

NAG10-153

NASA/CR-95- 207617

11-27-11  
078934

**INTERIM REPORT ON  
CHEMICAL AND THERMAL ANALYSIS**

**Prepared for: CAPP International Consortium**

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**Document Date: 31.6.95**

**Document Number: CAPP/T.3  
CONTENTS**

**Synopsis**

## **CONTENTS**

### **Synopsis**

#### **1.0 Hoop Stress Relaxation of Coflon Pipe**

#### **1.1 Elemental Analysis of Aged Coflon and Tefzel**

#### **1.2 Dynamic Mechanical Analysis of Coflon Pipe and Computer Accelerated Life Development Software**

#### **1.3 Differential Scanning Calorimetry of Aged Coflon and Tefzel**

#### **1.4 Fourier Transform Spectroscopy and Gas Chromatography/Mass Spectroscopy**

#### **1.5 Appendix One- DSC Results**

#### **1.6 Appendix Two- FTIR Results**

#### **1.7 Appendix Three- DMA Results**

#### **1.8 Appendix Four- Pipe Stress Relaxation Results**

#### **1.9 Appendix Five- Mass Spectra of Exudate From Coflon**

#### **2.0 Thermogravimetric Evaluation of Deplasticization of Coflon**

## SYNOPSIS

During the past six months we have conducted significant research in several domains in order to clarify and understanding the aging and chemical failure mechanism of thermoplastics (PVDF or Tefzel) for pipes. We organized numerous analytical studies with methods including Fourier Transform Infrared Spectroscopy, Dynamic Mechanical Analysis, Differential Scanning Calorimetry, and Stress Relaxation experiments. In addition we have reanalyzed previous thermogravimetric data concerning the rate of deplastization of Coflon pipe. We investigated a number of aged samples of both Tefzel and Coflon that were forwarded from MERL. We conducted stress relaxation experiments of Coflon pipe at several temperatures and determined an activation energy. We also examined the dynamic mechanical response PVDF during deplasticization and during methanol plastization. We performed numerous DSC analyses to research the changing crystalline morphology. We have noted significant changes in crystallinity upon aging for both PVDF and Tefzel. Little variation in elemental composition was noted for many of the aged Coflon and Tefzel samples tested.

## 1.0 Stress Relaxation of Coflon Pipe

We determined the stress relaxation characteristics of Coflon pipe sections in a splitting tension test emulating 200 psi differential internal pressure. The testing was conducted at three temperatures in order to determine the activation energy for the process. An activation energy was determined for the process of 3 Kcal/mol. Any activation below 5 Kcal/mol indicates that no primary bond breaking is occurring. The plots for the stress relaxation experiments are included in Appendix 4.

## 1.1 Elemental Analysis of Aged Coflon and Tefzel

Elemental analysis was accomplished on some of the aged Coflon and Tefzel samples obtained from MERL at the last CAPP meeting. Color changes were apparent with both the Tefzel and Coflon materials however there was little effect on the elemental composition of the material. Previously we reported substantial elemental changes in Coflon after exposure to a combination of temperature, H<sub>2</sub>S and aliphatic amine. We postulated at the last CAPP meeting that this was an elimination dehydrohalogenation type mechanism. This reaction occurs either in the presence of bases such as amines or hydroxides. These types of reactions are commonly known to occur with compounds such as PVC. Very little in the literature describes these processes occurring with PVDF. Considering the initial results after only thermal exposures it appears that Coflon and Tefzel are both relatively stable and undergoing no substantial elemental changes or reactions. This indicates that either the aliphatic amine and or the H<sub>2</sub>S are essential in addition to thermal activation to produce substantial elemental changes in Coflon. Some of the elemental results from the most recent tests are included below.

Sample Identification	Visual Appearance	%C, %H, %N, %F	Exposure
Control Tefzel	White	36.33, 2.74,	Laboratory Temperature and Conditions
	Translucent	0.00, 61.04	
T-9 Tefzel	White	36.19, 2.80, 0.00, 61.07	8 days methanol, 140°C, unstrained 5 ksi
T-19 Tefzel	White	36.54, 2.86, 0.00, 61.04	14 days methane, 140°C, strained 7% 5 ksi
Control Coflon	White	40.76, 4.11,	Laboratory Exposure and Conditions
	Translucent	0.00, 55.29	
T-7 Coflon	Very Light Brown	37.87, 3.33, 0.01, 58.40	14 days Nitrogen, 140°C, 7.5% strain
T-8 Coflon	Brown	37.54, 3.29, 0.01, 58.82	14 days methanol, 140°C, 7.5% strain, 5 ksi
T-12 Coflon	Brown	38.12, 3.28, 0.01, 58.95	8 days methanol, 140°C, unstrained reached

<b>T-23 Coflon</b>	Light Brown	37.62, 3.29, 0.01, 58.86	14 days methanol, 140°C unstrained, 5 ksi
<b>*Aged Coflon</b>	Dark Brown	71.47, 11.47, 0.00, <0.03	5% H <sub>2</sub> S 7days 130°C, methane permeation 25

\*Also found 1.29 % Sulfur

We conducted elemental analysis of a second batch of samples of aged Coflon and Tefzel test articles. This group of materials were again aged in various chemical and physical environments. From the Table it is obvious we are not observing any tremendous decreases in F as was observed for the initial Exxon test piece. This may be due to the severity of the conditions involved with the Exxon test piece.

<b>Sample ID</b>	<b>Visual Form</b>	<b>%C,%H, %N,%F</b>	<b>Exposure</b>
<b>T-28 Coflon</b>	Light Brown	37.74, 3.23, ,0.01, 58.99	6 days fluid A, 140°C vapor pressure
<b>T-29 Tefzel</b>	White	37.18, 2.75, 0.05, 59.61	6 days fluid A, 140°C vapor pressure
<b>T-30 Coflon</b>	White Porous	37.86, 3.18, 0.03, 56.36	13 days Fluid A, 140°C vapor pressure
<b>T-31 Coflon</b>	White Porous Foam ≈ 10PCF	38.02, 3.13, 0.03, 58.18	13 days Fluid A, 140°C vapor pressure
<b>T-36 Coflon</b>	Brown Wax	58.39, 8.55, 0.51, 11.84	13 days Fluid A, 140°C vapor pressure in glass ended cell, residue from evaporated fluid at end of test
<b>T-41 Coflon Skin</b>	Dark Brown Skin	41.80, 3.42, 0.70, 52.91	4 weeks Fluid F, 120oC, 5kpsi, tested in gas phase
<b>T-42 Tefzel</b>	White Inner	36.28, 2.71, 0.04, 60.83	4 weeks Fluid F, 120oC, 5kpsi, tested in gas phase
<b>T-52 Tefzel</b>	White	36.22, 2.81, 0.01, 60.82	4 weeks (gas phase) Fluid F, 120oC, 5kpsi, subsequent permeation in methane at 140oC 5ksi
<b>T-53 Coflon</b>	Dark Brown Skin White Inner	39.62, 3.69, 0.03, 56.37	4 weeks (gas phase) Fluid F, 120oC, 5kpsi, subsequent permeation in methane at 140oC 5ksi

Very few changes either elementally or visually were observed for the Tefzel material. It is commonly believed that the darkening of the Coflon is associated with dehydrohalogenation. We observed test specimens black or very dark in color that exhibited only minor changes in elemental composition. Considering the results it is imperative to test further samples under increasingly aggressive conditions to determine when dehydrohalogenation becomes a major mode of degradation.

## **1.2 Dynamic Mechanical Analysis of Coflon Pipe and Computer Accelerated Life Development Software**

Dynamic Mechanical Analysis (DMA) of the Coflon material was carried out and is contained in Appendix 3. The initial flexural modulus was in good agreement with previously published information. Upon heating the flexural modulus drops to a low of 268 MPa. After which it was noted that the flexural modulus increased to 312 MPa. We believe that the increase is due to the deplasticization. We also noted that the tan delta increases (0.105) until the sample reaches 100°C and then decreases to (0.100). After a long period we again see the tan delta rise during deplasticization to (0.102), as the sample becomes more lossy.

We also examined the viscoelastic response of Coflon using DMA while the sample was immersed in methanol at room temperature. During the first eighteen hours of immersion we notice a decrease in the flexural modulus indicating plasticization with methanol had occurred in the Coflon. The flexural modulus of the Coflon decreased over thirteen percent in the initial eighteen hours while immersed in methanol.

The sample was then removed from methanol and the dynamic mechanical analysis was continued in air for the next twenty two hours. We noticed an increase in the flexural modulus to a higher level than the initial value. The initial flexural modulus value had increased 1.3% at the end of twenty-two hours from the initial value. The increase in the flexural modulus at the end of the test could be due to the leaching of the plasticizer, an increase in crystallinity, or both of these processes.

A computer program has been written for construction of an accelerated test plan for thermoplastic pipe. The duty profile for the pipe is input and an activation energy is also included for the principle mode of degradation finally an acceleration factor is calculated for specific environmental exposures. We will present the program at the meeting and discuss what other exposures or information is needed from the clients to complete the computer program. The aspiration of the program is to assist the project clients in developing a comprehensive composite unit accelerated life prediction test plan based on the mission profile as well as user defined laboratory testing conditions. A complete mission profile for the thermoplastic pipe is necessary for the program. This software program upon completion will hopefully also allow the clients to forecast a commensurate age for thermoplastic pipes that have been in service and exposed to variant environmental conditions.

## **1.3 Differential Scanning Calorimetry of Aged Coflon and Tefzel**

We conducted DSC on many of the forwarded samples of Tefzel and Coflon. The DSC results of the Coflon materials indicated considerable variability in crystallinity depending on aging conditions. We generally observed an increase in the heat of fusion as a function of heating time and temperature. Some of this effect may be attributable to the loss of plasticizer. The residue from the evaporated fluid after 14 days exposure to fluid A at vapor pressure indicates the presence of three compounds with vastly different melt temperatures from Coflon. The three compounds are possibly plasticizer, the solvent, and the decomposed polymer. Based on the DSC information we are not observing any change from the  $\alpha$  form to the  $\beta$  crystalline form. The  $\beta$  form has a melting point of 190 C. We are clearly observing some changes in the relative amount of crystallinity of the Coflon based upon exposure. The DSC results for the samples, the heat of fusion's, the exposure conditions, and percentage crystallinity are given below.

Sample Identification #	Exposure Conditions	Heat of Fusion	Percentage Crystallinity
Coflon Baseline	Not aged	67.59 J/g	64.6%
Tefzel Baseline	Not Aged	39.00 J/g	
T-26 Coflon	14 days Fluid B, 140°C 5,000psi	77.96 J/g	74.5%
T-30 Coflon	13 days Fluid A, 140°C vapor pressure	48.30 J/g	46.2%
T-31 Coflon	13 days Fluid A, 140°C vapor pressure	44.23 J/g	42.3%
T-32 Coflon	13 days Fluid A, 140°C vapor pressure	67.16 J/g	64.2%
T-36 Residue from evaporated fluid at end of test Coflon	13 days Fluid A, 140°C vapor pressure	3 peaks none near the 150-160°C melt onset of Coflon	0
T-29 Tefzel	6 days fluid A, 140°C vapor pressure	51.50 J/g	32.1 % increase in crystallinity over unaged
T-33 Coflon	13 days Fluid A, 140°C vapor pressure	30.54 J/g	29.2%

Using the methods cited in the literature we dissolved PVDF in hot dimethylacetamide (DMAC) and cast a film drying the film at  $\approx 70^\circ\text{C}$  for 16 hours. We next performed FTIR and DSC analysis of the resultant film. Films were prepared for virgin PVDF, and aged PVDF (T-28) and compared with a sample of PVDF not dissolved and cast from PVDF. Solution of the PVDF into boiling DMAC was effected within thirty minutes. The DSC analysis (Appendix 1) and the FTIR analysis (Appendix 2) indicate some differences in  $T_g$  and the integration areas of the two DSC peaks around  $160^\circ\text{C}$

This could indicate some conversion from the alpha or beta form to the gamma form with resultant permeation and physical property changes. We also performed a derivative analysis of the DSC data in order to clearly resolve the peaks in the analyses.

#### 1.4 Fourier Transform Spectroscopy and Gas Chromatography/Mass Spectroscopy

We investigated accelerated high temperature aging of the Coflon material and analyzed the liquid exudate using gas chromatography coupled with mass spectrometry. The mass spectrum of the liquid exudate is provided in Appendix 5. The database search base provided the best match with a dibutyl ester of decanedioic acid. The search routine can only match those compounds catalogued in the library that is approximately seven hundred thousand compounds.

We have conducted FTIR analyses of Coflon and Tefzel test pieces after aging for selected times, temperature, and exposure conditions (Appendix 2). We are interested in the chemical functionality's or changes the samples exhibited upon aging. We were also interested whether the recrystallized PVDF deposits exhibited a change from the  $\alpha$  or the type 2 form to the  $\beta$  or type 1 crystalline form when the PVDF dissolved under strain. Below is a table that summarizes the results of the FTIR analyses conducted to date.

Sample Identification #	Exposure Conditions	Visual Appearance and Observations	Chemical Analysis and Observations
T-32 Coflon	14 days at 140°C	Solid retrieved by evaporation from fluids after exposure	Broad hydroxy functionality, decreased carbonyl absorption
T-36 Coflon	Residue from evaporated fluid A 140°C vapor pressure exposure with Coflon	Mixture of solids in fluid and retrieved from fluids after exposure, brown waxlike substance	Polyethylene or polypropylene type spectrum, hydrocarbon type
T-31 Coflon	Collection of deposited Coflon 13 days Fluid A exposure 140°C vapor pressure	Spongy residue deposits from bottom of cell: white, porous, extremely physically degraded	Splitting of 1200cm <sup>-1</sup> peak, decreased carbonyl absorption
T-29 Tefzel	Tefzel, 6 days fluid A 140°C vapor pressure exposure	White, translucent, good integrity	Few minor changes
T-35 Coflon	Debris collected from pressure cell after 14 days fluid A 140°C vapor pressure test of Coflon	Film from cell walls, light brown like paper	Hydroxy functionality evident, decreased carbonyl



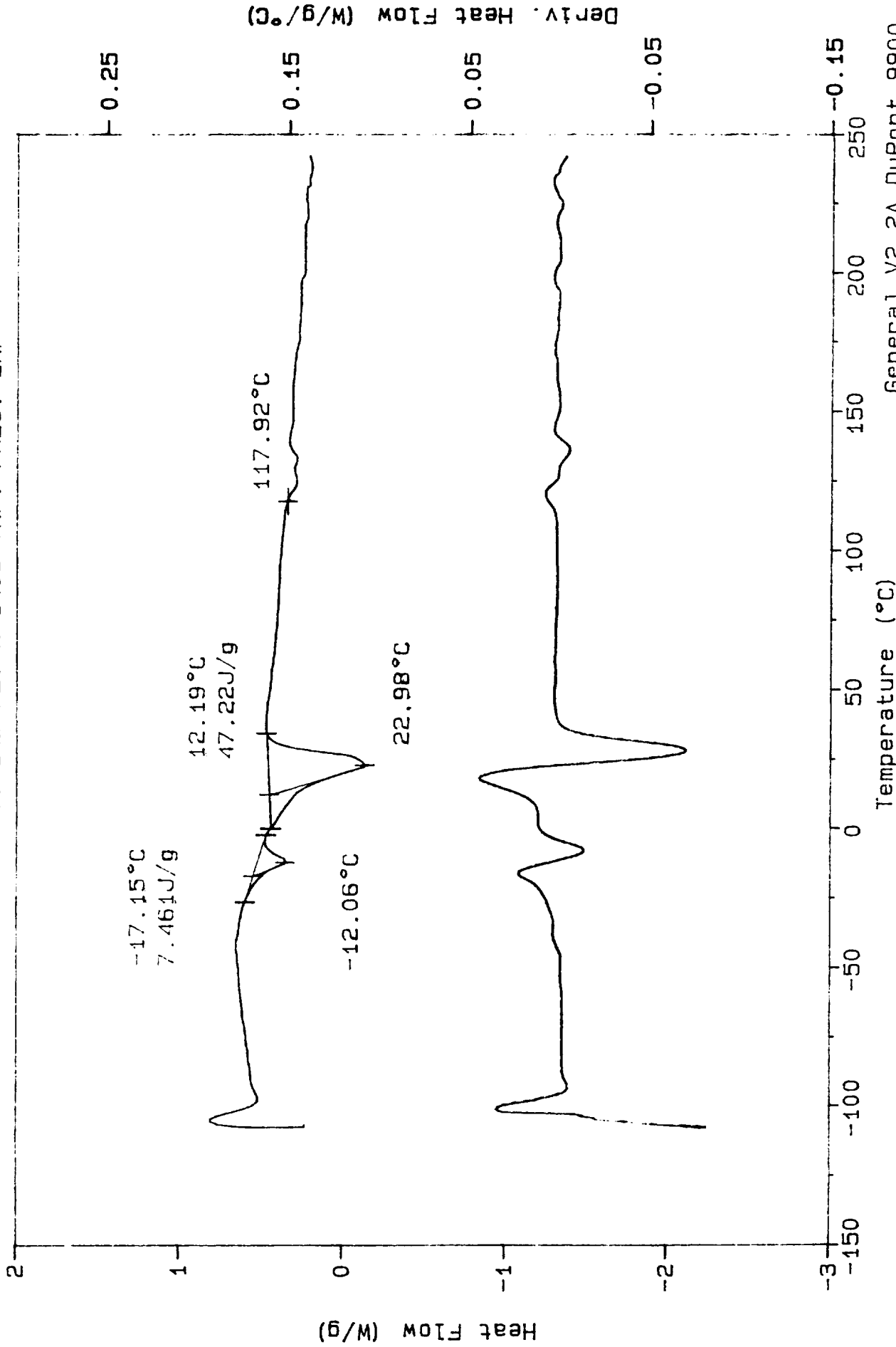
<b>T-30 Coflon</b>	Remains of Coflon 4 point bend	White spongy porous shell of sample fractured during test	Decreased carbonyl absorption
<b>T-26 Coflon</b>	Sample tested at 23oC, after 14 days in fluid B at 140°C 5000psi	White, opaque, with good integrity, ductile	Decreased Carbonyl absorption, new peaks at lower wavenumbers indicating increased hydrocarbon presence
<b>T-32 Coflon</b>	Residue of filtered methanol from 13 days exposure with Coflon sample 140°C vapor pressure	Extremely porous and brittle light brown material	Broad hydroxy absorption, decreased carbonyl absorption
<b>T-34 Coflon</b>	Unstrained Coflon bar fluid A at 140°C vapor pressure for 14 days	Dark skin to material, good physical integrity	Decreased carbonyl absorption, broad peaks at high wavenumbers

### **1.5 Appendix One- DSC Results**

Sample: CAPP T-36 COFLON  
Size: 8.4000 mg  
Method: 10R250  
Comment: RESIDUE FROM EVAP FLUID AFT. 14D FL. A 140C VAP. PRES. EXP

# DSC

File: CAP-DSC79.01  
Operator: RR  
Run Date: 7-Apr-95 10:51



Sample: T-33 COFLON

Size: 6.3000 mg

Method: 10R300

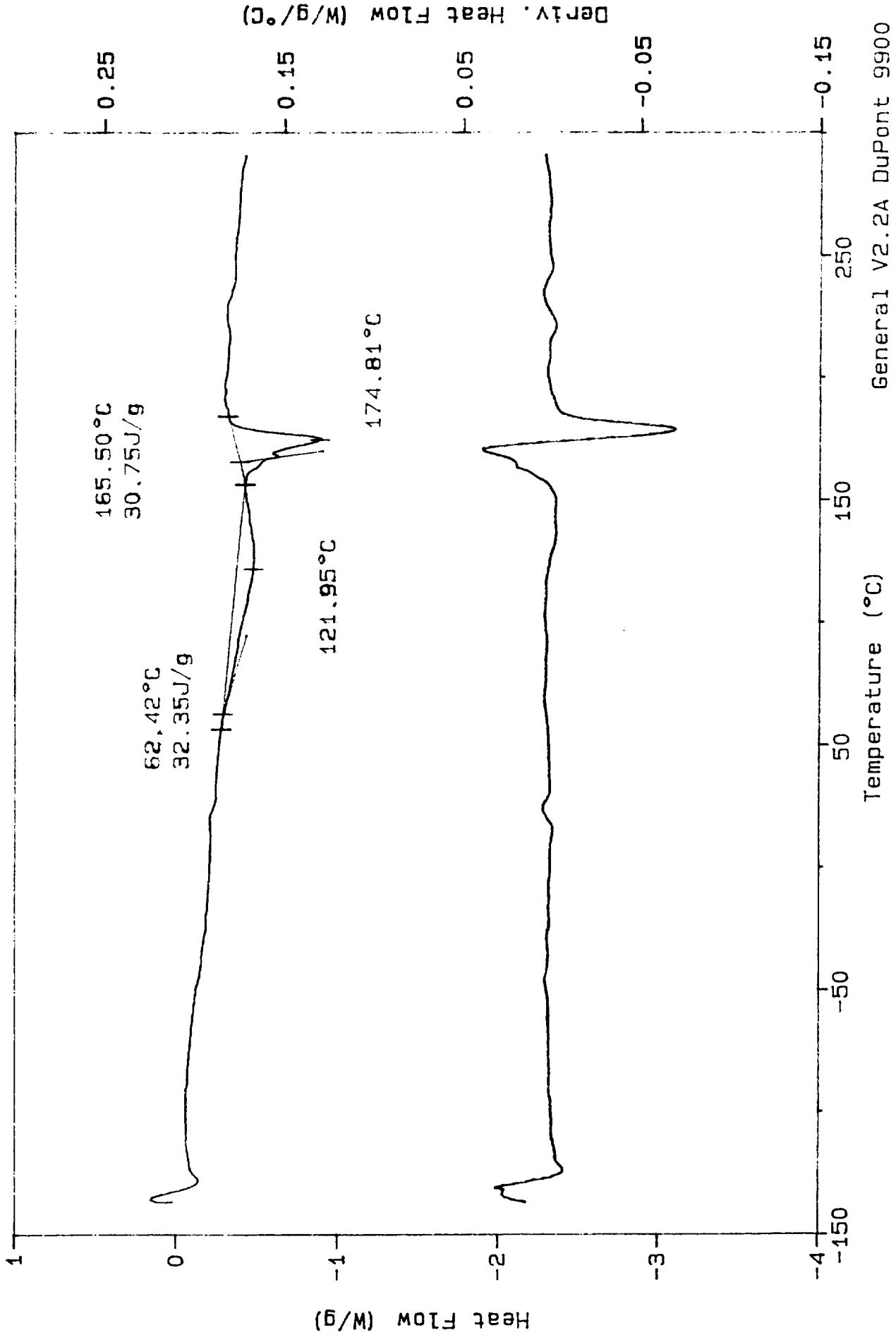
Comment: 4 PT BND 12% STRAIN FLUID A 140C VAP. PRESS.14D

File: CAP-DSC79.08

Operator: RR

Run Date: 1-May-95 14:58

# DSC



Sample: T32

Size: 2.5000 mg

Method: 10R250

Comment: RESIDUE FILTERED FROM METHANOL. 13D EXP COFLON 140C VAP PRESSURE

# DSC

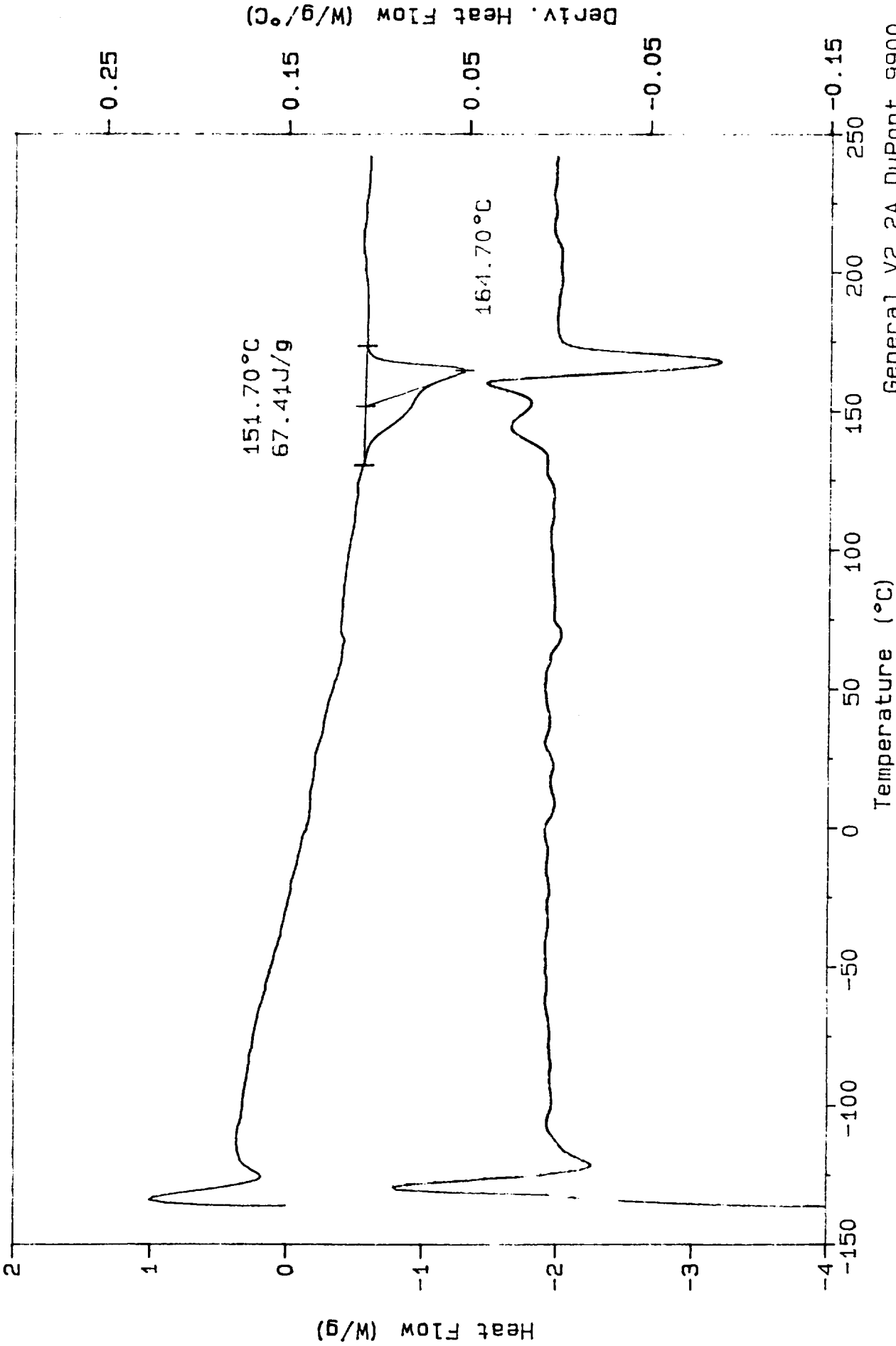
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Operator: RR

Run Date: 25-Apr-95 08:59

Method: 10R250

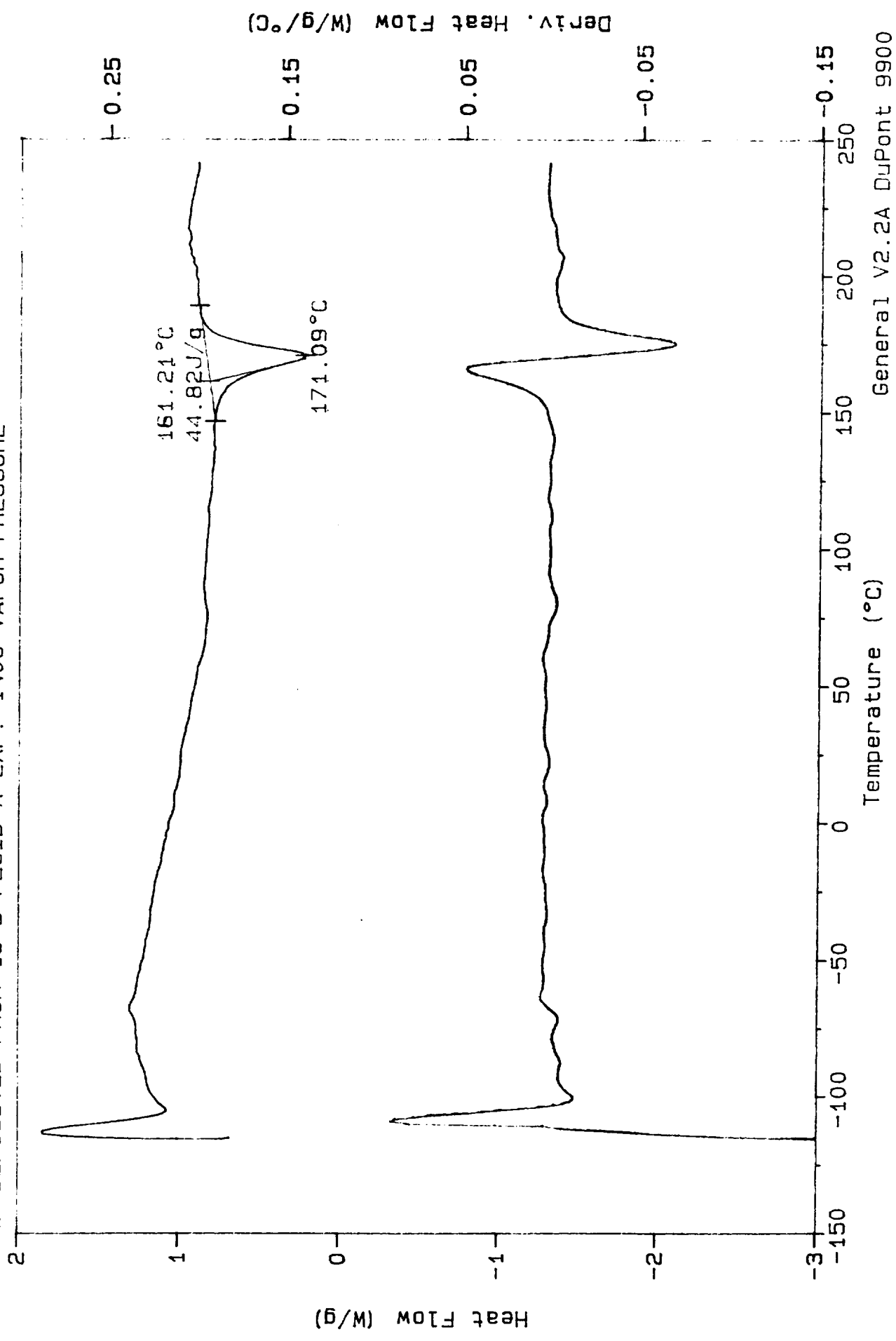
Comment: RESIDUE FILTERED FROM METHANOL. 13D EXP COFLON 140C VAP PRESSURE



Sample: CAPP T-31 COFLON  
Size: 4.2000 mg  
Method: 10R250  
Comment: DEPOSITED FROM 13 D FLUID A EXP. 140C VAPOR PRESSURE

# DSC

File: CAP-DSC79.02  
Operator: RR  
Run Date: 7-Apr-95 13:01



Sample: T-30

Size: 2.4000 mg

Method: 10R250

Comment: REMAINS OF COFLON 4 PT BEND AFTER 13D IN FLUID A AT 140C VAP PRS

# DSC

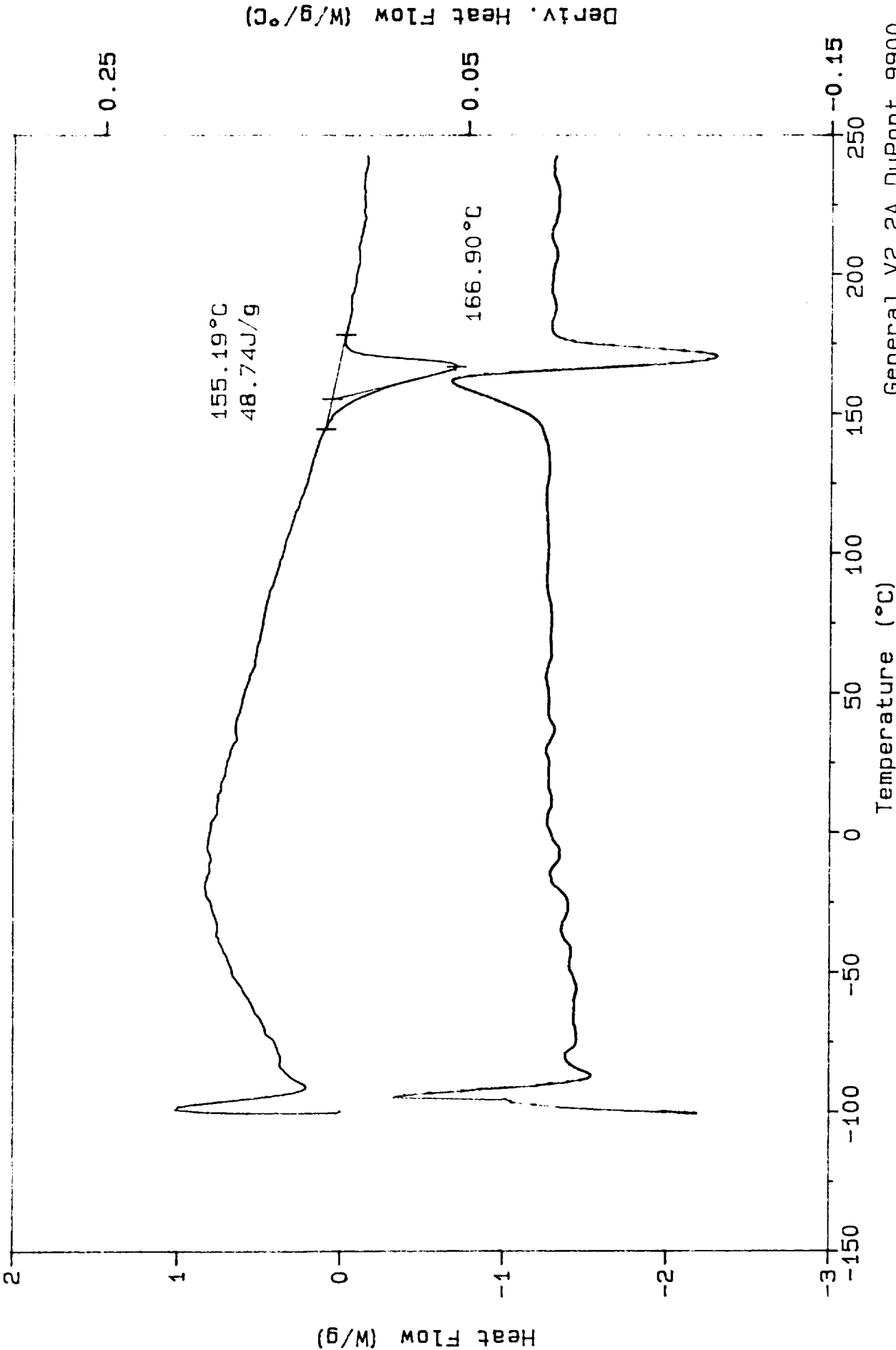
File: CAP-DSC79.03

Operator: RR

Run Date: 13-Apr-95 14:50

Method: 10R250

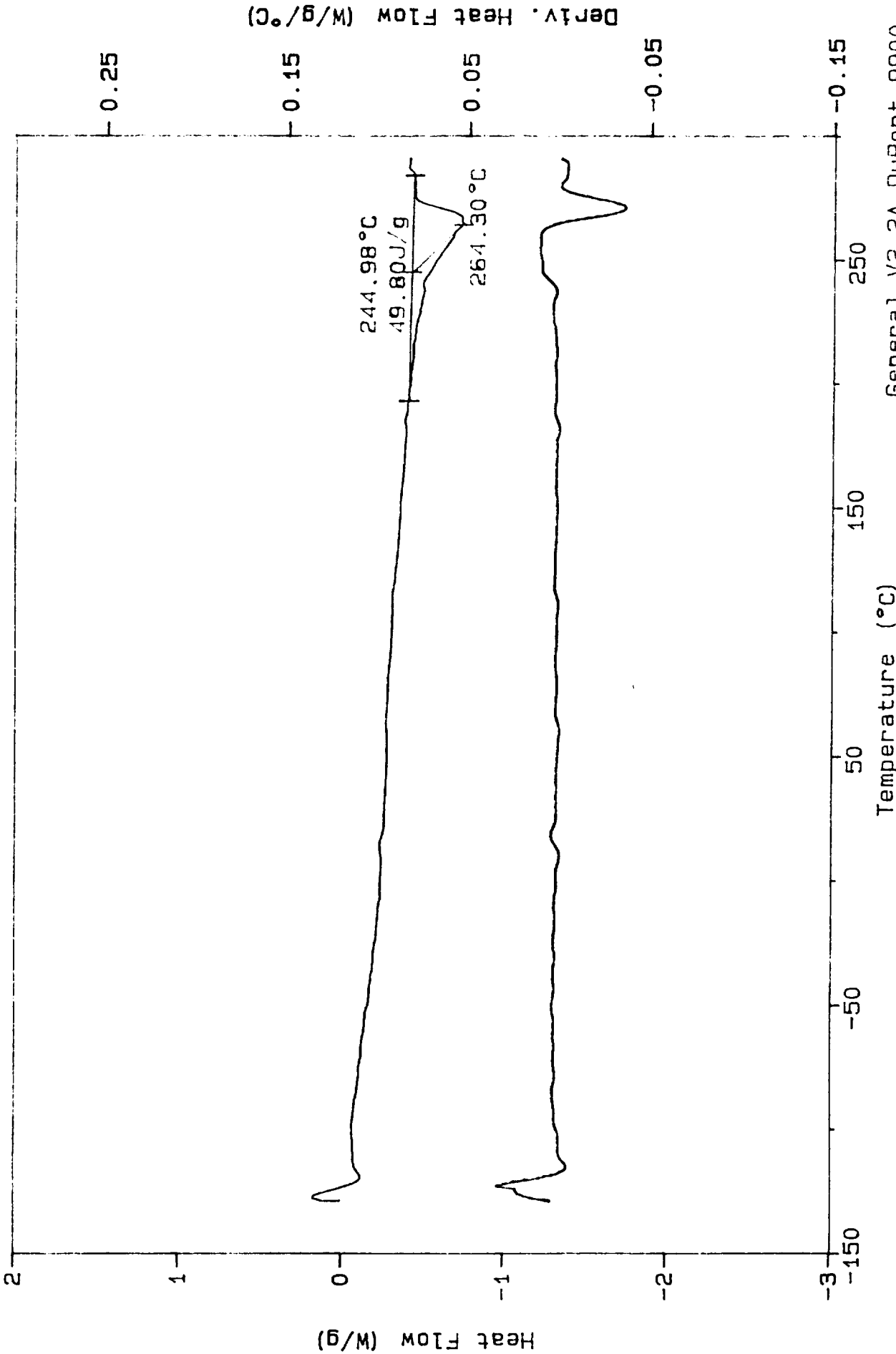
2



Sample: T-29 TEFZEL  
Size: 5.9000 mg  
Method: 10R300  
Comment: 4 PT BND AFTER 6D IN FLUID A AT 140C VAP. PRESS.

# DSC

File: CAP-DSC79.07  
Operator: RR  
Run Date: 1-May-95 12:36

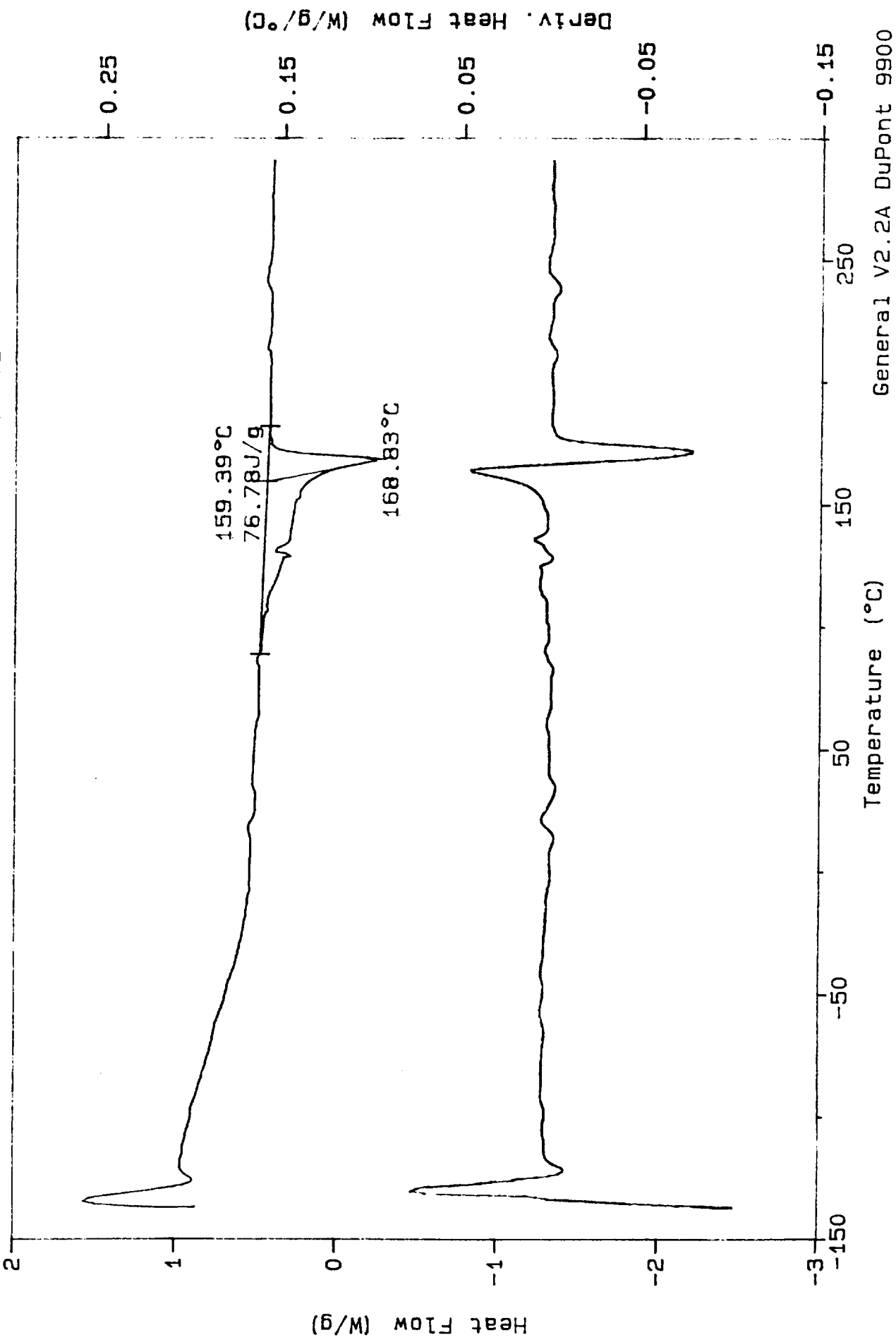




Sample: T-26 COFLON  
Size: 4.3000 mg  
Method: 10R300  
Comment: COFLON TESTED AT 23C AFT. 140 IN FLUID B AT 140C 5000 PSI

# DSC

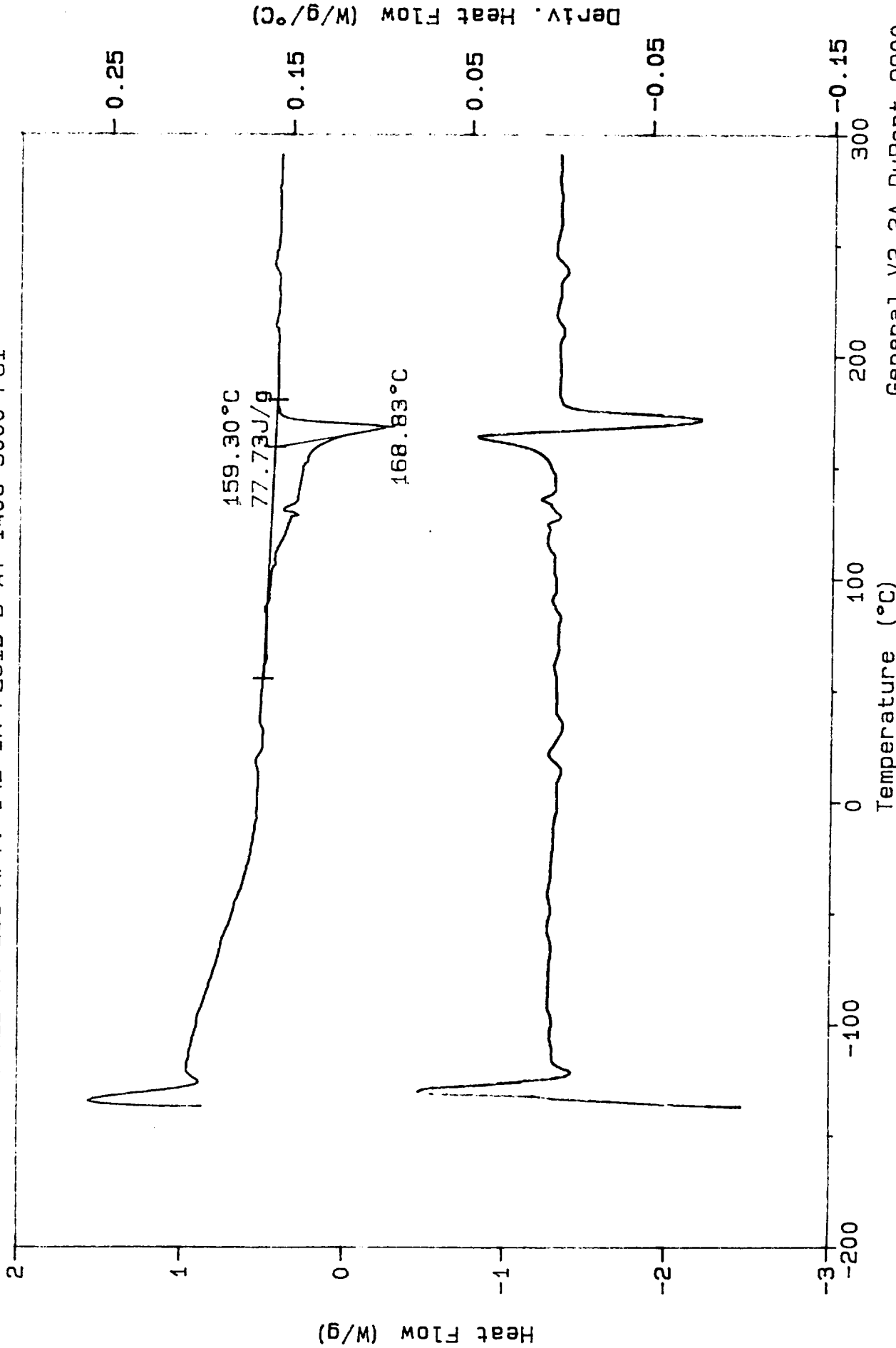
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Operator: RR  
Run Date: 1-May-95 11:19



Sample: T-26 COFLON  
Size: 4.3000 mg  
Method: 10R300  
Comment: COFLON TESTED AT 23C AFT. 14D IN FLUID B AT 140C 5000 PSI

# DSC

File: CAP-DSC79.06  
Operator: RR  
Run Date: 1-May-95 11:19



Sample: PVDF RECRYSTS. FROM DMAC (T-28)

Size: 1.3000 mg

Method: 10R250

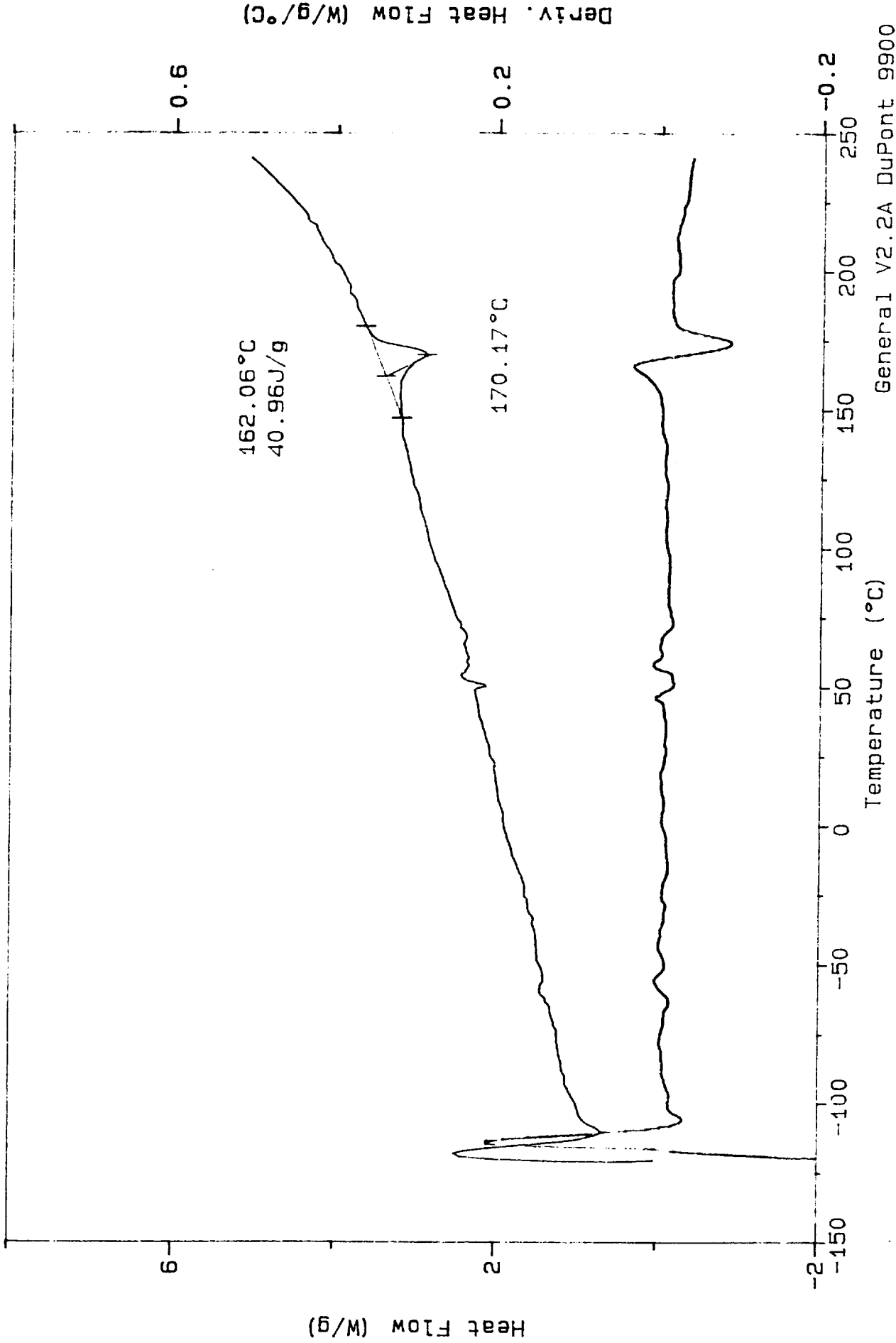
Comment: N2 PURGE

# DSC

File: CAPP-DSC87.02

Operator: RAR

Run Date: 31-May-95 10:46



Sample: PVDF RECRY. FROM DMAC (VIRGIN) DSC

Size: 1.0000 mg

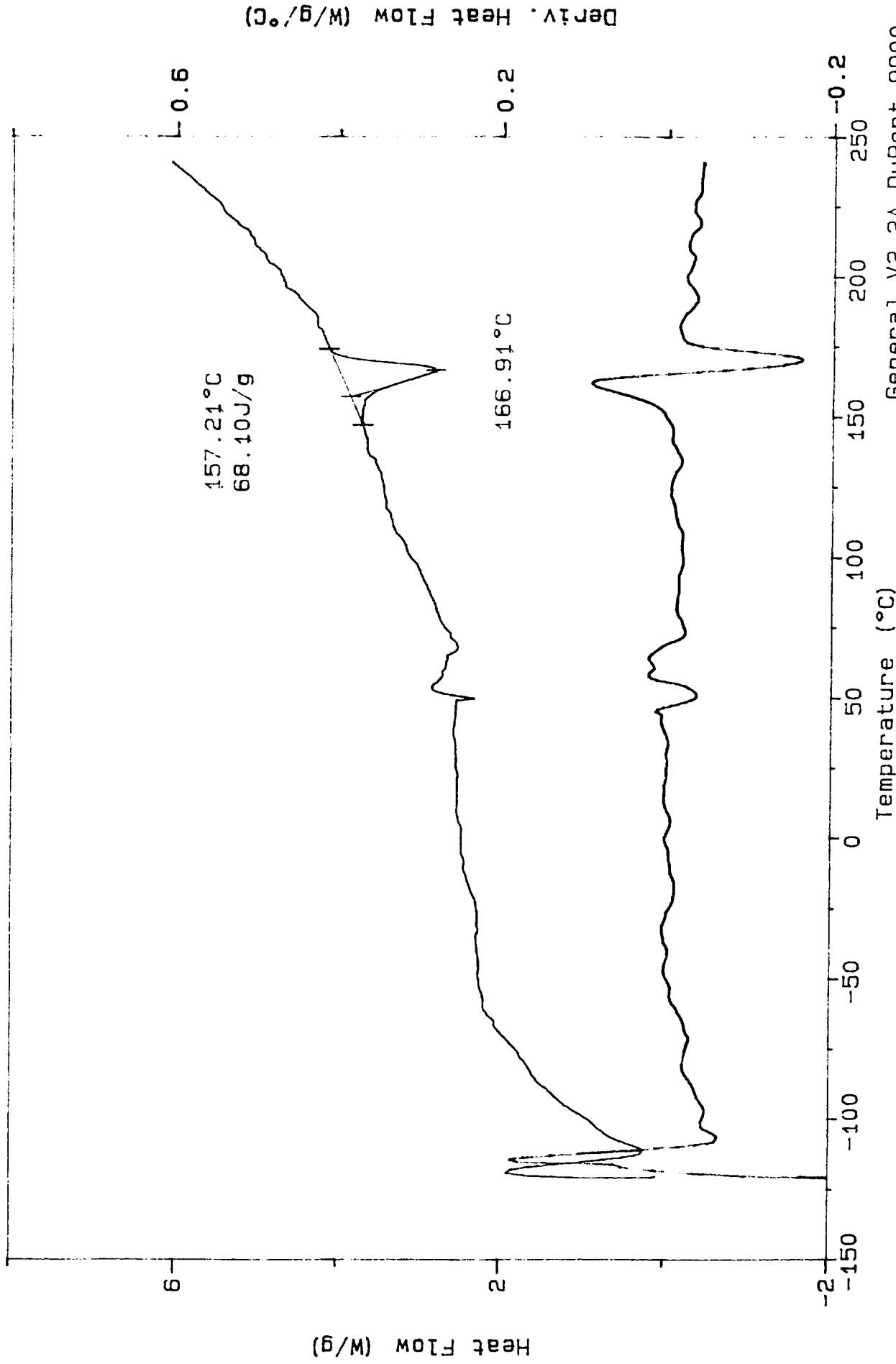
Method: 10R250

Comment: N2 PURGE

File: CAPP-DSC87.01

Operator: RAR

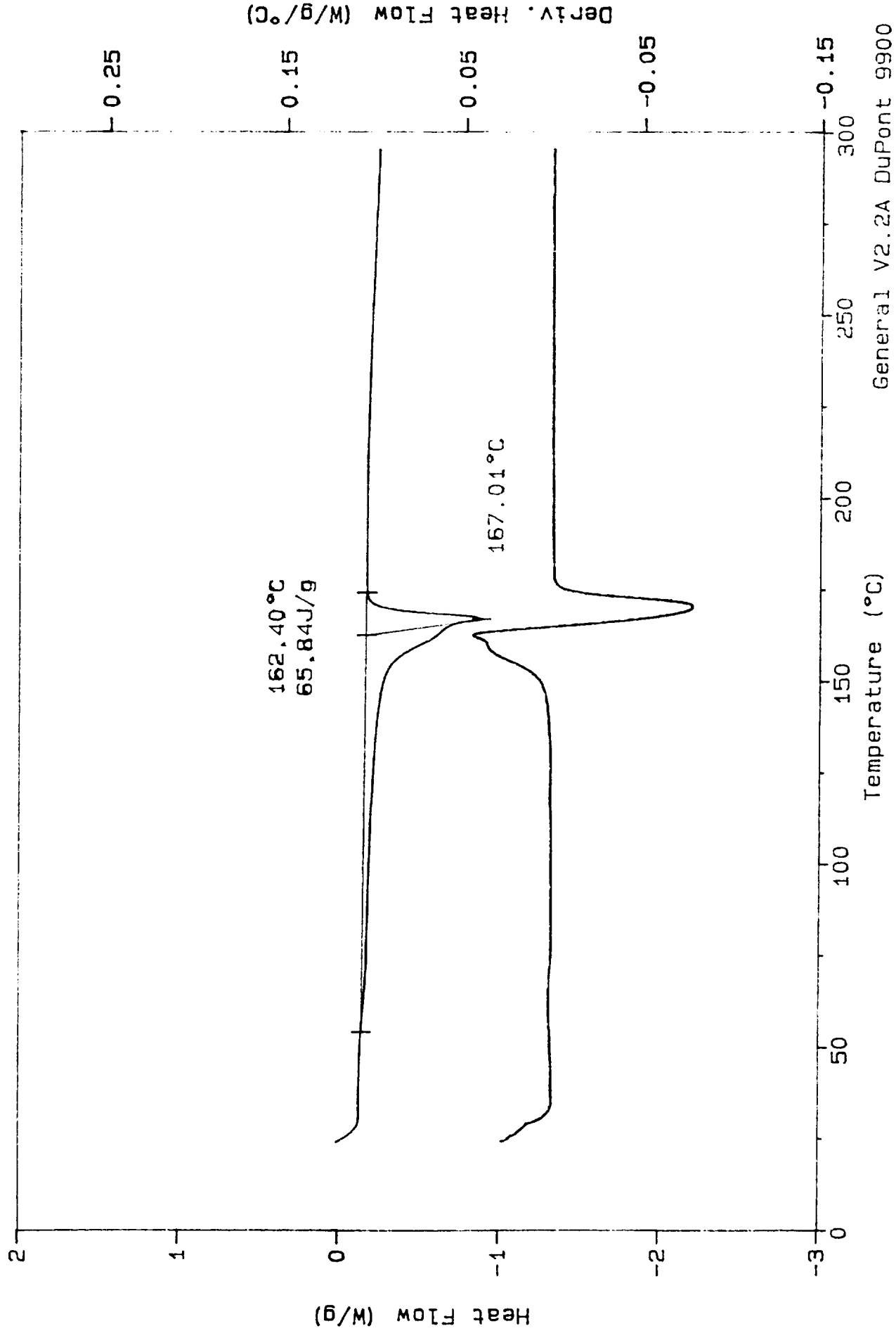
Run Date: 31-May-95 10:46



Sample: COFLON BASELINE NOT AGED  
Size: 3.3000 mg  
Method: 10R, 300

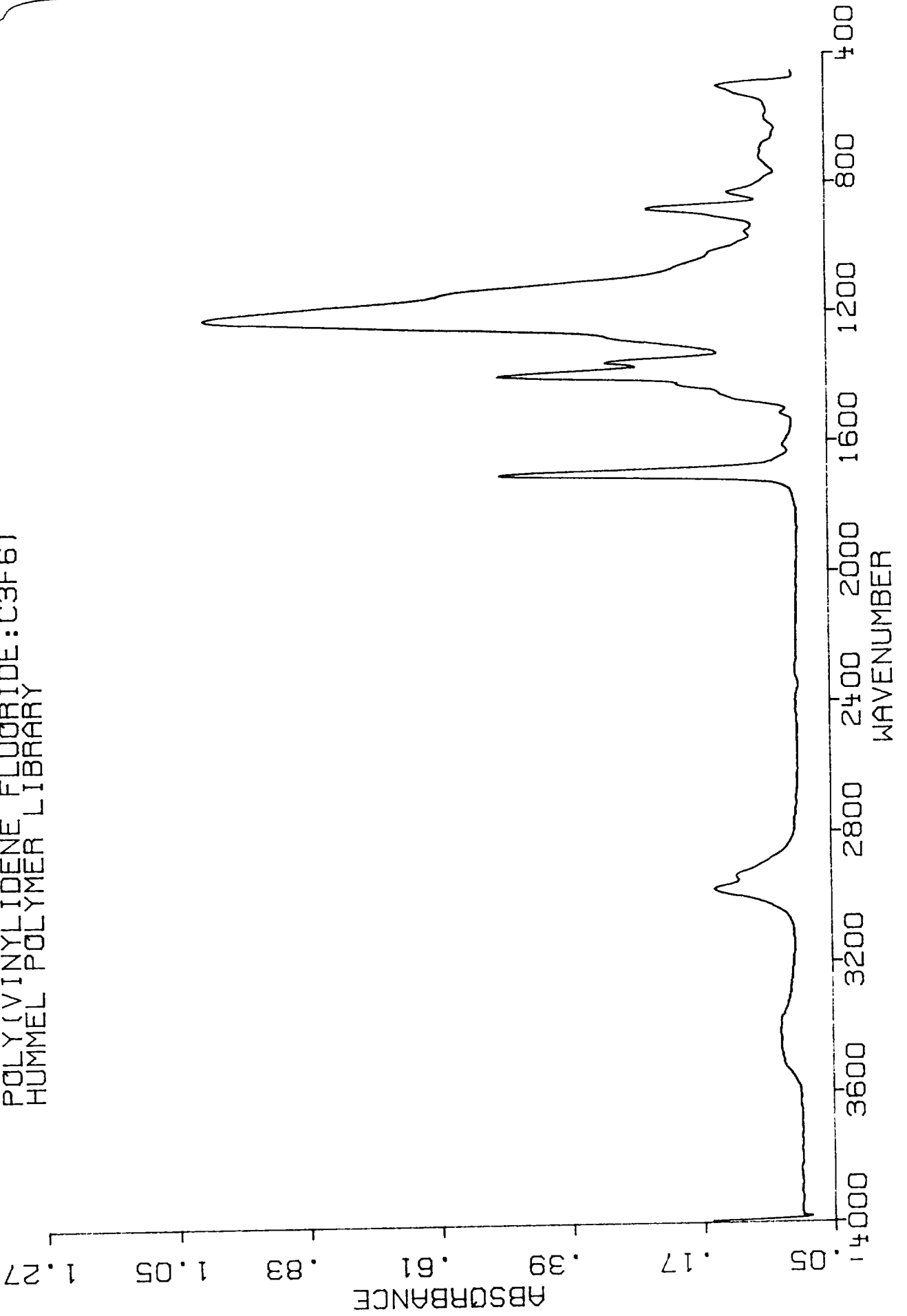
# DSC

File: A: COF-DSC01.08  
Operator: RR  
Run Date: 28-Apr--94 07:51

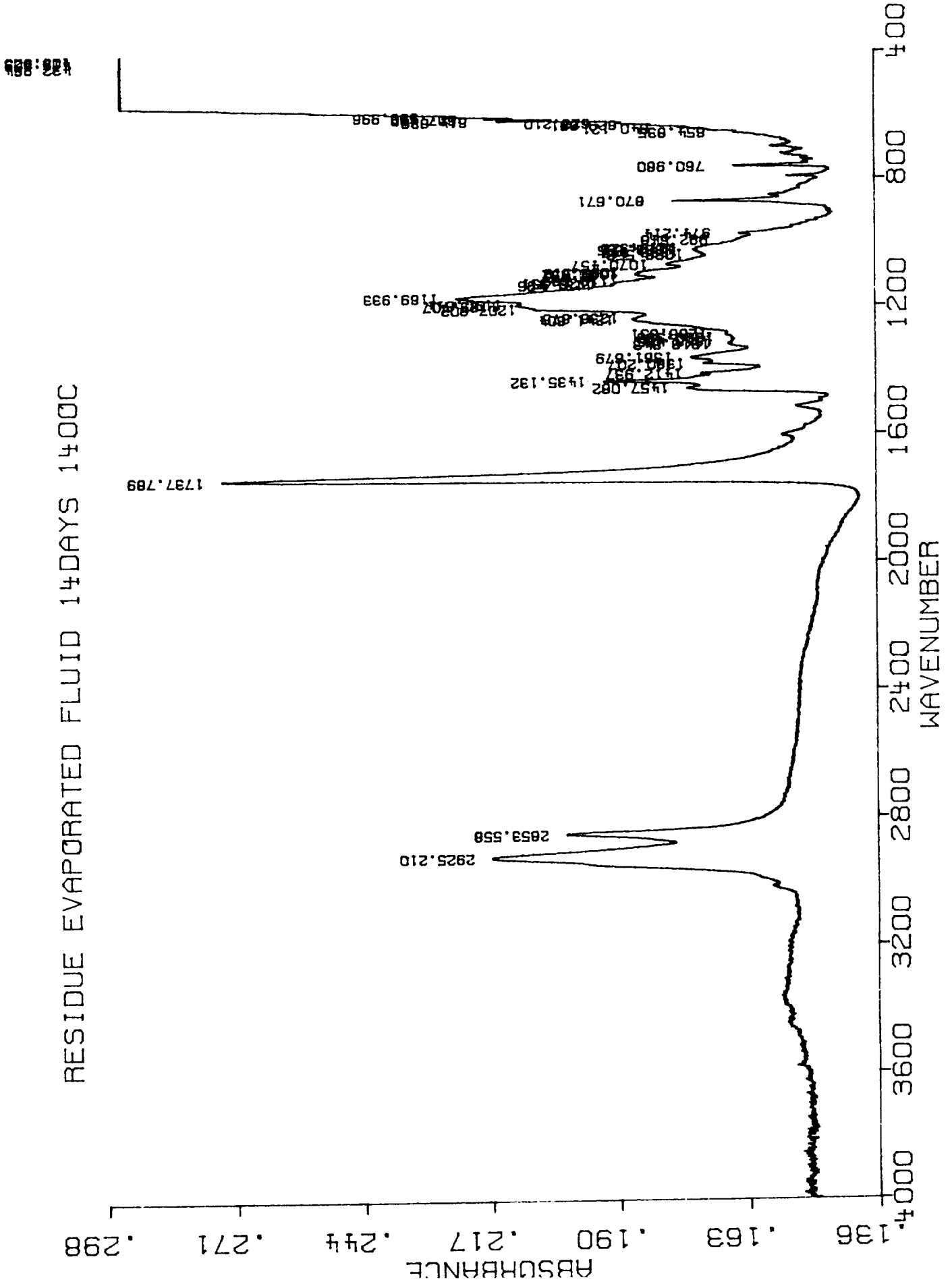


**1.6 Appendix Two- FTIR Results**

POLY(VINYLIENE FLUORIDE: C3F6)  
HUMMEL POLYMER LIBRARY

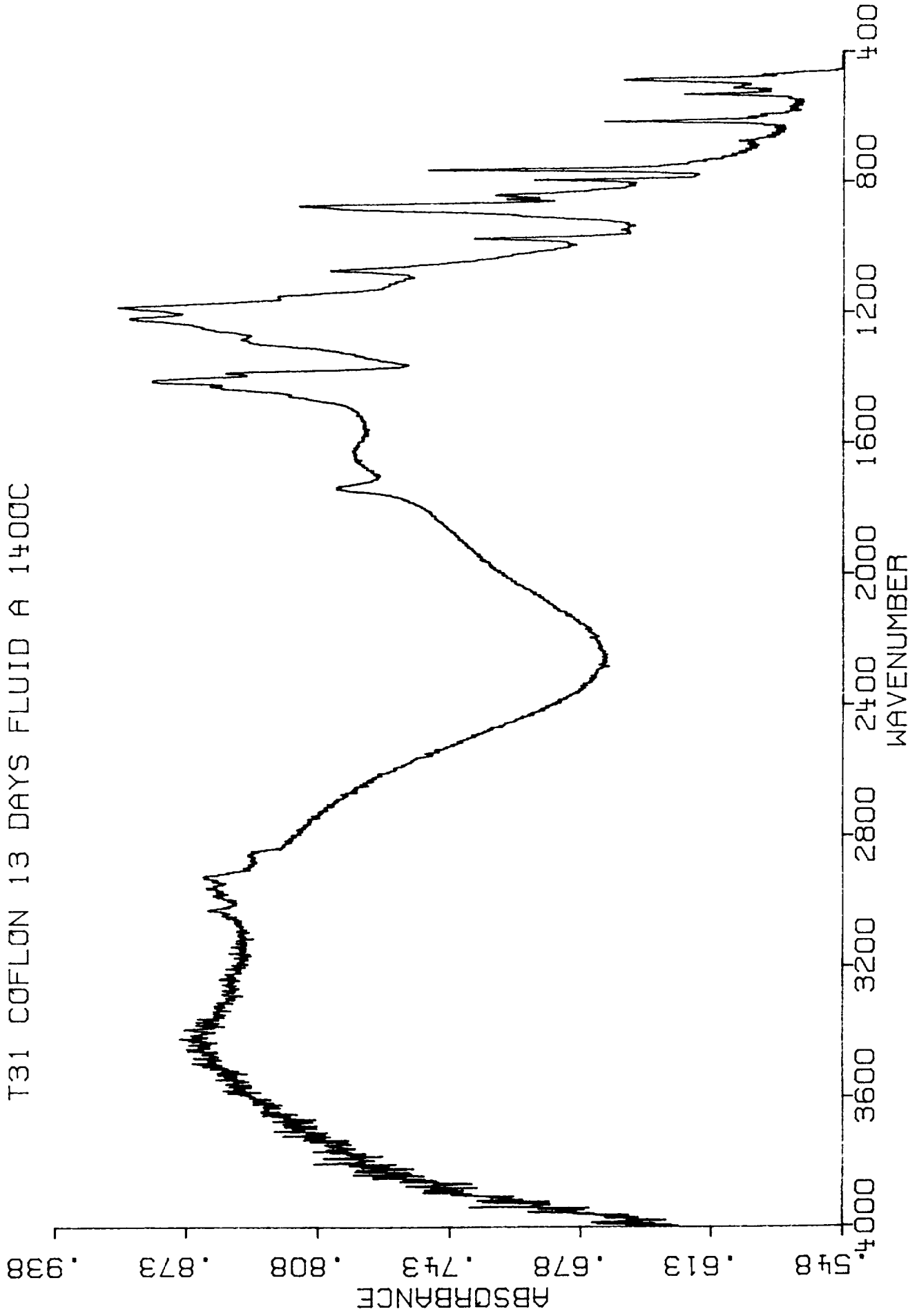


RESIDUE EVAPORATED FLUID 14 DAYS 1400C



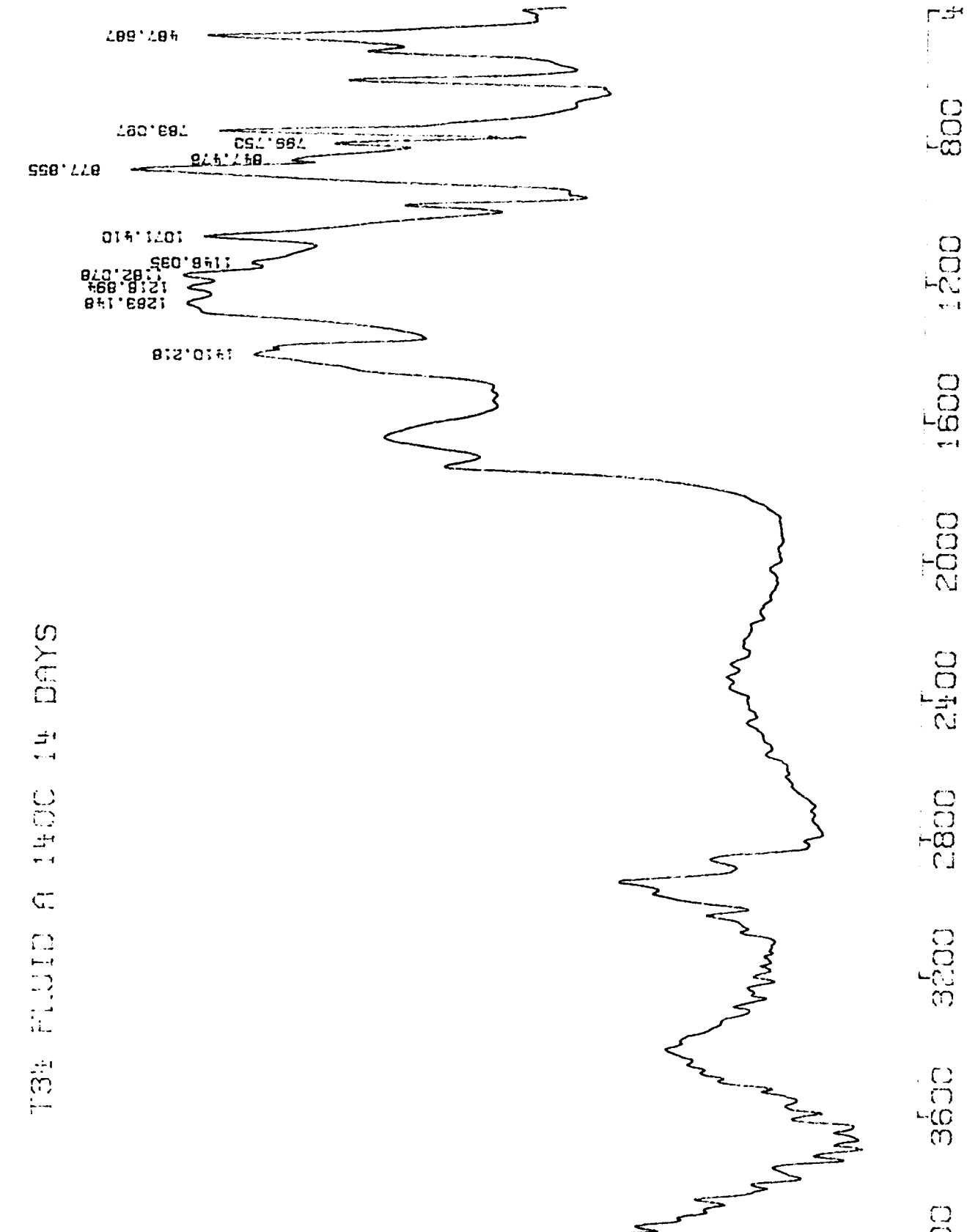


T31 COFLON 13 DAYS FLUID A 1400C



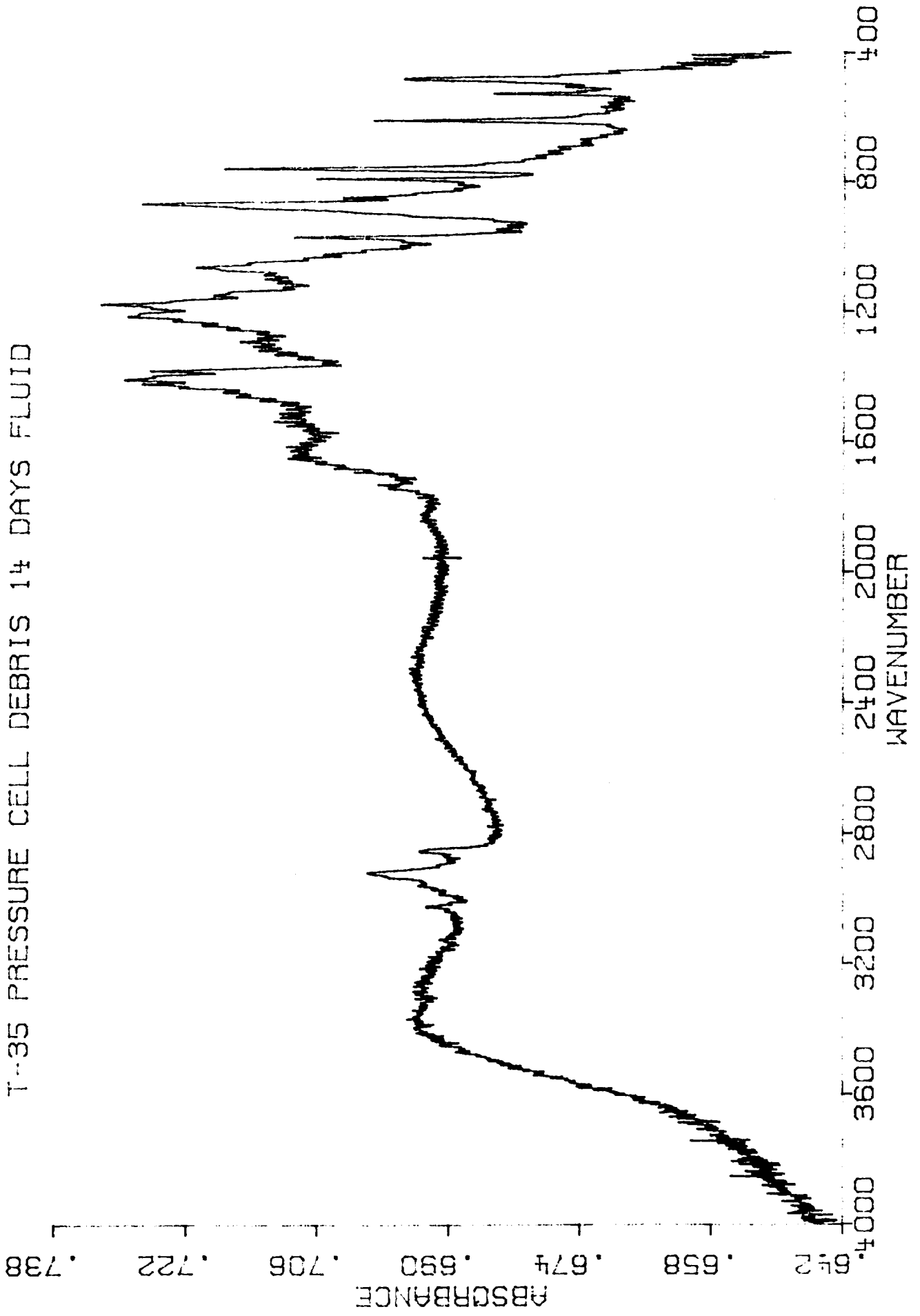
T34 FLUID @ 1400 14 DAYS

WAVENUMBER  
4000+ 3600 3200 2800 2400 2000 1600 1200 800 400

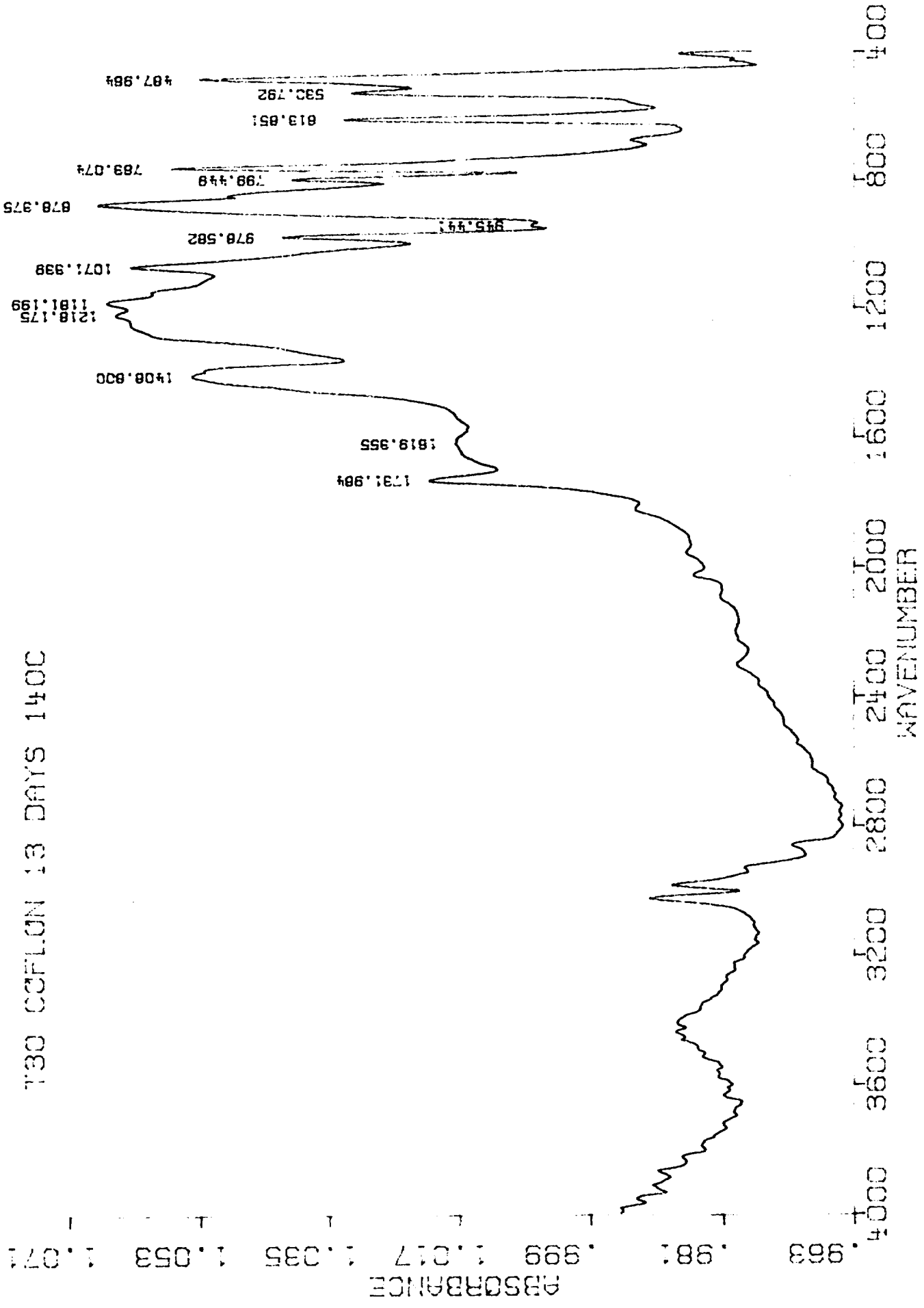


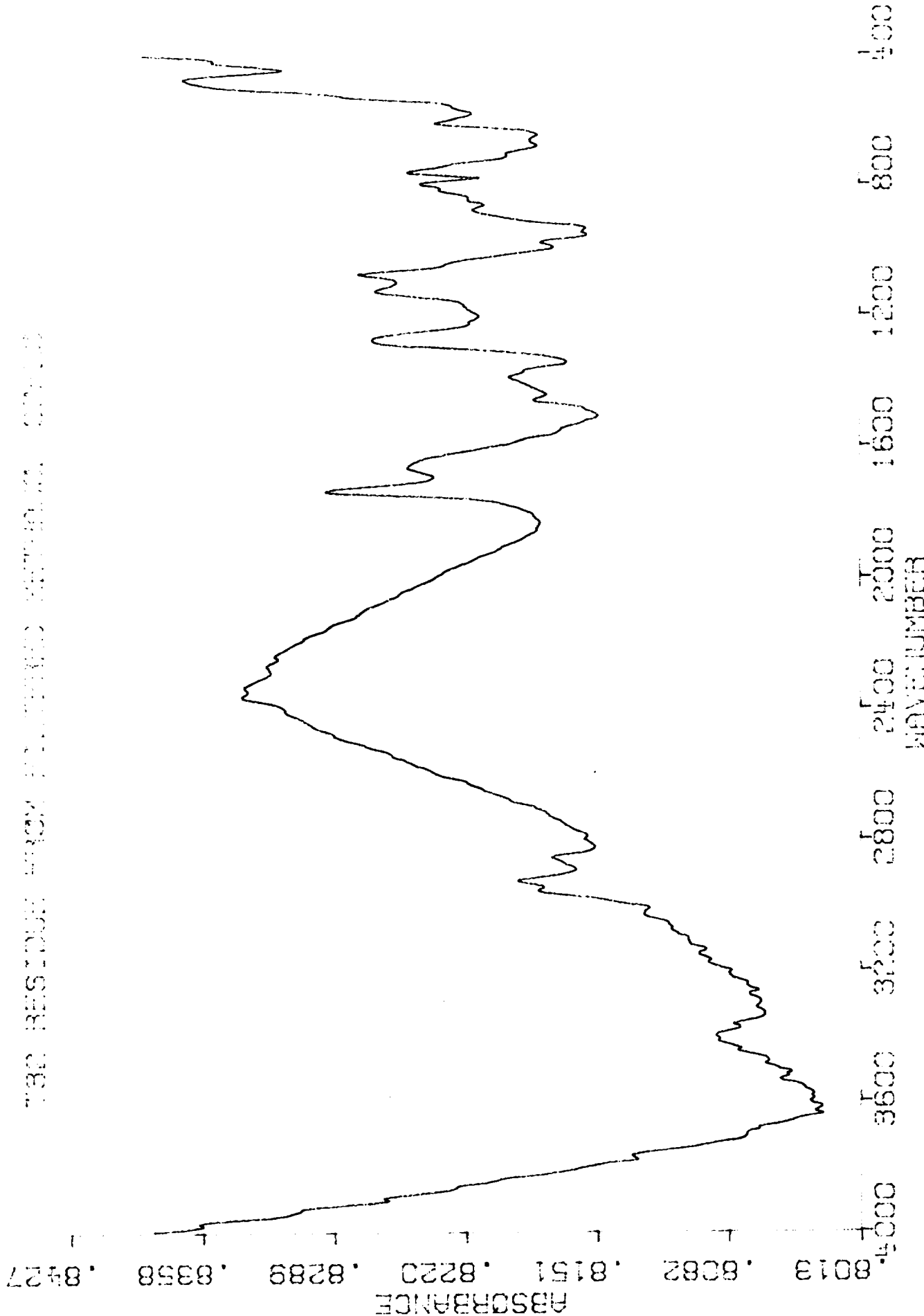
ABSORBANCE

T-35 PRESSURE CELL DEBRIS 14 DAYS FLUID



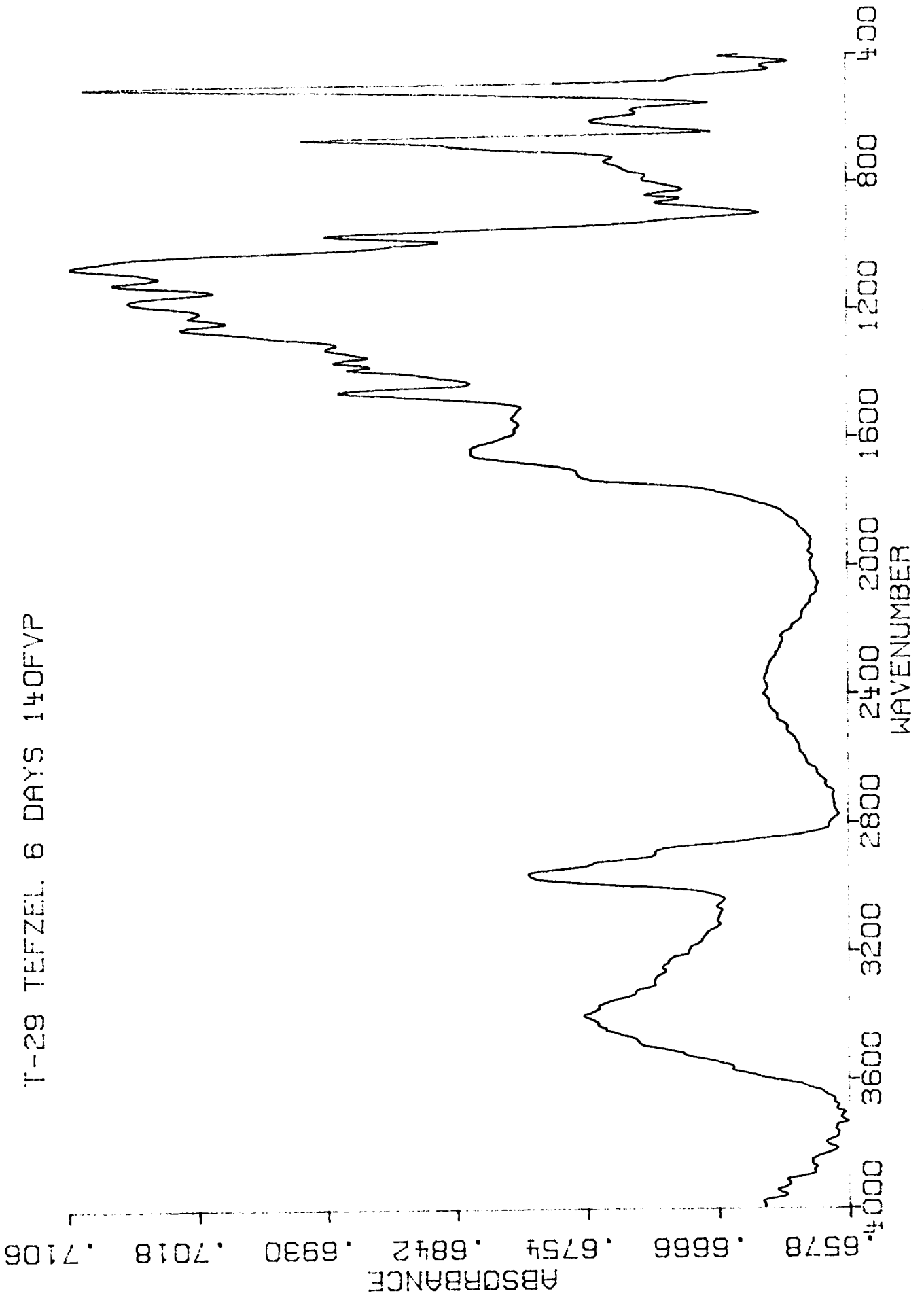
T30 CCFLON 13 DAYS 140C



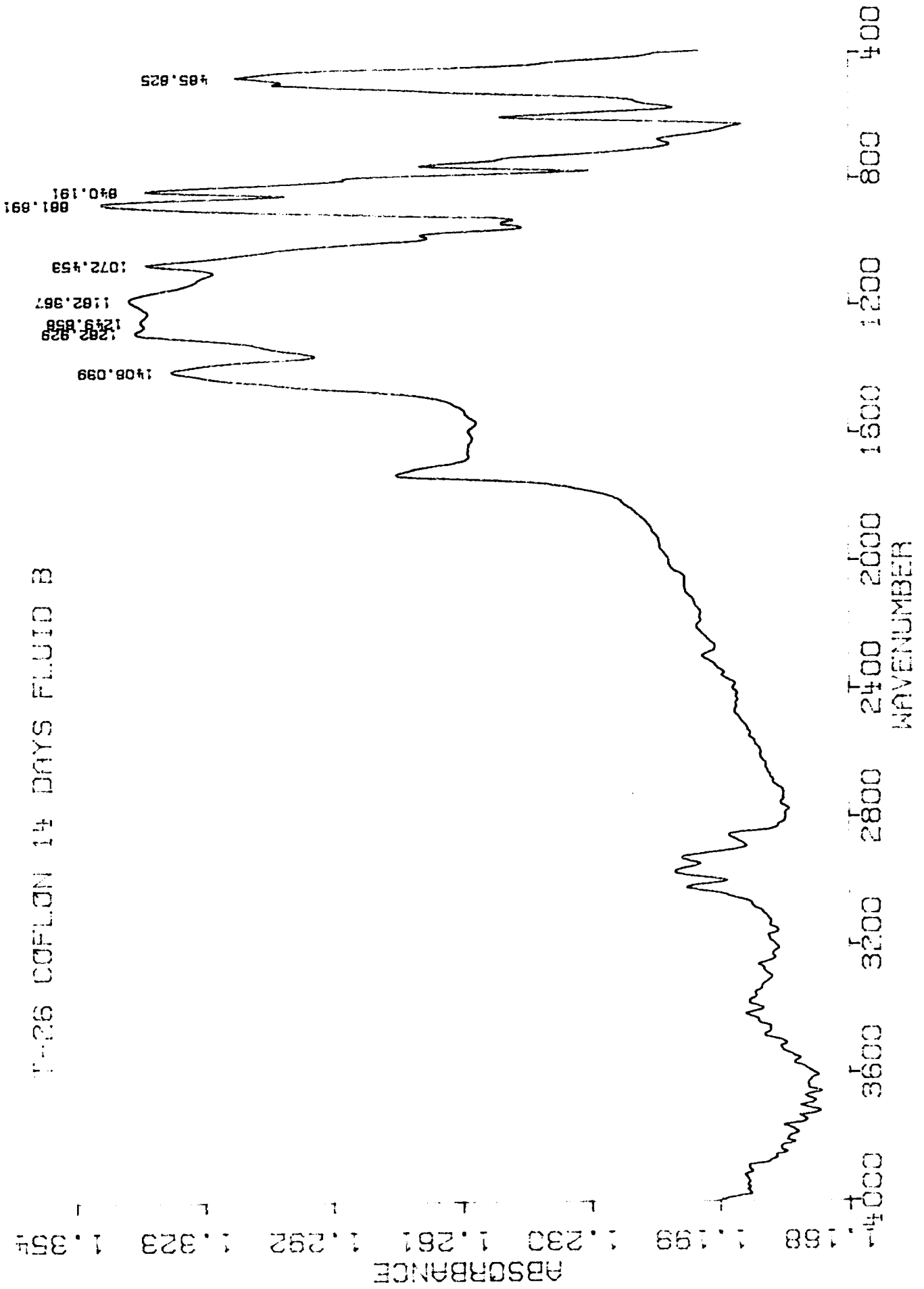


RESIDUE FROM POLYMERIZATION OF...

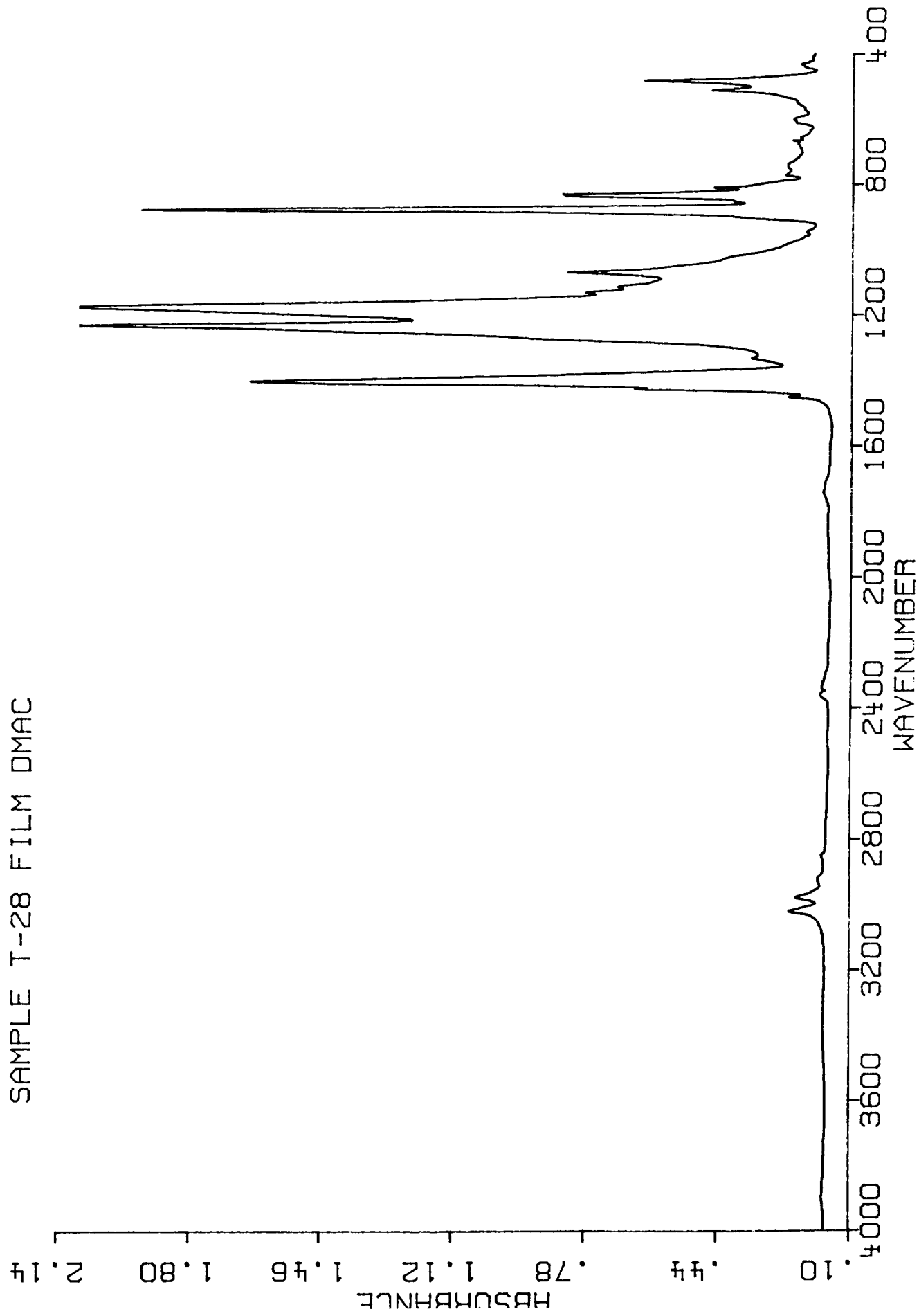
T-29 TEFZEL. 6 DAYS 140FVP



T-26 COFLON 14 DAYS FLUID B



SAMPLE T-28 FILM DMAC



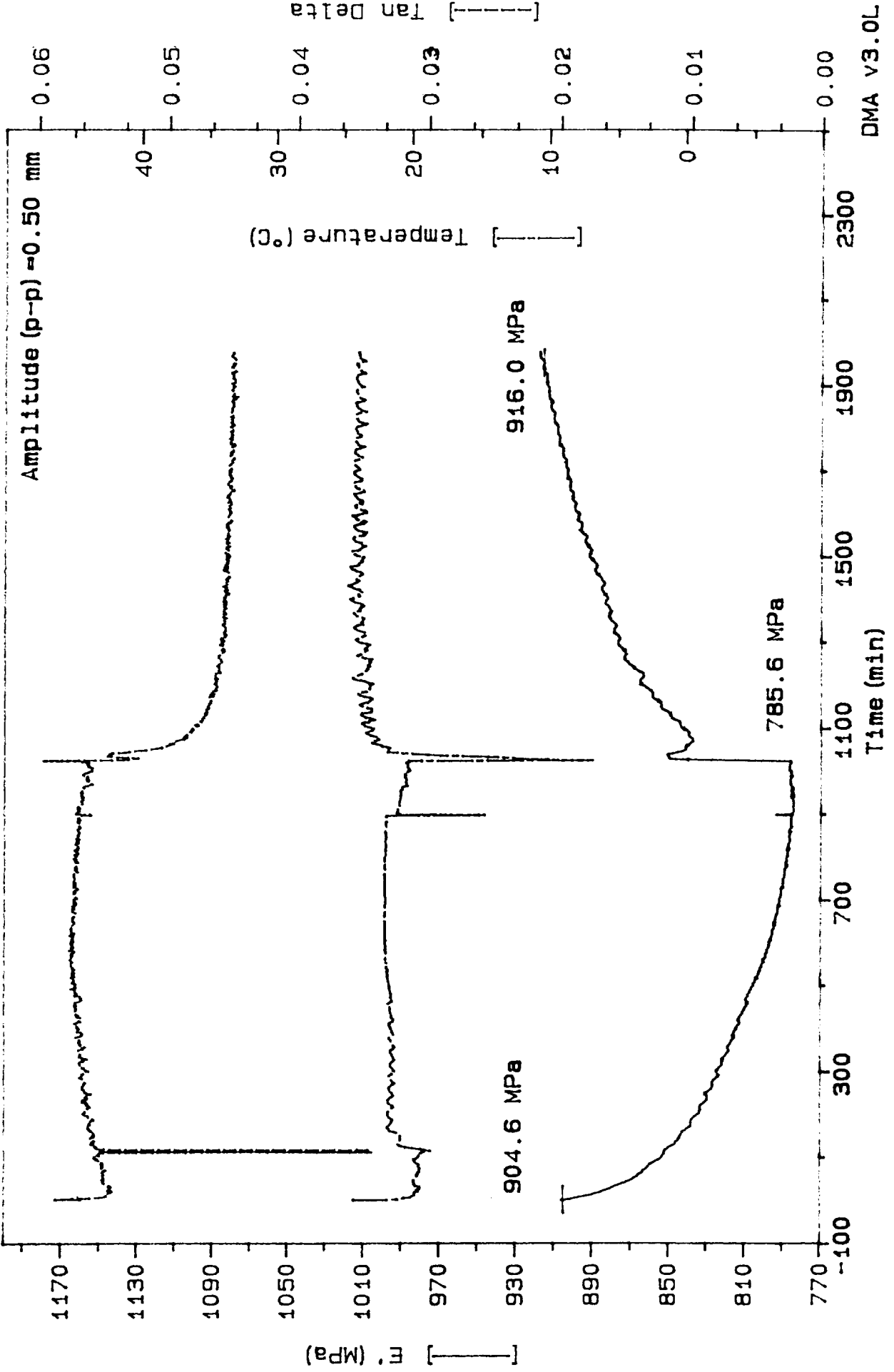


**1.7 Appendix Three- DMA Results**

Sample : COFLON IN METHANOL  
Size : 13.30 x 5.57 x 3.46 mm  
Method : 1 HZ AMBIENT  
Comment: SUBMERGED IN METHANOL

File : E: CAP-DMA45.04  
Operator: RR  
Run Date: 27-Apr-95 16:19

# DMA



Sample : COFLON

Size : 13.40 x 5.57 x 3.46 mm

Method : 1 HZ ISOTHERM ELEV TEMP

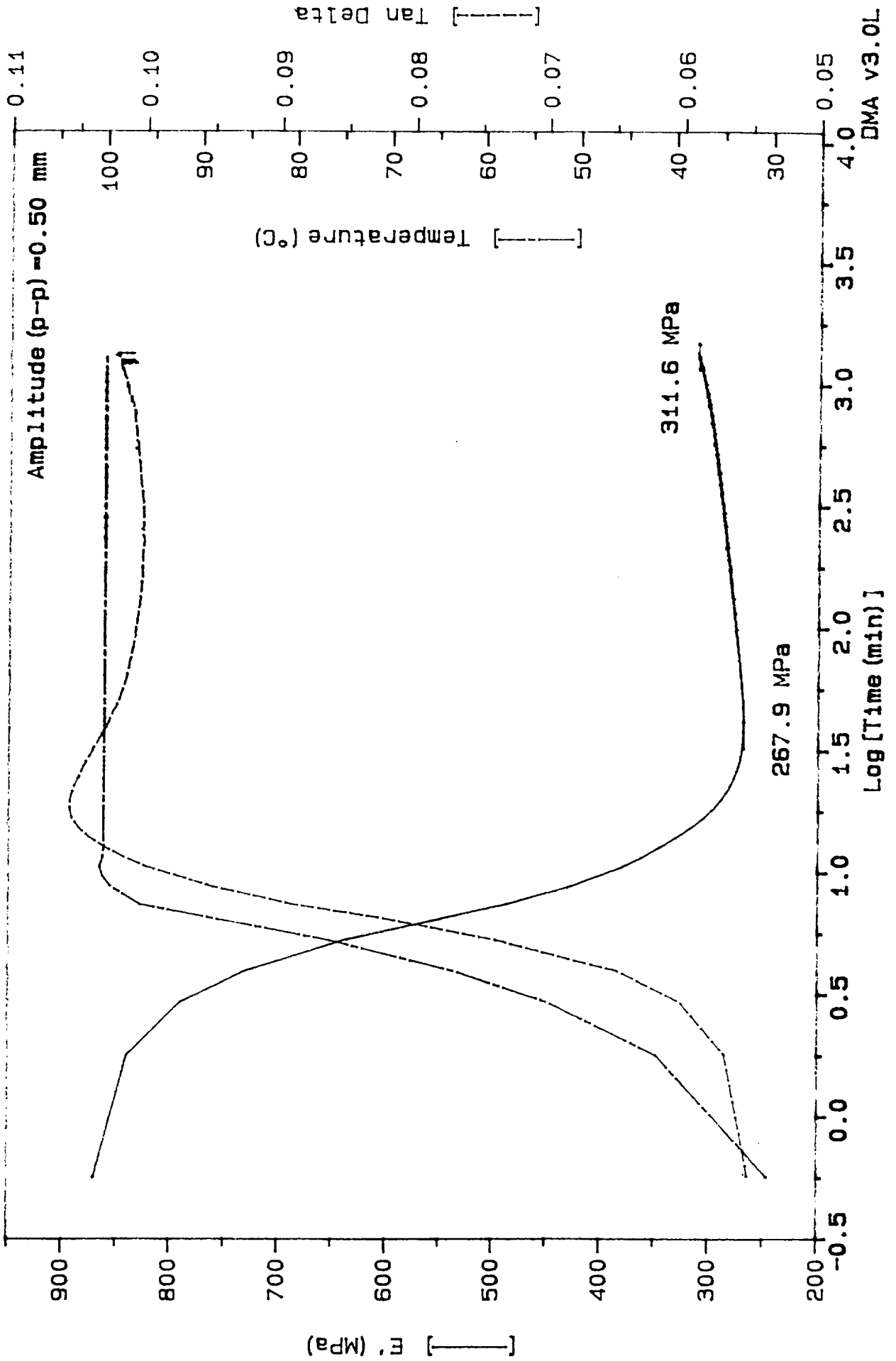
Comment:

File : E: CAP-DMA45.02

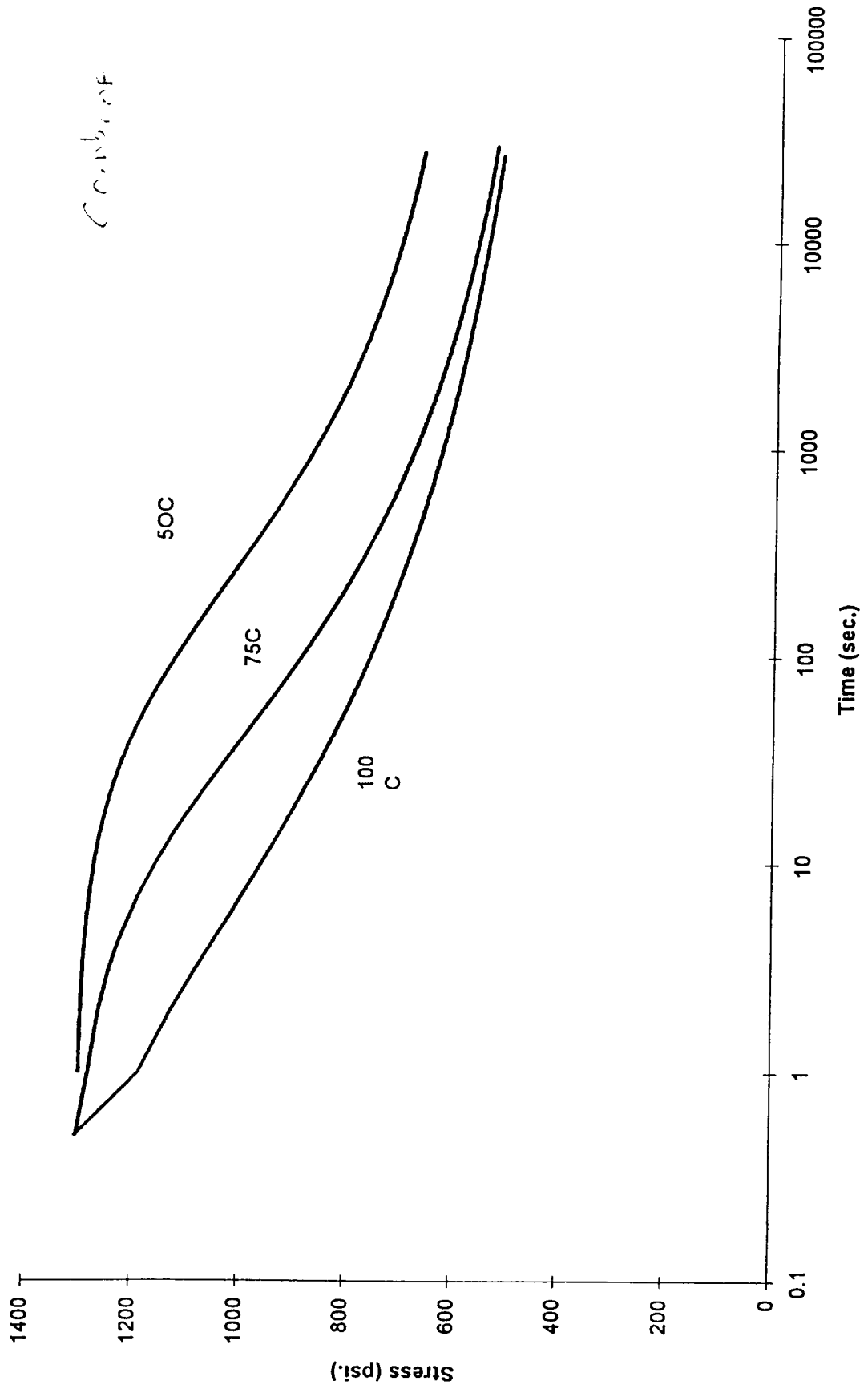
Operator: RR

Run Date: 25-Apr-95 09:34

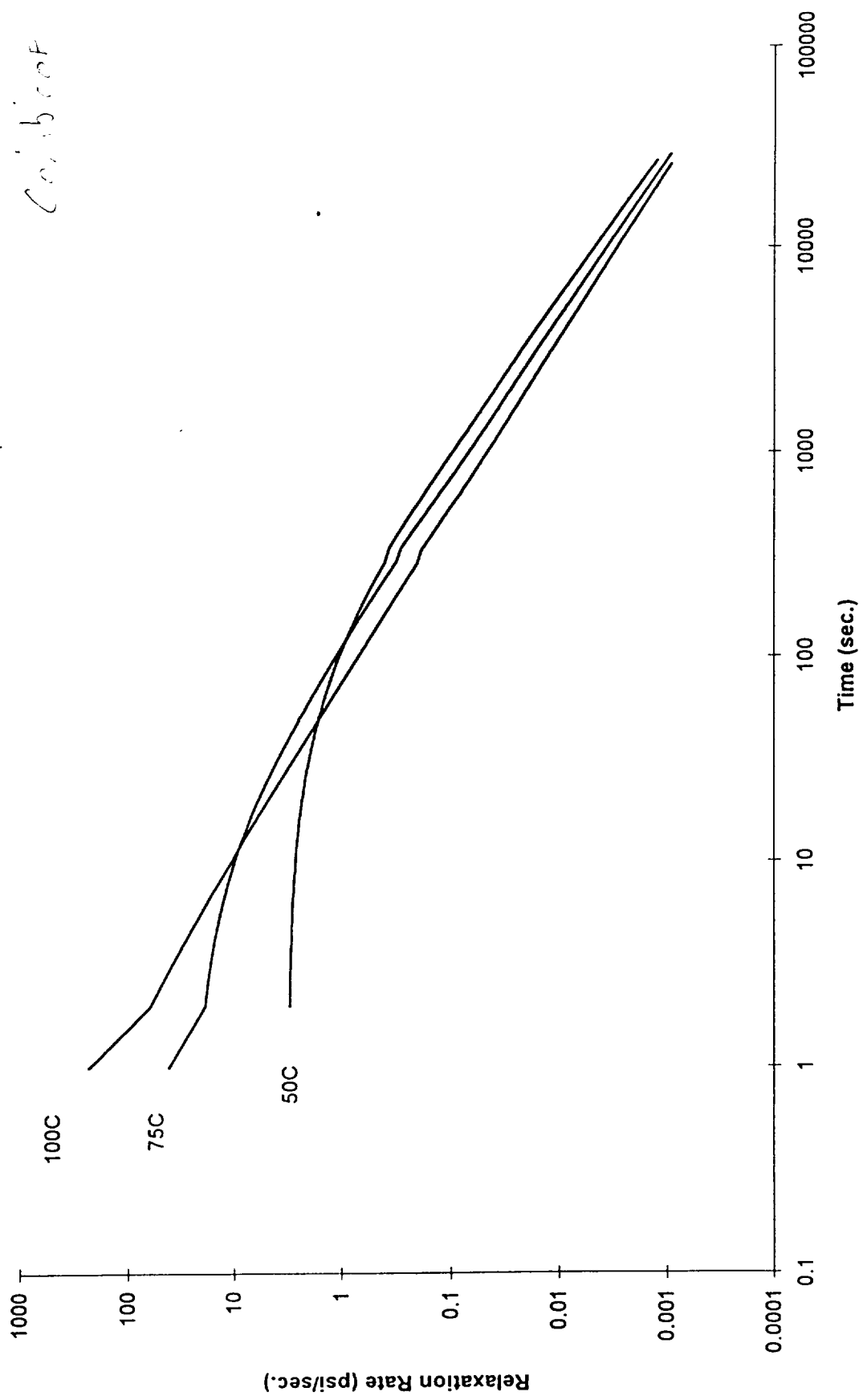
# DMA



### **1.8 Appendix Four- Pipe Stress Relaxation Results**



COFLON PIPE HOOP STRESS RELAXATION

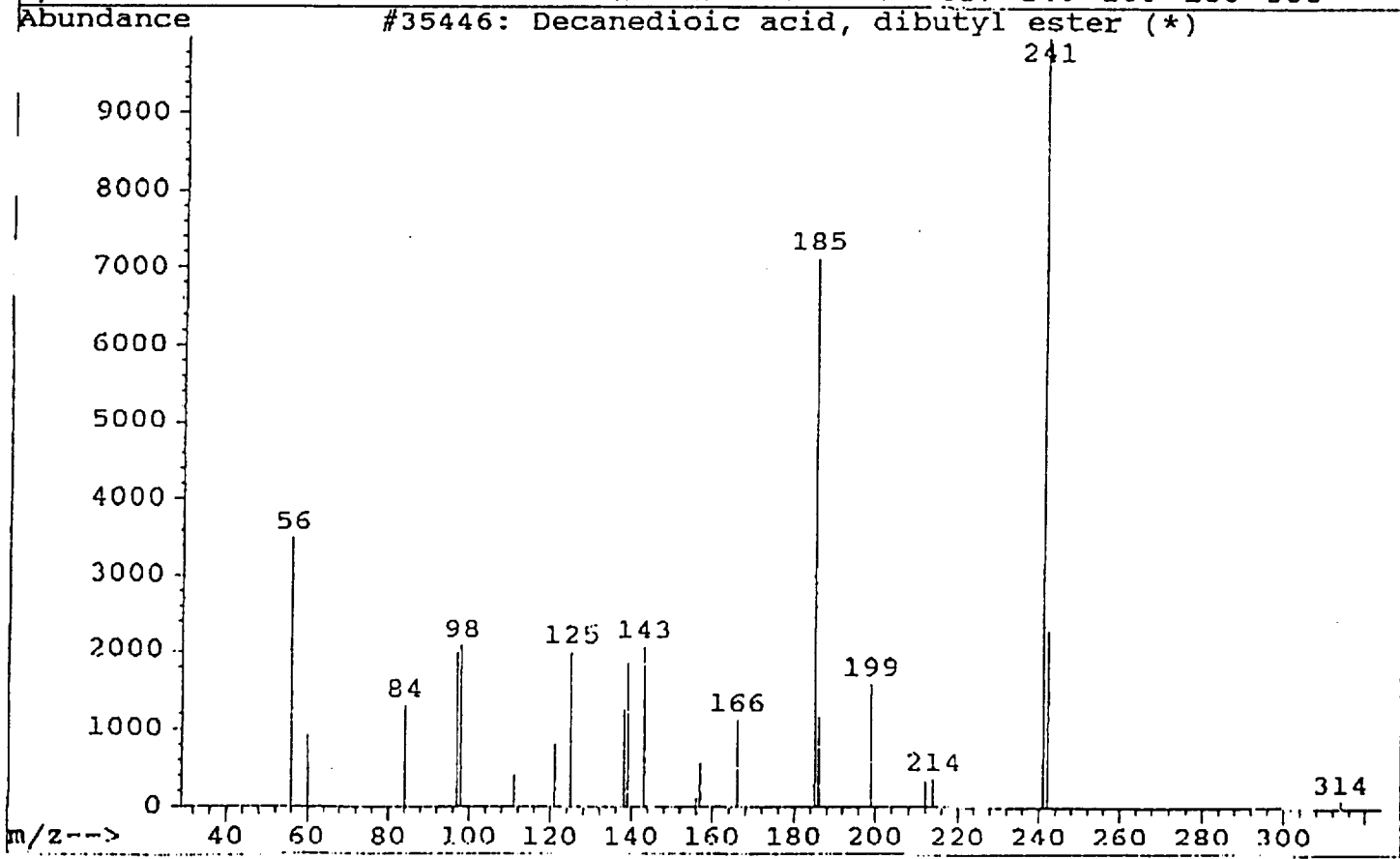
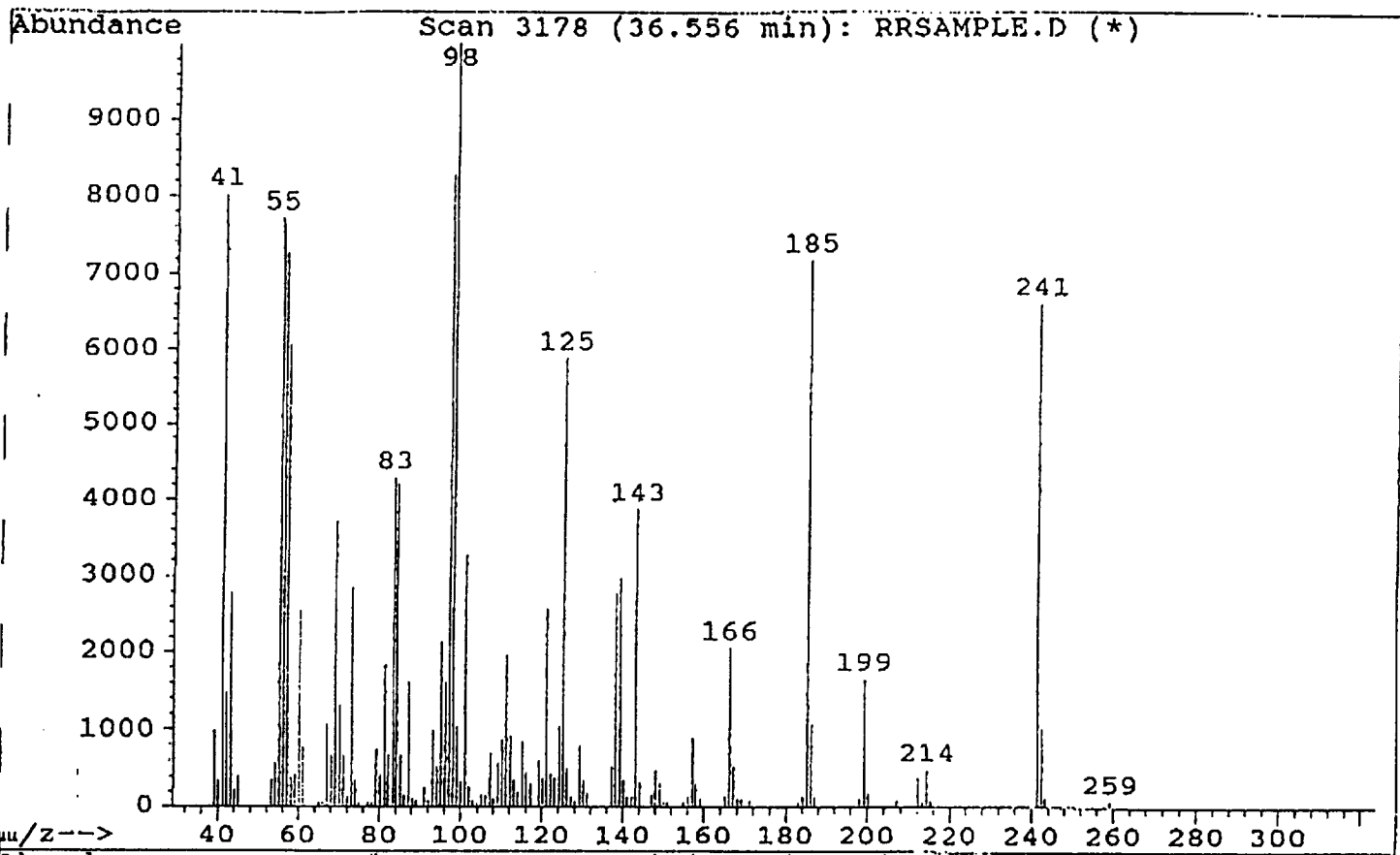


COFLON PIPE HOOP STRESS RELAXATION

Caribbea

## **1.9 Appendix Five- Mass Spectra of Exudate From Coflon**

Library Searched : C:\HPCHEM\DATABASE\NBS49K.L  
Quality : 38  
ID : Decanedioic acid, dibutyl ester



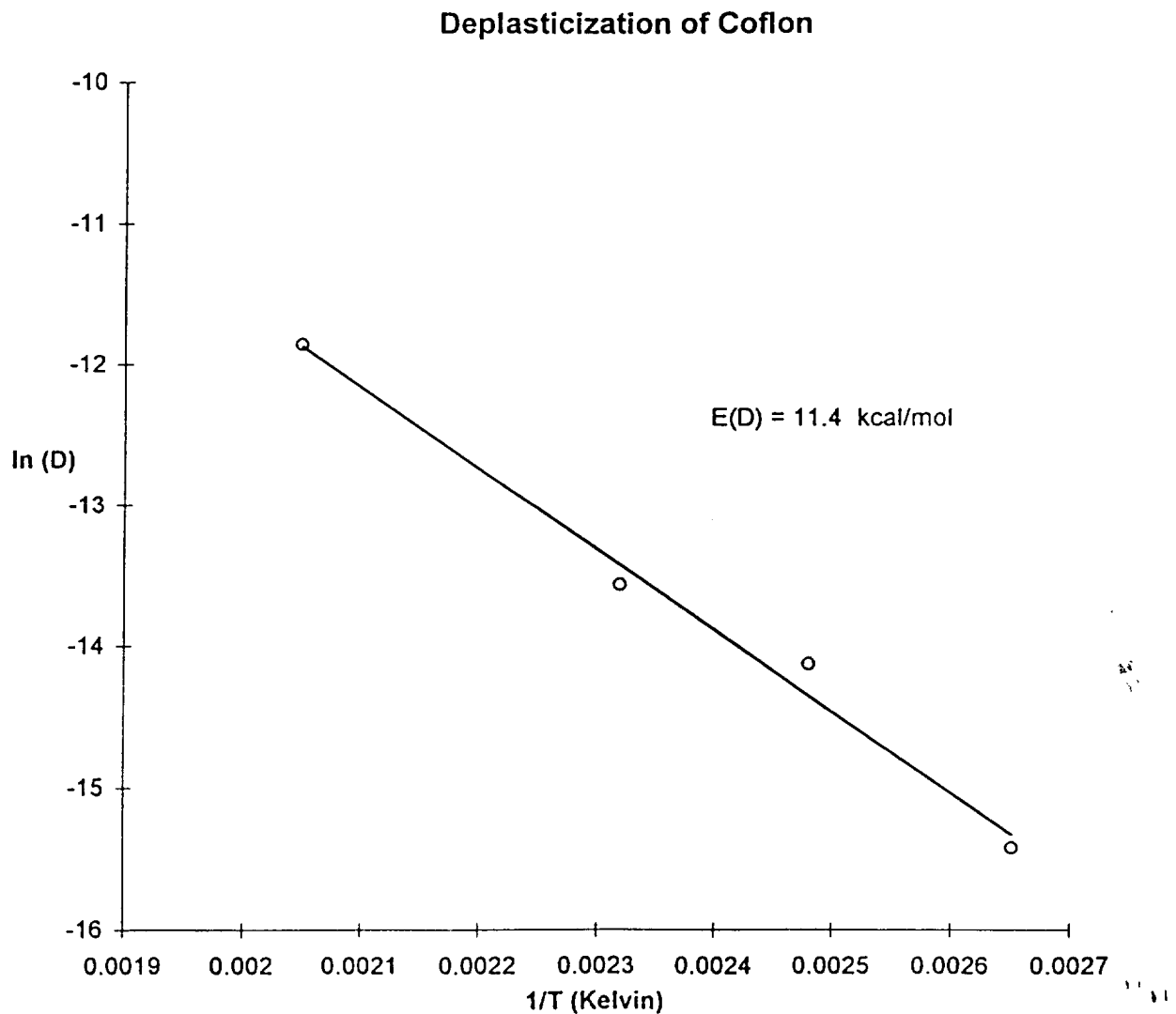


## **2.0 Thermogravimetric Evaluation of Deplasticization of Coflon**

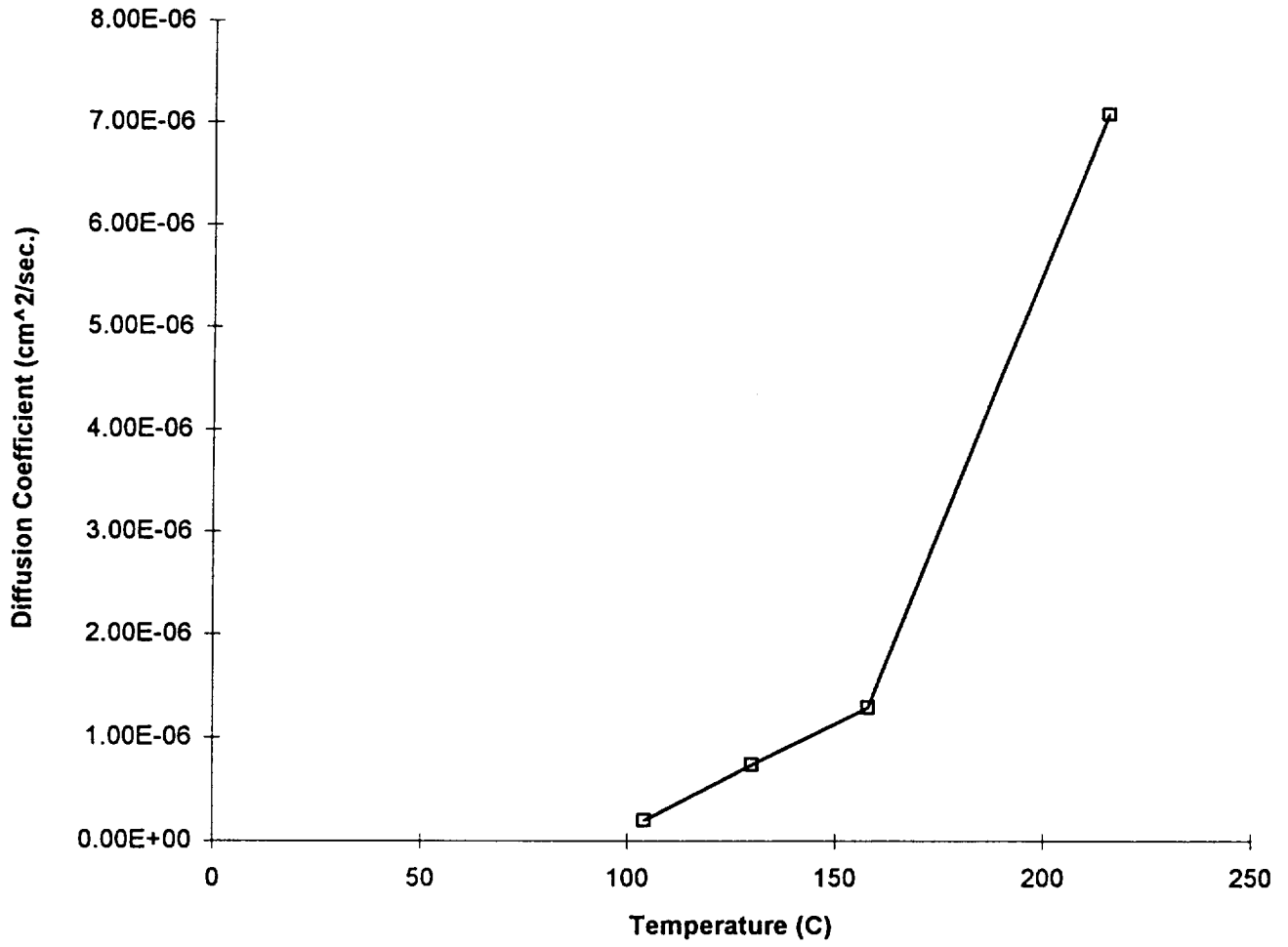
## **2.0 Thermogravimetric Evaluation of Deplasticization of Coflon**

Additional analysis of thermogravimetric data has been conducted. We are currently developing detailed examination of the deplasticization rates for Coflon. From this information we are calculating this diffusion coefficient of the plasticizer from the Coflon. These rates will be useful in future tests should preconditioning of specimens be required.

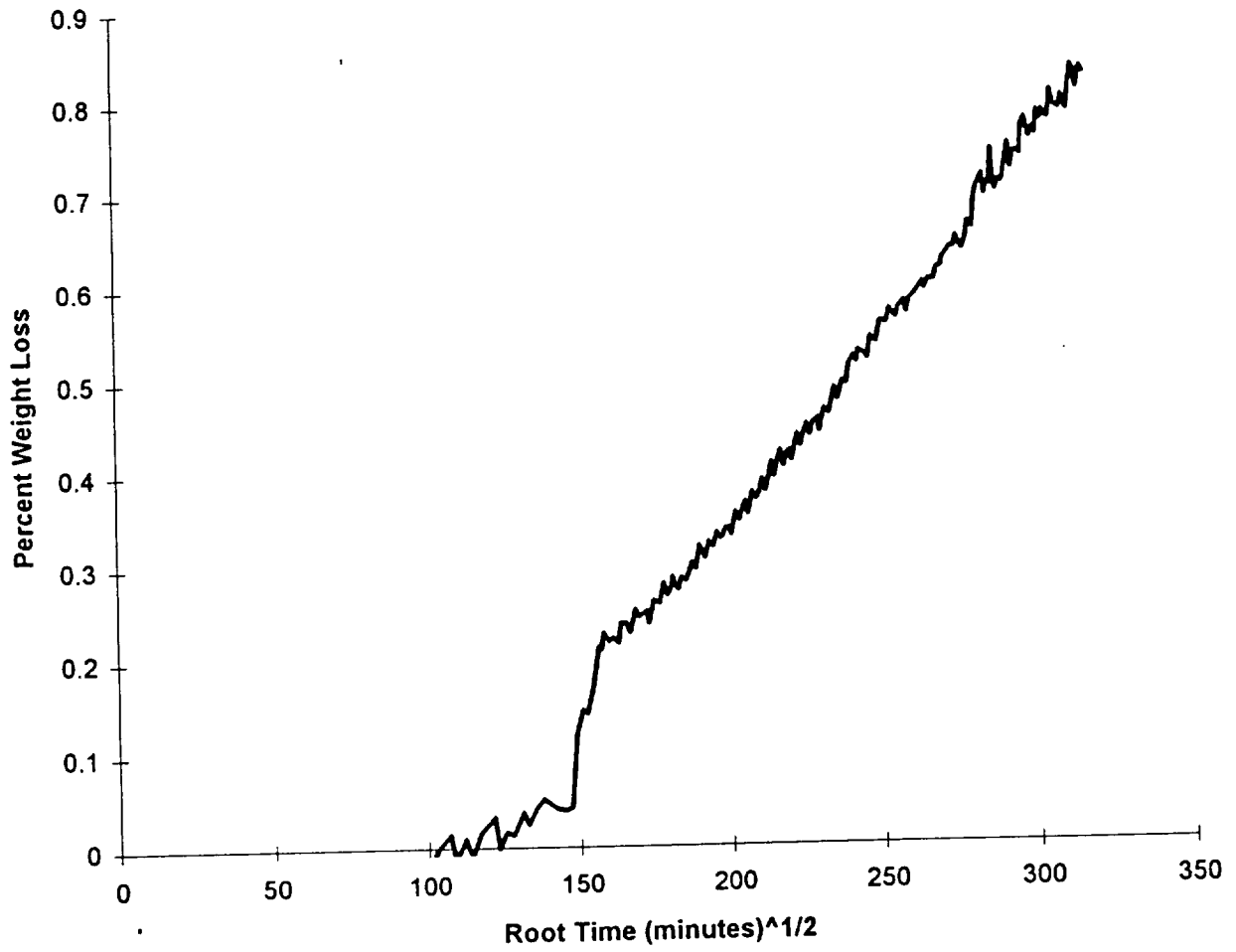
We reanalyzed the thermogravimetric information and recalculated the times associated with deplasticization for the Coflon pipe materials at specific temperatures. Below is the information that relates deplasticization of the Coflon to time and temperature.



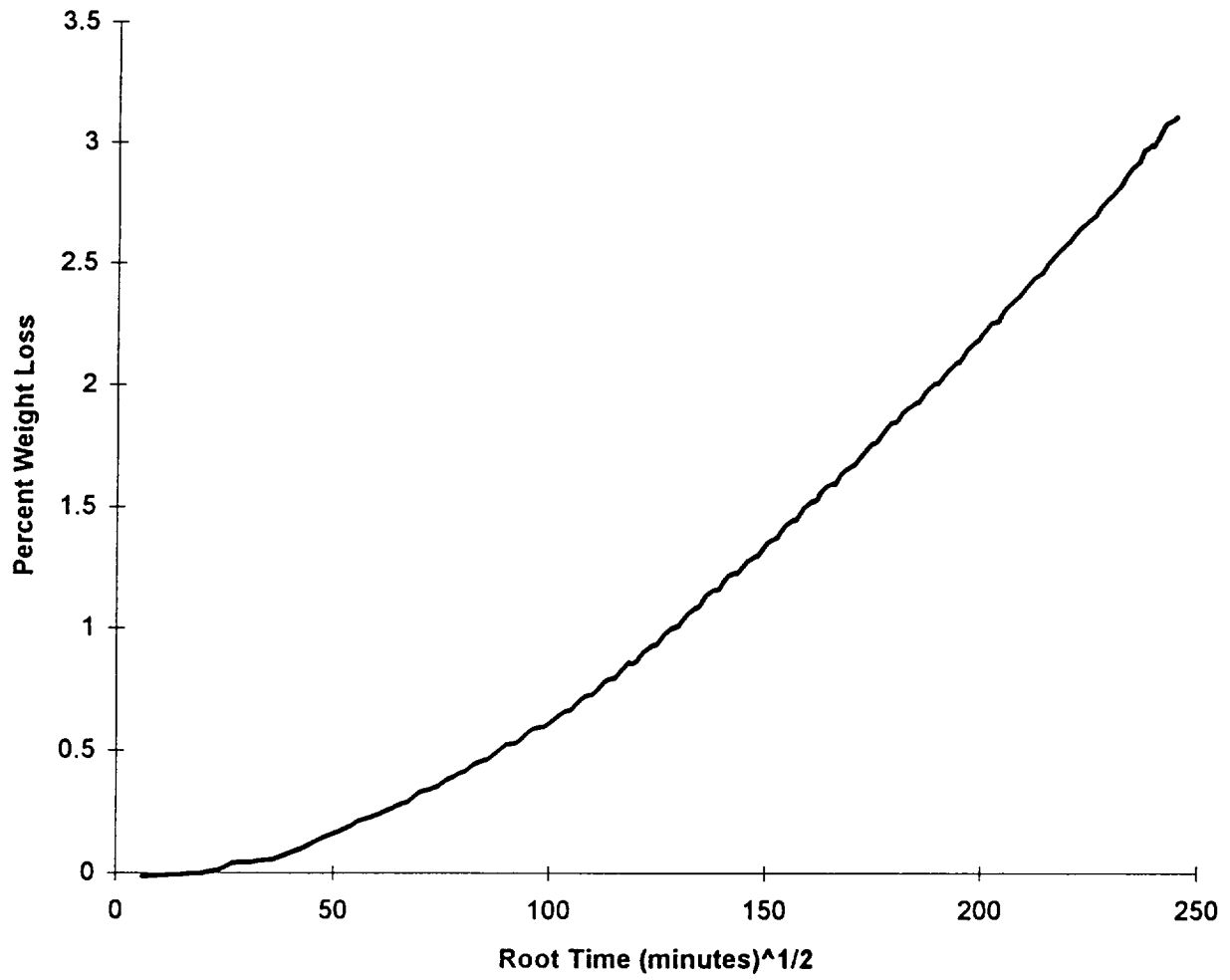
### Coflon Deplasticization



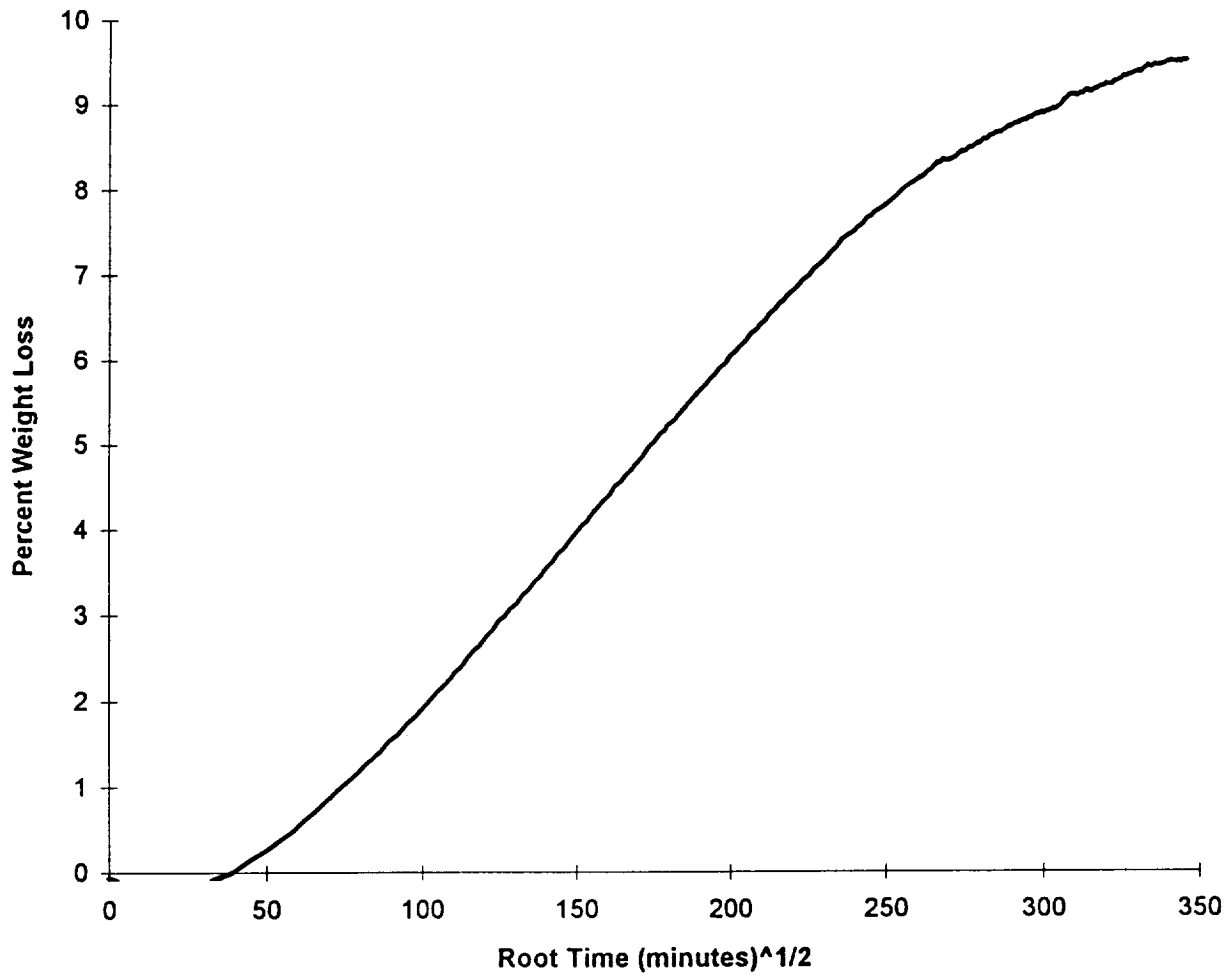
### Coflon Deplasticization at 104C



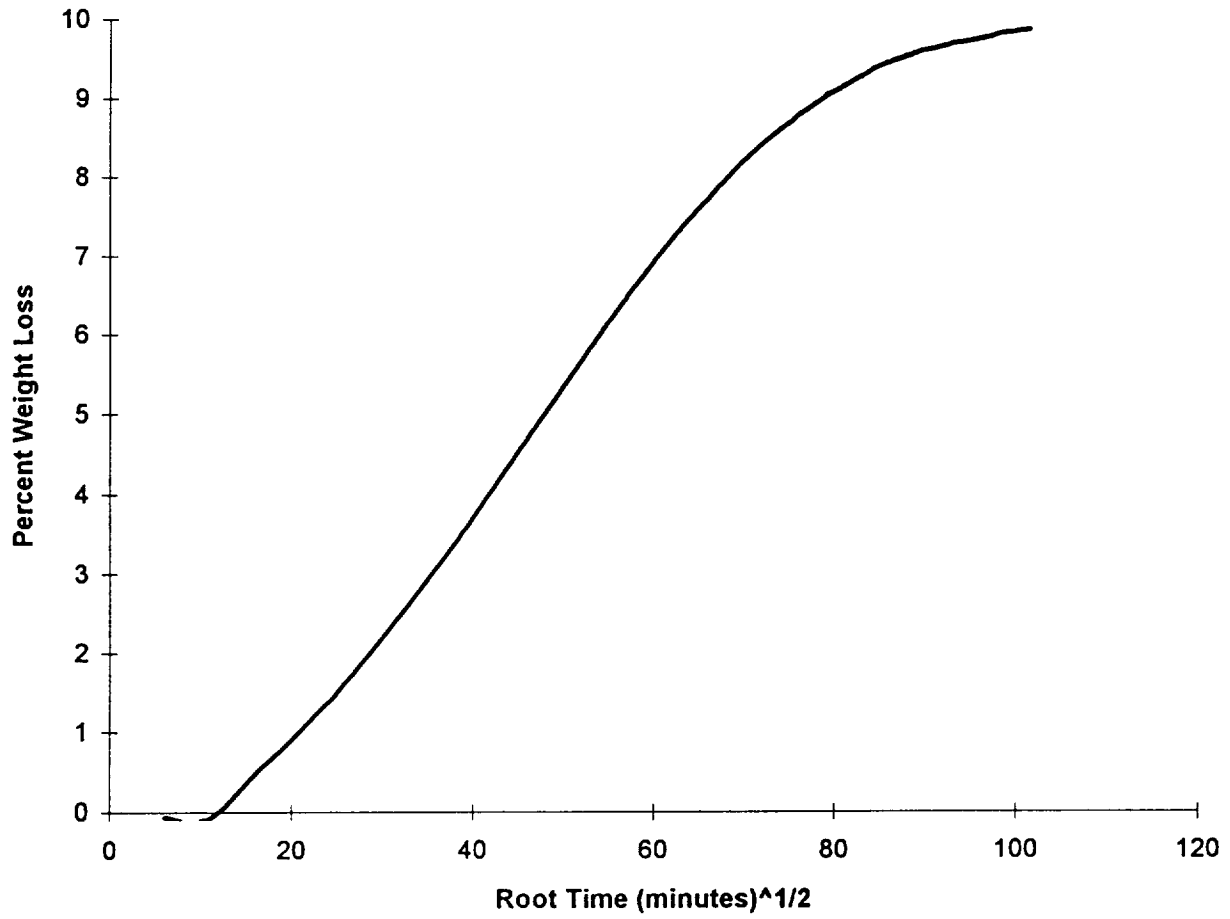
### Coflon Deplasticization at 130C



**Coflon Deplasticization  
at 158C**



Coflon Deplasticization  
at 215C





### Coflon Deplasticization at 264C

