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Analysis of bake-out monitoring data

TEC-QTE: Materials Space Evaluation & Radiation Effects Section

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1 INTRODUCTION

Many components of a spacecraft (SC) require a bake-out in thermal vacuum (TV) in order to reduce the risk of contamination of the SC. The effectiveness of a bake-out in reducing the contamination levels of the SC depends on many factors, such as the temperature and duration of the bake-out vs. the temperature and duration of the mission, geometry (view factor of contaminants with sensitive surfaces) and the outgassing characteristics of all materials present.

The bake-out temperature is often restricted by the maximum safe temperature of the hardware, or maximum temperature of the bake-out facility. Given a certain bake-out temperature, the effectiveness of the bake-out depends on the duration. As a general rule, the outgassing rate of volatile species during a bake-out is initially fast but decreasing over time. Moreover, the decrease in the rate of the outgassing itself tends to decrease over time, and the outgassing eventually becomes virtually linear in time. At this point further bake-out would not significantly reduce the outgassing rate under in-orbit conditions. Considering the cost associated with performing a vacuum bake-out of flight items, it is desirable to keep the bake-out duration to the minimum while still guaranteeing its effectiveness through a “best effort” approach. That is, the duration, and hence the stopping criterion of the bake-out, should be such that the bake-out removes the majority of the species that are volatile at the bake-out temperature but avoid going into the regime of diminishing returns.

Bake-out monitoring using a quartz crystal microbalance (QCM) is already quite common and included as a requirement by ESA when the criticality of the mission justifies it. The frequency of the QCM relates directly to the amount of deposition on the sensor, which in turns is related to the outgassing of the hardware. The outgassing from the hardware can thus be monitored continuously.

This TN describes how to use the QCM data to assess the effectiveness of the bake-out at a given bake-out temperature. Different stopping criteria that use QCM data already exist, e.g. requiring that a certain frequency rate or a certain rate reduction is reached. These methods are either arbitrary and/or facility dependent. For instance, a rate reduction requirement would lead to different results depending on the heating rate of the hardware.
The method described in this TN uses a physical model of the outgassing kinetics to derive a stopping criterion that depends only on the particular characteristics of the outgassing species. It thus ensures that a “best effort” bake-out is obtained at the chosen bake-out temperature.

It is important to note that although with this method it is possible to assess the effectiveness of the bake-out process, in order to assess the overall effectiveness of the bake-out with respect to the contamination requirements a system-level contamination analysis is required. This is typically discussed on a case-by-case basis and is outside the scope of this TN.

2 DOCUMENTS AND ABBREVIATIONS

2.1 Applicable Documents

AD1	ECSS-Q-TM-70-o1C	Cleanliness and contamination control

2.2 Reference Documents

2.3 Abbreviations

ESA	European Space Agency
ESTEC	European Space Research and Technology Centre
MOC	Molecular Organic Contamination
MPCB	Materials and Processes Control Board
PRT	Platinum Resistance Thermometer
QCM	Quartz Crystal Microbalance
r.m.s.	Root mean square
SC	Spacecraft
TEC-QTE	Materials Space Evaluation & Radiation Effects Section
TN	Technical Note
TV	Thermal Vacuum

2.4 List of symbols

Symbol	Description	Unit/value
a_i	Contribution of species i to the outgassing characteristic as measured with a QCM	Hz
f	Frequency of a QCM	Hz
F_q	View factor of a QCM with the hardware	cm^2
K_s	QCM mass sensitivity factor	$1.96 \cdot 10^{-9}$ $g \cdot cm^{-2} \cdot Hz^{-1}$
Q_i	Activation energy for desorption of species i	$kJ \cdot mol^{-1}$
R	Gas constant	8.31441 $J \cdot mol^{-1} \cdot °C^{-1}$
t	Time	h
T	Temperature	°C
T_{QCM}	Temperature of the QCM sensor	°C
t_s	Start time of the curve-fit time interval	°C
x	Numerical value of the deviation from linearity	
$\langle T \rangle$	Average temperature	
δT	r.m.s temperature variation	
ζ	Total deviation from linearity	%

ζ'	Deviation from linearity	%/h
τ_i	Time constant of species i at temperature T	h
Δf	Frequency change of a QCM	Hz
$\tau_{o,i}$	Pre-exponential factor	h
τ_{app}	Apparent residence time	h

3 METHODOLOGY

The outgassing from a material can usually be described with first order desorption kinetics. During isothermal TV bake-out, the outgassing characteristic is then given by a sum of exponential decay functions:

$$f(t) = \sum_i a_i \cdot \left(1 - e^{-t/\tau_i}\right) \quad , \tag{1}$$

where $f(t)$ is the outgassing characteristic that is being monitored, *e.g.* the frequency of a QCM kept at a certain temperature. a_i gives the contribution of species i to the total outgassing characteristic, t is time and τ_i the residence time of outgassing species i. A single material can have many outgassing species, although at any given time only a few may be dominant. However, since flight hardware generally contains many different types of outgassing materials, the number of outgassing species can be very large at any given point in time.

A QCM cannot discriminate the different outgassing species and treats the outgassing from the hardware as a black box instead. However, Eq. (1) is still a useful way to describe the outgassing in a phenomenological way, as its mathematical properties match the physical properties of the outgassing process. That is, it is a continuously increasing function with a continuously decreasing rate and decreasing higher order derivatives.

From Eq. (1) it follows that the outgassing rate $f'(t)$ is given by

$$f'(t) = \sum_i \frac{a_i}{\tau_i} \cdot e^{-t/\tau_i} \tag{2}$$

and the change of the rate is given by

$$f''(t) = -\sum_i \frac{a_i}{\tau_i^2} \cdot e^{-t/\tau_i} \tag{3}$$

In practice, the outgassing characteristic of flight hardware eventually appears linear in time, *i.e.* the rate becomes near constant. The linear and non-linear part of the outgassing characteristic can be separated using a Taylor expansion of the outgassing rate $f'(t)$:

$$f'(t+\Delta t) = f'(t) + f''(t)\cdot \Delta t + \ldots \quad . \tag{4}$$

The higher order terms can be safely ignored since we are interested in the bake-out time at which the deviation from linearity becomes small. Inserting Eq. (2) and Eq.(3) into Eq. (4) we get:

$$f'(t+\Delta t) = \sum_i \frac{a_i}{\tau_i}\cdot e^{-t/\tau_i} - \Delta t \cdot \sum_i \frac{a_i}{\tau_i^2}\cdot e^{-t/\tau_i} \; . \tag{5}$$

We can define the total deviation from linearity ζ as:

$$\zeta = \left|\frac{f''(t)}{f'(t)}\right| \cdot \Delta t \qquad , \tag{6}$$

or, the deviation from linearity per unit of time ζ' (hereafter referred to as simply the deviation from linearity):

$$\zeta' = \left|\frac{f''(t)}{f'(t)}\right| = \frac{\sum_i \frac{a_i}{\tau_i^2}\cdot e^{-t/\tau_i}}{\sum_i \frac{a_i}{\tau_i}\cdot e^{-t/\tau_i}} \quad . \tag{7}$$

The inverse of ζ' is also a useful quantity which we define as the apparent residence time τ_{app} according to

$$\tau_{app} = \frac{1}{\zeta'} = \left|\frac{f'(t)}{f''(t)}\right| \quad . \tag{8}$$

The apparent residence τ_{app} can be considered as a weighted average residence time of all species outgassing after a time t.

The deviation from linearity or the apparent residence time are convenient quantities on which to base the stopping criterion for bake-outs. Regardless of the actual distribution of the outgassing species and their individual temperature dependence, at any given bake-out temperature the most volatile species will always outgas first until their contribution becomes negligible compared to species with higher residence times. As follows from Eq. (1), for a single species i with residence time τ_i, the reservoir of species i after t= τ_i is just 37 % of the initial amount present. At $t = 3\tau_i$ this has decreased to just 5 % of the original, and less than 1% after t=5τ_i. Thus, over time, the contribution of the most volatile species (smallest τ_i) decreases. As a result the apparent residence time will increase and the deviation from linearity decreases. The time at which a deviation from linearity of less than x %/hour (or $\tau_{app} > 100/x$ hours) is reached *does* depend on the distribution of outgassing species after a certain bake-out time. It does *not* depend on the total amount of outgassing mass from the hardware nor on the heating rate of the facility, since the analysis is valid only for the isothermal part of the bake-out. Setting a stopping criterion below a deviation from linearity of x %/hour thus ensures that a “best effort” has been reached.

The value at which the stopping criterion is set can be decided on a case-by-case basis, depending on the expected efficiency of the bake-out temperature w.r.t. the nominal flight temperature, with a maximum value of 1 %/hour.

- REQUIREMENT 3.a: a value of χ' <= 1 %/hour shall be used

The actual time at which the stopping criterion $\zeta' < x$ %/h ($\tau_{app} > 100/x$ h) is reached will vary depending on the outgassing characteristics of the species involved, but usually this time is somewhere between 0.5×(100/x) hours up to 3×(100/x) hours. However, according to AD1, a minimum bake-out time of 72 hour shall be carried out.

- REQUIREMENT 3.b: This criterion shall not replace minimum bake-out durations as defined by ECSS-Q-ST-70-01C.

The practical implementation of the method requires Eq. (1) to be curve-fitted to the QCM data of the isothermal bake-out phase to avoid interference from *e.g.* temperature fluctuations. The deviation from linearity and/or the apparent residence time can then be calculated from the first and second derivative of the fit-function. The implementation of this will be discussed in section 5. First, in section 4 the basic test requirements with respect to for instance the temperature fluctuations will be discussed in order to understand the implementation method.

4 BASIC TEST REQUIREMENTS

The outgassing characteristics of the hardware during a TV bake-out can be monitored using a QCM. The measurement principle of a QCM is simple; the oscillation frequency of a quartz crystal is being monitored as a function of time. This oscillation frequency depends on the deposited mass on the quartz crystal. Thus the QCM can provide information on the kinetics of the outgassing species cf. Eq. (1), provided that:

1. The QCM is properly installed and operated;
2. The observed frequency change during the hardware test is large enough to avoid artefacts in the measurement while avoiding saturation of the sensor;
3. The bake-out can be considered as isothermal;
4. The temperature fluctuations and temperature drift remain within certain limits;
5. The QCM temperature is constant.

These points will now be discussed in the following sections.

4.1 QCM positioning

The proper installation and operation of the QCM during the bake-out are the responsibility of the technical officer performing the bake-out. The QCM shall be installed in such a way that it provides meaningful results. That is, the observed frequency change should be due mostly to the outgassing signal of the hardware and not the background of the facility. A QCM only produces meaningful results in high vacuum ($p < 10^{-4}$ mbar) and thus QCM monitoring is not an option during bake-out in *e.g.* GN2.

- NOTE 4.1.a: Monitoring of the background of the bake-out facility is required by the ECSS-Q-70-01C by either QCM and/or molecular witnesses. For the analysis method described in this TN it is not required to subtract the QCM signal of the background from the signal of the bake-out.
- REQUIREMENT 4.1.a: If the QCM signal observed during the facility background measurement is more than 50 % of the signal observed during the hardware bake-out during the same period of time as the background measurement, the analysis method described in this TN shall not be used. Instead the bake-out shall be performed for a duration of at least $3 \times 100/x$ hours.

Depending on which type of the QCM is used, the dynamic range of a QCM can be anywhere from a few kHz to a few 100 kHz. The actual observed frequency rate depends on the view factor (VF) of the QCM with the hardware. Ideally, the VF is such that the full range of the QCM is used. If the VF is too small, the observed frequency change may contain artefacts from the temperature dependence of the sensor crystals and/or electronics. These artefacts are typically of the order of a few Hz, so a sensor signal of 10s of Hz is necessary to avoid that the artefacts become dominant in the analysis. On the other hand, if the VF is too large, the risk is that the sensor saturates within hours making analysis impossible.

- NOTE 4.1.b: In practice bake-out facilities see a range of sample sizes and so a compromise between a typical outgassing sample size and VF has to be found.

4.2 Bake-out temperature considerations

4.2.1 Start of the bake-out

ECSS-Q-70-01C defines the start of the bake-out when the material has reached its pre-defined bake-out temperature. For large items of flight hardware, different parts may heat up at different rates, and reach different steady state temperatures. W.r.t. the analysis method described in Section 5, the bake-out starts when all parts have reached a temperature within 0.5 °C of the steady state temperature, and the system is at high vacuum.

- NOTE 4.2.1.a: the existence of temperature gradients over the sample does not affect the analysis. The analysis method treats the outgassing from the hardware as a black box, and having temperature gradients simply means that the same molecular species may be outgassing with a range of residence times, which is indistinguishable from having multiple molecular species with different residence times outgassing.

4.2.2 Temperature fluctuations

Due to the strong temperature dependence of the outgassing rate, fluctuations in the hardware temperature can generate changes in the outgassing rate that obscure the reduction in outgassing rate from the outgassing itself. Some temperature fluctuation is in practice however unavoidable. Fast temperature fluctuations, occurring over a duration of seconds to minutes, tend to be caused by fluctuations of the sensor itself and have little effect on the outgassing rate of the hardware as the thermal mass of the hardware dampens them out. However, there is often a temperature variation in the bake-out facility on a much longer time-scale, typically with a period of a day (e.g. day – night cycle on the power supply, room temperature fluctuations on the vacuum chamber wall).

Considering that the temperature dependence of the outgassing rate is usually described by an Arrhenius law, and considering that as a rule of thumb this approximates to a temperature dependence of outgassing of a factor 2 in rate per 10 °C, it follows that fluctuations of just ±1 °C will cause fluctuations in the outgassing rate of about 7 %. If these fluctuations take place in the span of an hour then the thermal fluctuations of 7%/hour may obscure the deviation from linearity of the outgassing rate caused by the outgassing itself. This can be circumvented to a large extend by using Eq. (1) as a trend line over at least 2 periods of the fluctuations. This averages out the fluctuations so that an analysis of the deviation from linearity will show the isothermal rate reduction rather than be dominated by the temperature fluctuations. In practice this means that the curve-fitting of Eq. (1) requires at least 48 hours of isothermal data.

- REQUIREMENT 4.2.2.a: Temperature fluctuations shall have a r.m.s. variation of no more than ±1.0 °C in an hour and no more than ±2.0 °C in a day.
- REQUIREMENT 4.2.2.b: Determining the outgassing change rates directly from the QCM data (e.g. determining Δf every n hours) shall not be done unless the temperature stability is much better than this (r.m.s. variation <=±0.1 °C).
- NOTE 4.2.2.a: the r.m.s. variation in the temperature δT is defined as

$$\delta T = \sqrt{\frac{1}{N}\sum_{j=1}^{N}\left(T_j - \langle T \rangle\right)^2} \quad (9)$$

,

where $\langle T \rangle$ denotes the average temperature.

4.2.3 Temperature stability and drift

Besides temperature fluctuations, the average temperature of the hardware may change during the bake-out, *e.g.* by failing heating elements or deliberate changes to the temperature set point. Usually such events tend to have clear demarcations.

- REQUIREMENT 4.2.3.a: Since the analysis of the deviation from linearity requires isothermal data, the analyses shall be restarted at the demarcation point.
- REQUIREMENT 4.2.3.b: A re-evaporation procedure of the QCM shall be performed after a bake-out temperature change (see Section 4.3.2), and after each occurrence the timer on the 48 hours of data requirement for the analysis shall be re-started.

Temperature drift, that is, a gradual systematic change in temperature over time is very detrimental to the analysis. If the temperature is gradually decreasing then the deviation from linearity criterion may not be reached at all as the outgassing rate continues to decrease, but this increase is then due to the lowering temperature rather than due to the decrease in rate over time. Alternatively, if the temperature is gradually increasing the temperature induced increase in outgassing rate may balance the decrease over time, making it appear that the deviation from linearity criterion has been reached when in fact considerable improvement could still be reached.

- REQUIREMENT 4.2.3.c: temperature drift shall not be more than a 1.0 °C change in the average temperature of consecutive 24 hour periods. However, if the drift occurs just once, *e.g.* at the start of the bake-out period but stabilizes later on then the drift period can simply be omitted from the analysis period. If the drift continues across the whole of the bake-out then instead the bake-out shall be performed for a duration of at least $3 \times 100/x$ hours.
- REQUIREMENT 4.2.3.d: for this reason, sample temperature and facility pressure data shall be provided along with the QCM data.
- NOTE 4.2.3.b: temperature drift may also invalidate system level analysis of the bake-out efficiency

4.3 QCM sensor considerations

4.3.1 QCM sensor temperature

Most QCM sensors for MOC monitoring have a reference crystal and a temperature control system to keep the measurement and reference crystal at the same constant temperature. The temperature control is typically performed with a PRT and either a heating element or a Peltier element (which allows control in both cooling and heating). The QCM itself should be attached to a heat sink to remove the heat pumped by the Peltier element. Depending on the quality of the heat sink the range of temperatures the QCM sensor can be maintained at may vary, or change when the facility is being heated to the bake-out temperature. It should be verified prior to the bake-out that the QCM can maintain its chosen set point throughout the bake-out.

- NOTE 4.3.1.a: this verification is usually provided by the facility bake-out or blank prior to the hardware bake-out.

For bake-out monitoring QCM sensor temperatures are typically maintained at temperatures in the range from -50 °C to 0 °C. Since the deposition rate on the QCM depends on the QCM temperature, with low sensor temperatures showing a higher deposition rate than high sensor temperatures, the QCM sensor temperature can be used to modify the QCM signal during the bake-out. If the observed frequency change is too low setting a lower QCM temperature may improve the signal. Likewise, if the frequency rate is too high, a higher sensor temperature may prevent early saturation. However the frequency at which the QCM saturates is itself a function of the sensor temperature. As a general rule, it decreases with increasing sensor temperature. Thus increasing the sensor temperature does not necessarily prevent early saturation.

- REQUIREMENT 4.3.1.a: A QCM sensor temperature change shall always be performed in combination with a re-evaporation procedure (see next Section), and after each occurrence the timer on the 48 hours of data requirement for the analysis shall be re-started..

4.3.2 QCM saturation and re-evaporation

QCM saturation can usually be recognized by a hyperbolic decrease in the frequency followed by sudden loss of frequency signal. A QCM re-evaporation can reset the QCM signal. A saturated QCM can be cleaned by thermal evaporation of the contaminants on the sensor crystal, by temporarily setting the sensor temperature to the maximum temperature before returning to the original (or new) set point. However this procedure may take up to an hour and if the saturation occurs on the same time-scale than it is better to keep the QCM sensor at 80 °C until the outgassing rate has decreased to a level where it can be measured within a reasonable amount of time.

- REQUIREMENT 4.3.2.a: After each re-evaporation procedure the timer on the 48 hours of data requirement for the analysis shall be re-started.
- REQUIREMENT 4.3.2.b: A re-evaporation procedure shall also be performed at the start of the bake-out (see Section 4.2.1) to remove the contaminants deposited on the measurement crystal during previous tests and during the heating up phase.

4.3.3 Re-emission

In principle, the contamination deposited on the QCM crystal during the early stages of the bake-out can have a non-negligible re-emission rate in the later stages of the bake-out. In rare cases, the re-emission rate of the contamination collected early during the bake-out can be even larger than the deposition rate of the contamination, resulting in a net decrease of the QCM frequency. In such a case, a re-evaporation of the sensor will restore the proper collection of contamination by removing all of the initial contamination.

5 IMPLEMENTATION OF THE METHOD

In this section the implementation of the method will be discussed using example data taken from a real sample bake-out. While the numbers will change on a case-by-case basis, the example discussed here shows the basics of the implementation.

5.1 Data treatment

Figure 1 shows an example of a bake-out monitoring data (QCM frequency, facility pressure, QCM sensor temperature and sample temperature). The data shown in Figure 1 are raw data which includes the pre-test phase (pumping down, cooling the cryo-panels and heating the sample). As can be seen in the graphs the bake-out phase itself starts at about 2.5 h. Due to a slight overshoot in the sample temperature (note: the overshoot was deliberate to speed up the heating, the thermal mass of the sample dampened out most of the overshoot), the analysis of the data was started after 5 h. From this point onward the bake-out is isothermal (in this case: temperature fluctuations are less than 0.1 °C, with a temperature drift less than 0.5 °C during the 122 h period of the bake-out).

To prepare the data for the fitting procedure described in the next Sections it is advisable to re-zero the QCM frequency change and the time at the start time of the analysis, t_s ($t_s = 5$ h in this case) as follows. The frequency change Δf is calculated as $\Delta f(t) = f(t) - f(t{=}t_s)$ and the time is replaced by $t' = t - t_s$.

- NOTE 5.1.a: re-zeroing the data before the fitting procedure is a matter of convenience. The data can either be re-zeroed, or else t_s and $f(t_s)$ have to be supplied to the fitting function itself.
- NOTE 5.1.b: In principle the choice of t_s makes little difference for the procedure, provided there is at least 48 h of isothermal bake-out time remaining for curve fitting. However it is advisable to use data from the full isothermal bake-out duration as this will make the convergence of the fit easier.

5.2 Fitting strategy

5.2.1 Fit function

As mentioned before, at any given time during the bake-out there can be just a few dominant species, or a wide distribution of species with different residence times. A fitting procedure of Eq. (1) to the bake-out data can never discriminate the residence times of all the species outgassing. This however is not the purpose of the curve-fitting of Eq. (1). The aim is to provide an accurate description of the measured data in such a way that the first and second derivative can be calculated from the fit-curve, in a way that minimizes systematic fitting errors. A polynomial fit can never satisfy this requirement, as its mathematical properties do not match the physical properties of the outgassing kinetics.
By adding enough terms to Eq. (1), in principle any smooth and continuously increasing function with smooth and continuously decreasing derivatives can be simulated.

In practice, using Eq. (1) with just 4 terms is sufficient to describe bake-out data. This is because, firstly, a fitting procedure of Eq. (1) cannot discriminate residence times that differ by less than a factor of ~4. Secondly, by the time the analysis of the bake-out starts all outgassing species with a residence time significantly smaller than t_s have already been removed. Thus the smallest residence time a fitting procedure can find tends to be of the order of t_s. Thirdly, the largest residence that can be found is limited by the total bake-out time (in practice, the largest residence time is less than 6× the total bake-out time).

With 4 terms, there are 8 adjustable fit parameters, a_i and τ_i.

5.2.2 Fitting method

A general least-squares fitting method is sufficient to obtain a good fit of the data to Eq. (1). A least-squares fitting procedure minimizes the sum of the squared differences χ^2 between the data points f_j and the fit curve y_j at those points:

$$\chi^2 = \sum_j \left(f_j - y_j \right)^2 \quad , \qquad (10)$$

More advanced fitting methods are in practice not necessary with this fit function and will not be discussed here. A least-squares fit can be performed with any data analysis software, or even with a spread sheet program such as Excel. In Annex A an example of a curve fitting procedure with Excel is described.

5.2.3 Fitting procedure

In the example of Figure 1, the fit to Eq. (1) was first performed when 48 hours of isothermal data was obtained (at the 53 hour mark in the graph of (Figure 1). The fit was then repeated for every 24 h afterward, adding the additional data, until such a time that the fit showed that the criterion was reached. In this particular test the criterion was set at having a deviation from linearity of less than 1%/hour, or an apparent residence time of more than 100 h.

Figures 2 to 5 show the data and fit-results at each of these analysis points (after 48 h, 72 h, 96 h and 120 h of isothermal data), as well as the first and second derivative of the fit curve

As can be seen, at each stage the fit-curve is nearly indistinguishable from the QCM data. only when looking into detail, by directly looking at the fit-residue as shown in Figure 6 can the difference between the fit-curve and data be seen.

- NOTE 5.2.3.a: in Figure 6 a clear cycle is visible in the fit-residue, corresponding to a day-night cycle. However as the fit-residues are evenly spread around 0, there is no systematic error in the fit and the day-night cycle has no influence on the results.

In this particular example, the apparent residence time of the outgassing species after 48 h of isothermal bake-out is 76 hours. After 72 h of isothermal bake-out the apparent residence time has barely increased, and is found to be 80 hours. After 96 h of isothermal bake-out the apparent residence time has increased to 92 h, just below the criterion and after 120 h of isothermal bake-out the apparent residence time is 125 h.

While this evolution of the apparent residence time with increasing bake-out time is particular to this example, it illustrates an important point of the method, which is that *the analysis has no predictive power*. The fact that the apparent residence time was already at 76 hours after 48 hours of bake-out cannot be used to assess when the criterion of a 100 h will be met. It may be that the hardware has a dominant species with a residence time somewhat below 100 h (in this particular example, there is a dominant species with a residence time of about 70 h). In that case the apparent residence time may hover around the same value for several days. Or it may be that there is a very even distribution of species with different residence times, in which case the criterion would be reached shortly afterwards. In fact, this illustrates the power of the analysis method to discriminate between the two extremes even though the hardware is treated as a black box, and thus ensure that a “best effort” bake-out is achieved.

6 FIGURES

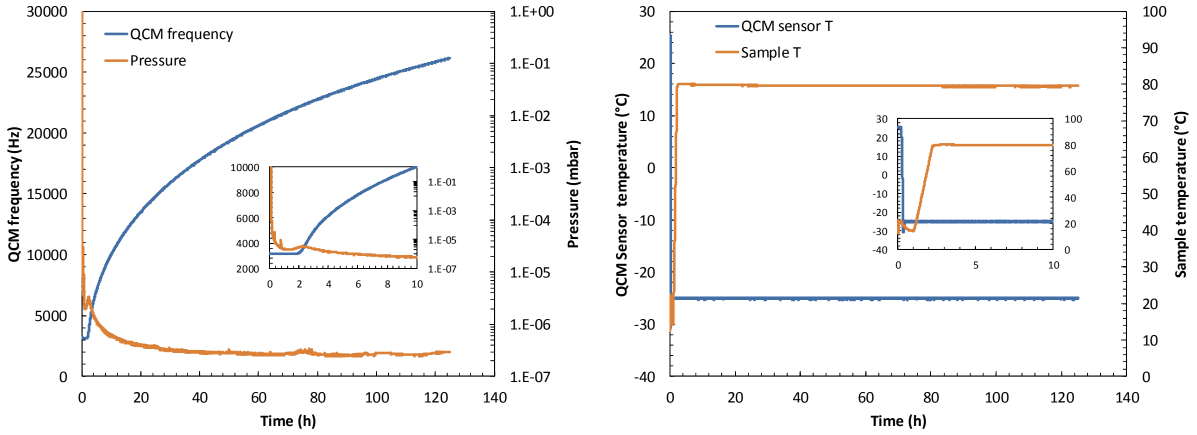


Figure 1: Example of bake-out monitoring data. (left): QCM frequency and facility pressure. (right) QCM sensor temperature and sample temperature. The insets show details of the first 10 hours of the test.

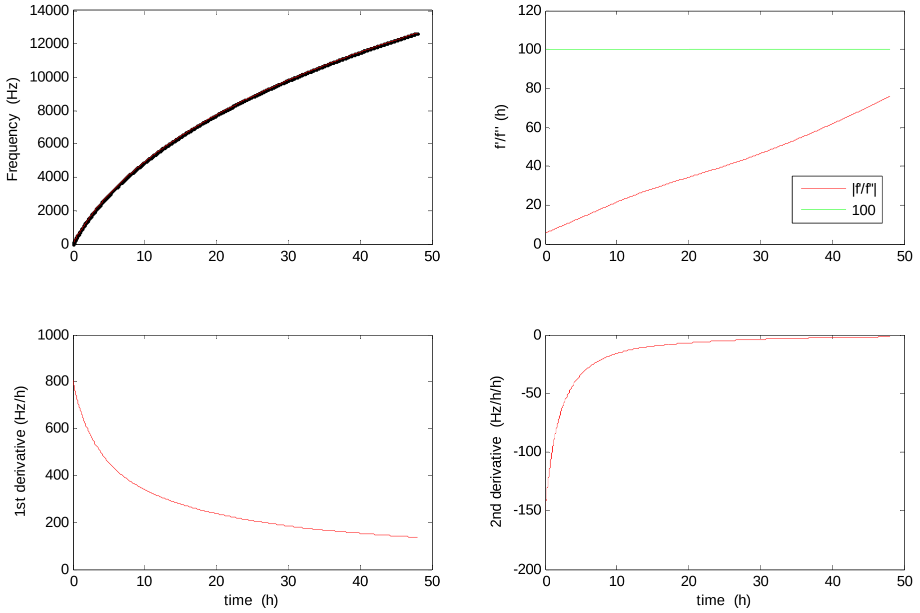


Figure 2: (Top left): Frequency change and fit curve after 48 h of analysis. (Bottom left and right): First and second derivative of the fit-curve. (Top right): Apparent residence time τ_{app} calculated according to Eq. (8).

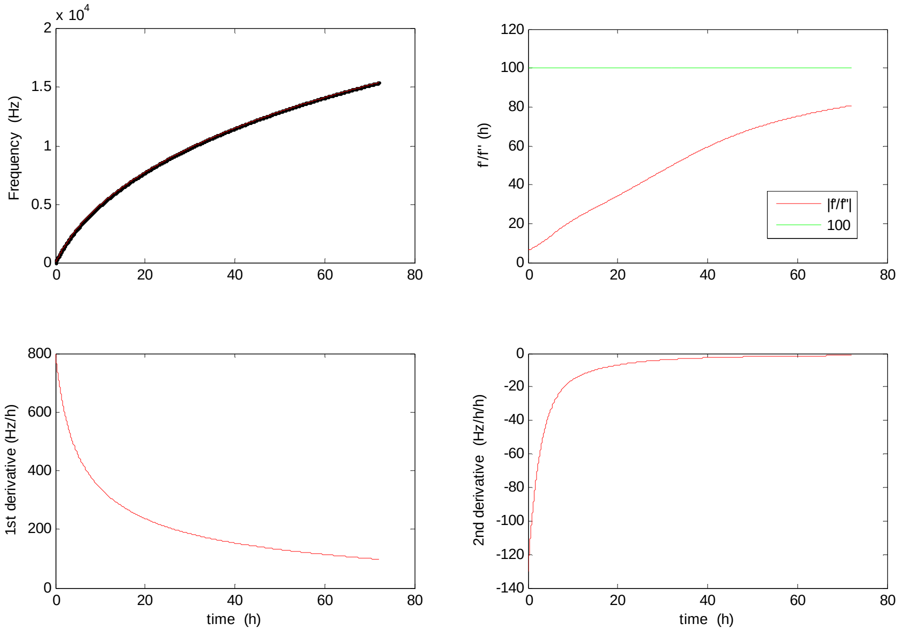


Figure 3: (Top left): Frequency change and fit curve after 72 h of analysis. (Bottom left and right): First and second derivative of the fit-curve. (Top right): Apparent residence time τ_{app} calculated according to Eq. (8).

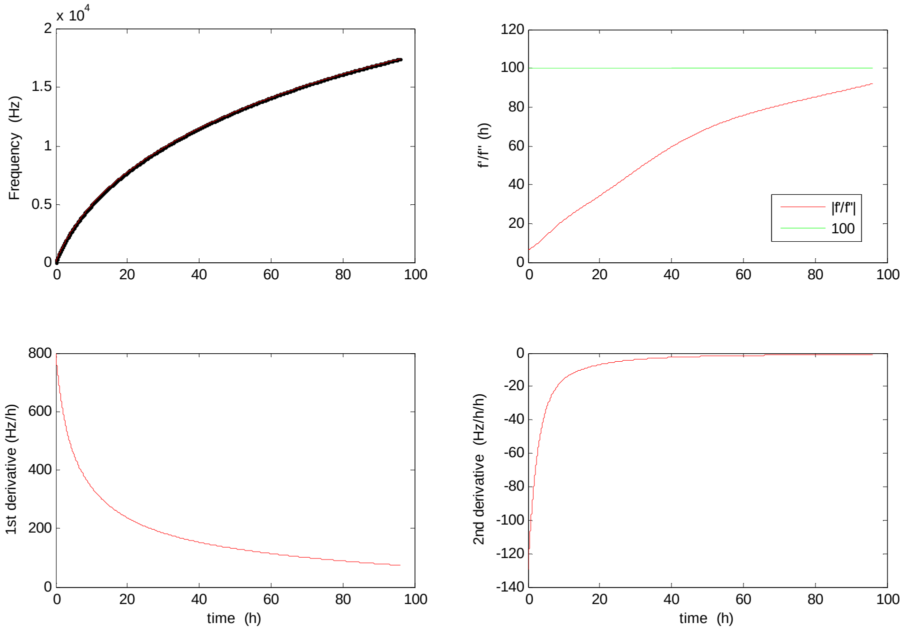


Figure 4: (Top left): Frequency change and fit curve after 96 h of analysis. (Bottom left and right): First and second derivative of the fit-curve. (Top right): Apparent residence time τ_{app} calculated according to Eq. (8).

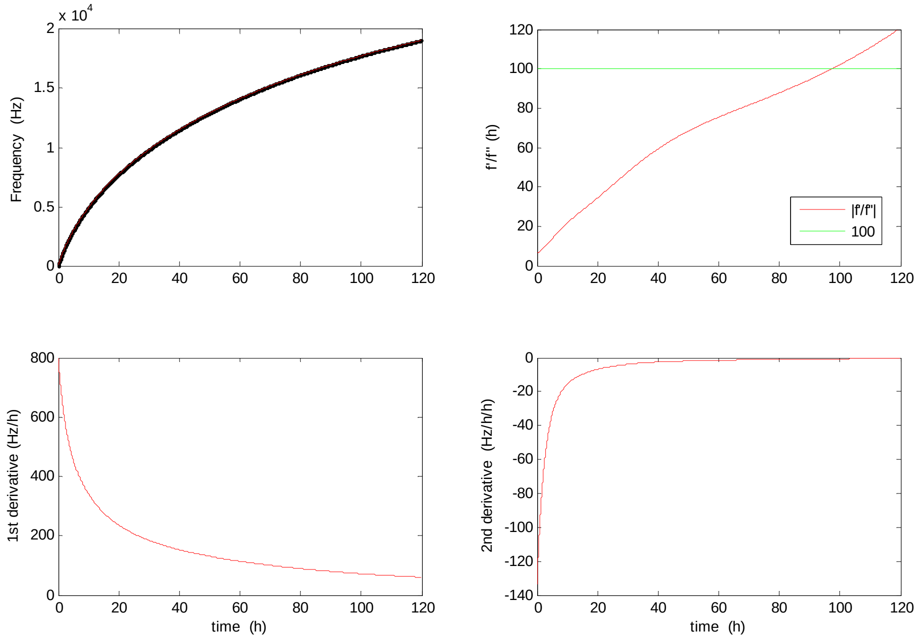


Figure 5: (Top left): Frequency change and fit curve after 120 h of analysis. (Bottom left and right): First and second derivative of the fit-curve. (Top right): Apparent residence time τ_{app} calculated according to Eq. (8).

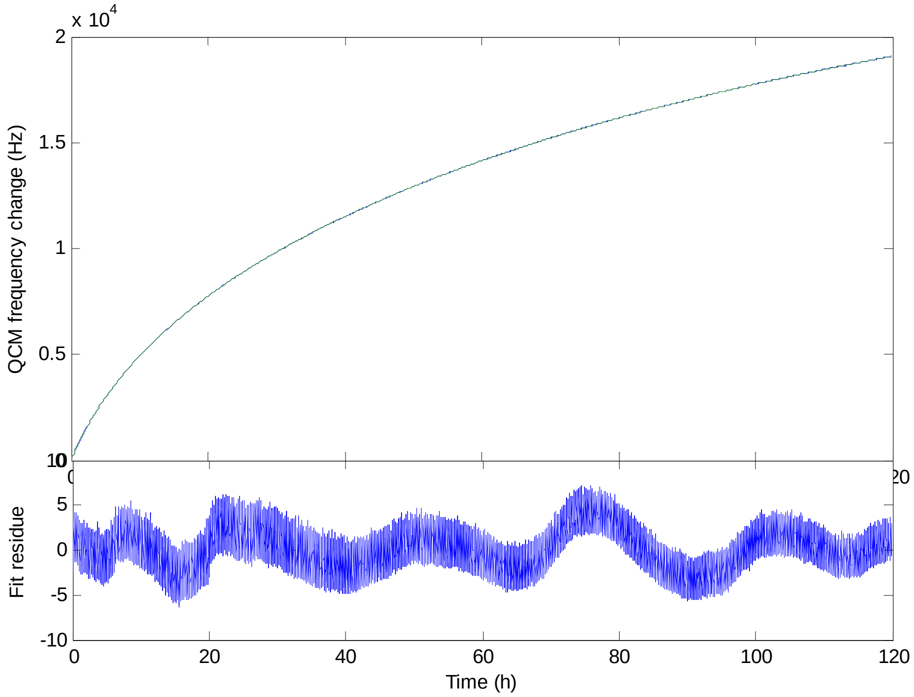
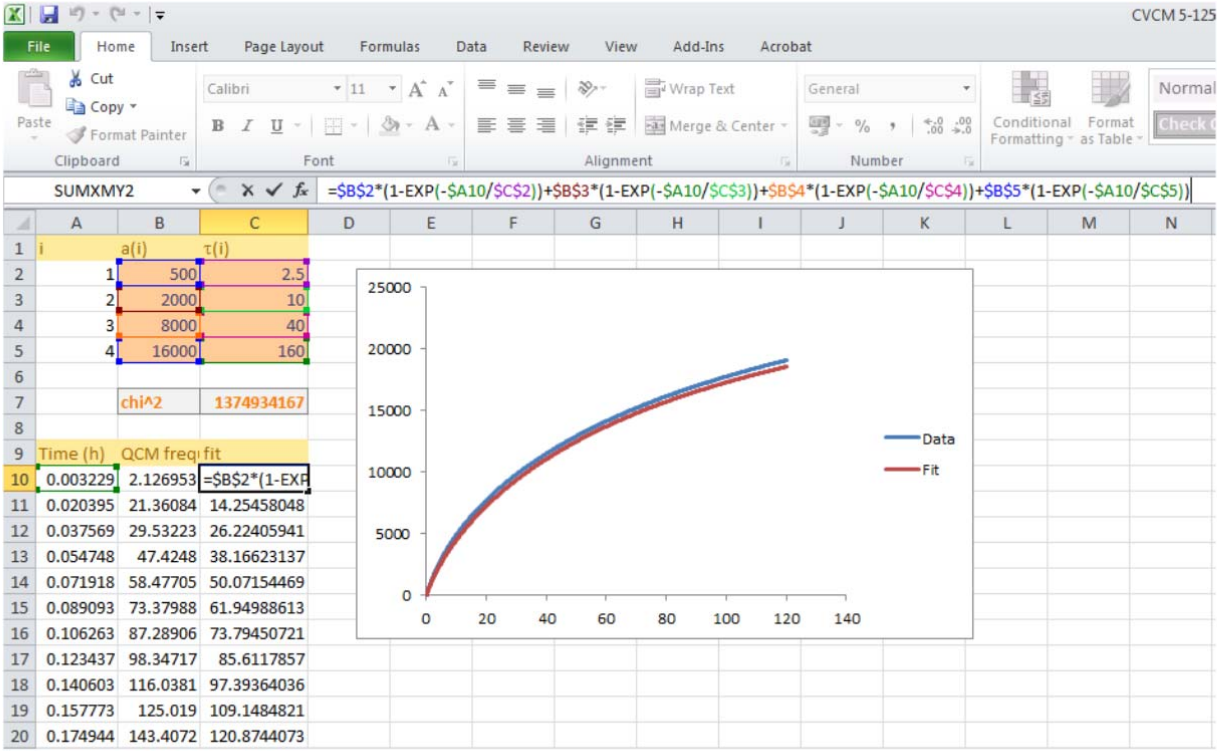


Figure 6: (top) Bake-out data and fit curve. (bottom) fit residue.

ANNEX A: EXAMPLE CURVE FITTING PROCEDURE WITH EXCEL

The screenshot below show an Excel spread sheet with the data from the example bake-out used before. The time and QCM frequency change (zeroed at the 5 h mark in Figure 1) are given in column A and B, starting at row 10. Initial guesses (see below) for the adjustable fit parameters are given in cells B2:C5. In column C the fit-function is entered as shown in the screenshot.



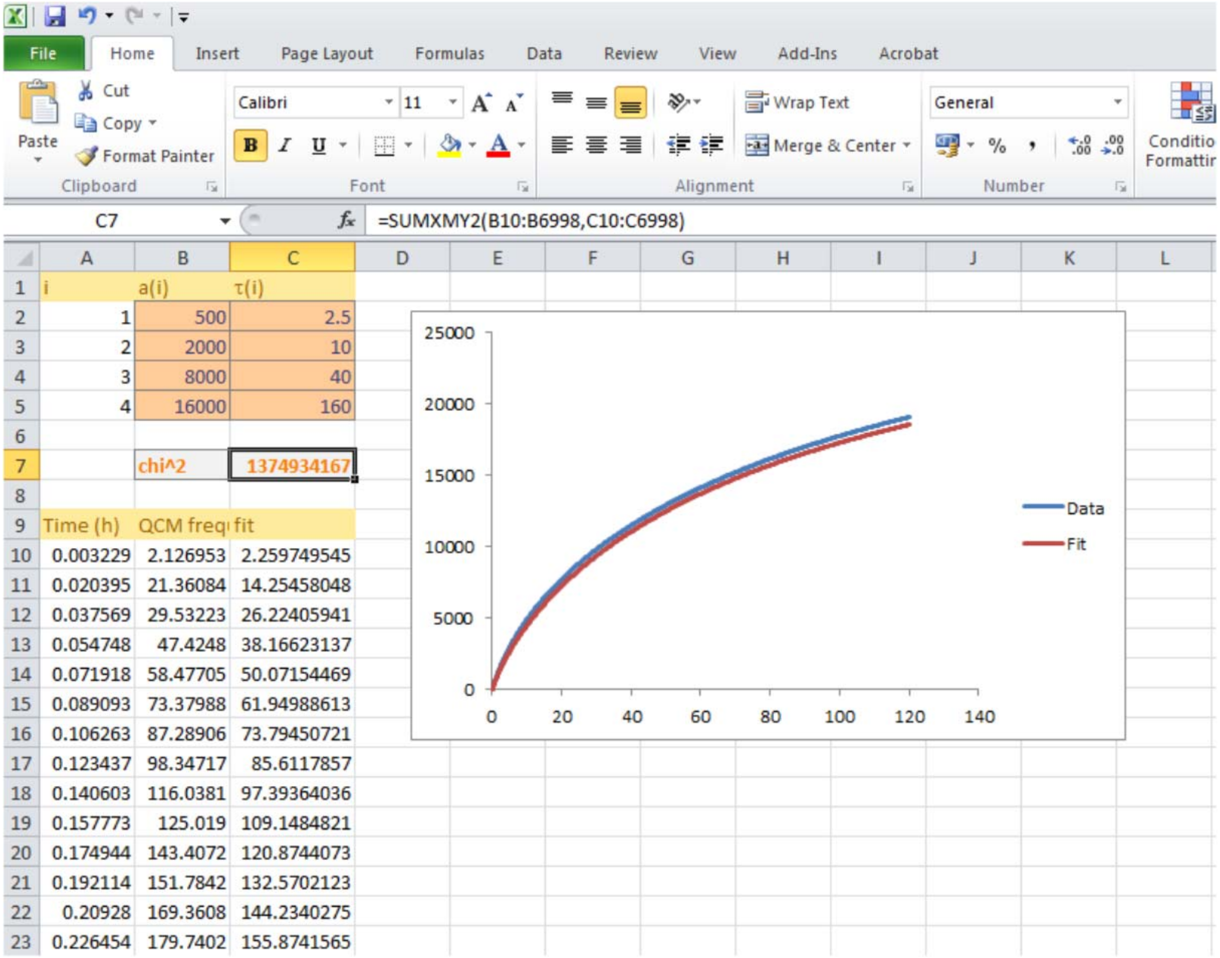
```
SUMXMY2
=$B$2*(1-EXP(-$A10/$C$2))+$B$3*(1-EXP(-$A10/$C$3))+$B$4*(1-EXP(-$A10/$C$4))+$B$5*(1-EXP(-$A10/$C$5))
```

	A	B	C
1	i	a(i)	τ(i)
2	1	500	2.5
3	2	2000	10
4	3	8000	40
5	4	16000	160
6			
7		chi^2	1374934167
8			
9	Time (h)	QCM freq	fit
10	0.003229	2.126953	=$B$2*(1-EXP
11	0.020395	21.36084	14.25458048
12	0.037569	29.53223	26.22405941
13	0.054748	47.4248	38.16623137
14	0.071918	58.47705	50.07154469
15	0.089093	73.37988	61.94988613
16	0.106263	87.28906	73.79450721
17	0.123437	98.34717	85.6117857
18	0.140603	116.0381	97.39364036
19	0.157773	125.019	109.1484821
20	0.174944	143.4072	120.8744073

The initial guesses for the adjustable parameters were obtained as follows. The lowest residence time in this example was set to 2.5 h (the difference between the start of the analysis and the time at which the set point was first reached), and the remaining three residence times are each a factor of 4 higher. The contributions of each "species" was adjusted manually until the difference between data and calculated curve was reasonable

- NOTE A.a: the choice of initial parameters is not critical but unphysical values should be avoided (e.g. residence times of 1000's or 0.001's of hours, contribution that are just a fraction of the total observed frequency change etc.)

The fit characteristic χ^2 can then be expressed with a single formula as shown in the screenshot below in cell C7.



C7 =SUMXMY2(B10:B6998,C10:C6998)

	A	B	C
1	i	a(i)	τ(i)
2	1	500	2.5
3	2	2000	10
4	3	8000	40
5	4	16000	160
6			
7		chi^2	1374934167
8			
9	Time (h)	QCM freq	fit
10	0.003229	2.126953	2.259749545
11	0.020395	21.36084	14.25458048
12	0.037569	29.53223	26.22405941
13	0.054748	47.4248	38.16623137
14	0.071918	58.47705	50.07154469
15	0.089093	73.37988	61.94988613
16	0.106263	87.28906	73.79450721
17	0.123437	98.34717	85.6117857
18	0.140603	116.0381	97.39364036
19	0.157773	125.019	109.1484821
20	0.174944	143.4072	120.8744073
21	0.192114	151.7842	132.5702123
22	0.20928	169.3608	144.2340275
23	0.226454	179.7402	155.8741565

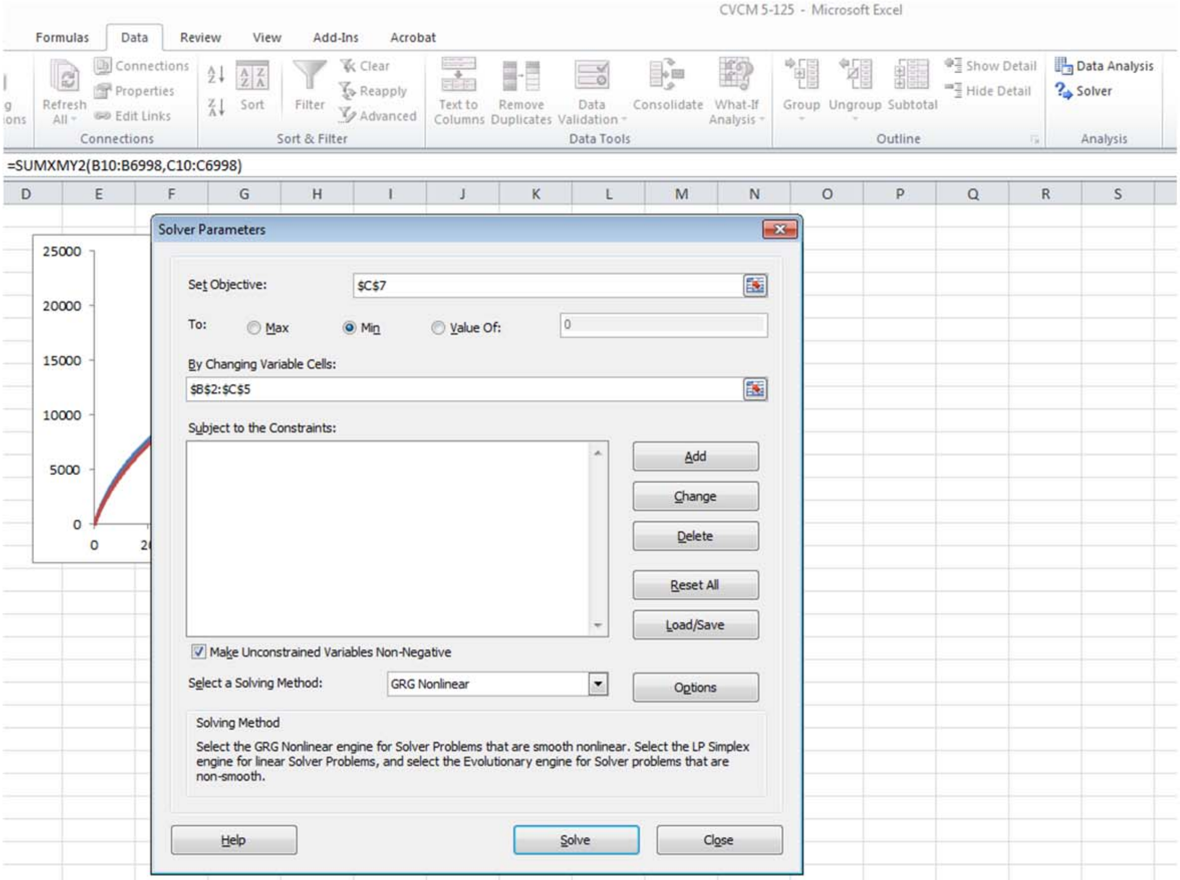
Next, using Excel's Solver add-in (may have to be loaded manually via the File-options menu, once loaded can be found in the Data-menu), the cell containing χ^2 can be minimised by changing the cells with the adjustable parameters, as shown in the screenshot below. The box that says "make unconstrained variable non-negative" should be flagged in this procedure.

The result of the Solver is shown in the next screenshot. Using the Solvers result, the first and second derivative of Eq. (1) can be calculated as a function of time as well as their ratio which is the deviation from linearity. This is shown in the final screenshot, where the 1st and 2nd derivative are given in column D and E, respectively, and the deviation from linearity in column F. The formulas used to calculate them are

Column D: =($B$2/$C$2)*EXP(-$A10/$C$2)+($B$3/$C$3)*EXP(-$A10/$C$3)+($B$4/$C$4)*EXP(-$A10/$C$4)+($B$5/$C$5)*EXP(-$A10/$C$5)

Column E: =($B$2/$C$2/$C$2)*EXP(-$A10/$C$2)+($B$3/$C$3/$C$3)*EXP(-$A10/$C$3)+($B$4/$C$4/$C$4)*EXP(-$A10/$C$4)+($B$5/$C$5/$C$5)*EXP(-$A10/$C$5)

Column F: =100*E10/D10



=SUMXMY2(B10:B6998,C10:C6998)

Solver Parameters

Set Objective: $C$7

To: ○ Max ● Min ○ Value Of: 0

By Changing Variable Cells: $B$2:$C$5

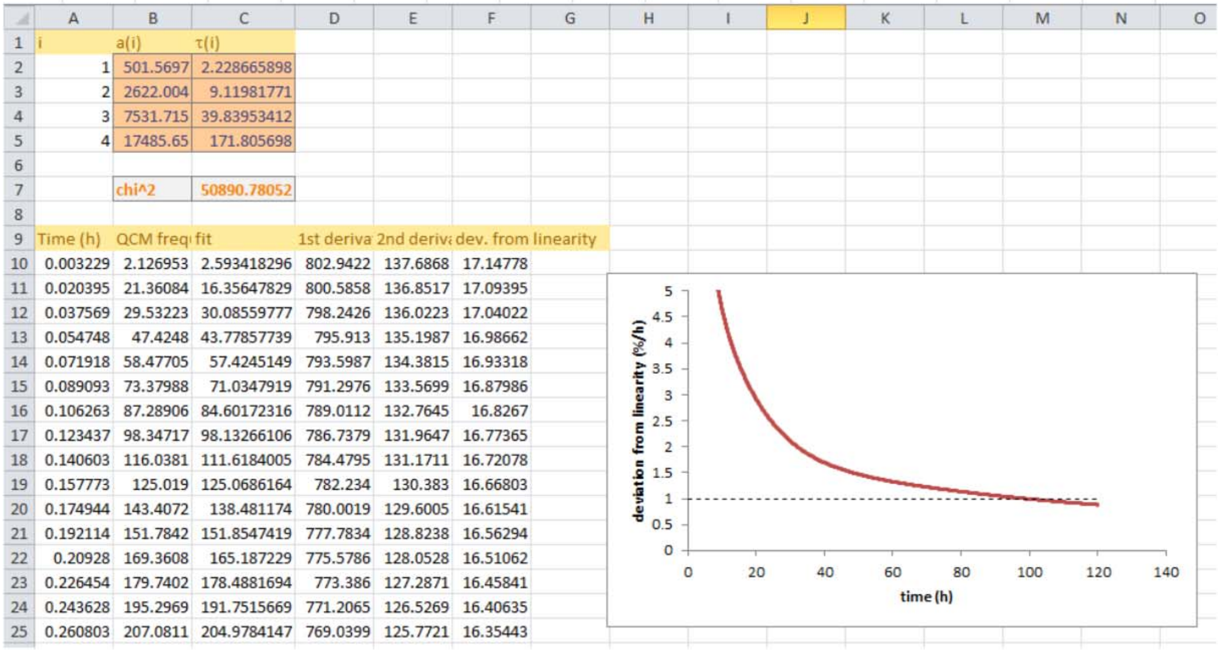
Subject to the Constraints:

☑ Make Unconstrained Variables Non-Negative

Select a Solving Method: GRG Nonlinear

Solving Method

Select the GRG Nonlinear engine for Solver Problems that are smooth nonlinear. Select the LP Simplex engine for linear Solver Problems, and select the Evolutionary engine for Solver problems that are non-smooth.



	A	B	C	D	E	F
1	i	a(i)	τ(i)			
2	1	501.5697	2.228665898			
3	2	2622.004	9.11981771			
4	3	7531.715	39.83953412			
5	4	17485.65	171.805698			
6						
7		chi^2	50890.78052			
8						
9	Time (h)	QCM freq	fit	1st deriva	2nd deriv	dev. from linearity
10	0.003229	2.126953	2.593418296	802.9422	137.6868	17.14778
11	0.020395	21.36084	16.35647829	800.5858	136.8517	17.09395
12	0.037569	29.53223	30.08559777	798.2426	136.0223	17.04022
13	0.054748	47.4248	43.77857739	795.913	135.1987	16.98662
14	0.071918	58.47705	57.4245149	793.5987	134.3815	16.93318
15	0.089093	73.37988	71.0347919	791.2976	133.5699	16.87986
16	0.106263	87.28906	84.60172316	789.0112	132.7645	16.8267
17	0.123437	98.34717	98.13266106	786.7379	131.9647	16.77365
18	0.140603	116.0381	111.6184005	784.4795	131.1711	16.72078
19	0.157773	125.019	125.0686164	782.234	130.383	16.66803
20	0.174944	143.4072	138.481174	780.0019	129.6005	16.61541
21	0.192114	151.7842	151.8547419	777.7834	128.8238	16.56294
22	0.20928	169.3608	165.187229	775.5786	128.0528	16.51062
23	0.226454	179.7402	178.4881694	773.386	127.2871	16.45841
24	0.243628	195.2969	191.7515669	771.2065	126.5269	16.40635
25	0.260803	207.0811	204.9784147	769.0399	125.7721	16.35443