The Effect of H_2O and Moisture on the Chemistry of B-KNO_3 (BKNO_3 Pellets) with respect to Delay-Times and Thermal-Energy Output

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Objective

For $BKNO_3$ (B-KNO_3) and Boron Powder Used in Igniters/Delay-Compositions:

- **To determine the major factors that influence the ballistic properties (e. g.; ignition-delay, thermal-energy output, and aging) of $BKNO_3$ pellets.**

- **To determine the effect of moisture and H_2O on the chemical reactivity of Boron powder used in Igniters and Delay-Compositions.**

$BKNO_3$ Physical Properties

Property	Virgin Pellets	"Clumped" Pellets
Weight, 15 pellets (g)	1.0000	1.0312
Calc. Density (g/cm^3)	2.0963	-
Calc. Surface Area (m^2/g)	1.1178×10^{-3}	-
Meas. Density (g/cm^3)	2.2477 ± 0.0081	2.1854 ± 0.0083
Meas. Surface Area (m^2/g)	1.6312	1.4491

$BKNO_3$-Related Physico-Chemical Properties

Property	Material	Value	Temp.
Specific Heat (cal/°C/g)			-
	Boron	0.263	
Specific Heat (cal/°C/g)	H_2O	1.000	-
DH_v (cal/g)	H_2O	+ 540.0	-
DH_v (kcal /mole)	H_2O	+ 9.71	100 °C
$DH_{Decomposition}$ (kcal /mole)	H_3BO_3	+	185 °C
$DH_{Decomposition}$ (kcal /mole)	KNO_3	+ 75.5*	400 °C (decomp.)
			337 °C (m. p.)

* $KNO_3 \rightarrow K_2O + N_2 + 2.5\ O_2$

$B + O_2 \rightarrow$ Exothermic reaction

Findings

“Pristine” $BKNO_3$: As-Received.

Findings

“Clumped” $BKNO_3$: As-Received.

Findings

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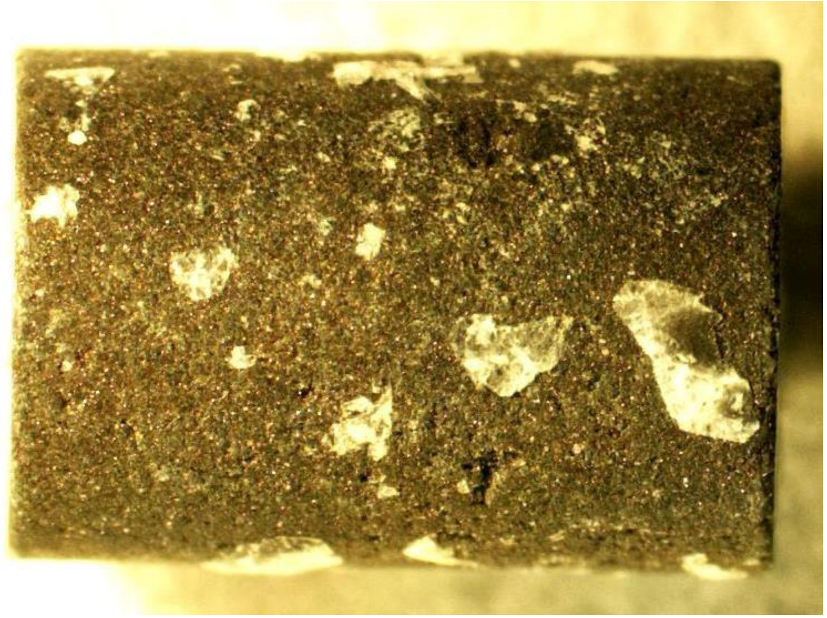
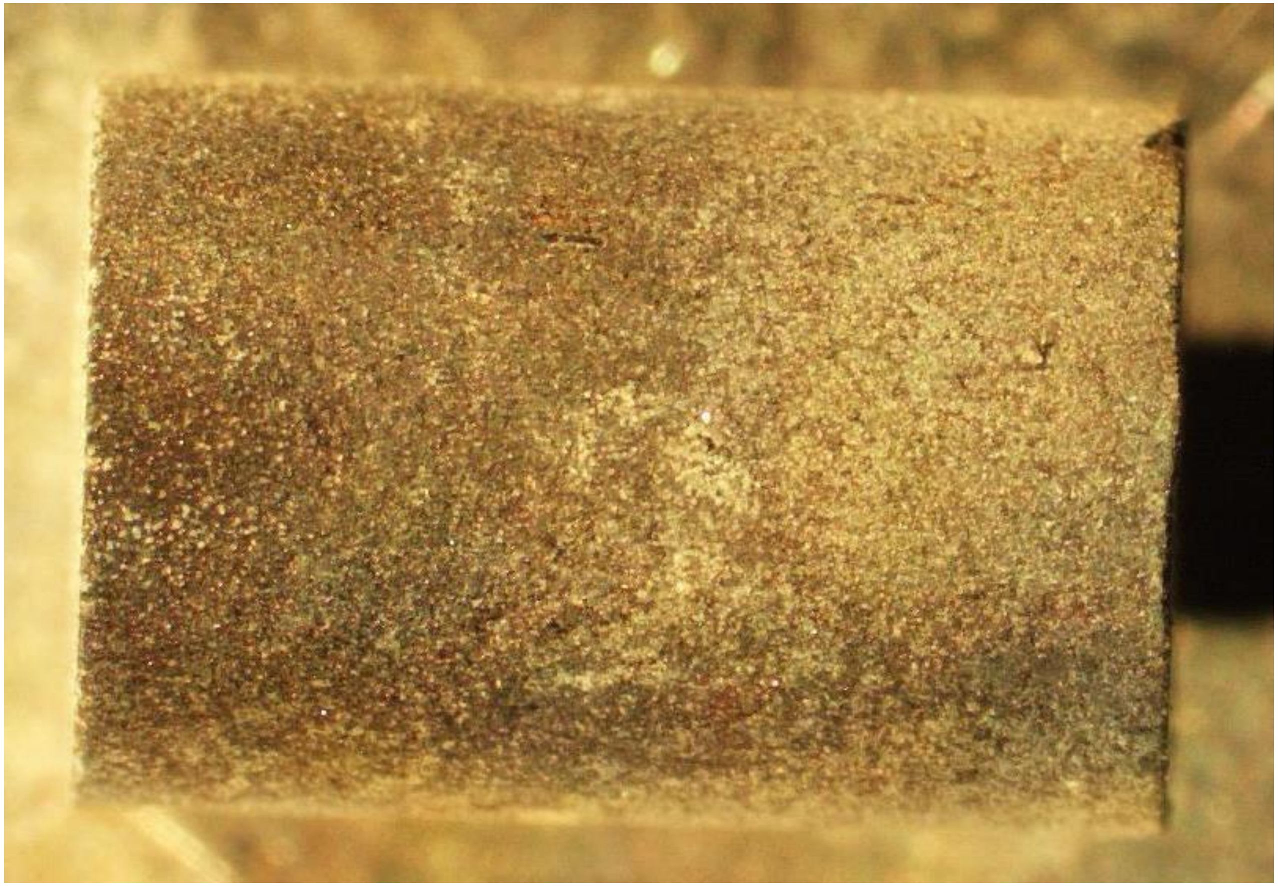
“Clumped” $BKNO_3$: As-Received.

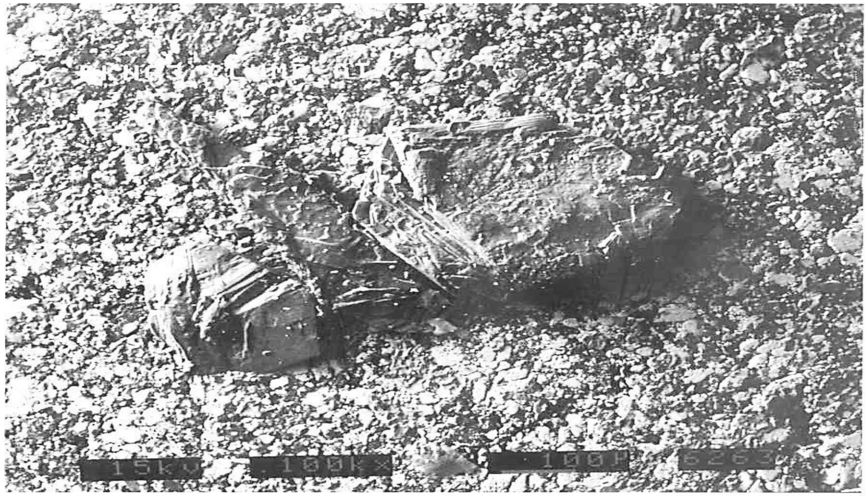


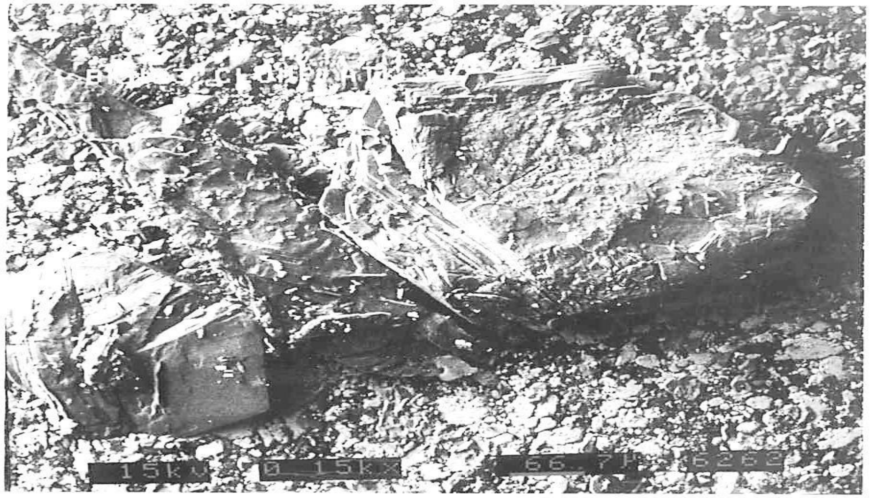
Findings

“Clumped” $BKNO_3$: Dried at 100°C.

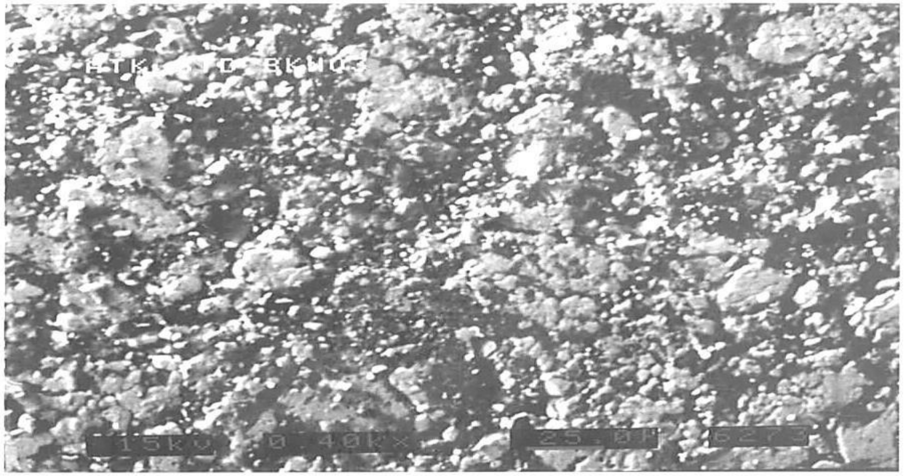


Boric Acid on Surface of $BKNO_3$ Pellet

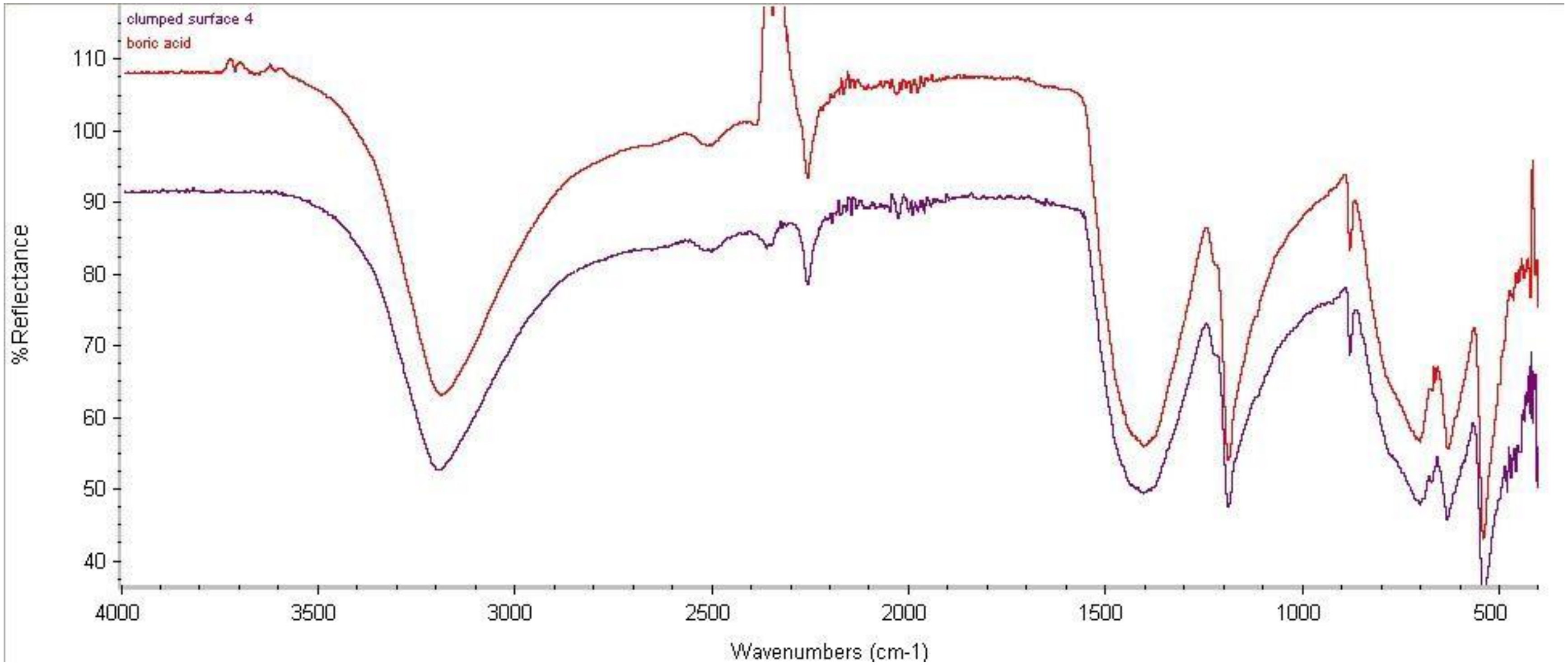




SEM: Virgin vs. Aged $BKNO_3$ Pellets

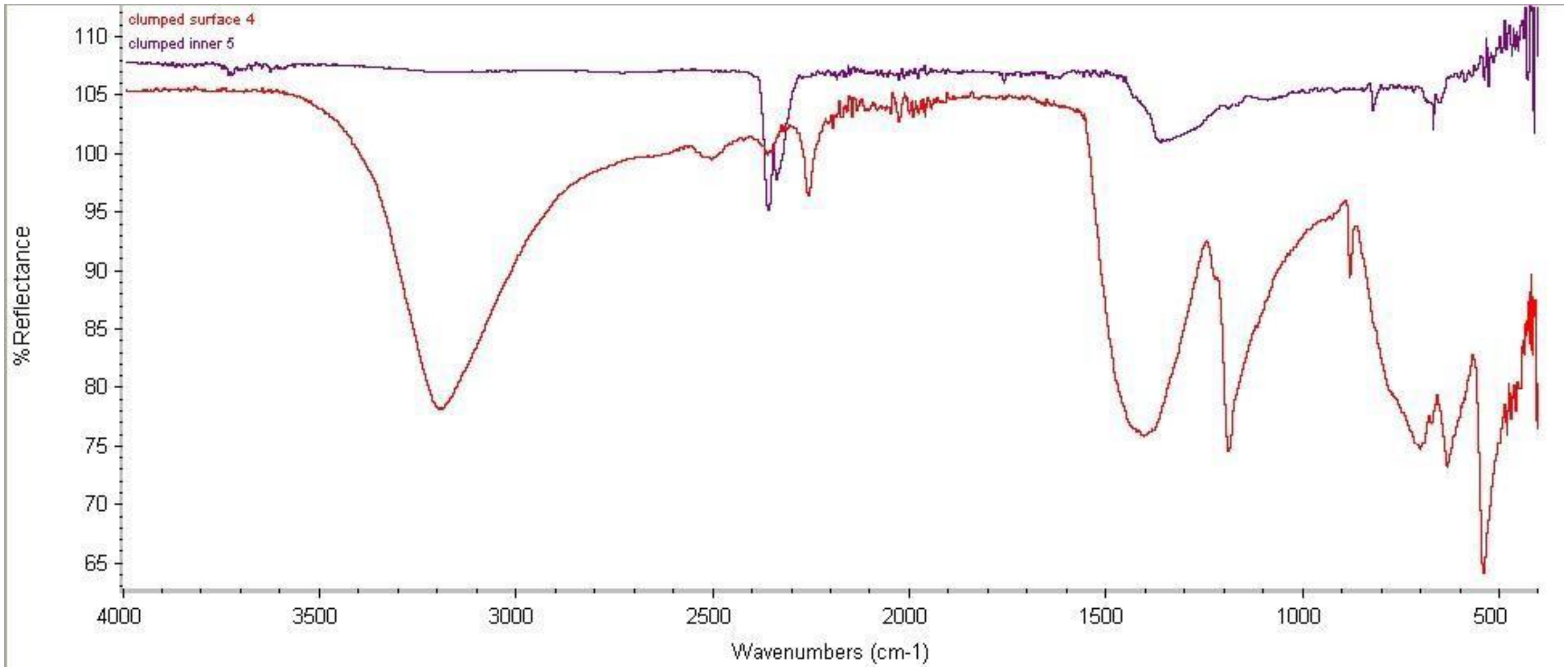


Boric Acid (H_3BO_3) - Reference Material



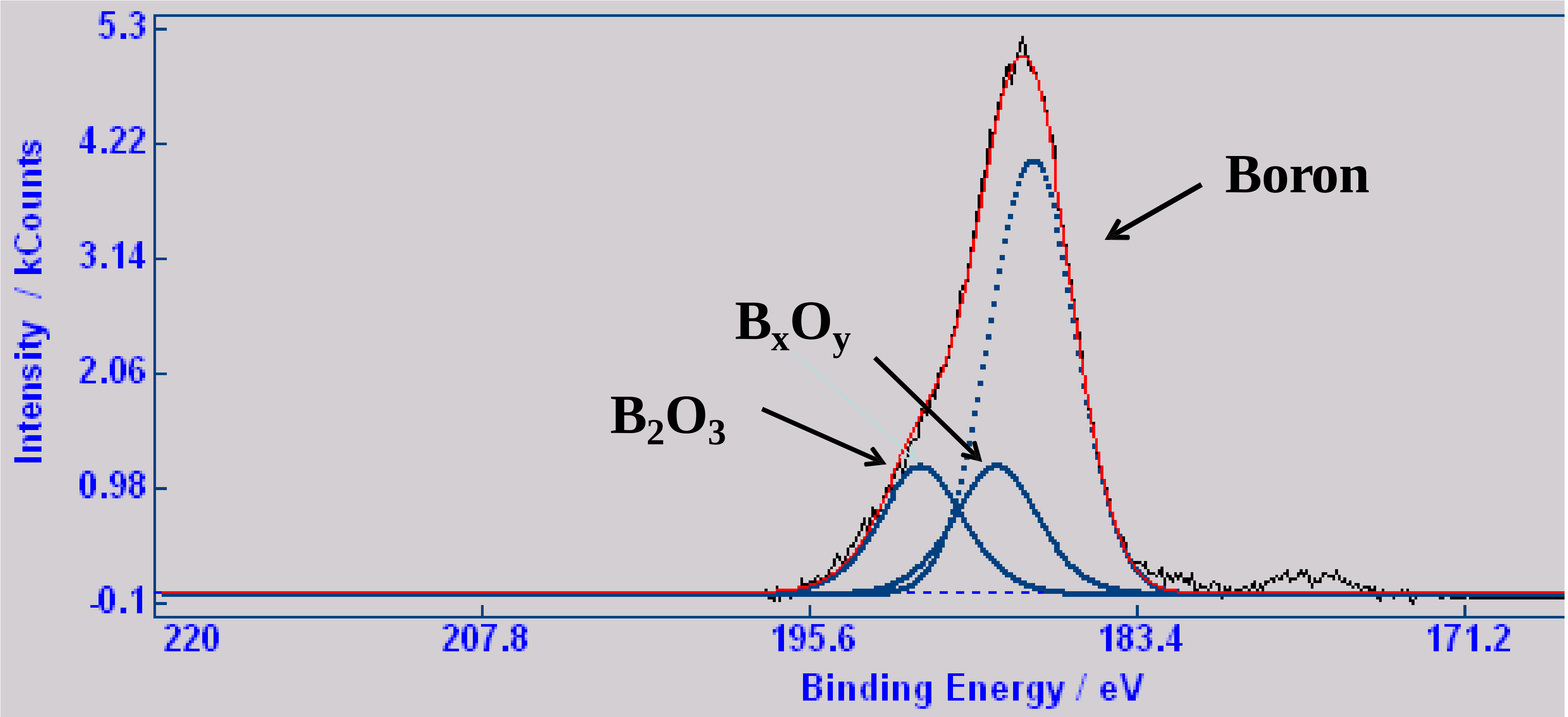
Surface crystals identified as primarily Boric Acid, H_3BO_3.

$BKNO_3$ Pellet - Inner vs. Surface

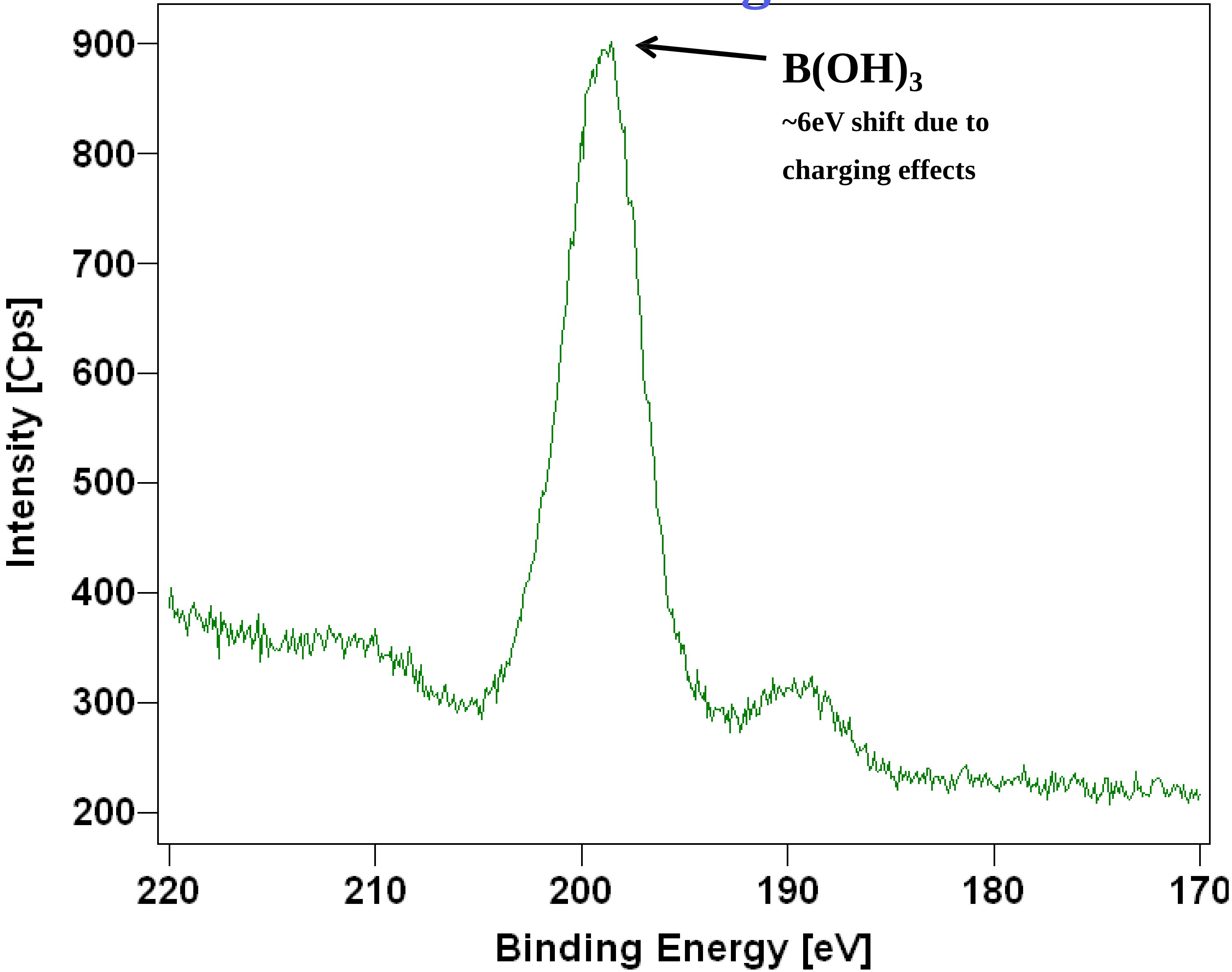


- **Significant crystal cover on cylinder face and sides.**
- **FTIR spectrum of surface vs. inner regions differ significantly.**
- **Spectrum of inner region consistent with that of virgin pellets.**
- **Surface crystals identified as primarily Boric Acid, H_3B0_3.**

Deconvoluted XPS Spectrum of Boron 1s Region Prewashed Sample



XPS Spectrum of Boric Acid (SPEX Standard) B1s region



Boric Acid - Experimental

Weight, Initial	**10.0008 g**
Weight after 24 hr. @ 150°C	**6.6446 g**
Δ Weight-Loss (24 hr. @ 150°C)	**3.3562 g**
% Weight-Loss	**33.6 %**
Weight after <u>additional</u> 24 hr. @ 179°C	**5.6439 g**
Δ Weight-Loss @ 179°C (<u>added</u> 24 hr. @ 179°C)	**1.0007 g**
% Weight-Loss	**10.01 %**
Δ Weight-Loss, Cumulative (150°C and 179°C):	**4.3569 g**
% Weight-Loss after 48 Hr.	**43.6 %**

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Energy-Consuming (Endothermic) Reaction Pathway of Boric Acid and Boron Oxide

$$H_3BO_3 \cdot H_2O \rightarrow HBO_2 \rightarrow H_2B_4O_7 \rightarrow B_2O_3 + (BO)_x \text{ compound}$$

M. P.	Meta-Boric	M. P.	Tetra-Boric	M. P.	M. P.
179 °C	Acid	236 °C	Acid	250 °C	450 °C

$$B_2O_3 + H_2O \rightarrow H_3BO_3$$

$$B + O_2 \rightarrow B_2O_3 \text{ (exothermic)}$$

Boron (found in the form of compounds; never as elemental Boron) is manufactured by reduction of B_2O_3 with Magnesium:

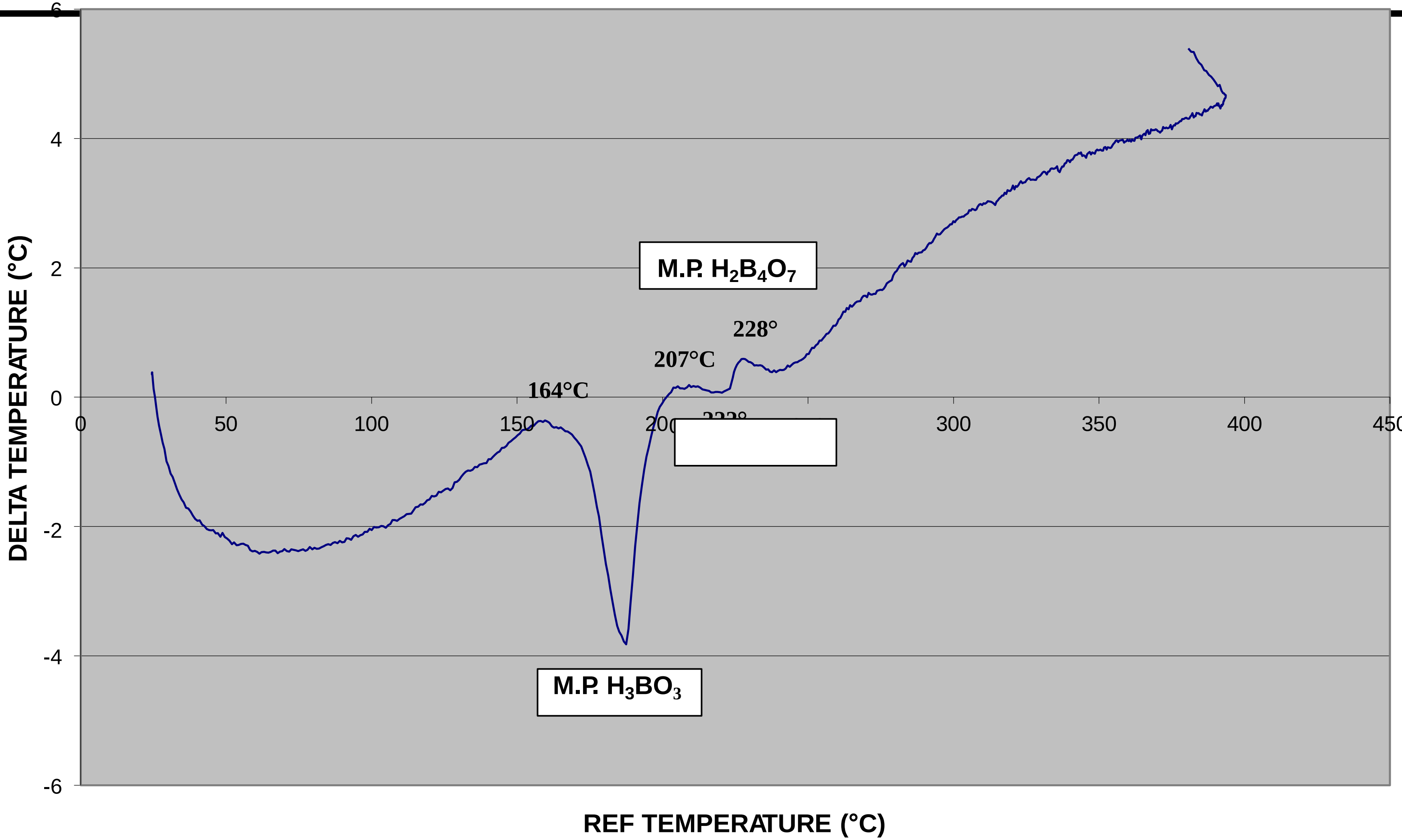
$$B_2O_3 + Mg \rightarrow B + B_2O_3 + Mg + MgO$$

In nature, a self-limiting reaction with O_2 occurs due to formation of B_2O_3 film.

This film evaporates above 1,000°C: $B + B_2O_3 \rightarrow BO$

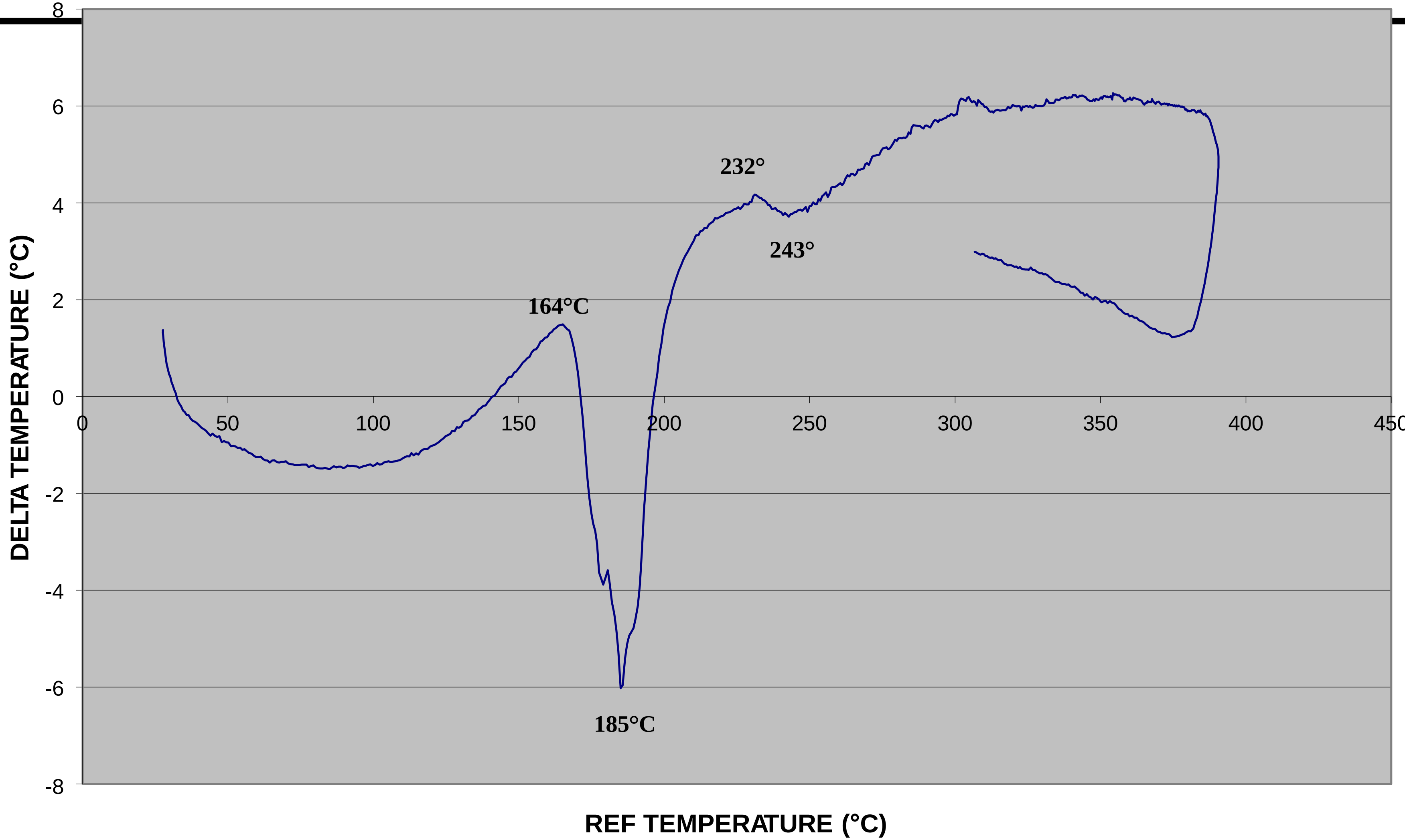
(1,050°C)

Boric Acid



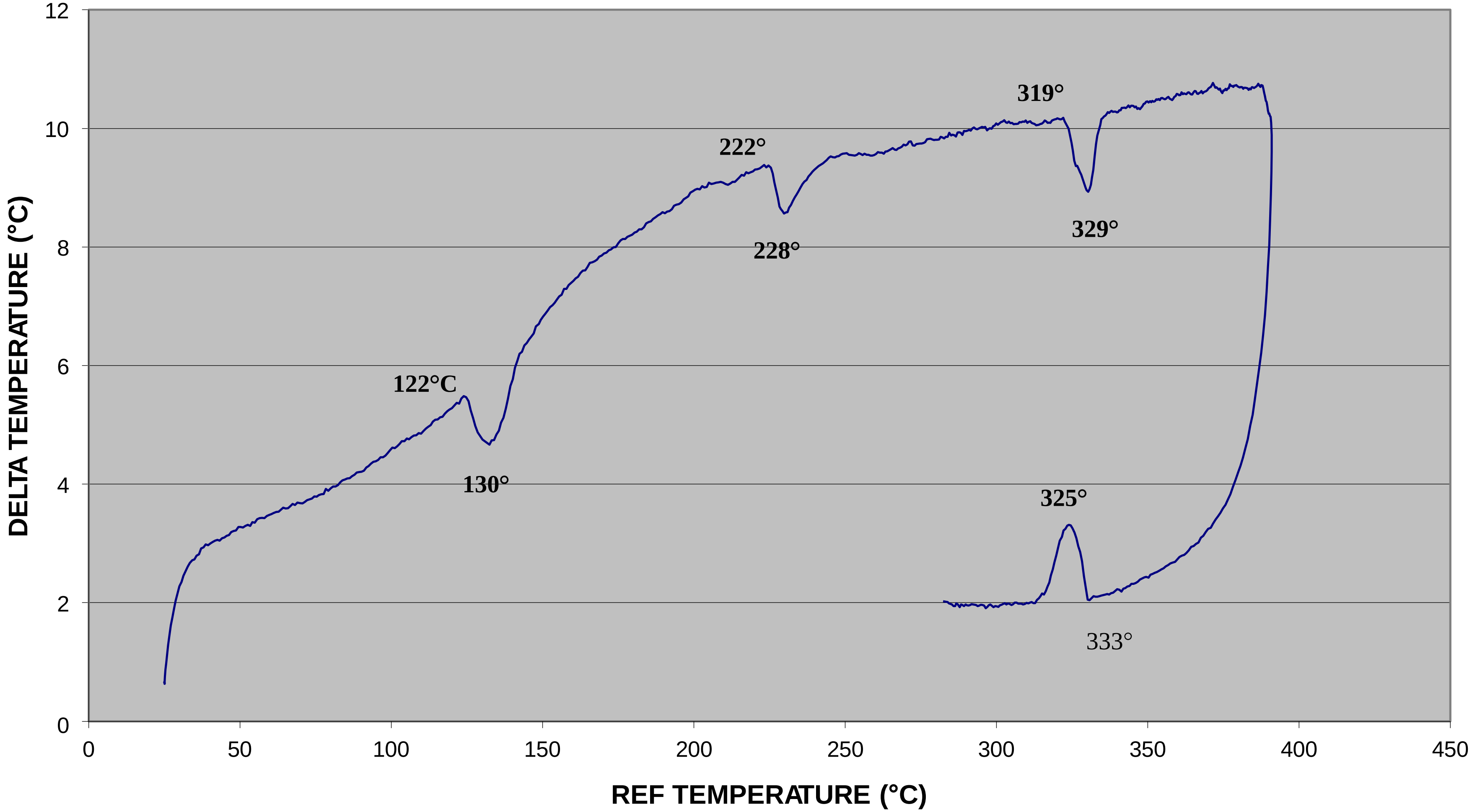
DELTA TEMPERATURE (°C)
6
4
2
0
-2
-4
-6
0
50
100
150
300
350
400
450
REF TEMPERATURE (°C)
M.P. $H_2B_4O_7$
228°
207°C
164°C
M.P. H_3BO_3

Boric Acid 2

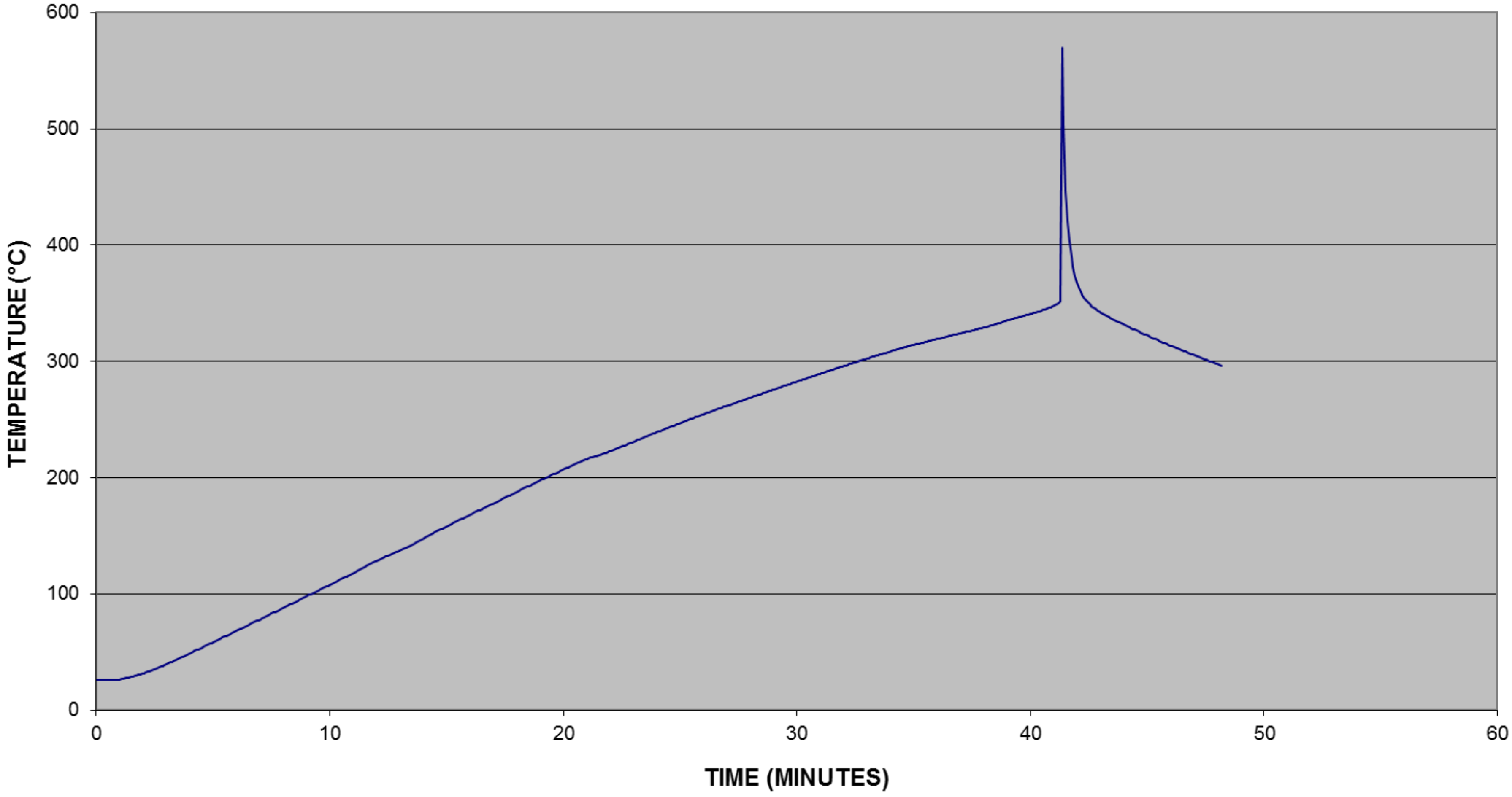

8
6
4
2
0
-2
-4
-6
-8
0
50
100
150
200
250
300
350
400
450
164°C
185°C
232°
243°
DELTA TEMPERATURE (°C)
REF TEMPERATURE (°C)

KNO_3

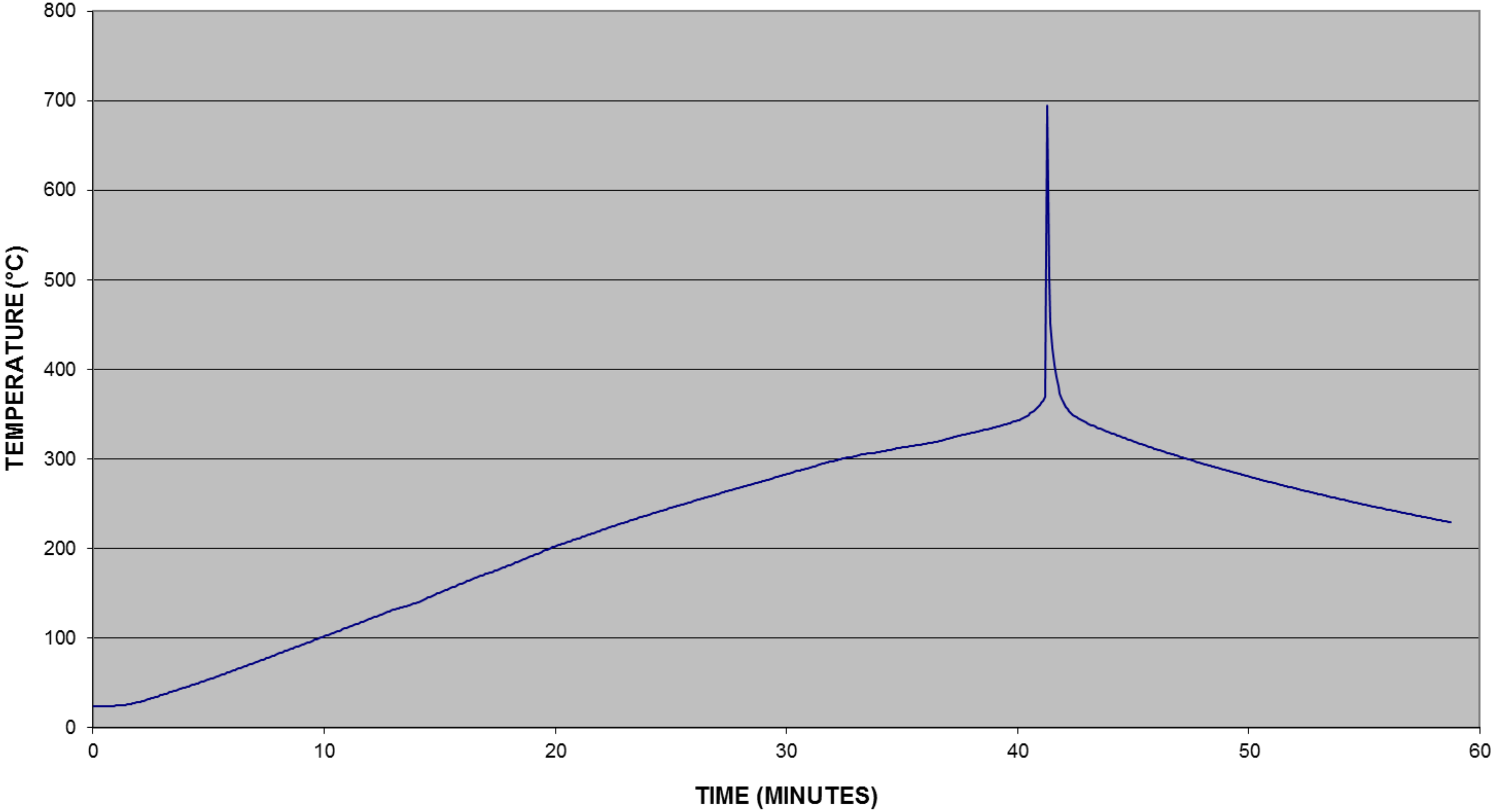
DRIED @175°C
3/31/08



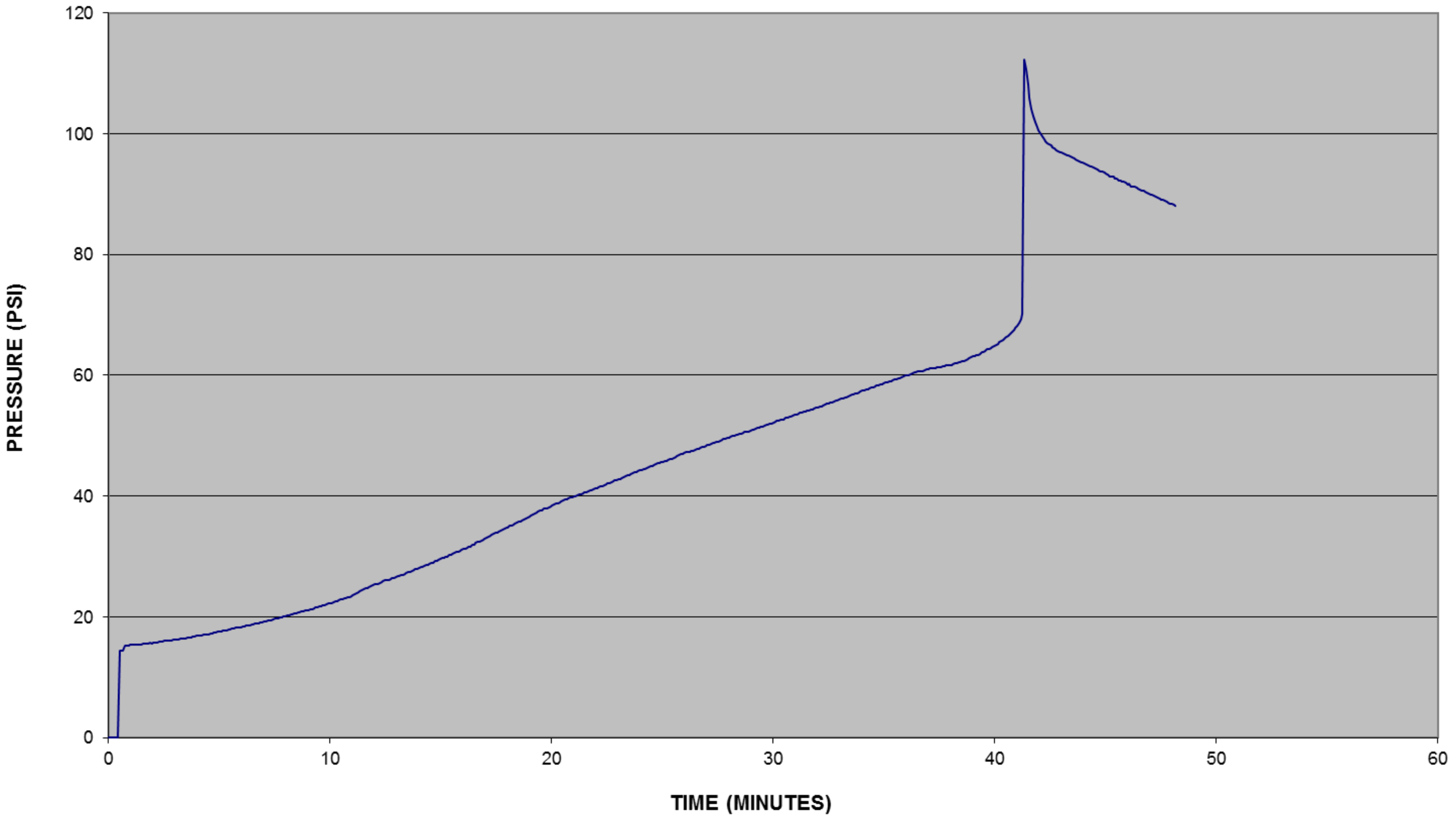
BKNO$_3$ CLUMP 2



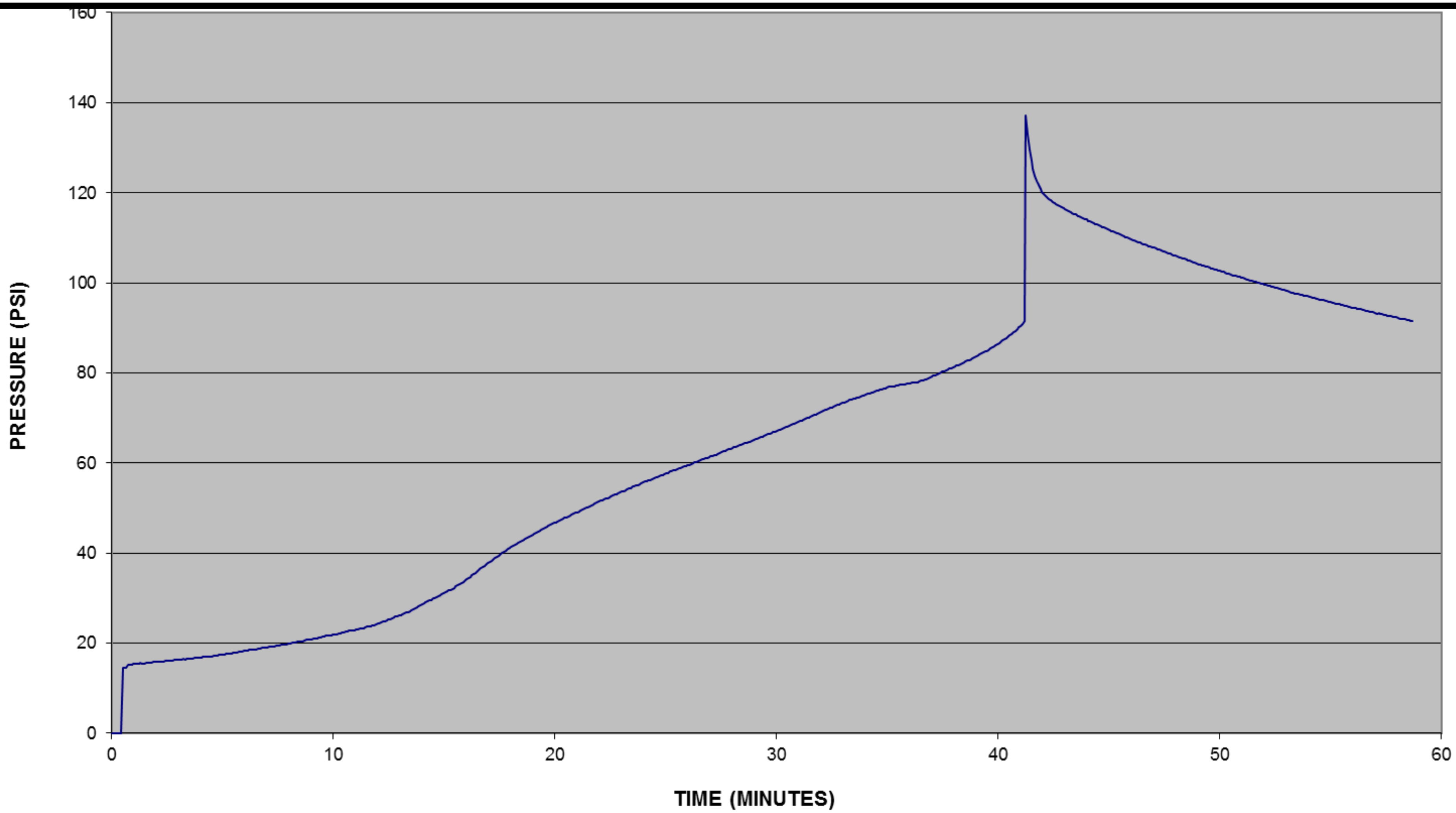
$BKNO_3$ CLUMP 3D
DRIED @110°C FOR 1 DAY

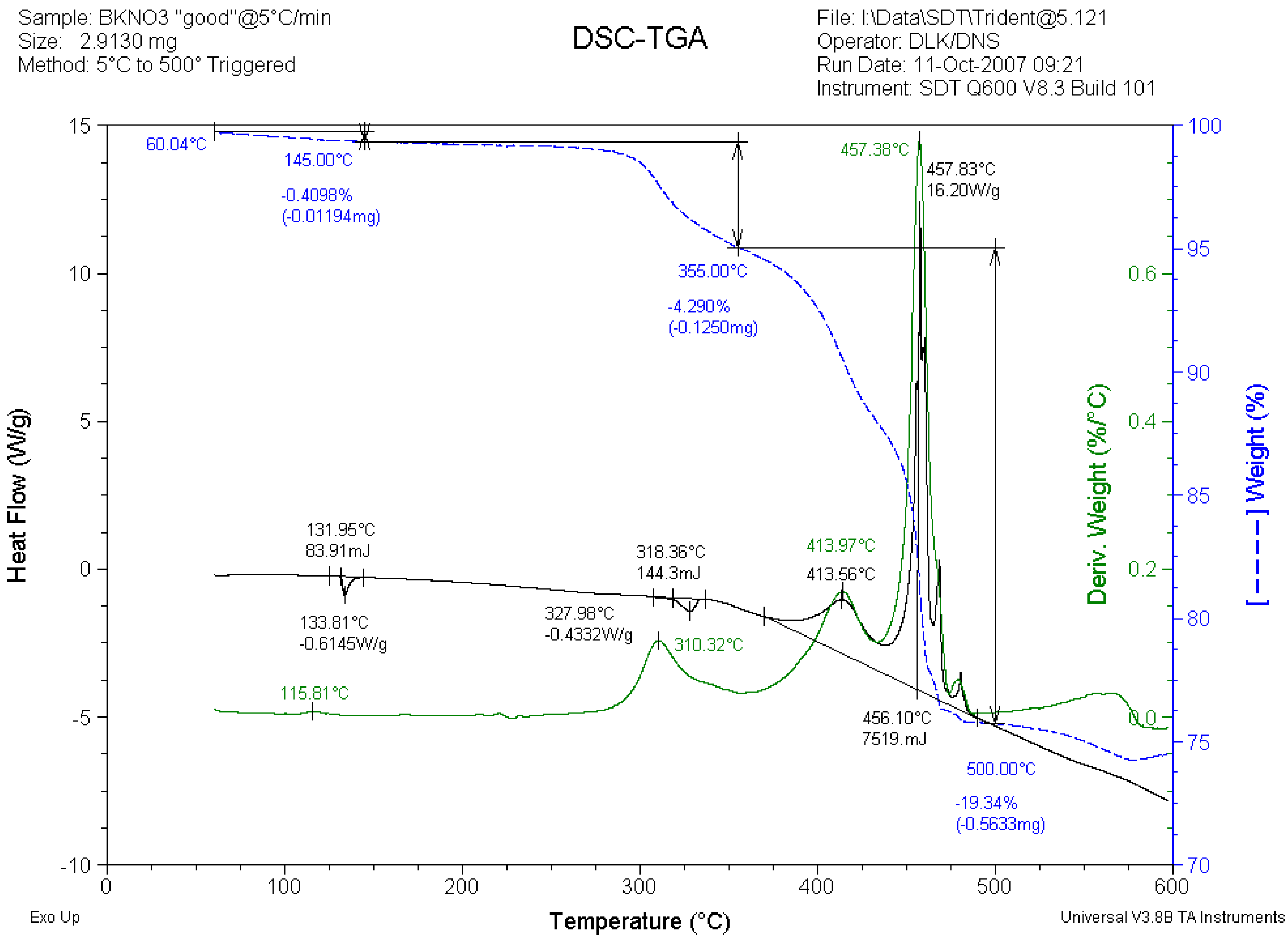


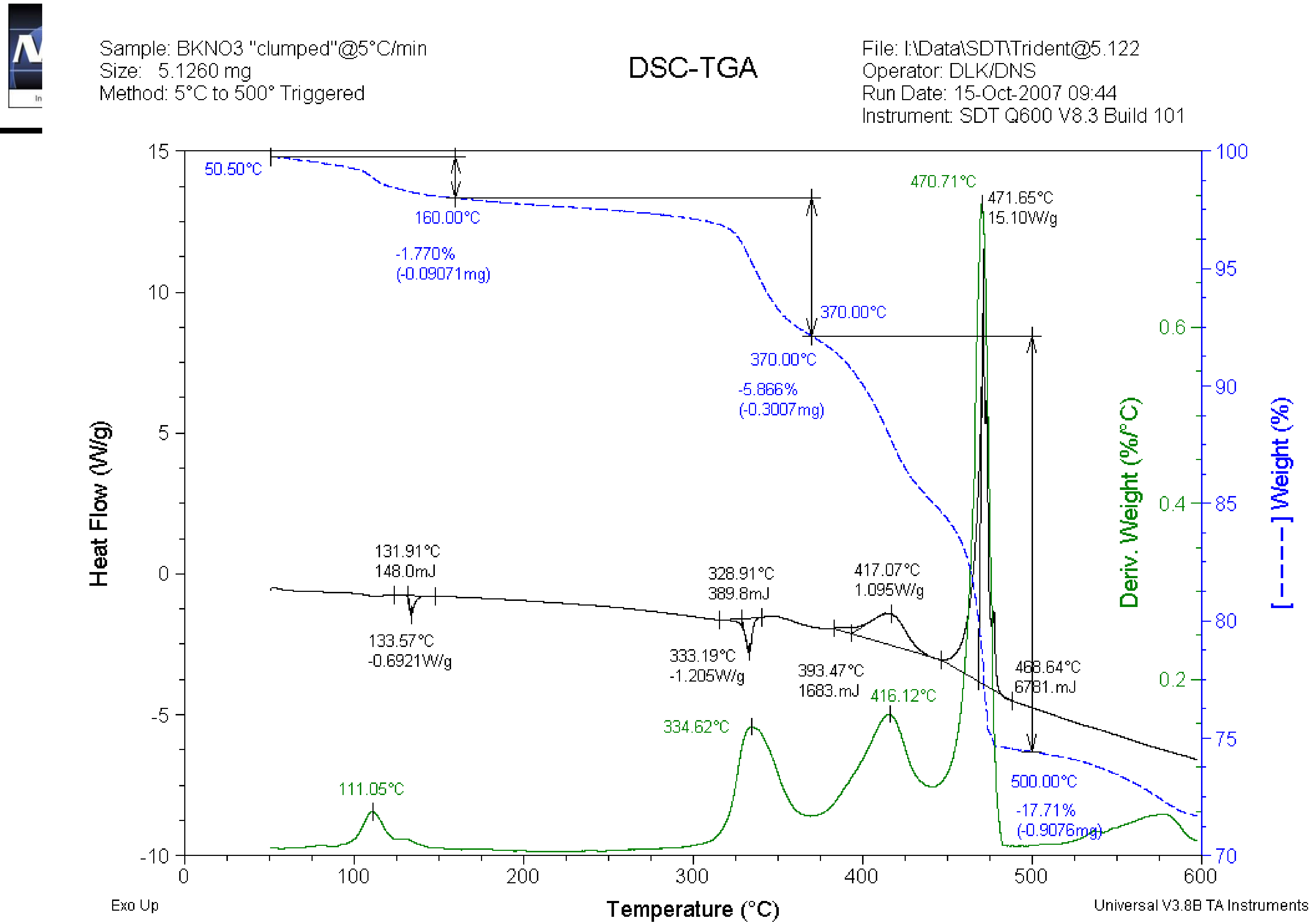
$BKNO_3$ CLUMP 2



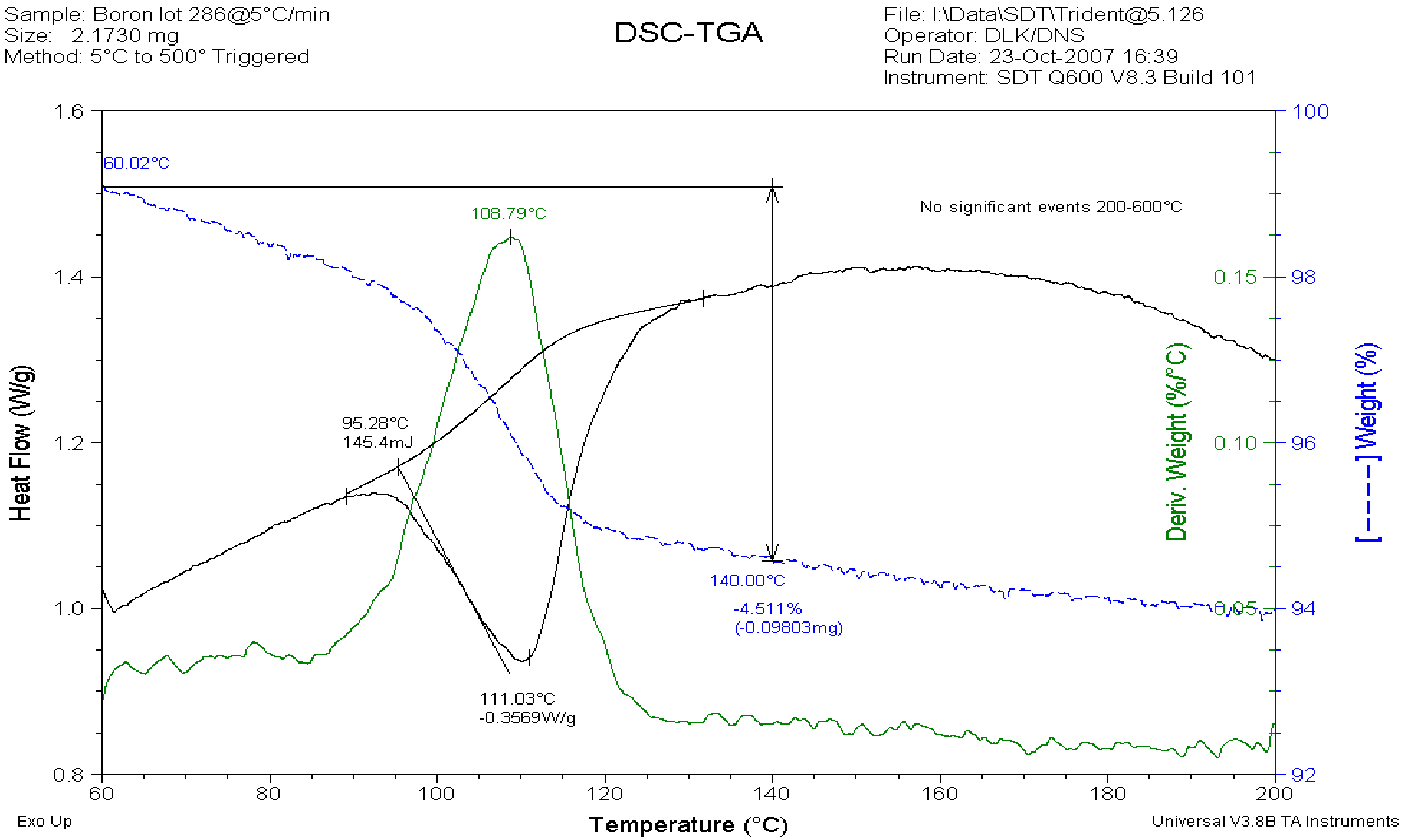
BKNO$_3$ CLUMP 3D
DRIED @110°C FOR 1 DAY




Sample: BKNO3 "good"@5°C/min
Size: 2.9130 mg
Method: 5°C to 500° Triggered
DSC-TGA
File: I:\Data\SDT\Trident@5.121
Operator: DLK/DNS
Run Date: 11-Oct-2007 09:21
Instrument: SDT Q600 V8.3 Build 101
60.04°C
145.00°C
-0.4098%
(-0.01194mg)
355.00°C
-4.290%
(-0.1250mg)
457.38°C
457.83°C
16.20W/g
131.95°C
83.91mJ
133.81°C
-0.6145W/g
318.36°C
144.3mJ
327.98°C
-0.4332W/g
310.32°C
413.97°C
413.56°C
115.81°C
456.10°C
7519.mJ
500.00°C
-19.34%
(-0.5633mg)
Heat Flow (W/g)
Deriv. Weight (%/°C)
[– – –] Weight (%)
Temperature (°C)
Exo Up
Universal V3.8B TA Instruments



Sample: BKNO3 "clumped"@5°C/min
Size: 5.1260 mg
Method: 5°C to 500° Triggered
DSC-TGA
File: I:\Data\SDT\Trident@5.122
Operator: DLK/DNS
Run Date: 15-Oct-2007 09:44
Instrument: SDT Q600 V8.3 Build 101
50.50°C
160.00°C
-1.770%
(-0.09071mg)
370.00°C
370.00°C
-5.866%
(-0.3007mg)
470.71°C
471.65°C
15.10W/g
131.91°C
148.0mJ
133.57°C
-0.6921W/g
328.91°C
389.8mJ
333.19°C
-1.205W/g
417.07°C
1.095W/g
393.47°C
1683.mJ
468.64°C
6781.mJ
416.12°C
334.62°C
111.05°C
500.00°C
-17.71%
(-0.9076mg)
Heat Flow (W/g)
Deriv. Weight (%/°C)
[– – –] Weight (%)
Temperature (°C)
Exo Up
Universal V3.8B TA Instruments


Sample: Boron lot 286@5°C/min
Size: 2.1730 mg
Method: 5°C to 500° Triggered
DSC-TGA
File: I:\Data\SDT\Trident@5.126
Operator: DLK/DNS
Run Date: 23-Oct-2007 16:39
Instrument: SDT Q600 V8.3 Build 101
60.02°C
108.79°C
No significant events 200-600°C
95.28°C
145.4mJ
140.00°C
-4.511%
(-0.09803mg)
111.03°C
-0.3569W/g
Heat Flow (W/g)
Deriv. Weight (%/°C)
[–––––] Weight (%)
Temperature (°C)
Exo Up
Universal V3.8B TA Instruments

Conclusions

- **Boric Acid covered about 25% of the analyzed $BKNO_3$ pellet surfaces. The Boric Acid did not infiltrate the interior (i. e.; the bulk) of the pellets.**

- **Boron reacts slowly with atmospheric O_2 to form B_2O_3 films on high surface-area Boron particles.**

- **Drying the clumped $BKNO_3$ pellets increased the thermal output of the pellets (i. e.; dT/dt, dp/dt).**

- **Moisture caused an increase in the particle-size of the KNO_3 and may be responsible for the clumping of the $BKNO_3$ pellets, thus hindering flame-spreading during ignition.**

- **Magnesium reacts with O_2 to increase the thermal-energy output of the $BKNO_3$ pellets and/or Boron powder (5.9 kcal/g).**