Digital Processing of Noise Experimental Sorption Data using Savitzky-Golay filter

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Introduction

The work deals with digital processing of experimental sorption data. Measured data on course of vapour sorption during sorption experiment are distorted by random noise together with unwanted vibrations of the measurement scales. Before processing of data is necessary to remove the vibrations of the quartz scales caused by pressure surge after injection of a sample of vapour or gas. Elimination of the vibrations and correction of the data is carried out interactively by an experienced expert. Then the data are smoothed again interactively by application of the Savitzky-Golay filter. The parameters of sorption kinetics are determined from the corrected and smoothed sorption data automatically by means of the least squares method. The optimum value of the goal function is searched by multidimensional nonlinear optimization. Used Nelder-Mead method of flexible polyhedron requires only a mathematical model of sorption process [2, 10]; that is derived from the 2nd Fick's law. The optimization process in addition to the value of diffusion coefficient calculates also the time delay of the signal and its initial and steady-state values.

Mathematical model of sorption kinetics

Mathematical model [2, 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 mass of sorbate $Q(t)$ at time t the following equation

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

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

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

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 mass of sorbed vapour reaches just half of those at sorption equilibrium. Then an approximated formula for the diffusion coefficient can be derived [1]

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

The value of the integral diffusion coefficient D can be determined by the least squares fitting of the measured values of mass of sorbed vapour $Q(t)$ using the equation (1). At 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 (McBain spiral quartz scales [11]) has its own dynamics.

Modifications of the theoretical mathematical model

Experimental data are influenced by own dynamics of the measuring scales, 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 scales cannot be identified by standard methods of experimental identification. So, it cannot be included into the modified theoretical model of vapour sorption in a flat sheet membrane and it has to be eliminated during digital processing of experimental data.
2. Manual switching on of parts of the measuring equipment causes that the sorption process does not at time $t = 0$ but is delayed by a time delay $T_d > 0$.
3. Inaccurate calibration of recording equipment shifts all the measured data in the vertical direction by a constant value Q_0.

From these reasons, the theoretical model of vapour sorption in a flat sheet membrane must be corrected into the following form:

$$\frac{Q(t)}{Q_\infty} = \left[1 - \frac{8}{\pi^2} \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2} \mathrm{e}^{-(2k+1)^2 \frac{D\pi^2}{L^2}(t-T_d)}\right] \eta(t - T_d) + \frac{Q_0}{Q_\infty} \tag{4}$$

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

Smoothing of experimental data

Experimental data are usually formed by superposition of the proper measured signal and a random noise. For processing of them it is necessary to smooth the data, thus to remove the random noise from them or at least it significantly suppressed. During this process it is important not to damage proper signal carrying information. Many smoothing methods are based on polynomial regression; experimental data are fitted by a polynomial using a modified method of least squares. All equations are simplified considerably if the experimental data are equidistant. Non-equidistant data must be appropriately interpolated to equidistant values of the independent variable. The end points cannot be interpolated; a suitable method of extrapolation has to be used. As interpolation and extrapolation methods are often used simple polynomial approximation; it is usually sufficient to use a linear, quadratic, or cubic polynomial.

Basic principles of Savitzky-Golay method of data smoothing.

Savitzky-Golay method (Savitzky-Golay low-pass FIR filter) for smoothing of experimental data

$$[t_k, y_k], \quad k = 0, 1, 2, \dots, N \tag{5}$$

is based on the assumption that the measured data are equidistant. Then linear transformation of independent variables can be performed

$$i_k = \frac{t_k - t_0}{\Delta}, \quad k = 0, 1, 2, \dots, N \tag{6}$$

Around each point a window (symmetric interval measured with the point as the central point of the interval) is created. From symmetry implies that the window must contain an odd number of points

$2m + 1$. Then the measured value at the central point of the window can be replaced by the weighted average of measured values for all points in the interval

$$z_k = \sum_{j=-m}^{m} c_j y_{k+j}\,, \quad k = m+1, m+2, \dots, N-m-1, N-m \tag{7}$$

where the weight coefficients $c_j,\ j = -m, -m+1, \dots, m-1, m$ are obtained by fitting the polynomial

$$f_n(i) = b_{n0} + b_{n1} i + b_{n2} i^2 + \cdots + b_{n,n-1} i^{n-1} + b_{nn} i^n \tag{8}$$

of degree $n < 2m + 1$ using the least squares method

$$\frac{\partial}{\partial\, b_{nk}} \left[\sum_{j=-m}^{m} (f(i) - y_i)^2 \right] = 0 \tag{9}$$

followed by normalization. The procedure can be generalized to the boundary points when the window is not symmetrical to the central point. When calculating the weights Savitzky and Golay [9] used direct solution of systems of linear algebraic equations. This procedure is complicated and difficult to generalize. Gorry [4] used the Gram polynomials, and acquired general recurrent formulas for weight coefficients. Press, Flannery, Teukolski and Vetterling [8] described compact explicit formulas for calculation of the weights. In all these publications is provided source program code for the calculation of weight coefficients for Savitzky-Golay filter. Signal Processing Toolbox, a part of the Matlab program system [6], contains function sgolay for calculation of the weight coefficients of Savitzky-Golay filter and function sgolayfilt for data smoothing.

Detecting and removing random errors and noise from data

Measuring of the mass of sorbed vapour in dependence on time can be affected by several 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, in our case the exact number one ($Q_{fail}(t) = 1$), is recorded as the result of measurement.
2. McBain spiral scales used in gravimetric sorption experiments have their own dynamics. It is influenced by the properties of the sorbent and sorbate. Vibrations of the quartz scales caused by sudden pressure change during injection of vapour or gas into the measuring chamber, although it is quickly damped, strongly influences results especially the start of measurement.
3. Measured values are not accurate; the random noise generated by various insufficiently identified processes superposes on them. This random noise may have a component with uniform power spectral density (white noise) and/or a frequency-dependent component.

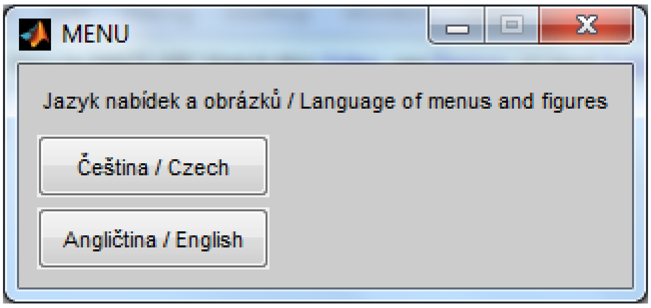
To eliminate these parasitic random events, the values corresponding to the failure of the measuring equipment and the oscillating but quickly dampened response of the scales are both searched. In both cases, the corrupted data are replaced by interpolated data together with the corresponding noise. After equidistant resampling of the data they are processed as follows:

1. The noise and other random phenomena are filtered out by the successively generated series of digital Savitzky-Golay filters [6, 9]. In the two-parameter filter (the degree of polynomial approximation, the window width for calculation of weighted average) is used a linear polynomial as the first parameter and as the second one integers starting at 41 and rising with 10 as the step. Smoothing procedure is interactively controlled by an experienced expert.
2. The Nelder-Mead method of flexible polyhedron [3, 5] is used for multi-dimensional nonlinear optimization of the modified mathematical model. The sum of squares of differences between smoothed values of sorbed vapour mass and values calculated using equation (4) is used as an objective function. The smoothed sorption curve is used for calculation of the integral diffusion coefficient D, the steady-state value of sorbed mass at sorption equilibrium Q_∞ and the shift of sorbed mass values (calibration of the sorption curve) Q_0.

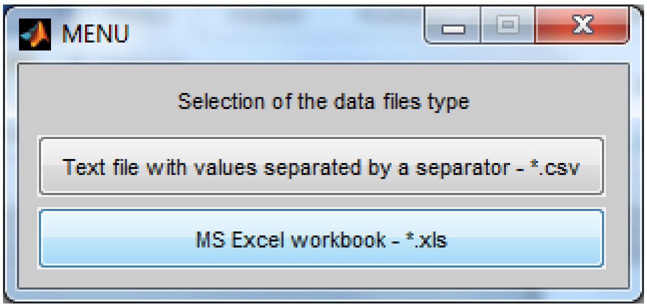
Procedure of digital processing of measured data

The result of gravimetric sorption experiments is a time series: the mass of sorbed vapour $Q(t)$ in dependence on time t with changing sampling periods. Its values are small at the start of measurement and increases as it approaches to steady-state. Data are written to a text file in a comma separated values format with semicolon as the separator. In case of failure of the measuring device the recording device generates as a result the exact number 1. The data are distorted by noise and random errors. The mass of vapour sorbed in a flat sheet membrane is recorded as the deviation of the position q of McBain spiral quartz scales from its initial position. All experimental and calculated values are automatically written into tables in a workbook of MS Excel spreadsheet.

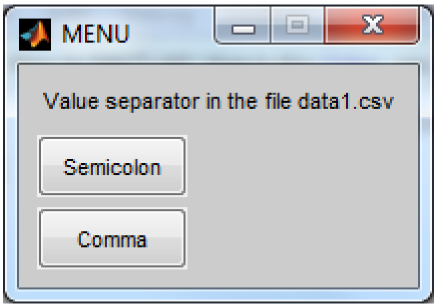
- **selection of the language of menus, figures and information messages**



- **selection of the data files type**



- **selection of the value separator**



- **entering the name of the data file and reading the data**

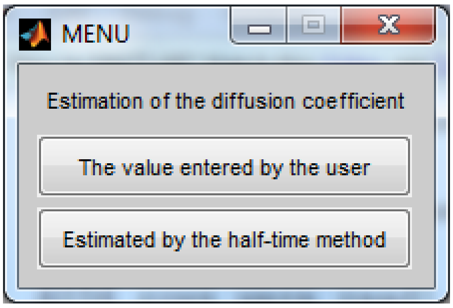
```
Enter the name of the data file: data1

Reading data from the input text file!!!

4034 rows were read!
```

- **writing the data into the MS Excel workbook of the same name, sheet Data**

```
Writing data to the output Excel spreadsheets!!
Wait, data entry may take a few seconds!!

4034 rows were written into the file data1.xls successfully !!!
```

Time	Prolongation	Pressure
[s]	[mm]	[Pa]
0,26215	-0,039545	-0,004115
1,196285	-0,039449	-0,00263
2,197159	-0,039725	-0,00742
3,197085	-0,039665	0,000251
4,197192	-0,039543	-0,007634
5,197326	-0,039608	-0,001603
6,19725	-0,039399	-0,002736
7,128857	-0,039575	-0,006792
8,197185	-0,039459	-0,000396
9,196875	-0,039529	-0,011182
10,197044	-0,039763	-0,00207
11,196578	-0,039704	-0,012496
12,19697	-0,039641	-0,002759
13,196904	-0,03939	-0,001125
14,196702	-0,039354	-0,00307
15,19675	-0,039575	0,000902
16,197063	-0,03955	-0,008878
17,196601	-0,039543	0,007253
18,196707	-0,03952	-0,001349
19,196735	-0,039434	0,009404
20,196707	-0,039618	0,004094

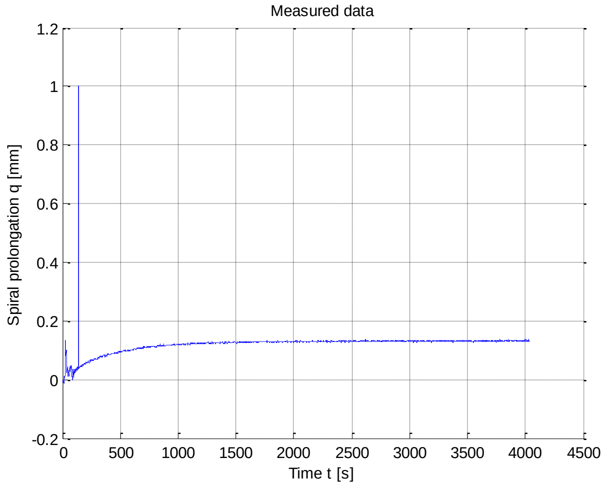
- **selection of the way for estimation of the diffusion coefficient**



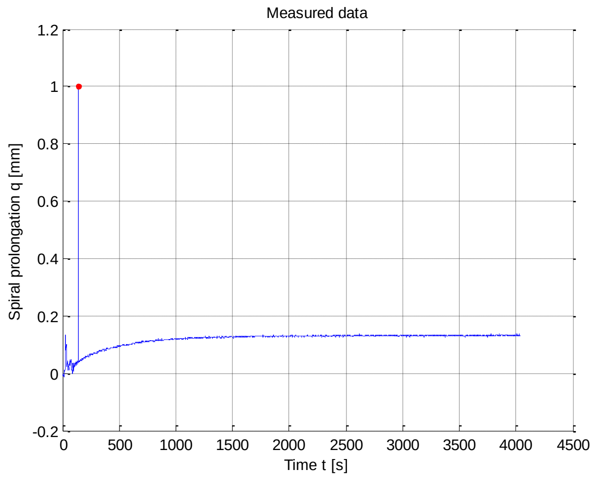
- **entering the input data**

```
Enter the value of the membrane thickness    L [m]    = 16e-6
Estimation of the diffusion coefficient      D [m2/s] = 4.6445e-14
```

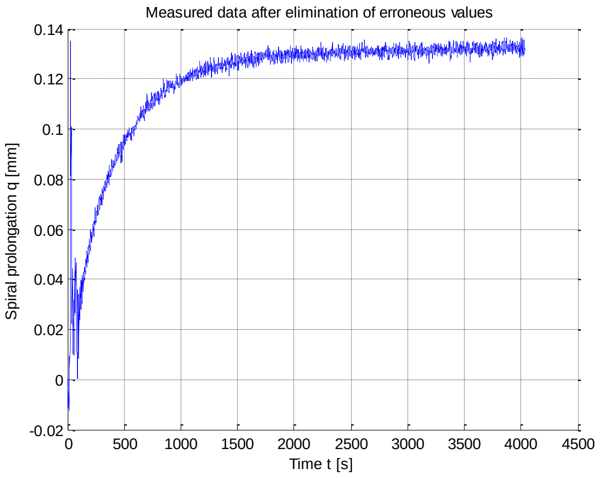
- **displaying the measured data**



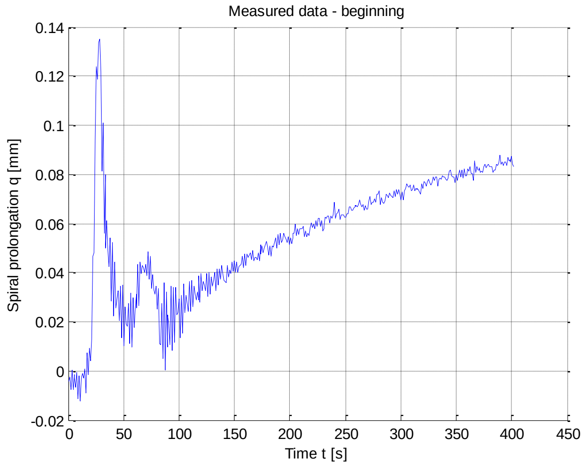
- **detection of failures of measuring device**: The program automatically finds sequences of failures (they are identified by the extreme value $q_{fail}(t) = 1$).



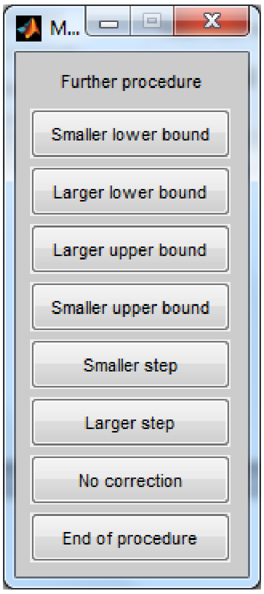
- **elimination of failures of measuring device**: Failure data are replaced by linear interpolation



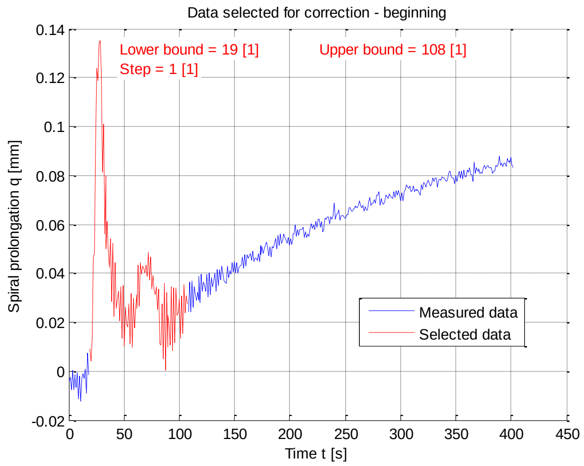
- **unwanted vibrations of spiral quartz scales**: Mechanical vibrations of McBain spiral quartz scales caused by pressure shock induced by injection of vapour or gas into the measuring chamber significantly influence the shape of the sorption curve at the start of.



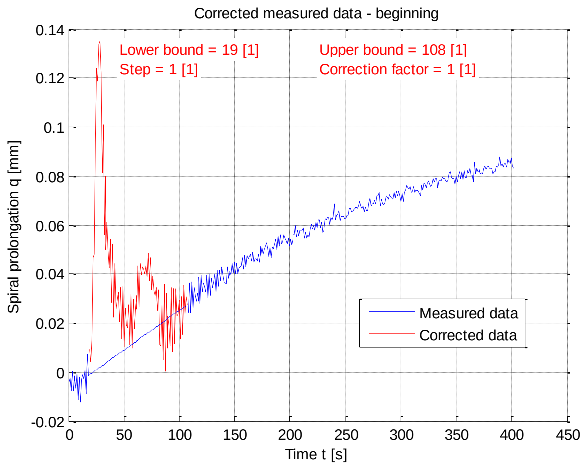
- **detection of unwanted vibrations of spiral quartz scales**: The range is selected by the user interactively using the menu.



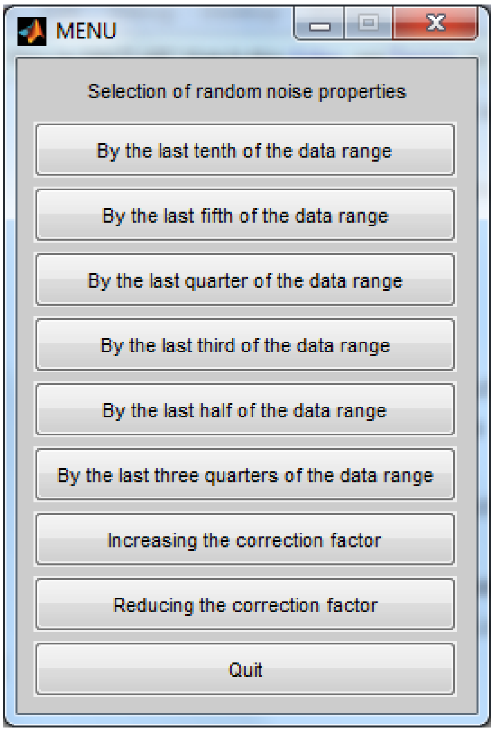
- **interactive selection of the vibrations range**



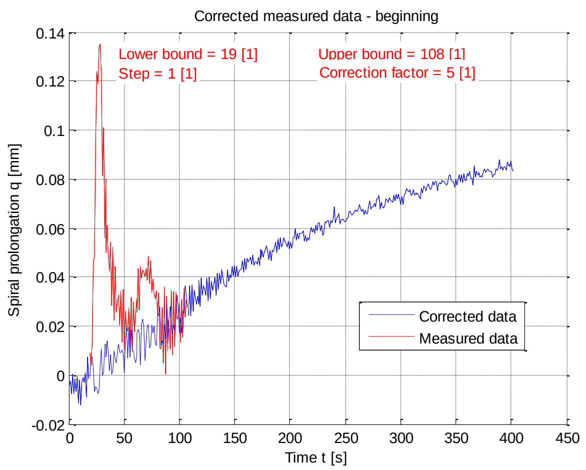
- **replacing the vibrations by linear interpolation**



- **selection of random noise properties**



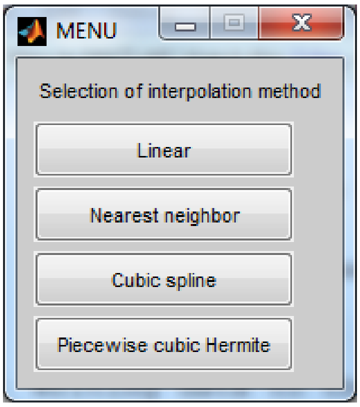
- **adding random noise to the interpolated values**



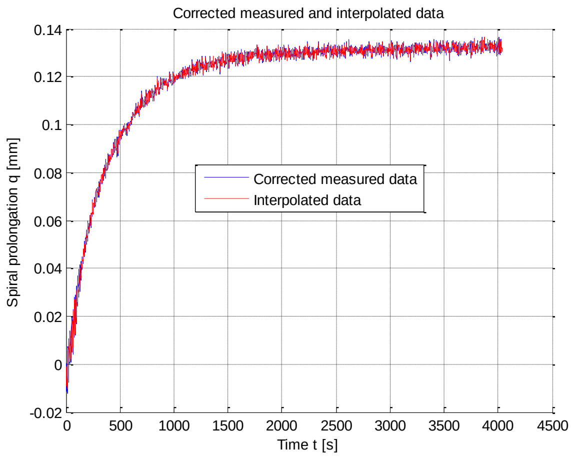
- **properties of recorded times and determination of the sampling period**

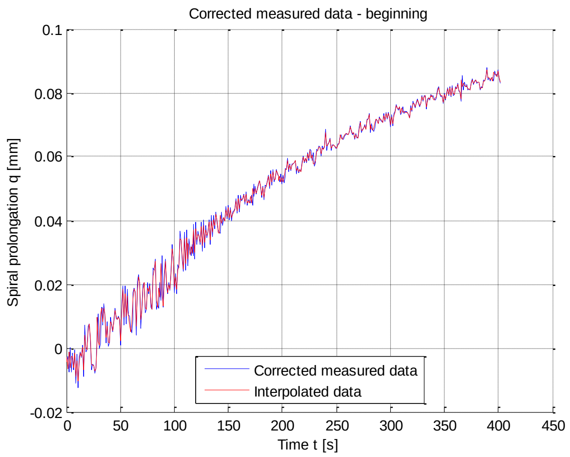
```
Characteristics of sampling periods:
The minimum of sampling periods [s] = 7.3370e-01
The maximum of sampling periods [s] = 1.9331e+00
The average of sampling periods [s] = 1.0002e+00
The median  of sampling periods [s] = 9.9997e-01
The modus   of sampling periods [s] = 9.9991e-01

The selected sampling period [s] = 1.0000e+00
```

- **selection of a interpolation method**

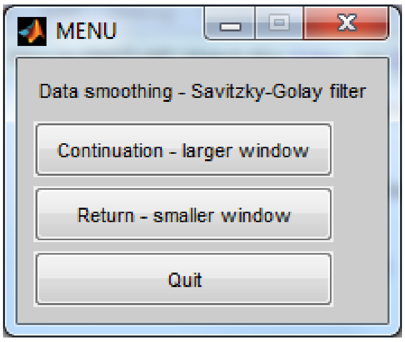


- **comparison of corrected measured and interpolated data**

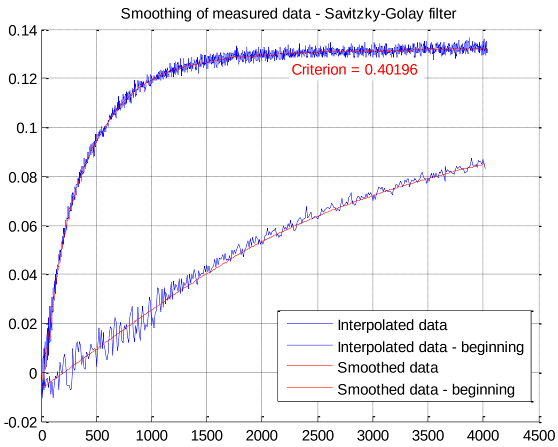




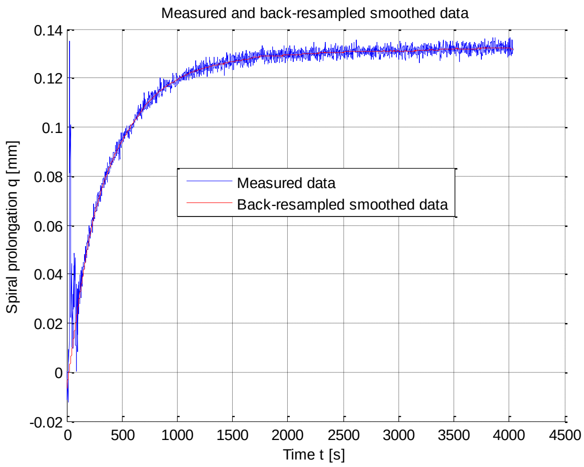
- **data smoothing by Sawitzky-Golay filter**: Process of smoothing is controlled by a simple menu

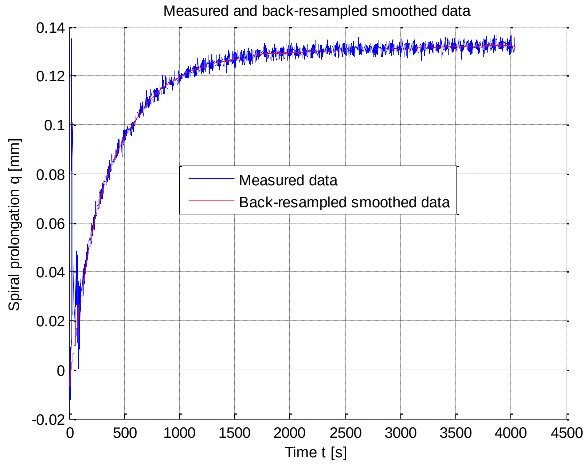


- **digital smoothing of data using a Savitzky-Golay filter**: Smoothing of modified experimental data is carried out interactively using the Savitzky-Golay low-pass filter. The function describing the process of vapour sorption on a flat sheet membrane (1) is continuous and monotone. So choice of a linear polynomial as the regression polynomial for the filter is sufficient. The initial value of the window width for smoothing after a series of numerical experiments is set to 41; it can increase with step of 10. An experienced expert evaluates the progress of smoothing by observing of changes the smoothed curve on the background of experimental data. He is able to simultaneously monitor data in both the entire range and its enlarged beginning. Progress of smoothing is interactively controlled by means of a simple menu where the window width can be changed (increased or reduced).



- **back resampling of the smoothed data**

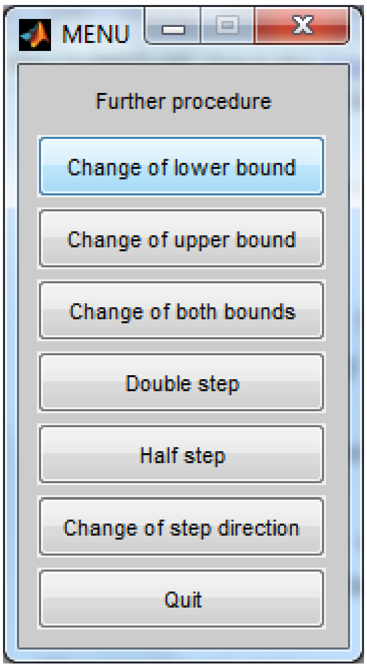




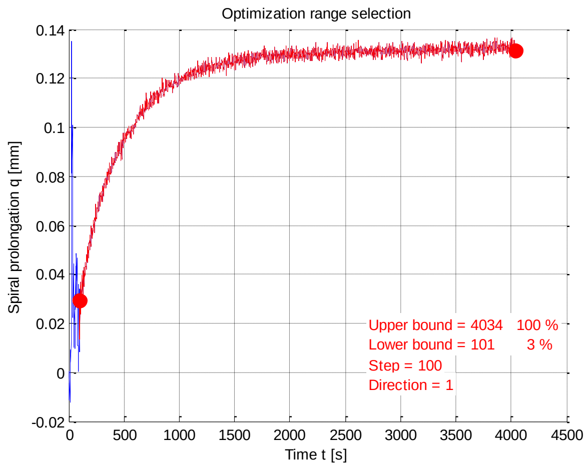
- **parameters of optimization process**: They are set-up automatically for the used optimization method (Nelder-Mead flexible polyhedron method – Mathlab function fminsearch)

```
Optimization parameters

Maximum number of iterations                     :       10000
Maximum number of function evaluations           :       10000
Termination tolerance on the variables           : 1.0313e-29
Termination tolerance on the function value      : 2.2737e-13
```

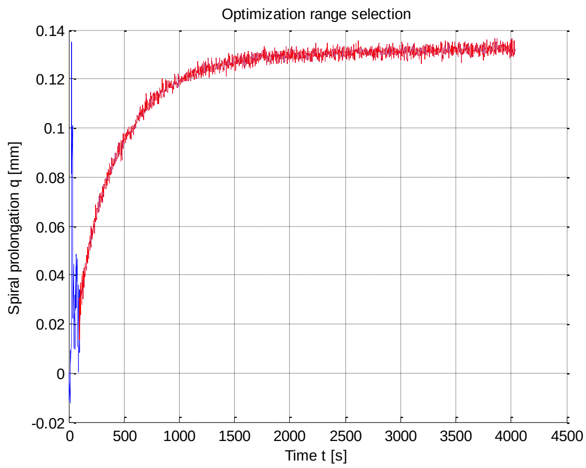
- **optimization subinterval**: The optimization process is possible to carry out optionally in the entire data range or an optimization subinterval can be interactively chosen. Selection of the interval should be carried out by an experienced expert. So it is possible to interactively choose such a partial range of data that has the highest information content for calculation of the integral diffusion coefficient. Selection of the interval should be carried out again by an experienced expert.



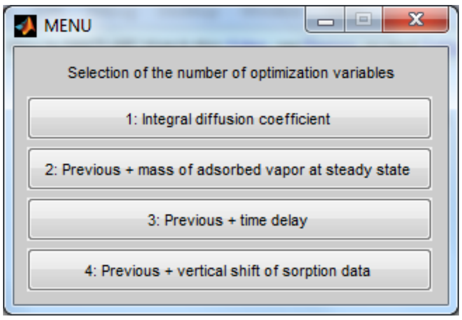
- **interactive selection of the optimization range**



- **selected optimization range**



- **choice of a version of the modified mathematical model**: The modified mathematical model (4) contains four parameters that can be used as optimization variables: integral diffusion coefficient D, mass of sorbed vapour at sorption equilibrium Q_{∞}, time delay T_d, and vertical shift of sorption data Q_0. Selection of a version of the mathematical model (the number of optimization parameters) will again be performed interactively.



- **the course and results of 1D optimization**

```
Optimization is in progress!!!
Wait, calculation may take several minutes!!!

Results of 1D-optimization for smoothed data

Diffusion coefficient : 5.2321e-14 [m2/s]

Optimum found successfully for      0.3648 s!!!

Writing results to the output Excel spreadsheets!!!
Wait, data entry may take a few seconds!!!

4034 rows were written into the file data1.xls successfully !!!
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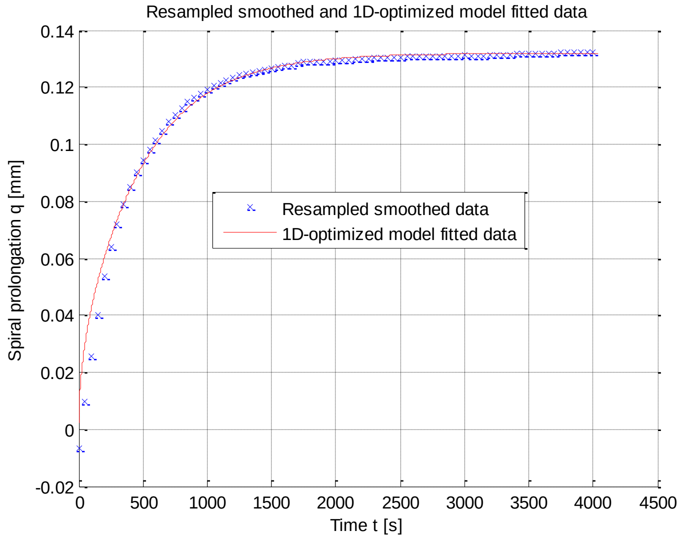

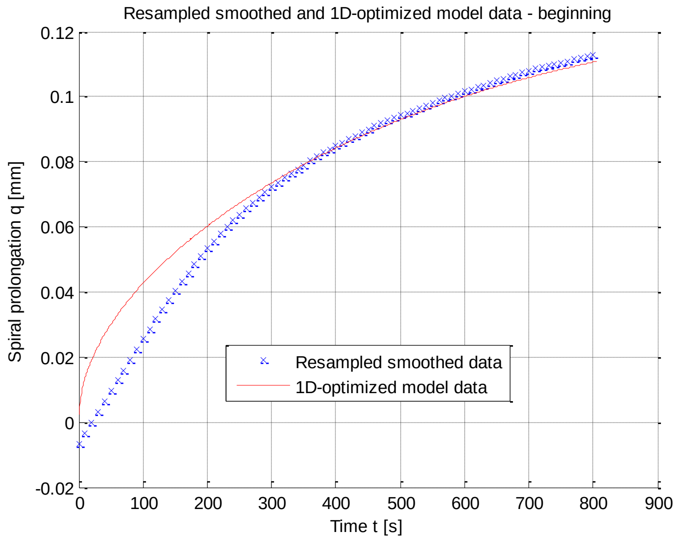

- **the course and results of 2D optimization**

```
Optimization is in progress!!!
Wait, calculation may take several minutes!!!

Results of 2D-optimization for smoothed data

Diffusion coefficient : 5.2483e-14 [m2/s]
Steady-state value    : 1.3181e-01 [mm]

Optimum found successfully for     0.5547 s!!!

Writing results to the output Excel spreadsheets!!!
Wait, data entry may take a few seconds!!!

4034 rows were written into the file data1.xls successfully !!!
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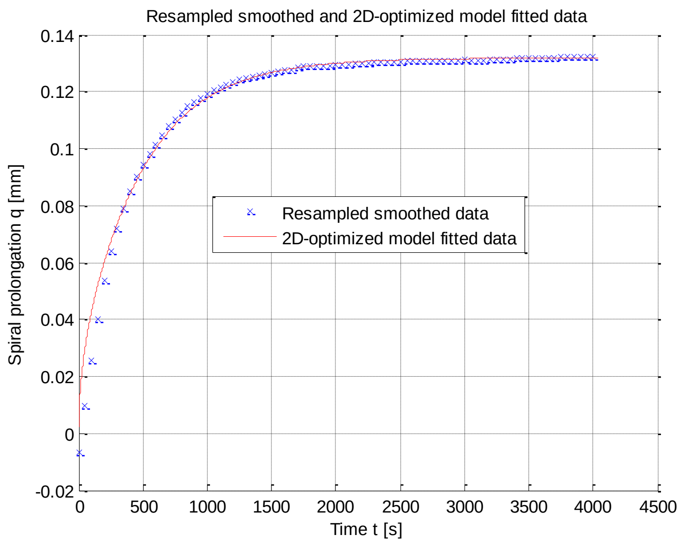
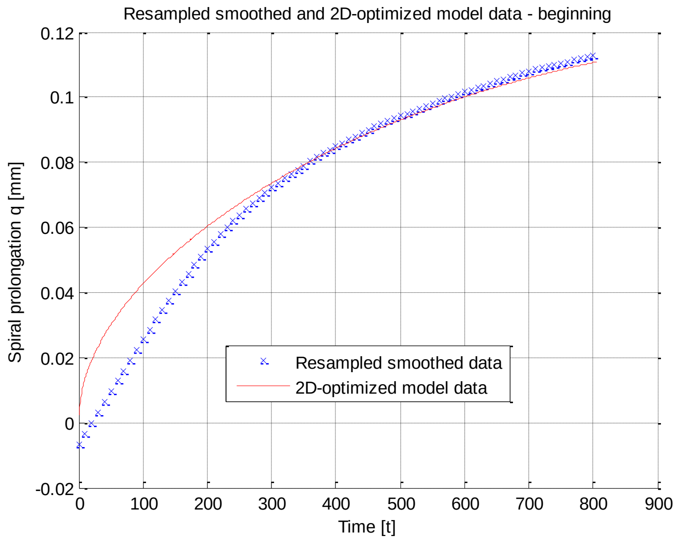
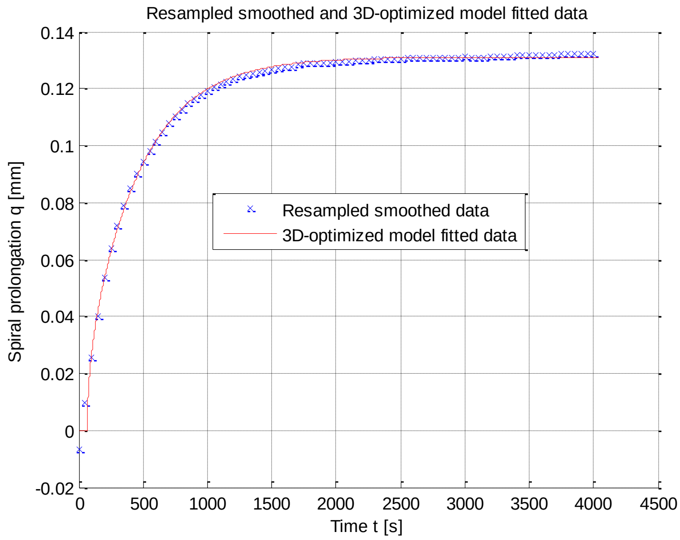
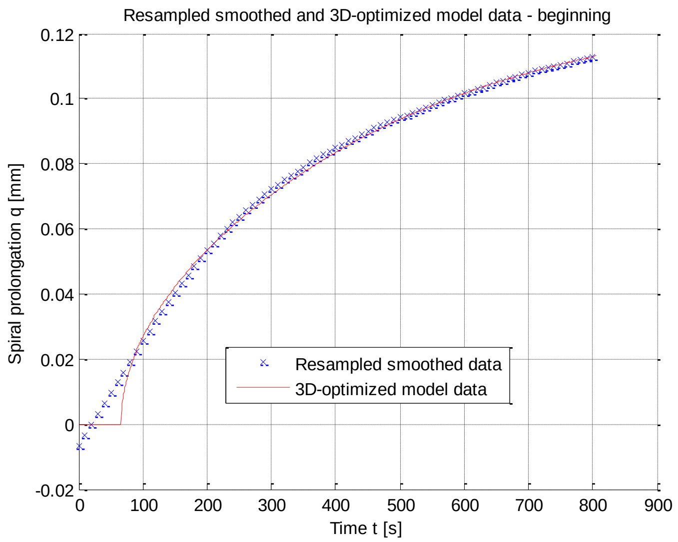




- **the course and results of 3D optimization**

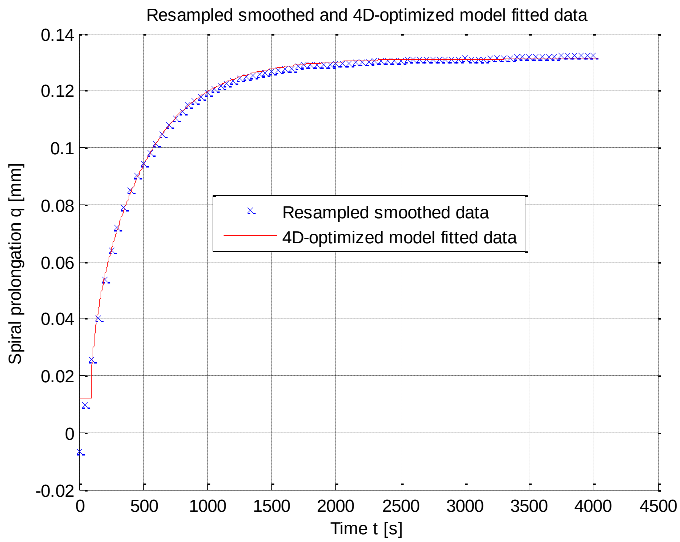
```
Optimization is in progress!!!
Wait, calculation may take several minutes!!!

Results of 3D-optimization for smoothed data

Diffusion coefficient : 6.2370e-14 [m2/s]
Steady-state value    : 1.3106e-01 [mm]
Signal time delay     : 6.6246e+01 [s]

Optimum found successfully for     1.1731 s!!!

Writing results to the output Excel spreadsheets!!!
Wait, data entry may take a few seconds!!!

4034 rows were written into the file data1.xls successfully !!!
```

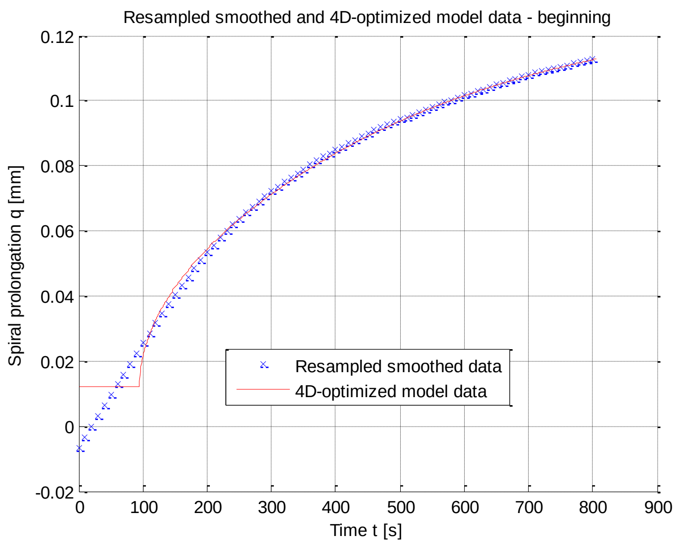




- **the course and results of 4D optimization**

```
Optimization is in progress!!!
Wait, calculation may take several minutes!!!

Results of 4D-optimization for smoothed data

Diffusion coefficient  : 6.0615e-14 [m2/s]
Steady-state value     : 1.1923e-01 [mm]
Signal time delay      : 9.4951e+01 [s]
Vertical shift of data : 1.1930e-02 [s]

Optimum found successfully for     3.5355 s!!!
Writing results to the output Excel spreadsheets!!!
Wait, data entry may take a few seconds!!!

4034 rows were written into the file data1.xls successfully !!!
```

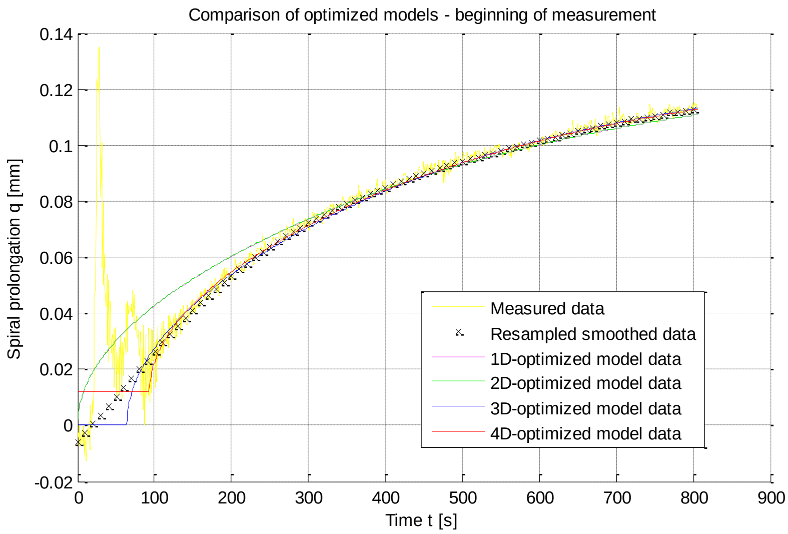




- **writing the results into the MS Excel workbook, sheet Results**

Time	Measured data	1D model data	2D model data	3D model data	4D model data
[s]	[mm]	[mm]	[mm]	[mm]	[mm]
0,26215	-0,004115	0,002180139	0,002181867	0	0,011947834
1,196285	-0,00263	0,004657219	0,00466091	0	0,011947834
2,197159	-0,00742	0,006311609	0,00631661	0	0,011947834
3,197085	0,000251	0,007613536	0,00761957	0	0,011947834
4,197192	-0,007634	0,008723459	0,008730372	0	0,011947834
5,197326	-0,001603	0,009707319	0,009715012	0	0,011947834
6,19725	-0,002736	0,010600072	0,010608472	0	0,011947834
7,128857	-0,006792	0,011368922	0,011377931	0	0,011947834
8,197185	-0,000396	0,012191066	0,012200727	0	0,011947834
9,196875	-0,011182	0,012913069	0,012923302	0	0,011947834
10,197044	-0,00207	0,013597106	0,013607881	0	0,011947834
11,196578	-0,012496	0,014247937	0,014259228	0	0,011947834
12,19697	-0,002759	0,014870833	0,014882618	0	0,011947834
13,196904	-0,001125	0,015468398	0,015480656	0	0,011947834
14,196702	-0,00307	0,016043645	0,016056359	0	0,011947834
15,19675	0,000902	0,016599105	0,016612259	0	0,011947834
16,197063	-0,008878	0,01713671	0,017150291	0	0,011947834
17,196601	0,007253	0,017657558	0,01767155	0	0,011947834
18,196707	-0,001349	0,018163759	0,018178153	0	0,011947834
19,196735	0,009404	0,018656192	0,018670976	0	0,011947834
20,196707	0,004094	0,019135931	0,019151096	0	0,011947834
...	...	...	...	...	...
61,194862	0,031399	0,033309399	0,033335796	0	0,011947834
62,194792	0,025574	0,033580436	0,033607047	0	0,011947834
63,194659	0,043592	0,033849286	0,03387611	0	0,011947834
64,195356	0,026414	0,034116237	0,034143273	0,001465688	0,011947834
65,194996	0,044358	0,034380838	0,034408083	0,004832281	0,011947834
66,194395	0,03966	0,034643354	0,034670807	0,006674469	0,011947834
67,194385	0,042778	0,034904049	0,034931709	0,008109171	0,011947834
68,194539	0,041986	0,035162854	0,035190719	0,009325892	0,011947834
69,195998	0,0403	0,035420102	0,035448171	0,010402574	0,011947834
70,195125	0,04324	0,035674903	0,035703173	0,011375648	0,011947834
71,194773	0,038853	0,035928028	0,035956499	0,012272254	0,011947834
72,194154	0,04832	0,036179315	0,036207985	0,013107457	0,011947834
73,19438	0,037182	0,036429079	0,036457947	0,013893184	0,011947834
74,194069	0,046616	0,036677009	0,036706074	0,014636403	0,011947834
75,193893	0,033658	0,036923308	0,036952568	0,015343758	0,011947834
76,193948	0,039112	0,037168031	0,037197485	0,016020063	0,011947834
77,193889	0,033029	0,037411126	0,037440773	0,016668878	0,011947834
78,194738	0,031173	0,03765287	0,037682708	0,017293925	0,011947834
79,193574	0,034565	0,03789259	0,037922618	0,017895963	0,011947834
80,193572	0,024984	0,038131079	0,038161296	0,018479063	0,011947834

- **calculation of parameters for the modified mathematical model**: An effective nonlinear multidimensional optimization method must be used for calculation of the parameters of the modified mathematical model. The Nelder-Mead method [3] of flexible polyhedron (implemented as function fminsearch in Optimization Toolbox of Matlab program system [5]) is selected for its reliability. In addition, this method requires no knowledge of objective function derivatives. The sum of squared deviations between the values of smoothed sorption curve and the values calculated from equation (4) of the modified mathematical model of sorption in a plain sheet membrane is used as an objective function.



Discussion and results

For digital processing of data from gravimetric sorption experiments Savitzky-Golay filter was chosen on the basis of previous experience. Frequency analysis of Butterworth filter application [3] showed that the random noise contained in data is not frequency dependent. This enabled the use of simpler Savitzky-Golay filter, which unlike Butterworth filter, performs calculations in the time domain only and need not go to the frequency domain and back. For design of Savitzky-Golay filter is sufficient to choose just two simple parameters: degree of approximating polynomial and the window width for linear regression. Based on analysis of properties of the sorption curve (continuity, monotonicity, slow changes of derivatives, …), that was confirmed by the numerical experiments, it was shown that choice a linear polynomial as a polynomial approximation is sufficient. This reduces smoothing of the sorption curve only on the choice of a single parameter: the window width in that the regression is performed. A user selects this parameter conversationally, he can see the result in graphical form on the display immediately and can then evaluate all by visual comparison.
After elimination of the noise from the measured data is performed calculation of the best parameters of the model (4). This model has up to four adjustable parameters. All four parameters or only some of them can be selected for optimization calculations. The values of the remaining parameters are estimated and are assumed to be constant during optimization. The initial estimate of the integral diffusion coefficient is calculated using the half-time method from the equation (3). Other parameters are calculated with help of optimization or are estimated by averaging of appropriately selected parts of the experimental data.

Conclusions

A complex algorithm for calculation of the integral diffusion coefficient from the measured data from the gravimetric sorption experiments is developed. This algorithm is implemented in the integrated environment for technical computing MATLAB®. Experimental and calculated data are being displayed in all steps of digital processing of this time series. Some decisions in the course of digital processing of experimental data cannot be completely algorithmized; decisions have to be made interactively by an experienced expert. Therefore, decision making, selection of options and parameter setting procedure are carried out conversationally in the graphical environment by means of the interactive system of dynamical graphs and menus. For processing of experimental data method and procedures from the following areas are used: mathematical modelling, simulation and visualization, digital processing of discrete data and multidimensional nonlinear optimization. The main advantages of the described algorithm are:

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

Acknowledgements

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