DOE/PC/91281--T18

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# Low Severity Coal Liquefaction Promoted by Cyclic Olefins

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

**Quarterly Report**
**April to June 1996**

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# 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.

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# Table of Contents

Page

# High Temperature Infrared Analysis of Cyclic Olefins

## FTIR at Combined Elevated Temperatures and Pressures

## 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.

The useful temperature range of the high temperature infrared cell has been 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. High temperature infrared analyses have been performed using isotetralin, tetralin, naphthalene, 1,4-dihydronaphthalene and 1,2-dihydronaphthalene. Stability studies have shown that naphthalene was quite stable at temperatures up to 230 °C, as were tetralin, decalin and 1,4-dihydronaphthalene. High temperature FTIR analysis of isotetralin and 1,2-dihydronaphthalene reacted at evelvated temperatures forming tetralin and 1,4-dihydronaphthalene, respectively. This quarter cell modification was completed to be able to perform high temperature and high pressure analysis. The system used for the initial study was naphthalene which is reported herein.

## Experimental Work

During this quarter, the mechanical modifications necessary to introduce a high pressure gas blanket over samples in the Aabspec cell were accomplished. These modifications included modifying the cell bracket and repositioning the cell, addition of mechanical connections for introducing high pressure into the cell and procurement and installation of appropriate high pressure regulators and tanks. The cell bracket was extended to allow the cell to be rotated 90 degrees. This allowed the sample ports to be in an upward position, thus insuring that the liquid sample was in the optical path and the gas blanket stayed above the solution. The length of the extension made it necessary to move the cell mount on the optical bench. This realignment resulted in an unexpected but welcomed reduction in the noise level, as is readily apparent by comparing any of the new spectra in this report to those published previously. Because of the mechanical connections, the cell is now held quite rigidly in its holder. Hopefully, this rigid positioning will provide reproducibility in the cell positioning.

With these modifications, the sample cell could then be pressurized. In order for the IR cell to be pressurized, high pressure gas was required to cover the sample in the sample chamber as well as a gas was needed to pressurize the external pressurization chamber. The gases can be the same or different depending upon experimental requirements. For the preliminary work of demonstrating the cell's ability to operate at combined elevated temperatures and pressures, nitrogen was chosen as both the blanket gas over the sample and the inert gas to pressurize the external pressurization chamber. The internal chamber was connected directly to the external pressurization chamber with

316 stainless steal ⅛ inch tubing. With this connection there could be no pressure difference across the internal (heated) salt windows. A solution of 1,2-dihydronaphthalene was chosen as the sample for this work.

The solution was scanned at 65 °C and atmospheric pressure to provide a baseline spectrum (see Figure 1). Then the pressure was increased to 500 psig, while holding the temperature at 65 °C (see Figure 2). Then the IR cell temperature was stepped up to 100 °C, 150 °C, 200 °C and 230 °C while maintaining a pressure of 500 psig. Figure 3 presents the spectra of 1,2-dihydronaphthalene in APF-240 at 230 °C under a 500 psig nitrogen blanket. This experiment was performed to evaluate the IR cell performance under combined high temperature and pressure conditions. It should be emphasized here that this was not a stability test. Only about eight minutes separated each temperature increase, whereas much longer times were used in the stability test.

## Naphthalene Stability Test

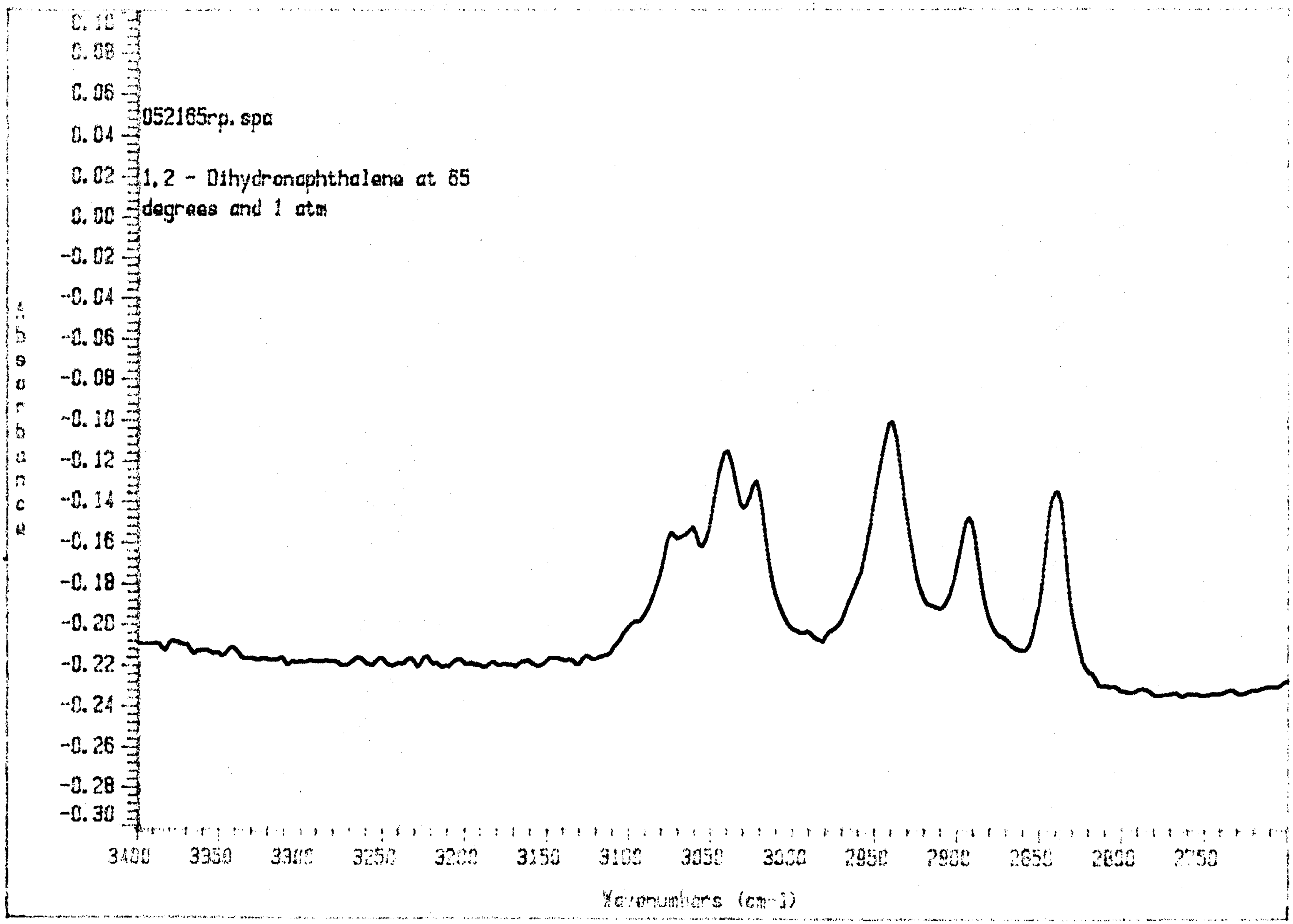
Having demonstrated the IR cell's ability to operate at combined elevated temperatures and pressures, the next step was to conduct stability studies. The initial experiment involved naphthalene. A 0.3 wt% solution of naphthalene in APF-240 was subjected to the routine stability test, the only difference being the 500 psig nitrogen blanket over the solution. The conditions for the stability test involved heating the sample to 65 °C and taking a spectrum. The temperature was held at 65 °C for 30 minutes and the spectrum was retaken. The temperature was then raised to 100 °C, then 150 and 200; the spectra were taken once the temperature was obtained and then 30 minutes later. The final temperature was 230 °C which was held for three to four hours. A spectrum was taken every 30 minutes during this time period. Figures 4, 5, 6 and 7 present the final scans at 65, 100, 150 and 200 °C, respectively. Figures 8 and 9 present the initial and final scans at 230 °C.

The naphthalene stability study under high pressure gave an anamolous result. When the stability study was performed at ambient pressure with the naphthalene solution filling the sealed cell and having no atmosphere present, the naphthalene appeared stable over the entire reaction sequence. However, when a nitrogen blanket was used, naphthalene appeared to be reacting under the nitrogen blanket. In Figure 9, a broad peak around 2950 $cm^{-1}$ became apparent at conditions of 200 °C. This may be characteristic of a tetralin peak which occurs around 2940 $cm^{-1}$. It was postulated that water and/or some other impurity in the nitrogen may be causing some reaction. Another possibility was that some residue in the IR cell became more apparent as high pressure was applied. The cell is being thoroughly cleaned before the next reactions are performed. A gas chromatography procedure is being developed to determine the contents of the IR cell after high temperature and pressure infrared analysis.

## Future Work

The high pressure stability studies will be extended to tetralin, isotetralin, 1,2-dihydronaphthalene and 1,4-dihydronaphthalene. Also, the high pressure stability studies will be conducted with a 500 psig hydrogen blanket over the sample. GC analysis will be used to confirm the identity of the products of the stability tests. In future research, the stability studies will be extended to 350 °C and 500 psig using a perfluoroether obtained from DuPont. The linear region of the absorbance versus 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 pressures will be determined.

**Figure 1**


052165rp.spa
1,2 - Dihydronaphthalene at 65
degrees and 1 atm
Absorbance
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
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

## Figure 2

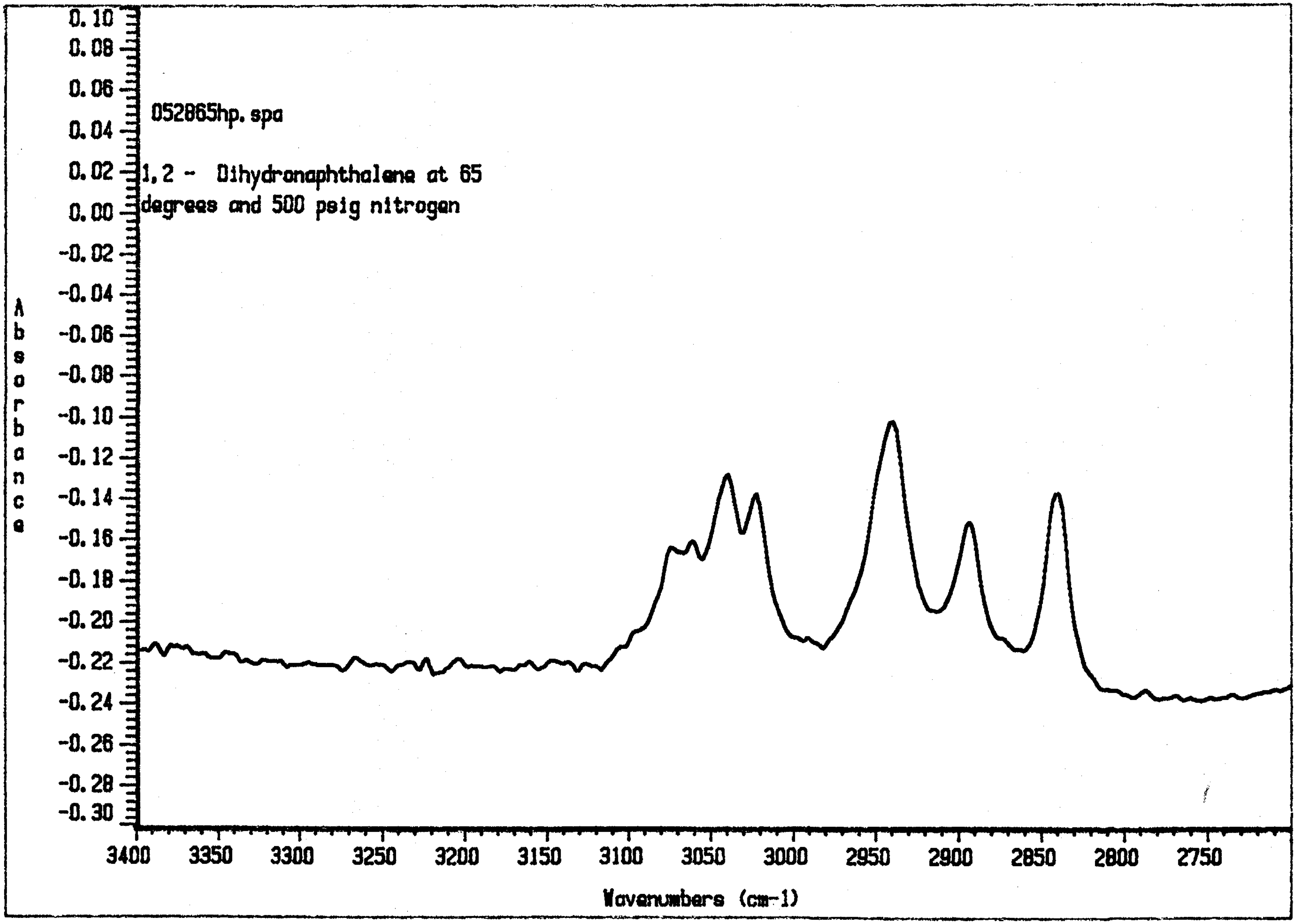

052865hp.spa
1,2 - Dihydronaphthalene at 65
degrees and 500 psig nitrogen
Absorbance
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
-0.12
-0.14
-0.16
-0.18
-0.20
-0.22
-0.24
-0.26
-0.28
-0.30
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 3

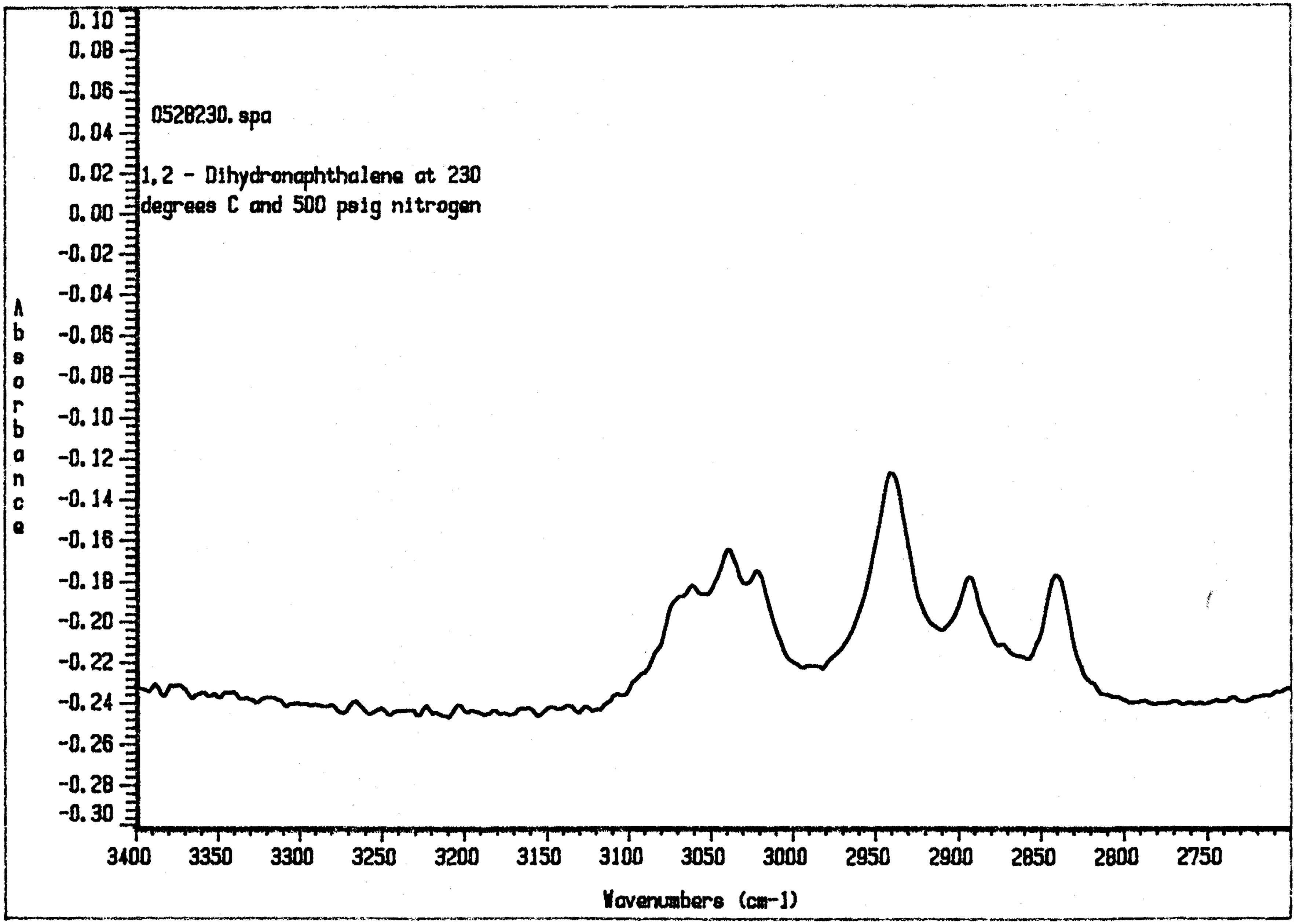

0528230.spa
1,2 - Dihydronaphthalene at 230
degrees C and 500 psig nitrogen
Absorbance
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
-0.12
-0.14
-0.16
-0.18
-0.20
-0.22
-0.24
-0.26
-0.28
-0.30
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 4

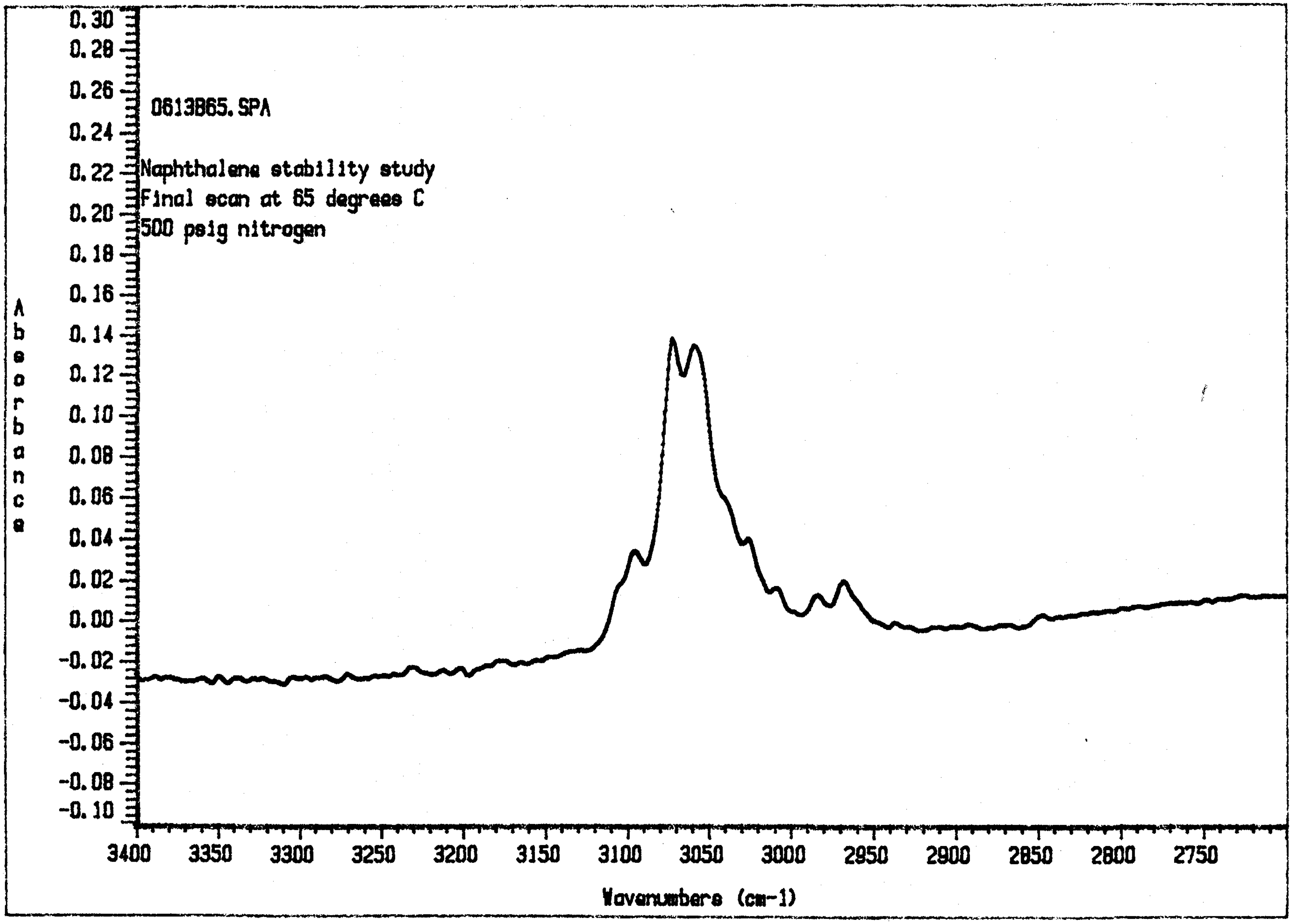
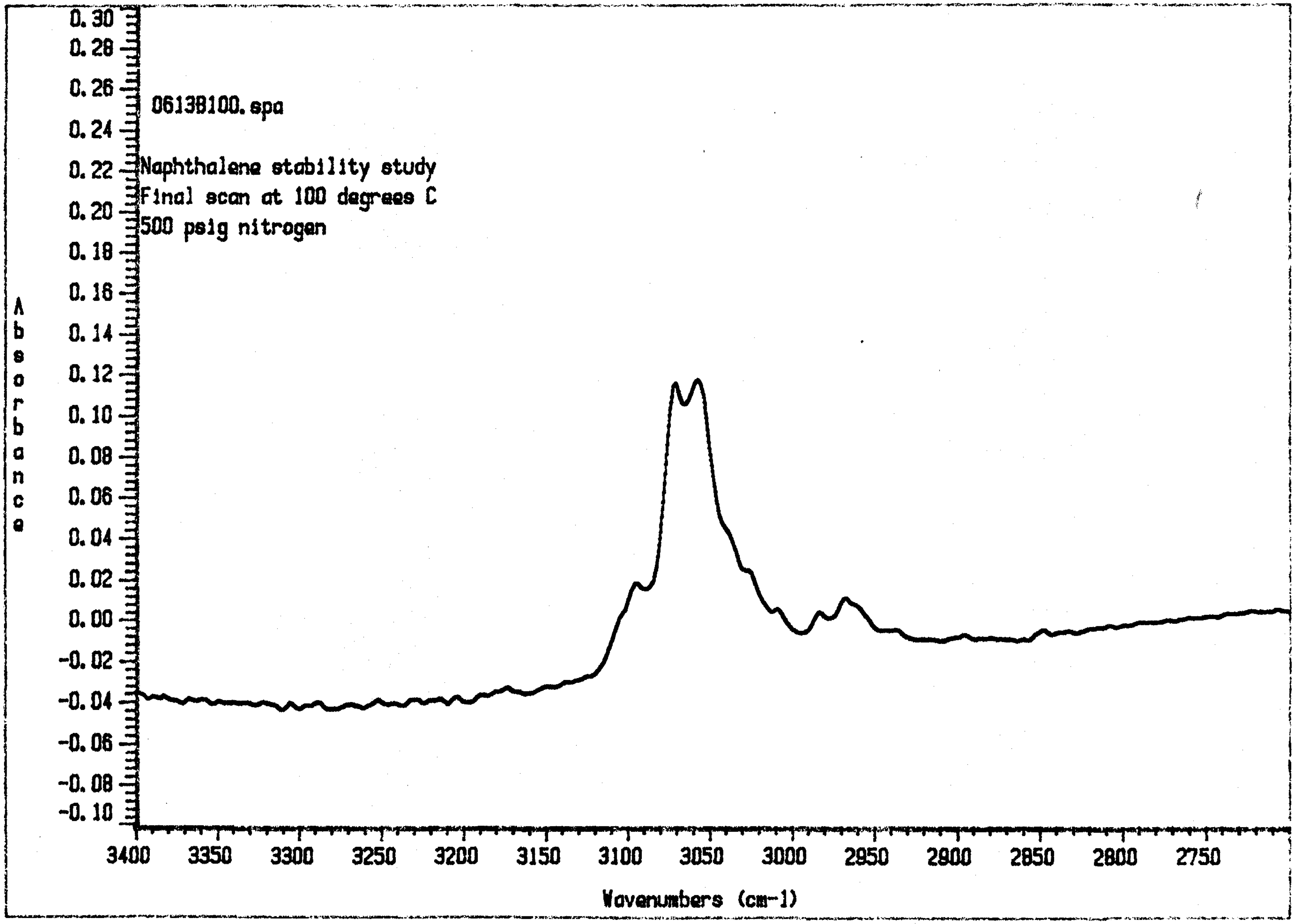
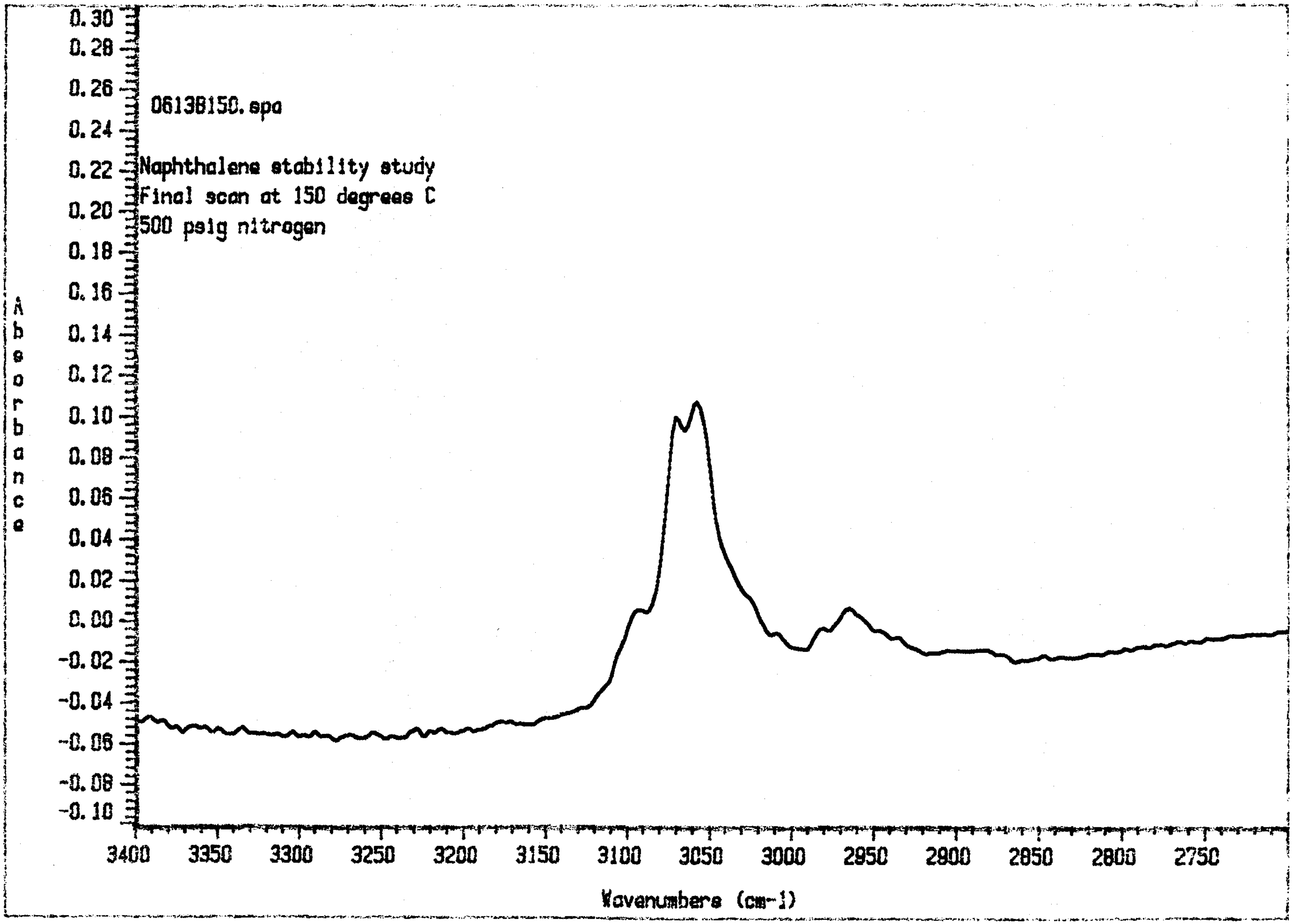

0613B65.SPA
Naphthalene stability study
Final scan at 65 degrees C
500 psig nitrogen
Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 5


06138100.spa
Naphthalene stability study
Final scan at 100 degrees C
500 psig nitrogen
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 6



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
06138150.spa
Naphthalene stability study
Final scan at 150 degrees C
500 psig nitrogen
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 7

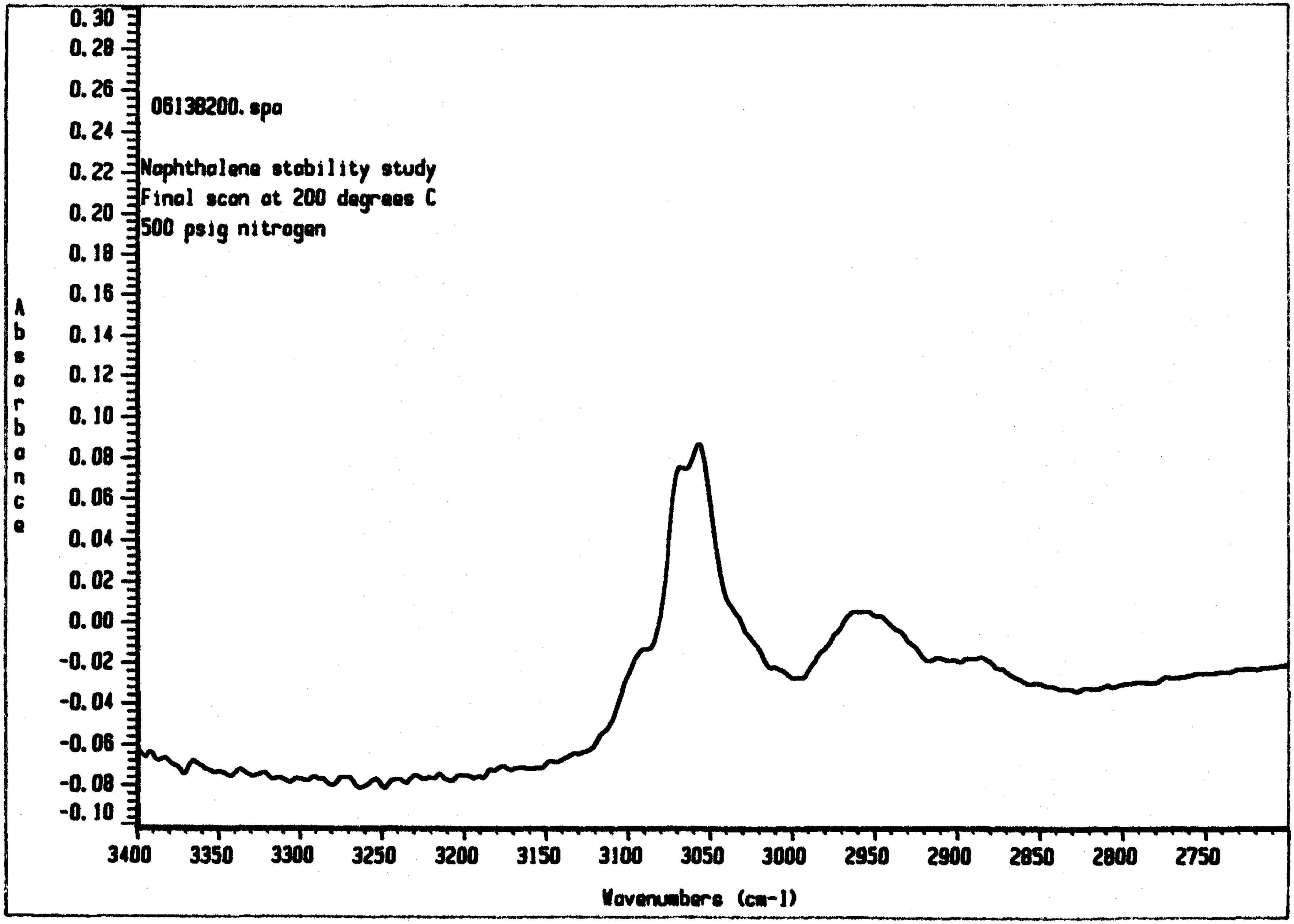
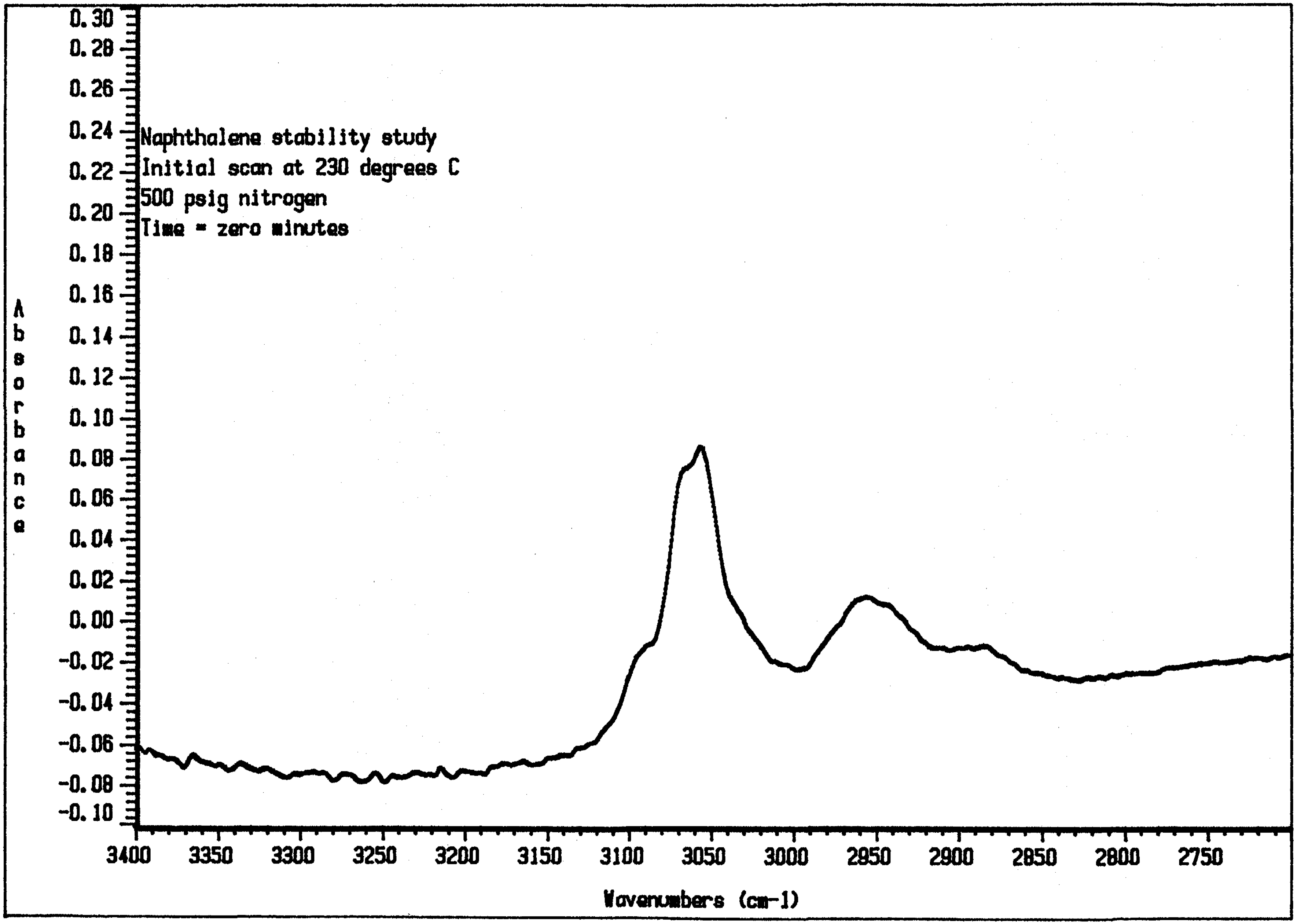
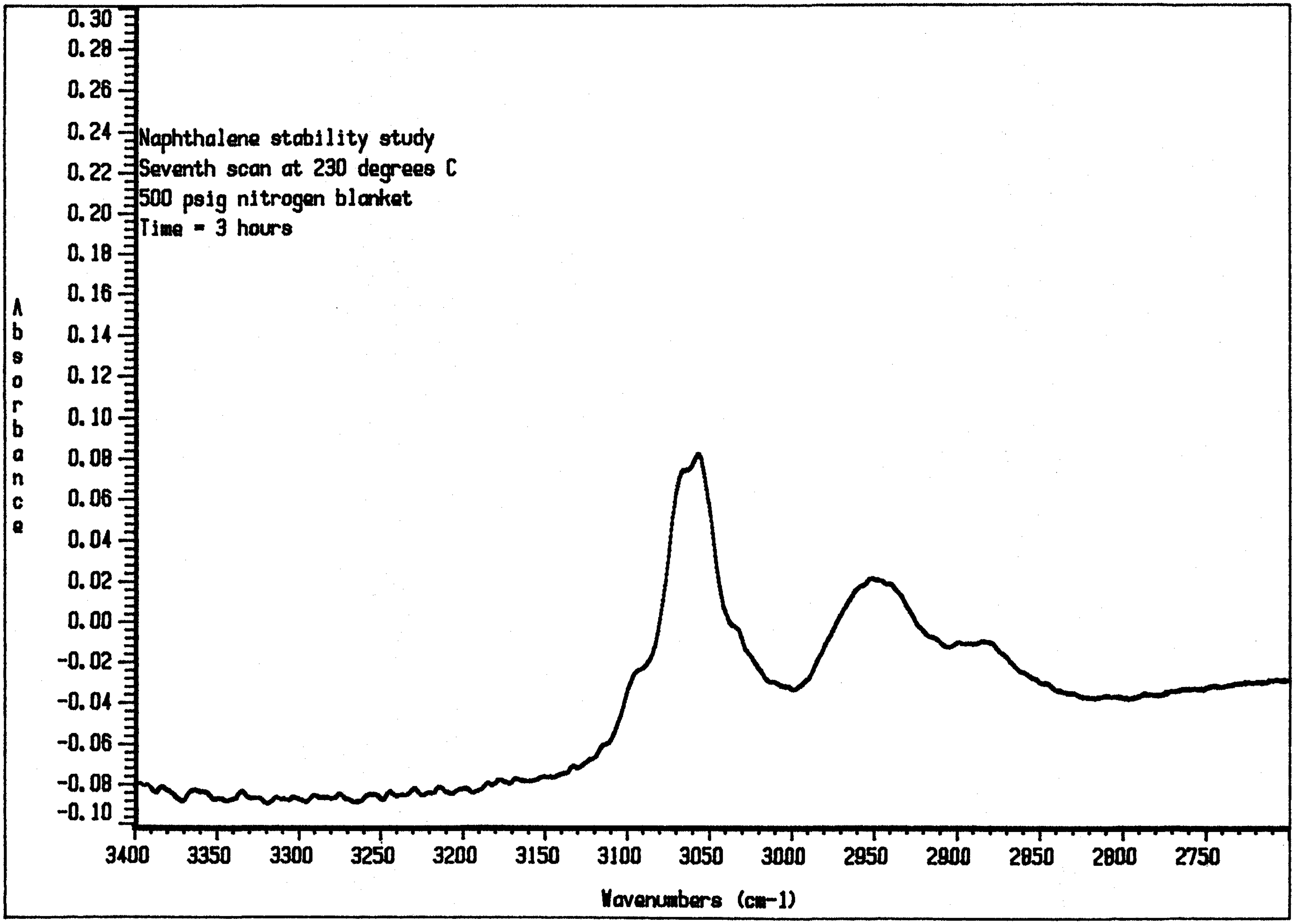

06138200.spa
Naphthalene stability study
Final scan at 200 degrees C
500 psig nitrogen
Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 8

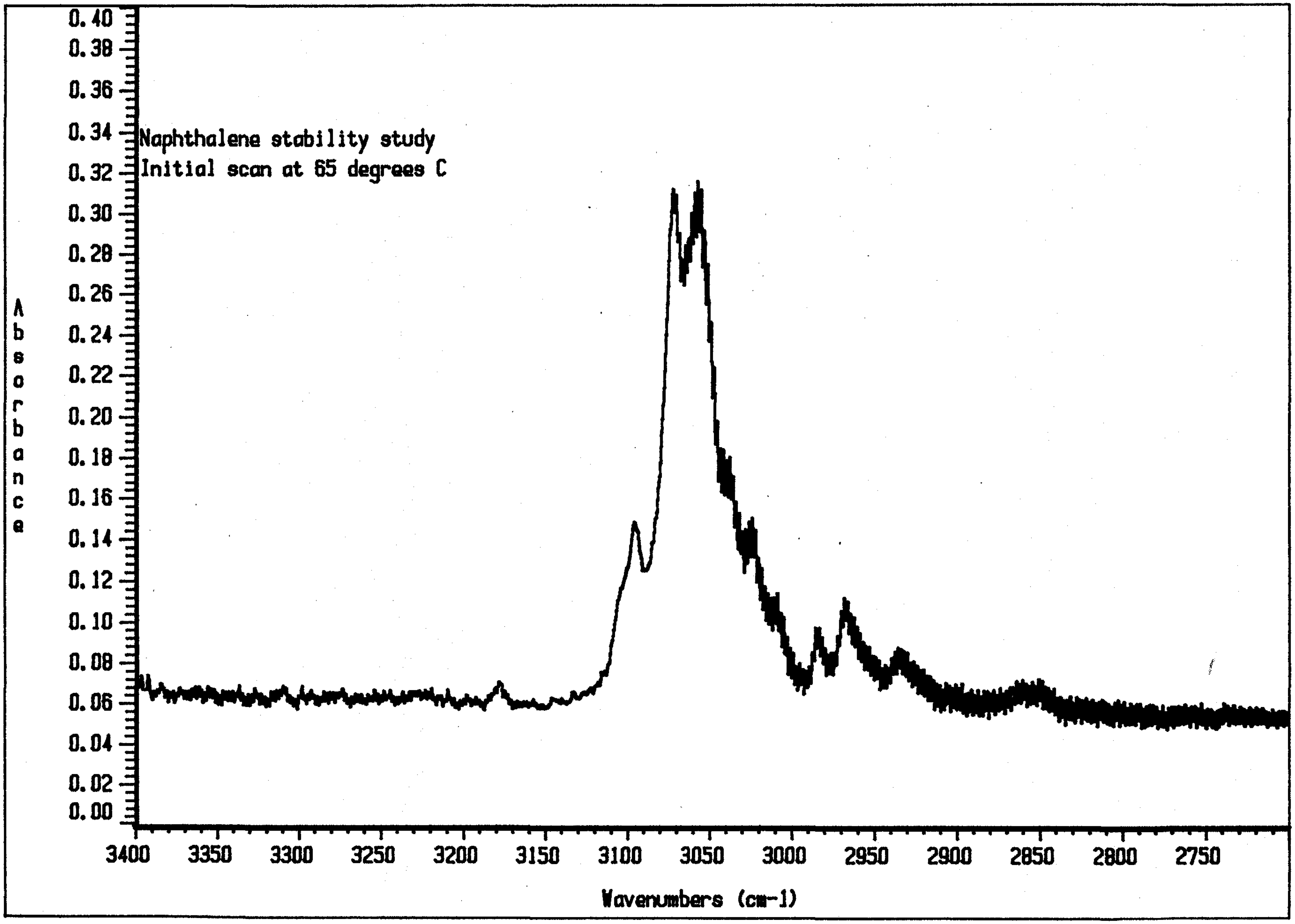

Naphthalene stability study
Initial scan at 230 degrees C
500 psig nitrogen
Time = zero minutes
Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

## Figure 9

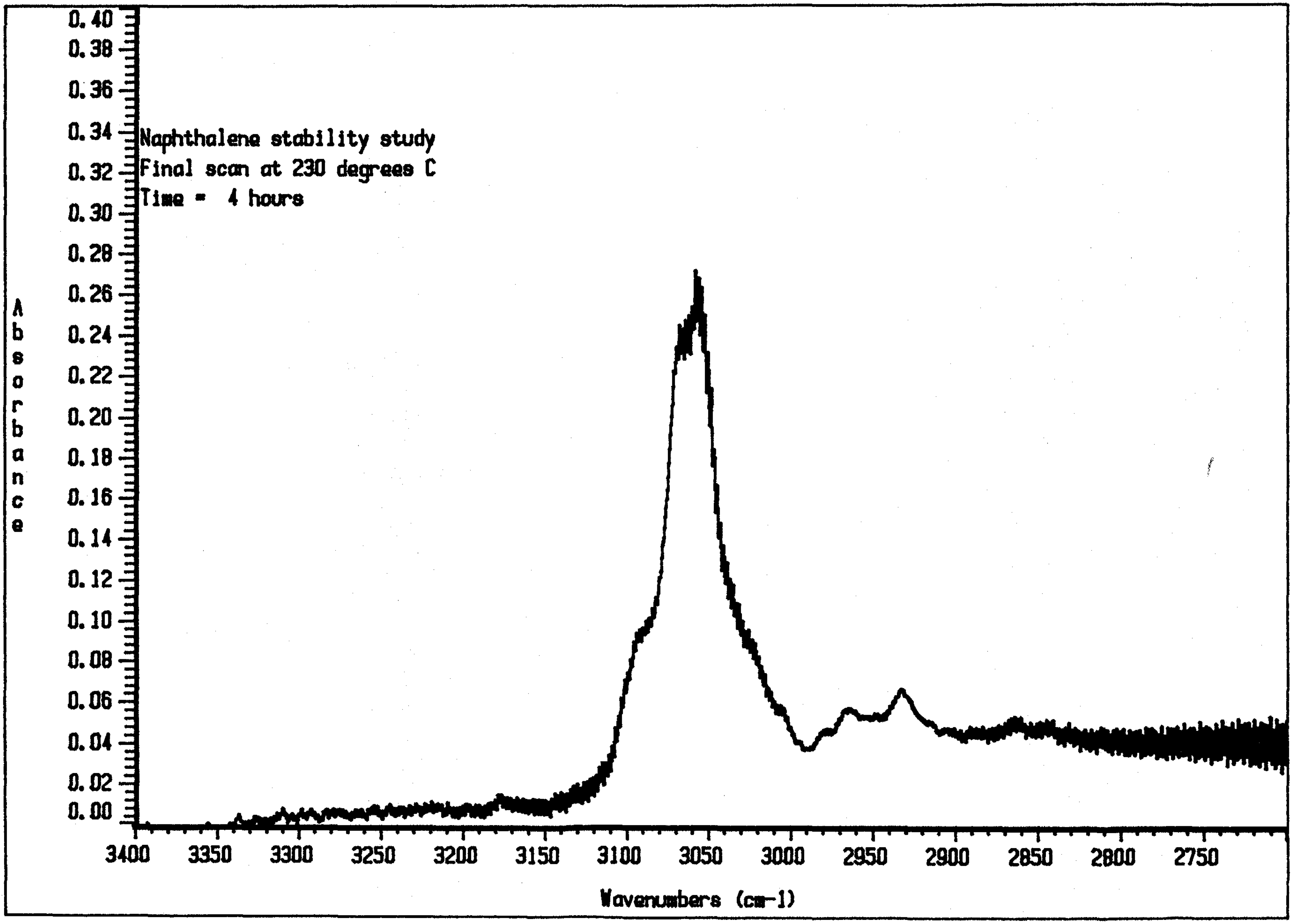


Naphthalene stability study
Seventh scan at 230 degrees C
500 psig nitrogen blanket
Time = 3 hours
Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
3400
3350
3300
3250
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
Wavenumbers (cm-1)

Figure 10


Naphthalene stability study
Initial scan at 65 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 11



Naphthalene stability study
Final scan at 230 degrees C
Time = 4 hours
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)

# Infrared Spectroscopy at Combined Elevated Temperatures and Pressures

## A Literature Review - An Update

A number of articles on infrared spectroscopy at elevated temperatures and pressures have appeared in the recent literature. The following is a brief review of some of the more noteworthy of those articles.

The earliest designs, such as those described by Noack,[1] and Tinker, et. al.,[2] employed a cell for the study of reactions carried out in a separate reactor. Essentially, these systems consisted of an autoclave with a IR cell located down steam for the analysis of reaction products. Since it is often desirable to do *in situ* studies of chemical reactions at elevated temperatures and pressures, several designs have been described in which the cell itself acts as the reactor. The cell developed by Penninger[3] is of the flow type and is primarily designed for chemical engineering purposes, e.g., *in situ* infrared recording of chemical reactions in gas-liquid systems, mixing characteristics of reactors under actual reaction conditions, and sensor device of an automatic reactor control system. This type of application is an extension of the earlier cell designs which were directed more towards pure chemistry. Since the window material and the metal-window seal present the most serious problems in the construction and use of a high pressure spectroscopic cell,[4] a substantial portion of the effort in the development of these cells went into improving the window seals.[5]

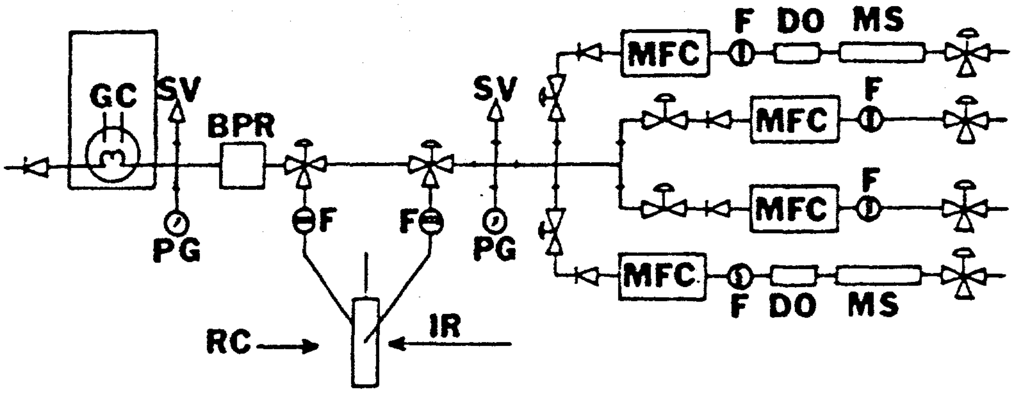
Whyman[6] provides an excellent review of the history of the development of infrared cells for use at elevated temperatures and pressures. In 1972, the details of only two or three such cells had been presented throughout the world. Over the next 15 years, many such cells were described and this technique became part of the traditional armory of physical methods, particularly in industrial laboratories. The reason for industrial interest is quite simply that it is essentially the only currently (1987) available spectroscopic technique for *in situ* monitoring of the species present under actual working conditions of pressure and temperature. It can therefore provide information which is directly relevant to industrial processes. Clearly the use of such a method provides a significant advance over the traditional method of withdrawal of samples from high pressure - high temperature vessels followed by analysis under ambient conditions.[7] The advent of Fourier transform instrumentation has considerably simplified the technique both in terms of enhancement of overall sensitivity and in terms of ease of operation when remote control is necessary. Commercial cells for the investigation of liquids, gases and solids under high pressures and temperatures are now available.

The cells described can be used to study a batch reaction or incorporated in a continuous flow system. One such design for catalytic studies in gas flow systems as described by Lavalley[8] is shown in Figure 12. The entire high pressure system is built directly on the FTIR spectrometer. The design is typical of flow systems for use with IR spectroscopy, and basically consists of high pressure gas cylinders which contain the reactant gases, mass flow controllers, a junction where the gases mix and flow through the IR cell which serves as the reactor, and a back pressure regulator. This particular design also incorporates a downstream gas chromatograph. The flow system can also be used to study the reactions of liquids or slurries, or liquids on a solid catalyst disc or catalyst particles.

Of particular interest to the current work is the study of liquids under pressures of gases. Spectroscopic cells which have been described for the measurement of spectra of liquids and/or solids under pressures of gases have generally been used for the study of catalytic reactions and the identification of reaction intermediates under process conditions. Whyman[9] provides a detailed description of three different designs, designated A, B and C respectively. Type A includes those cells which are self contained units, such as an autoclave fitted with windows, and which can be stirred and heated. Thus chemical reactions can be monitored continuously from start to finish without perturbing the system, i.e., a truly *in situ* experiment.

**Figure 12**

**Flow system with FTIR spectrometer**



| | | | |
|---|---|---|---|
| MFC | Mass flow controller | SV | Safety valve |
| DO | Deoxygen trap | RC | Reactor cell |
| MS | Molecular sieve trap | BPR | Back pressure regulator |
| F | Filter | GC | Gas chromatography |
| PG | Pressure gauge | | |

In the Type B cell design, the IR cell and autoclave are separate components which are operated in conjunction with each other. Thus, reacting solutions from the autoclave are circulated through the IR cell by means of either gravity or a pump.

Type C cells are closely related to those of Type B but have been designed specifically as flow cells for the study of liquid/solid (or gas/liquid/solid and gas/solid) systems and the examination of heterogeneous catalysts under working conditions. The cell described by Penninger[10] represents the latest in a series of developments in spectroscopic cells which were initially designed for the study of homogeneous catalysts.[11,12,13,14] The Penninger cell is a versatile piece of equipment which may be used for the study of either liquid-solid catalyst interactions (with or without dissolved gas) or gas-solid systems. Since Rossiter's[15] cell is similar in construction to the Penninger cell, it should be well suited to the purpose of following the reaction of isotetralin at low severity coal liquefaction conditions. It should also be suited, with some modifications, to the study of heterogeneous catalyst systems.

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