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Caliber Stab Detonators**

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List of Acronyms

ARDEC	Armament Research and Development Center (US Army)
BNCP	Tetraammine-nitro-tetrazolato cobalt perchlorate
DAATO 3.5	Diaminoazobistetrazine-3.5-oxide, Compound 29A
DAHA	Diamino-hexaazidocyclotetraphosphazene
DDT	Deflagration-to-detonation transition
DFeP	Diaminotetrazole, Fe(II) perchlorate complex, Compound 28A
DSC	Differential scanning calorimetry
ENTA	Ethylenedinitramino-tetraazidocyclotriphosphazene, Compound 30A
ETCP	Ethylenediamino-tetraazidocyclo-triphosphazene
HMX	Cyclo-tetramethylene-tetranitramine
NSWC-IHD	Naval Surface Warfare Center, Indian Head Division
PSEMC	Pacific Scientific Energetic Materials Company
RDX	Cyclo-trimethylene-trinitramine

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Preface

Acknowledgements: The following individuals participated in the joint SERDP/NSWC-IHD effort toward developing new, lead-free primary explosives:

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Executive Summary

All U.S. manufactured medium caliber stab detonators use a three component design consisting of initiation, transfer and output charges. Each of these components or materials is a distinct charge tailored specifically to the function it must perform. The initiation charge translates a mechanical energy strike into a rapid chemical event which in turn initiates a transfer charge which is typically an instantaneous detonant. This charge then initiates the output charge to a detonation velocity and pressure sufficient to then initiate a less sensitive main explosive charge. Typical stab detonator components are NOL-130 as the stab sensitive initiation charge, lead azide as the transfer charge and RDX or HMX as the output material. The present output charges are currently environmentally acceptable however current stab initiator materials contain objectionable elements such as lead, barium and antimony while the transfer charge is, without exception, lead azide which is a current target for replacement.

This effort addressed whether a new primary explosive could be developed that was made from environmentally desirable materials and that provided the functionality of a transition charge in a medium caliber detonator.

The replacement of lead azide is considered the most demanding task in the development of an environmentally benign detonator in that it is a point or instantaneous detonant in which detonation is realized in very short times (≤ 1 microsecond) and very short distances (≤ 1 mm). This type of sensitivity requires that rather simple chemical bond breaking and making reactions be occurring. Alternately, the stab primer used in the M59 detonator must react very rapidly but need not detonate, only effectively ignite the transfer charge (lead azide). Consequently, environmentally acceptable primer compositions should have more latitude in design approaches.

Current alternates to lead azide are either environmentally unacceptable in that they contain entities such as mercury, cobalt or perchlorate or are rapid deflagration-to-detonation transition (DDT) explosives. These materials require more distance and time to run-up (POP) to detonation and also require greater confinement to achieve effective DDT. Such materials are marginal to ineffective in detonator designs such as the M59. While current DDT detonants embody some of the attractive features for rapidly attaining detonation, some improvement is needed. The use of chemical sensitizers or trigger groups must be more effectively utilized within these materials to create the required lead azide replacement material. Examples of such sensitizer/trigger groups include azido, tetrazolato and diazo, which are endothermic in nature. More effective would mean using the trigger groups in a fashion to arrive at fewer (or simpler) bond breaking activities in the energetic molecule to achieve full reaction. Lead azide is an example of such a molecule.

For the present investigations into lead azide replacement candidates, the effort was concentrated on synthesis and testing of compounds containing the "trigger groups" briefly described above. The simplest and most obvious approach to replacing lead azide would be to look at the characteristics of other azide compounds. The explosive performance and thermal stability of silver azide is superior to lead azide. It was, quite naturally, considered as a lead azide replacement. The handling and discharge of silver is regulated by several states leading to concerns that this may not be a 'clean' environmental replacement material plus normally produced silver azide is much more electrostatically sensitive than lead azide, which would cause serious loading and handling problems. The only other known energetic azide compound is copper azide. It, however, is much more impact and friction sensitive than lead azide, which

again would cause handling and loading problems during production. As there are no other viable azide salts known at this time, the search for other candidates was of necessity focused on compounds other than azide salts, namely those containing the azido, triazole, and tetrazole trigger groups, as well as their salts and metallic complexes. The search was also expanded to include some of the more complex, hence larger trigger groups such as the tetrazines.

The originally proposed candidates, ENTA and DAATO 3.5 performed marginally and unsatisfactory in screening tests conducted in this effort. ENTA has performed marginally in the current screening tests, the synthesis process resulted in low yields and the quality of the synthesized material was suspect compared to previously synthesized materials by Geo-Centers/ARDEC. The other candidate, DAATO 3.5, did not indicate any tendency to behave as a detonant. This material is currently being studied as a high burn rate propellant.

As a consequence of these results it was decided to leverage the technology developed under a series of studies performed by the Naval Surface Warfare Center, Indian Head Division (NSWC-IHD) and their contractor Pacific Scientific Energetic Materials Company (PSEMC) over the past six years. These studies were conducted to establish alternates to lead azide and lead styphnate that would not contain environmentally objectionable elements. A listing of the lead azide candidates is provided in Table 1 in the text. One lead azide candidate, DFeP (Candidate 28A (FeII)) appeared to be promising based on initial evaluation in the M59 configuration as did a reduced sensitivity variant of silver azide tested at the request of the SERDP office near the end of the effort. Candidate 13A also performs well and should be included in future activities.

It is proposed that future efforts in the subject area take full advantage of the previous and current developments of the NSWC-IHD/PSEMC programs. Additionally, it is suggested that the reduced sensitivity silver azide be pursued if silver is not determined to be an environmental issue, since it is superior to lead azide as a point detonant. Also, copper(II) 5-chlorotetrazole, a Picatinny Arsenal developed material from the 1970's, should be reviewed. All promising lead azide candidates should ultimately be evaluated in M59 hardware.

This research is applicable to all chemically initiated detonators used in U.S. military munitions. Currently, there are no producers of lead azide in the United States. All detonator production is being accomplished by utilizing an existing stockpile of material produced in excess of ten years ago. It has recently been determined that half of this stockpile is no longer useable for detonator loading due to aging issues with the material. At current consumption rates (not accounting for any ramp up due to munitions consumption in the Middle East), the stockpile will last for approximately 5 years. At that time, materials will have to be procured from a foreign source or a U.S. company enticed to initiate production. As a result of this situation, there will be an excellent opportunity to introduce a non-lead based solution into the production base for detonator materials.

Objective:

Overall Objectives - This effort was conducted in response to SERDP PPSON-03-07, Environmentally Acceptable Stab Detonators for Medium Caliber Munitions. The objective of PPSON-03-07 is “to develop new, small, impact initiated devices (IID’s) that are environmentally benign compared to the current designs. The new IID’s will be designed such that the output from the device will cause a lead or main explosive charge to detonate. The small IID’s are to be sized such that they will be compatible with the current fuzes being produced for medium caliber (20-60mm) ammunition and have sufficient output energy to initiate lead and main charges containing the current explosives and may be required to initiate explosives that are militarily classified as 'insensitive’’. The objective of this effort was restricted to evaluating and testing environmentally benign compounds that can potentially be used as replacement materials for the current lead azide transfer charge in small stab detonator devices for medium caliber ammunition thereby eliminating a large source of lead from these rounds. As a result of this restriction, all M59 detonator testing was conducted with the existing NOL 130 lead based initiating compound. This effort was to culminate in a feasibility demonstration of these new explosives in the M59 detonator, a representative medium caliber stab detonator used in the M430 40mm high velocity grenade.

Specific Project Objectives –

The following are the specific objectives for the project:

1. Award a contract modification to PSEMC (contractor to NSWC-IHD) to synthesize and evaluate the polyazidocyclophosphazene compound ENTA.
2. Synthesize and evaluate the high nitrogen compound DAATO 3.5, which was first synthesized at the Los Alamos National Lab (LANL).
3. Monitor other compounds being evaluated at PSEMC/NSWC-IHD.
4. Conduct basic safety and handling tests on the replacement compounds.
5. Conduct witness plate tests on the selected compound.
6. Down select to the most promising compound based upon environmental and performance considerations
7. Conduct M59 detonator feasibility demonstration firings

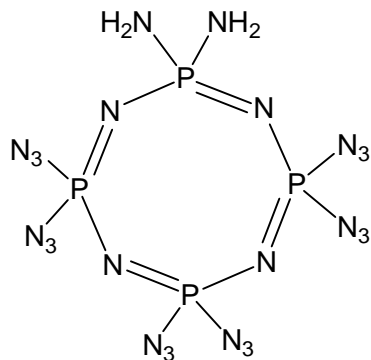
Background:

The Department of Defense initiated a program for the replacement of toxic material in response to executive order # 12856 of 1993, and subsequent executive orders and directives which ordered federal agencies to eliminate or reduce procurement of extremely hazardous substances and chemicals. One of the environmental areas that DoD has targeted for elimination is heavy metal contamination, which is a critical environmental problem. The DoD has accepted the responsibility for reducing the use of heavy metals, including lead (Pb), in the design, manufacture and operational use of its munitions. Lead compounds are environmentally hazardous materials and replacement compounds need to be sought. Lead compounds are listed on the EPA Toxic Chemical List (EPA List of 17 Toxic Chemicals). Further lead compounds are regulated under the Clean Air Act as Title III Hazardous Air Pollutants, included on the superfund list of hazardous substances, and are toxic pollutants under the Clean Water Act. The need for alternative primary explosives that are free from lead and other environmentally hazardous materials has been expressed for some time.

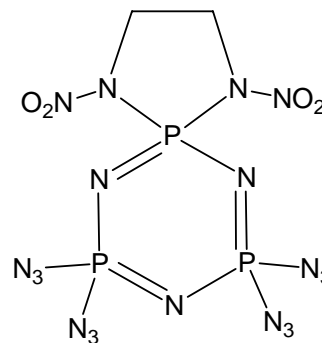
The Strategic Environmental Research and Development Program (SERDP) was established to identify, develop, and transition environmental technologies that relate directly to defense mission accomplishment. An umbrella program was initiated by SERDP in 2000 to investigate the medium caliber ammunition commodities for specific environmental issues and fund research to eliminate contributing components. One area of research identified as an environmental issue was the detonators used in all high explosive cartridges, since they all contain lead azide based initiating and transfer compounds. A proposal to specifically research the replacement of the lead azide transfer compound was funded under project SERDP PPSON-03-07, Environmentally Acceptable Stab Detonators for Medium Caliber Munitions. This effort combined previous work done by the U.S. Army ARDEC and the NWSC-IHD in this area.

ARDEC had previously investigated a family of compounds known as polyazidocyclophosphazenes. The most promising of these compounds are 1,1-diamino-3,3,5,5,7,7-hexaazidocyclotetraphosphazene (DAHA) and 1,1-(N,N'-ethylenedinitramino)-3,3,5,5-tetraazidocyclotriphosphazene (ENTA), whose molecular structure is shown in Figure 1. DAHA, however, has some issues related to its melting point and availability of the precursor compound and was thus not considered as part of the SERDP effort.

Figure 1 - Molecular Structure of DAHA and ENTA



DAHA
(Candidate 31A)



ENTA
(Candidate 30A)

The NSWC-IHD initiated a program in 1998 targeting the replacement of lead based primary explosive initiating compounds (lead styphnate and lead azide), which are used in a number of military systems as well as commercial items. Under the Indian Head program, a contract was awarded to PSEMC to conduct a market survey to determine the availability of a replacement compound. The data gathered during the survey suggested that an off the shelf replacement compound did not exist. Three follow-on contracts were awarded to PSEMC to develop, synthesize and evaluate possible lead azide replacement compounds as well as lead styphnate alternates. A study of the lead azide candidates studied under these programs is provided below in Table 1.

Table 1. Lead Azide Candidates Investigated

Code	Material	DSC (deg C)		Status
		Onset	Peak	
1A	Cis-tetraamminediazidocobalt(III) perchlorate			Eliminated, identical to 2A
2A	Trans-tetraamminediazidocobalt(III) perchlorate	188	194	Eliminated on 200 C criterion, evaluated
3A	3-amino-6-nitramino-1,2,4,5-tetrazine	180	183	Eliminated on 200 C criterion probably an LS candidate
4A	3,6-dihydrazino-1,2,4,5-tetrazine dperchlorate			Eliminated, highly soluble, acidic - should investigate dinitramide salt
5A	3,6-bis(5-aminotetrazol-1-yl)1,2,4,5-tetrazine			Eliminated
6A	2-picryl-5-nitrotetrazole	163	170	Eliminated on 200 C criterion, borderline LA candidate, may be hydrolytically unstable
7A	Potassium 6-azido-2,4-dinitrophenate	139	153	Eliminated on 200 C criterion, borderline LA candidate, may be hydrolytically unstable
8A	1,2-diazidoglyoxime			Borderline on 200 C criterion, may be hazardous
9A	4-nitro-2-(5-nitro-1,2,4-triazol-3-yl)-1,2,3-triazole			Low yields, difficulty with synthesis, eliminated
10A	Potassium 1,3-bis-nitroimido-1,2,3-triazole			Precursors very expensive, however should revisit
11A	5-nitrotetrazoyl-1,3,5-triazines			May not be chemically possible, may hydrolyze as product is formed
12A	Bis(5-nitrotetrazoyl)picric acid			Probably borderline as LA candidate, molecule too large, benzene ring not favorable
13A ₁	Copper(II) 5-nitrotetrazolate	270	283	Active LA candidate, requires crystal modification
13A ₂	Copper(II) 5-nitrotetrazolate	206	215, 301	Eliminated, hydrated version of 13A
14A	1,1'-azobis-3-nitro-1,2,4-triazole	244	335	Eliminated, SRI candidate (J. Bottaro), crystal habit change may aid performance
15A	Bis-furoxano-nitrophenol	203	209	Appears to be a LS candidate
16A	5-Azidotetrazole, Cu(II) complex	185	187	Eliminated, too sensitive to be practical
17A	3-Azido-5-nitro-1,2,4-triazole, Cu	185	190	Appears to be a dihydrate, work proceeding on anhydrous derivative
17A	3-Azido-5-nitro-1,2,4-triazole, Cu (dry)	183	189	
18A	3,5-Diazido-1,2,4-triazole	157	186	Eliminated, too sensitive to be practical
19A	2-Nitramino-4,6-diazido-1,3,5-triazine, Rb	200	227	Appears to be an LS candidate, using less electropositive metals may produce an LA candidate
19A	2-Nitramino-4,6-diazido-1,3,5-triazine, Cs	182	223	
20A	2-Azido-4,6-bisnitramino-1,3,5-triazine			Pending successful outcome with 19A
21A	6-Amino-tetrazolo[1,5-b]tetrazine	194	208	To be used as a precursor
22A	Triazolo[4,3-b]tetrazine-3,6-diamine	306	353	To be used as a precursor
23A	Tetraazido-hydrazo-triazine			In progress, molecule may be too large, even with four azide groups
24A	5-Azido-3-amino-1,2,4-triazole			Has been synthesized by M. Sitzmann (NSWC), will be a precursor to 25A
25A	5-Azido-3-nitramino-1,2,4-triazole			Synthesis in progress
26A	4-Azido-5-nitro-1,2,3-triazole	162	176	Good candidate, but complex synthesis (LLNL, P. Pagoria), more effective prep sought
27A	3-Azido-6-guanidiny-1,2,4,5-tetrazine	216	279	In progress
28A	1,5 Diaminotetrazole, Fe(II) complex	216	233	Both complexes show promise, alternative anions to perchlorate being investigated
28A	1,5 Diaminotetrazole, Cu(II) complex	235	240	
29A	DAATO 3.5	218	242	Eliminated, more propellant than explosive in nature
30A	ENTA	mp 143	266	Initial results not promising, higher purity and improved particle habit sought

Materials and Methods:

In the NSWC-IHD program, after a potential compound was theorized as either a lead azide or lead styphnate replacement primary explosive, plausible synthetic techniques were postulated and ranked in order of their likelihood of success and anticipated yield. Attempts were then made to synthesize a small quantity of each of the candidate compounds starting with the highest ranked process and preceding down the list until either an adequate process was developed or the list of processes exhausted. After the small quantity of each candidate material had been created, it was subjected to testing to determine safety characteristics and basic properties. Practical handling criteria of the following were adopted:

- 1) thermal stability (decomposition temperature $\geq 200^{\circ}$ C as indicated by DSC thermal analysis), and
- 2) sensitivity (impact, friction, and electrostatic discharge) of lead azide or better

The technique employed for impact sensitivity utilized a ball drop instrument fabricated at PSEMC and was designed to meet specifications per NATO AOP-7 registry number US/High Explosives/201.01.001. This apparatus was designed to release a 1/2 inch diameter chrome alloy steel ball bearing, weighing 8.35g, with a Rockwell C hardness of 64-66. The powder to be tested was spread in a 0.330mm (0.013") thick layer onto a polished steel block of Rockwell C hardness 60-62. The ball bearing was dropped from heights varying by 1" to be analyzed by the Bruceton technique. A new area on the steel block was used for each test and the ball bearings were either thoroughly cleaned or new for each run.

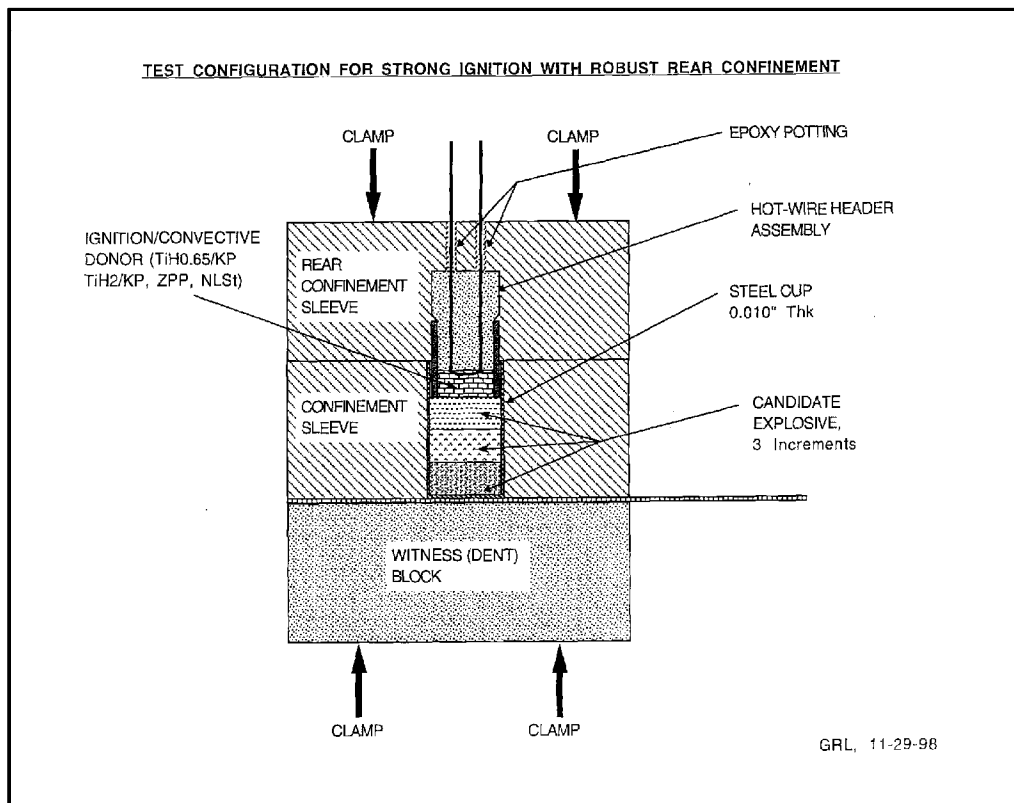
The apparatus was capable of delivering a drop no greater than 34"; for heights in excess of this, a 3/8 inch diameter bearing (16.80g) was substituted for the 1/2 inch bearing. Bearings of 23/32 inches (24.80g) and 25/32 inches (31.84g) were used when increased weights were required.

Friction sensitivity testing was conducted using a small BAM friction apparatus and test procedures as specified in MIL-STD-1751A.

The handling criteria indicated above were used to determine viable candidates for the next step of the evaluation process, the strong confinement test. Candidate materials to be included in the SERDP effort were screened with the additional criteria that the compounds contained no undesirable heavy metals and the synthesis process contained no environmentally objectionable materials.

The strong confinement screening test was used to determine if the material created would detonate. In the strong confinement screening test, a quantity of the material is loaded into a cavity at 10 kpsi loading pressure. An aluminum witness block is placed at the one end of the fixture while an initiating charge is placed at the other end. The material is initiated and consumed within the fixture. If a detonation wave is created by the reaction, its interface with the witness block will result in a dent. The dent in the witness is measured and recorded for comparison with other candidates and to a lead azide control sample. The depth of the dent in the witness block is directly related to the strength of the detonation reaction. If the material does not detonate no dent will be found in the witness plate. The apparatus used by PSEMC was a variant of that designed by G. Laib of NSWC-IHD, which is shown in Figure 2.

Figure 2- Strong Confinement Screening Test Apparatus



The final test in the selection of candidate materials for the actual detonator feasibility demonstration firing was the strong confinement test done at various loading pressures. Candidate materials whose results from the strong confinement screening test were comparable to lead azide were pressed at four different pressures into the strong confinement fixture. The samples were then initiated in the same manner as in the strong confinement screening tests and the dent in the witness plate measured, recorded and averaged for each charging pressure.

Candidate materials showing comparable performance to lead azide in the strong confinement test were then selected for feasibility demonstration firing in the M59 detonator. The demonstration material was loaded into the detonator at differing loading pressures and column lengths. All of the demonstration detonators utilized the standard NOL-130 initiation charge. The internal configuration (amount and/or presence of an output charge) of the detonators was varied based upon the column length of the transfer charge within the detonator.

Results and Accomplishments:

Under the combined NSWSC-IHD effort and SERDP SEED program, the following was accomplished:

Synthesis Efforts:

Under the NSWSC-IHD contracts and SERDP modification awarded to PSEMC to synthesize new compounds and conduct preliminary detonation tests, the compounds listed in Table 1 were synthesized.

Candidate 13A [copper(II)] was studied during the first NSWSC-IHD/PSEMC program. The base explosive is the readily available 5-nitrotetrazole (as the sodium salt, NaNT) used in the production of the DDT explosive BNCP.

A previously reported but relatively unknown compound, 3-azido-5-nitro-1,2,4-tetrazole (17A) was evaluated as the copper(II) complex. This was prepared in a three step process starting with the synthesis of 3,4,5-triamino-1,2,4-triazole (guanazine) from dimethylcyanamide and hydrazine followed by reaction of guanazine with two equivalents of nitrous acid and excess nitrite ion to produce the base 17A explosive.

Candidate 19A, 4,6-diazido-2-nitramino-1,3,5-triazine, is a previously unknown compound and was prepared in a three step synthesis. The readily available cyanuric chloride is aminated at low temperature to produce 2-amino-4,6-dichloro-1,3,5-triazine which in turn is reacted with sodium azide to give 2-amino-4,6-diazido-1,3,5-triazine. Finally, the last product is nitrated at low temperature with 100% nitric acid to produce 19A. The alkali metal candidates, Rb and Cs, are readily formed by reaction with the appropriate hydroxides.

The preparation of the most promising candidate, 28A (Fe(II) and Cu(II) 1,5-diaminotetrazole complexes as the perchlorate salts) were conducted in two steps. The heterocyclic ligand was prepared by the reaction of thiosemicarbazide, sodium azide and lead monoxide in dimethylformamide solvent. This product is then reacted with the appropriate iron(II) or copper(II) perchlorate to result in the final candidate. It is certainly obvious some modification is required in the preparation of the diaminotetrazole to eliminate the use of lead monoxide.

It was not necessary to synthesize DAATO 3.5 (Compound 29A) as it was supplied by Los Alamos National Laboratory.

A significant effort was expended in the synthesis of ENTA (Compound 30A). The synthesis is as follows. 1,1-(N,N-ethylenedinitramino)-3,3,5,5-tetraazidocyclotriphosphazene (ENTA) is a yellow/white crystalline solid which melts at 144-145°C. Preparation of ENTA proceeds from the commercially available hexachlorocyclotriphosphazene via reaction with 2.0 equivalents of ethylenediamine in diethyl ether to give 1,1-spiro(ethylenediamino)-3,3,5,5-tetrachlorocyclotriphosphazene. This material may be recrystallized from methylene chloride and hexane to give a white powder which is very susceptible to hydrolysis. Direct formation of the spiro(ethylenedinitramino) compound with N,N-dinitroethylenediamine (Haleite) failed to give any addition products, presumably due to the reduced nucleophilicity of the nitramines. Conversion to 1,1-spiro(ethylenediamino)-3,3,5,5-tetraazidocyclo-triphosphazene (ETCP) was, however, accomplished utilizing either lithium azide or sodium azide in dry acetone and afforded a clear gum which slowly crystallized under high vacuum. Nitration of ETCP with acetic anhydride/90% nitric acid failed to furnish ENTA in any appreciable amount. However, reaction

with nitronium tetrafluoroborate (NO₂BF₄) in dry acetonitrile produced the desired material (recrystallization from benzene/hexane). The nitration reaction was found to be very sensitive to the character of the NO₂BF₄, and since the commercially available material is of unpredictable quality, yields were also found to vary substantially.

It has been determined that candidate 15A is not a lead azide candidate but rather a possible alternate to lead styphnate and will not be discussed further.

Test Data/Results:

DSC analysis was performed on all lead-free compounds synthesized at PSEMC to obtain the thermal decomposition temperature for each. Additional safety testing (friction and impact sensitivity) has been completed on most. Compound 16A was found to be too sensitive to evaluate, and compound 26A is still undergoing evaluation. The safety test results are compared with normal lead styphnate in Table 2.

Table 2. Safety Test Results For Compounds Synthesized at PSEMC

Compound	DSC 20°C/minute		Impact (J)	Friction (grams)		Density (g/cc)
	Onset °C	Peak °C		No Fire	Low Fire	
13A	270	283	0.057±0.006	55	65	2.11
15A	203	209	0.009±0.002	20	30	2.07
16A	185	187	NA*	NA*	NA*	NA*
17A	185	190	-	2075	>2075	-
17A(dry)	183	189	0.015±0.002	975	1000	1.91
19A(Rb)	200	227	0.012±0.003	850	900	2.10
19A(Cs)	182	223	0.013±0.003	175	200	2.34
26A	162	176	TBD	TBD	TBD	TBD
28A(Fe)**	216	223	0.013±0.002	40	50	1.76
28A(Cu)**	235	240	0.011±0.003	100	110	1.86
29A	218	242	0.085±0.025	2075	>2075	1.85
30A	235	266	TBD	300	400	1.83
NLS	290	305	0.025±0.001	40	50	3.20

* - too sensitive to evaluate

** - perchlorate salt of the complex

Those compounds which had successfully completed safety testing were then subjected to a strong confinement screening test at 10 kpsi loading pressure. This test, which is conducted with a nominal 200 mg charge under strong confinement, is designed to determine whether any of the candidate compounds is capable of detonation, evidence of which is indicated by a significant dent in an aluminum witness block. Table 3 lists the results that were obtained, which are an average of three consecutive tests.

Table 3. Strong Confinement Test Results at 10.0 Kpsi Loading Pressure

Candidate	Description	Average Charge Density (g/cm ³)	Average Dent (mils)
13A	Copper(II) 5-nitrotetrazole	1.440	13.2
15A	Bis-furoxano-nitrophenol (KBFNP)	1.626	0.8
17A	3-Azido-5-nitro-[1,2,4]triazole, copper complex (dry)	1.421	2.3
19A	Diazido-nitramino-s-triazine, Rb	1.810	0.8
19A	Diazido-nitramino-s-triazine, Cs	2.026	0.5
28A	1,5 Diaminotetrazole, Fe(II) perchlorate complex	1.465	27.0
28A	1,5 Diaminotetrazole, Cu(II) perchlorate comp	1.412	16.8
29A	DAATO 3.5	1.203	0.0
30A	ENTA	1.756	1.3
LA	Lead Azide, RD1333, LN 40148	3.119	37.3

Of the compounds prepared and tested under the PSEMC or SERDP programs, both 13A and 28A were capable of relatively powerful detonation under the conditions of the 10 kpsi strong confinement test. While the present synthesis of compound 30A failed to detonate in the strong confinement test, previous testing of this compound at ARDEC has, in fact, produced detonations. Thus, it is expected that additional synthesis work on compound 30A would yield a detonable material. The most recent synthesis work produced new renderings of compound 30A which were of higher purity and larger crystal structure than the material tested above. It is expected that the newer material will have improved detonation characteristics, and present efforts are being focused on producing yields of sufficient quantity for testing under a NWSC-IHD continuation effort.

With reference to compound 17A, this complex was more sensitive to impact but considerably less friction sensitive as compared to normal lead styphnate. However, the strong confinement witness plate testing was disappointing, 2.3 mils versus 37.3 mils for lead azide at 10 kpsi loading pressure. This result may be due to the presence of water. Heating at 85°C resulted in a weight loss of 4.2%, or very close to a dihydrate (1.84 H₂O) which may have inhibited the DDT. This candidate should result in high performance detonants and it is believed anhydrous metal salts or complexes would result in such materials. It is suggested this candidate be pursued regarding this end. It is to be noted that 17A forms a silver salt having attractive particle characteristics using the Costain method of preparation.

Candidate 19A (Rb and Cs) failed to perform as a detonant. However, if less electropositive counter cations are employed, more promising results may be realized.

DAATO 3.5 (29A) does not appear to be a detonant and is probably better placed as its original intent, a high burn rate propellant.

Candidate 30A, ENTA, indicated a very marginal tendency to perform as a detonant as indicated above.

Additional strong confinement testing conducted on compound 13A in the earlier program revealed that optimum output (maximum dent) occurred at a loading pressure of 20 kpsi (1.53 g/cc density) and decreased slowly at higher densities. While these very encouraging test

results are indicative of fast deflagration-to-detonation (DDT) behavior, the extremely fine particle size of the material presents some serious handling and loading problems. As a result, some effort has been expended during the present program on recrystallizing compound 13A. So far, the results have failed to produce a suitable particle habitat, but the effort will be continued under the NSWC follow-on effort.

Based on the favorable results obtained with both Fe(II) and Cu(II) complexes of compound 28A, the full (Phase II) strong confinement test series was performed with each. The results are compared in Table 4 with those obtained earlier with Compound 13A and RD1333 lead azide.

Table 4. Phase II Strong Confinement Test Results

CODE	CANDIDATE	LOADING PRESSURE (kpsi)	AVERAGE CHARGE DENSITY (g/cm ³)	AVERAGE DENT (mils)
13A	Copper(II) Nitrotetrazole ¹	5	1.26	9.0
		10	1.38	22.6
		20	1.53	31.7
		40	1.77	29.0
28A	1,5 Diaminotetrazole, Cu(II) perchlorate complex	5	1.18	25.0
		10	1.33	23.7
		20	1.52	14.7
		40	1.62	7.7
28A	1,5 Diaminotetrazole, Fe(II) perchlorate complex	5	1.28	35.3
		10	1.40	40.3
		20	1.52	37.7
		40	1.63	23.3
LA	Lead Azide, RD1333, LN 40148	5	2.62	27.7
		10	2.99	33.7
		20	3.18	39.0
		40	3.55	46.3
Samples were dried at 65°C for >2 hours and stored in a dry box until tested 1 – Results from 1 st program, provided for comparison				

M59 Detonator Tests:

While both complexes of compound 28A showed good evidence of detonation at all loading pressures, the iron complex (DFeP) gave superior performance (deeper dent) and was selected for testing as a transition charge in the M59 detonator. The tests were conducted in Code 2210 test facilities at NSWC-IHD. Tests were also performed with a reduced sensitivity silver azide to evaluate its performance as a transition charge, and also with RD1333 lead azide to provide direct comparison with the DFeP and silver azide results. Late in the effort, SERDP requested that a reduced sensitivity silver azide be tested in the M59 to determine if a synthesis process existed to create this product and how the product compared to lead azide. The reduced sensitivity silver azide was synthesized using the “Costain” process, named for the Picatinny chemist that created the synthesis technique. The reduced sensitivity of the material was accomplished by creating larger crystal size using this specific synthesis technique. Because the chemical and physical characteristics of the DFeP have not been optimized, several different

transition/output charge configurations were tested. This approach allowed the full potential of the compound to be explored.

Table 5. Tabulated Properties of Costain Process Silver Azide

	Costain Process	Costain Process	RD1333 Lead Azide a
Property	<u>Lot 8702</u>	<u>Lot 8703</u>	
Bulk Density			
g/cc:	1.6	1.6	1.3
Granulation:			
%On 100	18	17	1
On 140	27	32	5
On 200	33	24	14
On 325	18	22	42
Thru 325	4	5	38
Assay:	99+%	99+%	97-98%
Hygroscopicity:	Nil	Nil	Very Slight
Vacuum Stability:			
1g/40 hrs/150°C	0.49	0.34	0.40
Impact Sensitivity			
P.A. 10% Point:	11 in	7 in	7 in
50% Point	17 in	10 in	8 in
Ball Drop 10%:	11 in	10 in.	10 in.
Electrostatic Sensitivity:	.0094 Joules	.018 Joules	.0005 Joules

a Data listed for comparison.

The M59 test results are summarized in Table 6, while the dent data is plotted against transition charge weight in Figure 3, and against output charge (RDX) weight in Figure 4. The DFeP results are plotted as three distinct tests.

Figure 3 – Aluminum Witness Block Indent Versus M59 Charge Weight For Various Transition Charges

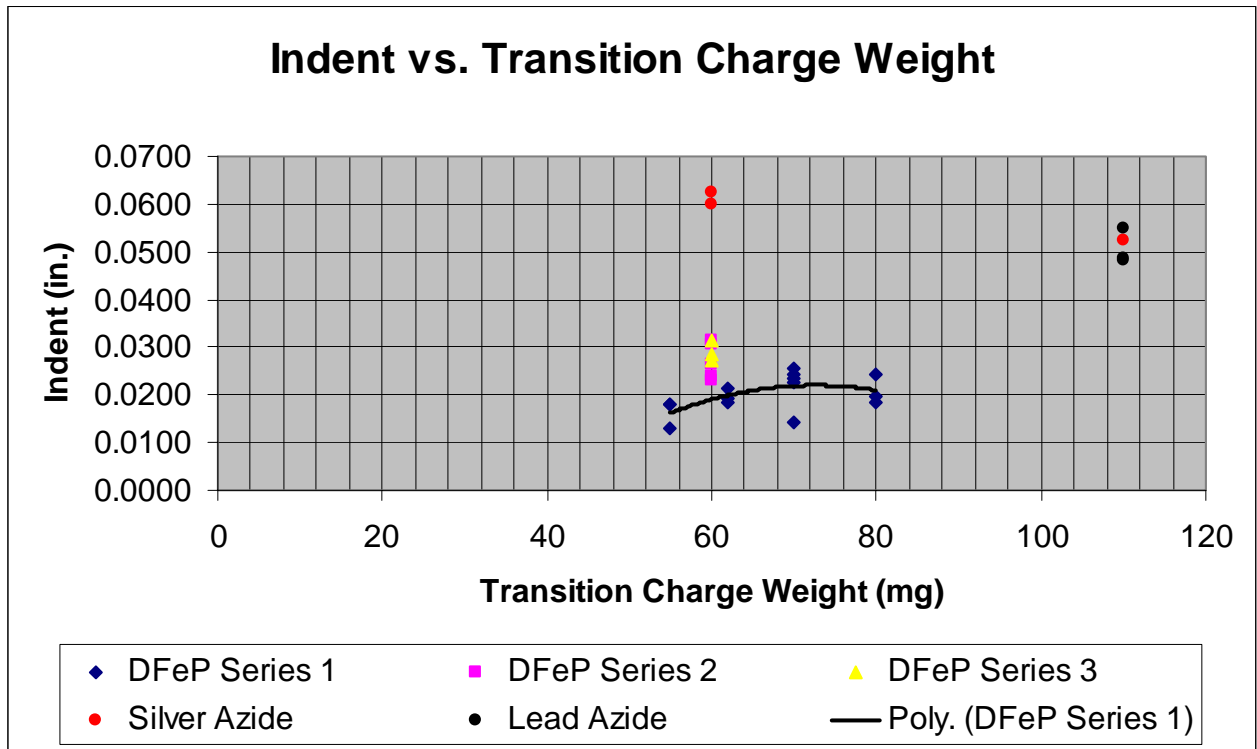


Figure 4 – Aluminum Witness Block Indent Versus M59 Output Charge Weight For Various Transition Charges

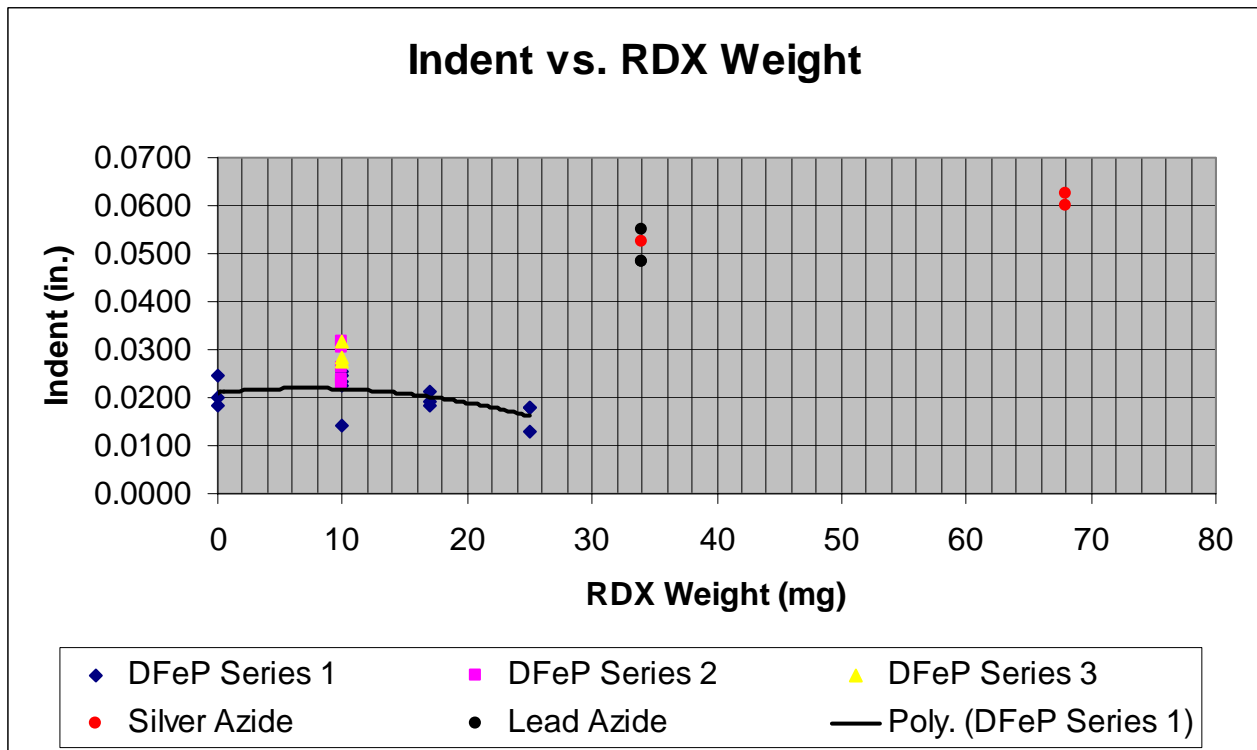


Table 6. M59 Detonator Transition Charge Test Results

Transition Charge Material	Weight (mg)	RDX Weight (mg)	Test Holder	Witness Material	Indent Depth (inches)
DFeP	55	34	Plastic	Lead	0.0643
DFeP	55	34	Plastic	Lead	0.0590
DFeP	55	34	Plastic	Lead	0.0538
DFeP	80	0	Brass	Lead	0.0278
DFeP	80	0	Plastic	Lead	0.0240
DFeP	80	0	Plastic	Lead	0.1033
DFeP	62	17	Plastic	Lead	0.0753
DFeP	62	17	Brass	Lead	0.3310
DFeP	80	0	Brass	Aluminum	0.0199
DFeP	80	0	Brass	Aluminum	0.0185
DFeP	80	0	Brass	Aluminum	0.0244
DFeP	62	17	Brass	Aluminum	0.0193
DFeP	62	17	Brass	Aluminum	0.0213
DFeP	62	17	Brass	Aluminum	0.0185
DFeP	55	25	Brass	Aluminum	0.0180
DFeP	55	25	Brass	Aluminum	0.0181
DFeP	55	25	Brass	Aluminum	0.0128
DFeP	60	10	Brass	Aluminum	0.0306
DFeP	60	10	Brass	Aluminum	0.0264
DFeP	60	10	Brass	Aluminum	0.0229
DFeP	70	10	Brass	Aluminum	0.0143
DFeP	70	10	Brass	Aluminum	0.0254
DFeP	70	10	Brass	Aluminum	0.0235
DFeP	60	10	Brass	Aluminum	0.0239
DFeP	60	10	Brass	Aluminum	0.0315
DFeP	70	10	Brass	Aluminum	0.0245
DFeP	70	10	Brass	Aluminum	0.0225
DFeP	60*	10	Brass	Aluminum	0.0316
DFeP	60*	10	Brass	Aluminum	0.0284
DFeP	60*	10	Brass	Aluminum	0.0273
AgN ₃	60	68	Brass	Aluminum	0.0599
AgN ₃	110	34	Brass	Aluminum	0.0520
AgN ₃	60	68	Brass	Aluminum	0.0630
Pb(N ₃) ₂	110	34	Brass	Aluminum	0.0548
Pb(N ₃) ₂	110	34	Brass	Aluminum	0.0483
Pb(N ₃) ₂	110	34	Brass	Aluminum	0.0485
Pb(N ₃) ₂	110	34	Brass	Lead	0.1975
Pb(N ₃) ₂	110	34	Brass	Lead	0.2144
Pb(N ₃) ₂	110	34	Plastic	Lead	0.1362
Pb(N ₃) ₂	110	34	Plastic	Lead	0.1429

* - 10 kpsi loading pressure

30 mg NOL 130 initiating charge loaded at 70 kpsi, transition and output charges loaded at 15 kpsi except where noted:

Series (1) 80 – 85 mg combined transition and output charge weight 15 kpsi loading pressure

Series (2) 70 mg combined transition and output charge weight 15 kpsi loading pressure

Series (3) 70 mg combined transition and output charge weight 10 kpsi loading pressure

The results of the M59 detonator tests showed definitively that the DFeP compound, when employed as a transition charge, was capable of strong detonation, although it requires more confinement (brass) than the usual lead azide transition charge. With brass confinement, the output was in general less than that of either lead azide or silver azide. Because of the charge weights investigated, a direct comparison of DFeP with the other two materials cannot be made, but the range of output dents with the DFeP was about half that of both lead azide and silver azide under the same confinement. The deeper dents produced by DFeP in the strong confinement test indicates that steel confinement will further increase DFeP performance.

It must be emphasized that the DFeP used in the present tests has not been optimized, and that under additional refinement of the crystal structure, significant improvement can be expected. Viewed in this respect, the present results are considered to be very encouraging.

While the use of perchlorate compounds may be objectionable for some explosive applications, the relative strength of the output from DFeP suggests that this compound contains sufficient chemical energy to warrant investigation into other, more acceptable, counter anions.

The present tests have also demonstrated that the reduced sensitivity silver azide is a viable transition charge in the M59 detonator, as at the same charge weights (110/34), the reduced sensitivity silver azide slightly outperformed lead azide.

These results provide several options for replacing the lead azide charge in the M59 detonator with a more environmentally acceptable explosive. In its present state of development, silver azide is essentially a drop-in replacement for lead azide, although compatibility testing with NOL-130 and other materials of interest must be completed to ensure that there are no compatibility problems with this material. The reduced sensitivity silver azide has been commercially manufactured by at least one U.S. manufacturer (Cartridge Actuated Devices) for a small detonator production contract. Since basic silver azide is already in commercial use, especially in Europe, such problems are not anticipated. Compounds 13A and 28A afford the opportunity of utilizing metals other than silver (copper and iron) that may be more environmentally and economically acceptable. Additional development work is required, however.

Conclusions / Recommendations:

A brief summary of the conclusions reached from the test results and recommendations for future development work of lead azide replacements is given below. In addition to follow-up work on the compounds that have been investigated to date, suggestions are also made for evaluation of some new compounds, and one (Copper(II) 5-chlorotetrazole) that has already been synthesized at ARDEC, but has not yet received sufficient attention.

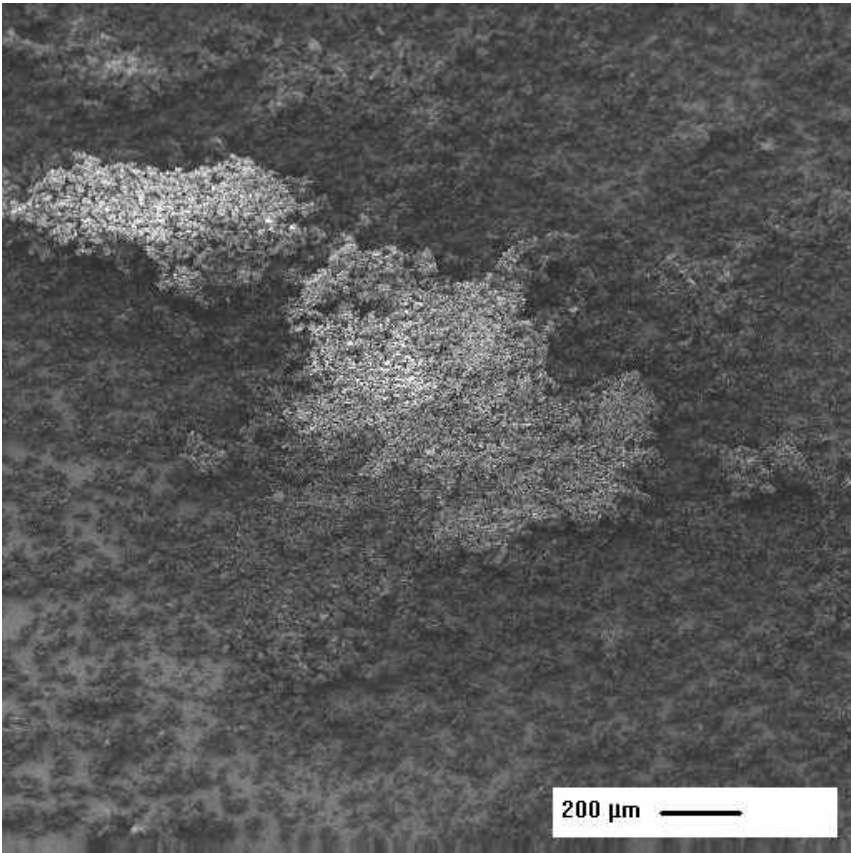
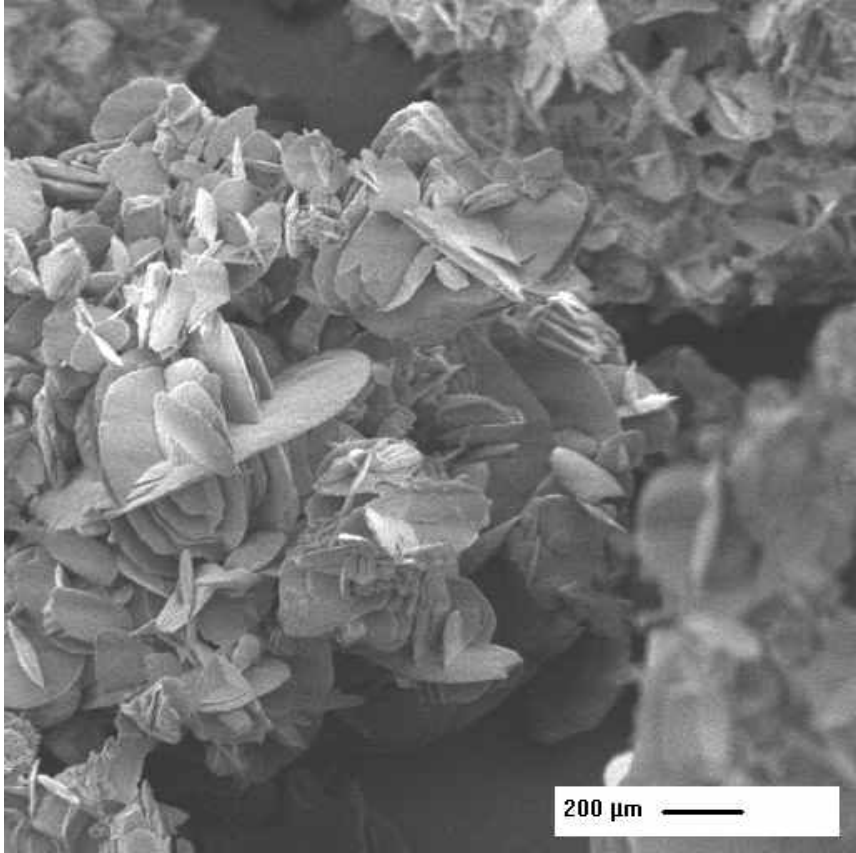
- DAATO 3.5 does not appear to warrant further consideration as a lead azide replacement.
- DFeP shows some promise based on M59 configuration testing. Further work is required in optimizing the detonator configuration, however. Also, if it is found suitable, sensitivity, stability and compatibility issues have to be addressed. Alternate oxidizing counter anions should be investigated.
- Reduced sensitivity silver azide is a viable, even superior, alternative to lead azide as it exhibits greater thermal stability and output. Further work is required regarding the method of preparation (e.g. Costain process) and subsequent effects on performance and

sensitivity. Also, compatibility issues with initiator materials may require additional attention.

- Additional effort should be devoted to several of the NSW-C-IHD/PSEMC candidates which show promise, such as Compounds 13A, 17A and 19A.
- Reconsideration should be given to a previously developed Picatinny Arsenal primary explosive, Copper(II) 5-chlorotetrazole
- Some consideration should be given to investigate the use of the highly sensitive azido azoles (Compounds 16A and 18A) in combination with less sensitive energetic ligands, e.g. ethylenedinitramine or dinitrobitriazole, in complexes with metals such as Cu(II) and Fe(II). These “mixed complexes” could possibly moderate the extreme sensitivity of these “trigger” compounds to result in useful detonants.
- Computational studies should be undertaken to evaluate structure-sensitivity relationships, reaction energetics, and molecular properties of these materials.
- All promising candidates would be evaluated in the M59 configuration.

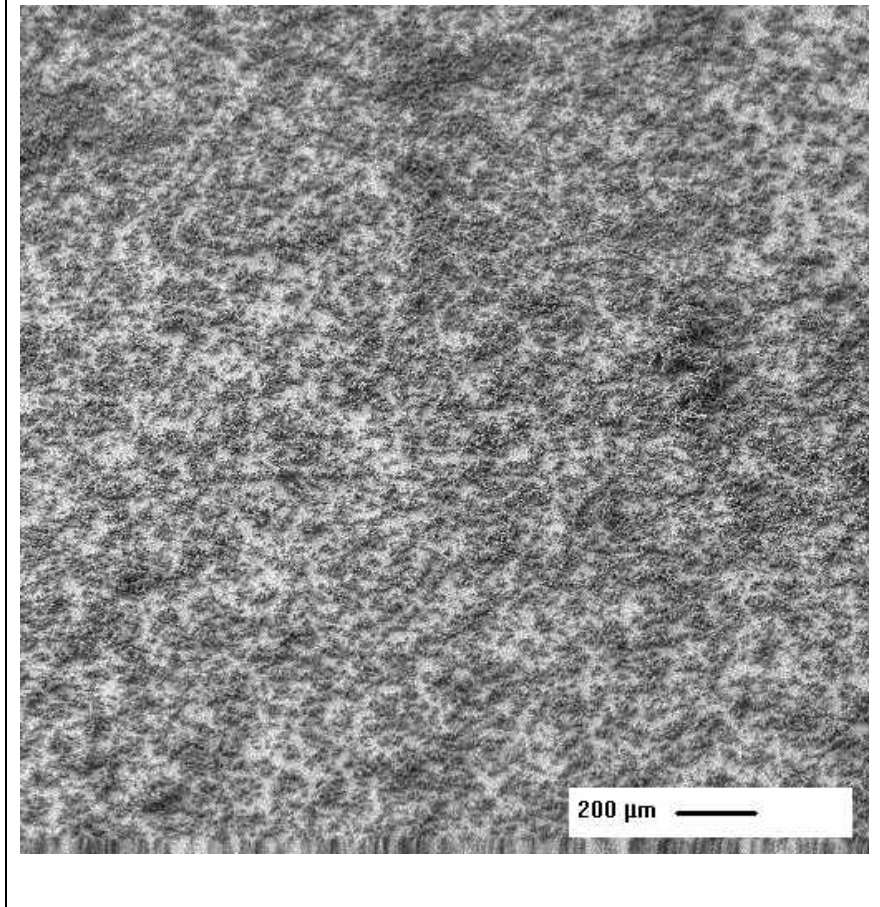
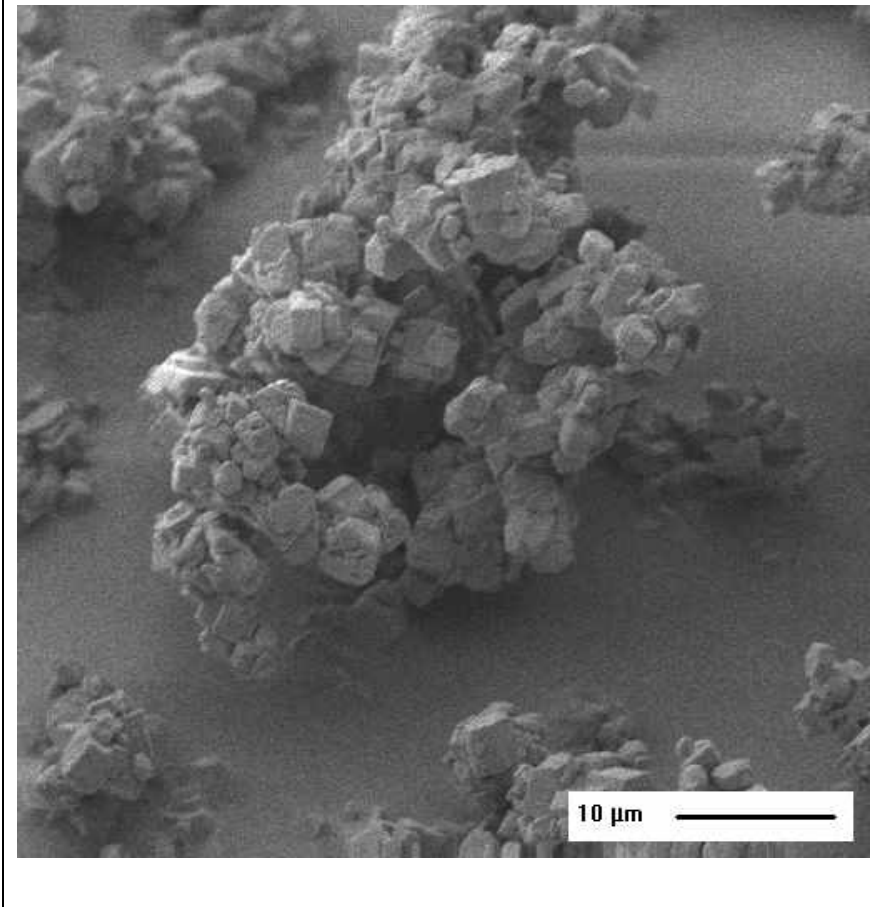
It has been a major effort throughout this program to consider candidate compounds that are both technically and economically producible. That is, all candidates that required synthesis that was either expensive, unduly time consuming, used arcane starting materials or those that were difficult to obtain, or entailed dangerous procedures were either directly omitted from consideration, or were dropped when such objections became evident. In this way, compounds with promising performance are envisioned to be viable replacements for lead azide. Scale-up of synthesis procedures to large production lots remains to be investigated, however.

APPENDIX A. SEM, DSC, TGA, IR AND NMR DATA

 <p data-bbox="743 1127 1022 1175">200 μm</p>	 <p data-bbox="1614 1127 1894 1175">200 μm</p>
<p data-bbox="359 1263 865 1295">EL20044A, 15A Candidate, K salt 50X</p>	<p data-bbox="1220 1263 1755 1295">EL20044A, 15A Candidate, K salt 2000X</p>

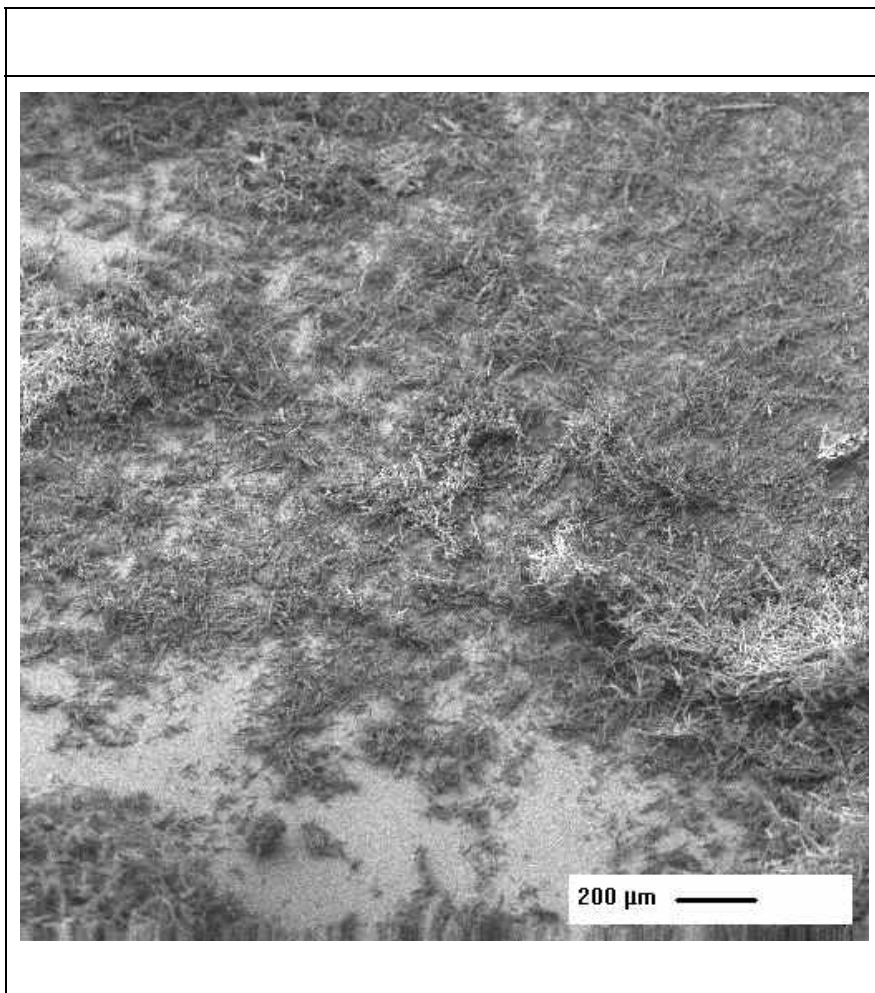
EL20044A, 15A Candidate, K salt 50X

EL20044A, 15A Candidate, K salt 2000X

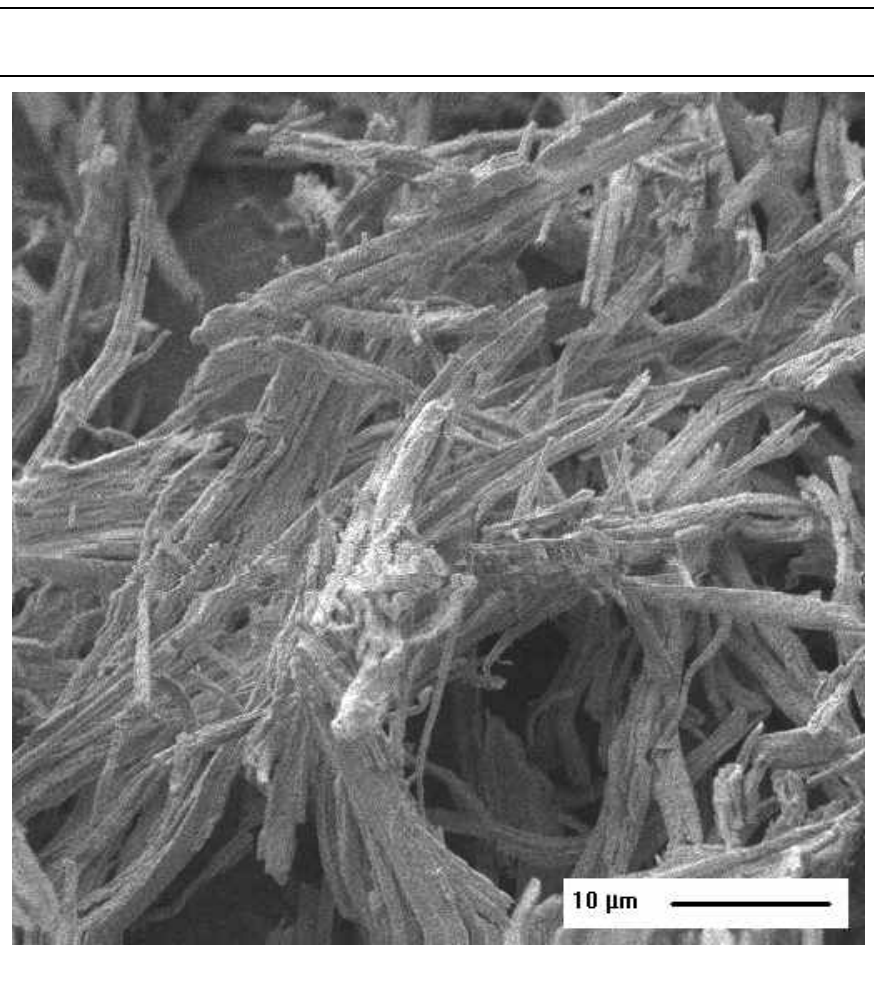
 <p data-bbox="737 1125 1016 1170">200 μm</p>	 <p data-bbox="1612 1125 1892 1170">10 μm</p>
<p data-bbox="352 1260 869 1287">EL2O056A, 17A Candidate, Cu salt 50X</p>	<p data-bbox="1213 1260 1751 1287">EL2O056A, 17A Candidate, Cu salt 2000X</p>

EL2O056A, 17A Candidate, Cu salt 50X

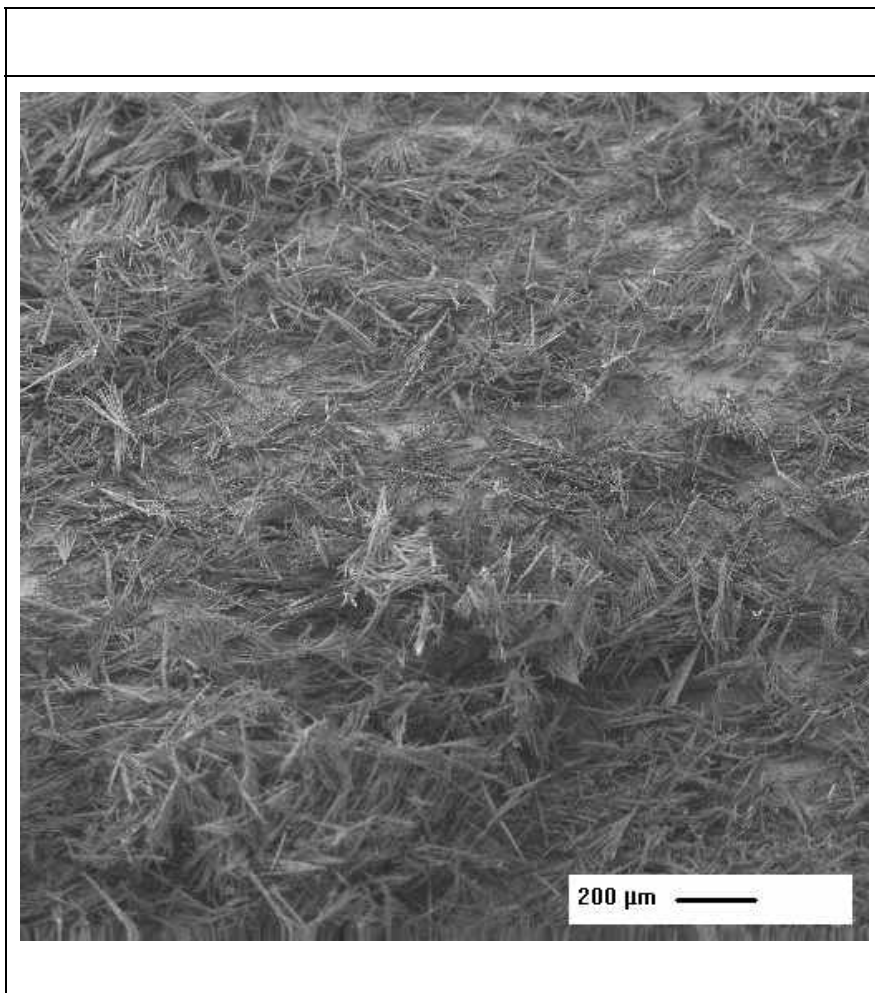
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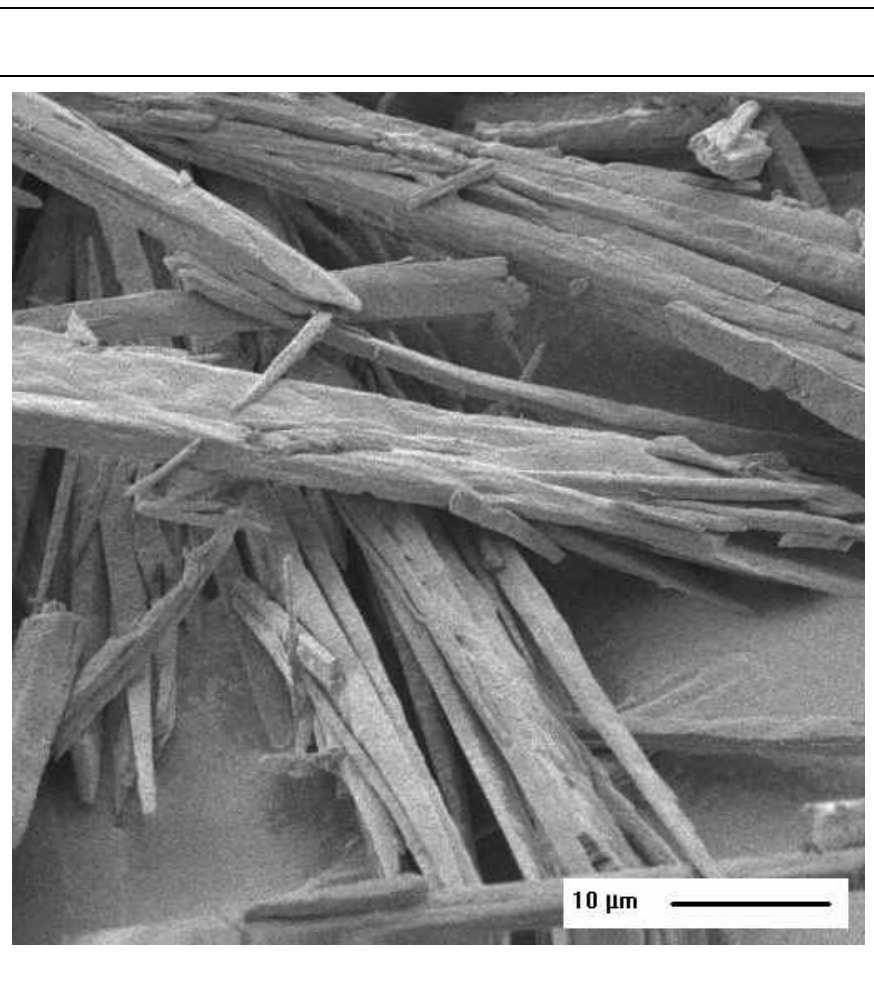
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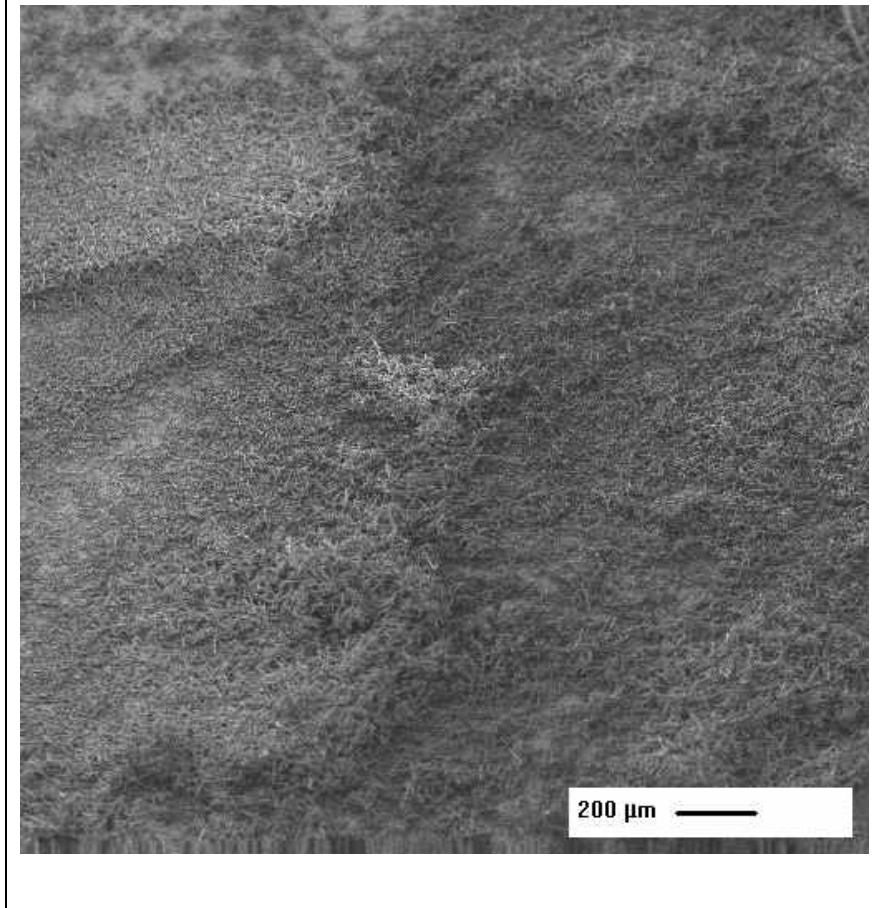
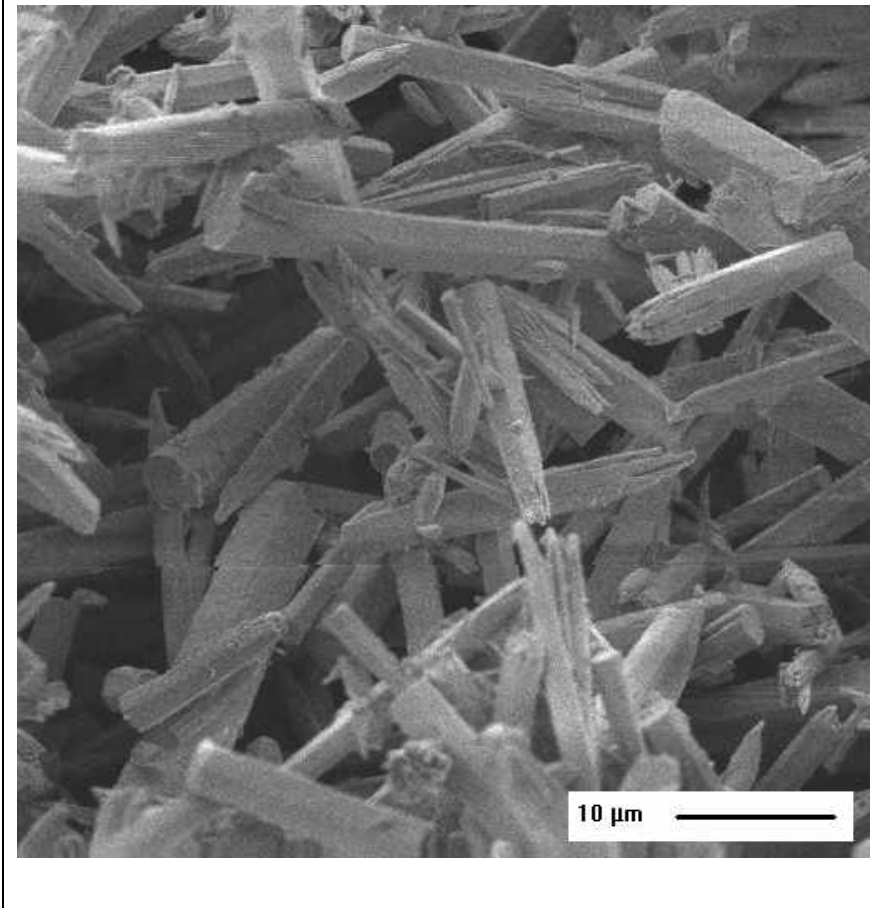
EL2O122A, 19A Candidate, Cs salt 2000X



EL2O117A, 19A Candidate, Rb salt 50X

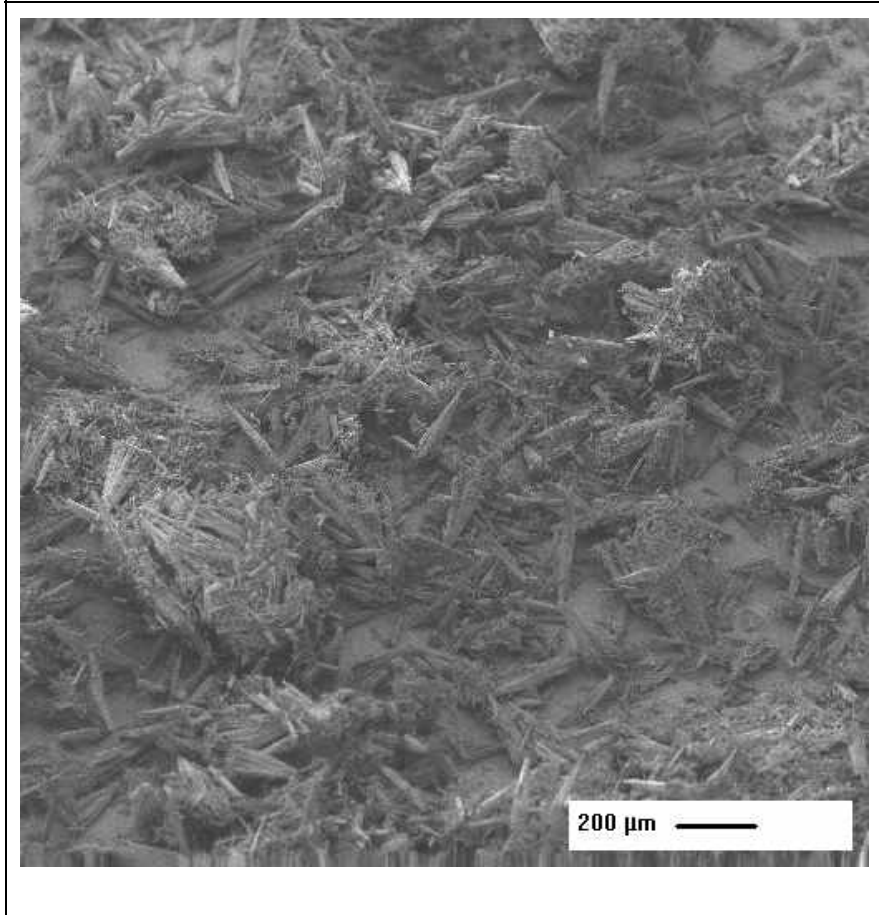
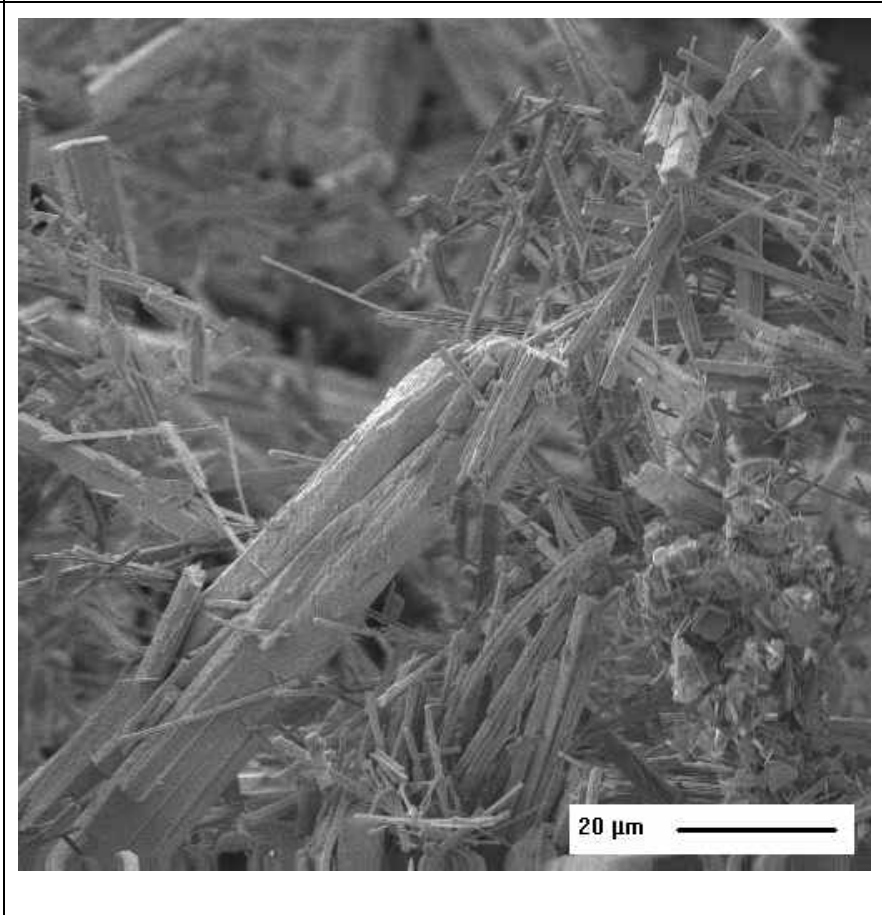


EL2O117A, 19A Candidate, Rb salt 2000X

 <p data-bbox="737 1122 1016 1170">200 μm</p>	 <p data-bbox="1612 1122 1892 1170">10 μm</p>
<p data-bbox="323 1260 905 1289">EL2O083A, 28A Candidate, Cu complex 50X</p>	<p data-bbox="1184 1260 1766 1289">EL2O083A, 28A Candidate, Cu complex 2000X</p>

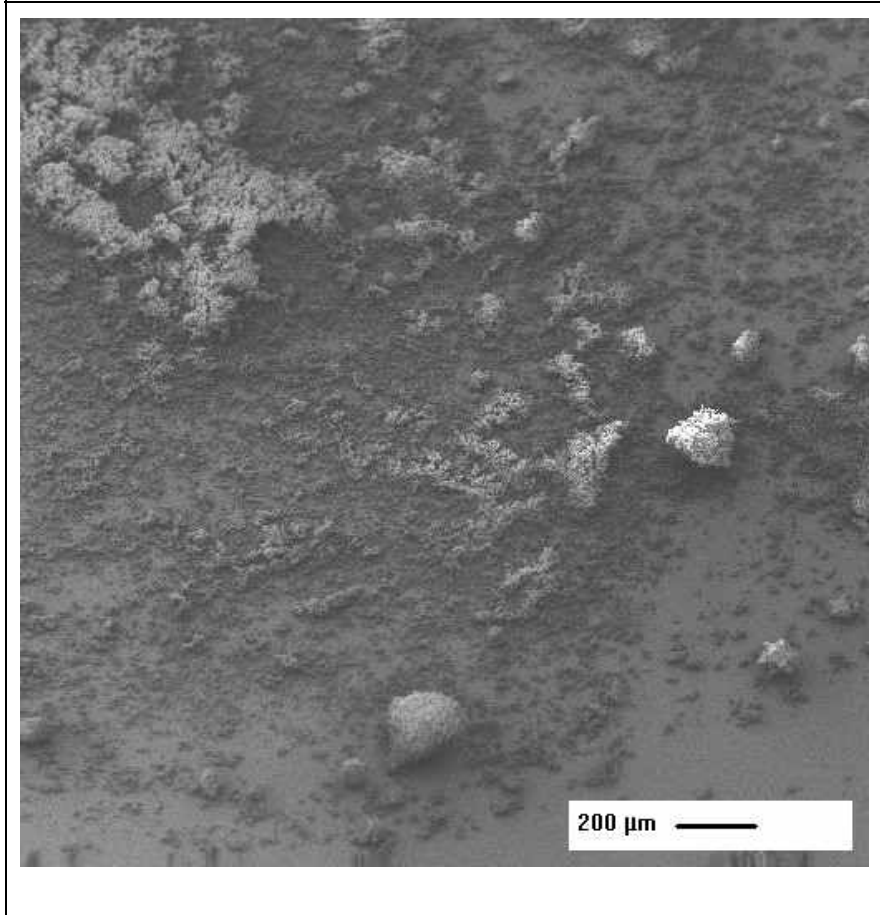
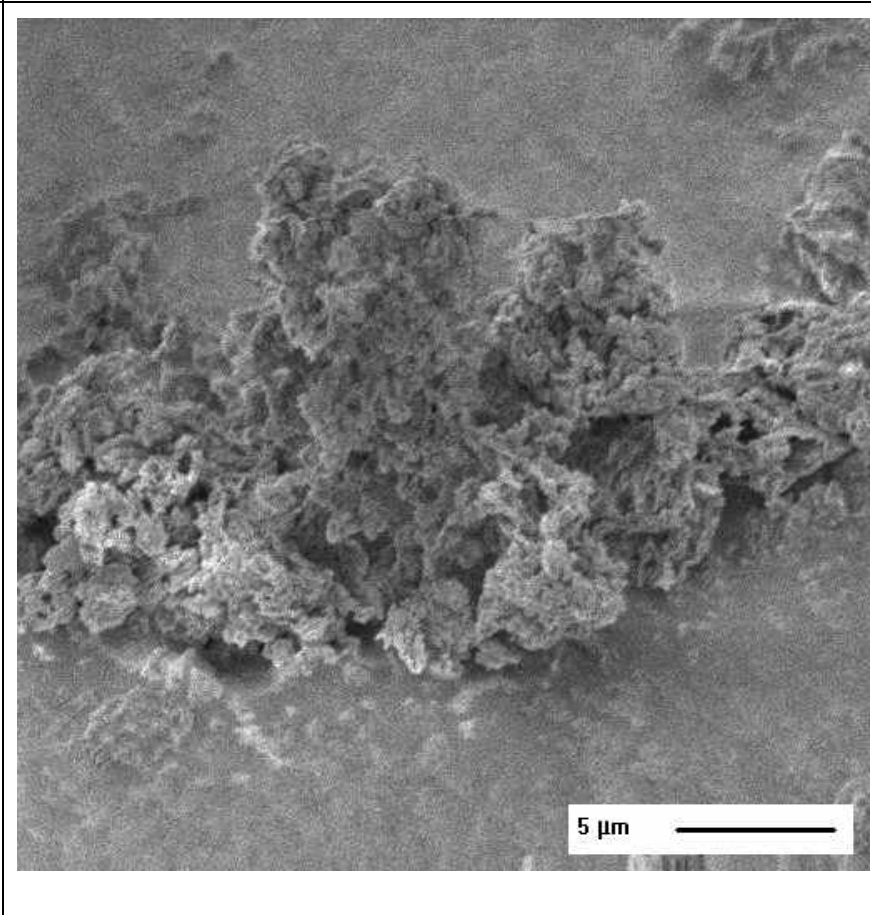
EL2O083A, 28A Candidate, Cu complex 50X

EL2O083A, 28A Candidate, Cu complex 2000X

 <p>Scanning electron micrograph (SEM) showing a dense field of small, needle-like or plate-like crystals. The crystals are oriented in various directions, creating a complex, interlocking texture. A scale bar in the bottom right corner indicates 200 μm.</p>	 <p>High-magnification scanning electron micrograph (SEM) of the same Fe complex. This view clearly shows the individual plate-like crystals, which appear as thin, flat, rectangular or irregular shapes. Some crystals are stacked or layered. A scale bar in the bottom right corner indicates 20 μm.</p>
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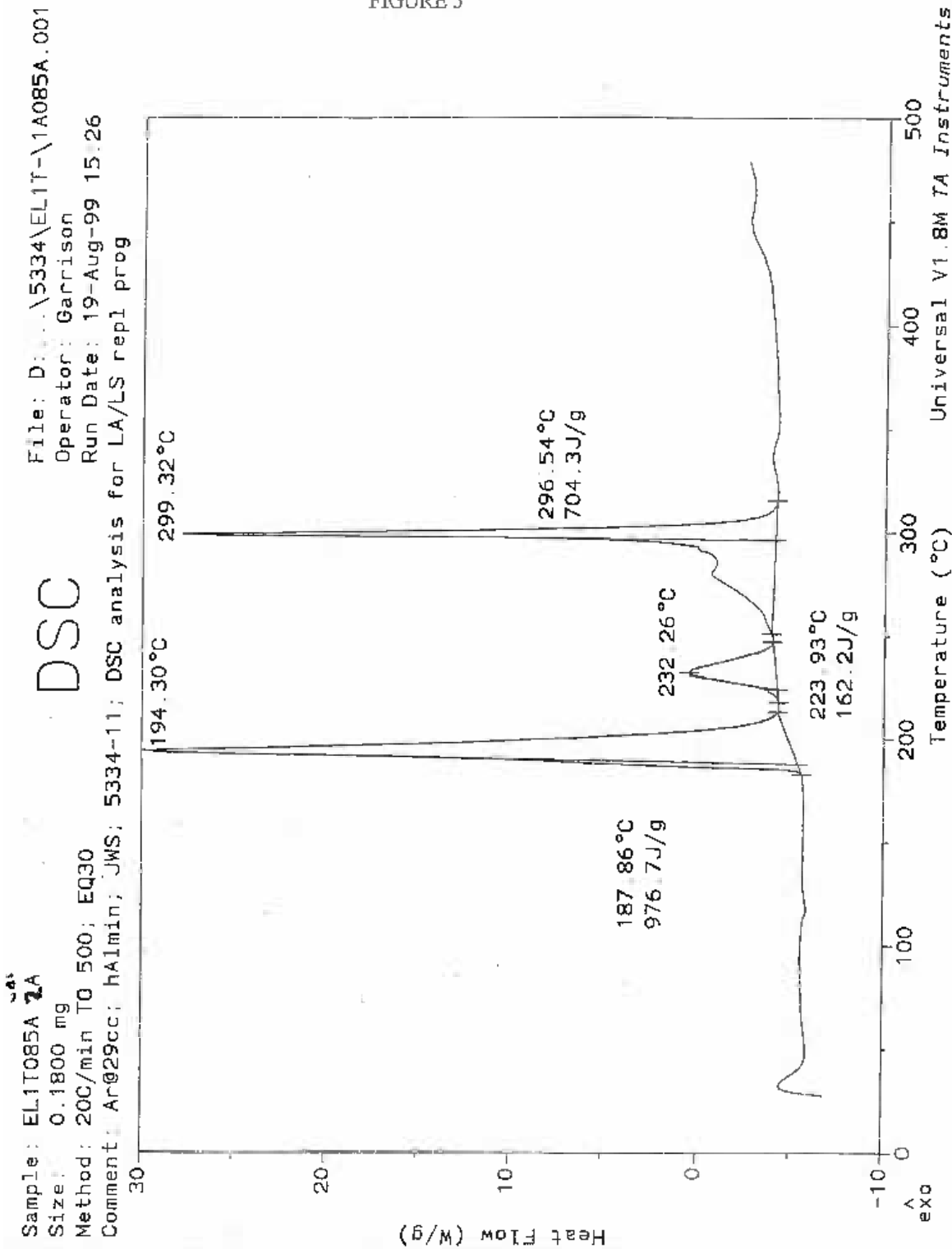
EL1O078A, 28A Candidate, Fe complex 50X

EL1O078A, 28A Candidate, Fe complex 1000X

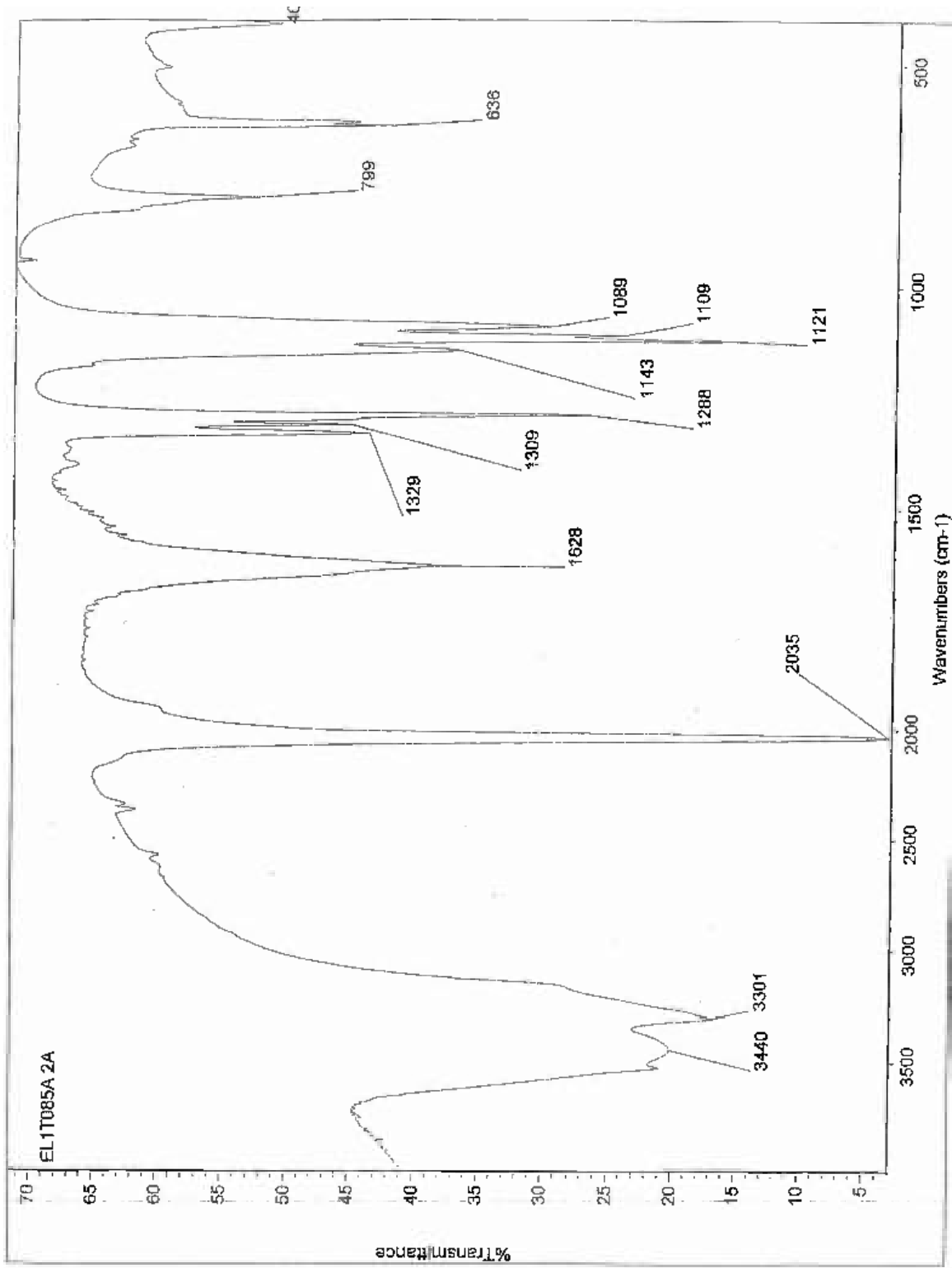
	
<p>DAATO 3.5, 29A 50X</p>	<p>DAATO 3.5, 29A 4000X</p>

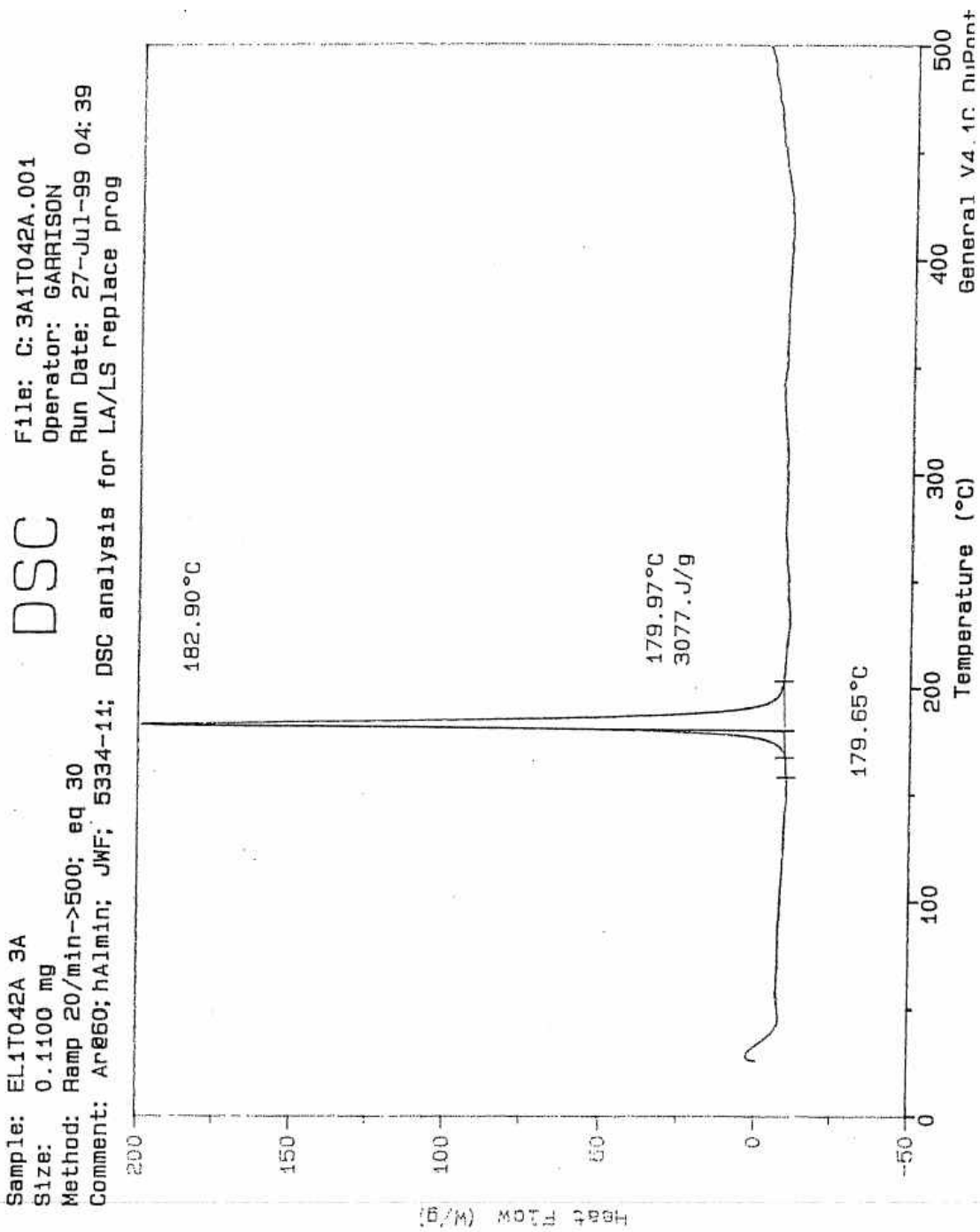
2A, EL1T085A

FIGURE 5

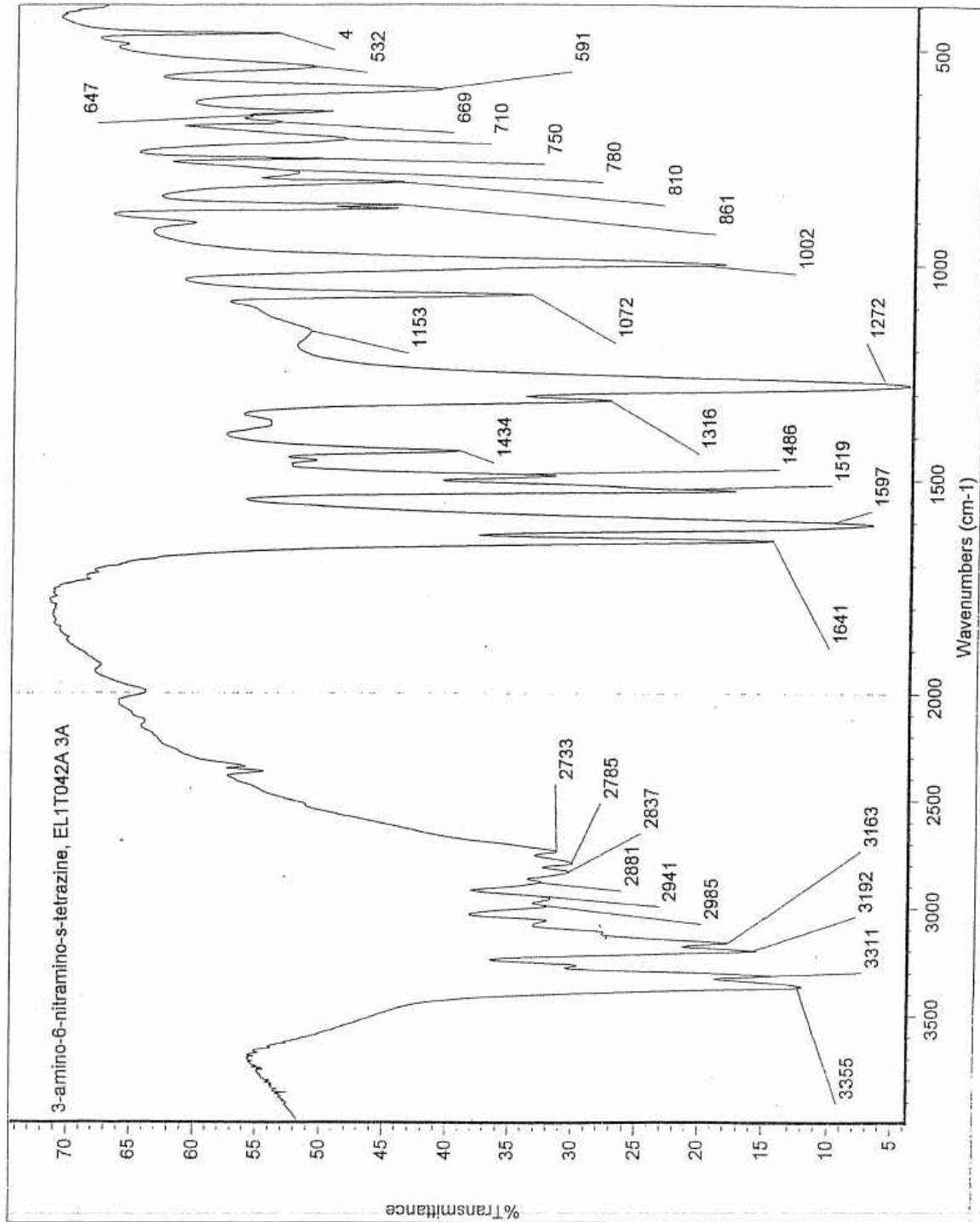


2A, EL1T085A





3A, EL1T042A



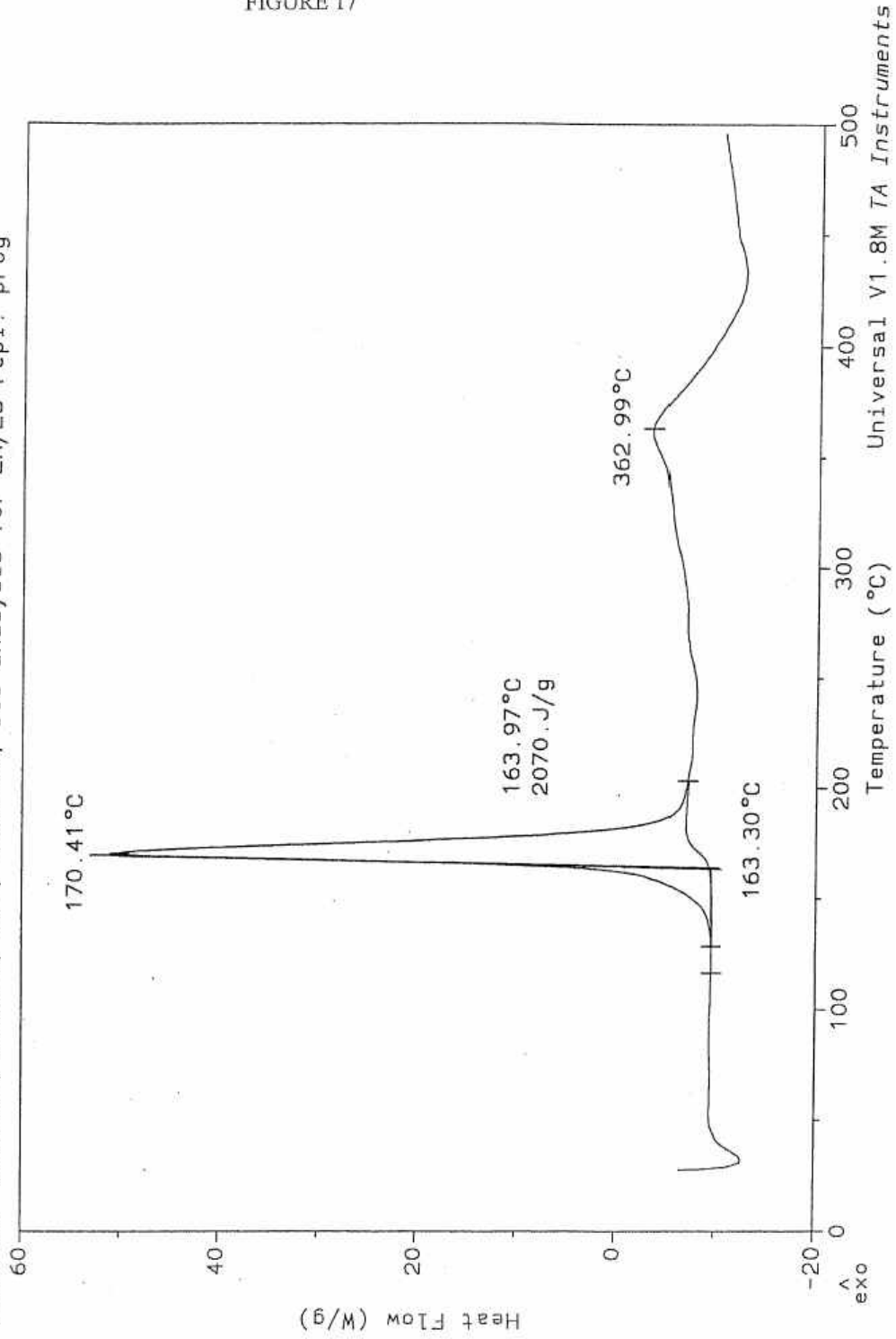
6A, EL1T072B

FIGURE 17

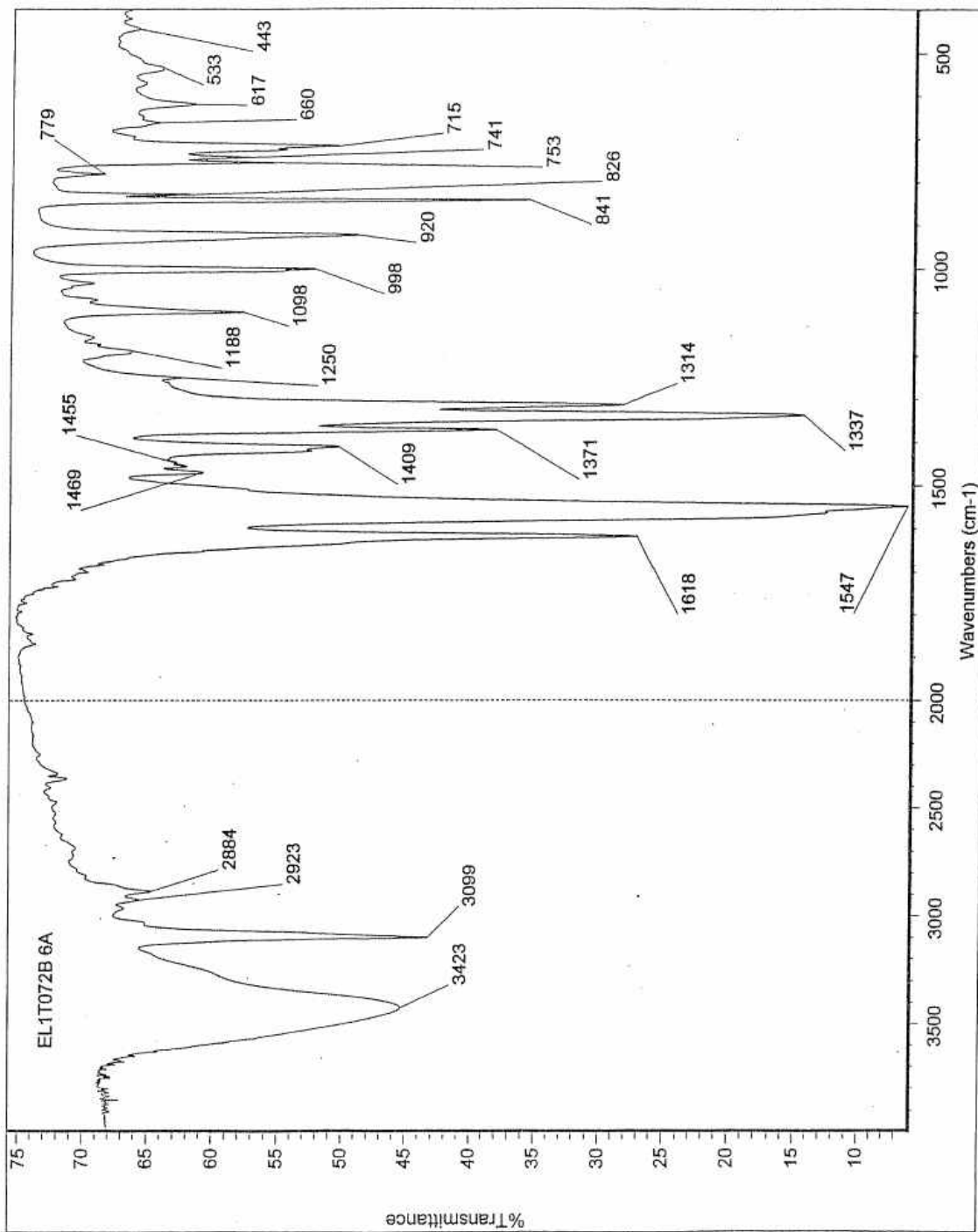
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Size: 0.1700 mg
Method: 20C/min TO 500; EQ30
Comment: Ar@29cc; hAlmin; JWF; 5334-11, DSC analysis for LA/LS repl. prog

DSC

File: D:\... \5334\EL1T-\6A072B.002
Operator: Damon
Run Date: 4-Aug-99 13:37



6A, EL1T072B



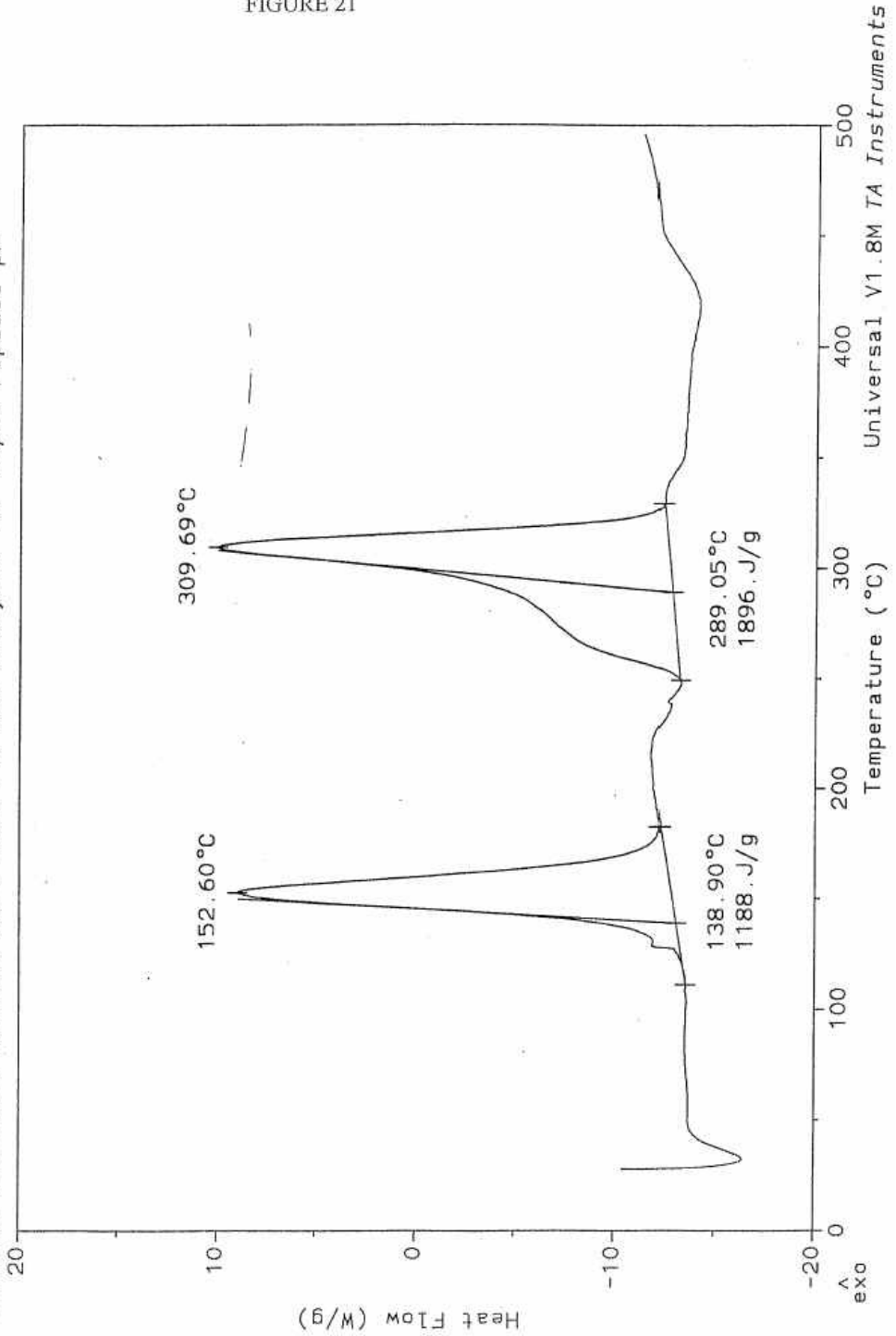
7A, EL1T079A

FIGURE 21

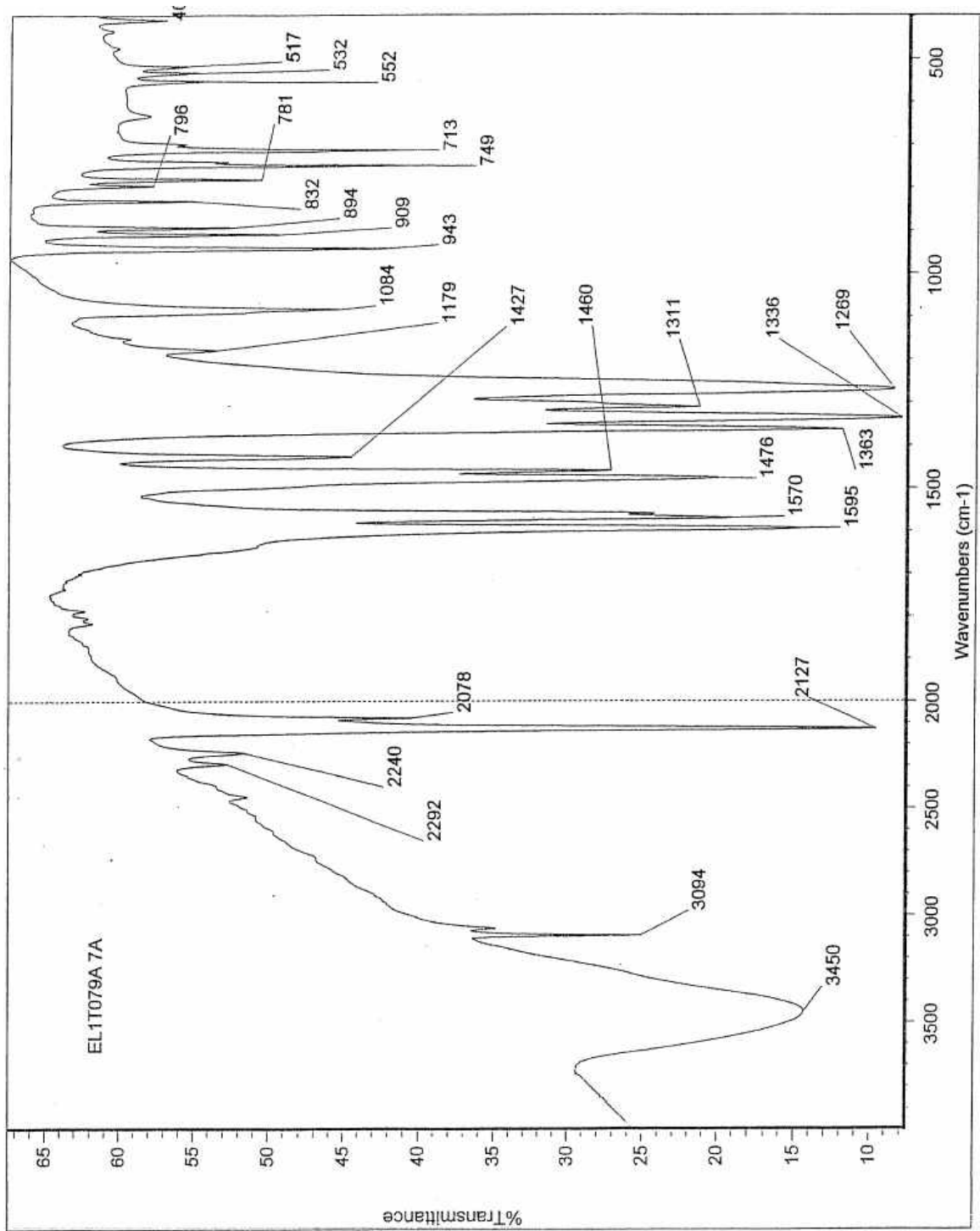
Sample: EL1T079A 7A
Size: 0.1100 mg
Method: 20C/min T0 500; EQ30
Comment: Ar@29cc; hAlmin; JWF; 5334-11; DSC analysis for LA/LS replace pr

DSC

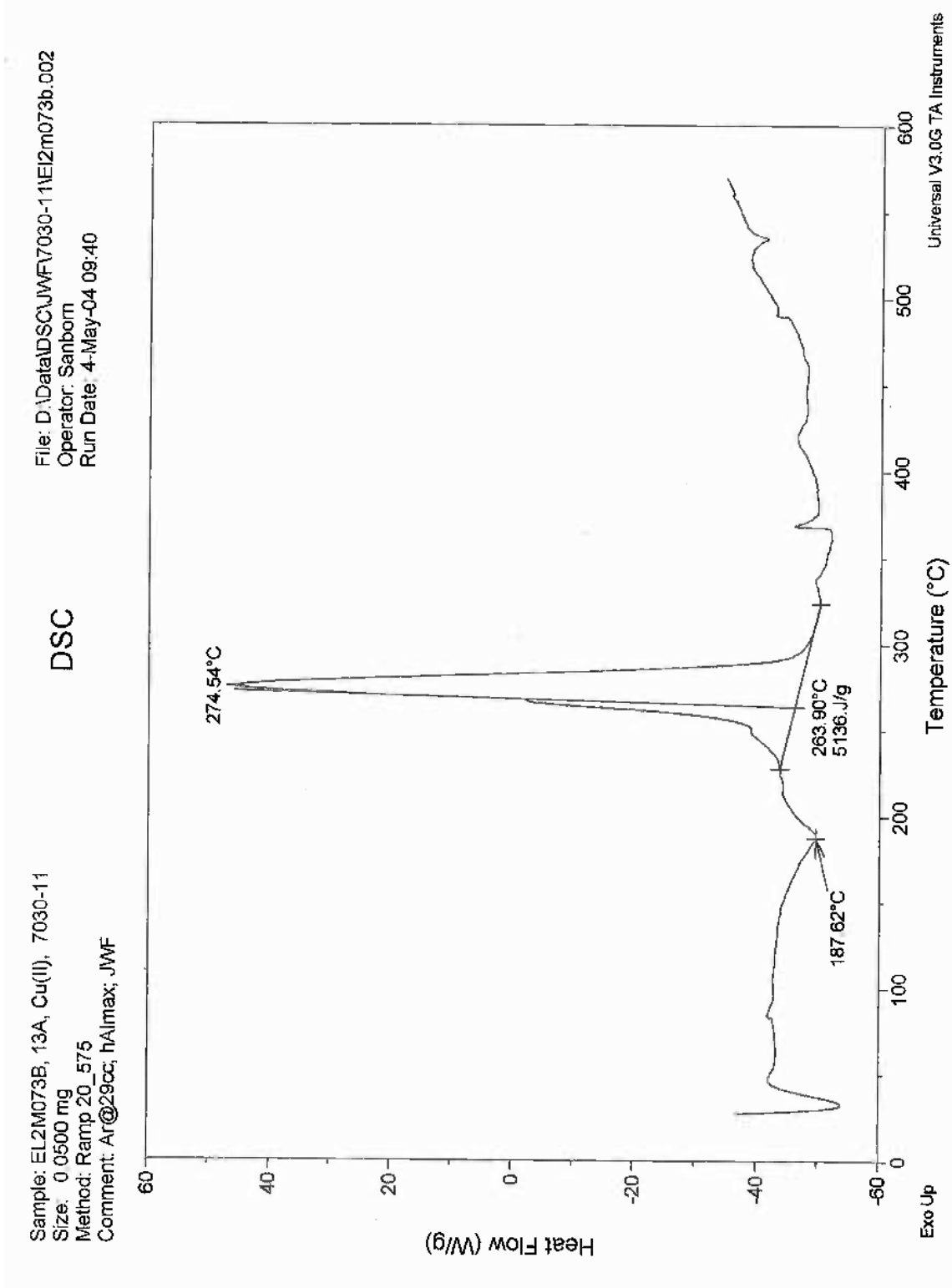
File: D:\...\5334\EL1T-7A079A.002
Operator: Garrison
Run Date: 12-Aug-99 09:55



7A, EL1T079A



(13A, A₁), EL2M073B



(13A, A₁), EL2M073B

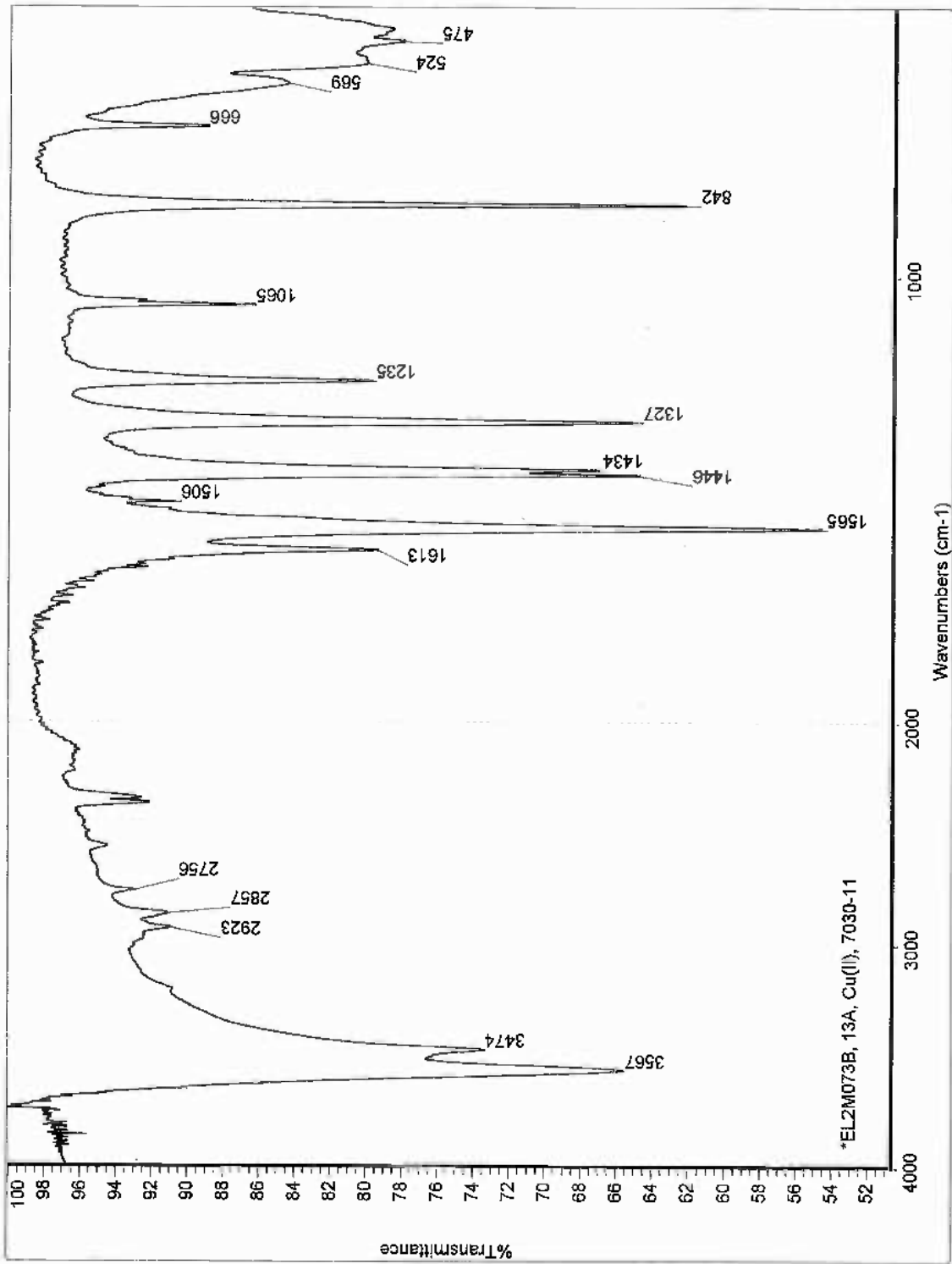
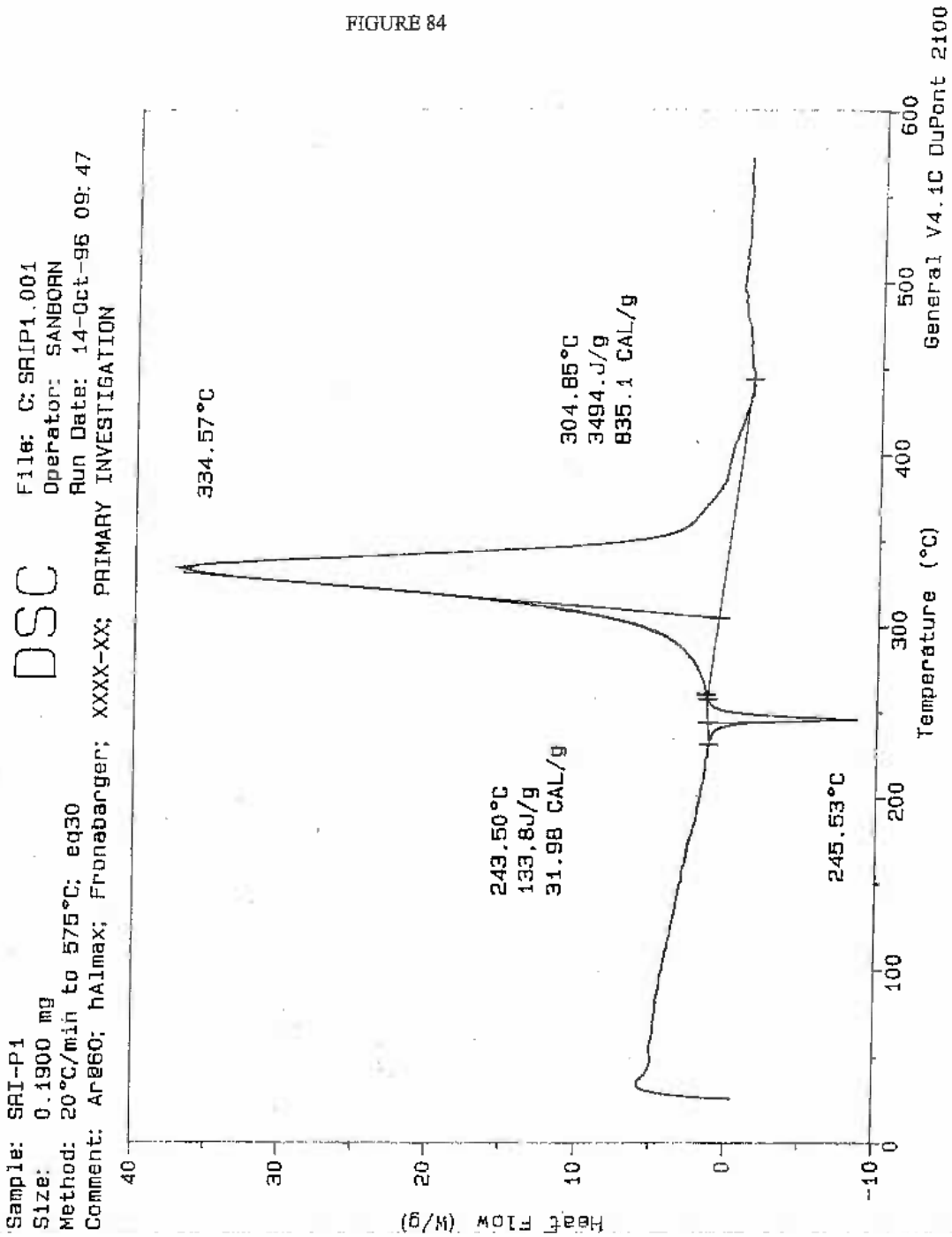


FIGURE 84

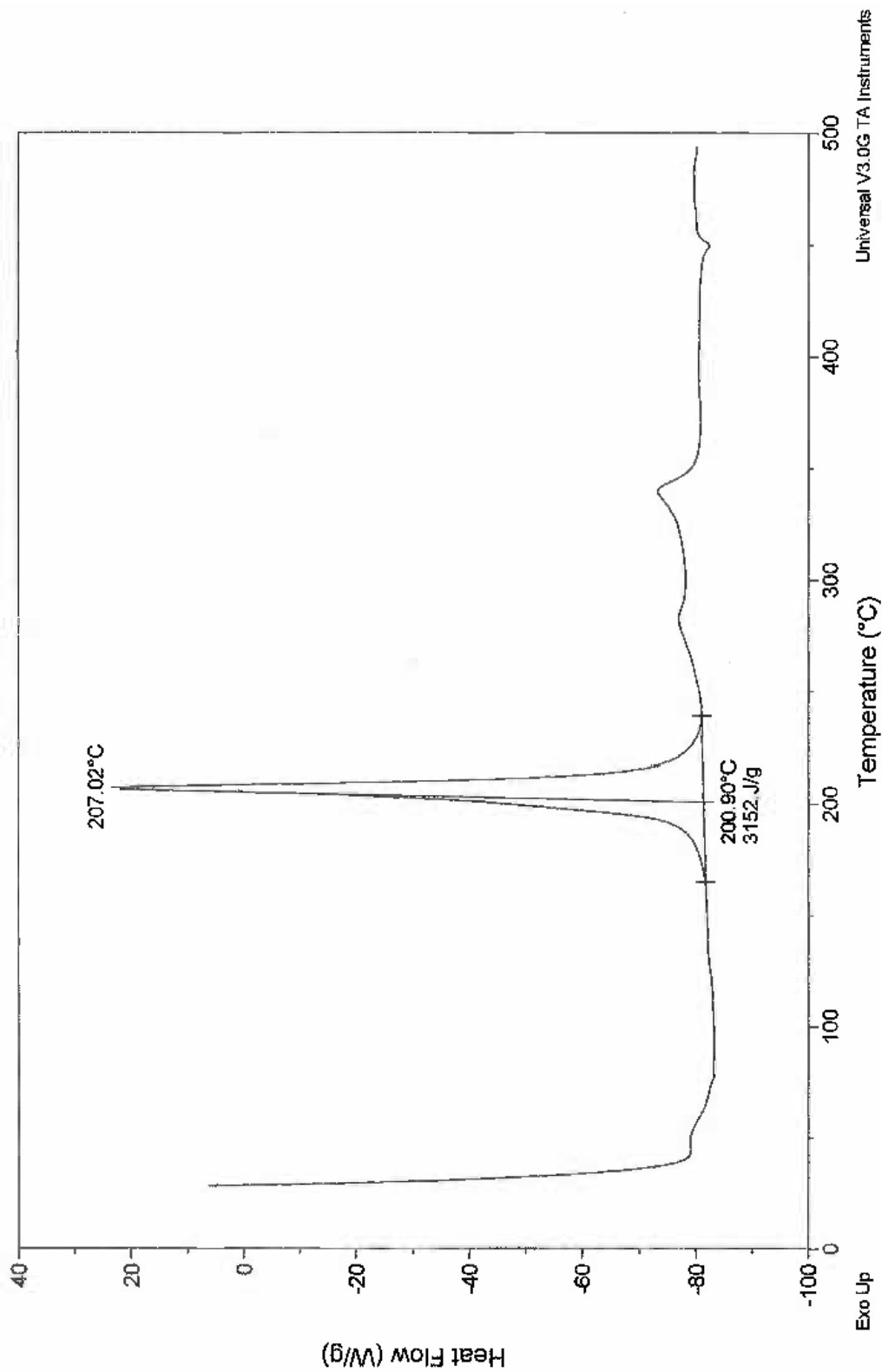


15A, potassium salt, EL2O048A

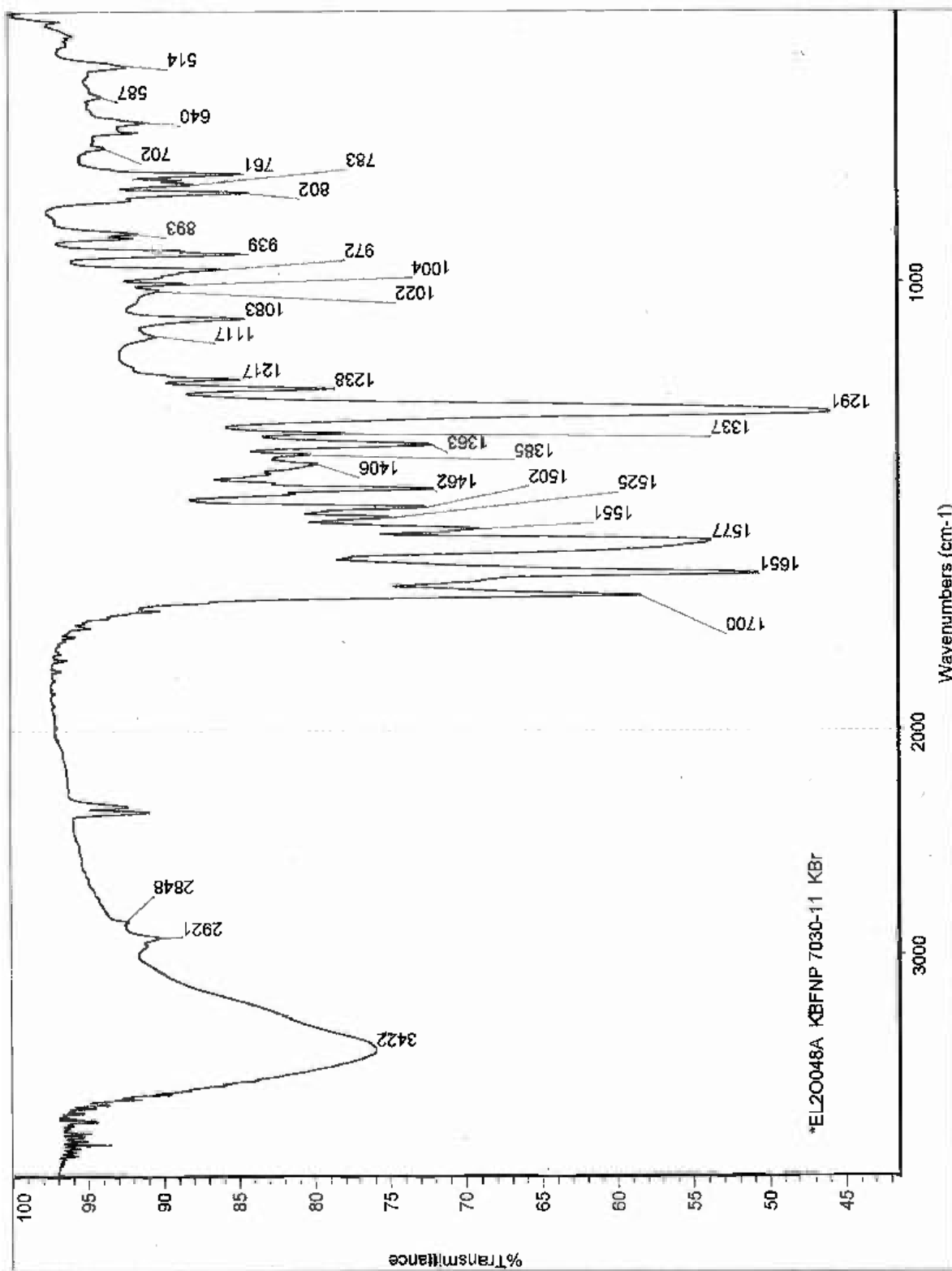
File: D:\Data\DSC\Mike WEL20\EL20048a.001
Operator: Grum
Run Date: 29-Jul-03 10:19

DSC

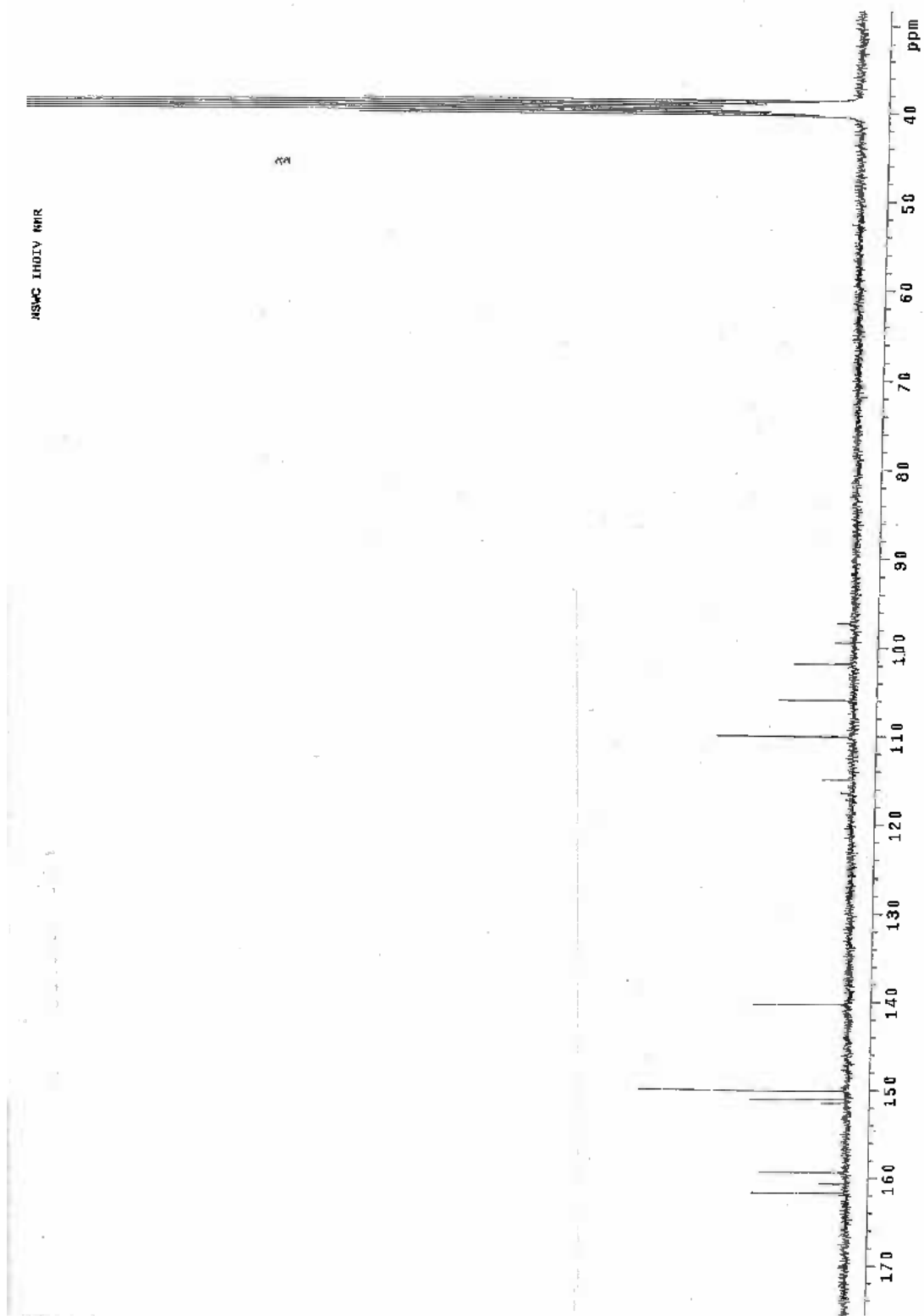
Sample: EL20048A
Size: 0.1700 mg
Method: 20C/min TO 500 EQ30
Comment: Ar@29cc/hAl/min;7030-11;MDW;samples



15A, potassium salt, EL2O048A



15A, potassium salt, EL2O048A

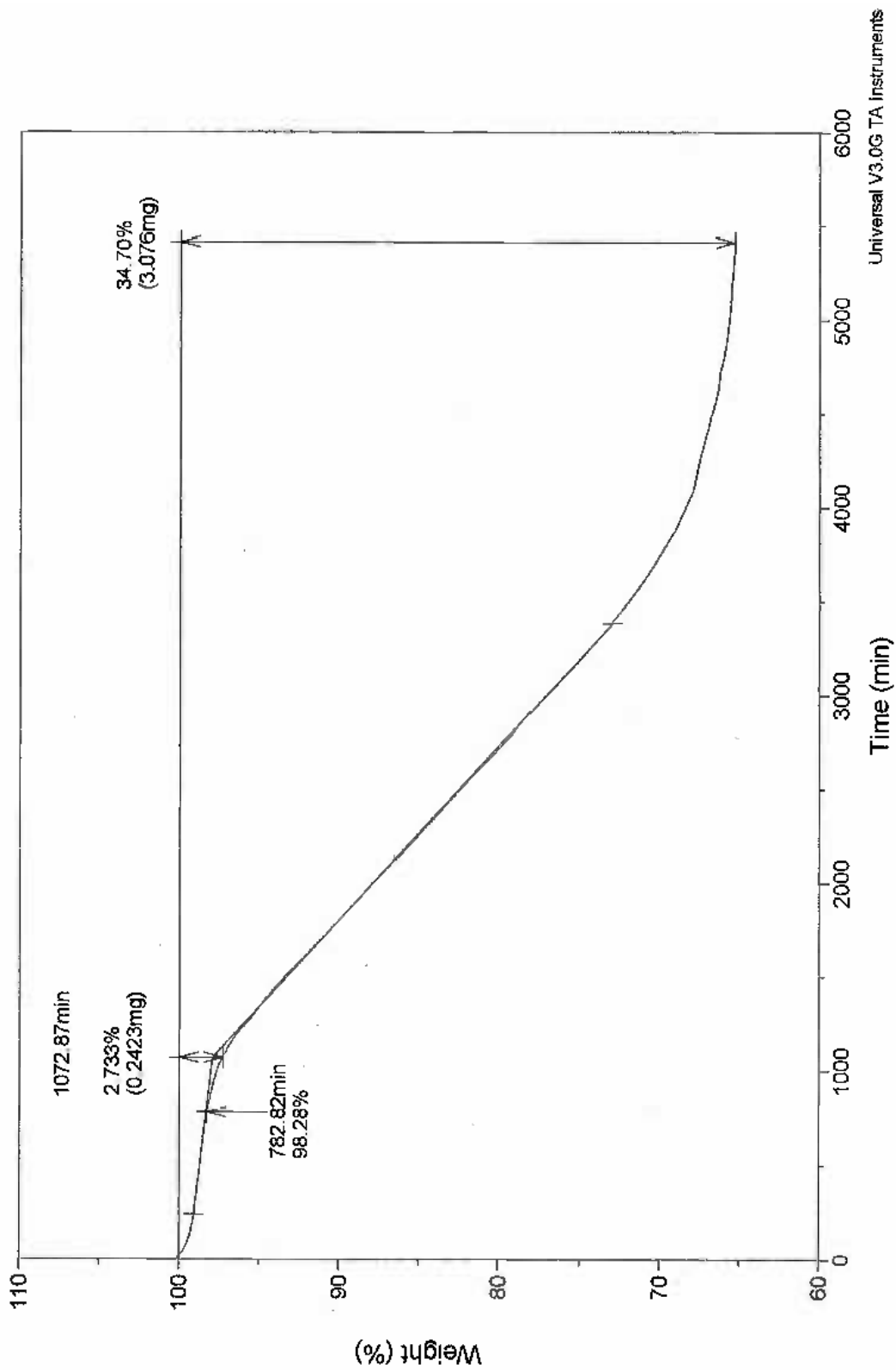


15A, potassium salt, TGA EL20044A

File: D:\Data\TGA\15A 20044a.300
Operator: Sanborn
Run Date: 27-Feb-04 14:22

TGA

Sample: 15A KBNFP LN 10044a
Size: 8.8650 mg
Method: ramp 5C/min-12C iso5400m
Comment: Argon @ 100 cc/min.; Al2O3Pan; thermal stability



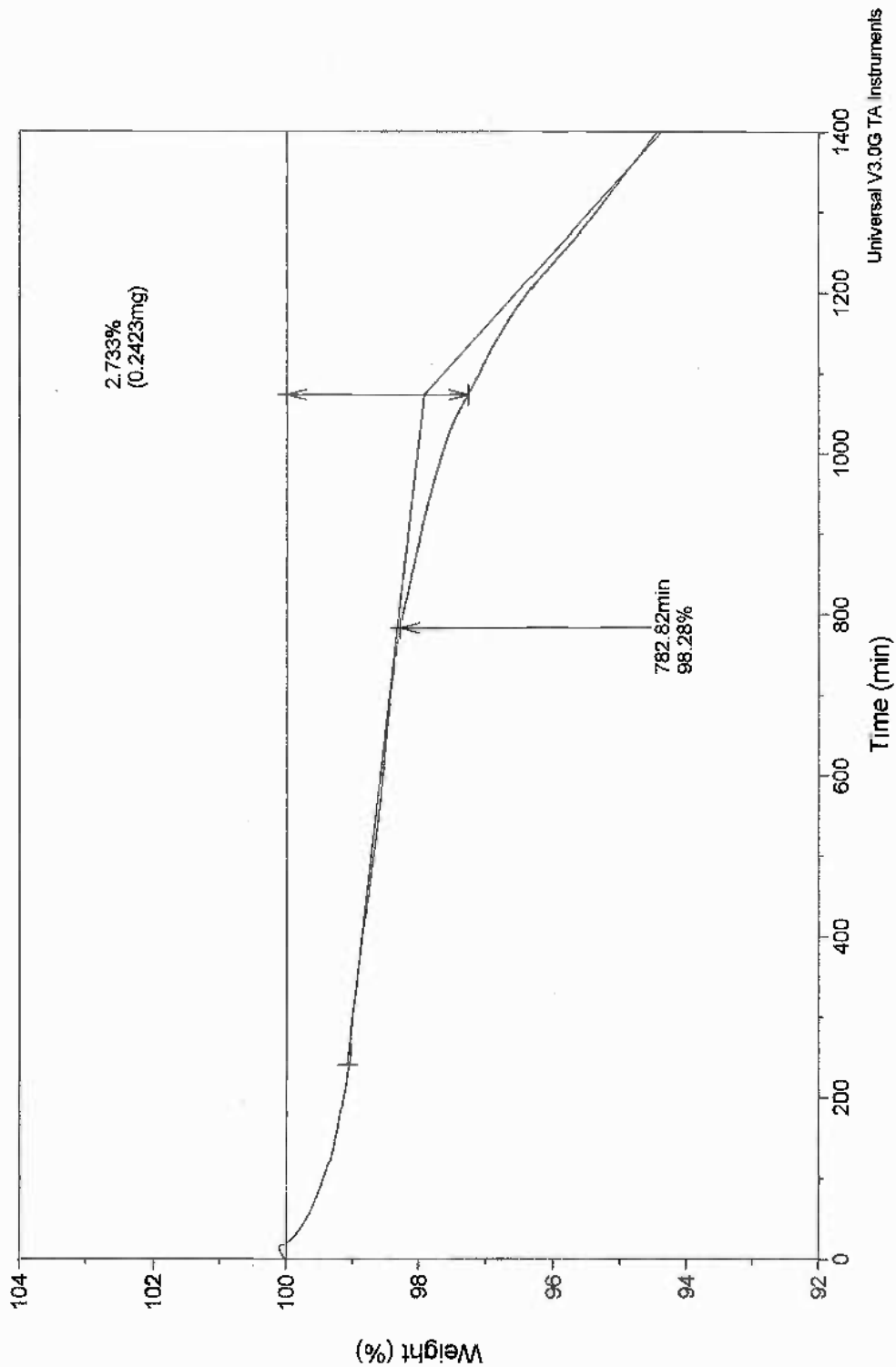
Universal V3.0G TA Instruments

15A, potassium salt, TGA EL20044A

File: D:\Data\TGA\15A 20044a.300
Operator: Sanborn
Run Date: 27-Feb-04 14:22

TGA

Sample: 15A KBNFP LN 10044a
Size: 8.8650 mg
Method: ramp 5C/min-12C iso5400m
Comment: Argon @ 100 cc/min.; Al2O3Pan; thermal stability

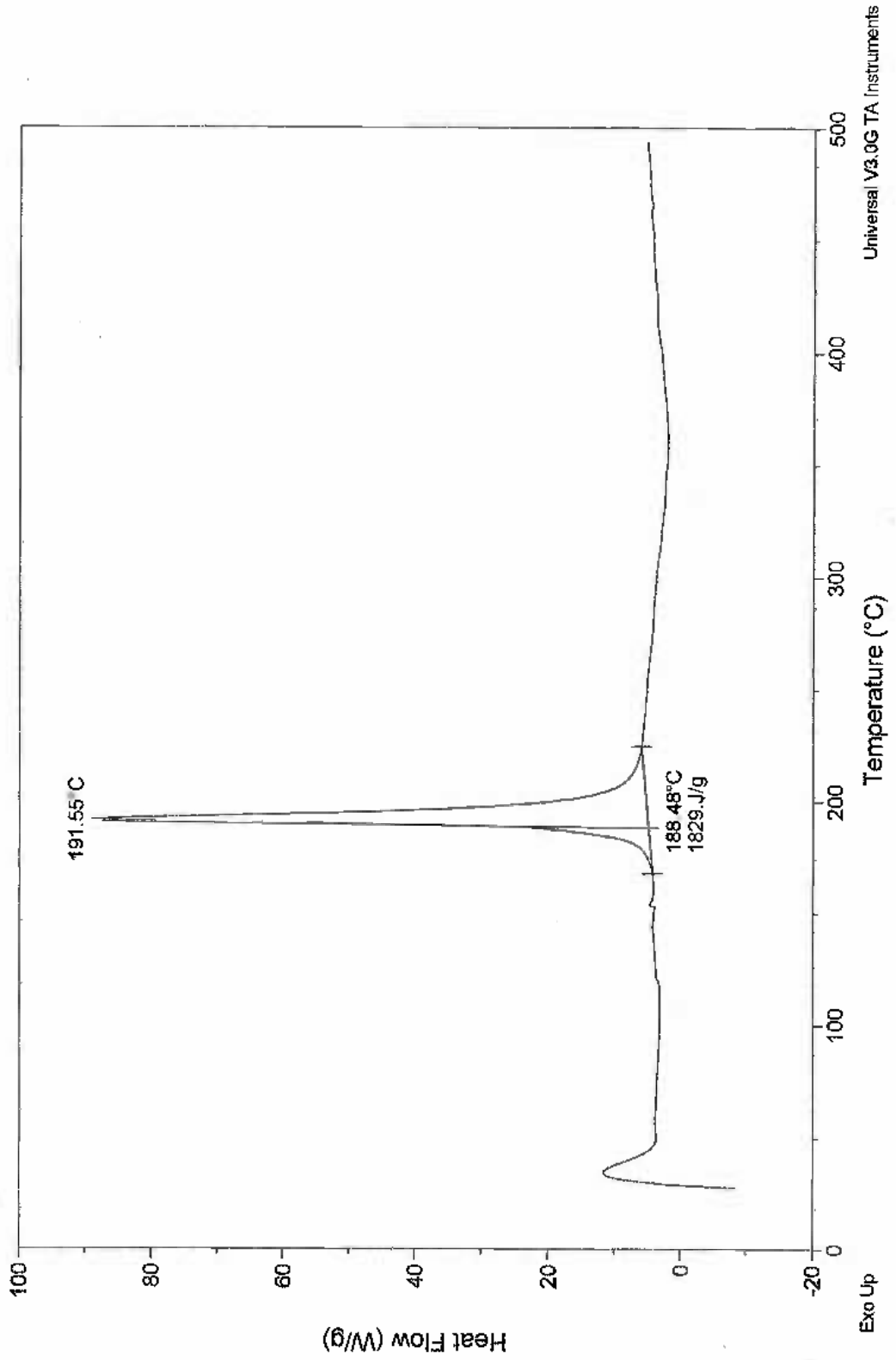


15A, rubidium salt, EL20177A

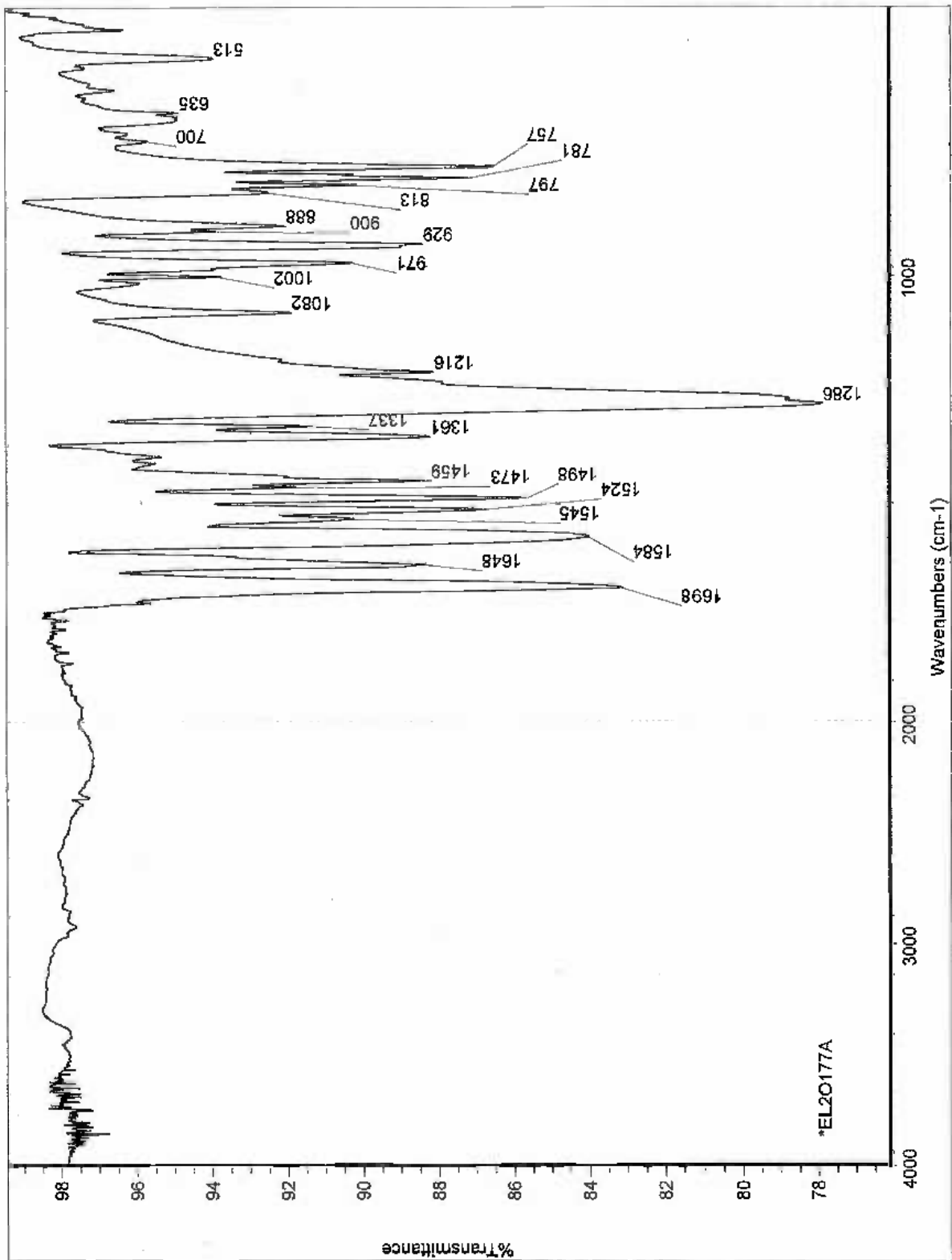
File: D:\Data\DSC\Mike WEL20\EL20177a.001
Operator: Grum
Run Date: 20-Apr-04 09:16

DSC

Sample: EL20177A, RbBFNP
Size: 0.0900 mg
Method: Ramp 20_500
Comment: Ar@29cc; hAlmax, MDW



15A, rubidium salt, EL20177A



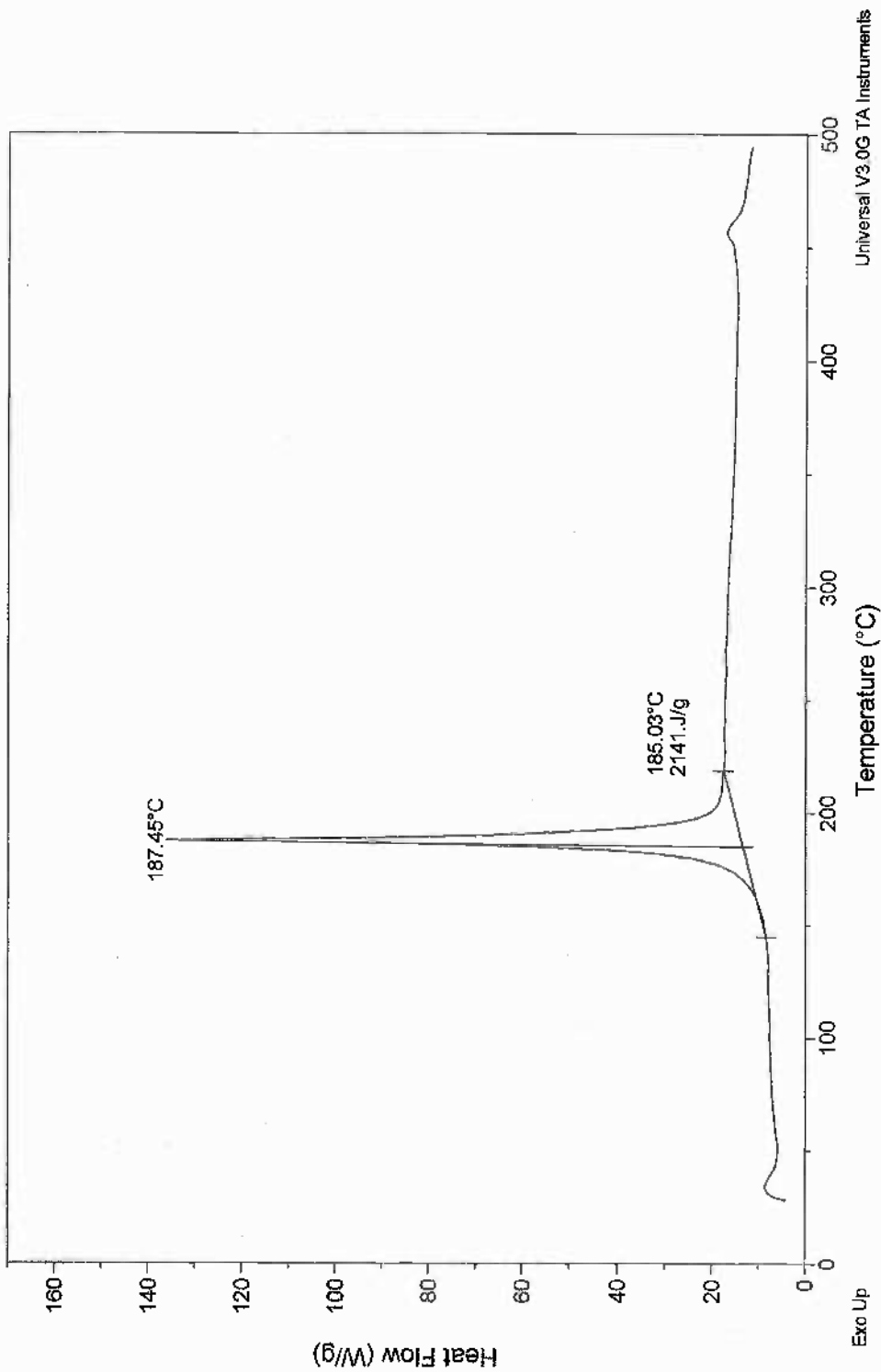
*EL20177A

16A, Cu, EL2J208A

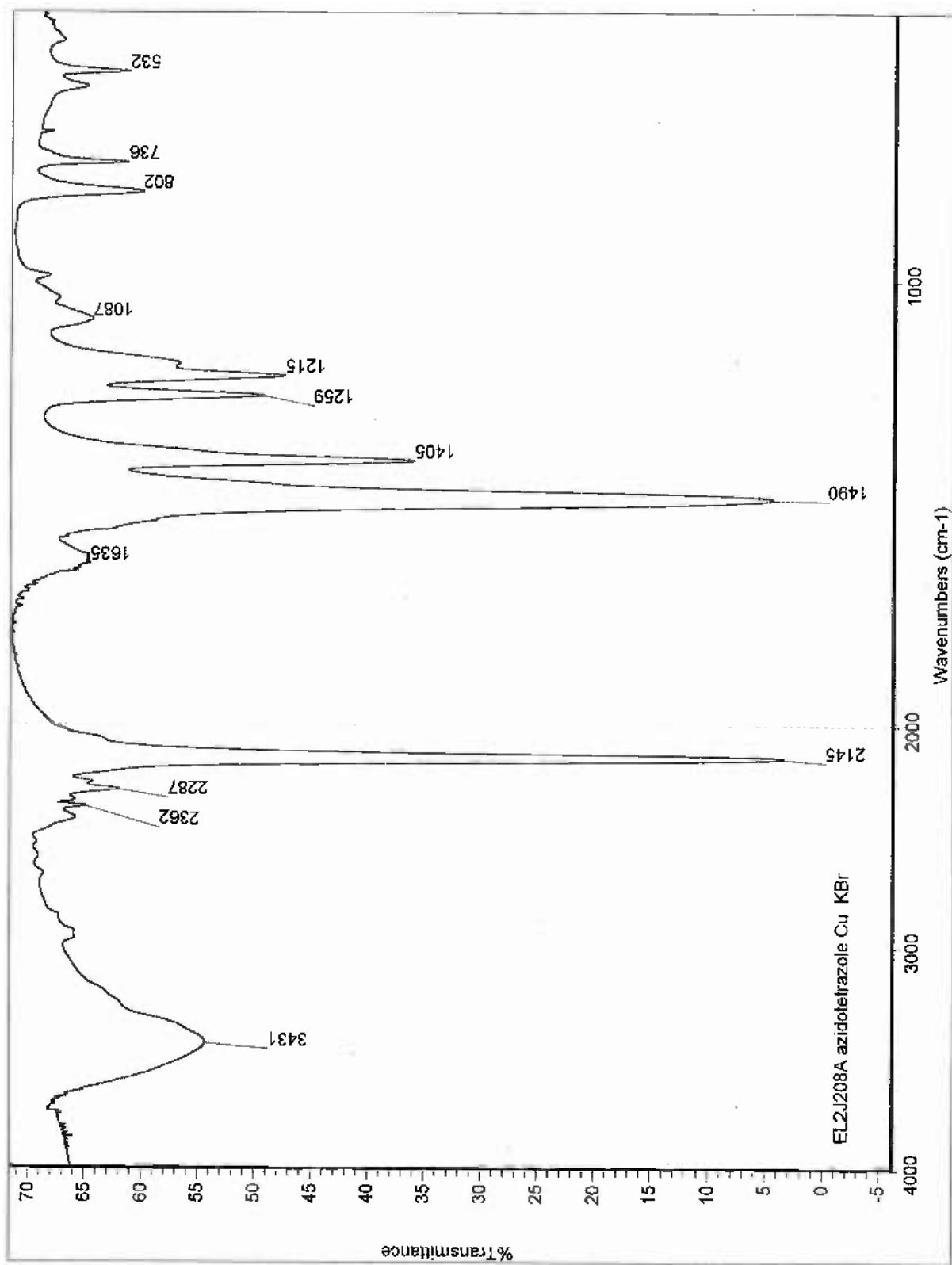
File: D:\Data\DSC\JWF\HP\Prime\EL2j208a.001
Operator: Grum
Run Date: 24-Oct-03 10:18

DSC

Sample: EL2J208A, azidotetrazole Cu
Size: 0.0900 mg
Method: 20C/min TO 500; EQ30
Comment: Ar@29cc;hAlmin;2304-1;JWF



16A, Cu, EL2J208A

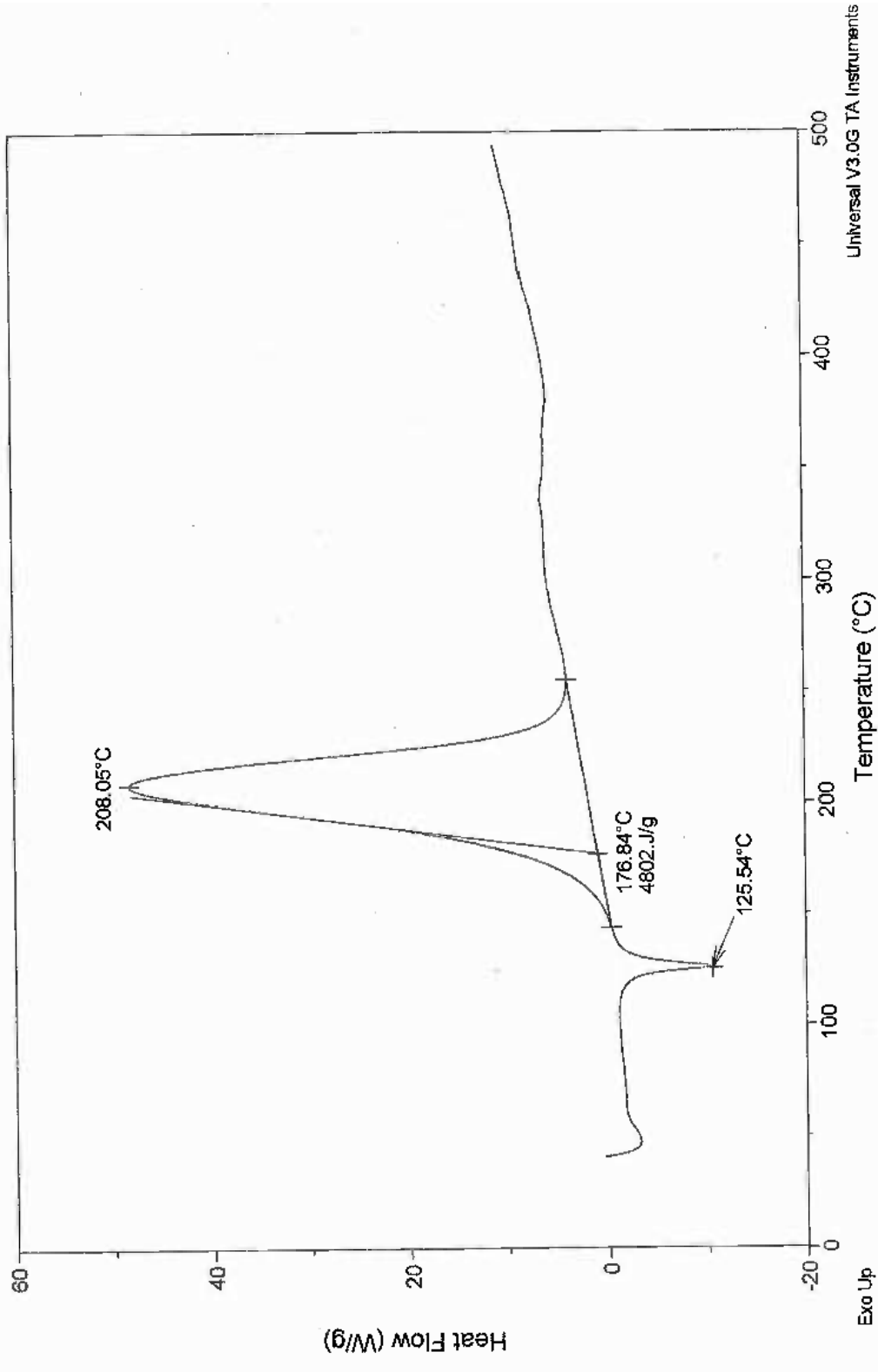


17A, Cu, EL2M048A

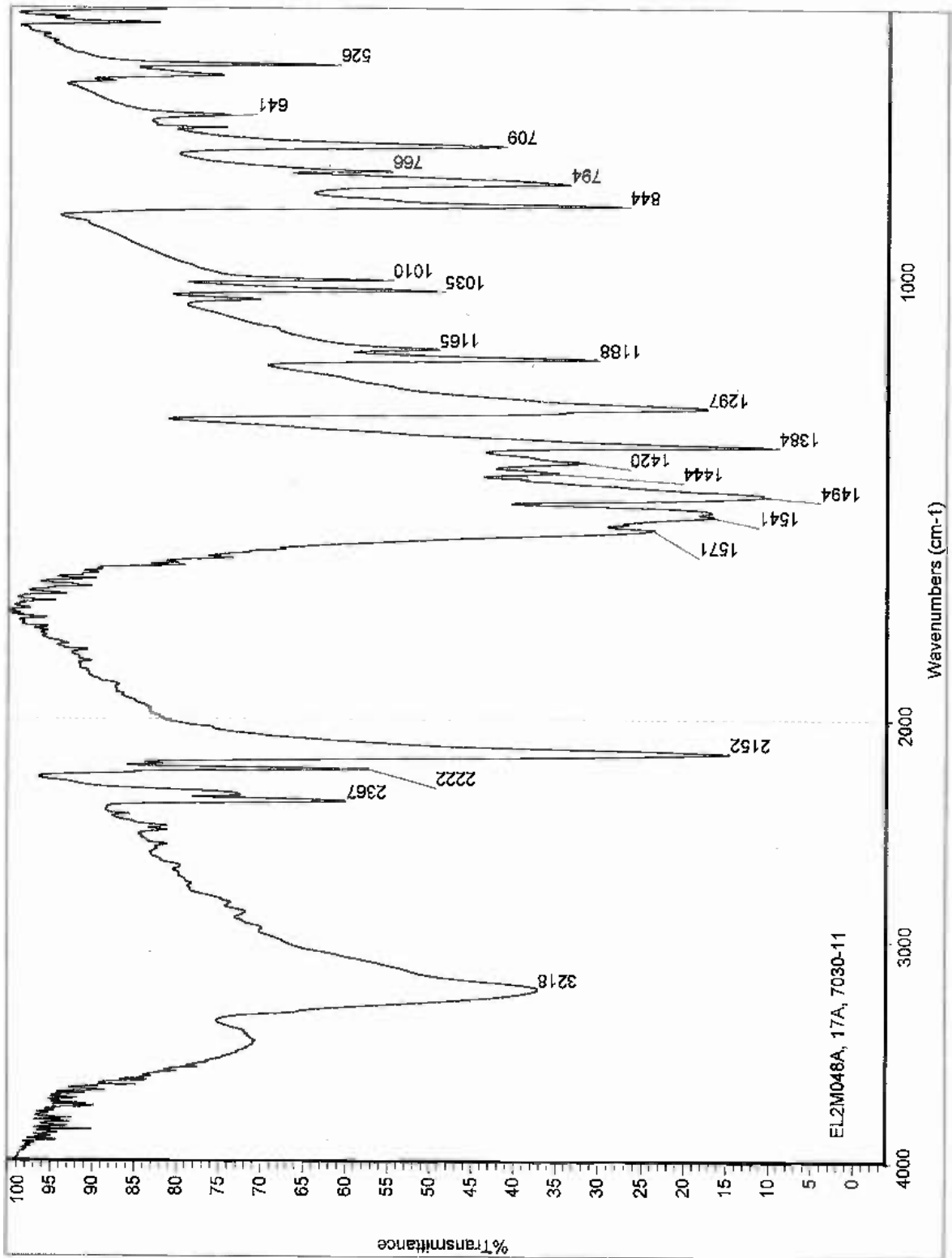
File: D:\Data\DSC\JWF\7030-11\EL2m048a.001
Operator: Williams
Run Date: 23-Sep-03 15:25

DSC

Sample: 17A\EL2M048A
Size: 0.1700 mg
Method: Ramp 20_575
Comment: At@29cc;hAlmin, 7030-11, JWF samples

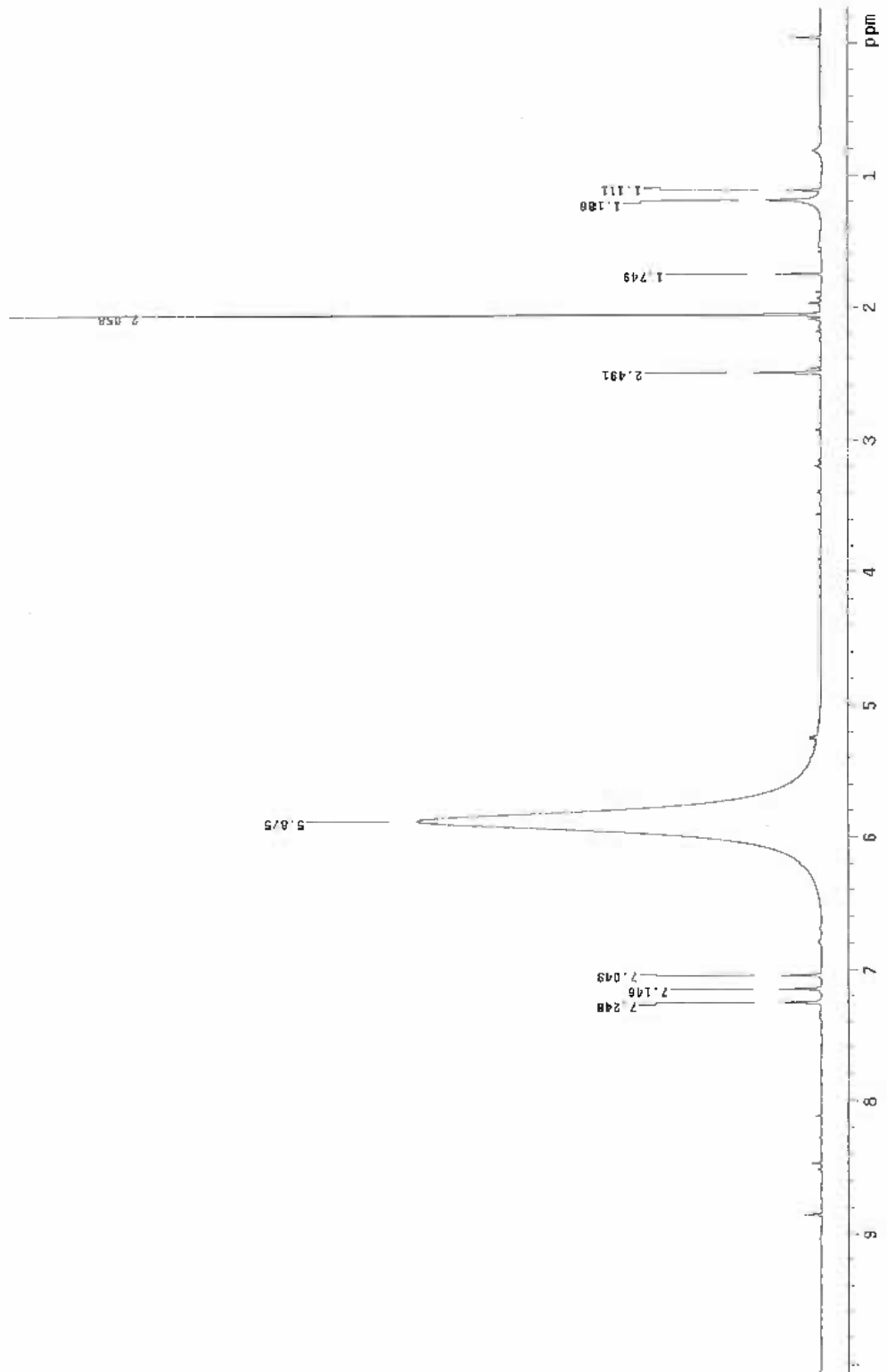


17A, Cu, EL2M048A



17A, Cu, EL2M048A

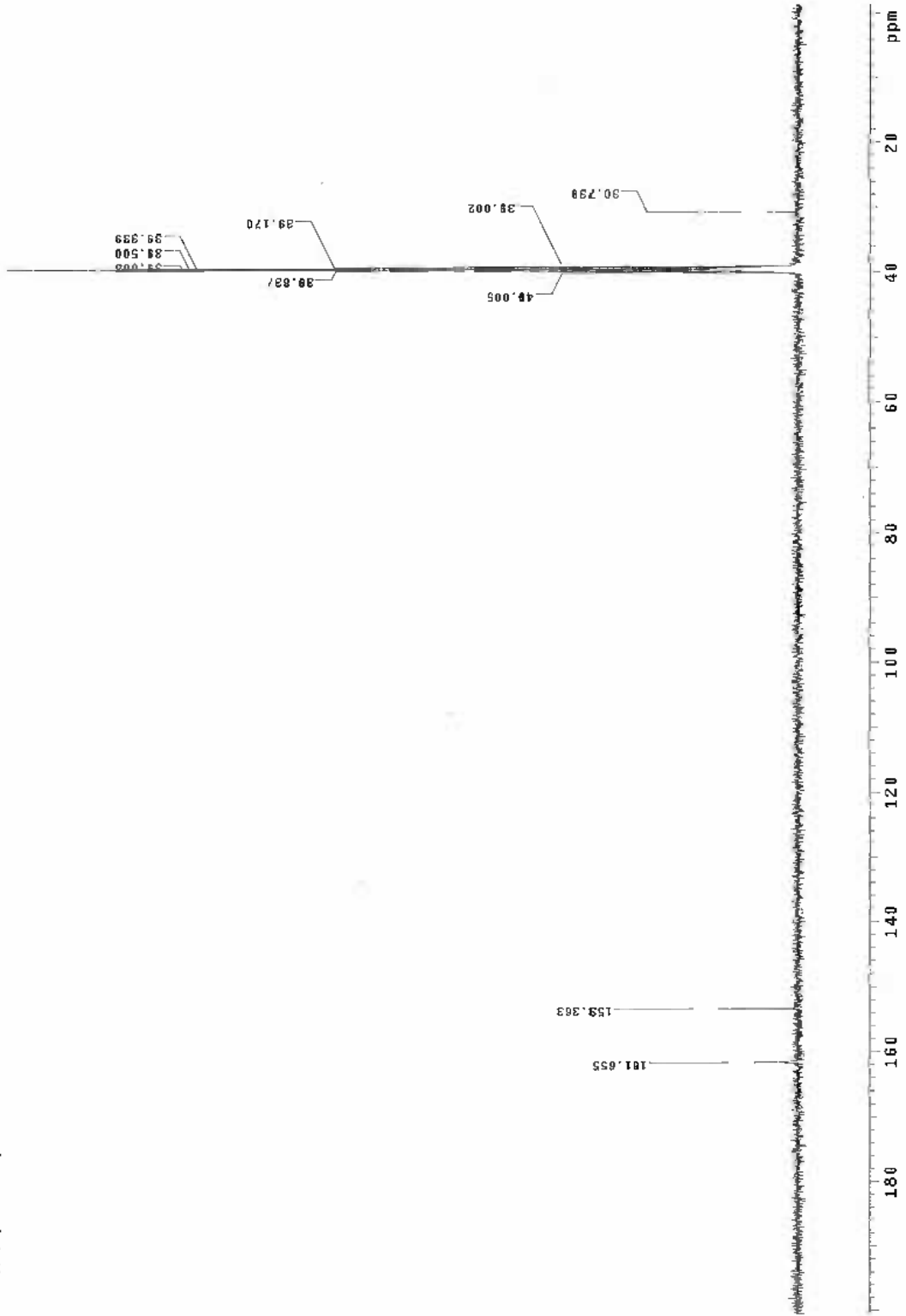
1H_EL2M007E, 25Mar03, mw
Pulse Sequence: s2pu1



17A, Cu, EL2M048A

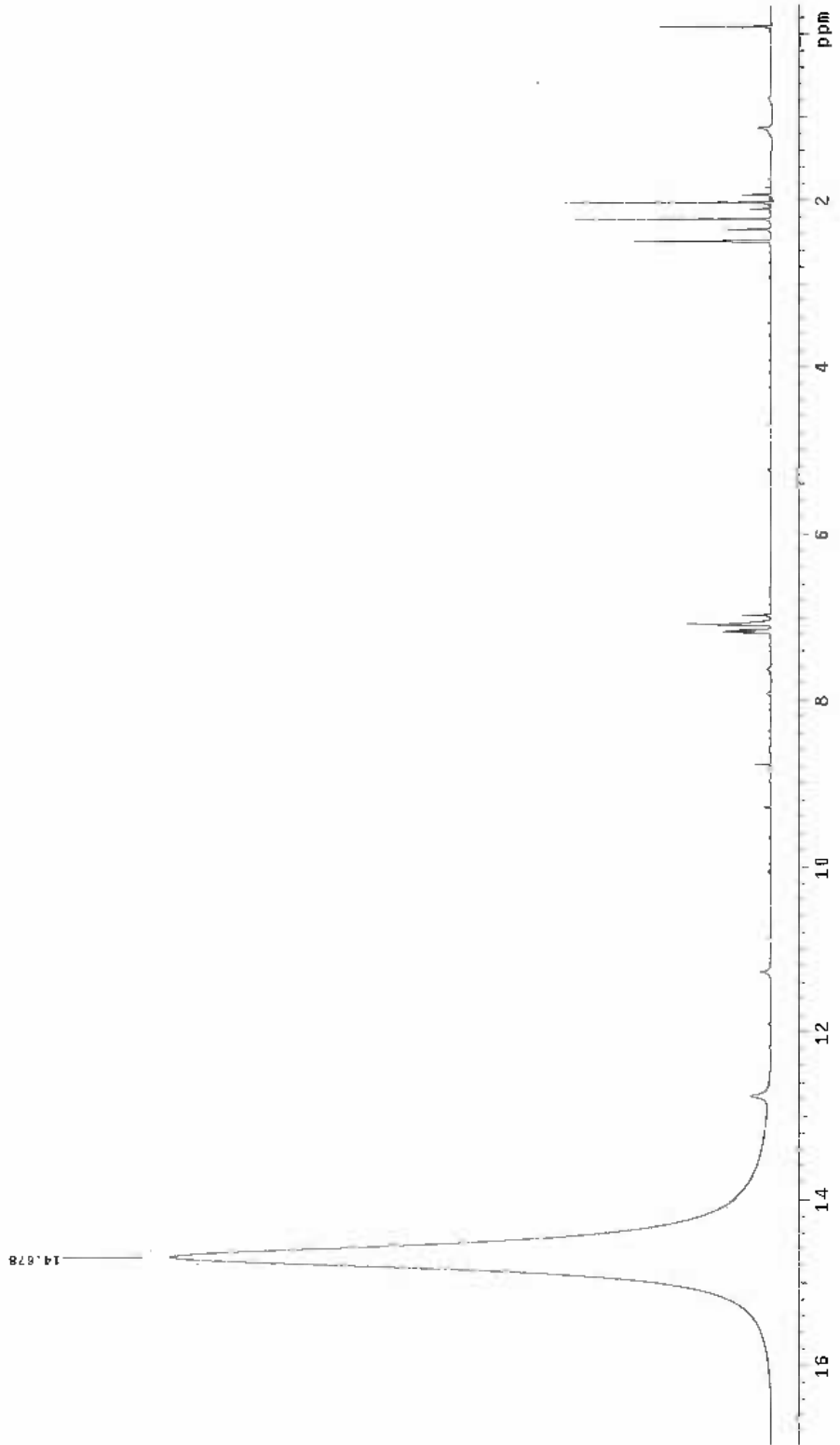
13C_EI_2H007E, 25Mar03, mw

Pulse Sequence: s2pu1



17A, Cu, EL2M048A

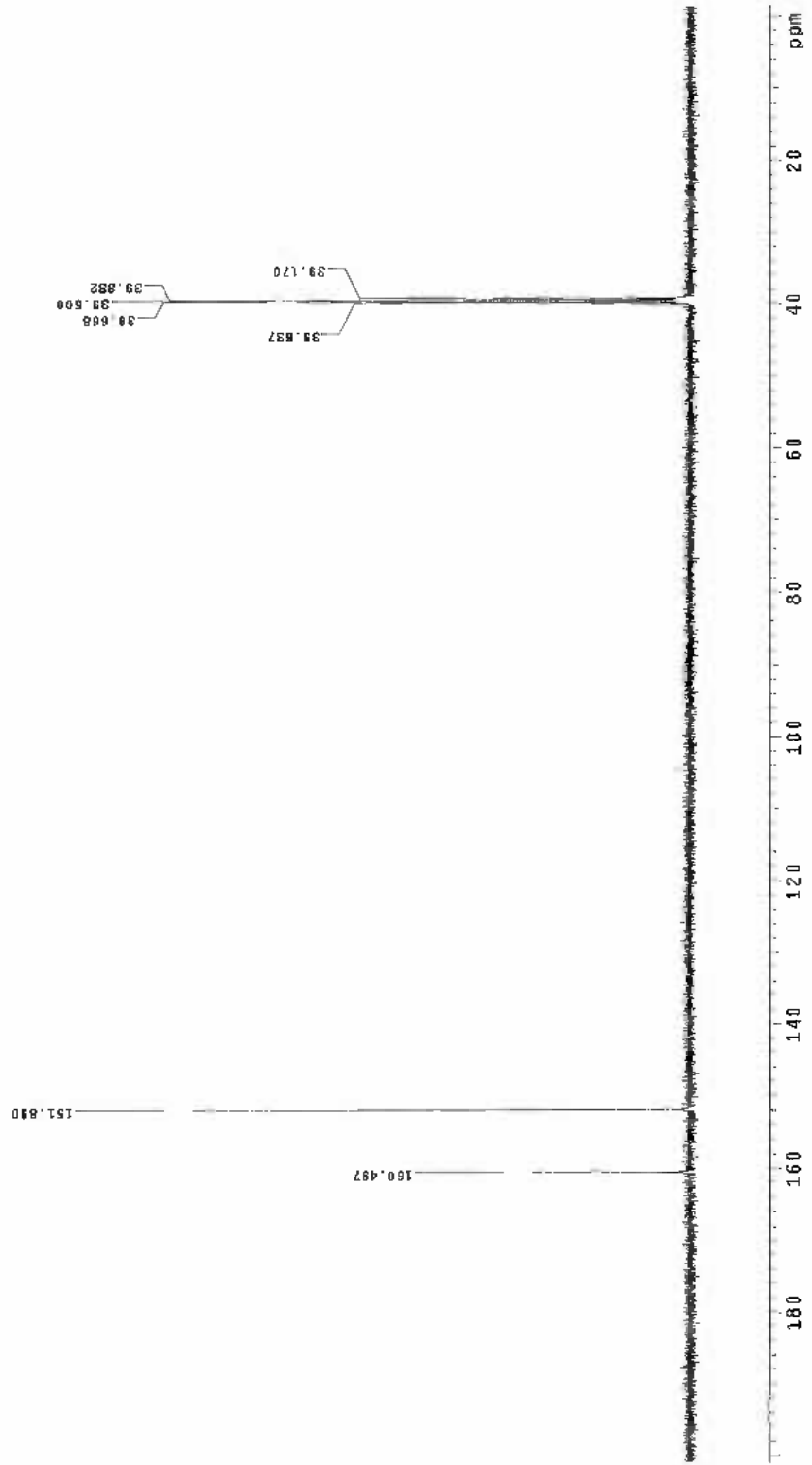
JH_LL2M07H, 25Mar08, mw
Pulse Sequence: #2pu1



17A, Cu, EL2M048A

19C_EL2M07H, 25Mar03, mw

Pulse Sequence: s2pul

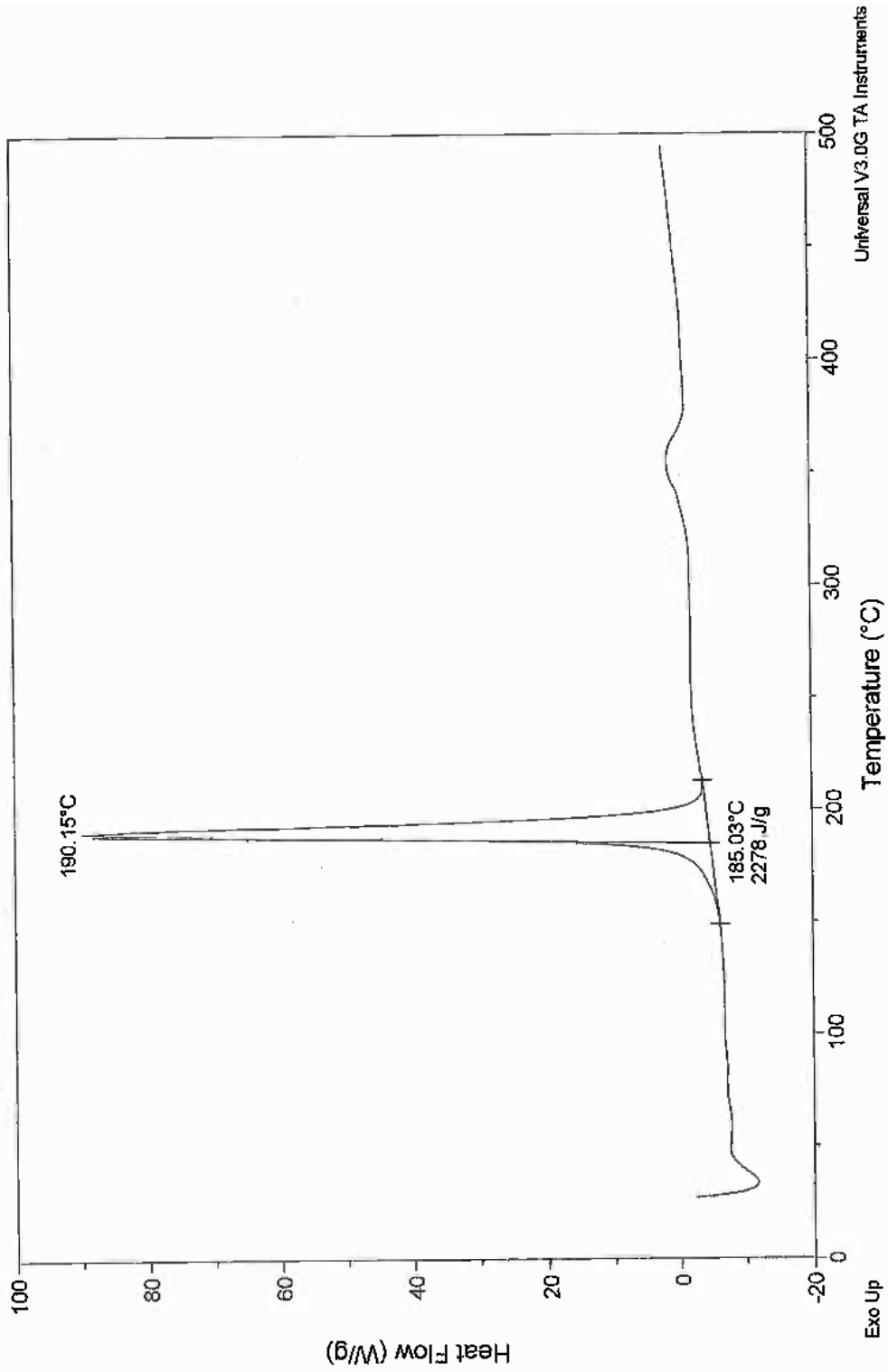


17A, Cu, EL2M056A

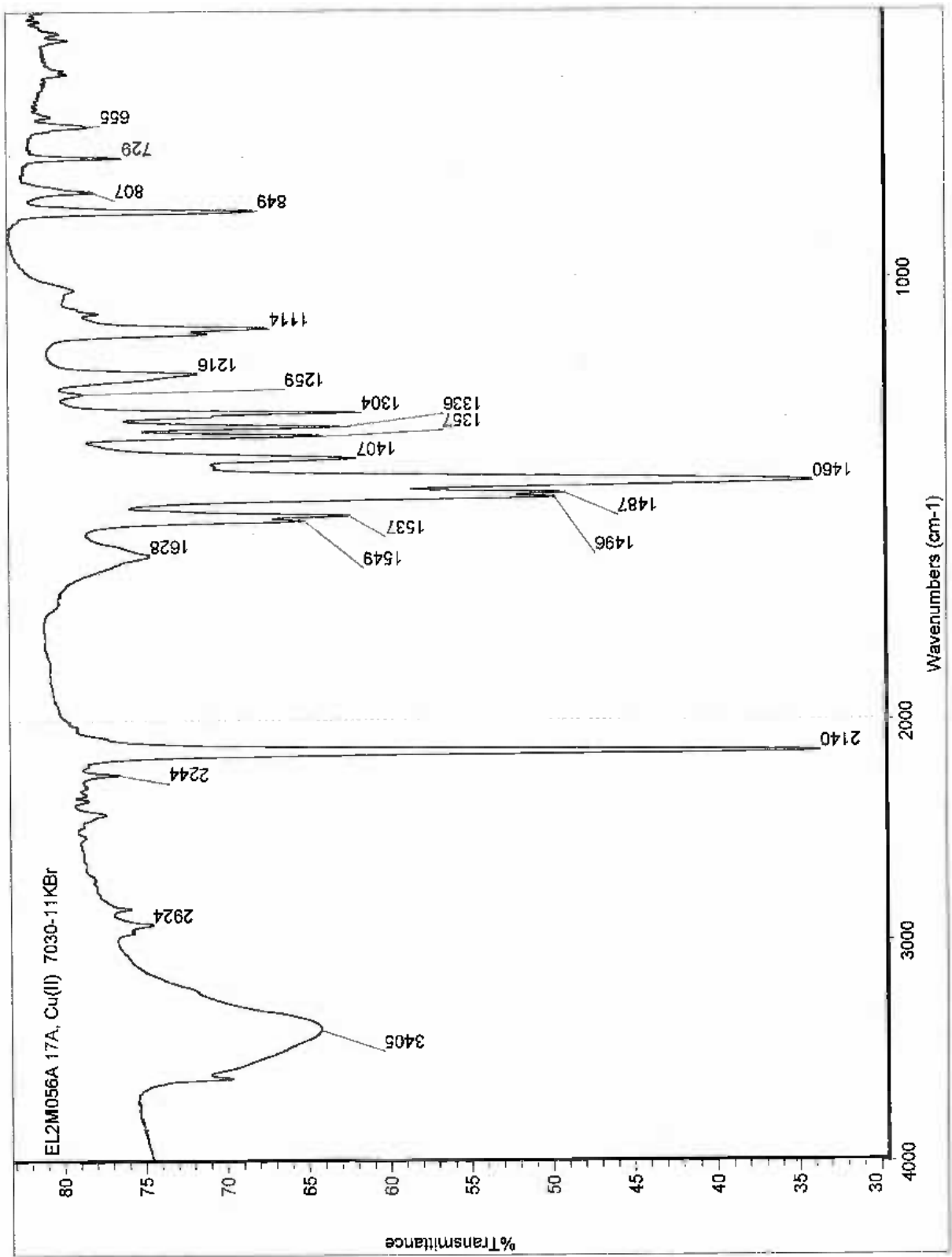
File: D:\Data\DS\JWF\7030-11\EI2m057a.002
Operator: Grum
Run Date: 16-Oct-03 10:09

DSC

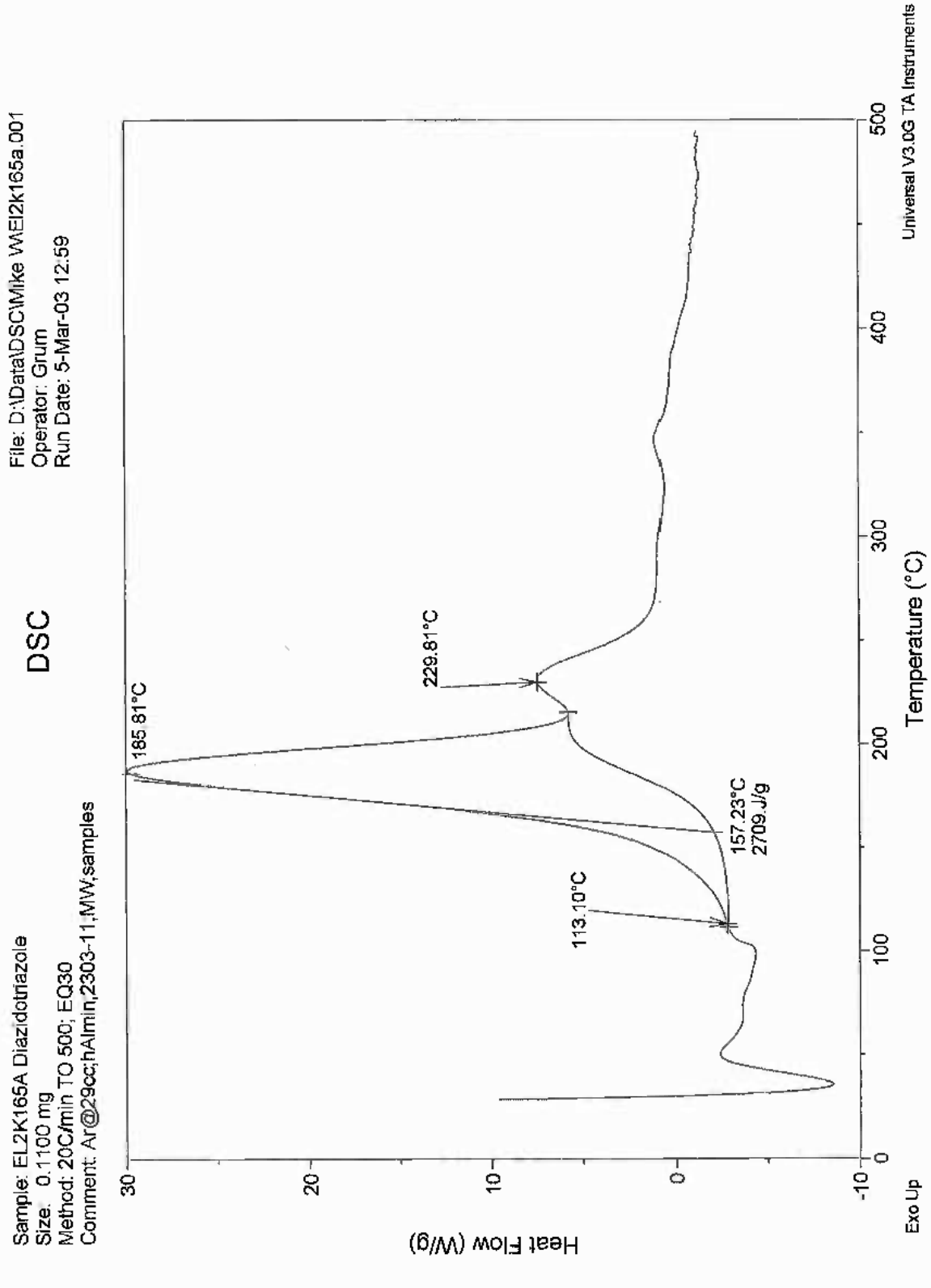
Sample: EL2M056A, 17A, Cu
Size: 0.1600 mg
Method: 20C/min TO 500; EQ30
Comment: Ar@29cc;hAlmin,7030-11, JWF



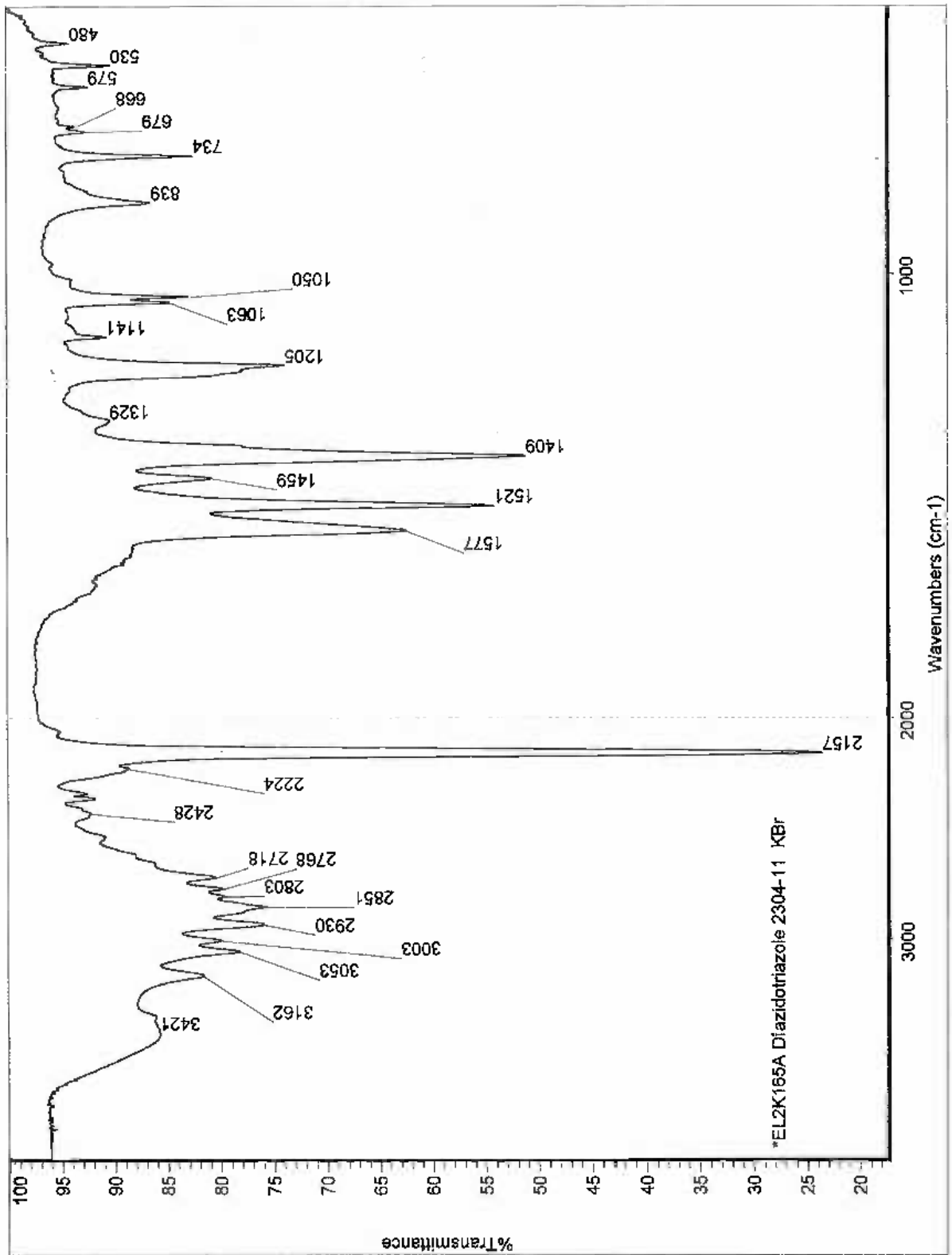
17A, Cu, EL2M056A



18A, Base material, EL2K165A

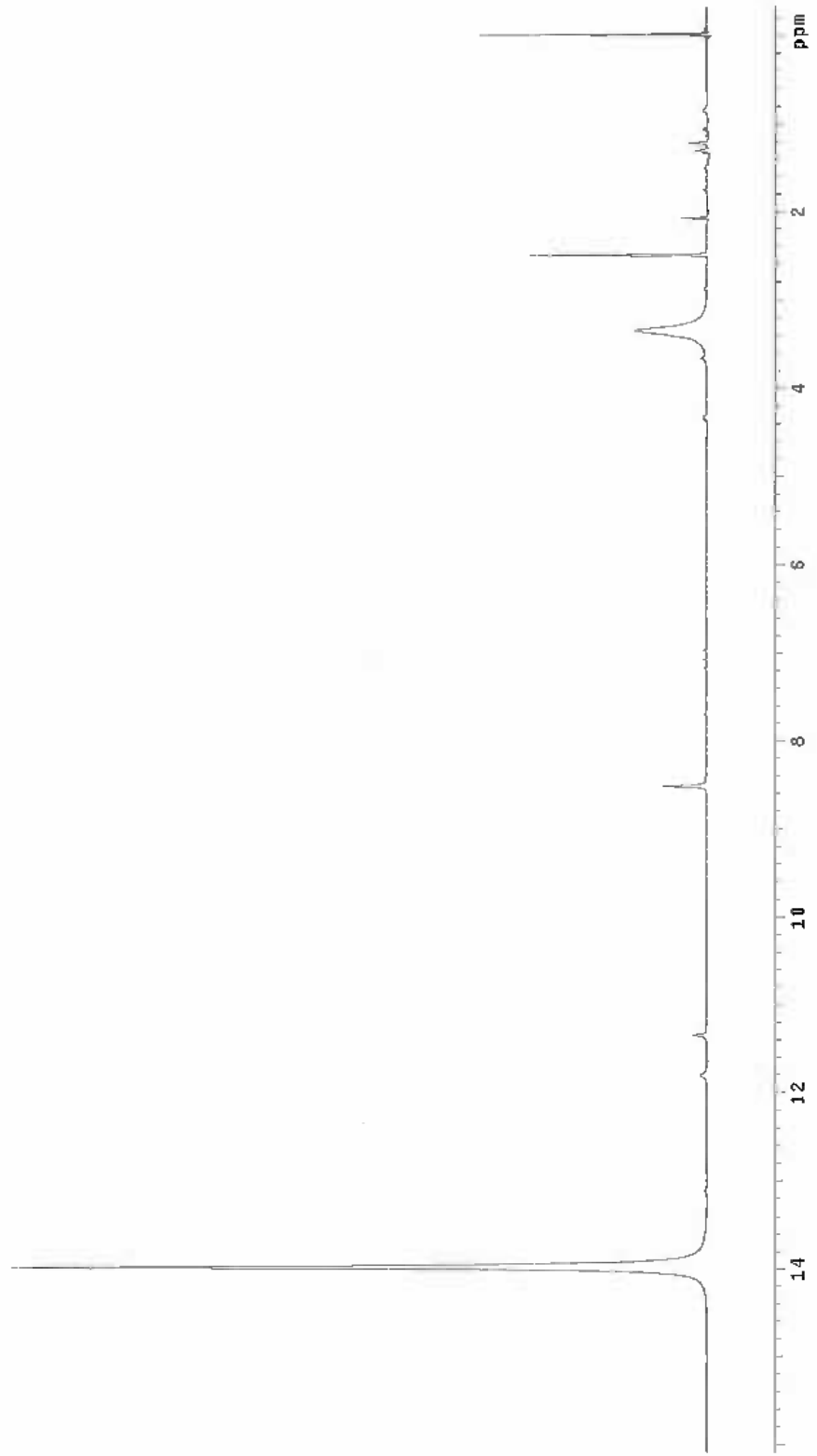


18A, Base material, EL2K165A



18A, Base material, EL2K165C

1H_EL2K165C, 25Mar03, mw
Pulse Sequence: zgpg30

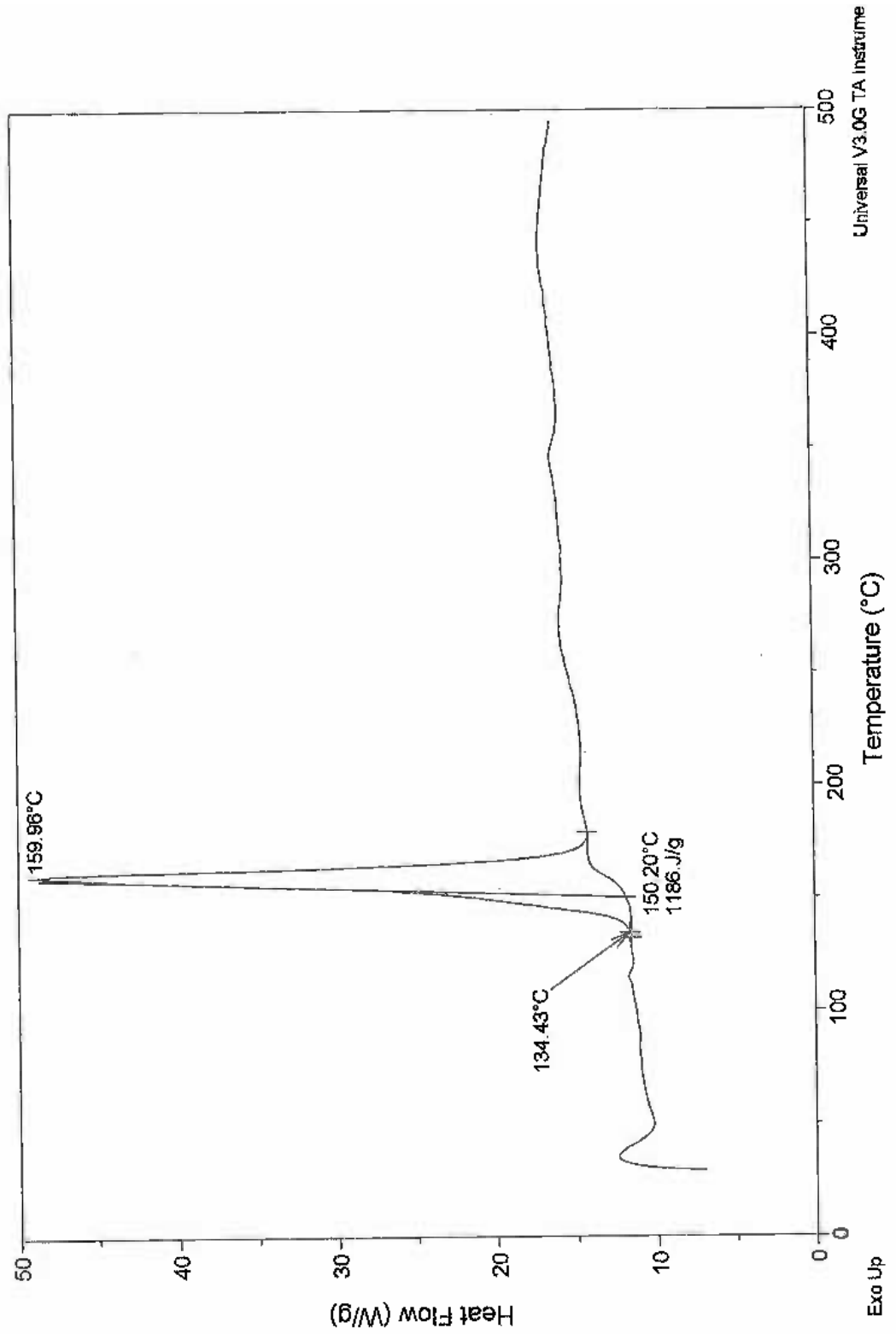


18A, Sr complex, EL2K103B

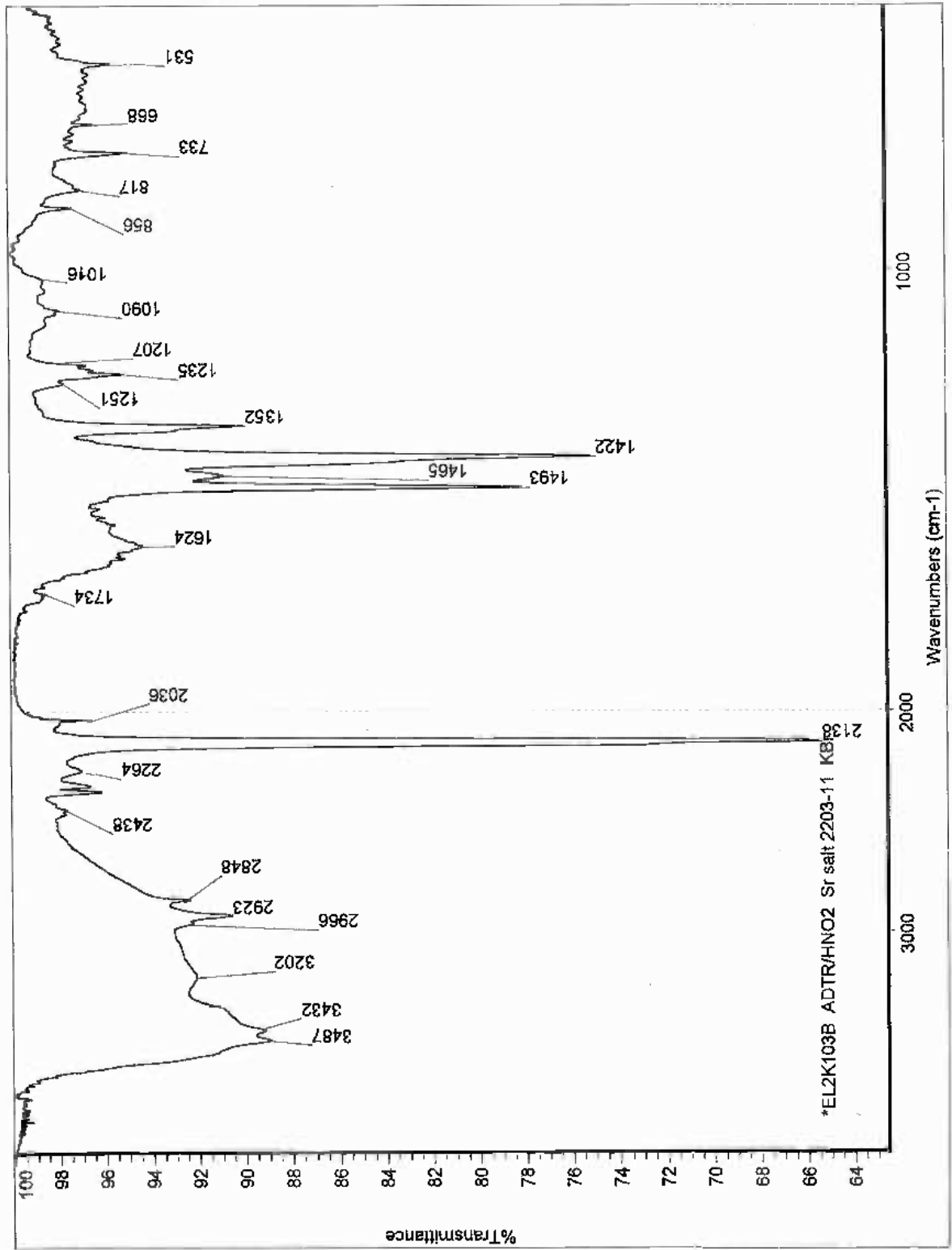
File: D:\Data\DSC\Mike WEI2k103b.001
Operator: Grum
Run Date: 18-Nov-02 10:02

DSC

Sample: EL 2K103B Sr salt
Size: 0.1000 mg
Method: 20C/min TO 500; EQ30
Comment: Ar@29cc;hAlmin;2203-11;MW;samples



18A, Sr complex, EL2K103B

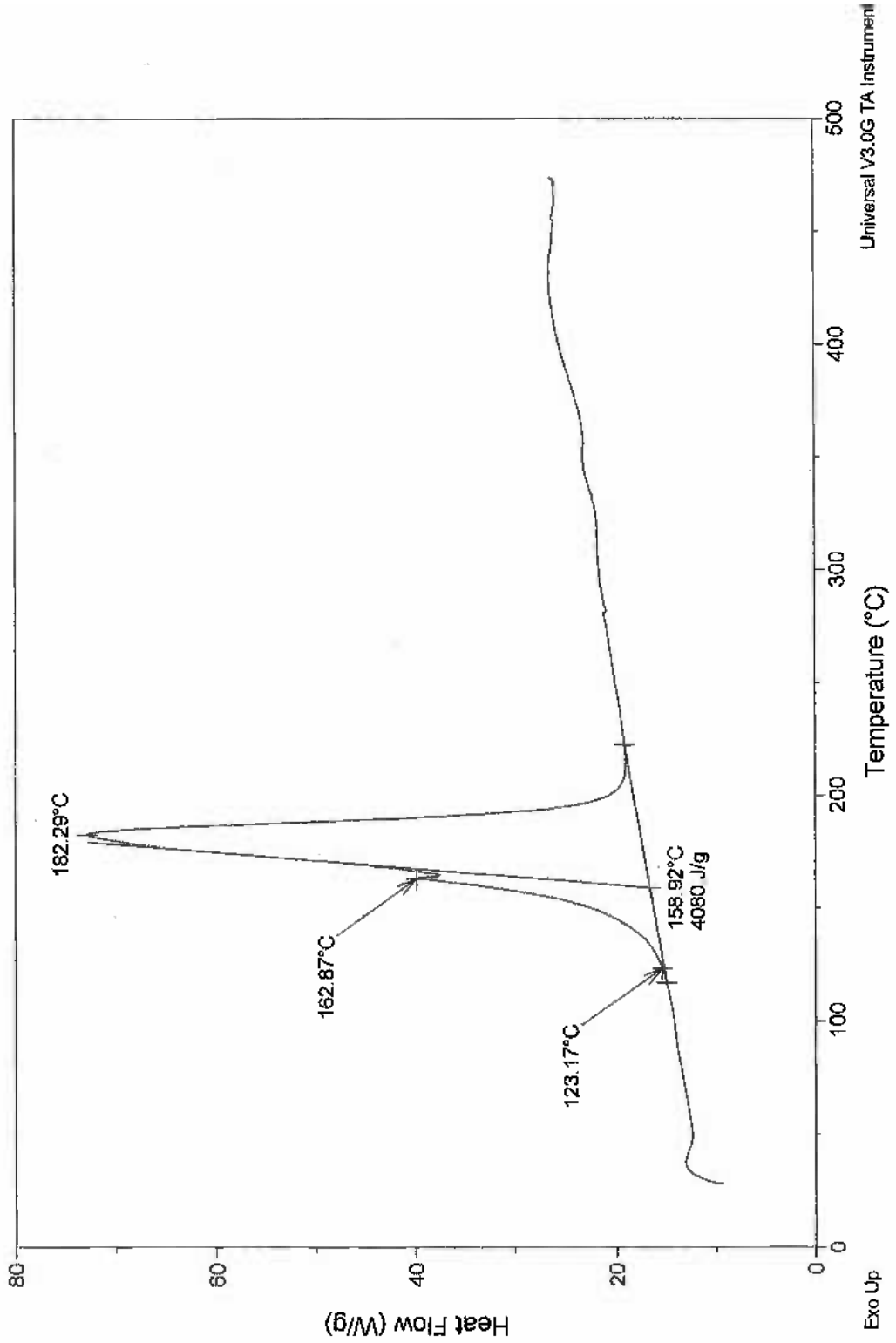


18A, Cu complex, EL2K110A

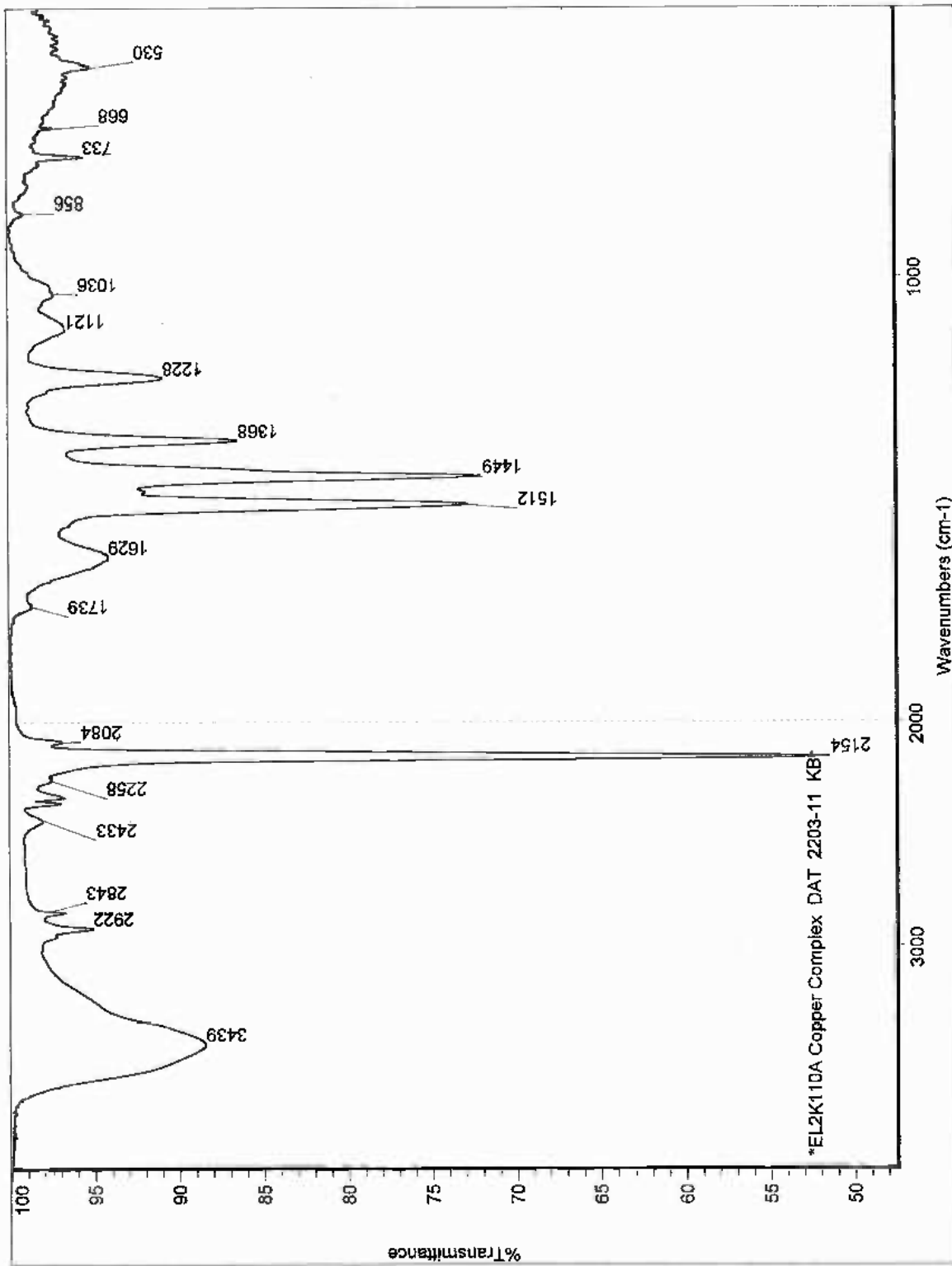
File: D:\Data\DSC\Mike W\EL2K110a.001
Operator: Grum
Run Date: 2-Dec-02 09:39

DSC

Sample: EL2K110A copper complex DAT
Size: 0.1000 mg
Method: 20C/min TO 500; EQ30
Comment: Ar@29cc; hAlmin;2203-11;MW:samples



18A, Cu complex, EL2K110A

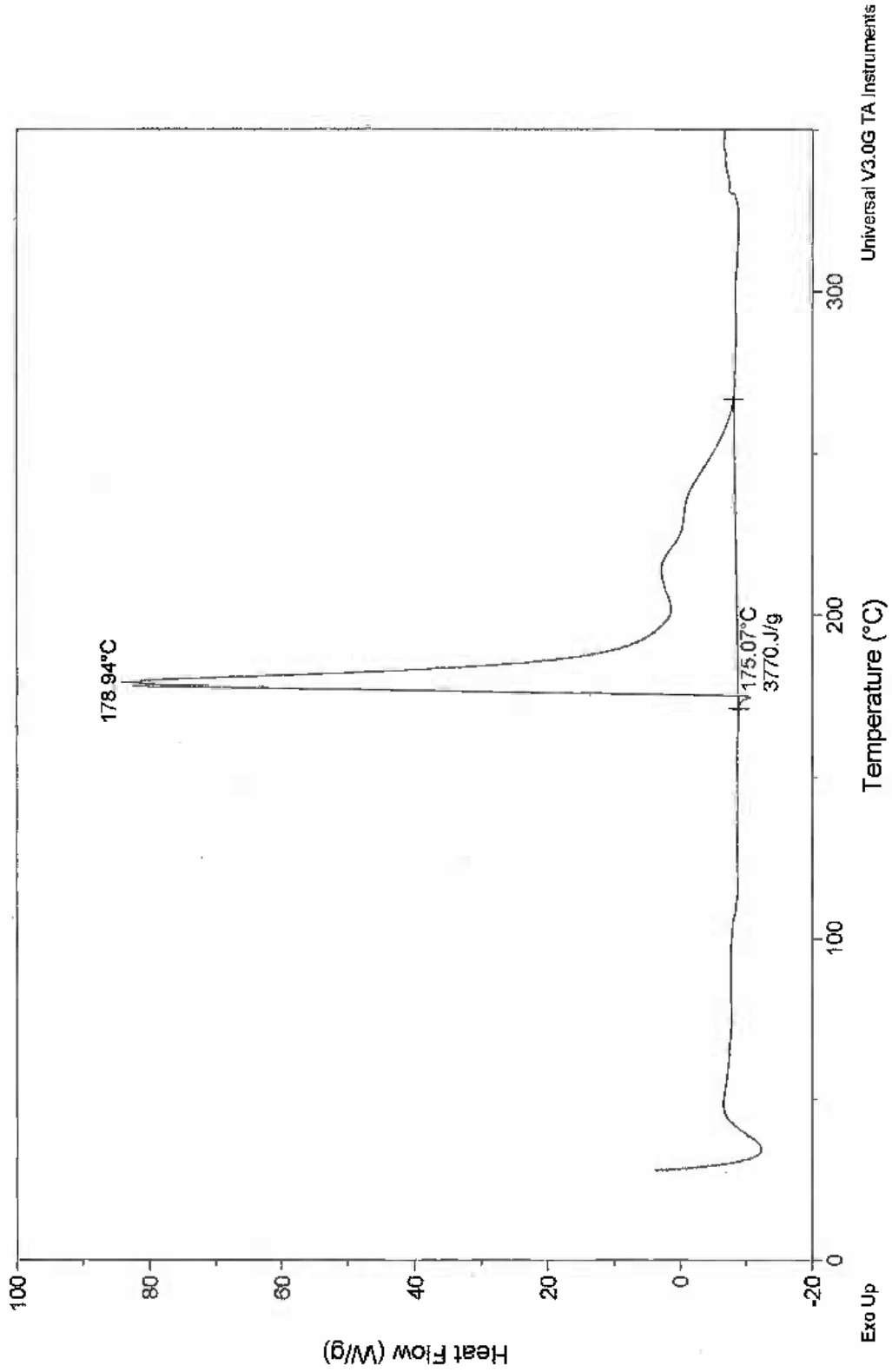


19A, Base material, EL20110A

File: D:\Data\DSC\Mike WEL20\EL20110a.001
Operator: Williams
Run Date: 6-Oct-03 08:43

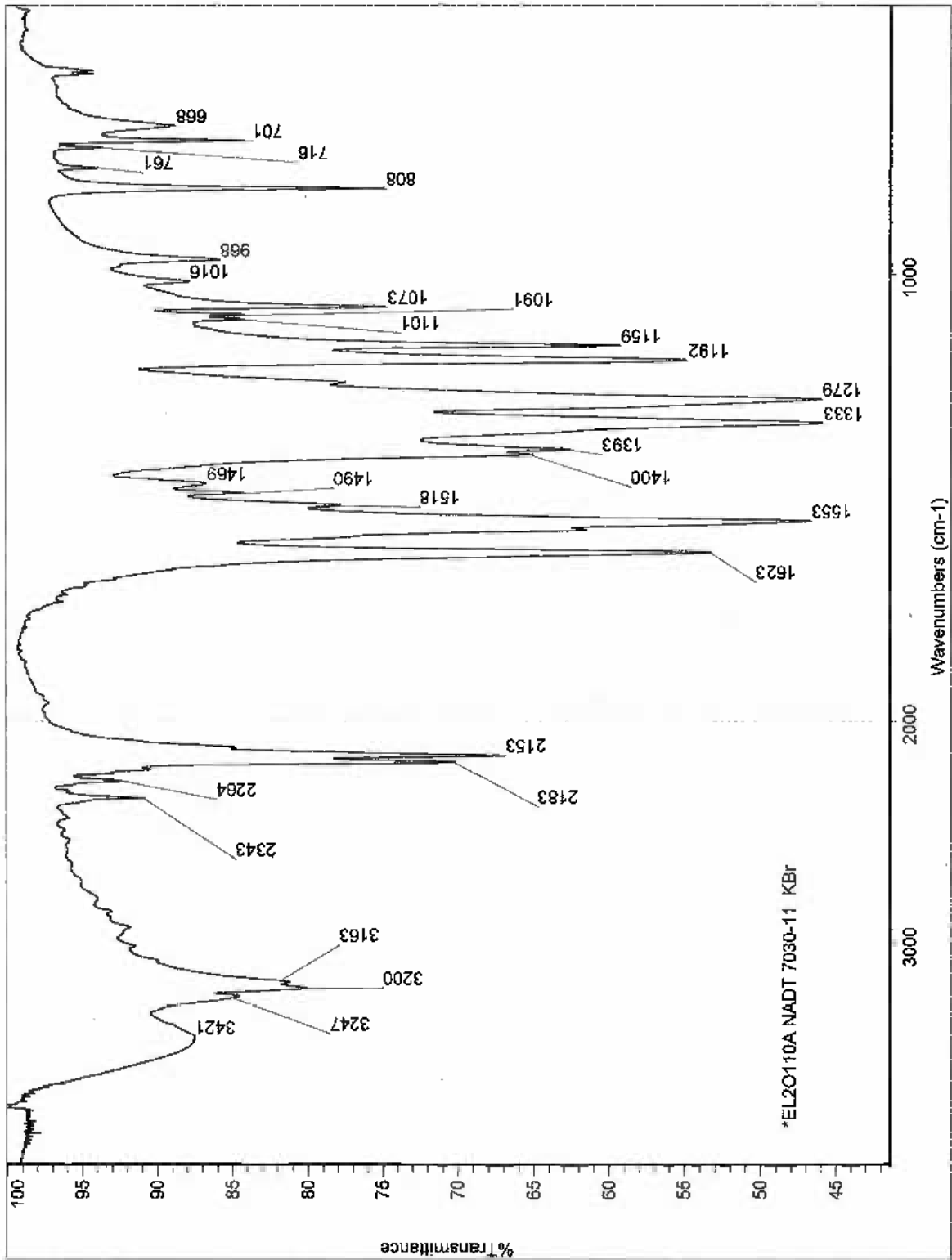
DSC

Sample: EL20110A, NACT
Size: 0.1300 mg
Method: Ramp 20_500
Comment: Ar@29cc;hAlmin, 7030-11, MDW

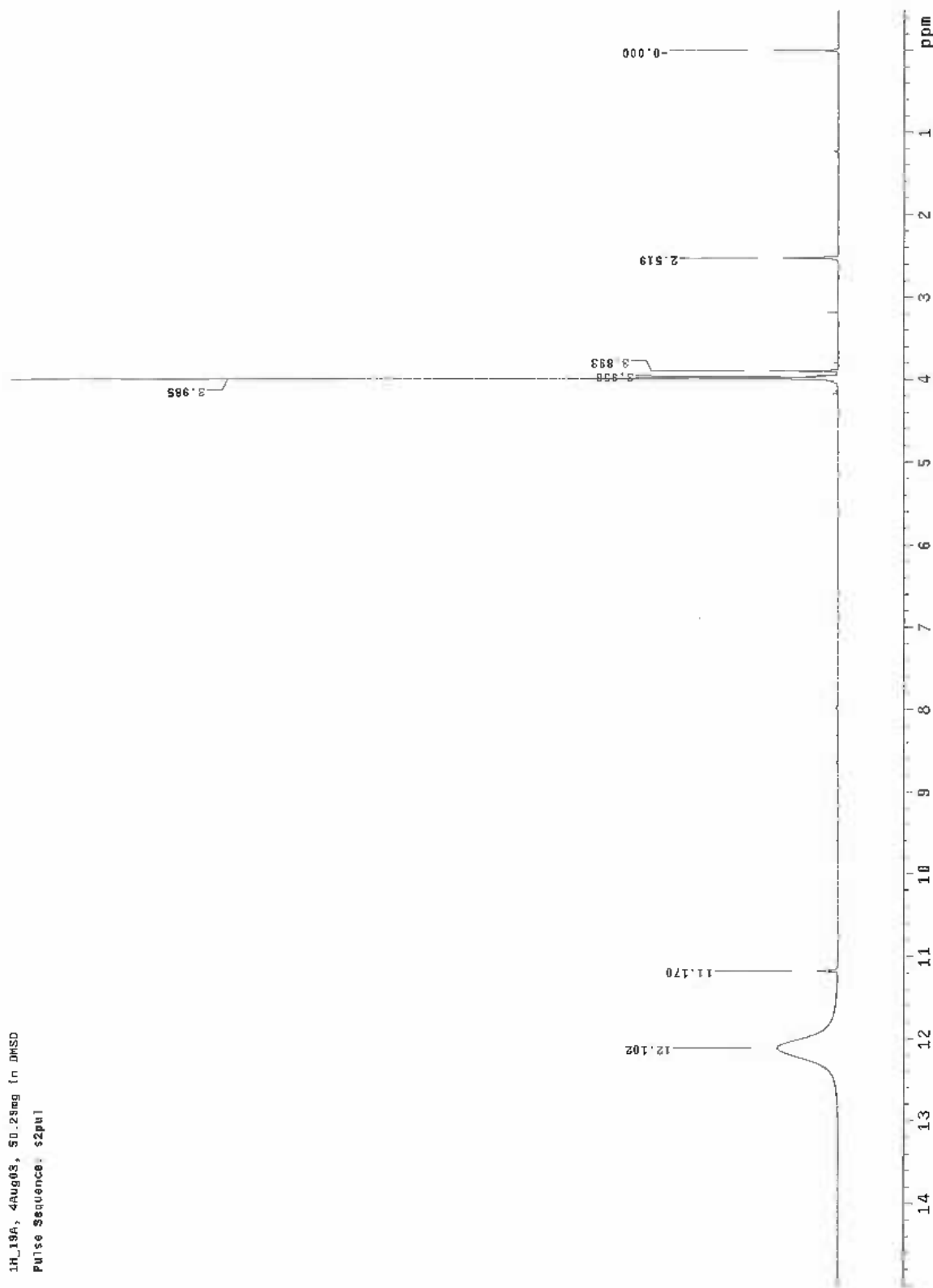


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19A, Base material, EL20110A



19A, Base material, EL2O110A

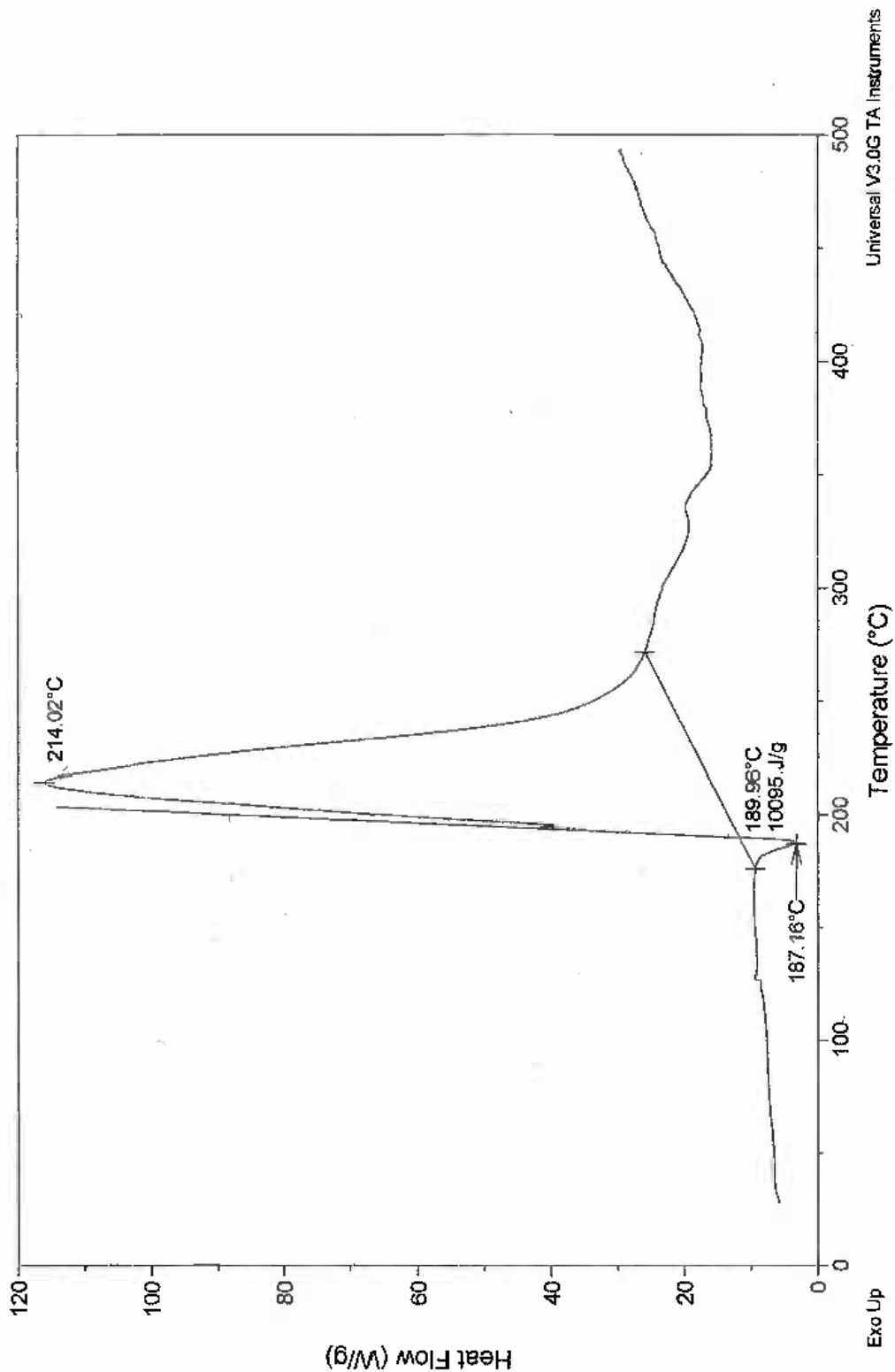


19A, rubidium salt, EL20117A

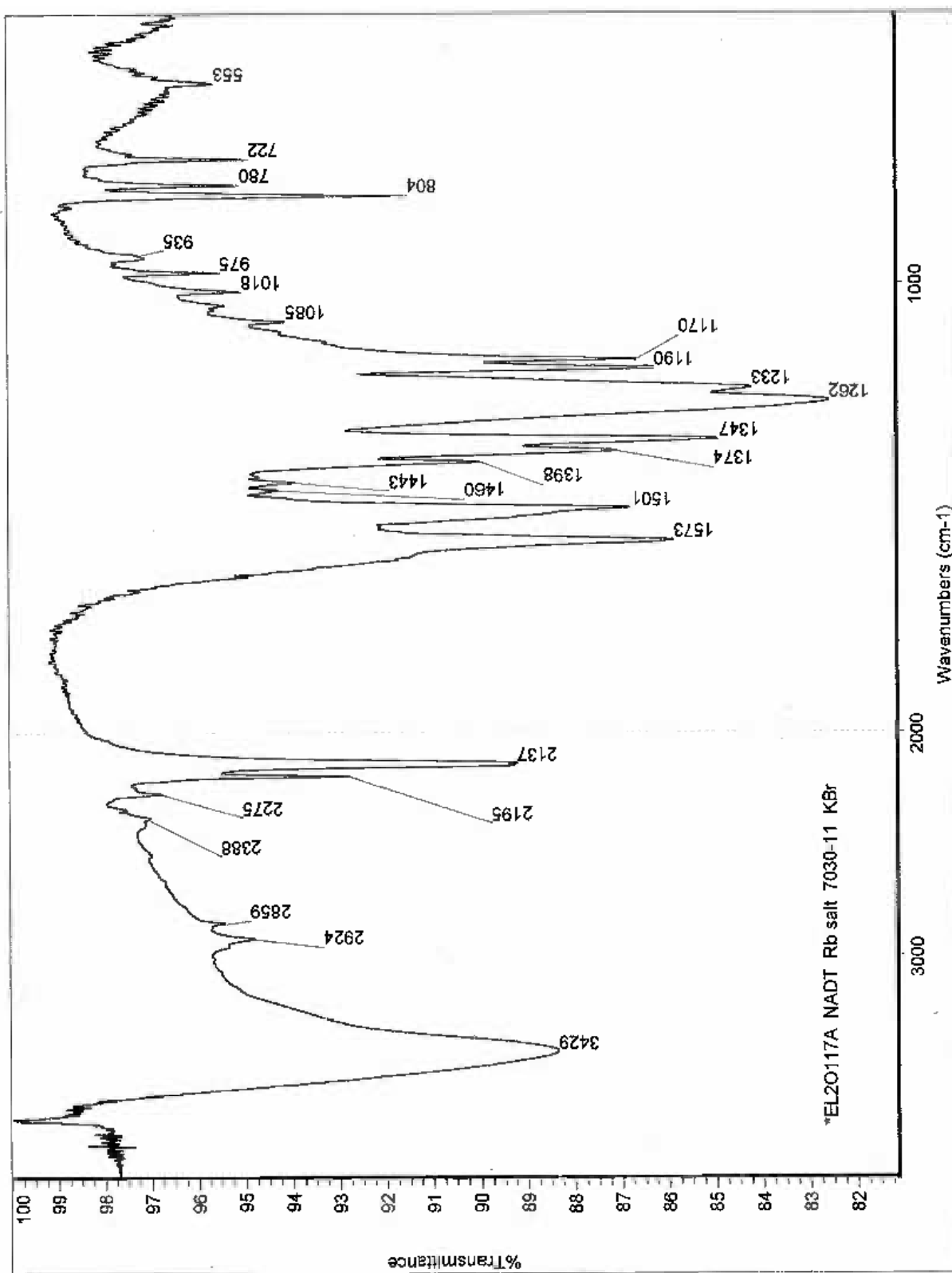
File: D:\Data\DSC\Mike W\EL20117a\17a.003
Operator: Grum
Run Date: 14-Oct-03 11:18

DSC

Sample: EL20117A NADT Rb salt
Size: 0.0600 mg
Method: 20C/min TO 500. EQ30
Comment: Ar@29cc;hAlmin 7030-11;MW



19A, rubidium salt, EL20117A

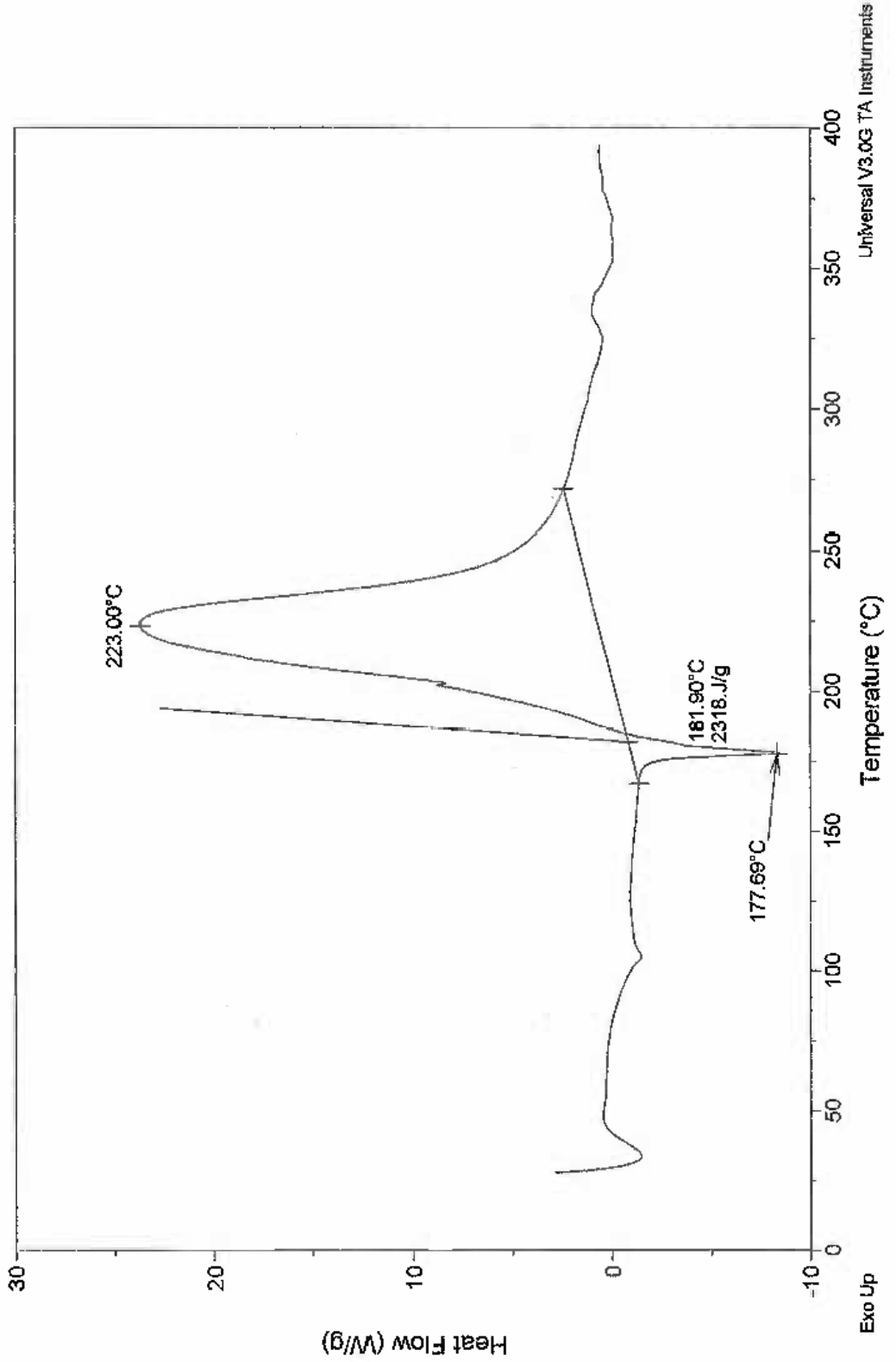


19A, cesium salt, EL20122A

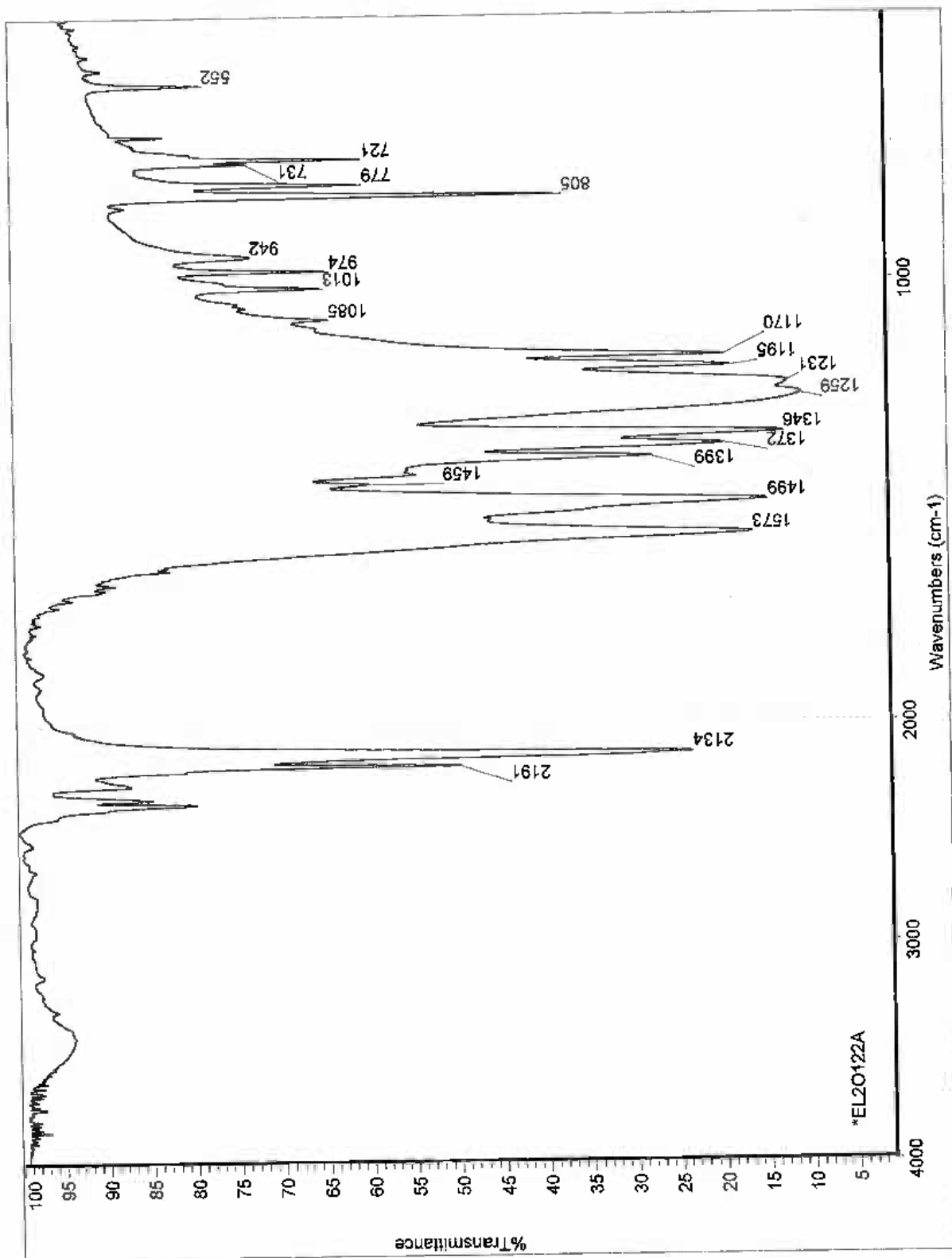
File: D:\Data\DSC\Mike WEL20\EL20122a.003
Operator: Grum
Run Date: 20-Oct-03 13:27

DSC

Sample: EL20122A, NADT, Cs salt
Size: 0.1400 mg
Method: BNCP 20C/min TO 400; EQ30
Comment: Ar@29cc;Almin, MDW



19A, cesium salt, EL20122A

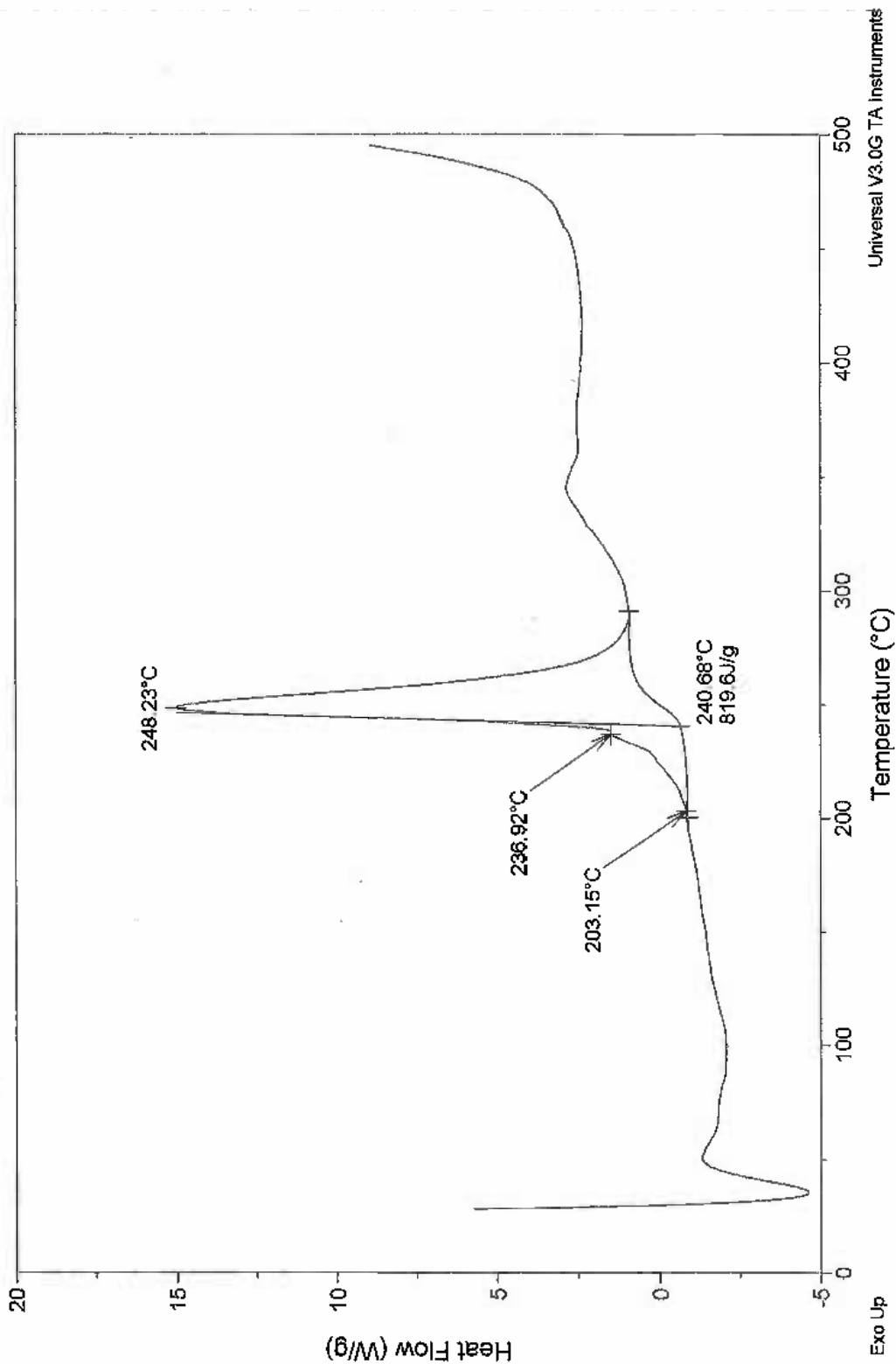


20A, precursor, EL2K199A

File: D:\Data\DSC\Mike WEI2k199a.001
Operator: Grum
Run Date: 22-Apr-03 14:13

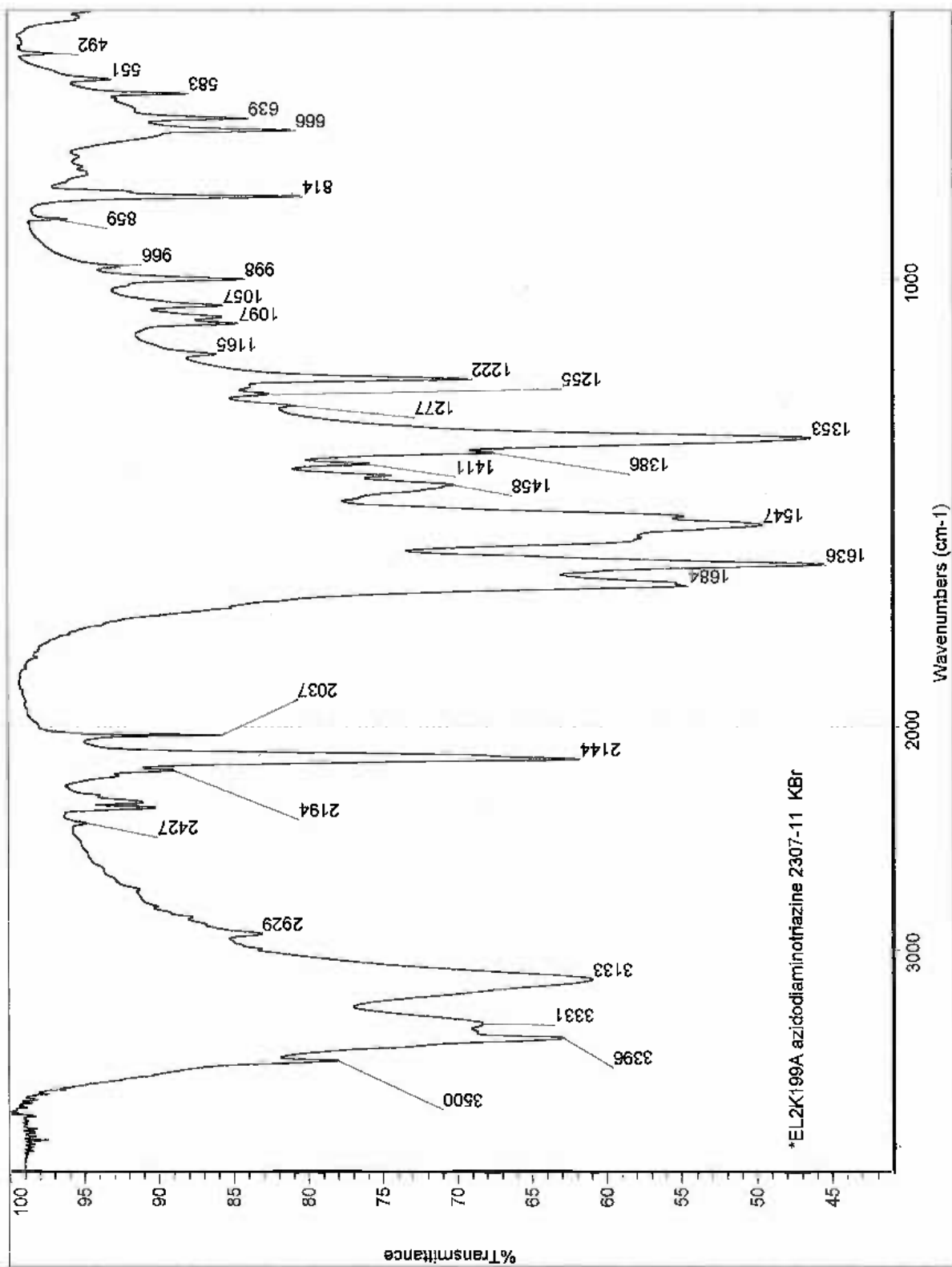
DSC

Sample: EL2K199A
Size: 0.1700 mg
Method: 20C/min TO 500, EQ30
Comment: Ar@29cc/hr/min; 2307-1; MW; samples

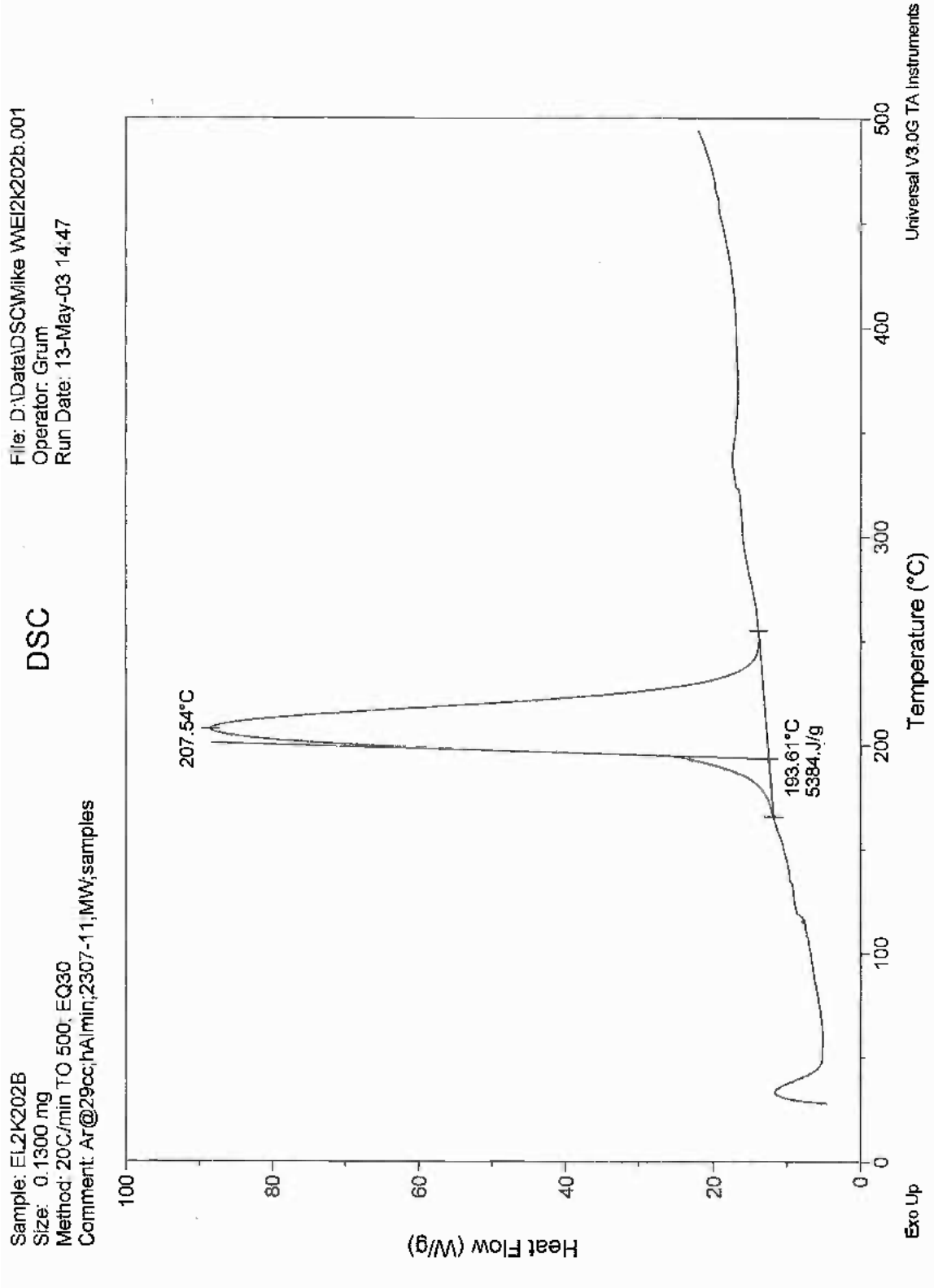


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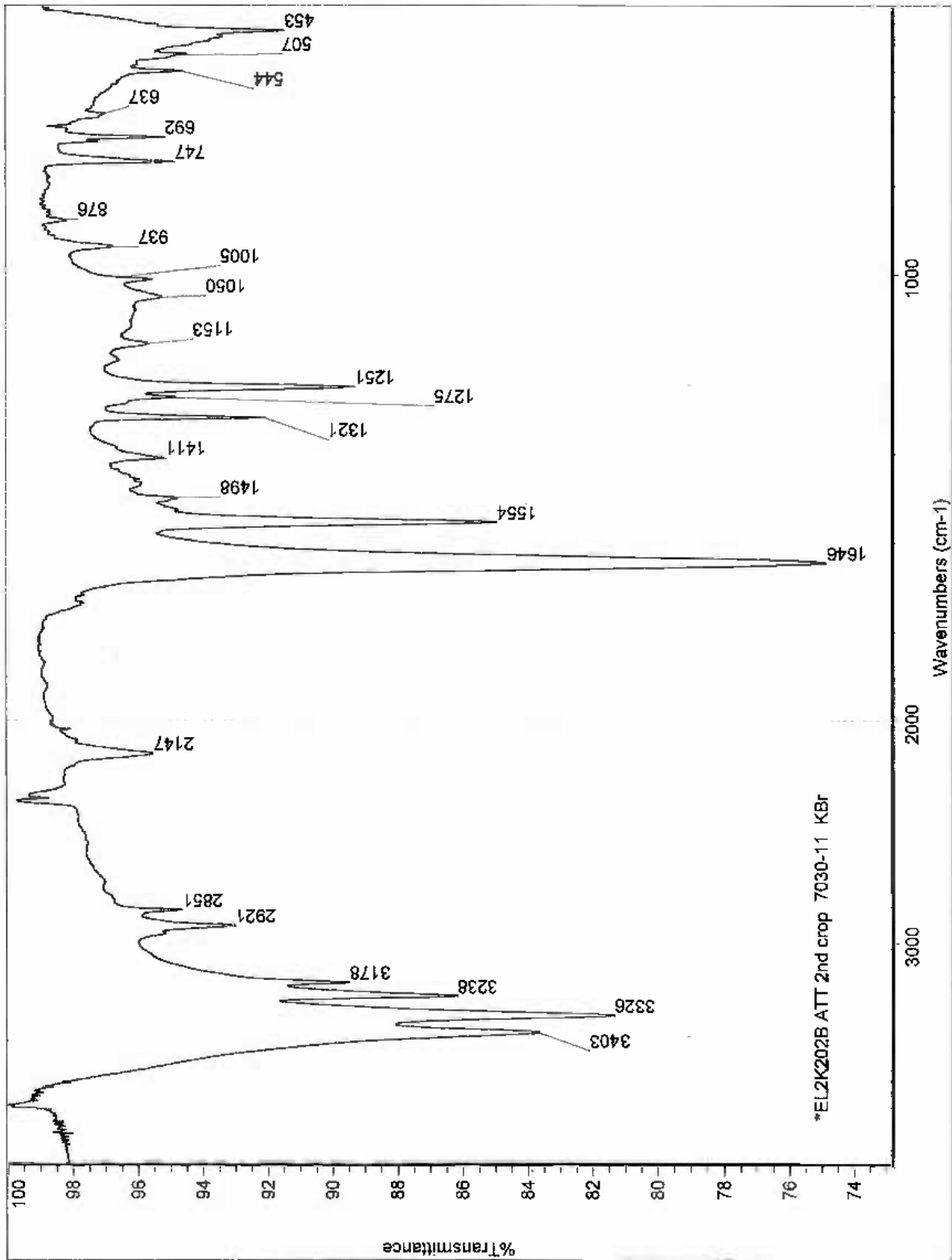
20A, precursor, EL2K199A



21A, Base material, EL2K202B



21A, Base material, EL2K202B

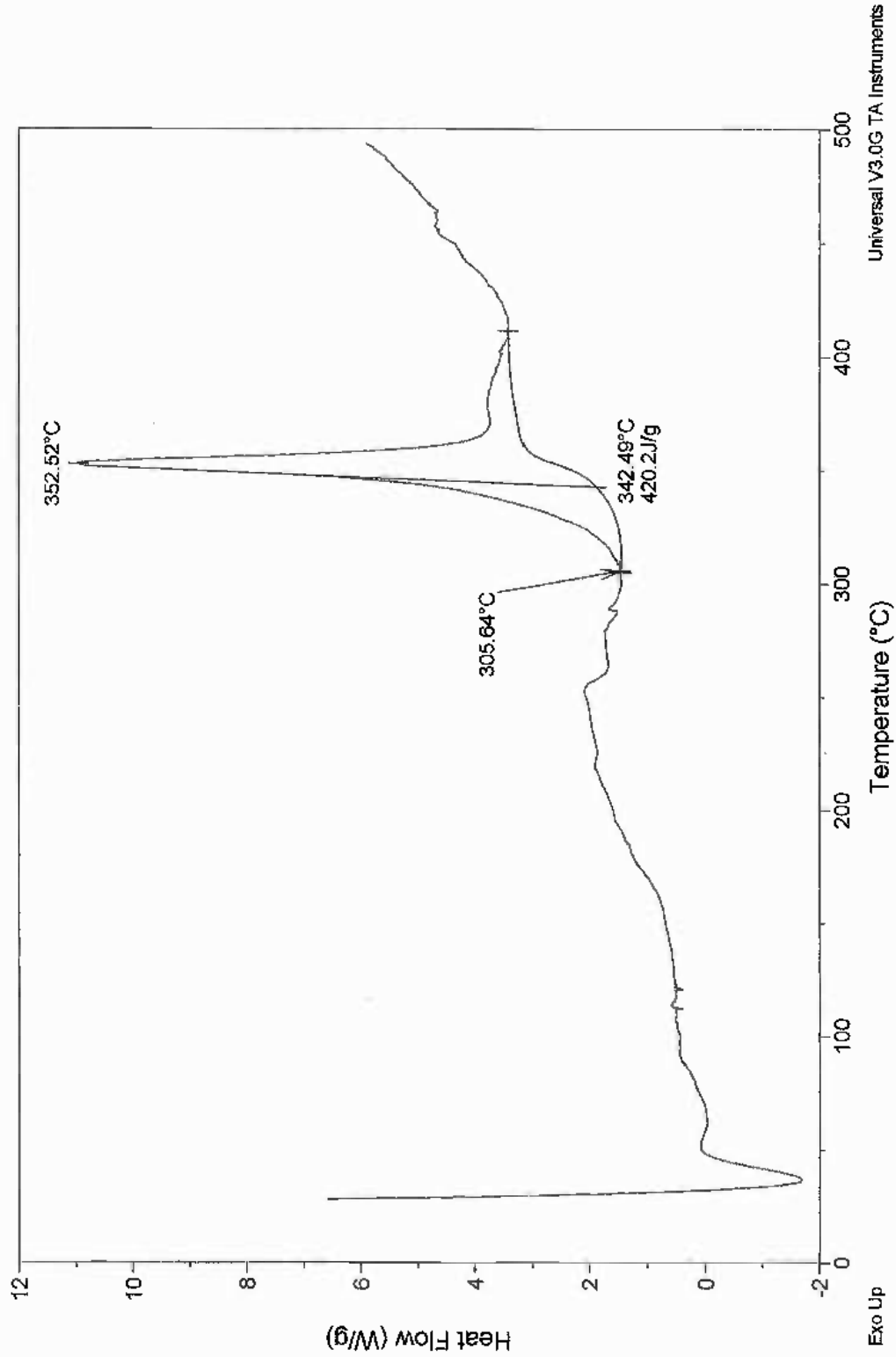


22A, Base material, EL20014B

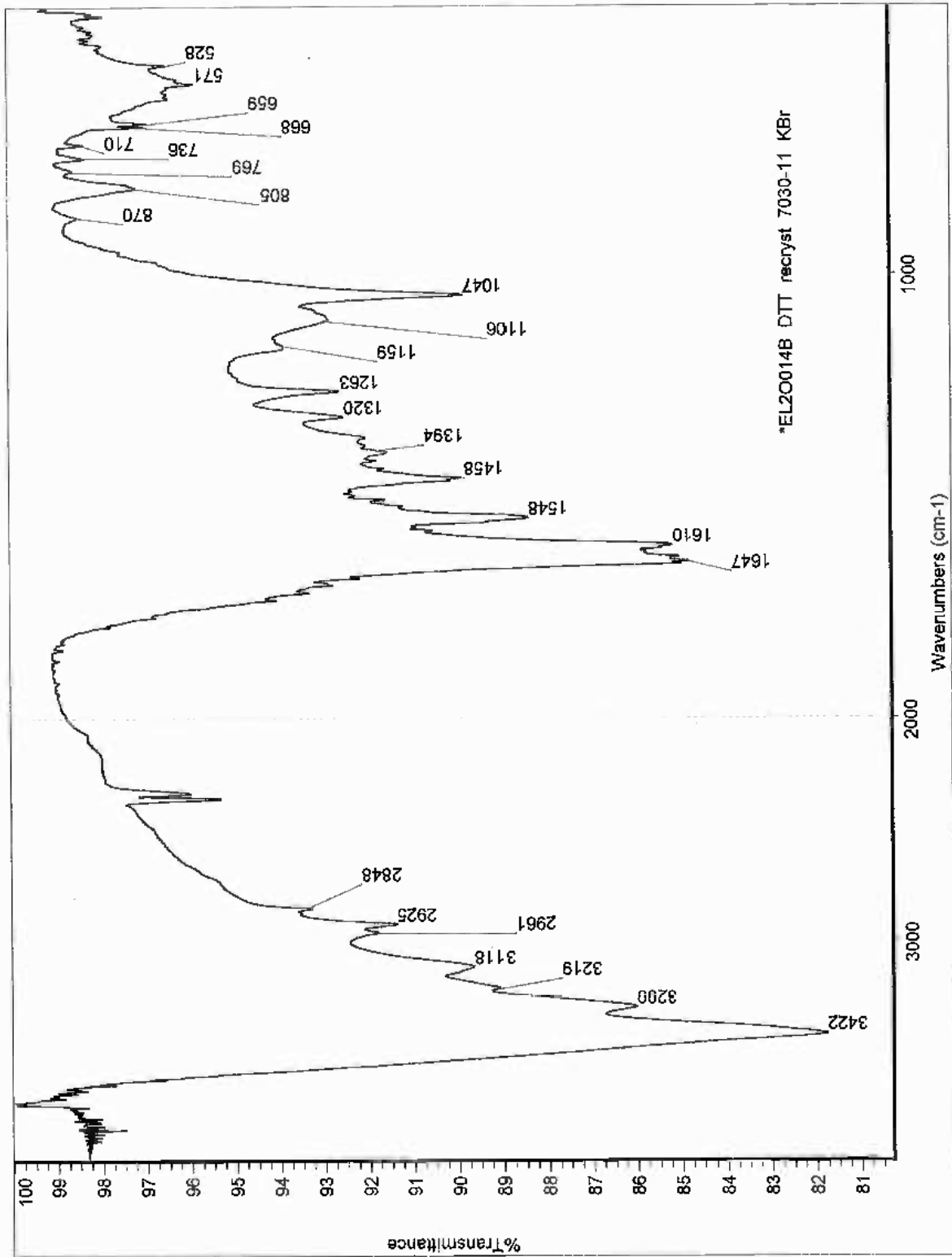
File: D:\Data\IDSC\Mike W\EL20\EL20014b.001
Operator: Grum
Run Date: 23-Jun-03 11:32

DSC

Sample: EL20014B recryst
Size: 0.1500 mg
Method: 20C/min TO 500; EQ30
Comment: Ar@29cc;hAlmin,2307-11;MW,samples



22A, Base material, EL20014B

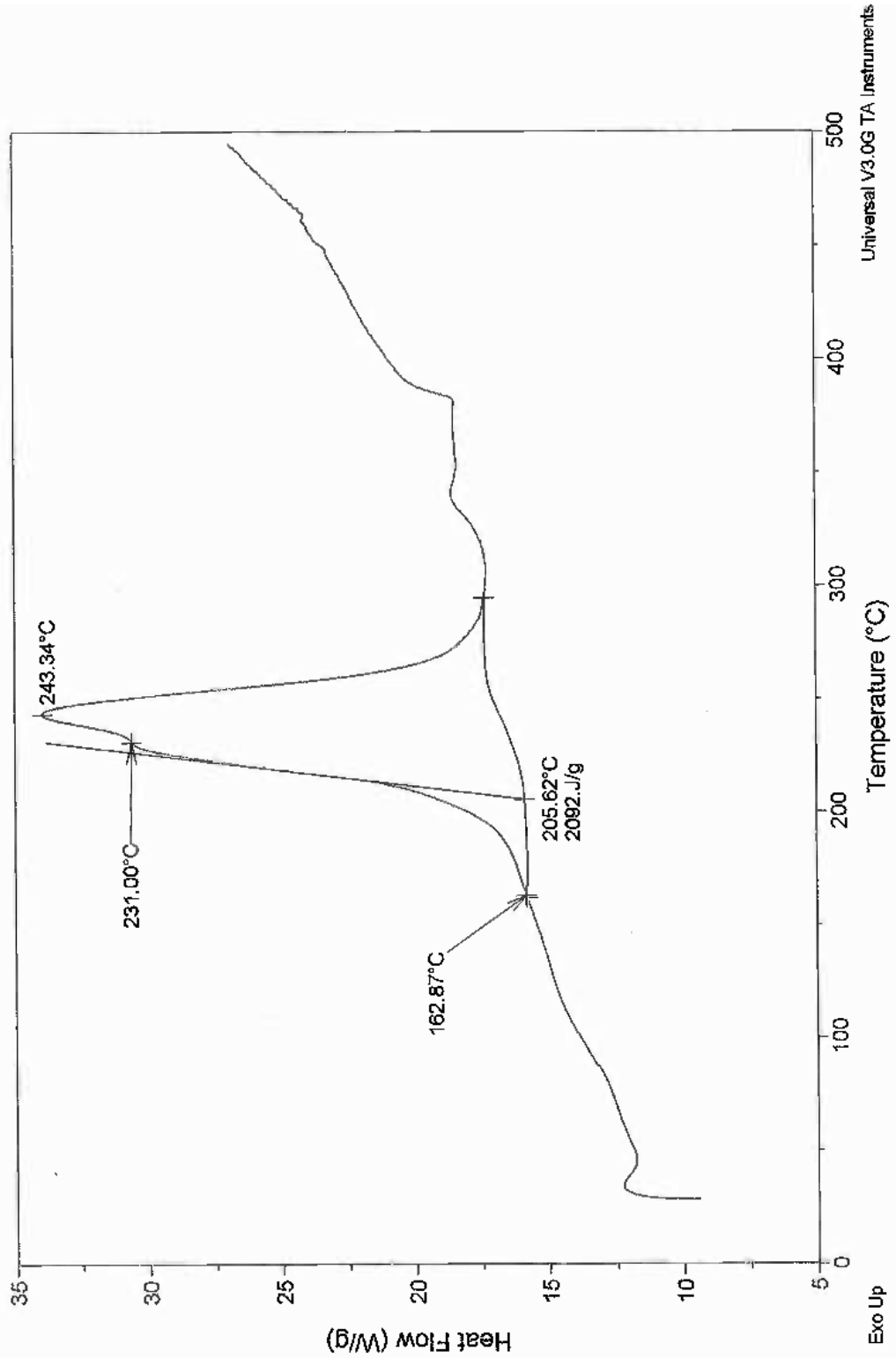


23A, Base material, EL2O013A

File: D:\Data\DSC\Mike W\EL2O\EL20013a.001
Operator: Grum
Run Date: 10-Jun-03 15:17

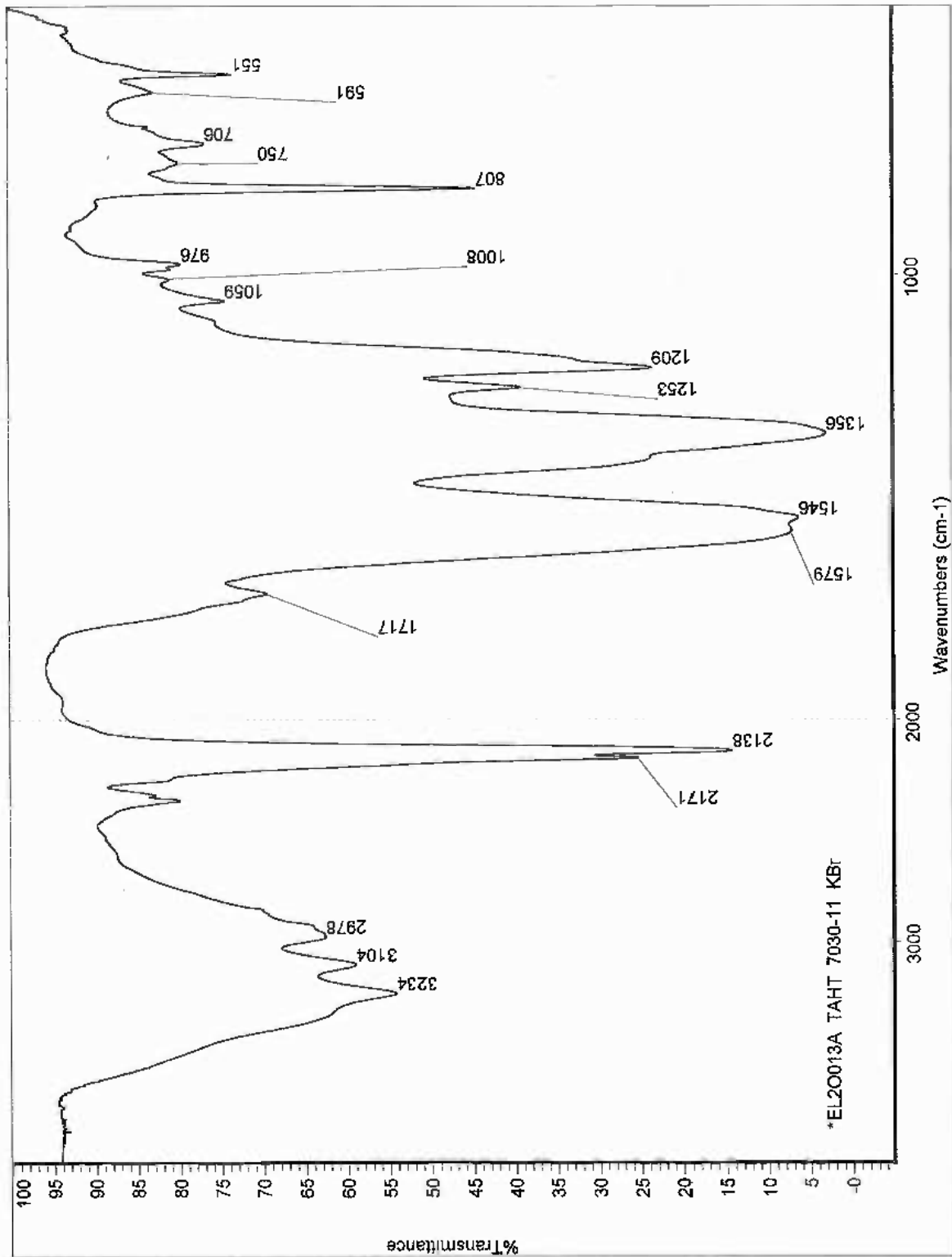
Sample: EL2O013A
Size: 0.1000 mg
Method: 20C/min TO 500: EQ30
Comment: Ar@29cc;hAlmin;7030-1;MW,samples

DSC

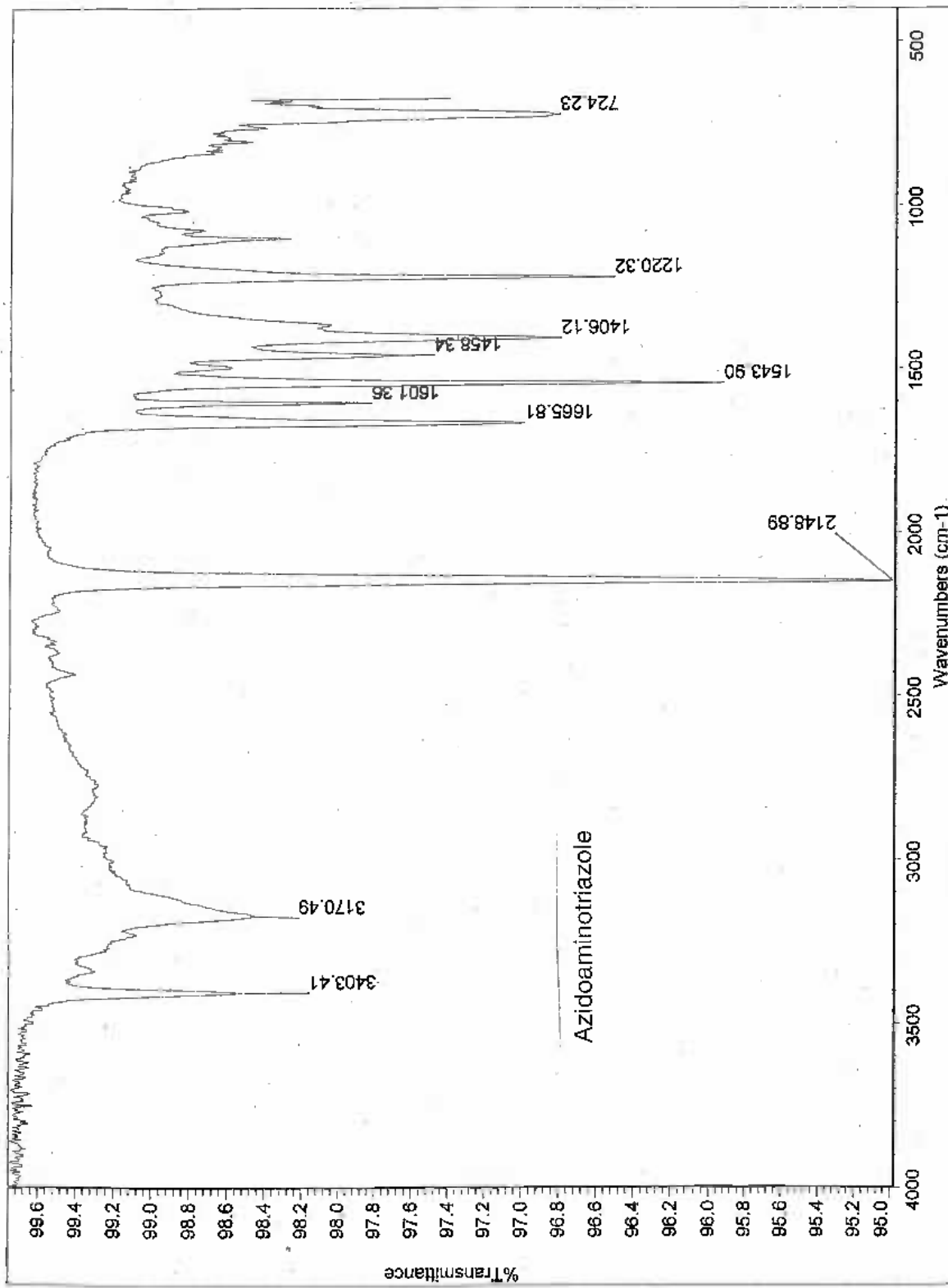


Universal V3.0G TA Instruments

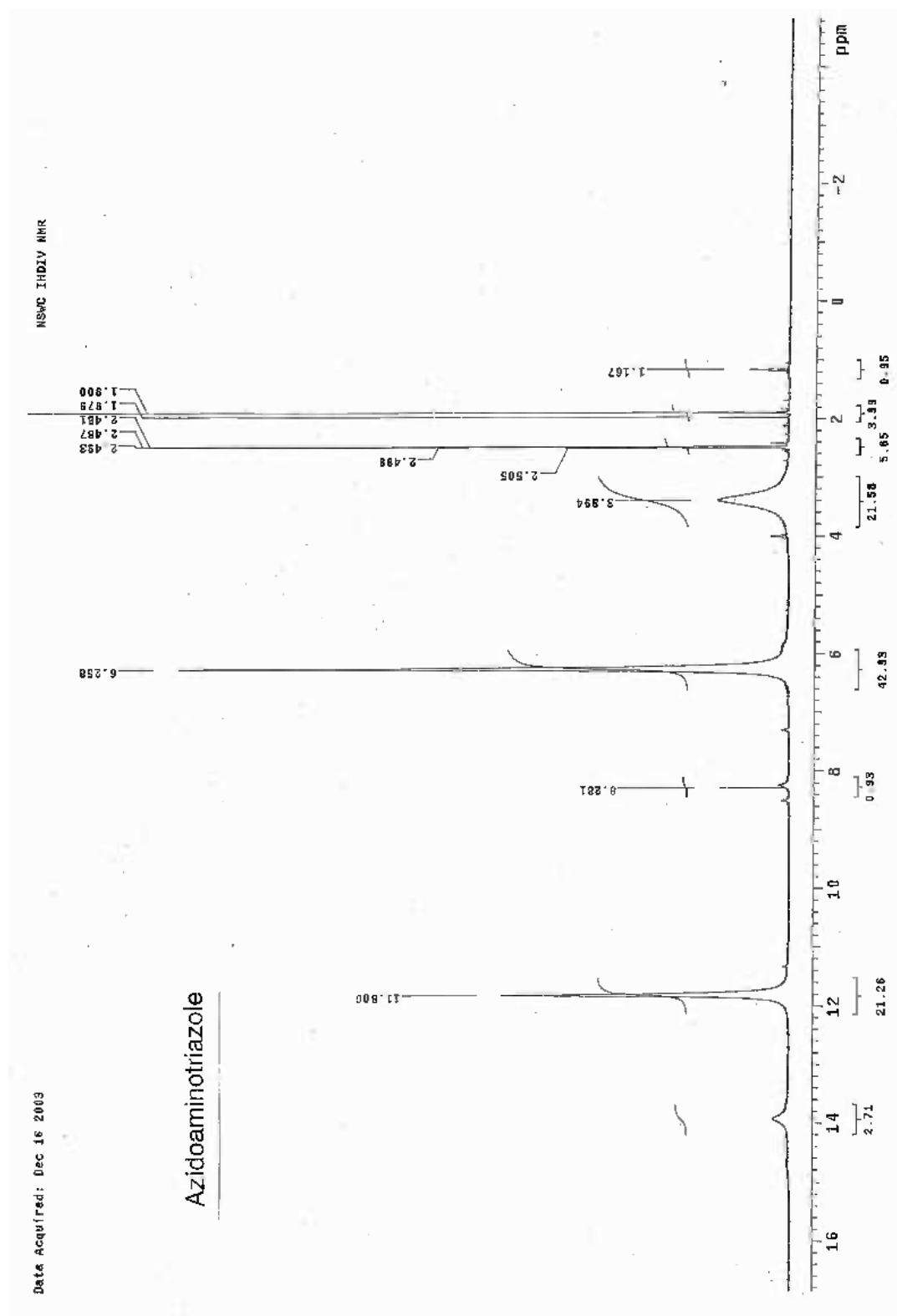
23A, Base material, EL2O013A



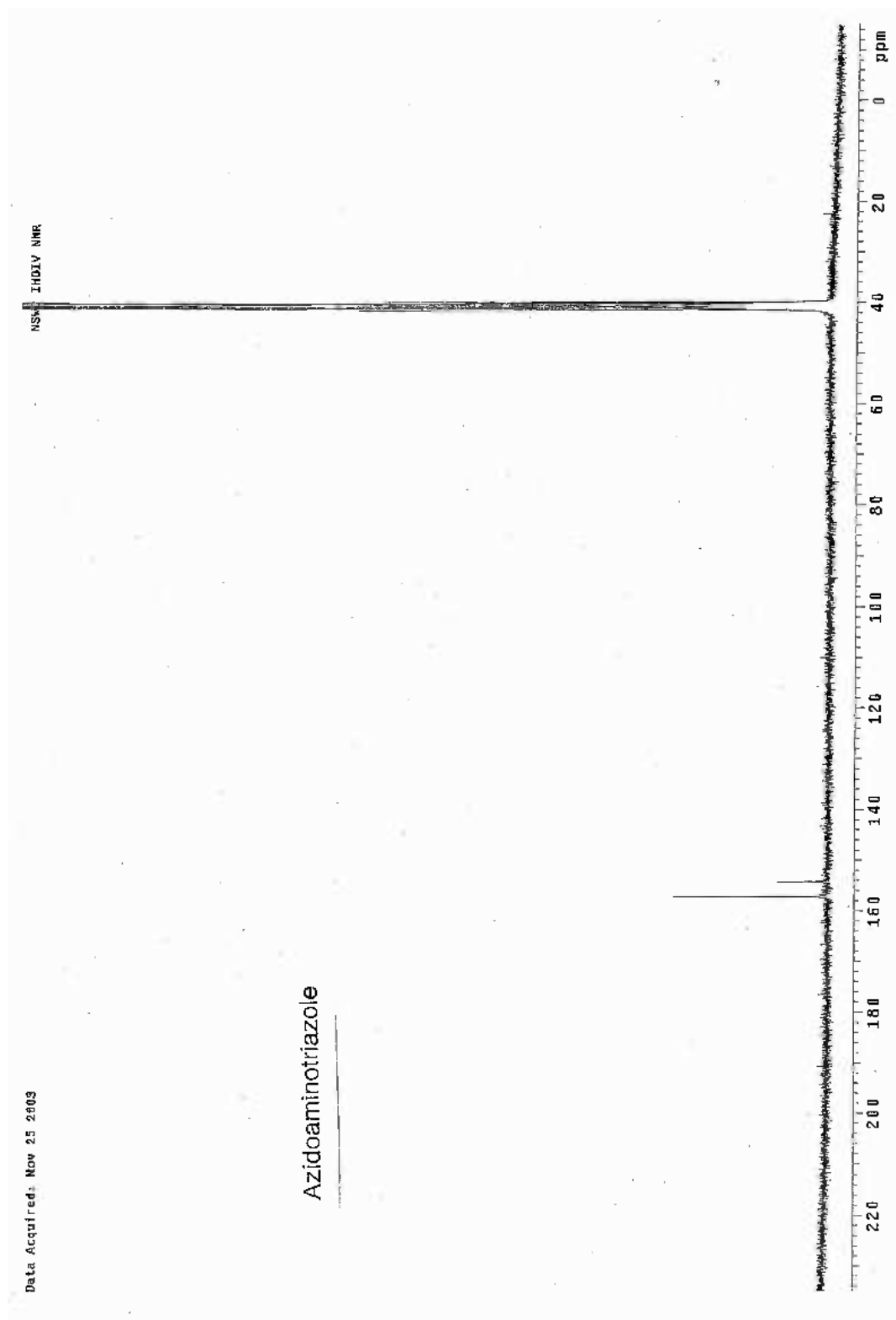
24A, Base material, 24A FTIR



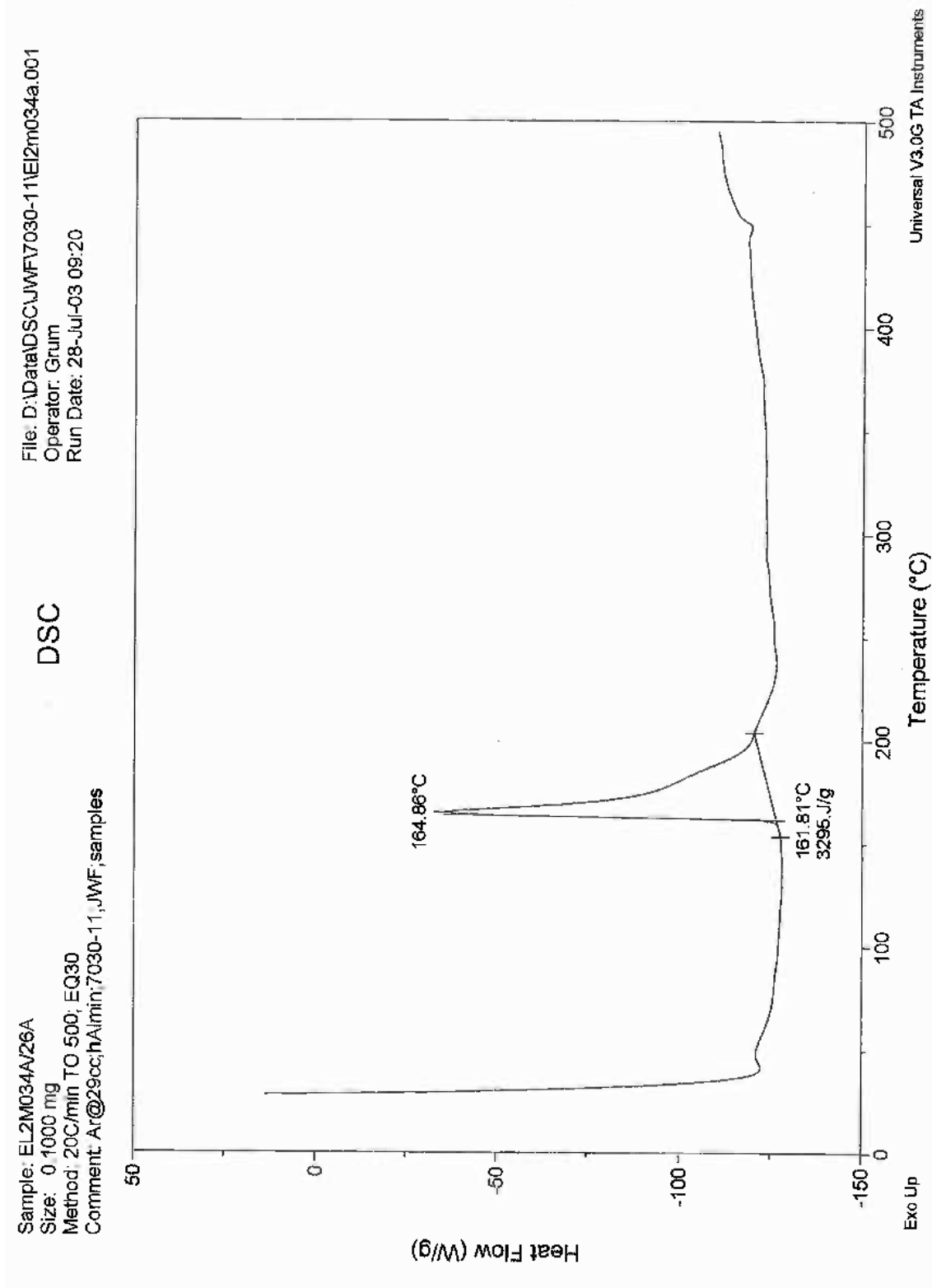
24A, Base material, 24A ¹H NMR



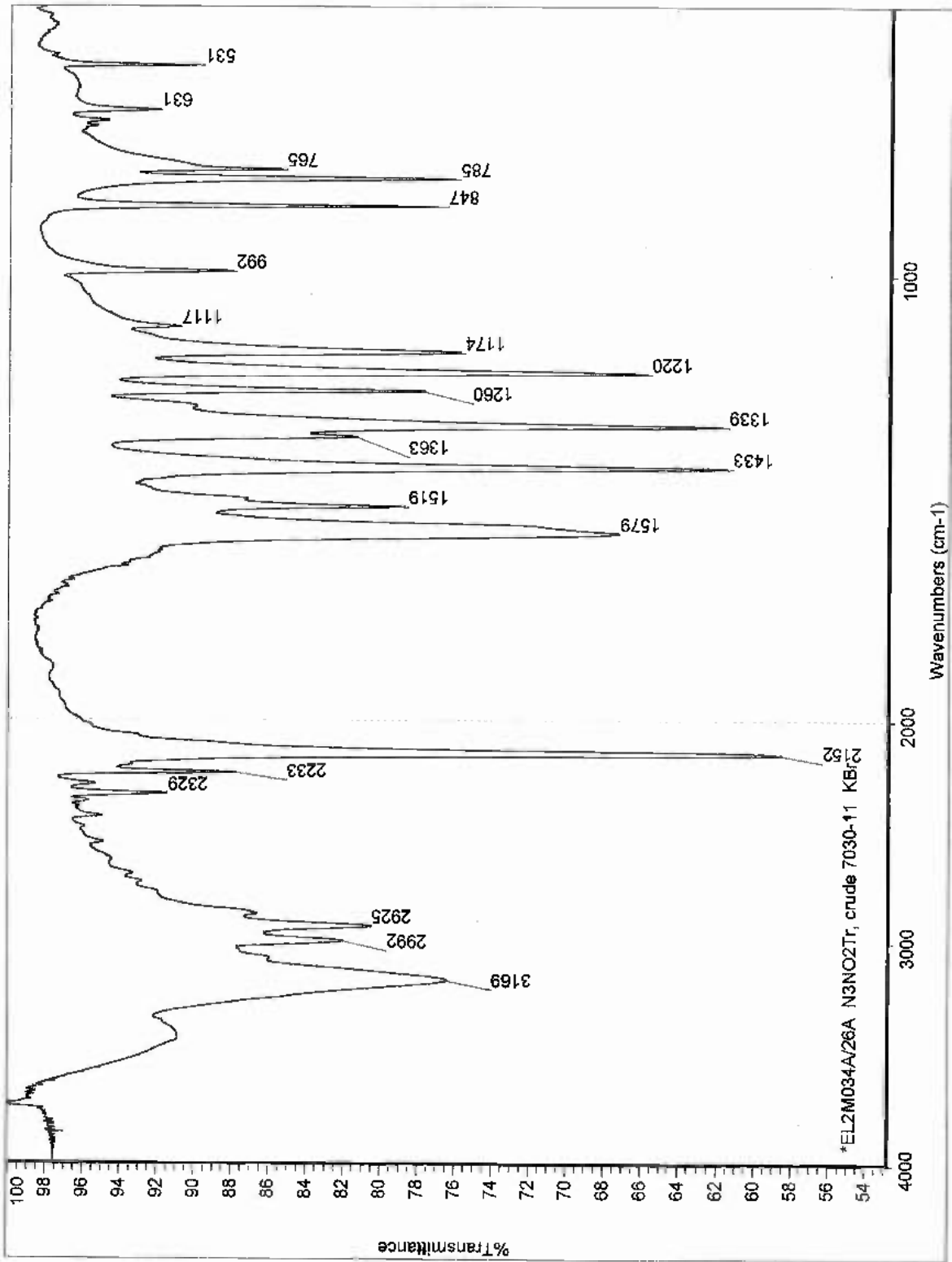
24A, Base material, 24A ¹³C NMR



26A precursor, EL2M034A



26A precursor, EL2M034A

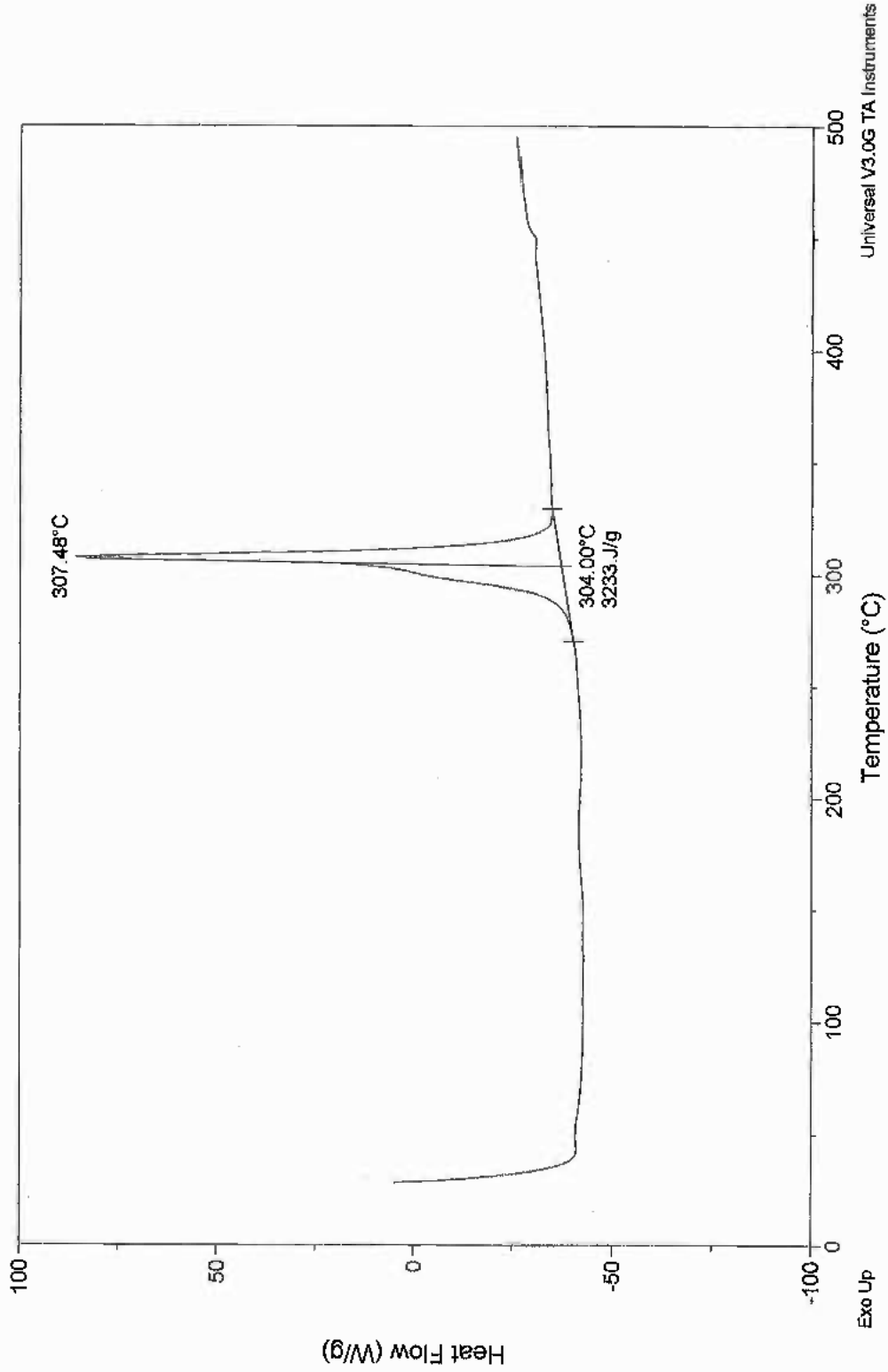


26A precursor, EL2M034B

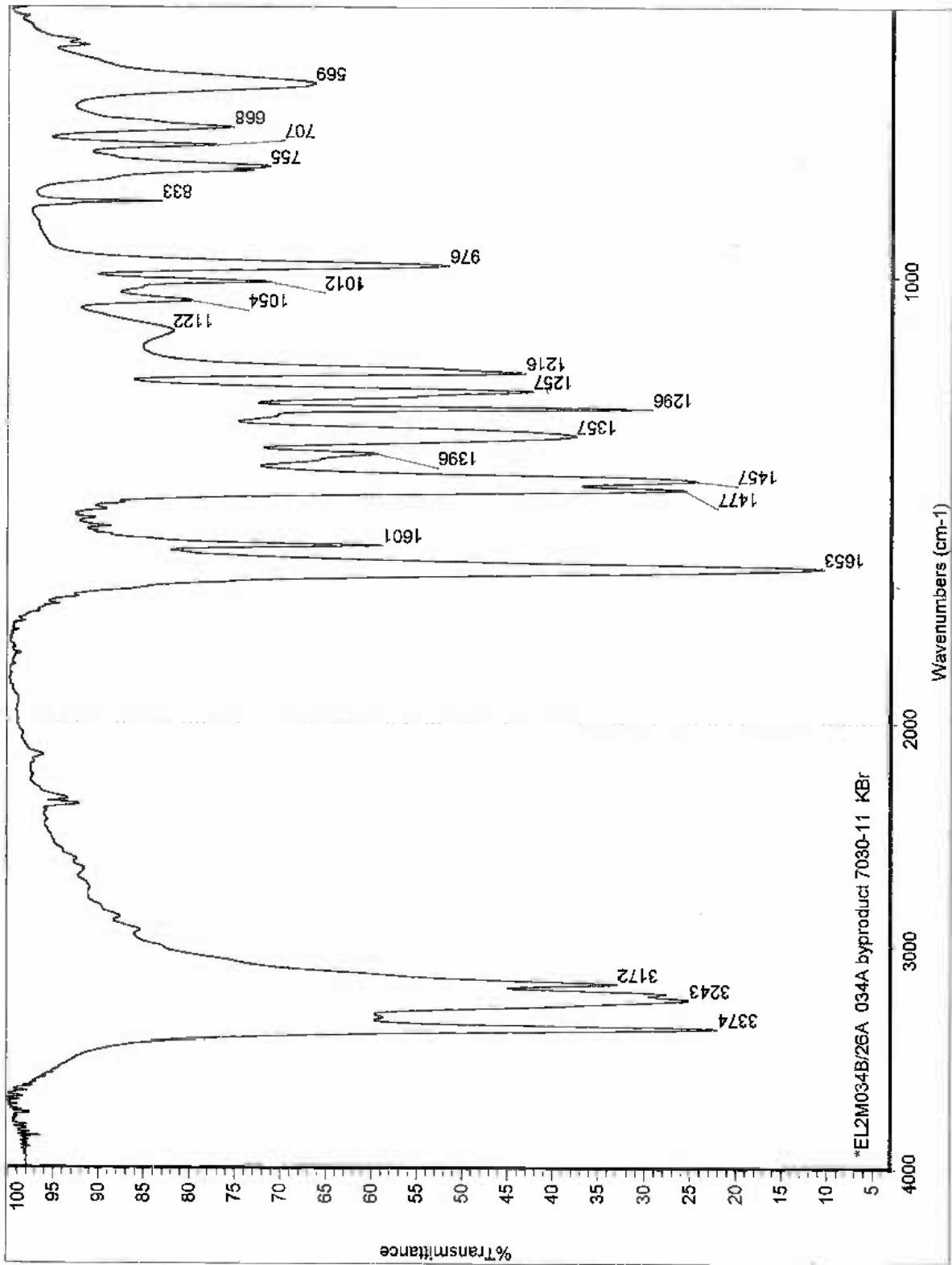
File: D:\Data\DSC\JWF\7030-11\El2m034b.001
Operator: Grum
Run Date: 28-Jul-03 14:30

DSC

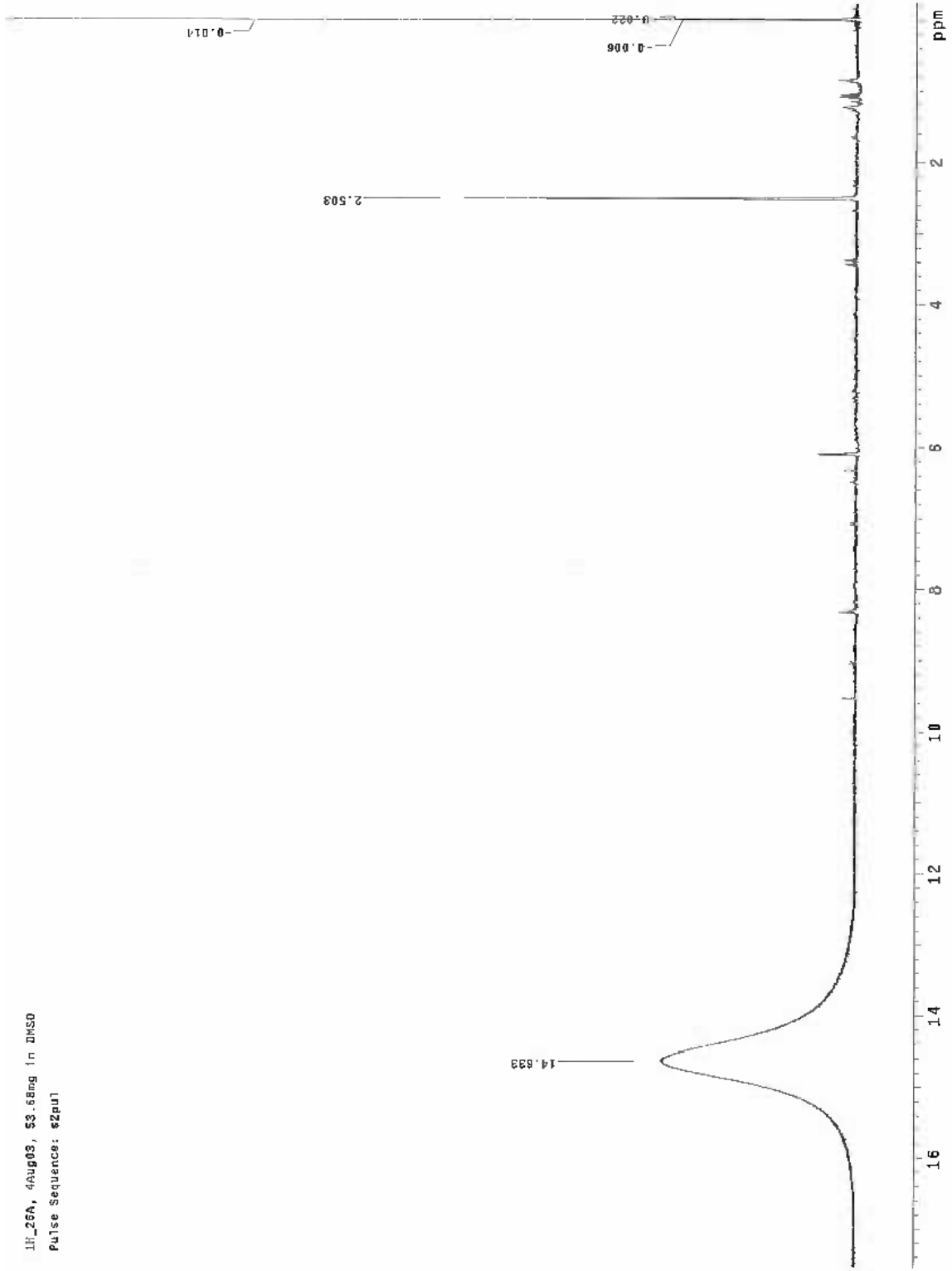
Sample: EL2M034B\26A 034A byproduct
Size: 0.2800 mg
Method: 20C/min TO 500; EQ30
Comment: Ar@29cc;hAlmin;7030-11,JWF;samples



26A precursor, EL2M034B

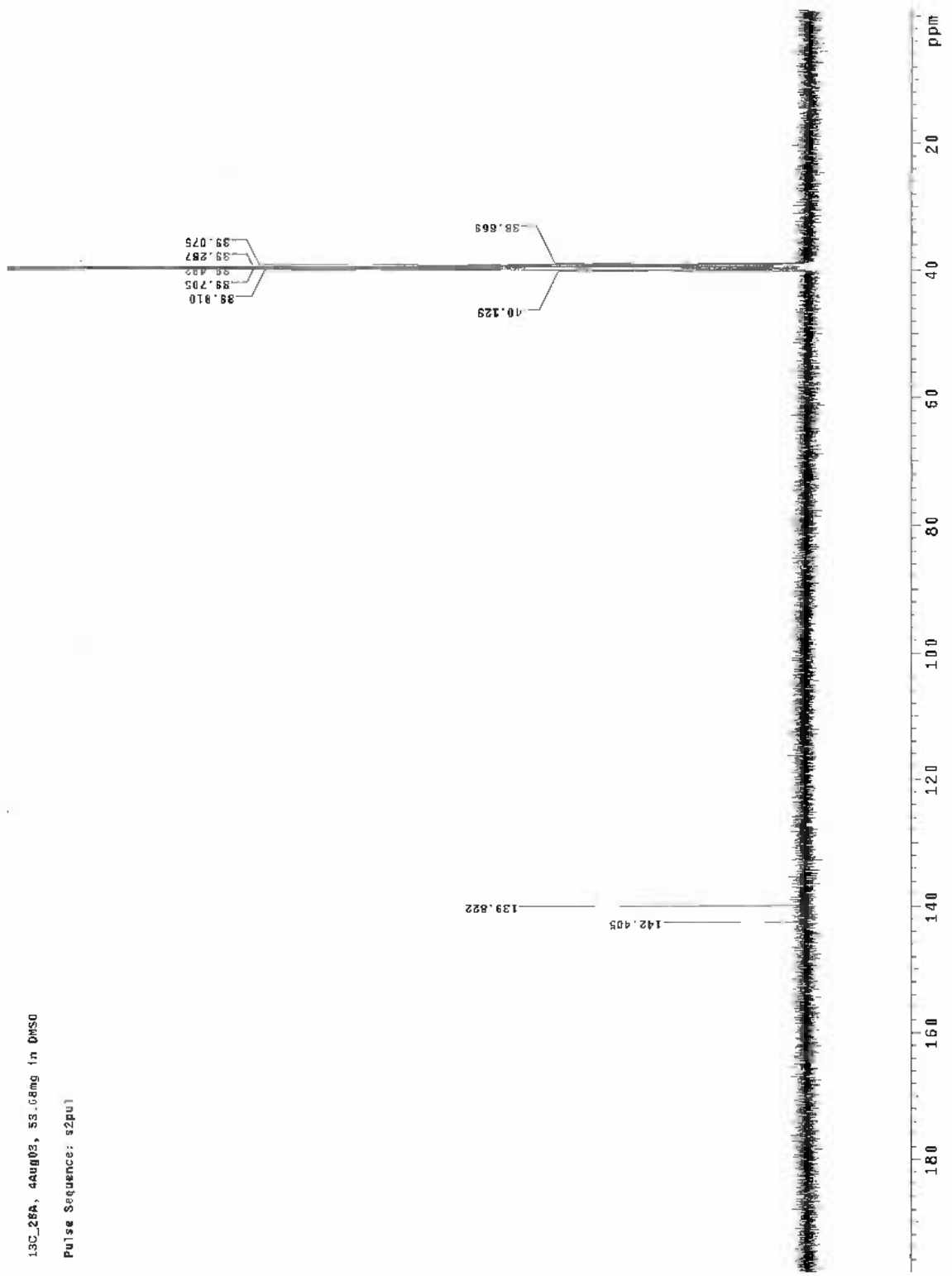


26A precursor, EL2M034B

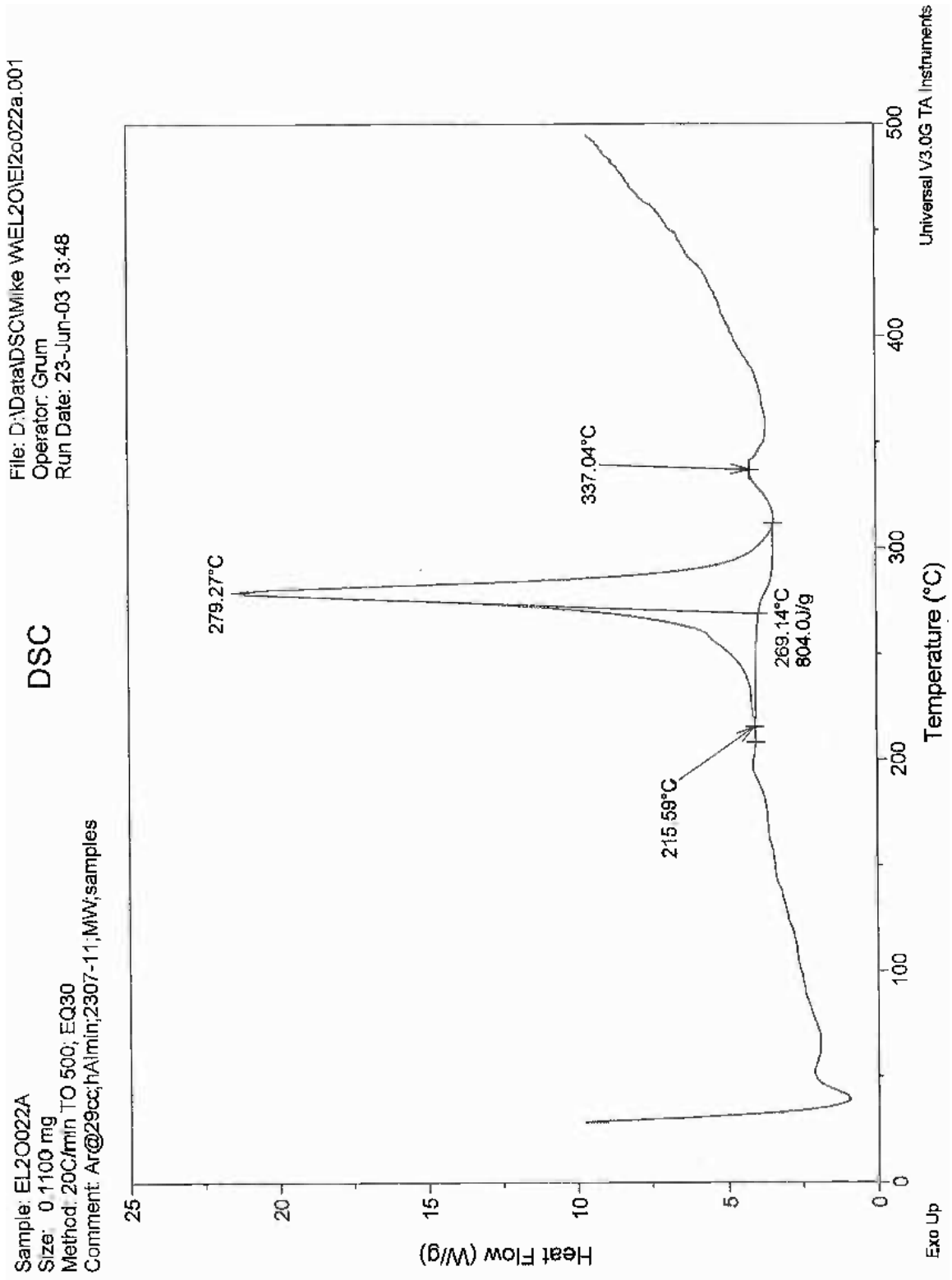


1H_26A, 40ug03, 53.68mg in DMSO
Pulse Sequence: zgpg1

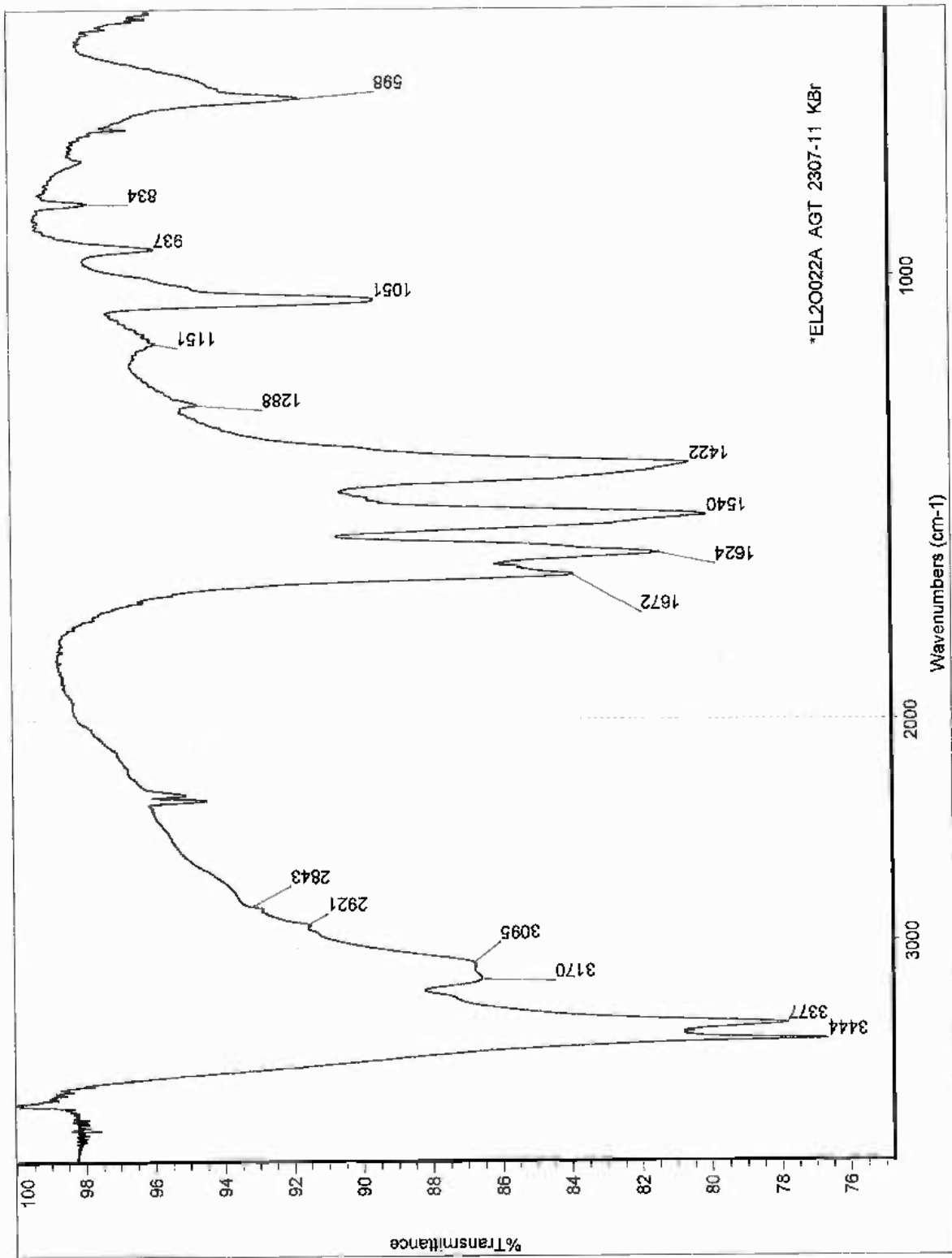
26A precursor, EL2M034B



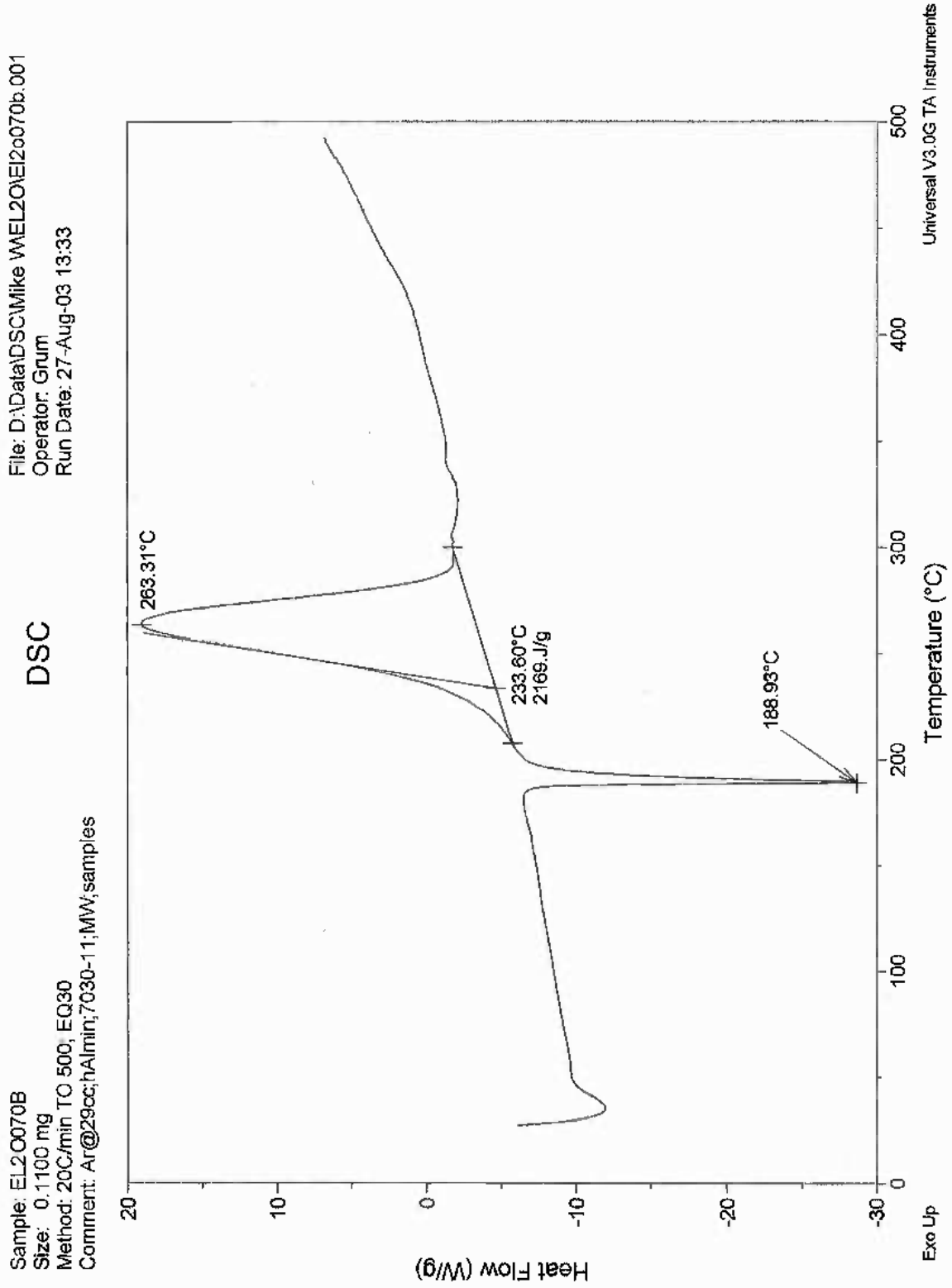
27A, Base material, EL2O022A



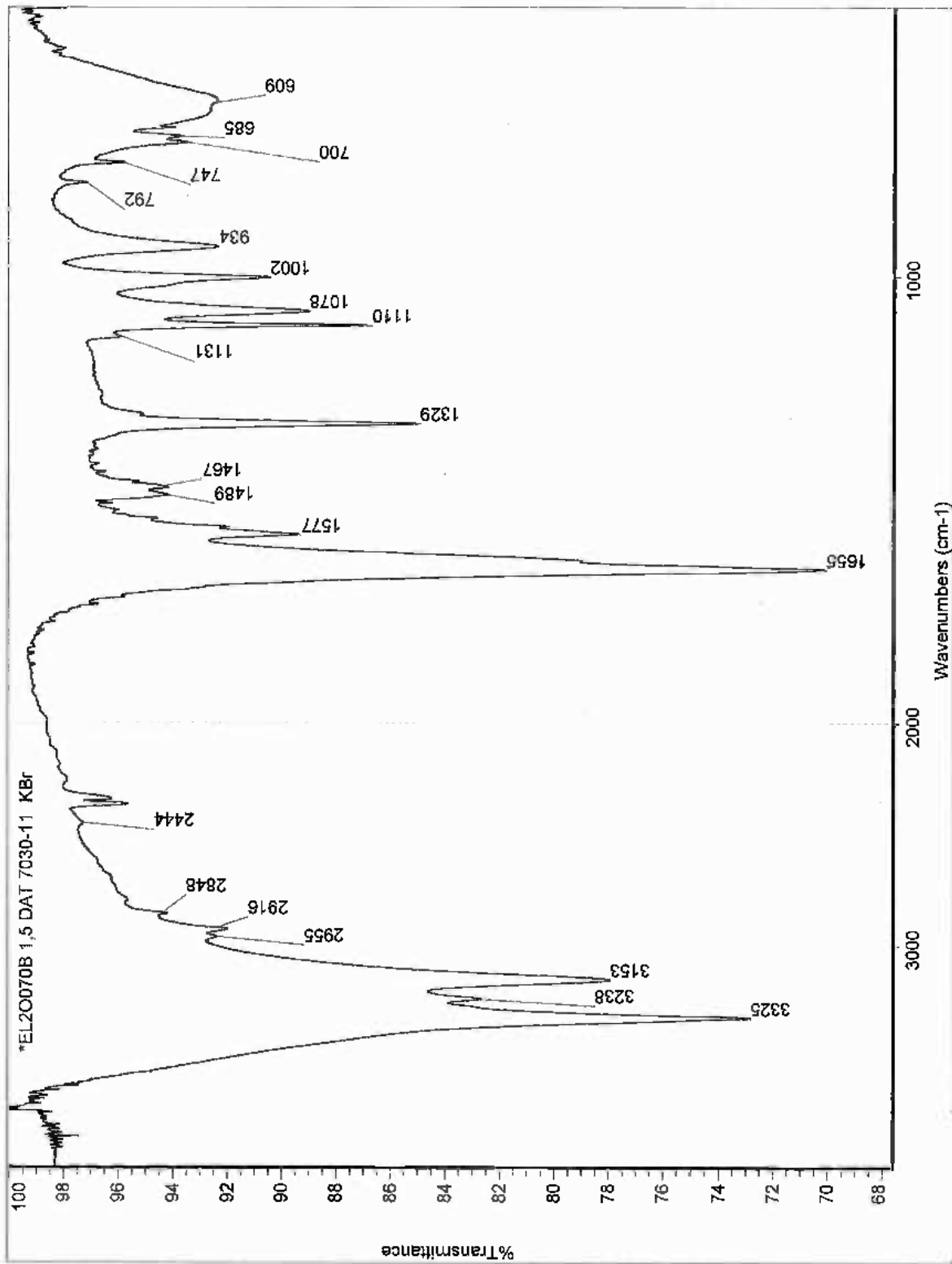
27A, Base material, EL2O022A



28A, precursor, EL20070B



28A, precursor, EL20070B

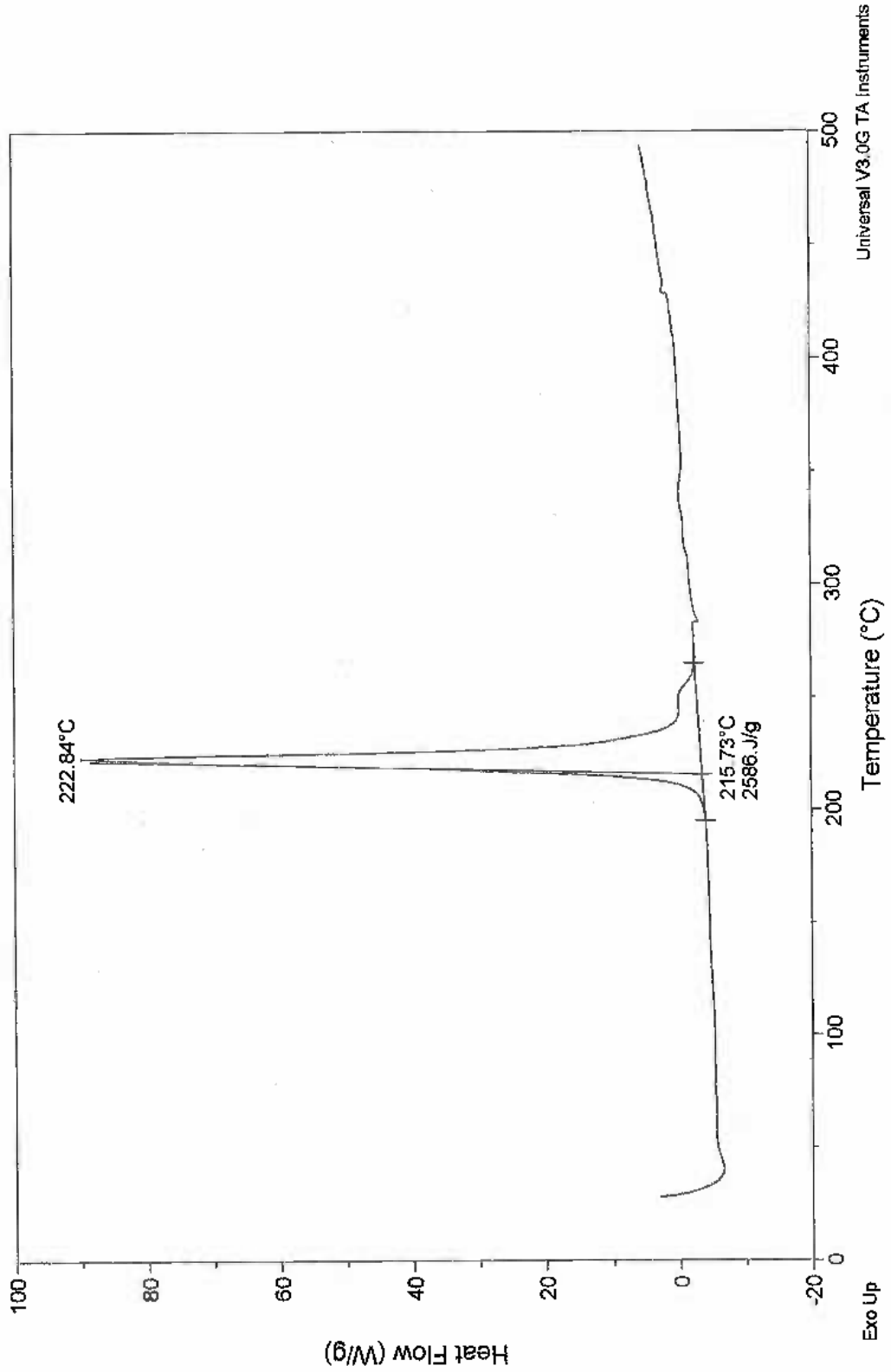


28A, Fe complex, EL2O078A

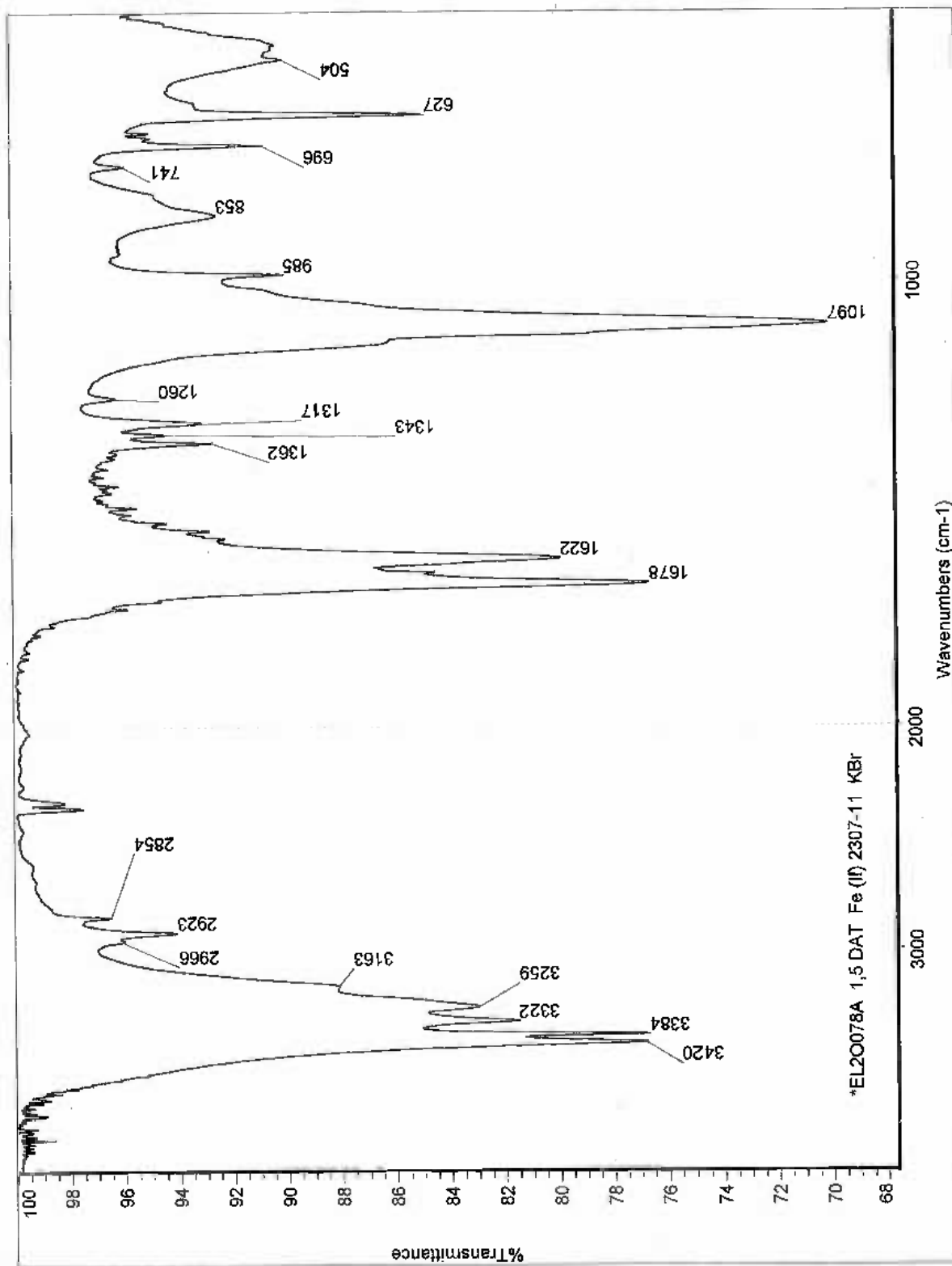
File: D:\Data\DSC\Mike WEL20\EL20078a.001
Operator: Grum
Run Date: 3-Sep-03 09:58

DSC

Sample: EL20078A
Size: 0.1000 mg
Method: 20C/min TO 500; EQ30
Comment: Ar@29cc;hAlm;2307-11,MDW;samples



28A, Fe complex, EL2O078A

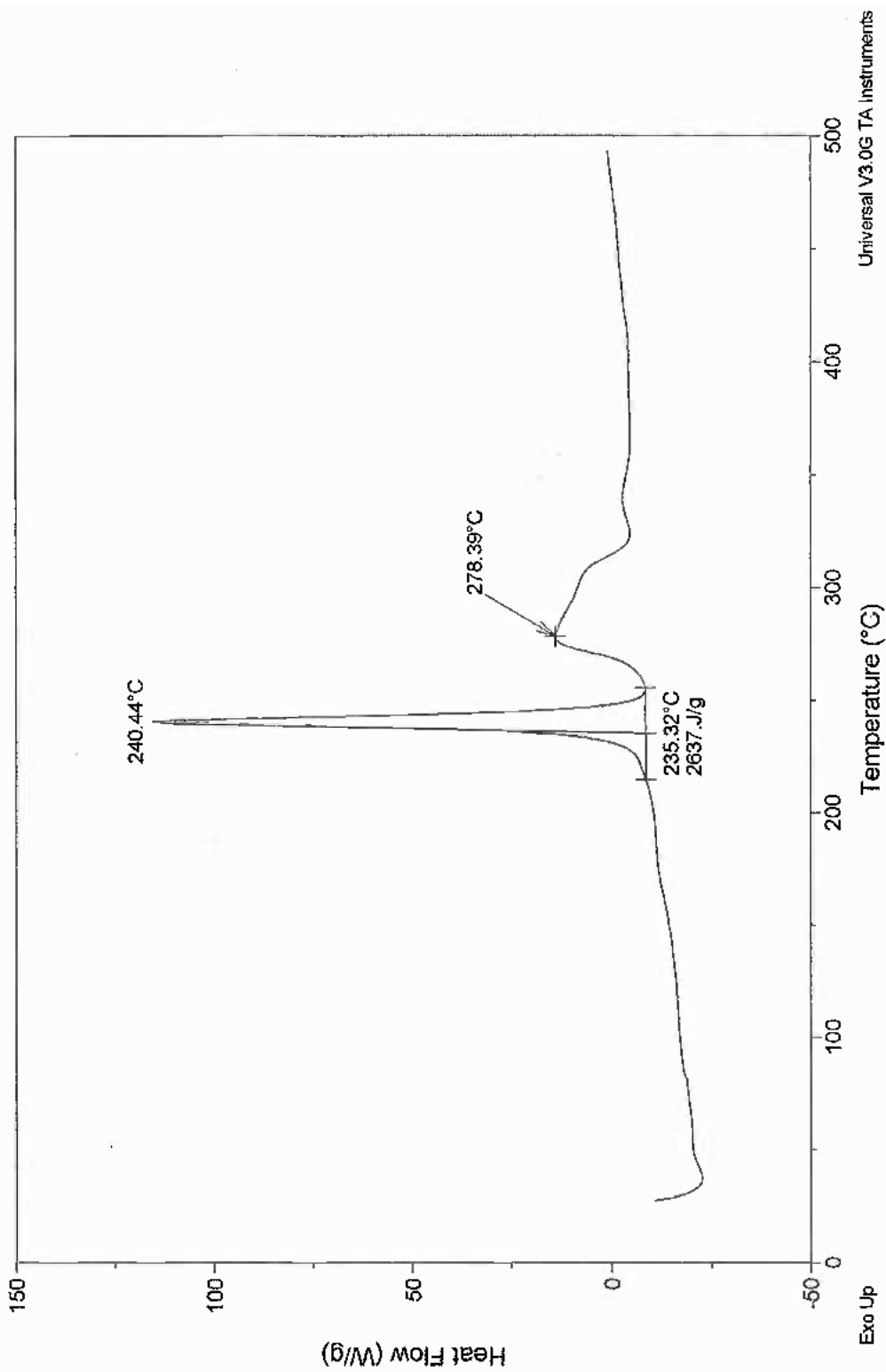


28A, Cu complex, EL20083A

File: D:\Data\IDSC\Mike WEL20\EL20083a-003
Operator: Grum
Run Date: 8-Sep-03 16:11

DSC

Sample: EL20083A
Size: 0.1000 mg
Method: 20C/min TO 615 EQ30
Comment: Ar@29cc;hAlmin,2307-11,mw samples



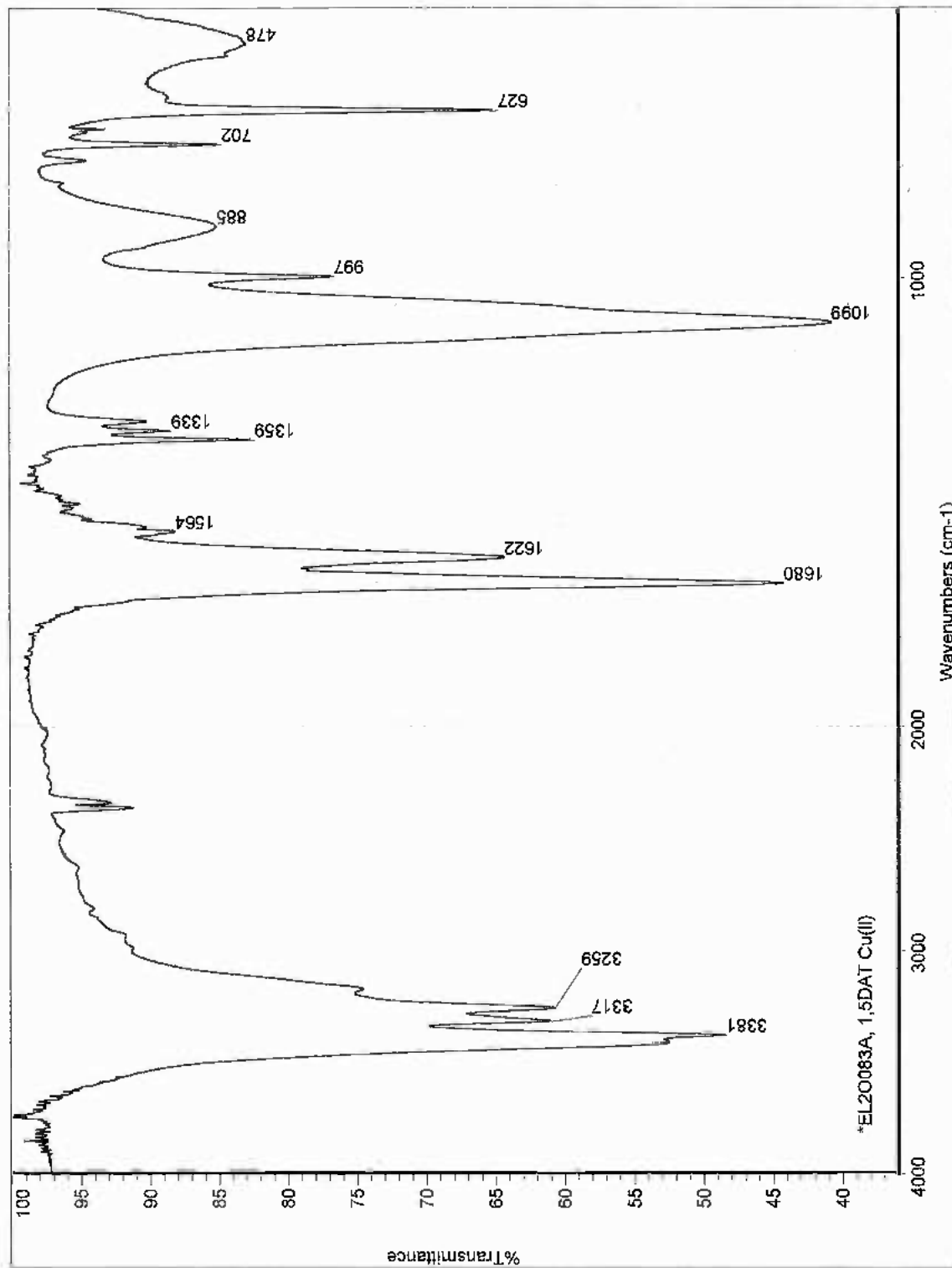
Universal V3.0G TA Instruments

Temperature (°C)

Heat Flow (W/g)

Exo Up

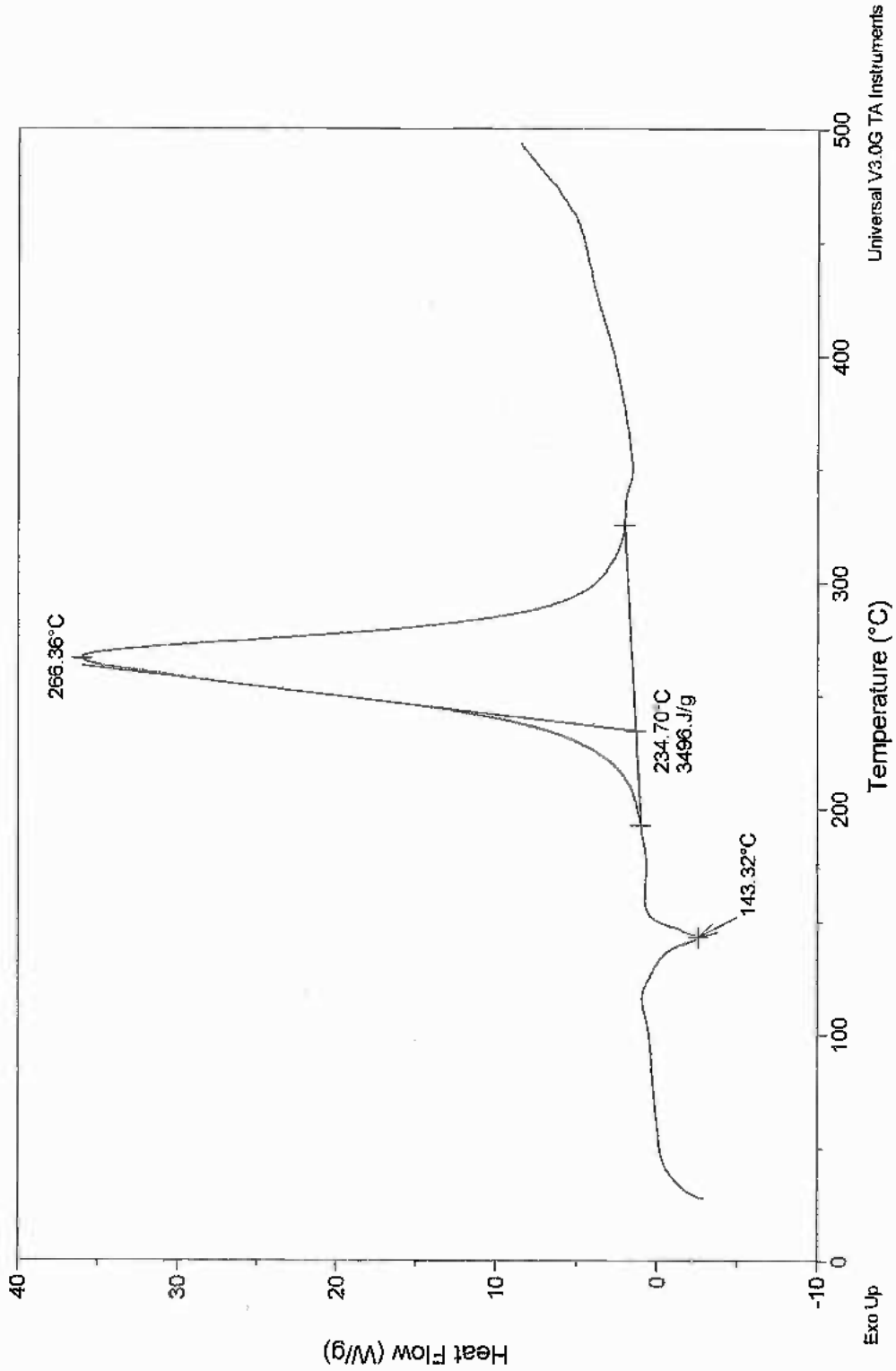
28A, Cu complex, EL2O083A



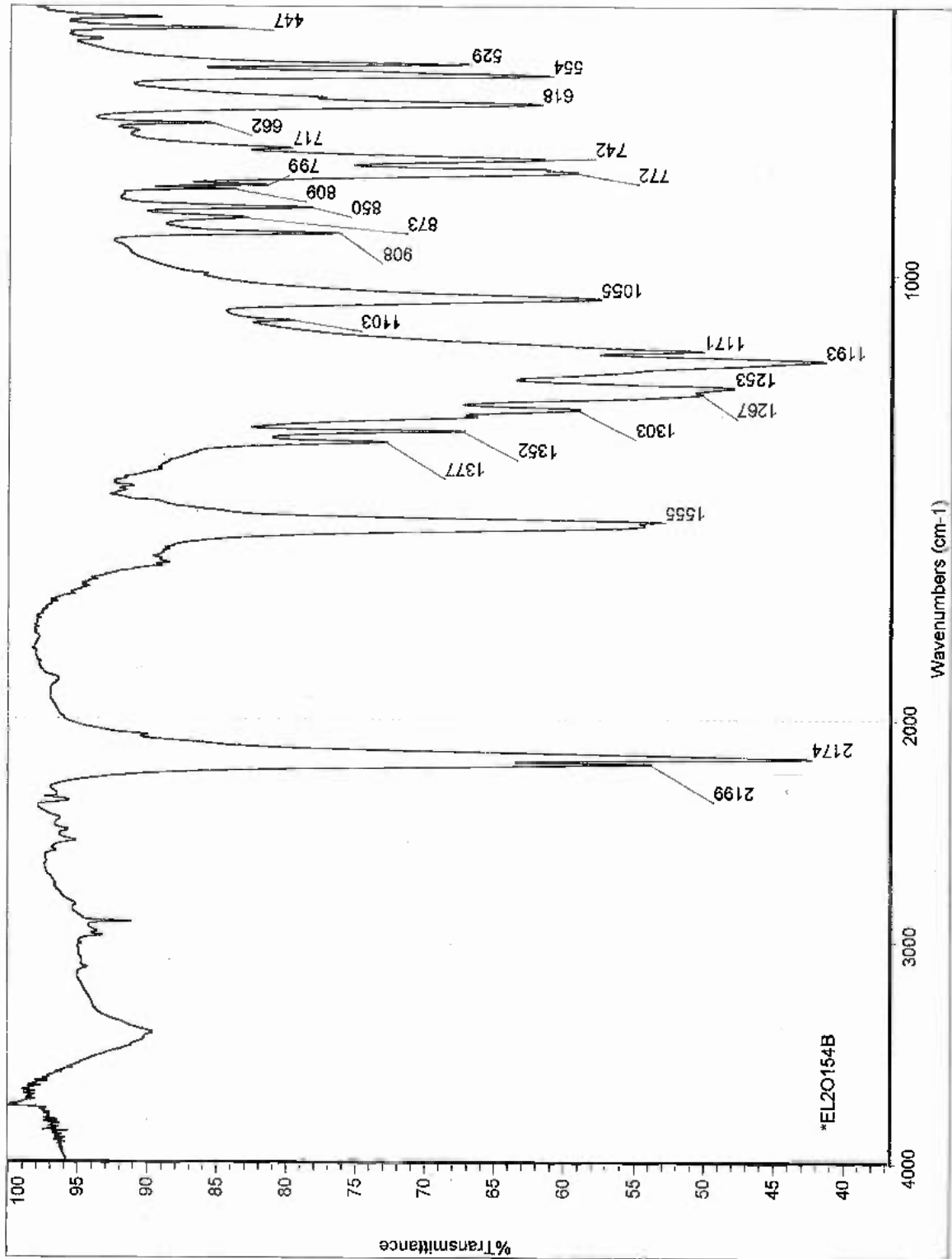
File: D:\Data\DSC\Mike W\EL20154b.001
Operator: Williams
Run Date: 3-Mar-04 15:49

DSC

Sample: EL20154B, ENTA
Size: 0.2200 mg
Method: Ramp 20_500
Comment: Ar@29cc; hAlmin; MDW



30A, EL2O154B



Appendix B

List of Technical Publications:

John Fronabarger, "*Final Report, Lead Azide and the Lead Styphnates, A Replacement Study*", Exothermics, Inc., Chandler, AZ May 1999 (Revised).

John W. Fronabarger and William B. Sanborn, "*Alternatives to Lead Azide and Normal Lead Styphnate*" Presented at the 2000 CAD/PAD Technical Exchange Workshop, NSWC Indian Head Division, Indian Head, MD, May 2000

John W. Fronabarger and Michael D. Williams, "*Final Report On The Investigation Of The Alternatives To Lead Azide And Lead Styphnate*" Pacific Scientific Energetic Materials Company, Chandler, AZ. July, 2000

John W. Fronabarger, William B. Sanborn, and Magdy Bichay "*An Investigation of Some Alternatives to Lead Based Primary Explosives*," Paper No. AIAA 2001-3633, Presented at the 37th AIAA Joint Propulsion Conference, Salt Lake City, UT. July 2001.

John W. Fronabarger, Michael D. Williams, and William B. Sanborn, "*Final Report On The Investigation Of The Alternatives To Lead Azide And Lead Styphnate*" Pacific Scientific Energetic Materials Company, Chandler, AZ. October, 2002

John W. Fronabarger, Michael D. Williams, and William B. Sanborn, "*Third Report On The Continued Investigation Of The Alternatives To Lead Azide And Lead Styphnate*" Pacific Scientific Energetic Materials Company, Chandler, AZ. September 2003

John W. Fronabarger, Michael D. Williams, William B. Sanborn, Michael E. Sitzmann, and Magdy M. Bichay "*Investigation of The Alternatives to Lead Azide and Lead Styphnate*" Presented at the 2004 CAD/PAD Technical Exchange Workshop, NSWC Indian Head Division, Indian Head, MD, April 2004

M. Sitzmann, M. Bichay, J. Fronabarger, M. Williams, W. Sanborn and R. Gilardi, "*Preparation, Characterization and Output Testing of the Novel Primary Explosive, Bis(furoxano)nitrophenol, Potassium Salt*", Proceedings of the 31st International Pyrotechnics Seminar, 729, Ft. Collins, CO. July 2004

Thomas Costain, "*A New Method for Making Silver Azide in a Granular Form*", U.S. Army Picatinny Arsenal, Dover, New Jersey, February 1974