



YUCCA MOUNTAIN PROJECT CONTROLLED SCIENTIFIC NOTEBOOK

Issued to: KIRK STAGGS Date: 12/20/04

Activity Number/Task: RESEARCH SUPPORTING ENVIRONMENTAL
CHEMISTRY EXPERIMENTS

12/20/04

THIS NOTEBOOK IS A QUALITY ASSURANCE RECORD



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MOL. 20060508.0188

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Scientific Notebook Identification and Control

SN Identifier: SN-LLNL-SCI-487-Y1V2 *9/10 1-10-06*

Title: Research Supporting Environmental Chemistry Experiments

Investigator: Sarah Roberts *(SIGNED IN VOLUME 1)*

Principal Investigator: Susan Carroll

Responsible Manager: Susan Carroll

Date: December 9, 2004

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QA:QA

Initial Entry

Work Package AWPTA4

Research Supporting Environmental Chemistry
Experiments

Technical Work Plan

TWP-WIS-MD-000011 Rev 00
*Waste Package and Drip Shield Materials Testing*Investigator Responsible for SN
Principal Investigator
Responsible ManagerSarah Roberts
Susan Carroll
Susan Carroll

Purpose

This scientific notebook (SN) exists to document controlled laboratory experiments to measure the pH of corrosion test solutions and the stability of deliquescent brines.

A. Work Related Items

1) Title, Objectives, Work Scope, Approach and Primary Tasks

Title

Research Supporting Environmental Chemistry Experiments

Objectives

To measure the pH of corrosion test solutions (AUZM21) and the stability of deliquescent brines (AWPTA4).

Work Scope

1. To measure pH of corrosion test solutions used in the localized corrosion model. 2. Research includes measuring the stability of NaCl-KNO₃-NaNO₃ and more complex salt mixtures at elevated temperatures and controlled RH to determine if gas volatility contributes to the dry out of these salt mixtures, measuring the stability of ammonium salts at temperature and possibly the stability of ammonium brines at temperature, measuring the stability of deliquescent brines that react with dust at 220C in autoclave experiments.

Post-test characterization may include analysis by optical microscopy, Raman spectroscopy, scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), x-ray diffraction (XRD), and ion chromatography (IC).

Approach

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Introduction

The approach for the pH measurements is straight forward. Corrosion solution will be synthesized at elevated temperature if needed, and pH will be measured at room temperature.

Several approaches will be used to measure chemical transformations in thin films. This include the use of the thermogravimetric analyzer under controlled temperature and relative humidity (RH) conditions (SN-LLNL-SCI-473-V1), environmental chamber at controlled RH and temperature, convection ovens at controlled temperature and ambient RH, and in autoclave experiments in saturated or unsaturated conditions at controlled temperature. Changes in sample weight, resistivity, or chemical composition or mineralogy will be used to address chemical changes in the thin film chemistry.

Measured parameters

The testing will yield the following information:

- Corrosion solution pH (25C), relative humidity, sample weight, chemical composition, and/or mineralogy

Uncertainty

Uncertainty in measurement of the following parameters will be characterized.

- Temperature
- Relative Humidity

Primary Tasks

The work is performed at Lawrence Livermore National Laboratory (LLNL) and consists of electrochemical testing and sample analysis.

2) Materials

- Reagent grade chemicals, such as NaCl and KNO₃
- De-ionized water from a Milli-Q source (>18M Ω)
- Platinum electrodes for resistivity measurements

3) Measuring and Test Equipment

The M&TE used will be documented in the scientific notebook and will include:

- Thermocouples (require vendor calibration every 12 months)
- Relative humidity sensors (require vendor calibration every 12 months)
 - RH calibrations will be checked using the high temperature water vapor technique prior to and after each test or every month, whichever is longer
- Analytical balance (calibrate before use, per TIP-CM-25-01)
- Raman spectrometer (calibrate before use, according to user's manual)
- XRD analyzer (calibration/frequency per TIP-AC-12)

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- IC analyzer (calibration/frequency per TIP-CM-59)
- Gamry potentiostat (requires calibration every 12 months)

4) Expected Procurement Activity

The procurement of general chemicals, lab supplies, and calibration services will be conducted through YMP approved suppliers, as applicable.

5) Software

Name	Excel 2000
Version	9.0 or later
Vendor	Microsoft
Address	Redmond, WA
Description	Data plotting
Computer Platform	Microsoft Windows
Operating System	Windows 2000
Qualification Status	Visual display or graphical representation of data. Qualification not needed, per LP-SI.11Q-BSC
STN	NA
Baseline Date	NA

Name	Gamry Framework: DC105 Corrosion Techniques
Version	4.30 or later
Vendor	Gamry Instruments
Address	Warminster, PA
Description	Potentiostat control
Computer Platform	Microsoft Windows
Operating System	Windows Me
Qualification Status	Potentiostat control. Qualification not needed, per LP-SI.11Q-BSC
STN	NA
Baseline Date	NA

Name	EChemAnalyst
Version	1.30 or later
Vendor	Gamry Instruments
Address	Warminster, PA
Description	Data plotting
Computer Platform	Microsoft Windows
Operating System	Windows 2000
Qualification Status	Visual display or graphical representation of data. Qualification not needed, per LP-SI.11Q-BSC
STN	NA
Baseline Date	NA

6) Standards, Criteria and Procedures

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No formal standards or criteria have been identified as applicable to this activity. Relevant procedures include:

TIP-CM-25 User calibration and Use of Sartorius Analytical Balance Model #MC210S

TIP-AC-12 Calibration of X-Ray Diffractometer

TIP-CM-59 Ion Chromatography: Calibration and Solution Anion Analysis

TIP-CM-42 User Verification of Gamry Potentiostats

TIP-CM-14 User Calibration of Reference Electrodes

LP-SI.11Q-BSC, Software Management

AP-12.1Q Control of Measuring and Test Equipment

AP-SIII.1Q Scientific Notebooks

AP-SIII.3Q Submittal and Incorporation of Data to the Technical Data Management System.

AP-SV.1Q Control of the Electronic Management of Data

LP-4.5Q.BSC Processing Purchase Requisitions and Procurement Documents

033-YMP-QP-3.8 Control of the Electronic Management of Data.

033-YMP-QP-8.0 Identification and Control of Samples.

7) Special Training/Qualification, Environmental Conditions, Accuracy/Precision Requirements, Potential Sources of Error

Special Training/Qualification

No prerequisites, special controls or processes, or any skills beyond those documented in the technical qualifications of the personnel performing the work are required. Laboratory studies will be conducted in Building 241 at LLNL.

Environmental Conditions

Standard laboratory conditions.

Accuracy/Precision Requirements

The accuracy and precision of all measurements shall comply with the requirements expressed in the TIP specific to the measurement being performed.

Potential Sources of Error

Potential sources of error due to measurement uncertainties and M&TE calibration status will be evaluated, and the results of such determinations will be recorded in this scientific notebook as appropriate and in the data spreadsheets submitted to the Technical Data Management System.

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8) **Miscellaneous**
N/A

9) **References**
N/A

10) **Electronic Control of Information**

At the time of data collection, a hard copy and an electronic copy (when appropriate) will be made. All data from these analyses will either be entered into this scientific notebook or stored in an attachment binder for this scientific notebook and/or on excel spreadsheets that are submitted to the TDMS for use by the Yucca Mountain Program. A backup copy of all electronic data is created on a weekly basis by the Energy and Environment Directorate Computer Staff. Electronic and/or hard copies of the data are contained in a locked fireproof safe during non-office hours.

A copy of the completed Process Control Evaluation for Supplement V and 033-YMP-QP-3.8 form, YMP 117 are attached to this scientific notebook.

11) **Affected Organizations**

This work supports the Engineered Barrier Systems (EBS) Process/Model Report, the Waste Package Group, and questions raised by the NWTRB and NRC project reviews.

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B. Personnel Authorized to Make Entries in this Scientific Notebook (SN)

Name: Signature: Initials: Date:

Sarah Roberts Signature in SN-LLNL-SCI-487 V1

Susan Carroll Signature in SN-LLNL-SCI-487-V1

Space below reserved for additional names.

S. Daniel Day ~~S. Daniel Day~~ SDA 1-11-05

Kirk Staggs ~~Kirk Staggs~~ KS 1-11-05

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C. Cross-References to Previous, Concurrent and Succeeding SNs and Attached Binders

This is the initial SN for this Activity. There are no concurrent, controlled SNs for this Activity. Documents that are too large to fit into this SN, if any, will be inserted into a supplement, identified below. Electronic files will be archived on a CD-ROM or other media as indicated below.

Supplement Supplement 1 "Research Supporting Environmental Chemistry Experiments"
Archive SN-LLNL-SCI 487 V2

Cross-References to Amendments to this Initial Entry

This space is reserved for the cross-referencing of any amendments that may be made to this initial entry.

SN _____ pages: _____

SN _____ pages: _____

D. Results of Initial Compliance Review

These are inserted in this SN.

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OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
PROCESS CONTROL EVALUATION FOR THE
ELECTRONIC MANAGEMENT OF INFORMATION

OA: OA
Page 1 of 1

A. Procedure/Work Activity Identification: (check one)

- Procedure (identify process procedure number, title, revision and ICN level being evaluated), or
- Work Activity (identify by work package number, Technical Work Plan, technical product, etc., including title and revision)
SN-LLNL-SCI-487-V1; TWP-WIS-MD-000011, Rev. 00, Waste Package Testing, Work Package (WP) AWPTA4

B1. Processes/Process Functions/Work Activities Evaluation

	Yes	No
1. Will, or does, the process/process function/work activity depend on a form of electronic media to store, maintain, retrieve, modify, update, or transmit information?	✓	
2. Will, or does, the process/process function/work activity manage, control, or use an electronic database, spreadsheet, set of files, or other holding system for information?	✓	
3. Will, or does, the process/process function/work activity transfer information electronically from one location to another? (The method may be File Transfer Protocol, electronic download, tape to tape, disk to disk, etc.)	✓	

If the answers in Section B1 are all "No," process in accordance with Paragraph 5.1 [2] g; otherwise proceed to Section B2.

B2. Processes/Process Functions/Work Activities Compliance Evaluation

	Yes	No	N/A
1. Is any Sensitive Unclassified electronic information produced from the work activities/processes/process functions?			✓
2. If any Sensitive Unclassified electronic information is produced, are the process controls in accordance with AP-SEC-001?			✓
3. Does the procedure or work activity document provide adequate controls to protect information from damage and destruction for its prescribed lifetime?	✓		
4. Does the procedure or work activity document provide adequate controls to ensure that information is readily retrievable?	✓		
5. Does the procedure or work activity document provide adequate controls to describe how information will be stored with respect to media, conditions, location, retention time, security, and access?	✓		
6. Does the procedure or work activity document provide adequate controls to properly identify storage and transfer media as to source, physical and logical format, and relevant date?	✓		
7. Does the procedure or work activity document provide adequate controls to ensure completeness and accuracy of the information input and any subsequent changes?	✓		
8. Does the procedure or work activity document provide adequate access to controls to maintain the security and integrity of the information?	✓		
9. Does the procedure or work activity document provide adequate controls to ensure that transfers are error free or within a defined permissible error rate? (e.g., copying raw information from notebook to electronic information form, electronic media to another electronic media, or File Transfer Protocols)	✓		

If a "No" answer is given for any question in Section B2, proceed to Section C; otherwise process in accordance with Paragraph 5.1 [2] g. Mark "N/A" for those items that are not applicable to the specific process or work activity.

C. Results of Evaluation

Provide a summary of the "as-is condition," proposed remedial actions, and expected completion date of document revision, for each item in Section B2 that was indicated as "No."
The correct response to B2.1 above is actually "No," because there is no sensitive unclassified electronic information produced from this scientific notebook. However, "N/A" was selected because a "no" response requires the above action but no action is required.

Responsible Manager
Susan Carroll

Date
12/10/2004

SCG

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University of California Lawrence Livermore National Laboratory YUCCA MOUNTAIN PROJECT	QA:QA <input checked="" type="checkbox"/> QA:N/A <input type="checkbox"/>	Page <u>1</u>
ELECTRONIC MANAGEMENT OF INFORMATION CHECKLIST		
A1 – Personnel with input/change access: <u>All persons listed under Scientific Notebook SN-LLNL-SCI-487-V1 SN Entry Authorization</u>		
A2 – Activity: <u>Research Supporting Environmental Chemistry Testing</u>		
A3 – Responsible Manager: <u>Susan Carroll</u>		
B. Document Controls used for the following:		
B1 – Controls for the protection of information from damage and destruction during the prescribed lifetime and methods to assure that information is readily accessible:		
<u>Hard copy of raw data will be kept as a back-up reference for all data entered/stored electronically.</u>		
B2 – How the security and integrity of the information will be maintained:		
<u>Electronic data will be compared with original hard copy files to assure completeness of information which will be stored in a locked file cabinet.</u>		
B3 – Controls for storage of information including media, conditions, location, retention time, security, and access:		
<u>Electronic media, scientific notebook, and its supplements will be stored in a locked office. Key analytical results will be maintained in both electronic and hard copy media.</u>		
B4 – Controls for information transfer media as to source, platforms and formats used, method and frequency for verification of transfers, and where performance of verifications will be documented:		
<u>Personal computer files are backed-up automatically every week. Visual verification of data to ensure completeness of copies. Results will be documented in the scientific notebook or supplement.</u>		
B5 – Controls for assurance of completeness and accuracy of information input and subsequent changes to the information. Verification of completeness and accuracy must address the specific method and frequency of verifications and where performance verification will be documented:		
<u>Visual examination of data to include a comparison of the number of rows and columns of data. Flows of data picked at random will also be compared. Results will be documented in the scientific notebook or supplement.</u>		
B6 – Identify if information transfers are to be error free or within a specified permissible error rate:		
<u>No errors permissible. Any error will be documented in notebook. Data file containing errors will be purged.</u>		
TAL/Responsible Manager Signature <u>Susan Carroll</u>		Date _____



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Supplement 1 has been created for this notebook. This supplement contains calibrations sheets, TGA validation records of the balance, and electronic media storage for files. Additional information and data may be added to this supplement as needed and will be indicated in this notebook.

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TGA-DSC Ammonium Salt Tests for the Yucca Mountain Project

Introduction

The ammonium salt stability testing program is being conducted to determine the decomposition rates and the various stages of ammonium chloride, ammonium nitrate, and ammonium sulfate salt decomposition nominally between 170°C to 220°C. This is part of a broader study to determine the possibility of dust particle deliquescence at the high temperature end of the nuclear waste package environment at the Yucca Mountain Repository in Nevada. The presence of these salts has been detected by dust collection operations in the repository tunnels. These salts are water soluble and release anions, particularly chloride (Cl⁻), that are agents of localized corrosion to Alloy 22. Alternatively, the ammonium nitrate can release nitrate anions (NO₃⁻) into solution, which are thought to have a mitigating effect on localized aqueous corrosion processes. Quantifying the thermal stability characteristics of these salts will help determine the temperature ranges over which the salts and their solid state decomposition products will occur.

Reagents

The reagents used for the TGA study are listed below:

Ammonium chloride (NH₄Cl)

- Manufacturer: Mallinkrodt
- Formula Weight: 53.49
- CAS No.: 12125-02-9
- Lot No.: 3384 A41612
- Assay: 99.9% NH₄Cl

Ammonium nitrate: (NH₄NO₃)

- Manufacturer: J.E. Baker
- Formula Weight: 80.04
- CAS No.: 6484-52-2
- Lot No.: A07655
- Assay: 100.2% NH₄NO₃

Ammonium Sulfate ((NH₄)₂SO₄)

- Manufacturer: J.E. Baker
- Formula Weight: 132.14
- CAS No.: 7783-20-2
- Lot No.: Y10334
- Assay: 99.4% (NH₄)₂SO₄

The reagents are all anhydrous crystalline solids, with morphological characteristics depicted in the following photographs/photomicrographs:

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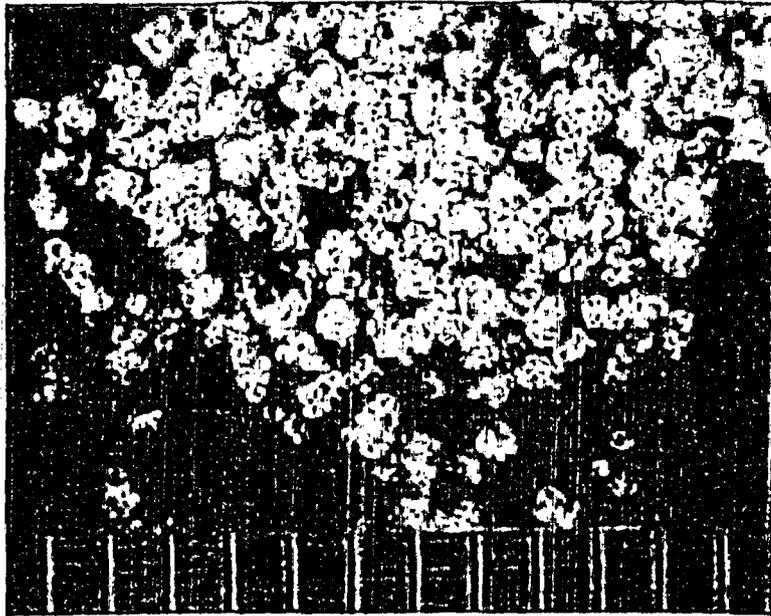


Figure 1 Ammonium chloride salt. 8X magnification. Scale marks = 1mm

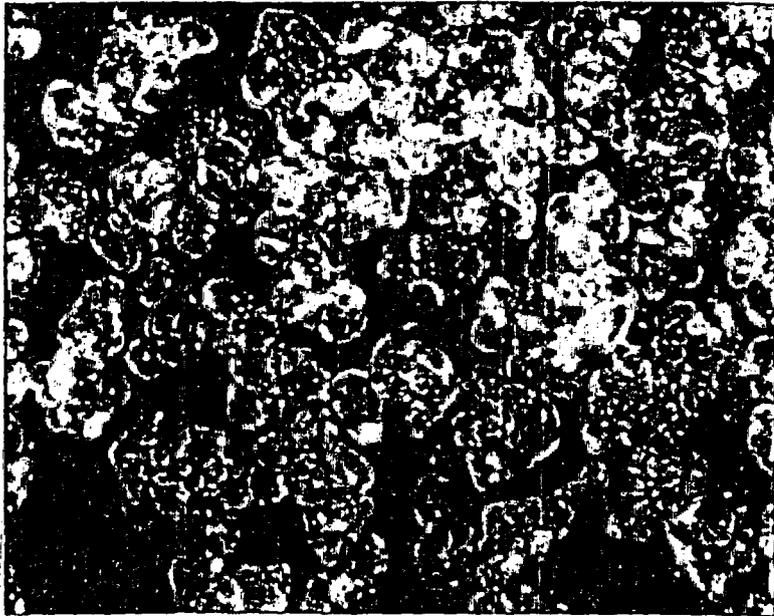


Figure 2 Ammonium chloride salt. 20X magnification.

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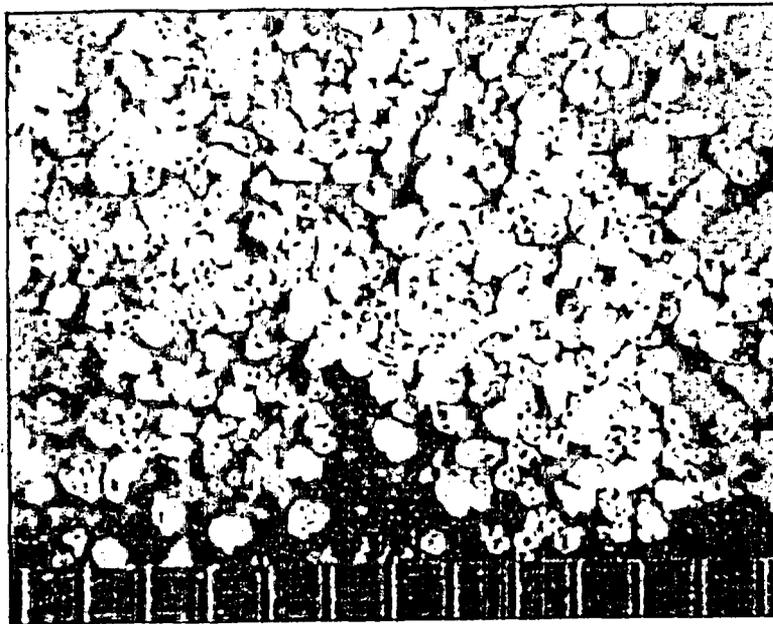


Figure 3 Ammonium nitrate salt. 8X magnification. Scale marks = 1mm

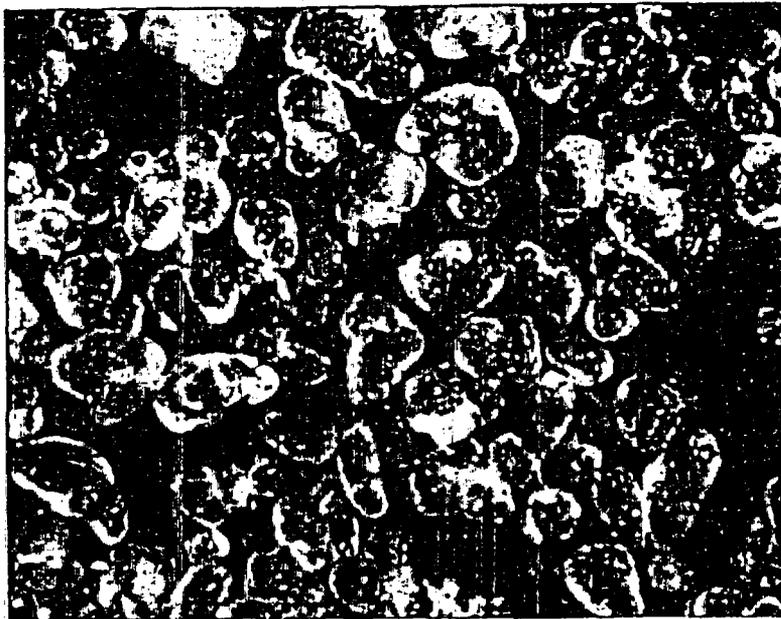


Figure 4 Ammonium nitrate salt. 20X magnification.

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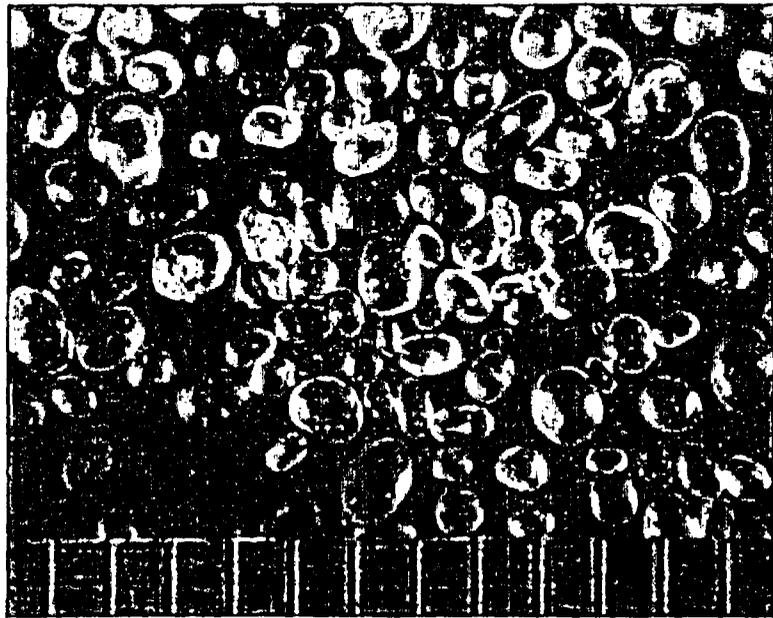


Figure 5 Ammonium sulfate salt. 8X magnification. Scale marks = 1mm

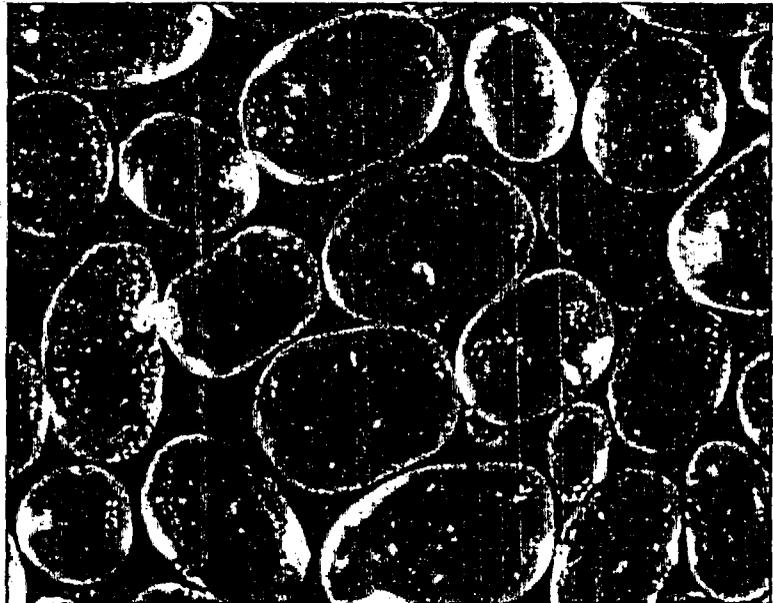


Figure 6 Ammonium sulfate salt. 20X magnification.

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Reagent descriptions:

Ammonium chloride: anhedral to subhedral clear individuals and polycrystalline agglomerates 0.5 to 1.5mm across. The crystals are 150 to 400 microns across, with an average diameter of 250 to 300 microns.

Ammonium nitrate: mostly clear and occasionally translucent subhedral single crystals and small polycrystalline agglomerates 250 to 1000 microns (1mm) in size. Individual crystals 300 to 750 microns in size have been "fused" together into agglomerates.

Ammonium sulfate: rounded to subhedral clear to frosted individuals, occasional polycrystalline agglomerates, and rare platelets measuring 600 microns by 375 microns to 1.75mm by 1.25mm across and averaging 1.25mm by 0.75mm across.

All three salts have a rounded morphology suggesting a spray formed manufacturing process.

Test Equipment

The apparatus used to measure the decomposition of the ammonium salts is a TA Instruments Hi Res TGA 2950, serial No. H2950-347; DOE #8541688. The TGA is operated by a TA Instruments Thermal Analyst 2100 computer using operating software version 8.9D (2.2B). The unit measures the amount and rate of weight change in a material either as a function of increasing temperature or isothermally as a function of time, under a controlled atmosphere. The unit can therefore characterize the weight gain or weight loss of a substance, and detect phase changes due to decomposition, oxidation, dehydration, or similar processes. The sample chamber and microbalance system is purged with facility air purified by passing it through a Parker Filtration/Balston Analytical Gas Systems Zero Air Generator to remove moisture and organics. The air is metered separately into the balance and furnace chambers to flush out volatiles. The balance flowmeter is set at 40 on the scale, and the furnace chamber flowmeter setting is 60. The TGA furnace itself is cooled by a circulating water system connected to a small external unit equipped with an electric pump and an air-cooled heat exchanger.

The TGA 2950 is a bench top model with a 23 inch by 17 inch footprint. Figures 7, 8, and 9 show the compact Hi Res TGA 2950 test module laboratory setup. The unit was positioned on a marble balance table to dampen vibrations, and was leveled to allow the platinum sample pan to hang freely in the cylindrical furnace chamber. Figures 8 and 9 are close-up views of the 375 mg platinum sample pan and the 1000°C cylindrical heating furnace. The pan is suspended from a thin platinum wire that connects it to the balance mechanism. The furnace sleeve is raised to enclose the suspended sample pan and makes a tight seal with the bottom of the black balance enclosure.

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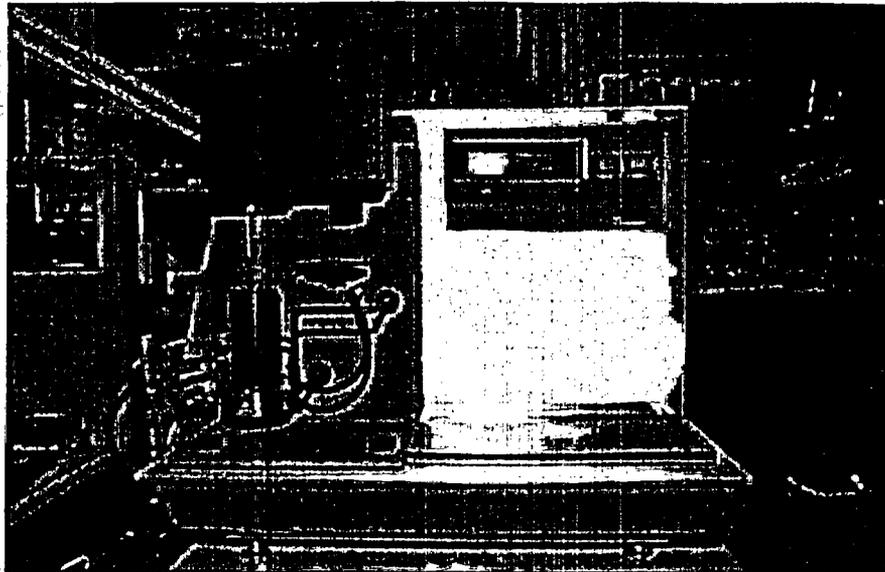


Figure 7 TA Instruments Hi Res TGA 2950 unit.

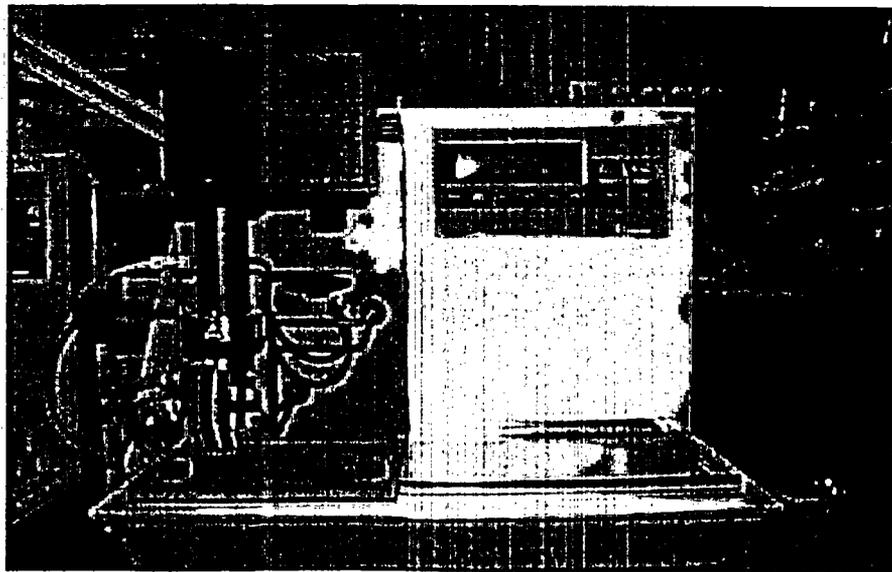


Figure 8 TGA 2950 unit with the furnace chamber in the closed position.

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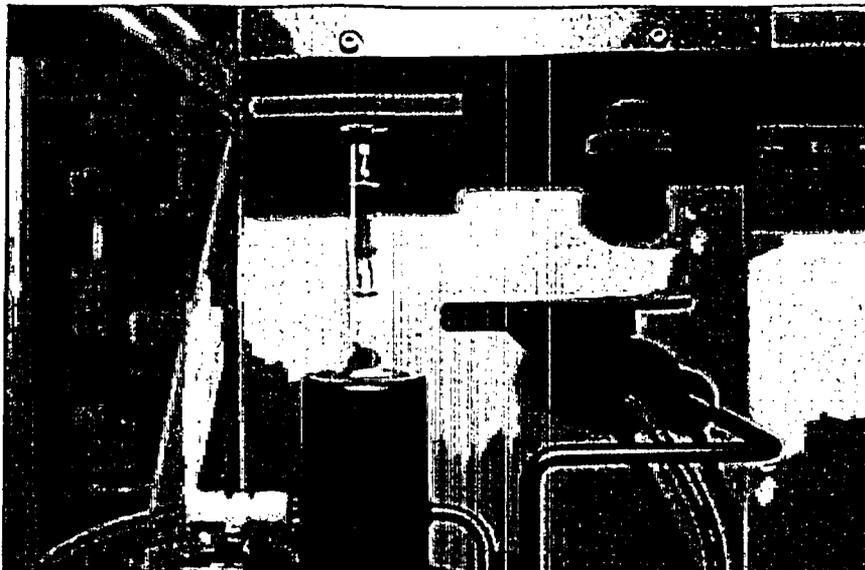


Figure 9 Close-up view of the platinum sample pan with the furnace in open position.

The five major TGA components are noted in the photos below. They include:

- the balance, which provides precise weight measurement (μg).
- the sample loading platform (stage).
- the furnace, which provides temperature and atmospheric control.
- the cabinet (not illustrated, but the base and back panel of the unit) which houses system electronics, controls, and mechanical devices.
- The heat exchanger (not shown), a $15 \times 6\frac{1}{2} \times 6\frac{1}{2}$ inch metal box enclosing a small water-wheel pump and fan-cooled radiator to dissipate furnace heat.

The furnace operates between 25°C and 1000°C with heating rates of 0.1 to $200^{\circ}\text{C}/\text{min}$. A small white Platinel II (Engelhard Industries) thermocouple is suspended near the 375 mg platinum sample pan to monitor test temperature (figures 10, 11, and 12). The platinum pan has a 100 μL volume capacity.

The TGA 2950 unit operates on a null balance principle. The balance mechanism is housed in the black box (figures 10 and 11) above the sample furnace and has a maximum weighing capacity of 1.0 g and a range of 1 μg to 1000 μg (1 gram). The balance assembly has a diamond-shaped arm from which two fine platinum hang-down wires are suspended. The arm is attached to a taut-band meter movement and is maintained in a horizontal position by an optically-actuated electronic servo loop with feedback from two photodiode detectors. The photodiodes are activated by a constant current LED that sends an equal amount of light to each of the photodiodes. When the balance arm is nulled (horizontal), the photodiodes receive equal amounts of light. Any sample weight loss or weight gain will offset the mechanism and the photodiodes will receive different intensities of infrared light. The unbalanced signal is noted by the servo circuitry, and the meter movement current is varied to create an electromagnetic force that rotates the balance beam back to the null position. The current compensation is measured by the electronics and translated into a weight change displayed on the computer screen. A small black cylindrical compartment on the bottom right side of the balance houses a platinum counterbalance pan. The tare pan holds small

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weights that keep the weight differential between the two pans to within ± 10 mg. The entire tare balance chamber and counter balance compartment are purged with air from the zero air generator to flush out any gaseous by-products.

To avoid operator damage to the sample suspension and the balance mechanism, the unit is equipped with an automatic loading stage (figures 10 and 11) that remotely loads the sample pan on the suspension wire. This operation is controlled by a system subroutine.

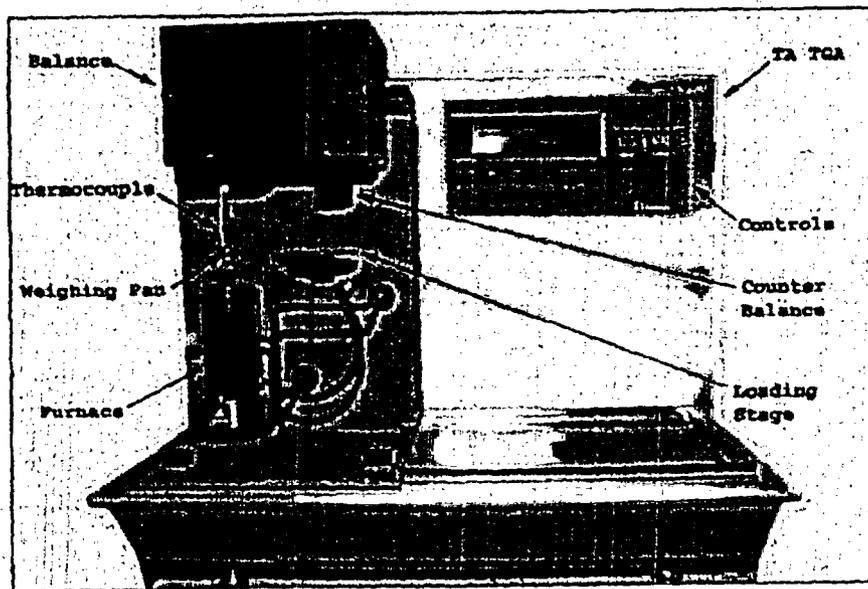


Figure 10 TA Instruments Hi Res TGA 2950 components.

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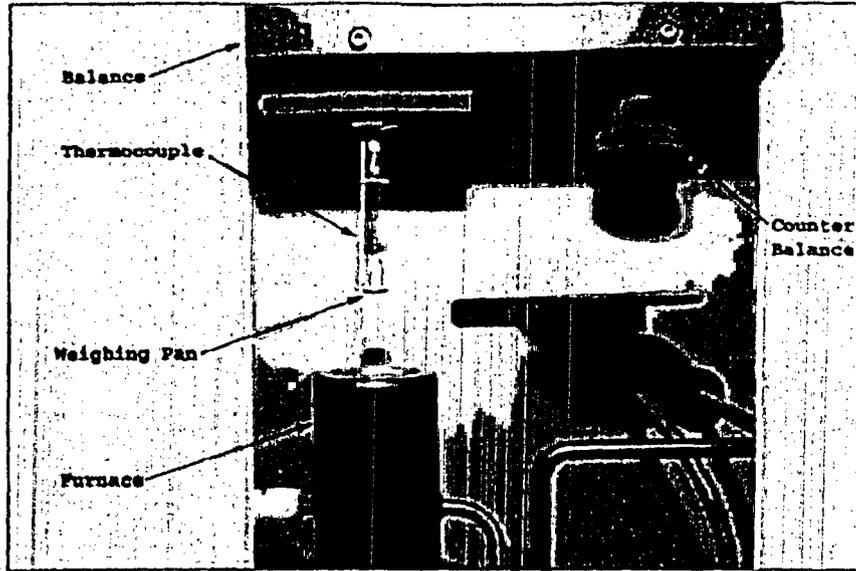


Figure 11 TA Instruments Hi Res TGA 2950 furnace, and sample balance assembly.

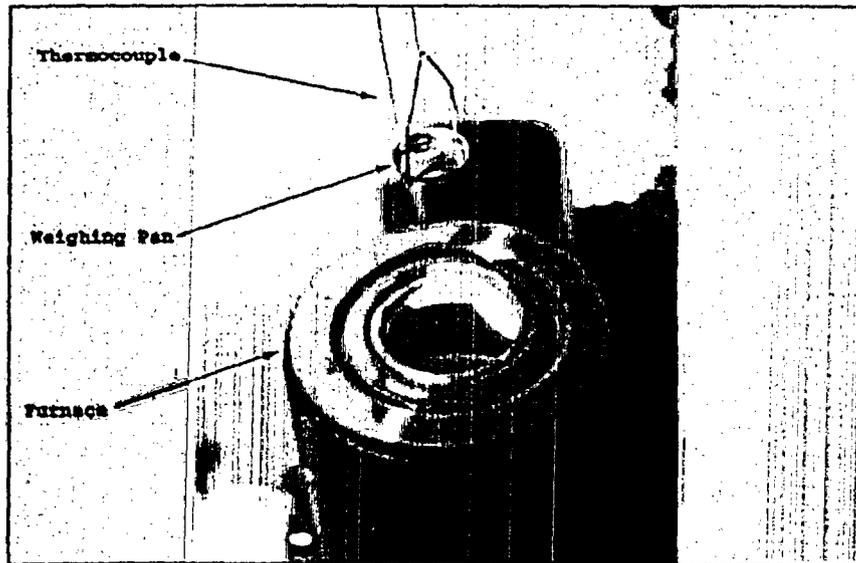


Figure 12 TA Instruments Hi Res TGA 2950 furnace and sample assembly, detail.

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Laboratory Analytical Procedure

Laboratory Housekeeping: Proper maintenance of the platinum sample pan was considered critical to achieving reproducible analytical results. The pan was always handled by its support wires using brass tweezers. As standard laboratory procedure, the operator also wore tight-fitting powder-free nitrile gloves during sample preparation, loading, and unloading activities. Between runs, test residue was removed from the pan by dipping it in 18 M Ω -cm grade deionized water and swabbing surfaces with a cotton Q-tip. The cleaned pan was air-dried using a VARITEMP heat gun and then rinsed, consecutively, with reagent grade acetone, isopropanol (isopropyl alcohol), and deionized water. Each step was interrupted with air-drying using the heat gun to evaporate all the residual liquid before proceeding with the next cleaning step. The pan was cooled to room temperature before continuing.

Reagent Preparation and Sample Pan Loading: The "as received" ammonium chloride, ammonium nitrate, and ammonium sulfate salts were not pretreated prior to analysis. The salts were transferred directly from the manufacturer's plastic bottle to the platinum pan using a clean (Kim-wiped with acetone) stainless steel micro-spatula. *The empty sample pan had been tared on the TGA 2950 balance prior to adding the test salt.* The pan was tared on a Sartorius MC210-S 5-place electronic balance. The salts were then transferred into the pan with the spatula and weighed. Any excess material was removed with brass microtweezers. The target weight was 10 \pm 0.5 mg, a nominal weight for accurate TGA 2950 analytical response. The sample weights were generally kept between 10.1 and 10.3 mg to permit acceptable analytical reproducibility. The accepted Sartorius MC210-S sample weight was recorded and the platinum pan was transferred to the TGA unit and placed on the automatic loading stage.

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Hi Res TGA 2950 Test Procedure

Equipment Calibration

Weight Calibration : The Hi Res TGA 2950 operator's manual provides specific procedures for temperature and weight calibrations. The weight calibration process uses standard reference weights and a special program, TGACal, to lead the operator through the calibration process. The first calibration step targets the 100 mg sample range. The latter involves balancing the tare pan against the empty sample pan in the closed furnace chamber, and adjusting the tare pan weight until the offset between the two pans is less than 10 mg. This was visually displayed on the computer screen by a color-coded bar indicating whether the weight differential is acceptable or unacceptable. Counterweight adjustments are made using the tare weight set provided with the TGA unit. Once the tare range is accepted, the program instructs the operator to calibrate in the 100 mg weight range. The empty sample pan is tared, then a calibrated 100 mg weight is placed on it and loaded into the furnace chamber. The calibrated weight value is entered on the screen. Once the balance has stabilized, the weight is accepted. The same procedure is followed using a 1000 mg (1 gram) calibrated weight. Accepting the 1000 mg weight completes the TGA 2950 weight calibration.

The TGA 2950 unit gave the following calibration readings on 1-10-05 using the Heusser-Neweigh Class S Metric weight set, Test #2115-04, Device No. 993465, Recalibration date December 15, 2005:

Standard Weight	Calibrated Weight Value	TGA Measured Weight
100 mg	99.9994 mg	96.234 mg
1000 mg	999.9890 mg	998.694 mg
20* mg	19.9951 mg	20.017 mg

The 20*mg weight from the Heusser-Neweigh set was weighed to validate the calibration accuracy in the approximate range where tests would be conducted.

*Added additional information
on page 86 of this notebook
to address Technical Review
comments.*

*ghf stop
12-22-05*

ghf stop 3-15-05

ghf

1/10/05

Temperature Calibration: The Hi Res TGA 2950 Thermogravimetric Analyzer temperature calibration was performed according to TA Instruments document "Traceable Temperature Calibration for TGA and SDT Using Curie Point Temperature Standards", PN 952386.001 Rev. F, Issued September, 2001.

This procedure uses the Curie point (demagnetization isotherm) temperature of a metal standard to calibrate the thermocouple-monitored temperature range of the unit. This is a one-point calibration process, but multiple readings can be taken over the desired test temperature range by using the appropriate metal standards. *The acquired Curie point temperature has not been used to correct the temperature output readings of the TGA 2950.*

The Curie point temperature calibration method was performed by placing a 35 to 40 mg piece of 40 mil nickel wire (TA Instruments Ni wire calibration standard PIN 952385.901, Lot No. CRM2-8058. This is an industrial standard.) in the cleaned and tared platinum sample tray, loading it onto the platinum suspension wire, and closing the furnace chamber. The sample tray was allowed to stabilize and a 1-inch square by 7-inch long permanent bar magnet was placed directly beneath the furnace to attract the sample and increase its weight by 2 to 5%. The TGA was programmed to equilibrate at 30.0°C and then ramp at 10.0°C/min to 500°C. The sample showed a slight weight gain up to Curie point threshold, attributed to the decreasing buoyancy effects of the heated furnace atmosphere. At the Curie point, its weight dropped sharply when it demagnetized. The weight was stable above the Curie temperature. A graphical plot of the temperature versus weight curve for the Curie point temperature calibration is shown in figure 13.

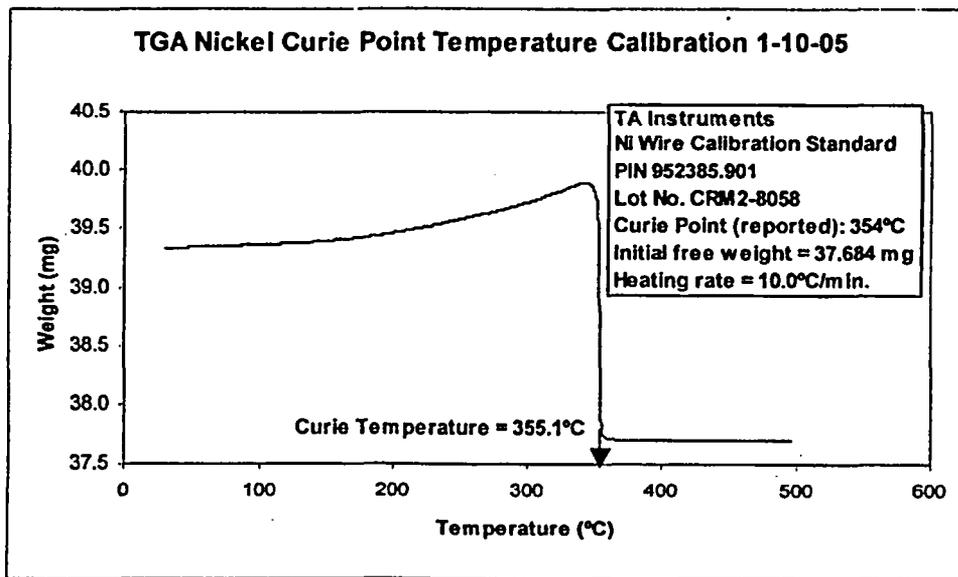


Figure 13 TGA Curie Point Temperature Calibration

The TA Instruments proprietary graphical analysis software's "Onset" subroutine was used to determine the Curie point temperature at the intersection of the curve tangents drawn just before the sudden weight loss occurs, and immediately below this point on the vertical section. The Curie point temperature determined from this curve is 355.1°C. The accepted value for nickel is 354°C (ASTM E 1582-93 Standard Practice for Calibration of Temperature Scale for Thermogravimetry). For the purposes of this study, the investigators felt the thermocouple temperature deviation from the actual Curie point was acceptable, and did not update the software to correct for this minor effect.

SWP

1/10/05

TGA Balance Calibration Verification

Before conducting TGA runs, the balance system that was calibrated on January 10, 2005, was checked using the Heusser-Neueigh Class S Metric weight set, Test #2115-04, Device No. 993465, Recalibration date December 15, 2005. The table below lists the weights used, the calibration weight value, and the TGA 2950 measured weight value. Each weight was loaded on the platinum sample pan using plastic tweezers, the pan was automatically loaded onto the balance wire, and the furnace jacket was raised to the closed position. The balance was allowed to stabilize for 5 minutes before each reading was made. The balance set did not contain a 10 mg weight, so the four smallest weight sizes were used to verify the TA Instruments balance calibration.

<u>Weight</u>	<u>Calibration Value</u>	<u>TGA Measured Weight</u>
20* mg	19.99513 mg	19.911 mg
50 mg	50.00195 mg	49.923 mg
100 mg	99.99938 mg	99.895 mg
200* mg	200.00596 mg	200.030 mg

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822

1/10/05
SHP 1/11/05

Test Procedure

The tests were run under two conditions: at constant ramping rate over a specified temperature range (thermal scan), and isothermally (constant temperature versus time). The thermal scan was selected to cover the stability range of the salts from 30°C ("room temperature") to above their decomposition points. Chemical literature supplied with the manufacturer MSDS documents states that ammonium nitrate and ammonium sulfate decompose slightly above their melting points (170°C and 235°C, respectively), whereas ammonium chloride sublimates at 338°C. The thermal scans were run first to confirm the stability range of the salts and to allow the experimenter to decide which temperatures were appropriate for subsequent decomposition rate studies. The nominal heating rate for the thermal scans is 10.0°C per minute. This rate will be varied when sample properties require test modification. The isothermal run times were arbitrarily selected to give a reasonably long decomposition time under stable conditions. Once runs were completed, the furnace automatically unloaded itself and was forced air cooled for 12 minutes. When the furnace had cooled to ambient temperature (25°C to 30°C), the residue or empty pan was reweighed at ambient temperature to confirm that the balance had not drifted. Post-test sample residues were saved.

Sample Clean-Up

The platinum test pan was cleaned after each run by dipping it into a beaker of 18 MΩ-cm deionized water and swabbing it with a cotton Q-tip. The pan was air dried using a Varitemp heat gun and then rinsed consecutively with acetone, isopropyl alcohol, and deionized water, with heat gun drying applied between each step. The pan was then visually examined for any contamination, the only notable flaws being very faint stain marks left by reagent that melted on the pan bottom.

Ammonium Salt Thermal Scan Test Results

For the two salts of interest in this study, ammonium chloride and ammonium sulfate, the decomposition scans were run from 30°C to 300°C at 10°C/min. for the chloride, and from 30°C to 500°C at 5°C/min. for the more refractory sulfate. The latter was terminated at 400°C when the sample had been completely spent at about 380°C. The dynamic decomposition curves for ammonium chloride (NH₄Cl) (file name YMP.001) and ammonium sulfate ((NH₄)₂SO₄) (file name YMP.008) are presented in figures 14 and 15.

gld stop 3-15-05

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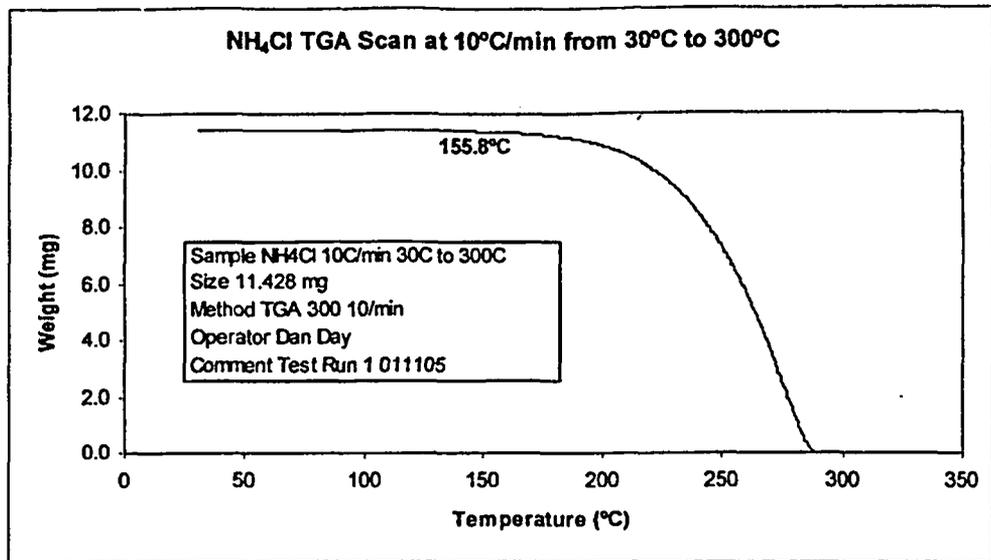


Figure 14 NH₄Cl TGA scan from 30°C to 300°C at 10°C/min. Decomposition onset is at 155.8°C.

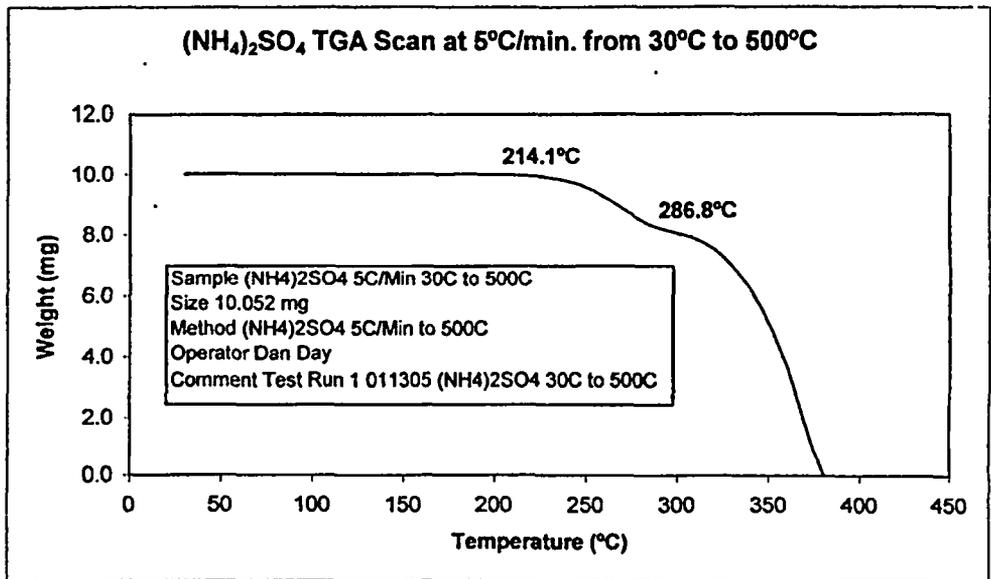


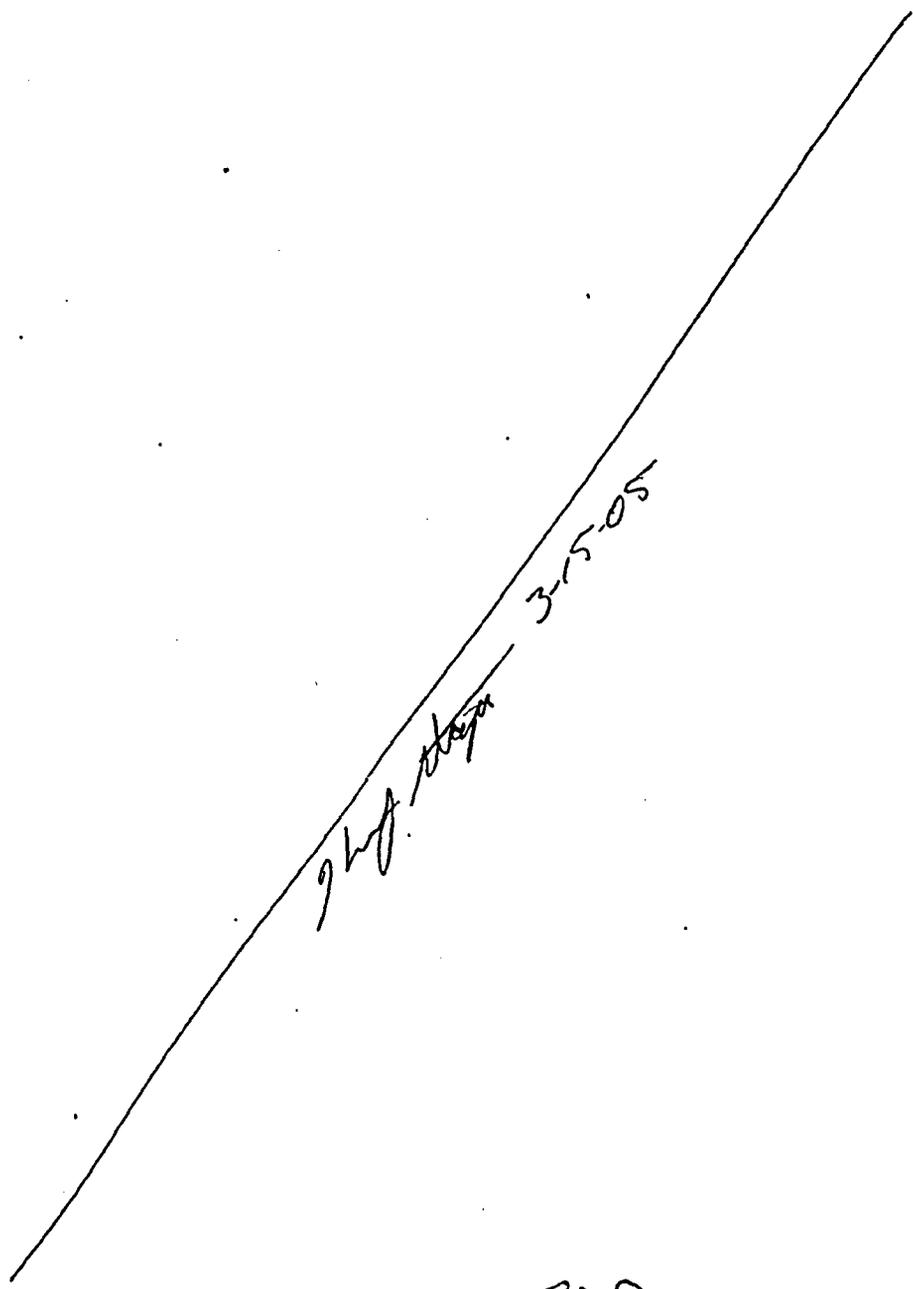
Figure 15 (NH₄)₂SO₄ TGA scan from 30°C to 500°C at 10°C/min. decomposition onset is at 214.1°C and decomposition transition point is at 286.8°C.

SWA

1/11/05

Ammonium Salt TGA Tests

The ammonium salt TGA tests described on the following pages were conducted using the parameters indicated on each test sheet. A graph of each test run accompanies each parameter sheet.



SWA

1/12/05

TA Instruments TGA-DSC Work Sheet

Date: 1/11/2005

Sample I.D.: NH₄Cl 10°C/min. 30°C to 300°C

Sample Weight: 11.428 mg

Operator: Dan Day

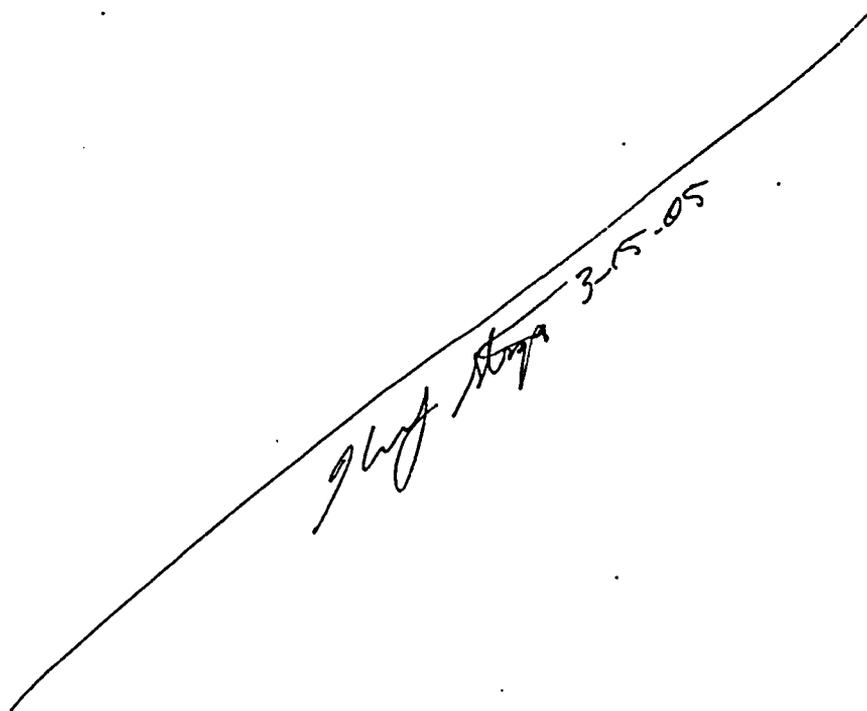
Comment: Test Run 1 011105 NH₄Cl 10°C/min. from 30°C to 300°C

File Name: YMP.001

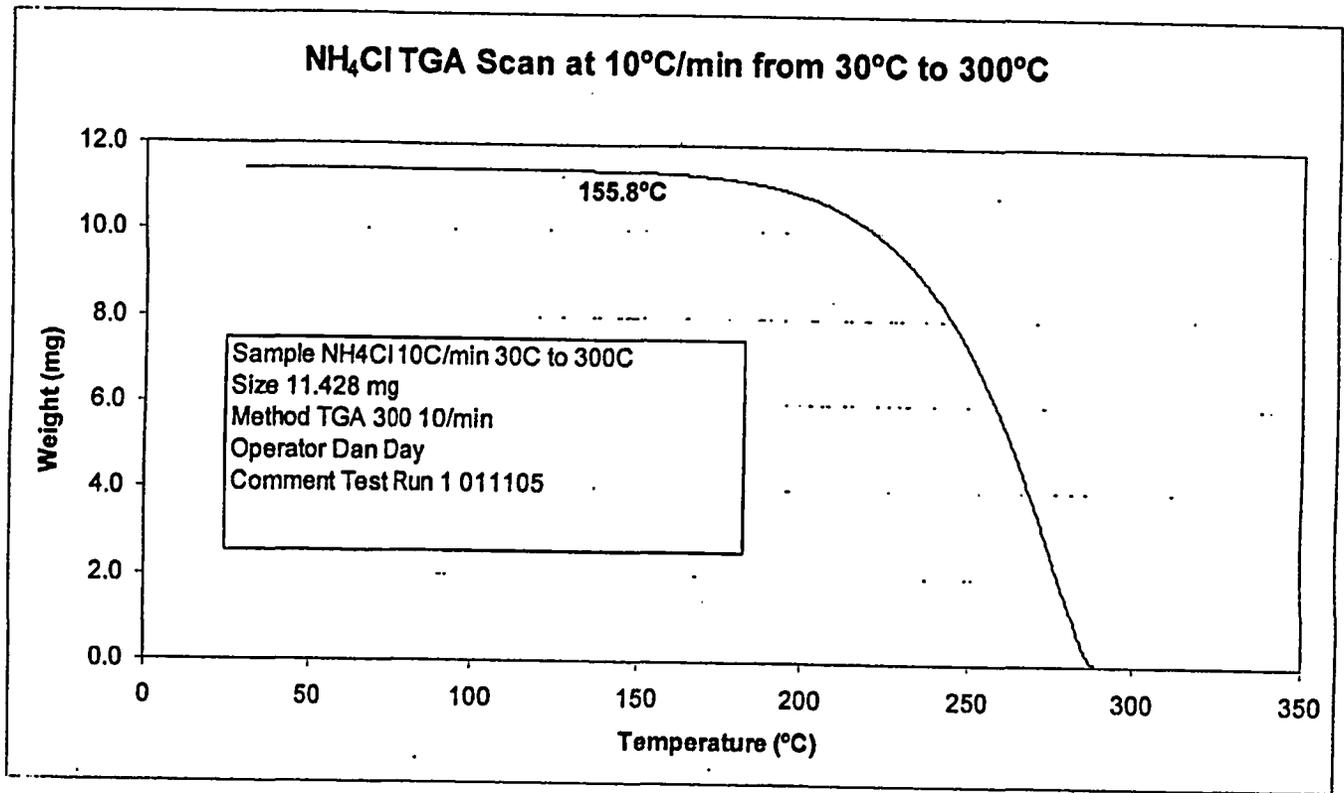
Method: TGA 300°C 10°C/min.

- Equilibrate at 30.0°C
- Ramp at 10.0°C/min. from 30.0°C to 300.0°C

Observations: The entire sample was consumed by about 288°C.



S.D. DL



8100

1/12/05

1/12/05

TA Instruments TGA-DSC Work Sheet

Date: 1/11/2005

Sample I.D.: NH₄Cl Iso at 143°C

Sample Weight: 10.760 mg

Operator: Dan Day

Comment: 3 hour NH₄Cl isothermal test at 143°C Test Run 2 011105

File Name: YMP.002

Method: TGA Iso at 143°C

- Equilibrate at 30.0°C
- Ramp at 10.0°C/min. to 143.0°C
- Isothermal at 143°C for 180 min.

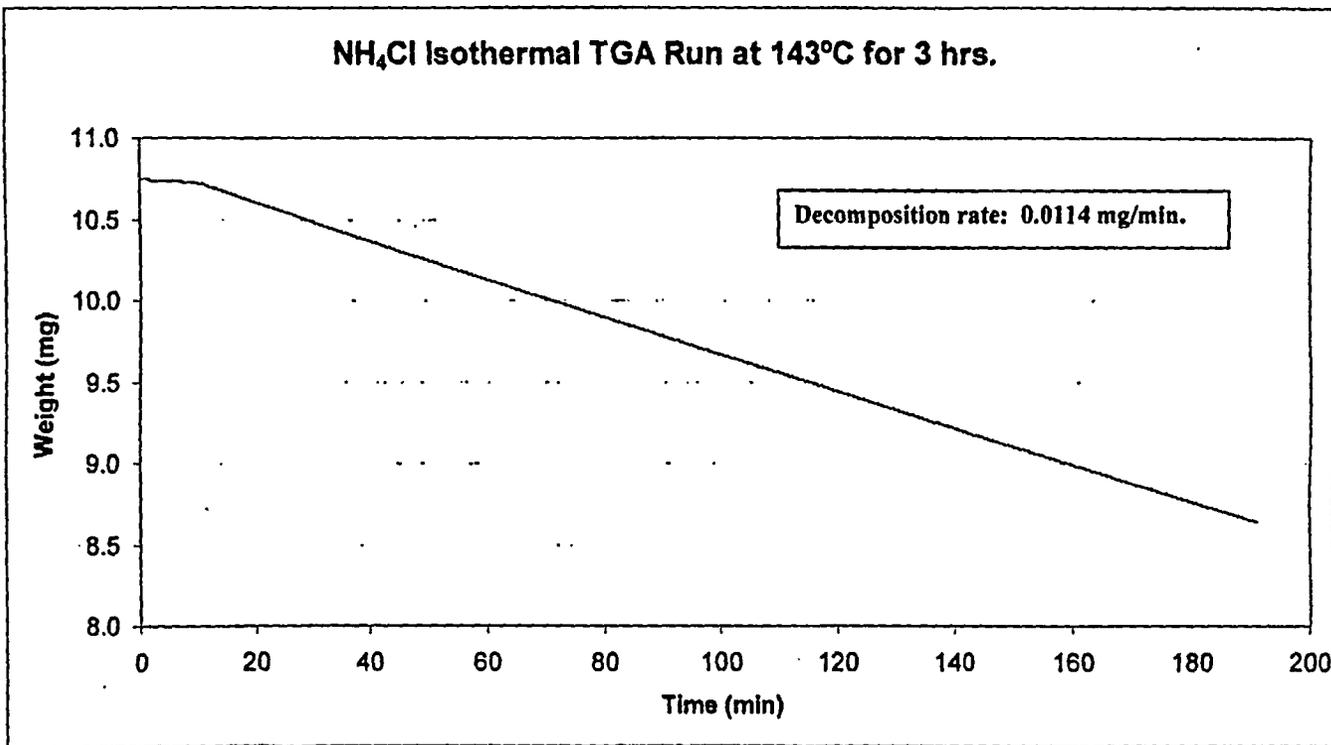
Final Sample Weight: 8.638 mg

Observations: The sample exhibits a linear weight loss versus time. After 3 hours it showed a weight loss slightly less than 20% the original weight. The 143°C isothermal temperature was selected from the TGA weight loss versus temperature curve (10.0°C/min. heat-up rate from 30°C to 300°C) because it was visually estimated to be the point where weight loss began. Linear weight loss versus time was observed at this temperature, with a 0.0114 mg/min. decomposition rate.

910 J. Day 3-15-05

SDR

NH₄Cl Isothermal TGA Run at 143°C for 3 hrs.



S.P.R.

1/12/05

H

1/12/05

TA Instruments TGA-DSC Work Sheet

Date: 1/11/2005

Sample I.D.: NH₄Cl Iso at 100°C

Sample Weight: 10.200 mg

Operator: Dan Day

Comment: Test Run 3 011105 NH₄Cl at 100°C for 12 hrs.

File Name: YMP.003

Method: TGA Iso at 100°C

- Equilibrate at 30.0°C
- Ramp at 10.0°C/min. to 100.0°C
- Isothermal at 100°C for 720 min.

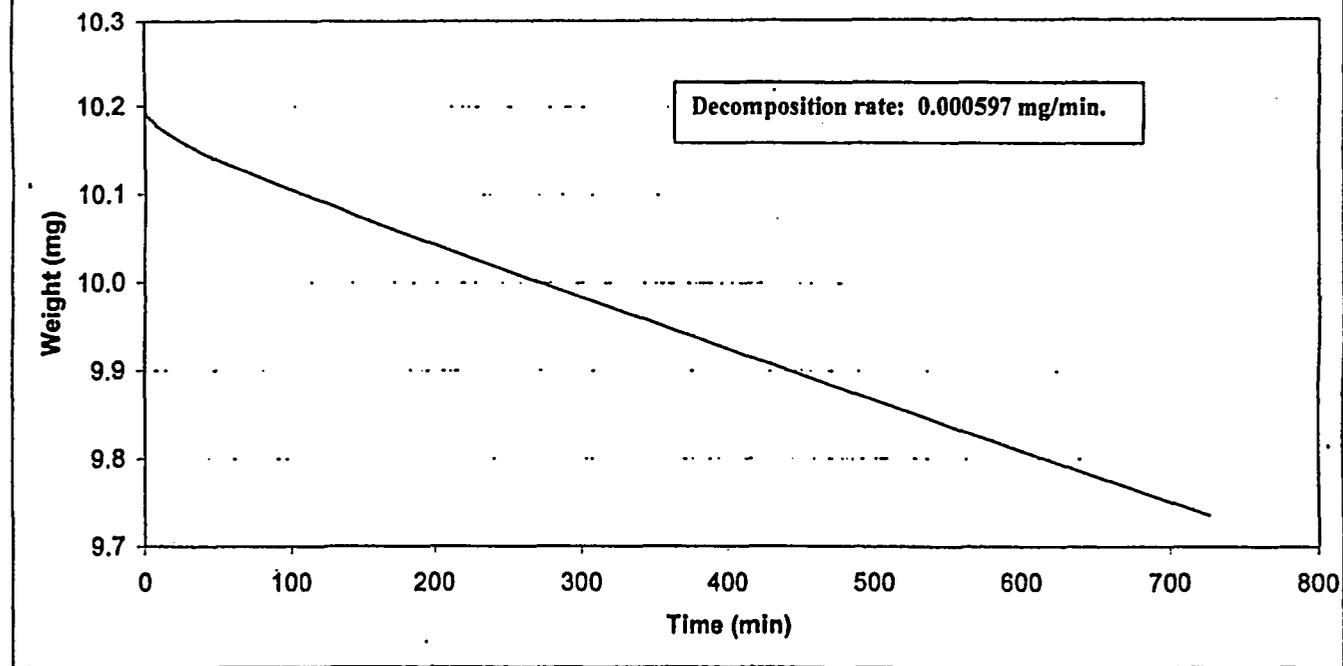
Final Sample Weight: 9.735 mg

Observations: The sample exhibits a linear weight loss versus time. After 12 hours the sample showed an ~4.6% weight loss. The residue is individual crystals of NH₄Cl reagent.

ghj stop 3-5-05

DD

NH₄Cl Isothermal TGA Run at 100°C for 12 hrs.



S. J. Hall

1/12/05

1/13/05

TA Instruments TGA-DSC Work Sheet

Date: 1/12/2005

Sample I.D.: NH₄Cl Iso at 250°C

Sample Weight: 10.374 mg

Operator: Dan Day

Comment: Test Run 1 011205 NH₄Cl at 250°C for 1 hr.

File Name: YMP.004

Method: NH₄Cl Iso at 250°C

- Equilibrate at 30.0°C
- Ramp at 200.0°C/min. to 250.0°C
- Isothermal at 250°C for 60 min.

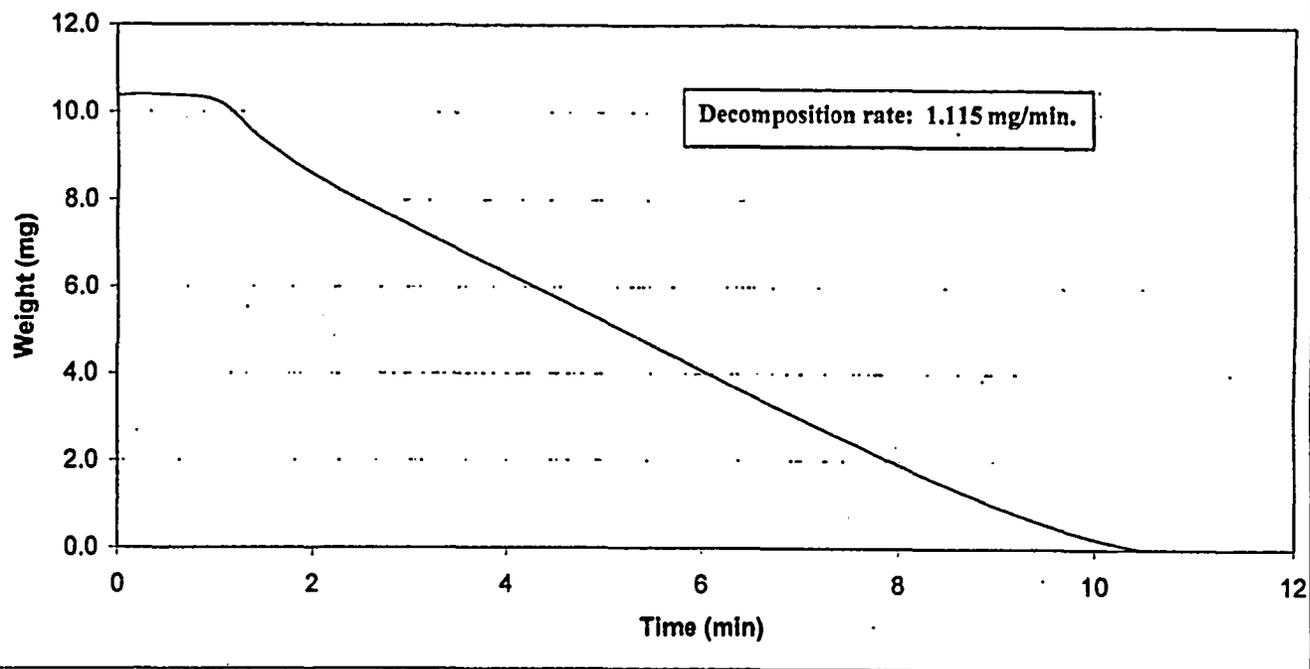
Sample Weight at 250°C set point: 8.884 mg

Observations: The sample was completely consumed in the first 11 minutes. The 200.0°C ramp rate is the fastest the TA Instruments TGA 2950 is capable of, and was used to minimize sample loss during the ramp up to the 250°C set point. There was still an ~15% weight loss when the sample reached 250°C.

9 hrs stop 3-15-05

S.D.L.

NH₄Cl Isothermal TGA Run at 250°C for 1 hr.



81812

1/13/05

1/13/05

TA Instruments TGA-DSC Work Sheet

Date: 1/12/2005**Sample I.D.:** NH₄Cl Iso at 200°C**Sample Weight:** 10.142 mg**Operator:** Dan Day**Comment:** Test Run 2 011205 NH₄Cl at 200°C for 1 hr.**File Name:** YMP.005**Method:** NH₄Cl Iso at 200°C

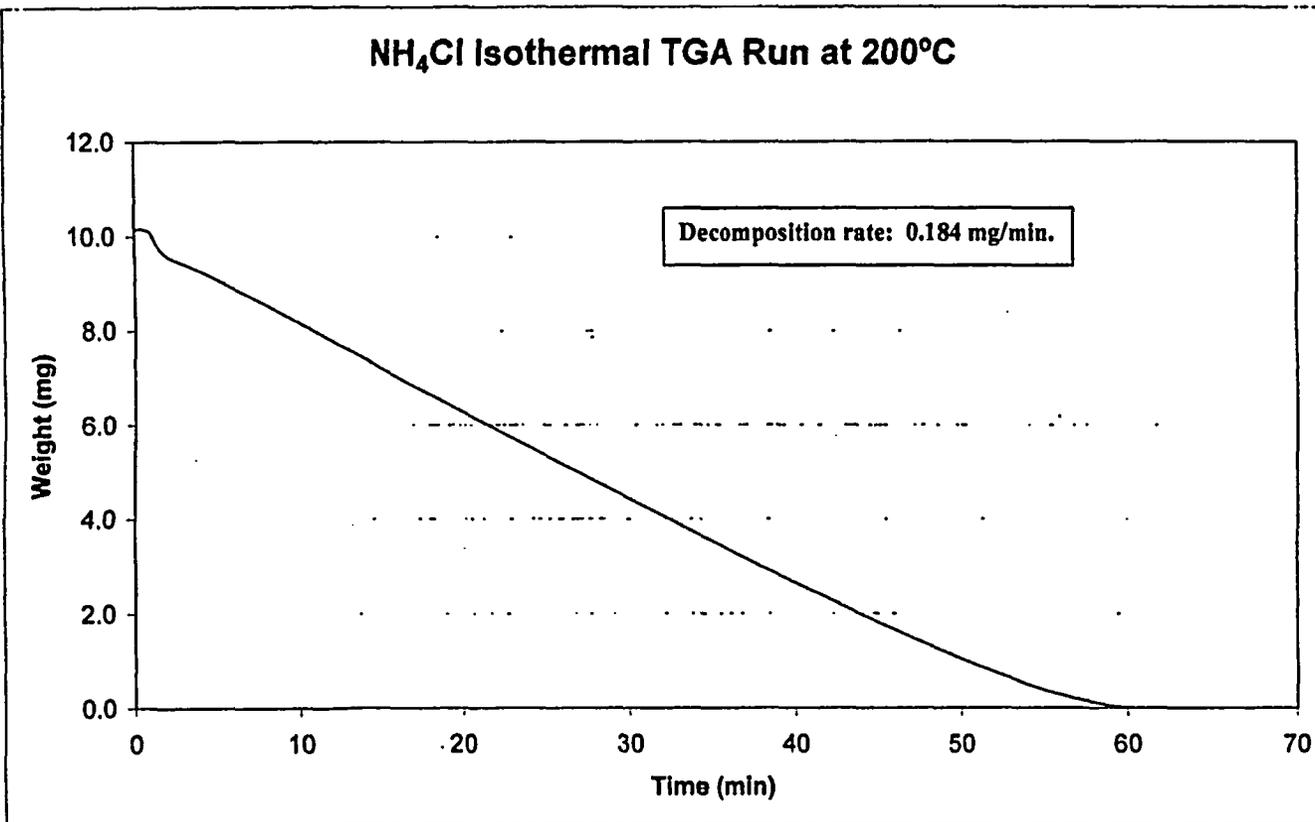
- Equilibrate at 30.0°C
- Ramp at 200.0°C/min. to 200.0°C
- Isothermal at 200°C for 60 min.

Sample Weight at 200°C set point: 9.848 mg**Observations:** The sample was completely consumed in just shy of 1 hour. The 200.0°C ramp rate was used to minimize sample loss during the ramp up to the 200°C set point. There was still an ~3% weight loss when the sample reached 200°C.

9.848 mg
3-15-05

S.H.D.

NH₄Cl Isothermal TGA Run at 200°C



SP

1/13/05

1/13/05

TA Instruments TGA-DSC Work Sheet

Date: 1/12/2005

Sample I.D.: $(\text{NH}_4)_2\text{SO}_4$ 10°C/min. from 30°C to 350°C

Sample Weight: 10.066 mg

Operator: Dan Day

Comment: Test Run 3 011205 $(\text{NH}_4)_2\text{SO}_4$ from 30°C to 350°C

File Name: YMP.006

Method: TGA 10C/min. to 350°C

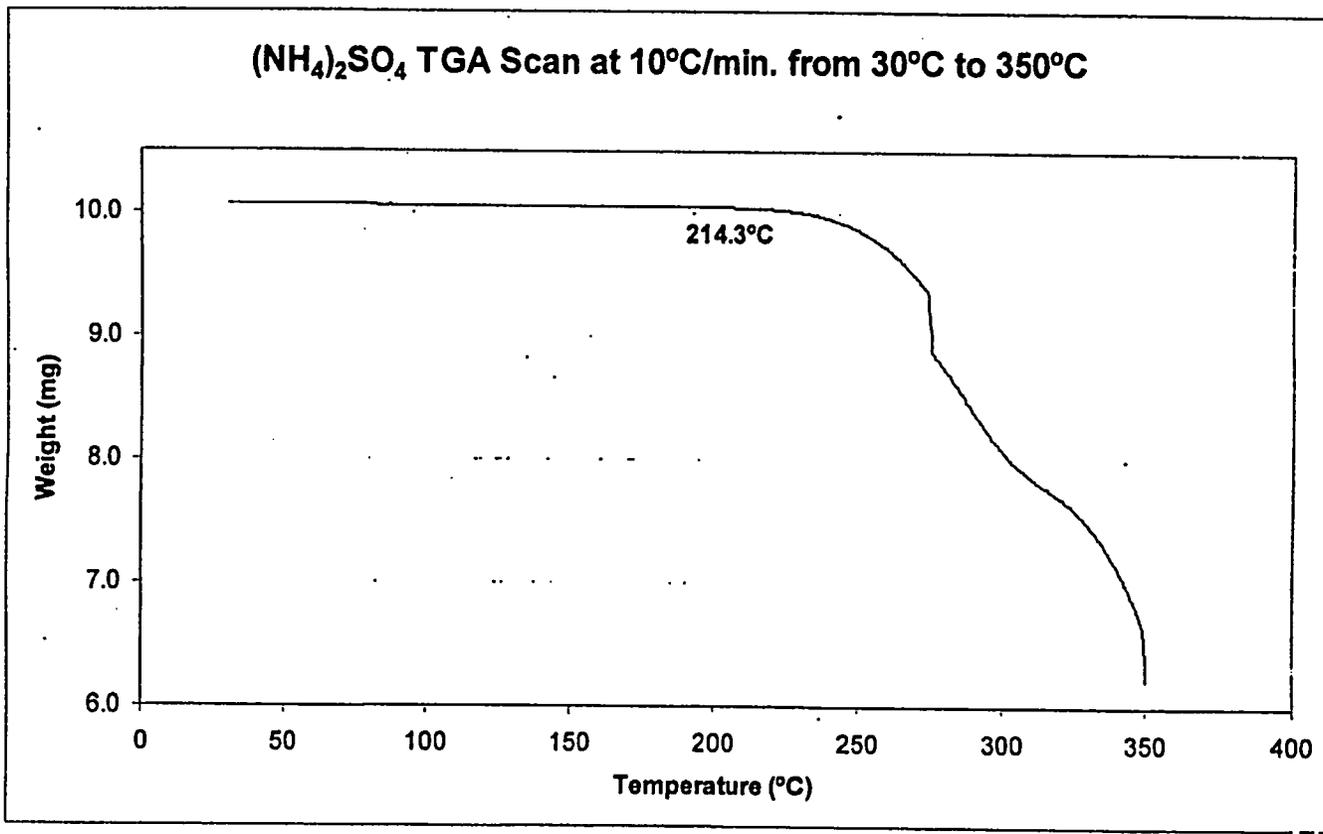
- Equilibrate at 30.0°C
- Ramp at 10.0°C/min. from 30.0°C to 350.0°C

Final Sample Weight: 6.216 mg

Observations: The sample was ~38% consumed by test end. The temperature versus weight curve showed weight loss initiation at about 210°C and an increasing loss rate with temperature. At ~275°C there was a sudden plunge in weight followed by an abrupt decrease in the weight loss rate as the curve apparently transitioned into a second phase decomposition field. The weight loss again accelerated and was dropping rapidly when the test ended. There was a brownish, pooled $(\text{NH}_4)_2\text{SO}_4$ derivative residue on the pan bottom indicating the second decomposition reaction had occurred in a melt phase.

g h y f j h y g g 3-15-05

S B D



SLL

1/13/05

1/13/05

TA Instruments TGA-DSC Work Sheet

Date: 1/12/2005

Sample I.D.: NH₄Cl Iso at 150°C

Sample Weight: 10.098 mg

Operator: Dan Day

Comment: Test Run 4 011205 NH₄Cl at 150°C for 12 hrs.

File Name: YMP.007

Method: NH₄Cl Iso at 150°C

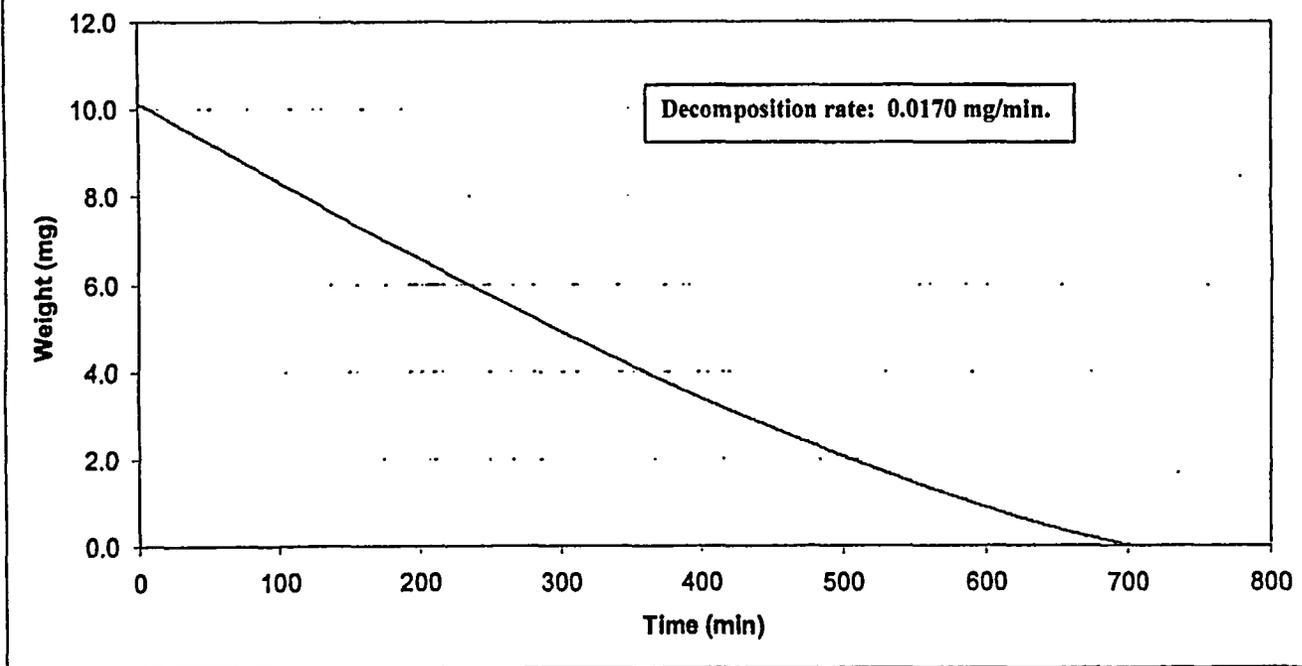
- Equilibrate at 30.0°C
- Ramp at 30.0°C/min. to 150.0°C
- Isothermal at 150°C for 720 min.

Observations: The sample was completely consumed after about 700 minutes (~11½ hrs.). There was a slight reaction rate flattening (roll over) near the end of the run. The 30°C/min. heat-up to 150°C was chosen to minimize sample loss ramping to the holding temperature, yet allow the sample to dry out before it reached that point.

7/1/05
3-15-05

S. L. S.

NH₄Cl Isothermal TGA Run at 150°C for 12 hrs.



SSS

1/13/05

1/14/05

TA Instruments TGA-DSC Work Sheet

Date: 1/13/2005

Sample I.D.: $(\text{NH}_4)_2\text{SO}_4$ 5°C/min. 30°C to 500°C

Sample Weight: 10.052 mg

Operator: Dan Day

Comment: Test Run 1 011305 $(\text{NH}_4)_2\text{SO}_4$ from 30°C to 500°C

File Name: YMP.008

Method: $(\text{NH}_4)_2\text{SO}_4$ 5°C/min. to 500°C

- Equilibrate at 30.0°C
- Ramp at 5.0°C/min. to 500.0°C

Observations: A slower heat-up ramping rate was used for this test because the $(\text{NH}_4)_2\text{SO}_4$ is more refractory than NH_4Cl . It was thought that a slower ramping rate would better pinpoint the onset of sulfate salt decomposition. The sample completely decomposed by ~380°C, and the test was operator terminated at 400°C. There were faintly detectable stain patterns where the final (second) decomposition product had pooled up on the pan bottom.

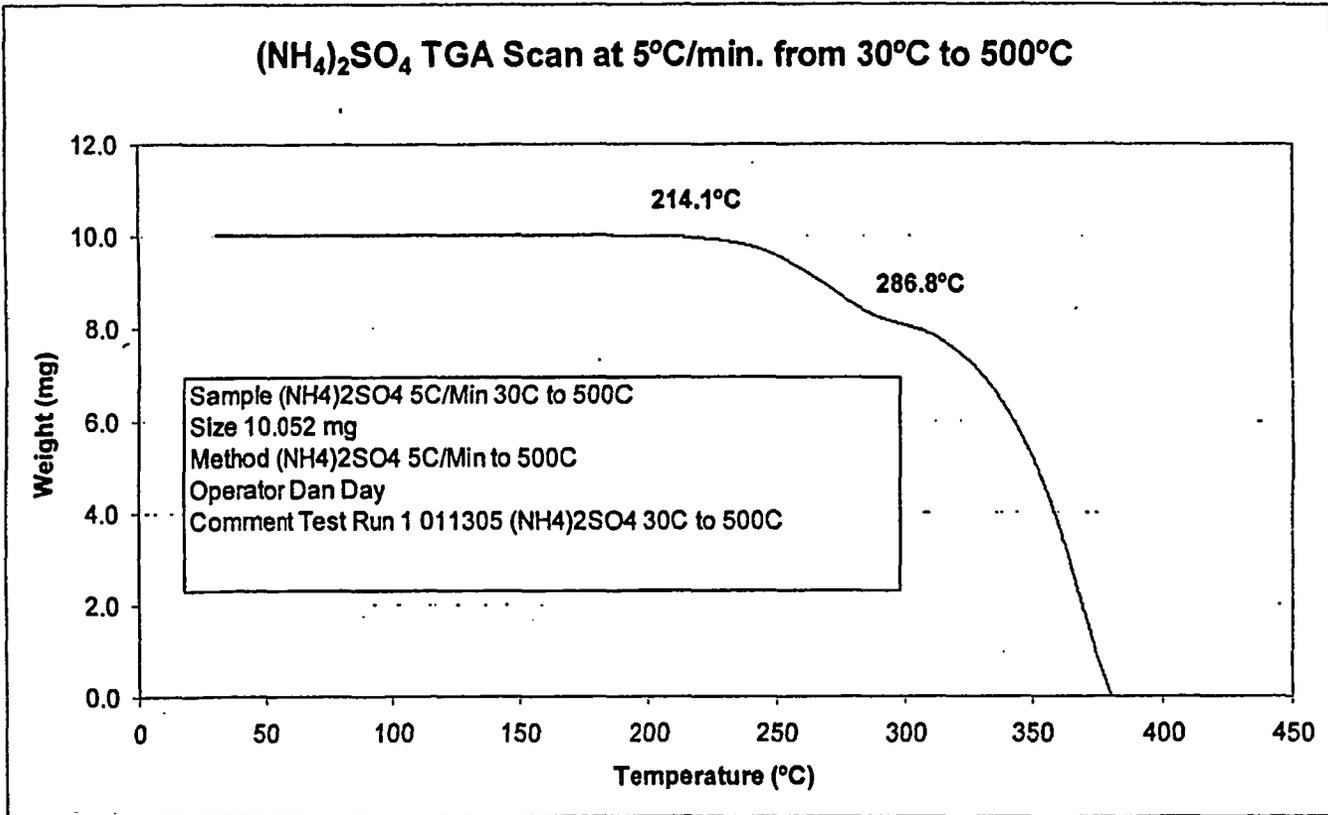
A validation of the TGA balance was conducted to ensure that it was working properly. This data is in SN-LLNL-SCI-487-V2 Supplement V1
SAD 3/10/05

SAD

010
1/10/05

//

(NH₄)₂SO₄ TGA Scan at 5°C/min. from 30°C to 500°C



DRR

1/14/05

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1/14/05

TA Instruments TGA-DSC Work Sheet

Date: 1/13/2005

Sample I.D.: $(\text{NH}_4)_2\text{SO}_4$ Iso at 250°C

Sample Weight: 10.189 mg

Operator: Dan Day

Comment: Test Run 2 011305 $(\text{NH}_4)_2\text{SO}_4$ Iso at 250°C for 2 hrs.

File Name: YMP.009

Method: TGA Iso at 250°C

- Equilibrate at 30.0°C
- Ramp at 200.0°C/min. to 250.0°C
- Isothermal for 120 min.

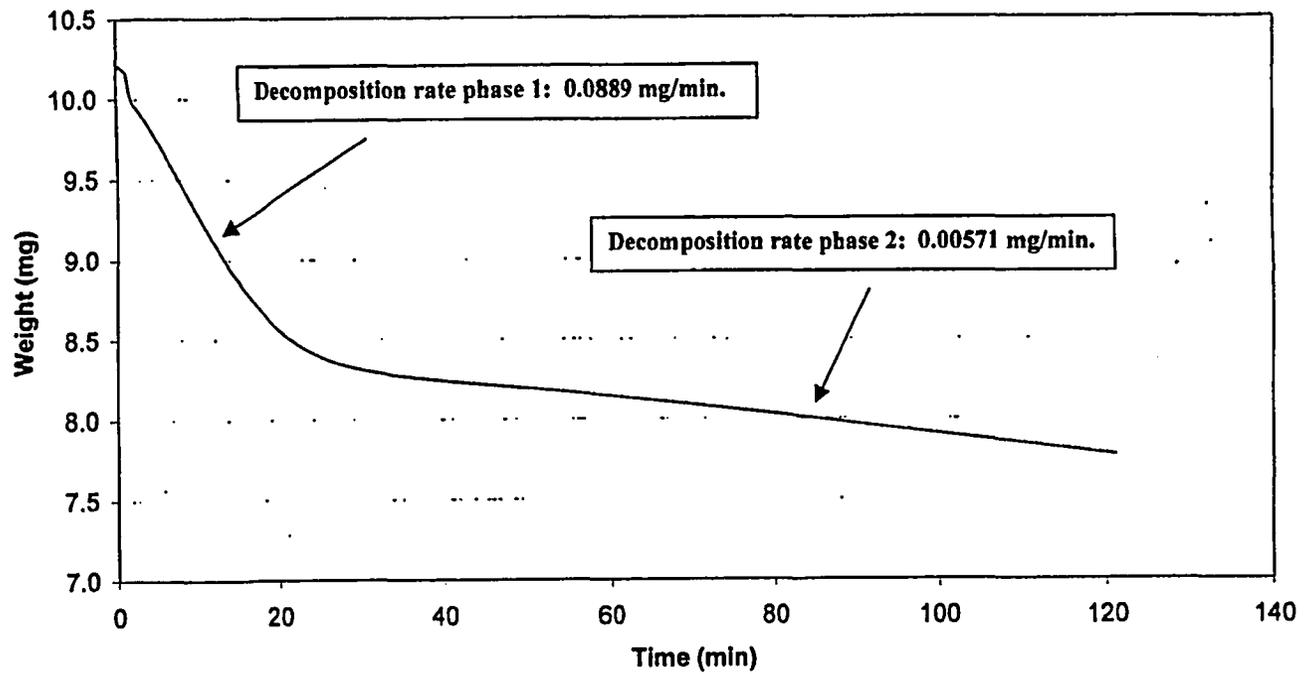
Final Sample Weight: 7.772 mg

Observations: The weight versus time plot had a knee about 20 minutes into the test that transitioned to a shallower slope (slower decomposition rate). The sample had a ~24% weight loss after 2 hours. At the projected decomposition rate the sample would likely have taken several days or more to fully decompose.

PhD *3-15-05*

Sal

$(\text{NH}_4)_2\text{SO}_4$ Isothermal TGA Run at 250°C for 2 hrs.



SRP

1/14/05

1/14/05

TA Instruments TGA-DSC Work Sheet

Date: 1/13/2005

Sample I.D.: $(\text{NH}_4)_2\text{SO}_4$ Iso at 200°C

Sample Weight: 10.211 mg

Operator: Dan Day

Comment: Test Run 3 011305 $(\text{NH}_4)_2\text{SO}_4$ Iso at 200°C for 24 hrs.

File Name: YMP.010

Method: TGA Iso at 200°C

- Equilibrate at 30.0°C
- Ramp at 200.0°C/min. to 200.0°C
- Isothermal for 1440 min.

Sample weight at 200°C set point: 10.184 mg

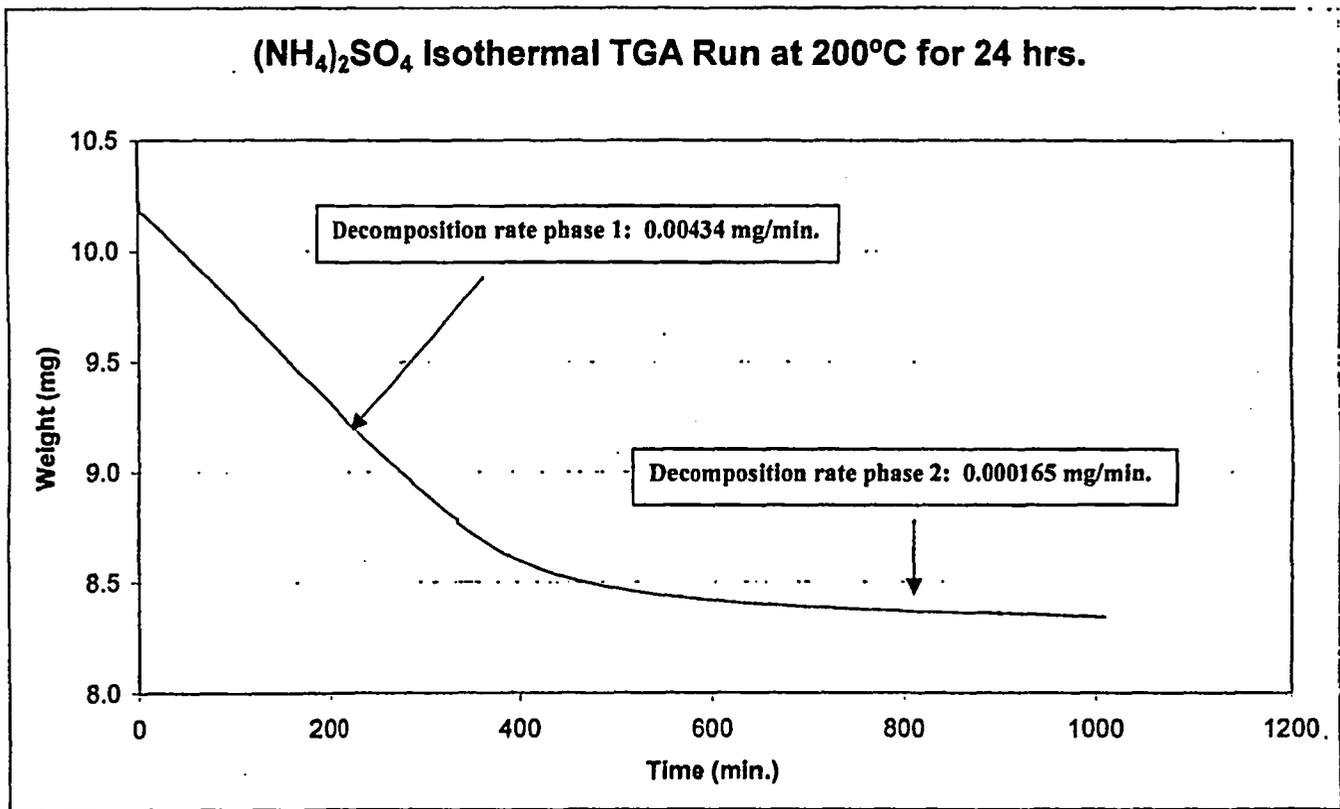
Final Sample Weight: 8.343 mg

Observations: The specimen has a linear weight loss versus time trajectory for the initial ~360 minutes (6 hrs.) and then has a knee transition to a slower and essentially flat weight loss versus time path (decomposition rate). The test was terminated after slightly over 1000 minutes (16 hrs.), leaving a pooled residue in the sample pan. Higher temperature runs are planned to study the secondary phase decomposition. The 200°C/min. ramp rate overshoot the 200°C set point to ~214°C, then dropped to ~198°C before stabilizing at 200°C. The sample lost ~18% its original weight by test end.

[Handwritten signature] 3-15-05

[Handwritten initials]

(NH₄)₂SO₄ Isothermal TGA Run at 200°C for 24 hrs.



S.P.P.

1/14/05

1/15/05 RDA 1/15/05

TA Instruments TGA-DSC Work Sheet

Date: 1/14/2005**Sample I.D.:** $(\text{NH}_4)_2\text{SO}_4$ Iso at 150°C**Sample Weight:** 10.546 mg**Operator:** Dan Day**Comment:** Test Run 1 011405 $(\text{NH}_4)_2\text{SO}_4$ Iso at 150°C for 12 hrs.**File Name:** YMP.011**Method:** TGA Iso at 150°C

- Equilibrate at 30.0°C
- Ramp at 30.0°C/min. to 150.0°C
- Isothermal for 720 min.

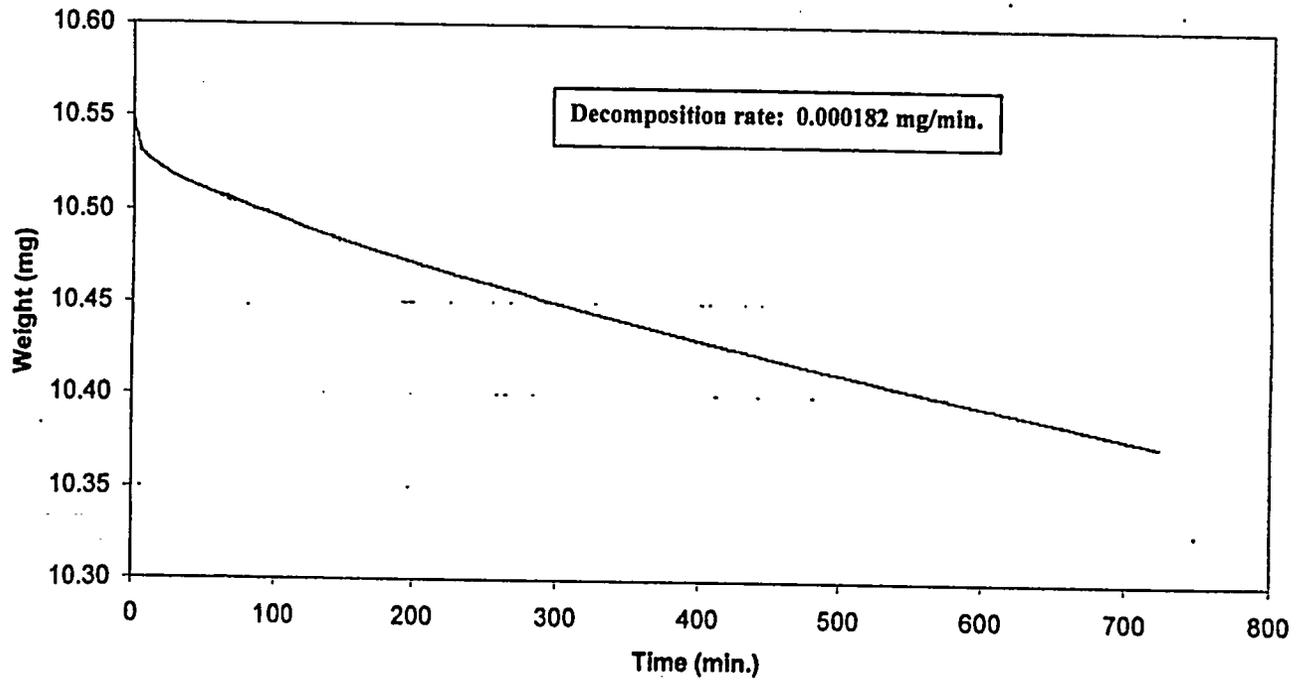
Sample weight at 150°C set point: 10.531 mg**Final Sample Weight:** 10.374 mg

Observations: After the 720 min. (12 hr.) test period the sample had a ~1.6% weight loss. The residue was saved. The latter was individual "as received" $(\text{NH}_4)_2\text{SO}_4$ crystals; no melting was noted. The decomposition (weight loss vs. time curve) was quasi-linear throughout most of the test. This reagent will be run at 175°C to get a higher material loss rate.

gloj *3-15-05*

SDR

$(\text{NH}_4)_2\text{SO}_4$ Isothermal TGA Run at 150°C for 12 hrs.



8/11/05

1/15/05

1/16/05

TA Instruments TGA-DSC Work Sheet

Date: 1/15/2005

Sample I.D.: $(\text{NH}_4)_2\text{SO}_4$ Iso at 175°C

Sample Weight: 10.289 mg

Operator: Dan Day

Comment: Test Run 1 011505 $(\text{NH}_4)_2\text{SO}_4$ Iso at 175°C for 12 hrs.

File Name: YMP.012

Method: TGA Iso at 175°C

- Equilibrate at 30.0°C
- Ramp at 200.0°C/min. to 175.0°C
- Isothermal for 720 min.

Sample weight at 150°C set point: 10.271 mg

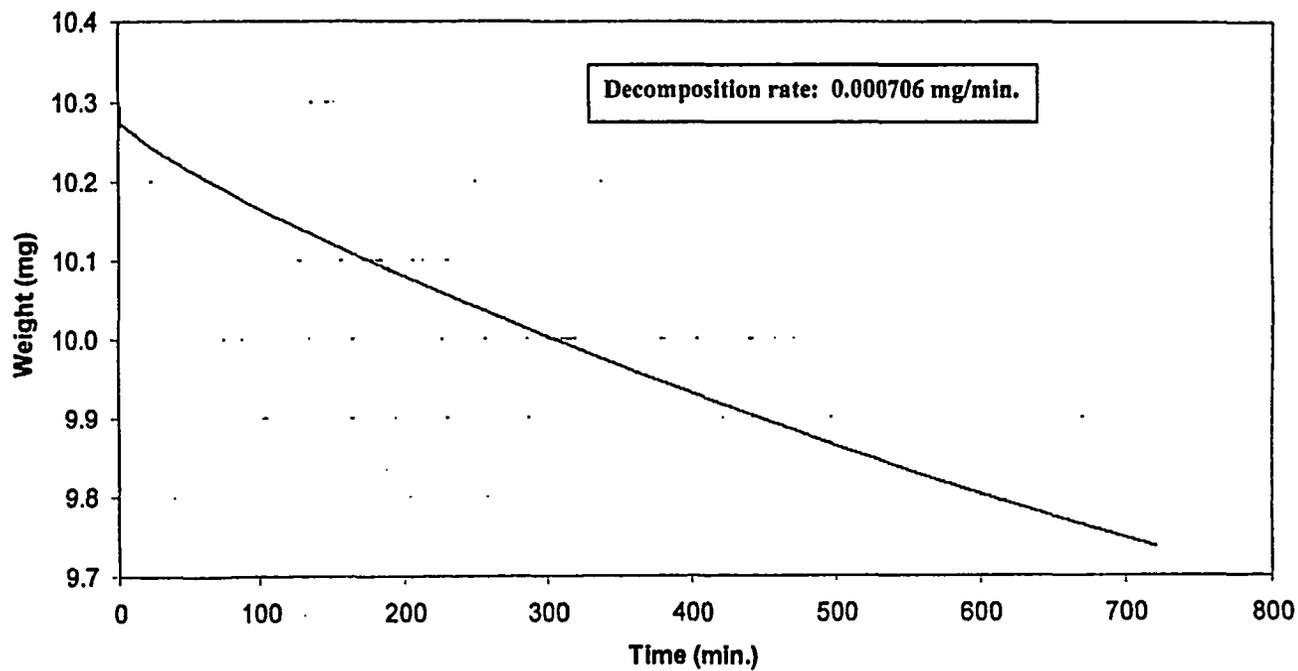
Final Sample Weight: 9.737 mg

Observations: The sample residue is individual reagent crystals, like were seen after the 150°C test. The residue is ~95% the original amount. The decomposition (weight loss vs. time) plot is slightly nonlinear and the same form as the 150°C isothermal test specimen. Ramp up rate increased to 200.0°C/min. to minimize sample loss during the transition to the set point.

ghyf stop 3-15-05

S.L.R.

$(\text{NH}_4)_2\text{SO}_4$ Isothermal TGA Run at 175°C for 12 hrs.



800

1/16/05

1/17/05

TA Instruments TGA-DSC Work Sheet

Date: 1/16/2005

Sample I.D.: $(\text{NH}_4)_2\text{SO}_4$ Iso at 300°C

Sample Weight: 10.269 mg

Operator: Dan Day

Comment: Test Run 1 011605 $(\text{NH}_4)_2\text{SO}_4$ Iso at 300°C for 12 hrs.

File Name: YMP.013

Method: TGA Iso at 300°C

- Equilibrate at 30.0°C
- Ramp at 200.0°C/min. to 300.0°C
- Isothermal for 720 min.

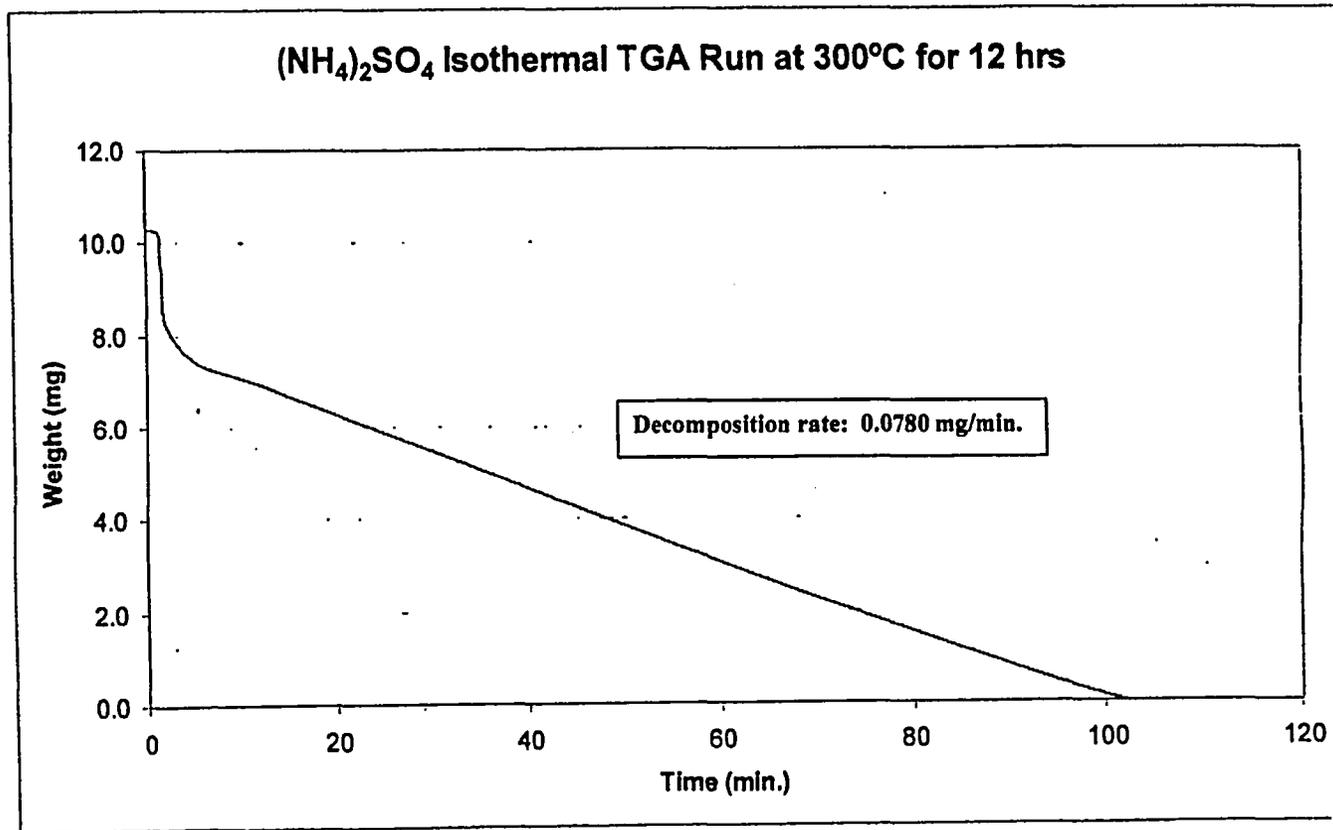
Sample weight at 300°C set point: 8.222 mg

Observations: There was a very rapid weight loss (~20%) during the initial 1.5 minute ramp up to the 300°C set point (isothermal holding temperature). The entire sample was consumed in 102 minutes. The initial sudden weight loss during the ramp up period was followed by a period of linear weight loss vs. time until the sample had been consumed.

g h j k l m n o p q r s t u v w x y z
3/5-05

g h j k l

$(\text{NH}_4)_2\text{SO}_4$ Isothermal TGA Run at 300°C for 12 hrs



S.D.P.

1/17/05

1/18/05

TA Instruments TGA-DSC Work Sheet

Date: 1/17/2005

Sample I.D.: $(\text{NH}_4)_2\text{SO}_4$ Iso at 325°C

Sample Weight: 10.070 mg

Operator: Dan Day

Comment: Test Run 1 011705 $(\text{NH}_4)_2\text{SO}_4$ Iso at 325°C for 90 min.

File Name: YMP.014

Method: TGA Iso at 325°C

- Equilibrate at 30.0°C
- Ramp at 200.0°C/min. to 325.0°C
- Isothermal for 90 min.

Sample weight at 325°C set point: 8.541 mg

Observations: The sample was completely consumed after 43 minutes. The sample lost over 20% weight in the first 4 minutes of the ramp up and isothermal hold at 325°C. There was a slight loss rate slowdown after the initial rapid weight drop, then the sample established a slightly steeper-sloped linear weight loss vs. time decomposition path until the sample had been consumed.

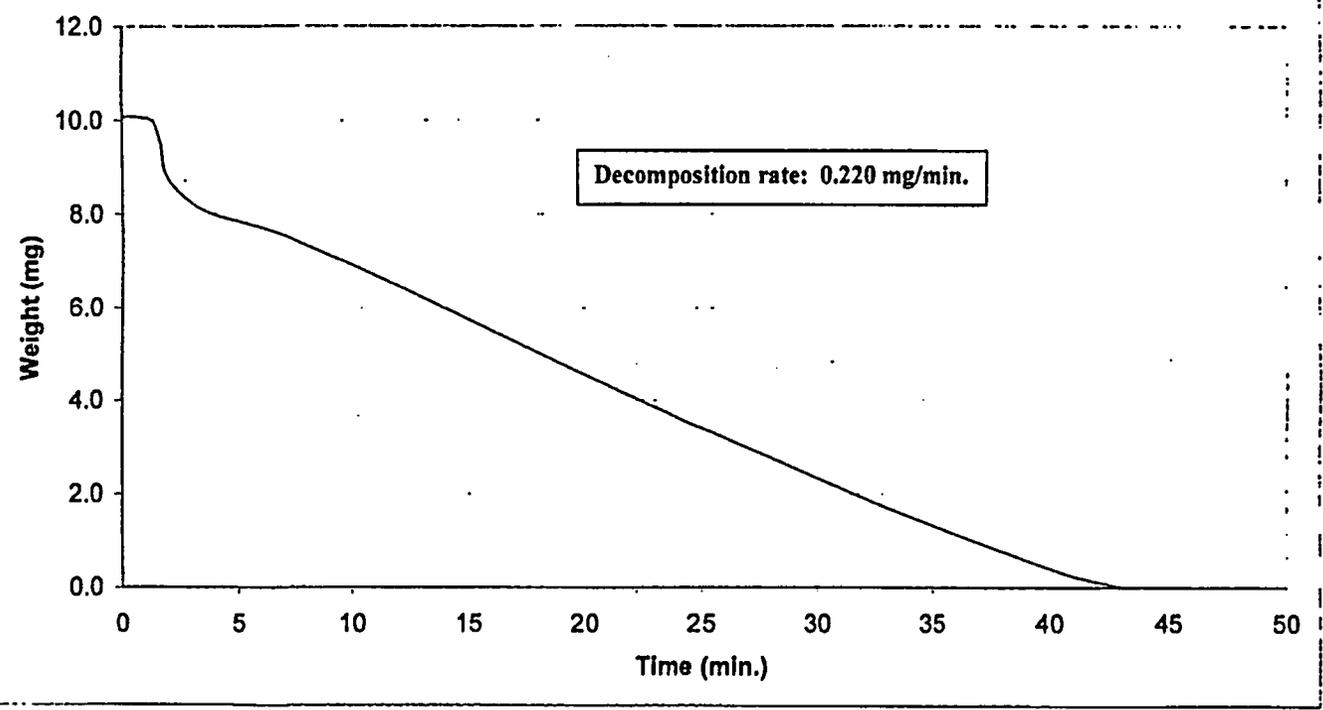
A validation of the TGA balance was conducted to ensure that it was working properly. This data is in SN-LLNL-SCI-487-V2 Supplement V1

SAD 3/10/05

SAD

//

(NH₄)₂SO₄ Isothermal TGA Run at 325°C for 90 min.



RRR

1/18/05

//

1/19/05

TA Instruments TGA-DSC Work Sheet

Date: 1/18/2005

Sample I.D.: $(\text{NH}_4)_2\text{SO}_4$ Iso at 350°C

Sample Weight: 10.284 mg

Operator: Dan Day

Comment: Test Run 1 011805 $(\text{NH}_4)_2\text{SO}_4$ Iso at 350°C for 30 min.

File Name: YMP.015

Method: TGA Iso at 350°C

- Equilibrate at 30.0°C
- Ramp at 200.0°C/min. to 350.0°C
- Isothermal for 30 min.

Sample weight at 350°C set point: 7.677 mg

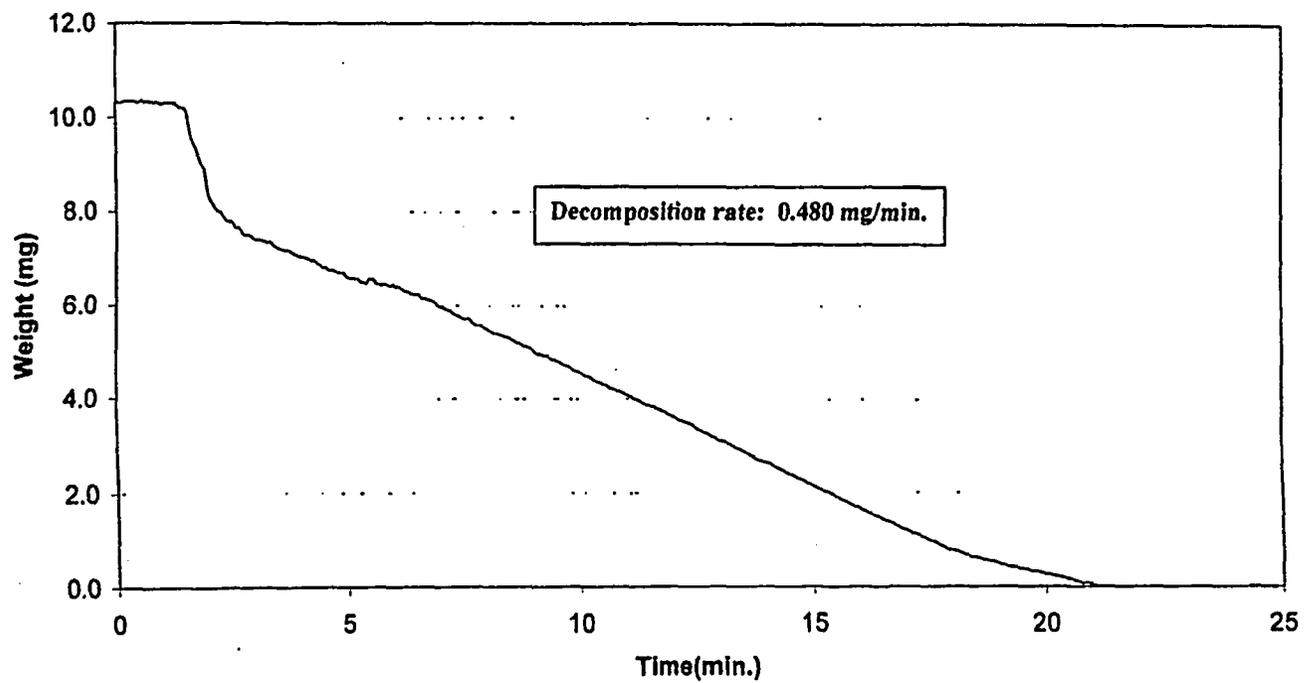
Observations: The sample was completely consumed after 21 minutes. It suffered a ~25% weight loss during ramp up to the 350°C holding temperature. As with the 325°C $(\text{NH}_4)_2\text{SO}_4$ isothermal run, the loss rate slowed down after the initial rapid weight loss during ramp up, then increased slightly and assumed a linear weight loss until the salt completely decomposed. There was a slight rate decrease (curve flattening or roll over) toward the very end of the experiment.

// A validation of the TGA balance was conducted to ensure that it was working properly. This data seen SN-LLNL-SCF-487-V2 Supplement V1

SJA 3/10/05

SJA

$(\text{NH}_4)_2\text{SO}_4$ Isothermal TGA Run at 350°C for 30 min.



SSP

1/19/05

1/20/05

TA Instruments TGA-DSC Work Sheet

Date: 1/19/2005

Sample I.D.: $(\text{NH}_4)_2\text{SO}_4$ Iso at 100°C

Sample Weight: 10.244 mg

Operator: Dan Day

Comment: Test Run 1 011905 $(\text{NH}_4)_2\text{SO}_4$ Iso at 100°C for 24 hrs.

File Name: YMP.016

Method: TGA Iso at 100°C and 30C/min.

- Equilibrate at 30.0°C
- Ramp at 30.0°C/min. to 100.0°C
- Isothermal for 1440 min.

Final Sample Weight: 10.189 mg

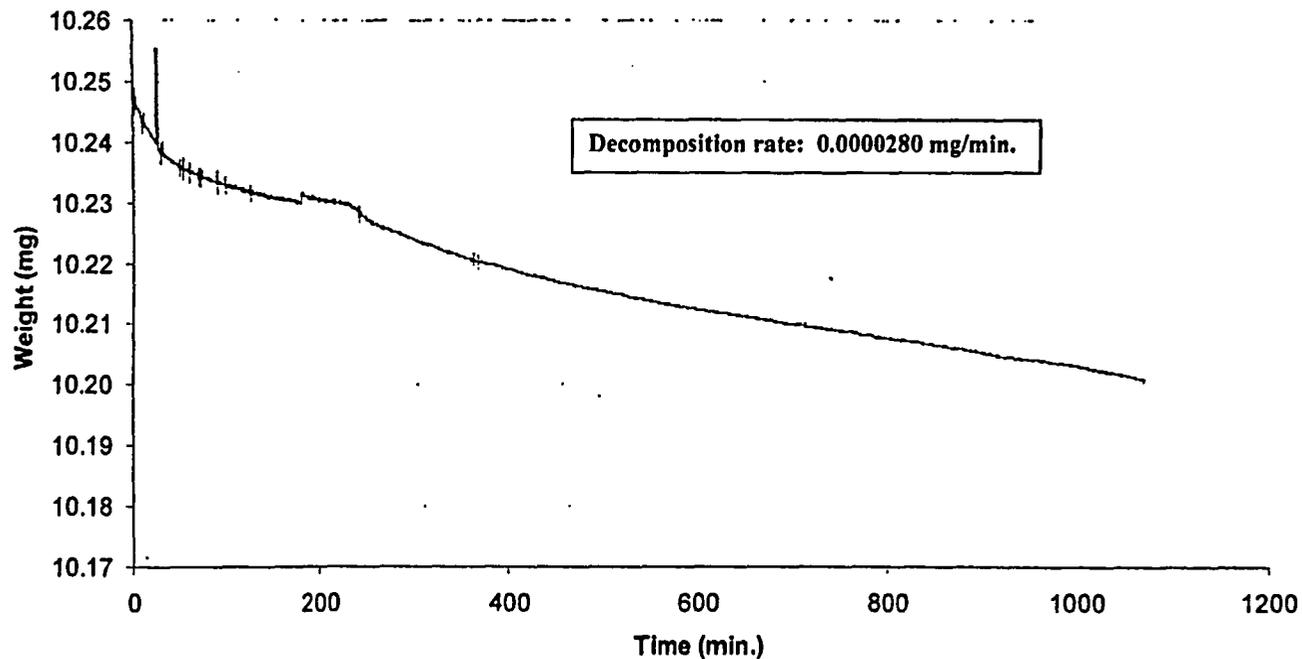
Observations: There was some noise at the beginning of this test, but it quieted down with time. The weight loss initially flattened out exponentially, then increased slightly and eventually assumed a quasi-linear weight loss vs. time relationship. The 30.0°C/min. ramp rate was selected to reach the 100°C hold temperature quickly, yet ensure that any free moisture was driven from the sample surface. The total weight loss was only ~0.5%. Sample residue was individual "as received" $(\text{NH}_4)_2\text{SO}_4$ crystals.

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$(\text{NH}_4)_2\text{SO}_4$ Isothermal TGA Run at 100°C for 24 hrs.



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1/21/05

TA Instruments TGA-DSC Work Sheet

Date: 1/20/2005

Sample I.D.: NH₄Cl Iso at 125°C

Sample Weight: 10.249 mg

Operator: Dan Day

Comment: Test Run 1 012005 NH₄Cl Iso at 125°C for 24 hrs.

File Name: YMP.017

Method: TGA Iso at 125°C

- Equilibrate at 30.0°C
- Ramp at 30.0°C/min. to 125.0°C
- Isothermal for 1440 min.

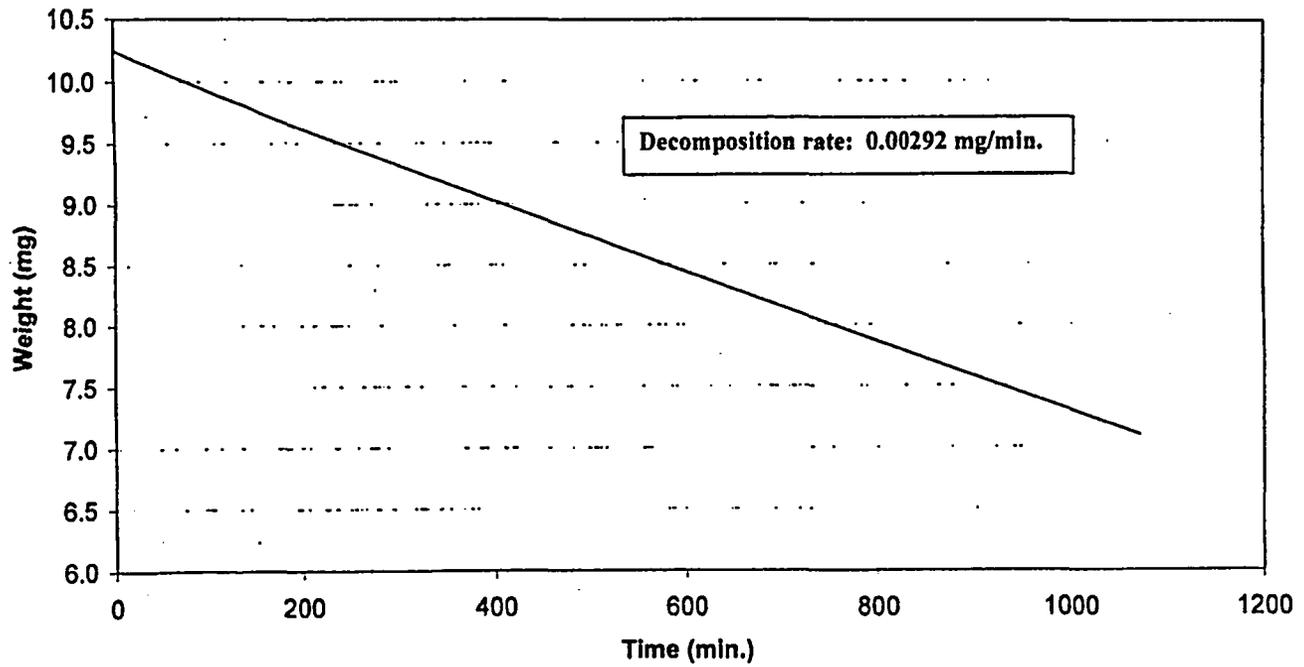
Final Sample Weight: 7.088 mg

Observations: The sample was originally meant to be (NH₄)₂SO₄, but the investigator accidentally took reagent from an NH₄Cl bottle. The error was not discovered until after the test was in progress. The test ran satisfactorily and was aborted after about 1075 minutes. The total weight loss was ~31%.

9/2/05
3-15-05

P.10.10

NH₄Cl Isothermal TGA Run at 125°C for 24 hrs.



8/2/05

1/21/05

1/22/05

TA Instruments TGA-DSC Work Sheet

Date: 1/21/2005

Sample I.D.: $(\text{NH}_4)_2\text{SO}_4$ Iso at 125°C

Sample Weight: 10.213 mg

Operator: Dan Day

Comment: Test Run 1 012105 $(\text{NH}_4)_2\text{SO}_4$ Iso at 125°C for 24 hrs.

File Name: YMP.018

Method: TGA Iso at 125°C

- Equilibrate at 30.0°C
- Ramp at 30.0°C/min. to 125.0°C
- Isothermal for 1440 min.

Final Sample Weight: 10.146 mg

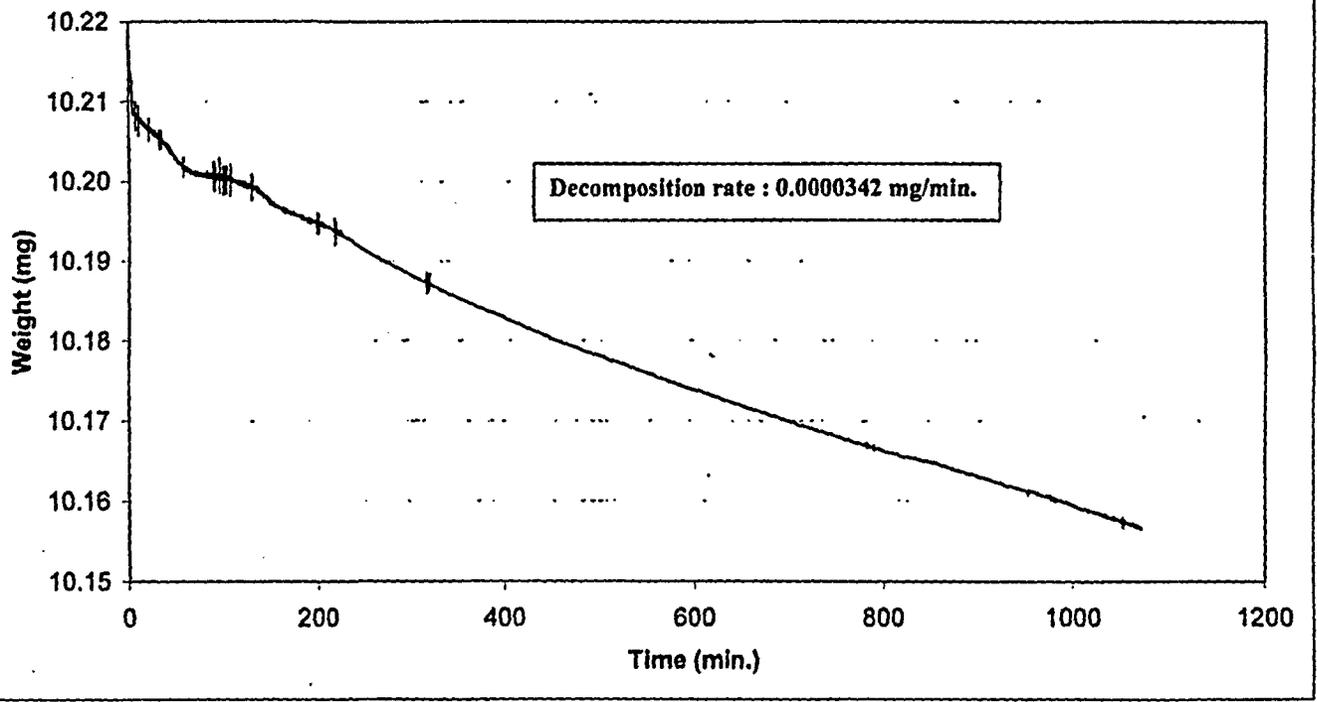
Observations: The sample gave a linear weight loss vs. time decomposition curve, but at test end, only lost 0.7% weight. The initial part of the test curve was somewhat noisy, but eventually became subdued. The residue was individual "as received" $(\text{NH}_4)_2\text{SO}_4$ crystals.

A validation of the TGA balance was conducted to ensure that it was working properly. This data will be in SN-LLNL-SCI-487-V2 Supplement V1.

DJD 3/10/05

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SJD

(NH₄)₂SO₄ Isothermal TGA Run at 125°C for 24 hrs.

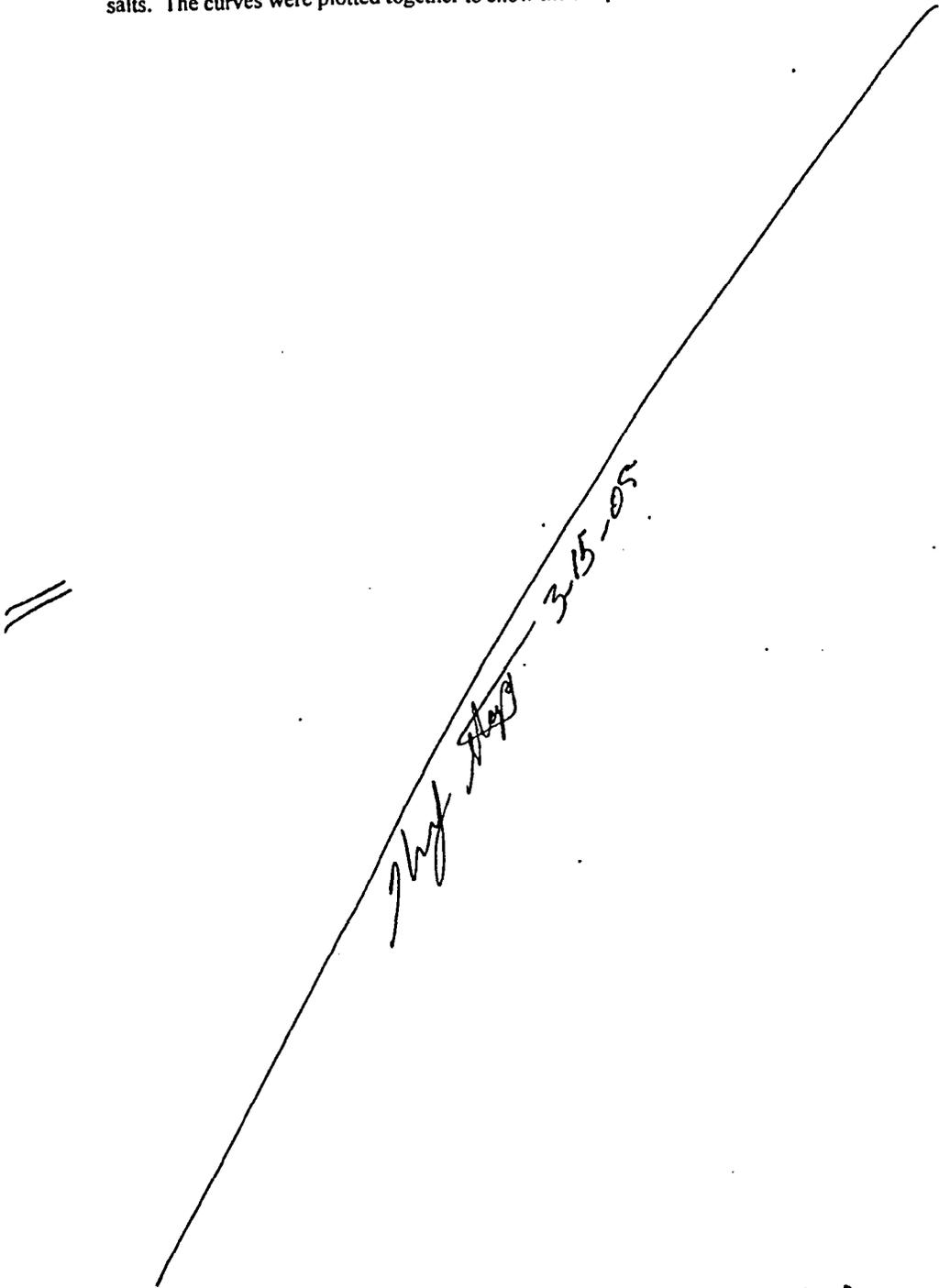


SA

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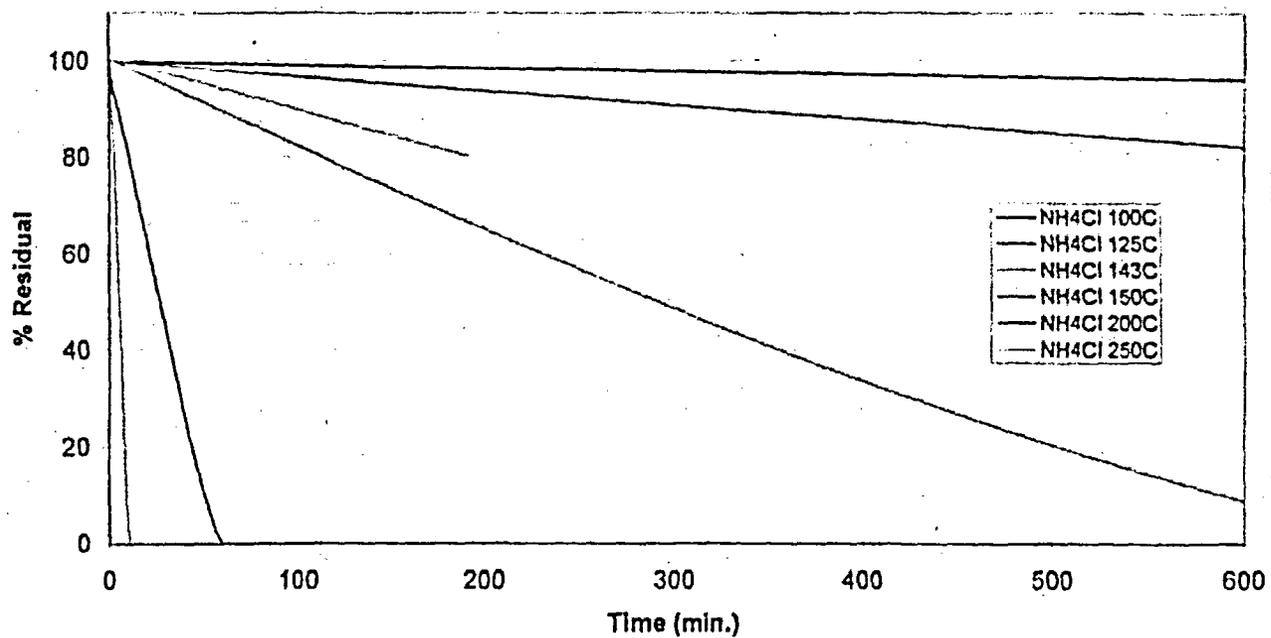
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The following four figures are graphs of the isothermal TGA runs for the NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$ salts. The curves were plotted together to show the temperature relationships.



S.S.S.

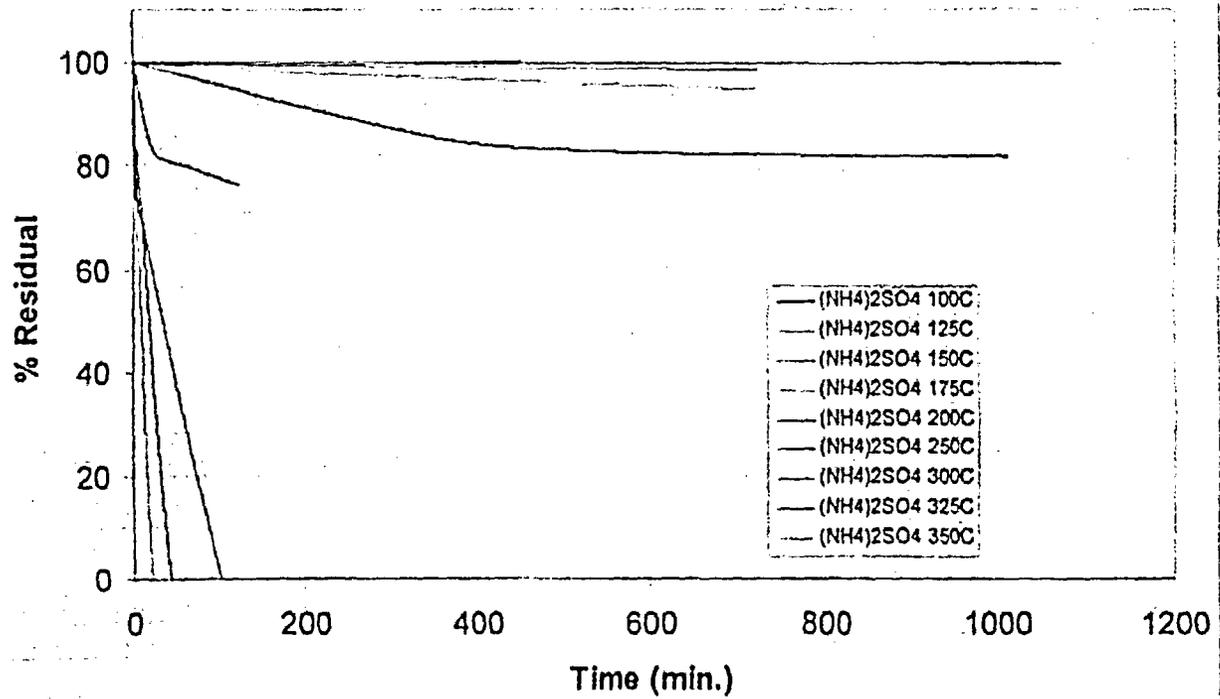
NH_4Cl Isothermal TGA Decomposition Curves 100°C to 250°C



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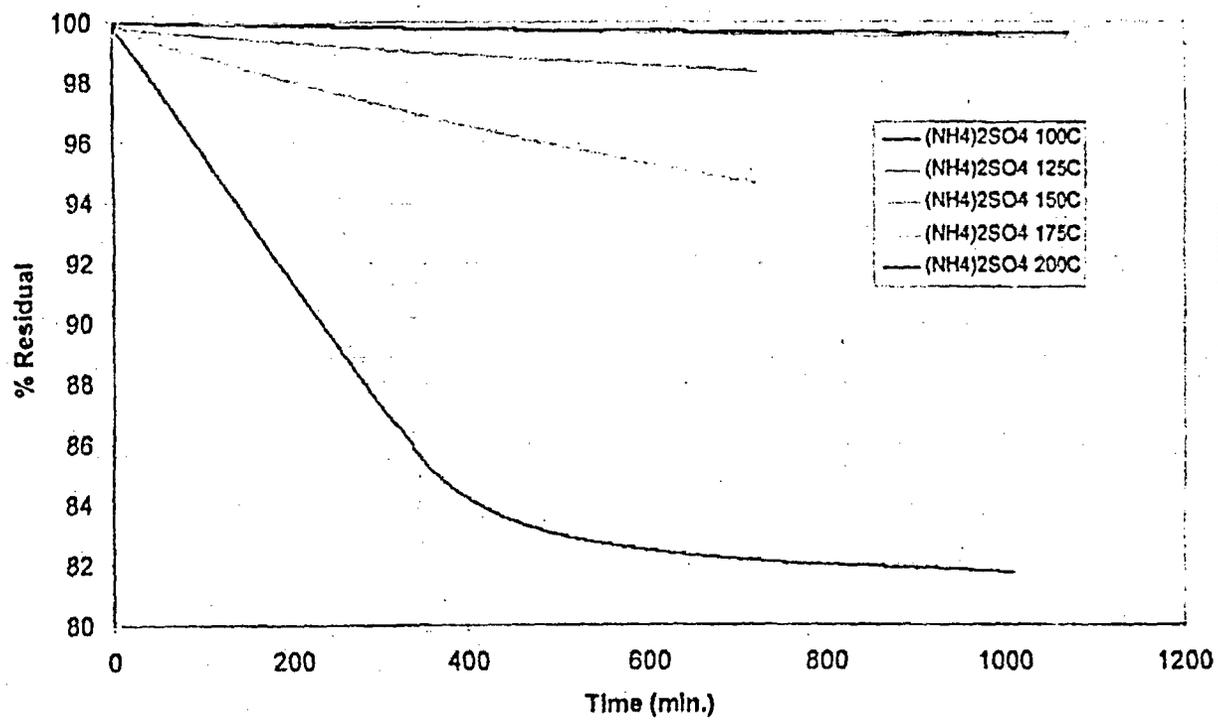
$(\text{NH}_4)_2\text{SO}_4$ Isothermal TGA Decomposition Curves 100°C to 350°C



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$(\text{NH}_4)_2\text{SO}_4$ Isothermal TGA Decomposition Curves 100°C to 200°C

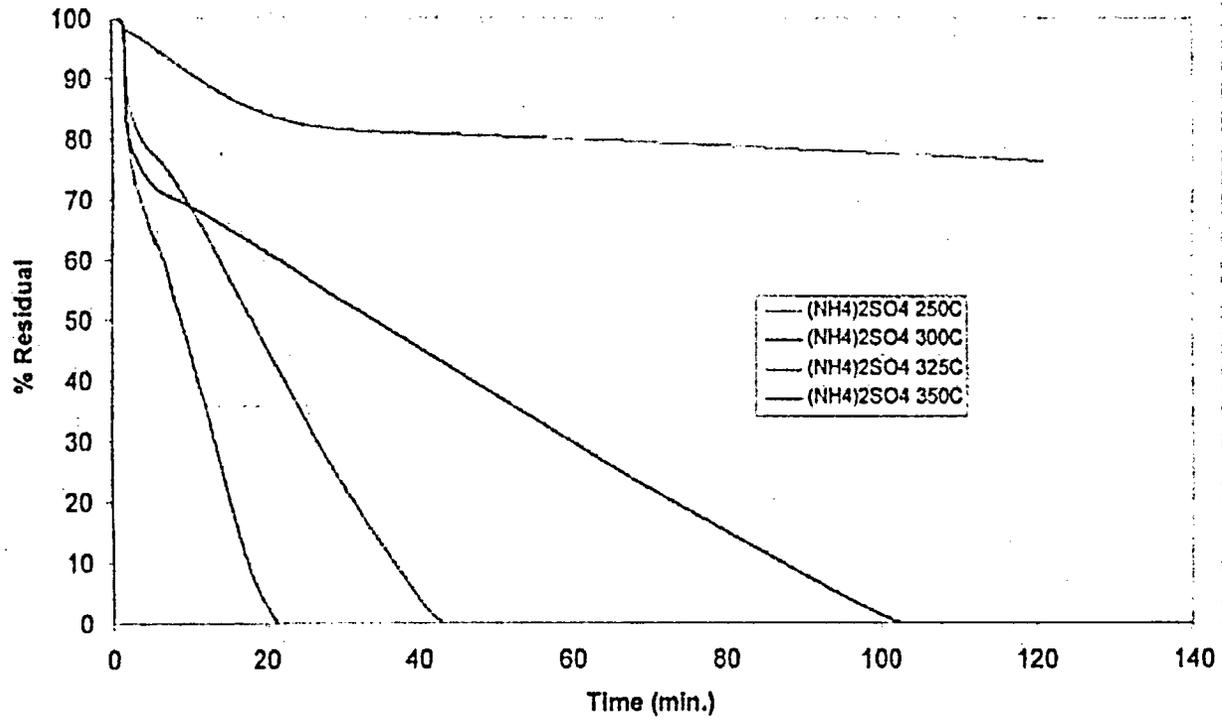


27
24
22

1/22/05

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$(\text{NH}_4)_2\text{SO}_4$ Isothermal TGA Decomposition Curves 250°C to 350°C



DRP

1/22/05

1/28/05

TGA Balance Closing Calibration

Balance Set: Heusser-Neueigh Class S Metric weight set
Test #2115-04, Device No. 993465,
Recalibration date December 15, 2005.

Procedure:

- Step 1: Press F11 Data Analysis
 - Press F1: Get new program.
 - Select C drive
 - Select TGA Cal
 - Press F1: Start program
- Step 2: Select F1 weight calibration.
- Step 3: manually tare the balance
 - Load an empty platinum sample pan on the balance and close the furnace chamber.
 - Remove the tare pan cover and expose the tare pan containing counter weights
 - Adjusting tare weight to 0.0±10 mg.
 - Add weight to the counterbalance pan if the monitor indicates the sample pan is outside of the acceptable range positive.
 - Remove weight if the monitor indicates the sample pan is outside the acceptable range negative.
 - Two 2 mg TA Instruments tare weights were added to bring the empty platinum sample pan into an acceptable empty (tare) weight range.
 - F8 weight was accepted.
 - Replace the tare pan cover.
- Step 5: Zero 100 mg range.
 - When the uncalibrated weight stabilizes, press F8 accept weight
- Step 6: Zero 1000 mg range.
 - When the uncalibrated weight stabilizes, press F8 accept weight
- Step 7: Calibrate the 100 mg range.
 - Unload the sample pan onto the loading stage and place the Heusser-Neueigh Class S 100 mg calibrated weight on the pan.
 - Reload the furnace.
 - Enter the exact standard weight (999.9890 mg)
 - Press F8: accept weight when the weight stabilizes.
 - Unload the furnace.

Weight	Calibration Value	TGA Measured Weight
100 mg	99.9938 mg	96.791 mg (25.5°C)

- Step 8: Calibrate the 1000 mg range
 - Unload the sample pan onto the loading stage and place the Heusser-Neueigh Class S 100 mg calibrated weight on the pan.
 - Reload the furnace.
 - Enter the exact standard weight (999.9890 mg)
 - Press F8: accept weight when the weight stabilizes.
 - Unload the furnace.

Weight	Calibration Value	TGA Measured Weight
1000 mg	999.9890 mg	993.246 mg (25.4°C)

The empty sample pan was tared and the four Heusser-Neueigh standards were weighed:

Weight	Calibration Value	TGA Measured Weight
20* mg	19.99513 mg	19.864 mg (25.1°C)
50 mg	50.00195 mg	49.559 mg (25.2°C)
100 mg	99.99938 mg	99.139 mg (25.1°C)
200* mg	200.00596 mg	199.983 mg (25.1°C)

The same set of weights was used to confirm the previous calibration:

Weight	Calibration Value	TGA Measured Weight
20* mg	19.99513 mg	20.012 mg (25.0°C)
50 mg	50.00195 mg	49.688 mg (25.0°C)
100 mg	99.99938 mg	99.723 mg (24.9°C)
200* mg	200.00596 mg	200.627 mg (25.0°C)

SNN
 A validation of the TGA balance was conducted to ensure it was working properly. This data is in *SNN* SN-LLNL-SCI-487-V2 Supplement V1. *SNN* 3/10/05
 See page 81 for TGA: Closing Temperature Calibration *SNN* 3/4/05

1/29/05

DSC (Differential Scanning Calorimetry) Tests

The investigators felt that differential scanning calorimetry (DSC) runs would be useful to supplement the TGA thermal scans and isothermal tests. The DSC tests were run on a sister unit, the DSC 2910 Differential Scanning Calorimeter, serial No. M2910-493, DOE #8541671. The unit measures the heat flow difference between the test piece and a sample blank (an empty crimped aluminum sample pan). The differential is plotted in a temperature vs. heat flow (mW, milliwatts) graph. Positive and negative peaks on the graphs correspond to exothermic and endothermic reactions, respectively. These in turn may correspond to melting, crystallization, decomposition, oxidation, or other reactions that occur as the specimen heats up.

DSC Calibrations

The DCS calibration procedure was taken from TA Instrument's **DSC 2910 Differential Scanning Calorimeter Operator's Manual**, PN 911004.001 Rev E, February, 1993 and **DSC Calibration Data Analysis Program, Version 5.0**, PN 996507.001 Rev G, January, 1993.

Baseline Slope Calibration

A baseline slope calibration and a temperature calibration were performed on the TA Instruments DSC 2910 unit. The former is run on an empty test cell and compares the responses of the two small sensing platforms on which the test sample and the empty (blank) sample are mounted during regular test runs. The software plots the calibration run as if it was an actual test and corrects for any difference between the two sensors. The parameters used in the baseline slope calibrations were:

Sample: Empty Cell

Sample weight: 0.0000 mg

Operator: Kirk Staggs

Comment: Baseline slope calibration with air flow setting at 50.

File Name: BLCAL.003

Method: Baseline Cal to 500C

- o Equilibrate at 30.0°C
- o Ramp at 10.0°C/min. to 500.0°C
- o Isothermal for 1.0 min.

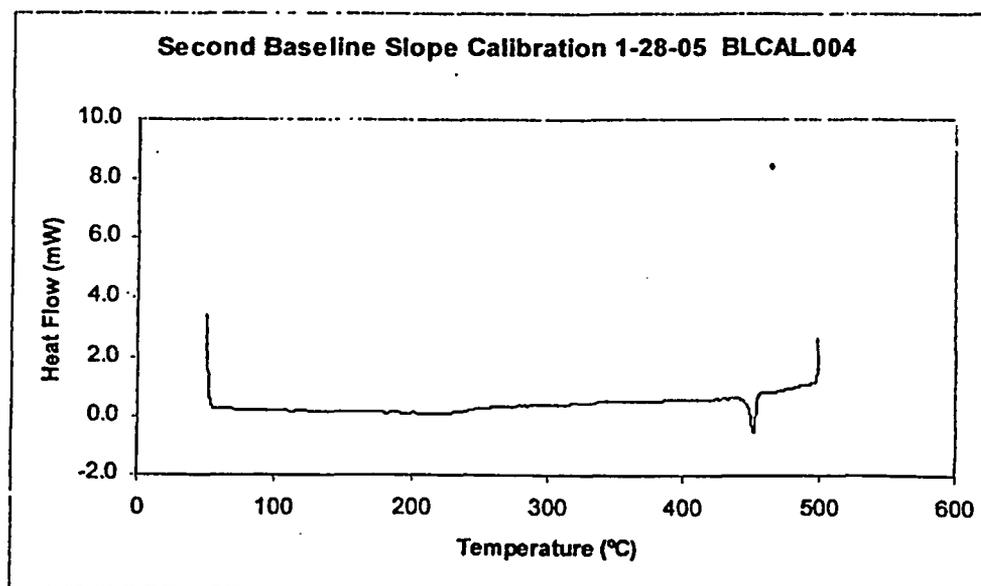
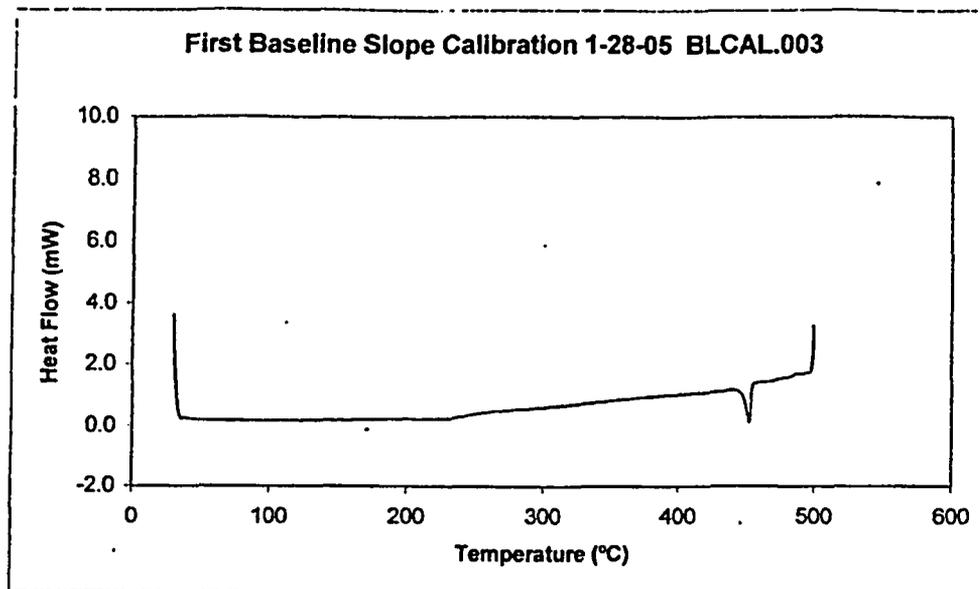
The first run (BLCAL.003) gave a small isotherm close to 450°C and it was decided to rerun the baseline calibration.

The second run, designated file BLCAL.004, was run under the same parameters and gave identical results. The baseline slope calibration curves are depicted below:

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Module parameters from the empty cell baseline slope calibration tests:

Cell constant: 1.0000
Baseline slope: 0.0778
Onset slope: 0.00 mW/°C
Offset: 49563.30

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Temperature Calibration

The DSC temperature calibration uses an Indium metal reference standard:

Certified Reference Material**LGC2601****Indium****Batch E1****Sample 0274****0.5 gram****Manufacturer:****Laboratory of the Government Chemist****Queens Road, Taddington, Middlesex, TW11 OLY, U.K.**

Melting point = 156.61°C (CRC Handbook of Chemistry & Physics, 56th Edition, 1975)

Note: The indium used for the DSC temperature calibration is an industrial standard.

The two-step method used for DSC temperature calibration with the indium standard, as outlined in the TA Instruments DSC 2910 manual, is:

- o Equilibrate at 125.0°C
- o Ramp 10.0°C/min. to 175.0°C.

The procedure used for the DSC calibration is based on these ASTM documents:

ASTM E 967-92 Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers.

ASTM E 968-83 Heat Flow Calibration of Differential Scanning Calorimeters.

A 10.02 mg Indium metal sample was placed in a ¼-inch diameter aluminum pan and a lid was crimped to seal it. The sample was mounted on the forward pedestal of the DSC test cell (the rear pedestal is for the blank (empty) pan), and the test chamber was closed. The following procedure was used:

Indium metal DSC Temperature Calibration**Sample: Indium Cal 012805****Sample Weight: 10.0200 mg****Cell Constant: 1.0183****Operator: Kirk Staggs****Comment: Indium calibration run.****File Name: CAL-IND.001****Method: Indium Cal**

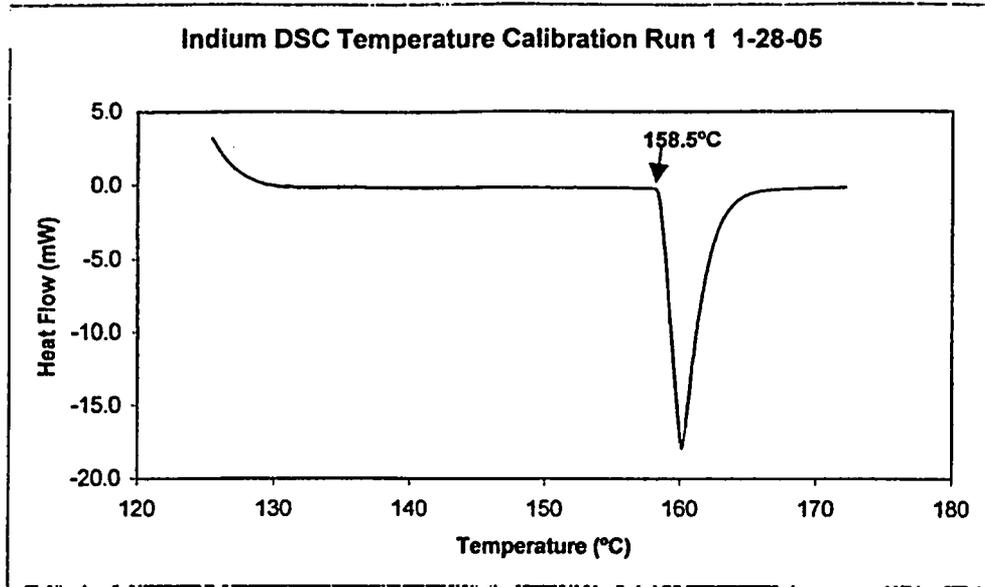
- o Equilibrate at 125.0°C
- o Ramp 10.0°C/min. to 175.0°C

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The temperature vs. heat flow curve is plotted below:



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A second calibration run was made to confirm the results of the initial Indium calibration.

Sample: Cal Check Indium 012805

Sample Weight: 10.0200 mg

Cell Constant: 1.0183

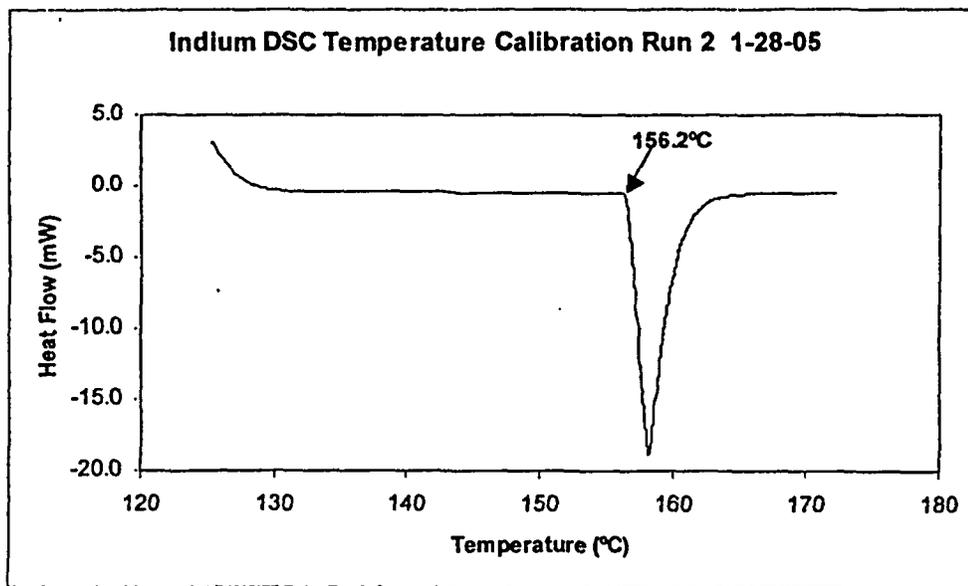
Operator: Kirk Staggs

Comment: Indium calibration check 012805

File Name: IND.001

Method: Indium Cal

- o Equilibrate at 125.0°C
- o Ramp 10.0°C/min. to 175.0°C



After calculating the baseline slope correction and determining the Indium temperature correction using the data file IND.001, the software calibration program calculated these module parameters:

Module Mode: DSC Calibration

Cell Constant: 1.0183

Baseline slope: 0.1305

Onset slope: -11.42 mW/°C

Offset: 49591.10

SRD

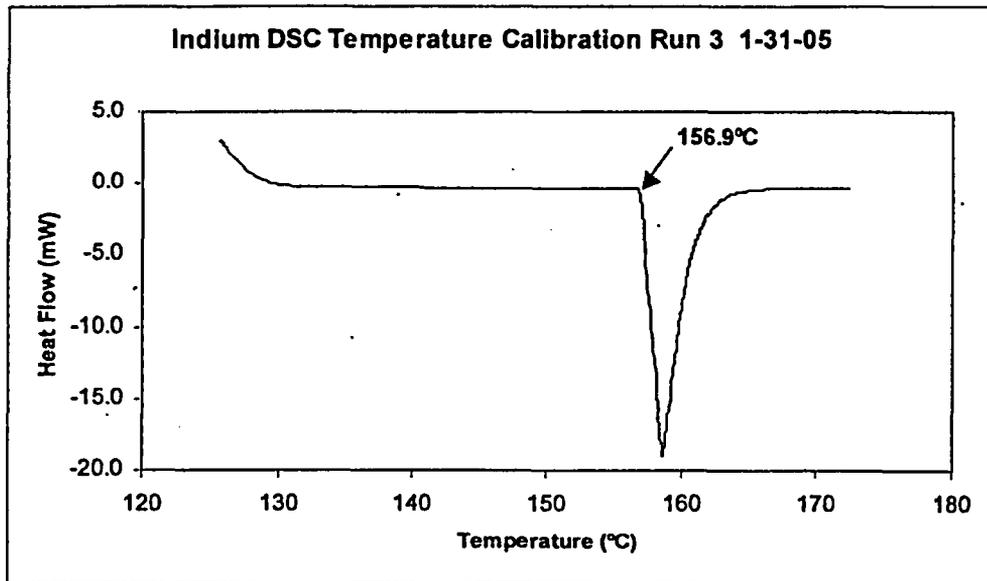
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On January 31, 2005, the investigators decided to run the Indium temperature calibration test once again, because the 1-28-05 calibrations had been conducted under higher air purge rates. The 1-31-05 Indium temperature calibration, and all subsequent DSC test runs were conducted at a flowmeter setting of 50.

Sample: Cal Check Indium 013105
Sample Weight: 10.0200 mg
Cell Constant: 1.0183
Operator: Kirk Staggs
Comment: Indium calibration check 013105
File Name: IND.002
Method: Indium Cal

- o Equilibrate at 125.0°C
- o Ramp 10.0°C/min. to 175.0°C



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DSC Testing of NH_4Cl . The sample was prepared in the conventional manner, encapsulating about 10 mg of the test reagent in a sealed aluminum pan, using Mallinkrodt ammonium chloride (Product No. 3384, Lot No. 3384 A41612). The sample pan was mounted on the specimen sensor platform and the following test parameters were applied:

Sample: NH_4Cl DSC 75°C to 220°C 020905

Sample Weight: 10.3100 mg

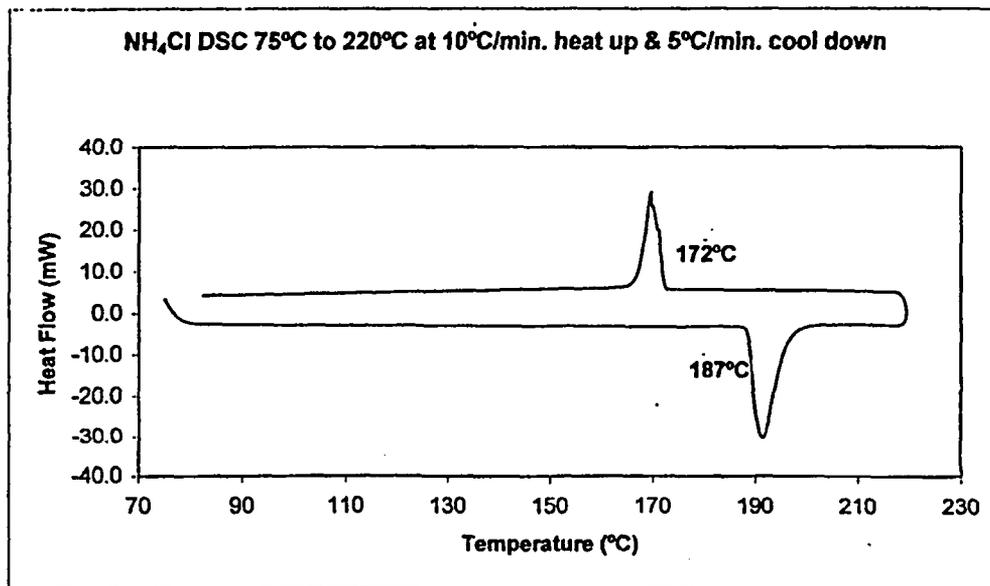
Operator: Dan Day

Comment: NH_4Cl DSC scan from 75°C to 220°C at 10°C/min. 020905.

File Name: YMP.019

Method: DSC 75°C to 220°C at 10°C/min.

- o Equilibrate at 75°C
- o Isothermal for 30.0 min.
- o Ramp 10.0°C/min. to 220.0°C
- o Ramp 5.0°C/min. to 30.0°C



The onset of melting on heat up was at 187°C. On cool down crystallization at the slower ramping rate occurred at 172°C.

SSB

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A second DSC test run covered the temperature range 75°C to 350°C, to quantify the onset of sample decomposition and to capture the form of the temperature vs. heat flow curve at the selected ramping rates. The following parameters were used:

Sample: NH_4Cl DSC 75°C to 350°C 020905

Sample Weight: 10.3100 mg

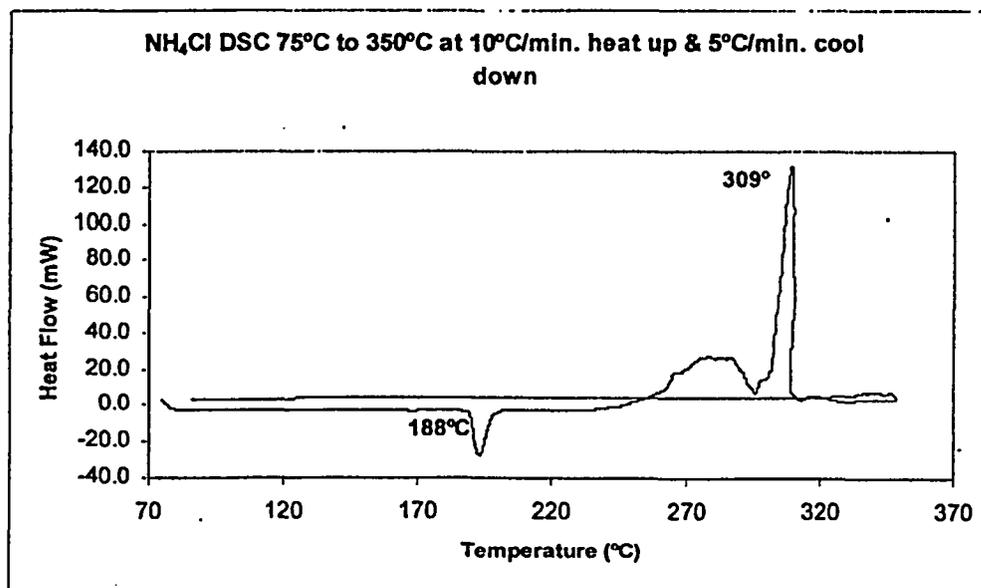
Operator: Dan Day

Comment: NH_4Cl DSC Run 2 from 75°C to 350°C at 10°C/min. 020905.

File Name: YMP.020

Method: DSC 75°C to 350°C at 10°C/min.

- o Equilibrate at 75°C
- o Isothermal for 30.0 min.
- o Ramp 10.0°C/min. to 350.0°C
- o Ramp 5.0°C/min. to 30.0°C



The melting endotherm initiated again at 187 to 188°C, but a large exotherm began at about 235°C and subsided at about 296°C. A sharper and more pronounced exotherm began a few degrees higher and peaked at ~309°C, then suddenly dropped off to background level. The exothermic activity probably represents buildup of decomposition products, likely hydrochloric acid (HCl) and ammonia (NH_3). The former apparently reacted with the aluminum test pan, and the solid residue vented out the seam, depositing a white powder around the pan. The latter is thought to have been aluminum chloride (AlCl_3). The pan showed evidence of corrosive attack, lending credence to the proposed reaction mechanism. No cool down crystallization peak was observed, implying the ammonium chloride completely decomposed during heat up.

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DSC Testing of $(\text{NH}_4)_2\text{SO}_4$. The aluminum test capsule was prepared the same as for the NH_4Cl . The DSC test cell was cleaned with a Q-Tip dipped in deionized water to remove the NH_4Cl reaction residue off the cell bottom. About 10 mg of $(\text{NH}_4)_2\text{SO}_4$ was weighed out and sealed in the aluminum pan, which was mounted on the test cell pedestal adjacent to the empty reference sample. The reagent was J.T. Baker granular ammonium sulfate, Product No. 0729-01, Lot No. Y10334. The test parameters were:

Sample: $(\text{NH}_4)_2\text{SO}_4$ DSC 105°C to 300°C 020905

Sample Weight: 10.1700 mg

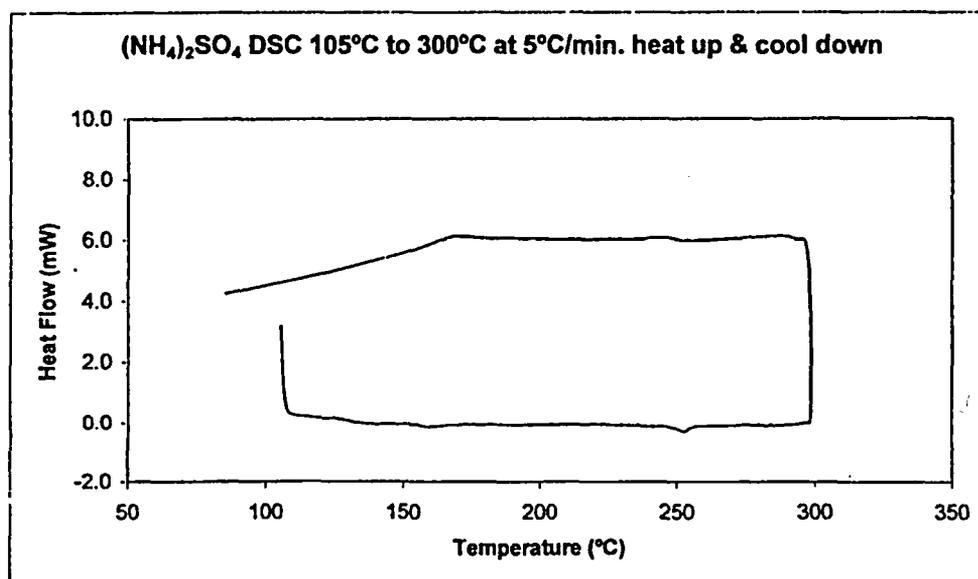
Operator: Dan Day

Comment: $(\text{NH}_4)_2\text{SO}_4$ DSC Run 1 from 105°C to 300°C at 5°C/min. 020905.

File Name: YMP.021

Method: DSC 105°C to 300°C at 5°C/min.

- o Equilibrate at 105.0°C
- o Isothermal for 30.0 min.
- o Ramp 5.0°C/min. to 300.0°C
- o Ramp 5.0°C/min. to 30.0°C



The temperature vs. heat flow curve was singularly uneventful, except for an unexplainable tiny endothermic peak at ~253°C. To better characterize the ammonium sulfate's thermal behavior, it was decided to make another test run and expand the temperature range to 450°C.

SIB

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The new test parameters were:

Sample: $(\text{NH}_4)_2\text{SO}_4$ DSC 105°C to 450°C 020905

Sample Weight: 10.1700 mg

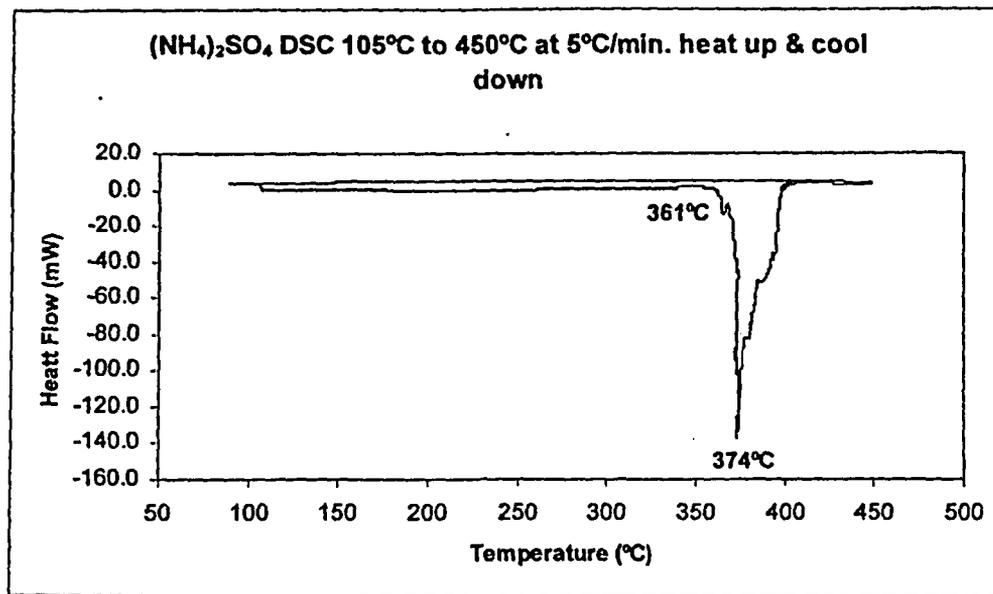
Operator: Dan Day

Comment: $(\text{NH}_4)_2\text{SO}_4$ DSC Run 2 from 105°C to 450°C at 5°C/min. 020905.

File Name: YMP.022

Method: DSC 105°C to 450°C at 5°C/min.

- o Equilibrate at 105.0°C
- o Isothermal for 30.0 min.
- o Ramp 5.0°C/min. to 450.0°C
- o Ramp 5.0°C/min. to 30.0°C



The run was uneventful until -361°C , when an endothermic reaction began. The endotherm peaked at 374°C and then diminished more slowly, with some secondary peak broadening that may represent slightly different reaction mechanisms. The event ended at about 402°C . Post-test DSC cell examination revealed that the lid to the test chamber was tightly sealed, perhaps by volatile condensates. It took some effort to remove it. The chamber bottom had a very faint tan-colored residue surrounding the test sample pedestal, there was some coating on the reference pan, and the sample pan had been displaced off the pedestal, apparently by the force of the escaping volatiles. The pan interior had a corroded appearance. The reaction products may have contained sulfuric acid (H_2SO_4) vapors. More experimentation is required to characterize this phenomenon. However, if volatilization and reaction with the aluminum pan had occurred, an exotherm rather than an endotherm would be expected.

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A closing temperature calibration on the DSC 2910 unit (Serial No. M2910-493, DOE No. 8541671) was conducted on March 3, 2005. The test parameters are as follows:

Sample: Indium Temperature Calibration 030305

Size: 10.0200 mg

Operator: Dan Day

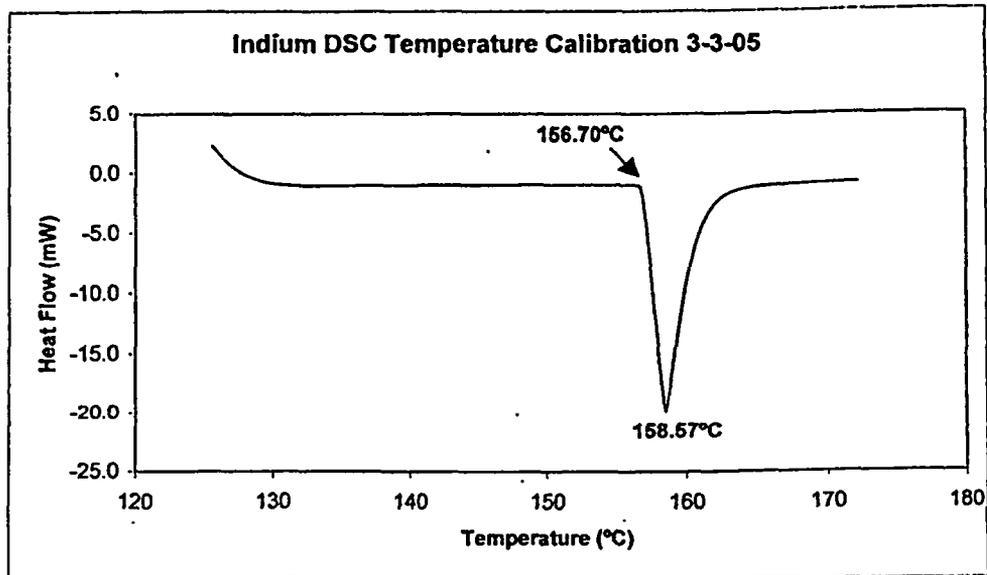
Comment: Indium close out DSC temperature calibration 030305

File Name: YMP.023

Method: Indium Cal

- Equilibrate at 125.0°C
- Ramp at 10.0°C/min. to 175.0°C

The test curve is displayed below. The onset melting point temperature from this run (156.7°C) is sufficiently close to the value reported in the CRC Handbook of Chemistry & Physics, 56th Edition, 1975 (156.61°C) to be considered acceptable for this one-point calibration. Based on these results, and the initial indium temperature calibrations, the investigators decided the intervening DSC test curves did not require a temperature correction.



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Hi Res TGA 2950 Temperature Closing Calibration

The Curie point temperature calibration method was used to do a closing temperature calibration on the TGA 2950 unit on January 28, 2005. This method was described in the Introduction under Equipment Calibration, and follows TA Instruments "Traceable Temperature Calibration for TGA and SDT Using Curie Point Temperature Standards", PN 952386.001 Rev. F, Issued September, 2001. The method uses the Curie point demagnetization properties of a nickel wire to accurately determine the Curie temperature and compare it with the accepted value of 354°C, taken from ASTM E 1582-93: Standard Practice for Calibration of Temperature Scale for Thermogravimetry, page 3, table 2: Curie Point standards.

Procedure:

Standard: nickel reference wire
P/N 952385.901
Lot No.: CRM2-8058

Pretest empty platinum sample pan weight = 0.073 mg at 23.6°C

Sample pan was tared through the Signal Control, Auto Zero option.

A small ~1/4-inch piece of 40 mil nickel wire was placed in the sample pan.

The static weight of the nickel wire and pan in the closed furnace chamber before testing was 37.352 mg at 23.7°C.

A 1-inch square by 7-inch long bar magnet was placed under the sealed furnace chamber containing the nickel wire and its magnetic attraction for the nickel increased the sample weight to 38.923 mg at 23.8°C (A weight gain of ~4.0%). The magnet should be positioned beneath the furnace to provide a nominal 2% weight gain.

The Curie temperature test calls for a thermal scan from room temperature (here chosen as 30°C) to 100°C above the standard's Curie temperature (in this case to 450°C) at a ramping rate of 10.0°C/min. The test parameters are listed below:

Sample: TGA 2950 Temp Calibration 012805

Sample Weight: 38.9200 mg

Operator: Dan Day

Comment: Nickel reference wire P/N 952385.901 Lot No. CRM2-8058

File Name: CAL.003

Method: TGA Temp Cal 500

- o Equilibrate at 30.0°C
- o Ramp at 10.0°C/min. to 500.0°C

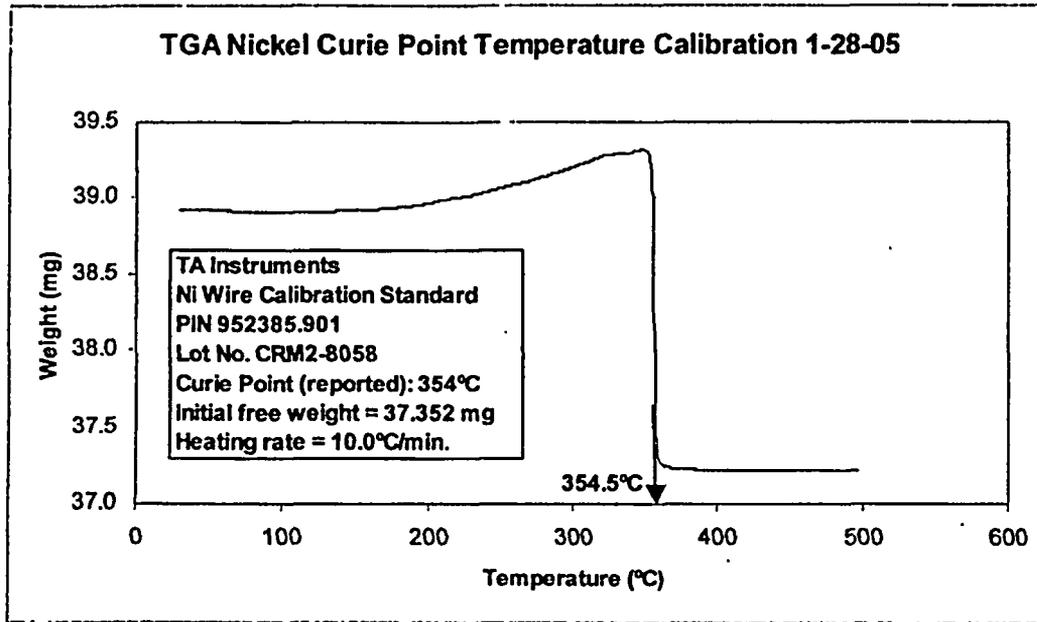
SD

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Sample weight at 30°C equilibration temperature = 38.916 mg

Post Curie Temperature demagnetized wire weight = 37.218 mg

The TA Instruments Thermal Analyst 2100 System Software, Serial No. 81078, Version 8.9D (2.2B) ONSET graphics utility was used to determine a Curie point temperature of 354.5°C from the temperature vs. weight curve for this test. The curve is plotted below:



This value is sufficiently close to the 354°C nickel Curie point temperature reported in ASTM E 1582-93 to declare the Hi-Res TGA 2950 unit's thermocouple readings accurate enough for the purposes of this study.

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Raw or original file name to Excel Spread sheet listed salt tests cross reference

Original File Name	NB page #	Test as listed in Excel Spread Sheet
YMP.001	28 & 29	NH ₄ Cl Ramp 30-300°C
YMP.002	30 & 31	NH ₄ Cl Isothermal at 143°C
YMP.003	32 & 33	NH ₄ Cl Isothermal at 100°C
YMP.004	34 & 35	NH ₄ Cl Isothermal at 250°C
YMP.005	36 & 37	NH ₄ Cl Isothermal at 200°C
YMP.006	38 & 39	(NH ₄) ₂ SO ₄ Ramp 30-350°C
YMP.007	40 & 41	NH ₄ Cl Isothermal at 150°C
YMP.008	42 & 43	(NH ₄) ₂ SO ₄ Ramp 30-500°C
YMP.009	44 & 45	(NH ₄) ₂ SO ₄ Isothermal at 250°C
YMP.010	46 & 47	(NH ₄) ₂ SO ₄ Isothermal at 200°C
YMP.011	48 & 49	(NH ₄) ₂ SO ₄ Isothermal at 150°C
YMP.012	50 & 51	(NH ₄) ₂ SO ₄ Isothermal at 175°C
YMP.013	52 & 53	(NH ₄) ₂ SO ₄ Isothermal at 300°C
YMP.014	54 & 55	(NH ₄) ₂ SO ₄ Isothermal at 325°C
YMP.015	56 & 57	(NH ₄) ₂ SO ₄ Isothermal at 350°C
YMP.016	58 & 59	(NH ₄) ₂ SO ₄ Isothermal at 100°C
YMP.017	60 & 61	NH ₄ Cl Isothermal at 125°C
YMP.018	62 & 63	(NH ₄) ₂ SO ₄ Isothermal at 125°C
YMP.019	76	NH ₄ Cl DSC 105°C to 300°C
YMP.020	77	NH ₄ Cl DSC 75°C to 350°C
YMP.021	78	(NH ₄) ₂ SO ₄ DSC 105°C to 300°C
YMP.022	79	(NH ₄) ₂ SO ₄ DSC 105°C to 450°C

The raw or original data files have been copied to a CD labeled "SN-LLNL-SCI-487-V2 CD-1" dated 03/11/2005. This CD also contains various Excel worksheets as follows:

(NH ₄) ₂ SO ₄ DSC Analysis.xls	DSC test runs of (NH ₄) ₂ SO ₄ salts, ramping temperature at fix rate
(NH ₄) ₂ SO ₄ TGA Analysis Linear Fits.xls	TGA isothermal runs of (NH ₄) ₂ SO ₄
DTN_LL050301723121_050.xls	Combined TGA isothermal runs of NH ₄ Cl & (NH ₄) ₂ SO ₄
NH ₄ Cl DSC Analysis.xls	DSC test runs of NH ₄ Cl salts, ramping temperature at fix rate
NH ₄ Cl TGA Analysis Linear Fits.xls	TGA isothermal runs of NH ₄ Cl
TGA Curie Point Temperature Calibrations.xls	Nickel Curie point temperature calibration files

SND

3/14/05

Each Converted excel file was compared to the original file for accuracy. This validation was made by comparing the screen image file on the TGA computer monitor to the plotted excel file(s).

Original File Name	Test as listed in Excel Spread Sheet	Acceptable
YMP.001	NH ₄ Cl Ramp 30-300°C	YES
YMP.002	NH ₄ Cl Isothermal at 143°C	YES
YMP.003	NH ₄ Cl Isothermal at 100°C	YES
YMP.004	NH ₄ Cl Isothermal at 250°C	YES
YMP.005	NH ₄ Cl Isothermal at 200°C	YES
YMP.006	(NH ₄) ₂ SO ₄ Ramp 30-350°C	YES
YMP.007	NH ₄ Cl Isothermal at 150°C	YES
YMP.008	(NH ₄) ₂ SO ₄ Ramp 30-500°C	YES
YMP.009	(NH ₄) ₂ SO ₄ Isothermal at 250°C	YES
YMP.010	(NH ₄) ₂ SO ₄ Isothermal at 200°C	YES
YMP.011	(NH ₄) ₂ SO ₄ Isothermal at 150°C	YES
YMP.012	(NH ₄) ₂ SO ₄ Isothermal at 175°C	YES
YMP.013	(NH ₄) ₂ SO ₄ Isothermal at 300°C	YES
YMP.014	(NH ₄) ₂ SO ₄ Isothermal at 325°C	YES
YMP.015	(NH ₄) ₂ SO ₄ Isothermal at 350°C	YES
YMP.016	(NH ₄) ₂ SO ₄ Isothermal at 100°C	YES
YMP.017	NH ₄ Cl Isothermal at 125°C	YES
YMP.018	(NH ₄) ₂ SO ₄ Isothermal at 125°C	YES
YMP.019	NH ₄ Cl DSC 105°C to 300°C	YES
YMP.020	NH ₄ Cl DSC 75°C to 350°C	YES
YMP.021	(NH ₄) ₂ SO ₄ DSC 105°C to 300°C	YES
YMP.022	(NH ₄) ₂ SO ₄ DSC 105°C to 450°C	YES
The following are calibration runs before and after testing		
CAL.001*	TEMP001 1-10-05	YES
CAL.003	CAL003 1-28-05	YES
BLCAL.003	BLCAL003 1-28-05	YES
BLCAL.004	BLCAL004 1-28-05	YES
CAL-IND.001	CALIN001 1-28-05	YES
IND.001	IND001 1-28-05	YES
IND.002	IND002 1-31-05	YES
YMP.023	IND003 3-3-05	YES

* This file was renamed TEMP001 when convert from the binary to ASCII file on the TGA computer and listed on CD labeled "SN-LLNL-SCI-487-V2 CD-1" as the Original Files TEMP001.

All converted files save to the CD were found to be accurate.

SBR

5-25-05

//

A new DTN LL050205223121.048 was created that included the temperature data from the files in DTN_LL050301723121.050 that are also listed below. A CD Labeled "SN-LLNL-SCI-487-V2 CD-2" contains the verified DTN file. The listed text from the raw files that were previously verified (see page 84 of this notebook) on the CD labeled "SN-LLNL-SCI-487-V2 CD-1" were used to verify this new DTN stored on disk CD-2.

Test Files include with DTN_LL050205223121.048	Raw File	Acceptable
NH ₄ Cl Isothermal at 143°C	YMP.002	Yes
NH ₄ Cl Isothermal at 100°C	YMP.003	Yes
NH ₄ Cl Isothermal at 250°C	YMP.004	Yes
NH ₄ Cl Isothermal at 200°C	YMP.005	Yes
NH ₄ Cl Isothermal at 150°C	YMP.007	Yes
NH ₄ Cl Isothermal at 125°C	YMP.017	Yes
(NH ₄) ₂ SO ₄ Isothermal at 250°C	YMP.009	Yes
(NH ₄) ₂ SO ₄ Isothermal at 200°C	YMP.010	Yes
(NH ₄) ₂ SO ₄ Isothermal at 150°C	YMP.011	Yes
(NH ₄) ₂ SO ₄ Isothermal at 175°C	YMP.012	Yes
(NH ₄) ₂ SO ₄ Isothermal at 300°C	YMP.013	Yes
(NH ₄) ₂ SO ₄ Isothermal at 325°C	YMP.014	Yes
(NH ₄) ₂ SO ₄ Isothermal at 350°C	YMP.015	Yes
(NH ₄) ₂ SO ₄ Isothermal at 100°C	YMP.016	Yes
(NH ₄) ₂ SO ₄ Isothermal at 125°C	YMP.018	Yes

The Excel file named LL050205223121.048.xls on the CD labeled "SN-LLNL-SCI-487-V2 CD-2" has been verified and found to be accurate.

This CD is included in the supplement to this notebook.

//

Phyllis King 5-25-05

12-22-05

Further clarifications on TGA calibration:

The TGA calibration software routine is provided by the manufacturer and initiates a series of instructions for the operator to perform as indicated on pages 22-24 of this notebook. The calibration of the TGA balance is a two-point calibration not considering defining the zero point of the balance. The two upper weight points were calibrated using 100mg and 1000mg from an YMP calibrated weight set as indicted on page 22 of this notebook. Calibration constants are generated by the program and stored in the TGA analyzer. The TGA analyzer displays the weight that is verified against the computer display. An additional YMP certified weight (20mg) was also used get a better determination of the accuracy of the TGA balance at the approximate specimen weight of 20mg. In addition, the balance was also checked between zero and 200mg using 20, 50, 100, and 200mg weights (see page 24 of this notebook). For all points the error was less than 0.5% of the reading which is acceptable for this analysis.

Temperature calibration was performed using a single point calibration as described on page 23 of this notebook. The type 'R' thermocouple (Platinum v 13% platinum Rhodium) is a fairly linear temperature to voltage device, especially below 700°C. Any shift in calibration would be easily recognized by significant shift in the temperature reading at ambient, at the calibration point, or both. As indicated by the Nickel Curie Point Calibration plot on page 23 of this notebook the temperature error was 1.1°C or 0.3% of the reading which is equivalent to the listed error for this thermocouple of 1.5°C or 0.25% whichever is greater. These readings were observed to be the same between the display on the TGA and the computer.

During all tests the readings on the TGA display were observed and compared to the readings on the computer display for both temperature and weight and found to be in agreement.

12-22-05

TECHNICAL REVIEWER

I have technically reviewed the portions of this notebook and supplements, as applicable, identified on the technical review form used to document my review. Technical comments have been resolved and the notebook entries are evaluated as being technically adequate.

Signature [Signature]
Printed name TIANGAN LIAN
Date Dec. 22, 2005

RESPONSIBLE MANAGER

The technical review is acceptable.

Signature [Signature]
Printed name Susan A. Carroll
Date 1-5-05

This Scientific Notebook (SN) is recommended for closure. A technical review has been completed, and any review comments have been resolved. The information contained in this SN is to the best of my knowledge both accurate and complete.

This SN does/does not (circle one) contain technical data. The work documented in this SN is continued in SN-LLNL-SCI-V 12/22/05

Principal Investigator _____ Date _____

Responsible Manager _____ Date _____

~~[Signature] 1-10-06~~

TECHNICAL REVIEW FOR SN-LLNL-SCI- 487 -V 2
 Scientific Notebook Page Range Reviewed ii to 85
 Supplemental Notebooks Reviewed (as applicable) Supplement 1
 Supplemental Notebook Page Range Reviewed all pages
 (Document each supplemental notebook and the inclusive pages/sections reviewed)

Review Type (check all that apply): Annual π /Interim π /Close-Out π

General Notebook Review Criteria (per LP-SIII.11Q-BSC, Rev 0, ICN 0)

Technical Reviewer: Tiangan Lian (Printed Name) Date: 12/08/2005

*Address the following criteria when performing this review. **DOCUMENT A JUSTIFICATION FOR ANY CRITERIA THAT ARE NOT APPLICABLE.***

1. The investigation is described in sufficient detail to retrace the investigation and confirm the results, or to repeat the investigation and achieve comparable results, without recourse to the original investigator.

Yes. The PI has done an excellent job in providing details of each experiment.

2. Software used is qualified and suitable to the problem being solved in accordance with LP-SI.11Q-BSC, *Software Management*.

See review comment in next page.

3. The documentation for any electronically managed information is in accordance with Initial Entry Requirements.

Yes.

1-10-06

The certificate of measurement provided by LGC (Queens Road, Teddington, Middlesex TW11 0LY, UK) indicates that the Indium standard should be good for at least 36 months after it has been shipped. The TA Instrument component list is dated 11-14-01; however the date the order was placed by YMP was placed in January of 2002 and probably shipped mid to late January of 2002. The first calibration series associated with the work in this notebook was conducted between 01-28-05 to 01-31-05 (see pages 72-75). The second calibration was conducted on 03-03-05 (see page 80).

The Indium standard is used to calibrate both temperature and energy (heat flow) coefficient of the DSC unit. The temperature calibration is based on the melting point of the standard and heat flow is a measure that is dependant on both the type and mass of the standard. LGC suggested use time after shipping of 36 months is based on the concern that over time some oxidation of the Indium standard can occur under certain adverse conditions. This oxidation will cause an error in weight related to the Indium purity, thus the amount of Indium metal available in the calibration sample for the heat flow calibration. Oxidation of the standard can cause a slight error in the heat flow calibration. However, the melting point of the Indium should not vary, within the sensitivity range of this DSC, with a small amount of oxidation that might form over time.

It should be noted that the standard was kept in the sealed container inside a lab and was not exposed to any adverse conditions. Based on this, only minimal oxidation would have been experience by the standard and it would not be expected that the melting point of the standard would have varied from its original temperature of 156.61°C.

The first calibration run shown on page 73 (CAL-IND.001) was a quick check of the instrument performance to see if it was responding properly. Cycling the sample pan with the Indium through the calibration temperature range also helps remove any contaminates on the pan that might interfere with the results. A second calibration run shown on page 75 (IND.001) was conducted to make any necessary adjustments. This run show that the DSC was with 0.1°C of the Indium standard without adjustment. It should be recognized that the temperature calibration values are taken during a ramping of the temperature and that some error is expected. This error is dependant on the ramp rate and data acquisition rate of the DSC unit. By experience an error of <1% would be considered acceptable for this calibration and the analysis that was conducted in this notebook.

A further check of the DSC calibration (see page 75) shows that the DSC responded within 0.8°C of the calibration standard, which gives and error of <0.2%. A final calibration run (page 80) post tests show an error of <0.2%.

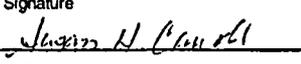
11
Phil J. Stoppa 1-10-06

BSC

Scientific Notebook Compliance Review Worksheet

QA: QA
Page 1 of 3

Complete only applicable items.

Scientific Notebook Identifier (from Scientific Notebook Register) SN-LLNL-SCI-487-V2		Investigator K. Staggs		
Scientific Notebook Title Research Supporting Environmental Chemistry Experiments				
Reviewed by: Print Name Leigh A. Gouvêa	Signature 	Organization LLNL-Engr. Assurance	Date 1/5/06	
Review Comment Resolution Satisfactory: Print Name Leigh A. Gouvêa	Signature 	Organization LLNL-Engr. Assurance	Date 1/10/06	
Review Acceptance (to be signed by Responsible Manager after the Compliance Review is complete): Print Name Susan A. Carroll				
Signature 		Organization LLNL-Technical Area Lead	Date 1-10-06	
Type of Compliance Review: Scientific Notebook page range reviewed <u>i</u> to <u>89 90 91 1/10/06</u>				
1. Initial Entry Review <input type="checkbox"/> Complete Parts 1 and 2 2. Interim Review <input checked="" type="checkbox"/> Complete Parts 1 and 3 3. Closure Review <input type="checkbox"/> Complete Parts 1, 3, and 4				
Additional Implementing Documents Identification (e.g., technical procedures, APs, etc., if applicable)				
Instructions for Completing This Form:				
1. If any part of a compound question in the Requirements/Criteria column cannot be answered YES, then mark the entire requirement NO, and provide an explanation in the COMMENTS column. 2. Marking the N/A box means the criteria is not applicable to this notebook. 3. All criteria marked NO require an explanation in the COMMENTS column and will be considered a non-compliance issue that the investigator must address in comment response. 4. The Review Acceptance box above will be completed by the Responsible Manager only after the Reviewer has signed above for satisfactory Comment Resolution.				
Comments (e.g., identification of Scientific Notebook Supplemental Records reviewed)				
Requirements/Criteria and Relevant Paragraph [LP-SIII.11Q-BSC, Paragraph No.]		CRITERIA MET		Comments
		Yes	No	
PART 1. GENERAL/IDENTIFICATION AND CONTROL OF SCIENTIFIC NOTEBOOKS				
1. Use of pre-bound notebook? [5.1.2]		<input checked="" type="checkbox"/>		
2. Consecutive pagination? [5.1.2]		<input checked="" type="checkbox"/>		
3. Loose material permanently attached? [5.1.3]		<input checked="" type="checkbox"/>		
4. Excessive open spaces lined through? [5.1.6]		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	Pg. 87 contains excessive open space. <i>Corrected</i>
5. Supplement contents properly cross-referenced? [5.1.7]		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	Pg. 8 should be updated to reference Supplement Binder #1. <i>updated</i>
6. All entries signed/initialed and dated? [5.1.10]		<input checked="" type="checkbox"/>		
7. Corrections lined through, initialed, and dated? [5.1.11]		<input checked="" type="checkbox"/>		
8. Table of Contents adequate? [5.1.13]		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	Should be updated to reflect the content of Pgs. 86-89. <i>updated</i>
9. First numbered page of Scientific Notebook contains the Scientific Notebook title, SNR ID, name of Investigator, and QA designator [5.2.2c]		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	Page 1 identifies the SN as SN-LLNL-SCI-487-V1, while the spine and Page i identify the SN as SN-LLNL-SCI-487-V2. <i>corrected</i>

BSC

Scientific Notebook Compliance Review Worksheet

 QA: QA
 Page 2 of 3

Complete only applicable items.

Scientific Notebook Identifier (from Scientific Notebook Register) SN-LLNL-SCI-487-V2				
Requirements/Criteria and Relevant Paragraph (LP-SIII.11Q-BSC, Paragraph No.)	CRITERIA MET			Comments
	Yes	No	N/A	
PART 2. SCIENTIFIC NOTEBOOK INITIAL ENTRY				
10. Statement of objective, identification of methods to be used and description of work? [5.3a) 1]]	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	Items 10-20 are not required for an Interim Compliance review.
11. List of sample types? [5.3a) 2]]	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	
12. List of test equipment to be used? [5.3a) 3]]	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	
13. Calibration information described? [5.3a) 3]]	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	
14. Description of procurement activity? [5.3a) 4]]	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	
15. All aspects required for software to be used [5.3.a) 5]]	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	
16. List of special training/qualification requirements, prerequisite actions, environmental conditions, and potential sources of error? [5.3a) 6]]	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	
17. Provisions for controls of any electronically managed information? [5.3a) 7]]	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	
18. Printed name, signature and initials of investigator? [5.3a) 8]]	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	
19. Initial entry initialed and dated? [5.3a)]	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	
20. Approved planning document noted [5.3a)]	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	
<p>Comments</p> <p>Part 3, Item 28: The certification for the Indium used for the DSC temperature calibration is valid for 36 months from the date of shipment provided the standard is stored under appropriate conditions. The issue date for the certificate is March 1996; TA Instruments appears to have provided the standard in November 2001; while the standard was used at LLNL in January 2005. The date of shipment should be determined, the method of storage of the Indium should be documented, and the adequacy of the standard should be established considering the shelf life restrictions identified on the certification.</p> <p style="text-align: center; font-style: italic;">See clarification provided on Page 90 of SN. J. Lawrence 11/10/06</p>				

BSC

Scientific Notebook Compliance Review Worksheet

 QA: QA
 Page 3 of 3

Complete only applicable items.

Scientific Notebook Identifier (from Scientific Notebook Register)				
SN-LLNL-SCI-487-V2				
Requirements/Criteria and Relevant Paragraph [LP-SIII.11Q-BSC, Paragraph No.]	CRITERIA MET			Comments
	Yes	No	N/A	
PART 3. SCIENTIFIC NOTEBOOK IN-PROCESS ENTRIES/SUBMITTAL AND TRACEABILITY OF DATA				
21. Names, signatures and initials of contributors to the notebook provided prior to making entries in the notebook? [5.3a) 8]]	✓			
22. Description of work performed? [5.4a) 1]]	✓			
23. Investigation results given? [5.4a) 1]]	✓			
24. Changes or additions to initial entry adequate? [5.4a) 4]]			✓	
25. Conditions described that might adversely affect the research? [5.4a) 5]]	✓			
26. Samples properly identified? [5.4a) 6]]	✓			
27. Test equipment properly identified? [5.4a) 6]]	✓			
28. M&TE calibration adequately documented? [5.4a) 6]]	✓ <i>5/4 1/10/06</i>	X		See comment in Comments section at the end of Part 2. <i>resolved</i>
29. Computer software properly identified? [5.4a) 6]]	✓			
30. Preliminary data used in the investigation identified? [5.4a) 7]]			✓	Data being generated.
31. For new volumes, initial entry copied into or referenced at the beginning of the volume? [5.4b) 1]]	✓			Pages 1-8.
32. Adequate controls documented for electronically managed information? [5.5.3a) 3]]	✓			
33. Input data obtained from the TDMS or TIC? [5.4a) 6]]			✓	Data being generated.
34. Data submitted to TDMS in accordance with AP-SIII.3Q? [5.6a]]	✓			See Page 85.
35. Identification of rejected or non-Q data [5.4a) 8]]			✓	
36. Adequate cross-reference to SN Supplements [5.4a) 9]]	✓			
PART 4. CLOSURE OF SCIENTIFIC NOTEBOOKS				
37. Concluding entry entered, signed, and dated? [5.7.1b]]			✓	Items 37-40 are not required for an Interim Compliance review.
38. Non-collection of data statement, if appropriate? [5.7.1b]]			✓	
39. Technical review completed? [5.7.1d]]			✓	
40. All supplements referenced in the notebook provided for the closure compliance review? [5.7.2a]]			✓	
Comments				

LP-SIII.11Q-BSC

FORM NO. LSIII11-1 (Rev. 10/12/2005)