CAPP

International Research Project on the Effects of Chemical Ageing of Polymers on Performance Properties

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INTERIM REPORT ON CHEMICAL ANALYSES

Prepared for: CAPP International Consortium

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1.0 Introduction

As a preliminary study on the effects of chemical aging of polymer materials MERL and TRI have examined two polymeric materials that are typically used for offshore umbilical applications. These two materials were Tefzel, a copolymer of ethylene and tetrafluoroethylene, and Coflon, polyvinylidene fluoride.

The Coflon specimens were cut from pipe sections and exposed to H_2S at various temperatures and pressures. One of these specimens was tested for methane permeation, and another for H_2S permeation.

The Tefzel specimens were cut from .05 mm. sheet stock material and were exposed to methanol at elevated temperature and pressure. One of these specimens was exposed to methanol permeation for 2 days at 100°C and 2500 psi. An additional specimen was exposed to liquid methanol for 3 days at 150°C and 15 Bar.

Virgin specimens of each material were similarly prepared and tested.

2.0 Analyses Performed

The specimens described above were subjected to the following tests following exposure.

- Thermogravimetric Analysis (TGA)
- Differential Scanning Calorimetry (DSC)
- Fourier Transform Infrared Analysis (FTIR)

The specimens were prepared by slicing a 0.015" surface section with a razor blade. TGA and DSC were performed using a nitrogen purge within the sample compartments. Percent crystallinity was determined by integration of the DSC melt curve to obtain heat of fusion. The resulting heat of fusion was then divided by the theoretical heat of fusion to obtain percent crystallinity.

FTIR was accomplished by scrapping very thin sections from the surface of the specimens and preparing a KBr pellet with this material for transmission analysis.

Two Coflon specimens were also analyzed using Electron Spectroscopy for Chemical Analysis (ESCA). One of these specimens was aged in 5% H_2S at 1000 psi and 140°C for 7 days and the other was virgin.

3.0 Results

3.1 Coflon TGA Results

As shown in Table 1 the aged specimens were exposed to 5% H_2S for 7 days at 1000 psi at either 100, 120 or 140°C. The first weight loss onset temperature was significantly higher for the unaged specimen while the second onset temperature remains relatively unchanged comparing the aged with unaged specimens. One possible reason for this behavior might be the loss of low molecular weight fractions produced by the aging process being eliminated at a lower temperature.

It also appears that the specimens that were exposed to high pressure permeation tests contain a smaller amount of the material evolving at the lower decomposition temperature (approximately 3% compared to 8% for the non-permeation specimens).

The highest secondary onset temperature was observed with the specimen that was exposed to high pressure H_2S as a permeant (10% H_2S at 130°C 2500 psi 1 day and 5000 psi 1 day). This may a result of bulk penetration of H_2S into the specimen causing sulphide crosslinking.

Another feature illustrated in Table 1 is the difference in char for the sample tested with methane as a permeant. The other three specimens produced char yields between 18 and 23 percent compared to 2.9% for the methane exposed specimen. An additional specimen was analyzed to confirm this result with similar results.

3.2 Coflon DSC Results

Table 2 illustrates the results for the DSC tests performed on the aged and unaged Coflon specimens. One of the most dramatic comparisons is the difference in melt onset temperature observed with the specimen exposed to methane permeation. This specimen exhibited an onset of 190°C compared to a range of 157 to 167°C for the other cases. In view of the fact that this material also displayed the highest degree of crystallinity it appears that the methane is displacing amorphous polymer from the specimen surface.

In contrast, exposure to high pressure H_2S produces a lower melt onset and percent crystallinity compared to the unaged material. If sulphide crosslinking is occurring it may result in disruption of crystallinity.

3.3 Coflon FTIR Results

Figure 1 displays the FTIR results for both the aged and unaged Coflon specimens. For reference purposes a library spectra of PVDF is shown also. The differences seen comparing the library spectra with the unaged Coflon specimen are likely due to the incorporation of stabilizers or residual processing additives in the latter. Another factor that may attribute to the differences is surface degradation of the polymer during processing. Specifically, the absorption band at approximately 1740 cm^{-1} seen in the unaged Coflon specimen is characteristic of carbonyl functionality. After aging in H_2S this peak lessens in intensity dramatically.

The peak at 1440 cm^{-1} that is associated with C=C and CH_2 functionalities decreases in relative intensity after aging also. The presence of a band at 850 cm^{-1}, after aging in H_2S at 140°C confirms that the changes are due to a decrease in CH_2 and not C=C. Loss of intensity of the CF_2 band at 1200 cm^{-1} after aging is consistent with the loss of HF associated with thermal degradation.

The specimen that was both aged in H_2S and exposed to high pressure methane shows indications of sulphide crosslinking as evidenced by the band visible at 1250 cm^{-1} that is associated with CH_2-S. In addition this specimen has partially lost some C=C character as seen by the decrease in the absorption band at 850 cm^{-1}.

The specimen that was aged in H_2S and exposed to high pressure H_2S shows even more pronounced indications of sulphide crosslinking by the band at 1250 cm^{-1} that is associated with CH_2-S.

3.4 Coflon ESCA Results

Two specimens were tested using ESCA, unaged and aged in 5% H_2S at 140°C 1000 psi for 7 days with no permeation exposure. Table 3 shows these results. A dramatic decrease in fluorine is seen after aging accompanied by an increase in sulphur content. This agrees with the FTIR results that indicate unsaturation resulting from loss of HF followed by sulphide crosslinking.

Interestingly, there was also a substantial increase in oxygen observed in the aged specimen. This may be due to oxidation occurring after the aged specimen was exposed to ambient atmosphere or may be a result of adsorbed moisture adhering to the aged surface that is likely to be more hydrophilic than the unaged material.

3.5 Tefzel TGA Results

The Tefzel specimens as tested consisted of the following:

- Unaged;
- Methanol permeation specimen exposed for 2 days at 100°C and 2500 psi;
- Methanol absorption specimen exposed for 3 days at 150°C and 15 Bar.

One thermal degradation event occurred with all of Tefzel specimens tested. The onset temperatures for this event observed for the three cases were very similar, with the range being 516 to 523°C. Because of instrumentation difficulties the char yields obtained are not reportable at this time.

3.6 Tefzel DSC Results

Melt temperature onsets, shown in Table 4, were similar for all of the specimens (252-253°C) with the exception of the low pressure side of the methanol permeation specimen exposed for 2 days at 100°C and 2500 psi. In this case the melt onset was 246°C. The heats of fusion ranged from 39 J/g for the unaged specimen to 75 J/g for the low pressure side of the methanol permeation specimen exposed for 2 days at 100°C and 2500 psi.

3.7 Tefzel FTIR Specimens

As shown in Figure 2 no significant differences were observed comparing the aged and unaged Tefzel specimens.

4.0 Conclusions

Significant changes in the surface chemical composition, as indicated by FTIR, were observed with the Coflon materials after aging in H_2S. Additional alterations in surface composition were observed after exposure to methane permeation, which seems to leave the surface on the high pressure side a highly crosslinked material. A significant increase in melt onset was observed with the

H_2S/methane exposed specimen. However, the char yield from TGA analysis of the Coflon exposed to high pressure methane was 2.9% compared to 18 to 23 percent for the other aged specimens.

ESCA analysis of the Coflon aged in H_2S showed a much lower concentration of fluorine, and an increase in both sulfur and oxygen compared to unaged specimen.

The Tefzel specimens were not exposed to H_2S and showed no significant indication of chemical degradation as a result of exposure to methanol at high pressure. The grade of Tefzel that was tested in this preliminary work is not intended for pipe applications and results included herein should be regarded with this in mind. Future work will include the pipe grade Tefzel material.

Aging Temperature[1] (°C)	Permeation Conditions	1st Weight Loss Onset	2nd Weight Loss Onset	Char Remaining
Unaged	None	267°C (8.1%)	482°C (69%)	22.33
100	10% H_2S 130°C 2500 psi 1 day 5000 psi 1 day	225°C (2.7%)	497°C (79%)	18.1%
120	methane 130°C 2500 psi 1 day	170°C (3.2%)	478°C (94%)	2.9%
140	None	176°C (7.2%)	488°C (70%)	22.9%

1 = Aged samples were exposed to 5% H^2S for 7 days at 1000 psi. Specimens were 0.015" shavings from exposed high pressure surface

Table 1 - Thermogravimetric Analysis Results for Coflon

Aging Temperature[1] (°C)	Permeation Conditions	Melt Onset (°C)	Percent Crystallinity
Unaged	None	162	54
100	10% H_2S 130°C 2500 psi 1 day 5000 psi 1 day	157	34
120	methane 130°C 2500 psi 1 day	190	72
140	None	167	41

1 = Aged samples were exposed to 5% H_2S for 7 days at 1000 psi.
Specimens were 0.015" shavings from exposed high pressure surface

Table 2 - Differential Scanning Calorimetry Results for Coflon

Specimen	C	N	O	F	Si	S	Fe	Zn
Coflon COF4 . Aged in 5% H_2S at 140°C 1000 psi for 7 days No Permeation	75	3.1	14	1.6	4.1	1.3	0.5?	0.4
Coflon Control (unaged)	52	---	3.1	44	0.3	0.1?	---	---

Note: ? = weak signal
--- = no signal detected

Table 3 - ESCA Results for Coflon: Elemental Composition data measured from the surface (approximately the top 100 Angstroms) of each sample and expressed in atomic percent units for the elements detected.

Aging Temperature (°C)	Permeation Conditions	Melt Onset (°C)	Heat of Fusion (J/g)
Unaged	None	252	39
150 (methanol, 15 Bar)	None	252	62
	Methanol 2500 psi 100°C (low pressure side)	246	75
	Methanol 2500 psi 100°C (high pressure side)	253	55

Specimens were 0.015" shavings

Table 4 - Differential Scanning Calorimetry Results for Tefzel

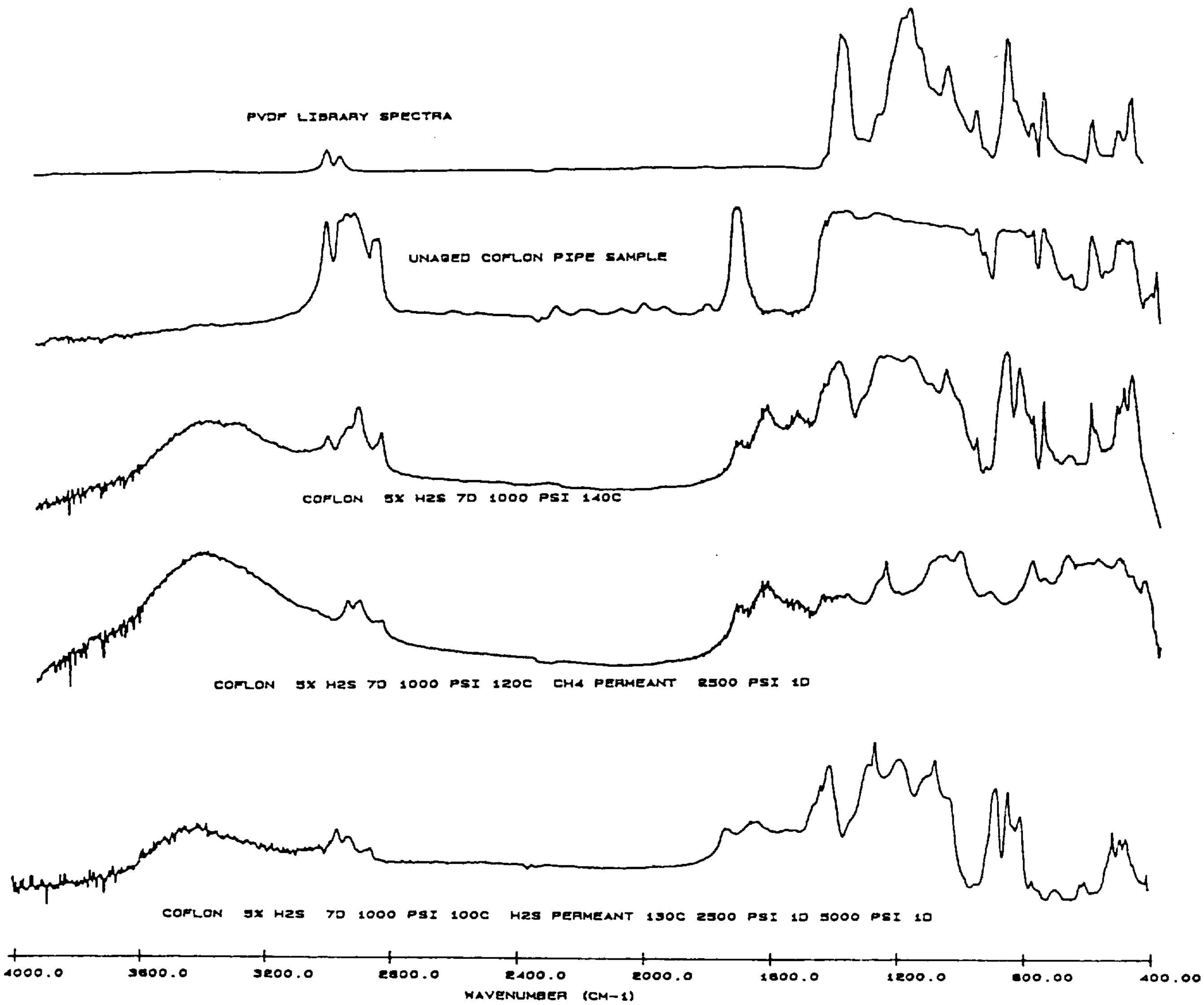


Figure 1 - Coflon FTIR Scans

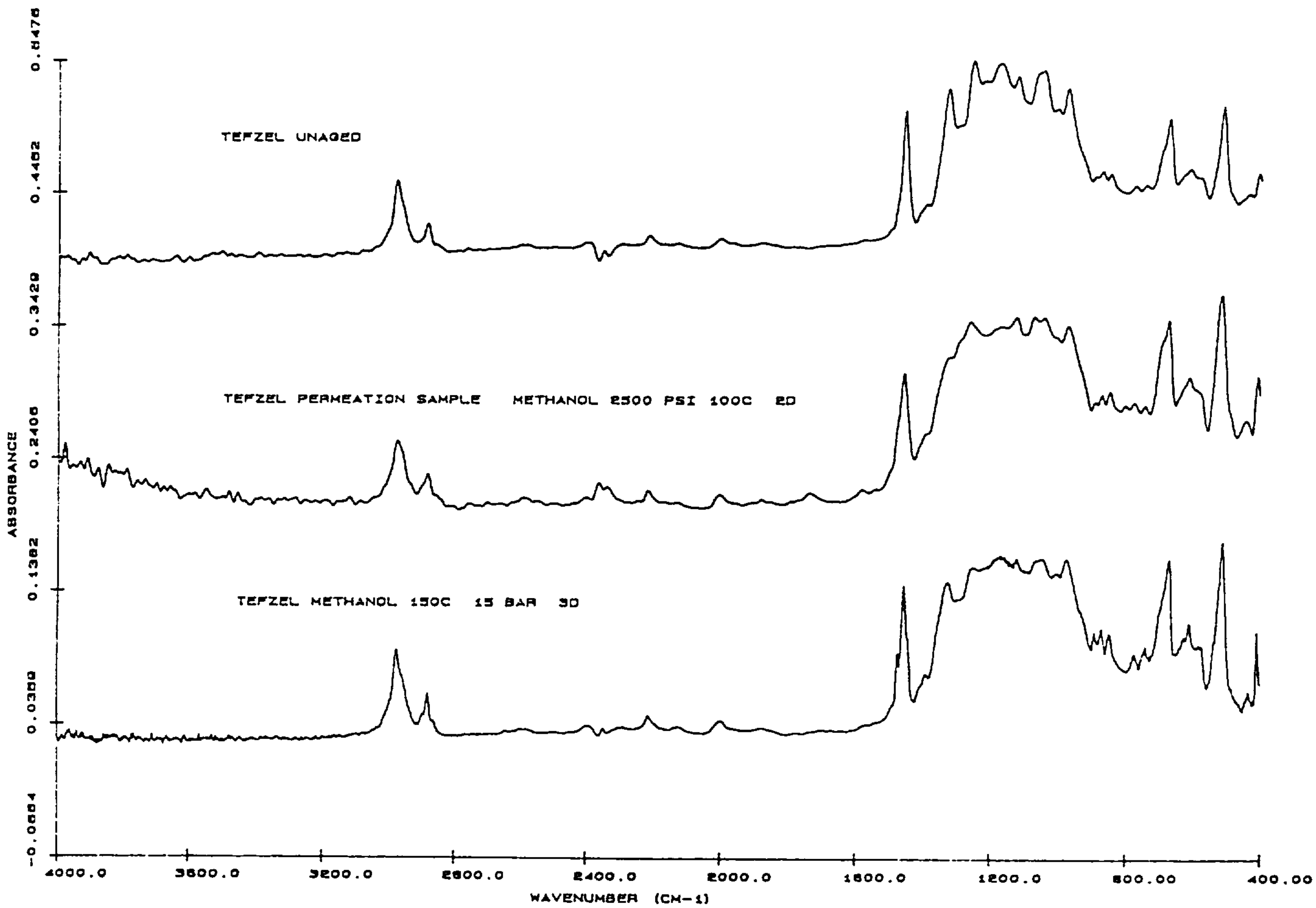


Figure 2 - Tefzel FTIR Scans

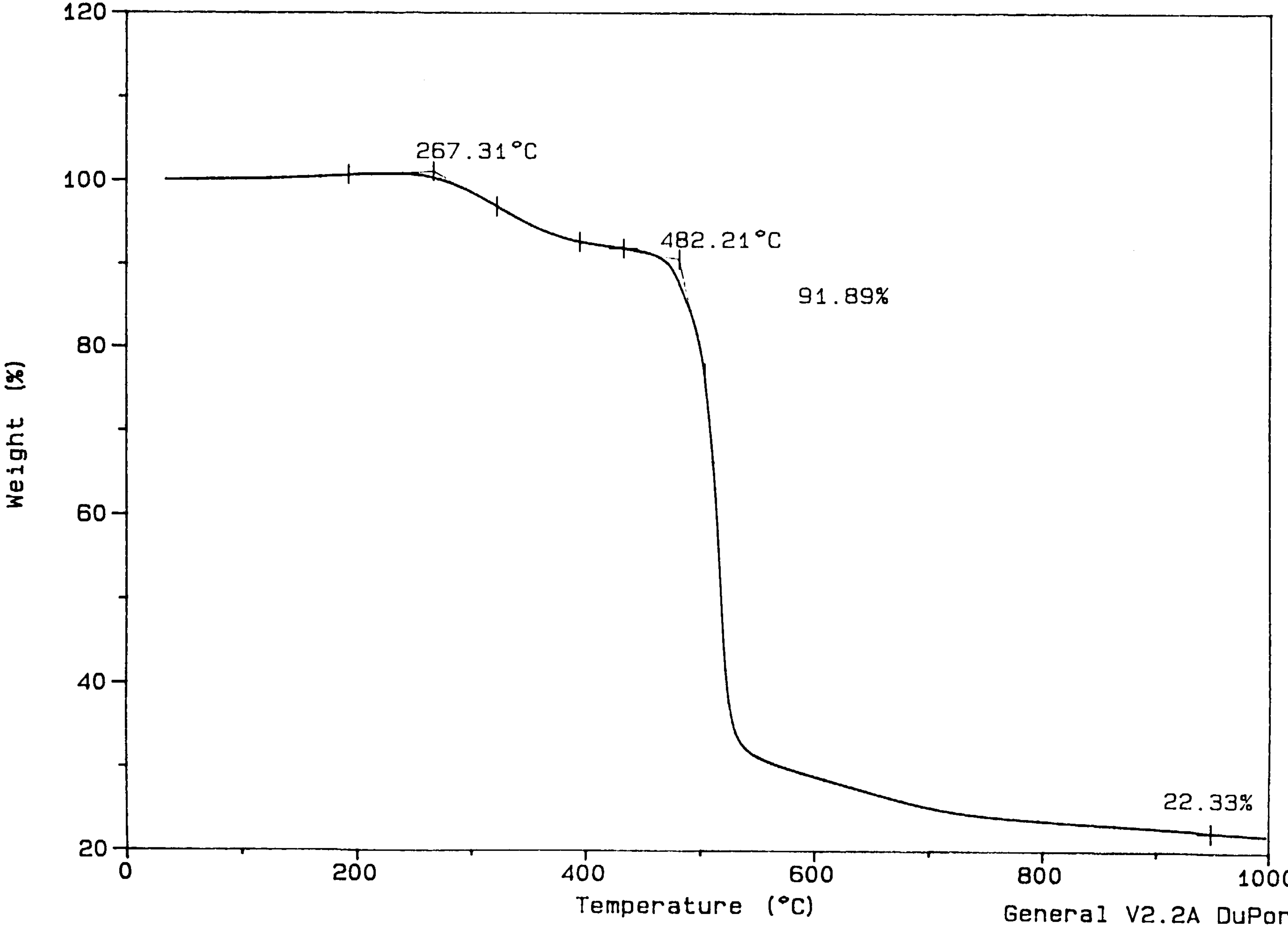
APPENDIX

THERMAL ANALYSIS AND ESCA PLOTS

Sample: COFLON UNAGED
Size: 14.4383 mg
Method: 20R/1000
Comment: N2 PURGE

TGA

File: COF-TGA01.02
Operator: RR
Run Date: 26-Apr-94 08:55

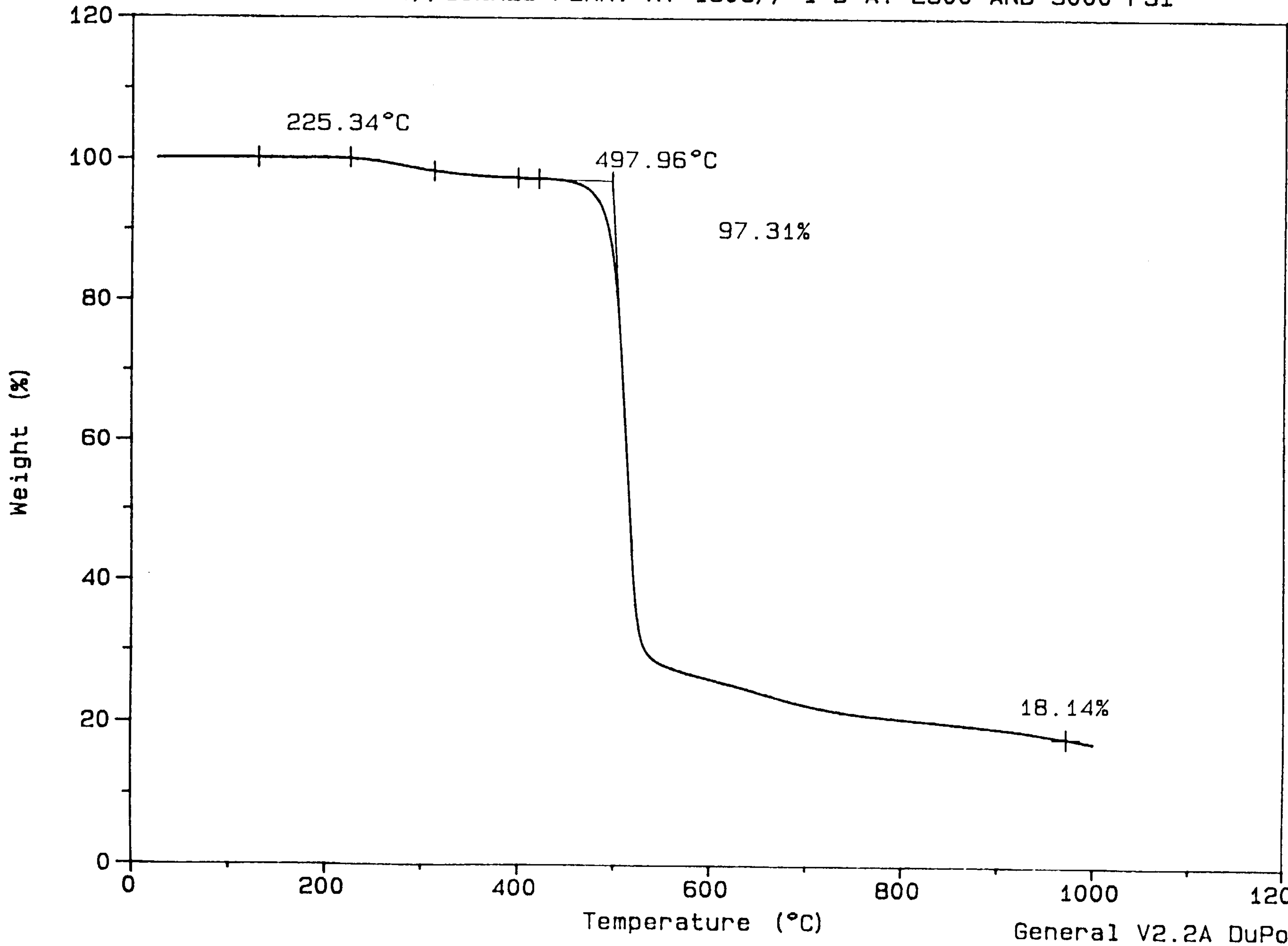


General V2.2A DuPont 9900

Sample: COFLON C33 AGED 7D 5 % H2S 100C
Size: 13.0714 mg
Method: 20R/1000
Comment: 1000 PSI FOR 7D//10%H2S PERM. AT 130C// 1 D AT 2500 AND 5000 PSI

TGA

File: COF-TGA05.03
Operator: RR
Run Date: 2-May-94 14:10



General V2.2A DuPont 9900

Sample: COFLON C28 AGED IN 5% H2S 120C

Size: 13.9053 mg

Method: 20R/1000

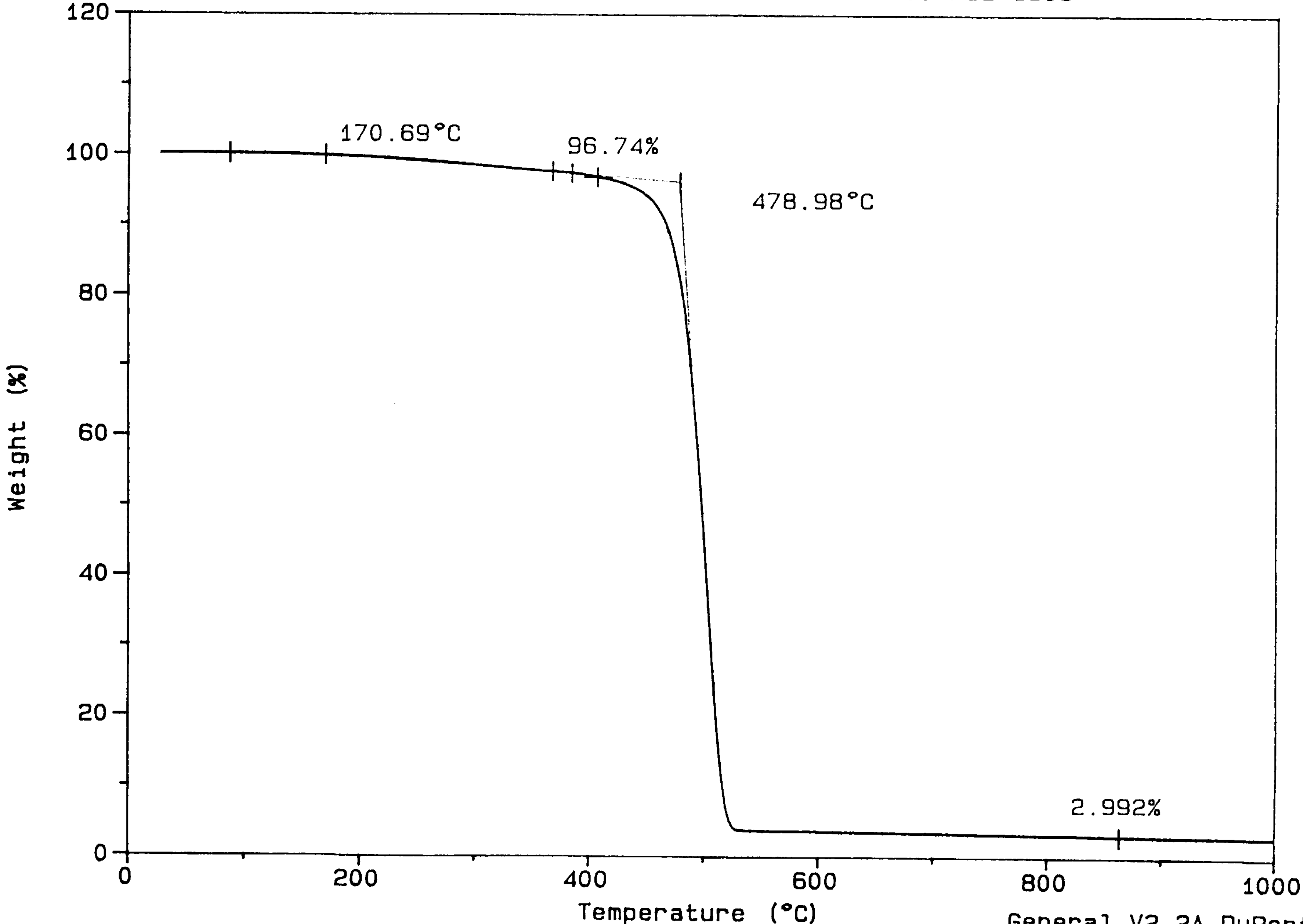
Comment: AGED 7DAYS 1000 PSI CH4 PENETRANT 1 DAY AT 2500 PSI 130C

TGA

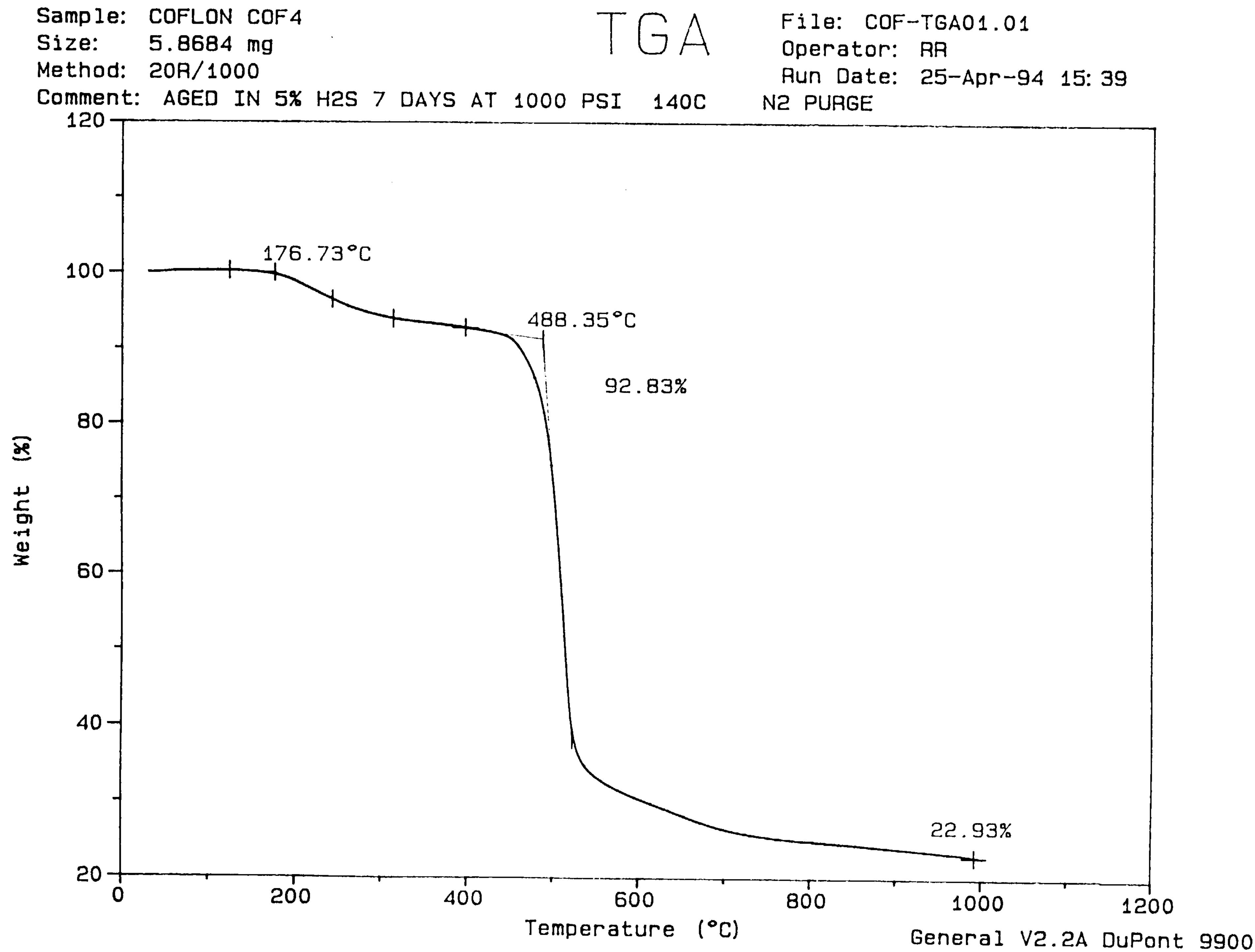
File: COF-TGA01.04

Operator: RR

Run Date: 27-Apr-94 08:29



General V2.2A DuPont 9900

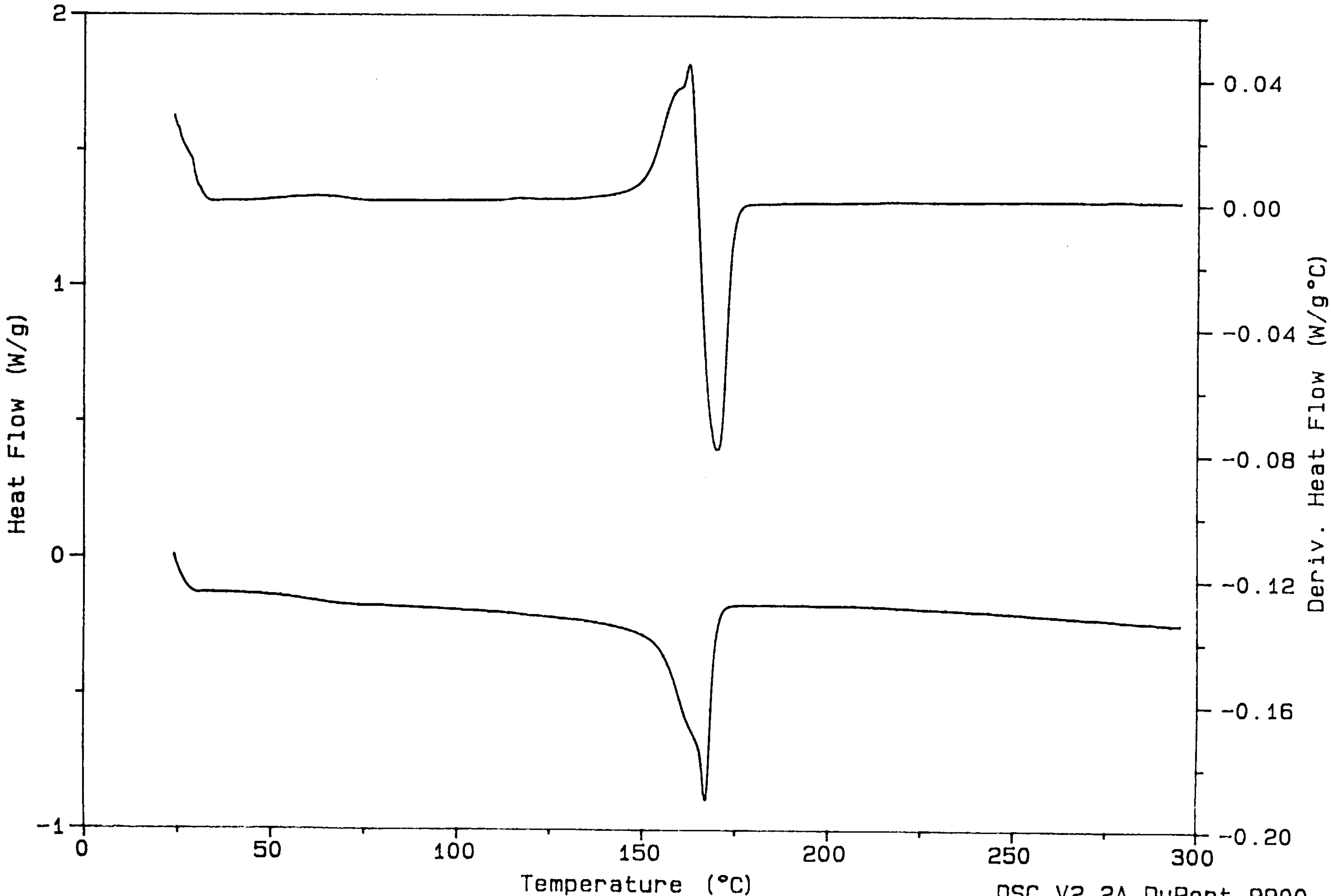


Sample: COFLON COF4
Size: 5.8684 mg
Method: 20R/1000
Comment: AGED IN 5% H2S 7 DAYS AT 1000 PSI 140C N2 PURGE
TGA
File: COF-TGA01.01
Operator: RR
Run Date: 25-Apr-94 15: 39
176.73°C
488.35°C
92.83%
22.93%
Weight (%)
Temperature (°C)
120
100
80
60
40
20
0
200
400
600
800
1000
1200
General V2.2A DuPont 9900

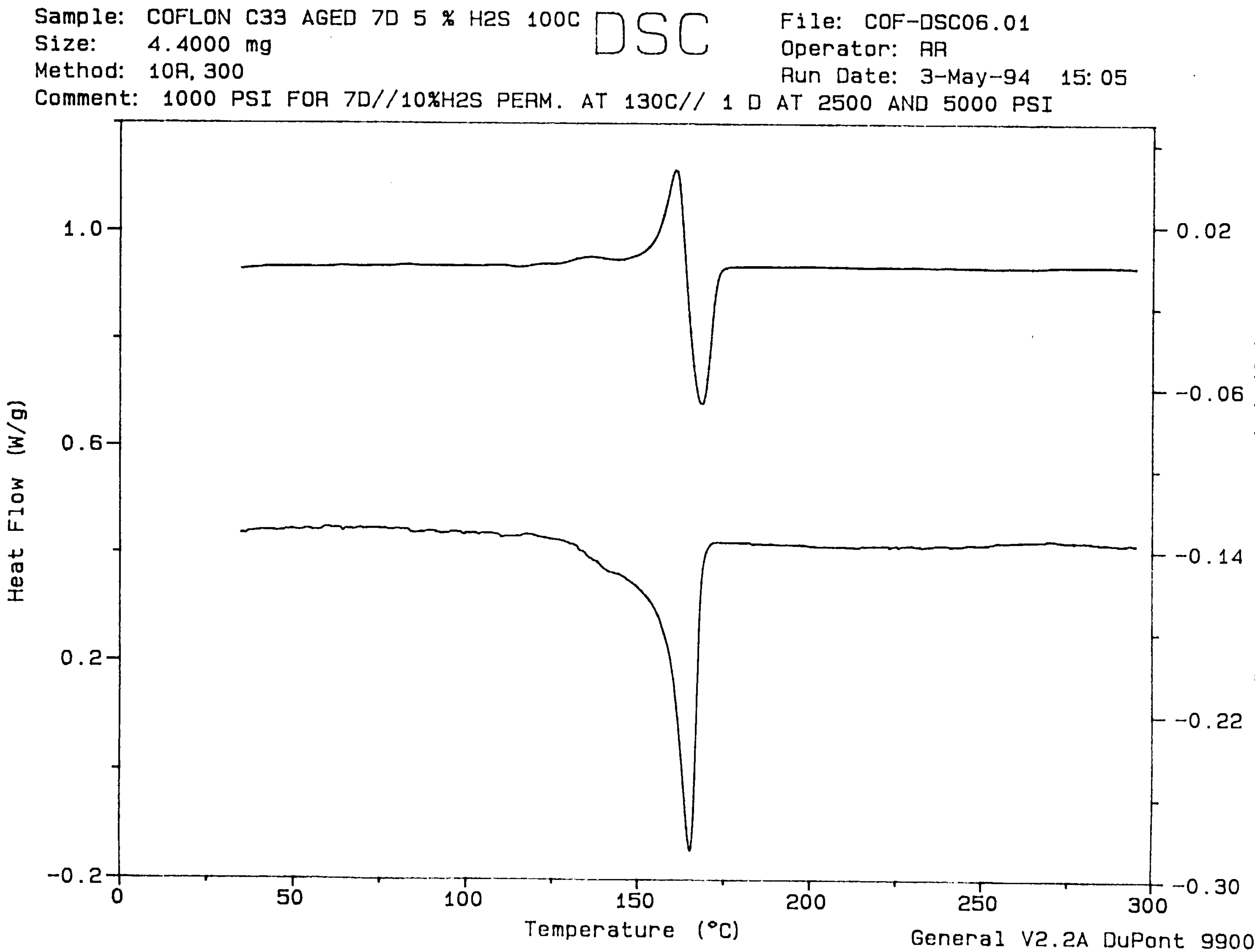
Sample: COFLON BASELINE NOT AGED
Size: 3.3000 mg
Method: 10R, 300

DSC

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



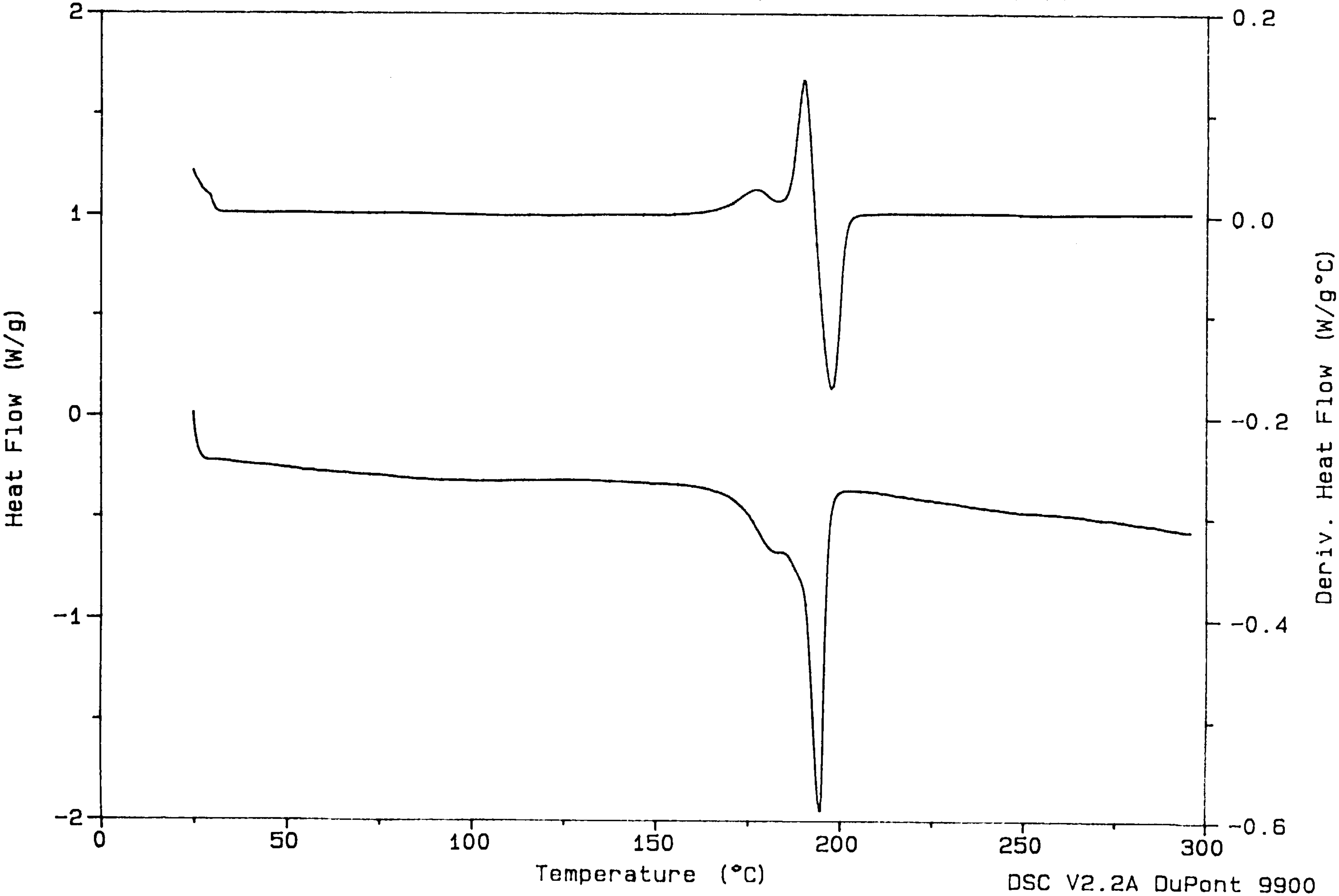
DSC V2.2A DuPont 9900


Sample: COFLON C33 AGED 7D 5 % H2S 100C
Size: 4.4000 mg
Method: 10R, 300
Comment: 1000 PSI FOR 7D//10%H2S PERM. AT 130C// 1 D AT 2500 AND 5000 PSI
DSC
File: COF-DSC06.01
Operator: RR
Run Date: 3-May-94 15:05
Heat Flow (W/g)
1.0
0.6
0.2
-0.2
Deriv. Heat Flow (W/g/°C)
0.02
-0.06
-0.14
-0.22
-0.30
0
50
100
150
200
250
300
Temperature (°C)
General V2.2A DuPont 9900

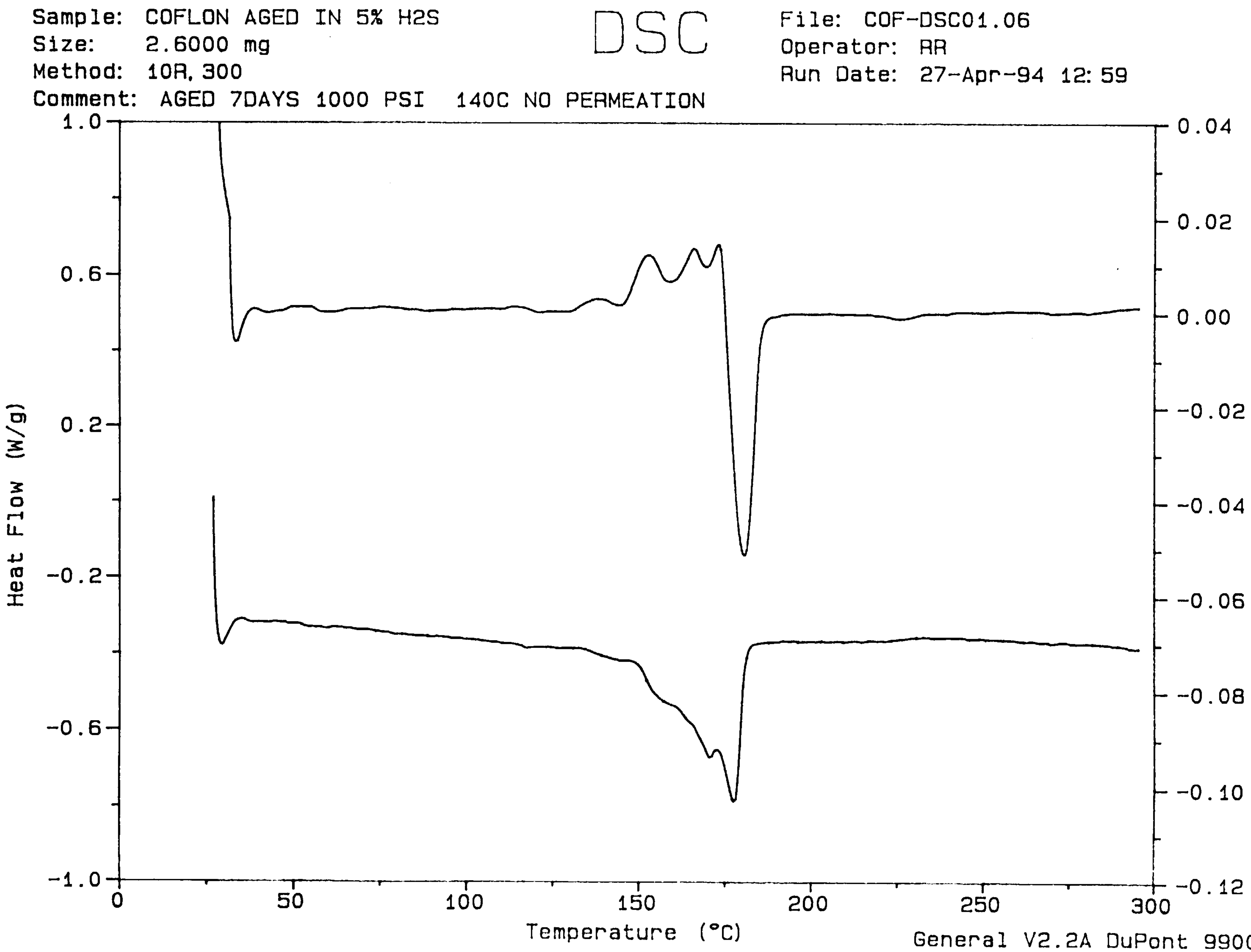
Sample: COFLON AGED IN 5% H2S
Size: 1.9000 mg
Method: 10R, 300
Comment: AGED 7DAYS 1000 PSI 120C/ CH4 PENETRANT / 1 DAY 2500 PSI 130C

DSC

File: COF-DSC01.07
Operator: RR
Run Date: 27-Apr-94 14:34



DSC V2.2A DuPont 9900

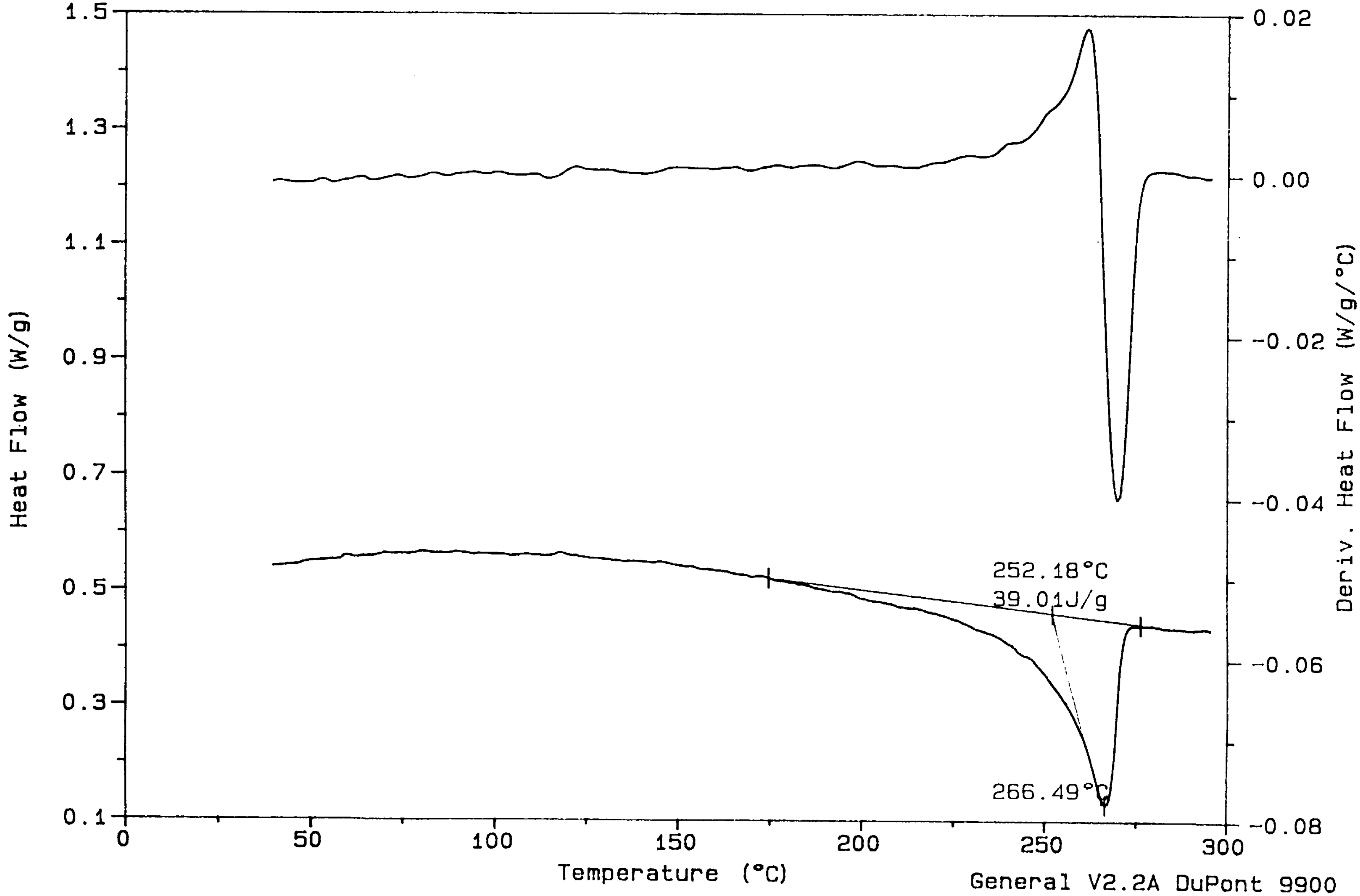


Sample: COFLON AGED IN 5% H2S
Size: 2.6000 mg
Method: 10R, 300
Comment: AGED 7DAYS 1000 PSI 140C NO PERMEATION
DSC
File: COF-DSC01.06
Operator: RR
Run Date: 27-Apr-94 12:59
Heat Flow (W/g)
1.0
0.6
0.2
-0.2
-0.6
-1.0
Deriv. Heat Flow (W/g/°C)
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
-0.12
0
50
100
150
200
250
300
Temperature (°C)
General V2.2A DuPont 9900

Sample: TEFZEL BASELINE
Size: 3.1000 mg
Method: 10R, 300

DSC

File: TEF-DSC01.04
Operator: RR
Run Date: 4-May-94 15: 15

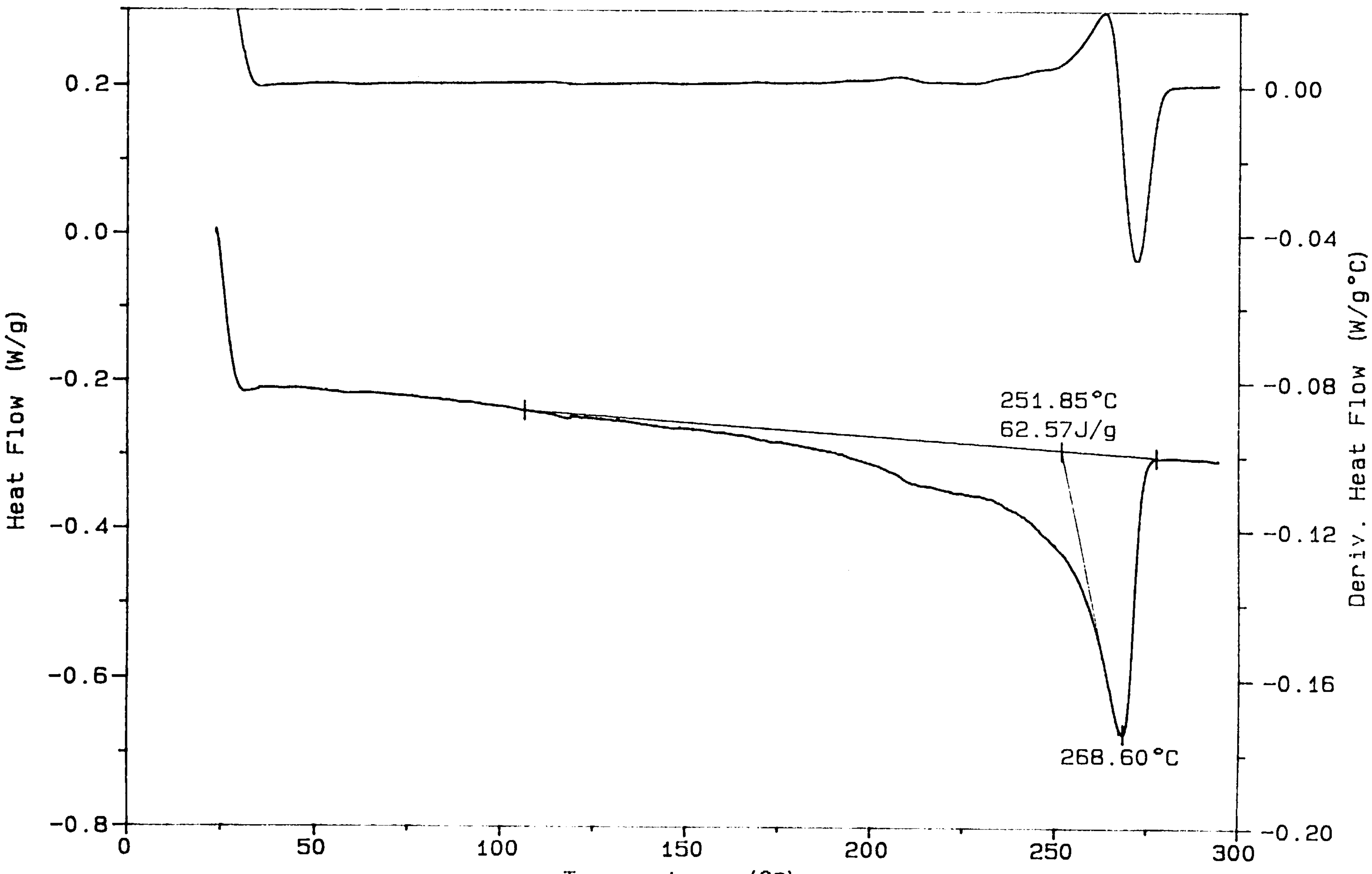


General V2.2A DuPont 9900

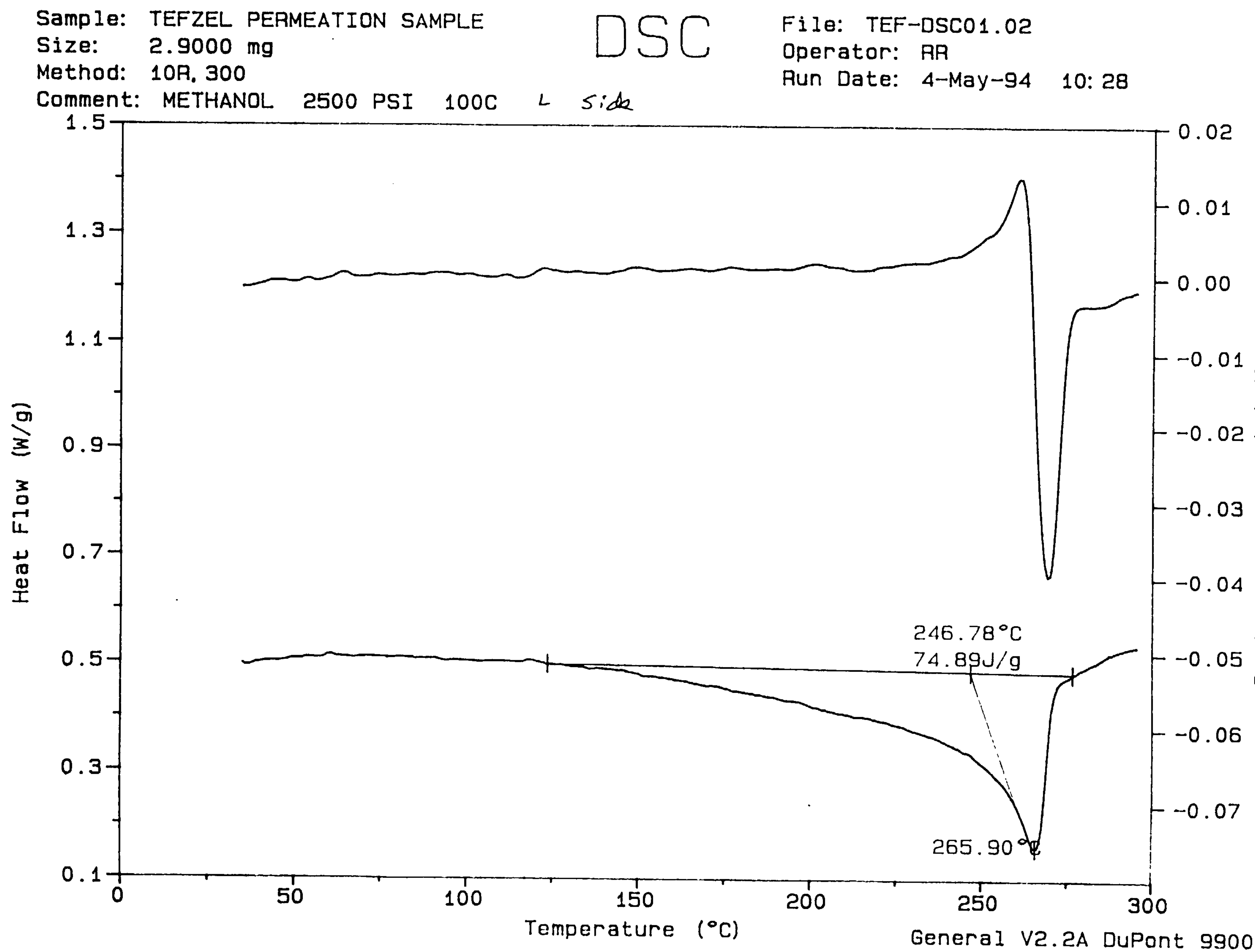
Sample: TEFZEL LIQUID ABSORPTION SAMP.
Size: 7.1000 mg
Method: 10 R 200
Comment: METHANOL 150C 3 DAYS NOMINALLY 15 BAR

DSC

File: TEF-DSC03.01
Operator: RR
Run Date: 3-Jun-94 16:42



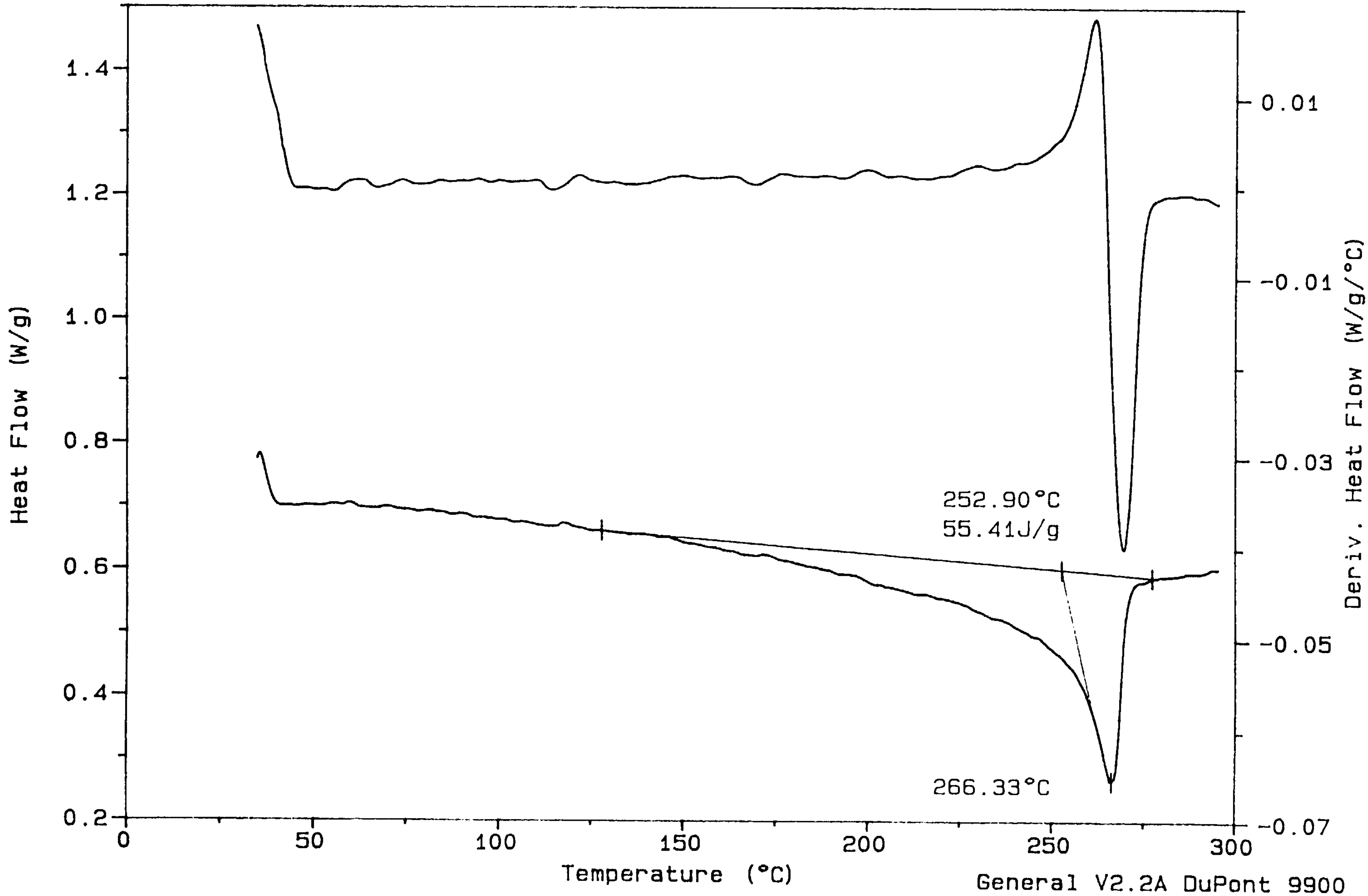
DSC V2.2A DuPont 9900


Sample: TEFZEL PERMEATION SAMPLE
Size: 2.9000 mg
Method: 10R, 300
Comment: METHANOL 2500 PSI 100C L side
DSC
File: TEF-DSC01.02
Operator: RR
Run Date: 4-May-94 10:28
Heat Flow (W/g)
1.5
1.3
1.1
0.9
0.7
0.5
0.3
0.1
0.02
0.01
0.00
-0.01
-0.02
-0.03
-0.04
-0.05
-0.06
-0.07
Deriv. Heat Flow (W/g/°C)
246.78°C
74.89J/g
265.90°C
0
50
100
150
200
250
300
Temperature (°C)
General V2.2A DuPont 9900

Sample: TEFZEL PERMEATION SAMPLE
Size: 2.9000 mg
Method: 10R, 300
Comment: METHANOL 2500 PSI 100C H side

DSC

File: TEF-DSC01.03
Operator: RR
Run Date: 4-May-94 12: 48



General V2.2A DuPont 9900

Table 2. High resolution ESCA data: Binding energies, atom percentages and peak assignments. (Binding energies were corrected to the binding energy of the $-(CH_2)_n-$ signal at 284.6 eV. Atom percentages were calculated from the high resolution data. Peak assignments were based on the binding energies of reference compounds).

Sample Description	C_1	C_2	C_3	C_4	C_5
Coflon aged in 5% H_2S					
Binding energy (eV)	284.6	286.0	287.5	288.8	?
Atom Percent	66.	5.5	1.7	2.2	?
Control Coflon (unaged)					
Binding energy (eV)	284.6	285.9	---	288.2	290.4
Atom Percent	4.4	25.	---	0.8	22.

Peak Assignments:

C_1 = $\underline{C}$-R (R = C, H)

C_2 = $\underline{C}$-OR, $\underline{C}$-N, $-(\underline{C}H_2-CF_2)_n-$

C_3 = R-$\underline{C}$=O, N-$\underline{C}$=O

C_4 = O=$\underline{C}$-OR

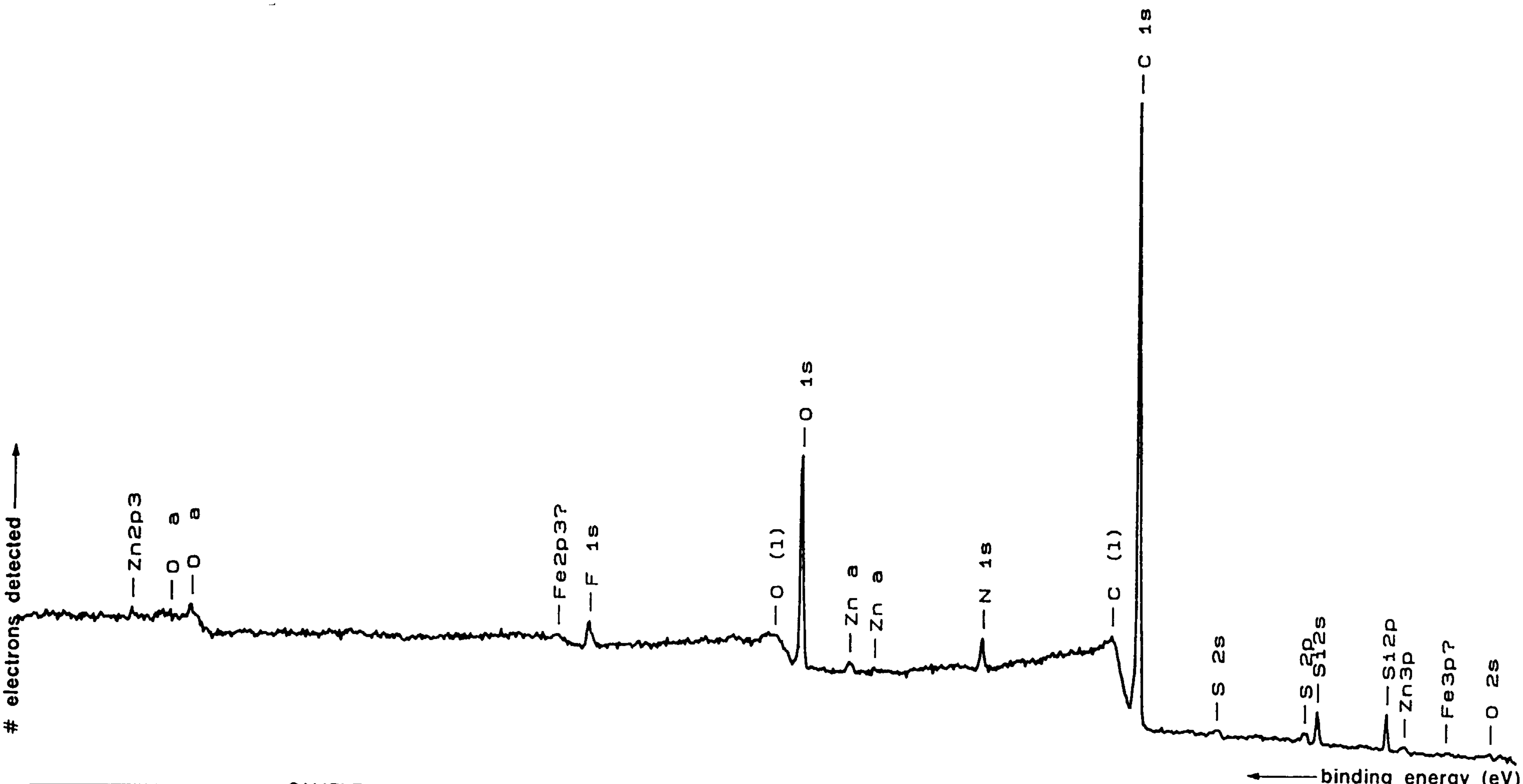
C_5 = $-(CH_2-\underline{C}F_2)_n-$

X-Ray Power: ______ Flood Gun: 5.0 Operator ERL Spot: 600 u Resolution: 4

VERTICAL SCALE 4000 COUNTS/INCH

ESCA SPECTRUM

CURSOR BINDING ENERGY



1100.0
UPPER BINDING ENERGY (eV)

SAMPLE:

COMMENTS:

Disc: B515

DATE 5/10/1994

DATA FILE # ERL1014A

Region 1

0.0
LOWER BINDING ENERGY (eV)

Coflon aged in 5% H2S for 7 days at 140C/1000 psi

6 # SCANS

CALIFORMS

SURFACE SCIENCE LABORATORIES 1206 Charleston Rd Mountain View California 94043 (415) 962-8767

Report #1014-0594

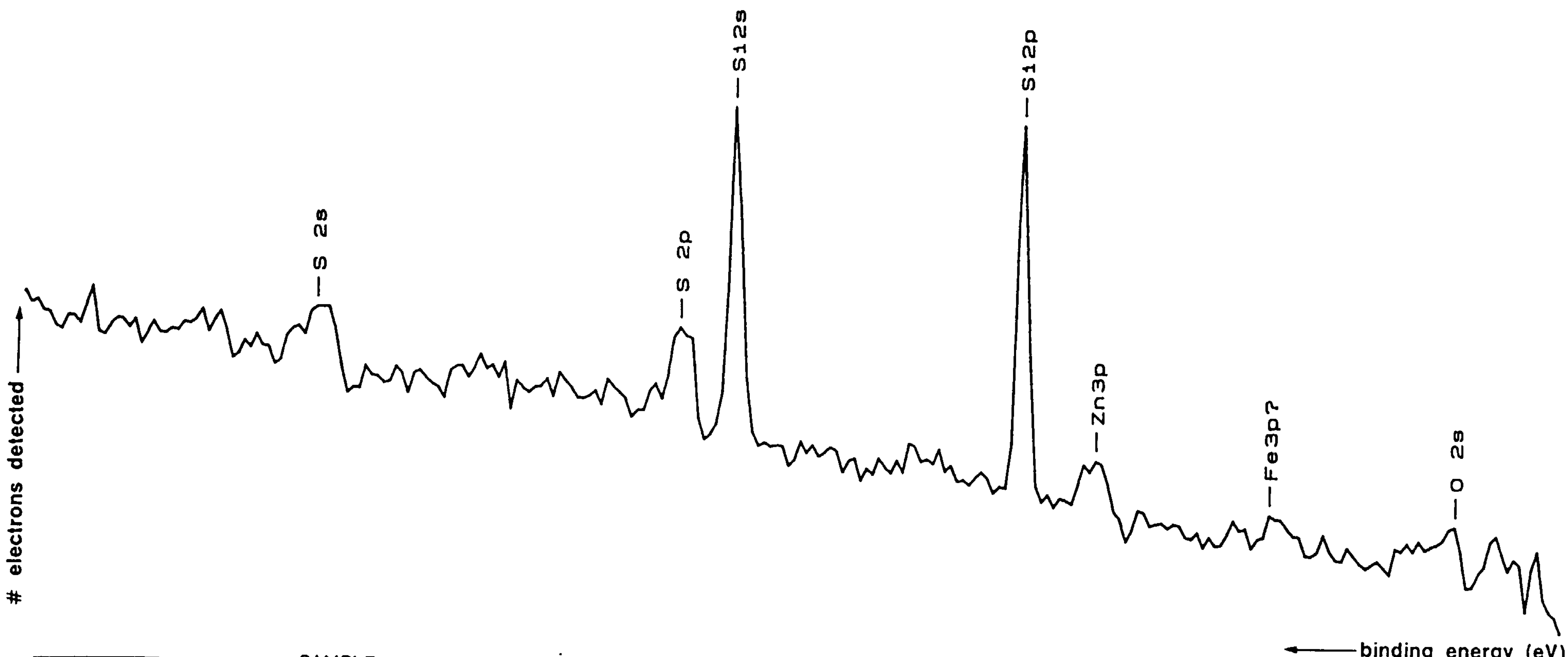
Spectrum #: 1

X-Ray Power: ______ Flood Gun: 5.0 Operator ERL Spot: 600 u Resolution: 4

VERTICAL SCALE 400 COUNTS/INCH

ESCA SPECTRUM

CURSOR BINDING ENERGY



275.0
UPPER BINDING ENERGY (eV)

SAMPLE:

COMMENTS: Disc: B515

DATE 5/10/1994

DATA FILE # ERL1014A

Region 1

0.0
LOWER BINDING ENERGY (eV)

Cof-lon aged in 5% H2S for 7 days at 140C/1000 psi

6 # SCANS

CALIFORMS

SURFACE SCIENCE LABORATORIES 1206 Charleston Rd. Mountain View California 94043 (415) 962-8767

Report #1014-0594

Spectrum #: 1-EXP

SURFACE SCIENCE

X-Ray Power: ______ Flood Gun: 5.0 Operator ERL Spot: 600 u Resolution: 2

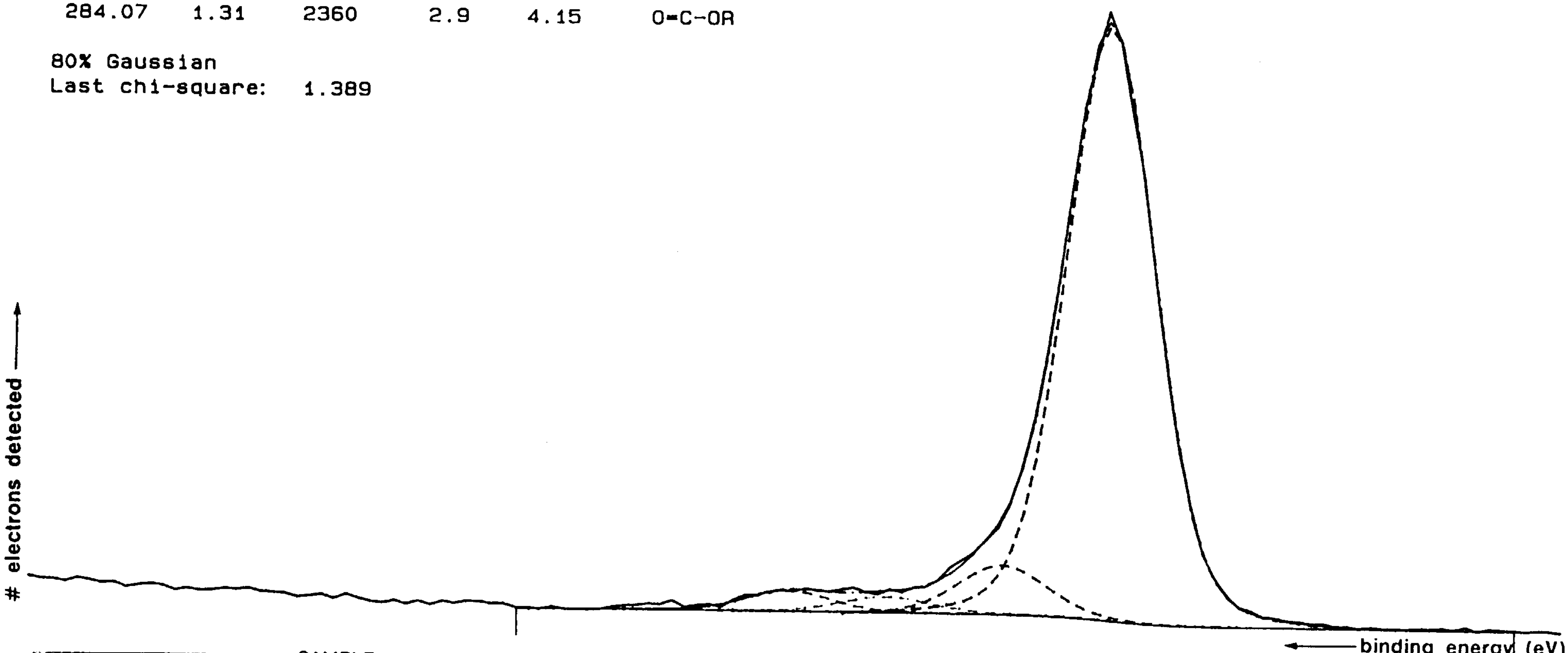
VERTICAL SCALE
2000
COUNTS/INCH

ESCA SPECTRUM

CURSOR BINDING ENERGY

Energy	Width	Area	%	Delta BE	
279.92	1.35	70498	87.6	0.00	C-R (R=C, H)
281.30	1.34	5864	7.3	1.38	C-OR, C-N
282.81	1.32	1774	2.2	2.89	R-C=O
284.07	1.31	2360	2.9	4.15	O=C-OR

80% Gaussian
Last chi-square: 1.389



294.0
UPPER BINDING ENERGY (eV)

SAMPLE:
COMMENTS: Disc: B515

DATE 5/10/1994
DATA FILE # ERL1014A
Region 2

274.0
LOWER BINDING ENERGY (eV)

Coflon aged in 5% H2S for 7 days at 140C/1000 psi

7 # SCANS
CALIFORNIA

SURFACE SCIENCE LABORATORIES 1206 Charleston Rd Mountain View California 94043 (415) 962-8767

Report #1014-0594
Spectrum #: 1A

X-Ray Power: ______ Flood Gun: 5.0 Operator ERL Spot: 600 u Resolution: 2

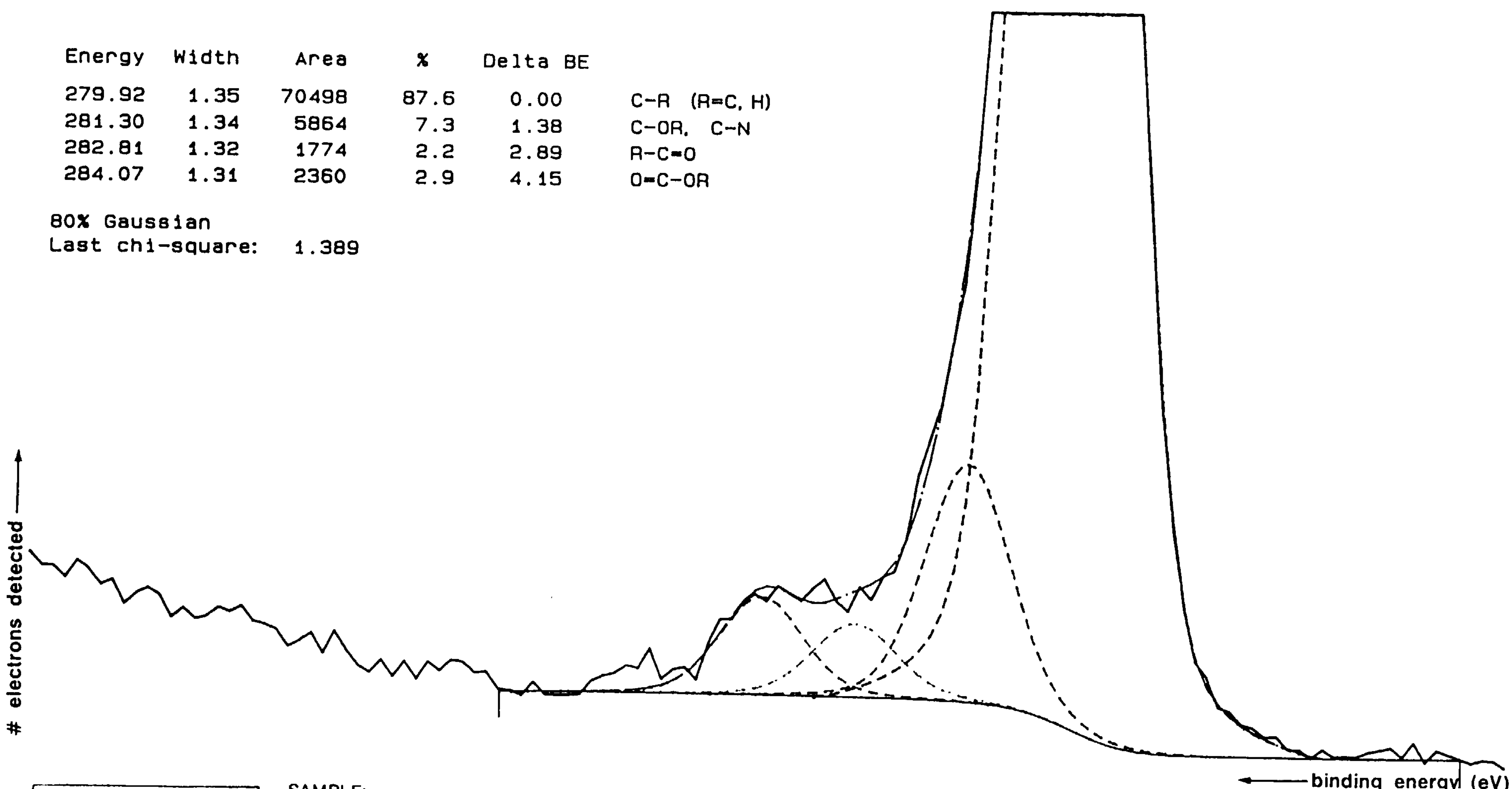
VERTICAL SCALE 400 COUNTS/INCH

ESCA SPECTRUM

CURSOR BINDING ENERGY

Energy	Width	Area	%	Delta BE	
279.92	1.35	70498	87.6	0.00	C-R (R=C, H)
281.30	1.34	5864	7.3	1.38	C-OR, C-N
282.81	1.32	1774	2.2	2.89	R-C=O
284.07	1.31	2360	2.9	4.15	O=C-OR

80% Gaussian
Last chi-square: 1.389



294.0 UPPER BINDING ENERGY (eV)

SAMPLE:

COMMENTS:

Disc: B515

DATE 5/10/1994

DATA FILE # ERL1014A

Region 2

274.0 LOWER BINDING ENERGY (eV)

Coflon aged in 5% H2S for 7 days at 140C/1000 psi

7 # SCANS

CALIFORMS

SURFACE SCIENCE LABORATORIES 1206 Charleston Rd Mountain View California 94043 (415) 962-8767

Report #1014-0594

Spectrum #: 1A-EXP

SURFACE SCIENCE

X-Ray Power: ______ Flood Gun: 5.0 Operator ERL Spot: 600 u Resolution: 4

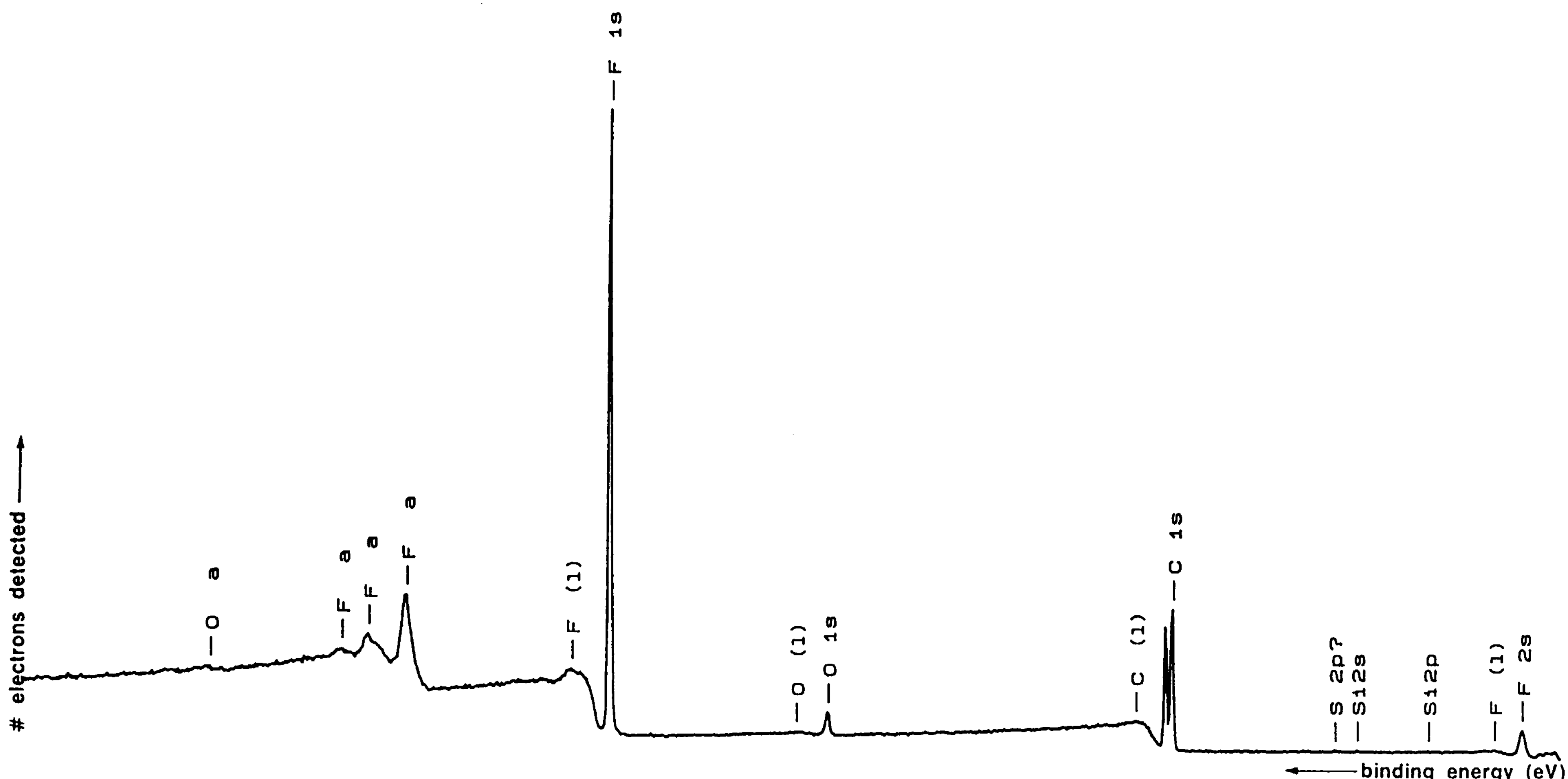
VERTICAL SCALE

10000

COUNTS/INCH

ESCA SPECTRUM

CURSOR BINDING ENERGY



1100.0

UPPER BINDING ENERGY (eV)

SAMPLE: DATE 5/10/1994

COMMENTS: Disc: B515 DATA FILE #ERL1014B

Region 2

Control Coflon (unaged)

0.0

LOWER BINDING ENERGY (eV)

6 # SCANS

CALIFORMS

Report #1014-0594

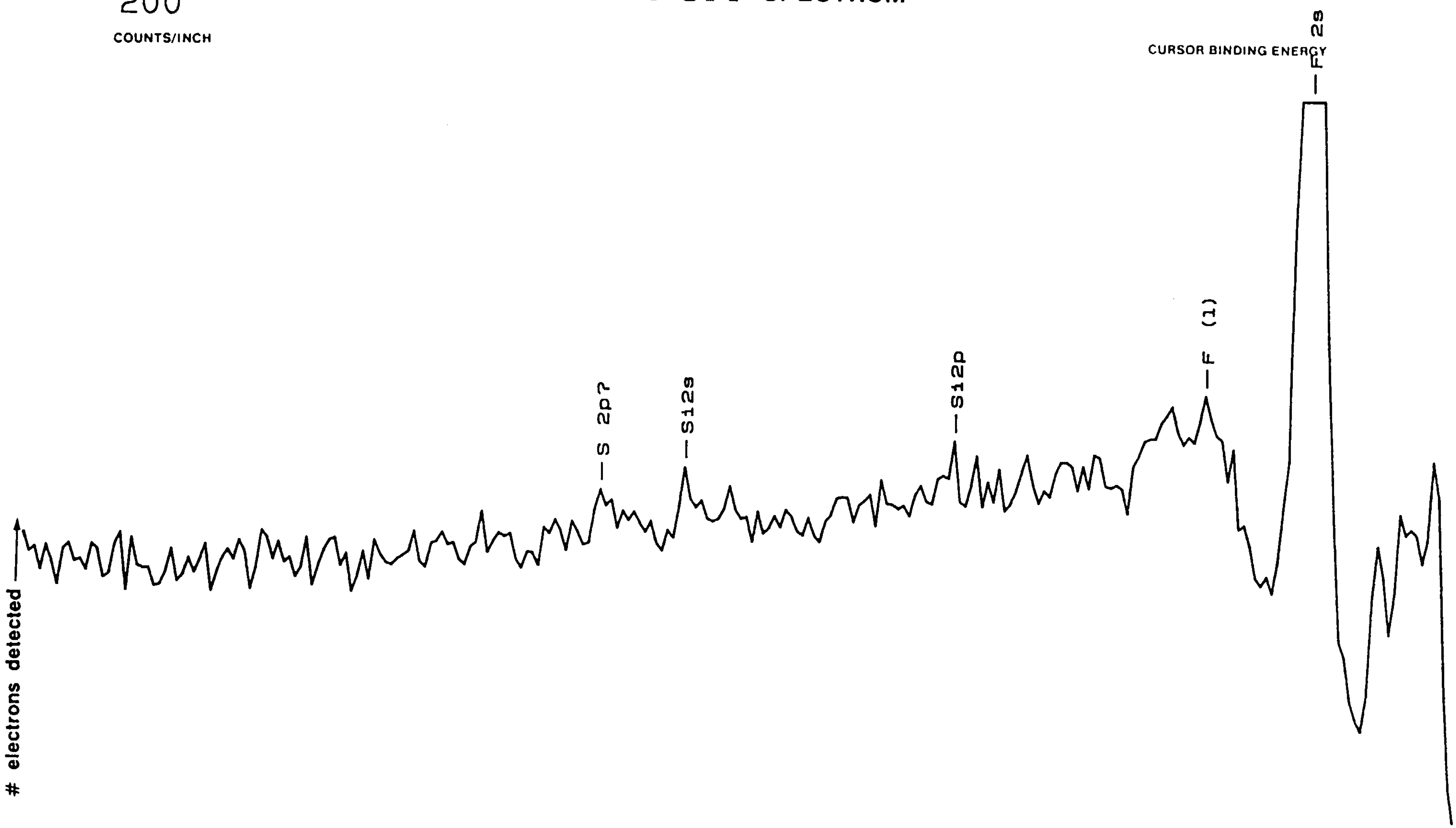
Spectrum #: 2

SURFACE SCIENCE LABORATORIES 1206 Charleston Rd. Mountain View California 94043 (415) 962-8767

X-Ray Power: ______ Flood Gun: 5.0 Operator ERL Spot: 600 u Resolution: 4

VERTICAL SCALE
200
COUNTS/INCH

ESCA SPECTRUM



275.0
UPPER BINDING ENERGY (eV)

SAMPLE:
COMMENTS: Disc: B515

DATE 5/10/1994
DATA FILE # ERL1014B
Region 2

Control Coflon (unaged)

0.0
LOWER BINDING ENERGY (eV)

6 # SCANS
CALIFORMS

SURFACE SCIENCE LABORATORIES 1206 Charleston Rd. Mountain View California 94043 (415) 962-8767

Report #1014-0594
Spectrum #: 2-EXP

SURFACE SCIENCE

X-Ray Power: ______ Flood Gun: 5.0 Operator ERL Spot: 600 u Resolution: 2

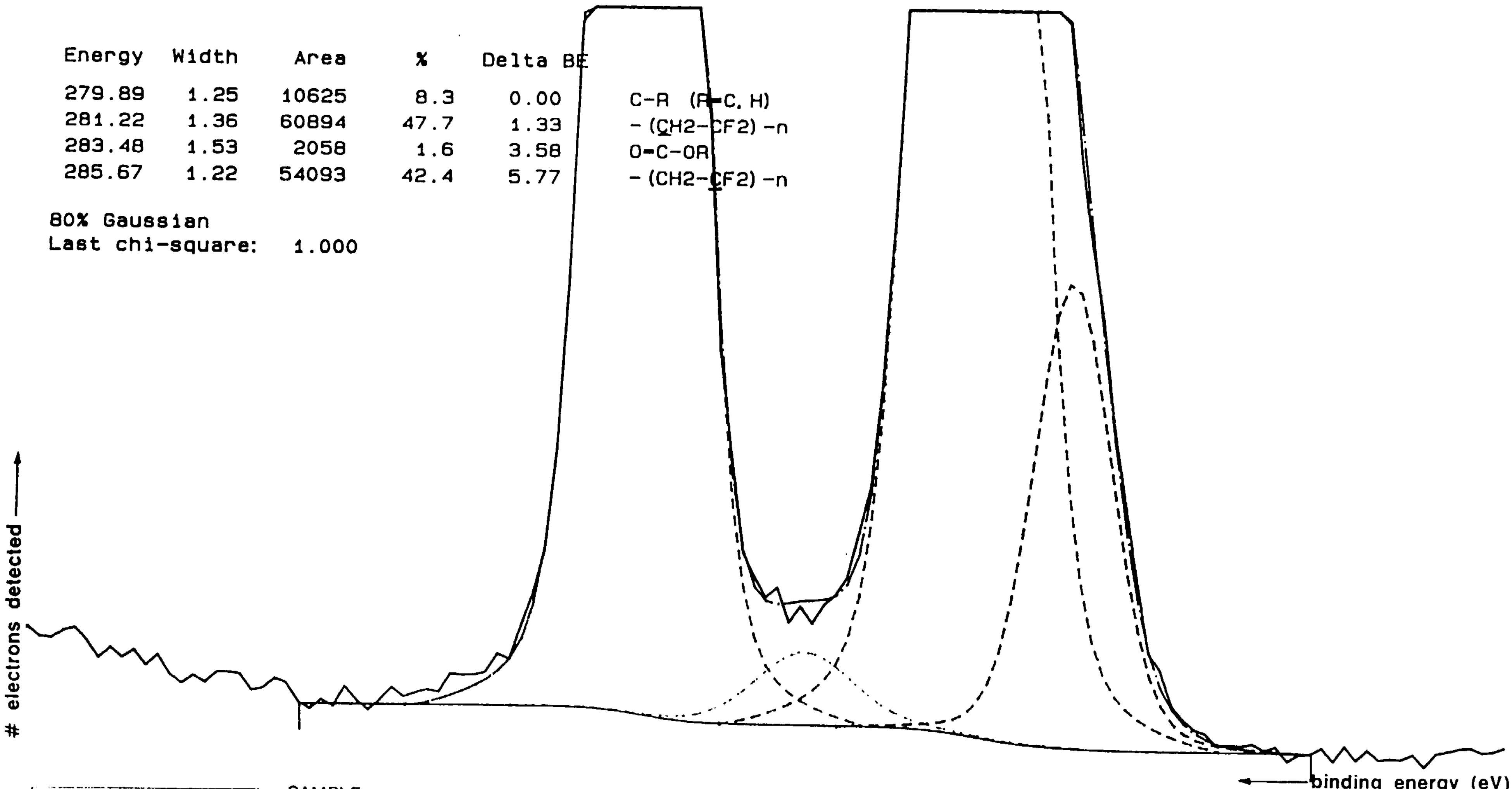
VERTICAL SCALE 400 COUNTS/INCH

ESCA SPECTRUM

CURSOR BINDING ENERGY

Energy	Width	Area	%	Delta BE	
279.89	1.25	10625	8.3	0.00	C-R (R=C, H)
281.22	1.36	60894	47.7	1.33	-(CH2-CF2)-n
283.48	1.53	2058	1.6	3.58	O=C-OR
285.67	1.22	54093	42.4	5.77	-(CH2-CF2)-n

80% Gaussian
Last chi-square: 1.000



294.0 UPPER BINDING ENERGY (eV)

SAMPLE:
COMMENTS:
Control Coflon (unaged)

Disc: B515

DATE 5/10/1994
DATA FILE # ERL1014B
Region 1

274.0 LOWER BINDING ENERGY (eV)

10 # SCANS

Report #1014-0594
Spectrum #:

SURFACE SCIENCE LABORATORIES 1206 Charleston Rd Mountain View California 94043 (415) 962-8767

X-Ray Power: ______ Flood Gun: 5.0 Operator ERL Spot: 600 u Resolution: 2

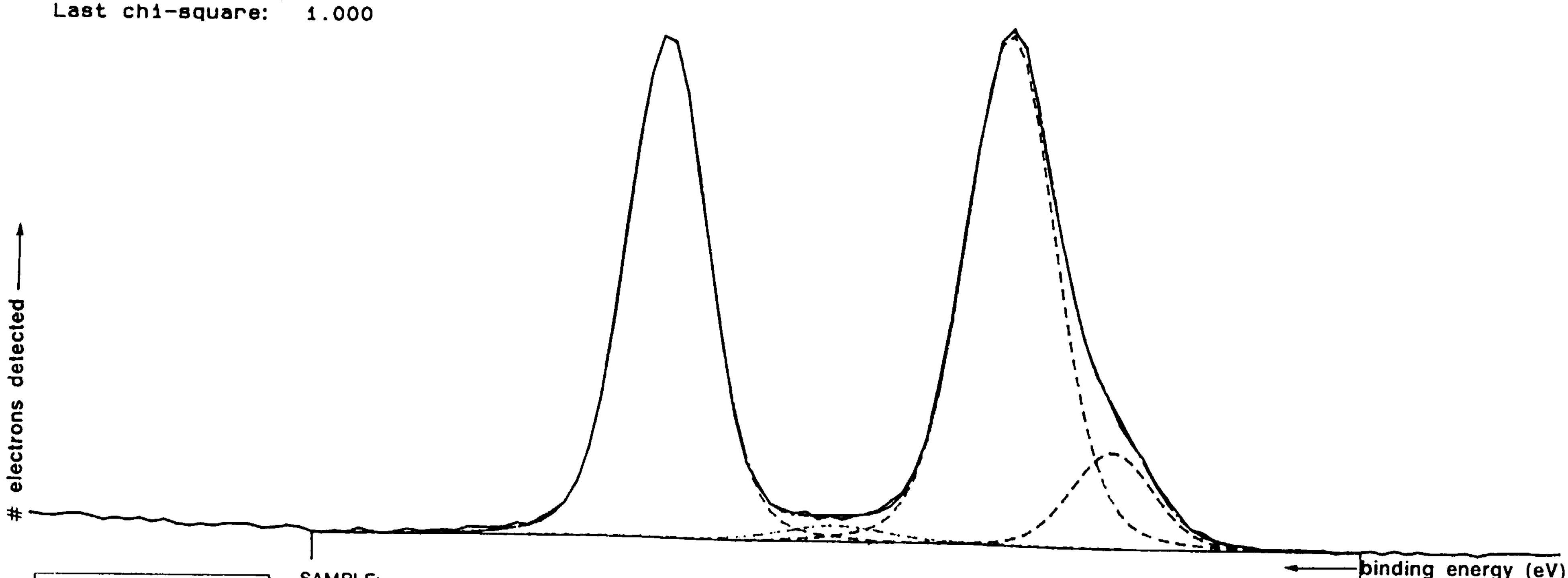
VERTICAL SCALE 2000 COUNTS/INCH

ESCA SPECTRUM

CURSOR BINDING ENERGY

Energy	Width	Area	%	Delta BE	
279.89	1.25	10625	8.3	0.00	C-R (R=C, H)
281.22	1.36	60894	47.7	1.33	-(C̲H2-CF2)-n
283.48	1.53	2058	1.6	3.58	O=C-OR
285.67	1.22	54093	42.4	5.77	-(CH2-C̲F2)-n

80% Gaussian
Last chi-square: 1.000



294.0 UPPER BINDING ENERGY (eV)

274.0 LOWER BINDING ENERGY (eV)

SAMPLE:

COMMENTS: Disc: B515

DATE 5/10/1994

DATA FILE # ERL1014B

Region 1

Control Coflon (unaged)

10 # SCANS

CALIFORMS

SURFACE SCIENCE LABORATORIES 1206 Charleston Rd. Mountain View California 94043 (415) 962-8767

Report #1014-0594

Spectrum #: 2r