DOE/PC/91281--T17

Low Severity Coal Liquefaction Promoted by Cyclic Olefins

Grant No. DE-FG22-91-PC-91281

Quarterly Report
October to December 1995

Christine W. Curtis
Chemical Engineering Department
Auburn University, AL 36849

Acknowledgments

The research of Jeffrey Snelling is sincerely appreciated. The technical support of Joe Aderholdt, Henry Cobb, and Michael Hornsby is appreciated by all of us. The word processing performed by Melanie Butcher is gratefully acknowledged.

Table of Contents

High Temperature Infrared Analysis of Cyclic Olefins

Introduction

The goal of this research is to develop a methodology for analyzing the reactivity of cyclic olefins in situ in a high temperature and high pressure infrared cell. Cyclic olefins, such as 1,4,5,8-tetrahydronaphthalene (isotetralin) and 1,4,5,8,9,10-hexahydroanthracene (HHA), are highly reactive donor compounds that readily donate their hydrogen to coal and model acceptors when heated to temperatures of 200 °C and above. These donors are active donors in the low severity liquefaction of coal at 350 °C as shown in the research performed in this project. The infrared studies are being performed in a high temperature infrared cell that was obtained from AABSPEC. Modifications to that cell have been made and have been reported in previous progress reports.

During this last quarter the useful temperature range of the high temperature infrared cell was extended to 230 °C through the use of a high-boiling perfluorocarbon solvent. The solvent used was an Air Products and Chemicals Company proprietary product trade named Multifluor APF-240. Solubilities of aromatics and cyclic olefins were quite low in APF-240, usually less than 0.1 wt% at room temperature, but were found to be a strong function of temperature, increasing markedly when the mixtures were heated to 65 °C. Spectra have been obtained of n-hexadecane and naphthalene at temperatures of 65, 100, 125, 150, 175, 200 and 230 °C. This demonstration of the safe operation of the high temperature IR cell and the acquisition of spectra at elevated temperatures paves the way for kinetic studies of the hydrogen donor capability of isotetralin. A perfluoroether has been obtained from Dupont which should extend the useful temperature range of the high temperature IR cell to 350 °C.

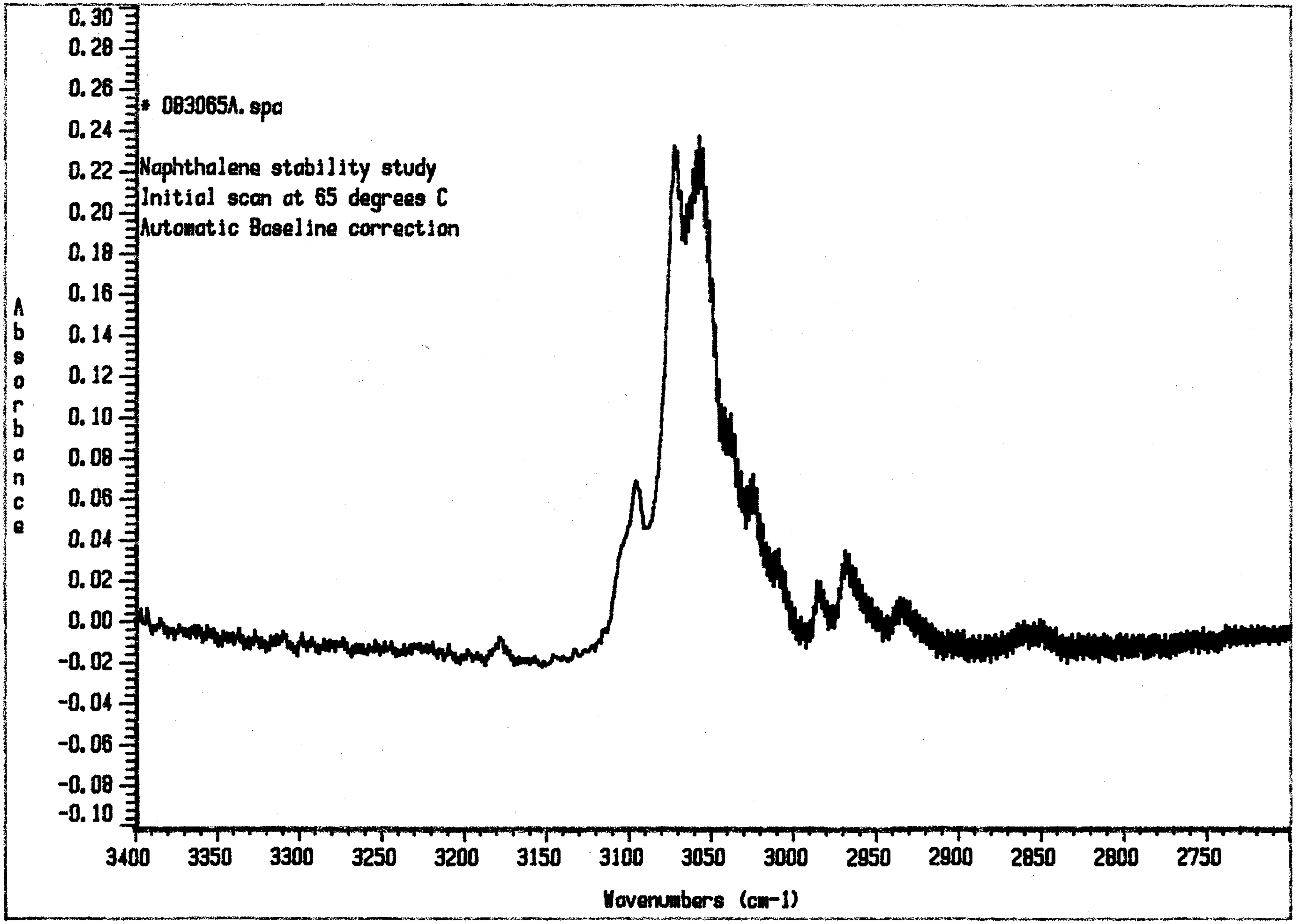
The research performed during Fall quarter 1995 focused upon evaluating the stability of naphthalene, decalin, tetralin and isotetralin at elevated temperatures in a Fourier transform infrared (FTIR) cell. Previous studies had shown that naphthalene was quite stable at temperatures up to 230 °C, but a more definitive stability study was conducted to confirm this observation. Stability studies also confirmed the non-reactivity of decalin and tetralin at elevated temperatures up to 230 °C. Preliminary investigations with isotetralin showed that isotetralin reacted at temperatures of 230 °C and lower. In order to investigate the effect of temperature on the reactivity of isotetralin, an experimental design for the stability test was devised. Naphthalene, decalin and tetralin were also subjected to the same experimental regimen.

The stability studies consisted of increasing the temperature of the samples from 65 °C to 100 °C, 150 °C, 200 °C, and finally to 230 °C, while holding the initial temperature and each intermediate temperature constant for thirty minutes. Scans were obtained before and after each step, and a scan was taken every thirty minutes at the final temperature for a period of three to four hours. Since isotetralin was reactive at 230 °C, additional studies were conducted with the final temperature being reduced to 200 °C, 150 °C and 100 °C.

Research Performed During this Quarter

Interpretation of Results. The stability studies indicated that naphthalene, decalin and tetralin are all quite stable at temperatures up to 230 °C, as indicated in Figures 1 through 6. Since the scans at the intermediate temperatures are virtually identical to the initial and final scans, only the initial scan at 65 °C and the final scan at 230 °C are presented. It should be noted that the peak height ratios for the initial scan at 65 °C are virtually identical to those for the final scan at 230 °C.

Figure 1



083065A.spa
Naphthalene stability study
Initial scan at 65 degrees C
Automatic Baseline correction
Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 2

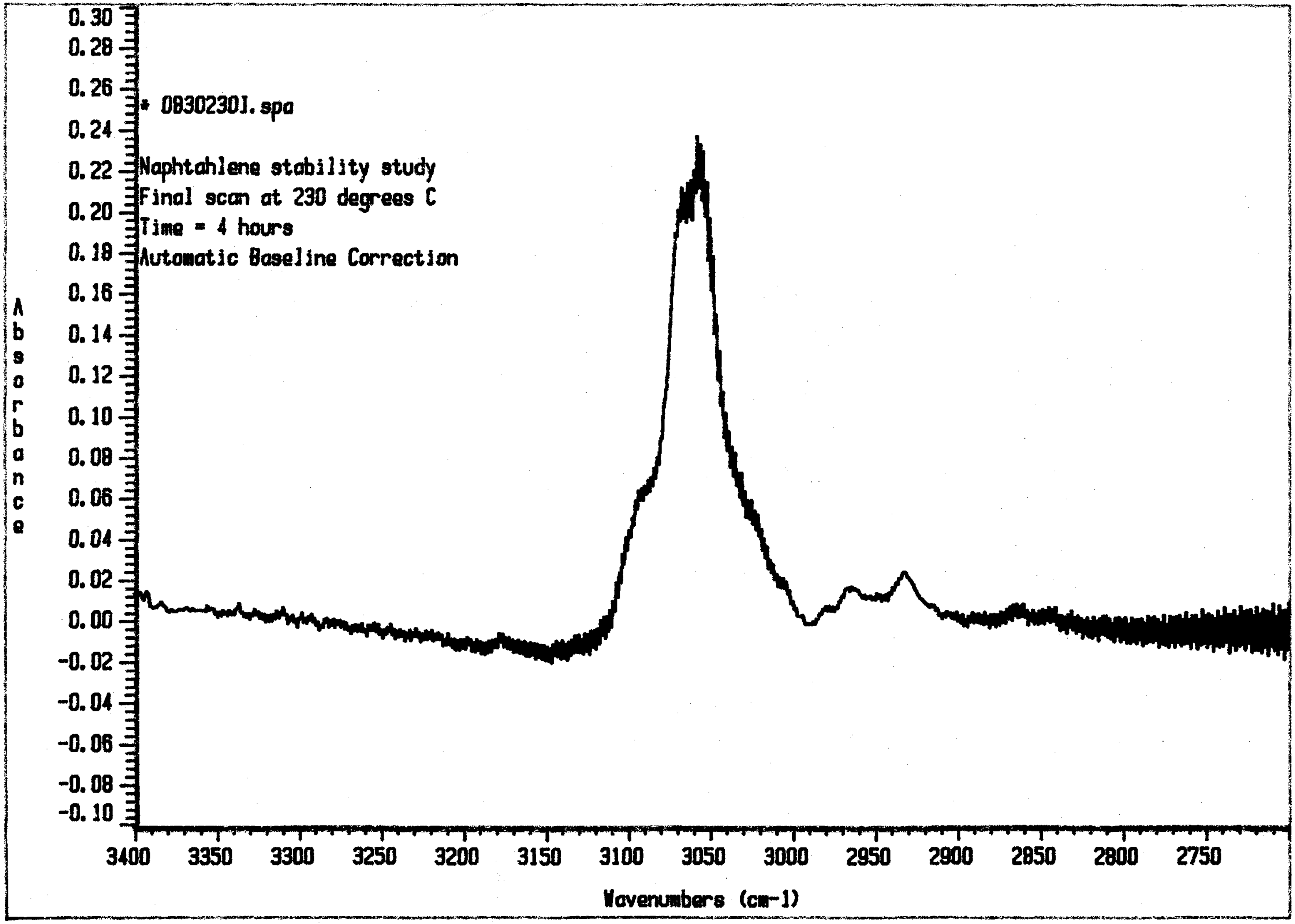
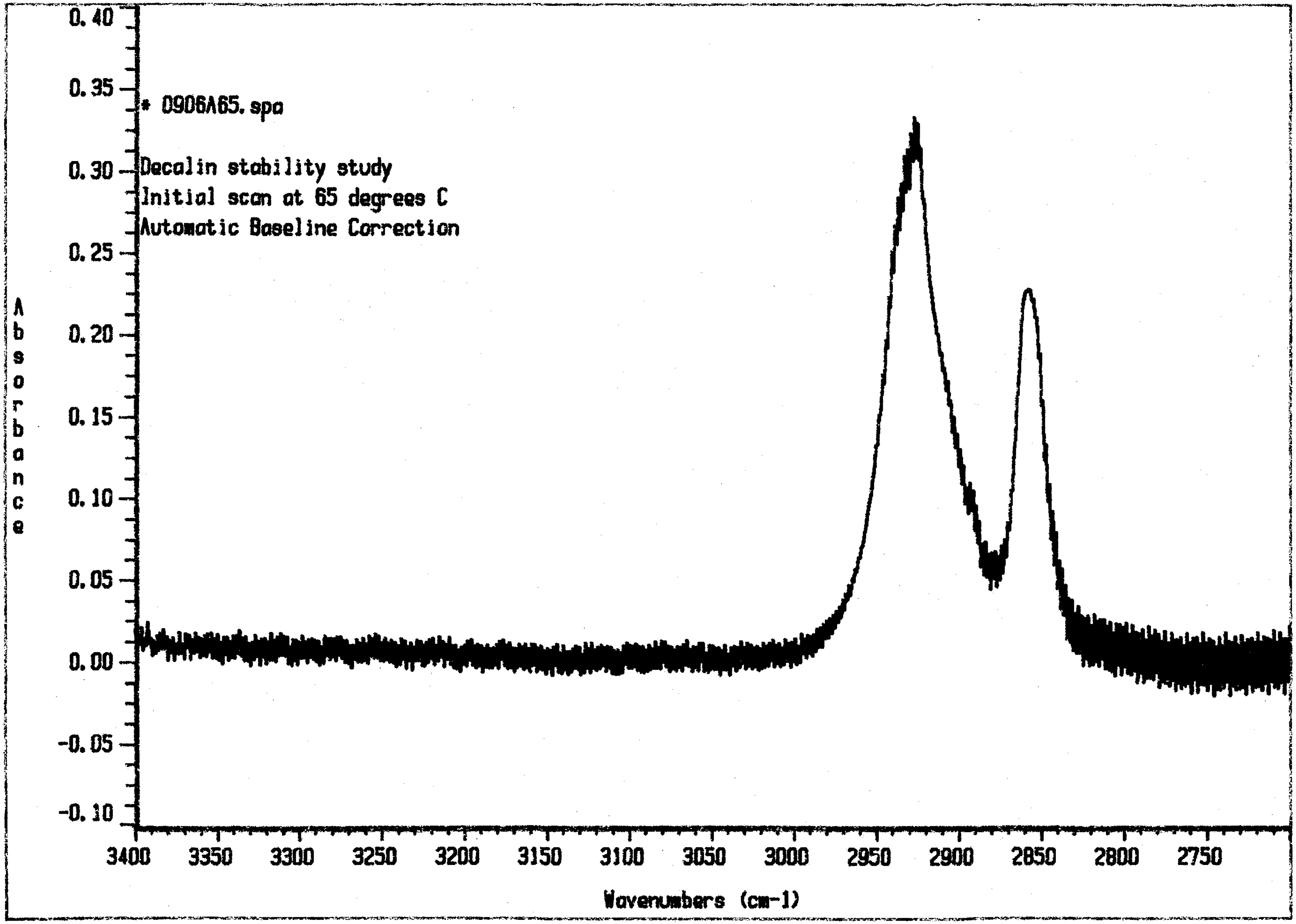

* 0830230I.spa
Naphtahlene stability study
Final scan at 230 degrees C
Time = 4 hours
Automatic Baseline Correction
Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 3



ma4.3rd.qt

Figure 4

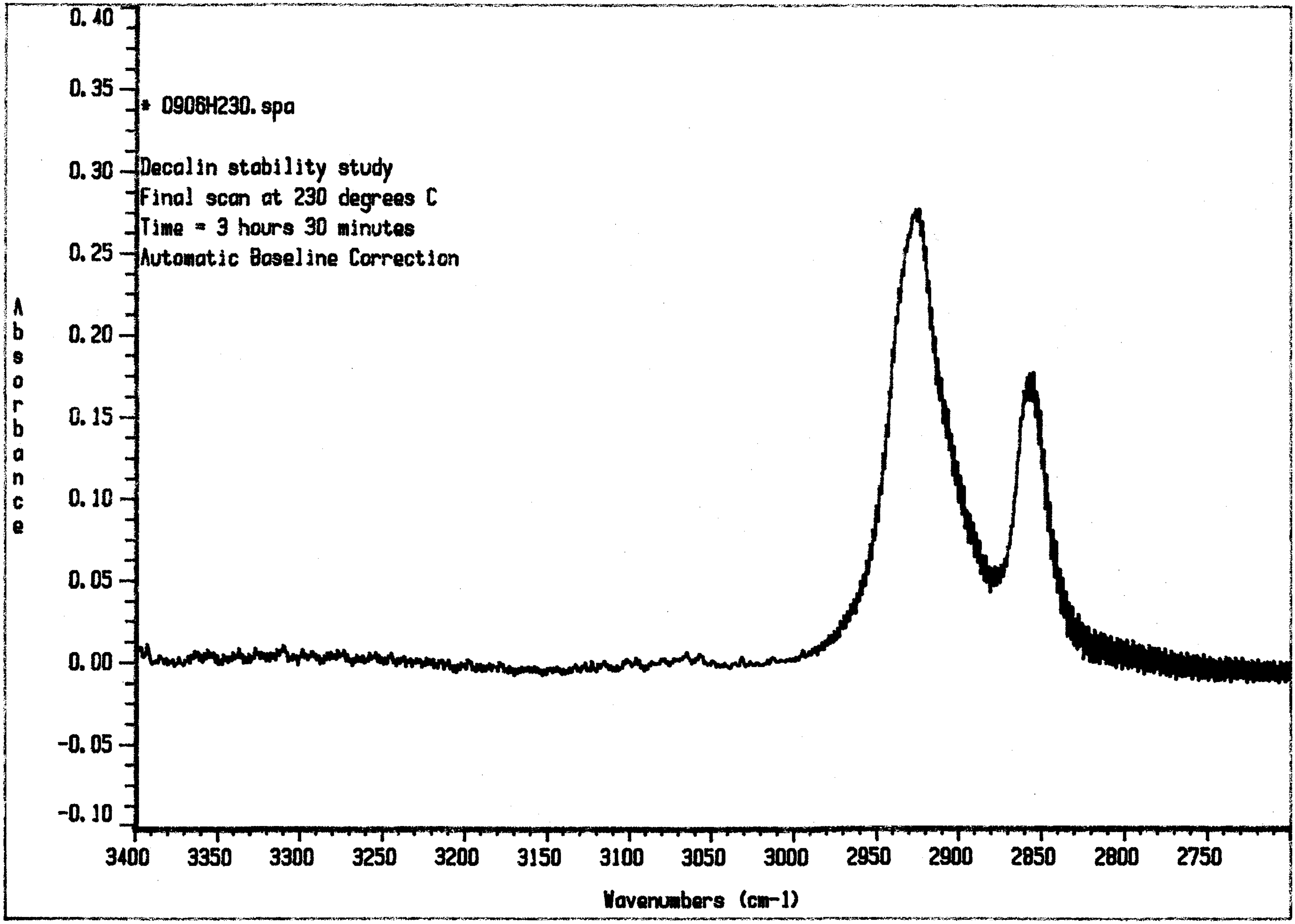

* 0906H230.spa
Decalin stability study
Final scan at 230 degrees C
Time = 3 hours 30 minutes
Automatic Baseline Correction
Absorbance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 5

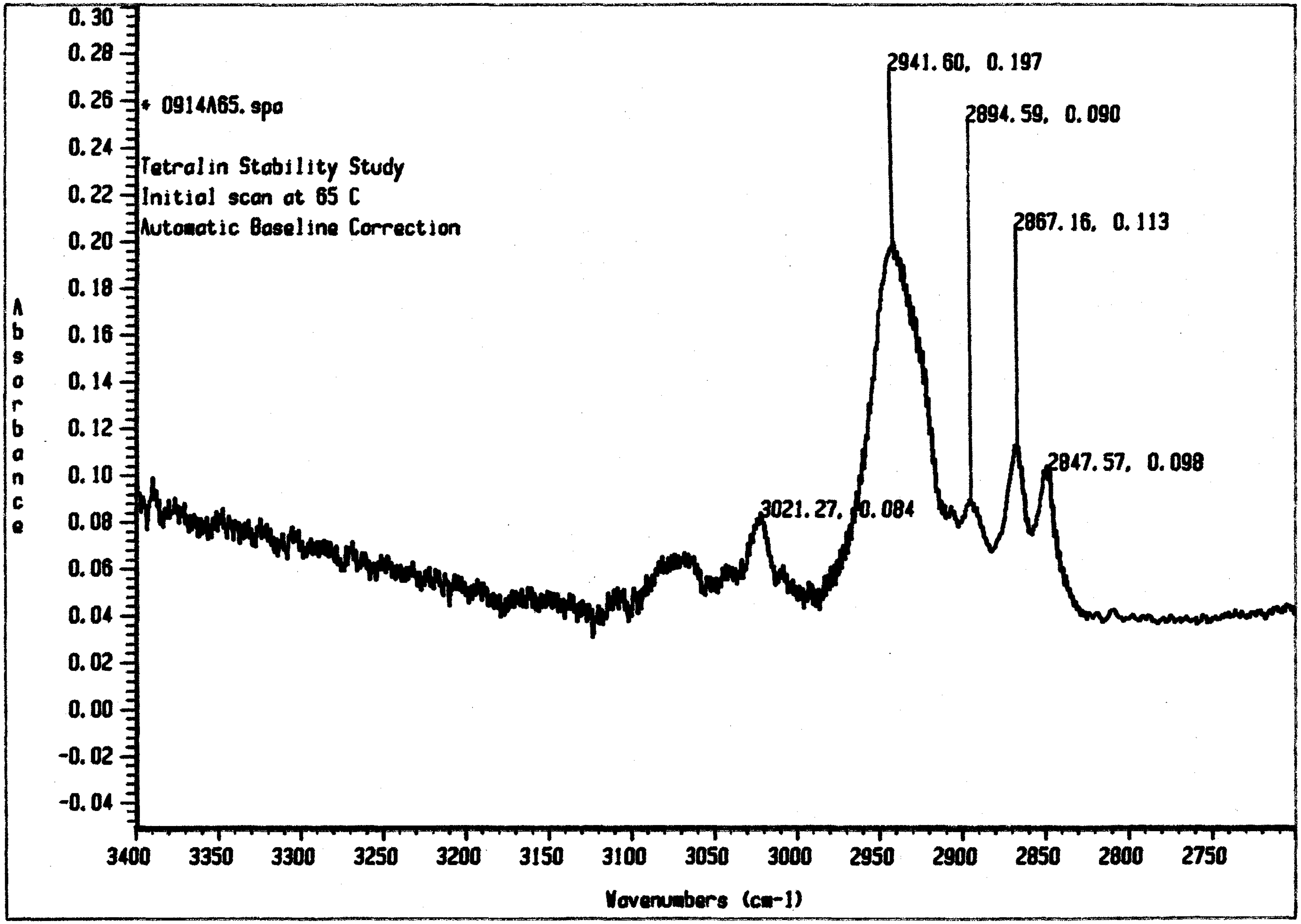
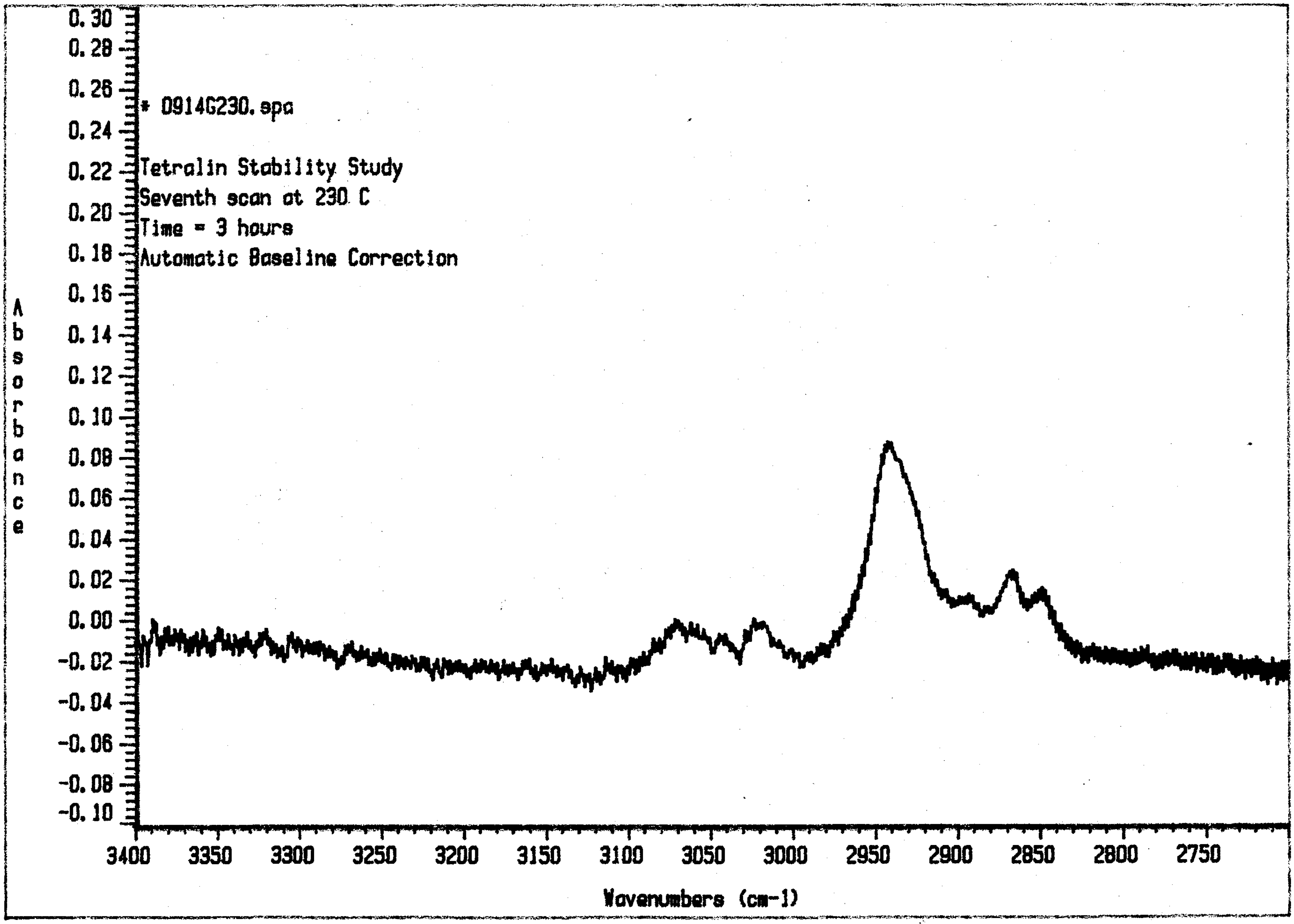

* 0914A65.spa
Tetralin Stability Study
Initial scan at 65 C
Automatic Baseline Correction
2941.60, 0.197
2894.59, 0.090
2867.16, 0.113
2847.57, 0.098
3021.27, 0.084
Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 6



* 0914G230.spa
Tetralin Stability Study
Seventh scan at 230 C
Time = 3 hours
Automatic Baseline Correction
Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Isotetralin, on the other hand, proved to be quite reactive. A detailed discussion of the reaction will necessarily involve the assignment of peak locations to definite structural features in the isotetralin molecule and its presumed products. Some of this work was accomplished this quarter with the rest being undertaken next quarter. Two of the peaks in the isotetralin spectra have been tentatively identified. The peak at 2855 cm^{-1} has been identified with a symmetrical CH_2 stretch (Silverstein[1] places the value at 2853 plus or minus 10 cm^{-1}) and the olefinic CH stretch at 3035 cm^{-1}. Generally, any C-H stretching bands above 3000 cm^{-1} result from aromatic, heteroaromatic, acetylenic, or olefinic stretching.[2] In the case of isotetralin, where these absorbance are present, they are limited to olefinic stretching.

Figures 7 through 17 present some of the spectra obtained from the isotetralin stability study. Figure 7 presents the initial scan at 65 °C. Figures 8 and 9 present the first and last scans at 230 °C, respectively. Figures 10 and 11 present the first and last scans at 200 °C, respectively. Figures 12 and 13 present the first and last scans at 150 °C, respectively. Figure 16 presents the initial scan at 65 °C and the final scan at 230 °C on the same display, to show clearly the extent of reaction that occurs at the higher reaction temperature. Figure 17 presents the last isotetralin scan at 230 °C which represent the reaction products for this study, and the scan of naphthalene on the same display. The increase in the broad peak between 3100 and 3000 cm^{-1} is suggestive of an increase in the aromaticity of the reaction products as compared to isotetralin.

Noise Reduction

Many of the spectra obtained at elevated temperatures have been plagued by considerable amounts of noise. The problem was addressed and a noticeable reduction in the noise level has been achieved. Specifically, three actions were taken. First, it was noted that background scans

Figure 7

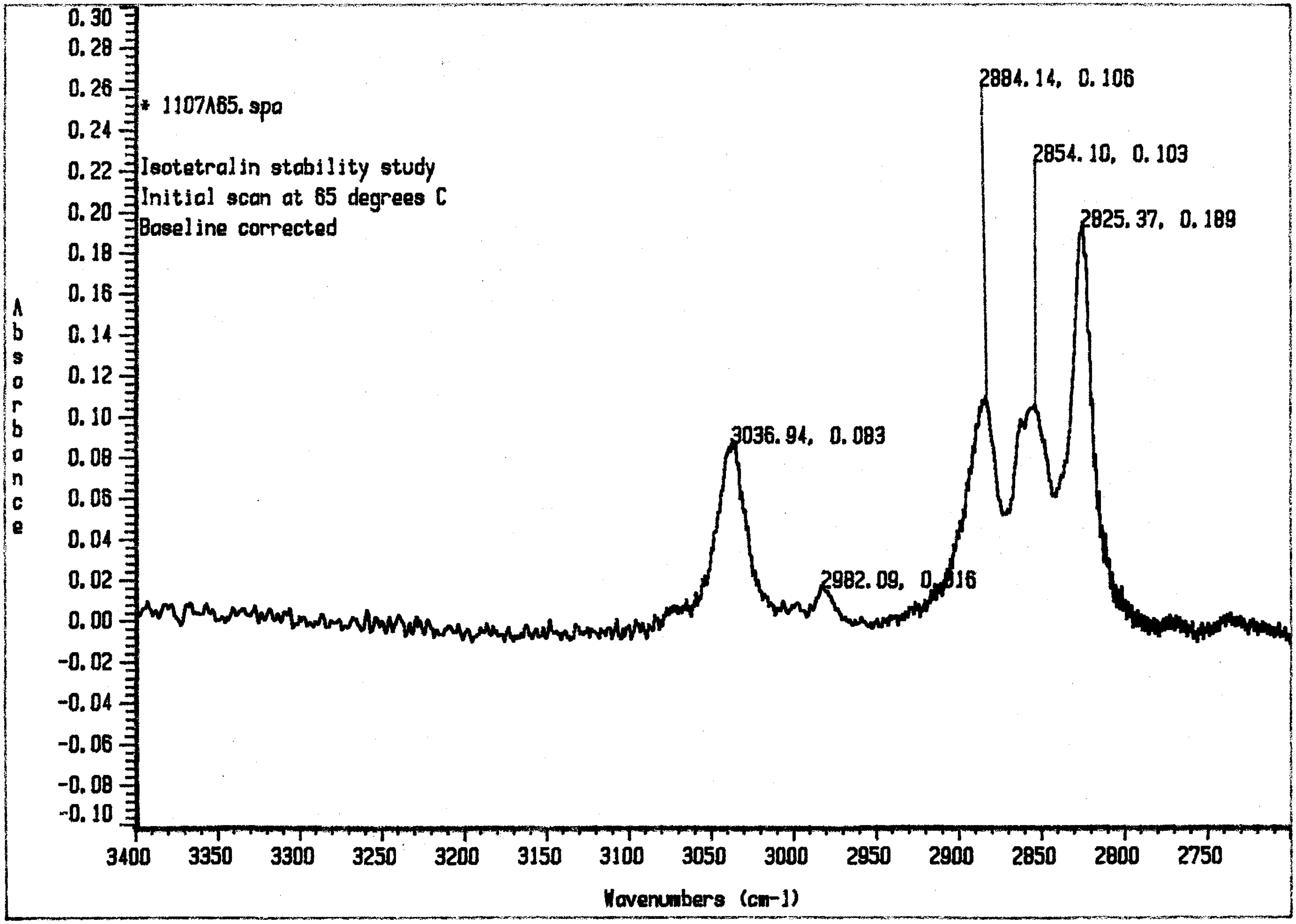
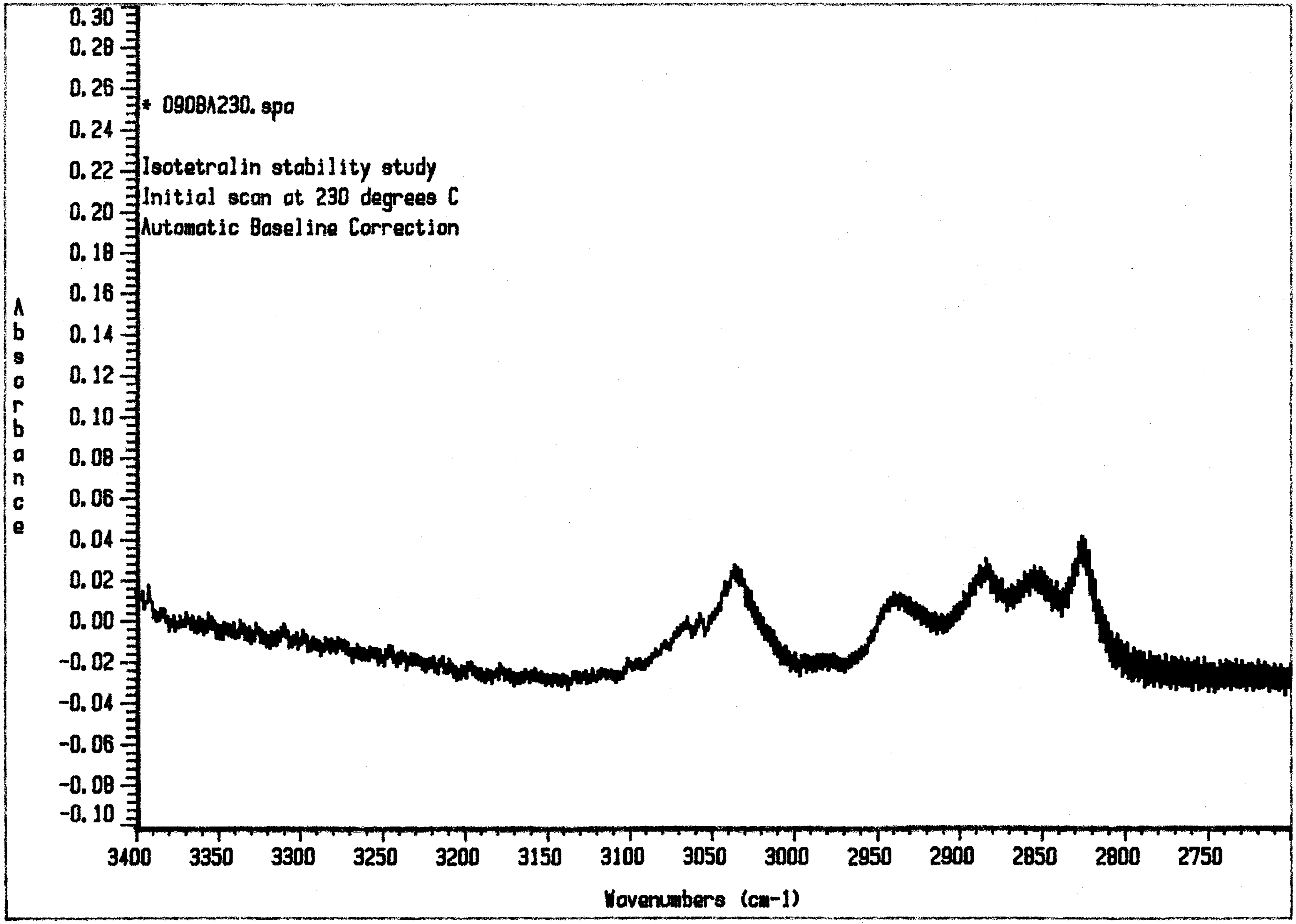

0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
Absorbance
* 1107A65.spa
Isotetralin stability study
Initial scan at 65 degrees C
Baseline corrected
2884.14, 0.106
2854.10, 0.103
2825.37, 0.189
3036.94, 0.083
2982.09, 0.016
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 8



* 0908A230.spa
Isotetralin stability study
Initial scan at 230 degrees C
Automatic Baseline Correction
Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 9

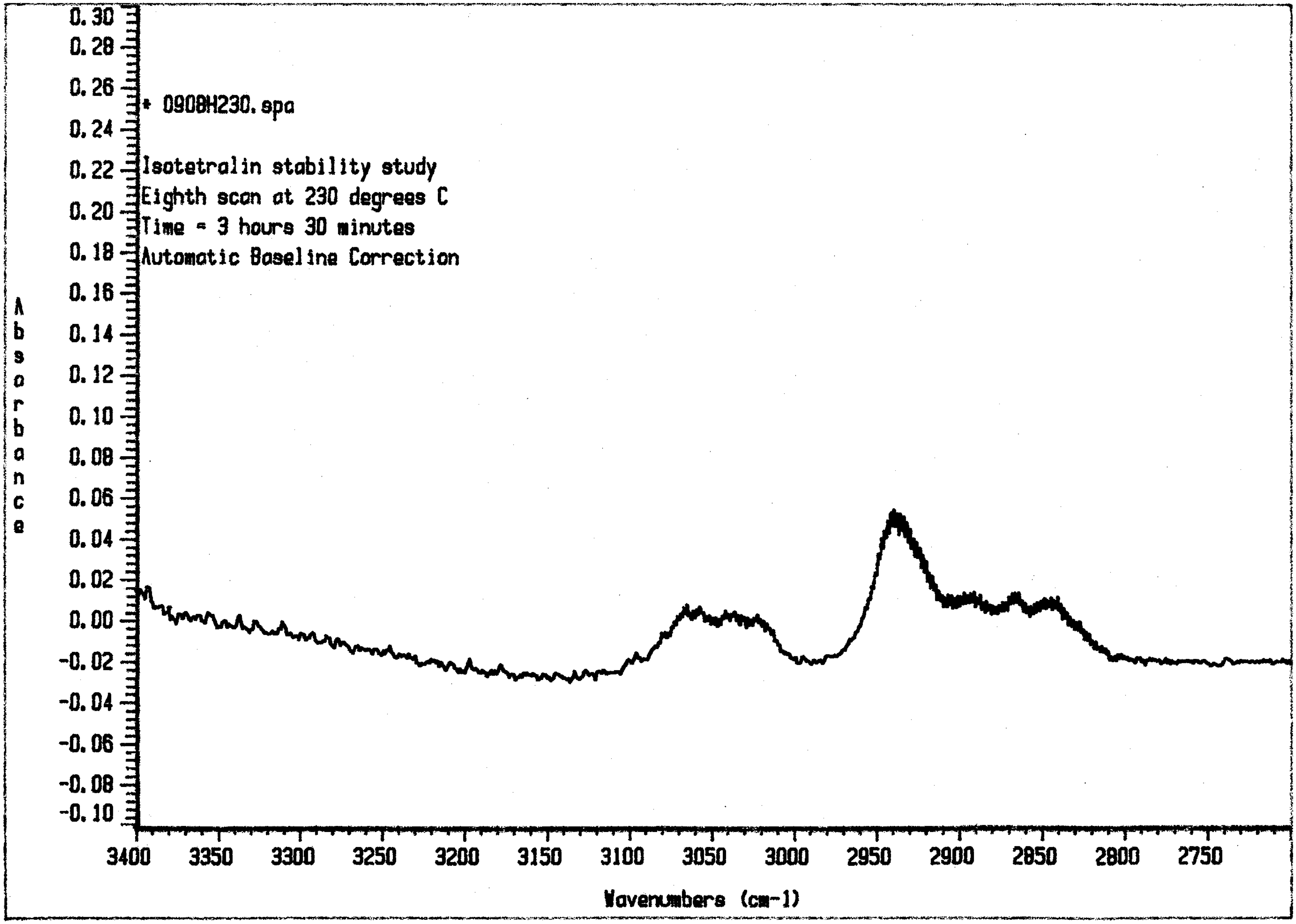
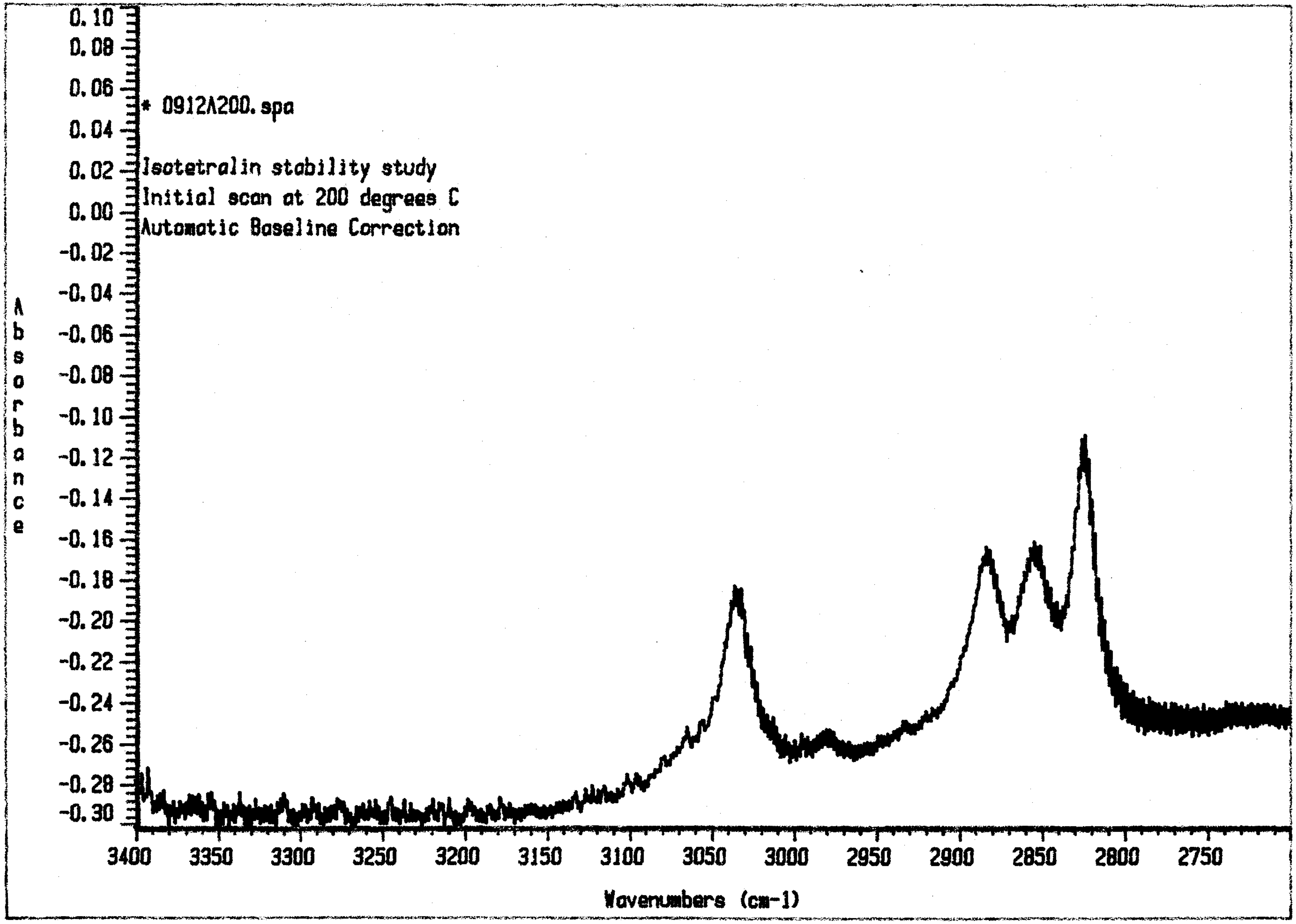

* 0908H230.spa
Isotetralin stability study
Eighth scan at 230 degrees C
Time = 3 hours 30 minutes
Automatic Baseline Correction
Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 10



0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
-0.12
-0.14
-0.16
-0.18
-0.20
-0.22
-0.24
-0.26
-0.28
-0.30
Absorbance
* 0912A200.spa
Isotetralin stability study
Initial scan at 200 degrees C
Automatic Baseline Correction
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 11

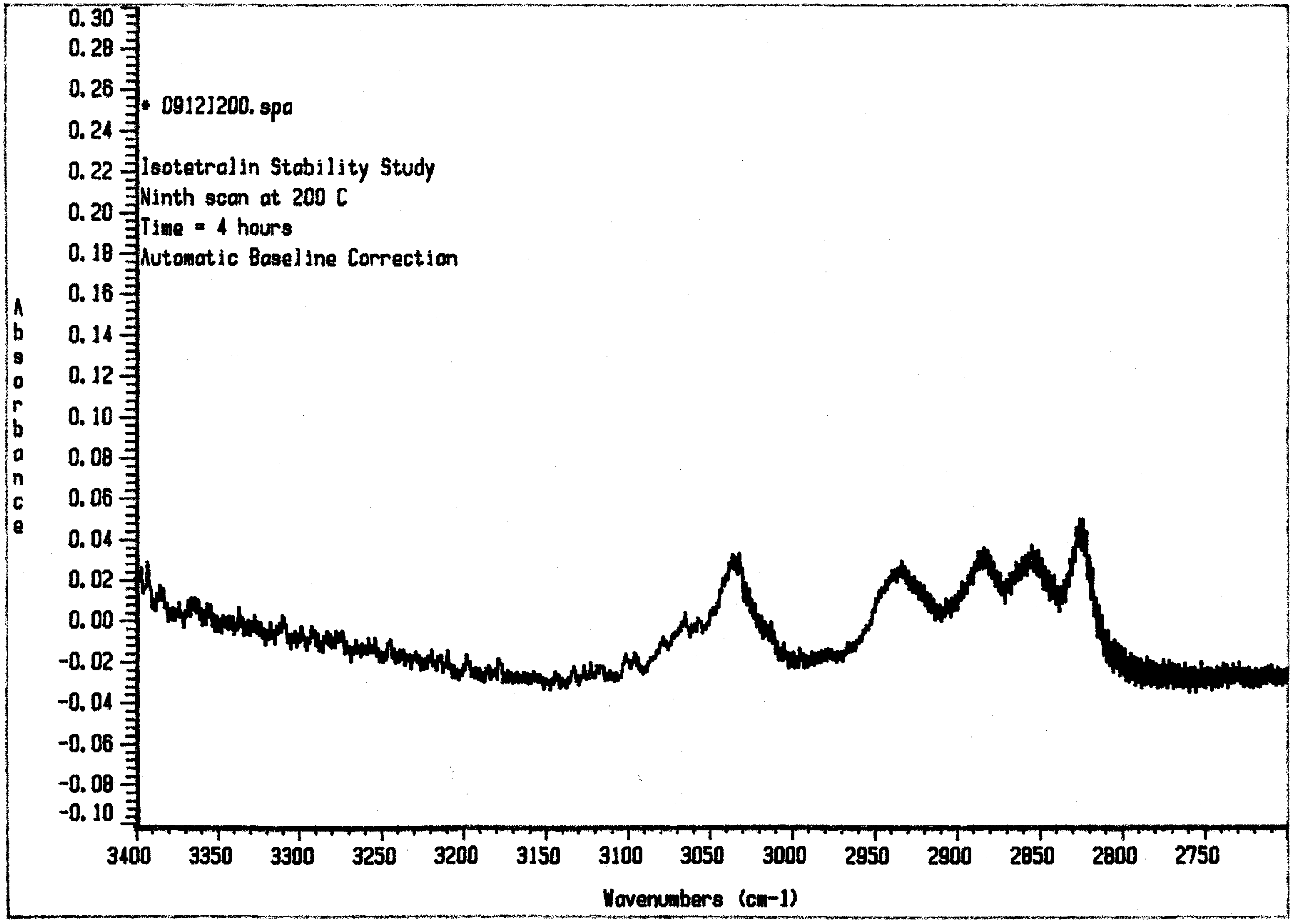
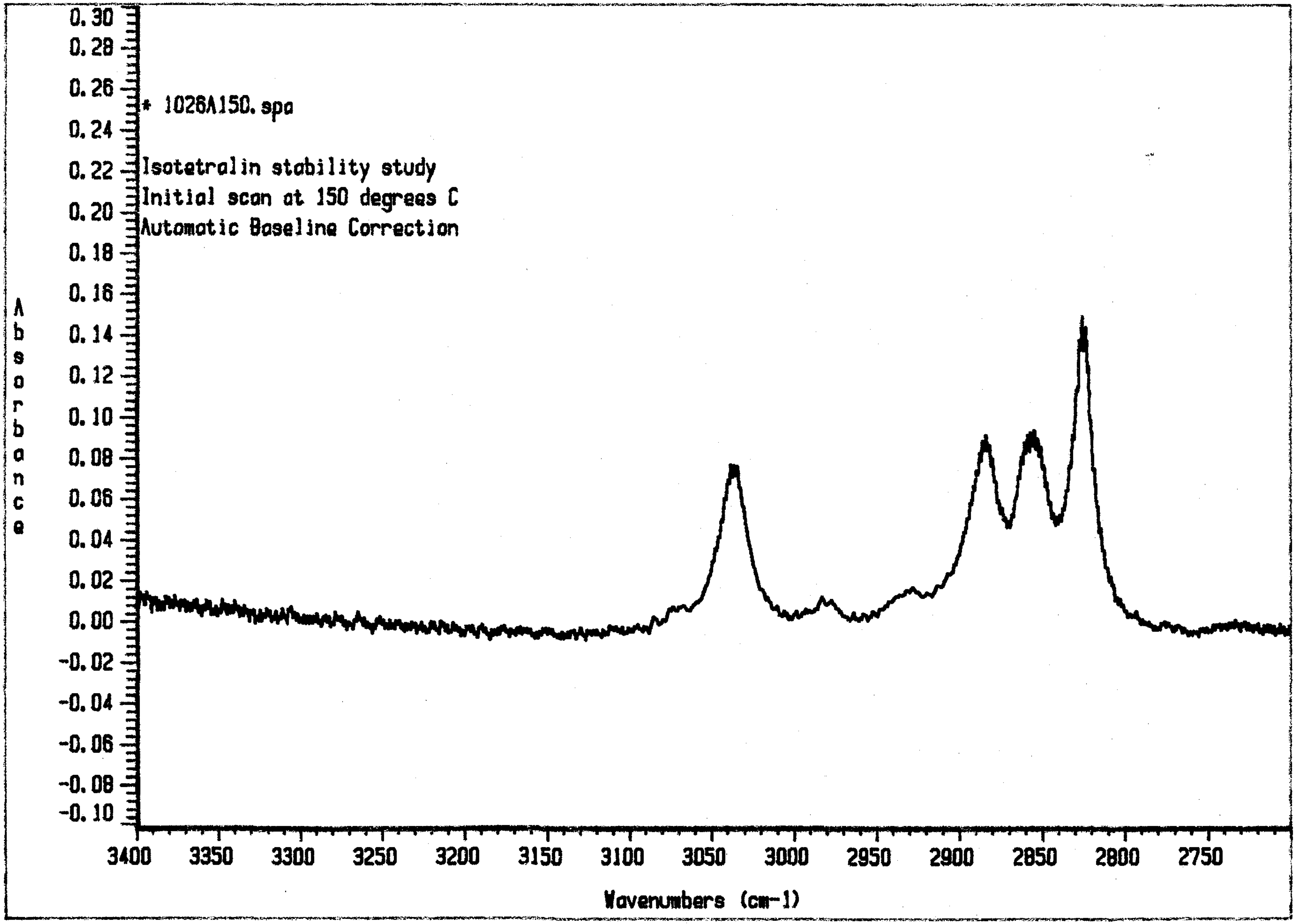
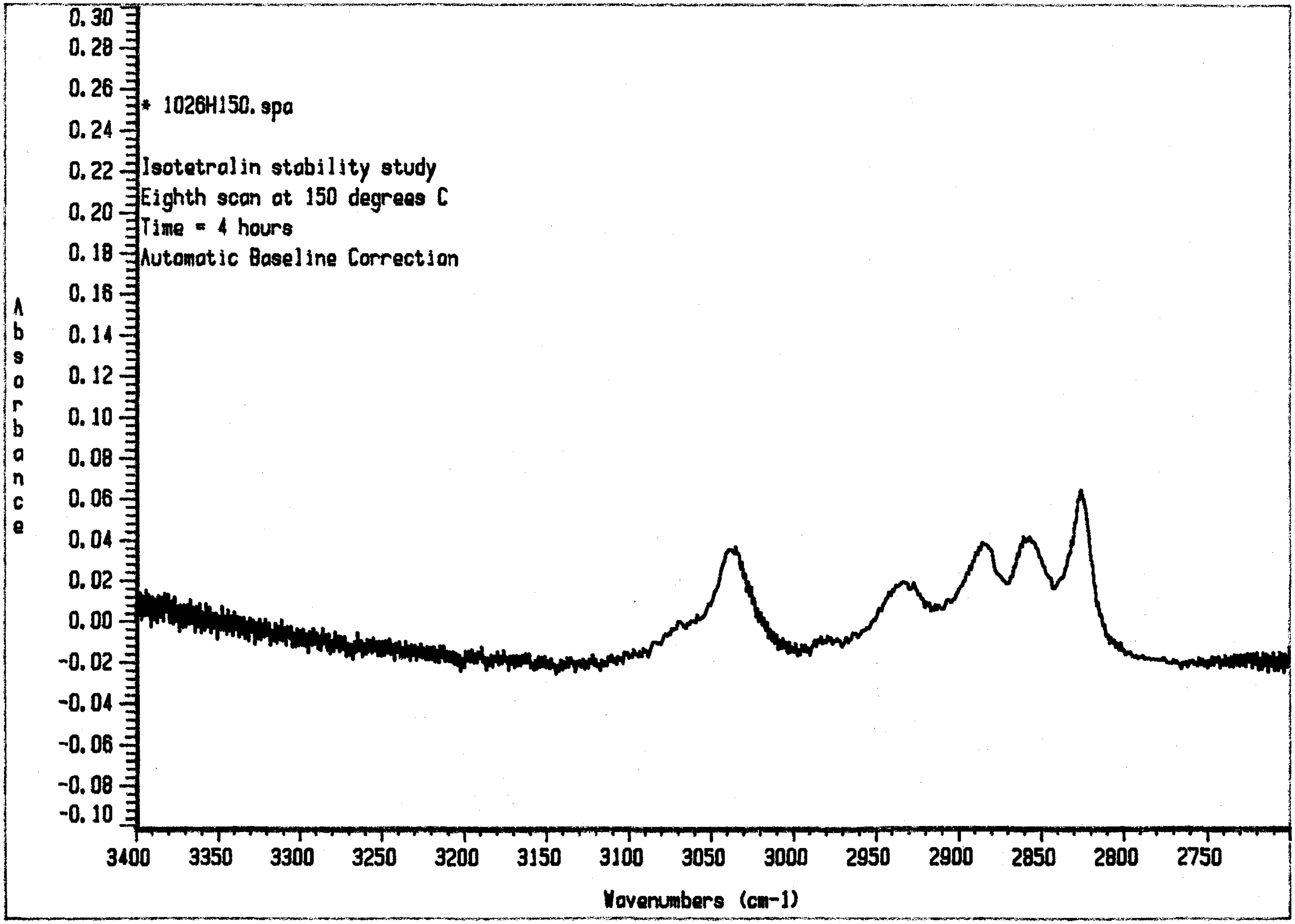

* 09121200.spa
Isotetralin Stability Study
Ninth scan at 200 C
Time = 4 hours
Automatic Baseline Correction
Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 12



ma4.3rd.qt

Figure 13



* 1026H150.spa
Isotetralin stability study
Eighth scan at 150 degrees C
Time = 4 hours
Automatic Baseline Correction
Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 14

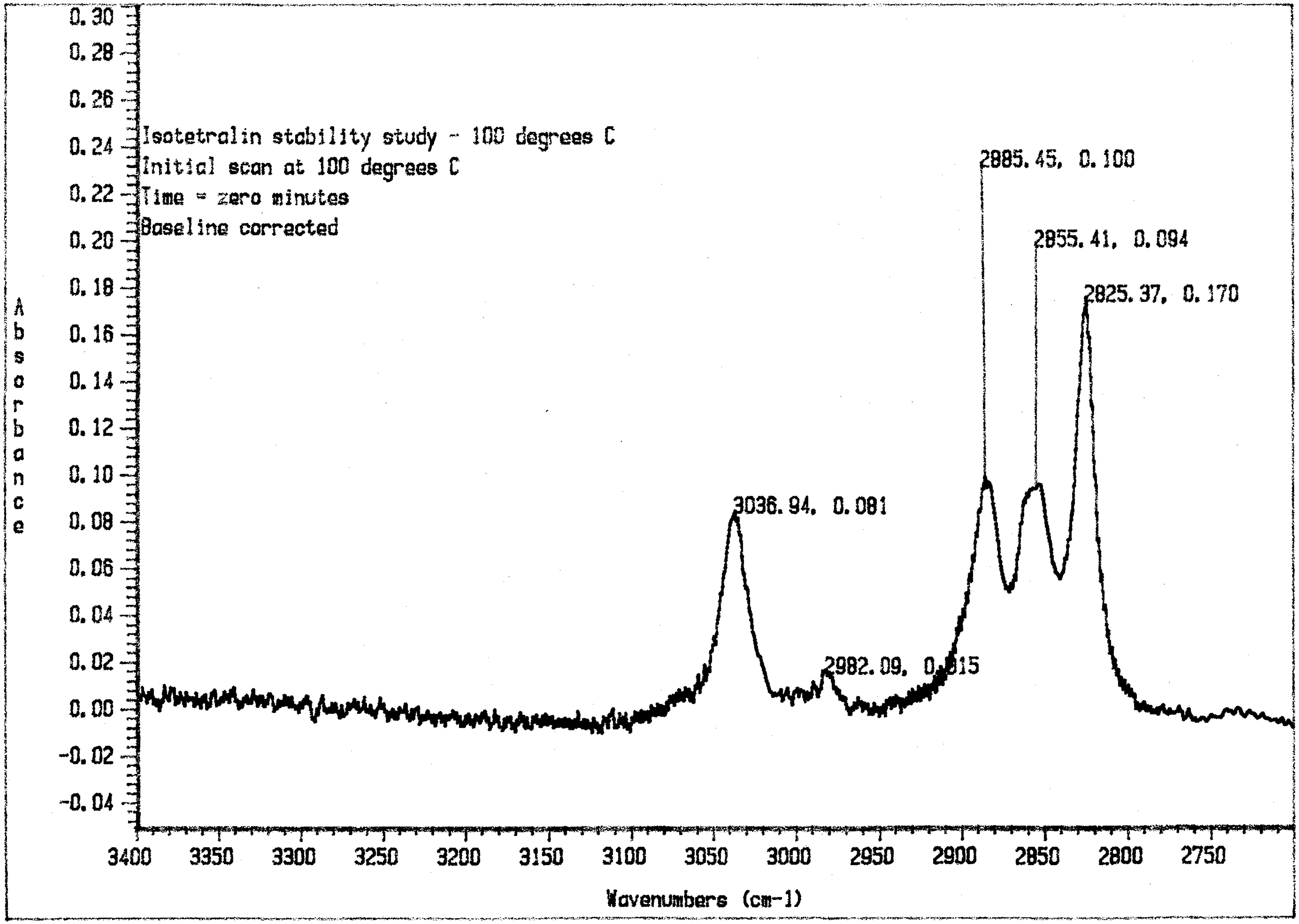

Isotetralin stability study - 100 degrees C
Initial scan at 100 degrees C
Time = zero minutes
Baseline corrected
2885.45, 0.100
2855.41, 0.094
2825.37, 0.170
3036.94, 0.081
2982.09, 0.015
Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 15

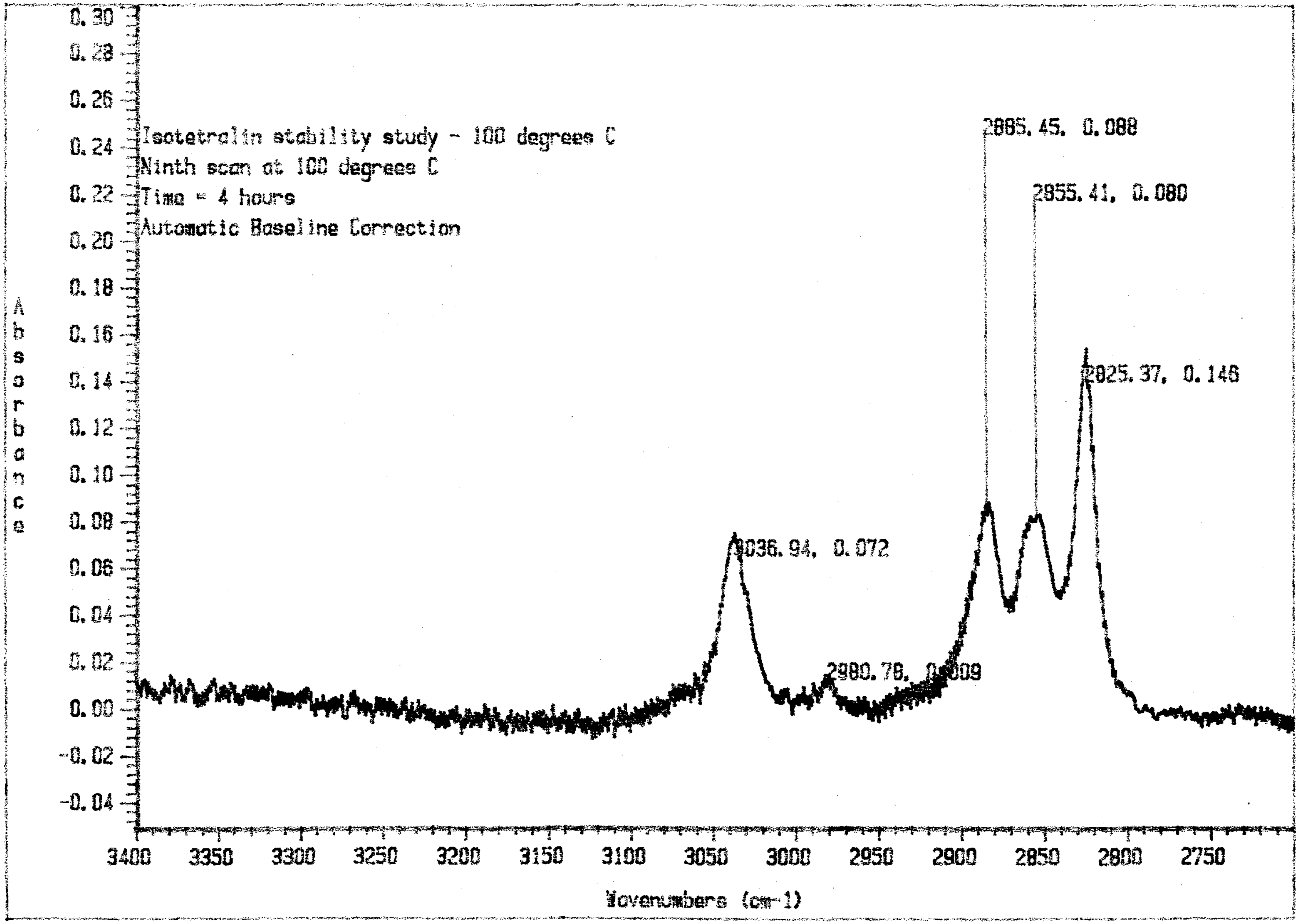

Isotetralin stability study - 100 degrees C
Ninth scan at 100 degrees C
Time = 4 hours
Automatic Baseline Correction
2885.45, 0.088
2855.41, 0.080
2825.37, 0.146
3036.94, 0.072
2980.78, 0.009
Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 16

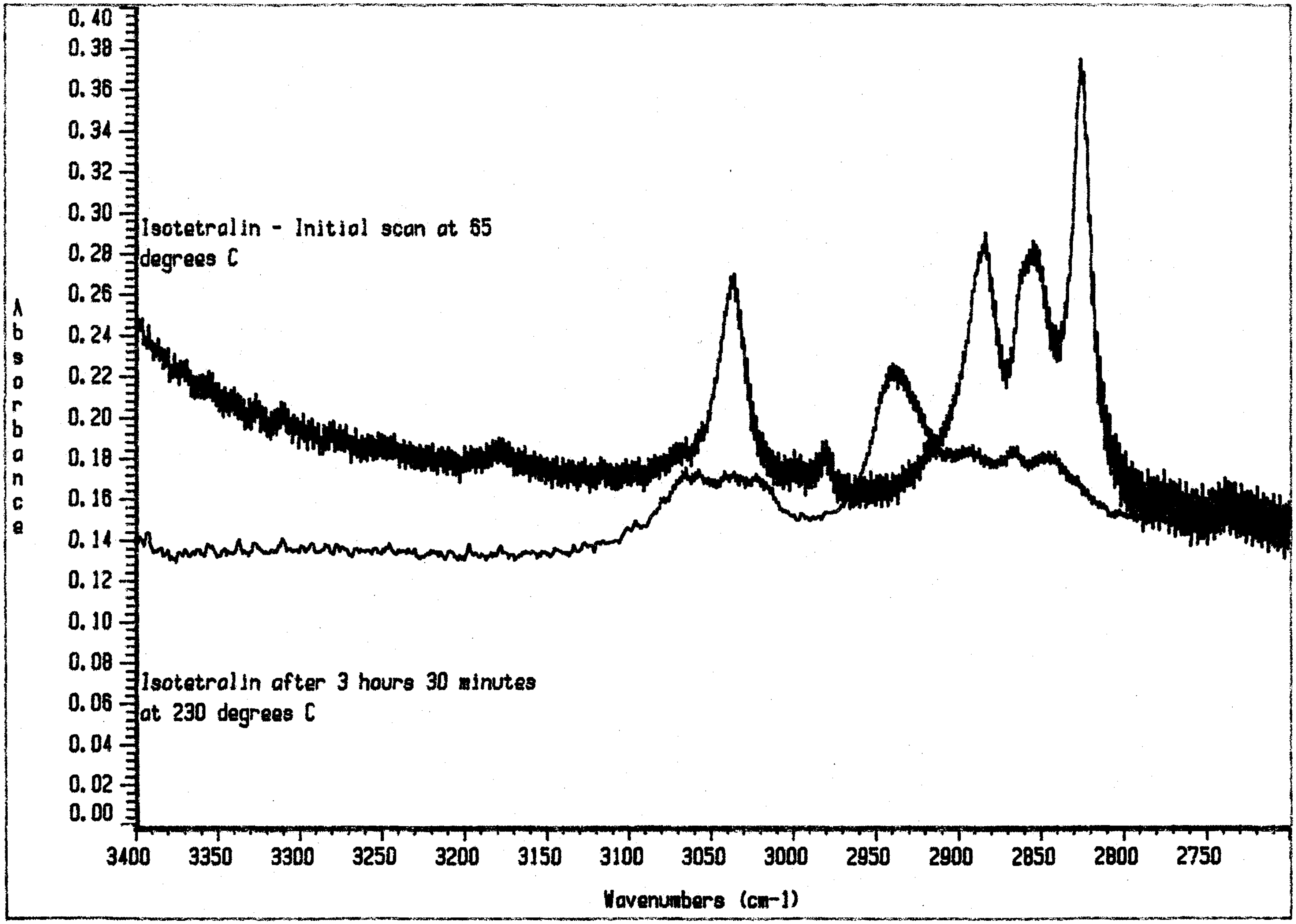
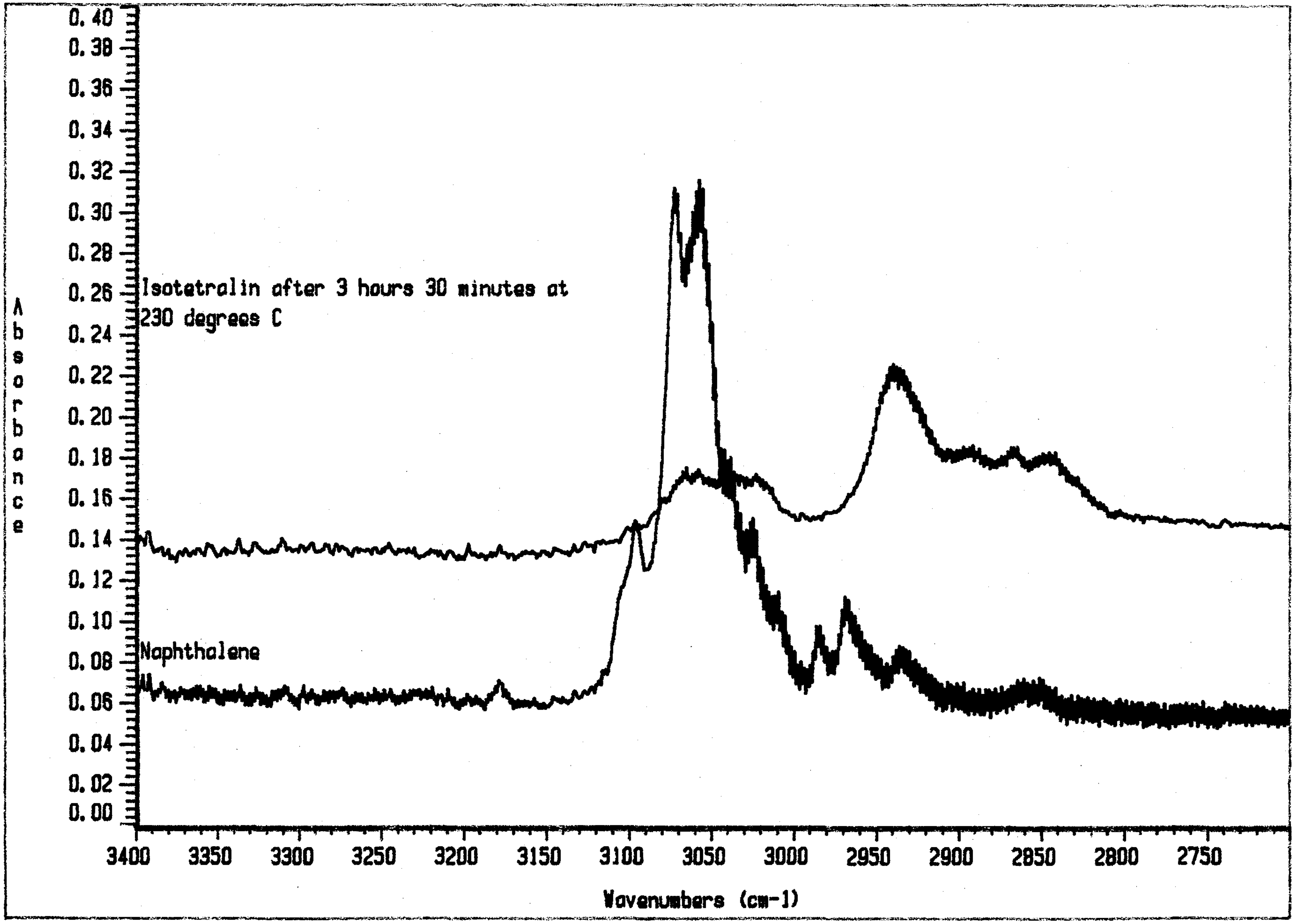

Isotetralin - Initial scan at 65 degrees C
Isotetralin after 3 hours 30 minutes at 230 degrees C
Absorbance
0.40
0.38
0.36
0.34
0.32
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 17


0.40
0.38
0.36
0.34
0.32
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Absorbance
Isotetralin after 3 hours 30 minutes at 230 degrees C
Naphthalene
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

obtained at elevated temperatures show more curvature and more noise than scans obtained at 65 °C. Subsequently, all sample scans have been compared to backgrounds obtained at the same temperature as the sample scans, resulting in a noticeable reduction in the noise level. Secondly, it was noted that the software, if allowed to autogain, will scan a sample at a different gain than the gain of the background to which the sample is to be compared. Consequently, the procedure was modified to allow the software to autogain for the background scan, but force the sample gain to match the background gain. Once again, noticeable noise reduction was achieved. Lastly, increasing the number of scans per sample can sometimes increase the signal-to-noise ratio (also referred to as "post-processing the noise"). The number of scans per sample was increased from the usual 32 to 64, 128 and 256 scans per sample. No reduction in the noise level was noticed, the number of scans per sample was returned to 32. The noise level continues to be a problem and constitutes a project for future work.

Future Work

The current elevated temperature work is to be extended to an elevated pressure as well (500 psi) by application of a nitrogen or hydrogen blanket. The cell will need to be rotated 90 degrees in its holder in order to introduce gas above the liquid phase. Hopefully, the anchoring of the cell to insure reproducibility of positioning in the optical path can also be accomplished with these mechanical alterations. Noise continues to be a problem which will need to be addressed. The peaks appearing in the spectra of isotetralin and its products will need to be assigned to definite structural features in these molecules. The stability studies will be extended to 350 °C and 500 psi using a polyperfluoroether obtained from DuPont. This work may also be extended to 1,2 and 1,4-dihydronaphthalene. The linear region of the absorbance vs. concentration curves at elevated temperatures and pressures will be determined. It may be necessary to use the least squares and/or deconvolution software packages in connection with this determination. The kinetics of the reaction of isotetralin at elevated temperatures and pressure will be determined.

References

1. Silverstein, R.M., et.al., *Spectrometric Identification of Organic Compounds,* John Wiley & Sons, New York, N.Y., 1974, 3rd edition, p. 85.
2. Silverstein, op. cit., p. 88.