Chemical and Biological Stability of Solvent Refined Coal Liquids

**C. W. Wright
W. C. Weimer**

January 1984

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FOREWORD

This report presents results of both long-term and short-term stability studies of the chemical composition and biological activity of solvent refined coal (SRC) I and II liquids which were provided by the Pittsburgh and Midway Coal Mining Co. Sample constituency was monitored as a function of storage temperature, dilution, cover atmosphere, and ambient light. Biological activity was measured using the histidine reversion microbial mutagenicity assay with S. typhimurium TA98. Chemical composition was monitored using high resolution gas chromatography (GC) and high resolution gas chromatography/mass spectrometry (GC/MS). The relative amounts of major components were computed in relation to an internal standard which had been added. Data were analyzed by computer-based analysis of variance techniques.

EXECUTIVE SUMMARY

Both long-term and short-term stability studies of the chemical composition and biological activity of solvent refined coal (SRC) I and II liquids have been performed. Concentrations of major sample components were monitored as a function of storage time, temperature, dilution, cover atmosphere, and ambient lighting conditions. Biological activity was measured with a histidine reversion assay for mutagenicity against S. typhimurium TA98 with S-9 rat-liver homogenate metabolic activation. Chemical composition was monitored using high resolution gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). The data were analyzed by computer-based analysis of variance techniques (ANOVA). A brief synopsis of parameters of the experiments performed at 4°C, 20°C, 60°C, and 100°C and the results obtained are given below.

A total of seventeen samples consisting of SRC-I light oil, wash solvent, and process solvents, and SRC-II naphthas, middle distillates, heavy distillates, and fuel oil blends (FOB) were monitored during storage in a repository. Conditions of repository storage were 4°C, in the dark, under a nitrogen atmosphere, in inert (glass or Teflon-lined stainless steel) containers. After storage for four years under these conditions, there was no significant change in the chemical composition or biological activity of the SRC materials. Certain of the heavy end samples, however, tended to form layers upon standing. Hence, without adequate mixing prior to sampling or use, the chemical characteristics of these samples would deviate from the bulk composition due to inhomogeneity in the bulk oil.

SRC-II FOB was chosen as a sample to undergo storage at harsher conditions than those of the repository, since many of the components found in this sample are representative of the components found in the other SRC materials. Changes that occurred in the FOB under harsher conditions are probably analogous to changes that may occur over longer periods of time in the repository. Samples of FOB were stored in duplicate under storage parameters of cover atmosphere (air vs. nitrogen), ambient lighting (light vs. darkness), and dilution (undiluted vs. dilution in methylene chloride) at -20°C and at room temperature (~20°C) for one year. There was no significant change in the major chemical

constituency for any of the samples stored under these conditions, except the samples stored diluted in methylene chloride, under an air atmosphere, in the light. For this sample the cresols and more highly alkylated phenols, indan and alkylated indans, indanol, and tetralin peaks showed a significant decrease in concentration. Similar decomposition occurred with SRC-II FOB diluted in methylene chloride and stored at -20°C for three years. The only significant changes in biological activity as measured by the microbial mutagenicity test occurred in the samples stored either diluted or undiluted at room temperature, in the light, under an air atmosphere. When diluted, the activity was completely eliminated, while undiluted it decreased by about a factor of two after storage for one year. When diluted and stored at -20°C for three years the mutagenicity was also significantly decreased.

Eighteen and three FOB samples were stored at 60°C and 100°C , respectively, in the dark under an air atmosphere. The samples were monitored seven times over a 32-week period under these severe conditions. Of the major chemical constituents, the cresols, alkylated indans, and indanol decreased in concentration most significantly. In addition, after storage at 100°C for 16 weeks, the indole and amino-polycyclic aromatic hydrocarbons (amino-PAH) degraded. This was determined when the nitrogen-containing polycyclic aromatic fraction was studied more closely. Biological activity was completely eliminated after storage at these increased temperatures.

Overall, when degradation occurred, biological activity decreased and concentrations of hydroxylated PAH, partially hydrogenated PAH, indoles, and amino-PAH decreased. Thus far (four years), degradation of materials stored neat in the repository has not been detected.

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1.0 INTRODUCTION

The Pacific Northwest Laboratory (PNL) maintains a repository of synfuel materials. The materials in this repository are utilized for comparative purposes between synfuels technologies, for evaluation of sample characteristics from various process streams within a single technology, and for biological testing. These research materials are stored in a refrigerated repository maintained at approximately 4°C. A computerized materials accounting system is used to track the quantity of each material remaining in the repository and to identify the investigators to whom subsamples of these materials have been released.

Several solvent refined coal (SRC) I and II liquids have been obtained in large quantities (>25L) and have been stored and subsampled throughout long-running biological or ecological testing regimes. Since the coal liquids are used over long periods of time, it is necessary to determine if the integrity of the chemical composition and biological activity is maintained during storage. The chemical compositions of these materials were determined initially and have been monitored during their storage in the repository at 4°C. Along with this monitoring, several experiments designed to monitor the chemical composition of the SRC materials under other storage conditions chosen to accelerate the kinetics of the reactions causing chemical change have been performed. The effects of storage at -20°C, 20°C, 60°C, and 100°C as well as cover atmosphere, dilution, and ambient lighting conditions were investigated. Results of these experiments serve as benchmarks for changes in chemical composition which may occur over a longer period of time in the repository. Results also give insight into the environmental degradation of the coal liquids. The same SRC coal liquid samples stored in the repository and under the harsher experimental conditions were monitored for changes in mutagenicity by a microbial bioassay against S. typhimurium TA98.

Several other studies have been conducted on the aging characteristics of synthetic fuels. Kershaw and Gray (1) found that there was no significant change in the IR, ¹H NMR spectra, or average molecular weight of coal hydrogenation liquids stored at room temperature while bubbling oxygen or nitrogen

through the liquids. The viscosity did increase over a period of time, with the greatest increase found in the samples stored under oxygen. Studies by Karn et al. (2-4) gave similar results. SYNTHOIL products were stored under a variety of conditions which included ambient temperatures as well as 30°C and 61°C, atmospheres of nitrogen, air, and oxygen, stirred and unstirred samples, and ambient light versus darkness. They found that the greatest effect of exposure to oxygen was increased viscosity. Accelerated carbonyl formation giving rise to an increased average molecular weight under storage conditions with oxygen and elevated temperatures was noted from IR spectral analysis. Frankenfeld et al. (5-7) found that the addition of nitrogen compounds, particularly alkylated heterocyclic nitrogen compounds, promoted sediment formation upon storage of petroleum-derived jet fuels and shale liquids. Oxygen promoted sediment formation to a significant degree. Results of these experiments also showed an increase in viscosity of the products upon storage over time and at elevated temperature.

Studies involving SRC products have implicated oxidative coupling of phenolic compounds as a major aging mechanism (8,9). A 3:7 blend of solid SRC-I product and SRC-II middle distillate were aged in the presence of Cu and O₂ by Hara et al. (10). Viscosity increased significantly with time and was attributed to the formation of higher molecular weight components. White et al. (11) quantified individual phenolic compounds in an SRC-II middle distillate before and after accelerated aging in the presence of Cu and O₂. The concentration of phenolic constituents decreased during aging. Dimers, trimers, tetramers, and larger oligomers formed by the condensation of phenols were characterized in the aging product by high resolution mass spectrometry (HRMS).

The stability studies of synthetic fuels described in the present report differ from those previously presented in the literature in several ways. Most notably, the aging investigations have been carried out over a long period of time, four years. Secondly, the aging characteristics were related to the biological activities of the aged products. Finally, the data analysis methods in the present study were more rigorous than those utilized by other investigators. The samples were analyzed on a peak-to-peak basis by high resolution gas chromatography (GC). Individual components were identified by gas

chromatography/mass spectrometry (GC/MS) and were monitored over a period of time under the various storage conditions previously mentioned. Changes in composition were represented by changes in the amounts of individual components. Results were analyzed by computer-based analysis of variance to determine when a sample's composition had changed. The experiments allowed the acquisition of data to determine under what conditions the composition of SRC materials changed, which specific components were being modified, and whether storage under the conditions of the repository is a viable means of maintenance for coal liquids over long periods of time without experiencing chemical changes.

2.0 EXPERIMENTAL METHODS

2.1 SAMPLE MATERIALS

The following SRC-I materials (with number of replicates) were subsampled in small volumes (<1 L) and stored for monitoring purposes: one light oil (LO); one wash solvent (WS); and two process solvents (PS). In addition to these SRC-I materials, the following SRC-II materials (with number of replicates) were stored for monitoring purposes: two naphthas (N); four middle distillates (MD); three heavy distillates (HD); and four fuel oil blends (FOB), a mixture of 2.9 parts middle distillate to 1 part heavy distillate. Table 2.1 summarizes the samples stored for monitoring purposes and their approximate boiling point ranges. All samples were supplied by the Pittsburgh and Midway

TABLE 2.1. SRC Samples Stored for Monitoring Purposes

<u>Sample</u>	<u>Identification Number</u>	<u>Approximate Boiling Point Range</u>
SRC-I Light Oil	3317-073-16	ambient - 380°F
SRC-I Wash Solvent	3317-075-19	380 - 480°F
SRC-I Process Solvent	3317-066-26	480 - 850°F
SRC-I Process Solvent	3317-066-27	
SRC-II Naphtha	3317-125-01B	ambient - 350°F
SRC-II Naphtha	3317-055-04	
SRC-II Middle Distillate	3317-129-02	350 - 550°F
SRC-II Middle Distillate	3317-130-02	
SRC-II Middle Distillate	3317-131-02	
SRC-II Middle Distillate	3317-058-02	
SRC-II Fuel Oil Blend	3317-079-23	350 - 850°F
SRC-II Fuel Oil Blend	3317-079-24	
SRC-II Fuel Oil Blend	3317-079-25	
SRC-II Fuel Oil Blend	3317-079-26	
SRC-II Heavy Distillate	3317-132-02	550 - 850°F
SRC-II Heavy Distillate	3317-134-02	
SRC-II Heavy Distillate	3317-015-11	

Coal Mining Co. Each replicate represents a discrete sample collected from the Ft. Lewis, WA, pilot plant during a period of stable, lined-out operating conditions. While these operating conditions have been defined for each sample, the samples may not be representative of materials that will be produced at commercial coal liquefaction facilities.

2.2 STABILITY STUDIES PARAMETERS

2.2.1 4°C

The 17 subsamples of distillates from the SRC-I and II processes, described in the preceding section, were stored under the same identical conditions as have all of the larger-volume coal liquefaction research materials in the repository. They were stored in the dark in inert containers at a temperature of 4°C under a blanket of nitrogen atmosphere. (Teflon-lined stainless steel drums are used for storing large-volume samples. The smaller samples were stored in glass jars with aluminum-lined caps or in Teflon bottles.) The chemical composition and biological activity of each of the 17 subsamples were monitored every two to four years. (The methods used for this monitoring are presented in the Data Acquisition Section 2.3, page 2.6.) Monitoring of the 17 samples stored under these conditions over time has shown the long-term chemical and biological effects of storage of coal liquefaction materials.

In addition to the biennial monitoring of samples stored under repository conditions, studies at -20°C, 20°C, 60°C and 100°C were performed with an SRC-II fuel oil blend sample. Changes in the FOB components under the accelerated aging conditions of these studies are assumed to be analogous to changes that may occur over longer periods of time in the repository. The FOB was chosen for these additional stability studies because, due to its wide boiling range (350° to 850°F), many of the components found in this sample are also found in the other SRC distillate materials stored in the repository.

2.2.2 -20°C, 20°C

Ten-mL samples of the SRC-II FOB were stored in glass vials in duplicate in a freezer at -20°C. The effect of cover atmosphere was monitored by

blanketing one sample set with nitrogen (the control) and the other sample set with air (condition 1). This control also served as the control for the studies at 20°C.

Ten-mL samples of the SRC-II FOB were stored in glass vials in duplicate at room temperature (approximately 20°C). The effects of ambient light, cover atmosphere, and dilution were studied by storing these sample sets under the following conditions: (A) undiluted in the light and covered with an inert nitrogen atmosphere (condition 2); (B) diluted 1:200 or 1:20 FOB:methylene chloride, stored in the light, and covered with an air atmosphere (condition 3); (C) undiluted in the light and covered with an air atmosphere (condition 4); (D) undiluted in the dark and covered with a nitrogen atmosphere (condition 5); and (E) undiluted in the dark and covered with an air atmosphere (condition 6). A schematic diagram of the stability study parameters of the -20°C and 20°C studies is shown in Figure 2.1. The labeled conditions correspond with those given in the text.

The effects of dilution, cover atmosphere, temperature, and ambient light were monitored by the comparison of both chemical composition and biological activity data for the samples shown in Table 2.2. The effects of singular and multiple parameters were monitored for the samples as shown in the table.

2.2.3 60°C

One-mL samples of an SRC-II FOB were placed in each of 18 inert glass vials which served as replicates for this study. They were sealed with screw-on caps under an air atmosphere and were stored in an oven at 60°C in the dark. The vials were subsampled in duplicate according to the schedule shown in Table 2.3. At each subsampling occasion, three of the replicate vials were opened and subsampled for the first time. These same vials were opened and subsampled a second time at the next subsampling occasion along with the three others being subsampled for the first time. The subsampling proceeded in this manner with each vial opened and subsampled on no more than three subsequent subsampling occasions.

FIGURE 2.1. Schematic Diagram of -20°C and 20°C Stability Study Parameters of Temperature, Light, Cover Atmosphere, and Dilution

TABLE 2.2. Intercomparison from -20°C and 20°C Studies to Monitor the Effects of Storage Under Various Conditions

<u>Sample Comparison^(a)</u>	<u>Parameter(s) Monitored</u>
Condition 3 versus Condition 4	Dilution
Control versus Condition 1 Condition 2 versus Condition 4 Condition 5 versus Condition 6	Air Atmosphere
Control versus Condition 5 Condition 1 versus Condition 6	Room Temperature
Condition 2 versus Condition 5 Condition 4 versus Condition 6	Ambient Light
Control versus Condition 2 Condition 1 versus Condition 4	Ambient Light plus room temperature
Control versus Condition 6	Air atmosphere plus room temperature
Control versus Condition 4	Ambient Light plus air atmosphere and room temperature
Control versus Condition 3	Ambient Light plus air atmosphere, room temperature, and dilution

(a) Conditions correspond to those shown in Figure 2.1

Following this subsampling procedure allowed the effects, if any, of numerous samplings from a particular vial to be monitored. It also provided a large number of replicate analyses for statistical purposes. For example, at the 32 week subsampling, 18 subsamples were taken from 9 vials stored under the same conditions. Each of the 18 subsamples were analyzed four times by high resolution gas chromatography (explained in the Data Acquisition Section 2.3, page 2.6) to give a total of 72 sets of data for analysis of one subsampling of the 60°C stability study.

2.2.4 100°C

One-mL samples of an SRC-II FOB were placed in each of three inert glass vials for the stability study at 100°C. The vials were sealed with screw-on

TABLE 2.3. Subsampling Schedule for the 60°C Stability Study of an SRC-II Fuel Oil Blend

Time	Vial Number ^(a)																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 week	X ^(b) X	X X	X X															
2 weeks	X X	X X	X X	X X	X X	X X												
4 weeks	X X	X X	X X	X X	X X	X X	X X	X X	X X									
8 weeks				X X	X X	X X	X X	X X	X X	X X	X X							
16 weeks							X X	X X	X X	X X	X X	X X	X X	X X	X X			
32 weeks										X X	X X	X X	X X	X X	X X	X X	X X	X X

(a) Represents replicate samples stored in the oven.

(b) Each X represents a subsampling of the vial for analysis.

caps under an air atmosphere and were stored in an oven at 100°C in the dark. Each vial was subsampled in duplicate at 1 week, 2 weeks, 4 weeks, 8 weeks, 16 weeks, and 32 weeks from the first day they were placed in the oven. The changes which occur under these harsh conditions, chosen to accelerate the kinetics of reactions which cause chemical change, serve as benchmarks for changes that may occur under mild conditions of storage over longer periods of time.

2.3 DATA ACQUISITION

2.3.1 High Resolution Gas Chromatography

Samples stored under the conditions described in the Stability Studies Parameters Section 2.2 were analyzed for chemical composition by high resolution gas chromatography using 15-30 M fused silica columns coated with SE-52. Samples were diluted approximately 25 μ L in 5 mL of methylene chloride containing a known quantity of an internal standard for the 4°C study. Samples

were diluted approximately 50 μL in 5 mL of methylene chloride containing a known quantity of an internal standard for the -20°C , 20°C and 60°C studies. Samples were diluted approximately 40 μL in 5 mL of methylene chloride containing a known quantity of an internal standard for the 100°C study. (Volumes were approximate since small volumes of viscous liquids were measured.) Samples of SRC-II naphthas and SRC-I light oil were analyzed neat, with the addition of an internal standard, using a 90 M glass capillary column coated with SF-96. The 5 mL of diluted sample were placed equally in three separate vials for analysis.

Internal standards were chosen that would not cause any interference in the gas chromatographic analysis. Straight-chain aliphatic hydrocarbons were used because a large selection of compounds with different elution times was available and their presence would not be expected to chemically modify any of the constituents already present in the complex synfuel mixtures. Since the samples analyzed were rough distillate cuts of SRC products, each different sample type needed a different internal standard (ISTD) to ensure there was no co-elution of internal standard with a component already present at a significant level in the material. This was particularly important since some aliphatic hydrocarbons are expected to be found in the SRC materials studied. Table 2.4 contains the list of SRC materials studied and the internal standards which were added for gas chromatography analysis.

After dilution and the addition of an internal standard, the diluted samples in two of the three vials prepared were analyzed by high resolution gas chromatography using the conditions summarized in Table 2.5. The third vial was stored for other analyses. The amounts of the major peaks in the chromatograms were calculated by normalizing the peak area or height of the individual peaks of interest to the internal standard peak. The following equation was used:

$$\frac{\text{Area or height of peak of interest}}{\text{Area or height of internal standard}} \cdot 100 = \text{Amount of peak of interest (1)}$$

TABLE 2.4. Internal Standards Added for High Resolution Gas Chromatography Analysis

<u>SRC Material</u>	<u>Internal Standard</u>
Naphtha ^(a)	C ₁₁ H ₂₄ n-Undecane
Middle Distillate ^(a)	C ₁₉ H ₄₀ n-Nonadecane
Fuel Oil Blend ^(a)	C ₁₉ H ₄₀ n-Nonadecane
Heavy Distillate ^(a)	C ₁₅ H ₃₂ n-Pentadecane
Light Oil ^(b)	C ₁₁ H ₂₄ n-Undecane
Wash Solvent ^(b)	C ₁₅ H ₃₂ n-Pentadecane
Process Solvent ^(b)	C ₁₂ H ₂₆ & C ₁₉ H ₄₀ n-Dodecane & n-Nonadecane

(a) SRC-II material.

(b) SRC-I material.

The amount of the peak of interest was calculated as a percent of the internal standard peak response. At the end of every gas chromatographic run, a table of data similar to that shown in Table 2.6 was acquired. The retention time of each peak was reported with the amount present. Multiple injections of each sample vial were performed for statistical purposes. Each diluted sample was analyzed a minimum of four times.

The individual peaks that were monitored were identified through gas chromatography/mass spectrometry (GC/MS) using the third vial of diluted samples which had been previously set aside. An Hewlett-Packard 5992 benchtop GC/MS system equipped with a 30 M SE-52 fused silica column was used for the SRC-I WS and PS and the SRC-II MD, HD, and FOB. An Hewlett Packard 5982A GC/MS system equipped with a 90M SF-96 glass capillary column and split injection was used for the analysis of the SRC-I LO and the SRC-II N.

2.3.2 Chemical Fractionation

One-hundred-mg samples of the FOB stored under the control condition (-20°C, nitrogen atmosphere, in the dark) and the conditions of 100°C, air atmosphere, in the dark for 16 weeks were chemically fractionated in triplicate to identify any measurable changes in chemical class composition. The fractionation scheme used is depicted in Figure 2.2 (12). Briefly, the samples were eluted through a column packed with 9 g of neutral alumina. Aliphatic

TABLE 2.5. Conditions for Gas Chromatography Analysis

Stability Study Temperature	Sample	Capillary Column	Carrier Gas-Velocity	Injection Technique	Oven Temperature Program
4°C	SRC-II N ^(a)	90 M SF-96	He-30 cm/s	split 1:71	12 min @ 35°C, then 8°C/min to 175°C
4°C	SRC-II MD ^(a)	30 M SE-52	He-50 cm/s	splitless ^(c)	2 min @ 40°C, then 2°C/min to 170°C; and 15°C/min to 250°C
4°C	SRC-II HD ^(a)	15 M SE-52	H ₂ -100 cm/s	splitless ^(c)	2 min @ 50°C, then 10°C/min to 100°C; 2°C/min to 225°C; and 15°C/min to 225°C
4°C, 100°C	SRC-II FOB ^(a)	30 M SE-52	He-50 cm/s	splitless ^(c)	2 min @ 40°C, then 2°C/min to 200°C; and 15°C/min to 250°C
4°C	SRC-I LO ^(a)	90 M SF-96	He-30 cm/s	split 1:71	12 min @ 35°C, then 8°C/min to 175°C
4°C	SRC-I WS ^(a)	30 M SE-52	He-50 cm/s	splitless ^(c)	2 min @ 40°C, then 2°C/min to 120°C; and 15°C/min to 250°C
4°C	SRC-I PS ^(a)	15 M SE-52	H ₂ -100 cm/s	splitless ^(c)	2 min @ 50°C, then 2°C/min to 200°C
-20°C, 20°C, 60°C	SRC-II FOB ^(b)	30 M SE-52	He-50 cm/s	splitless ^(c)	2 min @ 70°C, then 2°C/min to 200°C

(a) Chromatographed on an Hewlett-Packard 5880A gas chromatograph.

(b) Chromatographed on an Hewlett-Packard 5710 gas chromatograph.

(c) An autosampler was used for injection at time = 2 years, manual injection was used in all other cases.

TABLE 2.6. Sample Data Table From an SRC-II Fuel Oil Blend Sample Stored in the Repository at 4°C

<u>Retention Time</u>	<u>Amount(a)</u>	<u>Standard Deviation of Amount (6 Runs)</u>
11.35	77.1	6.1
11.49	13.0	1.1
13.85	20.9	2.0
15.70	46.4	3.5
17.21	78.2	8.1
20.57	17.0	1.3
21.28	30.2	2.1
21.87	23.4	1.4
22.04	58.0	4.6
23.23	21.5	0.73
23.43	132.8	8.5
25.72	16.4	1.0
29.11	42.6	2.2
29.60	35.4	1.4
30.95	117.0	4.9
31.95	27.9	1.0
33.07	20.7	0.81
34.62	19.7	1.6
35.40	31.0	1.1
36.30	14.9	1.5
36.68	37.5	1.2
37.47	40.3	1.1
38.14	34.0	1.2
38.38	64.7	1.0
42.46	18.3	0.78
42.92	18.9	0.43
44.41	15.5	0.50
48.79	14.0	1.0
49.49	10.8	0.97
50.01	11.6	0.57
59.54	36.7	1.5
75.60	11.8	0.88

(a) Percent of internal standard based on 2.50 mg/mL C₁₉ ISTD.

FIGURE 2.2. Chemical Class Fractionation Using Alumina and Silicic Acid Column Chromatography

hydrocarbons were eluted with hexane (fraction A-1), polycyclic aromatic hydrocarbons (PAH) were eluted with benzene (fraction A-2), nitrogen-containing polycyclic aromatic compounds (N-PAC) were eluted with 99:1 chloroform:ethanol (fraction A-3), and hydroxylated PAH (HPAH) were eluted with methanol. To further fractionate the nitrogen-containing PAC for the analysis of mutagenically

active aromatic amines, the A-3 fraction was eluted through a silicic acid column. The carbazoles were eluted with 1:1 hexane:benzene (fraction S-1), an amino-PAH rich fraction was eluted with benzene (fraction S-2), and the azarenes were eluted with 1:1 benzene:ethyl ether. The weight percent of the sample eluting in each of the seven fractions monitored the chemical composition of classes of organic compounds found in the FOB under the harshest storage conditions versus the mildest storage conditions (-20°C).

Individual components in the A-2, A-3, and S-2 fractions were quantitated through high resolution GC using SE-54 bonded phase fused silica columns to monitor the more trace level constituents of the FOB under the harshest versus mildest storage conditions. These fractions were chosen since they contain the greatest quantities of mutagenic or carcinogenic constituents (13-16). Response factors were calculated for standards at seven different concentrations ranging over two orders of magnitude. If a standard was not available, a response factor for a standard of similar retention time and chemical class was used. Samples were analyzed at three different concentration levels, i.e., 10 mg/mL, 5.0 mg/mL, and 2.5 mg/mL with 2-chloroanthracene added as an internal standard at a final concentration of 50 ng/ μ L. The amino-PAH were quantitated through the use of an electron capture detector after derivatization with pentafluoropropionic anhydride (PFP) to the corresponding fluoroamides (17).

2.3.3 Direct Probe Mass Spectrometry

Several samples of SRC-II heavy distillate were taken from varying depths of the Teflon-lined stainless steel container (60 L capacity) used to store the sample in the repository. The container was pressurized with nitrogen and material was forced out from specific depths with the use of a Teflon sampling hose. Six samples were obtained from the 29 cm depth of HD sample in the repository. The first sampling depth was two cm from the top of the undisturbed container, the second was five cm from the bottom of the undisturbed container, and the third was from the bottom of the undisturbed container. The sample from the bottom of the container was noted to contain both light and heavy sludges, which formed the fourth and fifth samples when separated. The sixth sample of SRC-II HD was taken after the container was mixed continuously for 18 h at room temperature.

Five μL of each of these six samples were analyzed by low-voltage probe mass spectrometry on a VG-ZAB-1F mass spectrometer at 10 eV with a 6 kV accelerating voltage. The probe was brought from ambient to 250°C while scanning a mass range of 60-500 amu. The dynamic mass resolution was 1:2000. The source temperature was 250°C. Data were acquired and processed by a VG 2035 data system.

2.3.4 Microbial Mutagenicity

Microbial mutagenicity was measured against S. typhimurium TA98 after metabolic activation with S-9 rat liver homogenate (18). The two SRC-II naphthas, four middle distillates, three heavy distillates, and four fuel oil blends, along with the SRC-I light oil, wash solvent, and two process solvents which were stored in the repository, under a nitrogen atmosphere, in the dark, were monitored for changes in biological activity after four years. A sample of the control and those under conditions 1 through 6 from Figure 2.1 (-20°C and 20°C studies with additional parameters of cover atmosphere, dilution, light, and dark) were monitored for microbial mutagenicity after one year and after three years for a sample of FOB diluted in methylene chloride and stored at -20°C. Samples of SRC-II FOB exposed to 32 weeks at 60°C and 6 and 26 weeks at 100°C under an air atmosphere in the dark were also monitored for changes in microbial mutagenicity. In addition, the microbial mutagenicity of the samples of SRC-II HD from varying depths in the storage container were compared with the homogenized sample.

2.3.5 Summary

Table 2.7 contains a summary of the types of analyses that were performed on the samples stored under the various conditions of the stability studies. Results of these analyses are given in the Results and Discussion Section, page 3.1.

2.4 STATISTICAL ANALYSIS

Each peak concentration relative to the internal standard was identified with a descriptive vector of values. Variables defined by these values included the SRC material studied (N, LO, MD, FOB, etc.), the storage

TABLE 2.7. Summary of Analyses of Stability Study Samples

<u>Samples</u>	<u>GC</u>	<u>GC/MS</u>	<u>Bioassay</u>	<u>Chemical Fractionation/ Quantitation</u>	<u>Direct Probe</u>
SRC-II N, 4°C	X	X	X		
SRC-II MD, 4°C	X	X	X		
SRC-II HD, 4°C	X	X	X		X
SRC-II FOB, 4°C	X	X	X		
SRC-I LO, 4°C	X	X	X		
SRC-I WS, 4°C	X	X	X		
SRC-I PS, 4°C	X	X	X		
SRC-II FOB, -20°C (control)	X	X	X	X	
SRC-II FOB, -20°C (condition 1)(a)	X		X		
SRC-II FOB, 20°C (condition 2)(a)	X		X		
SRC-II FOB, 20°C (condition 3)(a)	X	X	X		
SRC-II FOB, 20°C (condition 4)(a)	X		X		
SRC-II FOB, 20°C (condition 5)(a)	X		X		
SRC-II FOB, 20°C (condition 6)(a)	X		X		
SRC-II FOB, 60°C	X	X	X		
SRC-II FOB, 100°C	X		X	X	

(a) Conditions refer to those given in Figure 2.1.

conditions, the time of analysis, the replicate, the vial after dilution, the chromatographic run, and peak number. With each relative concentration characterized by a unique vector of values, the data in each analysis set were described by summary statistics and further explored using ARTHUR (19), a collection of pattern recognition routines; PNL-enhanced MINITAB (20), a linear algebra/database management tool; and RUMMAGE (21), an analysis of variance statistical package.

Through interactive color graphics, relative concentrations versus peak number were displayed on a high resolution screen. These graphs were enhanced by the use of background indicator variables such as time or replicate to determine the color of each plotted point. Offset plotting where the data at one treatment level was plotted near the data from another level was also utilized. In this manner, a summary chromatogram was created. This use of graphics allowed for an efficient determination of global characteristics or patterns in an analysis set as well as specific data characteristics such as the identification of outliers and other data anomalies.

Several characteristics common to all the data sets were identified. The displays and summary statistics revealed that the variation increased with increase in the mean relative concentration. Under this circumstance, analysis of variance (ANOVA) techniques are not optimal. To increase the power of the analysis, the natural logarithm transform for each relative concentration was calculated; the transformed data set replaced the original in further analysis. The transform reduced the dependent relationship between the mean and variance in the relative concentration data distribution. The log transformed data were then assumed normally distributed and analyzed through ANOVA techniques (22) suitable for unbalanced designs (21).

ANOVA is a statistical technique whereby measures of variation for each factor are calculated and then compared to a measure of variation assigned to the pure experimental error. The comparison statistic is called an F statistic:

$$F = \frac{MS \text{ (factor)}}{MS \text{ (error)}} \quad (2)$$

Under assumption of no factor effect, the ratio would equal 1 because any variation measured for the factor would be pure experimental error. The further this ratio deviates from 1, the stronger the effect of the factor on the relative concentrations. For ANOVA, it is assumed that the numerator and denominator of the F statistic are estimated independently. A relative error of 20% or the estimate of the pure error (which ever was larger) was used for the MS (error) value (0.04 for 20% error). The 20% error determination is considered a true experimental error determined in experiments presented in the Results and Discussion Section page 3.14. Peak-to-peak statistical analysis was used so that specific compositional changes could be monitored. General compositional trends can be observed from the specific peak changes in the samples.

The relative concentrations of the 4°C data set were adjusted for variation in the concentration of the internal standard from the initial measurement to the after-storage measurements. A multiplication factor, the ratio of the ISTD concentration in the initial analysis to the ISTD concentration in the analysis after storage, was used to correct for these differences induced by the experimental procedure. For the 60°C and 100°C data sets, a reference peak was chosen for normalization of dilution over the long-running experiments.

3.0 RESULTS AND DISCUSSION

3.1 HIGH RESOLUTION GAS CHROMATOGRAPHY

The complete list of individual compounds monitored in all the stability studies is given in Table 3.1. The numbers refer to peaks designated in the chromatograms shown in Figures 3.1 through 3.10, which are representative gas chromatograms of the SRC-II naphthas, SRC-I light oil, SRC-II middle distillates, SRC-II fuel oil blends, SRC-I wash solvent, SRC-II heavy distillates, and SRC-I process solvents. Numbered peaks, identified in Table 3.1, are those monitored in the sample while being stored in the repository at 4°C, in the dark, and under a nitrogen atmosphere. The internal standard added to each of the samples is labeled in the chromatograms. The components were identified by GC/MS. It should be noted that the identifications given in Table 3.1 are for major components found in particular peaks and that minor components can co-elute with these peaks.

Representative gas chromatograms from the accelerated stability studies using an SRC-II FOB are presented in Figures 3.8 through 3.10. Figure 3.8 is an example of the sample kept under the control conditions (-20°C, dark, under nitrogen atmosphere) and shows the peaks monitored in the -20°C and 20°C studies. Figures 3.9 and 3.10 show the peaks monitored in the 60°C and 100°C studies, respectively, through the example of the time=0 samples. Identification of the peaks is also given in Table 3.1. For Figures 3.1 through 3.10, all peaks labeled with the same number represent the same compound. This allows the intercomparison of data for a specific compound between different SRC materials.

Appendix I is a compendium of the data gathered during the accelerated stability studies as well as the data for the repository samples. The mean values of all GC runs calculating the individual peak heights or areas, normalized to an internal standard, for the seventeen materials stored in the repository at 4°C, in the dark, and under a nitrogen atmosphere are presented in Tables 7.1-7.17 of Appendix I. Tables 7.18 and 7.19 in Appendix I contain two sets of mean values of GC data collected for the -20°C and 20°C study.

TABLE 3.1. Compounds Monitored in the Stability Studies

Peak No. (a)	Compound (b)	Peak No. (a)	Compound (b)
1	C ₁ -Butane	32	Indan
2	Pentane	33	<u>o</u> -Cresol
3	Pentene	34	C ₄ -Benzene
4	C ₂ -Butane	35	<u>m</u> - & <u>p</u> -Cresol, C ₁ -Indan
5	C ₁ -Pentane	36	n-Undecane
6	n-Hexane	37	C ₂ -Phenol
7	Hexene	38	C ₁ -Indan
8	Benzene	39	C ₁ -Indan
9	Cyclohexane	40	C ₂ -Phenol
10	Cyclohexene	41	Tetralin
11	C ₇ H ₁₆	42	C ₂ -Phenol
12	Heptene	43	Naphthalene
13	n-Heptane	44	C ₂ -Phenol
14	C ₁ -Cyclohexane	45	C ₃ -Phenol
15	C ₂ -Pentene	46	C ₁ -Dihydronaphthalene
16	Toluene	47	C ₁ -Tetralin
17	C ₈ H ₁₈	48	C ₁ -Tetralin
18	C ₈ H ₁₈	49	C ₁ -Tetralin, C ₃ -Phenol
19	C ₂ -Cyclohexane	50	C ₁ -Dihydronaphthalene
20	n-Octane	51	C ₃ -Phenol
21	C ₃ -Cyclohexane	52	C ₃ -Phenol
22	<u>o</u> -Xylene	53	C ₂ -Indan
23	<u>m</u> -Xylene	54	C ₂ -Indan
24	<u>p</u> -Xylene	55	C ₂ -Indan
25	n-Nonane	56	2-Methylnaphthalene
26	C ₄ -Cyclohexane	57	1-Methylnaphthalene
27	C ₃ -Benzene	58	C ₃ -Indan
28	Phenol	59	C ₃ -Indan
29	C ₃ -Benzene	60	Indanol
30	C ₃ -Benzene	61	C ₂ -Tetralin
31	n-Decane		

TABLE 3.1. (contd)

Peak No. (a)	Compound (b)	Peak No. (a)	Compound (b)
62	C ₄ -Phenol	82	C ₁ -Fluorene
63	C ₄ -Phenol, C ₃ -Indan	83	Dibenzothiophene
64	Biphenyl	84	Tetrahydrophenanthrene
65	2-Ethyl naphthalene	85	Phenanthrene
66	2,6-Dimethyl naphthalene	86	C ₂ -Fluorene
67	C ₂ -Naphthalene	87	C ₂ -Fluorene
68	C ₂ -Naphthalene, Diphenylether	88	C ₂ -Fluorene
69	Acenaphthene	89	Carbazole
70	C ₃ -Naphthalene	90	3-Methylphenanthrene
71	C ₃ -Naphthalene	91	2-Methylphenanthrene
72	Dibenzofuran	92	1-Methylphenanthrene
73	Isopropyl naphthalene	93	C ₂ -Xanthene
74	Fluorene	94	Phenyl naphthalene
75	C ₁ -Acenaphthene, C ₂ -Biphenyl	95	C ₂ -Phenanthrene
76	C ₄ -Naphthalene	96	Fluoranthene
77	C ₄ -Naphthalene	97	Pyrene
78	Xanthene	98	Dihdropyrene
79	C ₁ -Fluorene	99	Benzo[b]fluorene, 2- or 4-Methylpyrene
80	C ₁ -Fluorene	100	C ₁ -Benzo[b]fluorene, C ₂ -Pyrene
81	C ₁ -Fluorene	101	C ₁ -Chrysene

(a) Numbers refer to peaks in Figures 3.1-3.10.

(b) Compounds tentatively identified by GC/MS.

Tables 7.20 and 7.21 in Appendix I contain the mean values of GC data collected during the 60°C and 100°C accelerated studies, respectively. Table 7.22 in Appendix I contains the mean values of GC data collected for an FOB sample diluted in methylene chloride and stored at -20°C for three years.

FIGURE 3.1. High Resolution Gas Chromatogram of an SRC-II Naphtha. Conditions: 90 M x 0.28 mm i.d. Glass Capillary Column Coated with SF-96; 1:71 Split Ratio Injection; Helium Carrier Gas; 12 min Isothermal at 35°C then Temperature Programmed to 175°C at 8°C/min. Numbers Refer to Identifications Given in Table 3.1.

FIGURE 3.2. High Resolution Gas Chromatogram of an SRC-I Light Oil. Conditions: Same as in Figure 3.1. Numbers Refer to Identifications Given in Table 3.1.

FIGURE 3.3. High Resolution Gas Chromatogram of an SRC-II Middle Distillate. Conditions: 30 M x 0.25 mm i.d. Fused Silica Capillary Column Coated with SE-52; Splitless Injection; Helium Carrier Gas at 50cm/s Linear Velocity; 2 min Isothermal at 40°C then Temperature Programmed to 170°C at 2°C/min and to 250°C at 15°C/min. Numbers Refer to Identifications Given in Table 3.1.

FIGURE 3.4. High Resolution Gas Chromatogram of an SRC-II Fuel Oil Blend. Conditions: Same as in Figure 3.3, Except Temperature Programmed to 200°C at 2°C/min. Numbers Refer to Identifications Given in Table 3.1.

FIGURE 3.5. High Resolution Gas Chromatogram of an SRC-I Wash Solvent. Conditions: Same as in Figure 3.3, Except Temperature Programmed to 120°C at 2°C/min. Numbers Refer to Identifications Given in Table 3.1.

FIGURE 3.6. High Resolution Gas Chromatogram of an SRC-II Heavy Distillate. Conditions: 15 M x 0.25 mm i.d. Fused Silica Capillary Column Coated with SE-52; Splitless Injection; Hydrogen Carrier Gas at 100 cm/s Linear Velocity; 2 min Isothermal at 50°C then Temperature Programmed to 100°C at 10°C/min, to 225°C at 2°C/min, and to 300°C at 15°C/min. Numbers Refer to Identifications Given in Table 3.1.

FIGURE 3.7. High Resolution Gas Chromatogram of an SRC-I Process Solvent. Conditions: Same as in Figure 3.6, Except Temperature Programmed from 50°C to 200°C at 2°C/min Only. Numbers Refer to Identifications Given in Table 3.1.

FIGURE 3.8. High Resolution Gas Chromatogram of the Control Sample from the -20°C and 20°C Studies of an SRC-II Fuel Oil Blend. Conditions: 30 M x 0.25 mm i.d. Fused Silica Capillary Column, Splitless Injection, Helium Carrier Gas at 50 cm/s Linear Velocity, 2 min Isothermal at 70°C then Temperature Programmed to 200°C at 2°C/min. Numbers Refer to Identifications Given in Table 3.1.

FIGURE 3.9. High Resolution Gas Chromatogram of the Time=0 Sample from the 60°C Study of an SRC-II Fuel Oil Blend. Conditions: Same as in Figure 3.8. Numbers Refer to Identifications Given in Table 3.1.

FIGURE 3.10. High Resolution Gas Chromatogram of the Time=0 Sample from the 100°C Study of an SRC-II Fuel Oil Blend. Conditions: 30 M x 0.25 mm i.d. Fused Silica Capillary Column Coated with SE-52, Splitless Injection, Helium Carrier Gas at 50 cm/s Linear Velocity, 2 min Isothermal at 40°C then Temperature Programmed to 200°C at 2°C/min and to 250°C at 15°C/min. Numbers Refer to Identifications Given in Table 3.1.

Analysis of the GC data to detect changes in composition over a period of time requires the ability to distinguish between actual changes in the sample and changes in the data which were due to differences in the GC experimental set-up. Data changes which might have been interpreted as changes may have been, in actuality, discrete differences caused by dissimilarities in chromatographic parameters. Flow rates through the column and the detector, injection technique, method of integration, column resolution, and/or differences in dilution all effect the data collected. To establish the level of error introduced by these parameters, four experiments were conducted. The first compared integration of area versus measurement of height in computing the relative amounts of components in the SRC materials compared to the internal standard. The second experiment consisted of chromatographing, under the same conditions, the same sample one day after it was originally analyzed; however, other samples were chromatographed in between the analyses. The third experiment compared results using split injection with split ratios varying by $\pm 10\%$. Finally, an experiment was performed in which all chromatographic parameters were reset to their initial settings after a complete modification of the instrument.

To compare integration using peak heights versus peak areas, two chromatographic runs were performed on the same SRC-II MD sample. After each run, two report tables were printed. The first used the heights of the peaks to calculate the relative amounts of components in the complex mixture based on the height of the internal standard. The second report used areas of the same peaks to calculate the relative amounts of the same components based on the area of the same internal standard. The results in Table 3.2 varied from a range of a +30% change in relative amount to a -38% change for particular peaks integrated by height versus area in the same run, with the duplicate runs giving similar results. There were no consistent trends in the same run except a tendency for early eluting peaks to yield smaller relative amounts when integrated using areas versus heights and late eluting peaks to yield greater relative amounts when integrated using areas versus heights. There were some exceptions to this trend. These data lead to the conclusion that one method of integration must be used for an entire series of samples; experiments

TABLE 3.2. Comparison of Peak Area versus Height for Computing Relative Amounts of Components in SRC-II Middle Distillate

<u>Retention Time (min)</u>	<u>Relative Area^(a)</u>	<u>Relative Height^(a)</u>	<u>Percent Changes Area versus Height</u>
11.4	62.5	76.6	-18.4
11.5	11.7	17.0	-31.1
13.9	19.0	29.5	-35.6
15.7	36.7	51.8	-29.1
17.2	83.5	76.0	+9.87
17.3	47.5	77.1	-38.4
20.6	14.8	18.3	-19.1
21.3	25.9	30.9	-16.2
21.9	18.7	21.6	-13.4
22.1	55.9	54.3	+2.95
23.3	19.5	19.4	+0.515
23.5	106	102	+3.92
29.1	35.2	35.3	-0.283
29.6	33.1	27.4	+20.8
31.0	91.1	88.7	+2.71
32.0	15.3	18.3	-16.4
33.1	18.8	16.5	+13.9
34.7	17.5	16.1	+8.70
37.5	38.3	30.2	+26.8
38.2	32.0	26.1	+22.6
43.5	21.0	18.7	+12.3
44.5	22.3	19.8	+12.6
50.1	22.8	17.5	+30.3

(a) Based on 3.59 mg/mL C₁₉ ISTD, SRC-II MD Sample, 1:16 dilution.

conducted using peak height integration (4°C, 100°C) cannot be correlated to experiments using peak area integration (-20°C, 20°C, 60°C) for the computation of relative amounts of major components under the chromatographic conditions used.

Results of the second experiment to establish a level of error caused solely by experimental variability showed that results varied up to 13% for individual peaks. After chromatographing a SRC-II MD sample five times and calculating a mean and standard deviation of the mean for the relative amounts of components based on an internal standard, another suite of samples was chromatographed. The next day, using the exact same set-up, the original

sample was again chromatographed and the results, given in Table 3.3, were compared to the original means and standard deviation of the means previously calculated. Although the majority of results obtained on the second day were within two standard deviations of the mean, a few were not. Results under these conditions varied by a maximum of -13% of the original data.

Since the SRC-II N and SRC-I L0 samples were chromatographed using a split injection technique, $\pm 10\%$ modifications of the split ratio (representing the estimated experimental error of this measurement) were made to check the variability of results. Figure 3.11 shows a plot of the relative amounts of specific peaks in an SRC-II N sample at three different split ratios. The amounts for each peak were connected to form a graphical representation of each chromatogram. As can be seen in the figure, wide variabilities were computed, with the least variability in the late eluting components closest to the internal standard. Slight variations in the split ratio can easily account for 50% error in the relative amounts calculated.

The final experiment was designed to analyze the variability of results due to irreproducibility of chromatographic parameters. Initial flow rates of helium carrier gas and hydrogen and air gases for the flame ionization detector (FID) were measured. A sample of an SRC-II FOB was then chromatographed in duplicate. Means and standard deviations of the mean were calculated for the relative amounts of components based on the internal standard for the two chromatographic runs. The chromatographic column was then removed, the FID turned off, and all gas flows modified. One loop of each end of the column was then broken off (to simulate normal attrition), the column was reinstalled in the oven, the injection port liner was changed, and all gas flows were set to the initial conditions. The same sample was then chromatographed and relative amounts of the same components were calculated. These results were compared to the initial results and are given in Table 3.4. The data varied up to a maximum of 26% for some particular peaks. Variability averaged 10-12%. It was decided from these four experimental studies that a 20% change in the relative amount of a peak was necessary before it was considered to be a change due to degradation at a 5% α level.

TABLE 3.3. Comparison of Chromatographic Variability After One Day
Using the Same Experimental Set-Up

Retention Time (min)	Relative Amount ^(a)		Percent Change ^(b)
	Day One	Day Two	
11.4	74.4 ± 3.73 ^(c)	71.0	
11.5	17.3 ± 0.245	15.0	-13.3
13.9	31.0 ± 1.22	27.6	-11.0
15.7	51.7 ± 1.99	48.9	
17.2	75.3 ± 4.37	73.1	
17.3	75.6 ± 3.63	-- ^(d)	
20.6	19.3 ± 0.935	18.1	
21.3	32.1 ± 1.47	30.5	
21.9	22.3 ± 1.15	21.3	
22.1	57.7 ± 4.55	53.6	
23.3	19.7 ± 0.737	19.6	
23.5	105 ± 5.05	101	
29.1	37.0 ± 1.59	35.8	
29.6	27.5 ± 0.606	27.4	
31.0	89.0 ± 2.71	89.1	
32.0	20.1 ± 1.33	20.5	
33.1	17.0 ± 0.360	16.8	
34.7	15.4 ± 1.24	16.1	
35.4	22.6 ± 0.696	22.8	
37.5	31.2 ± 0.808	31.4	
38.2	27.0 ± 0.608	27.1	
43.5	18.8 ± 0.404	19.3	
44.5	18.7 ± 0.792	18.6	
50.1	17.6 ± 0.353	17.8	

(a) Based on 3.59 mg/mL C₁₉ ISTD,
SRC-II MD Sample, 1:16 dilution.

(b) Only given when change is greater
than 10%, day one versus day two.

(c) Based on five chromatographic
determinations.

(d) No data.

FIGURE 3.11. Relative Amounts of Components in SRC-II Naphtha Sample 3317-055-04 Using Three Different Split Ratios for Injection. Amounts for Specific Peaks Were Connected for Graphical Representation.

TABLE 3.4. Comparison of Chromatographic Variability After Modification of Experimental Set-Up

Retention Time (min)	Relative Amount ^(a)		Percent Change ^(d)
	Before	After ^(b)	
9.93	26.7 ± 2.79	31.0	+16.1
12.1	4.75 ± 0.49	5.46	+14.9
14.0	16.9 ± 1.68	18.4	
15.5	ND ^(d)	36.5	
18.5	9.88 ± 1.14	10.9	+10.3
19.2	12.0 ± 1.31	12.6	
19.9	44.2 ± 4.82	43.9	
21.3	78.7 ± 7.55	75.1	
21.6	29.4 ± 2.60	26.9	
23.5	12.8 ± 1.50	13.6	
24.8	7.99 ± 0.800	9.61	+20.3
25.9	7.59 ± 0.544	7.23	
26.9	35.7 ± 3.98	35.4	
27.7	23.1 ± 2.10	23.7	
28.7	96.0 ± 9.00	96.5	
29.6	27.7 ± 2.61	28.6	
31.0	10.9 ± 1.06	11.3	
32.5	7.02 ± 0.485	8.38	+19.4
33.1	15.7 ± 1.53	16.6	
33.9	12.7 ± 1.15	11.9	
34.3	39.1 ± 3.19	40.5	
35.1	39.9 ± 2.04	40.2	
35.8	47.0 ± 3.97	49.3	
36.1	66.1 ± 5.35	67.3	
40.4	18.1 ± 1.14	20.2	
41.0	24.0 ± 1.93	27.0	
42.0	16.2 ± 1.74	19.5	+20.4
42.3	12.6 ± 1.56	15.9	+26.2
42.9	11.8 ± 1.60	12.9	
46.2	13.9 ± 1.15	15.4	
46.8	15.0 ± 0.680	16.0	
47.5	17.8 ± 0.643	20.6	+13.6
53.1	10.1 ± 0.424	11.9	+17.8
56.9	47.6 ± 0.448	48.5	
70.4	13.8 ± 0.610	15.6	+13.0
72.7	22.6 ± 0.937	24.7	

(a) Based on 0.400 mg/mL C₁₉ ISTD, SRC-II FOB, 1:201 dilution.

(b) After readjustment of carrier gas, gas flows in FID, and breaking a loop off each end of the capillary column.

(c) No data.

(d) Only given when change is greater than 10%, before versus after.

3.1.1 4°C Study

Log transformed data from the ANOVA statistical analysis are presented for the four SRC-II FOB replicates stored in the repository in Figure 3.12. The data are shown as paired sets which compare the results of these samples at time zero and after two years of storage. Table 3.5 presents the F values for the peak-to-peak statistical analysis of the FOB. An F value greater than 18.51 shows a significant change in composition for a particular peak. The obvious overlap of data in Figure 3.12 and the lack of statistical significance at a 5% α level in Table 3.2 show that there was no change in the chemical composition of the FOB after two years in the repository, as measured by the components monitored.

Similar results were achieved from the statistical analyses of chromatographic data from the SRC-I LO, WS and PS, and SRC-II N, MD, and HD. No significant degradation changes in the chemical composition (as monitored by the compounds in Table 3.1) greater than chromatographic error occurred in any of the 17 SRC materials stored in the repository at 4°C, in inert containers, in the dark, under a nitrogen atmosphere over a two year period. Some statistically significant increases in the concentration of some components did occur, however, but they cannot be attributed to decomposition. In addition, if inconsistent results were achieved between replicates, no conclusions as to decomposition were drawn. Log transformed plots of all the SRC materials stored in the repository along with tables of calculated F values are presented in Figures and Tables 8.1 through 8.6 of Appendix II.

3.1.2 -20°C, 20°C Study

Log transformed data from the chromatographic analysis of SRC-II FOB samples stored at -20°C and room temperature under various parameters of ambient light, cover atmosphere, and dilution are presented in Figure 3.13. The top portion of the figure shows the results of all the FOB samples stored undiluted, each offset from the others. The bottom portion of the figure shows the results of the samples stored diluted 1:20 and 1:200 in methylene chloride versus the sample stored under the same conditions except not diluted (in the light, under an air atmosphere, at room temperature). F Values for the data

FIGURE 3.12. Log Transformed Data from Chromatographic Results for SRC-II Fuel Oil Blend Samples Stored in the Repository. Data Points After Two Years are Offset by 0.3 Peak Units.

TABLE 3.5. F Values From the ANOVA Techniques Applied to the SRC-II Fuel Oil Blend Chromatographic Data After Storage in the Repository for Two Years

Peak ^(a)	Calculated F Value	Critical F Value (5% α Level)
28	5.54	18.51 ^(d)
30	2.48	18.51
32	5.62	18.51
33	3.75	18.51
35	0.02	18.51
38	1.80	18.51
39	9.52	18.51
40	1.12	18.51
41	3.95	18.51
42	0.39	18.51
43	0.0025	18.51
48	0.0025	18.51
54	0.05	18.51
55	2.94	18.51
56	0.08	18.51
57	10.39	18.51
59	6.32	18.51
60	9.34	18.51
61, 62	0.82	18.51
63	ND ^(b)	
64	2.84	18.51
65	1.29	18.51
66	5.10	18.51
68	4.36	18.51
69	10.62	18.51
70	4.42	18.51
71	7.56	18.51
74	ND	
75	29.01 ^(c)	18.51
77	6.48	18.51
85	4.31	4.30 ^(e)
97	ND	

(a) Peaks refer to compounds identified by GC/MS contained in Table 3.1 and shown in Figure 3.4.

(b) No data collected.

(c) Although significant, this change was thought to be attributed to chromatography, not degradation. The amount of the peak increased, not decreased.

(d) Based on 20% error.

(e) Based on calculated statistical error.

FIGURE 3.13. Log Transformed Data from Chromatographic Results for SRC-II Fuel Oil Blend Samples Stored at -20°C and 20°C Under Various Parameters of Cover Atmosphere, Ambient Light, and Dilution (See Figure 2.1) Top: All Samples Stored Undiluted Offset by 0.1 Peak Units. Bottom: Condition 4 Versus 1:20 and 1:200 Dilutions with Methylene Chloride Offset by 0.25 and 0.5 Peak Units, Respectively.

presented in the figure are in Table 3.6. Values greater than 19.3 or 19.0 show significant (greater than 20%) changes in composition of particular peaks.

No replicate (samples stored in duplicate) or vial effects were significant. There was no significant chemical composition difference for any of the undiluted FOB samples regardless of increased temperature, ambient light, or air atmosphere during storage for one year. This is shown by the tight cluster of data in the top portion of Figure 3.13 and by the F Values given for the undiluted samples in Table 3.6 all being less than 19.3. There were, however, significant degradation changes in the chemical composition of the samples stored diluted in methylene chloride in the light, under an air atmosphere, at room temperature (see Figure 3.13, bottom, and Table 3.6, F Values for diluted samples). Under these conditions the peaks numbered 32 (indan), 33 (o-cresol), 35 (m & p-cresol and C_1 -indan), 59 (C_3 -indan), and 60 (indanol) showed degradation significant at a 5% α level. (Similar degradation of the phenol, indan, o, m, and p-cresol was noted after storage of the FOB diluted in methylene chloride for three years, at -20°C , in the dark, under a nitrogen atmosphere. See Table 7.22 in Appendix I for chromatographic data.) Degradation in methylene chloride can likely be attributed to trace hydrochloric acid residues which are commonly found in this solvent.

3.1.3 60°C, 100°C Study

Log transformed data from the chromatographic results obtained for the samples of SRC-II FOB stored at 60°C are presented in Figure 3.14. Three data sets are presented offset from each other: before accelerated storage (time=0); after 16 weeks of storage at 60°C ; and after 32 weeks of storage at 60°C . F Values from the ANOVA techniques are shown in Table 3.7. The data variability increased with time. Even though the vials were sealed there tended to be an increase in heavier molecular weight compounds and decrease in lighter materials due to volatility effects which were significant at the 5% α level. Peaks which were the most significantly effected by storage, giving changes greater than the experimental error, and showing consistent decrease in concentration over time were those labeled 33 (o-cresol), 38 (C_1 -indan), 58 (C_3 -indan), and 60 (indanol).

TABLE 3.6. F Values From the ANOVA Techniques Applied to the SRC-II Fuel Oil Blend Chromatographic Data After Storage at -20°C and Room Temperature Under Various Parameters of Light, Atmosphere, and Dilution for One Year

Peak (a)	Undiluted Samples ^(b)		Diluted Samples ^(c)	
	Calculated F Value	Critical F Value (5% α Level)	Calculated F Value	Critical F Value (5% α Level)
28	1.59	19.3	0.339	19.0 ^(e)
32	2.86		32.55	19.0
33	3.86		81.83	19.0
35	1.38		63.45	19.0
38	1.69		19.3	19.0
39	2.27		10.675	19.0
41	2.71		18.50	19.0
43	2.44		2.88	19.0
48	2.56		6.246	19.0
54	3.12		180.1 ^(d)	19.0
56	3.38		0.178	19.0
57	1.88		3.14	19.0
59	1.37		33.36	19.0
60	1.83		40.07	19.0
62	3.75		5.76	19.0
63	2.04		5.82	19.0
64	1.99		2.66	19.0
65	1.73		3.95	19.0
68	2.24		1.66	19.0
69	0.88		12.2	19.0
70	1.59		0.58	19.0
71	2.72		2.42	19.0
74	1.59		0.868	19.0
75	1.62		2.67	19.0
77	1.61		3.46	19.0
85	0.88		2.89	5.14 ^(f)
97	0.25		3.96	5.14

(a) Peak numbers refer to compounds identified by GC/MS contained in Table 3.1 and shown in Figure 3.8

(b) Samples stored under control and conditions 1,2,4-6 as outlined in Figure 2.1

(c) Samples stored under conditions 3 and 4 as outlined in Figure 2.1

(d) One dilution showed a significant change, but the other did not, therefore no conclusions regarding this peak were included.

(e) Based on 20% error.

(f) Based on calculated statistical error.

FIGURE 3.14. Log Transformed Data from Chromatographic Results for SRC-II Fuel Oil Blend Samples Stored at 60°C, Under an Air Atmosphere, in the Dark. Data Points for Time = 0 are Offset by 0.0 Peak Units, 16 Weeks by 0.25 Peak Units, and 32 Weeks by 0.5 Peak Units.

TABLE 3.7. F Values from the ANOVA Techniques Applied to the SRC-II Fuel Oil Blend Chromatographic Data After Storage at 60°C in the Dark, Under an Air Atmosphere for 16 and 32 weeks.

Peak ^(a)	Calculated F Value	Critical F Value (5% α Level)
28	33.48	3.91 ^(e)
32	23.63	3.91
33	139.16	3.91
35	25.98	3.91
38	159.8	3.91
39	2.5	19.0 ^(f)
41	16.8	19.0
43	0.02	19.0
48	18.2	19.0
54	132.0 ^(b)	19.0
56	14.75	19.0
57	67.50	19.0
58	178.50	19.0
60	127.3	19.0
61	ND ^(c)	
62	5.75	19.0
64	10.75	19.0
65	80.5	19.0
68	2.25	19.0
69	22.0	19.0
70	82.0	19.0
71	67.5	19.0
74	45.5	19.0
75	14.25	19.0
77	116.25 ^(d)	19.0
85	65.0	19.0
97	384.0 ^(d)	19.0

- (a) Peak numbers refer the compounds identified by GC/MS contained in Table 3.1 and shown in Figure 3.9
- (b) After 16 weeks, it appeared degradation had occurred, however, at 32 weeks the component had not degraded, therefore, no conclusions about this peak were made.
- (c) No data.
- (d) Data showed increase in component, therefore not a component which degrades.
- (e) Based on calculated statistical error.
- (f) Based on 20% error.

Results of the 100°C study were similar to those of the 60°C study, although the volatility effects were greater. Log transformed data and F Values are given in Figure and Table 8.7 of Appendix II, respectively.

3.1.4 Summary

After two years, the SRC samples stored in the repository at 4°C, in inert containers, under a nitrogen atmosphere, in the dark have shown no chemical composition changes as monitored by high resolution gas chromatography. When degradation did occur under harsher storage conditions of 60°C, 100°C, or room temperature diluted in methylene chloride under air atmospheres, the hydroxylated PAH (phenols, cresols, indanol) and partially hydrogenated PAH (indans, tetralin) showed the greatest amount of degradation. Degradation of more than 20% of the original amount had to occur before chromatographic differences were interpreted as actual differences in the sample. Dilution with methylene chloride and storage in the freezer at -20°C for three years caused similar degradation of phenolic materials as occurred in the samples stored under harsh conditions.

For all data sets analyzed, the differences in vial subsamples (after dilution) and chromatographic runs were not found to be significant. Therefore, for statistical purposes, the emphasis of replication should be placed on duplicating the storage vials not the subsamples from these vials or the subsequent number of chromatographic runs. Though not significant in a statistical sense, the order in which the chromatographic runs were made showed a definite trend; the later chromatograms had lower relative concentrations than the earlier runs. This shows that samples should be analyzed on a random basis to exhibit errors found in the chromatography. Instead of running a diluted sample four times in a row, as was done in this study, replicate chromatographic runs should be made randomly throughout the analysis of all other diluted samples.

3.2 CHEMICAL FRACTIONATION

After fractionation into chemical classes, as previously described, each fraction was analyzed by GC after dilution to a consistent volume. The total area counts were computed relative to the internal standard and corrected for differences in initial starting material. Table 3.8 gives the comparison of the approximate total area of the chromatographable peaks for each fraction from the alumina separation. After storage at 100°C for 16 weeks, the aliphatic hydrocarbon (A-1), N-PAC (A-3), and hydroxylated PAH (A-4) fractions decreased in total chromatographable materials; the PAH (A-2) fraction increased. Overall, about 20% less material was chromatographable after storage at 100°C, in the dark, under an air atmosphere for 16 weeks. (This was based on the fractionation of 100 mg of material before and after harsh storage conditions and dilution of all fractions to a consistent volume before chromatography.)

The components in the PAH fraction (A-2) were chromatographed and normalized to pyrene to see if the peak profile of any components changed after storage at 100°C. Table 3.9 presents the means of the normalized data for 25 polycyclic aromatic compounds in the A-2 fraction. Means were determined from six chromatographic runs for the "before" sample and three chromatographic runs for the "after" sample. Applying an error margin of $\pm 20\%$ (determined as previously described), the peak profile of the components monitored did not change in the PAH fraction.

TABLE 3.8. Total Area Counts Chromatographed per mg
Crude SRC-II Fuel Oil Blend Before and After
Storage at 100°C for 16 Weeks

<u>Alumina Fractions</u>	<u>Before</u>	<u>After</u>
aliphatics (A-1)	3300 ^(a)	2400
PAH (A-2)	1400	1800
N-PAC (A-3)	640	240
hydroxylated PAH (A-4)	<u>4600</u>	<u>3700</u>
Total	9940	8140

(a) All values were normalized to the addition
of 2-Chloroanthracene as an internal standard

TABLE 3.9. Mean of PAH Compound Concentration in the PAH Fraction of an SRC-II Fuel Oil Blend Before and After Storage at 100°C, in the Dark, Under an Air Atmosphere for 16 Weeks

Compound	Amount(a)	
	Before	After
Naphthalene	46	51
2-Methylnaphthalene	180	170
1-Methylnaphthalene	41	38
Biphenyl	92	75
1,7-Dimethylnaphthalene	30	26
1,6-Dimethylnaphthalene	18	16
Dibenzofuran	45	43
Fluorene	57	48
2-Methylfluorene	41	32
1-Methylfluorene	13	10
Dibenzothiophene	33	26
Phenanthrene	230	201
3-Methylphenanthrene	39	39
2-Methylphenanthrene	43	41
Fluoranthene	53	51
Pyrene	100	100
Benzo[a]fluorene	12	8.9
Benzo[b]fluorene(b)	37	32
1-Methylpyrene	4.8	4.6
Benz[a]anthracene	6.7	7.1
Chrysene	12	12
6- or 4-Methylchrysene	4.3	3.7
Benzo[j or b]fluoranthene	3.5	3.9
Benzo[k]fluoranthene	2.0	2.2
Benzo[e]pyrene	2.7	2.8
Benzo[a]pyrene	1.9	2.1

(a) Normalized to pyrene

(b) Co-elutes with 2- or 4-methylpyrene

The components in the N-PAC fraction (A-3) were also chromatographed and were normalized to carbazole to see if the peak profile of any components changed after storage at 100°C. Table 3.10 presents the means of the normalized data for 12 of the nitrogen heterocycles in the fraction. The data were obtained and analyzed in the same fashion as the A-2 fraction. The aniline,

TABLE 3.10 Mean of Nitrogen Heterocycle Compound Concentration in the in the N-PAC Fraction of an SRC-II Fuel Oil Blend Before and After Storage at 100°C, in the Dark, Under an Air Atmosphere for 16 Weeks

Compound	Amount ^(a)	
	Before	After
Aniline	13	--(c)
C ₁ -Aniline	62	0.83
Quinoline	74	94
Indole	120	13
7-Methylquinoline	74	62
3-Methylquinoline	54	62
Benzo[f]quinoline	20	23
Carbazole	100	100
1-Methylcarbazole	15	18
3-Methylcarbazole	29	23
2-Methylcarbazole	18	15
Benzo[a]carbazole	13	16

(a) Normalized to Carbazole

(b) Co-elutes with phenanthridine

(c) None detected

methylaniline, and indole showed significant decreases in concentration after storage at 100°C, in the dark, under an air atmosphere.

When the N-PAC fraction was further fractionated on silicic acid obtaining the amino-PAH fraction, the total area which was chromatographable in this fraction decreased in comparison to the control. The amino-PAH fraction was derivatized with pentafluoropropionic anhydride and chromatographed using an electron capture detector for primary aromatic amine-specific detection. The sample fractionated before storage at 100°C had over two times the total primary aromatic amine content of that fractionated after exposure ($5.5 \pm 0.5 \times 10^6$ versus $2.4 \pm 0.7 \times 10^6$ area counts). Figure 3.15 shows the comparison of amines before (top) and after (bottom) storage at 100°C under an air atmosphere.

FIGURE 3.15. ECD Chromatograms of Derivatized Amino-PAH Fractions from an SRC-II FOB Before (Top) and After (Bottom) Storage at 100°C for 16 Weeks. Conditions: 50°C to 300°C at 3°C/min, 15 M x 0.25 mm i.d. DB-5 Column, Helium Carrier at 50 cm/s Linear Velocity.

3.2.1 Summary

The more-trace component analysis of the SRC-II FOB stored under harsh conditions showed that amino-PAH and indole degraded after 16 weeks at 100°C, in the dark, under an air atmosphere. The overall material which was chromatographable had decreased by 20%, with decreases in the aliphatic, N-PAC, and HPAH fractions. The integrity of the PAH fraction (as monitored) was maintained.

3.3 DIRECT PROBE MASS SPECTROMETRY

The top of Figure 3.16 shows the results of the probe analysis of the SRC-II heavy distillate which had been mixed to homogeneity. The major components had masses of 178 (phenanthrene/anthracene), 192 (C₁-phenanthrene/anthracenes), 202 (pyrene/fluoranthene), and 216 (C₁-pyrene/fluoranthenes, benzofluorenes). The middle of Figure 3.16 shows the major components from the subsampling 2 cm from the top of the undisturbed container to be similar to the mixed sample. The sample taken 5 cm from the bottom of the undisturbed container (Figure 3.16, bottom), however, shows the lower molecular weight component of mass 178 to be significantly less than those of masses 192, 202, and 216. In this case, the components of mass 181 (C₁-carbazoles) were in higher concentration than the phenanthrene/anthracene.

Figure 3.17 presents the direct probe results for the SRC-II HD taken from the bottom of the undisturbed container and the subsequent partitions into a light and heavy sludge. It appears that components of mass 167 (carbazole) settle to the bottom of the container or partition preferentially into the sludge-like bottom materials which form when stored undisturbed in the repository for long periods of time. (Probably a solubility effect.) These results highlight the need to mix synthetic fuel samples thoroughly prior to subsampling for any purpose.

FIGURE 3.16. Direct Probe Results for SRC-II Heavy Distillate Sampled from a Mixed Container (top), Two cm from the Top of an Undisturbed Container (middle), and Five cm from the Bottom of an Undisturbed Container (bottom).

FIGURE 3.17. Direct Probe Results for SRC-II Heavy Distillate Sampled from the Bottom of an Undisturbed Container (top), and from the Subsequently Partitioned Light (middle), and Heavy (bottom) Sludges.

3.4 MICROBIAL MUTAGENICITY

3.4.1 4°C

Results of the histidine reversion assay for mutagenicity at 12 doses ranging from 0.2 µg/plate to 50 µg/plate are given in Table 3.11. Means and standard deviations of the means are given for the initial data collected in 1979 (23) and those in 1983. An initial (1979) value was not available for the SRC-II FOB; for comparative purposes the 1983 value of the SRC-II FOB that had been stored at -20°C, under a nitrogen atmosphere, in the dark was used. As can be seen in Table 3.11 and Figure 3.18, there was no significant change at the 95% confidence level in microbial mutagenicity after storage in the repository for four years. All samples had overlapping values when comparing the means and standard deviations of the mean from 1979 to 1983 determinations.

Table 3.12 presents mutagenicity data for the samples of SRC-II HD taken from varying depths of the undisturbed container (Teflon-lined stainless steel drum) stored at 4°C. Results for the sample after mixing are also given. There were no significant differences at the 95% confidence limit. There was, however, a trend for the samples taken from the bottom of the container to have lower mutagenicity values than the samples taken nearer to the top of the container. Although the chemical data indicated the partitioning of carbazole into the sludge-like layers, there apparently is not a similar partitioning of the amino-PAH, the determinant mutagens in these samples.^(15,16)

3.4.2 -20°, 20°C

Results of the histidine reversion bioassay for the -20°C and 20°C samples against TA98 at 12 doses ranging from 0.2 µg/plate to 50 µg/plate are given in Table 3.13 and shown in Figure 3.19. Comparisons of mutagenicity data under the various sample storage conditions are given in Table 3.14. This table contains a list of the samples which were compared, the storage parameters which were monitored, and the conclusions which were drawn from the mutagenicity data.

Overall results showed a slight (although not significant at the 95% level) decrease in mutagenicity for the samples stored at room temperature in the darkness (conditions 5 and 6) versus those stored at -20°C (control,

TABLE 3.11. Results of Microbial Mutagenicity Tests After Storage at 4°C, in the Dark, Under a Nitrogen Atmosphere for Four Years

Sample	1979 ^(a)	1983
SRC-I Light Oil 3317-073-16	<0.01	0 ^(b)
SRC-I Wash Solvent 3317-075-19	<0.01	0
SRC-I Process Solvent 3317-066-26	12.3 ± 1.9	11.6 ± 4.5
3317-066-27		11.0 ± 3.3
SRC-II Naphtha 3317-125-01B	<0.01	0
3317-055-04		0
SRC-II Middle Distillate 3317-058-02	<0.01	0
3317-129-02		0
3317-130-02		0
3317-131-02		0
SRC-II Fuel Oil Blend 3317-079-23	11.4 ± 3.2 ^(c)	7.8 ± 1.4
3317-079-24		6.8 ± 1.7
3317-079-25		6.4 ± 1.6
3317-079-26		8.5 ± 0.6
SRC-II Heavy Distillate 3317-32-02	40 ± 23	26.9 ± 1.8
3317-134-02		34.7 ± 8.5
3317-015-11		31.9 ± 8.0

(a) From reference 23.

(b) No mutagenic activity detected.

(c) No data available from 1979, the value from the sample stored at -20°C, under nitrogen, in the dark was used for reference.

FIGURE 3.18. Comparison of Microbial Mutagenicity for SRC Materials in 1979 Versus Those Stored in the Repository at 4°C, in the Dark, Under a Nitrogen Atmosphere in 1983. Replicates Refer to Those Identified in Table 3.11.

TABLE 3.12. Results of Microbial Mutagenicity Tests for Samples from Varying Depths of an Undisturbed Container of SRC-II Heavy Distillate Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

<u>Sample Location</u>	<u>Mutagenicity (rev/ug)</u>
Mixed	21.8 ± 9.0
2 cm from the Top	27.6 ± 10.1
5 cm from the Bottom	27.3 ± 6.3
Bottom	21.4 ± 7.5
Light Sludge ^(a)	15.0 ± 6.1
Heavy Sludge ^(a)	17.9 ± 4.5

(a) The two sludges were partitioned from the sample taken from the bottom of the storage container.

TABLE 3.13. Results of Microbial Mutagenicity Tests Against S. typhimurium TA98, -20°C and 20°C Stability Study

<u>Sample</u>	<u>Rev/ug</u>
3317-079-25 FOB, Control	11.4 ± 3.2
3317-079-25 FOB, Condition 1 ^(a)	9.8 ± 0.5
3317-079-25 FOB, Condition 2	7.0 ± 1.4
3317-079-25 FOB, Condition 3	0 ^(b)
3317-079-25 FOB, Condition 4	4.4 ± 0.3
3317-079-25 FOB, Condition 5	6.9 ± 0.6
3317-079-25 FOB, Condition 6	7.0 ± 0.6
FOB diluted in MeCl ₂ at -20°C for three years	3.1 ± 1.6

(a) Refers to conditions explained in Experimental Methods Section, Figure 2.1.

(b) No mutagenic activity detected.

FIGURE 3.19. Comparison of Microbial Mutagenicity for an SRC-II Fuel Oil Blend Stored Under Various Conditions at -20°C and 20°C. Conditions Refer to Those in Figure 2.1 of the Experimental Methods Section 2.0.

TABLE 3.14. Mutagenic Effects^(a) of Storage Under Various Conditions at -20°C and 20°C for One Year

Sample Comparison ^(b)	Parameter(s) Monitored	Conclusions
Condition 3 versus Condition 4	Dilution in Methylene Chloride	- Dilution of a sample in Methylene chloride eliminated the mutagenic response with other conditions of light, air atmosphere, and room temperature held constant (under these conditions the mutagenicity only decreased significantly)
Control versus Condition 1	Nitrogen versus Air Atmosphere	- No change in mutagenicity between an air or nitrogen atmosphere at -20°C in the dark
Condition 2 versus Condition 4	Nitrogen versus Air Atmosphere	- Mutagenicity decreased under an air atmosphere versus a nitrogen atmosphere in the light at room temperature
Condition 5 versus Condition 6	Nitrogen versus Air Atmosphere	- No change in mutagenicity between an air or nitrogen atmosphere in the dark at room temperature
Control versus Condition 5 Condition 1 versus Condition 6	Temperatures of -20°C versus 20°C	- Storage of a sample in the dark at an elevated temperature decreased the mutagenic response slightly but not significantly regardless of air or nitrogen cover atmospheres
Condition 2 versus Condition 5	Light versus Dark	- No change in mutagenic response between light or darkness under a nitrogen atmosphere at room temperature
Condition 4 versus Condition 6	Light versus Dark	- Light decreased the mutagenicity when stored under an air atmosphere at room temperature
Control versus Condition 2 Condition 1 versus Condition 4	Light plus Elevated Temperature	- Mutagenicity only decreased significantly under conditions of light and room temperature under an air atmosphere. Under a nitrogen atmosphere there was a slight but not significant decrease.
Control versus Condition 6	Air Atmosphere plus Elevated Temperature	- Storage of a sample at room temperature under an air atmosphere decreased the mutagenicity slightly but not significantly
Control versus Condition 4	Air Atmosphere, Elevated Temperature, Light	- Mutagenicity decreased significantly in the light under an air atmosphere at room temperature.
Control versus Condition 3	Air Atmosphere, Elevated Temperature, Light, Dilution	- Mutagenicity was eliminated by storage diluted 1:20 or 1:200 in methylene chloride in the light under an air atmosphere at room temperature

(a) As expressed in the histidine reversion test against TA98.

(b) Conditions correspond to those shown in Figure 2.1, Experimental Methods Section 2.0.

condition 1). A significant change in mutagenicity was noted when the FOB sample was left stored at room temperature, in the light, under an air atmosphere (condition 4); the mutagenicity decreased by more than a factor of two from the control. However, the mutagenic response of the sample stored under the same conditions except under a nitrogen atmosphere (condition 2) did not show a similar mutagenicity decrease. Mutagenic response was completely eliminated when the sample was stored diluted in methylene chloride at room temperature, in the light, under an air atmosphere. Mutagenic response was also significantly decreased after storage at -20°C diluted in methylene chloride under nitrogen for three years.

Dilution in methylene chloride proved to be the harshest storage condition with regard to maintenance of sample mutagenicity. The combination of air atmosphere, room temperature, and light was another storage condition which caused significant mutagenicity decrease. Since the chromatographic data showed no change in the chemical composition of this sample, trace component degradation is probably leading to the decreased mutagenicity. Amino-PAH are the likely candidates which are degrading. Mutagenicity of all other storage samples was not significantly changed from the control (Table 3.14).

3.4.3 60°, 100°C

Results of the microbial mutagenicity test at 12 doses with means and standard deviations calculated from a dose response two times that of background and a correlation coefficient greater the 0.8 are given in Figure 3.20. The data indicated an elimination of mutagenicity when the sample was stored at 60°C for 32 weeks and at 100°C for 26 weeks. (Mutagenicity may have been eliminated prior to these points, but mutagenicity tests were not performed on a weekly basis to monitor when mutagenicity was gone.) After storage at 100°C for 6 weeks, mutagenicity had decreased by more than a factor of three from the control.

3.4.4 Summary

Mutagenicity of samples stored for four years in the repository at 4°C, in the dark, under a nitrogen atmosphere, was not significantly altered. Conditions which decreased or eliminated mutagenicity were storage at room temperature, in the light, under an air atmosphere either diluted in methylene F3.20

FIGURE 3.20. Comparison of Microbial Mutagenicity Data for SRC-II Fuel Oil Blend Under Accelerated Conditions of Elevated Temperatures of 60°C and 100°C.

chloride or undiluted for one year, or storage at 60°C and 100°C in the dark under an air atmosphere for an extended period of time (32 weeks, 26 weeks, respectively). Mutagenicity was also significantly decreased when stored for three years at -20°C after dilution with methylene chloride. There was no significant difference in mutagenicity from samples of SRC-II HD taken from varying depths of the unmixed container stored at 4°C.

The histidine reversion assay is particularly sensitive to concentration changes in the trace constituent amino-PAH^(15,16). Because of this, it has been used in the past as a principal indicator of synfuel biological activity. The mutagenicity data for the repository samples, together with the chemical analysis data, indicated that the method used for sample storage at PNL has maintained the integrity of the biological activity of the samples stored in the repository. These samples can continue to be used in biological testing programs with assurance that the data obtained today are comparable with data obtained as long as four years ago.

4.0 CONCLUSIONS

The stability studies performed on seventeen SRC samples ranging in boiling point from ambient to 850°F showed that the major chemical composition of the materials as monitored by high resolution gas chromatography did not change under the storage conditions of the repository, which were 4°C, in inert containers, under a nitrogen atmosphere, in the dark. Samples were monitored after two years of storage. It was also found from microbial mutagenicity studies that after four years in the repository there was no significant change in the biological activity of any of the SRC materials. The materials which originally displayed mutagenicity maintained the same mutagenicity, and materials which originally were not mutagenic were still inactive. The SRC liquids have maintained their integrity upon storage in the repository. It was found from sampling varying depths of a storage container, however, that gross changes in the chemical composition occur due to the formation of a sludge-like material in the SRC-II heavy distillate. This sludge-like material contains elevated concentrations of carbazole. However, this sludge-like material can be completely eliminated by thorough mixing. Samples must be mixed to homogeneity after storage to ensure that the overall chemical composition remains unchanged.

Studies comparing the stability of an SRC-II FOB at room temperature versus storage in the freezer at -20°C showed there was no change in the chemical composition as monitored by high resolution gas chromatography. Samples stored under various parameters of air versus nitrogen atmosphere and ambient light versus darkness at room temperature and -20°C for one year showed there was no significant differences in the chemical composition of any of the samples. There was evidence, however, that trace components such as amino-PAH degraded at room temperature, in the light, under an air atmosphere since the microbial mutagenicity of samples stored under these conditions for one year decreased significantly.

Both the chemical composition and mutagenicity of FOB samples changed when stored diluted in methylene chloride, in the light, under an air atmosphere at room temperature. After one year of storage under these conditions, the

microbial mutagenicity was eliminated. The major chemical constituents which degraded were hydroxylated PAH, such as the cresols, indanol, and more highly alkylated phenols, and partially hydrogenated PAH, such as alkylated indans, and tetralin (or any co-eluting species of the above). Similar results were noted for samples stored for three years at -20°C, diluted in methylene chloride, under a nitrogen atmosphere.

Storage of SRC-II FOB at increased temperatures of 60°C and 100°C showed significant changes in chemical composition due to volatility effects; early eluting peaks decreased in concentration while later eluting peaks increased in concentration. Components which showed consistent degradation (rather than volatility changes) over time were hydroxylated PAH, such as the cresols and indanol, and partially hydrogenated PAH, such as alkylated indans (or any co-eluting species of the previously mentioned components). Further study into the more trace components in the sample showed the nitrogen heterocycles of indole almost completely degraded and the total amino-PAH content decreased by more than a factor of two after storage at 100°C for 16 weeks. The microbial mutagenicity of this sample had significantly decreased after 6 weeks of storage. The microbial mutagenicity of the FOB samples was completely eliminated after storage at 60°C for 32 weeks and 100°C for 26 weeks.

It appears that the amino-PAH and phenolic materials are the most susceptible components to degradation in the complex SRC materials. These components may be used as benchmark compounds to monitor the decomposition of SRC materials over long periods of time in the repository.

From a statistical standpoint, emphasis of replication should be placed on duplicating storage vials, since the differences in vial subsamples (after dilution) and chromatographic runs were not found to be significant. Samples should also be analyzed on a random rather than ordered basis. The order in which chromatographic runs were made showed a definite (although not significant) trend; the later chromatograms had lower relative concentrations than the earlier runs.

5.0 ABBREVIATIONS

ANOVA	Analysis of Variance
Amino-PAH	Amino-Substituted Polycyclic Aromatic Hydrocarbons
FOB	Fuel Oil Blend
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
HD	Heavy Distillate
HPAH	Hydroxylated PAH
HRMS	High Resolution Mass Spectrometry
ISTD	Internal Standard
LO	Light Oil
MD	Middle Distillate
N	Naphtha
N-PAC	Nitrogen-Containing PAC
PNL	Pacific Northwest Laboratory
PAC	Polycyclic Aromatic Compound
PAH	Polycyclic Aromatic Hydrocarbon
PFP	Pentafluoropropionic Anhydride
PS	Process Solvent
rev/ μ g	Revertants Per Microgram
S.	Salmonella
SRC	Solvent Refined Coal
T	Time
WS	Wash Solvent

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7.0 APPENDIX I

MEANS AND STANDARD DEVIATIONS OF NORMALIZED AMOUNTS OF INDIVIDUAL COMPONENTS OF SRC MATERIALS

The tables on the following pages present the results of chromatographic analyses of the stability samples under all storage conditions. Tables 7.1 to 7.17 contain the mean and standard deviation of the mean for each peak monitored in the 17 samples stored in the repository, at 4°C, in the dark. The first two columns in each of these tables represent the normalized means correcting the time = 2 years to the same dilution made at the beginning of the experiment (time = 0). The data under the columns labeled "Raw Data" are the uncorrected means and standard deviations determined using different dilution factors at time = 2 years. All dilutions are noted in the legends.

Tables 7.18 and 7.19 contain the means and standard deviations of the mean for the peaks monitored in the -20°C and 20°C studies. Two sets are presented because the data were collected on two separate occasions using slightly different operating parameters and dilutions. Tables 7.20 and 7.21 contain the results of the 60°C and 100°C accelerated stability studies, respectively.

Table 7.22 contains the chromatographic results from the four SRC-II FOB samples after dilution in methylene chloride and storage at -20°C, under a nitrogen atmosphere, in the dark, for three years. This table should be compared to Tables 7.8-7.11 for time = 0 data.

The numbers in the column labeled "Peak No." correspond to discrete chemical compounds which have been identified by GC/MS and their identifications are given. It should be noted that a compound with a specific number, e.g. 15, always refers to the same chemical component throughout Tables 7.1 to 7.22. It should also be noted that trace component species could co-elute with the major component identifications given.

TABLE 7.1. Chromatographic Results for SRC-II Naphtha Sample 3317-125-01B
Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. ^(b)	Compound ^(c)	Normalized Percent to n-Undecane ISTD ^(a)	
		T = 0 ^(d)	T = 2 years ^(e)
1	C ₁ -Butane	67.7 ± 4.6 ^(f)	67.8 ± 7.4 ^(g)
2	Pentane	216.9 ± 10.6	202.0 ± 23.7
3	Pentene	132.8 ± 7.6	128.7 ± 10.2
4	C ₂ -Butane	75.3 ± 5.1	65.7 ± 6.6
5	C ₁ -Pentane	40.2 ± 3.7	43.0 ± 3.9
6	n-Hexane	170.5 ± 13.9	165.8 ± 13.1
7	Hexene	202.0 ± 14.6	224.6 ± 19.1
8	Benzene	80.7 ± 8.1	62.2 ± 4.8
9	Cyclohexane	259.8 ± 22.0	248.1 ± 17.5
10	Cyclohexene	35.4 ± 4.8	23.9 ± 2.0
11	C ₇ H ₁₆	58.9 ± 6.3	43.5 ± 3.6
12	Heptene	48.0 ± 4.8	26.9 ± 2.1
13	n-Heptane	106.1 ± 10.0	53.5 ± 5.8
14	C ₁ -Cyclohexane	214.2 ± 21.2	132.1 ± 10.4
15	C ₂ -Pentene	61.8 ± 6.6	32.4 ± 2.6
16	Toluene	229.4 ± 25.2	143.8 ± 10.8
18	C ₈ H ₁₈	36.9 ± 4.6	ND ^(h)
19	C ₂ -Cyclohexane	36.8 ± 3.9	14.9 ± 1.0
20	n-Octane	90.9 ± 9.6	37.8 ± 3.2
21	C ₃ -Cyclohexane	87.0 ± 9.2	55.4 ± 3.8
22	<u>o</u> -Xylene	96.8 ± 9.0	63.1 ± 3.6
23	<u>m</u> -Xylene	123.2 ± 11.4	77.8 ± 5.2
24	<u>p</u> -Xylene	86.6 ± 7.5	68.2 ± 4.9
25	n-Nonane	59.8 ± 4.9	44.2 ± 2.1
26	C ₄ -Cyclohexane	22.2 ± 1.6	18.4 ± 0.8
27	C ₃ -Benzene	27.0 ± 1.5	20.6 ± 1.0
28	Phenol	107.5 ± 10.3	75.1 ± 2.0

(a) Based on the integration of peak heights

(b) Numbers refer to peaks in Figure 3.1, Results and Discussion Section.

(c) Identified by GC/MS

(d) Based on approximately 26 mg/mL n-Undecane ISTD, neat, manual injections, 1980.

(e) Based on an unknown amount of n-Undecane ISTD, neat, manual injections, 1982.

(f) Based on 5 runs.

(g) Based on 3 runs.

(h) No data.

TABLE 7.2. Chromatographic Results for SRC-II Naphtha Sample 3317-055-04
Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. ^(b)	Compound ^(c)	Normalized Percent to n-Undecane ISTD ^(a)	
		T = 0 ^(d)	T = 2 years ^(e)
1	C ₁ -Butane	ND ^(f)	20.8 ± 3.2 ^(g)
2	Pentane	130.5 ± 18.1 ^(f)	73.9 ± 9.6
3	Pentene	100.6 ± 11.3	65.9 ± 9.0
4	C ₂ -Butane	56.5 ± 5.0	34.9 ± 4.6
5	C ₁ -Pentane	28.4 ± 2.5	20.8 ± 2.9
6	n-Hexane	123.2 ± 9.3	87.8 ± 11.7
7	Hexene	155.1 ± 9.6	121.1 ± 15.1
8	Benzene	52.9 ± 2.6	31.3 ± 3.0
9	Cyclohexane	193.7 ± 8.5	131.4 ± 16.9
10	Cyclohexene	27.7 ± 1.6	14.7 ± 2.0
11	C ₇ H ₁₆	43.4 ± 1.5	24.3 ± 2.8
12	Heptene	35.9 ± 3.8	16.7 ± 2.1
13	n-Heptane	93.3 ± 3.0	35.9 ± 4.5
14	C ₁ -Cyclohexane	174.5 ± 4.9	76.5 ± 9.0
15	C ₂ -Pentene	56.0 ± 1.4	21.7 ± 2.9
16	Toluene	154.7 ± 3.4	69.0 ± 7.1
18	C ₈ H ₁₈	31.2 ± 0.6	ND
19	C ₂ -Cyclohexane	31.8 ± 0.6	10.7 ± 1.6
20	n-Octane	81.5 ± 2.0	26.8 ± 3.3
21	C ₃ -Cyclohexane	82.1 ± 1.0	38.0 ± 3.9
22	<u>o</u> -Xylene	75.1 ± 1.1	36.3 ± 3.9
23	<u>m</u> -Xylene	103.2 ± 1.2	48.0 ± 4.0
24	<u>p</u> -Xylene	81.7 ± 1.4	49.5 ± 4.0
25	n-Nonane	56.0 ± 0.8	33.5 ± 3.2
26	C ₄ -Cyclohexane	31.4 ± 0.5	19.8 ± 1.3
27	C ₃ -Benzene	68.6 ± 1.7	43.6 ± 1.0
28	Phenol	275.2 ± 9.1	132.7 ± 31.0

(a) Based on the integration of peak heights.

(b) Numbers refer to peaks in Figure 3.1, Results and Discussion Section.

(c) Identified by GC/MS.

(d) Based on approximately 23.2 mg/mL n-Undecane ISTD, neat, manual injections, 1980.

(e) Based on an unknown amount of n-Undecane ISTD, neat, manual injections, 1981.

(f) No data.

(g) Based on 4 runs.

TABLE 7.3. Chromatographic Results for SRC-I Light Oil Sample 3317-073-16 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. (b)	Compound (c)	Normalized Percent to n-Undecane ISTD (a)	
		T = 0 (d)	T = 2 years (e)
1	C ₁ -Butane	49.1 ± 5.9 ^(f)	56.2 ± 7.9 ^(g)
2	Pentane	177.6 ± 10.4	211.3 ± 33.6
3	Pentene	119.8 ± 5.0	164.3 ± 23.1
4	C ₂ -Butane	82.7 ± 5.0	107.0 ± 13.6
5	C ₁ -Pentane	36.7 ± 2.4	60.5 ± 7.6
6	n-Hexane	162.4 ± 12.1	232.6 ± 32.7
7	Hexene	172.0 ± 14.7	275.5 ± 35.3
8	Benzene	55.4 ± 4.0	48.4 ± 6.1
9	Cyclohexane	145.2 ± 14.0	193.1 ± 23.6
10	Cyclohexene	30.4 ± 3.1	27.6 ± 3.5
11	C ₇ H ₁₆	51.8 ± 5.1	53.5 ± 6.3
12	Heptene	36.9 ± 3.8	30.5 ± 3.6
13	n-Heptane	103.3 ± 11.1	68.0 ± 7.4
14	C ₁ -Cyclohexane	102.2 ± 11.2	76.1 ± 7.8
15	C ₂ -Pentene	42.1 ± 4.4	28.5 ± 3.2
16	Toluene	76.7 ± 7.8	50.5 ± 4.7
17	C ₈ H ₁₈	21.7 ± 2.9	ND ^(h)
18	C ₈ H ₁₈	16.6 ± 2.3	ND
19	C ₂ -Cyclohexane	19.9 ± 2.0	9.4 ± 0.8
20	n-Octane	56.1 ± 5.4	29.2 ± 3.5
21	C ₃ -Cyclohexane	31.5 ± 4.3	22.1 ± 2.1
22	<u>o</u> -Xylene	28.0 ± 3.2	19.1 ± 1.5
23	<u>m</u> -Xylene	37.1 ± 3.3	20.9 ± 1.7
24	<u>p</u> -Xylene	20.8 ± 2.0	15.3 ± 0.4
25	n-Nonane	33.9 ± 2.6	25.4 ± 2.0
26	C ₄ -Cyclohexane	9.3 ± 0.9	7.4 ± 0.5
27	C ₃ -Benzene	19.0 ± 1.6	13.3 ± 1.3
28	Phenol	106.7 ± 6.1	82.4 ± 4.2
29	C ₃ -Benzene	16.0 ± 1.6	12.4 ± 0.6
30	C ₃ -Benzene	25.9 ± 2.3	20.2 ± 1.0
31	n-Decane	19.2 ± 1.3	15.9 ± 0.4
32	Indan	58.4 ± 3.7	23.1 ± 1.2
33	<u>o</u> -Cresol	24.1 ± 1.1	ND

(a) Based on the integration of peak heights.

(b) Numbers refer to peaks in Figure 3.2, Results and Discussion Section.

(c) Identified by GC/MS.

(d) Based on approximately 22.4 mg/mL n-Undecane ISTD, neat, manual injection, 1980.

(e) Based on an unknown amount of n-Undecane ISTD, neat, manual injection, 1982.

(f) Based on 4 runs.

(g) Based on 6 runs.

(h) No data.

TABLE 7.4. Chromatographic Results for SRC-II Middle Distillate Sample 3317-129-02 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. ^(c)	Compound ^(d)	Normalized Percent to n-Nonadecane ISTD ^(a)		Raw Data ^(b)
		T = 0	T = 2 years	T = 2 years
28	Phenol	136.2 ± 14.6 ^(e)	121.6 ± 1.8 ^(f)	38.7 ± 0.6 ^(f)
30	C ₃ -Benzene	25.4 ± 2.8	24.2 ± 0.4	7.7 ± 0.1
32	Indan	45.0 ± 4.6	39.9 ± 1.4	12.7 ± 0.4
33	<u>o</u> -Cresol	86.9 ± 5.3	75.0 ± 0.9	23.9 ± 0.3
35a	<u>m</u> - & <u>p</u> -Cresol, C ₁ -Indan	127.8 ± 11.6	ND ^(g)	ND
35b		132.0 ± 11.1	127.7 ± 1.4	40.7 ± 0.5
38	C ₁ -Indan	29.0 ± 1.5	27.5 ± 0.4	8.8 ± 0.1
39	C ₁ -Indan	50.6 ± 2.9	43.4 ± 0.5	13.8 ± 0.2
40	C ₂ -Phenol	36.6 ± 1.9	38.5 ± 0.3	12.3 ± 0.1
41	Tetralin	82.0 ± 4.6	73.0 ± 1.0	23.3 ± 0.3
42	C ₂ -Phenol	32.7 ± 1.6	ND	ND
43	Naphthalene	169.8 ± 9.9	165.1 ± 2.0	52.6 ± 0.6
54	C ₂ -Indan	53.1 ± 2.6	52.5 ± 0.9	16.7 ± 0.3
55	C ₂ -Indan	46.2 ± 2.0	49.9 ± 0.4	16.0 ± 0.1
56	2-Methylnaphthalene	146.0 ± 7.4	148.5 ± 2.5	47.3 ± 0.8
57	1-Methylnaphthalene	33.3 ± 1.3	43.0 ± 0.5	13.7 ± 0.2
59	C ₃ -Indan	27.0 ± 0.9	30.0 ± 0.3	9.5 ± 0.1
60	Indanol	25.9 ± 2.6	30.5 ± 0.5	9.7 ± 0.2
61	C ₂ -Tetralin	35.3 ± 2.3	35.3 ± 0.6	11.2 ± 0.2
62	C ₄ -Phenol			
65	C ₂ -Naphthalene	50.3 ± 1.6	52.7 ± 0.5	16.8 ± 0.2
66	C ₂ -Naphthalene	42.3 ± 1.5	48.3 ± 0.6	15.4 ± 0.2
70	C ₃ -Naphthalene	29.9 ± 0.9	35.1 ± 0.9	11.2 ± 0.3
71	C ₃ -Naphthalene	29.9 ± 0.9	35.0 ± 1.4	11.2 ± 0.4
77	C ₄ -Naphthalene	43.6 ± 1.3	57.3 ± 0.4	18.2 ± 0.1

(a) Based on 1.6 mg/mL n-Nonadecane ISTD, 1:16 dilution, based on the integration of peak heights, T=0 was 1980, T=2 years was 1982.

(b) Based on 0.40 mg/mL n-Nonadecane ISTD, 1:201 dilution.

(c) Numbers refer to peaks in Figure 3.3, Results and Discussion section.

(d) Identified by GC/MS.

(e) Based on 5 GC runs.

(f) Based on 4 GC runs.

(g) No data.

TABLE 7.5. Chromatographic Results for SRC-II Middle Distillate Sample 3317-130-02 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. (c)	Compound (d)	Normalized Percent to n-Nonadecane ISTD (a)		Raw Data (b)
		T = 0	T = 2 years	T = 2 years
28	Phenol	72.8 ± 3.9 ^(e)	52.1 ± 1.5 ^(f)	37.2 ± 1.1 ^(f)
30	C ₃ -Benzene	16.8 ± 1.0	11.7 ± 0.4	8.3 ± 0.3
32	Indan	30.1 ± 1.8	20.6 ± 0.8	14.7 ± 0.6
33	<u>o</u> -Cresol	50.5 ± 2.5	35.7 ± 0.9	25.5 ± 0.7
35a } 35b }	<u>m</u> - & <u>p</u> -Cresol, C ₁ -Indan	73.9 ± 4.2	ND ^(g)	ND
		74.4 ± 4.1	62.1 ± 1.3	44.3 ± 0.9
38	C ₁ -Indan	18.6 ± 1.3	14.5 ± 0.5	10.3 ± 0.4
39	C ₁ -Indan	31.2 ± 1.9	22.9 ± 0.8	16.4 ± 0.6
40	C ₂ -Phenol	21.8 ± 1.3	19.5 ± 0.6	13.9 ± 0.4
41	Tetralin	56.1 ± 4.7	40.8 ± 1.3	29.1 ± 0.9
42	C ₂ -Phenol	19.1 ± 1.7	ND	ND
43	Naphthalene	102.4 ± 6.4	82.6 ± 2.0	59.0 ± 1.5
54	C ₂ -Indan	36.2 ± 2.1	30.8 ± 0.8	22.0 ± 0.5
55	C ₂ -Indan	27.1 ± 1.1	26.4 ± 0.6	18.8 ± 0.4
56	2-Methylnaphthalene	87.9 ± 3.8	78.2 ± 1.6	55.8 ± 1.2
57	1-Methylnaphthalene	20.0 ± 1.2	22.4 ± 0.5	16.0 ± 0.4
59	C ₃ -Indan	16.7 ± 0.6	16.3 ± 0.3	11.7 ± 0.2
60	Indanol	15.4 ± 1.1	16.8 ± 0.3	12.0 ± 0.2
61 } 62 }	C ₂ -Tetralin } C ₄ -Phenol }	22.4 ± 1.0	20.9 ± 0.4	14.9 ± 0.3
65	C ₂ -Naphthalene			
66	C ₂ -Naphthalene	26.8 ± 0.7	27.6 ± 0.5	19.7 ± 0.3
70	C ₃ -Naphthalene	18.8 ± 0.6	19.8 ± 0.8	14.2 ± 0.6
71	C ₃ -Naphthalene	18.4 ± 1.0	19.0 ± 1.0	13.6 ± 0.7
77	C ₄ -Naphthalene	17.6 ± 0.4	21.3 ± 0.6	15.2 ± 0.4

(a) Based on 3.6 mg/mL n-Nonadecane ISTD, 1:16 dilution, based on the integration of peak heights, T=0 was 1980, T=2 years was 1982.

(b) Based on 0.40 mg/mL n-Nonadecane ISTD, 1:201 dilution.

(c) Numbers refer to peaks in Figure 3.3, Results and Discussion section.

(d) Identified by GC/MS.

(e) Based on 6 GC runs.

(f) Based on 4 GC runs.

(g) No data.

TABLE 7.6. Chromatographic Results for SRC-II Middle Distillate Sample 3317-131-02 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. ^(c)	Compound ^(d)	Normalized Percent to n-Nonadecane ISTD ^(a)		Raw Data ^(b)
		T = 0	T = 2 years	T = 2 years
28	Phenol	181.1 ± 14.9 ^(e)	149.4 ± 5.9 ^(f)	41.5 ± 1.6 ^(f)
30	C ₃ -Benzene	49.7 ± 2.8	36.7 ± 1.4	10.2 ± 0.4
32	Indan	75.0 ± 5.5	53.6 ± 2.3	14.9 ± 0.6
33	<u>o</u> -Cresol	105.4 ± 5.9	84.7 ± 4.3	23.5 ± 1.2
35a	<u>m</u> - & <u>p</u> -Cresol, C ₁ -Indan	144.3 ± 17.2	148.7 ± 4.3	41.3 ± 1.2
35b		145.4 ± 16.2	ND ^(g)	ND
38	C ₁ -Indan	40.7 ± 2.6	33.2 ± 1.4	9.2 ± 0.4
39	C ₁ -Indan	68.0 ± 3.5	51.7 ± 2.2	14.4 ± 0.6
40	C ₂ -Phenol	42.3 ± 3.4	44.7 ± 1.6	12.4 ± 0.4
41	Tetralin	114.2 ± 10.1	96.4 ± 3.5	26.8 ± 1.0
42	C ₂ -Phenol	38.9 ± 3.2	ND	ND
43	Naphthalene	200.0 ± 16.5	197.3 ± 5.1	54.8 ± 1.4
54	C ₂ -Indan	73.8 ± 4.2	74.4 ± 1.8	20.7 ± 0.5
55	C ₂ -Indan	52.6 ± 4.4	60.0 ± 1.2	16.7 ± 0.3
56	2-Methylnaphthalene	174.0 ± 14.0	187.2 ± 5.6	52.0 ± 1.6
57	1-Methylnaphthalene	41.4 ± 2.1	52.9 ± 1.0	14.7 ± 0.3
59	C ₃ -Indan	32.4 ± 1.9	35.5 ± 1.5	9.9 ± 0.4
60	Indanol	28.1 ± 4.4	38.5 ± 0.5	10.7 ± 0.1
61	C ₂ -Tetralin	47.0 ± 2.1	49.2 ± 0.6	13.7 ± 0.2
62	C ₄ -Phenol			
65	C ₂ -Naphthalene	63.0 ± 3.0	70.6 ± 1.4	19.6 ± 0.4
66	C ₂ -Naphthalene	55.1 ± 2.5	66.7 ± 1.3	18.5 ± 0.4
70	C ₃ -Naphthalene	39.0 ± 2.2	48.8 ± 0.8	13.6 ± 0.2
71	C ₃ -Naphthalene	37.8 ± 2.5	46.1 ± 1.7	12.8 ± 0.5
77	C ₄ -Naphthalene	35.3 ± 1.2	50.7 ± 0.5	14.1 ± 0.1

(a) Based on 1.4 mg/mL n-Nonadecane ISTD, 1:16 dilution, based on the integration of peak heights, T=0 was 1980, T=2 years was 1982.

(b) Based on 0.40 mg/mL n-Nonadecane ISTD, 1:201 dilution.

(c) Numbers refer to peaks in Figure 3.3, Results and Discussion.

(d) Identified by GC/MS.

(e) Based on 6 GC runs.

(f) Based on 4 GC runs.

(g) No data.

TABLE 7.7. Chromatographic Results for SRC-II Middle Distillate Sample 3317-058-01 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. (c)	Compound (d)	Normalized Percent to n-Undecane ISTD (a)		Raw Data (b)
		T = 0	T = 2 years	T = 2 years
28	Phenol	76.2 ± 4.7 ^(e)	60.5 ± 3.5 ^(f)	23.3 ± 1.3 ^(f)
30	C ₃ -Benzene	12.1 ± 1.2	10.9 ± 0.4	4.2 ± 0.2
32	Indan	20.2 ± 1.8	18.0 ± 1.1	6.9 ± 0.4
33	o-Cresol	40.4 ± 2.2	34.4 ± 2.1	13.2 ± 0.8
35a	m- & p-Cresol, C ₁ -Indan	ND ^(g)	ND	ND
35b		78.4 ± 6.8	74.5 ± 2.4	28.7 ± 0.9
38	C ₁ -Indan	16.6 ± 1.4	15.8 ± 0.7	6.1 ± 0.3
39	C ₁ -Indan	25.4 ± 2.6	22.1 ± 1.0	8.5 ± 0.4
40	C ₂ -Phenol	22.5 ± 1.5	23.0 ± 0.9	8.9 ± 0.3
41	Tetralin	73.1 ± 5.6	65.9 ± 2.5	25.3 ± 1.0
42	C ₂ -Phenol	16.1 ± 1.1	15.8 ± 0.3	6.1 ± 0.1
43	Naphthalene	168.5 ± 10.8	173.6 ± 4.5	66.8 ± 1.7
54	C ₂ -Indan	56.5 ± 4.7	58.2 ± 1.5	22.4 ± 0.6
55	C ₂ -Indan	37.2 ± 2.6	42.2 ± 0.7	16.2 ± 0.3
56	2-Methylnaphthalene	171.7 ± 11.1	177.1 ± 4.1	68.1 ± 1.6
57	1-Methylnaphthalene	32.3 ± 3.2	46.5 ± 0.8	17.9 ± 0.3
59	C ₃ -Indan	20.9 ± 2.0	26.1 ± 0.5	10.0 ± 0.2
60	Indanol	22.2 ± 2.1	27.3 ± 0.6	10.5 ± 0.2
61	C ₂ -Tetralin	37.7 ± 3.1	41.7 ± 0.7	16.0 ± 0.3
62	C ₄ -Phenol			
65	C ₂ -Naphthalene	62.8 ± 4.3	70.5 ± 1.5	27.1 ± 0.6
66	C ₂ -Naphthalene	60.3 ± 4.3	74.5 ± 1.6	28.7 ± 0.6
70	C ₃ -Naphthalene	47.8 ± 2.8	57.9 ± 1.7	22.3 ± 0.7
71	C ₃ -Naphthalene	30.7 ± 1.9	38.8 ± 1.5	14.9 ± 0.6
77	C ₄ -Naphthalene	26.4 ± 1.9	39.0 ± 0.8	15.0 ± 0.3

(a) Based on 1.95 mg/mL n-Nonadecane ISTD, 1:16 dilution, based on the integration of peak heights, T=0 was 1980, T=2 years was 1982.

(b) Based on 0.40 mg/mL n-Nonadecane ISTD, 1:201 dilution.

(c) Numbers refer to peaks in Figure 3.3, Results and Discussion.

(d) Identified by GC/MS.

(e) Based on 4 GC runs.

(f) Based on 8 GC runs.

(g) No data.

Table 7.8. Chromatographic Results for SRC-II Fuel Oil Blend Sample 3317-079-23 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. (c)	Compound (d)	Normalized Percent to n-Nonadecane ISTD (a)		Raw Data (b)
		T=0	T=2 years	T=2 years
28	Phenol	80.5 ± 6.9 ^(e)	81.0 ± 0.6 ^(f)	40.5 ± 0.3 ^(f)
30	C ₃ Benzene	18.2 ± 2.3	15.7 ± 0.1	7.8 ± 0.1
32	Indan	30.6 ± 3.5	23.9 ± 0.5	11.9 ± 0.2
33	<u>o</u> -Cresol	55.5 ± 4.7	51.9 ± 0.6	25.9 ± 0.3
35a }	<u>m</u> - & <u>p</u> -Cresol, C ₁ -Indan	67.8 ± 6.4	ND	ND
35b }		77.3 ± 6.2	91.6 ± 0.4	45.8 ± 0.2
38	C ₁ -Indan	23.8 ± 2.4	20.3 ± 0.3	10.2 ± 0.1
39	C ₁ -Indan	41.1 ± 3.5	31.6 ± 0.3	15.8 ± 0.1
40	C ₂ -Phenol	28.1 ± 2.8	30.4 ± 0.2	15.2 ± 0.1
41	Tetralin	74.6 ± 5.5	64.2 ± 0.3	32.1 ± 0.2
42	C ₂ -Phenol	ND ^(g)	23.7 ± 0.1	11.9 ± 0.1
43	Naphthalene	144.1 ± 7.7	157.4 ± 1.4	78.7 ± 0.7
48	C ₁ -Tetralin	21.6 ± 1.5	19.6 ± 0.1	9.8 ± 0.1
54	C ₂ -Indan	52.3 ± 2.6	52.1 ± 0.5	26.0 ± 0.2
55	C ₂ -Indan	38.6 ± 2.0	45.4 ± 0.7	22.7 ± 0.4
56	2-Methylnaphthalene	123.8 ± 5.5	140.0 ± 2.2	70.0 ± 1.1
57	1-Methylnaphthalene	34.4 ± 1.8	40.9 ± 0.6	20.4 ± 0.3
59	C ₃ -Indan	23.8 ± 1.8	28.5 ± 0.3	14.3 ± 0.2
50	Indanol	24.1 ± 1.5	29.3 ± 0.4	14.6 ± 0.2
61	C ₂ -Tetralin }	34.2 ± 2.1	36.5 ± 0.8	18.3 ± 0.4
62	C ₄ -Phenol }			
63	C ₄ -Phenol, C ₃ -Indan	25.6 ± 2.7	ND	ND
64	Biphenyl	45.4 ± 2.0	48.2 ± 1.0	24.1 ± 0.5
65	C ₂ -Naphthalene	50.0 ± 2.3	51.1 ± 0.6	25.6 ± 0.3
66	C ₃ -Naphthalene	42.8 ± 2.0	46.3 ± 0.2	23.2 ± 0.1
68	C ₂ -Naphthalene, Diphenylether	73.0 ± 2.9	85.8 ± 1.2	42.9 ± 0.6
69	Acenaphthene	24.2 ± 1.5	26.7 ± 0.5	13.3 ± 0.2
70	C ₄ -Naphthalene	23.5 ± 1.3	25.4 ± 0.5	12.7 ± 0.3
71	C ₃ -Naphthalene	19.9 ± 1.4	21.7 ± 0.3	10.8 ± 0.1
74	Fluorene	18.8 ± 1.3	ND	ND
76	C ₁ -Acenaphthene, C ₃ -Biphenyl	14.9 ± 0.8	18.7 ± 0.3	9.3 ± 0.2
77	C ₄ -Naphthalene	14.9 ± 0.8	11.4 ± 0.2	5.7 ± 0.1
80	Phenanthrene	42.4 ± 1.8	62.9 ± 0.5	31.5 ± 0.2
97	Pyrene	16.1 ± 1.6	ND	ND

(a) Based on 4.0 mg/mL n-Nonadecane ISTD, 1:10 dilution, based on the integration of peak heights, T=0 was 1980, T=2 years was 1982.

(b) Based on 0.40 mg/mL n-Nonadecane ISTD, 1:201 dilution.

(c) Numbers refer to peaks in Figure 3.4, Results and Discussion Section.

(d) Identified by GC/MS.

(e) Based on 5 GC runs.

(f) Based on 4 GC runs.

(g) No data.

TABLE 7.9. Chromatographic Results for SRC-II Fuel Oil Blend Sample 3317-079-24 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. (c)	Compound (d)	Normalized Percent to n-Nonadecane ISTD (a)		Raw Data (b)
		T=0	T=2 years	T=2 years
28	Phenol	86.3 ± 10.3 (e)	64.4 ± 2.7 (e)	40.3 ± 1.7 (e)
30	C ₃ -Benzene	14.6 ± 1.9	12.4 ± 0.5	7.8 ± 0.3
32	Indan	22.6 ± 2.7	19.0 ± 1.0	11.9 ± 0.6
33	o-Cresol	49.9 ± 4.2	40.6 ± 2.3	25.4 ± 1.5
35	m- & p-Cresol, C ₁ -Indan	86.3 ± 9.3	72.6 ± 3.2	45.4 ± 2.0
38	C ₁ -Indan	18.0 ± 1.4	16.0 ± 0.9	10.0 ± 0.6
39	C ₁ -Indan	32.2 ± 2.3	25.1 ± 1.0	15.7 ± 0.7
40	C ₂ -Phenol	25.1 ± 2.2	24.3 ± 0.9	15.2 ± 0.5
41	Tetralin	62.5 ± 5.1	50.9 ± 2.4	31.8 ± 1.5
42	C ₂ -Phenol	22.3 ± 1.1	19.3 ± 0.1	12.1 ± 0.1
43	Naphthalene	143.3 ± 10.7	125.6 ± 5.0	78.5 ± 3.1
48	C ₁ -Tetralin	17.2 ± 1.0	15.7 ± 0.6	9.8 ± 0.4
54	C ₂ -Indan	45.0 ± 2.6	41.9 ± 1.5	26.2 ± 0.9
55	C ₂ -Indan	35.8 ± 2.2	36.4 ± 0.9	22.7 ± 0.6
56	2-Methylnaphthalene	128.0 ± 8.2	112.2 ± 2.9	70.1 ± 1.8
57	1-Methylnaphthalene	28.7 ± 1.2	32.6 ± 0.9	20.4 ± 0.5
59	C ₃ -Indan	20.9 ± 0.9	23.0 ± 0.6	14.4 ± 0.4
60	Indanol	22.0 ± 2.2	23.5 ± 0.6	14.7 ± 0.4
61	C ₂ -Tetralin	29.3 ± 0.6	29.5 ± 0.8	18.4 ± 0.5
62	C ₄ -Phenol			
63	C ₄ -Phenol, C ₃ -Indan	13.4 ± 0.5	ND (f)	ND
64	Biphenyl	37.4 ± 1.7	38.9 ± 1.1	24.3 ± 0.7
65	C ₂ -Naphthalene	40.8 ± 1.6	41.2 ± 0.8	25.7 ± 0.5
66	C ₂ -Naphthalene	34.1 ± 0.9	37.5 ± 0.8	23.5 ± 0.5
68	C ₂ -Naphthalene, Diphenylether	66.6 ± 2.1	68.7 ± 1.6	43.0 ± 1.0
69	Acenaphthene	18.2 ± 0.4	21.7 ± 0.6	13.6 ± 0.4
70	C ₃ -Naphthalene	19.1 ± 0.6	20.5 ± 0.7	12.8 ± 0.4
71	C ₃ -Naphthalene	15.2 ± 0.2	17.4 ± 0.4	10.9 ± 0.3
74	Fluorene	14.2 ± 0.4	ND	ND
75	C ₁ -Acenaphthene, C ₂ -Biphenyl	11.0 ± 0.2	15.1 ± 0.3	9.4 ± 0.2
77	C ₄ -Naphthalene	11.7 ± 0.2	9.3 ± 0.2	5.8 ± 0.1
81	Phenanthrene	38.4 ± 1.3	50.8 ± 0.3	31.7 ± 0.2
97	Pyrene	13.0 ± 1.2	ND	ND

(a) Based on 2.5 mg/mL n-Nonadecane ISTD, 1:20 dilution, based on the integration of peak heights, T=0 was 1980, T=2 years was 1982.

(b) Based on 0.40 mg/mL n-Nonadecane ISTD, 1:200 dilution.

(c) Numbers refer to peaks in Figure 3.9, Results and Discussion Section.

(d) Identified by GC/MS.

(e) Based on 4 GC runs.

(f) No data.

TABLE 7.10. Chromatographic Results for SRC-II Fuel Oil Blend Sample 3317-079-25 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. (c)	Compound (d)	Normalized Percent to n-Nonadecane ISTD (a)		Raw Data (b)
		T=0	T=2 years	T=2 years
28	Phenol	77.1 ± 6.1 (e)	62.7 ± 1.2 (f)	39.2 ± 0.7 (f)
30	C ₃ -Benzene	13.0 ± 1.1	12.0 ± 0.2	7.5 ± 0.1
32	Indan	20.9 ± 2.0	18.4 ± 0.4	11.5 ± 0.3
33	o-Cresol	46.4 ± 3.5	39.2 ± 1.0	24.5 ± 0.6
35	m- & p-Cresol, C ₁ -Indan	78.2 ± 8.1	71.5 ± 1.1	44.7 ± 0.7
38	C ₁ -Indan	17.0 ± 1.3	15.5 ± 0.3	9.7 ± 0.2
39	C ₁ -Indan	30.2 ± 2.1	24.0 ± 0.4	15.0 ± 0.3
40	C ₂ -Phenol	23.4 ± 1.4	23.6 ± 0.5	14.7 ± 0.3
41	Tetralin	58.0 ± 4.6	49.1 ± 1.1	30.7 ± 0.7
42	C ₂ -Phenol	21.5 ± 0.7	18.4 ± 0.3	11.5 ± 0.2
43	Naphthalene	132.8 ± 8.5	123.2 ± 2.5	77.0 ± 1.6
48	C ₁ -Tetralin	16.4 ± 1.0	15.2 ± 0.3	9.5 ± 0.2
54	C ₂ -Indan	42.6 ± 2.2	40.5 ± 0.9	25.3 ± 0.5
55	C ₂ -Indan	35.4 ± 1.4	35.8 ± 0.6	22.4 ± 0.4
56	2-Methylnaphthalene	117.0 ± 4.9	110.0 ± 2.5	68.7 ± 1.6
57	1-Methylnaphthalene	27.9 ± 1.0	32.5 ± 0.4	20.3 ± 0.3
59	C ₃ -Indan	20.7 ± 0.8	22.4 ± 0.3	14.0 ± 0.2
60	Indanol	19.8 ± 1.6	23.1 ± 0.4	14.4 ± 0.3
61	C ₂ -Tetralin	31.0 ± 1.2	28.7 ± 0.3	17.9 ± 0.2
62	C ₄ -Phenol			
63	C ₄ -Phenol, C ₃ -Indan	15.0 ± 1.5	ND (g)	ND
64	Biphenyl	37.5 ± 1.2	38.1 ± 0.3	23.8 ± 0.2
65	C ₂ -Naphthalene	40.3 ± 1.1	40.0 ± 0.4	25.0 ± 0.3
66	C ₂ -Naphthalene	34.0 ± 1.2	36.2 ± 0.6	22.6 ± 0.4
68	C ₂ -Naphthalene, Diphenylether	64.7 ± 1.0	67.3 ± 0.7	42.0 ± 0.4
69	Acenaphthene	18.4 ± 0.8	21.0 ± 0.4	13.1 ± 0.2
70	C ₃ -Naphthalene	19.0 ± 0.4	20.2 ± 0.6	12.6 ± 0.4
71	C ₃ -Naphthalene	15.5 ± 0.5	17.1 ± 0.3	10.7 ± 0.2
74	Fluorene	14.0 ± 1.0	ND	ND
75	C ₁ -Acenaphthene, C ₂ -Biphenyl	10.8 ± 0.9	14.6 ± 0.2	9.1 ± 0.1
76	C ₄ -Naphthalene	11.6 ± 0.6	9.1 ± 0.1	5.7 ± 0.1
77	Phenanthrene	36.7 ± 1.5	49.9 ± 0.7	31.2 ± 0.4
78	Pyrene	11.8 ± 0.9	ND	ND

(a) Based on 2.5 mg/mL n-Nonadecane ISTD, 1:20 dilution, based on the integration of peak heights, T=0 was 1980, T=2 years was 1982.

(b) Based on 0.40 mg/mL n-Nonadecane ISTD, 1:201 dilution.

(c) Numbers refer to peaks in Figure 3.4, Results and Discussion Section.

(d) Identified by GC/MS.

(e) Based on 5 GC runs.

(f) Based on 4 GC runs.

(g) No data.

TABLE 7.11. Chromatographic Results for SRC-II Fuel Oil Blend Sample 3317-079-26 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. ^(c)	Compound ^(c)	Normalized Percent to n-Nonadecane ISTD ^(a)		Raw Data ^(b)
		T=0	T=2 years	T=2 years
28	Phenol	88.0 ± 5.2 ^(e)	73.9 ± 1.7 ^(f)	41.0 ± 1.0 ^(f)
30	C ₃ -Benzene	15.3 ± 0.9	14.3 ± 0.4	7.9 ± 0.2
32	Indan	24.1 ± 1.5	22.0 ± 0.7	12.2 ± 0.4
33	<i>o</i> -Cresol	50.3 ± 2.2	46.4 ± 0.9	25.8 ± 0.5
35	<i>m</i> - & <i>p</i> -Cresol, C ₁ -Indan	84.8 ± 8.1	83.3 ± 1.5	46.3 ± 0.8
38	C ₁ -Indan	18.3 ± 0.8	18.5 ± 0.5	10.3 ± 0.3
39	C ₁ -Indan	31.6 ± 1.6	28.8 ± 0.9	16.0 ± 0.5
40	C ₂ -Phenol	24.4 ± 1.5	28.0 ± 0.9	15.5 ± 0.5
41	Tetralin	60.6 ± 3.3	58.5 ± 1.5	32.5 ± 0.8
42	C ₂ -Phenol	21.8 ± 1.6	21.2 ± 0.5	11.8 ± 0.3
43	Naphthalene	136.8 ± 9.5	144.2 ± 3.3	80.1 ± 1.8
48	C ₁ -Tetralin	16.6 ± 1.0	18.1 ± 0.6	10.1 ± 0.3
54	C ₂ -Indan	42.0 ± 2.4	48.0 ± 1.3	26.7 ± 0.7
55	C ₂ -Indan	34.6 ± 2.2	42.2 ± 1.2	23.5 ± 0.7
56	2-Methylnaphthalene	117.5 ± 8.2	128.3 ± 3.0	71.3 ± 1.7
57	1-Methylnaphthalene	26.8 ± 1.6	37.5 ± 1.0	20.8 ± 0.6
59	C ₃ -Indan	20.5 ± 1.2	26.3 ± 0.8	14.6 ± 0.4
60	Indanol	20.4 ± 1.5	26.8 ± 0.6	14.9 ± 0.4
61	C ₂ -Tetralin	27.9 ± 1.5	33.7 ± 1.0	18.7 ± 0.6
62	C ₄ -Phenol			
63	C ₄ -Phenol, C ₃ -Indan	12.5 ± 1.2	ND ^(g)	ND
64	Biphenyl	34.4 ± 1.9	44.0 ± 1.0	24.5 ± 0.5
65	C ₂ -Naphthalene	37.4 ± 1.7	44.7 ± 6.1	24.9 ± 3.4
66	C ₂ -Naphthalene	31.4 ± 1.6	42.5 ± 1.4	23.6 ± 0.8
68	C ₂ -Naphthalene, Diphenylether	60.9 ± 3.2	78.9 ± 2.5	43.8 ± 1.4
69	Acenaphthene	16.5 ± 0.7	24.6 ± 0.8	13.6 ± 0.4
70	C ₃ -Naphthalene	17.2 ± 0.8	23.3 ± 0.8	12.9 ± 0.4
71	C ₃ -Naphthalene	13.8 ± 0.5	19.7 ± 0.7	11.0 ± 0.4
74	Fluorene	12.6 ± 0.9	ND	ND
75	C ₁ -Acenaphthene, C ₂ -Biphenyl	9.5 ± 0.6	17.0 ± 0.7	9.5 ± 0.4
77	C ₄ -Naphthalene	10.3 ± 0.6	10.4 ± 0.5	5.8 ± 0.3
85	Phenanthrene	33.9 ± 1.5	57.0 ± 2.2	31.7 ± 1.2
97	Pyrene	11.2 ± 0.9	ND	ND

(a) Based on 2.2 mg/mL n-Nonadecane ISTD, 1:20 dilution, based on the integration of peak heights, T=0 was 1980, T=2 years was 1982.

(b) Based on 0.40 mg/mL n-Nonadecane ISTD, 1:201 dilution.

(c) Numbers refer to peaks in Figure 3.4, Results and Discussion Section.

(d) Identified by GC/MS.

(e) Based on 5 GC runs.

(f) Based on 8 GC runs.

(g) No data.

Table 7.12. Chromatographic Results for SRC-I Wash Solvent Sample 3317-075-19 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. (c)	Compound (d)	Normalized Percent to n-Pentadecane ISTD (a)		Raw Data (b)
		T=0	T=2 years	T=2 years
23	C ₂ -Benzene	23.4 ± 2.0 (e)	23.6 ± 0.3 (f)	7.0 ± 0.1 (f)
24	C ₂ -Benzene	19.6 ± 1.7	19.4 ± 0.3	5.8 ± 0.1
27	C ₃ -Benzene	26.8 ± 1.4	25.6 ± 0.4	7.6 ± 0.1
28	Phenol	135.0 ± 9.8	136.4 ± 1.6	40.7 ± 0.5
30	C ₃ -Benzene	28.7 ± 3.0	22.0 ± 0.3	6.6 ± 0.1
32	Indan	67.2 ± 4.1	60.1 ± 0.6	17.9 ± 0.2
33	o-Cresol	108.0 ± 5.9	104.5 ± 1.1	31.2 ± 0.3
34	C ₄ -Benzene	20.8 ± 1.9	17.1 ± 0.2	5.1 ± 0.1
35a	m- & p-Cresol, C ₁ -Indan	90.6 ± 4.4	92.3 ± 1.1	27.6 ± 0.3
35b		139.4 ± 10.1	135.1 ± 1.8	40.3 ± 0.6
36	n-Undecane	42.4 ± 3.3	30.6 ± 0.5	9.1 ± 0.1
37	C ₂ -Phenol	23.3 ± 1.1	22.4 ± 0.3	6.7 ± 0.1
38	C ₁ -Indan	42.8 ± 2.2	40.2 ± 0.5	12.0 ± 0.2
39	C ₁ -Indan	66.0 ± 3.2	72.1 ± 0.9	21.5 ± 0.3
41	Tetralin	190.8 ± 11.1	181.7 ± 2.6	54.2 ± 0.8
43a	Naphthalene	244.4 ± 18.7	233.3 ± 2.6	69.6 ± 0.8
43b		93.8 ± 8.7	95.9 ± 1.9	28.6 ± 0.6
44	C ₂ -Phenol	53.5 ± 3.3	39.1 ± 0.5	11.7 ± 0.2
45	C ₃ -Phenol	23.2 ± 1.4	22.8 ± 0.3	6.8 ± 0.1
46	C ₁ -Dihydronaphthalene	29.0 ± 0.2	30.6 ± 0.8	9.1 ± 0.3
47	C ₁ -Tetralin	47.9 ± 2.4	34.0 ± 0.6	10.1 ± 0.2
48	C ₁ -Tetralin	49.1 ± 2.1	46.5 ± 0.7	13.9 ± 0.2
49	C ₁ -Tetralin, C ₃ -Phenol	21.7 ± 0.9	14.0 ± 0.2	4.2 ± 0.1
50	C ₁ -Dihydronaphthalene	19.9 ± 0.8	18.0 ± 0.3	5.4 ± 0.1
51	C ₃ -Phenol	19.2 ± 0.7	16.2 ± 0.4	4.8 ± 0.1
52	C ₃ -Phenol	19.5 ± 0.3	18.5 ± 0.4	5.5 ± 0.1
53	C ₂ -Indan	23.8 ± 1.4	21.0 ± 0.4	6.3 ± 0.1
54	C ₂ -Indan	48.2 ± 2.0	47.8 ± 0.6	14.3 ± 0.2
55	C ₂ -Indan	25.3 ± 0.3	28.7 ± 0.8	8.6 ± 0.3
56	2-Methylnaphthalene	36.6 ± 1.0	36.4 ± 0.6	10.9 ± 0.2
57	1-Methylnaphthalene	34.2 ± 1.5	31.9 ± 0.4	9.5 ± 0.1

(a) Based on 2.0 mg/mL n-Pentadecane ISTD, 1:12 dilution, based on the integration of peak heights, T=0 was 1980, T=2 years was 1982.

(b) Based on 0.40 mg/mL n-Pentadecane ISTD, 1:201 dilution.

(c) Numbers refer to peaks in Figure 3.5, Results and Discussion Section.

(d) Identified by GC/MS.

(e) Based on 4 GC runs.

(f) Based on 8 GC runs.

Table 7.13. Chromatographic Results for SRC-II Heavy Distillate Sample 3317-132-02 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No.(c)	Compound(d)	Normalized Percent to n-Nonadecane ISTD(a)		Raw Data(b)
		T=0	T=2 years	T=2 years
74	Fluorene	5.7 ± 0.2(e)	2.4 ± 0.1(e)	4.8 ± 0.1(e)
75	C ₁ -Acenaphthene, C ₂ -Biphenyl	7.0 ± 0.3	3.0 ± 0.1	6.0 ± 0.1
77	C ₄ -Naphthalene	6.2 ± 0.3	4.4 ± 0.1	8.8 ± 0.1
78	Xanthene	4.6 ± 0.2	2.4 ± 0.1	4.8 ± 0.1
79	C ₁ -Fluorene	4.8 ± 0.2	2.5 ± 0.4	5.0 ± 0.7
80	C ₁ -Fluorene	6.2 ± 0.4	5.4 ± 0.1	10.8 ± 0.2
81	C ₁ -Fluorene	13.1 ± 0.8	10.0 ± 0.2	20.1 ± 0.4
82	C ₁ -Fluorene	4.2 ± 0.3	3.5 ± 0.1	7.2 ± 0.3
83	Dibenzothiophene	9.1 ± 0.5	10.0 ± 0.3	19.9 ± 0.7
84	Tetrahydrophenanthrene	5.6 ± 0.4	4.4 ± 0.2	8.7 ± 0.5
85	Phenanthrene	50.1 ± 4.5	49.5 ± 1.1	98.9 ± 2.2
86	C ₂ -Fluorene	3.8 ± 0.4	2.9 ± 0.5	5.9 ± 1.0
87	C ₂ -Fluorene	2.9 ± 0.2	5.1 ± 0.7	10.2 ± 1.4
88	C ₂ -Fluorene	3.0 ± 0.3	3.1 ± 0.6	6.3 ± 1.2
89	Carbazole	10.9 ± 0.5	10.7 ± 1.2	21.5 ± 2.4
90	3-Methylphenanthrene	10.5 ± 1.0	10.4 ± 0.5	20.7 ± 1.0
91	2-Methylphenanthrene	18.9 ± 1.6	16.3 ± 0.5	32.7 ± 1.0
92	1-Methylphenanthrene	3.2 ± 0.3	4.8 ± 0.9	9.6 ± 1.8
93	C ₂ -Xanthene	4.1 ± 0.3	3.1 ± 0.2	6.2 ± 0.4
94	Dihydrofluoranthene	5.2 ± 0.4	8.9 ± 0.4	17.8 ± 0.7
95	C ₂ -Phenanthrene	3.6 ± 0.2	3.6 ± 0.1	7.3 ± 0.1
96	Fluoranthene	4.8 ± 0.2	5.2 ± 0.3	10.5 ± 0.5
97	Pyrene	22.2 ± 1.9	28.3 ± 0.2	56.6 ± 0.4
98	Dihdropyrene	2.8 ± 0.2	2.9 ± 0.1	5.8 ± 0.1
99	2- or 4-Methylpyrene, Benzo(b)fluorene	13.5 ± 0.7	14.5 ± 0.3	29.1 ± 0.5
100	2-Pyrene, C ₁ -Benzo(b)fluorene	2.5 ± 0.2	3.9 ± 0.1	7.7 ± 0.2
101	C ₁ -Chrysene	3.9 ± 0.4	ND(f)	ND

(a) Based on 1.0 µg/mL n-Pentadecane ISTD, 1:50 dilution, based on the integration of peak heights, T=0 was 1980, T=2 years was 1982.

(b) Based on 0.40 µg/mL n-Pentadecane ISTD, 1:101 dilution.

(c) Numbers refer to peaks in Figure 3.6, Results and Discussion Section.

(d) Identified by GC/MS.

(e) Based on 5 GC runs.

(f) No data

TABLE 7.14. Chromatographic Results for SRC-II Heavy Distillate Sample 3317-134-02 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. ^(c)	Compound ^(d)	Normalized Percent to n-Nonadecane ISTD ^(a)		Raw Data ^(b)
		T=0	T=2 years	T=2 years
74	Fluorene	16.5 ± 0.7 ^(e)	7.9 ± 0.1 ^(f)	9.8 ± 0.1 ^(f)
75	C ₁ -Acenaphthene, C ₂ -Biphenyl	18.6 ± 0.9	9.3 ± 0.4	11.6 ± 0.5
77	C ₄ -Naphthalene	16.8 ± 1.1	14.3 ± 0.4	17.9 ± 0.4
78	Xanthene	12.2 ± 0.6	7.7 ± 0.6	9.7 ± 0.7
79	C ₁ -Fluorene	11.4 ± 0.4	8.7 ± 1.4	10.8 ± 1.8
80	C ₁ -Fluorene	13.0 ± 0.7	13.0 ± 0.9	16.3 ± 1.1
81	C ₁ -Fluorene	25.4 ± 1.6	22.2 ± 1.0	27.8 ± 1.3
82	C ₁ -Fluorene	9.0 ± 1.0	8.2 ± 0.6	10.3 ± 0.8
83	Dibenzothiophene	15.8 ± 0.9	18.8 ± 1.5	23.5 ± 1.9
84	Tetrahydrophenanthrene	8.3 ± 0.5	7.2 ± 1.1	9.0 ± 1.3
85	Phenanthrene	81.9 ± 8.8	85.8 ± 5.1	107.3 ± 6.4
86	C ₂ -Fluorene	6.6 ± 0.2	5.4 ± 1.0	6.7 ± 1.3
87	C ₂ -Fluorene	5.0 ± 0.1	9.2 ± 1.3	11.5 ± 1.6
88	C ₂ -Fluorene	5.4 ± 0.2	5.8 ± 1.1	7.2 ± 1.4
89	Carbazole	19.6 ± 1.0	20.6 ± 1.8	25.7 ± 2.3
90	3-Methylphenanthrene	16.5 ± 1.3	17.9 ± 0.4	22.3 ± 0.5
91	2-Methylphenanthrene	29.6 ± 1.6	27.9 ± 0.2	34.8 ± 0.3
92	1-Methylphenanthrene	4.7 ± 0.4	9.0 ± 0.3	11.3 ± 0.4
93	C ₂ -Xanthene	7.4 ± 0.6	5.4 ± 0.1	6.7 ± 0.1
94	Dihydrofluoranthene	8.3 ± 0.5	15.4 ± 0.1	19.2 ± 0.2
95	C ₂ -Phenanthrene	5.4 ± 0.3	6.1 ± 0.1	7.6 ± 0.1
96	Fluoranthene	6.9 ± 0.5	8.1 ± 0.6	10.1 ± 0.8
97	Pyrene	36.6 ± 5.7	49.6 ± 1.5	62.0 ± 1.8
98	Dihdropyrene	4.2 ± 0.4	4.7 ± 0.2	5.8 ± 0.2
99	2- or 4-Methylpyrene, Benzo(b)fluorene	21.0 ± 2.5	24.9 ± 0.7	31.1 ± 0.9
100	C ₂ -Pyrene, C ₁ -Benzo(b)fluorene	4.1 ± 0.5	6.6 ± 0.5	8.2 ± 0.6
101	C ₁ -Chrysene	5.5 ± 0.5	ND ^(g)	ND

(a) Based on 1.0 mg/mL n-Pentadecane ISTD, 1:50 dilution, based on the integration of peak heights, T=0 was 1980, T=2 years was 1982.

(b) Based on 0.4 mg/mL n-Pentadecane ISTD, 1:101 dilution.

(c) Numbers refer to peaks in Figure 3.6, Results and Discussion Section.

(d) Identified by GC/MS.

(e) Based on 5 GC runs.

(f) Based on 4 GC runs.

(g) No data.

TABLE 7.15. Chromatographic Results for SRC-II Heavy Distillate Sample 3317-015-11 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. ^(c)	Compound ^(d)	Normalized Percent to n-Pentadecane ISTD ^(a)		Raw Data ^(b)
		T=0	T=2 years	T=2 years
74	Fluorene	34.0 ± 1.6 ^(e)	14.5 ± 0.8 ^(f)	14.5 ± 0.8 ^(f)
75	C ₁ -Acenaphthene, C ₂ -Biphenyl	27.4 ± 1.8	11.6 ± 0.4	11.6 ± 0.4
77	C ₄ -Naphthalene	24.0 ± 1.2	16.7 ± 0.7	16.7 ± 0.7
78	Xanthene	16.4 ± 1.4	8.3 ± 0.6	8.3 ± 0.6
79	C ₁ -Fluorene	14.6 ± 1.2	7.4 ± 0.9	7.4 ± 0.9
80	C ₁ -Fluorene	20.2 ± 1.1	16.8 ± 0.7	16.8 ± 0.7
81	C ₁ -Fluorene	42.2 ± 2.6	27.4 ± 1.1	27.4 ± 1.1
82	C ₁ -Fluorene	11.0 ± 0.9	6.9 ± 0.3	6.9 ± 0.3
83	Dibenzothiophene	21.9 ± 1.8	19.7 ± 1.0	19.7 ± 1.0
84	Tetrahydrophenanthrene	12.7 ± 1.2	8.0 ± 0.5	8.0 ± 0.5
85	Phenanthrene	100.4 ± 6.7	107.6 ± 5.2	107.6 ± 5.2
86	C ₂ -Fluorene	11.9 ± 0.7	7.6 ± 1.1	7.6 ± 1.1
87	C ₂ -Fluorene	8.7 ± 0.7	9.4 ± 1.6	9.4 ± 1.6
88	C ₂ -Fluorene	9.4 ± 0.7	6.1 ± 1.4	6.1 ± 1.4
89	Carbazole	35.3 ± 2.2	34.5 ± 4.3	34.5 ± 4.3
90	3-Methylphenanthrene	22.6 ± 1.0	21.2 ± 1.4	21.2 ± 1.4
91	2-Methylphenanthrene	43.3 ± 2.4	32.9 ± 2.1	32.9 ± 2.1
92	1-Methylphenanthrene	8.9 ± 0.9	10.3 ± 1.4	10.3 ± 1.4
93	C ₂ -Xanthene	10.0 ± 0.8	7.1 ± 0.7	7.1 ± 0.7
94	Dihydrofluoranthene	14.3 ± 0.9	17.6 ± 1.4	17.6 ± 1.4
95	C ₂ -Phenanthrene	8.8 ± 1.0	6.8 ± 0.5	6.8 ± 0.5
96	Fluoranthene	13.4 ± 0.8	11.1 ± 1.5	11.1 ± 1.5
97	Pyrene	42.8 ± 3.8	56.0 ± 2.3	56.0 ± 2.3
98	Dihdropyrene	7.9 ± 0.5	6.8 ± 0.5	6.8 ± 0.5
99	2- or 4-Methylpyrene, Benzo(b)fluorene	30.1 ± 4.2	29.1 ± 0.9	29.1 ± 0.9
100	C ₂ -Pyrene, C ₁ -Benzo(b)fluorene	6.1 ± 0.9	7.5 ± 0.7	7.5 ± 0.7
101	C ₁ -Chrysene	3.0 ± 0.4	ND ^(g)	ND

(a) Based on 0.80 mg/mL n-Pentadecane ISTD, 1:50 dilution, based on the integration of peak heights, T=0 was 1980, T=2 years was 1982.

(b) Based on 0.40 mg/mL n-Pentadecane ISTD, 1:101 dilution.

(c) Numbers refer to peaks in Figure 3.6, Results and Discussion Section.

(d) Identified by GC/MS.

(e) Based on 5 GC runs.

(f) Based on 8 GC runs.

(g) No data.

TABLE 7.16. Chromatographic Results for SRC-I Process Solvent Sample 3317-066-26 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. ^(a)	Compound ^(b)	Normalized Percent to ISTD ^(c,g)		Raw Data ^(b)
		T=0	T=2 years	T=2 years
43	Naphthalene	11.9 ± 1.3 ^(c,d)	16.4 ± 0.1 ^(e)	11.7 ± 0.1 ^(e,f)
54	C ₂ -Indan	17.4 ± 0.6 ^(c)	13.4 ± 0.1	9.6 ± 0.1 ^(f)
55	C ₂ -Indan	24.9 ± 1.9 ^(c)	26.2 ± 0.1	18.7 ± 0.1 ^(f)
56	2-Methylnaphthalene	96.1 ± 12.2 ^(c)	81.1 ± 0.2	57.9 ± 0.2 ^(f)
57	1-Methylnaphthalene	20.4 ± 1.0 ^(c)	16.5 ± 0.1	11.8 ± 0.1 ^(f)
60	Indanol	12.6 ± 0.8 ^(c)	9.7 ± 0.1	6.3 ± 0.1 ^(f)
61	C ₂ -Tetralin } C ₄ -Phenol }	13.3 ± 3.0 ^(c)	14 ± 0.1	10.3 ± 0.1 ^(f)
62				
63	C ₄ -Phenol, C ₃ -Indan	11.6 ± 2.3 ^(c)	12.0 ± 0.1	8.6 ± 0.1 ^(f)
64	Biphenyl	26.4 ± 2.7 ^(c)	27.0 ± 0.1	19.3 ± 0.1 ^(f)
65	C ₂ -Naphthalene	23.0 ± 2.3 ^(c)	23.2 ± 0.1	16.6 ± 0.1 ^(f)
66	C ₂ -Naphthalene	20.8 ± 1.8 ^(c)	24.2 ± 0.1	17.3 ± 0.1 ^(f)
67	C ₂ -Naphthalene	10.3 ± 1.0 ^(c)	6.6 ± 0.1	4.7 ± 0.1 ^(f)
68	C ₂ -Naphthalene, Diphenylether	27.2 ± 2.6 ^(c)	27.6 ± 0.2	19.7 ± 0.1 ^(f)
69	Acenaphthene	15.2 ± 1.6 ^(c)	18.7 ± 0.2	13.4 ± 0.1 ^(f)
70	C ₃ -Naphthalene	10.6 ± 1.3 ^(c)	15.6 ± 0.1	11.1 ± 0.1 ^(f)
71	C ₃ -Naphthalene	7.2 ± 1.0 ^(c)	10.2 ± 0.2	7.3 ± 0.2 ^(f)
72	Dibenzofuran	21.3 ± 2.9 ^(c)	27.0 ± 0.1	19.3 ± 0.1 ^(f)
74	Fluorene	35.2 ± 3.2 ^(g)	25.0 ± 0.3	15.6 ± 0.2 ^(h)
75	C ₁ -Acenaphthene, C ₂ -Biphenyl	17.3 ± 1.8 ^(g)	14.0 ± 0.3	8.7 ± 0.2 ^(h)
76	C ₄ -Naphthalene	15.2 ± 1.7 ^(g)	10.7 ± 0.3	6.7 ± 0.2 ^(h)
77	C ₄ -Naphthalene	27.6 ± 3.1 ^(g)	31.5 ± 1.0	19.7 ± 0.6 ^(h)
78	Xanthene	12.8 ± 1.3 ^(g)	10.9 ± 0.2	6.8 ± 0.1 ^(h)
79	C ₁ -Fluorene	12.6 ± 1.2 ^(g)	10.4 ± 0.6	6.5 ± 0.4 ^(h)
81	C ₁ -Fluorene	12.6 ± 1.1 ^(g)	10.6 ± 0.2	6.7 ± 0.1 ^(h)
85	Phenanthrene	92.4 ± 6.2 ^(g)	111.7 ± 2.1	69.8 ± 1.3 ^(h)
90	3-Methylphenanthrene	9.4 ± 0.6 ^(g)	11.0 ± 0.3	6.8 ± 0.2 ^(h)
91	2-Methylphenanthrene	12.4 ± 0.8 ^(g)	13.5 ± 0.3	8.5 ± 0.2 ^(h)
96	Fluoranthene	9.5 ± 1.3 ^(g)	14.5 ± 0.4	9.1 ± 0.2 ^(h)
97	Pyrene	11.1 ± 1.6 ^(g)	16.9 ± 0.5	10.5 ± 0.3 ^(h)
99	2- or 4-Methylpyrene, Benzo(b)fluorene	13.1 ± 2.1 ^(g)	ND ⁽ⁱ⁾	ND

(a) Numbers refer to peaks in Figure 3.7, Results and Discussion Section.

(b) Identified by GC/ms.

(c) Based on 1.0 mg/mL n-Dodecane ISTD, 1:50 dilution, based on the integration of peak heights, T=0 was 1980, T=2 years was 1982.

(d) Based on 5 GC runs.

(e) Based on 4 GC runs.

(f) Based on 0.35 mg/mL n-Dodecane ISTD, 1:201 dilution.

(g) Based on 1.0 mg/mL n-Nonadecane ISTD, 1:50 dilution.

(h) Based on 0.40 mg/mL n-Nonadecane ISTD, 1:201 dilution.

(i) No data.

TABLE 7.17. Chromatographic Results for SRC-I Process Solvent Sample 3317-066-27 Stored at 4°C, in the Dark, Under a Nitrogen Atmosphere

Peak No. (a)	Compound (b)	Normalized Percent to ISTD		Raw Data
		T = 0	T = 2 years	T = 2 years
43	Naphthalene	22.6 ± 1.7 ^(c,d)	13.8 ± 0.4 ^(e)	11.5 ± 0.3 ^(e,f)
54	C ₂ -Indan	9.6 ± 1.3 ^(c)	11.2 ± 0.3	9.3 ± 0.2 ^(f)
55	C ₂ -Indan	16.5 ± 1.8 ^(c)	21.7 ± 0.6	18.1 ± 0.5 ^(f)
56	2-Methylnaphthalene	65.1 ± 6.4 ^(c)	67.5 ± 1.8	56.2 ± 1.5 ^(f)
57	1-Methylnaphthalene	12.8 ± 1.6 ^(c)	13.7 ± 0.4	11.4 ± 0.3 ^(f)
60	Indanol	8.3 ± 0.9 ^(c)	8.1 ± 0.2	6.7 ± 0.2 ^(f)
61	C ₂ -Tetralin	9.7 ± 1.7 ^(c)	12.0 ± 0.4	10.0 ± 0.3 ^(f)
62	C ₄ -Phenol			
63	C ₄ -Phenol, C ₃ -Indan	8.2 ± 1.4 ^(c)	10.0 ± 0.4	8.3 ± 0.3 ^(f)
64	Biphenyl	18.3 ± 2.5 ^(c)	22.5 ± 0.8	18.7 ± 0.6 ^(f)
65	C ₂ -Naphthalene	16.7 ± 1.7 ^(c)	19.4 ± 0.7	16.2 ± 0.5 ^(f)
66	C ₂ -Naphthalene	15.3 ± 1.8 ^(c)	20.1 ± 0.6	16.8 ± 0.5 ^(f)
67	C ₂ -Naphthalene	7.6 ± 1.0 ^(c)	5.5 ± 0.2	4.6 ± 0.2 ^(f)
68	C ₂ -Naphthalene, Diphenylether	20.0 ± 2.2 ^(c)	23.0 ± 0.8	19.2 ± 0.6 ^(f)
69	Acenaphthene	12.2 ± 1.7 ^(c)	15.3 ± 1.8	12.8 ± 1.5 ^(f)
70	C ₃ -Naphthalene	8.1 ± 1.0 ^(c)	13.0 ± 0.6	10.8 ± 0.5 ^(f)
71	C ₃ -Naphthalene	6.0 ± 1.2 ^(c)	8.4 ± 0.4	7.0 ± 0.3 ^(f)
72	Dibenzofuran	17.7 ± 2.9 ^(c)	22.6 ± 0.8	18.8 ± 0.7 ^(f)
74	Fluorene	21.7 ± 2.7 ^(g)	15.4 ± 0.6	15.4 ± 0.6 ^(h)
75	C ₁ -Acenaphthene, C ₂ -Biphenyl	10.6 ± 1.5 ^(g)	8.5 ± 0.3	8.5 ± 0.3 ^(h)
76	C ₄ -Naphthalene	9.3 ± 1.4 ^(g)	6.6 ± 0.2	6.6 ± 0.2 ^(h)
77	C ₄ -Naphthalene	17.1 ± 2.5 ^(g)	19.3 ± 0.6	19.3 ± 0.6 ^(h)
78	Xanthene	8.1 ± 1.1 ^(g)	6.7 ± 0.3	6.7 ± 0.3 ^(h)
79	C ₁ -Fluorene	7.8 ± 0.8 ^(g)	6.5 ± 0.6	6.5 ± 0.6 ^(h)
81	C ₁ -Fluorene	8.3 ± 1.1 ^(g)	6.6 ± 0.2	6.6 ± 0.2 ^(h)
85	Phenanthrene	63.2 ± 0.7 ^(g)	68.7 ± 2.8	68.7 ± 2.8 ^(h)
90	3-Methylphenanthrene	6.6 ± 0.4 ^(g)	6.6 ± 0.3	6.6 ± 0.3 ^(h)
91	2-Methylphenanthrene	9.0 ± 0.9 ^(g)	8.1 ± 0.3	8.1 ± 0.3 ^(h)
92	Fluoranthene	7.1 ± 0.7 ^(g)	8.8 ± 0.4	8.8 ± 0.4 ^(h)
97	Pyrene	9.1 ± 0.8 ^(g)	9.8 ± 0.5	9.8 ± 0.5 ^(h)
99	2- or 4-Methylpyrene, Benzo(b)fluorene	12.3 ± 3.3 ^(g)	ND ⁽ⁱ⁾	ND

(a) Numbers refer to peaks in Figure 3.7, Results and Discussion Section.

(b) Identified by GC/MS.

(c) Based on 1.15 mg/mL n-Dodecane ISTD, 1:50 dilution, based on the integration of peak height.

(d) Based on 6 GC runs, T=0 was 1980.

(e) Based on 8 GC runs, T=2 years was 1982.

(f) Based on 0.35 mg/mL n-Dodecane ISTD, 1:201 dilution.

(g) Based on 1.7 mg/mL n-Nonadecane ISTD, 1:50 dilution.

(h) Based on 0.40 mg/mL n-Nonadecane ISTD, 1:201 dilution.

(i) No data.

TABLE 7.18. Chromatographic Results for SRC-II Fuel Oil Blend Sample 3317-079-25 Stored at -20°C and 20°C Under Various Conditions for One Year - Set 1

Peak No.(b)	Compound(c)	Normalized Percent to n-Nonadecane Internal Standard(a)						
		Control(d)	Condition 1(e)	Condition 2(f)	Condition 3(g)	Condition 4(h)	Condition 5(i)	Condition 6(j)
28	Phenol	19.3 ± 2.2(k)	22.4 ± 2.7(l)	23.7 ± 1.2(m)	ND(n)	20.1 ± 3.8(o)	25.3 ± 1.0(p)	24.1 ± 2.2(q)
32	Indan	5.0 ± 0.5	6.5 ± 1.0	6.0 ± 0.3	ND	5.1 ± 1.0	6.5 ± 0.8	6.1 ± 0.9
33	o-Cresol	12.1 ± 1.4	14.0 ± 1.6	15.1 ± 0.7	ND	12.8 ± 2.4	15.8 ± 0.9	15.3 ± 1.4
35	m- & p-Cresol, C ₁ -Indan	49.0 ± 3.2	55.0 ± 5.1	57.6 ± 2.1	ND	51.7 ± 5.3	60.2 ± 2.4	60.2 ± 5.2
38	C ₁ -Indan	19.3 ± 2.0	22.1 ± 2.3	23.9 ± 0.8	ND	20.8 ± 3.2	24.5 ± 1.0	24.3 ± 1.9
39	C ₁ -Indan	20.3 ± 2.1	22.9 ± 2.3	24.7 ± 1.0	ND	21.7 ± 3.0	25.2 ± 1.1	24.9 ± 1.7
41	Tetralin	39.5 ± 3.9	45.3 ± 4.2	49.1 ± 1.5	ND	43.1 ± 6.1	50.3 ± 1.9	50.1 ± 3.8
43	Naphthalene	37.9 ± 3.6	42.7 ± 4.0	46.2 ± 1.5	ND	40.7 ± 5.5	47.3 ± 1.8	46.7 ± 3.2
48	C ₁ -Tetralin	5.7 ± 0.5	6.9 ± 0.6	7.2 ± 0.5	ND	6.4 ± 1.2	7.4 ± 0.4	7.4 ± 0.6
54	C ₂ -Indan	41.8 ± 4.7	50.2 ± 3.8	53.8 ± 1.3	ND	47.5 ± 5.9	56.6 ± 2.5	54.7 ± 4.1
56	2-Methylnaphthalene	69.3 ± 10.5	90.3 ± 12.9	82.5 ± 2.1	ND	72.8 ± 8.7	103.6 ± 14.9	83.7 ± 6.2
57	1-Methylnaphthalene	13.7 ± 1.0	14.7 ± 3.1	16.8 ± 0.4	ND	14.9 ± 1.6	17.3 ± 0.4	16.9 ± 1.2
59	C ₃ -Indan	11.0 ± 0.7	12.2 ± 0.8	13.3 ± 0.6	ND	11.9 ± 0.3	13.2 ± 0.5	13.0 ± 0.8
60	Indanol	13.3 ± 1.0	15.6 ± 1.0	16.6 ± 0.3	ND	14.9 ± 1.4	17.0 ± 0.4	16.8 ± 1.3
62	C ₄ -Phenol	10.0 ± 1.7	10.1 ± 1.5	11.9 ± 2.1	ND	12.3 ± 1.2	11.2 ± 2.1	12.6 ± 1.6
63	C ₄ -Phenol, C ₃ -Indan	6.0 ± 0.5	6.9 ± 0.6	7.3 ± 0.1	ND	6.6 ± 0.6	7.6 ± 0.7	7.5 ± 0.5
64	Biphenyl	19.1 ± 1.3	21.6 ± 1.5	23.2 ± 0.5	ND	20.8 ± 1.8	24.0 ± 1.6	23.5 ± 1.6
65	C ₂ -Naphthalene	27.3 ± 1.6	30.2 ± 2.2	33.0 ± 0.6	ND	29.6 ± 2.6	33.9 ± 2.0	33.2 ± 2.4
68	C ₂ -Naphthalene, Diphenylether	59.4 ± 4.1	69.0 ± 4.1	71.7 ± 1.3	ND	64.8 ± 5.0	79.1 ± 3.7	72.6 ± 4.7
69	Acenaphthene	10.1 ± 0.7	11.7 ± 0.6	11.7 ± 0.9	ND	10.8 ± 1.0	12.9 ± 0.3	11.8 ± 1.1
70	C ₃ -Naphthalene	17.5 ± 3.7	20.2 ± 3.6	19.3 ± 3.0	ND	17.5 ± 0.9	21.8 ± 3.3	20.5 ± 2.5
71	C ₃ -Naphthalene	14.3 ± 1.8	17.9 ± 1.0	18.0 ± 1.5	ND	16.1 ± 2.2	19.2 ± 3.7	18.2 ± 1.6
74	Fluorene	9.6 ± 0.4	11.6 ± 1.1	12.0 ± 1.0	ND	10.9 ± 1.3	13.0 ± 1.2	11.5 ± 0.9
75	C ₁ -Acenaphthene, C ₂ -Biphenyl	7.2 ± 0.3	7.8 ± 2.9	8.8 ± 0.3	ND	8.0 ± 0.3	9.6 ± 0.9	8.5 ± 0.6
77	C ₄ -Naphthalene	14.6 ± 0.7	17.1 ± 1.2	17.7 ± 0.6	ND	15.9 ± 0.6	19.2 ± 1.6	16.8 ± 0.8
85	Phenanthrene	32.4 ± 1.4	34.5 ± 0.6	38.7 ± 0.7	ND	36.1 ± 0.2	38.9 ± 0.2	37.1 ± 1.7
97	Pyrene	10.6 ± 0.5	12.5 ± 1.2	12.2 ± 0.4	ND	11.6 ± 0.7	12.0 ± 1.2	11.5 ± 0.6

(a) Based on 0.40 mg/mL n-Nonadecane ISTD, 1:201 dilution, based on the integration of peak areas.

(b) Numbers refer to peaks in Figure 3.8, Results and Discussion Section.

(c) Identified by GC/MS.

(d) Stored at -20°C, in the dark, under a nitrogen atmosphere.

(e) Stored at -20°C, in the dark, under an air atmosphere.

(f) Stored at 20°C, in the light, under a nitrogen atmosphere.

(g) Stored at 20°C, in the light, under an air atmosphere, diluted in methylene chloride.

(h) Stored at 20°C, in the light, under an air atmosphere.

(i) Stored at 20°C, in the dark, under a nitrogen atmosphere.

(j) Stored at 20°C, in the dark, under an air atmosphere.

(k) Based on 6 GC runs.

(l) Based on 11 GC runs.

(m) Based on 4 GC runs.

(n) No data collected.

(o) Based on 2 GC runs.

(p) Based on 9 GC runs.

(q) Based on 8 GC runs.

TABLE 7.19. Chromatographic Results for SRC-II Fuel Oil Blend Sample 3317-079-25
Stored at -20°C and 20°C Under Various Conditions - Set 2(a)

Peak No.(c)	Compound(d)	Normalized Percent to n-Nonadecane Internal Standard(b)							
		Control(e)	Condition 1(f)	Condition 2(g)	Condition 3(h)		Condition 4(i)	Condition 5(j)	Condition 6(k)
28	Phenol	9.8 ± 0.4(l)	ND(m)	12.1 ± 0.1(n)	12.4 ± 0.1(o)	11.1 ± 0.3(o)	10.8 ± 0.3(p)	8.6 ± 0.2(n)	9.6 ± 0.4(l)
32	Indan	4.5 ± 1.4	ND	5.0 ± 0.9	1.4 ± 0.5	6.4 ± 0.1	4.3 ± 0.6	3.2 ± 0.1	3.5 ± 0.1
33	o-Cresol	8.8 ± 1.1	ND	11.5 ± 0.2	1.5 ± 0.5	2.8 ± 1.0	10.5 ± 0.3	8.4 ± 0.2	9.5 ± 0.6
35	m- & p-Cresol, C ₁ -Indan	39.8 ± 2.0	ND	50.3 ± 0.9	8.6 ± 2.0	12.2 ± 0.4	45.4 ± 1.5	35.9 ± 0.7	40.5 ± 2.8
38	C ₁ -Indan	6.2 ± 1.1(q)	ND	7.7 ± 0.2	2.2 ± 0.4	4.1 ± 0.2	6.9 ± 0.1	5.4 ± 0.3	6.0 ± 0.2
39	C ₁ -Indan	10.1 ± 0.3	ND	13.0 ± 0.2	7.9 ± 1.8	13.0 ± 0.9	11.5 ± 0.3	9.2 ± 0.3	10.6 ± 0.6
41	Tetralin	15.9 ± 0.7	ND	22.1 ± 0.4	7.4 ± 1.3	10.4 ± 0.1	19.1 ± 0.9	14.6 ± 0.1	16.5 ± 0.9
43	Naphthalene	16.6 ± 0.5	ND	21.4 ± 0.3	13.8 ± 3.5	21.4 ± 0.9	19.0 ± 0.5	15.1 ± 0.4	16.9 ± 1.0
48	C ₁ -Tetralin	6.6 ± 0.6	ND	9.0 ± 0.6	7.6 ± 0.2	13.9 ± 1.4	8.0 ± 0.3	6.2 ± 0.2	7.0 ± 0.5
54	C ₂ -Indan	19.1 ± 1.0	ND	25.3 ± 0.6	13.4 ± 2.5	26.0 ± 1.0	22.8 ± 0.8	17.7 ± 0.3	19.3 ± 0.6
56	2-Methylnaphthalene	29.5 ± 1.9	ND	38.6 ± 1.3	38.7 ± 6.9	39.3 ± --	35.2 ± 1.6	27.1 ± 0.3	28.9 ± --
57	1-Methylnaphthalene	5.9 ± 1.1	ND	8.2 ± 0.4	5.3 ± 1.9	7.8 ± 1.3	7.5 ± 0.5	6.1 ± 1.1	5.2 ± 0.8
59	C ₃ -Indan	4.3 ± 0.3	ND	5.6 ± 0.2	1.6 ± 0.7	2.2 ± 0.9	5.1 ± 0.2	4.1 ± 0.1	3.7 ± 0.5
60	Indanol	6.5 ± 0.5	ND	7.9 ± 0.2	1.3 ± --	2.2 ± --	5.8 ± 3.2	6.3 ± 0.1	5.0 ± 1.0
62	C ₄ -Phenol	4.8 ± 0.4	ND	6.8 ± 0.4	3.5 ± 1.5	5.2 ± 1.4	5.8 ± 0.5	4.6 ± 0.1	3.8 ± 0.7
63	C ₄ -Phenol, C ₃ -Indan	3.7 ± 0.3	ND	5.1 ± 0.2	2.7 ± 1.2	4.1 ± 0.9	4.4 ± 0.4	3.4 ± 0.1	2.9 ± 0.5
64	Biphenyl	8.6 ± 0.5	ND	13.7 ± 1.8	7.7 ± 2.5	11.3 ± 1.1	10.8 ± 1.8	8.1 ± 0.1	7.4 ± 0.7
65	C ₂ -Naphthalene	16.8 ± 1.1	ND	15.3 ± 0.4	8.7 ± 2.7	12.7 ± 0.9	13.5 ± 1.1	11.1 ± 0.1	10.7 ± 2.3
68	C ₂ -Naphthalene, Diphenylether	24.1 ± 1.2	ND	34.2 ± 3.1	24.3 ± 5.2	34.5 ± 1.2	29.5 ± 1.2	22.7 ± 0.2	25.0 ± 1.7
69	Acenaphthene	5.3 ± 1.2	ND	6.7 ± 0.2	3.0 ± 0.3	4.3 ± 0.5	6.7 ± 0.9	5.2 ± 0.7	5.1 ± 0.3
70	C ₃ -Naphthalene	6.5 ± 0.6	ND	9.0 ± 0.3	7.5 ± 2.7	9.0 ± 0.6	8.1 ± 0.3	6.4 ± 0.1	6.9 ± 0.4
71	C ₃ -Naphthalene	6.6 ± 0.6	ND	9.0 ± 0.3	5.9 ± 0.8	8.4 ± 0.6	8.3 ± 0.2	6.6 ± 0.1	7.2 ± 0.4
74	Fluorene	4.6 ± 0.7	ND	6.7 ± 0.3	5.1 ± 1.1	6.3 ± 1.2	6.2 ± 0.2	4.9 ± 0.1	5.2 ± 0.3
75	C ₁ -Acenaphthene, C ₂ -Biphenyl	3.3 ± 0.4	ND	4.8 ± 0.2	3.0 ± 0.3	4.2 ± 1.7	4.4 ± 0.1	3.5 ± 0.1	3.7 ± 0.2
77	C ₄ -Naphthalene	7.0 ± 0.4	ND	9.4 ± 0.3	5.6 ± 0.7	7.5 ± 0.7	8.6 ± 0.3	6.7 ± 0.1	7.2 ± 0.5
85	Phenanthrene	40.7 ± 5.2	ND	47.8 ± 2.0	36.6 ± 3.6	42.7 ± 34.0	48.4 ± 3.6	42.6 ± 2.3	44.7 ± 0.8
97	Pyrene	4.9 ± 1.3	ND	5.2 ± 0.1	3.3 ± 0.5	6.2 ± 3.7	5.2 ± 0.7	4.1 ± 0.4	4.0 ± 0.4

(a) Set 1 and Set 2 were acquired using different chromatographic parameters, based on the integration of peaks areas.

(b) Based on 0.40 mg/mL n-Nonadecane ISTD, 1:401 dilution.

(c) Numbers refer to peaks in Figure 3.8, Results and Discussion Section.

(d) Identified by GC/MS.

(e) Stored at -20°C, in the dark, under a nitrogen atmosphere.

(f) Stored at -20°C, in the dark, under an air atmosphere.

(g) Stored at 20°C, in the light, under a nitrogen atmosphere.

(h) Stored at 20°C, in the light, under an air atmosphere, diluted in methylene chloride, 1:20 & 1:200.

(i) Stored at 20°C, in the light, under an air atmosphere.

(j) Stored at 20°C, in the dark, under a nitrogen atmosphere.

(k) Stored at 20°C, in the dark, under an air atmosphere.

(l) Based on 4 GC runs.

(m) No data collected.

(n) Based on 3 GC runs.

(o) Based on 1 GC runs.

(p) Based on 1 GC runs.

(q) Result of only 1 GC run.

TABLE 7.20. Chromatographic Results for SRC-II Fuel Oil Blend Sample 3317-079-25 Stored at 60°C, in the Dark, Under an Air Atmosphere

Peak No. ^(b)	Compound ^(c)	Normalized Percent to n-Nonadecane Internal Standard ^(a)				
		T = 0	T = 1 week	T = 2 weeks	T = 16 weeks	T = 32 weeks
28	Phenol	58.7 ± 4.1 ^(d)	55.6 ± 1.9 ^(e)	51.2 ± 3.0 ^(f)	38.4 ± 9.3 ^(g)	17.0 ± 6.3 ^(g)
32	Indan	13.9 ± 1.3	12.8 ± 0.9	11.9 ± 1.1	7.2 ± 2.1	7.0 ± 1.2
33	p-Cresol	40.2 ± 4.0	37.6 ± 2.7	34.8 ± 3.6	23.5 ± 3.8	10.7 ± 1.9
35	m- & p-Cresol, C ₁ -Indan	99.7 ± 7.9	97.1 ± 3.4	90.2 ± 7.6	62.5 ± 9.5	43.6 ± 10.4
38	C ₁ -Indan	47.4 ± 6.8	47.6 ± 1.6	44.9 ± 2.6	18.0 ± 3.5	18.9 ± 2.7
39	C ₁ -Indan	44.4 ± 3.4	42.0 ± 2.2	40.9 ± 2.6	34.7 ± 5.4	21.5 ± 6.1
41	Tetralin	75.0 ± 5.2	74.8 ± 2.2	69.9 ± 5.0	50.2 ± 6.5	34.7 ± 5.2
43	Naphthalene	70.5 ± 10.6	71.6 ± 2.3	67.8 ± 3.5	60.2 ± 8.0	41.8 ± 8.7
48	C ₁ -Tetralin	13.3 ± 0.8	12.9 ± 0.4	12.4 ± 1.0	13.5 ± 2.8	7.6 ± 1.7
54	C ₂ -Indan	86.5 ± 5.8	87.5 ± 3.3	83.3 ± 5.6	40.9 ± 5.9	47.9 ± 4.8
56	2-Methylnaphthalene	148.4 ± 16.3	143.8 ± 13.6	137.9 ± 14.2	157.3 ± 26.5	106.3 ± 19.2
57	1-Methylnaphthalene	26.7 ± 1.5	26.4 ± 0.8	25.4 ± 1.9	18.5 ± 3.0	16.1 ± 2.9
58	C ₂ -Indan	34.5 ± 2.0	33.9 ± 1.0	32.3 ± 2.3	12.4 ± 5.6	9.5 ± 1.2
60	Indanol	24.8 ± 1.5	24.2 ± 0.7	22.5 ± 3.4	9.8 ± 3.6	10.4 ± 2.2
61	C ₂ -Tetralin	22.0 ± 1.4	21.9 ± 1.0	20.7 ± 1.6	ND ^(h)	ND
62	C ₄ -Phenol	14.6 ± 1.2	14.5 ± 2.0	13.4 ± 1.5	ND	9.8 ± 1.4
64	Biphenyl	31.9 ± 2.1	32.4 ± 3.6	31.0 ± 3.4	28.5 ± 3.8	23.7 ± 4.2
65	C ₂ -Naphthalene	53.4 ± 3.9	53.5 ± 3.2	49.8 ± 4.2	31.8 ± 4.0	27.9 ± 2.7
68	C ₂ -Naphthalene, Diphenylether	124.2 ± 12.5	121.9 ± 12.1	109.6 ± 10.7	94.5 ± 12.3	78.4 ± 9.1
69	Acenaphthene	17.7 ± 3.4	17.9 ± 0.6	17.4 ± 1.1	14.5 ± 1.9	13.5 ± 2.2
70	C ₃ -Naphthalene	27.6 ± 1.5	27.2 ± 0.6	26.3 ± 1.3	20.2 ± 2.6	22.6 ± 4.8
71	C ₃ -Naphthalene	19.8 ± 1.1	19.4 ± 0.5	19.1 ± 1.0	18.9 ± 2.5	19.2 ± 3.0
74	Fluorene	14.5 ± 0.8	14.3 ± 0.3	13.8 ± 0.7	13.4 ± 2.1	12.7 ± 1.9
75	C ₁ -Acenaphthene, C ₂ -Biphenyl	14.1 ± 0.9	13.7 ± 0.9	13.7 ± 0.7	ND	10.2 ± 1.4
77	C ₄ -Naphthalene	21.5 ± 1.1	21.2 ± 0.3	21.2 ± 1.2	20.4 ± 4.5	23.6 ± 3.0
85	Phenanthrene	39.7 ± 1.4	40.1 ± 1.0	39.8 ± 1.2	51.5 ± 12.0	40.9 ± 5.0
97	Pyrene	10.7 ± 1.7	11.6 ± 1.5	12.1 ± 0.8	32.1 ± 12.0	11.4 ± 3.9

^(a) Based on 0.40 mg/mL n-Nonadecane ISTD, 1:101 dilution, based on the integration of peak areas.

^(b) Numbers refer to peaks in Figure 3.9, Results and Discussion Section.

^(c) Identified by GC/MS.

^(d) Based on 25 GC runs.

^(e) Based on 24 GC runs.

^(f) Based on 48 GC runs.

^(g) Based on 72 GC runs.

^(h) No data collected.

TABLE 7.21. Chromatographic Results for SRC-II Fuel Oil Blend Sample 3317-079-25 Stored at 100°C, in the Dark, Under an Air Atmosphere

Peak No. (b)	Compound(s)	Normalized Percent to N-Nonadecane Internal Standard(a)						
		T = 0	T = 1 week	T = 2 weeks	T = 4 weeks	T = 8 weeks	T = 16 weeks	T = 32 weeks(g)
26	C ₆ -Benzene	1.1 ± 0.2(d)	2.1 ± 0.4(d)	1.6 ± 0.6(d)	1.0 ± 0.9(d)	0.0 ± --(d)	0.2 ± 1.0(e)	0.0 ± --(d)
27	C ₃ -Benzene	1.1 ± 0.4	4.2 ± 0.7	3.8 ± 0.8	2.5 ± 1.3	1.5 ± 1.6	1.8 ± 1.8	0.0 ± --
28	Phenol	40.2 ± 3.8	40.4 ± 3.2	38.7 ± 3.2	28.7 ± 6.7	21.0 ± 8.4	20.1 ± 10.8	1.6 ± 0.2
32	Indan	9.6 ± 2.1	8.7 ± 1.0	8.6 ± 0.9	6.3 ± 1.8	4.3 ± 2.3	4.8 ± 3.3	0.2 ± 0.1
33	o-Cresol	22.0 ± 1.3	21.0 ± 1.5	20.0 ± 2.1	15.7 ± 2.9	11.7 ± 3.3	12.8 ± 5.6	1.6 ± 0.1
35	m- & p-Cresol, C ₁ -Indan	77.3 ± 5.7	76.7 ± 4.6	75.5 ± 7.7	70.8 ± 10.9	50.7 ± 9.2	46.9 ± 13.3	5.4 ± 3.9
38	C ₁ -Indan	10.5 ± 0.6	10.3 ± 0.6	10.3 ± 0.5	8.5 ± 1.2	6.6 ± 1.3	7.7 ± 2.3	1.1 ± 0.1
39	C ₁ -Indan	11.2 ± 0.5	15.1 ± 2.8	11.6 ± 0.5	8.9 ± 1.1	7.0 ± 1.3	8.3 ± 2.1	0.7 ± 0.5
41	Tetralin	53.0 ± 3.2	55.9 ± 3.0	54.5 ± 5.8	38.4 ± 4.8	36.1 ± 6.0	32.6 ± 8.2	3.0 ± 2.9
43	Naphthalene	80.0 ± 5.3	78.3 ± 3.7	77.7 ± 2.8	60.0 ± 5.0	52.0 ± 3.7	52.5 ± 7.3	4.6 ± 5.5
44	C ₂ -Phenol	39.9 ± 2.3	34.9 ± 3.4	38.4 ± 2.0	36.0 ± 4.5	27.8 ± 2.9	39.2 ± 10.0	4.3 ± 1.7
48	C ₁ -Tetralin	9.9 ± 0.6	10.1 ± 0.6	10.4 ± 0.4	8.9 ± 0.8	7.5 ± 0.4	11.2 ± 1.9	1.2 ± 0.9
50	C ₁ dihydronaphthalene	11.1 ± 0.8	11.5 ± 1.5	11.7 ± 0.6	10.3 ± 1.2	10.6 ± 0.4	7.7 ± 2.7	1.7 ± 0.9
53	C ₂ -Indan	11.4 ± 1.1	10.8 ± 0.7	10.9 ± 1.4	8.9 ± 0.8	7.1 ± 0.8	ND(f)	0.6 ± 0.3
54	C ₂ -Indan	31.1 ± 1.7	30.9 ± 1.8	31.9 ± 1.4	27.6 ± 2.2	23.3 ± 1.2	27.6 ± 4.0	3.7 ± 5.3
55	C ₂ -Indan	37.8 ± 5.0	37.6 ± 2.5	38.9 ± 1.3	33.1 ± 2.7	22.6 ± 2.3	31.7 ± 6.9	4.6 ± 2.8
56	Methylnaphthalene	97.9 ± 5.8	98.0 ± 4.6	104.5 ± 4.2	91.4 ± 6.2	80.7 ± 2.1	96.0 ± 8.7	14.0 ± 10.3
57	1-Methylnaphthalene	21.0 ± 1.3	19.2 ± 1.4	20.0 ± 1.0	18.3 ± 1.4	17.5 ± 1.4	19.3 ± 1.7	3.4 ± 1.9
59	C ₃ -indan	19.0 ± 1.1	19.4 ± 1.1	19.8 ± 2.3	14.4 ± 1.8	10.3 ± 1.0	12.5 ± 4.2	2.2 ± 0.9
60	Indanol	20.9 ± 1.4	14.9 ± 2.1	17.1 ± 2.2	14.4 ± 1.7	10.6 ± 1.5	8.3 ± 3.0	1.2 ± 0.7
61	C ₄ -Phenol	13.8 ± 0.8	18.1 ± 3.7	14.4 ± 0.7	11.6 ± 1.0	9.4 ± 0.7	10.7 ± 1.4	1.4 ± 0.9
62	C ₄ -Phenol, C ₃ -Indan	11.6 ± 0.4	14.4 ± 2.3	10.5 ± 0.7	8.5 ± 0.7	7.7 ± 0.8	7.3 ± 2.0	0.9 ± 0.7
64	Biphenyl	28.4 ± 1.6	29.3 ± 2.7	29.8 ± 1.1	26.4 ± 1.8	24.7 ± 1.4	35.0 ± 3.8	8.3 ± 2.9
65	C ₂ -Naphthalene	40.6 ± 4.4	41.8 ± 3.5	43.6 ± 2.3	31.2 ± 3.4	28.5 ± 1.0	32.8 ± 3.1	5.5 ± 4.1
66	C ₂ -Naphthalene	37.8 ± 3.5	42.6 ± 3.1	44.4 ± 2.3	39.2 ± 3.2	33.2 ± 1.4	44.8 ± 4.0	7.6 ± 5.1
68	C ₂ -Naphthalene, Diphenylether	43.6 ± 2.2	44.1 ± 2.0	45.8 ± 1.8	43.1 ± 2.7	41.3 ± 1.9	44.9 ± 3.5	9.4 ± 6.5
69	Acenaphthene	13.4 ± 1.9	16.5 ± 2.9	13.9 ± 3.2	15.4 ± 0.9	11.1 ± 1.0	14.4 ± 2.0	2.9 ± 1.7
70	C ₃ -Naphthalene	17.1 ± 1.4	18.8 ± 2.2	18.3 ± 0.8	16.8 ± 0.9	16.1 ± 0.8	17.0 ± 1.2	4.2 ± 2.5
71	C ₃ -Naphthalene	13.3 ± 1.0	14.1 ± 1.0	14.1 ± 0.9	12.6 ± 0.7	12.1 ± 0.8	12.0 ± 1.5	3.3 ± 1.7
72	Dibenzofuran	16.4 ± 1.5	16.4 ± 3.7	17.5 ± 2.1	16.4 ± 1.4	15.4 ± 2.0	12.2 ± 2.0	4.0 ± 1.9
73	Isopropylnaphthalene	10.0 ± 0.8	10.3 ± 1.5	10.2 ± 0.9	9.5 ± 0.6	8.7 ± 0.7	9.1 ± 0.9	1.7 ± 1.0
74	Fluorene	11.8 ± 0.6	12.0 ± 1.5	11.8 ± 0.7	10.0 ± 1.0	9.9 ± 0.6	9.8 ± 1.0	2.4 ± 0.8
75	C ₁ -Acenaphthene, C ₂ -Biphenyl	8.8 ± 1.0	9.2 ± 0.9	8.9 ± 1.0	7.9 ± 1.1	8.2 ± 0.7	9.6 ± 0.9	3.1 ± 1.1
77	C ₄ -Naphthalene	9.9 ± 1.9	11.2 ± 0.5	11.4 ± 0.5	11.3 ± 0.7	10.0 ± 0.2	11.8 ± 0.7	6.4 ± 2.7
81	C ₁ -Fluorene	7.7 ± 0.5	7.8 ± 0.7	8.2 ± 0.3	7.0 ± 0.3	7.7 ± 0.3	7.2 ± 0.6	2.7 ± 0.5
85	Phenanthrene	35.9 ± 2.0	37.2 ± 1.3	37.8 ± 1.5	34.1 ± 2.0	39.5 ± 2.3	39.0 ± 3.1	23.1 ± 5.3
96	Fluoranthene	7.8 ± 0.5	8.0 ± 0.9	8.9 ± 0.4	7.5 ± 0.4	9.7 ± 0.8	8.8 ± 0.8	5.9 ± 2.3
97	Pyrene	15.0 ± 0.5	15.0 ± 1.3	15.4 ± 2.1	13.3 ± 0.8	17.8 ± 1.3	16.1 ± 1.8	10.9 ± 4.0

(d) Based on 0.40 µg/mL n-Nonadecane ISID, 1:126 dilution, based on the integration of peak heights.

(b) Numbers refer to peaks in Figure 3.10, Results and Discussion Section.

(c) Identified by GC/MS.

(d) Based on 24 GC runs.

(e) Based on 36 GC runs.

(f) No data collected.

(g) Volatility effects were too large to use 32 week data for chemical compositional changes.

TABLE 7.22. Chromatographic Results for SRC-II Fuel Oil Blend Samples Stored at -20°C, in the Dark, Under a Nitrogen Atmosphere for Three Years Diluted in Methylene Chloride

Peak No. (a)	Compound (b)	Normalized Percent to n-Tridecane ISTD			
		FOB 3317-79-23 (c)	FOB 3317-79-24 (d)	FOB 3317-79-25 (e)	FOB 3317-79-26 (f)
28	Phenol	28.6 ± 0.6	31.1 ± 0.9	40.4 ± 3.2	28.8 ± 1.2
30	C ₃ -Benzene	13.3 ± 0.2	11.2 ± 0.1	ND (f)	9.7 ± 0.1
32	Indan	11.4 ± 0.3	8.3 ± 0.1	14.0 ± 0.8	8.2 ± 0.1
33	<i>o</i> -Cresol	22.3 ± 0.5	23.0 ± 0.2	26.8 ± 1.1	22.2 ± 0.5
35	<i>m</i> & <i>p</i> -Cresol, C ₁ -Indan	50.0 ± 0.4	49.2 ± 0.5	44.8 ± 1.9	45.4 ± 0.7
38	C ₁ -Indan	11.7 ± 0.3	10.0 ± 0.1	13.1 ± 0.5	10.1 ± 0.1
39	C ₁ -Indan	19.5 ± 0.2	17.7 ± 0.3	21.5 ± 0.6	18.3 ± 0.1
40	C ₂ -Phenol	13.7 ± 0.2	12.3 ± 0.2	19.3 ± -- (h)	14.4 ± 0.1
41	Tetralin	48.8 ± 0.3	39.5 ± 0.5	44.6 ± 4.3	39.9 ± 0.1
42	C ₂ -Phenol	13.7 ± 0.1	12.5 ± 0.2	ND	14.2 ± 0.1
43	Naphthalene	100.2 ± 0.7	93.9 ± 1.1	87.6 ± 2.6	95.4 ± 0.4
48	C ₁ -Tetralin	12.2 ± 0.2	11.3 ± 0.1	15.3 ± 0.2	11.3 ± 0.1
54	C ₂ -Indan	32.4 ± 0.3	30.4 ± 0.3	33.8 ± 0.9	30.1 ± 0.2
55	C ₂ -Indan	26.2 ± 0.3	25.5 ± 0.2	25.7 ± 0.6	26.8 ± 0.1
56	2-Methylnaphthalene	95.7 ± 0.7	91.5 ± 0.9	80.2 ± 1.3	86.4 ± 0.1
57	1-Methylnaphthalene	20.6 ± 0.2	20.2 ± 0.3	27.7 ± 2.6	20.9 ± 0.1
59	C ₃ -Indan	13.2 ± 0.2	12.4 ± 0.5	16.4 ± 1.6	13.9 ± 0.1
60	Indanol	14.6 ± 0.1	13.7 ± 0.2	13.6 ± --	14.9 ± 0.1
61	C ₂ -Tetralin	21.9 ± 0.3	22.2 ± 0.3	24.3 ± 0.5	24.4 ± 1.2
62	C ₄ -Phenol				
63	C ₄ -Phenol, C ₃ -Indan	11.4 ± 0.1	11.3 ± 0.1	16.6 ± 3.4	13.3 ± 0.2
64	Biphenyl	29.8 ± 0.3	29.1 ± 0.3	32.5 ± 2.3	30.4 ± 0.1
65	C ₂ -Naphthalene	34.0 ± 0.2	33.0 ± 0.3	38.6 ± 2.3	34.6 ± 0.3
66	C ₂ -Naphthalene	28.3 ± 0.2	27.5 ± 0.3	34.4 ± 1.1	29.0 ± 0.4
68	C ₂ -Naphthalene, Diphenylether	53.6 ± 0.1	52.0 ± 0.7	54.6 ± 2.1	52.6 ± 0.2
69	Acenaphthene	15.0 ± 0.1	14.8 ± 0.1	18.4 ± 1.9	15.4 ± 0.1
70	C ₃ -Naphthalene	16.1 ± 0.1	16.0 ± 0.2	20.2 ± 1.8	16.8 ± 0.1
71	C ₃ -Naphthalene	14.8 ± 0.1	14.6 ± 0.1	18.6 ± 1.8	15.4 ± 0.2
74	Fluorene	11.9 ± 0.1	11.8 ± 0.1	18.1 ± 2.3	13.4 ± 0.3
75	C ₁ -Acenaphthene, C ₂ -Biphenyl	10.4 ± 0.1	10.4 ± 0.1	14.5 ± 2.0	11.2 ± 0.1
77	C ₄ -Naphthalene	11.9 ± 0.1	11.8 ± 0.1	15.7 ± 1.3	12.9 ± 0.1
85	Phenanthrene	30.1 ± 0.2	31.4 ± 0.3	40.0 ± 0.8	35.0 ± 0.4
97	Pyrene	13.6 ± 0.4	14.0 ± 0.2	18.7 ± 2.7	16.1 ± 0.1

(a) Numbers refer to peaks in Figure 3.4, Results and Discussion section.

(b) Identified by GC/MS.

(c) Based on 4.0 mg/mL ISTD, 1:10 dilution in methylene chloride, 3 determinations, compare to Table 7.8 for time = 0 results.

(d) Based on 2.5 mg/mL ISTD, 1:20 dilution in methylene chloride, 3 determinations, compared to Table 7.9 for time = 0 results.

(e) Based on 2.5 mg/mL ISTD, 1:20 dilution in methylene chloride, 3 determinations, compare to Table 7.10 for time = 0 results.

(f) No data received.

(g) Based on 2.2 mg/mL ISTD, 1:20 dilution in methylene chloride, 3 determinations, compare to Table 7.11 for time = 0 results.

(h) Value from one determination only.

8.0 APPENDIX II

PLOTS AND F VALUES FROM STATISTICAL ANALYSIS OF CHROMATOGRAPHIC DATA

The plots and tables on the following pages present results of ANOVA techniques applied to the chromatographic data. Figure 8.1 and Table 8.1 present the log transformed results and F values from the SRC-II naphtha samples stored in the repository. Figure 8.2 and Table 8.2 present the results from the SRC-I light oil samples stored in the repository. Figures 8.3 and 8.4 and Tables 8.3 and 8.4 present the results from the SRC-II middle and heavy distillates, respectively. Figures 8.5 and 8.6 and Tables 8.5 and 8.6 present the results from the SRC-I wash solvent and process solvents stored in the repository, respectively. The data for the SRC-II FOB is in the text of the status report.

The data from the studies at -20°C and 20°C under various parameters of light versus darkness, air versus nitrogen atmosphere, and diluted in methylene chloride versus undiluted are given in the text of the status report.

Figure 8.7 and Table 8.7 present the log transformed results and F values from the chromatographic data acquired from the accelerated study of an SRC-II FOB stored at 100°C under an air atmosphere. The results from the 60°C study are in the text.

FIGURE 8.1. Log Transformed Data from Chromatographic Results for SRC-II Naphtha Samples Stored in the Repository. Data points after two years are offset by 0.3 peak units

TABLE 8.1. F Values from the ANOVA Techniques Applied to the SRC-II Naphtha Chromatographic Data After Storage in the Repository for Two Years

<u>Peak^(a)</u>	<u>Calculated F Value^(b)</u>	<u>Critical F Value (5% α Level)</u>
1	3.30	4.54 ^(d)
2	2.81	4.54
3	3.13	4.54
4	11.72	18.51 ^(e)
5	2.21	18.51
6	4.40	18.51
7	0.82	18.51
8	18.50	18.51
9	0.36	18.51
10	ND ^(c)	
11	ND	
12	40.27	18.51
13	72.52	18.51
14	49.08	18.51
15	68.14	18.51
16	46.80	18.51
18	ND	
19	ND	
20	106.1	18.51
21	39.96	18.51
22	37.01	18.51
23	41.09	18.51
24	14.77	18.51
25	17.80	18.51
26	4.42	4.54
27	1.96	4.54
28	5.81	4.54

(a) Peaks refer to compounds identified by GC/MS contained in Table 3.1 and shown in Figure 3.1.

(b) Values greater than the 5% α level were considered chromatographic differences caused by the split injection. Therefore, no conclusions were made regarding decomposition of these compounds.

(c) No data.

(d) Based on calculated statistical error.

(e) Based on 20% error.

FIGURE 8.2. Log Transformed Data from Chromatographic Results for SRC-I Light Oil Samples Stored in the Repository. Data points after two years are offset by 0.3 peak units

TABLE 8.2. F Values from the ANOVA Techniques Applied to the SRC-I Light Oil Chromatographic Data After Storage in the Repository for Two Years

Peak(a)	Calculated F Value(b)	Critical F Value (5% α Level)
1	1.06	18.51 ^(d)
2	1.64	18.51
3	5.72	18.51
4	3.84	18.51
5	12.48	18.51
6	5.75	18.51
7	10.33	18.51
8	1.95	18.51
9	3.00	18.51
10	ND ^(c)	
11	ND	
12	ND	
13	13.93	18.51
14	7.68	18.51
15	12.32	18.51
16	13.24	18.51
17	ND	
18	ND	
19	ND	
20	29.69	18.51
21	9.79	18.51
22	11.28	18.51
23	22.43	18.51
24	4.83	18.51
25	6.25	18.51
26	4.30	18.51
27	6.95	18.51
28	4.20	18.51
29	4.23	18.51
30	4.56	18.51
31	2.02	18.51
32	45.28	18.51
33	ND	

(a) Peaks refer to compounds identified by GC/MS contained in Table 3.1 and shown in Figure 3.2.

(b) Values greater than the 5% α level were considered chromatographic differences caused by the split injection. No value was greater than the 1% α value of 98.49.

(c) No data.

(d) Based on 20% error.

FIGURE 8.3. Log Transformed Data from Chromatographic Results for SRC-II Middle Distillate Samples Stored in the Repository. Data points after two years are offset by 0.3 peak units

TABLE 8.3. F Values from the ANOVA Techniques Applied to the SRC-II Middle Distillate Chromatographic Data After Storage in the Repository for Two Years

Peak(a)	Calculated F Value	Critical F Value (5% α Level)
28	4.11	4.11(b)
30	2.10	4.11
32	5.60(c)	4.11
33	6.03(c)	4.11
35	1.70	4.11
38	3.31	4.11
39	6.22(c)	4.11
40	0.00	4.11
41	2.83	4.11
42	ND(d)	
43	0.03	4.11
54	0.09	4.11
55	1.48	4.11
56	1.04	4.11
57	11.07(e)	4.11
59	2.16	4.11
60	7.14(e)	4.11
61,62	1.04	4.11
65	2.65	4.11
66	5.98(e)	4.11
70	6.44(e)	4.11
71	13.67	18.51(f)
77	9.31(e)	4.11

- (a) Peaks refer to compounds identified by GC/MS contained in Table 3.1 and shown in Figure 3.3.
- (b) Based on calculated statistical error.
- (c) Data among 4 replicates did not show consistent degradation, see Tables 7.4 - 7.7 in Appendix I.
- (d) No data.
- (e) Peaks showed increase in concentration, not degradation.
- (f) Based on 20% error.

FIGURE 8.4. Log Transformed Data from Chromatographic Results for SRC-II Heavy Distillate Samples Stored in the Repository. Data points after two years are offset by 0.3 peak units

TABLE 8.4. F Values from the ANOVA Techniques Applied to the SRC-11 Heavy Distillate Chromatographic Data After Storage in the Repository for Two Years

Peak (a)	Calculated F Value	Critical F Value (5% α Level)
74	6.27 ^(b)	4.22 ^(e)
75	11.66 ^(b)	4.22
77	1.09	4.22
78	5.84 ^(b)	4.22
79	5.68 ^(b)	4.22
80	0.04	4.22
81	1.69	4.22
82	2.69	4.22
83	0.47	4.22
84	12.33	18.51 ^(f)
85	0.58	4.22
86	2.10	4.22
87	9.76 ^(c)	4.22
88	0.47	4.22
89	0.00	4.22
90	0.17	4.22
91	0.94	4.22
92	7.75 ^(c)	4.22
93	3.42	4.22
94	13.92 ^(c)	4.22
95	0.00	4.22
96	0.36	4.22
97	19.81	18.51
98	0.21	4.22
99	0.94	4.22
100	11.61 ^(c)	4.22
101	ND ^(d)	4.22

(a) Peaks refer to compounds identified by GC/MS contained in Table 3.1 and shown in Figure 3.6.

(b) Due to sample handling and volatility effects.

(c) Peaks showed increase in concentration, not degradation.

(d) No data.

(e) Based on calculated statistical error.

(f) Based on 20% error.

FIGURE 8.5. Log Transformed Data from Chromatographic Results for SRC-I Wash Solvent Sample Stored in the Repository. Data points after two years are offset by 0.3 peak units

TABLE 8.5. F Values from the ANOVA Techniques Applied to the SRC-I Wash Solvent Chromatographic Data After Storage in the Repository for Two Years

Peak (a)	Calculated F Value	Critical F Value (5% α Level)
23	0.004	18.51 ^(b)
24	0.006	18.51
27	0.104	18.51
28	0.011	18.51
30	4.53	18.51
32	0.822	18.51
33	0.068	18.51
34	2.42	18.51
35a	0.026	18.51
35b	0.059	18.51
36	7.03	18.51
37	0.085	18.51
38	0.255	18.51
39	0.54	18.51
41	0.15	18.51
43a	0.13	18.51
43b	0.042	18.51
44	6.48	18.51
45	0.018	18.51
46	0.19	18.51
47	6.25	18.51
48	0.21	18.51
49	12.71	18.51
50	0.66	18.51
51	1.83	18.51
52	0.18	18.51
53	1.06	18.51
54	5.23	18.51
55	1.08	18.51
56	0.001	18.51
57	0.54	18.51

(a) Peaks refer to compounds identified by GC/MS contained in Table 3.1 and shown in Figure 3.5.

(b) Based on 20% error.

FIGURE 8.6. Log Transformed Data from Chromatographic Results for SRC-I Process Solvent Samples Stored in the Repository. Data points after two years are offset by 0.3 peak units

TABLE 8.6. F Values from the ANOVA Techniques Applied to the SRC-I Process Solvent Chromatographic Data After Storage in the Repository for Two Years

Peak(a)	Calculated F Value	Critical F Value (5% α Level)
43	73.75(b)	18.51(e)
54	0.59	18.51
55	3.65	18.51
56	1.17	18.51
57	1.27	18.51
60	4.10	18.51
61,62	2.77	18.51
63	1.16	18.51
64	0.995	18.51
65	0.69	18.51
66	5.85	18.51
67	22.17(c)	18.51
68	0.618	18.51
69	5.45	18.51
70	24.67(d)	18.51
71	15.44	18.51
72	7.50	18.51
74	22.72(c)	18.51
75	10.52	18.51
76	23.62(c)	18.51
77	0.725	18.51
78	7.44	18.51
79	9.74	18.51
81	9.45	18.51
85	0.095	18.51
90	0.008	18.51
91	0.795	18.51
96	8.99	18.51
97	7.46	18.51
99	ND	

(a) Peaks refer to compounds identified by GC/MS contained in Table 3.1 and shown in Figure 3.7.

(b) Due to sample handling and volatility effects.

(c) Data among 2 replicates did not show consistent degradation, see Tables 7.16 and 7.17 in Appendix I.

(d) Peak showed an increase in concentration, not degradation.

(e) Based on 20% error.

FIGURE 8.7. Log Transformed Data from Chromatographic Results for SRC-II FOB Stored at 100°C, Under an Air Atmosphere, in the Dark. Data points for Time = 0 are offset by 0.0 peak units, 16 weeks by 0.3 peak units

TABLE 8.7. F Values from the ANOVA Techniques
Applied to the SRC-II Fuel Oil
Blend Chromatographic Data After
Storage at 100 C for 16 Weeks

Peak (a)	Calculated F Value (b)	Critical F Value (5% α Level)
24	25.5	4.0 ^(d)
27	46.1	4.0
28	76.6	4.0
32	49.4	4.0
33	59.3	4.0
35	80.2	4.0
38	37.8	4.0
39	20.6	4.0
41	117.3	4.0
43	66.75	18.51 ^(e)
44	0.90	18.51
48	2.80	18.51
50	64.50	18.51
53	ND ^(c)	
54	10.83	18.51
55	18.58	18.51
56	0.82	18.51
57	4.60	18.51
59	81.5	18.51
60	328.3	18.51
62	14.28	18.51
63	67.5	18.51
64	11.58	18.51
65	21.6	18.51
66	7.38	18.51
68	0.00	18.51
69	0.30	18.51
70	0.49	18.51
71	6.08	18.51
72	38.8	18.51
73	6.6	18.51
74	17.5	18.51
75	0.48	18.51
77	1.78	18.51
81	3.25	18.51
85	1.00	18.51
96	2.58	18.51
97	0.55	18.51

(a) Peaks refer to compounds identified by GC/MS contained in Table 3.1 and shown in Figure 3.10.

(b) Peaks, 28 (phenol), 35 (m & p-cresol), 41 (tetralin), 59 (C₃-indan), and 60 (indanol) showed the greatest degradation over time.

(c) No data.

(d) Based on calculated statistical error.

(e) Based on 20% error.

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