INTERVAL APPROACH TO IDENTIFICATION OF PARAMETERS OF EXPERIMENTAL PROCESS

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Topics of presentation

I. Experimental process and its models.

II. Conditions of uncertainty and diffficulties in identification of parameters.

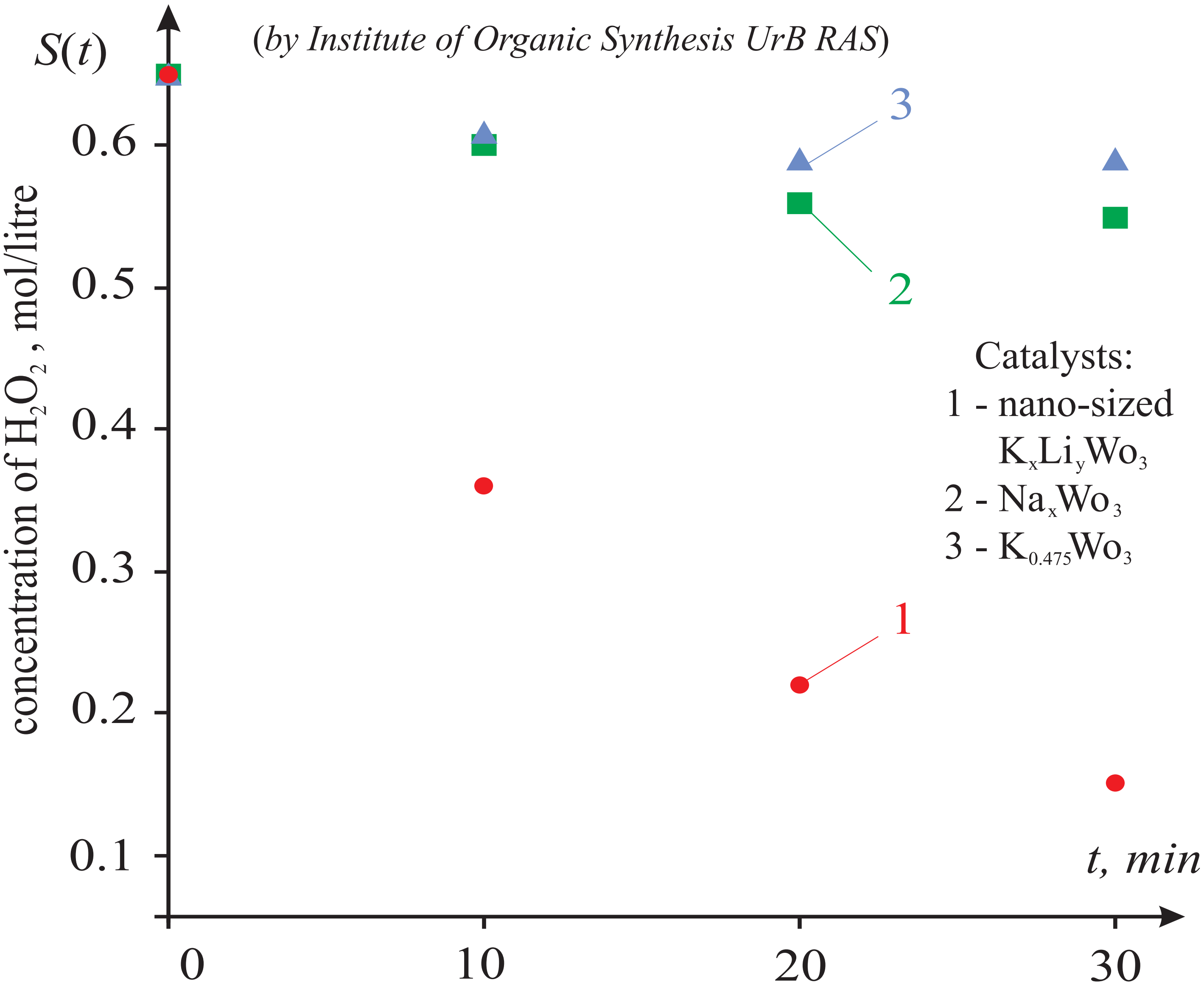
III. Inability of the standard statistical approach.

IV. Interval approach.

V. Practical examples.

VI. Conclusions.

I. Experimental process [1]: decomposition of H_2O_2 on bronzes; experiments with high accuracy



Possible models of the experimental process [2 – 4]

Polynomial: $S(t) = At^3 + Bt^2 + Ct + D,\ \ A > 0.$

Single exponent: $S(t) = A\exp(\alpha t),\ \ A > 0,\ \alpha < 0.$

Exponent with a background: $S(t) = A\exp(\alpha t) + BG$, $A > 0,\ \alpha < 0,\ BG > 0.$

Sophisticated exponent with a background: $S(t) = A\exp(\alpha t + \beta t^2) + BG$, $A > 0,\ \alpha < 0,\ \beta < 0,\ BG > 0.$

Various catalysts (including advanced nano-sized ones) are investigated: the process curve, values of its parameters, and activity (the process on the derivative).

Conditions of the experiment: fixed volume and initial concentration of the standard reactant H_2O_2; fixed volume and initial concentration of various catalysts to be tested; the same (standard) environmental conditions of the experiment (temperature, pressure, etc.); the same (standard) procedures of measuring the reactant concentration versus the time of the decomposition reaction.

The measuring procedure is indirect that implies appearance not only the primary measuring errors, but, also, additional chaotic corruptions in measured values of the reactant concentration.

II. Identification of the process parameters

Several topics of interest:
– previous validity analysis of various models of the the process;
– for valid model, finding pointwise estimates of its parameters that could serve as approximate "trend" values.

The main problem is to construct the set of admissible values of the process parameters with more subtle description of its structure than by usual rough outer approximate box-estimation.

Peculiarities of the experimental data to be processed:
– very short sample and relatively short time interval of observation of the reaction;
– as mentioned above, there are both usual (small) fluctuation error and possible chaotic component in the summary error of each measurement;
– complete absence of any probabilistic characteristics of both components in the error.

Conditions of uncertainty and model of measurement corruption

As a result, one should work under conditions of uncertainty. The following practical information about corruptions in measurements could be reasoned:

– it is possible to show an approximate bound onto the maximal (in modulus) value of the summary error;

– the model of corrupting each measurement, for example, the most popular is one

$$s_n = S(t_n) = S^*(t_n) + e_n,\ n = 1, N,$$
$$e_n = e_n^{\text{eqp}} + \chi_n,$$
$$|e_n| \leq e_{\text{max}},$$

where s_n is a measurement at the instant t_n; $S^*(t_n)$ is an unknown true value to be measured; N is the sample length; e_n is the summary error constrained in modulus by the value e_{max} and comprising of the equipment e_n^{eqp} and chaotic χ_n components.

Violations of conditions for application of the statistical approaches [5 – 7] *lead to serious consequences*

The sample is too short.

No information on probability characteristics of the measuring error.

Measuring error contains possible chaotic component, *i.e.*, shifts.

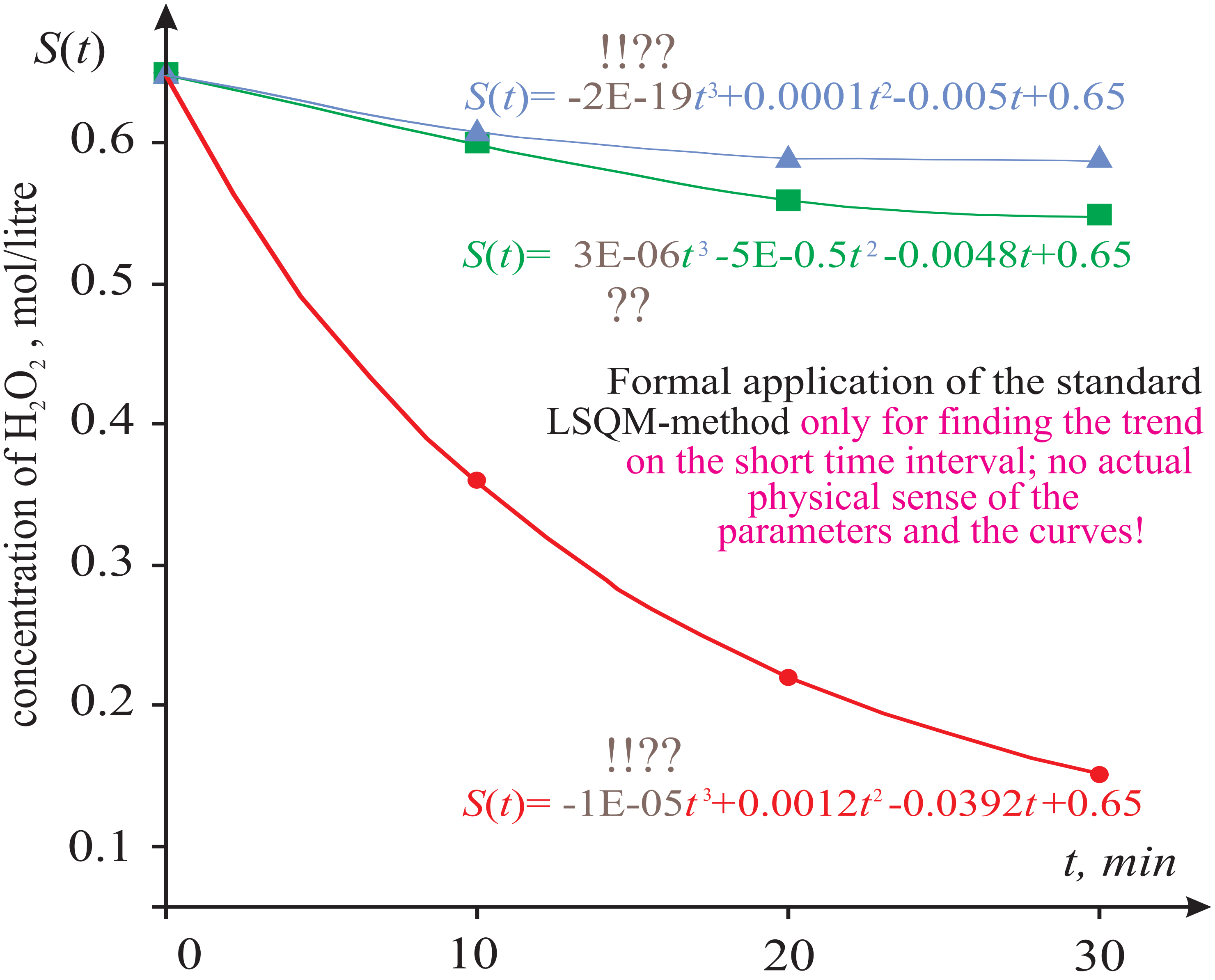
No information on possible dependence of errors between neighbor measurements.

The notions of the "confidence probability" and corresponding "confidence interval of parameter" lose the sense.

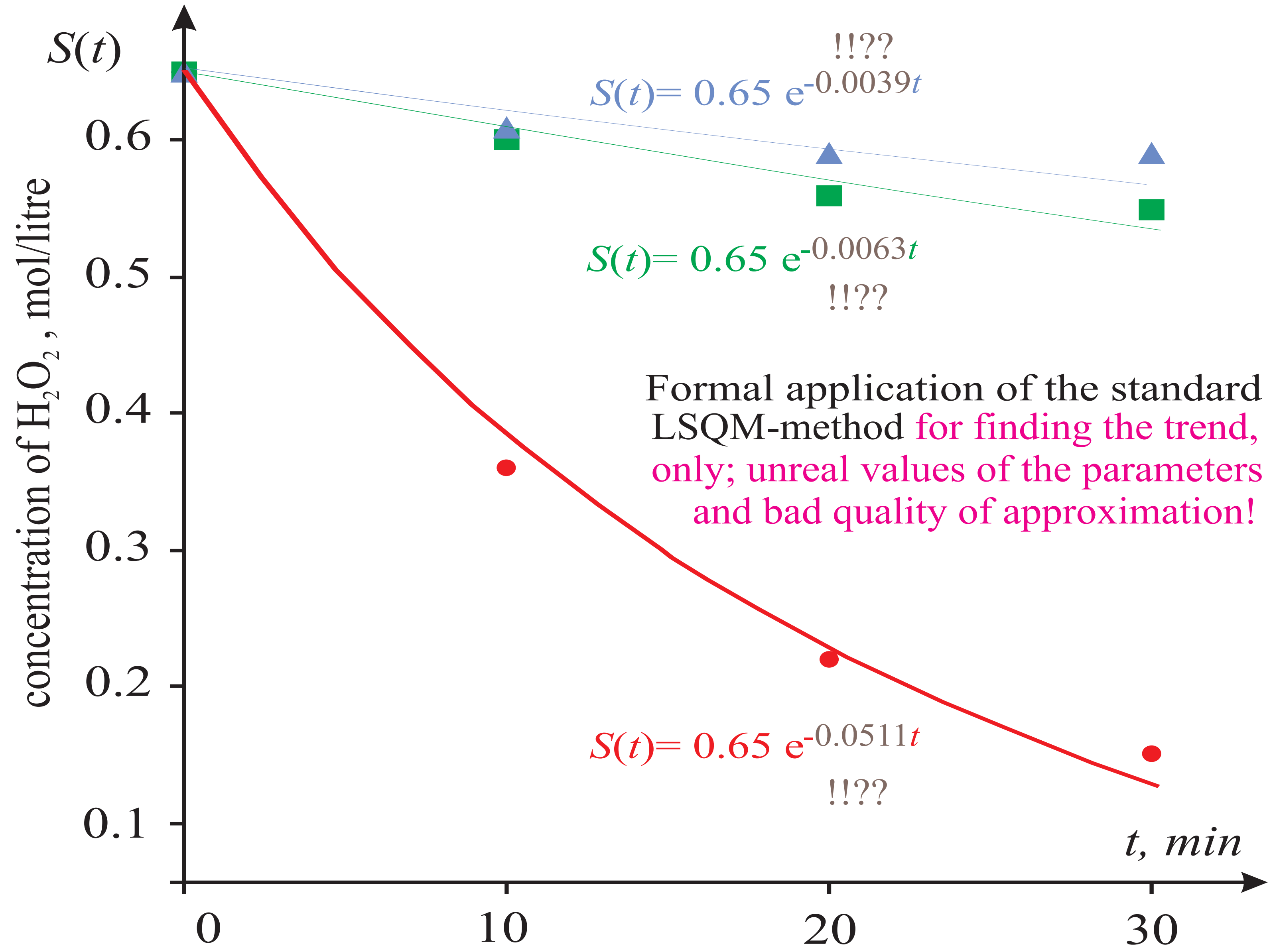
As a result, it becomes problematic to find any intervals of possible parameter values and corresponding tube of possible trajectories of the process under investigation.

Now, it would be very interesting to illustrate these consequences on practical examples.

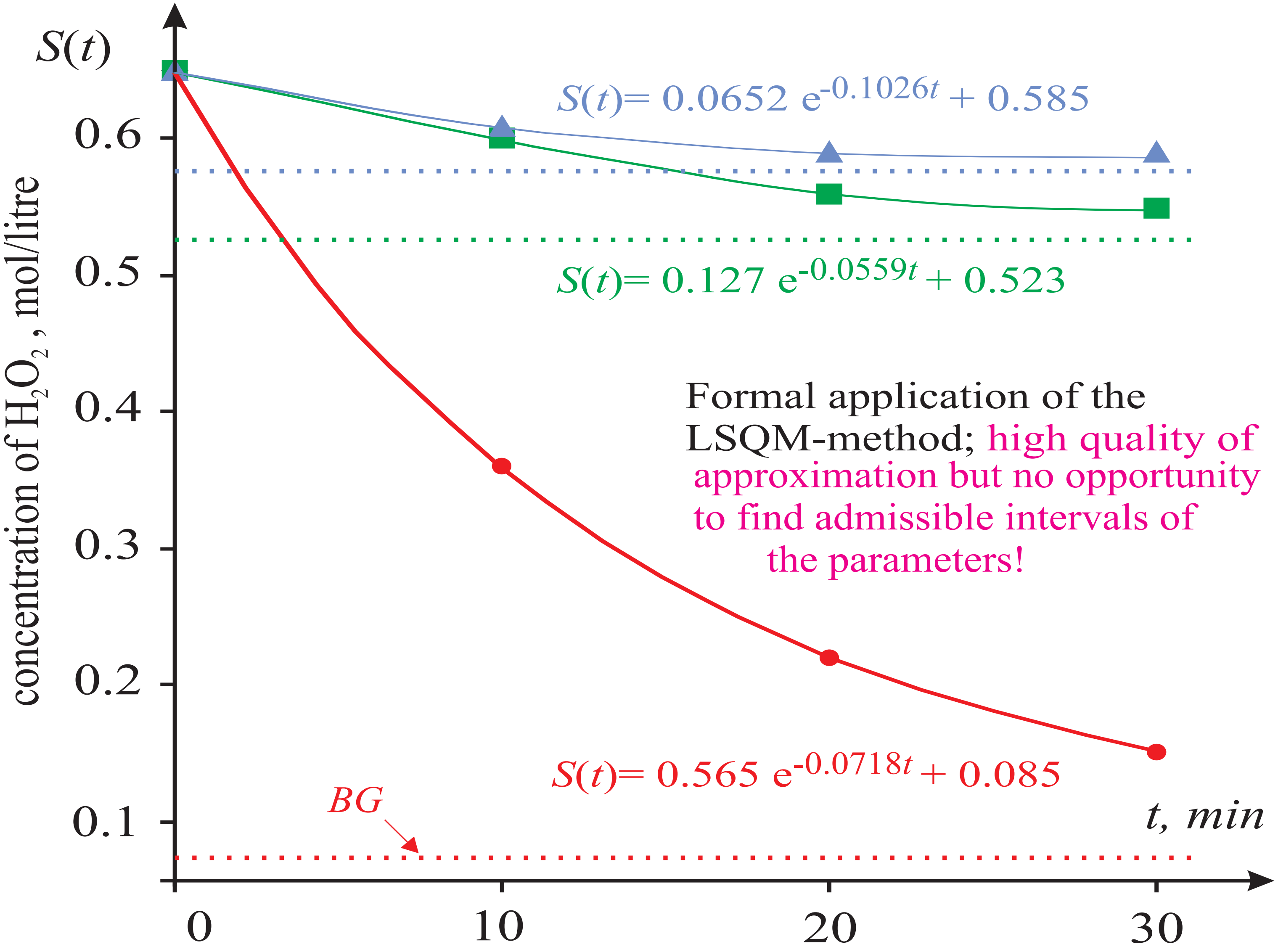
III. Inability of the standard statistical approach. Polynomial model of the process is invalid



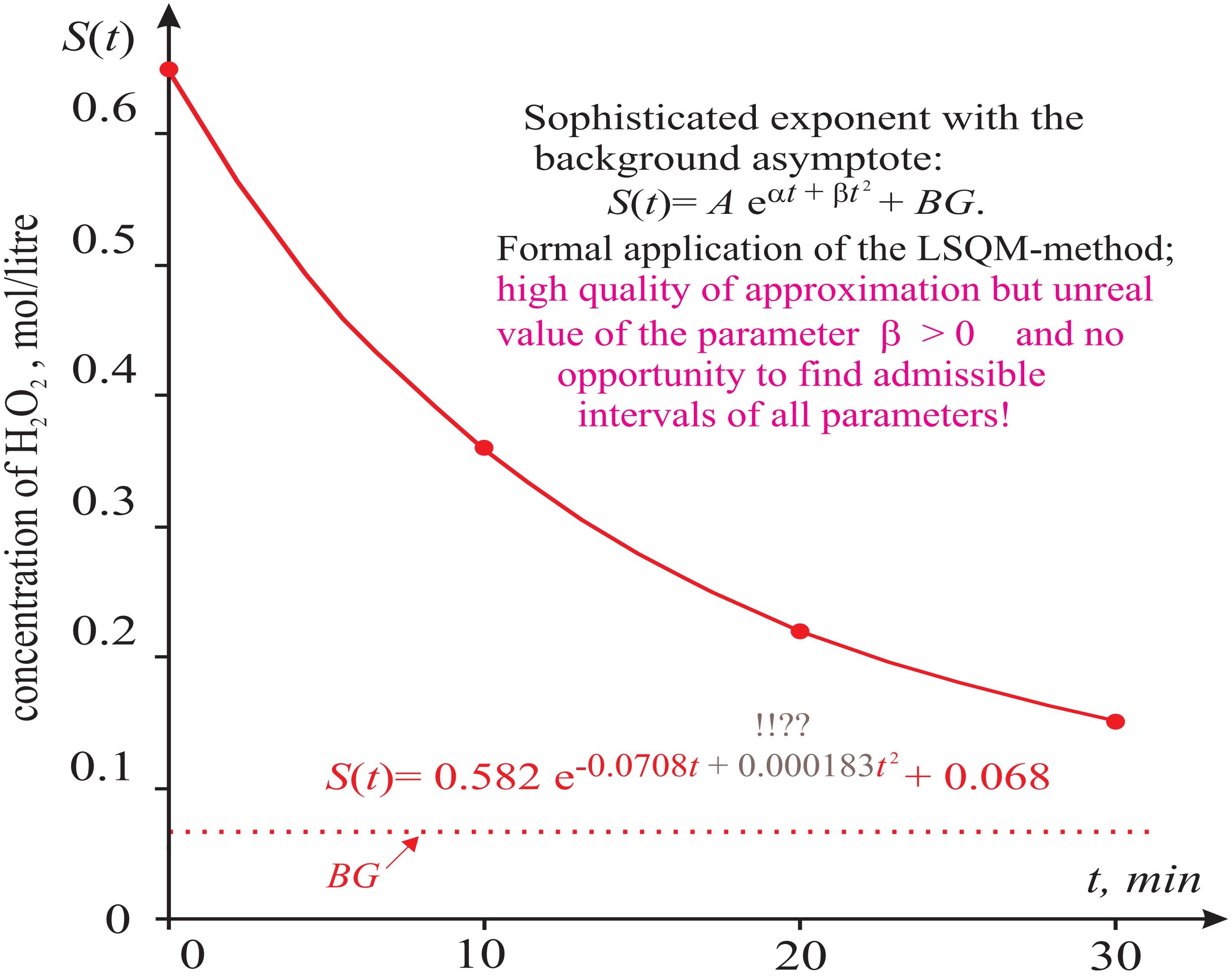
Inability of the standard statistical approach. Single exponent model contradicts to accuracy of the experiment



Exponent with the background asymptote; inability of the standard statistical approach even with additional information about exhausting the catalyst



The most active nano-sized catalyst; sophisticated exponent; inability of the standard statistical approach even with information about exhausting the catalyst



Then, what should be done to overcome the heritage of uncertainty and to construct the desirable set of the process parameters?

After refusal of the statistical paradigm and passage to the interval description of the summary corruption in measurements, the situation changes crucially and becomes constructive.

IV. Interval approach [8 – 10]*; the main notions* [11 – 13]

A sample $\{t_n, s_n\}$, $n = 1, N$;

A model of corruption $s_n = S^*(t_n) + e_n$, $n = 1, N$, with the interval constraint (bound) onto the summary error $|e_n| \le e_{\text{max}}$;

A describing function (dependence) $S(t) = f(t, p)$ with the argument t and the parameter vector p.

Uncertainty set of each measurement (USM), *i.e.*, the interval $\mathbf{s}_n = [\underline{s}_n, \overline{s}_n]$, $\underline{s}_n = s_n - e_{\text{max}}$, $\overline{s}_n = s_n + e_{\text{max}}$.

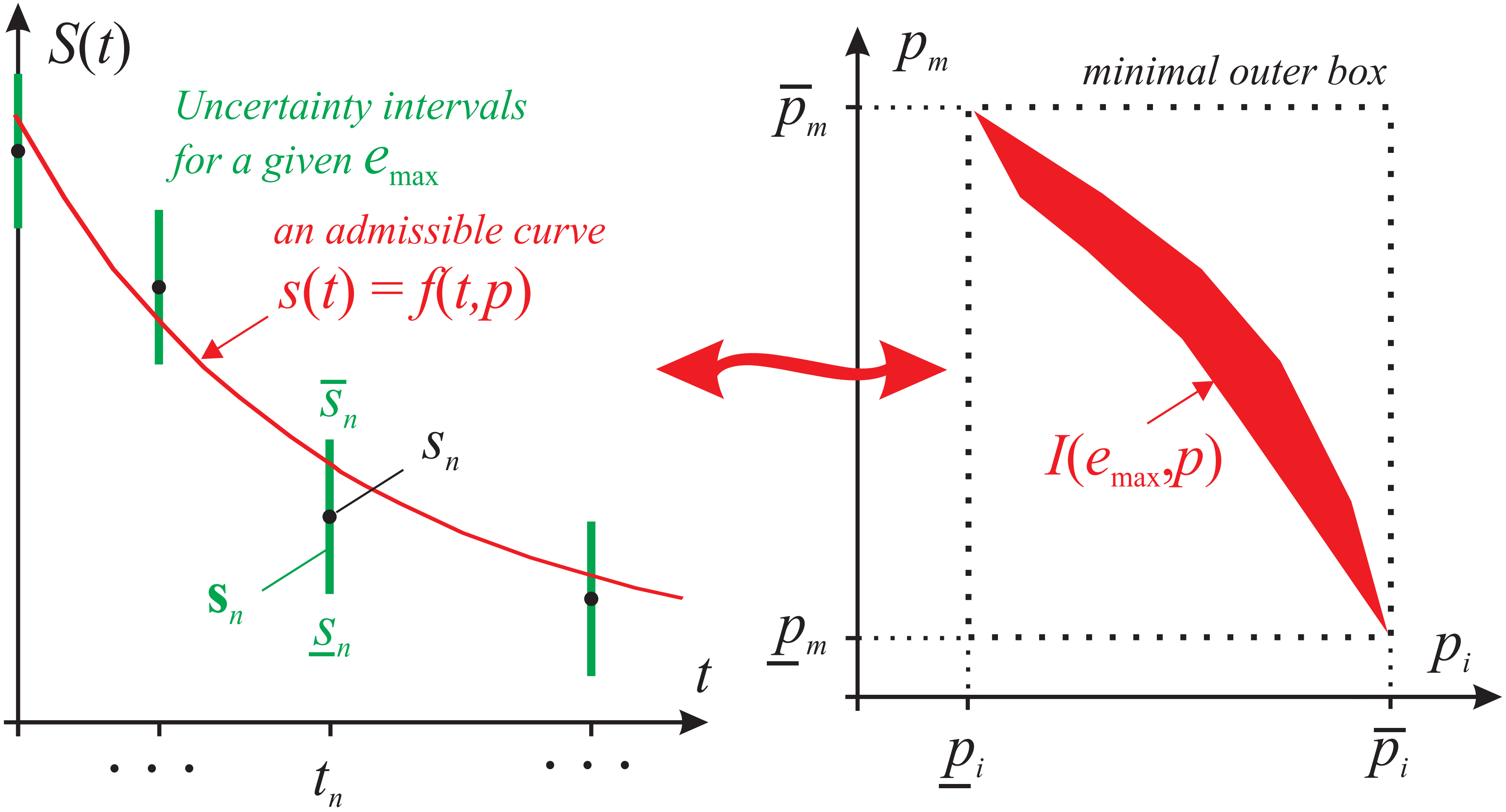
Admissible value p of the parameter vector and corresponding admissible dependence $\big(p, f(t, p)\big)$: $f(t_n, p) \in \mathbf{s}_n$, for all $n = 1, N$.

Informational set (INFS) (the set of membership), *i.e.*, the totality of all values p, for which $I(e_{\text{max}}, p) = \Big\{p : f(t_n, p) \in \mathbf{s}_n,$ for all $n = 1, N\Big\}$.

Consistent sample: if for the given e_{max}, $I(e_{\text{max}}, p) \ne \varnothing$, or inconsistent sample: if $I(e_{\text{max}}, p) = \varnothing$.

The tube of admissible dependences (TAD), *i.e.*, the totality of all dependences, for which $T(t) = \Big\{f(t, p) : f(t_n, p) \in \mathbf{s}_n,$ for all $n = 1, N$ and $p \in I(e_{\text{max}}, p)\Big\}$.

Illustration to the notions



Interval approach, developed "grid–analytical" technology [11 – 13] ***with exact description of the INFS sections***

1. Transformation [7,11-13] of the original nonlinear (in a general case) function to one with linear dependence on the parameters to be estimated. For example, in the case under consideration (Model 2):
$S(t) = A\exp(\alpha t + \beta t^2) + BG \Rightarrow \left(S(t) - BG\right) = A\exp(\alpha t + \beta t^2) \Rightarrow \mathrm{Ln}\left(S(t) - BG\right) = \mathrm{Ln}A + \alpha t + \beta t^2 \Rightarrow \mathrm{Ln}\left(S(t) - BG\right) - \beta t^2 = \mathrm{Ln}A + \alpha t.$
2. Introducing the grid $\{\beta_k,\ k = 1, K\}$ in β on some possible (by practical reasons) interval $\beta_{\min} = \underline{\beta}$, $\beta_{\max} = \overline{\beta}$. Similarly, introducing the grid $\{BG_j,\ j = 1, J\}$ in BG on some possible (by practical reasons) its interval $BG_{\min} = \underline{BG}$, $BG_{\max} = \overline{BG}$.
3. As a result, under given value of the bound $e_{\max}$, for the interval $\mathbf{s}_n$ of each measurement s_n, each node β_k, and each node BG_j, we obtain the following system of interval linear double-side inequalities for parameters $\mathrm{Ln}A$ and α: $\mathrm{Ln}A + \alpha t_n \in \mathrm{Ln}\left(\mathbf{s}_n - BG_j\right) - \beta_k t_n^2$, $n = 1, N$, $k = 1, K$, $j = 1, J$.
4. Solving the system, the desirable informational set $I(e_{\max}, \mathrm{Ln}A, \alpha, \beta, BG)$ is constructed as a collection of its exact cross-sections in the plane $\mathrm{Ln}A \times \alpha$: $\left\{I(e_{\max}, \mathrm{Ln}A, \alpha, \beta_k, \{BG_j(\beta_k)\}\right\}$ for each node $k = 1, K$, $j = 1, J(\beta_k)$.

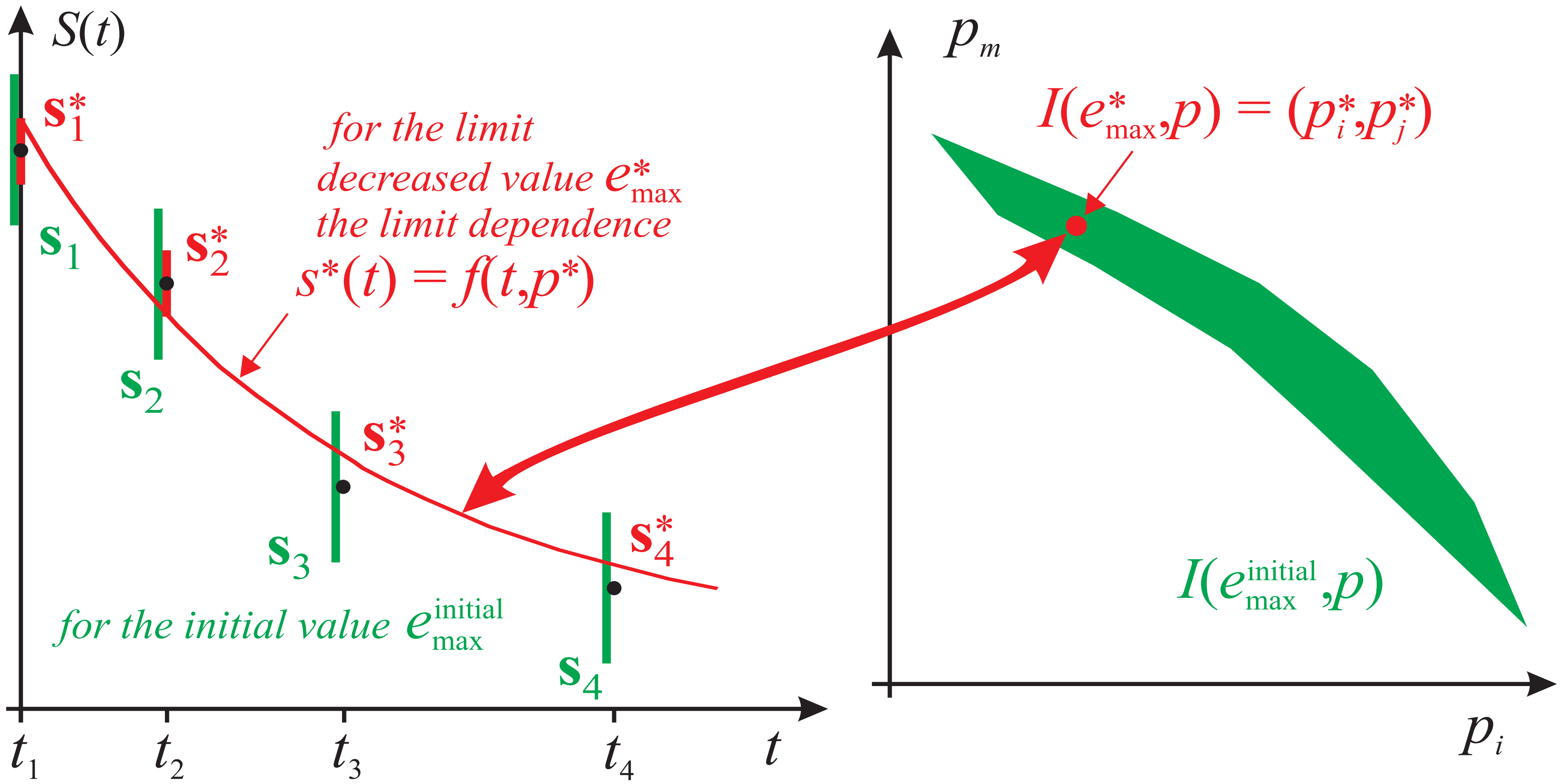
Interval approach, developed "grid–analytical" technology [11 − 13] *with exact description of the INFS sections; another techniques of linearization*

For Model 2 (similarly for Model 1), introducing the grid $\{\beta_k,\ k = 1, K\}$ in β on some possible (by practical reasons) interval $\beta_{\text{min}} = \underline{\beta}$, $\beta_{\text{max}} = \overline{\beta}$ and, similarly, introducing the grid $\{\alpha_j,\ j = 1, J\}$ in α on some possible (by practical reasons) its interval $\alpha_{\text{min}} = \underline{\alpha}$, $\alpha_{\text{max}} = \overline{\alpha}$, one obtains:

$$S(t) = A\exp(\alpha t + \beta t^2) + BG \ \Rightarrow\ S(t_n) = A\ \exp(\alpha_j t_n + \beta_k t_n^2) + BG \ \Rightarrow$$
$$S(t_n) = A z_{n,j,k} + BG, \quad \text{where, } z_{n,j,k} = \exp(\alpha_j t_n + \beta_k t_n^2).$$

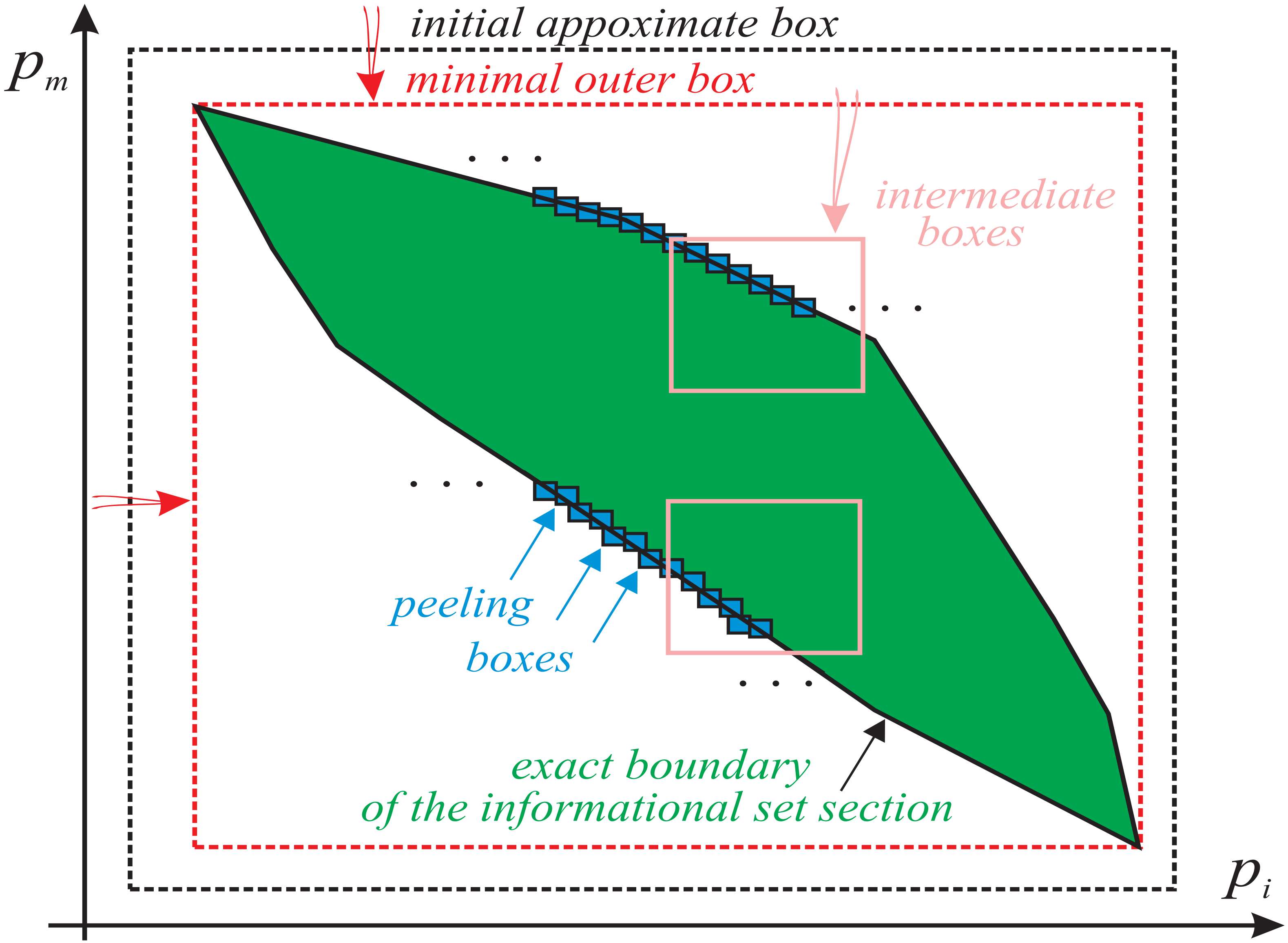
Again, under a given value of the bound e_{max}, for the interval $\mathbf{s}_n$ of each measurement s_n, each node α_j, and each node β_k, we obtain the following system of interval linear double-side inequalities for parameters A and BG: $\quad A z_{n,j,k} + BG \in \mathbf{s}_n,\ \ n = 1, N,\ k = 1, K,\ j = 1, J.$

Interval approach. Special procedure [11 – 13]*: opportunity of estimating (from below) the actual level of corruptions in the sample*

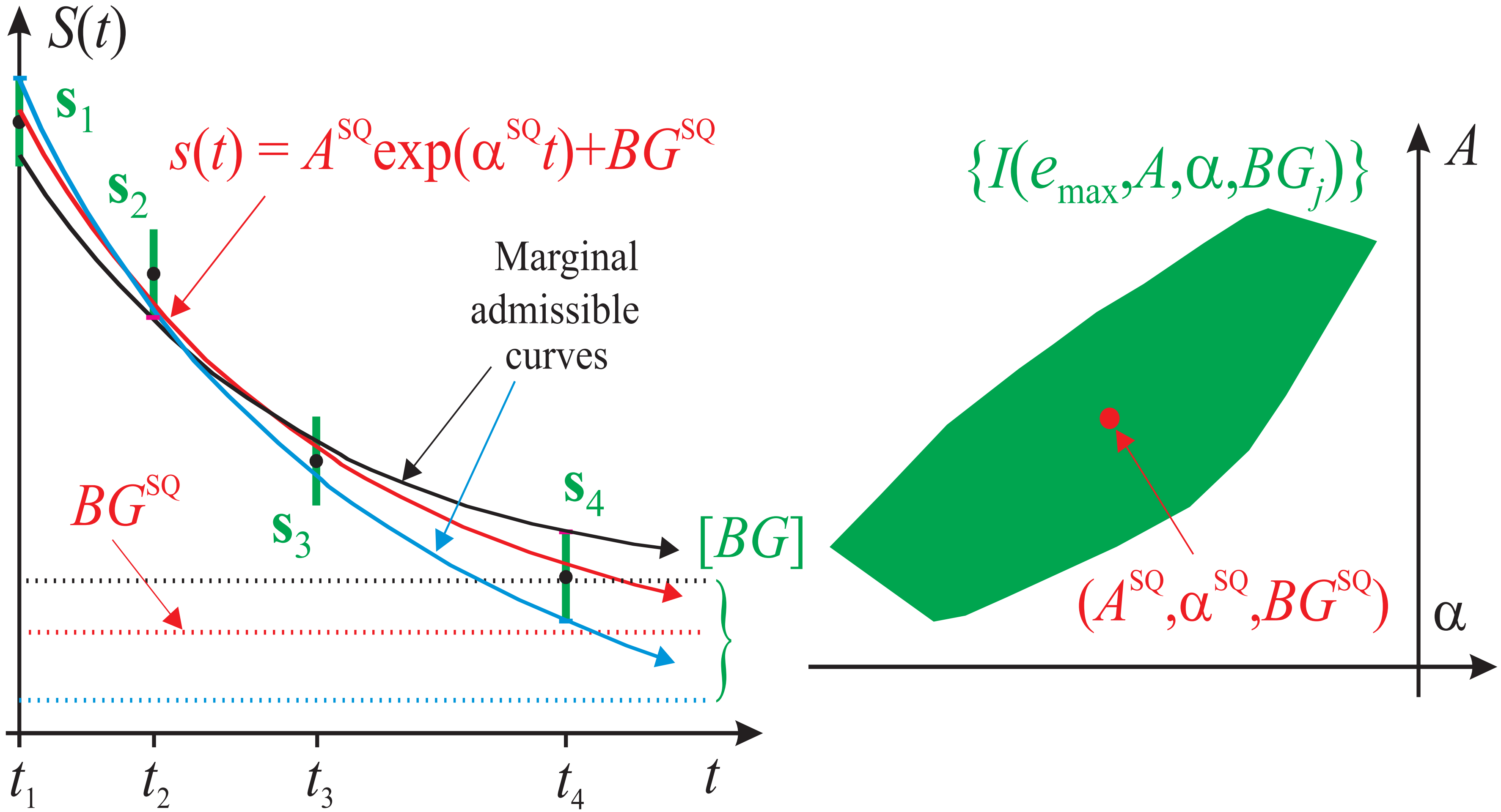


Limit values for Model 1, e^*_{max} : 0.0015 , 0.0042 , and 0.0050 for curves 1, 2, and 3.

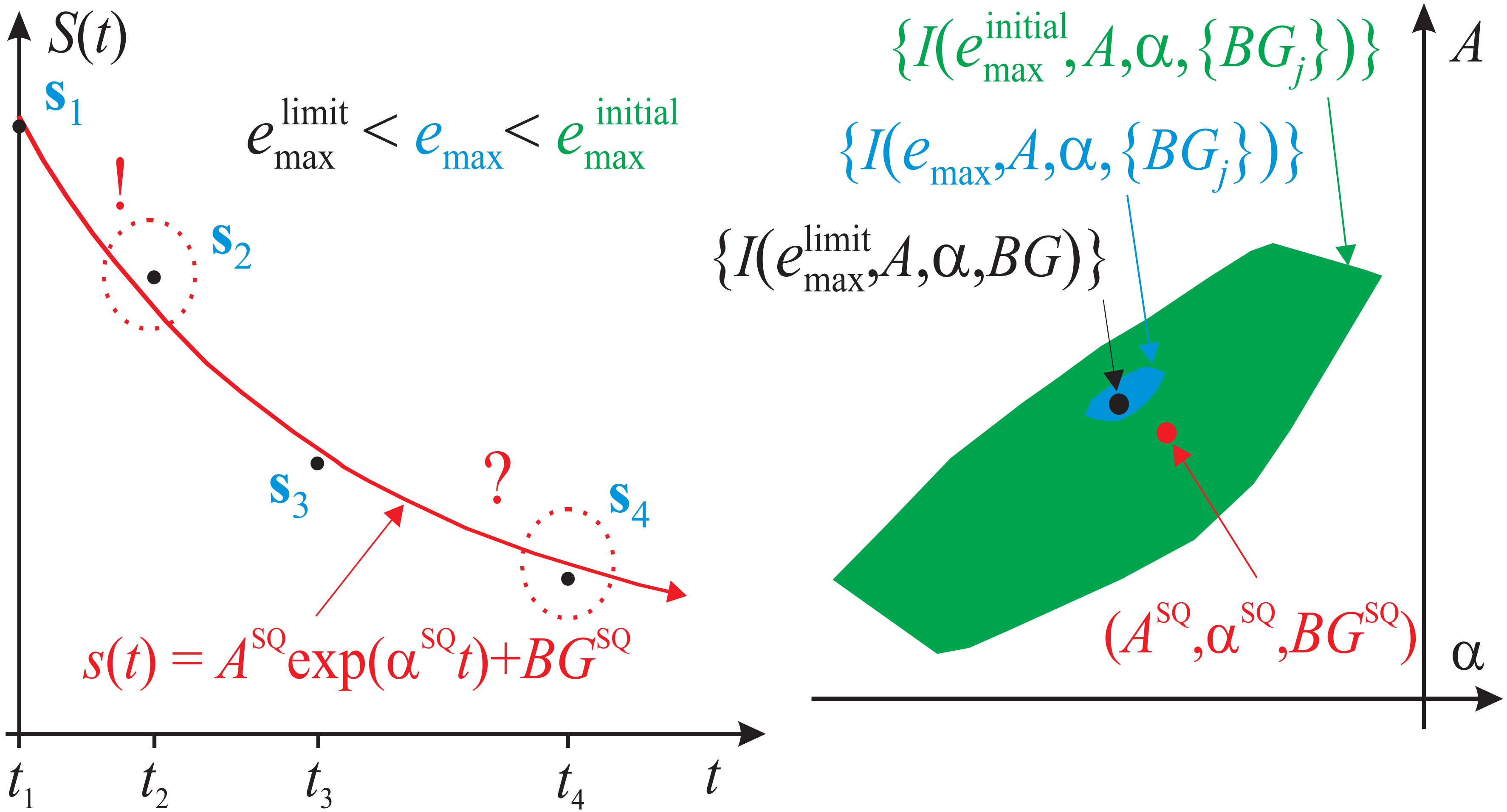
Role of transforming the initial dependence to linear one on parameters; usual box (parallelotope) procedures



Incompleteness of the statistical approach results when formally applied!



Inadmissible results of formal application of the statistical approach!

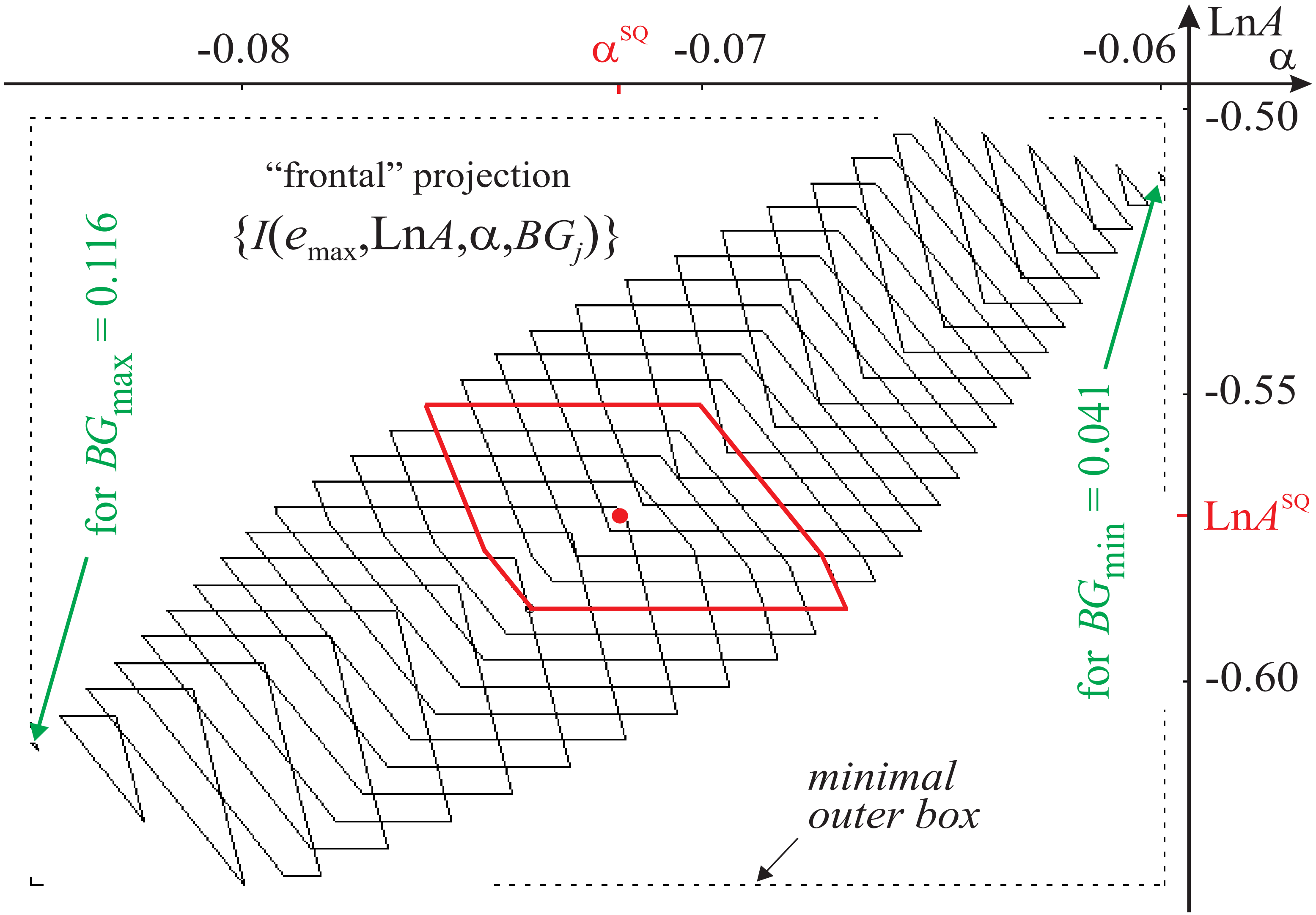


Important detail of the interval approach

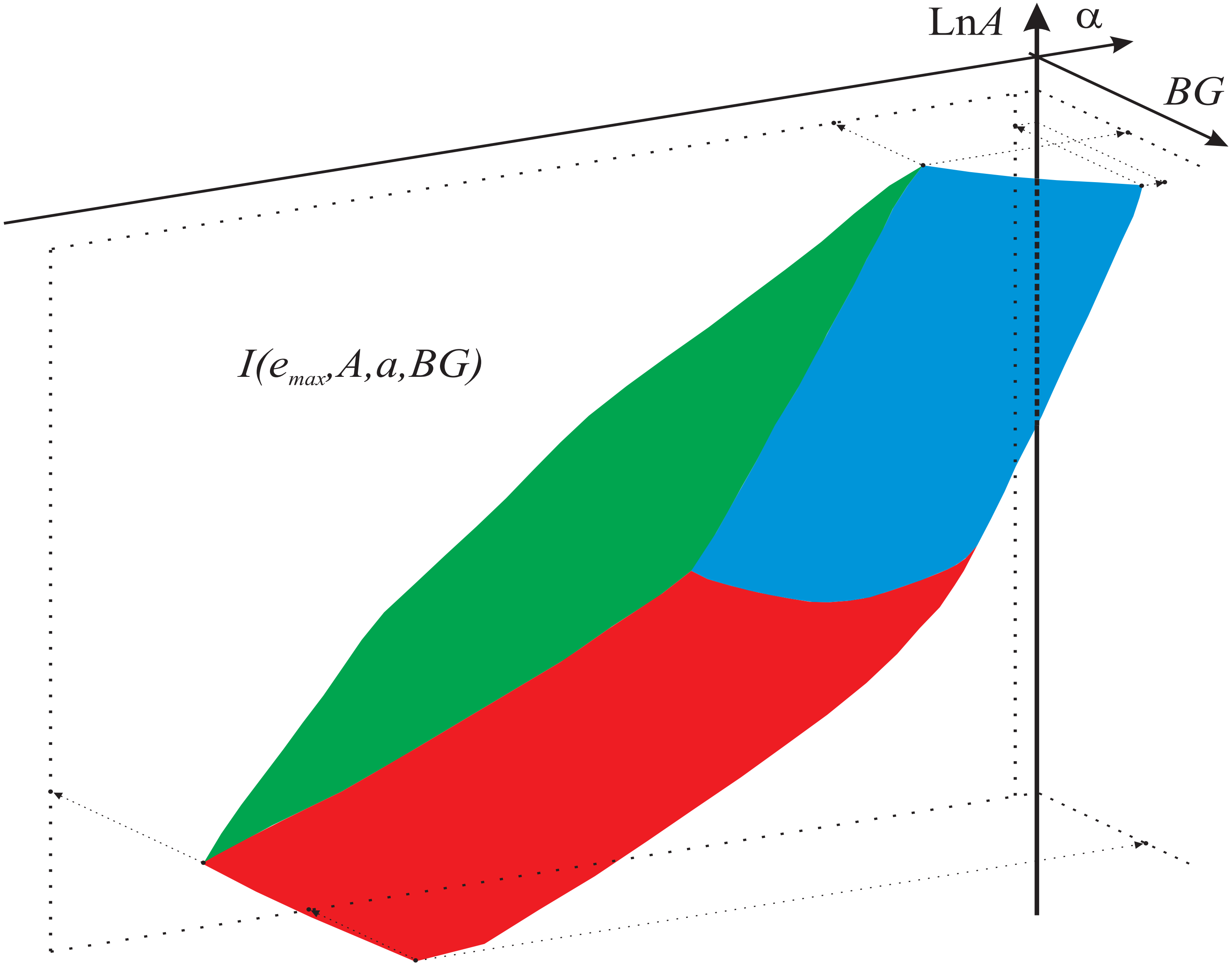
Under mentioned uncertainty, the notion of "confidence probability" loses the sense. Its role is played by the bound $e_{\max}$ of a variable level.

The work with the variable value $e_{\max}$ is absolutely transparent and convenient for the researcher.

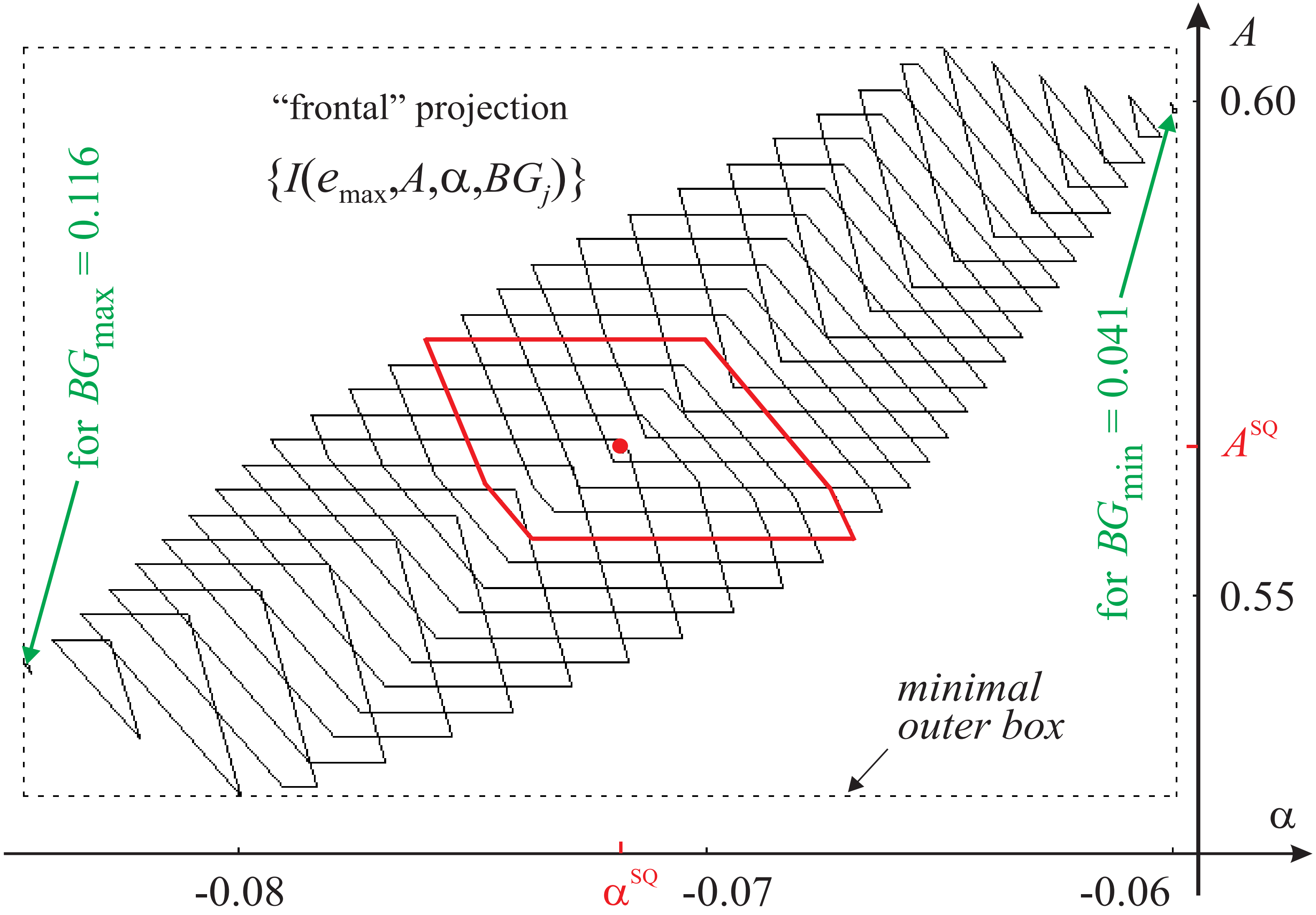
V. Practical examples. Model 1 ($\beta \equiv 0$), curve 1, sections of the informational sets on the grid $\{BG_j\}$, $e_{\max} = 0.01$



Practical examples. Model 1 ($\beta \equiv 0$), curve 1, informational set, general three-dimensional image



Practical examples. Model 1 ($\beta \equiv 0$)*, curve 1, sections of the informational sets on the grid* $\{BG_j\}$, $e_{\max} = 0.01$*, in the natural scale*



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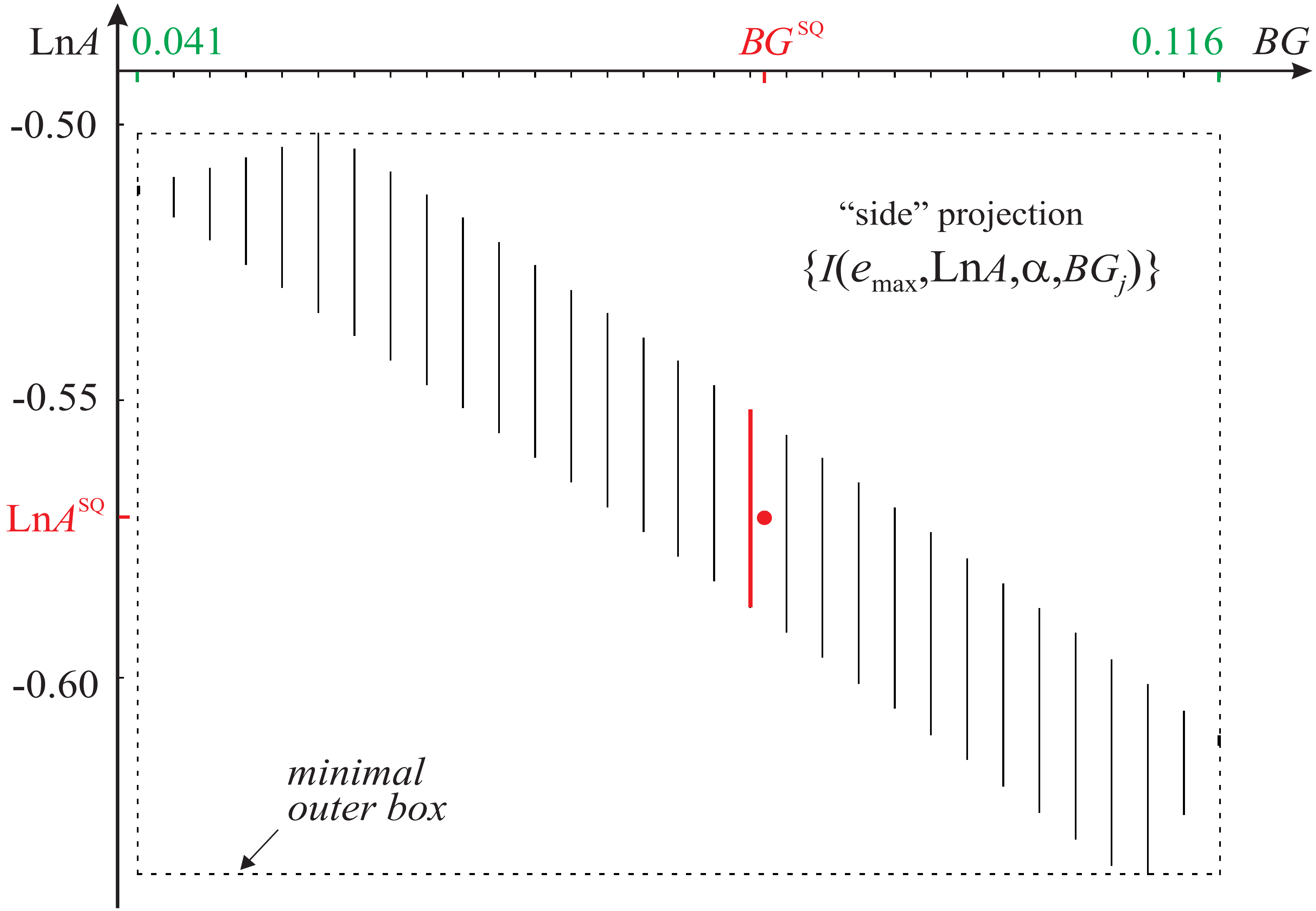
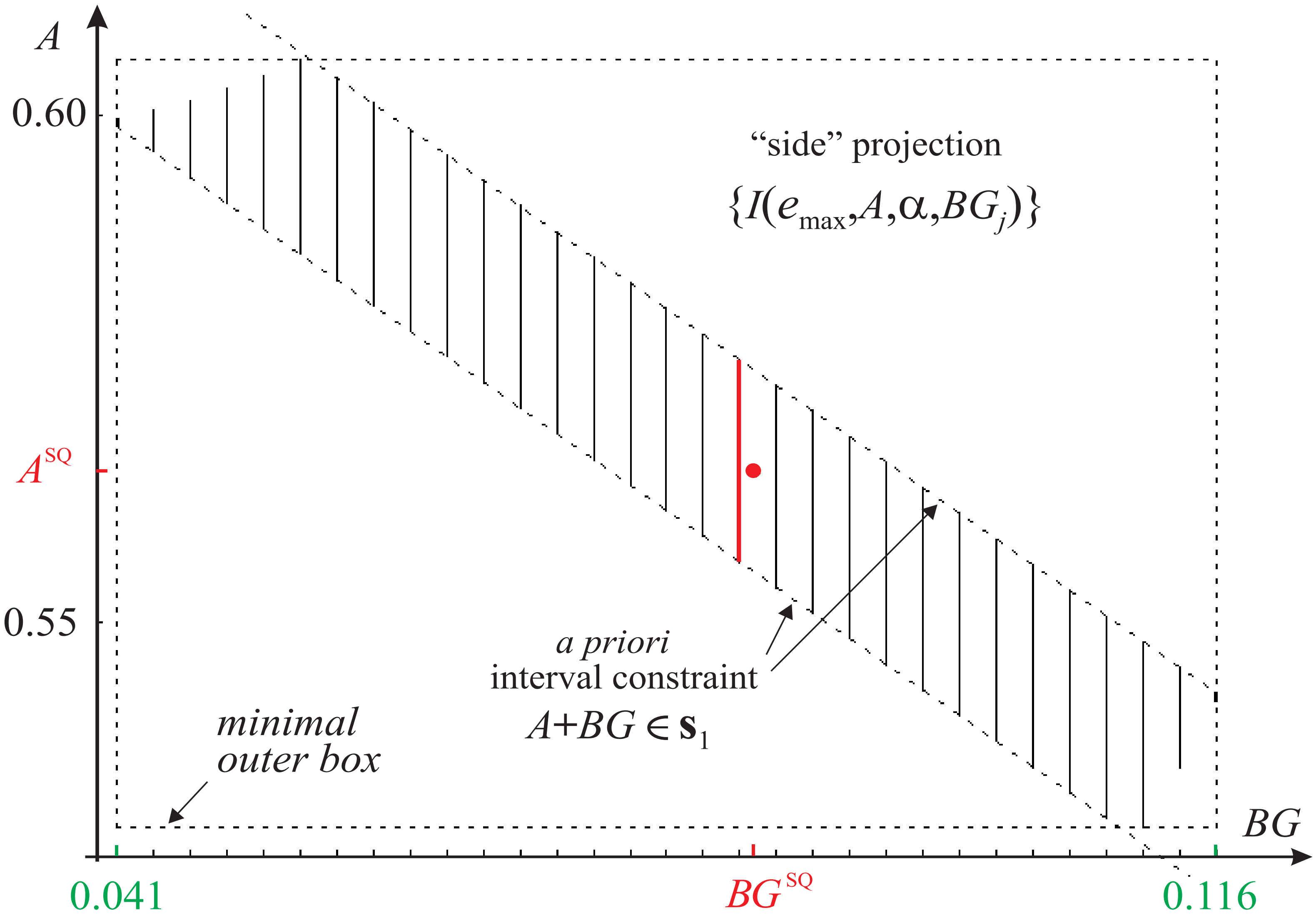
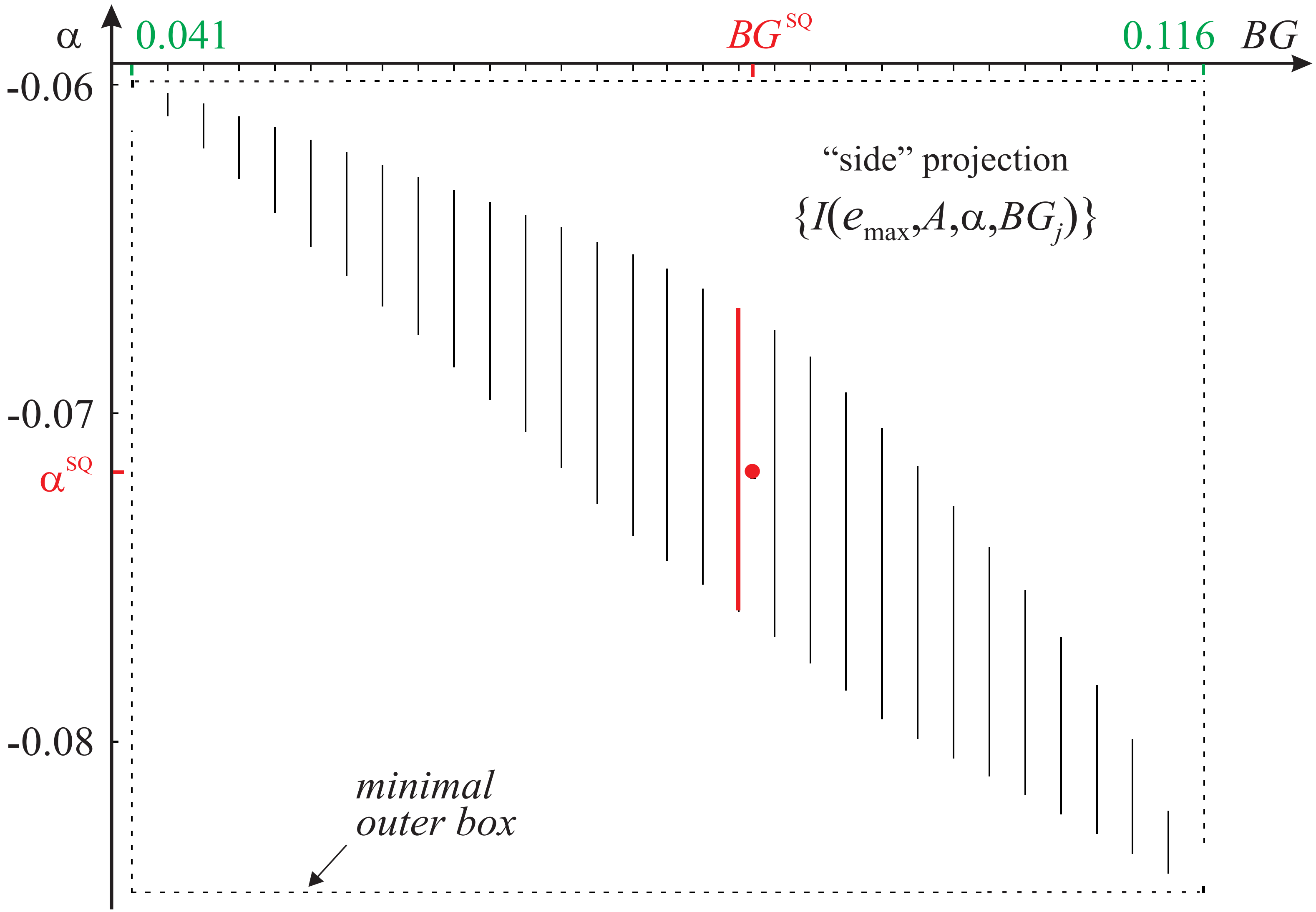


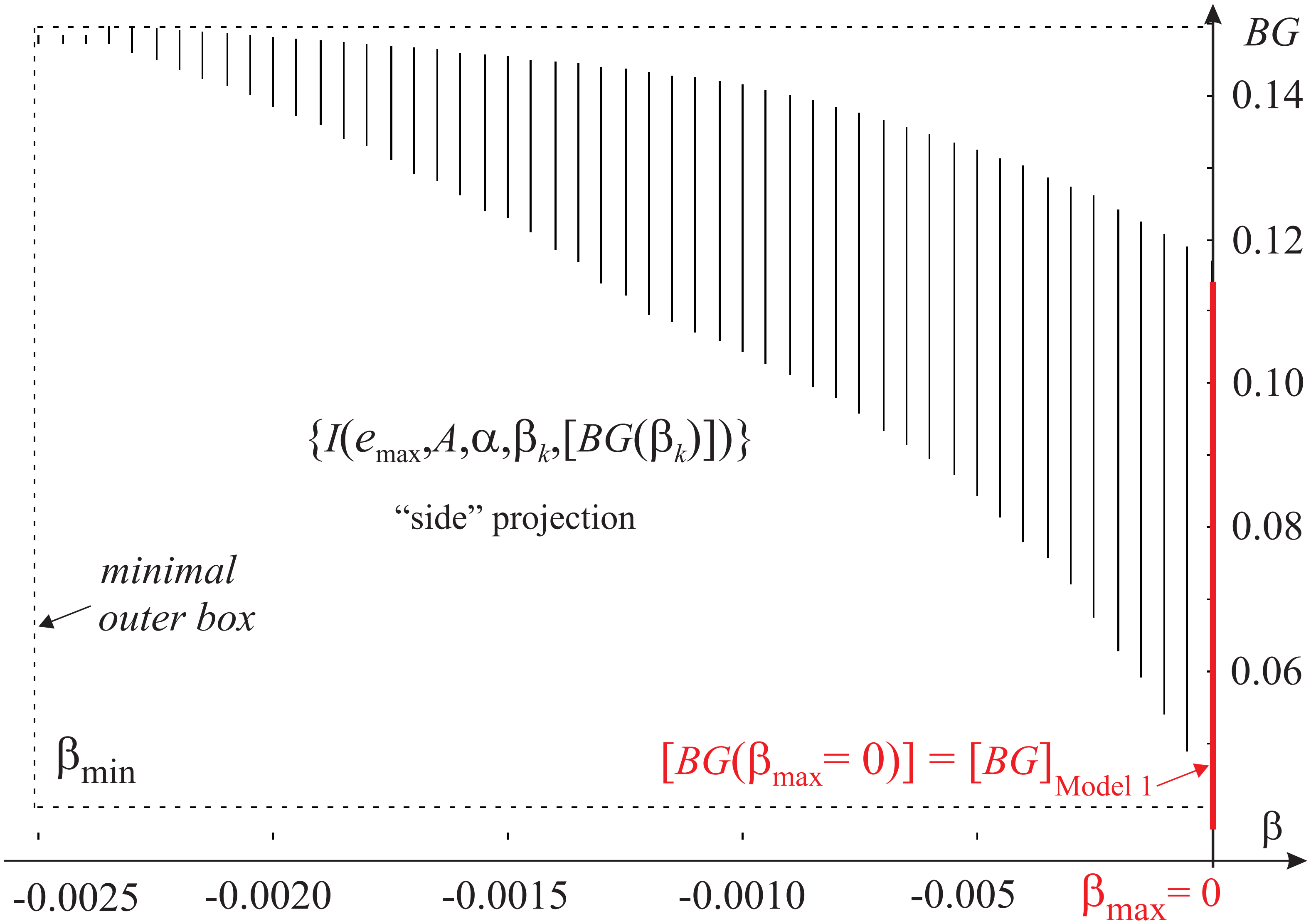
Practical examples. Model 1 ($\beta \equiv 0$), curve 1, sections of the informational sets on the grid $\{BG_j\}$, $e_{\max} = 0.01$, in the natural scale



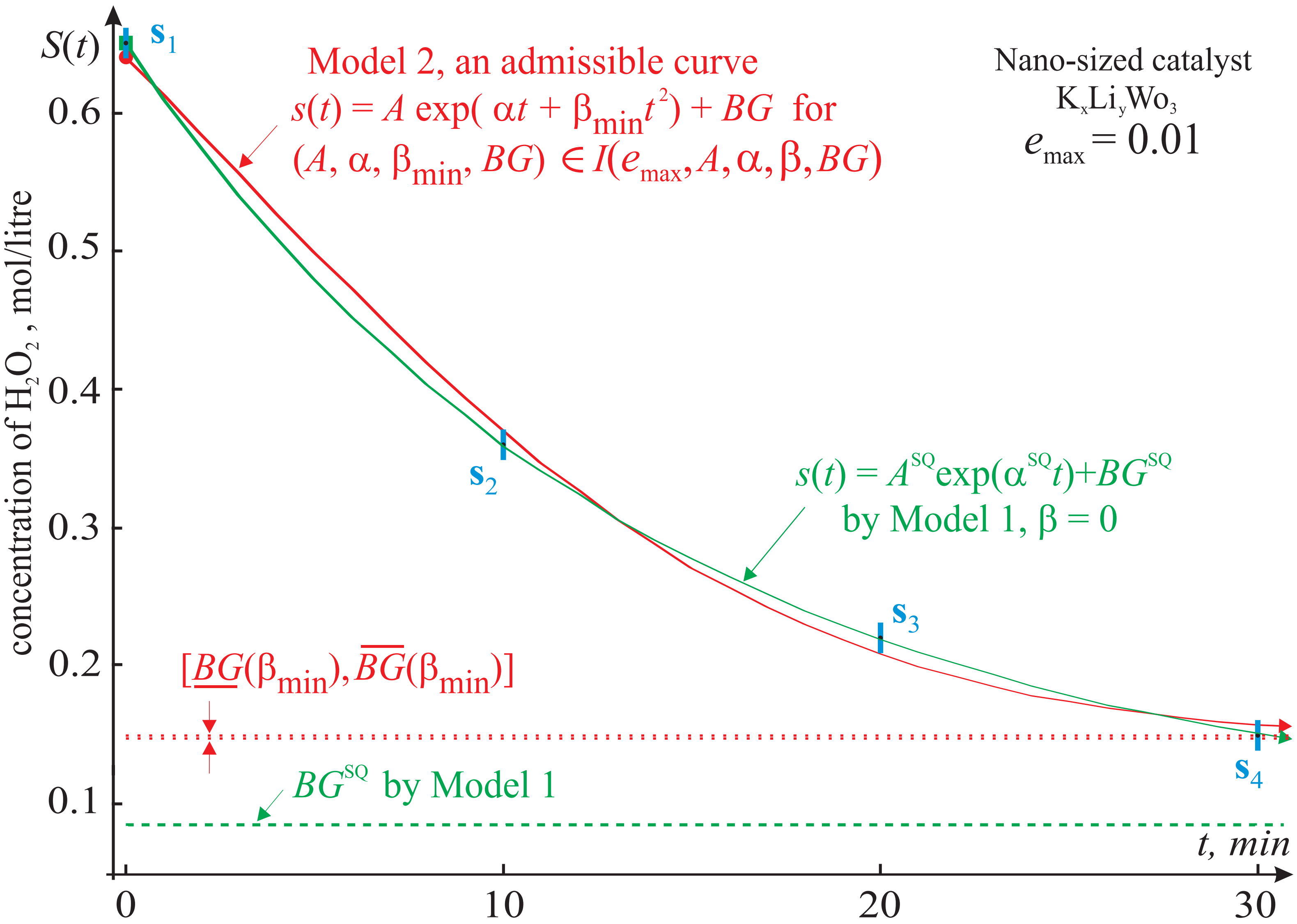
Practical examples. Model 1 ($\beta \equiv 0$), curve 1, sections of the informational sets on the grid $\{BG_j\}$, $e_{\max} = 0.01$, in the natural scale



Practical examples. Model 2, curve 1, admissible intervals $[BG(\beta_k)]$, on the grid $\{\beta_k\}$, $e_{\max} = 0.01$



Practical examples. Model 2, curve 1, an admissible curve for $\beta_{\min}$, $e_{\max} = 0.01$



VI. Conclusions

Under mentioned conditions of uncertainty, the interval approach overcomes the dead-lock situation and gives constructive description for the subtle structure of the informational set of parameters. This allows one to analyze validity of various models of the investigated process.

In practical cases, the developed hybrid "grid–analytical" algorithms for constructing the informational sets of parameters (together with transformation of variables) lead to fast computational procedures and provide obtaining exact description of boundaries of informational set sections.

The limit values of the bounds e^*_{max} onto the summary measuring error were found by the mentioned special interval procedure. The bounds were at the level (1.0–1.5)%. It allows one to conclude that the chaotic components of the measuring error are very small, the experiments were performed with very high quality and sufficiently accurate results.

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Thanks for attention