IMSERC User Manual for Netzsch STA 449

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INTRODUCTION

Use of this instrument is allowed only by qualified users after receiving training by a staff member. Do not run this instrument without approval from IMSERC staff. Failure to do so may cause damage to the instrument, produce invalid data, and result in additional fees and/or removal of all IMSERC privileges. This set of instructions is meant to serve as a guide for 'routine' data collection on the instrument. For custom experiments that are not covered in this user manual, contact a staff member. For the full list of modes, capabilities, and potential custom experiments that could be run on this instrument, please either contact a staff member or check the corresponding capabilities section at http://imserc.northwestern.edu/pcm-instruments.html. Please read this user manual and acquaint yourself with the instrument.

A hard copy of this user manual can be found near the instrument. An electronic version of this user manual is linked to the desktop of the instrument computer and also available under the corresponding instrument section at http://imserc.northwestern.edu/pcm-instruments.html by pressing on the 'User manual' button. If while using the system, something happens that you do not understand, please ***stop***, and ***get help***. In any event, be completely prepared to justify your actions. The cost of even minor repairs could be considerable.

SAFETY

All users of IMSERC must review the general safety policies at http://imserc.northwestern.edu/about-policies.html. To become an independent user of this instrument, you must have the following safety training and certificates under your LUMEN profile:

- Hazardous Chemical Waste Management
- Laboratory Safety
- Personal Protective Equipment

You need the above certificates to be able to reserve time for this instrument on NUcore. Online classes and certification are offered at https://learn.northwestern.edu. Upon completion of the certificate, it will take an overnight to filter through the different systems and get into the files that NUcore uses. Additionally, familiarize yourself with the location of standard safety stations like eye wash and shower stations found in outside of room B172 at the north side. Protective eyewear is required in this room, and gloves should be removed when using the computer.

DATA MANAGEMENT

Your personal data folder is created during training. Please save data under your personal folder, which must be located under your supervisor's group folder, otherwise you might not be able to access your data remotely. See a staff member if you do not have a personal folder on this instrument yet. For users that prefer to name their data folders using dates, use the order of YYYY-MM-DD or YYYYMMDD in the name, so that folders can be sorted chronologically by the operating system if needed.

Data from this instrument are copied on your group folder on 'imsercdata.northwestern.edu' under 'others/STA' every few seconds. Please follow instructions at http://imserc.northwestern.edu/about-general-faq.html#data for details about data access.

SOFTWARE

Data reduction and analysis of thermal data can be performed with the 'Proteus' software. GC-MS data processing can be performed with the 'ChemStation' software. Software is installed on the instrument computer. For offline analysis after your instrument reservation is complete, please use the following resources:

- For registered IMSERC users, the licensed to IMSERC 'Proteus' and 'ChemStation' software can be downloaded from 'imsercdata.northwestern.edu' under the folder 'public/STA'. Software is available for Windows only. Please follow instructions under 'Data Access' at http://imserc.northwestern.edu/about-general-faq.html#data on how to connect to the 'public' folder
- Remotely via NUWorkspace which is operating system independent. After logging in with your netID credentials, please launch the 'IMSERC' workspace which contains the thermal analysis (no GC-MS) software
- You have the option to use the instrument computer for analyses, but you must reserve instrument time through NUcore

DEFAULT INSTRUMENT STATUS

The default measurement mode of NETZSCH STA 449F3 is ***TGA/DTA under inert gas (Helium or Nitrogen)***. Please notify the appropriate staff member well in advance if you would like to run an experiment in a different mode than TGA/DTA or using a different gas environment. For the full list of modes and capabilities, please check at http://imserc.northwestern.edu/pcm-instruments.html#sta. Additionally, put a note on your NUcore reservation indicating the preferred mode of your measurement.

The default working condition of NETZSCH STA 449F3 is as follows:

1. Computer screen is by default deactivated. You must start your reservation through NUcore to be able to turn on the computer screen. If screen is already on, start your reservation through NUcore
2. The default 'STA' user account should be logged in. In case the computer was restarted, the password for the 'STA' account is (see hardcopy by the instrument)
3. Acquisition software (Proteus) should be running. Leave the acquisition software open when you are done with the measurement
4. There should be no error messages on either the front panel of the instrument or the acquisition software. Please check the 'Troubleshooting' session for a potential solution before reporting the error
5. Type of crucible mounted on the TGA/DTA carrier will depend on the selection of the crucible used by the user before you. If needed, exchange crucibles according to the instructions and training you have been given. Crucibles, standards, and various attachments are in the yellow compartmentalized container (figure 5) located in the second drawer of the cabinet under the instrument computer. When exchanging ceramic crucibles, please place uncontaminated ceramic crucibles back into the yellow container. Do not leave exchanged ceramic crucibles at the area near the instrument, as they might role, drop, and crack or break

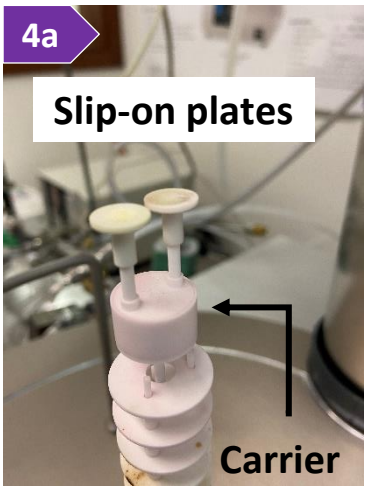
If there is an error or problem with the instrument that is not covered under the 'Troubleshooting' section, please report the issue by following at least one of the steps below:

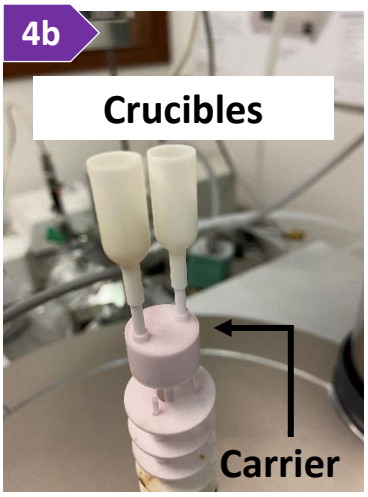
1. If you have already started your reservation using NUcore, please end your reservation and select the error reporting option with a brief description about the issue. Place the 'Stop' sign near the instrument computer to notify users immediately after you. 'Stop' signs are located on the shelf above the computers in BG51
2. If you have not started your reservation using NUcore, please report problems with the instrument at http://imserc.northwestern.edu/contact-issue.html and place the 'Stop' sign near the instrument computer
3. Contact a staff member for instructions

LOADING A SAMPLE INTO THE INSTRUMENT

The following procedure should be followed by the users who want to use the default instrument configuration, which is 'TGA/DTA'. If you need to measure DSC, please talk to a Staff for installing the DSC carrier for you.

1. Verify that the instrument is idle, and temperature of the furnace is near room temperature (25-45 °C) as indicated on the display panel in the front of the device (figure 1). System will let you raise the furnace at any temperature when instrument is idle. Please verify that the temperature of the furnace is near room temperature before going to the next step. Start your reservation in NUcore to have the screen of the instrument computer turned on
2. To load your sample, move the furnace into the upper end position by pressing and holding simultaneously the 'Up' button in front of the instrument and the 'Safety' button on the right side of the instrument. Watch the 'sta-raising-lowering-furnace' video for a visual demonstration on raising and lowering the furnace. Keep holding the two buttons until the furnace has stopped moving
3. (Optional) When the furnace is at the upper end position, the furnace can be swung out by 30° to the left (parking position) which gives you more room to mount your crucible. Watch the 'sta-raising-rotating-lowering-furnace' video for a visual demonstration on how to swing a furnace
4. If needed, exchange crucibles on the TGA/DTA carrier with the crucibles required for your measurement. Slip-on plates (figure 4a) and crucibles of different volume (figure 4b) are available. Watch the 'sta-exchanging-crucibles' video for a visual demonstration on how to exchange crucibles. Remember that crucibles and carrier sit on a delicate microbalance that can be damaged if excessive force is used during crucible exchange
5. Select the appropriate furnace for your experiment. STA is equipped with two furnaces which are labeled. The Silicon Carbide furnace (installed on the right side of the furnace mount) is used for open crucible measurements (TGA, DTA/TG with or without GC-MS) and the stainless-steel furnace (installed on the left side of the furnace mount) is used for sealed crucibles (DTA or DSC) under inert conditions. To select the appropriate furnace, rotate the furnace to the position that is aligned





with the carrier of where the sample mounts. Watch the 'sta-raising-rotating-lowering-furnace' video for a visual demonstration on how to select and position a furnace.

6. Measure the mass of your sample using any of the microbalances in the room. Watch the 'sta-microbalance' video for a visual demonstration on how to use the microbalance
7. Using tweezers, gently place your sample crucible onto the sample carrier (sample in front/reference back). Watch the 'sta-loading-unloading-tga-sample' video for a visual demonstration on how to load and unload a crucible on the carrier. Use the beam in front of the carrier to support your hand during sample mounting. Sample carrier is installed on a very sensitive micro-balance, please be careful when you (un)mount your sample. With the default carrier, you can measure simultaneously TGA and DTA. If you need to measure DSC, please talk to a staff
8. Lower the furnace by pressing simultaneously the 'Down' button and 'Safety' button. Hold both buttons until the furnace has stopped moving. This step is part of the 'sta-raising-lowering-furnace' video used for step 2 under this section

MEASUREMENT TYPES FOR THERMAL ANALYSIS EXPERIMENTS

Start the STA 449F3 measurement program (icon on the desktop) in case it is not running. It will take a few seconds for the software to connect to the instrument and look for the current configuration, i.e., sample carrier, furnace, and attachments. Once synchronization between the software and instrument is successful, a notification window will pop up at the bottom right corner of the software window.

Depending on the measurement type, i.e., baseline, sample, or combination of both, you have different options with the software for measuring:

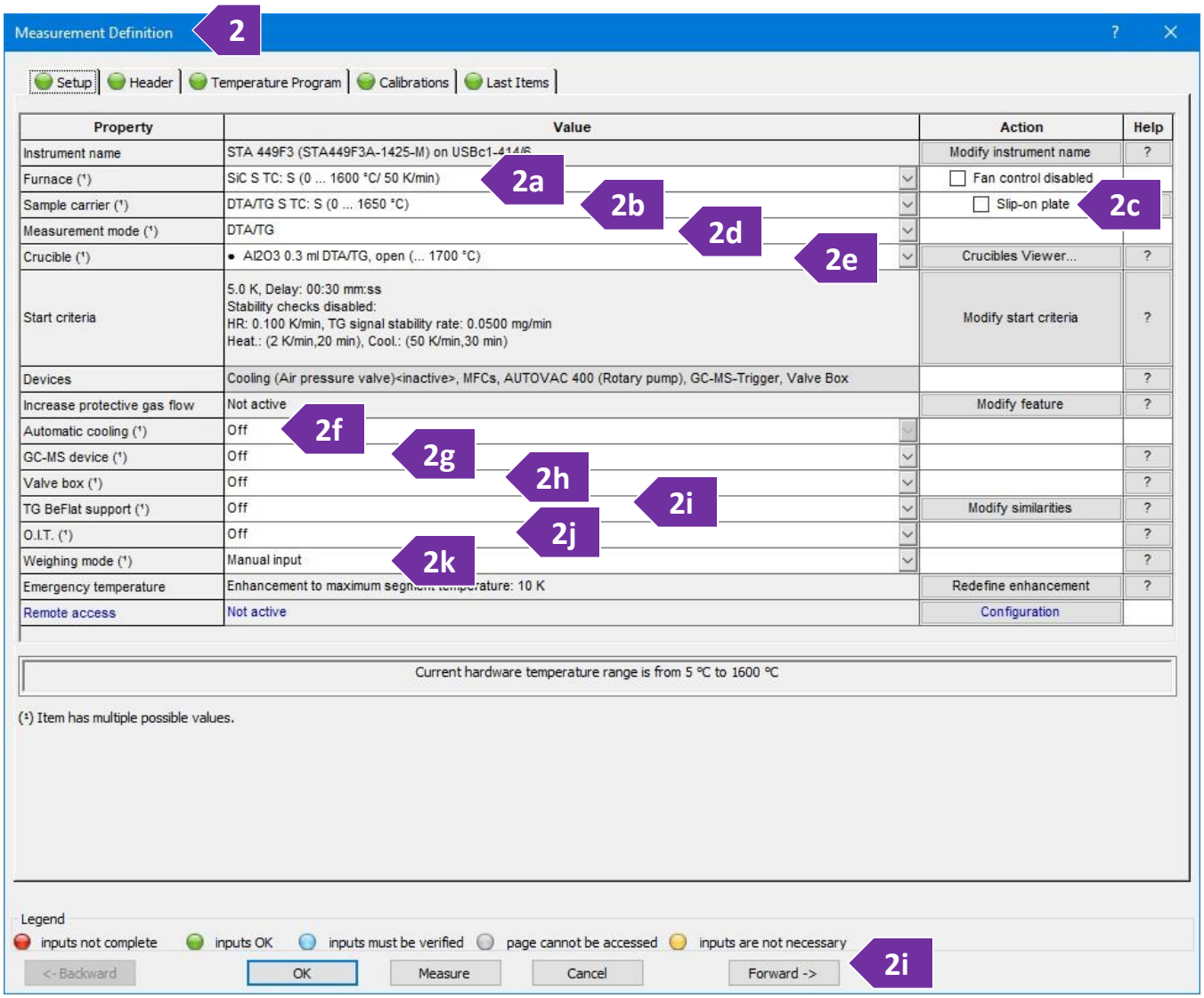
- a sample without a pre-existing baseline or pre-existing settings (new procedure). This measurement type is called 'Sample' on the software
- a baseline for samples to be measured. This selection has the same type of settings and options used for the creation of new procedure. This measurement type is called 'Correction'
- a sample using a pre-existing baseline. This selection does not allow for any changes in the settings, e.g., temperature range, and assumes that you want to repeat the same experiment used for the baseline. This measurement type is called 'Correction + Sample'
- a baseline for a pre-existing sample measurement. This selection does not allow for any changes in the settings, e.g., temperature range, and assumes that you want to apply a baseline correction to an existing collection that may or may not include a measured baseline. This measurement type is called 'Sample + Correction'
- a sample with pre-existing settings. In this case, all you must do is open an old sample collection

Please read the detailed instructions below based on the measurement type of your choice.

A. TGA/DTA SAMPLE MEASUREMENT WITHOUT A CORRECTION FILE OR EXISTING PROCEDURE

To create a completely new measurement without a pre-collected correction file (baseline) or existing procedure that is part of an old measurement:

1. Press on the 'File' menu and select 'New'. If an existing procedure is loaded, select 'OK' in the warning message regarding the deletion of the current procedure. The 'Measurement Definition' window opens
2. On the 'Setup' tab of the 'Measurement Definition' window, you are going to set the main configuration parameters of your measurement (figure 2):



a. 'Furnace' option will be pre-selected for you by the software based on your physical selection of the furnace (figure 2a)

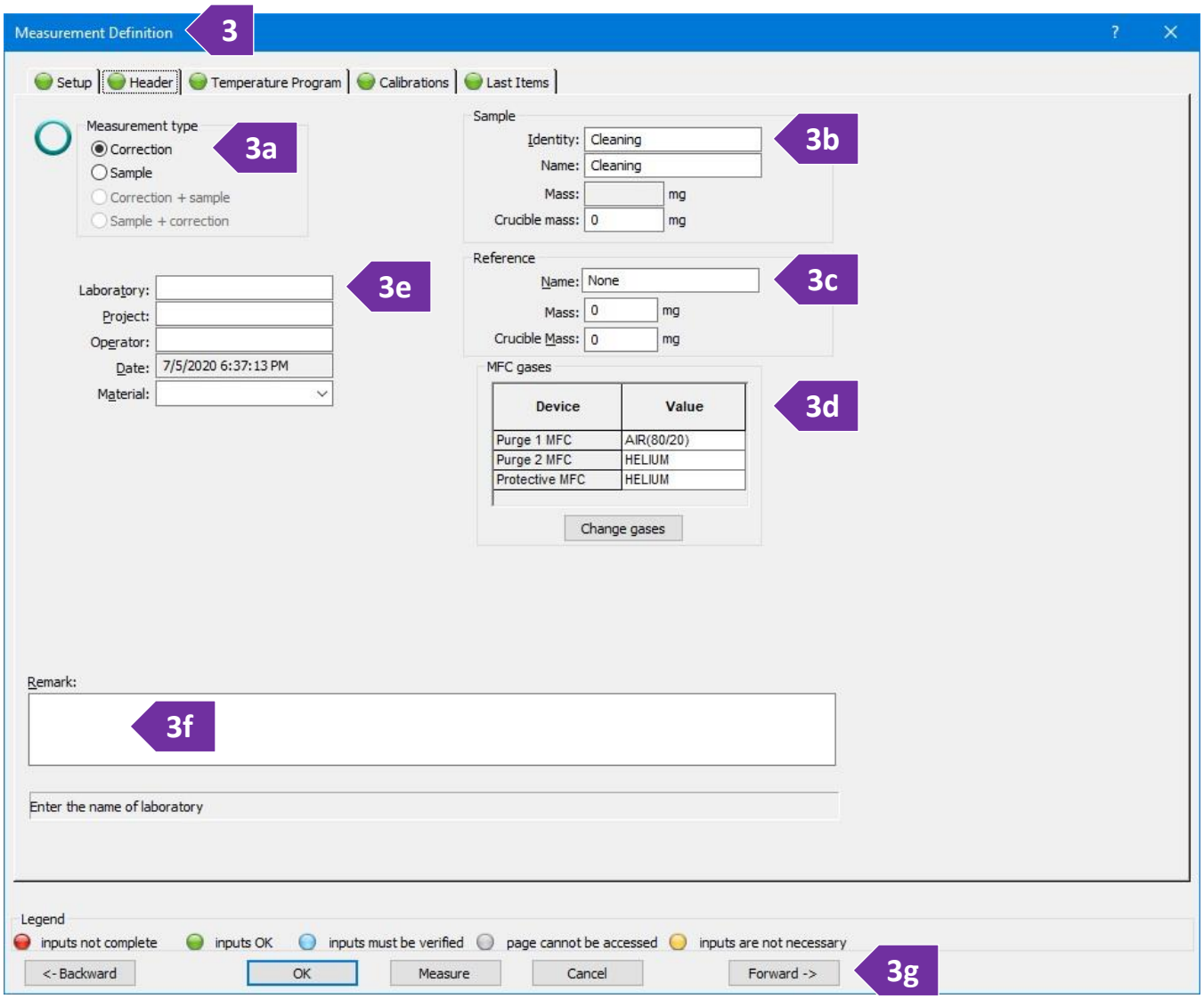
b. 'Sample carrier' option will be pre-selected for you by the software based on the carrier installed, i.e., DTA default, DSC, or TGA only

c. 'Slip-on plate' must be selected when using the slip-on mounting plates (figure 4a). This option will also populate the crucible list (step 2e) with pan-like crucible options

d. 'Measurement mode' requires your input depending on what signal (TGA only, or DTA/TG) you would like to record. It is highly recommended to record DTA or DSC with the TGA data since you can get data for two measurements simultaneously

e. 'Crucible' needs to be set based on the type of crucible you are about to use, e.g., selecting Aluminum crucibles will automatically limit the maximum allowable temperature to 600C. Please verify that you have selected the 'Slip-on plate' option (step 2c) to see the correct list of crucible options
f. 'Automatic cooling' is available only for the stainless-steel furnace and not for the Silicon Carbide one. Use the 'Automatic cooling option' to control cooling below ~ 150C
g. 'GC-MS device' should be enabled only when GC-MS is needed. Only the Silicon Carbide furnace (and not the Stainless-Steel furnace) is connected to the GC-MS with the transfer line. See more details under the 'GC-MS with TGA/DTA sample measurement' section
h. 'Valve box' should be set to 'Off' since this attachment is not available on our system
i. 'TG BeFlat support' should be set to 'Off'. Measuring experimentally the baseline is highly recommended instead of using a 'BeFlat' correction which is an algorithm for correcting of the buoyancy affect
j. 'O.I.T.' should be set to 'Off'
k. 'Weighing mode' should be set to 'Manual input' when mass of the sample is known. Use any of the other options in case you have extremely air sensitive samples and you would like to use the STA microbalance to measure the mass of the sample while being protected by the flowing gas
l. Press on the 'Forward ->' button or press on the 'Header' tab

3. On the 'Header' tab (figure 3) of the 'Measurement Definition' window (red disc-like symbol next to each tab name and textbox indicates required fields), you are going to provide some sample specific information:
   a. In the 'Measurement type' panel, select 'Sample'. Measuring a correction (baseline) is highly recommended for accurate mass changes. Uncorrected measurements may have overestimated weight values that depend on the type of flowing gas due to buoyancy affects, e.g., ~ 0.2 mg under He or ~ 0.8 mg under air flow. Correction can be measured either before or after a sample measurement. Correction files can be reused for future sample corrections only if the conditions of the experiment remain the same. Please refer to the corresponding sections in this user manual depending on the order of the sample and correction measurement (correction first and then sample or sample first and then correction)
   b. In the 'Sample' panel provide
      i. 'Identity' such as sample code, composition, etc.
      ii. 'Name' such as sample code, composition, etc.
      iii. 'Mass' for the sample mass (without the crucible). The mass value will be used by the software to calculate the corresponding percentage weigh value as a function of temperature
      iv. 'Crucible mass' for the mass of the empty crucible placed in the sample position of the carrier (front side). The mass value is not used for any calculation, but value serves as an important info about the



size of the crucible used for the measurement. Size/volume of the crucible is important for the baseline correction process

c. In the 'Reference' panel, which is relevant only for DTA or DSC measurements, please provide:

   i. 'Name' for the name of the standard used, e.g., Al_2O_3 or empty crucible

   ii. 'Mass' for the standard mass (without the crucible). For the sealed ampoule Al_2O_3 standard, please check the latest mass values under 'procedures/reference.txt'

   iii. 'Crucible mass' for the mass of the empty crucible placed in the reference position of the carrier (back side)

d. In the 'MFC gases' panel (figure 3d), ***check to see if the appropriate gas for your experiment is selected***. The type of gas for 'Purge 1' is controlled via a separate script as described in the 'Change type of gas' section. 'Purge 2' is connected to ultra-high purity Helium. In case you need a special gas for your

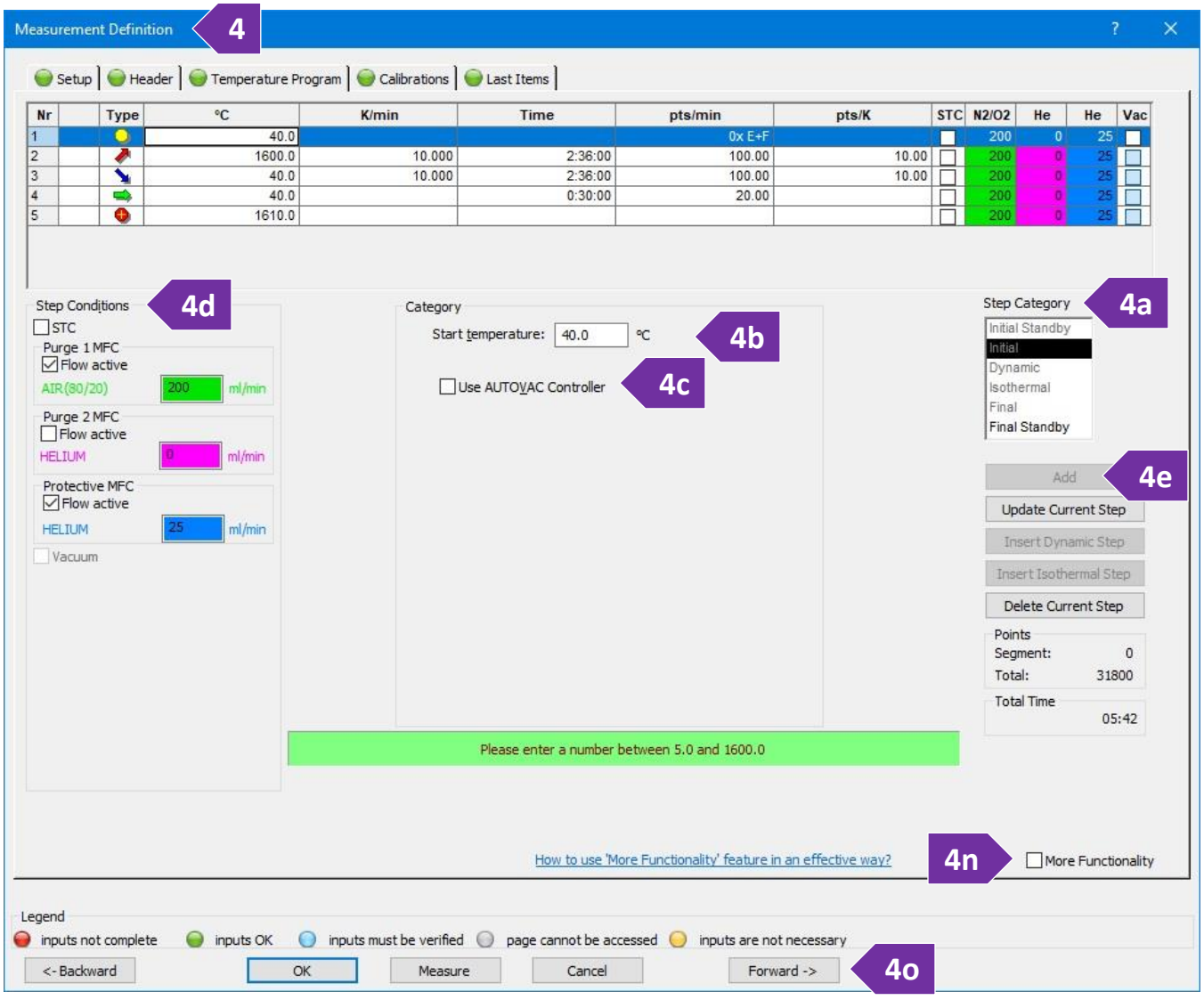
measurement that is different than the existing gases (nitrogen 5% hydrogen balanced with nitrogen, air, or argon), please talk to a staff

e. (Optional) Provide details about 'Laboratory', 'Project', 'Operator', and 'Materials'

f. In the 'Remark' field please provide any additional details you feel are important for reproducing the experiment. Temperature profile, type and flow of gases are automatically recorded during your measurement

g. Press on the 'Forward ->' button or press on the 'Temperature Program' tab

4. On the 'Temperature Program' tab (figure 4), you are about to build the detailed temperature profile for your variable temperature measurement. The workflow on this tab starts by selecting the appropriate category from the 'Step Category' panel, then by selecting the temperature conditions from the 'Category' panel, and



finally by selecting the environment from the 'Step Conditions'. Once all selections are made, you press on the 'Add' button to add the temperature segment in the profile. The recommended sequence of segments is:

a. Select 'Initial' from the 'Step Category' panel (figure 4a)
b. Type the starting temperature in 'Start temperature' in the 'Category' panel (figure 4b). Starting temperature can be either a temperature point
   - Near (±8 degrees) the actual temperature of the furnace. Please check the front panel on the instrument for the actual temperature, or
   - Well above the actual temperature. In this case, software will preheat the furnace before automatically starting the measurement, or
   - Well below the actual temperature only when a cooling attachment is connected (available only for the stainless-steel furnace)
c. Leave the 'Use AUTOVAC Controller' unselected unless you need to evacuate (apply vacuum) the furnace before starting the measurement (figure 4c)
d. Under the 'Step Conditions' panel (figure 4d)
   i. ***Uncheck the 'STC' option.*** See step 4k below for more details about the 'STC' option in combination with an isothermal step
   ii. (Mandatory) Set the 'Protective MFC' gas (Helium or Nitrogen) to at least 25 ml/min. This gas flow option must be always on regardless of your other gas settings. Failure to use a protective flow might result in contamination and/or damage of the microbalance electronics
   iii. Set the 'Purge 1 MFC' or 'Purge 2 MFC' based on the type of gas needed for your experiment. Type of gas (e.g., Helium, air, etc.) per MFC is shown next to the flow setting. A flow of at least 50 ml/min is recommended. Use higher flow (150 ml/min or so) in case your sample releases highly corrosive gases
e. Press on the 'Add' button to add the initial segment into the temperature profile (figure 4e)
f. You need to make sure that gas flow is equilibrated, and furnace is purged with the gas of your choice before increasing temperature. Therefore, select 'Isothermal' from the 'Step Category' and under the 'Category' panel type either
   - 5 mins or longer for measurements under air, or
   - 10 mins or longer for any inert or special gas
g. For all temperature segments in your profile, leave the gas type and flow as is (most common) unless you need to change them for special experiments. Note that any changes to the type or flow of the gas will affect the continuity of the weight trace due to changes to the buoyancy
h. Press on the 'Add' button to add the isothermal segment into the temperature profile

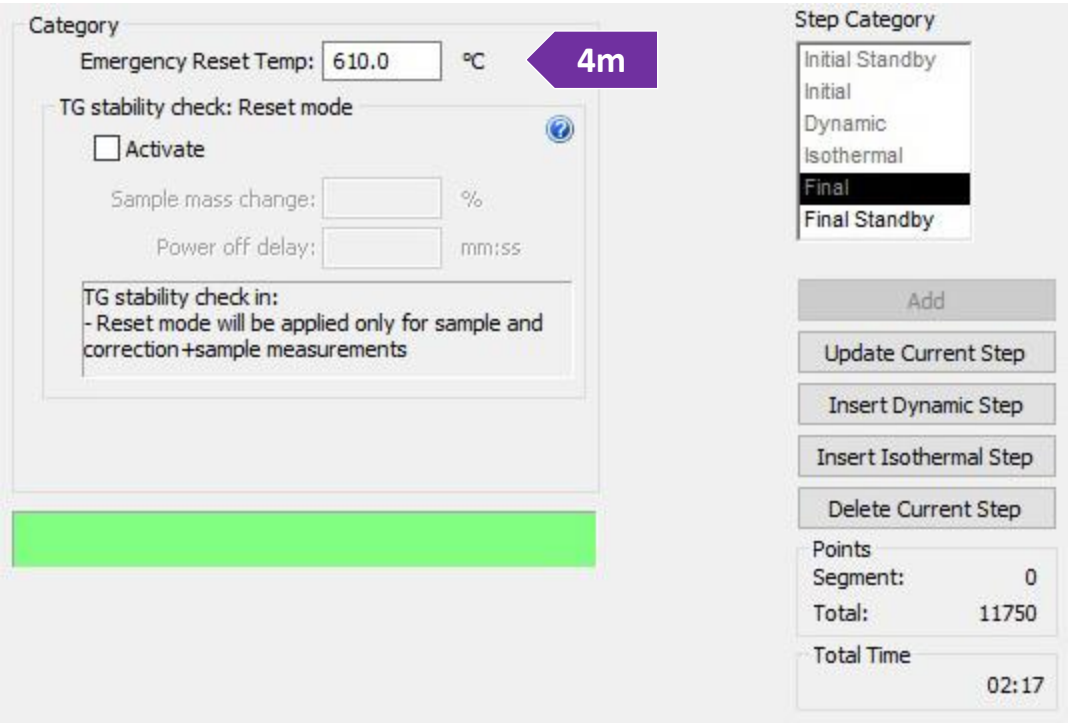
i. Select 'Dynamic' from the 'Step Category' panel and provide the target temperature and rate. Minimum and maximum allowable values of each setting are shown in the green text field under the 'Category' panel. Set the gases at the 'Step Conditions' panel and press on the 'Add' button to add the dynamic segment into the temperature profile

j. Keep adding temperature segments according to the temperature profile of your choice

k. For isothermal steps of where the actual temperature of the sample (and not the furnace) is important, enable the 'STC' option. By default, the temperature you provide in any step of the temperature program, e.g., dynamic or isothermal, corresponds to the temperature of the furnace (thermocouple on the furnace) and not necessarily of the sample (thermocouple on the carrier and under the sample). This temperature difference between the sample and the furnace will depend mainly on the type of the gas flowing in the furnace, the flow rate, the temperature ramp rate, and the absolute temperature point. The temperature data plotted on the screen and recorded in the exported file correspond to the actual temperature of the sample and not the furnace. It is not recommended to enable 'STC' on a dynamic step

l. The last dynamic segment in your temperature profile must end near a room temperature value (25-40 C) even if you are not interested in collecting/analyzing data on cooling. This step is important to ensure STA is immediately ready for the next measurement after the end of your collection

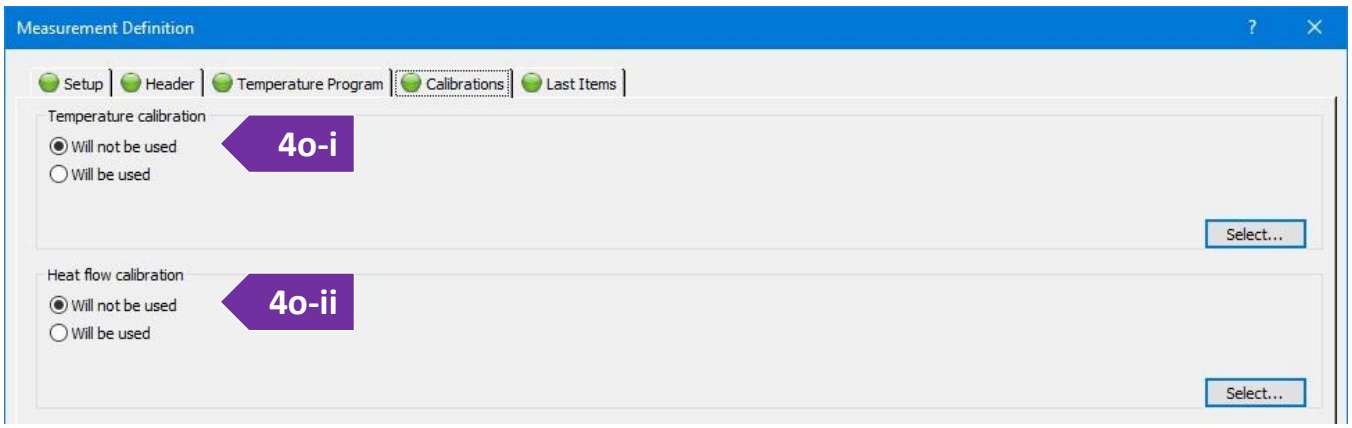
m. Once you have added all temperature segments needed for your temperature profile, select 'Final' under the 'Step Category' panel (figure 4m), accept the default values (which is 10 degrees on top of your highest temperature point in your profile), and press on the 'Add' button. This 'Final' step is more like an



overtemperature safety step in case of a hardware failure during collection. Please do not use the 'Final Standby' option since this will turn off all gases and create a mild vacuum in the furnace that will require the next use to refill the furnace with gas

n. (Optional) Select the 'More Functionality' option to see a graph of your temperature profile that might help you overview and verify your settings (figure 4n)

o. Press on the 'Forward ->' button or press on the 'Calibrations' tab (figure 4o)



i. (Optional) On the 'Temperature calibration' panel, select a calibration file you might have (figure 4o-i). Calibration files are used to correct for any temperature offsets between the actual temperature of the sample and thermocouple of the carrier. For example, if you sample is in a thick ceramic crucible or sealed in an ampoule, the actual temperature of the sample will be a little bit lower than the temperature recorded by the carrier thermocouple. A temperature calibration file requires separate measurements of materials with known melting points under the same conditions used for measuring your samples

ii. (Optional) On the 'Heat flow calibration' panel, select a heat flow calibration file (figure 4o-ii). This option is more relevant for DSC measurements of where the raw signal on the carrier (µV/mg) must be converted to energy units (e.g., J/mg). The heat flow calibration file is created by measuring a standard, i.e., Sapphire disc, under the same conditions used for the sample and the creation of a calibration curve by using the software. See a staff if a calibration file for the temperature range or environment of interest does not exist

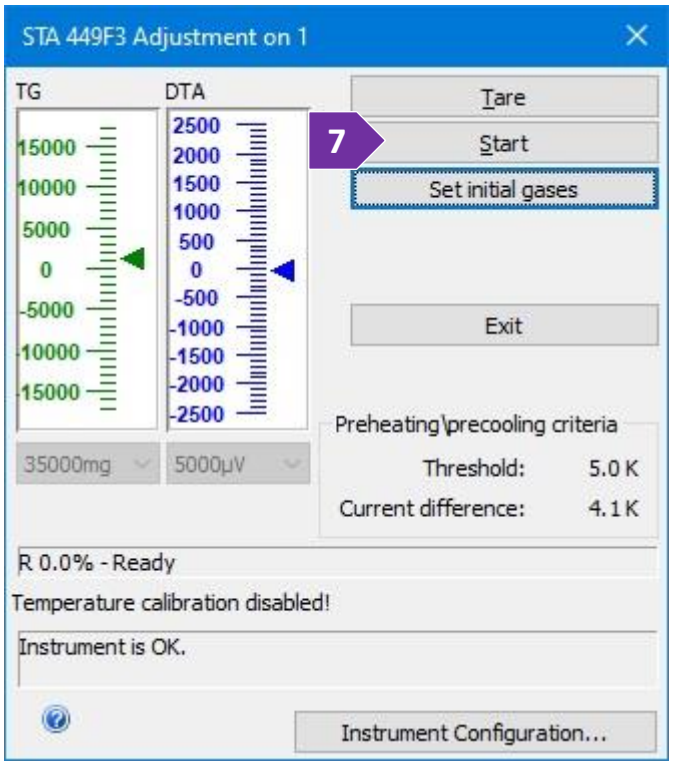
iii. Press on the 'Forward ->' button or press on the 'Last Items' tab

5. On the 'Last Items' tab, you need to provide the path and filename of the sample file. Use your personal folder under your group folder on the 'D' drive to save the file

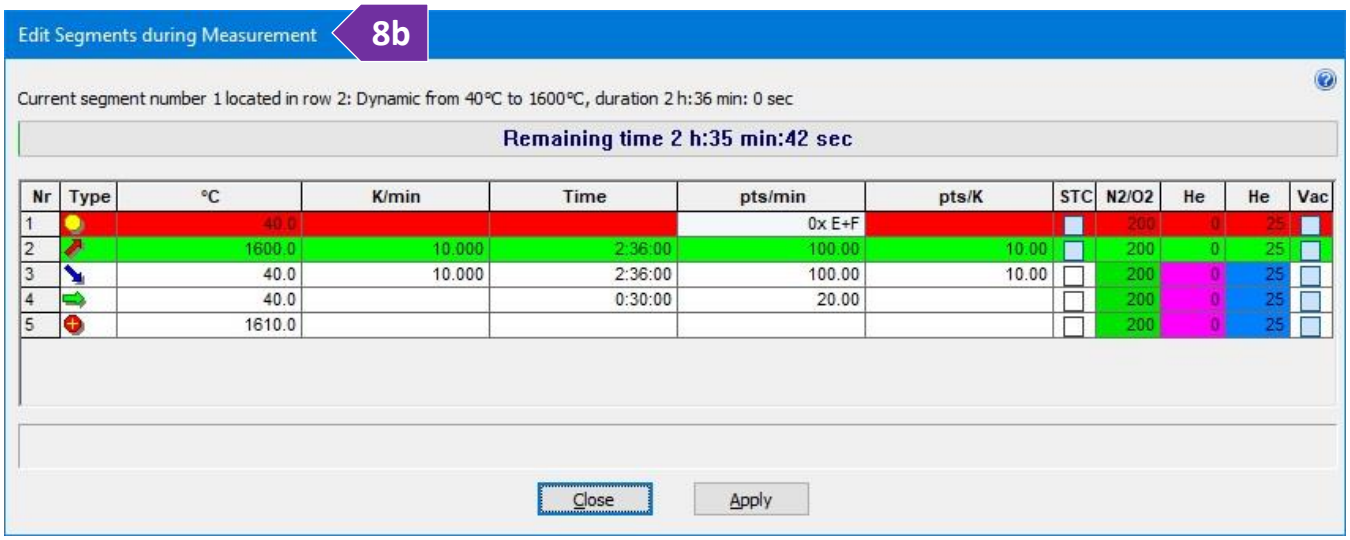
6. Go to the next step to start the measurement by pressing on either:
   - the 'Measure' button, or

- the 'OK' button, and then pressing on the green play button on the toolbox

7. The final window for starting the measurement will open. When actual temperature is within the temperature threshold under the 'Preheating\precooling criteria' panel, the 'Start' button will be enabled (figure 7). Press on the 'Start' button to start the measurement. A countdown timer will be visible on the screen with the remaining time of your measurement. Press on the 'Tare' button only if you are using a 'Weighing mode' (step 2k) that is different than 'Manual input' when working with extremely air-sensitive samples



8. (Optional) In case you need to edit acquisition parameters on-the-fly while your measurement is running, e.g., extending an isothermal step:
   a. On the main window, under the menu 'Measurement', press on the 'View/Edit Running Measurement Program'
   b. The 'Edit Segments during Measurement' window opens (figure 8b)

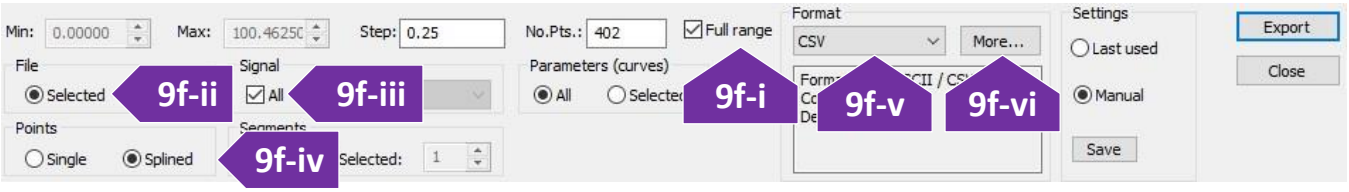


   i. Software colors segments that are completed in red, running segments in green, and pending segments in white
   ii. Remaining time of the running segment (in green) is shown as a progress bar on the top of the window

iii. Double press on any parameter and/or select a tick box on either a running and/or pending segment to edit their values

iv. Press on the 'Apply' button to apply the new settings

9. When measurement is done:
   a. Remove your sample and lower the furnace as described in step 2, 3, 5, and 6 under the 'Loading a sample into the instrument' section
   b. Place contaminated ceramic (Al_2O_3) crucibles and ceramic lids into the 'For STA Al_2O_3 crucibles' labeled vial located in the hood across the STA
   c. Dispose of any used Aluminum pans/lids into the 'Hazardous - For STA Al crucibles' labeled vial located in the hood across the STA
   d. Remove any vials, weighing paper, etc. you may have left in the room
   e. End your reservation in NUcore
10. To convert your data to an ASCII text file:
   a. Start the 'Proteus Analysis' software (icon on desktop). More details about exporting/converting data can be found under the 'Exporting data' section
   b. Load your file
   c. (Optional) Press on the 'T/t' icon (X-Time / X-Temperature) to plot the data as a function of temperature
   d. Select either the TGA or DTA (if applicable) curve in the plot by clicking on it
   e. Under the 'Extras' menu, select 'Export Data'
   f. On the menu above your plot:



i. Tick 'Full range' (figure 9f-i)

ii. Under the 'File' panel, select 'Selected' (figure 9f-ii)

iii. Under the 'Signal' panel, tick on 'All' (figure 9f-iii)

iv. Under the 'Points' panel, select 'Splined' (figure 9f-iv)

v. Under the 'Format' panel, select 'CSV' (most common) (figure 9f-v)

vi. (Optional) Press on the 'More…' button and change the output type of the file to be exported (figure 9f-vi)

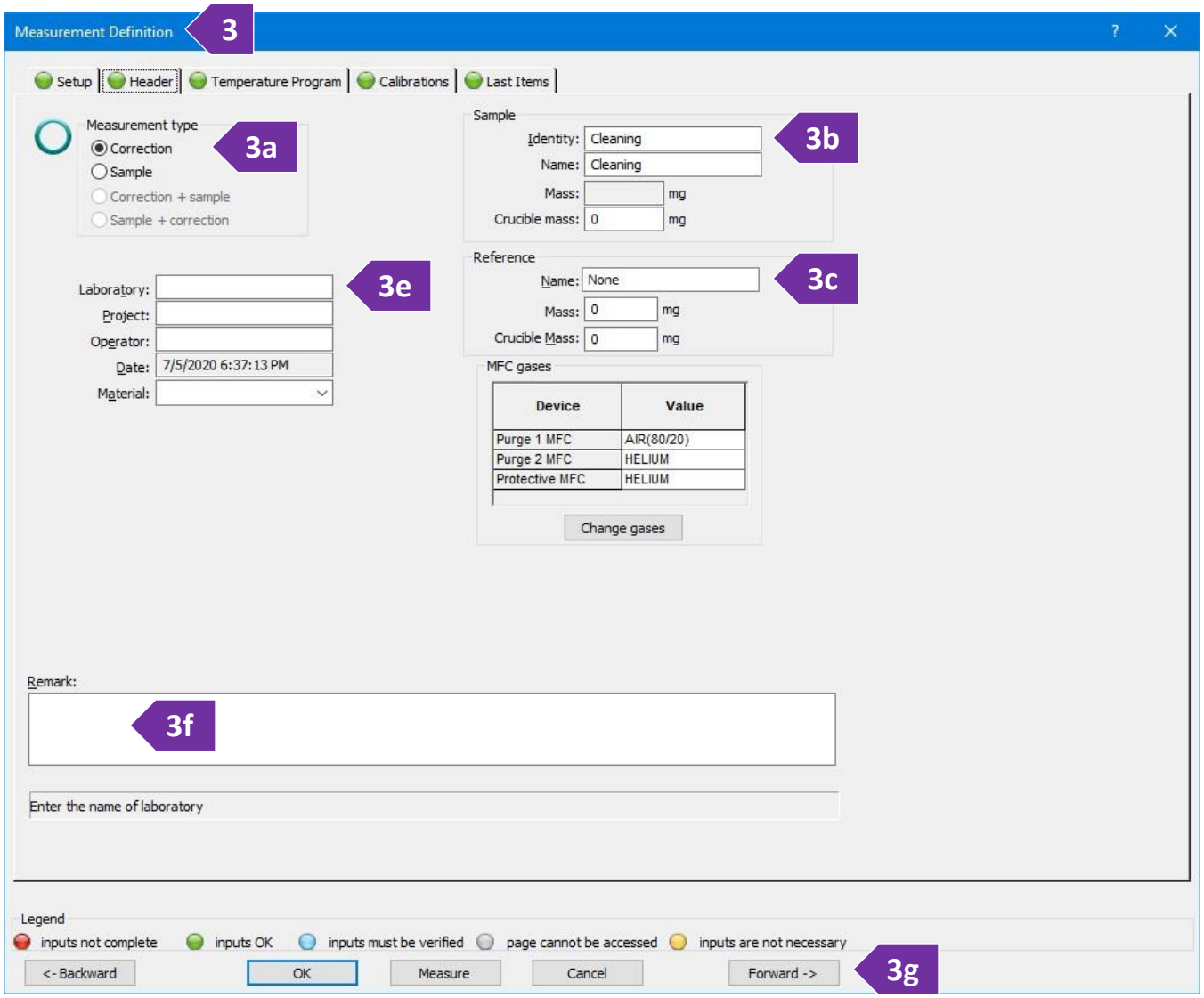
vii. Press on the 'Export' button

viii. Set the file name and verify that you are saving into your group folder

B. TGA/DTA CORRECTION FILE MEASUREMENT

To create a baseline-corrected measurement from a previously measured baseline/correction file:

1. Load the file that contains the baseline measurement by pressing on the 'File' menu and selecting 'Open'
2. On the 'Setup' tab, all options will be pre-selected based on the options used for the baseline measurement you loaded
3. On the 'Header' tab (figure 3) of the 'Measurement Definition' window (red disc-like symbol next to each tab name and textbox indicates required fields), you are going to provide some sample specific information:



   a. In the 'Measurement type' panel, select 'Correction + Sample'
   b. In the 'Sample' panel provide
      i. 'Identity' such as sample code, composition, etc.

ii. 'Name' such as sample code, composition, etc.

iii. 'Mass' for the sample mass (without the crucible). The mass value will be used by the software to calculate the corresponding percentage weigh value as a function of temperature

iv. 'Crucible mass' for the mass of the empty crucible placed in the sample position of the carrier (front side). The mass value is not used for any calculation, but value serves as an important info about the size of the crucible used for the measurement. Size/volume of the crucible is important for the baseline correction process

c. In the 'Reference' panel, which is relevant only for DTA or DSC measurements, please provide:

i. 'Name' for the name of the standard used, e.g., Al_2O_3 or empty crucible

ii. 'Mass' for the standard mass (without the crucible). For the sealed ampoule Al_2O_3 standard, please check the latest mass values under 'procedures/reference.txt'

iii. 'Crucible mass' for the mass of the empty crucible placed in the reference position of the carrier (back side)

d. ***Ensure that the proper gas is selected both physically and electronically***, see 'Change type of gas' section for more details

e. (Optional) Provide details about 'Laboratory', 'Project', 'Operator', and 'Materials' (figure 3e)

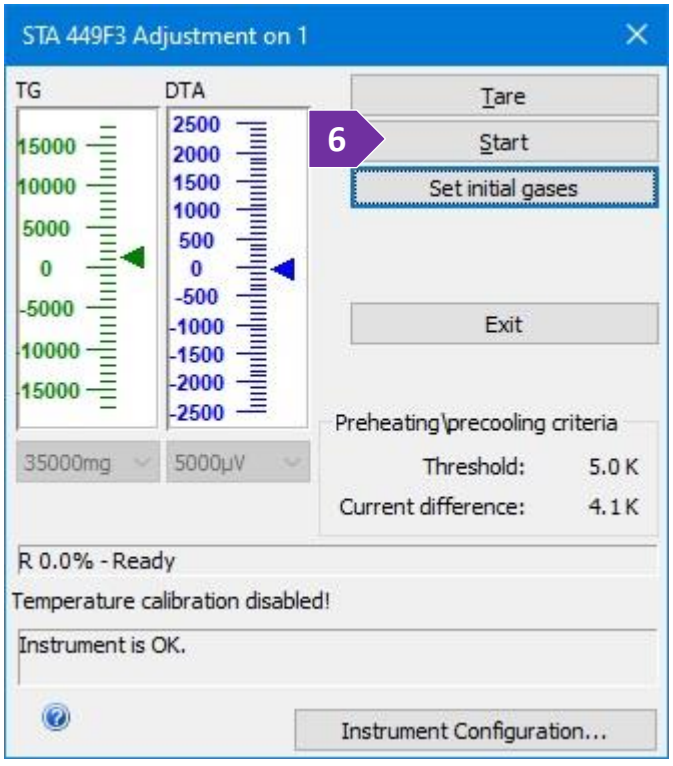
f. In the 'Remark' field (figure 3f) please provide any additional details you feel are important for reproducing the experiment. Temperature profile, type and flow of gases are automatically recorded during your measurement

g. Press on the 'Forward ->' button (figure 3g) or press on the 'Temperature Program' tab

4. On the 'Last Items' tab, you need to provide the path and filename of the sample file. Use your personal folder under your group folder on the 'D' drive to save the file

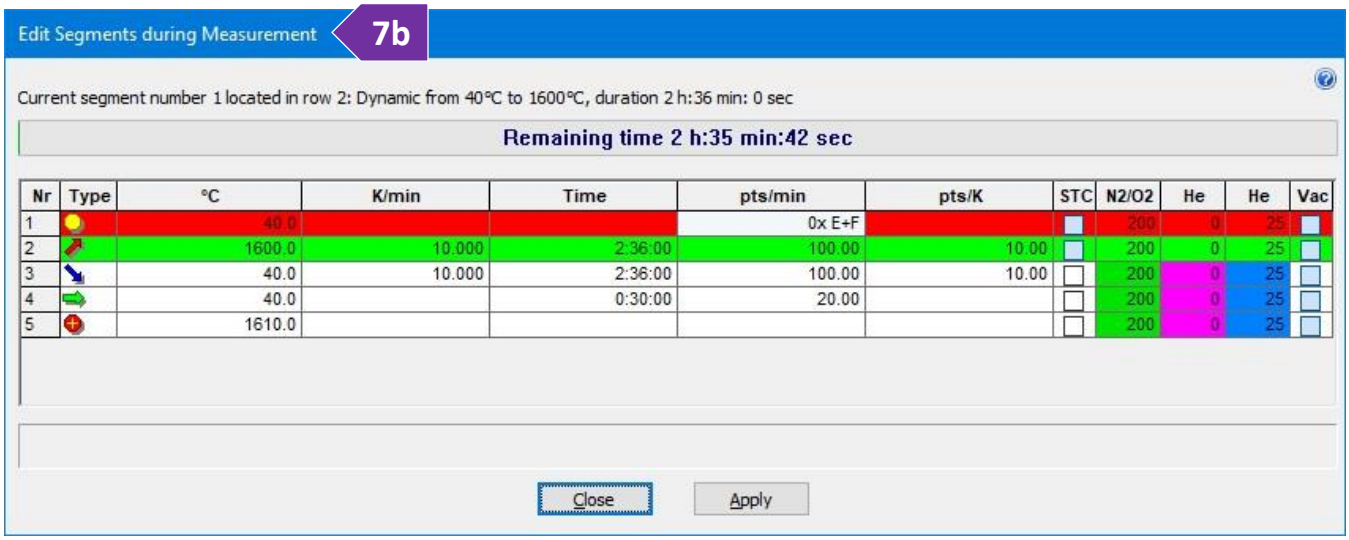
5. Go to the next step to start the measurement by pressing on either:
   - the 'Measure' button, or
   - the 'OK' button, and then pressing on the green play button on the toolbox

6. The final window for starting the measurement will open. When actual temperature is within the



temperature threshold under the 'Preheating\precooling criteria' panel, the 'Start' button will be enabled (figure 6). Press on the 'Start' button to start the measurement. A countdown timer will be visible on the screen with the remaining time of your measurement. Press on the 'Tare' button only if you are using a 'Weighing mode' (step 2k) that is different than 'Manual input' when working with extremely air-sensitive samples

7. (Optional) In case you need to edit acquisition parameters on-the-fly while your measurement is running, e.g., extending an isothermal step:
   a. On the main window, under the menu 'Measurement', press on the 'View/Edit Running Measurement Program'
   b. The 'Edit Segments during Measurement' window opens (figure 7b)



      i. Software colors segments that are completed in red, running segments in green, and pending segments in white
      ii. Remaining time of the running segment (in green) is shown as a progress bar on the top of the window
      iii. Double press on any parameter and/or select a tick box on either a running and/or pending segment to edit their values
      iv. Press on the 'Apply' button to apply the new settings
8. When measurement is done:
   a. Remove your sample and lower the furnace as described in step 2, 3, 5, and 6 under the 'Loading a sample into the instrument' section
   b. Place contaminated ceramic (Al_2O_3) crucibles and ceramic lids into the 'For STA Al_2O_3 crucibles' labeled vial located in the hood across the STA

c. Dispose of any used Aluminum pans/lids into the 'Hazardous - For STA Al crucibles' labeled vial located in the hood across the STA

d. Remove any vials, weighing paper, etc. you may have left in the room

e. End your reservation in NUcore

9. To convert your data to an ASCII text file:

a. Start the 'Proteus Analysis' software (icon on desktop). More details about exporting/converting data can be found under the 'Exporting data' section

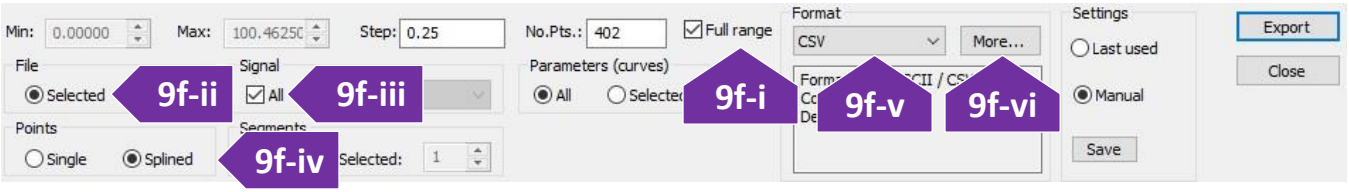
b. Load your file

c. (Optional) Press on the 'T/t' icon (X-Time / X-Temperature) to plot the data as a function of temperature

d. Select either the TGA or DTA (if applicable) curve in the plot by clicking on it

e. Under the 'Extras' menu, select 'Export Data'

f. On the menu above your plot:



i. Tick 'Full range' (figure 9f-i)

ii. Under the 'File' panel, select 'Selected' (figure 9f-ii)

iii. Under the 'Signal' panel, tick on 'All' (figure 9f-iii)

iv. Under the 'Points' panel, select 'Splined' (figure 9f-iv)

v. Under the 'Format' panel, select 'CSV' (most common) (figure 9f-v)

vi. (Optional) Press on the 'More…' button and change the output type of the file to be exported (figure 9f-vi)

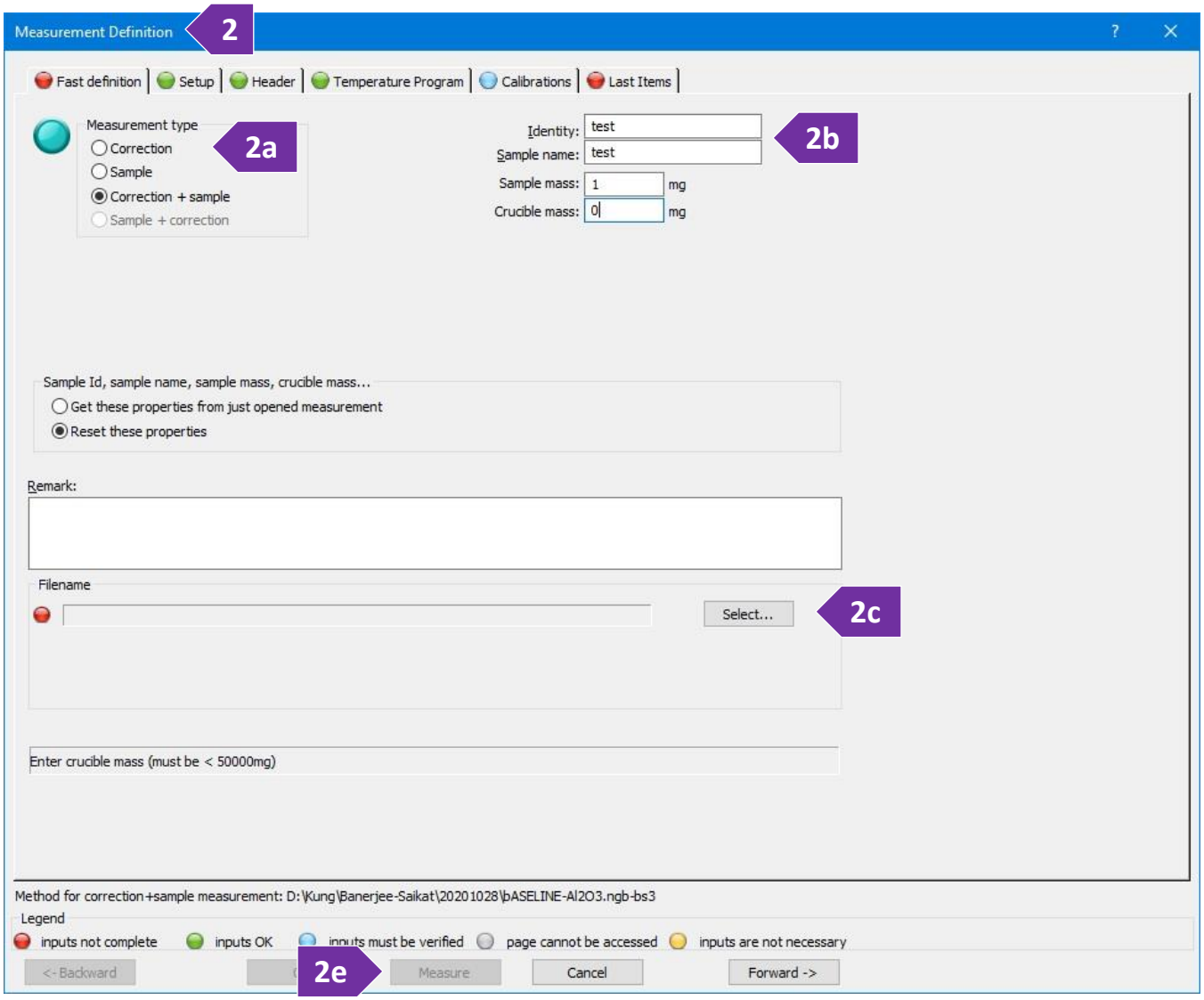
vii. Press on the 'Export' button

viii. Set the file name and verify that you are saving into your group folder

C. TGA/DTA MEASUREMENT WITH A CORRECTION FILE

To create a new corrected sample measurement based on a pre-collected correction file (baseline):

1. Press on the 'File' menu and select 'Open. If an existing procedure is loaded, select 'OK' in the warning message regarding the deletion of the current procedure. The 'Measurement Definition' window opens
2. On the 'Fast definition' tab (figure 2) of the 'Measurement Definition' window (red disc-like symbol next to each tab name and textbox indicates required fields), you are going to provide some sample specific information:



   a. In the 'Measurement type' panel, select 'Correction + Sample'. Measuring a correction (baseline) is highly recommended for accurate mass changes. Uncorrected measurements may have overestimated weight values that depend on the type of flowing gas due to buoyancy affects, e.g., ~ 0.2 mg under He or ~ 0.8

mg under air flow. Correction can be measured either before or after a sample measurement. Correction files can be reused for future sample corrections only if the conditions of the experiment remain the same. Please refer to the corresponding sections in this user manual depending on the order of the sample and correction measurement (correction first and then sample or sample first and then correction)

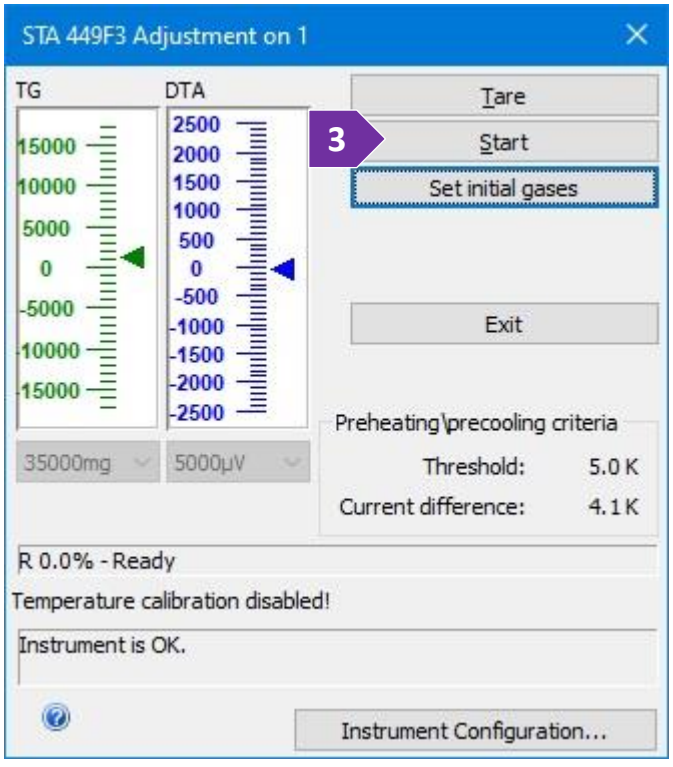
b. In the 'Sample' panel provide
   i. 'Identity' such as sample code, composition, etc. (figure 2b)
   ii. 'Name' such as sample code, composition, etc. (figure 2b)
   iii. 'Mass' for the sample mass (without the crucible). The mass value will be used by the software to calculate the corresponding percentage weigh value as a function of temperature
   iv. 'Crucible mass' for the mass of the empty crucible placed in the sample position of the carrier (front side). The mass value is not used for any calculation, but value serves as an important info about the size of the crucible used for the measurement. Size/volume of the crucible is important for the baseline correction process

c. Press on the 'Select…' button to define the file path and filename for the data collection (figure 2c). This is the path for the corrected data of your sample

d. ***Ensure that the proper gas is selected both physically and electronically***, see 'Change type of gas' section for more details

e. Press on the 'Measure' button (figure 2e)

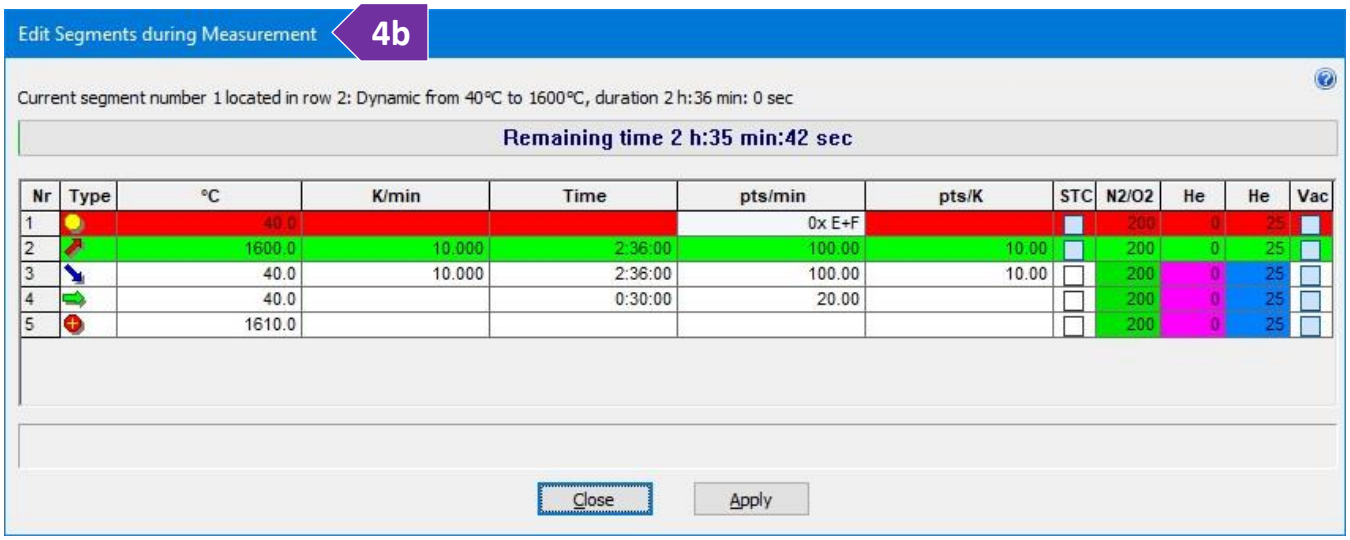
3. The final window for starting the measurement will open. When actual temperature is within the temperature threshold under the 'Preheating\precooling criteria' panel, the 'Start' button will be enabled (figure 3). Press on the 'Start' button to start the measurement. A countdown timer will be visible on the screen with the remaining time of your measurement. Press on the 'Tare' button only if you are using a 'Weighing mode' (step 2k) that is different than 'Manual input' when working with extremely air-sensitive samples



4. (Optional) In case you need to edit acquisition parameters on-the-fly while your measurement is running, e.g., extending an isothermal step:

a. On the main window, under the menu 'Measurement', press on the 'View/Edit Running Measurement Program'

b. The 'Edit Segments during Measurement' window opens (figure 4b)



i. Software colors segments that are completed in red, running segments in green, and pending segments in white

ii. Remaining time of the running segment (in green) is shown as a progress bar on the top of the window

iii. Double press on any parameter and/or select a tick box on either a running and/or pending segment to edit their values

iv. Press on the 'Apply' button to apply the new settings

5. When measurement is done:

a. Remove your sample and lower the furnace as described in step 2, 3, 5, and 6 under the 'Loading a sample into the instrument' section

b. Place contaminated ceramic (Al_2O_3) crucibles and ceramic lids into the 'For STA Al_2O_3 crucibles' labeled vial located in the hood across the STA

c. Dispose of any used Aluminum pans/lids into the 'Hazardous - For STA Al crucibles' labeled vial located in the hood across the STA

d. Remove any vials, weighing paper, etc. you may have left in the room

e. End your reservation in NUcore

6. To convert your data to an ASCII text file:

a. Start the 'Proteus Analysis' software (icon on desktop). More details about exporting/converting data can be found under the 'Exporting data' section

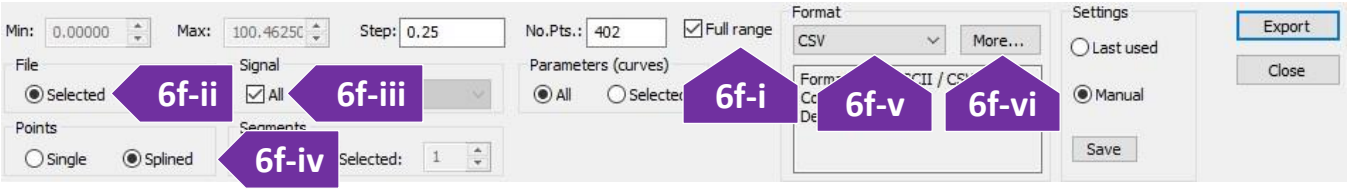
b. Load your file

c. (Optional) Press on the 'T/t' icon (X-Time / X-Temperature) to plot the data as a function of temperature

d. Select either the TGA or DTA (if applicable) curve in the plot by clicking on it

e. Under the 'Extras' menu, select 'Export Data'

f. On the menu above your plot:



i. Tick 'Full range' (figure 6f-i)

ii. Under the 'File' panel, select 'Selected' (figure 6f-ii)

iii. Under the 'Signal' panel, tick on 'All' (figure 6f-iii)

iv. Under the 'Points' panel, select 'Splined' (figure 6f-iv)

v. Under the 'Format' panel, select 'CSV' (most common) (figure 6f-v)

vi. (Optional) Press on the 'More…' button and change the output type of the file to be exported (figure 6f-vi)

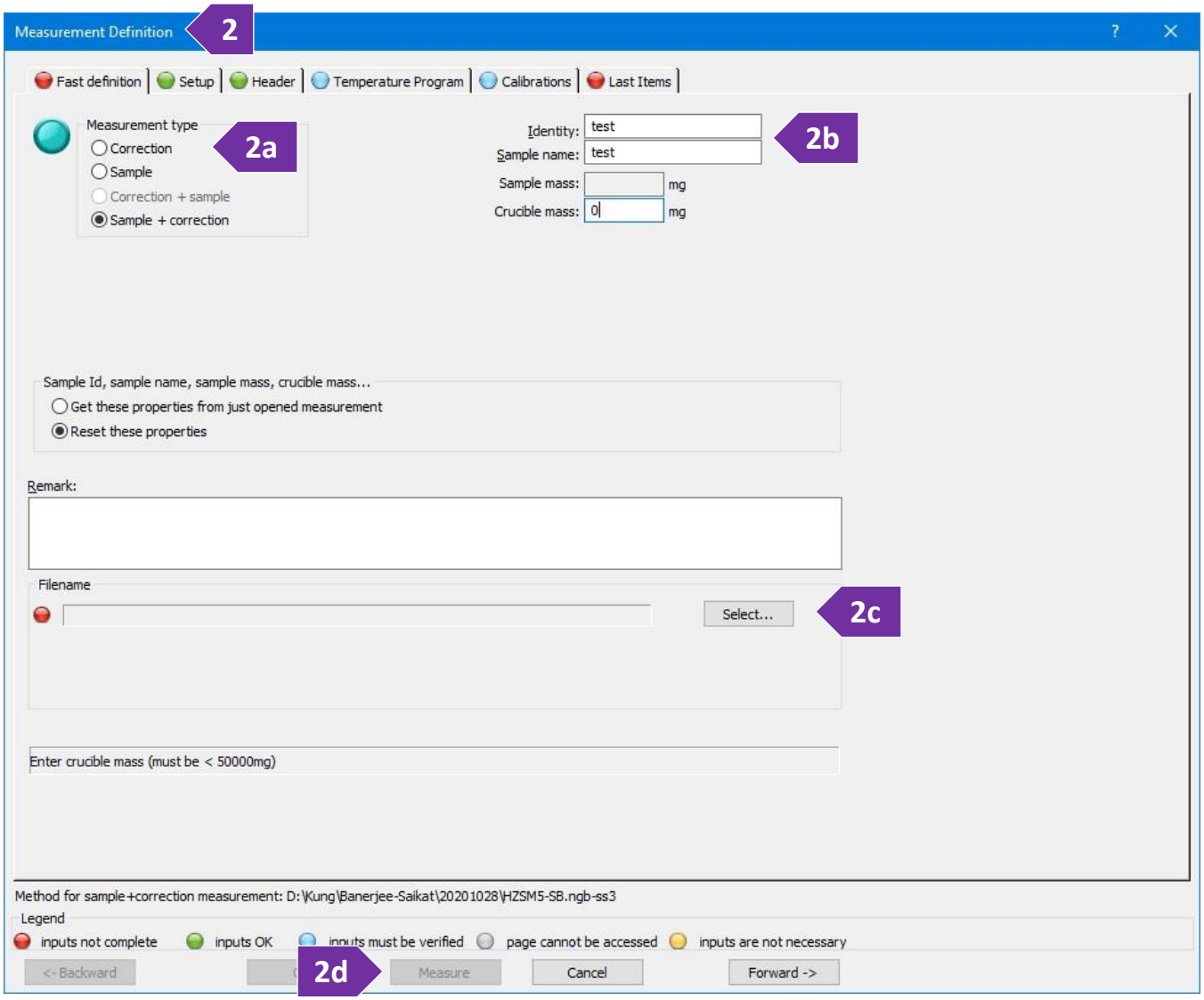
vii. Press on the 'Export' button

viii. Set the file name and verify that you are saving into your group folder

D. TGA/DTA CORRECTION MEASUREMENT WITH A SAMPLE FILE

To create a new corrected sample measurement based on a pre-collected correction file (baseline):

1. Press on the 'File' menu and select 'Open. If an existing procedure is loaded, select 'OK' in the warning message regarding the deletion of the current procedure. The 'Measurement Definition' window opens
2. On the 'Fast definition' tab (figure 2) of the 'Measurement Definition' window (red disc-like symbol next to each tab name and textbox indicates required fields), you are going to provide some sample specific information:



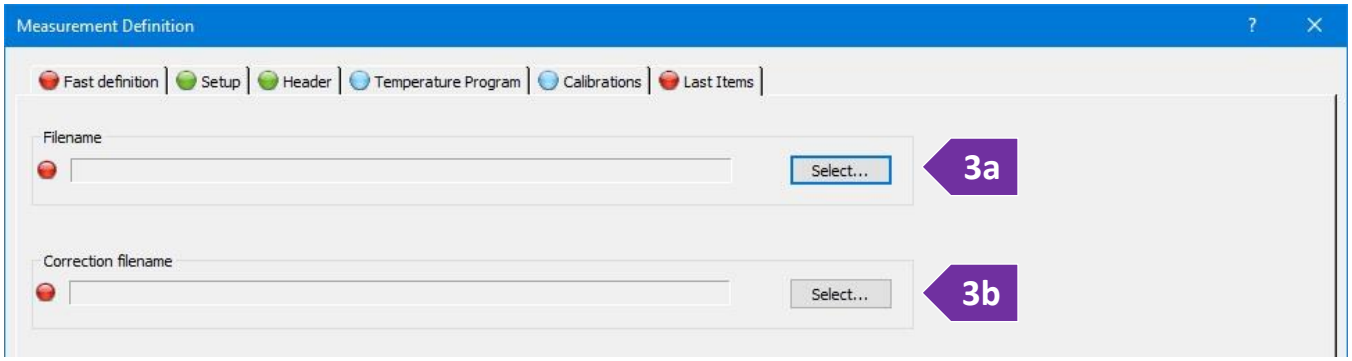
   a. In the 'Measurement type' panel, select 'Sample + Correction'. Measuring a correction (baseline) is highly recommended for accurate mass changes. Uncorrected measurements may have overestimated weight values that depend on the type of flowing gas due to buoyancy affects, e.g., ~ 0.2 mg under He or ~ 0.8

mg under air flow. Correction can be measured either before or after a sample measurement. Correction files can be reused for future sample corrections only if the conditions of the experiment remain the same. Please refer to the corresponding sections in this user manual depending on the order of the sample and correction measurement (correction first and then sample or sample first and then correction)

b. In the 'Sample' panel provide
   i. 'Identity' such as sample code, composition, etc. (figure 2b)
   ii. 'Name' such as sample code, composition, etc. (figure 2b)
   iii. 'Mass' for the sample mass (without the crucible). The mass value will be used by the software to calculate the corresponding percentage weigh value as a function of temperature
   iv. 'Crucible mass' for the mass of the empty crucible placed in the sample position of the carrier (front side). The mass value is not used for any calculation, but value serves as an important info about the size of the crucible used for the measurement. Size/volume of the crucible is important for the baseline correction process

c. Press on the 'Select…' button to define the file path and filename for the data collection (figure 2c). This is the path for the corrected data of your sample. At the next step, you will provide the path of the correction (baseline) file which can be used for any future runs

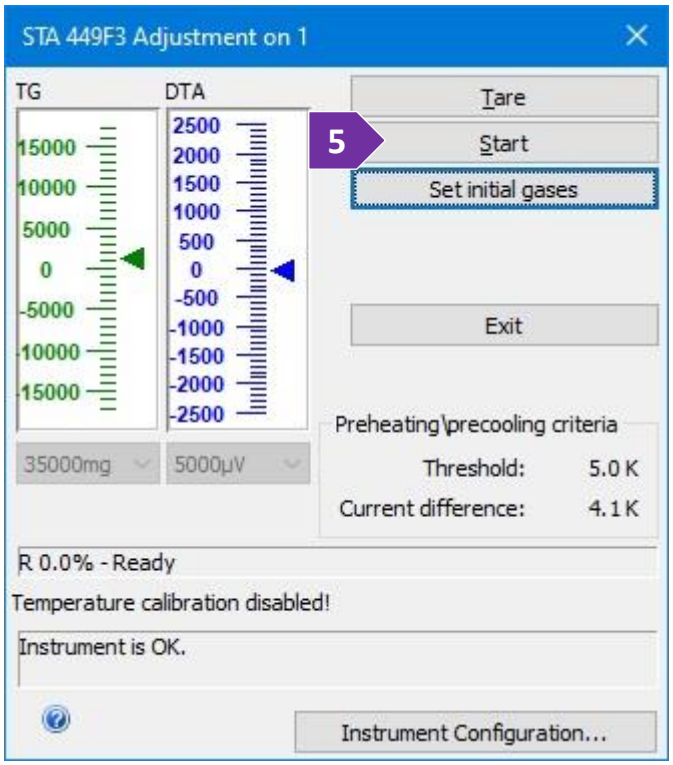
3. Select the 'Last Items' tab for providing the filename of the baseline file.



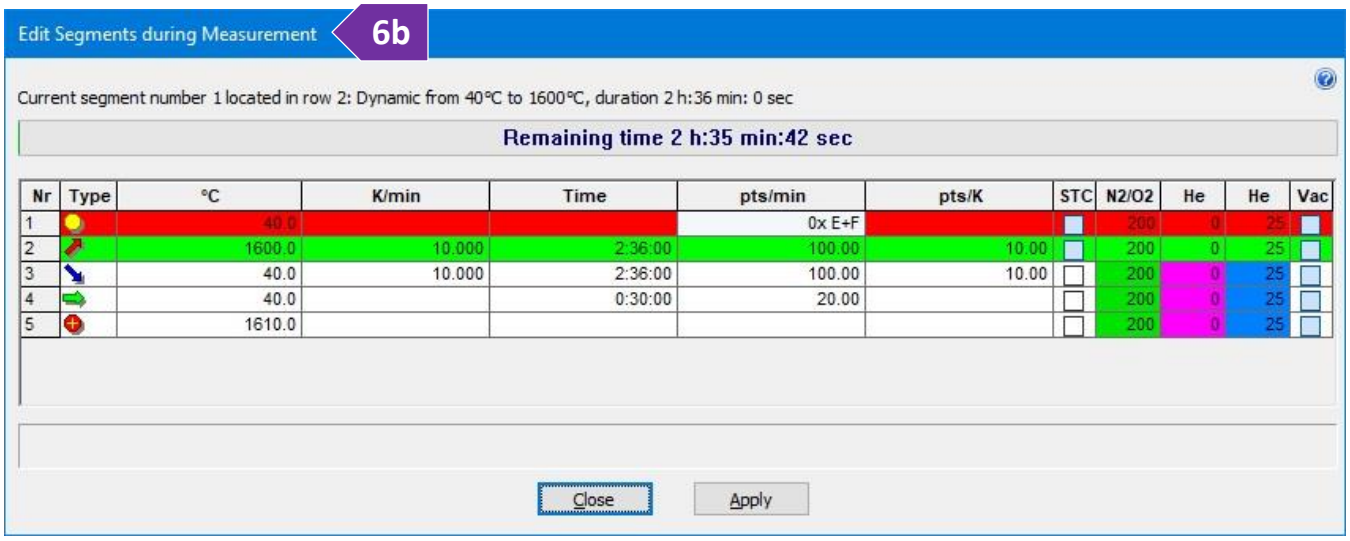
   a. The filename for the corrected data of your sample should be already populated from the previous step. If not, press on the top 'Select…' button (figure 3a) to provide the path and filename of your corrected data
   b. Press on the bottom 'Select…' button (figure 3b) to provide the path and filename of your correction (baseline) file

4. ***Ensure that the proper gas is selected both physically and electronically***, see 'Change type of gas' section for more details
5. Press on the 'Measure' button (figure 2d)

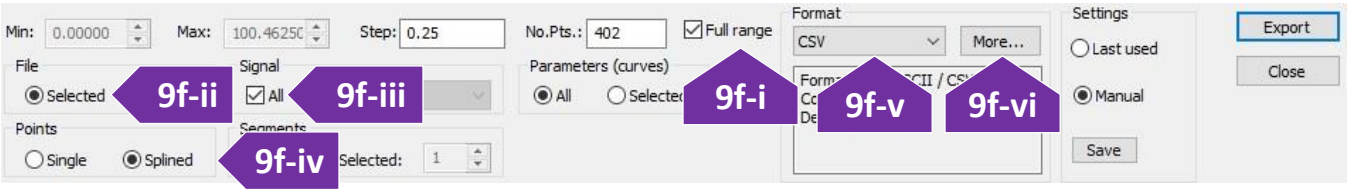
6. The final window for starting the measurement will open. When actual temperature is within the temperature threshold under the 'Preheating\precooling criteria' panel, the 'Start' button will be enabled (figure 5). Press on the 'Start' button to start the measurement. A countdown timer will be visible on the screen with the remaining time of your measurement. Press on the 'Tare' button only if you are using a 'Weighing mode' (step 2k) that is different than 'Manual input' when working with extremely air-sensitive samples



7. (Optional) In case you need to edit acquisition parameters on-the-fly while your measurement is running, e.g., extending an isothermal step:
   a. On the main window, under the menu 'Measurement', press on the 'View/Edit Running Measurement Program'
   b. The 'Edit Segments during Measurement' window opens (figure 6b)
      i. Software colors segments that are completed in red, running segments in green, and pending segments in white
      ii. Remaining time of the running segment (in green) is shown as a progress bar on the top of the window
      iii. Double press on any parameter and/or select a tick box on either a running and/or pending segment to edit their values
      iv. Press on the 'Apply' button to apply the new settings



8. When measurement is done:
    a. Remove your sample and lower the furnace as described in step 2, 3, 5, and 6 under the 'Loading a sample into the instrument' section
    b. Place contaminated ceramic (Al_2O_3) crucibles and ceramic lids into the 'For STA Al_2O_3 crucibles' labeled vial located in the hood across the STA
    c. Dispose of any used Aluminum pans/lids into the 'Hazardous - For STA Al crucibles' labeled vial located in the hood across the STA
    d. Remove any vials, weighing paper, etc. you may have left in the room
    e. End your reservation in NUcore
9. To convert your data to an ASCII text file:
    a. Start the 'Proteus Analysis' software (icon on desktop). More details about exporting/converting data can be found under the 'Exporting data' section
    b. Load your file
    c. (Optional) Press on the 'T/t' icon (X-Time / X-Temperature) to plot the data as a function of temperature
    d. Select either the TGA or DTA (if applicable) curve in the plot by clicking on it
    e. Under the 'Extras' menu, select 'Export Data'
    f. On the menu above your plot:

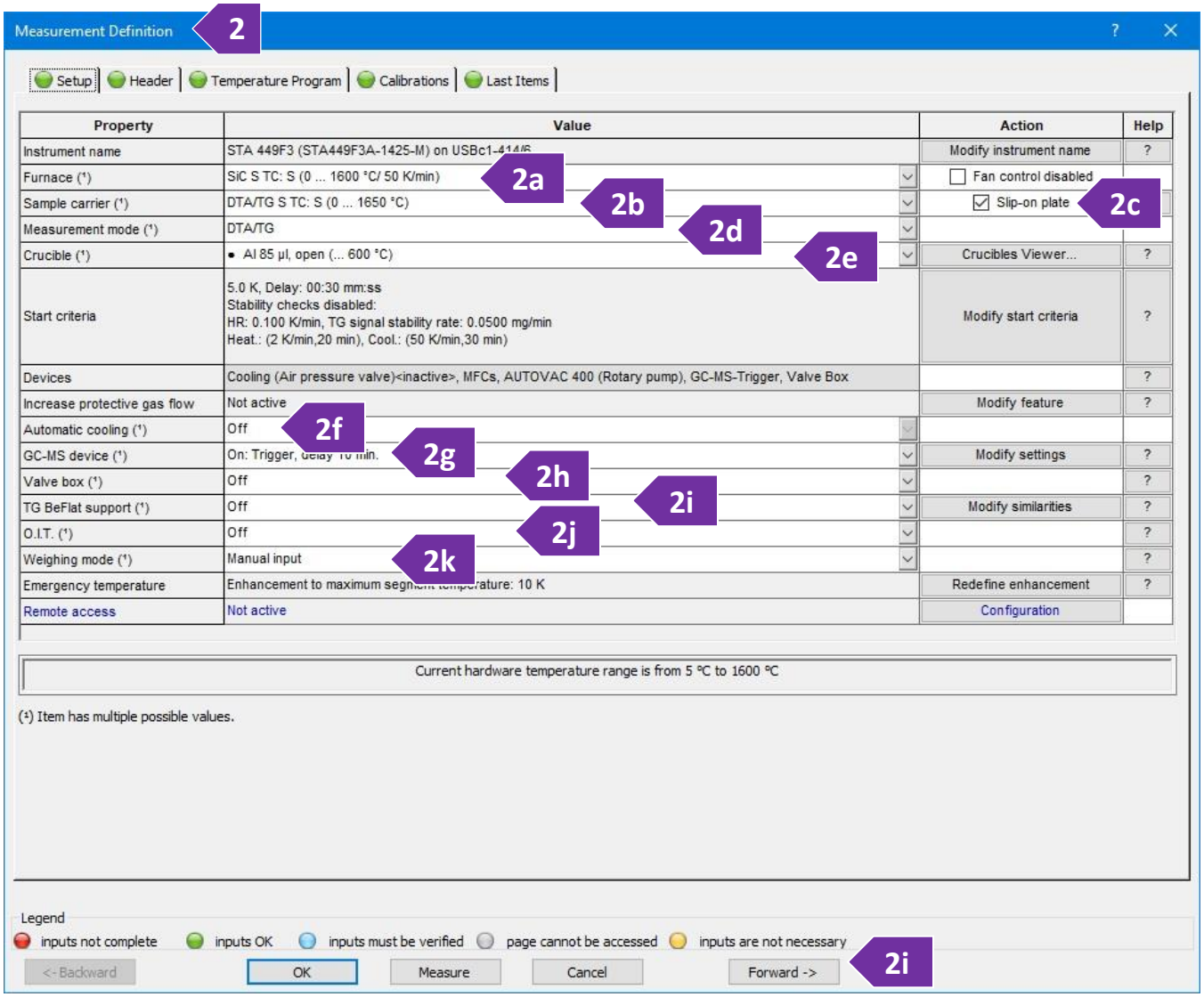


    i. Tick 'Full range' (figure 9f-i)
    ii. Under the 'File' panel, select 'Selected' (figure 9f-ii)
    iii. Under the 'Signal' panel, tick on 'All' (figure 9f-iii)
    iv. Under the 'Points' panel, select 'Splined' (figure 9f-iv)
    v. Under the 'Format' panel, select 'CSV' (most common) (figure 9f-v)
    vi. (Optional) Press on the 'More…' button and change the output type of the file to be exported (figure 9f-vi)
    vii. Press on the 'Export' button
    viii. Set the file name and verify that you are saving into your group folder

E. GC-MS WITH TGA/DTA MEASUREMENT

To create a completely new measurement with GC-MS and without a pre-collected correction file (baseline) or existing procedure that is part of an old measurement:

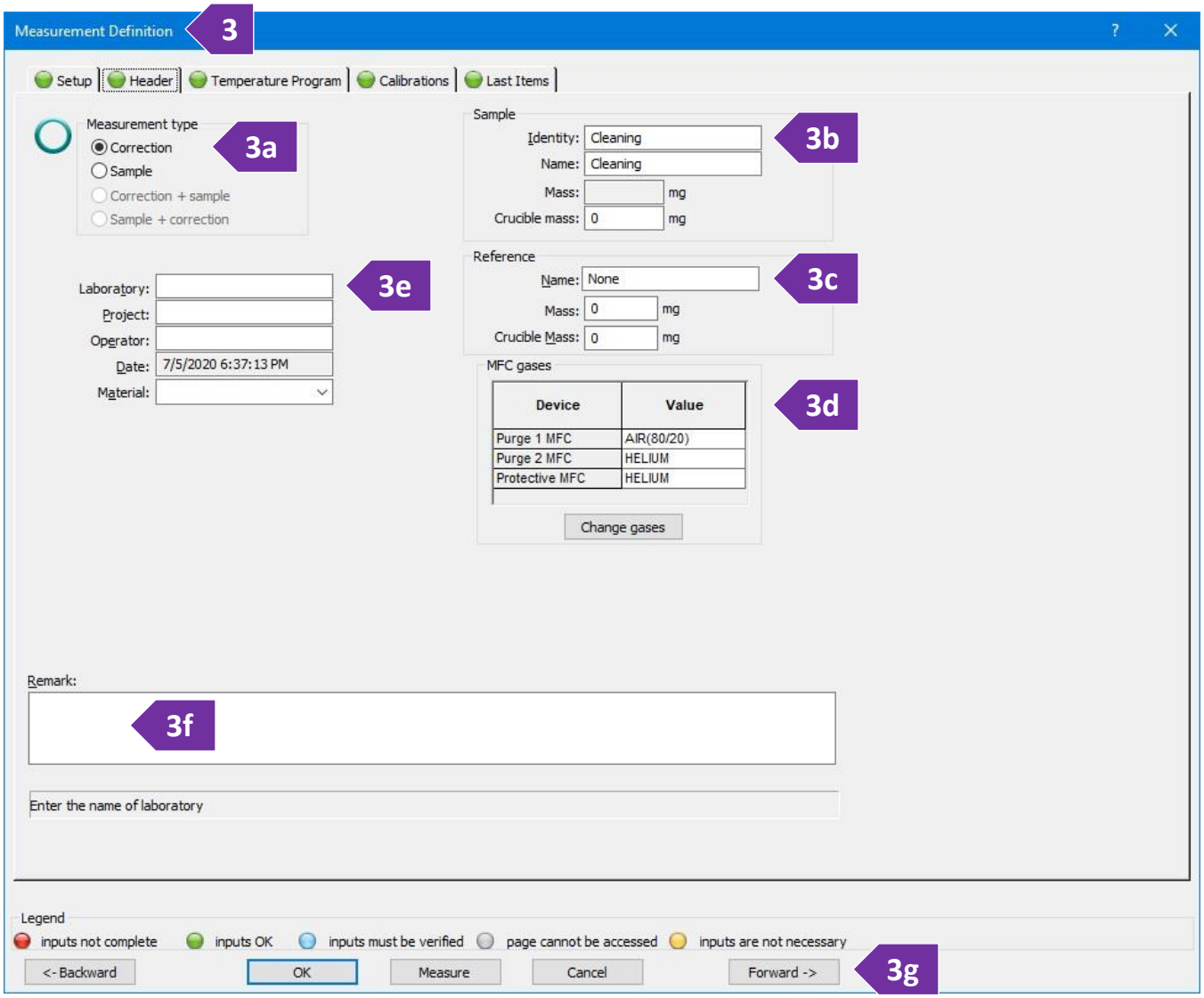
1. Press on the 'File' menu and select 'New'. If an existing procedure is loaded, select 'OK' in the warning message regarding the deletion of the current procedure. The 'Measurement Definition' window opens
2. On the 'Setup' tab of the 'Measurement Definition' window, you are going to set the main configuration parameters of your measurement (figure 2):



   a. 'Furnace' option will be pre-selected for you by the software based on your physical selection of the furnace (figure 2a). Only the Silicon Carbide furnace (and not the Stainless-Steel furnace) is connected to the GC-MS with the transfer line

b. 'Sample carrier' option will be pre-selected for you by the software based on the carrier installed, i.e., DTA default, DSC, or TGA only
c. 'Slip-on plate' must be selected when using the slip-on mounting plates (figure 4a). This option will also populate the crucible list (step 2e) with pan-like crucible options
d. 'Measurement mode' requires your input depending on what signal (TGA only, or DTA/TG) you would like to record. It is highly recommended to record DTA or DSC with the TGA data since you can get data for two measurements simultaneously
e. 'Crucible' needs to be set based on the type of crucible you are about to use, e.g., selecting Aluminum crucibles will automatically limit the maximum allowable temperature to 600C. Please verify that you have selected the 'Slip-on plate' option (step 2c) to see the correct list of crucible options
f. 'Automatic cooling' is available only for the stainless-steel furnace and not for the Silicon Carbide one. Use the 'Automatic cooling option' to control cooling below ~ 150C
g. 'GC-MS device' should be 'On'. Only the Silicon Carbide furnace (and not the Stainless-Steel furnace) is connected to the GC-MS with the transfer line
h. 'Valve box' should be set to 'Off' since this attachment is not available on our system
i. 'TG BeFlat support' should be set to 'Off'. Measuring experimentally the baseline is highly recommended instead of using a 'BeFlat' correction which is an algorithm for correcting of the buoyancy affect
j. 'O.I.T.' should be set to 'Off'
k. 'Weighing mode' should be set to 'Manual input' when mass of the sample is known. Use any of the other options in case you have extremely air sensitive samples and you would like to use the STA microbalance to measure the mass of the sample while being protected by the flowing gas
l. Press on the 'Forward ->' button or press on the 'Header' tab

3. On the 'Header' tab (figure 3) of the 'Measurement Definition' window (red disc-like symbol next to each tab name and textbox indicates required fields), you are going to provide some sample specific information:
   a. In the 'Measurement type' panel, select 'Sample'. Measuring a correction (baseline) is highly recommended for accurate mass changes. Uncorrected measurements may have overestimated weight values that depend on the type of flowing gas due to buoyancy affects, e.g., ~ 0.2 mg under He or ~ 0.8 mg under air flow. Correction can be measured either before or after a sample measurement. Correction files can be reused for future sample corrections only if the conditions of the experiment remain the same. Please refer to the corresponding sections in this user manual depending on the order of the sample and correction measurement (correction first and then sample or sample first and then correction)
   b. In the 'Sample' panel provide



i. 'Identity' such as sample code, composition, etc.

ii. 'Name' such as sample code, composition, etc.

iii. 'Mass' for the sample mass (without the crucible). The mass value will be used by the software to calculate the corresponding percentage weigh value as a function of temperature

iv. 'Crucible mass' for the mass of the empty crucible placed in the sample position of the carrier (front side). The mass value is not used for any calculation, but value serves as an important info about the size of the crucible used for the measurement. Size/volume of the crucible is important for the baseline correction process

c. In the 'Reference' panel, which is relevant only for DTA or DSC measurements, please provide:

i. 'Name' for the name of the standard used, e.g., Al_2O_3 or empty crucible

ii. 'Mass' for the standard mass (without the crucible). For the sealed ampoule Al_2O_3 standard, please check the latest mass values under 'procedures/reference.txt'

iii. 'Crucible mass' for the mass of the empty crucible placed in the reference position of the carrier (back side)

d. In the 'MFC gases' panel (figure 3d), ***check to see if the appropriate gas for your experiment is selected***. The type of gas for 'Purge 1' is controlled via a separate script as described in the 'Change type of gas' section. 'Purge 2' is connected to ultra-high purity Helium. In case you need a special gas for your measurement that is different than the existing gases (nitrogen 5% hydrogen balanced with nitrogen, air, or argon), please talk to a staff

e. (Optional) Provide details about 'Laboratory', 'Project', 'Operator', and 'Materials'

f. In the 'Remark' field please provide any additional details you feel are important for reproducing the experiment. Temperature profile, type and flow of gases are automatically recorded during your measurement

g. Press on the 'Forward ->' button or press on the 'Temperature Program' tab

4. On the 'Temperature Program' tab (figure 4), you are about to build the detailed temperature profile for your variable temperature measurement. The workflow on this tab starts by selecting the appropriate category from the 'Step Category' panel, then by selecting the temperature conditions from the 'Category' panel, and finally by selecting the environment from the 'Step Conditions'. Once all selections are made, you press on the 'Add' button to add the temperature segment in the profile. The recommended sequence of segments is:

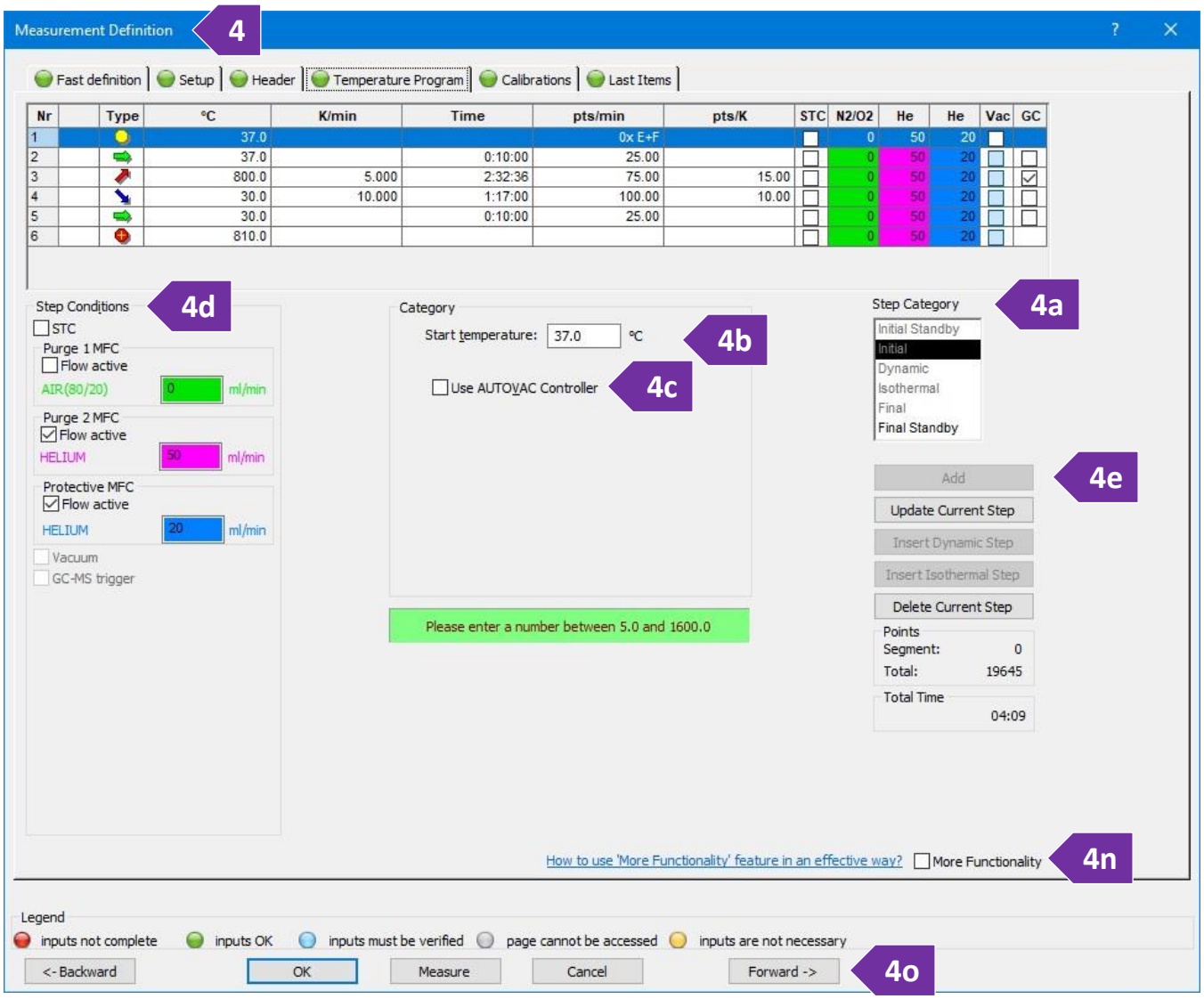
   a. Select 'Initial' from the 'Step Category' panel (figure 4a)

   b. Type the starting temperature in 'Start temperature' in the 'Category' panel (figure 4b). Starting temperature can be either a temperature point

      - Near (±8 degrees) the actual temperature of the furnace. Please check the front panel on the instrument for the actual temperature, or
      - Well above the actual temperature. In this case, software will preheat the furnace before automatically starting the measurement, or
      - Well below the actual temperature only when a cooling attachment is connected (available only for the stainless-steel furnace)

   c. Leave the 'Use AUTOVAC Controller' unselected unless you need to evacuate (apply vacuum) the furnace before starting the measurement (figure 4c)

   d. Under the 'Step Conditions' panel (figure 4d)



i. ***Uncheck the 'STC' option.*** See step 4k below for more details about the 'STC' option in combination with an isothermal step

ii. (Mandatory) Set the 'Protective MFC' gas (Helium or Nitrogen) to at least 25 ml/min. This gas flow option must be always on regardless of your other gas settings. Failure to use a protective flow might result in contamination and/or damage of the microbalance electronics

iii. Set the 'Purge 1 MFC' or 'Purge 2 MFC' based on the type of gas needed for your experiment. Type of gas (e.g., Helium, air, etc.) per MFC is shown next to the flow setting. A flow of at least 50 ml/min is recommended. Use higher flow (150 ml/min or so) in case your sample releases highly corrosive gases

e. Press on the 'Add' button to add the initial segment into the temperature profile (figure 4e)

f. You need to make sure that gas flow is equilibrated, and furnace is purged with the gas of your choice before increasing temperature. Therefore, select 'Isothermal' from the 'Step Category' and under the 'Category' panel type either
   - 5 mins or longer for measurements under air, or
   - 10 mins or longer for any inert or special gas. Using Helium for GC-MS runs is highly recommended for minimizing the background of total measured ions

g. For all temperature segments in your profile, leave the gas type and flow as is (most common) unless you need to change them for special experiments. Note that any changes to the type or flow of the gas will affect the continuity of the weight trace due to changes to the buoyancy

h. Press on the 'Add' button to add the isothermal segment into the temperature profile

i. Select 'Dynamic' from the 'Step Category' panel and provide the target temperature and rate. Minimum and maximum allowable values of each setting are shown in the green text field under the 'Category' panel. Set the gases at the 'Step Conditions' panel. Tick on the 'GC-MS' option to trigger the acquisition of the GC-MS method (to be defined later). Press on the 'Add' button to add the dynamic segment into the temperature profile

j. Keep adding temperature segments according to the temperature profile of your choice and ensure that the 'GC-MS' option is un-ticked for any temperature segment you might add, i.e., you need only one triggering point for the GC-MS method which is usually at the beginning of the heating step defined on the previous step

k. For isothermal steps of where the actual temperature of the sample (and not the furnace) is important, enable the 'STC' option. By default, the temperature you provide in any step of the temperature program, e.g., dynamic or isothermal, corresponds to the temperature of the furnace (thermocouple on the furnace) and not necessarily of the sample (thermocouple on the carrier and under the sample). This temperature difference between the sample and the furnace will depend mainly on the type of the gas flowing in the furnace, the flow rate, the temperature ramp rate, and the absolute temperature point. The temperature data plotted on the screen and recorded in the exported file correspond to the actual temperature of the sample and not the furnace. It is not recommended to enable 'STC' on a dynamic step

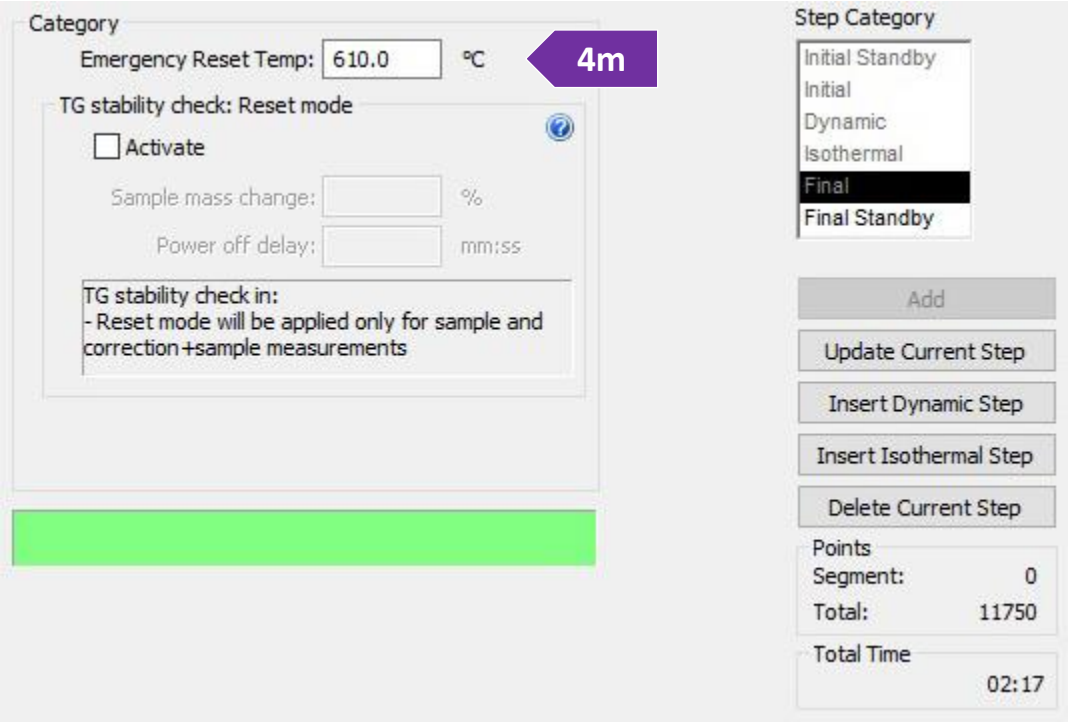
l. The last dynamic segment in your temperature profile must end near a room temperature value (25-40 C) even if you are not interested in collecting/analyzing data on cooling. This step is important to ensure STA is immediately ready for the next measurement after the end of your collection

m. Once you have added all temperature segments needed for your temperature profile, select 'Final' under the 'Step Category' panel (figure 4m), accept the default values (which is 10 degrees on top of your highest

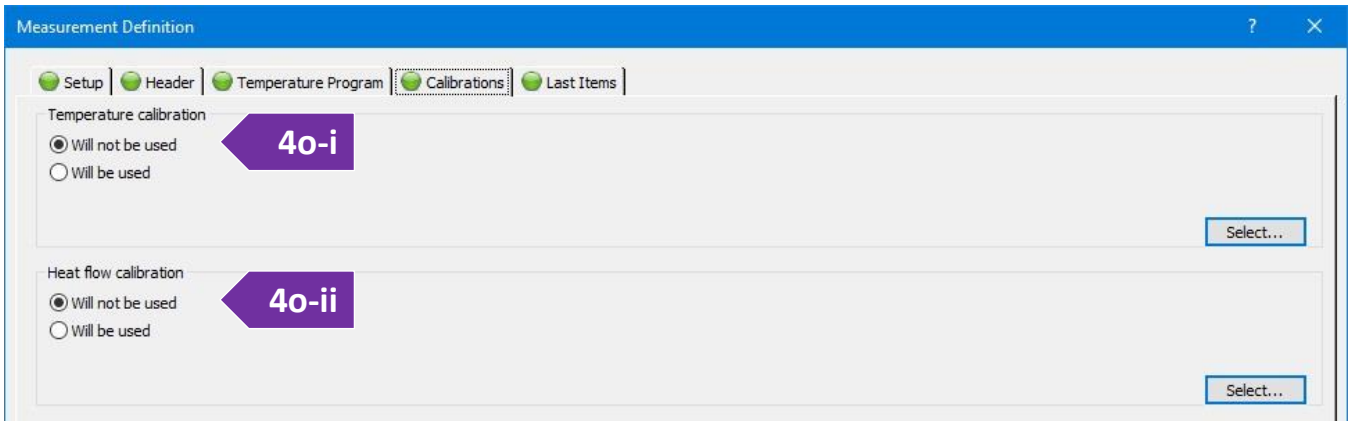
temperature point in your profile), and press on the 'Add' button. This 'Final' step is more like an overtemperature safety step in case of a hardware failure during collection. Please do not use the 'Final Standby' option since this will turn off all gases and create a mild vacuum in the furnace that will require the next use to refill the furnace with gas

n. (Optional) Select the 'More Functionality' option to see a graph of your temperature profile that might help you overview and verify your settings (figure 4n)

o. Press on the 'Forward ->' button or press on the 'Calibrations' tab (figure 4o)



i. (Optional) On the 'Temperature calibration' panel, select a calibration file you might have (figure 4o-i). Calibration files are used to correct for any temperature offsets between the actual temperature of the sample and thermocouple of the carrier. For example, if you sample is in a thick ceramic crucible or sealed in an ampoule, the actual temperature of the sample will be a little bit lower than the

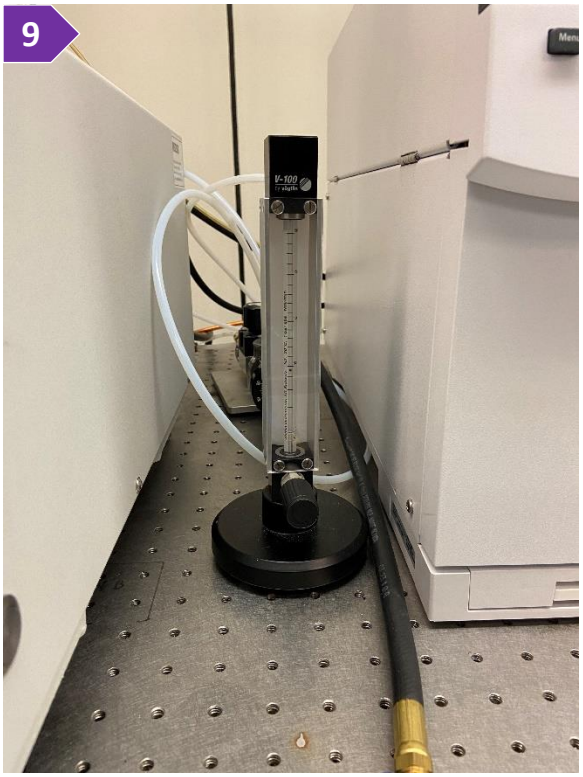


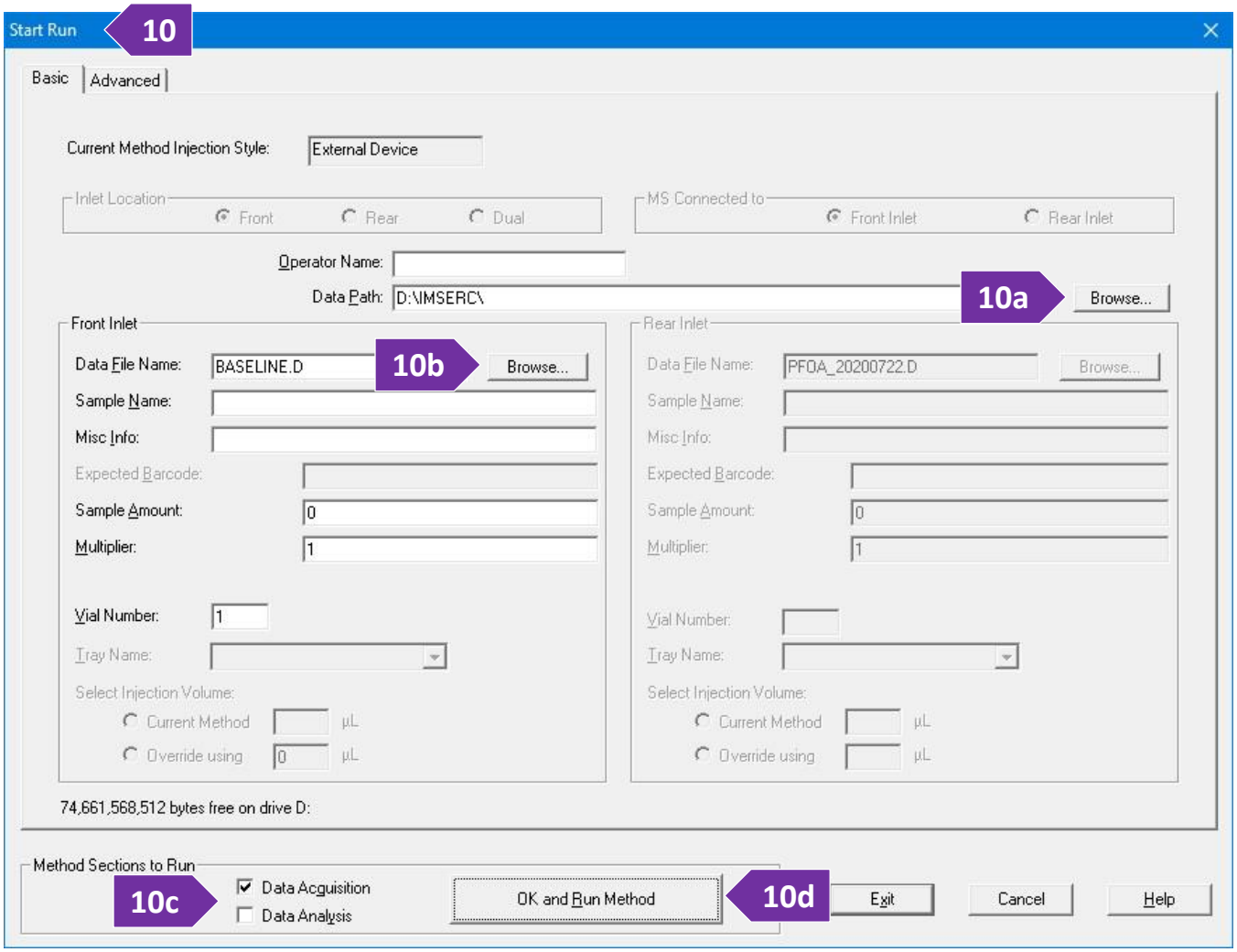
temperature recorded by the carrier thermocouple. A temperature calibration file requires separate measurements of materials with known melting points under the same conditions used for measuring your samples

ii. (Optional) On the 'Heat flow calibration' panel, select a heat flow calibration file (figure 4o-ii). This option is more relevant for DSC measurements of where the raw signal on the carrier (µV/mg) must be converted to energy units (e.g., J/mg). The heat flow calibration file is created by measuring a standard, i.e., Sapphire disc, under the same conditions used for the sample and the creation of a calibration curve by using the software. See a staff if a calibration file for the temperature range or environment of interest does not exist

iii. Press on the 'Forward ->' button or press on the 'Last Items' tab

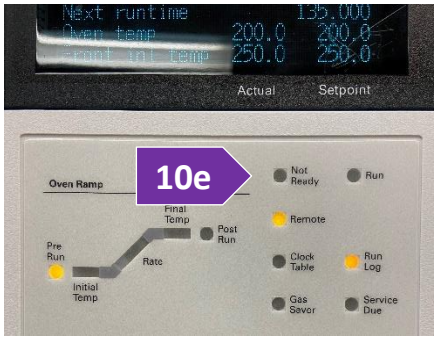
5. On the 'Last Items' tab, you need to provide the path and filename of the sample file. Use your personal folder under your group folder on the 'D' drive to save the file
6. Press on the 'OK' button to store the procedure
7. Launch the GC-MS acquisition software (ChemStation) in case is not running already. Icon of the GC-MS software is on the desktop labels as 'TGA-GC-MS'
8. Load the method that was created for you during your training session by pressing on the 'Method' menu and selecting 'Load Method'. Wait for a few seconds until the method is loaded and the cursor becomes responsive again
9. Ensure that the flow in the flow meter between the STA and MSD is around 50 µl/min (figure 9). If there is no flow, please contact a staff
10. Run your method by pressing on the 'Method' menu and selecting 'Run Method'
    a. On the 'Start Run' window (figure 10), provide the path for where your GC-MS data will be saved under by pressing on the 'Browse' button next to the 'Data Path' field (figure 10a)
    b. Provide the folder name of where the GC-MS will be saved under by pressing on the 'Browse' button next to the 'Data File Name' field (figure 10b)
    c. At the bottom-left corner of the window, tick the option 'Data Acquisition' and untick the option 'Data Analysis' (figure 10c)





d. Press on the 'OK and Run Method' to run the method (figure 10d). Within a few seconds, GC-MS instrument will go into standby mode and instrument will wait for the trigger signal from the thermal analysis software

e. The 'Not Ready' light indicator should be off (figure 10e) before going to the next step

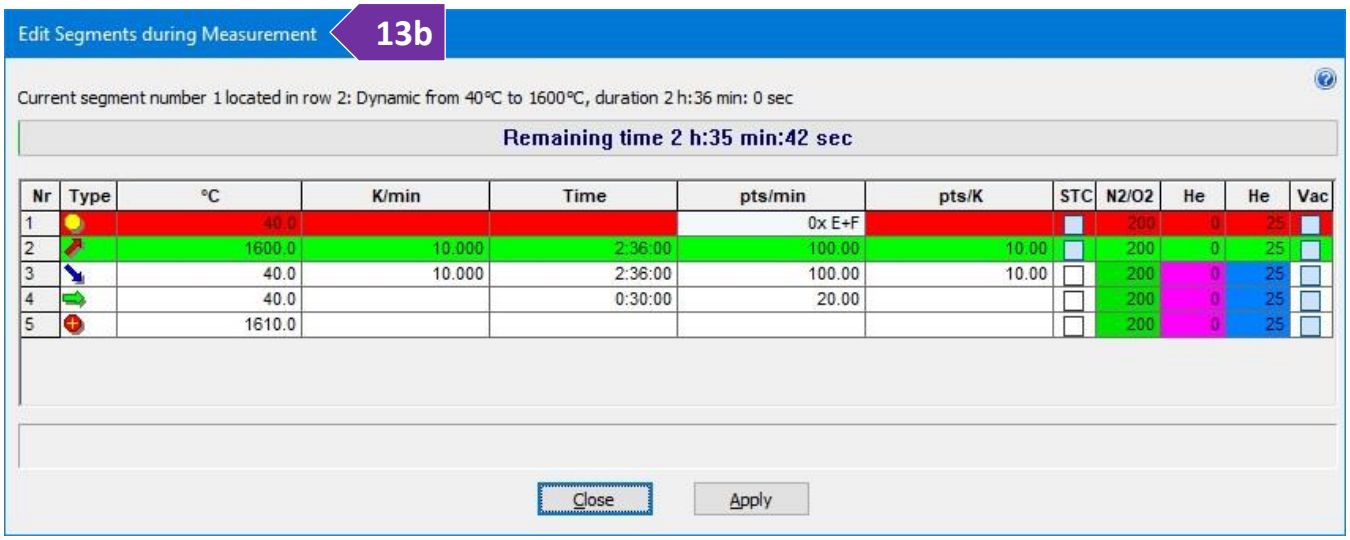


11. Select the thermal analysis program again and press on the green play button on the toolbox

12. The final window for starting the measurement will open. When actual temperature is within the temperature threshold under the 'Preheating\precooling criteria' panel, the 'Start' button will be enabled (figure 12). Press on the 'Start' button to start the measurement. A countdown timer will be visible on the screen with the remaining time of your

measurement. Press on the 'Tare' button only if you are using a 'Weighing mode' (step 2k) that is different than 'Manual input' when working with extremely air-sensitive samples

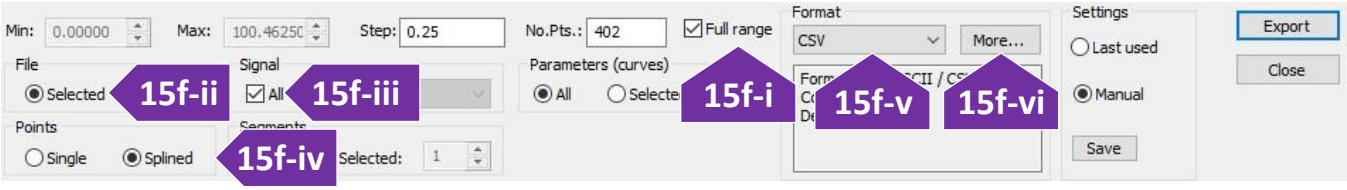
13. (Optional) In case you need to edit acquisition parameters on-the-fly while your measurement is running, e.g., extending an isothermal step:
    a. On the main window, under the menu 'Measurement', press on the 'View/Edit Running Measurement Program'
    b. The 'Edit Segments during Measurement' window opens (figure 13b)
        i. Software colors segments that are completed in red, running segments in green, and pending segments in white



        ii. Remaining time of the running segment (in green) is shown as a progress bar on the top of the window
        iii. Double press on any parameter and/or select a tick box on either a running and/or pending segment to edit their values
        iv. Press on the 'Apply' button to apply the new settings

14. When measurement is done:
    a. Remove your sample and lower the furnace as described in step 2, 3, 5, and 6 under the 'Loading a sample into the instrument' section
    b. Place contaminated ceramic (Al_2O_3) crucibles and ceramic lids into the 'For STA Al_2O_3 crucibles' labeled vial located in the hood across the STA
    c. Dispose of any used Aluminum pans/lids into the 'Hazardous - For STA Al crucibles' labeled vial located in the hood across the STA
    d. Remove any vials, weighing paper, etc. you may have left in the room
    e. End your reservation in NUcore

15. To convert your data to an ASCII text file:
    a. Start the 'Proteus Analysis' software (icon on desktop). More details about exporting/converting data can be found under the 'Exporting data' section
    b. Load your file
    c. (Optional) Press on the 'T/t' icon (X-Time / X-Temperature) to plot the data as a function of temperature
    d. Select either the TGA or DTA (if applicable) curve in the plot by clicking on it
    e. Under the 'Extras' menu, select 'Export Data'
    f. On the menu above your plot:
        i. Tick 'Full range' (figure 15f-i)

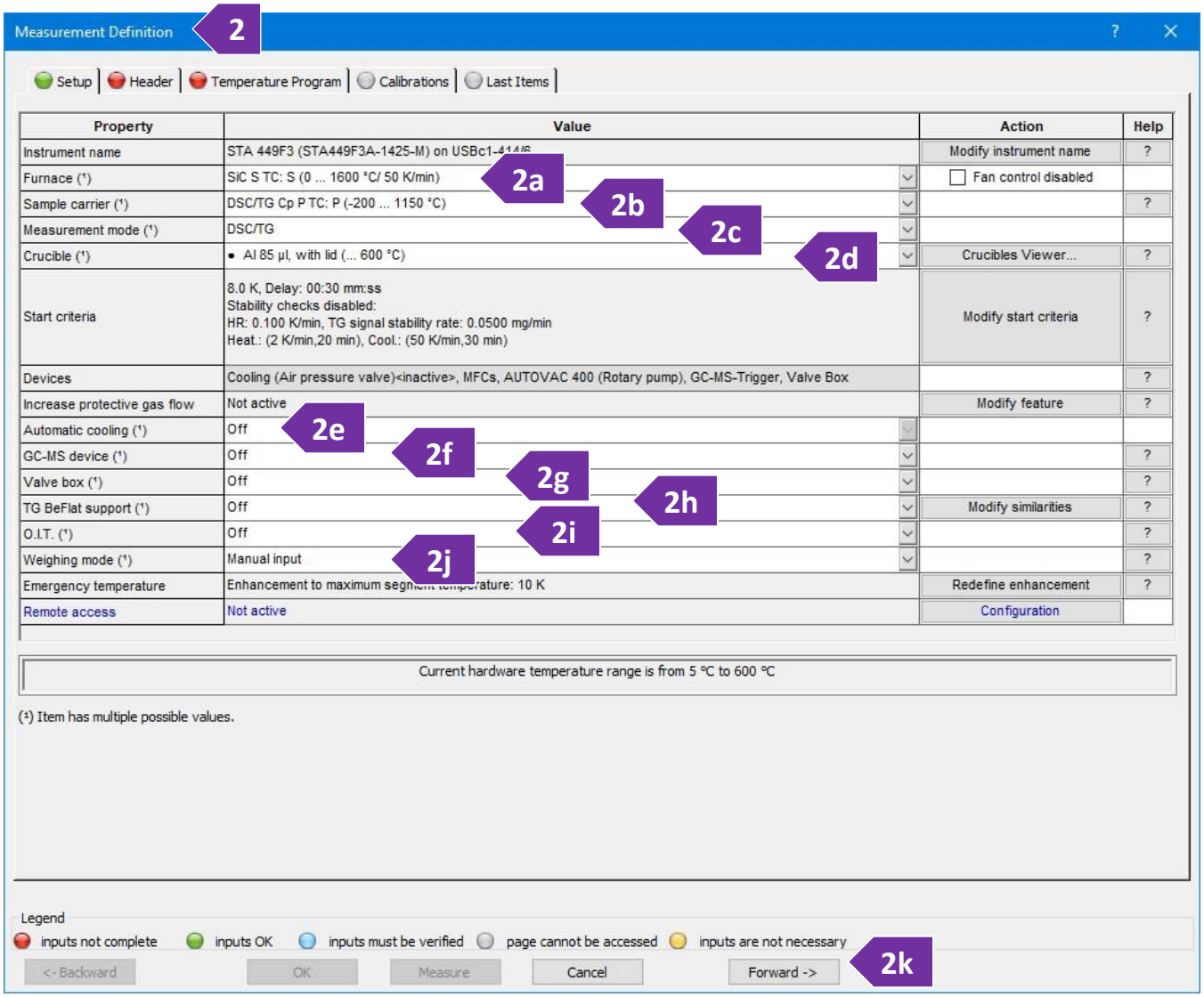


        ii. Under the 'File' panel, select 'Selected' (figure 15f-ii)
        iii. Under the 'Signal' panel, tick on 'All' (figure 15f-iii)
        iv. Under the 'Points' panel, select 'Splined' (figure 15f-iv)
        v. Under the 'Format' panel, select 'CSV' (most common) (figure 15f-v)
        vi. (Optional) Press on the 'More…' button and change the output type of the file to be exported (figure 15f-vi)
        vii. Press on the 'Export' button
        viii. Set the file name and verify that you are saving into your group folder

F. DSC/TGA MEASUREMENT WITHOUT A CORRECTION FILE OR EXISTING PROCEDURE

To create a completely new DSC measurement without a pre-collected correction file (baseline) or existing procedure that is part of an old measurement. The workflow for creating a new DSC measurement is identical to the workflow described above for creating a new DTA/TGA measurement:

1. Press on the 'File' menu and select 'New'. If an existing procedure is loaded, select 'OK' in the warning message regarding the deletion of the current procedure. The 'Measurement Definition' window opens
2. On the 'Setup' tab of the 'Measurement Definition' window, you are going to set the main configuration parameters of your measurement (figure 2):
   a. 'Furnace' option will be pre-selected for you by the software based on your physical selection of the furnace (figure 2a)



b. 'Sample carrier' option will be pre-selected for you by the software based on the carrier installed, i.e., DSC/TG

c. 'Measurement mode' requires your input depending on what signal (TGA only, or DSC/TG) you would like to record. It is highly recommended to record TGA with the DSC data since you can get data for two measurements simultaneously

d. 'Crucible' needs to be set based on the type of crucible you are about to use, e.g., selecting Aluminum crucibles will automatically limit the maximum allowable temperature to 600C

e. 'Automatic cooling' is available only for the stainless-steel furnace and not for the Silicon Carbide one. Use the 'Automatic cooling option' to control cooling below ~ 150C

f. 'GC-MS device' should be enabled only when GC-MS is needed. Only the Silicon Carbide furnace (and not the Stainless-Steel furnace) is connected to the GC-MS with the transfer line. See more details under the 'GC-MS with TGA/DTA sample measurement' section

g. 'Valve box' should be set to 'Off' since this attachment is not available on our system

h. 'TG BeFlat support' should be set to 'Off'. Measuring experimentally the baseline is highly recommended instead of using a 'BeFlat' correction which is an algorithm for correcting of the buoyancy affect

i. 'O.I.T.' should be set to 'Off'

j. 'Weighing mode' should be set to 'Manual input' when mass of the sample is known. Use any of the other options in case you have extremely air sensitive samples and you would like to use the STA microbalance to measure the mass of the sample while being protected by the flowing gas

k. Press on the 'Forward ->' button or press on the 'Header' tab

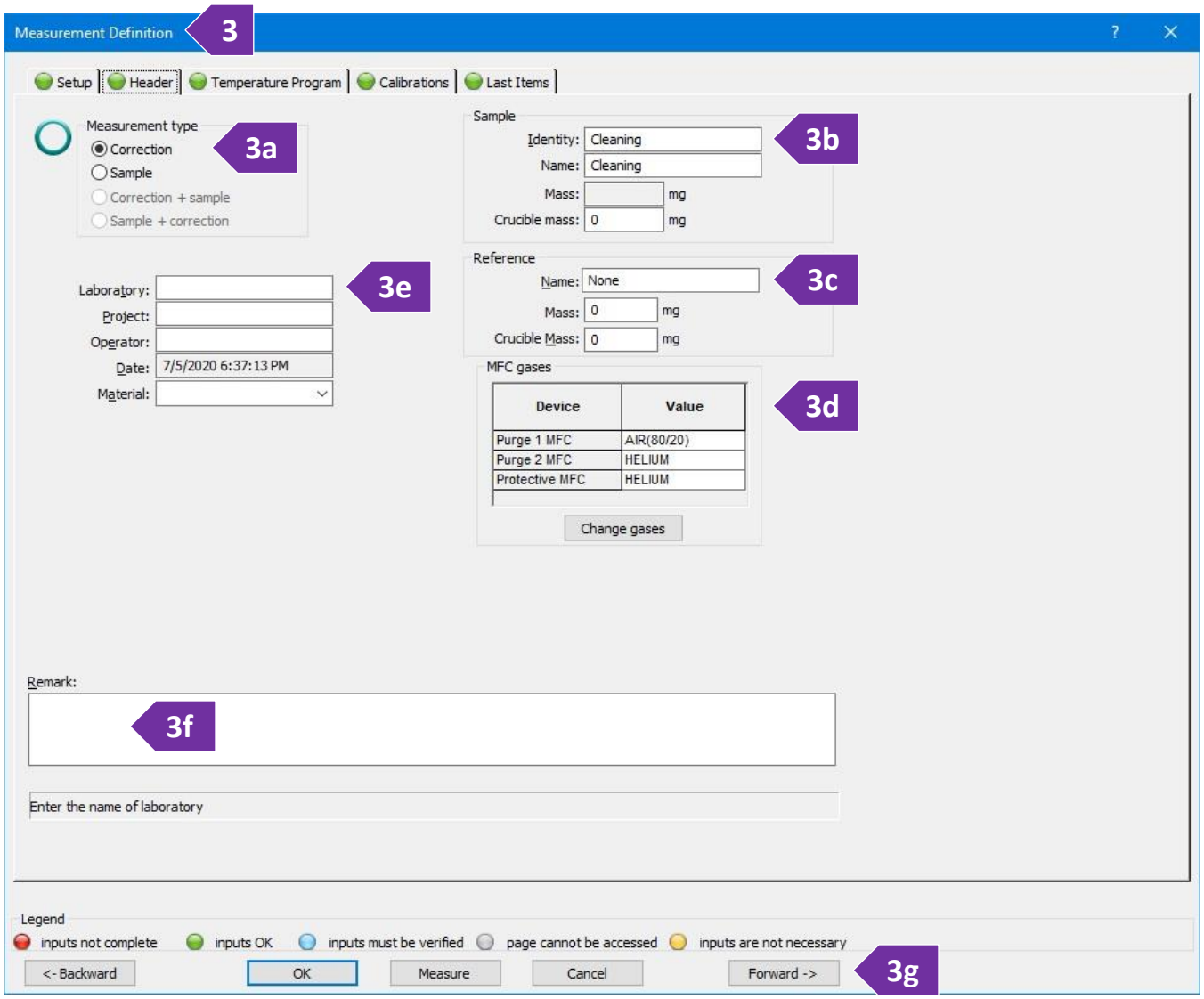
3. On the 'Header' tab (figure 3) of the 'Measurement Definition' window (red disc-like symbol next to each tab name and textbox indicates required fields), you are going to provide some sample specific information:

   a. In the 'Measurement type' panel, select 'Sample'. Measuring a correction (baseline) is highly recommended for accurate mass changes. Uncorrected measurements may have overestimated weight values that depend on the type of flowing gas due to buoyancy affects, e.g., ~ 0.2 mg under He or ~ 0.8 mg under air flow. Correction can be measured either before or after a sample measurement. Correction files can be reused for future sample corrections only if the conditions of the experiment remain the same. Please refer to the corresponding sections in this user manual depending on the order of the sample and correction measurement (correction first and then sample or sample first and then correction)

   b. In the 'Sample' panel provide

      i. 'Identity' such as sample code, composition, etc. (figure 3b)

      ii. 'Name' such as sample code, composition, etc. (figure 3b)



iii. 'Mass' for the sample mass (without the crucible). The mass value will be used by the software to calculate the corresponding percentage weigh value as a function of temperature

iv. 'Crucible mass' for the mass of the empty crucible placed in the sample position of the carrier (front side). The mass value is not used for any calculation, but value serves as an important info about the size of the crucible used for the measurement. Size/volume of the crucible is important for the baseline correction process

c. In the 'Reference' panel (figure 3c), which is relevant only for DTA or DSC measurements, please provide:

i. 'Name' for the name of the standard used, e.g., Al_2O_3 or empty crucible

ii. 'Mass' for the standard mass (without the crucible). For the sealed ampoule Al_2O_3 standard, please check the latest mass values under 'procedures/reference.txt'

iii. 'Crucible mass' for the mass of the empty crucible placed in the reference position of the carrier (back side)

d. In the 'MFC gases' panel (figure 3d), check to see if the appropriate gas for your experiment is selected. The type of gas for 'Purge 1' is controlled via a separate script as described in the 'Change type of gas' section. 'Purge 2' is connected to ultra-high purity Helium. In case you need a special gas for your measurement that is different than the existing gases (nitrogen 5% hydrogen balanced with nitrogen, air, or argon), please talk to a staff

e. (Optional) Provide details about 'Laboratory', 'Project', 'Operator', and 'Materials' (figure 3e)

f. In the 'Remark' field (figure 3f) please provide any additional details you feel are important for reproducing the experiment. Temperature profile, type and flow of gases are automatically recorded during your measurement

g. Press on the 'Forward ->' button (figure 3g) or press on the 'Temperature Program' tab

4. On the 'Temperature Program' tab (figure 4), you are about to build the detailed temperature profile for your variable temperature measurement. The workflow on this tab starts by selecting the appropriate category from the 'Step Category' panel, then by selecting the temperature conditions from the 'Category' panel, and finally by selecting the environment from the 'Step Conditions'. Once all selections are made, you press on the 'Add' button to add the temperature segment in the profile. The recommended sequence of segments is:

a. Select 'Initial' from the 'Step Category' panel (figure 4a)

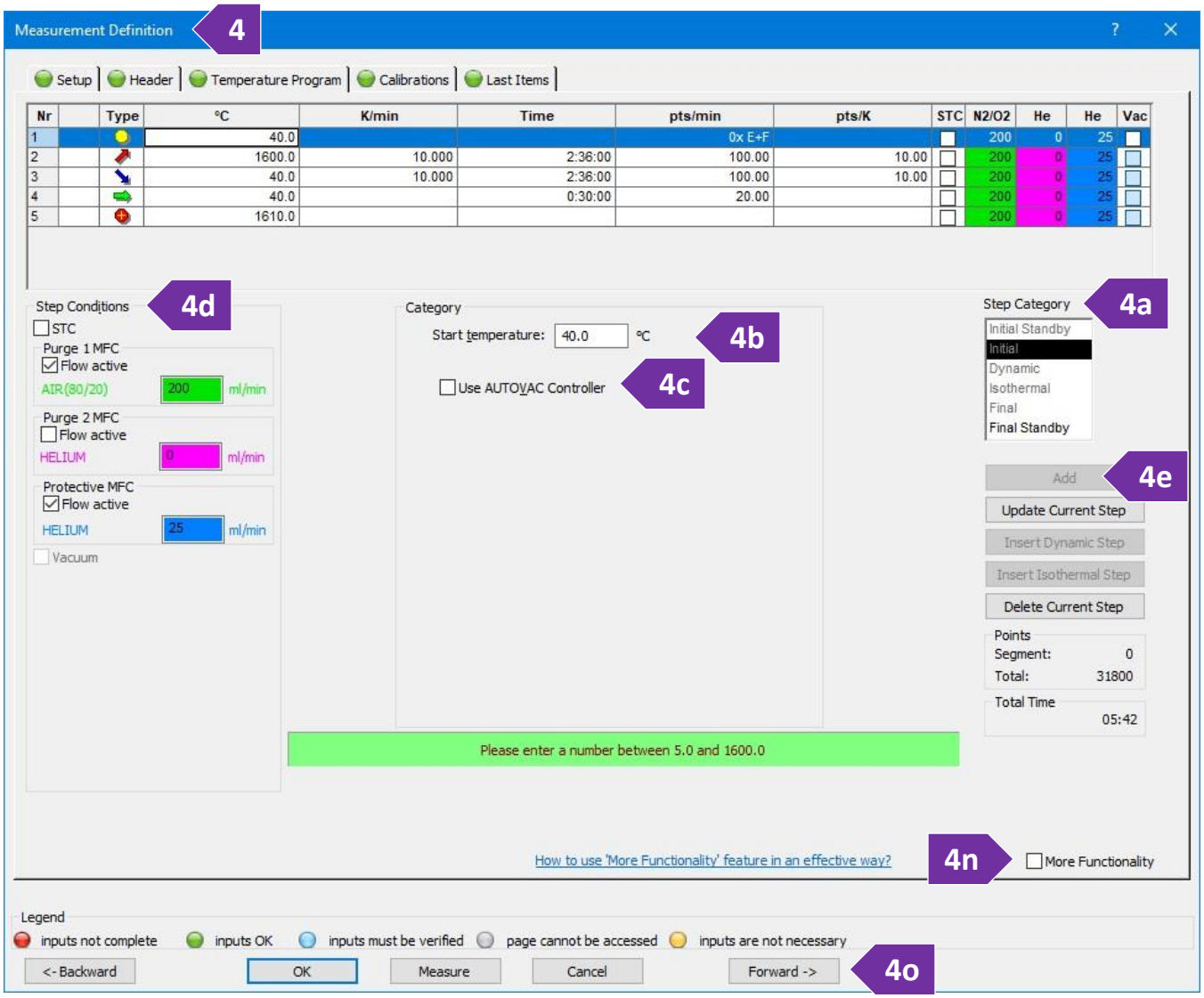
b. Type the starting temperature in 'Start temperature' in the 'Category' panel (figure 4b). Starting temperature can be either a temperature point

- Near (±8 degrees) the actual temperature of the furnace. Please check the front panel on the instrument for the actual temperature, or
- Well above the actual temperature. In this case, software will preheat the furnace before automatically starting the measurement, or
- Well below the actual temperature only when a cooling attachment is connected (available only for the stainless-steel furnace)

c. Leave the 'Use AUTOVAC Controller' unselected unless you need to evacuate (apply vacuum) the furnace before starting the measurement (figure 4c)

d. Under the 'Step Conditions' panel (figure 4d)

i. ***Uncheck the 'STC' option.*** See step 4k below for more details about the 'STC' option in combination with an isothermal step



ii. (Mandatory) Set the 'Protective MFC' gas (Helium or Nitrogen) to at least 25 ml/min. This gas flow option must be always on regardless of your other gas settings. Failure to use a protective flow might result in contamination and/or damage of the microbalance electronics

iii. Set the 'Purge 1 MFC' or 'Purge 2 MFC' based on the type of gas needed for your experiment. Type of gas (e.g., Helium, air, etc.) per MFC is shown next to the flow setting. A flow of at least 50 ml/min is recommended. Use higher flow (150 ml/min or so) in case your sample releases highly corrosive gases

e. Press on the 'Add' button to add the initial segment into the temperature profile (figure 4e)

f. You need to make sure that gas flow is equilibrated, and furnace is purged with the gas of your choice before increasing temperature. Therefore, select 'Isothermal' from the 'Step Category' and under the 'Category' panel type either

- 5 mins or longer for measurements under air, or

- 10 mins or longer for any inert or special gas

g. For all temperature segments in your profile, leave the gas type and flow as is (most common) unless you need to change them for special experiments. Note that any changes to the type or flow of the gas will affect the continuity of the weight trace due to changes to the buoyancy

h. Press on the 'Add' button to add the isothermal segment into the temperature profile

i. Select 'Dynamic' from the 'Step Category' panel and provide the target temperature and rate. Minimum and maximum allowable values of each setting are shown in the green text field under the 'Category' panel. Set the gases at the 'Step Conditions' panel and press on the 'Add' button to add the dynamic segment into the temperature profile

j. Keep adding temperature segments according to the temperature profile of your choice

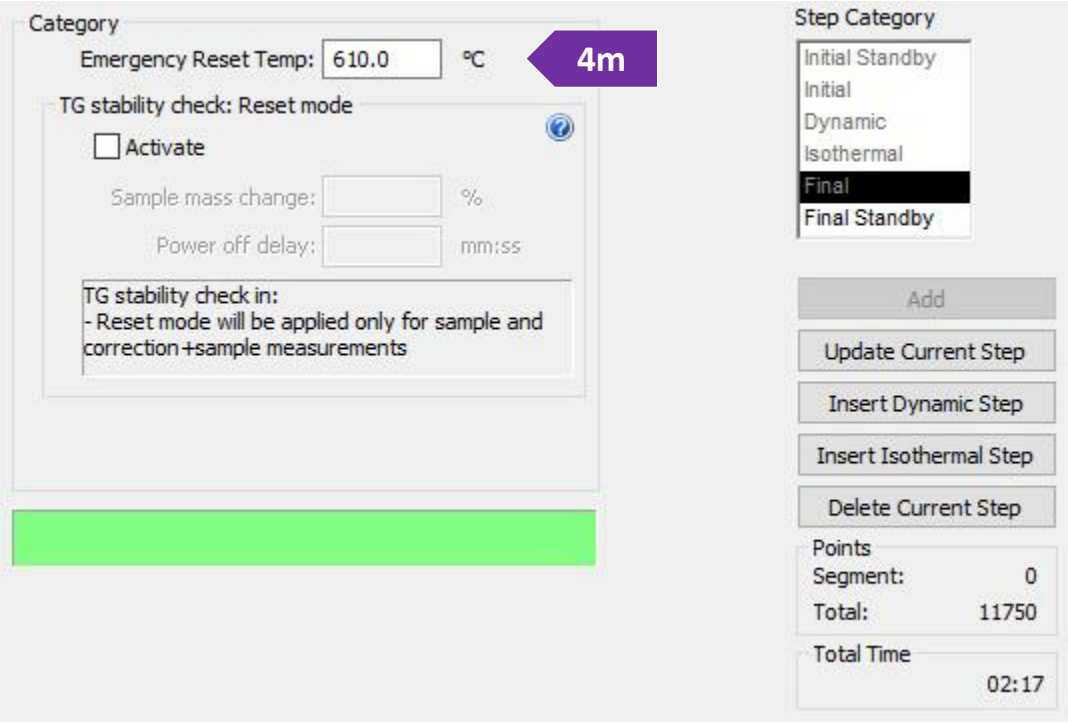
k. For isothermal steps of where the actual temperature of the sample (and not the furnace) is important, enable the 'STC' option. By default, the temperature you provide in any step of the temperature program, e.g., dynamic or isothermal, corresponds to the temperature of the furnace (thermocouple on the furnace) and not necessarily of the sample (thermocouple on the carrier and under the sample). This temperature difference between the sample and the furnace will depend mainly on the type of the gas flowing in the furnace, the flow rate, the temperature ramp rate, and the absolute temperature point. The temperature data plotted on the screen and recorded in the exported file correspond to the actual temperature of the sample and not the furnace. It is not recommended to enable 'STC' on a dynamic step

l. The last dynamic segment in your temperature profile must end near a room temperature value (25-40 C) even if you are not interested in collecting/analyzing data on cooling. This step is important to ensure STA is immediately ready for the next measurement after the end of your collection

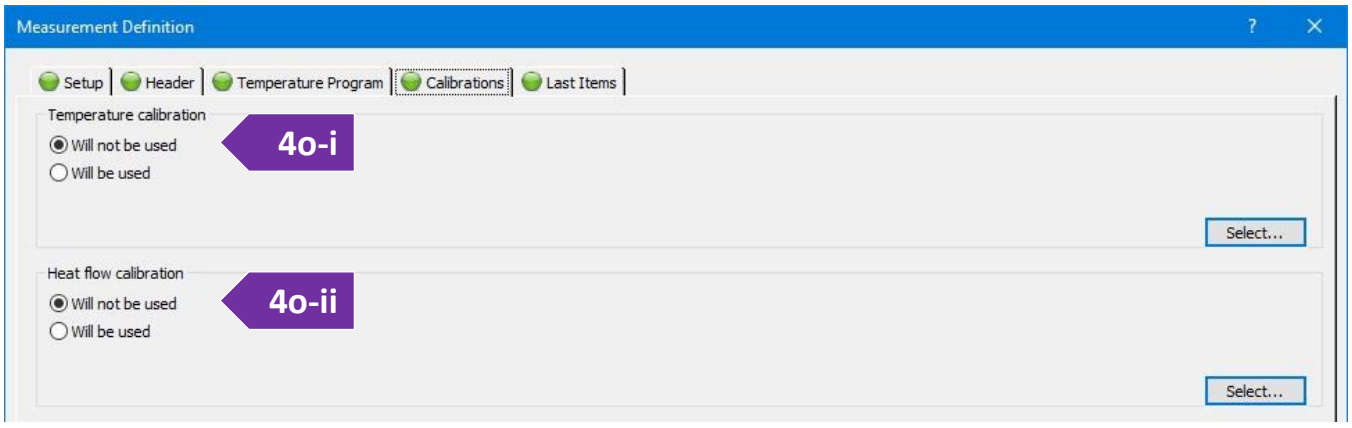
m. Once you have added all temperature segments needed for your temperature profile, select 'Final' under the 'Step Category' panel (figure 4m), accept the default values (which is 10 degrees on top of your highest temperature point in your profile), and press on the 'Add' button. This 'Final' step is more like an overtemperature safety step in case of a hardware failure during collection. Please do not use the 'Final Standby' option since this will turn off all gases and create a mild vacuum in the furnace that will require the next use to refill the furnace with gas

n. (Optional) Select the 'More Functionality' option to see a graph of your temperature profile that might help you overview and verify your settings (figure 4n)

o. Press on the 'Forward ->' button or press on the 'Calibrations' tab (figure 4o)



i. (Optional) On the 'Temperature calibration' panel, select a calibration file you might have (figure 4o-i). Calibration files are used to correct for any temperature offsets between the actual temperature of the sample and thermocouple of the carrier. For example, if you sample is in a thick ceramic crucible or sealed in an ampoule, the actual temperature of the sample will be a little bit lower than the temperature recorded by the carrier thermocouple. A temperature calibration file requires separate measurements of materials with known melting points under the same conditions used for measuring your samples

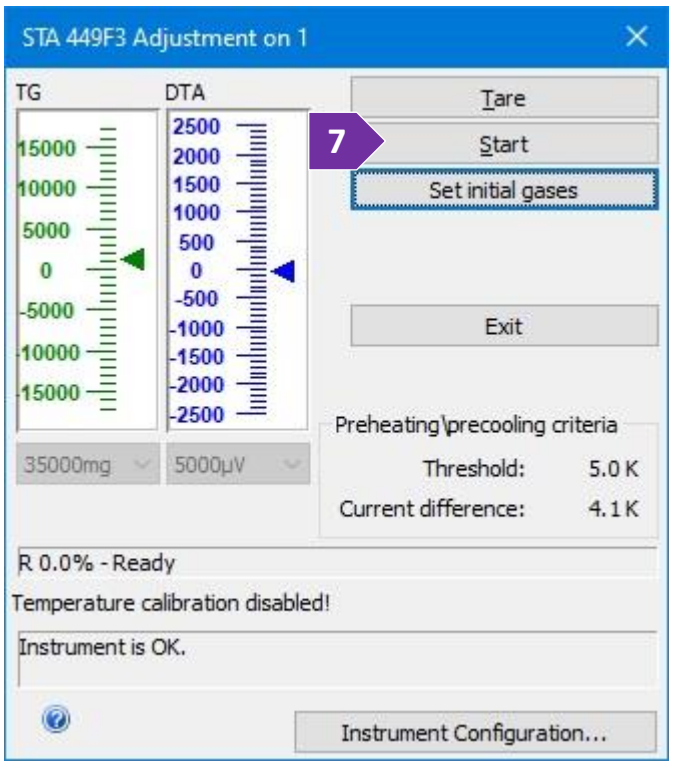


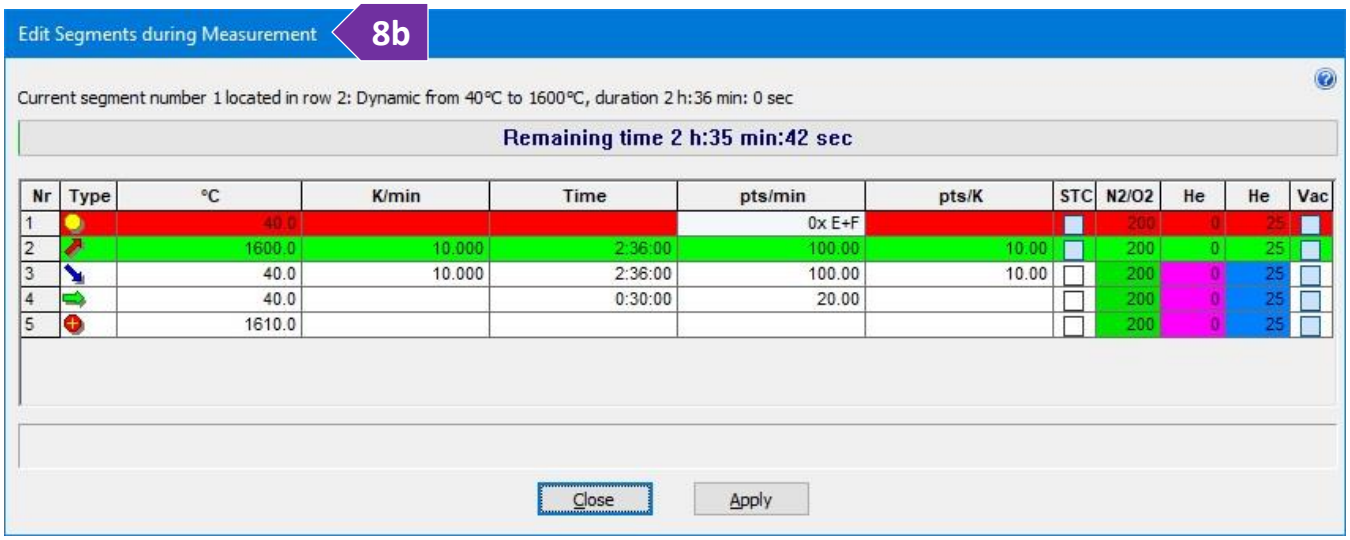
ii. (Optional) On the 'Heat flow calibration' panel, select a heat flow calibration file (figure 4o-ii). This option is important for DSC measurements of where the raw signal on the carrier (µV/mg) must be converted to energy units (e.g., J/mg). The heat flow calibration file is created by measuring a standard, i.e., Sapphire disc, under the same conditions used for the sample and the creation of a

calibration curve by using the software. See a staff if a calibration file for the temperature range or environment of interest does not exist

iii. Press on the 'Forward ->' button or press on the 'Last Items' tab

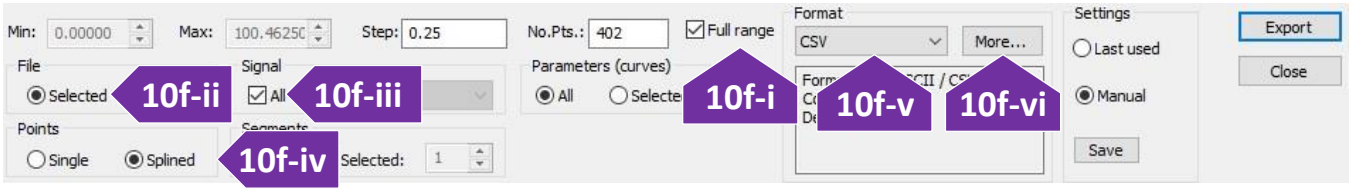
5. On the 'Last Items' tab, you need to provide the path and filename of the sample file. Use your personal folder under your group folder on the 'D' drive to save the file
6. Go to the next step to start the measurement by pressing on either:
   - the 'Measure' button, or
   - the 'OK' button, and then pressing on the green play button on the toolbox
7. The final window for starting the measurement will open. When actual temperature is within the temperature threshold under the 'Preheating\precooling criteria' panel, the 'Start' button will be enabled (figure 7). Press on the 'Start' button to start the measurement. A countdown timer will be visible on the screen with the remaining time of your measurement. Press on the 'Tare' button only if you are using a 'Weighing mode' (step 2k) that is different than 'Manual input' when working with air-sensitive samples
8. (Optional) In case you need to edit acquisition parameters on-the-fly while your measurement is running, e.g., extending an isothermal step:





a. On the main window, under the menu 'Measurement', press on the 'View/Edit Running Measurement Program'
b. The 'Edit Segments during Measurement' window opens (figure 8b)
   i. Software colors segments that are completed in red, running segments in green, and pending segments in white
   ii. Remaining time of the running segment (in green) is shown as a progress bar on the top of the window
   iii. Double press on any parameter and/or select a tick box on either a running and/or pending segment to edit their values
   iv. Press on the 'Apply' button to apply the new settings

9. When measurement is done:
   a. Remove your sample and lower the furnace as described in step 2, 3, 5, and 6 under the 'Loading a sample into the instrument' section
   b. Place contaminated ceramic (Al_2O_3) crucibles and ceramic lids into the 'For STA Al_2O_3 crucibles' labeled vial located in the hood across the STA
   c. Dispose of any used Aluminum pans/lids into the 'Hazardous - For STA Al crucibles' labeled vial located in the hood across the STA
   d. Remove any vials, weighing paper, etc. you may have left in the room
   e. End your reservation in NUcore
10. To convert your data to an ASCII text file:
   a. Start the 'Proteus Analysis' software (icon on desktop). More details about exporting/converting data can be found under the 'Exporting data' section
   b. Load your file
   c. (Optional) Press on the 'T/t' icon (X-Time / X-Temperature) to plot the data as a function of temperature
   d. Select either the TGA or DTA (if applicable) curve in the plot by clicking on it
   e. Under the 'Extras' menu, select 'Export Data'
   f. On the menu above your plot:



   i. Tick 'Full range' (figure 10f-i)
   ii. Under the 'File' panel, select 'Selected' (figure 10f-ii)
   iii. Under the 'Signal' panel, tick on 'All' (figure 10f-iii)

iv. Under the ‘Points’ panel, select ‘Splined’ (figure 10f-iv)

v. Under the ‘Format’ panel, select ‘CSV’ (most common) (figure 10f-v)

vi. (Optional) Press on the ‘More…’ button and change the output type of the file to be exported (figure 10f-vi)

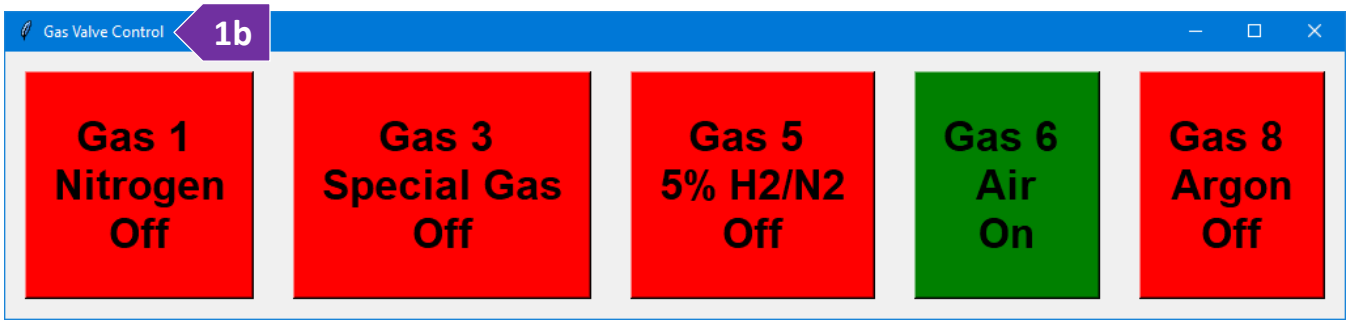
vii. Press on the ‘Export’ button

viii. Set the file name and verify that you are saving into your group folder

CHANGE TYPE OF GAS

The STA is equipped with two mass flow controllers (MFCs) for an accurate control of the gases flowing through the furnace during a measurement. The two controllers are labeled as 'Purge 1' and 'Purge 2'. The 'Purge 2' controller is connected to an ultra-high purity Helium tank for experiments that require Helium, e.g., TGA-GC-MS and/or low temperature runs. The 'Purge 1' controller is dedicated for any other inert or special gas needed for your measurement. To change the type of gas flowing through the 'Purge 1' controller, you need to follow two steps. First step is to select the appropriate gas using a valve control script, and the second step is to change the digital label of the gas defined in the acquisition software:

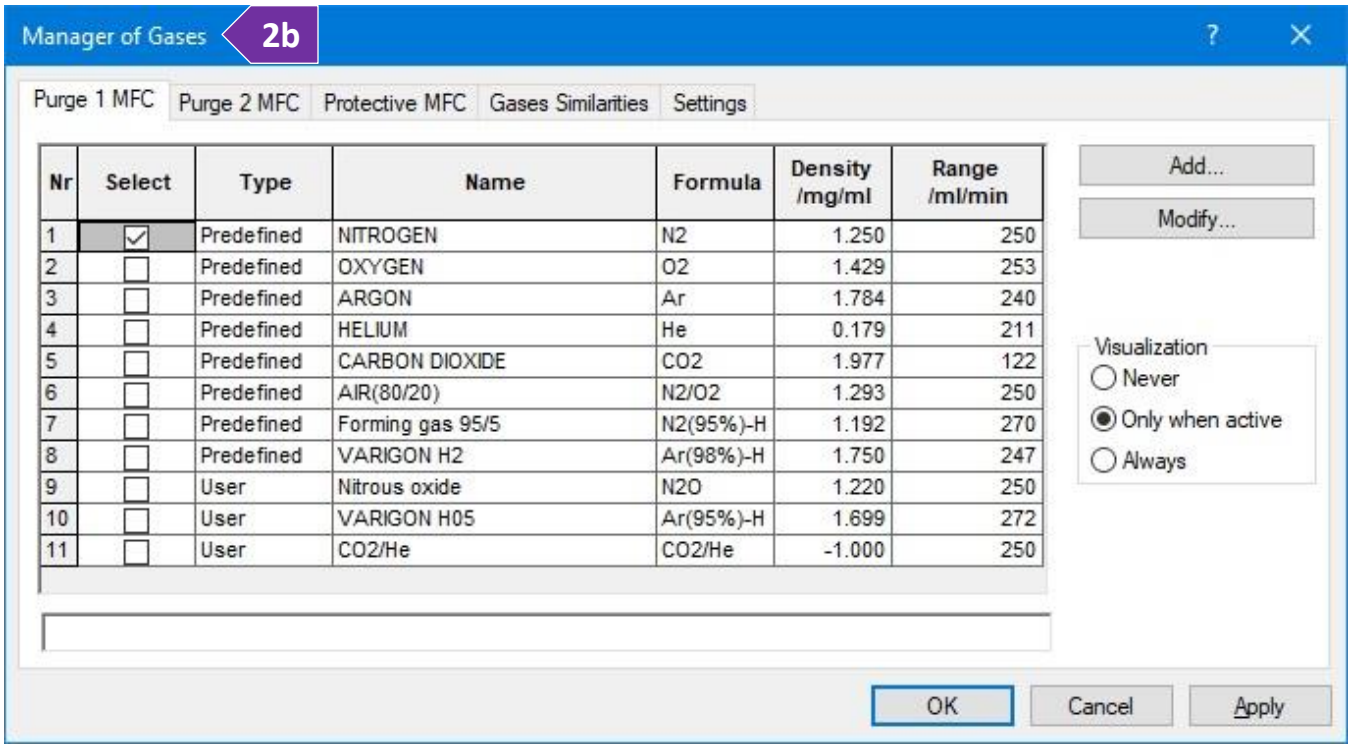
1. To change the type of gas to what is needed for your measurement, use the 'sta_gas_port_control' script:
   a. Look at the windows taskbar to see if the script is running (circled in figure 1a). If script is not running, double press on the 'sta_gas_port_control' icon on the desktop
   a. Press anywhere on the large red button with the label of the preferred gas (figure 1b). Button of the selected gas should turn green within five seconds. If this is not the case, please press again on the button showing the gas of interest. Gases that are always available include nitrogen (ultra-high purity), 5% hydrogen balanced by nitrogen, dry air, and argon. For any other special gas, please talk to a staff before scheduling your experiment. Additionally, add a note in NUcore about the special gas request
   b. Minimize the 'sta_gas_port_control' script. In case you accidentally closed the script, the selected gas valve will remain open



2. To change the digital label of the gas in the acquisition software, under the 'Header' tab on the 'Measurement Definition' window:
   a. Press on the 'Change gases' button to see the 'Manager of Gases' window
   b. Ensure that the 'Purge 1 MFC' tab is selected (figure 2b)
   c. Select the appropriate gas using the tick box and press on the 'OK' button. ***Ensure that the correct gas is physically selected via the 'Gas Valve Control' script as described in step #1. Do not assume that the***

digital label set during the measurement session before yours is correct since loading a procedure might reset the digital labels

d. The correct gas label should be visible in the 'MFC gases' panel



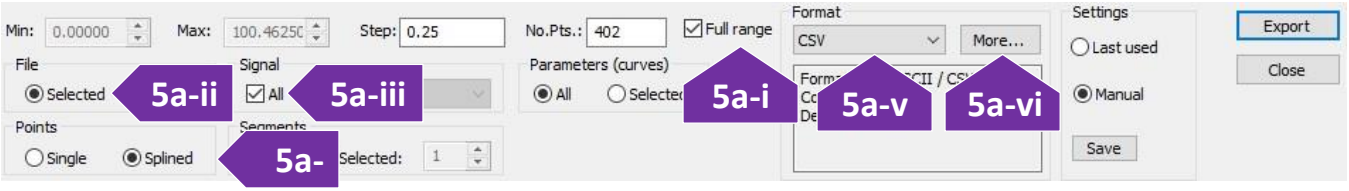
Nr	Select	Type	Name	Formula	Density /mg/ml	Range /ml/min
1	☑	Predefined	NITROGEN	N2	1.250	250
2	☐	Predefined	OXYGEN	O2	1.429	253
3	☐	Predefined	ARGON	Ar	1.784	240
4	☐	Predefined	HELIUM	He	0.179	211
5	☐	Predefined	CARBON DIOXIDE	CO2	1.977	122
6	☐	Predefined	AIR(80/20)	N2/O2	1.293	250
7	☐	Predefined	Forming gas 95/5	N2(95%)-H	1.192	270
8	☐	Predefined	VARIGON H2	Ar(98%)-H	1.750	247
9	☐	User	Nitrous oxide	N2O	1.220	250
10	☐	User	VARIGON H05	Ar(95%)-H	1.699	272
11	☐	User	CO2/He	CO2/He	-1.000	250

EXPORTING DATA

To export/convert your data to an ASCII text file:

1. Start the 'Proteus Analysis' software (icon on desktop)
2. Open your file by pressing either on the 'Open' icon (figure 2) or selecting 'Open' under the 'File' menu

3. (Optional) Press on the 'T/t' icon (figure 3) to plot the data as a function of temperature or time
4. Select either the TGA or DTA (if applicable) curve in the plot by clicking on it
5. Under the 'Extras' menu, select 'Export Data'
   a. On the menu above your plot:



   i. Tick 'Full range' (figure 5a-i)
   ii. Under the 'File' panel, select 'Selected' (figure 5a-ii)
   iii. Under the 'Signal' panel, tick on 'All' (figure 5a-iii)
   iv. Under the 'Points' panel, select 'Splined' (figure 5a-iv)
   v. Under the 'Format' panel, select 'CSV' (most common) (figure 5a-v)
   vi. (Optional) Press on the 'More…' button and change the output type of the file to be exported (figure 5a-vi)
   vii. Press on the 'Export' button
   viii. Set the file name and verify that you are saving into your group folder
6. To export data from a different file, unload the current file by pressing on the trash can icon (figure 5), and repeat steps 2-5

PUBLICATION

A. EXPERIMENTAL SECTION

Modify the text below according to the setup and conditions you used during the measurement:

"Thermogravimetric thermal analyses were performed in a Netzsch STA 449 F3 Jupiter Simultaneous Thermal Analysis (STA) instrument. ***XX mg*** of sample ***YY*** were placed in an ***Alumina | Aluminum XX ml*** crucible with weight of ***ZZ mg***. Sample was measured under ***ultra-high purity Helium gas (XX ml/min) | dry air (YY ml/min)***. Buoyancy effect for ***Helium | air*** was corrected by measuring the empty crucible under the same measurement conditions used for the samples. Temperature was increased at a rate of ***XX C/min*** and gases were transferred to the GC/MS instrumentation via a heated (250 °C) transfer line. An Agilent Technologies 7890A GC system equipped with a non-polar capillary column (Agilent J&B HP-5 packed with (5%-Phenyl)-methylpolysiloxane) coupled with a 5975 MSD spectrometer was used for the analyses of the gases released from the samples. A gas injection was triggered every ***XX minutes*** from the beginning of the heating cycle and 0.25 ml of gas was sampled from the gases released by the compound and carrier gas (Helium). Detection limit is typically better than 100 fg but this value can be larger, and it highly depends on the ionization efficiency of the different molecules in the compound. Mass spectra were scanned in the range of ***XX-YY u***. Performance of the thermobalance of the STA was verified by using a certified sample of calcium oxalate monohydrate (European Pharmacopoeia Reference Standard) up to 1000 °C."

B. ACKNOWLEDGEMENT

"This work made use of the IMSERC X-RAY facility at Northwestern University, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-2025633), and Northwestern University."

TROUBLESHOOTING

A. THE COMPUTER SCREEN WILL NOT TURN ON

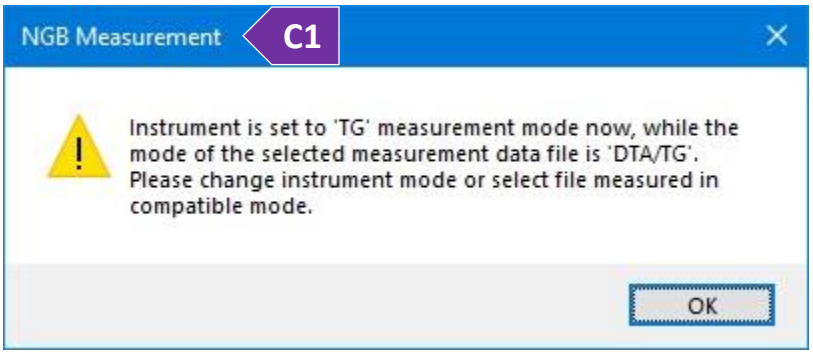
Begin your reservation in NUcore to initiate access to the instrument

B. COMPUTER REQUIRES LOGIN AND A PASSWORD

The default 'STA' user account should be logged in. In case the computer was restarted, the password for the 'STA' account is (see hardcopy by the instrument). See 'Default instrument status' section for more details.

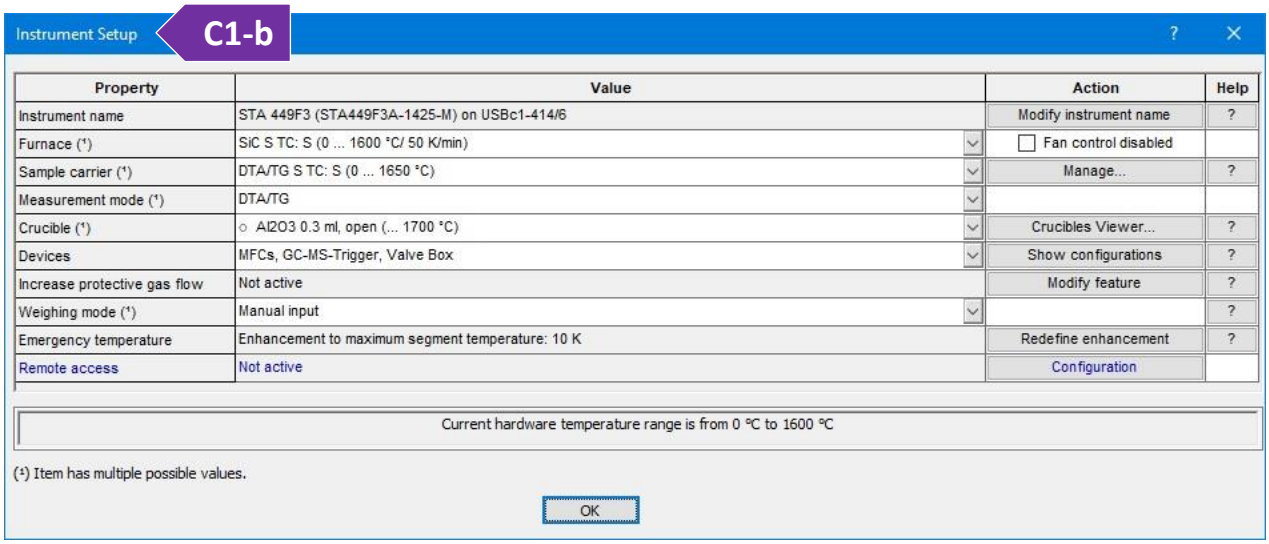
C. SPECIFIC ERROR MESSAGES

1. ***Measurement mode related when trying to load an existing procedure***. Error message will be like the one shown in figure C1 where current mode, e.g., 'TG' might be different than the one being loaded, e.g., 'DTA/TG'.

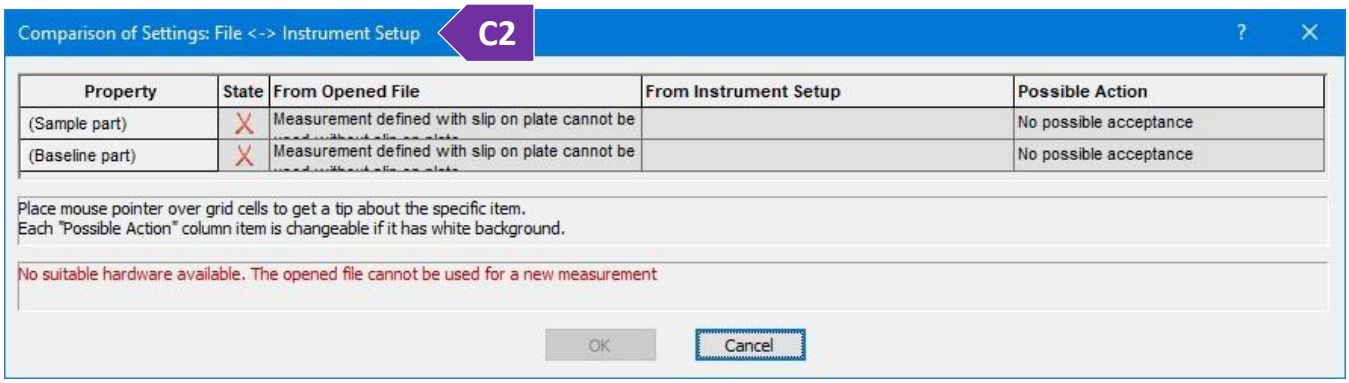


To overcome this error message and successfully load your procedure:

a. On the main window, under the 'File' menu, select 'Instrument Setup'
b. On the 'Instrument Setup' window (figure C1-b), select the appropriate 'Measurement mode' that matches the one in the procedure file you are trying to load, and press on the 'OK' button. Now, you should be able to load your procedure



2. ***Discrepancy between current instrument setup and loaded settings***. Error message will be like the one shown in figure C2 where current instrument setup is different than the one being loaded, e.g., measurement was done with a different carrier and/or furnace. Most of the times, you can change settings directly from the drop-down menus on the 'Comparison of Settings' window to match the loaded setting with the current instrument setup. A particular error message related to the 'slip-on' plates (figure C2) gives no drop-down menus and the only way to clear the error message is:



   a. On the main window, under the 'File' menu, select 'New'
   b. Tick the 'Slip-on plate' option, and
   c. Press on the 'Cancel' button
   d. Now, you should be able to load your procedure

D. THERE IS AN ERROR/PROBLEM WITH THE INSTRUMENT THAT IS NOT ADDRESSED UNDER THE TROUBLESHOOTING SECTION

If there is an error or problem with the instrument which is not addressed under the troubleshooting section, please report the issue by following at least one of the steps below:

1. If you have already started your reservation using NUcore, please end your reservation and select the error reporting option with a brief description about the issue
2. If you have not started your reservation using NUcore, please report problems with the instrument at http://imserc.northwestern.edu/contact-issue.html add place the 'Stop' sign near the instrument computer. 'Stop' signs are located on the shelf above the computers in BG51 and online at the link above. Email or talk to a staff member
3. Email or talk to a staff member

REVISIONS

v1.35 2022/10/19	• 'Change type of gas' section added and appropriate links were added • Picture of the GC-MS flowmeter was updated with current arrangement
v1.32 2021/09/22	• 'Troubleshooting' section updated • Separate 'Exporting data' section created • Training video files transferred from Box to OneDrive, and all relevant links were updated
v1.30 2020/11/13	• Improvements and more pictures added for facilitating remote training: ○ Sample loading has its own section now ○ Links to online video modules added for demonstrating (un)mounting processes using crucibles and samples ○ Each measurement mode was separated to its own section • Figures were updated for the latest Proteus software v8.0.1 and Win10 theme
v1.20 2020/03/10	• Reformatted according to the latest template. Sections about 'Safety', 'Data management', 'Software', 'Publication', and 'Troubleshooting' were added
v1.16 2016/09/01	• Release of original version of the user manual for the acquisition software Proteus v6