



# Nordic PhD course in Analytical Techniques in Combustion

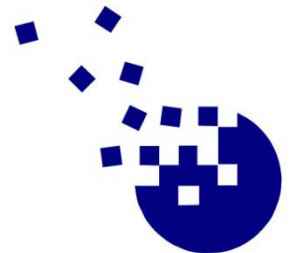
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NTNU, Trondheim, Norway

## Introduction to kinetic models for biomass pyrolysis. Part 2. Numerical techniques.

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## Subtopics:

Can we evaluate the DTG curves instead of the TG curves without introducing mathematical errors/artifacts? (How to get reliable DTG?)

What numerical methods are well worth to use in the solution of the kinetic equations and in the minimization of the least squares sum?

## ***Determination of the DTG curve (1)***

If the errors are random, we can estimate the noise level of a given curve by simple statistical checks, then we can find a “smooth”  $f(t)$  function approximating the experimental data within the given noise level:

$$\text{average smoothness of } f(t) \approx \text{maximum} \quad (1)$$

$$\sum_{i=1}^N w_i^2 (f(t_i) - X_i)^2 \leq N \sigma^2 \quad (2)$$

Here  $N$ ,  $f(t)$ ,  $t$ ,  $X_i$  and  $\sigma$  denote the number of data, the smoothing function, the time, the observations, and the noise level, respectively. The use of weight factors  $w_i$  is optional. (We can use  $w_i \equiv 1$  values). This type of smoothing was invented by Whittaker & Robinson more than 70 years ago! (Their book, *The Calculus of Observations* is a treasure for science history.) Later Reinsch developed an effective algorithm for the calculation of cubic spline functions satisfying conditions (1) – (2). This method is now part of every major mathematical program library.

## *Determination of the DTG curve (2)*

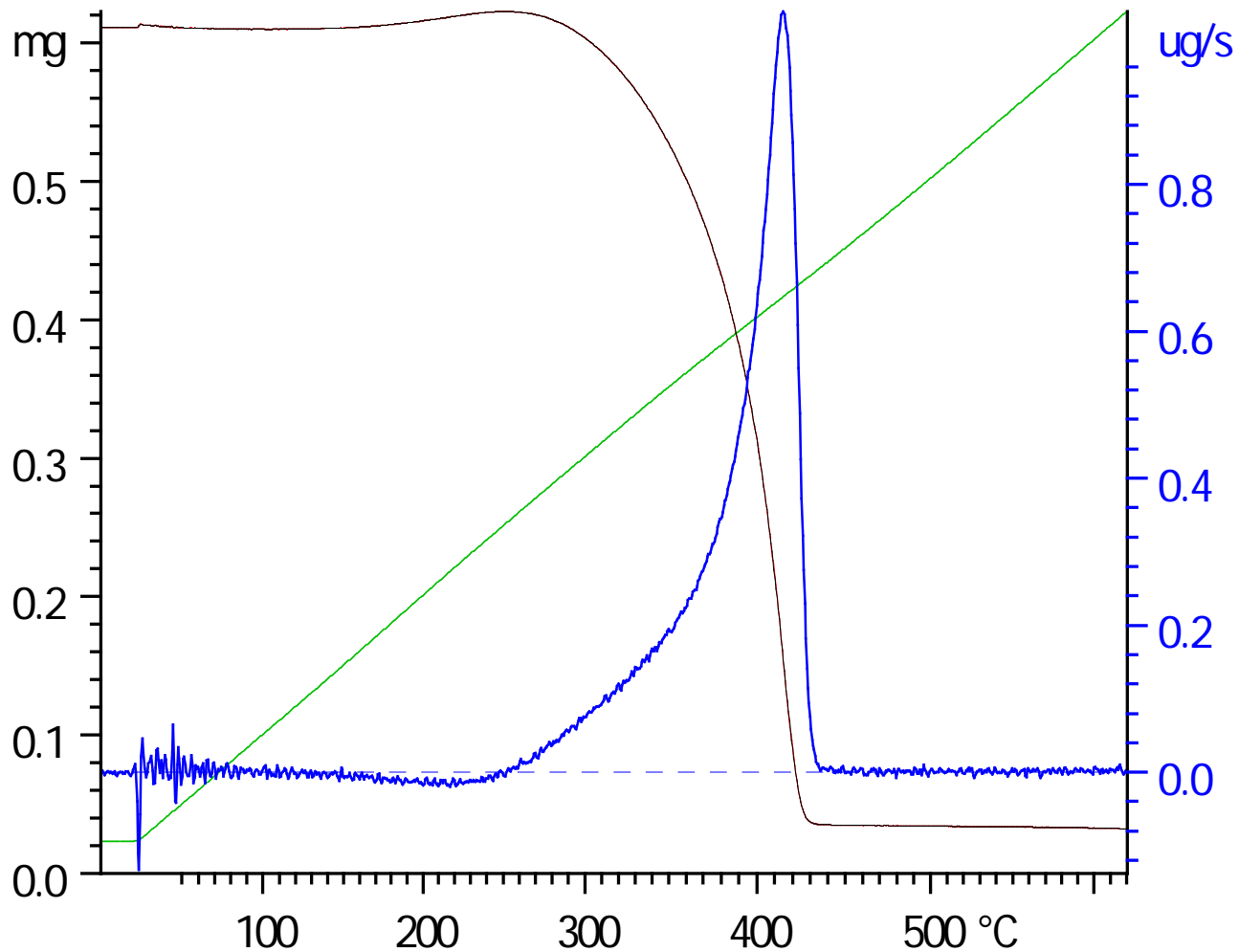
*The noise level can be estimated by simple statistical checks.*

**The smoothing of the random noise, however, is not enough due to wave-like errors! We must increase  $\sigma$  gradually till we got an acceptable compromise.**

For example, let us suppose that the random noise is  $0.3\mu\text{g}$  and we get the acceptable compromise at  $0.5\mu\text{g}$ . Then the systematic error is not higher than  $0.2\mu\text{g}$ . It is surely negligible at a sample mass of  $2\text{ mg}$  and acceptable at a sample mass of  $0.2\text{ mg}$ .

If the TG system is in a good shape and carefully cleaned from tar deposits, etc., even better values can be achieved, as the following examples show.

# Determination of the DTG curve: Smoothing a the statistic noise



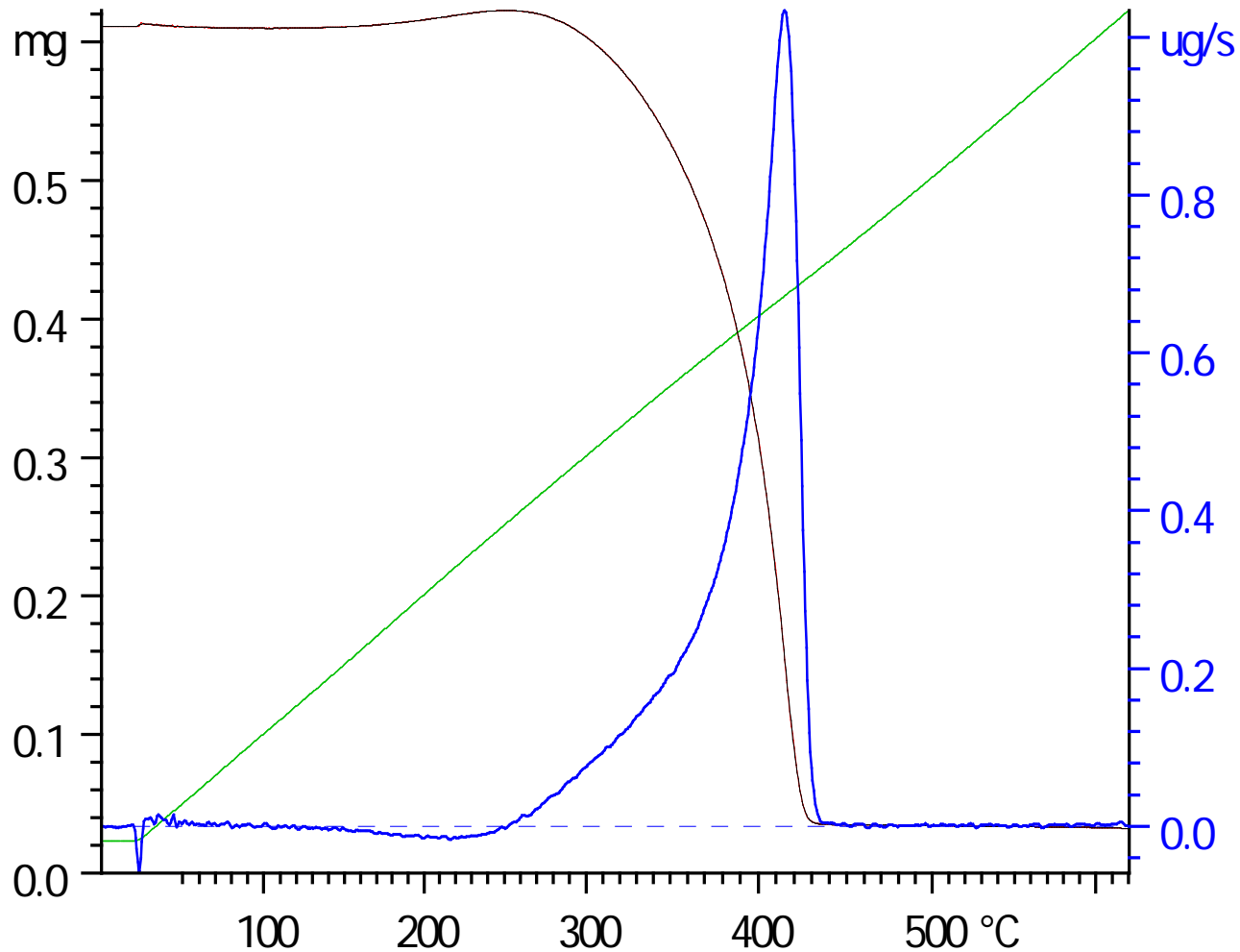
Corn cob charcoal 03.12.31, middle section,  $\varnothing$  10.6  $\mu\text{m}$  (10 min grinding)

$m_0 = 0.613$  mg,  $\text{O}_2$ : 140 ml/min, 5  $^\circ\text{C}/\text{min}$

total deviation of G = .056 microgram

4E-01%/s ( 1.035E-03 mg/s) at 415.0 $^\circ\text{C}$

# Determination of the DTG curve: Smoothing more than the statistic noise

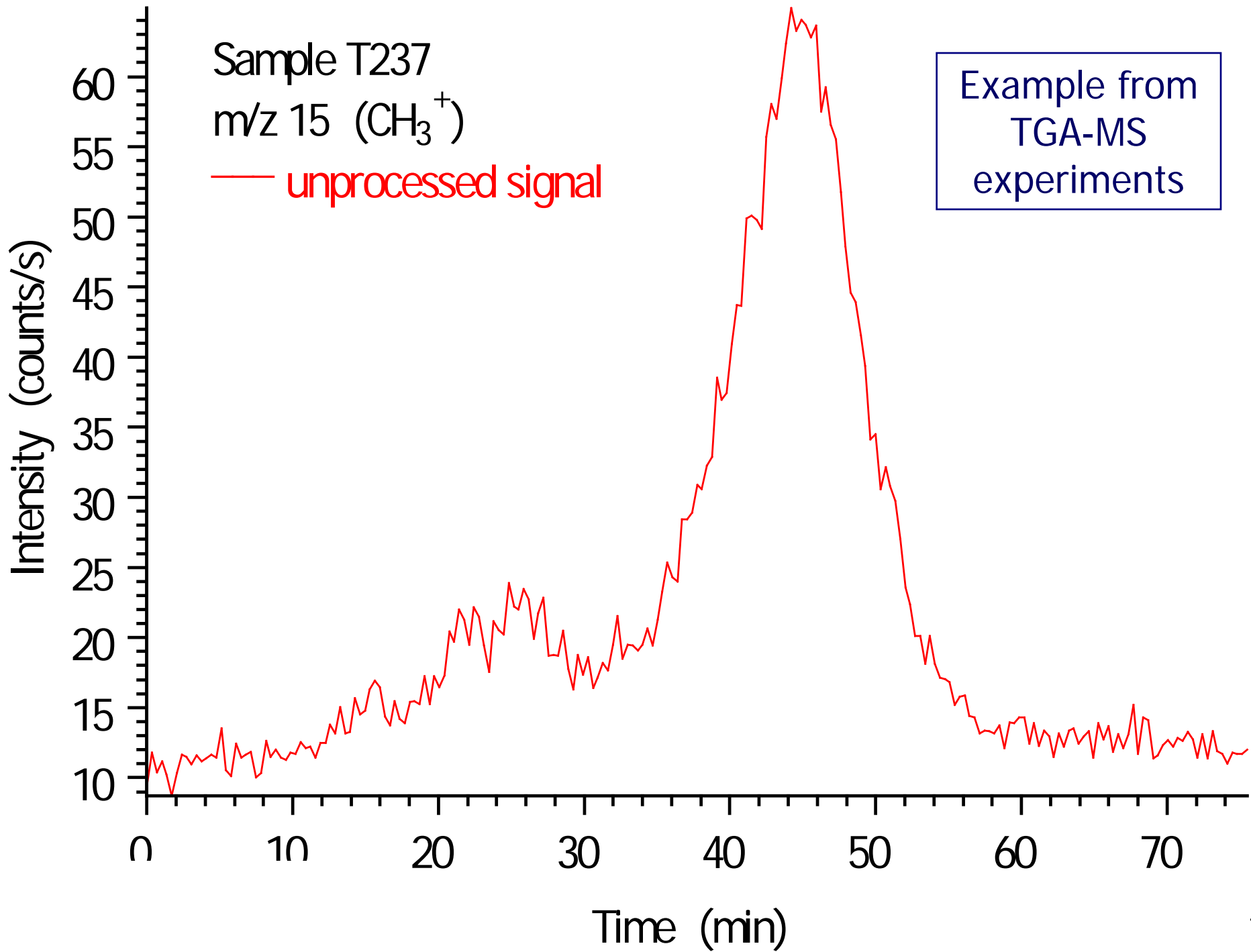


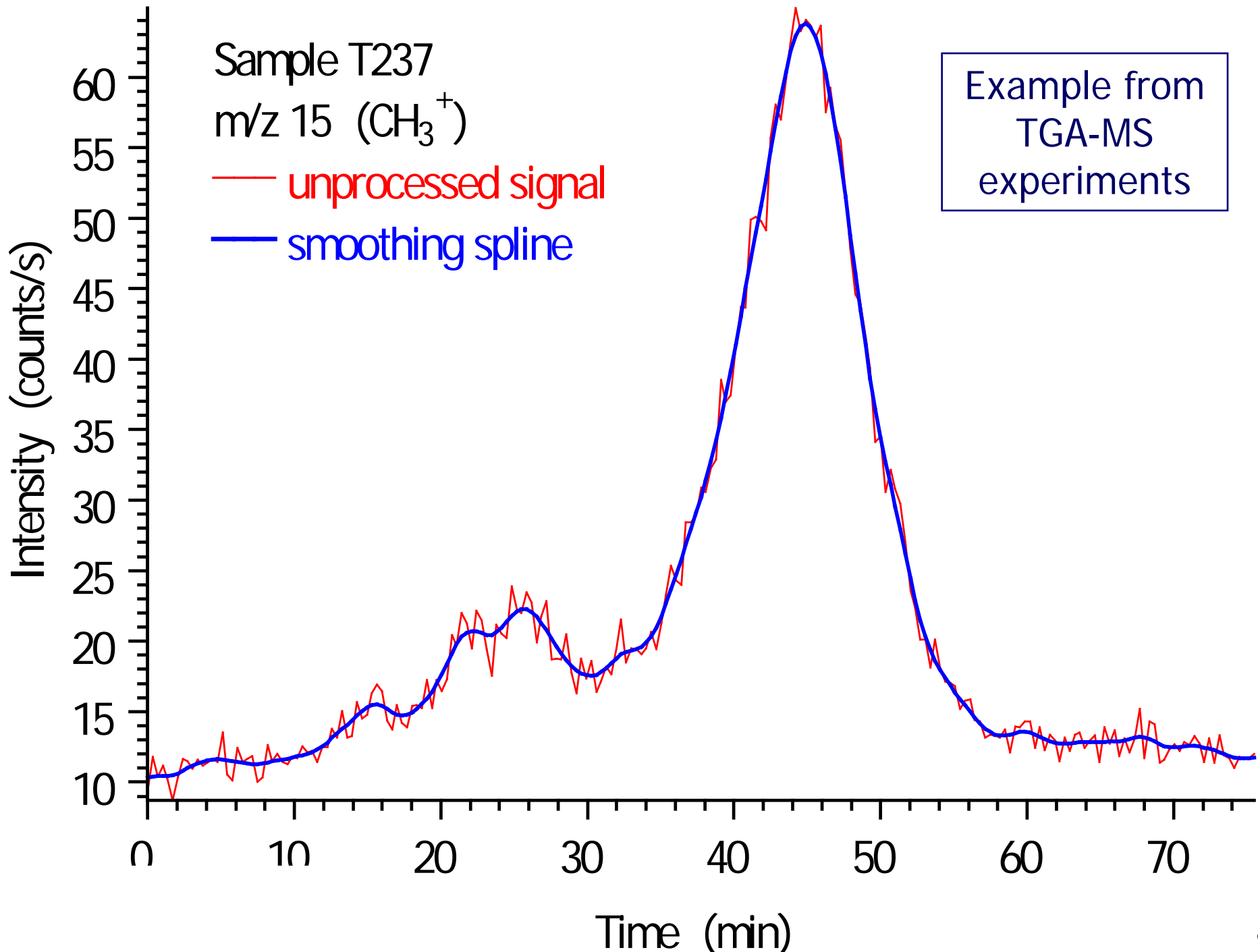
Corn cob charcoal 03.12.31, middle section,  $\varnothing$  10.6  $\mu\text{m}$  (10 min grinding)

$m_0 = 0.613$  mg,  $\text{O}_2$ : 140 ml/min, 5  $^\circ\text{C}/\text{min}$

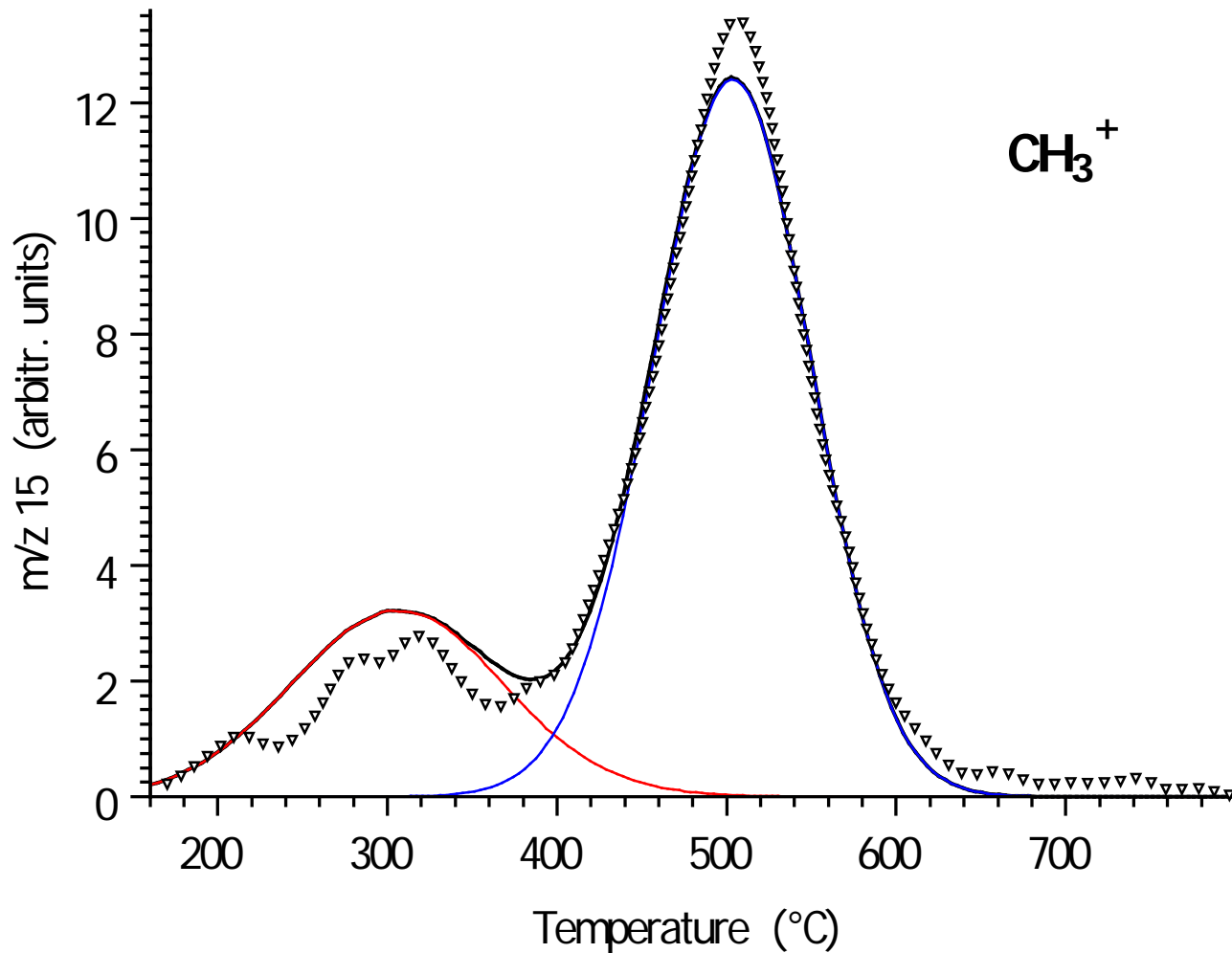
deviation of G = .086 microgram

01%/s ( 1.034E-03 mg/s) at 414.8 $^\circ\text{C}$









Example from  
TGA-MS  
experiments

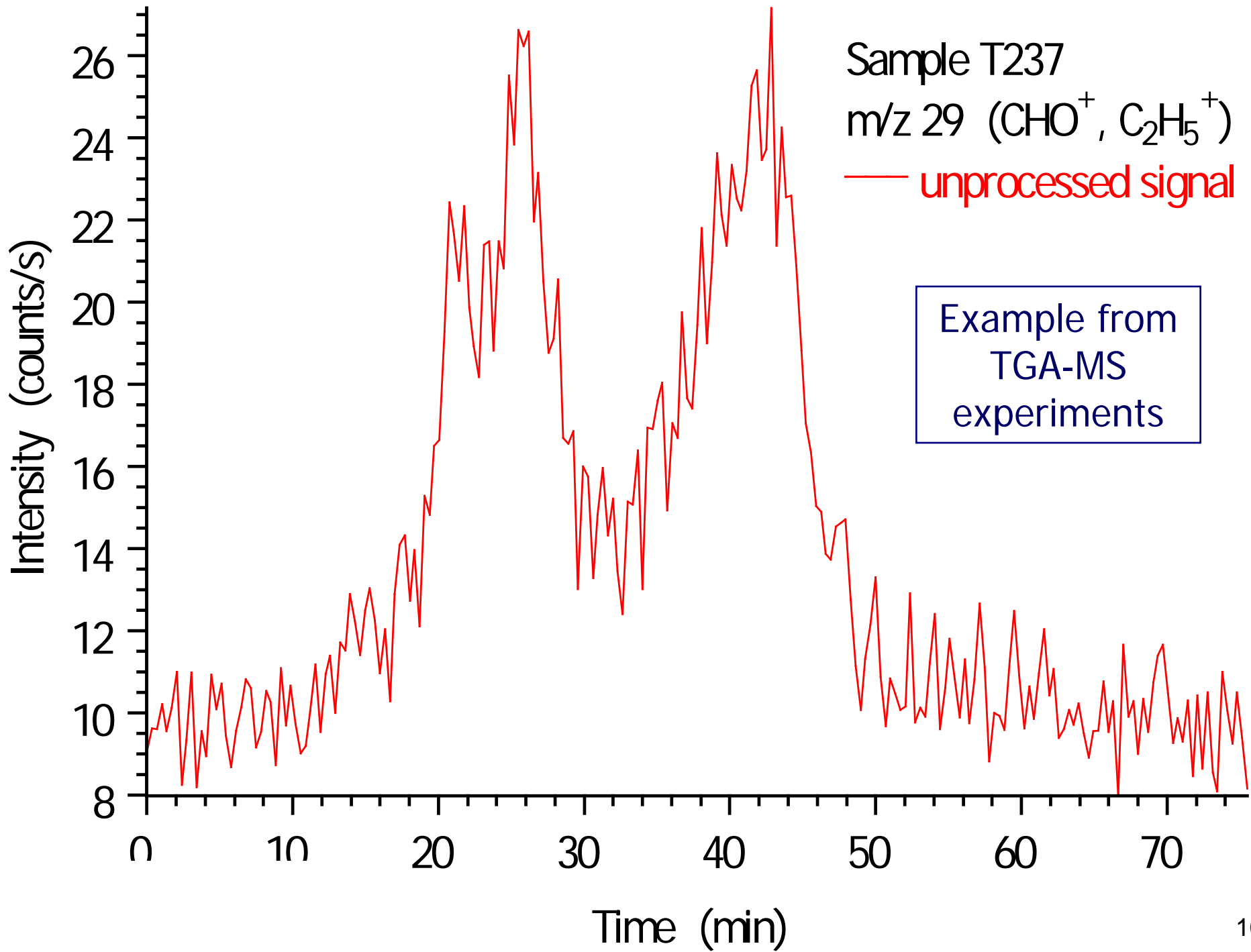
**BAT tobacco T237  $G_0=4.1\text{mg}$ , Ar,  $10^\circ\text{C}/\text{min}$**

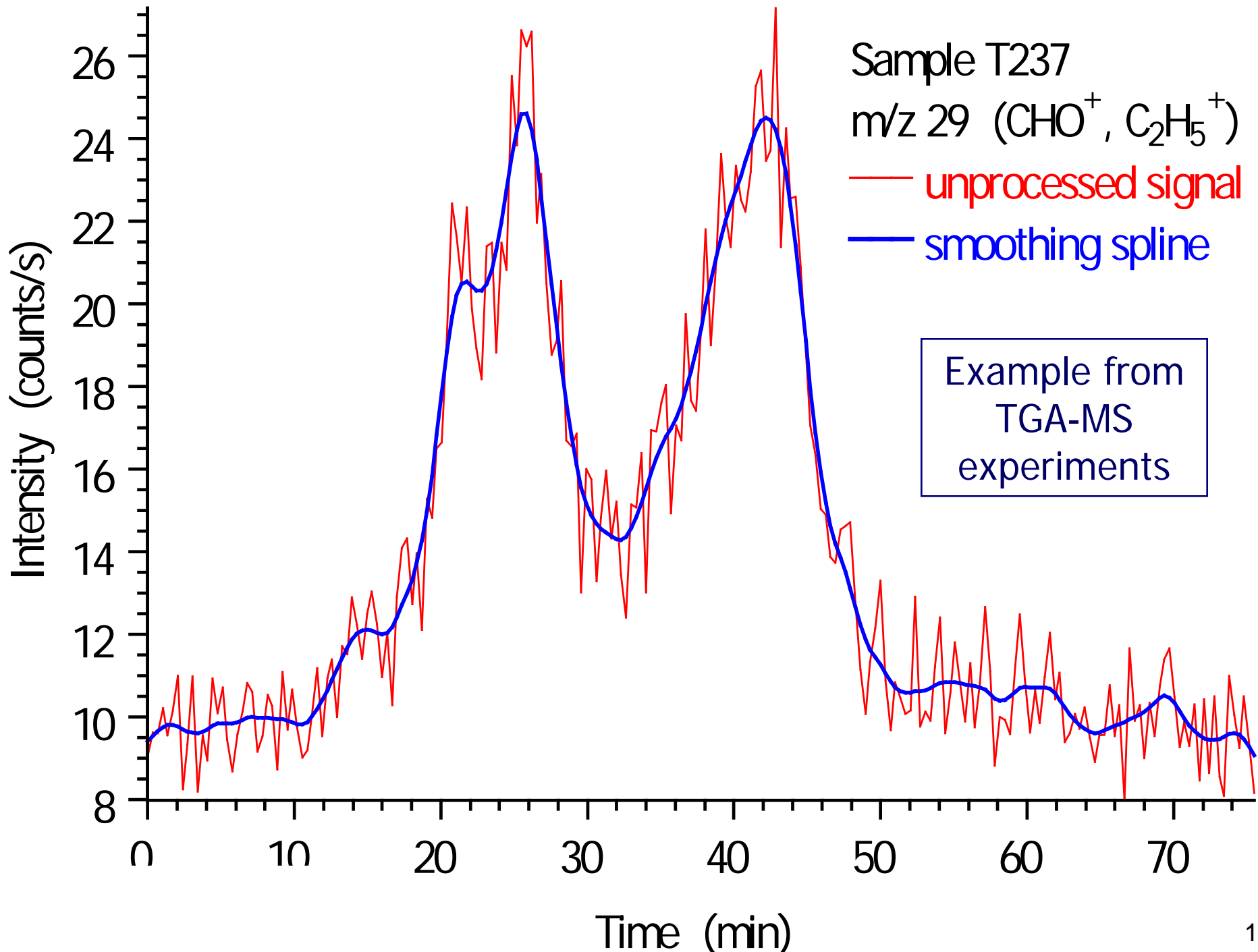
Relative deviation: 3.36%; rms rel. dev. of all experiments: 3.83%

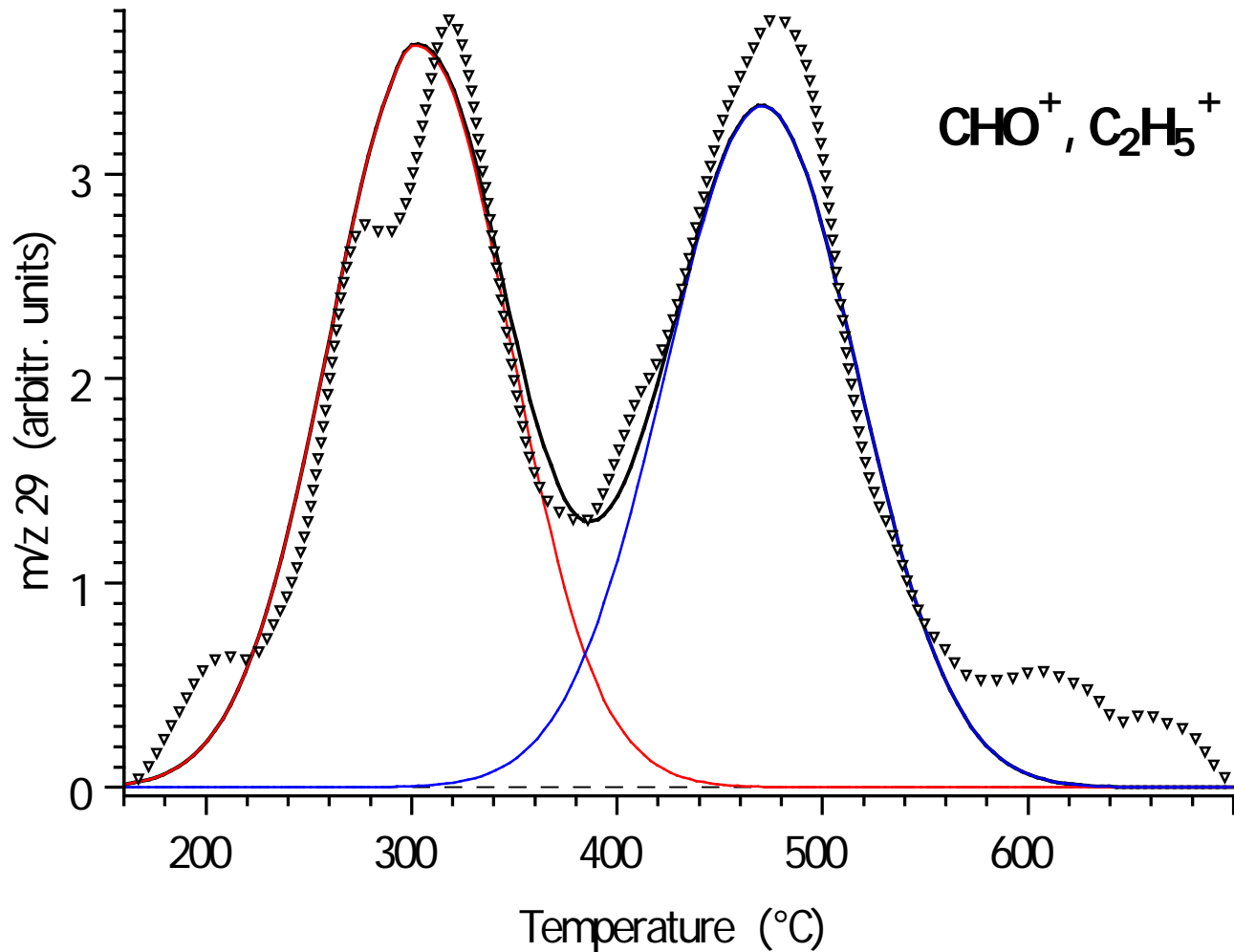
1:  $E=268.5$   $\log_{10}A=22.11$   $\sigma(E)=29.1$   $\delta I=9.3\%$   
 2:  $E=245.9$   $\log_{10}A=14.29$   $\sigma(E)=13.0$

8668

DAEM kinetics,  
2 pseudokomponenten,  
simultaneous evaluation  
of 5 experiments.







Example from  
TGA-MS  
experiments

**BAT tobacco T237  $G_0=4.1\text{mg}$ , Ar,  $10^\circ\text{C}/\text{min}$**

Relative deviation: 8.12%; rms rel. dev. of all experiments: 6.45%

1:  $E = 222.6$   $\log_{10} A = 18.03$   $\sigma(E) = 16.3$   $\delta I = -1.9\%$

2:  $E = 259.4$   $\log_{10} A = 16.02$   $\sigma(E) = 14.8$

2387

DAEM kinetics,  
2 pseudokomponenten,  
simultaneous evaluation  
of 5 experiments.

## *Methods for a general least squares process:*

### **I. Basic considerations:**

The time of the programmers is much more expensive than the time of the computer.

An ordinary desktop PC in the order of € 400 can do the job. Since invention of the ~3 GHz processors, simple runs take only seconds. Nowadays the longest runs take less than a night (unattended) or a day (as a low priority background job). 15 years ago the evaluation of a huge data set by a complex model required 1 month. During a longer run, the program saves the results in every 15 minutes automatically. (No problem with blackouts, if any. Besides, we can survey after an unattended run what happened, how the optimum was found).

The complexity of the programs should be kept within limits, otherwise we cannot modify them for different tasks / mechanisms / evaluation strategies.

**Accordingly, simple, but safe techniques should be selected.**

## *Methods for a general least squares process II. ODE solution*

### *Part 1: Independent 1<sup>st</sup> order reactions:*

The solution of the 1<sup>st</sup> order kinetic equation can be carried out via a simple, fast integration at any T(t).

Let us separate the variables and integrate both sides:

$$d\alpha/dt = k(T) (1-\alpha)$$

$$d\alpha/(1-\alpha) = k(T) dt$$

$$\int (1-\alpha)^{-1} d\alpha = \int k(T) dt$$

The left hand side is the logarithm function, the right-hand side can be easily integrated numerically by well-known methods to any precision ...

This is applicable if a biomass is described by assuming independent, parallel reactions. **Cannot be employed, however, for successive and/or competitive reactions; in such cases a general ODE solving algorithm is more straightforward.**

## *Methods for a general least squares process II. ODE solution*

### **Part 2. Solution of a general system of ordinary differential equations:**

One of the simplest methods is the Runge Kutta family of ODE solvers.

If the step size is continuously adjusted, it can safely keep any reasonable precision. (Except in the case of a stiff system of ODEs!). I usually set a precision of  $10^{-8}$ , and refine the results with another run of the evaluation software with a precision of  $10^{-10}$ . Why to use such tight precision requirements?

(Just to be absolutely sure that the found optimum is not affected by mathematical artifacts. It's free!)

One could hope larger step sizes by a more advanced technique.

*But can a step size be higher than the step size of the observations?*

No! We measure discrete temperature values. In my programs, the  $T(t)$  functions are constructed by simple interpolation. One could use spline approximations, too. In both cases, however, either  $T(t)$  or its derivatives are not smooth in the points of the observations. Accordingly, we can solve the ODEs separately, in each intervals:

$[t_1, t_2], [t_2, t_3], [t_3, t_4], \dots$

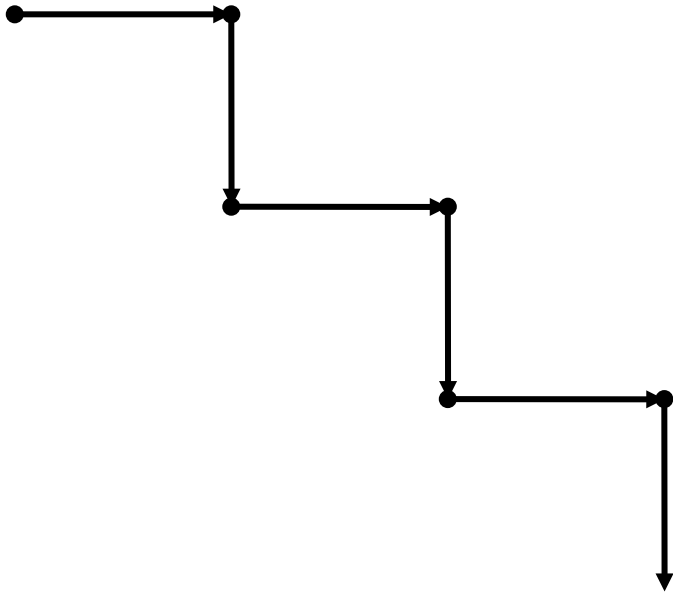
## *Methods for a general least squares process:*

### **III. Optimization:**

Which is a simple, but safe method?

Should we bother with finding analytical or numerical derivatives?

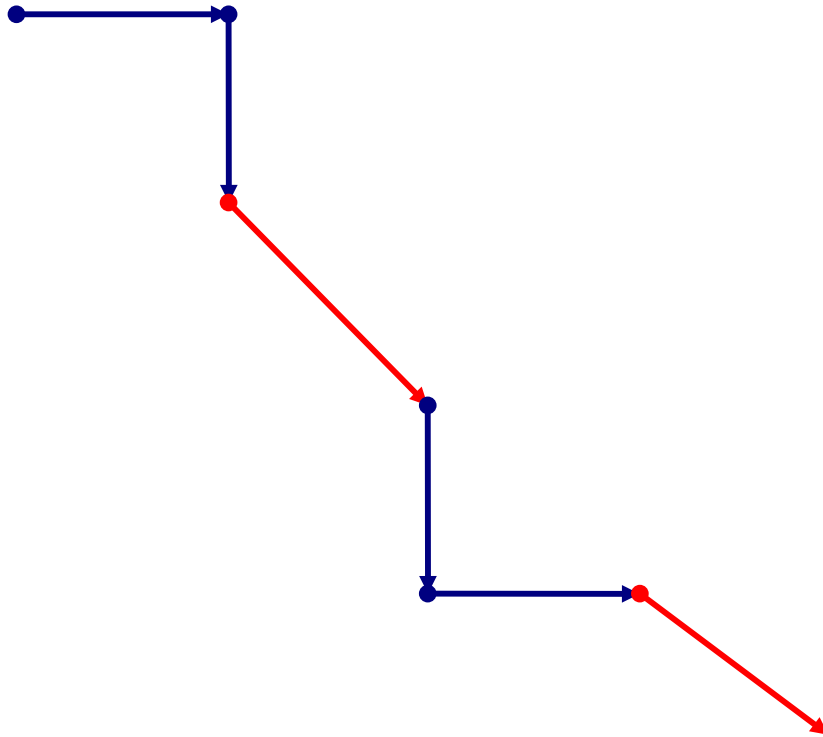
In the fifties, discrete steps were made in each direction, successively:





## *Methods for a general least squares process III. Optimization*

Later, in 1961, Hook and Jeeves added a step in the direction of the valley found in each cycle (see the red arrows in the figure.)



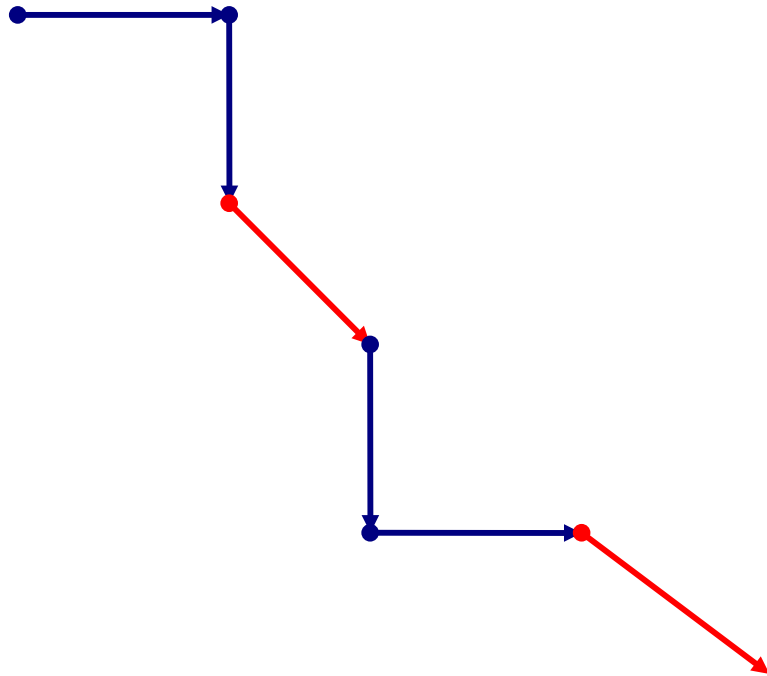
This invention improved the speed. This simple algorithm is very stable and finds a minimum at any topography. [See the recent results of Torczon et al.]

Contrary to the Simplex method of Nelder and Mead: the simplex sometime flatten, and one dimension is loss.

One can easily supplement this method by refining the step-length by parabolic interpolation/extrapolation in each step. (Its result is used only when it is significantly better than the unrefined step.)

## Methods for a general least squares process III. Optimization

Further advantages of the Hook – Jeeves method:



(1) Works simple and safely in the case of interval bounds on the variables, e.g.:

$$0 \leq n \leq 3; \quad 30 \leq E \leq 300$$

(2) In our case, several parameters affect only one ODE in the system. For example, if we evaluate a series of experiments with common  $E$ , while each experiment has its own  $\ln A$  and  $m_\infty$  then each  $\ln A$  and  $m_\infty$  affect only one ODE. In the steps in the direction of these parameters only one ODE should be solved.

## Methods for a general least squares process V. Separation of the linear and non-linear parameters

$$-dm/dt = \sum_{j=1}^M c_j d\alpha_j / dt$$

$$S_N = \sum_{k=1}^N \sum_{i=1}^{N_k} \frac{[X_k^{obs}(t_i) - X_k^{calc}(t_i)]^2}{N_k h_k^2} = \min$$

$S_N$  is quadratic for parameters  $c_j$ . They can be obtained by solving a system of linear equation by any set of  $E_j$  and  $A_j$ . Accordingly, only  $E_j$  and  $A_j$  should be searched by a general minimization algorithm.

**Safety considerations:** Whatever combinations arise temporarily during the minimization of  $S_N$ , the algorithm must not go astray. Accordingly, the program should automatically employ some strategy (e.g. a Tikhonov's regularization) for finding meaningful parameters if it observes ill-definition. Besides, the program must not allow negative  $c_j$  (except if the user explicitly tells such exception at the very beginning of the run).

## *Methods for a general least squares process VI. Parameter transformations*

The parameters can compensate each other to some extent. For example, a change of  $E$  can be counterbalanced more or less by a proper change of  $A$ . Many authors believed in deeper physical content behind this simple mathematical consequence that can be deduced easily from the properties of the Arrhenius type equations at non-isothermal  $T(t)$  programs.

The compensation effects can slow down the evaluation. One can fight against them by simple parameter transformations that decrease the dependence between the unknown parameters.

Nowadays I am not sure that such transformations are important, except a simple and trivial one:

In  $A$  or  $\log_{10} A$  should be used instead of  $A$

to avoid unpleasant geometries. Try to visualize an Arrhenius equation in the following way:

$$k(T) = \exp(\ln A - E/RT)$$

*End of these lectures.  
Thanks for your attention. 😊  
See you tomorrow! 😊*

