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ACTIVITY/PROJECT SPECIFIC PROCEDURE

SP 12-16
THERMAL GRAVIMETRIC ANALYSIS/DIFFERENTIAL SCANNING CALORIMETRY
Revision 1

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1.0 Purpose and Scope

The purpose of this procedure is to establish a method for making thermal gravimetric analysis (TGA) measurements, differential scanning calorimetry measurements (DSC), and differential temperature analysis (DTA) measurements.

This document is a supplement to manufacturer's manuals for the operation of Netzsch STA 409. This supplement is not intended to be formal instrument documentation, nor does it cover all features or use of the instrument, but rather a hands-on user's guide to the typical operation of the instrument. Details of instrument operation can be found in the user's manuals located in the laboratory and/or in the online help.

Acronyms and definitions for terms used in this procedure may be found in the Glossary located at the Sandia National Laboratories (SNL) WIPP Online Documents web site.

2.0 Implementation Actions

2.1 Responsibility

The Principal Investigator (PI) or designee is responsible for implementing the requirements of this procedure.

The Technical Staff is responsible for performing the measurements following the requirements of this procedure, documenting all required information described in this SP, and assuring the latest revision of this document is followed.

If the procedure cannot be worked as written, the user has the responsibility to stop work and resolve all concerns with the PI/designee or safety, as appropriate, prior to proceeding with the work.

2.2 Qualification and Training

Qualification and training of users will be documented on the instrument qualified users form. Users should not use this instrument without on the job training from an experienced user.

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2.3 Safety

The activities described in this SP shall conform to SNL Environmental Safety and Health programs (ES&H). All activities described in this SP are also subject to ES&H requirements governed by the WIPP Industrial Safety Program and the WIPP Industrial Hygiene Program.

2.4 Data Collection and Storage

Data collected on this instrument will be collected on printouts, in scientific notebooks (SN), or on electronic media. Records of instrument use, calibrations, maintenance, and other information that is not project specific will be made in the instrument log book. Notes on what measurements were performed will be documented in the scientific notebook or in the instrument log book.

2.5 Instrument Procedures

Follow the instructions in the user's manuals and the online help section. Details on how to perform these operations are contained in these references. Some features in the below text may have alternative control methods (such as control/panel or computer control) which are available and described in the user's manuals and online help section.

Diagrams showing the location of various parts of the instrument are in the user's manual.

2.5.1 Turning on the STA 409 Instrument (if not already on)

A. Turn on the water-circulator system. There are three on/off switches, one on the water tank and two on the control panel. If you intend to do TG measurements then the water circulator should be on for 6 to 8 hours prior to starting a measurement so that the balance achieves thermal stability. If you intend to do only DSC/DTA measurements then it is not necessary to wait. It is only necessary that the circulator be on.

Make sure the water level in the circulator is at the proper fill level. This is a mandatory responsibility of the user to check the water level and make sure that it is maintained properly.

B. Turn on the computer system.

C. Turn on the STA409 unit. The power on switch is located on the back of the unit where the 120 VAC line plugs in.

D. Turn on the furnace transformer. The switch is located on the front of the unit.

2.5.2 Condition of the Instrument

A. The instrument should be left in this state after measurements.

1. The helium tank valve should be open. The secondary regulator should be set to 0.6 bar. The secondary should not go above 1 bar and there is a pressure safety valve after the regulator set to 1 bar.
2. The balance protective gas valve on the back of the instrument should be open.
   a. The rotometer that controls the balance protective gas should be open to about 5 ml/min.

3. The valve on the STA 409 (not on the GC/MS) connecting the STA 409 to the Varian GC/MS should be open. It should always be open.
4. The 2-way valve on the Varian GC/MS should be turned so that the GC is connected to the MS, not the STA 409.

Closing the valve connecting the STA 409 to the Varian GC/MS will break the capillary column that runs between the two instruments and will require replacement of this column.

2.5.3 Opening/Closing STA 409 Instrument & Crucible Placement

2.5.3.1 Opening/Closing the Unit

A. To raise the furnace: place one finger on the "Safety" button located on the right side of the STA 409 unit. At the same time place another finger on the "Up" arrow located on the front panel of the instrument. Hold both buttons in until the furnace reaches the desired location or until it's parked and stops moving.

The system will not open or close unless the safety button is held down simultaneously with the respective arrows. This is a safety feature that prevents the furnace from opening during a measurement or from fingers being trapped under the hoist mechanism when lowering the furnace. If the LED on the Safety button is RED then you will not be able to raise the furnace. RED means that either the system is running or there is negative pressure inside the balance.

B. To lower the furnace: press the "Down" arrow button and the "Safety" button.

*Be **VERY** careful to check the alignment of the carrier to the furnace opening as it is being lowered over the carrier and also over the radiation shield. STOP lowering the furnace if there appears to be any risk of contacting the carrier or the radiation discs. Make any necessary adjustments then finish lowering the furnace.*

2.5.3.2 Crucible Placement

A. After sample weight has been recorded in the scientific notebook (using the laboratory balance not the TGA balance), raise the furnace.

B. Wear powder free gloves or use clean tweezers for crucible placement.

C. Place the Reference crucible on back position of the crucible holder (for DTA and DSC).

D. Place the sample crucible (contains sample/ or contains no sample for a baseline) on the front position of the crucible holder (the TG head only has one stem for a single crucible).

*When placing a crucible onto a stem you must be **VERY** careful not to apply any torque to the stem or it will break. There is a guide rail in front of the furnace to assist you in this task. You must obtain training from a qualified user before you attempt this.*

E. Lower the furnace as described in Subsection 0.

The crucibles often contain traces or coatings (mostly water) that will burn off in the TGA and slightly alter your measurements. You can condition the crucible by heating it up in the high temperature furnace in the wet lab. Heat the crucible to the highest temperature to be used in the TGA, for a few minutes, and then let it cool. You should use the crucible soon after, or store in a dessicator, because water will immediately begin condensing onto the crucible.

You can remove water by adding a step to your TGA program that first heats to about 60 ºC for a while (~10 minutes).

2.5.4 Purge and Backfill of the STA 409

Purging the system may remove a significant fraction of moisture from your sample. If you want to determine moisture content, this step probably should not be performed. You can also record the weight change during the purge/backfill step by following the directions in 2.5.4.1. If you do not purge and backfill you will still need to remove air (oxygen) by allowing the gases to flow through the system (for a while ~ 30 min) if you are going to use the MS or if oxygen will affect your sample. In any case, the TGA only tracks mass from when you start a measurement to when you finish a measurement. Thus you may need to record (in your scientific notebook or logbook) the mass loss before and after purge/backfill before you press Start in step 0.

A. Close all gas inlet valves and the main exhaust valve but not the exhaust valve on the STA 409 to the Varian GC/MS. At this point the GC should be connected to the MS by way of the 2-way valve.

B. Turn on the vacuum pump.

C. Introduce the vacuum by slowly opening the vacuum valve on the back of the instrument.

When working with fine powders you should have a lid on the crucible and you must be very careful introducing gas or vacuum into the system. As you are purging or filling with gas, you should keep an eye on the TG mass measurement. If you have lost a significant weight by the time you finish purging and backfilling, probably some powder has escaped the crucible. At this point you will need to open the furnace (if cool) and clean up using the small vacuum. ***Try not to let this happen.***

D. When the pressure in the TGA is sufficiently low (not changing any more) connect the STA 409 to the MS by way of the 2-way valve on the Varian instrument, if MS is desired.

Immediately after the vacuum has started you will see the pressure on the vacuum gauge begin to decrease. Although the vacuum gauge will indicate maximum vacuum (around -0.9 bar), it is a good idea to open the View Signals window in the Measurement program and watch the TG values. The TG will stabilize when the maximum vacuum has been achieved inside the balance chamber.

E. Once vacuum is achieved **stop the vacuum pump** and close the vacuum valve. Slowly open the Protective Gas valve and observe the vacuum gauge and the rotometer. Check the gauge and the rotometer to make sure gas is flowing into the system.

F. Slowly open the Purge Gas valve and observe the vacuum gauge and the rotometer.

G. When the vacuum gauge indicates a slight over pressure or pressure close to atmospheric, then slowly open the exhaust valve.

H. Allow the system to stabilize before beginning the measurement.

Immediately after the gas has begun to flow into the system, the TG starts to decrease in weight due to the buoyant force of the gas. Allow the system sufficient time to achieve equilibrium. The rotometer balls will stop bouncing when the gas flow has reached equilibrium.

I. Recommended settings for the gas flow rates are 50 ml/min for the purge gas and 15 ml/min for the protective gas.

The rotometers are not calibrated and should not be removed from the system. ***We don't want to open fittings unless absolutely necessary.*** *For most TGA/DSC measurements it is not critical that the rotometers have accurate flow rates. What is critical is that you don't change the flow rates when comparing two measurements. If accurate flow rates are needed (say for a chemical reaction rate experiment), one can use the calibrated digital flow meter on the main exhaust port to set the rotometers to the desired flow rates.*

J. After the system has stabilized, and gas (not oxygen) has been flowing through the system for a while (10 min) you can turn on the heated transfer line (if needed). Refer to the instruction manual in the laboratory.

2.5.4.1 Purge and Backfill as Part of the TGA Measurement

A. Create an initial long isothermal leg at room temperature (see Subsection 0).

B. Start the instrument as described in Subsection 0.

C. Purge and Backfill as described above in Subsection 0.

D. Alter the running program to end the initial isothermal leg by going to View/Edit Running Measurement Program under the Measurement pulldown.

2.5.5 New Measurement

2.5.5.1 Instrument setup

A. Open the STA 409 program on the computer.

B. Before every measurement you need to check the instrument parameters:

1. Go to File and Instrument Setup.
2. Check the instrument parameters to make sure they match what you are doing. Follow the online instructions under help.
3. On the back of the instrument is a knob that tells the instrument what type of thermocouple you are using (T, S, W, etc.). Be sure this knob is set to the correct thermocouple type.

2.5.5.2 Measurement Setup and Startup

A. Select New under File.

B. A screen will then appear that allows the user to enter in the experimental information which will be stored in an external file. This information is not used for making the measurement.

1. Select Measurement type (Sample, Sample + Correction, Correction)

If you are using helium as the purge gas, performing a baseline correction is probably not necessary and may add errors to your measurement. For argon, baseline correction may be necessary depending on the width (in time or temperature) of your peaks.

2. Enter other information asked for. You need to put something in for name, ID and sample mass (except for baselines)

If you do not put down a sample mass on this screen (except for baselines) it is a bit harder to add this into the file later on. Recommend doing this now.

3. Click on Continue.

C. A screen will then appear that allows the user to select the appropriate calibration files:

1. Select the appropriate temperature calibration file. If no temperature calibration is necessary then select “Tcalzero.”
2. Click OK.

D. If you are in the measurement mode for TG/DSC or DSC, a screen will then appear that allows the user to select the appropriate sensitivity calibration file:

1. Select the sensitivity calibration file that matches the heating rate, gas atmosphere, and crucible type that will be used during the baseline run. If no Sensitivity calibration curve is necessary then select “Senszero”.
2. Click OK.

E. A screen will then appear that allows the user to set up the appropriate heating program for the run. Below is a list of possible but not all choices for the heating program. Refer to the online help section for a complete explanation of the various options.

*Many temperature steps have the STC (Sample Temperature Control) option. With STC on, the heating program will follow the TG thermocouple reading. With STC off, the heating program will follow the furnace thermocouple reading. Recommend keeping STC off. STC **must** be off for temperature calibration runs.*

Initial - select the initial temperature to be room temperature (usually 20ºC-25ºC).

Dynamic- enter the end temperature of this step in the temperature program.

Enter the rate at which this dynamic is to occur.

If another dynamic is required follow the above steps. The user is given the option to perform an unlimited amount of heating and cooling dynamics.

Isotherm- enter the time of the isotherm that is to be performed.

If an isotherm is not needed, click on the next dynamic that needs to be performed or click on FINAL.

Final- this step is an emergency safety step that shuts the system down if the temperature of the system reaches ten degrees more than the highest dynamic temperature.

The default automatically sets the reset temperature to 10°C higher than the highest programmed temperature; however, the user can change the emergency reset temperature.

Final Standby – this step enables the operator to prevent the furnace from being raised after the FINAL step has been entered. There will be no data collected. This step is strongly recommended as a Safety mechanism. The Operator can override this segment at any time it is activated by clicking on “Measurement” in the STA409 program and deactivating “Stop Stand-by”.

1. After choosing a step, click on ADD to add this step to the program. This step in the temperature program will then appear in the box. This box allows the user to observe the temperature program, and make any changes.
2. Click on CONTINUE.

F. A screen will then appear that allows the user to save the measurement in the appropriate file. Enter the name of the file (e.g. Baseline or Sample). It is not necessary to add the file extension. This is automatically done for you. Click Save.

G. A screen will then appear that allows the user to start the initial conditions of the baseline, and then the measurement.

H. Click Start. Watch the instrument for a few minutes to be sure everything is going ok. You can cancel a measurement at any time by clicking Stop Measurement under the Measurement pull down.

I. After the measurement is complete you can run the Proteus analysis software or click on Run Analysis Software under the Tools pull down. Analyses using software will be conducted under NP 9-1.

2.5.6 Calibration

2.5.6.1 Thermocouple Calibration

Thermocouple calibration is a lengthy process and therefore cannot be performed before every use. The thermocouples used in this instrument cannot be calibrated by the standards laboratory. The stem thermocouple needs to be calibrated at least once a year.

A. Perform measurements on a set of standards (at least three) that covers the temperature range up to about 1500ºC (Going up to around 1000ºC is usually good enough). Currently we have a set of 8 melting point standards from Netzsch. The instrument requires that the measurement of each melting point standard agree within 20ºC of the expected value. If

the stem thermocouple is more than 20ºC off from the expected values, determine the cause, correct the problem and repeat the calibration measurements.

1. You can program the instrument to heat at 20 K/min up to a temperature about 75-100°C below the melting point (mp) of the material.
2. From 75-100°C below to about 20°C above the melting point, heat at a rate around 2-5 K/min (i.e. slowly).
3. Program the instrument to make at least two measurements at each melting point. You can program it to heat to 20°C above the mp then cool to 75°C below, then reheat to 20°C above, etc. Duplicate measurements should be within 10% (or 20°C which ever is smaller). If not, determine the cause, correct the problem, and repeat the measurements.

B. Run the Proteus analysis program.

1. Perform a c-DTA ® (calculated differential temperature analysis) analysis on the temperature versus time curve, which can be found under the Evaluation pull-down menu.
2. Do Onset... under Evaluation on the c-DTA ® curve. Select the region around where the first sharp change occurs. You can then use Set Value... under Evaluation on the temperature versus time curve to find the temperature at the onset time.
3. Follow the online help instructions for creating a calibration file. Netzsch normally gives indium (In) a regression weight of 10, the other melting points a regression weight of 1.000 for thermocouple calibration, and zinc a regression weight of 0.8 for the DSC calibration. This comes from Netzsch's experimental experience (of the variance of each melting point) and we should not alter these weights unless we have good evidence to do so.
4. The Proteus program requires measurement or dummy value(s) at the beginning and end of the calibration range (i.e., 0°C and 1500°C) such that no part of the calibration curve has more than a 20°C difference between experimental and expected values.

2.5.6.2 Thermocouple Check

Thermocouple checks take several hours and therefore cannot be done before every use. This needs to be performed once a month.

Follow the steps under Subsection A for a single measurement (single melting point determination). Record the melting point value (corrected) in the instrument log book and compare to the expected value. If the (corrected and/or uncorrected) experimental value is more that 20ºC from the expected value, determine the cause, correct the problem, and repeat the measurement.

2.5.6.3 Balance Calibration

The STA 409 has an internal weight for balance calibration. Balance Calibration may be found under the Diagnostics pull down menu. You can also measure the weight of your sample (using the lab balance) after the TGA/DSC measurement is complete, but you must keep in mind that the purge/backfill can remove a large mass of moisture and the TGA only tracks mass from when you start a measurement to when you finish a measurement. Thus you should record (in your scientific notebook, or the instrument log book for instrument checking) the mass loss after purge/backfill before you press Start in step 0.

2.5.6.4 Acceptance Criteria for Duplicate Measurements

Wide variations in the TG and or DSC (DTA) measurements can occur due to a variety of issues including sample inhomogeneity, slow rates of decomposition, and differences in how different users determine a peak. Furthermore very small weight changes (below 1 wt %) can be measured which will have a correspondingly high uncertainty. Herein we only claim that duplicate measurements should be within 40 % which is the uncertainty that has been observed for small weight changes (below 1 wt %). We leave it up to the PI to decide whether or not to develop more stringent acceptance criteria for their particular experiments.

3.0 Records

The following records, generated through implementation of this procedure, shall be prepared and submitted to the WIPP Records Center in accordance with NP 17-1 (Records):

QA Record

- SN (Scientific Notebook) and supporting documentation
- Instrument Log Book

Non Quality (NQ) Record

- Any electronic media

4.0 Appendices

There are no appendices in this SP.

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