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Selection of Formal Baseline Correction Methods in Thermal Analysis

Baseline correction is a key step in processing of thermal analysis data. Whilst this is a common step, techniques range from linear baselines to use of high-order polynomials. When considering a formal baseline correction (those without physical or experimental justification), only linear correction methods should be used: linear with time, linear with temperature, and linear with extent of reaction. The absence of baseline correction should also be considered. An in silico study shows that the wrong baseline correction can significantly impact the parameters obtained from kinetic modeling. The four baseline correction methods are demonstrated with a mass spectrometry dataset. It is recommended that the selection of correction method should be based on comparison of Akaike weights.

Keywords: Akaike weights, Baseline correction, Kinetics, Thermogravimetric analysis

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1 Introduction

Thermal analysis is an invaluable tool in materials research and development [1]. This class of experimentation can be used to extract information on mass changes and thermodynamics, kinetics, sintering and heat capacity, crystalline formations and oxygen content, amongst others [1]. In many of these thermal analysis experiments, baseline drifts are observed, and this must be accounted for prior to the extraction of kinetic information from the data. A rigorous and accurate methodology for baseline correction is required, as quantitative data analysis is being carried out more frequently with thermal analysis data [2–4], with the aim of extracting kinetic and mechanistic information.

A baseline is the signal produced when no detectable thermal events are occurring. These baselines are used to identify the start and end of the thermal events taking place during an experiment. To extract meaningful kinetic parameters from these thermal analysis experiments, the data must be treated with a baseline correction method [5], which is a function subtracted from the data. Some papers refer to the need for baseline correction, but do not identify the methods used to carry out this subtraction [6,7]. Similarly, while the issues with extracting information from unstable baselines is referred to in Maciejewski [2], methods to overcome them are not addressed. Most of the literature which discusses thermal analysis does not refer to baseline correction. It may be that the data were deemed to be free from baseline drift (which can be the case), or that correction methods have been used but not stated. In some cases, the figures presented in the literature appear to contain baseline drift, but this issue is not addressed [8,9].

It is common to use computer software in the fitting of these baseline corrections [10]. These programs often require the experimenter to assign the initial and final baseline points, which can be subjective and based on experience. This work aims to remove the subjective nature of baseline correction and to show how the selection of a baseline correction should be based on a statistical approach.

Many factors can cause the baseline to change during an experiment, and this change must be accounted for prior to extracting information from the data. For kinetic studies using thermogravimetric analysis (TGA) data, the first derivative is required. The baseline drift present in these data are recognized and mainly associated with buoyancy effects or changes in these effects [4]. The impact of these depends upon the experimental setup. For example, buoyancy effects may have a larger impact when using a vertical flow arrangement rather than a horizontal setup. The appearance of this baseline drift also depends on the instrument setup, as buoyancy can be observed as either a weight loss or weight gain depending on the instrument used.

Baseline drifts within differential scanning calorimetry (DSC) measurements are well known, and it is recognized that the baseline originates from the temperature dependence of the heat capacities, reactants, intermediates, products, and the amount by which these change throughout the process [4].

For temperature-programmed reduction/temperature-programmed desorption (TPR/TPD) experiments there are several

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possible sources of baseline drift: pressure, an increase in pressure caused by a contraction/flow restriction, volume of gas, a leak in the system which would decrease the volume of gas passing the detector, water ingress, changes to the composition of the gas stream, and hence the conductivity detected by the thermal conductivity detector (TCD). For mass spectrometry (MS), changes in baseline shown in the data may be due to the presence of ambient gases in the supplied carrier gas, more than one species with a given mass-charge ratio or variation in vacuum within the equipment.

It is common, but not necessary [11], for peaks observed in thermal analysis experiments to be deconvoluted prior to kinetic modeling. Michael et al. [12] and Hemminger and Sarge [5] both recommend that this deconvolution be carried out prior to the baseline correction, such that each thermal event has its own baseline. Baselines based on the individual thermal event would not apply if the reasons for the baseline drift occur due to a process condition, such as a leak. This means that using this method of baseline correction would not account for these types of baseline drifts, though use of an overall baseline correction would. This study of baseline correction methods will be combined with the methodology reported by Gibson et al. [11], which does not require peak deconvolution, hence overall baselines are considered in this work.

The International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommends that for kinetic analysis which requires multiple heating rate experiments, the same baseline correction method should be applied to all data sets [4]. Additionally, various baseline correction methods should be trialled, with the kinetic modeling completed and statistics for each method compared before a method is selected. This would, importantly, reveal the impact on the kinetic parameters estimated [4]. This work aims to present a methodology for comparing baseline correction methods, through the use of Akaike weights [13]. This statistical technique evaluates the amount of information lost through modeling and indicates which of the well-fitting models considered would be the most likely to describe the system.

Hemminger and Sarge [5] described the use of three groups of baseline correction methods, i.e., formal methods (these lack physical justification), methods based on physicochemical assumptions, and experimental methods. Although Hem-

minger and Sarge [5] study the baseline construction for DSC curves, these baseline categories can be extended to most thermal analysis experiments.

Experimental methods to establish a baseline are common within thermal analysis. For a TGA experiment, the buoyancy effects causing the baseline drift can be captured by carrying out a blank TGA run with an empty sample pan. The curve produced from this experiment would then be subtracted from the TGA curve when the sample is present [14]. This is the simplest form of obtaining a baseline experimentally. Other similar experiments can be run using inert samples [5]. Other more complex examples use simultaneous experimental techniques to identify suitable baselines for correction [5, 15].

Physicochemical methods require physical reasoning. Niet et al. [16] use a step-change baseline correction for their TPD work, explained by the water used in the TPD adsorbing onto the stainless-steel walls of the reaction chamber. For DSC measurements it has been established that the tangential area-proportional baseline should be used to capture the heat capacity temperature dependencies [17]. Svoboda [18–20] has discussed this baseline correction technique in detail, including a comparison with interpolations commonly preprogrammed into commercial software. Schematics of these physicochemical baselines are displayed in Fig. 1.

It is advised that where possible and where a physical basis is present, either experimental or physicochemical baseline correction methods should be attempted, e.g., the use of a tangential area-proportional baseline correction. However, this paper will focus on formal baseline correction techniques. These should only be considered in the absence of any physical or experimental reasoning for a baseline drift.

There are many possible options for the type of function to be constructed between two data points (initial and final baseline). Theoretical/nonphysical methods can range from a simple function such as straight lines to more complex ones such as sigmoidal curves [5]. It has been well established that models should use as few parameters as is practical whilst giving an accurate representation of the data [21, 22]. Overparameterization may lead to an improved closeness of fit by capturing more of the variance in the measured data and yet decrease the quality of fit for a model by introducing bias in the model [22]. To avoid overparameterization, the only function which can be
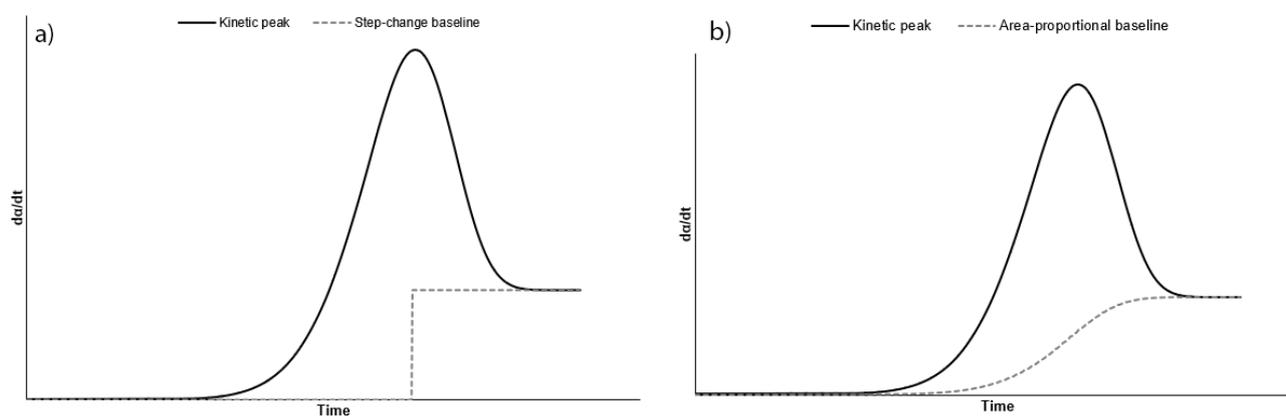

Figure 1. Schematic representation of (a) step-change baseline, (b) area-proportional baseline.

justified for connecting two points is a linear function, i.e., a straight line. In the absence of further data, other possible functions would be ill-constrained. This straight line can use either the time, temperature, or extent of reaction as its independent variable. Other functions such as final point backwards (extrapolating from the final baseline back to the start time of the experiment), have no justification and should be avoided. Similarly, high-order polynomials [23] and other curves should be avoided, as these have too many degrees of freedom. Along with these linear baseline correction methods, the absence of correction should also be considered.

In this work, a method of selecting the most statistically likely formal baseline correction technique will be discussed and demonstrated with both in silico and experimental datasets. In silico data, representing a temperature-programmed experiment, will be used to demonstrate the internal consistency of the baseline correction models, the impact of selecting an unsuitable correction method, and the use of Akaike weights to select the most suitable correction method. The experimental case study, a zinc nitrate catalyst precursor decomposition, demonstrates the applicability of the proposed methodology using real data. The aim of this work is to remove the human or experiential element which is often present in baseline correction of thermal analysis data.

2 Modeling Methods

The baseline correction methods are combined with the Sestak-Berggren modeling in Athena Visual Studio and are estimated alongside the Sestak-Berggren model itself. The four baseline correction methods considered in this work take the forms given in Eqs. (1)–(4):

$$\text{No correction}: \varepsilon_{\text{BL}} = 0.0 \tag{1}$$

$$\text{Linear with time}: \varepsilon_{\text{BL}} = Mt + C \tag{2}$$

$$\text{Linear with temperature}: \varepsilon_{\text{BL}} = MT + C \tag{3}$$

$$\text{Linear with extent of reaction}: \varepsilon_{\text{BL}} = M\left(\sum F_{\text{v,i}}\alpha_i\right) + C \tag{4}$$

where $M^{1)}$ represents the baseline (BL) gradient, C is the y-intercept of the baseline, t is time (h), T temperature (K), α is the extent of reaction, and $F_{\text{v,i}}$ represents the contribution of each thermal event (i) signal to the overall curve. No constraints have been placed on the values of M and C.

The kinetic modeling used in this work is based on the modified Sestak-Berggren equation [11], Eq. (5). This methodology does not require a priori peak deconvolution. Nonlinear least-squares regression has been used in Athena Visual Studio, with default tolerances [24], with the aim of minimizing the residual on dα/dt, the dimensionless signal. The model report-

ed elsewhere [11] is extended with the addition of the contribution from the unknown baseline.

$$\frac{d\alpha}{dt} = \sum_{i=1}^{n_{\text{events}}} F_{\text{v,i}} A_i \exp\left(\frac{E_{\text{a,i}}}{RT_{\text{b,i}}}\left(1 - \frac{T_{\text{b,i}}}{T}\right)\right)(1 - \alpha_i)^{n_i}\alpha_i^{m_i} + \varepsilon_{\text{BL}} \tag{5}$$

where α is the extent of reaction (–), A is the pre-exponential factor (s^{-1}), E_a is the activation energy (kJ mol^{-1}), R is the universal gas constant (kJ mol^{-1}K^{-1}), T_b is the base temperature of the peak (K), T is the temperature (K), n and m are fitted exponent parameters (–), and F_v is a contribution term (–) which represents the relative contribution of each thermal event (at full conversion) to the overall signal.

Whilst this truncated form of the Sestak-Berggren equation can represent a range of solid-state reactions [25–27], it should not be viewed as a general model for all possible mechanisms [28]. This methodology is also based on the assumption of independent thermal events. There may be cases which contain energetically similar sequential reactions or competing reactions [27, 29], for which this model would not be suitable.

This empirical kinetic model is used in this work to demonstrate the incorporation of the formal baseline into a regression, and the use of Akaike weights. The choice of a kinetic model would not impact the baseline correction methodology described in this paper; the modified Sestak-Berggren equation could be replaced with any other kinetic model.

Data are regressed with each of the four candidate formal baseline models. Akaike weights [13], which are based on the Akaike information criterion (AIC) [30], can be applied to discriminate candidate baseline correction methods in this work. Akaike information criteria assumes that model errors are independent and normally distributed. The use of time-series data means the difference in AIC or Akaike weights for models would be overestimated, hence these values should be used qualitatively.

Eq. (6) shows a specific case of the corrected second-order AIC, for least squares regression [31]. The second term $\left(\frac{2K(K+1)}{\sigma - K - 1}\right)$ is only necessary for small sample sizes (when $\sigma/K < 40$). Eqs. (7) and (8) display the method for calculating the Akaike weights. The most statistically likely model is represented by the smallest value of AICc and the highest value of Akaike weights.

$$\text{AICc} = \sigma\ln\left(\frac{\text{RSS}}{\sigma}\right) + 2K + \frac{2K(K+1)}{\sigma - K - 1} \tag{6}$$

$$\Delta_j = \text{AICc}_j - \text{AICc}_{\min} \tag{7}$$

$$w_j = \frac{\exp\left(-\frac{\Delta_j}{2}\right)}{\sum_{s=1}^{S} \exp\left(-\frac{\Delta_s}{2}\right)} \tag{8}$$

where σ is the number of data points, K is the number of estimable parameters (which is the number of explicit parameters in the model plus the variance of the error), and RSS represents the residual sum of squares. Δ_j is the difference in the

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1) List of symbols at the end of the paper.

calculated AICc value for the model and the most statistically likely model (that with the smallest value of AICc), $AICc_{min}$ is the AICc of the most statistically likely model, i.e., the smallest value of AICc, and w_j is the Akaike weight.

This Akaike weights methodology incorporates the closeness of model fit through the RSS value and the number of estimated parameters in a model (K). This avoids the selection of overparametrized models. Tab. 1 displays a theoretical case of two models A and B, which have the same RSS value and number of datapoints but differ in the number of parameters estimated.

Table 1. Comparison of Akaike weights for theoretical models.

Metric	Model A	Model B
Number of parameters	9	11
RSS	6.79×10^{-6}	6.79×10^{-6}
σ	3910	3910
aicc	$-78\,852$	$-78\,848$
Δj	0.00	4.02
w_j	0.88	0.12

Even though both models in Tab. 1 would provide a good closeness of fit, reflected in the RSS value, model A with the lower number of estimated parameters has a clear majority share of the Akaike weights. This emphasizes the need to justify the addition of parameters to a model.

3   Experimental

3.1   In Silico Data Generation

To verify the models added to the Athena Visual Studio script, an in silico study was carried out. The benefit to this kind of modeling study is that the internal consistency of a model can be confirmed, as the correct values for the parameter estimates are known prior to modeling. Four in silico datasets were produced, one for each baseline correction method.

For each dataset, five dimensionless temperature ramp rates are simulated (2, 4, 6, 8, 10 K min^{-1}) [11]. For the single-peak system, the temperature ramp was between 315 and 700 K, and for the multipeak system between 315 and 1273 K. A 15-min temperature hold was simulated at the end of the temperature ramp to establish the end point for the baseline. Tabs. 2 and 3 show the kinetic parameters used to produce the "no baseline added" dataset, for the single-peak and multipeak datasets, respectively. For the single-peak case, the base temperature was 420 K. For the multipeak case, the base temperature values for the low and high temperature peaks were 420 K and 700 K, respectively.

The parameters used to generate the in silico baselines are indicated in Tab. 4. These values were used for both the single- and multipeak datasets.

Example curves with the simulated baselines added are illustrated in Figs. 2 and 3 for single- and multipeak cases, respective-

Table 2. Kinetic parameters for in silico data generation, single-peak dataset.

Parameter	Expected value
A_1 [s^{-1}]	2.23×10^9
$E_{a,1}$ [kJ mol^{-1}]	4.02×10^1
n_1 [–]	1.00×10^0
m_1 [–]	0.00×10^0
$F_{v,1}$ [–]	1.00×10^0

Table 3. Kinetic parameters for in silico data generation, multi-peak dataset.

Parameter	Expected value
Low-temperature peak	
A_1 [s^{-1}]	2.23×10^9
$E_{a,1}$ [kJ mol^{-1}]	4.02×10^1
n_1 [–]	8.07×10^{-1}
m_1 [–]	5.15×10^{-1}
$F_{v,1}$ [–]	6.00×10^{-1}
High-temperature peak	
A_2 [s^{-1}]	1.01×10^{16}
$E_{a,2}$ [kJ mol^{-1}]	1.47×10^2
n_2 [–]	0.93×10^{-1}
m_2 [–]	-1.01×10^0
$F_{v,2}$ [–]	4.00×10^{-1}

Table 4. Parameters used to generate simulated baselines.

Known baseline model	Parameter	
No baseline correction	Gradient	0.0000
	Intercept	0.0000
Linear with time	Gradient	0.2000
	Intercept	0.0000
Linear with temperature	Gradient	0.0008
	Intercept	-2.6624
Linear with extent of reaction	Gradient	0.3000
	Intercept	0.0000

ly. The figures demonstrate how similar these types of baselines can be, thus determining the correct baseline correction method by eye can be difficult. A rigorous statistical method should be applied when selecting a baseline correction technique.

When baseline correcting thermal analysis data, only a single curve would be present compared to the four shown in Figs. 2 and 3. To reliably recognize the shape of an individual baseline
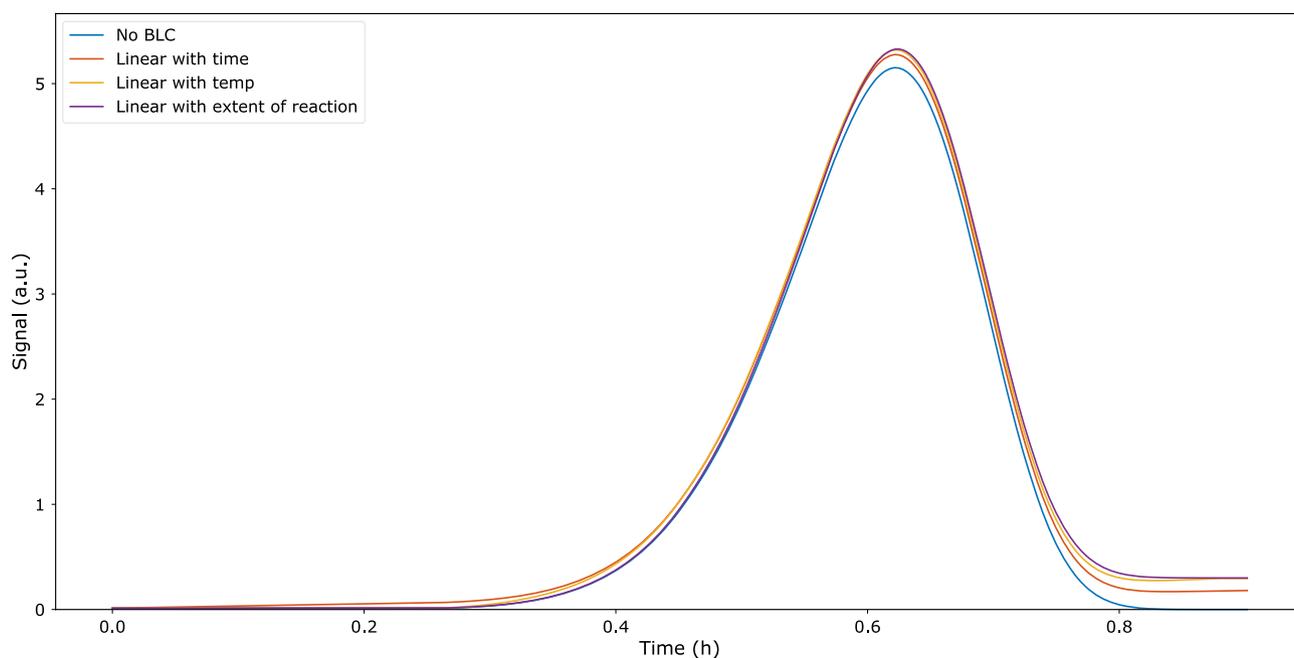
Figure 2. Single-peak $10\,\mathrm{K\,min^{-1}}$ in silico dataset with no baseline added, linear with time baseline added, linear with temperature baseline added, and linear with extent of reaction baseline added.
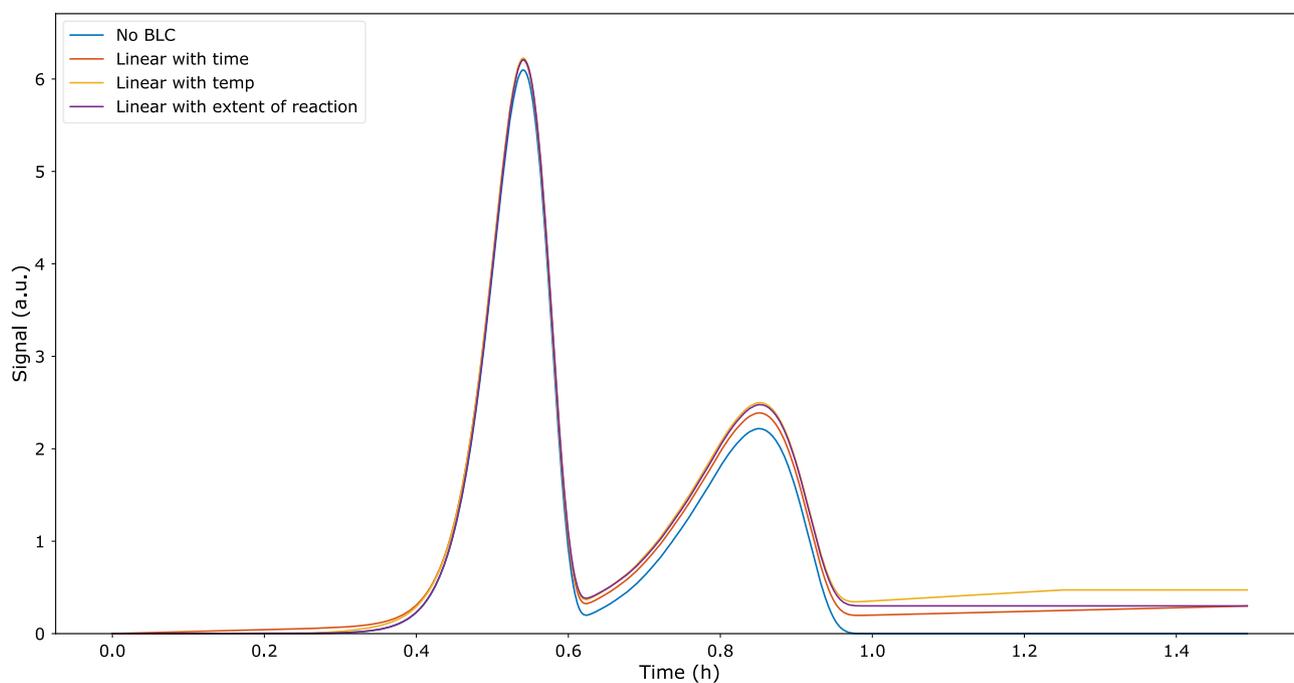
Figure 3. Multiple peak $10\,\mathrm{K\,min^{-1}}$ in silico dataset with no baseline added, linear with time baseline added, linear with temperature baseline added, and linear with extent of reaction baseline added.

by looking at a single curve is difficult, even with significant experience. Removing this experiential factor from baseline correction is one of the key aims of this work.

3.2 Mass Spectrometry Case Study

3.2.1 Material

The $Zn(NO_3)_2/Al_2O_3$ model catalyst precursor was prepared using incipient wetness impregnation, with a notional zinc

loading of 10 wt %, assuming the decomposed oxidized state, i.e., ZnO/Al_2O_3. Alumina (Sasol SCCA 100/100, 18.01 g) was combined with a solution of zinc nitrate hexahydrate (Alfa Aesar, 9.11 g) in water (6.0 mL) and mixed in a Speedmixer at 2000 rpm for 30 s. The material was dried in air at 378 K for 35 min.

3.2.2 Thermogravimetric Analysis

Thermal analyses were conducted in a Netzsch Jupiter STA 449 F3 TGA/DSC unit, coupled with a Netzsch Aëolos QMS 403 D quadrupolar mass spectrometer. The mass spectrometer was programmed to operate in multiple ion detection (MID) mode, in which specified mass-charge ratios are followed with time. Mass-charge signals for 18, 30, and 46 were of interest in this study, and results for m/z 30 are discussed below.

Seven temperature ramp rate experiments were carried out, in a random order, heating between 313 and 1273 K at 8, 10, 12, 14, 16, 18, and 20 K min^{-1}. The sample mass was 20.9 ± 0.5 mg for each experiment and a flow rate of 20 mL min^{-1} of air (under standard conditions) was used. The ramp rates and gas flow rates were chosen in the interests of maximizing the signal-to-noise ratio of the resultant data and minimizing the buoyancy effects on the TG signal.

Although both TG and MS data are simultaneously gathered, these two data types represent the experiment at different points of time and space. This is due to a lag between the thermal event occurring captured by the TG data and the gathering of the volatiles captured by the MS data. Due to this lag and the different measurement techniques, it would not be expected that the two datasets would experience the same baseline drift. The MS data has been selected to highlight the application of the formal baseline correction technique.

4 Results and Discussion

4.1 In Silico Case Study

For the in silico datasets, the values for the baseline gradient and intercept are known prior to carrying out the modeling.

The models can thus be checked for internal consistency and for a single global solution by comparing parameter estimation results to the input values. Tab. 5 indicates that for each dataset with an in silico baseline added (linear with time, temperature, and extent of reaction) the correct input values are obtained through the parameter estimation regression for both single- and multipeak cases. This means that the models for each baseline correction are internally consistent and achieve global minima values.

When faced with experimental data that shows a baseline drift, the source of this drift is not always clear, hence the best method of baseline correction may not be known. For each in silico dataset, all four correction methods have been regressed. Akaike weights have been used to compare the results from these four methods and establish which technique is the most statistically significant.

Tabs. 6 and 7 show, for a single-peak and multiple-peak case, respectively, the comparison of fits using the four baseline correction methods on each of the four datasets. It should be noted that RSS and Akaike weight are only comparable within the same dataset.

Tab. 6 emphasizes that even when models achieve the same closeness of fit (reflected in the RSS value), the Akaike weights will select the model with fewest parameters. This should avoid overfitting.

The discrepancies between RSS values for the "no drift added" case (Tab. 7) are caused by the parameter tolerances for M and C in the linear baseline correction methods, as these parameters are attempting to converge to zero in this case.

The results of the Akaike weights comparison show that for each dataset the correct method was identified as the most statistically probable (the largest Akaike weight), often giving a considerably better fit shown by the lowest values for RSS. This has been established for both single-peak and multiple-peak systems.

This methodology can thus be used to identify the most statistically likely baseline correction methodology, including whether a correction is required or not. This should be used for experimental data when the best baseline correction method is not known prior to modeling.

Table 5. Parameter estimation results, in silico data.

Method for baseline addition	Correction method	Parameter	Input value	Single peak		Multiple peaks	
				Estimate	95 % confidence interval	Estimate	95 % confidence interval
Linear with time	Linear with time	M	2.0×10^{-1}	2.0×10^{-1}	4.1×10^{-6}	2.0×10^{-1}	2.3×10^{-6}
		C	0.0×10^{0}	1.6×10^{-6}	4.6×10^{-6}	3.0×10^{-6}	5.9×10^{-6}
Linear with temperature	Linear with temperature	M	8.0×10^{-4}	8.0×10^{-4}	2.1×10^{-8}	8.0×10^{-4}	5.5×10^{-8}
		C	-2.7×10^{-1}	-2.7×10^{-1}	1.0×10^{-5}	-2.7×10^{-1}	3.6×10^{-5}
Linear with extent of reaction	Linear with extent of reaction	M	3.0×10^{-1}	3.0×10^{-1}	3.5×10^{-5}	3.0×10^{-1}	2.5×10^{-5}
		C	0.0×10^{0}	2.9×10^{-4}	2.2×10^{-5}	2.8×10^{-4}	1.9×10^{-5}

Table 6. Comparison of Akaike weights, in silico data, single peak, $\sigma = 2402$.

Dataset	Metric	No baseline correction method	Linear with time method	Linear with temperature method	Linear with alpha method
No drift added	RSS	5.75×10^{-7}	5.75×10^{-7}	5.75×10^{-7}	5.75×10^{-7}
	Akaike weight	0.70	0.10	0.10	0.10
Drift with time added	RSS	7.38×10^{0}	8.35×10^{-7}	1.41×10^{0}	1.08×10^{0}
	Akaike weight	0.0	1.0	0.0	0.0
Drift with temperature added	RSS	3.37×10^{0}	5.58×10^{-1}	5.92×10^{-7}	6.66×10^{-2}
	Akaike weight	0.0	0.0	1.0	0.0
Drift with alpha added	RSS	4.21×10^{0}	2.01×10^{2}	5.56×10^{-1}	2.15×10^{-5}
	Akaike weight	0.0	0.0	0.0	1.0

Table 7. Comparison of Akaike weights, in silico data, multiple peaks, $\sigma = 3899$.

Dataset	Metric	No baseline correction method	Linear with time method	Linear with temperature method	Linear with alpha method
No drift added	RSS	1.22×10^{-4}	1.25×10^{-4}	1.24×10^{-4}	1.25×10^{-4}
	Akaike weight	1.0	0.0	0.0	0.0
Drift with time added	RSS	4.39×10^{3}	1.95×10^{-4}	5.44×10^{2}	5.53×10^{2}
	Akaike weight	0.0	1.0	0.0	0.0
Drift with temperature added	RSS	1.27×10^{3}	1.38×10^{2}	1.84×10^{-3}	4.68×10^{1}
	Akaike weight	0.0	0.0	1.0	0.0
Drift with alpha added	RSS	8.19×10^{2}	2.09×10^{1}	6.50×10^{1}	1.44×10^{-3}
	Akaike weight	0.0	0.0	0.0	1.0

4.2 Impact of Incorrect Method

The accuracy of the rate determined through kinetic analysis can be negatively affected by the inaccuracy of the baseline determined [4]. Hemminger and Sarge [5] recommend a linear baseline correction with respect to time unless additional information is known. These authors found that when using an "incorrect" baseline, the relative error of the enthalpy of melting could be as high as 3.2 %, when compared to the exponential baseline correction function, which was taken as the "true" function. This is outside the repeatability range of the instrument used and can greatly impact the kinetic information extracted from the data.

With the in silico data used in this study the parameters for the kinetic modeling are also known, so the impact of correcting a baseline drift with the incorrect method can be determined. Tab. 8 shows the percentage errors achieved when using the incorrect baseline methods for each dataset. The table focuses on the activation energy parameter for simplicity; however, similar results are obtained for all the parameters used in the modified Sestak-Berggren model.

Tab. 8 indicates that errors of up to 8.33 % can be obtained when using the wrong baseline correction technique. This means selecting the wrong correction method could impact the kinetic parameters estimated severely. These errors in activation energy cannot be detected visually when interrogating quality of fit graphically. This reinforces the need to consider all four baseline correction methods and to have a rigorous statistical method to select the most suitable.

The use of this Akaike weights method would remove the experiential element which is currently associated with baseline correction in thermal analysis data. In some cases, such as the single peak linear with extent of reaction dataset, when different baseline correction methods are applied multiple could appear feasible, shown in Fig. 4.

Whilst in this case the no baseline correction may appear to be "obviously" wrong, the linear with time baseline correction could be plausible for this system. If selected, this linear with time baseline correction would still result in an error of ∼5 % on the activation energy estimated. This Akaike weights method comparing multiple baseline correction options would allow even novice thermal analysis users to interpret data in a rigorous manner, accounting for the possibility of baseline drift. This comparison of baseline correction methods should be applied consistently to thermal analysis data, even in case which appear "obvious" to avoid bias fittings.

Table 8. Errors due to wrong baseline correction method.

Dataset			No baseline correction method	Linear with time method	Linear with temp. method	Linear with alpha method
Single peak	Drift with time added	$E_{a,1}$	6.19 %	–	2.46 %	–3.09 %
	Drift with temperature added	$E_{a,1}$	3.14 %	0.39 %	–	–3.84 %
	Drift with extent of reaction added	$E_{a,1}$	8.33 %	4.78 %	Failed	–
Multiple peaks	Drift with time added	$E_{a,1}$	1.37 %	–	0.82 %	–3.76 %
		$E_{a,2}$	5.55 %	–	7.70 %	–1.99 %
	Drift with temperature added	$E_{a,1}$	0.68 %	–0.03 %	–	–2.57%
		$E_{a,2}$	4.37 %	0.18 %	–	–3.36 %
	Drift with extent of reaction added	$E_{a,1}$	2.32 %	2.00 %	2.05 %	–
		$E_{a,2}$	4.16 %	4.04 %	6.12 %	–
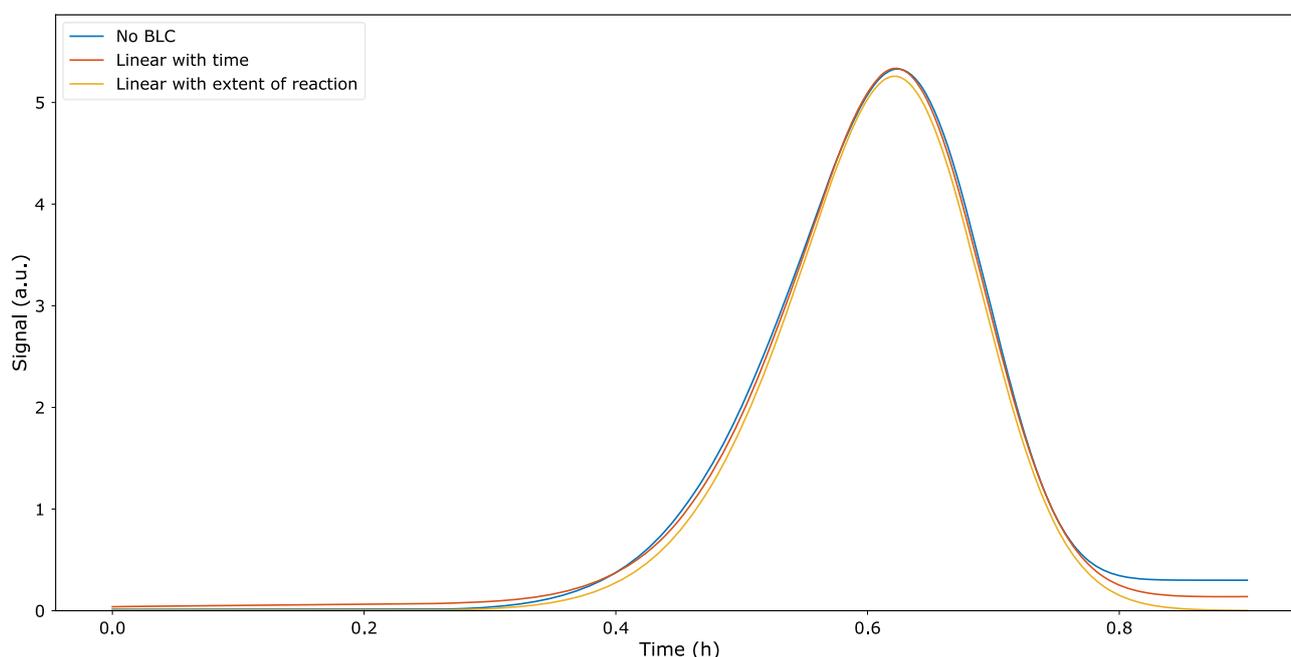
Figure 4. Baseline correction of single peak, drift with extent of reaction dataset, 10 K min^{-1} examples.

4.3 Experimental Mass Spectrometry Study

This section aims to present and discuss experimental data. The raw experimental data for m/z 30 are presented in Fig. 5.

The four baseline correction methods outlined above were considered for this mass spectrometry data. Akaike weights were used to identify which method was the most statistically likely, presented in Tab. 9.

When the linear with extent of reaction baseline correction method was selected, not all kinetic parameters required were estimated. This could be due to the strong correlation between the parameters. This means this model was poor and has been discounted from the Akaike weights comparison, as Akaike weights should only be used to discriminate good-quality mod-

els [13]. Since this is a simple example of baseline drift, it implies this linear with alpha baseline correction method may also fail when used in more complex cases.

For this data, the most appropriate baseline correction method was linear with temperature. This was used for all temperature ramp rate experiments (seven in total) and resulted in a good fit, with R^2 of 0.994 and an RSS of 24.40.

Tab. 10 shows the baseline gradient and intercept estimated for this data, with Fig. 6 illustrating an example of the baseline and overall curve fit using the modified Sestak-Berggren equation [11].

This example demonstrates that Akaike weights can be used to identify the most statistically likely formal baseline correction method for experimental thermal analysis data. This
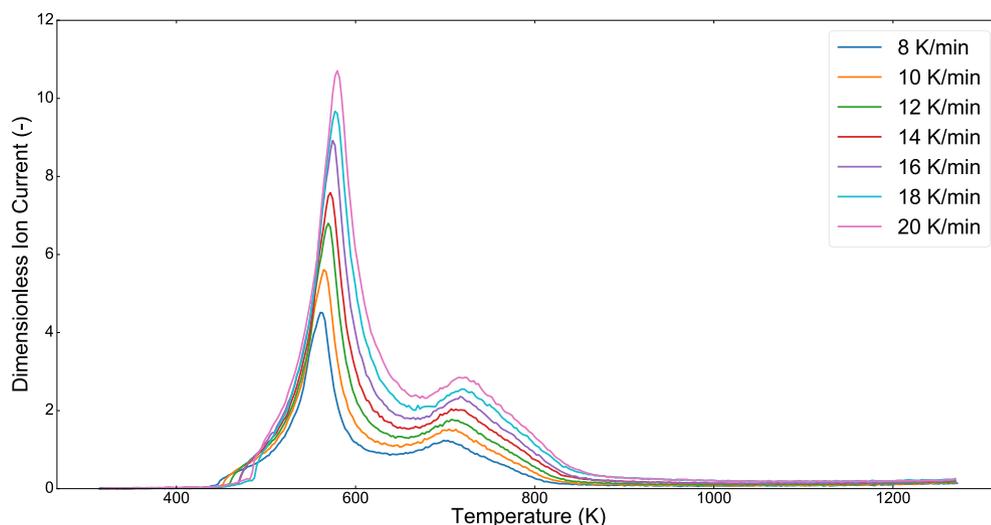
Figure 5. Mass spectrometry data for *m/z* 30.

Table 9. Comparison of Akaike weights, MS data.

Dataset	No baseline correction method	Linear with time method	Linear with temperature method	Linear with alpha method
RSS	3.05×10^{1}	3.56×10^{2}	2.44×10^{1}	$2.23 \ 10^{1}$
Akaike weight	0.0	0.0	1.0	Discounted

Table 10. Parameter estimation results.

Parameter	Estimate	95 % confidence interval	Coefficient of variation
BL gradient	0.04	9.49×10^{-3}	1.10×10^{-1}
BL intercept	0.02	7.57×10^{-3}	2.23×10^{-1}

methodology should be applied to all modeling of thermal analysis data as this has a rigorous statistical basis for the cor-rection method selection which importantly includes the possibility that no baseline correction is necessary.

5 Conclusions

This work has highlighted the importance of selecting a suitable baseline correction method for thermal analysis data. To remove the human/experiential factor which can be associated with this preprocessing step, this work has recommended the
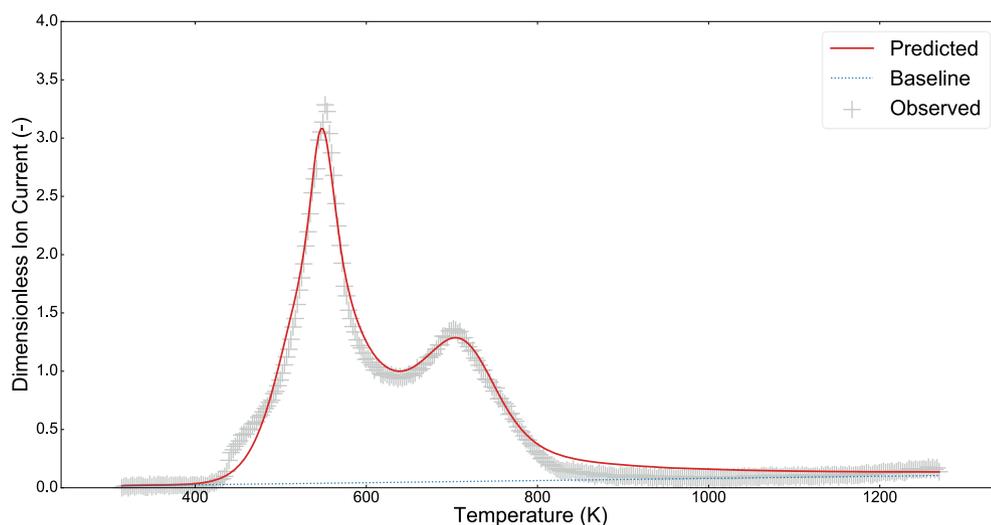

Figure 6. Example of predicted baseline, 8 K min^{-1} experiment. Predicted refers to the estimated Sestak-Berggren model prediction for a three-thermal event system [32].

use of a statistical basis for the choice of baseline correction, Akaike weights.

Formal baseline correction methods should only be applied in the absence of a justifiable physiochemical or experimental baseline correction method. This work does not deconvolute thermal events or baseline drift prior to kinetic modeling, instead an overall baseline is accounted for.

This in silico case study illustrated that the choice of baseline correction can have a significant impact on the kinetic parameters estimated and that the correction method used may be selected using Akaike weights comparison of four formal baseline correction methods, i.e., no baseline correction, linear with time, linear with temperature, and linear with extent of reaction. Once selected, the same baseline correction method should be applied across different ramp rate experiments for a single dataset.

An experimental case study of mass spectrometry data demonstrated the applicability of these baseline correction methods and Akaike weight comparison for a real system. The Akaike weights comparison indicated that a baseline which was linear with temperature was the most statistically likely. This baseline correction was applied to all ramp rate experiments and results in a good fit for the experimental data once the modified Sestak-Berggren model had been applied.

This paper has outlined a procedure to select the appropriate baseline correction method using Akaike weights, with formal baseline correction methods as examples. However, this selection technique is based on information theory and could be applied to any baseline correction method, including those with a physical basis. The modified Sestak-Berggren equation has been used to exemplify the coupling of the baseline correction methods with a kinetic model. This kinetic model could also be replaced with a model more suitable for a specific system.

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Symbols used

A	[s^{-1}]	pre-exponential factor
C	[various]	y-intercept of baseline function
E_a	[kJ mol^{-1}]	activation energy
F_v	[–]	contribution term
Δj	[–]	difference in calculated AICc value for the model and the most statistically likely model
K	[–]	number of parameters
m	[–]	Sestak-Berggren exponent
M	[various]	gradient of baseline function
n	[–]	Sestak-Berggren exponent
n_{events}	[–]	number of thermal events
R	[kJ kmol^{-1}K^{-1}]	universal gas constant
t	[s]	time
T	[K]	temperature
w	[–]	Akaike weight

Greek letters

α	[–]	extent of reaction
ε_{BL}	[various]	baseline function
σ	[–]	number of datapoints

Subscripts

1	first thermal event
2	second thermal event
b	base
i	thermal event
j	model
min	minimum

Abbreviations

AICc	corrected Akaike information criteria
DSC	differential scanning calorimetry
m/z	mass to charge
MS	mass spectroscopy
RSS	residual sum of squares
TCD	thermal conductivity detector
TGA	thermogravimetric analysis
TPD	temperature-programmed desorption
TPR	temperature-programmed reduction

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Research Article: Recommendations for formal baseline correction methods for thermal analysis data are given. When lacking physical or experimental justification, only linear baseline correction methods should be used, i.e., linear with time, linear with temperature, and linear with extent of reaction. The absence of baseline correction should also be considered. In silico and experimental data are demonstrated.

Selection of Formal Baseline Correction Methods in Thermal Analysis

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