

RECOVERY AND PROCESSING OF GRAVIMETRIC SORPTION DATA

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Abstract

Data obtained during gravimetric sorption experiments are often distorted by random noise and also can be corrupted with random or systematic gross errors. Noise and errors do not contain any useful information and can significantly affect the results of diffusion coefficient calculations.

Knowledge of different disciplines is applied in the paper to utilize the information contained in experimental data as much as possible. The computational procedure is based on modelling and simulation, control theory, experimental identification, digital signal filtering and processing and nonlinear optimization. The standard theoretical model describing the dynamics of sorption of organic vapours in polymeric membranes is modified in view of dynamic characteristics of the measuring chamber. Calculated values of vapour pressure after its injection into the measuring chamber fit then to measured data better. Random noise is eliminated from effective signal by use of a low-pass Butterworth digital filter with a suitably chosen cut-off frequency. Parameters of mathematical model (diffusion coefficient, time constant of the measuring chamber, the initial and final value of the signal and its time delay) are calculated using the Nelder-Mead flexible polyhedron method.

1 Mathematical model of sorption kinetics

Mathematical model [3, 1] describing the kinetics of sorption of gases or vapours in non-porous polymer flat sheet membranes can be derived by solving of the second Fick's law under assumption of independence of diffusion coefficient on concentration and under relatively simple initial and boundary conditions. Solving of this partial differential equation using separation of variables gives for the amount of sorbate $Q(t)$ at time t the following equation

$$\frac{Q(t)}{Q_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2} e^{-\frac{D(2k+1)^2\pi^2 t}{L^2}} \quad (1)$$

where D is the integral diffusion coefficient, L is the thickness of the membrane and Q_{∞} is the amount of vapour sorbed at sorption equilibrium. Using the Laplace transform for solution of the diffusion equation another form of the equation (1) can be obtained

$$\frac{Q(t)}{Q_{\infty}} = 4 \sqrt{\frac{Dt}{L^2}} \left[\frac{1}{\sqrt{\pi}} + 2 \sum_{k=1}^{\infty} (-1)^k \operatorname{ierfc} \frac{kL}{2\sqrt{Dt}} \right] \quad (2)$$

Equation (1) is useful for larger values of time, because the higher members of the series quickly converge to zero. And vice versa, equation (2) is more useful for lower values of time because then the series can be neglected.

Equation (2) is helpful for determination of an estimate of the diffusion coefficient D using the half-time method. The half-time value $t_{1/2}$ corresponds to the time at which the amount sorbed reaches just half of the amount sorbed at sorption equilibrium. Then an approximated formula for the diffusion coefficient can be derived [1]

$$D = \frac{\pi}{64} \frac{L^2}{t_{1/2}} = 0,4909 \frac{L^2}{t_{1/2}} \quad (3)$$

The value of the integral diffusion coefficient D can be easily determined by the least squares fitting of the measured values of sorbed amount $Q(t)$ using the equation (1). At the practical solving of this task there are several problems caused mainly by random events during the measurement process and also by the fact that the measuring equipment is of finite dimensions.

2 Modifications of the theoretical mathematical model

Experimental data are influenced by the finite size of the measuring chamber, the final speed of the consecutive starting of parts of the measuring equipment and its calibration (the zero adjustment):

1. The own dynamics of the measuring chamber causes that the pressure input is not in the form of unit step, but it is delayed and deformed [8]. For needs of its identification four different models were used:

- a first-order system

$$\frac{a}{s+a}$$

- a second-order system with the same time constants (poles)

$$\frac{a^2}{(s+a)^2} \quad (4)$$

- a second-order system with different time constants (poles)

$$\frac{ab}{(s+a)(s+b)}$$

- a third-order system with the same time constants (poles)

$$\frac{a^3}{(s+a)^3}$$

It was shown by experimental identification using the least squares method that the measuring chamber is the second-order system with the same time constants described by equation (4).

2. Manual switching of measuring equipment parts causes that the start of pressure increase does not begin at $t = 0$ but is delayed by the time delay $T_d > 0$.
3. Inaccurate calibration of recording equipment shifts all the measured data by the same value in the vertical direction p_0 or Q_0 , respectively.

After corresponding corrections of the theoretical mathematical model the modified equation for pressure $p(t)$ depending on time t can be expressed in the following form

$$\frac{p(t)}{p_\infty} = [1 - e^{-a(t-T_d)}(1 + a(t - T_d))] \eta(t - T_d) + \frac{p_0}{p_\infty} \quad (5)$$

The analogous equation for the sorbed amount $Q(t)$ depending on time t must be modified as follows

$$\frac{Q(t)}{Q_\infty} = \left[\begin{aligned} & 1 - e^{-a(t-T_d)}(1 + a(t - T_d)) - \frac{8}{\pi^2} \times \\ & \times \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2} \left(A e^{-(2k+1)^2 \frac{D\pi^2}{L^2}(t-T_d)} + (C(t - T_d) - A) e^{-a(t-T_d)} \right) \end{aligned} \right] \eta(t - T_d) + \frac{Q_0}{Q_\infty} \quad (6)$$

where the following expressions can be obtained for the expressions A and C [8]

$$A = \frac{a^2}{a^2 - 2a \frac{D\pi^2}{L^2} (2k+1)^2 + \left(\frac{D\pi^2}{L^2} \right)^2 (2k+1)^4}$$

$$C = \frac{a^2}{\frac{D\pi^2}{L^2} (2k+1)^2 - a}$$

and $\eta(t)$ is Heaviside unit function (unit step function).

3 Detecting and removing random errors and noise from data

Measuring of the sorbed amount in dependence on time can be affected by a variety of random processes. Measured values are most of all influenced by the following processes:

1. Random failure of the measuring device caused by different causes. In this case, an exact extreme value, usually the exact number one or zero, is recorded as the result of measurement.
2. McBain spiral quartz balances used in gravimetric sorption experiments have their own dynamics. It is influenced by the properties of the sorbent and sorbate. Vibrations of the balance caused by sudden pressure change during injection of measured vapour or gas into the measuring chamber, although it is quickly damped, strongly influences results especially the beginning of measurement.
3. Measured values are not accurate; the random noise generated by various insufficiently identified processes superposes on them. This random noise can have a component with uniform power spectral density (white noise) and/or a frequency-dependent component.

To eliminate these parasitic random events, the values corresponding to the failure of the measuring apparatus and the time interval of oscillating and rapidly becoming stable response of the balance are both searched. In both cases, the corrupted data are replaced by interpolated data together with the corresponding noise. After equidistant resampling of the data they are processed as follows:

1. The noise and random phenomena are filtered out by the successively generated digital Butterworth low-pass filters. Characteristics of the filters are set up by changes of their cut-off frequencies interactively in graphical environment consisting of menus and figures interconnected with each other. In such a way both curves of pressure $p(t)$ and sorbed amount $Q(t)$ are smoothed by filtering out the noise. If the measured data contain frequency dependent noise then the noise frequency spectrum is also calculated using the fast Fourier transformation. Before this processing of the data, the trend, a deterministic component of the data, is removed from them. For estimation of the integral diffusion coefficient needed for calculation of the trend equation (3) is used.
2. The Nelder-Mead method of flexible polyhedron [6] is used for multi-dimensional nonlinear optimization of the modified mathematical model. The sum of squares of differences between filtered and smoothed values of pressure and values calculated using equation (5), respectively smoothed values of sorbed amount and values calculated using equation (6) is used as an objective function. The smoothed pressure curve is used for calculation of the double real pole of the measuring chamber transfer function a , the time delay between starting of recording device and injection of measured vapour or gas T_d , the steady state value of pressure in sorption equilibrium p_∞ and the shift of pressure values (calibration of the pressure curve) p_0 . The smoothed sorption curve is used for calculation of the integral diffusion coefficient D , the steady-state value of amount sorbed at sorption equilibrium Q_∞ and the shift of sorbed amount values (calibration of the sorption curve) Q_0 . The needed values of double pole of the measuring chamber transfer function a and the time delay between the start of recording device and the beginning of the sorption experiment T_d can be taken from evaluation of the pressure curve or may be determined independently.

4 Procedure of digital processing of measured data

The result of gravimetric sorption experiments are two time series: the pressure $p(t)$ and the sorbed amount $Q(t)$ in dependence on time t with a variable sampling period. Its value is smaller at the beginning and increases with rising time. Data are written to a text file in CSV format (comma separated values); a semicolon is used as a separator. In case of failure of the measuring device the recording device generates as a result the exact number one. The data are distorted by noise and random errors; the pressure curve is smoother than the sorption curve. The amount of sorbed gas or vapour is measured as the deviation of the position q of McBain spiral quartz balances from the initial position. All measured and calculated values are automatically written into tables in a workbook of MS Excel spreadsheet.

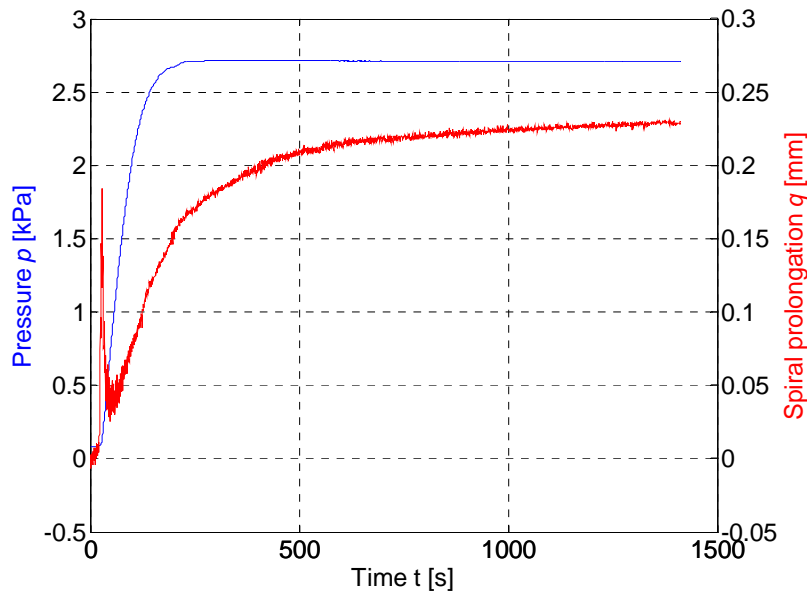


Figure 1: The full course of pressure and sorption curves

4.1 Indication of measuring and recording device failures

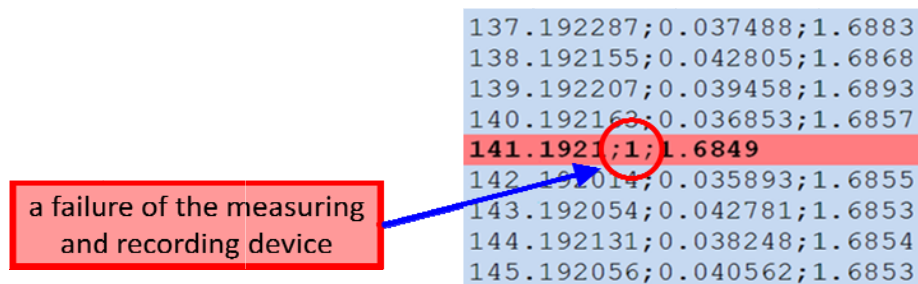


Figure 2: Indication of failure of the measuring and recording device

Errors caused by an accidental failure of the measuring or recording device are written into the data file as the exact number one. These values are automatically searched for in the data file and they are replaced by interpolated values with added random noise with the same characteristics as correctly measured and recorded values. If this algorithmic search fails or provides incorrect values then the results can be interactively corrected using an automatically generated dynamic figure controlled by a menu system. The menu system allows to carry out simple actions; they enable conversationally repair or modify the results of automated searches.

A detailed description of the measuring device is given in [7].

4.2 Detection of measuring and recording device failures

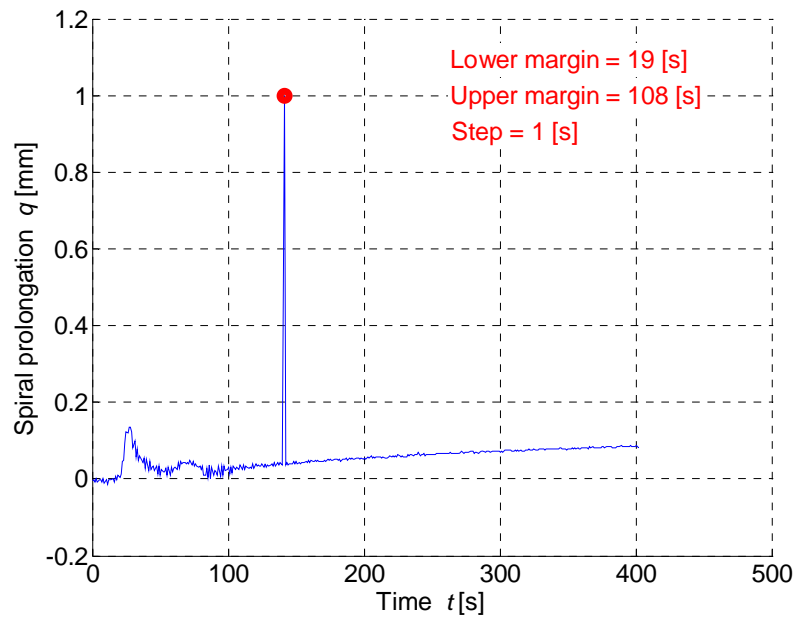


Figure 3: Automatic detection of failures of measuring and recording equipment

4.3 Elimination of measuring and recording device failures

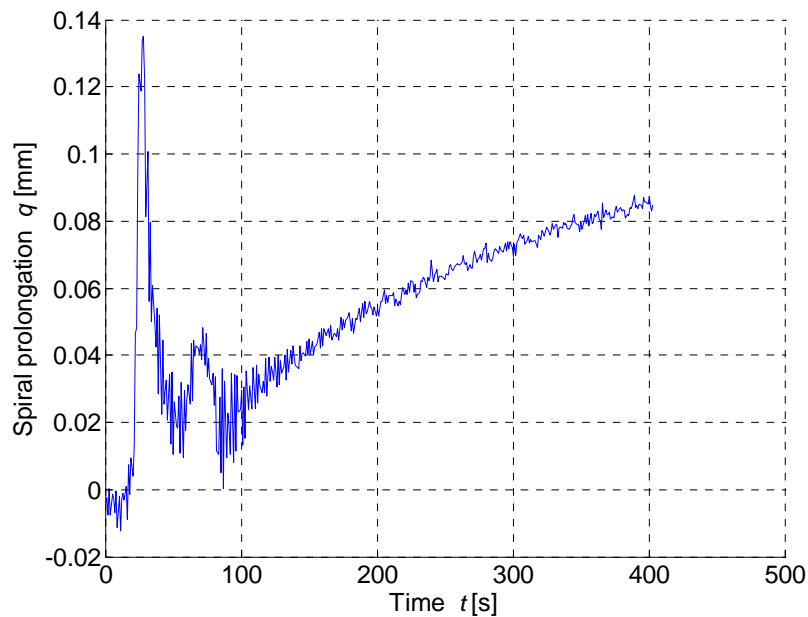


Figure 4: Data after removing values indicating failure of the measuring device

4.4 Detection of unwanted vibrations of spiral quartz balance

Mechanical vibrations of McBain spiral quartz balances caused by pressure shock induced by injection of vapour or gas into the measuring chamber significantly influence the shape of the sorption curve at the beginning of measurement. With regard to the small time constants of spiral balances these unwanted vibrations are quickly damped down. In spite of this they can sometimes spoil the whole course of measurement and therefore they must be identified and localized. They bring no usable information for determination of the integral diffusion coefficient. It is suitable and useful to clean the sorption curve from them in an adequate range.

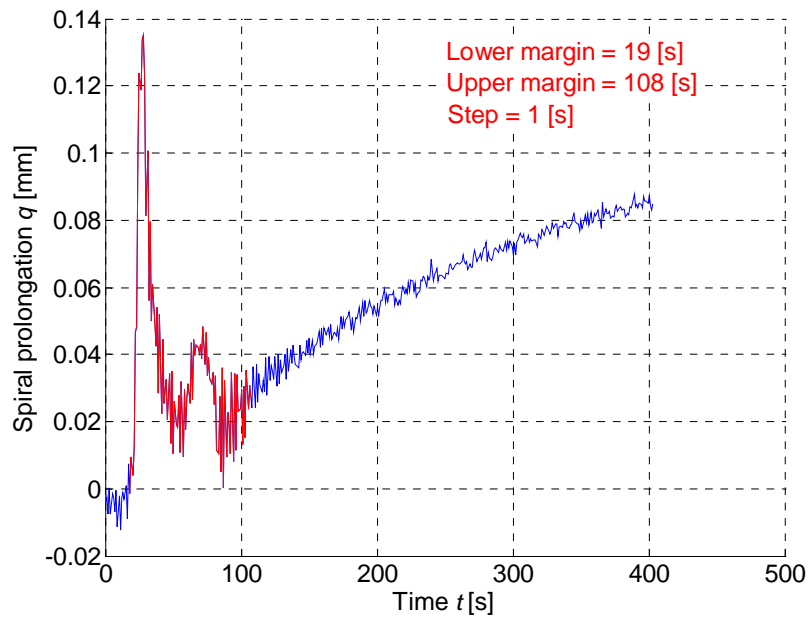


Figure 5: Detection of the values affected by unwanted vibrations

4.5 Data cleaning from unwanted vibrations by interpolation

The measured values affected by vibrations of spiral balances are reconstructed by interpolation. The method of linear interpolation seems to be the best one; but if it is necessary other interpolation methods can be used.

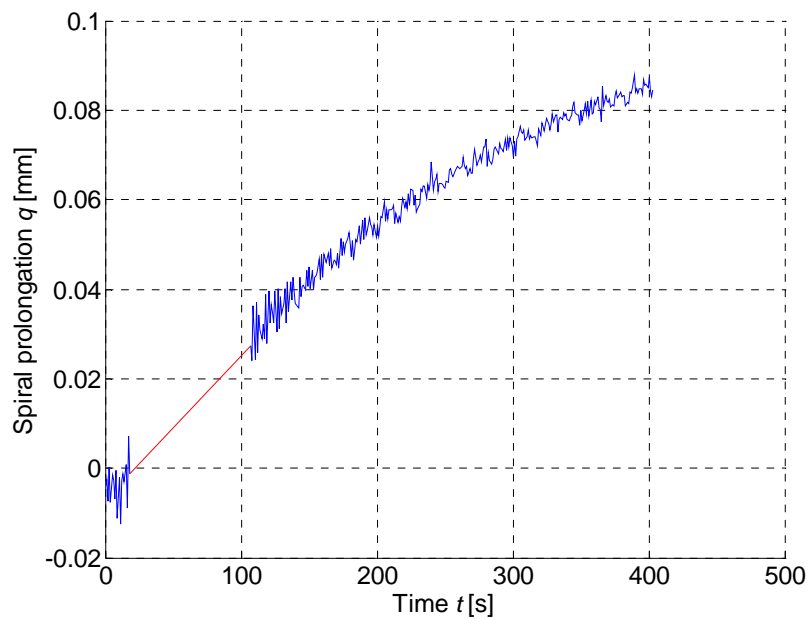


Figure 6: Reconstruction of the vibration affected values by interpolation

4.6 Interpolated data completion with random noise

The process of data recovery after elimination of unwanted vibration is completed by adding of random noise with the same characteristics as the original noise.

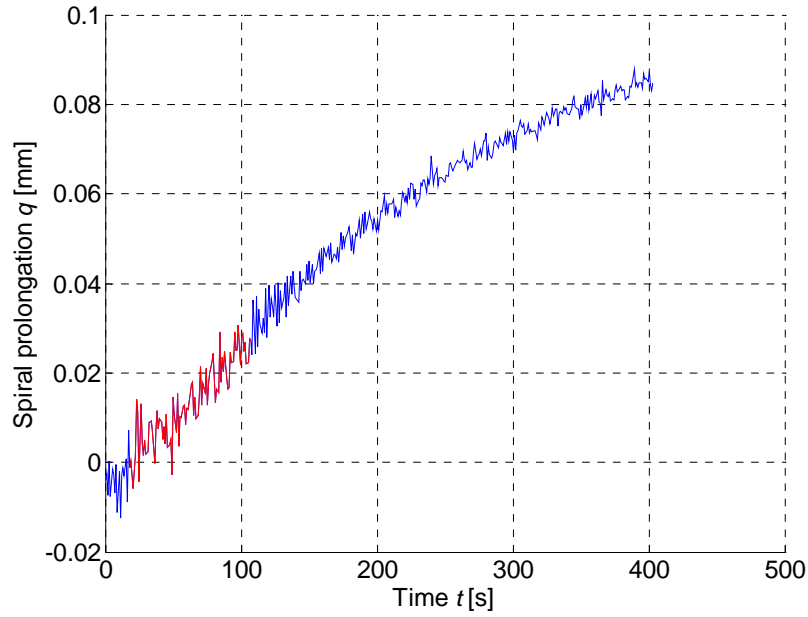


Figure 7: Completion of experimental data recovery by superposition of random noise

4.7 Digital filtering and smoothing of data using a Butterworth low-pass filter

The data that no longer contain any random gross or systematic errors are treated by the process of digital processing [2]. First they are resampled to equidistant sampling data with constant sampling period. Resampling is carried out by means of an interpolation method. Optionally, linear interpolation, nearest-neighbour method, cubic spline interpolation or piecewise cubic Hermitian interpolation can be used. Then the half-time method (3) is applied for estimation of the integral diffusion coefficient needed for determination of the trend. After removing the trend the frequency spectrum of the noise signal is calculated using the discrete fast Fourier transform. The appropriate cut-off frequency may be possibly determined from the frequency spectrum to eliminate frequency-dependent component of noise. Subsequently different variants of fourth-order low-pass Butterworth filters are calculated interactively for various values of normalized cut-off frequency. The number 0.5 is used as a suitable initial value of the normalized cut-off frequency. The goal is to maximize the smoothing of the data especially in the area of measurement that has the highest information content in terms of determining the diffusion coefficient. Only an expert with experience in evaluating sorption curves should perform this work to achieve good results. As the best for the tested data is determined the Butterworth low-pass filter with the following transfer function

$$H(z) = \frac{0,0241 + 0,0965z^{-1} + 0,1448z^{-2} + 0,0965z^{-3} + 0,0241z^{-4}}{1 - 3,9343z^{-1} + 5,8051z^{-2} - 3,8072z^{-3} + 0,9364z^{-4}} \times 10^{-6} \quad (7)$$

When determining an appropriate cut-off frequency and calculating coefficients of Butterworth low-pass filter transfer function (7) smoothing can be performed across the all measurement interval. As an alternative it is possible to interactively choose such a measurement subinterval that has the highest information content considering the integral diffusion coefficient. Selection of the interval should be carried out by an experienced expert.

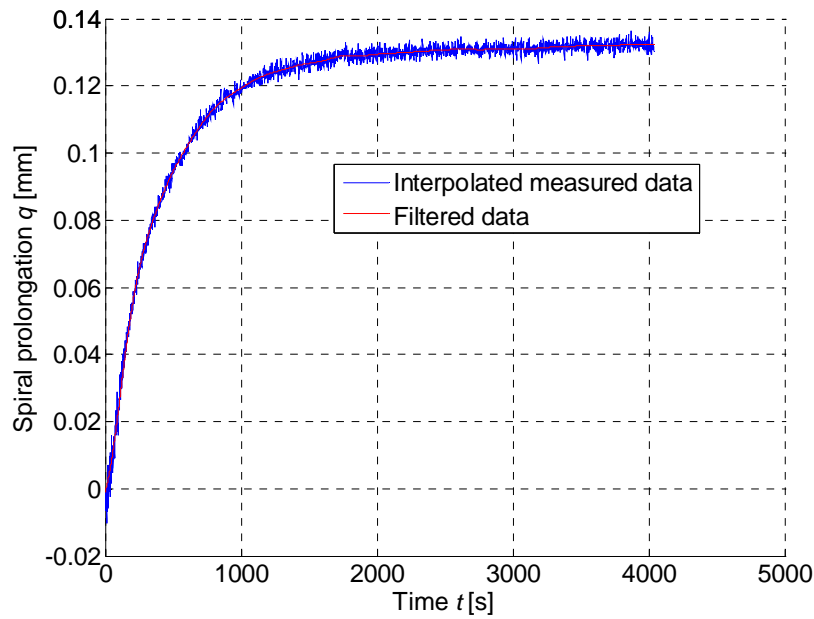


Figure 8: Data smoothing by means of Butterworth low-pass filter

4.8 Calculation of the modified mathematical model parameters

An effective nonlinear multidimensional optimization method must be used for calculation of the parameters of the modified mathematical model. The Nelder-Mead method of flexible polyhedron is selected for its reliability. In addition, this method requires no knowledge of objective function derivatives. As an objective function the sum of squared deviations between the values of smoothed pressure and sorption curve, respectively, and the values calculated from equation (5) or equation (6), respectively, of the modified mathematical model of sorption in a plain sheet membrane is used. The optimization process is again possible to carry out optionally on the whole interval measurements or a measurement subinterval can be interactively chosen.

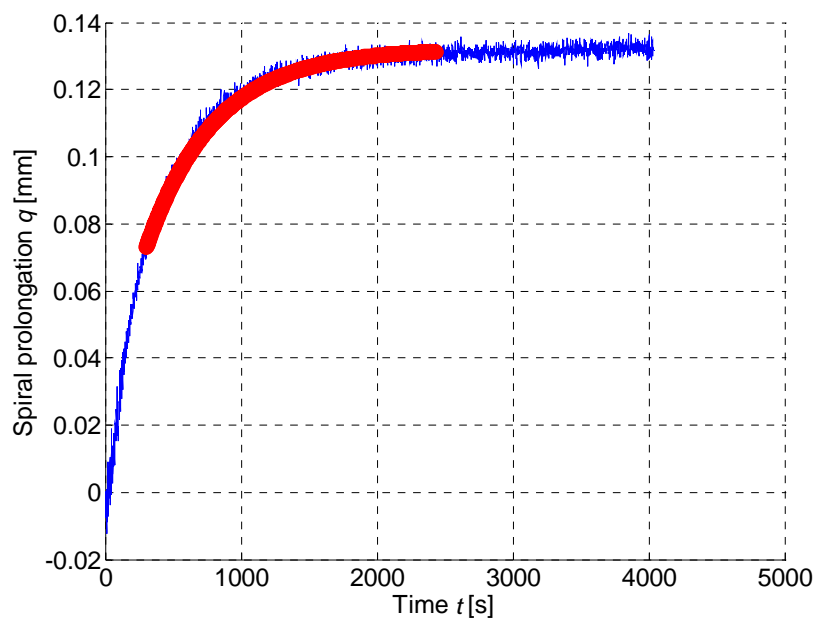


Figure 9: Selection of a suitable interval for optimization of model parameters

Optimization can be optionally carried out for one up to five parameters of the modified model. After processing of the tested pressure and sorption curves were found the following values of the model parameters:

1. integral diffusion coefficient $D = 5,6405 \times 10^{-14}$ [m²/s],
2. amount vapour sorbed at sorption equilibrium $Q_{\infty} = 1,3536 \times 10^{-1}$ [mm],
3. time delay $T_d = 20.4032$ [s],
4. vertical shift of sorption data $Q_0 = 0,00263$ [mm],
5. pole of the measuring chamber transfer function $a = 0,0332$ [s⁻¹] (time constant $T = 30,1$ [s]).

5 Results

An algorithm for calculation of the integral diffusion coefficient from the measured data obtained during the gravimetric sorption experiments was developed. This algorithm was implemented in the integrated environment for technical computing MATLAB[®]. Experimental and calculated data (pressure and sorption curve) are being displayed in all steps of digital processing of these time series. The model of the dynamics of the measuring chamber that most closely corresponds to the measured data was selected from four investigated models by means of experimental identification. Some decisions in the course of digital processing of experimental data can not be completely algorithmized. Therefore, decision making, selection of options and parameter setting procedure are carried out conversationally in the graphical environment using an interactive system of dynamical figures and menus. The following methods for processing of the measured experimental data are used: mathematical modelling, simulation and visualization, digital processing of discrete data and multidimensional nonlinear optimization. The main advantages of the described procedure are:

- usage of the modified mathematical model that is closer to the real measurement conditions,
- automation of data processing,
- significantly faster and more accurate calculation of the integral diffusion coefficients from gravimetric sorption experiments,
- possibility of processing such experimental data that has been corrupted so much that the traditional methods of their processing fail.

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