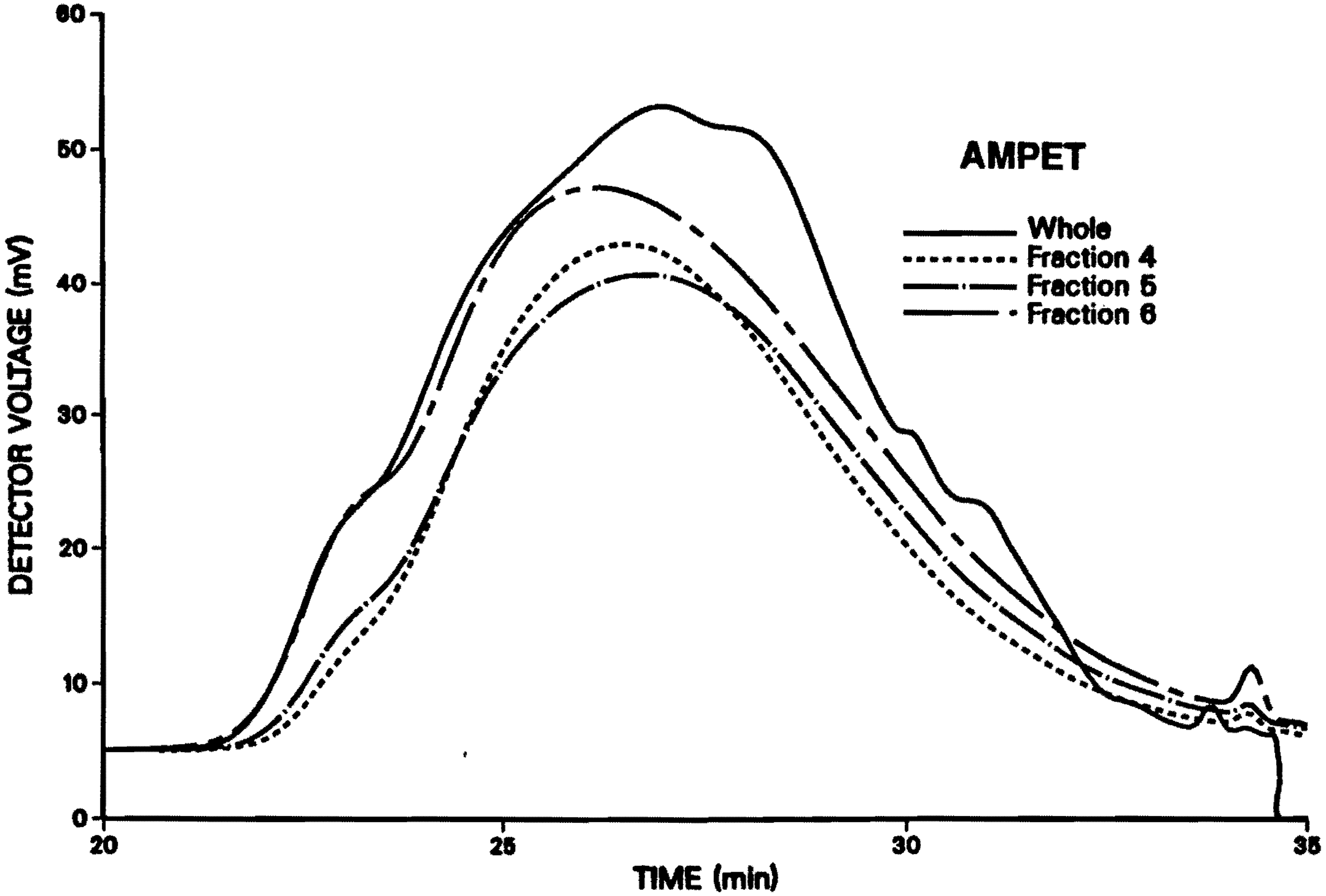

Figure B-11
GPC Chromatograms of Ampet
Naphthene Aromatic Whole and Fractions 4-6

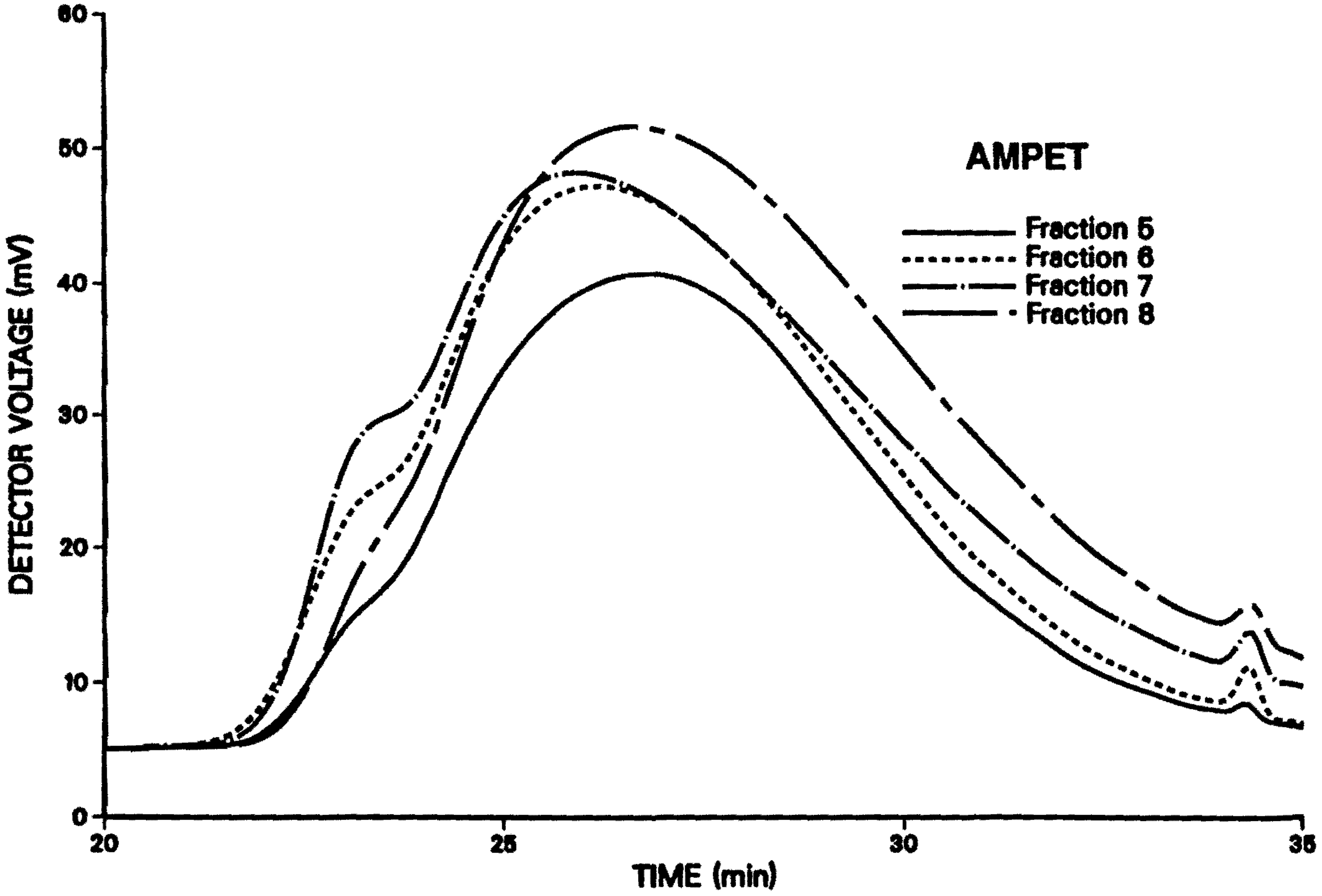

Figure B-12
GPC Chromatograms of Ampet
Naphthene Aromatic Fractions 5-8

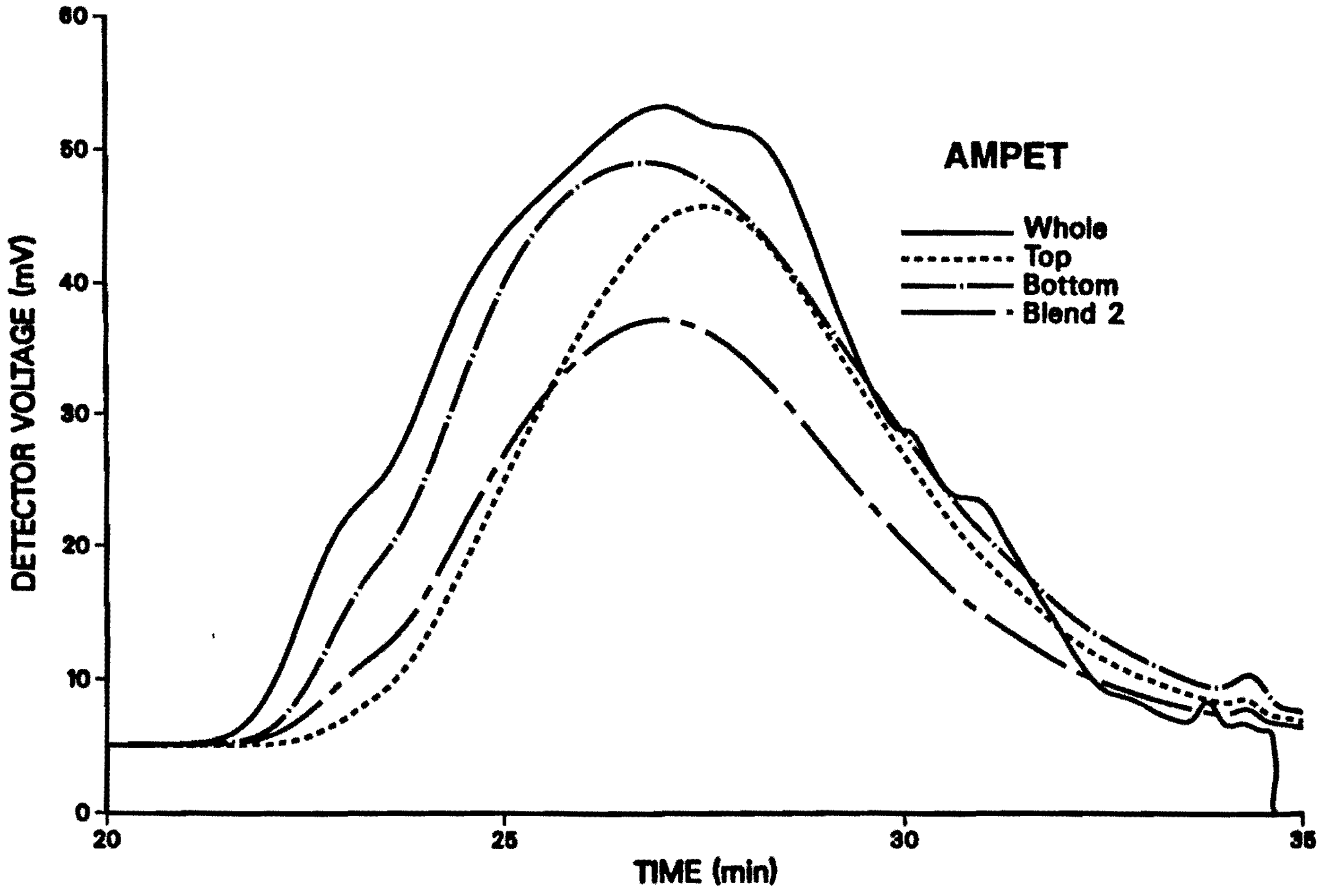

Figure B-13
GPC Chromatograms of Ampet Naphthene Aromatic
Whole, Top, Bottom, and Blend 2

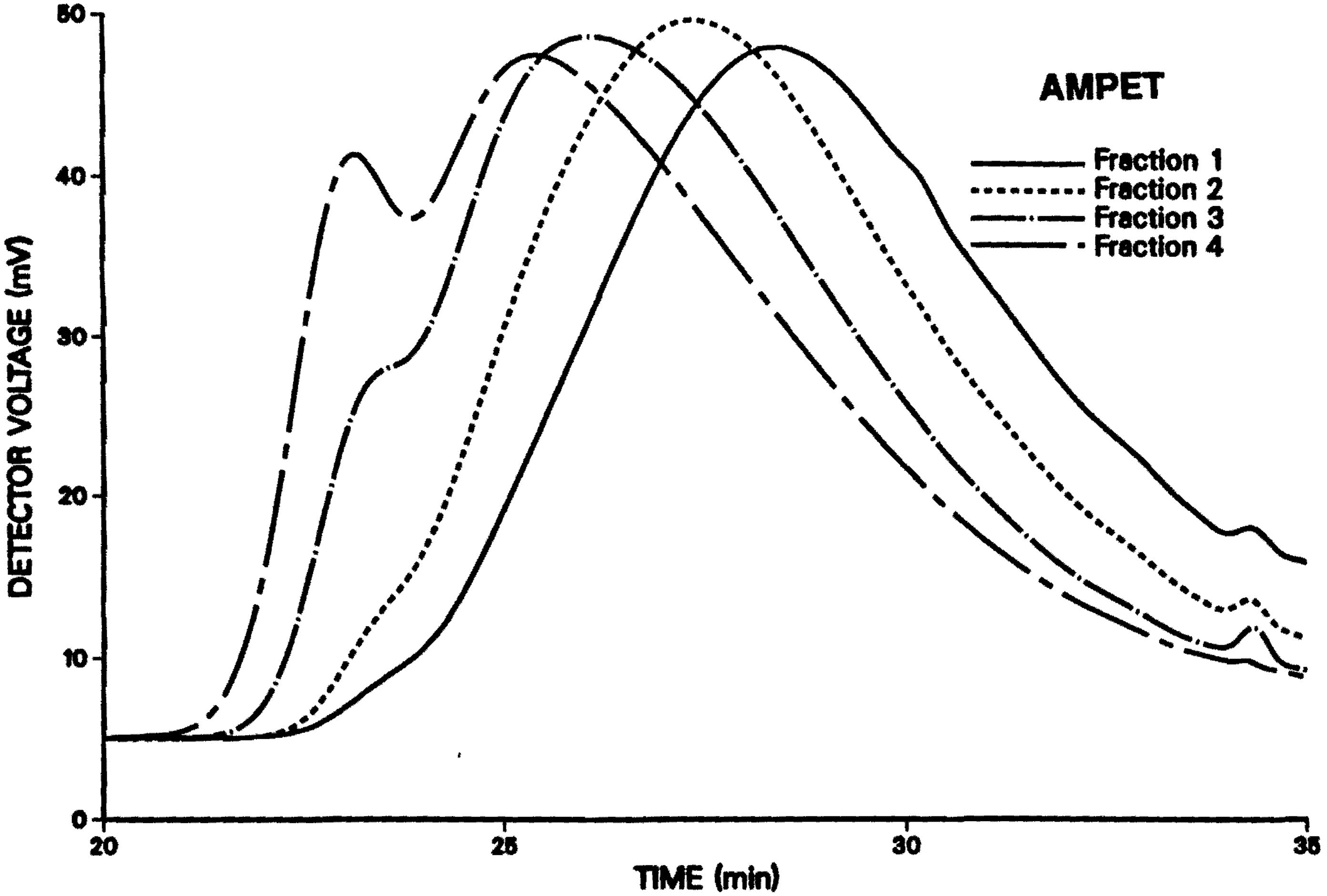

Figure B-14
GPC Chromatograms of Ampet
Polar Aromatic Fractions 1-4

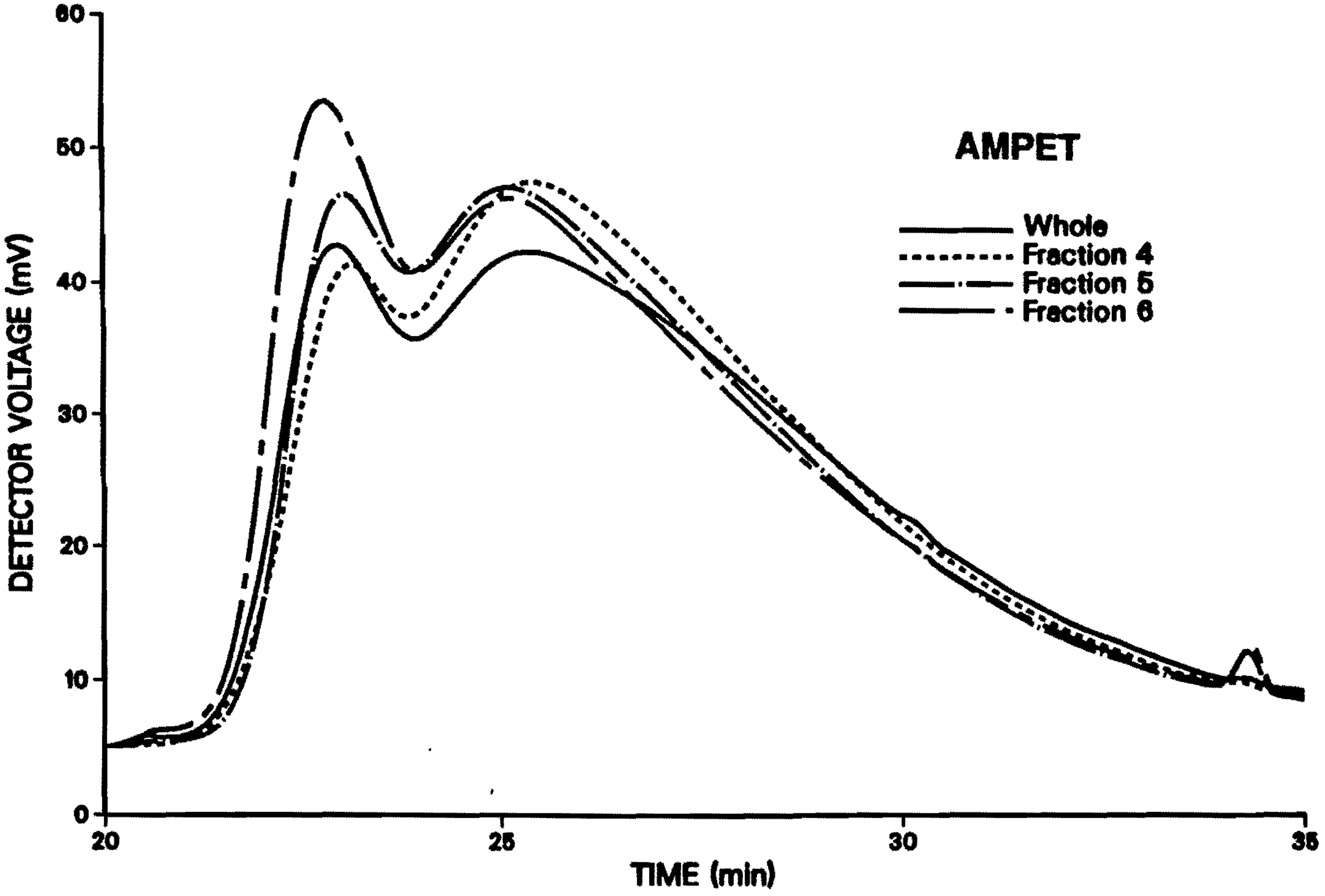

Figure B-15
GPC Chromatograms of Ampet Polar Aromatic
Whole and Fractions 4-6

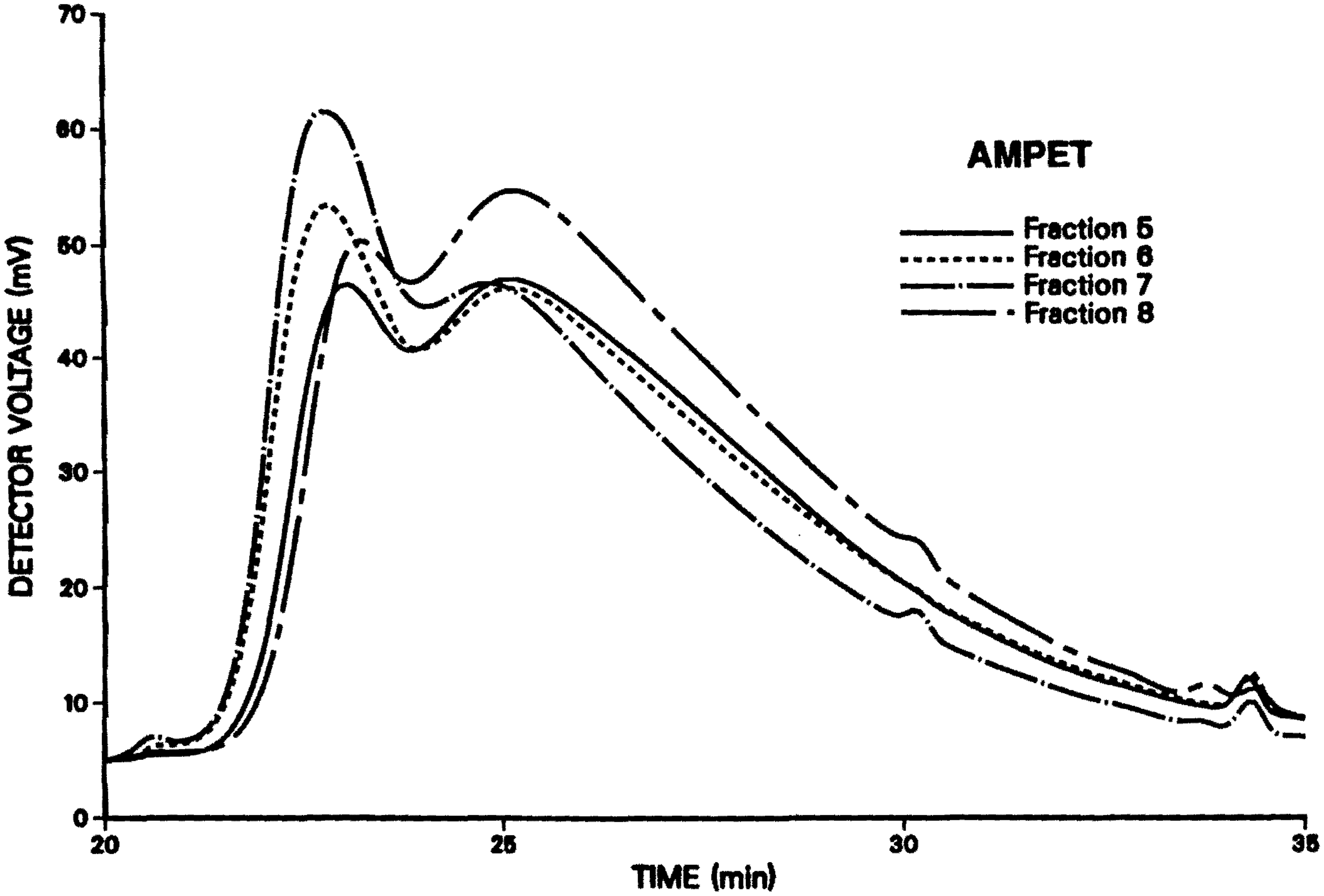

Figure B-16
GPC Chromatograms of Ampet
Polar Aromatic Fractions 5-8

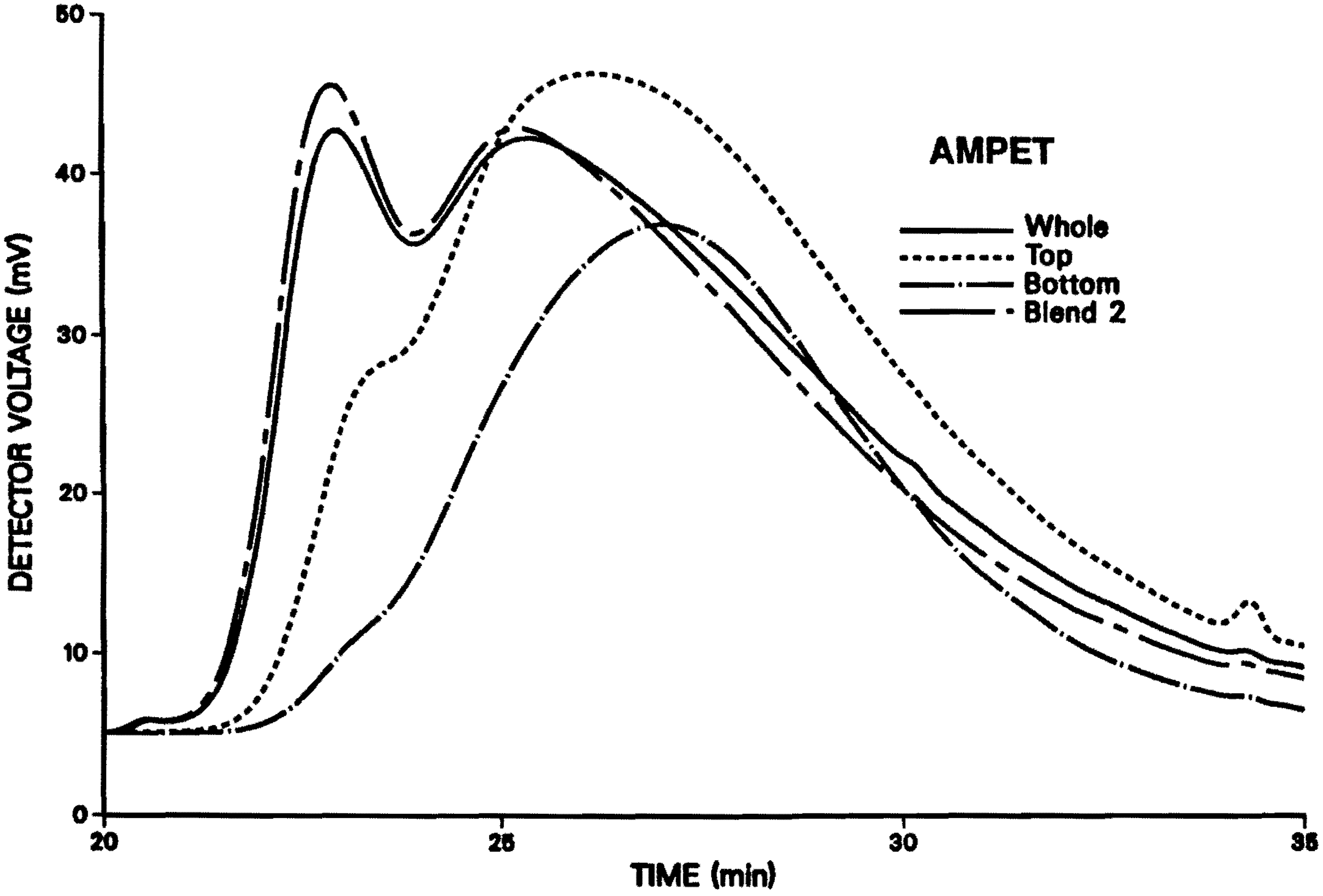

Figure B-17
GPC Chromatograms of Ampet Polar Aromatic
Whole, Top, Bottom, and Blend 2

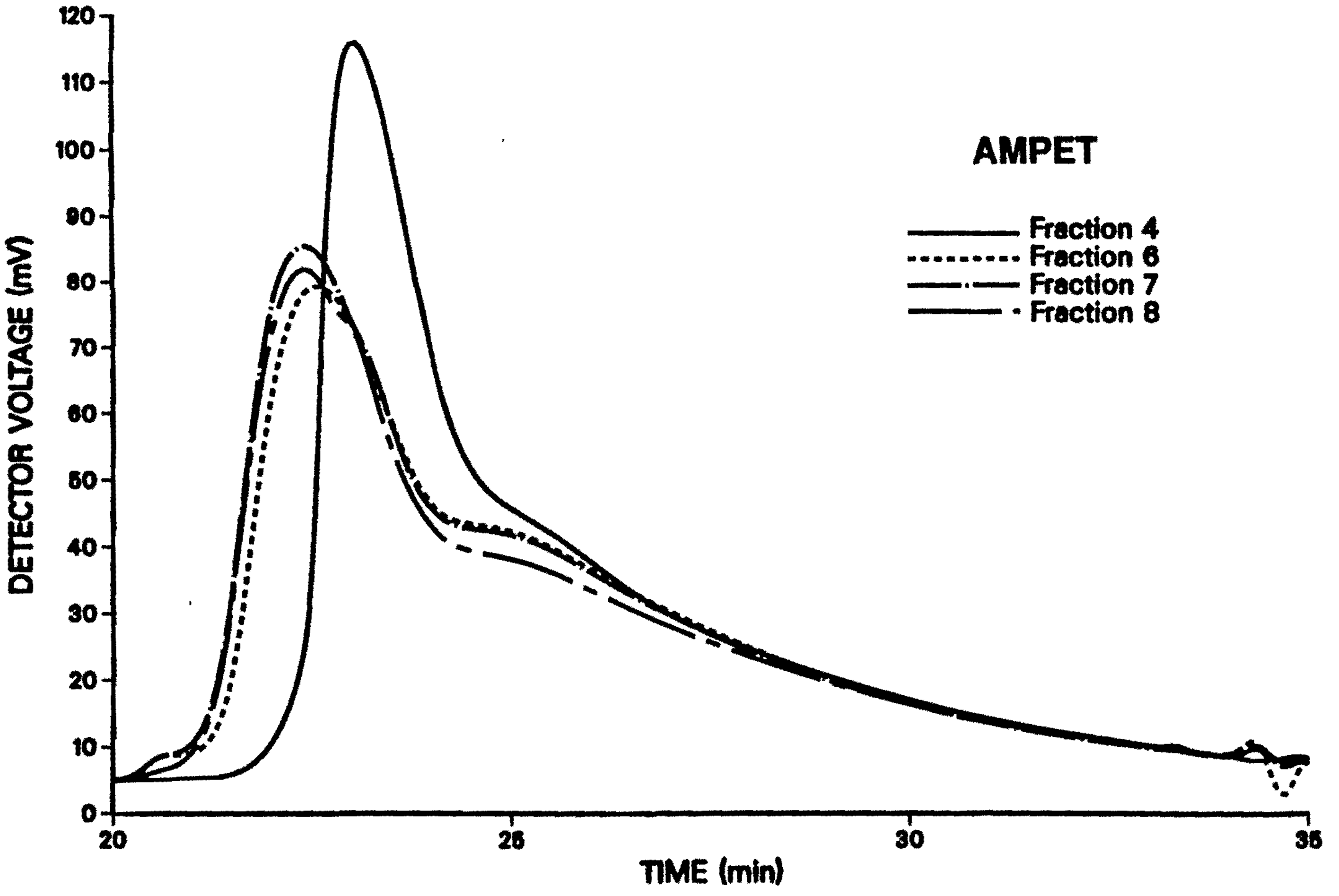

Figure B-18
GPC Chromatograms of Ampet
Asphaltene Fractions 4 and 6-8

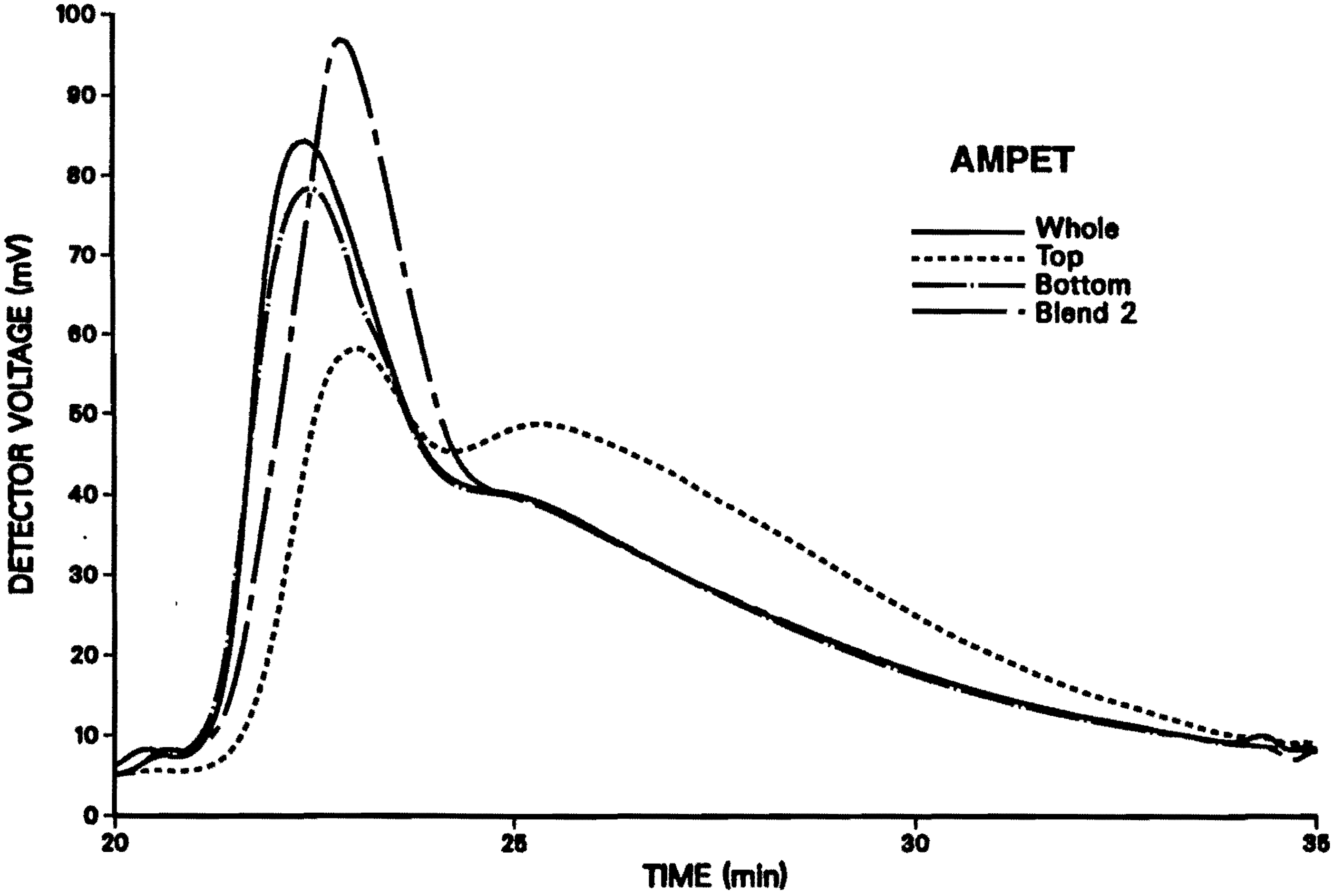

Figure B-19
GPC Chromatograms of Ampet Asphaltene
Whole, Top, Bottom, and Blend 2

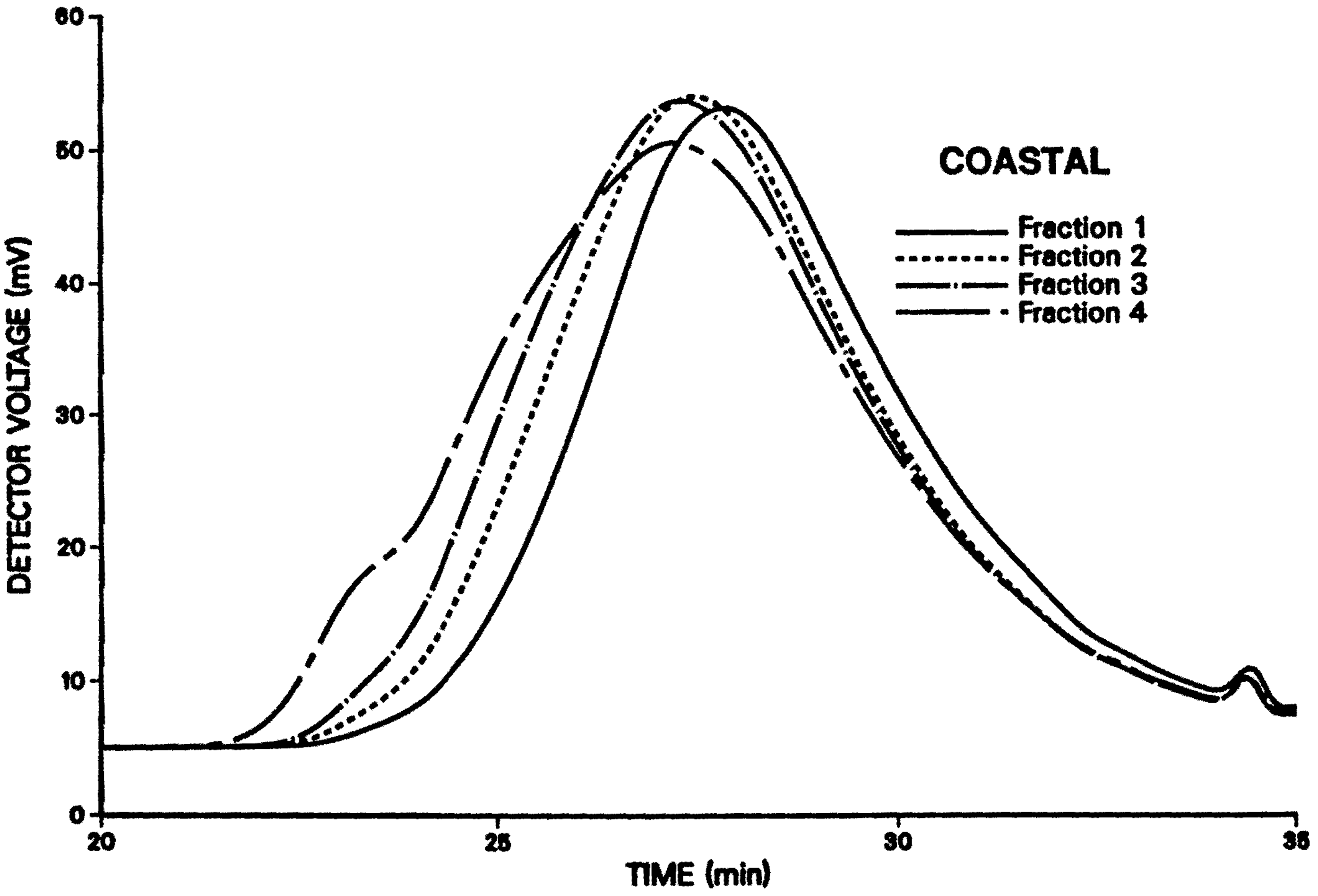

Figure B-20
GPC Chromatograms of Coastal Fractions 1-4

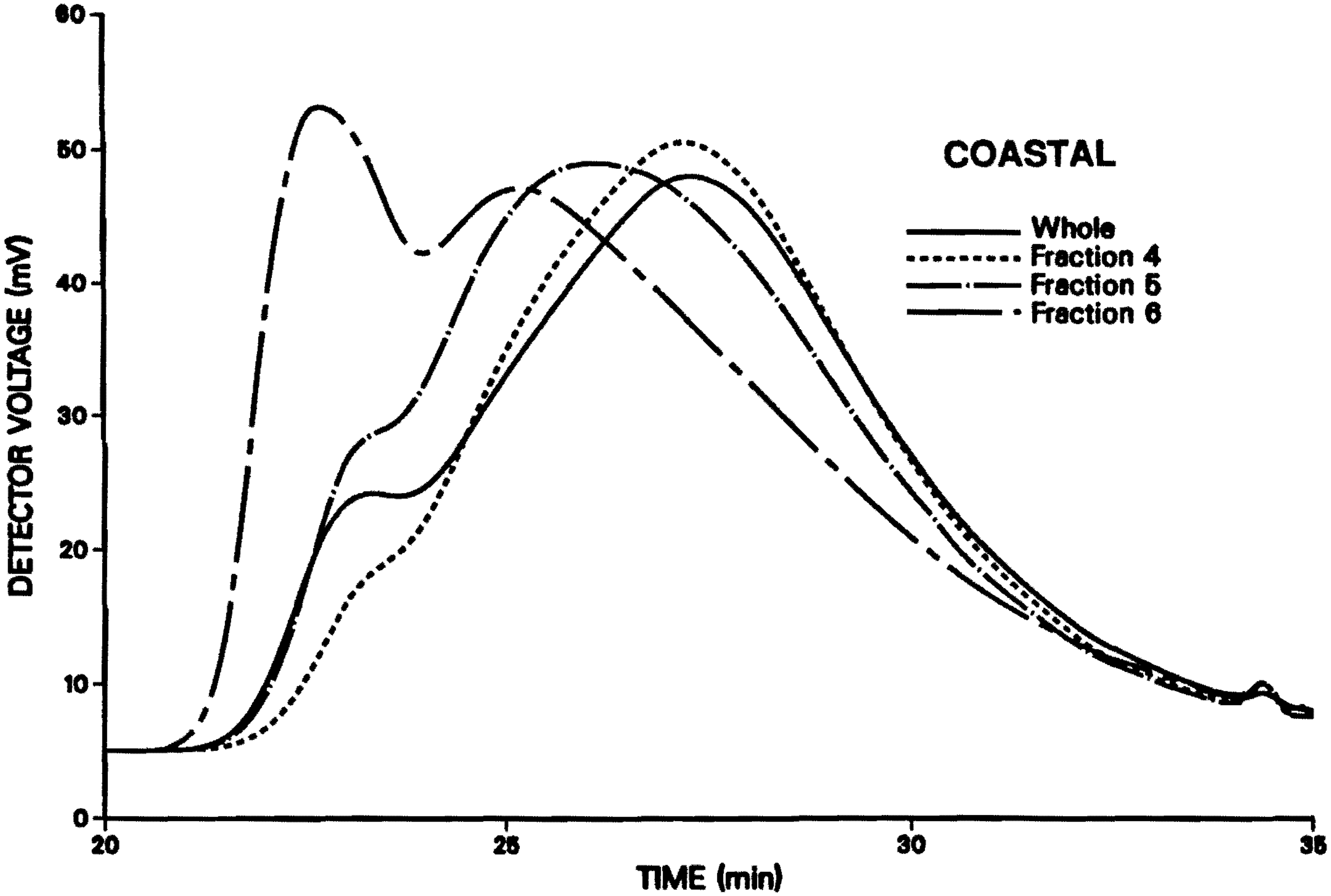

Figure B-21
GPC Chromatograms of Coastal Whole and Fractions 4-6

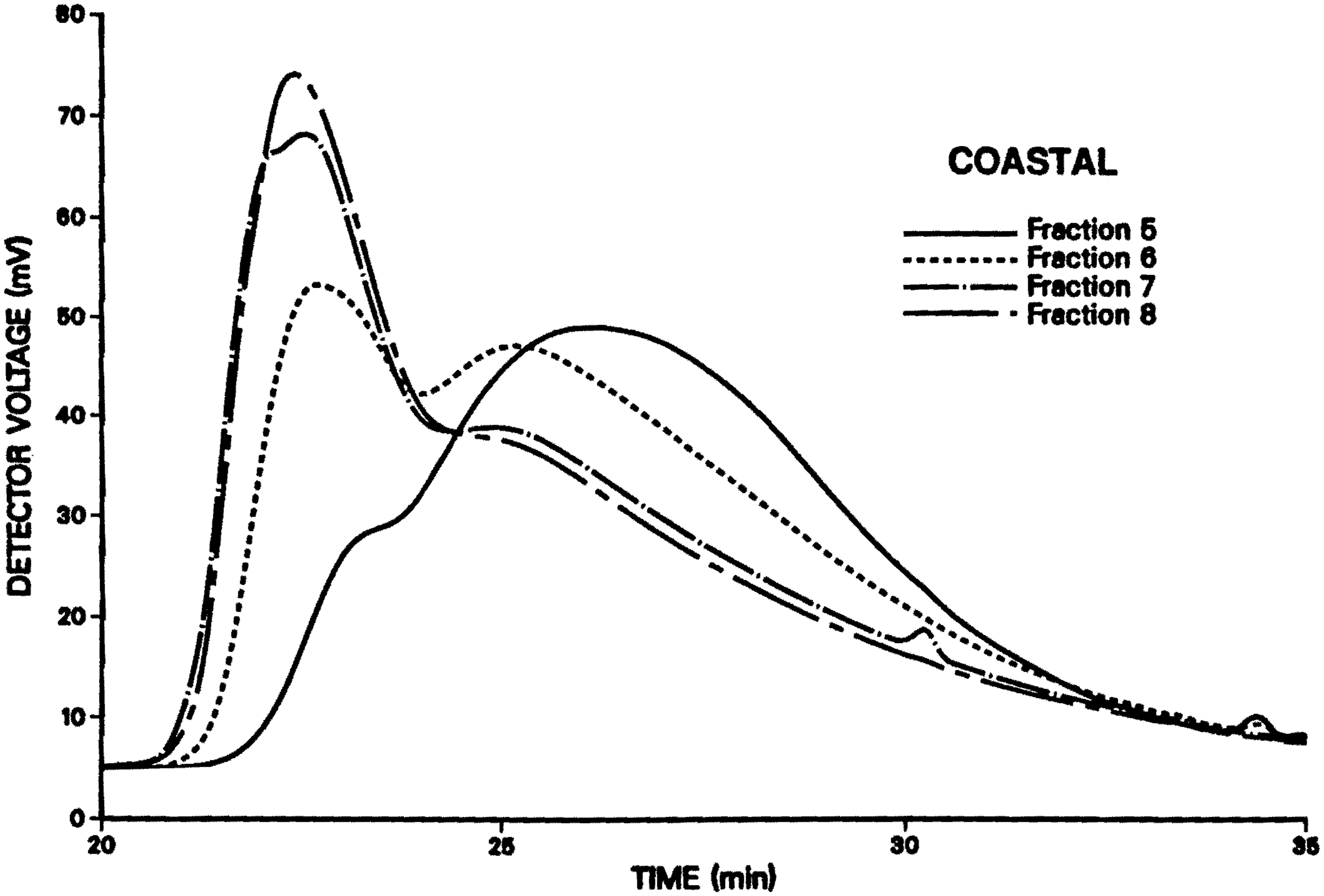

Figure B-22
GPC Chromatograms of Coastal Fractions 5-8

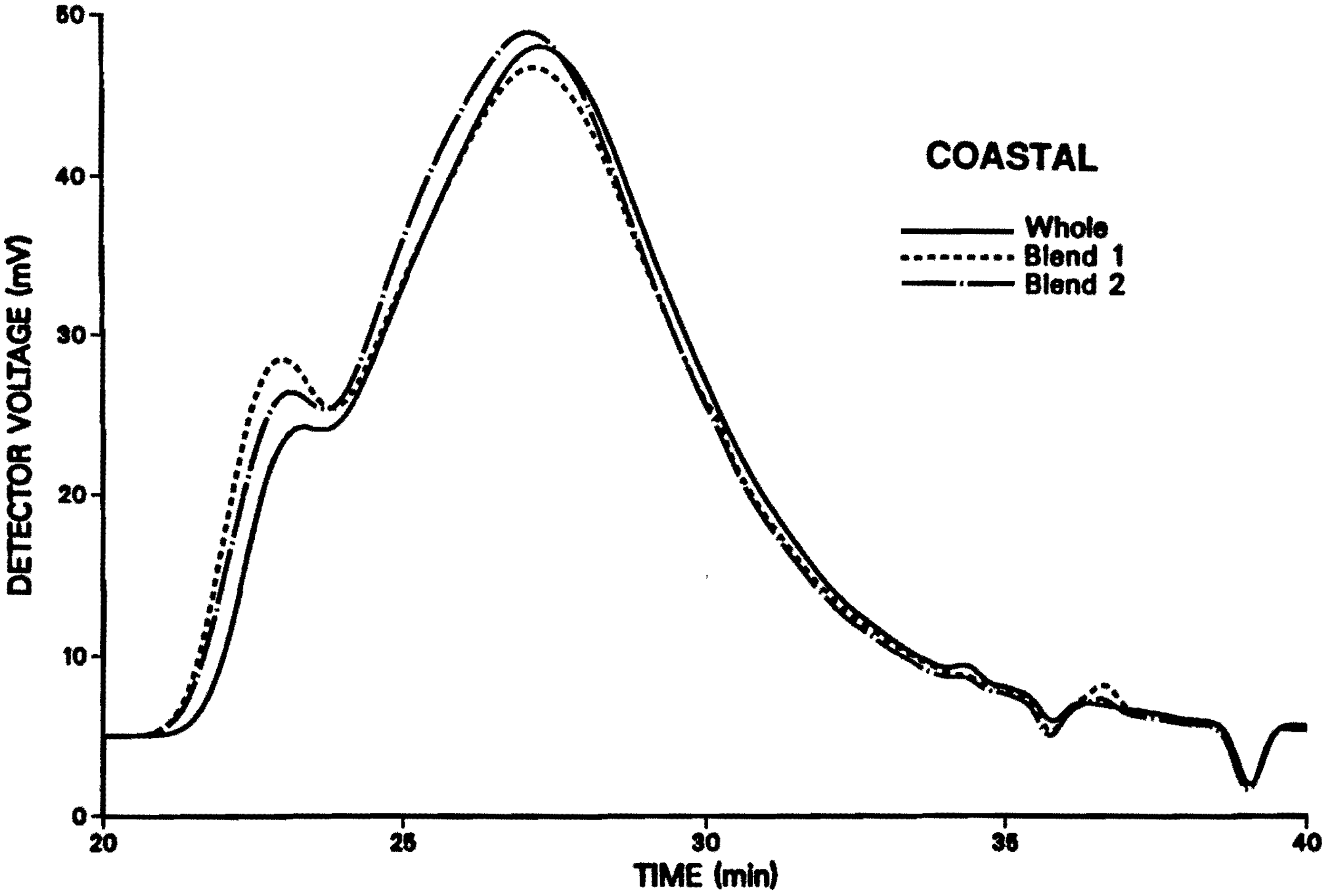

Figure B-23
GPC Chromatograms of Coastal Whole and Blends 1 and 2

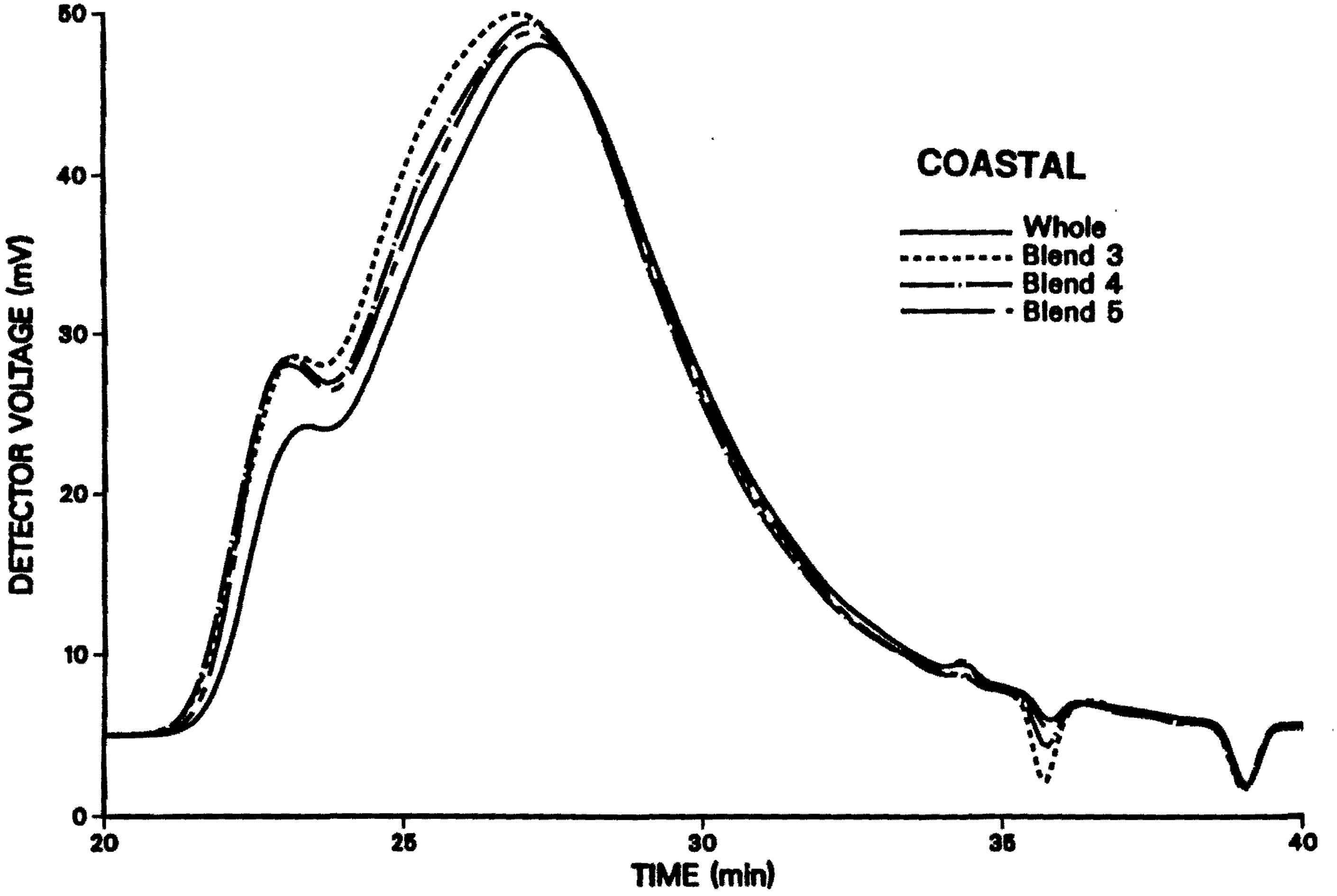

Figure B-24
GPC Chromatograms of Coastal Whole and Blends 3-5

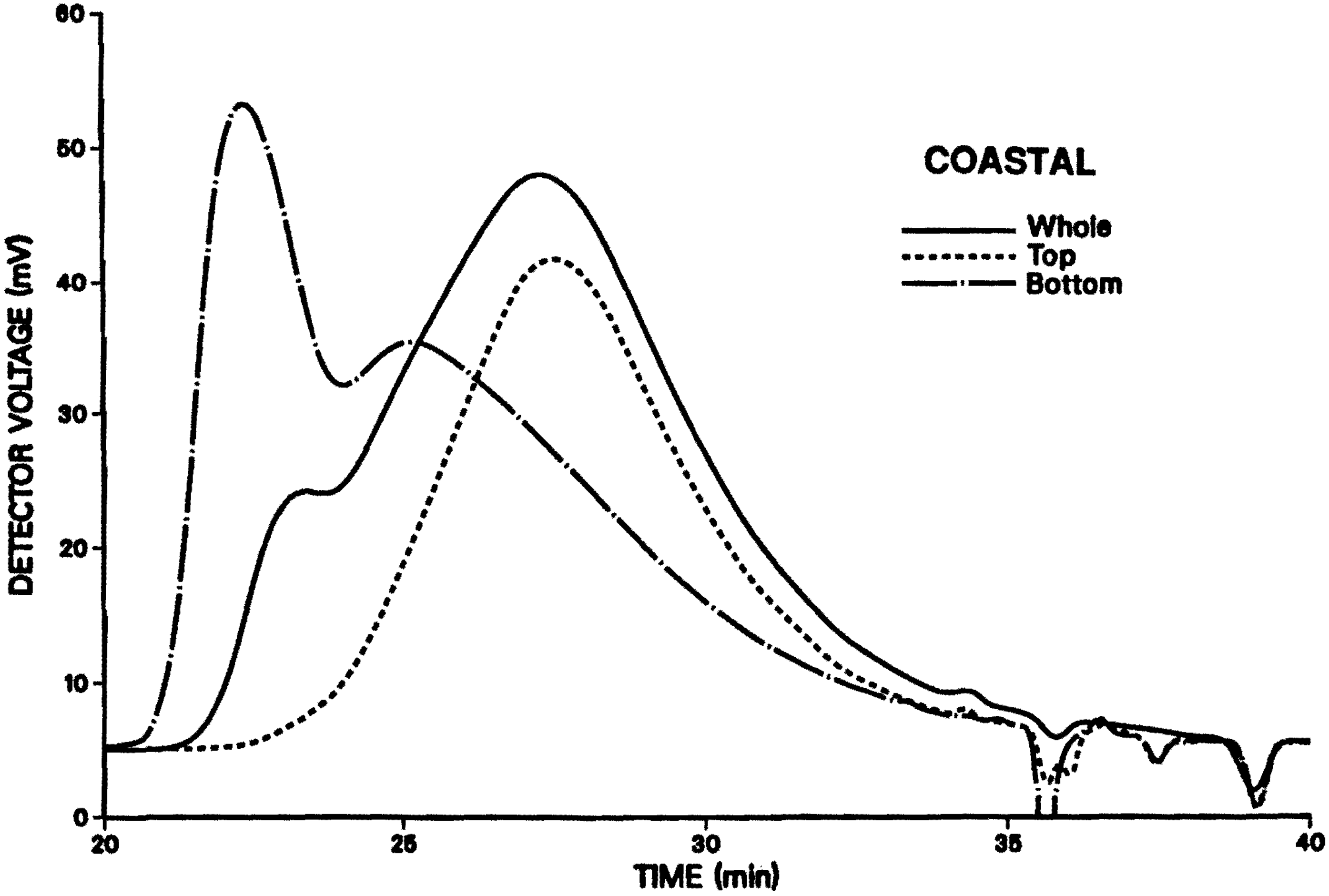

Figure B-25
GPC Chromatograms of Coastal Whole, Top, and Bottom

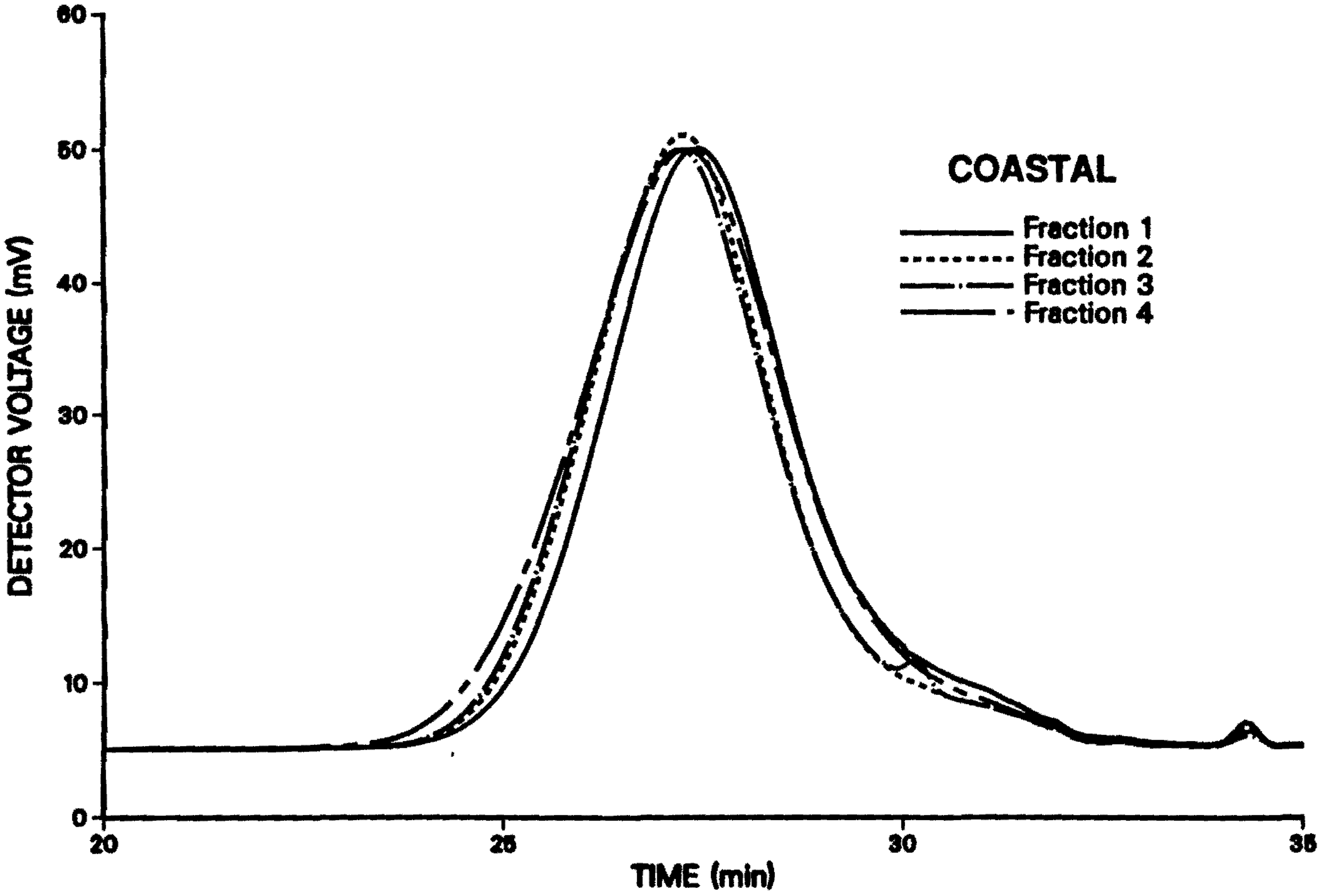

Figure B-26
GPC Chromatograms of Coastal Saturate Fractions 1-4

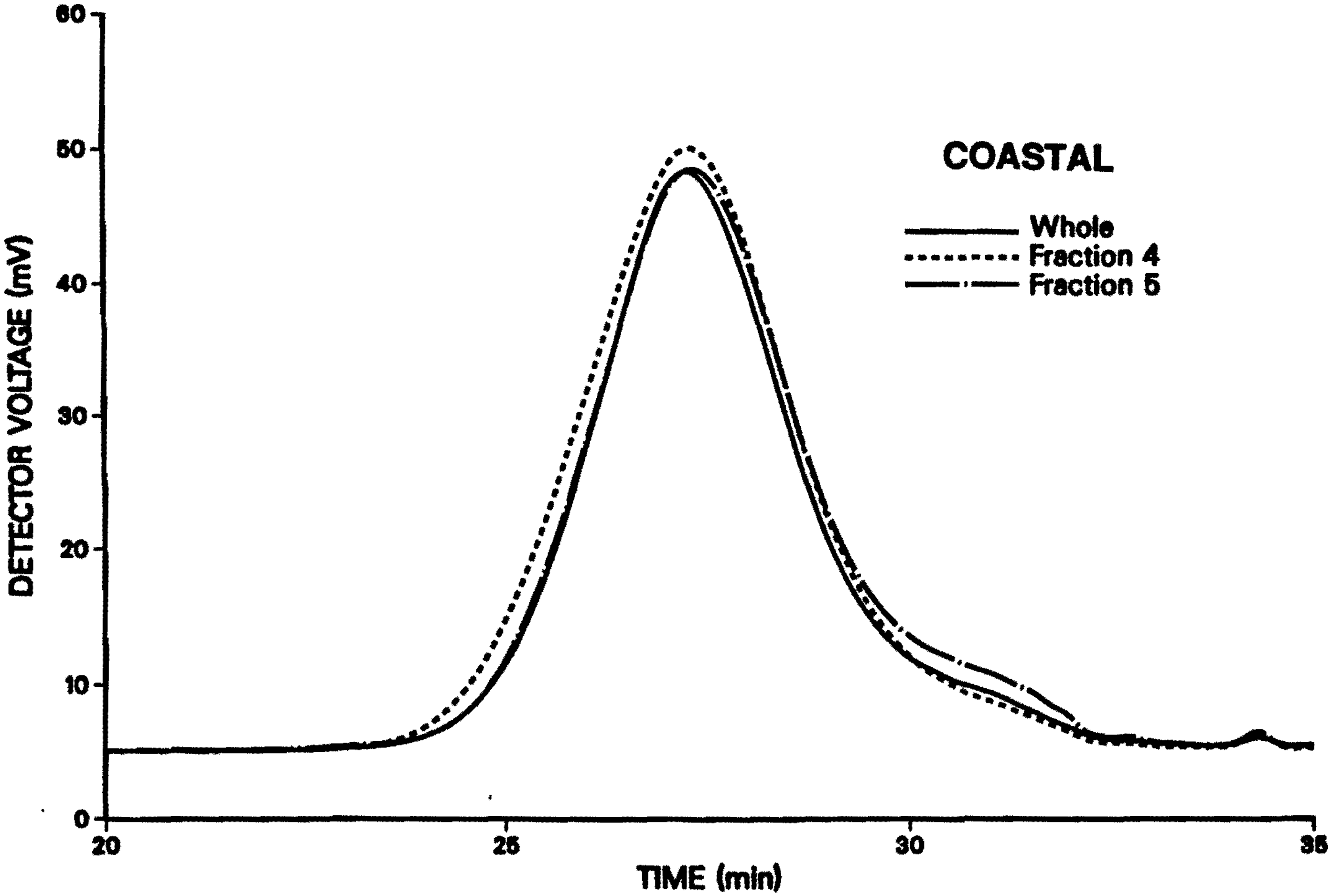

Figure B-27
GPC Chromatograms of Coastal Saturate
Whole and Fractions 4 and 5

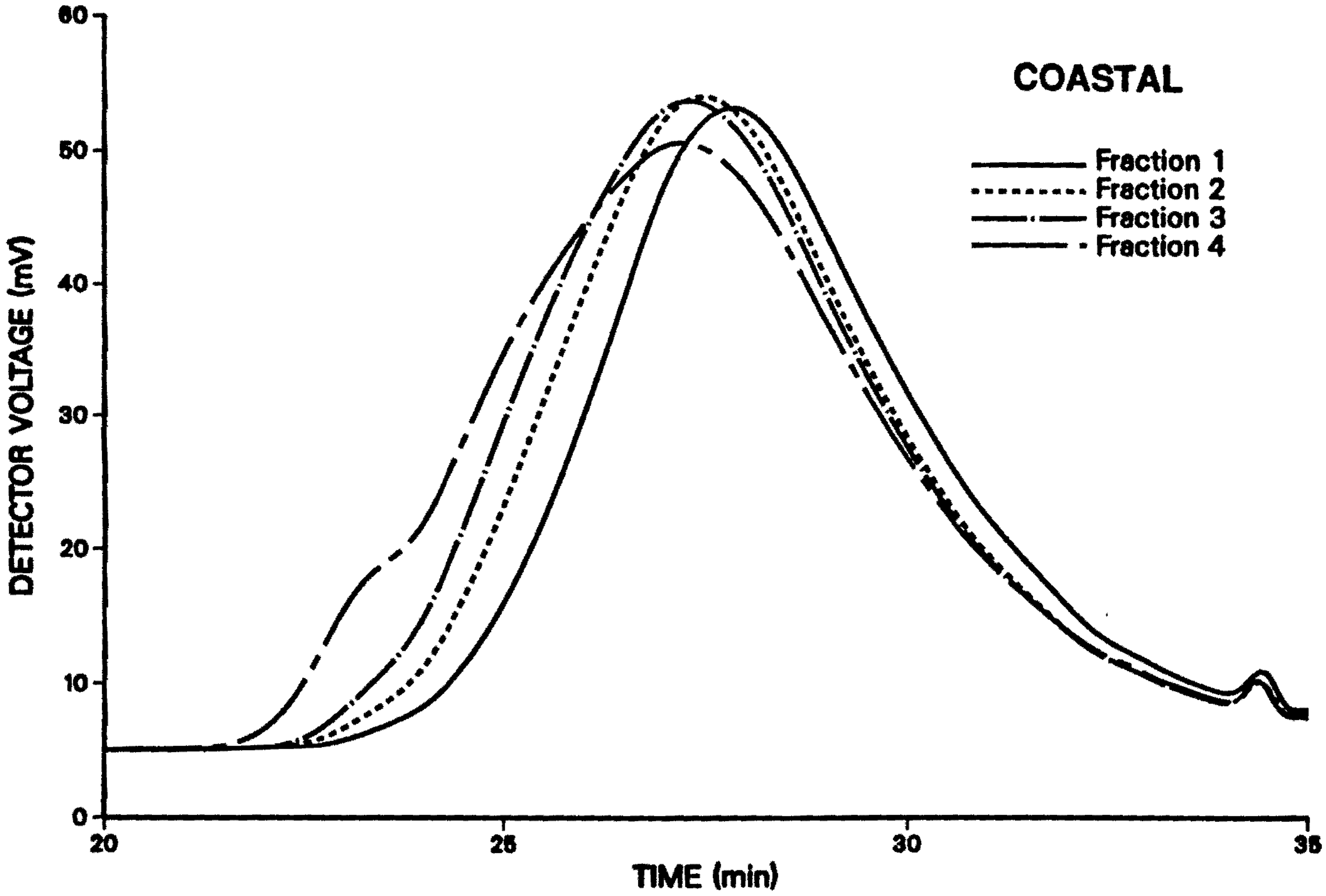

Figure B-28
GPC Chromatograms of Coastal
Naphthene Aromatic Fractions 1-4

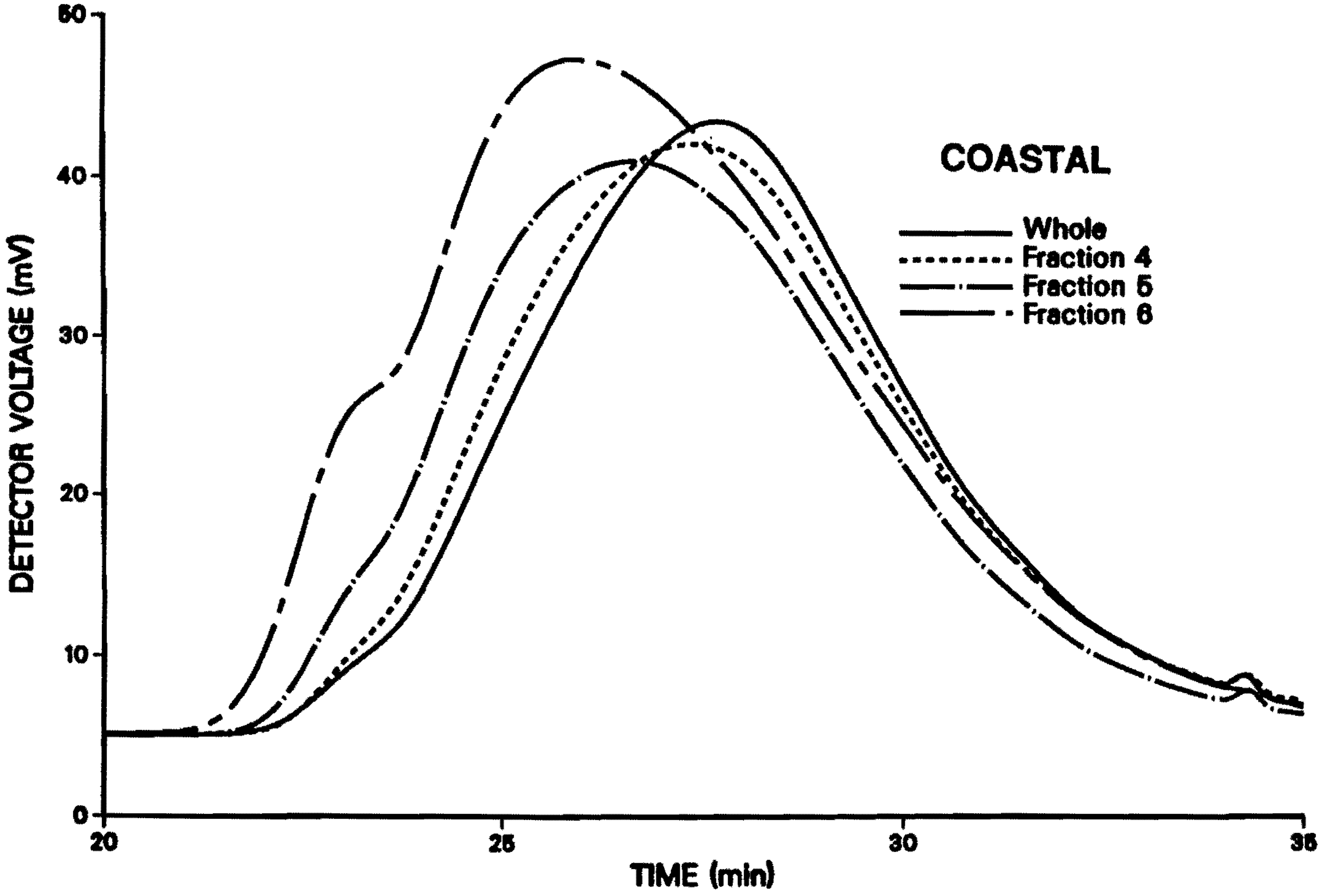

Figure B-29
GPC Chromatograms of Coastal Naphthene Aromatic
Whole and Fractions 4-6

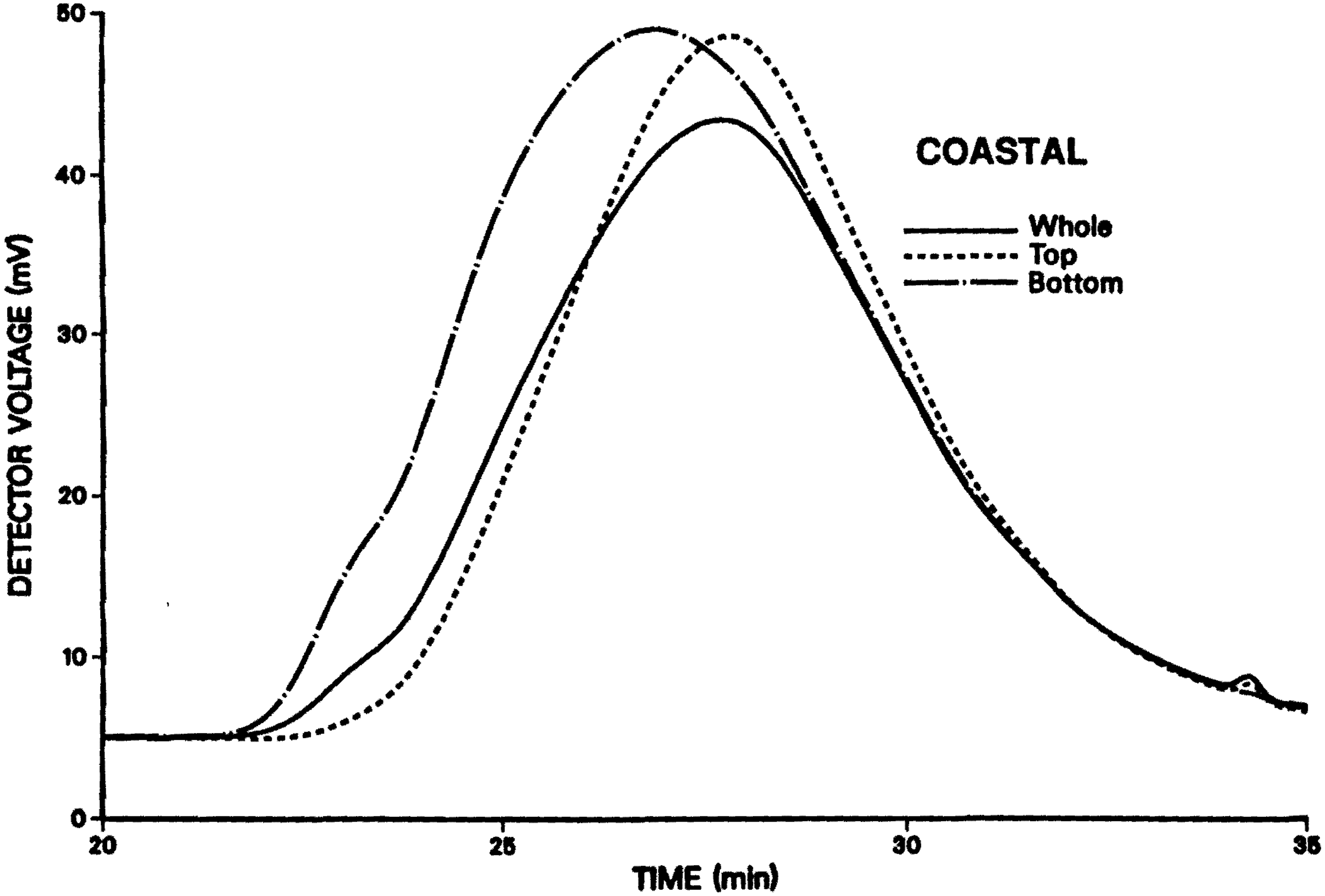

Figure B-30
GPC Chromatograms of Coastal Naphthene Aromatic
Whole, Top, and Bottom

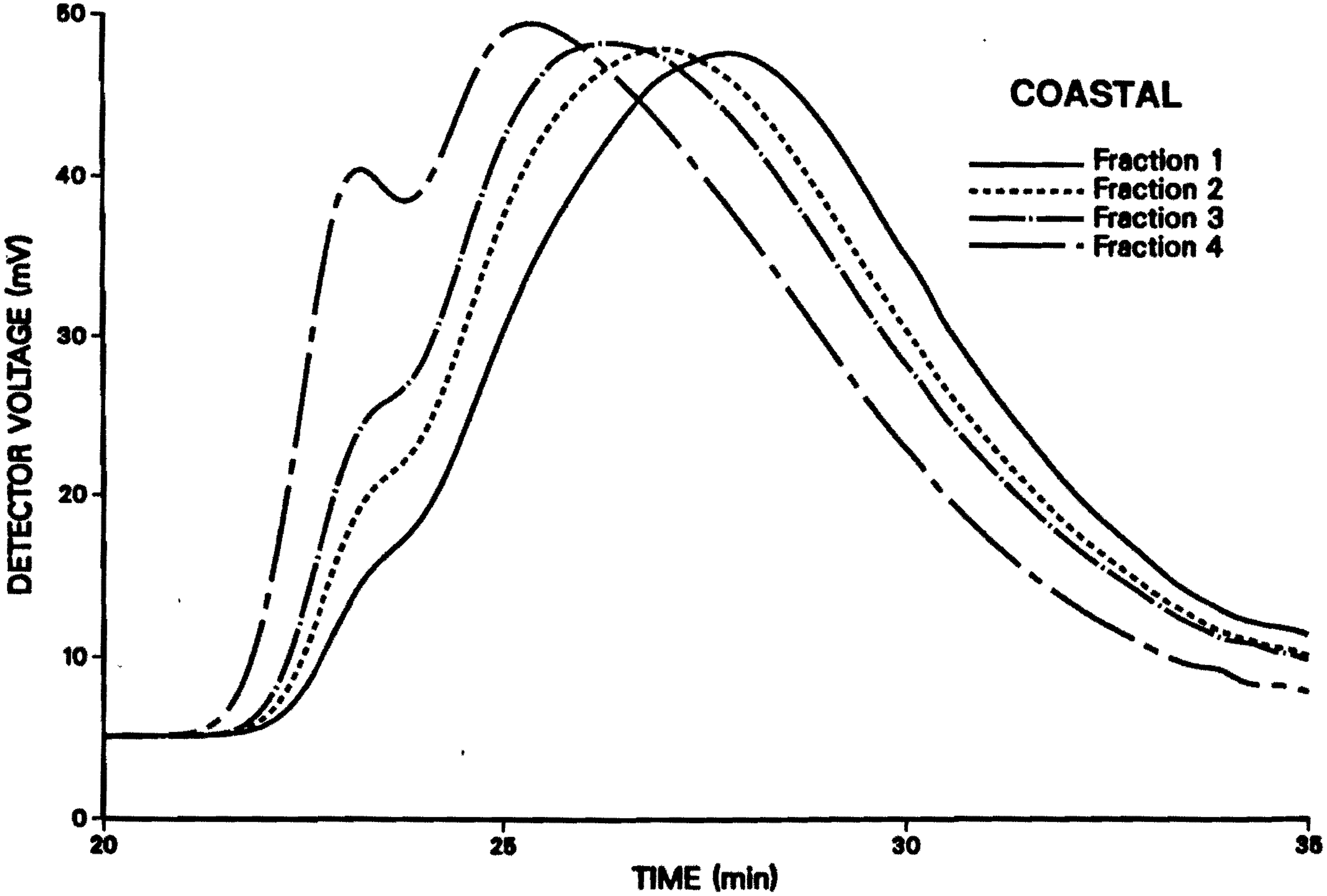

Figure B-31
GPC Chromatograms of Coastal Polar Aromatic Fractions 1-4

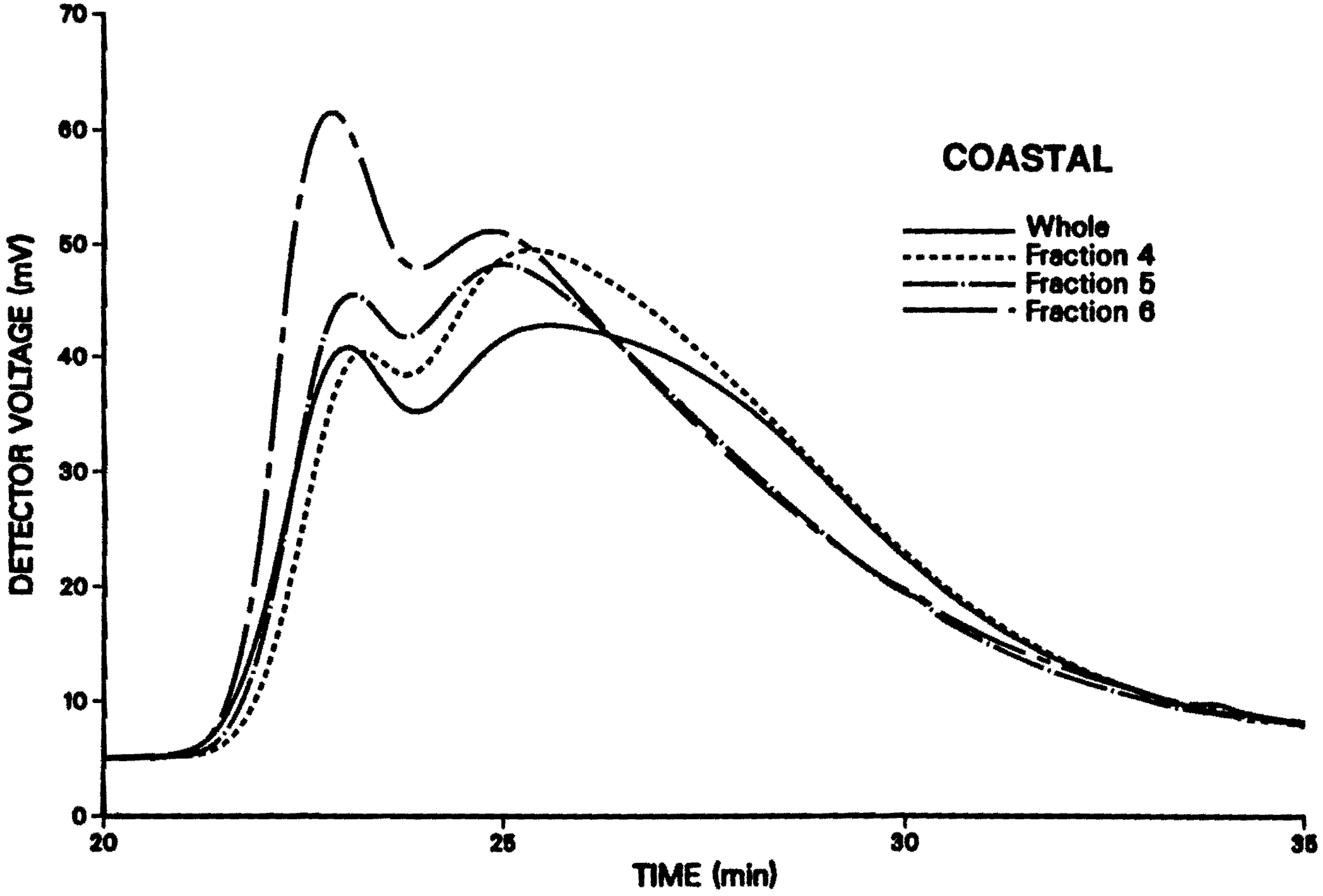

Figure B-32
GPC Chromatograms of Coastal
Polar Aromatic Whole and Fractions 4-6

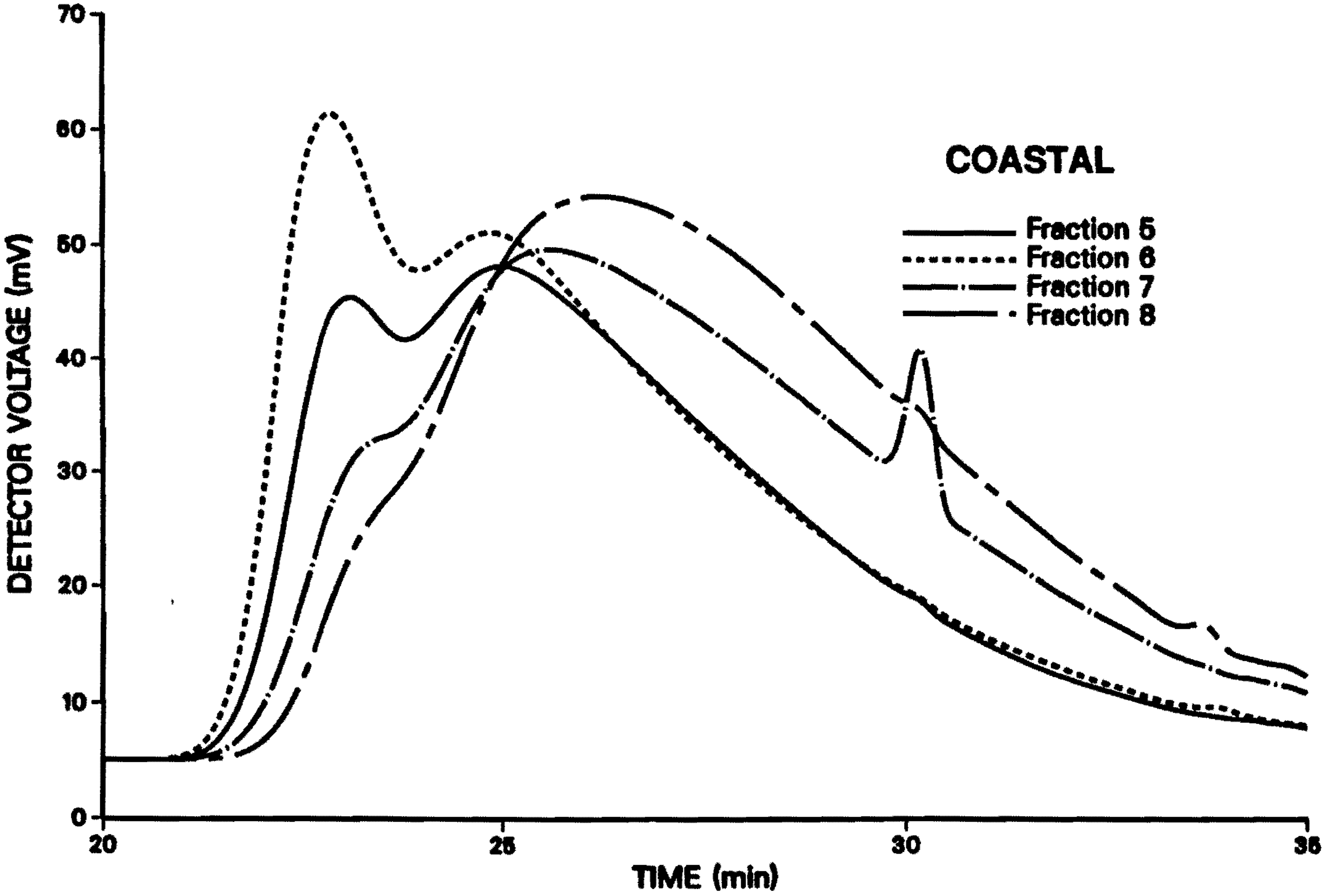

Figure B-33
GPC Chromatograms of Coastal Polar Aromatic Fractions 5-8

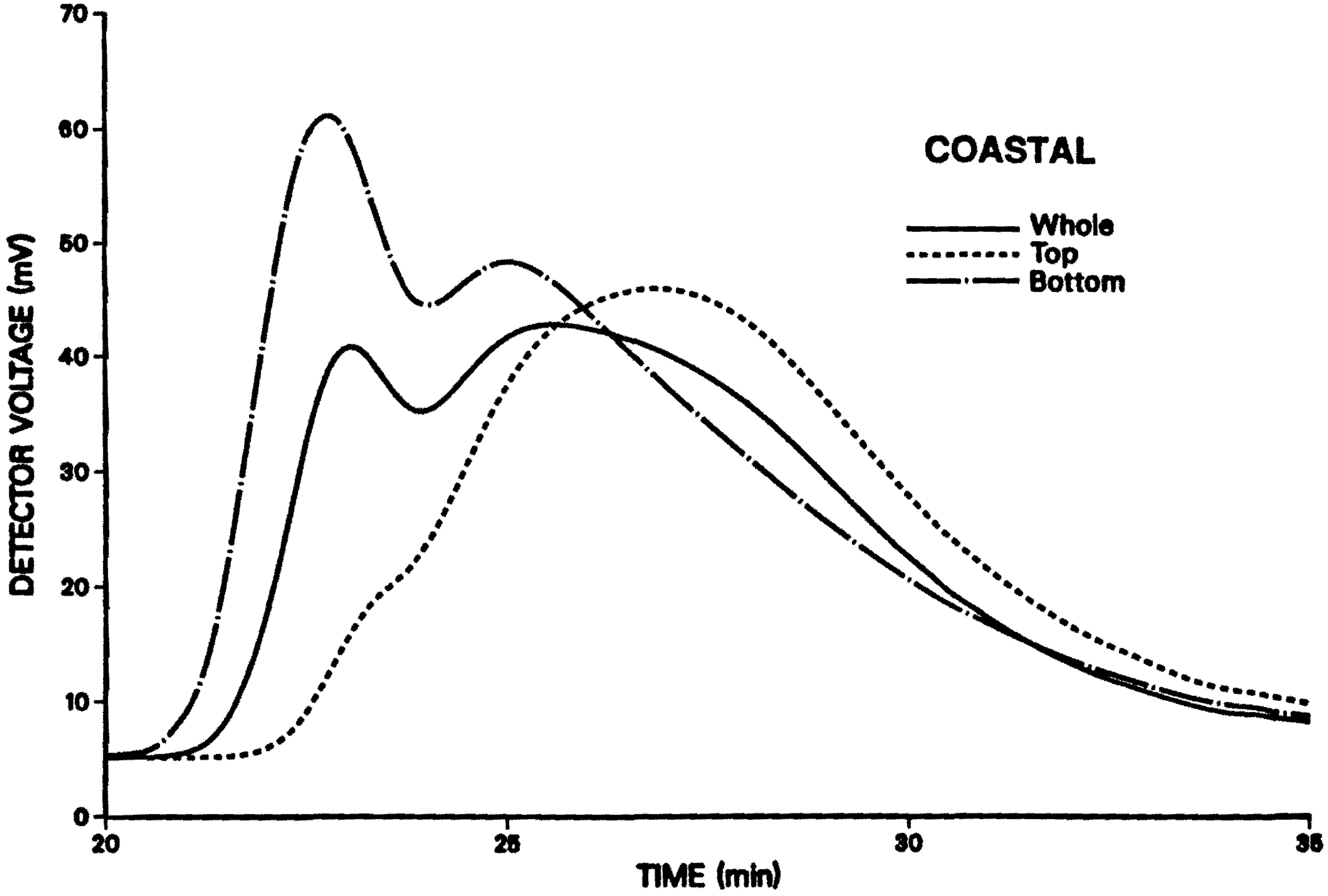

Figure B-34
GPC Chromatograms of Coastal Polar Aromatic
Whole, Top, and Bottom

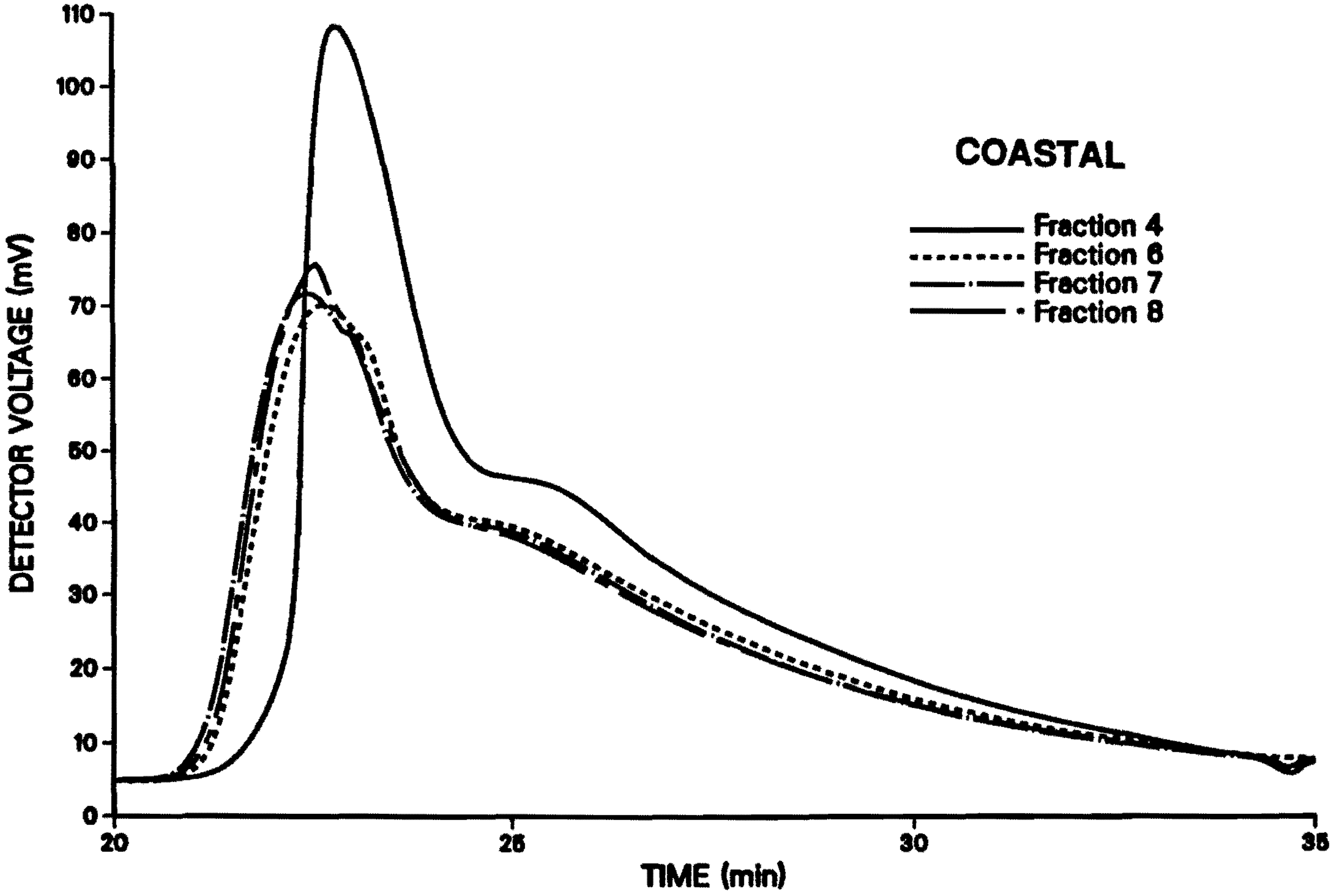

Figure B-35
GPC Chromatograms of Coastal
Asphaltene Fractions 4 and 6-8

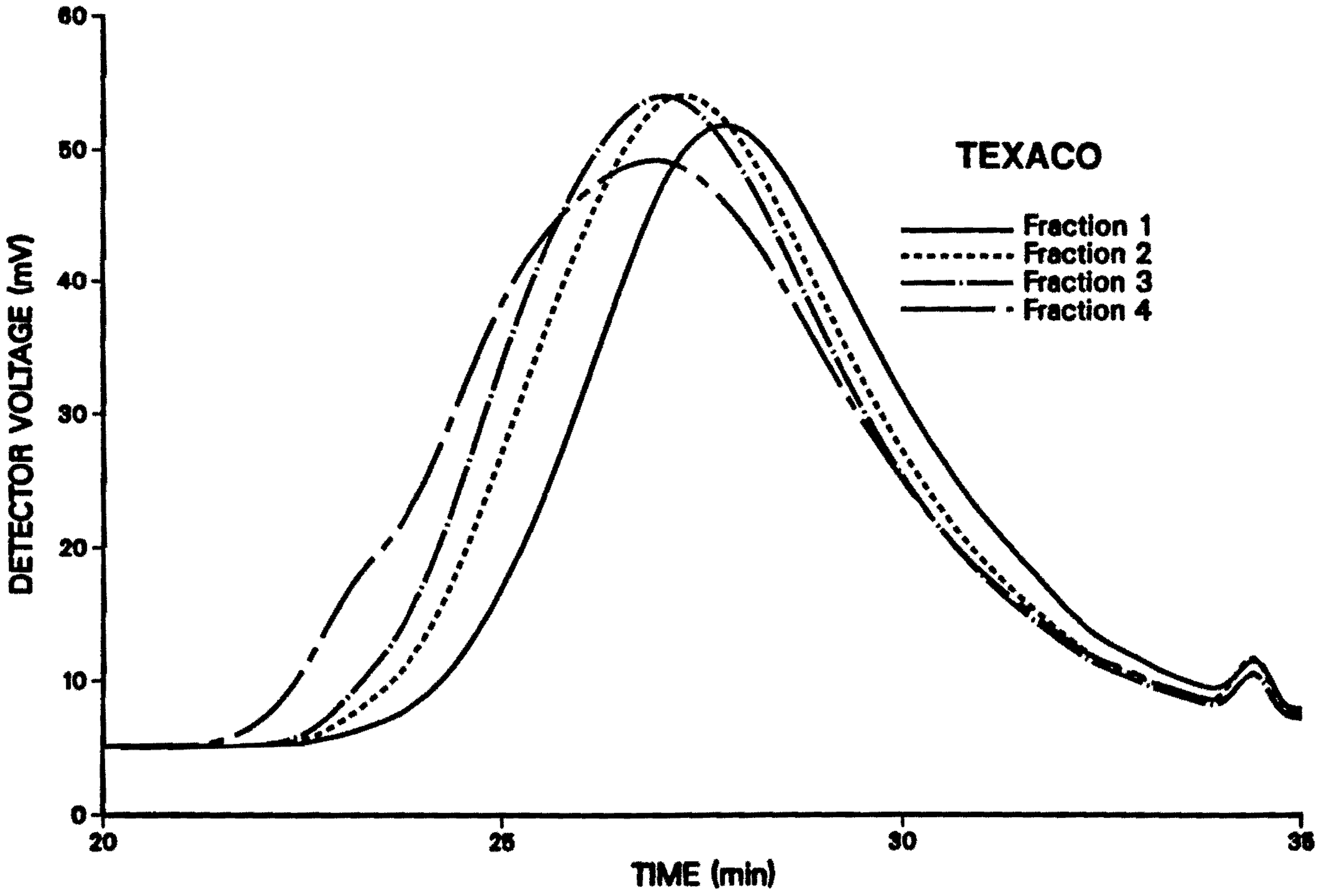

Figure B-36
GPC Chromatograms of Texaco Fractions 1-4

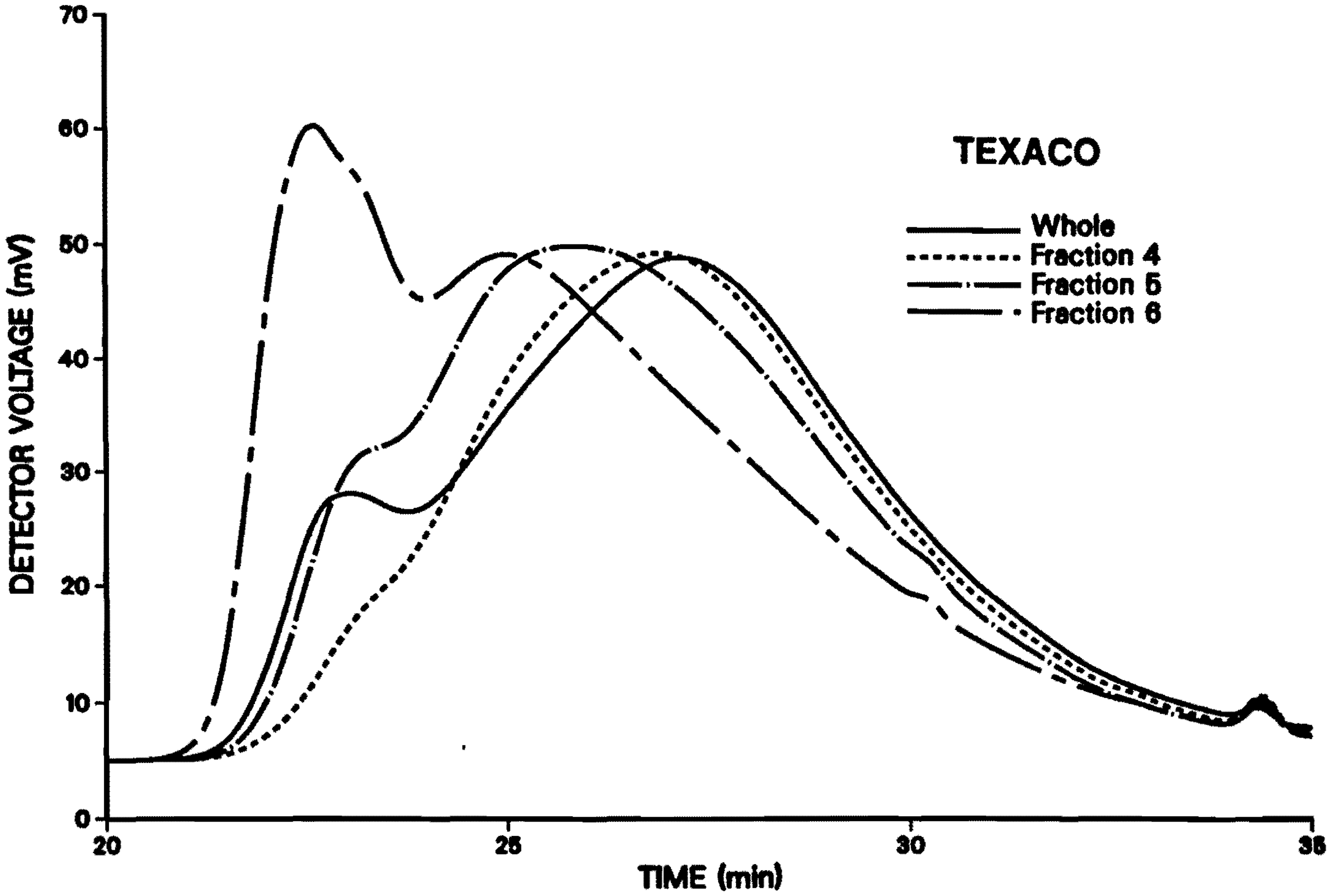

Figure B-37
GPC Chromatograms of Texaco Whole and Fractions 4-6

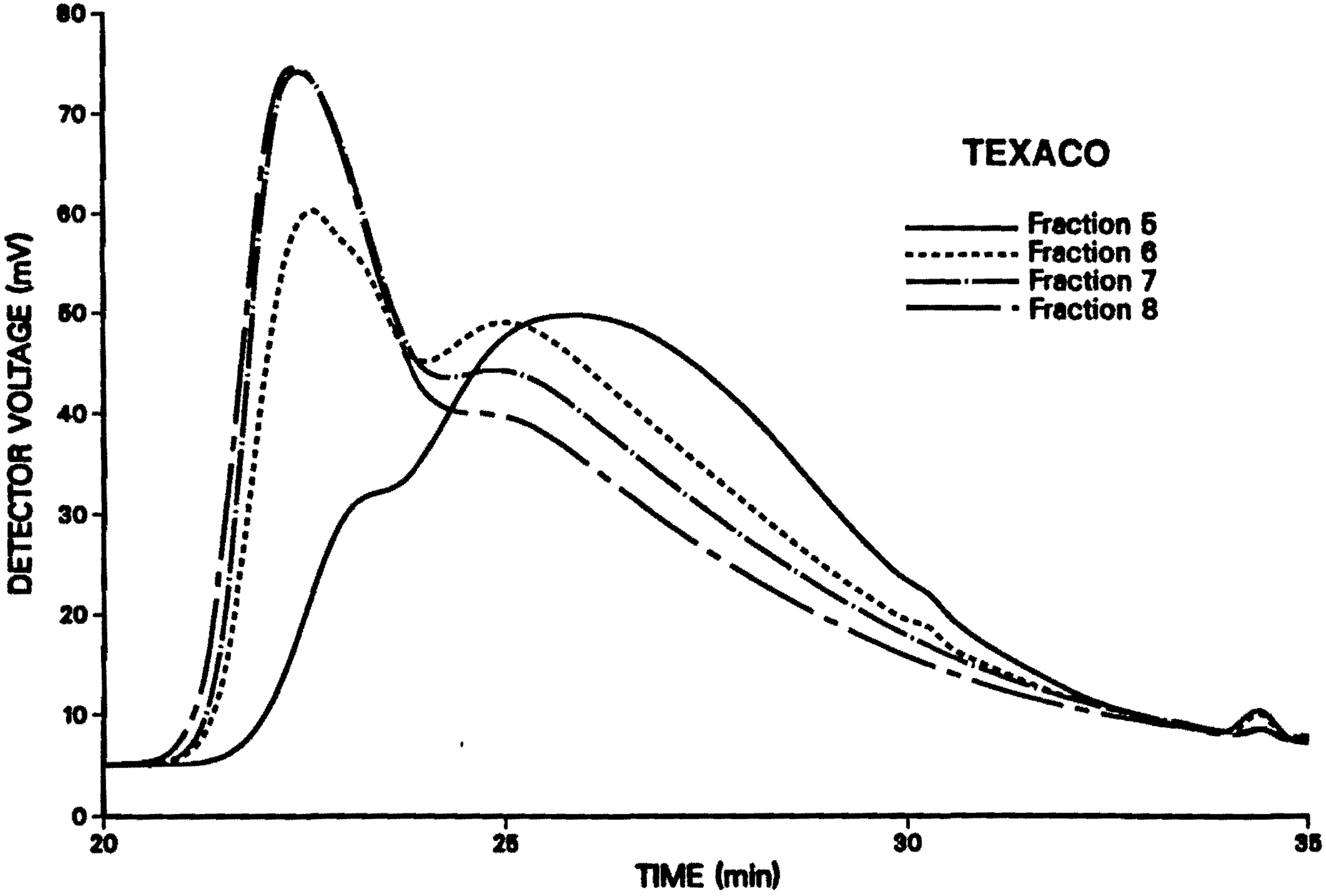

Figure B-38
GPC Chromatograms of Texaco Fractions 5-8

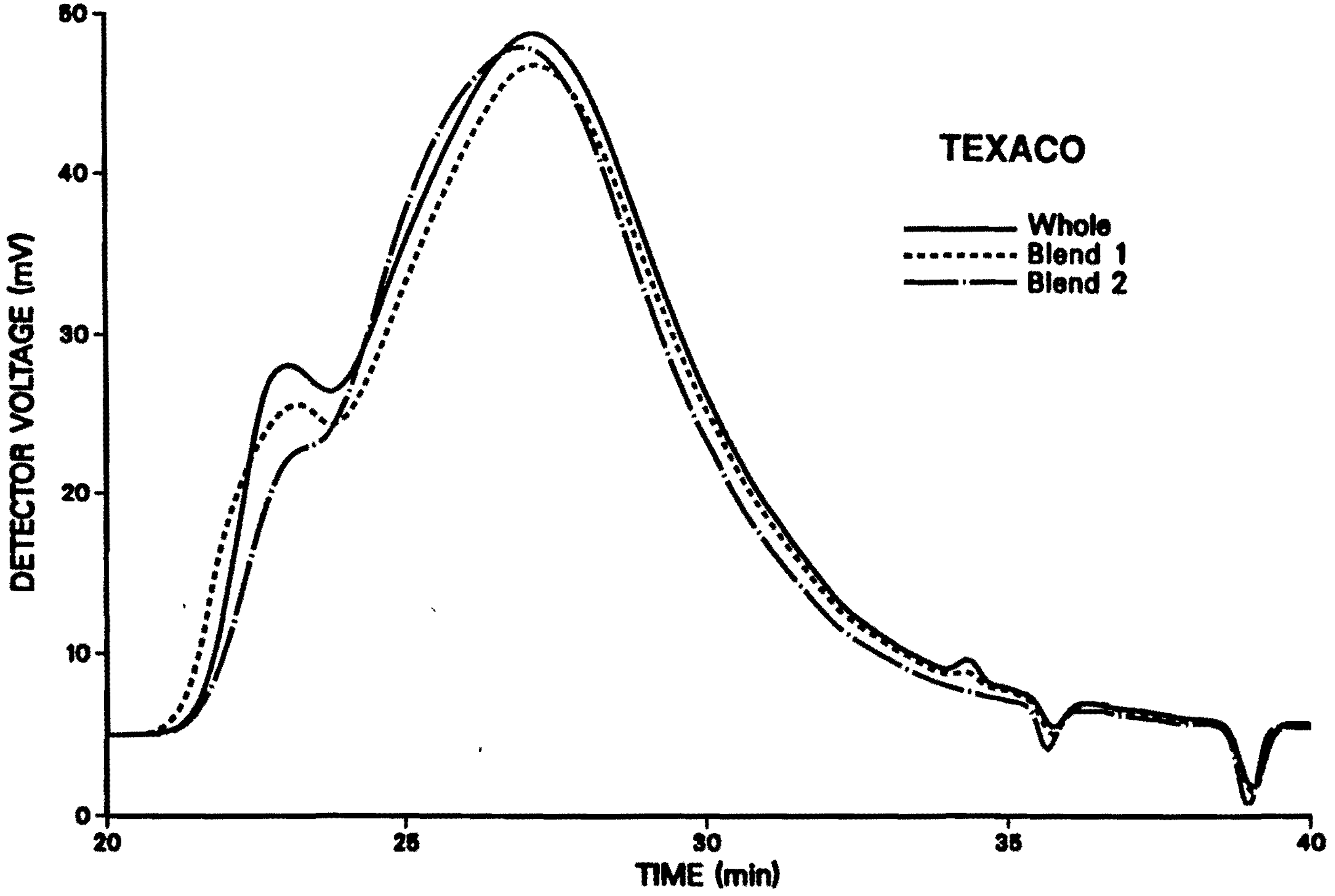

Figure B-39
GPC Chromatograms of Texaco Whole and Blends 1 and 2

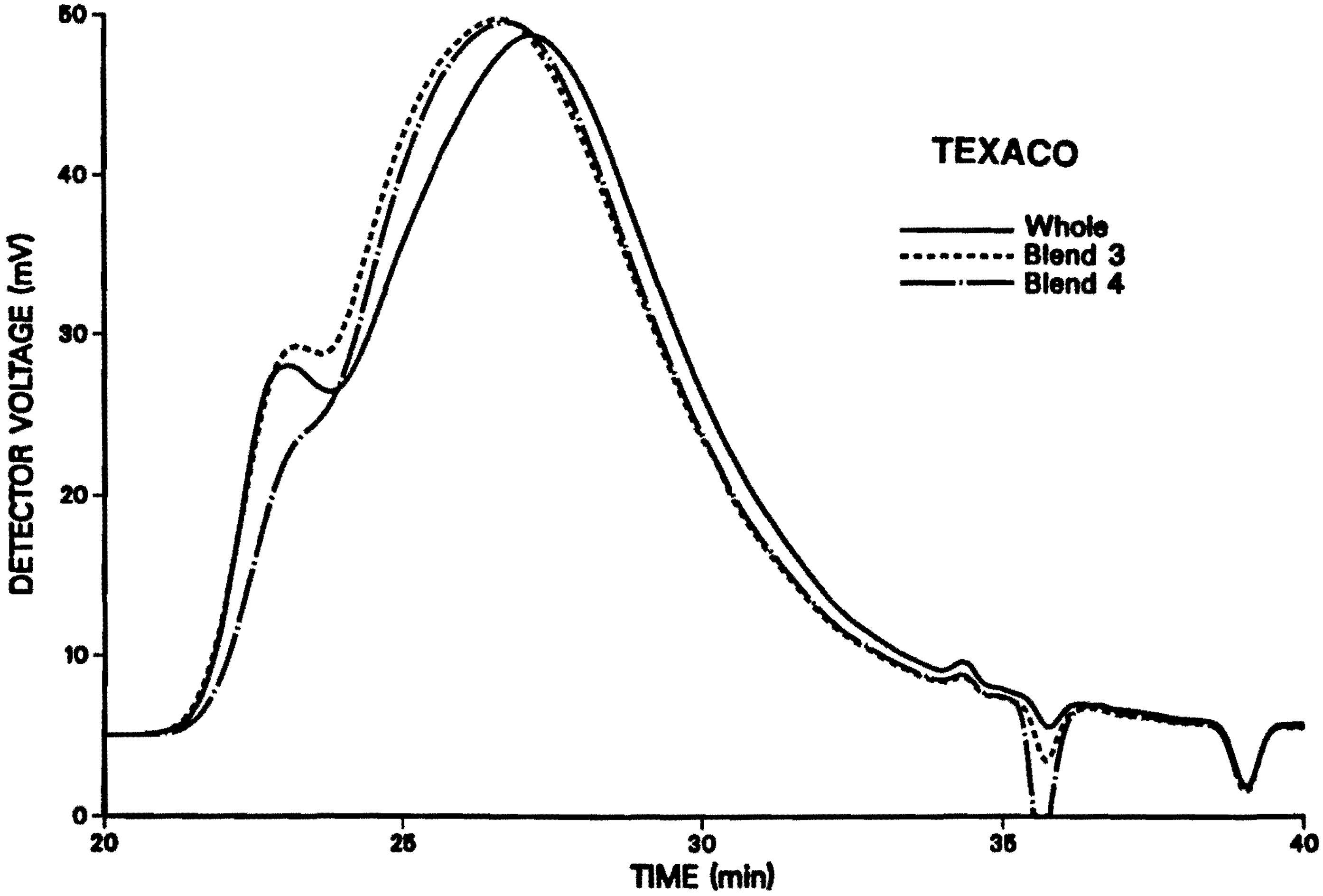

Figure B-40
GPC Chromatograms of Texaco Whole and Blends 3 and 4

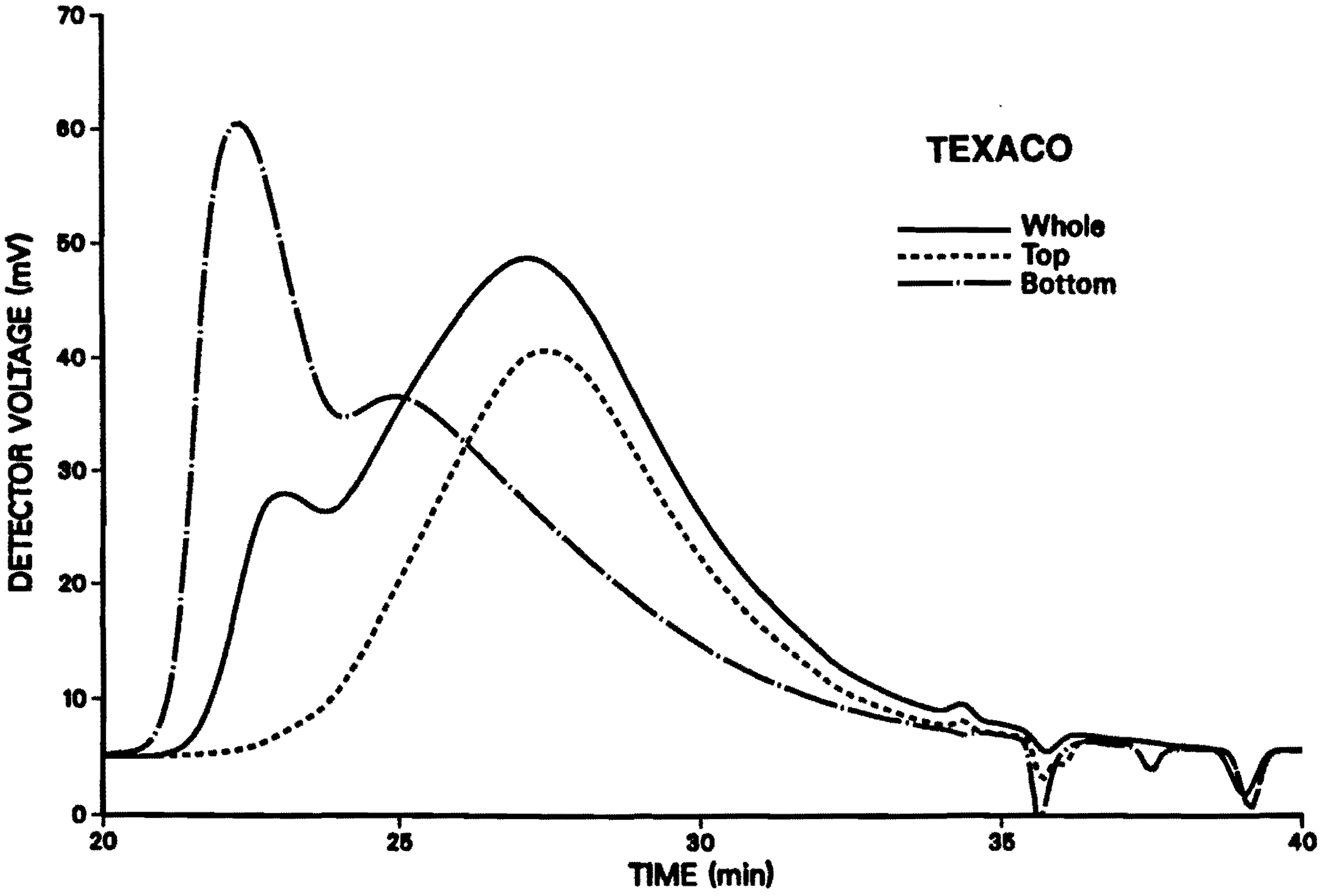

Figure B-41
GPC Chromatograms of Texaco Whole, Top, and Bottom

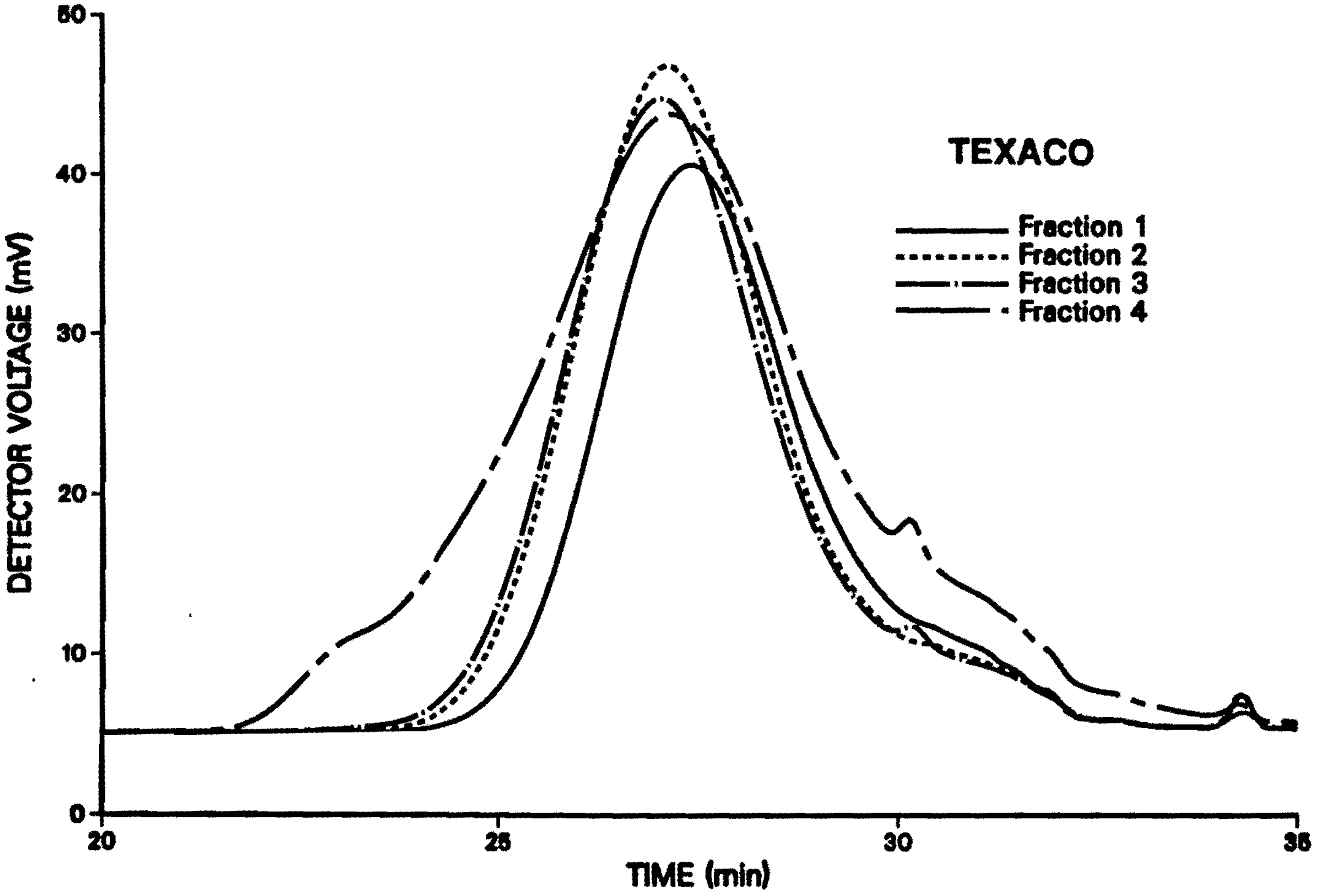

Figure B-42
GPC Chromatograms of Texaco Saturate Fractions 1-4

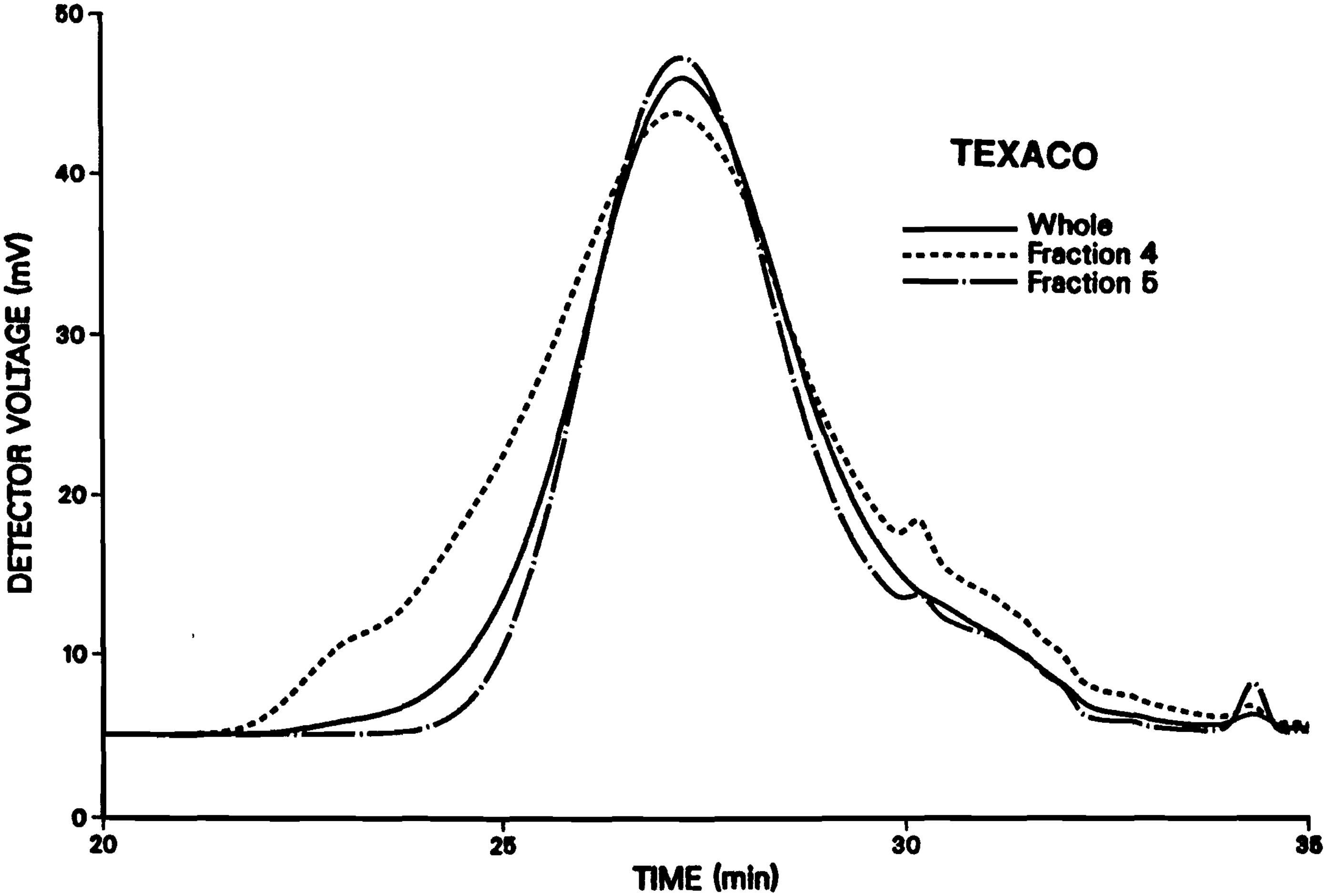

Figure B-43
GPC Chromatograms of Texaco Saturate
Whole and Fractions 4 and 5

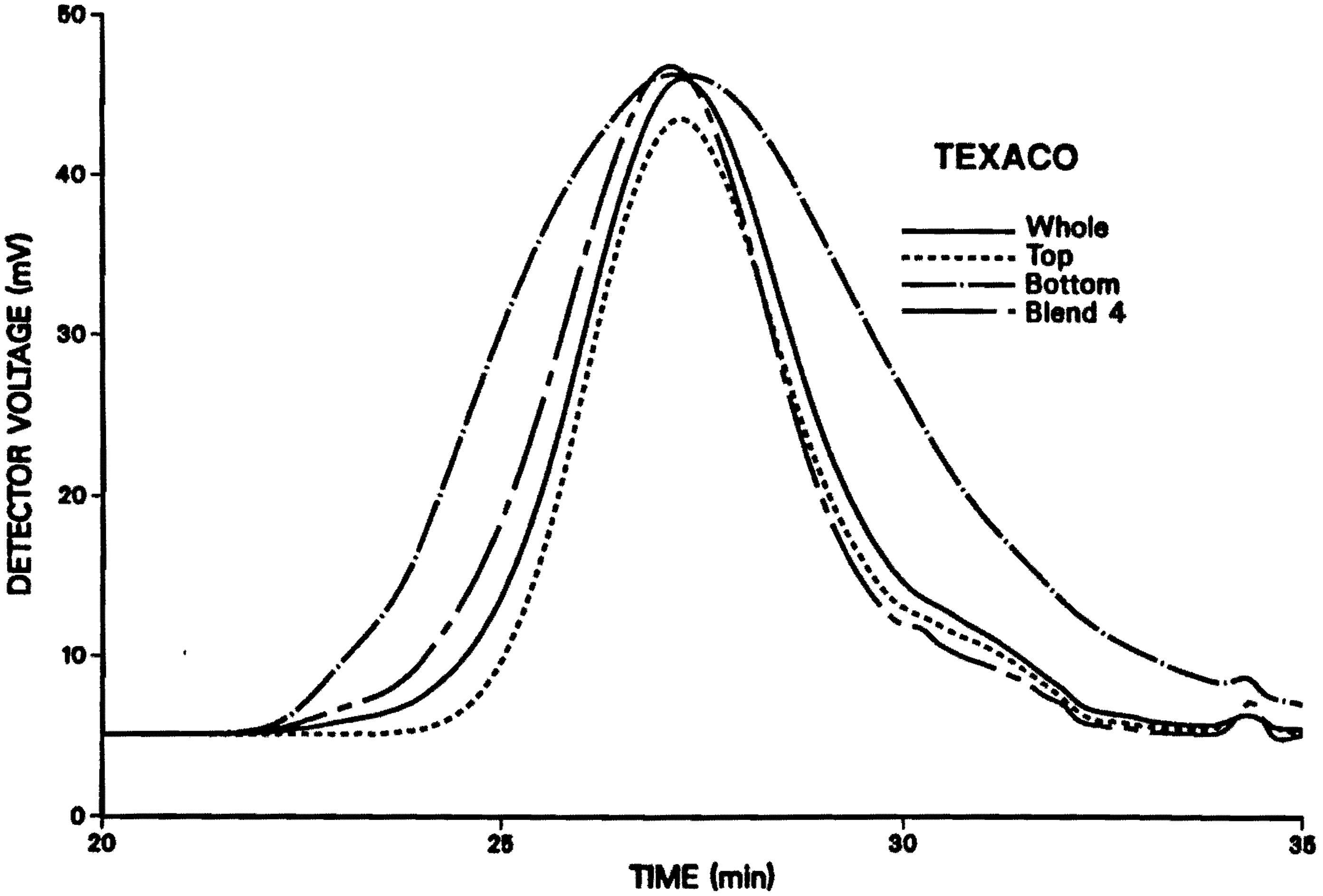

Figure B-44
GPC Chromatograms of Texaco Saturate
Whole, Top, Bottom, and Blend 4

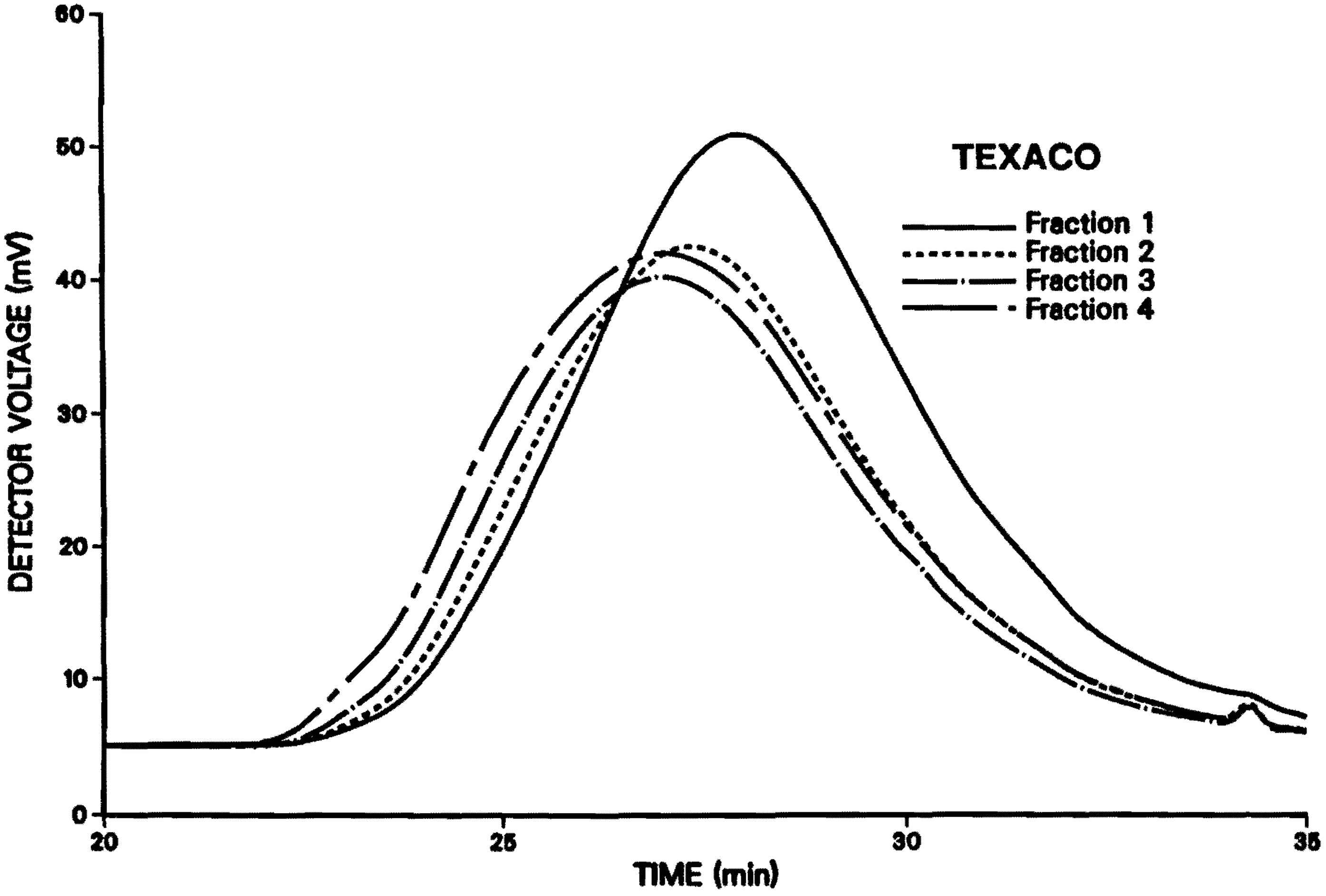

Figure B-45
GPC Chromatograms of Texaco
Naphthene Aromatic Fractions 1-4

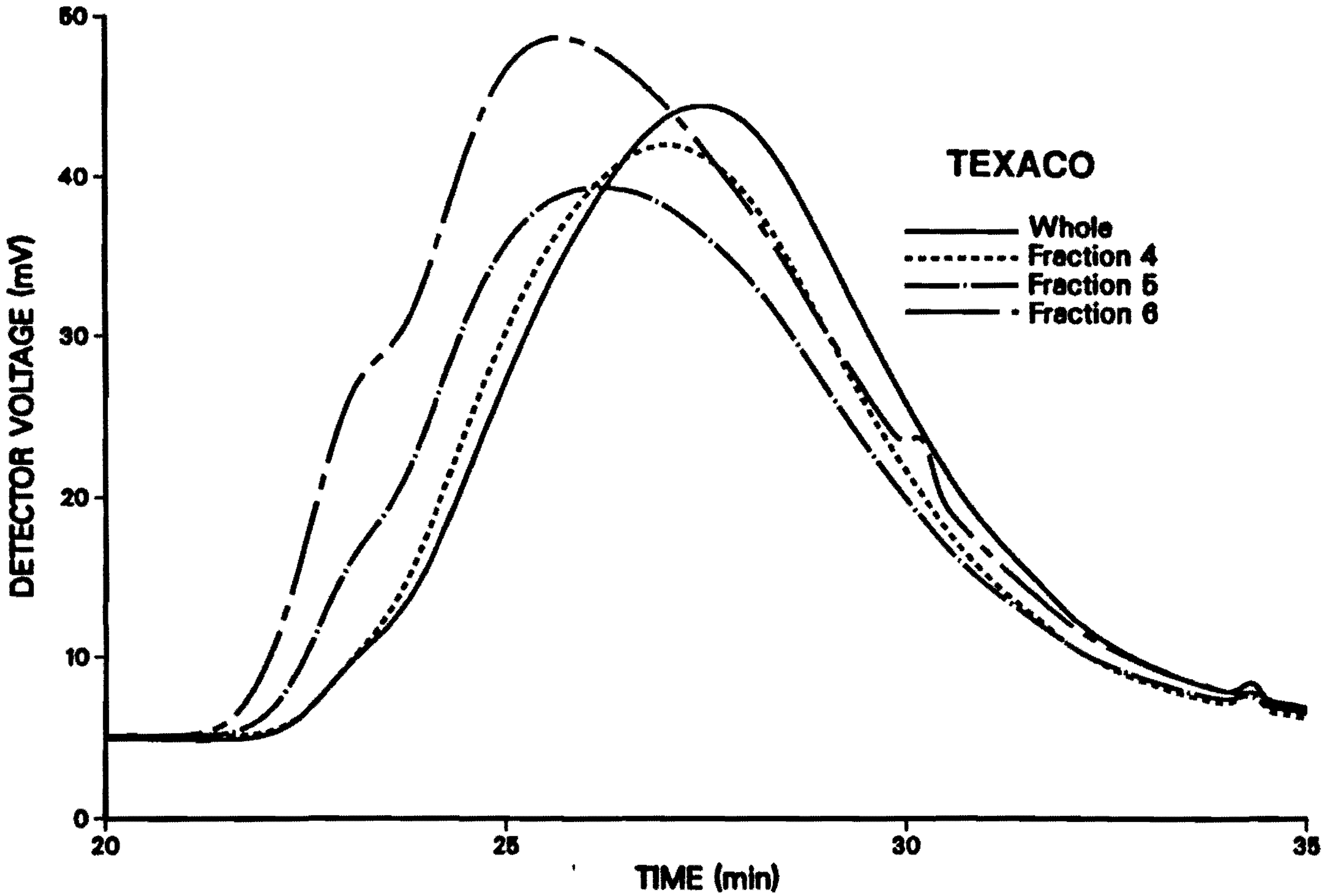

Figure B-46
GPC Chromatograms of Texaco
Naphthene Aromatic Whole and Fractions 4-6

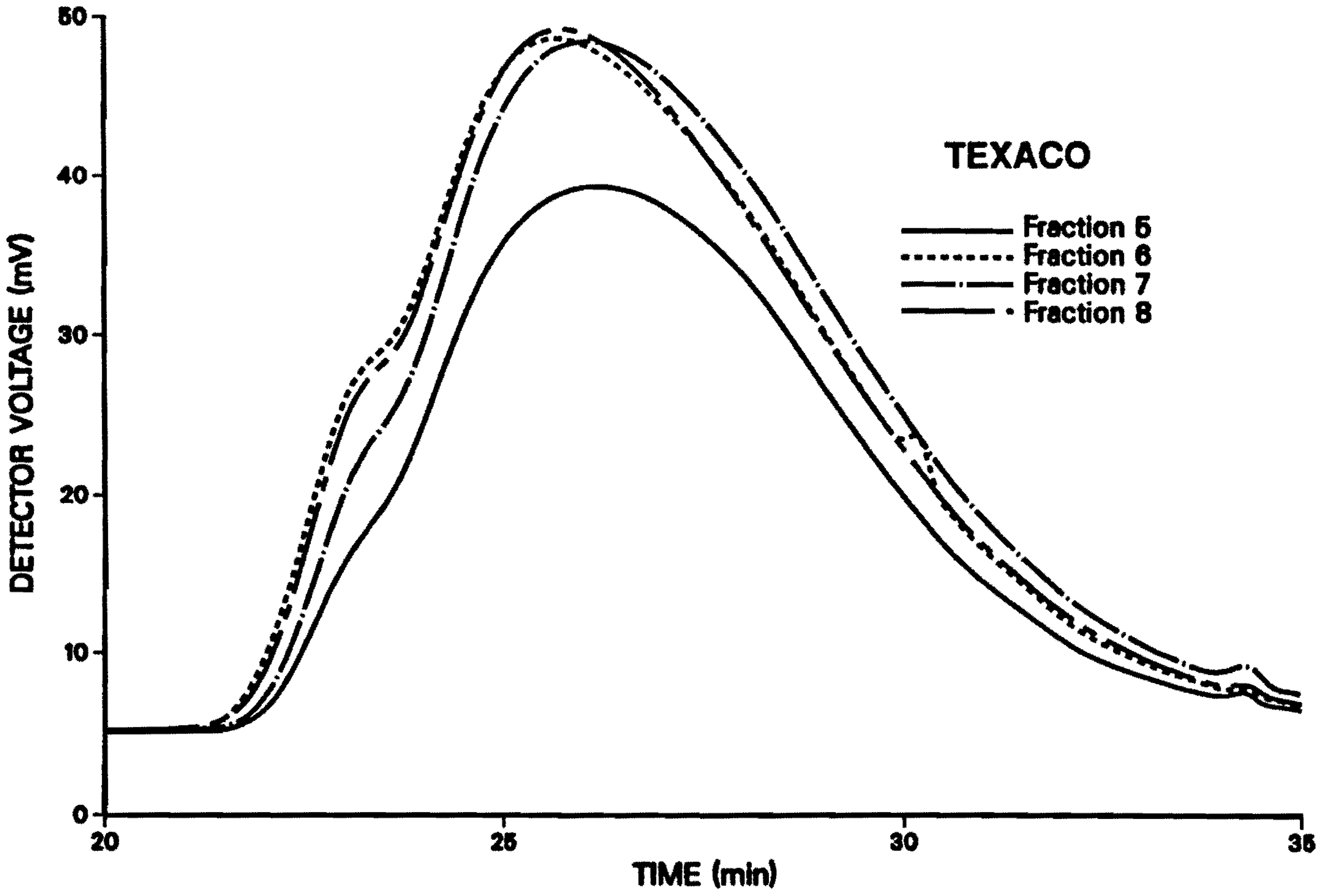

Figure B-47
GPC Chromatograms of Texaco
Naphthene Aromatic Fractions 5-8

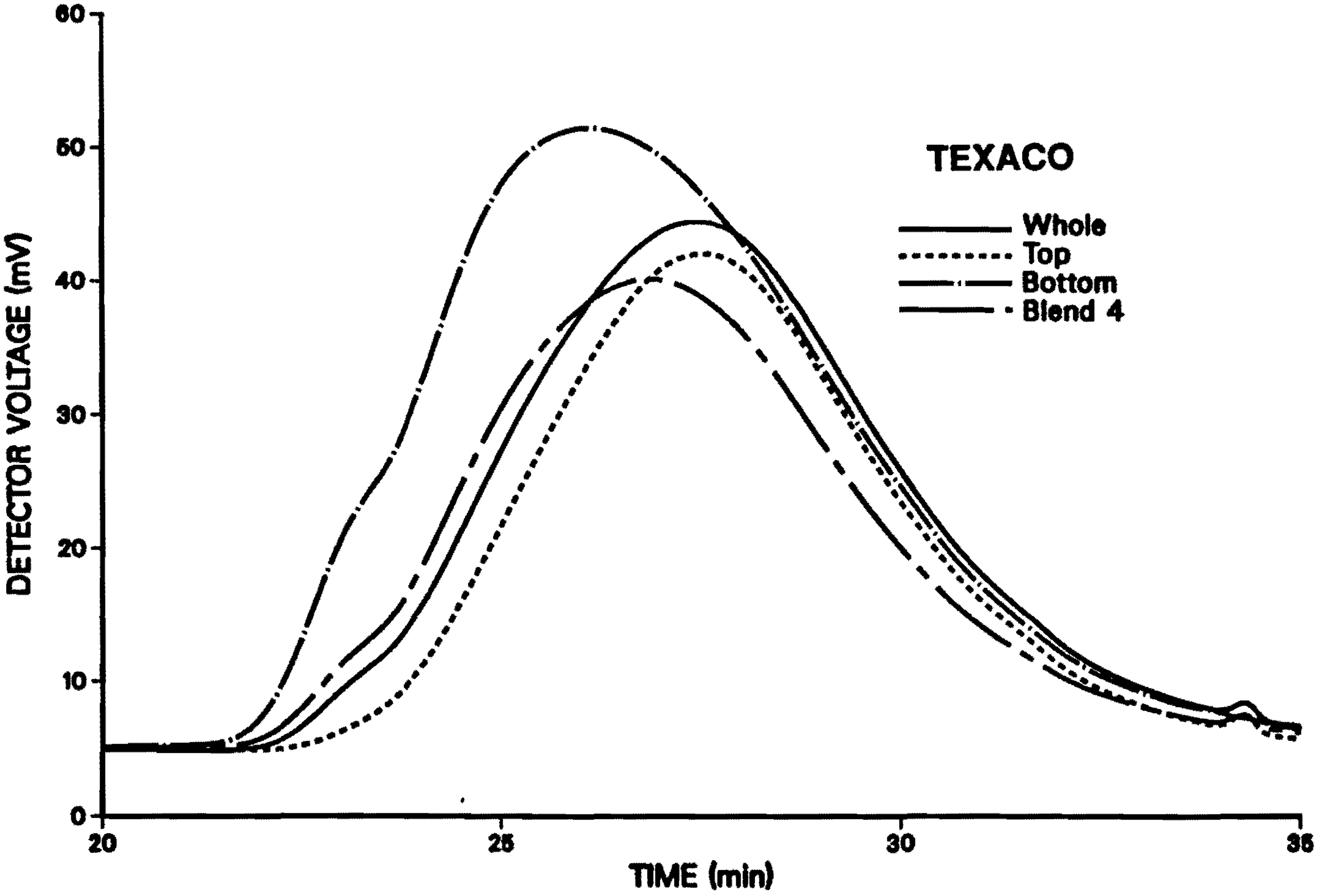

Figure B-48
GPC Chromatograms of Texaco Naphthene Aromatic
Whole, Top, Bottom, and Blend 4

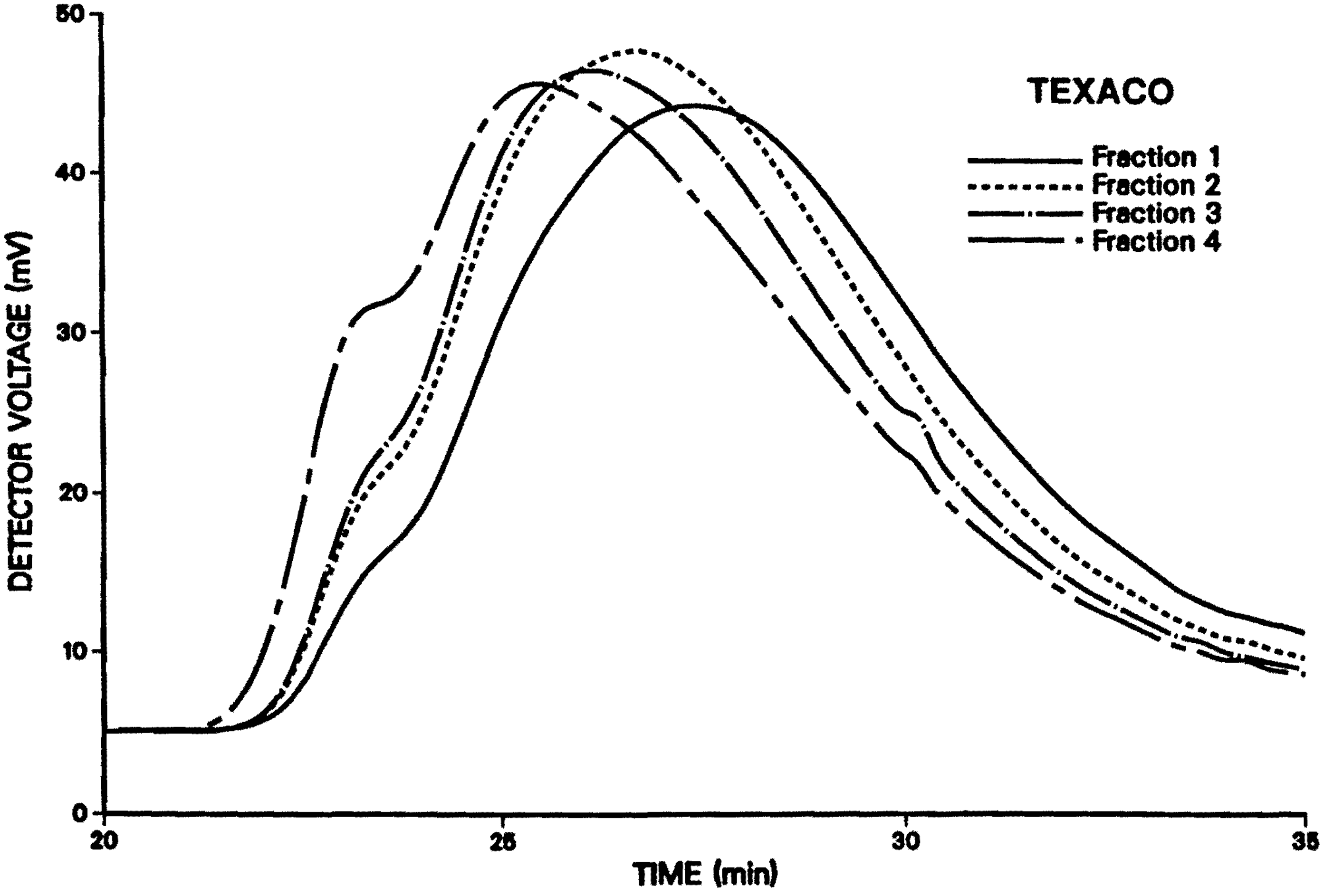

Figure B-49
GPC Chromatograms of Texaco
Polar Aromatic Fractions 1-4

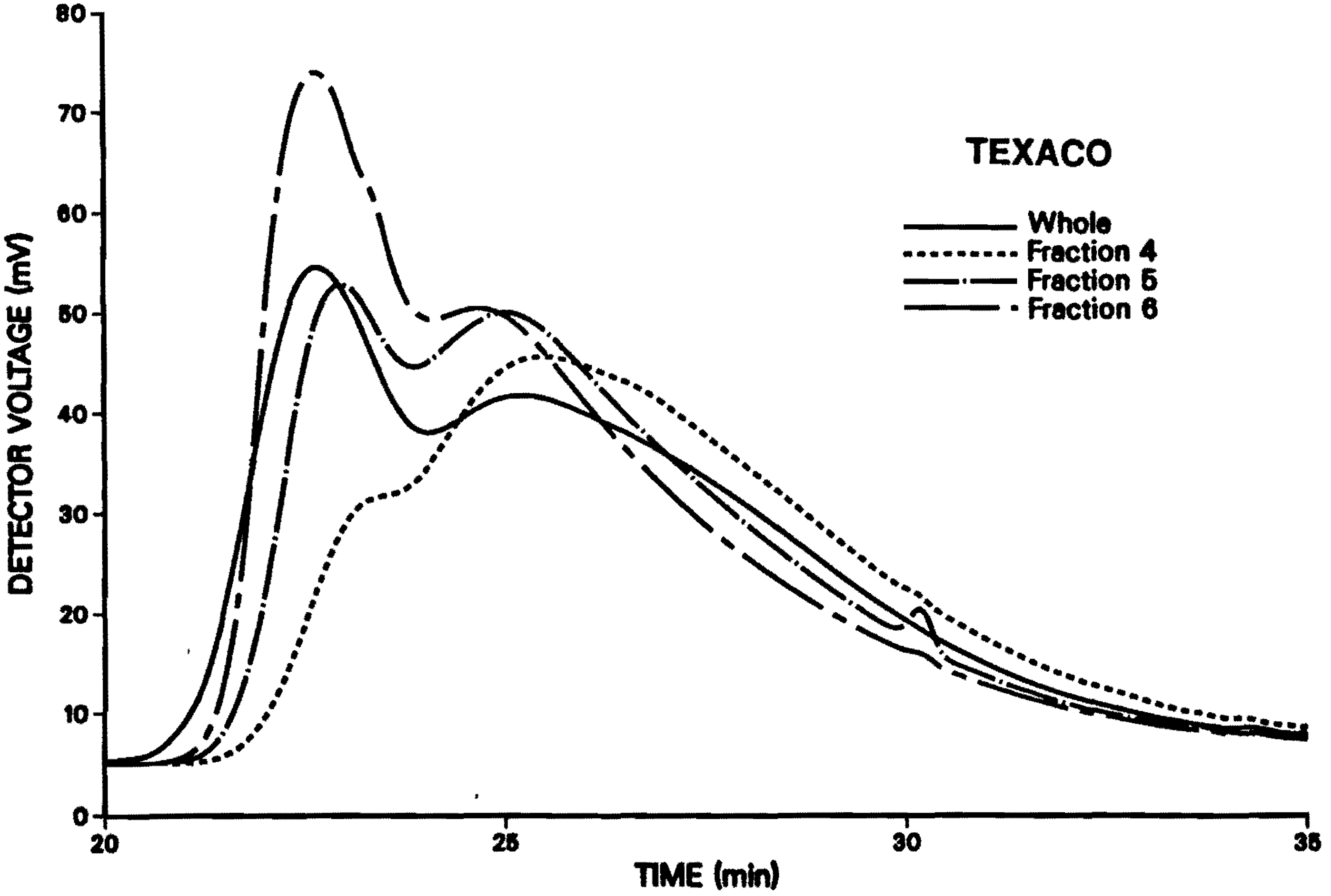

Figure B-50
GPC Chromatograms of Texaco
Polar Aromatic Whole and Fractions 4-6

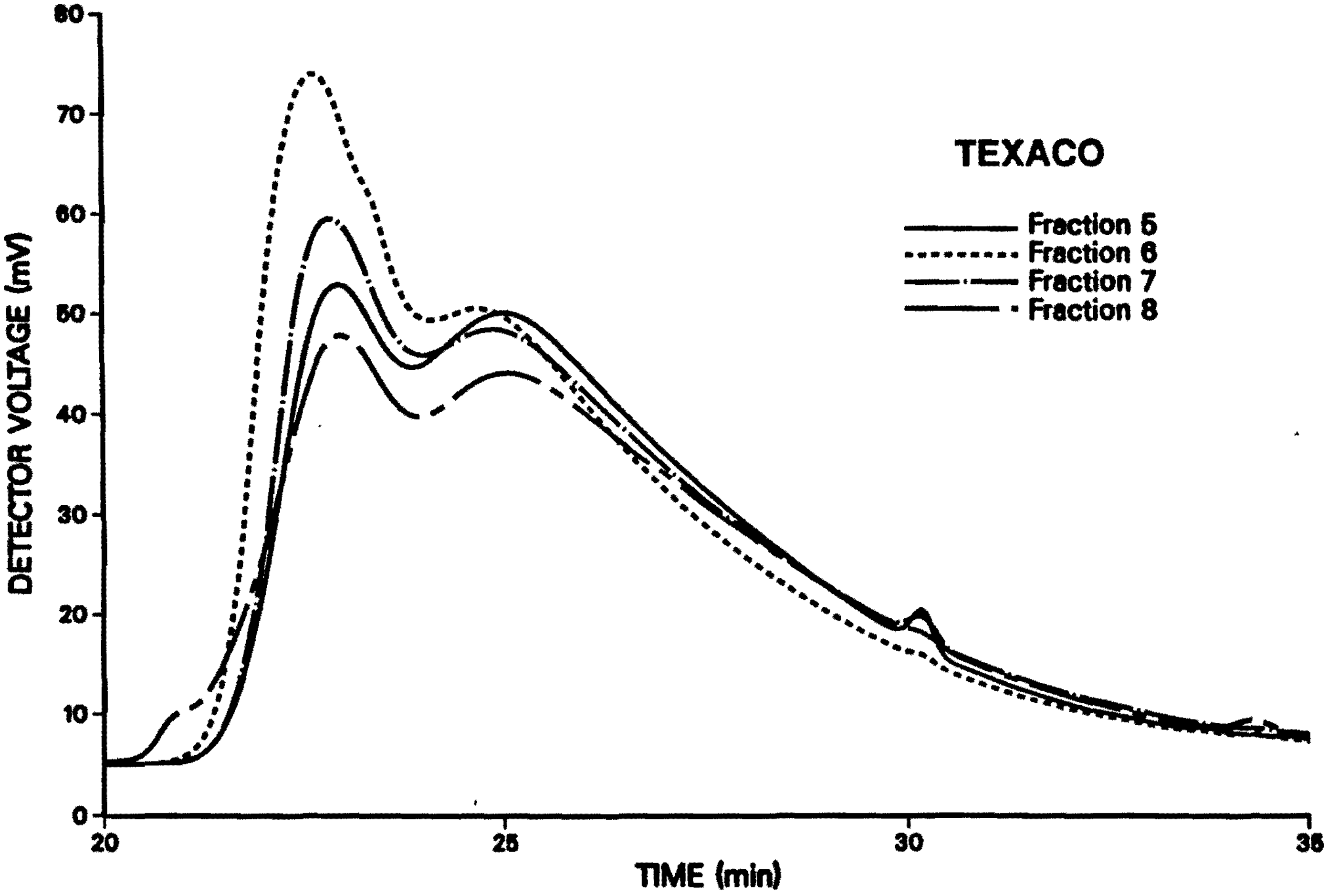

Figure B-51
GPC Chromatograms of Texaco
Polar Aromatic Fractions 5-8

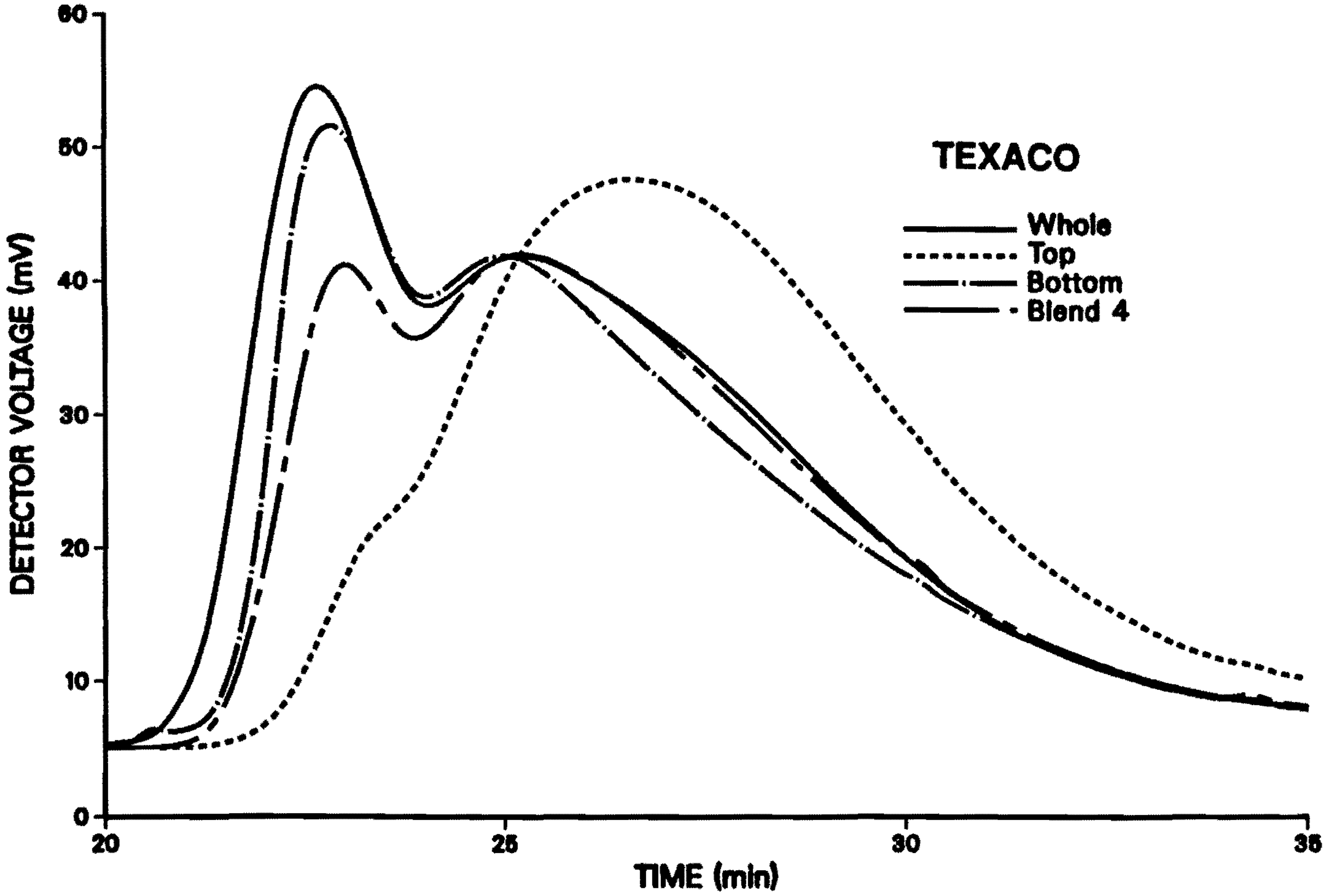

Figure B-52
GPC Chromatograms of Texaco Polar Aromatic
Whole, Top, Bottom, and Blend 4

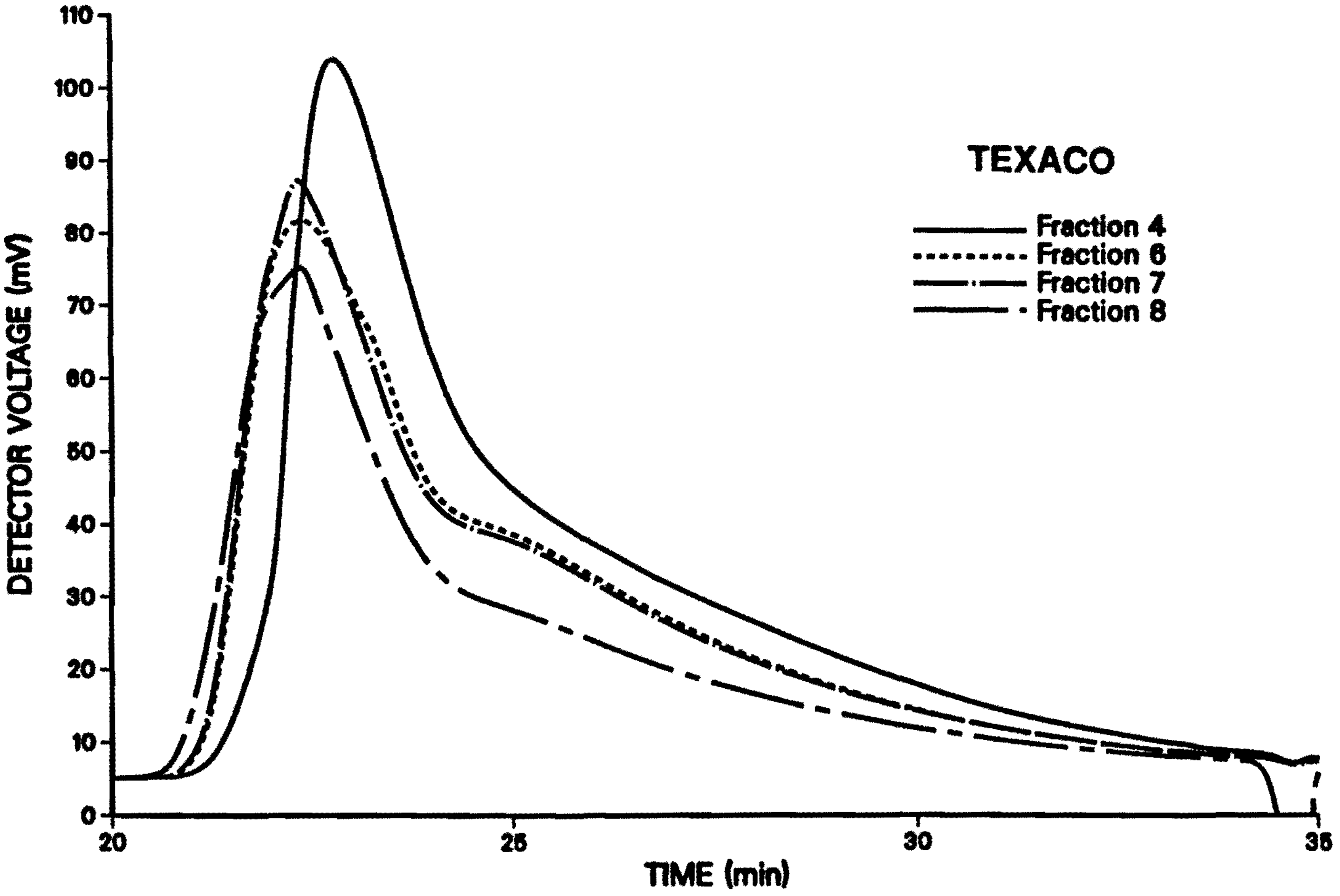

Figure B-53
GPC Chromatograms of Texaco
Asphaltene Fractions 4 and 6-8

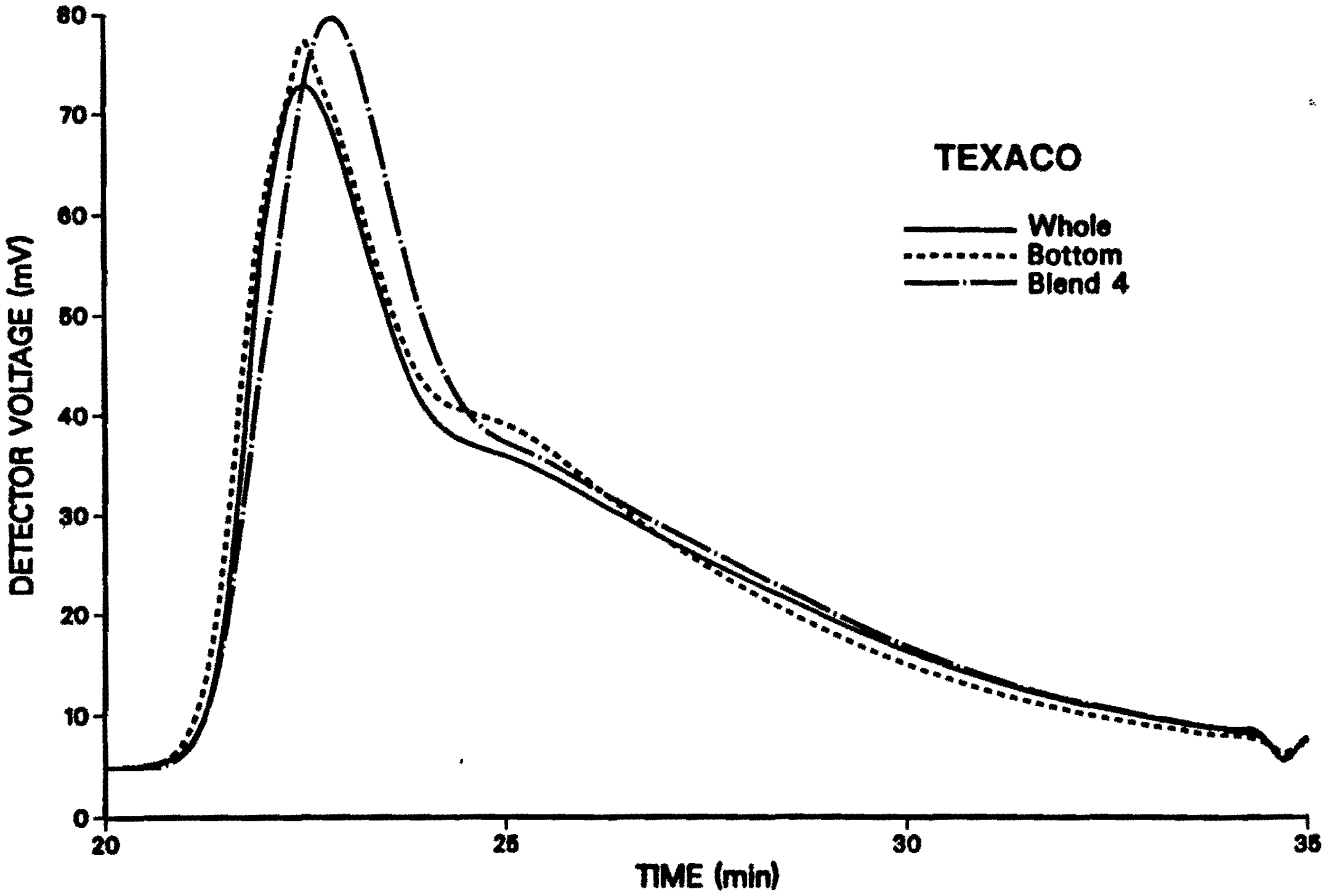

Figure B-54
GPC Chromatograms of Texaco Asphaltene
Whole, Bottom, and Blend 4