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THE INFLUENCE OF THE DYNAMIC PARAMETERS OF THE CALORIMETRIC SYSTEM ON THE ACCURACY OF THE DETERMINATION OF THE THERMOKINETICS

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ABSTRACT

This work presents the influence of external and internal noises on the accuracy of the determination of thermokinetics as the function of the dynamic parameters of the calorimetric system at a given noise-to-signal ratio.

INTRODUCTION

The important problem in calorimetry is the determination of thermokinetics, that is the function describing the changes of heat power in time, connected with the examined heat process on the basis of the measurement of the calorimetric signal and the assumed model of the calorimetric system. Each measurement of the calorimetric signal is encumbered with a certain error connected with the external noise or the precision of the measurement itself.

This work discusses the choice of the sampling period at the given noise-to-signal ratio so as to eliminate the influence of noise on the quality of thermokinetic determinations. The dependence of the optimal sampling period on the order of the calorimetric system is demonstrated. The considerations were carried out on the basis of the multi-body theory.

FUNDAMENTAL EQUATIONS

Considering the calorimetric system as the system of bodies, which is placed in the constant temperature environment (shield), the general equation of heat balance has the form [1]

$$C_j \, d\Theta_j(t) + G_{0j}\Theta_j(t) \, dt + \sum_{i=1}^{N} G_{ij}\left[\Theta_j(t) - \Theta_i(t)\right] dt = dQ_j(t) \tag{1}$$

$j = 1, 2, \ldots, N; \; i \neq j$

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where N is the number of distinguished bodies, C_j is the heat capacity of body j, G_{0j} is the heat loss coefficient between body j and the environment, G_{ij} is the heat loss coefficient between body j and body i, $\Theta_j(t)$ is the function describing the changes of temperature of body j in time with respect to the environment temperature and $dQ_j(t)$ is the amount of heat generated in body j in the interval time dt.

The differential equation (1) normalized in the dimension of temperature is called the dynamic equation of the calorimetric system and has the form [1]

$$T_j \frac{d\Theta_j(t)}{dt} + \Theta_j(t) = \sum_{i=1}^{N} k_{ij}\Theta_i(t) + p_j f_j(t) \tag{2}$$

$j = 1, 2, \ldots, N;\ i \neq j$

where T_j is the time constant of body j, k_{ij} is the interaction coefficient between body j and body i, $f_j(t)$ is the forcing function whose course is proportional to the heat power generated in body j and p_j is a dimensionless coefficient, which is chosen so that the increment of temperature $\Theta_j(t)$ in the steady state (stationary state of exchange heat) is equal to the increment of the forcing function $f_j(t)$.

TRANSMITTANCE

The system of differential equations (2) can be written in matrix form as follows

$$\mathbf{T}\dot{\boldsymbol{\Theta}}(t) + \mathbf{A}\boldsymbol{\Theta}(t) = \mathbf{P}\mathbf{f}(t) \tag{3}$$

where $\mathbf{T}$ is the diagonal matrix whose elements are the time constants T_j, $\mathbf{P}$ is the diagonal matrix whose elements are the coefficients p_j, $\mathbf{A}$ is the matrix whose elements are $a_{jj} = 1$ and $a_{ij} = -k_{ij}$ for $i \neq j$, $\boldsymbol{\Theta}$ is the state vector, $\boldsymbol{\Theta}^{T} = [\Theta_1, \Theta_2, \ldots, \Theta_N]$, and $\mathbf{f}$ is the forcing vector, $\mathbf{f}^{T} = [f_1, f_2, \ldots, f_N]$.

Applying the Laplace transformation to eqn. (3) at zero initial conditions, we obtain

$$(s\mathbf{T} + \mathbf{A})\boldsymbol{\Theta}(s) = \mathbf{P}\mathbf{f}(s) \tag{4}$$

where $\boldsymbol{\Theta}(s)$ is the Laplace transform of the state vector $\boldsymbol{\Theta}(t)$ and $\mathbf{f}(s)$ is the Laplace transform of the forcing vector $\mathbf{f}(t)$. The solution of eqn. (4) is

$$\boldsymbol{\Theta}(s) = (s\mathbf{T} + \mathbf{A})^{-1}\mathbf{P}\mathbf{f}(s) \tag{5}$$

or

$$\boldsymbol{\Theta}(s) = \mathbf{H}(s)\mathbf{f}(s) \tag{6}$$

where

$$\mathbf{H}(s) = (s\mathbf{T} + \mathbf{A})^{-1}\mathbf{P} \tag{7}$$

is the transfer matrix and its elements are the transmittances $H_{ij}(s)$, which have the form

$$H_{ij}(s)=\frac{(-1)^{i+j}\,|s\mathbf{T}+\mathbf{A}|_{ji}\,|\mathbf{P}|}{|s\mathbf{T}+\mathbf{A}|} \tag{8}$$

where $|s\mathbf{T}+\mathbf{A}|$ is the determinant of the matrix $s\mathbf{T}+\mathbf{A}$, $|s\mathbf{T}+\mathbf{A}|_{ji}$ is the corresponding minor of the matrix $s\mathbf{T}+\mathbf{A}$ and $|\mathbf{P}|$ is the determinant of the matrix $\mathbf{P}$. These determinants, after development into a power series with respect to s, give polynomials of Nth- and Mth-degree, $(M<N)$, respectively

$$|s\mathbf{T}+\mathbf{A}|=\sum_{n=0}^{N} a_n s^n = F(s) \tag{9}$$

$$(-1)^{i+j}\,|s\mathbf{T}+\mathbf{A}|_{ji}\,|\mathbf{P}|=\sum_{k=0}^{M} b_{ij,k}s^k = F_{ij}(s) \tag{10}$$

Thus, the transmittance (8) can be written in the form

$$H_{ij}(s)=\sum_{k=0}^{M} b_{ij,k}s^k \Big/ \sum_{n=0}^{N} a_n s^n \tag{11}$$

or developing the nominator and the denominator of the transmittance (11) into first-degree factors

$$H_{ij}(s)=S_{ij}\prod_{k=1}^{M}\left(1+sL_{ij,k}\right)\Big/\prod_{n=1}^{N}\left(1+sM_n\right) \tag{12}$$

where $S_{ij}=b_{ij,0}/a_0$ is the static gain, $-1/L_{ij,k}$ is the root of the nominator of transmittance (the zero of the transmittance) and $-1/M_n$ is the root of the denominator of transmittance (the pole of the transmittance).

As can readily be observed, the poles of transmittance depend only on the parameters of the calorimetric system, but the zeros of the transmittance depend on the mutual localization of the heat source and the temperature sensor.

AMPLITUDE CHARACTERISTICS

Putting $s=j\omega$ in relationship (12), we obtain the spectrum transmittance $H_{ij}(j\omega)$ in the frequency domain ω

$$H_{ij}(j\omega)=S_{ij}\prod_{k=1}^{M}\left(1+j\omega L_{ij,k}\right)\Big/\prod_{n=1}^{N}\left(1+j\omega M_n\right) \tag{13}$$

The amplitude characteristics $A_{ij}(\omega)$ are described by the function

$$A_{ij}(\omega)=S_{ij}\prod_{k=1}^{M}\left(1+\omega^2L_{ij,k}^2\right)^{1/2}\Big/\prod_{n=1}^{N}\left(1+\omega^2M_n^2\right)^{1/2} \tag{14}$$

For sufficiently large values of frequency ω, the function $A_{ij}(\omega)$ can be approximated by the expession

$$\bar{A}_{ij}(\omega) = S_{ij}\omega^{-m} \prod_{k=1}^{M} L_{ij,k} \Big/ \prod_{n=1}^{N} M_n \tag{15}$$

where $m = N - M$. Taking logarithms of both sides of relationship (15)

$$y = -mx + p \tag{16}$$

where

$$y = \log \bar{A}_{ij},\ x = \log \omega,\ p = \log\left(S_{ij} \prod_{k=1}^{M} L_{ij,k} \Big/ \prod_{n=1}^{N} M_n \right) \tag{17}$$

As a result of relationship (16), the plot of the amplitude in co-ordinates ($\log \omega$, $\log A$) asymptotically approaches the line having a direction coefficient, $-m$, equal to the difference between the degree of the nominator and the degree of the denominator of the transmittance. Thus, the asymptotical plot enables the evaluation of the difference between the number of zeros and the number of poles the transmittance.

OPTIMAL SAMPLING PERIOD

As the criterion of choosing the optimal sampling period, it is assumed that

$$A_{ij}(\omega) = 10^{-q} \tag{18}$$

where 10^{-q} denotes the noise-to-signal ratio, and q corresponds to the number of the certain digits in the measurement of the calorimetric signal. In order to estimate the values of the sampling period h instead of $A_{ij}(\omega)$, the approximate values

$$\bar{A}_{ij}(\omega) = 10^{-q} \tag{19}$$

are assumed in eqn. (15). From relationships (15) and (19)

$$\omega^{-m} S_{ij} \prod_{k=1}^{M} L_{ij,k} \Big/ \prod_{n=1}^{N} M_n = 10^{-q} \tag{20}$$

Applying relationship (20), the formula of the optimal sampling period $h = 1/\omega$ has the form

$$h = 10^{-q/m} \left(S_{ij} \prod_{k=1}^{M} L_{ij,k} \Big/ \prod_{n=1}^{N} \right) M_n^{-1/m} \tag{21}$$

Thus the values of the constants $L_{ij,k}$ and M_n must be bigger than the sampling period with respect to the stability of the numerical solution. In the particular case when the number of the certain digits in the calorimetric measurement is equal to the difference between the number of poles and the number of zeros of the transmittance ($q = m$), the formula of the optimal sampling period takes the form

$$h = 0.1\left(S_{ij}\prod_{k=1}^{M} L_{ij,k} \Bigg/ \prod_{n=1}^{N} M_n\right)^{-1/m} \tag{22}$$

DISCUSSION

If the calorimetric system is the first-order inertial object with time constant M, which is described by the following equation

$$M\frac{\mathrm{d}\Theta(t)}{\mathrm{d}t} + \Theta(t) = f(t) \tag{23}$$

and assuming, that the input signal $f(t)$ has the shape of the sinusoidal vibration of amplitude A_{in} and frequency ν ($\nu = 2\pi/T$; T is the vibration period)

$$f(t) = A_{\mathrm{in}}\sin(\nu t) \tag{24}$$

then the ratio of the amplitude A_{ou} of the output signal and the amplitude A_{in} of the input signal is

$$A_{\mathrm{ou}}/A_{\mathrm{in}} = (1 + \nu^2 M^2)^{-1/2} \tag{25}$$

From relationship (25), it follows that the influence of external noise on the measured signal becomes smaller and smaller as the time constant M or the frequency ν becomes bigger. Thus, this influence decreases due to the number of time constants (poles). On the other hand, in the case of the determination of the input signal, the situation becomes completely different. Each time constant of the system increases the influence of the noise connected with the measured signal on the quality of the determination of the input signal.

The inverse situation occurs when the transmittance has zeros. The zeros increase the influence of the external noise on the accuracy of the calorimetric measurement. On the other hand, they reduce the influence of the internal noise on the accuracy of the determination of the input signal.

Consider, for example, a calorimetric system of time constant $M = 100$ s and sampling period $h = 1$ s. The reconstruction of an input signal $f(t)$, when the measured calorimetric signal is noise of normal distribution and amplitude $A_{\mathrm{ou}} = 0.05$, is shown in Fig. 1. This corresponds to the change in base line. As can be seen from this figure, a certain band around the average value of zero is obtained instead of the input signal $f(t)$.

Figure 2 shows the reconstruction of a constant input signal $f(t) = 100$ when the measured calorimetric signal $\Theta(t)$ is the response of the calorimet-

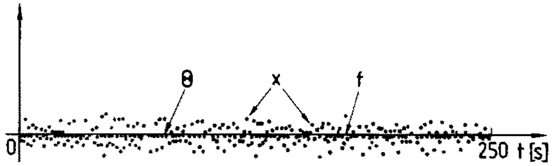

Fig. 1. Plots of the output signal Θ (continuous line), the known null input signal f (continuous line) and the reconstructed input signal x (dots).

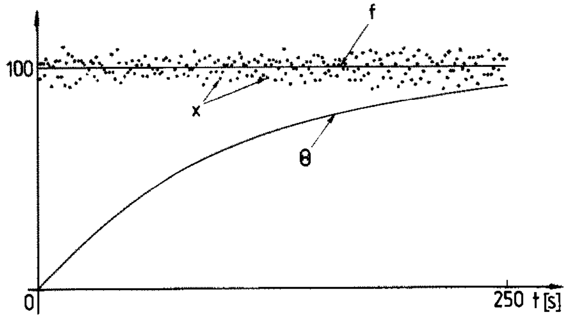

Fig. 2. Plots of the output signal Θ (continuous line), the known constant input signal f (continuous line) and the reconstructed input signal x (dots).

ric system to this effect, modulated by noise of normal distribution of amplitude $A_{ou} = 0.05$.

The reconstruction of an input signal $f(t)$

$$f(t) = 400\ [\exp(-t/40) - \exp(-t/20)]$$

when the measured calorimetric signal $\Theta(t)$ is the response of the calorimetric system to this effect, modulated by noise of normal distribution of amplitude $A_{ou} = 0.05$, is given in Fig. 3.

As can be seen in these figures, a band around the input signal $f(t)$ is obtained instead of the signal. A similar phenomenon was observed in the

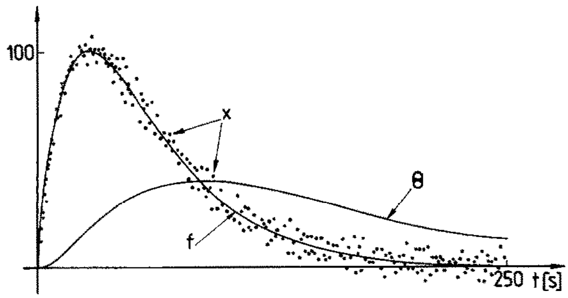

Fig. 3. Plots of the output signal Θ (continuous line), the known changing input signal f (continuous line) and the reconstructed input signal x (dots).

calorimetric investigations of calcium phosphate precipitation in relation to solution composition and temperature [2]. The problem of kinetic limits in the determination of thermokinetics was discussed in a previous paper [3]. The conditions of uniqueness for the determination of thermokinetics were reported in other papers [4,5].

CONCLUSIONS

As a result of these considerations, at a given precision of the measurement, it is possible to determine the input signal with a certain accuracy in spite of the optimal sampling period used. In order to increase the accuracy of the determination of the input signal, it is necessary to increase the precision of the measurement.

As a result of these considerations, there is a relationship between the number of determined parameters of the calorimetric system and the quality of the measured signal. When the signal-to-noise ratio is low, it is not reasonable to take into account a great number of dynamic parameters. While choosing a dynamic model of a given calorimetric system and determining its parameters by different methods, it is necessary to evaluate the adequacy of the model when describing the real system.

All calorimetric systems have similar relative frequency characteristics. This permits the estimation of the dynamic possibilities of an apparatus and the measurements for a given value of the signal-to-noise ratio. It is necessary to choose a sampling period which would eliminate the influence of noise on the accuracy of the determination of thermokinetics as much as possible.

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