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Temperature-programmed Desorption / Reduction / Oxidation (TPD/TPR/TPO) and Pulse-Sorption / Chemisorption
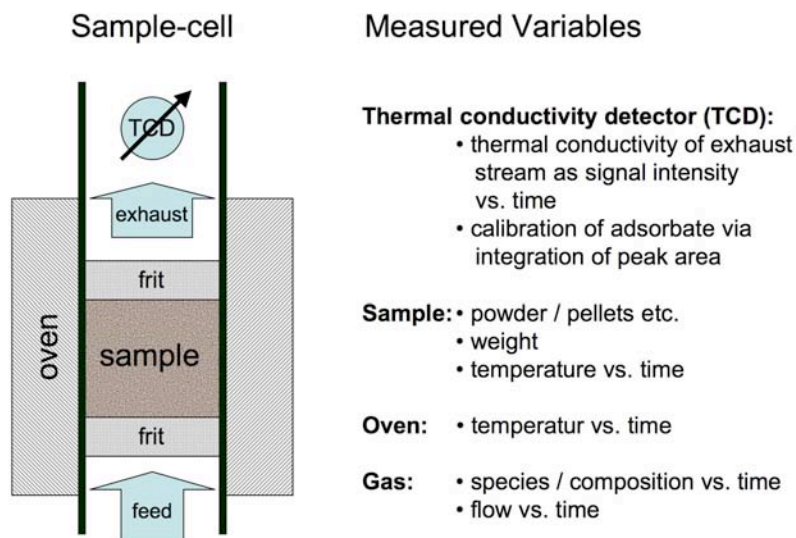# Instrument: TPD/R/O 1100 by Thermo Scientific

Measurement Principle

This technique offers the ability to investigate the temperature-dependence of specific ad- or desorption processes of samples in a well-defined gas-atmosphere - as in the case of ammonia-TPD for the evaluation of acidic centers of zeolite samples or by pulse-chemisorption for the determination of active metal sites in heterogeneous catalysts.

Depending of the kind of sample, approximately 0.1-1 g of material is needed, which is filled between fused silica frits in a quartz-glass tube with tight contact to a heating mantle. All of the following steps - sample pretreatment, adsorption (or chemisorption) and desorption – may be monitored by a thermal conductivity detector (TCD) in the exhaust gas stream with variation of the parameters: temperature, gas-flow, gas species or gas composition. Data treatment is based upon the calibration of the TCD via the injection of different amounts of pure sorbate in carrier-gas by the evaluation of the peak area.

Sample-cell

Measured Variables

Thermal conductivity detector (TCD):
• thermal conductivity of exhaust stream as signal intensity vs. time
• calibration of adsorbate via integration of peak area

Sample:
• powder / pellets etc.
• weight
• temperature vs. time

Oven:
• temperatur vs. time

Gas:
• species / composition vs. time
• flow vs. time

Pre-treatment

The first step consists of to bringing the sample to a well-defined state, which is ensured by complete desorption to reach maximum adsorption capacity. The activation procedure is conducted employing a temperature ramp under a constant flow of pure inert gas to remove all adsorbed material with special respect to the thermal stability of the sample material. In the case of zeolites the activation is equivalent to the usual calcination procedure.

Further sample pretreatment is method-dependent: while chemisorption / pulse sorption experiments start from this sample state with maximum loading capacity, TPD-measurements need an additional loading step to follow the temperature-dependency of the desorption of the specific adsorbate.

For ammonia-TPD of zeolites, the adsorption procedure is followed by a second, well defined desorption procedure prior to the measurement to remove unspecifically adsorbed ammonia.

Measurement

Typical measurement protocols and -types can be found in the attached excerpt from the machine manual. The most often required experiments are TPD-measurements (pp. 86ff) for zeolites or pulse-sorption / chemisorption (p. 87ff) for heterogeneous catalysts and adsorbents. If a specific desorption peak can be detected, the determination of adsorption energy is possible (p. 91ff).

Eligible adsorbates are not restricted to gaseous compounds only: as long as they show a non-negligible vapor pressure, adsorbates can be manually injected with a micro-syringe into the feeding gas-stream for pulse-sorption experiments. Also possible is a combined experiment: feeding of adsorbate analogue to pulse-sorption experiments at a constant temperature followed by desorption employing a temperature gradient analogue to TPD-experiments.

Technical Data

Sample mass (typical):	0.5 g
Sample types:	powder, pellets etc. up to 1 cm in diameter
Temperature range:	RT to 1,100 °C
Heating rate:	1 – 40 K/min
Available gas species:	He, Ar, N_2
...by request:	H_2, O_2, CO, NO_x, synthetic air, etc…
Pulse-gases:	NH_3, ... C_nH_m and by request
Gas-flow:	10 – 200 ml/min
Detector:	Tungsten

Contact

Please contact us for further information or details - or about possibilities to develop experimental layouts to solve your specific problem:

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9   Calculation Methods

In the following chapter the following abbreviations and symbols will be used:

S_m	Sample Mass [g]
X_{met}	Metal Percentage [%]
F_s	Stoichiometric Factor [metal mole / gas mole]
M_{met}	Metal Atomic Weight [g/mole]
M_{sam}	Molecular Weight of Sample Active Phase [g/mole]
ρ_{met}	Metal Density [g/mL]
a_{met}	Square Section of a Metal Atom [^{2}/metal atom]
M_{gas}	Gas Molecular Weight [g/mole]
t	Time [s]
V_{loop}	Total Loop Volume [mL]
V_{syr}	Syringe Injection Volume [mL]
T_{inj}	Injection Temperature [K]
P_{inj}	Injection Pressure [hPa]
X_{gas}	Reactive Gas Percentage [%]
R	Constant of Gases (8.314451 [J/mole K])
$\int_{man}$	Peak Area in Manual Injections [mV s]
$\int_{av\ man}$	Average Peak Area in Manual Injections [mV s]
$\int_{pulse}$	Peak Area in Pulse Injections [mV s]
$\int_{av\ pulse}$	Average Peak Area in Pulse Injections [mV s]
$\int_{sum}$	Total sum of peaks area [mV s]
N_p	Total Pulse Number
N_h	Number of Hidden Peaks in Pulse Chemisorption
N_d	Total Detected Peaks
N_s	Number of Last Peaks showing the same area in Pulse Chemisorption
$\int_{dro}$	Detected Peak Area in TPD/R/O Analyses [mV s]
C_F	Calibration Factor [mmole/mV s]
$C_{F\ int}$	Internal Calibration Factor (Pulse Chemisorption) [mmole/mV s]
n_{ads}	Amount of Gas Adsorbed in Pulse Chemisorption[mmole/g]
n_{des}	Amount of Gas Desorbed in TPD [mmole/g]
n_{rea}	Amount of Gas Reacted in TPR/TPO [mmole/g]
S_f	Shape Factor
L	Avogadro number (6.023 10^{23} [molecule/mole])
A_{met}	Metal Surface Area [m^2/g of metal]
A_{sam}	Metal Surface Area [m^2/g of sample]
A_{sup}	Metal Surface Area [m^2/g of support]
D_{met}	Metal Dispersion [adsorbing metal atoms/total metal atoms]
d_{met}	Mean Metal Aggregate Diameter [nm]

9.1 Loop Calibration

Perform the Loop Calibration procedure as previously described in this manual. When the Loop Calibration run is over, load in memory the saved file. The following graph is obtained.
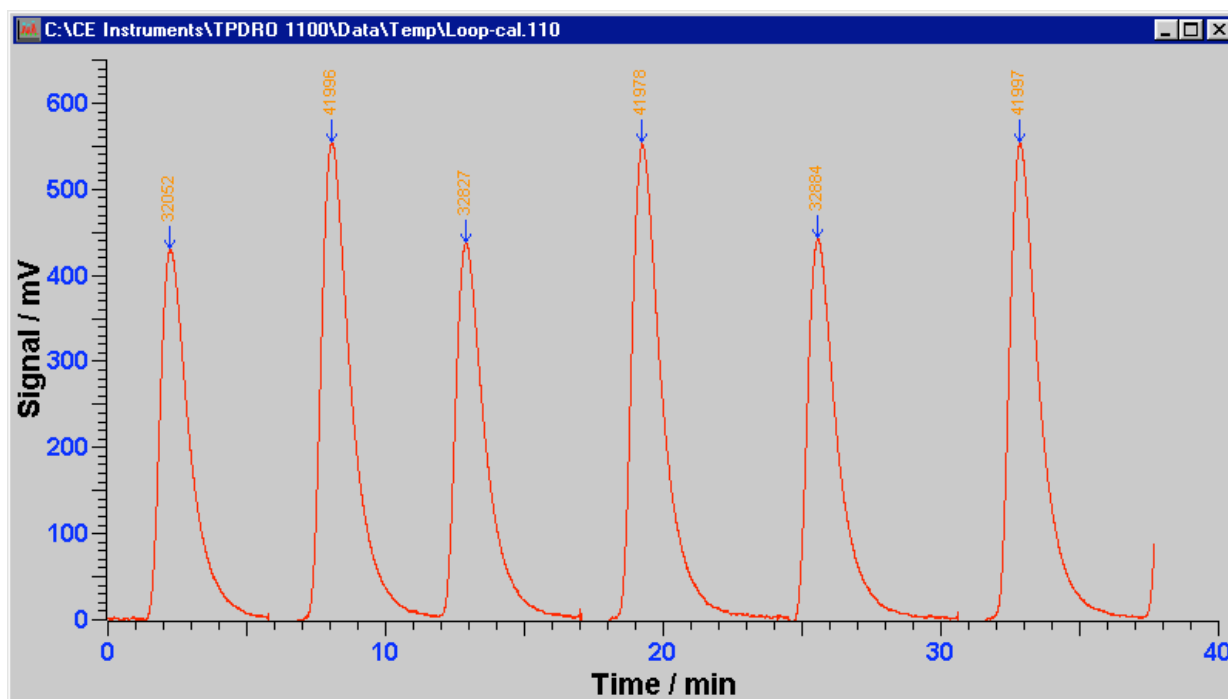

Figure 84

Perform now the previously described procedures for baseline subtraction and peaks integration. In the following example only three automatic injections and three manual injections have been performed. Anyway, the recommended number of automatic and manual injections is five each. In the above graph the smaller peaks are related to the automatic injections performed by the loop valve (unknown loop volume) while the higher peaks result from the syringe manual injections (known syringe volume). When the integration is performed, save again the file with the same file name. The calculation of the loop volume is done manually.

ATTENTION: The total volume of the injections (in mL) results from the sum of the Loop Volume and the valve dead volume. For instance, if a loop of nearly 0.2 mL is prepared and installed, the total injection volume will be the sum of 0.2 mL of the loop plus about 0.1 mL of the valve dead volume. Therefore the real value will be about 0.3 mL.

When the integration has been properly done, calculate the loop volume as follows (values are taken from the above example):

Loop Volume Calculation	Automatic Injections (unknown volume V_{loop}) $\int_{pulse}$ [mV s]	Manual Injections (known volume V_{syr} = 0.5 mL) $\int_{man}$ [mV s]
Injection 1	32052	41996
Injection 2	32827	41987
Injection 3	32884	41997
Average values [mV.s]:	$\int_{av\,pulse}$ = 32587.7	$\int_{av\,man}$ = 41993.3

Table 3

V_{loop} is calculated according to the following relation:

1) $V_{loop} / V_{syr} = \int_{av\,pulse} / \int_{av\,man}$ -> $V_{loop} = (V_{syr} \int_{av\,pulse}) / \int_{av\,man}$

That is to say in the above example:

$V_{loop} = 0.5 \cdot 32587.7 / 41993.3 = 0.388$ [mL]

The found value of the loop volume must be typed in the relevant label in every Pulse Chemisorption method. When the loop is changed, the calibration must be repeated and the new value must be replaced.

9.2   Calibration factors calculation

The calibration factor is a parameter that must be measured and used if quantitative calculations are required. The calibration factor puts in relation the peak integration value with the amount of reactive gas chemisorbed or desorbed by the sample. A typical calibration run consists in an experiment performed in the same analytical conditions (i.e. flow, temperature rates, starting and final temperature, etc.) and with the same detected component.

9.2.1   By Manual Injections

The calibration by manual injections consists in injecting in the system known doses of reactive gas by a calibrated syringe for gases. The resulting calibration factor can be used for the quantitative computation in the experiments of TPD and Pulse Chemisorption. The following example of manual calibration has been performed using the parameters:

Carrier   = nitrogen
Flow   = 20 mL/min
Probe gas   = 5% hydrogen in nitrogen
Syringe volume   = 1 mL
Atmospheric pressure   = 1000 hPa
Room Temperature   = 25 C
Number of injections   = 4

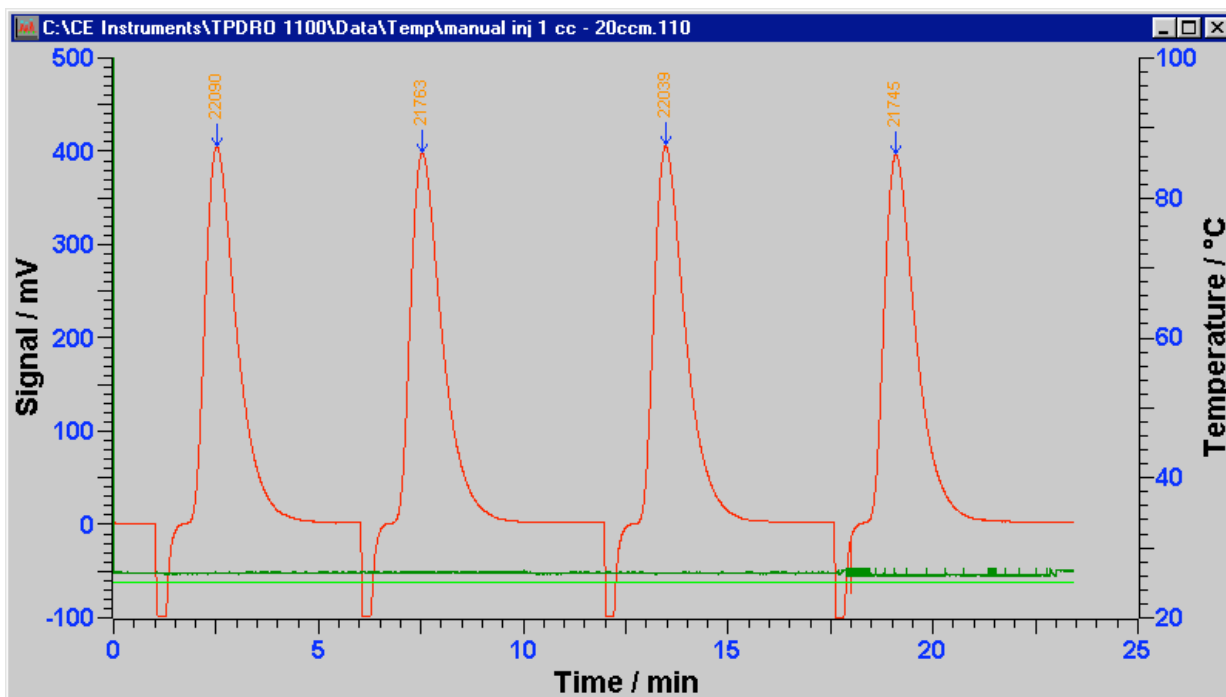This is the resulting graph after baseline subtraction and peaks integration:

Figure 85

The integration values are the following:

N_d	$\int_{man}$ (mV s)
1	22090
2	21763
3	22039
4	21745
$\int_{sum}$	87637

The calculation formula is the following:

2) $C_F = (N_d \ V_{syr} \ X_{gas} \ P_{inj} \ 10^{-3)} \ / \ (R \ T_{inj} \ \int_{sum})$

The same equation by dimensional expression gives:

[mmole/mV s] = [mL][hPa][m^3/mL][1/100][Pa/hPa][mmole/mole][mole K m^2/m^3 N][1/K][1/mV s]

NOTE: 1 N/m^2 = 1 Pa

In the above example, substituting the calibration values, we obtain:

$C_F = (4 . 1 . 5 . 1000 . 0.001) / (8.314451 . 293 . 87590) = 9.36788 \ E^{-8}$

9.2.2   By Automatic Pulse Injections

The equation used to compute the calibration factor using the automatic pulse injection procedure is the same as equation (2) but instead of the syringe volume (V_{syr}) the loop volume (V_{loop}) is used.

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9.2.3   TPR of Copper (II) Oxide

Calibration runs for TPR and/or TPO experiments can be performed with a suitable pure sample that reacts with the probe gas according to a well-known stoichiometry. The recommended samples are copper (II) oxide (CuO) for TPR experiments and copper (I) oxide (Cu2O) for TPO.
In TPR/TPO calibration runs the calibration factor depends mainly by the carrier flow rate. Assuming that the carrier composition is always the same, only the carrier flow rate strongly influences the C_F value. The best calibration conditions are anyway obtained performing the analysis with the same temperature rate used during the calibration run. In the following paragraph the example of TPR calibration will be considered.

NOTE: Only use substances having purity not lower than 99.99%.

Sample	= copper (II) oxide -CuO
Active Phase Molecular Weight	= 79.54 g/mole
Sample Mass	= 0.0033 g
Carrier	= H_2 5% in nitrogen
Flow	= 60 mL/min
Start T	= room T
Final T	= 800 C
Rate	= 15 C/min
Room T	= 26 C
Atmospheric pressure	= 1000 hPa
Stoichiometric Factor	= 1

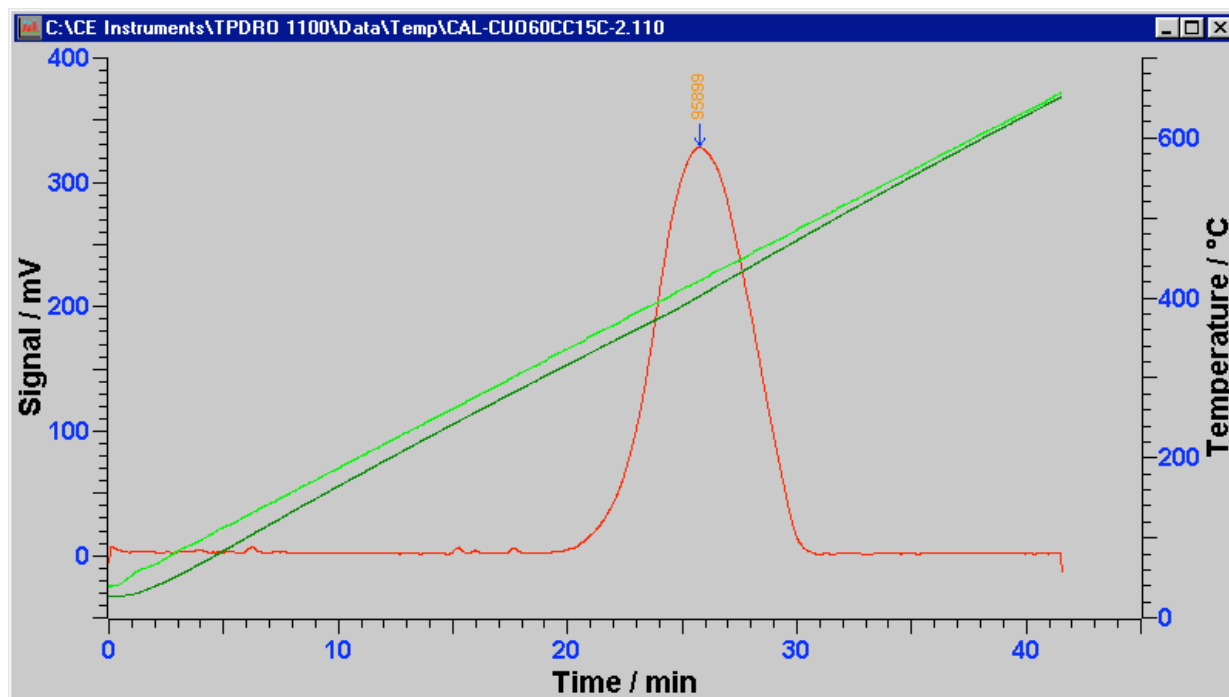The chemical reaction is $H_2 + CuO = Cu + H_2O$ giving the following result:

Figure 86

Detected peak area $\int_{dro}$ = 95899 [mV s]

The equation used for the calibration factor calculation in TPR/TPO is:

3) $C_F = (S_m \ 1000) / (F_s \ M_{sam} \ \int_{dro})$

The same equation by dimensional expression gives:

[mmole/mV.s] = [g sam.][mmole/mole][gas mole/sam. mole][sam. mole/g sam.][1/mV s]

In the above example, substituting the calibration values, we obtain:

$C_F = (0.0033 \ 1000) / (1 \ 79.54 \ 95899) = 4.33 \ E^{-7}$

9.2.4   Internal Calibration Factor in Pulse Chemisorption

The TPD/R/O software, in the case of Pulse Chemisorption analysis, calculate a special calibration factor, named as "internal". This procedure is completely automated when, during the automatic peak detection and integration procedure, the calibration factor is not selected (C_F empty). Therefore, the software computes automatically the internal calibration factor ($C_{F \ int}$). $C_{F \ int}$ is evaluated according to the last peaks of the experiment, that is the peaks generated by non-chemisorbed probe gas.

Consider the example of a pulse chemisorption experiment on platinum catalyst. The analytical conditions are the follows:

Sample	= platinum 2% on Al2O3
Sample Mass	= 0.2595 g
Carrier	= nitrogen
Flow	= 10 mL/min
Pulse Gas	= hydrogen 5% in nitrogen
Analysis temperature	= 30 C
Room Temperature	= 30 C
Atmospheric pressure	= 1000 hPa
Number of pulses	= 20
Loop Volume	= 0.7496 mL

In the following example, only the calculations regarding the internal calibration factor will be described. The same analysis file will be later used like example for the result calculation.

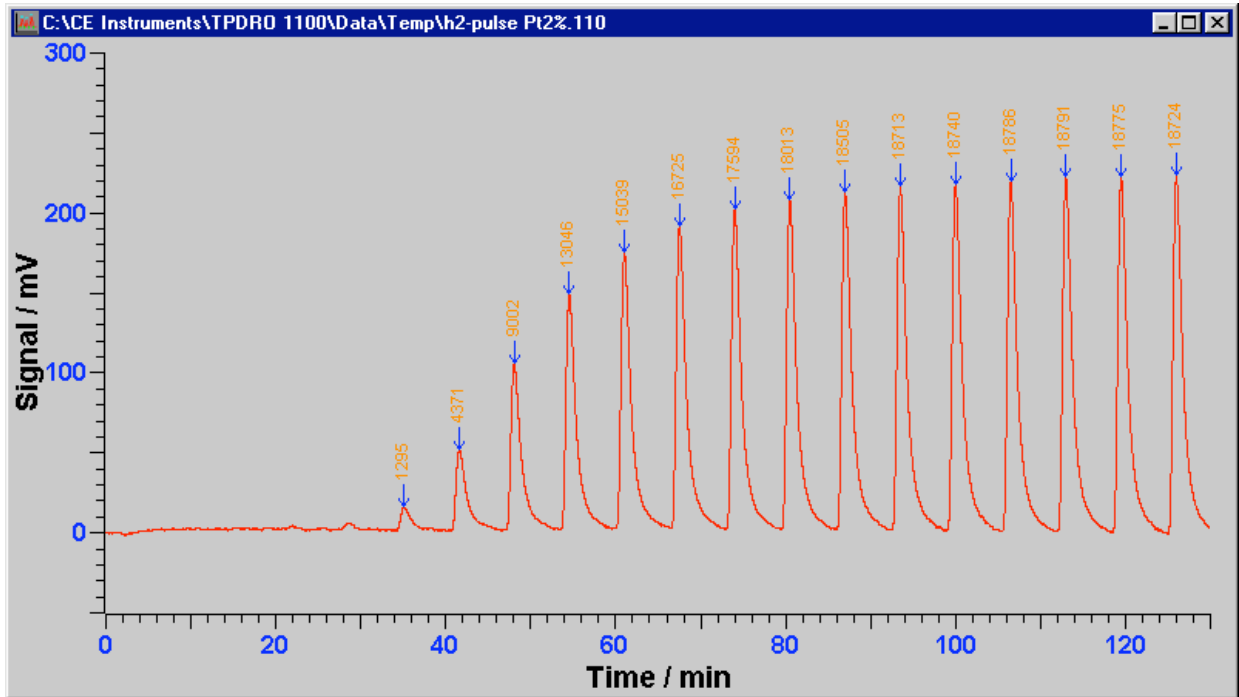The analytical graph is the following:

Figure 87

The first five peaks (N_h) are hidden because the sample has completely chemisorbed the probe gas. The displayed peaks are related to the not-chemisorbed probe gas and show these results:

N_d	$\int_{pulse}$
1	1295.36
2	4370.82
3	9002.24
4	13045.74
5	15039.47
6	16725.06
7	17594.40
8	18012.50
9	18505.34
10	18713.10
11	18739.80
12	18785.75
13	18791.05
14	18775.40
15	18724.36

In the above table, only the 15 displayed peaks are represented (N_d). In fact the first 5 peaks (N_h) have been totally chemisorbed by the catalyst. The last 6 peaks (N_s) represent the catalyst saturation status, as the probe gas (hydrogen) is passing unchanged through the catalyst bed. The internal calibration factor will be calculated according to these last peaks (N_s).
We apply a modified equation number 2:

4) $\qquad C_{F\,int} = (N_s \; V_{loop} \; X_{gas} \; P_{inj} \; 10^{-3)}) / (R \; T_{inj} \int_{sum})$

where:

N_s = number of last pulses with the same area (= 6)
$\int_{sum}$ = total sum of last peaks area (= 112529.46)

Dimensionally:

$[\text{mmole/mV s}] = [\text{mL}][\text{hPa}][\text{m}^3/\text{mL}][1/100][\text{Pa/hPa}][\text{mmole/mole}][\text{mole K m}^2/\text{m}^3 \text{ N}][1/\text{K}][1/\text{mV s}]$

NOTE: 1 N/m^2= 1 Pa

The calculated internal calibration factor using the above values is:

$C_{F\ int} = 7.932\ \text{E}^{-8}\ [\text{mmole/mV s}]$

9.3   Results Calculation

The results given by the TPD/R/O software are derived by the information taken from the database system. We strongly recommend checking that all the parameter related to the experiment under test are contained in the database system. In case some information is missing, the correlated result cannot be computed. In the following picture, some of the possible relationship during the analytical and reporting process are represented.
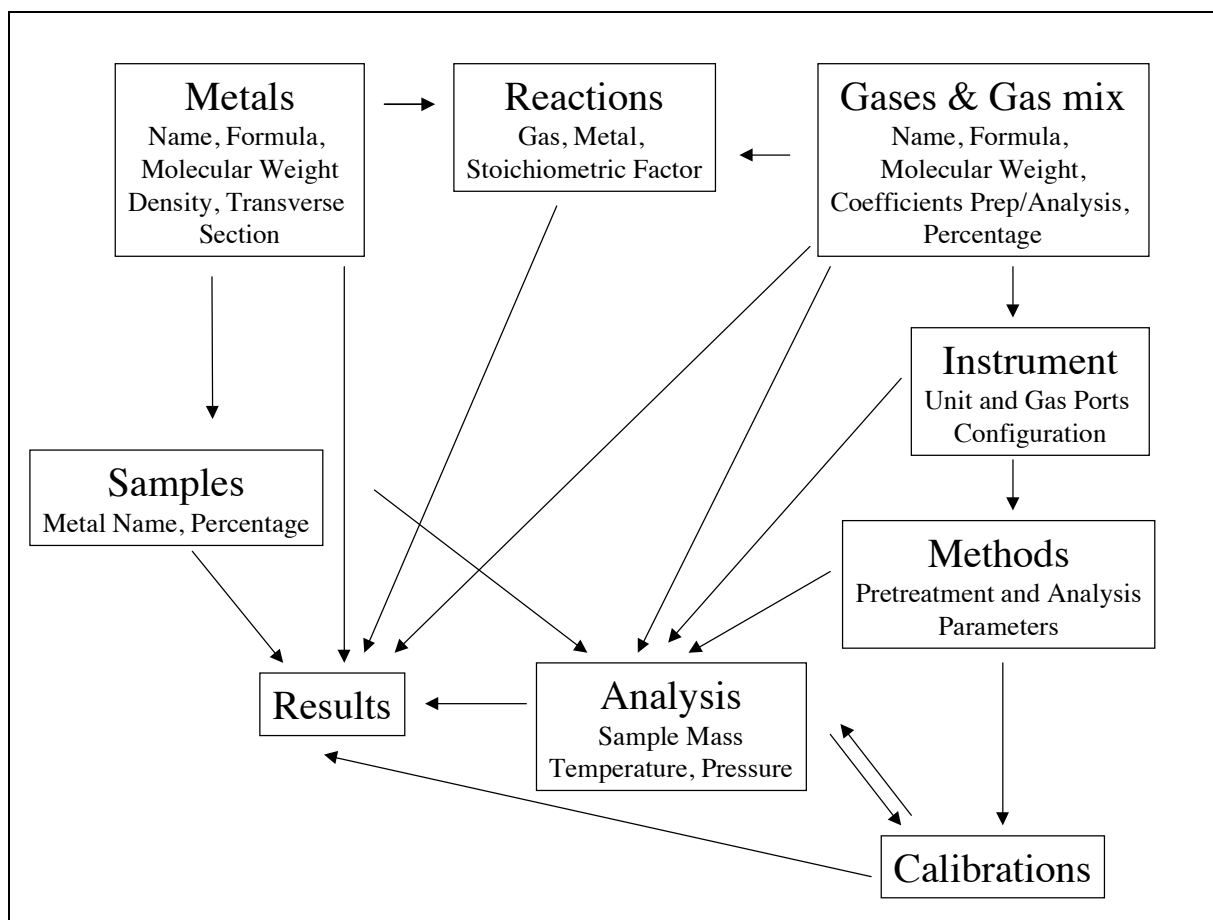
Figure 88

9.3.1 Calculation of desorbed gas quantity (TPD)

TPD experiment provides the amount of gas desorbed from a catalyst in function of temperature. In case the sample has been properly prepared, that is when the available active surface has been properly saturated, the amount of gas desorbed can be used to evaluate the metal surface area and dispersion (see later).
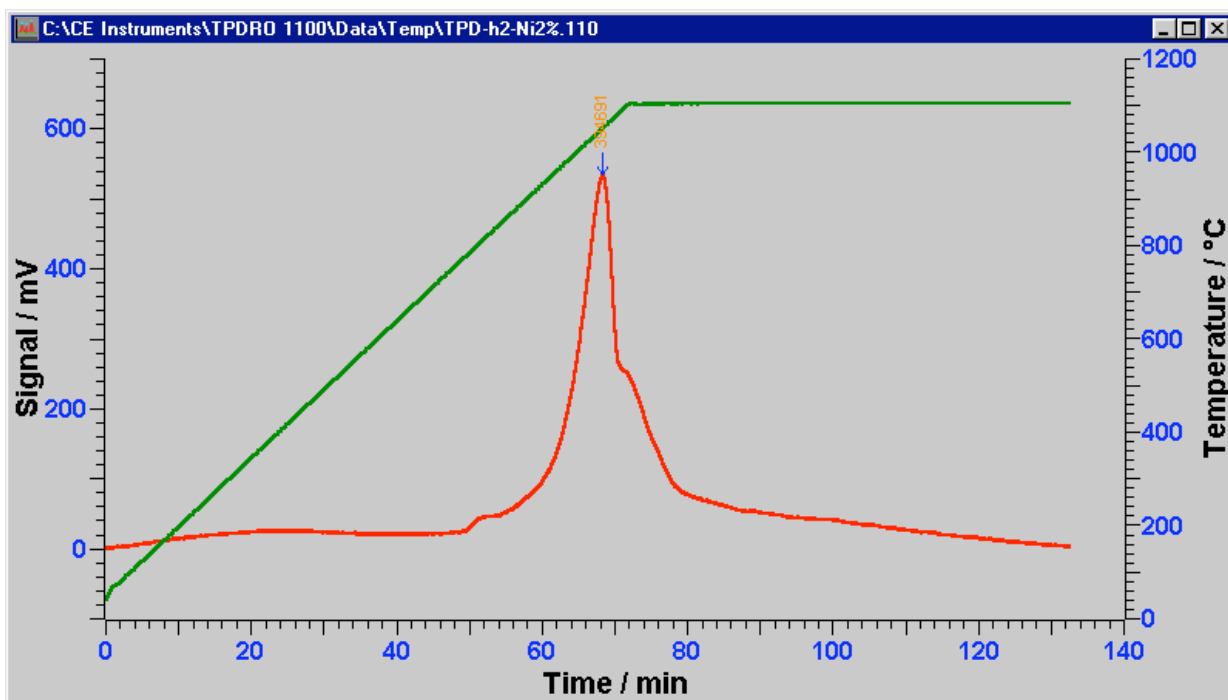
Consider the following TPD example.

Figure 89

The integration provides the following result:

#	Start[min]	Stop[min]	Maximum[min]	T[°C]	Integral[mVs]	Integral[µmol/g]
1	45.183	105	68.4	1051	394690.8	27.655696

Figure 90

The amount of gas desorbed is calculated according the following equation:

5) $\qquad n_{des} = (\int_{dro} C_F) / S_m$

The same equation using dimensions:

[mmole/g] = [mVs] [mmole/mVs] [1/g]

Substituting the values and considering $S_m = 0.7136$ [g]:

$n_{des} = (394690.8 \; 5.00014308 \; 10^{-8})/0.7136 = 0.0276557$ [mmole/g]

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9.3.2   Calculation of reacted gas quantity (TPR/TPO)

Equation number (5) is used also to evaluate the amount of gas reacted in TPR/TPO experiments (n_{rea}). Of course, the resulting peak area is calculated on the TPR or TPO profile.

9.3.3   Calculation of chemisorbed gas quantity (Pulse Chemisorption)

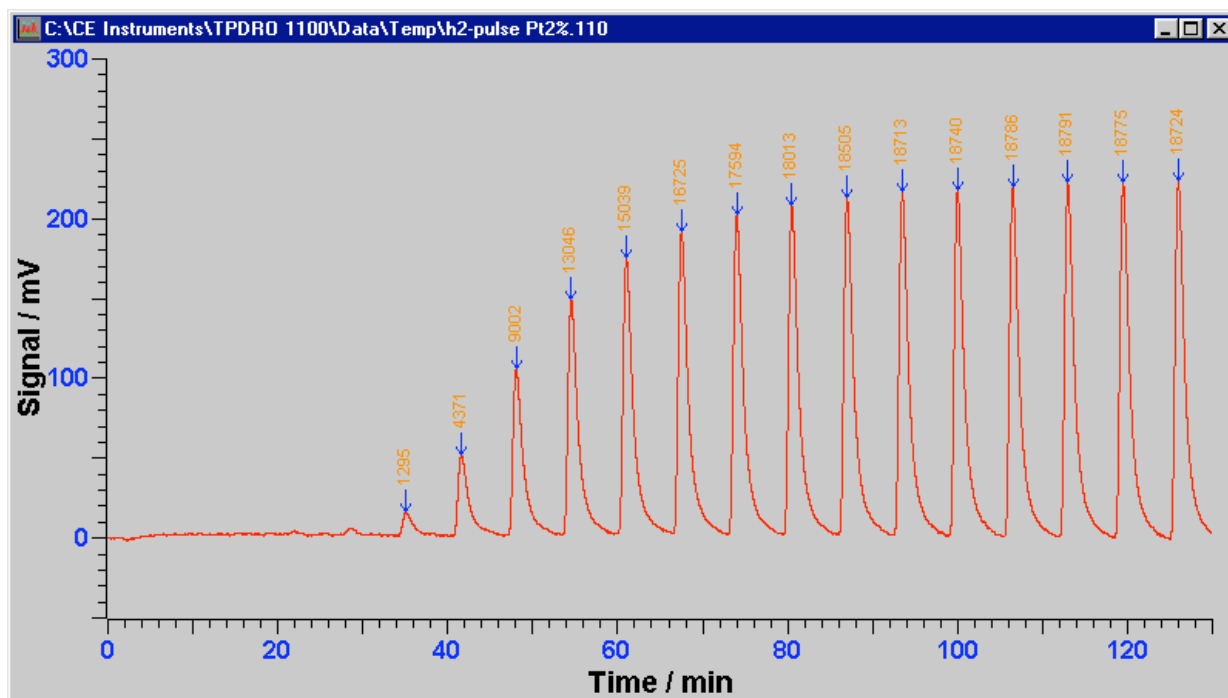Considering the pulse chemisorption example already mentioned:

Figure 91

N_d	$\int_{pulse}$
1	1295.36
2	4370.82
3	9002.24
4	13045.74
5	15039.47
6	16725.06
7	17594.40
8	18012.50
9	18505.34
10	18713.10
11	18739.80
12	18785.75
13	18791.05
14	18775.40
15	18724.36

In the above analysis there are 5 hidden peaks (N_h) at the beginning of the experiment. The first 5 gas pulses have been completely chemisorbed by the catalyst active phase, whereas the last 6 peaks

(N_s) can be used for the computation of the internal calibration factor ($C_{F\,int}$) . From the above table the following parameters are calculated:

$\int_{av\,pulse}$ = 18754.91   (Average area related to N_s)

In case the calibration factor C_F was previously determined and selected from the relevant database, it is not necessary to know parameters like V_{loop}, T_{inj} and P_{inj}.

6) $n_{ads} = \left\{ \sum_{Nd} \left(\int_{av\,pulse} - \int_{pulse\,N_d} \right) + N_h \int_{av\,pulse} \right\} C_F / S_m$

Dimensionally:

[mmole/g]   = [mV s][mmole/mV s][1/g]

In case a proper calibration run was not performed, the software will automatically compute the relevant internal calibration factor ($C_{F\,int}$) according to equation (4).

7) $n_{ads} = \left\{ \sum_{Nd} \left(\int_{av\,pulse} - \int_{pulse\,N_d} \right) + N_h \int_{av\,pulse} \right\} C_{F\,int} / S_m$

The equation number (7) gives the following figures:

$C_{F\,int}$ = 7.932 E^{-8} [mmole/mV s]
$\int_{av\,pulse}$ = 18754.91 [mV s]
S_m = 0.2595 [g]
N_p = 20
N_d = 15
N_h = 5
n_{ads} = (55203.26 + 93774.55) 7.932 E^{-8} / 0.2595 = 0.0455373 [mmole/g]

9.3.4   Calculation of Metal Surface Area

The computation of metal surface area, dispersion and aggregate size is limited to the experiments of thermal programmed desorption and pulse chemisorption, in case the catalyst has been previously pretreated in order to obtain the above information. In fact, TPR and TPO experiments produce the reduction or oxidation of all the species, present in the catalyst that can be reduced or oxidized. Once the amount of gas chemisorbed on (or desorbed by) a monolayer has been determined (n_{ads}), the following equation gives the metal surface area:

8) $A_{sam} = L\ n_{ads}\ F_s\ a_{met}\ 10^{-23}$

Dimensionally:

[m^2/g] = [metal atoms/metal mole][gas mmole/g][metal mole / gas mole][^{2}/metal atom][m^2/ ^{2}][gas mole/gas mmole]

In the above example of pulse chemisorption:

$$L \quad = 6.023 \ 10^{23}$$
$$N_{ads} \quad = 0.0455373$$
$$F_s \quad = 2$$
$$a_{met} \quad = 8.9$$
$$A_{sam} \quad = 4.88 \ [m^2/g]$$

The metal surface area can be conveniently expressed as referred to the metal weight in the catalyst (A_{met}) or to the support weight in the catalyst (A_{sup})

8) $A_{met} = A_{sam} \ (1/ X_{met}) \ 10^2$

The above example gives:

$$A_{met} \quad = 4.88 \ (1/2) \ 100 = 244 \ [m^2/g \ metal]$$

Referring the metal surface area to the support mass unit:

9) $A_{sup} = A_{sam} \ 10^2 \ / \ (10^2 - X_{met})$

9.3.5   Calculation of Metal Dispersion

The metal dispersion is defined as the number of adsorbing metal atoms (or moles) referred to the total number of metal atoms (or moles) that are contained in the catalyst.

10) $D_{met} = (N_{ads} \ F_s \ 10 \ M_{met}) \ / X_{met}$

Dimensionally:

$$D_{met} \quad = [gas \ mmole \ /g][met \ mole/gas \ mole][met \ g/met \ mole][gas \ mole/gas \ mmole][g/met \ g] \ 100$$

In the above example:

$$M_{met} \quad = 195.09 \ [met \ g/met \ mole]$$
$$F_s \quad = 2$$
$$X_{met} \quad = 2$$
$$N_{ads} \quad = 0.0455373 \ [gas \ mmole/g]$$

Therefore:

$$D_{met} \quad = (0.0455373 \ 2 \ 10 \ 195.09)/ \ 2 = 88.84 \ [\%]$$

9.3.6   Calculation of Metal Aggregate Size

The calculation of the average metal aggregate size is based on the assumption that the aggregate is of spherical shape laying on the support surface. In the software calculation the shape factor (S_f) of 6 will be used.

11) $d_{met} = S_f \ 10^3 \ / \ (A_{met} \ \rho_{met})$

Dimensionally:

$$[nm] = [g/m^2][cm^3/g][m^3/cm^3][nm/m]$$

In the above example for platinum catalyst:

A_{met} = 244 [m^2/g met]
ρ_{met} = 21.45 [g/cm^3]

d_{met} = 6 10^3 / (244 21.45) = 1.15 [nm]

9.4   Parameters Calculation for Multi-metallic Catalysts

In case more than one metal is present on the catalyst surface (multi-metallic catalysts), the result related to the single active phases cannot be evaluated. The results are computed according to the average values with respect to the relative percentages of each metal.

9.4.1   Stoichiometric Factor and Transverse Section for Multi-metallic Catalysts

12) $F_s = \sum_i \left(F_{s\,i} X_{met\,i} \right) / \sum_i \left(X_{met\,i} \right)$

Where "i" is the index identifying each different metal.

13) $a_{met} = \sum_i \left(a_{met\,i} X_{met\,i} \right) / \sum_i \left(X_{met\,i} \right)$

The average metal atomic weight and metal density are also calculated according to the above equations.

10 Desorption Energy Calculation

The calculation of the desorption energy NH_3 on a zeolite is reported as example.

10.1 Calculation of the Desorption Energy NH_3 on a Zeolite

Operatine sequenze:

1. Perform an adsorbment of pure NH3 or in percentage on the sample through flow or performing an analysis of "Pulse Chrmisorption" up to the complete saturation.

2. Perform a TPD analysis, by using He as carrier gas, up to a temperature of 120 C. Maintain this temperature for one hour, with the purpose to remove the part of NH_3 physisorbed..

3. Eseguire un analisi TPD, utilizzando He come gas di trasporto (carrier), con una temperatura Tin = 120 C fino ad arrivare alla temperatura di completo desorbimento della NH_3 chemisorbita (nell esempio, 800 C) e mantenere questa temperatura per 30 minuti.

4. Perform a TPD analysis, by using He as carrier gas, with a temperature Tin = 120 C up to reach the temperature of complete desorption of the chemisorbed NH_3 (in the example, 800 C) and maintain this temperature for 30 minutes.

Perform this operating sequence on a minimum of three batches of the same sample by using the the same parameters (flows, initial temperature, final temperature and hold time). Exclusively change the rate of the analysis temperature at the point 3. In the example rates of 10, 15 and 20 C/min have been used.
At the end of every analysis perform the integration of the peaks.

5. From the program press Load Data , then load the analysis performed at the point 3 keeping the Control button pressed and selecting the files with the mouse as shown figure 92.
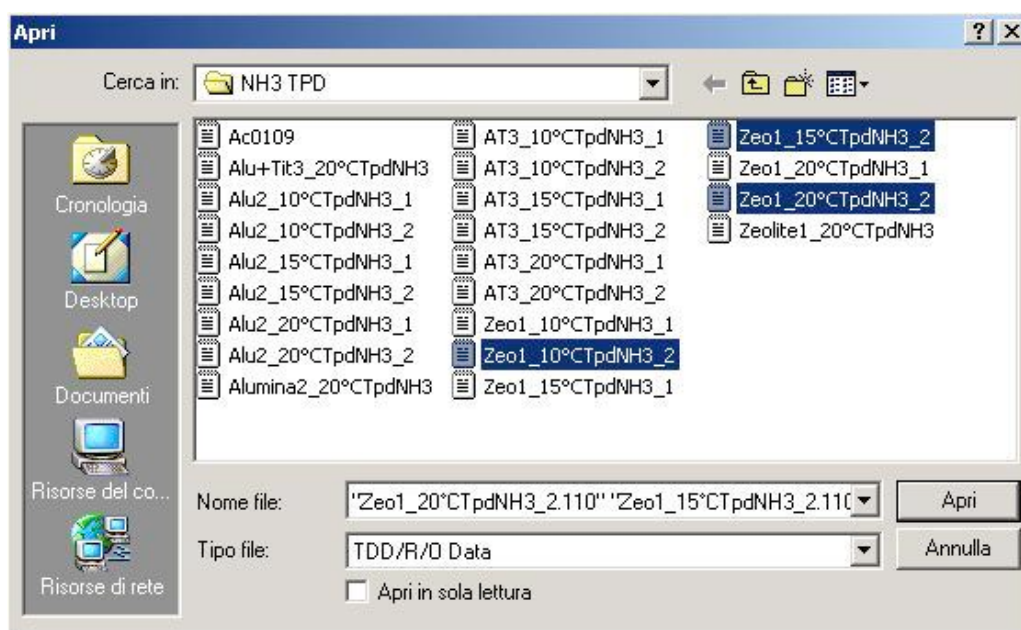

Figure 92

91

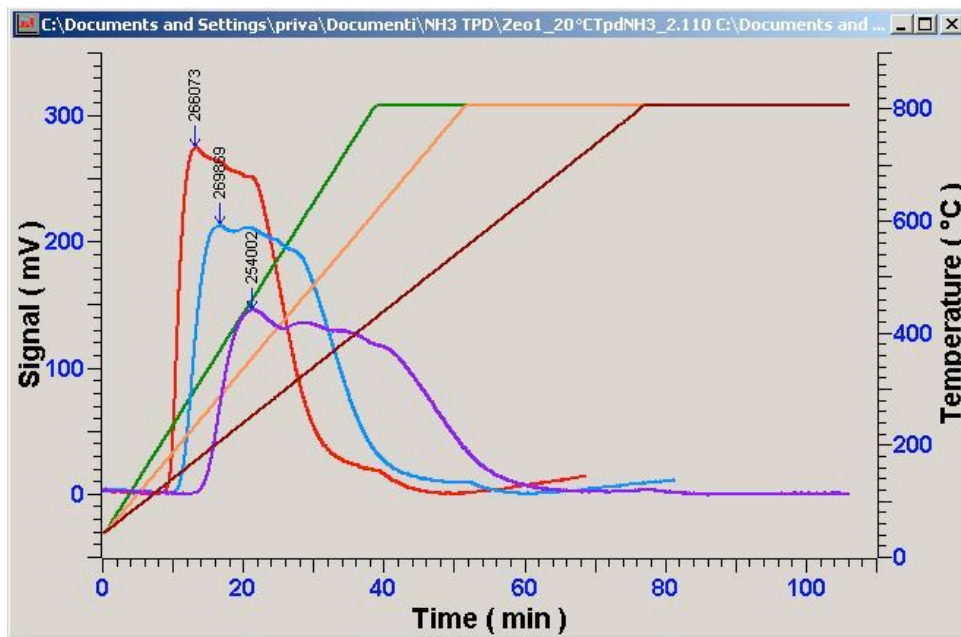6. Press ⌐Open⌐ (Apri) button. A graph similar to that reported in figure 93 is visualized.

Figure 93

7. Press ⌐File Information⌐ button. The program visualizes a summary page reporting all the information regarding the sample. Use the sliding bar to scroll the page up to reach the lower section. The ⌐Memorize⌐ and ⌐Desorption Energy⌐ buttons are present. See figure 94.
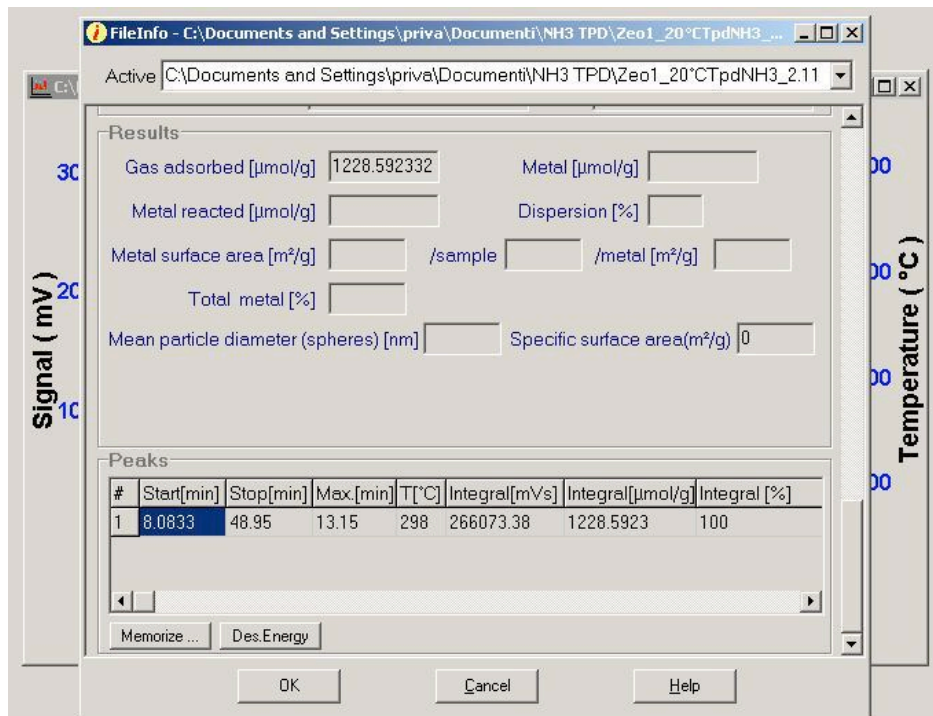

Figure 94

8. From the ⌐Active⌐ text bar, select the file of the analysis performed using the lower temperature rate .

9. Press   Memorize   button. Repeat the operation using the other temperature rates (see figure 95) thin to have memorized all the necessary parameters of the analyses performed at the point 3.
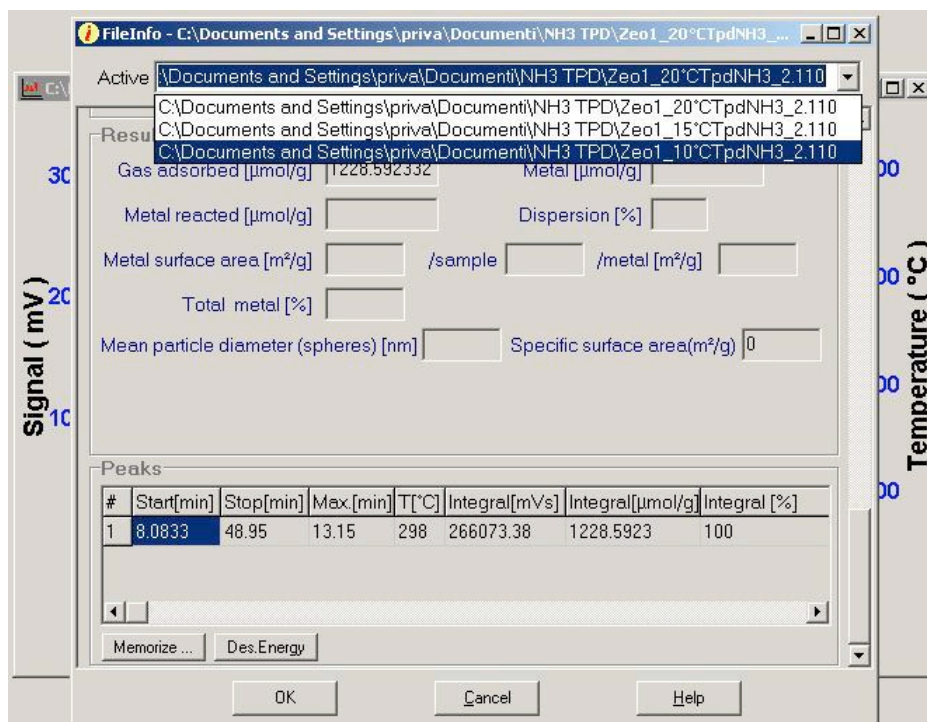

Figure 95

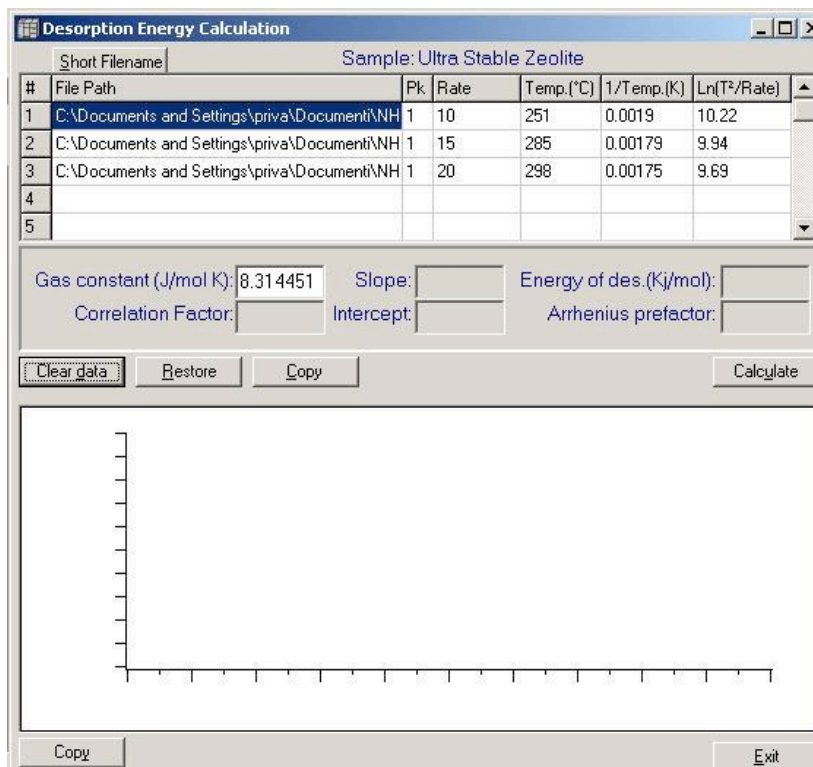10. Press   Desorption Energy   button. Figure 96 is visualized.

Figure 96

11. Press Calculate button. A graph reporting the desorption energy calculations is visualized. See figure 97.
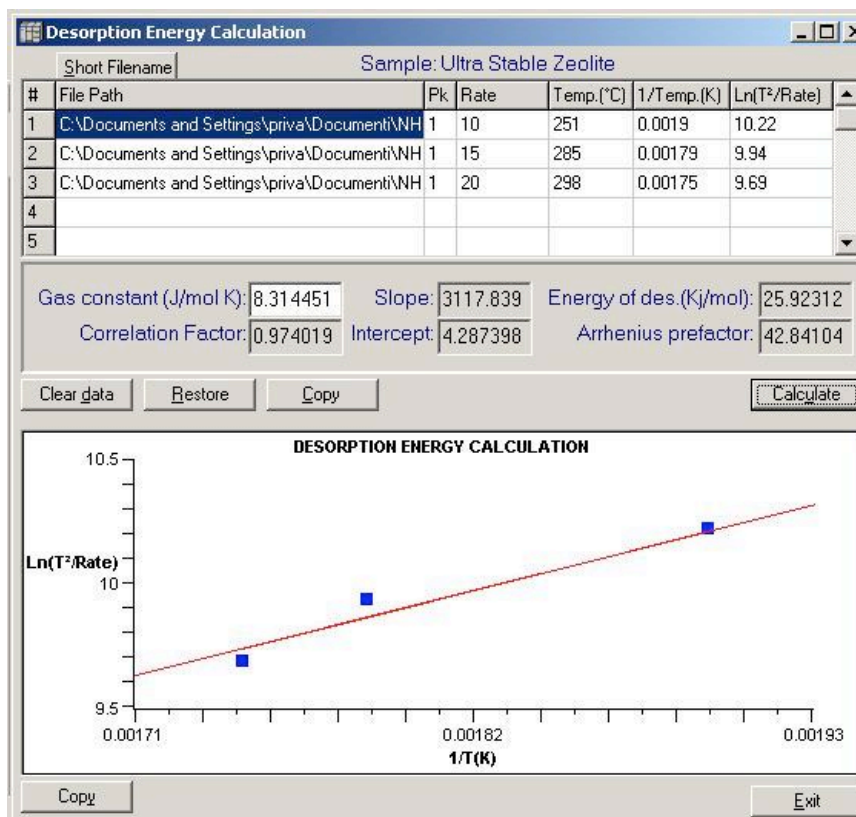

Figura 97

12. The data and the graph can be exported both in Excel and in Word and saved. Open Excel or Word and press Copy . Enter in Excel (or Word) then paste.

The file can be saved with the extension related to the used program.