Procedure for the Deconvolution of TPD Data

by Francisco Zaera

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It is often the case that the interpretation of TPD data is obscured by the overlap of signals from the desorption of several compounds. This is a particularly common problem when studying the surface chemistry of hydrocarbons, because most organic molecules display complex cracking patterns in their mass spectra, with significant signals for many amus. It is therefore desirable to deconvolute the cracking patterns from the raw TPD data in order to identify the desorption peaks for each product. Below a procedure is described for such deconvolution.

1. Masses to be followed

The first thing that needs to be done in order to carry out TPD of complex systems is to identify the potential products to be followed. This is done by using chemical intuition in order to predict the molecules that may be produced, and by obtaining survey TPD data following a large number of amus. Simple inspection of those data usually provides clues on what products may be forming in the TPD experiments. In particular, each TPD peak, with its unique shape and position, represents the desorption of one product. Of course, the same species may desorb in more than one temperature regime, and, conversely, peaks seen in different traces (for different amus) may also correspond to the same species. To check on this latter issue, it is important to compare the peak shape and position of features among the traces for different amus. If a peak for one amu can be superimposed, after appropriate scaling, to another for another amu, chances are that both peaks correspond to the same species. Comparison of the scaling factors used in these comparisons with reported or measured mass spectra cracking patterns can help identify the nature of that compound.

Initially, it is recommended to take several survey TPD spectra for the same conditions, typically saturation adsorption at liquid nitrogen temperatures. Many (10-15) masses should be recorded in any given experiment, and, if more than one experiment is required, a small set of representative amus should be used in all as references to make sure that the experiments are reproducible. In choosing the masses to look at, consideration should be given to the main cracking peaks of the species expected to form based on the possible chemistry of the adsorbate. Typical products are hydrogen, carbon monoxide, carbon dioxide, and water, as well as

hydrogenation and dehydrogenation products, products from fragmentation of the original molecule (sometimes followed by hydrogenation-dehydrogenation), and products from dimerization/coupling. In the case of coadsorbed systems, products from combinations of both species may form as well. For instance, in oxygen covered species, oxygen insertion may lead to the production of alcohols, aldehydes, ketones, etc. from hydrocarbons. If deuterium is co-deposited on the surface, products from (multiple) H-D exchange should be search for.

Once all desorbing products have been identified, a set of amus needs to be chosen to carry out the remaining of the TPD experiments, to explore the effect of other parameters such as coverage and adsorption temperature dependence on the surface chemistry of interest. For the deconvolution, one different amu is required for each possible product. The main criteria to choose those are: (a) the amus should be as unique as possible to the compound they represent, that is, they should not show up in the MS cracking pattern of the other products (this can be typically accomplished by picking a high mass, the molecular peak if possible); and (b) the sensitivity factor for the amus chosen should be reasonably high, although they do not need to be the stronger peak in the mass spectra.

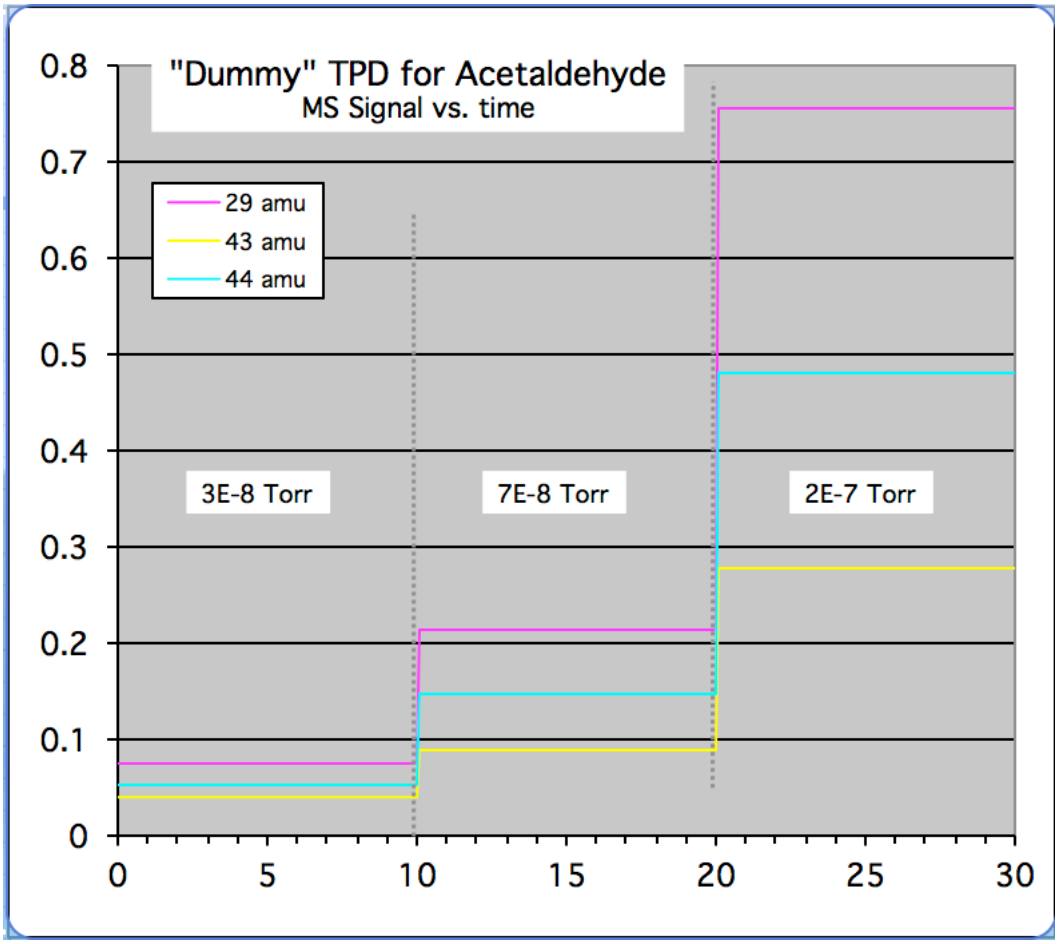
2. Sensitivity factors

Once the masses to be followed in the TPD experiments are chosen, a set of sensitivity factors for them needs to be determined. Ideally, those should be measured with the same instrument and conditions used for the TPD studies, but if that is not possible, it may be required to resource to reported literature data and/or guessing. In any case, the initial sensitivity factors may need to be adjusted during the deconvoluting process (see later). Several procedures are described below to measure sensitivity factors. Note that: (a) one amu needs to be chosen for each of the products to be deconvoluted from the TPD data; and (b) sensitivity factors for all the amus chosen are needed for each of the possible products.

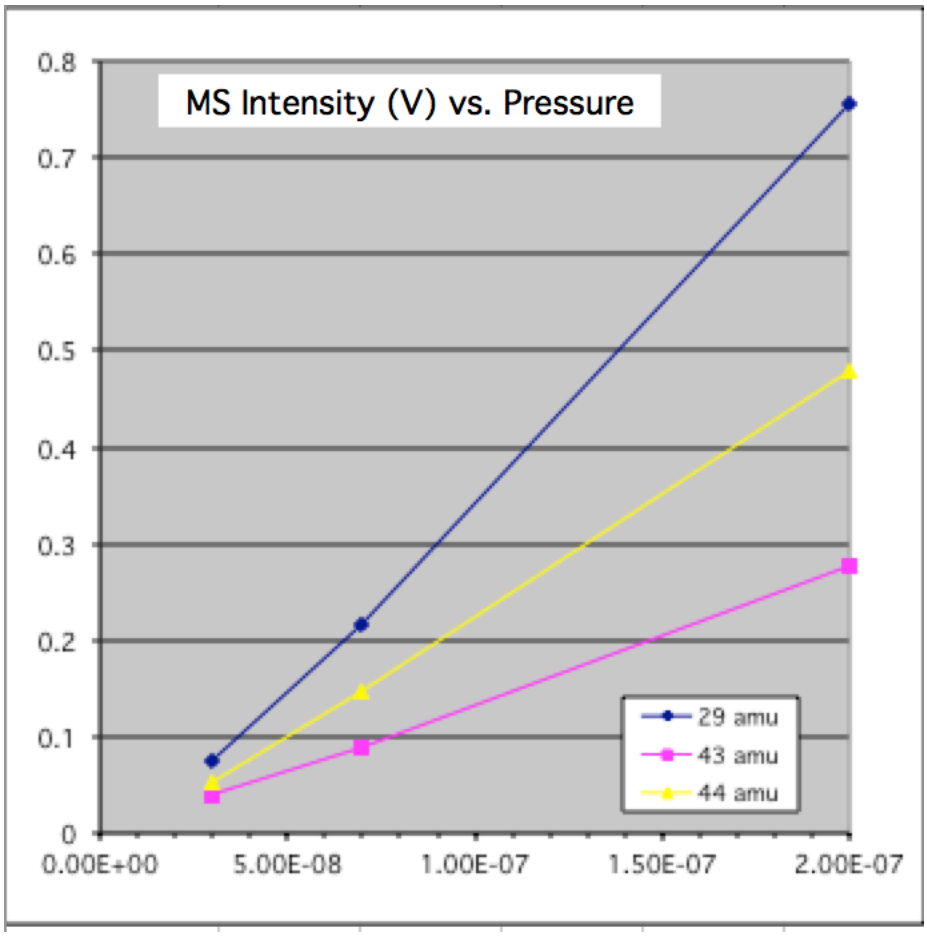
2.1. Acquisition of "dummy" TPD.

The best method for determining sensitivity factors is to run "dummy" TPDs with the compounds of interest and follow the masses needed. In those experiments, the crystal does not need to be cleaned, cooled or heated, since the temperature data will not be used. The same TPD program used for real TPD experiments needs to be run. What needs to be done is to leak each of the compounds into the vacuum chamber up to a given pressure, and to start the TPD acquisition program, which needs to be set to record all the masses needed (all the amus selected to represent all the desorbing products). After a few (5-10) seconds, the pressure needs to be increased to a new value while the TPD is still running and recording data. The same procedure needs to be repeated for a number of pressures (somewhere between 5 and 10), to obtain mass

spectroscopy signal intensities versus pressure. The resulting "TPDs" are exemplified for the case of the 29, 43 and 44 amu signals for acetaldehyde and three ($3\cdot10^{-8}$, $7\cdot10^{-8}$, and $2\cdot10^{-7}$ Torr) pressures in the accompanying excel file named "data_mssensitivities_example.xlsx". The key data are reproduced below:



From this, values of MS signal intensity versus pressure are extracted, and plotted:

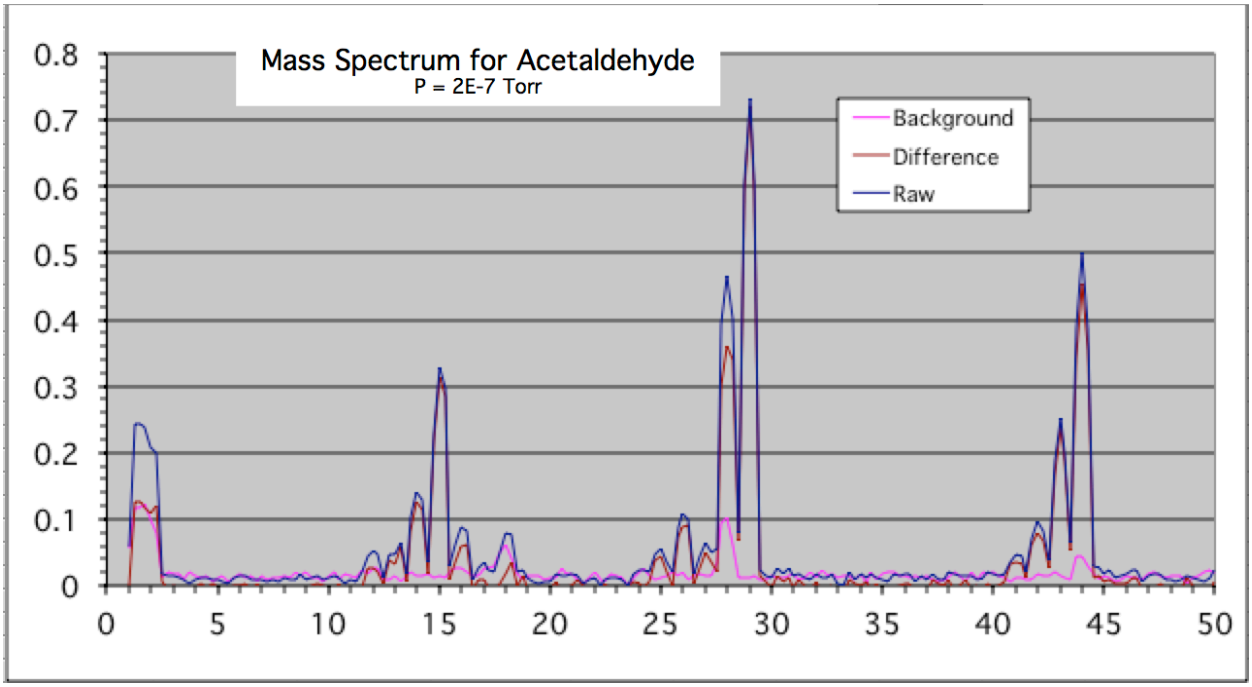


Linear square fit of the data provides the final sensitivity factors:

Calculated Sensitivity Factors (From the slopes of the plots)			
amu	29 amu	43 amu	44 amu
S (V/Torr)=	4.04E+06	1.42E+06	2.53E+06
1/S (Torr/V)	2.48E-07	7.07E-07	3.96E-07

2.2. Acquisition of mass spectra.

Less desirable, but still viable, is a method based on recording mass spectra for the compounds of interest and reading the intensity of the different amu peaks directly from those data. In this case, it is important to record and subtract a background spectrum of the UHV gases before introducing the compound of interest. It is also better to take data at different pressures and plot intensities versus pressures, in a way similar to that shown in the previous section. The mass spectrum for acetaldehyde corresponding to our example is shown below:



2.3. Literature data.

When the compound is not available in the lab, there may be a need to use literature data. When possible, the most reliable data available should be used, preferably those taken using similar instruments and/or conditions than those available in our lab. One important parameter to look

for is the electron ionization energy, which in our instruments is typically set to 70 V. Luckily, this is also the most common value used in the literature. Useful sources of MS data are:

1. "TRC Spectral Data-Mass (formerly Selected Mass Spectral Data)," American Petroleum Institute Research Project 44 (Thermodynamics Research Center Hydrocarbon Project), TRC, Texas Engineering Experimental Station, Texas A&M University, College Station, 1984.

2. Stenhagen, Einar, Sixten Abrahamsson and Fred W. McLafferty, "Registry of Mass Spectral Data," New York, Wiley, 1974.

3. "Index of mass spectral data, listed by molecular weight and the six strongest peaks," ASTM Committee E-14 on Mass Spectrometry. Subcommittee IV on Data and Information Problems. Philadelphia, American Society for Testing and Materials, 1969.

4. The NIST web site: http://webbook.nist.gov/chemistry/

2.4. Deuteriated compounds.

Work is often performed in our laboratory with (partially) deuteriated compounds. Also, experiments are sometimes performed to look into the deuteriation of adsorbates by coadsorbing deuterium on the surface. In those cases, if the spectra of the deuteriated compounds are not

available, they may need to be estimated from that of the associated normal compound using statistical arguments. For instance, given that the spectrum for normal ethylene, CH_2=CH_2, shows peaks for 26, 27 and 28 amu with approximately 60:60:100% relative intensities, it can be speculated that, to a first approximation, the spectrum of perdeuterioethylene, CD_2=CD_2, will show the same ratios for 28, 30 and 32 amu (the real values are quite close to this). For partially substituted molecules, a statistical analysis needs to be factored in. For instance, for monodeuteriated ethylene, CHD=CH_2, there are three out of four possible ways of producing $C_2H_2D^+$ ions, so the relative intensity for its 28 amu peak should be (3/4)·60% = 45% of 29 amu (the molecular CHD=CH_2^+ peak). The real value is approximately 55%. Finally, when looking into a cracking fragment, it is important to determine what moiety of the molecule that fragment corresponds to in order to apply the proper statistical calculations. For instance, the main peak in the mass spectrum of ethanol, CH_3CH_2OH, is seen at 31 amu, with an intensity about 460% that of the molecular 46 amu signal. This 31 amu peak comes from the CH_2OH^+ moiety, which means that the same intensity ratio (in this case for 31/49 amu) is expected for CD_3CH_2OH; in reality, that value is 625%.

The procedure described above is only meant to provide first approximation values for the sensitivity factors. They may deviate from the real values because:

1. Ionization and scission probabilities are different for C–D versus C–H bonds. The C–H bond is typically easier to break, so, in a case such as a CHD moiety, the ratio of CD^+/CH^+ intensities is usually larger than one. This typically introduces an error on the order of 5-10%.

2. There may be significant isotope scrambling and/or hydrogenation reactions with H^+ from the background in the ionizing region of the mass spectrometer. This is the reason why, for instance, the 31 amu signal from perdeuterioethylene (CD_2=CD_2) is not zero. Again, this error may amount to 5-10% of the total signal, but in many instances is less significant than the first effect cited above (although in others it is more, this changes a lot with the specifics of the chemical system).

If data are available for some deuterium-substituted compounds, but not for the one needed, some corrections may be introduced to deal with that. Also, mass spectra data acquired in our laboratory may be blended with those from the literature to get the best cracking pattern possible. Below is an example for ethanol:

amu	CH3CH2OH (exp)	CH3CH2OH (Rep)	CD3CH2OH(Rep)	CD3CH2OH(Calc)	CH2DCH2OH (calc)
31	4.00	4.60	6.25	5.43	4.48
45	1.60	2.00			
46	1.00	1.00			1.73
47					1.00
48			2.50	2.00	
49			1.00	1.00	

In this case, the normal ethanol spectrum obtained in our lab is compared to that from the literature (first two columns). Then, the reported spectrum for CD_3CH_2OH (third column) is scaled to estimate the values expected for the same compound in our instrument (fourth column). Finally, the effect of H-D scrambling for CH_2DCH_2OH is estimated as one third of that seen between CH_3CH_2OH and CD_3CH_2OH (last column).

3. Deconvolution

Once the sensitivity factors are available, it is possible to use them for the deconvolution of the raw TPD data. Below, an algorithm is described for this based on matrix algebra. The steps will be illustrated by using the example provided in the accompanying "data_tpddeconvolution_example.xlsx" for the case of 8.0 L of 2-iodoethanol adsorbed on Ni(100) at 100 K.

3.1. General protocol.

The raw TPD data consist of a set of TPD intensity values for the selected amus as a function of temperature. The data may look something like this:

T/K	27 amu	29 amu	31 amu	43 amu
90.32	0.688278	0.663858	0.566178	0.574481
92.91	0.716606	0.661416	0.566667	0.581807
92.91	0.757631	0.679976	0.564713	0.578877
95.46	0.821612	0.68779	0.566178	0.587668
97.97	0.913431	0.683883	0.570574	0.581319
100.44	0.916361	0.681929	0.564713	0.579853
102.87	0.890965	0.707326	0.564225	0.583272
105.26	0.829915	0.705861	0.564225	0.587668
109.94	0.792796	0.693162	0.566178	0.581807
114.48	0.776191	0.699023	0.566178	0.590598
118.9	0.77326	0.69072	0.565201	0.588156
123.19	0.760562	0.7	0.567643	0.593529
125.29	0.782051	0.745421	0.564225	0.612576
131.42	0.753724	0.749817	0.564225	0.61453
135.38	0.766422	0.747863	0.564225	0.596948
139.24	0.77326	0.717582	0.562271	0.599878

etc.

Here, 27, 29, 31 and 43 amu were chosen to extract information on the desorption of ethylene (C_2H_4), acetaldehyde (CH_3CHO), ethanol (CH_3CH_2OH), and 2-iodoethanol (ICH_2CH_2OH), respectively. Each row, for a given temperature, contains the intensity values for each mass. These can be represented by a $[I_j]$ vector:

$$[I_j] = [I_{27\ amu}, I_{29\ amu}, I_{31\ amu}, I_{43\ amu}] \qquad (1),$$

where, in the generic expression, j stands for the different amus measured. There is one vector for each temperature recorded, that is, for each row in the table with the raw TPD data. Each TPD intensity (for each amu) results from the sum of the intensities originating from each of the desorbing products, which are given by their partial pressures, P_i, times their corresponding sensitivity factors, S_{ij}. For instance, for 27 amu:

$$\begin{aligned} I_{27\ amu} = {} & P_{C2H4} \cdot S_{C2H4,27\ amu} \\ & + P_{CH3CHO} \cdot S_{CH3CHO,27\ amu} \\ & + P_{CH3CH2OH} \cdot S_{CH3CH2OH,27\ amu} \\ & + P_{ICH2CH2OH} \cdot S_{ICH2CH2OH,27\ amu} \end{aligned} \qquad (2).$$

Here, the i and j indices are used to represent the different compounds and the amus recorded in the TPD, respectively. In general terms:

$$I_j = \sum_i P_i \cdot S_{ij} \qquad (3).$$

There is one equation like Equation 3 for each amu j recorded in the TPD experiment, as reflected by the $[I_j]$ matrix. A $[S_{ij}]$ matrix can be constructed for the sensitivity factors, with the different rows corresponding to the compounds that desorb (i), and the columns to the amus detected (j). In our example, that matrix looks as follows (the values in $1 \cdot 10^{-6}$ V/Torr):

	27amu	29amu	31amu	43amu
C2H4	5.6	0.2	0	0
CH3CHO	0.224	4.69	0	1.26
CH3CH2OH	0.78	1.09	2.69	0.377
ICH2CH2OH	0.375	0.5	0.067	0.422

Remember that, when making this matrix, one amu is needed per compound. They should be organized in the same order (the respective amus listed in the order used for the compounds), so that there are no zero values in the diagonal of the matrix. Otherwise, it will not be possible to invert this matrix (see later).

A $[P_i]$ vector can now be defined for the partial pressures of all the products that desorb:

$$[P_i] = [P_{C2H4}, P_{CH3CHO}, P_{CH3CH2OH}, P_{ICH2CH2OH}] \qquad (4),$$

and the operations reported above (Equations 2 or 3) can then be summarized in matrix form as follows:

$$[I_j] = [P_i] \cdot [S_{ij}] \qquad (5).$$

To solve this problem, that is, to obtain an expression for $[P_i]$, both sides of Equation 5 need to be multiplied by the inverse of the sensitivity matrix:

$$[I_j]\cdot[S_{ij}]^{-1} = [P_i]\cdot\{[S_{ij}]\cdot[S_{ij}]^{-1}\} = [P_i] \qquad (6).$$

3.2. Implementation in excel.

The preceding derivation shows that, in order to deconvolute the raw data, $[I_j]$, for each temperature, and obtain the corresponding set of partial pressures of the different products, $[P_i]$, what is needed is to multiply each row of the raw data table by the inverse of the sensitivity factor. This is what was done in our example, in the excel spread sheet named "Deconvolution." The sensitivity factor matrix, $[S_{ij}]$, reported in cells H4:K7 (and reproduced above), was inverted in cells H12:K15 to obtained $[S_{ij}]^{-1}$:

	C2H4	CH3CHO	CH3CH2OH	ICH2CH2OH
27amu	0.17689409	-0.0108991	-0.000829	0.03328283
29amu	0.04696534	0.30517403	0.02321137	-0.9319194
31amu	-0.0414157	-0.0727997	0.37467013	-0.117353
43amu	-0.2062633	-0.3403372	-0.0862505	3.462894

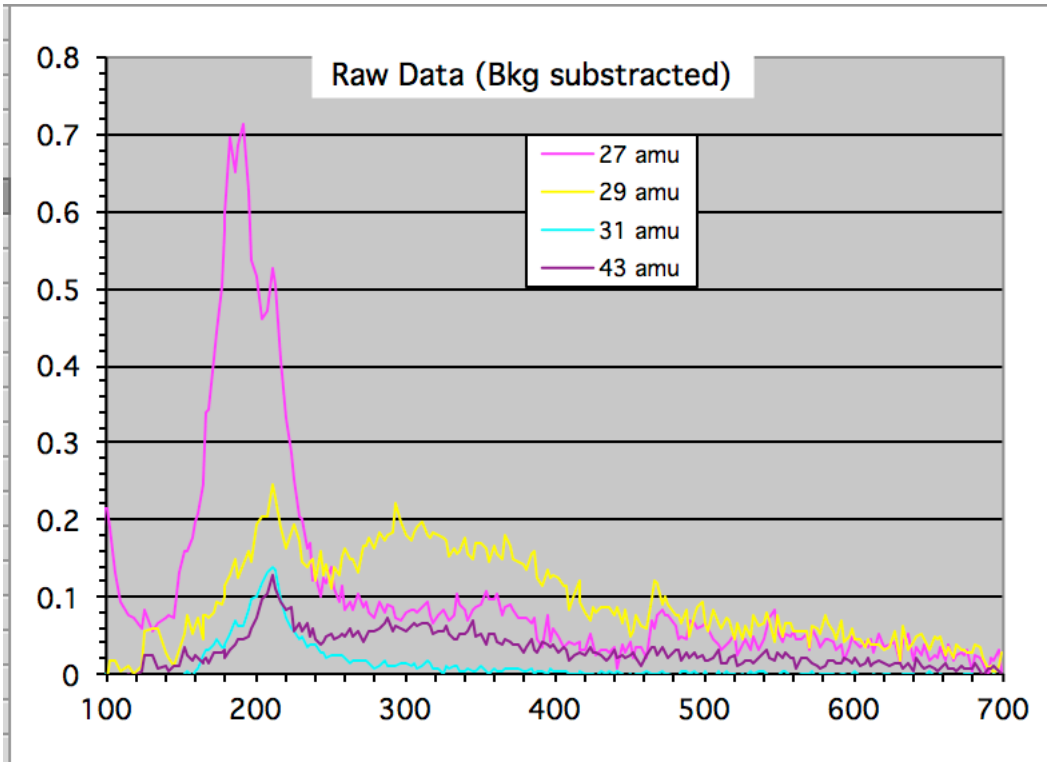
and then each row was multiplied as described above. For the first row, the raw data, cells B31:E31:

T/K	27 amu	29 amu	31 amu	43 amu
90.32	-0.011722	-0.026142	-0.003822	-0.015519

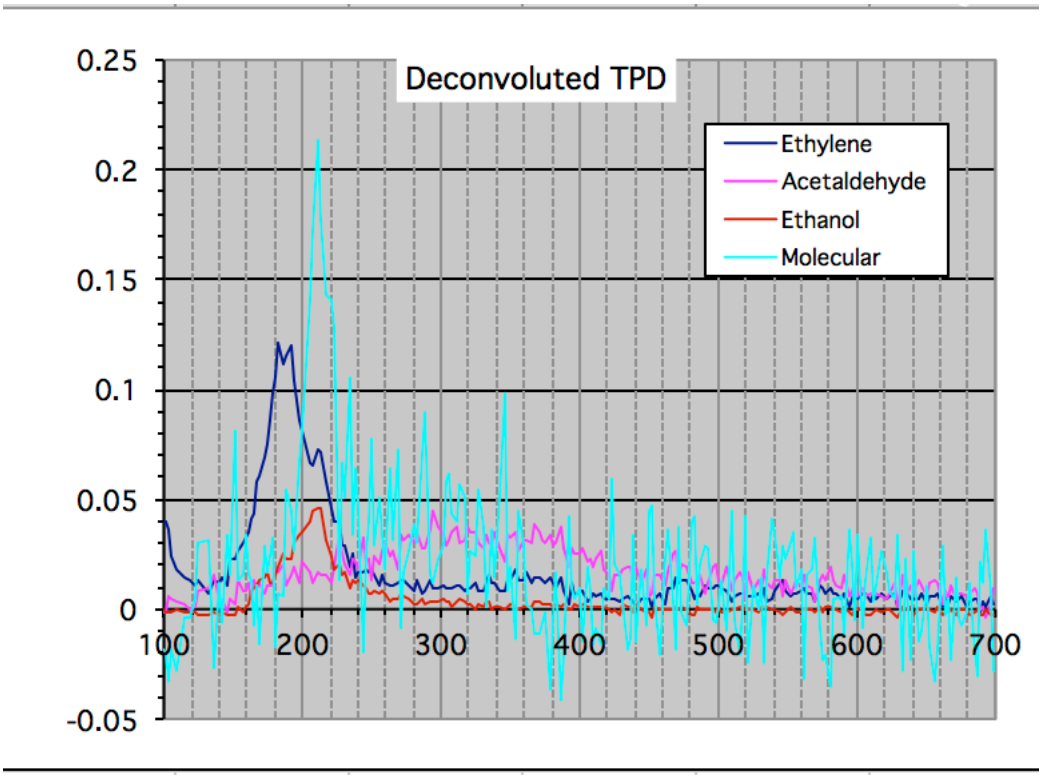
were multiplied by $[S_{ij}]^{-1}$ (only the four data points on the right are involved in this operation, the temperature value is included here only for reference) to yield the partial pressure values, cells H31:K31:

T/K	C2H4	CH3CHO	CH3CH2OH	ICH2CH2OH
90.32	5.797E-05	-0.0022902	-0.0006905	-0.02932

This operation was then copied for all rows, for all temperatures. The end result is that the raw TPD traces:



Becomes:



Note that this procedure not only deconvolutes the different components from the raw TPD traces, but also scales the data in terms of partial pressures (in this case, in 10^{-6} Torr units). The sensitivity factors have been factored in. Also, it is important to point out that the background was subtracted from the raw data in this analysis before the deconvolution. This is actually not necessary, but it is still highly desirable, because it does help visualize the relative desorption traces better.

3.3. Fine corrections.

Although mathematically the process described above is exact, a number of problems may arise during its application to practical cases. Therefore, once done, this analysis must be checked for possible pitfalls. In particular:

1. The deconvolution process introduces noise in the spectra. The more masses that are deconvoluted simultaneously, the more noise that is introduced into the final data. Problems also arise when the sensitivity factor for one particular compound is much lower than those for the others. Notice in particular the high noise in the molecular desorption trace in our example. The best way to avoid this problem is to choose amus for each compound with minimum overlap with the other compounds. In this example, the traces for 27 and 31 amu are almost exclusively due to ethylene and ethanol, hence the small changes between their raw and processed traces. In those cases, the final TPD figures can be made by directly using the raw data (after appropriate scaling). Those data still need to be included in the deconvolution, though, to extract their contributions from the other traces.

2. Sometimes, negative features are introduced in the final desorption traces. These are physically unreasonable, and indicate that the sensitivity factors used in the analysis are not correct, and need to be adjusted. There is no set way of doing this adjustment other than by trial and error. Fortunately, the excel spread sheet is interactive, so the consequences of the changes introduced in the sensitivity factor table can be immediately seen in final TPD plots. The best procedure to improve on the values for the sensitivity factors is to systematically change them, one at a time, giving priority to those with the

larger numbers. At the end, it needs to be remembered that: (a) the final sensitivity numbers should not excessively deviate from the original values; (b) the changes introduced have to make physical sense; and (c) the same sensitivity factors should work for all data in a given data set, such as a collection of TPDs versus initial coverage taken using the same parameters.

3.4. Additional tips.

Two more things can be done to optimize the results from this deconvoluting analysis:

1. First, deconvolution should be performed on the least number of traces possible at one time, rather than blindly on all compounds from all traces. If two desorbing products (say, hydrogen and carbon monoxide) do not interfere with each other, no deconvolution is needed, only scaling of the data by the respective sensitivity factors. Deconvoluting the data in those cases only adds to the noise, and provides no gain.

2. It is also possible to carry out deconvolutions only over the appropriate temperature range, rather than over the whole data set. For instance, lets assume that in a given experiment, two peaks are seen for the 28 amu trace, one around 150 K, accompanied with significant signal from other amus, and another at 400 K, only seen in this amu. Such results can most likely be interpreted as the 400 K peak corresponding exclusively to CO, and therefore not needing any deconvolution. The peak at 150 K, on the other

hand, may be do to, say, ethylene and propane. If no better amu choices are available to represent those compounds in the TPD, the 28 amu trace may be used for ethylene, and possibly that for 44 amu for propylene. The two can then be deconvoluted only to the end of the first peak (perhaps up to ~300 K).

3.5. Analysis of isotope exchange TPDs.

Finally, for the analysis of deuteriated compounds, the sensitivity factor matrix contains all zeros in one half, above or below the diagonal, which means that the data analysis can alternatively be done manually by iterative calculations. For example, for studies on the desorption of deuteriated ethylenes, $C_2D_xH_{4-x}$, the molecular masses may be employed in the TPD experiments, from 28 (normal non-deuteriated C_2H_4) to 32 (perdeuterioethylene, C_2D_4) amu. Note that the signals from the heavier compounds show no interferences from the light ones. Therefore, if only ethylene desorbs from this system, the 32 amu signal must correspond exclusively to C_2D_4; no deconvolution is needed there. In addition, the 31 amu must also correspond to only one compound, in this case C_2D_3H, because C_2D_4 can only form ions with (28–2·n) amu (since it can only loose deuterium atoms, and those have 2 amu masses). Next, the desorption of $C_2D_2H_2$ can be extracted from the 30 amu trace after subtraction of the contributions from C_2D_4 and C_2D_3H, which can be calculated by multiplying the 32 and 31 amu traces by $S_{C2D4,30\ amu}/S_{C2D4,32\ amu}$ and $S_{C2D3H,30\ amu}/S_{C2D3H,30\ amu}$, respectively. The desorption for C_2DH_3 can be then extracted from the signal for 29 amu, after subtracting the contributions from

C_2D_3H and $C_2D_2H_2$, in the same way as before; C_2D_4 does not have any signal at 29 amu, and therefore does not interfere with this mass. Finally, the trace for normal ethylene, C_2H_4, is obtained from the data for 28 amu, in this case after subtracting the contributions from all other isotopologues. It is worth noticing that, since many times the TPD experiments being carried out in our studies involve the normal hydrocarbon and deuterium, there is often only limited H-D exchange within the original molecule. This means that the amounts of deuteriated products is much smaller than those from the non-substituted molecule, which means that the corrections on the signal of the latter due to the former may be small (and, in some cases, may be neglected, at least when considering the original non-deuteriated reactant).