



EDGEWOOD

CHEMICAL BIOLOGICAL CENTER

U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND

ECBC-TR-439

**CHARACTERIZATION OF SOLID AND
LIQUID GB SAMPLES COLLECTED
FROM M55 ROCKETS PROCESSED
AT ANNISTON CHEMICAL AGENT DISPOSAL FACILITY
(ANCDF)**

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ABERDEEN PROVING GROUND, MD 21010-5424

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PREFACE

The work described in this report was authorized under Project No. 622622. The work was started in May 2004 and completed in September 2004.

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CHARACTERIZATION OF SOLID AND LIQUID GB SAMPLES COLLECTED FROM M55 ROCKETS PROCESSED AT ANNISTON CHEMICAL AGENT DISPOSAL FACILITY (ANCDF)

1.0 INTRODUCTION

The Program Manager Assembled Chemical Weapon Alternatives (PM-ACWA) requested that Edgewood Chemical Biological Center (ECBC) conduct a full analytical characterization of a Sarin, GB, sample collected at the Anniston Chemical Agent Disposal Facility (ANCDF). The liquid samples were manually collected from two warheads prior to the M55 Rockets being drained of agent and processed for incineration. The solid samples were collected separately from a drained agent filter upon completion of a plant operational shift processing M55 Rockets. It was expected to find GB liquid and GB "gel" in the rocket, however no "gel" was observed. The only solid was residual solid strained from the liquid GB.

ECBC developed and implemented an analysis plan using several analytical techniques including Nuclear Magnetic Resonance (NMR), Gas Chromatography/Mass Spectrometry (GCMS), Inductively Coupled-Mass Spectrometry (ICPMS), Light Microscopy, Density Determination, Viscometry, and Differential Scanning Calorimetry. This report contains the details of the sampling and analysis activities and results of the characterization effort. It is believed to be the first such in-depth study of the chemical and physical properties of GB solids obtained from an operating disposal plant and a side-by-side comparison of the GB solids with laboratory synthesized standards.

2.0 SIGNIFICANT FINDINGS

2.1 Liquid GB Sample

The liquid GB was 75 weight percent pure and the major impurity was 12 weight percent diisopropyl methylphosphonate (DIMP, $\text{CH}_3\text{P}(\text{O})(\text{O } i\text{-C}_3\text{H}_7)_2$). The GB in the M55 rockets was originally stabilized with two compounds, tri-*n*-butylamine (TBA, $(n\text{-C}_4\text{H}_9)_3\text{N}$) and 1,3-diisopropylcarbodiimide (DICDI, $i\text{-C}_3\text{H}_7\text{-N}=\text{C}=\text{N-}i\text{-C}_3\text{H}_7$). However, under long-term storage, both stabilizers were consumed by reacting with water and acidic degradation compounds of GB. These degradation compounds are isopropyl methylphosphonic acid (IMPA, $\text{CH}_3\text{P}(\text{O})(\text{O } i\text{-C}_3\text{H}_7)\text{OH}$), the major hydrolysis product of GB, methylphosphonofluoric acid (fluoracid, $\text{FCH}_2\text{P}(\text{O})\text{OH}$), and hydrofluoric acid (HF). The original TBA was presumably converted to its ammonium salt, which was detected by NMR but difficult to measure accurately by GC/MS techniques. The diphosphonate ($[\text{CH}_3\text{P}(\text{O})(\text{O } i\text{-C}_3\text{H}_7)]_2\text{O}$), which could be produced from the reaction of IMPA and DICDI, was not detected. Almost all of the original DICDI was converted to the corresponding hydrolysis product, *N,N'*-diisopropylurea (DIPU, $i\text{-C}_3\text{H}_7\text{-NH-C(O)-NH-}i\text{-C}_3\text{H}_7$), about 0.8 weight percent of which was still soluble in the liquid GB, but the rest was separated from the GB liquid as crystalline solids in the rocket. The DIPU was often referred to as “GB Crystals” in the field.

The liquid sample contained low levels of metals including 0.12 weight percent aluminum and 0.016 weight percent iron. Although the GB purity is relatively low, visual inspection showed the sample to be a clear liquid of low viscosity (Photo 2.1). The color of the liquid was not as dark as those GB samples containing higher iron (e.g., 0.2 weight percent) from corrosion of steel containers or projectiles. Relative to pure GB, the viscosity of the liquid sample was slightly higher and the density was slightly lower.



Photo 2.1 Liquid Sample As Received



Photo 2.2 Gelled Residue Found in the Bottom of the Liquid GB Sample Container

2.2 Solid GB Sample and GB Crystals

The solid GB samples contained DIPU crystals (GB crystals) and debris from the punch and drain operation during sample collection, as shown in Photo 2.3. The samples looked dry and any liquid GB adhered to the solid surfaces must have evaporated or reacted by the time the samples reached the laboratory. The DIPU component in the sample, as well as DIPU crystals independently synthesized in the laboratory, are soluble in a range of polar and non-polar organic solvents, particularly in isopropanol with about 7.5 weight percent solubility at 26°C. The DIPU is insoluble in water under both acidic and alkaline pH, nor is it soluble in a bleach solution. However, it was observed that reaction between DIPU and bleach occurred slowly at the interface.

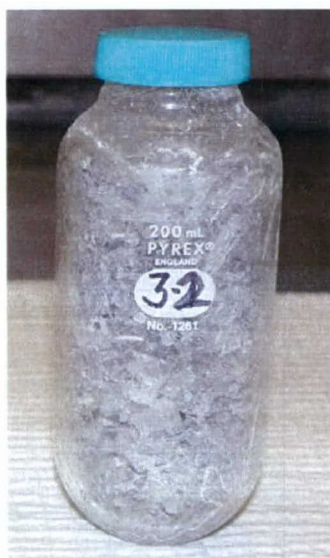


Photo 2.3 Solid GB Samples As Received

The debris found in the solid sample was a cluster of fibrous materials unrelated to GB and was insoluble in any of the solvents tested. It is composed mainly of fiberglass, polymers, and white and gray colored dust. Aromatic compounds were detected in the debris. The DIPU portion of the solid sample can be separated from the debris by dissolving the DIPU in methanol and filtering the debris from the solution. The methanol solution typically contained DIPU, IMPA, and only a trace amount of GB. It is believed that most of the GB on the solid surfaces was hydrolyzed to IMPA prior to mixing with methanol. As a comparison, in a 1996 Report from Tooele Chemical Agent Disposal Facility (TOCDF), wet needle-like solid samples were collected from GB processing lines and equipment and were analyzed by GC/MS. There were almost equal amounts of DIPU and GB in these wet needles. So, the amount of GB contamination on the DIPU surfaces was strongly dependent on sampling conditions. About 3.7 weight percent aluminum and 13 weight percent calcium were found in the debris.

Single DIPU crystals were cleaned to remove GB, IMPA, and other impurities adhering to the surfaces. The crystals were carefully selected from the solid clusters and cleaned by repetitive washing with copious amounts of a solvent such as acetone. Such "cleaned" crystals contained over 95 weight percent DIPU and up to 0.9 weight percent GB as the major impurity. This residual GB was apparently trapped in the interstitial spaces in the crystalline lattice and was difficult to remove by solvent washing. The solid GB samples may be decontaminated by an

aqueous solution of 90 volume percent monoethanolamine (MEA, $\text{HOCH}_2\text{CH}_2\text{NH}_2$), in which both DIPU and GB dissolve. GB reacts with MEA rapidly. Alternatively, isopropanol (IPA) can be used to dissolve the DIPU. Addition of sodium hydroxide (NaOH) or potassium hydroxide (KOH) to the isopropanol solution can accelerate the decontamination of GB.

The DIPU crystals are composed of small needle and chunk particles ranging in lengths from approximately 0.9 to 13 mm. The morphologies of the samples are similar to some of the laboratory synthesized pure DIPU crystals. The larger chunks and needles can be easily broken into smaller sizes by pressing them with a glass rod. So fractured, the larger needles and chunks broke into tiny needle fragments, which seemed to be the basic microstructures of DIPU crystals. The melting point of the DIPU crystals in the solid sample was typically 172°C , which is lower than that of the pure synthesized DIPU that has a melting point of 190°C . The literature value for the melting point of DIPU is 192°C . Only a trace amount of aluminum was detected in the DIPU crystals.

2.3 Detection of Gelled Substance in Liquid GB Sample.

Consistent with Anniston Chemical Agent Disposal Facility (ANCDF) observations, the liquid GB sample flowed and was not gelled. However, in the bottom of the liquid sample bottle, a gel-like substance, at about 0.3-0.4 weight percent of the total liquid sample was found, as can be seen in Photo 2.2. In addition to GB, both IMPA and aluminum were detected in this material. These components are consistent with previous studies that aluminophosphonates might be the species responsible for gel formation in liquid GB. This material is currently being characterized further.

3.0 SAMPLE COLLECTION, STORAGE, AND DELIVERY

3.1 Sampling

The purpose of the Program Manager Assembled Chemical Weapon Alternatives (PM-ACWA) sampling mission at ANCDF was to collect liquid, gelled GB agent, and crystal material from the warheads of M55 rockets for chemical and physical characterization and for use in hydrolysis studies.

During the PM-ACWA sample collection activities at ANCDF, no GB gel material was encountered. Therefore, only liquid GB agent and GB crystal material were collected.

The Anniston Army Depot (ANAD) delivered a lot of M55 rockets, suspected to contain gelled GB, to ANCDF for processing and agreed to collect samples of the agent cavity materials for PM-ACWA. The lot of M55 rockets was suspected to contain gelled GB based on agent inventory records of documented anomalies. However, upon processing of the rocket lot through the ANCDF over several days, Anniston personnel informed PM-ACWA that they were not encountering any gelled GB. During the punch and drain step, a crystal-like material was observed and captured by the Agent Quantification System (AQS) filter of the rocket shear machine punch and drain station. The decision was made by PM-ACWA to collect liquid GB to support the planned GB neutralization studies and to collect and analyze the crystals recovered from the rockets to determine their chemical composition and physical characteristics.

Samples of liquid GB agent were collected from two M55 rockets at ANCDF. The rockets were physically opened using the vent hole punches at the punch and drain station of the rocket shear machine. The agent-filled warheads were then accessed from the upper vent holes of the rockets to collect the liquid GB agent. A sample of the crystal material was collected from an AQS filter that had captured the crystal material from several rockets processed during a one-day shift operation. Table 3.1 below provides the sample collection date, the volume of samples collected, the agent type, and the munition and agent lot numbers:

Table 3.1 Agent Lot and Sample Collection Information

Date of Collection	19-21 Jan 2004
Amount Collected	1600 mL – liquid GB 400 mL – crystals
Agent Type Designation	PRO-RS
Munition Lot Number	1033-45-183
Agent Lot Number	1034-45-1235

3.1.1 Liquid Samples

An ordinary "turkey baster" was used to collect the liquid GB sample. This device was chosen due to the ease of use by the operators (sample collectors) in Demilitarization Protective Ensemble (DPE) suits. Each use of the "turkey baster" allowed for the collection of an aliquot of approximately 60 mL of liquid agent. Enough agent was collected to fill eight individual 200 mL Pyrex glass vials with Teflon[®] lined screw top lids for a total GB liquid agent sample of 1600 mL.

3.1.2 Solid Samples

The crystals were collected from the AQS filter using a scoop. A total of 400 mL of solids were placed into two 200 mL Pyrex glass vials. Much of the crystal sample included debris from the mechanically punched and accessed rocket, such as fiberglass shards from the rocket shipping/firing tube and aluminum particles from the aluminum warhead. The deputy Plant Manager mentioned that during the trial burn process, the rocket lots encountered were draining approximately a "full shot glass" of crystals per rocket. A rough estimate can be concluded from this observation that each rocket drained approximately one ounce of crystals or ~29.5 mL/warhead.

3.1.3 Sample Processing

During the collection, there was a minimum exposure of the liquid samples to the air inside the Munitions Demilitarization Building (MDB), until the vials were sealed with Teflon[®]-lined screw-top lids. Crystal samples also had a minimum exposure to air. The AQS filter, which had been removed as a plant maintenance procedure, was bagged and placed in a plastic bucket and left in the MDB until the sampling team could collect a sample the next evening. Air exposure would have occurred when the sample of the crystals was scooped from the AQS filter and placed inside glass vials. All of the sample vials had a nominal headspace. The Westinghouse Anniston Standing Operating Procedure, SOP Number AN-SOP-056, describes the procedures in detail for the manual agent sampling of the M55 rockets.

The outside surfaces of the sample vials were decontaminated. A 1 weight percent solution of NaOH was soaked on a towelette and used to decontaminate any spilled agent on the threads of the glass vials. All glass threads were wiped with the towelette after filling the vials with liquid agent. The vials were decontaminated by submerging the closed vial in a 5-gallon bucket filled with 18 weight percent NaOH followed by submerging in 1 weight percent NaOH. The vials were transferred to the A airlock where they were bagged and monitored for clearing overnight. Once cleared, they were transferred to the B airlock where they were packaged for transport to the two laboratories. The samples were packaged in Multiple Round Containers (MRC) for subsequent shipment by the Technical Escort Unit (TEU). The sample aliquots for use by the Battelle laboratories in the BGCAPP TRRP activities were shipped via TEU from ANAD to Battelle. The sample aliquots for use by Edgewood Chemical Biological Center (ECBC) laboratories for characterization were shipped via TEU from ANAD to the ECBC.

A waiver from the U.S. Army, AMSCM-OPS to collect and ship in a primary container larger than the standard 40-mL ampoules had been approved on 29 Jan 2004. This waiver allowed for packaging of larger quantities of agent and facilitates collection of solid crystalline material.

3.2 Sample Storage

The samples were transferred from ANCDF to ANAD for temporary igloo storage prior to TEU shipment. The samples destined for ECBC analysis were stored from January 2004 until May 2004. A portion of the GB liquid agent and solid crystal samples were shipped to ECBC, Edgewood, MD from Anniston, AL on 18 May 2004. Table 3.2 shows the temperature range to which the MRCs were exposed during storage inside the igloo.

Table 3.2 Temperatures of the Igloo During Sample Storage

Temperature Range (°F)			
Week of	High	Low	Remarks
1/23/2004	45	44	
1/26/2004	45	42	
2/3/2004	46	44	
2/10/2004	NA	NA	Missing data card
2/17/2004	NA	NA	Recorder malfunction
2/24/2004	48	46	
3/2/2004	51	48	
3/10/2004	51	48	
3/17/2004	52	51	
3/23/2004	54	51	
3/30/2004	54	52	
4/6/2004	56	52	
4/13/2004	56	53	
4/21/2004	59	56	
4/27/2004	59	58	
5/4/2004	62	59	
5/11/2004	62	60	
5/18/2004	62	60	

4.0 RESULTS OF ANALYSIS OF GB LIQUID

4.1 Sample Distribution within ECBC

Four aliquots of the GB liquid sample were distributed to various laboratories for analyses. Distribution aliquots, analyses, and laboratory identification numbers are shown in Table 4.1.

Table 4.1 Sample Origin, Distribution, and Identification

Sample Name	Distribution Aliquot	Determination	Lab ID
GB Liquid GB/ACWA-1 GB10005	Vial #1	Density, Viscosity	GB10005
	Vial #2	GC/MS	ms04032
	Vial #3	NMR	010069-123
	CTF Preparation	ICP/MS	MB040763

4.2 Gas Chromatography/Mass Spectrometry

LAB I.D. NO: ms04032
CUSTOMER SAMPLE NO: GB/ACWA-1 (GB10005) Vial #2
DATE RECEIVED: 21 June 2004
DATE(S) ANALYZED: 22 June 2004
CONDITION OF SAMPLE: Light brown liquid
ANALYST: Dennis Rohrbaugh
METHOD NO: ACT-008, "GC/MS analysis for the identification of impurities in neat samples"
INSTRUMENT: HP 5972 MSD
METHOD DETECTION LIMIT: ~ 0.01 area %

4.2.1 Qualitative Characterization

On 22 June 2004, GB liquid was analyzed as received and after derivatization (1:1 with BSTFA/1 % TMCS at 60°C for 30 minutes). Results from each analysis are listed separately in Table 4.2. The validity of the fluoracid detection is unknown. In the past, fluoracid has been observed in derivatized GB samples but has not been confirmed by NMR. Higher TBA levels are also observed in the derivatized sample. One possible explanation is that derivatization breaks up TBA-fluoracid to give free TBA and derivatized fluoracid. Another possible source of fluoracid is reaction of methylphosphonic difluoride with BSTFA during GC analysis.

4.2.2 Quantitative Characterization

Weight percent GB and DIMP quantification was performed on 13 and 14 July 2004 using 4-point external calibration curves. The results are provided in Table 4.3.

Table 4.2 GC/MS Characterization of GB10005

Analyte	Structure	Area %	
		Underivatized	Derivatized
Difluorodimethylsilane	$(\text{CH}_3)_2\text{SiF}_2$	0.2	ND
Methylphosphonic difluoride (DF)	$\text{CH}_3\text{P}(\text{O})\text{F}_2$	0.2	ND
Isopropyl alcohol	$i\text{-C}_3\text{H}_7\text{OH}$	0.6	1.2 ^a
Isopropyl methylphosphonofluoridate (GB)	$\text{CH}_3\text{P}(\text{O})(\text{O}i\text{-C}_3\text{H}_7)\text{F}$	75.6	62.8
Methylphosphonofluoridic acid (fluoracid)	$\text{CH}_3\text{P}(\text{O})(\text{OH})\text{F}$	ND	3.6 ^{a,b}
Unknown		0.3	0.2
Diisopropyl methylphosphonate (DIMP)	$\text{CH}_3\text{P}(\text{O})(\text{O}i\text{-C}_3\text{H}_7)_2$	20.5	21.8
Isopropyl methylphosphonic Acid (IMPA)	$\text{CH}_3\text{P}(\text{O})(\text{O}i\text{-C}_3\text{H}_7)\text{OH}$	ND	3.5 ^a
Tributylamine (TBA)	$(n\text{-C}_4\text{H}_9)_3\text{N}$	1.7	6.3 ^c
N,N'-Diisopropylurea (DIPU)	$i\text{-C}_3\text{H}_7\text{NHC}(\text{O})\text{NH}i\text{-C}_3\text{H}_7$	0.8	0.6

ND None detected

^a Detected as trimethylsilyl derivative

^b Cannot rule out that detection of fluoracid is an artifact of the analysis (reaction of DF with BSTFA?)

^c Higher concentration of TBA in derivatized samples could result from release of free TBA from salts during derivatization

Table 4.3 GC/MS Determination of Weight % GB and DIMP in GB10005

Analyte	Weight %
GB	75.8 ± 3.3^a
DIMP	11.8 ± 3.2^b

^a Average of 4 runs

^b Average of 3 runs

4.3 NMR Analysis

LAB I.D. NO: 010069-123
 CUSTOMER SAMPLE NO: GB/ACWA-1 (GB10005) Vial #3
 DATE RECEIVED: 24 June 2004
 DATE(S) ANALYZED: 14 July 2004
 CONDITION OF SAMPLE: Clear transparent light brown liquid
 ANALYST: George Hondrogiannis
 METHOD NO: AM-084, "NMR Procedure for the Characterization of Organic Compounds"
 INSTRUMENT: Bruker Avance 300 MHz
 METHOD DETECTION LIMIT: ~ 0.005 weight %

This method is semi-quantitative in that only the ratios of those compounds detected in the ^{31}P , ^{13}C , ^{19}F and ^1H spectra are measured. The method does not give an absolute amount of any component in the sample (i.e., $\mu\text{g/mL}$) because no internal/external standards are used.

Table 4.4 NMR Analysis of GB10005

Compound	Mole %	Weight %
Isopropyl methylphosphonofluoridate (GB), $\text{CH}_3\text{P}(\text{O})(\text{Oi}-\text{C}_3\text{H}_7)\text{F}$	81.44	81.04
Diisopropyl methylphosphonate (DIMP), $\text{CH}_3\text{P}(\text{O})(\text{Oi}-\text{C}_3\text{H}_7)_2$	8.85	11.33
Methylphosphonic difluoride (DF), $(\text{CH}_3)\text{P}(\text{O})\text{F}_2$	0.26	0.18
Ethyl methylphosphonofluoridate, $\text{CH}_3\text{P}(\text{O})(\text{OCH}_2\text{CH}_3)\text{F}$	0.002	0.002
Methylphosphonofluoridic acid (FA), $\text{CH}_3\text{P}(\text{O})(\text{OH})\text{F}$	2.82	1.96
Diisopropyl phosphorofluoridate, $(\text{i}-\text{C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{F}$	0.14	0.18
Dimethylphosphinic fluoride, $(\text{CH}_3)_2\text{P}(\text{O})\text{F}$	0.03	0.02
Acids, HF/F^-	1.56	0.22
$(\text{CH}_3\text{CH}_2\text{O})\text{P}(\text{O})(\text{OR})\text{F}$ (t)*	0.03	0.03
Isopropyl fluoride, $(\text{CH}_3)_2\text{CHF}$ (t)	0.07	0.03
Tri-n-butylamine-HF, TBA-HF, $(\text{n}-\text{C}_4\text{H}_9)_3\text{N}-\text{HF}$	1.86	2.71
Urea like Unknown	0.33	0.34
N-N'-Diisopropylurea, (DIPU) $\text{i}-\text{C}_3\text{H}_7\text{NHC}(\text{O})\text{NH}-\text{i}-\text{C}_3\text{H}_7$	0.76	0.78
Chloroform, CHCl_3 (t)	0.080	0.07
Isopropyl alcohol, $(\text{CH}_3)_2\text{CHOH}$	1.13	0.48
Isopropyl methylphosphonic acid (IMPA), $\text{CH}_3\text{P}(\text{O})(\text{Oi}-\text{C}_3\text{H}_7)\text{OH}$	0.55	0.54
Hexafluorophosphoric acid, HPF_6	0.04	0.04
Dimethylphosphinic Acid, $(\text{CH}_3)_2\text{P}(\text{O})(\text{OH})(\text{t})$	0.04	0.03
Isopropyl ethylphosphonofluoridate, $\text{CH}_3\text{CH}_2\text{P}(\text{O})(\text{Oi}-\text{C}_3\text{H}_7)\text{F}$	0.006	0.007
$(\text{i}-\text{C}_3\text{H}_7\text{O})\text{P}(\text{O})(\text{OH})\text{F}(\text{t})$	0.0045	0.005

* R group is not identified, but is likely either ethyl, propyl, isopropyl or another small carbon group of this type

4.4 Elemental Analysis Using ICP-MS

LAB I.D. NO: MB040763
CUSTOMER SAMPLE NO: GB10005
DATE RECEIVED: 5 August 2004. Received from CTF after digestion
DATE(S) ANALYZED: 5 August 2004
CONDITION OF SAMPLE: Sample received as clear, colorless digestate
SAMPLE PREPARATION: John Loss
ANALYST(S): Craig Taylor and Steven Norman
METHOD NO: IOP MT-07, "Operation and Maintenance of the ELAN 9000 Inductively Coupled-Mass Spectrometer (ICP-MS) for the Analysis of Metals in Various Matrices"
INSTRUMENT: Perkin Elmer SCIEX ICP Mass Spectrometer ELAN 9000
RESULTS: Results are shown in Table 4.5

4.5 Density

SAMPLE ID: GB/ACWA-1 (GB10005) Vial # 1
RECEIPT DATE: 22 June 2004
STORAGE: Ambient
ANALYSTS: Ann Butrow and Patrice Abercrombie
Agent Chemistry Team/R&T Directorate
TEST DATE: 15 July 2004
METHOD: ASTM D 4052 Density and Relative Density of Liquids by Digital Density Meter
INSTRUMENTATION: Anton Parr DMA 58 Digital Density Meter
CALIBRATION: Instrument calibration was validated at each temperature using NIST standard toluene
DOCUMENTATION: See ECBC Lab Notebook 03-0172, p. 78 (Abercrombie) and Density Meter Logbook
RESULTS: Experimental data are listed in Table 4.6 and plotted in Figure 4.1. (Literature data for GB are included for comparison)

Table 4.5 ICP-MS Analysis of GB10005

Lab ID:	MB040763	
Sample ID:	GB10005	
Analytical Aliquot (g):	1.115	
Batch:	04080201	
	Results (Weight %)	Qual
Aluminum	0.12	D
Calcium	0.061	D
Iron	0.016	D
Phosphorus	21	D
Silicon	0.070	D
Sodium	0.012	D
	Results (ng/g)	Qual
Barium	510	
Chromium	3,300	
Cobalt	21	
Copper	23,000	E
Lead	1,100	
Magnesium	1,900	
Manganese	1,200	
Molybdenum	290	
Nickel	600	
Potassium	8,700	
Sulfur	33,000	J
Tin	2,600	
Titanium	3,600	
Vanadium	260	
Zinc	25,000	

Qualifiers: D = Sample diluted to bring response into calibration range
E = Sample response higher than highest calibration standard
J = Estimated value

All results are reported to two significant figures. Units of ng/g correspond to parts per billion (weight)

Table 4.6 Density Results for GB10005

Temperature (°C)	Density (g/mL)	
	Experimental	Literature (GB)*
25	1.07143 ± 0.00002	1.089
35	1.06037 ± 0.00004	1.077
50	1.04389 ± 0.00015	1.059

*Source: Samuel, J.B., Penski, E.C., Callahan, J.J., "Physical Properties of Standard Agents, Candidate Agents, and Related Compounds at Several Temperatures", ARCSL-SP-83015, Chemical Systems Laboratory, APG, MD, June 1983.

Linear equation (for experimental data):

$$d = 1.09895 - 1.10 \times 10^{-3} (t)$$

where d = density, g/mL

t = temperature, °C

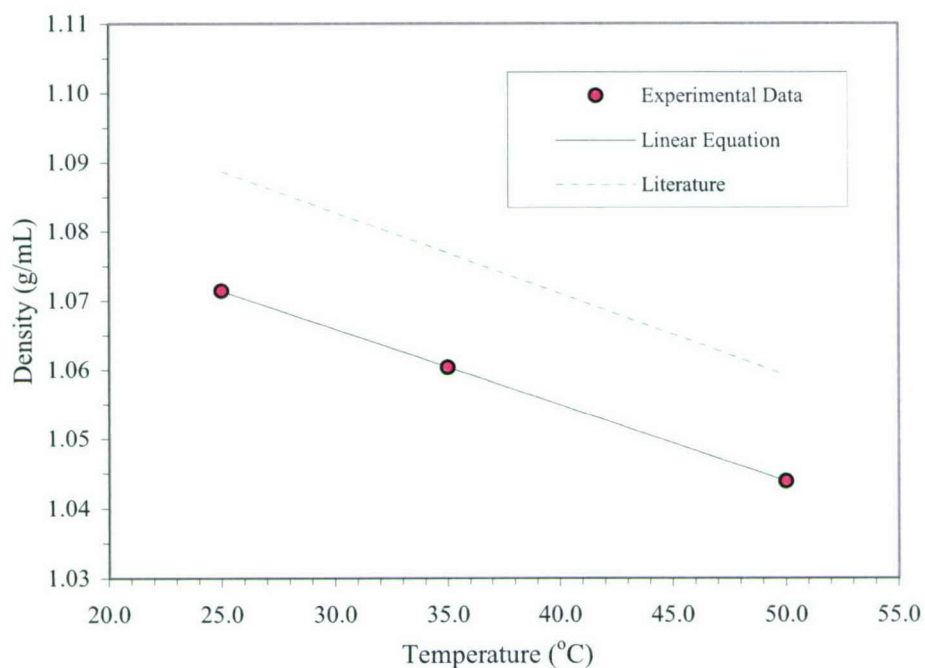


Figure 4.1 Density of Anniston GB

4.6 Viscosity

SAMPLE ID: GB/ACWA-1 (GB10005) Vial # 1
RECEIPT DATE: 22 June 2004
STORAGE: Ambient
ANALYSTS: Ann Butrow and Patrice Abercrombie
Agent Chemistry Team/R&T Directorate
TEST DATE: 20 July 2004
METHOD: ASTM D 445 Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)
INSTRUMENTATION: Cannon-Manning semi-micro viscometer and Cannon CT-1000 Constant Temperature Bath
CALIBRATION: The viscometer was calibrated by the manufacturer
DOCUMENTATION: See ECBC Lab Notebook 03-0172, p. 79 (Abercrombie)
RESULTS: Experimental data are listed in Table 4.7 and plotted in Figure 4.2 (Literature data for GB are included for comparison)

Table 4.7 Viscosity Results for GB10005

Temperature (°C)	Viscosity (centistokes)	
	Experimental	Literature (GB) *
25	1.652 ± 0.001	1.283
35	1.393 ± 0.002	1.090
50	1.116 ± 0.001	0.893

*Source: Samuel, J. B., Penski, E.C., Callahan, J.J., "Physical Properties of Standard Agents, Candidate Agents, and Related Compounds at Several Temperatures", ARCSL-SP-83015, Chemical Systems Laboratory, APG, MD, June 1983.

Antoine equation (for experimental data):

$$\log \eta = A - B/(C + t)$$

where:

η = viscosity, centistokes
 t = temperature, °C
 A = -1.9415
 B = -623.02
 C = 263.37

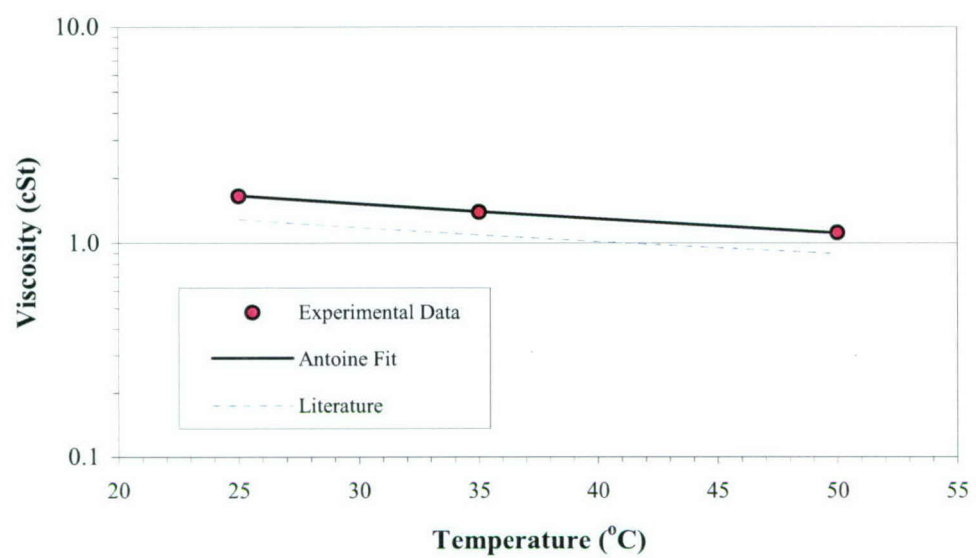


Figure 4.2 Viscosity of Anniston GB

5.0 RESULTS OF ANALYSIS OF GB SOLIDS

5.1 Sample Distribution

Aliquots of the GB solid sample, a portion of which is shown in Photo 5.1, were distributed for analysis by the CTF. Subsamples of the aliquots were dissolved or washed by one analyst and distributed for further characterization. Finally, synthesized DIPU (described in Section 6.0) was distributed for comparison to results obtained for the crystal samples. Distribution aliquots, analyses, and laboratory identification numbers of solid materials are shown in Table 5.1.

Table 5.1 Origin, Distribution, and Identification Systems of Solid Samples

Sample Name	Distribution Aliquot	Measurement	ID	Subsample	Lab ID
Shell Casing Fiber	(none)	GC/MS			ms04034
Anniston GB Solid GB/ACWA-2 GB10006	Vial #21	Heat of Fusion, Melting Point	(none)	Needles	GBC.01
				Chunks	GBC.03
				Chunks	GBC.04
		Microscopy			GB10006/Vial #21
	Vial #22	GC/MS	ms04033	White Chunk	030147-06901
				White Needle	030147-06902
				Gray Solid	030147-06903
	Vial #5	GC/MS			ms04029
	Vial #6	GC/MS	ms04030	Solid	030147-06904
				Needle	(none)
	Vial #7	GC/MS			ms04031
	CTF Preparation	ICP/MS	(none)	GB Solid – White	MB040761
				GB Solid – Gray	MB040762
	Vial #23	ICP/MS	0100069-124	GB Solid Dissolved in MeOH	MB040530
				GB Solid Debris	MB040531
		NMR		Acetone-washed GB Crystals	010069-118bH
				Acetonitrile-washed GB Crystals	010069-127H
		Heat of Fusion, Melting Point		Acetone-washed GB Solid	010069-118A
				Acetone-washed GB Crystals	010069-140
		Microscopy		Acetone-washed GB Solid	010069-118A
				Acetone-washed GB Crystals	010069-140
	Vial #24	Microscopy			GB10006/Vial #24
Synthesized N,N'-Diisopropyl Urea	010069-115A	Solubility			010069-117
	010069-115B	Microscopy			Synthesized Needles #2
	020034-039A	Heat of Fusion, Melting Point	Sample 1 (Powder)		Sample 1 (Powder)
		Microscopy			Urea Powder
	020034-017	Heat of Fusion, Melting Point	Sample 2 (Needles)		Sample 2 (Needles)

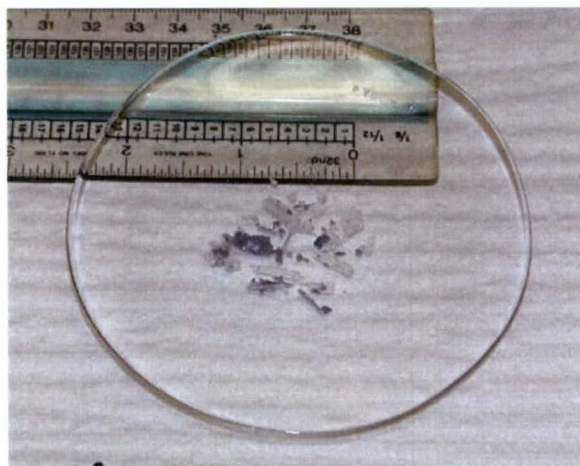


Photo 5.1 GB Crystals, Dust, and Debris on a Watch Glass

5.2 Mass Spectral Characterization

The following GB liquid and solid samples were received 21 June 2004:

- Vial #5 containing 0.0506 g GB solid in 2 mL chloroform (ms04029)
- Vial #6 containing 0.0514 g GB solid in 2 mL acetonitrile (ms04030)
- Vial #7 containing 0.0468 g GB solid in 2 mL isopropanol (ms04031)
- Vial #22 containing 0.48 g GB solid GB10006; GB/ACWA-2 (ms04033)

Vials #5, #6, and #7 contained a small amount of residual solids in addition to the GB solution.

5.2.1 GB Solid in Solution - Qualitative

The liquid portions of vials 5, 6 and 7 (ms04029, ms04030, ms04031) were analyzed on 21 June 2004 by GC/MS/EI (Method ACT-008). Liquids were analyzed as received and after derivatization with BSTFA/1 % TMCS (60°C for 30 min). The results in Tables 5.2 through 5.4 represent a combination of the analyses using DIMP as the common compound for quantification. Tributylamine (TBA) was only observed after derivatization.

Table 5.2 GC/MS Characterization of GB Solid in Chloroform

Compound	GC/MS Area %
GB	0.25
Diisopropyl methylphosphonate (DIMP)	1.5
Isopropyl methylphosphonic Acid (IMPA)	17.1
Tri- <i>n</i> -butylamine (TBA)	0.6
N,N'-Diisopropylurea	80.5

Table 5.3 GC/MS Characterization of GB Solid in Acetonitrile

Compound	GC/MS Area %
GB	0.18
Diisopropyl methylphosphonate (DIMP)	4.5
Isopropyl methylphosphonic Acid (IMPA)	47.4
Tri- <i>n</i> -butylamine (TBA)	2.3
N,N'-Diisopropylurea	45.6

Table 5.4 GC/MS Characterization of GB Solid in Isopropanol

Compound	GC/MS Area %
GB	0.58
Diisopropyl methylphosphonate (DIMP)	3.3
Isopropyl methylphosphonic Acid (IMPA)	35.2
Tri- <i>n</i> -butylamine (TBA)	1.7
N,N'-Diisopropylurea	59.2

5.2.2 Quantitative Determination of GB in GB Solid Sample Added to Solvent

A chloroform solution containing 0.0506 grams of Anniston GB solid, received from the CTF on 21 June 2004 (Vial #5), was analyzed by GC/MS for GB content on 31 August 2004. Some solid was still present in the solution. 40 μ L of solution was diluted to 1 mL in chloroform (1:25 dilution). The diluted sample was analyzed by GC/MSD (HP 5972) in the SIM/EI mode (ions 79, 81, 99, 125, 140). Quantification was performed using the m/z 99 ion and a 3-point external calibration curve (1.0, 2.5 and 5.0 μ g/mL GB; $r^2 = 0.9985$). Duplicate runs gave 3.50 and 3.27 μ g/mL GB (average 3.39 μ g/mL) in the diluted sample. Taking into account dilution factors, this corresponds to a concentration of 0.34 weight percent GB in the solid (wt/wt), assuming all GB was extracted into the solvent.

5.2.3 Analysis of Solid GB Samples

Vial #22 contained GB solid consisting primarily of 1) white solid chunks, 2) white crystalline needles, and 3) a gray solid. Attempts were made to isolate each of the solids for analysis. The solid chunks appeared to break up into the white crystalline needles. Solids were analyzed directly by direct exposure probe (DEP) mass spectral analysis in both the EI and methane CI modes (Finnigan TSQ-7000). In addition to vial #22, clear/white needles present in the acetonitrile solution (Vial #6) were analyzed. EI and CI mass spectra of IMPA, DIMP and DIPU were compared to library spectra.

Probe analysis lacks the sensitivity and selectivity to reliably detect GB at the levels indicated in the solutions.

5.2.3.1 Vial #22 White Solid Chunk

This sample is identified as 030147-06901, with analysis on 23 June 2004. Both EI and CI spectra are consistent with identification of this solid as N,N'-diisopropylurea. Small ions present at m/z 97 and 123 (less than 2 % total ion intensity) suggest a small amount of IMPA/DIMP may be present.

5.2.3.2 Vial #22 White Crystalline Needles

This sample is identified as 030147-06902, with analysis on 23 June 2004. Obtained spectra are identical to those obtained for the white chunk solid, indicating the needles are N,N'-diisopropylurea with a trace of IMPA/DIMP.

5.2.3.3 Vial #22 Gray Solid

This sample is identified as 030147-06903, with analysis on 23 June 2004. DEP/MS EI and CI analysis of the gray solid revealed much higher concentrations of IMPA and DIMP than in the white solids. Significant amounts (greater than 10 %) of each of the following were observed:

IMPA
DIMP
DIPU
Aromatic compounds

Ions associated with aromatic compounds are indicative of vinyl and phthalic acid type aromatic compounds. Specifically, ions are present which are consistent with the presence of ethenylmethylbenzene ($\phi\text{CH}_2\text{CH}=\text{CH}_2$) and phthalic acid, monomethyl ester.

5.2.3.4 Vial #6 (acetonitrile solution) White Solid

This sample is identified as 030147-06904, with analysis on 23 June 2004. DEP/MS EI and CI spectra indicate the solid analyzed was almost exclusively N,N'-diisopropylurea. IMPA and DIMP ions at 79, 97 and 123 were barely observable.

A second white needle-type fiber with a similar appearance was also analyzed from this solution. The spectrum of this particular fiber (EI only) was consistent with the presence of aromatic compounds related to ethenylmethylbenzene ($\phi\text{CH}_2\text{CH}=\text{CH}_2$) and phthalic acid, monomethyl ester.

5.2.3.5 GB Shell Casing Fiber

This sample, identified as ms04034, was received 25 June and analyzed on 29 June 2004. Grayish needle-like fibers obtained from a GB shell casing were also analyzed by DEP/MS in the EI and CI modes to see if aromatic compounds observed in GB solids might come from casing material. The ion at m/z 104 (EI) was the most abundant ion in both the shell casing fiber and GB solid fiber spectra. However, the shell casing 104 appeared to come from styrene and the GB solid 104 from phthalic acid. Other than the aromatic-related ions at 104 and 91, the casing and GB fiber spectra did not match.

5.3 NMR Analysis

5.3.1 GB Crystal Washed with Acetone

LAB I.D. NO: 010069-118bH
FIELD SAMPLE ID NO: GB/ACWA-2 (GB10006) Vial # 23
DATE RECEIVED: 24 Jun 2004
DATES ANALYZED: 29 Jun 2004, 20 Jul 2004
CONDITION OF SAMPLE: Cleaned crystal about $0.3 \times 0.2 \times 0.2 \text{ cm}^3$, white and glassy, shown in Photo 5.2

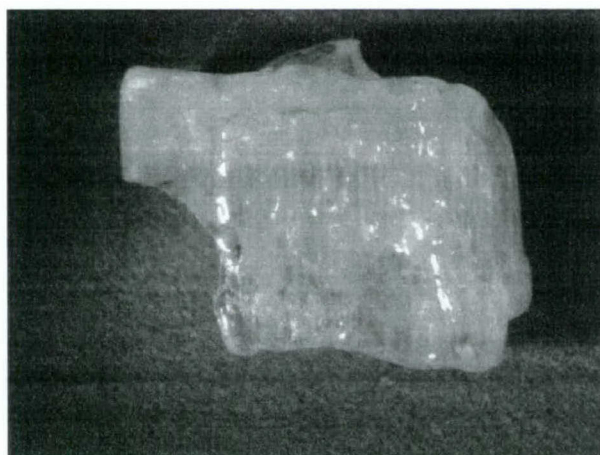


Photo 5.2 Cleaned DIPU Crystal

OBJECTIVE OF ANALYSIS: Determine identity of cleaned crystal
ANALYST: G. Hondrogiannis
METHOD NO: AM-084(*), "NMR Procedure for the Characterization of Organic Compounds"
INSTRUMENT: Bruker Avance 500 MHz (^1H), (^{31}P); 300 MHz (^{19}F)
SAMPLE PREPARATION: 0.179 g of bulk solid was washed with 32 g of acetone. A selected cleaned single crystal (0.0542 g) was dissolved in methanol- d and transferred into an NMR tube for analysis
METHOD DETECTION LIMIT: ~ 0.005 weight % (for this sample based on its concentration and the number of scans accumulated in ^1H and ^{19}F NMR)

Table 5.5 NMR Characterization of GB Crystals Washed with Acetone

Compound	Weight %
N-N'-Diisopropylurea (DIPU) $i\text{-C}_3\text{H}_7\text{NHC(O)NH}i\text{-C}_3\text{H}_7$	97.75
Isopropyl methylphosphonofluoridate (GB), $\text{CH}_3\text{P(O)(O}i\text{-C}_3\text{H}_7\text{)F}$	0.83
Unknown compound structurally similar to DIPU	0.52
Hydrofluoric acid (HF)	0.39
Isopropyl methylphosphonic acid (IMPA), $\text{CH}_3\text{P(O)(O}i\text{-C}_3\text{H}_7\text{)OH}$	0.24
Diisopropyl methylphosphonate (DIMP), $\text{CH}_3\text{P(O)(O}i\text{-C}_3\text{H}_7\text{)}_2$	0.23
Methylphosphonofluoridic acid (FA), $\text{CH}_3\text{P(O)(F)OH}$	0.04

(*) This method is semi-quantitative in that only the ratios of those compounds detected in the ^{31}P , ^{13}C , ^{19}F and ^1H spectra are measured. The method does not give an absolute amount of any component in the sample (i.e., $\mu\text{g/mL}$) since no internal/external standards are used.

On July 20 2004 the NMR tube containing the solution analyzed above was spiked with 0.0049g of Bromoform to be used as an internal standard for the absolute quantification of the amount of GB in the cleaned solid. This was calculated as 0.00053 g or $(0.00053/0.0542) \times 100 = 0.978 \%$.

5.3.2 GB Crystal Washed with Acetonitrile

LAB I.D. NO: 010069-127H

FIELD SAMPLE ID NO: GB/ACWA-2 (GB10006) Vial # 23

DATE RECEIVED: 24 Jun 2004

DATES ANALYZED: 22 Jul 2004, 27 Jul 2004

CONDITION OF SAMPLE: Cleaned crystal. Long (1.5 cm), white, and glassy

OBJECTIVE OF ANALYSIS: Determine identity of cleaned crystal

ANALYST: G. Hondrogiannis

METHOD NO: AM-084(*), "NMR Procedure for the Characterization of Organic Compounds"

INSTRUMENT: Bruker Avance 500 MHz (^1H), (^{31}P); 300 MHz (^{19}F)

SAMPLE PREPARATION: 0.1823 g of bulk solid was washed with 2.5 g of acetonitrile- d_3 . The remaining 0.1467 g of cleaned crystal was dried and then dissolved in methanol- d and transferred into an NMR tube for analysis.

METHOD DETECTION LIMIT: ~ 0.005 weight % (for this sample based on its concentration and the number of scans accumulated in ^1H and ^{19}F NMR)

Table 5.6 NMR Characterization of GB Crystals Washed with Acetonitrile

Compound	Weight %
N-N'-Diisopropylurea (DIPU) $i\text{-C}_3\text{H}_7\text{NHC(O)NH-}i\text{-C}_3\text{H}_7$	97.13
Hydrofluoric acid (HF)	1.4
Isopropyl methylphosphonofluoridate (GB), $\text{CH}_3\text{P(O)(O } i\text{-C}_3\text{H}_7\text{)F}$	0.68
Isopropyl methylphosphonic acid (IMPA), $\text{CH}_3\text{P(O)(O } i\text{-C}_3\text{H}_7\text{)OH}$	0.50
Diisopropyl methylphosphonate (DIMP), $\text{CH}_3\text{P(O)(O } i\text{-C}_3\text{H}_7\text{)}_2$	0.21
Unknown C-F compound (assumed MW=140)	0.08

(*) This method is semi-quantitative in that only the ratios of those compounds detected in the ^{31}P , ^{13}C , ^{19}F and ^1H spectra are measured. The method does not give an absolute amount of any component in the sample (i.e., $\mu\text{g/mL}$) since no internal/external standards are used.

On July 27 2004, the NMR tube containing the solution analyzed above was spiked with 0.0022g of 1,4-Difluorobenzene to be used as an internal standard for the absolute quantification of the amount of GB in the cleaned solid. This was calculated as 0.00117 g or $(0.00117/0.1467) \times 100 = 0.798 \%$.

5.4 Elemental Analysis Using ICP-MS

5.4.1 Bulk Solid

LAB I.D. NO:	As shown in Table 5.7
CUSTOMER SAMPLE NO:	As shown in Table 5.7
DATE RECEIVED:	5 August 2004. Received from CTF after digestion
DATES ANALYZED:	5 August 2004
CONDITION OF SAMPLE:	Samples received as clear, colorless digestates. The GB solid consisted primarily of 1) white solid chunks, 2) white crystalline needles, and 3) a gray solid. The white material was manually isolated from the gray by visual identification.
SAMPLE PREPARATION:	John Loss
ANALYSTS:	Craig Taylor and Steven Norman
METHOD NO:	IOP MT-07, "Operation and Maintenance of the ELAN 9000 Inductively Coupled-Mass Spectrometer (ICP-MS) for the Analysis of Metals in Various Matrices"
INSTRUMENT:	Perkin Elmer SCIEX ICP Mass Spectrometer ELAN 9000

Table 5.7 ICP-MS Results for Bulk Solid

Lab ID: Sample ID: Analytical Aliquot (g): Batch:	MB040761		MB040762	
	GB Solid – White		GB Solid – Gray	
	1.043		0.963	
	04080201		04080201	
	Results (Weight %)	Qual	Results (Weight %)	Qual
Aluminum	0.17	D	0.30	D
Barium	0.035	D	0.046	D
Calcium	0.73	D	1.3	D
Iron	0.012	E	0.015	JD
Magnesium	0.053	D	4.3	D
Phosphorus	0.62	D	9.9	D
Potassium	0.0014		0.034	D
Silicon	0.0084	D	0.020	D
Sodium	0.12	D	3.7	D
	Results (ng/g)	Qual	Results (ng/g)	Qual
Chromium	5,700		13,000	
Cobalt	3,500		14,000	
Copper	200,000	E	23,000	JD
Lead	1,700		1,500	
Manganese	2,500		2,500	
Molybdenum	89		65	
Nickel	2,200		3,000	
Sulfur	21,000	J	30,000	J
Tin	360		66	J
Titanium	19,000		220,000	D
Vanadium	1,000		190,000	D
Zinc	26,000	E	30,000	E

Qualifiers: D = Sample diluted to bring response into calibration range.

E = Sample response higher than highest calibration standard

J = Estimated Value

All results reported to two significant figures. Units of ng/g correspond to parts per billion (weight).

5.4.2 Purified Crystal and Debris

Initial Sample Preparation:

LAB I.D. NO: 010069-124

FIELD SAMPLE ID NO: GB/ACWA-2 (GB10006) Vial #23

DATE RECEIVED: 24 Jun 2004

DATES ANALYZED: 12, 14 Jul 2004

CONDITION OF SAMPLE: Well mixed and very homogeneous mixture of bulk solid

ANALYSTS: G. Hondrogiannis

METHOD NO:

N/A

SAMPLE PREPARATION:

2.4438 g of bulk solid was treated with 100 mL of anhydrous methanol with continuous stirring for 1 hour. Not all of the material dissolved. The residue is shown in Photo 5.3.

The resulting solution was transferred into an HPLC jar. Its weight was 77.30 g. The solid left behind was air dried for 48 hours. Its weight was 0.401g. Both liquid and solid were delivered for ICPMS analysis.



Photo 5.3 Dried Residue After the DIPU Component in the Solid GB Sample was Dissolved and Removed from the Residual

Sample Digestion and Analysis:

LAB I.D. NO:

As shown in Table 5.8

CUSTOMER SAMPLE NO:

As shown in Table 5.8

DATE RECEIVED:

21 July 2004

DATE ANALYZED:

5 August 2004

CONDITION OF SAMPLE:

Clear, colorless liquid in jar and white residue in flask

SAMPLE PREPARATION:

Craig Taylor

ANALYSTS:

Craig Taylor and Steven Norman

METHOD NO:

IOP MT-07, "Operation and Maintenance of the ELAN 9000 Inductively Coupled-Mass Spectrometer (ICP-MS) for the Analysis of Metals in Various Matrices"

INSTRUMENT:

Perkin Elmer SCIEX ICP Mass Spectrometer ELAN 9000

Table 5.8 ICP-MS Results for MeOH-Treated GB Solid

Lab ID:	MB040530		MB040531	
Sample ID:	Crystal Dissolved in MeOH		GB Crystal Debris	
Analytical Aliquot (g):	0.0419		0.312	
Batch:	04072301		04072301	
	Results (Weight %)	Qual	Results (Weight %)	Qual
Aluminum	0.061		3.7	D
Barium	0.0022		0.29	D
Calcium	0.33	JD	13	D
Iron	0.034		0.022	E
Magnesium	0.023		0.85	D
Phosphorus	3.1	D	0.52	D
Potassium	0.0055		0.0087	
Silicon	0.0080		0.28	JD
Sodium	0.040		0.67	D
	Results (ng/g)	Qual	Results (ng/g)	Qual
Chromium	17,000		19,000	
Cobalt	15,000		7,300	
Copper	420,000		110,000	
Lead	< 1,400		55,000	
Manganese	6,100		3,900	
Molybdenum	< 1,400		< 190	
Nickel	5,600		3,300	
Sulfur	830,000		150,000	J
Tin	< 6,200		< 830	
Titanium	27,000		140,000	
Vanadium	9,800		5,800	
Zinc	72,000		66,000	

Qualifiers: D = Sample diluted to bring response into calibration range.
E = Sample response higher than highest calibration standard
J = Estimated Value

All results reported to two significant figures.

A less than symbol (<) indicates that the element was not found at a concentration greater than or equal to the Practical Quantitation Limit (PQL), which is the number shown.

5.5 Heat of Fusion and Melting Point

5.5.1 DIPU And GB Solid

BACKGROUND:

High-purity, synthesized samples of N,N'-diisopropylurea were compared to the bulk solid sample and selected crystals from the Anniston GB sample. Refer to Table 5.1 (page 19) for a sample summary.

SAMPLE IDs: Sample 1: DIPU (powder), 020034-039A; off-white, fine powder; synthesized by G. Hondrogiannis, CBFAC

Sample 2: DIPU (needles), 020034-017; single, long (ca. 1 cm) thin crystal; synthesized by G. Hondrogiannis, CBFAC

Sample 3: GB solid, GB/ACWA-2, Vial #21 (GB10006); non-homogeneous solids; wet, brown "chunks" and off-white "needles;" received on 22 June 2004

ANALYSTS: Ann Butrow
Patrice Abercrombie
Agent Chemistry Team/R&T Directorate

TEST DATES: 6 – 7 July 2004

INSTRUMENTATION: TA Instruments 910 Differential Scanning Calorimeter and 2200 Controller

CALIBRATION METHODS: ASTM E 967 Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

ASTM E 968 Heat Flow Calibration of Differential Scanning Calorimeters

- Standards: tin (temperature) and indium (temperature and energy)
- Heating rate: 5 deg/min
- Pans: sealed aluminum

ANALYSIS METHODS: ASTM E793-01 Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry

ASTM 794-01 Melting and Crystallization Temperatures by Thermal Analysis

- Heating rate: 5 deg/min
- Sample pans: sealed aluminum
- Each sample was run in triplicate (three separate specimens from each sample). After heating through the melting point, the first specimen from each sample was cooled to ambient to permit recrystallization and reheated through the melting region

DOCUMENTATION: See ECBC Lab Notebook 03-0172, p. 82 (Abercrombie)

RESULTS:

Melting points are determined from the intersection of tangents to the melting peak (or melting endotherm) at the onset of melting. This onset temperature is defined as the melting point. Heat of fusion is determined from integration of the area under the melting endotherm.

Calibration: The results for the calibration standards are listed in Table 5.9.

Table 5.9 DSC Calibration Results

Standard	Melting Point (°C)		Heat of Fusion (Joules/gram)	
	Literature	Observed*	Literature	Observed*
Indium	156.60	156.44 ± 0.04	28.58	28.2 ± 0.2
Tin	231.93	230.7 ± 0.6	-	-

*Mean of three determinations

Samples: The thermal curves for the two diisopropyl ureas and the GB solid are shown in Appendix A, Figures A.1 through A.16. These figures include the melting endotherms from each specimen run with the melting points and heats of fusion indicated. These plots also include selected other temperatures calculated by the instrument software (such as peak minimum temperature) which were not used for this work and are crossed out. For the specimens that were cooled and reheated to check for recrystallization, only the heating curves are shown. (Cooling curves were not recorded.) For each sample, a summary plot comparing the melting curves is shown. In addition, a plot comparing the two ureas and the GB solid is included.

Heats of fusion and melting (onset) temperatures for the three samples are listed in Table 5.10.

Table 5.10 DSC Results for DIPU and GB Solid

DSC File	Melting Point (°C)	Heat of Fusion (Joules/g)
DIPU (powder)		
UREAP.01	190.20	165.4
UREAP.02 (rerun of UREAP.01)	189.45*	157.1*
UREAP.03	190.19	161.4
UREAP.04	190.22	157.0
Mean	190.20 ± 0.02	161 ± 4

Table 5.10 DSC Results for DIPU and GB Solid (continued)

DSC File	Melting Point (°C)	Heat of Fusion (Joules/g)
DIPU (needles)		
UREAN.01	189.17	162.1
UREAN.02 (rerun of UREAN.01)	187.96*	153.5*
UREAN.03	190.65	155.2
UREAN.04	189.60	157.8
Mean	189.8 ± 0.8	158 ± 3
GB Solid		
GBC.01 (needles)	176.43	85.66
GBC.02 (rerun of GBC.01)	180.41*	60.82*
GBC.03 (chunks)	163.15	73.79
GBC.04 (chunks)	175.01	98.96
Mean	172 ± 7	86 ± 13

*The results from this run were not used in calculation of the means.

Sample 1: DIPU (powder)

The thermal curve for this sample consisted of a single, reasonably sharp melting endotherm around 190°C. The peak was “clean” with no accompanying spikes or bumps. The melting points for the three specimens (files UREAP.01, .03, .04) were reproducible. On reheating (file UREAP.02), the first specimen melted at a temperature within 1 degree of the initial melting point. Determination of heat of fusion (area under the melting endotherm) was straightforward due to the flat baselines before and after the melting peak.

Sample 2: DIPU (needles)

The thermal curve for this sample also consisted of a single, “clean,” reasonably sharp melting endotherm around 190°C. The three specimens (files UREAN.01, .03, .04) gave reproducible melting points. Reheating the specimen (file UREAN.02) gave a melting point slightly lower than the initial value. As with the “powder” urea sample, heat of fusion was easily determined due to the flat baselines before and after melting.

Sample 3: GB Solid

Because this sample was non-homogeneous, the two main types of solid material were characterized. The first specimen contained primarily the off-white “needles” and the second and third contained primarily the wet, brown “chunks.”

The resulting thermal curve for this sample consisted of a melting peak around 172°C (files GBC.01, .03, .04) that was broad and “noisy” (erratic and spiky). The baselines before and after the melting endotherm were also “noisy”. The standard deviation for both the melting point and heat of fusion of this sample was much larger than for either urea sample. In contrast to the urea samples, the reheated specimen (file GBC.02) melted four degrees higher than the initial melting point. Additional erratic and non-reproducible endothermic events were observed at temperatures well above the melting point.

DISCUSSION:

The results for the synthesized diisopropylurea powder and needle samples were similar both qualitatively (the melting endotherms were similarly shaped) and quantitatively (the melting points and heats of fusion were essentially the same). The reproducible melting point detected for both samples on reheating suggests that they readily recrystallize on cooling to ambient in the DSC.

In contrast, the GB solid exhibited a number of differences from the urea samples. Overall, the melting peaks were broader and the baselines were more erratic for the GB solid than the urea. The melting points were considerably lower (18 degrees) and the heats of fusion were about half of the values measured for the ureas.

These differences are not surprising, given the source and nature of the samples (synthesis versus munition). The GB solid samples collected also contained varied bits of debris (fiberglass, etc.) and are assumed to be wet with some amount of neat GB. The peak broadening, erratic baselines, and lower melting points observed for the GB solid are all consistent with impure material. The reduced heats of fusion and additional endotherms observed beyond the melting point for the GB solid are assumed to be due to the presence of these impurities.

The four degree increase in melting point detected on reheating of the first GB solid specimen is further evidence of the presence of impurities. Impurities in solution typically depress the melting point (the phenomenon of freezing point depression). It is postulated that the GB solid, as received, contained impurities that depressed the melting point. The increase in melting point after the initial melting and recrystallization suggests that impurities initially trapped in the crystal lattice were excluded upon crystal reformation.

For sharp, well-defined melting endotherms with smooth, flat baselines, determination of both onset temperature and peak area is straightforward. In this case, there is little uncertainty regarding placement of onset tangents or peak integration limits. However, for broad or “noisy” endotherms with poorly-defined melting onsets or irregularly-shaped baselines, accurate determination of both melting point and heat of fusion can be a challenge. This explains the larger standard deviations for the mean melting points and heats of fusion for the GB solid as compared to the urea samples.

5.5.2 Washed GB Solid

In light of the results described in Section 5.5.1, the thermal measurements were repeated on crystals, i.e., GB solid that was washed to remove the liquid agent contamination and GB solid that was hand sorted to remove inert debris.

SAMPLE IDs: Sample 1: Acetone-washed GB solid from Anniston, 010069-118A, non-homogeneous white/grey particles (long “needle” and short “fiber” particles); prepared by G. Hondrogiannis, CBFAC, ECBC

Sample 2: Acetone-washed GB solid from Anniston, 010069-140, homogeneous, single, large (0.150 mg) white crystal; isolated and prepared by G. Hondrogiannis, CBFAC, ECBC

ANALYSTS: Ann Butrow
Patrice Abercrombie
Agent Chemistry Team/R&T Directorate/ECBC

TEST DATES: 24, 27 September 2004

INSTRUMENTATION: TA Instruments 910 Differential Scanning Calorimeter and 2200 Controller

CALIBRATION METHODS: ASTM E 967 Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

ASTM E 968 Heat Flow Calibration of Differential Scanning Calorimeters

Standards: tin (temperature) and indium (temperature and energy)

- Heating rate: 5 deg/min
- Pans: sealed aluminum

ANALYSIS METHODS: ASTM E793-01 Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry

ASTM 794-01 Melting and Crystallization Temperatures by Thermal Analysis

- Heating rate: 5 deg/min
- Sample pans: sealed aluminum
- Each sample was run in triplicate (three separate specimens from each sample). After heating through the melting point, the first specimen from each sample was cooled to ambient to permit recrystallization and reheated through the melting region

DOCUMENTATION: See ECBC Lab Notebook 03-0172, p. 92 (Abercrombie)

RESULTS:

Melting points are determined from the intersection of tangents to the melting peak (or melting endotherm) at the onset of melting. This onset temperature is defined as the melting point. Heat of fusion is determined from integration of the area under the melting endotherm.

Calibration:

The results for the calibration standards are listed in Table 5.11.

Table 5.11 DSC Calibration Results

Standard	Melting Point (°C)		Heat of Fusion (Joules/gram)	
	Literature	Observed*	Literature	Observed*
Indium	156.60	157.06 ± 0.06	28.58	28.96 ± 0.88
Tin	231.93	231.63 ± 0.09	-	-

*Mean of three determinations

Samples:

The thermal curves for the two acetone-washed GB samples are shown in Appendix A, Figures A.17 through A.26. These figures include the melting endotherms from each specimen run with the melting points and heats of fusion indicated. (These plots also include other selected temperatures calculated by the instrument software, such as peak minimum temperature, which were not used for this work and are crossed out.)

For the specimens that were cooled and reheated to check for recrystallization, only the heating curves are shown. (Cooling curves were not recorded.) For each sample, a summary plot comparing the melting curves is also provided.

Heats of fusion and melting (onset) temperatures for the samples are listed in Table 5.12.

Table 5.12 DSC Results for Washed GB Samples

DSC File	Melting Point (°C)	Heat of Fusion (Joules/g)
010069-0118A		
GBC2.01	185.53	50.0
GBC2.02 (rerun of GBC1.01)	179.42*	40.2*
GBC2.03	182.79	17.5
GBC2.04	187.45	116.9
Mean	185 ± 2	61 ± 51
010069-140		
GBC3.01	184.37	135.6
GBC3.02 (rerun of GBC3.01)	186.37*	28.0*
GBC3.03	189.03	152.0
GBC3.04	188.75	156.0
Mean	187 ± 3	148 ± 11

*The results from this run were not used in calculation of the means.

Sample 1: 010069-0118A

The thermal curve for this sample consisted of a single, reasonably sharp melting endotherm around 185°C. Two of the specimens also showed an additional small endothermic peak around 200°C. The baselines before and after melting were somewhat “noisy” and sloped. The melting points for the three specimens (files GBC2.01, .03, .04) were in reasonable agreement. On reheating (file GBC2.02), the first specimen melted more than 6 degrees lower than the initial melting point. The heats of fusion for this sample varied significantly from specimen to specimen.

Sample 2: 010069-140

The thermal curve for this sample consisted of a single, reasonably sharp melting endotherm around 187°C. The first specimen also showed a large, “noisy” endotherm with an onset around 220°C. The baselines before and after melting for this sample were less “noisy” than for Sample 1. The melting points for the three specimens (files GBC3.01, .03, .04) were also in reasonable agreement. Reheating specimen 1 (file GBC3.02) gave a melting point two degrees higher than the initial value. The heats of fusion for this material were more consistent than those detected for Sample 1.

DISCUSSION:

Washed Sample 1 versus Washed Sample 2

While both of these samples are acetone-washed and their melting points are similar (within 2 degrees), the measured heats of fusion were quite different. These results suggest that solvent washing was more effective for Sample 2 and that Sample 1 still contains residual contamination. This is consistent with the appearance of the samples as received.

The presence of an inert contaminant that does not dissolve in the melt and causes a subsequent reduction in the melting point due to freezing point depression would yield similar melting points for Samples 1 and 2. However, the presence of an inert contaminant that contributes to the specimen mass but not to the thermal energy transferred during melting would yield a drastically different heat of fusion for Sample 1 relative to Sample 2. The results in Table 5.12 reflect this behavior.

The large standard deviation in the mean heat of fusion for Sample 1 (61 ± 51 J/g or ± 82 %) is consistent with a wide range of contaminant content among the three specimens run. The significantly smaller standard deviation for the heat of fusion of Sample 2 (148 ± 11 J/g or ± 7 %) suggests a more homogeneous material. In addition, the visual observation of two different types of particles in Sample 1 supports the hypothesis of residual contamination.

The additional endotherms beyond the melting point observed for both samples were also detected in the earlier studies and are assumed to be due to impurities.

Washed GB Solid versus As-Received GB Solid

A comparison of these results with those described in Section 5.5.1 for the GB solid clearly indicates that solvent washing has removed some contamination that was contributing to the lower melting point and a reduction in the measured heat of fusion. The melting point for the GB solid as received was 172°C as compared with the 185 and 187°C for acetone-washed

Samples 1 and 2, respectively. The mean heat of fusion for the GB solid as received was 86 Joules/gram as compared to 148 Joules/gram for washed Sample 2.

The elevation in both melting point and heat of fusion for the washed GB samples brings these values closer to those for DIPU. The literature melting point for DIPU is 192°C and the mean value determined during the earlier studies for the two synthesized urea samples was 190°C. The mean heat of fusion for the two synthesized samples was determined to be 160 Joules/gram. The results from washed Sample 2 (melting point: 187°C and heat of fusion: 148 Joules/gram) are consistent with the proposed identification of the GB crystals as DIPU. While none of the data reported here conflicts with that conclusion, it is important to note that it also does not confirm it. These results indicate that acetone-washed GB crystals display thermal behavior similar to DIPU; additional tests beyond thermal analysis would be required to conclusively identify the GB crystals.

6.0 SYNTHESIS OF N,N'-DIISOPROPYLUREA

6.1 Synthesis of DIPU

6.1.1 For Solubility Measurements

LAB I.D. NO: 010069-115A
LOCATION: E5100-28
TEMPERATURE: 25.9°C
DATE PREPARED: 06/29/04
ANALYST: G. Hondrogiannis
CHEMICALS USED: 1,3-Diisopropylcarbodiimide, 99 %
Hydrofluoric acid, 48 %
Deionized Water

SAMPLE PREPARATION: To a 10-mL round-bottomed flask, equipped with a magnetic stirring bar and a condenser, were added 5.812 g (0.323 moles) of deionized water and 0.749 g (0.0059 moles) of 1,3-diisopropylcarbodiimide. This resulted in a two-phase solution in which the carbodiimide was the top phase and the water the bottom. No mixing was achieved despite vigorous agitation. While stirring, 1 drop (0.032 g) of 48 % aqueous HF solution was added at room temperature, followed by a brief reflux to achieve a homogeneous almost clear solution. This was allowed to cool to room temperature.

Upon cooling the solution was full of short (2mm) very fine needle-like crystals of DIPU. The pH of the solution was 4-5.

The crystals were collected and washed with water under vacuum in a glass-frit hose-connection Buckner funnel until the pH of the aqueous washing was neutral. The crystals were allowed to dry in the Buckner funnel under vacuum for 2 hours and then collected. The amount of dry crystals collected was 0.320 g. The yield of the reaction was 38.0 %.

6.1.2 For Melting Point and Other Measurements

LAB I.D. NO: 020034-039A
LOCATION: E5100-28
TEMPERATURE: Ambient
DATE PREPARED: 05/01/03
CONDITION OF SAMPLE: Amorphous white powder
ANALYST: G. Hondrogiannis

CHEMICAL USED: 1,3-Diisopropylcarbodiimide 99 %
Hydrofluoric Acid, 48 %
Deionized Water

SAMPLE PREPARATION: To a 12-mL Wheaton glass sample vial (screw-cap size 15 mm), equipped with a magnetic stirring bar, were added 5.654 g (0.314 moles) of distilled water, and 0.815 g (0.0065 moles) of 1,3-diisopropylcarbodiimide. This resulted in a two-phase solution in which the carbodiimide was the top phase and the water the bottom. No mixing was achieved despite vigorous agitation; the top layer was clear but the bottom was white and a bit cloudy. No crystals were visible. While stirring, 3 drops (0.090 g) of 48 % aqueous HF solution were added at room temperature. Upon mixing it was observed that the top phase became white and a bit cloudy, whereas the bottom phase became clear. After 5 minutes, coarse white crystals appeared to float in solution. After 30 minutes, coagulates of white particles adhered to the vial walls. The reaction was stopped after 1 hour. The pH of the solution was 3-4.

The crystals were collected and washed with water under vacuum in a Buckner funnel until the pH of the aqueous washing was neutral. The crystals were allowed to dry in the Buckner funnel under vacuum for 2 hours. The amount of dry crystals was 0.574 g. The yield of the reaction was 61.3 %.

6.1.3 Long Needle Sample

LAB I.D. NO: 020034-017

LOCATION: E5100-28

TEMPERATURE: Ambient

DATE PREPARED: 03/04/03

CONDITION OF SAMPLE: Single, transparent, off white, long (2.5 – 3 cm), thin (0.1 – 0.3 mm) needle-like crystal

ANALYST: G. Hondrogiannis

CHEMICALS USED: IMPA, synthesized, not purchased
DIMP, synthesized, not purchased
1,3-Diisopropylcarbodiimide, 99 %

SAMPLE PREPARATION: To a 5-mm NMR tube equipped with a pressure cap were added 0.393 g (0.0022 moles) of diisopropyl methylphosphonate and 0.065 g (0.0005 moles) of isopropyl methylphosphonic acid. To it was added 0.019 g (0.0002 moles) of 1,3-diisopropylcarbodiimide. This resulted in the formation of few crystals $\frac{3}{4}$ the length to the top of the NMR tube. The solution was briefly hand shaken and characterized by NMR spectroscopy. The NMR tube was allowed to stand without mixing at room temperature.

After 2 months it was observed that a long (2 – 3 cm) thin needle-like crystal of DIPU had formed. 1 mL of chloroform was added to wash the crystal out of the NMR tube, and the crystal was washed carefully with about 2 mL of distilled water. The long crystal was then air dried in a petri dish.

6.1.4 Thin Short Needles Sample

LAB I.D. NO: 010069-115B
LOCATION: E5100-28
TEMPERATURE: Ambient
DATE PREPARED: 06/29/04
CONDITION OF SAMPLE: White, short (0.2-1 cm), fine, needle-like crystals, plus some crystal flakes, as shown in Photo 6.1.



Photo 6.1 Synthesized DIPU By Addition of DICDI to Water

ANALYST: G. Hondrogiannis
CHEMICALS USED: 1,3-Diisopropylcarbodiimide, 99 %
DI Water
SAMPLE PREPARATION: To a 125-mL Pyrex Erlenmeyer flask, equipped with a stopper and a magnetic stirring bar, were added 63.500 g (3.528 moles) of distilled water and 1.1102 g (0.0088 moles) of

1,3-diisopropyl carbodiimide. This resulted in a two-phase solution in which the carbodiimide was the top phase and the water the bottom. No mixing was achieved despite vigorous stirring at 80 °C for 30 min. The reaction flask was allowed to stand (no mixing) at room temperature.

Within 3 weeks thin relatively long (0.6 – 0.8 cm) needle-like crystals of DIPU started to form. More crystals formed within a month, but the size of the crystals originally observed did not appear to grow any longer. The pH of the solution was 8-9.

The crystals were collected and washed under vacuum with sufficient water until the pH of the aqueous washing was neutral. The crystals were allowed to dry under vacuum for 3 hours and then collected. The amount of dry crystals collected was 0.688 g. The yield of the reaction was 54.3 %.

6.2 Urea Solubility

LAB I.D. NO: 010069-117

CONDITION OF SAMPLE: Fine short white fibers of synthesized DIPU

ANALYST: G. Hondrogiannis

SAMPLE PREPARATION: A given amount of synthesized urea was added to 500µl of the given solvent. The solubility was noted. Increments of 250 µL of solvent were added until the solid was estimated to have a visual solubility index of ≥ 8 . The only exception was water. The weight of the solvent was then recorded.

METHOD DETECTION LIMIT: A Visual Index of 10 was given for complete solubility of urea in the given solvent and 0 for complete insolubility. The solubility data are expressed as:

$$\text{Weight \%} = \frac{\text{urea weight}}{\text{solvent weight}} \times 100$$

Thus isopropyl alcohol shows the largest solubility per amount of solvent added. However, care should be exercised since the solubility study is qualitative.

Table 6.1 DIPU Solubility

Study Date: 24 July 2004

Temperature (°C): 26.6

Solvent	Solvent density (g/mL)	Urea Weight (g)	Solvent Weight (g)	Urea Weight %	Visual Solubility Index ^A
Acetonitrile, 99.9 %	0.786	0.0109	1.269	0.86	10
Bleach, 6.42 weight %	1.07	0.0244	6.698	0.36	8
Isopropanol, 99.9 %	0.785	0.0095	0.370	2.57	10

Table 6.1 DIPU Solubility (continued)

Solvent	Solvent density (g/mL)	Urea Weight (g)	Solvent Weight (g)	Urea Weight %	Visual Solubility Index [^]
N-Ethyldiethanolamine, 98 %	1.038	0.0133	1.393	0.96	9.9
N-Methyldiethanolamine, 99 %	0.887	0.0122	1.212	1.01	10
Water	1.000	0.0191	3.640	0.53	5
Benzene, 99.9 %	0.874	0.0116	1.350	0.86	8
Isobutyl alcohol, 99.5 %	0.803	0.0093	0.403	2.31	10
Chloroform, 99+ %	1.492	0.0100	2.072	0.48	10
Acetone, 99.5 %	0.791	0.0108	1.368	0.79	10
Ethylene glycol, > 99.5 %	1.113	0.0131	8.611	0.15	10
Tetrahydrofuran, 99.9 %	0.889	0.0116	1.359	0.85	7-8
Ethanolamine, 99.5 %	1.012	0.0162	3.5797	0.45	9-10

[^]Numerical Indicator of complete solubility = 10

Numerical Indicator of complete insolubility =0

Another set of solubility experiments were conducted between 13 and 22 July 2004. For this experiment, solvent was added to DIPU crystals to achieve approximately 2 % solute by weight and observations were recorded. Additional solvent was then added to achieve approximately 1 % solute by weight; again, observations were recorded. The results are given in Table 6.2.

Table 6.2 Dissolution of DIPU at Approximately 2 and 1 Weight %

Study Date: 13 – 22 July 2004

Temperature (°C): Ambient

Solvent	Solvent density (g/mL)	Crystal Weight (g)	Solvent Weight (g)	Urea Weight %	Visual Solubility Index ^(A)	Location of Crystals in Solvent
Acetonitrile	0.786	0.0109	0.502	2.1	4-5	Top
			1.269	0.90	10	Gone
Bleach	1.07	0.0244	1.418	1.7	0-1	Top
			6.698	0.40	8 ⁽¹⁾	Bottom
Isopropyl alcohol 99.9 %	0.785	0.0095	0.370	2.5	10	Gone
N-Methyldiethanolamine	1.038	0.0133	0.603	2.2	3-4	Mostly top
			1.393	0.90	9.9	Trace top
N,N-Dimethylethanolamine	0.887	0.0122	0.434	2.70	6	Dispersed
			1.212	1.00	10	Gone

Table 6.2 Dissolution of DIPU at Approximately 2 and 1 Weight % (continued)

Solvent	Solvent density (g/mL)	Crystal Weight (g)	Solvent Weight (g)	Urea Weight %	Visual Solubility Index ^(A)	Location of Crystals in Solvent
Water	1.000	0.0191	1.005	1.9	0	Top
			3.640	0.50	5 ⁽²⁾	Top
Methanol	0.791	0.0098	0.516	1.9	10	Gone
Benzene	0.874	0.0116	0.521	2.2	5-6	Mostly bottom
			1.350	0.90	8	Bottom
Isobutyl alcohol	0.803	0.0093	0.403	2.3	10	Gone
				0.50	10	Gone
Chloroform	1.492	0.0100	0.704	1.4	7-8	Top
			2.072	0.50	10	Gone
Acetone	0.791	0.0108	0.387	2.7	2-3	Bottom
			1.368	0.80	10	Gone
Ethylene glycol	1.113	0.0131	0.528	2.4	3	Top
			8.611	0.20	10	Gone
Tetrahydrofuran	0.889	0.0116	0.512	2.2	2-3	Bottom
			1.359	0.80	7-8	Bottom
Monoethanolamine	1.012	0.0162	1.125	1.4	2-3	Top
			3.5797	0.45	9-10	Top

^A Numerical Indicator of complete solubility = 10. Numerical Indicator of complete insolubility = 0

- (1) In the 10 ml vial a few tiny oily droplets were observed. Also, the bottom of the 10 ml vial was covered with a thin, loose, cotton-like white material. No resemblance to the original urea crystals.
- (2) It would appear that a few of the urea crystals might have actually have dissolved. At least this is the impression one could get visually.

Finally, the solubility of DIPU in isopropanol was investigated by sequentially adding solvent to a known weight of crystal. After each solvent addition, the solution was observed. The results are presented in Table 6.3.

Table 6.3 Solubility of DIPU in Isopropanol

Study Date: 24 July 2004

Temperature (°C): 26.0

Crystal Weight (mg)	Solvent Weight (g)	Solvent Density	Crystal Weight %	Visual Solubility Index ^(A)	Location of crystals in solvent
28.8	0.3167	0.785	8.3	7	Top
	0.3318		8.0	8	Top
	0.3514		7.6	9	Top
	0.3723		7.2	10	
	0.3911		6.9	10	

Numerical Indicator of complete solubility = 10

Numerical Indicator of complete insolubility = 0

7.0 OPTICAL MICROSCOPY

Anniston GB crystal samples contain two major types of material: 1) N,N'-diisopropylurea in the form of crystalline needles and 2) N,N'-diisopropylurea in the form of crystalline chunks. At times there is also gray-colored debris. The gray-colored debris apparently does not dissolve in methanol, whereas the needles and chunks do. These crystalline samples and chunks were photographed using a digital camera and measured using microscopic scalar techniques.

SAMPLES: Urea Powder (from Ann Butrow (ECBC))
 GB 10006/Vial #21 (from Ann Butrow (ECBC) on 29 July 2004)
 GB 10006/vial #24 (via TEU on 5 August 2004)
 010069-118A (from George Hondrogiannis (ECBC) on 12 August 2004)
 Synthesized Needles #2 (from Yu Chu Yang (ECBC) on
 31 August 2004)
 010069-140 (from George Hondrogiannis (ECBC) on
 13 September 2004)

DATES ANALYZED: 29 July to 22 September 2004

ANALYST: J. Michael Lochner

EQUIPMENT: Optical Microscope - Daigger MBC-10 Five-Way Magnification Stereo
 Microscope
 Pictures - Nikon COOLPIX 950 Digital Camera, processed using
 HotShots 1.5 software.
 Microscope Calibration - "Biological Stage Micrometer" slide
 (1 mm/100 divisions)
 Calibration Eyepiece - OLYMPUS SWHK 10X eyepiece containing a
 Scale Reticle (100 divisions)

INSTRUMENTAL TECHNIQUE:

The MBC-10 microscope was initially placed in a fume hood. A "Biological Stage Micrometer" slide was used to calibrate the OLYMPUS SWHK 10X eyepiece, which contained a 100-division reticle scale. Each division on the reticle scale was calibrated against the "Biological Stage Micrometer" slide which was placed on the viewing stage. For very large crystals, a 2 cm section of plastic ruler was used for comparison. A conversion factor was determined and used for each magnification employed in examining each crystal.

Crystals were selected as representative of each sample provided. If possible, the entire sample was initially photographed using the Nikon camera alone. An approximately 8.7 cm diameter piece of circular blue poster board was used as a background for contrast. The blue cardboard was placed in a Petri dish, and the sample was placed onto the blue background. An initial photograph was taken. Several representative crystal/chunk pieces were selected from each

sample and arranged in a clockwise fashion around the perimeter of the Petri dish; a total of thirteen items were selected. Each piece was photographed through the microscope eyepiece using the Nikon camera. Each photograph contained an overlay of the reticle scale and the crystal/chunk examined. Sample width and lengths were estimated (using the appropriate scale factor) and recorded.

RESULTS:

Sample pictures and associated data are attached as addenda.

Table 7.1 Optical Microscopy Results

Sample	Size Distribution Needles	Size Distribution Chunks/Platelets
Synthesized Urea Powder	0.64 mm x 0.12 mm (large) 0.48 mm x 0.11 mm (small)	0.03 mm x 0.04 mm
GB 10006/VIAL#21	12.24 mm x 1.29 mm (large) 3.29 mm x 0.86 mm (small)	10.66 mm x 2.62 mm (large) 3.24 mm x 1.76 mm (small)
GB 10006/VIAL#24	12.89 mm x 1.11 mm (large) 3.07 mm x 0.67 mm (small)	13.02 mm x 3.02 mm (large) 5.56 mm x 1.51 mm (small)
010069-118A	3.56 mm x 0.43 mm (large) 2.61 mm x 0.31 mm (small)	2.11 mm x 1.06 mm (large) 1.58 mm x 1.16 mm (small)
Synthesized Needles #2	8.22 mm x 0.93 mm (large) 2.67 mm x 0.29 mm (small)	3.56 mm x 4.18 mm (large) 0.91 mm x 0.91 mm (small)
010069-140	N/A	10.33 mm x 7.42 mm (single crystal)

DISCUSSION:

Samples were recorded and examined as received. A representative sample of each was photographed and analyzed for measurement comparison.

- The Urea Powder sample was the most uniform sample, consisting mostly of small particles, when magnified similar to rice grains in appearance. The powder sample also contained particles as small as 0.03 mm x 0.04 mm.
- The two samples of “GB 10006” (Vial #21 and Vial #24) were composed of large and small “chunks” and “needles.” The chunks seemed to be of no particular shape, but appeared layered and were easily broken. Many pieces appeared to have other particulate smaller “chunks” attached.
- Sample 010069-118A was composed of one large long crystal in addition to many smaller chunks and needles. Sample 118A also contained many smaller particles of approximately 0.03 mm x 0.04 mm size.
- The Synthesized Needles #2 sample was evenly divided between large needles, small needles and large “platelets.” The largest needle was 1.40 cm x 0.78 mm.
- Sample 010069-140 consisted of a single crystal “chunk,” 10.33 mm x 7.42 mm in size.

Most needles, chunks and platelets were observed to be composed of multiple facets, junctures, and striations. Examples of each of these can be seen in Appendix B.1.

Samples also revealed other smaller particulate matter attached to the main needle or chunk, as shown in the appendices.

SUMMARY:

Six samples containing different morphologies were examined, particles measured, and measurements compared. Detailed pictures and measurements are provided in Appendix B.2 through B.7.

APPENDIXES:

APPENDIX B.1 - Samples arranged in Petri dishes (Photos B.1 through B.6)

APPENDIX B.2 - Measurements of selected crystals/chunks from sample "Urea Powder"
(Photo B.7 through B.9)

APPENDIX B.3 - Measurements of selected crystals/chunks from sample "GB 10006/Vial#21"
(Photo B.10)

APPENDIX B.4 - Measurements of selected crystals/chunks from sample "GB 10006/Vial#24"
(Photo B.11)

APPENDIX B.5 - Measurements of selected crystals/chunks from sample "010069-118A"
(Photo B.12)

APPENDIX B.6 - Measurements of selected crystals/chunks from sample "Synthesized
Needles #2" (Photo B.13)

APPENDIX B.7 - Measurements of selected crystals/chunks from sample "010069140"
(Photo B.14)

ABBREVIATIONS AND ACRONYMS

ACWA	Assembled Chemical Weapons Alternatives
ANAD	Anniston Army Depot
ANCDF	Anniston Chemical Agent Disposal Facility
AQS	Agent Quantification System
BGCAPP	Blue Grass Chemical Agent Destruction Pilot Plant
BSTFA	N,O-bis(trimethylsilyl)trifluoroacetamide
DF	Methylphosphonic difluoride
DICDI	Diisopropylcarbodiimide
DIMP	Diisopropyl methylphosphonate
DIPU	N,N'-diisopropylurea
DPE	Demilitarization Protective Ensemble
ECBC	Edgewood Chemical Biological Center
GB	Isopropyl methylphosphonofluoridate
GC/MS	Gas Chromatography/Mass Spectrometry
Fluoracid	Methylphosphonofluoridic acid
HF	Hydrofluoric acid
IMPA	Isopropyl methylphosphonic acid
IPA	Isopropanol
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
MDB	Munitions Demilitarization Building
MRC	Multiple Round Containers
NMR	Nuclear Magnetic Resonance
PM-ACWA	Program Manager Assembled Chemical Weapons Assessment
TBA	Tri-n-butylamine
TEU	Technical Escort Unit
TMCS	Trimethylchlorosilane
TOCDF	Tooele Chemical Agent Disposal Facility
TRRP	Technical Risk Reduction Program

Blank

APPENDIX A
THERMAL CURVES FOR SPECIMENS

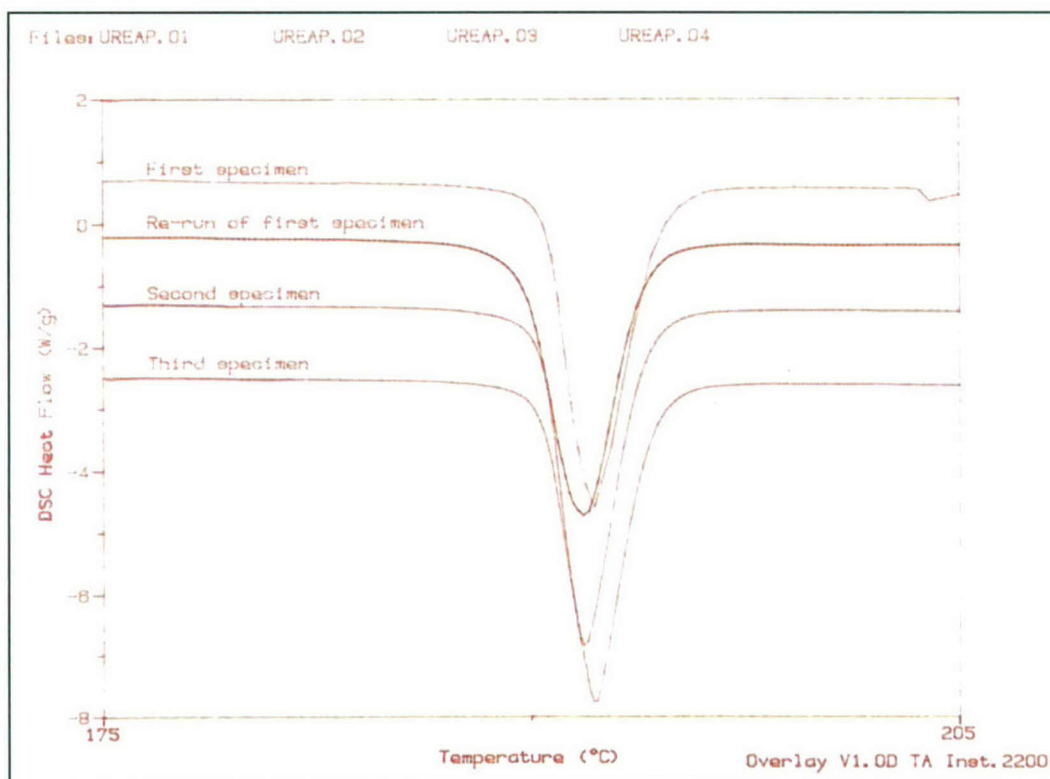


Figure A.1 Melting Curve Summary for DIPU Powder

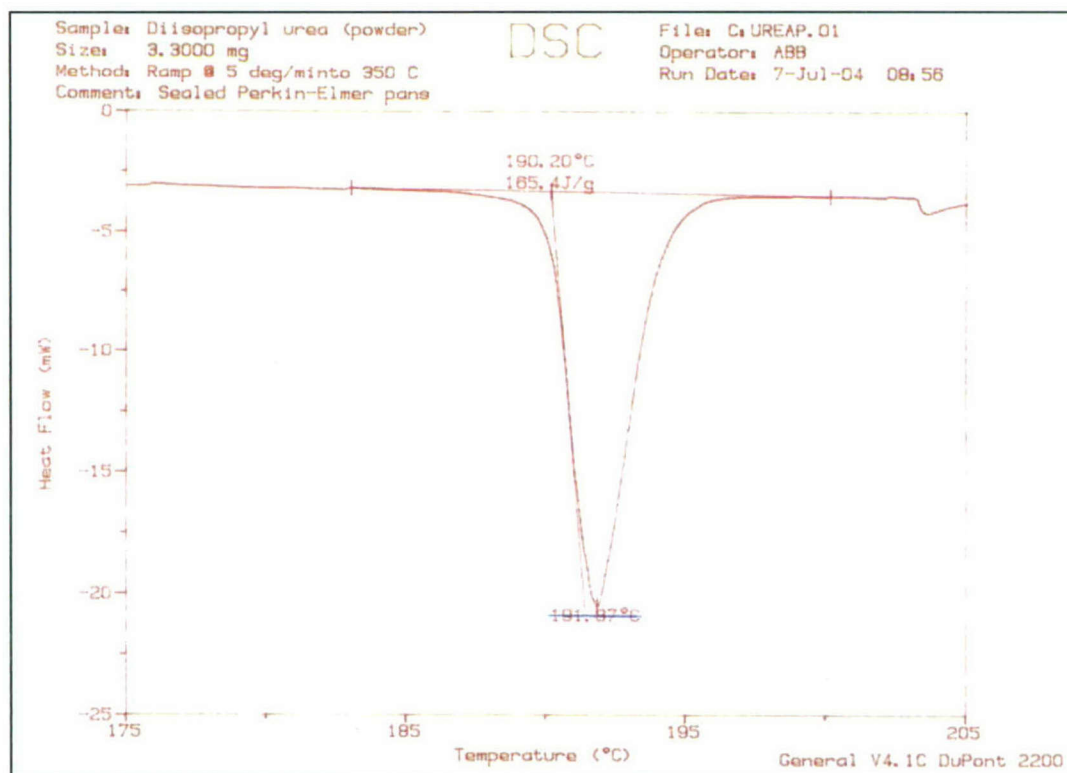


Figure A.2 Melting Endotherm for DIPU Powder Specimen 1

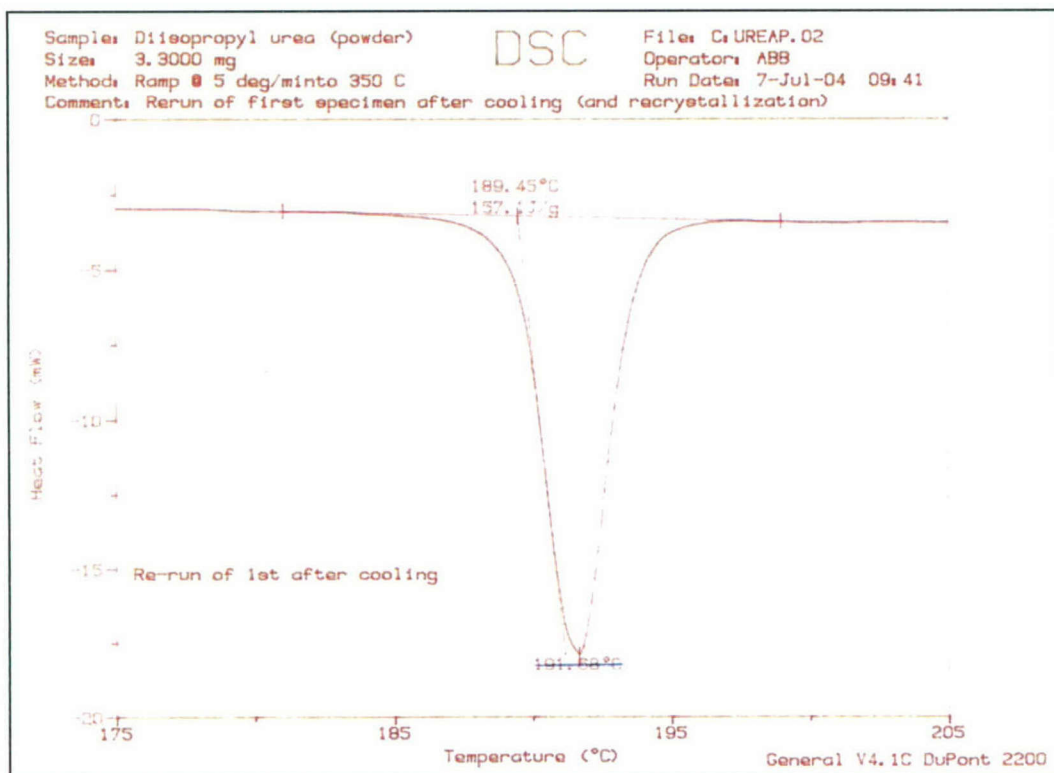


Figure A.3 Melting Endotherm for DIPU Powder Specimen 1 Rerun

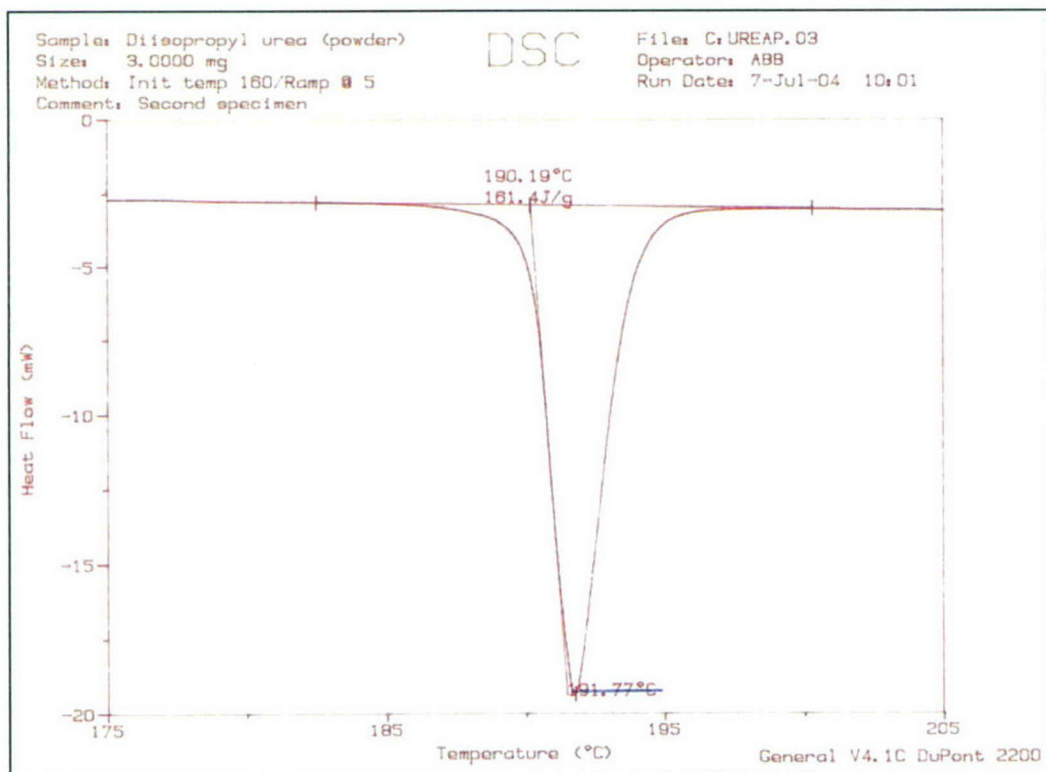


Figure A.4 Melting Endotherm for DIPU Powder Specimen 2

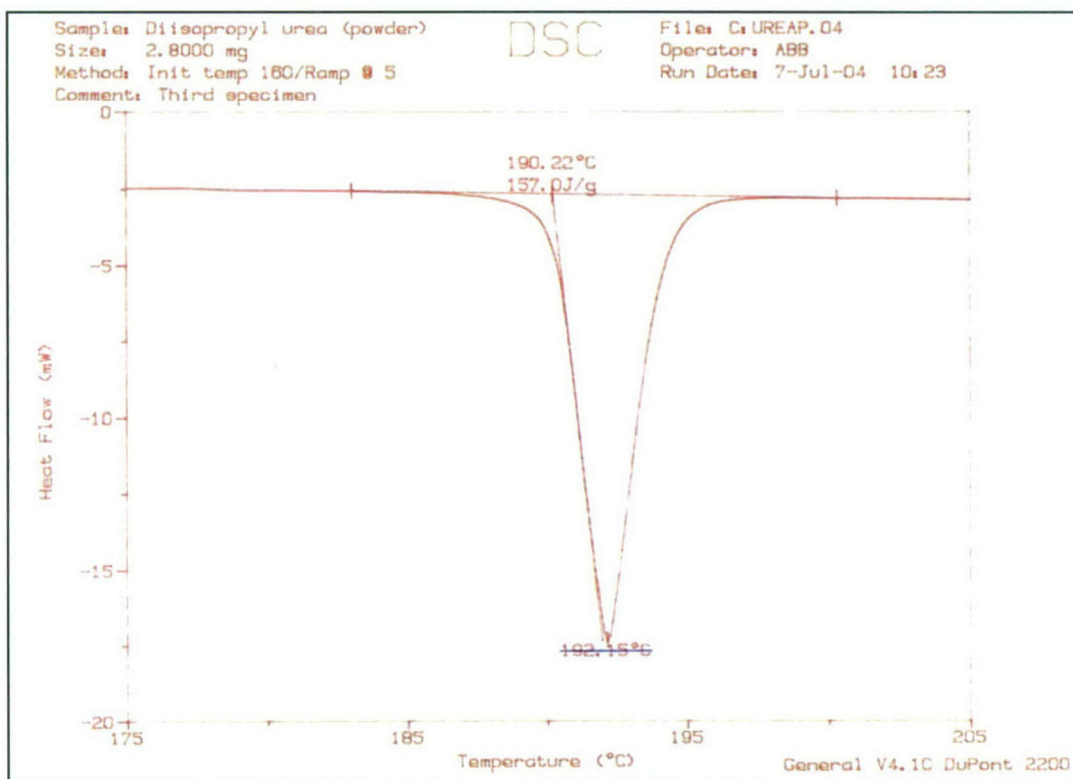


Figure A.5 Melting Endotherm for DIPU Powder Specimen 3

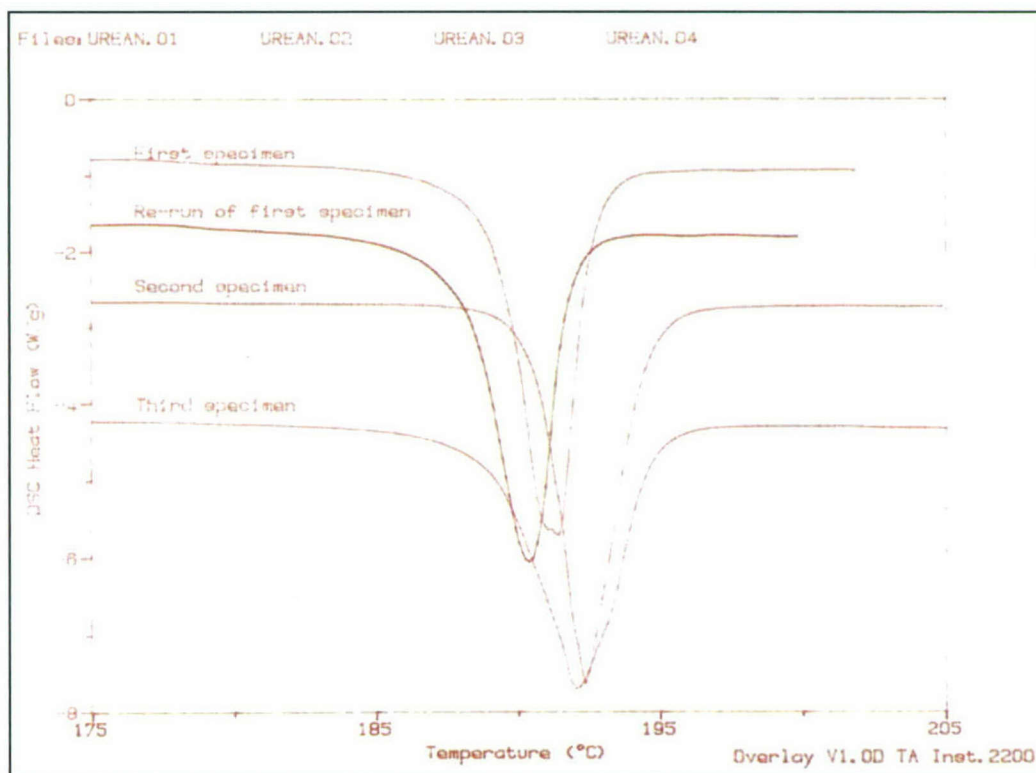


Figure A.6 Melting Curve Summary for DIPU Needles

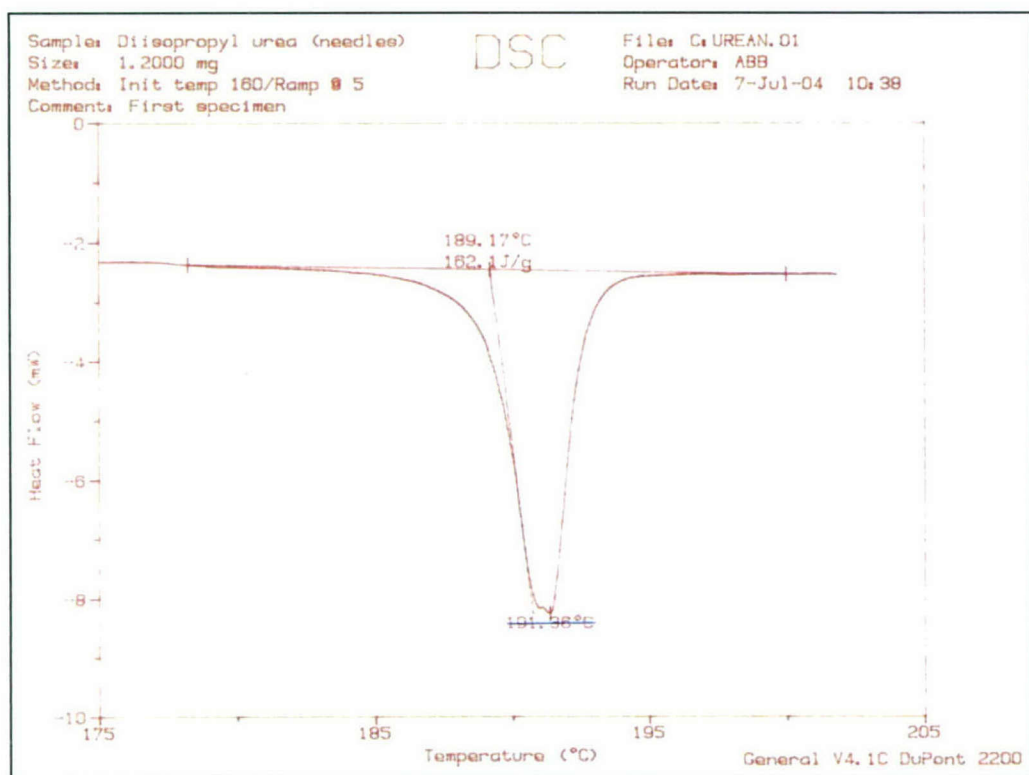


Figure A.7 Melting Endotherm for DIPU Needles Specimen 1

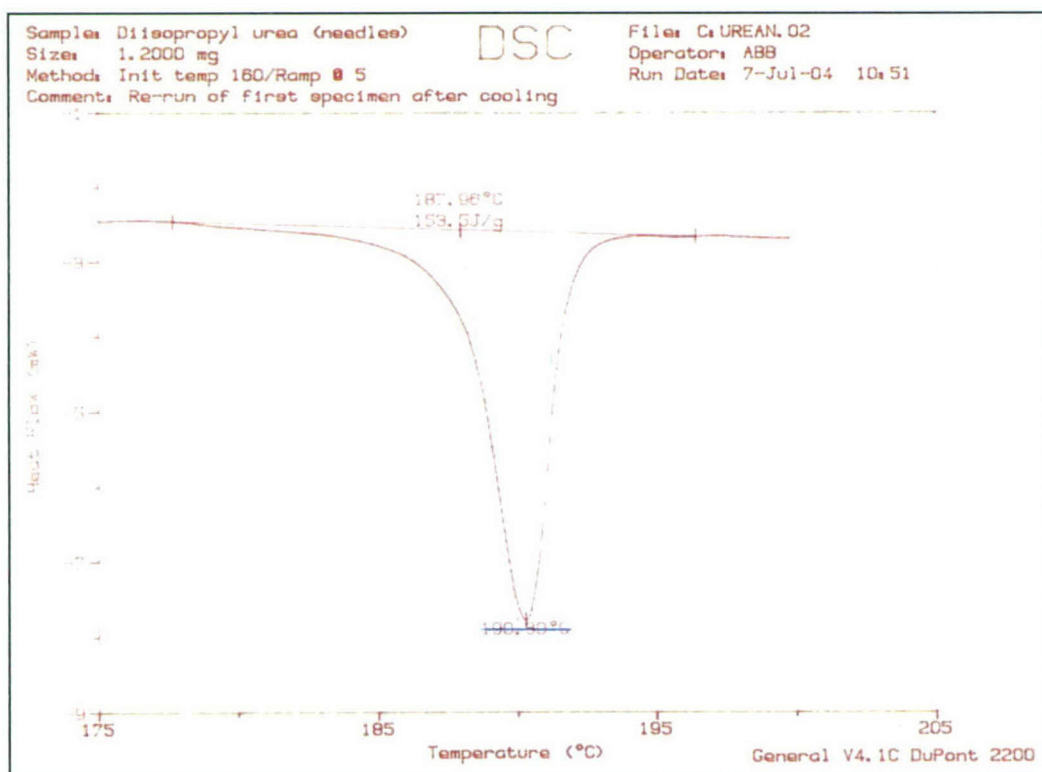


Figure A.8 Melting Endotherm for DIPU Needles Specimen 1 Rerun

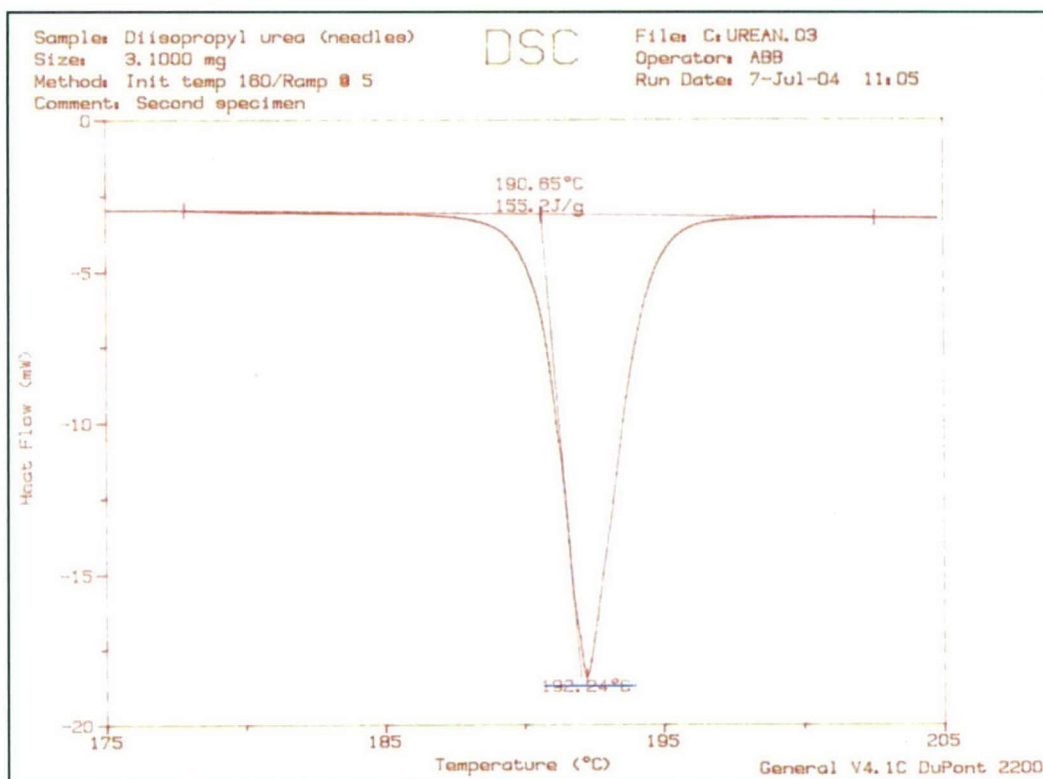


Figure A.9 Melting Endotherm for DIPU Needles Specimen 2

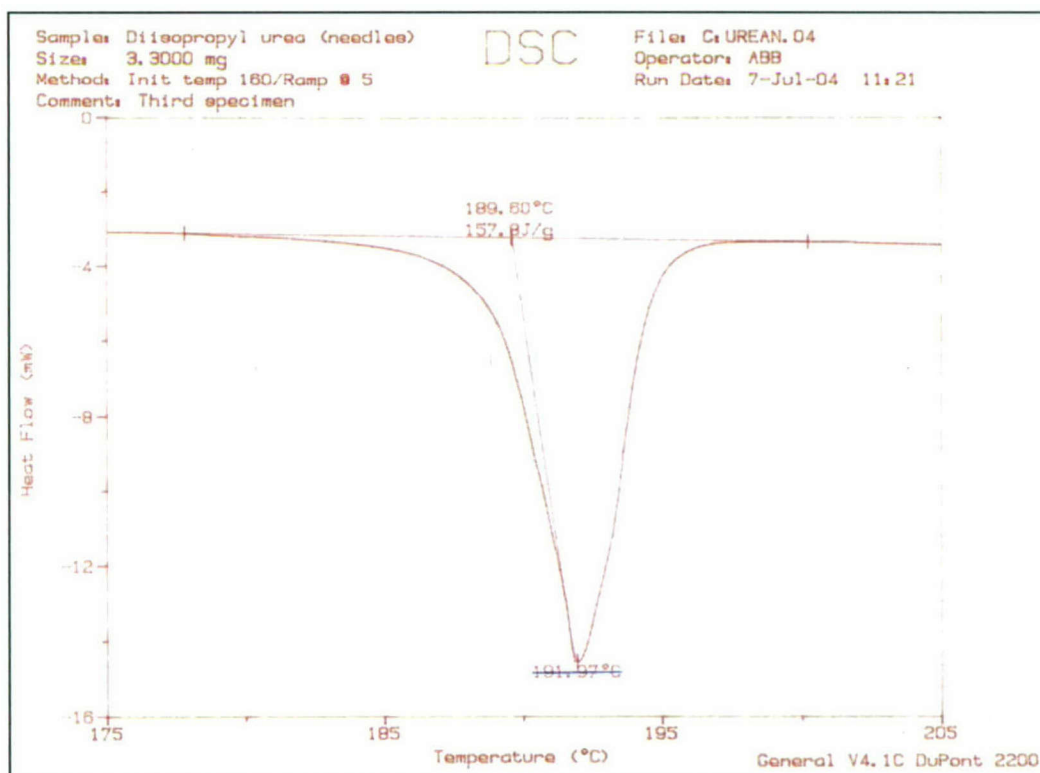


Figure A.10 Melting Endotherm for DIPU Needles Specimen 3

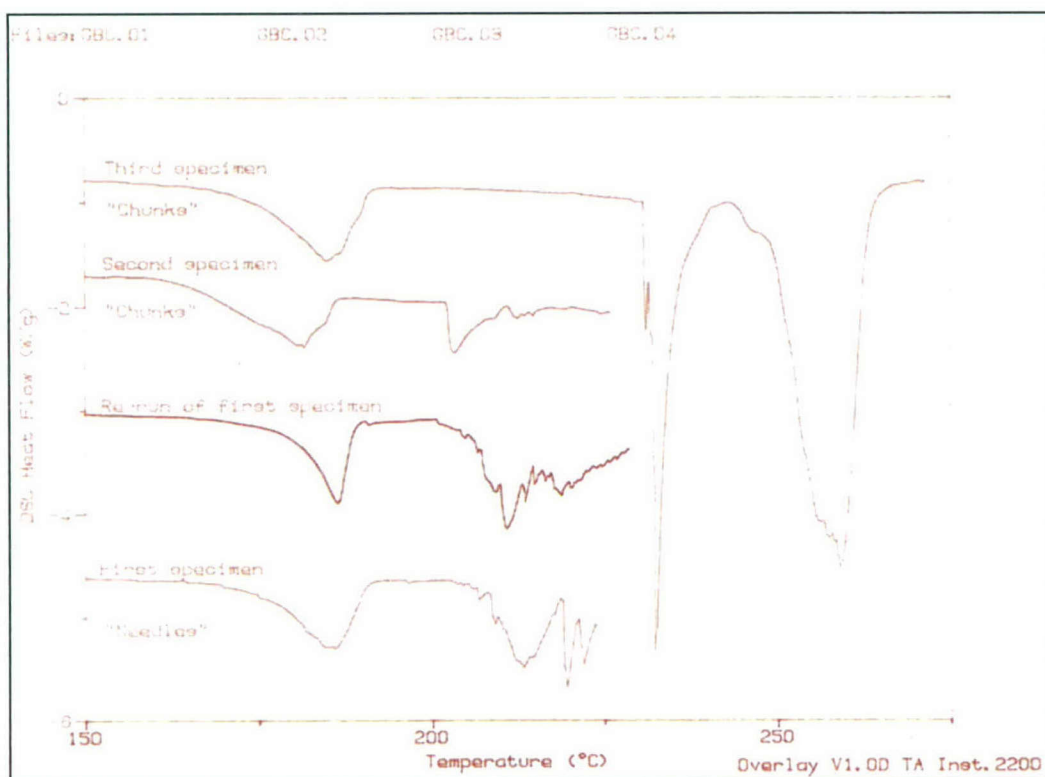


Figure A.11 Melting Curve Summary for GB Solid

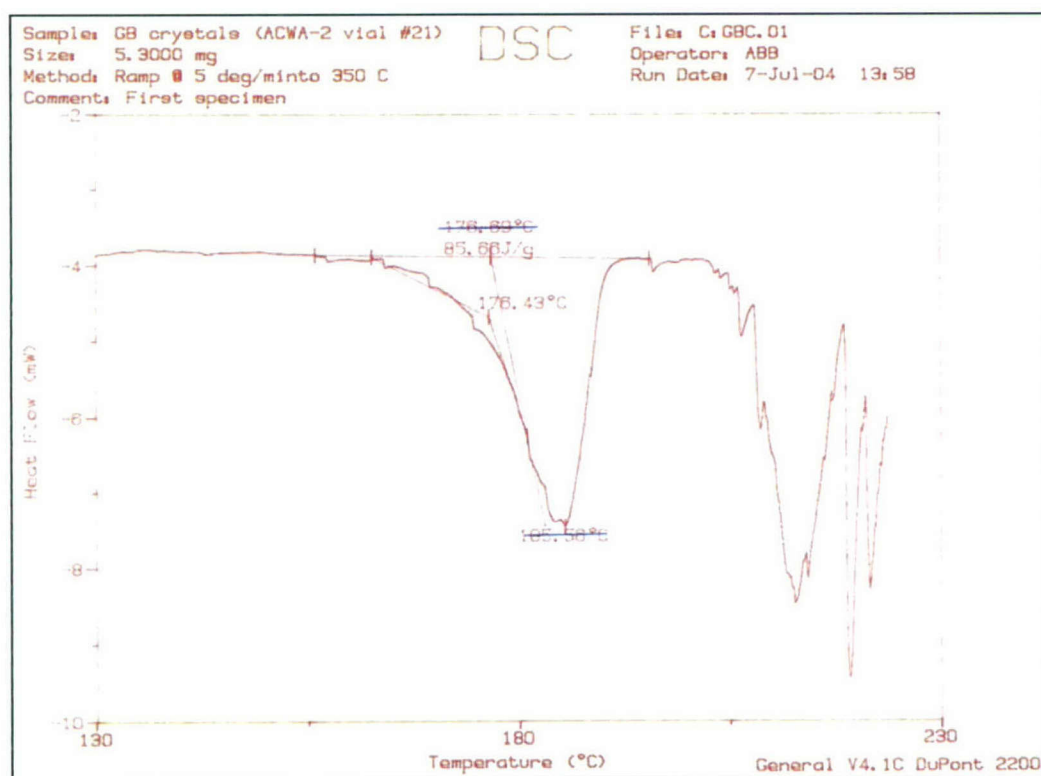


Figure A.12 Melting Endotherm for GB Solid Specimen 1 (Needles)

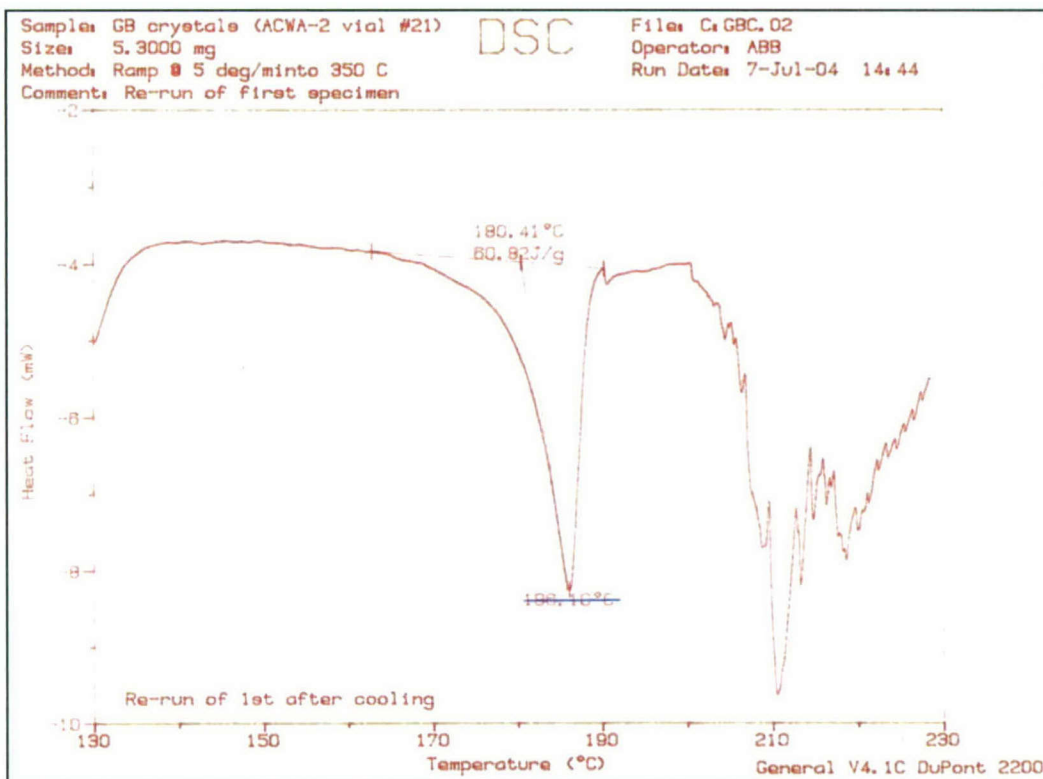


Figure A.13 Melting Endotherm for GB Solid Specimen 1 (Needles) Rerun

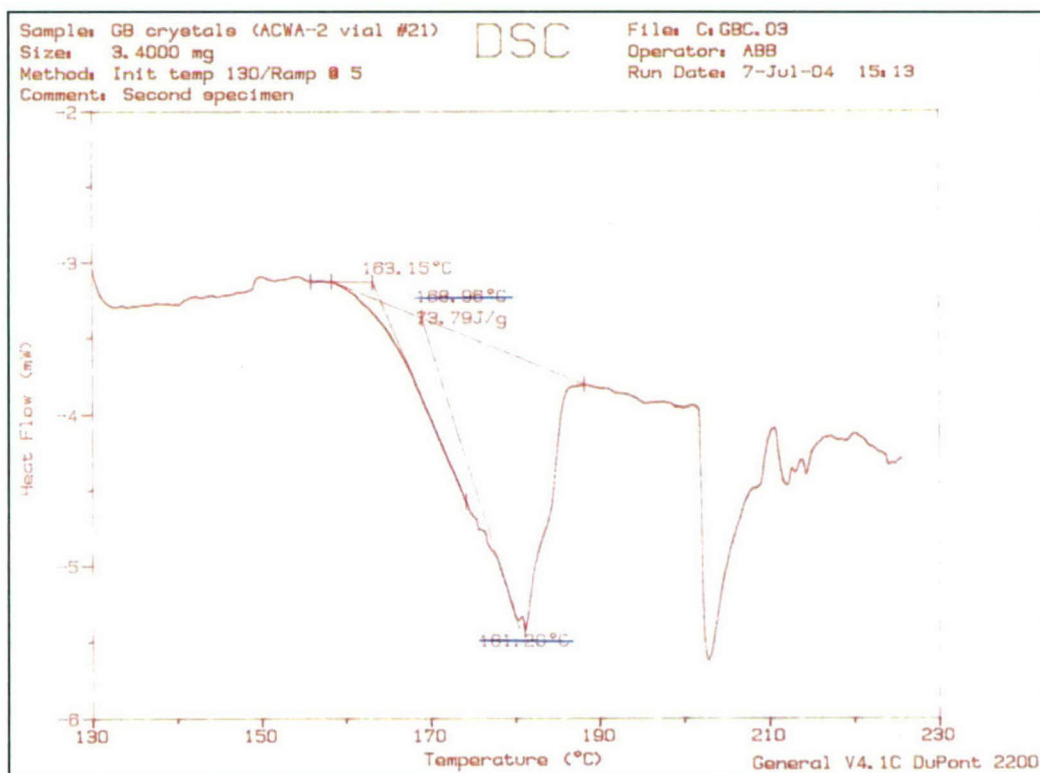


Figure A.14 Melting Endotherm for GB Solid Specimen 2

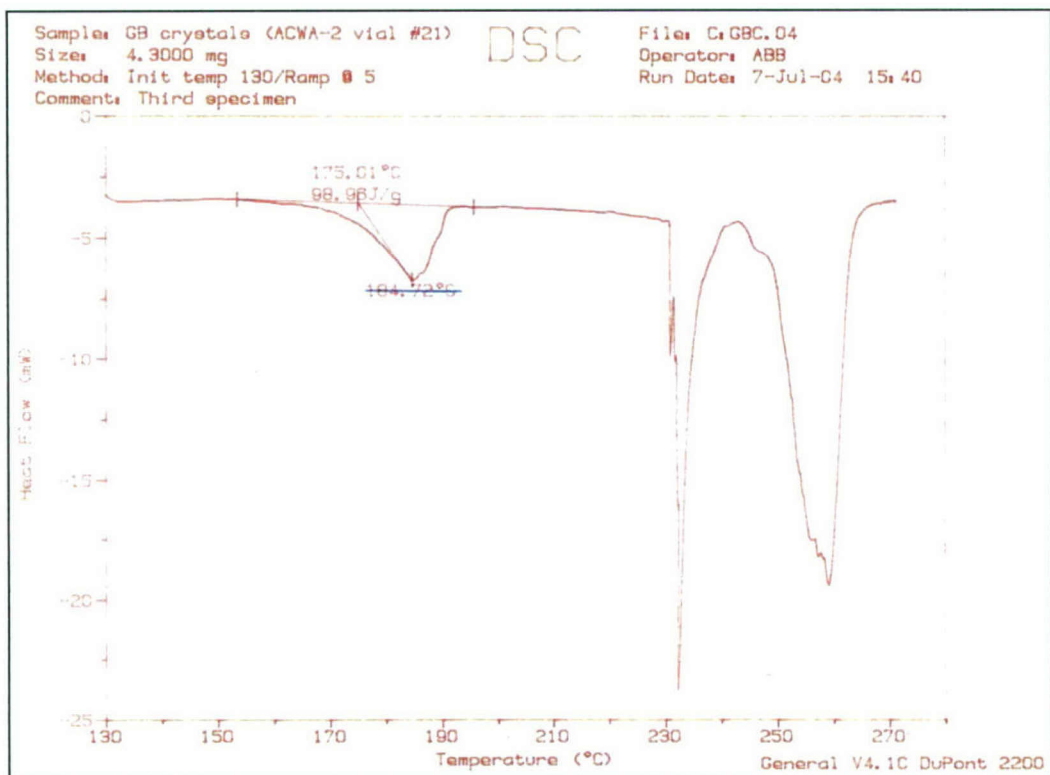


Figure A.15 Melting Endotherm for GB Solid Specimen 3

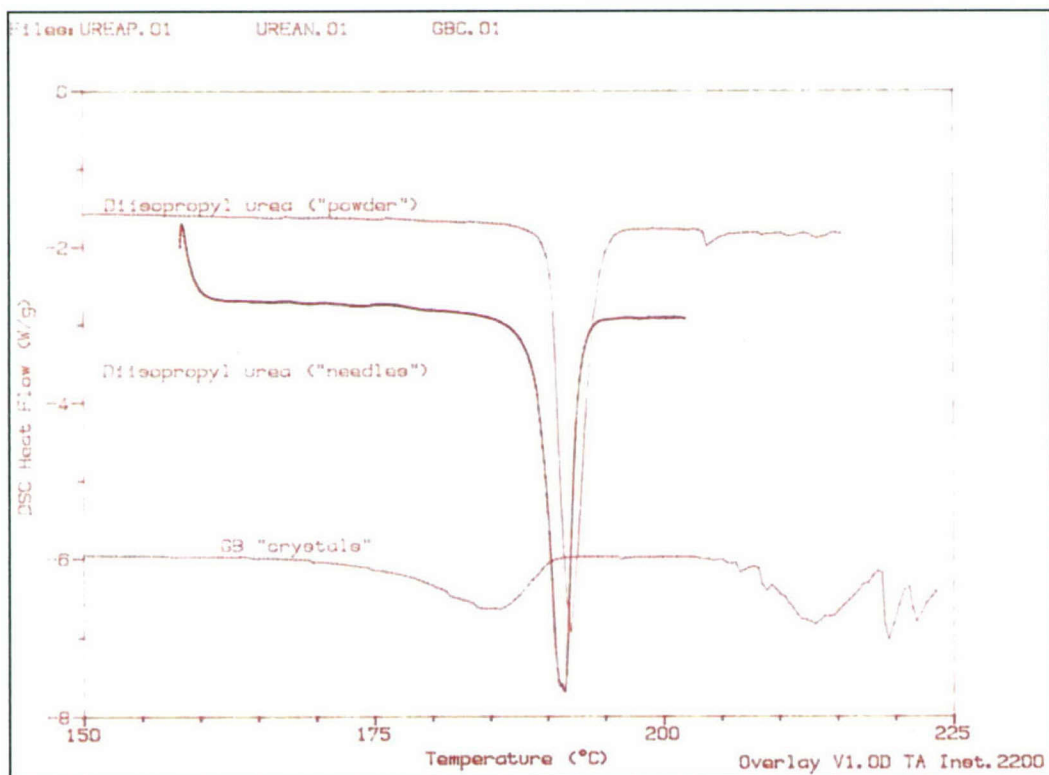


Figure A.16 Melting Endotherm Comparison of DIPU Powder, DIPU Needles, and GB Solid

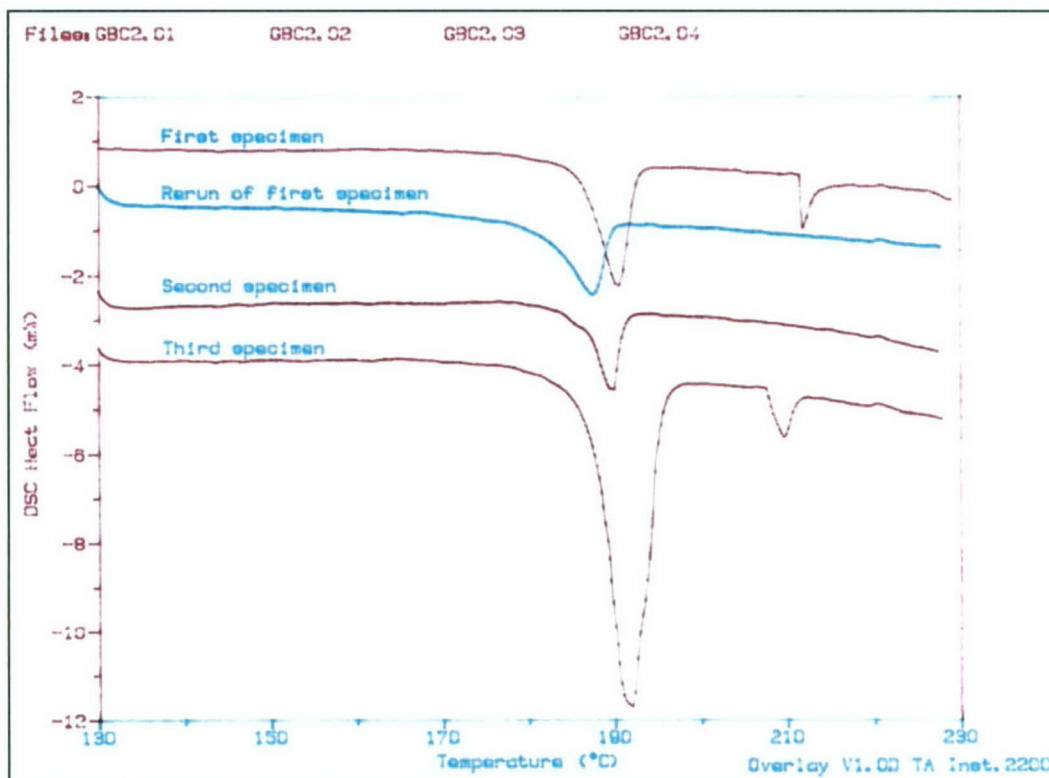


Figure A.17 Melting Curve Summary for Acetone-Washed GB Sample, 010069-0118A

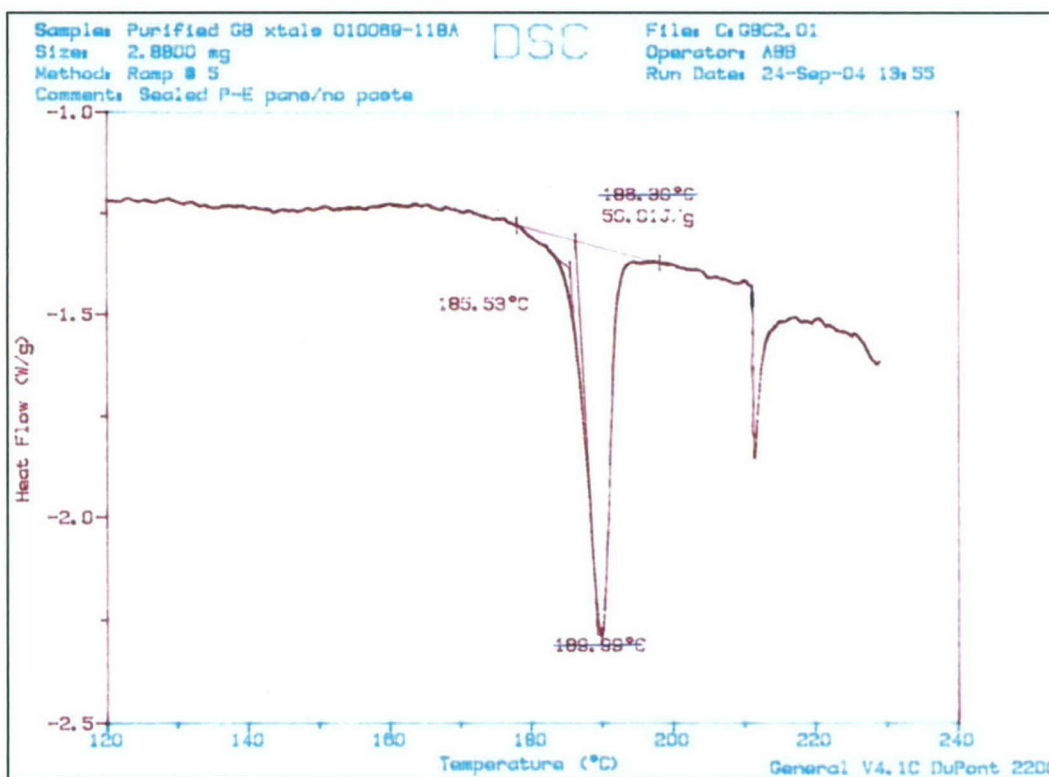


Figure A.18 Melting Endotherm for Acetone-Washed GB Sample, 010069-0118A, Specimen 1

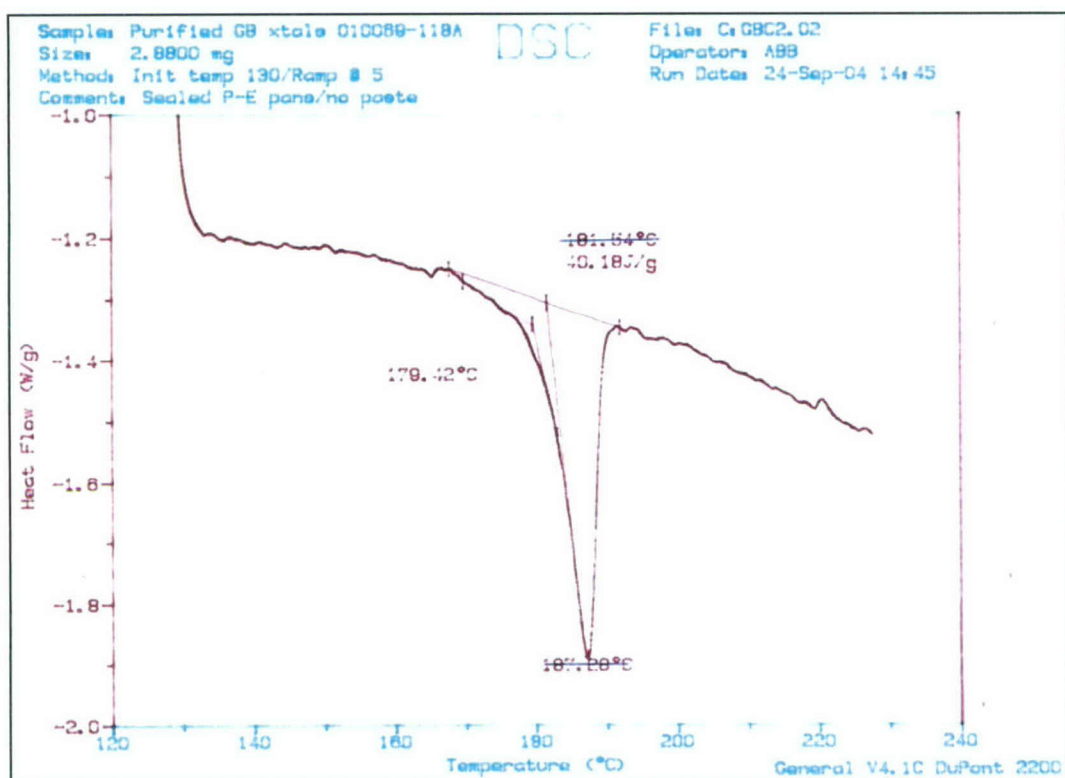


Figure A.19 Melting Endotherm for Acetone-Washed GB Sample, 010069-0118A, Specimen 1 Rerun

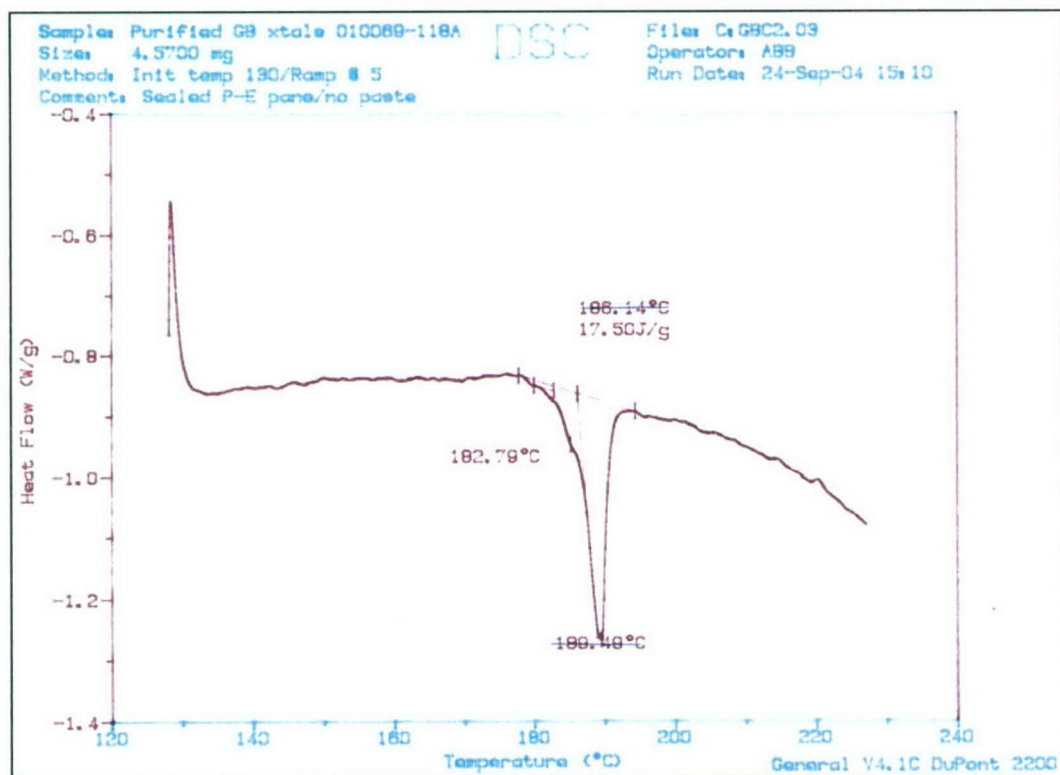


Figure A.20 Melting Endotherm for Acetone-Washed GB Sample, 010069-0118A, Specimen 2

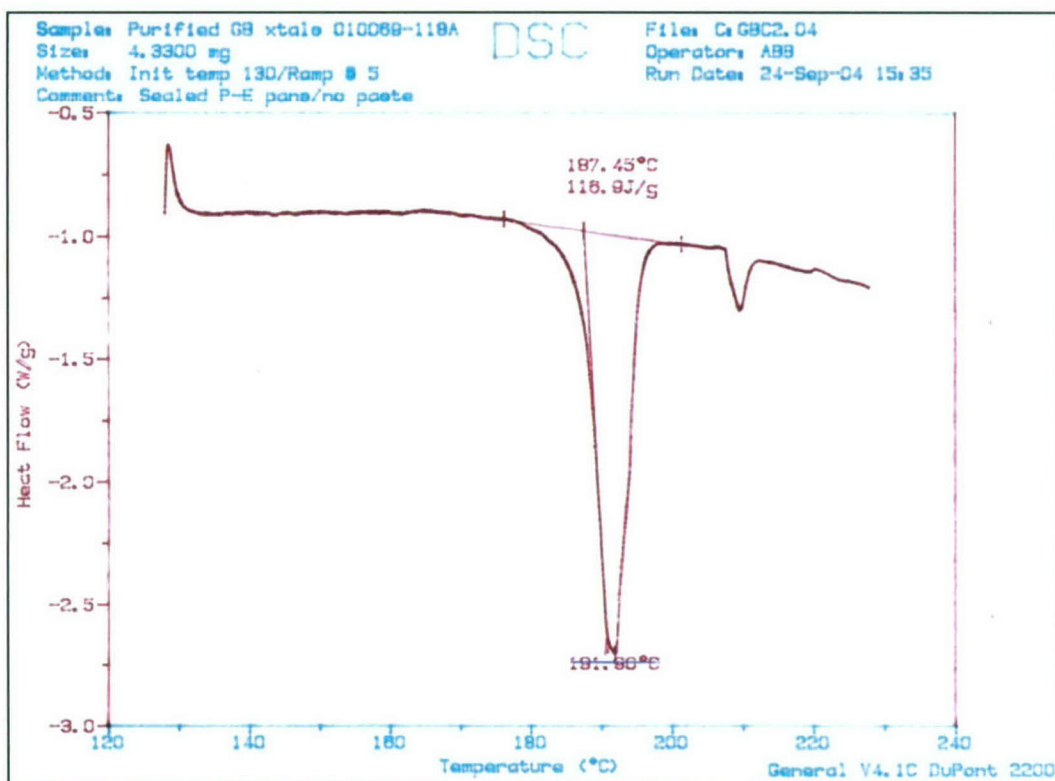


Figure A.21 Melting Endotherm for Acetone-Washed GB Sample, 010069-0118A, Specimen 3

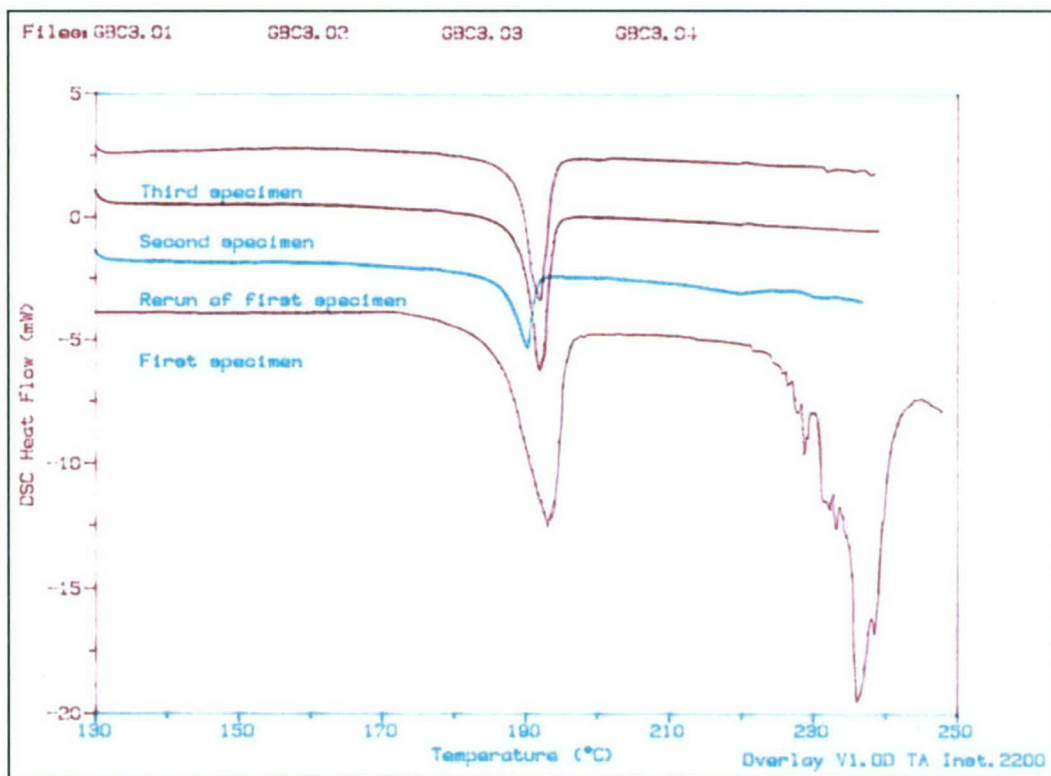


Figure A.22 Melting Curve Summary for Acetone-Washed GB Sample, 010069-140

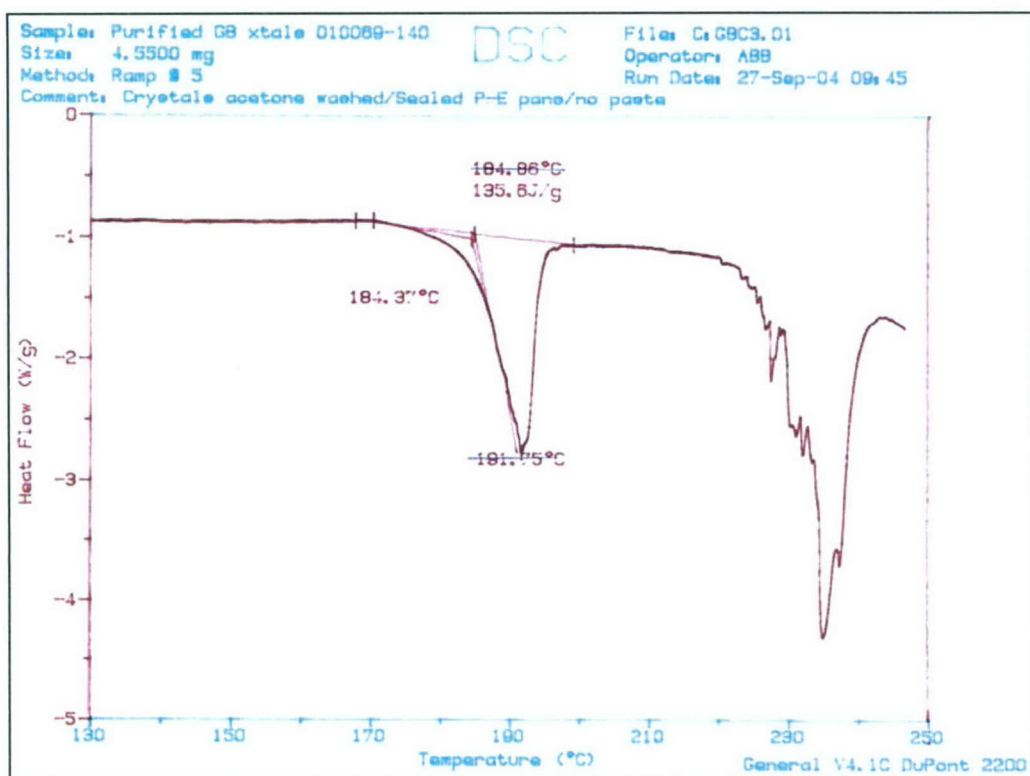


Figure A.23 Melting Endotherm for Acetone-Washed GB Sample, 010069-140, Specimen 1

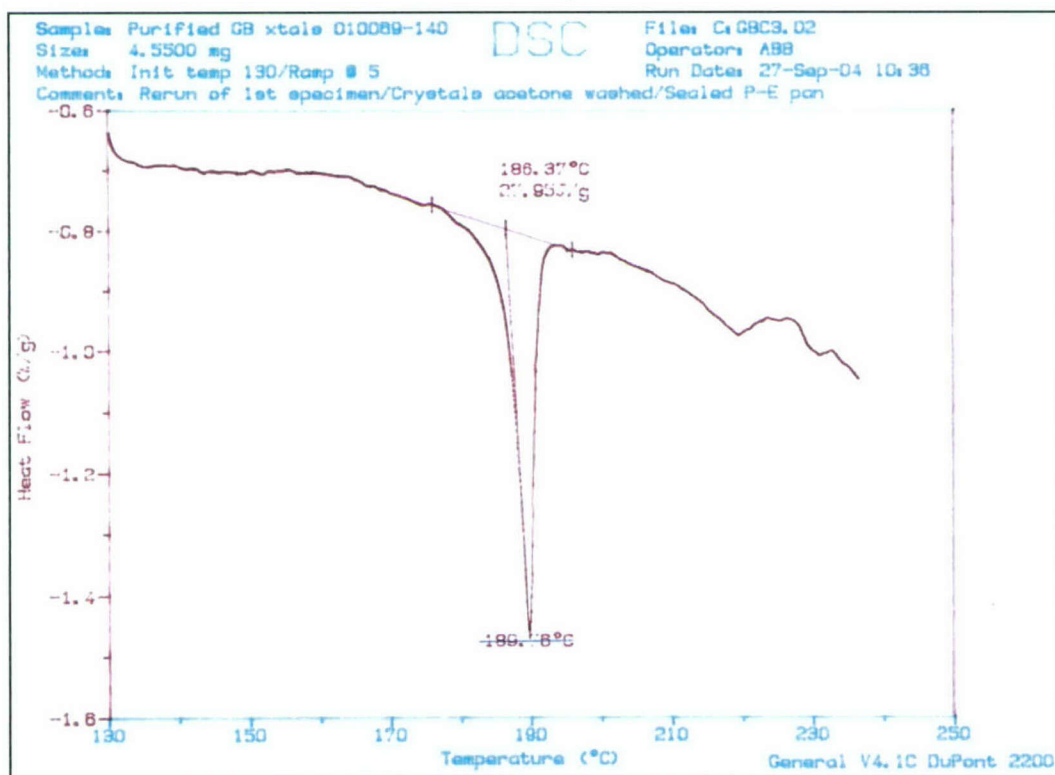
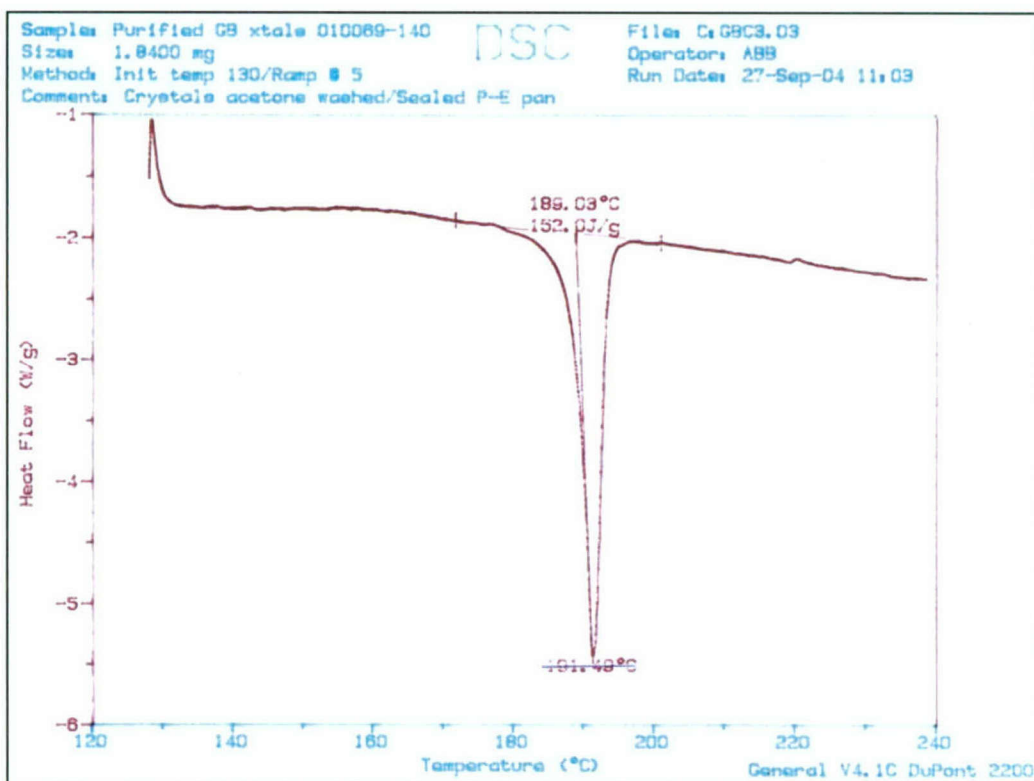
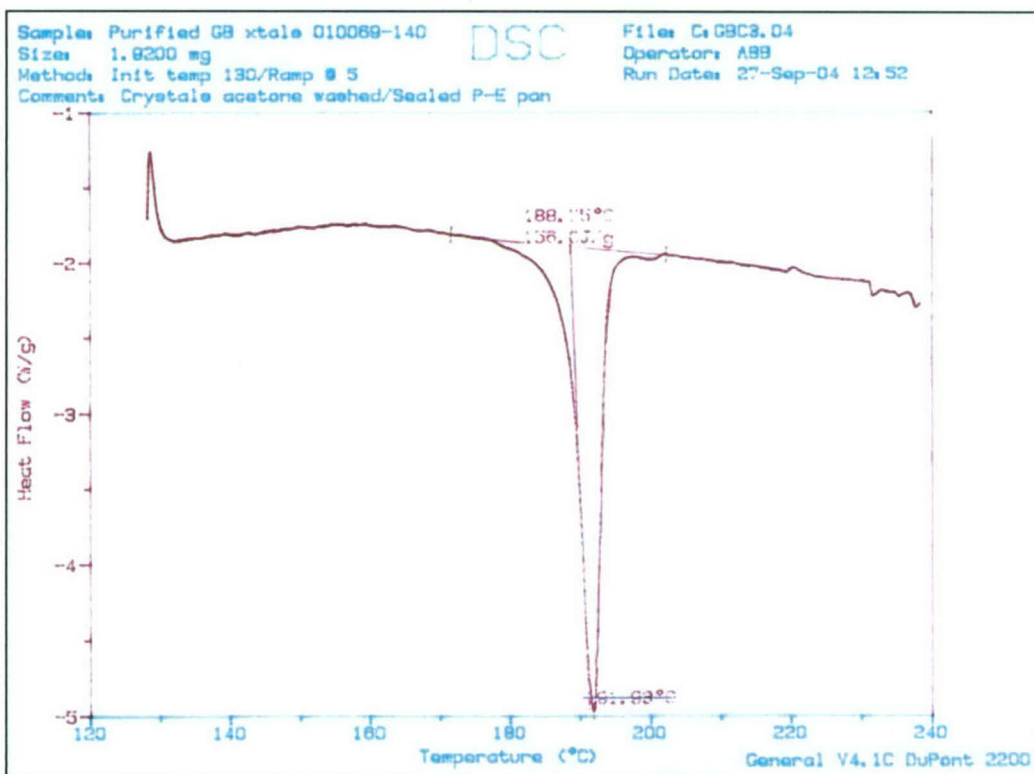


Figure A.24 Melting Endotherm for Acetone-Washed GB Sample, 010069-140, Specimen 1 Rerun



**Figure A.25 Melting Endotherm for Acetone-Washed GB
 Sample, 010069-140, Specimen 2**



**Figure A.26 Melting Endotherm for Acetone-Washed GB
 Sample, 010069-140, Specimen 3**

APPENDIX B
OPTICAL MICROSCOPY RESULTS

Appendix B.1 Representative Examples of Each Sample Type

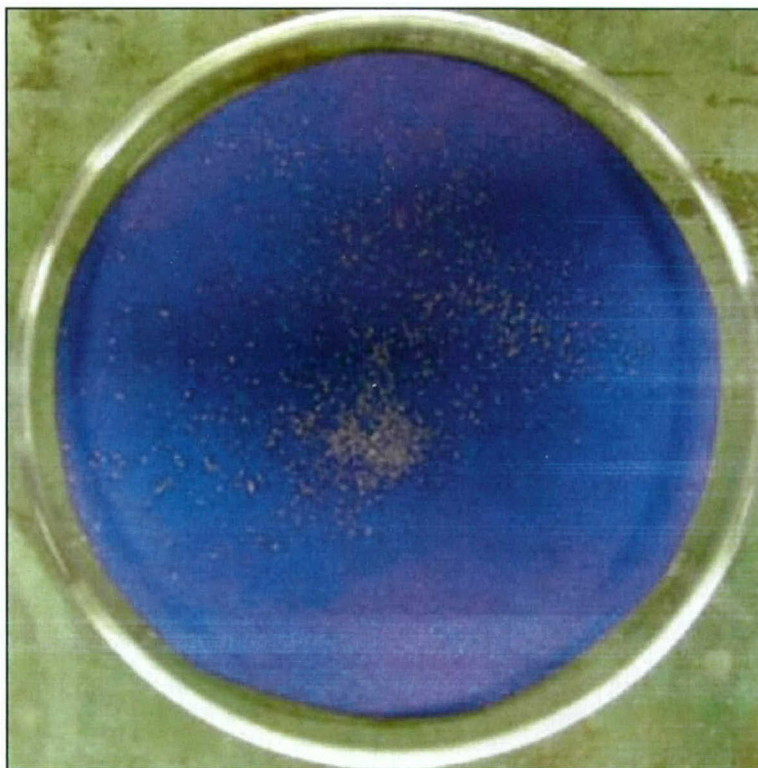


Photo B.1 Urea Powder

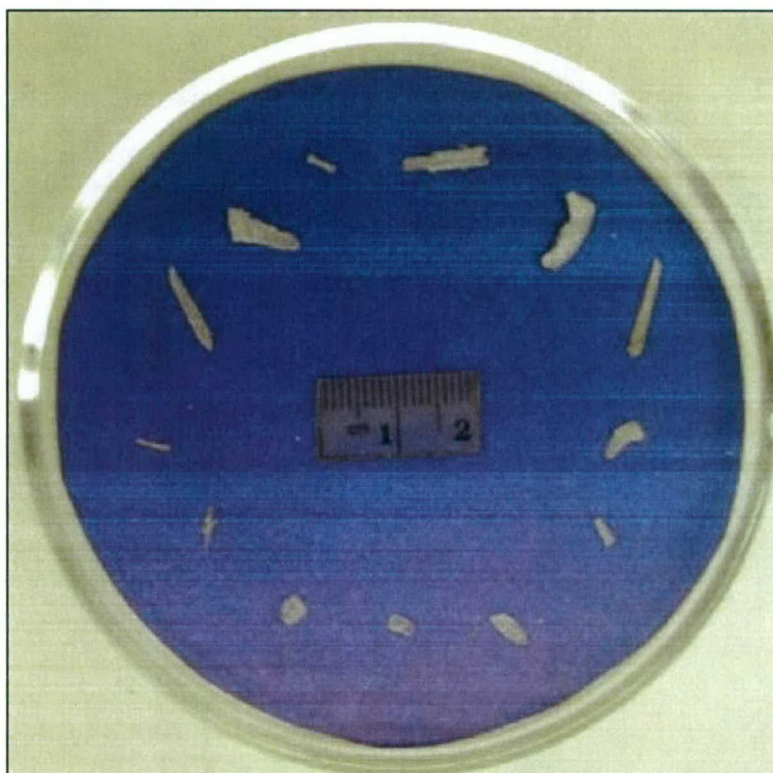


Photo B.2 GB 10006/Vial #21

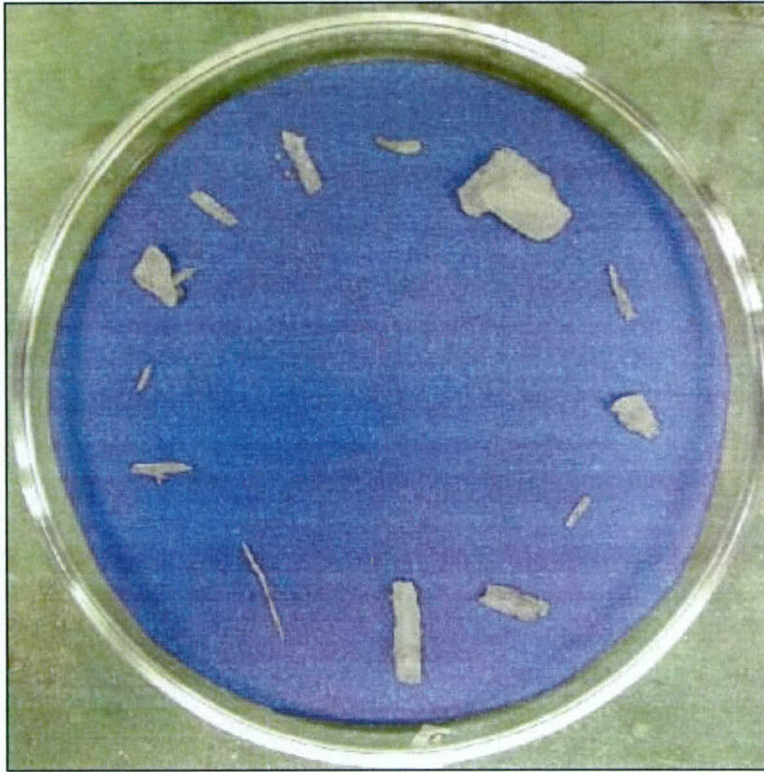


Photo B.3 GB 10006/Vial #24

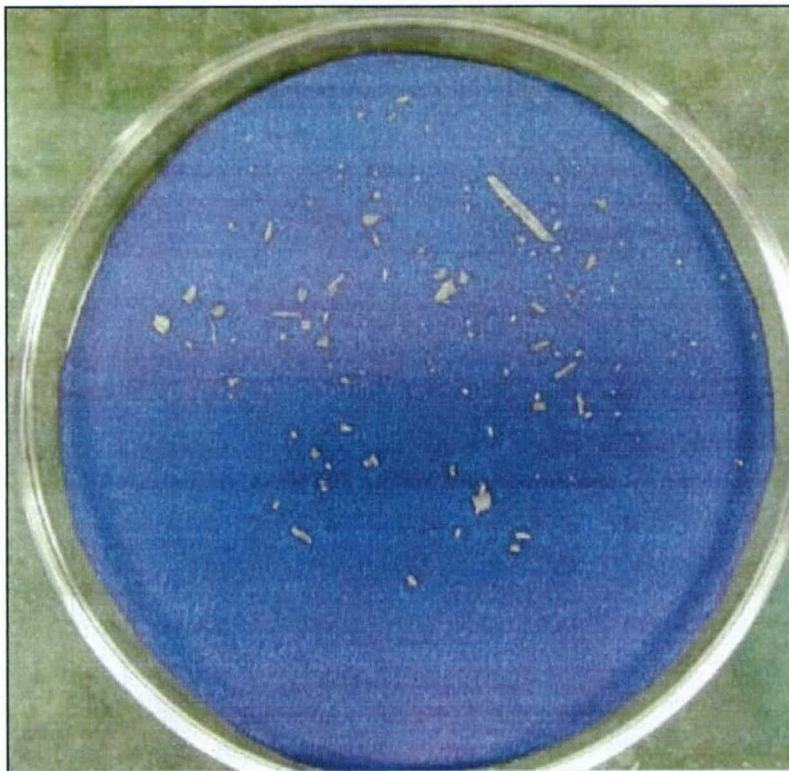


Photo B.4 010069-0118A

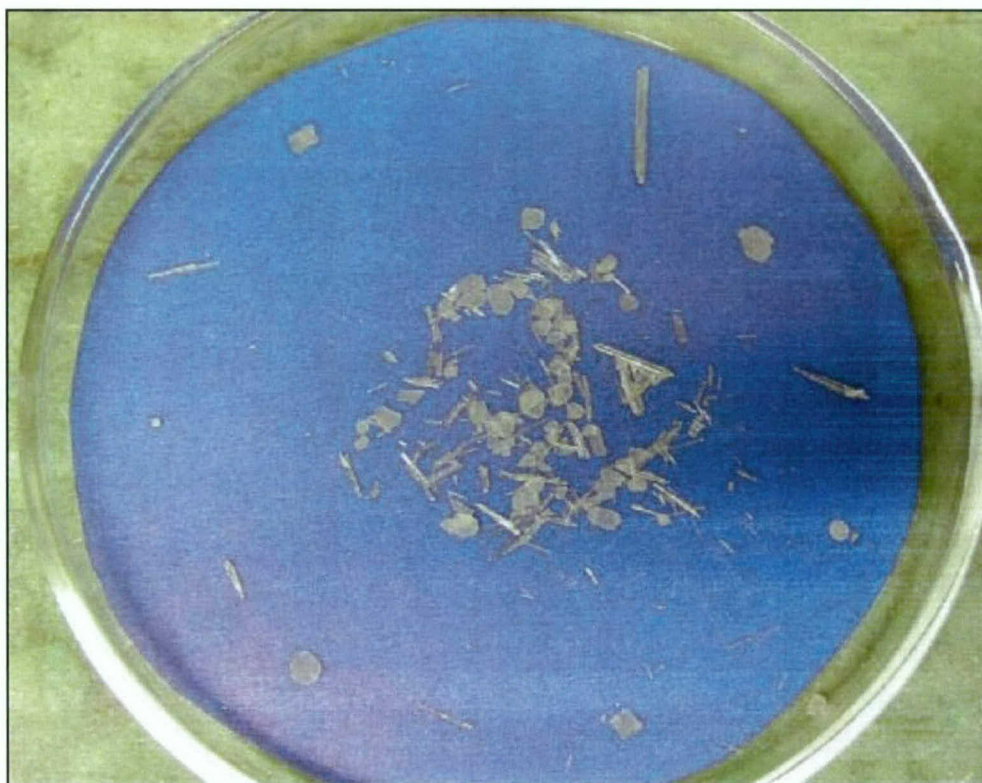


Photo B.5 Synthesized Needles #2

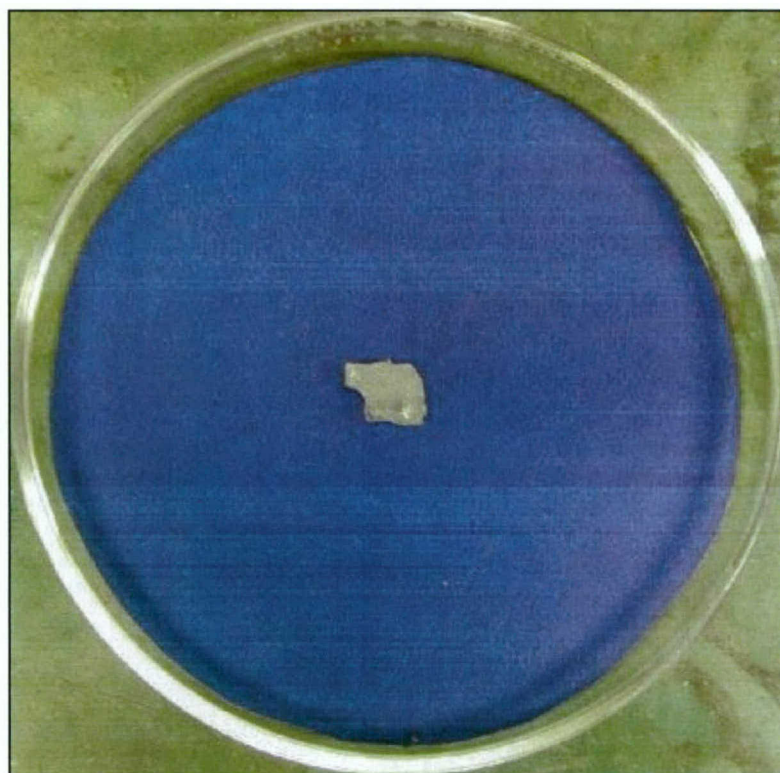


Photo B.6 010069-140

Appendix B.2 Measurements of Selected Crystals/Chunks from Urea Powder Sample

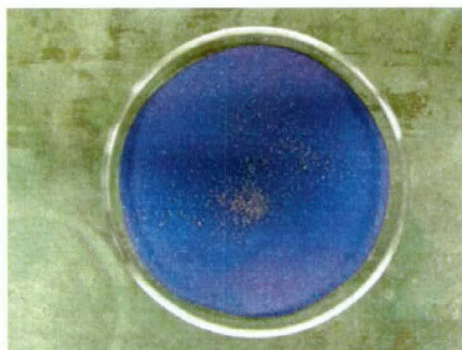


Photo B.7 Urea Powder Using MBC10 Microscope and Nikon Camera



Photo B.8 Urea Powder with 2x10 Magnification



Photo B.9 Urea Powder with 4x10 Magnification

Table B.1 Representative Crystal Measurements for Urea Powder

0.64 mm x 0.12 mm
0.55 mm x 0.33 mm
0.53 mm x 0.11 mm
0.48 mm x 0.11 mm

Appendix B.3 Measurements of Selected Crystals/Chunks from Sampe GB 10006/Vial #21

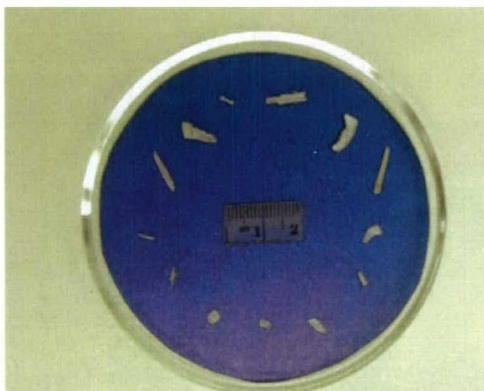


Photo B.10 GB 10006/Vial #21 Using MBC10 Microscope and Nikon Camera

Table B.2 Representative Photos and Crystal Measurements for GB 10006/Vial #21

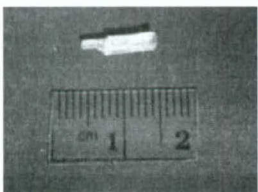
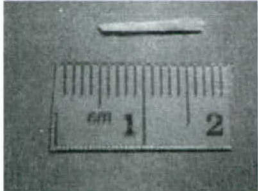
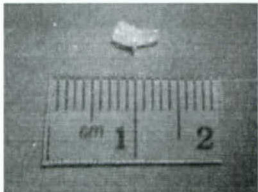
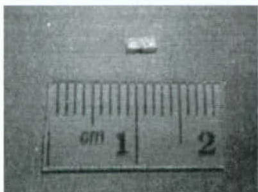
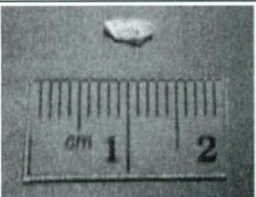
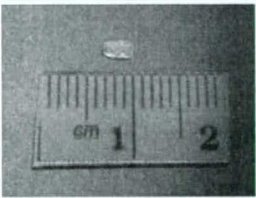
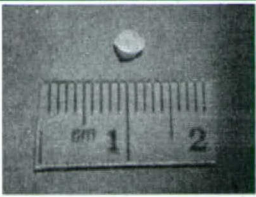
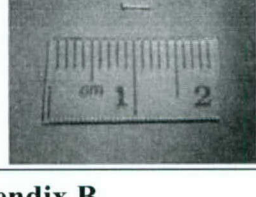
Photograph	Nikon	Nikon and MBC10 Microscope
	10.36 mm x 2.68 mm	10.89 mm x 2.22 mm
	10.66 mm x 2.62 mm	10.22 mm x 2.00 mm
	12.24 mm x 1.29 mm	12.67 mm x 1.44 mm
	5.59 mm x 2.35 mm	6.00 mm x 2.22 mm
	3.62 mm x 1.45 mm	3.78 mm x 1.38 mm

Table B.2 Representative Photos and Crystal Measurements for GB 10006/Vial #21 (continued)

Photograph	Nikon	Nikon and MBC10 Microscope
	5.19 mm x 2.34 mm	5.56 mm x 2.22 mm
	3.24 mm x 1.76 mm	3.56 mm x 1.62 mm
	3.48 mm x 2.75 mm	3.78 mm x 2.89 mm
	5.00 mm x 0.59 mm	5.78 mm x 0.44 mm
	4.14 mm x 0.71 mm	4.22 mm x 0.51 mm
	11.08 mm x 1.69 mm	12.00 mm x 1.69 mm
	8.75 mm x 2.50 mm	9.78 mm x 2.80 mm
	3.29 mm x 0.86 mm	3.78 mm x 0.73 mm

Appendix B.4 Measurements of Selected Crystals/Chunks from Sample GB 10006/Vial #24

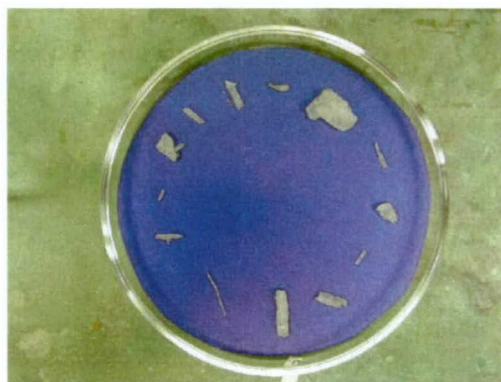


Photo B.11 GB 10006/Vial #24 Using MBC10 Microscope and Nikon Camera

Table B.3 Representative Photos and Crystal Measurements for GB 10006/Vial #24

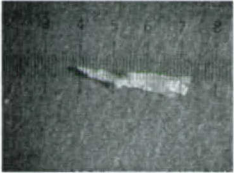
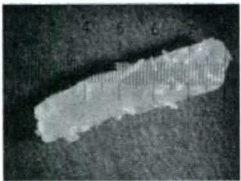
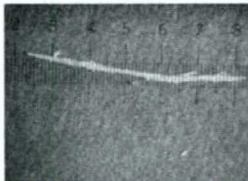
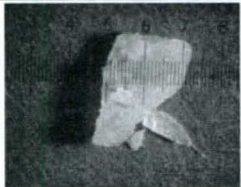
Photograph	Nikon and MBC10 Microscope
	12.33 mm x 7.73 mm
	7.44 mm x 1.15 mm
	6.53 mm x 3.78 mm
	4.58 mm x 0.89 mm
	6.78 mm x 3.07 mm

Table B.3 Representative Photos and Crystal Measurements for GB 10006/Vial #24 (continued)

Photograph	Nikon and MBC10 Microscope
	13.02 mm x 3.20 mm
	12.89 mm x 1.11 mm
	7.56 mm x 1.22 mm
	3.07 mm x 0.67 mm
	7.33 mm x 4.67 mm
	7.11 mm x 1.56 mm
	8.67 mm x 1.91 mm
	5.56 mm x 1.51 mm

Appendix B.5 Measurements of Selected Crystals/Chunks from Sample 010069-0118A

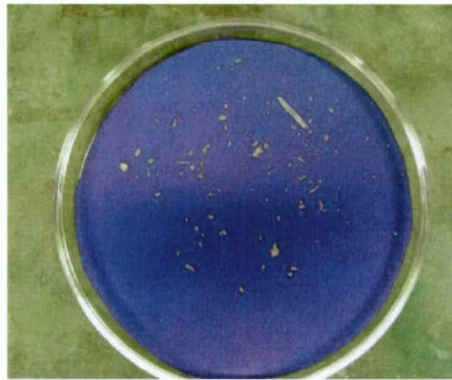


Photo B.12 Sample 010069-0118A Using MBC10 Microscope and Nikon Camera

Table B.4 Representative Photos and Crystal Measurements for 010069-0118A

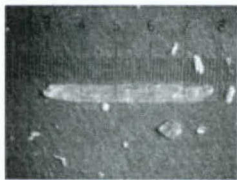
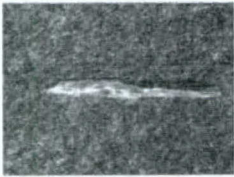
Photograph	Nikon and MBC10 Microscope
	10.89 mm x 1.29 mm
	1.98 mm x 1.91 mm
	2.11 mm x 1.06 mm
	3.53 mm x 0.22 mm
	3.56 mm x 0.43 mm

Table B.4 Representative Photos and Crystal Measurements for 010069-0118A (continued)

	3.15 mm x 0.62 mm
	2.19 mm x 1.26 mm
	2.60 mm x 0.83 mm
	2.61 mm x 0.31 mm
	1.81 mm x 0.63 mm
	2.63 mm x 0.31 mm
	1.58 mm x 1.16 mm
	2.94 mm x 0.74 mm

Appendix B.6 Measurements of Selected Crystals/Chunks from Synthesized Needles #2

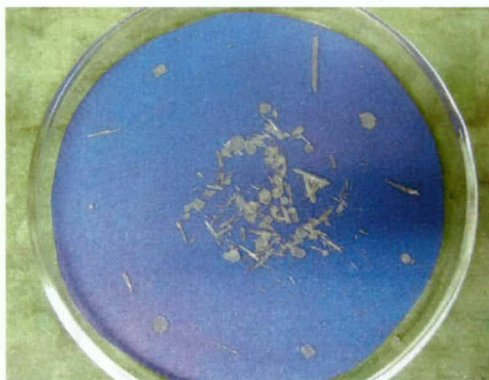


Photo B.13 Synthesized Needles #2 Using MBC10 Microscope and Nikon Camera

Table B.5 Representative Photos and Crystal Measurements for Synthesized Needles #2

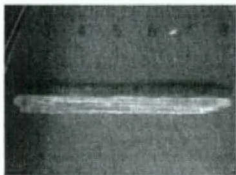
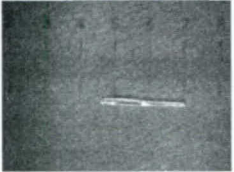
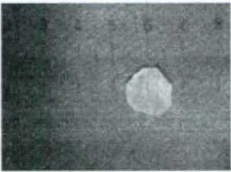
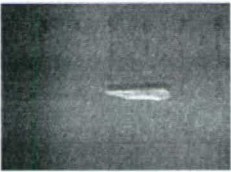
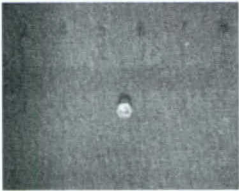
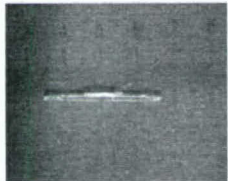
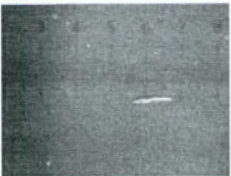
Photograph	Nikon and MBC10 Microscope
	14.00 mm x 0.78 mm
	3.56 mm x 4.18 mm
	8.22 mm x 0.93 mm
	2.00 mm x 2.11 mm
	6.22 mm x 0.42 mm

Table B.5 Representative Photos and Crystal Measurements for Synthesized Needles #2 (continued)

Photograph	Nikon and MBC10 Microscope
	2.22 mm x 2.44 mm
	5.78 mm x 0.44 mm
	3.24 mm x 3.18 mm
	4.22 mm x 0.80 mm
	0.91 mm x 0.91 mm
	7.56 mm x 0.56 mm
	3.53 mm x 2.00 mm
	2.67 mm x 0.29 mm

Appendix B.7 Measurements of Selected Crystals/Chunks from Sample 010069-140

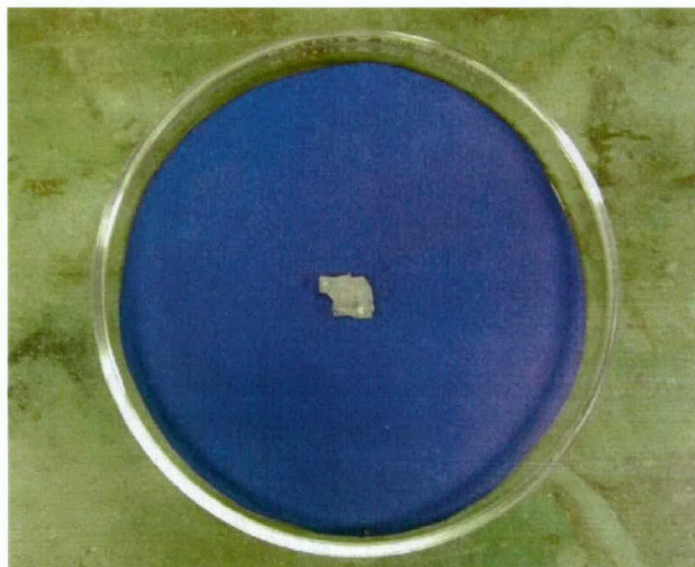


Photo B.14 Sample 010069-140 Using MBC10 Microscope and Nikon Camera

Table B.6 Representative Photo and Crystal Measurement for Sample 010069-140

Photograph	Nikon and MBC10 Microscope
	10.33 mm x 7.42 mm