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July 1993

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Gel Permeation Chromatography Analysis of Asphalt-Based Joint Sealants

by Rogers T. Graham, Larry N. Lynch
Geotechnical Laboratory

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by Rogers T. Graham, Larry N. Lynch
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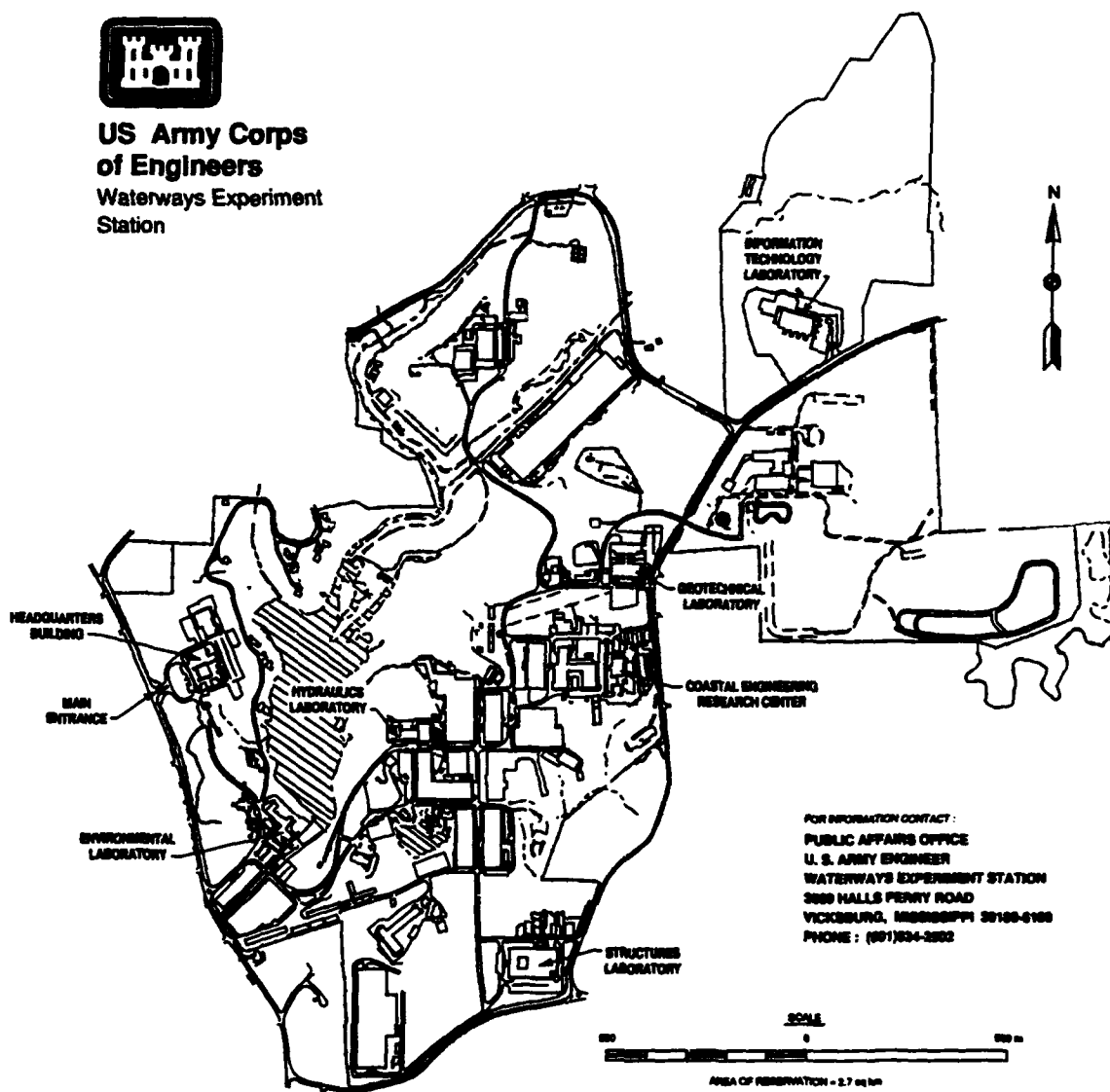
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Conversion Factors, Non-SI to SI Units of Measurement

Non-SI units of measurement used in this report can be converted to SI units as follows:

Multiply	By	To Obtain
degrees (angle)	0.01745329	radians
Fahrenheit degrees	5/9	Celsius degrees or kelvins ¹
feet	0.3048	meters
inches	2.54	centimeters
ounces (mass)	28.34952	grams
pounds (force)	4.448222	newtons
pounds (force) per square inch	6.894757	kilopascals

¹ To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use the following formula: $C = (5/9)(F - 32)$. To obtain kelvin (K) readings, use: $K = (5/9)(F - 32) + 273.15$.

Preface

This investigation was conducted by the Geotechnical Laboratory (GL), U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, MS, for the Federal Aviation Administration (FAA), and the Air Force Engineering Support Agency during the period April through December 1991.

The study was conducted under the general supervision of Dr. William F. Marcuson III, Director, GL, Mr. Harry H. Ulery, Jr., former Chief, Pavement Systems Division (PSD), and Dr. George M. Hammitt, Chief, PSD. This report was written by Messrs. Rogers T. Graham and Larry N. Lynch under the direct supervision of Mr. Timothy W. Vollor, Chief, Materials Research and Construction Technology Branch, PSD. PSD personnel, in addition to the authors, engaged in the sampling, testing, analyzing, and evaluation of this project included Mr. Herbert McKnight and CPT Laurand Lewandowski.

The Director of WES during this project was Dr. Robert W. Whalin. The Commander was COL Leonard G. Hassell, EN.

1 Introduction

Background

The field performance of most field molded pavement joint sealant materials (those sealants that are liquid at the time of installation and mold to the shape of the joint reservoir) has been less than desirable and is becoming an ever increasing focus of the pavement engineer. The increased focus has been generated by two factors. First, joint sealant materials can extend the life of a pavement by protecting the pavement structure. Secondly, fiscal problems at the local city and state level as well as the federal level have greatly reduced the amount of funds available to the pavement engineer for infrastructure maintenance. Therefore, maintenance funds that are expended have to provide a high-quality, long-term solution to the problem being solved, whether it is patching potholes or sealing joints and cracks.

Pavement joint sealant materials are designed to perform two basic functions; prevent the retention of incompressible debris in the joint and prevent or minimize the infiltration of water through the joint into moisture susceptible base and subbase materials. There are other functions such as fuel resistance that are designed into some sealants, but all sealants must perform the two basic functions to provide satisfactory field performance. If a sealant does not prevent the retention of incompressible debris, the thermal stress relief provided to the pavement through the joint will be negated often causing the joint edges to spall. Water infiltration through the joint can cause a weakening of the pavement structure by softening a moisture susceptible base or subbase material and creating voids under the pavement. Pumping of pavement slabs is a typical example of a weakened pavement structure that could be caused by water infiltration.

Field surveys conducted by the U.S. Army Engineers Waterways Experiment Station (WES) (Lynch 1989) and the Naval Civil Engineering Laboratory (NCEL) (Inaba, Hironaka, and Novison 1988) indicate that portland cement concrete (PCC) pavement joint sealant materials are generally performing their designed function for approximately 1 to 2 years. Some user agencies are reporting joint sealant failures within 6 months after application. This is a considerable difference from verbal claims of some manufacturers which state their material will perform satisfactorily for 10 to 15 years when "properly installed." One manufacturer offered to substantiate the performance claims of their material by offering a 5 to 10 year warranty

(Gaus 1984) but this offer has not gained wide acceptance in the sealant industry.

The suspected reason for the discrepancy between the verbal performance claims, the proposed warranty period, and the actual field performance experienced in the field will vary depending upon the party providing the explanation. From the manufacturer's viewpoint, the natural explanation of poor joint sealant field performance is poor workmanship or poorly written project specifications. The user agency will cite the reason for failure as poor workmanship or poor quality material and the contractor will cite inferior materials or flawed project specifications.

The actual cause of poor field performance could be any one or all of the above mentioned explanations, but whatever the reason, the premature sealant failure affects the bottom line of the user agency. For example, it is estimated that the U.S. Department of the Navy spends \$12 million annually resealing joints in PCC pavements (Inaba, Hironaka, and Novison 1988). Expenditures for the U.S. Departments of the Army and Air Force are not as easy to estimate because joint resealing projects are often included in maintenance contracts or performed by in-house crews; however, it is expected that similar funding would be required by both agencies. Therefore, it is estimated that \$36 million is being spent annually by the Department of Defense (DOD) to reseal PCC pavements with joint sealant materials whose life cycles are less than half of that claimed by the manufacturers. If a method could be found to double the actual field performance of pavement joint sealants, the DOD could save an estimated \$18 million annually.

To examine the potential benefits of increased joint sealant field performance in the civilian sector instead of focusing on the narrower DOD use of sealants, it is necessary to determine the quantity of sealant materials used on an annual basis. Joint sealant manufacturers estimate that the total United States market for field-molded pavement joint sealant materials is 100,000,000 to 125,000,000 pounds per year. If one assumes a joint reservoir size of 3/4 in. wide by 3/4 in. deep, the total linear feet of joints sealed each year would be 356,000,000 to 445,000,000. The actual cost savings to the user agencies is difficult to estimate because the material cost for joint sealant materials range from 40 to 60 cents per pound for hot-applied joint sealants up to \$3.20 per pound for some cold-applied sealants. Regardless of the actual material cost, the potential savings to user agencies could be astronomical.

To improve the field performance of pavement joint sealants, the three suspected causes of poor field performance should be investigated. Workmanship could be improved by implementing quality control and quality assurance measures. Educating contractor personnel and user agency inspectors on proper joint preparation and sealant application techniques and why these procedures are important would be one method of accomplishing this goal. Comparing project specifications with recently updated U.S. Army Corps of Engineers guide specifications, technical manuals, and manufacturer's literature could reduce the defects contained within project specifications, and testing the sealant material to the appropriate material specification will

minimize the use of inferior materials (assuming material specification conformance implies a superior material). However, there are joint sealing projects in which all three areas of concern were reported to be correct, but the field performance of the sealant was still unsatisfactory.

The forensic analysis of these perfect projects indicates that problem areas exist in determining the exact cause of sealant failure. The largest deficiency is the fact that satisfactory field tests are not available to determine if the physical properties evaluated in the laboratory are being obtained in the field.

Field tests which are currently available include a coin test, twist test, and peel test. These tests are used to indicate a sealant's resilience and/or adhesion to the joint face. The coin test is conducted by pressing a coin, usually a quarter, into the sealant material to a depth of approximately 1/4 in. The coin is then released to allow the sealant to rebound. If the sealant rebounds to its original shape and the coin is completely pushed out of the sealant, the sealant is considered to have satisfactory resilience. The twist test is conducted by pressing a flat piece of metal (generally 1/2 in. wide by 1/8 in. thick by 12 in. long) into the sealant material to a depth of approximately 1/4 in. and twisting it 90 deg or until it touches the joint face. If the sealant does not crack or pull loose from the joint face, it is considered to be in satisfactory condition. The peel test is conducted by cutting loose a 6-in. piece of the in-place sealant material. Two marks are placed 2 in. apart on the sealant and the loose end of the sealant is stretched to a specified elongation. This test has been modified by some user agencies to include a scale. The scale is attached to the loose end of the sealant so that the force required to stretch the sealant to the specified elongation can be measured.

The limited field tests that do exist are highly dependent upon the operator conducting the test, the environmental conditions during the test, and the shape factor used during the installation of the sealant being tested. Because of these factors, the tests are not reproducible and cannot necessarily distinguish between properly and improperly applied sealants. The only method currently available to determine if a sealant has been properly prepared and installed is for the user agency to require 100 percent inspection during the project. Due to manpower shortages and lack of funding, this type of inspection is difficult if not impossible to obtain. It would therefore be advantageous to develop or modify a test procedure that could identify improperly prepared and/or applied joint sealant materials.

One method that has been used to identify different types of asphalt cements and provide an indication of the physical properties of the asphalt cement is gel permeation chromatography (GPC). In this method, the asphalt cement is dissolved in a solvent and is injected into the GPC. The injected sample travels through a series of columns which separates the sample based on molecular size. The larger molecular size particles exit the columns first and are detected by the system's detectors. The smaller molecular size particles travel into the pores of the columns and, therefore, have longer retention times. A molecular size distribution (which can be thought of as analogous to a type of sieve analysis of the sample) is obtained. One study (Price 1988)

indicates that asphalt cements which have a higher concentration of large molecular size particles are more brittle than asphalts which contain high concentrations of small molecular size particles.

It is expected that similar trends may be found in joint sealant materials and that the change can be detected by the GPC, especially for hot-applied joint sealant materials. As the sealant is heated before application, volatiles (small molecular size particles) will be driven off. If the sealant is over-heated or exposed to prolonged heating, a greater amount of the volatiles will be driven off causing the sealant to become brittle.

Objective

The objective of this research was to determine if a laboratory test method could be used to identify joint sealant materials that have been improperly prepared and to predict how the improper preparation will affect the physical properties of the sealant.

Scope

The scope of this research included a literature review, a three-phase laboratory study, and analysis of the laboratory data. Phase I of the laboratory study consisted of testing two different joint sealant materials in accordance with Federal Specification SS-S-1401C (Federal Specification SS-S-1401C 1984).

Phase II of the laboratory study was a modification of Phase I. In Phase II the heating times of the hot-applied sealants were changed to simulate different exposures to application temperatures. Test criteria outlined in the federal specification were then conducted to determine the physical property changes caused by the preparation conditions.

Additional tests were conducted on each sealant in both the Phase I and Phase II portions of the laboratory study. The additional tests consisted of penetration and resilience tests on artificially aged specimens. The penetration and resilience tests were conducted in accordance with Federal Specification SS-S-1401C except the specimens were conditioned in the weather-o-meter for 160 hr as specified by Federal Specification SS-S-200E, Amendment 1 (Federal Specification SS-S-200E 1988).

Phase III of the laboratory study was the GPC analysis of each of the conditioned sealant materials. Samples of the as-received sealants were also analyzed using the GPC to establish a base line fingerprint of each sealant. The fingerprint was then compared to the chromatograms obtained from the

conditioned sealants to determine if a significant change had occurred.
Replicates of each GPC sample were conducted to verify reproducibility.

2 Review of Literature

History

The literature review did not reveal any published information concerning GPC or size exclusion chromatography (SEC) analysis of pavement joint sealant materials. However, there had been considerable work concerning polymeric materials, asphalt cements, coal tar derivatives, adhesives, and nonpavement sealants using GPC.

The major rationales for GPC analysis of pavement joint sealants are basically the same as those that precipitated the invention of the GPC. The rationales are to discover sources of product deficiencies in samples that have been returned by customers, determine the source of deficiencies that occur during production which cause faulty batches to be produced, check raw materials and finished products for routine quality control, and evaluate competitor products for comparison purposes (Habash and Hutchinson 1985).

The work that has been conducted using the GPC to analyze asphalt cements is important when considering the analysis of hot-applied joint sealants because a large number of these sealants are asphalt based. Therefore, if conclusions can be drawn about the performance of the asphalt cements, conclusions should be obtainable between the sealants manufactured from those products and their performance.

GPC was developed in 1963 (Garrick and Wood 1988) as a method for determining the molecular weight distribution of polymer materials. Since its inception, GPC has gained acceptance by many industries as a quality control tool. The wide acceptance of GPC has occurred because it can provide a fingerprint of polymer materials, distinguishing important changes in the chemical composition and characterizing individual constituents which contribute to the polymer's overall performance (Prince, Woodzell, and Kuge 1983). Also, GPC is relatively quick and easy to perform.

Chemical changes which can be detected by GPC would include those caused by an impurity or those caused by aging of the polymer. For example, the chromatogram obtained by conducting a GPC analysis of urethanes that had undergone aging exhibited an increase in the low molecular weight fraction and a decrease in the high molecular weight fraction as compared to the

chromatograms of urethanes that had not been aged. The shift in quantity or concentration of the high molecular weight fraction indicated that the urethane polymer chain was undergoing scission or breaking down during the aging process. Chromatograms obtained from epoxy systems indicated an increase in the high molecular weight fraction and a decrease in the low molecular weight fraction upon aging (Prince, Woodzell, and Kuge 1983).

The ability of the GPC to characterize chemical constituents of a polymer, and, therefore, predict the performance of the polymer and differentiate between aged and nonaged materials led researchers to adapt the technique for macromolecules. In 1965 Algelt added heavy petroleum fractions to the list of nonpolymers being analyzed by GPC (Brule 1980). The earliest efforts at characterizing asphalt cements were undertaken in 1916 when Marcuson developed a solvent extraction process for fractionating asphalts (Garrick and Wood 1988). Other types of fractionation methods such as chemical precipitation and thermal diffusion were also tried, and are still used today, but GPC has been given considerable attention. It is believed to be one of the more useful physio-chemical analytical techniques for analyzing asphalt cement (Brule 1980).

In a review of chromatography applications to asphalt pavements conducted in 1986 (Stock 1986), it was concluded that the GPC could be used to differentiate between asphalt cements from different sources, but valid correlations still could not be made between physical properties, pavement performance, and the chromatograms of the asphalt cement. The lack of correlation was attributed to the complexity of the asphalt cement structure, or more simply, trying to use an analytical tool developed for polymers on a nonhomogenous nonpolymer. The apparent insufficient degree of correlation did not deter researchers from investigating GPC techniques for asphalt cement analysis. The efforts continued because the performance of other materials could be predicted by GPC and a method to relate compositional parameters of asphalt cement with actual performance was greatly needed. The relationships are desired for two reasons; the performance of many newly constructed asphalt pavements is much less than their designed performance, and the large quantity of asphalt cement that is used annually results in major economic leverage for any technology that may lead to longer life. For example, France alone uses over 3,000,000 tons of asphalt cement annually (Brule 1980).

One possible explanation of the poor field performance of pavements is a decrease in the quality of the asphalt cement being manufactured. A common but unproven belief among asphalt cement users is that changes in the oil refinery industry which occurred because of the 1973 oil embargo have adversely affected the physical properties of asphalt cements to the detriment of pavement performance. Specific reasons given as evidence by the users include observations that premature pavement cracking and tender mixes appear more prevalent in recent times (Garrick and Wood 1986). It is therefore tempting to assume that changes in physical properties associated with the asphalt cement have also affected the field performance of asphalt-based sealants manufactured to meet the requirements of Federal Specification SS-S-1401C.

Factors that Affect GPC

There are several factors which affect the chromatograms obtained when analyzing asphalt cements, or polymeric materials using GPC. The factors are as follows (Price 1988):

- a. Type of solvent and mobile phase or carrier solvent used.
- b. Mobile phase flow rate.
- c. Sensitivity of the detectors to the compounds being analyzed.
- d. Aggregation and absorption of sample components in the system.
- e. Sample size and concentration.
- f. Ultra-violet (UV) detector wavelength.
- g. Refractive index (RI) detector sensitivity.
- h. Column pore size.
- i. Solution age effects caused by the length of time the sample remains in solution.

GPC parameters used in other studies were reviewed to determine how these factors would affect the analysis of joint sealants.

The methods reviewed (Price 1988; Prince, Woodzell, and Kuge 1983, Brule 1980, Garrick and Wood 1986; Brule, Ramond, and Such 1986) used tetrahydrofuran (THF) as both the mobile phase and the solvent. THF was used in these studies because it provided a higher state of association between the asphalt molecules, and, therefore, should be more representative of the natural state of asphalt cement (Brule, Ramond, and Such 1986). Therefore, THF was selected as the mobile phase for this joint sealant analysis.

The effects of aggregation and absorption of the material components in the system can be eliminated from consideration because in a comparative analysis all areas of the procedure will remain constant.

Normally, a RI detector and/or a UV absorbance detector are used to obtain the molecular size distribution. The UV detector appeared to be more sensitive to the smaller molecular sized particles and the RI detector appeared to be more sensitive to the larger molecular sized particles (Stock 1986). Since asphalt cements have longer elution times, the UV detector was selected for the joint sealant evaluations. By selecting the UV detector, the RI detector sensitivity factor was eliminated.

The number of columns used for the various procedures reviewed ranged from a single column to six columns. The column pore size ranged from 10^6 Å to 100 Å. Brulé, Ramond, and Such (1986) concluded that when several columns were used in series and very dilute solutions were injected into the GPC, the resulting chromatograms did not show significant differences from various asphalt cement production methods. Therefore, it was desirable to use as few columns as possible while still maintaining high resolution.

The single column approach was termed "ultra-fast" GPC method. This procedure was called ultra-fast because the chromatogram was obtained in approximately 10 min or less as compared to approximately 1 hr when three columns were used. By using only one column, it was believed that the qualitative characterization of the complex equilibrium existing within the asphalt cement could be evaluated. The equilibrium in the asphalt cement can be represented as follows (Brulé 1986):



The molecules are the smallest quantity of matter of the asphalt cement. For an asphalt cement the molecule would probably be an aromatic sheet, a small carbon chain, and/or nitrogen compounds. Micelles are a grouping or layering of the aromatic sheets caused by interactions between π electrons of the sheets, and aggregates are formed by the association of several micelles. The quick throughput of the material through a single column does not allow sufficient time for micelles to disassociate nor does it allow time for additional aggregates to form. The disadvantage of this method is that resolution is diminished (Brulé 1986).

The three column technique would increase the resolution of the chromatograms, but it was not known if the asphalt-based sealants would show an aging or increase in the larger molecular weight fraction when left in solution for an extended period of time. Asphalt cement samples that are allowed to remain in solution for an hour or longer tend to exhibit an increase in the larger molecular weight fraction. The time in solution includes the time the sample remains in solution before it is injected into the GPC and the time required for the sample to completely exit the columns. Samples that have remained in solution for various lengths of time must be injected into the GPC to determine the solution effects on each type of material being analyzed. Figure 1 provides an example of chromatograms of a sealant material that has remained in a solution of THF for various lengths of time.

Sample concentration also affects the chromatographic results obtained for a specific material. Figure 2 indicates how the chromatogram of a sealant changes as the sample concentration in mass of sealant to volume of THF is varied. It is believed that an increase in concentration leads to an associated or natural state when analyzing asphalt cements, assuming that the detector is not overloaded (Brulé 1980). Therefore, to provide a laboratory analysis of an asphalt material that is most representative of its natural state; it is desirable to use the highest sample concentration that does not overload the detector.

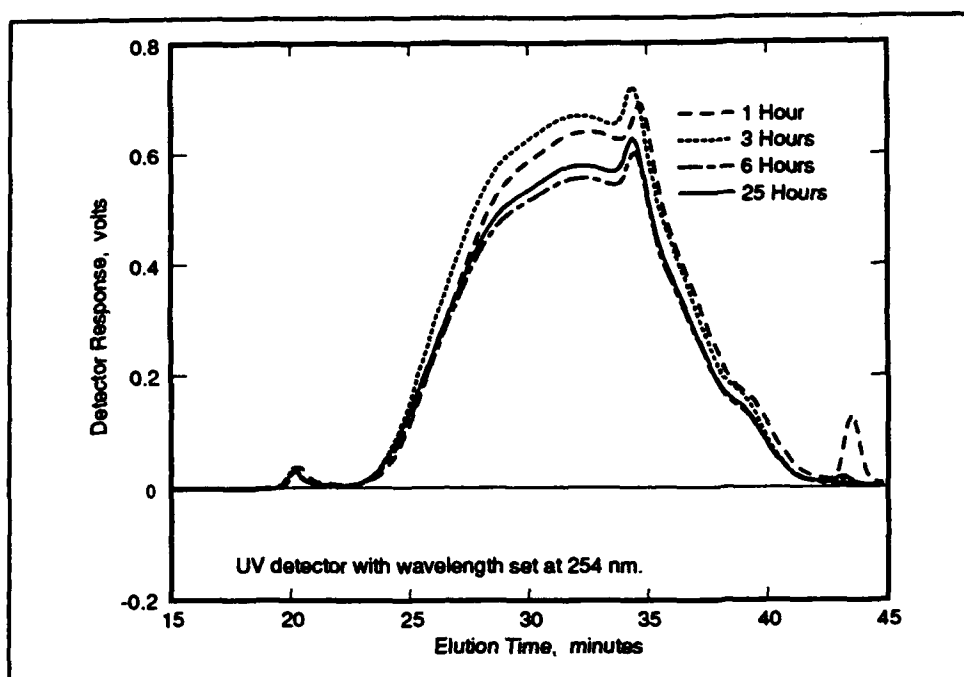


Figure 1. Chromatograms obtained by varying sample solution time

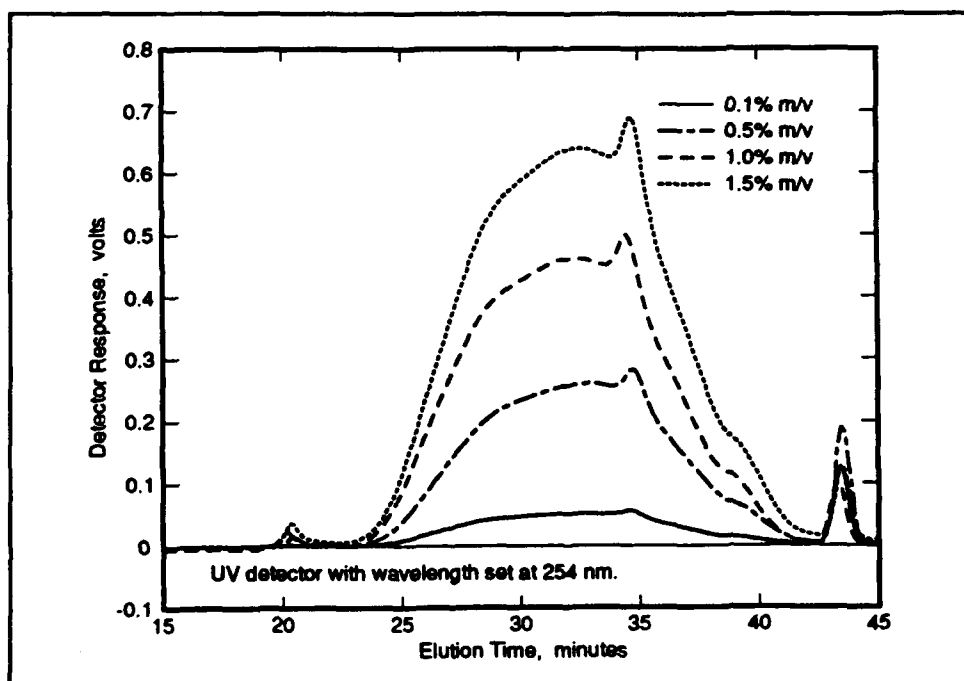


Figure 2. Chromatograms obtained by varying sample concentration

Another parameter which affects the chromatograph is the wavelength of the UV detector. Most of the studies which have been conducted on asphalt cements used a UV detector wavelength of 254 n. m. However, Brulé (Brulé 1980) concluded that when evaluating high penetration asphalt cements, a wavelength of 350 n. m. could detect more significant differences. The study stated that differences in asphalt cements were associated with the relative content of polycondensed compounds (defined above as micelles) instead of the molecular weight distribution of the constituents or the distribution of aromaticity (defined above as molecules). The polycondensed compounds would be detected using a UV detector wavelength of 350 n. m. The molecular weight distribution of the constituents would be detected using an RI detector, while the distribution of aromaticity would be detected using a UV detector wavelength of 254 n. m. It is possible that the same phenomena could apply to the asphalt-based sealants.

Calibration

The GPC was developed to provide a molecular size distribution of an analyzed sample thereby providing the molecular weight distribution. The ability to obtain the molecular weight distribution is possible because the molecular size of a polymer is related to its molecular weight. By providing the molecular weight distribution, information such as the number average and weight average molecular weight of the polymer can be determined. The two molecular weights provide valuable information for processing the polymers into a final product and can be used as a quality control tool. But for the molecular weight information to be accurate, some type of calibration curve has to be established for the material being analyzed. The common method of establishing a calibration curve for GPC polymer analysis is to use polystyrene samples with varying molecular weights; however, asphalt cements are not polymers. Therefore, the calibration curves for these materials and their fractions will not be the same as the calibration curve for polymers (Brulé, Ramond, and Such 1986).

Calibration curves for different asphalt cements have been established for GPC analysis (Brulé 1980). The calibration curves were established by separating the specific asphalt cement into different fraction sizes by vapor pressure osmometry and ultracentrifugation. These fractions were then injected into the GPC using the specific parameters that would be used to analyze the asphalt cements.

Even after calibration curves have been established, it is possible that the chromatograms of asphalt cements obtained using GPC are broader than the true molecular weight distribution. One possible explanation for the variance from the "true" molecular weight is the chemical composition of the asphalt cement. The micelles and aggregates that are in existence during evaluation can distort the molecular weight distribution. Therefore, the molecular weight obtained by GPC is not considered to be accurate. But Ambler and Mate (Ambler and Mate 1972) question the accuracy of other "absolute" methods.

For example, methods such as membrane osmometry have limits on the pore size obtainable in the membrane and may not provide the actual molecular weight of the material being analyzed. To obtain a correlation between membrane osmometry and GPC, Ambler and Mate truncated the chromatogram at a molecular weight which corresponded to approximately 25,000 grams/mole. The molecular weight of most asphalt cements is below 25,000 grams/mole. Thus, the limit placed on the chromatogram eliminates the portion of a chromatogram where the asphalt molecular weight distribution would be detected.

Analyzing Chromatograms

The work conducted on asphalt cements using GPC has not answered many questions and often the answers that have been provided are contradictory (Brule 1980). One of the main reasons for the contradictory results could be that the molecular types and sizes vary widely with chain and ring shapes found in asphalt cements. Therefore, it is very difficult, if not impossible, to develop a consistent relationship between molecular size and molecular weight (Stock 1986). But if the chromatograms obtained from asphalt cements are analyzed using a comparative analysis, the actual molecular weight is not as important as the differences between different chromatograms. Therefore, a method to systematically analyze the chromatograms is needed. It would also be desirable that the systematic evaluation method be extrapolated to predict the field performance of the material being analyzed (Price and Burati 1989).

One of the most common methods of analyzing asphalt cement chromatograms is to divide them into three sections or partitions (Stock 1986, Price 1989, Leite et al 1989, Jennings 1985). The partitions are normally established by dividing the chromatogram into equal sections based on elution time. The area in each section is then calculated by slice integration.

The labeling or terminology used to classify the three partitions has also been standardized. The section which elutes first has traditionally been referred to as the large molecular size fraction, the second fraction as the intermediate or medium molecular size fraction, and the last fraction as the small molecular size fraction. However, since the solvent may not separate all of the aggregates and micelles in an asphalt, it is probable that some of the material that elutes in the large or intermediate size molecular fraction is actually a grouping of small molecules. A more appropriate method of labeling these sections would be to eliminate the molecular size wording and replace it with early fraction for the portion of the chromatogram that elutes as the large molecular size, intermediate fraction for intermediate molecular size, and late fraction for small molecular size (Stock 1986). Figure 3 illustrates a chromatogram which has been divided into three partitions and the terminology used to describe the sections. Early, intermediate, and late fractions will be used to describe portions of chromatograms for the joint sealant analysis.

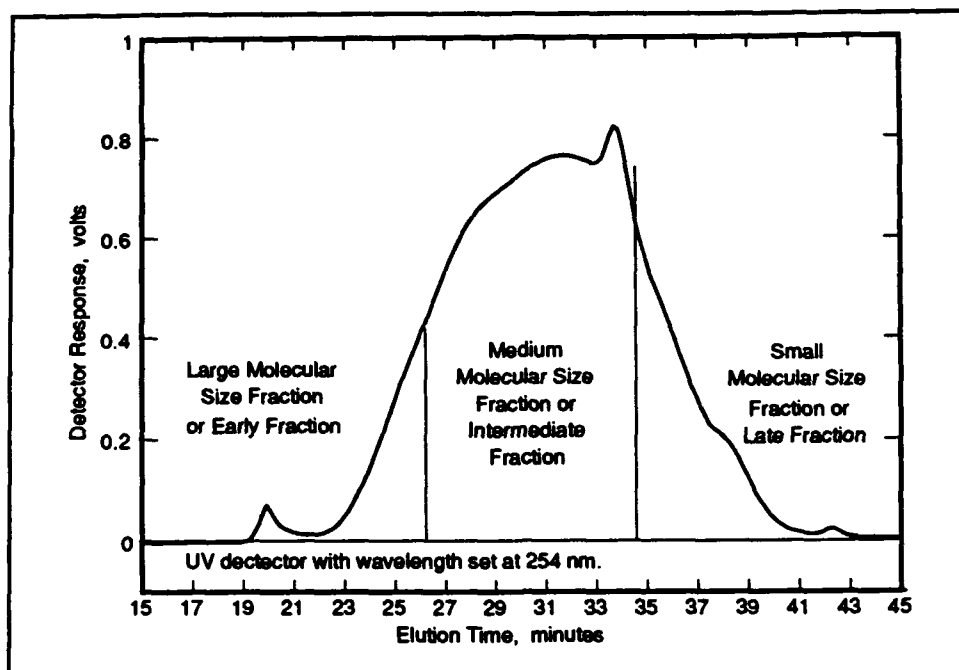


Figure 3. Chromatogram partitioned into thirds with descriptive terminology

A second possibility for the contradictory results sometimes obtained when analyzing the chromatograms could be that it was only divided into three partitions. Price (1988) performed studies in which the chromatograms were first divided into thirds as described by earlier researchers. The chromatograms were then reevaluated by dividing them into fourths and tenths. By dividing the chromatograms into fourths, the asphaltene fraction of the asphalt cement was better approximated by the upper fourth or early fraction. Dividing the chromatograms into tenths provided better resolution for analysis and thus provided an improved statistical correlation with physical data.

Each partition of the chromatogram was divided by the total area under the curve to normalize the comparisons of one chromatogram with another. The chromatograms that were partitioned into tenths indicated that different sections correlate to different rheological tests such as specific gravity, kinematic viscosity, thin film oven loss, pen-vis number, viscosity-temperature susceptibility, and kinetic viscosity of thin-film oven residue (Price and Burati 1989). The equations obtained from the analysis were validated using a different asphalt cement (AC-20). In five of the six models tested, the predicted values were within 10 percent of the actual value. This strengthens the hypothesis that HP-GPC characterization of asphalt can be used to predict performance in physical properties regardless of source or crude oil origin (Price and Burati 1989). The joint sealant chromatograms in this study will be analyzed by determining the initial detection and final detection and partitioning them into tenths to provide better resolution.

3 Laboratory Test Plan

Phase I

Phase I of the laboratory study consisted of testing the joint sealant materials to the appropriate Federal Specification, the SS-S-1401C in this case. The Federal Specification has several criteria requirements that the sealant must meet in order to conform to the specification. Failure of any one of the criteria is classified as nonconformance. Table 1 list the criteria and their requirements for the specification.

Additional tests were established and conducted on the sealants to allow each material to be tested for the same physical characteristics under various aging conditions. For example, notice in Table 1 that the test criteria for Federal Specification SS-S-1401C includes a penetration and an aged and unaged resilience. Therefore, the additional test criteria for the SS-S-1401C sealants are an aged penetration, a penetration conditioned in the weather-o-meter, and a resilience conditioned in the weather-o-meter. The specific additional tests conducted on each sealant are provided in Table 2.

Federal Specification SS-S-1401C requires the penetration test to be conducted by filling a 6-oz container flush with sealant material. The specifications require that the penetration be conducted in accordance with American Society for Testing and Materials (ASTM) D 5-86 (ASTM 1989) using the penetrometer and optional cone described in ASTM D 217-86 (ASTM 1989). The penetrometer and optional cone are illustrated in Photo 1. All unaged penetrations were prepared and tested using this procedure. The weather-o-meter and oven-aged penetration specimens were prepared and tested in accordance with the Federal Specification except the specimens were conditioned in a twin-enclosed, carbon arc weather-o-meter or a forced-draft oven (Photo 2).

The penetration specimens conditioned in the twin-enclosed carbon arc weather-o-meter shown in Photo 2 were exposed to 160 cycles of 51 min of UV radiation with a controlled black panel temperature of 140°F and 9 min of UV combined with a water spray as described in Federal Specification SS-S-200E. This conditioning was conducted to simulate exposure to the natural weathering conditions of sunlight and rain. The penetration specimens conditioned in the forced-draft oven were exposed to 158°F for 7 days. This conditioning was conducted to accelerate the aging of the sealant.

Table 1
Federal Specification SS-S-1401C Test Requirements

Test	Requirement
Application Temperature (°F) ¹	Pouring temperature shall be the safe heating temperature and shall be determined by the manufacturer.
Melting Time	3 hr
Penetration, 77°F (mm)	Shall not exceed 9.0
Flow at 140 F, (mm)	Shall not exceed 3.0
Resilience: Unaged: ² Initial indentation, (mm) Recovery, percent Aged: ³ Initial indentation, (mm) Recovery, percent	0.5 to 1.5 Minimum of 80 0.5 to 1.5 Minimum of 80
Bond to concrete, (-20°F) Nonimmersed Water-immersed	None of the specimens shall develop any separation or other opening in the sealing compound or between the sealing compound and the concrete block Same as nonimmersed bond
Compatibility with Asphalt	Shall be no failure in adhesion, formation of any oily exudate at the interface between the sealing compound and the asphaltic concrete, softening or other deleterious effects on the asphaltic concrete

¹ The safe heating temperature is the highest use temperature permitted by the manufacturer and is a temperature to which the sealant can be heated for a duration of at least 3 hr, and still conform to all of the requirements specified.

² Unaged specimens are cured for 24 hr at standard conditions (73 ± 4°F temperature and 50 ± 5 percent relative humidity) then conditioned for 1 hr in a water bath at 77 ± 0.5°F prior to testing.

³ Aged specimens are cured for 24 hr at standard conditions, overaged in a forced draft oven at 158 ± 2°F for 168 ± 2 hr, cooled under standard conditions for 1 hr, then conditioned for 1 hr in a water bath at 77 ± 0.5°F prior to testing.

Table 2
Additional Tests Conducted on Each Sealant Type

Sealant Type	Additional Test
SS-S-1401C	(a) 2 - penetrations one oven-aged and one conditioned in the weather-o-meter ¹ (b) 1 - weather-o-meter conditioned resilience

¹ Oven-aged specimens are cured for 24 hr at standard conditions (73 ± 4°F temperature and 50 ± 5 percent humidity), oven-aged in a forced-draft oven at 158 ± 2°F for 168 ± 2 hr, cooled under standard conditions for 1 hr, then conditioned for 1 hr in a water bath at 77 ± 0.5°F prior to testing. Weather-o-meter conditioned specimens are cured for 24 hr at standard conditions, exposed to 160 cycles of 51 min of UV radiation with a controlled black panel temperature of 140°F and 9 min of UV combined with a water spray, then conditioned for 1 hr in a water bath at 77 ± 0.5°F prior to testing.

Federal Specification SS-S-1401C includes unaged and aged resilience testing. The specifications require a 6-oz container to be filled flush with the sealant material. The penetrometer specified in ASTM D 217 using a ball penetration tool substituted for the penetration needle is used to conduct the test. The ball is placed in contact with the sealant surface, then released and allowed to penetrate the specimen for 5 sec. The penetration at 5 sec is recorded in tenth-millimeter units. The ball is then pressed into the sealant material an additional 100 units (10.0 mm) within 10 sec at a uniform rate. The ball is held at the additional depth for 5 sec and is then allowed to rebound for 20 sec. The final reading is subtracted from 100 plus the initial reading to determine the resilience. The unaged specimens were conditioned at standard laboratory conditions for 24 hr before testing. The oven-aged and weather-o-meter aged resilience specimens were conditioned in the same manner as the oven-aged and weather-o-meter aged penetration specimens.

The Phase I testing data were used as the baseline against which all other test data were compared. The Federal Specification testing provided an indication of the physical characteristics and the additional testing provided an indication of how various artificial aging techniques affect selected physical properties.

Phase II

Phase II of the laboratory study used the same type of conditioning and testing procedures as Phase I; however, the heating times for hot-applied sealants were varied. The sealants were exposed to the manufacturer's recommended safe heating temperature as required by the Federal Specification for the following times:

- a. Heating Time A - sealant was poured into the specimen molds as soon as the sealant reached the safe heating temperature.
- b. Heating Time B - sealant was maintained at the safe heating temperature for 90 min and then poured into the specimen molds.
- c. Heating Time C - sealant was maintained at the safe heating temperature for 3 hr and then poured into the specimen molds. This is the heating time used in Phase I per Federal Specification SS-S-1401C test requirements; therefore, it was not repeated in Phase II.
- d. Heating Time D - sealant was maintained at the safe heating temperature for 6 hr and then poured into the specimen molds.

Phase III

Phase III of the laboratory study consisted of the GPC analysis of the joint sealant materials. To conduct this portion of the study, a water's GPC system consisting of a Model 590 programmable solvent delivery system, a Model U6K universal injector, a column heater module, and a Model 484 variable wavelength detector were used. The data acquisition and analysis were conducted on a FlexCache 20386DT portable computer.

The GPC parameters used for the joint sealant analysis were as follows:

- a. Mobile phase and solvent used was THF.
- b. Three columns were used in series, an Ultrastyrigel 1000 Å, an Ultrastyrigel 500 Å, and an Ultrastyrigel 100 Å. All columns were packed with styrenedivinylbenzene in THF and were 7.8 by 300 mm.
- c. Column temperature was maintained at 104°F.
- d. The flow rate was 0.8 ml/min.
- e. The injection volume was 0.25 ml.
- f. Sample concentration was 1.5 percent m/v.
- g. Sample time in solution was less than 2 hr.
- h. The samples were filtered using a prefilter and a 0.005 µl filter to prevent clogging of the columns.
- i. Polystyrene standards ranging from a molecular weight of 530 to 1,300,000 gram/mole were used to develop the calibration curve.
- j. UV detector wavelength was 350 n. m.

Before the parameters listed above were established, several areas had to be investigated. The first area of investigation was the column configuration to be used. Two different column configurations were evaluated for the analysis of joint sealants. The first configuration was a single 1000 Å column and the second was a series of three columns consisting of a 1000 Å, a 500 Å, and a 100 Å column. Typical results obtained from the single column "ultra-fast" method are shown in Figure 4, and typical results obtained using the three column method are provided in Figure 5. The ultra-fast method did provide much quicker results but the resolution was greatly reduced. The three column method was selected to provide greater resolution.

To determine if the solvent aging effects occurred with sealants in the same manner as asphalt cements, several samples were prepared and allowed to remain in solution for 1.0, 3.0, 6.0, or 25.0 hr before being injected into the GPC. Figure 4 illustrates the resulting chromatograms from the various

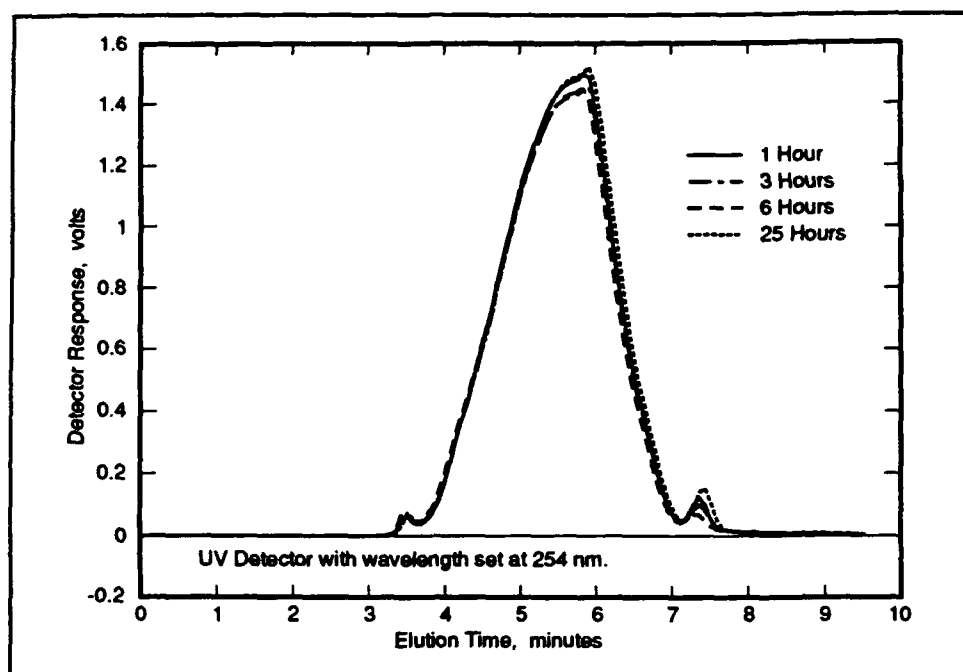


Figure 4. Chromatograms obtained by varying sample solution time using ultra-fast method

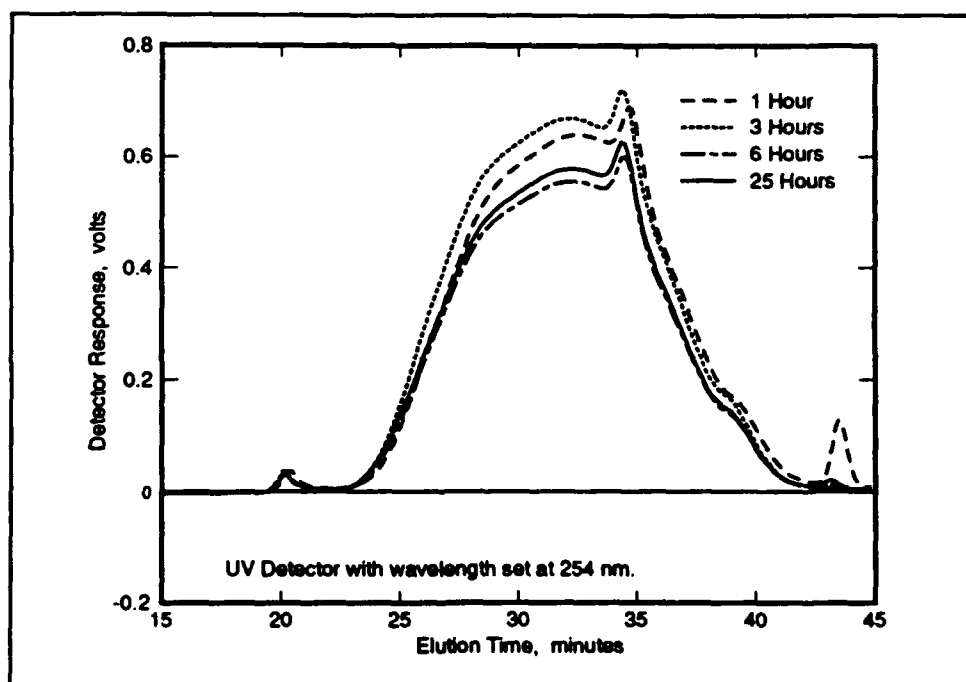


Figure 5. Chromatograms obtained by varying sample solution time using three column method

solution times using the ultra-fast method, and Figure 5 illustrates the resulting chromatograms using the three column method. As shown the sample time in solution affected the chromatograms more for the three column method. One hour was originally selected as the solution time for the sealant analysis based previous studies that concluded shorter solution times provided a more natural state analysis. However, to determine the reproducibility of GPC analysis of joint sealant materials, it was desirable to have four different runs for each sealant condition, i.e., unaged from the melter, oven-aged, weather-o-meter aged, and as-received before heating. To accomplish this, two samples were prepared from each sealant condition by dissolving the material in THF. The sample was filtered and two injections were made from each prepared sample. The run time for each injection was approximately 45 min. The second specimen from each sample was injected immediately after the first run allowing two chromatograms to be obtained from each sample. The total time in solution for the second specimen was less than 2 hr.

The effect of sample concentration was determined by preparing samples with varying concentrations and injecting them into the GPC. The concentrations were determined in tens of the ratio of the mass of sealant to volume of THF. Figure 2 illustrates the chromatograms obtained from varying the concentrations. Based on these chromatograms, a concentration of 1.5 percent sealant mass/solvent volume (m/v) was selected.

Based on the work conducted by Brulé (Brule 1980), the asphalt-based samples were analyzed using an initial wavelength of 254 n. m. which was changed to 350 n. m. before main tests were begun. Figures 6 and 7 illustrate typical results obtained using a wavelength of 254 and 350, respectively, on an asphalt based sealant. In Figure 6, the shift toward the early fraction is noticed only in the first third of the chromatogram while the shift encompasses the entire chromatogram in Figure 7. Because of the overall shift noted in Figure 7, the UV detector wavelength was set at 350 n. m. for analyzing the asphalt-based sealants.

Polystyrene was used to establish the calibration curve for the joint sealant analysis conducted during this project. The calibration curve was reestablished on a weekly basis to verify that the columns had not become clogged or damaged. The calibration curves were not used to determine the molecular weight of the sealants. As a result, the chromatograms obtained were used to provide a comparative analysis between sealant materials instead of an exact analysis of the material. The comparative analysis was performed by normalizing the chromatogram, dividing it into sections, calculating the area of each section, and determining the changes in area caused by specific conditioning. Also, since only a comparative analysis was performed, the detector response in volts was used as the ordinate for simplification.

An as-received sample of each sealant was analyzed using the GPC to establish a before conditioning baseline or fingerprint of each material. Samples were then prepared from each of the unaged, oven-aged, and weather-o-meter conditioned penetration samples from Phases I and II of the laboratory study.

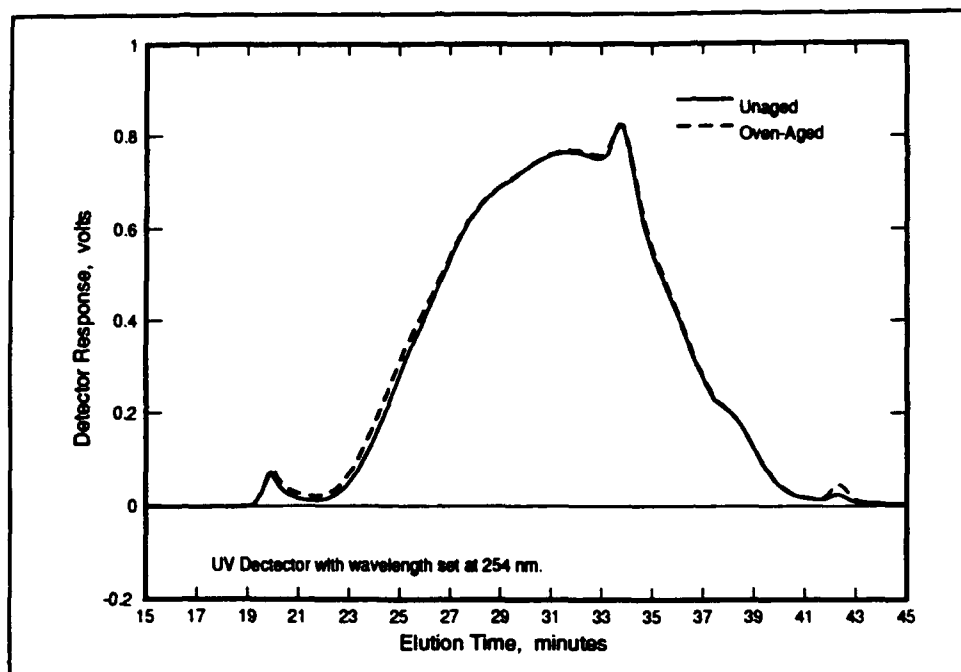


Figure 6. Chromatograms of conditioned SS-S-1401C sealant using UV detector wavelength of 254 n. m.

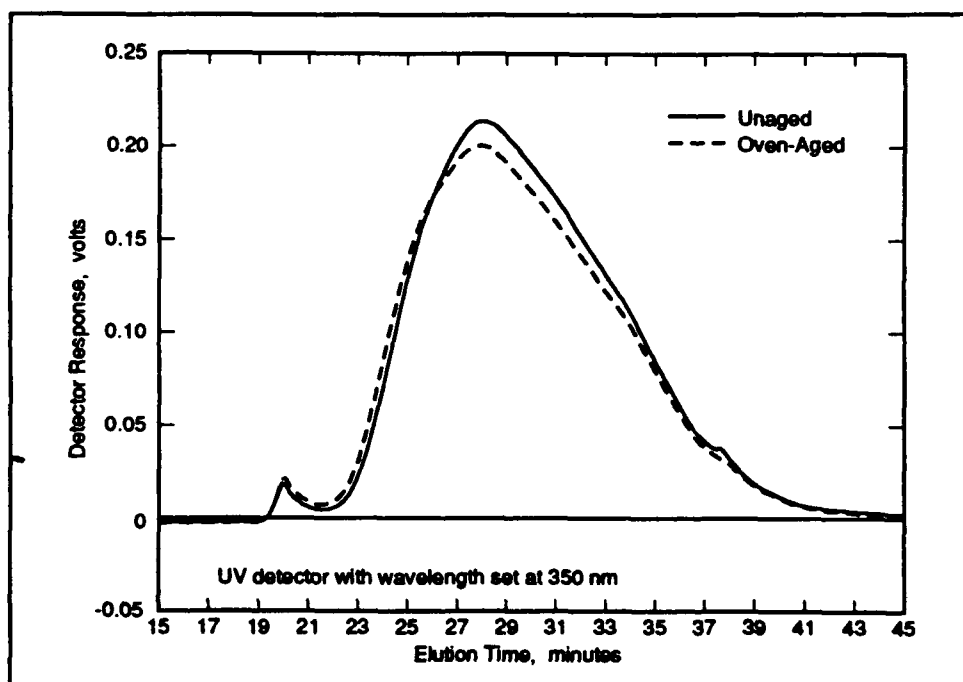


Figure 7. Chromatograms of conditioned SS-S-1401C sealant using UV detector wavelength of 350 n. m.

4 Phases I and II - Presentation and Analysis of Data

Phases I and II data will be discussed together since the only difference between the two phases is a change in the length of heating time before the samples were poured into the molds. Phase I data are designated by a C following the sealant identification, and Phase II data are designated by an A, B, or D following the sealant identification. Table 3 provides the nomenclature used to describe the sealants which were evaluated.

Table 3
Nomenclature Used for Sealant Analysis

Nomenclature	Definition
6522	Sealant manufactured to meet Federal Specification SS-S-1401C obtained from Manufacturer A
6527	Sealant manufactured to meet Federal Specification SS-S-1401C obtained from Manufacturer B
6522-A 6527-A	Sealant samples poured as soon as the material reached the safe heating temperature
6522-B 6527-B	Sealant samples poured after 90 min of heating at the safe heating temperature
6522-C 6527-C	Sealant samples poured after 3 hr of heating at the safe heating temperature.
6522-D 6527-D ¹	Sealant samples poured after 6 hr of heating at the safe heating temperature.
¹ Testing was not conducted due to a lack of material.	

Federal Specification SS-S-1401C

Two sealants, one each from two manufacturers, were obtained for the Phase I and Phase II analyses. These two sealants were manufactured to meet the requirements of Federal Specification SS-S-1401C and were selected based

on the fact that the two materials are often submitted for specification conformance testing for use on military projects. When the sealants arrived at the laboratory, they were logged in using a flexible pavement laboratory (FPL) number. The FPL number is an in-house method used to track materials that have been received for testing. The FPL number will be used to represent the different sealants instead of using product names. The FPL numbers for the two sealants are 6522 and 6527.

The as-received samples of both FPL 6522 and FPL 6527 did not meet the requirements of Federal Specification SS-S-1401C. FPL 6522 sample failed the unaged resilience initial indentation requirement, and the FPL 6527 sample failed both the unaged and aged resilience initial indentation requirements. Federal Specification SS-S-1401C allows a retest of a specific test if it is not in compliance. Both samples were retested and both samples failed the retest. Summaries of the Federal Specification SS-S-1401C test results for the two materials are provided in Column C of Tables 4 and 5.

Table 4 Federal Specification SS-S-1401C Test Results of FPL 6522				
Test/Heat Time After Safe Heating Temperature ¹	A (0)	B (1½ hr)	C (3 hr)	D (6 hr)
Safe Heating Temperature (Deg F)	Used ²	Used	Used	Used
Penetration (cm)				
Unaged	0.80	0.86	0.87	0.96 ³
Oven-Aged ⁴	0.80	0.81	0.79	0.88
Weather-O-Metered Aged ⁴	0.76	0.76	0.79	0.99 ³
Flow (cm)	0.0	0.0	0.0	0.0
Resilience				
Unaged				
Initial indentation (cm)	0.16 ³	0.15	0.18 ³	0.21 ³
Percent recovery	67%	69%	68%	67%
Oven-Aged				
Initial indentation (cm)	0.14	0.13	0.15	0.15
Percent recovery	67%	70%	65%	65%
Weather-O-Meter Aged ⁴				
Initial indentation (cm)	0.14	0.14	0.15	0.15
Percent recovery	62%	65%	62%	63%
Bond to Concrete (-20 Deg F)				
Nonimmersed	Sat. ⁵	Sat. ⁵	Sat. ⁵	Sat. ⁵
Water-immersed	Sat. ⁵	Sat. ⁵	Sat. ⁵	Sat. ⁵
¹ Compatibility with asphalt testing not conducted. ² Manufacturer's recommended value was used. The number is not reported to prevent identification of the manufacturer. ³ Does not meet specification requirements. ⁴ Additional tests not included in SS-S-1401C. ⁵ Satisfactory.				

The noncompliance of the two materials was unexpected but not necessarily surprising. Historical test data on sealants tested by the WES indicate that approximately 25 to 30 percent of all sealant materials submitted for

Table 5 Federal Specification SS-S-1401C Test Results of FPL 6527			
Test/Heat Time ¹	A	B	C
Safe Heating Temperature (Deg F)	Used	Used	Used
Penetration (cm)			
Unaged	0.70	0.71	0.79
Oven-Aged ²	0.67	0.69	0.80
Weather-O-Metered Aged ²	0.62	0.66	0.68
Flow (cm)	0.0	0.0	0.0
Resilience			
Unaged			
Initial indentation (cm)	0.14	0.14	0.18 ³
Percent recovery	68%	69%	65%
Oven-Aged			
Initial indentation (cm)	0.13	0.15	0.17 ³
Percent recovery	63%	64%	64%
Weather-O-Meter Aged ²			
Initial indentation (cm)	0.11	0.11	0.14
Percent recovery	63%	62%	63%
Bond to Concrete (-20 Deg F)			
Nonimmersed	Sat. ⁴	Sat. ⁴	Sat. ⁴
Water-immersed	Unsat. ⁵	Unsat. ⁵	Sat. ⁴
¹ Compatibility testing not conducted. ² Additional tests not included in SS-S-1401C. ³ Does not meet specification requirements. ⁴ Satisfactory. ⁵ Unsatisfactory.			

specification conformance testing do not conform to the specification to which it was manufactured. These two materials would not be accepted for use on a Government sealing project, but their failure does not negate the objective of the research effort for two primary reasons. The research effort is a comparative analysis to determine if changes caused by aging or over-heating can be detected by GPC. All user agencies do not require the contractor to have the sealant materials tested for specification compliance. Therefore, the test results may be indicative of materials actually being used in the field.

FPL 6522

The penetration testing of FPL 6522 did indicate a hardening or stiffening of the material during the artificial aging processes at each of the heating times with two exceptions. The first exception was noted in 6522-A in which the unaged and oven-aged specimens both had a penetration of 0.80 cm. The second exception was 6522-D in which the weather-o-meter aged specimen exhibited an increase in penetration versus the unaged specimen, 0.99 cm versus 0.96 cm. There was no consistency concerning which type of aging, oven or weather-o-meter, caused the greater amount of hardening.

Setting aside the two exceptions for the moment and considering the specimens as either unaged or aged, a distinctive hardening was noted as would be expected. The hardening upon aging was indicated by a decrease in penetration values.

Similar trends to those observed in the penetration testing should be noticed in the resilience testing. The specific area in which the trends should be similar would be the initial indentation testing. However, the only similarity between the penetration testing and the initial indentation testing was that when comparing unaged versus aged specimens for each heating time, hardening was exhibited by a decrease in the test results. The decrease was observed for each of the heating times. Also, the oven-aged and weather-o-meter aged specimens had almost identical initial indentations indicating that both types of aging affect the materials in a similar fashion. The percent recovery indicated a hardening of the material by a decrease in the material's ability to rebound after loading with two exceptions. The oven-aged and unaged percent recovery were identical for 6522-A, and the oven-aged percent recovery for 6522-B was slightly higher than the corresponding unaged percent recovery.

The unaged resilience initial indentation results indicated a softening of the sealant with an increase in the heating time similar to that exhibited by the unaged penetration results. The oven-aged and weather-o-meter specimens, with the exception of heating time D, indicated almost no change between the various heating times. It was suspected that the lack of change was observed because the artificial aging affected the specimens more significantly than the extended heating times. It was also believed that the polymers and extender oils added to the sealant by the manufacturer compensate for the hardening of the asphalt cement during extended heating times. This conclusion was drawn from the fact that the manufacturer's literature states that the sealant is manufactured to endure heating times of up to 6 hr and still meet the requirements of Federal Specification SS-S-1401C.

The summarized test data in Table 4 generate several questions or inconsistencies. First, the sealant exhibited aging as depicted by a decrease in the penetration test results for the same heating times, but there were inconsistent exceptions to the trend. Secondly, the extended heating times to which the sealant was exposed either softened the material or apparently had no affect on it as depicted by an increase or no change in the penetration test results. This is opposite to the trend that would be expected.

Several areas were investigated in an effort to determine why exceptions were noted in the hardening trend. First, the specific tests in question were conducted again using the same test specimen. The results of the retests were almost identical to the initial test results thereby indicating that the noted differences were not caused by testing technique. Secondly, the surface of the test specimens was examined for any defects which could have affected the results. When no surface flaws were detected, the specimens were cut into sections to visually examine the homogeneity of the specimen. The specimens appeared to be homogeneous with no internal voids or unmelted chunks of

sealant. Therefore, the differences in the test results did not appear to be related to the specimens or their preparation.

The as-received sealant samples were examined to determine if there was something inherent to the material that could have caused the inconsistencies. FPL 6522 is manufactured by combining rubber, extender oils, reinforcing fillers, and polymers with an asphalt cement.

The exact type of these ingredients is not disclosed in product data sheets or material safety data sheets for obvious reasons. But when reviewing the production procedures used to produce these materials, it was discovered that the materials are packed into shipping containers while they are still hot from the mixing process. As the materials cool, some segregation of the ingredients may occur. The segregation does not pose a problem if the entire sealant package is placed in a melter for application into joints or cracks in a pavement, but it can be a significant problem if only small sections of the material are being used for laboratory testing. In an effort to minimize the effects of segregation and to obtain a representative sample from the sealant material, the material taken from the sealant was cut vertically from the top to the bottom of the container. This method allowed material from each layer to be incorporated into the material used for testing.

Based on these investigations, there was no apparent reason for the noted exceptions in the penetration results of 6522-A and 6522-D. The last possibility for the discrepancy could be a combination of the type of melter used and segregation of the as-received sealant. The melter used to heat the sealants consisted of two melting pots in which the sealant was inserted. The two melting pots are enclosed in a larger container which contains the heating elements and a heat transfer oil. The melter used to prepare the sealant materials is shown in Photo 3. It is possible that the two melting pots were not evenly filled with sealant from each of the segregated layers especially since the segregated layers are not visibly distinguishable. If two of the penetration specimens were poured out of one of the pots and the other penetration specimen was poured out of the second pot, there could be slight differences between the test specimens. These differences could explain the noted exceptions in the hardening trends within a specific heating time and the inconsistent resilience results. Information concerning which melting pot each specimen was poured out of is not known. Therefore, the exact reasons for these discrepancies cannot be determined.

Since a decrease in penetration was noted as the sealant specimens were aged, one would also expect a decrease in penetration values as the heating time for the sealant increased. However, the trend observed in the unaged specimens was an increase in both penetration and resilience initial indentation results. The largest difference was noticed with heating time D (6 hrs). The penetration results for the oven-aged and weather-o-meter aged specimens indicated a softening of the sealant as the heating time was extended, but not to the extent exhibited by the unaged specimens. The one exception to the limited difference was heating time D. The oven-aged and weather-o-meter aged resilience specimens indicated almost no difference between the various

heating times. It was suspected that this lack of change was observed because the amount of artificial aging on the specimens contributes more to the end result than the heating time. It was also believed that the polymers and extender oils compensate for the hardening of the asphalt cement during extended heating times. This conclusion was drawn from the fact that the manufacturer's literature states the sealant is manufactured to accept heating times of up to 6 hr and still meet the requirements of Federal Specification SS-S-1401C.

The test results for heating times A and B are very similar. The similarity was to be expected since there was only 90 min difference between the two results, and since the material was manufactured to withstand heating times of 3 to 6 hr. There was a noted difference in the unaged results for heating time D as compared to the other heating times. The oven-aged and weather-o-meter aged resilience specimens initial indentation results for the various heating times indicated no significant differences. This indicated that the artificial aging surface effects were greater than the aging effects caused by extended heating. The decrease in penetration within a specific heating time was probably caused by surface effects. The surface of the specimen was exposed to the artificial aging thereby concentrating the weathering effects on the surface. The increase in penetration values observed as the heating time increases was probably caused by a breakdown of the polymer system of the sealant.

FPL 6527

The penetration and resilience initial indentation results indicate that FPL 6527 exhibited hardening as it was aged. The hardening was identified by a decrease in the respective test values. Two exceptions were noted to this trend. One exception was observed in 6527-C where the oven-aged penetration was slightly higher than the unaged value, 0.80 cm versus 0.79 cm. An exception was also noted in 6527-B where the oven-aged initial indentation was higher than the unaged initial indentation, 0.15 cm versus 0.14 cm.

Excluding these two exceptions, 6527 demonstrated definite trends between unaged versus aged and between the different types of aging. The 6527 results indicate that the material hardens as it is aged and that the specimens exposed to the weather-o-meter harden more than the specimens exposed to oven aging.

The 6527-A and 6527-B specimens failed the water-immersed bond to concrete. In both cases, two of the three specimens failed in adhesion. That is, the bond between the sealant and the concrete block was broken. It is possible that, since the material is manufactured to meet Federal Specification SS-S-1401C, the material may require 3 hr of heating to obtain the desired adhesion properties. Another possible reason for the adhesion failure could be improper preparation of the bond specimens. To evaluate the preparation procedures, the failed specimens were observed. The most common type of improper preparation associated with adhesion failure is the accidental

application of a release agent to the concrete blocks. The release agent is used on the spacers that separate the concrete blocks and form the reservoir for the sealant. The block surfaces that were exposed because of the adhesion failure had a small amount of sealant residue or discoloration on them. Normally, if the release agent had been accidentally applied to the concrete block, the separation between the sealant and the block would be clean, i.e., no sealant residue. Thus, specimen preparation error is an unlikely cause of the failure.

The possible reasons for the discrepancies noted in the resilience and penetration testing are the same as those noted for sealant 6522.

5 Phase III - Presentation and Analysis of Data

Physical testing of the pavement joint sealant materials conducted in Phases I and II indicated that the inconsistent changes that occur due to extended heating and artificial aging can be physically detected. The objective of Phase III was to determine if those changes could be detected using GPC. The same nomenclature provided in Table 3 was used to describe the evaluated sealants.

Two specimens were prepared for each sealant condition and two injections were made from each of the prepared specimens. For example, two pieces of sealant were obtained from the unaged penetration test specimen of FPL 6522-A. Each piece of sealant was placed into a separate vial and the appropriate amount of THF was added to the vial. After the sealant dissolved in the THF, the sealant/THF solution was filtered to remove the inert fillers from the specimen. Two samples were taken from each vial and injected into the GPC, thus providing four runs for each sealant condition. Figure 8 illustrates typical results obtained from the four GPC runs. In this figure, samples 1 and 2 were taken from the first vial, and samples 3 and 4 were taken from the second vial. If the GPC is to be used to provide meaningful comparative data, then all four runs should overlay directly on each other as illustrated in Figure 8. Unfortunately, not all of the chromatograms for each of the sealant conditions yielded the near ideal results depicted in Figure 6.

The GPC analysis indicated considerable inconsistencies between the four runs of some of the sealant samples. Because of the inconsistencies, average chromatograms were calculated to assist in the comparative analysis. Standard deviations of the chromatograms were also calculated so that a 95 percent confidence region chromatogram could be constructed. The 95 percent confidence region was constructed by taking the average chromatogram and then adding and subtracting two standard deviations from the average. The ± 2.0 standard deviations provided the upper and lower limit for the 95 percent confidence region.

The chromatograms for the two sealants which were manufactured to meet the requirements of Federal Specification SS-S-1401C had similar profiles. The chromatograms exhibited two peaks. The first peak was small and was initially detected at an elution time of approximately 18 to 19 min. The

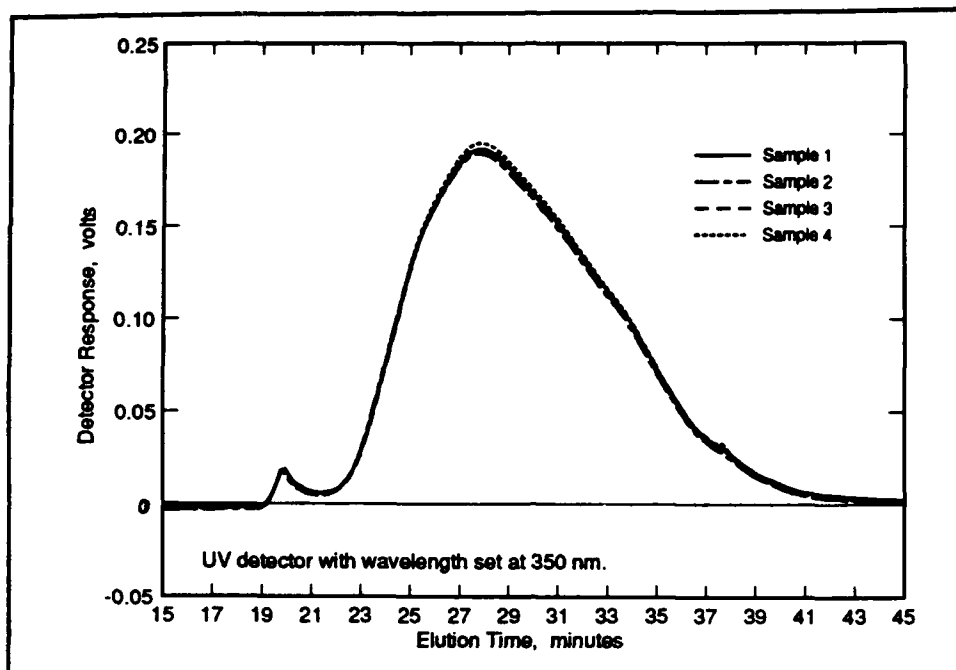


Figure 8. Chromatograms obtained from one sealant penetration specimen

chromatogram then approached the base line again at an elution time of approximately 21 to 22 min. The second peak was much larger and broader. The second peak began at an elution time of approximately 21 to 22 min and returned to base line at approximately 45 min. The first peak was suspected to be a polymer that had been added to the sealant, and the second peak was characteristic of chromatograms obtained when analyzing asphalt cements. Therefore, the second peak was believed to be the base asphalt material.

FPL 6522

A total of 13 FPL 6522 sealant conditions were analyzed using GPC. Only five of the 13 sealant conditions had a 95 percent confidence region that was approximately 0.05 or less at the widest point. The five sealant conditions which had a 95 percent confidence region of approximately 0.05 or less were FPL 6522 as-received, 6522-A unaged, 6522-B oven-aged, 6522-C oven-aged, and 6522-D unaged. Evaluating the other eight sealant conditions more closely allowed two more sealant conditions to be included in the 95 percent confidence region of 0.05 or less by eliminating one of the chromatograms. The sealant conditions were FPL 6522-C weather-o-meter aged in which sample 1 was eliminated, and 6522-D weather-o-meter aged in which sample 4 was eliminated. The fact that approximately 50 percent of the total number of sealant conditions tested had a confidence region less than 0.05 and the large fluctuation in the maximum peak heights precluded meaningful quantitative analysis of the data. However, generalized trends can be discussed.

The four chromatograms for each FPL 6522 sealant condition and the 95 percent confidence region for each sealant condition are provided in Appendix A. The FPL 6522 as-received sample was taken from the block of sealant after it had been logged into the laboratory. Figure 9 illustrates the average chromatograms obtained from the FPL 6522-A sealant conditions as well as the as-received chromatogram. The intermediate fraction, or in this case the second peak of these chromatograms indicated a decrease as the sealant was heated to pour into the Federal Specification SS-S-1401C test specimen molds. A greater reduction in the second peak was observed as the sealant was aged in the oven and the weather-o-meter. The decrease in the intermediate region resembled the decrease caused by a decrease in sample concentration, as shown in Figure 2. The decrease in size of this second peak could have been caused by a decrease in the concentration or by a conversion of the intermediate fraction material into compounds that would be detected using a different wavelength. A visual change in the amount of filler material collected on the filter paper was observed between the various samples. Therefore, it is believed that even though the exact mass of sealant to volume of solvent ratio was maintained, changes in the sample concentration occurred. Figure 2 indicated that the early fraction of the chromatograms was not as affected by changes in concentration as the intermediate fraction, and the changes that did occur in the early fraction were consistent with the changes observed in the intermediate fraction. For example, the 1.5 percent mass to volume ratio sample exhibited the highest peak in both the early and intermediate fractions. Therefore, differences in the profiles of the chromatograms must be considered instead of depending solely upon a shifting of the chromatograms as would be expected in the analysis of polymers.

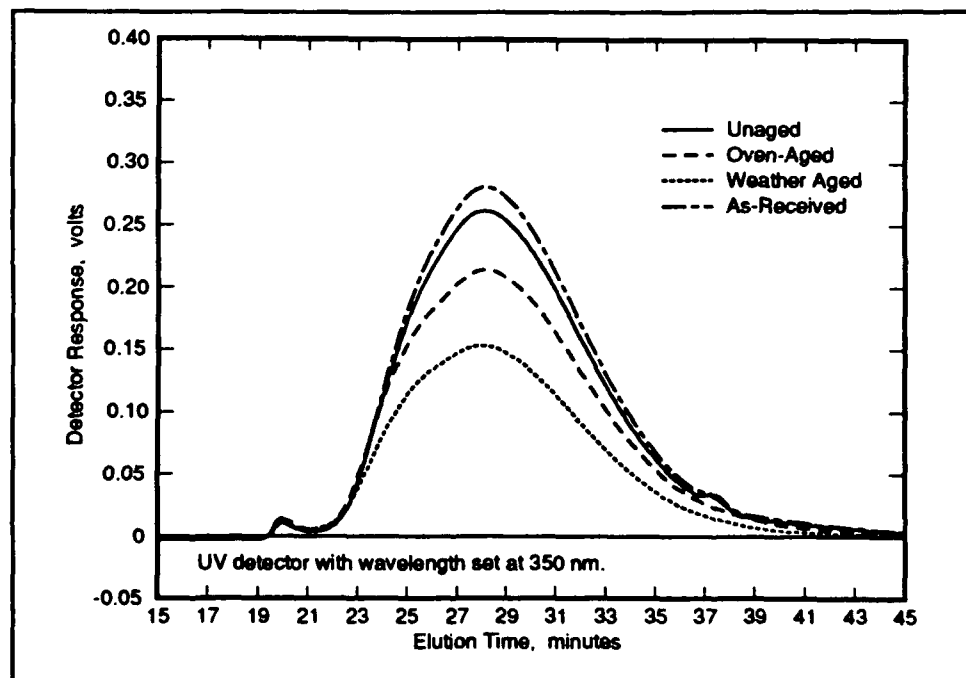


Figure 9. FPL 6522-A average chromatograms

The expected overall shift of the chromatograms of FPL 6522-A as a result of aging to the early fraction did not occur, but a change in the profile was exhibited. A shoulder in the intermediate fraction began to appear at approximately 25 min indicating an increase in the larger sized molecular weight fraction. The shoulder was indicated by a change in slope of the chromatogram which became more pronounced as the sealant samples were aged. Accompanying the development of the shoulder, an increase in the early fraction between 19 and 22 min would be expected. Figure 10 provides a closer view of the first peak for the average chromatograms. Figure 10 indicates that between 19 and 20 min, a consistent increase in the early fraction from the as-received to the various aged samples did not exist. However, in the saddle area between the two peaks which eluted from 20 to 22 min, a slight increase in the early fraction of the two aged samples was observed when compared to the as-received and unaged samples. The specification test results of 6522-A in Table 4 indicated very little change in the penetration values of the unaged sample versus the oven-aged and weather-o-meter aged samples. It is possible that the small changes in the early fraction portion of the average chromatograms of FPL 6522-A explain the lack of change in the penetration values. Since the change in the early fraction was small and inconsistent, the penetration value changes should be small and inconsistent.

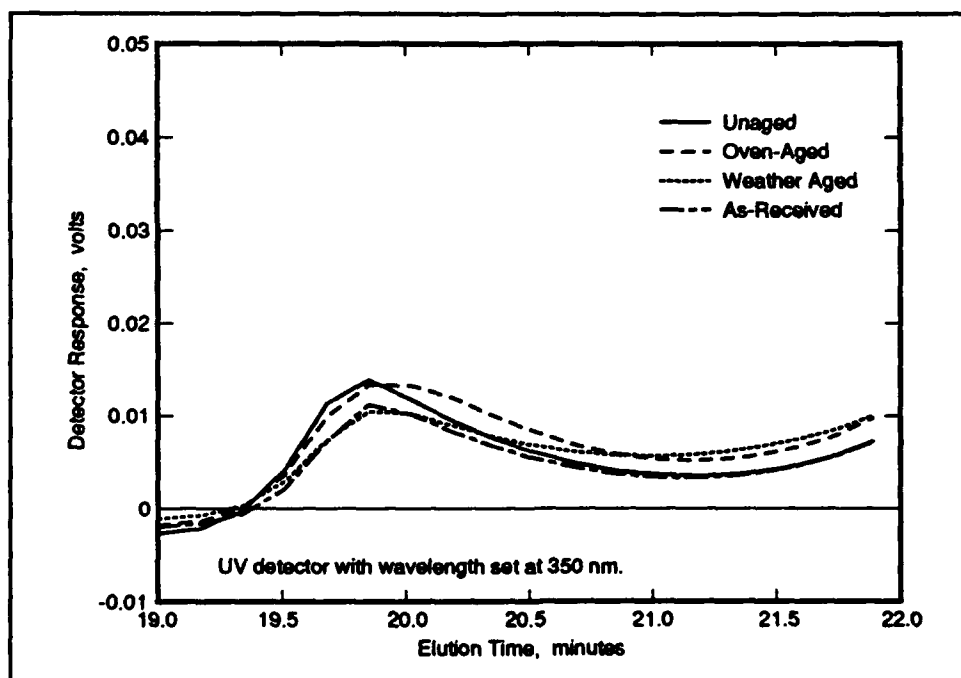


Figure 10. FPL 6522-A average chromatograms from 19 to 22 min

The average chromatograms of FPL 6522-B as shown in Figure 11 exhibited a shift toward the early fraction as the materials were aged. A change in sample concentration was also indicated by the differences in peak heights, and the longer tailing of the weather-o-meter aged chromatogram.

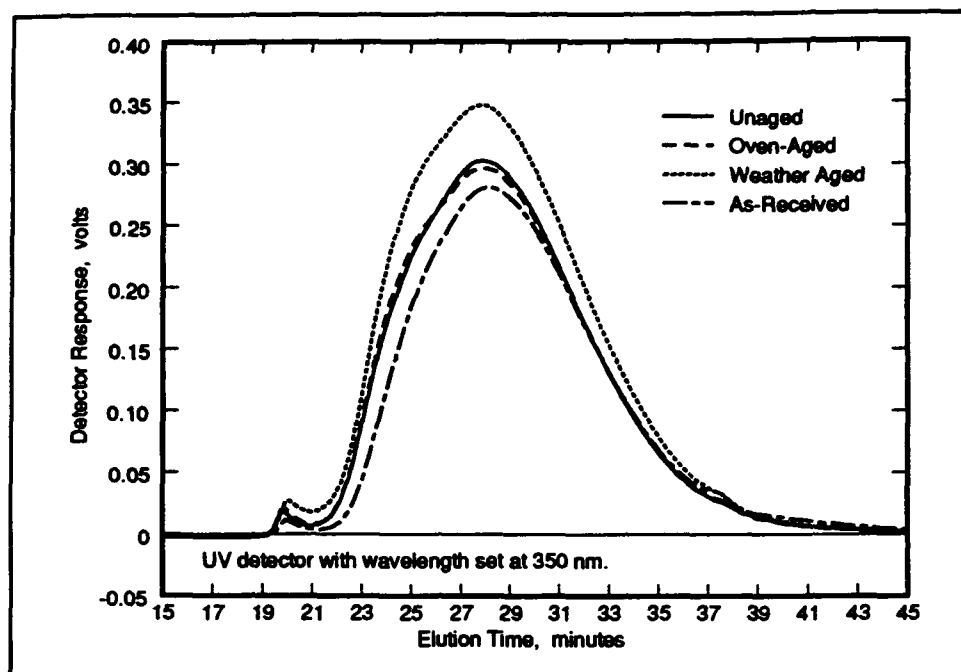


Figure 11. FPL 6522-B average chromatograms

The development of the shoulder at approximately 24 to 25 min was similar to the shoulder which developed in the FPL 6522-A chromatograms. An increase in the early fraction between 19 and 22 min was also present. The increase in this portion of the chromatograms is highlighted in Figure 12 which indicates that the sample exposed to UV radiation in the weather-o-meter had the greatest increase of the early fraction. The oven-aged sample had a slight increase over the unaged sample, and both the unaged and oven-aged samples exhibited an increase over the as-received sample. The penetration values of FPL 6522-B from Table 4 exhibited the same trend as the increase in the early fraction.

FPL 6522-C

Average chromatograms illustrated in Figure 13 exhibited similar trends to those observed in the FPL 6522-B chromatograms. A shift toward the early fraction was noticed as the samples were aged. This shift was accompanied by a corresponding increase in the early fraction, and the shoulder was evident at approximately 24 to 25 min as shown in Figure 13. Sample concentrations varied as indicated by the difference in peak heights, but the extended heating increased the early fraction significantly enough to cause a crossover of the unaged sample as compared to the as-received sample. For example, the unaged sample had a higher first peak than the as-received sample but a lower second peak. The same type of crossover was exhibited between the oven-aged and weather-o-meter aged samples but to a lesser extent.

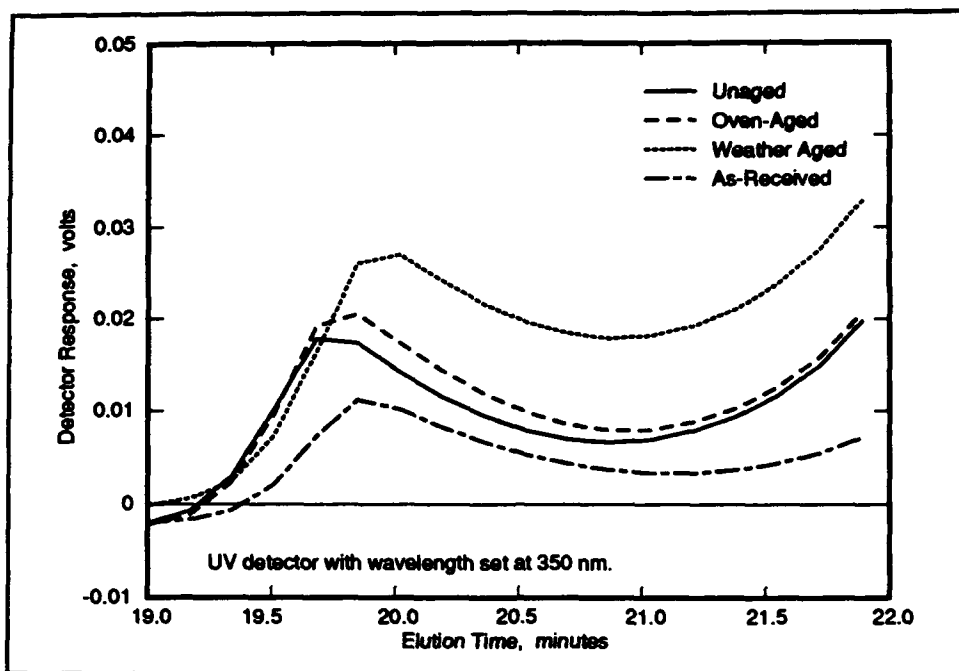


Figure 12. FPL 6522-B chromatograms from 19 to 22 min

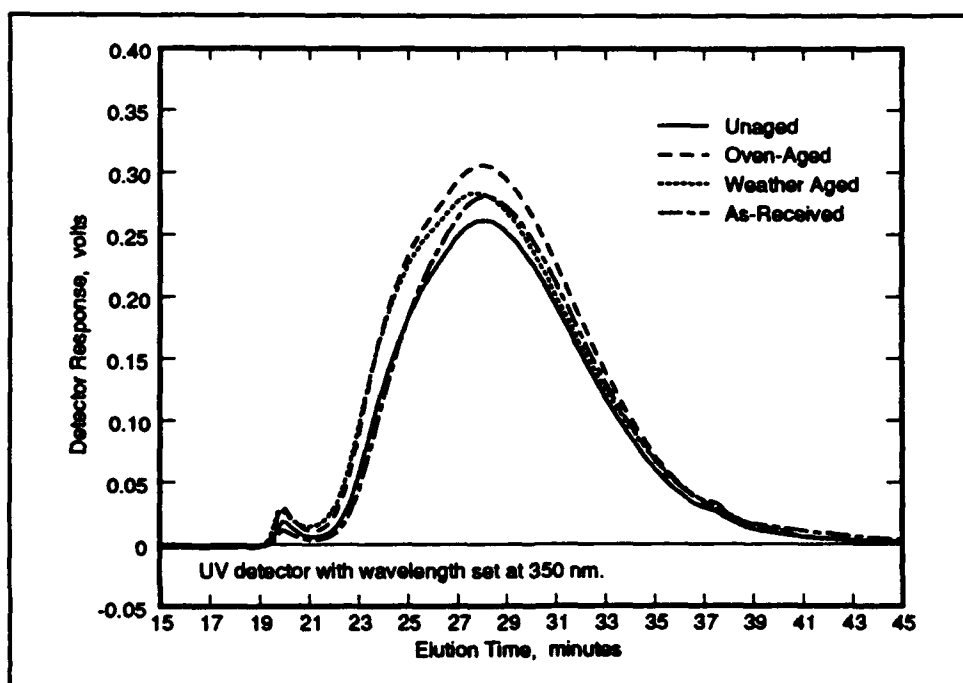


Figure 13. FPL 6522-C average chromatograms

Figure 14 illustrates the early fraction between 19 and 22 min of FPL 6522-C. Comparison of the chromatograms with the FPL 6522-C penetration values from Table 4 indicated similar trends as both the FPL 6522-A and B resulted. The penetration results indicated a hardening of the sealant as it was aged and the chromatograms exhibited an increase in the early fraction with aging. The oven-aged and weather-o-meter aged samples had identical penetration results and the corresponding chromatograms were very similar.

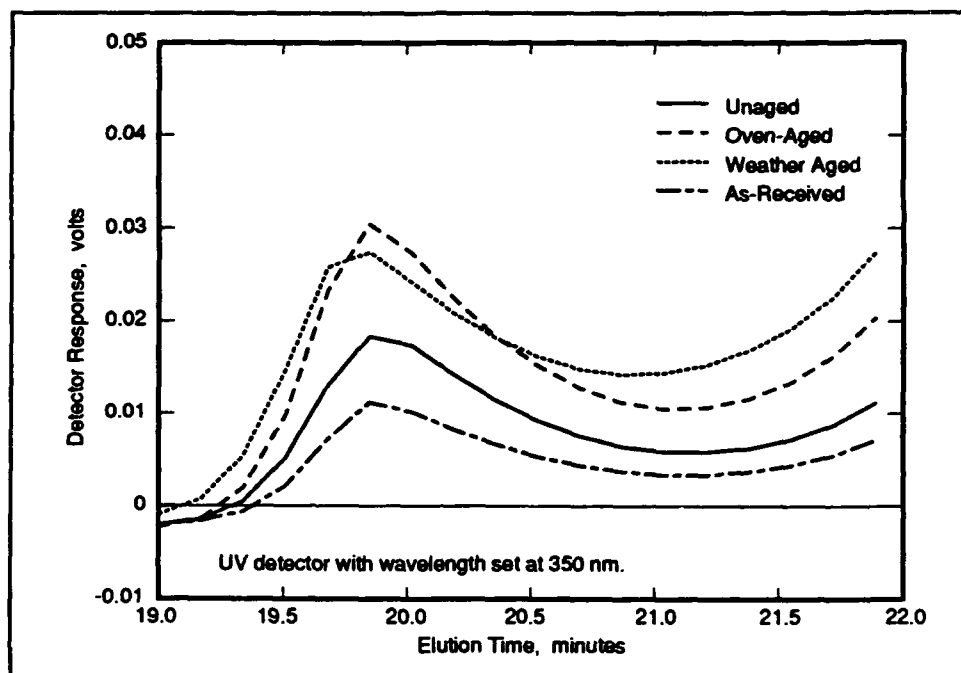


Figure 14. FPL 6522-C chromatograms from 19 to 22 min

The average chromatograms of FPL 6522-D provided in Figure 15, with the exception of the weather-o-meter aged chromatogram, do not have the development of a shoulder in the unaged and oven-aged samples as was evident in the previous FPL 6522 chromatograms. The weather-o-meter aged sample, however, exhibited a shoulder at approximately 24 to 25 min. The FPL 6522-D chromatograms also appeared to have different sample concentrations as indicated by the change in the second peak height. The most significant difference between the FPL 6522-D chromatograms and the previous FPL 6522 chromatograms was the fact that the unaged and oven-aged samples as shown in Figure 16 had very similar first peaks in the early fraction while the weather-o-meter aged sample peak was less intense. From the previous chromatographic versus penetration trends, the weather-o-meter aged penetration value should be higher than the unaged and oven-aged penetration values and the unaged and oven-aged values should be similar. The FPL 6522-C penetration data in Table 4 did not follow this trend. The weather-o-meter aged value was the highest at 0.99 cm., but there was a 0.08 cm difference between the unaged and oven-aged values. The exact reason for this discrepancy is not known; however, one possible cause could be sampling error. Since the unaged and oven-aged samples did not exhibit the development of a

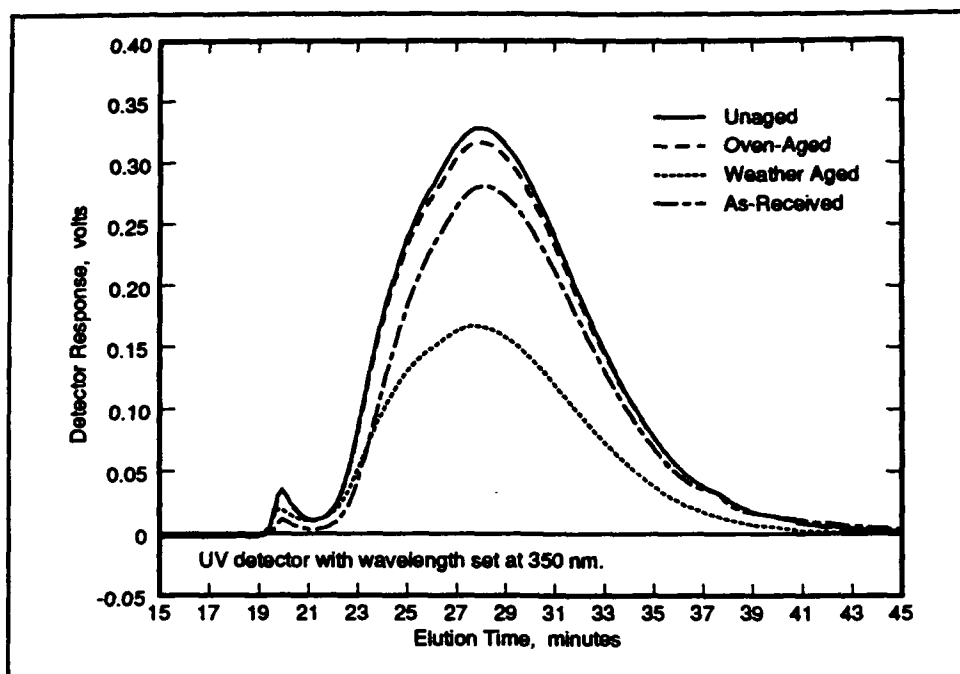


Figure 15. FPL 6522-D average chromatograms

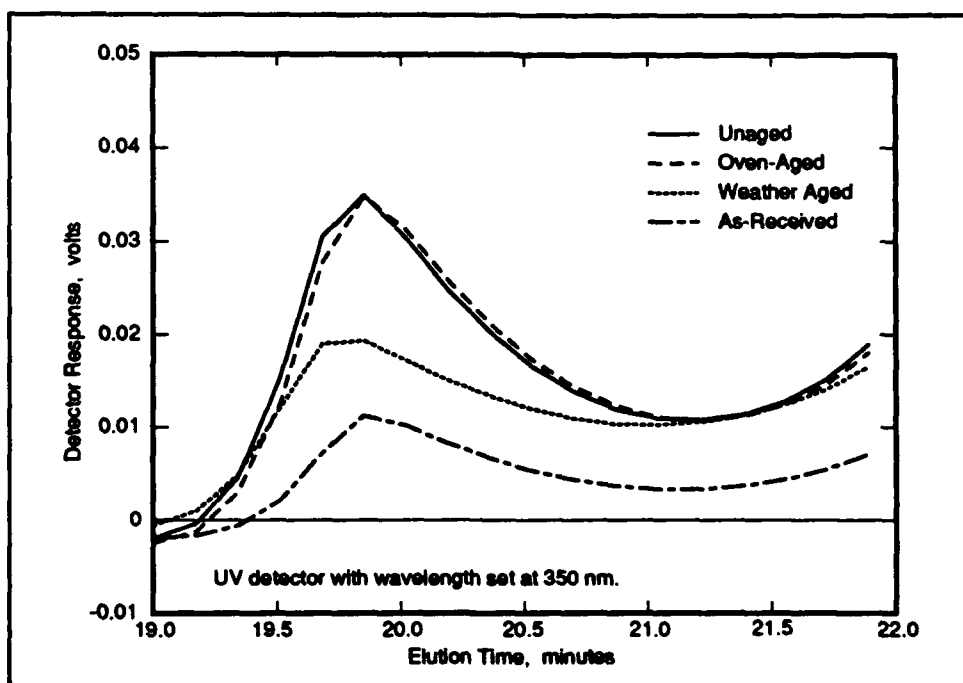


Figure 16. FPL 6522-D chromatograms from 19 to 22 min

shoulder, it is possible that the original material placed in the sealant melter was not representative.

The chromatographic results of FPL 6522 within specific heating times did not follow the expected trend of exhibiting an increase as the sealant sample was aged. However, the chromatograms, with the exception of FPL 6522-D, seemed to reinforce the trends exhibited in the FPL 6522 penetration tests. Samples with lower penetration values exhibited an increase in the early fraction. From the literature review, the expected trend between heating times would be an increase in the early fraction as the heating time was extended. For example, the FPL 6522-B unaged sample should exhibit an increase in the early fraction as compared to the FPL 6522-A sample. From the penetration results shown in Table 4, it was expected that when comparing the unaged samples, FPL 6522-B should have the highest peak in the 19 to 22 min region. FPL 6522-B and C should have peaks that are approximately the same height, but smaller than the FPL 6522-A peak. The FPL 6522-D peak should be the smallest in height of the four heating times. The early fraction chromatograms of the unaged samples follow more closely to the trend expected from the literature. The FPL 6522-A unaged chromatogram exhibited the smallest peak height, FPL 6522-B and C had intermediate peak heights, and FPL 6522-D had the largest peak height. The FPL 6522-B and C chromatograms were very similar as expected from the penetration results, but the FPL 6522-A and D chromatograms were reversed from the expected order indicated by the penetration results.

The FPL 6522 oven-aged chromatograms follow the trend expected by the literature. There does not appear to be any correlation between the penetration test result and the chromatogram results. The weather-o-meter aged chromatograms do not follow either trend; the one expected from the literature or the one expected from the penetration results.

The FPL 6522 chromatograms indicate that differences can be detected as a sealant was aged and as the heating time was extended. But these visual differences do not follow a consistent trend, and the changes that occurred may be defined as insignificant since the 95 percent confidence region for the various sealant conditions overlap. Some of the inconsistencies may have been caused by a change in sample concentration which occurred during the preparation of the samples; therefore, the area defined by the chromatograms was calculated and the chromatograms were partitioned into tenths for further evaluation. Figure 17 illustrates the 10 slices used for evaluation. Slice data for each sealant condition and summarized percent average area per slice data are provided in Appendix B.

The percentage of the total area of the first two slices were arbitrarily selected and added together to establish an aging index. By taking the percentage of the total area of the first two slices or a normalized area, effects caused by changes in sample concentration are minimized. The calculated aging index of each of the FPL 6522 samples is shown in Figure 18. The calculated aging index for all of the FPL 6522 sealant conditions indicated that the percentage of material eluting in the early fraction increased as the sealant

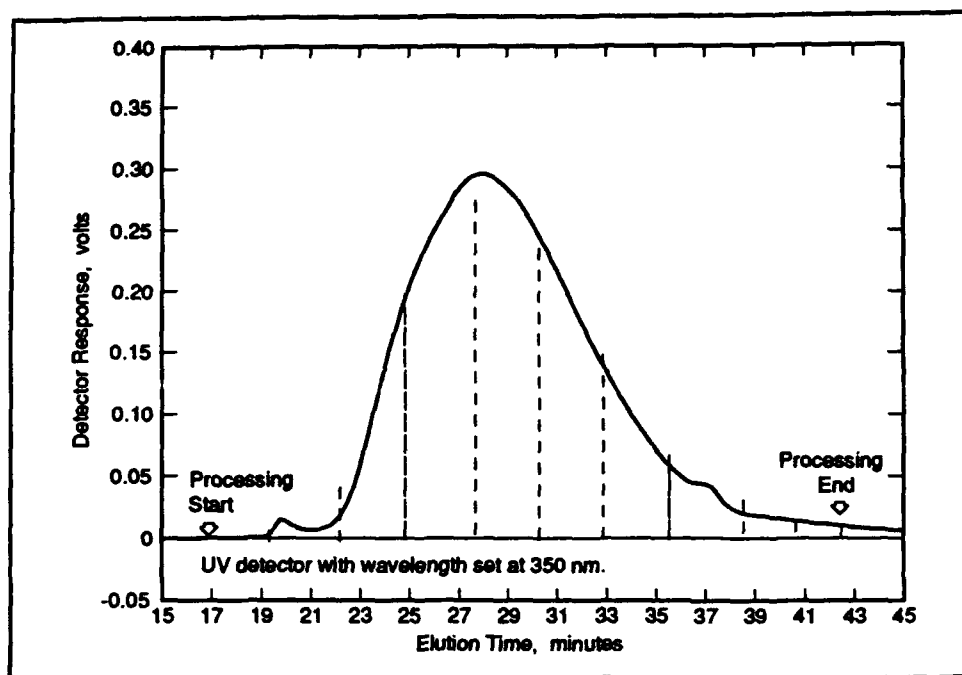


Figure 17. Chromatogram portioned into tenths

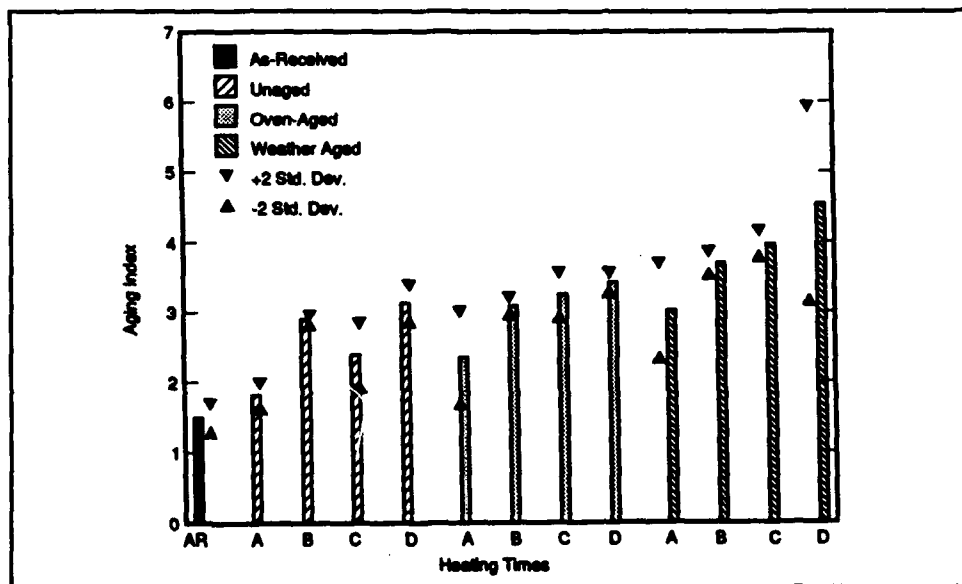


Figure 18. Aging index of FPL 6522 using area percentages of slices 1 and 2

was exposed to aging. The percentage of material eluting in the early fraction also increased as the sealant was exposed to longer heating times with the one exception, the FPL 6522-C unaged sample. The trend indicated by the calculated aging index was similar to the increase in the early fraction predicted by the literature, but it did not correlate with the physical test data obtained in Phases I and II. Also, when ± 2.0 standard deviations were included with the aging index, the variability in the GPC test procedure or the nonuniformity of the sealant was evident.

FPL 6527

A total of 10 FPL 6527 sealant conditions were analyzed using GPC. All 10 of the sealant conditions had a 95 percent confidence region that was approximately 0.05 or less at the widest point. The reproducibility of the FPL 6527 samples improved as compared to the FPL 6522 samples based on the 0.05 criteria and by the fact that the maximum peak heights of the FPL 6527 chromatograms were more consistent than the maximum peak heights of the FPL 6522 chromatograms. The consistency of the maximum peak heights allowed a confidence region maximum width of approximately 10 percent of the maximum detector response or 0.03 to be selected. Seven of the 10 FPL 6527 sealant conditions had a confidence region width of 0.03 or less at the widest point. The sealant conditions which did not meet the 0.03 criteria were the 6527 as-received, 6527-C oven-aged, and 6527-C weather-o-meter aged chromatograms. These three confidence regions had a maximum width of 0.05. Even though an increase in reproducibility of the GPC technique was exhibited, the confidence regions of the various sealant conditions overlapped one another. Therefore, only generalized trends can be discussed concerning FPL 6527.

The improvement in reproducibility could possibly be attributed to either a change in sample preparation procedures or a change in the material characteristics between the two sealants. A change in sample preparation could have occurred because the operator had become more familiar with the GPC technique and with the sensitivity of the GPC technique to sample preparation. However, the more probable cause of the increased reproducibility was the fact that FPL 6527 appeared to be a more uniform material and was more soluble in THF than FPL 6522. The increase in solubility of FPL 6527 was based upon an observable decrease in the amount of filler material remaining on the filter paper during sample preparation. The reduction in filler material translated to a more consistent sample being injected into the GPC.

The four chromatograms for each FPL 6527 sealant condition and the 95 percent confidence region for each sealant condition are provided in Appendix C. The FPL 6527 as-received sample was taken from the block of sealant after it had been logged into the laboratory in the same manner as the as-received sample of FPL 6522.

The FPL 6527-A sealant condition chromatograms and the FPL 6527 as-received chromatogram are provided in Figure 19. The second peak of these chromatograms exhibited an increase as the sealant was heated to pour into the Federal Specification SS-S-1401C test specimen molds. But the sealant exhibited a decrease as it was aged in the oven and the weather-o-meter. The decrease observed in these chromatograms was not the same type of decrease detected in the FPL 6522-A average chromatograms illustrated in Figure 9, and consequently, was not believed to be a result of varying sample concentration. A shift in the second peak toward the early fraction and the development of a shoulder at approximately 23 min indicated that the sealant hardened as it was heated and aged.

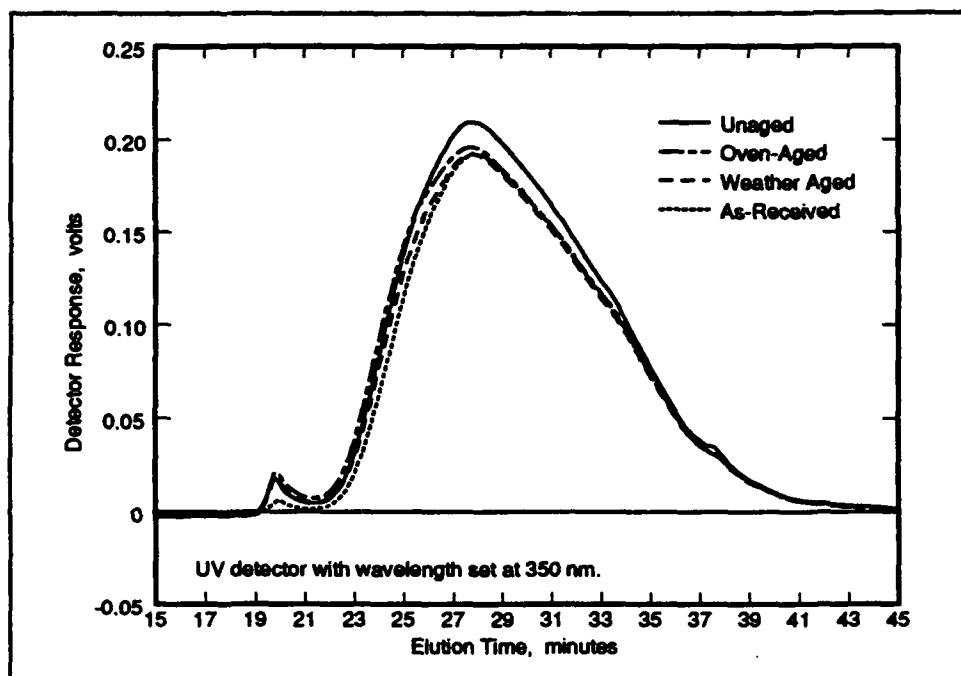


Figure 19. FPL 6527-A average chromatograms

The first peak of FPL 6527-A as illustrated in Figure 20, occurred at approximately 19 min. The peak exhibited an increase from the as-received to the unaged and aged specimens. From the chromatograms shown in Figure 20, it would be expected that the unaged penetration value should be the highest, followed closely by the weather-o-meter aged penetration value, and the oven-aged penetration value should be the lowest. The results in Table 5 for FPL 6527-A did not follow this trend.

The average chromatograms of FPL 6527-B illustrated in Figure 21 also indicated a shift toward the early fraction as the material was aged. The shifting toward the early fraction was accompanied with the development of a shoulder between 23 and 25 min, and an increase in height of the first peak. The change in profiles from the as-received to the unaged and aged chromatograms was similar to those typically expected from the literature review for a material that has been aged. The relative hardness of the sealant material as

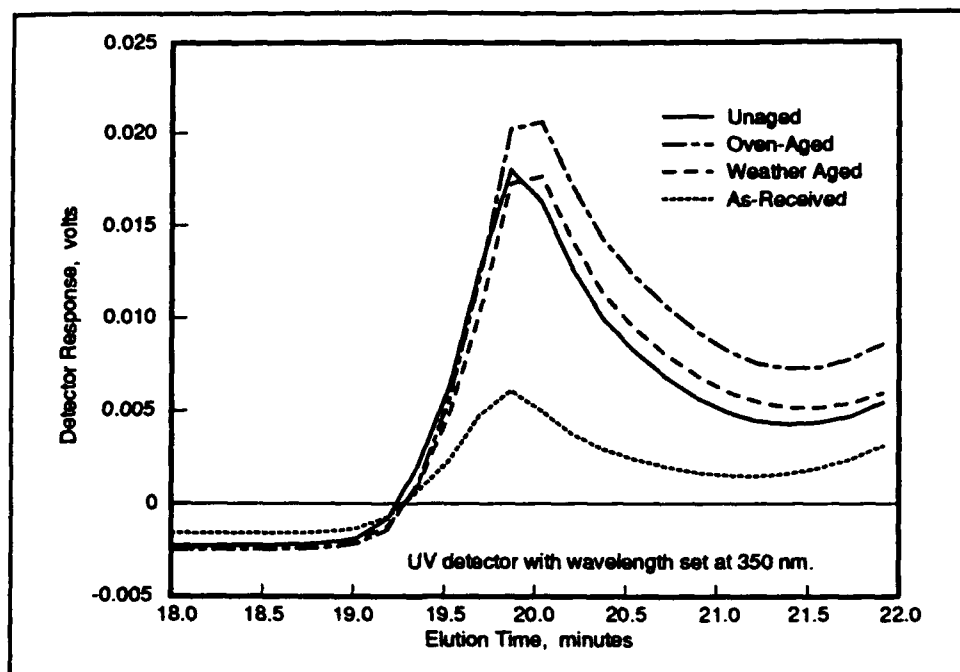


Figure 20. FPL 6527-A average chromatograms from 18 to 22 min

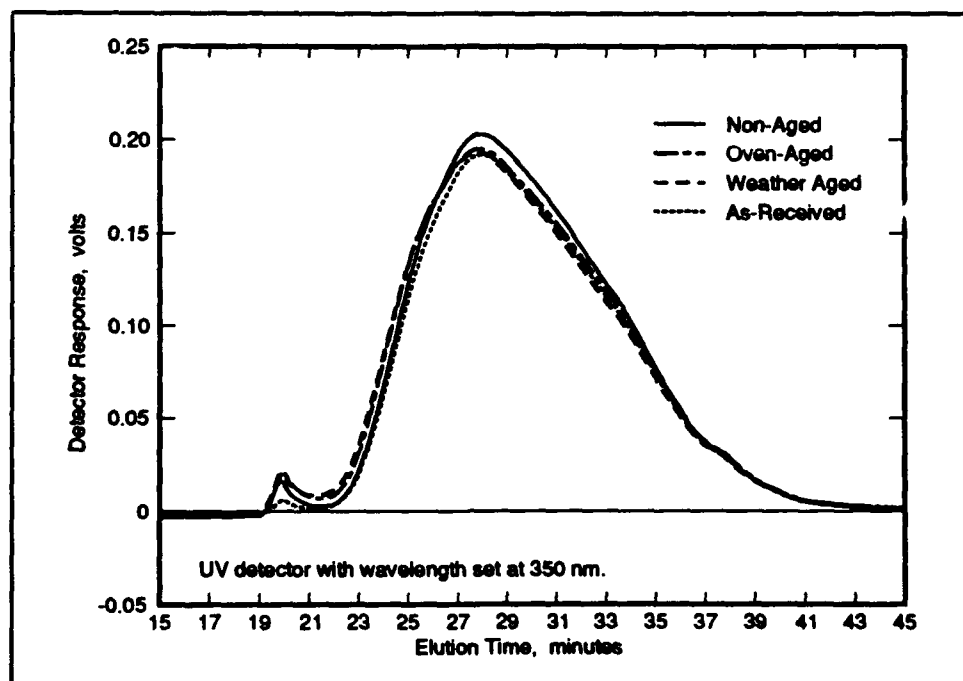


Figure 21. FPL 6527-B average chromatograms

predicted by visual evaluation of the first peak chromatograms shown in Figure 22 would be that the weather-o-meter aged specimen should be harder than the oven-aged specimen, and the unaged specimen should be softer than both of the aged specimens. The penetration values provided in Table 5 for FPL 6527-B followed the expected trend.

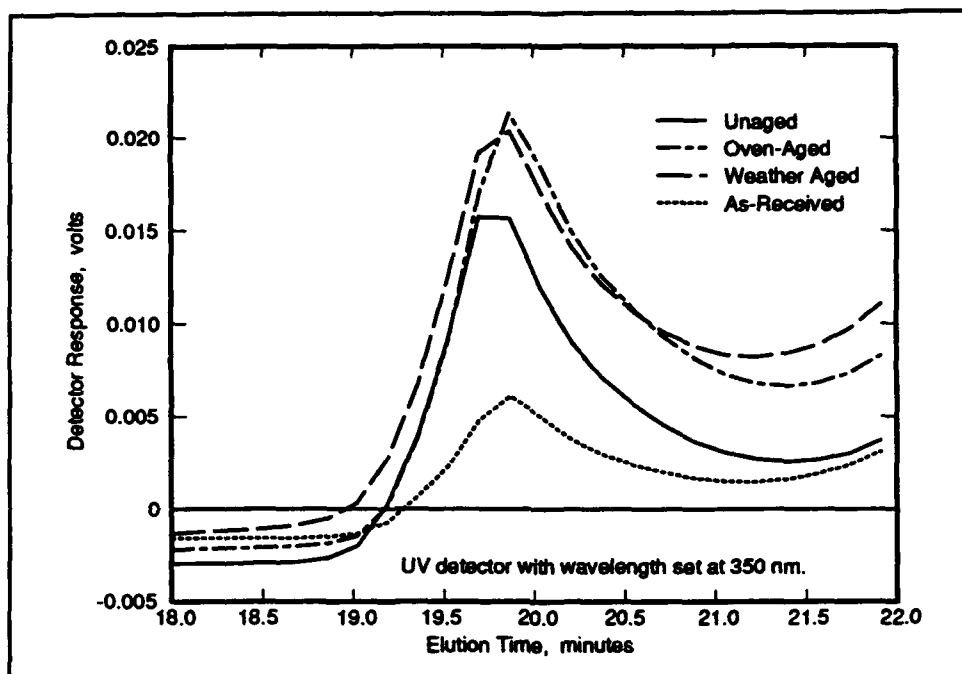


Figure 22. FPL 6527-B average chromatograms from 18 to 22 min

The average chromatograms for FPL 6527-C in Figure 23 also exhibited a shift toward the early fraction coupled with the development of a shoulder between 23 and 25 min and a significant increase in the height of the first peak. Figure 24 presents a closer examination of the first peak. In Figure 24 the ordinate was increased from a maximum of 0.025 to 0.05. This increase indicated that heating the sealant for 3 hr greatly increased the large molecular size fraction. The chromatograms in Figure 24 also indicate that the oven-aged and weather-o-meter aged specimens should have very similar penetration values. However, the penetration results from Table 5 did not agree with the chromatogram results.

The FPL 6527 chromatograms indicated that differences can be detected as a sealant was aged and as the heating time was extended. But, as with the FPL 6522 chromatograms, these visual differences were inconsistent, and the changes that occurred may be defined as insignificant because some of the 95 percent confidence regions of the chromatograms overlapped. The slice data for each sealant condition and summarized percent average area per slice data are provided in Appendix D.

The aging index was calculated for each of the FPL 6527 sealant conditions and the results are illustrated in Figure 25. The calculated aging index

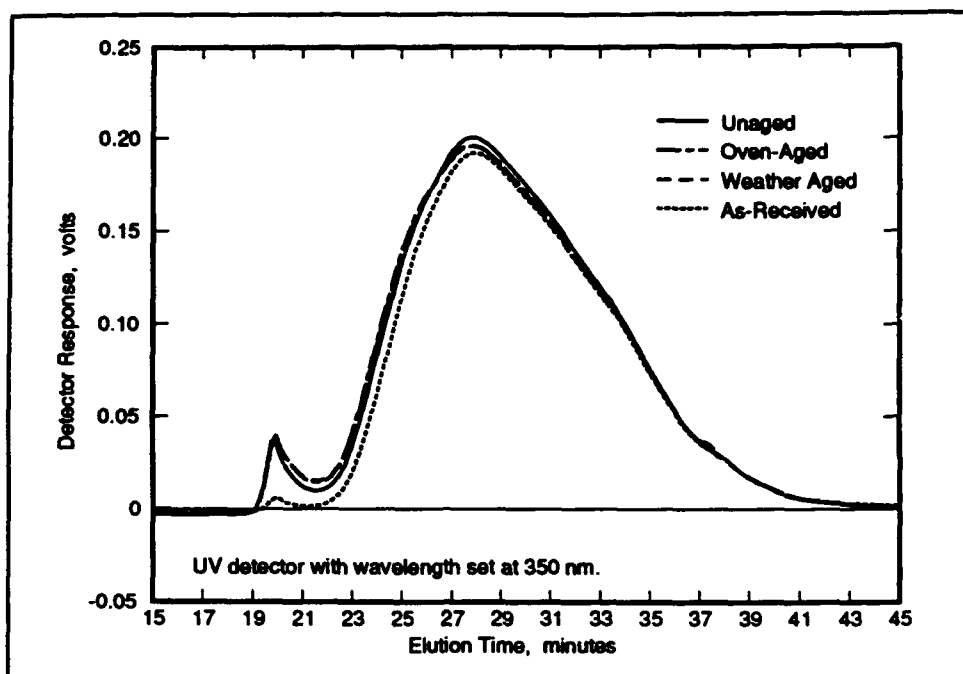


Figure 23. FPL 6527-C average chromatograms

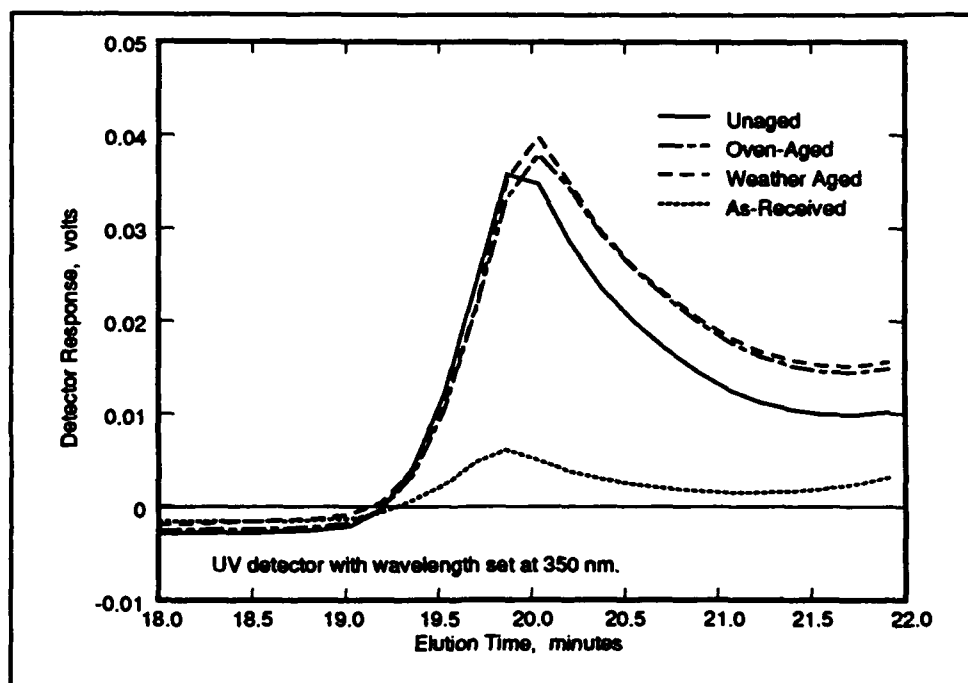


Figure 24. FPL 6527-C average chromatograms from 18 to 22 min

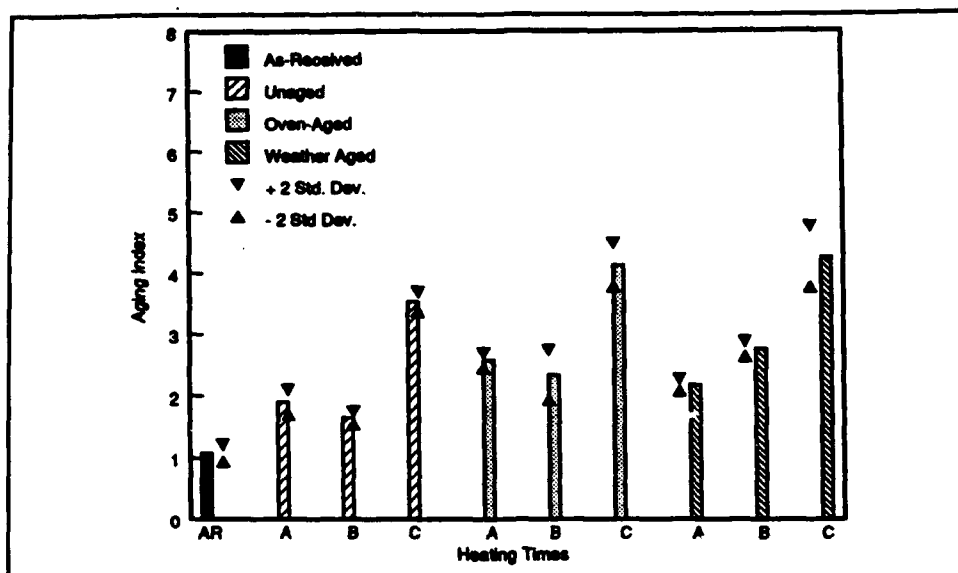


Figure 25. Aging index of FPL 6527 using area percentages of slices 1 and 2

for all of the FPL 6527 sealant conditions indicated that the percentage of material eluting in the early fraction increased as the sealant was exposed to aging. With the exception of the FPL 6527-A results, the weather-o-meter aged samples had a higher aging index than the oven-aged samples. The percentage of material eluting in the early fraction also increased as the sealant was exposed to longer heating times with the exception of the FPL 6522-B unaged and oven-aged samples. The trend indicated by the calculated aging index was similar to the increase in the early fraction predicted by the literature, but it did not correlate with the physical test data obtained in Phases I and II. When ± 2.0 standard deviations were included with the aging index, the variability in the GPC test procedure and/or the nonuniformity of the sealant was again evident.

6 Summary, Conclusions, and Recommendations

Summary

This research program was conducted to evaluate the use of GPC as a test method to identify improperly prepared hot-applied pavement joint sealants and to detect changes in the sealant materials caused by aging. The research effort consisted of a literature review and a three-phase laboratory study on laboratory prepared and aged specimens. Phases I and II of the laboratory study involved material property testing of two pavement joint sealant materials. The two sealants tested were hot-applied asphalt-based materials manufactured to meet the requirements of Federal Specification SS-S-1401C. Phase III testing was the GPC analysis of sealants tested in Phases I and II. The objective of this research was to determine if GPC could be used to identify or detect changes in the sealants caused by prolonged heating and/or aging. The research objective was partially achieved. The GPC technique did detect changes in the various sealant samples, but the changes were inconsistent and did not correlate to physical test data.

The review of the literature indicated that GPC had been used extensively to analyze polymeric materials, and attempts had been made to analyze non-polymeric materials such as asphalt cements. However, no data were found concerning the GPC analysis of pavement joint sealant materials. The majority of the literature concluded that changes in the analyzed materials which were caused by aging could be detected using GPC. Opinions varied concerning the significance of changes that are detected when analyzing non-polymeric materials using GPC, but the literature generally agreed that an increase in the early fraction portion of the chromatogram indicates a hardening of the material being analyzed.

The Phase I testing indicated that both of the sealants which were manufactured to meet the requirements of Federal Specification SS-S-1401C did not meet those requirements. Phase II testing was designed to determine the effects different heating times and various types of artificial aging on the physical properties specified in the Federal Specifications. The Phase II testing indicated that changes could be detected in the penetration results of most of the sealants, but the changes did not necessarily follow expected trends, and

the changes detected within a specific sealant were inconsistent. The expected trend would be for the penetration values to decrease as the sealant is aged, and as it is exposed to extended heating times.

During the Phase III testing, an aging index was developed in an attempt to define increases in the early fraction that were expected to occur during aging and extended heating. It was determined that visual evaluation of the chromatograms would not be sufficient for a comparative analysis because of fluctuations in the base lines of the chromatograms. To compensate for these changes, the chromatograms were partitioned into 10 slices and the area in each of these slices was normalized to give an area percentage of each slice. The aging index was arbitrarily chosen to be the sum of the normalized area of the first two slices of the chromatograms. It was believed that the aging index would be more representative of any changes that occurred in the early fraction. Table 6 provides the summarized trends for the two sealants. The specific trends include penetration testing, analysis of the first peak of the chromatograms, and the aging index.

Table 6 Summarized Trend Analysis ¹			
Sealant Material	Penetration Results	First Peak	Aging Index
FPL 6522	General decrease as sealant was aged but increase with extended heating time.	No consistent trend as the sealant was aged or as heating time increased.	General increase as sealant was aged and as heating time increased.
FPL 6527	General decrease as sealant was aged but increase with extended heating time.	General increase as sealant was aged and as heating time was extended.	General increase as sealant was aged but no consistent trend with extended heating.
¹ Only generalized trends are presented here. There were several exceptions to the trends and overlapping of the 95 percent confidence region occurred between specimens.			

Conclusions

Based on the results of the investigation including the literature review and the three-phase laboratory study, the following conclusions were made concerning the use of GPC as a method to identify joint sealants which have been improperly prepared, and how the improper preparation affects the physical properties of the sealant:

- a. GPC can be used to detect changes in a sealant caused by extended heating or aging if the original material has been evaluated. The changes that were detected are qualitative not quantitative, and the changes did not correlate with physical tests such as penetration.

- b.* The aging index established for the joint sealant materials during the GPC analysis exhibited a trend which indicated that extended heating and aging of the sealants increased the early fraction of the chromatogram. However, the trend was not consistent for both joint sealant materials.
- c.* The chromatograms obtained by analyzing the joint sealant materials had significant variability. When 95 percent confidence regions were established for individual sealant conditions, several of them overlapped. Therefore, GPC analysis of unknown sealant samples would be difficult.
- d.* The procedures used to conduct the GPC analysis are extremely important. The procedures must be carefully thought out and patiently followed. Any deviation from the prescribed procedures will adversely affect the resulting chromatograms.
- e.* Any changes in equipment, especially in the columns, will affect the resulting chromatograms. Therefore, reproducibility of GPC analysis of pavement joint sealants between laboratories will be difficult.
- f.* Penetration values of the sealants generally exhibited a change as the sealants were exposed to extended heating or to artificial aging. The changes in penetration were not consistent with expected trends, and the amount of change varied with each sealant.
- g.* Changes experienced in the penetration values did not appear to affect the various sealants' ability to adhere to concrete as demonstrated by satisfactory results of almost all of the bond testing. Subsequently, correlations between field performance characteristics such as adhesion and the penetration results were not exhibited.

Recommendations

Based on the literature review and laboratory analysis of this research effort, the following recommendations were made:

- a.* To maximize the potential use of GPC in the analysis of sealants, alternate detection methods such as a photodiode array (PDA) should be investigated. The PDA can analyze several wavelengths at the same time, and, therefore, may provide a clearer "fingerprint" of the sealant being evaluated. The PDA could also allow the variability of the sealant materials to be more readily defined.
- b.* Investigations which combine techniques such as fourier transform infrared spectroscopy (FTIR) with GPC should be conducted. This type of analysis should provide a more quantitative analysis of the sealants.

- c. Round robin testing should be conducted on the laboratory test procedures used to evaluate the physical properties of joint sealants and on GPC analysis of nonpolymeric materials. The round robin testing would allow significant changes in penetration and resilience testing, and chromatograms to be defined.
- d. Research is still required to develop a test method that more accurately detects sealant materials that have been improperly prepared and installed. Investigations are also required to determine realistic life cycles and working ranges of pavement joint sealant materials.
- e. There is a need to standardize a sampling procedure for joint sealing materials that are solid at room temperature to assure that the same material as that which is mixed in the melter in the field is tested.

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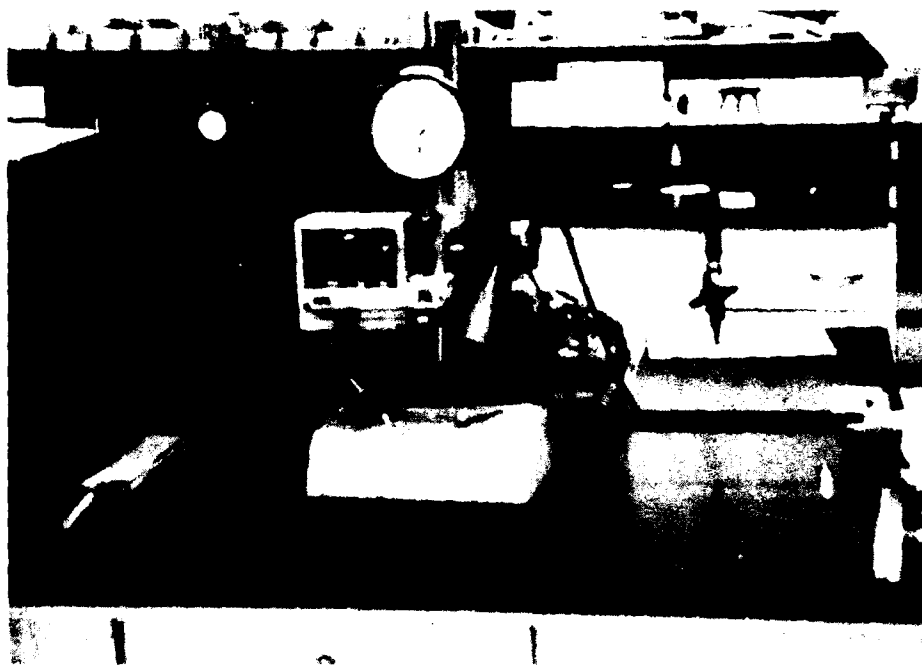


Photo 1. Penetrometer with optional cone

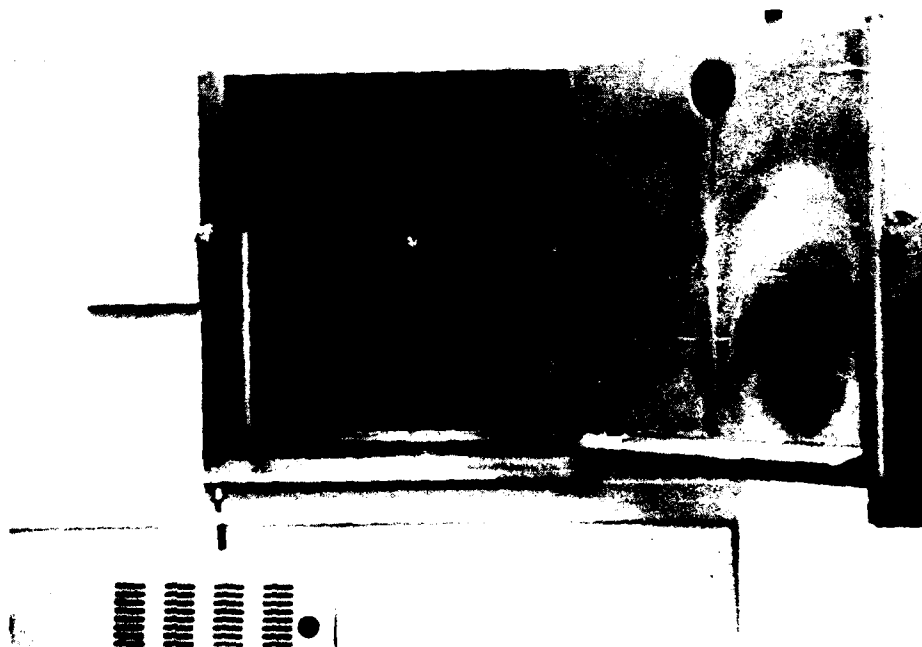


Photo 2. Twin-enclosed carbon arc weather-o-meter

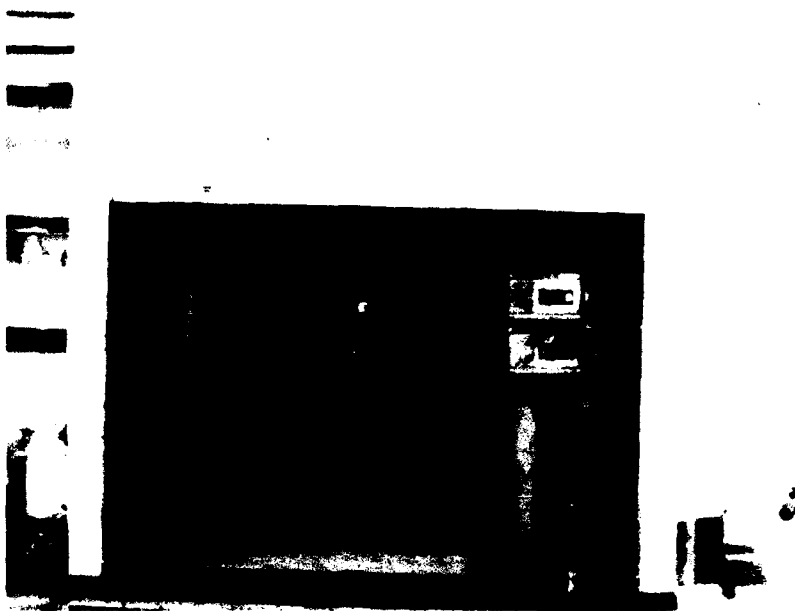


Photo 3. Melter used to prepare hot-applied sealants

Appendix A

FPL 6522 Chromatograms

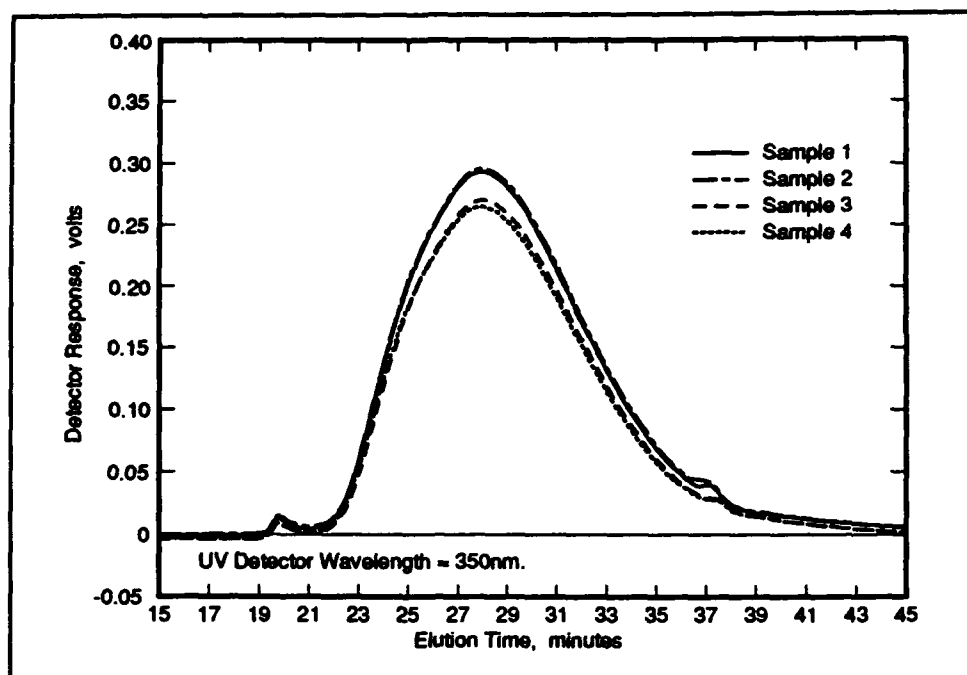


Figure A1. FPL 6522 as-received chromatograms

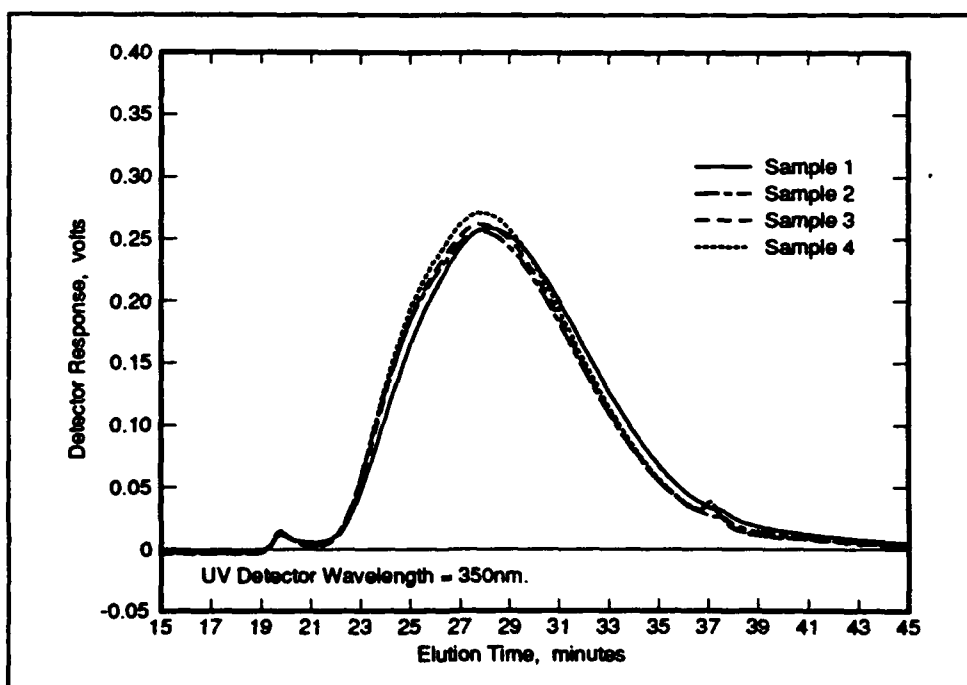


Figure A2. FPL 6522-A unaged chromatograms

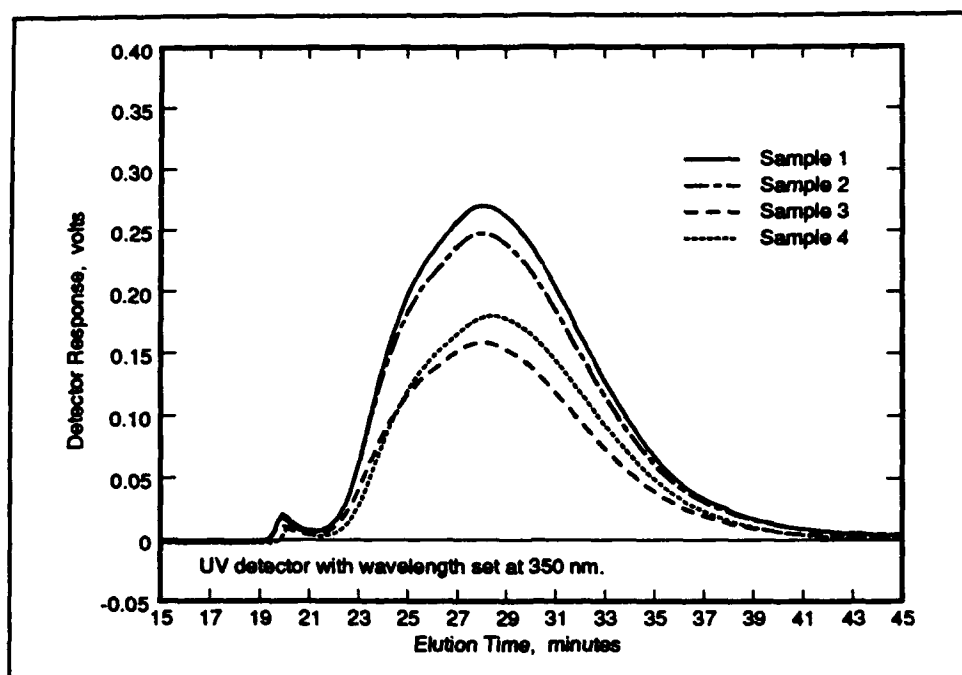


Figure A3. FPL 6522-A oven-aged chromatograms

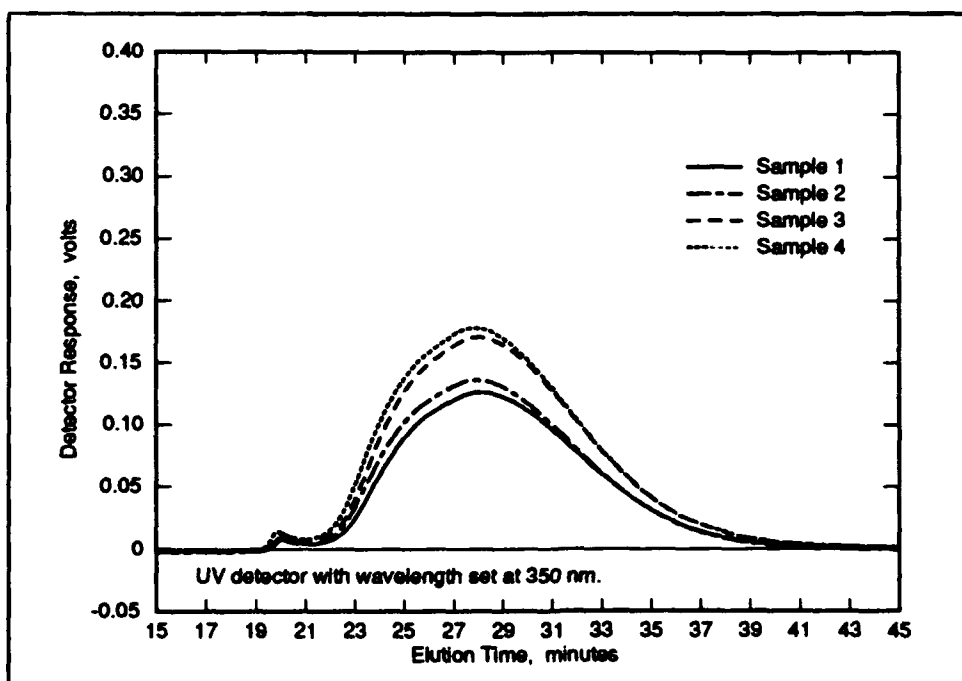


Figure A4. FPL 6522-A weather-o-meter aged chromatograms

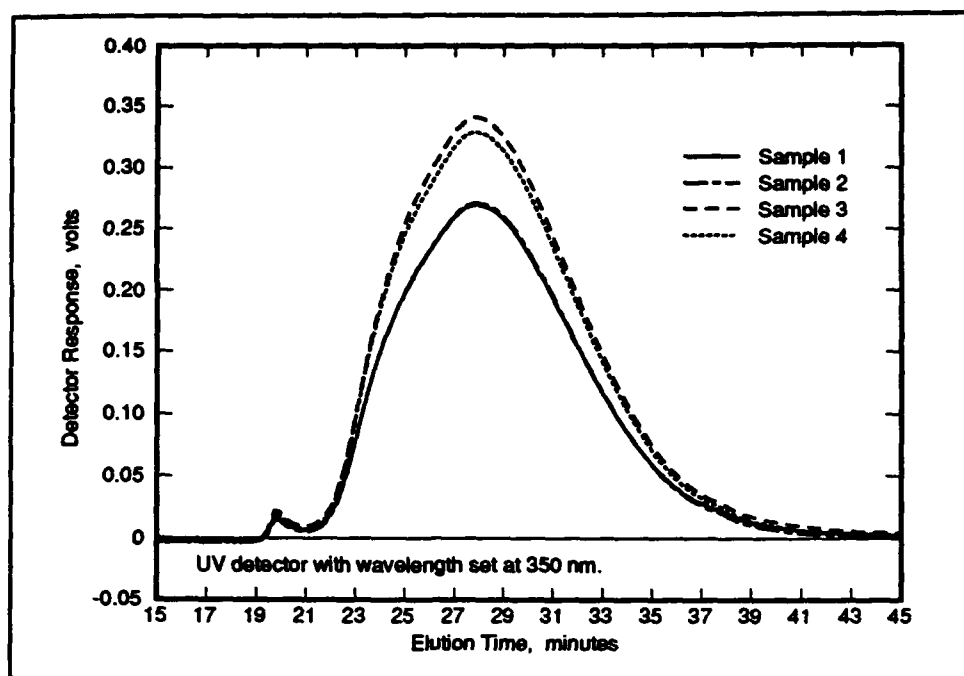


Figure A5. FPL 6522-B unaged chromatograms

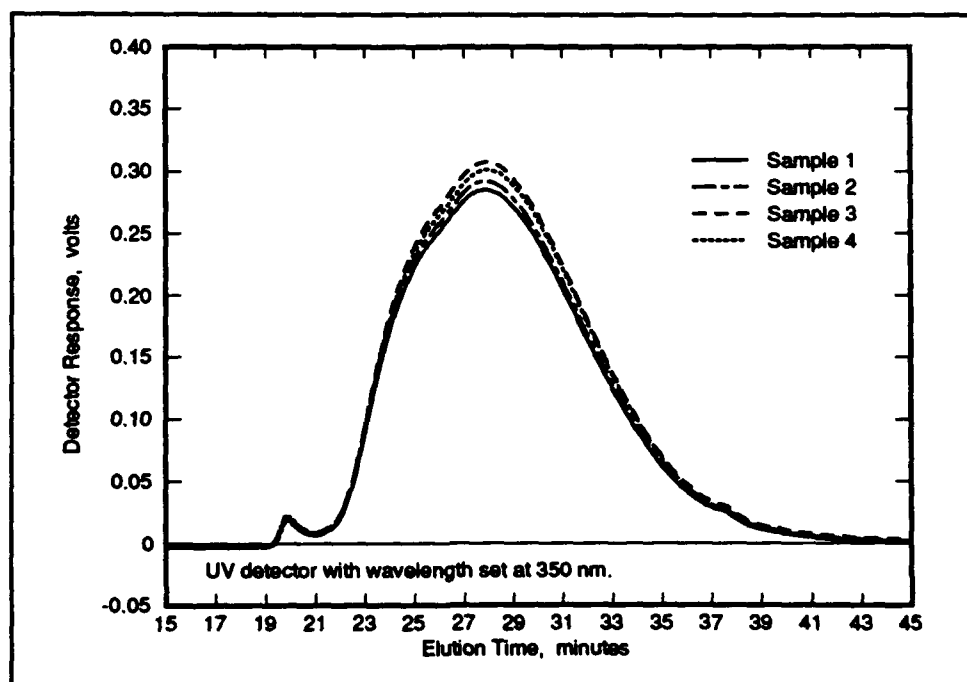


Figure A6. FPL 6522-B oven-aged chromatograms

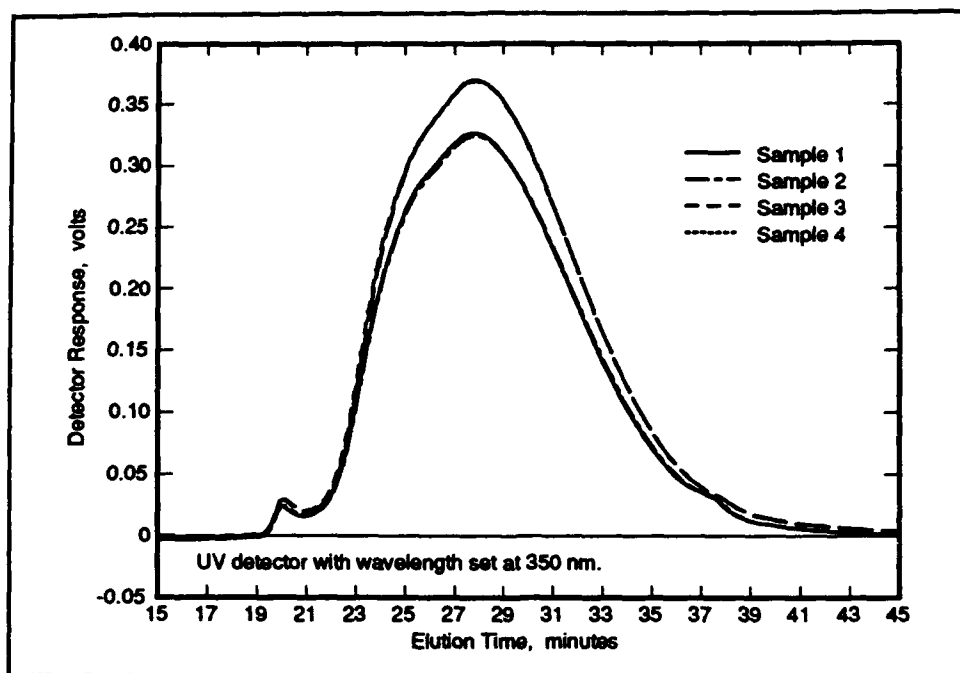


Figure A7. FPL 6522-B weather-o-meter aged chromatograms

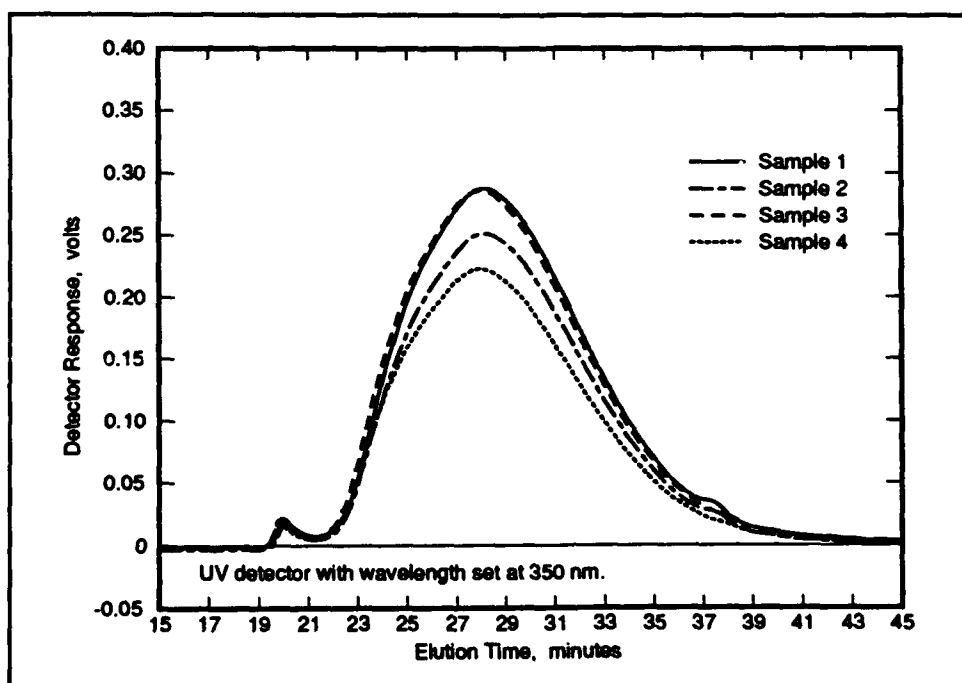


Figure A8. FPL 6522-C unaged chromatograms

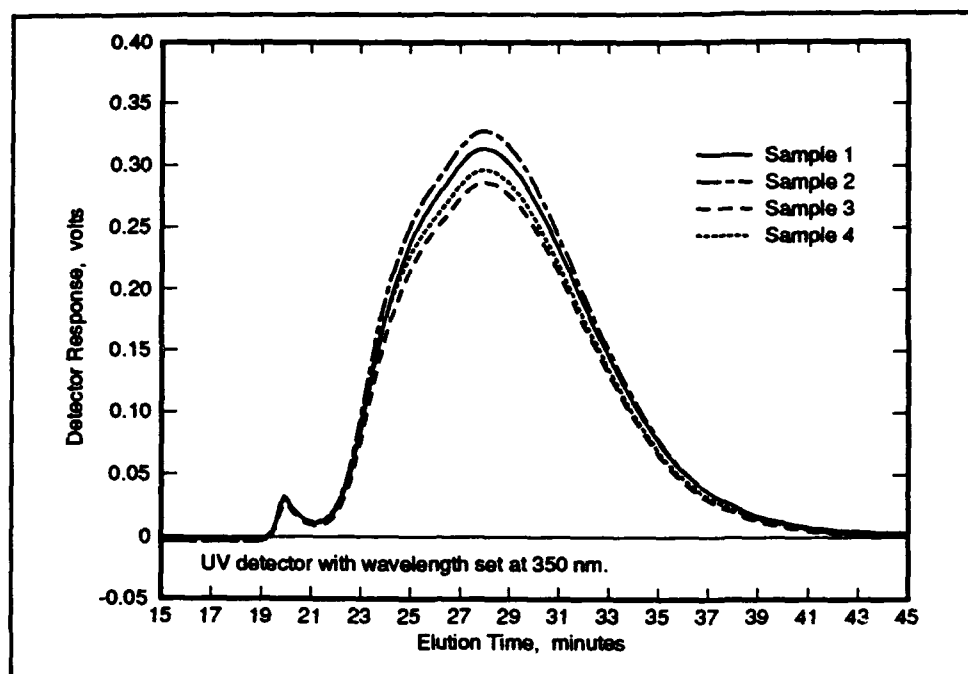


Figure A9. FPL 6522-C oven-aged chromatograms

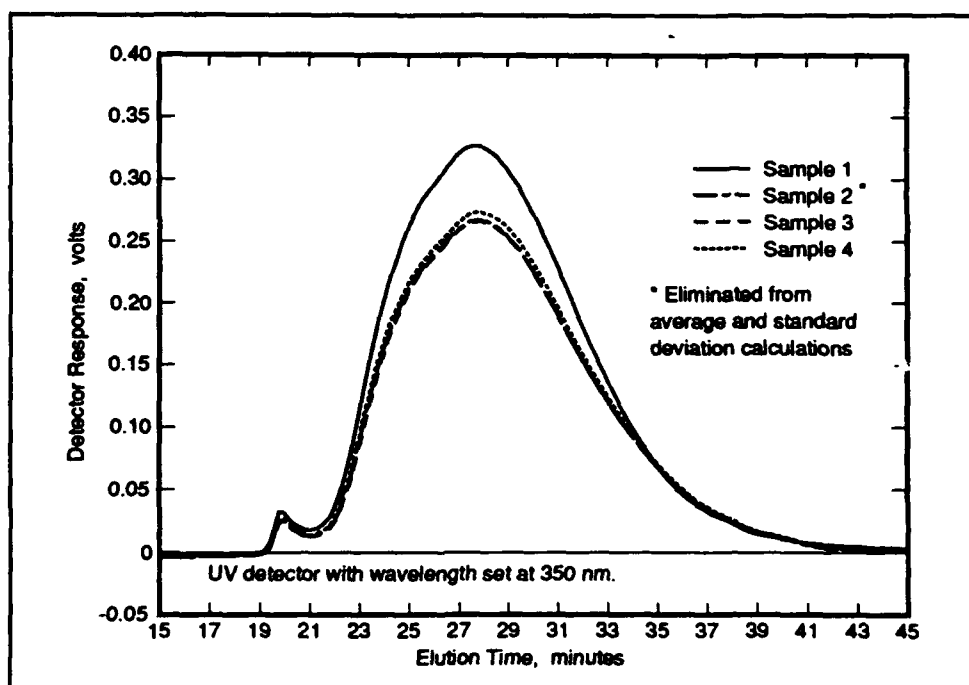


Figure A10. FPL 6522-C weather-o-meter aged chromatograms

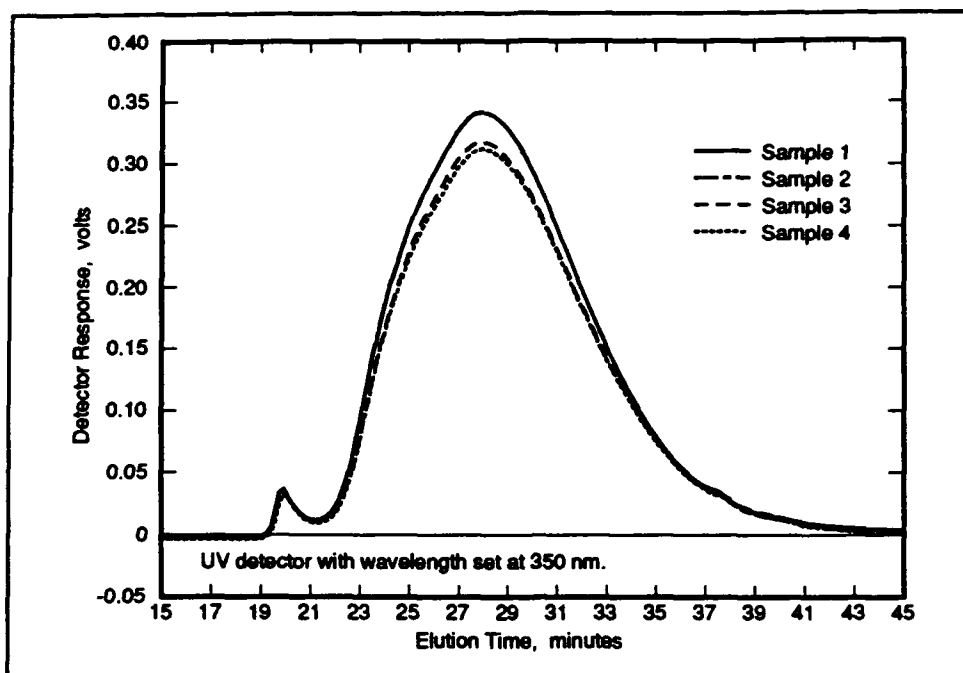


Figure A11. FPL 6522-D unaged chromatograms

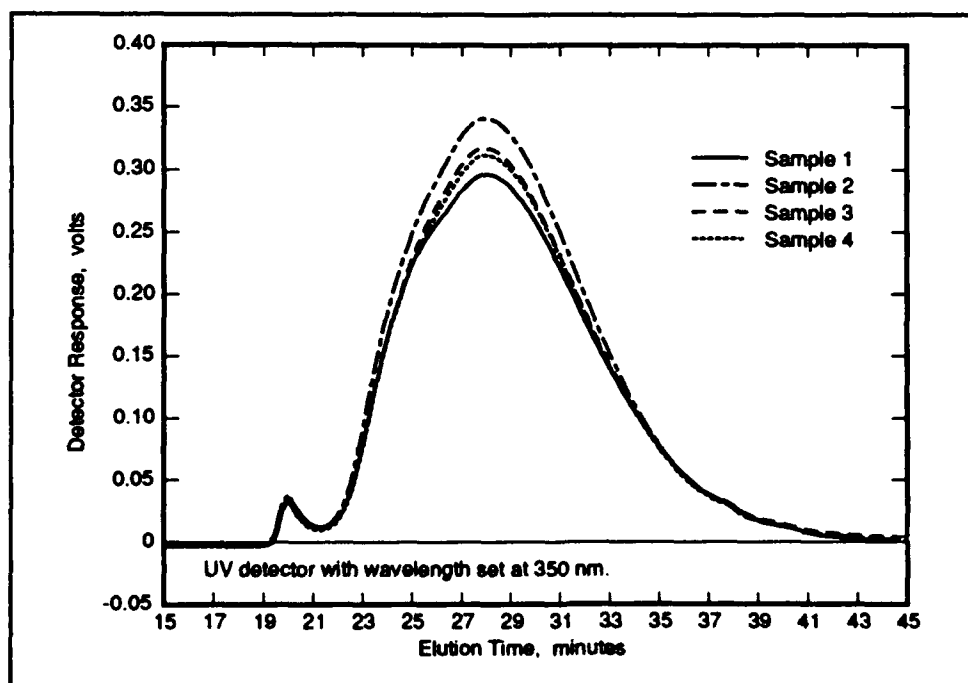


Figure A12. FPL 6522-D oven-aged chromatograms

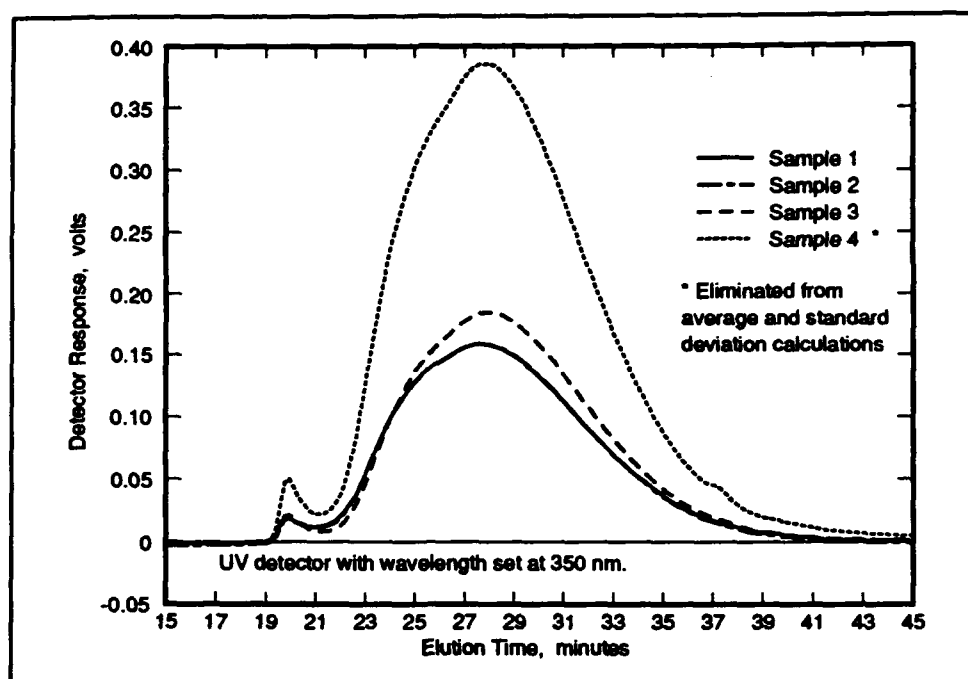


Figure A13. FPL 6522-D weather-o-meter aged chromatograms

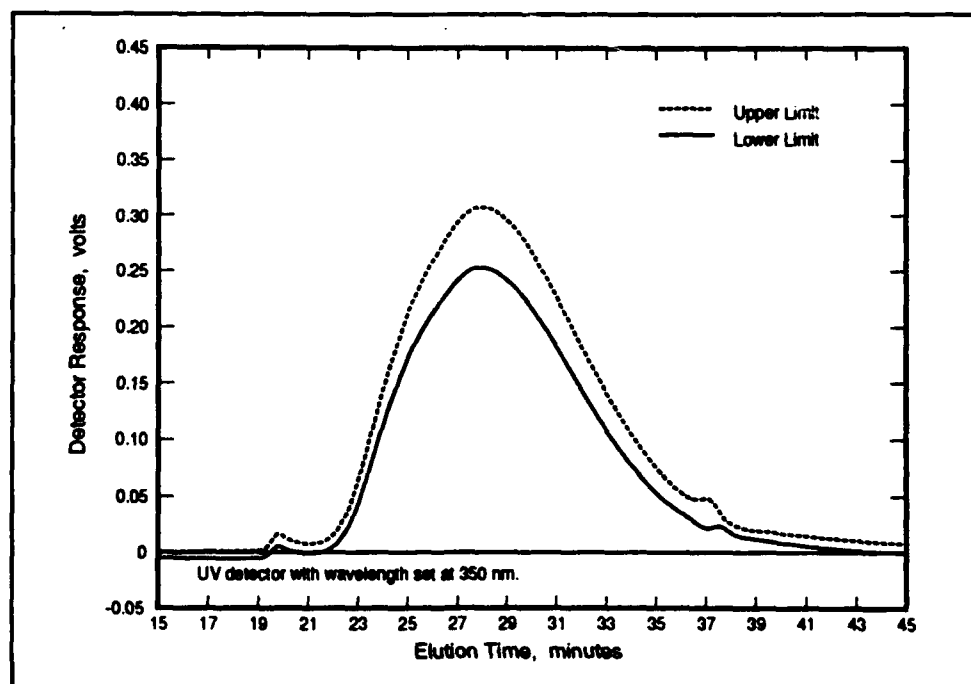


Figure A14. FPL 6522 as-received chromatogram 95 percent confidence region

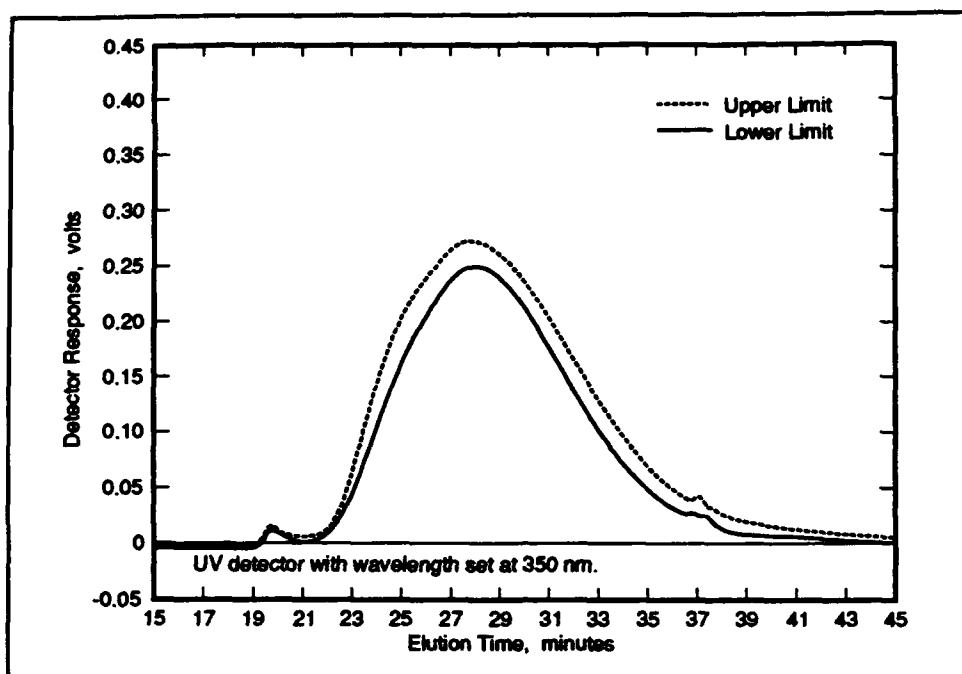


Figure A15. FPL 6522-A chromatogram 95 percent confidence region

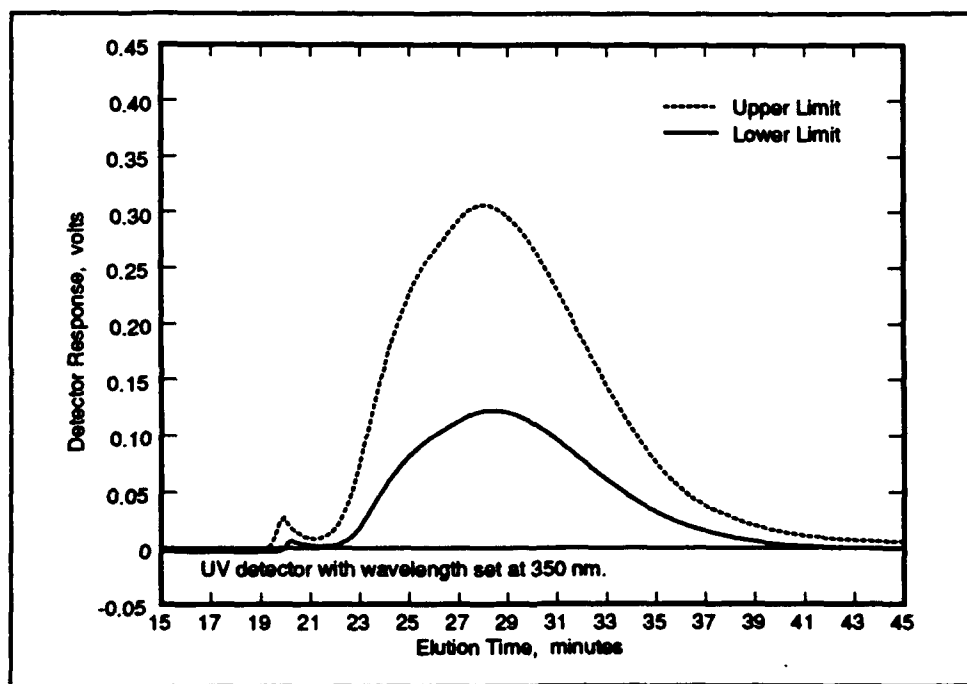


Figure A16. FPL 6522-A oven-aged chromatogram 95 percent confidence region

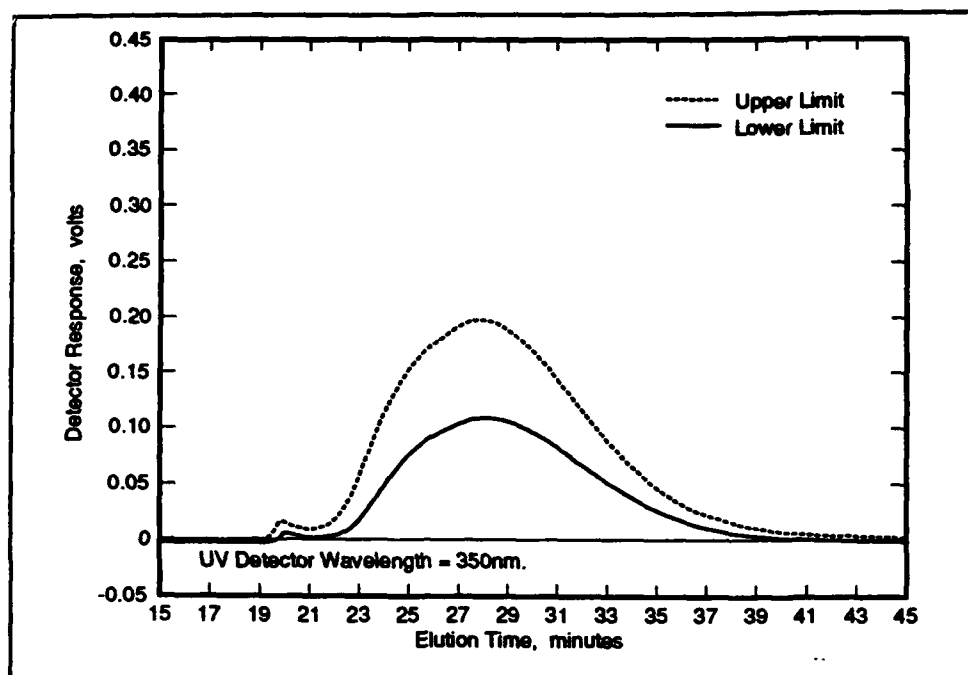


Figure A17. FPL 6522-A weather-o-meter aged chromatogram 95 percent confidence region

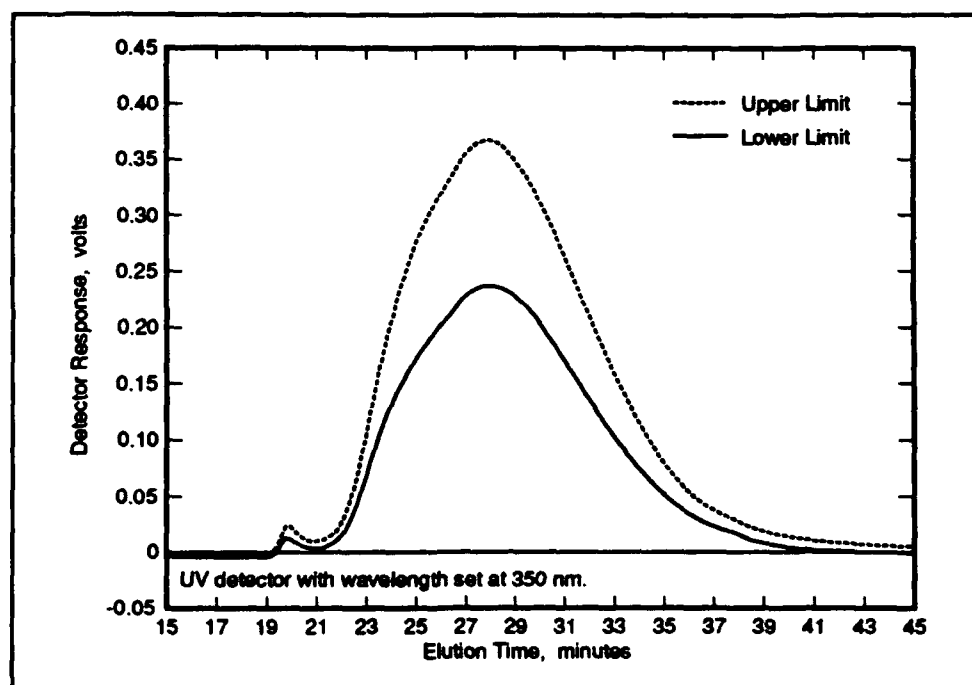


Figure A18. FPL 6522-B unaged chromatogram 95 percent confidence region

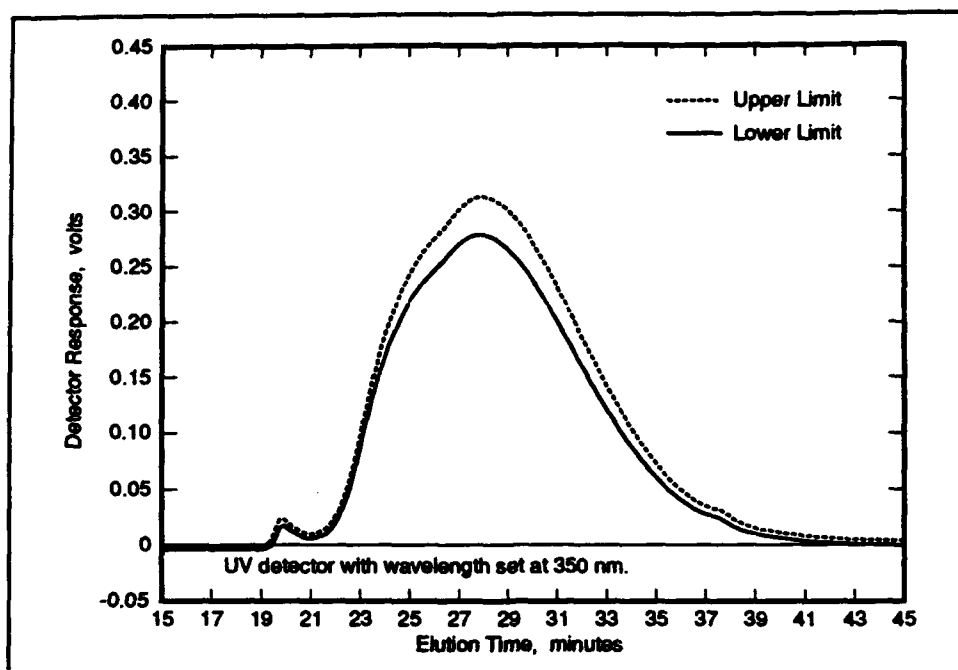


Figure A19. FPL 6522-B oven-aged chromatogram 95 percent confidence region

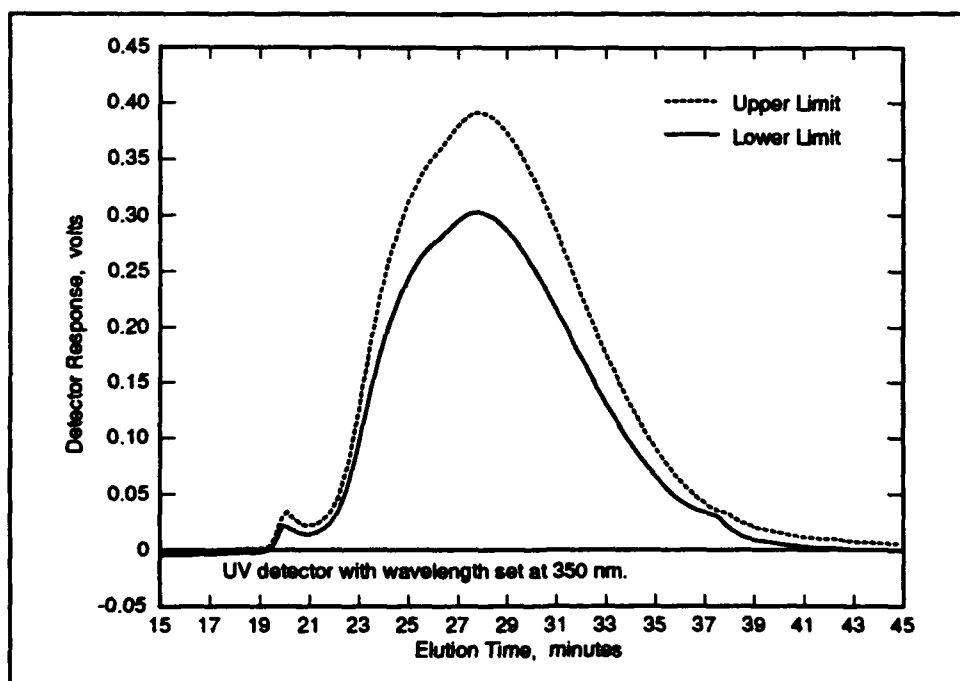


Figure A20. FPL 6522-B weather-o-meter aged chromatogram 95 percent confidence region

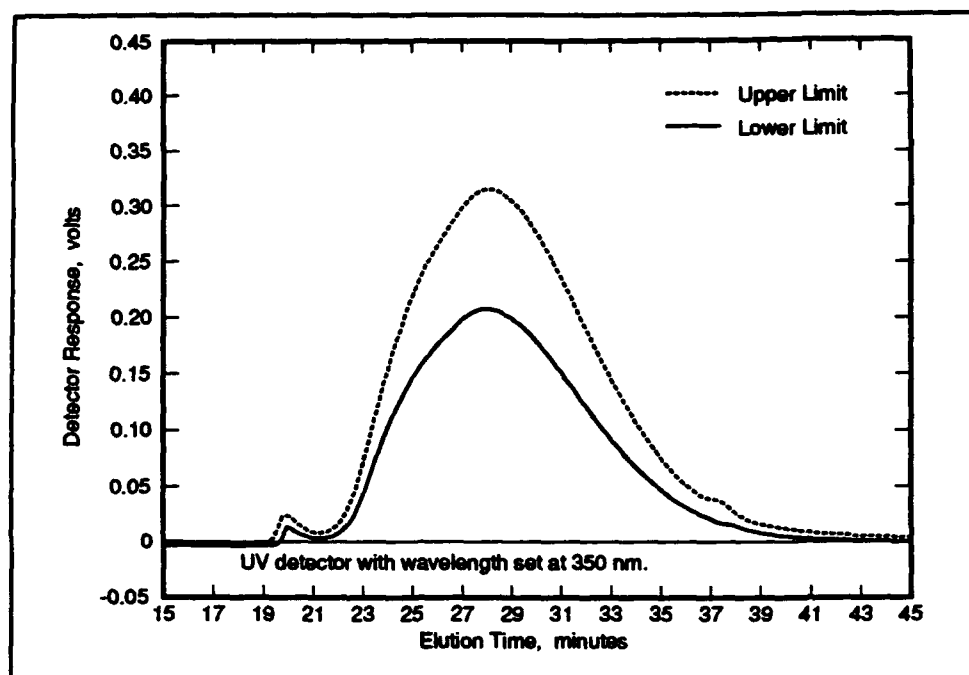


Figure A21. FPL 6522-C unaged chromatogram 95 percent confidence region

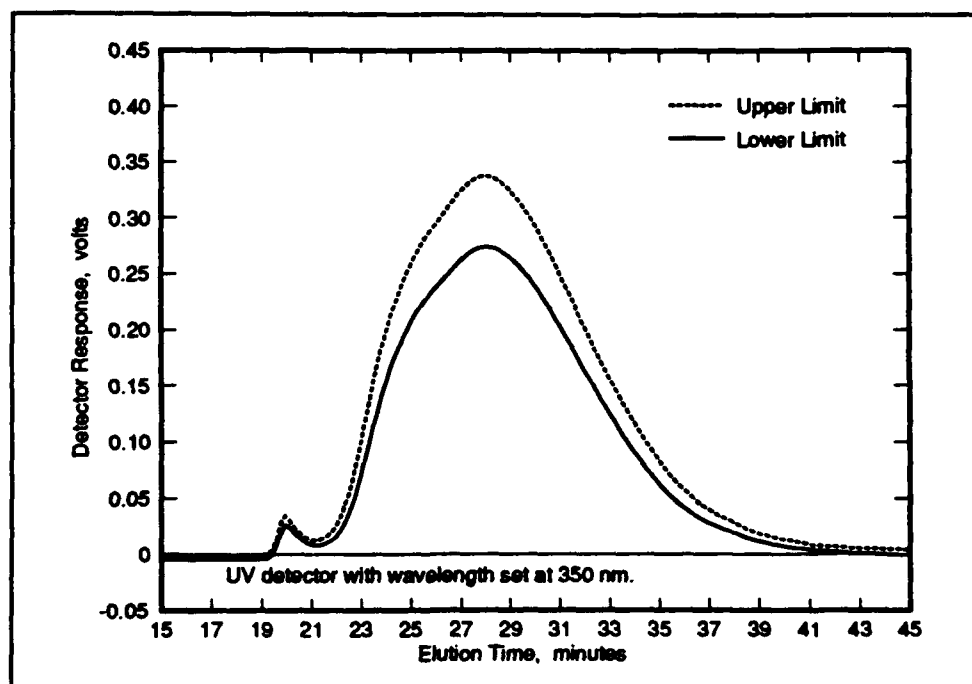


Figure A22. FPL 6522-C oven-aged chromatogram 95 percent confidence region

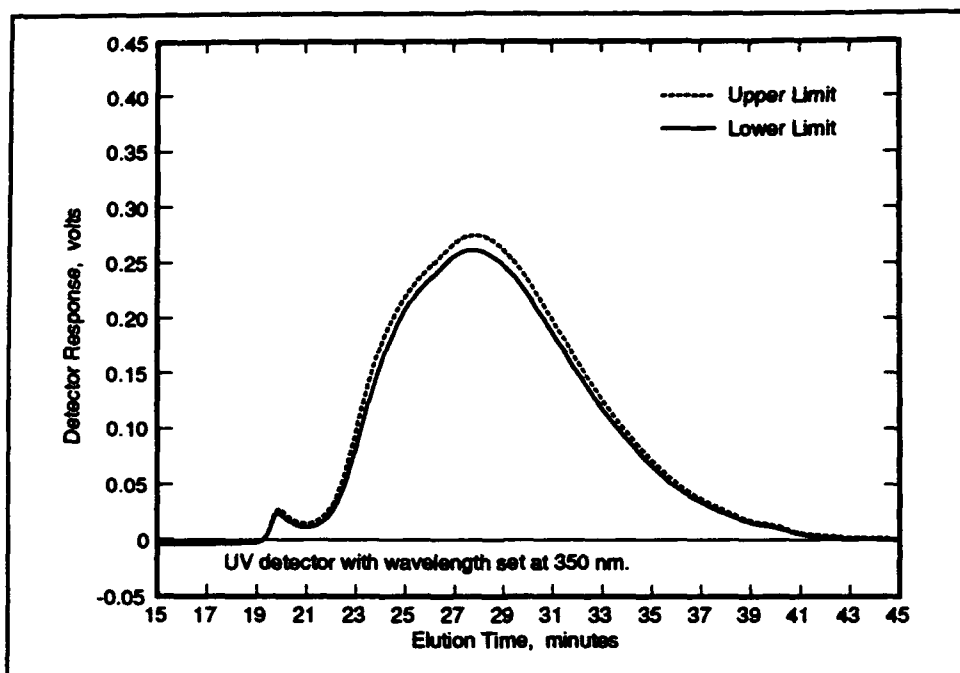


Figure A23. FPL 6522-C weather-0-meter aged chromatogram 95 percent confidence region

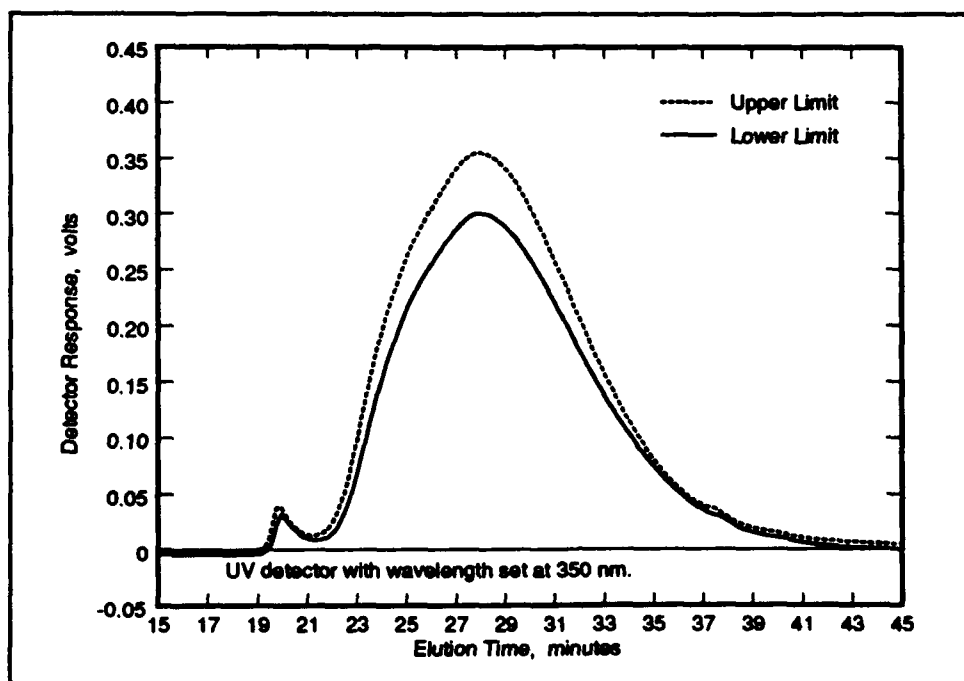


Figure A24. FPL 6522-D unaged chromatogram 95 percent confidence region

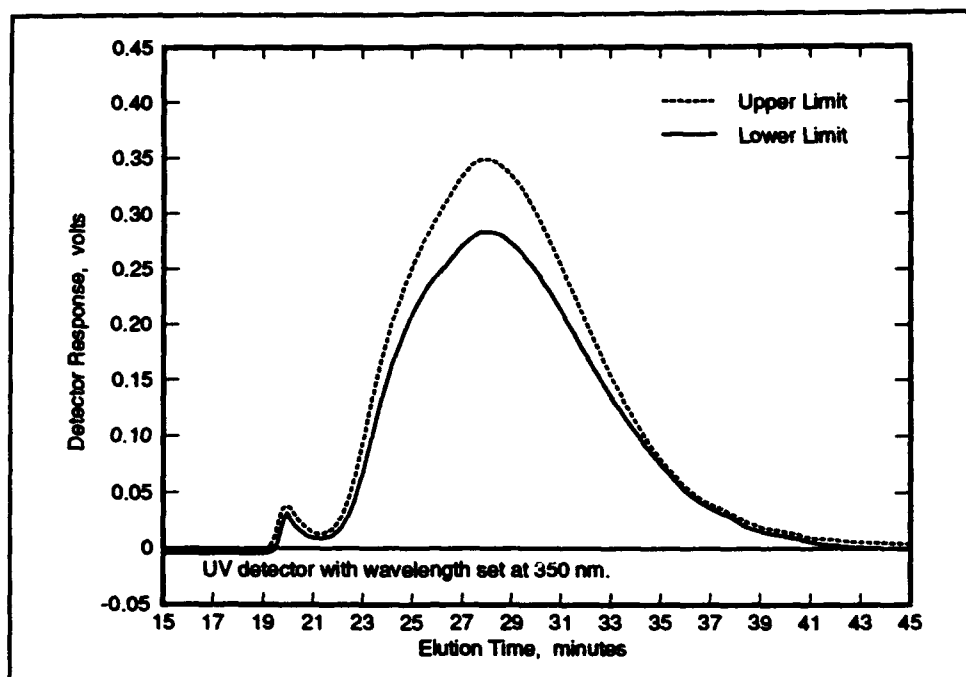


Figure A25. 6522-D oven-aged chromatogram 95 percent confidence region

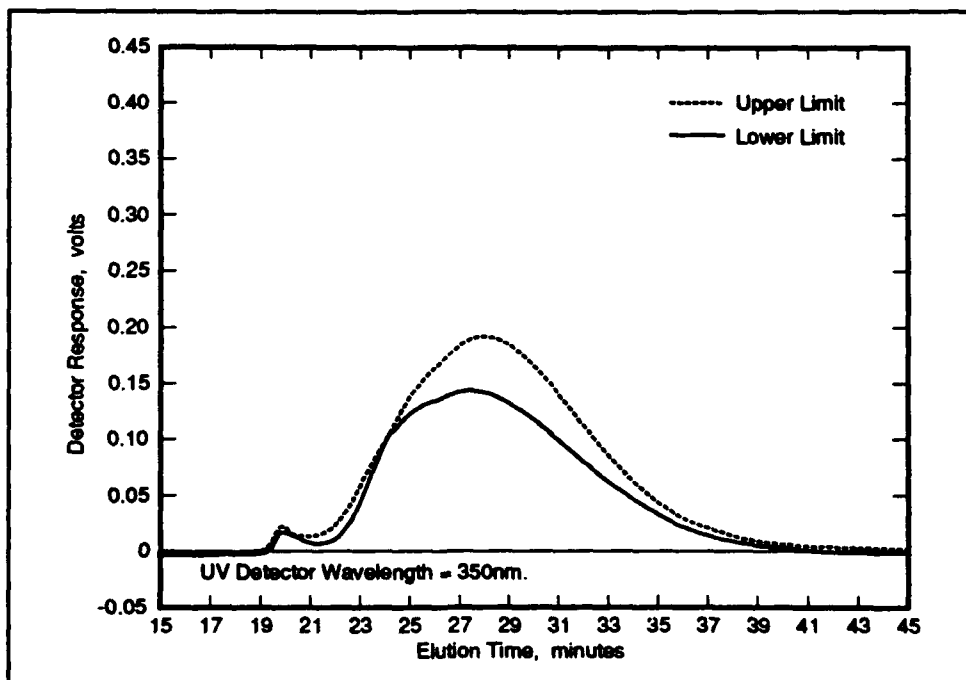


Figure A26. FPL 6522-D weather-o-meter aged chromatogram 95 percent confidence region

Appendix B

FPL 6522 Slice Data

Table B1
Slice Data for FPL 6522 As-Received Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	548709	66663	12.15
Slice 2	1618779	151568	9.36
Slice 3	17084779	824718	4.83
Slice 4	34046172	1455804	4.28
Slice 5	37649807	1642447	4.36
Slice 6	28037697	1303876	4.65
Slice 7	15492677	835766	5.39
Slice 8	6858482	470069	6.85
Slice 9	2995483	152235	5.08
Slice 10	1321189	37344	2.83
Total	145653772	6815938	4.68
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.38	0.03	7.68
Slice 2	1.11	0.07	5.93
Slice 3	11.73	0.23	1.97
Slice 4	23.38	0.11	0.49
Slice 5	25.85	0.11	0.43
Slice 6	19.25	0.11	0.59
Slice 7	10.63	0.11	1.07
Slice 8	4.70	0.11	2.44
Slice 9	2.06	0.02	1.17
Slice 10	0.91	0.02	2.02
¹ Average of four samples.			

Table B2
Slice Data for FPL 6522-A Unaged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	723827	59045	8.16
Slice 2	1743739	754858	4.33
Slice 3	16463672	1274320	7.74
Slice 4	32058729	1225974	3.82
Slice 5	35165758	771628	2.19
Slice 6	26199017	851189	3.25
Slice 7	14413947	810757	5.62
Slice 8	6348771	485506	7.65
Slice 9	2800342	204379	7.30
Slice 10	1197937	119719	9.99
Total	137115738	2818664	2.06
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.53	0.04	7.71
Slice 2	1.27	0.05	4.29
Slice 3	12.01	0.88	7.35
Slice 4	23.38	0.69	2.96
Slice 5	25.65	0.07	0.27
Slice 6	19.11	0.51	2.65
Slice 7	10.51	0.57	5.46
Slice 8	4.63	0.35	7.52
Slice 9	2.04	0.15	7.33
Slice 10	0.87	0.09	10.79
¹ Average of four samples.			

Table B3
Slice Data for FPL 6522-A Oven-Aged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	728661	215241	29.54
Slice 2	2018205	511850	25.36
Slice 3	15539264	3741241	24.08
Slice 4	26722111	5910164	22.12
Slice 5	28832969	6031103	20.92
Slice 6	21704366	4400235	20.27
Slice 7	12155353	2407940	19.81
Slice 8	5454753	1051418	19.28
Slice 9	2313562	489735	21.17
Slice 10	850329	204193	24.01
Total	116319571	24628797	21.17
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.62	0.10	15.33
Slice 2	1.73	0.23	13.17
Slice 3	13.31	0.95	7.11
Slice 4	22.93	0.46	2.02
Slice 5	24.80	0.17	0.70
Slice 6	18.70	0.59	3.15
Slice 7	10.48	0.52	5.01
Slice 8	4.71	0.28	6.04
Slice 9	1.99	0.12	6.01
Slice 10	0.73	0.05	6.60
¹ Average of four samples.			

Table B4
Slice Data for FPL 6522-A Weather-O-Meter Aged Chromatograms

Slice Number	Average Area¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	651874	149338	22.91
Slice 2	1905413	466824	24.50
Slice 3	11651762	2171475	18.64
Slice 4	19605250	2916995	14.88
Slice 5	20531160	2829210	13.78
Slice 6	15153339	1977737	13.05
Slice 7	8385132	1044533	12.46
Slice 8	3700582	465036	12.57
Slice 9	1443122	221271	15.33
Slice 10	511384	73961	14.46
Total	83539017	12195459	14.60
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.77	0.08	9.92
Slice 2	2.25	0.26	11.71
Slice 3	13.87	0.74	5.37
Slice 4	23.46	0.12	0.52
Slice 5	24.61	0.26	1.07
Slice 6	18.18	0.42	2.29
Slice 7	10.07	0.33	3.27
Slice 8	4.45	0.16	3.50
Slice 9	1.73	0.05	2.68
Slice 10	0.61	0.02	2.54
¹ Average of four samples.			

Table B5
Slice Data for FPL 6522-B Unaged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	998797	116652	11.68
Slice 2	3663641	400298	10.93
Slice 3	23872495	2599199	10.89
Slice 4	38278901	4167727	10.89
Slice 5	40146685	4185730	10.43
Slice 6	28869215	3042580	10.54
Slice 7	15424001	1593565	10.33
Slice 8	6510361	640115	9.83
Slice 9	2592117	286588	11.06
Slice 10	900206	152161	16.90
Total	161256418	17175206	10.65
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.62	0.02	2.49
Slice 2	2.27	0.01	0.65
Slice 3	14.80	0.07	0.45
Slice 4	23.73	0.06	0.27
Slice 5	24.90	0.06	0.25
Slice 6	17.90	0.04	0.20
Slice 7	9.57	0.04	0.46
Slice 8	4.04	0.03	0.86
Slice 9	1.61	0.01	0.70
Slice 10	0.55	0.04	6.72
¹ Average of four samples.			

Table B6
Slice Data for FPL 6522-B Oven-Aged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1122529	34734	3.09
Slice 2	6878196	111007	2.86
Slice 3	24911890	587991	2.36
Slice 4	38002631	964252	2.54
Slice 5	39440957	1144633	2.90
Slice 6	28795303	981761	3.41
Slice 7	15628553	590774	3.78
Slice 8	6657645	255059	3.83
Slice 9	2647003	124285	4.70
Slice 10	861703	52244	6.06
Total	161946408	4764739	2.94
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.69	0.01	1.79
Slice 2	2.40	0.05	2.29
Slice 3	15.39	0.13	0.81
Slice 4	23.47	0.12	0.50
Slice 5	24.35	0.04	0.15
Slice 6	17.78	0.10	0.57
Slice 7	9.65	0.09	0.97
Slice 8	4.11	0.04	1.04
Slice 9	1.63	0.03	1.92
Slice 10	0.53	0.02	3.50

¹ Average of four samples.

Table B7
Slice Data for FPL 6522-B Weather-O-Meter Aged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1538446	74393	4.84
Slice 2	5552577	294400	5.30
Slice 3	29957106	1729191	5.77
Slice 4	45133162	2648321	5.87
Slice 5	45967455	2853825	6.21
Slice 6	33433410	2165911	6.48
Slice 7	18221821	1190481	6.53
Slice 8	7855484	448583	5.71
Slice 9	3066312	175310	5.72
Slice 10	1003485	121537	12.11
Total	191729258	11621323	6.06

Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.80	0.02	2.71
Slice 2	2.90	0.07	2.43
Slice 3	15.63	0.13	0.85
Slice 4	23.54	0.09	0.36
Slice 5	23.97	0.05	0.21
Slice 6	17.43	0.10	0.56
Slice 7	9.50	0.08	0.85
Slice 8	4.10	0.05	1.11
Slice 9	1.60	0.02	1.45
Slice 10	0.52	0.03	6.51

¹ Average of four samples.

Table B8
Slice Data for FPL 6522-C Unaged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	941603	102762	10.91
Slice 2	2353842	249151	10.58
Slice 3	18344132	1750327	9.54
Slice 4	32439666	3218737	9.92
Slice 5	34979559	3583270	10.24
Slice 6	25737027	2748045	10.68
Slice 7	14087200	1532574	10.88
Slice 8	6112135	682195	11.16
Slice 9	2460507	313033	12.72
Slice 10	804774	100117	12.44
Total	138260446	13847129	10.02
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.68	0.06	9.15
Slice 2	1.71	0.17	9.99
Slice 3	13.29	0.55	4.16
Slice 4	23.47	0.19	0.79
Slice 5	25.29	0.17	0.68
Slice 6	18.60	0.33	1.78
Slice 7	10.18	0.24	2.33
Slice 8	4.42	0.12	2.82
Slice 9	1.78	0.09	5.21
Slice 10	0.58	0.02	2.86
¹ Average of four samples.			

Table B9
Slice Data for FPL 6522-C Oven-Aged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1525794	102119	6.69
Slice 2	3939920	349706	8.88
Slice 3	24826860	1533202	6.18
Slice 4	38833820	2079205	5.35
Slice 5	40905985	2094899	5.12
Slice 6	30251638	1556123	5.14
Slice 7	16686655	986976	5.91
Slice 8	7252336	549763	7.58
Slice 9	2888126	264945	9.17
Slice 10	984586	101687	10.33
Total	168095720	9434151	5.61
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.91	0.02	1.83
Slice 2	2.34	0.14	5.92
Slice 3	14.77	0.26	1.79
Slice 4	23.11	0.08	0.36
Slice 5	24.34	0.14	0.59
Slice 6	18.00	0.12	0.68
Slice 7	9.93	0.10	0.96
Slice 8	4.31	0.10	2.36
Slice 9	1.71	0.06	3.72
Slice 10	0.58	0.03	4.78
¹ Average of four samples.			

Table B10 Slice Data for FPL 6522-C Weather-O-Meter Aged Chromatograms			
Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1570032	23137	1.47
Slice 2	4489904	181727	4.05
Slice 3	23278970	511685	2.20
Slice 4	34986708	360179	1.03
Slice 5	35681956	432663	1.21
Slice 6	25857494	358239	1.39
Slice 7	14920133	217062	1.45
Slice 8	7311266	107875	1.48
Slice 9	3231555	41985	1.30
Slice 10	1172331	7387	0.63
Total	152500349	2201322	1.44
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1.03	0.01	0.83
Slice 2	2.94	0.08	2.72
Slice 3	15.26	0.13	0.84
Slice 4	22.94	0.09	0.41
Slice 5	23.40	0.06	0.27
Slice 6	16.96	0.04	0.25
Slice 7	9.78	0.03	0.26
Slice 8	4.79	0.01	0.28
Slice 9	2.12	0.01	0.42
Slice 10	0.77	0.01	1.15
¹ Average of three samples.			

Table B11
Slice Data for FPL 6522-D Unaged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1794837	116360	6.48
Slice 2	3750399	320980	8.56
Slice 3	24697341	1425175	5.77
Slice 4	41093630	1763555	4.29
Slice 5	43662873	1783808	4.09
Slice 6	31864016	1213649	3.81
Slice 7	17548658	502970	2.87
Slice 8	7817753	88039	1.13
Slice 9	3305970	23149	0.70
Slice 10	1217894	14250	1.17
Total	176753370	7159587	4.05
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1.01	0.03	2.67
Slice 2	2.12	0.10	4.53
Slice 3	13.96	0.24	1.73
Slice 4	23.25	0.10	0.43
Slice 5	24.70	0.02	0.10
Slice 6	18.03	0.06	0.34
Slice 7	9.93	0.13	1.27
Slice 8	4.43	0.13	3.03
Slice 9	1.87	0.09	4.64
Slice 10	0.69	0.04	5.19
¹ Average of four samples.			

Table B12
Slice Data for FPL 6522-D Oven-Aged Chromatograms

Slice Number	Average Area¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1941833	128334	6.61
Slice 2	4196622	347192	8.27
Slice 3	25492382	1812237	7.11
Slice 4	40755175	2852511	7.00
Slice 5	43405894	3178403	7.32
Slice 6	32444745	2396055	7.39
Slice 7	18209960	912690	5.01
Slice 8	8188571	190277	2.32
Slice 9	3407519	252555	7.41
Slice 10	1250160	91529	7.32
Total	179292859	11211409	6.25
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1.08	0.02	1.53
Slice 2	2.34	0.05	2.04
Slice 3	14.21	0.14	0.95
Slice 4	22.72	0.21	0.91
Slice 5	24.19	0.27	1.11
Slice 6	18.08	0.21	1.14
Slice 7	10.16	0.15	1.51
Slice 8	4.59	0.35	7.54
Slice 9	1.92	0.25	13.23
Slice 10	0.70	0.09	13.08
¹ Average of four samples.			

Table B13
Slice Data for FPL 6522-D Weather-O-Meter Aged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1257609	40008	3.18
Slice 2	2924757	417110	14.26
Slice 3	13963058	87315	0.63
Slice 4	21782510	1148385	5.27
Slice 5	22179147	1698877	7.66
Slice 6	16029249	1298119	8.10
Slice 7	8868560	600312	6.77
Slice 8	3897929	206155	5.29
Slice 9	1505634	50531	3.36
Slice 10	513452	3506	0.68
Total	92921906	4537922	4.88
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1.36	0.11	7.77
Slice 2	3.18	0.58	18.32
Slice 3	15.06	0.72	4.81
Slice 4	23.44	0.11	0.49
Slice 5	23.84	0.65	2.71
Slice 6	17.22	0.54	3.13
Slice 7	9.54	0.17	1.83
Slice 8	4.19	0.02	0.49
Slice 9	1.62	0.02	1.50
Slice 10	0.55	0.03	5.36
¹ Average of three samples.			

Table B14
Percent Average Area Per Slice for FPL 6522 As-Received and
Unaged Chromatograms

Slice Number	As-Received	Heating Time			
		A	B	C	D
Slice 1	0.38	0.53	0.62	0.68	1.01
Slice 2	1.11	1.27	2.27	1.71	2.12
Slice 3	11.73	12.01	14.80	13.29	13.96
Slice 4	23.85	23.38	23.73	23.47	23.25
Slice 5	25.85	25.65	24.90	25.29	24.70
Slice 6	19.25	19.11	17.90	18.60	18.03
Slice 7	10.63	10.51	9.57	10.18	9.93
Slice 8	4.70	4.63	4.04	4.42	4.43
Slice 9	2.06	2.04	1.61	1.78	1.87
Slice 10	0.91	0.87	0.55	0.58	0.69

Table B15
Percent Average Area Per Slice for FPL 6522 Oven-Aged
Chromatograms

Slice Number	Heating Time			
	A	B	C	D
Slice 1	0.62	0.69	0.91	1.08
Slice 2	1.73	2.40	2.34	2.34
Slice 3	13.31	15.39	14.77	14.21
Slice 4	22.93	23.47	23.11	22.72
Slice 5	24.80	24.35	24.34	24.19
Slice 6	18.70	17.78	18.00	18.08
Slice 7	10.48	9.65	9.93	10.16
Slice 8	4.71	4.11	4.31	4.59
Slice 9	1.99	1.63	1.71	1.92
Slice 10	0.73	0.53	0.58	0.70

Table B16
Percent Average Area Per Slice for FPL 6522 Weather-O-Meter
Aged Chromatograms

Slice Number	Heating Time			
	A	B	C	D
Slice 1	0.77	0.80	1.03	1.36
Slice 2	2.25	2.90	2.94	3.18
Slice 3	13.87	15.63	15.26	15.06
Slice 4	23.46	23.54	22.94	23.44
Slice 5	24.61	23.97	23.40	23.84
Slice 6	18.18	17.43	16.96	17.22
Slice 7	10.07	9.50	9.78	9.54
Slice 8	4.45	4.10	4.79	4.19
Slice 9	1.73	1.60	2.12	1.62
Slice 10	0.61	0.52	0.77	0.55

Appendix C

FPL 6527 Chromatograms

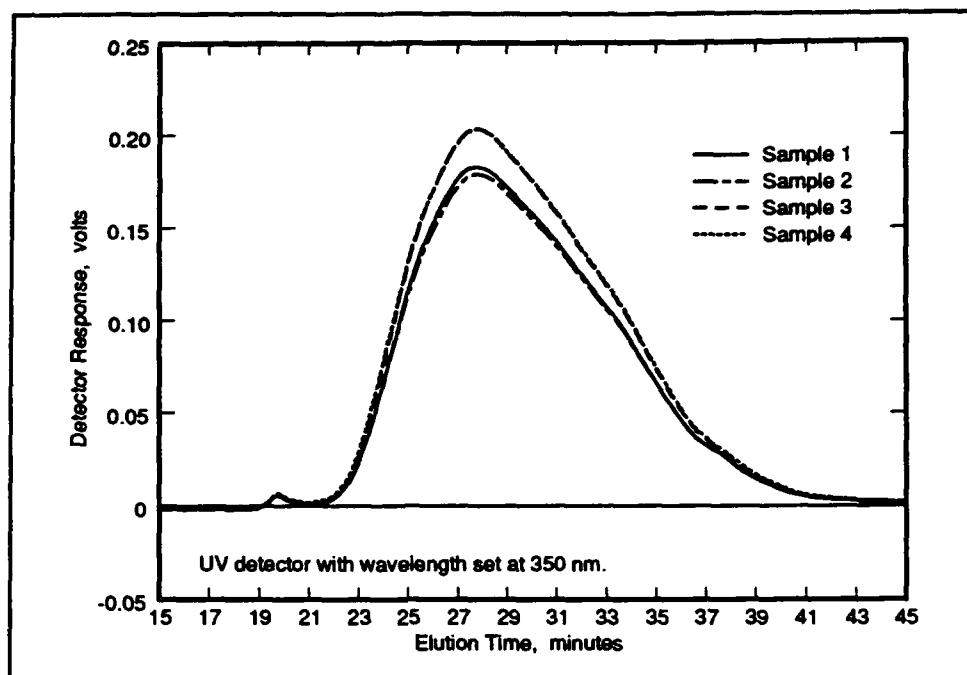


Figure C1. FPL 6527 as-received chromatograms

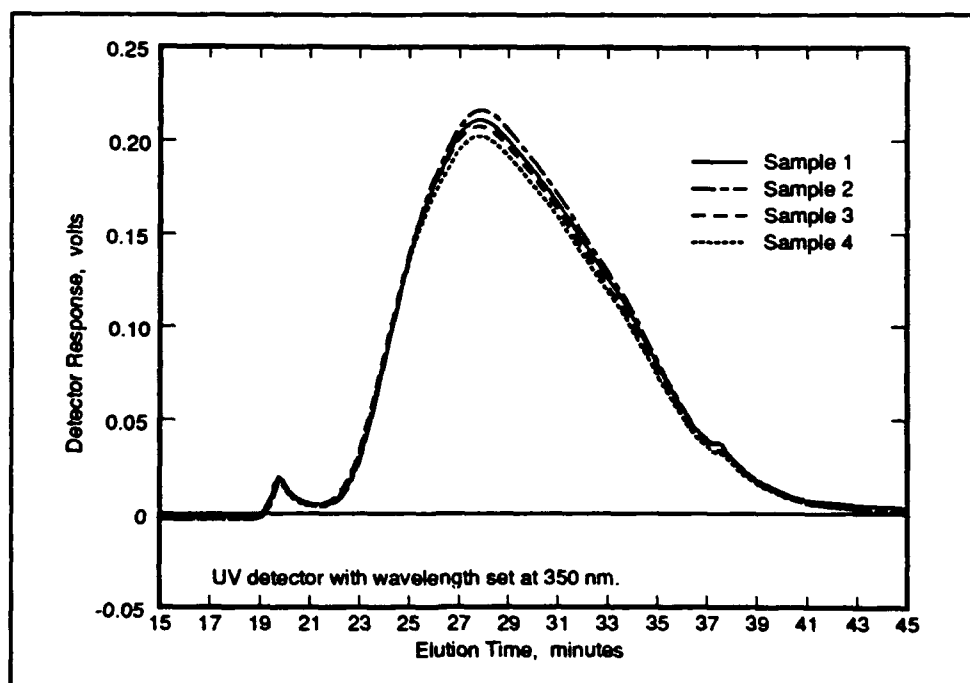


Figure C2. FPL 6527-A unaged chromatograms

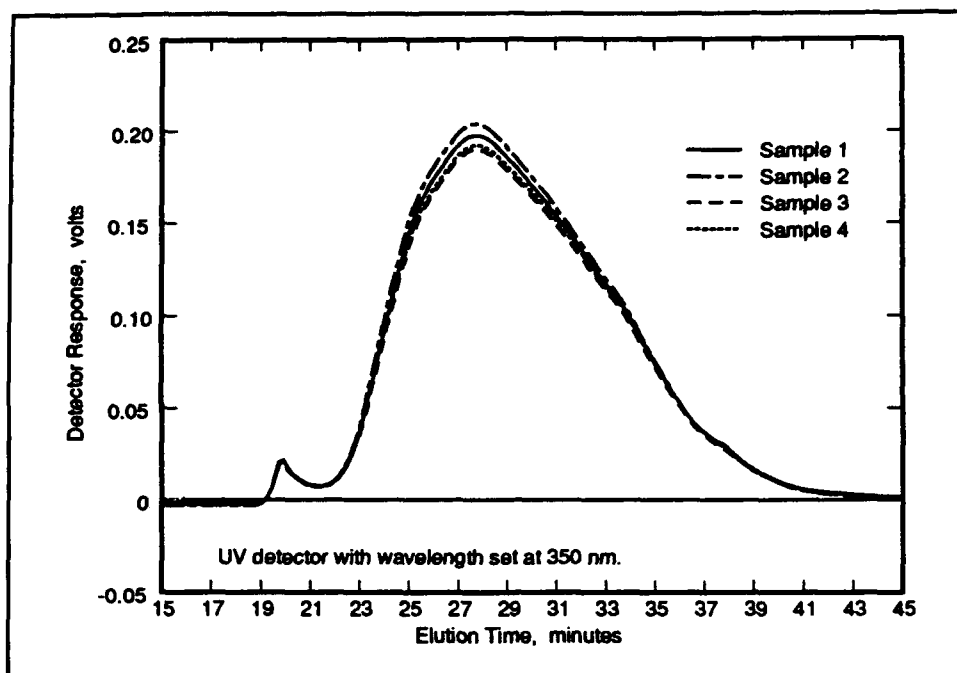


Figure C3. FPL 6527-A oven-aged chromatograms

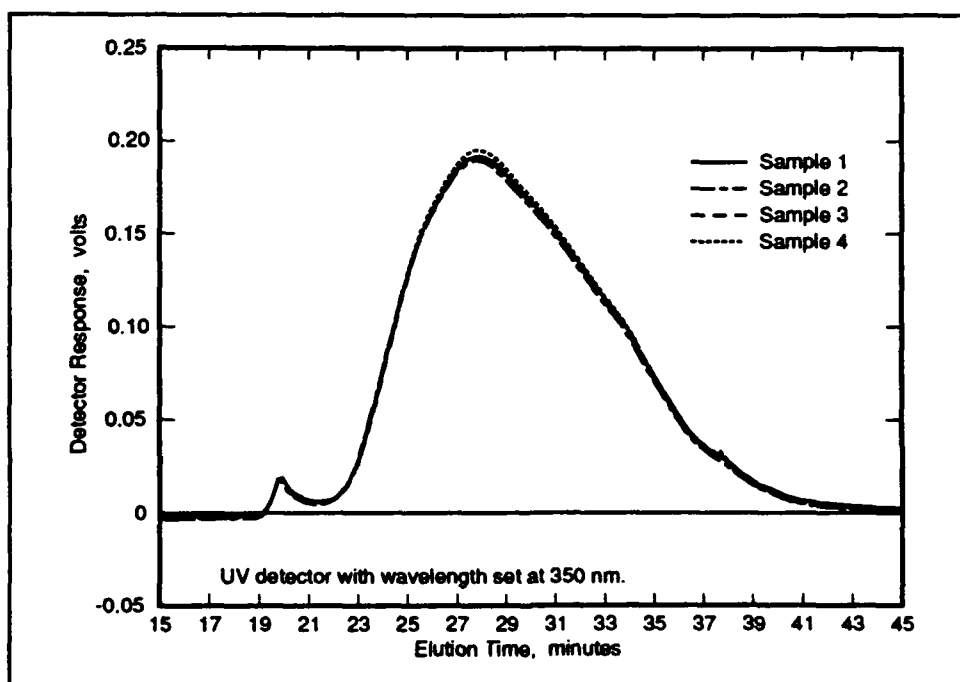


Figure C4. FPL 6527-A weather-o-meter aged chromatograms

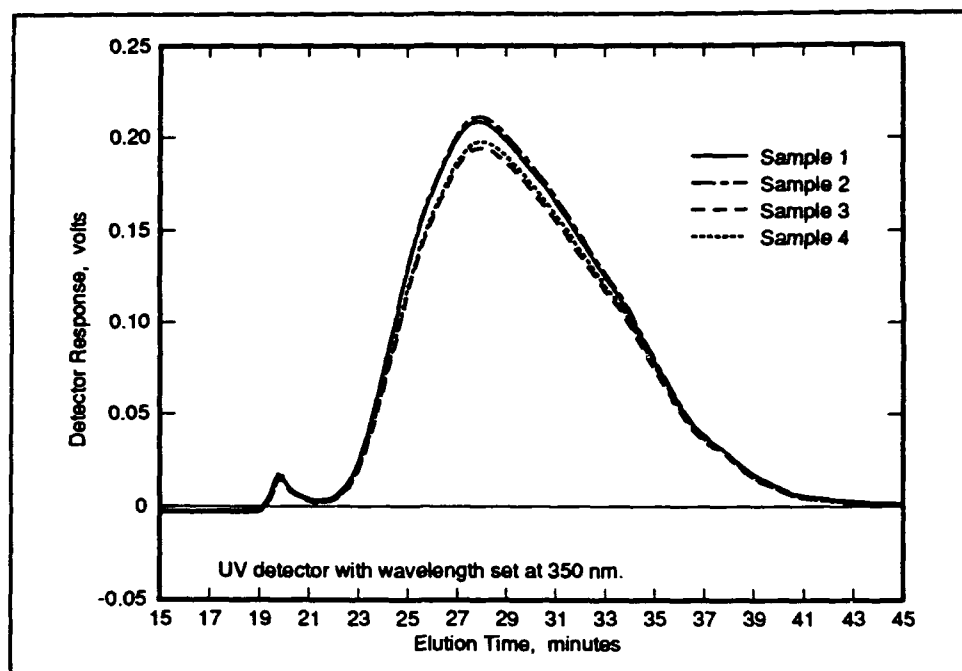


Figure C5. FPL 6527-B unaged chromatograms

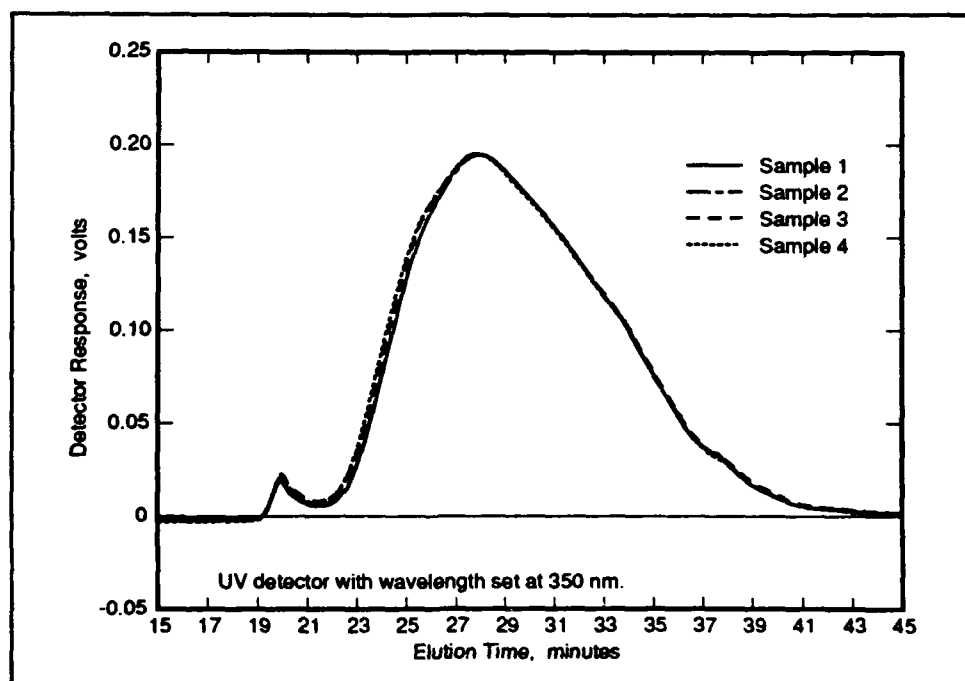


Figure C6. FPL 6527-B oven-aged chromatograms

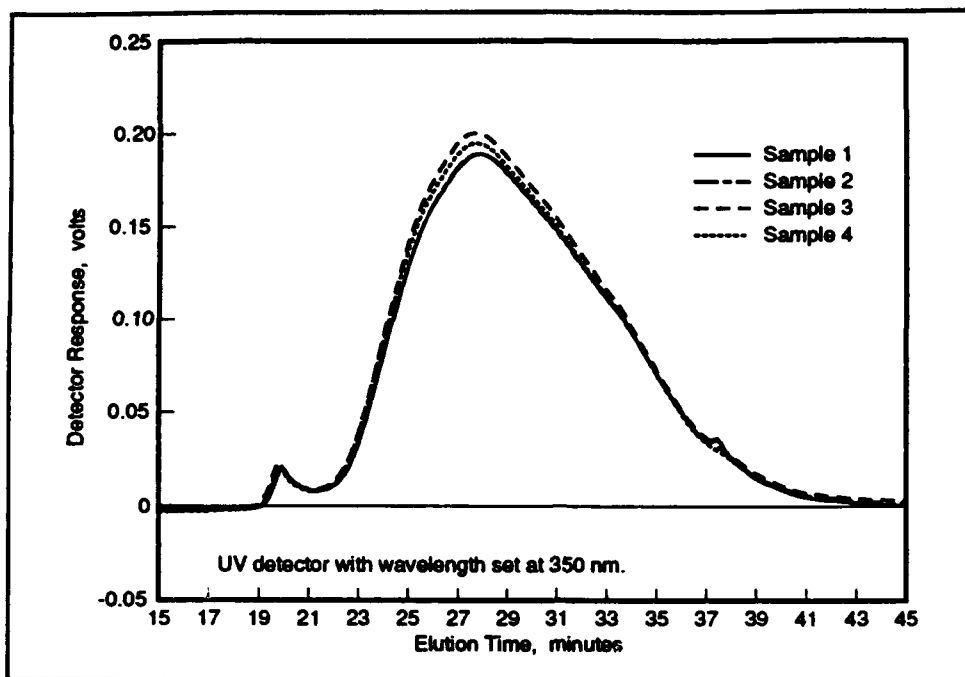


Figure C7. FPL 6527-B weather-o-meter aged chromatograms

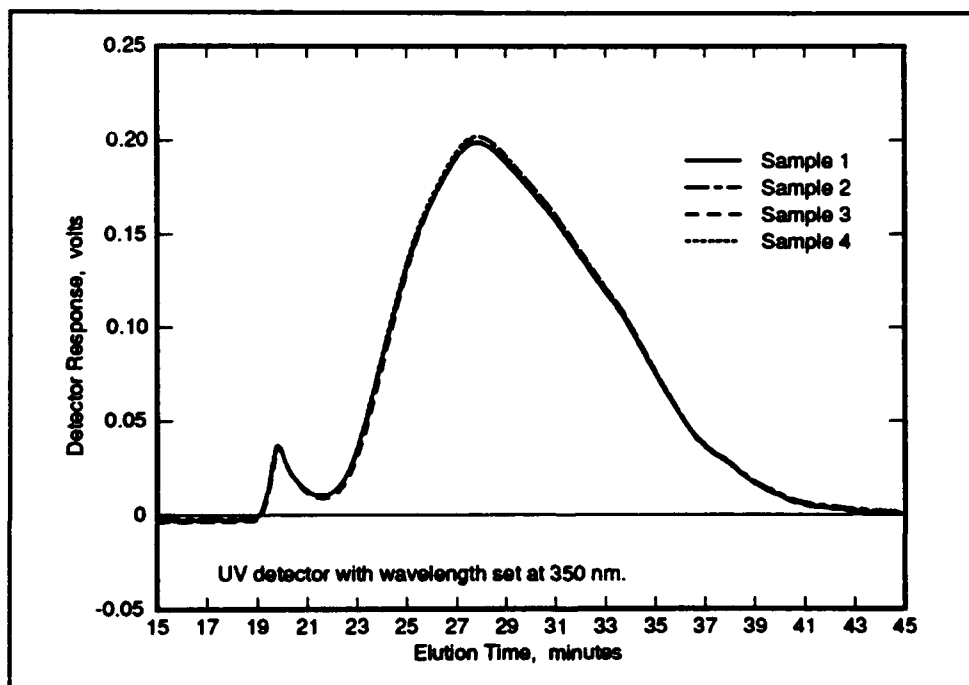


Figure C8. FPL 6527-C unaged chromatograms

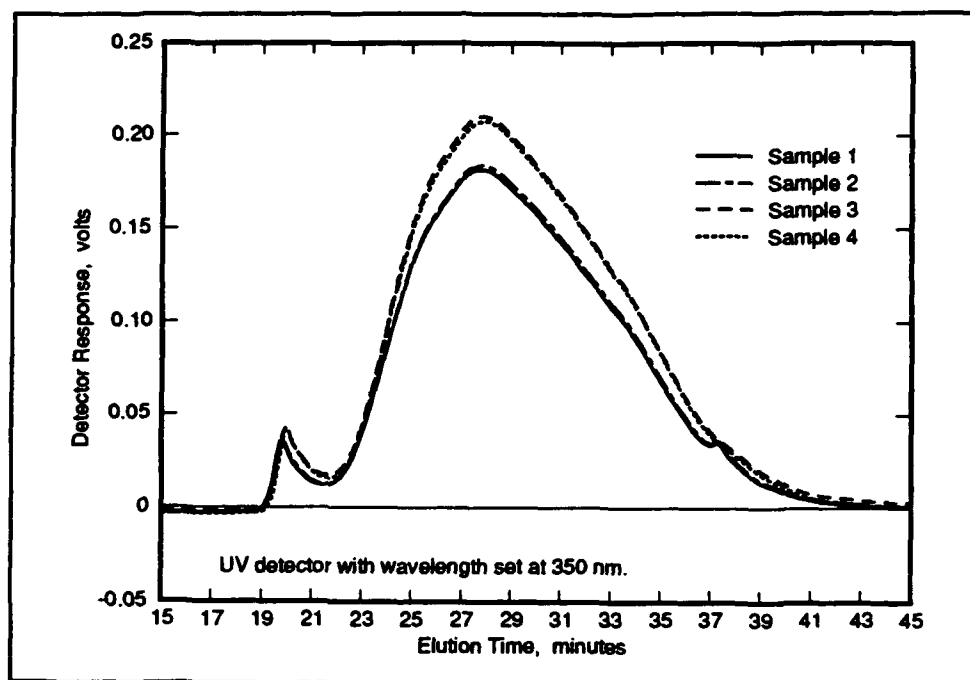


Figure C9. FPL 6527-C oven-aged chromatograms

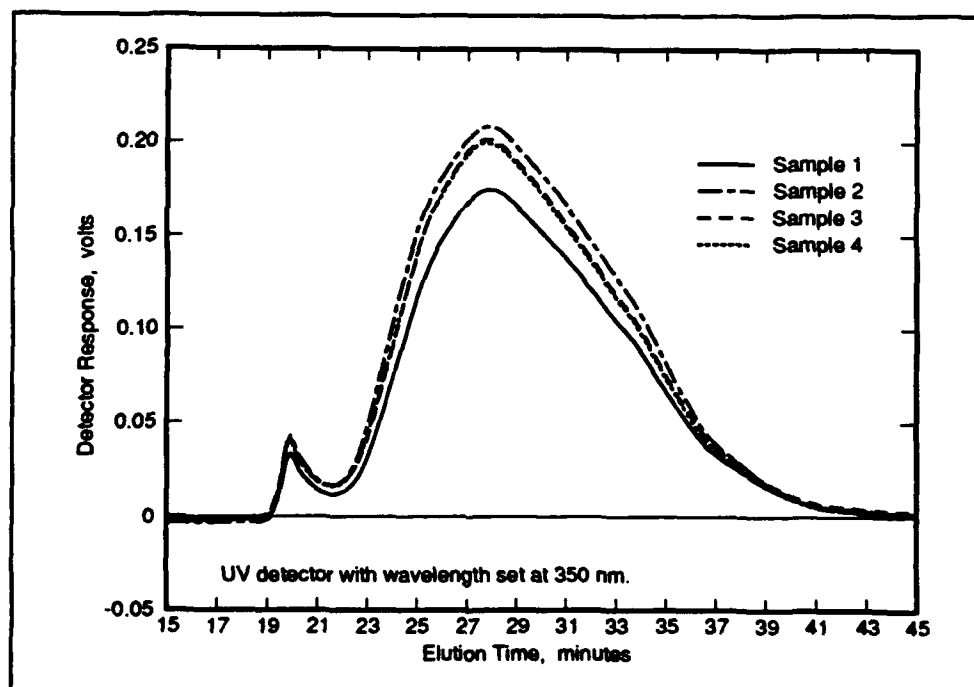


Figure C10. FPL 6527-C weather-o-meter aged chromatograms

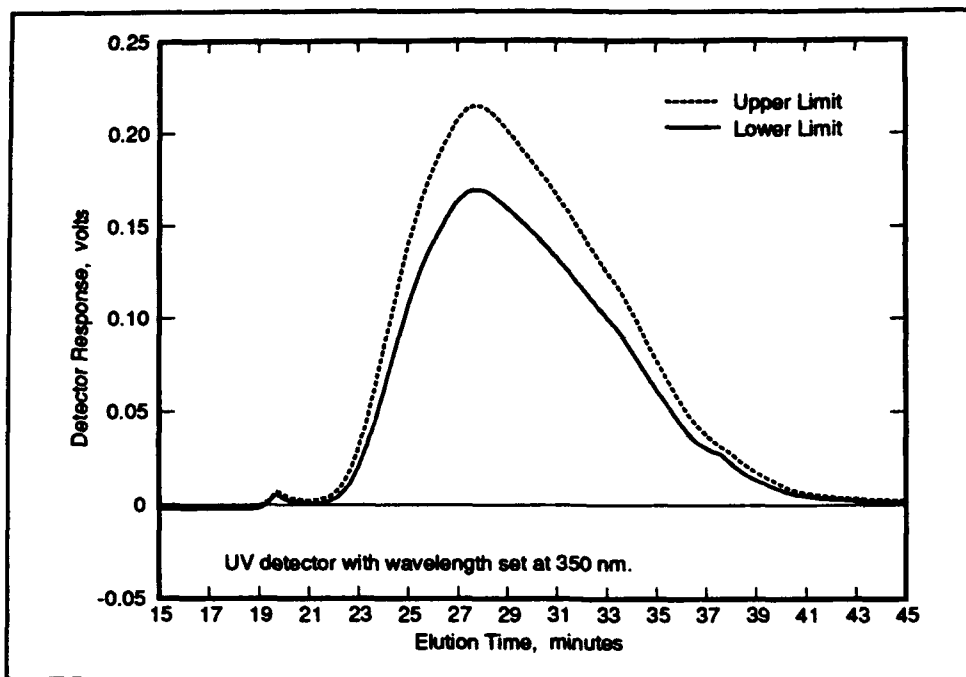


Figure C11. FPL 6527 as-received chromatogram 95 percent confidence region

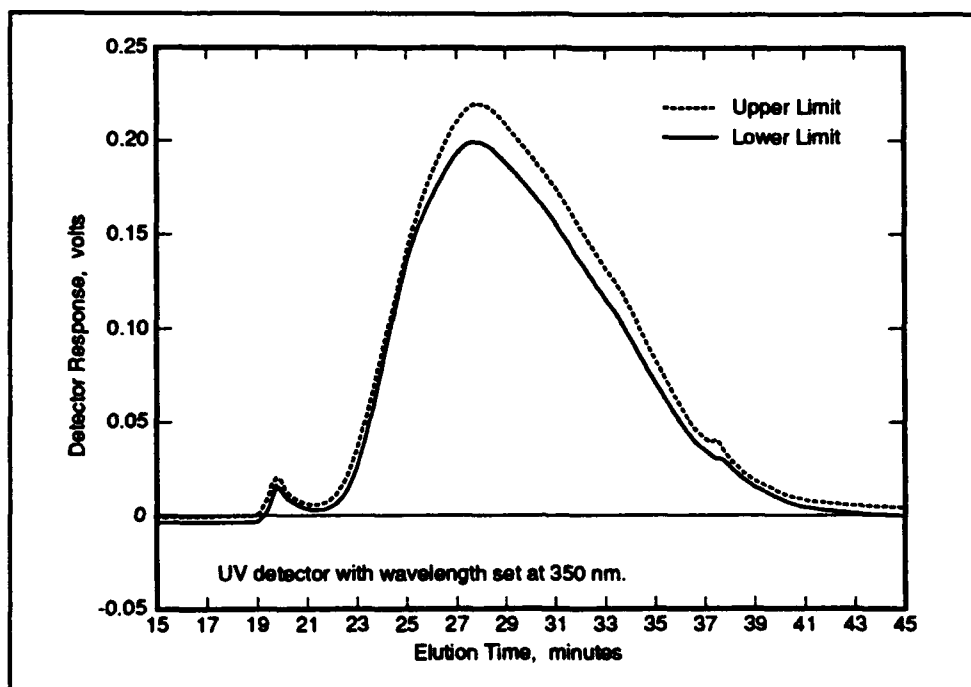


Figure C12. FPL 6527-A unaged chromatogram 95 percent confidence region

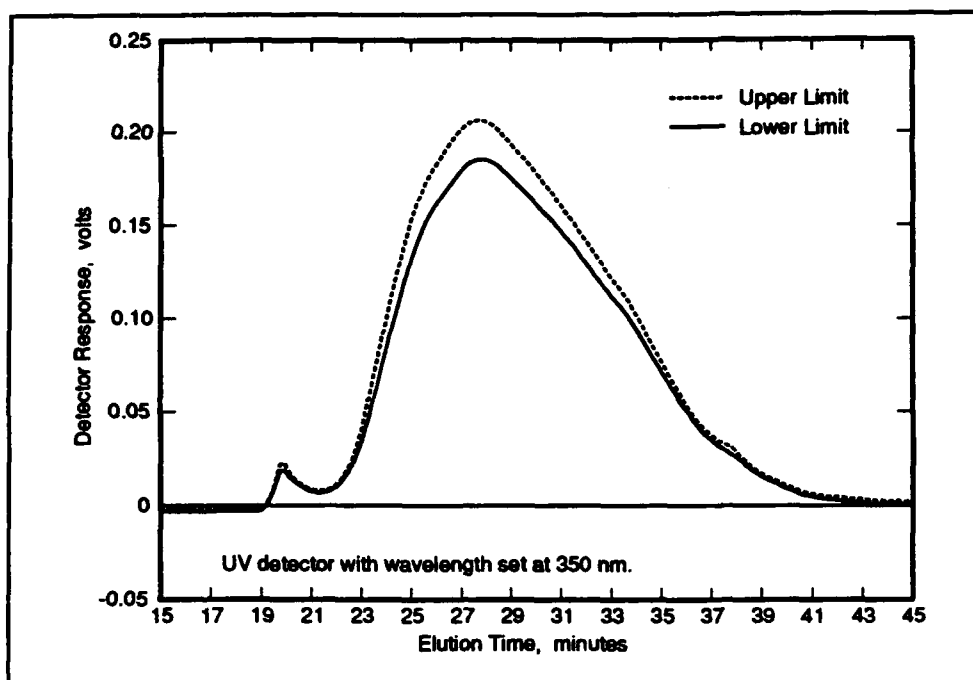


Figure C13. FPL 6527-A oven-aged chromatogram 95 percent confidence region

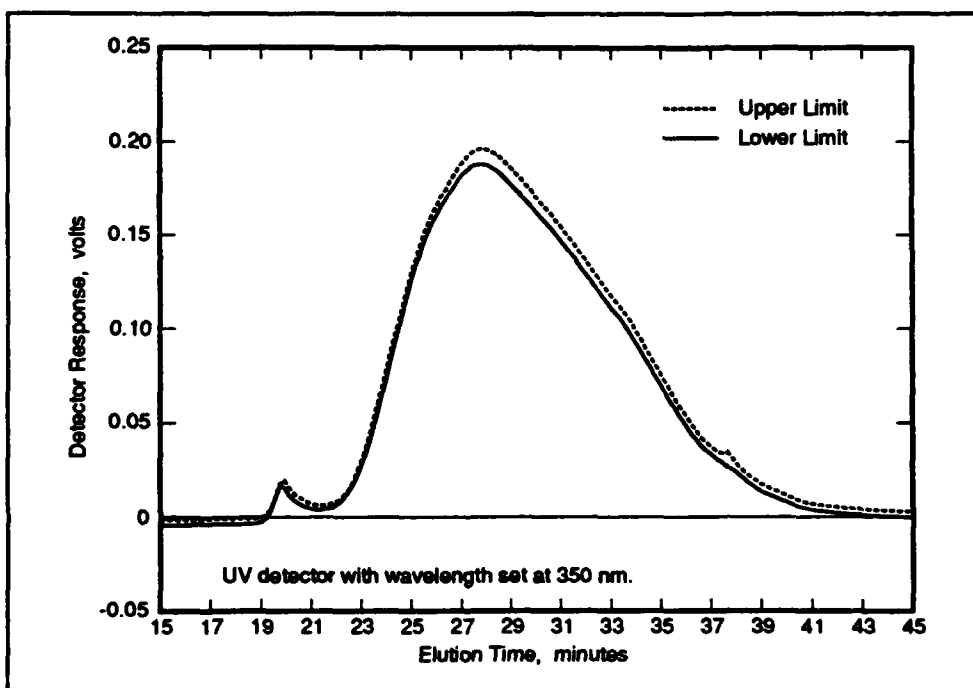


Figure C14. FPL 6527-A weather-o-meter aged chromatogram 95 percent confidence region

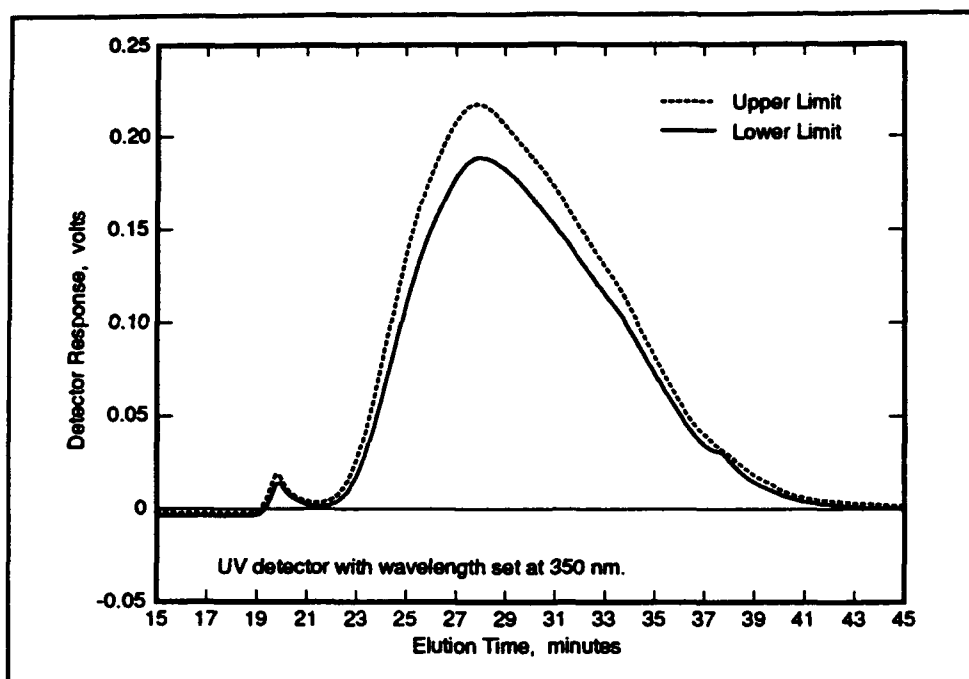


Figure C15. FPL 6527-B unaged chromatogram 95 percent confidence region

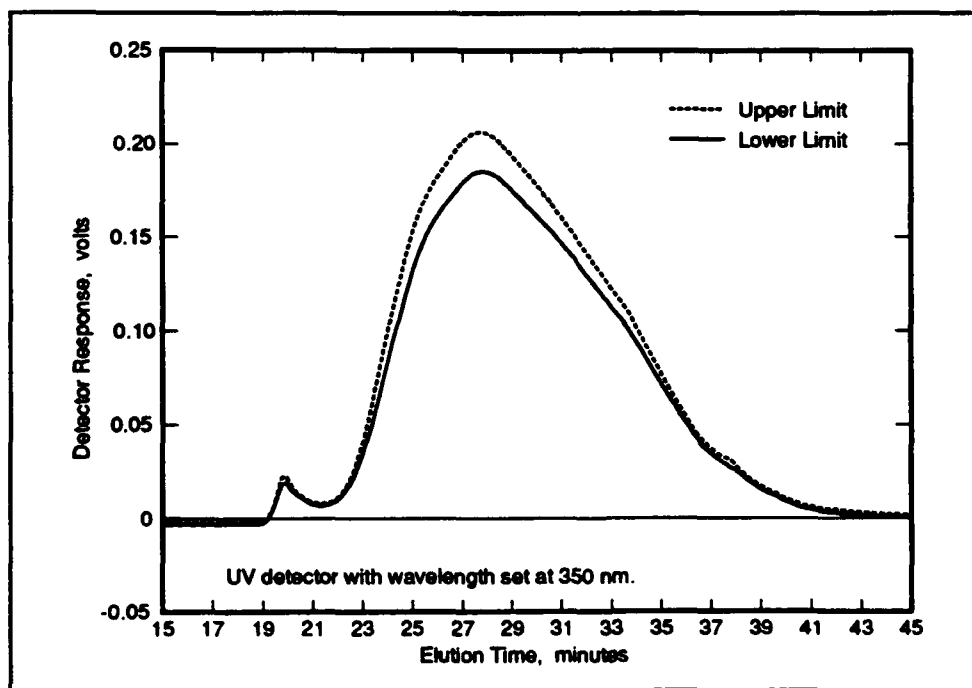


Figure C16. FPL 6527-B oven-aged chromatogram 95 percent confidence region

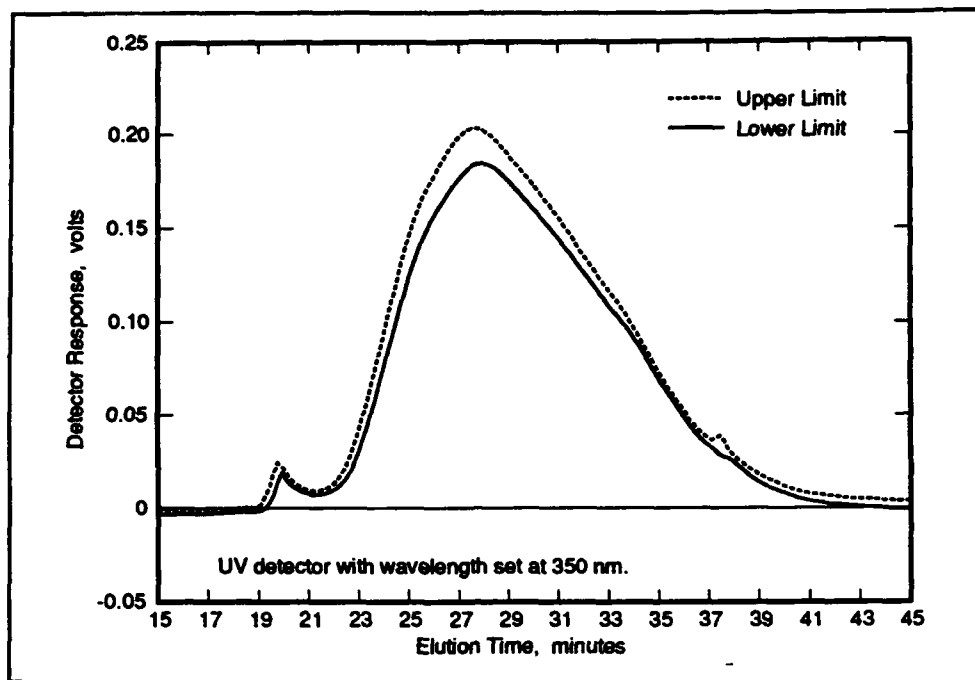


Figure C17. FPL 6527-B weather-o-meter aged chromatogram 95 percent confidence region

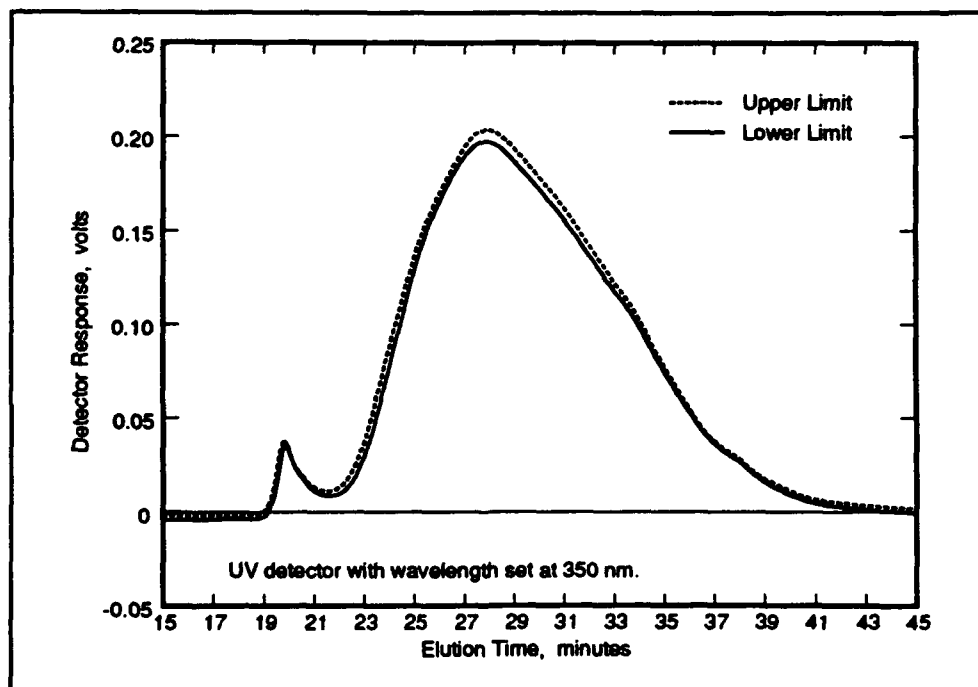


Figure C18. FPL 6527-C unaged chromatogram 95 percent confidence region

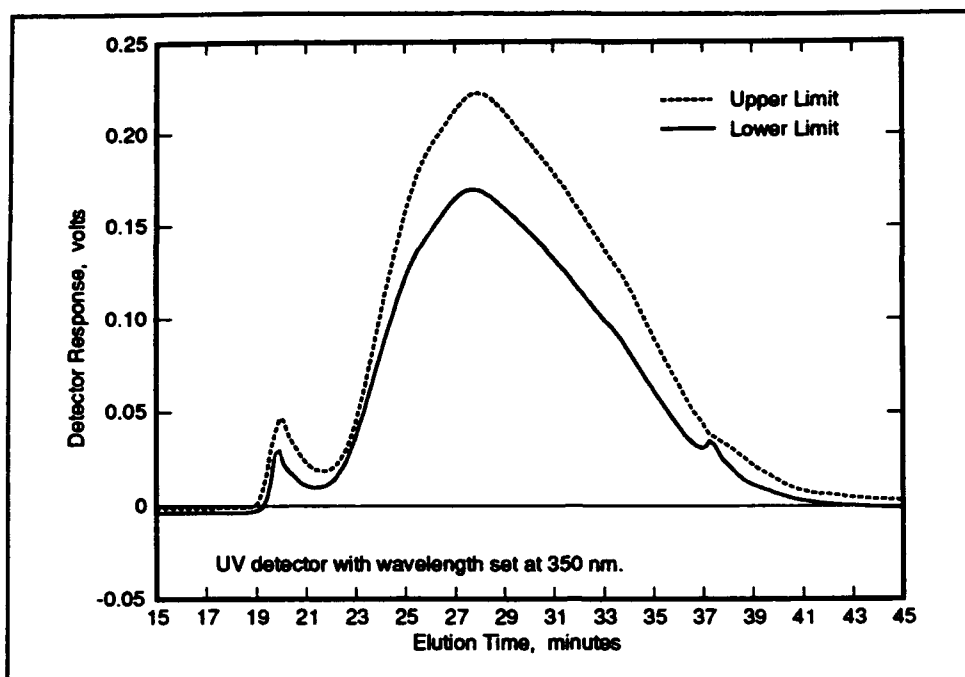


Figure C19. FPL 6527-C oven-aged chromatogram 95 percent confidence region

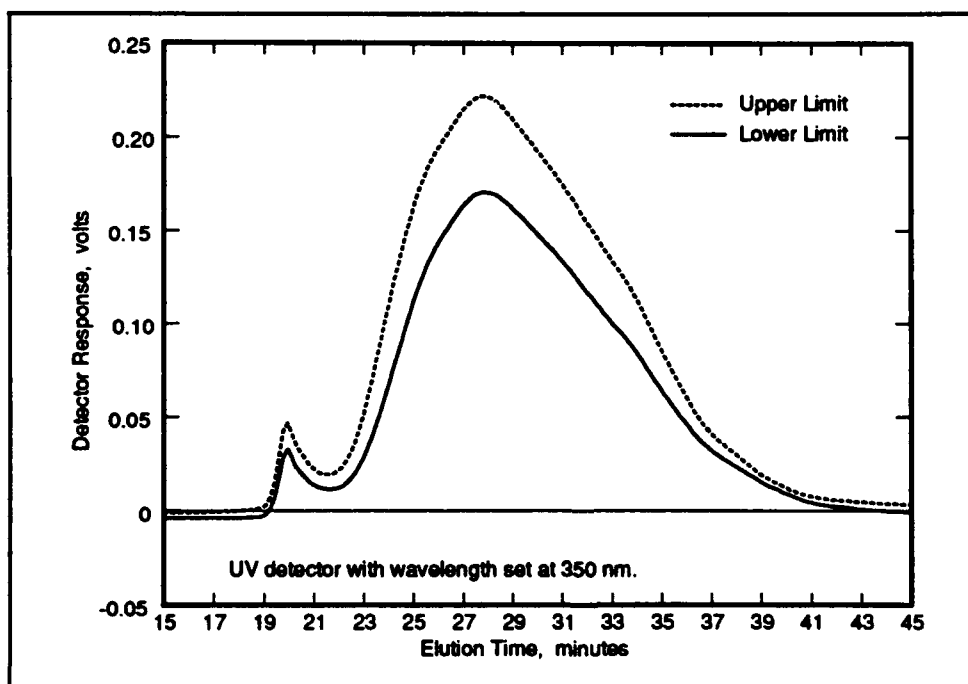


Figure C20. FPL 6527-C weather-o-meter aged chromatogram 95 percent confidence region

Appendix D

FPL 6527 Slice Data

Table D1
Slice Data for FPL 6527 As-Received Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	349564	26044	7.45
Slice 2	798199	110161	13.80
Slice 3	9826803	746009	7.59
Slice 4	23206174	1426575	6.15
Slice 5	25538856	1502627	5.88
Slice 6	20659119	1190571	5.76
Slice 7	14539762	837832	5.76
Slice 8	7484923	449493	6.01
Slice 9	3182034	188357	5.92
Slice 10	914500	81632	8.93
Total	106499932	6541132	6.14
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.33	0.01	3.57
Slice 2	0.75	0.06	7.98
Slice 3	9.22	0.14	1.56
Slice 4	21.79	0.09	0.42
Slice 5	23.98	0.08	0.34
Slice 6	19.40	0.08	0.39
Slice 7	13.66	0.06	0.42
Slice 8	7.03	0.03	0.47
Slice 9	2.99	0.02	0.52
Slice 10	0.86	0.03	3.19
¹ Average of four samples.			

Table D2 Slice Data for FPL 6527-A Unaged Chromatograms			
Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	940352	8541	0.91
Slice 2	1325070	70164	5.30
Slice 3	11375698	259134	2.28
Slice 4	25474491	471053	1.85
Slice 5	28031393	714771	2.55
Slice 6	22777742	653836	2.87
Slice 7	16058329	570193	3.55
Slice 8	8415845	346492	4.12
Slice 9	3663067	142191	3.88
Slice 10	1079725	26144	2.42
Total	119141712	2726263	2.29
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.79	0.02	1.90
Slice 2	1.11	0.08	6.86
Slice 3	9.55	0.37	3.82
Slice 4	21.38	0.12	0.54
Slice 5	23.53	0.09	0.37
Slice 6	19.12	0.12	0.64
Slice 7	13.47	0.19	1.37
Slice 8	7.06	0.14	1.94
Slice 9	3.07	0.05	1.70
Slice 10	0.91	0.03	2.98
¹ Average of four samples.			

Table D3
Slice Data for FPL 6527-A Oven-Aged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1101180	41534	3.77
Slice 2	1884705	59560	3.16
Slice 3	12463995	546634	4.39
Slice 4	24706372	778915	3.15
Slice 5	26182783	700654	2.68
Slice 6	21312959	507596	2.38
Slice 7	15295219	338195	2.21
Slice 8	8126014	145636	1.79
Slice 9	3510228	63280	1.80
Slice 10	1070817	18431	1.72
Total	115654270	3144628	2.72

Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.95	0.01	1.17
Slice 2	1.63	0.05	2.84
Slice 3	10.77	0.18	1.69
Slice 4	21.36	0.11	0.53
Slice 5	22.64	0.06	0.28
Slice 6	18.43	0.06	0.35
Slice 7	13.23	0.07	0.50
Slice 8	7.03	0.07	0.99
Slice 9	3.04	0.04	1.18
Slice 10	0.93	0.02	2.37

¹ Average of four samples.

Table D4
Slice Data for FPL 6527-A Weather-O-Meter Aged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	973110	24405	2.51
Slice 2	1433434	40106	2.80
Slice 3	10539007	213529	2.03
Slice 4	23513005	202447	0.86
Slice 5	25743806	273584	1.06
Slice 6	20927391	233494	1.12
Slice 7	14900911	185762	1.25
Slice 8	7913889	126137	1.59
Slice 9	3416603	82189	2.41
Slice 10	1025703	19466	1.90
Total	110386656	1174902	1.06
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.88	0.02	1.96
Slice 2	1.30	0.03	2.12
Slice 3	9.55	0.19	1.99
Slice 4	21.30	0.07	0.31
Slice 5	23.32	0.06	0.27
Slice 6	18.96	0.06	0.32
Slice 7	13.50	0.06	0.44
Slice 8	7.17	0.06	0.79
Slice 9	3.09	0.05	1.49
Slice 10	0.93	0.01	1.29
¹ Average of four samples.			

Table D5
Slice Data for FPL 6527-B Unaged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	854625	49501	5.79
Slice 2	1043861	62390	5.98
Slice 3	9639814	568253	5.89
Slice 4	24087025	979268	4.07
Slice 5	27433863	863587	3.15
Slice 6	22516848	660917	2.94
Slice 7	16035143	454691	2.84
Slice 8	8477325	230001	2.71
Slice 9	3628562	91855	2.53
Slice 10	1063294	48631	4.57
Total	114780158	3970139	3.46

Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.74	0.02	2.69
Slice 2	0.91	0.03	2.79
Slice 3	8.39	0.21	2.49
Slice 4	20.98	0.16	0.76
Slice 5	23.90	0.08	0.34
Slice 6	19.62	0.11	0.56
Slice 7	13.97	0.10	0.73
Slice 8	7.39	0.08	1.08
Slice 9	3.16	0.05	1.56
Slice 10	0.93	0.02	2.01

¹ Average of four samples.

Table D6
Slice Data for FPL 6527-B Oven-Aged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1028357	42678	4.15
Slice 2	1647629	217744	13.22
Slice 3	11162181	750417	6.72
Slice 4	23998307	312848	1.30
Slice 5	26216235	22112	0.08
Slice 6	21534323	33682	0.16
Slice 7	15539816	52071	0.34
Slice 8	8396921	80835	0.96
Slice 9	3663813	46104	1.26
Slice 10	1073322	54522	5.08
Total	114260902	1457599	1.28
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	0.90	0.03	2.90
Slice 2	1.44	0.17	11.96
Slice 3	9.76	0.53	5.45
Slice 4	21.00	0.06	0.30
Slice 5	22.95	0.30	1.30
Slice 6	18.85	0.26	1.38
Slice 7	13.60	0.15	1.09
Slice 8	7.35	0.07	0.89
Slice 9	3.21	0.03	0.94
Slice 10	0.94	0.04	3.89
¹ Average of four samples.			

Table D7
Slice Data for FPL 6527-B Weather-O-Meter Aged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1177763	59254	5.03
Slice 2	1922540	60375	3.14
Slice 3	11594030	563494	4.86
Slice 4	23998857	711372	2.96
Slice 5	25785934	482267	1.87
Slice 6	20739797	318784	1.54
Slice 7	14660996	171004	1.17
Slice 8	7785643	62321	0.80
Slice 9	3427662	75024	2.19
Slice 10	1032584	17157	1.66
Total	112125804	2296057	2.05
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1.05	0.03	3.11
Slice 2	1.71	0.03	1.64
Slice 3	10.33	0.30	2.92
Slice 4	21.40	0.21	0.96
Slice 5	23.00	0.06	0.25
Slice 6	18.50	0.10	0.56
Slice 7	13.08	0.13	0.98
Slice 8	6.95	0.14	2.01
Slice 9	3.06	0.12	3.99
Slice 10	0.92	0.01	0.97
¹ Average of four samples.			

Table D8 Slice Data for FPL 6527-C Unaged Chromatograms			
Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1892346	39214	2.07
Slice 2	2256602	52185	2.31
Slice 3	11403355	294435	2.58
Slice 4	24425017	178708	0.73
Slice 5	26959619	274581	1.02
Slice 6	22042038	262496	1.19
Slice 7	15729527	205930	1.31
Slice 8	8373700	117511	1.40
Slice 9	3623117	53177	1.47
Slice 10	1134064	6618	0.58
Total	117839385	1090307	0.93
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1.61	0.03	1.76
Slice 2	1.92	0.05	2.36
Slice 3	9.68	0.24	2.51
Slice 4	20.73	0.06	0.29
Slice 5	22.88	0.09	0.39
Slice 6	18.70	0.10	0.51
Slice 7	13.35	0.09	0.64
Slice 8	7.11	0.06	0.85
Slice 9	3.07	0.03	0.87
Slice 10	0.96	0.01	0.91
¹ Average of four samples.			

Table D9
Slice Data for FPL 6527-C Oven-Aged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1956739	34924	1.78
Slice 2	2928254	306907	10.48
Slice 3	12493536	676521	5.41
Slice 4	24417678	1532968	6.28
Slice 5	26303528	1764242	6.71
Slice 6	21582211	1549724	7.18
Slice 7	15579831	1238357	7.95
Slice 8	8349074	771199	9.24
Slice 9	3640867	252910	6.95
Slice 10	1098752	135763	12.36
Total	118350469	8248898	6.97
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1.66	0.09	5.63
Slice 2	2.47	0.09	3.57
Slice 3	10.57	0.17	1.59
Slice 4	20.64	0.16	0.78
Slice 5	22.23	0.06	0.28
Slice 6	18.23	0.04	0.23
Slice 7	13.16	0.13	1.00
Slice 8	7.04	0.16	2.33
Slice 9	3.08	0.02	0.78
Slice 10	0.92	0.05	5.51
¹ Average of four samples.			

Table D10
Slice Data for FPL 6527-C Weather-O-Meter Aged Chromatograms

Slice Number	Average Area ¹ (microvolt-sec)	Standard Deviation	Coefficient of Variance (%)
Slice 1	2045110	217493	10.63
Slice 2	2972565	407337	13.70
Slice 3	12223173	1438564	11.77
Slice 4	24346047	1825984	7.50
Slice 5	26275439	1742712	6.63
Slice 6	21346710	1482590	6.95
Slice 7	15252665	1155389	7.57
Slice 8	8175066	630134	7.71
Slice 9	3508554	258980	7.38
Slice 10	1115449	80378	7.21
Total	117260775	9142221	7.80
Slice Number	Average Area (%)	Standard Deviation	Coefficient of Variance (%)
Slice 1	1.74	0.09	5.41
Slice 2	2.52	0.16	6.49
Slice 3	10.39	0.44	4.22
Slice 4	20.77	0.19	0.92
Slice 5	22.43	0.30	1.35
Slice 6	18.22	0.18	0.98
Slice 7	13.01	0.16	1.19
Slice 8	6.97	0.12	1.70
Slice 9	2.99	0.06	1.96
Slice 10	0.95	0.02	2.60
¹ Average of four samples.			

Table D11
Percent Average Area Per Slice for FPL 6527 As-Received and
Unaged Chromatograms

Slice Number	As-Received	Heating Time		
		A	B	C
Slice 1	0.33	0.79	0.74	1.61
Slice 2	0.75	1.11	0.91	1.92
Slice 3	9.22	9.55	8.39	9.68
Slice 4	21.79	21.38	20.98	20.73
Slice 5	23.98	23.53	23.90	22.88
Slice 6	19.40	19.12	19.62	18.70
Slice 7	13.66	13.47	13.62	13.35
Slice 8	7.03	7.06	7.39	7.11
Slice 9	2.99	3.07	3.16	3.07
Slice 10	0.86	0.91	0.93	0.96

Table D12
Percent Average Area Per Slice for FPL 6527 Oven-Aged
Chromatograms

Slice Number	Heating Time		
	A	B	C
Slice 1	0.95	0.90	1.66
Slice 2	1.63	1.44	2.47
Slice 3	10.77	9.76	10.57
Slice 4	21.36	21.00	20.64
Slice 5	22.64	22.95	22.23
Slice 6	18.43	18.85	18.23
Slice 7	13.23	13.60	13.16
Slice 8	7.03	7.35	7.04
Slice 9	3.04	3.21	3.08
Slice 10	0.93	0.94	0.92

Table D13
Percent Average Area Per Slice for FPL 6527 Weather-O-Meter
Aged Chromatograms

Slice Number	Heating Time		
	A	B	C
Slice 1	0.88	1.05	1.74
Slice 2	1.30	1.71	2.52
Slice 3	9.55	10.33	10.39
Slice 4	21.30	21.40	20.77
Slice 5	23.32	23.00	22.43
Slice 6	18.96	18.50	18.22
Slice 7	13.50	13.08	13.01
Slice 8	7.17	6.95	6.97
Slice 9	3.09	3.06	2.99
Slice 10	0.93	0.92	0.95

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13. ABSTRACT (Maximum 200 words) The premature failure of field molded pavement joint sealants has led to increased maintenance cost and can reduce the life cycle of a pavement structure. Two possible causes of premature failure of pavement joint sealants are prolonged heating prior to installation and excessive aging after it has been installed into the joint. This laboratory study was conducted to evaluate the use of gel permeation chromatography (GPC) as a method for identifying sealants that have been exposed to prolonged heating or that have aged because of natural weathering. This research consisted of a literature review and a three-phase laboratory study. Material specification testing and GPC analysis were conducted to determine if physical and/or molecular size distribution changes could be detected in the sealants. The conclusions of the laboratory study indicated that GPC analysis could be used to detect changes in sealant materials caused by exposure to extended heating and aging, but that the detected changes were inconsistent and could not be correlated with physical test properties.				
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