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Simulations for evaluation of kinetic methods in differential scanning calorimetry. Part 2. Effect of additional noise on single-peak methods

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Abstract

Theoretical data with various amounts of random gaussian errors have been used to test the validity of single-peak methods. This procedure was applied to various multiple linear regression algorithms with one or two kinetic exponents, and to the Achar–Brindley–Sharp, the Freeman–Carroll and the Ellerstein methods. Simulations were performed according to the results previously obtained for an experimental polymerization of an epoxy-novolac resin. The test of validity of the methods was performed using the LSM parameter which represents the fit between the mathematical treatment used in the kinetic model and known data, relative errors and standard deviations. The study shows in our case the lack of robustness of the Freeman–Carroll and of the Ellerstein methods in the presence of noise, and their sensitivity to temperature errors. The effect of smoothing has also been studied.

Keywords: Differential scanning calorimetry; Epoxy resins; Kinetics; Noise; Simulations

1. Introduction

In our previous paper [1], a comparative kinetic study from simulated thermoanalytical curves was presented. The validity of single-peak methods such as the multiple linear regression [2,3], the Achar–Brindley–Sharp [4], the Freeman–Carroll and the Ellerstein methods [5,6] was discussed. Assuming the hypothesis of a single-step reaction, the test of validity of the methods was performed using a parameter called LSM which represents the fit between the mathematical treatment used in the kinetic model and known data [7], relative errors and standard deviations. The parameter

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LSM is defined as

$$\mathrm{LSM} = \frac{1}{N}\sum_i (Y_{i,\,\mathrm{exp}} - Y_{i,\,\mathrm{calc}})^2$$

where N is the number of experimental values and Y represents the heat flow measured (exp) or calculated (calc) from the kinetic parameters. Relative errors have been computed by comparing the values obtained to those of a reference (the values mentioned are always absolute relative errors). The study revealed the importance of the resolution of the thermal curve recording, especially for the Freeman–Carroll and Ellerstein methods, with an increase in the relative errors on all the kinetic parameters when the number of points is decreased [1]. The Freeman–Carroll method, which has been the subject of criticism, gave accurate results for relative errors on the kinetic parameters, while for modelling purposes, the LSM values were always higher than with the Achar–Brindley–Sharp and multiple linear regression methods. This first study may at least explain the disagreement between authors in regard to this method. It is known that this method is sensitive to the scattering of the data; hence the series of simulations with additional noise presented here will allow investigation of the effect of experimental errors on the determination of the kinetic parameters.

2. Numerical simulations

Thermal analysis is an important tool in the characterization of reaction kinetics in thermosetting systems. Our interest in this field is not recent, and since our first investigation of crosslinking in epoxy-novolac resin [8], we have attempted to show the various sources of errors that can arise in these kinds of characterizations. Simulations may be used after evaluation of the level of noise, depending on the apparatus used, and of the order of magnitude of the thermodynamic and kinetic parameters involved by the transformation studied. The generation of the simulated data was previously presented [1]. In this study, the parameters used in the simulations were taken as: heat of cure Q, -77 J (taken as negative for an exothermic reaction); scanning rate V, $5^\circ\,\mathrm{min}^{-1}$; kinetic order n, 2; logarithm of the pre-exponential factor $\ln k_0$, 19; activation energy E_a, $77\,\mathrm{kJ\,mol}^{-1}$. These values were previously obtained from an experimental polymerization [9] that can be fitted [10] in the 10–80% kinetic interval with the kinetic homogeneous law. This law is expressed as $f(\alpha_i) = (1 - \alpha_i)^n$, where α_i is the degree of conversion at time i. So, each α_i can be computed as previously mentioned [1], and the computation is stopped for an α_i value near to one (> 0.999999). Because of the very precise results previously obtained with 6932 points (that is to say 780 points in the kinetic interval of 10–90% retained for the simulations), this value has been kept in this work and in that condition; the relative error on the heat of reaction was 9.66×10^{-6} for simulated data without noise, using a linear baseline extrapolation and a trapezoidal integration [1].

In the case of experimental measurements of temperature and power, simulations must take into account the effect of noise on these two measurements. To test the effect of noise in the recovery of reaction kinetic parameters, two types of pseudo-random noise can be generated, a pseudo-gaussian random noise and a pseudo-random noise. The accuracy of the methods was evaluated using different amounts of noise. The noise values were chosen in regard to the standard deviation of the noise on the power of the apparatus used (DSC-111 Setaram), which was evaluated in the temperature domain of our interest to a value of about 0.07.

3. Results of numerical simulations

Evaluation of the kinetic parameters was performed on the artificial created data by using a computer program described elsewhere [7]. In this program, the multiple linear regression method using a Sestak–Berggren model with two kinetic exponents m and n, denoted MLR(m,n), was added. This equation was solved using three multiple linear regression algorithms, the gaussian-elimination, the partial-pivoting and the gauss-seidel methods. In this case, this method may be performed taking the logarithmic form of the reaction rate equation

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_i = \ln k_0 - \frac{E_a}{\mathrm{R}T_i} + m\ln(\alpha_i) + n\ln(1-\alpha_i)$$

with

$$\alpha_i = H_i/Q$$

where R is the universal gas constant (8.31 J mol^{-1} K^{-1}), H_i the partial area computed at time i and T_i the absolute temperature at time i.

Simulations performed using non-gaussian noise led to similar conclusions as those with gaussian noise, so we present here only the results obtained with gaussian noise. Variations between simulations for the same level of noise were studied, and the average of five separate simulations was used to obtain the mean relative errors on

Table 1
Kinetic parameters obtained for simulated data without noise [1] using the Achar–Brindley–Sharp (ABS), multiple linear regression (MLR(n)), Freeman–Carroll (FC) and Ellerstein (EL) methods

	n[a,b]	$\ln k_0$[a,b]	E_a[a,b]	r_1[c]	r[c]	LSM[d]	
ABS	2.00	18.99520	76.96786		−1.0000000	2.36×10^{-6}	Step 10^{-2}
	1.99986	18.99322	76.96193		−1.0000000	9.68×10^{-8}	Step 10^{-6}
MLR(n)	1.99987	18.99330	76.96216			8.20×10^{-8}	
FC	1.99987	18.99339	76.96273	−1.0000000	−1.0000000	5.90×10^{-5}	
EL	1.99984	18.99300	76.96167	−1.0000000	−1.0000000	1.12×10^{-4}	

[a] n, kinetic exponent; $\ln k_0$, logarithm of pre-exponential factor; E_a, activation energy (kJ mol^{-1}).

[b] Theoretical parameters: $n = 2$; $\ln k_0 = 19$; $E_a = 77$ kJ mol^{-1}.

[c] r_1, correlation coefficient of the first-step calculation of the Freeman–Carroll and Ellerstein methods; r, correlation coefficient.

[d] LSM, fit of the calculated curve with the simulated one.

the kinetic parameters. In order to estimate the amplitude of the noise compared to the signal, a parameter is given (npmr) that represents the noise to peak-maximum ratio.

To perform comparisons, Table 1 gives the results previously obtained without noise with the Achar–Brindley–Sharp, Freeman–Carroll, Ellerstein and multiple linear regression MLR(n) methods [1]. The results obtained with the three other multiple linear regression algorithms: the gaussian-elimination, the partial-pivoting algorithm and the gauss-seidel algorithm presented in Table 2 are very different from those previously obtained in Table 1. The gauss-seidel algorithm is able to find a solution for a tolerance of 10^{-10}, but the exponent m obtained is not equal to zero and the kinetic parameters are different from the reference value. Furthermore, the very good accuracy between simulated and computed data (LSM) would not allow the elimination of these methods, in the case of the study of an unknown transformation. Absolute relative errors are reported in Table 3.

Table 2

Kinetic parameters obtained for simulated data without noise, using various algorithms (GE, PP, GS) for the multiple linear regression method MLR(m, n)

	E_a [a]	m [b]	n [b]	$\ln k_0^{\circ}$ [a]	LSM [a]
GE/PP [c]	74.00431	0.03582	1.96451	18.06491	2.48×10^{-8}
GS [c]	45.14953	0.38521	1.61957	9.00814	6.02×10^{-6}

[a] For abbreviations see Table 1.

[b] m and n are kinetic exponents.

[c] MLR(m, n), multiple linear regression method with two kinetic exponents; GE, gaussian-elimination; PP, partial-pivoting; GS, gauss-seidel (tolerance, 10^{-10}).

Table 3

Relative errors (RE) for the Achar–Brindley–Sharp (ABS), multiple linear regression (MLR(n), GE, PP, GS), Freeman–Carroll (FC) and Ellerstein (EL) methods (simulated data without noise)

	RE(n) [a,b,c]	RE($\ln k_0$) [a,b,c]	RE(E_a) [a,b,c]	LSM [a]	
ABS	5.00×10^{-3}	2.52×10^{-4}	4.17×10^{-4}	2.36×10^{-6}	Step 10^{-2}
	7.00×10^{-5}	3.57×10^{-4}	4.94×10^{-4}	9.68×10^{-8}	Step 10^{-6}
MLR (n)	6.73×10^{-5}	3.53×10^{-4}	4.91×10^{-4}	8.20×10^{-8}	
FC	6.40×10^{-5}	3.48×10^{-4}	4.84×10^{-4}	5.90×10^{-5}	
EL	7.77×10^{-5}	3.68×10^{-4}	4.98×10^{-4}	1.12×10^{-4}	
MLR(m, n)					
GE/PP	1.77×10^{-2}	4.92×10^{-2}	3.89×10^{-2}	2.48×10^{-8}	
GS	1.90×10^{-1}	5.26×10^{-1}	4.14×10^{-1}	6.20×10^{-6}	

[a] For abbreviations see Tables 1 and 2.

[b] RE(x), relative error on the parameter x.

[c] Total heat of cure $Q = -76\,999.26$ mJ, RE(Q) $= 9.66 \times 10^{-6}$.

3.1. *Noise on the power signal*

In a first step, the noise was only added to the power signal, in order to simulate experiments where only the power is measured and to separate each effect. This is effectively performed in some commercial calorimeters. In that case, the temperature T of a flux-meter differential scanning calorimeter is simply computed from the temperature at the beginning of the experiment (T_0).

The results presented in Tables 4–6 give an example of the values obtained for a simulation performed using additional gaussian noise (mean $m = 0$ and standard deviation $\sigma = 0.2$). The discrimination between methods is achieved by comparing the average of the relative errors for various sets of five separate simulations with a same level of noise, presented in Table 7. If we compare the kinetic parameters recovered from the simulations with the lowest power noise ($\sigma = 0.05$, Table 7) and without noise (Table 3), the activation energy is the parameter least sensitive to the noise (an increase in the factor of the relative error of about 10); whereas for the logarithm of the pre-exponential factor, a factor of about 100 is observed in the increase in the relative error on the pre-exponential factor (not given in the tables) and on the reaction order.

The variations of the LSM vs. the level of noise were not reported in this study but show a high increase for a level of noise greater than 0.2. The Freeman–Carroll and

Table 4
Kinetic parameters obtained for simulated data with gaussian random noise on the power[a], using the Achar–Brindley–Sharp (ABS), multiple linear regression (MLR(n)), Freeman–Carroll (FC) and Ellerstein (EL) methods

	n[b]	$\ln k_0$[b]	E_a[b]	r_1[b]	r[b]	LSM[b]	
ABS	1.94	18.56976	75.71		−0.9999930	8.81×10^{-2}	Step 10^{-2}
	1.94	18.59916	75.80		−0.9999931	8.49×10^{-2}	Step 10^{-6}
MLR(n)	1.94	18.59328	75.78			8.55×10^{-2}	
FC	1.96	18.87051	76.86	−0.6660603	−0.9999897	3.84×10^{1}	
EL	1.93	18.40760	75.66	−0.8041024	−0.9999913	1.13×10^{2}	

[a] Characteristics of the noise: mean = 0, standard deviation = 0.2.
[b] For abbreviations see Table 1.

Table 5
Kinetic parameters obtained for simulated data with gaussian random noise on the power[a] using various algorithms (GE, PP, GS) for the multiple linear regression method MLR(m, n)

	E_a[b]	m[b]	n[b]	$\ln k_0$[b]	LSM[b]
GE/PP	−15.51219	1.09546	0.86958	−10.05836	4.43×10^{-2}
GS[b]	45.20313	3.67001	1.58259	8.99612	6.21×10^{-2}

[a] Characteristics of the noise: mean = 0, standard deviation = 0.2.
[b] For abbreviations see Tables 1 and 2.
[c] Tolerance, 10^{-7}.

Table 6
Relative errors (RE) obtained for simulated data with gaussian random noise on the power, using the Achar–Brindley–Sharp (ABS), multiple linear regression (MLR(n), GE, PP, GS), Freeman–Carroll (FC) and Ellerstein (EL) methods

	RE(n)[a,b]	RE($\ln k_0$)[a,b]	RE(E_a)[a,b]	LSM[a]	
ABS	3.00×10^{-2}	2.26×10^{-2}	1.67×10^{-2}	8.81×10^{-2}	Step 10^{-2}
	2.90×10^{-2}	2.11×10^{-2}	1.56×10^{-2}	8.49×10^{-2}	Step 10^{-6}
MLR (n)	2.92×10^{-2}	2.14×10^{-2}	1.58×10^{-2}	8.55×10^{-2}	
FC	1.95×10^{-2}	6.82×10^{-3}	1.78×10^{-3}	3.84×10^{1}	
EL	3.57×10^{-2}	3.12×10^{-2}	1.74×10^{-2}	1.13×10^{2}	
MLR(m, n)					
GE/PP	5.65×10^{-1}	1.53×10^{0}	1.20×10^{0}	4.43×10^{-2}	$E_a, n < 0$
GS	2.09×10^{-1}	5.27×10^{-1}	4.13×10^{-1}	6.21×10^{-2}	

[a] For abbreviations see Tables 1–3.

[b] Total heat of cure $Q = -76\,193.39$ mJ, RE $(Q) = 1.05 \times 10^{-2}$.

[c] Characteristics of the noise: mean = 0, standard deviation = 0.2.

Ellerstein methods led to higher LSM values (as an example 38.4 and 113 respectively for the Freeman–Carroll and Ellerstein methods in Table 6). This confirms the hypothesis previously formulated [1] that the Freeman–Carroll method may be more accurate in the determination of the kinetic parameters if the number of data points is sufficient, but is not the more efficient method for modelling purposes [8,10].

The use of a sharper iterative step involving an increase in the computation time for the Achar–Brindley–Sharp method (Tables 4 and 6, step 10^{-6}), induces little decrease in the relative errors and LSM values. In the presence of noise, the decrease in the LSM value is weak compared to that obtained with noiseless data.

As with the noiseless data of Table 2, multiple linear regression algorithms performed for two kinetic exponents give an example of the existence of local minima, leading to negative values for the activation energy and the reaction order (gaussian-elimination and partial-pivoting algorithms, Table 5). This explains the high values observed for the relative errors, while the LSM values are of the same order as with the Achar–Brindley–Sharp and the multiple linear regression MLR(n) methods.

Tables 6 and 7 show that all the methods presented gave a reasonable estimation of the activation energy and of the reaction order for a noise level of 0.2. Beyond that, the relative errors are significantly increased, especially for the pre-exponential factor and for the reaction order, when the noise level is increased from 0.2 to 0.4 (Fig. 1 for E_a) and then from 0.4 to 0.6. When the noise level is increased up to 0.8, the relative error on the logarithm of the pre-exponential factor and on the reaction order becomes higher for the Freeman–Carroll method than for the multiple linear MLR(n) method. The Ellerstein method led to the highest relative errors, while, in most cases, the Freeman–Carroll method led to the lowest. The Achar–Brindley–Sharp and the multiple linear MLR(n) methods always led to accurate results. As with noiseless simulation, the lowest accuracy is found for the pre-exponential factor because, obviously, taking the antilogarithm of the logarithmic form magnifies the errors. As an example, for a 0.2

Table 7
Average relative errors obtained for simulated data with various amounts of gaussian random noise on the power, using the Achar–Brindley–Sharp (ABS), multiple linear regression MLR(*n*), Freeman–Carroll (FC) and Ellerstein (EL) methods

σ[c]	RE(Q)[a]	npmr[b]	Method	RE(n)[a]	RE($\ln k_0$)[a]	RE(E_a)[a]
0.05	2.90×10^{-3}	0.36%				
			ABS	1.20×10^{-2}	1.03×10^{-2}	7.73×10^{-3}
			MLR(n)	1.04×10^{-2}	7.93×10^{-3}	6.01×10^{-3}
			FC	8.71×10^{-3}	5.32×10^{-3}	2.82×10^{-3}
			EL	1.24×10^{-2}	1.09×10^{-2}	6.68×10^{-3}
0.1	5.00×10^{-3}	0.82%				
			ABS	2.20×10^{-2}	1.73×10^{-2}	1.29×10^{-2}
			MLR(n)	2.13×10^{-2}	1.63×10^{-2}	1.21×10^{-2}
			FC	1.78×10^{-2}	1.43×10^{-2}	8.93×10^{-3}
			EL	2.55×10^{-2}	2.26×10^{-2}	1.36×10^{-2}
0.2	1.15×10^{-2}	1.45%				
			ABS	4.60×10^{-2}	3.49×10^{-2}	2.55×10^{-2}
			MLR(n)	4.56×10^{-2}	3.44×10^{-2}	2.51×10^{-2}
			FC	3.95×10^{-2}	2.54×10^{-2}	1.34×10^{-2}
			EL	5.54×10^{-2}	4.89×10^{-2}	2.79×10^{-2}
0.4	2.16×10^{-2}	3.18%				
			ABS	1.31×10^{-1}	1.04×10^{-1}	7.58×10^{-2}
			MLR(n)	1.27×10^{-1}	9.77×10^{-2}	7.12×10^{-2}
			FC	1.10×10^{-1}	7.37×10^{-2}	3.80×10^{-2}
			EL	1.47×10^{-1}	1.27×10^{-1}	7.36×10^{-2}
0.8	3.67×10^{-2}	6.36%				
			ABS	2.04×10^{-1}	1.61×10^{-1}	1.17×10^{-1}
			MLR(n)	1.95×10^{-1}	1.47×10^{-1}	1.07×10^{-1}
			FC	2.02×10^{-1}	1.58×10^{-1}	8.30×10^{-2}
			EL	2.27×10^{-1}	1.94×10^{-1}	1.07×10^{-1}

[a] For abbreviations see Tables 1 and 3.
[b] npmr, noise to peak-maximum ratio.
[c] Characteristics of the noise: mean = 0, standard deviation $\sigma = 0.2$.

noise level, a mean value of 161% is found for the pre-exponential factor with the Ellerstein method, while the relative error on its logarithm corresponds only to 4.89% (Table 7). As the pre-exponential factor is used in the computation of the LSM, this statement, associated with the low correlation coefficients of the first step (r_1, Table 4), explains the high LSM values obtained with this method. The Freeman–Carroll method often led to the lowest average relative error for the kinetic parameters, within an approximate range of 0.3–8% for the activation energy, 0.9–20% for the reaction order, and 0.5–16% for the logarithm of the pre-exponential factor (Table 7). The results obtained from the Achar–Brindley–Sharp and multiple linear regression MLR(*n*) methods are very similar, these last two methods leading to the lowest LSM values. As an example, with the multiple linear regression method (MLR(*n*) Table 7), an approximate range of 0.6–11% is found for the activation energy, 1–19.5% for the reaction order, and 0.8–15% for the logarithm of the pre-exponential factor.

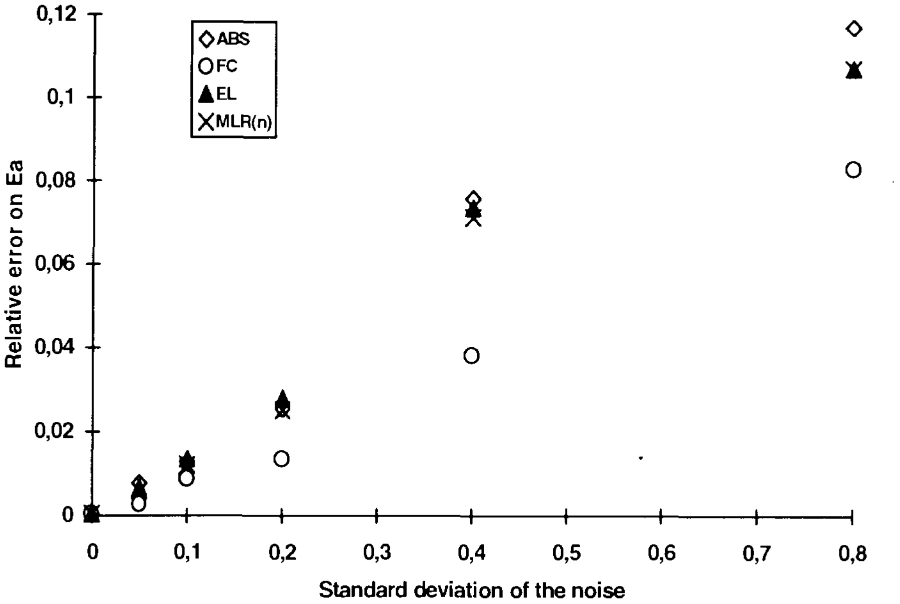

Fig. 1. Average relative errors on the activation energy vs. the standard deviation of gaussian noise applied on the power, for the multiple linear regression (MLR(n)), the Achar–Brindley–Sharp (ABS), the Freeman–Carroll (FC) and the Ellerstein (EL) methods.

The analysis of the standard deviations of the kinetic parameters shows that the lowest values are found for the reaction order, then for the activation energy, and finally for the pre-exponential factor. When the noise is increased from $\sigma = 0.05$ to $\sigma = 0.2$, a multiplying factor of approximately ten is found for the reaction order and for the activation energy, while this factor is about twenty for the pre-exponential factor. For the same level of noise, the different methods give very similar standard deviations except for that of Ellerstein, for which the values are always higher. There is a tendency for the Freeman–Carroll method to give the lowest deviations.

The parameter called Δn has been calculated for the Freeman–Carroll method according to Jerez [11]. This parameter is expressed as $\Delta n = \sigma_y(1 - r^2)^{1/2}$, where σ_y represents the standard deviation of the ordinates, and gives an estimation of the absolute error on the reaction order. Fig. 2 shows a good correlation between various relative errors on the reaction order for each level of noise and this parameter (divided by the reference value of the reaction order). Nevertheless, the values given by these two parameters are different (all these values are the average for 5 sets).

3.2. *Noise on the power and temperature signals*

In the case of joint power and temperature noise, the standard deviation of the noise was increased from 0.01 up to a maximum level of 0.4. The Achar–Brindley–Sharp and multiple linear regression MLR(n) methods show a similar level of accuracy (Tables

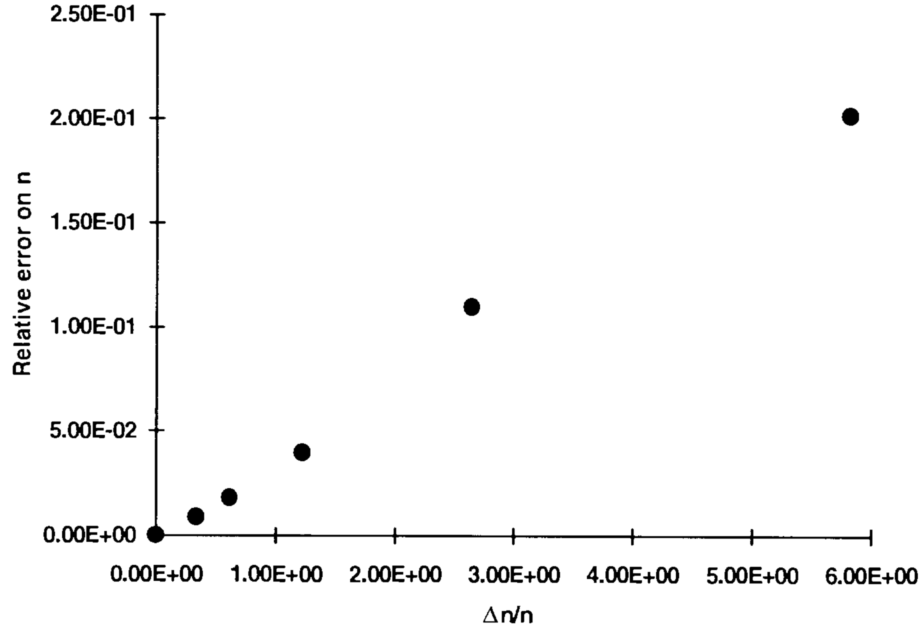

Fig. 2. Average relative errors on the reaction order obtained with the Freeman–Carroll (FC) method vs. the parameter Δn, for various standard deviations of gaussian noise (0, 0.05, 0.1, 0.2, 0.4 and 0.8), applied on the power.

Table 8
Kinetic parameters obtained for simulated data with gaussian random noise on the power and on the temperature[a], using the Achar–Brindley–Sharp (ABS), multiple linear regression (MLR(n)), Freeman–Carroll (FC) and Ellerstein (EL) methods

	n[b]	$\ln k_0$[b]	E_a[b]	r_1[b]	r[b]	LSM[b]	
ABS	2.03	19.18981	77.54	–	−0.9999353	1.27×10^0	Step 10^{-2}
	2.03	19.16683	77.47	–	−0.9999353	1.26×10^0	Step 10^{-6}
MLR(n)	2.02	19.10889	77.30	–	–	1.26×10^0	
FC	−0.50	−16.51624	3.79	−0.1798115	−0.7512439	6.77×10^3	
EL	1.21	7.54782	61.67	−0.0571958	−0.9814389	6.74×10^3	

[a] Characteristics of the noise: mean = 0, standard deviation $\sigma = 0.2$.
[b] For abbreviations see Table 1.

8–10). The multiple regression methods with two kinetic exponents led to very different parameters from those of the reference (Table 9), while the LSM values are the lowest. The average of the relative errors for five separate sets is presented in Table 11 where the parameter noted ΔT gives the amplitude of the noise on the temperature. For the lowest noise level (a temperature accuracy of $\Delta T = 0.1$ K and a noise to peak-maximum ratio npmr = 0.082%), similar relative errors are found for the Achar–Brindley–Sharp, Ellerstein and multiple regression methods, while the relative error on the logarithm of

Table 9
Kinetic parameters obtained for simulated data with gaussian random noise on the power and on the temperature[a], using various algorithms (GE, PP, GS) for the multiple linear regression method MLR(m, n)

Line	E_a [b]	m [b]	n [b]	$\ln k_0$ [b]	LSM [b]
GE/PP	0.08729	9.36774	1.09357	−5.12547	4.36×10^{-2}
GS[c]	45.14758	3.91325	1.63778	9.01945	4.58×10^{-1}

[a] Characteristics of the noise: mean = 0, standard deviation $\sigma = 0.2$.
[b] For abbreviations see Tables 1 and 2.
[c] Tolerance, 10^{-6}.

Table 10
Relative errors (RE) for simulated data with gaussian random noise on the power and on the temperature[a], using the Achar–Brindley–Sharp (ABS), multiple linear regression (MLR(n), MLR(m, n)), Freeman–Carroll (FC) and Ellerstein (EL) methods

	RE(n) [b,c]	RE($\ln k_0$) [b,c]	RE(E_a) [b,c]	LSM [b,c]	
ABS	1.50×10^{-2}	9.99×10^{-3}	7.03×10^{-3}	1.27×10^{0}	Step 10^{-2}
	1.42×10^{-2}	8.78×10^{-3}	6.14×10^{-3}	1.26×10^{0}	Step 10^{-6}
MLR (n)	1.21×10^{-2}	5.73×10^{-3}	3.89×10^{-3}	1.26×10^{0}	
FC	1.25×10^{0}	1.87×10^{0}	9.51×10^{-1}	6.77×10^{3}	
EL	3.97×10^{-1}	6.03×10^{-1}	1.99×10^{-1}	6.74×10^{3}	
MLR(m, n)					
GE/PP	4.53×10^{-1}	1.27×10^{0}	9.99×10^{-1}	4.36×10^{-2}	
GS	1.81×10^{-1}	5.25×10^{-1}	4.14×10^{-1}	4.58×10^{-1}	

[a] Characteristics of the noise: mean = 0, standard deviation $\sigma = 0.2$.
[b] For abbreviations see Table 3.
[c] Total heat of cure $Q = -77\,233.33$ mJ, RE(Q) $= 3.03 \times 10^{-3}$.

the pre-exponential factor of the Ellerstein method is higher. All the values obtained with the Freeman–Carroll method are higher. As the noise level increases to 0.05, i.e. $\Delta T = 0.5$ K and npmr = 0.36%, this tendency increases drastically, leading to a distinguishable set of values between the Freeman–Carroll and Ellerstein methods, and the other two methods (Fig. 3). So, the Freeman–Carroll method gives an average activation energy, reaction order and logarithm of the pre-exponential factor which deviate from the reference values by about 66, 86 and 129%, respectively; for the Ellerstein method, the errors are respectively 58, 63 and 94%. Because of the scatter of the data kinetic points, the Freeman–Carroll method is unable to describe the reaction kinetics, being too susceptible to low temperature and power noises. The example presented in Table 8 ($\sigma = 0.2$) confirms the previous conclusion drawn for the correlation coefficients r_1 of the Freeman–Carroll and Ellerstein methods, which explains the very high LSM values found, and this is in agreement with the results obtained experimentally [8–10]. This was also observed in the reduced interval (10–80%) for experimental data, where it has been shown that the reaction order model gives an accurate fit of the data.

Table 11
Average relative errors obtained for simulated data with various amounts of gaussian random noise on the power and on the temperature, using the Achar–Brindley–Sharp (ABS), multiple linear regression (MLR(n)), Freeman–Carroll (FC) and Ellerstein (EL) methods

σ [a]	RE(Q) [b]	npmr [b]	ΔT [c]	Method	RE(n) [b]	RE($\ln k_0$) [b]	RE(E_a) [b]
0.01	5.56×10^{-4}	0.082%	0.1				
				ABS	5.00×10^{-3}	1.92×10^{-3}	1.45×10^{-3}
				MLR(n)	2.03×10^{-3}	1.58×10^{-3}	1.30×10^{-3}
				FC	1.01×10^{-1}	1.51×10^{-1}	7.72×10^{-2}
				EL	7.38×10^{-3}	1.06×10^{-2}	6.78×10^{-3}
0.05	1.41×10^{-3}	0.36%	0.4				
				ABS	8.00×10^{-3}	6.38×10^{-3}	4.73×10^{-3}
				MLR(n)	7.99×10^{-3}	6.19×10^{-3}	4.59×10^{-3}
				FC	8.64×10^{-1}	1.29×10^{0}	6.58×10^{-1}
				EL	6.32×10^{-1}	9.40×10^{-1}	5.76×10^{-1}
0.1	5.59×10^{-3}	0.82%	0.9				
				ABS	3.20×10^{-2}	2.44×10^{-2}	1.81×10^{-2}
				MLR(n)	3.16×10^{-2}	2.39×10^{-2}	1.77×10^{-2}
				FC	1.18×10^{0}	1.75×10^{0}	8.86×10^{-1}
				EL	5.54×10^{-1}	8.27×10^{-1}	5.53×10^{-1}
0.2	5.05×10^{-3}	1.45%	1.6				
				ABS	1.90×10^{-2}	1.48×10^{-2}	1.10×10^{-2}
				MLR(n)	1.97×10^{-2}	1.58×10^{-2}	1.17×10^{-2}
				FC	1.26×10^{0}	1.88×10^{0}	9.58×10^{-1}
				EL	1.76×10^{0}	2.64×10^{0}	1.46×10^{0}
0.4	2.05×10^{-2}	3.18%	3.5				
				ABS	9.30×10^{-2}	7.08×10^{-2}	5.17×10^{-2}
				MLR(n)	9.18×10^{-2}	6.94×10^{-2}	5.06×10^{-2}
				FC	1.29×10^{0}	1.94×10^{0}	9.88×10^{-1}
				EL	1.81×10^{0}	2.71×10^{0}	1.61×10^{0}

[a] Characteristics of the noise: mean = 0, standard deviation σ.
[b] For abbreviations see Tables 1–3.
[c] Amplitude of the error on the temperature.

For these last two methods the parameters are very different to those of the reference, even leading to negative values for the Freeman–Carroll method.

3.3. Smoothing data

The interest in a pre-treatment of noisy data such as filtering, or the elaboration of kinetic methods less sensitive to noisy signals, is obvious for kinetic or modelling treatments. Smoothing crude data is a simple technique, often used in analytical chemistry. Here we show the results obtained using such a treatment, and we will give comparisons with other techniques in a future paper. In the present work, the convolution method applied used a polynomial with intervals of seven successive points [12], which was found adequate in regard to the dual effect of smoothing. Smoothing was also applied on the pure signals: in fact, it is known that running

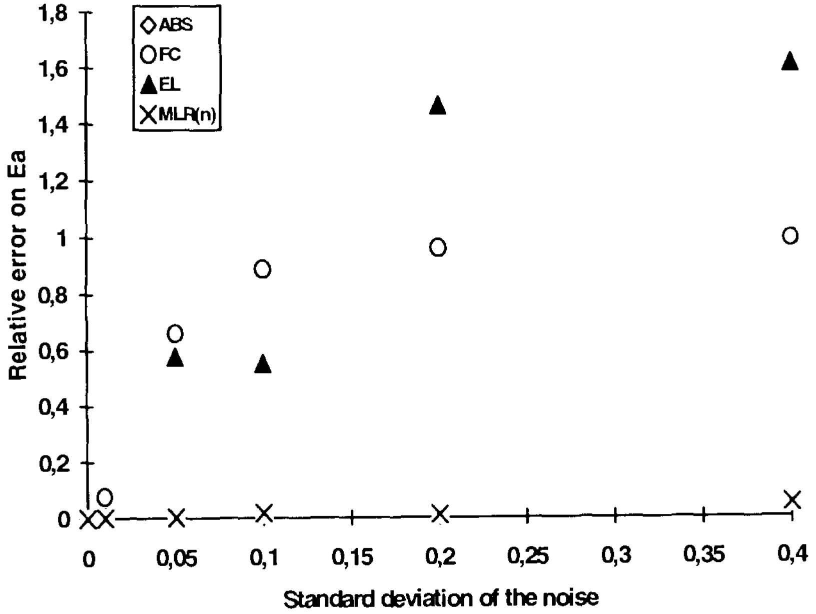

Fig. 3. Average relative errors on the activation energy factor vs. the standard deviation of gaussian noise applied on the power and on the temperature, for the multiple linear regression (MLR(*n*)), the Achar–Brindley–Sharp (ABS), the Freeman–Carroll (FC) and the Ellerstein (EL) methods.

averages may distort values that are already smooth. The relative error on the heat of cure is significantly decreased for noisy data (factor 100) by using this technique.

Results on pure and noisy signals are presented in Tables 12 and 13 in order to evaluate the filtering ability as well as the effect of smoothing itself. Applied to the pure

Table 12

Relative errors obtained for simulated data without noise, using the Achar–Brindley–Sharp (ABS), multiple linear regression (MLR(*n*)), Freeman–Carroll (FC) and Ellerstein (EL) methods, before and after smoothing data

	RE(n)[a,b]	RE($\ln k_0$)[a,b]	RE(E_a)[a,b]	LSM[a]	
ABS	5.00×10^{-3}	2.52×10^{-4}	4.17×10^{-4}	2.36×10^{-6}	
	5.00×10^{-3}	2.54×10^{-4}	4.17×10^{-4}	2.39×10^{-6}	Smooth[c]
MLR (n)	6.73×10^{-5}	3.53×10^{-4}	4.91×10^{-4}	8.20×10^{-8}	
	6.78×10^{-5}	3.53×10^{-4}	4.92×10^{-4}	8.43×10^{-8}	Smooth[c]
FC	6.40×10^{-5}	3.48×10^{-4}	4.84×10^{-4}	5.90×10^{-5}	
	6.44×10^{-5}	3.48×10^{-4}	4.84×10^{-4}	6.02×10^{-5}	Smooth[c]
EL	7.77×10^{-5}	3.68×10^{-4}	4.98×10^{-4}	1.12×10^{-4}	
	7.83×10^{-5}	3.69×10^{-4}	4.98×10^{-4}	1.14×10^{-4}	Smooth[c]

[a] For abbreviations see Tables 1 and 3.

[b] RE(Q) = 9.66×10^{-6} before smoothing and Re(Q) = 1.08×10^{-5} after smoothing.

[c] Parameters obtained after smoothing data.

Table 13
Relative errors obtained for simulated data with gaussian random noise on the power[a], using the Achar–Brindley–Sharp (ABS), multiple linear regression (MLR(n)), Freeman–Carroll (FC) and Ellerstein (EL) methods, before and after smoothing data

	RE(n)[b,c]	RE($\ln k_0$)[b,c]	RE(E_a)[b,c]	LSM[b]	
ABS	3.00×10^{-2}	2.26×10^{-2}	1.67×10^{-2}	8.81×10^{-2}	
	1.00×10^{-2}	1.02×10^{-2}	7.82×10^{-3}	2.14×10^{-2}	Smooth[d]
MLR (n)	2.92×10^{-2}	2.14×10^{-2}	1.58×10^{-2}	8.55×10^{-2}	
	7.90×10^{-3}	7.12×10^{-3}	5.51×10^{-3}	1.67×10^{-2}	Smooth[d]
FC	1.95×10^{-2}	6.82×10^{-3}	1.78×10^{-3}	3.84×10^{1}	
	1.25×10^{-2}	1.40×10^{-2}	8.26×10^{-3}	2.06×10^{1}	Smooth[d]
EL	3.57×10^{-2}	3.12×10^{-2}	1.74×10^{-2}	1.13×10^{2}	
	1.48×10^{-2}	1.74×10^{-2}	1.11×10^{-2}	1.55×10^{1}	Smooth[d]

[a] Characteristics of the noise, same set as in Table 6.
[b] For abbreviations see Tables 1 and 3.
[c] $RE(Q) = 1.05 \times 10^{-2}$ before smoothing and $RE(Q) = 5.80 \times 10^{-4}$ after smoothing.
[d] Parameters obtained after smoothing data.

signal, relative errors as well as LSM are found to be of the same order or a little less accurate (Table 12). Little decrease in the relative errors is observed when gaussian random noise is added onto the power (the same example as in Table 6, $m = 0$, $\sigma = 0.2$). Nevertheless, the results remain of the same order of magnitude. For the Freeman–Carroll method, the relative errors on the logarithm of the pre-exponential factor and on the activation energy are increased, while only the relative error on the reaction order (intercept of the Arrhenius plot) shows a little decrease. The correlation coefficient of the first step is increased by smoothing the data (we found -0.93273 instead of -0.66606 in Table 4).

3.4. Discussion

For multiple linear regression algorithms MLR(m,n) performed with two kinetic exponents, the simulations reveal a very important problem which deals with the existence of several local minima in the phase space that represent the solutions of the problem, and are in agreement with the conclusion of Sestak and Malek [13], relative to the statement that multiple linear regression methods can lead to incorrect results because any thermal analysis curve can be interpreted within the scope of several apparent kinetic models (reaction order or Sestak–Berggren) depending on the value of the apparent activation energy. In our case, this problem was only encountered for the Sestak–Berggren model (MLR(m,n)).

The precision that could be obtained on the kinetic parameters would depend on the peak shape, i.e. on the kinetic parameters, and on the inherent noise of the apparatus (this latter is generally much lower than the maximal values tested here). For fast reactions involving high energy exchanges, the thermal gradients inside the sample may induce large errors on the temperature, and so the kinetic parameter accuracy would be lower. In that case, the increase of thermal gradients represents part of the errors [8, 9], and may sometimes be reduced by using a lower heating rate. We proposed [9] the use of the sample temperature measurement as an interesting way of evaluating thermal gradients and their effects on kinetic parameters, in order to select the proper experimental conditions. In such a case, the sample temperature (measured) is not linearly increased; its value may sometimes be quite constant between two time intervals leading to very small numerators or zero-value numerators and so to the lack of application of the Ellerstein method. Furthermore, the kinetic parameters obtained with the Freeman–Carroll or the Ellerstein method may be very different from those computed by other methods, because these methods are very sensitive to the presence of noise, especially on the temperature. This remark concerns particularly the Freeman–Carroll method, the Ellerstein method always being the less accurate. In the presence of noise on the power and on the temperature, the Freeman–Carroll and Ellerstein methods led to very high relative errors (100–270%) for the highest level of noise tested ($\sigma = 0.4$, $\Delta T = 3.5$, npmr = 3%), while for the multiple linear regression MLR(n) or the Achar–Brindley–Sharp methods, these errors vary from 5 to 9% for all the kinetic parameters. For the same level of power noise, the relative errors vary from 7 to 13% for these last methods and from 4 to 15% for the former. A lower value for the multiple linear regression MLR(n) and the Achar–Brindley–Sharp methods is found in the case of a curve simulated with two noise components (in this case some errors may compensate themselves, Table 11). In this case, the precision on the temperature is about 4 K which is low, and we still observe a good accuracy for these last methods. So, the robustness of the methods vs. noise may be very different. This conclusion confirms the statement of Flynn [14] that the temperature imprecision is probably the greatest source of errors in thermal analysis and demonstrates that difference-differential methods are especially sensitive to this error. Nevertheless, systematic errors in temperature measurements (as with experimental data) may have much less effect than random errors [14], if the number of experimental points is sufficient [1].

In the presence of noise, the analysis of the correlation coefficients (Tables 4 and 8) confirms the great difference between r_1 (first-step calculation) and r (second-step calculation). This is in agreement with the results obtained experimentally [8,10], and explains the differences observed between the Freeman–Carroll and Ellerstein methods and the others. The correlation coefficient r_1 may become too removed from unity to evaluate the activation energy and the reaction order from the slope and intercept of the Arrhenius line. These methods do not retain the parameters that correspond to the best linearization of the Arrhenius plot, and so in the presence of noise the validity of the Arrhenius equation is not verified. This explains the great sensitivity of the Freeman–Carroll and Ellerstein methods to the presence of noise in the temperature measurements. However, for the Achar–Brindley–Sharp method, the reaction order retained is the one that gives the best linearization of the Arrhenius plot (involving E_a, n and $\ln k_0$), and then the activation energy and the logarithm of the pre-exponential factor are deduced. For the multiple linear regression MLR(n) method, the parameters (E_a, n and $\ln k_0$) are computed by minimizing the residual between the data and the plot of the Arrhenius line. Indeed, in the Freeman–Carroll or Ellerstein methods, the reaction order and the activation energy are computed in a first step from one Arrhenius plot (involving E_a and n). Then the logarithm of the pre-exponential factor is deduced, with a correlation coefficient of the first-step calculation generally low, and a correlation coefficient of the second step generally nearest to unity. So, the difference between these last methods and the Achar–Brindley–Sharp or the multiple linear regression MLR(n) methods may result in very good agreement between the kinetic parameters computed by these last kinds of methods in regard to the assumption made.

We can confirm that the use of the LSM values provides a good method for the choice between the Freeman–Carroll, Ellerstein, Achar–Brindley–Sharp and multiple linear regression MLR(n) methods.

4. Conclusion

The simulations with additional noise on power and on temperature were used as a way of selecting kinetic methods for an example of the given kinetic parameters of a cure. Discrimination between methods was achieved by comparing the average relative errors, the standard deviations and the fit between the kinetic model and known data. The differential methods used are not supported by mathematical approximations so that the multiple linear regression method for a reaction order model and the Achar–Brindley–Sharp method led to accurate relative errors and LSM values even when noise is added on both temperature and power signals, with relatively high amounts of noise. The simulations prompt us to take care using the multiple linear regression algorithms performed with two kinetic exponents, methods of modellization rather than kinetic methods for which the LSM values and the relative errors are not always correlated. The existence of local minima, in the modelling of a thermal curve constructed using a single-step model, clearly indicates that for the description of complex phenomena, requiring more than one kinetic exponent, the parameters obtained with a multiple linear regression method should be modelling parameters, depending on the experimental conditions, and not real kinetic parameters.

On simulated thermoanalytical curves without noise, the Freeman–Carroll and Ellerstein methods led to precise results when the highest number of kinetic points was used; these methods are still accurate with gaussian power noise for the determination of the kinetic parameters, but not for modelling purposes. Nevertheless, the Ellerstein method often led to the worst results. When gaussian random noise is added on both power and temperature, the Freeman–Carroll method is very sensitive to small amounts of noise. These simulations give an explanation for the high LSM values that can be obtained for the Freeman–Carroll and the Ellerstein methods and show the importance of the knowledge of the correlation coefficient of the first-step calculation. This study clearly shows the limit of these two difference-differential methods for which the postulated assumption of the linearization of the Arrhenius plot is not always respected.

A simple smoothing data technique led to a decrease in the error on the heat of cure and on the kinetic parameters, with an exception for the Freeman–Carroll method. Therefore, this technique may be recommended after having quantified the effect of running averages. In that case, simulations are useful to select the optimal equation depending on the data that have to be smoothed. A future work will present the interesting results obtained in filtering thermoanalytical data, by applying new techniques.

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