The non-Anderson-Schulz-Flory distribution for the alkylbenzenes suggest that they were not made by successive chain growth of the alkylbenzenes. Rather, it appears that these compounds were individually made from Fischer-Tropsch paraffins and/or olefins with different carbon numbers.

The increase in the alkylbenzene concentration at carbon numbers C_{14} through C_{17}, C_{18} through C_{20} suggest that the tendency for the aromatization of linear Fischer-Tropsch products increases with carbon number.

The low concentration of alkylbenzenes at C_{14}, C_{18} and C_{22} may be explained by high selectivity for new ring formation to produce the polynuclear aromatics. For instance, at C_{14} most of the aromatics may be in the form of alkyl naphthalenes rather than octyl benzenes. Similarly, at C_{18} three-ring compounds like anthracene and phenantrene may be selectively formed compared to dodecyl benzene.

5.3.5.2.4.2 Analyses of Material Extracted from Modified Ruthenium Catalyst 4966-180 Used in Run 46 and from Unmodified Ruthenium Catalyst 4966-198 Used in Run 47

The soxhlet extraction steps were conducted by the procedure used for Run 39 catalyst, as explained in the previous section. Percent materials removed in each extraction from Catalyst 4966-180 and Catalyst 4966-198 are summarized in Table 5-62. After extractions were completed, a much higher Leco carbon value was measured on the unmodified catalyst.

Table 5-62

Materials Removed by Soxhlet Extraction from Modified and Unmodified Ruthenium Catalysts

After Extraction with	Modified Catalyst 4966-180 Run 46	Unmodified Catalyst 4966-198 Run 47
Cyclohexane	57.9%	50.4%
Toluene	2%	3%
Methylene Chloride/Methanol	3%	3%
Leco Carbon After Methylene Chloride/Methanol	1.46	5.41

Only the extracts obtained with methylene chloride/methanol were analyzed by HRMS and fluorescence.

According to HRMS analysis (Table 5-63), the majority of the extract material, from both catalysts, was saturated and oxygenated hydrocarbons.

Table 5-63

Analyses of Soxhlet Extracts from Modified and Unmodified Ruthenium Catalysts by HRMS and Fluorescence

Detected Compounds	Amount %		Carbon Number Range Detected
	Modified Ruthenium Catalyst 4966-180 (Run 46)	Unmodified Ruthenium Catalyst 4966-198 (Run 47)	
Saturated Hydrocarbons C_NH_{2N+2}	25-70%	47-82%	
Oxygenated Hydrocarbons mostly $C_NH_{2N}O_2$ (acids and/or esters, most likely)	30-75%	15-50%	N $\leq$35
Aromatic Hydrocarbons C_NH_{2N-Z} (Z = 6, 8, 12, 14)	Much less than in Run 47	<3%	N = 16-29
Aromatic Oxygenates $C_NH_{2N-Z}O$ (Z = 6,8)			N = 6-9 (Run 46) N = 18-26 (Run 47)
Aromatic Dioxygenates $C_NH_{2N-6}O_2$			
Polynuclear Aromatics (3-5 rings)	Not Detected	Detected	

The oxygenates made up 30-75% of the extract from the modified catalyst and 15-50% of the extract from the unmodified catalyst. They were mostly $C_NH_{2N}O_2$-type compounds and could be long chain olefinic oxygenates and/or cyclic oxygenates with $\leq$35 carbon numbers. Based on the strong fragmentation peak at m/z = 60.0211, they appear to be mainly acids and/or esters. The remaining oxygenated species may be alcohols.

The alkylbenzene distribution for the unmodified ruthenium catalyst is illustrated in Table 5-64. These results were consistent with the ones obtained with Al_2O_3-TiO_2 supported-ruthenium Catalyst 4966-124. The tendency to form the aromatic, apparently from Fischer-Tropsch paraffinic or olefinic linear compounds increased with carbon number. The peak intensities at C_{18}, C_{22} and C_{26} were low, probably suggesting selective formation of polynuclear aromatics from alkyl benzenes at these carbon numbers.

Table 5-64

Alkylbenzenes in Run 47

C No.	Peak Intensity
C_{16}	575
C_{17}	316
C_{18}	285
C_{19}	380
C_{20}	154
C_{21}	179
C_{22}	153
C_{23}	216
C_{24}	118
C_{25}	121
C_{26}	27
C_{27}	116
C_{28}	128
C_{29}	216

Aromatics amounted to less than 3% of the total amount of material extracted from the unmodified Catalyst 4966-198, while it was much less for the modified Catalyst 4966-180. Aromatic hydrocarbons of the type C_NH_{2N-Z} (Z = 6, 8, 12, 14), aromatic oxygenates of the type $C_NH_{2N-Z}O$ (Z = 6, 8) and aromatic dioxygenates of the type $C_NH_{2N-6}O_2$ were detected. The carbon number range for detected aromatic oxygenates were 6-9 for the modified Catalyst 4966-180 and 18-26 for the unmodified Catalyst 4966-198.

Fluorescence analysis of the two extracts are in Figure 5-335. Polynuclear aromatics (PNA) with 3-5 rings were detected at 390, 440 and 460 nm only with the unmodified Catalyst 4966-198. The increase in background with increase in wavelength for the modified Catalyst 4966-180 is believed to be due to the interference from Fischer-Tropsch wax and oxygenates and not the PNA's.

The long chain olefinic and/or cyclic oxygenates removed from used catalysts during extraction with methylene chloride/methanol may be the XPS-detected carbon that was bound to oxygen.

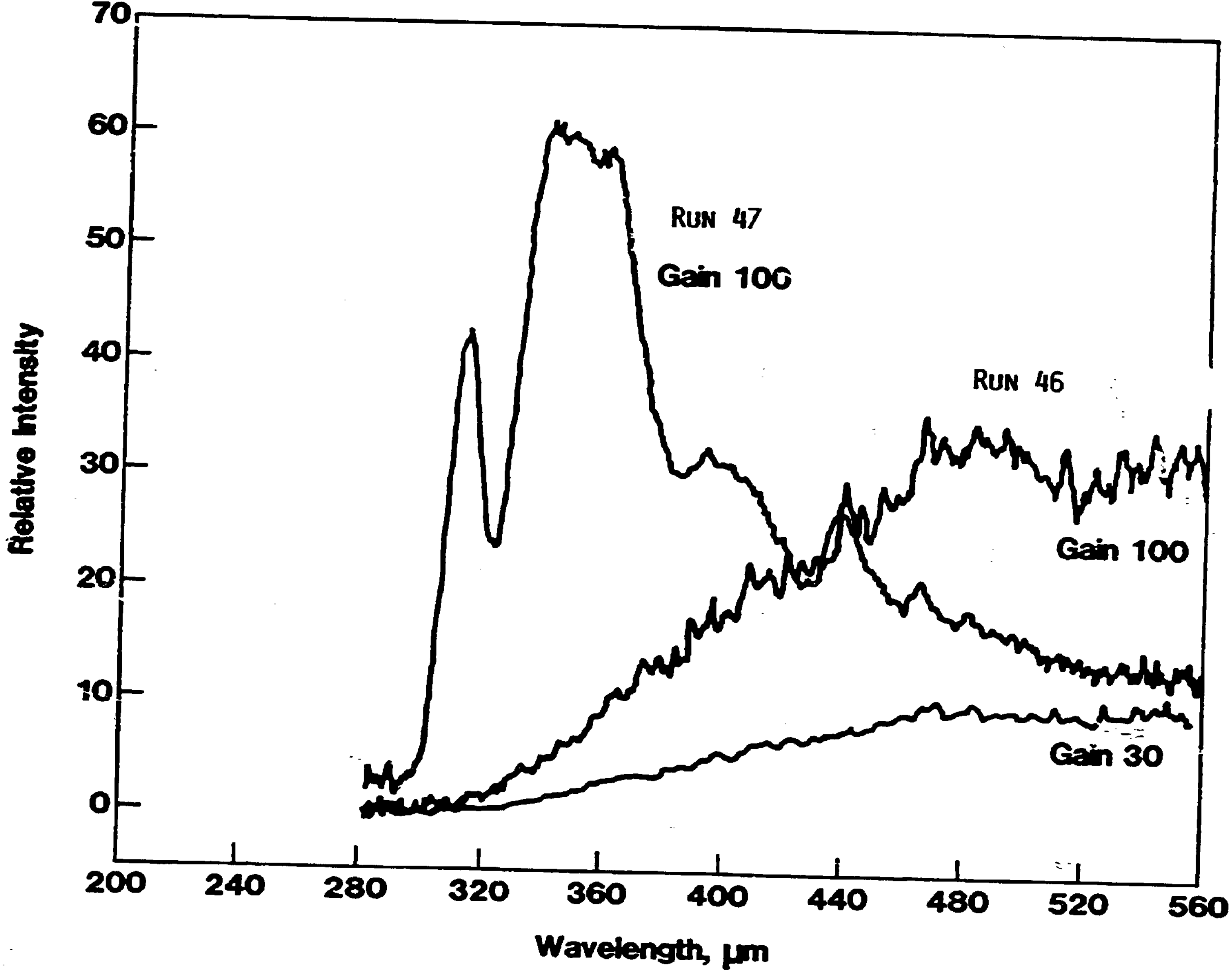
Although relatively small amounts of aromatics and polynuclear aromatics were detected in extract solutions, these compounds may be present in high concentration on the catalyst surface, but may be hard to remove with the extraction techniques used. High aromatic concentration would make the catalyst surface graphitic. Since the C 1s binding energy differences between graphite and hydrocarbon are small, XPS measurements do not provide clear evidence about the amount of polynuclear aromatics on the catalyst surface.

5.3.5.2.5 Burning Characteristics of Carbon on Used Catalysts

5.3.5.2.5.1 Establishment of DSC and TGA Experimental Procedures with Catalyst 4966-124 Tested in Run 39

In an attempt to establish coke characterization procedures for used catalysts by examining coke's burning characteristics, Al_2O_3-TiO_2 supported-ruthenium Catalyst 4966-124 tested in Run 39 was analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) after various soxhlet extraction steps. The reactor inlet portion of the used catalyst was used for these measurements.

Figure 5-335. Fluorescence Spectra for Methylene Chloride/Methanol Extracts from Modified Ruthenium Catalyst 4966-180 Tested in Run 46 and from Unmodified Ruthenium Catalyst 4966-198 Tested in Run 47



In DSC experiments, the used catalyst was heated from room temperature to 625°C at 5°C/min under air flow and the heat flow to or from the catalyst was measured. A maximum in the DSC curve indicates the occurrence of an exothermic reaction, like burning of coke. A minimum in the DSC curve indicates the occurrence of an endothermic reaction, like volatilization of ruthenium oxide.

In TGA experiments, the percent weight loss from the used catalyst is measured as the catalyst is heated to 625°C at 5°C/min under air flow. The TGA experiment also provides the derivative of the catalyst weight loss with respect to time. A maximum in the derivative curve illustrates the temperature at which the rate of weight loss becomes maximum.

The wax extracted from the reactor inlet portion of Catalyst 4966-124 tested in Run 39 started to burn at about 200°C according to a TGA experiment (Figure 5-336). Over 60% of the weight was lost by the time the temperature reached 300°C. The rest of the wax burned between 300 and 500°C.

The onset temperature for burning of wax was the same when the wax was inside the catalyst pores, as is illustrated by the TGA and DSC experiments with used Catalyst 4966-124 before soxhlet extraction (Figures 5-337 and 5-338). This sample had 56% wax according to soxhlet extraction measurements previously discussed. However, the same set of experiments also indicate that, in addition to the Fischer-Tropsch wax, the used catalyst had a second type of carbon which started to burn at about 275°C, with a DSC maxima at 345°C. Further analyses were done with soxhlet extracted catalyst in order to examine more closely this second type of carbon, which will be, from now on, referred to as coke.

TGA of used Catalyst 4966-124 after extraction with cyclohexane indicated that substantial weight loss did not essentially occur below 300°C. The ~2% weight loss between room temperature and 100°C may be explained by water

Figure 5-336. TGA of Wax Extracted from Catalyst 4966-124

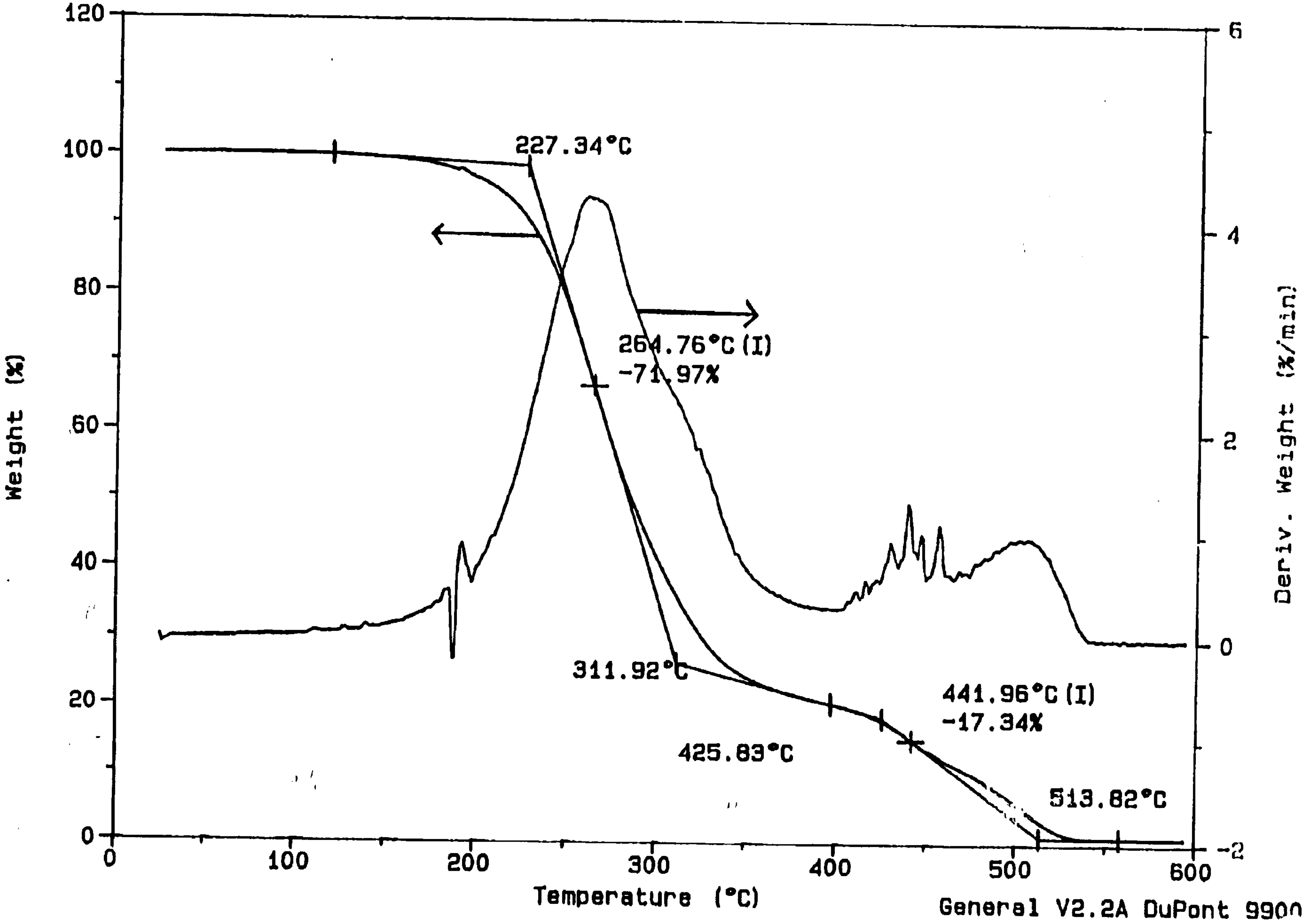


Figure 5-337. TGA of Used Catalyst 4966-124 Before Soxhlet Extraction

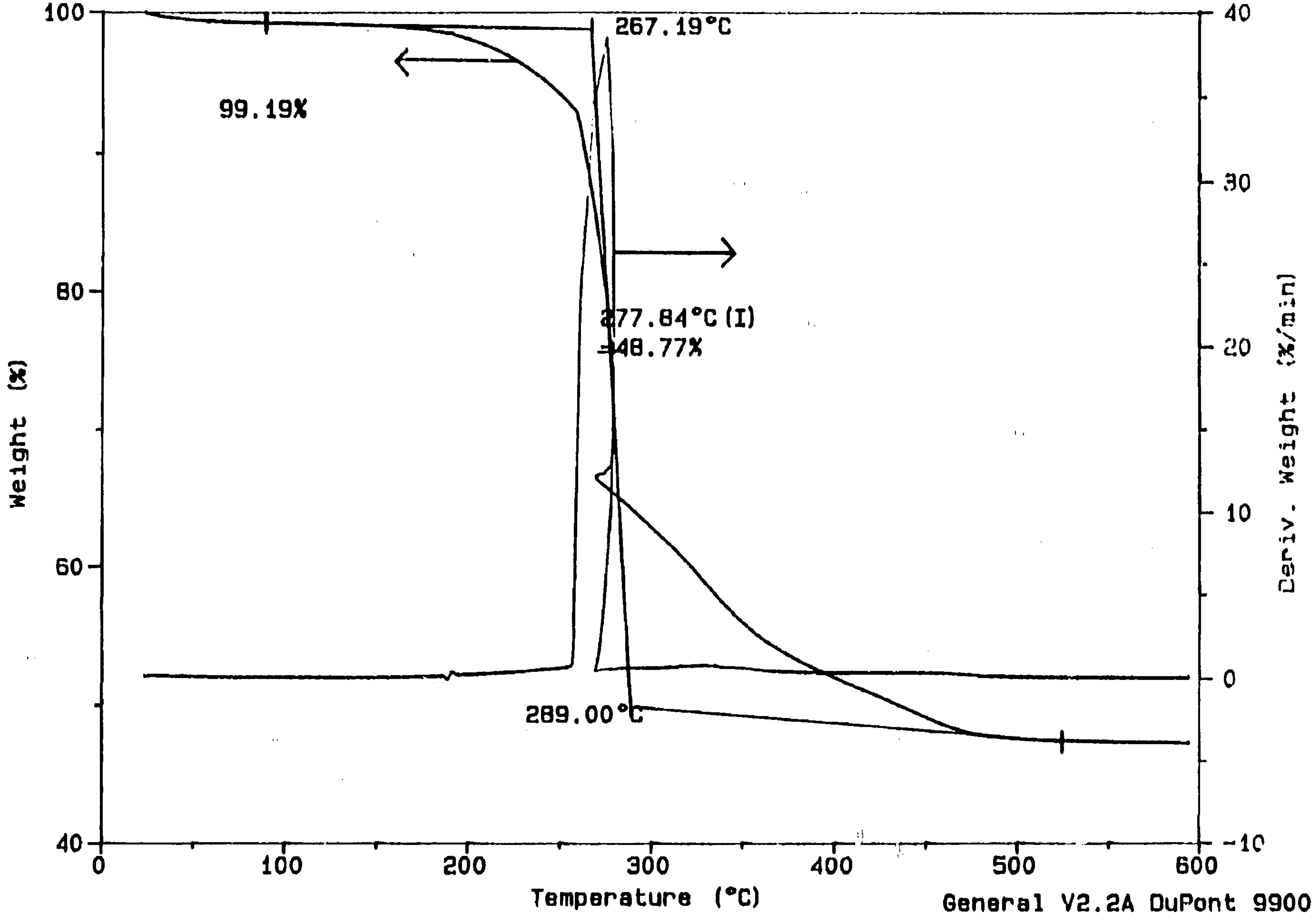
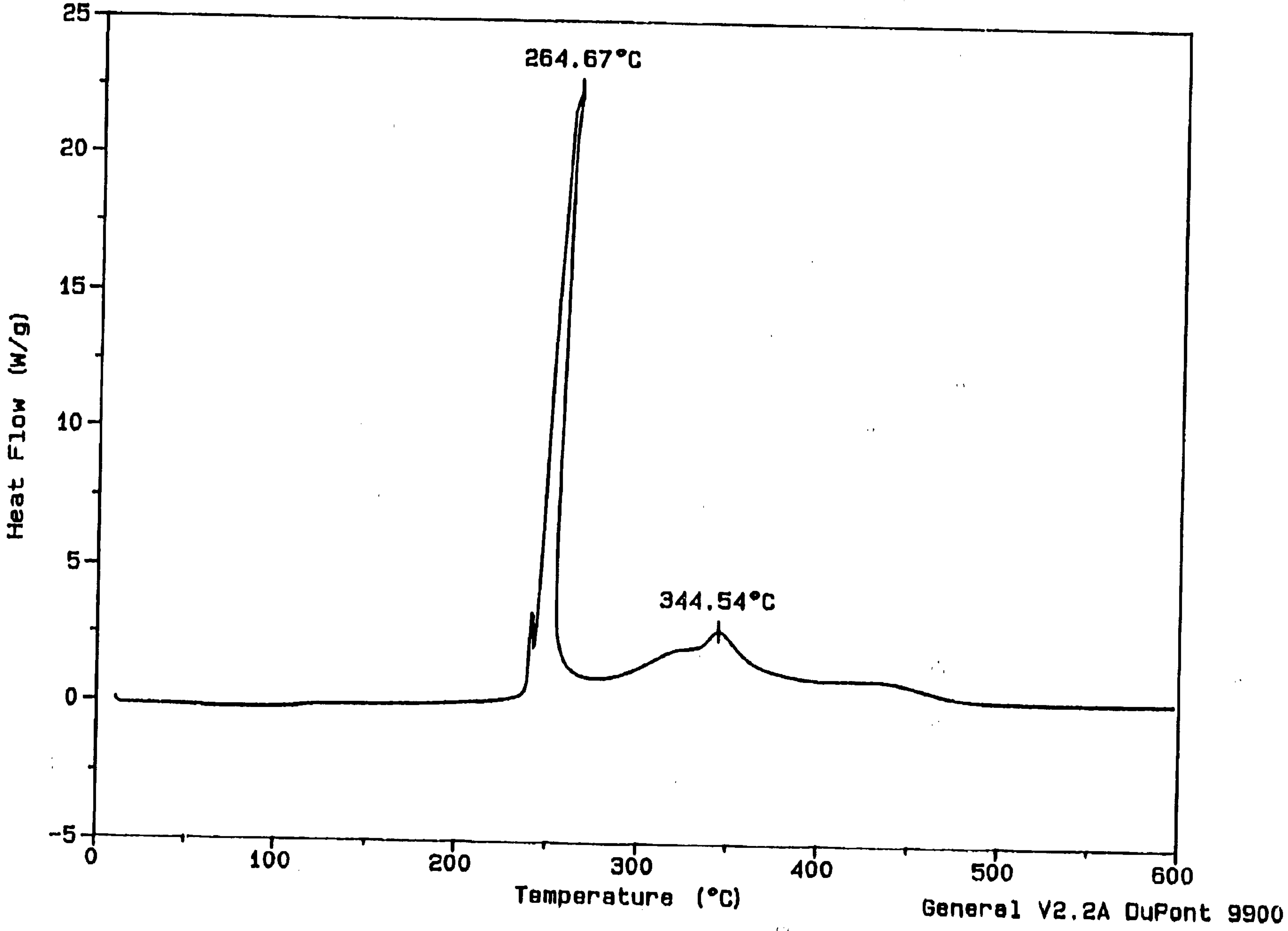


Figure 5-338. DSC of Used Catalyst 4966-124 Before Soxhlet Extraction



evolution from the sample. This result may indicate that the overwhelming majority of the wax was removed during soxhlet extraction with cyclohexane (Figure 5-339).

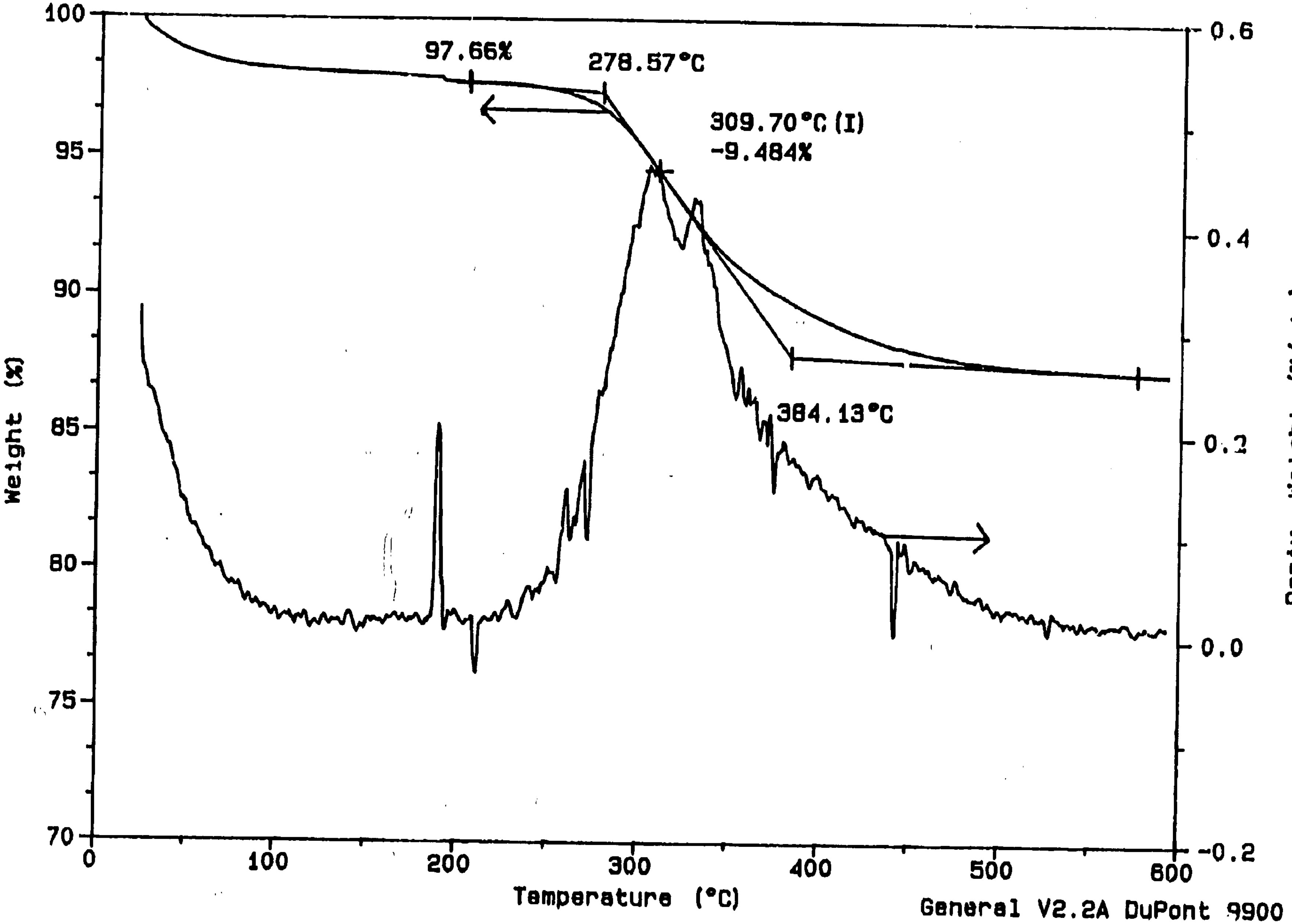
The 9.5% weight loss that occurred between 200°C and 500°C is slightly higher than the % Leco carbon measured on this sample. The balance can be explained by hydrogen in coke and also by further water evolution. According to DSC of the same sample, there were two unresolved peaks; one at about 290°C and the other at 324°C (Figure 5-340).

Subsequent TGA measurements after soxhlet extraction with toluene and with methylene chloride/methanol showed only small differences in weight loss compared to the cyclohexane extracted sample, indicating that only small amounts of material were removed with toluene and with methylene chloride/methanol (Figures 5-341 and 5-342). Nevertheless, there was a noticeable decrease in the DSC maximum which decreased from 324°C with cyclohexane extracted sample to 311°C with methylene chloride/methanol extracted sample (Figures 5-343 and 5-344). Also, the lower temperature peak decreased significantly in intensity.

5.3.5.2.5.2 DSC and TGA Analyses with Modified Ruthenium Catalyst 4966-180 After Use in Run 46 and with Unmodified Ruthenium Catalyst 4966-198 After Use in Run 47

The DSC of unmodified ruthenium Catalyst 4966-198 shows one DSC maximum at 346°C and a secondary maximum at about 320°C after cyclohexane extraction. Further extraction with toluene and with methylene chloride/methanol shifted the DSC maximum to 332°C and caused disappearance of the secondary maxima. The DSC minimum at 515-520°C may be explained by volatization of ruthenium via the volatile ruthenium tetroxide species (Figure 5-345).

Figure 5-359. TGA of Used Catalyst 4966-124 After Soxhlet Extraction with Cylcohexane



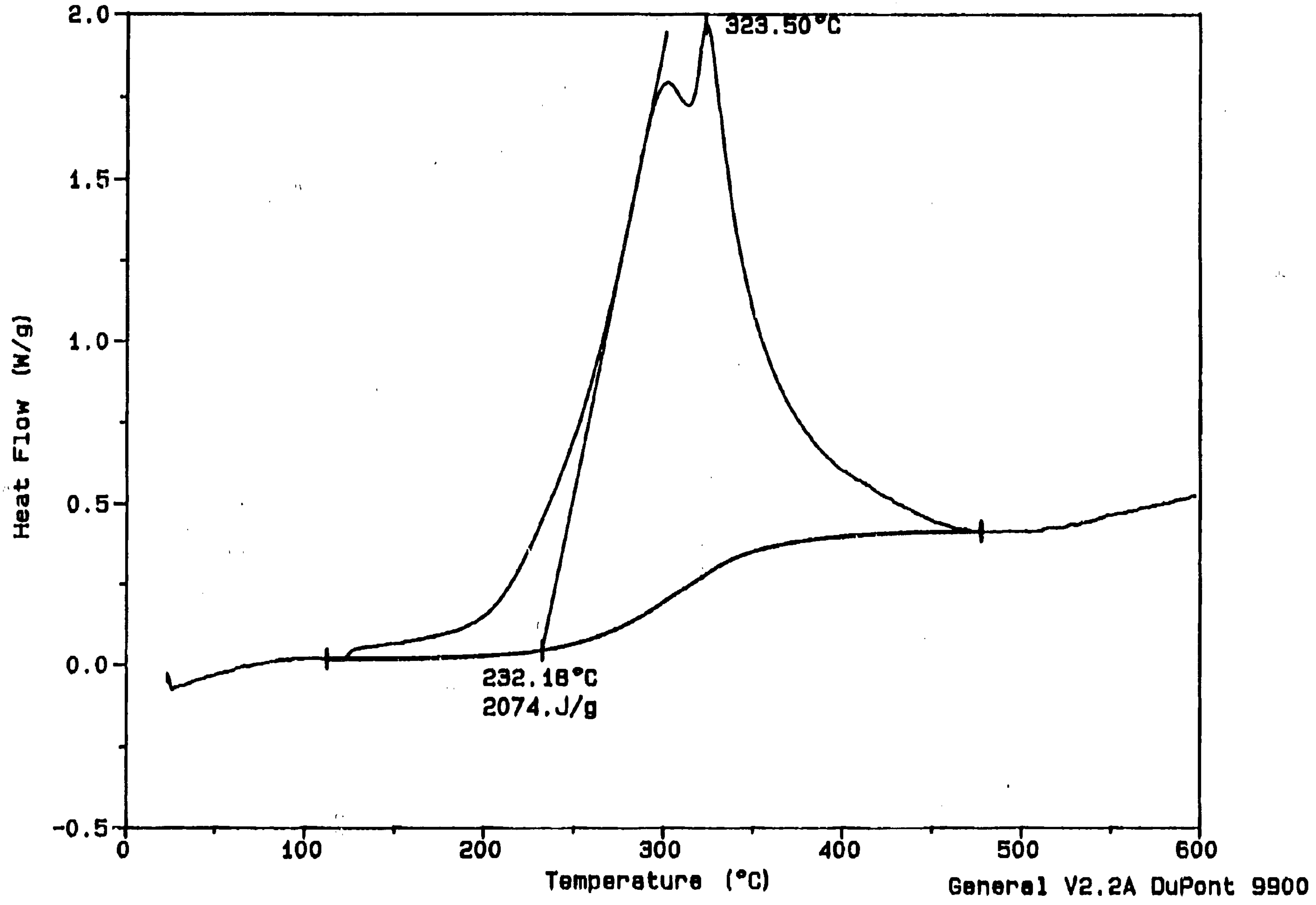


Figure 5-340. DSC of Used Catalyst 4966-124 After Soxhlet Extraction with Cyclohexane

Figure 5-341. TGA of Used Catalyst 4966-124 After Soxhlet Extraction with Toluene

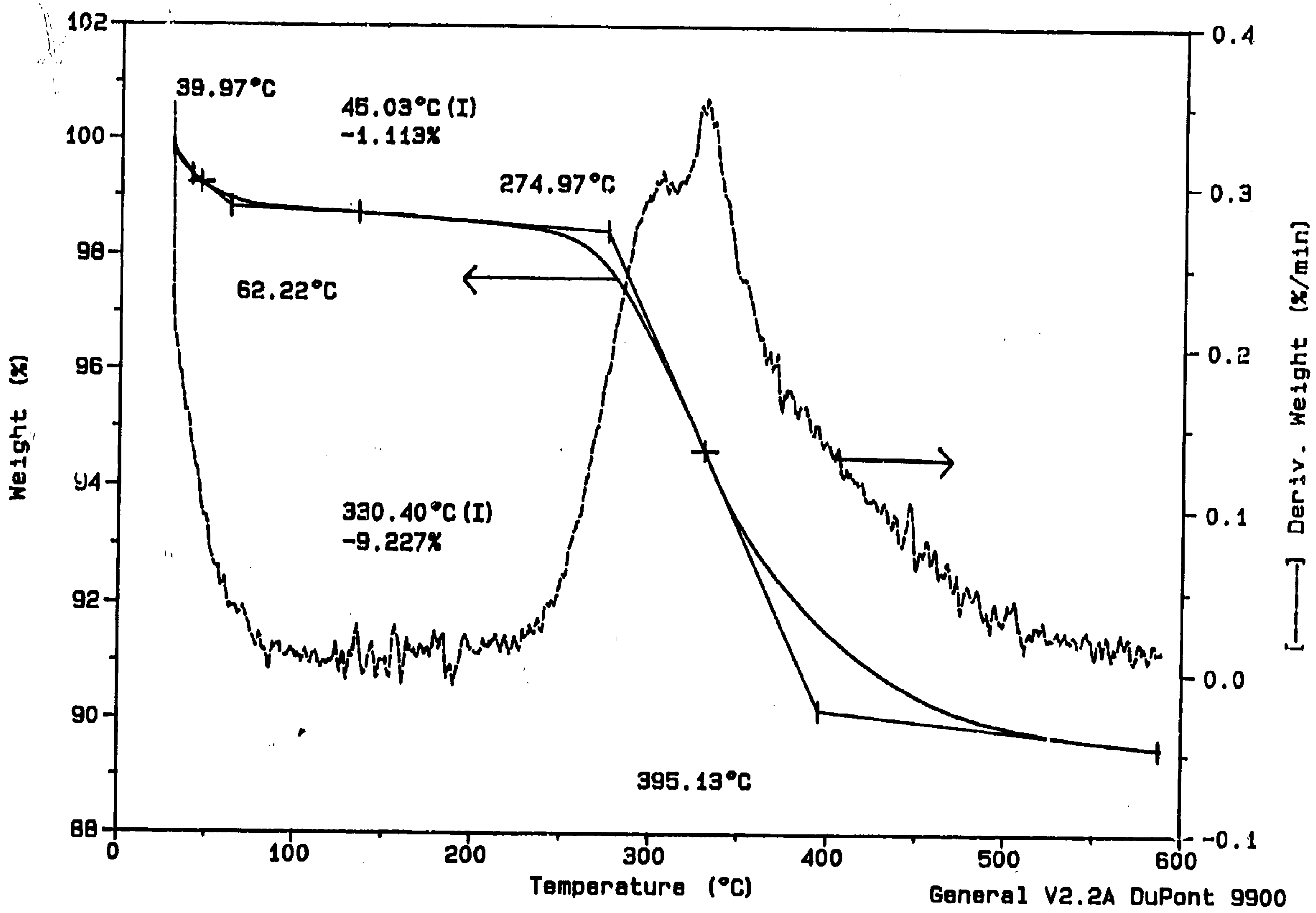


Figure 5-342. TGA of Used Catalyst 4966-124 After Soxhlet Extraction with Methylene Chloride/Methanol

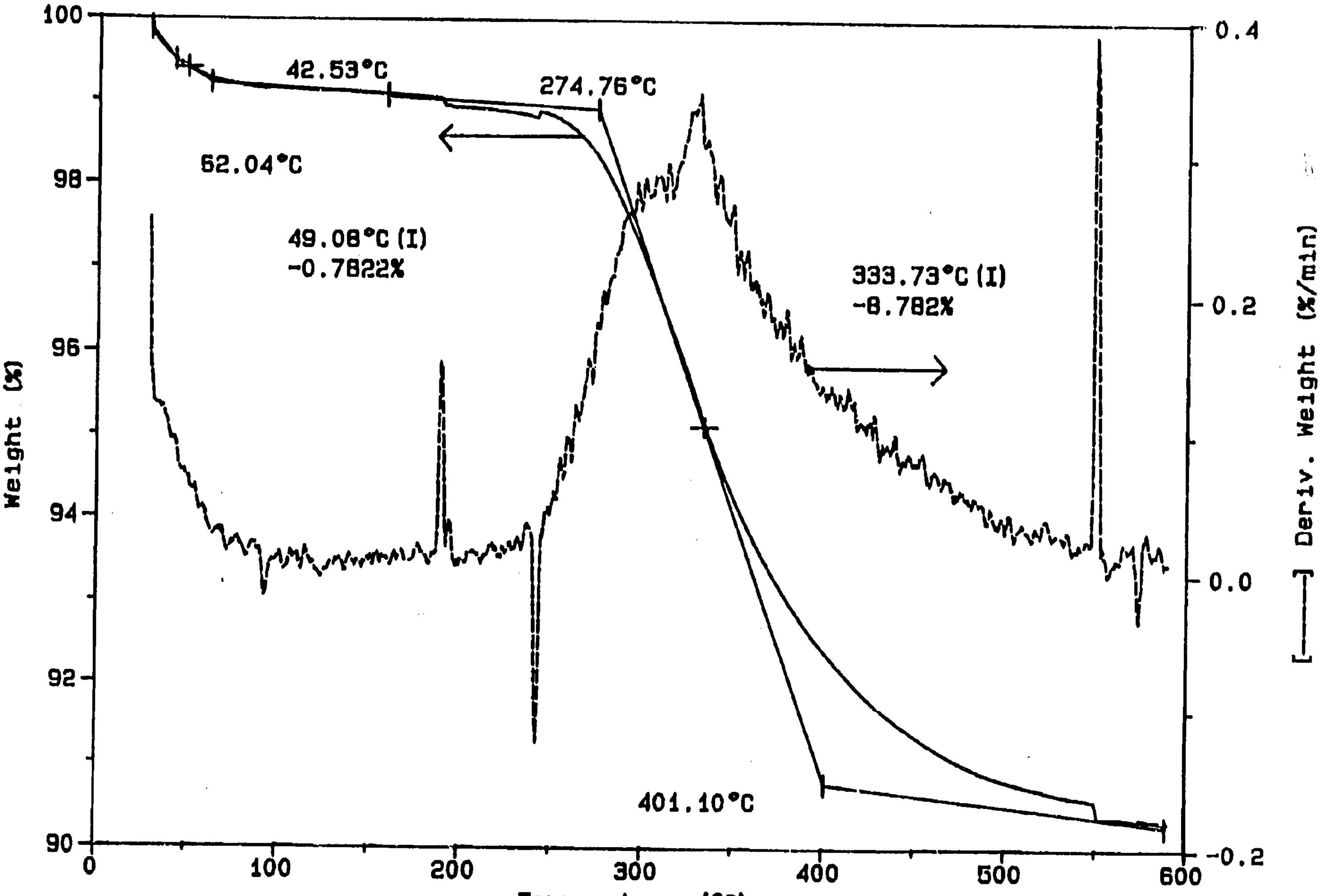


Figure 5-343. DSC of Used Catalyst 4966-124 After Soxhlet Extraction with Toluene

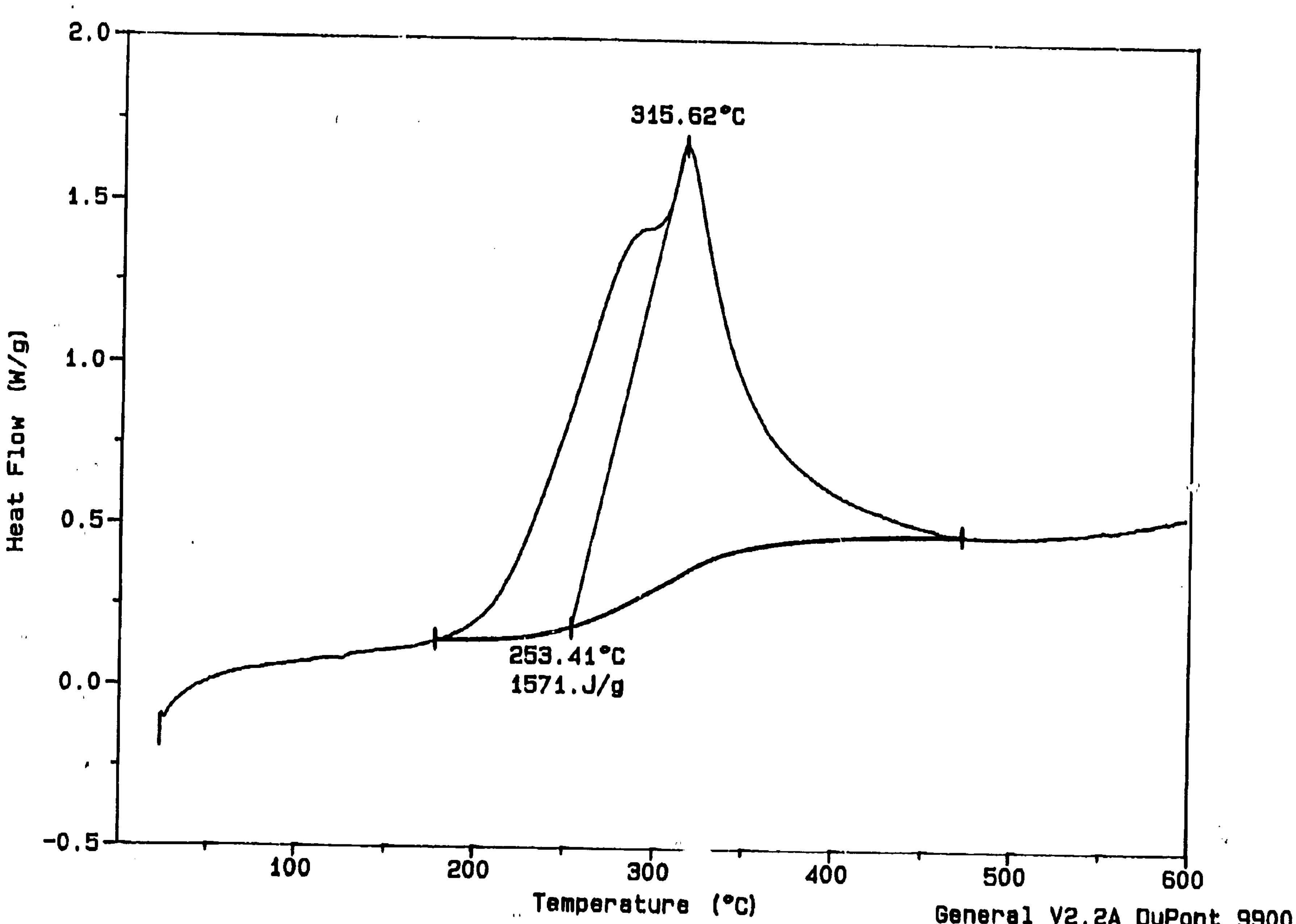


Figure 5-344. DSC of Used Catalyst 4966-124 After Soxhlet Extraction with Methylene Chloride/Methanol

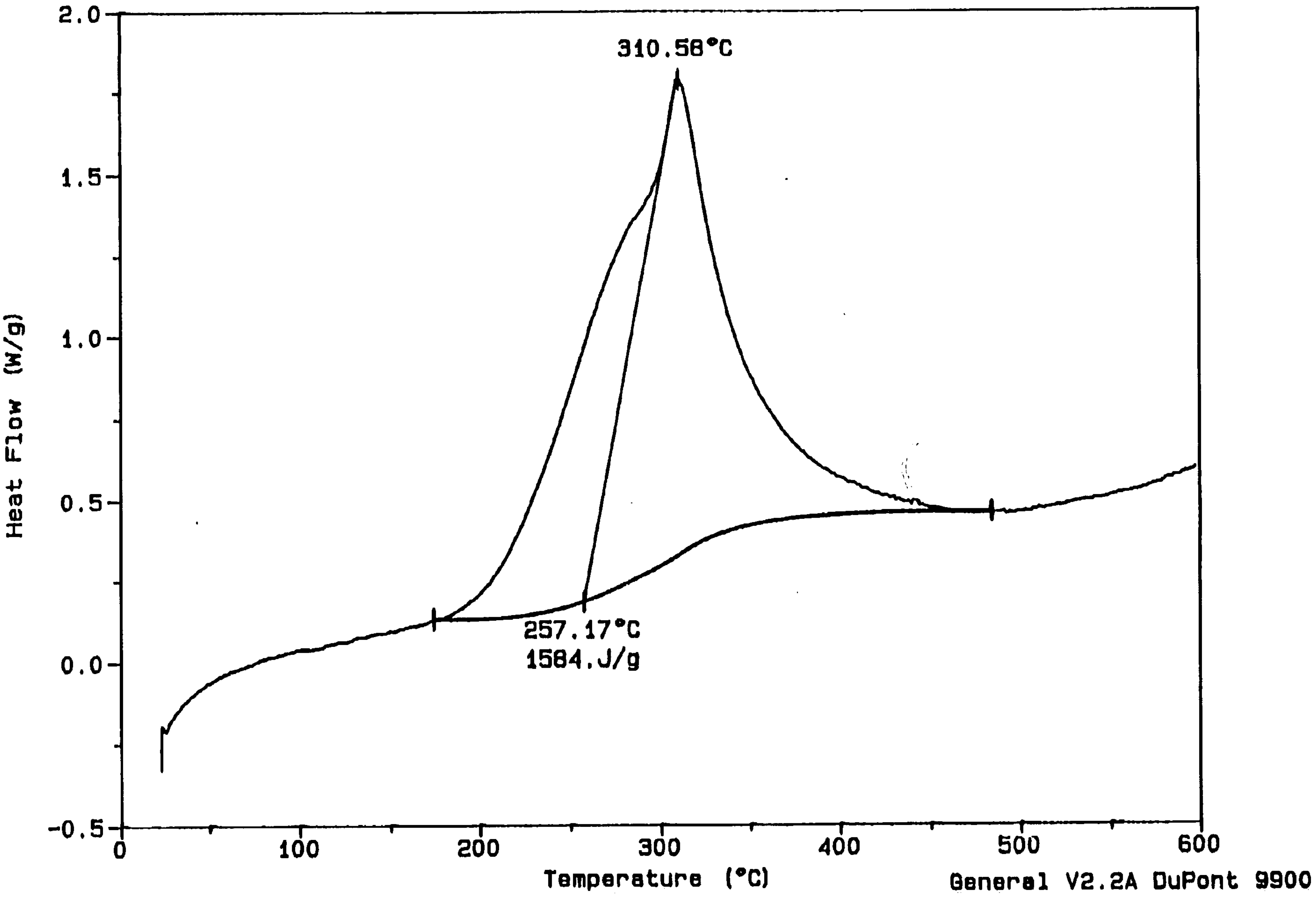
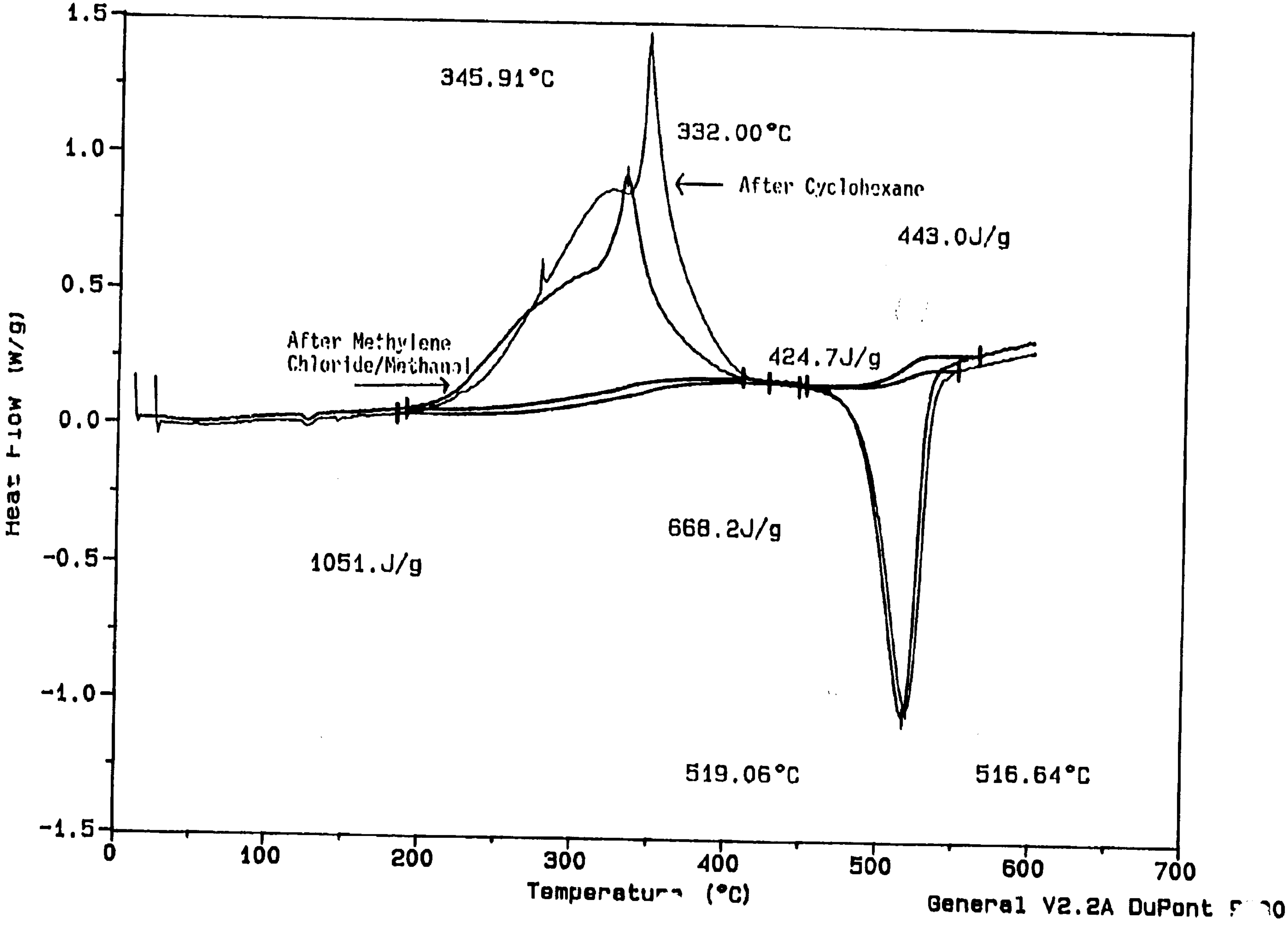


Figure 5-345. DSC of Used Unmodified Ruthenium Catalyst 4966-198 After Soxhlet Extraction with Cyclohexane and After Methylene Chloride/Methanol



According to TGA experiment with the methylene chloride/methanol extracted sample, the weight loss between 250°C and 450°C is 3-4%, which is slightly lower than 5.41% carbon measured on this sample (Figure 5-346). The discrepancy can be explained by weight gain through bulk oxidation of ruthenium in the catalyst. Since RuO_4 is volatile, a subsequent weight loss is expected at higher temperature. A maximum of 5% weight loss may occur through volatilization of 2.8% ruthenium in the catalyst in the form of volatile tetroxide species. The actual weight loss between 450°C and 550°C was higher, about 9%. The causes for the 4% difference between actual and expected weight loss are not clear but may be partly explained by dehydration of alumina in this temperature range.

The effects of various extraction steps on the nature of coke in the modified ruthenium Catalyst 4966-180 were qualitatively similar to those observed with the unmodified Catalyst 4966-198 (Figures 5-347 and 5-348).

Results summarized in Figures 5-348 through 5-352 indicate, however, two important differences between Catalysts 4966-180 and 4966-198.

1. The coke in the modified ruthenium catalyst was much less than that of the unmodified ruthenium catalyst based on the weight loss between 250°C and 450°C.

2. The coke in the modified catalyst burned at about 30°C lower temperature relative to the coke in the unmodified ruthenium catalyst. Since coke with higher hydrogen content is expected to burn at lower temperature, the coke in the modified catalyst may have higher hydrogen content relative to the unmodified catalyst.

Figure 5-346. TGA of Used Unmodified Ruthenium Catalyst 4966-198 After Extraction with Cyclohexane and After Methylene Chloride/Methanol

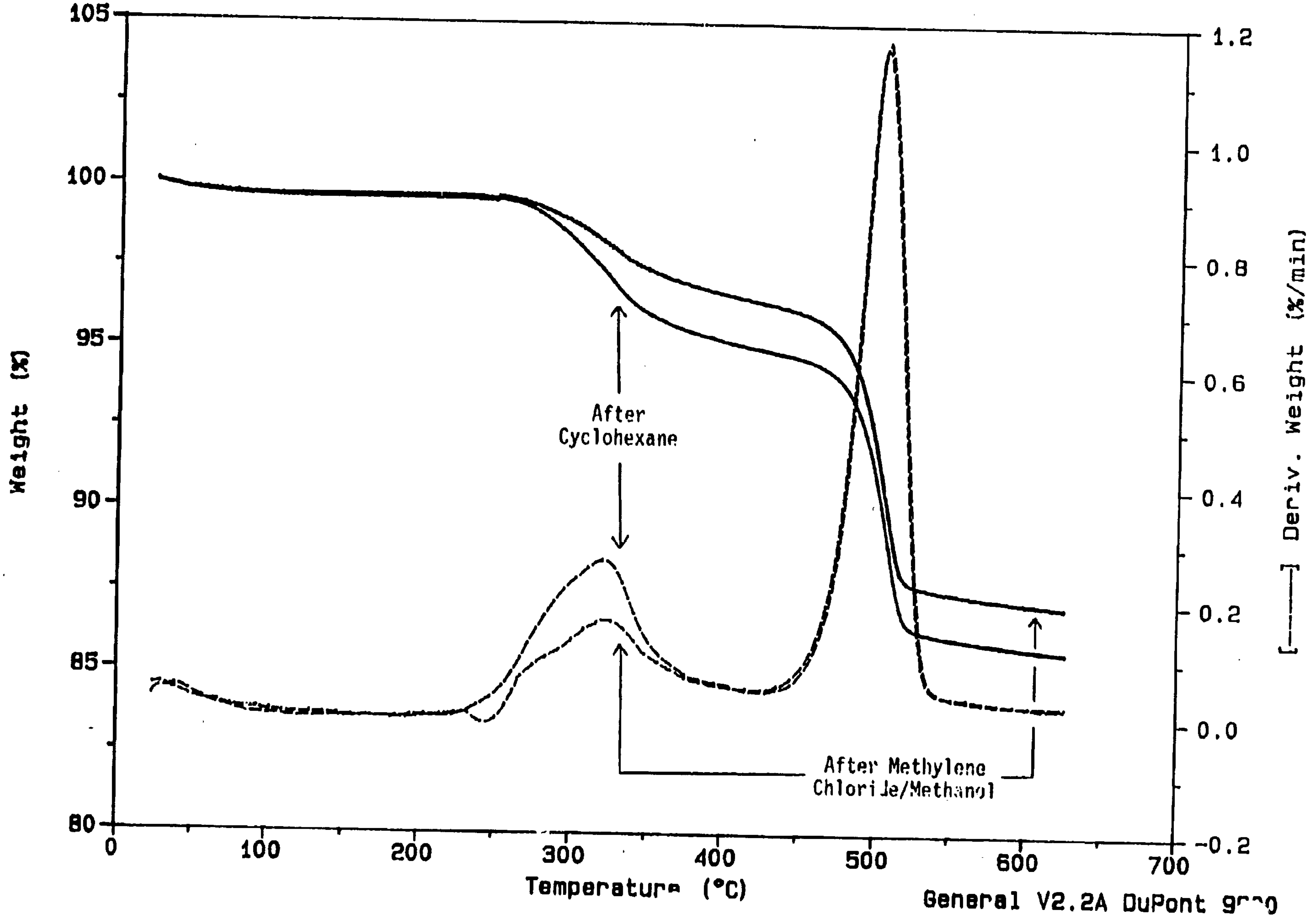


Figure 5-347. DSC of Used Modified Catalyst 4966-180 After Soxhlet Extraction with Cyclohexane and Methylene Chloride/Methanol

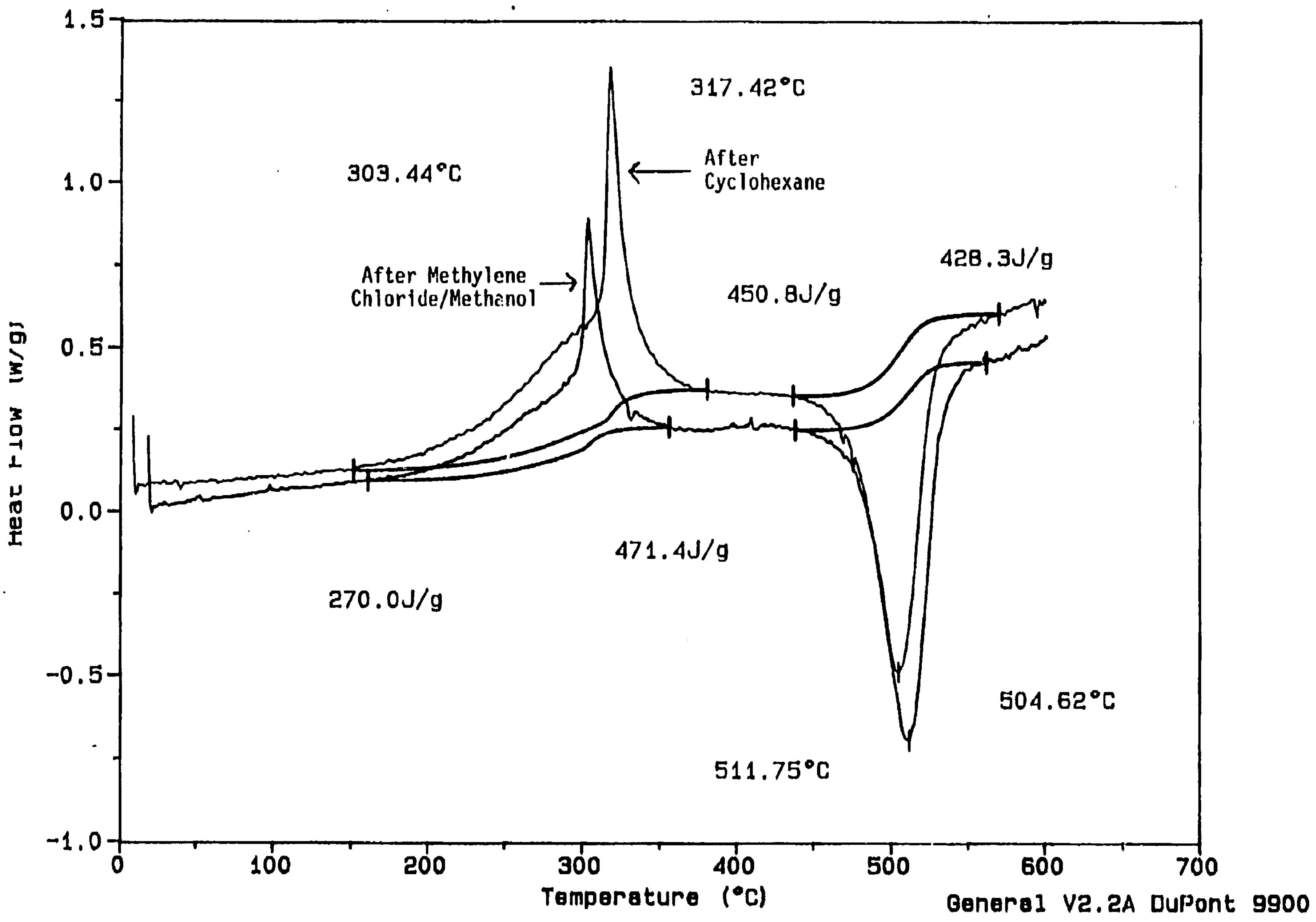


Figure 5-348. TGA of Used Modified Ruthenium Catalyst 4966-180 After Soxhlet Extraction with Cyclohexane and Methylene Chloride/Methanol

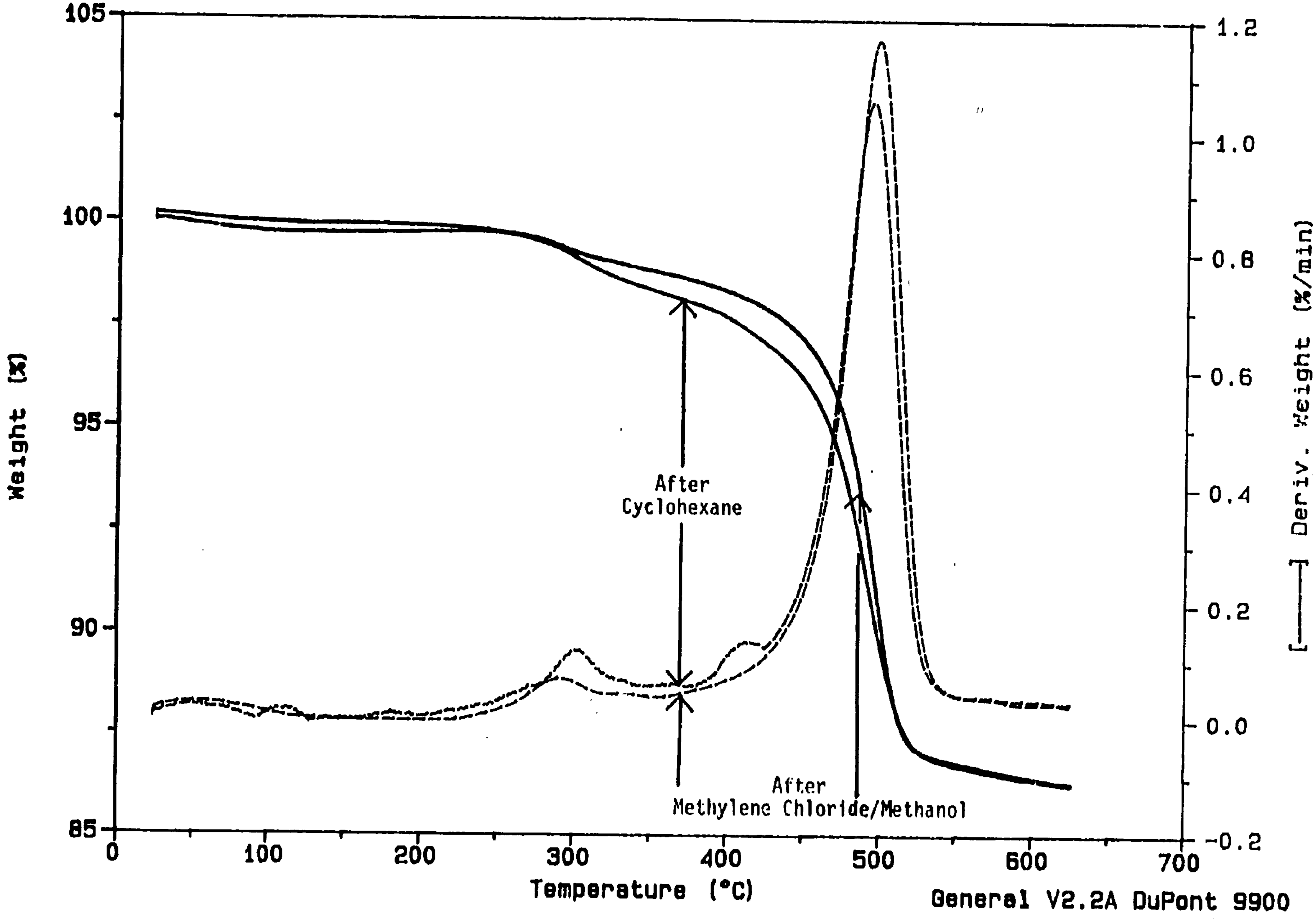


Figure 5-349. DSC of Used Modified and Unmodified Ruthenium Catalysts After Soxhlet Extraction with Cyclohexane

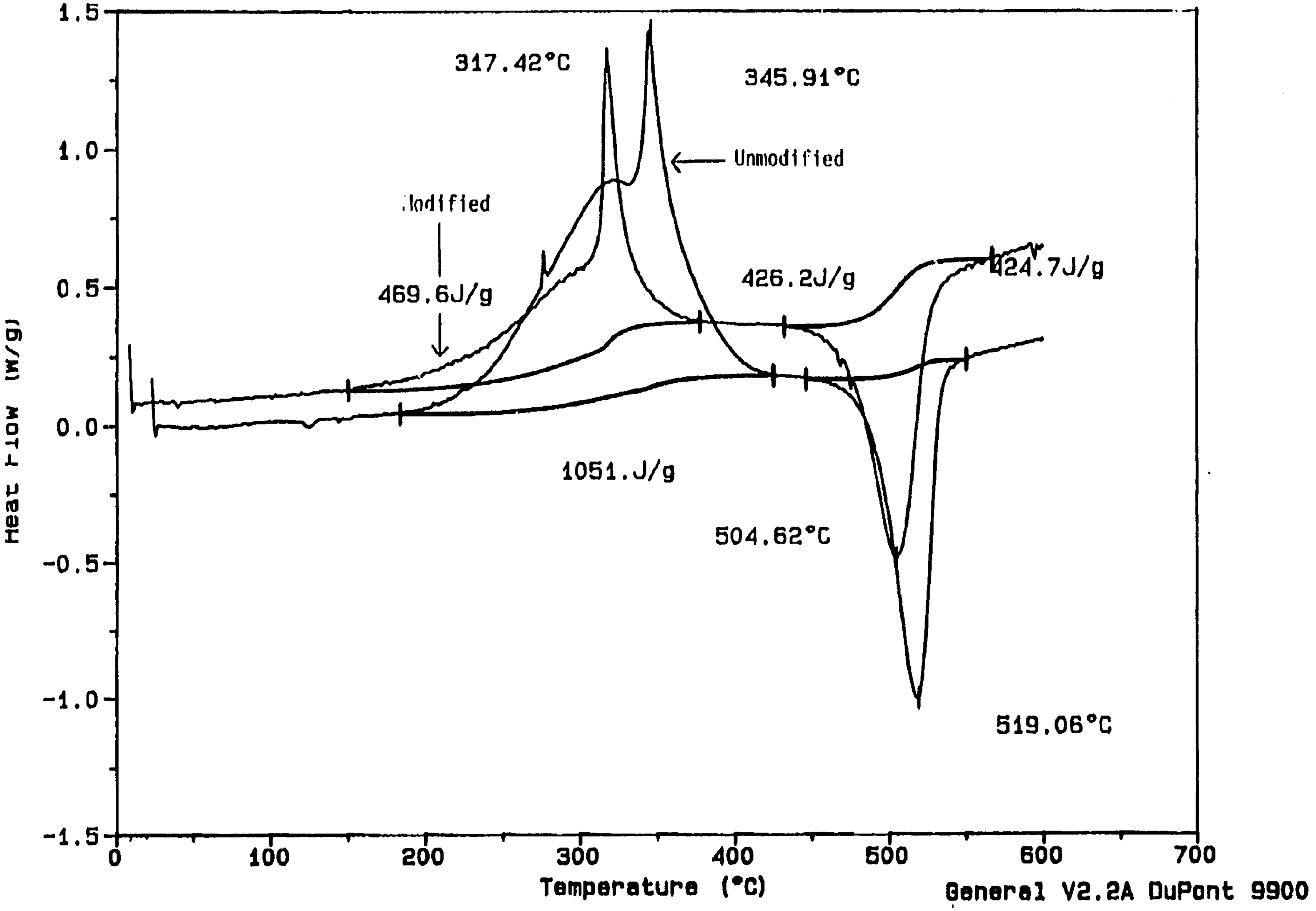


Figure 5-350. TGA of Used Modified and Unmodified Ruthenium Catalysts After Soxhlet Extraction with Cyclohexane

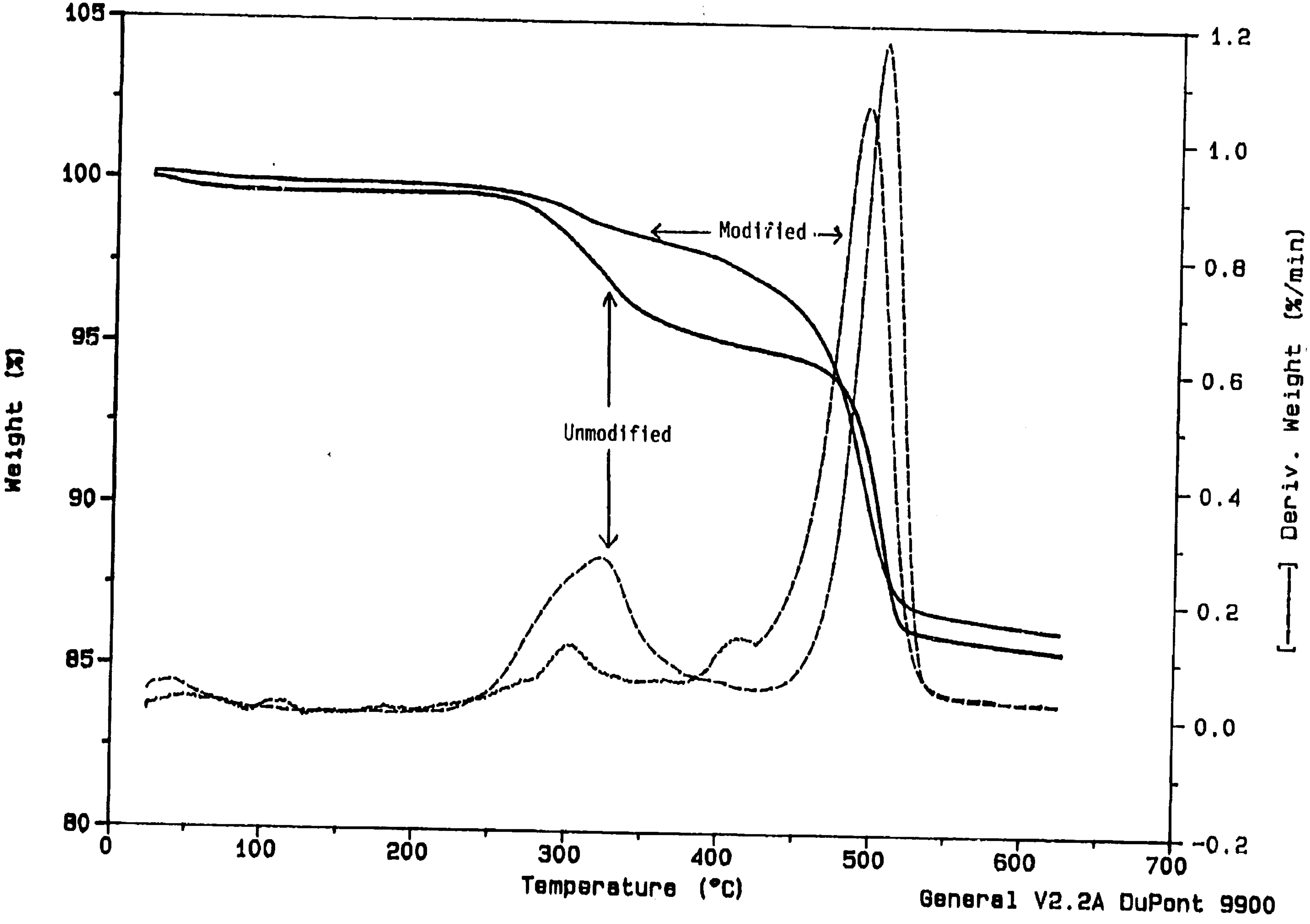


Figure 5-351. DSC of Used Modified and Unmodified Ruthenium Catalysts After Soxhlet Extraction with Methylene Chloride/Methanol

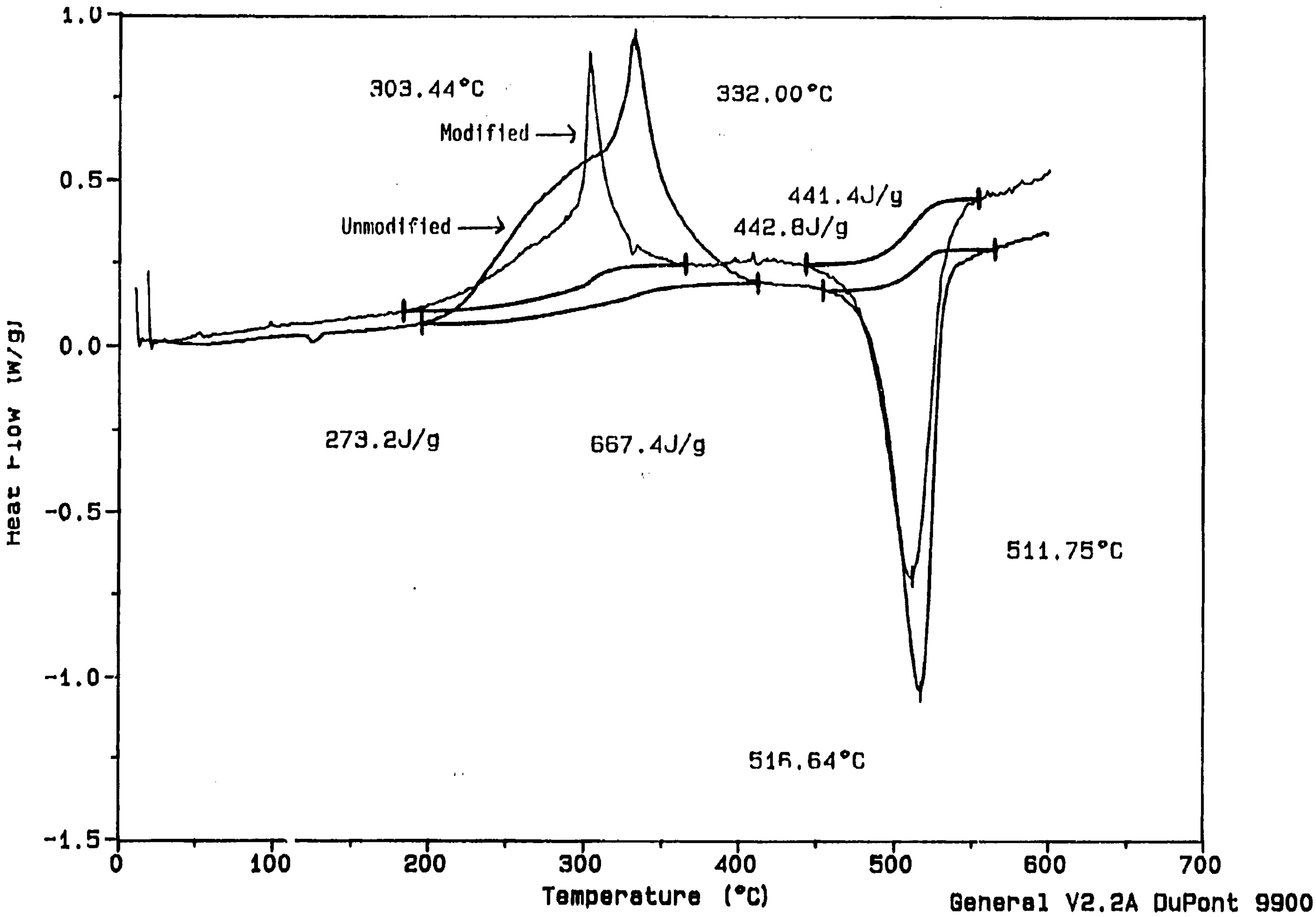


Figure 5-352. TGA of Used Modified and Unmodified Ruthenium Catalysts After Soxhlet Extraction with Methylene Chloride/Methanol