

**K BASIN SLUDGE CONDITIONING
PROCESS TESTING PROJECT**

**RESULTS FROM TEST 4, "ACID DIGESTION OF
MIXED-BED ION EXCHANGE RESIN"**

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Executive Summary

Purolite NRW37, a mixed bed ion exchange resin which consists of 40% by volume Purolite NRW-100 (strong acid cation exchange resin) and 60% by volume Purolite NRW-400 (strong based anion exchange resin) has been used to treat K Basin waters for 5 to 12 years. The anion resin is initially amber in color, and is a hydroxyl form trimethylamine functionalized polystyrene-divinyl benzene copolymer. The cation resin is initially nearly black in color and is the hydrogen form sulfonic acid functionalized polystyrene-divinyl benzene copolymer. Accidental discharge of this resin is known to have occurred during this time. These resin beads have been tentatively identified as components of sludge samples retrieved from K East basin floor and Weasel Pit. The tests and results discussed in this report describe the fate of Purolite NRW37 during the nitric acid based sludge dissolution process. Specifically, the change in chemical functionality of the resin (e.g., loss of ion exchange functional groups and addition of nitro or nitroso moieties to the resin matrix) was investigated. In addition, the thermal stability of the rinsed product resins and their propensity to undergo rapid exothermic events when heated were evaluated. The organic carbon concentrations of the digestion solution were also determined.

Significant changes in measured properties of resin beads were observed only at the most extreme digestion conditions (95° C; 7 and 24 hr). At less rigorous conditions, only very small losses of ion exchange functionality were seen. The extent of resin bead matrix disruption, as measured by TOC of digestion filtrates, was only significant at the most extreme processing conditions.

Radionuclides sorbed or associated with the organic ion exchange resins (OIER) can restrict disposal of this solid to the Environmental Restoration Disposal Facility (ERDF). Solids to be delivered to the ERDF must meet Waste Acceptance Criteria (WAC) for radionuclide concentrations (*ERDF Waste Acceptance Criteria*, BHI-00139, Rev. 2, Table 4-1). The radionuclides most likely controlling the ERDF acceptance of K Basins' solid residues are ¹³⁷Cs (32 Ci/m³ or 32 µCi/mL) and the transuranics (TRU; 100 nCi/g). The transuranic isotopes have individual limits; ²⁴¹Am is 0.05 Ci/m³ (50 nCi/mL), ²³⁸Pu is 1.5 Ci/m³ (1,500 nCi/mL), and ²³⁹Pu and ²⁴⁰Pu are each 0.029 Ci/m³ (29 nCi/mL). The effective uranium limit for disposal to ERDF, 0.0026 g U/mL¹, may also foreclose ERDF disposal of certain K Basins residues. The radionuclide activities of OIER retrieved from the K Basins must be decontaminated to these levels to allow ERDF disposal. The TRU content of rinsed OIER retrieved from the K East Basin (Sample KES-H-08) has been found to range from about 650 to 850 nCi/g dried resin. The unrinsed OIER also contains 144 µCi ¹³⁷Cs and 0.003 g U per gram of dried resin (Schmidt et al. 1999).

Based on the above radionuclide concentrations in the actual OIER in KE Basin sludge and the levels of defunctionalization achieved during the cold OIER testing (i.e., 3% to 34% defunctionalization for the cation and 3% to 13% for the anion resin material), acid digestion in 15.7 M HNO₃ is predicted to be insufficient to decontaminate the OIER to the levels necessary to meet the ERDF WAC. However,

¹ The ERDF WAC limit for ²³⁸U and its daughters is 0.012 Ci/m³. With 8 alpha and 6 beta decays in the ²³⁸U decay chain and a specific activity of 3.36x10⁻⁷ Ci ²³⁸U/g, the specific activity of the ²³⁸U chain is 4.7x10⁻⁶ Ci/g. The ERDF limit for ²³⁸U thus is 0.00256 g ²³⁸U/mL. The ERDF limit for ²³⁵U (daughters *not* included) is 0.0027 Ci/m³ and the specific activity of ²³⁵U is 2.16x10⁻⁶ Ci/g. Thus the ERDF limit for ²³⁵U is 0.0013 g ²³⁵U/mL. The relative limits of the two uranium isotopes, and the nominal 0.7% enrichment of the K Basins sludge, mean that ²³⁸U concentration limits ERDF disposal. Therefore, the effective uranium limit for disposal to ERDF is 0.0026 g U/mL.

recent results from digestion of actual OIER from KE Basin sludge in 10 M HNO₃ indicate that higher levels of decontamination were achieved than predicted from the cold OIER digestion (Schmidt et al. 1999). For sieved and rinsed OIER from sample KES-H-08, at ratios of about 1 g resin per 20 mL acid, about 80% of the uranium, 25% of the plutonium, and 70% or more of the americium activity were removed. Cesium distributions were not measured but high removals would be expected. Residual activities in the acid-treated OIER were 160 to 340 nCi/g TRU (110-190 nCi ^{239,240}Pu/g, 20-120 nCi ²⁴¹Am/g), and 1.5-34 μCi ¹³⁷Cs/g (uranium concentrations were not detectable but likely were near 0.0003 g U/g based on K_d tests at higher loadings).

The differences in results obtained from the digestions performed on the cold OIER and the digestions performed on the hot OIER collected from KE Basin sludge can be partially attributed to the following factors: 1) the cold testing examined defunctionalization, whereas the decontamination achieved during the hot testing included the effects of both defunctionalization and displacement, 2) the initial radionuclide concentrations associated with the hot OIER may have included particulate matter that was easily digested (i.e., possibly inflating the initial concentrations of the OIER), and 3) The ion exchange capacity in the cold work was determined with Na⁺ (cation resin) and Cl⁻ (anion resin). The binding affinity of OIER for ¹³⁷Cs, ^{239,240}Pu, and ²⁴¹Am differ from that of Na⁺ and Cl⁻.

Based on the results obtained for the digestions of the hot OIER, it may be possible to remove cesium, uranium, and americium to meet ERDF criteria by performing multiple washing contacts of retrieved OIER with strong HNO₃. However, such an approach would be less successful for plutonium where strong anion exchange sorption occurs at high HNO₃ concentrations and strong cation exchange sorption occurs at low HNO₃ concentrations, especially considering that very little defunctionalization occurs to either the anion or cation resin. Consequently, a more sophisticated leaching approach will likely be required to decontaminate the OIER to the levels necessary to meet the ERDF WAC.

FTIR spectra of digested resins show evidence for formation of small amounts of nitroaromatic compounds (nitrated resin matrix). Thermal analyses suggest that nitric acid treated resin beads can undergo exothermic decomposition reactions in the 160°C to 400°C temperature range. The largest exothermic event (1015 J/g) was observed for sample C100-3. These results indicate that some level of safety evaluation will likely be required if the OIER will be digested or leached with nitric acid. After nitric acid leaching or digestion, it may be necessary to contact the OIER with base to hydrolyze nitroaromatics and neutralize and remove residual acid.

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1.0 INTRODUCTION

Approximately 73 m³ of heterogeneous solid material, "sludge," (upper bound estimate, Packer 1997) have accumulated at the bottom of the K Basins in the 100 K Area of the Hanford Site. This sludge is a mixture of spent fuel element corrosion products, ion exchange materials (organic and inorganic), graphite-based gasket materials, iron and aluminum metal corrosion products, sand, and debris (Makenas et al. 1996, 1997). In addition, small amounts of polychlorinated biphenyls (PCBs) have been found. Ultimately, it is planned to transfer the K Basins sludge to the Hanford double shell tanks (DSTs). The Hanford Spent Nuclear Fuel (HSNF) project has conducted a number of evaluations to examine technology and processing alternatives to pretreat K Basin sludge to meet storage and disposal requirements. From these evaluations, chemical pretreatment has been selected to address criticality issues, reactivity, and the destruction or removal of PCBs before the K Basin sludge can be transferred to the DSTs. Chemical pretreatment, referred to as the K Basin sludge conditioning process, includes nitric acid dissolution of the sludge (with removal of acid insoluble solids), neutrons absorber addition, neutralization, and reprecipitation. Laboratory testing is being conducted by the Pacific Northwest National Laboratory (PNNL) to provide data necessary to develop the sludge conditioning process.

The proposed K Basin sludge conditioning process for removal, processing, and ultimate disposal of K Basin sludges includes a nitric acid digestion/dissolution step intended primarily to dissolve uranium metal and/or oxides known to be major sludge components. During this nitric acid treatment step, ion exchange materials (specifically polystyrene-divinylbenzene based resins) consequently would be disposed of as a part of the acid insoluble solid waste. It is planned to dispose the acid insoluble fraction generated from the sludge conditioning process to the Environmental Restoration Disposal Facility (ERDF) (Hatch 1997).

Purolite NRW37, a mixed bed ion exchange resin which consists of 40% by volume Purolite NRW-100 (strong acid cation exchange resin) and 60% by volume Purolite NRW-400 (strong based anion exchange resin) has been used to treat K Basin waters for 5 to 12 years. The anion resin is initially amber in color, and is a hydroxyl form trimethylamine functionalized polystyrene-divinyl benzene copolymer. The cation resin is initially nearly black in color and is the hydrogen form sulfonic acid functionalized polystyrene-divinyl benzene copolymer. Accidental discharge of this resin is known to have occurred during this time. These resin beads have been tentatively identified as components of sludge samples retrieved from K East basin floor and Weasel Pit. The tests and results discussed in this report describe the fate of Purolite NRW37 during the nitric acid based sludge dissolution process.

The work described in this report was performed in accordance with the "Fiscal Year 1998 Cold Testing Work Plan in Support of K-Basin Sludge Conditioning System Process Development" (Silvers 1997) and the associated test instruction. In accordance with the work plan, the following items were evaluated:

- change in chemical functionality of the resin e.g., loss of ion exchange functional groups and addition of nitro or nitroso moieties to the resin matrix,
- thermal stability of the rinsed product resins and their propensity to undergo rapid exothermic events when heated, and
- organic carbon concentration of the digestion solution.

2.0 EXPERIMENTAL

2.1 Preparation of Ion Exchange Resins

Cation ion-exchange resin, Purolite NRW-100 in H⁺ form, and anion ion-exchange resin, Purolite NRW-400 in OH⁻ form, were washed repeatedly with deionized water (DIW) until the specific conductivity of the washings were less than 2 μ S/cm following overnight exposure. The thoroughly washed resins were then dried overnight at 50°C and subsequently stored in a desiccator (Drierite) until prepared for the nitric acid digestion tests described below. A portion of each resin type was further dried at 110°C for 4.75 hours to determine moisture content remaining after 50°C drying. Weight losses were 12.2% and 8.3% for cation and anion resins respectively.

2.2 Nitric Acid Digestion of Ion Exchange Resin Beads

Digestions were carried out using concentrated HNO₃ (~15.7 M) at three temperatures: room temperature (~22°C), 60°C, and 95°C. All digestions were carried out unstirred except that room temperature digestions of anion resin samples were gently stirred by means of a small magnetic stir bar. For cation resin samples, 17 mL of concentrated HNO₃/g resin was used and for anion resin samples the ratio was 22 mL concentrated HNO₃/g resin. These acid/resin ratios were chosen based on the following assumptions:

- dry resin copolymer matrix is composed of six styrene moieties for each divinylbenzene,
- there are four ion exchange groups per six styrenes,
- the reaction products are CO₂, H₂O, and NO₂, and
- the resins are completely reacted to these products.

Digestions of each resin type were performed for nominally 1 hour, 7 hours, and 24 hours at each test temperature. Following the digestions, resin beads from each test were filtered (Millipore HA type, 0.45 μ m pore size), and rinsed five times with DIW. The combined filtrate and rinsings were diluted to a known volume and set aside for total organic carbon (TOC) analyses.

The rinsed resin beads from each test were dried overnight at 50°C and stored in a desiccator until prepared for tests to determine 1) residual ion-exchange capacity, 2) thermal behavior (DSC/TGA), and 3) presence or absence of nitro/nitroso compounds (FTIR).

2.3 Total Organic Carbon Analyses of Digestion Supernates

Initial attempts to determine TOC of these samples were fraught with difficulties. Results were widely scattered and not reproducible. It is believed that the high nitrate content and/or high acidity of the samples introduced an uncontrollable interference in the actual analyses. To circumvent the problem, a sample pretreatment procedure was designed and used. This pretreatment procedure consisted of adding well washed aliquots of anion exchange resin (OH⁻ form) to the digestion supernates, in quantities sufficient to neutralize the H⁺ and bind nitrate, agitating the resin and supernate on a laboratory shaker to

achieve ion exchange equilibrium, and analyzing the treated supernate by the usual acidify and sparge TOC procedure. Blanks, i.e., fresh nitric acid diluted to same concentration as that of samples, were similarly treated with hydroxide form anion exchange resins and included in the TOC analysis campaign. The TOC content of the blanks could not be neglected relative to those of digestion supernates. Each sample and blank were analyzed 3 to 5 times and the mean and standard deviations for the replicates were calculated. Net TOC content of digestion supernates as given in the results section of this report were blank corrected and experimental uncertainty values (standard deviations) were calculated from the usual "propagation of errors" algorithm.

2.4 Ion Exchange Capacity Tests/Cation Resin Samples

Approximately 0.2 g aliquots of each digested cation exchange resin sample and an untreated resin sample were placed in glass scintillation vials and contacted with a known volume of known concentration of NaOH solution. These vials and contents were agitated on a laboratory shaker table for approximately 60 hours. The supernates, along with an aliquot of the sodium hydroxide solution used, were analyzed for sodium content by ICP-AES (Procedure PNL-ALO-211.2, Rev. 0). (Section 7.2.6 of referenced procedure was not implemented because it is not applicable to the instrument used.) From the known total quantity of Na⁺ introduced to each sample and the residual quantity of sodium ion found in supernates after ion exchange equilibration, the amount of sodium bound by the resin was calculated by difference.

2.5 Anion Resin Samples

Approximately 0.5 g aliquots of each digested anion exchange resin sample and an untreated resin sample were placed in glass scintillation vials and contacted with a known quantity of known concentration sodium sulfate solution. These vials and contents were agitated on a laboratory shaker table for approximately 60 hours. The supernate and an aliquot of Na₂SO₄ contacting solution were analyzed by ICP-AES for sulfur content according to the procedure cited above. The ion exchange capacity for each sample was then calculated as described in the previous section of this report. Results were confusing and deemed unreliable mainly because the calculations were based on the assumption that the sulfate introduced to each sample would behave as a divalent ion for ion exchange purposes. Tests of the equilibrated supernates revealed that the pH for digested samples was acidic (pH ~2 by pH indicator paper) and the pH of supernate over undigested anion resin was definitely basic. At pHs of 2 or less, sulfate ion is known to exist primarily in the monovalent, bisulfate, form. Therefore, the basic assumption of divalent behavior of the sulfate in ion exchange capacity calculations is suspect at best, invalid at worst.

The supernates for all samples were discarded and replaced with 1.0 M NaOH, equilibrated as usual by means of the shaker platform agitation. The supernate was discarded, replaced with DIW, agitated again, supernate discarded, replaced with DIW, etc. until the DIW washing pH <9. A fresh aliquot of 1.0 M NaOH was then added to each vial, and the equilibration, washing procedure used until pH of supernates was less than 9. This procedure was intended to ensure that virtually all of the anion exchange sites of the resin samples were occupied by hydroxide ion. These samples were then contacted with a known quantity of known concentration HCl. After equilibration by shaker platform agitation, the supernates along with an aliquot of HCl contacting solution were analyzed for chloride content by ion chromatography (procedure PNL-ALO-212). Ion exchange capacity of these anion resin samples was calculated based on chloride balance as described above for cation resin samples.

2.6 Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA)

Samples of dried digested resins and undigested resins were pulverized to powder by standard methods. Thermal behavior tests (DSC and TGA) were conducted under a nitrogen gas blanket atmosphere, using a 10°C/min temperature ramp rate from ambient temperature (20°C) to a maximum temperature of 750°C. Weight change as a function of temperature (time) and heat absorption or liberation as a function of temperature (time) were recorded.

2.7 Fourier Transform Infrared Analyses

Portions of powdered resin beads were mixed with KBr, pressed into pellets, and analyzed by FTIR for the presence of significant functional groups such as nitro or nitroso moieties.

3.0 RESULTS

3.1 Qualitative Observations During Digestions

1. Anion resin floats, cation resin sinks when exposed to 15.7 M HNO₃.
2. Immediate and sustained evolution of brown gas (NO_x) from anion samples when exposed to conc. HNO₃ at all temperatures.
3. Room temperature digestion: Cation resin - no obvious gas evolution. Digestion supernates yellow in color; cation resin digests darker than those from anion resin.
4. 60°C Digestions: Anion resin samples: immediate white vapor evolved followed quickly by brown gas (NO_x). Cation resin samples: immediate white vapor; brown gas observed as samples heat up to near 60°C.
5. 95°C Digestions: anion resin samples same observations as above. Also it should be noted that a fine white precipitate appears to form a film on digestion vial walls which slowly settles to bottom during digestion. No attempt was made to isolate and analyze this white precipitate. This was also observed for room temperature and 60°C digestions. More brown gas evolution observed at 95°C than 60°C.
6. Cation resin samples after digestion, filtering, and washing were progressively lighter in color as digestion conditions increased in severity. Supernates were progressively darker yellow in color as digestion conditions increased in vigor. Anion resin color differences not as apparent but showed same trend.

3.2 Sample Identifications

Samples of resins and filtrates derived from digestions were given the identifications as summarized in Table 3.1 for reference.

Table 3.1 Sample Identifications

Cation Sample ID	Anion Sample ID	Digestion Time (hr)	Digestion Temperature (°C)	Comments
C0	A0	0	-	Starting materials
C1	A1	1	22	room temperature digestions
C2	A2	6.5	22	room temperature digestions
C3	A3	24	22	room temperature digestions
C60-1	A60-1	1	60	60°C digestions
C60-2	A60-2	7	60	60°C digestions
C60-3	A60-3	24	60	60°C digestions
C100-1	A100-1	1	95	95°C digestions
C100-2	A100-2	7.25	95	95°C digestions
C100-3	A100-3	24	95	95°C digestions

3.3 Weight Changes Following Digestions

Weight changes of resin samples following digestions and drying at 50°C varied widely. The range of observed weight changes was +5.6% to -8.4% for cation resin samples and +0.65% to -5.5% for anion resin sample. The largest weight losses for both cation and anion resin samples were seen in the 95°C, 24 hr digested cases. There was no discernable trend in weight changes for resin samples involved in the other digestion conditions.

3.4 Total Organic Carbon Content of Digestion Filtrates

The TOC content of digestion filtrates of cation resin and anion resin samples was determined and results calculated as described in the experimental section of this report. Results are summarized in Table 3.2.

Table 3.2 TOC Found in Digestion Filtrates

Cation Resin Sample ID	Cation Resin Sample Net TOC & Std Dev. (mg C/g resin)	Anion Resin Sample ID	Anion Resin Sample Net TOC & Std Dev. (mg C/g resin)
C1	1.09 ± 0.27	A1	1.83 ± 0.83
C2	0.78 ± 0.38	A2	1.30 ± 0.78
C3	1.23 ± 0.37	A3	2.68 ± 0.86
C60-1	1.44 ± 0.31	A60-1	2.18 ± 0.95
C60-2	2.18 ± 0.26	A60-2	2.23 ± 0.84
C60-3	0.72 ± 0.23	A60-3	2.92 ± 0.82
C100-1	1.85 ± 0.43	A100-1	3.41 ± 0.87
C100-2	2.06 ± 0.27	A100-2	12.7 ± 1.0
C100-3	6.74 ± 0.34	A100-3	40.1 ± 3.6

Based on the assumed composition (see Section 2.2) and residual moisture content of dried (50°C) resin beads, the carbon content of beads was estimated to be approximately 70%. The overall mass loss observed for anion resin digested for 24 hr at 95°C was 5.5%. Of this overall mass loss, 3.85% (0.7 x 5.5) is attributable to carbon. The TOC content of the digestate derived from sample A100-3, as given in Table 3.2, was found to be 4.0%. Correlation of bead mass loss and TOC of digestates for other samples was poor compared to the good correlation found for A100-3 sample.

3.5 Ion Exchange Capacity of Digested Resins

The ion exchange capacity of nitric acid digested resin samples and untreated starting materials was determined as described in the experimental section. Results are summarized in Table 3.3. Accuracy of these values is estimated from "continuing calibration verification standard" (CCV) results to be ±3%. Precision is conservatively estimated to be ±1.5% based on agreement of analytical duplicates.

Table 3.3 Ion Exchange Capacity of Digested Resin Samples and Starting Materials

Cation Resin Sample ID	Cation Resin Sample Ion Exchange Capacity (meq/gm)	Anon Resin Sample ID	Anion Resin Sample Ion Exchange Capacity (meq/gm)
Vendor Spec.	4.9 (dry weight basis)	Vendor Spec.	3.7 (dry weight basis)
C0	4.62	A0	2.37
C1	4.31	A1	2.07
C2	4.47	A2	2.10
C3	4.47	A3	2.09
C60-1	4.42	A60-1	2.10
C60-2	4.46	A60-2	2.21
C60-3	4.25	A60-3	2.22
C100-1	3.82	A100-1	2.29
C100-2	3.52	A100-2	2.30
C100-3	3.04	A100-3	2.31

Note: All ion exchange capacity measurements (other than vendor specs) were made on resin material dried overnight at 50°C.

3.6 Thermal Analyses

DSC and TGA analyses of predigestion and post nitric acid digested resin samples were performed by Todd Hart of PNNL under conditions described in the experimental section. The DSC and TGA traces are appended to this report (Appendix A). Table 3.4 below summarizes the thermal behavior features of the samples observed in the temperature range of 150°C and 400°C. Weight losses and heat flows at temperatures below ~150°C are believed to be associated with loss of residual moisture. Above ~400°C, weight losses and heat flows are believed to be due to charring of the basic hydrocarbon bead matrix. Between 150°C and 400°C, weight losses and heat flows are believed to be associated with loss of ion-exchange functional groups and possibly decomposition of nitro or nitroso organic moieties.

Table 3.4 Thermal Behavior of Ion Exchange Resin Samples in the Temperature Range, 150 to 400°C

Sample ID	Reaction Heat Flow Onset Temperature (°C)	Heat Flow (J/g)	Estimated Weight Loss Accompanying Thermal Event (%)
C0	250	+111	20
C1	258	+127	22
C2	252	+90	22
C3	262	+89	24
C60-1	271	+102	25
C60-2	217	-154	25
C60-3	236	-348	25
C100-1	234	-280	20
C100-2 (a)	183	-6	-
C100-2 (b)	237	-668	30
C100-3 (a)	167	-28*	-
C100-3 (b)	239	-797*	26
A0	164	+219	22
A1	244	-534	29
A2	245	-398	31
A3 (a)	170	-9.2	-
A3 (b)	243	-508	29
A60-1 (a)	180	-11	-
A60-1 (b)	246	-388	26
A60-2 (a)	179	-7.7	-
A60-2 (b)	242	-463	29
A60-3 (a)	186	-1.7	-
A60-3 (b)	243	-352	30
A100-1 (a)	177	-18	-
A100-1 (b)	236	-472	28
A100-2 (a)	185**	-45	-
A100-2 (b)	242**	-404	28
A100-3 (a)	177***	-62	-
A100-3 (b)	241***	-368	35

* Integration of heat flow exotherms from beginning of first event to end of second event yields an overall exotherm of 1015 J/gm.

** Integration of heat flow exotherms from beginning of first event to end of second event yields an overall exotherm of 559 J/g.

*** Integration of heat flow exotherms from beginning of first event to end of second event yields an overall exotherm of 648 J/g.

3.7 Infrared Analysis of Nitric Acid Treated Sulfonated (Cation) and Quaternary Ammonium (Anion) Polystyrene Copolymer Ion Exchange Resins

Two ion exchange resins were treated with varying concentrations of nitric acid at various times and temperatures followed by analysis by FTIR spectroscopy.

The treatment of the cation exchange resin (sulfonated polystyrene copolymer) with concentrated HNO₃ at 60 and 95°C showed evidence of nitro-aromatic (Ar-NO₂) formation. The anion exchange resin (alkyl quaternary ammonium polystyrene copolymer) treated with concentrated HNO₃ at 95°C showed evidence of nitro-aromatic (Ar-NO₂) formation. The treatment with less concentrated nitric acid (10M HNO₃) showed no evidence of nitro-aromatic or nitro-alkyl formation. Treatment of anion exchanger with concentrated HNO₃ at room temperature for 1hr also showed no evidence of nitro-aromatic or nitro-alkyl formation. The cation exchange resin (sulfonated polystyrene copolymer) is discussed in the first section and the anion exchange resin (alkyl quaternary ammonium polystyrene copolymer) is discussed in the second section.

3.7.1 Cation Exchanger - Nitric Acid Treatment

Table 3.5 contains the temperatures and times for acid treatments of the cation exchange resin. The infrared spectra were performed on finely ground and dry resins using the KBr pellet method of sample preparation (Silverstein et al. 1991).

Table 3.5 Treatment Conditions for Cation Exchange Resin Samples

Treatment ID	Conditions	Sample ID
(a)	fresh resin, no acid treatment	CO
(b)	10M HNO ₃ , 60°C, 8h	*
(c)	conc HNO ₃ , 60°C, 7h	C60-2
(d)	conc HNO ₃ , 95°C, 24h	C100-3

* Sample from scoping test

(a) Fresh Resin, No Acid Treatment: The infrared spectra of the untreated cation exchange resins and the nitric acid treated resin were measured and are shown in Figures 3.1 and 3.2. The spectrum of the untreated fresh resin (spectrum (a) in Figures 3.1 and 3.2), contains the general features expected for a hydrated, sulfonated polystyrene polymer. The observed broad and intense absorbance in the 3600-2800 cm⁻¹ region is typical of acid hydrates (Silverstein et al. 1991); absorbances at 3000 – 2900 cm⁻¹ are assigned to C-H stretching mode (Silverstein et al. 1991; Lin-Vien et al. 1991); absorbances found at 1650-1450 cm⁻¹ are due to substituted aromatics (Silverstein et al. 1991; Lin-Vien et al. 1991); intense bands located at 1210-1150 and 1035 cm⁻¹ are assigned to the asymmetric and symmetric sulfonate S=O stretching frequencies respectively (Silverstein et al. 1991; Lin-Vien et al. 1991). The higher energy

asymmetric S=O band found at 1210-1150 cm^{-1} is broad due to the fact that for all sulfonates this band is expected to appear as a doublet.

(b) 10M HNO_3 , 60°C, 8hr Treatment: The infrared spectrum of the 10M nitric acid, 60°C washed cation resin (spectrum (b) in Figures 3.1 and 3.2) shows the same general features as found for the untreated resin discussed above. Specifically, this spectrum is consistent for an aromatic sulfonated ion-exchange resin and shows no additional features. No evidence was seen by infrared spectroscopy to suggest that either nitroalkanes or nitroaromatic complexes were produced from the resin under the 10M HNO_3 treatment at 60°C for 8 h.

(c) and (d) CONC HNO_3 , 60°C-7hr and 90°C, 24hr Treatment: The infrared spectra for cation resin treatment with concentrated HNO_3 under 60°C and 7hr, and 95°C and 24hr (spectra (c) and (d) respectively, Figures 3.1 and 3.2) show varying degrees of evidence for aromatic nitration of the copolymer of the resin in addition to the general features of the untreated resin. Absorption bands from aromatic nitrate (Ar-NO_2) formation are observed in these spectra at 1530 cm^{-1} (asymmetric NO_2 ν) and 1350 cm^{-1} (symmetric NO_2 ν) consistent with literature values (Silverstein et al. 1991; Lin-Vien et al. 1991). There is evidence of a trace of “free” nitrate in the 95°C, 24h, concentrated nitric acid treatment, in spectrum (d). The 1385 cm^{-1} absorption band is indicative of a non-covalently bound nitrate associated within the sample matrix. The “free” nitrate was undoubtedly left from the treatment with concentrated nitric acid.

3.7.2 Anion Exchanger - Nitric Acid Treatment

Table 3.6 contains the temperatures and times for acid treatments of the anion exchange resin. The infrared spectra of these resin samples were performed on finely ground and dry resins using the KBr pellet method of sample preparation (Silverstein et al. 1991).

Table 3.6 Treatment Conditions for Anion Exchange Resin Samples.

Treatment ID	Conditions	Sample ID
(a)	fresh resin, no acid treatment	AO
(b)	10M HNO_3 , 60°C, 8h	*
(c)	conc HNO_3 , room temp, 1hr	A1
(d)	conc HNO_3 , 95°C, 24h	A100-3

*Sample from scoping test

(a) Fresh Resin, No Acid Treatment: The infrared spectra of the untreated anion exchange resins and the nitric acid treated resin were measured and are shown in Figures 3.3 and 3.4. The spectrum of the untreated fresh resin (spectrum (a) in Figure 3.3 and 3.4), contain the general features expected for a hydrated, quaternary ammonium polystyrene polymer. The observed broad and intense absorbance in the 3600-2800 cm^{-1} region is typical of acid hydrates (Silverstein et al. 1991); absorbances at 3000 – 2900

cm^{-1} are assigned to C-H stretching mode (Silverstein et al. 1991; Lin-Vien et al. 1991); absorbances found at 1650-1450 cm^{-1} are due to substituted aromatics (Silverstein et al. 1991; Lin-Vien et al. 1991).

(b) 10M HNO_3 , 60°C, 8hr, and (c) CONC HNO_3 , room temp, 1hr Treatment: The infrared spectrum of the 10M nitric acid, 60°C, 8hr treatment and concentrated HNO_3 , room temperature-1 hr treatments (spectra (b) and (c) respectively, Figures 3.3 and 3.4) shows the same general features as found for the untreated resin discussed above in addition to an intense band at 1385 cm^{-1} due to unbound nitrate. Specifically, these spectra are consistent for an aromatic quaternary substituted anion-exchange resin loaded with “free” nitrate. The “free” nitrate denotes that the nitrate ion associated with the resin is from the anion exchange of nitrate for hydroxide after nitric acid treatment and *not* due to covalently bound nitrate from nitration reactions. No evidence was seen by infrared spectroscopy to suggest that either nitroalkanes or nitroaromatic complexes were produced from the resin under the 10M HNO_3 treatment at 60°C for 8 hr or concentrated HNO_3 , room temperature-1 hr treatment.

(d) CONC HNO_3 , 95°C, 24 hr Treatment: The infrared spectra for anion resin treatment with concentrated HNO_3 under 95°C and 24 hr (spectrum (d) Figures 3.3 and 3.4) shows evidence for aromatic nitration of the copolymer of the resin in addition to the general features of the untreated resin and associated “free” nitrate. The “free” nitrate denotes that the nitrate ion associated with the resin is from the anion exchange of nitrate for hydroxide after nitric acid treatment and *not* due to covalently bound nitrate from nitration reactions. Absorption bands from aromatic nitrate (Ar-NO_2) formation are observed in these spectra at 1530 cm^{-1} (asymmetric NO_2 ν) and ~1370 cm^{-1} (symmetric NO_2 ν) consistent with literature values (Silverstein et al. 1991; Lin-Vien et al. 1991). The 1370 cm^{-1} symmetric NO_2 ν band is a shoulder on the more intense “free” nitrate absorption band (1385 cm^{-1}).

sulfonated polystyrene copolymer, cation exchange resin

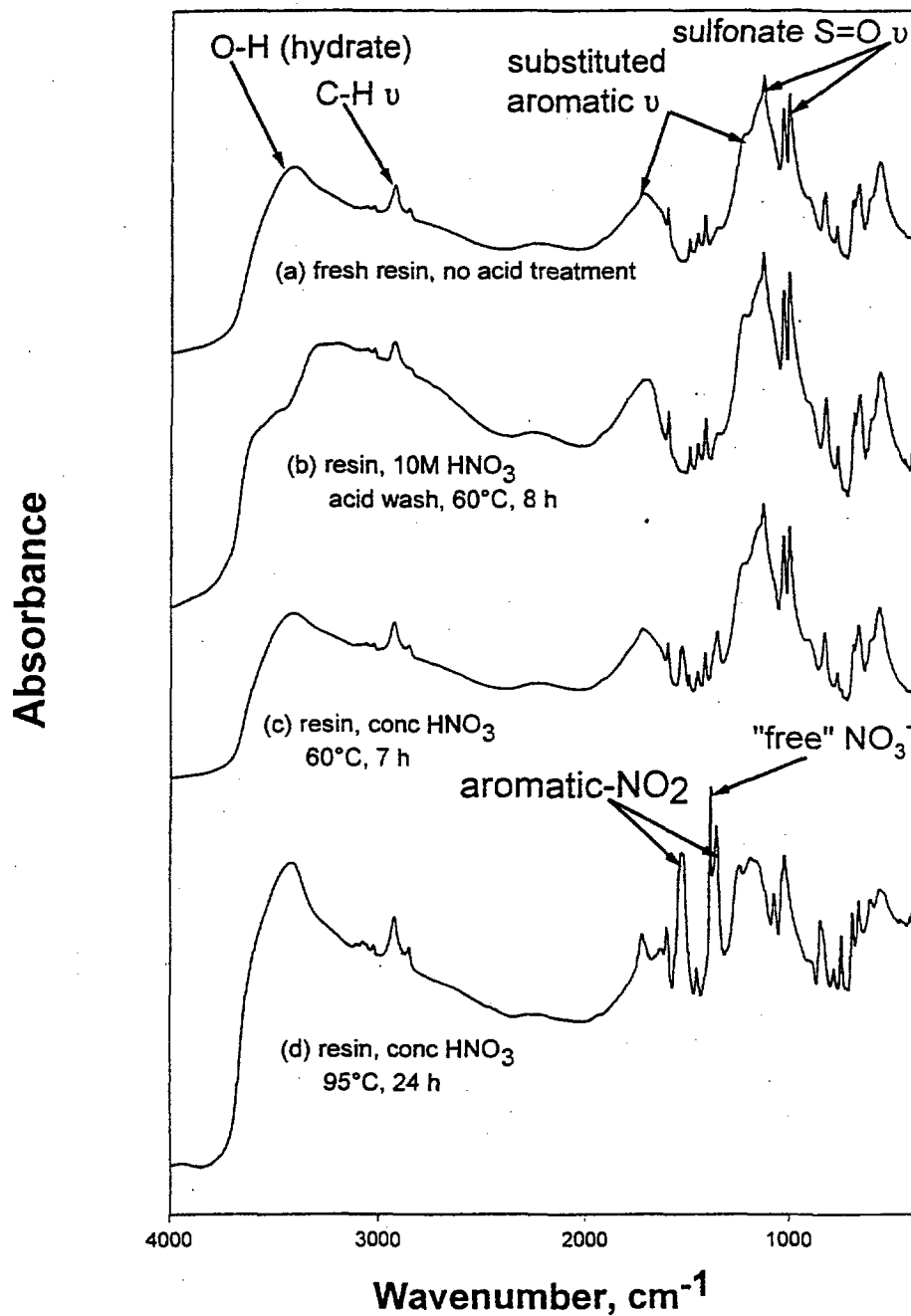


Figure 3.1 Infrared Spectra of Sulfonated Polystyrene Copolymer, Cation Exchange Resin; 4000 – 400 cm^{-1} Region. Resin was treated as follows (a) fresh resin, no acid treatment (b) 10M HNO_3 , 60°C , 8h, (c) conc HNO_3 , 60°C , 7h, (d) conc HNO_3 , 95°C , 24h

sulfonated polystyrene copolymer, cation exchange resin

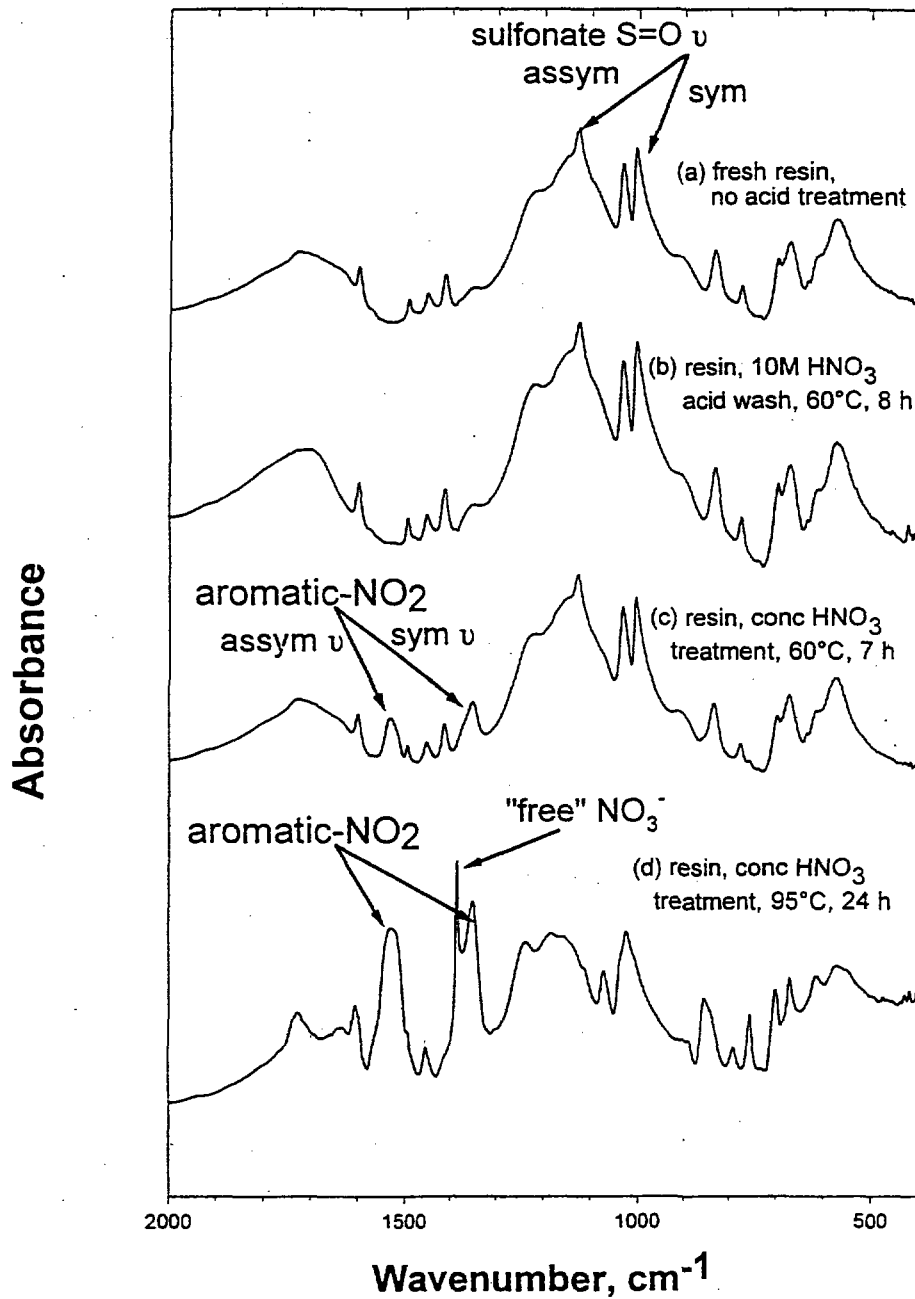


Figure 3.2 Infrared Spectra of Sulfonated Polystyrene Copolymer, Cation Exchange Resin; 2000 – 400 cm⁻¹ Region. Resin was treated as follows (a) fresh resin, no acid treatment (b) 10M HNO₃, 60°C, 8h, (c) conc HNO₃, 60°C, 7h, (d) conc HNO₃, 95°C, 24h

quaternary ammonium polystyrene copolymer,
anion exchange resin

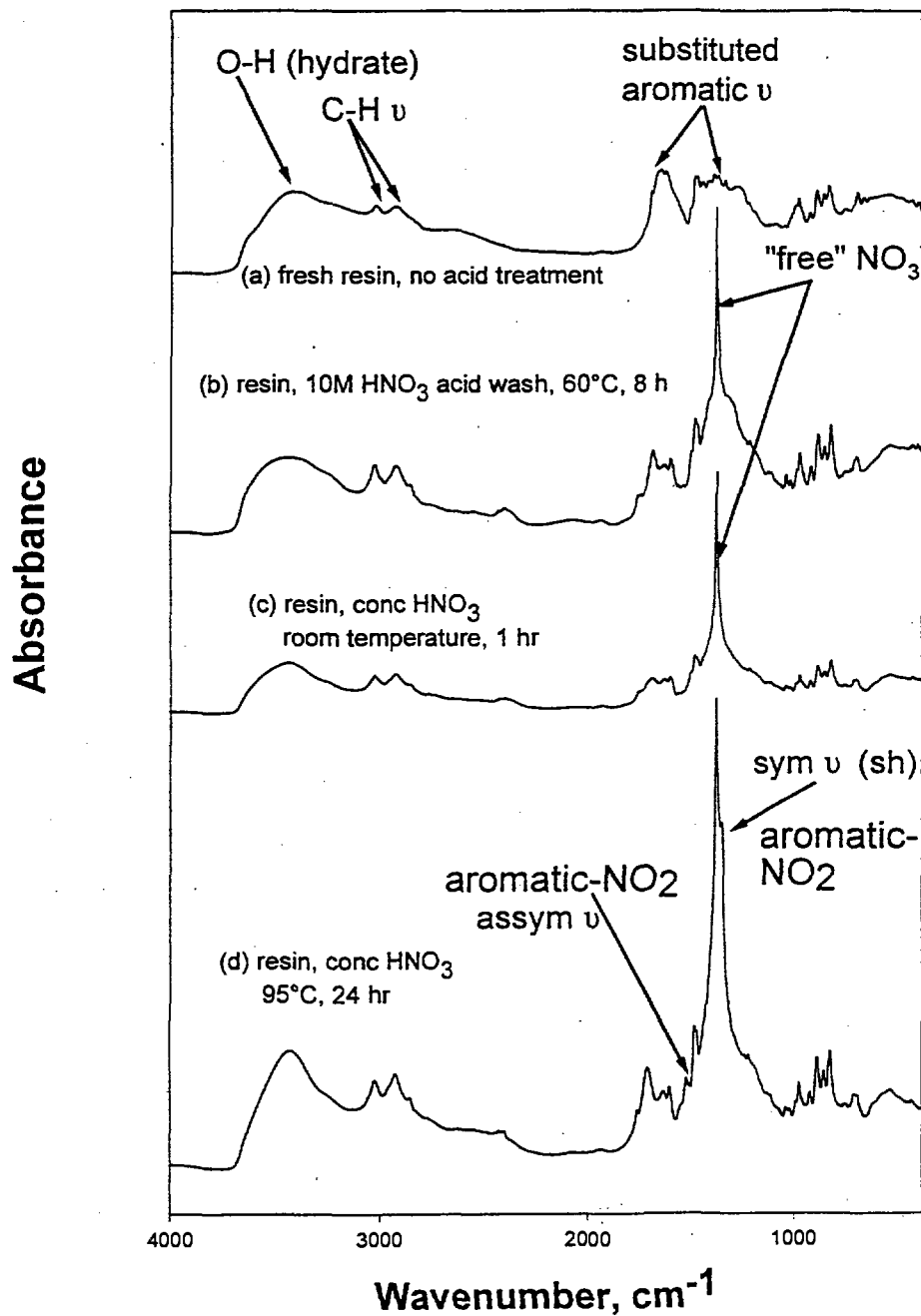


Figure 3.3 Infrared Spectra of Quaternary Ammonium Polystyrene Copolymer, Anion Exchange Resin; 4000 – 400 cm^{-1} Region. Resin was treated as follows (a) fresh resin, no acid treatment (b) 10M HNO_3 , 60°C, 8h, (c) conc HNO_3 , room temp, 1h (d) conc HNO_3 , 95°C, 24h

quaternary ammonium polystyrene copolymer,
anion exchange resin

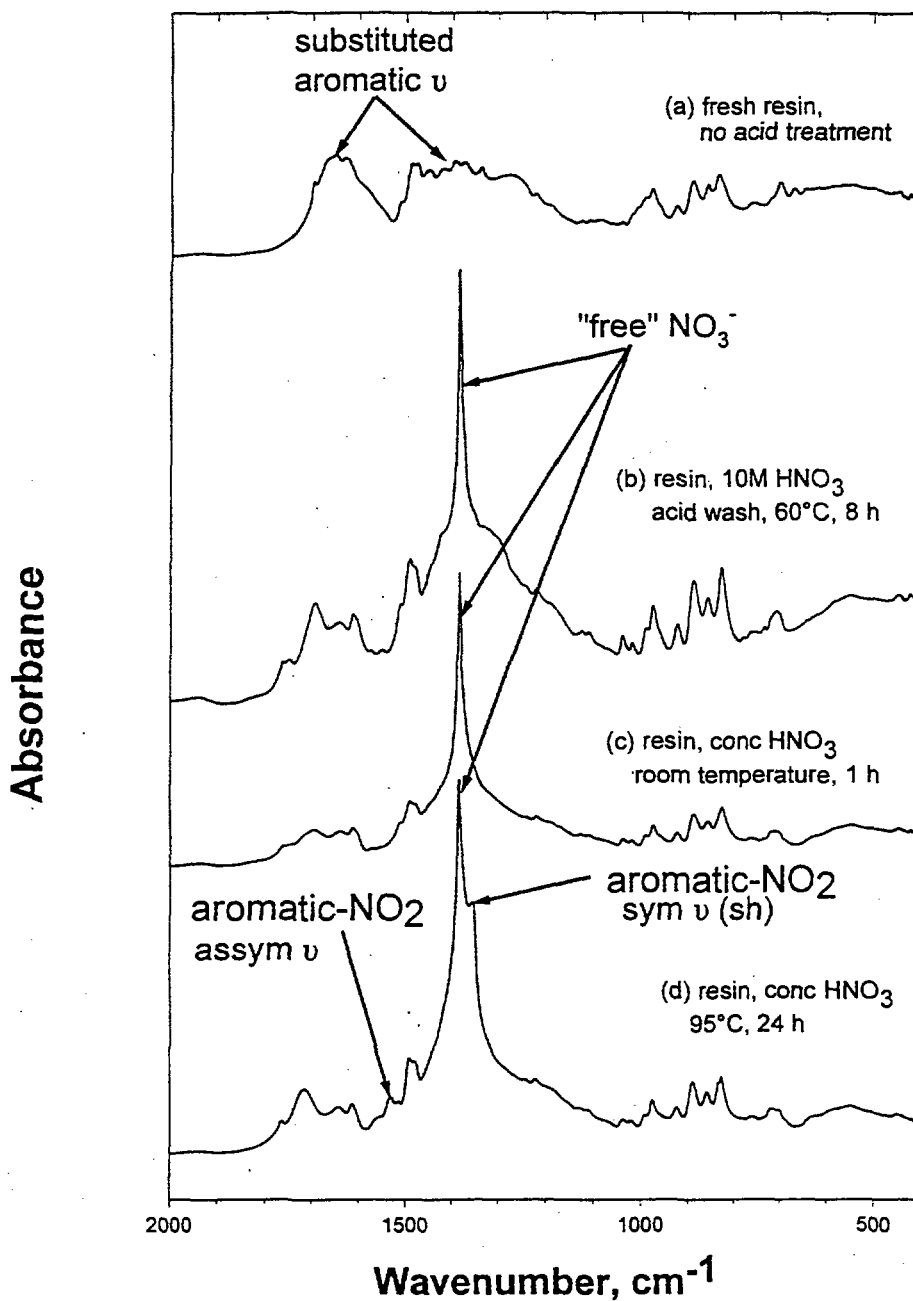


Figure 3.4 Infrared Spectra of Quaternary Ammonium Polystyrene Copolymer, Anion Exchange Resin; 2000 – 400 cm⁻¹ Region. Resin was treated as follows (a) fresh resin, no acid treatment (b) 10M HNO₃, 60°C, 8h, (c) conc HNO₃, room temp, 1h (d) conc HNO₃, 95°C, 24h

4.0 SUMMARY

Results for tests performed in the course of this work are summarized in Table 4.1 below.

Table 4.1 Results Summary

Sample ID	Ion Exchange Capacity (maq/g)	Digestate TOC (mgC/g resin)	DSC Results ^(a) (J/g)	Presence of ^(b) Nitroaromatics	Other Observations - Comments
CO	4.62	N/A	+111	no	starting material
C1	4.31	1.1	+127	na	no obvious gas evolution Supernates yellow; darker with larger exposure
C2	4.47	0.8	+9.0	na	
C3	4.47	1.2	+89	na	
C60-1	4.42	1.4	+102	na	Some NO _x evolved as reaction mixture heats up
C60-2	4.46	2.2	-154	na	
C60-3	4.25	0.7	-348	na	
C100-1	3.82	1.9	-280	na	
C100-2	3.52	2.1	-674	na	
C100-3	3.04	6.7	-1015	yes	
A0	2.37	N/A	+219	no	starting material
A1	2.07	1.8	-534	no	Resin floats in conc HNO ₃ . Brown gas (NO _x) evolved upon contact with conc HNO ₃ . More NO _x at higher T. Digestates not as yellow as corresponding cation resin digestates
A2	2.10	1.3	-398	na	
A3	2.09	2.7	-517	na	
A60-1	2.10	2.2	-399	na	
A60-2	2.21	2.2	-471	na	
A60-3	2.22	2.9	-354	na	
A100-1	2.29	3.4	-354	na	
A100-2	2.30	13	-490	na	
A100-3	2.31	40	-648	yes	

(a) Heat absorbed (+) or liberated (-) in the 150°C to 400°C range

(b) From FTIR measurement

N/A = not applicable; na = not analyzed.

5.0 CONCLUSIONS

Significant changes in measured properties of resin beads were observed only at the most extreme digestion conditions (95° C; 7 and 24 hr). At less rigorous conditions, only very small losses of ion exchange functionality were seen. The extent of resin bead matrix disruption, as measured by TOC of digestion filtrates, was only significant at the most extreme processing conditions.

Radionuclides sorbed or associated with the organic ion exchange resins (OIER) can restrict disposal of this solid to the Environmental Restoration Disposal Facility (ERDF). Solids to be delivered to the ERDF must meet Waste Acceptance Criteria (WAC) for radionuclide concentrations (*ERDF Waste Acceptance Criteria*, BHI-00139, Rev. 2, Table 4-1). The radionuclides most likely controlling the ERDF acceptance of K Basins' solid residues are ¹³⁷Cs (32 Ci/m³ or 32 µCi/mL) and the transuranics (TRU; 100 nCi/g). The transuranic isotopes have individual limits; ²⁴¹Am is 0.05 Ci/m³ (50 nCi/mL), ²³⁸Pu is 1.5 Ci/m³ (1,500 nCi/mL), and ²³⁹Pu and ²⁴⁰Pu are each 0.029 Ci/m³ (29 nCi/mL). The effective uranium limit for disposal to ERDF, 0.0026 g U/mL², may also foreclose ERDF disposal of certain K Basins residues. The radionuclide activities of OIER retrieved from the K Basins must be decontaminated to these levels to allow ERDF disposal. The TRU content of rinsed OIER retrieved from the K East Basin (Sample KES-H-08) has been found to range from about 650 to 850 nCi/g dried resin. The unrinsed OIER also contains 144 µCi ¹³⁷Cs and 0.003 g U per gram of dried resin (Schmidt et al. 1999).

Based on the above radionuclide concentrations in the actual OIER in KE Basin sludge and the levels of defunctionalization achieved during the cold OIER testing (i.e., 3% to 34% defunctionalization for the cation and 3% to 13% for the anion resin material), acid digestion in 15.7 M HNO₃ is predicted to be insufficient to decontaminate the OIER to the levels necessary to meet the ERDF WAC. However, recent results from digestion of actual OIER from KE Basin sludge in 10 M HNO₃ indicate that higher levels of decontamination were achieved than predicted from the cold OIER digestion (Schmidt et al. 1999). For sieved and rinsed OIER from sample KES-H-08, at ratios of about 1 g resin per 20 mL acid, about 80% of the uranium, 25% of the plutonium, and 70% or more of the americium activity were removed. Cesium distributions were not measured but high removals would be expected. Residual activities in the acid-treated OIER were 160 to 340 nCi/g TRU (110-190 nCi ^{239,240}Pu/g, 20-120 nCi ²⁴¹Am/g), and 1.5-34 µCi ¹³⁷Cs/g (uranium concentrations were not detectable but likely were near 0.0003 g U/g based on K_d tests at higher loadings).

The differences in results obtained from the digestions performed on the cold OIER and the digestions performed on the hot OIER collected from KE Basin sludge can be partially attributed to the following factors: 1) the cold testing examined defunctionalization, whereas the decontamination achieved during the hot testing included the effects of both defunctionalization and displacement, 2) the initial radionuclide concentrations associated with the hot OIER may have included particulate mater that was easily digested (i.e., possibly inflating the initial concentrations of the OIER), and 3) the ion exchange

² The ERDF WAC limit for ²³⁸U and its daughters is 0.012 Ci/m³. With 8 alpha and 6 beta decays in the ²³⁸U decay chain and a specific activity of 3.36x10⁻⁷ Ci ²³⁸U /g, the specific activity of the ²³⁸U chain is 4.7x10⁻⁶ Ci/g. The ERDF limit for ²³⁸U thus is 0.00256 g ²³⁸U/mL. The ERDF limit for ²³⁵U (daughters not included) is 0.0027 Ci/m³ and the specific activity of ²³⁵U is 2.16x10⁻⁶ Ci/g. Thus the ERDF limit for ²³⁵U is 0.0013 g ²³⁵U/mL. The relative limits of the two uranium isotopes, and the nominal 0.7% enrichment of the K Basins sludge, mean that ²³⁸U concentration limits ERDF disposal. Therefore, the effective uranium limit for disposal to ERDF is 0.0026 g U/mL.

capacity in the cold work was determined with Na⁺ (cation resin) and Cl⁻ (anion resin). The binding affinity of OIER for ¹³⁷Cs, ^{239,240}Pu, and ²⁴¹Am differ from that of Na⁺ and Cl⁻.

Based on the results obtained for the digestions of the hot OIER, it may be possible to remove cesium, uranium, and americium to meet ERDF criteria by performing multiple washing contacts of retrieved OIER with strong HNO₃. However, such an approach would be less successful for plutonium where strong anion exchange sorption occurs at high HNO₃ concentrations and strong cation exchange sorption occurs at low HNO₃ concentrations, especial considering that very little defunctionalization occurs to either the anion or cation resin. Consequently, a more sophisticated leaching approach will likely be required to decontaminate the OIER to the levels necessary to meet the ERDF WAC.

FTIR spectra of digested resins show evidence for formation of small amounts of nitroaromatic compounds (nitrated resin matrix). Thermal analyses suggest that nitric acid treated resin beads can undergo exothermic decomposition reactions in the 160°C to 400°C temperature range. The largest exothermic event (1015 J/g) was observed for sample C100-3. These results indicate that some level of safety evaluation will likely be required if the OIER will be digested or leached with nitric acid. After nitric acid leaching or digestion, it may be necessary to contact the OIER with base to hydrolyze nitroaromatics and neutralize and remove residual acid.

Acknowledgments

Contributors to this report include SA Bryan, TR Hart, RL Sell, SO Slate, LMP Thomas, and GK Ruebsamen.

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Appendix A

Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) Traces for Nitric Acid Digested Purolite Ion Exchange Resin Samples

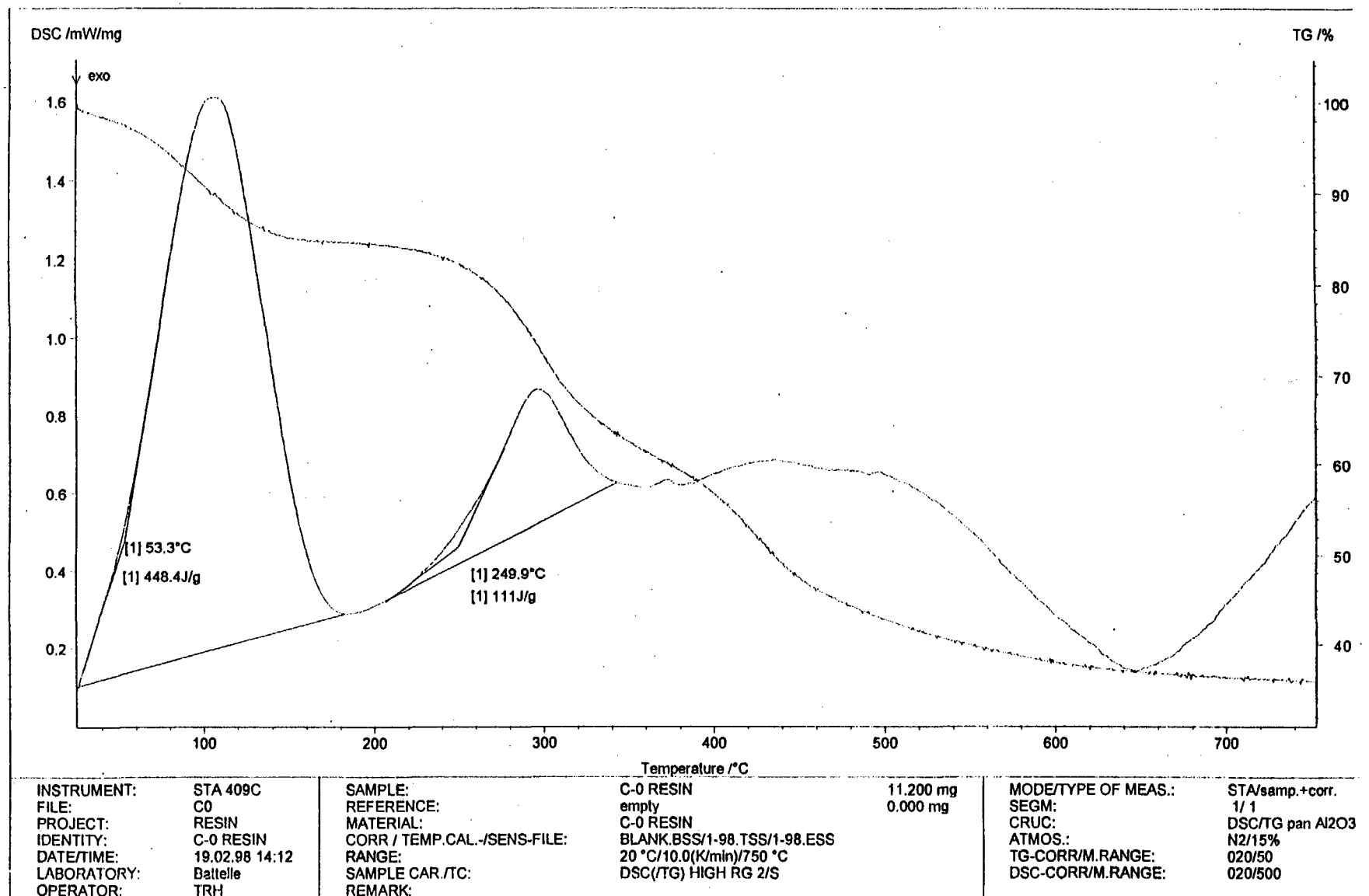


Figure A.1 TGA and DSC Traces for Sample C0

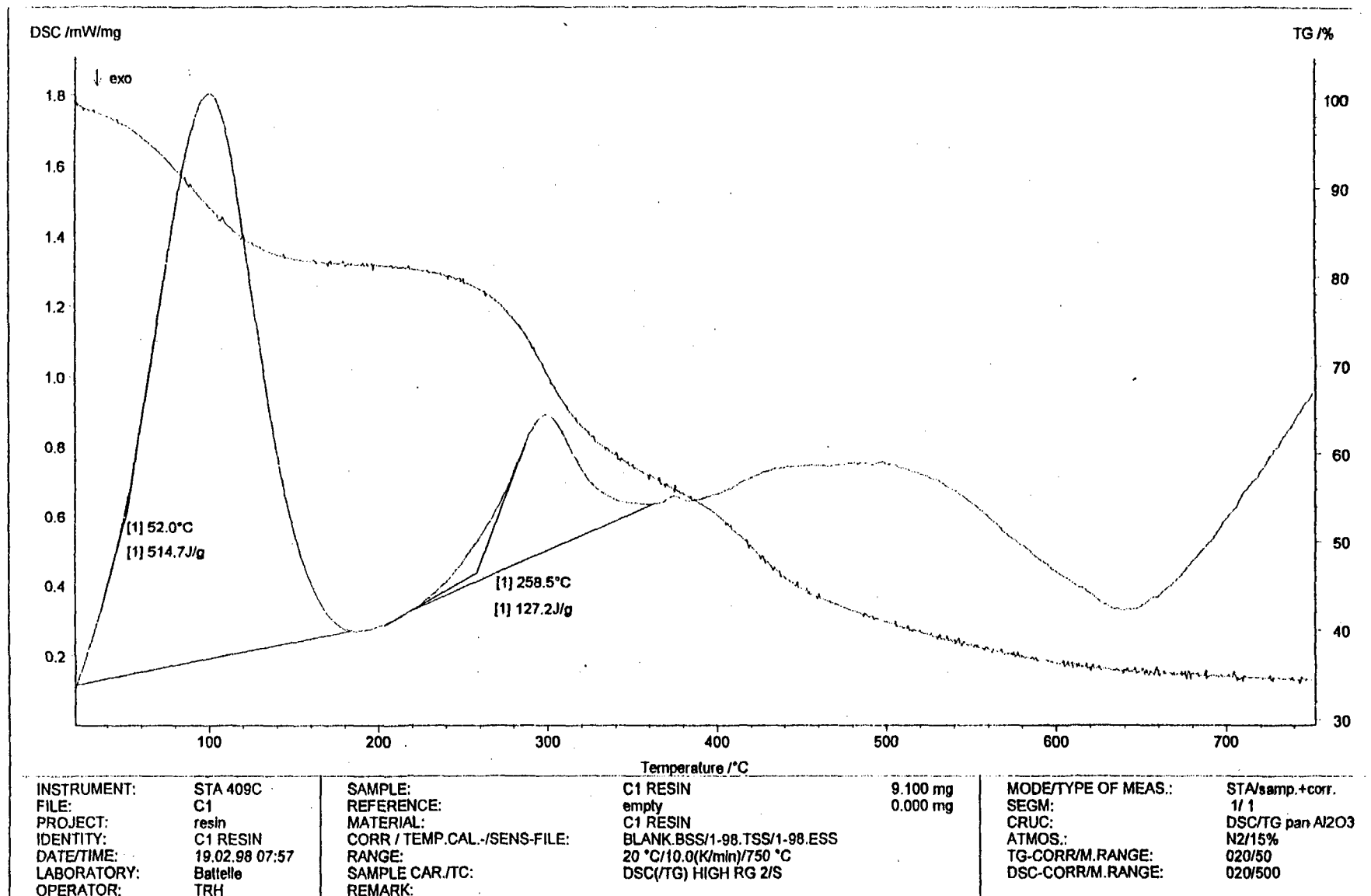


Figure A.2 TGA and DSC Traces for Sample C1

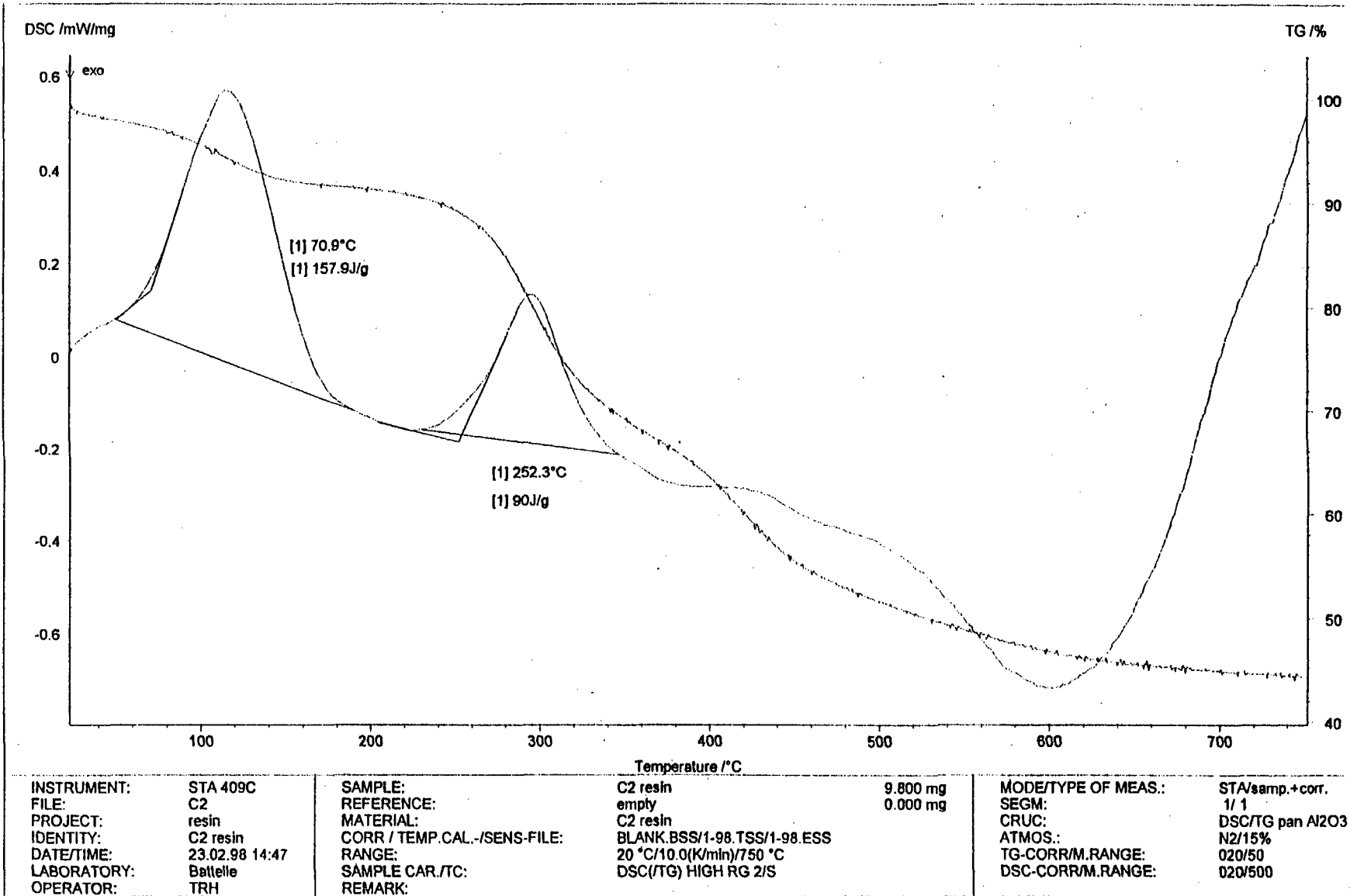


Figure A.3 TGA and DSC Traces for Sample C2

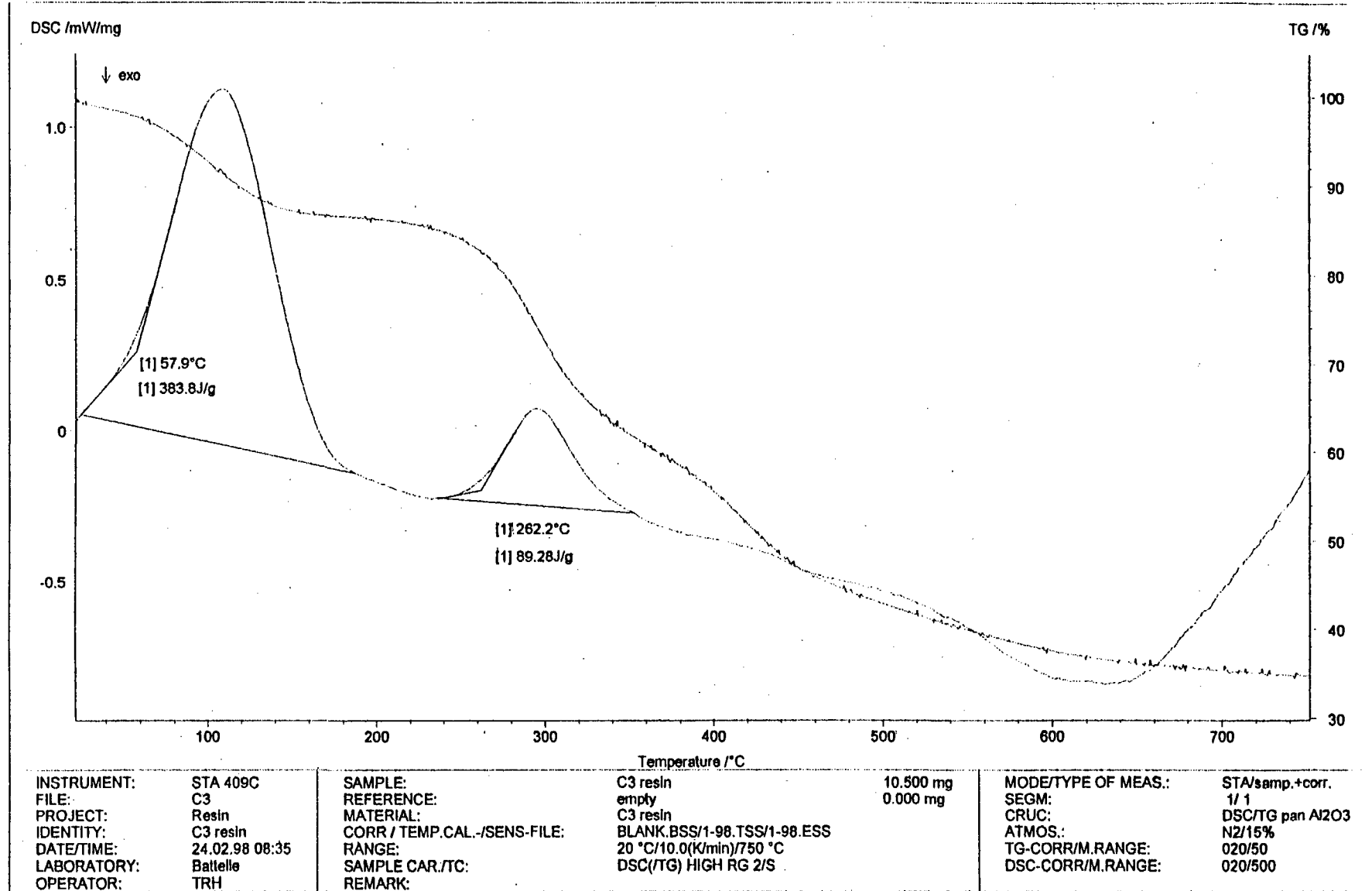


Figure A.4 TGA and DSC Traces for Sample C3

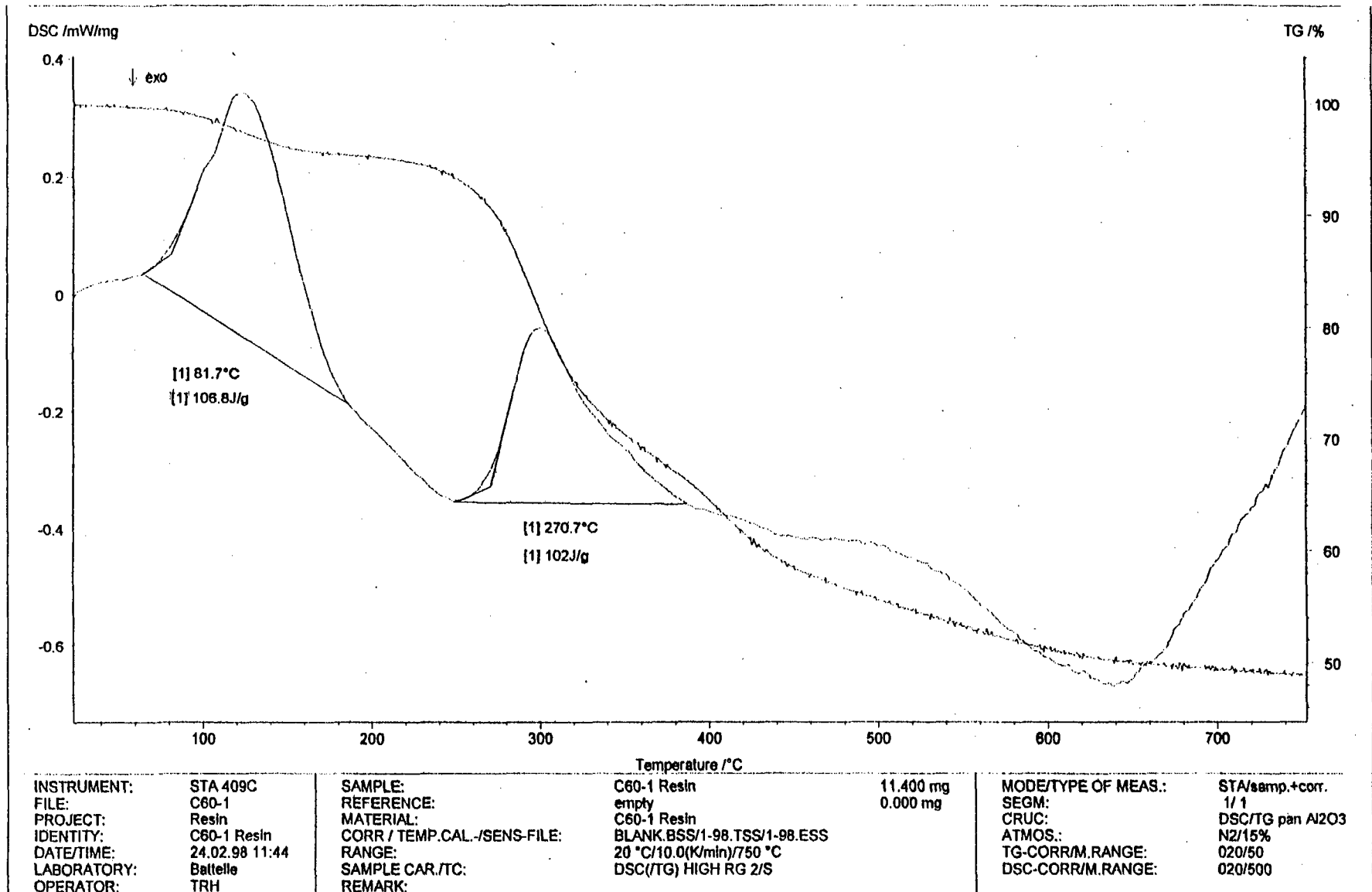


Figure A.5 TGA and DSC Traces for Sample C60-1

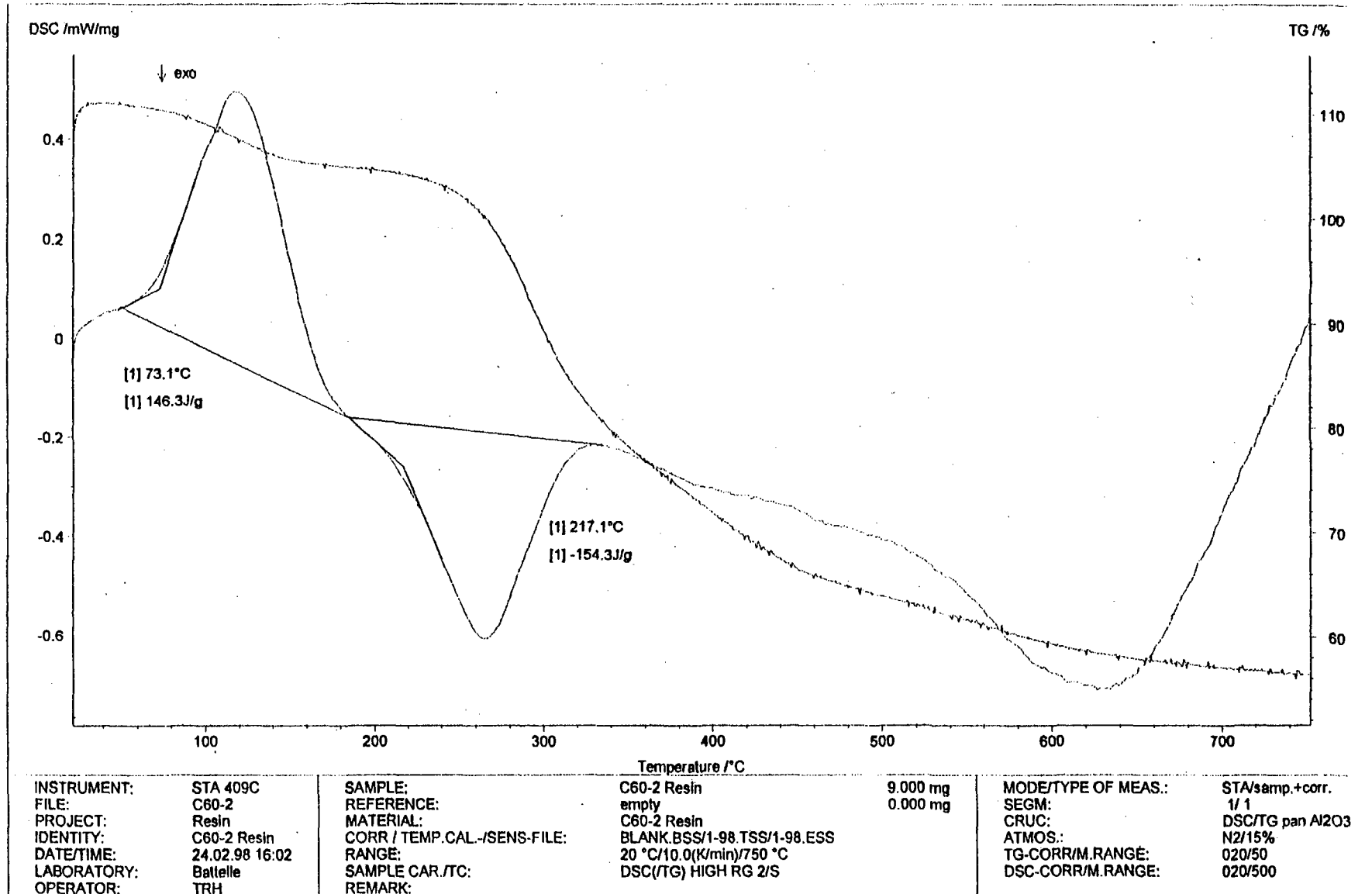


Figure A.6 TGA and DSC Traces for Sample C60-2

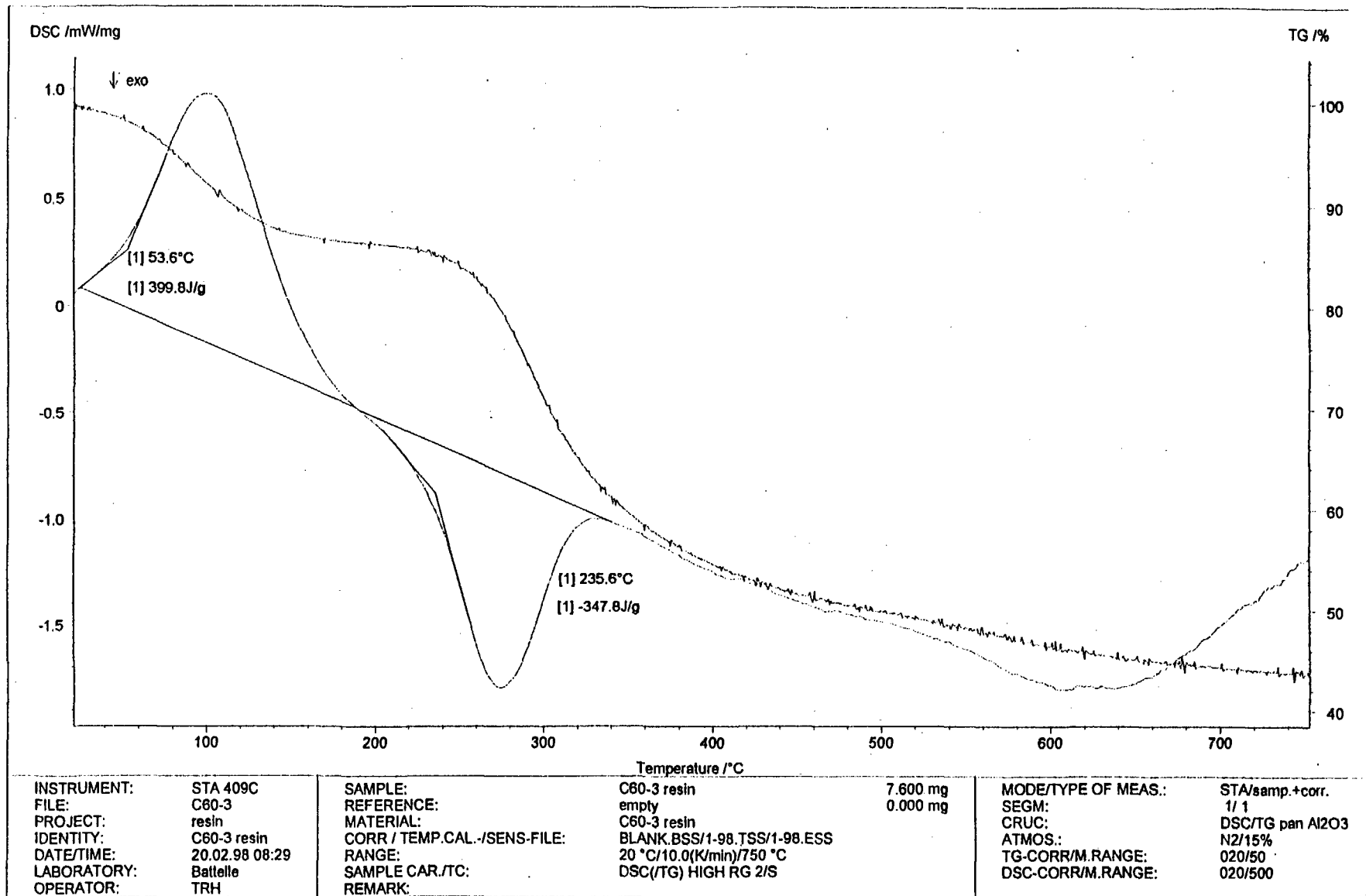


Figure A.7 TGA and DSC Traces for Sample C60-3

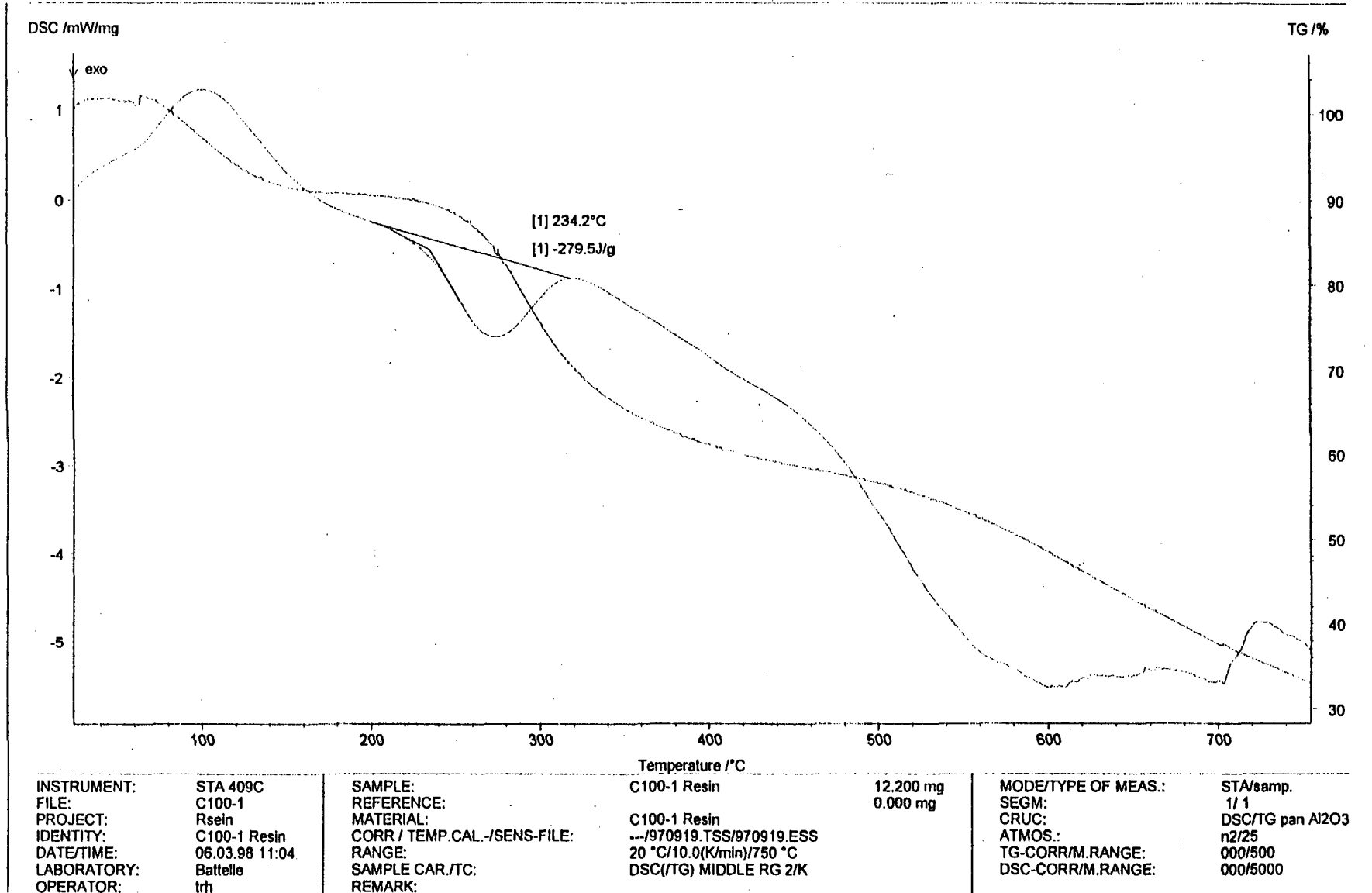
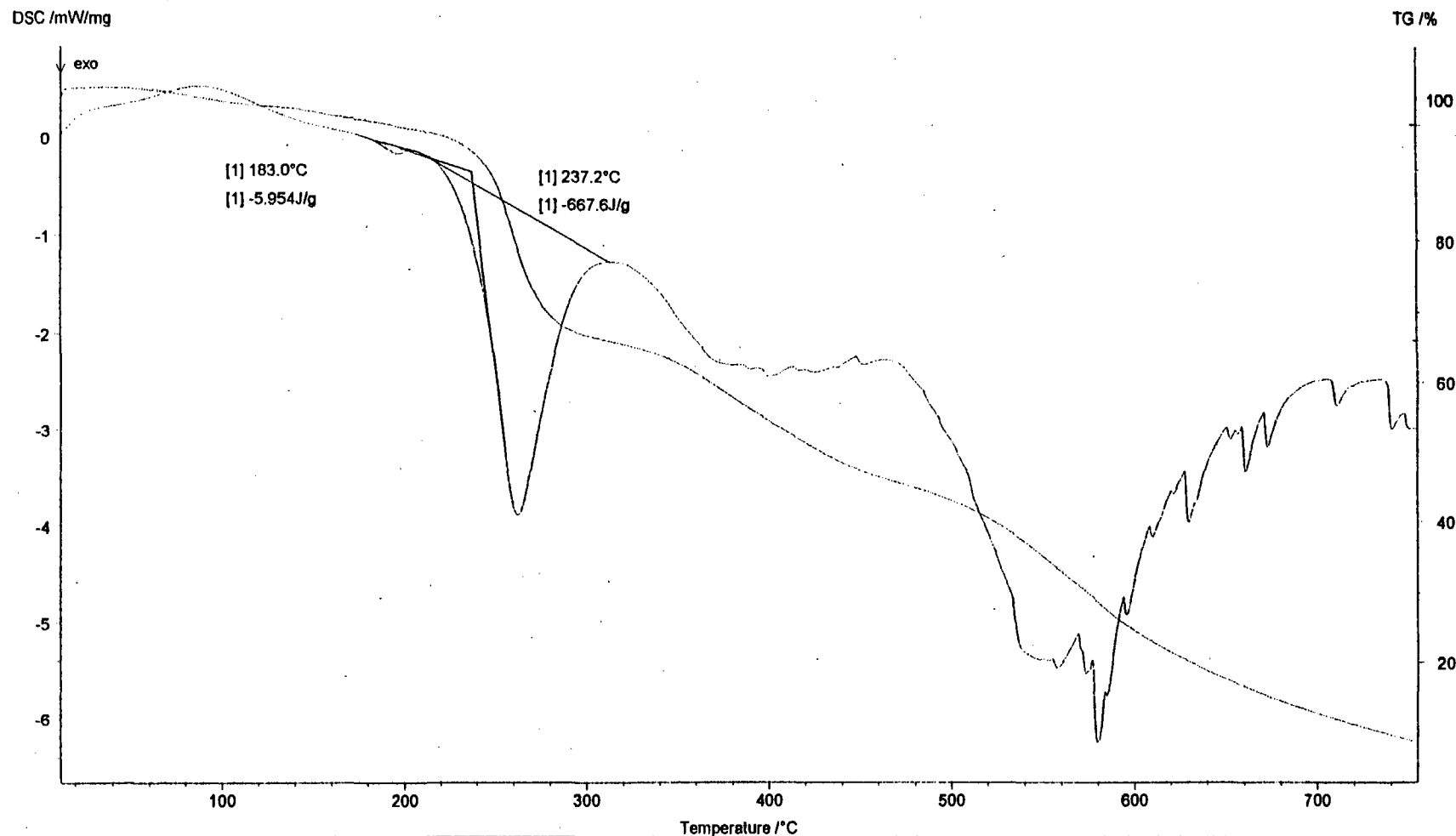


Figure A.8 TGA and DSC Traces for Sample C100-1



INSTRUMENT:	STA 409C	SAMPLE:	C100-2 Resin	17.200 mg	MODE/TYPE OF MEAS.:	STA/samp.
FILE:	C100-2	REFERENCE:		0.000 mg	SEGM:	1/1
PROJECT:	Rsein	MATERIAL:	C100-2 Resin		CRUC:	DSC/TG pan Al2O3
IDENTITY:	C100-2 Resin	CORR / TEMP.CAL./SENS-FILE:	---/970919.TSS/970919.ESS		ATMOS.:	n2/25
DATE/TIME:	06.03.98 15:35	RANGE:	20 °C/10.0(K/min)/750 °C		TG-CORR/M.RANGE:	000/500
LABORATORY:	Battelle	SAMPLE CAR./TC:	DSC(TG) MIDDLE RG 2/K		DSC-CORR/M.RANGE:	000/5000
OPERATOR:	lrh	REMARK:				

Figure A.9 TGA and DSC Traces for Sample C100-2

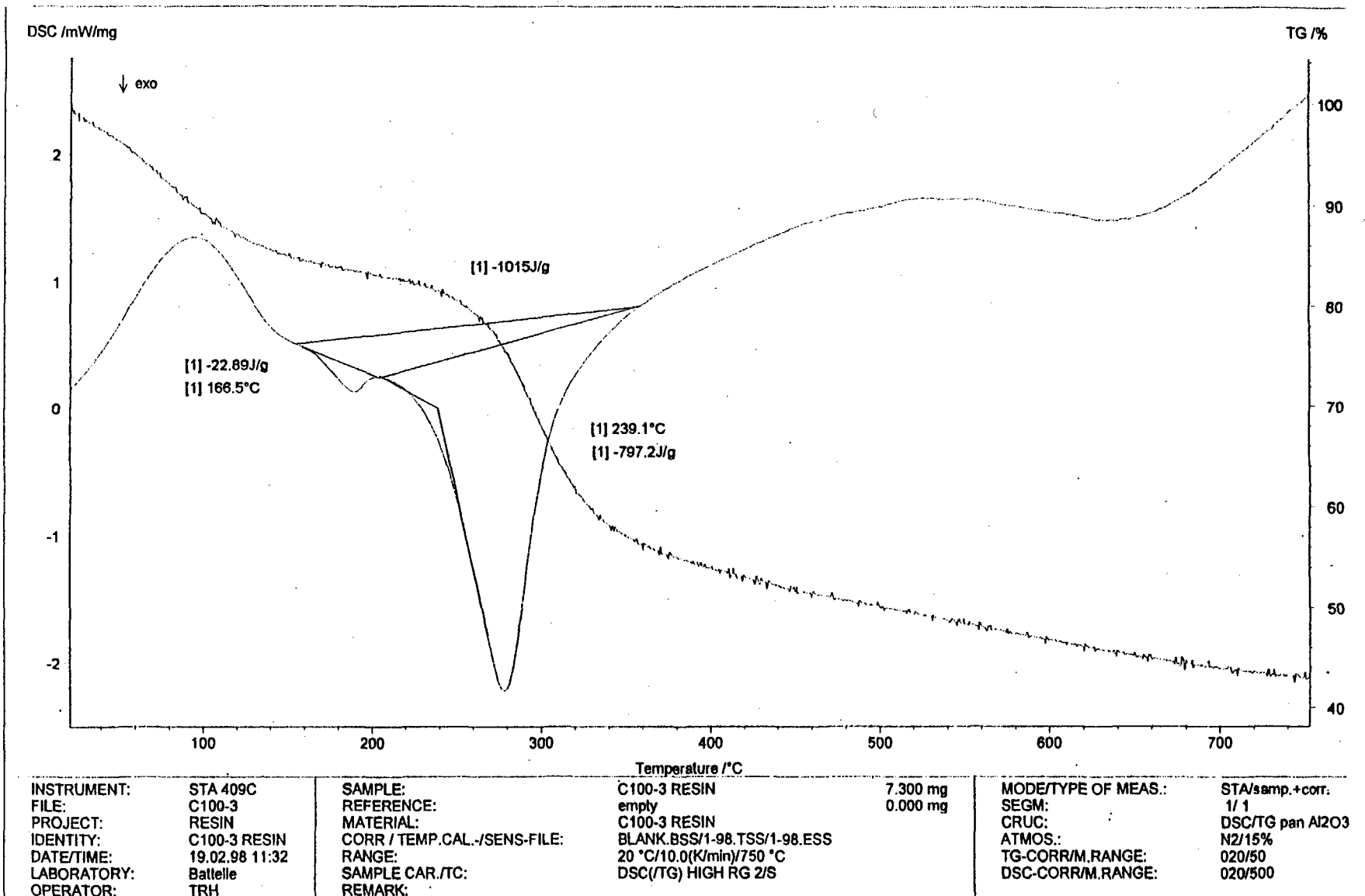


Figure A.10 TGA and DSC Traces for Sample C100-3

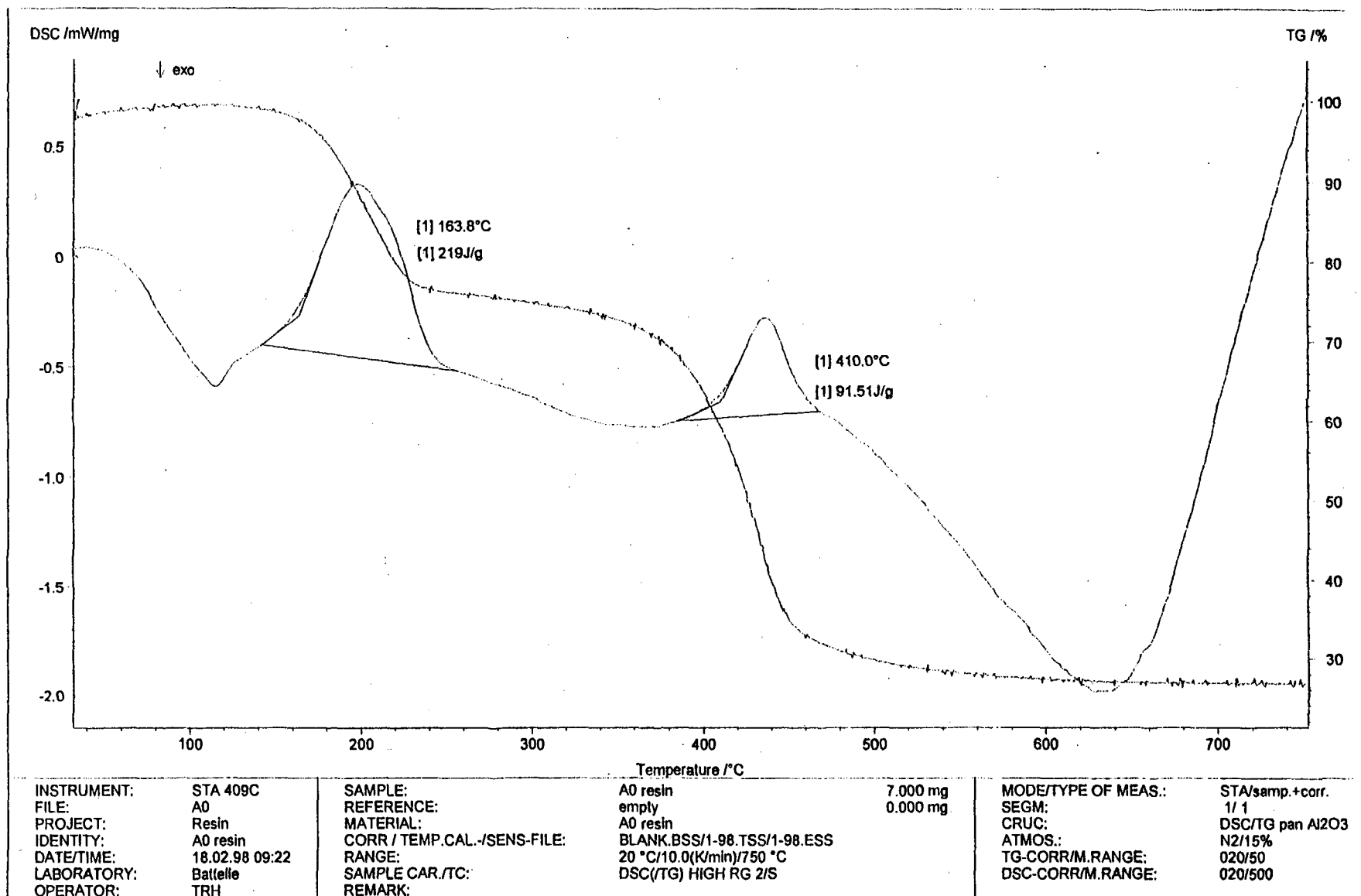


Figure A.11 TGA and DSC Traces for Sample A0

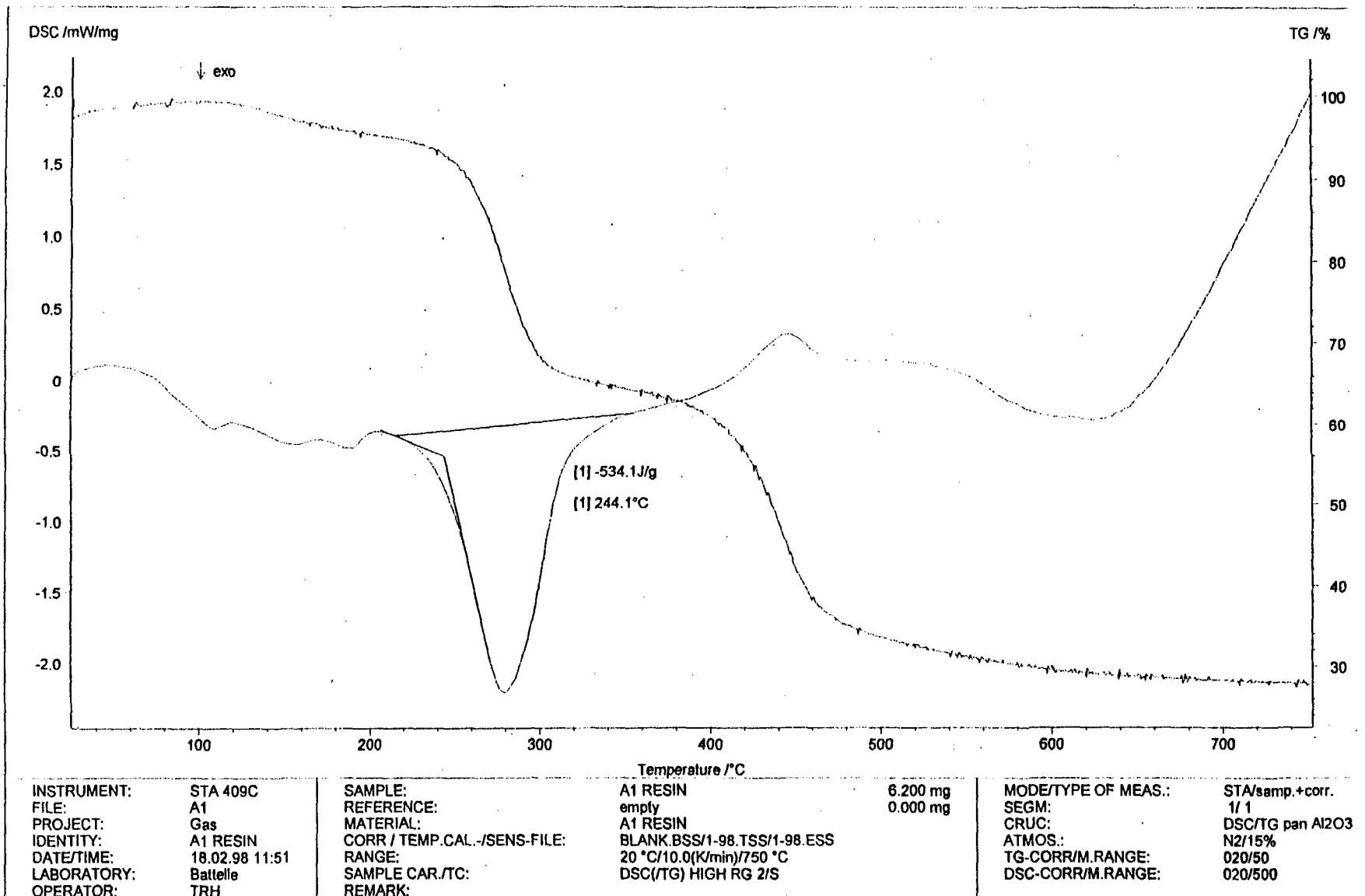


Figure A.12 TGA and DSC Traces for Sample A1

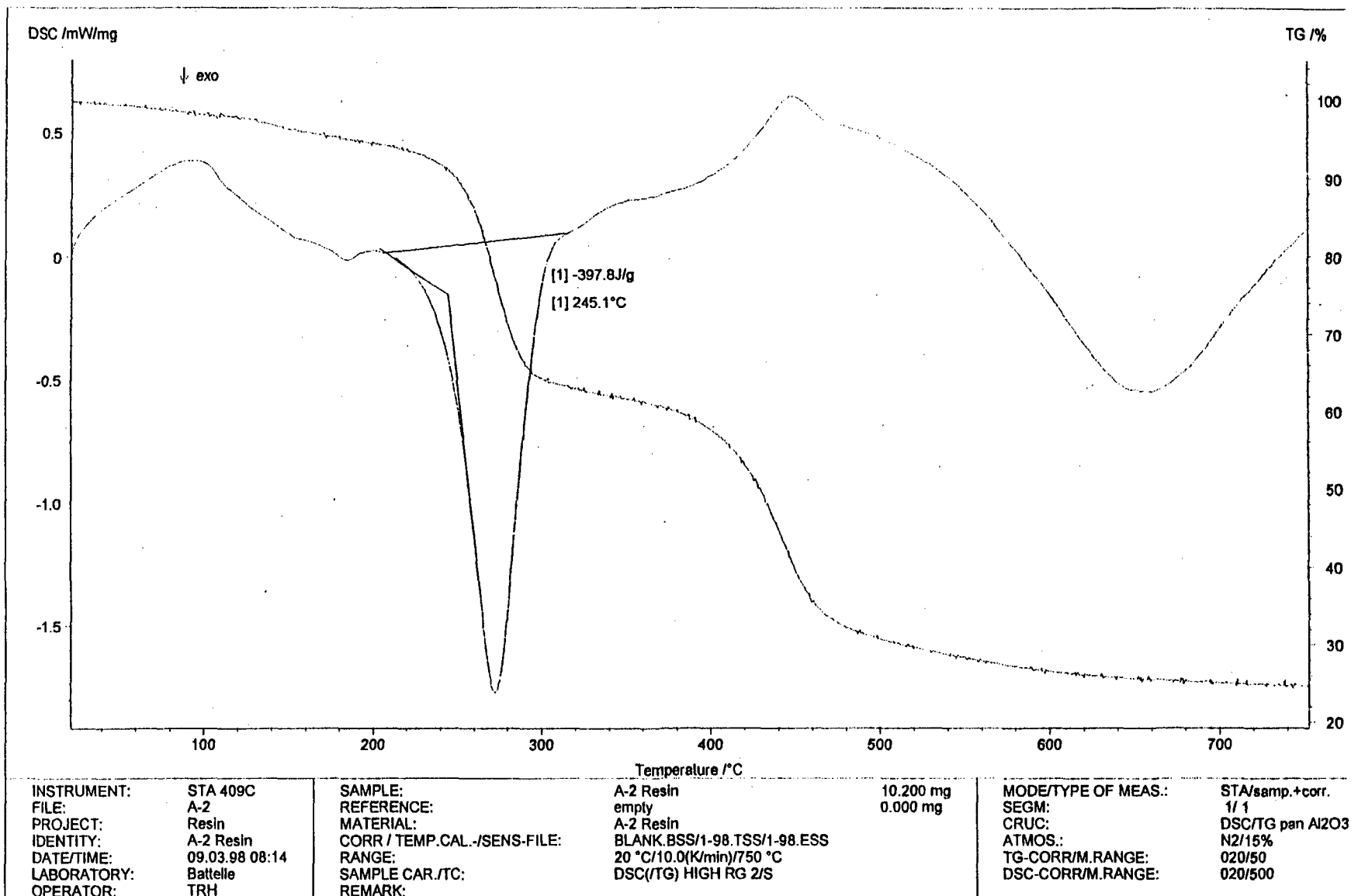


Figure A.13 TGA and DSC Traces for Sample A2

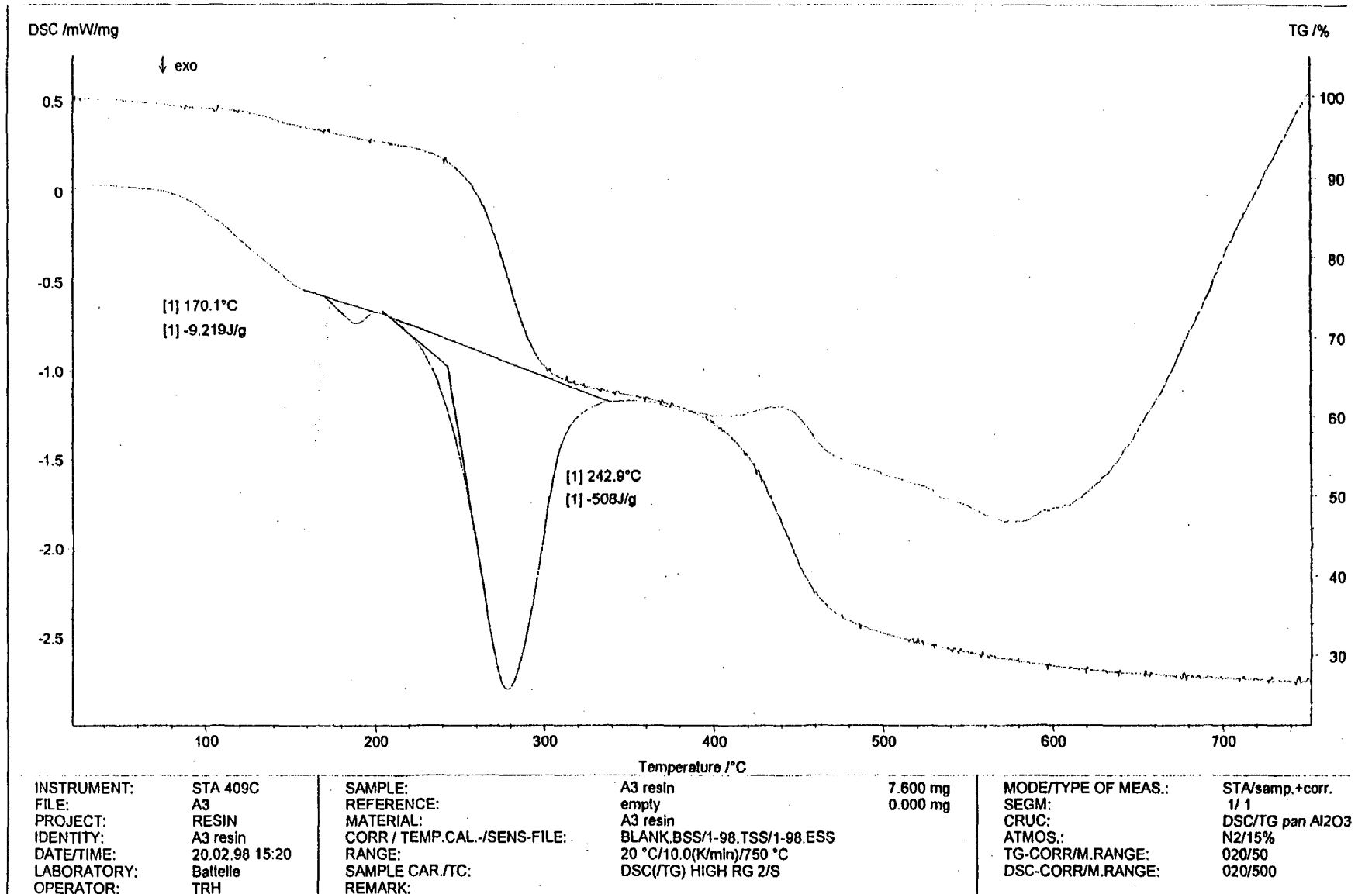


Figure A.14 TGA and DSC Traces for Sample A3

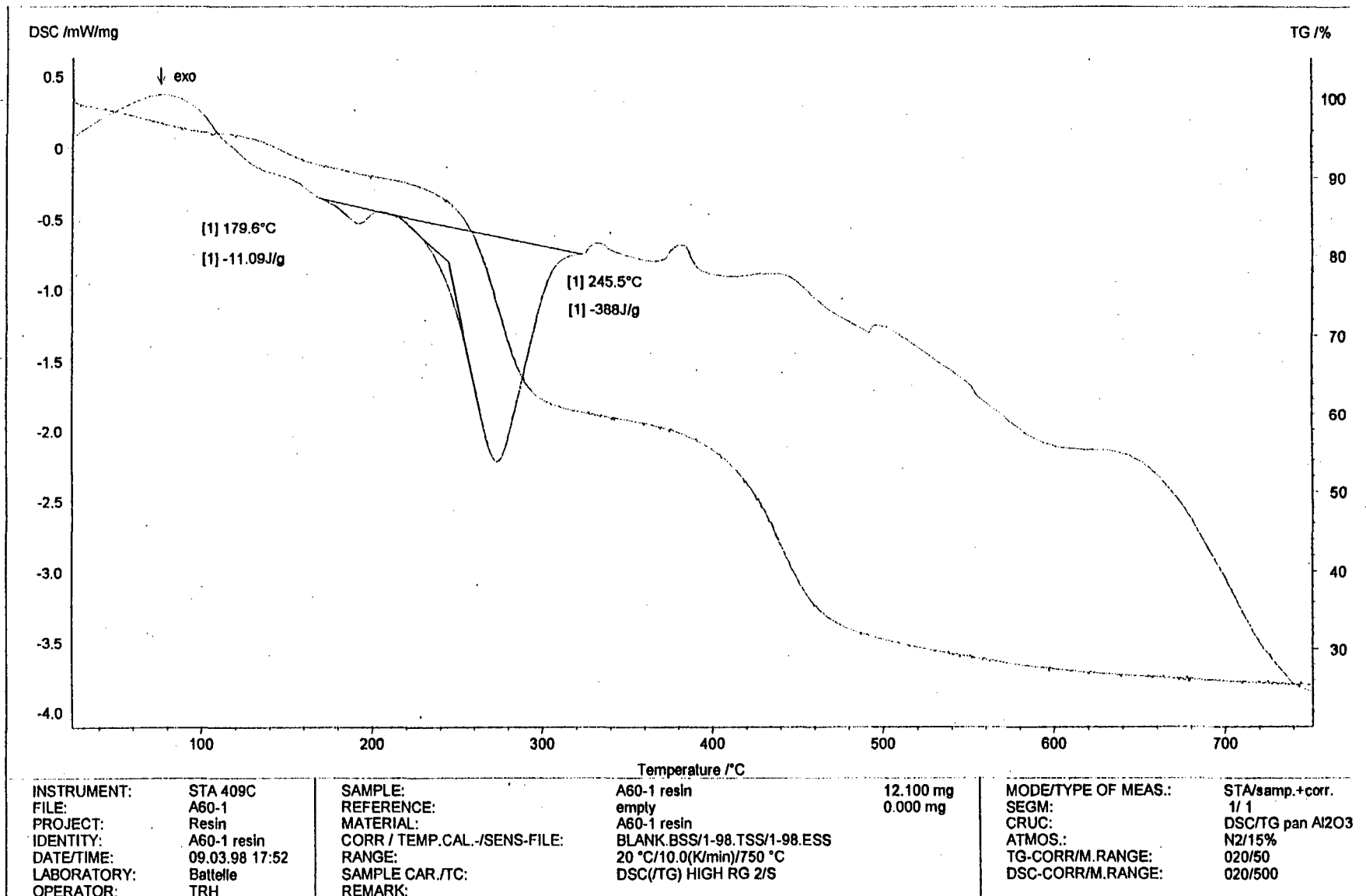


Figure A.15 TGA and DSC Traces for Sample A60-1

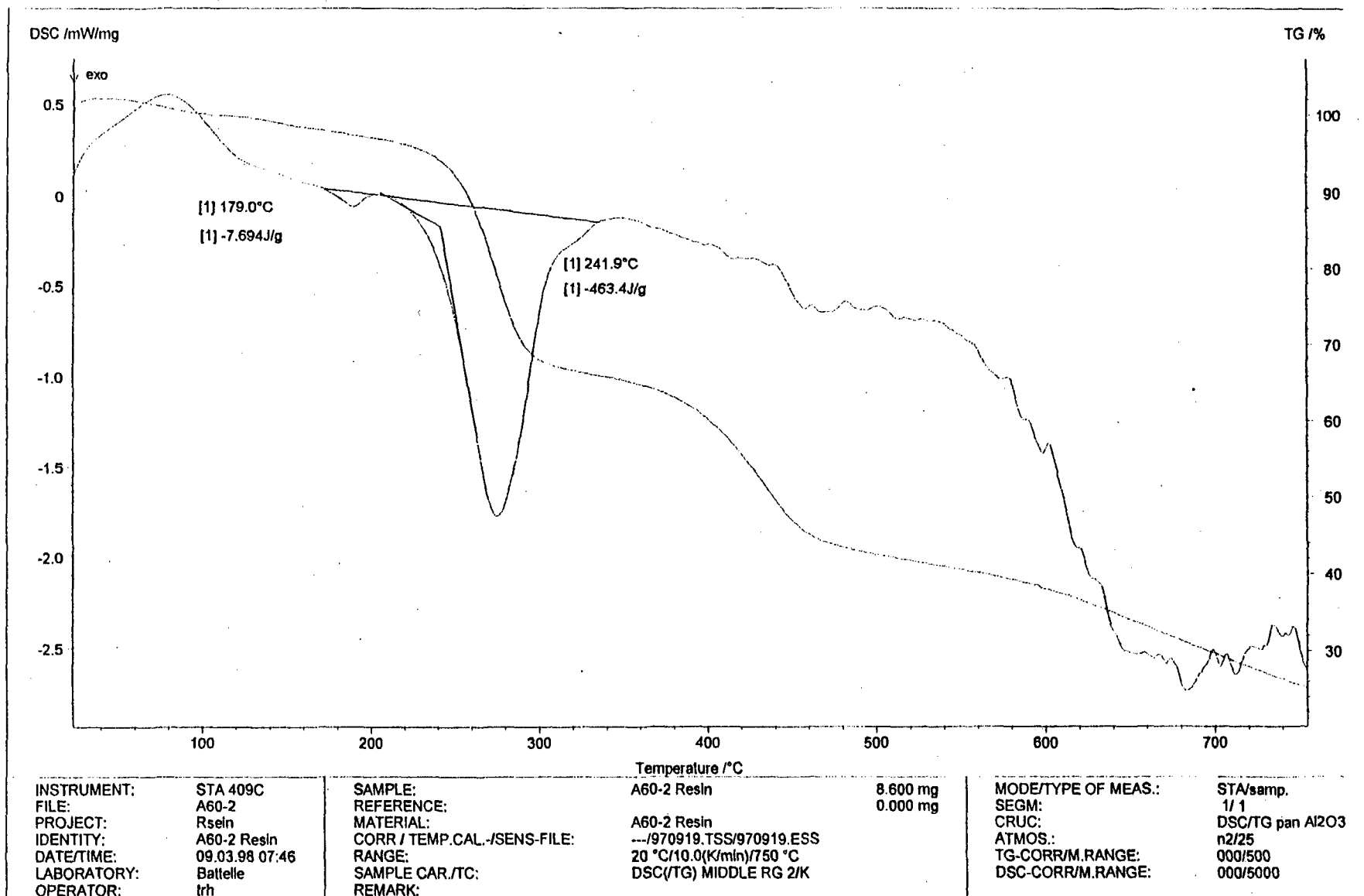


Figure A.16 TGA and DSC Traces for Sample A60-2

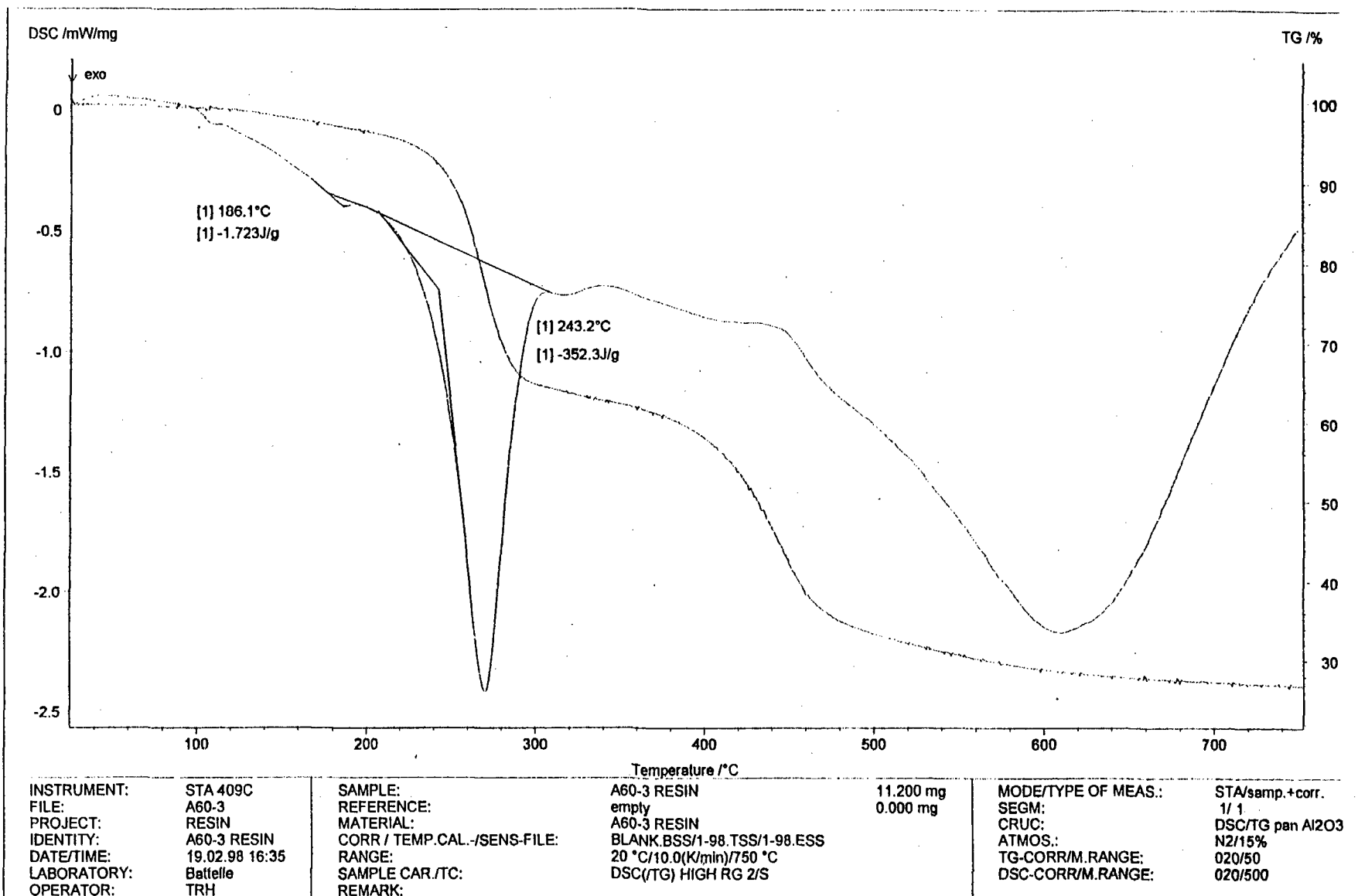


Figure A.17 TGA and DSC Traces for Sample A60-3

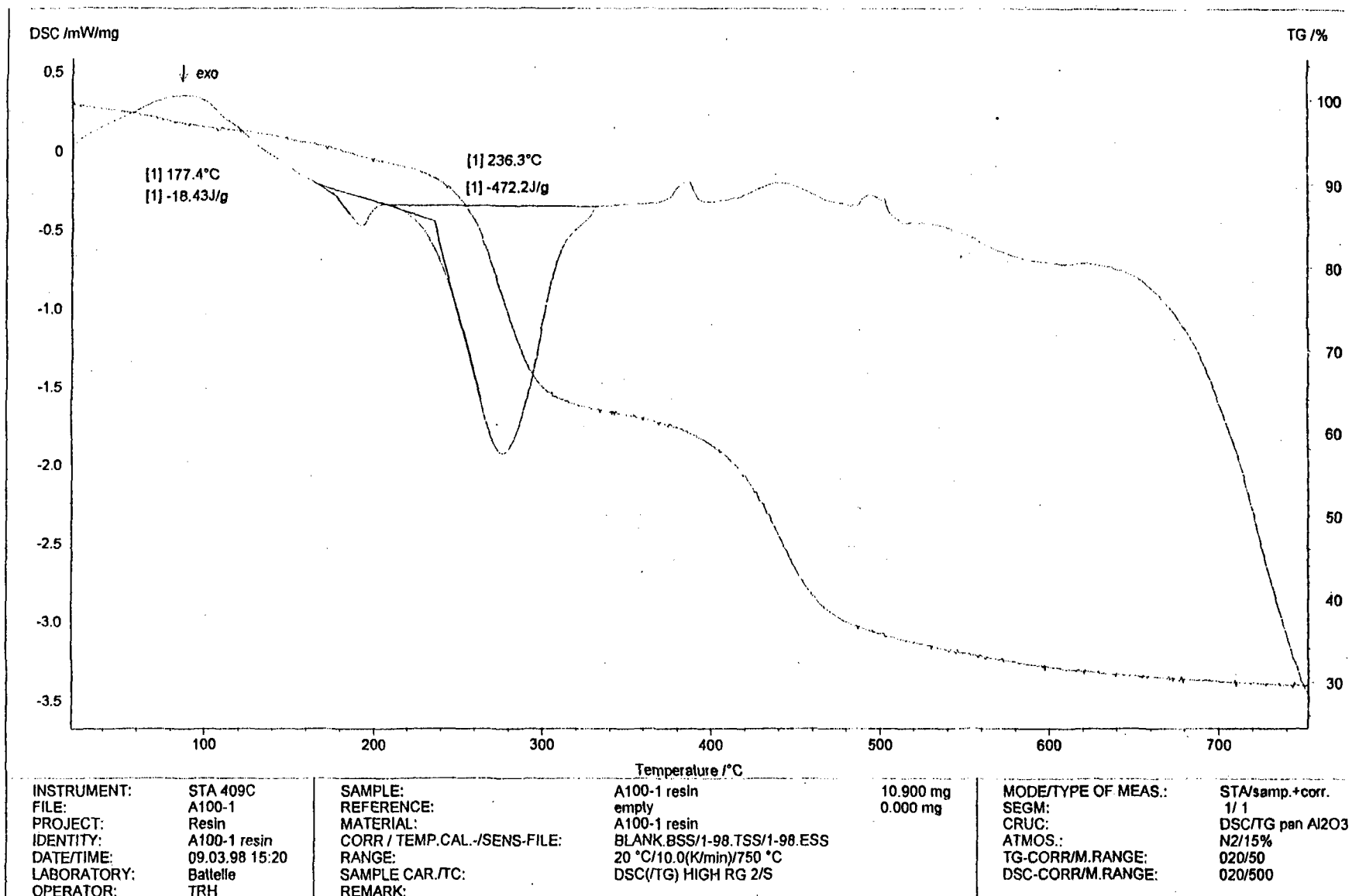


Figure A.18 TGA and DSC Traces for Sample A100-1

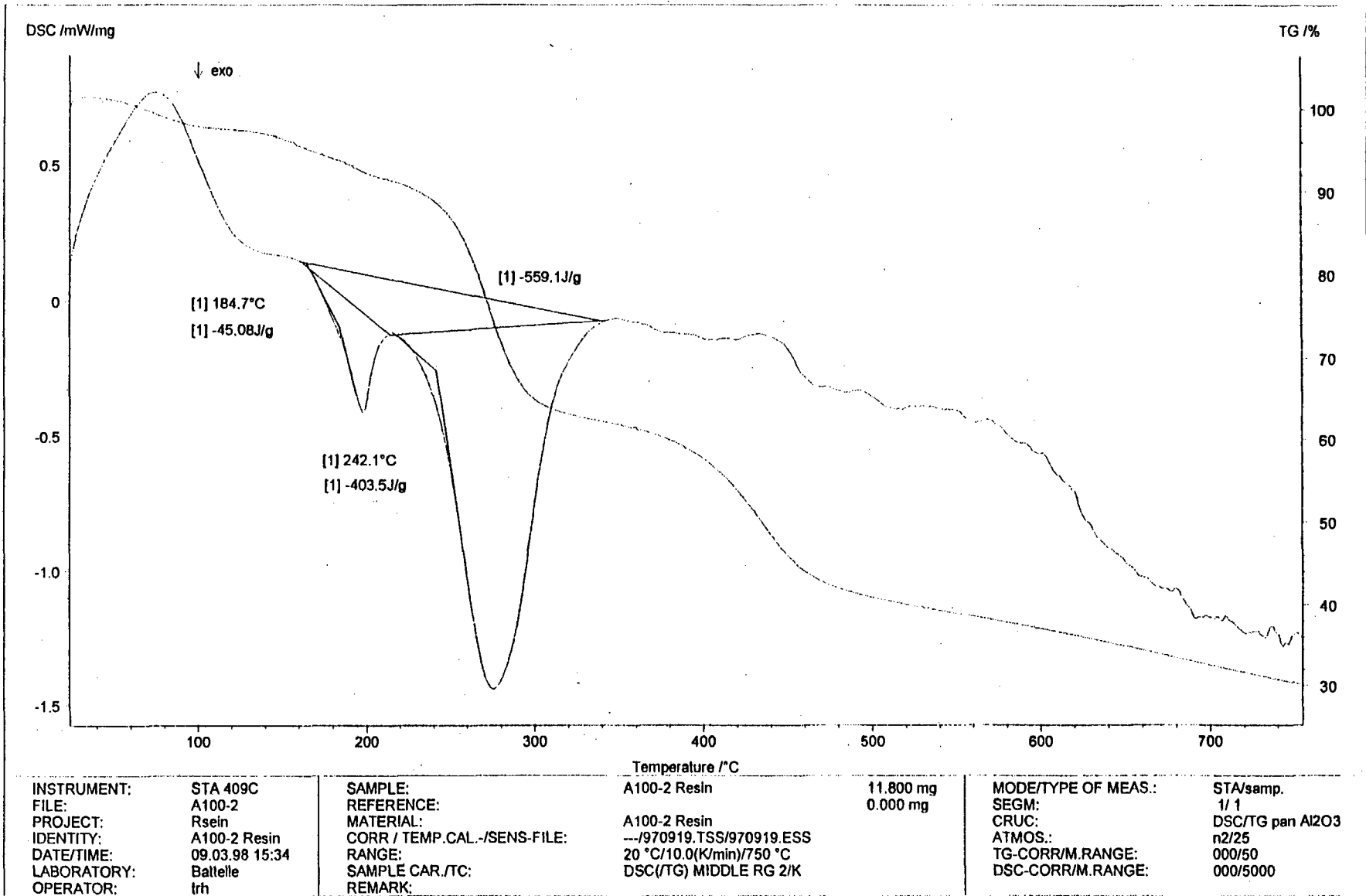


Figure A.19 TGA and DSC Traces for Sample A100-2

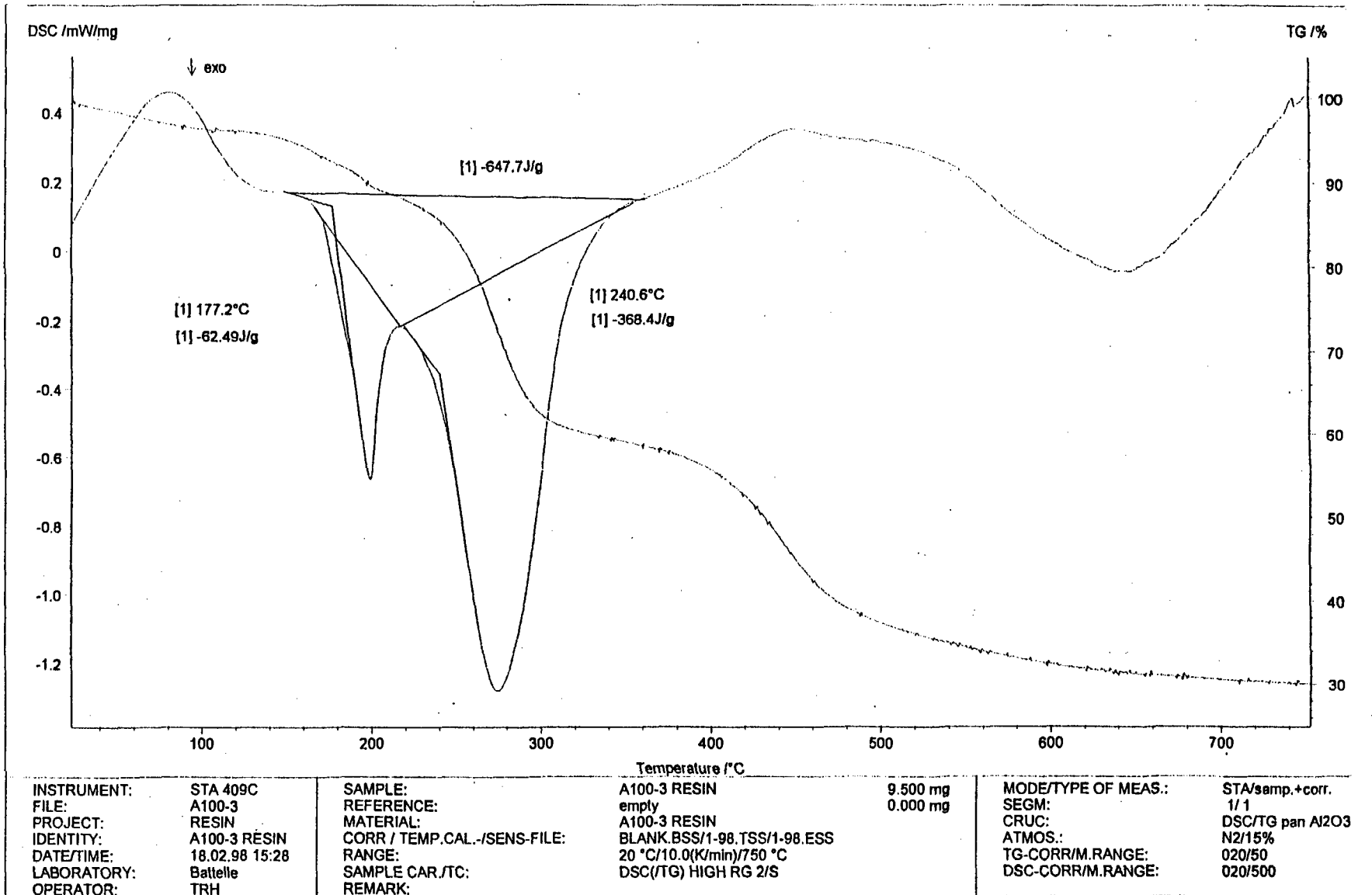


Figure A.20 TGA and DSC Traces for Sample A100-3