Thermo
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Internal procedure for TPDRO 1100 validation by ammonia TPD from a saturated zeolite

Internal reference material: Zeolite powder, supplier code 96096 (flask 100g)
Purchased by: Fluka
Notes: irritant to eyes, respiratory system and skin. Avoid contact and inhalation. For R&D use only. Not for drug use.

TPDRO configuration

Port A:	argon
Port B:	helium
Port C:	not necessary
Port D:	not necessary
Pulse Port:	not necessary

Port 3 (pretreatment):	helium
Port 2:	not necessary
Port 1:	not necessary

ATTENTION: the procedure requires the use of ammonia. Take care to connect the waste ports of the TPDRO to a suitable waste system to avoid that gaseous ammonia is released in the lab environment. Please, strictly follow the local rules that are in due in your country for the use of gaseous ammonia.

Additional required gases:
Pure gaseous ammonia or mixed in helium (10 to 20% in volume)

Recommended filter
Use soda lime as filter media before the TCD detector. Soda lime will stop water but not ammonia.

Recommended sample mass
Use a balance with a precision of at least 0.1 mg weigh between 0.1 and 0.2 g

TPDRO firmware and software version
Use firmware version 2.1 and software version 2.1

Sample preparation
Use a clean and dry reactor. Assemble the reactor as described in the TPDRO instruction manual. Weigh the sample using a balance with a precision at least of 0.1 mg. Place the zeolite in the reactor between two layers of quartz wool. Use the internal volume reducer and firmly close the reactor.

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Important notes and preliminary operations

The described procedure and the results can internally validate the TPDRO in use provided that:

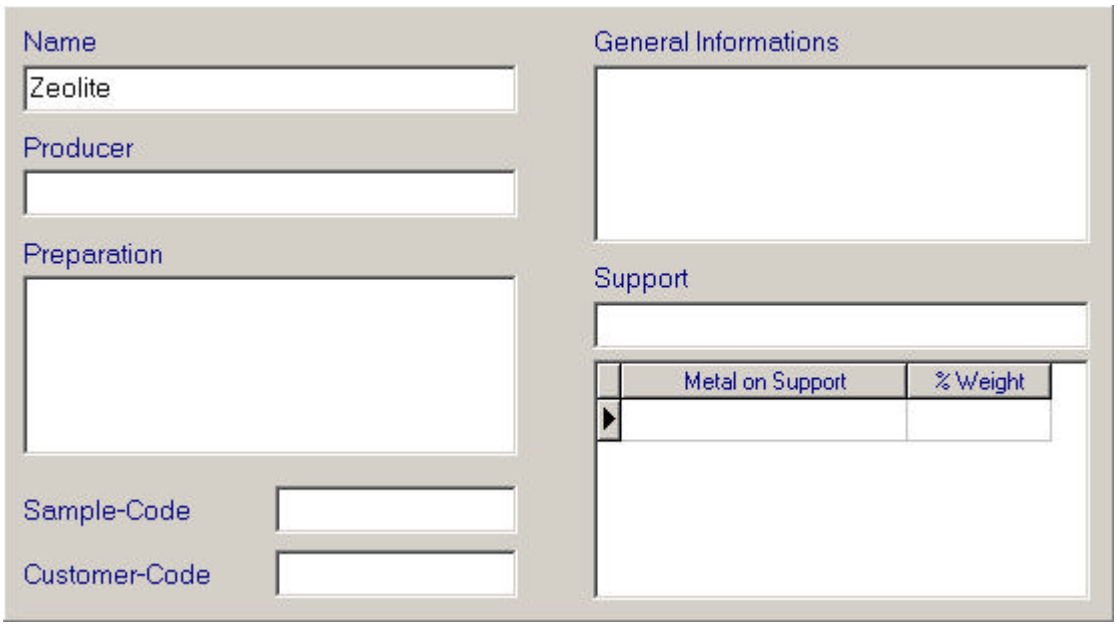
- the instrument is properly installed and configured according to the instructions and the installation is done by trained service operators
- the gases are pure and dry, the gas lines clean
- the instrument has been properly calibrated (loop volume, ovens linearization, mass flow controllers, etc.)
- the filter for water is new and activated (soda lime)
- the instrument is leak free

Software set up

Open the TPDRO software and input the following data in the relevant database.

Sample database

Open the sample database click NEW and a sample cards as indicated below.



Leave the other fields empty.

Analytical procedure

The analytical procedure consists into four sequential steps:

1- Zeolite activation at high temperature in flow of inert gas
2- Zeolite saturation with gaseous ammonia
3- Removal of physisorbed ammonia
4- Temperature programmed desorption of chemisorbed ammonia
5- Ammonia signal quantitative calibration
6- Example of data processing and results

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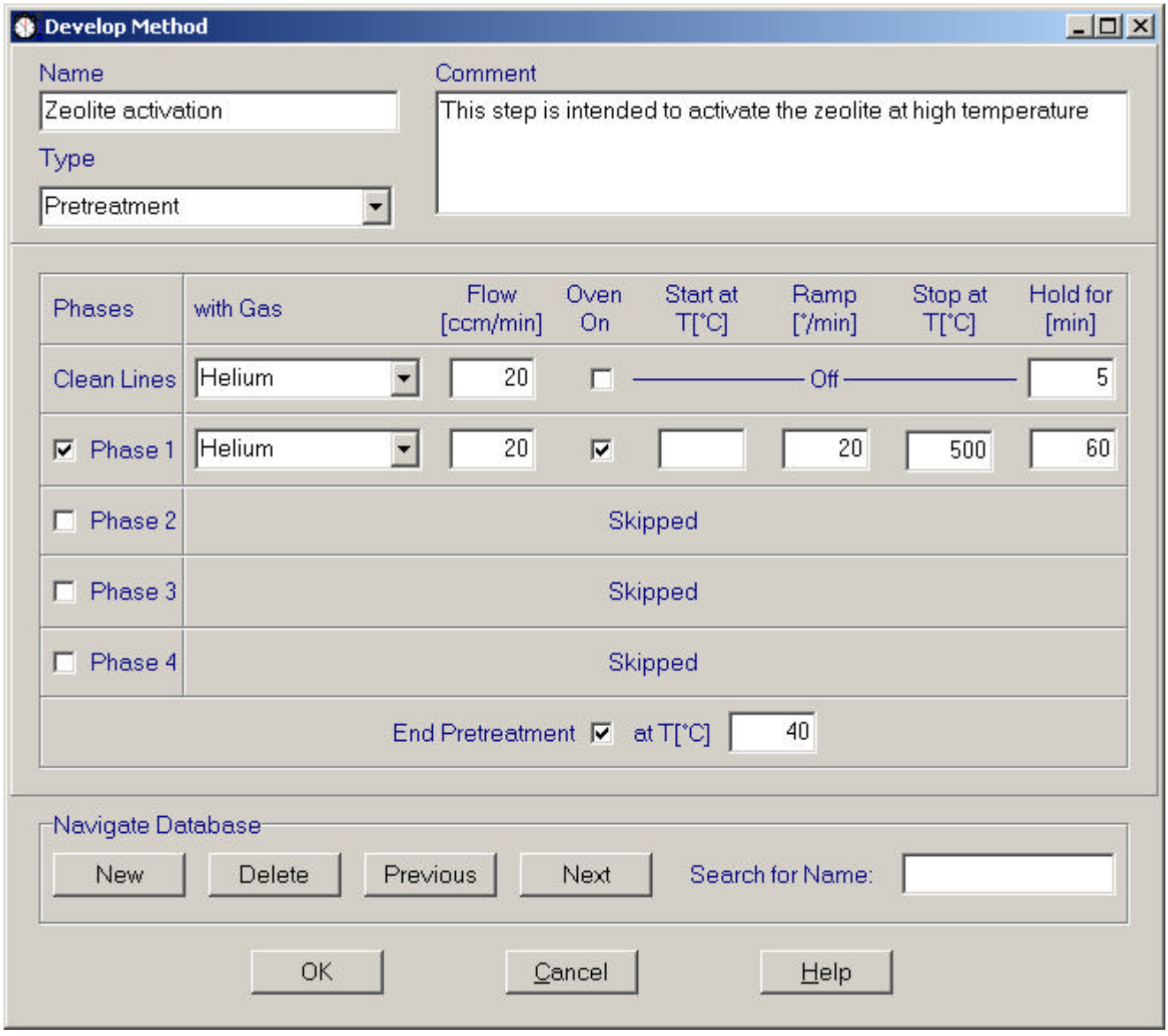
1 – Zeolite activation

Open the Method Database, click NEW and select PRETREATMENT. Fill the method according to the following.



Place the reactor with the zeolite in one of the oven (i.e. left oven). Then for the TPDRO software select “Run Control”

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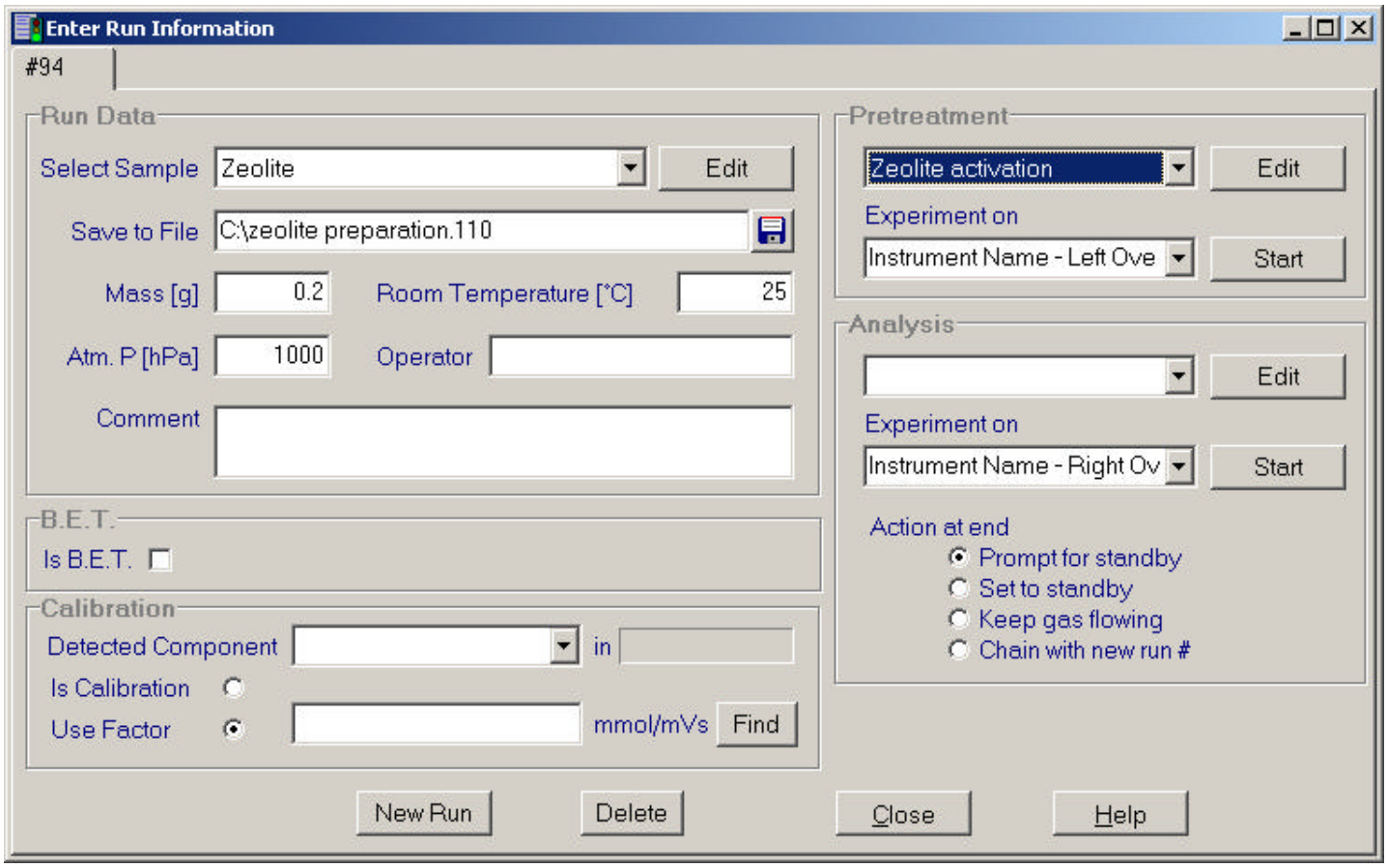
Prepare to start a pretreatment on the left oven:



Once the sample activation is over, remove the reactor and perform the sample saturation.

2 – Ammonia saturation

ATTENTION

Ammonia is a dangerous gas. Be sure that the lab and the operators are fully compliant to local rules for the use of this gas.

The saturation using pure gaseous ammonia or in a mixture 10 to 20% in helium MUST be performed under a suitable fume hood in a completely safe environment.

From the TPDRO, close the reactor and transfer it under a fume hood. Connect the ammonia gas cylinder to the reactor, open the reactor and flow ammonia (or the mix) for 30 minutes at room temperature. After the saturation is over, close the reactor and disconnect the tubing. A purge line with inert gas (helium) is recommended to remove the excess of ammonia from the tubing and from the reactor. Transfer the reactor to the TPDRO.

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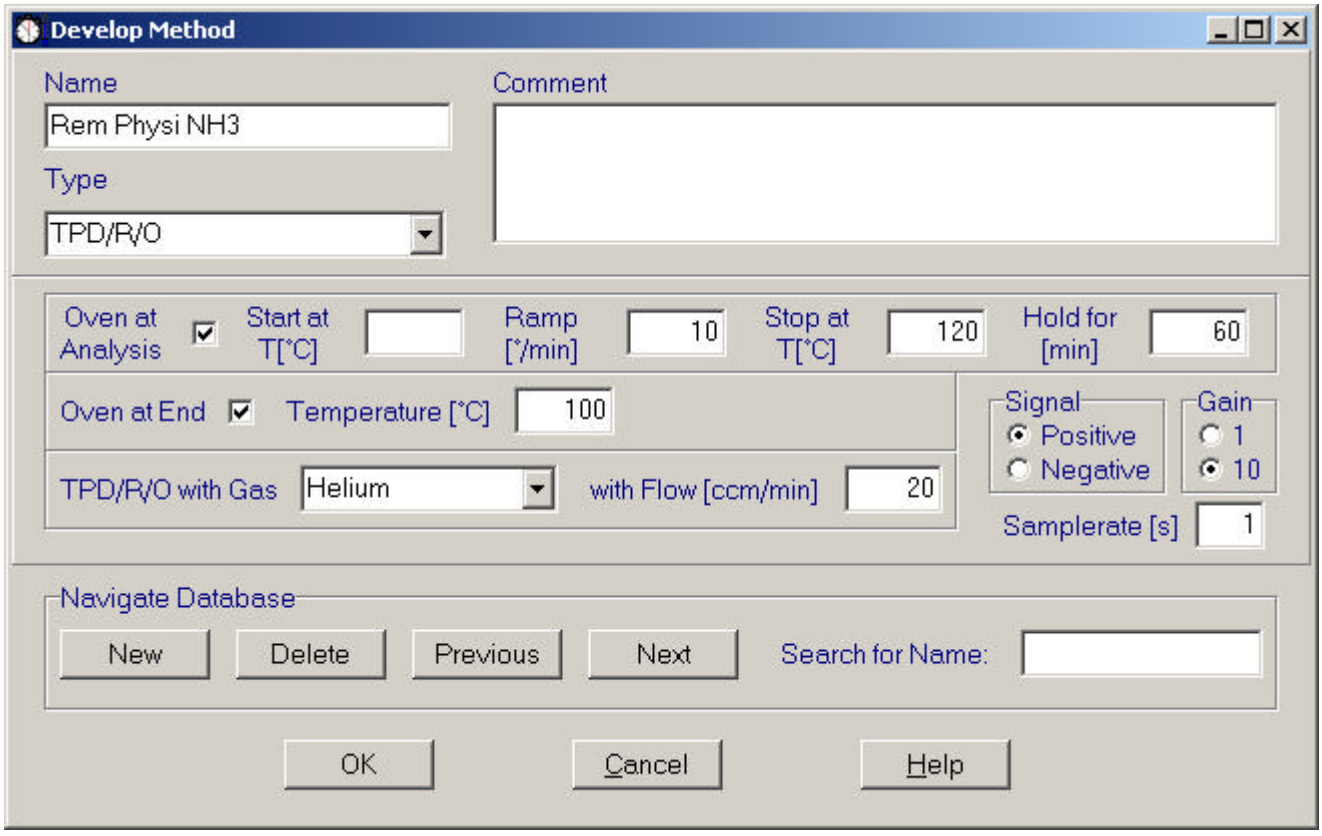
3/4 – removal of physisorbed ammonia and TPD analysis

Ammonia usually is partially physisorbed and partially chemisorbed. In order to evaluate the acidic sites concentration only it is necessary to degas the zeolite to remove the physisorbed ammonia. The operation of ammonia degassing and TPD experiment can be done in an automatic sequence. Thus, prepare the following two methods, one for physisorbed ammonia degassing and the second for ammonia TPD.



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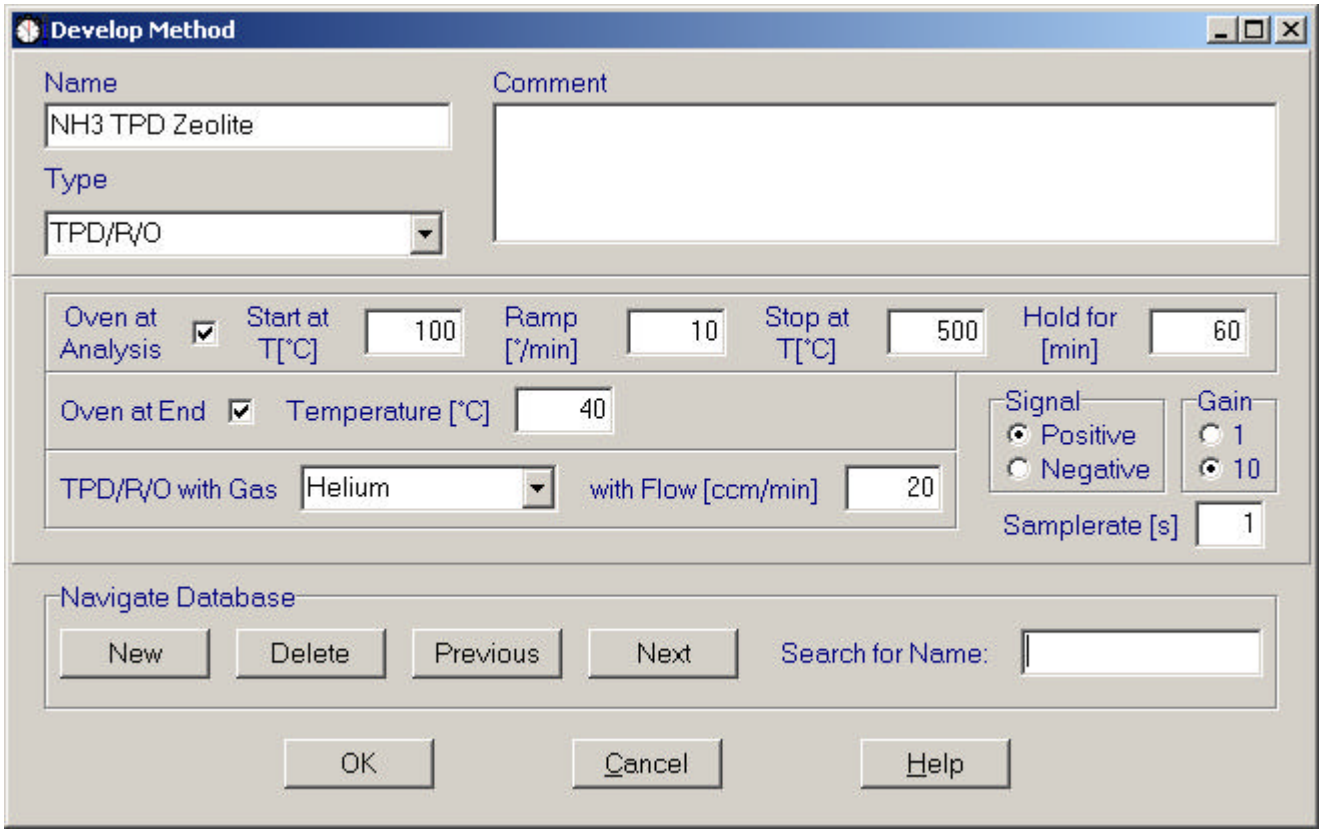

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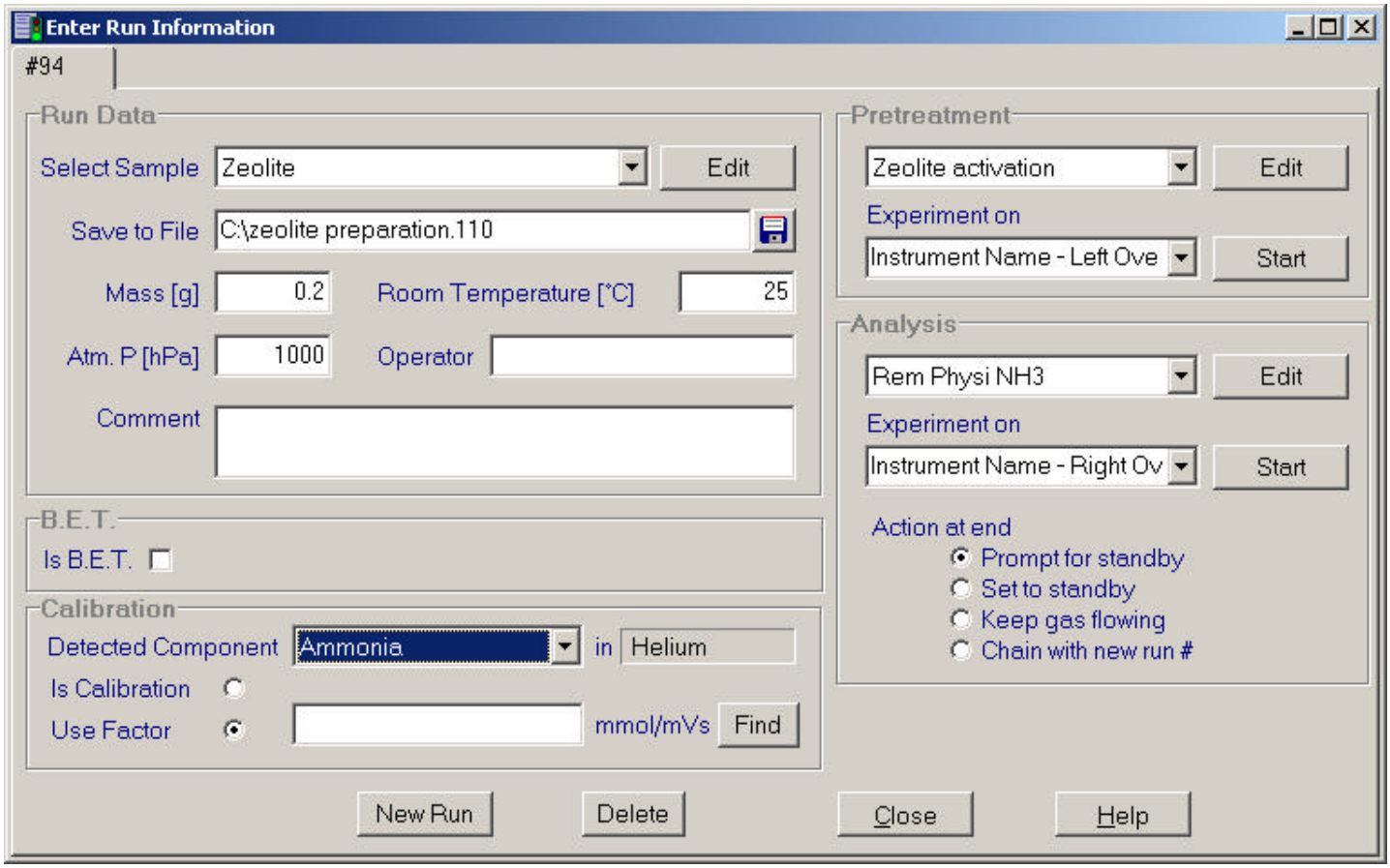
Start the analytical sequence

Open the Run Control page and fill out the following sequence by using the previous run number implemented for the sample activation. In the box position named “Analysis” click on EDIT button and select the method previously prepared named “Rem Physi NH3”:

Fill out all the boxes as indicated above by manually selecting the “Detected Component” box, choose Ammonia.



When all the fields ad filled click on the tick mark “Chain with new run #” and a new card (in the above example number 95) will be available. Select then the new card number and prepare the card for the TPD experiment by selecting the analytical method previously named “NH3 TPD Zeolite”. In this page you have to select a new file name and again choose “Ammonia” in the “Detected Component” field.

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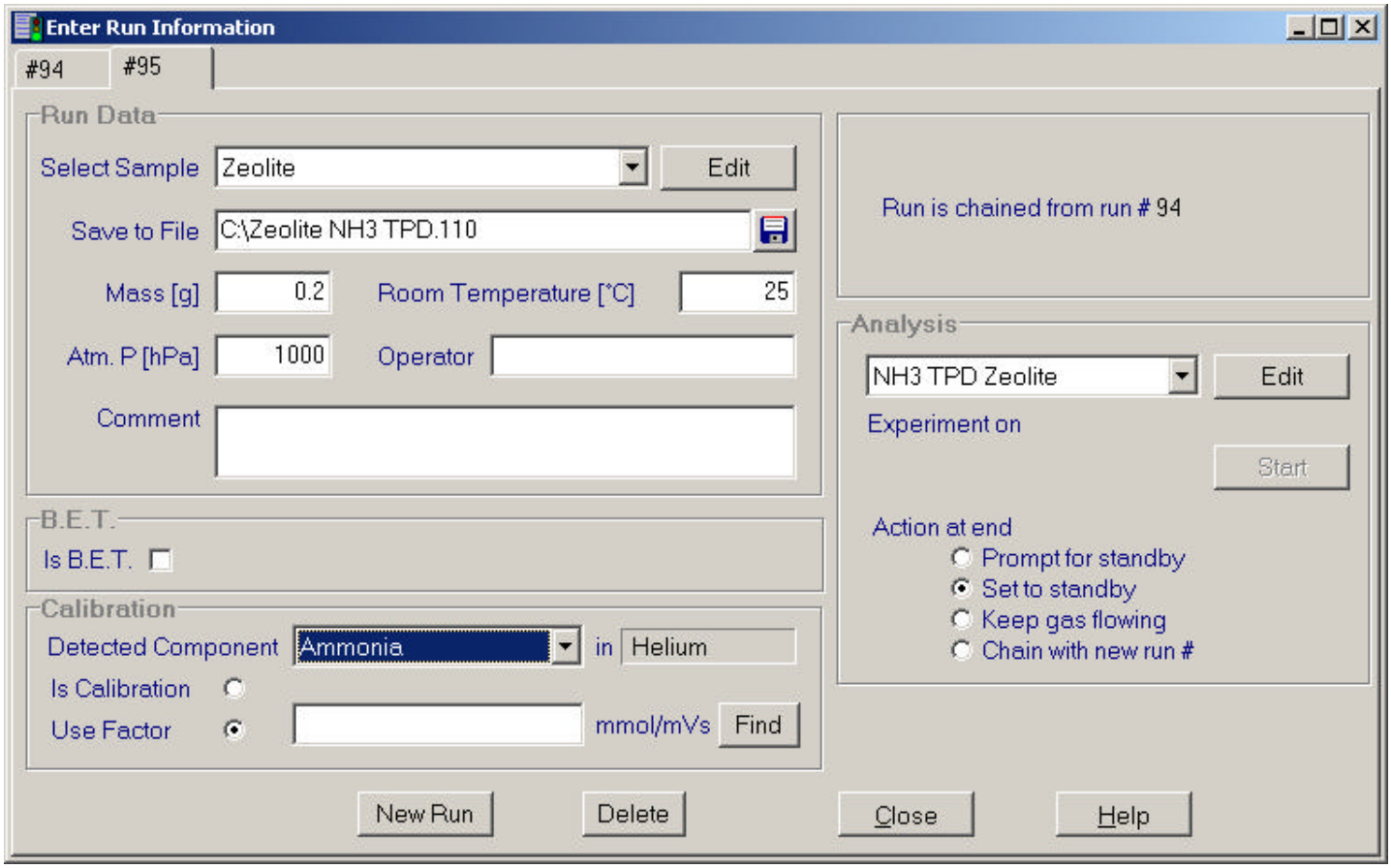
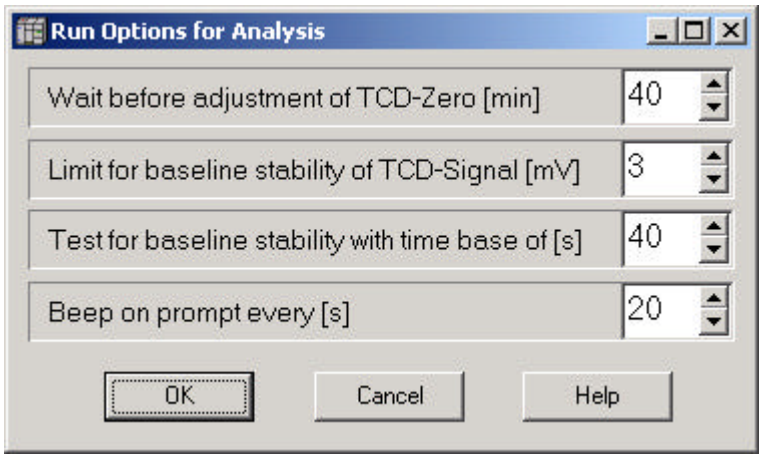


When all the boxes and properly filled click on “Set to stand by”

Prepare now the Run Options parameters as follow:



Return to the Start page, select the first prepared card, check that the oven selection is the proper one and eventually change it, then click on the START button. The total sequence will last for some hours. It is possible to start the procedure running the experiments during the night.

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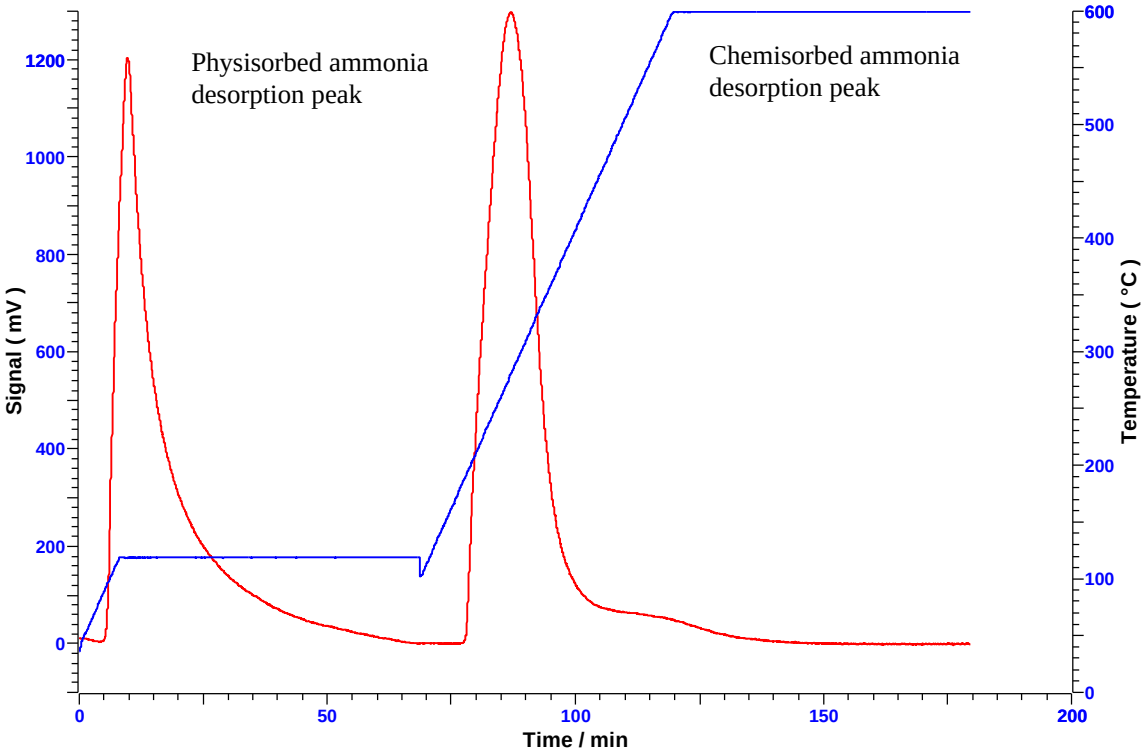
Data reduction

The total preparation / analysis sequence will generate 2 different files. The most important one is relevant to the ammonia TPD (the second analysis). The complete sequence is represented in the following linked graph:



Where the blue line represents the temperature profile, the first peak is relevant to the physisorbed ammonia desorption at 120 °C while the second peak is relevant to the strong acid sites of the zeolite.

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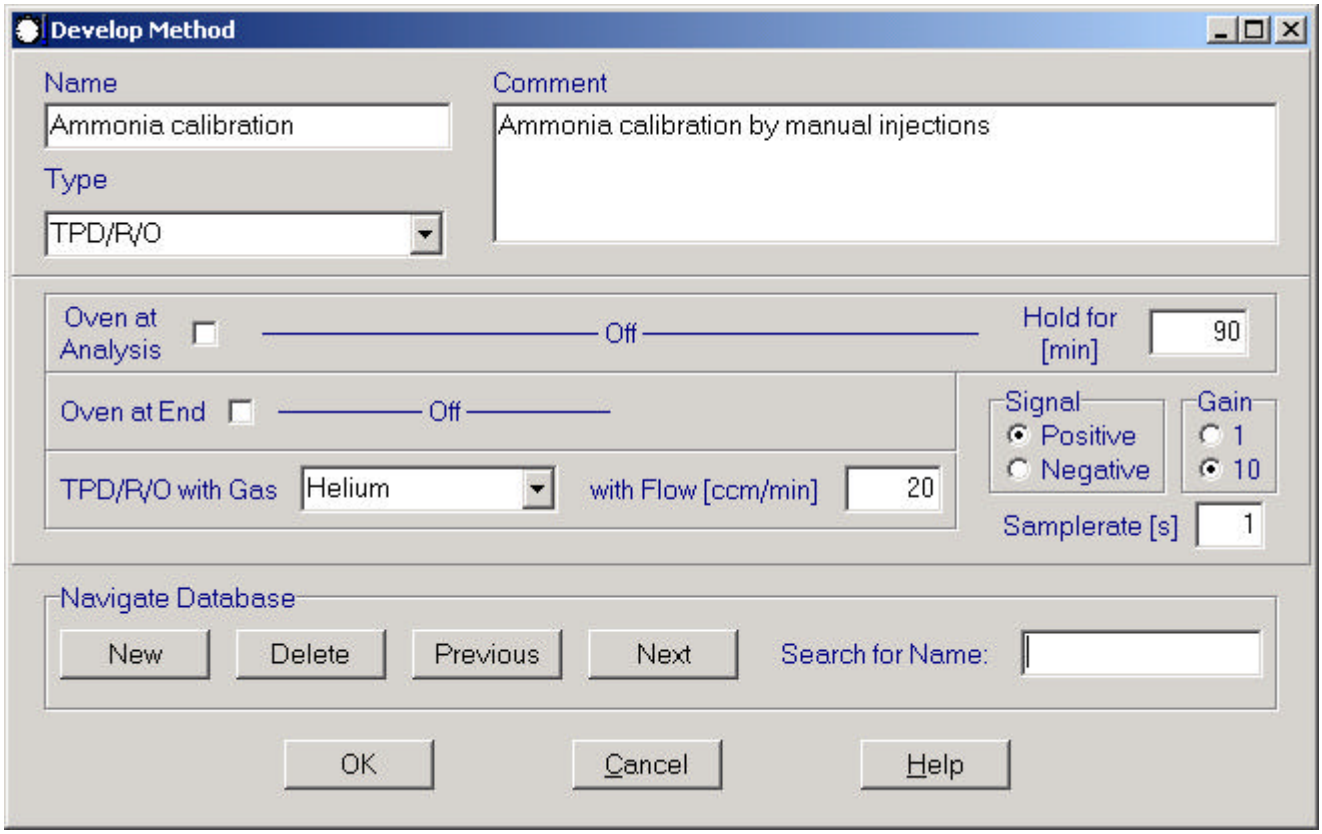
5 – Ammonia signal calibration

An ammonia signal calibration is required for quantitative measurement of the desorbed amount of gas. The calibration can be performed by a manual injection of pure gaseous ammonia in an empty reactor. Refer to the relevant instruction manual for the proper calibration procedure.

Prepare a method as follow:



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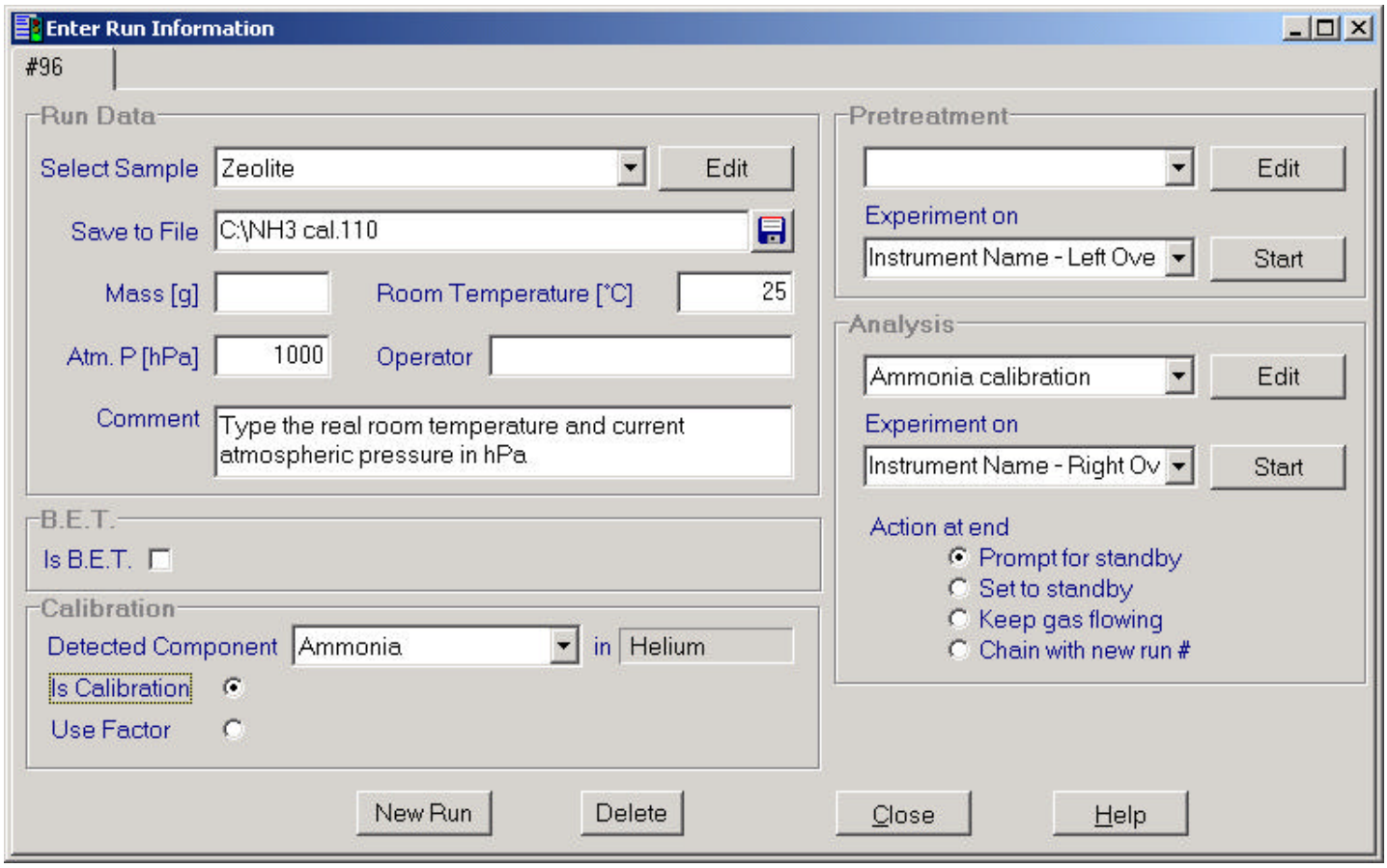
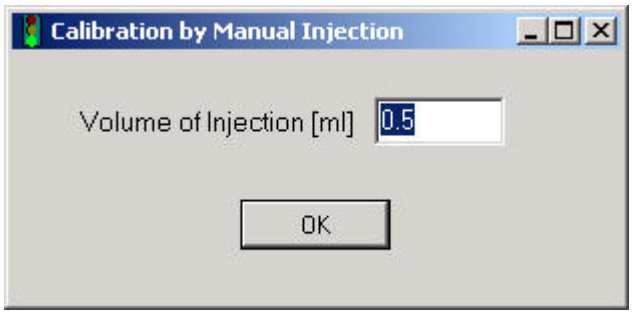
Prepare the Run Page as follow:



Press start. As Start button is pressed, the software recognizes that it is a calibration by manual injections and requires to type the desired injection volume. In the example it is recommended to use at least 0.5 ml:



When the software starts to detect the tcd signal, prepare a clean gas syringe. Fill the syringe using pure ammonia and make at least two injections (refer to the instrument instruction manual).
At the end of the calibration, properly subtract the baseline and integrate the two peaks. For best results, it is recommended to integrate the peaks manually. Once the peak start is detected, place the peak stop indicator as the tcd goes back to the baseline. Record the timing between and integrate the second peak accordingly (time lapse between the peak start and peak stop for the two peaks should be the same).

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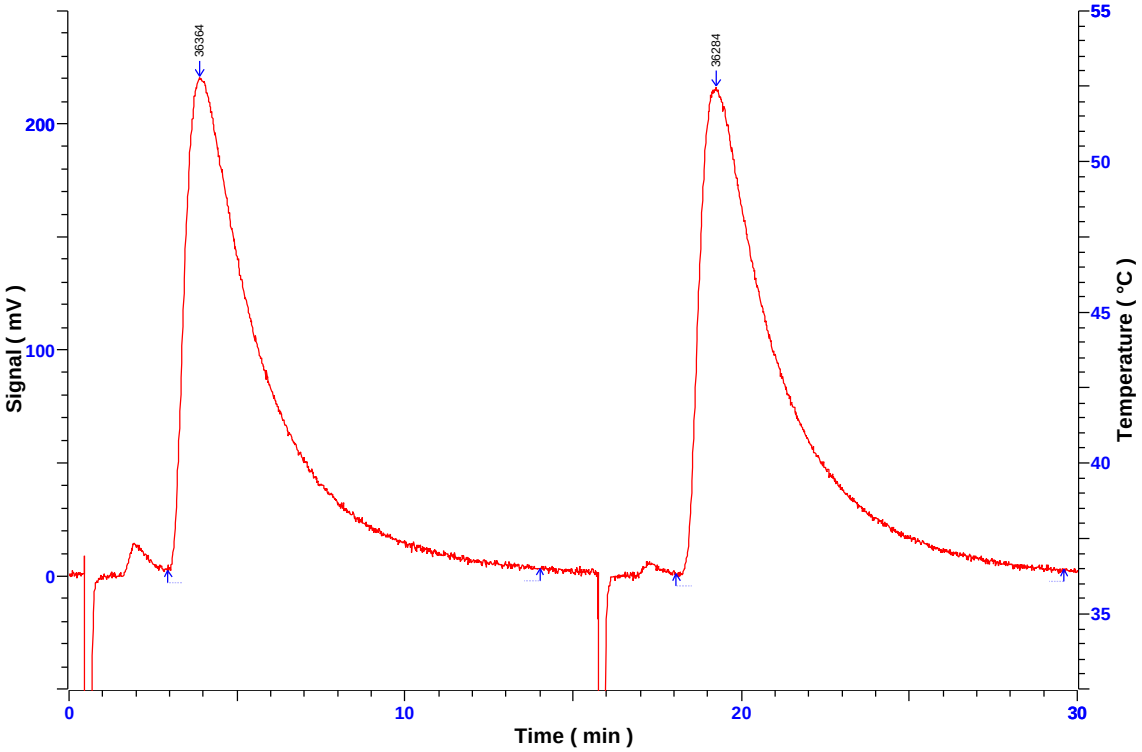

Save the file again to record the calibration factor.

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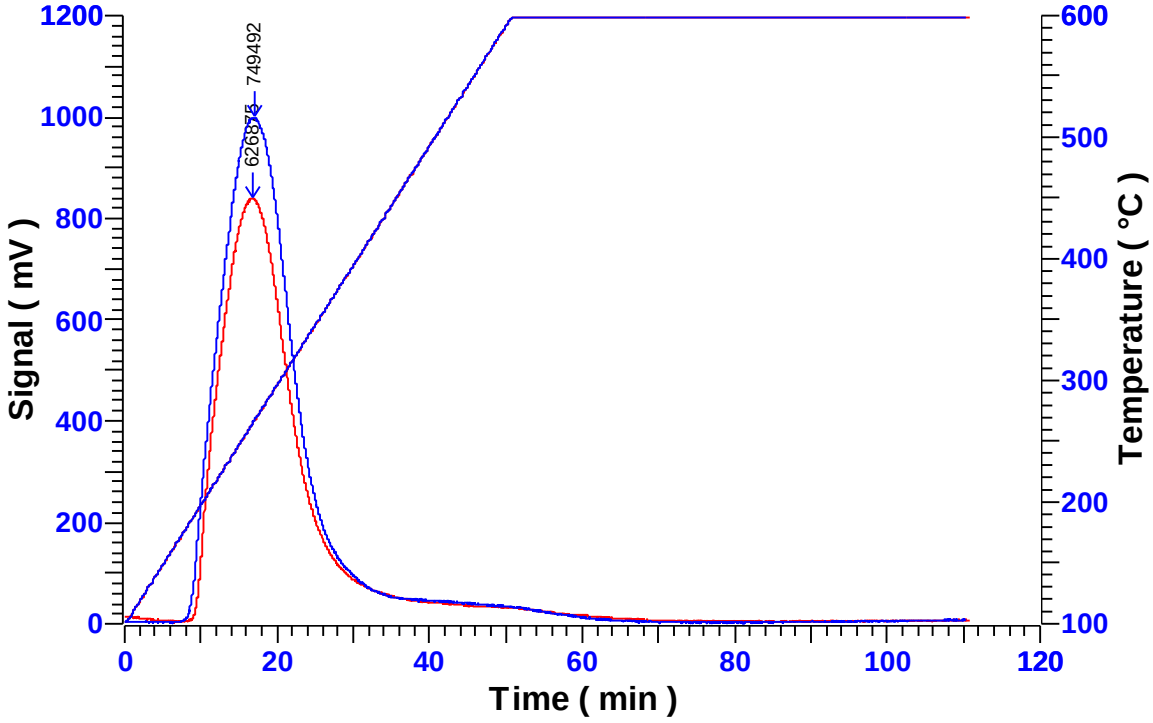
Example of data processing and results

The zeolite sample used as internal reference is quite reproducible. Following the example of two repeated tests by changing the sample mass. Graphs are built using the TCD signal referred to sample mass versus time and temperature.

TCD (mv) vs time for run 1 + 2



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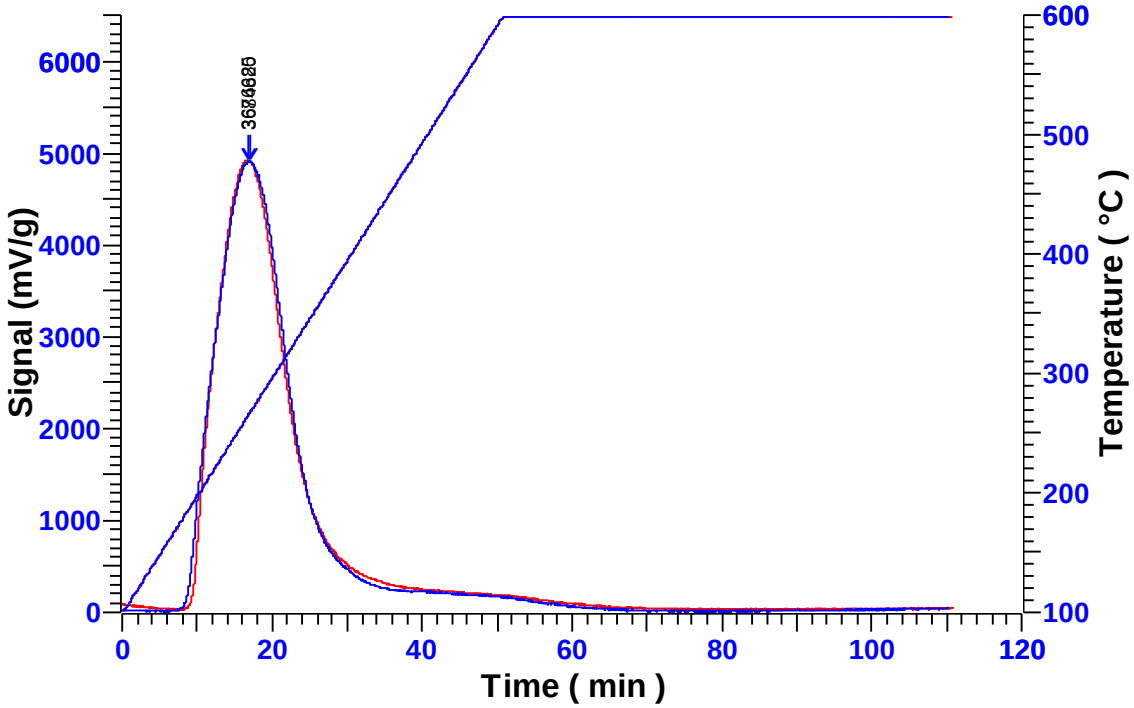
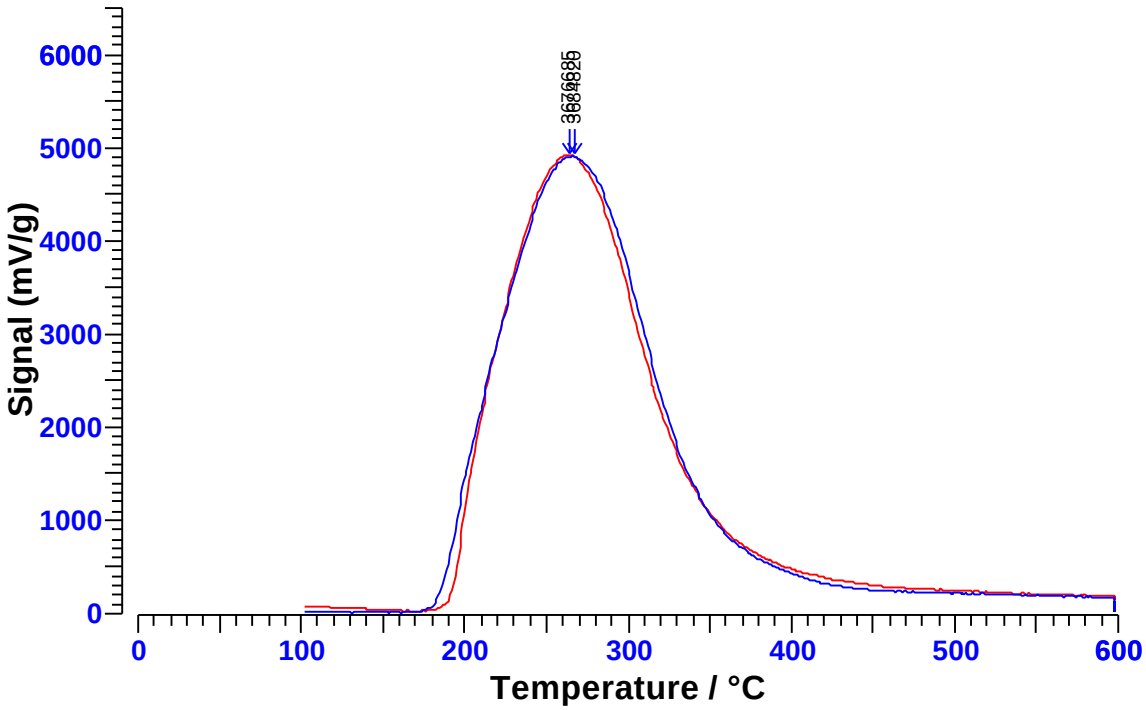
TCD (mv/g) vs time for run 1 + 2



TCD (mv/g) vs Temperature for run 1 + 2



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Results

	Sample Mass	Adsorb. NH3	Peak Temp.
	(g)	micromole/g	°C
Sample 1	0.2034	2028	267
Sample 2	0.1705	2023	264