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16. Abstract

Gel permeation chromatography (GPC), Corbett analysis, Heithaus test and other physical and chemical tests have been used to characterize asphalts and to relate chemical properties, physical properties and performance. The GPC analytical methods were developed extensively to increase the sensitivity to asphalts. A series of pure compounds and an asphalt standard were used to insure accuracy and reproducibility. The GPC can be used to determine changes with time in asphalts from a particular supplier and to detect excessive changes in asphalts during the hot-mix process.

Corbett fractions of the virgin asphalts and cores from Study 287 test pavements were analyzed by GPC. This showed that rather large changes in the size of the Corbett fractions from virgin asphalts to cores were accompanied by relatively slight changes in molecular sizes within the various Corbett fractions.

A method was also developed to indicate asphalt tenderness based on the Heithaus test, asphaltene analysis or GPC analysis.

The extensive analytical results from this study will serve as an excellent data base for further characterization of Texas asphalts and development of superior asphalts to conform to particular aggregate characteristics and climate.

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CHARACTERIZATION OF ASPHALTS USING GEL PERMEATION CHROMATOGRAPHY AND OTHER METHODS

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SUMMARY

Gel permeation chromatography (GPC), Corbett analysis, Heithaus test, and other physical and chemical tests have been used to characterize asphalts and to relate chemical properties, physical properties and performance. The asphalts used in the present study consisted of periodic samples of virgin asphalt from the various suppliers to Texas over the last two years, the test pavement asphalts in Dickens, Dumas, and Lufkin, Texas from Study 287, and a group of asphalts which had been rated according to tenderness.

The GPC analytical methods were developed extensively during the project. Changes in carrier solvent, column pore size and injection size have improved the sensitivity of the method. The development work showed that it was necessary to use a series of pure compounds and a standard asphalt to insure accuracy and reproducibility. With the development of the GPC analytical methodology, it can be used to determine changes with time in asphalts from a particular supplier and to detect excessive changes in asphalts during the hot–mix process.

The virgin asphalts and cores from Study 287 test pavements were fractionated by the Corbett analysis. Further analysis of these fractions by GPC showed that rather large changes in the size of the Corbett fractions from virgin asphalts to cores were accompanied by relatively slight changes in molecular sizes within the various Corbett fractions. The primary change in molecular weight was in the asphaltene fraction.

A method was also developed to indicate asphalt tenderness based on the Heithaus test, asphaltene analysis, or GPC analysis. The method is quite flexible since any one of these tests may be used to predict potential tenderness.

The extensive analytical results from this study will serve as an excellent data base for further characterization of Texas asphalts and development of superior asphalts to conform to particular aggregate characteristics and climate.

METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

LENGTH

Symbol	When You Know	Multiply by	To Find	Symbol
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km

AREA

Symbol	When You Know	Multiply by	To Find	Symbol
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha

MASS (weight)

Symbol	When You Know	Multiply by	To Find	Symbol
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t

VOLUME

Symbol	When You Know	Multiply by	To Find	Symbol
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3

TEMPERATURE (exact)

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

Approximate Conversions from Metric Measures

LENGTH

Symbol	When You Know	Multiply by	To Find	Symbol
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi

AREA

Symbol	When You Know	Multiply by	To Find	Symbol
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	

MASS (weight)

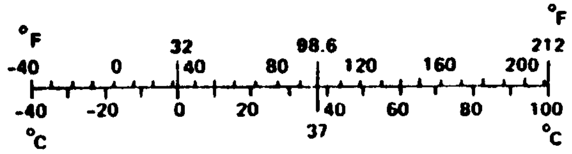
Symbol	When You Know	Multiply by	To Find	Symbol
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	

VOLUME

Symbol	When You Know	Multiply by	To Find	Symbol
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3

TEMPERATURE (exact)

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



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*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.

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IMPLEMENTATION

The results from this study may be implemented in several ways. The gel permeation chromatograph (GPC) has been demonstrated to be a reliable quality control test for asphalts. GPC analysis can be used to determine if the composition of asphalts from a particular supplier is changing with time. The GPC also can be a valuable quality control tool in another respect. If large changes are noted in the GPC results between a virgin asphalt and the asphalt after the hot–mix process, the asphalt quality should be closely examined for potential problems and deficiencies. A method to indicate tender asphalts has also been developed based on a Heithaus Test, asphaltene analysis, or GPC analysis. The method is quite flexible, since the results from any one of these three tests may be used to predict potential tenderness. The extensive analytical results from this study will serve as an excellent data base for further characterization of Texas asphalts.

DISCLAIMER

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

Introduction

Asphalts are very complex mixtures of components ranging from light aromatic and paraffinic materials to very heavy aromatic compounds known as asphaltenes. The exact composition of an asphalt varies greatly depending upon the original crude oil from which it was produced as well as the refining processes. Additionally, blending with other materials also affects the final composition of an asphalt cement. Finally, once a virgin asphalt is obtained for use in paving, additional changes take place during the hot mixing process that result in chemical changes in the asphalt. Evaporation, oxidation, and polymerization all are factors which combine to produce an asphalt cement which hopefully will have the appropriate physical properties.

In spite of known differences in asphalt composition, the current asphalt specifications do not directly indicate composition. Laboratory physical property tests have been disappointing in their ability to detect problem asphalts or to accurately predict asphalt performance. Usual specifications generally include the determination of asphalt penetration and viscosity, neither of which directly measures the chemical composition of the asphalt, nor necessarily relates to performance. These standard tests are not able to reflect changes in composition of an asphalt from a particular supplier and many engineers feel that the tests do not identify the important properties which affect pavement performance.

The generally unsatisfying results of current tests have led researchers to attempt to correlate composition with performance. Due to the wide variety of compounds, complete separation and identification of all chemical species is virtually impossible. As a result, chemical characterization techniques are employed to partially separate the asphalt into generic fractions.

Without a reliable predictor of performance based on properties measured in the laboratory, it is difficult to (1) accurately predict performance, (2) screen asphalts to determine those which will provide adequate performance, and (3) design blends or additives which will insure good performance for stated conditions. Consequently, roadway durability and life expectancy are unknown quantities. The price paid for poor performance is astronomically high, involving not just the cost of the pavement materials, but more importantly the costs of installation including the time the road is out of service as well as the direct construction cost. Consequently, there is a great need to better characterize asphalts by relating chemical properties to roadway performance.

Objectives. The objectives of this study are:

(1) To develop gel permeation chromatography (GPC) as a quality inspection tool for asphalts. The GPC can be used to determine if the composition of asphalts from a particular supplier is changing with time.

(2) To develop methods to determine asphalt properties and performance.

(3) To coordinate the effort with state highway research personnel (D-9) to insure technological and procedural compatibility.

(4) To determine the analytical methods which show the best potential for characterizing asphalt cement quality that will be further studied.

Gel Permeation Chromatography

Gel permeation chromatography (GPC) has been used by numerous researchers to investigate the asphalt fractions contributing to pavement performance. Others (Goodrich et al., 1985), have pointed out its limitations and doubted it would ever provide sufficient information to identify good and bad asphalts. Presently, it does have limitations but still it has shown as much accuracy as any alternative asphalt test in predicting asphalt life, at least in so far as cracking is concerned, and also probably in regard to tenderness and rutting. GPC gives a rough representation of molecular size distribution but tells us nothing directly about molecular structure. The fact that GPC has correlated with asphalt performance at all is probably because of widespread similarity in molecular species in many asphalts. Some asphalts whose performance is better or worse than might be predicted from the GPC have indeed been shown to be structurally anomalous at the molecular level.

Principles of GPC. The basic principle of GPC, or size exclusion chromatography as it is often called, is quite simple. If one passes a solvent containing a solute over a substrate containing pores, the solute molecules will diffuse into the pores. If the pore is large compared to the molecule, equilibrium will be reached when the concentrations within and without the pore are the same. If the pore is of a size larger than but of the same order of magnitude as the solute molecule, diffusion within the pore will be restricted and the concentration within the pore will be less than that in the bulk solvent. For instance, in a very simple model (Yau et al., 1979) where the molecules are spheres of diameter R and the pores are cylinders of diameter r, the equilibrium distribution is given by

$$K = \left(1 - \frac{R}{r}\right)^2$$

where K is the ratio of concentration in the pore to that in the bulk solvent. If R is equal to or greater than r then K is zero, as the solute molecules cannot enter the pore. Similarly, K approaches unity as the pore size becomes large relative to the size of the solute molecules.

Similar relations may be obtained for different pore geometries and molecular geometries. If the pores are cylinders and the solute molecules are polymers that form random coils, it can be shown that K is equal to the ratio of the allowed conformations within the pore to those in the bulk phase. In this case, $\log(1 - K)$ is linear in $\log(M / r^2)$ where M is the molecular weight. This correlation has been shown to apply to a large number of polymers (Basedow and Ebert, 1980). These equations assume that the substrate surface is inert to the solute, for if adsorption occurs, much higher values of K can result.

The relation between the retention volume, V_R, the exclusion volume, V_0, and pore volume, V_i, is given by

$$V_R = V_0 + KV_i$$

from which

$$K = \frac{V_R - V_0}{V_i}$$

A useful correlation is that combining the molecular weight, M, with the intrinsic viscosity, $[\eta]$, defined by

$$[\eta] = \lim_{C \to 0} \frac{\eta_{\text{solution}} / \eta_{\text{solvent}} - 1}{C}$$

where C is the concentration of the polymer in the solution and η is viscosity. According to theory, $[\eta]M$ is directly proportional to the hydrodynamic volume for a polymer chain. Correlations of V_R versus $\log[\eta]M$ have been shown to give a universal plot for a large number of polymers in a given solvent-column system.

Though useful, this correlation is far from universal, depending on the nature of the solvent, solute and substrate. Figueruelo et al. (1980) show plots of $\log M[\eta]$ vs. V_R for polystyrene in a wide range of solvent systems. While tetrahydrofuran (THF), chloroform, methyl ethyl ketone (MEK) and benzene did give essentially the same curve, MEK and heptane and a variety of solvents with methanol differed considerably.

Assuming the relation

$$\ln(V_R - V_0) = -\frac{R}{r} + \ln\frac{2K}{r}$$

plots of $\ln(V_R - V_0)$ versus R in various solvents (Basedow and Ebert, 1980) gave a range of pore sizes, r, for the same substrate with the pore size decreasing with increasing solvent strength as defined by Snyder and Saunders (1969). This was explained by increasing adsorption of the solvent within the pores effectively decreasing the diameters. The values of K obtained from the intercept of these plots indicated that at higher solute molecular weights and with poorer solvents, adsorption of the solute in the gel increases and can even lead to a situation where the solute is difficult to recover.

The separation of two molecules depends on the difference in their retention times which in turn depends on their respective values of K which, as shown, vary with the ratio of molecular size to pore size. Thus, there is an optimum pore size for a range of molecular sizes. The actual separation of retention volumes depends on many factors. For instance, increasing column length increases separation proportionately.

The separation ability of a column is conveniently expressed in terms of the number of plates. This may be expressed approximately in terms of the retention volume and peak spreading by

$$N = 5.54\left(\frac{V_R}{W_{0.5}}\right)^2$$

where N is the number of plates and $W_{0.5}$ is the peak width at half its height. The height of a plate is then the column length divided by the number of plates. There are a number of factors that affect the plate height besides K. It is very sensitive to particle diameter and the use of small particle sizes in higher pressure systems has greatly improved the separation and reduced the time in GPC analysis. Flow rate has little effect on the plate height for small molecules, but for larger sizes the height increases with flow. This is likely the result of the small diffusivity of large molecules. Concentration can have an effect at large molecular weights through molecular association in the bulk phase and in the pores.

GPC and Asphalt Analysis. When GPC is applied to asphalt analysis, all the complications above are encountered in addition to others. We have not yet mentioned the problem of detectors. Generally, either refractive index (RI) or ultraviolet (UV) detectors are used. The former is linear in mass only if the refractive index is linear in concentration as molecular weight changes, and the latter only if the UV absorption remains constant as the molecular weight changes. With a polymer which changes little in molecular structure, this may be true, but with a complex mixture such as asphalt there is little chance that this will be so.

Very different chromatograms are obtained with refractive index and UV and the latter varies with absorption wave length. Therefore, if one wishes the instrument signal to be related to the mass of the material, the detector must be calibrated. This has generally been done by taking GPC fractions, evaporating the solvent and weighing the solute for comparison with the detector signal.

Similarly, the molecular weight does not follow the universal correlations determined for polymers. At low molecular weight, the apparent molecular weight is lower because of the percentage of compact aromatic molecules which also may adsorb, and at high molecular weight the analysis is complicated by association. Indeed, intrinsic viscosity measurements (Altgelt and Gouw, 1975, Brulé, 1980, and Huynh et al., 1977) have shown that association is occurring at the concentrations used to determine molecular weights for calibration, such as by vapor pressure osmometry (VPO). Boduszynski (1981) reports that molecular weights of the asphaltene fraction as determined by Field-Ionization Mass Spectrometry (FIMS) were about a fifth of that determined by VPO.

Attempts to relate the GPC to asphalt performance generally have not tried to correct the chromatograms for association or agglomeration of molecules, a reasonable approach because the tendency to associate is a characteristic of asphalts that probably relates to performance. Association increases the apparent large molecular size fraction, and this seems to be related to both cracking (Heithaus, 1960) and tenderness (Chapter 5) for most asphalts.

The detector correction is greater when UV is used. However, the deviation of the UV from linearity does give structural information (Brulé and Such, 1979, Brulé, 1980, and Snyder, 1969). For instance, a large hump in the large molecular size region at 350 nm indicates a high fraction of polycondensed compounds (Brulé, 1980). A much lower peak in the mid range indicates a high percentage of paraffins (Huynh et al., 1977). At 254 nm, (sensitive to aromaticity) this hump is not present and, in fact, less large molecular size material is exhibited than with refractive index (Jennings et al. 1982).

A large sample injection may overload the detectors, but with asphalts a more common effect is association that increases the large molecular size fraction (Brulé, 1980, Brulé et al., 1986, and Snyder, 1969).

The general effect of solvent flow rate was discussed above but with asphalts there is an additional complication arising from the kinetics of dissociation (Brulé, 1980, Brulé et al., 1986) so that at higher flow rates the large molecular size materials may be more associated and the LMS part of the chromatogram will be larger. Brulé (1980) studied the effect of time elapse between sample preparation and injection in THF solvent at intervals of 4 hours, 7, 14, and 21 days. There was significant change in the chromatograms between 4 hours and 7 days.

The choice of solvents with asphalts is complicated by the tendency of asphaltenes to adsorb on the columns (Altgelt and Gouw, 1975, Jennings et al. 1982, and Snyder, 1969). Because of this tendency and the tendency of association, dramatically different chromatograms may be obtained with different solvents. Jennings et al. (1982) reported that the relative percentage of large molecular size molecules between asphalts could be reversed by using chloroform instead of THF; however, he reported that rapid fouling of the column occurred with chloroform, trichloroethylene and methylchloride. Altgelt and Gouw (1975) report that 5 percent methanol in chloroform or benzene are excellent solvents. Brulé (1980) compared benzonitrile, chloroform, THF and tetralin. The first two gave much lower LMS regions than the latter two indicating less association. The best solvent, benzonitrile, has the highest dielectric constant and the worst, tetralin, has the lowest. Chloroform and THF, however, are reversed though their solubility parameters are nearly identical.

Air blowing of asphalts leads to an increase in the LMS region. Brulé et al. (1986) and Brulé (1980) reported that using UV detectors at 350 nm, ordinary asphalt chromatograms are bimodal while blown asphalts are trimodal. Boduszynski (1981) compared GPC results with FIMS determinations of molecular weights on whole asphalt and asphaltene fractions. There was a large increase in the LMS region as determined by GPC but the FIMS determination showed only a slight increase in molecular weight for the asphalt and an actual decrease for the asphaltene fraction. They conclude that the growth in the LMS part of the GPC on blowing is due entirely to an increase in active sights that leads to association.

GPC and Asphalt Performance. Various oven tests for aging, especially the Thin Film Oven Test (TFOT) (ASTM D 1754), and the Rolling Thin Film Oven Test (RTFOT) (ASTM D 2872) and variations such as the Extended Thin Film Oven Test (ETFOT) have been used to reproduce the changes that occur in the hot mix plant and during pavement aging. These tests definitely cause changes that occur during aging, such as an increase in asphaltene content and in viscosity and a decrease in ductility. Whether they actually predict road performance is hotly debated, for example, Anderson et al. (1976), Goodrich et al. (1985). GPC tests on asphalts from the oven tests generally show an increase in the LMS region (Brulé et al., 1986, Hattingh, 1984). There are two features of these tests that may reduce their utility. First, the temperature is too high and probably causes changes that do not occur on the road. Second, and probably of greater importance, is that they do not include the aggregate which has been shown to catalyze the hardening reactions which can differ for each asphalt-aggregate combination (Jennings and Pribanic, 1984, Plancher et al. 1977, Ensley et al., 1984, Barbour et al., 1974, Petersen et al., 1982, Petersen et al. 1974a). An alternative procedure to aging asphalt with aggregate is described by Jennings et al. (1982).

To determine if asphalt molecular size distributions would correlate with asphalt cracking, Plummer and Zimmerman (1984) collected eleven pavement samples in Michigan and eight in Indiana. The Indiana results were more consistent than those for Michigan, but both showed more cracking with an increase in molecular size. Results from the Michigan roads showed that asphalts extracted immediately after construction were harder for the roads that eventually cracked (a mean penetration of 48 vs. 62).

Bynum and Traxler (1970) determined GPC chromatograms on virgin asphalts and pavement cores from nine test sections in Texas. Rheological properties and vanadium concentrations were also determined. The GPC columns were 50, 500, 1000 and 10,000Å arranged in series. Refractive index detection was used and THF was the solvent. Considerable difference was noted between asphalts from different sources. Also the chromatograms obtained from asphalts from a given source often showed change with time. After two years, three of the road sections were reported as inadequate, two as fair, one as good, one as very good and two as excellent. After this short time, no consistent pattern between molecular size and performance emerged though the chromatograms for the poorer asphalts seemed to change more with time. Fortunately, the vanadium content was determined and all the inadequate asphalts contained high vanadium.

Hattingh (1984) used GPC and high pressure liquid chromatography (HPLC) to study four South African road asphalts. Two roads were in good condition after nine and three years, respectively, and two exhibited serious setting properties. The two good asphalts showed a much higher LMS fraction than the tender asphalts.

Hattingh, also used HPLC and a series of solvents to separate both whole asphalt and the maltenes into nine fractions following hexane precipitation of asphaltenes. The fractions were subsequently tested on the GPC. For the whole asphalt, fractions 1 and 2, hexane eluted, were mostly low molecular size. Fraction 3, containing most of the asphaltenes and eluted by chloroform, was mostly of intermediate molecular size. Fractions 4, 5, and 6, eluted by chloroform + 10 percent ether, ether + 3 percent ethanol, and methanol, respectively, varied from large to small molecular size. Fractions 7, 8 and 9 eluted by chloroform + 3 percent ethanol, THF + 3 percent ethanol, and Pyridine + 3 percent ethanol, respectively, were mostly of high molecular size. Interestingly, fractions 1 and 2, hexane eluted and low molecular size, contained small amounts of asphaltenes, and fractions 7 and 9, generally large moleculer size, also contained asphaltenes though the largest amount was in fraction 3. The relatively long retention time of all the maltene fractions indicate that the largest molecules were removed with the asphaltene precipitation.

Following ETFOT on the asphalts used in the roads, the two tender asphalts showed smaller decreases in fraction 1 and much smaller increases in fractions 7, 8 and 9 than the other 2 asphalts. In other words, the tender asphalts did not gain the larger molecular size molecules on aging. This is a reverse of the situation with cracking asphalts. Hattingh, thus concluded that too high an asphaltene or LMS percentage causes cracking and too low causes setting problems.

By far the most extensive studies of the use of GPC in predicting asphalt pavement performance have been those of Jennings and co-workers (Jennings et al. 1980, Jennings et al., 1981, Jennings et al. 1982, Jennings et al. 1985b, Jennings et al. 1985a). Jennings et al. (1980) took cores from 39 roads in Montana representing asphalts from all of Montana's four refiners including five penetration grades and representing a variety of pavement ages. The asphalts were extracted and tested on the GPC with THF as solvent and with a six-column array consisting of three 500, one 1000, one 10^5 and one 10^6Å. The chromatograms were divided in equal time segments into large molecular size (LMS) medium molecular size (MMS) and small molecular size (SMS). In addition, the roads were graded as to their condition. The only defect included was cracking, and an attempt was made to eliminate roads that suffered from construction faults. Roads were classified as follows:

Excellent	Older than 14 yrs. and little cracking
Good	Newer than 14 yrs. and few cracks
Poor	Extensive cracking or newer than 10 yrs. and cracking
Bad	Extensive cracking

Jennings chose a 19 year old road in excellent condition and used it as a standard or model asphalt. He found a high degree of correlation between pavement performance and the similarity of the asphalt's GPC to that of the standard, particularly in the LMS region. He determined that low LMS is desirable to reduce cracking.

Jennings also determined the asphaltene content by heptane solubility. All samples containing more than 19 percent asphaltenes were poor or bad. All with less than 15% were good or excellent with only two exceptions. One road with 17.4% asphaltene rated bad and one with 17.8% rated excellent. However, the bad road contained considerably more LMS, as measured on the GPC, than the excellent road and the model.

Penetration and ductility correlated only fairly well with performance. Asphaltene content correlated better. But the best correlating factor was the similarity of an asphalt's chromatogram to that of the model asphalt, particularly in the LMS region.

Based on all these data, he made the following recommendations for Montana:

LMS	8–10%
MMS	46–48%
SMS	44–46%
Asphaltenes	12.5–16.5%
Penetration	> 120

Jennings noted that asphalts from each of the four refineries gave distinctive chromatograms, and he discussed this relative to the refining processes. It was not known, however, how closely present refinery methods represented that used when the roads were built.

Jennings noted that a section of road containing lime had a larger LMS fraction than unlimed sections. Later, Jennings, et al. (1981) performed some experiments heating asphalt alone as well as asphalt mixed with lime, fly ash or aggregate for one hour at 163°C (325°F). No change occurred in asphalt exposed to oxygen or nitrogen or in the lime-asphalt mixture. However, heating with aggregate, with lime plus aggregate, or with fly ash plus aggregate increased the LMS fractions. Later, Jennings et al. (1982) studied aging in asphalts from six roads by changes in GPC. Increases in LMS during the hot-mixing operation and construction averaged about 43 percent. Cores taken after two years showed no significant increase, and in fact, averaged a small decrease. One pavement contained fly ash and another, lime. Both showed a large increase in LMS through the construction stage and a decrease during the two years of aging. On the basis of comparison with the GPC model asphalt, four of the six roads would be expected to crack. Two of these were showing cracks after two years. The other roads were all in good condition after two years.

Further work was reported on the effect of heating under nitrogen (to prohibit oxidation) as well as with oxygen with and without additives. Samples from all four refineries were included. Heating was at 163°C (325°F) and 115°C (240°F) with samples taken at 1/2 and one hour. Heating was not in a thin film. In the absence of additives, no significant change was seen in the molecular size distribution. All asphalts underwent immediate change in molecular size distribution on contact with hot aggregate at 115°C, particularly showing an increase in the LMS region. There was usually further change following 1/2 hour and 1 hour heating, but this was asphalt dependent.

Further data were obtained on heating asphalt with lime, and unlike the 1981 laboratory results, but in agreement with the road results of 1980, the LMS was increased in the presence of lime. When asphalts were heated with aggregate plus lime at 115°C for 1/2 hour, a much larger increase in LMS occurred than with aggregate alone. Heating with fly ash plus aggregate exhibited a similar increase.

Four antistripping agents were tested with one asphalt, and all of them upon exposure to heat increased the LMS fraction as compared with aggregate alone. In another asphalt, the effect of antistripping agent ranged from none to a decrease in LMS. All of these effects varied with the asphalt, the aggregate and the particular agent added.

Because of these changes, Jennings concluded that GPC tests on virgin asphalts are not a good predictor of asphalt performance. Jennings et al. (1982) compared various heating methods with changes that occurred during paving of four roads in 1980. Mixtures of asphalt and aggregates were heated at 115°C and 163°C and sampled at 5 minute intervals. The samples were all analyzed by GPC and compared with cores from the corresponding roads. Good correspondence was obtained on samples heated at 115°C for 5 to 10 minutes. Even up to forty minutes, the results, though less precise, were close.

Jennings et al. (1985b) expanded their road study to include samples in 15 other states covering a wide range of climate conditions. The nation was divided into zones of similar climate and the conditions of roads within each zone were compared on the basis of molecular size distribution. In general, in each zone, there was an LMS level above which all the roads were bad, and most of the good and excellent roads in each zone were those with lower LMS. There was however, a very large difference between the LMS percent that could be tolerated in warm zones and in very cold zones. Interestingly, several roads in Georgia with low LMS were exhibiting rutting.

There were quite a few exceptions. Some could be accounted for by construction practice or traffic loads, but others could not. There were, for instance, some quite low LMS asphalts that had cracked badly as well as high LMS asphalts that were performing well. Texas was included with samples from District 4 in the Panhandle. The number of samples was not large and were mostly from special projects including asphalt recycle and road overlays. The results were inconclusive.

Penetration/viscosity numbers (PVN) were available on some virgin asphalts used in test sections in Pennsylvania and Montana. Two of these were from bad roads that had low LMS fractions and these two roads showed the highest temperature susceptibility. Jennings suggested that high temperature susceptibility may account for the anomalous performance of the low LMS roads.

Most of the states submitted virgin asphalts used in the pavements. Some refineries showed identical GPC for the different viscosity grades, some showed consistent variation with grade and others random variation. Some old pavements exhibited GPC chromatograms that could not be derived from any of the asphalts now used in the state.

Florida submitted samples in which the effect of mixing temperature was studied using different aggregates. In two cases, there was almost no difference in the percent LMS as the mixing temperature was varied from 204°to 310°F and from 215 to 285°F. There was some increase after six months and one year which was larger for the asphalts mixed at the higher temperature. In a third test, there was a significant temperature effect and a much larger increase with aging. In all cases, newly constructed roads show a higher fraction of LMS than the corresponding virgin asphalt.

Adams and Holmgreen (1985) report some GPC results for test pavements at Dumas, Dickens and Lufkin. There were ten asphalts and six to seven were used at each location. They used THF as solvent with a 100Å column. This column gives a sharp peak at the beginning of the chromatogram due to exclusion of the larger size molecules. There was similarity in the common asphalts used at different locations and essentially no variation with viscosity grades (either AC-10 or 20). Three asphalts from Lufkin were evaluated for early aging. Both viscosity and GPC tests were performed. While all viscosities increased, as did the fraction of LMS, the two properties did not correlate in this small sample. There was also no correlation found between the chromatograms of the virgin asphalts and tensile strength of the paving mixture.

Asphalt Fractions and Their Aging

Many methods have been proposed for fractionating asphalt in addition to GPC and HPLC. Most of these are chromatographic while others involve solvent extraction, or chemical precipitation. A number of these methods are discussed by Altgelt and Gouw (1975) and Goodrich et al. (1985).

Perhaps the two most frequently used methods for characterizing asphalt by fractions is that of Rostler and Sternberg (1949), ASTM D 2006, and that of Corbett and Swarbrick (1960) Corbett (1969) ASTM D 4124. The method of Rostler and Sternberg has been most widely used in attempts to correlate fractions with performance, but as it is destructive and does not yield material for further study, we will focus on the Corbett procedure. This latter method involves precipitation of the asphaltene with n-heptane and separation of the remaining material into three fractions on calcined alumina. A saturate fraction is the material not adsorbed on percolation with n-heptane; a naphthene aromatic fraction is desorbed by toluene, and a polar aromatic fraction is desorbed by toluene and trichloroethylene.

One must realize that, to a considerable degree, these fractions are an artifact of the method and many similar separation procedures have been proposed and each gives a somewhat different fractionation. Asphaltenes are defined as the heptane (or sometimes hexane or pentane) precipitated fraction, but Long (1981) points out that in some asphalts waxes precipitate in the asphaltenes. Yet most would agree that some degree of fractionation, which will always be incomplete, greatly facilitates the study of these complex mixtures. Generally, though, the asphaltenes are the most polar fraction and are thus precipitated by hydrocarbons.

Hoiberg and Garris (1944) precipitated asphaltenes with hexane and then used a series of solvents to separate the remaining maltenes into four fractions. There was a hard resin that was probably the more polar part of Corbett's polar aromatics; a soft resin, likely a mixture of polar and naphthenic aromatics; waxes, the higher molecular weight and linear paraffins; and oils, paraffins and naphthenic aromatics. Upon decreasing penetration by vacuum distillation of the asphalt, asphaltenes and hard resins increased, oils decreased sharply, soft resins and waxes increased and then decreased. When penetration was decreased by air blowing, asphaltenes increased, hard and soft resins decreased, and oils and waxes were unchanged.

Hubbard and Stanfield (1948) reference a number of separating procedures that had been tried to that date. They describe a procedure in which asphaltenes are precipitated by pentane, and maltenes separated on alumina into oils and resins using first pentane and then methanol-benzene elution. The resins would appear to approximate Corbett's polar aromatics while the oils include the paraffins and naphthenic aromatics.

A procedure very similar to that of Corbett was used by Griffin et al. (1959). Asphaltenes were precipitated by isopentane, saturates (paraffins) were eluted from a silica gel column with isopentane. Aromatics, containing the naphthenic aromatic and much of the polar aromatic fractions were eluted with benzene; and the resins, the remaining polar aromatics, were eluted with ethanol-benzene. A microfilm oven test was performed on a variety of asphalts and their fractions and an aging index calculated from viscosity measurements. There was a very large increase in viscosity in going from saturate to aromatics to resins. The viscosities of the different saturate fractions varied rather uniformly with molecular weight, but this was not the case with the aromatic and resin fractions. There were order of magnitude differences between asphalts for these fractions of the same molecular weight.

Saturates from two asphalts showed no aging, while the aging index of a third saturate fraction, from a California valley asphalt, varied from 1.4 to 2.8. Aromatics from the California valley asphalt showed aging indexes from 1 to 4 while all others were below 2. The resins had the highest aging index among the maltene fractions. Synthetic asphalts prepared from various asphalt fractions showed high aging indexes whenever asphaltenes from California coastal asphalt were used. The conclusion is that poor aging characteristics for an asphalt may be due to the characteristics of one fraction of that asphalt.

In the original paper of Corbett and Swarbrick (1958), a different procedure was used that produced only three fractions: 1) asphaltenes by hexane precipitation, and then, by maltene separation on a porocell column, 2) a paraffin plus naphthene fraction by hexane elution, and 3) an aromatic oil fraction by elution with pyridine.

The effects of air blowing and hardening in the thin film oven test were studied. In neither test did the paraffins plus naphthenes fraction change appreciably. The aromatic oils fraction was very reactive. During air blowing highly condensed aryl groups with short side chains were reacted to asphaltenes, so the resulting molecules showed a decrease in aromatic rings per aryl group and an increase in aryl groups per molecule. During the oven test, molecules with fewer aryl groups and lower molecular weight reacted preferentially. The fraction of asphaltenes increased in both instances. Blowing increased asphaltene aryl condensation but not the oven hardening.

In their next paper, Corbett and Swarbrick (1960) describe a process that separated asphalt into five fractions in a procedure very similar to that used now. Asphaltenes were heptane precipitated. The paraffins plus naphthenes (P+N) were eluted from an activated alumina column with heptane. A single ring aromatic (SRA) fraction was recovered with heptane plus benzene, and a light multi-ring

(LMA) fraction with benzene. These two fractions approximate the naphthene aromatic fraction of the standard method. A heavy multi-ring aromatic (HMA) fraction, approximating the polar aromatics is eluted with pyridine. Air blowing caused no change in the (P + N) fraction and a small change in the (SRA) fraction. The (LMA) fraction decreased slightly, and the (HMA) fraction decreased considerably. The predominate change was (HMA) to asphaltene.

A three year old core was compared to the virgin asphalt. The (HMA) material was found to decrease in carbon side chains and increase in aromatic rings. Again, the main quantitative change was (HMA) to asphaltene. The approximate compositions of the five fractions were as follows:

P + N	A mixture of pure paraffin plus naphthene hydrocarbons with alkyl side chains
SRA	Primarily single ring aromatics with several long aliphatic side chains
LMA	A mixture of multi-ring aromatics with shorter side chains than in the (SRA) fraction
HMA	Multi-ring similar to (LMA) but of higher molecular weight
Asphaltenes	Multi-ring aromatics with short side chains and of still higher molecular weight

Corbett (1969) describes a procedure essentially the same as that of ASTM D 4124. He performed chemical analyses on the fractions from several asphalts and summarized the results as in Table 1-1.

Lamb and Cooper (1958), using a procedure similar to Corbett's five fraction method, found that asphaltenes and heavy aromatics increased with aging while light aromatics and paraffins decreased. They were unable to correlate rheological properties with the fractional composition but inclusion of the coefficient of thermal expansion improved the correlation.

Girdler (1965) described a method very similar to Corbett's in which asphaltenes were precipitated with heptane and paraffins eluted from the column with iso-octane. "Cyclics" were recovered with benzene, and resins with benzene-ethanol. This work was primarily concerned with the properties of the asphaltene fraction. In discussing the complex problem of asphaltene molecular weights, he notes that reported values vary dramatically according to measurement technique: 300,000 by ultracentrifuge, 80,000 by osmotic pressure, 2500–5000 by an ebullioscopic method, 600–4000 by cryogenics and 900–4000 by viscosimetry. Girdler favors 2000–5000. Boduszynski (1981) reports an average value of 1000 measured by field ionization mass spectrometry. Girdler reports that oxygen, sulfur and ni-

Table 1-1
Fractions Obtained Using the Corbett Analysis

Group	Average Mol. Wt.	Fraction Aromatic	Rings/Mole Naph.	Rings/Mole Arom.	Description
Saturates	650	0	3	0	Pure paraffins, pure naphthenes + mixed paraffins-naphthenes
Naphthene-Aromatics	725	0.25	3.5	2.6	Mixed paraffins-naphthene-aromatics + sulfur containing compounds
Polar Aromatics	1150	0.42	3.6	7.4	Mixed paraffin-naphthene-aromatics in multi-ring structures + sulfur, oxygen, and nitrogen compounds
Asphaltenes	3500	0.5	—	—	Mixed paraffins-naphthene aromatics in polycyclic structures + sulfur, oxygen, nitrogen compounds

trogen are present in chemically stable configurations, probably in rings. By precipitating asphaltenes with a series of hydrocarbons, he showed that nickel and vanadium are uniformly distributed throughout the asphaltene fraction. Diluting asphaltenes one part to 25,000 in benzene, he obtained a fair correlation between color of the solution and the carbon to hydrogen ratio and a somewhat poorer correlation with the aromatic to aliphatic ratio.

Corbett (1970) presents typical compositions and molecular weights for all 4 fractions. These values are illustrated in Table 1-2.

Petersen, et al. (1974a) studied oxidation of asphalt and Corbett fractions on quartzite and flouropak 80 and on other materials (1974b). They found that quartzite catalyzed oxidation of paraffins and naphthene aromatics but not polar aromatics and asphaltenes. They concluded that adsorption of polar compounds in the latter fractions deactivated the catalytic effect, but catalysts present in the polar fractions catalyzed oxidation in the non-polar fractions as well as in the whole asphalt.

Analysis by Corbett and Merz (1975) of six asphalts used in Michigan road tests showed a consistent decrease in naphthene aromatics which convert to polar aromatics and, in turn, to asphaltenes. There was a fair correlation between the asphaltene content of these 18 year old sections and the absolute viscosity at 140°F and a fair correlation showing a decrease in performance rating with an increase in asphaltene content.

In studies of air blowing of asphalts, Corbett (1975) reported that some naphthene aromatics convert to polar aromatics and some polar aromatics convert to asphaltenes. However, while both of these aromatic fractions tended to decrease in size in these air blowing studies, in the road studies above the polar aromatics often did not. Using P_2O_5 and $FeCl_3$ as catalysts increases this rate of conversion of one fraction to another 2–3 fold and gives a higher penetration at the same softening point, especially with $FeCl_3$.

Corbett and Petrossi (1978) use Corbett fractions to compare the asphalts obtained by distillation to those obtained by hydrocarbon extraction. Distillation separates on the basis of boiling point which tends to concentrate the higher molecular weight fractions. Hydrocarbon solvents extract the more saturated hydrocarbons and then the lower molecular weights. Generally though, paraffins are removed preferentially by both procedures, then naphthenic aromatics, etc. Hydrocarbon extraction can produce a much harder asphalt predominating in asphaltenes

Table 1-2
Elemental Characterization of Corbett Fractions

	Average number of atoms per molecule in			
Element	Saturates	Naphthene Aromatics	Polar Aromatics	Asphaltenes
Carbon				
Paraffin chain	31	21	24	85
Naphthene ring	14	17	18	29
Aromatic ring	0	13	25	115
Hydrogen	85	94	105	350
Sulfur	0	0.5	1	4
Nitrogen	0	0	1	3
Oxygen	0	0	1	2.5
Average Molecular Weight	625	730	970	3400

and polar aromatics.

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 shows poor temperature susceptibility and poor low temperature ductility. A saturates/asphaltenes blend was not homogeneous but still displayed a good temperature susceptibility, but the mixture had 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 durability. Asphaltenes give the highest values of viscosity. The saturates which are always present in all asphalts make no contribution to good test quality."

Corbett notes 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, 1976, Garrick and Wood 1986, Newcomer and Soltav, 1982).

CHAPTER 2

ANALYSIS TECHNIQUES

A number of chemical, physical, and thermodynamic properties were used in this study to evaluate and characterize asphalts. Development of an improved gel permeation chromatography (GPC) technique for asphalts has been a paramount objective and this work is described in some detail. Other procedures that have been used in this study are outlined in varying detail. These other tests, apart from providing additional information that may be useful in predicting asphalt performance directly, are helpful in understanding and interpreting the GPC chromatograms. Descriptions of the techniques are presented in this chapter. Results for the various asphalts are presented in other chapters, where appropriate.

Development of GPC Analysis Technique

Introduction. Gel permeation chromatography (GPC) is an analysis technique that provides rapid fractionation of an asphalt sample, primarily on the basis of molecular size. The dissolved sample is injected into a continually flowing stream of solvent, also called the mobile phase or carrier, which carries the sample through a column packed with highly porous particles. Smaller molecules take longer to elute from the column since they are more likely to diffuse into the pores of the column. Larger molecules diffuse into fewer pores so they take less time to elute.

GPC columns are manufactured in a variety of well regulated pore sizes. Thus, with proper selection of column pore size, the technique can be used to separate molecules over a wide range of molecular sizes. This feature makes GPC a prime candidate for analyzing of asphalts.

Suggested techniques and procedures of Jennings and co-workers (Jennings, 1977, Jennings, et al., 1980, 1981, 1982, 1985a, 1985b, Jennings and Pribanic, 1984) have been evaluated extensively. One of the most important procedures adopted for this study is the inclusion of an asphalt standard with each sample set. Also Jennings' technique of quantifying the asphalt chromatogram was employed. In two key areas, the techniques used in the present study have deviated from Jennings and other researchers. For reasons that will be discussed later, a larger sample size was adopted. Brulé et al. (1986) also increased sample size in order to emphasize the aggregation of large molecular size components. In this research, an even larger sample than that used by Brulé (7 mg compared to 1 mg) was employed. In addition, a method for using toluene as a carrier has been developed in the present study. Jennings et al. (1982) and other researchers have shown the possibilities of using other carriers, but before this tetrahydrofuron (THF) was the only carrier that had been used with asphalt on a long term basis where questions of reproducibility could be addressed.

Objectives. A major goal of the current study was to develop GPC as a tool for asphalt evaluation. As will be discussed in more detail in the operating parameters portion, chromatographic conditions can have a great impact on a GPC separation. This is especially true for asphalt, which is composed of a wide variety of chemical species. For example, the large molecular size region, which is chiefly asphaltenic in nature, can be spread out in a broad shoulder or it can be concentrated in a sharp peak, depending on the choice of column pore size. Therefore, a great deal of work went into developing operating conditions that produce chromatograms which emphasize the differences between asphalts. Once distinctive profiles were obtained, attempts were made to relate the characteristics of GPC profiles to asphalt performance.

Apparatus. In this work an IBM LC-9533 ternary gradient liquid chromatograph was employed. The pump in the LC-9533 was a three-piston pump designed to give a very well controlled flow rate with minimal pressure fluctuation. The original IBM system was slightly modified by replacing all the teflon tubing with stainless steel, it being more resistant to THF. The columns were made by Polymer Laboratories and they contain 5 micron, PL Gel Packing and were 60 cm in length. Two refractive index (RI) detectors were used in series. The first was a Waters Model 401 while the second was an Laboratory Data Control Detector supplied by IBM (IBM Model 9525). To aid in processing a large number of samples, an IBM 9505 Autosample Handler was used. A Rheodyne 6-port injection valve was also available for manual injections. An IBM 9002 Bench top computer equipped with 10 megabyte hard disk and dual floppy drives was used to collect and store the data and to control the autosampler and chromatograph. The computer was also used in the analysis of data.

Experimental Procedure. Before THF was used as a carrier, the peroxides and water were removed by refluxing the THF over sodium metal for 40 to 60 minutes and then distilling to a solvent reservoir and storing under a helium blanket. Toluene was purified in a similar manner before use as a carrier. To prepare the asphalt samples for injection, the asphalt was weighed to 0.001 gm accuracy and dissolved in distilled solvent measured to 0.1 ml to give a concentration of 7%. The sample concentration was closely controlled since sample size has a very large impact on the results. After dissolution, the sample was filtered through a 0.45 micron filter to remove particles that might damage the column. An American Petrofina AC-10 asphalt was selected for use as an asphalt standard and was injected at the beginning and end of each batch of samples being analyzed. Also, a mixture of known pure compounds (2×10^6 molecular weight Polystyrene, 2350 molecular weight Polystyrene, normal Octacosane and Orthodichlorobenzene [ODCB]) were injected. The ODCB peak was used to calculate plate counts (see Chapter 1) to regularly monitor the column condition. Injecting the standard asphalt and known compounds were essential for monitoring performance and obtaining reproducible data. Typical reproducibility that was obtained when proper procedures were followed is shown in Figure 2-1 for toluene carrier solvent and Figure 2-2 for THF.

Operating Parameters. There are several operating conditions or parameters which may be changed to optimize GPC analyses. These include column pore size, injected sample size, type of detector, and the carrier solvent. The importance of each of these parameters and the conditions chosen for this study, are discussed in the following paragraphs of this subsection. Extended discussions of solvent effects and reproducibility are presented in later subsections.

In this work, two column arrangements were used for most analyses. One arrangement consisted of a single 100 Å column. This small pore-size column causes the larger species in the asphalt to be totally excluded from the pores of the gel and to elute in a single, narrow peak. The second configuration used was a 500 Å column. In some cases a 50 Å column was added. The 500 Å column provided some fractionization of the largest molecular size species. The 50 Å column (when used) provided some further separation of the smaller molecular size species. The objective was to obtain more fractionation and therefore more distinctive chromatograms. Previous work performed at Texas A&M (Adams and Holmgreen, 1985) used the 100 Å column exclusively.

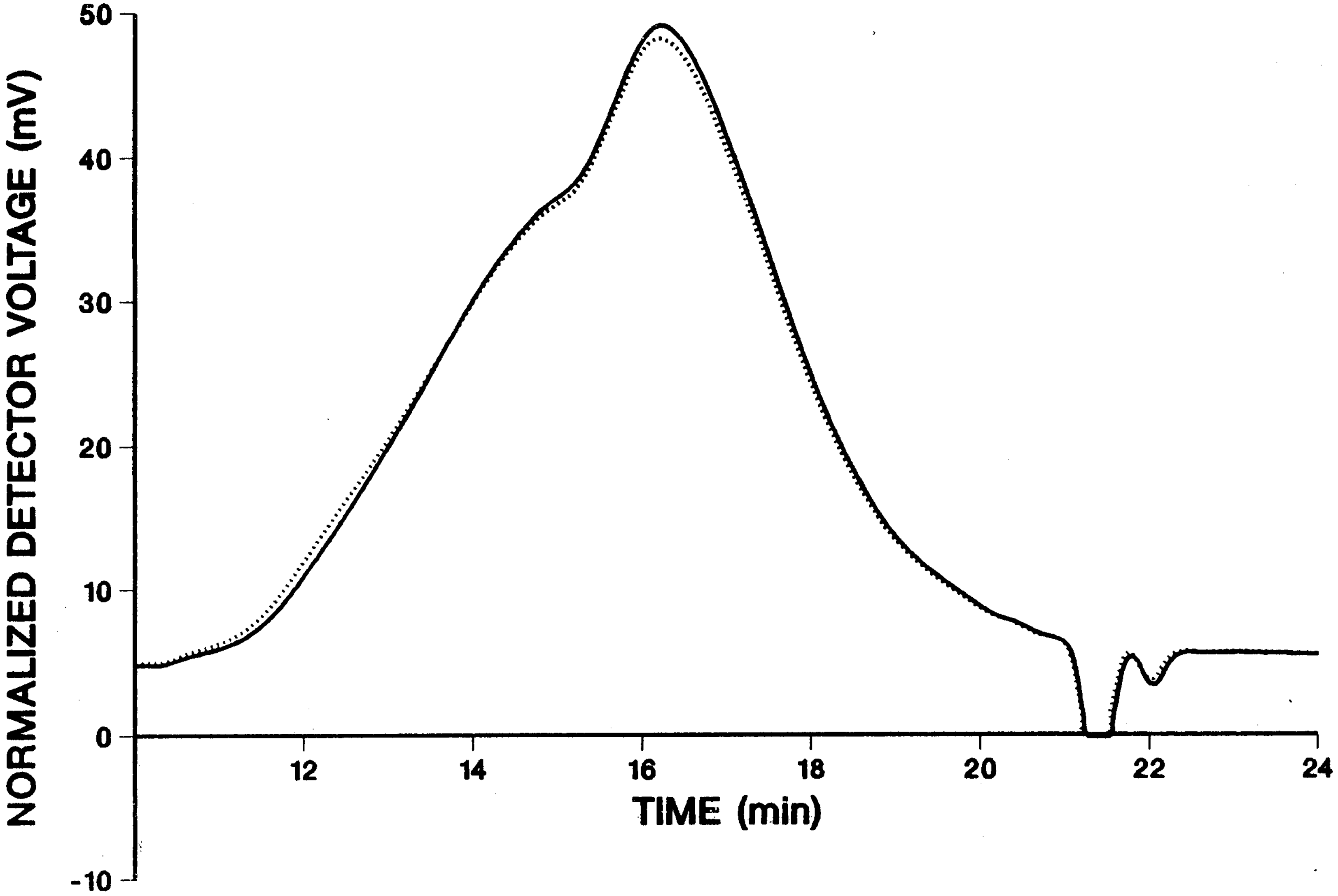


Figure 2-1
Reproducibility of Two Asphalt Standard Chromatograms in Toluene
500 Å Column/Toluene/100 μl/7%

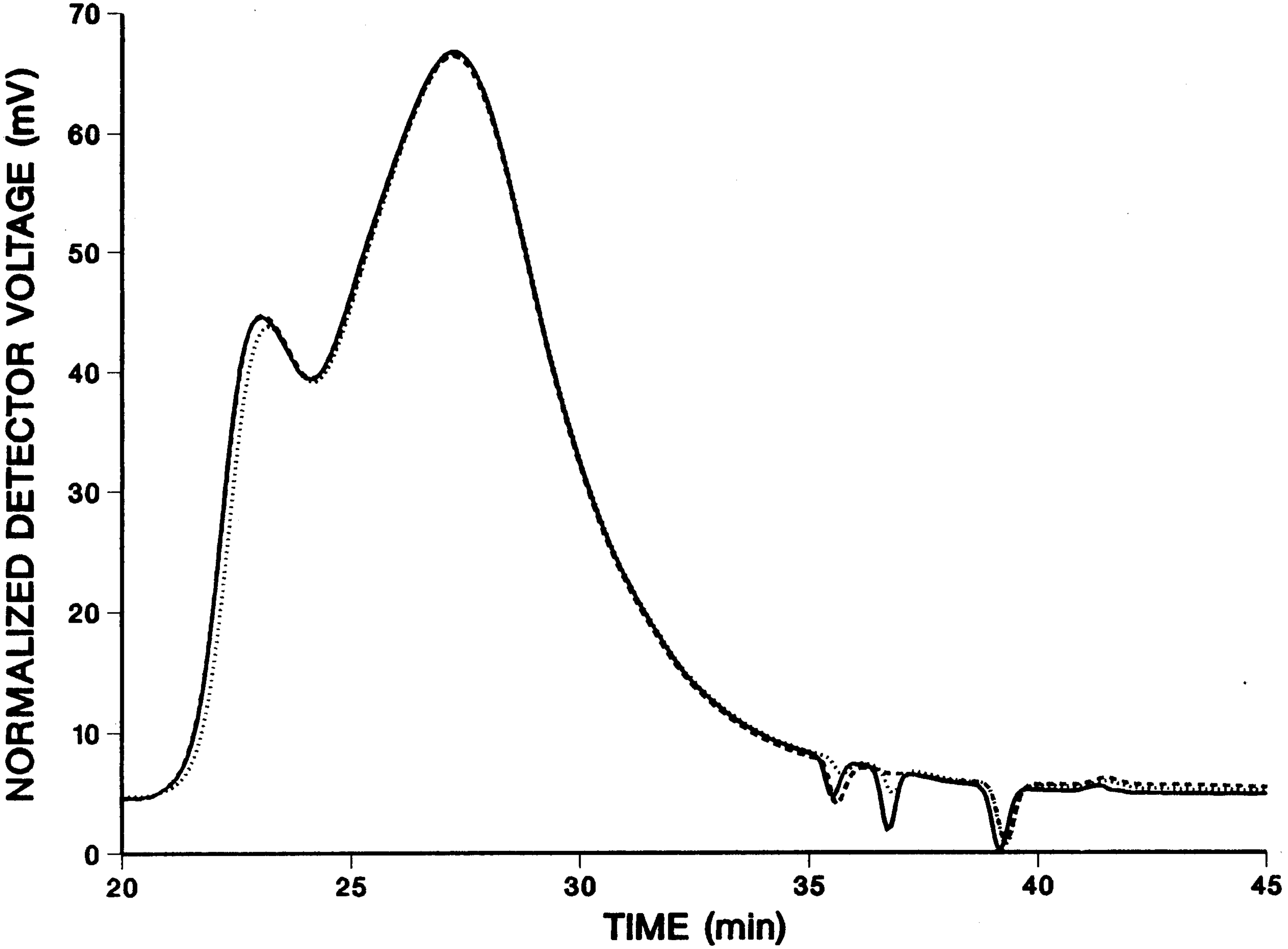


Figure 2-2
Reproducibility of Three Asphalt Standard Chromatograms in THF
500 Å and 50 Å Columns/THF/100 μl/7%

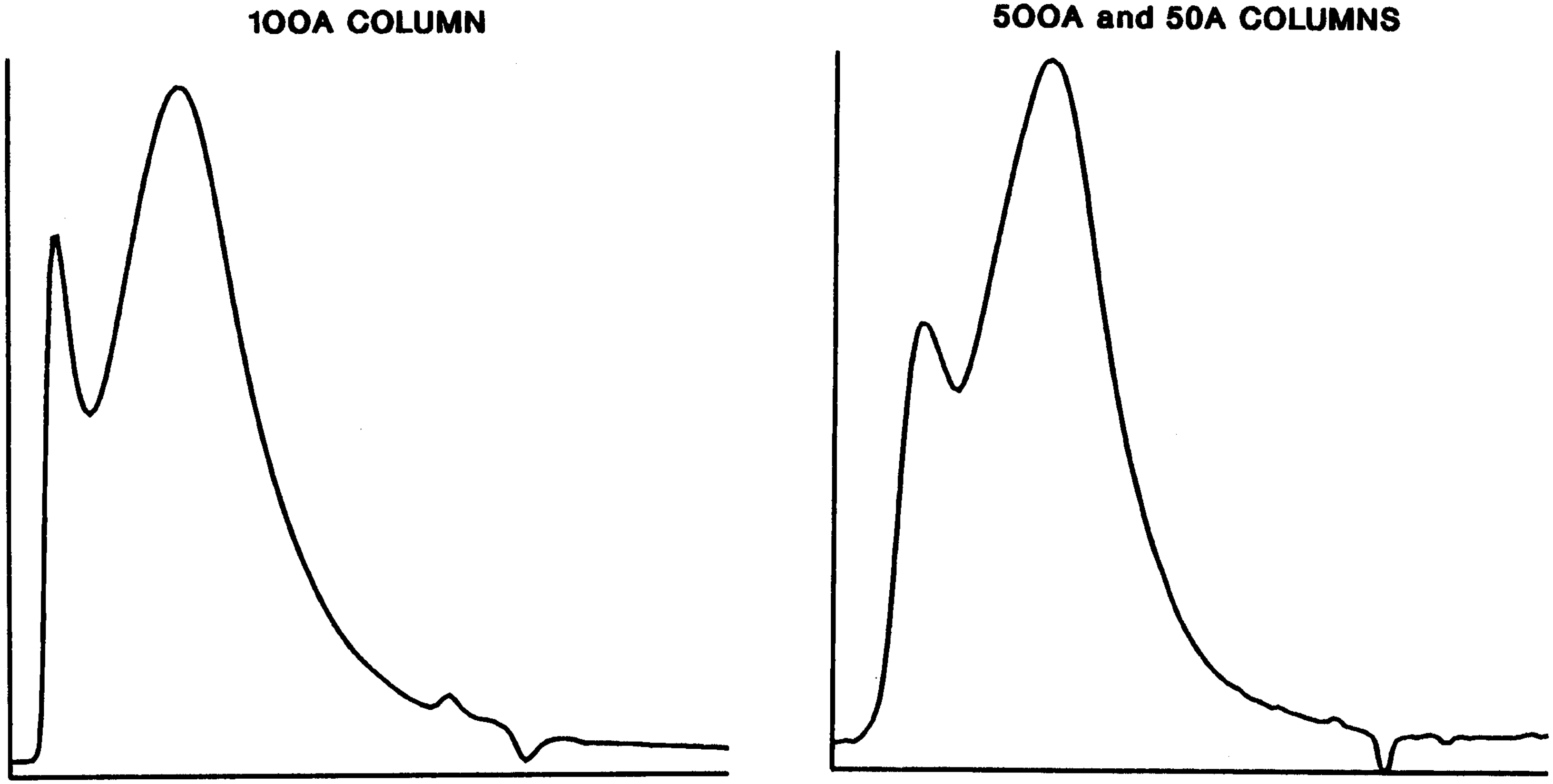
Figure 2-3 shows the effect pore size selection can have on the separation. In general, the exclusion of a large fraction of the species is not desirable since this could mask valuable information. There is a possibility that all of the information which is important to asphalt performance could be contained in the leading peak of the excluded species.

Solvents Effects. In this study two types of refractive index detectors were used. The first detector was an IBM Model Number 9525 manufactured by Laboratory Data Control. It measured the refractive index difference indirectly using Fresnal's Law. This detector was found to be susceptible to light absorption or scattering by the sample. The other detector was a Waters Model 401 and was less sensitive to light scattering since it measured the position of the light deflection caused by the change in refractive index. The Waters 401 detector was of the type that has been typically used in asphalt studies. Figure 2-4 shows representative data from the two detectors.

Although the negative peak given by the IBM detector is not fully understood, data for all samples using this IBM detector were recorded throughout the study. The size of the negative peak appears to correlate with asphaltene content and may be of use in future studies.

The amount of sample injected has also been found to have a large effect on GPC results. This was shown by Jennings and Pribanic (1984) who found the amount of LMS (Large Molecular Size) material increases with increasing sample size. As shown in Figure 2-5, this characteristic is confirmed in the present study. As the concentration of sample is increased, the leading peak clearly grows. The growth of this LMS region is probably attributable to agglomeration of molecules into clusters which then act as very large molecules. These species probably exist as agglomerations in the asphalt binder as well. In the current work, the largest practical sample size was used since this emphasized the differences in the asphalts so that measuring and understanding this effect likely is important to asphalt performance. For both toluene and THF carrier solvents, the injected sample was 100 microliters of a 7 weight percent solution.

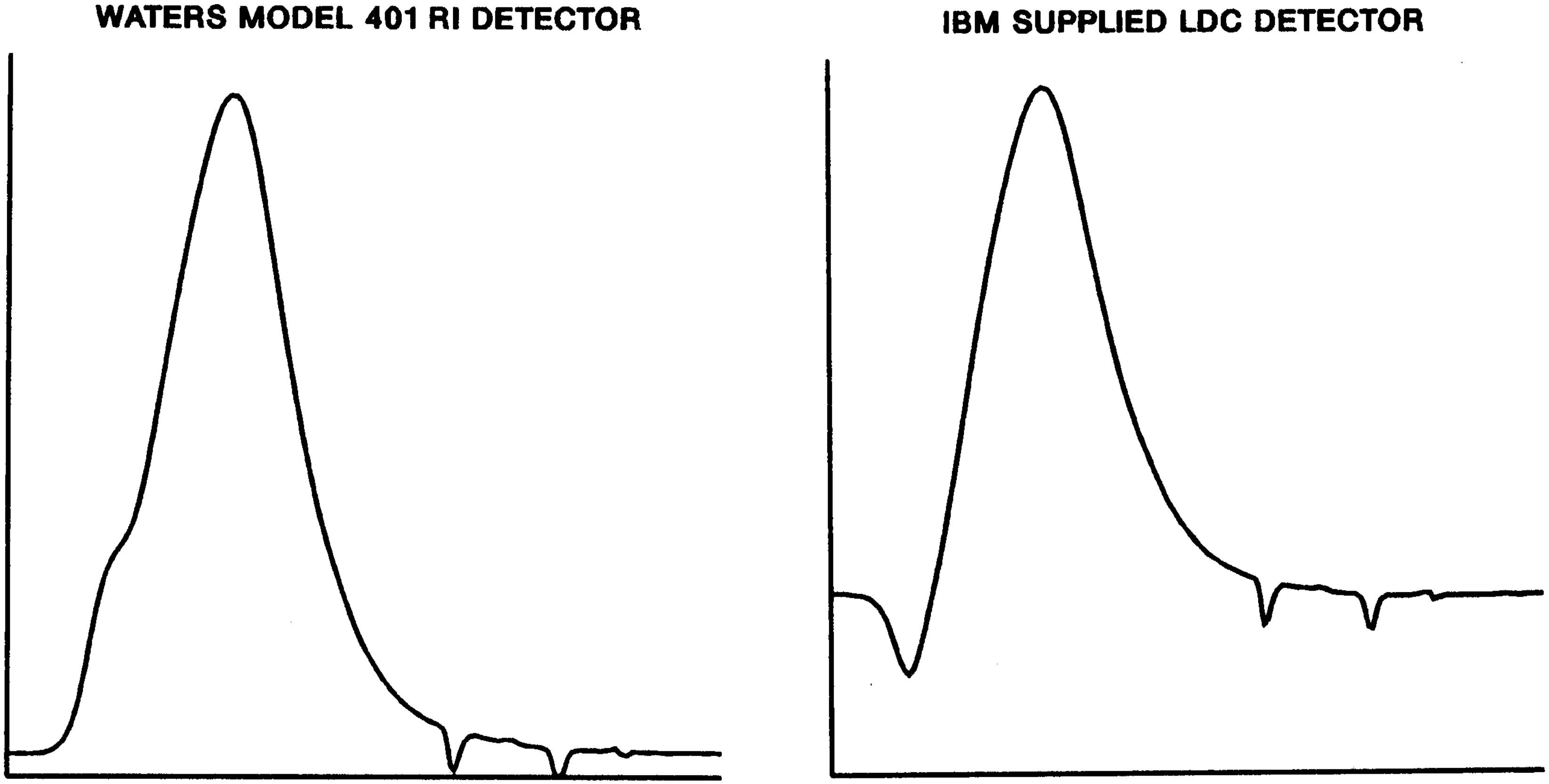
The carrier solvent can have a large impact on the GPC results in two ways. First, the refractive index of the carrier is important since RI detectors operate by comparing the refractive index of the sample stream to a reference stream of pure carrier. If the sample has a refractive index similar to that of the carrier it will not give a strong response. Thus, since different components of the asphalt will have



100A COLUMN

500A and 50A COLUMNS

Figure 2-3
Effect of Column Pore Size on Chromatography
Dorchester AC-20/Dickens Tank/THF/100μl/7%



WATERS MODEL 401 RI DETECTOR

IBM SUPPLIED LDC DETECTOR

Figure 2-4
Differences in Refractive Index Detector Response
Exxon AC-10/500 Å and 50 Å Columns/THF/100 μl/7%

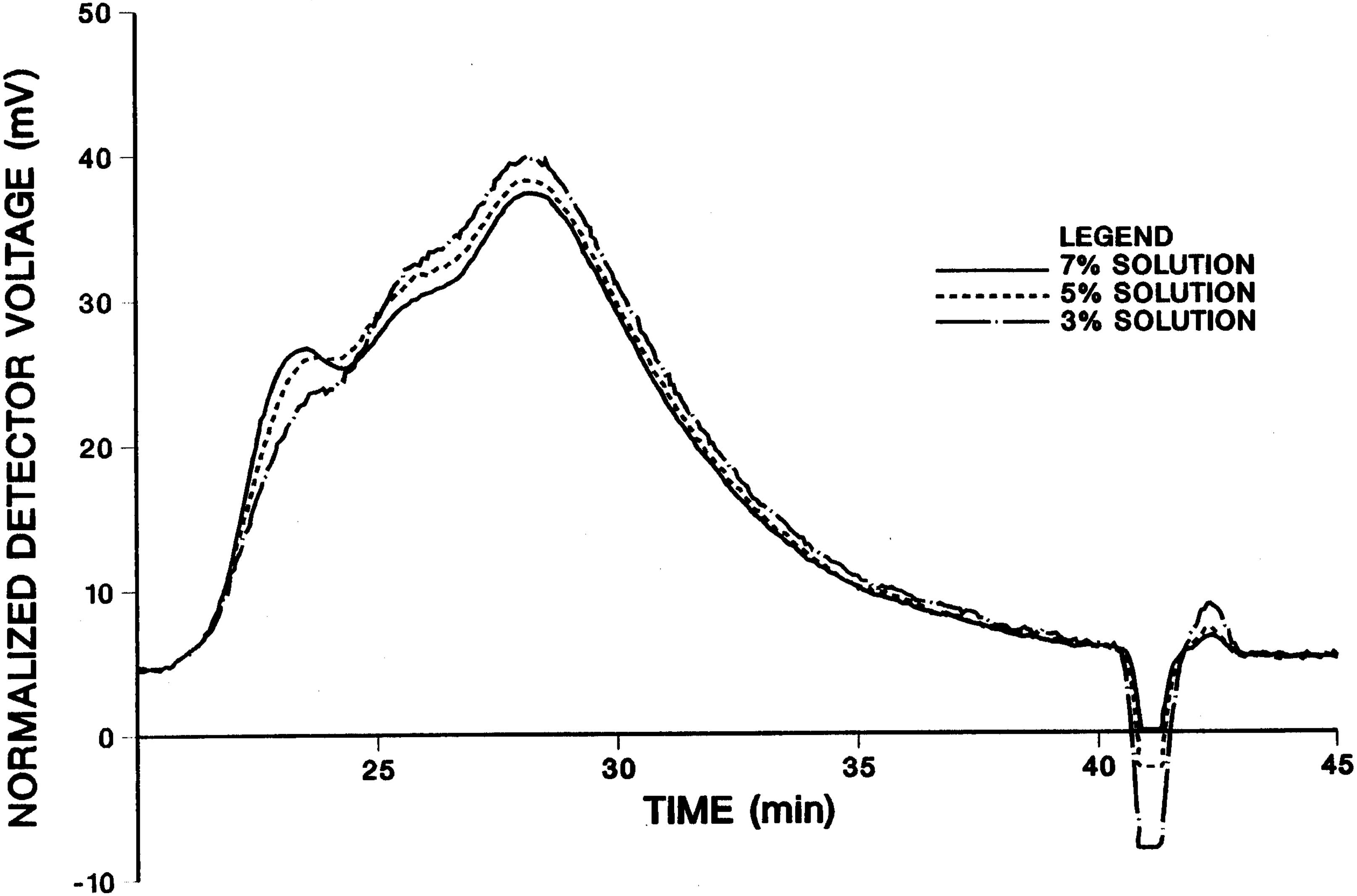


Figure 2-5
Concentration Effects on Gel Permation Chromatography
500 Å and 50 Å Columns/Toluene/100 μl

different refractive indices, the carrier can affect the results given by GPC. Second, solute/solvent and solute/column interactions both play important roles in determining the elution time of components. Since asphalts are made up of a wide variety of components, the type of solvent can have a large impact on the time various constituents take to travel through the column. Furthermore, a poor solvent can increase the formation of aggregates of smaller molecules forming apparently larger molecules that elute sooner.

THF has been the most commonly used solvent for GPC analysis of asphalts due to its strong solvent power. Toluene was selected as a second carrier in this study due to its widely different solvent characteristics. Other researchers at Texas A&M (Anthony and Philip, 1979) have studied the influence of carrier on the retention time of pure compounds. They concluded that THF hydrogen bonds with some molecules forming larger agglomerates that elute from the column sooner.

To give further insight into solute/solvent interactions, several pure compounds were analyzed in this study using both THF and toluene as the carrier solvent. Five classes of compounds were analyzed: normal paraffins, polystyrene, straight chain alcohols, straight chain aldehydes and polyethers. The results of these experiments are discussed below and presented in Table 2-1.

Straight chain hydrocarbons of 36, 28, 12 and 7 carbons in length were analyzed. No significant differences in retention times using the two carriers was noted.

Polystyrenes of 470,000, 20,000, 8,000 and 2,350 molecular weight were analyzed in toluene and THF. Again, since the polystyrenes have no functional groups, little difference in retention times between the two carriers was found.

Figure 2-6 shows a comparison of straight chain alcohols to normal paraffins having the same carbon numbers analyzed using THF. The –OH group causes the molecule to elute faster due to THF hydrogen bonding and the associated increase in size of the molecule and also by reducing any tendency for solute adsorption. On the other hand, in toluene, alcohols take longer to elute than normal paraffins of the same carbon number.

Aldehydes demonstrate the same interaction with the solvent as alcohols although not as drastically. The apparent size increases in THF and decreases in toluene.

Table 2-1

Comparison of Elution Order in THF and Toluene

THF		Toluene	
Compound	Retention Time (min)	Compound	Retention Time (min)
PS[1] 470,000 MW	20.09	PS 470,000 MW	20.37
PS 20,000 MW	21.33	PS 20,000 MW	20.80
PS 8,000 MW	22.14	PS 8,000 MW	22.62
IGEPAL-CO® 990	23.12	IGEPAL-CO® 990	24.65
PS 2,350 MW	24.50	PS 2,350 MW	25.11
IGEPAL-CO® 890	24.74	IGEPAL-CO® 890	26.27
Tripalmitine	26.62	Tripalmitine	27.18
IGEPAL-CO® 720	27.30	Hexatriacontane (C_{36})	28.00
Cholesteryl Stearate	27.65	Cholesteryl Stearate	28.00
Hexatriacontane (C_{36})	27.66	IGEPAL-CO® 720	28.56
Octacosane (C_{28})	28.64	Octacosane (C_{28})	29.05
IGEPAL-CO® 520	29.14	Vitamin E Acetate	29.95
Vitamin E Acetate	29.19	Octadecane (C_{18})	31.05
1-octadecanol (C_{18}-OH)	29.73	IGEPAL-CO® 520	31.94
Octadecane (C_{18})	30.50	1-octadecanol (C_{18}-OH)	32.20
IGEPAL-CO® 210	30.87	Dodecane (C_{12})	32.95
1-undecanol (C_{11}-OH)	31.40	1-dodecanal (C_{12} =O)	33.38
1-dodecanal (C_{12} =O)	32.01	IGEPAL-CO® 210	34.11
Dodecane (C_{12})	32.28	1-undecanol (C_{11}-OH)	34.86
1-heptanol (C_7-OH)	32.76	heptane (C_7)	35.55
1-heptanal (C_7 =O)	34.18	1-heptanal (C_7 =O)	36.15
Heptane (C_7)	34.60	1-heptanol (C_7-OH)	37.48

*PS–Polystyrene

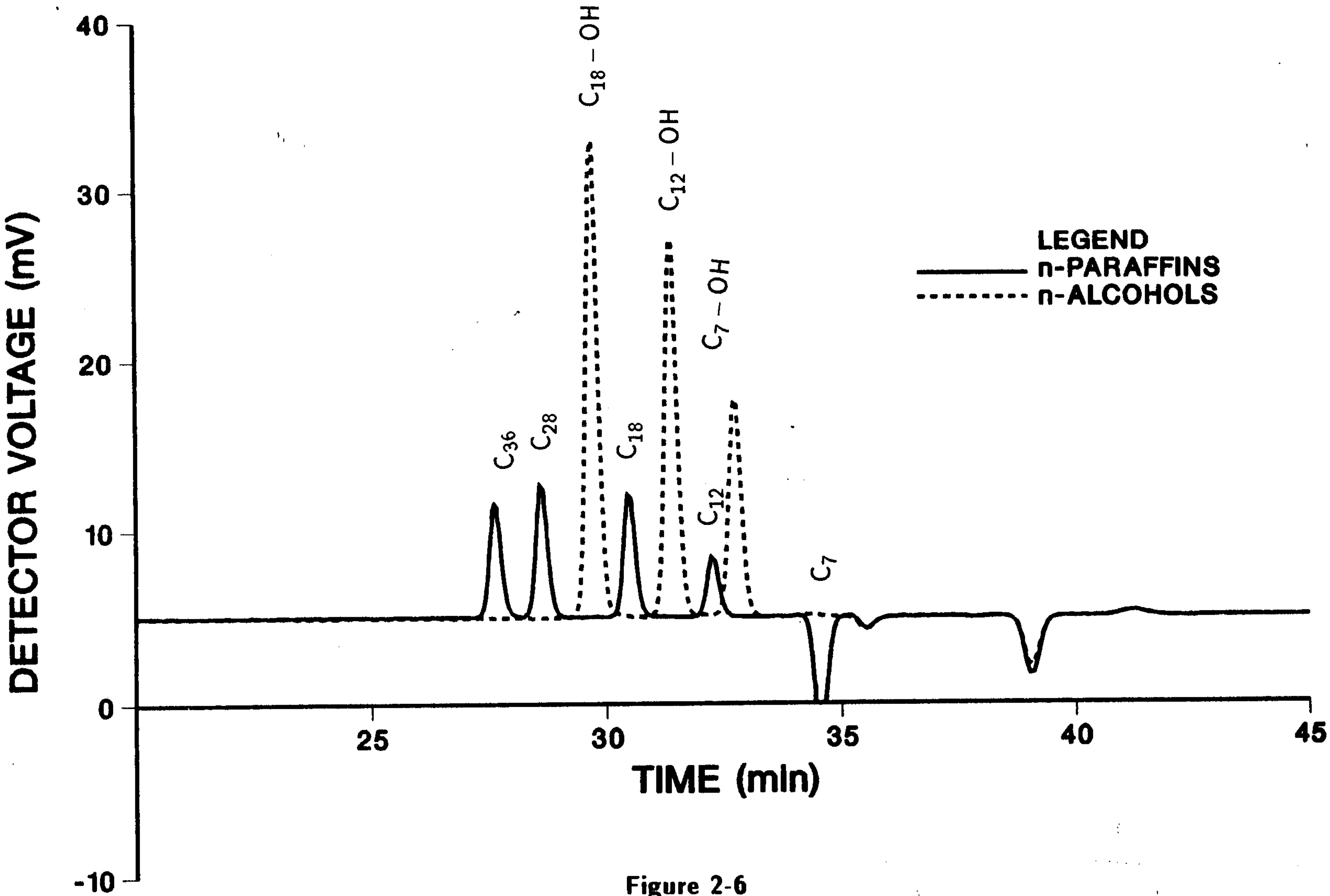


Figure 2-6
Retention Time Comparison of n-Alcohols and n-Paraffins in THF
500 Å and 50 Å Columns/THF/100 μl/approx. 1%

A series of polyethers IGEPAL-CO® compounds of various molecular weights were studied. IGEPAL-CO has the formula:

$$4(C_9H_{19})C_6H_4O(CH_2CH_2O)_xCH_2CH_2OH$$

where x=1, 4, 11, 39 and 99 giving molecular weights ranging from 308 to 4,625. As might be expected, these compounds eluted sooner in THF than in toluene.

These results support the concept that the stronger the interactions of the carrier solvent are with a given compound, the sooner the compound will elute from the column. Since THF is strongly polar, it interacts strongly with the polar constituents in asphalts and these molecules elute sooner from the column than the less polar ones of equivalent molecular weight and size. Conversely, with a toluene carrier solvent, which is less polar than THF, the polar constituents of asphalt would be held in the column longer than they are in THF. Thus, toluene can give different separations than THF.

Another way in which a less polar solvent (say toluene) can create different chromatograms from the strongly polar THF is by causing aggregation of asphalt molecules which are difficult to hold in solution. Asphaltenes, being the largest molecular weight species in asphalt and also the highest in polarity, are the most difficult to maintain in solution. It has been suggested that they can associate or agglomerate in solution to form micelles, according to the model of Yen (1979) to form still larger species. For these molecules, a less polar solvent, rather than leading to a longer elution time through effects discussed in the preceding paragraph, could well produce a shorter time, relative to the strongly polar THF. This aggregation effect has been suggested by both Snyder (1969) and Brulé (1980) as being responsible for the growth of the early eluted region of an asphalt chromatogram with an increase in the injected sample size.

The characteristic differences in using THF and toluene as carriers is demonstrated for the whole asphalt in Figure 2-7. Marked differences in chromatograms of whole asphalts are observed. Generally, the toluene profiles are more disperse and have more peaks or shoulders than do those with THF.

GPC analyses of Corbett fractions (Corbett, 1969) provide insight as to why these differences occur, in the context of the effects discussed above (Figures 2-8 and 2-9). First, we see some shifts in the elution times of the Corbett fractions, relative to each other. Direct comparisons of elution times in Figures 2-8 and 2-9

IGEPAL-CO is a registered trademark of GAF corporation should not be made, since two columns in series were used with THF, whereas, only one column was used for toluene analyses. This resulted in twice the void volume with THF compared with toluene. Comparisons of elution times of the fractions relative to each other for a given solvent can be made, however. The saturates peak center elutes sooner in toluene than both the polar aromatics and naphthene aromatic fractions whereas in THF it elutes later. Second, significant refractive index effects exist and are most obvious for the saturates which have a lower refractive index than toluene (and hence give a positive peak in toluene) but a larger refractive index than THF (and hence give a positive peak in THF). Third, the naphthene aromatics fraction appears much larger relative to the polar aromatics or asphaltene fractions in toluene, probably again due to refractive index differences. Also, there is some alteration of the peak shapes in that the polar aromatics profile in toluene does not have the leading peak observed in THF but is instead a smooth, nearly symmetric, single peak. The combination of these effects produces the significantly different profiles.

The net effect of these results is that the THF and toluene chromatograms are, to some extent, seeing different parts of the asphalt cements. Analyses using THF tend to emphasize the asphaltene and polar aromatic fractions and de-emphasize the naphthene aromatic fraction. Analyses in toluene tend to de-emphasize the asphaltenes and polar aromatics in favor of the naphthene aromatics.

Reproducibility of Chromatograms. Using several different carriers, Jennings et al. (1982) demonstrated that the carrier type has an enormous impact on GPC analysis of asphalts. Jennings did not however, determine if analyses using other carriers could be performed reproducibly.

In the present work, extensive effort was required to demonstrate the reproducibility of the method. It was found that the asphalt fouled the column when toluene was employed as the carrier, drastically reducing the separation efficiency of the column. This problem seemed to affect the smaller pore size (100 Å, 50 Å) columns most. Therefore, only the 500 Å column was used. Fortunately, the fouling process was found to be reversible by using appropriate time intervals between injections. As a result, approximately three column volumes of toluene were allowed to pass through the column between asphalt injections. An orthodichlorobenzene (ODCB) injection before each asphalt injection was used to monitor the plate count for the column.

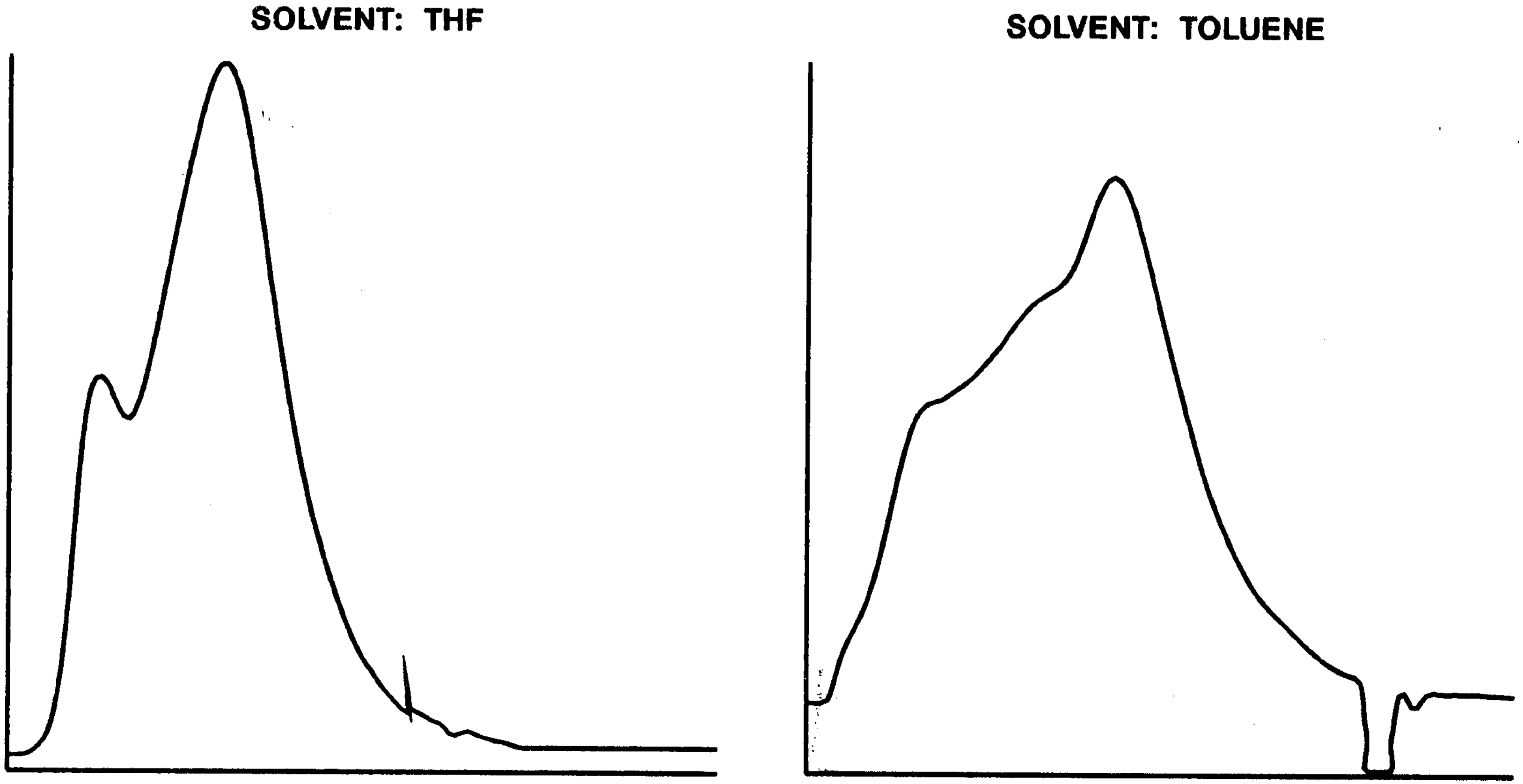


Figure 2-7
Solvent Effects on Chomatography
Dorchester AC-10/100 μl/7%

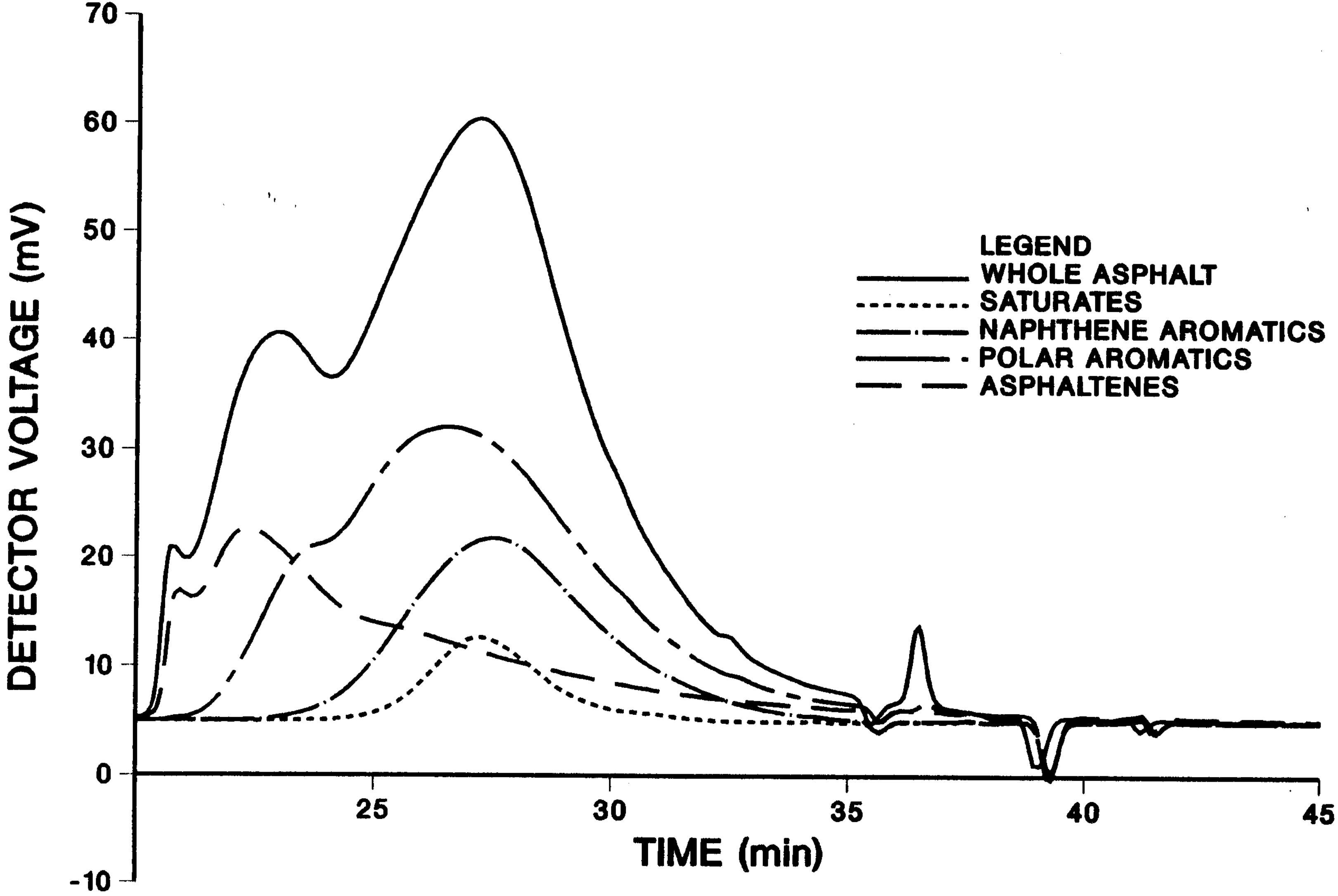


Figure 2-8
Overlaid Chromatograms of the Individual Corbett Fractions in THF
Macmillan AC-20/Dickens 1984 Core/500 Å and 50 Å Columns

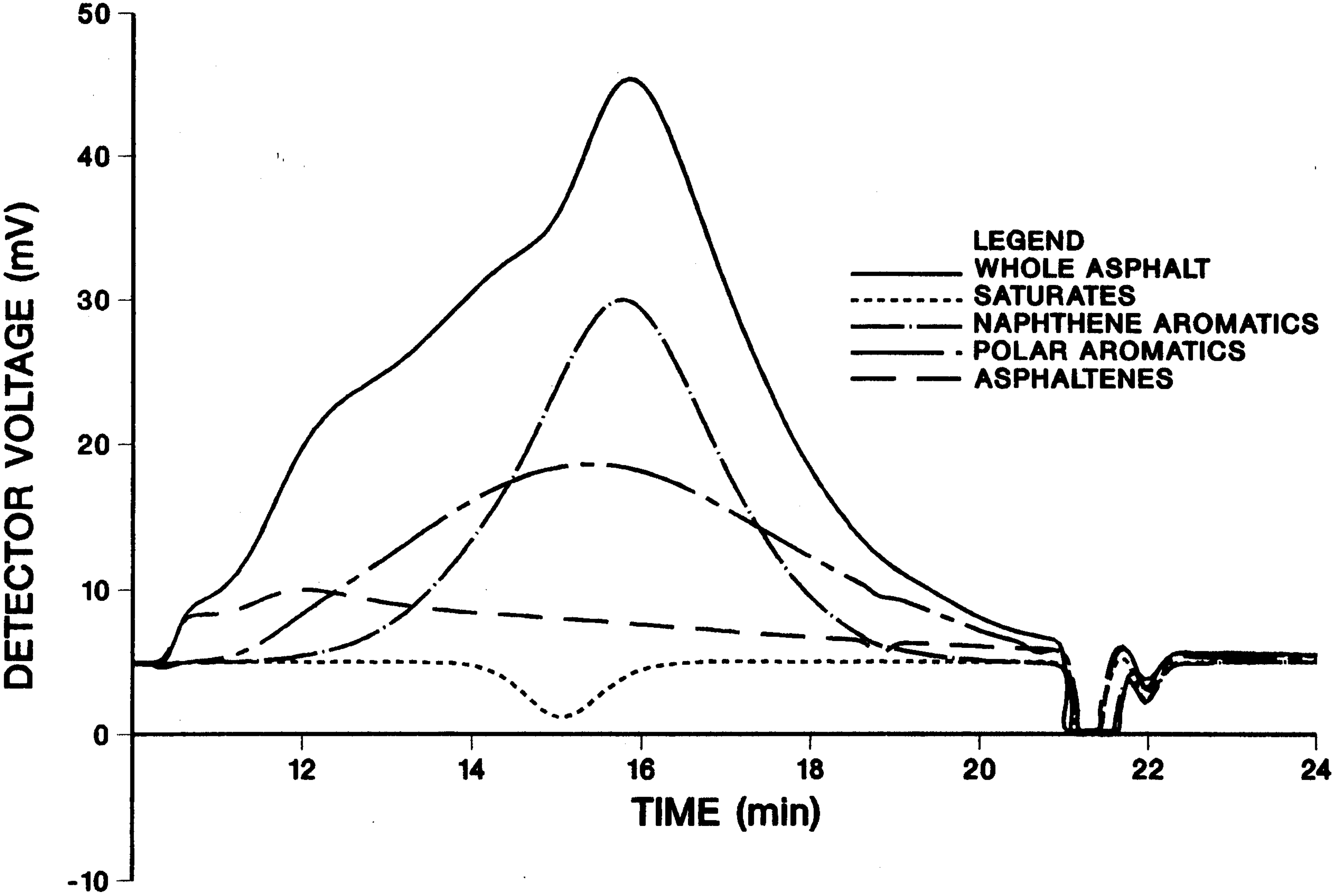


Figure 2-9
Overlaid Chromatagrams of the Individual Corbett Fractions in Toluene
MacMillan AC-20/Dickens 1984 Core/500 Å Column

Quantitative Representation of Chromatograms. A method to quantify the GPC results was also desired for this study and an adaptation of the technique used by Jennings (1977) Jennings et al. 1981, 1982 was chosen. In this method, the chromatogram was broken into three sections and the area under the curve in each of these sections was found by numerical integration. In the present work, this corresponded to dividing the chromatogram into three five minute sections between 20 and 35 minutes for the 500 Å and 50 Å column arrangement. When a single column was used, the chromatogram was broken into four minute sections from 10 to 22 minutes in retention time. As discussed in Chapter 1, Jennings used the terms large molecular size (LMS), medium molecular size (MMS) and small molecular size (SMS) for the three regions. A sample chromatogram showing the three areas is shown in Figure 2-10.

Conclusions. GPC techniques for the analysis of asphalts were developed using toluene and THF as carrier solvents. The development study showed that using toluene as a carrier solvent could add valuable information on asphalt composition to that obtained using THF. The study also showed that operating at higher sample concentrations would help produce chromatograms which emphasize the differences between different asphalts. The column pore size chosen was demonstrated to have a great effect on results. A two-column 500/50 Å series combination in THF and a single 500 Å column in toluene proved adequate for the asphalt separations. A standard asphalt and several pure compounds were used to insure reproducibility of the GPC methods. The resultant GPC chromatograms were also found useful for identifying asphalts, since the chromatograms of different asphalts appear markedly different.

Combined GPC/GC-MS Analysis

An analytical procedure based on the combined use of three separations and identification techniques was devised to study virgin road asphalts, recovered asphalts from road pavements and asphalts modified by the use of additives. Vacuum distillation was used to separate the asphalt into volatiles and non-volatiles. The volatiles were analyzed by capillary gas chromatography-mass spectrometry (GC-MS). The asphalt samples as well as both the volatile and non-volatile vacuum distillation products were analyzed by GPC. These analytical procedures provided additional detail on the chemical composition of asphalt samples.

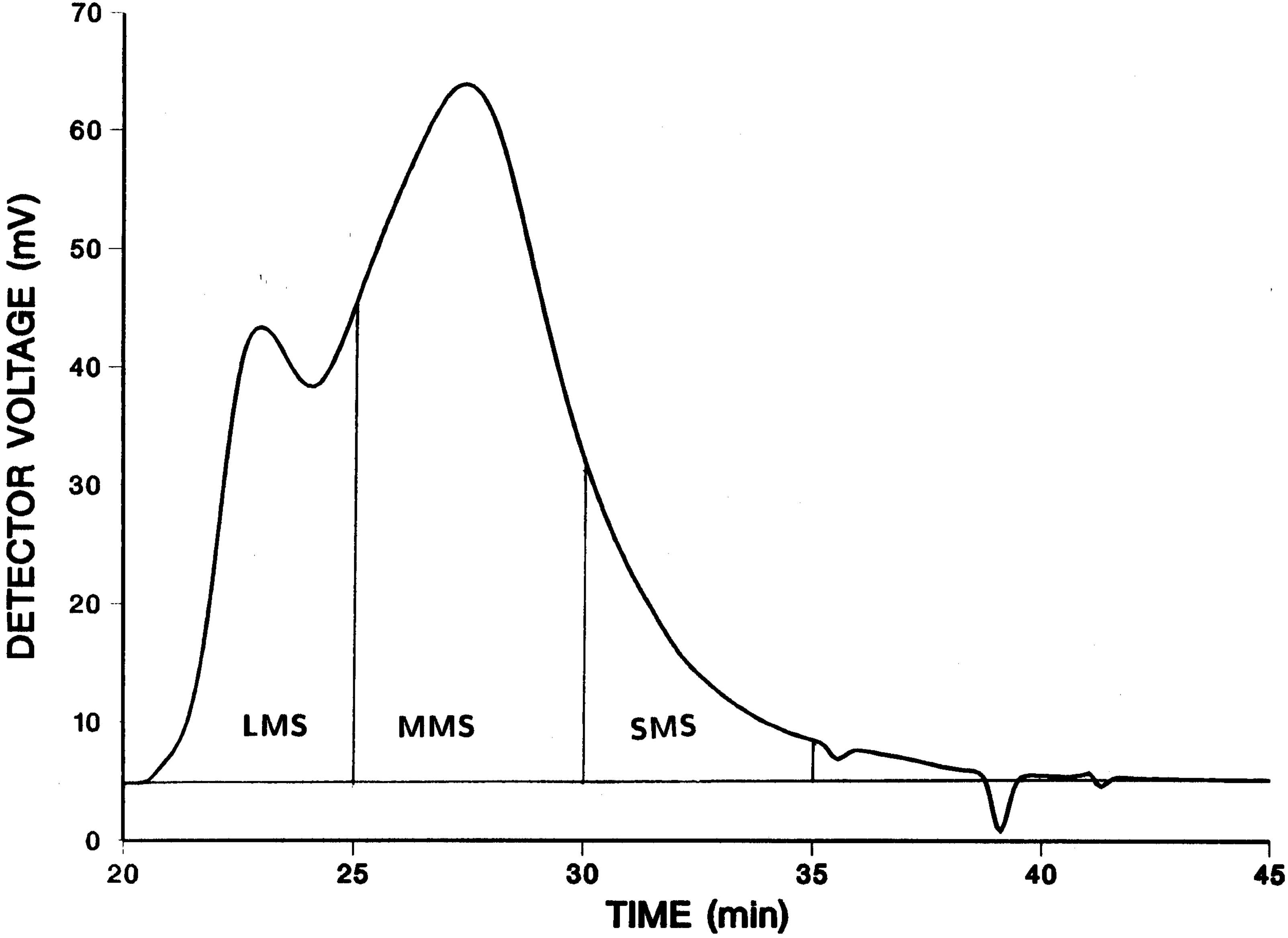


Figure 2-10
LMS, MMS, SMS Regions of The GPC Chromatograms
Dorchester AC-5/500 Å and 50 Å Columns/100 μl/7%

Asphalt Distillation. Vacuum distillations of asphalt samples were carried out using a distillation system. Temperature was controlled by a Thermolyn Furnatol I temperature controller. The schematic representation of the distillation apparatus is shown in Figure 2-11. The outside of the glass vessel was heated and the vapors deposited on an inside liquid nitrogen cold finger. The sample was maintained at 10^{-2} torr by a single stage vacuum pump and the degree of vacuum was monitored by a mercury manometer. The mercury manometer could not accurately measure the volume but could check for any leaks. The sample was normally heated slowly from room temperature to the distillation temperature limit, which varied from 572 to 670°F. Heat-up time was increased for certain samples which showed greater tendency for splashing.

Gel Permeation Chromatography. Samples were dissolved in additive–free tetrahydrofuran (THF) to obtain a 10% solution. The complete dissolution of asphalt in THF was aided by placing the samples in an ultrasonic bath for 15 minutes. The solutions were filtered using a $0.5\,\mu$m membrane filter (Supelco). The asphalt sample solutions were analyzed by a Water's Liquid Chromatograph (ALC 202) equipped with a $5\,\mu$m 100 Å PL gel column (stainless steel, 60 cm long, 7.8 cm ID) and a refractive index detector (Water's Model 401, $10\,\mu$m cell). Dry additive–free THF stored under a helium blanket was used as the mobile phase. The THF flow through the gel column was set at 1 ml per minute. The chromatographic data were collected by an IBM 9000 microcomputer with 1 megabyte RAM memory and two 8" floppy disk drives. Each 8" disk has about one megabyte storage capacity. The chromatograms can be displayed on the CRT or plotted on the printer-plotter on a real time basis. The raw data storage and post chromatographic calculations were performed with the aid of the Chromatography Application Program (CAP) and Gel Permeation Program from IBM.

GC-MS Analysis of Asphalt Volatiles. The volatiles from the asphalt samples collected on the liquid nitrogen cold finger were analyzed by high resolution gas chromatography-mass spectrometry (GC-MS). The instrumentation consisted of a Varian gas chromatographic system (VISTA 44) and Finnigan Ion Trap Detector (ITD), and a mass spectrometric detector for capillary gas chromatography. The samples ($0.2\,\mu$l size) were injected into the column using a cold, on-column injector (Scientific Glass Engineering, SGE). The samples were separated on a 25 m wide-bore (0.32 mm ID) fused silica capillary column with BP-1 bonded phase coating ($0.25\,\mu$m thickness). The capillary columns connected to the heated trans-

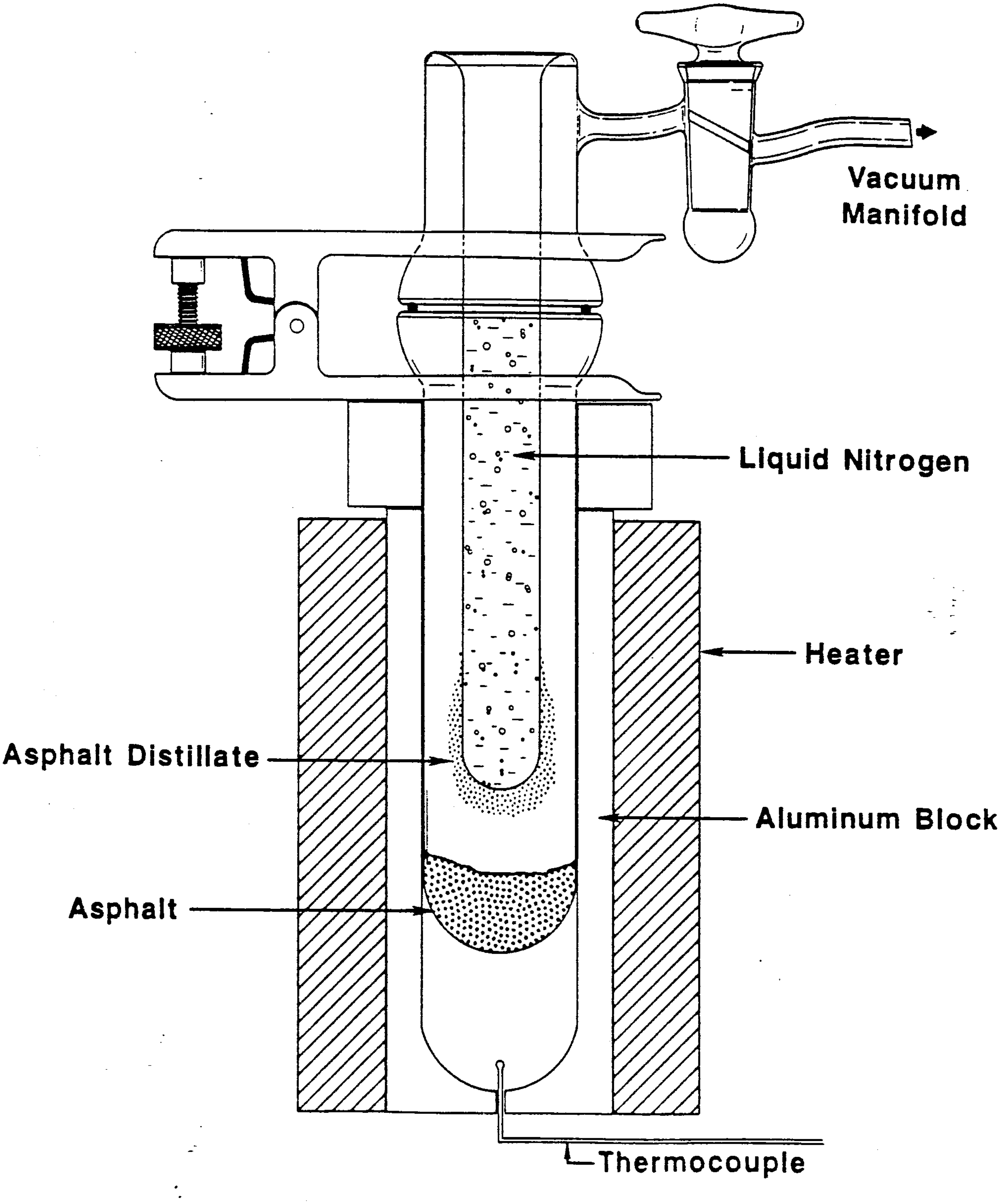


Figure 2-11

Schematic Representation of the Vacuum Distillation Unit

Philip and Anthony (1978)

fer line which has linked the gas chromatograph to the ITD, by an open split interface. The control and data collection of the ITD was managed by an IBM PC-XT computer with 10 megabyte hard disk drive and a 5-1/4" floppy drive. All the ITD operational programs were stored on the hard disk. The GC output was collected as the mass spectral fragmentation pattern. The total ion chromatogram displays a mass based GC output. The mass spectral fragmentation pattern of each GC peak was analyzed by a library search program using the National Bureau of Standards (NBS) Mass Spectral Data Base, a collection of MS fragmentation patterns of about 4000 known organic compounds. In cases where the MS data of known compounds were not available in the library, the GC peaks were labeled as to the probable compound by using the information available on similar chemical species.

Results Obtained. Vacuum distillation provides a quantitative separation of the distillable portion of an asphalt from the non-distillable portion. Typically, the amount of volatile in an asphalt ranges from 3% to 15%, depending on the particular asphalt and the type and amount of additives used. GPC and GC-MS then can be used to analyze these two portions for distinctive features which can be used to characterize asphalts.

GPC analyses of the whole asphalt, of the non-volatile components, and of the volatile components provides molecular weight profiles which can be used to compare asphalts. Separation of species by GPC, is based primarily on linear molecular size. Large molecules elute first and small molecules elute last. The range of separation varies depending on the pore size of the column used. For an asphalt sample, the separation of large molecular size asphaltenes from the rest of the organic material can be achieved by the use of a single 100 Å pore size column. The non-asphaltene components, which account for almost 80 to 90% of most road asphalts, are dispersed by fractionation in the column and appear as a broad GPC profile. The asphaltenes, being totally excluded from the small pores of the column, remain relatively undispersed and appear as a relatively sharp peak. Using a larger pore size column, for example a 500 Å column, produces broadening of this asphaltene peak and consequently better differentiation between various asphalts.

GC-MS data for the volatile portion provides detailed structural information on the volatile components in asphalts. Typically for asphalts, most of the sharp peaks in the total ion chromatogram are due to straight chain saturated hydrocarbons, namely normal alkanes. The region between two alkane peaks, which is flat but displaced well above the normal base line, also shows mass spectral fragmentation patterns similar to that of alkanes indicating that they are isomeric alkanes of similar molecular weights. Mass spectral fragmentation patterns characteristic of aromatics were rarely seen in the GC-MS of asphalt derived from volatiles.

Application of this technique to asphalts suspected of hot-mix fuel oil contamination is presented in Chapter 6.

Other Chemical Analysis Procedures

Corbett Analysis. Due to the complexity of asphalt cements, a separation process was necessary so that chemically similar groups in the mixture could be analyzed using Gel Permeation Chromatography (GPC). The Corbett Analysis (ASTM Procedure D 4124-82) allows an asphalt or crude stock sample to be separated into four generic fractions:

(1) Saturates
(2) Naphthene Aromatics
(3) Polar Aromatics
(4) Asphaltenes

The average molecular weight of the saturates fraction is the lowest while that of the asphaltenes is the highest.

These four fractions are distinct in color and physical appearance. The saturates generally produce a light yellow or clear solution. The saturates themselves resemble paraffin wax. The naphthene aromatics are normally dark red in color and are quite viscous and sticky. The polar aromatics are brown to black and still more viscous. The asphaltenes are black and solid-like or crystalline.

The separation process used in the Corbett procedure utilizes an F-20 alumina chromatographic column. Initially a known mass of asphalt cement is dissolved in n-heptane so that the asphaltenes (n-heptane insolubles) may be separated from the petrolenes (n-heptane solubles). After filtering the solid asphaltene cake from the petrolene solution, the petrolenes are introduced onto the alumina chromatographic column. Saturates are first collected from the column by using benzene or toluene as the eluting solvent. After the saturates have been separated from the petrolenes, the naphthene aromatics are collected by using a more polar methanol/toluene mixture. The final fraction to be removed from the column is the polar aromatic fraction which is eluted by using trichloroethylene as the eluant.

The cut point between the saturates and naphthene aromatic fractions is occasionally difficult to detect accurately but the cut point between the naphthene aromatics and polar aromatics is easily observed by the movement of the black polar aromatic ring down the column.

Several other techniques which may be used to separate asphalt into various fractions have been introduced. One such process is known as the Rostler analysis (Rostler and Sternberg, 1949). The Corbett procedure was chosen over the Rostler procedure because of the destructive nature of the sulfuric acid in the Rostler process. Since the reagents used in the Corbett analysis were not reactive with the asphalt, the fractions collected from the chromatographic separation could be recombined into a mixture that could be further analyzed.

Elemental Analyses. In order to obtain as much information as possible on the test section asphalts, elemental analyses were performed on many of the Dumas virgin and core samples. This analysis provides the percentages of various elements in the sample irrespective of the type of compound in which the element is present. The elements of interest were carbon, hydrogen, oxygen, nitrogen, and sulfur. Two laboratories were contracted to do all of the elemental analyses except those for sulfur. The first laboratory was located at the Center for Trace Characterization at Texas A&M University and the second was Galbraith Laboratories, Inc. in Knoxville, Tennessee.

All analyses except that for oxygen conducted at the Center for Trace Characterization were performed by burning the sample in a combustion chamber at 900°C. The gases given off in this process were then swept from the combustion chamber by a helium carrier to a column on which they were separated and measured in a thermal conductivity detector (TCD). Oxygen analyses at the Center for Trace Characterization were performed by neutron activation. This process results in a highly accurate measurement of oxygen content.

Carbon and hydrogen analyses performed at Galbraith were done similar to those done at the Center for Trace Characterization. Galbraith determined oxygen content of the samples by pyrolyzing the oxygen in the sample to carbon monoxide followed by oxidation to carbon dioxide. The resulting carbon dioxide was then measured using a TCD. Nitrogen analyses were performed using the Kjeldahl method. In this process the sample is oxidized in hot, concentrated sulfuric acid so that any bound nitrogen may be converted to ammonium ions. The solution is then treated with a strong alkaline solution to liberate ammonia. The liberated ammonia is then bubbled through a known amount of acid solution and then back titrated with a standard base.

Sulfur analyses were conducted by project personnel using a Leco Induction Furnace which utilized the combustion idiometric procedure (ASTM C816-85). The asphalt sample was burned at high temperatures in the presence of oxygen. The sulfur present in the sample was thus converted to sulfur dioxide (SO_2). The resulting SO_2 was then titrated according to the following reactions:

$$KIO_3 + 5KI + 6HCl \rightarrow 6KCl + 3I_2 + 3H_2O$$

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$$

Thus, the SO_2 from the combustion process was bubbled through a dilute hydrochloric acid solution containing excess potassium iodide (KI) and a starch indicator. Initially a small amount of potassium iodate solution (KIO_3) of known concentration was added to the solution so that free iodine (I_2) would be released as indicated by the first reaction above. This was noted by the starch indicator giving the solution a blue tint. As SO_2 was being evolved by the combustion of the asphalt, free I_2 in the solution would be consumed and more KIO_3 would need to be added to keep the solution blue. The endpoint of the titration was noted when no more KIO_3 was necessary to keep a blue color.

Heithaus Compatibility Test. The Shell-Heithaus peptization test (Heithaus, 1960) was investigated for the purpose of evaluating thermodynamic and compatibility relationships among the many components in asphalts. This test gives a measure of how well the asphaltenes are solubilized or held in solution by the resins and oils in the asphalt. The technique previously has been reported in the literature and is a routine test procedure. Consequently, the method is not given here in great detail but instead is presented only briefly.

In this work an abbreviated version of the Heithaus state of peptization test was used for determining the flocculation ratio. The procedure is described below:

1. To a 250 ml Erlenmeyer flask add 1 ± 0.1 g of asphalt.
2. Add from a burette 5 ± 0.05 ml of toluene.
3. Heat gently on a steam bath or hot plate set at 200°F, the Erlenmeyer flask, asphalt and toluene until asphalt softens.

4. Stir with a glass stirring rod until asphalt is well mixed into a uniform cutback. CAUTION–be careful not to lose toluene. It may be helpful to weigh flask, asphalt, toluene and rod before heating and then replace any evaporation after cutback is made.
5. Cool in a water bath at 70°–80°F.
6. With a magnetic stirrer, mixing constantly, add heptane slowly. Intermittently stop mixing and place a drop of the mix on a slide, cover with a cover glass and observe under a microscope at 100 or more power. Continue examination after additional increments of addition. With continued heptane addition, small individual transparent asphaltene particles will be seen in suspension.
7. No change will be observed with further heptane addition for a few ml. Then, suddenly, with addition of another increment, a definite change will be observed as the individual asphaltene particles begin to agglomerate or clump into loose floccules. Additional heptane (1–3 ml) completes flocculation of the asphaltenes.
8. On initial evaluation, large increments of heptane, perhaps 10 ml, should be added. After the approximate volume for flocculation has been determined, another sample should be taken and the heptane added in smaller increments as the volume is approached where flocculation occurs.

The weight of asphalt, volume of toluene and volume of heptane required to initiate precipitation are recorded. The flocculation ratio (FR) is computed as follows:

$$FR = \frac{\text{(volume of toluene)}}{\text{(volume of toluene + volume of heptane)}}$$

The full procedure (Skog, et al., 1966, Venable et al., 1983) can be used to compute additional parameters called (1) peptizability of asphaltenes, (2) peptizing power of asphaltenes, and (3) state of peptization of asphaltenes. The plan is to continue and expand this work to determine if correlations between these parameters and asphalt performance can be achieved.

CHAPTER 3

CHARACTERIZATION OF ASPHALTS BY GPC AND OTHER METHODS

A large number of asphalts used in Texas highways have been analyzed for their GPC profiles. These include asphalts of several viscosity grades supplied throughout the year by a number of producers. Additionally, some results on asphalts used for seal coats are given.

Monthly Samples

Monthly samples from twelve different refineries as shown in Table 3-1 were examined by GPC analysis. Not every refinery furnished a sample every month. Data are reported which span a time period of over one year. Results obtained using toluene as the carrier solvent and a 100 Å column are shown in Figures 3-1 to 3-4. Some results obtained using THF and a 50 Å-500 Å column configuration are shown in Figures 3-5 to 3-11. The chromatograms from the two experimental systems are quite different and are affected by both solvent and column configuration.

Each refinery tends to have its own characteristic shape in each system. Typical chromatograms for some of these are shown in Figures 3-1 and 3-5. Figures 3-4 and 3-11 show refineries that are apparently obtaining the same grades of asphalt from different crudes.

Figure 3-5 compares typical chromatograms of 6 asphalts using THF. The Diamond Shamrock asphalt differs significantly from others in that it consists of considerably higher molecular weight material. All the others are somewhat similar, having a small leading peak and one large peak, yet the differences are usually sufficient to be recognizable. Chevron has the sharpest main peak tailing down sooner than the others. The main peaks of Cosden and Texaco are similar but Cosden shows a very small leading peak. Texaco and Texas Fuel and Asphalt are similar. Gulf States is also very similar to Texaco and Cosden but its leading peak is intermediate in size and location.

Figures 3-2 and 3-3 indicate a rather dramatic change in composition in February, March and April in both the Texaco and Exxon refineries and a return to the previous composition by July. Unfortunately the data with THF for the same months was not available. All refineries show substantial composition variation in

Table 3-1

Asphalt Monthly Samples Supplied by Different Refiners

Refiner	Asphalt Grades Supplied AC-5	AC-10	AC-20
Calumet		●	
Chevron		●	●
Cosden	●	●	●
Diamond Shamrock		●	
Dorchester		●	
Exxon	●	●	●
Gulf States Houston			●
Gulf States Corpus Christi			●
Texaco	●	●	●
Texas Fuel & Asphalt		●	●
Total Refining		●	●

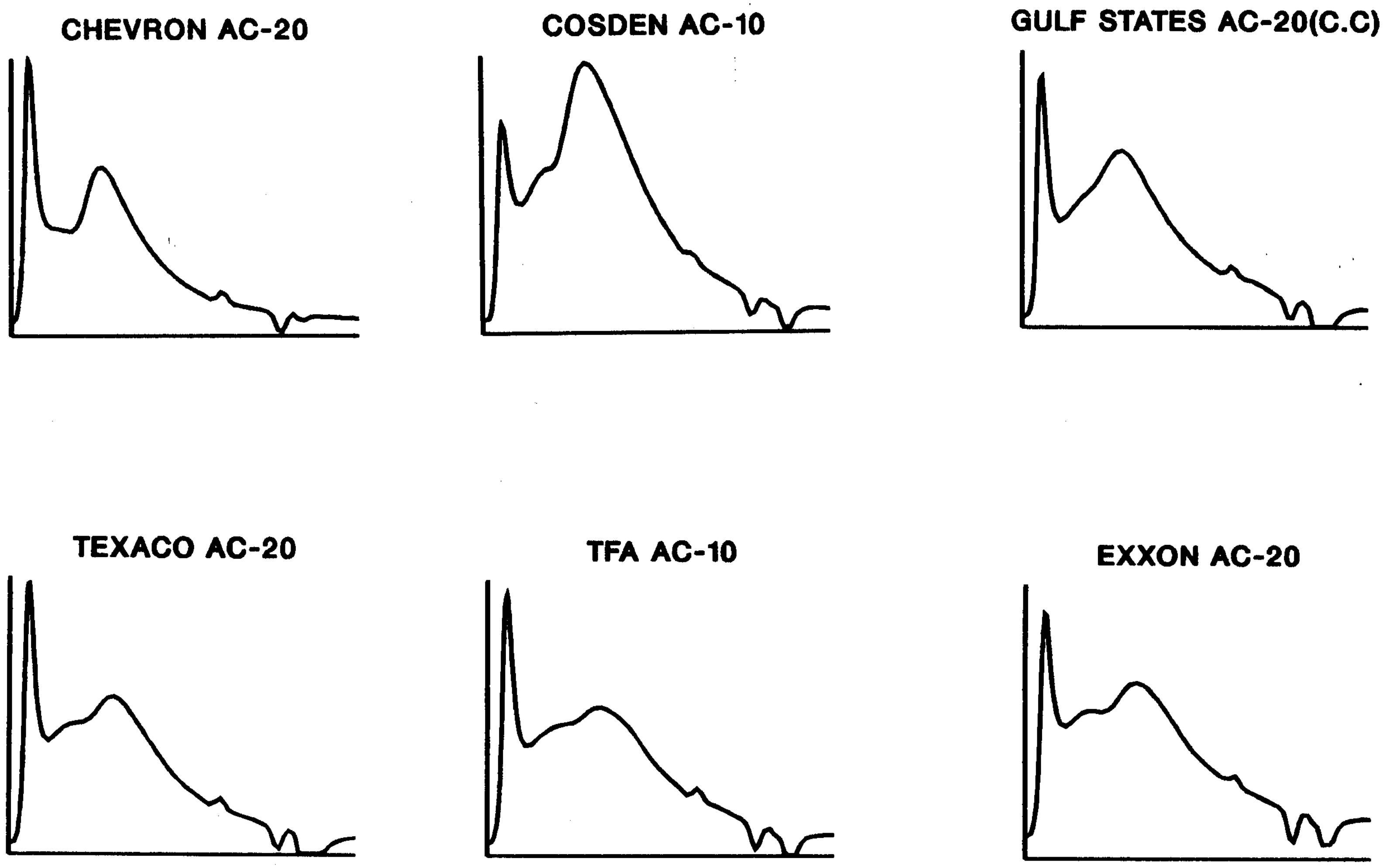


Figure 3-1
Representative Chromatograms For Several Refiners in Toluene
100 Å Column/Toluene/100 μl/7%

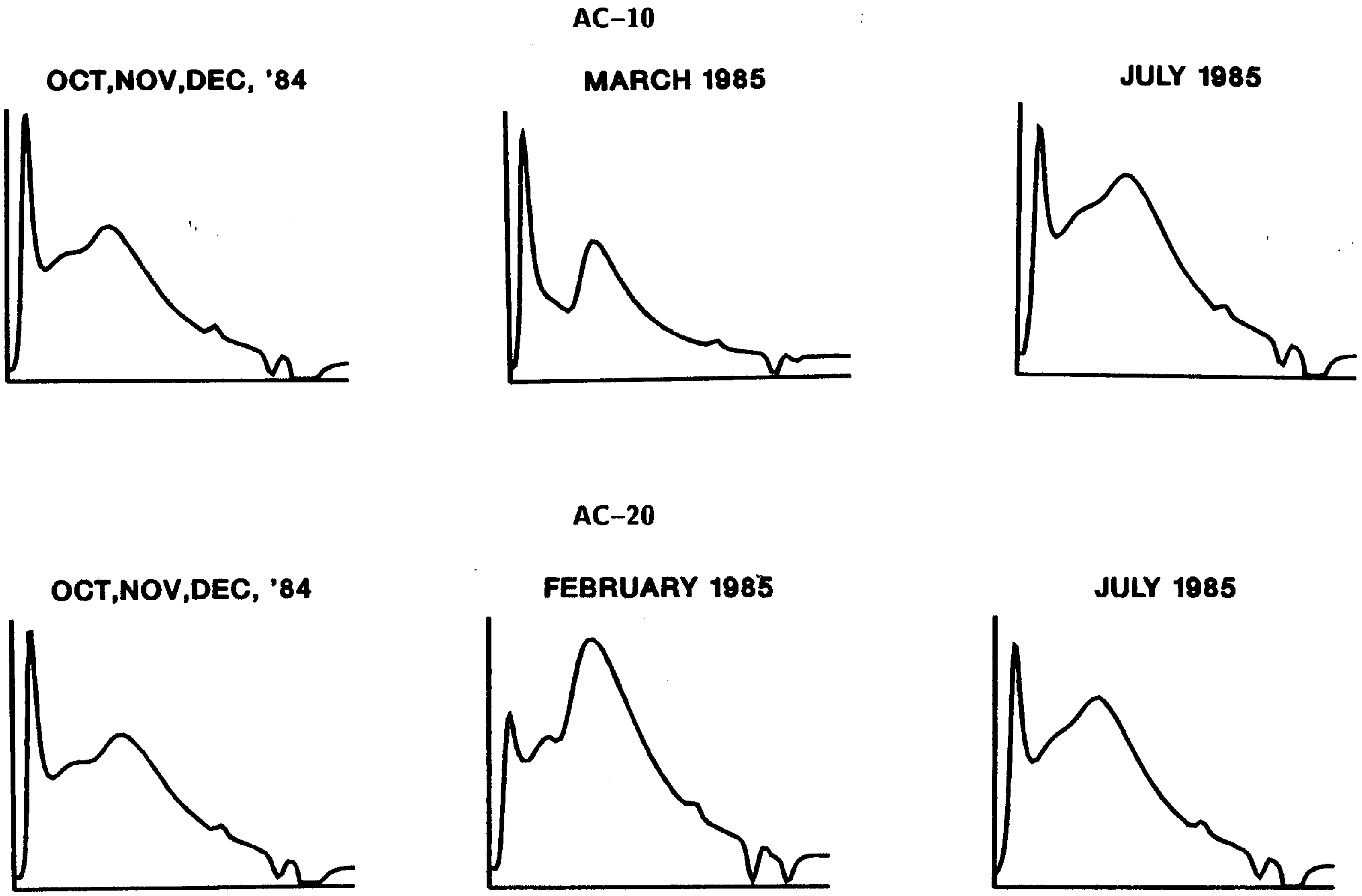


Figure 3-2
Chromatograms of Monthly Samples From Texaco
100 Å Column/Toluene/100 μl/7%

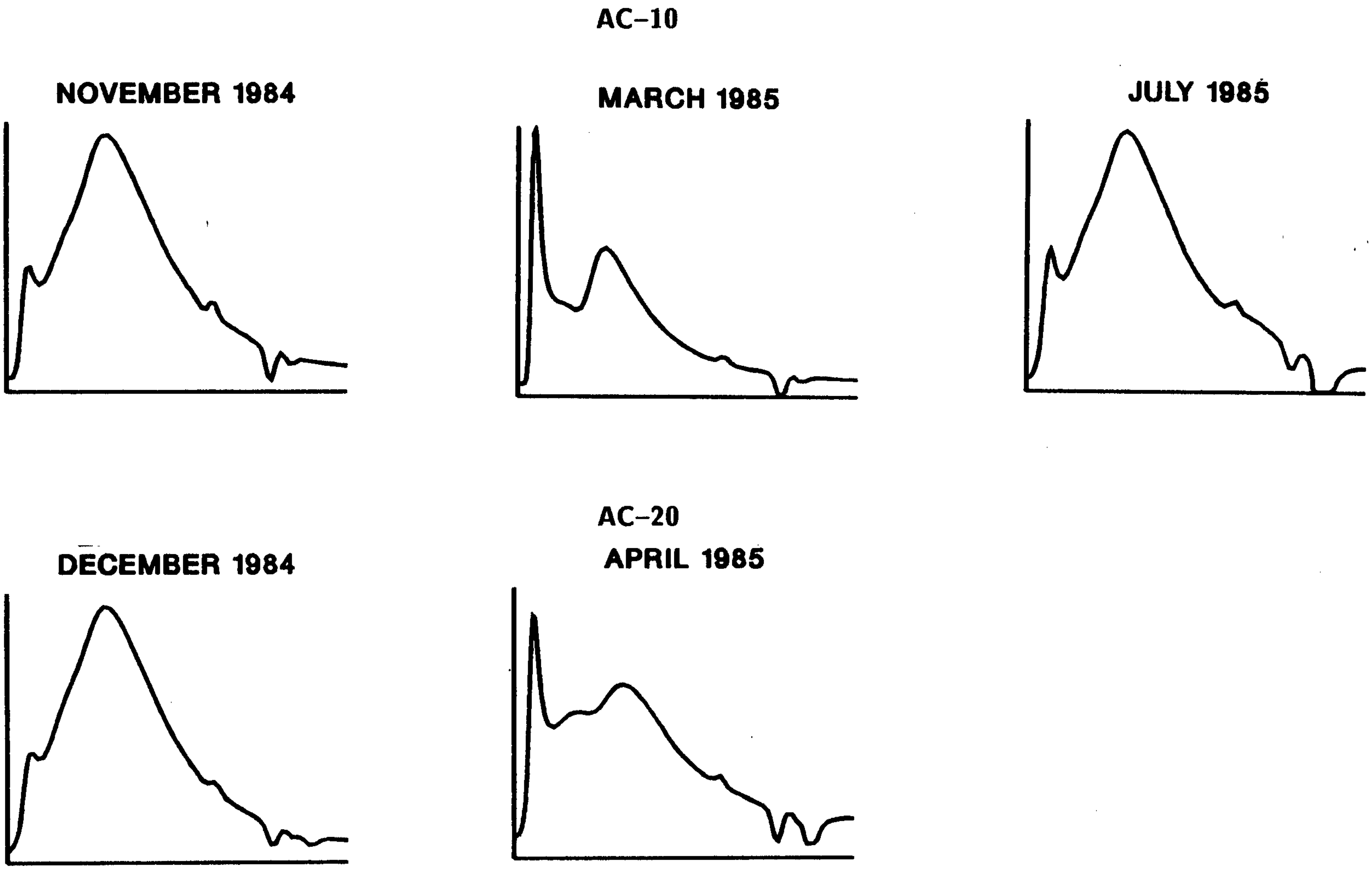


Figure 3-3
Chromatograms of Monthly Samples From Exxon
100 Å Column/Toluene/100 μl/7%

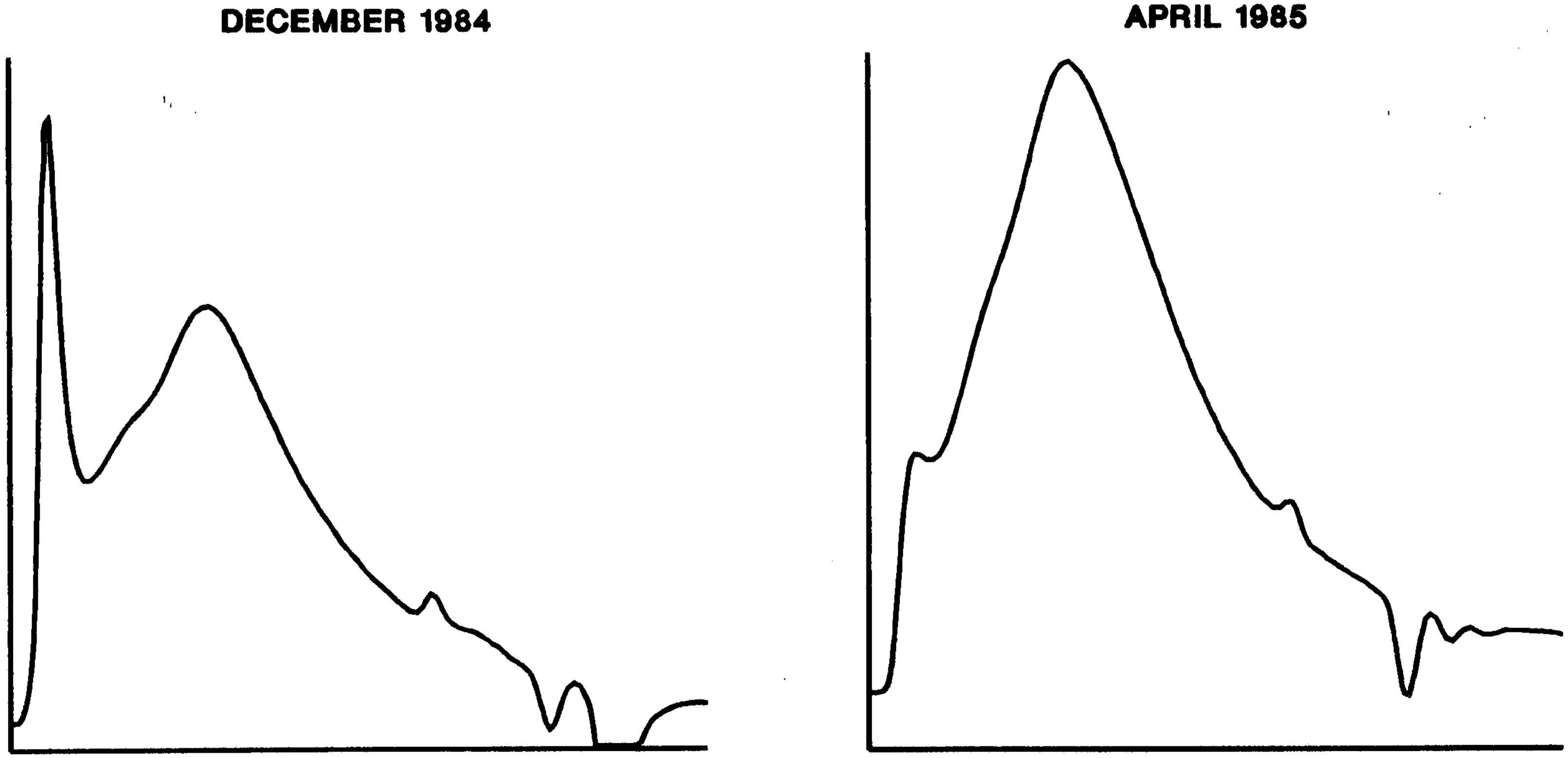


Figure 3-4
Chromatagrams of Monthly Samples of Gulf States AC-20, Houston
100 Å Column/Toluene/100 µl/7%

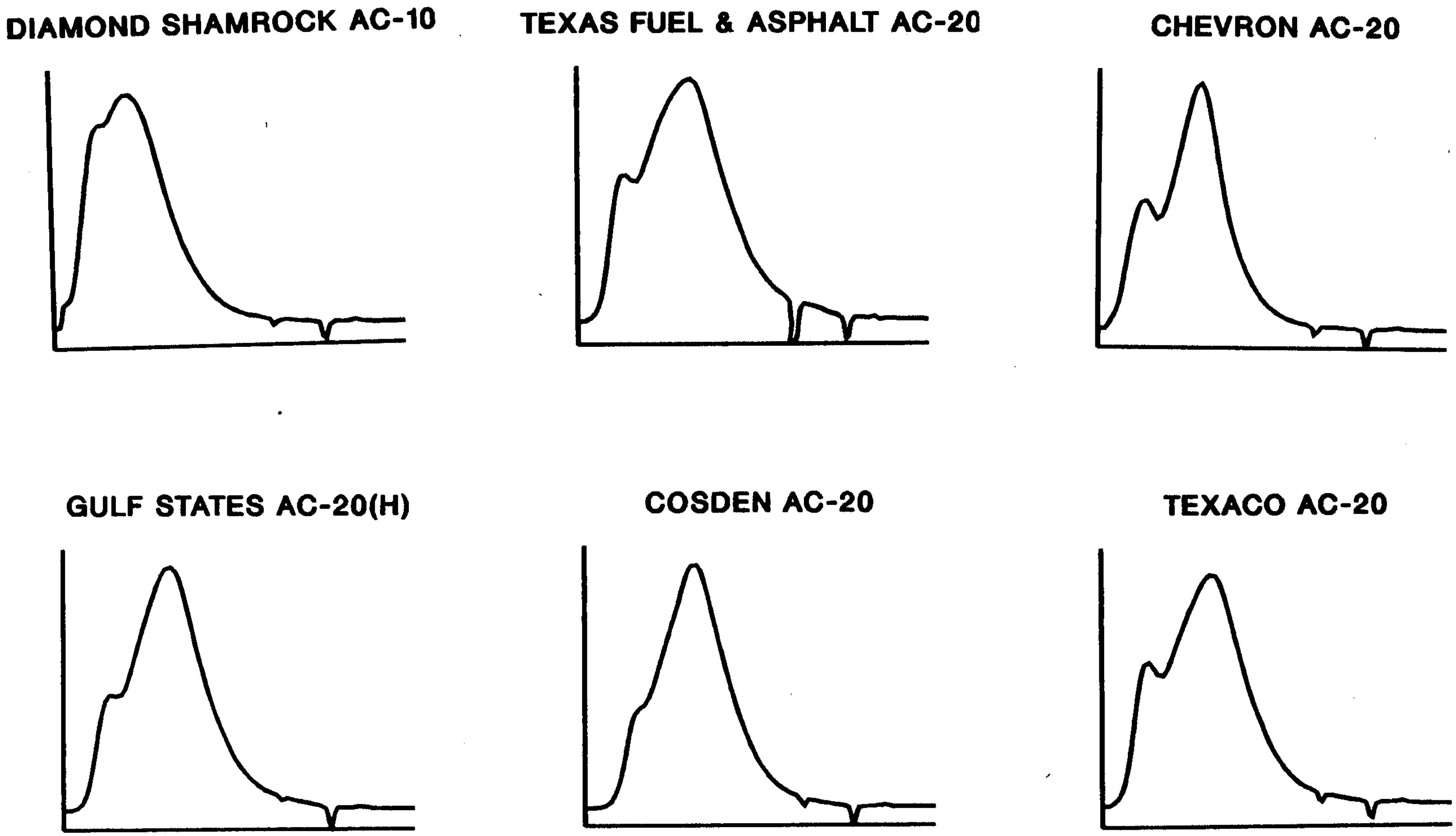


Figure 3-5
Representative Chromatagrams for Several Refiners in THF
500 Å and 50 Å Columns/THF/100 μl/7%

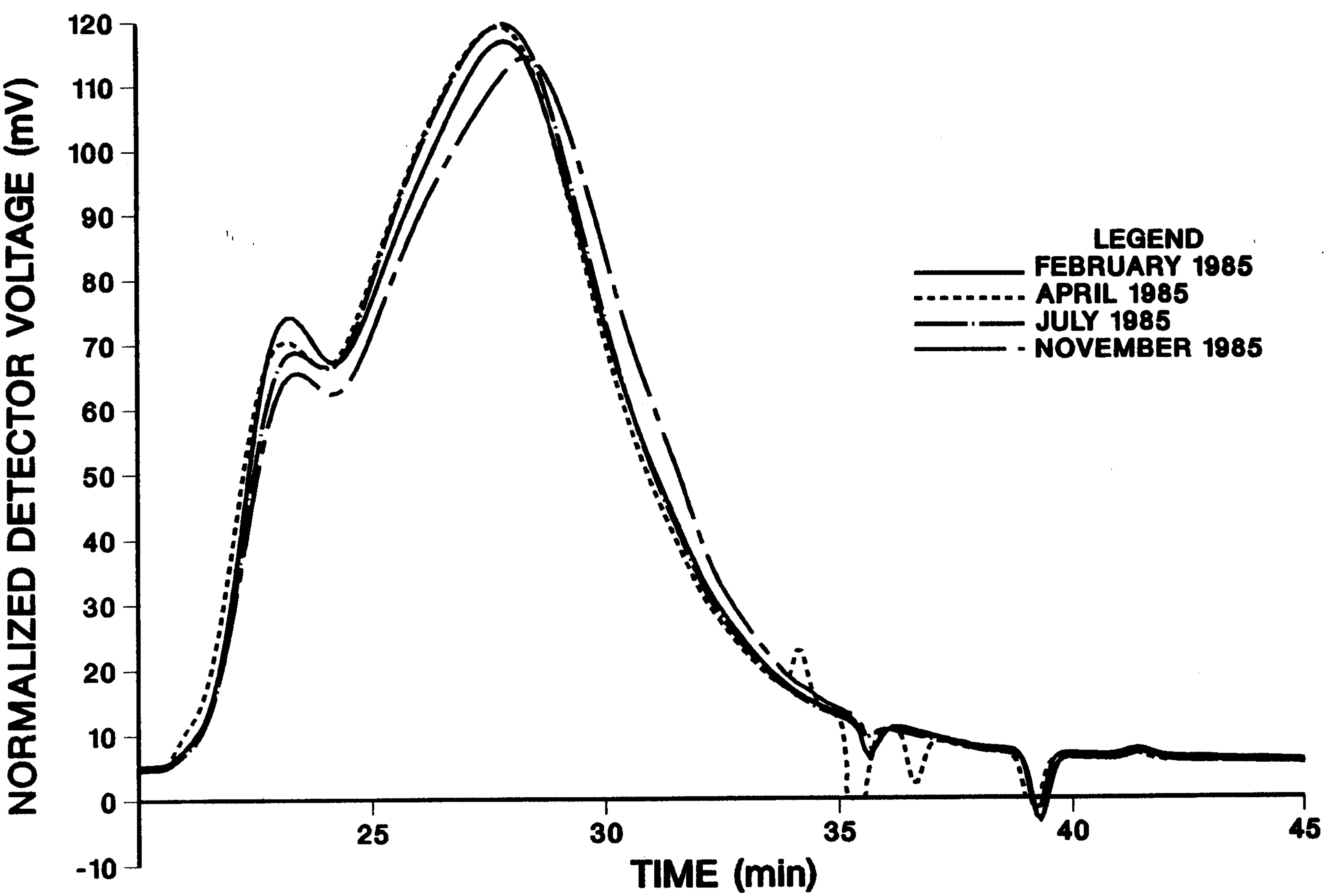


Figure 3-6
Variability of Texaco AC-20 Over Time
500 Å and 50 Å Columns/THF/100 μl/7%

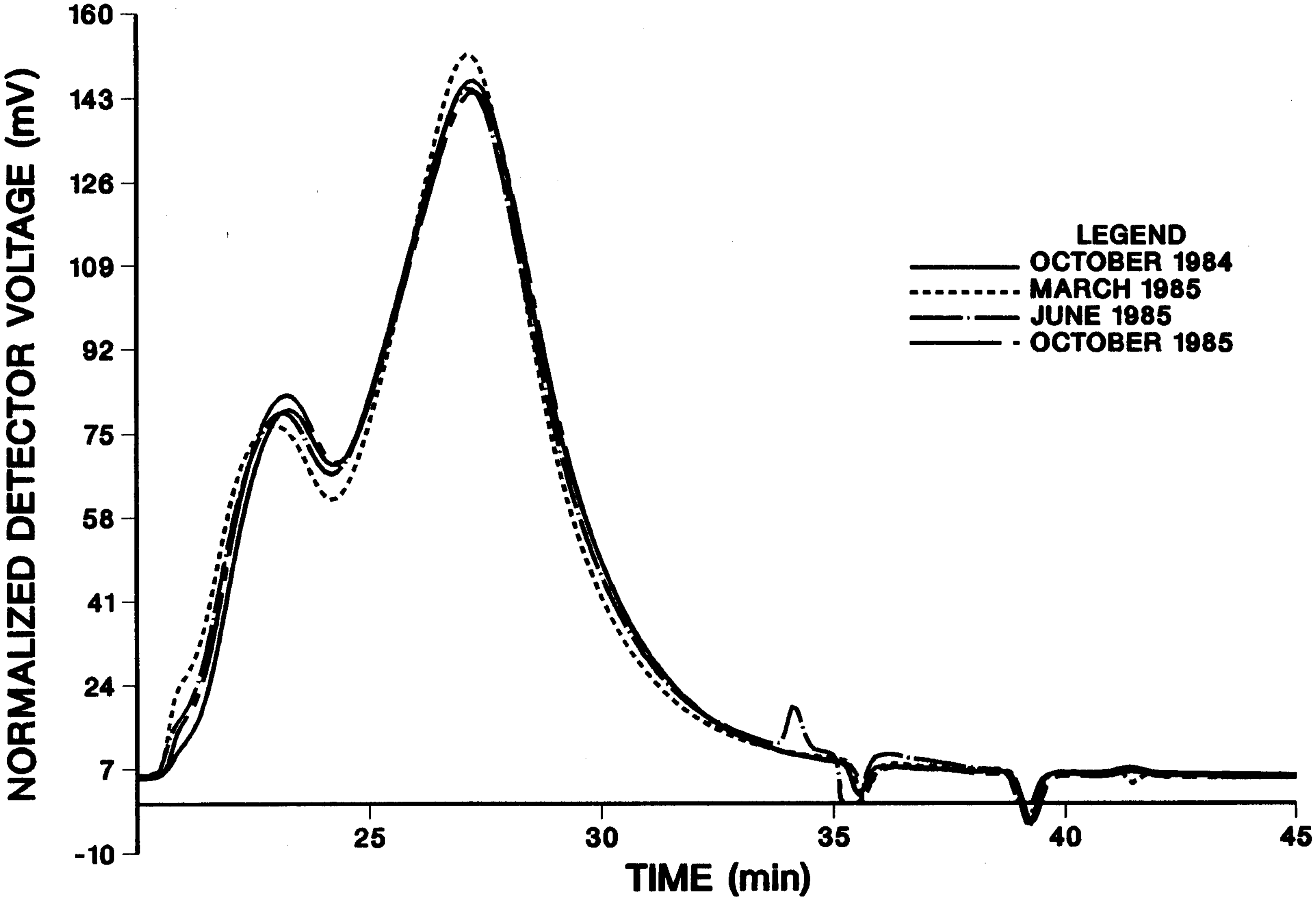


Figure 3-7
Variability of Chevron AC-20 Over Time
500 Å and 50 Å Columns/THF/100 μl/7%

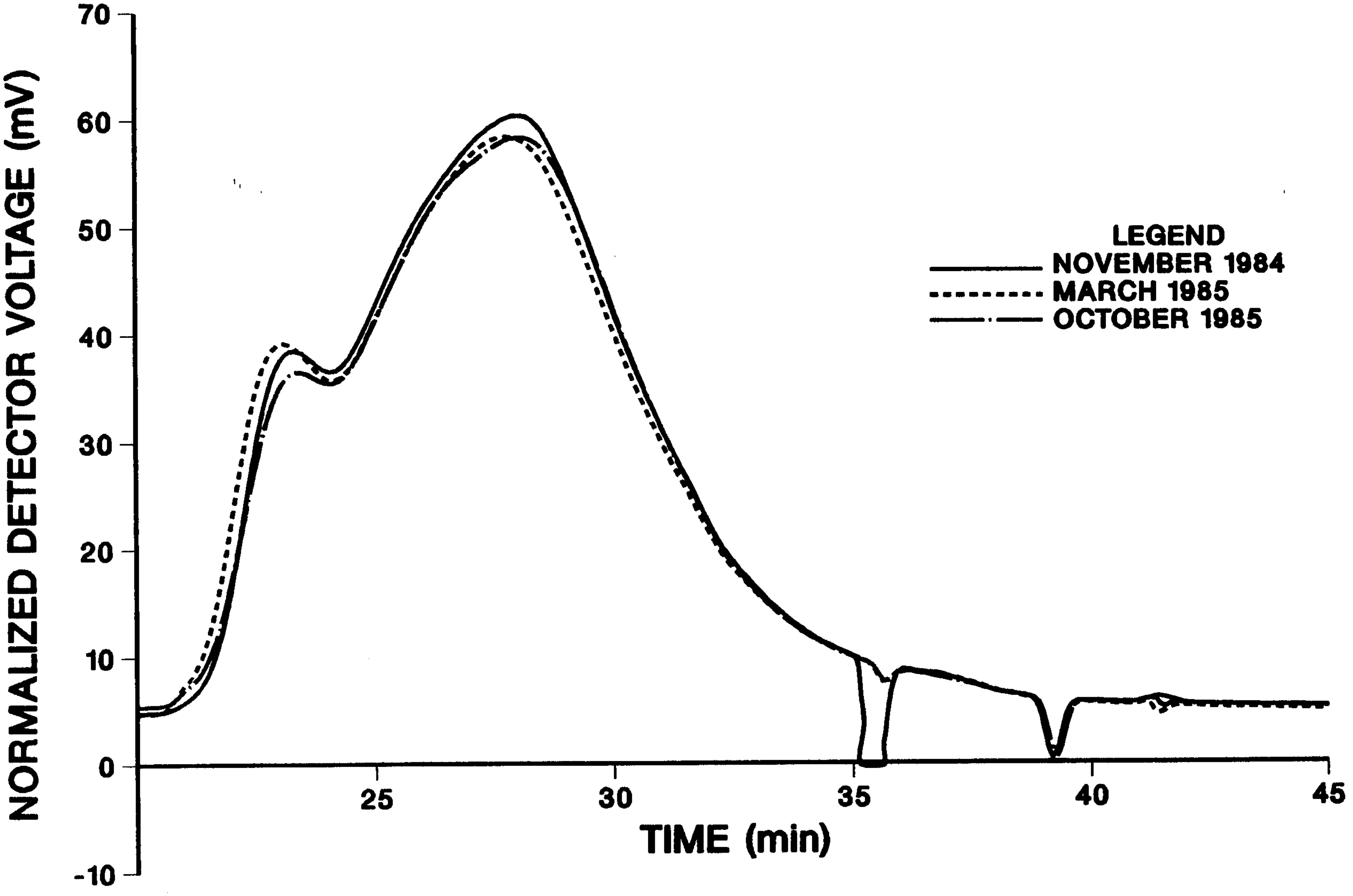


Figure 3-8
Variability of Texas Fuel and Asphalt AC-10 Over Time
500 Å and 50 Å Columns/THF/100 μl/7%

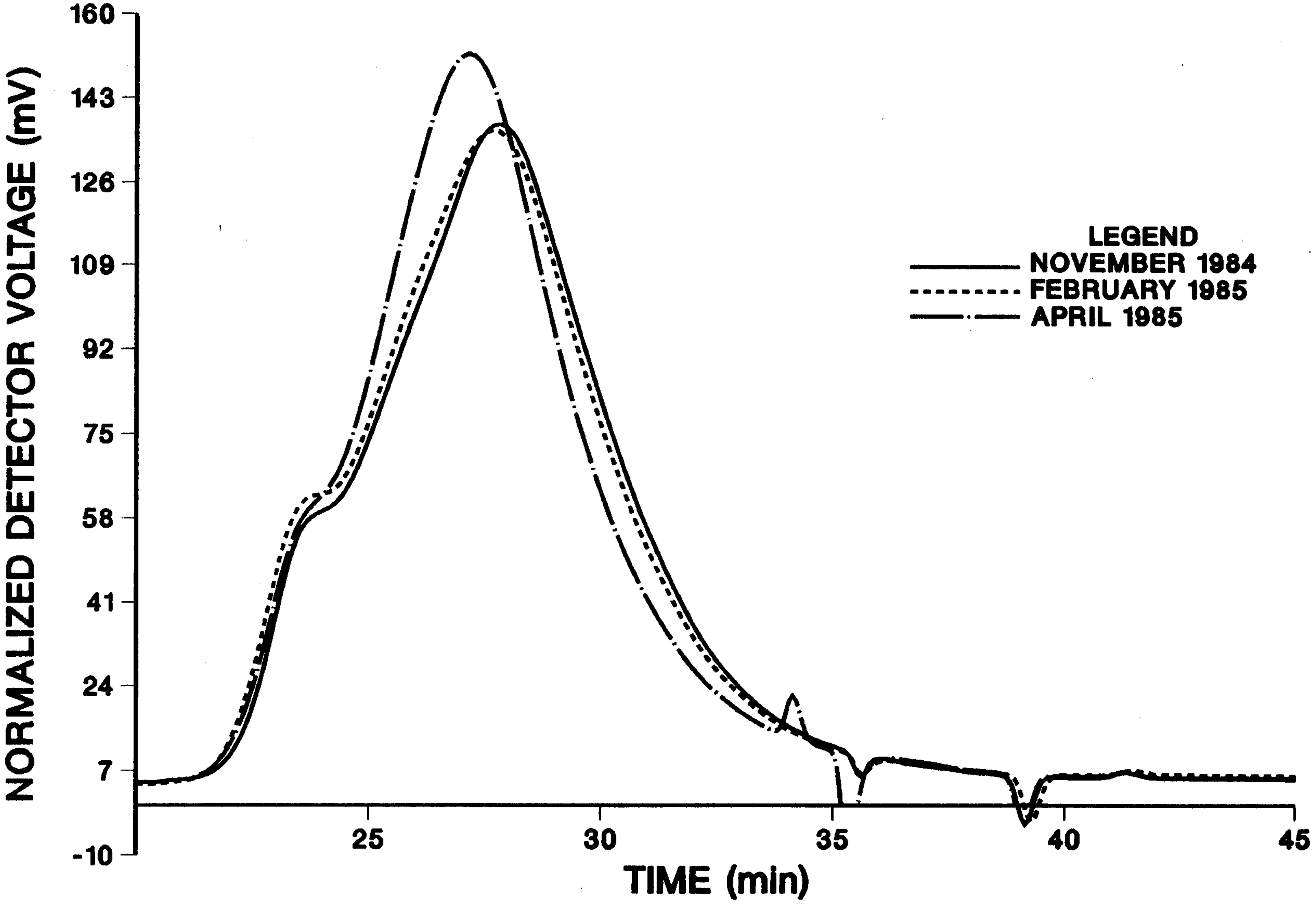


Figure 3-9
Variability of Cosden AC-20 Over Time
500 Å and 50 Å Columns/THF/100 μl/7%

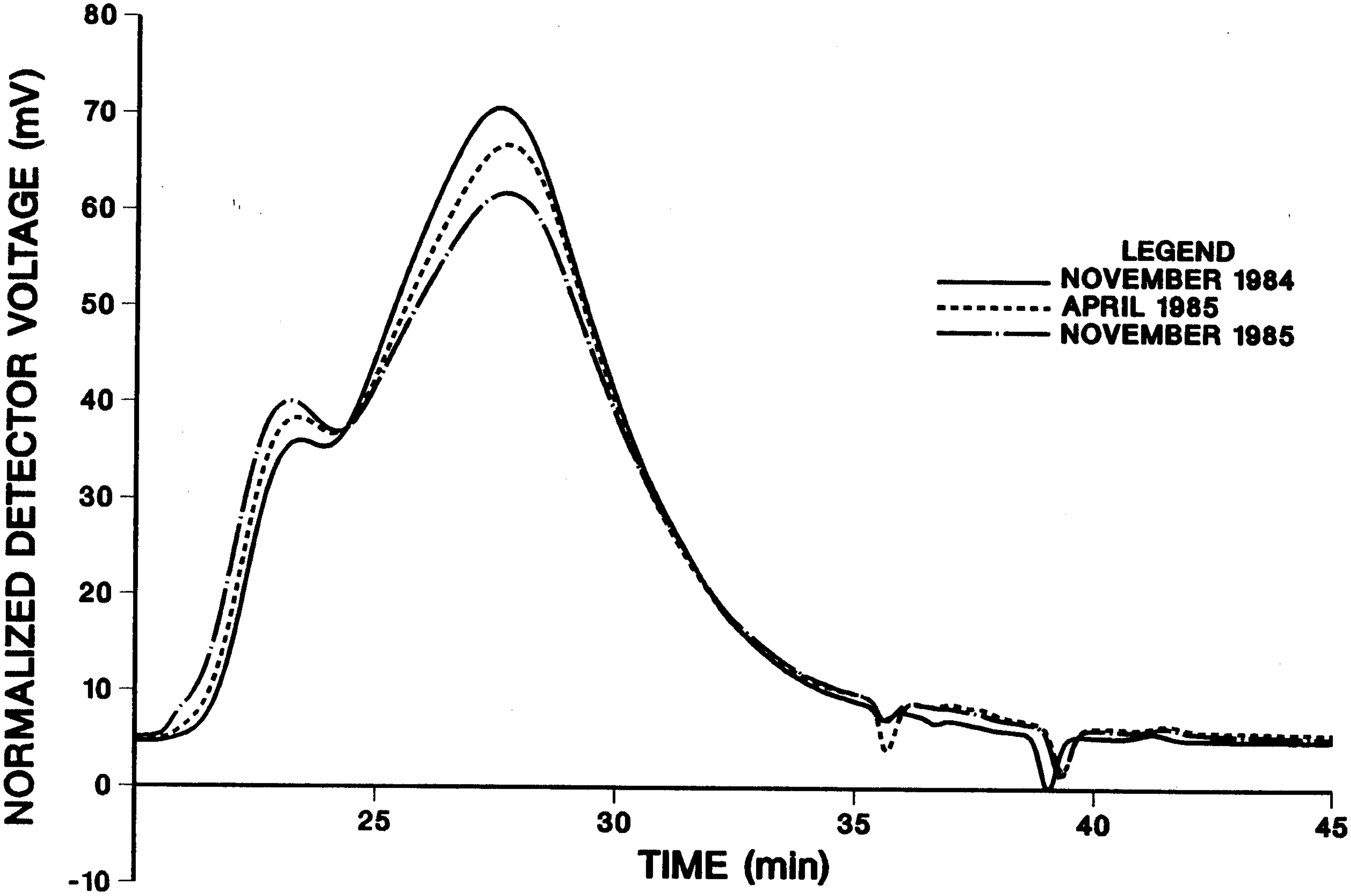


Figure 3-10
Variability of Gulf States AC-20, Corpus Christi Over Time
500 Å and 50 Å Columns/THF/100 μl/7%

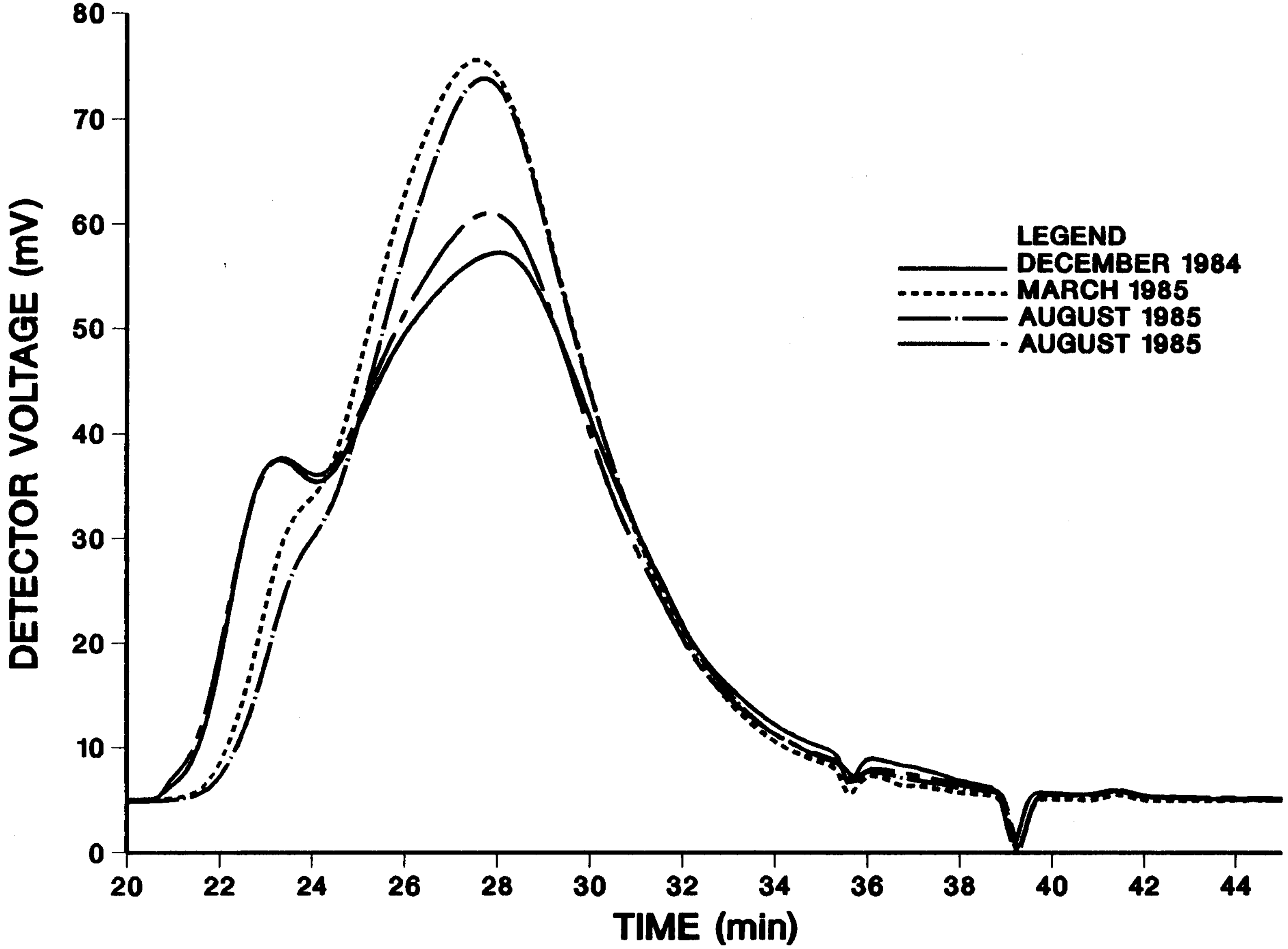


Figure 3-11
Variability of Gulf States AC-20, Houston Over Time
500 Å and 50 Å Columns/THF/100 μl/7%

THF, but it is much less dramatic and more random than with toluene. Texaco does show a small but undirectional change from February to November 1985.

At this time, the significance of the dramatic changes shown in Figures 3-2 to 3-4 is not known. In the first place the 100 Å column is producing total exclusion of a considerable portion of the large molecular size material as shown by the sharp leading peaks. This is no doubt accentuated by the poorer solvent power of toluene and the resulting increased association of the high molecular weight polar material as discussed in Chapter 2. A second factor is that a deterioration in separation efficiency or plate count was noted with toluene, especially with the 100 Å column, due to slowly reversible adsorption.

This causes us to question the reproducibility of some of the data as partial plugging would likely decrease effective pore size and increase exclusion still further. The cyclic nature of the data in both Figure 3-2 and 3-3 make this explanation seem unlikely.

From the sampling that has been done to date we believe that GPC can be very useful in detecting changes in processing and crude. Most asphalts are sufficiently different from one another to be distinguishable by GPC analysis. The changes that affect viscosity are not always detectable by GPC.

Asphalt chemists involved with GPC generally believe that the components of an asphalt which elute first from a GPC column are primarily asphaltenes. The present work, as well as that of others (Boduzynski et al., 1980), suggests that this is not necessarily so. Figure 3-12 is a comparison of two asphalts, one from Cosden and the other from Diamond Shamrock. The Diamond Shamrock profile begins eluting considerably earlier than the Cosden one, suggesting that it is higher in asphaltenes. However, in fact, the reverse is true, the Diamond Shamrock being about 2% asphaltenes while the Cosden is about 11%. The correlation given in Chapter 5, Figure 5-7 indicates that this is rather uncommon.

Seal Coat Asphalts.

These asphalts were used in seal coat test sections in four Texas highway districts. Their physical properties before and after thin film oven tests are given in Table 3-2.

By their GPC analyses, these asphalts look similar to the monthly samples and, where comparisons can be made, to test section asphalts which will be dis-

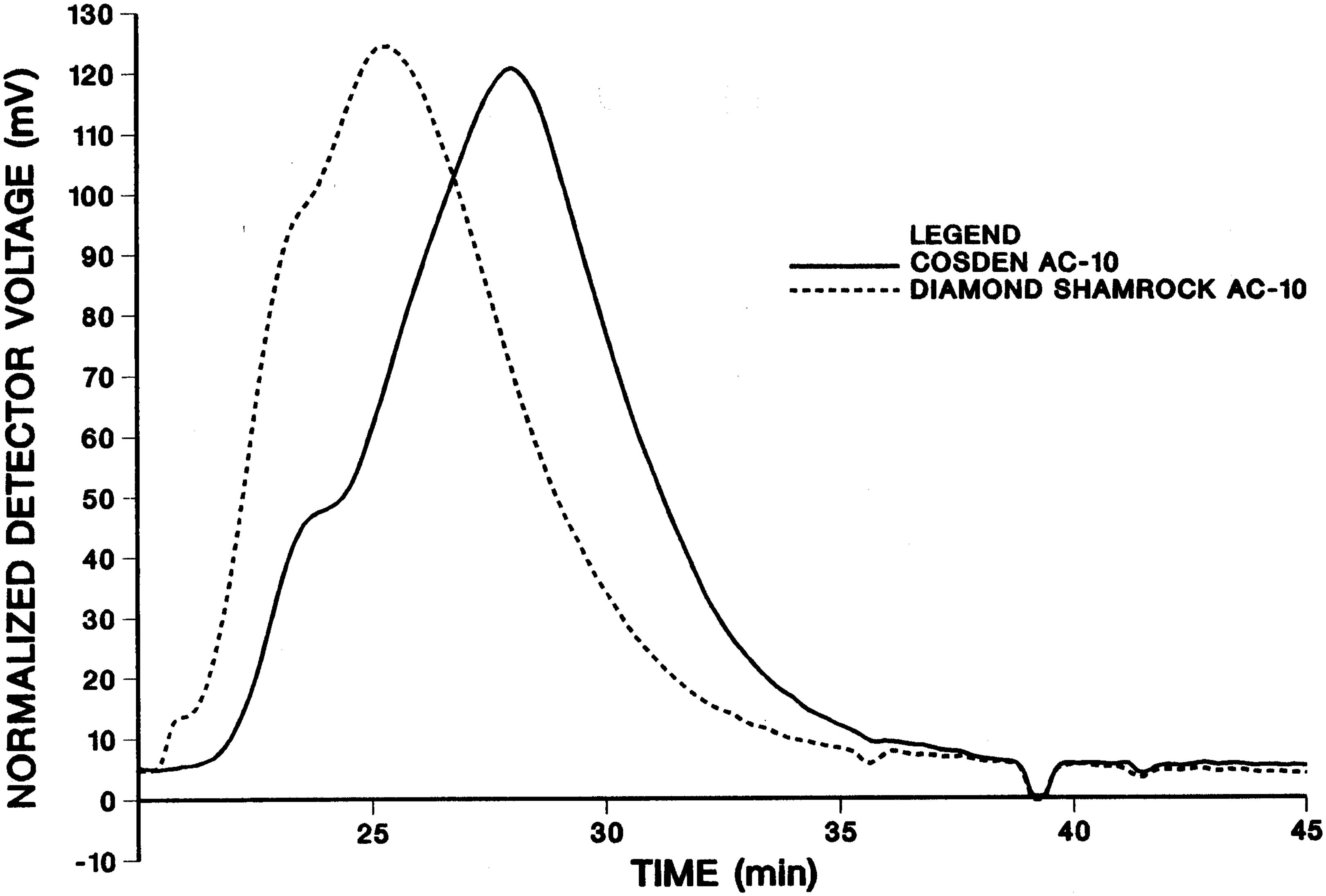


Figure 3-12
Comparison of Cosden AC-10 and Diamond Shamrock AC-10
500 Å and 50 Å Columns/THF/100 μl/7%/Dumas

Table 3-2
Asphalt Data from Seal Coat Test Pavements
Reported 2-5-86 by the SDHPT

			Before Thin Film Oven Test					
District Containing Test Pavement	Producer of Asphalt	Grade of Asphalt	Kinematic Viscosity at 140°F (stokes)	Kinematic Viscosity at 275°F (stokes)	Penetration at 77°F (mm)	Specific Gravity at 60°F	Specific Gravity at 77°F	Flash Point (°F) COC
6	Cosden	AC-5	628	2.1	121	1.025	1.019	585
6	Texas Fuel	AC-10	1087	2.9	85	1.021	1.015	570
6	Dia. Sham.	AC-10	1066	5.3	110	0.985	0.979	600
6	Dorchester	AC-10	414	2.1	220	1.020	1.014	600
6	Exxon	AC-10	1156	2.8	96	1.031	1.025	600
6	Exxon	AC-10	1248	3.8	113	1.027	1.021	600
6	Cosden	AC-10	968	2.4	74	1.036	1.030	575
5	Texaco	AC-10	949	3.2	99	1.020	1.014	565
5	Texas Fuel	AC-10	1195	2.7	90	1.016	1.010	590
5	Exxon	AC-10	1199	2.7	103	1.028	1.022	560
5	Dorchester	AC-10	1089	3.4	105	1.027	1.021	600
5	Dia. Sham.	AC-10	1170	5.4	110	0.985	0.979	600
5	Cosden	AC-5	513	1.8	111	1.026	1.020	600
5	Cosden	AC-10	1970	3.7	71	1.034	1.028	600
15	Cosden	AC-5	507	1.8	121	1.026	1.020	560
15	Texaco	AC-10	1150	3.4	112	1.025	1.019	600
15	Dorchester	AC-10	1011	3.1	120	1.026	1.020	585
15	Texas Fuel	AC-10	1038	—	98	1.017	1.011	560
15	Cosden	AC-10	926	2.4	89	1.032	1.026	580
15	Exxon	AC-10	1376	3.3	88	1.021	1.015	595
20	Texaco	AC-10	1137	3.4	113	1.030	1.024	600
20	Dorchester	AC-10	989	3.0	114	1.024	1.018	580
20	Texas Fuel	AC-10	1251	2.8	75	1.027	1.021	550
20	Cosden	AC-10	1056	2.5	78	1.032	1.026	585
20	Cosden	AC-5	467	1.3	116	1.017	1.010	585
20	Exxon	AC-10	1176	2.6	105	1.033	1.027	600
20	Dia. Sham.	AC-10	1085	5.4	114	0.981	0.975	600

Table 3-2 (Continued)
Asphalt Data from Seal Coat Test Pavements
Reported 2-5-86 by the SDHPT

District Containing Test Pavement	Producer of Asphalt	Grade of Asphalt	After Thin Film Oven Test		
			Kinematic Viscosity at 140°F (stokes)	Penetration at 77°F (mm)	Ductility at 77°F (cm)
6	Cosden	AC-5	1257	72	141
6	Texas Fuel	AC-10	2790	60	141
6	Dia. Sham.	AC-10	1703	76	141
6	Dorchester	AC-10	1815	63	141
6	Exxon	AC-10	2342	60	141
6	Exxon	AC-10	2077	76	141
6	Cosden	AC-10	2087	55	141
5	Texaco	AC-10	2198	70	141
5	Texas Fuel	AC-10	3817	51	141
5	Exxon	AC-10	2552	60	141
5	Dorchester	AC-10	2432	70	141
5	Dia. Sham.	AC-10	1986	75	141
5	Cosden	AC-5	1182	80	141
5	Cosden	AC-10	4114	47	141
15	Cosden	AC-5	1064	99	141
15	Texaco	AC-10	1935	81	141
15	Dorchester	AC-10	2198	81	141
15	Texas Fuel	AC-10	3125	52	141
15	Cosden	AC-10	1918	55	141
15	Exxon	AC-10	2468	55	141
20	Texaco	AC-10	2194	76	141
20	Dorchester	AC-10	2462	57	141
20	Texas Fuel	AC-10	2833	53	141
20	Cosden	AC-10	2187	56	141
20	Cosden	AC-5	1039	99	141
20	Exxon	AC-10	2003	63	141
20	Dia. Sham.	AC-10	1823	76	141

cussed in Chapter 4. Chromatograms are given in Figures 3-13 to 3-18. No performance data on these seal coats are available and further evaluation must be deferred until such results are obtained.

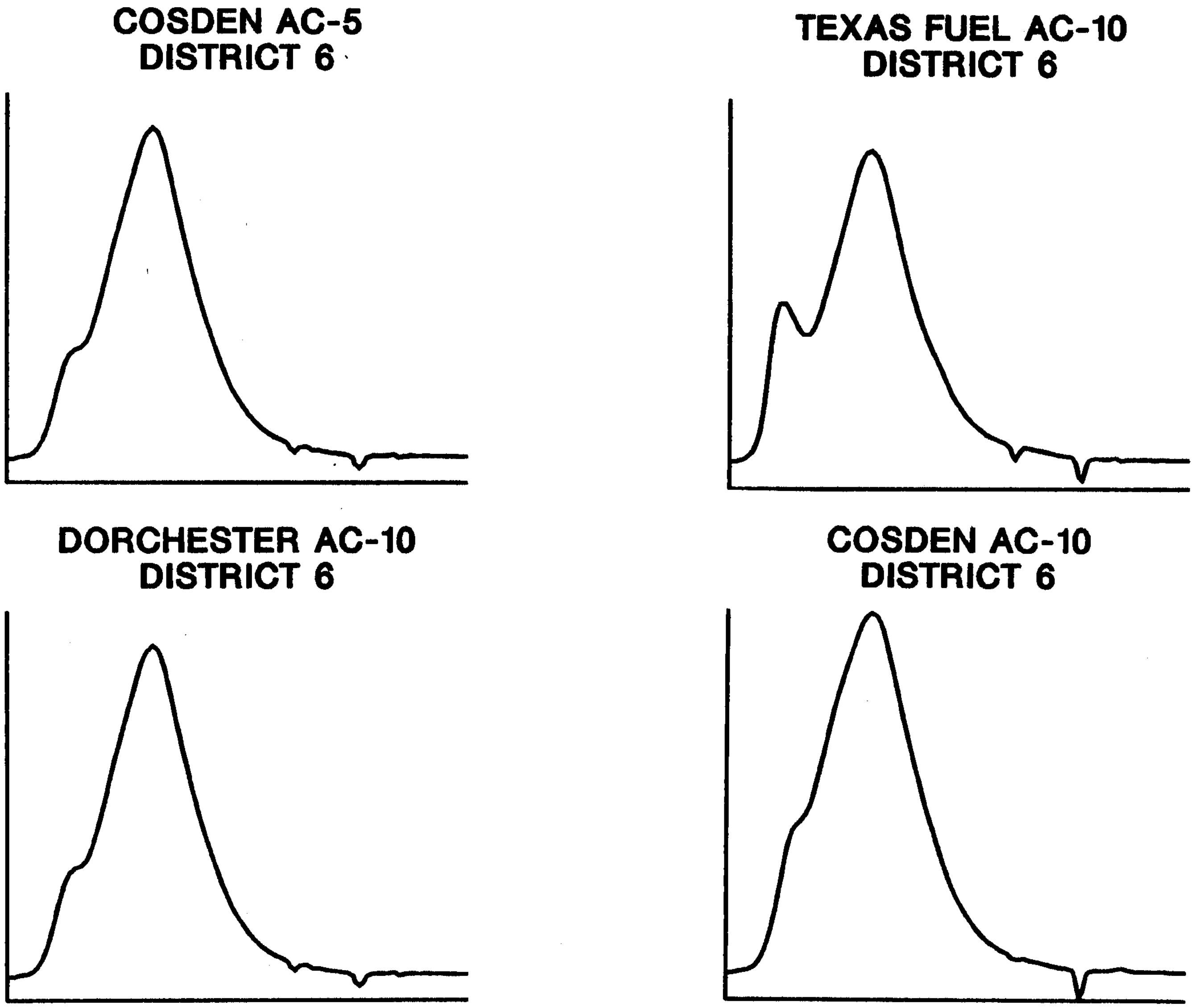


Figure 3-13
Chromatograms of Seal Coats From District 6
500 Å and 50 Å Columns/THF/100μl/7%

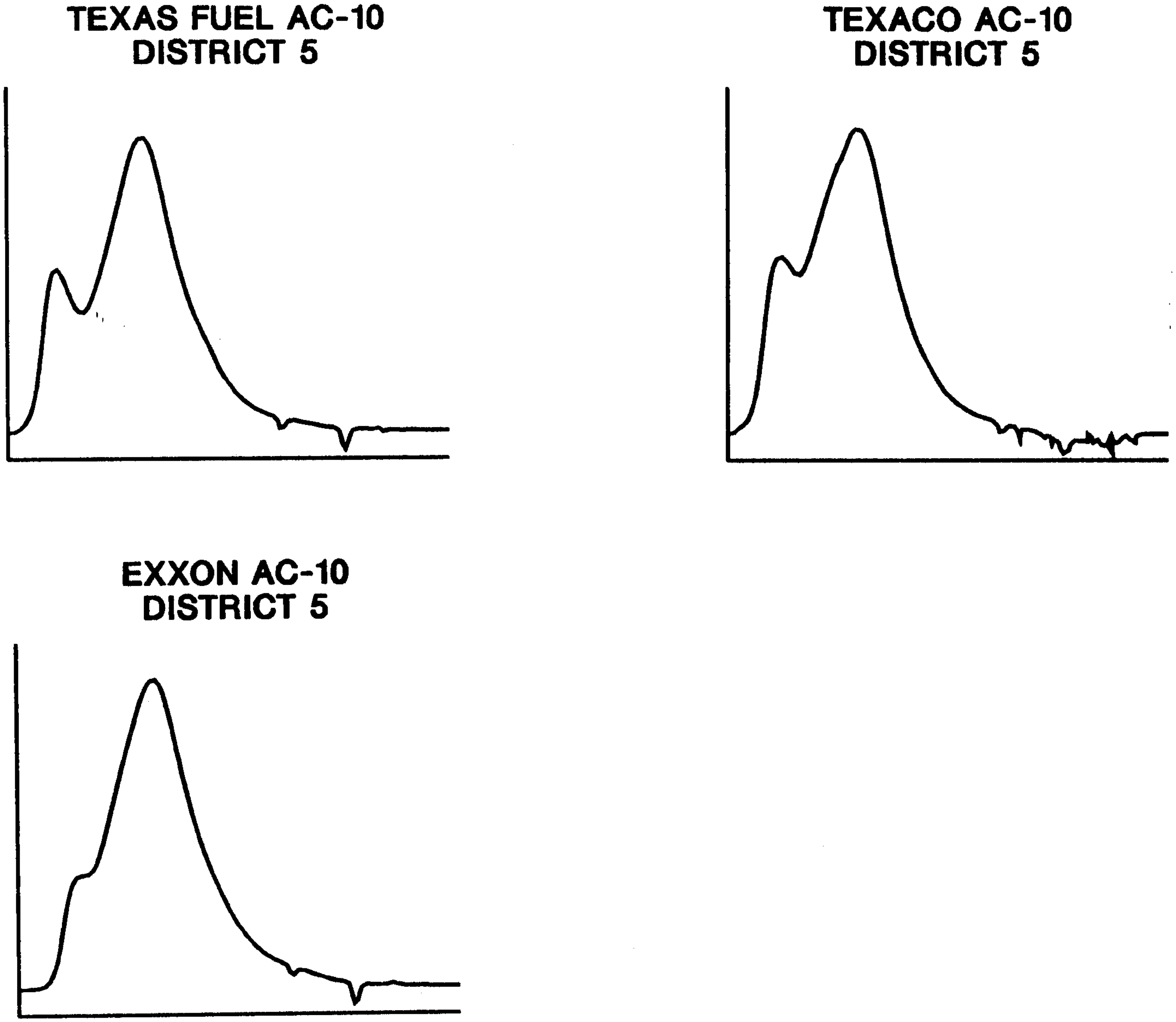
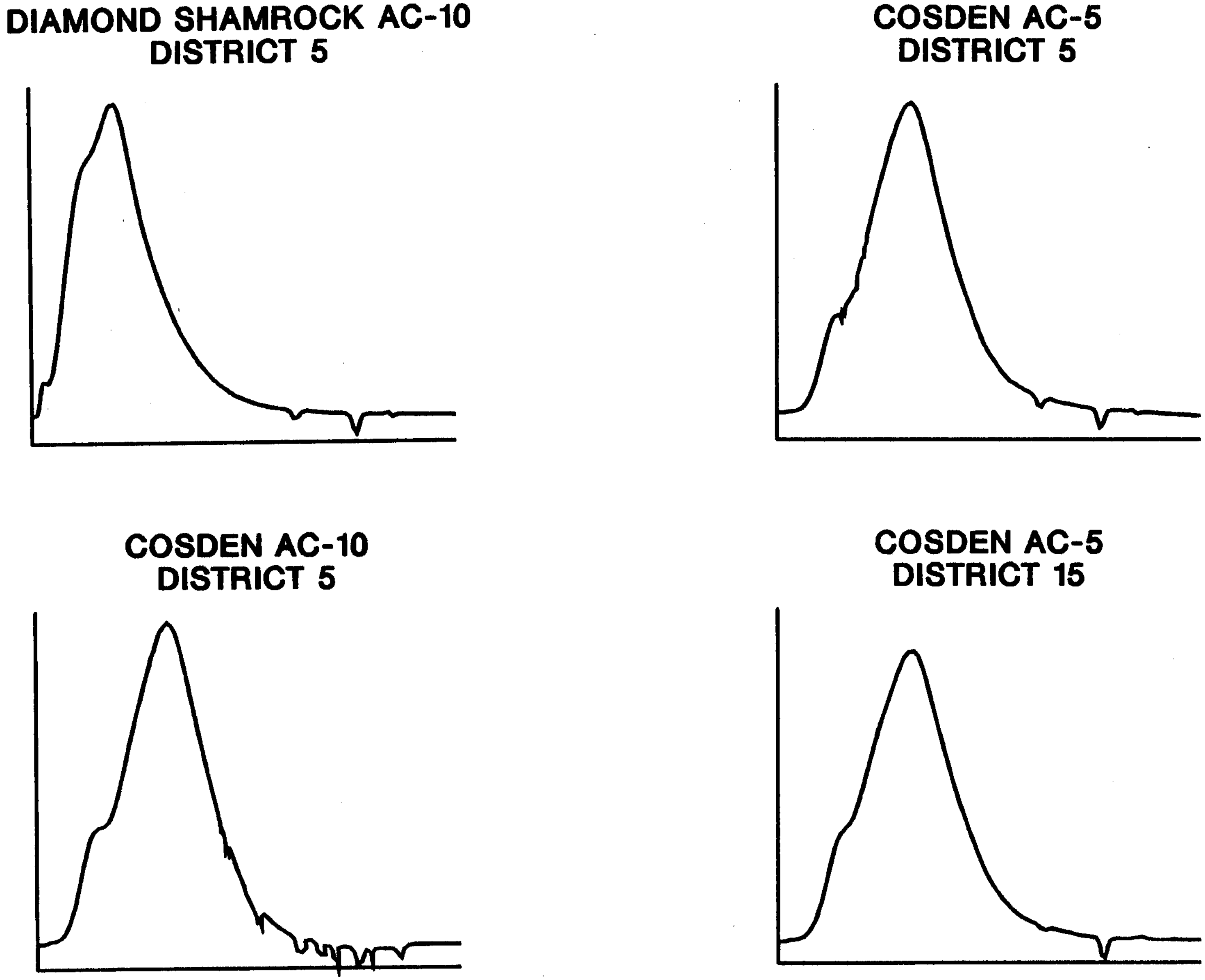


Figure 3-14
Chromatograms of Seal Coats From District 5
500 Å and 50 Å Columns/THF/100 μl/7%



DIAMOND SHAMROCK AC-10
DISTRICT 5

COSDEN AC-5
DISTRICT 5

COSDEN AC-10
DISTRICT 5

COSDEN AC-5
DISTRICT 15

Figure 3-15
Chromatograms of Seal Coats From Districts 5 and 15
500 Å and 50 Å Columns/THF/100 μl/7%

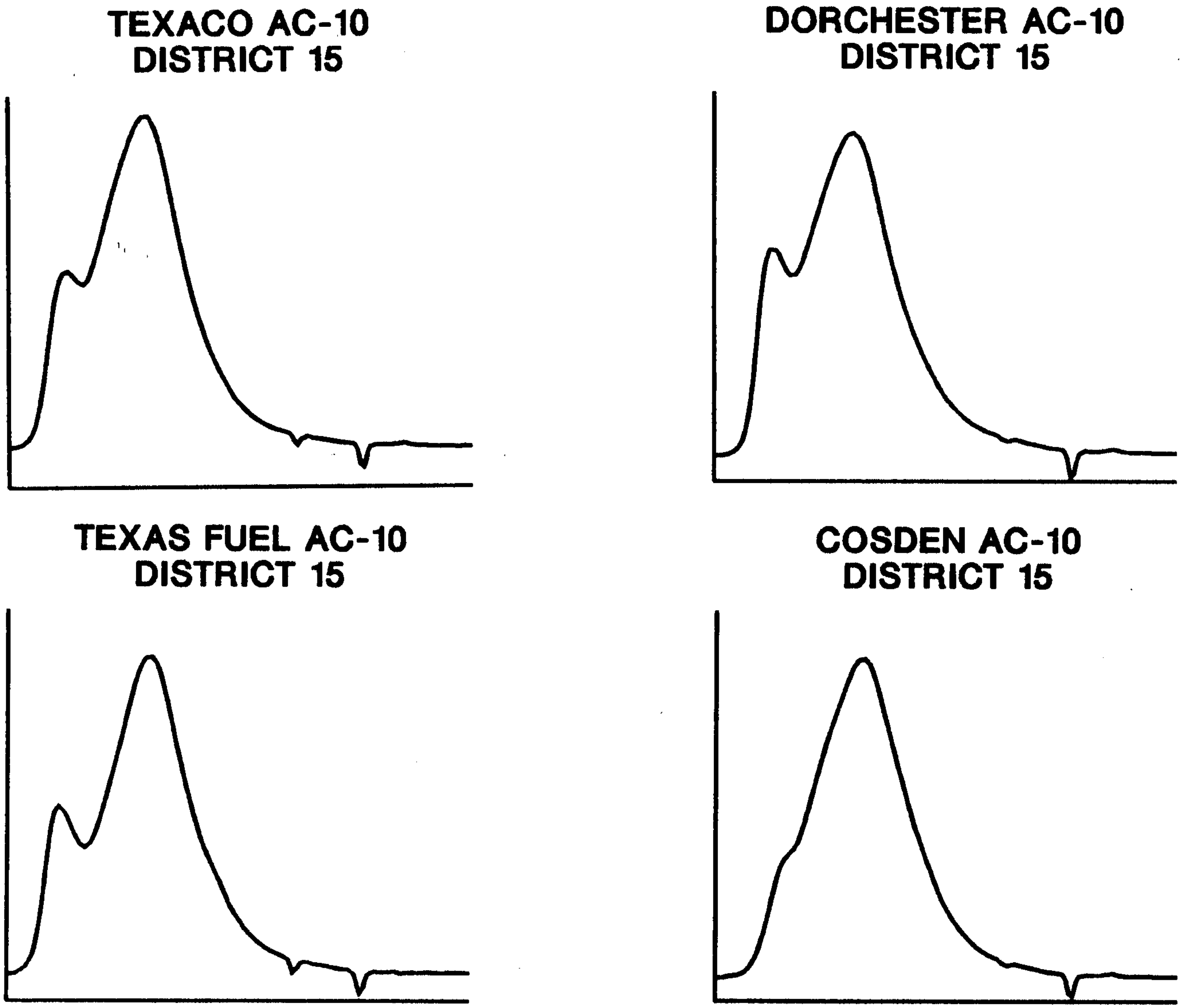
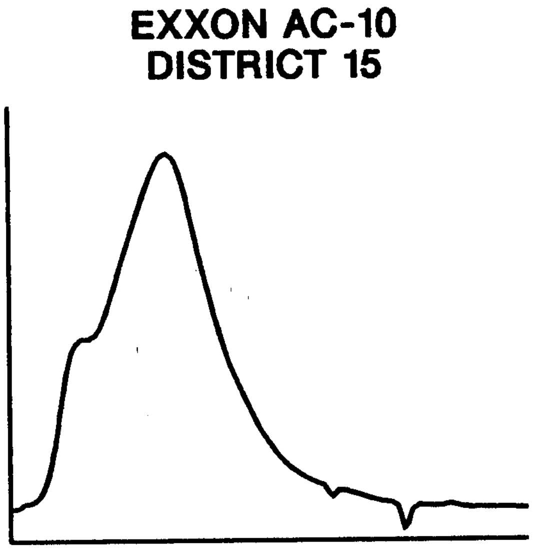
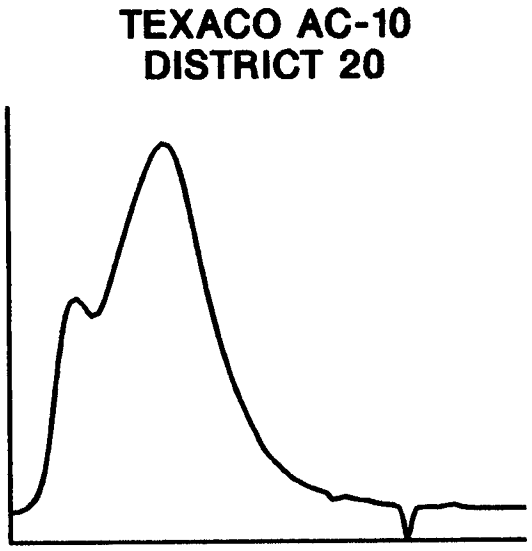
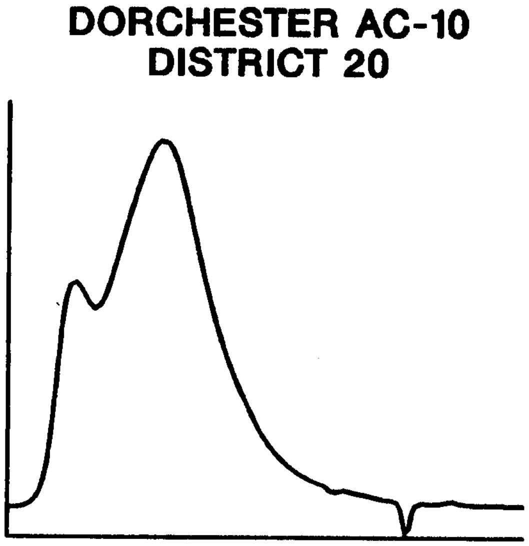


Figure 3-16
Chromatagrams of Seal Coats From District 15
500 Å and 50 Å Columns/THF/100 μl/7%







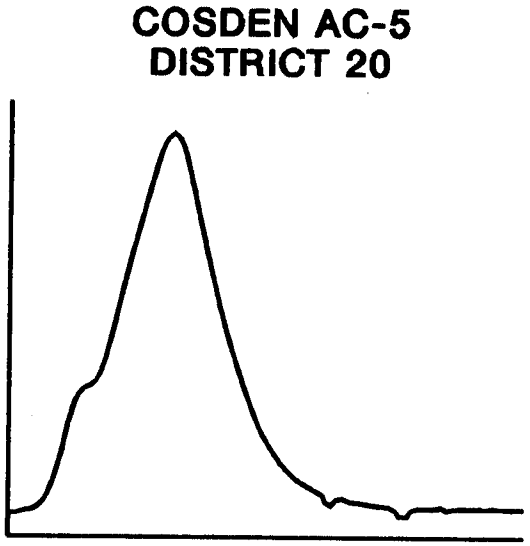


Figure 3-17
Chromatograms of the Seal Coats from Districts 15 and 20
500 and 50 Å Columns/THF/100 μl/7%

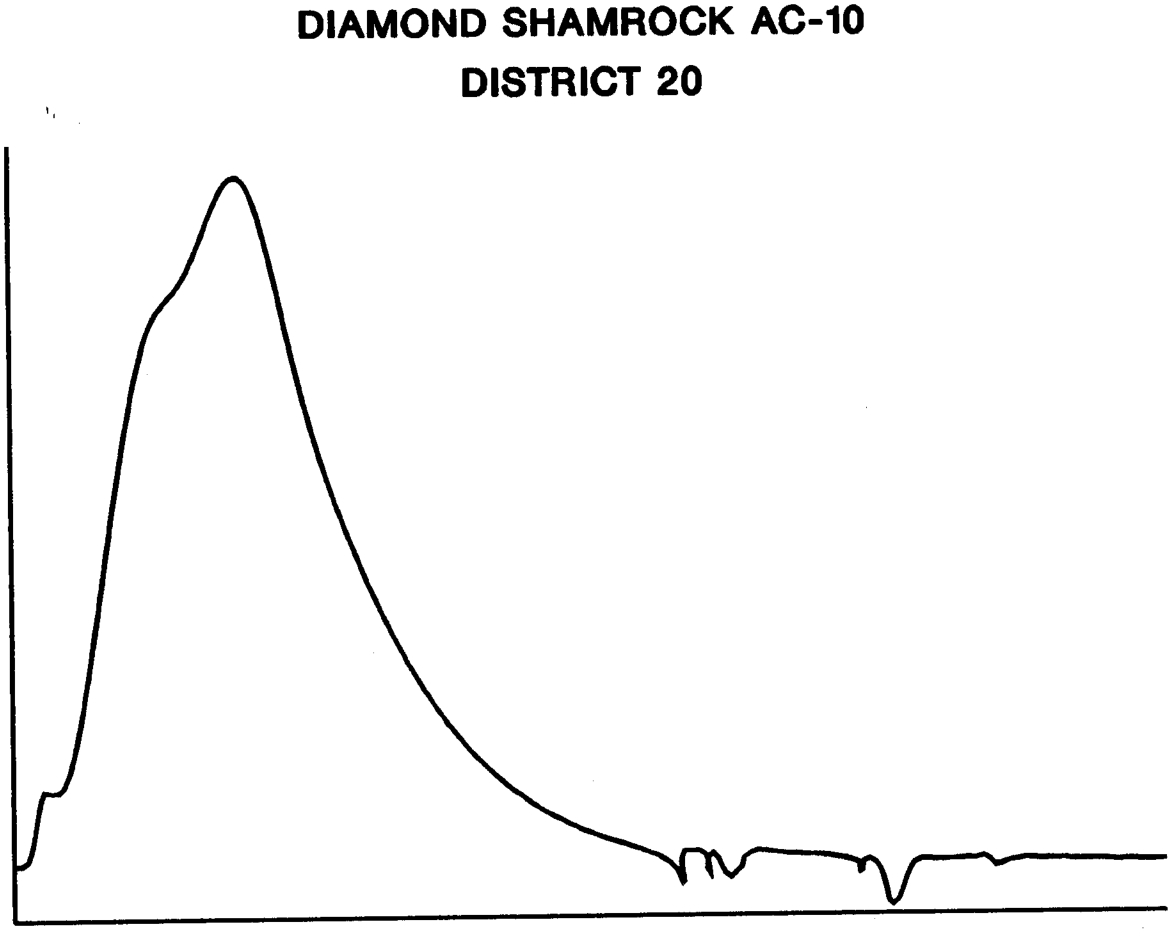


Figure 3-18
Chromatagram of Seal Coat From District 20
500 Å and 50 Å Columns/THF/100 μl/7%

CHAPTER 4

EVALUATION OF HOT MIX TEST PAVEMENTS IN TEXAS

In this chapter, chemical and physical test results on the hot mix test sections of Study 287 are summarized. These include analyses on virgin asphalts as well as recent core samples. Also reported are current performance evaluations of the test sections. Discussion and interpretation of these data with regard to performance are presented in Chapter 5.

Introduction

In 1981, an investigation of the performance of asphalt cements from several suppliers was sponsored by the State Department of Highways and Public Transportation (SDHPT) as Study Number 287 (Adams and Holmgreen, 1985). Test pavements were constructed in three different locations selected to represent different climatic zones within Texas. The study included gel permeation chromatography (GPC) analysis of the asphalt cement as well as measurements of the properties of the asphalt cements and the mechanical properties of the mixes. Plant operations and construction techniques were controlled in an attempt to control air voids and other construction parameters. Subsequent evaluation of the pavements, however, showed considerable variation in air voids, a problem to be considered in evaluating pavement performance.

Fortunately, samples of the materials used in Study No. 287 were preserved for future analyses with improved or new techniques. This provided a unique opportunity for on-going studies of asphalt characterization and performance. Virgin asphalt, and core samples were retained.

One goal of the present study was to provide additional analyses and evaluation of these test sections. Specifically, the objectives for the asphalts from the test sections included (1) performing gel permeation chromatography and other chemical tests of the virgin asphalt and pavement test section cores, (2) collecting and reviewing the physical property data of cores taken from the test sections, (3) evaluating the field performance of the test sections with regard to tenderness, water susceptibility, rutting, and other performance characteristics, (4), and relating the physical properties measured in the laboratory and the field performance of the test sections to the measured chemical properties and characterization, to the extent possible. The results of these efforts are reported below.

Summary of Test Pavements

Three hot mixed asphalt concrete pavement (overlay) test sites were located at Dickens, Dumas, and Lufkin, Texas as shown in Figure 4-1. The pavement at Dickens was placed July, 1982, Dumas in September, 1982, and Lufkin in July, 1983. The study included AC-10 and AC-20 asphalts from five different refineries, designated as Diamond Shamrock, MacMillan, Exxon, Dorchester, and Cosden, as shown in Table 4-1. Not all grades of asphalt cement were used at all sites.

The aggregate used at each site was locally available crushed rock, meeting SDHPT specifications. The Dickens aggregate was a crushed gravel-conglomerate, the Dumas aggregate was crushed limestone and the Lufkin aggregate was a combination of limestone and sandstone, both of which were absorptive. All mixes contained field sand to improve workability. Drum mix plants were utilized for mixing. Placement and compaction were accomplished in the conventional manner. Further details of the construction processes can be obtained from Adams and Holmgreen (1985), and Button et al. (1983).

Pavement Performance

At Dickens, the test pavements appeared to be satisfactory after construction. After one year's service, there were no signs of distress but the surface appeared dry and coarse. The surface was subsequently fog sealed. There were no visually discernible differences in performance between the asphalts from the different sources or of different grades. In the spring of 1985, the pavements were sealed to offset a slight raveling problem, otherwise, no distress was evident.

At Dumas, the pavement appeared to be satisfactory after construction. Within two months, the sections containing asphalts from MacMillan and Exxon had begun to ravel severely, in some cases completely through to the old asphalt pavement. At the end of one year of service, the section containing Exxon asphalt was replaced and the section containing MacMillan asphalt was partially replaced.

Figure 4-1

Location of Test Pavement Sites

Table 4-1

Physical Properties of Asphalts Obtained at Different Stages Before, During and After Construction*

Asphalt Refinery & Grade	Location of Test Pavement	Directly from Refinery					As Delivered to Construction Site					After TFOT		
		Viscosity			Penetration		Viscosity			Penetration		Viscosity	Penetration	Weight Loss
		77	140	275	39.2	77	77	140	275	39.2	77	140	77	Percent
Dia. Sham.	**	0.66	973	2.76	20	106	–	–	–	–	–	1280	69	0
AC-10	Dickens	-	-	-	-	-	1.35	1220	4.51	15	95			
	Dumas	-	-	-	-	-	0.56	958	4.65	16	104			
Dia. Sham.	**	3.55	2240	6.42	-	-	-	-	-	-	-	4680	41	0
AC-20	Dickens	-	-	-	-	-	4.00	2180	7.15	8	65			
	Dumas	-	-	-	-	-	1.90	2160	6.39	16	61			
	Lufkin	-	-	-	-	-	1.80	1730	5.05	16	70			
MacMillan	**	0.22	773	2.76	35	166	–	–	–	–	–	1210	121	0.04
AC-10	Dumas	-	-	-	-	-	0.36	961	3.63	39	133			
	Lufkin	-	-	-	-	-	0.76	932	3.63	25	95			
MacMillan	**	1.55	3010	5.33	26	64	–	–	–	–	–	5010	53	0.04
AC-20	Dickens	-	-	-	-	-	1.20	2520	4.64	27	77			
Exxon	**	0.66	1268	2.85	16	80	–	–	–	–	–	2540	50	0.03
AC-10	Dumas	-	-	-	-	-	0.83	1388	3.06	15	74			
Exxon	**	1.70	2180	3.22	18	58	–	–	–	–	–	4020	32	0.05
AC-20	Dickens	-	-	-	-	-	2.75	2580	3.55	7	43			
	Lufkin	-	-	-	-	-	1.55	1810	3.19	6	64			
Dorchester	**	0.50	930	3.18	35	113	–	–	–	–	–	2380	68	0.13
AC-10	Dumas	-	-	-	-	-	0.53	1030	3.21	30	105			
	Lufkin	-	-	-	-	-	0.42	1040	2.88	33	111			
Dorchester	**	1.11	1810	4.09	26	81	–	–	–	–	–	3240	56	0.05
AC-20	Dickens	-	-	-	-	-	2.50	2150	4.53	22	69			
	Lufkin	-	-	-	-	-	0.96	1910	3.96	23	79			
Cosden	**	0.88	955	2.34	17	80	–	–	–	–	–	2440	42	0.37
AC-10	Dickens	-	-	-	-	-	1.15	1260	2.55	15	72			
	Dumas	-	-	-	-	-	0.97	1038	2.48	16	71			
Cosden	**	2.25	1910	3.10	13	45	–	–	–	–	–	4280	32	0.15
AC-20	Dickens	-	-	-	-	-	1.90	1520	2.87	9	53			
	Dumas	-	-	-	-	-	1.60	2350	3.17	10	54			

*Viscosity at 77°F given in poise × 10^6
Viscosity at 140 and 275°F given in poise

**These data are representative of asphalts obtained directly from refineries, not from a specific construction site

Table 4-1 (Continued)

Physical Properties of Asphalts Obtained at Different Stages Before, During and After Construction*

Asphalt Refinery & Grade	Location of Test Pavement	Recovered from Lab Mixes					Recovered from Cores				
		Viscosity			Penetration		Viscosity			Penetration	
		77	140	275	39.2	77	77	140	275	39.2	77
Dia. Sham. AC-10	Dickens	12.0	2000	5.93	21	62	17.0	12,400	7.29	15	37
	Dumas	1.6	1723	5.24	20	75	2.0	2600	4.81	15	57
Dia. Sham. AC-20	Dickens	18.4	9560	11.0	14	20	12.0	12,300	11.8	5	25
	Dumas	3.4	2980	7.13	12	51	5.8	4470	8.41	10	41
	Lufkin	4.5	3780	7.45	15	52	3.55	3470	6.92	10	48
MacMillan AC-10	Dumas	0.56	1360	3.49	57	107	0.7	1450	3.59	30	90
	Lufkin	3.45	3600	5.46	22	57	3.70	3890	6.26	7	56
MacMillan AC-20	Dickens	7.0	11,250	8.30	20	38	21.0	9790	5.67	3	17
Exxon AC-10	Dumas	2.9	3000	3.86	7	45	2.06	2480	4.41	15	62
Exxon AC-20	Dickens	16.0	8670	6.06	8	21	8.00	5520	8.08	8	32
	Lufkin	3.3	2939	4.40	9	48	3.80	2750	3.87	10	46
Dorchester AC-10	Dumas	1.5	1990	3.98	26	66	1.28	1930	4.04	26	71
	Lufkin	1.28	1870	3.90	19	73	1.20	2420	4.44	16	63
Dorchester AC-20	Dickens	1.40	11,400	8.74	21	32	21.0	8670	5.79	2	20
	Lufkin	4.10	5940	5.77	5	45	3.80	2975	4.98	12	52
Cosden AC-10	Dickens	1.30	4322	4.16	8	28	18.5	23,100	9.70	10	21
	Dumas	2.00	1940	3.08	12	47	–	–	–	–	–
Cosden AC-20	Dickens	14.0	4750	4.49	9	29	30.0	15,500	7.45	0	18
	Dumas	5.0	2374	3.42	12	41	14.5	8790	5.06	4	23

*Viscosity at 77°F given in poise × 10^6
Viscosity at 140 and 275°F given in poise

At Lufkin, the pavement appeared to be satisfactory after construction and also after one year of service.

Physical Tests on Asphalt Cements

Five gallon samples of the asphalt cements were collected directly from the respective refineries about one month before construction of the test pavements. Five gallons of each asphalt were also collected from the transports at the three construction sites. In addition, asphalt samples were extracted from the laboratory molded plant mixes and pavement cores obtained at various periods after construction. Physical tests on these asphalts included penetration at 39.2 and 77°F, viscosity at 77, 140 and 275°F, ring and ball softening point, and thin film oven test with rheological properties thereafter (Adams and Holmgreen, 1985). Selected values are given in Table 4-1.

Composition Analyses

Compositional evaluations of the virgin asphalts and asphalts extracted from pavement cores from the three test sections were made using gel permeation chromatography, Corbett analyses, GPC analyses of the Corbett fractions, and elemental analyses. These techniques and procedures are described in Chapter 2. The results are presented below.

GPC Analysis with THF. Chromatograms for the Dumas location are given in Figures 4-2 to 4-8. For these tests, THF was the carrier solvent and one 500 Å and one 50 Å column were used in series. Shown in each figure are profiles for both the virgin asphalt used and asphalt obtained from pavement core samples. Analyses of the Dickens and Lufkin test sections also have been completed and appear in Figures A-1 to A-11 of Appendix A.

The asphalts used in the test sections at the various locations have quite distinctive chromatograms in both profile and retention time. Exxon profiles tend to have a very small leading peak which is better described as a small shoulder on the second, broader peak. By contrast, Cosden asphalts have a larger leading peak, indicating a larger fraction of large molecular size or asphaltene material. The Diamond Shamrock asphalt is even more distinctive in that the average retention time for the entire asphalt is much shorter than any of the other asphalts we have an-

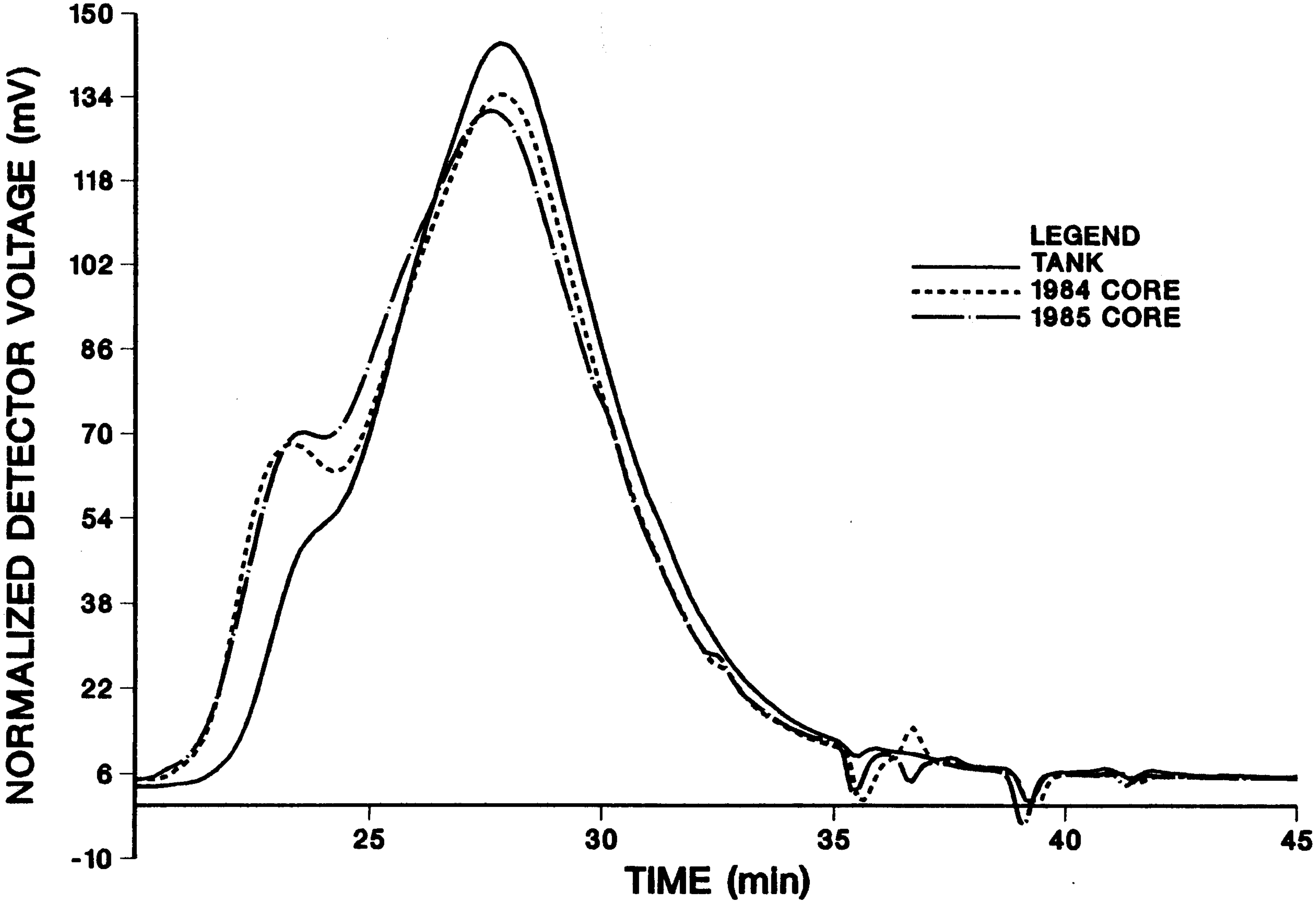


Figure 4-2
Comparison of Core Samples to the Original Asphalt in THF
Cosden AC-10, Dumas Test Site
500 Å and 50 Å Columns/THF/100 μl/7%

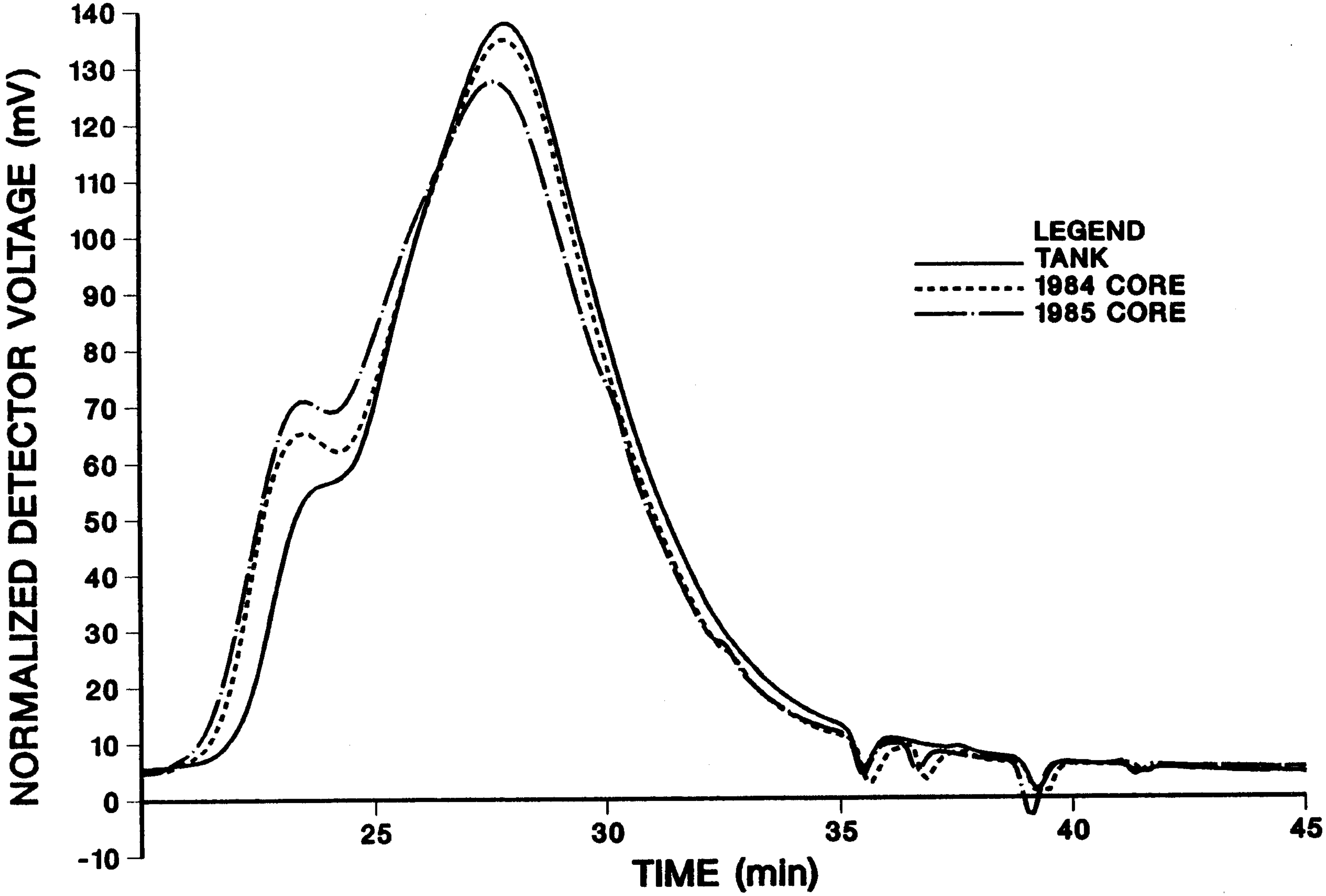


Figure 4-3
Comparison of Core Samples to the Original Asphalt in THF
Cosden AC-20, Dumas Test Site
500 Å and 50 Å Columns/THF/100 μl/7%

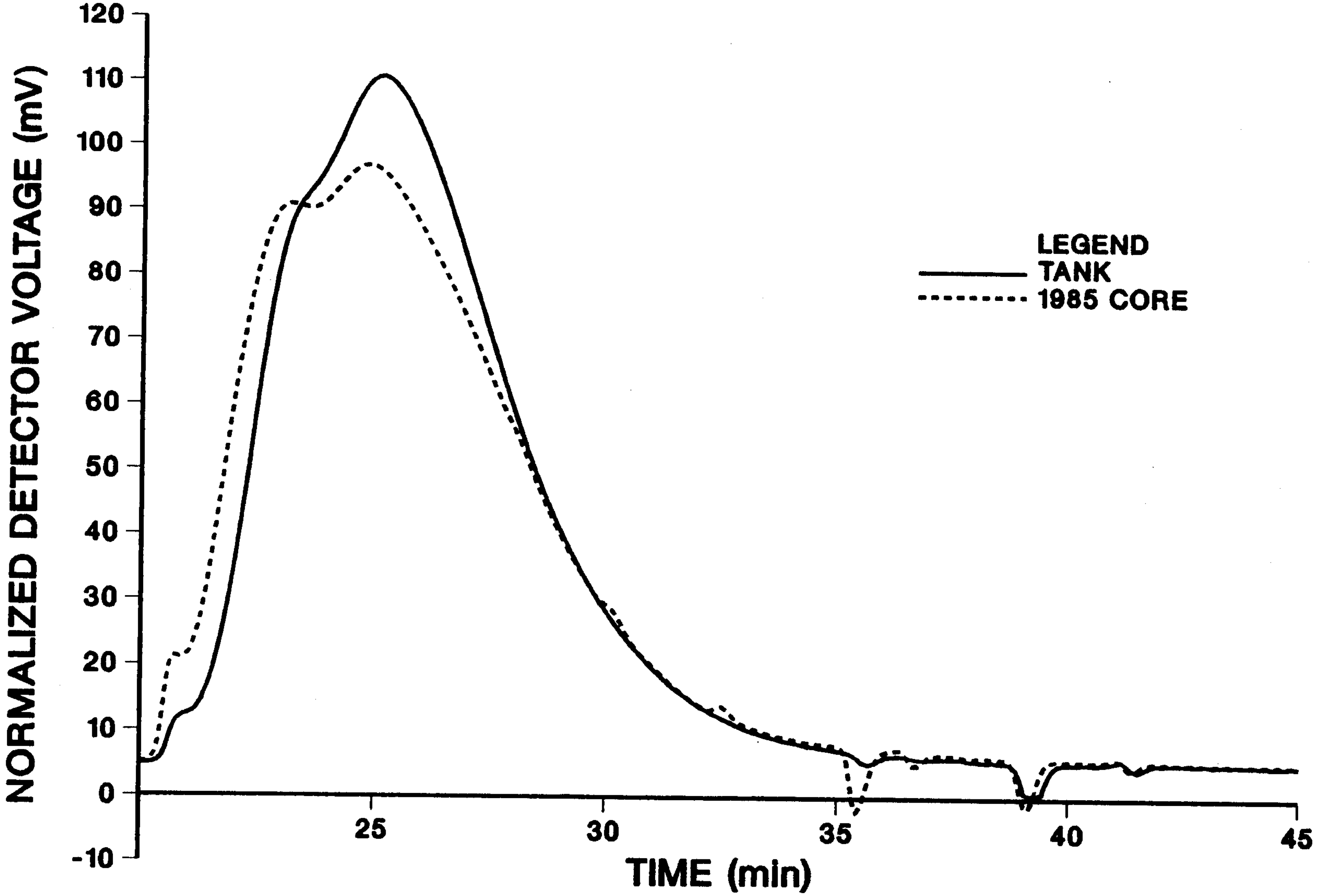


Figure 4-4
Comparison of Core Samples to the Original Asphalt in THF
Diamond Shamrock AC-10, Dumas Test Site
500 Å and 50 Å Columns/THF/100μl/7%

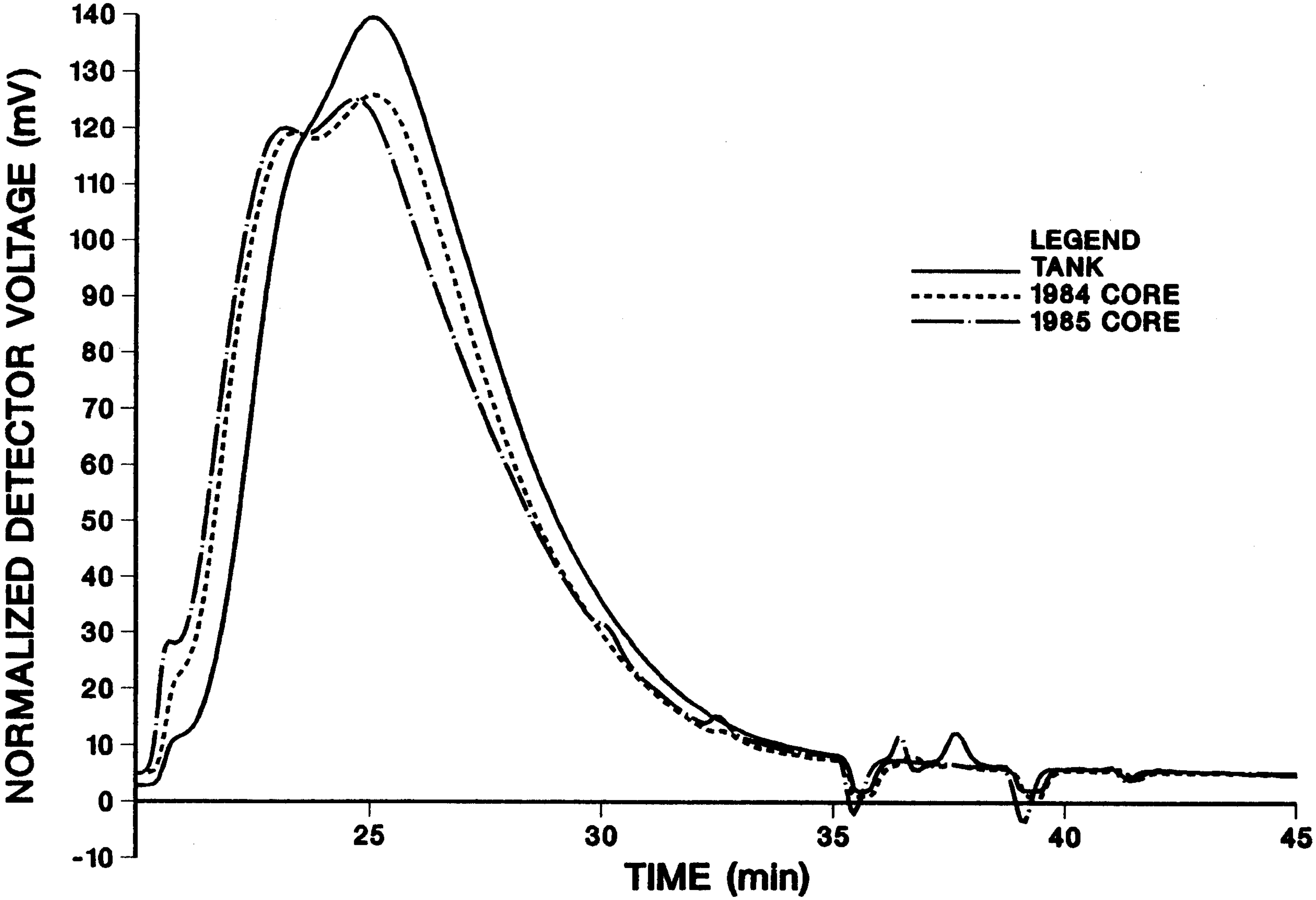


Figure 4-5
Comparison of Core Samples to the Original Asphalt in THF
Diamond Shamrock AC-20, Dumas Test Site
500 Å and 50 Å Columns/THF/100 μl/7%

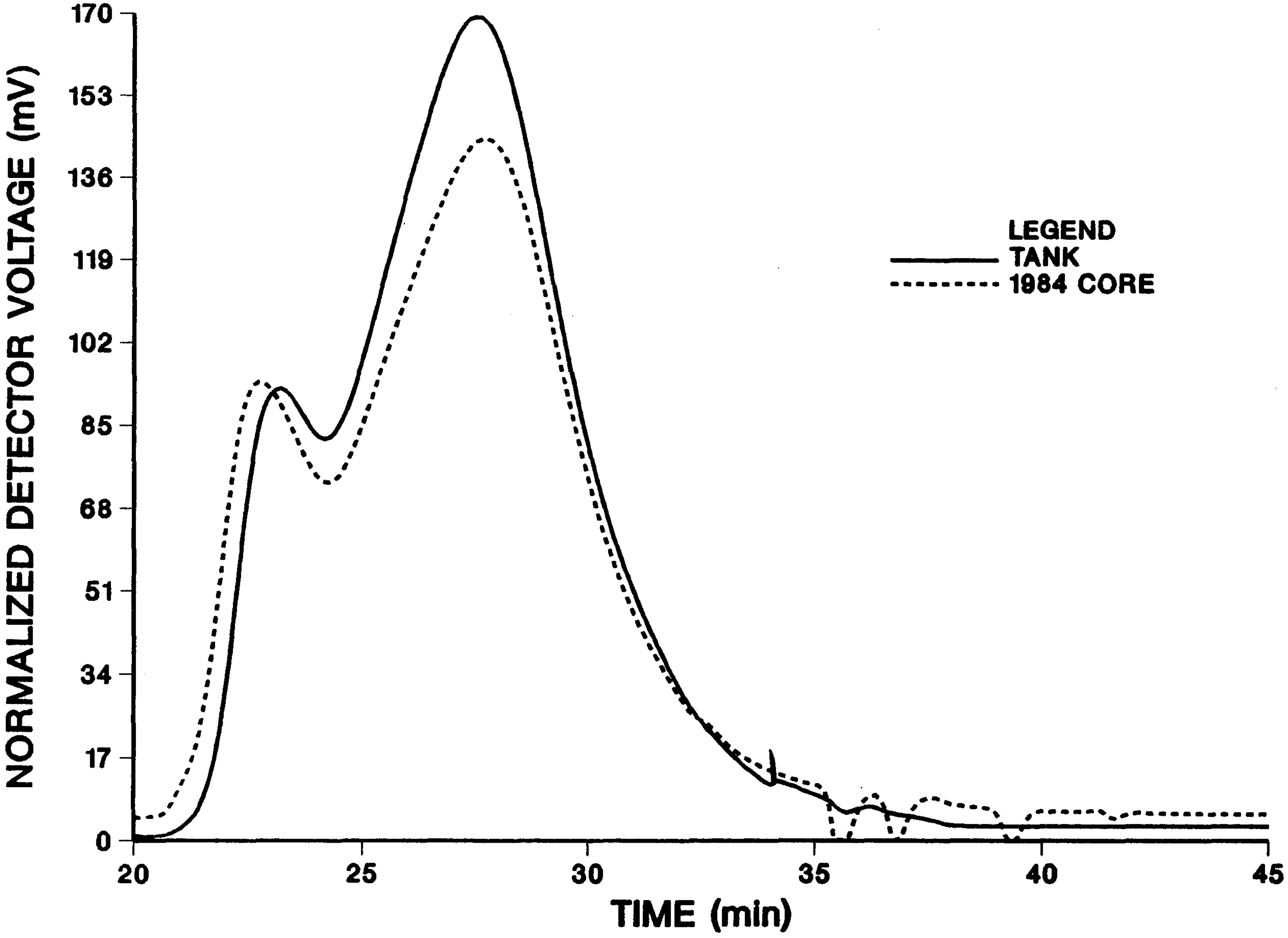


Figure 4-6
Comparison of Core Samples to the Original Asphalt in THF
Dorchester AC-10, Dumas Test Site
500 Å and 50 Å Columns/THF/100 μl/7%

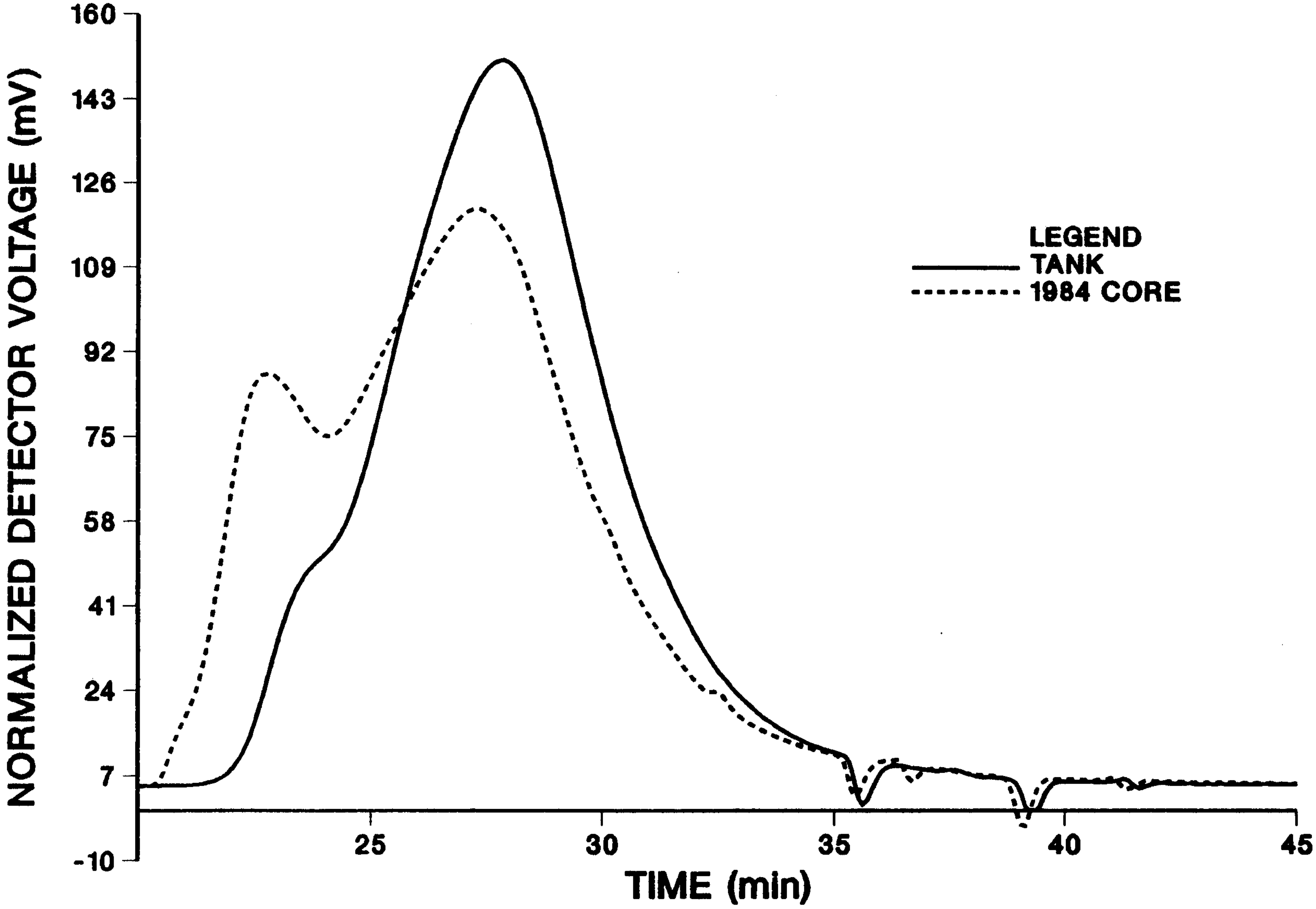


Figure 4-7
Comparison of Core Samples to the Original Asphalt in THF
Exxon AC-10, Dumas Test Site
500 Å and 50 Å Columns/THF/100 μl/7%

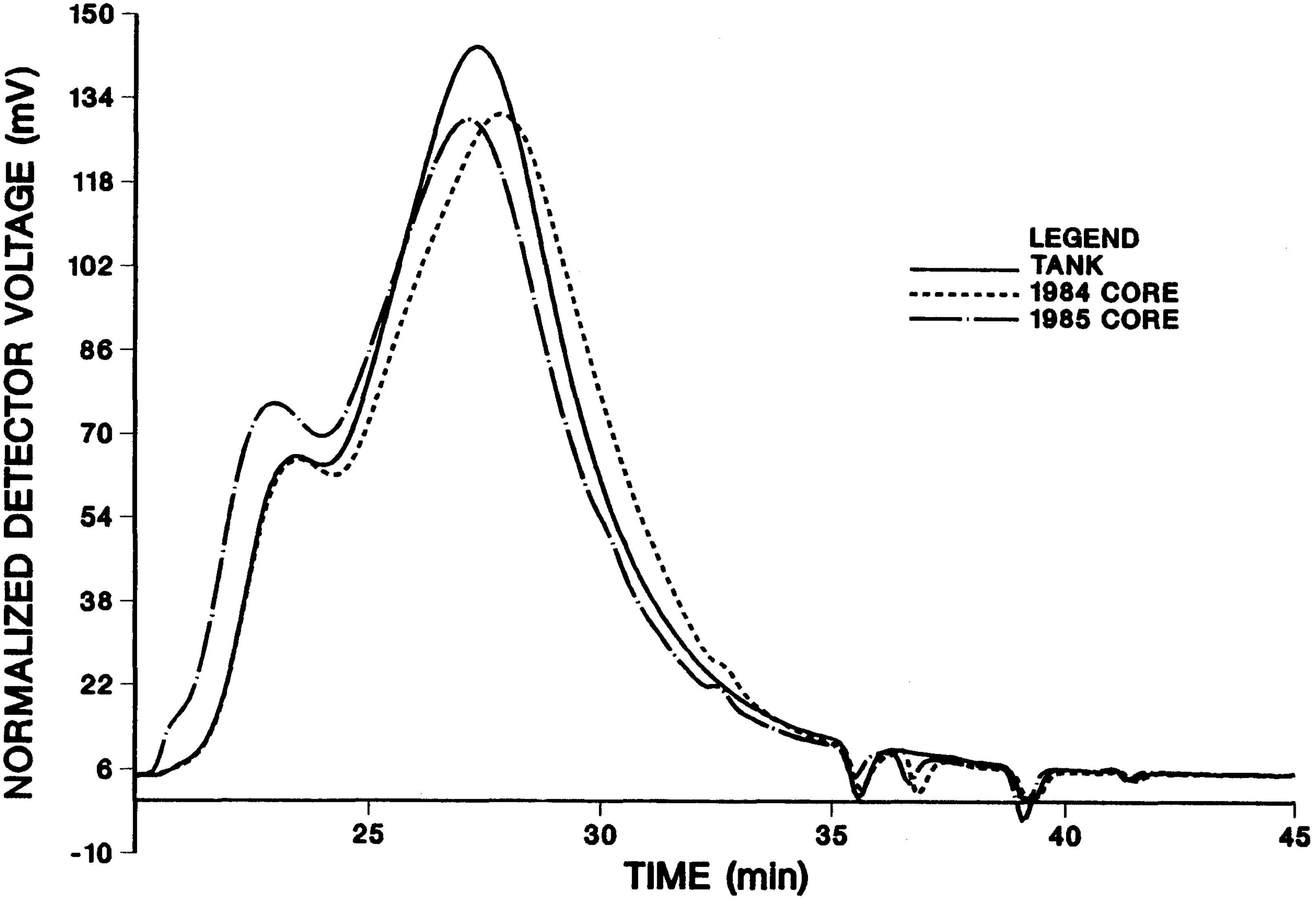


Figure 4-8
Comparison of Core Samples to the Original Asphalt in THF
MacMillan AC-10, Dumas Test Site
500 Å and 50 Å Columns/THF/100μl/7%

alyzed. Additionally, the entire profile is not as broad as for other asphalts. The Diamond Shamrock asphalt tends to be unique by all the various analytical techniques and is somewhat of an enigma in that it is low in asphaltenes, as defined by alkane precipitation, and yet has a higher fraction of large molecular size species than do the other asphalts. Petersen (1986) recently has shed some light on this puzzle, concluding that the large molecular size species in the Diamond Shamrock asphalt are highly branched and hence behave as polar aromatics in the Corbett fractionation analysis and are soluble in alkanes.

A comparison of the chromatograms of the virgin asphalts with core samples of the test sections shows that changes which occur in the asphalt during the hot mixing process and in pavement service are quite consistent between asphalts. Considered as a whole, the asphalts, upon aging, show an increase in large molecular size species (or at least in species that behave as larger sizes in the GPC) at the expense of the smaller sizes.

This behavior is characteristic of most, but not all, of the asphalts. The Exxon and MacMillan asphalts at Dumas are atypical. The Exxon asphalt was excessive in the degree of change and the MacMillan asphalt showed little change in the LMS region between the tank and the 1984 core and then a large change in the 1985 core. We believe the 1984 results are suspect. The toluene results, Figure 4-15, confirm this. The Exxon results are probably meaningless as this section failed and was replaced in 1983.

GPC Analysis with Toluene. Figure 4-9 to 4-15 show GPC results for Dumas using toluene as solvent with a 500 Å column. Results for Dickens and Lufkin are shown in Figures A-12 to A-22 in Appendix A.

The general increase in the LMS region with aging is again confirmed and more or less agrees with the THF results as to degree. Exxon and MacMillan are exceptions but as already noted there are problems with both of these asphalts.

The shapes of the chromatograms for each are strikingly different using toluene instead of THF. The trimodal behavior of Diamond Shamrock may be seen with both solvents, though it is more evident with toluene. Both Dorchester and MacMillan are bimodal in THF but trimodal in toluene though for each asphalt the peaks are less prominent than with Diamond Shamrock. With both Cosden and Exxon on the other hand, bimodal profiles are obtained with both solvents although in each case the leading peak is much more evident with THF. Overall the profiles in toluene are more distinctive than in THF.

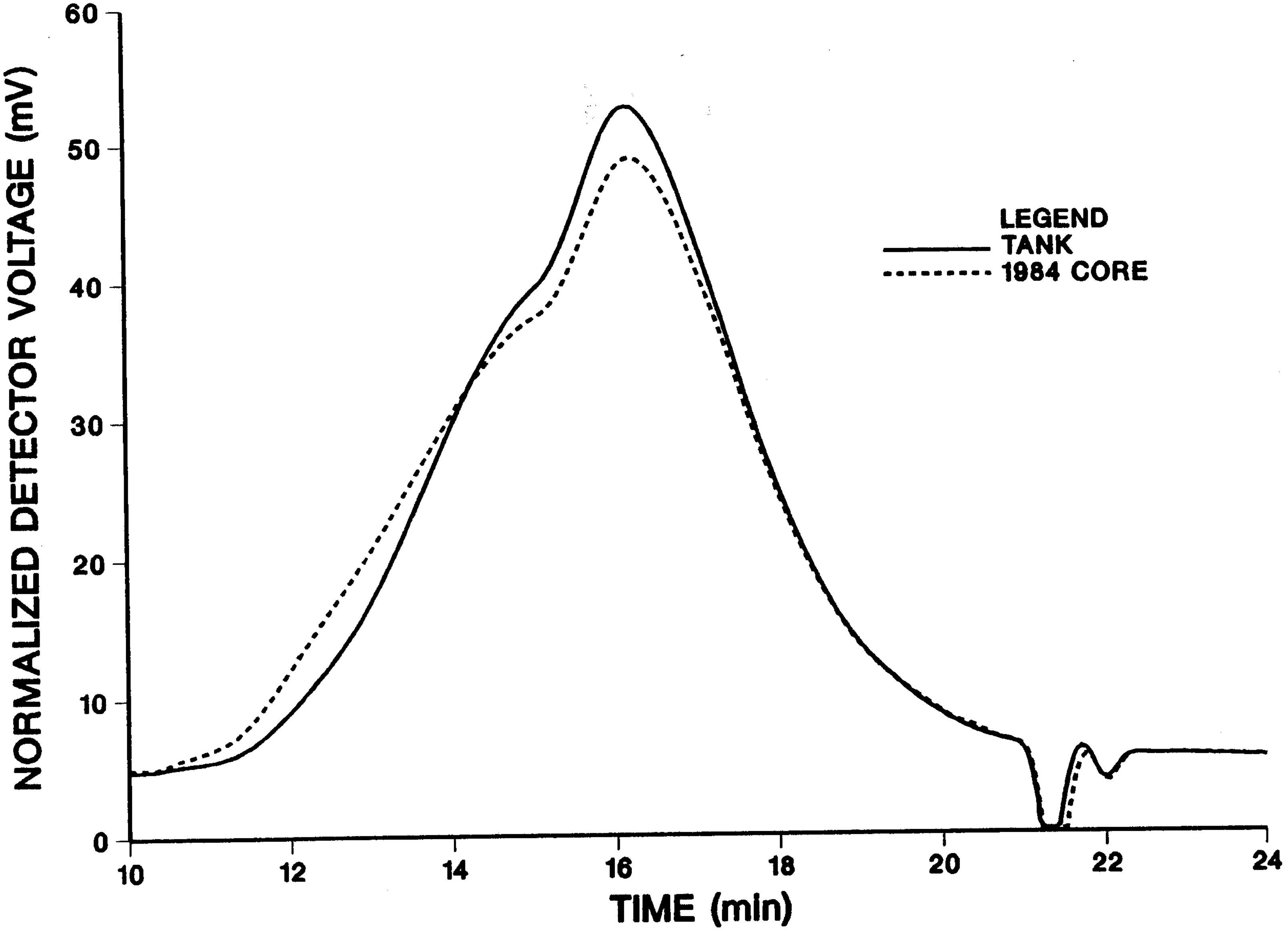


Figure 4-9
Comparison of Core Samples to the Original Asphalt in Toluene
Cosden AC-10, Dumas Test Site
500 Å Column/Toluene/100 μl/7%

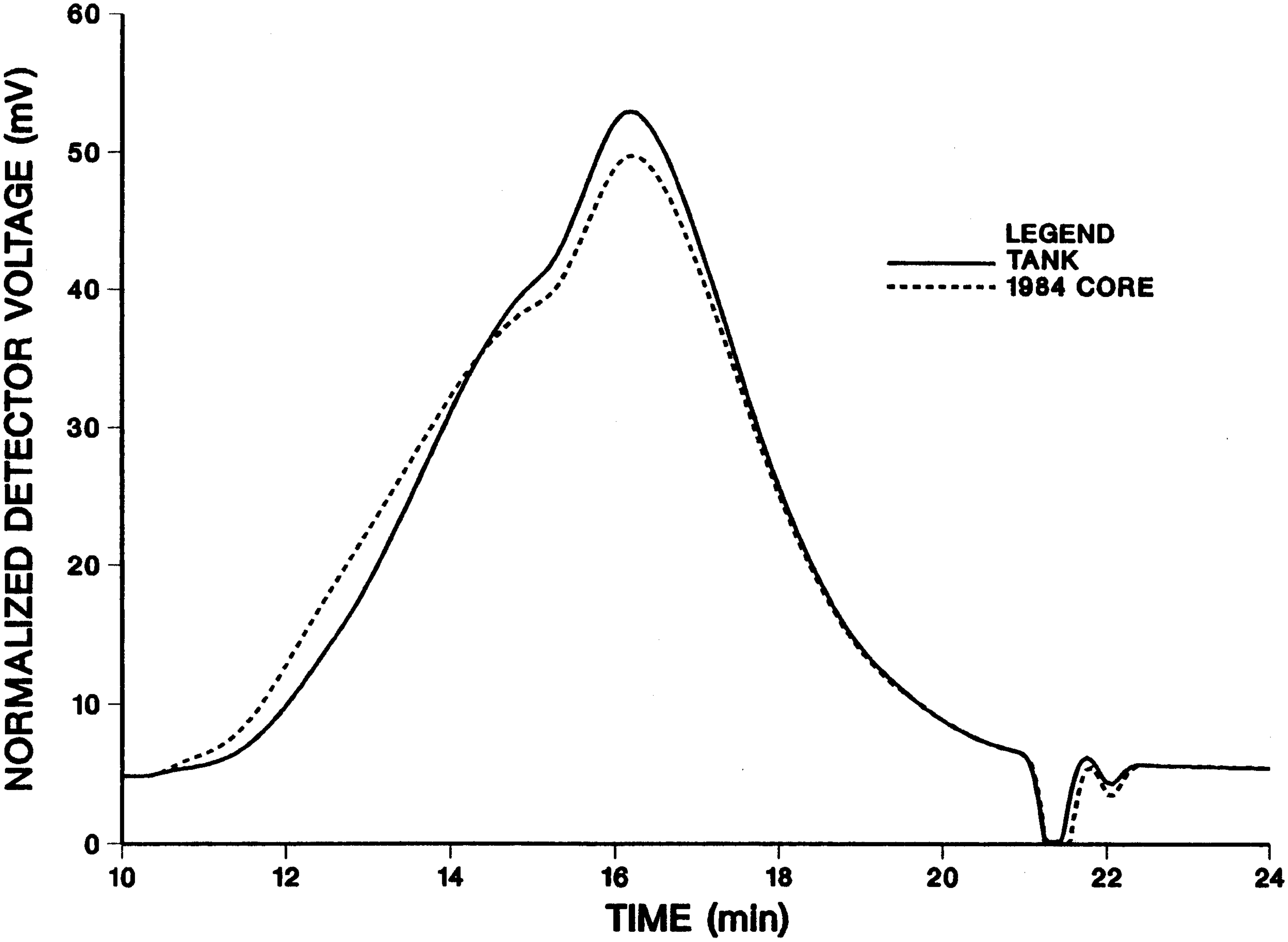


Figure 4-10
Comparison of Core Samples to the Original Asphalt in Toluene
Cosden AC-20, Dumas Test Site
500 Å Column/Toluene/100 μl/7%

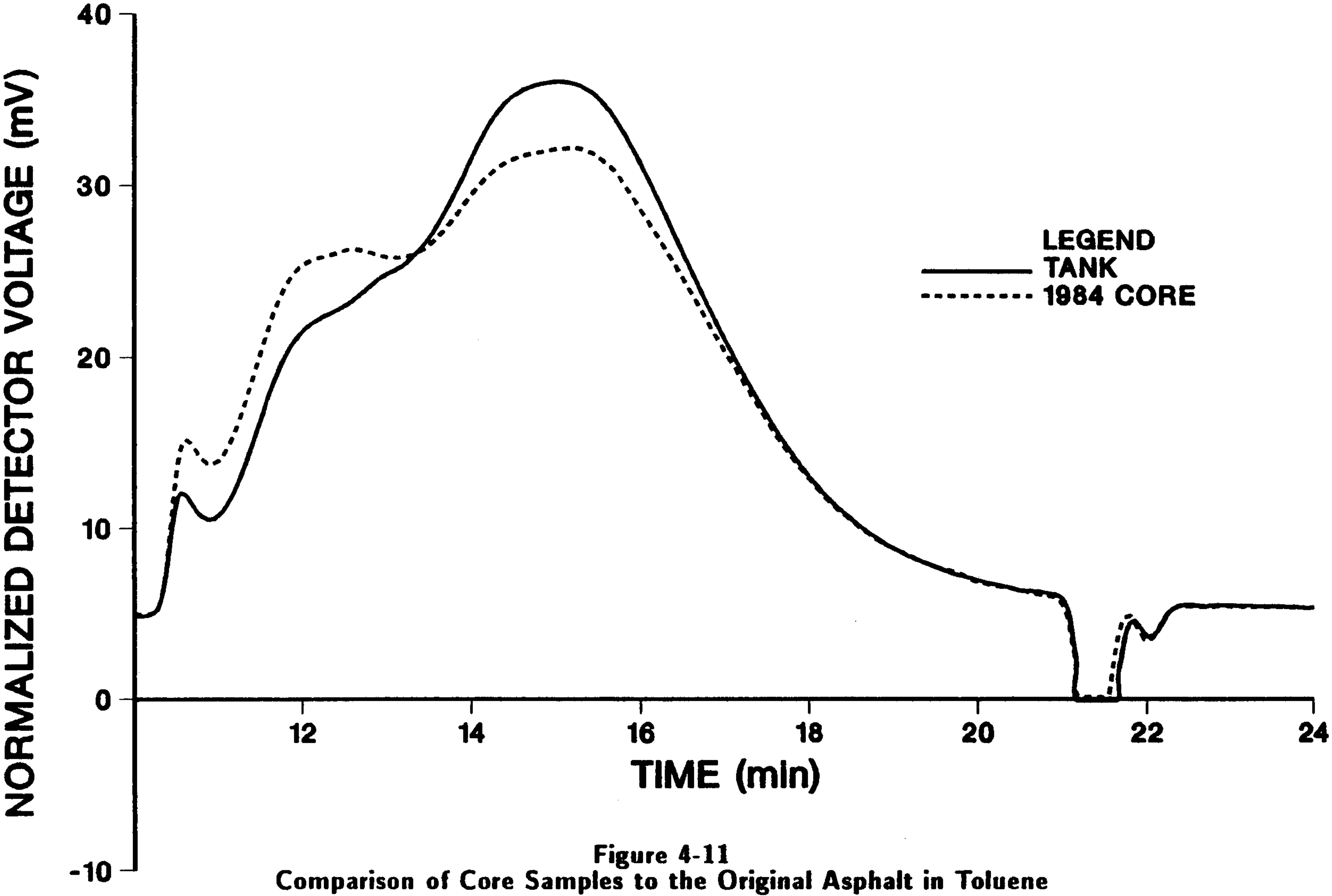


Figure 4-11
Comparison of Core Samples to the Original Asphalt in Toluene
Diamond Shamrock AC-10, Dumas Test Site
500 Å Column/Toluene/100 μl/7%

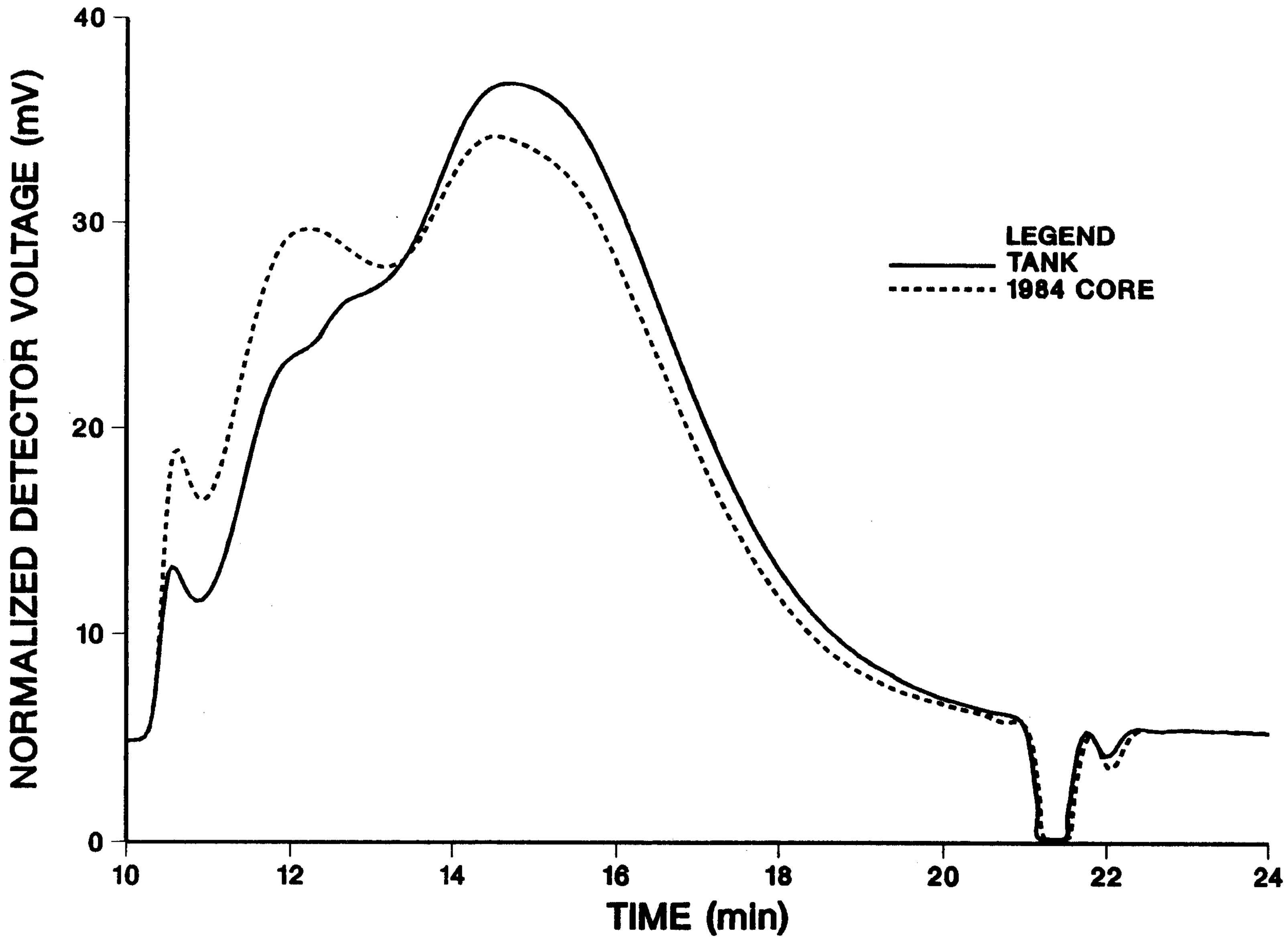


Figure 4-12
Comparison of Core Samples to the Original Asphalt in Toluene
Diamond Shamrock AC-20, Dumas Test Site
500 Å Column/Toluene/100 μl/7%

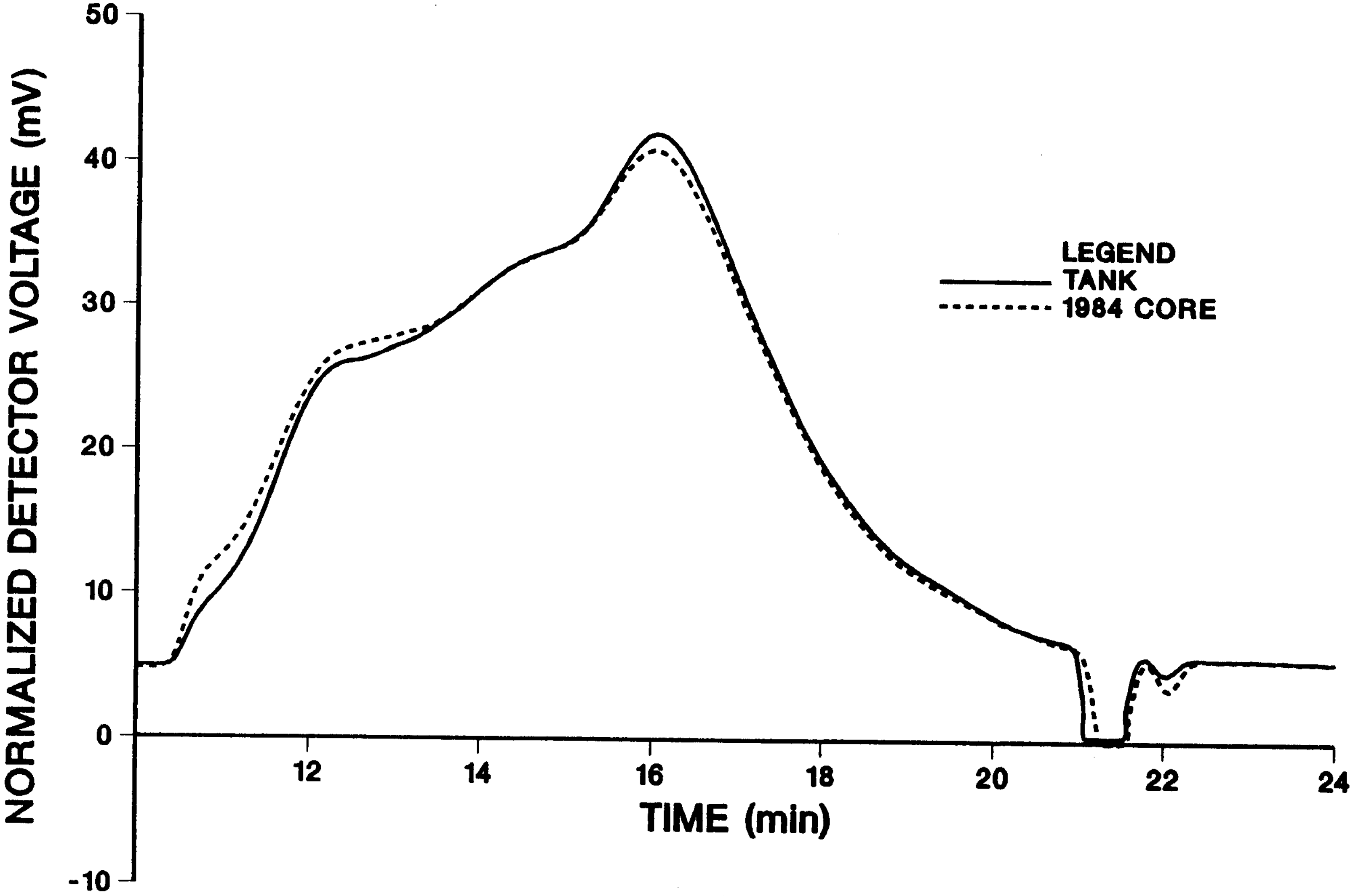


Figure 4-13
Comparison of Core Samples to the Original Asphalt in Toluene
Dorchester AC-10, Dumas Test Site
500 Å Column/Toluene/100 μl/7%

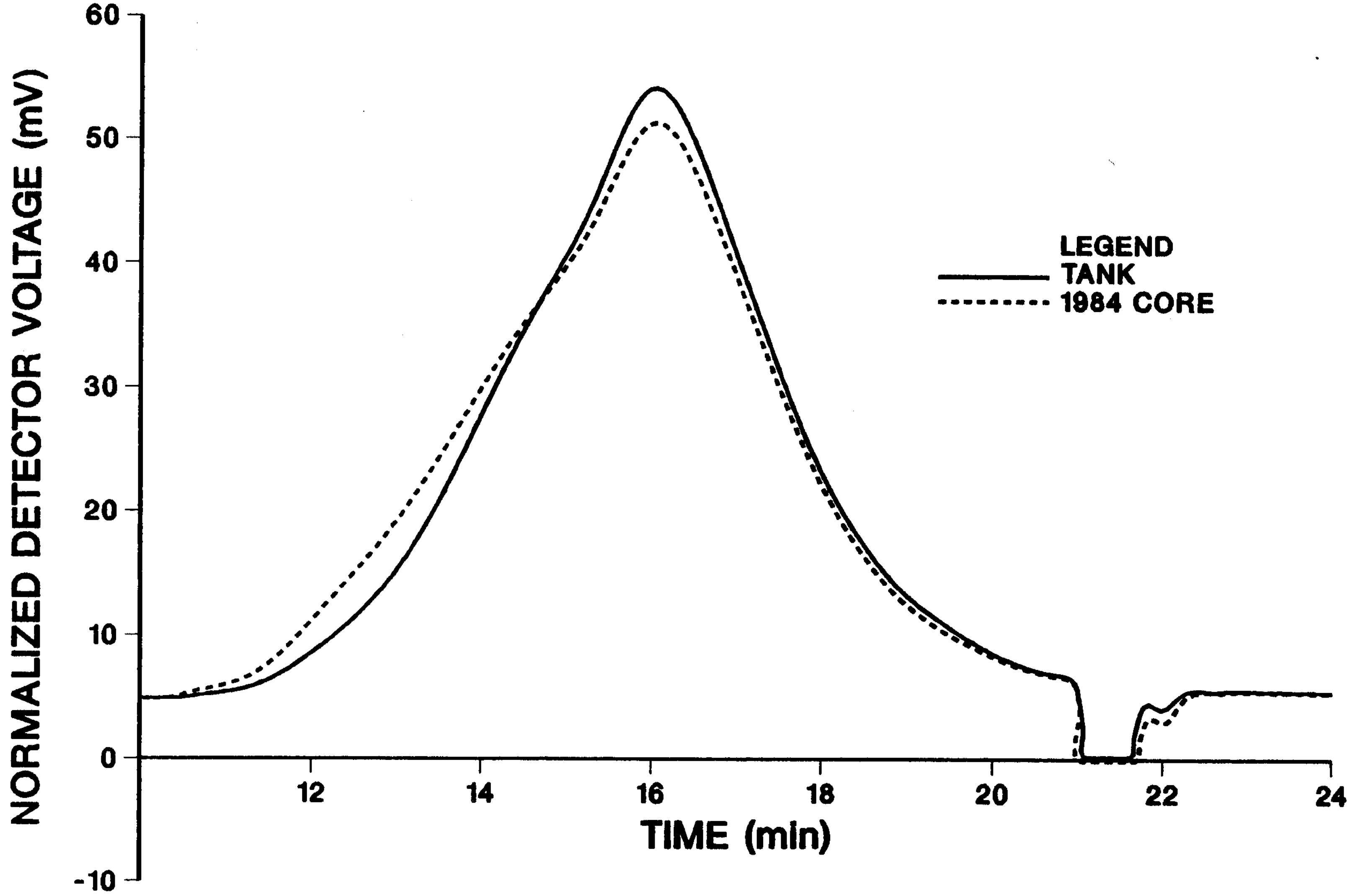


Figure 4-14
Comparison of Core Samples to the Original Asphalt in Toluene
Exxon AC-10, Dumas Test Site
500 Å Column/Toluene/100 μl/7%

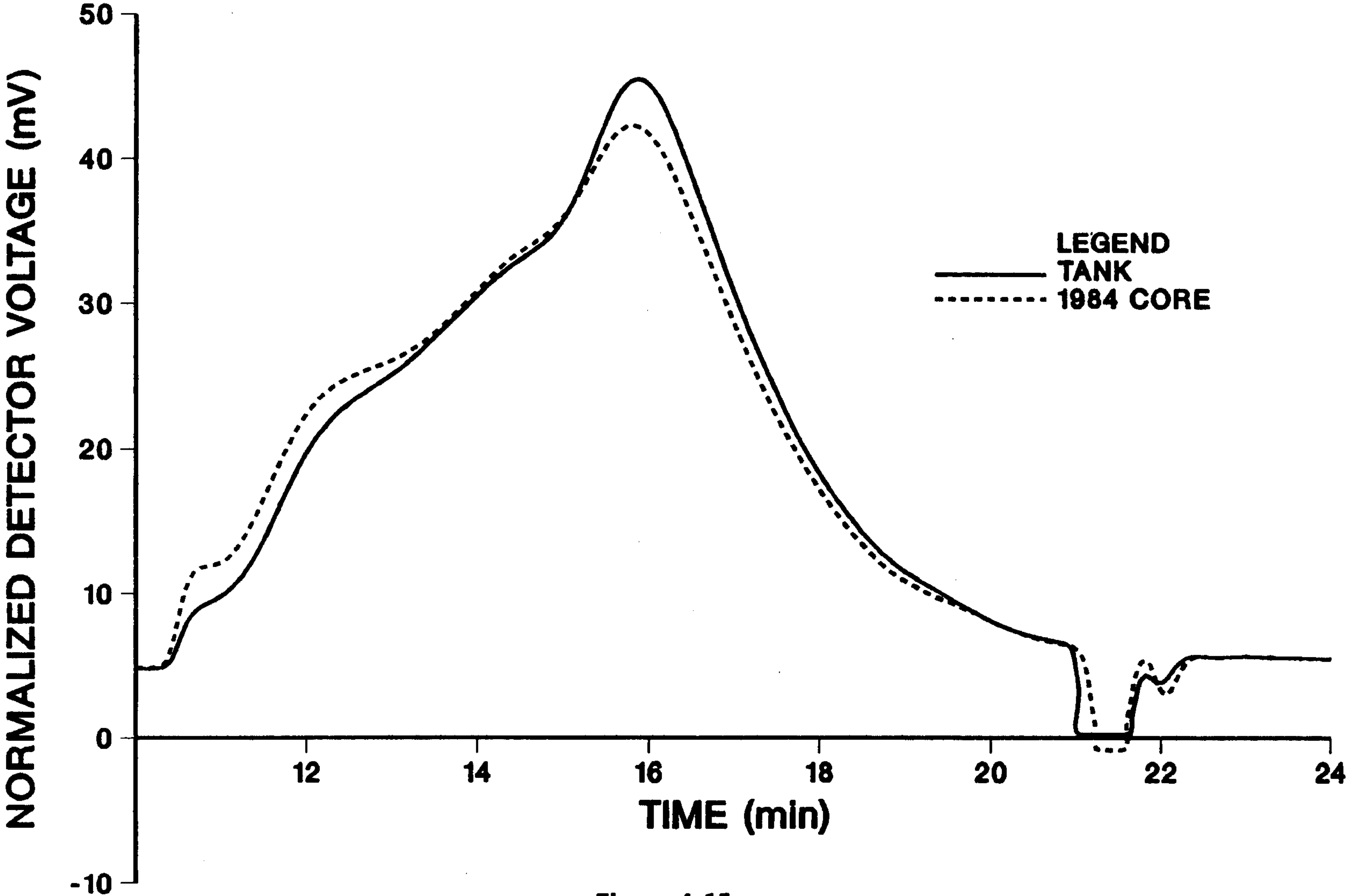


Figure 4-15
Comparison of Core Samples to the Original Asphalt in Toluene
MacMillan AC-10, Dumas Test Site
500 Å Column/Toluene/100 μl/7%

Corbett Fraction Analyses. Results for the tank and core samples for the three test locations are shown in Tables 4-2 through 4-4. As with the GPC results, differences in the Corbett analyses for the different asphalts are evident. The Diamond Shamrock asphalts are very low in asphaltene and saturates content (less than 1% and about 5% or less, respectively) while the other asphalts are more typical (in the range of 10 to 15% for both asphaltenes and saturates). Generally, the reproducibility for any one of the fractions is of the order of 1 or 2 percentage points.

Based on a comparison of the Corbett fraction analyses of the virgin asphalts with the corresponding core samples, typical changes for the asphalts were noted. The saturate fraction, in most instances, does not change significantly. It may increase or decrease, but by a fairly small amount. The notable exception is Diamond Shamrock in one test section which shows an increase to 10% from 2.2%. This analysis was not repeated and thus was not confirmed. The saturates fraction is considered to consist largely of saturated hydrocarbon molecules, which are characterized by low reactivity. Consequently, they were not expected to age significantly. The naphthene aromatic fraction, consisting of somewhat larger molecules with a higher degree of polarity, and, presumably, a higher degree of reactivity, was usually observed to undergo significant changes upon aging. This fraction typically decreases during the combined hot mixing/pavement aging processes. In the cores, naphthene aromatic fractions that were significantly lower than the virgin asphalt fractions were observed. The polar aromatic fraction likewise underwent changes. Usually, there was a net increase in the size of this fraction, although, in some cases, there was a decrease or little change at all. The net change in polar aromatics is the result of increases due to aging of the naphthene aromatic fractions coupled with decreases due to aging of the original polar aromatic species which become asphaltenes. Thus the net change is determined by which effect is greater. The asphaltene fraction almost always increases, although there are some deviations from this trend. However, this may be due to experimental error.

It should be re-emphasized that the names given to the various fractions are names only. They do not necessarily represent either the size or chemical functionality of any particular species in the group. Generally, the groups are ranked with respect to molecular size according to

$$\text{asphaltenes} > \text{polar aromatics} > \text{naphthene aromatics} > \text{saturates}.$$

Table 4-2

Corbett Analysis for Performance Test Pavements

Dumas Tank vs. Core

Description	Recovery	A	S	NA	PA
Cosden AC-10 (Tank)	100.7	9.8	12.0	40.9	37.3
Cosden AC-10 (Core)	97.6	13.1	14.2	26.6	46.1
Cosden AC-20 (Tank)	99.1	11.0	10.3	39.7	39.0
Cosden AC-20 (Core)	98.5	16.7	11.9	28.0	43.4
Dia. Shamrock AC-10 (Tank)	97.3	0.8	2.2	55.1	42.0
Dia. Shamrock AC-10 (Core)	98.1	0	10.0	36.7	53.3
Dia. Shamrock AC-20 (Tank)	109.0	0.3	3.1	51.4	45.0
Dia. Shamrock AC-20 (Core)	95.7	0	1.5	40.1	58.4
Exxon AC-10 (Tank)	101.0	10.0	9.1	45.2	35.6
Exxon AC-10 (Core)	98.9	13.1	11.3	26.3	49.3
MacMillan AC-10 (Tank)	96.5	11.0	9.1	52.0	28.0
MacMillan AC-10 (Core)	101.1	8.1	6.9	40.6	44.4
Dorchester AC-10 (Tank)	98.5	14.7	10.2	44.6	30.5
Dorchester AC-10 (Core)	96.9	15.8	9.9	33.3	40.9

A – Asphaltenes precipitated by n-heptane
S – Saturates
NA – Naphthenic Aromatics
PA – Polar Aromatics

Table 4-3

Corbett Analysis for Performance Test Pavements

Dickens Tank vs. Core

Description	Recovery	A	S	NA	PA
Cosden AC-10 (Tank)	99.1	10.3	13.4	30.0	46.2
Cosden AC-10 (Core)	95.6	20.1	14.7	17.8	47.3
Cosden AC-20 (Tank)	100.8	11.8	12.8	32.7	42.8
Cosden AC-20 (Core)	98.0	20.3	11.2	22.8	45.8
Dia. Shamrock AC-10 (Tank)	98.4	0.2	5.2	43.3	51.3
Dia. Shamrock AC-10 (Core)	94.0	0	3.3	33.3	63.5
Dia. Shamrock AC-20 (Tank)	99.2	0.1	1.9	48.3	49.7
Dia. Shamrock AC-20 (Core)	97.3	0	3.0	42.4	54.6
Exxon AC-20 (Tank)	98.7	8.9	11.4	31.8	47.9
Exxon AC-20 (Core)	90.6	16.2	11.0	24.2	48.5
MacMillan AC-20 (Tank)					
MacMillan AC-20 (Core)	91.7	19.9	12.0	25.8	42.4
Dorchester AC-20 (Tank)	99.4	17.8	10.4	39.6	32.3
Dorchester AC-20 (Core)	96.1	21.3	12.4	21.9	44.3

A – Asphaltenes precipitated by n-heptane
S – Saturates
NA – Naphthenic Aromatics
PA – Polar Aromatics

Table 4-4

Corbett Analysis for Performance Test Pavements

Lufkin Tank vs. Core

Description	Recovery	A	S	NA	PA
Cosden AC-20 (Tank)	100.6	8.7	10.9	36.4	44.0
Cosden AC-20 (Core)	97.2	12.7	10.2	30.7	46.5
Dia. Shamrock AC-20 (Tank)	106.7	6.6	4.7	39.8	48.9
Exxon AC-20 (Tank)	98.5	14.3	10.6	36.5	38.5
Exxon AC-20 (Core)	94.1	11.8	9.6	24.8	53.8
MacMillan AC-20 (Tank)	98.7	9.1	11.2	42.6	37.1
MacMillan AC-20 (Core)	96.0	13.0	10.8	32.4	43.9
Dorchester AC-10 (Tank)	97.9	11.9	11.2	34.1	42.8
Dorchester AC-10 (Core)	97.7	14.2	14.8	27.5	43.5
Dorchester AC-20 (Tank)	99.8	11.4	10.7	28.0	49.9
Dorchester AC-20 (Core)	96.7	14.3	10.2	27.5	48.0

A – Asphaltenes precipitated by n-heptane
S – Saturates
NA – Naphthenic Aromatics
PA – Polar Aromatics

However, this is not necessarily true for every molecule in any particular group compared to every molecule in any other group. Likewise, even though the groups follow the same ranking with respect to polarity, one cannot say that this holds true for every molecule in a group relative to every molecule in any other group. Consequently, considering what happens to any specific molecule in the aging process, one cannot say with certainty or universality that, e.g., naphthene aromatic molecules become polar aromatic molecules as the result of aging. Future studies with more detailed chemical analyses should give a much improved understanding of the chemical composition of asphalts and their changes during the hot mix and pavement aging processes.

GPC Analyses of the Corbett fractions. As a first effort at learning more about the way specific parts of the asphalt cement change as a result of the hot mixing/pavement aging process, GPC analyses of the four Corbett fractions have been made for all of the asphalts from Study 287. Figures 4-16 to 4-22 show GPC chromatograms for the whole asphalts as well as the chromatograms for the individual Corbett fractions for 1984 samples of all test sections at Dickens. The asphaltene fraction, being, on average, a higher molecular weight than the other fractions, was eluted sooner; but it also indicates a wide range for the molecular weight of this fraction. This is not surprising as asphaltenes result as much from polarity as molecular weight, and even the higher molecular weight species probably result from association of smaller molecules. There is also a possibility that some of the apparently smaller molecular size material is actually of larger size but because of its polarity is weakly adsorbed on the column resulting in an increased retention time. It is interesting that the other three groups do not differ greatly in maximum peak location but there is a trend of decreasing size from polar aromatics to saturates.

The Diamond Shamrock asphalt (Figures 4-18 and 4-19) is extremely anomalous being composed almost entirely of polar aromatics and naphthene aromatics. Corbett (1979) has shown that good asphalts can be obtained by combining only those two fractions extracted from normal asphalts. As with all the chromatograms the peaks beyond 35 minutes are such compounds as water or unrecovered solvent. Note, however, that the peak at 30 minutes in Figure 4-17 also is present in the 1985 cores, Figures 4-4 and 4-5.

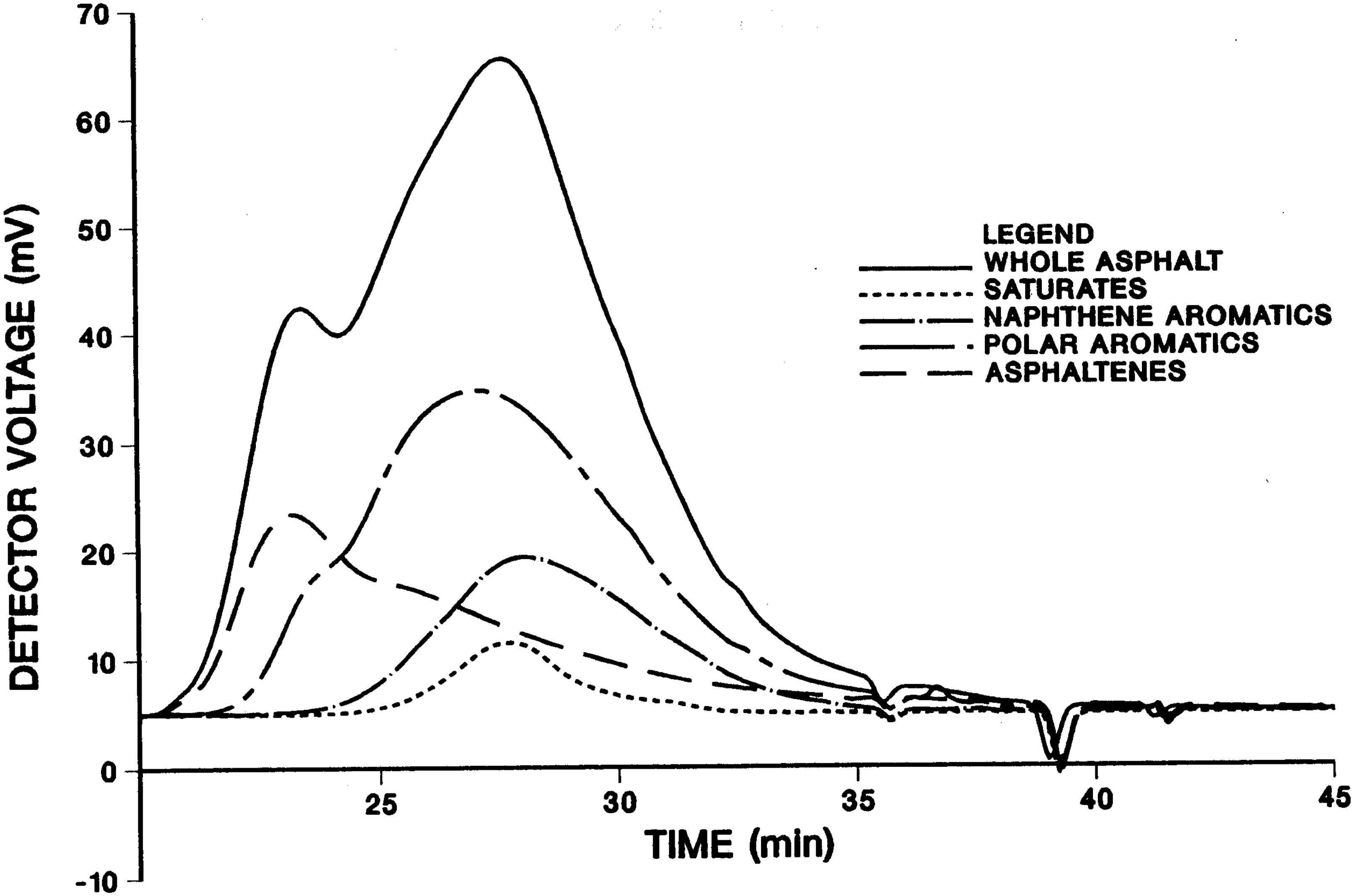


Figure 4-16
Individual Corbett Fractions Overlaid With The Whole Asphalt
Cosden AC-10,Dickens Test Site, 1984 Core
500 Å and 50 Å Columns/THF/100 μl/7%

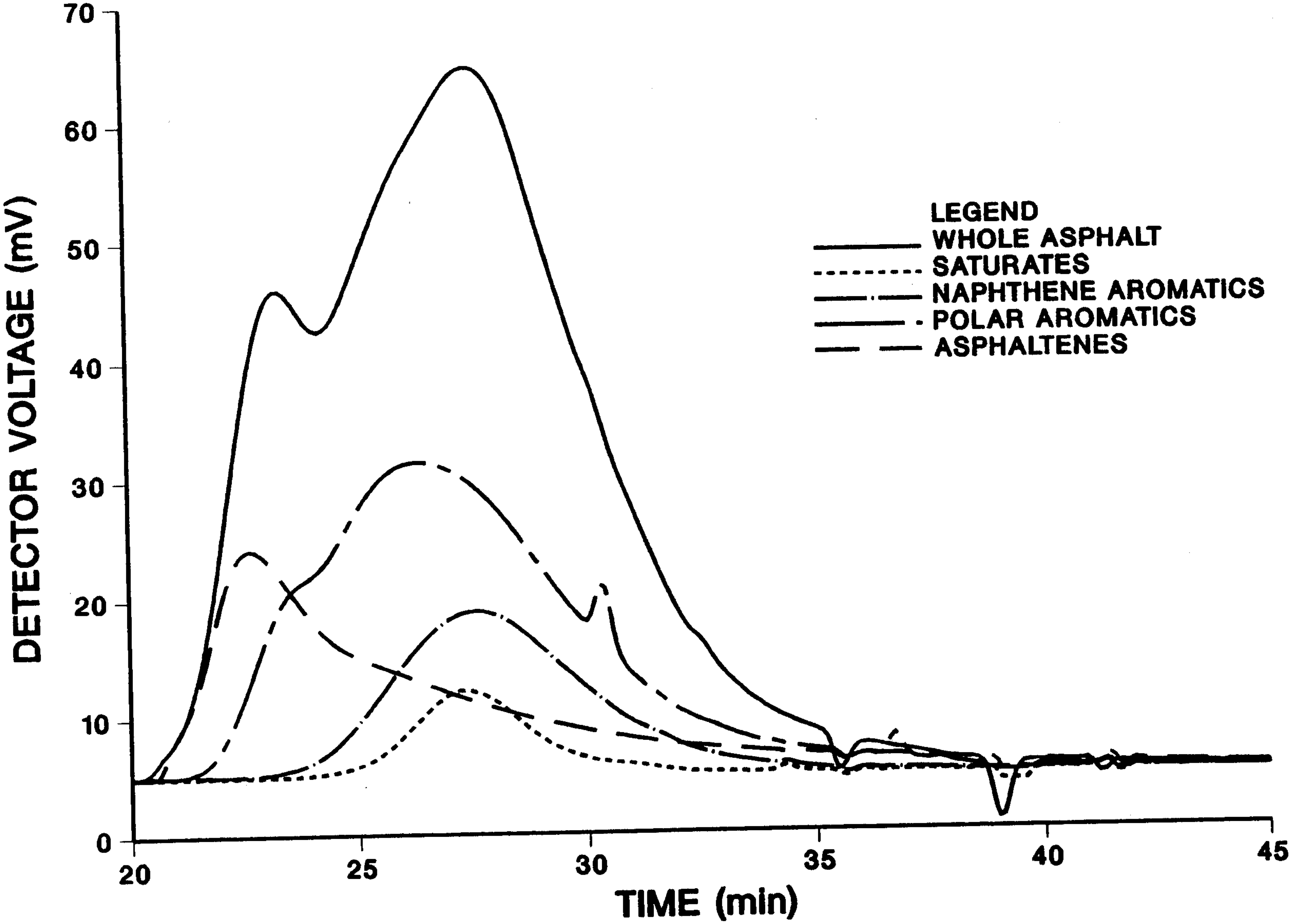


Figure 4-17
Individual Corbett Fractions Overlaid With The Whole Asphalt
Cosden AC-20, Dickens Test Site, 1984 Core
500 Å and 50 Å Columns/THF/100 μl

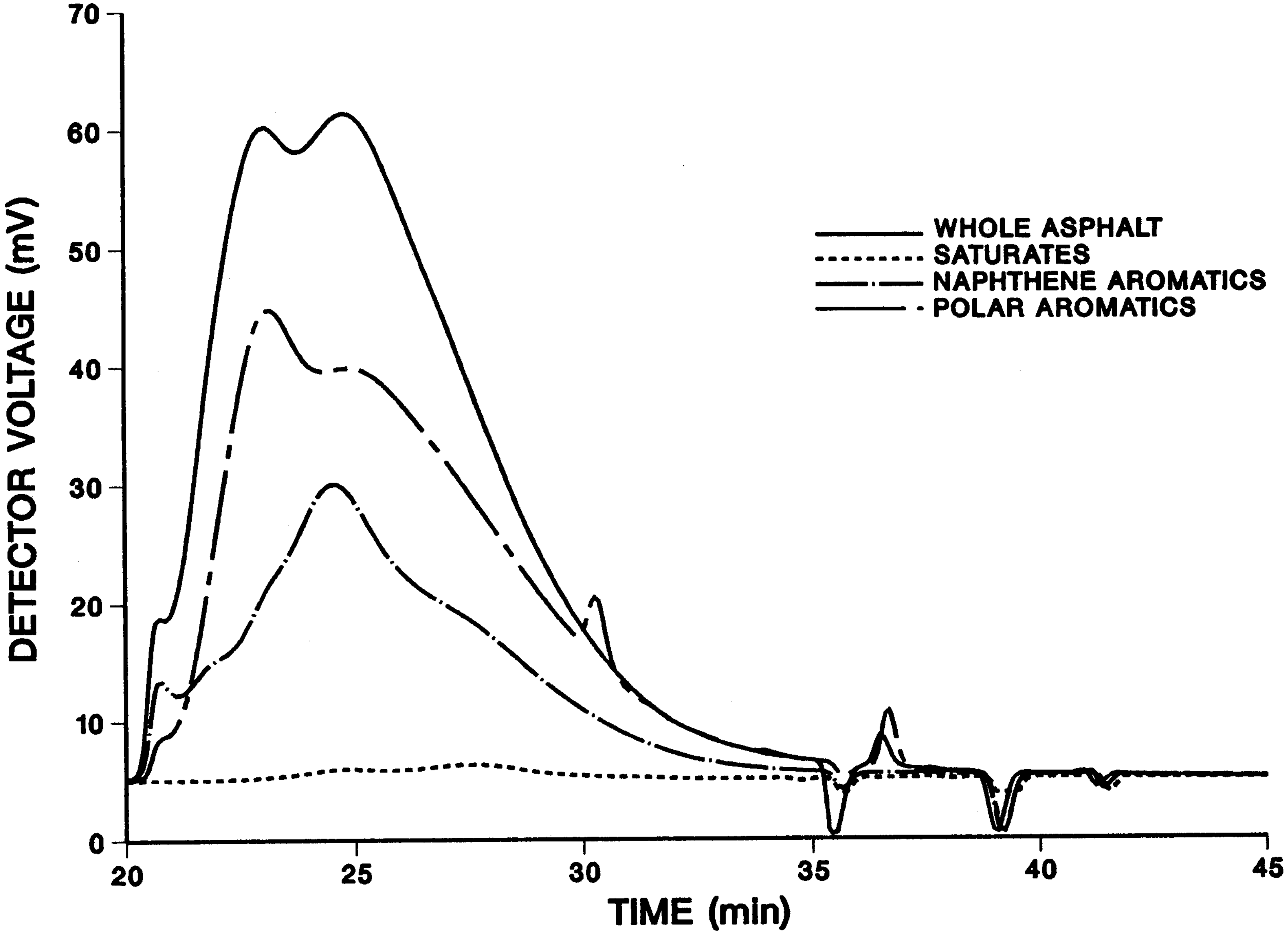


Figure 4-18
Individual Corbett Fractions Overlaid With The Whole Asphalt
Diamond Shamrock AC-10, Dickens Test Site, 1984 Core
500 Å and 50 Å Columns/THF/100 μl

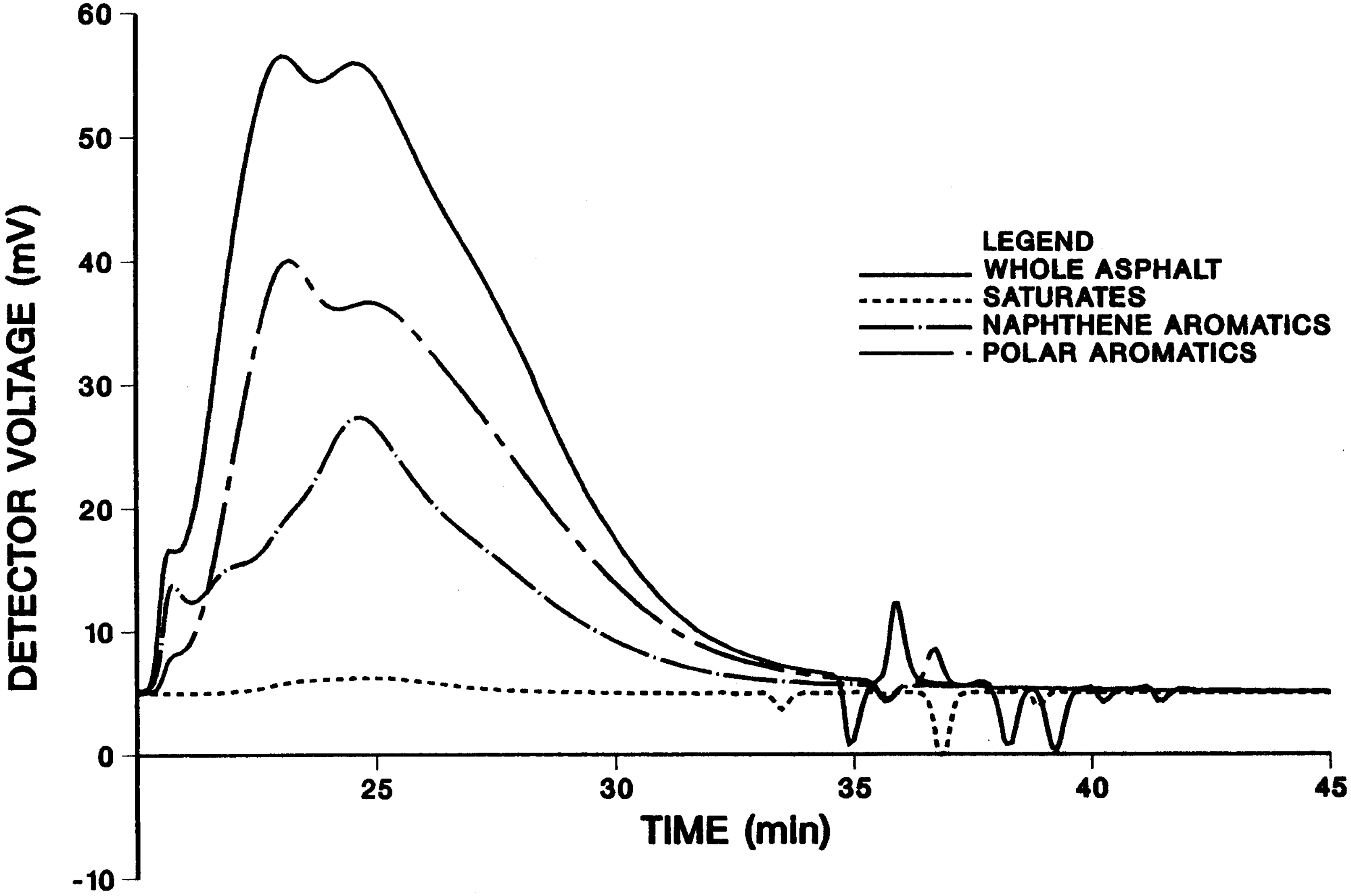


Figure 4-19
Individual Corbett Fractions Overlaid With The Whole Asphalt
Diamond Shamrock AC-20, Dickens Test Site, 1984 Core
500 Å and 50 Å Columns/THF/100 μl

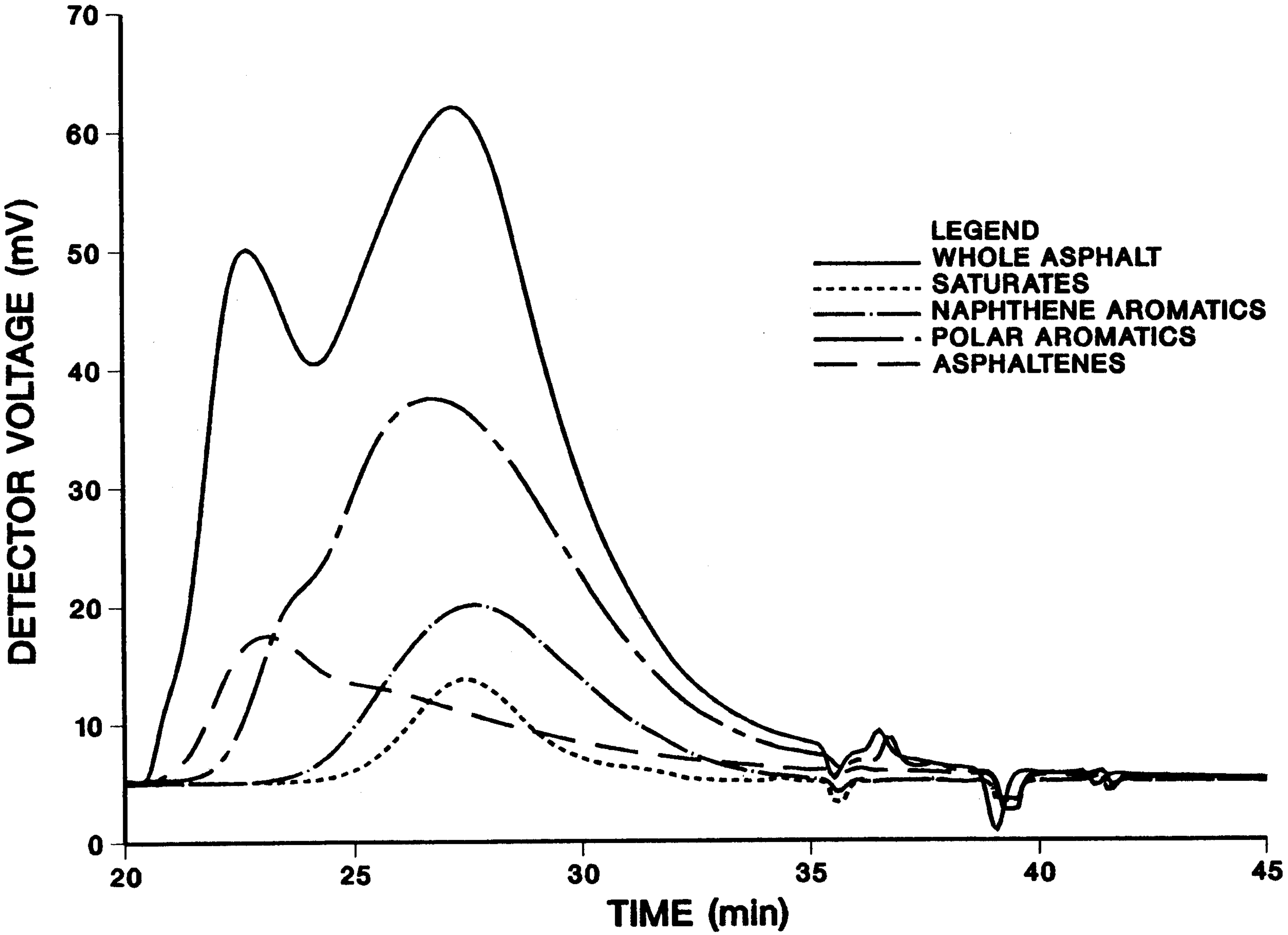


Figure 4-20
Individual Corbett Fractions Overlaid With The Whole Asphalt
Dorchester AC-20, Dickens Test Site, 1984 Core
500 Å and 50 Å Columns/THF/100 μl

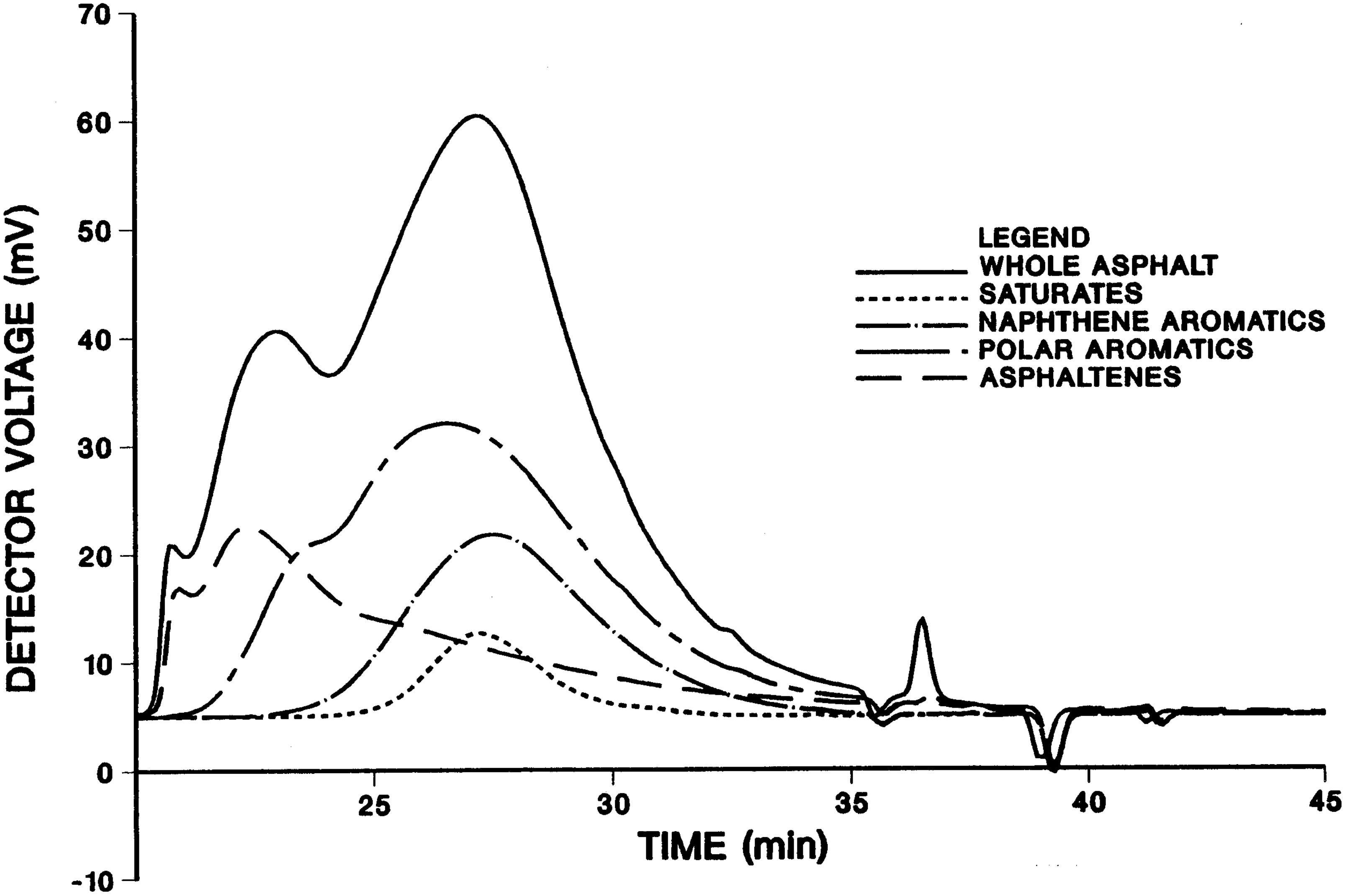


Figure 4-21
Individual Corbett Fractions Overlaid With The Whole Asphalt
MacMillan AC-20, Dickens Test Site, 1984 Core
500 Å and 50 Å Columns/THF/100 μl

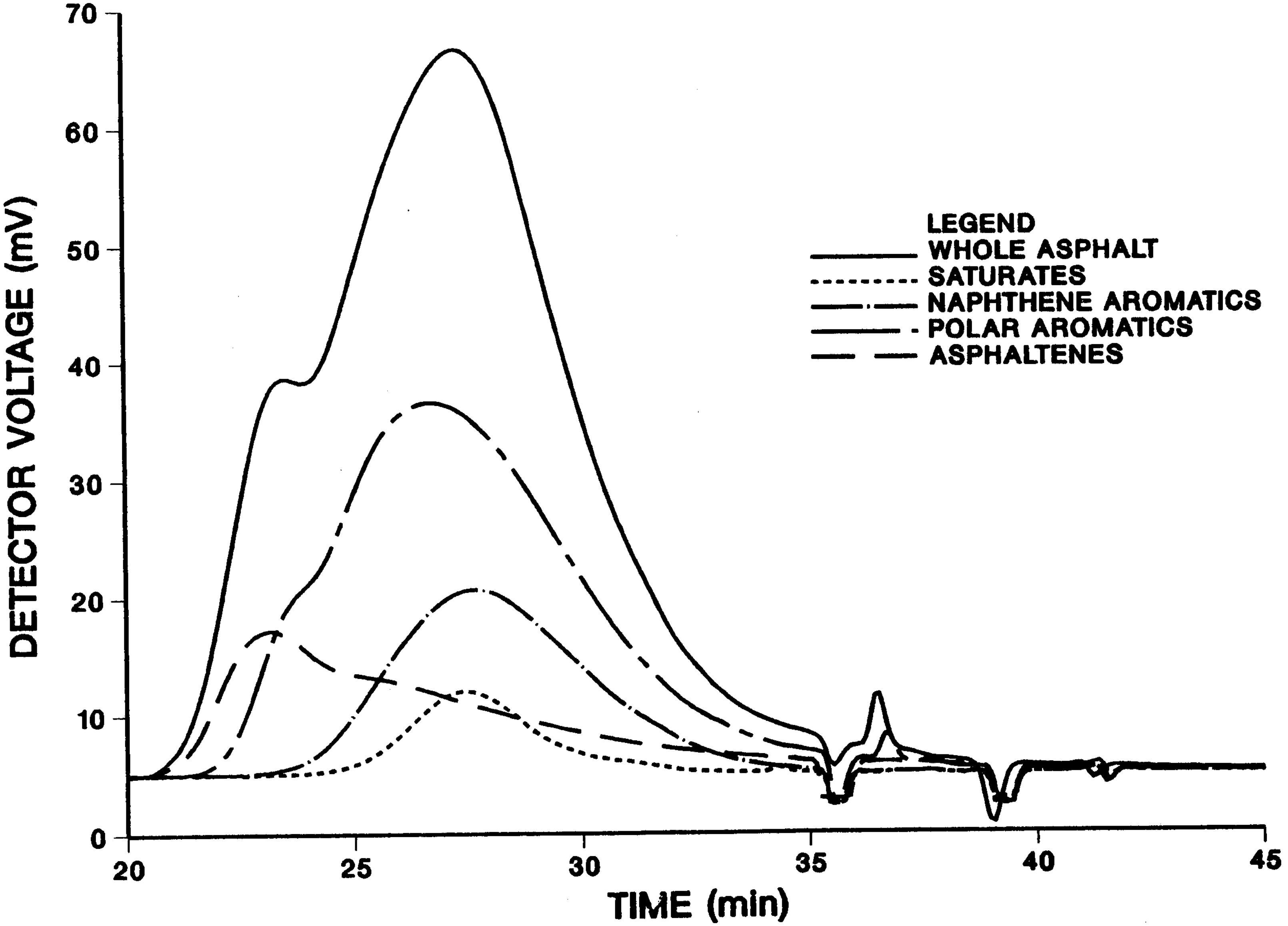


Figure 4-22
Individual Corbett Fractions Overlaid With The Whole Asphalt
Exxon AC-20, Dickens Test Site, 1984 Core
500 Å and 50 Å Columns/THF/100 μl

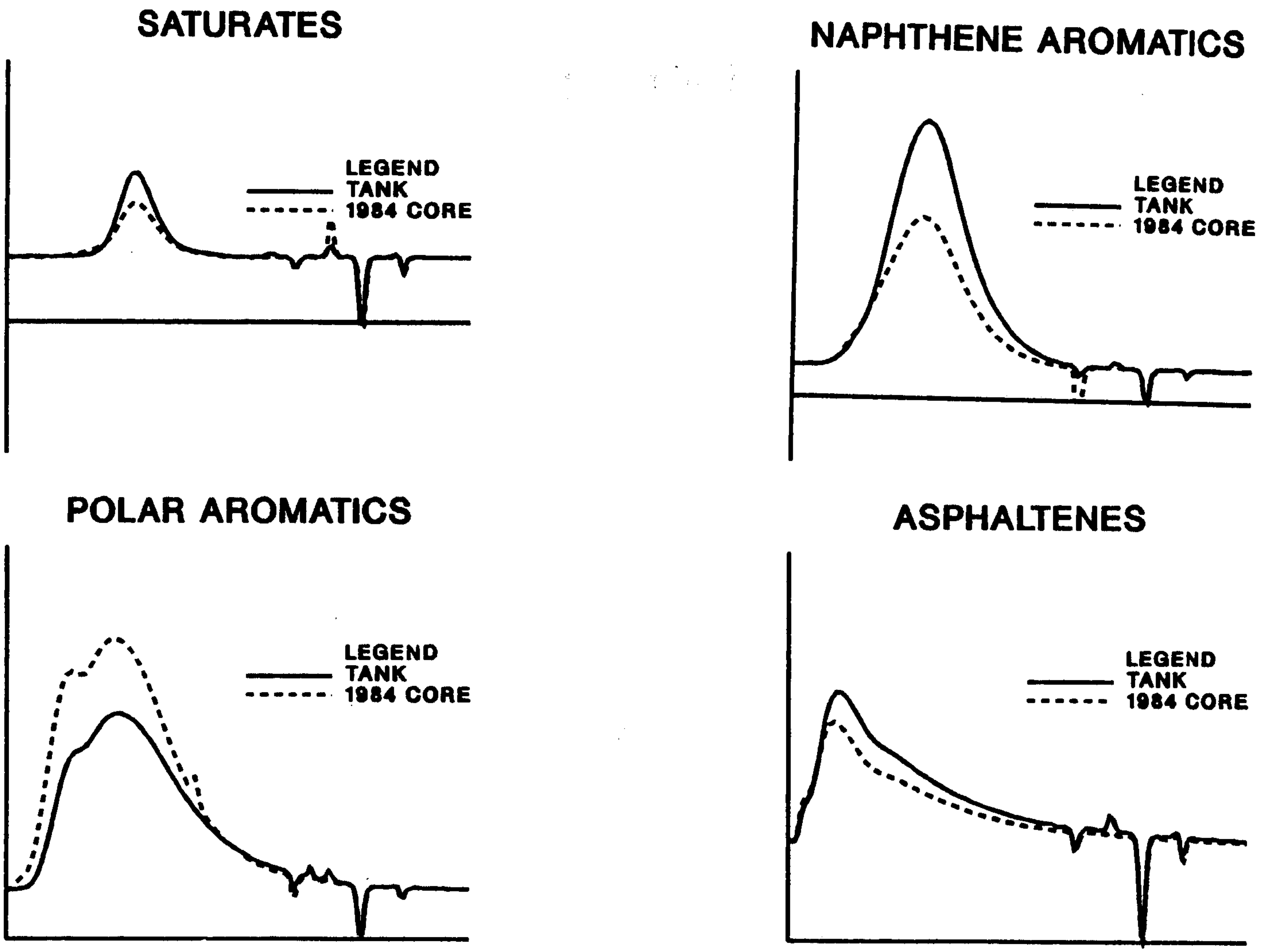
Figures 4-23 through 4-29 show chromatograms for each of the Corbett fractions in the virgin asphalts from Dumas compared with the corresponding fractions from the 1984 cores. The Diamond Shamrock asphalt typically has little or no asphaltenes, as defined by alkane precipitation. For each analysis, a sample was prepared to give us the same injected concentration of a fraction as would exist in the whole asphalt. That is, if 40% of an asphalt was determined by the Corbett procedure to be polar aromatics, then a 2.8% solution of polar aromatics was prepared for injection instead of the usual 7% used for the whole asphalt. This method of "normalization" discounts interactive effects on measurements of the whole asphalt but should, nevertheless, provide a reasonable basis for comparison. Specifically, we were interested in how and to what extent the shapes of the various fractions changed upon aging. Somewhat unexpectedly we found that in virtually every case where a fraction changes in size, it was a change which occurs primarily across the entire fraction so that the chromatogram shapes of the fractions were preserved.

There is, in most cases, a small shift to higher molecular sizes in the asphaltene and polar aromatic fractions. There is essentially no change in molecular size of the saturates, which was expected as they are unreactive. The large changes in the quantity of naphthene aromatics are generally accompanied by very slight changes in molecular size.

Anomalies occur in the quantity of asphaltenes in the MacMillan and Exxon asphalts. It has already been noted that there are problems with these two samples. In the case of MacMillan the lower asphaltene in the core is the result of a low Corbett analysis which, however, is not confirmed by the LMS region of the whole asphalt, Figure 4-8. The lower value of asphaltene in the Exxon core, Figure 4-24, cannot be explained by Corbett analysis and so is probably an error in the sample preparation.

The small changes in molecular size that accompany large changes in the Corbett fraction size indicate that minimal chemical change (such as the addition of an oxygen to a large molecule) can result in a large change in polarity. It is the polarity change that primarily causes a shift in material from one Corbett fraction to another rather than a change in molecular size.

Elemental Analyses. All of the asphalts from tank samples used at the Dumas test site and the asphalts recovered from the cores taken 3 years later were submitted for elemental analysis at the Center for Trace Charaterization at Texas A&M University. The results are tabulated in Table 4-5. Although there are no ap-


SATURATES

NAPHTHENE AROMATICS

POLAR AROMATICS

ASPHALTENES

Figure 4-23
Comparison of Corbett Fractions From Tank And Core Samples
MacMillan AC-10, Dumas Test Site
500 Å and 50 Å Columns/THF/100 μl

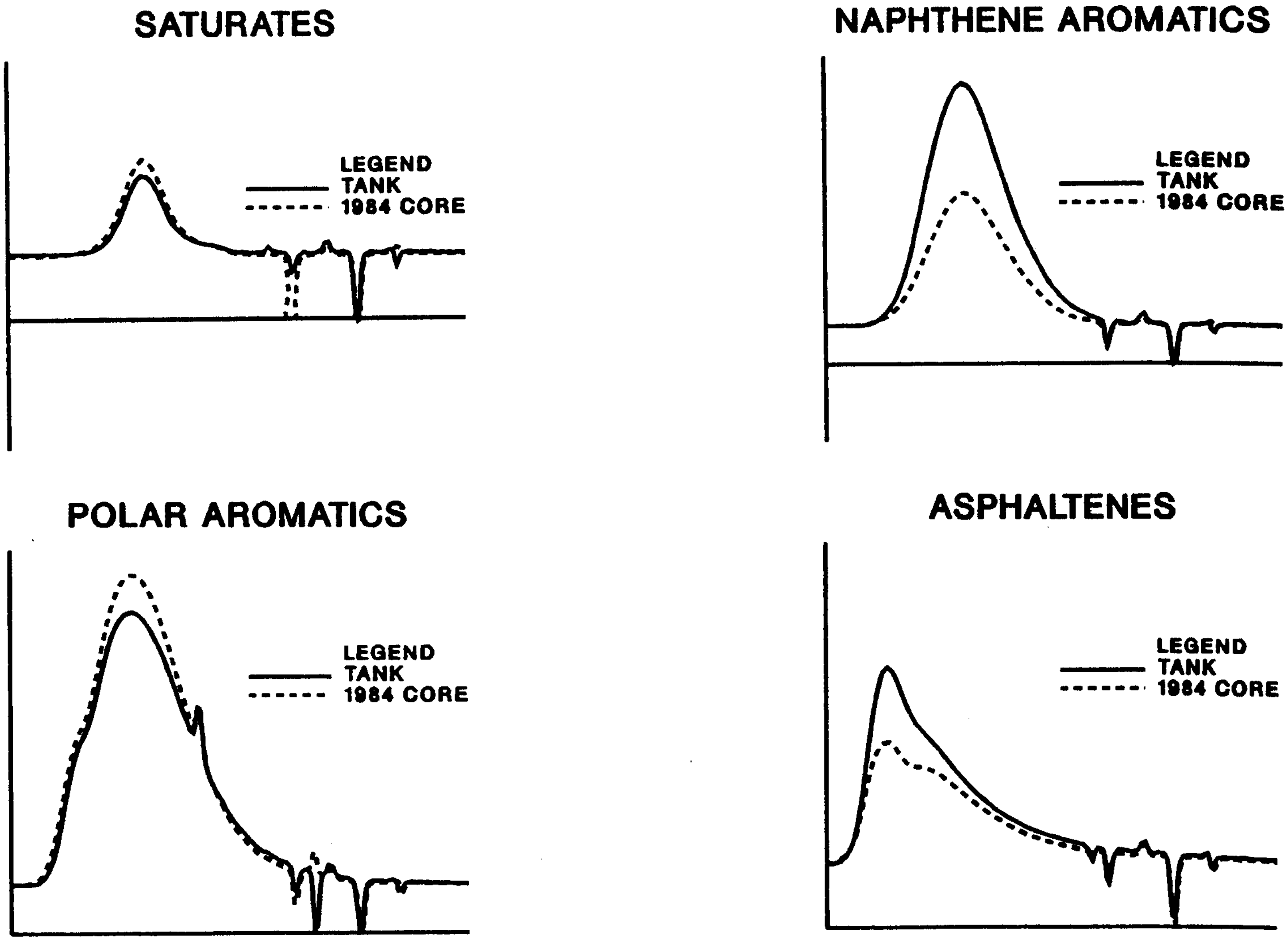


Figure 4-24
Comparison of Corbett Fractions From Tank And Core Samples
Exxon AC-10, Dumas Test Site
500 Å and 50 Å Columns/THF/100 μl

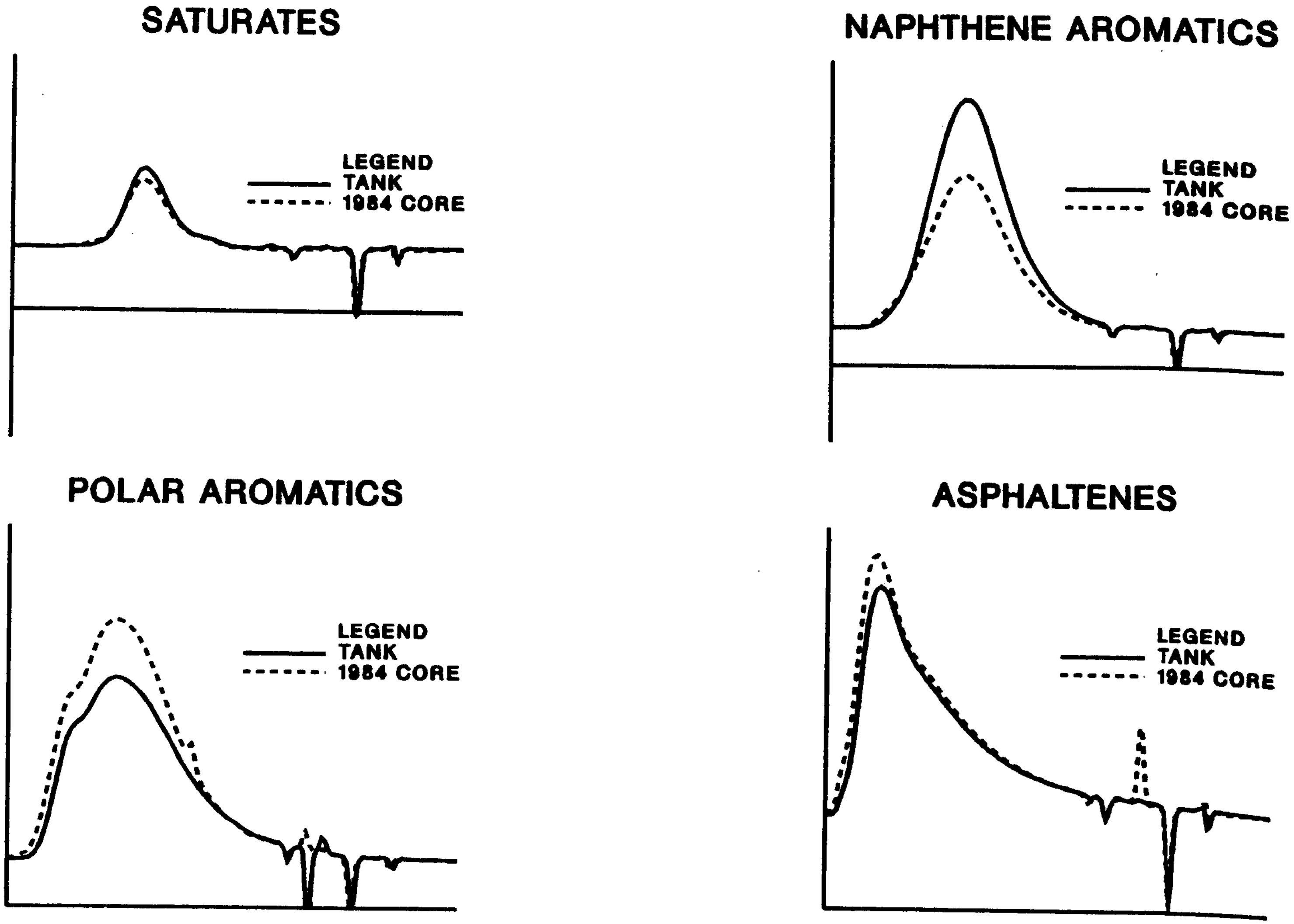


Figure 4-25
Comparison of Corbett Fractions From Tank And Core Samples
Dorchester AC-10, Dumas Test Site
500 Å and 50 Å Columns/THF/100 μl

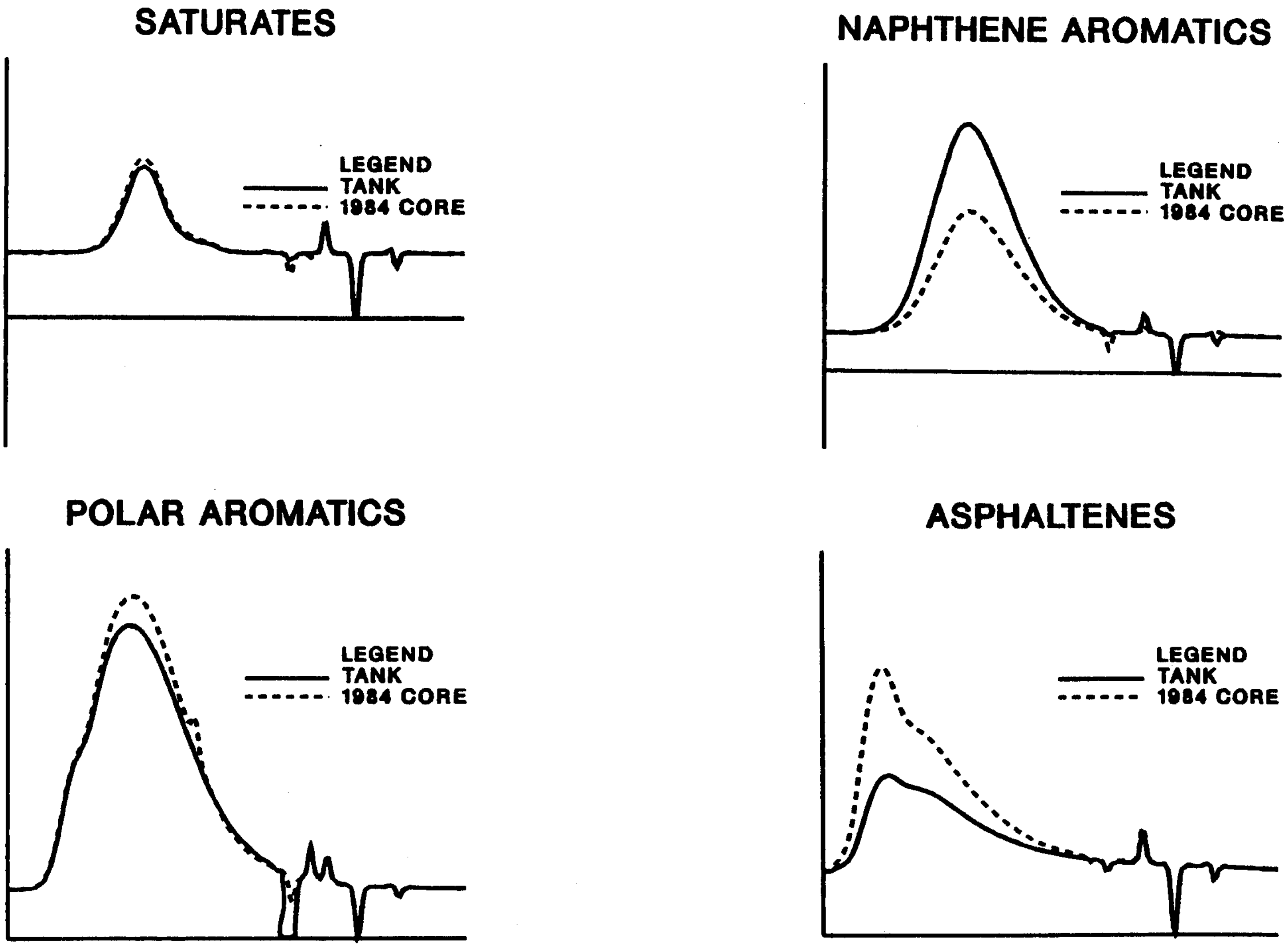
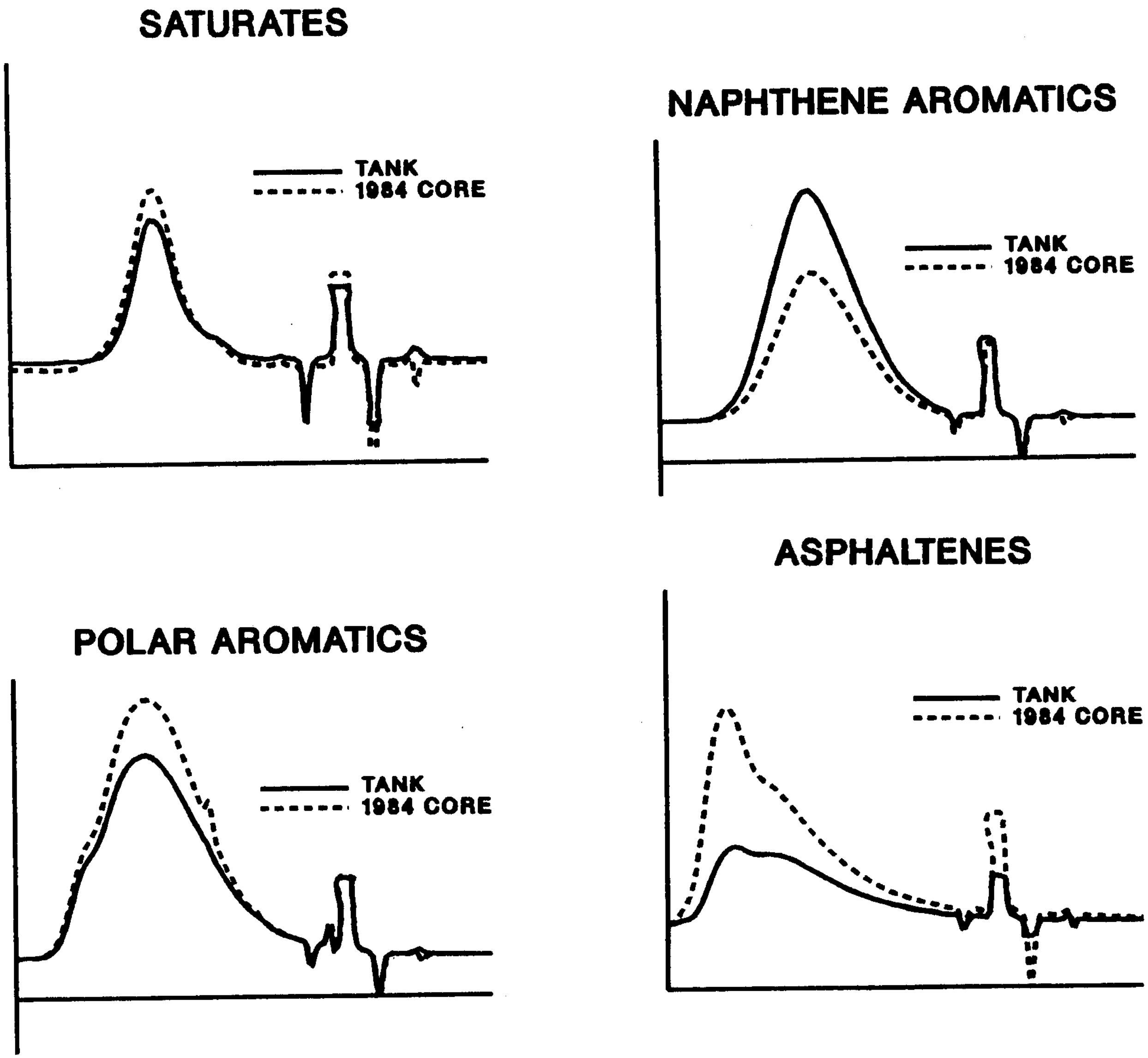


Figure 4-26
Comparison of Corbett Fractions From Tank And Core Samples
Cosden AC-20, Dumas Test Site
500 Å and 50 Å Columns/THF/100 μl


SATURATES

NAPHTHENE AROMATICS

POLAR AROMATICS

ASPHALTENES

Figure 4-27
Comparison of Corbett Fractions From Tank And Core Samples
Cosden AC-10, Dumas Test Site
500 Å and 50 Å Columns/THF/100μl

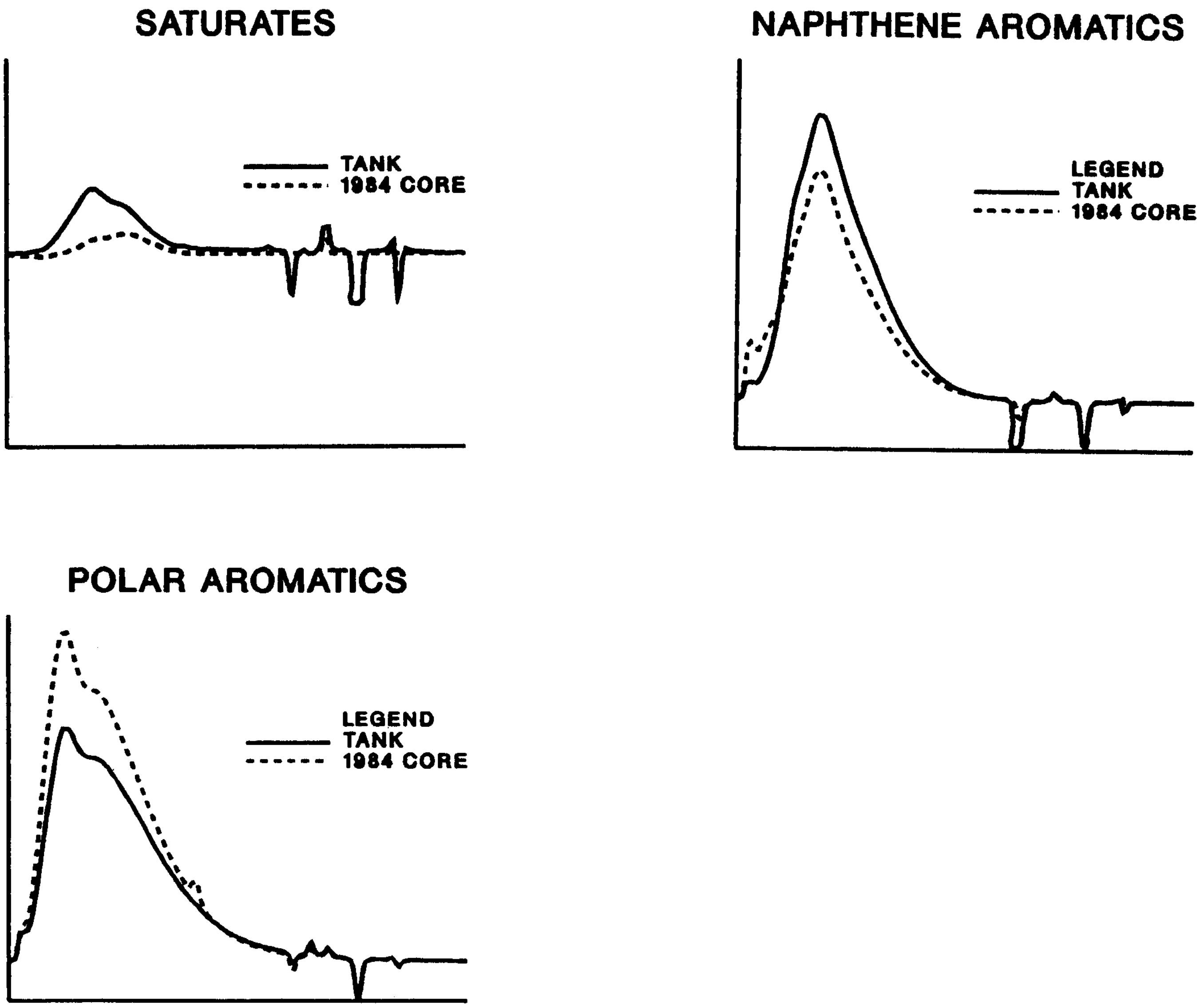


Figure 4-28
Comparison of Corbett Fractions From Tank And Core Samples
Diamond Shamrock AC-20, Dumas Test Site
500 Å and 50 Å Columns/THF/100 μl

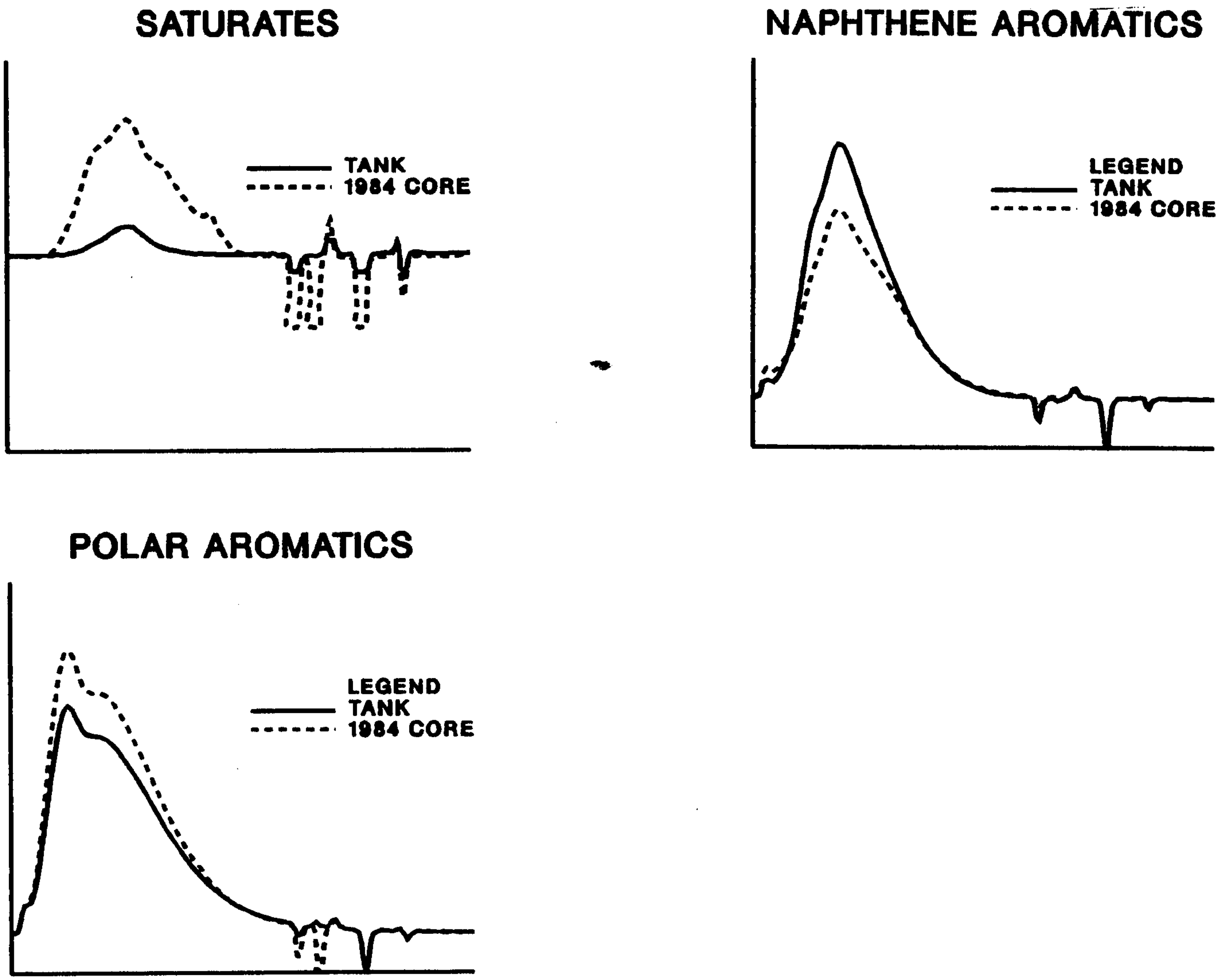


Figure 4-29
Comparison of Corbett Fractions From Tank And Core Samples
Diamond Shamrock AC-10, Dumas Test Site
500 Å and 50 Å Columns/THF/100 μl

parent trends in the individual carbon, hydrogen and nitrogen analyses, there are some significant differences in the totals which range from a low of 93% to a high of 100%. The differences represent primarily sulfur and oxygen content and experimental error. Seven percent would be a very large amount of sulfur and oxygen and most certainly would have very significant consequences on the asphalt properties.

Table 4-5
Elemental Analyses of the Performance Test Sections

	Carbon		Hydrogen		Nitrogen		Residue		Total C + H + N		Sulfur	
	Tank	Core	Tank	Core	Tank	Core	Tank	Core	Tank	Core	Tank	Core
Cosden AC-20	86.3	82.74	10.00	9.72	0.56	0.34	0.0	0.5	96.9	92.8	4.12	
Diamond Shamrock AC-10	89.99	86.82	10.38	10.70		1.07	0.0	0.0	100.4	98.6	0.85	
Exxon AC-10	86.06	87.38	10.34	10.94	0.18	0.20	0.0	0.0	96.6	98.5		4.17
Cosden AC-10	85.48	85.71	10.12	10.05	0.22	0.48	0.0	0.0	95.8	96.2		1.81
Diamond Shamrock AC-20	88.50	88.25	11.06	10.88	0.26	0.52	0.0	0.0	99.8	99.7	0.84	
Mt. Pleasant AC-10	86.85	86.57	10.27	10.91	0.20	0.26		0.0	97.3	97.0		
MacMillan AC-10	82.40	86.40	9.74	10.05	0.69	0.45	0.0	0.0	92.8	96.9	4.60	

CHAPTER 5

CORRELATION OF ASPHALT CEMENT PROPERTIES TO PAVEMENT PERFORMANCE

From an historical perspective, the correlation of asphalt properties with pavement performance has been an elusive goal. In this chapter, correlations of all the results reported in earlier chapters to highway performance and to laboratory physical properties are considered. Significant progress has been made.

Asphalt Pavement Tenderness

Heithaus State of Peptization Test. The word "peptize" means to cause to disperse in a medium or to bring into a colloidal solution. According to Heithaus (Heithaus, 1960), "Asphalt consists of a highly aromatic material (asphaltenes) of moderate molecular weight (ca. 2,000-1,000) dispersed or dissolved in a lower molecular-weight medium (maltenes)." Considerable evidence exists, which indicates that the "apparent" high-molecular-weight often reported for asphaltenes is due to association of lower molecular-weight molecules. (Venable, 1983). Heithaus discussed the importance of the peptizability of the asphaltenes and of the peptizing power of the maltenes in determining the mutual solubility of these asphalt fractions. The state of peptization of the asphaltenes plays a major role in determining the rheological properties of an asphalt and the susceptibility of these properties to change in asphalt composition and environmental factors. Heithaus points out that, in a neat asphalt, there is probably no physical basis for a distinction between dissolved and dispersed phases. Altgelt and Harle (1975) showed that the polarity of the so-called asphaltenes in petroleum asphalt greatly influenced their self-association and that the dispersibility of these asphaltenes in the asphalt was a dominant factor influencing asphalt viscosity.

The term "compatibility", as used herein, relates to mutual solubility of the molecular components in asphalt to produce homogeneity in the asphalt system and is thus a function of the state of peptization of the asphalt. By definition then, as highly associated molecular agglomerates in the asphalt become separated from their dispersing or solubilizing components, the system will have reduced component compatibility. An extreme example of poor compatibility might be a highly polar (high heteroatom content or highly condensed aromatic ring systems) asphalt containing an excess of a low-molecular-weight non-polar paraffinic blending stock (Venable, 1983). Research (Button and Little, 1986 and Little et al., 1986) has shown that asphalts which contain mutually compatible components are also more likely to be compatible with polymeric additives.

Heithaus (1960) applied the principles developed earlier by van Kerkvoort et al. (1952) to investigate asphaltene peptizability or degree of dispersion, the dispersion power of maltenes, and the state of peptization of asphalts. Little application of the state of peptization parameters applied by Heithaus appears in the literature. The California Highway Department in extensive pavement performance studies (Kemp, 1972 and Predoehl and Kemp, 1974) indicates that the parameters used by Heithaus for state of peptization of asphalt may be useful in predicting pavement durability. Researchers at the University of New Mexico (Kiggundu, et al., 1985 and Newcomb, et al., 1984) have related Heithaus results to compatibility of asphalt with modifiers. Good component compatibility is most likely a necessary requirement for good pavement durability. Akzo Chemie America (Dybalski, 1985) uses the test to measure emulsibility of asphalts.

The objectives of this segment of the study were to determine how well asphalt setting rate or tender mix problems could be predicted by an abbreviated version of the Heithaus procedure (Heithaus, 1960). This was accomplished by relating flocculation ratio to asphaltene content (Venable, 1983), rheological properties (Altgelt and Harle, 1975), compatibility (Anonymous, 1984) and durability of asphalt cement (Little, et al., 1986).

Flocculation ratios were measured, using the Heithaus procedure to analyze more than 30 asphalts of various paving grades from different sources. Generally, state of peptization of the asphalt increases as flocculation ratio decreases. The results from the present work on peptization are depicted in Figures 5-1 through 5-4.

Figure 5-1 shows a reasonable correlation between flocculation ratio and pavement tenderness. Pavement tenderness (Button, et al., 1983) is based on user comments pertaining to the asphalt's general performance history with particular emphasis on construction and early pavement performance. The tenderness rating is based on a scale from 0 to 5; zero indicates that tenderness or slow setting problems are never associated with the asphalt and five indicates these problems are always associated with the asphalt. This was expected since highly peptized asphalts had been associated with slow setting mixtures by Hveem et al. (1963) in

1963, although no data were presented.

A general trend of increasing flocculation ratio with increasing asphaltene content is shown in Figure 5-2 for the present work. That is, lower asphaltene contents are indicative of more highly peptized systems. The dashed lines in Figure 5-2 are included to represent the bounds of the data.

A rather weak correlation between flocculation ratio and asphalt hardening (increase in viscosity at 140°F) by the thin film oven test (TFOT) was found as shown in Figure 5-3. More highly peptized materials would generally be expected to exhibit less hardening upon exposure to heat in the presence of oxygen. That is, the more compatible materials exhibited greater durability.

Based on a limited number of asphalt sources (only four), a very slight increase in flocculation ratio with increasing viscosity grade was noted as shown in Figure 5-4. Lower viscosity grade asphalts from a given source should have a slightly higher percentage of oils and resins and, therefore, should be a more highly peptized system than the higher grade asphalts. However, the source of the asphalt had a far greater impact on the flocculation ratio than the differences in viscosity grades. Additionally, the Texaco (1985) and California Valley (1985) asphalts were used in asphalt additive studies (Button and Little 1986). The California Valley asphalt, which is shown to be highly peptized, was very compatible with the polymer additives; whereas, the Texaco asphalt, which exhibited a comparatively low state of peptization, was not compatible with any of the polymer additives. Compatibility means that the polymers dispersed well in the asphalt thus yielding smooth, homogeneous blends. No correlations were apparent between flocculation ratio and asphalt temperature susceptibility or shear susceptibility.

GPC and Tenderness. Hattingh (1984) and Jennings, et al. (1985a) have suggested that low values for the large molecular size (LMS) fraction as determined by gel permeation chromatography are an indicator of tenderness. The asphalts represented in Figure 5-1 have been correlated with LMS. These results are shown in Figure 5-5. The quality of fit is about the same as in Figure 5-1, but one asphalt, a Diamond Shamrock AC-10, could not be plotted as it was off the graph in LMS size even though it is a tender asphalt. Asphalt tenderness is compared with asphaltene content in Figure 5-6. On this plot Diamond Shamrock, denoted by DS, plots very well. With the exception of this one asphalt, all the techniques plot about equally well with much of the scatter undoubtedly due to the subjectivity of the tenderness rating. Basically, asphalts may be broken into two families

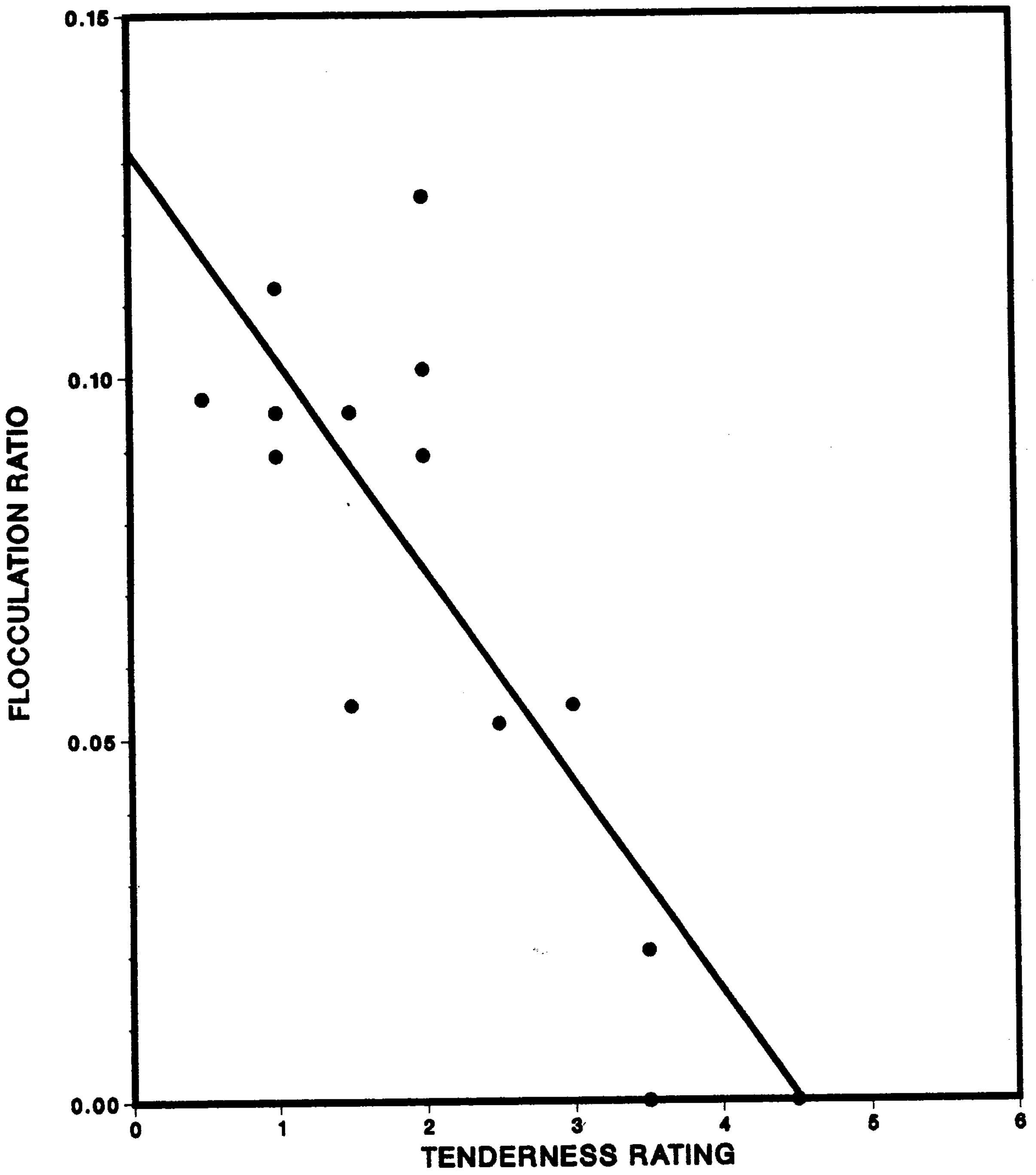


Figure 5-1

Flocculation Ratio as a Function of Tenderness Rating

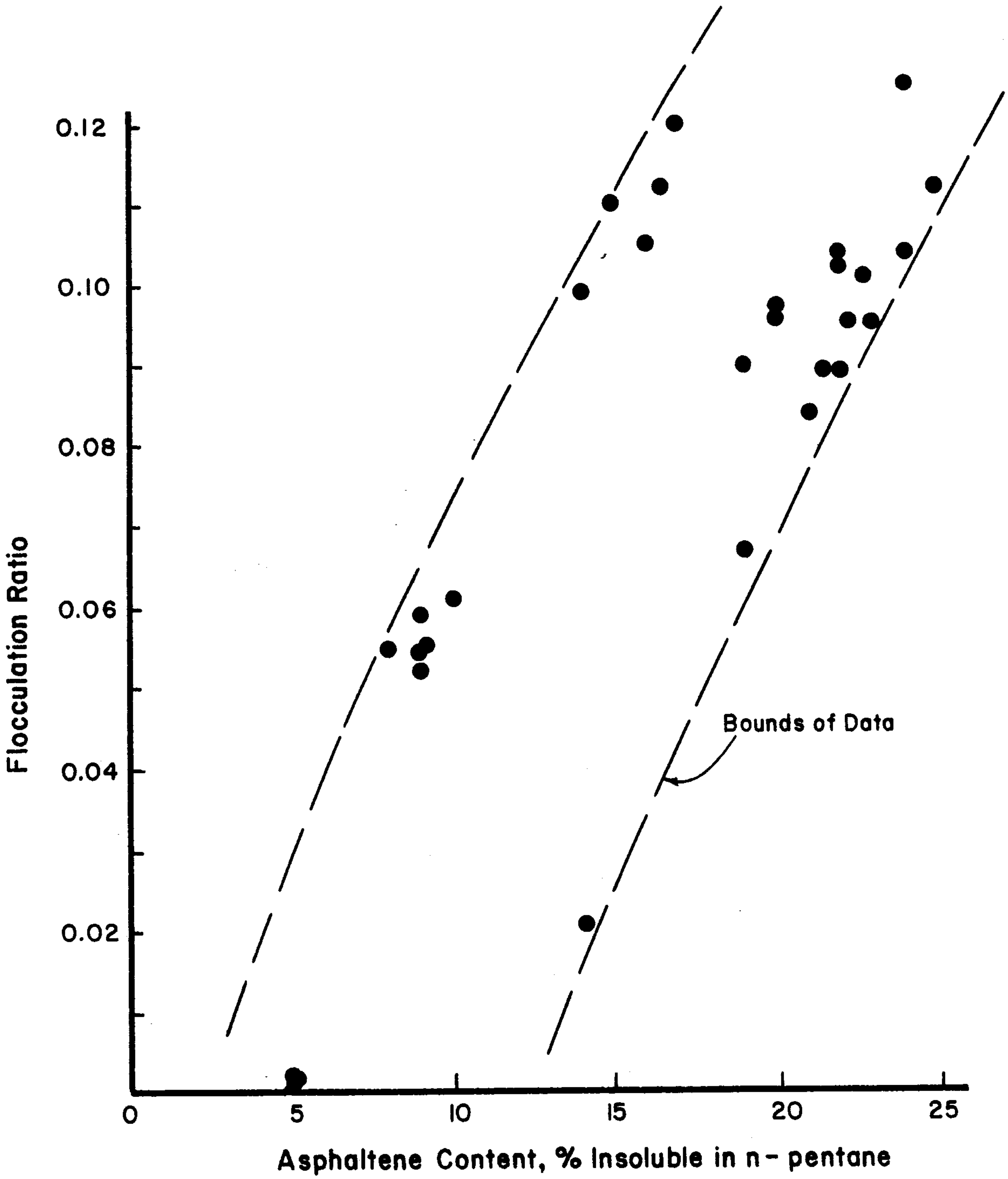


Figure 5-2

Flocculation Ratio as a Function of Asphaltene Content

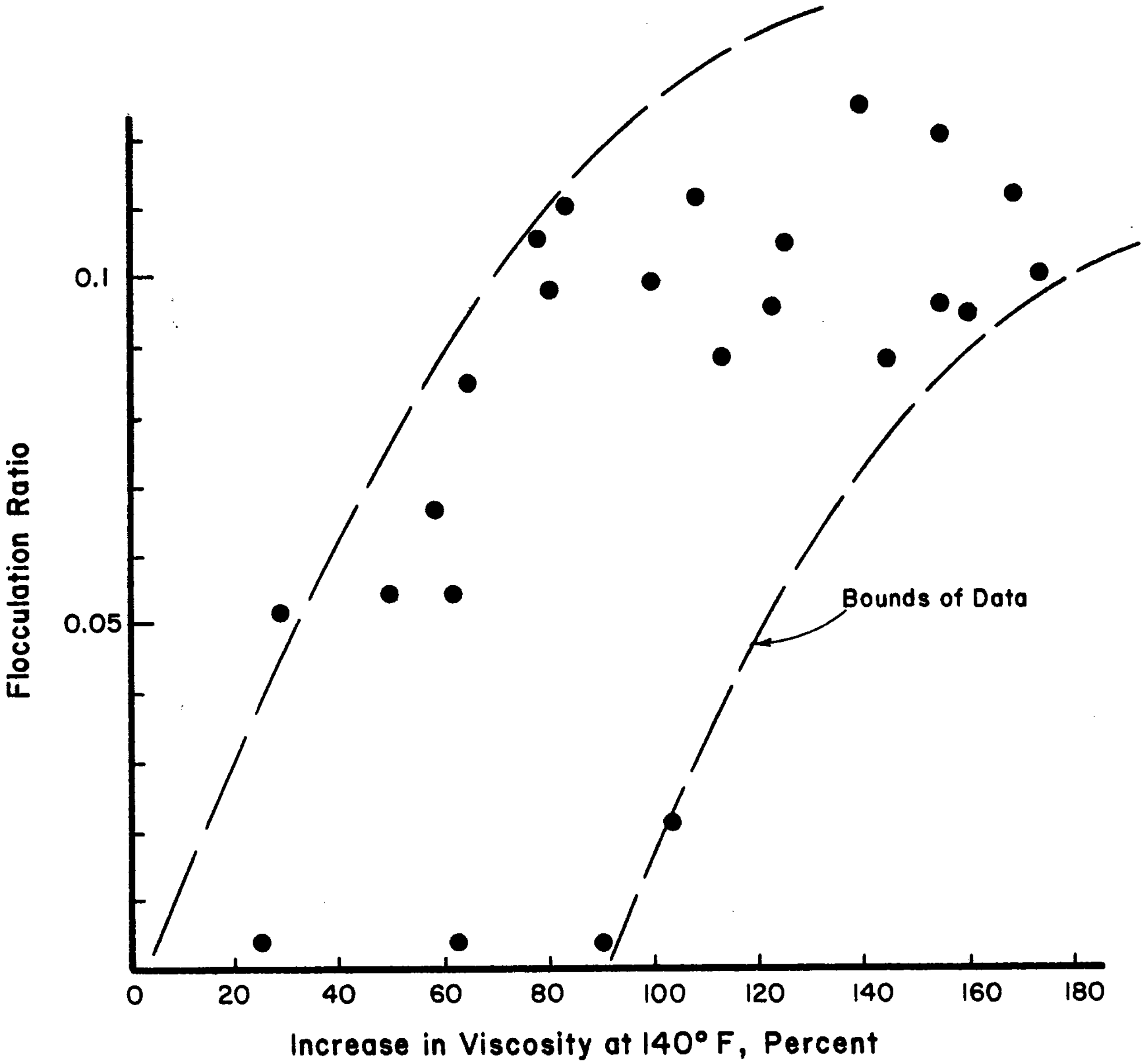


Figure 5-3

Relationship between Flocculation Ratio and Increase in Viscosity at 140°F after the Thin Film Oven Test

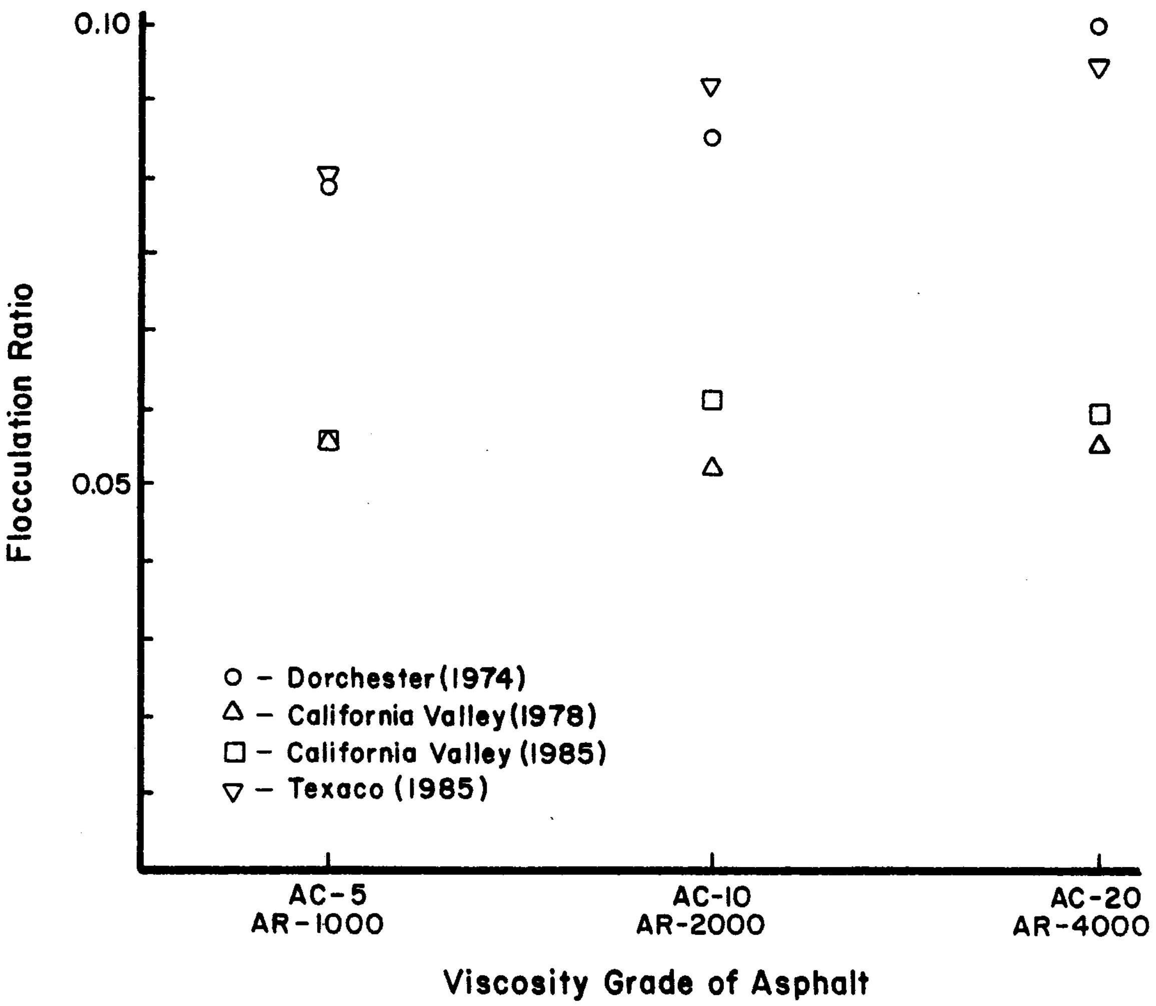


Figure 5-4

Flocculation Ratio as a Function of Asphalt Viscosity Grade

with regard to tenderness. The tender asphalts consist of those with tenderness ratings above two. These asphalts have low flocculation ratios, low LMS (with the exception of the Diamond Shamrock asphalt) and low asphaltene content. The non-tender asphalts have tenderness ratings at two or below. Accordingly, they have high flocculation ratios, high LMS, and high asphaltene content. This implies that there is a strong cross correlation between the factors presented on the ordinates of Figures 5-1, 5-5 and 5-6. A plot showing the variation of LMS with asphaltene content is shown in Figure 5-7. With the exception of Diamond Shamrock which is again off the graph, the correlation is very nearly within the accuracy of the data, so that in most cases when high LMS is found it means high asphaltenes.

A comparison of GPC chromatograms for asphalts with high and low tenderness ratings is given in Figure 5-8. While there is not a perfect correlation between LMS and the tenderness rating, the difference between the two groups is obvious. Thus, considering the speed of performing a GPC analysis as compared with the other procedures, the GPC is a useful tool for identifying asphalts with tenderness problems. This knowledge could be of particular value when using the asphalt with marginal aggregate.

Relationship Between GPC and Pavement Performance. Pioneering work in relating chromatograms of asphalt fractions to the performance of pavements was sponsored by the Texas Highway Department (now the State Department of Highways and Public Transportation) as early as 1963. The results of this study were reported to the Association of Asphalt Paving Technologists at their 1970 Annual Meeting and subsequently published in the proceedings (Bynum and Traxler, 1970). This early research showed that the techniques can be useful in studying the behavior of asphalt binders in highway pavements, though the authors did note on occasion that "there is really no satisfactory explanation for the results."

There is, to date, relatively little distress and almost no difference in pavement performance of the field trials in Dickens, Dumas and Lufkin with which to relate GPC. The raveling observed in two sections at the Dumas test site (Exxon and MacMillan Asphalts) was most likely promoted by poor compaction of the mix. However, all test sections were compacted to approximately equivalent air void contents and only two of the mixes exhibited significant raveling. The raveling reportedly occurred shortly after extended periods of exposure to snow, ice and

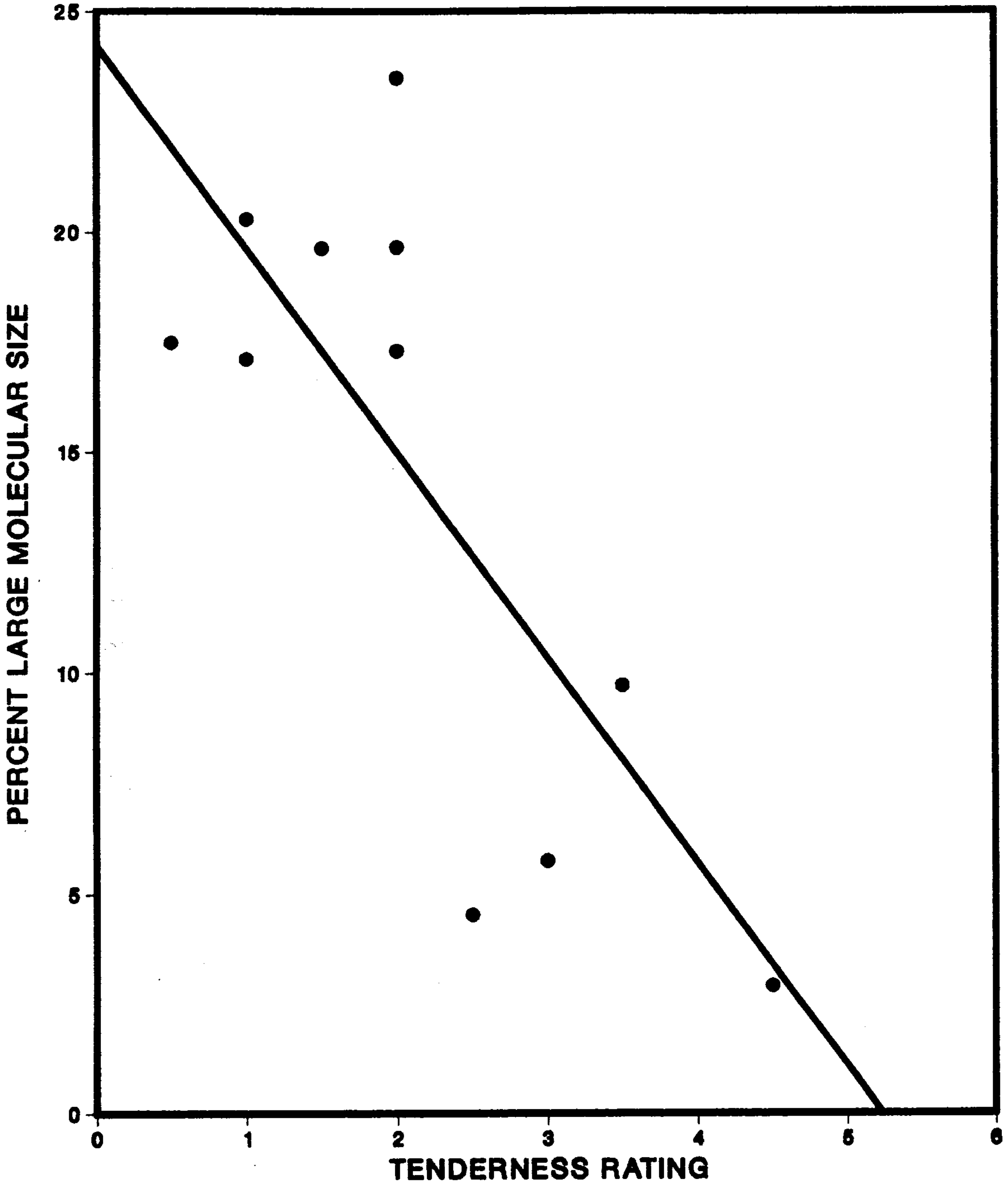


Figure 5-5

Large Molecular Size Fraction vs. Tenderness Rating

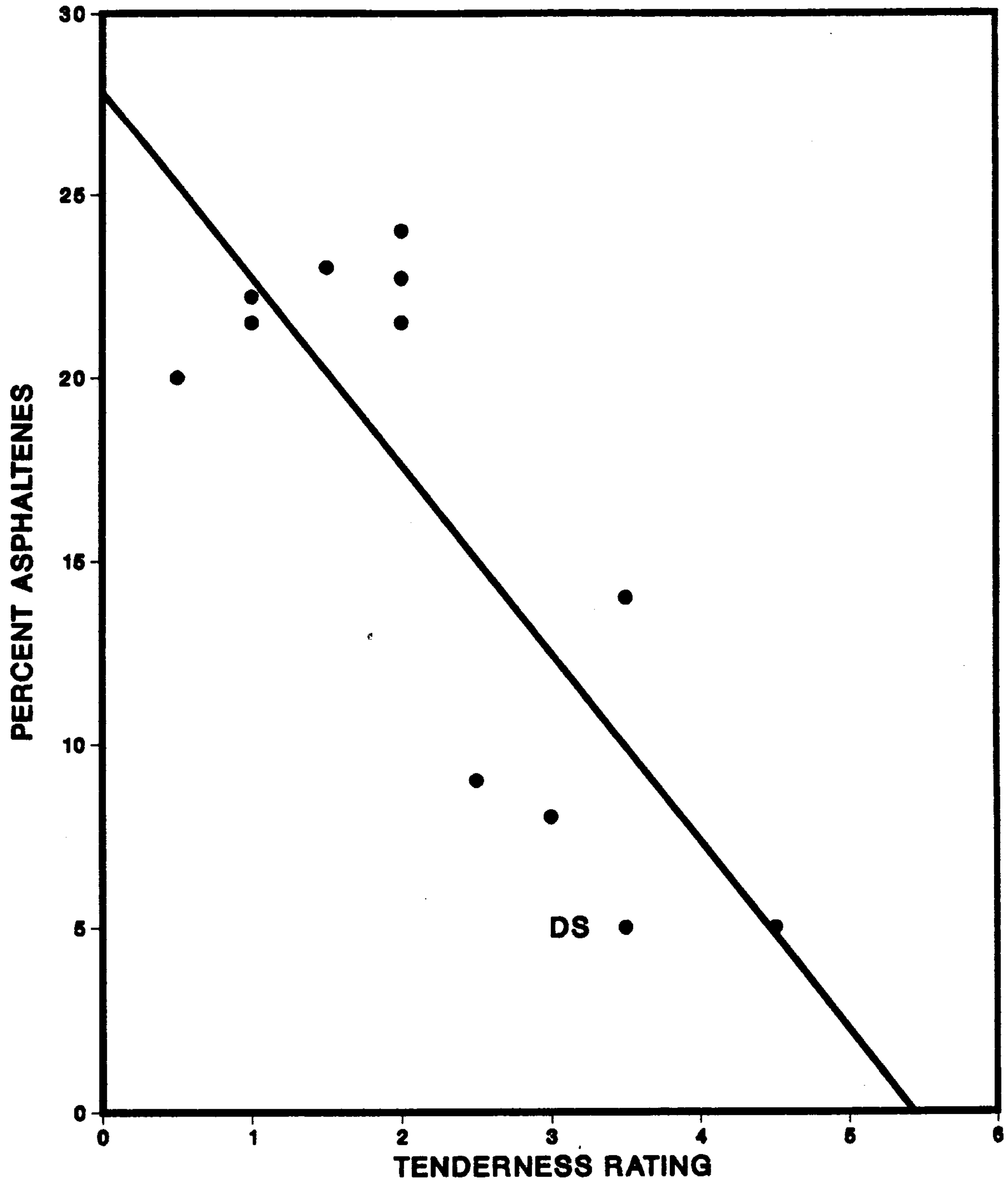


Figure 5-6

Asphaltene Fraction vs. Tenderness Rating

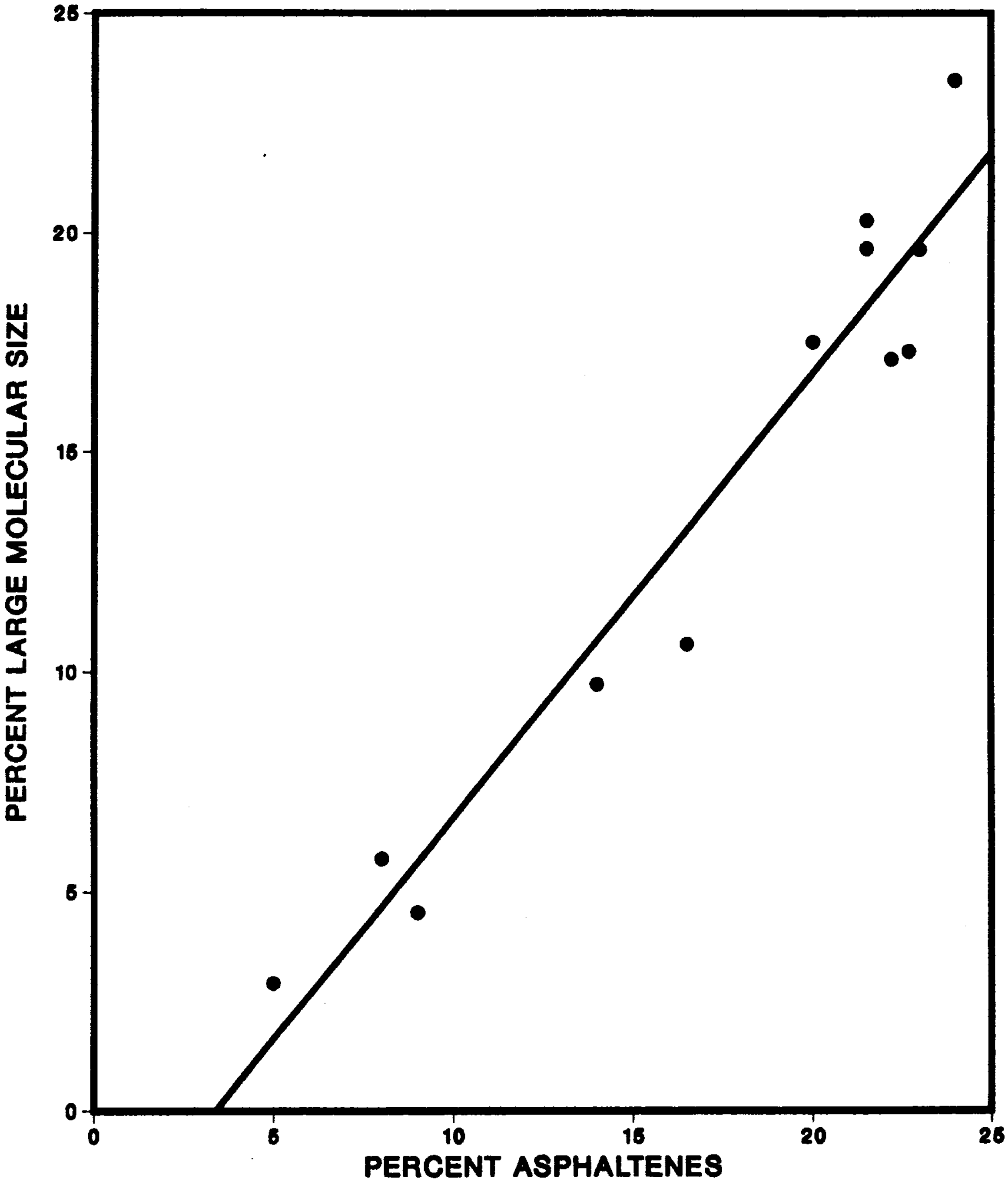
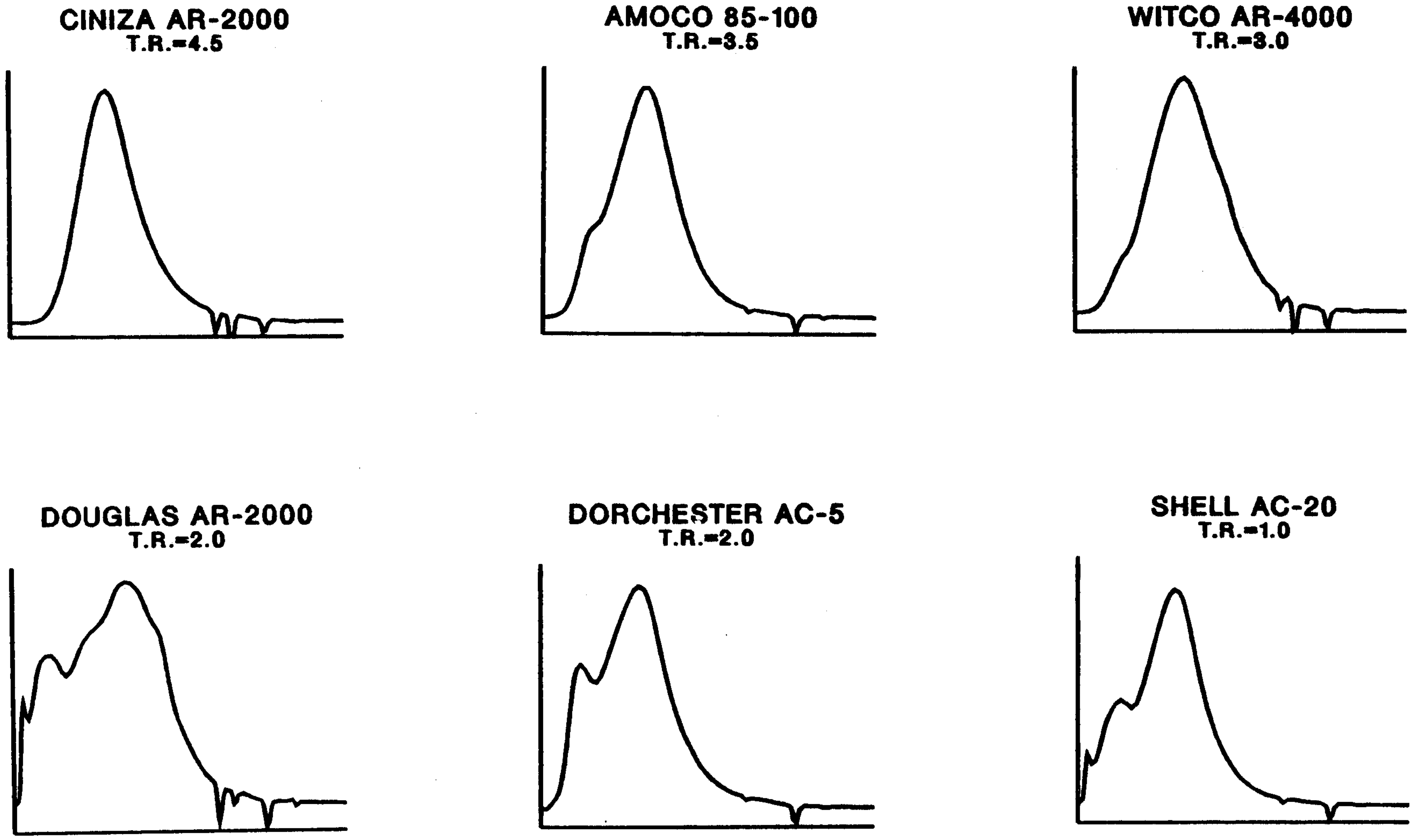


Figure 5-7

Large Molecular Size Fraction vs. Asphaltene Fraction



CINIZA AR-2000
T.R.=4.5

AMOCO 85-100
T.R.=3.5

WITCO AR-4000
T.R.=3.0

DOUGLAS AR-2000
T.R.=2.0

DORCHESTER AC-5
T.R.=2.0

SHELL AC-20
T.R.=1.0

Figure 5-8
Comparison of GPC Profiles To Tenderness Rating
500 Å 50 Å Columns/THF/100 μl/7%

moisture. One test section (Exxon Asphalt) exhibited extremely severe raveling. With all other construction factors being constant, the raveling in the two sections at Dumas may be due to the character of the asphalt cements. The test sections at Dickens and Lufkin containing these same asphalts, showed no visible signs of distress after three years of service. These inconsistencies in field performance and the limited quantity of data make it difficult to derive and support conclusions regarding asphalt quality.

However, an important point on relating GPC data to the performance of asphalt pavements should be made. Even though poor performance may be the result of poor asphalt, it also is possible that other factors are involved. For example, while pavement disintegration may be the result of poor adhesive characteristics of the asphalt, it may also result from aggregate surface characteristics or inadequate compaction. Similarly, while laboratory tests show that fatigue-type cracking is related to the characteristics of the asphalt in the mix, studies also show that fatigue-type cracking may be related to the volume fraction of asphalt cement in the mix. That is, low binder content or poor compaction can lead to cracking in a mix with a perfectly satisfactory binder. Even if the mix is well compacted and contains adequate asphalt cement, a weak substrate will subject the pavement to large tensile strains and it will crack.

This discussion could be extended to other forms of cracking as well as other distress modes. The point is that careful monitoring and investigation of pavement performance is necessary in order to obtain meaningful correlations with GPC and other test results.

Laboratory Physical Properties

An intermediate objective in reaching the goal of predicting roadway performance from chemical analyses is to be able to correlate chemical properties and composition to laboratory physical properties. Past efforts at achieving this have fallen short. Efforts of this project have included analysis of data from Study 287 as well as new data from this study.

Asphalt Viscosity. Inspection of the Study 287 Corbett analyses for the test section virgin asphalts (Tables 4-2 to 4-4) suggests that a higher viscosity grade tends to be associated with a higher asphaltene content and a lower saturates content.

If viscosity is assumed to be related exponentially to the weight fraction asphaltenes and saturates, then

$$\ln \eta = \alpha + \beta w_{A_s} + \gamma w_S$$

where η is viscosity and w_{A_s} and w_S are the weight fraction of asphaltenes and saturates in the asphalt. Multiple linear regression analyses were performed at each temperature for these five asphalt producers to obtain the constants α, β, and γ at all three temperatures (Table 5-1). Calculated values of viscosity are compared with the reported experimental values in Figures 5-9 through 5-11. There is certain to be considerable variation in α, β, and γ for the different asphalts resulting in scatter for the correlation. Correlation coefficients range from 0.5 to 0.55 perhaps due to this variability in types of asphalt as well as to uncertainties in the Corbett analyses. The values of β and γ support the notion that higher asphaltene content and lower saturates produce higher viscosity with changes in saturates concentration having a larger effect than asphaltenes.

A more detailed analysis accounting for the polar aromatic and naphthene aromatic fractions did not produce any improvements in the correlation.

Effect of Temperature on Viscosity. Analysis of the Study 287 viscosity data did not reveal any reasonable correlation between the variation of viscosity with temperature and the Corbett analyses. This conclusion is consistent with that of the Study 287 final report concerning viscosity temperature susceptibility.

While correlations must exist, more precise viscosity and chemical data apparently are required to reveal them. Asphalts, being viscoelastic in nature do not subject themselves to easy rheological analysis; viscosity is a function of shear rate and measurement methods must be rigorously defined and analyzed. The standard viscosity tests for specification purposes are suspected to be inadequate for correlating viscosity to chemical composition. Such difficulties are especially pronounced over a range in temperature (77 to 275°F) which cause viscosity changes of six orders of magnitude. Measurements of viscosity at a single temperature on several asphalts may still be expected to have reasonable correlation with composition (as above) in spite of these difficulties, since at a single temperature the relative effects of elastic and viscous behavior may be about the same in the different asphalts.

Table 5-1

Correlation of Asphalt Viscosity[a]

Temperature (°F)	α	β	γ
77	16.0	0.83	-2.49
140	7.30	0.0687	-0.0831
275	1.60	0.0287	-0.0697

[a] $\ln \eta = \alpha + \beta w_{A_s} + \gamma w_S$, η in poise

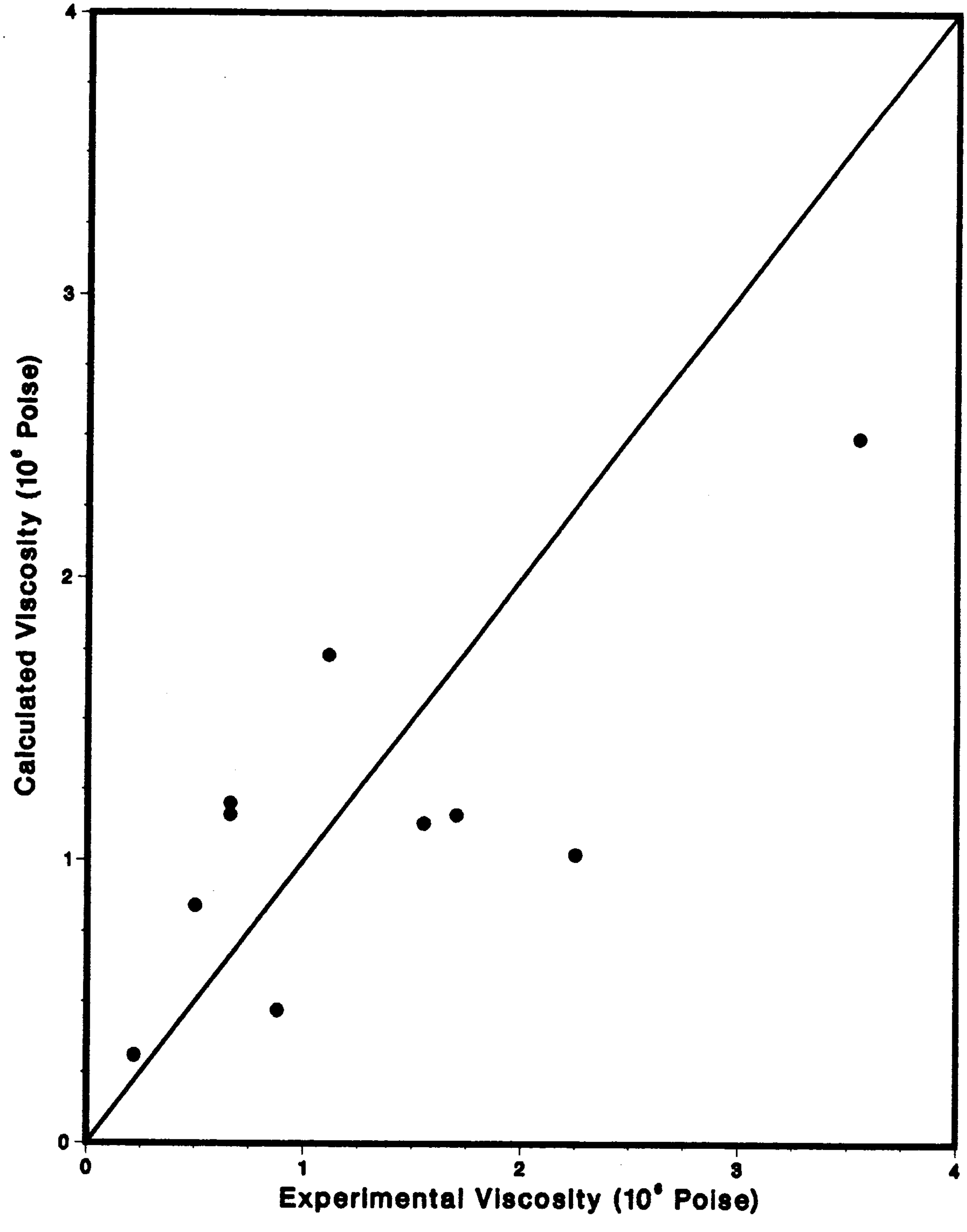


Figure 5-9

Comparison of Experimental Asphalt Viscosity to Predicted Viscosity (77°F)

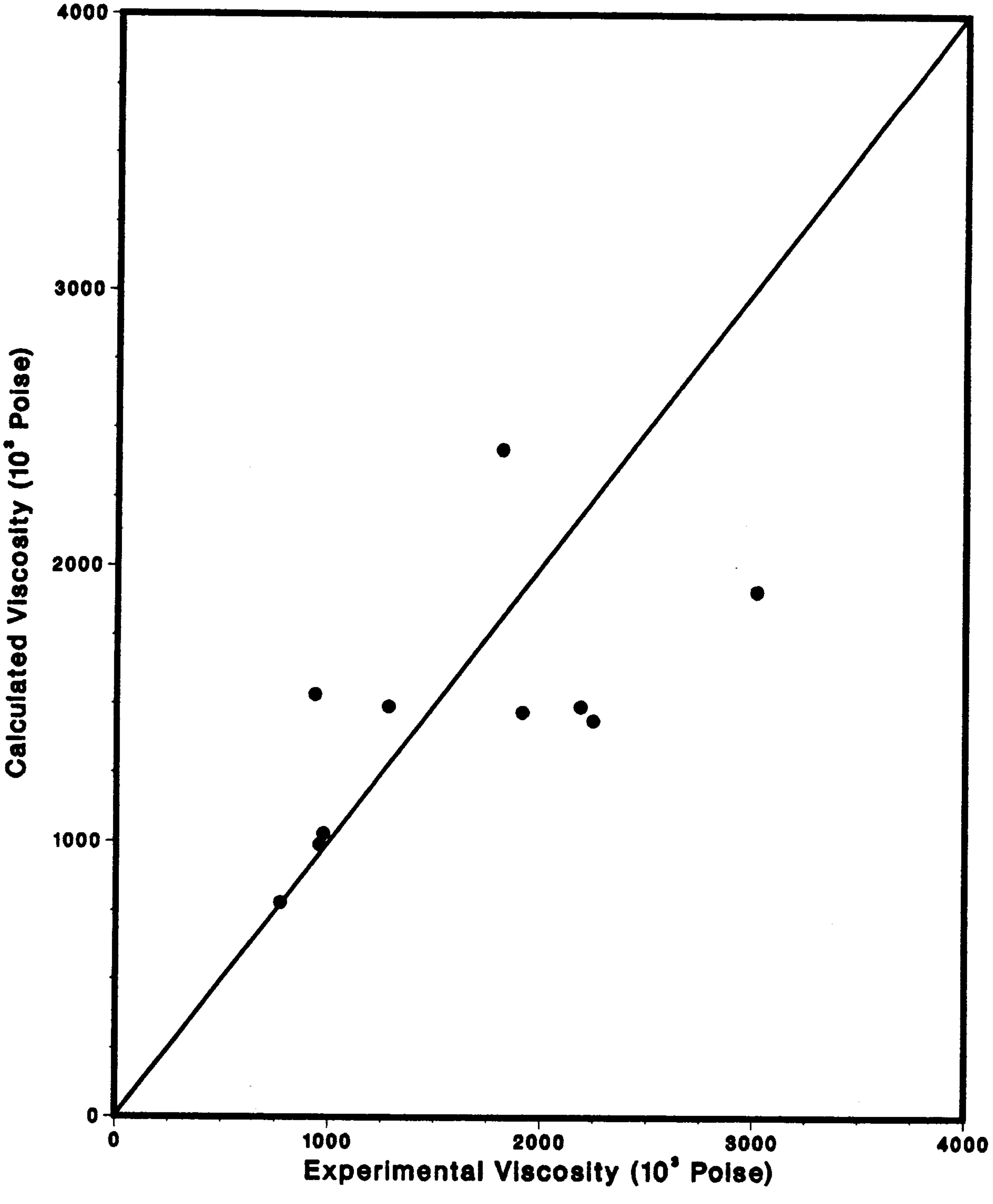


Figure 5-10

Comparison of Experimental Asphalt Viscosity to Predicted Viscosity (140°F)

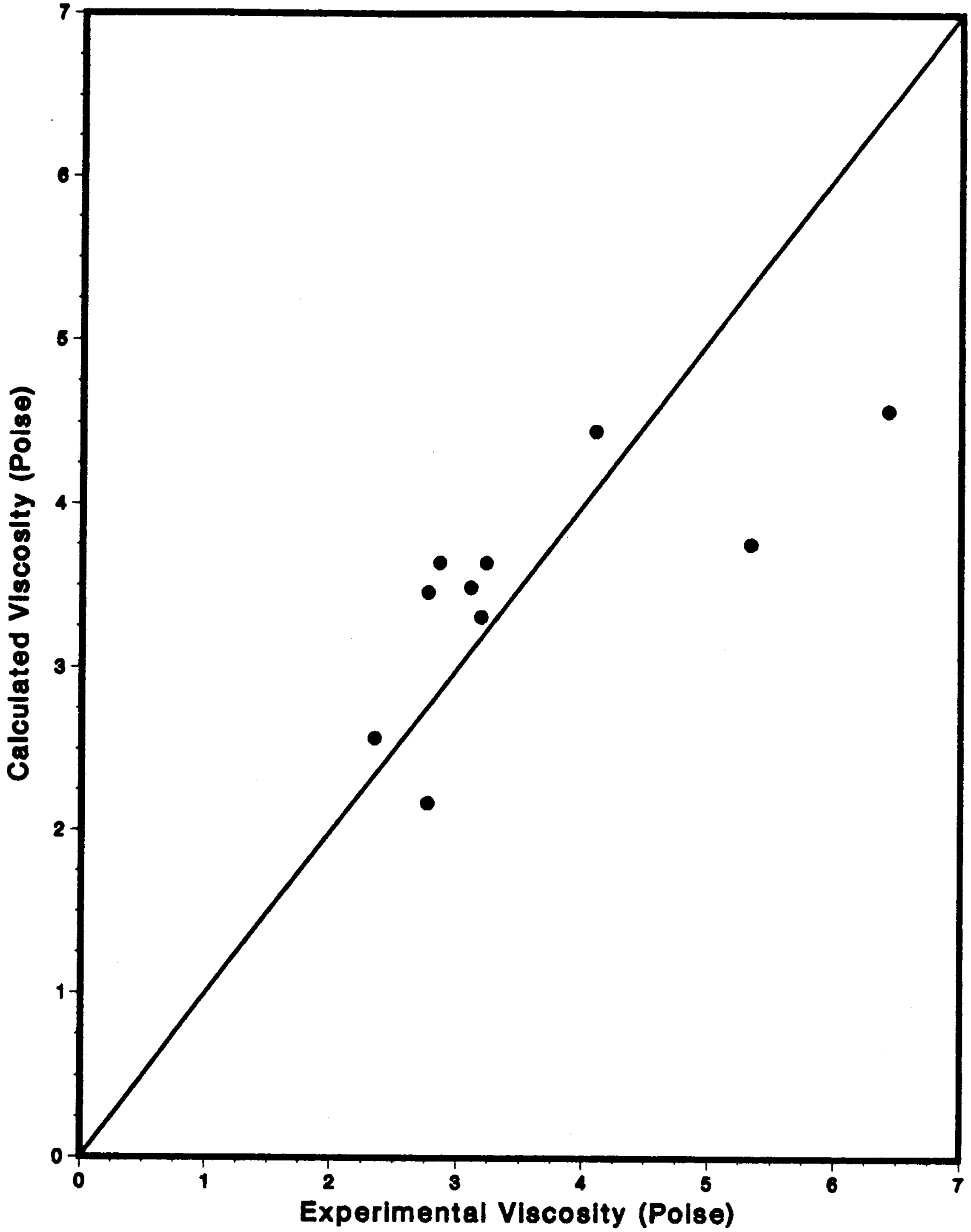


Figure 5-11

Comparison of Experimental Asphalt Viscosity to Predicted Viscosity (275°F)

Viscosity Temperature Susceptibility and Penetration Index. The GPC chromatograms for the asphalts from the Study 287 test sections were divided into large (LMS), medium (MMS) and small (SMS) molecular sizes as discussed earlier. These measurements were made for the virgin asphalts, the 1984 cores and the available 1985 cores. The results are reported in Table 5-2 along with the viscosity-temperature-susceptibility (VTS) and penetration index (PI). The GPC profiles were obtained using the methods described in Chapter 2.

The penetration index was determined from

$$\mathrm{PI} = \frac{20 - 500A}{1 + 50A}$$

where

$$A = \frac{\log(\mathrm{pen}_{T_1}) - \log(\mathrm{pen}_{T_2})}{T_1 - T_2}$$

and

pen_{T_1} =penetration at temperature T_1

pen_{T_2} =penetration at temperature T_2

and Viscosity-Temperature Susceptibility (VTS) (Puzinauskas, 1979) was determined from

$$\mathrm{VTS} = \frac{\log\log(100\eta_1) - \log\log(100\eta_2)}{\log T_2 - \log T_1}$$

where

η_1 =viscosity at T_1, poise

η_2 =viscosity at T_2, poise

T =temperature, Kelvin

Attempts to correlate LMS fraction of the asphalts with VTS showed that essentially no correlation for these data. Nevertheless, we still suspect that a relation exists. The asphalts were divided according to AC-10 and AC-20 groupings for the analysis.

Table 5-2

Selected Asphalt GPC (LMS, MMS, and SMS) and Physical (VTS, PI) Properties

Dickens Tank Samples

Solvent or Property	Region of GPC Chromatogram	Cosden AC-10	Cosden AC-20	Dia. Sham. AC-10	Dia. Sham. AC-20	Dorch. AC-20	Exxon AC-20	MacMillan AC-20
THF	LMS	8.32	9.07	23.94	26.55	17.54	6.84	18.88
	MMS	47.61	48.23	57.72	56.42	49.49	52.54	49.30
	SMS	44.08	42.69	18.34	47.07	32.97	40.63	31.81
Toluene	LMS	8.72	10.15	26.88	28.28	26.11	9.76	25.51
	MMS	57.47	57.55	56.45	56.08	51.88	60.64	52.79
	SMS	33.81	32.30	16.67	15.64	22.01	29.60	21.71
VTS		3.71	3.68	3.21	3.09	3.44	3.71	3.48
PI		1.4	0.59	0.31	-0.53	3.8	0.43	4.3

1984 Dickens Cores

Solvent or Property	Region of GPC Chromatogram	Cosden AC-10	Cosden AC-20	Dia. Sham. AC-10	Dia. Sham. AC-20	Dorch. AC-20	Exxon AC-20	MacMillan AC-20
THF	LMS	17.46	19.36	36.27	36.20	25.41	15.77	24.87
	MMS	47.89	47.67	49.00	48.09	47.36	51.55	48.15
	SMS	34.65	32.97	14.73	15.70	27.22	32.68	26.98
Toluene	LMS	15.09	17.37	37.14	34.78	28.70	11.65	25.77
	MMS	54.14	53.88	48.62	49.35	49.63	60.31	51.05
	SMS	30.77	28.75	14.23	15.87	21.67	28.04	23.19
VTS		3.83	3.81	3.66	3.44	3.75	3.61	3.64
PI		3.6	-0.48	5.1	9.5	0.74	6.7	6.7

Table 5-2 (Continued)

Selected Asphalt GPC (LMS, MMS, and SMS) and Physical (VTS, PI) Properties

1985 Dickens Cores

Solvent or Property	Region of GPC Chromatogram	Cosden AC-10	Cosden AC-20	Dia. Sham. AC-10	Dia. Sham. AC-20	Dorch. AC-20	Exxon AC-20	MacMillan AC-20
THF	LMS		25.02		38.60		15.77	23.06
	MMS		47.00		47.07		51.55	48.27
	SMS		27.98		14.33		33.12	28.67
Toluene	LMS							
	MMS							
	SMS							
VTS		3.82	3.87	3.75	3.82	3.96	3.64	4.08
PI		7.5	3.4	8.8	6.2	6.0	3.2	0.52

Dumas Tank Samples

Solvent or Property	Region of GPC Chromatogram	Cosden AC-10	Cosden AC-20	Dia. Sham. AC-10	Dia. Sham. AC-20	Dorch. AC-10	Exxon AC-10	MacMillan AC-10
THF	LMS	7.46	8.81	25.85	25.42	15.96	6.82	13.73
	MMS	49.22	48.88	57.40	56.89	49.90	50.74	53.44
	SMS	43.14	42.31	16.75	17.69	34.13	42.44	32.83
Toluene	LMS	7.62	8.54	25.85	27.71	22.35	6.71	19.83
	MMS	60.12	59.54	57.76	56.46	53.82	62.50	57.26
	SMS	32.26	31.92	16.39	15.82	23.83	30.80	22.91
VTS		3.65	3.77	3.08	3.17	3.42	3.58	3.29
PI		1.8	0.93	0.22	2.6	3.1	1.3	3.2

Table 5-2 (Continued)

Selected Asphalt GPC (LMS, MMS, and SMS) and Physical (VTS, PI) Properties

1984 Dumas Cores

Solvent or Property	Region of GPC Chromatogram	Cosden AC-10	Cosden AC-20	Dia. Sham. AC-10	Dia. Sham. AC-20	Dorch. AC-10	Exxon AC-10	MacMillan AC-10
THF	LMS	14.92	13.42		32.89	20.49		13.52
	MMS	47.15	47.86		52.59	46.41		47.55
	SMS	37.93	38.72		14.52	33.10		38.93
Toluene	LMS	11.09	11.88	31.42	35.21	24.33	10.12	23.24
	MMS	57.70	57.51	52.56	51.61	52.78	61.24	55.74
	SMS	31.21	30.61	16.01	13.19	22.90	28.63	21.03
VTS		3.71	4.11	3.18	3.30	3.45		3.42
PI		0.52	2.3	2.5	2.9	3.0		3.4

1985 Dumas Cores

Solvent or Property	Region of GPC Chromatogram	Cosden AC-10	Cosden AC-20	Dia. Sham. AC-10	Dia. Sham. AC-20	Dorch. AC-10	Exxon AC-10	MacMillan AC-10
THF	LMS	14.63	15.18	32.72	36.22		23.85	20.70
	MMS	49.31	49.02	50.61	49.29		47.92	51.45
	SMS	36.06	35.80	16.67	14.49		28.72	27.86
Toluene	LMS							
	MMS							
	SMS							
VTS		3.81	3.82	3.30	3.28	3.61		3.48
PI		5.4	3.4	3.8	2.7	3.2		3.0

Table 5-2 (Continued)

Selected Asphalt GPC (LMS, MMS, and SMS) and Physical (VTS, PI) Properties

Lufkin Tank Samples

Solvent or Property	Region of GPC Chromatogram	Cosden AC-20	Dia. Sham. AC-20	Dorch. AC-10	Dorch. AC-20	Exxon AC-20	MacMillan AC-20
THF	LMS	8.70	24.37	14.92		7.01	18.50
	MMS	50.38	53.90	46.95		52.99	52.39
	SMS	40.93	21.73	38.13		39.99	29.11
Toluene	LMS	10.30	27.08	20.17	19.14	7.43	21.23
	MMS	60.37	55.19	54.01	53.88	62.87	56.70
	SMS	29.33	17.73	25.82	26.98	29.70	22.06
VTS		3.78	3.26	3.52	3.50	3.66	3.27
PI		0.65	1.9	3.3	3.2	-1.3	2.6

Lufkin 84/85 Cores

Solvent or Property	Region of GPC Chromatogram	Cosden AC-20	Dia. Sham. AC-20	Dorch. AC-10	Dorch. AC-20	Exxon AC-20	MacMillan AC-20
THF	LMS	16.40		20.70		12.83	24.97
	MMS	50.82		48.38		53.31	49.53
	SMS	32.78		30.92		33.86	25.50
Toluene	LMS	16.24		25.14		11.58	28.19
	MMS	57.19		51.50		60.39	51.27
	SMS	26.57		23.36		28.03	20.54
VTS		3.52	5.01	3.49	3.69	3.74	3.67
PI		2.1			2.3		0.13

CHAPTER 6

EVALUATION OF ASPHALT CONTAMINATION USING GPC AND GC-MS

It is possible for binder failure to result from contamination of the asphalt mix by fuel oil from the hot-mix process. Three asphalt mixes that were suspected of fuel oil contamination were evaluated in this study. Boyd and East Texas Asphalt (ETA) samples were from District 11 and the South Texas sample was from District 21. Samples of both virgin asphalt and fuel oil were available for the Boyd and ETA mix. Only a pavement sample was available for the South Texas mix.

Gel Permeation Chromatography (GPC) alone did not reveal any contamination of these asphalts. Further GPC analyses were made of both the volatile and non-volatile fractions obtained by vacuum distillation, and the volatile fraction was also analyzed by GC-MS. Chapter 2 contains a description of this technique and procedure.

Vacuum Distillation

Vacuum distillation was used to determine the volatile content of all of the samples (Table 6-1). The volatile fraction of asphalt is less than 20%, whereas the volatile fraction of the fuel oil is greater than 90%. The ETA mix showed little change in volatile content while the Boyd mix showed some increase.

GPC Analysis

The samples, vacuum residues, and distillates were analyzed by GPC using a 60 cm long, 5 μm 100 Å PL Gel column. The chromatograms of the samples are shown in Figures 6-1 to 6-7. Unfortunately, vacuum distillation of ETA Plant Fuel Oil did not yield a sufficient amount of vacuum residue for analysis. Because of slight variations in sample concentration, the distillable and non-distillable curves do not necessarily add up to the profile for the whole asphalt. Figures 6-3 and 6-6 show the chromatograms of the fuel oils. These profiles demonstrate that although the fuel oil is chiefly low molecular weight, volatile species, there is a small amount of non-volatile material that is fairly large in molecular size. While these large molecular weight species are possible candidates for contaminating an as-

Table 6-1

Volatile Fractions of Vacuum Distilled Asphalts

Sample	Temperature (°F)	Time (min)	% Distillables
South Texas Mix	572	30	16.3
ETA Asphalt	572	30	14.9
ETA Mix	572	30	14.4
ETA Fuel Oil	572	39	95.0
Boyd Asphalt	572	30	12.3
Boyd Mix	572	30	14.8
Boyd Fuel Oil	572	30	93.6

phalt, there is no suggestion that this has occurred for either the Boyd or ETA asphalts, based upon their GPC volatile profiles.

The ETA asphalt shows a shift in its profile toward large molecular size material as a result of the hot-mix process (compare Figures 6-1 and 6-2). The Boyd asphalt shows a similar shift but to a lesser extent. This shift is typical of the chemical changes that are seen during the hot-mix process and which were discussed in Chapter 4.

GC-MS Analysis

Volatile fractions from the virgin asphalt and mix samples as well as Boyd and ETA fuel oil samples were analyzed by GC-MS. The total ion chromatograms are shown in Figures 6-8 to 6-14. Figures 6-9 and 6-12 show low boiling point components which are not found either in the suspected fuel oil sample, or in the virgin asphalt sample. Both ETA and Boyd asphalt mixes contained almost identical contaminating species but in different proportions. Table 6-2 lists these species. These species were identified by the Finnigan mass spectral (MS) library search programs using National Bureau of Standards (NBS) Mass Spectral Data Base which has mass spectral fragmentation patterns of about 40,000 organic species. The MS library search may not establish the exact identity of all species as there are several millions of possible organic compounds. The GC-MS analysis in most cases identifies molecular parameters such as molecular weights, molecular formula and probable functional groups.

In conclusion, the analysis identified a few volatile contaminants but could not identify any non-volatile material which might have contaminated the asphalt. Vacuum distillation data suggest but do not prove that the ETA mix may have gained some additional non-volatiles in the hot-mix process. This analysis was performed at an exploratory level. Both GC-FTIR (Gas Chromatography-Fourier Transform Infrared) of volatiles and FTIR of non-volatiles may provide additional information.

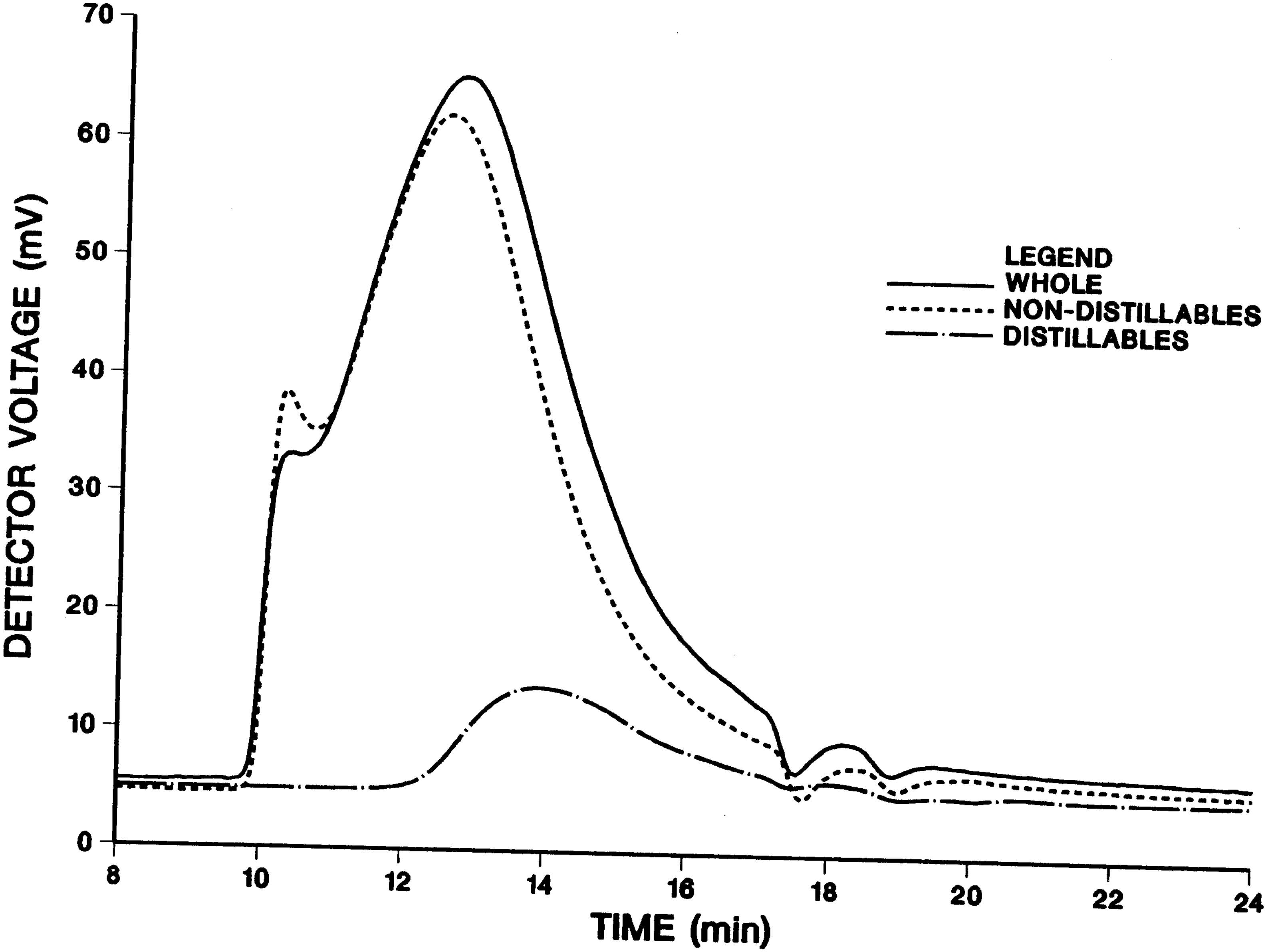


Figure 6-1
GPC Profiles of ETA Plant Asphalt
100 Å Column/THF/100 μl/5%

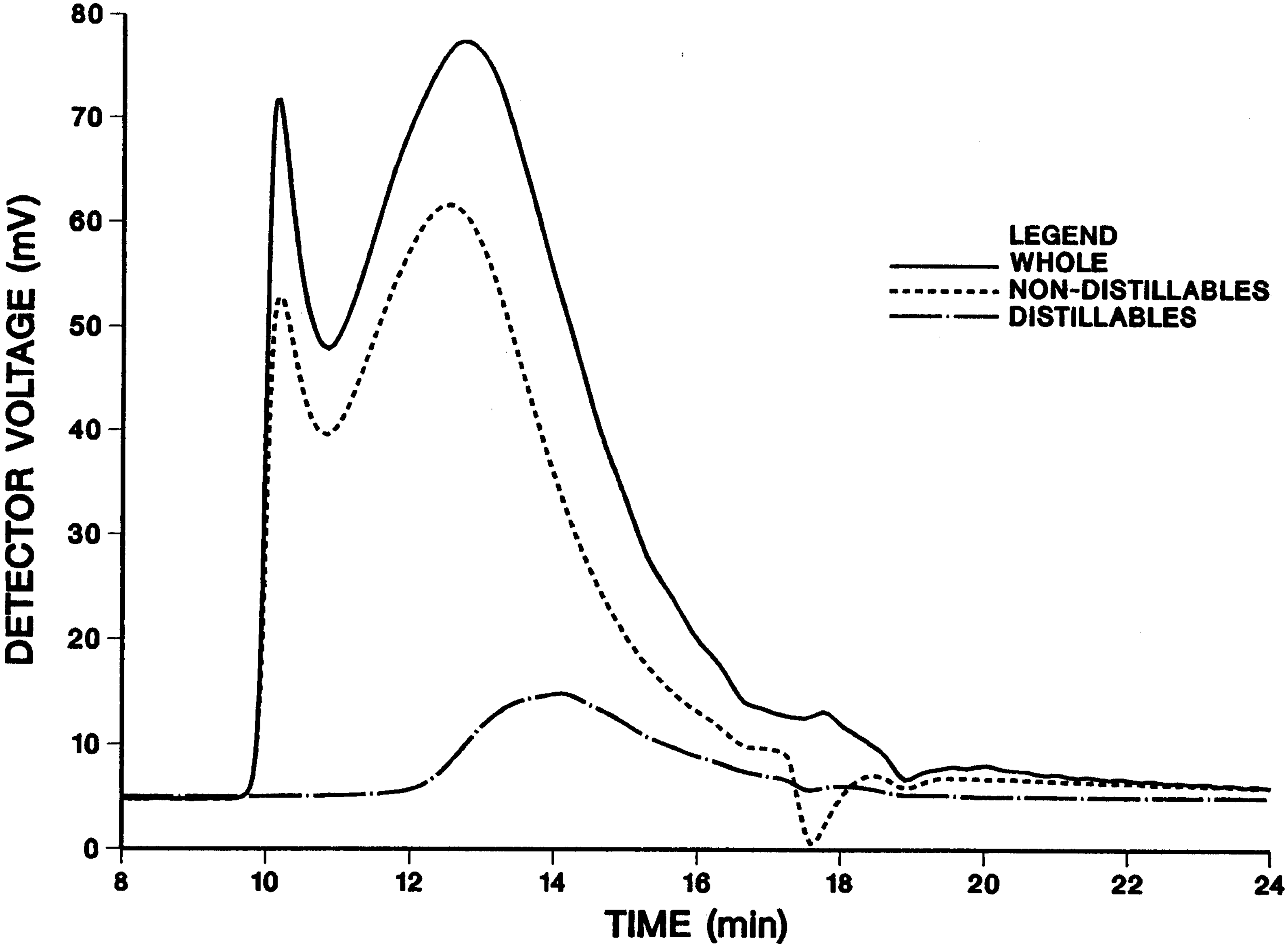


Figure 6-2
GPC Profiles of ETA Plant Asphalt Mix
100 Å Column/THF/100 μl/5%

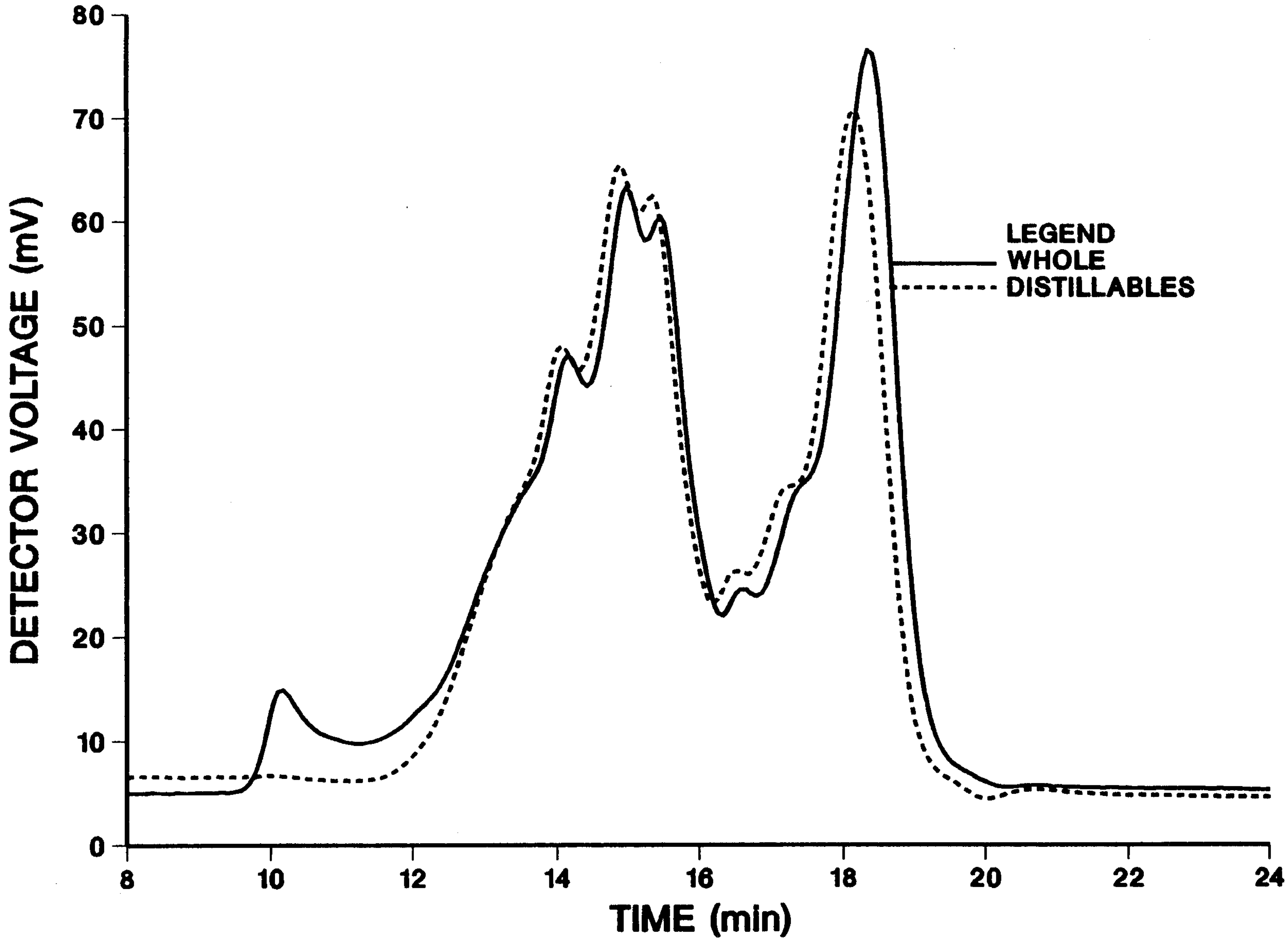


Figure 6-3
GPC Profiles of ETA Plant Fuel Oil
100 Å Column/THF/100 μl/5%

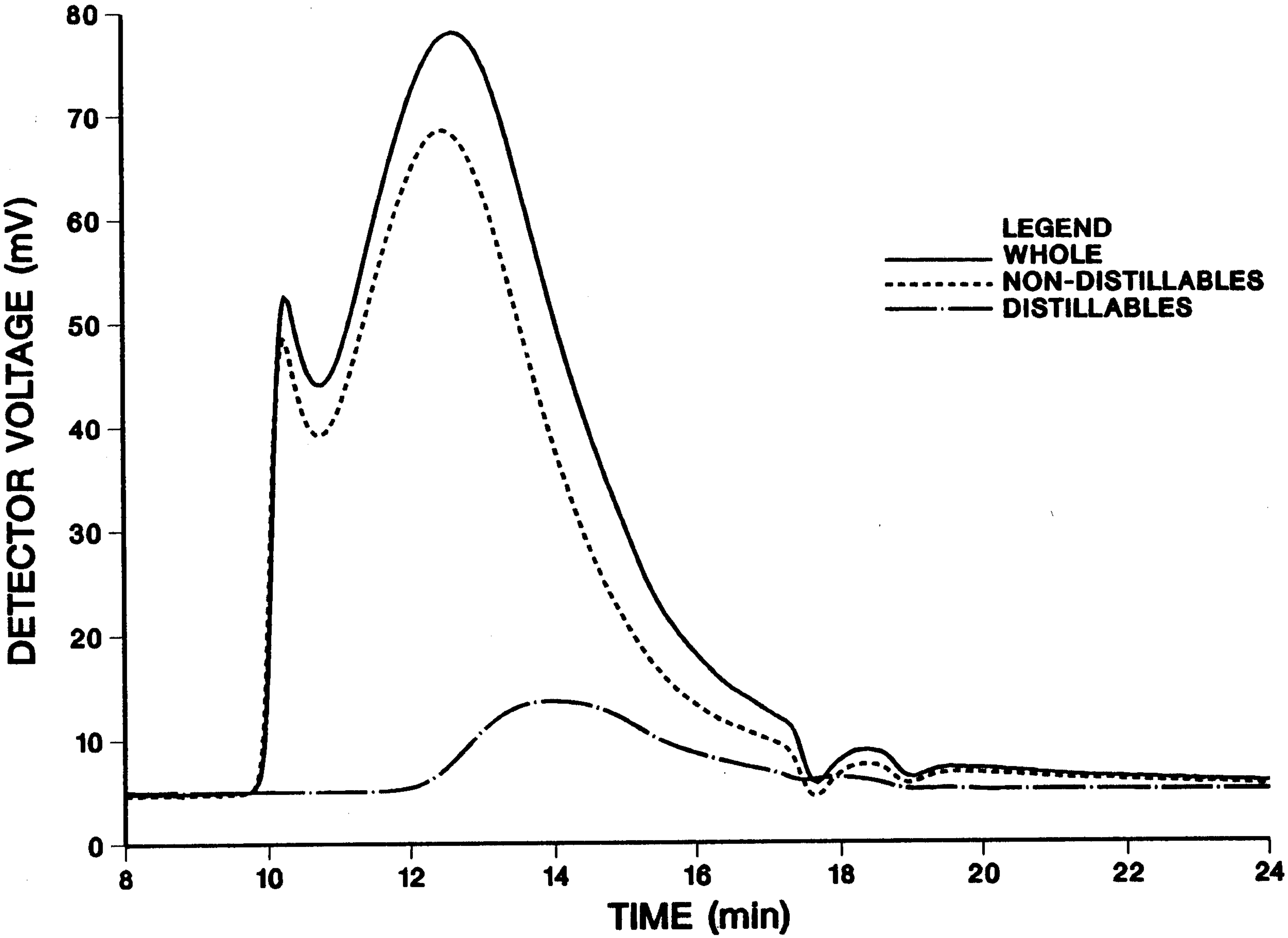


Figure 6-4
GPC Profiles of Boyd Plant Asphalt
100 Å Column/THF/100 μl/5%

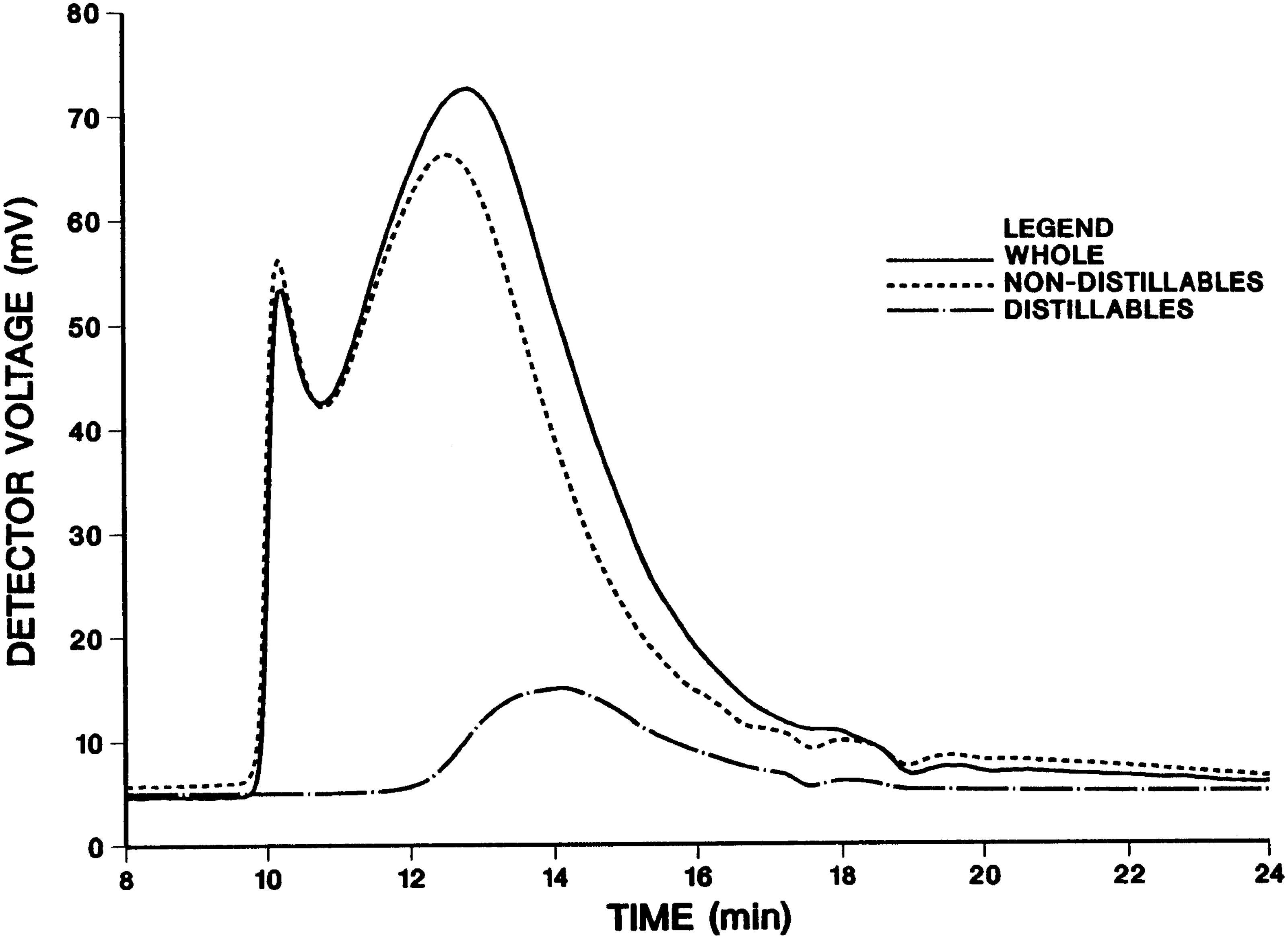


Figure 6-5
GPC Profiles of Boyd Plant Asphalt Mix
100 Å Column/THF/100 μl/5%

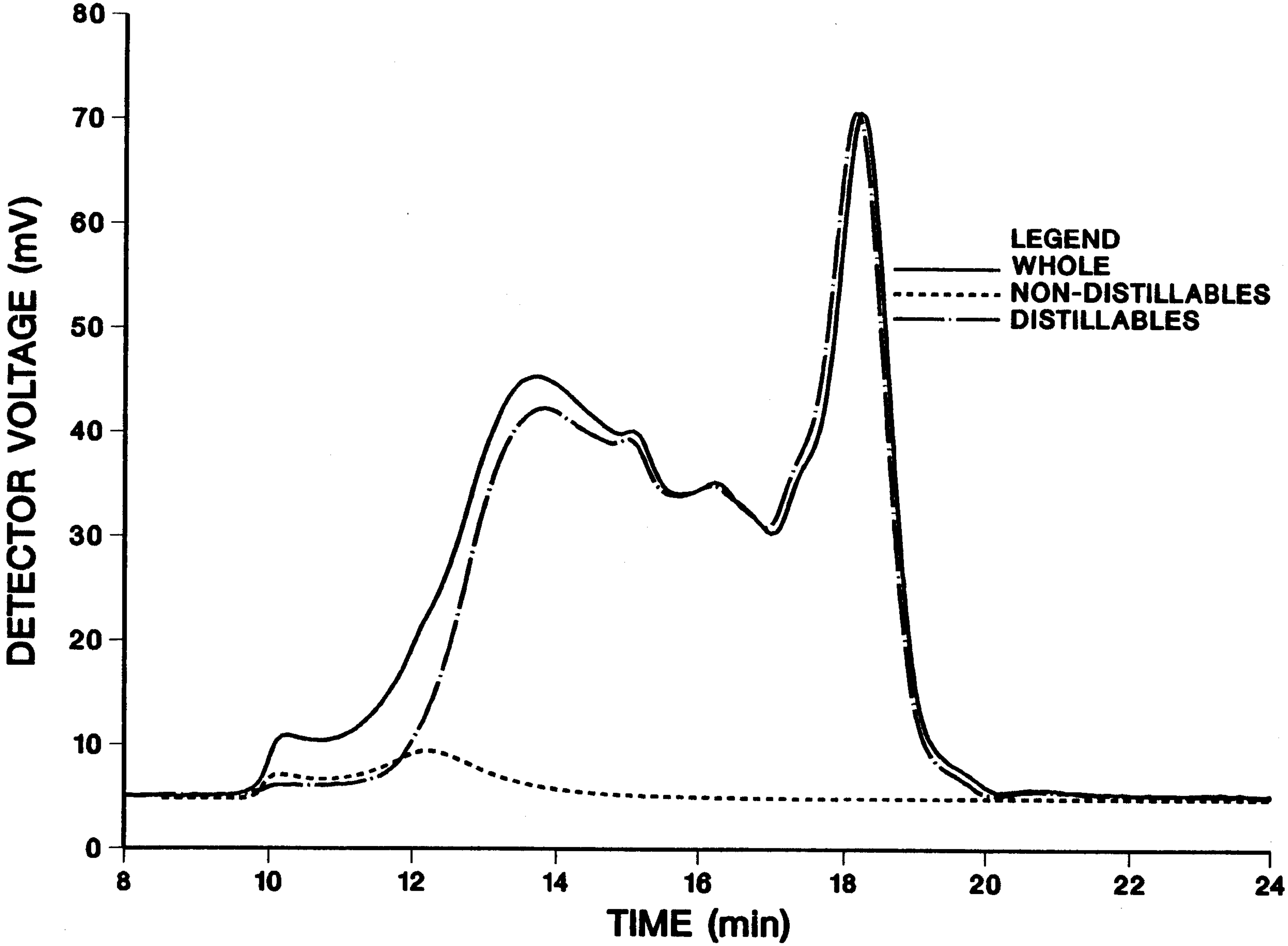


Figure 6-6
GPC Profiles of Boyd Plant Fuel Oil
100 Å Column/THF/100 μl/5%

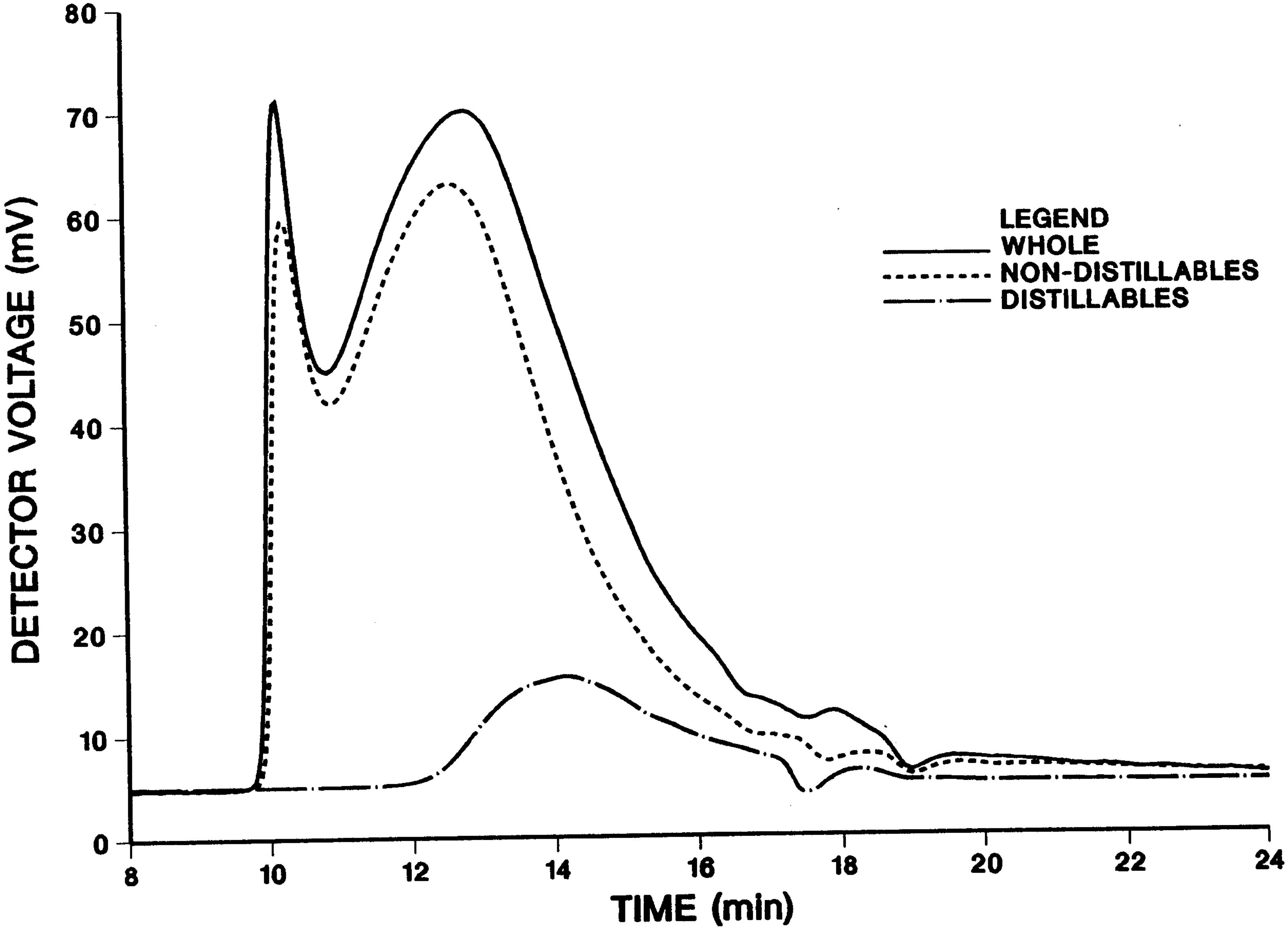


Figure 6-7
GPC Profiles of South Texas Mix
100 Å Column/THF/100 μl/5%

Table 6-2

Probable Compounds Identified by GC-MS

Retention Time (min:sec)	Probable Compound
21:17	C_4 alkyl phenol
23:02	Propanoic acid, 2-methyl-,2,2-dimethyl 1-(2-hydroxy-1-methyl ethyl) PR 1 $C_{12}H_{24}O_3$
23:28	Propanoic acid, 2-methyl, -3-hydroxy-2, 4, 4-trimethylpentyl ester $C_{12}H_{24}O_3$
44:34	1,2-Benzenedicarboxylic acid, diheptyl ester $C_{22}H_{34}O_4$
46:04	1,2-Benzenedicarboxylic acid, diisooctyl ester $C_{24}H_{38}O_4$

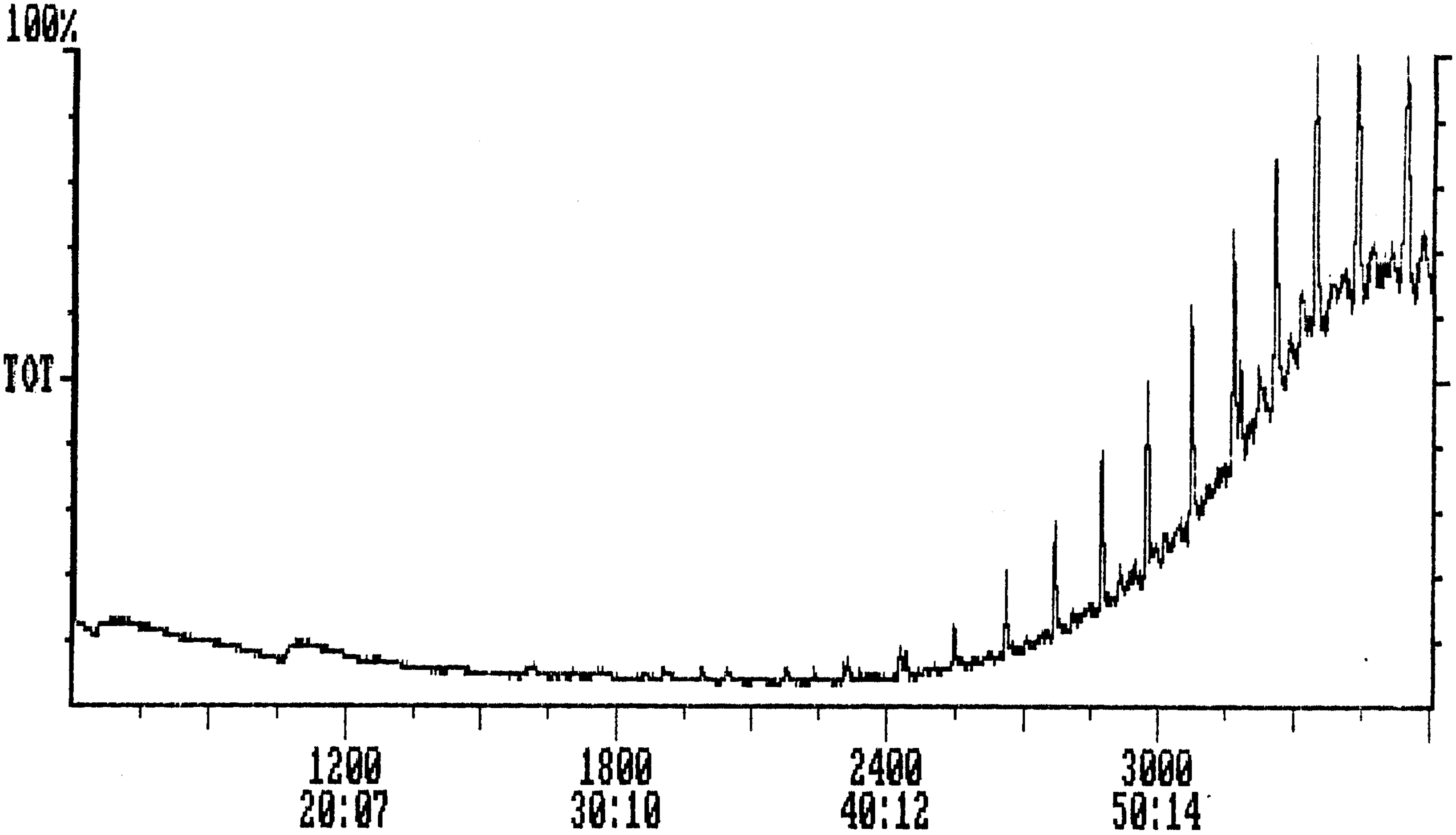


Figure 6-8
Distillables Fraction of ETA Asphalt by GC-MS
0.2 μl/THF/Scan Range: 601-3600

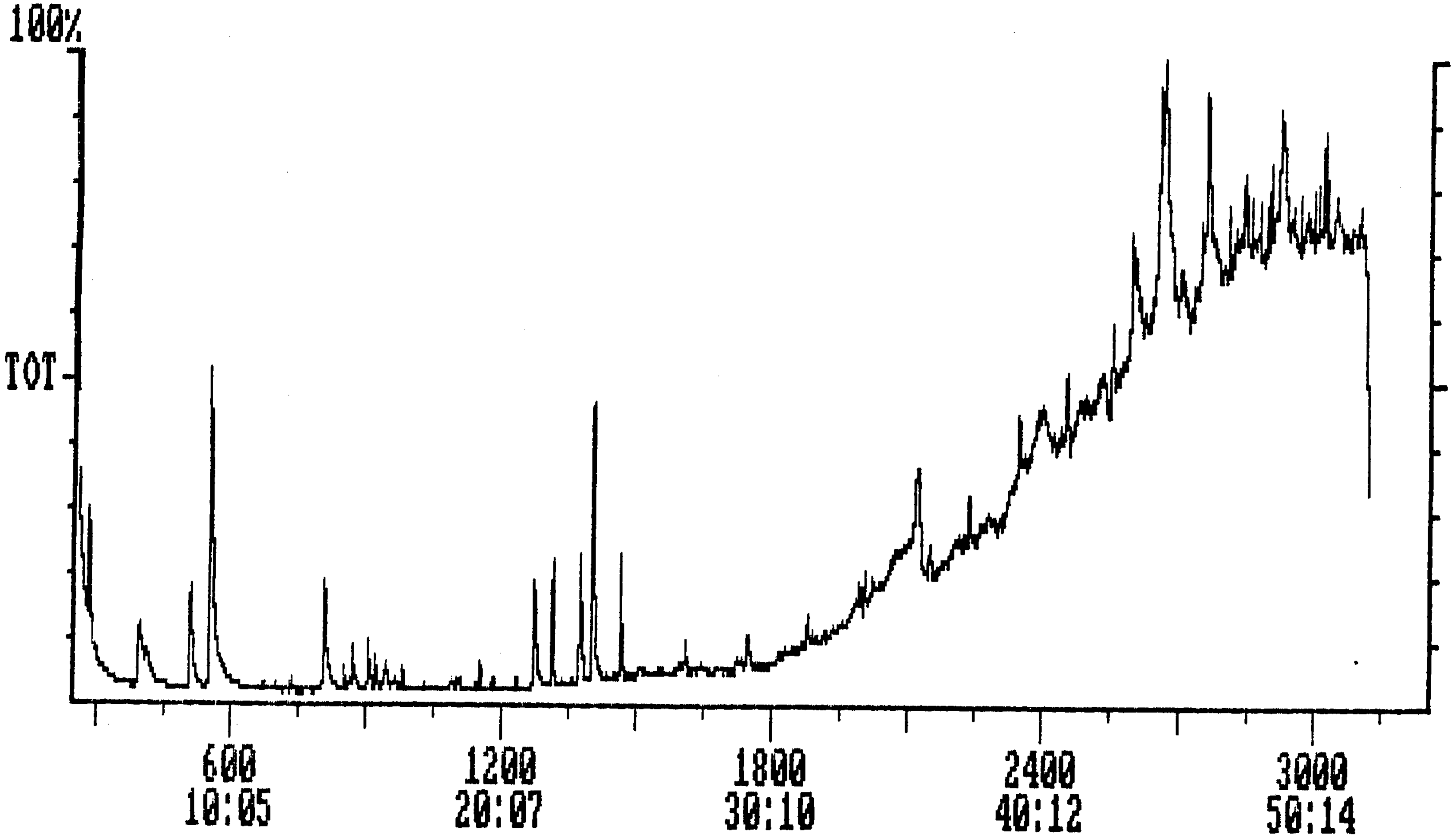


Figure 6-9
Distillables Fraction of ETA Mix by GC-MS
0.2 μl/THF/Scan Range: 251-3120

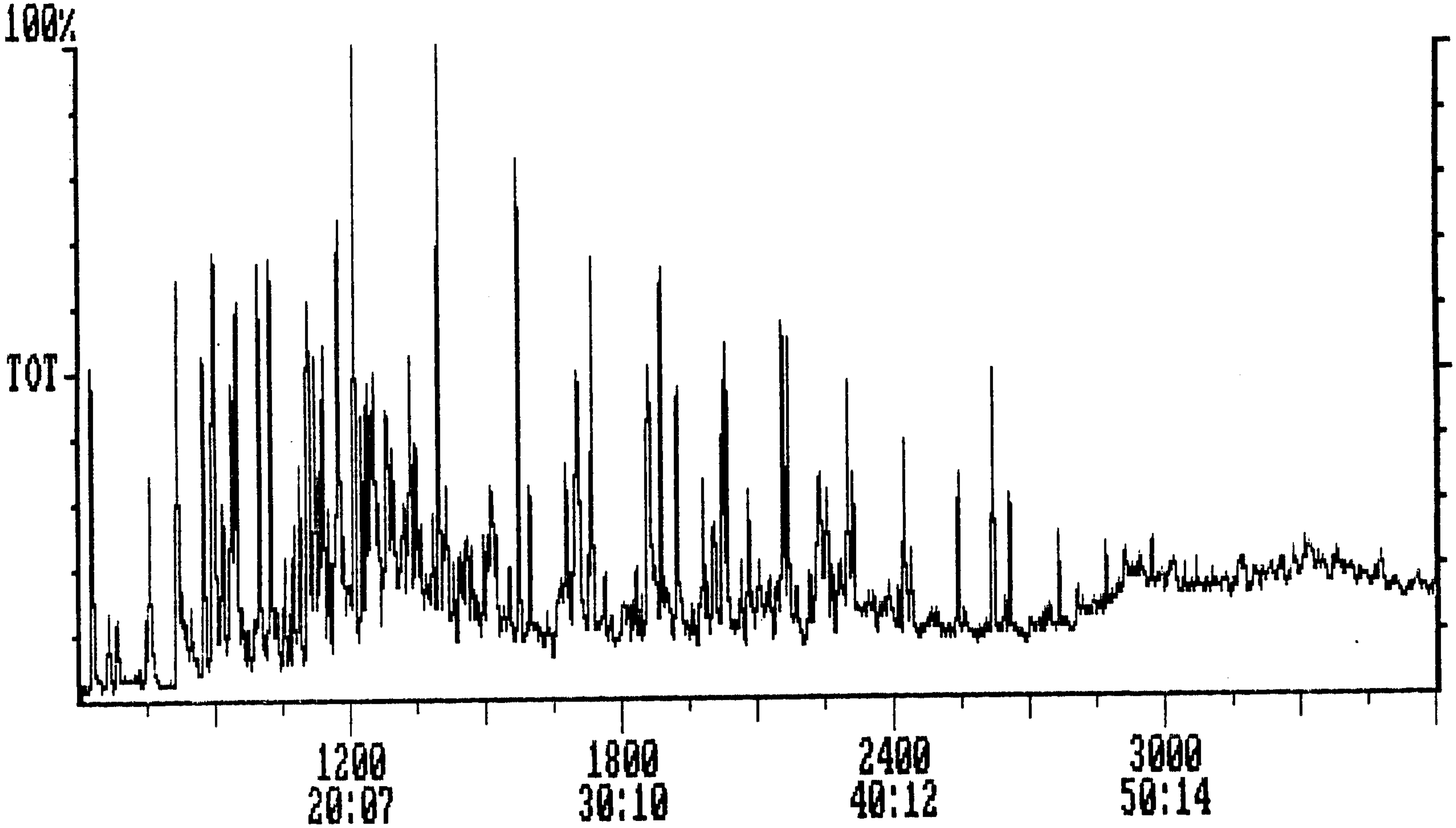


Figure 6-10
Distillables Fraction of ETA Fuel Oil by GC-MS
0.2μl/THF/Scan Range: 601-3600

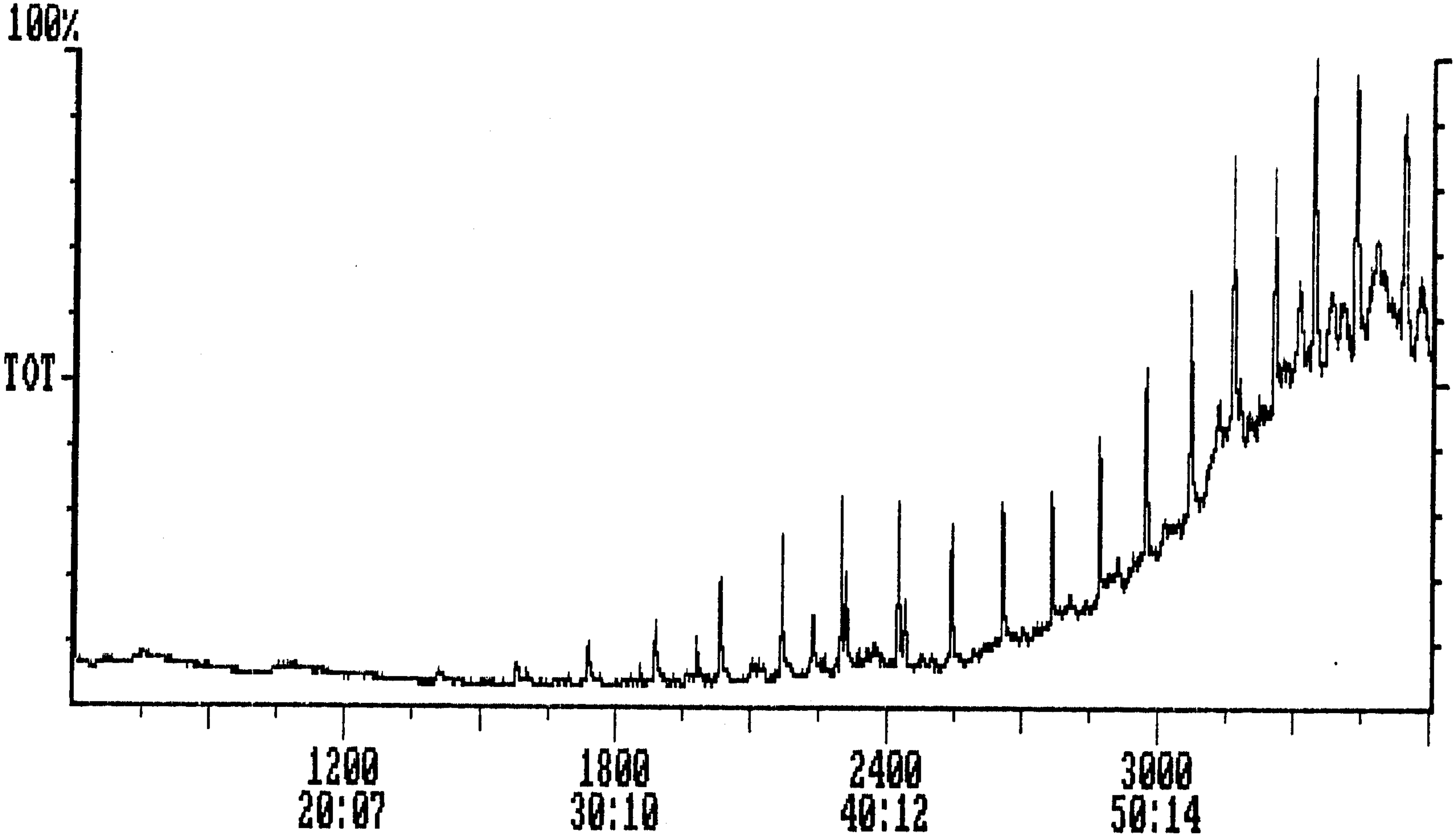


Figure 6-11
Distillables Fraction of Boyd Asphalt by GC-MS
0.2 μl/THF/Scan Range: 601-3600

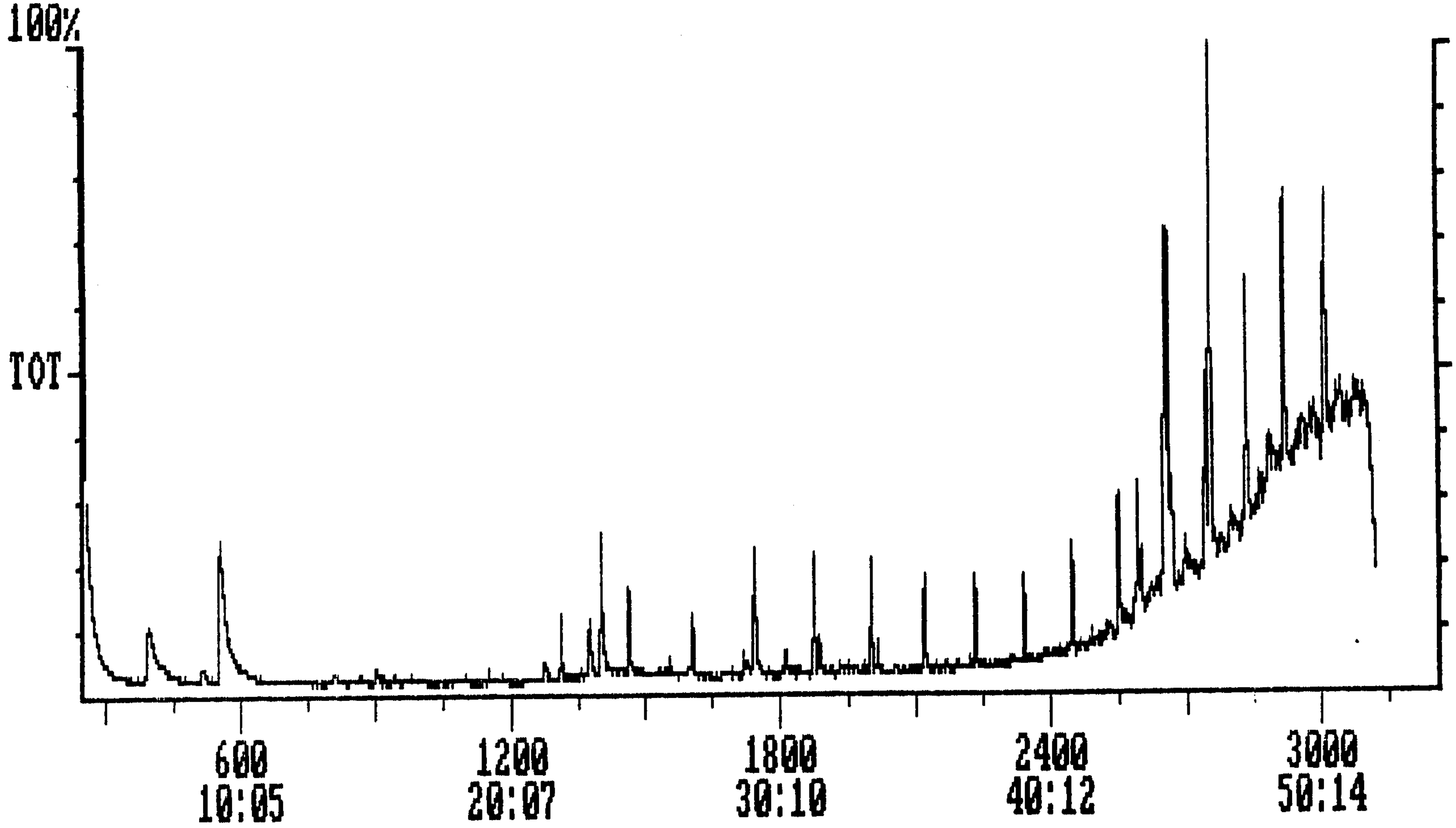
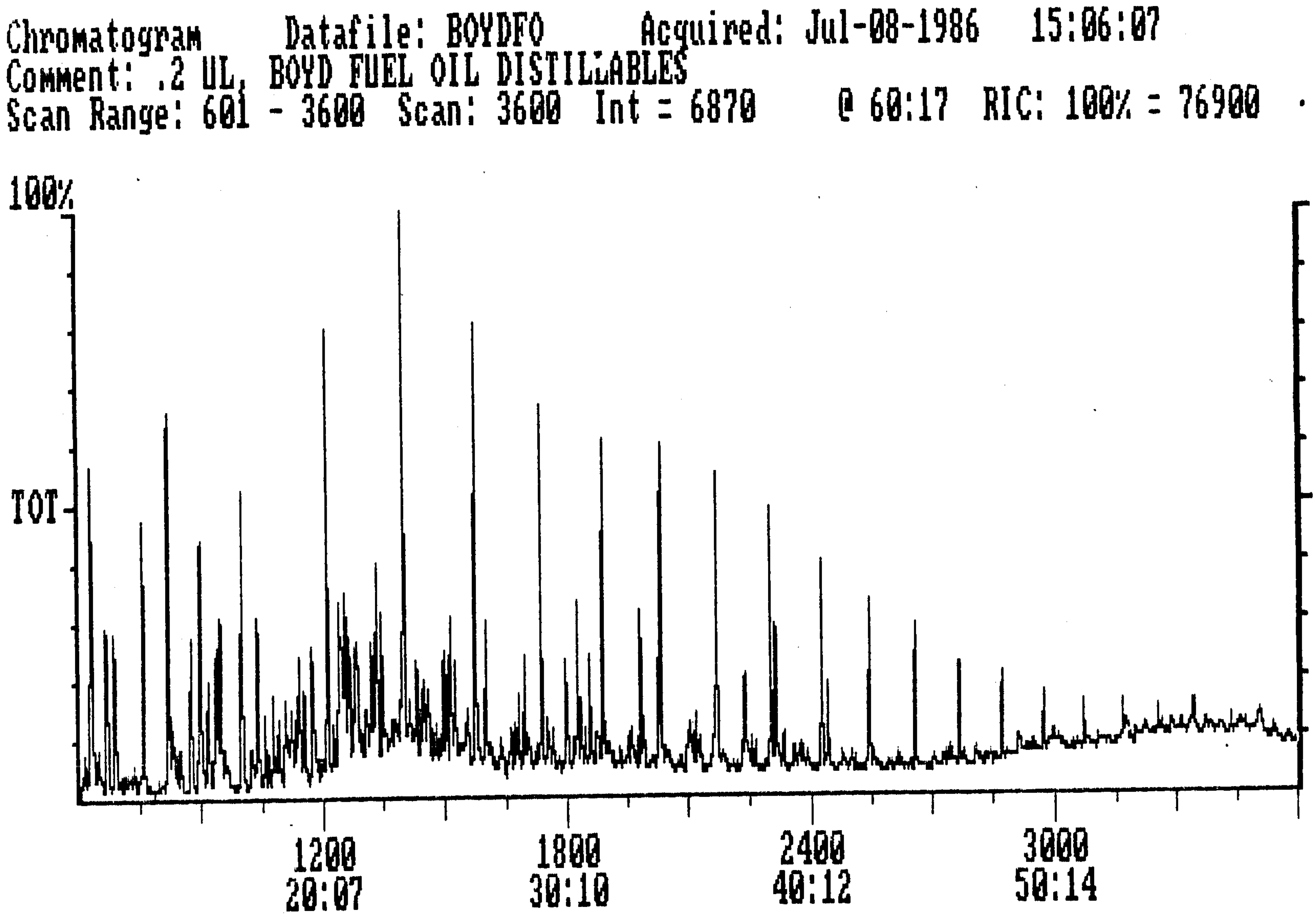


Figure 6-12
Distillables Fraction of Boyd Mix by GC-MS
0.2 μl/THF/Scan Range: 251-3120



```
Chromatogram    Datafile: BOYDFO     Acquired: Jul-08-1986   15:06:07
Comment: .2 UL, BOYD FUEL OIL DISTILLABLES
Scan Range: 601 - 3600  Scan: 3600  Int = 6870    @ 60:17  RIC: 100% = 76900
```

Figure 6-13
Distillables Fraction of Boyd Fuel Oil by GC-MS
0.2μl/THF/Scan Range: 601-3600

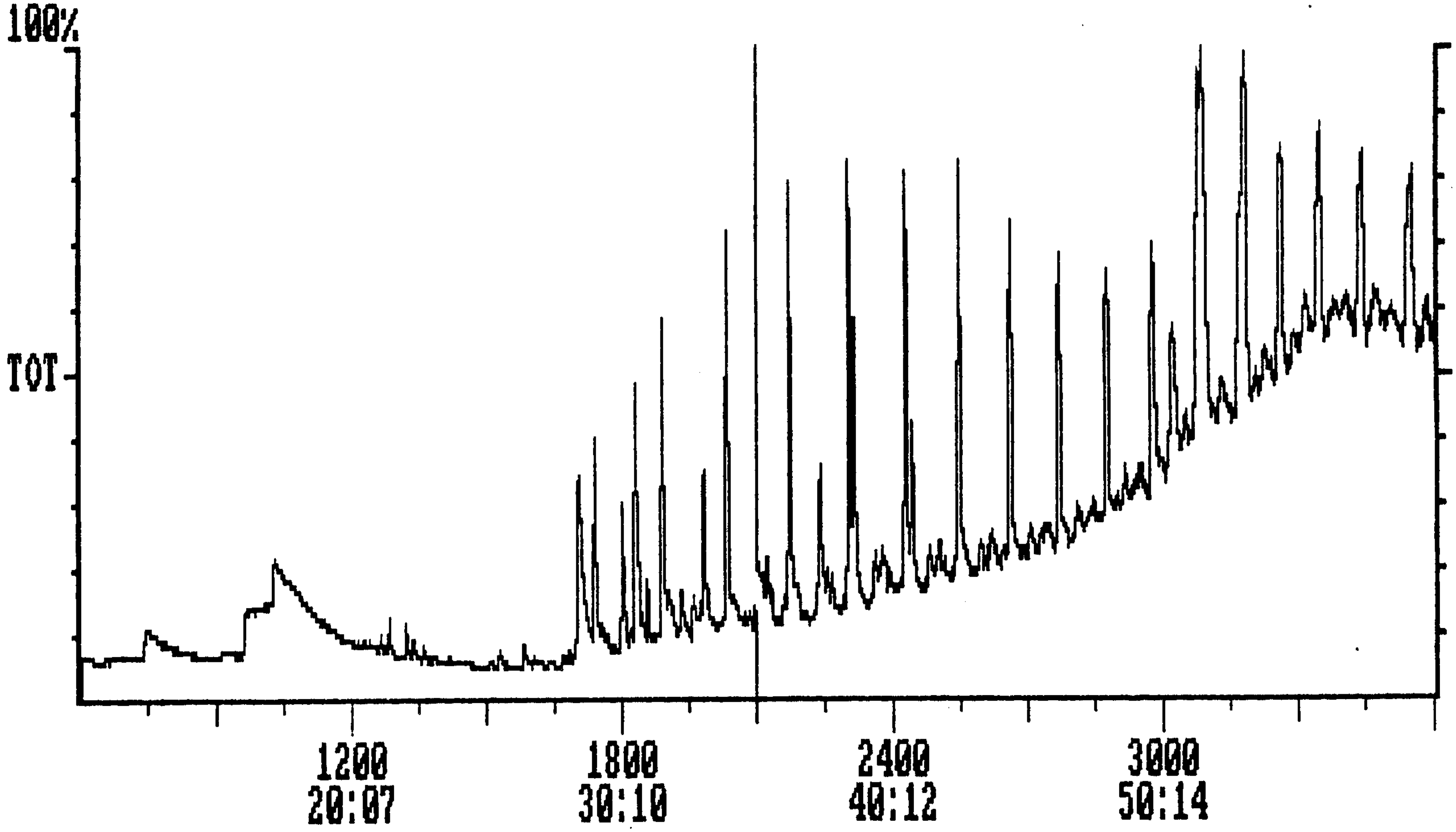


Figure 6-14
Distillables Fraction of South Texas Mix by GC-MS
0.2μl/THF/Scan Range: 601-3600

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Work described in this report leads to the following conclusions:

1. Gel Permeation Chromatography (GPC) is a very rapid procedure for asphalt characterization. There is a considerable body of literature indicating that it is also a useful tool for identifying asphalt changes and for correlating cracking and tenderness in asphalts.
2. To produce reproducible GPC chromatograms, a number of operating conditions (solvent, solvent flow, detector characteristics and type, column size and solute concentration) must be closely controlled.
3. Higher than normal solute concentrations can enhance differences between the chromatograms of different asphalts.
4. Reproducible chromatograms can be obtained with toluene even though it is a relatively poor solvent for asphalt.
5. By using solvents of very different solvency such as THF and toluene, component elution times can be changed so that the order of elution may be reversed. The change in elution time of asphalt components can provide additional information about the asphalt.
6. The change in detector sensitivity in toluene relative to that in THF changes the relative response of different asphalt fractions. For instance in toluene the response to the paraffin and asphaltene Corbett fractions is suppressed emphasizing the polar and naphthene aromatic fractions.
7. Changes in asphalt composition caused by changes in processing and feedstock can be detected by GPC. In most instances the differences between asphalts from various sources are distinguishable.
8. For all cores taken from the Study No. 287 test sections, the GPC large molecular size (LMS) region increased relative to the virgin asphalt, and changes in the Corbett fractions from virgin asphalt to cores were similar to those reported by others. That is, there was little change in paraffins, an increase in asphaltenes, a decrease in naphthene aromatics, and either an increase, a decrease, or little change in polar aromat-

ics.

9. Rather large changes in the size of Corbett fractions from virgin asphalt to core were accompanied by relatively slight if any changes in the shape of the GPC chromatograms of the Corbett fractions. In general there was a measurable shift to larger molecular size in the asphaltene and polar aromatic fractions.
10. Tenderness in asphalts was about equally well correlated by the Heithaus flocculation ratio, the percent LMS, and the percent asphaltene fraction. There was for most asphalts a good correlation between asphaltene content and the percent LMS. The Diamond Shamrock asphalt was an exception in all LMS relationships.

Based on research thus far and an extensive literature survey the authors have formulated several concepts or hypotheses which could lead to greatly improved asphalts.

1. Paraffins are not desirable in asphalts and serve only to reduce viscosity.
2. An asphaltene content which is too high causes cracking while that which is too low causes setting problems.
3. Aging tests with aggregate are of considerable value as aggregate catalyzes significant changes in the asphalt.

The problem with implementing items 1 and 2 is that there is such variation in the viscosity of the fractions of particular asphalts that frequently considerable paraffin is required to lower viscosity and it is unknown to what extent and in what manner asphaltenes affect viscosity temperature susceptibility and other asphalt properties. The optimum asphaltene content is definitely a function of climate, but it also depends to some unknown extent on the chemical nature of the asphaltenes and other fractions.

We believe that it is likely that most asphalts could be improved by fractionation followed by optimum recombination of the fractions. To accomplish these ends a reliable aging test that includes the aggregate is needed. This could be accomplished by reproducing from virgin asphalt and aggregate an asphalt chemically and physically resembling the aged cores taken from test sections. Only with a reliable aging test can the effects of changes in asphalt composition be studied. As the data from test sections are limited, they should be supplemented by the sampling of roads of various ages and conditions to better correlate various chemical markers with these conditions.

By supplementing the GPC and Corbett analyses with infrared and elemental analysis coupled to aging tests, we believe that the characteristics of asphalt that lead to undesirable changes can be identified. By extending these results to recombinations of asphalt fractions we believe that superior asphalts can be designed to conform to a particular aggregate characteristic and climate.

Recommendations

Significant results have been produced which will provide guidelines for the future. In general, too much asphaltene content (especially large molecular size asphaltenes) results in pavement cracking. On the other hand, large molecular size compounds (which are usually asphaltenes) are necessary to prevent tenderness. There is thus likely to be a trade–off which will vary with climate. We believe that a study of this relationship can result in asphalt specifications. It is also believed that temperature susceptibility can be related to GPC chromatograms and to Corbett fractions. Finally, as stated above, the GPC analysis is sensitive to aging and the extent of change of an asphalt GPC chromatogram with time seems to relate to performance.

Thus, we believe that with further work, specifications can be formulated to improve the quality of asphalts by placing limits to protect against (1) cracking, (2) tenderness, (3) temperature susceptibility, and (4) excessive hardening. Furthermore, GPC analysis can be used routinely as an early warning of changes in the asphalt from any supplier.

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NOTATION

C = concentration of polymer in the solvent

FIMS = Field-Ionization Mass Spectrometry

K = ratio of concentration in a pore to that in the bulk solvent

LMS = Large Molecular Size region of a gel permeation chromatogram

MMS = Middle Molecular Size region of a gel permeation chromatogram

M = molecular weight

ODCB = Orthodichlorobenzene

N = number of theoretical plates in a GPC column

pen = penetration

PI = penetration index

R = diameter of molecule in the GPC model of Yau et al. (1979)

r = diameter of pores in the GPC model of Yau et al. (1979)

SDHPT = State Department of Highways and Public Transportation

SMS = Small Molecular Size region of a gel permeation chromatogram

THF = tetrahydrofuran

V_i = GPC pore volume

V_o = total exclusion volume in a GPC column

V_R = retention volume

VTS = Viscosity–Temperature Susceptibility

$W_{0.5}$ = width of a GPC response peak at half its height

w_{A_s} = weight fraction of asphaltenes in the asphalt

w_S = weight fraction of saturates in the asphalt

Greek Letters

α, β, γ = Parameters in the viscosity equation, Table 5-1

η = viscosity

$[\eta]$ = intrinsic viscosity

Appendix A

Chromatograms from the Dickens and Lufkin Test Pavements

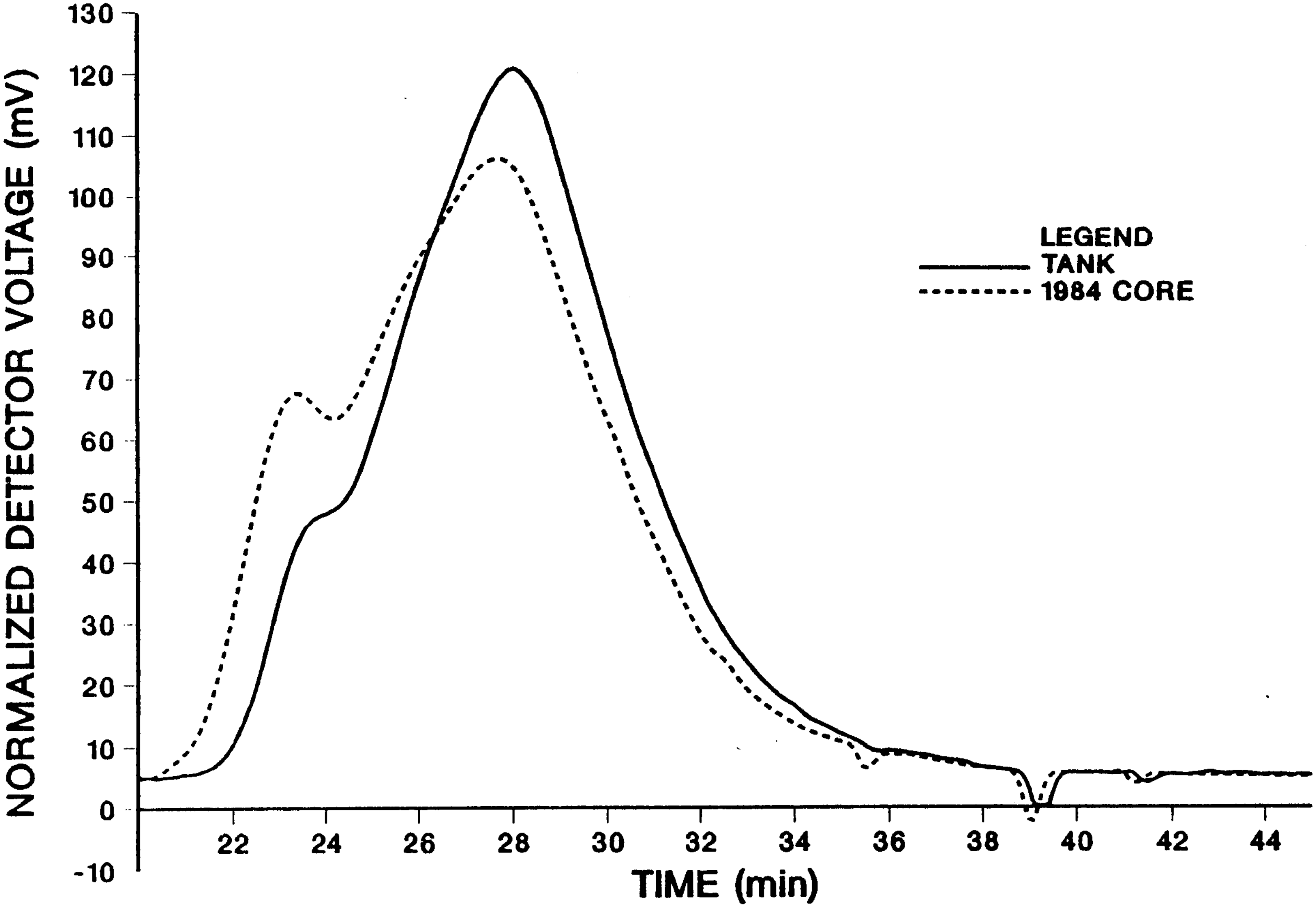

Figure A-1
Comparison of Core Samples to the Original Asphalt in THF
Cosden AC-10, Dickens Test Site
500 Å and 50 Å Columns/THF/100 μl/7%

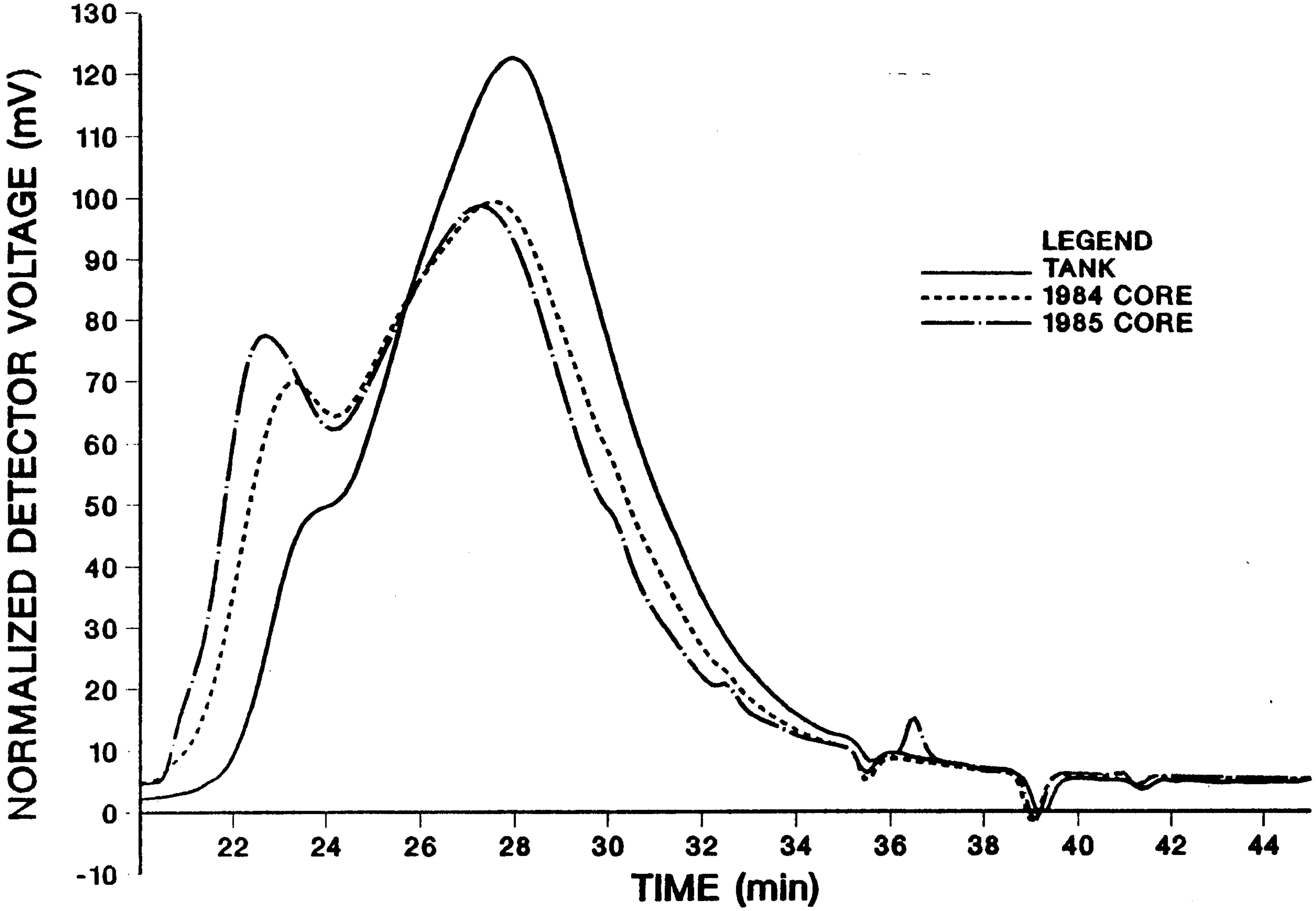

Figure A-2
Comparison of Core Samples to the Original Asphalt in THF
Cosden AC-20, Dickens Test Site
500 Å and 50 Å Columns/THF/100 μl/7%

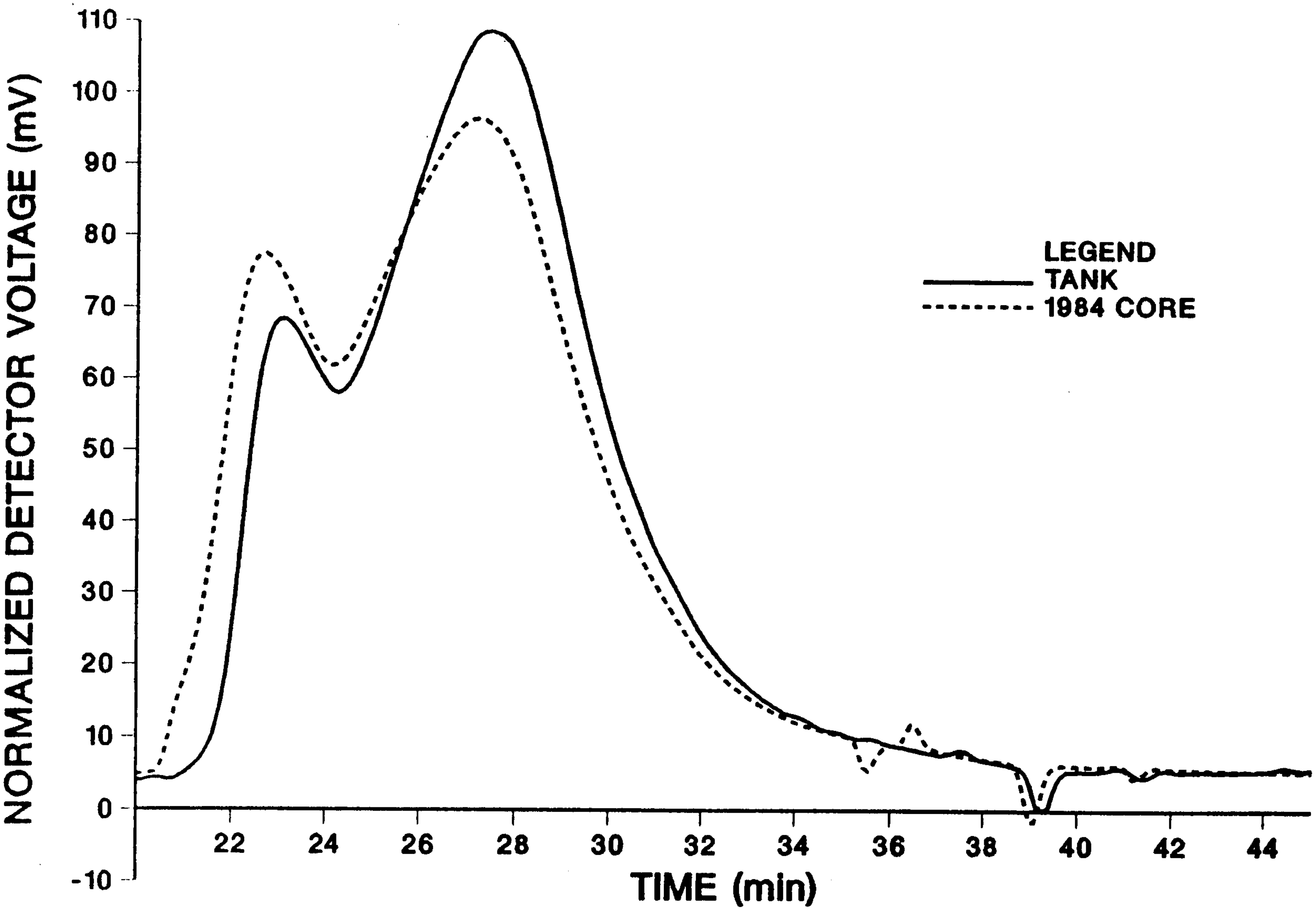

Figure A-3
Comparison of Core Samples to the Original Asphalt in THF
Dorchester AC-20, Dickens Test Site
500 Å and 50 Å Columns/THF/100μl/7%

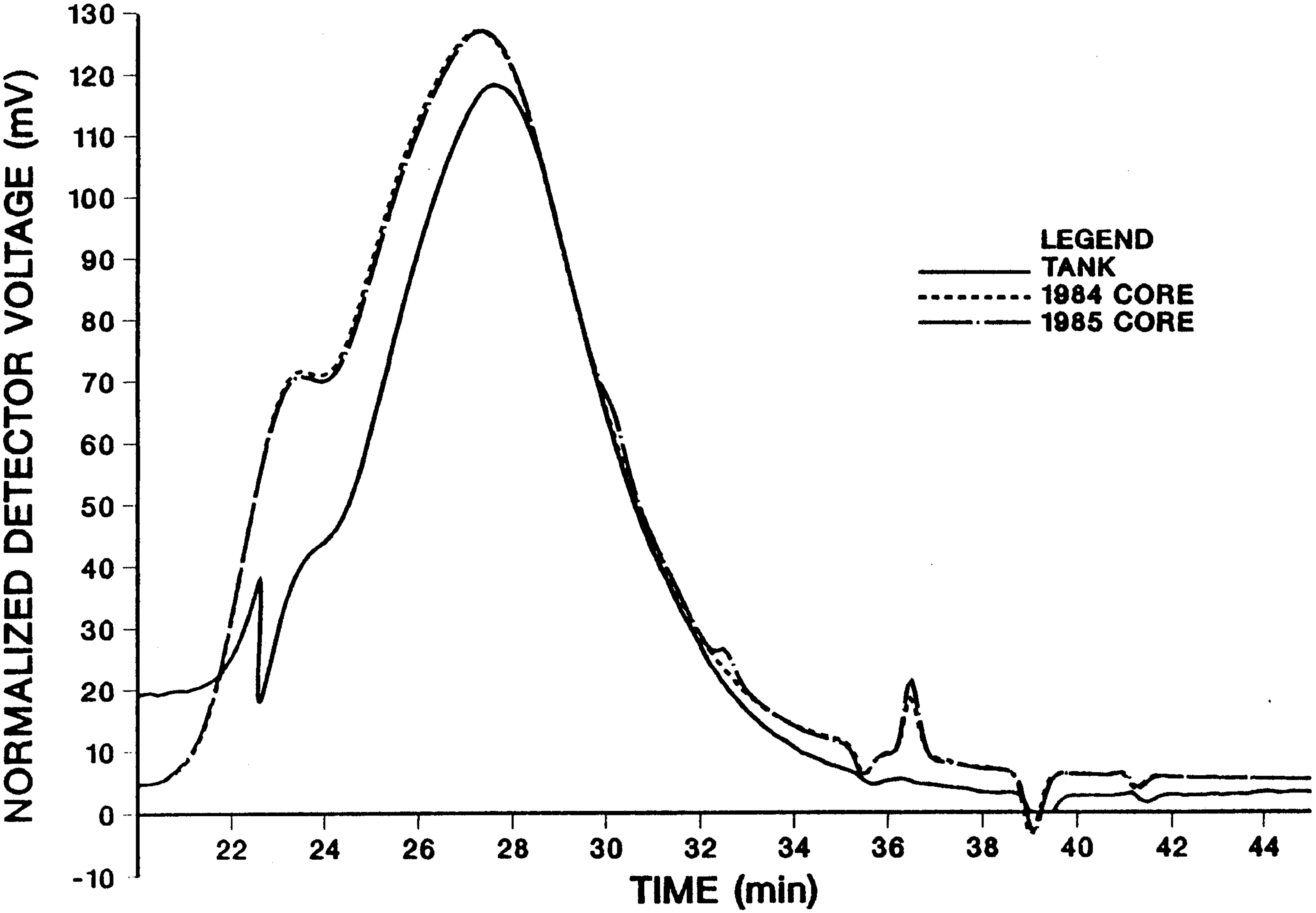

Figure A-4
Comparison of Core Samples to the Original Asphalt in THF
Exxon AC-20, Dickens Test Site
500 Å and 50 Å Columns/THF/100 μl/7%

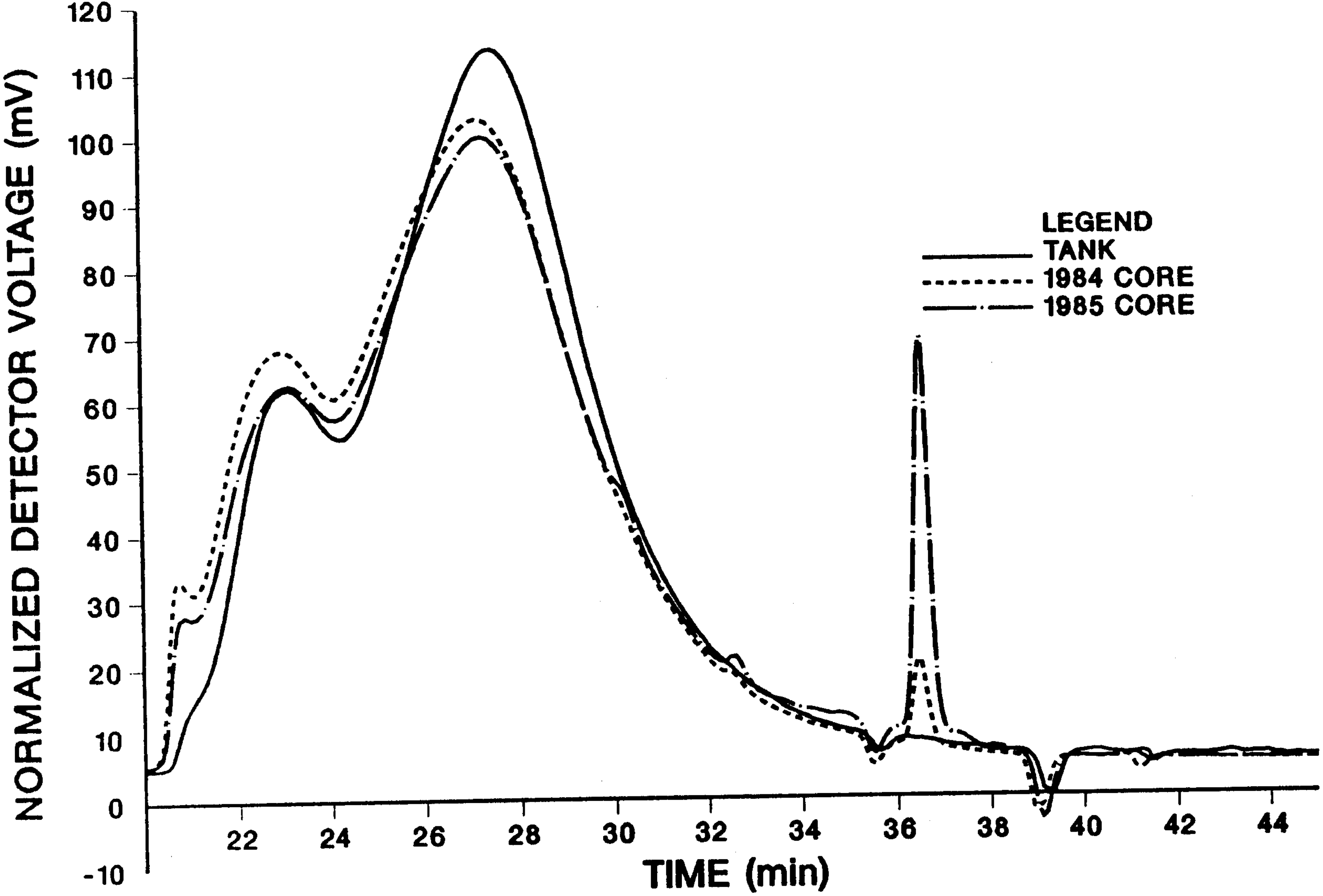

Figure A-5
Comparison of Core Samples to the Original Asphalt in THF
MacMillan AC-20, Dickens Test Site
500 Å and 50 Å Columns/THF/100 μl/7%

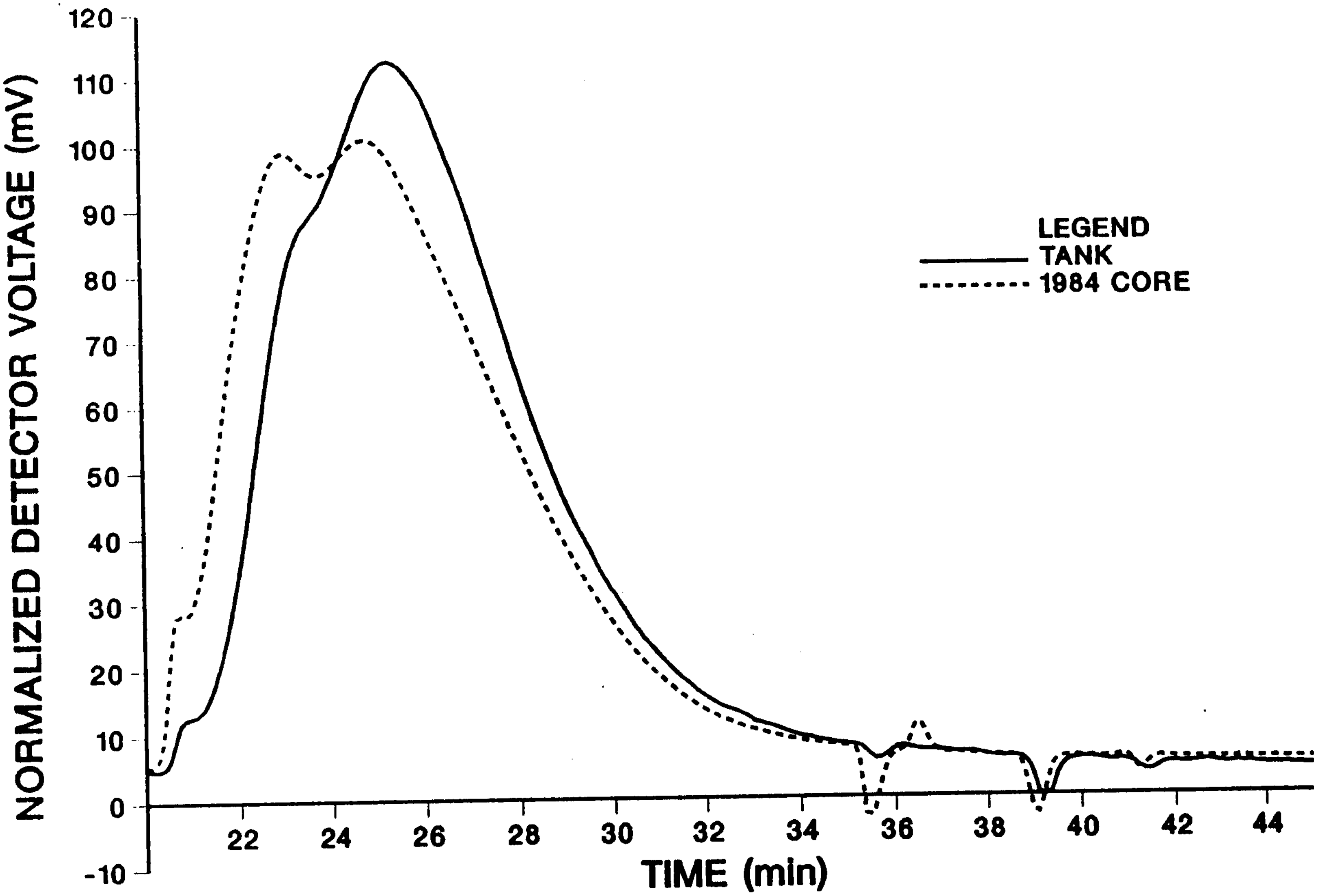

Figure A-6
Comparison of Core Samples to the Original Asphalt in THF
Diamond Shamrock AC-10, Dickens Test Site
500 Å and 50 Å Columns/THF/100 μl/7%

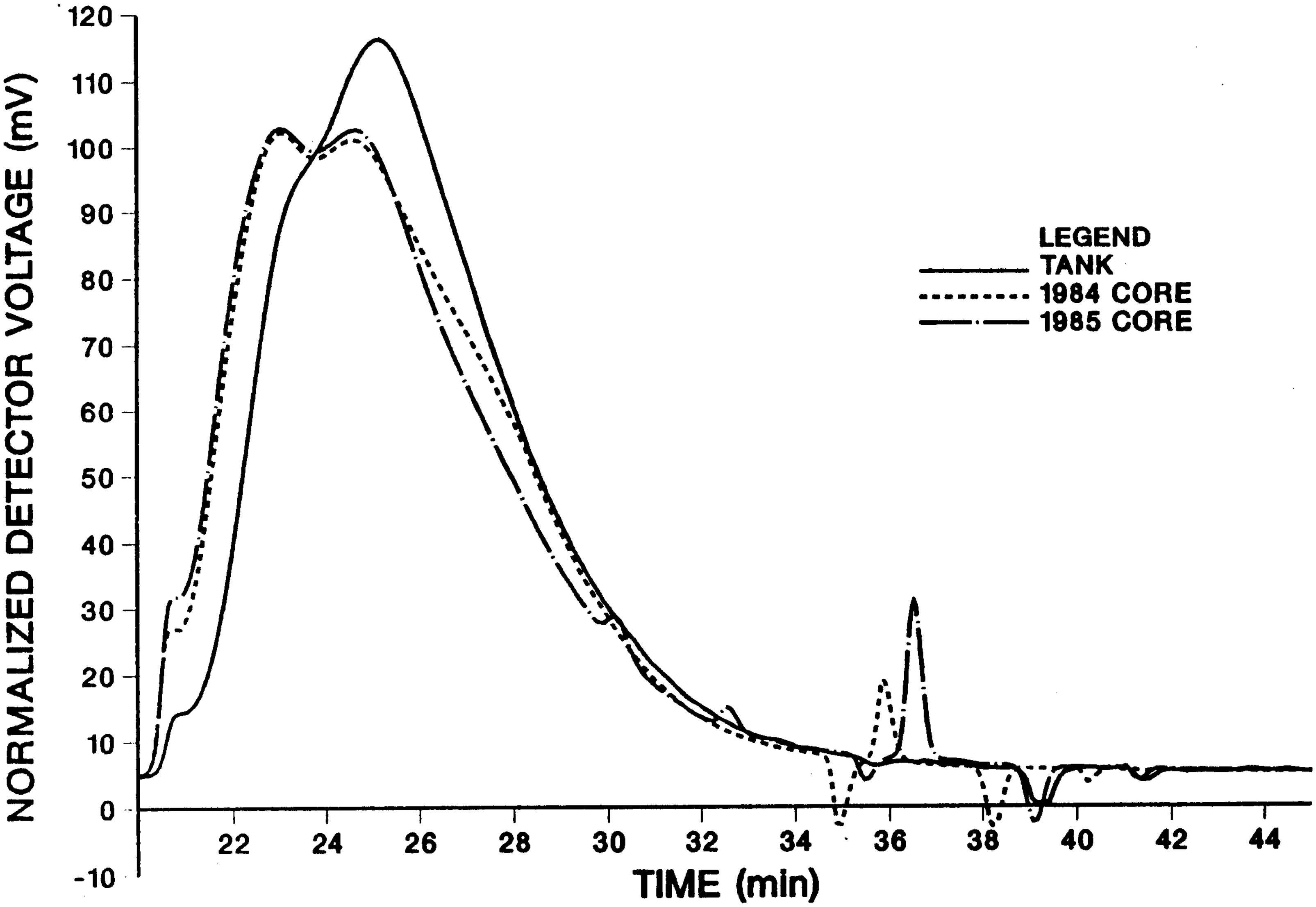

Figure A-7
Comparison of Core Samples to the Original Asphalt in THF
Diamond Shamrock AC-20, Dickens Test Site
500 Å and 50 Å Columns/THF/100 μl/7%

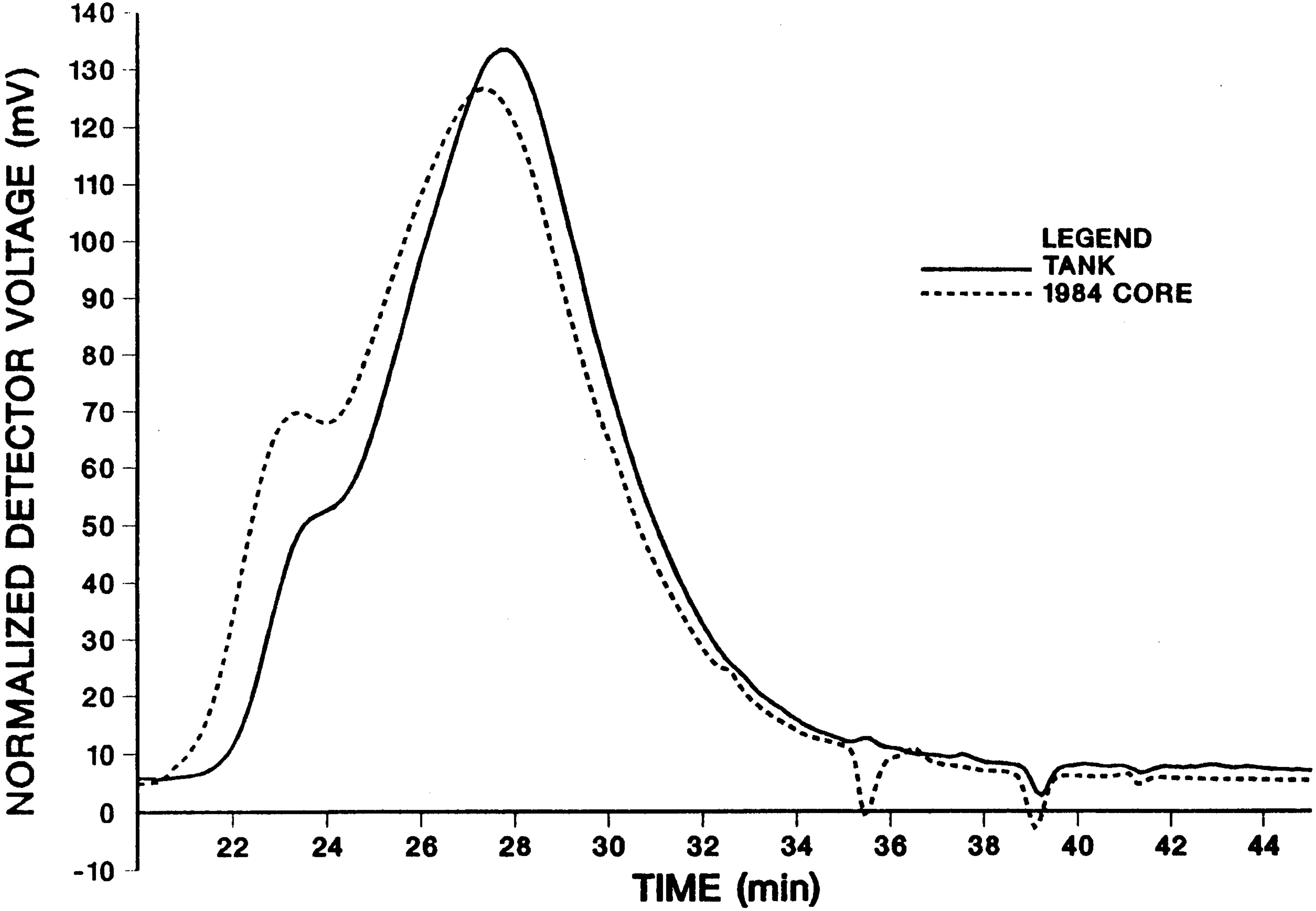

Figure A-8
Comparison of Core Samples to the Original Asphalt in THF
Cosden AC-20, Lufkin Test Site
500 Å and 50 Å Columns/THF/100μl/7%

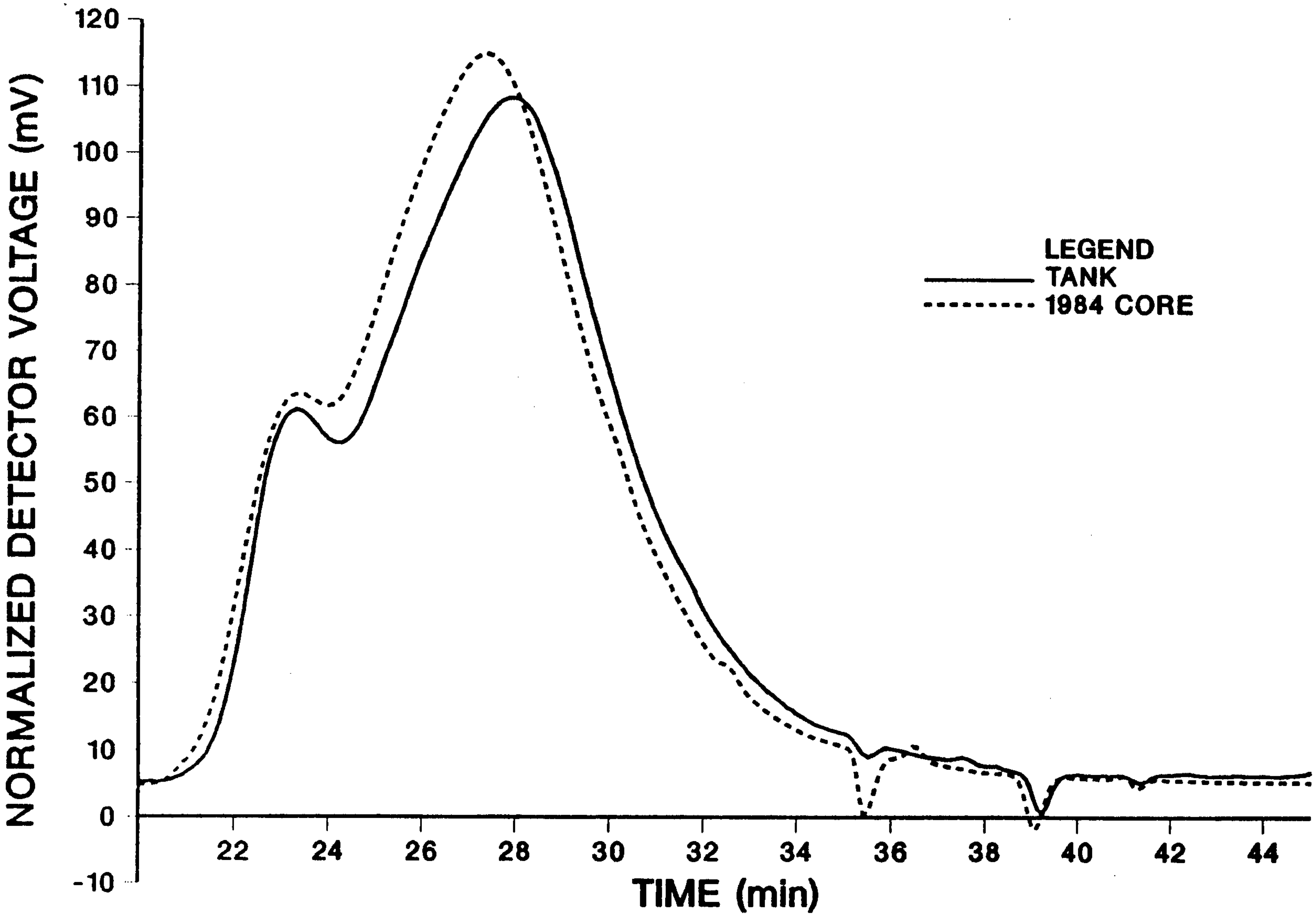

Figure A-9
Comparison of Core Samples to the Original Asphalt in THF
Dorchester AC-20, Lufkin Test Site
500 Å and 50 Å Columns/THF/100 μl/7%

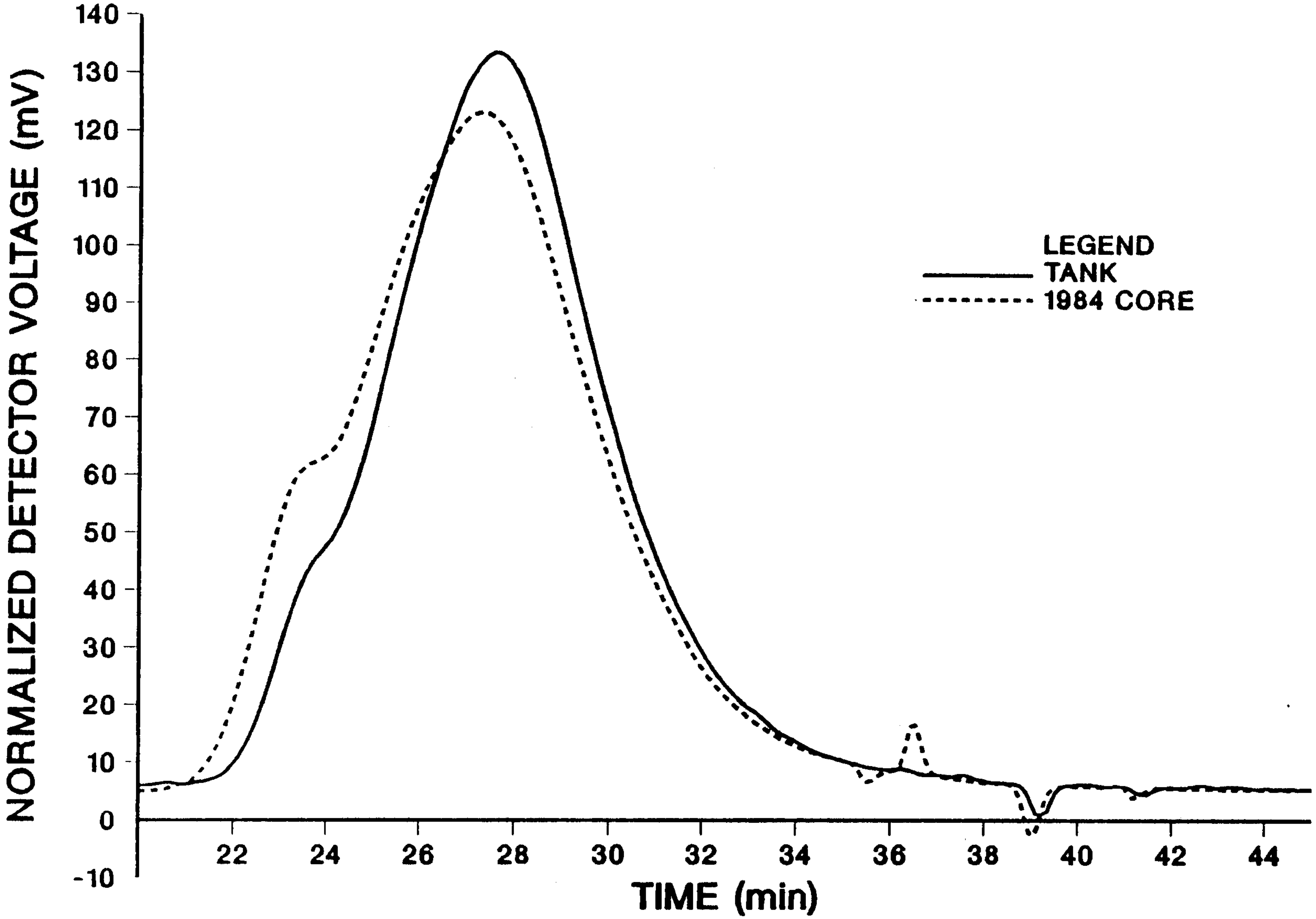

Figure A-10
Comparison of Core Samples to the Original Asphalt in THF
Exxon AC-20, Lufkin Test Site
500 Å and 50 Å Columns/THF/100 μl/7%

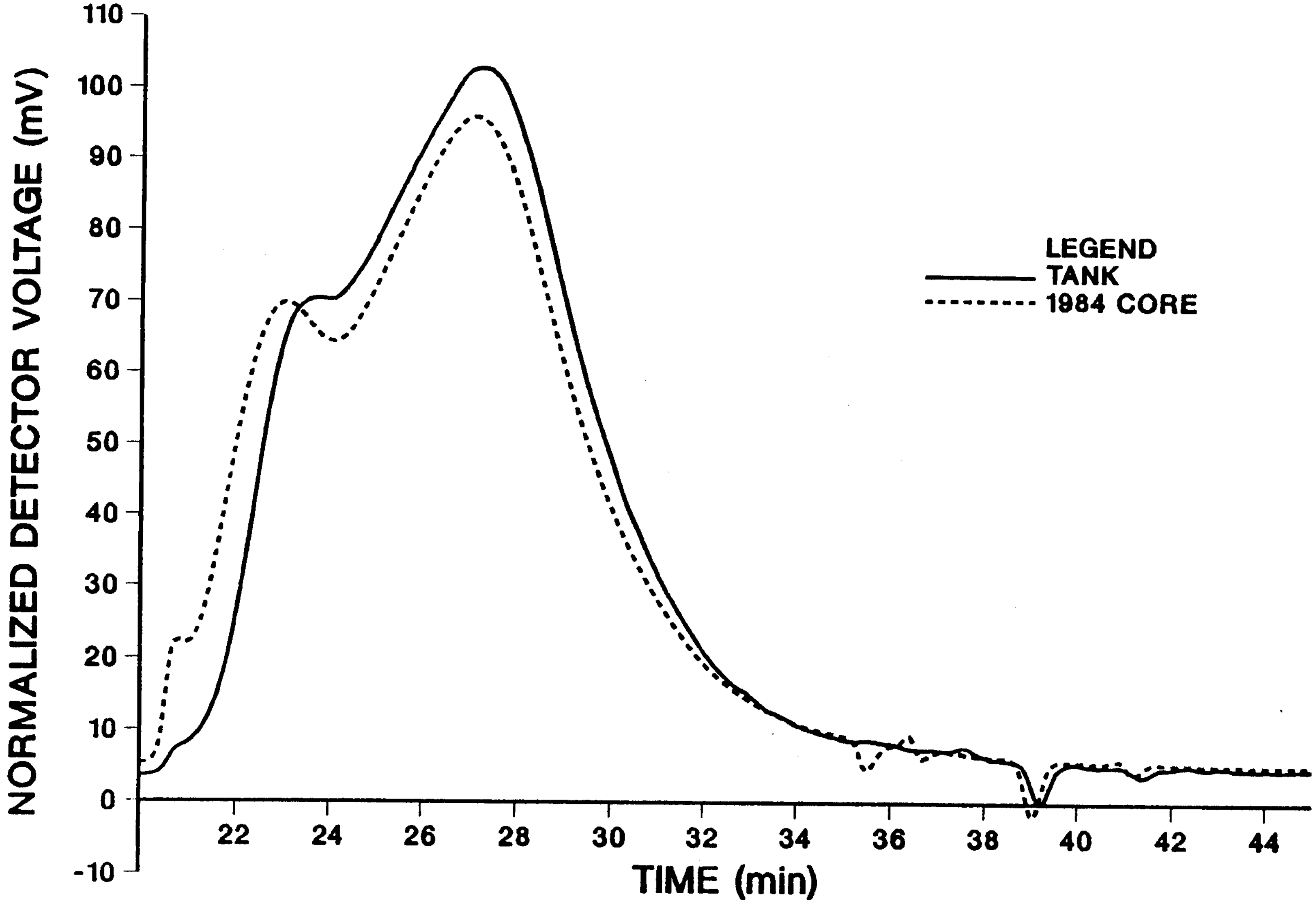

Figure A-11
Comparison of Core Samples to the Original Asphalt in THF
MacMillan AC-10, Lufkin Test Site
500 Å and 50 Å Columns/THF/100μl/7%

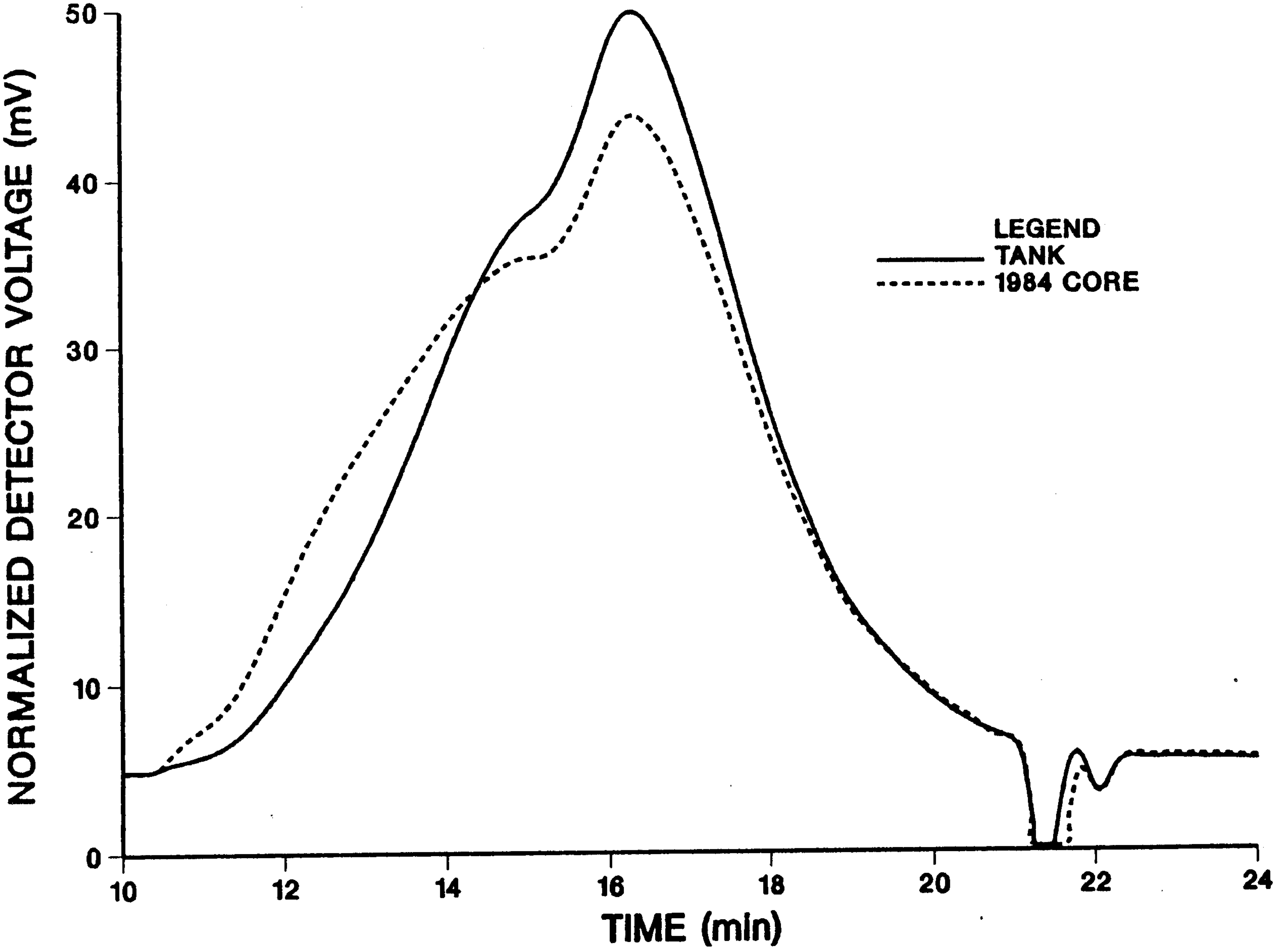

Figure A-12
Comparison of Core Samples to the Original Asphalt in Toluene
Cosden AC-10, Dickens Test Site
500 Å Column/Toluene/100 μl/7%

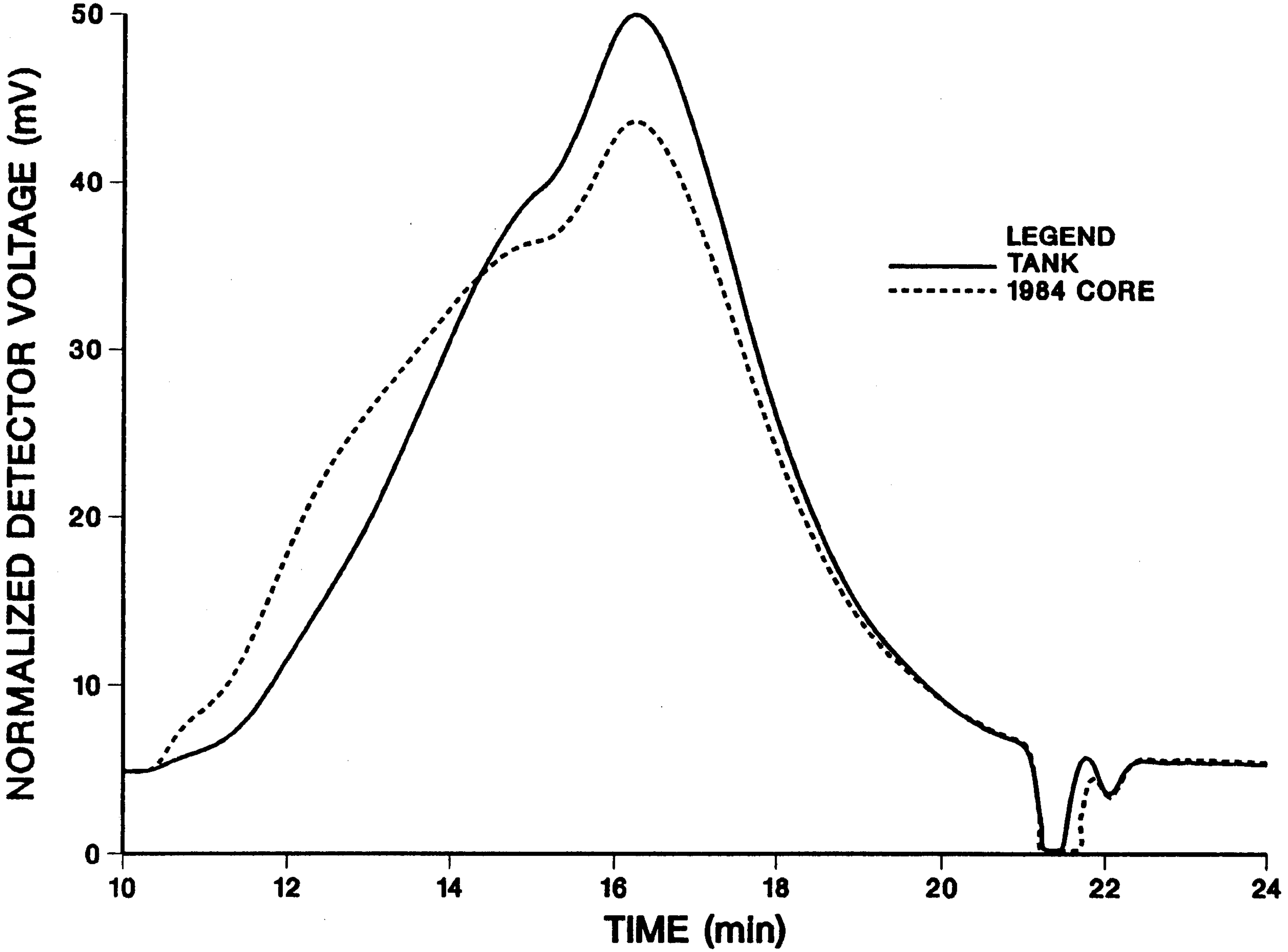

Figure A-13
Comparison of Core Samples to the Original Asphalt in Toluene
Cosden AC-20, Dickens Test Site
500 Å Column/Toluene/100 μl/7%

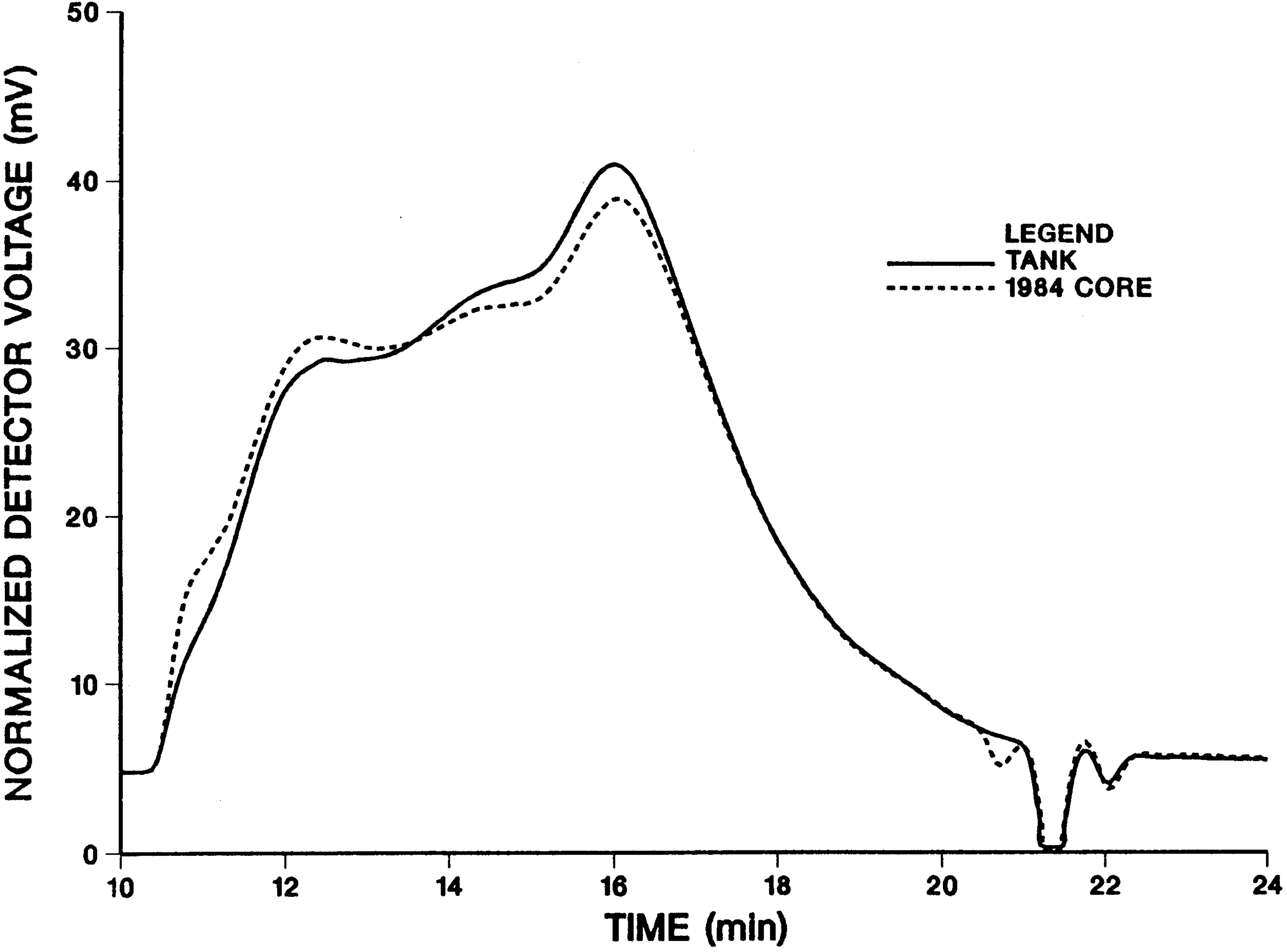

Figure A-14
Comparison of Core Samples to the Original Asphalt in Toluene
Dorchester AC-20, Dickens Test Site
500 Å Column/Toluene/100 μl/7%

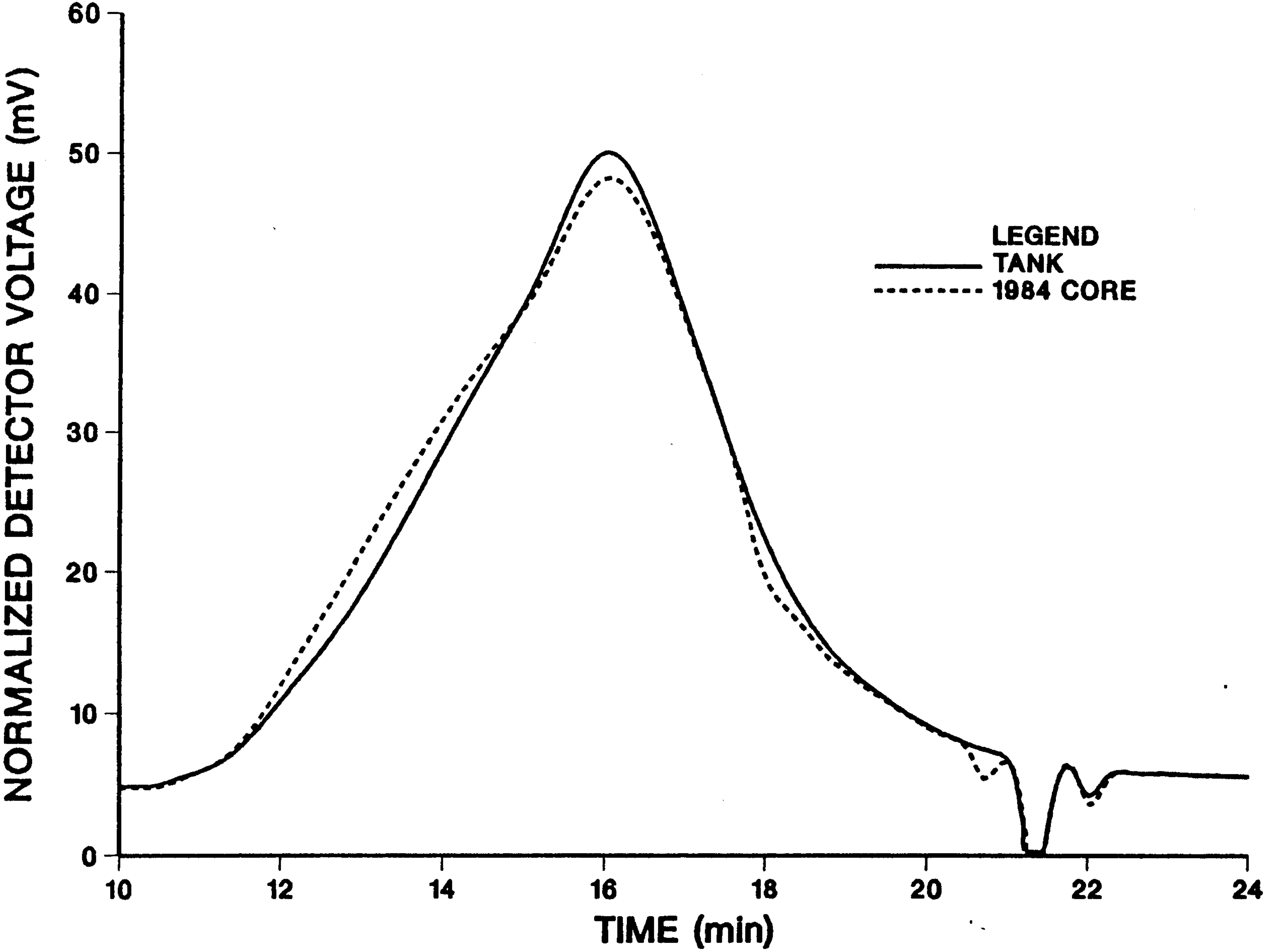

Figure A-15
Comparison of Core Samples to the Original Asphalt in Toluene
Exxon AC-20, Dickens Test Site
500 Å Column/Toluene/100 μl/7%

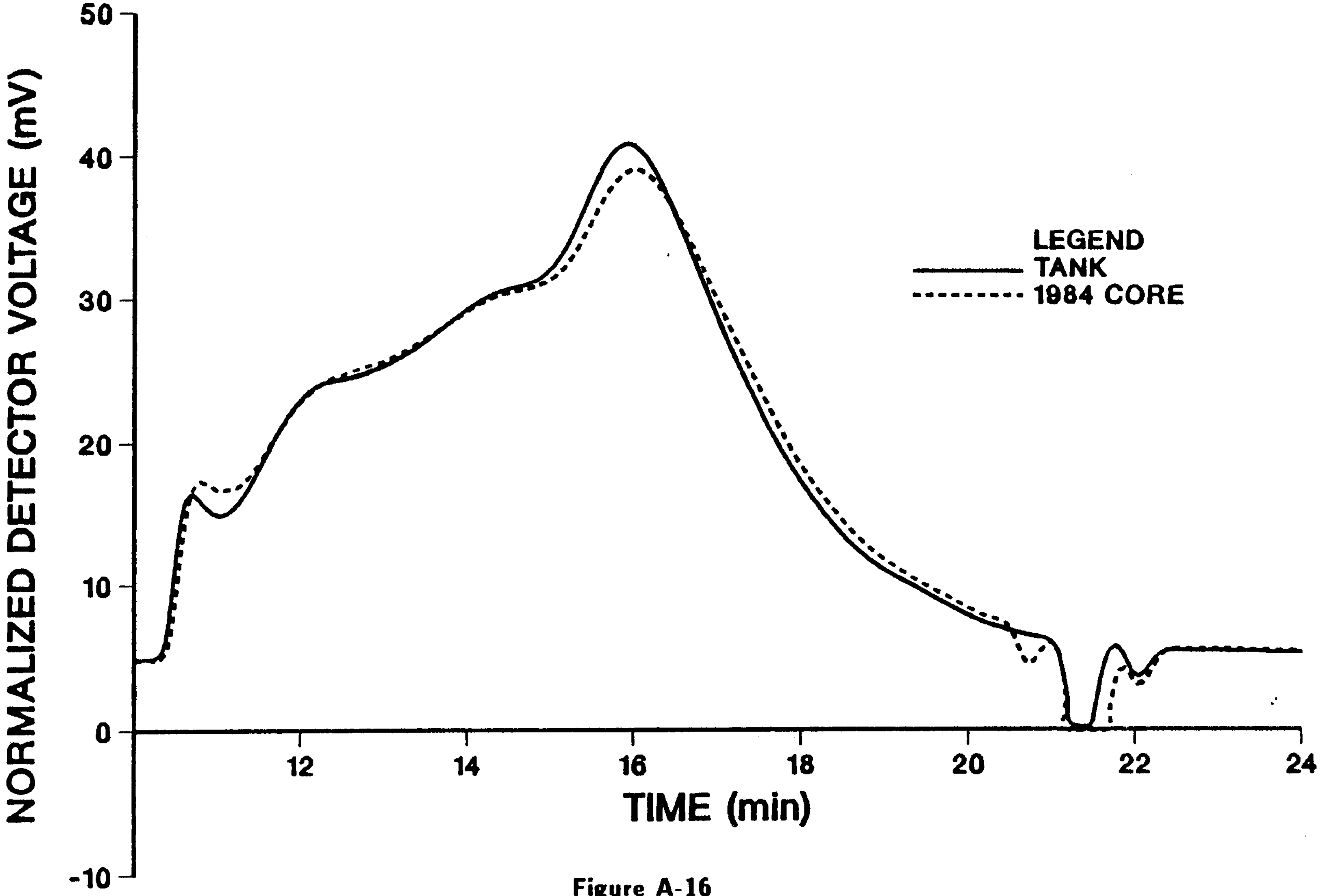

Figure A-16
Comparison of Core Samples to the Original Asphalt in Toluene
MacMillan AC-10, Dickens Test Site
500 Å Column/Toluene/100 μl/7%

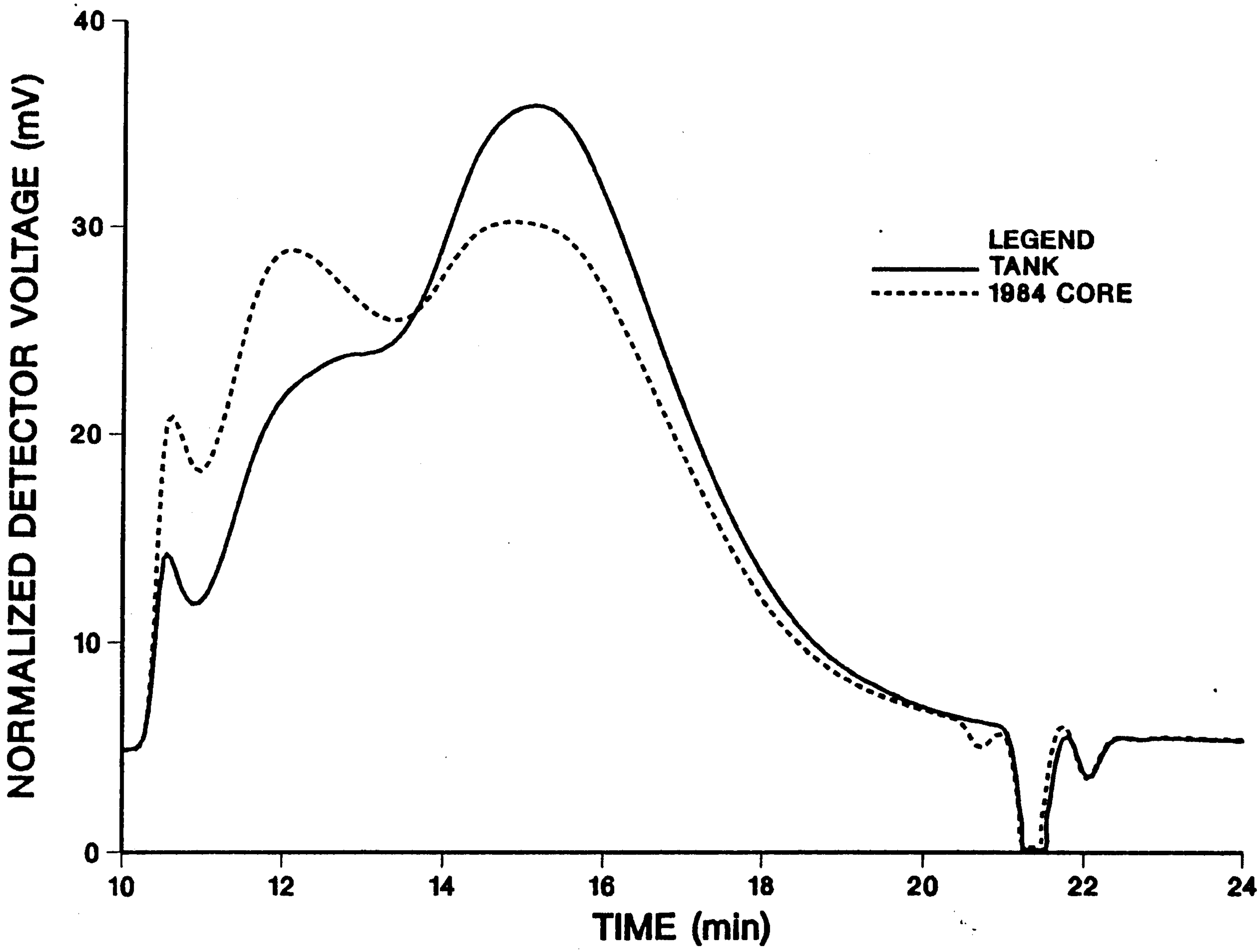

Figure A-17
Comparison of Core Samples to the Original Asphalt in Toluene
Diamond Shamrock AC-10, Dickens Test Site
500 Å Column/Toluene/100 μl/7%

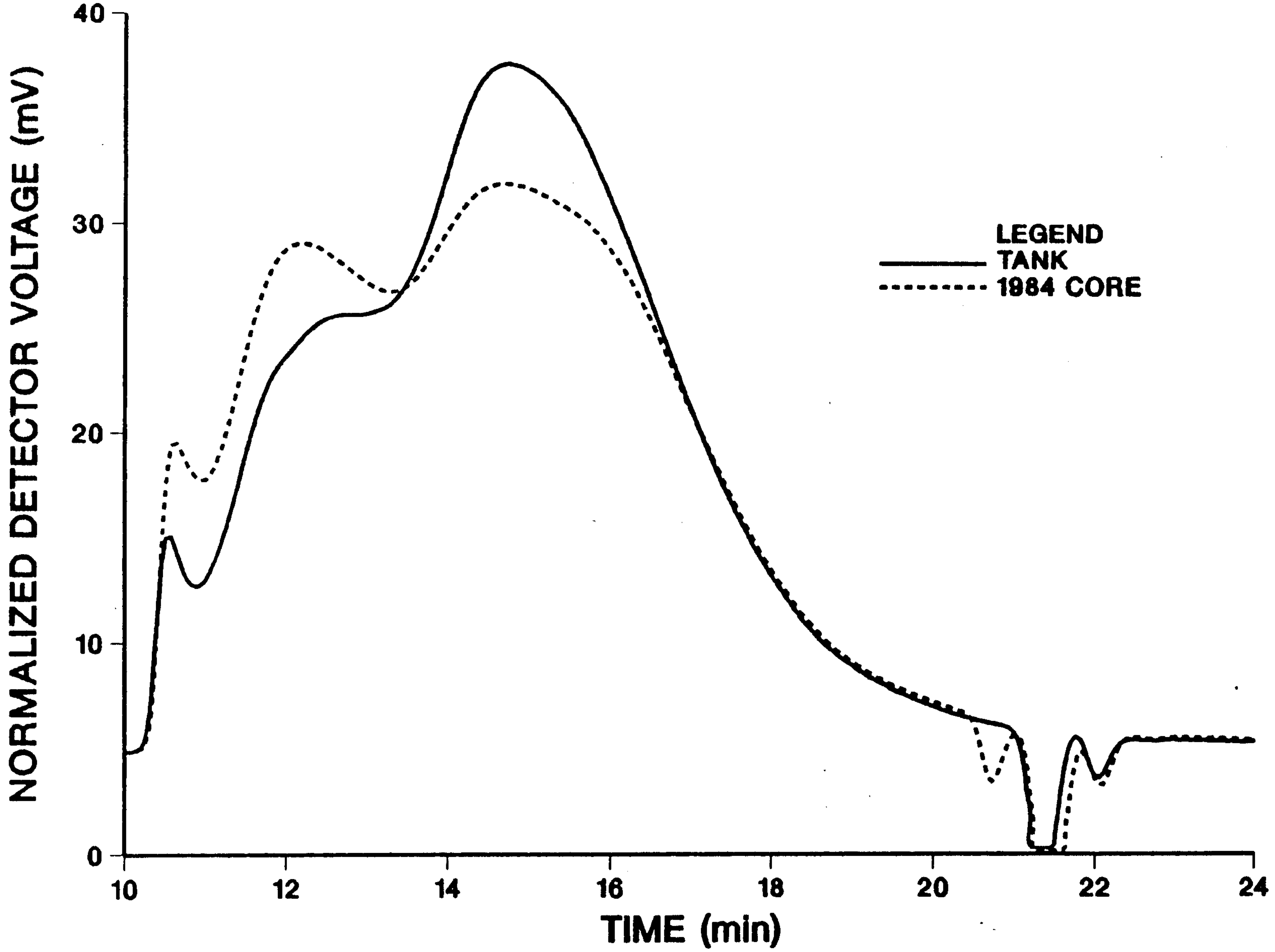

Figure A-18
Comparison of Core Samples to the Original Asphalt in Toluene
Diamond Shamrock AC-20, Dickens Test Site
500 Å Column/Toluene/100 μl/7%

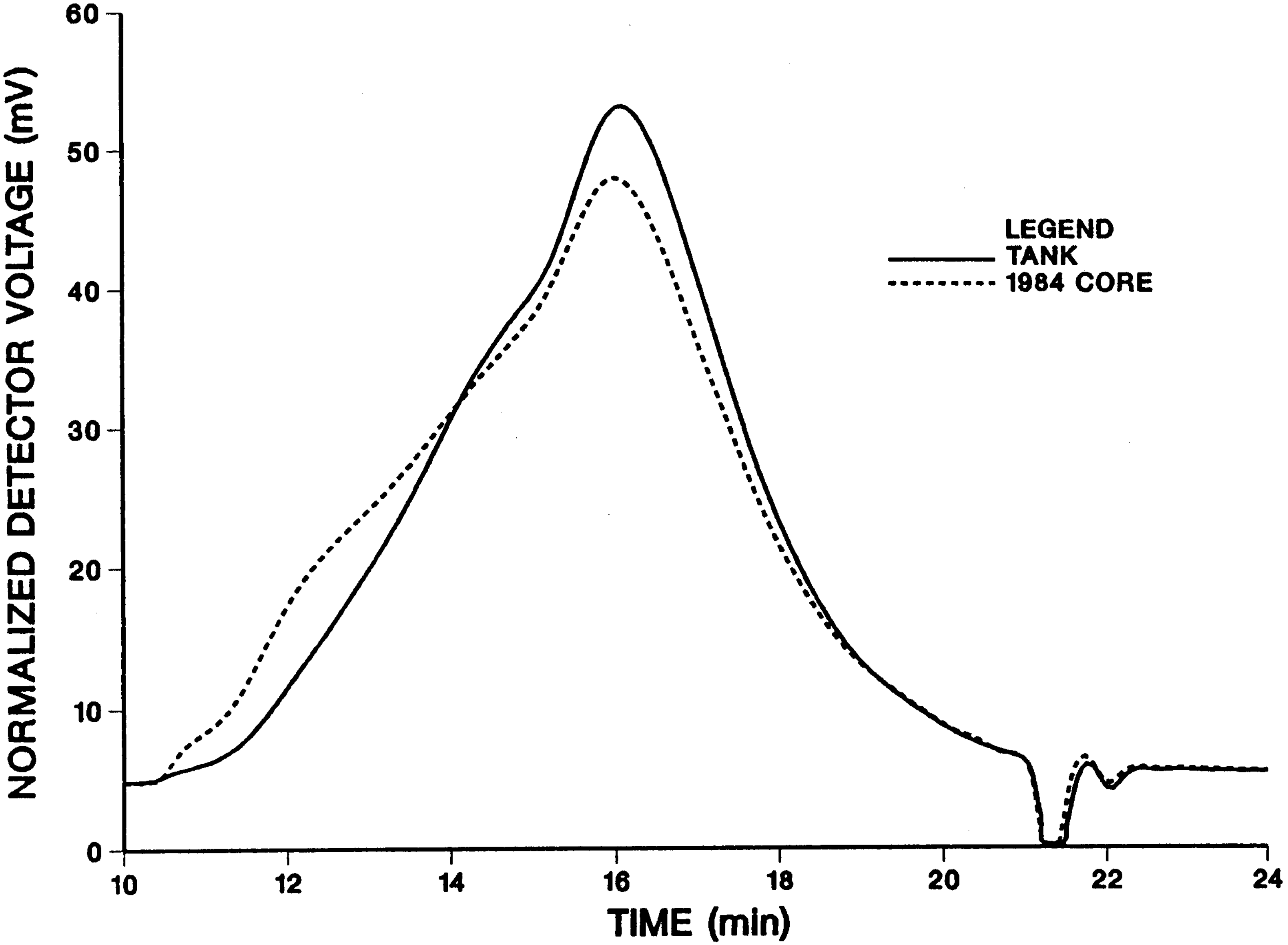

Figure A-19
Comparison of Core Samples to the Original Asphalt in Toluene
Cosden AC-20, Lufkin Test Site
500 Å Column/Toluene/100 µl/7%

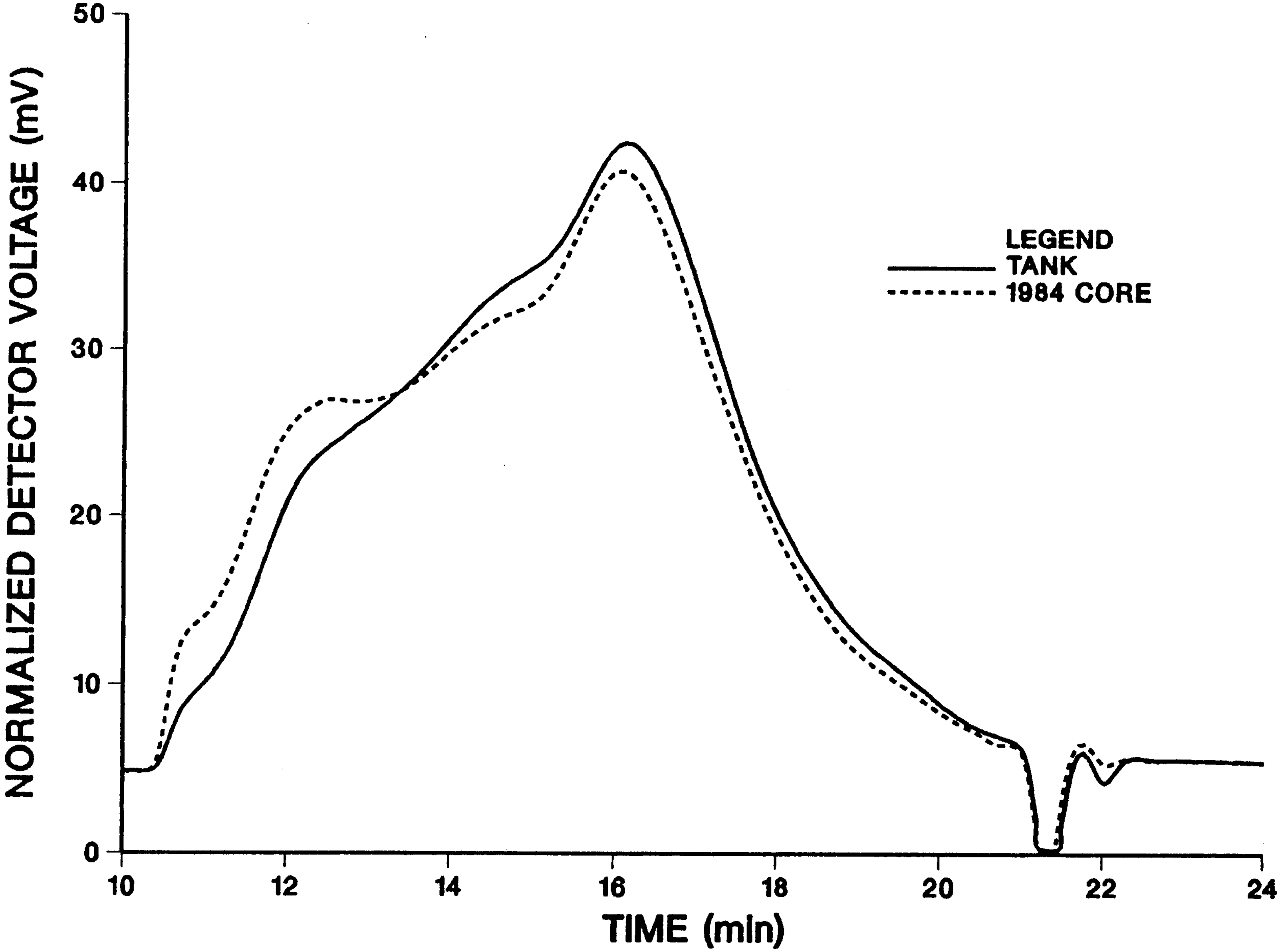

Figure A-20
Comparison of Core Samples to the Original Asphalt in Toluene
Dorchester AC-20, Lufkin Test Site
500 Å Column/Toluene/100 μl/7%

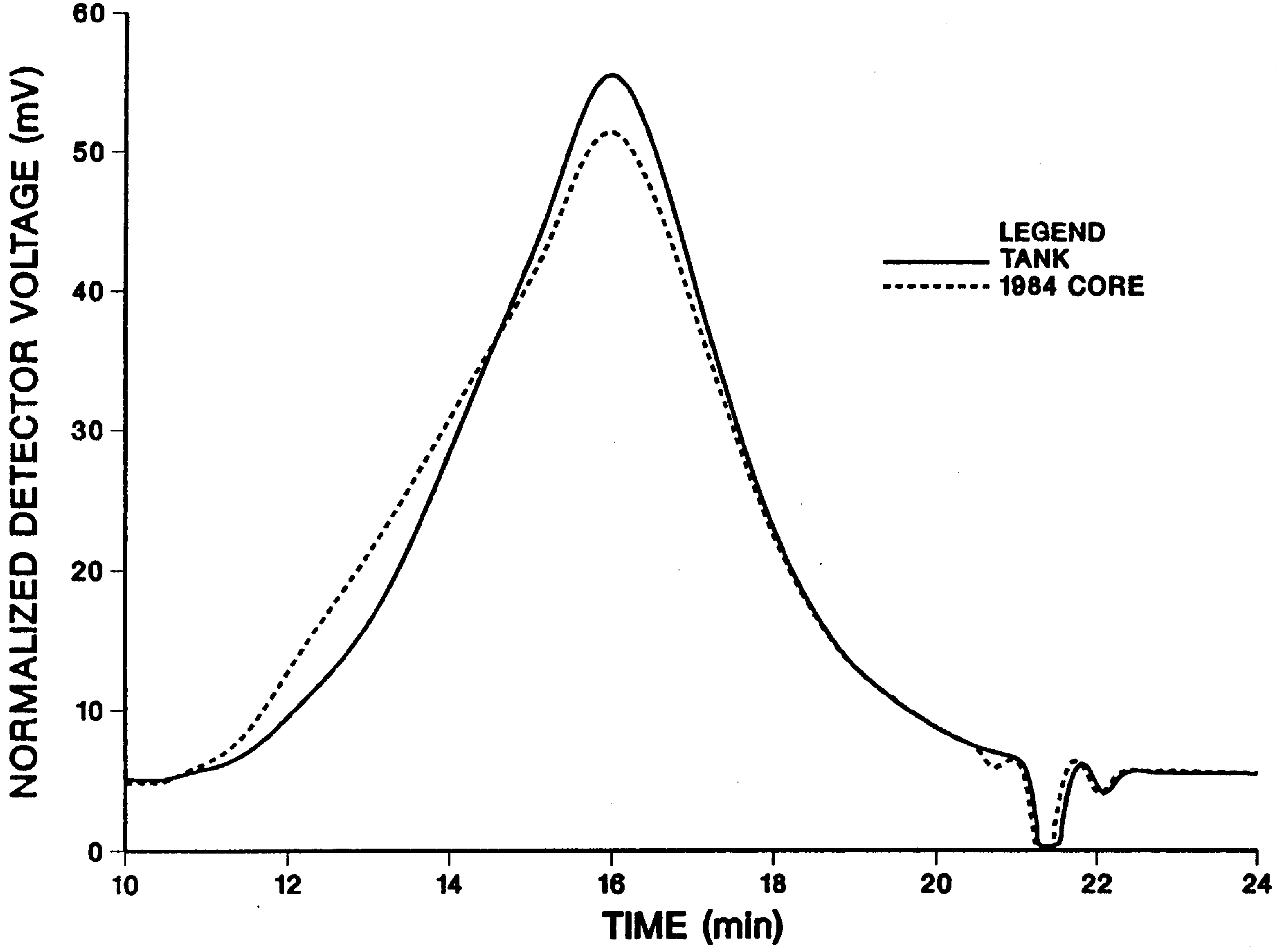

Figure A-21
Comparison of Core Samples to the Original Asphalt in Toluene
Exxon AC-20, Lufkin Test Site
500 Å Column/Toluene/100 μl/7%

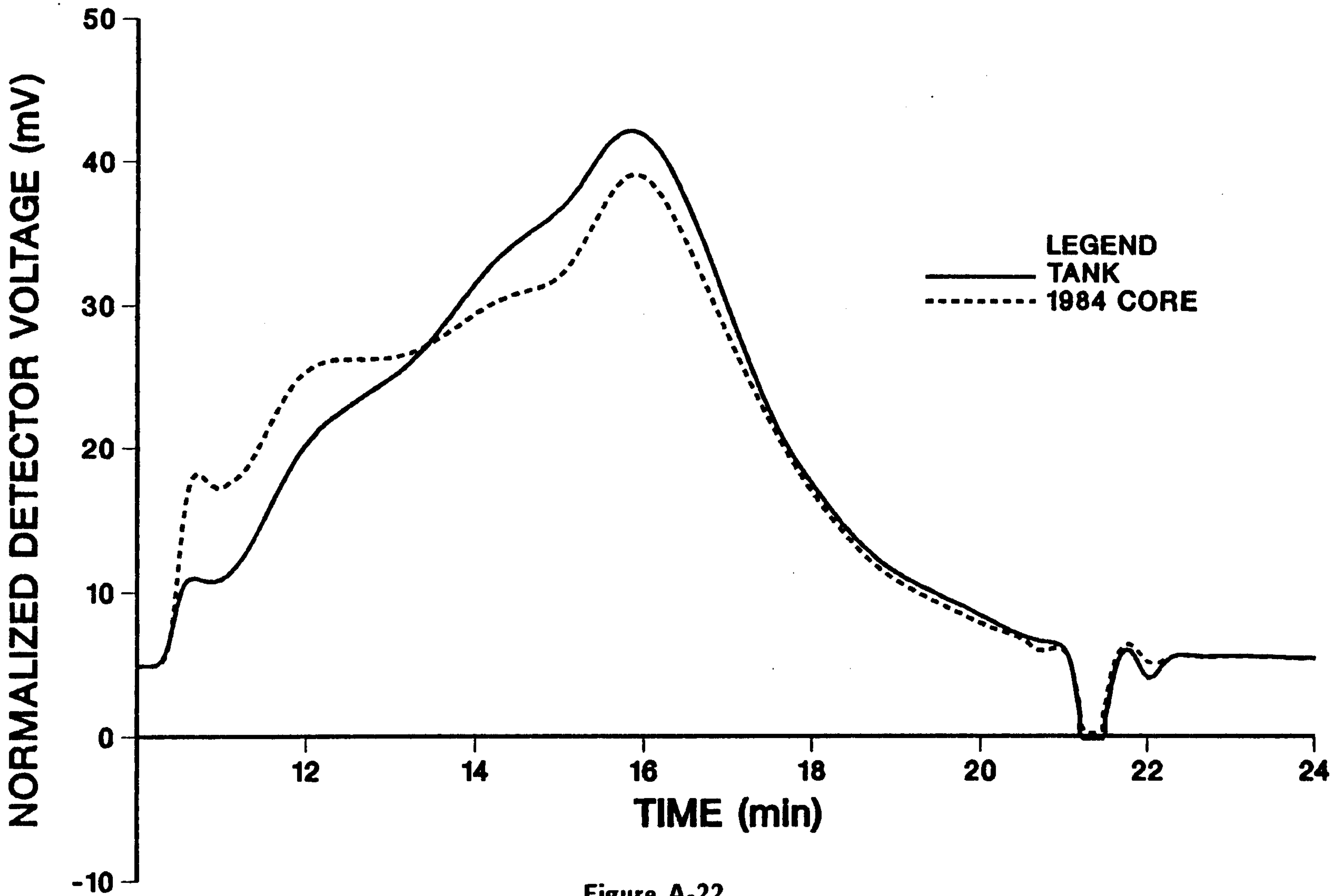

Figure A-22
Comparison of Core Samples to the Original Asphalt in Toluene
MacMillan AC-20, Lufkin Test Site
500 Å Column/Toluene/100 μl/7%