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Sequential experimental design for model discrimination Taking into account the posterior covariance matrix of differences between model predictions

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Abstract

Techniques for experimental design of experiments for model discrimination constitute important tools for scientists and engineers, as analyzed phenomena can very often be described fairly well by different mathematical models. As interpretation and use of available experimental data depend on the model structure, techniques for design of experiments for selection of the best model are of fundamental importance. Besides, experiments must often be designed for estimation of model parameters and reduction of variances of model predictions (or parameter estimates). These two classes of experimental design techniques generally lead to different experimental designs, although model discrimination and reduction of variances of parameter estimates are closely related to each other. In this work the posterior covariance matrix of difference between model predictions is taken into account during the design for model discrimination for the first time. The obtained results show that the model discrimination power becomes much higher when the posterior covariance matrix of difference between model predictions are considered during the experimental design, increasing the capability of model discrimination and simultaneously leading to improved parameter estimates.

Keywords: Model discrimination; Experimental design; Parameter estimation; Posterior covariance matrix; Mathematical modeling

1. Introduction

The scientific investigation of physical phenomena and/or processes follows a well-known iterative procedure, where available experimental data are interpreted in terms of theories, which in turn are based on the formulation of hypotheses that must be confirmed through experiments, which may eventually lead to new interpretations and new theories. This iterative behavior is repeated until achievement of the pursued objectives of the investigation. However, as experimentation is expensive both in terms of time and money, experiments should be designed to allow for achievement of the objectives with fewest possible experiments.

For engineering purposes, theories normally must be translated into mathematical equations to facilitate its use for design, control and optimization of the analyzed processes. During the initial stages of the experimental investigation, the available results can usually be explained by several different mechanistic interpretations. A typical example is the mechanistic interpretation of catalytic reactions, which can lead to several different rate equations (Froment, 1975). In order to select the best model among the proposed ones, new experiments must be designed. (The best model can be regarded as the one that is valid in a broader range of the experimental range and allows for improved extrapolations of the available data.)

Several criteria for experimental design for model discrimination have been proposed in literature. Hunter and Reiner (1965) developed a simple criterion for discrimination between two rival single response models, where the new experimental condition must be selected where the difference between model responses is maximum, according to:

$$D(\mathbf{x}) = (y_1 - y_2)^2. \tag{1}$$

In Eq. (1), D is the discriminant value, y_1 and y_2 are the expected responses of Models 1 and 2 at experimental condition $\mathbf{x}$ and with model parameters $\boldsymbol{\theta}_1$ and $\boldsymbol{\theta}_2$ estimated from the

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available experiments ($\mathbf{x}$, $\boldsymbol{\theta}_1$ and $\boldsymbol{\theta}_2$ were omitted for simplicity). Experimental observations of $\mathbf{x}$ and $\mathbf{y}$ are subject to random noise (assumed here to follow a normal distribution, with zero mean and covariance $\mathbf{V_x} = \mathbf{0}$ and $\mathbf{V_y} = \mathbf{V}$, unless stated otherwise). This criterion can be extended for discrimination among M rival models as follows (Froment, 1975):

$$D(\mathbf{x}) = \sum_{m=1}^{M-1} \sum_{n=m+1}^{M} (y_m - y_n)^2. \tag{2}$$

The major drawback of criteria defined in Eqs. (1) and (2) is the assumption that the variances of model predictions are constant throughout the experimental region. In order to take into account the change of model prediction variances, Box and Hill (1967) developed a different design criterion by making use of the Information Theory and of a Bayesian approach, assigning probabilities for models to concentrate the efforts in discriminating the most probable models. The Box and Hill's criterion can be written as

$$D(\mathbf{x}) = \sum_{m=1}^{M-1} \sum_{n=m+1}^{M} P_m P_n \left[\frac{(\sigma_m^2 - \sigma_n^2)^2}{(\sigma^2 + \sigma_m^2)(\sigma^2 + \sigma_n^2)} + (y_m - y_n)^2 \left(\frac{1}{\sigma^2 + \sigma_m^2} + \frac{1}{\sigma^2 + \sigma_n^2} \right) \right], \tag{3}$$

where P_m is the probability for model m to be the best model, σ^2 and σ_m^2 are, respectively, the experimental variance and the prediction variance of model m, both dependent of experimental condition $\mathbf{x}$. An interesting feature of this criterion is that experimental design and model evaluation are performed simultaneously through model probabilities (Hill, 1978).

Although Box and Hill's criterion take into account the experimental and the model prediction variances, Dumez et al. (1977) and Atkinson (1978) did not observe any systematic difference between experiments designed with either the Box and Hill's or the simpler Hunter and Reiner's criterion. Atkinson (1978) also observed that the use of model probabilities might lead to selection of one model even when all models are bad. Besides, due to the recursive law that was originally proposed by Box and Hill (1967) to update model probabilities, the obtained results may depend on the ordering of the experimental observations, as observed by Buzzi-Ferraris and Forzatti (1983). They also observed that, due to the structure of Eq. (3), experiments can be selected where the variances of the difference between model predictions are large and not where differences of model responses are large. In order to overcome these difficulties, alternative design criteria for model discrimination have been proposed in the literature.

Buzzi-Ferraris and Forzatti (1983) proposed a criterion for sequential model discrimination where the new experimental condition should maximize the ratio between the variance of model deviations and the mean value of model prediction variances, as follows:

$$D(\mathbf{x}) = \frac{\sum_{m=1}^{M-1} \sum_{n=m+1}^{M} (y_m - y_n)^2}{(M-1)(M\sigma^2 + \sum_{m=1}^{M} \sigma_m^2)}. \tag{4}$$

Eq. (4) takes into account all M models and the selected experimental condition can be placed in regions where the divergence among all rival models is not very large. For this reason, it may be preferable to discriminate pairs of rival models instead of all models simultaneously (Buzzi-Ferraris and Forzatti, 1983). Then, for discrimination between two rival models, Eq. (4) becomes:

$$D_{m,n}(\mathbf{x}) = \frac{(y_m - y_n)^2}{2\sigma^2 + \sigma_m^2 + \sigma_n^2}. \tag{5}$$

One should then maximize the maximum value of $D_{m,n}$ during the design phase and eliminate bad models during the data analysis phase, in order to avoid the repetitive design of experiments for elimination of bad model candidates. The criterion defined in Eq. (5) can be extended for models with multiple responses (Buzzi-Ferraris et al., 1984) as follows:

$$D_{m,n}(\mathbf{x}) = (\mathbf{y}_m - \mathbf{y}_n)^{\mathrm{T}} \mathbf{V}_{m,n}^{-1} (\mathbf{y}_m - \mathbf{y}_n), \tag{6}$$

where $\mathbf{y}_m$ is a vector of responses of model m and $\mathbf{V}_{m,n}$ is defined as

$$\mathbf{V}_{m,n} = 2\mathbf{V} + \mathbf{V}_m + \mathbf{V}_n, \tag{7}$$

where $\mathbf{V}$ is the covariance matrix of experimental deviations and $\mathbf{V}_m$ is the covariance matrix of model prediction deviations calculated from model m.

Buzzi-Ferraris et al. (1990) presented an improved version of the design criterion defined in Eq. (6), in order to correctly take the experimental errors into consideration during the design phase, given by

$$D_{m,n}(\mathbf{x}) = (\mathbf{y}_m - \mathbf{y}_n)^{\mathrm{T}} \mathbf{V}_{m,n}^{-1} (\mathbf{y}_m - \mathbf{y}_n) + \mathrm{trace}(2\mathbf{V}\mathbf{V}_{m,n}^{-1}). \tag{8}$$

Differently from Box and Hill's procedure, the sequences of designed experiments obtained with the criteria developed by Buzzi-Ferraris and coworkers (1983, 1984, 1990) do not depend on the ordering of the experimental observations. Buzzi-Ferraris and coworkers (1983, 1984, 1990) also suggested the *a priori* evaluation of the discrimination power associated with the new designed experiment. According to them, the optimum value of discriminant $D_{m,n}$ (calculated from Eq. (5), (6) or (8)) must be larger than the number of model responses; otherwise, discrimination is not possible and the experimental procedure must be halted. The adequacy of model evaluations must be performed with the classical χ^2-test for model adequacy (or any other statistical test developed for analysis of model adequacy).

Detailed surveys on available mathematical (and numerical) procedures for model discrimination are presented by Hill (1978) and Forzatti et al. (1986). Interesting applications of model discrimination procedures in dynamic problems are presented by Asprey and Macchieto (2000) and Ucinski and Bogacka (2005). The public literature concerning the optimal experimental design for model discrimination is huge and one should refer to Atkinson and Fedorov (1975a, b) and Atkinson et al. (2007) for detailed description of batch optimum design procedures (which can be regarded as preliminary experimental designs in a sequential experimental design strategy).

Recently, Schwaab et al. (2006) proposed the use of model probabilities to formulate a design criterion for model discrimination defined in Eq. (6). In order to concentrate the experimental efforts on discriminating the more plausible models, the discrimination is based on the performance of pairs of models as

$$D_{m,n}(\mathbf{x}) = (P_m P_n)^Z (\mathbf{y}_m - \mathbf{y}_n)^{\mathrm{T}} \mathbf{V}_{m,n}^{-1} (\mathbf{y}_m - \mathbf{y}_n), \tag{9}$$

where Z resembles the Tsallis' parameter, used for generalization of the entropy and information content (Tsallis, 1988). In the proposed model discrimination procedure, Z is a parameter used to modulate the relative importance of the rival models: if Z is greater than 1, model prediction differences are magnified; if Z is smaller than 1, model prediction differences are minimized. P_m is the relative probability for model m to be the best model, calculated from the absolute model probabilities as

$$P_m = \frac{\phi_m}{\sum_{n=1}^{M} \phi_n}, \tag{10}$$

where ϕ_m is the absolute probability for model m to be the best model, as defined in Eq. (11). Assuming that model m is perfect, that experiments are well done and that experimental deviations follow the normal distribution, the objective function presented in Eq. (12) approximately follows a χ^2-distribution with υ degrees of freedom ($\upsilon = \mathrm{NE}–\mathrm{NP}_m$, where NE is the total number of experimental points and NP_m is the number of estimated parameters in model m). Consequently, a value can be assigned to each model probability in the form:

$$\phi_m = 1 - p[\chi_\upsilon^2 \leqslant F_m], \tag{11}$$

where F_m is the minimum value of the objective function obtained in the parameter estimation of model m, defined as

$$F_m = \sum_{i=1}^{N} (\mathbf{y}_{i,m} - \mathbf{y}_i^e)^{\mathrm{T}} \mathbf{V}_i^{-1} (\mathbf{y}_{i,m} - \mathbf{y}_i^e), \tag{12}$$

where $\mathbf{y}_{i,m}$ is the vector of model responses, $\mathbf{y}_i^e$ is the vector of experimental responses and $\mathbf{V}_i$ is the covariance matrix of experimental deviations for experiment i. As the objective function does not depend on ordering of the experimental observations, the absolute probabilities calculated from Eq. (11) do not depend on ordering of experimentation either. Schwaab et al. (2006) claimed that model analysis and comparison of model performances become simpler and unambiguous when a quantitative measure of model adequacy is provided, such as the model probabilities, which were also used for model discrimination. Besides, the absolute model probabilities, calculated from the χ^2-distribution, can be readily used as a classical χ^2-test for model adequacy, allowing for evaluation of absolute model performances and analysis of the relative performances.

After selecting the best model, one may also need to design additional experiments to increase the precision of model parameters and model predictions. This task is closely related with the posterior covariance matrix of parameter estimates (Bard, 1974); that is, the expected covariance matrix of parameter estimates after the addition of new k experiments to the set of available experimental data and re-estimation of model parameters.

The criteria used for selection of new experiments for minimization of variances of parameter estimates normally minimize some norm of the posterior covariance matrix of the parameter estimates. The first criterion defined in the literature for minimization of variances of parameter estimates consists in the minimization of the determinant of the posterior covariance matrix of the parameter estimates (Box and Lucas, 1959), since this determinant is proportional to the volume of the hyper-ellipsoid that defines the parameter confidence region. Consequently, minimizing the determinant is equivalent to increasing the confidence in the parameter estimates.

Experiments can also be designed for reduction of the parameter correlations (Hosten, 1974; Pritchard and Bacon, 1978), as parameter correlations make the parameter estimation and parameter identification much more difficult. (Schwaab and Pinto (2007) and Schwaab et al. (2008b) have recently proposed a two-step parameter estimation procedure for minimization of parameter correlations, based on the reparameterization of model parameters, which does not require the design of new experiments.) The design for precise parameter estimation can also be performed through the minimization of the trace of the posterior covariance matrix of the parameter estimates (Pinto et al., 1990), where the sum of the posterior variances of parameter estimates should be minimized. (Pinto et al. (1991) developed and proposed the use of the relative posterior covariance matrix of parameter estimates for minimization of relative parameter deviations, since the orders of magnitude of the absolute parameter values can differ greatly in many problems).

Based on the previous paragraphs, one can propose the execution of two blocks of experimental design: the first one for model discrimination and the second one for precise parameter estimation, after selection of the best model. As sometimes this may lead to long and expensive experimental plans, some authors suggested the formulation of a single design criterion for simultaneous model discrimination and precise parameter estimation. Hill et al. (1968) were the first to suggest a joint design criterion, defined as

$$C(\mathbf{x}) = w \frac{D(\mathbf{x})}{D_{\max}} + (1 - w) \sum_{m=1}^{M} P_m \frac{E_m(\mathbf{x})}{E_{m,\max}}, \tag{13}$$

where D represents a model discrimination criterion and E_m represents a criterion for precise parameter estimation for model m. In order to provide a suitable normalization of the joint criterion, $D_{\max}$ and $E_{m,\max}$ represent the maximum value of D and E over the experimental design region, respectively. P_m is the probability of model m, as defined previously. w is a relative weight defined as

$$w = \left[\frac{M(1 - P_b)}{M - 1} \right]^{\lambda}, \tag{14}$$

where P_b is the probability of the best model, M is the total number of rival models and λ is a positive number that allows the experimenter to control the relative importance of the

discrimination procedure and the precise parameter estimation procedure during the experimental design.

As a matter of fact, Cochran (1973) observed that the best experimental conditions for model discrimination are not necessarily good for precise parameter estimation, and vice versa. For this reason, when the criterion defined in Eq. (13) is used for planning experiments, the selected experimental conditions are composed of a series of experiments designed for model discrimination and of a series of experiments designed for parameter estimation (sometimes, for bad models). As the model discrimination proceeds, more "estimation conditions" and fewer "discrimination conditions" are selected (Hill, 1978). As a consequence, both model discrimination and precise parameter estimation are prejudiced to some extent. This explains why the literature does not recommend the simultaneous design of experiments for model discrimination and precise parameter estimation (Hill, 1978).

In spite of that, it must be clear that good model discrimination is closely related with the estimation of precise parameters. The more precise are the model parameters (and, consequently, the model predictions), the easier is the discrimination between model responses. When model predictions are very uncertain, no model discrimination is possible. From Eq. (5) one can see that discrimination is not possible when model prediction variances are high, as the ratio between model predictions and the sum of prediction variances becomes less than 1. Similar comments can be easily extended for problems involving multiple response models.

Surprisingly, the literature review indicates that the effect of the new designed experiment on the model prediction variance has been neglected in all proposed design criteria for model discrimination. However, when a new experiment is performed and added to the set of available experimental data, the variance of model prediction decreases, as the model is adjusted to this new set of experimental conditions during parameter estimation. This is well known by those who design experiments for precise parameter estimation. Therefore, according to Eq. (5), the discrimination power is underestimated when the decrease of prediction variances is not considered, as the model performances will be compared after re-estimation of model parameters, not before.

In order to take into account the decrease of variances of model predictions during the experimental design, it is proposed here that the posterior covariance matrix of parameter estimates be used for calculation of the covariance matrix of model predictions during model discrimination procedures. This modification may allow for more accurate calculation of the discrimination power and for improved experimental designs. As a consequence the next experiment is selected in regions where the model divergences are high and/or the posterior variances of model predictions are small. It is expected that this approach may allow for model discrimination and simultaneous reduction of the variances of the parameter estimates, as reduction of variances of parameter estimates exerts a beneficial effect on model discrimination. It is important to observe that the use of the posterior covariance matrix of parameter estimates for model discrimination does not define a joint design criterion for simultaneous model discrimination and precise parameter estimation, since the decrease of the variances of the parameter estimates are obtained as a secondary effect, because the primary objective is the increase of discrimination power.

2. Methodology

The traditional procedure used for model discrimination does not make use of the posterior covariance matrix of parameter estimates. According to the usual approach, the calculations begin with the estimation of parameters for M rival models, using N available experiments. Tests of model adequacy are then performed for all proposed models. Adequate models are then used for design of the new experimental condition.

The covariance matrix of parameter estimates, based on the N available experiments can be calculated as follows (Bard, 1974):

$$\mathbf{V}_{\boldsymbol{\theta},m} = \left[\sum_{i=1}^{N} \mathbf{B}_m^{\mathrm{T}}(\mathbf{x}_i)\mathbf{V}^{-1}(\mathbf{x}_i)\mathbf{B}_m(\mathbf{x}_i)\right]^{-1}, \tag{15}$$

where $\mathbf{V}_{\theta,m}$ is the covariance matrix of parameter estimates for model m, $\mathbf{V}$ is the covariance matrix of experimental deviations and $\mathbf{B}_m$ is the sensitivity matrix that contains the first derivatives of model m responses with respect to its parameters, as

$$\mathbf{B}_m = [b_m]_{r,s} = \frac{\partial y_{r,m}}{\partial \theta_s}. \tag{16}$$

The covariance matrix of model predictions $\mathbf{V}_m$ at the new experimental condition $\mathbf{x}_{N+1}$ can be calculated as follows (Bard, 1974):

$$\mathbf{V}_m(\mathbf{x}_{N+1}) = \mathbf{B}_m(\mathbf{x}_{N+1})\mathbf{V}_{\boldsymbol{\theta},m}\mathbf{B}_m^{\mathrm{T}}(\mathbf{x}_{N+1}). \tag{17}$$

One should observe that the sensitivity matrix $\mathbf{B}_m$ in Eq. (17) is calculated at the new experimental condition, while the covariance matrix of parameter estimates $\mathbf{V}_{\boldsymbol{\theta},m}$ seems to be independent of the new experimental condition. The procedure continues with the calculation of the covariance matrix of the differences between model predictions as

$$\mathbf{V}_{m,n}(\mathbf{x}_{N+1}) = 2\mathbf{V}(\mathbf{x}_{N+1}) + \mathbf{V}_m(\mathbf{x}_{N+1}) + \mathbf{V}_n(\mathbf{x}_{N+1}). \tag{18}$$

The design criterion developed by Schwaab et al. (2006) is used here for experimental design (when Z is equal to 0, Schwaab et al.'s criterion becomes similar to the criterion proposed by Buzzi-Ferraris et al., 1984). Then, the discriminant can be written as

$$D_{m,n}(\mathbf{x}_{N+1}) = (P_m P_n)^Z [\mathbf{y}_m(\mathbf{x}_{N+1}) - \mathbf{y}_n(\mathbf{x}_{N+1})]^{\mathrm{T}} \times \mathbf{V}_{m,n}^{-1}(\mathbf{x}_{N+1})[\mathbf{y}_m(\mathbf{x}_{N+1}) - \mathbf{y}_n(\mathbf{x}_{N+1})]. \tag{19}$$

The new experimental condition $\mathbf{x}_{N+1}$ is the one that allows for maximization of Eq. (19). Maximization can be performed through extensive search in a proposed experimental grid or with the help of a proper numerical procedure. However, some care should be taken during maximization due to the possible existence of multiple points of maximum, as shown by Schwaab et al. (2006).

It is proposed here that the posterior covariance matrix of parameter estimates be used for model discrimination in Eqs. (15)–(19). The use of the posterior covariance matrix of parameter estimates can be justified by the fact that model performances are compared after execution of the designed experiment and re-estimation of model parameters for all models. The posterior covariance matrix of model parameters can be defined as (Bard, 1974)

$$\hat{\mathbf{V}}_{\theta,m}(\mathbf{x}_{N+1}) = [\mathbf{B}_m^{\mathrm{T}}(\mathbf{x}_{N+1})\mathbf{V}^{-1}(\mathbf{x}_{N+1})\mathbf{B}_m(\mathbf{x}_{N+1}) + \mathbf{V}_{\theta,m}^{-1}]^{-1}, \tag{20}$$

where $\hat{}$ is used to differentiate the posterior covariance matrix from the current covariance matrix of parameter estimates. Comparing Eqs. (15) and (20), the difference is the inclusion of the next experiment for computation of the posterior covariance matrix of parameter estimates. Therefore, the calculation of the posterior covariance matrix of model predictions should be performed as

$$\hat{\mathbf{V}}_m(\mathbf{x}_{N+1}) = \mathbf{B}_m(\mathbf{x}_{N+1})\hat{\mathbf{V}}_{\theta,m}(\mathbf{x}_{N+1})\mathbf{B}_m^{\mathrm{T}}(\mathbf{x}_{N+1}). \tag{21}$$

In Eq. (21) all terms are calculated as functions of the new selected experimental condition $\mathbf{x}_{N+1}$, differently from Eq. (17), where the covariance matrix of parameter estimates is not a function of $\mathbf{x}_{N+1}$. Finally, the posterior covariance matrix of the differences between model predictions becomes

$$\hat{\mathbf{V}}_{m,n}(\mathbf{x}_{N+1}) = 2\mathbf{V}(\mathbf{x}_{N+1}) + \hat{\mathbf{V}}_m(\mathbf{x}_{N+1}) + \hat{\mathbf{V}}_n(\mathbf{x}_{N+1}) \tag{22}$$

and the discriminant becomes

$$\hat{D}_{m,n}(\mathbf{x}_{N+1}) = (P_m P_n)^Z[\mathbf{y}_m(\mathbf{x}_{N+1}) - \mathbf{y}_n(\mathbf{x}_{N+1})]^{\mathrm{T}} \times \hat{\mathbf{V}}_{m,n}^{-1}(\mathbf{x}_{N+1})[\mathbf{y}_m(\mathbf{x}_{N+1}) - \mathbf{y}_n(\mathbf{x}_{N+1})]. \tag{23}$$

In Eqs. (21), (22) and (23), $\hat{}$ was used to indicate that the posterior covariance matrix of parameter estimates was used during calculations. One must observe that the design criteria depend on the values of the parameter estimates, which has been omitted from the equations for the sake of simplicity.

The main advantage of using the posterior covariance matrix of the differences between model predictions for model discrimination is that the discriminant values becomes higher (that is, the discriminant calculated with Eq. (23) is higher than the discriminant calculated with Eq. (17)), indicating easier discrimination of rival models. Besides, the use of Eq. (23) is much more realistic, since after execution and use of the new experimental condition for parameter estimation, prediction variances become usually lower than calculated with Eq. (17). (Obviously, the covariance matrix calculated with Eq. (21) will not be equal to the one obtained after execution and re-estimation, although it can certainly be regarded as a better approximation of the true covariance matrix of model predictions after re-estimation of model parameters.)

The sequential procedure used in this work is illustrated in Fig. 1. It is assumed that a set of preliminary experiments is available, as usual. (The preliminary set of experiments may be designed with the help of batch optimum experimental design procedures.) The model discrimination procedure is required when more than one model is able to describe the available experimental data appropriately, in accordance with standard statistical analysis. In this case, additional experiments must be designed in order to allow for determination of the best model.

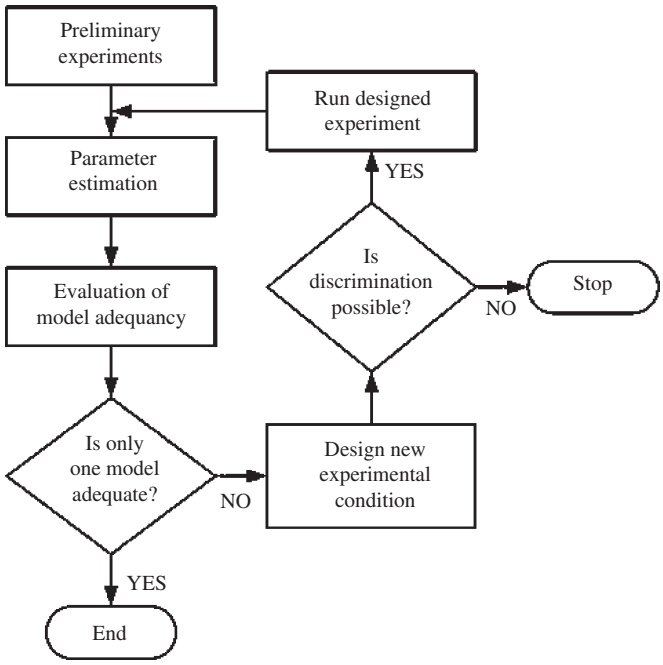

Fig. 1. Sequential experimental procedure for model discrimination.

The first step consists in estimating model parameters for all rival models. Minimum objective function values (Eq. (12)), the optimum parameter estimates and the covariance matrixes of parameter estimates (Eq. (15)) can then be obtained for each model. Afterwards, model adequacy can be evaluated for each model with the help of Eq. (10). When only one model can be regarded as adequate, the desired objective is attained; otherwise, a new experimental condition must be designed.

The design step consists in searching for the experimental conditions that allow for maximization of the selected design criterion (Eq. (19) or (23)). One must observe that it is necessary to know the optimum parameter estimates and the covariance matrix of parameter estimates in order to perform this step. The search can be performed with the help of standard numerical optimization procedures (or, as performed here, through exhaustive grid search).

After maximization of the design criterion, it is necessary to analyze whether model discrimination is indeed possible; otherwise, the procedure must be halted and the problem must be reviewed. If it is concluded that model discrimination is possible, the designed experiment is performed and the experimental results are added to the set of available experiments. Then, the whole procedure is repeated again. The sequential design procedure must be performed until achievement of one of the two stopping criteria: successful model discrimination or conclusion that model discrimination is not possible within the proposed experimental grid.

3. Results and discussion

In the first example the model discrimination procedure is studied for discrimination between two linear models, in order to illustrate the effect of the inclusion of the posterior covariance matrix of parameter estimates in the design criterion used for model discrimination.

The following two examples regard real model discrimination problems. In these examples, the minimization of the objective function during the parameter estimation procedure is performed with a hybrid method. The search is initiated with the Particle Swarm Optimization method (Kennedy and Eberhart, 1995), which performs a global search in order to locate the global minimum and provide the likelihood confidence region of parameter estimates (Schwaab et al., 2008a). The best point located by the Particle Swarm Optimization is then used as the initial guess for a Gauss–Newton based procedure (Noronha et al., 1993), which assures the precision of the final point estimate and provides the covariance matrix of parameter estimates, used for confidence evaluation of the parameter estimates and for calculation of the posterior covariance matrix of parameter estimates.

3.1. Example 1: linear models discrimination

The proposed model discrimination procedure is initially applied for discrimination of two rival linear models, defined as

$$\text{Model 1:} \quad y_1 = \theta_{1,1} x, \tag{24a}$$

$$\text{Model 2:} \quad y_2 = \theta_{2,1} x + \theta_{2,2}, \tag{24b}$$

where $\theta_{m,p}$ is the parameter p of model m, x is the independent variable and y is the dependent variable. The main objective here is providing a simple example where analytical solutions are available, in order to illustrate how important the use of the posterior covariance matrix of parameter estimates can be for proper model discrimination.

Let us assume that N experimental data points are available. Then, the objective function for parameter estimation can be written as

$$F_m = \sum_{i=1}^{N} \frac{(y_{m,i} - y_i^e)^2}{\sigma^2}, \tag{25}$$

where σ^2 is the experimental variance, assumed to be constant along the experimental region for the sake of simplicity. The covariance matrixes of parameter estimates for each of the rival linear models are (Eq. (15))

$$\mathbf{V}_{\theta_1} = \sigma^2 \left[\sum_{i=1}^{N} x_i^2 \right]^{-1}, \tag{26a}$$

$$\mathbf{V}_{\theta_2} = \sigma^2 \begin{bmatrix} \sum_{i=1}^{N} x_i^2 & \sum_{i=1}^{N} x_i \\ \sum_{i=1}^{N} x_i & N \end{bmatrix}^{-1}. \tag{26b}$$

The variances of model predictions at the new experimental condition x_{N+1} are then equal to (Eq. (17))

$$\mathbf{V}_1(x_{N+1}) = \sigma^2 \frac{x_{N+1}^2}{\sum_{i=1}^{N} x_i^2}, \tag{27a}$$

$$\mathbf{V}_2(x_{N+1}) = \sigma^2 \frac{N x_{N+1}^2 - 2x_{N+1} \sum_{i=1}^{N} x_i + \sum_{i=1}^{N} x_i^2}{N \sum_{i=1}^{N} x_i^2 - (\sum_{i=1}^{N} x_i)^2}. \tag{27b}$$

One can observe that the variances of model predictions for both models increase as a quadratic function of the new experimental condition x_{N+1}. It is possible to calculate the covariance matrix of the differences between predictions of models m and n, in accordance with Eq. (18), as

$$\mathbf{V}_{1,2}(x_{N+1}) = \sigma^2 \left[2 + \frac{x_{N+1}^2}{\sum_{i=1}^{N} x_i^2} + \frac{N x_{N+1}^2 - 2x_{N+1} \sum_{i=1}^{N} x_i + \sum_{i=1}^{N} x_i^2}{N \sum_{i=1}^{N} x_i^2 - (\sum_{i=1}^{N} x_i)^2} \right]. \tag{28}$$

Again, the variances of the differences between predictions of the linear models increase as a quadratic function of the new experimental condition x_{N+1}. The discriminant can be written as (Eq. (5))

$$D_{1,2}(x_{N+1}) = \frac{[(\theta_{1,1} - \theta_{2,1}) x_{N+1} - \theta_{2,2}]^2}{\sigma^2 \left[2 + \frac{x_{N+1}^2}{\sum_{i=1}^{N} x_i^2} + \frac{N x_{N+1}^2 - 2x_{N+1} \sum_{i=1}^{N} x_i + \sum_{i=1}^{N} x_i^2}{N \sum_{i=1}^{N} x_i^2 - (\sum_{i=1}^{N} x_i)^2} \right]}. \tag{29}$$

As the value of x_{N+1} increases, the discriminant tends to a constant, since both numerator and denominator are second-order polynomials. This indicates that model discrimination cannot be improved when x_{N+1} is increased arbitrarily, because the variances of model predictions increase with x_{N+1}^2. However, this is indeed a very strange result, because the performances of distinct linear models tend to infinity when x_{N+1} is increased arbitrarily.

Considering now the posterior covariance matrix of parameter estimates, then

$$\hat{\mathbf{V}}_{\theta_1}(x_{N+1}) = \sigma^2 \left[x_{N+1}^2 + \sum_{i=1}^{N} x_i^2 \right]^{-1}, \tag{30a}$$

$$\hat{\mathbf{V}}_{\theta_2} = \sigma^2 \begin{bmatrix} x_{N+1}^2 + \sum_{i=1}^{N} x_i^2 & x_{N+1} + \sum_{i=1}^{N} x_i \\ x_{N+1} + \sum_{i=1}^{N} x_i & N+1 \end{bmatrix}^{-1}. \tag{30b}$$

Taking into account the posterior covariance matrix of parameter estimates after inclusion of a new experimental condition x_{N+1}, the model prediction errors become (Eq. (21))

$$\hat{\mathbf{V}}_1(x_{N+1}) = \sigma^2 \frac{x_{N+1}^2}{x_{N+1}^2 + \sum_{i=1}^{N} x_i^2}, \tag{31a}$$

$$\hat{\mathbf{V}}_2(x_{N+1}) = \sigma^2 \frac{Nx_{N+1}^2 - 2x_{N+1}\sum_{i=1}^{N} x_i + \sum_{i=1}^{N} x_i^2}{Nx_{N+1}^2 - 2x_{N+1}\sum_{i=1}^{N} x_i + (N+1)\sum_{i=1}^{N} x_i^2 - (\sum_{i=1}^{N} x_i)^2}. \quad (31b)$$

One can observe now that the model prediction variances of both linear models present an asymptotic behavior as x_{N+1} increases. In both cases, the prediction variances become equal to the experimental variance σ^2. This means that prediction variances do not increase arbitrarily as x_{N+1} increases, when the models are updated with the new experimental data. This makes a lot of sense, as variances of model predictions are high before execution of the experiment, but are significantly smaller after obtainment of the new experimental point. Similar behavior is found for the variances of the differences between model predictions

$$\hat{\mathbf{V}}_{1,2}(x_{N+1}) = \sigma^2 \left[2 + \frac{x_{N+1}^2}{x_{N+1}^2 + \sum_{i=1}^{N} x_i^2} + \frac{Nx_{N+1}^2 - 2x_{N+1}\sum_{i=1}^{N} x_i + \sum_{i=1}^{N} x_i^2}{Nx_{N+1}^2 - 2x_{N+1}\sum_{i=1}^{N} x_i + (N+1)\sum_{i=1}^{N} x_i^2 - (\sum_{i=1}^{N} x_i)^2} \right]. \quad (32)$$

Finally, the discriminant becomes

$$\hat{D}_{1,2}(x_{N+1}) = \frac{[(\theta_{1,1} - \theta_{2,1})x_{N+1} - \theta_{2,2}]^2}{\sigma^2 \left[2 + \frac{x_{N+1}^2}{x_{N+1}^2 + \sum_{i=1}^{N} x_i^2} + \frac{Nx_{N+1}^2 - 2x_{N+1}\sum_{i=1}^{N} x_i + \sum_{i=1}^{N} x_i^2}{Nx_{N+1}^2 - 2x_{N+1}\sum_{i=1}^{N} x_i + (N+1)\sum_{i=1}^{N} x_i^2 - (\sum_{i=1}^{N} x_i)^2} \right]}. \quad (33)$$

When the posterior covariance matrix of parameter estimates is taken into account for calculation of the model prediction variances, the value of the discriminant increases arbitrarily as the value of x_{N+1} increases. This happens because the numerator increases with x_{N+1}^2, while the denominator tends to a constant as x_{N+1} increases. Therefore, Eq. (33) indicates very clearly that x_{N+1} must be large for model discrimination, as one might already expect. Besides, as clearly indicated in Eq. (30), model parameters are improved very significantly when x_{N+1} is allowed to increase. Therefore, selection of large x_{N+1} values contributes simultaneously with model discrimination and improved parameter estimation. This very simple example shows that posterior covariance matrix of parameter estimates should not be neglected during model discrimination.

3.2. Example 2: discrimination of rival adsorption models

This second example consists in discriminating between two single response models. The problem regards the adsorption of a gaseous component on a solid matrix and one is interested in describing the equilibrium adsorbate concentration as a function of the gas pressure. Model 1 is the Langmuir adsorption isotherm and Model 2 is the Freundlich adsorption isotherm, as described below:

$$\text{Model 1:} \quad y_1 = \theta_{1,1} \frac{\theta_{1,2} x}{1 + \theta_{1,2} x}, \quad (34a)$$

$$\text{Model 2:} \quad y_2 = \theta_{2,1} x^{\theta_{2,2}}, \quad (34b)$$

where $\theta_{m,p}$ is the parameter p of model m, x is the pressure in bar and y is the concentration of adsorbate on a solid material in mol kg^{-1}.

Table 1
Initial experimental data set for Example 2

Run	x (bar)	y (mol kg^{-1})
1	0.50	1.40
2	1.00	1.99
3	2.00	2.41

Table 2
Initial parameter estimates in Example 2

Model	F_m	P_m	$\theta_{m,1} \pm \Delta\theta_{m,1}$	$\theta_{m,2} \pm \Delta\theta_{m,2}$
1	0.135	76.1	3.175 ± 0.283	1.613 ± 0.402
2	1.478	23.9	1.892 ± 0.060	0.372 ± 0.055

Model 1 is assumed to be the correct one and is used to generate the experimental data, which are corrupted by a random normal deviation with zero mean and variance of 0.01. Parameters used to generate the "experimental" data were $\theta_{1,1}$ equal to 3 mol kg^{-1} and $\theta_{1,2}$ equal to 2 bar^{-1}. Table 1 presents the three initial experiments. Using these experimental points, the parameters of both models were estimated, as presented in Table 2. F_m and P_m in Table 2 are, respectively, the minimum value of the objective function and the relative probability of model m, as defined in Eq. (10). $\Delta\theta_{m,p}$ is the standard deviation of the parameter $\theta_{m,p}$.

Despite the higher relative probability of Model 1, when compared with Model 2, both models are statistically significant and new experiments must be designed in order to discriminate between them. In order to design a new experimental condition, two design criteria were used. The first one is the criterion defined in Eq. (6) (Buzzi-Ferraris et al., 1984), while the second is the new proposed criterion, as defined in Eq. (23). Since only two models are considered, the use of the model probabilities (and definition of Z) does not affect the design of experiments. Therefore, the only difference between Eqs. (6) and (23) is the use of the posterior covariance matrix of the parameter estimates for calculation of the prediction variances in Eq. (23).

The selection of the best experimental condition was performed through a direct search in the range $0.05 \leqslant x \leqslant 5.00$, with steps of 0.05 bar. Using the criterion defined in Eq. (6) the new selected experimental condition was x equal to 0.05 bar; that is, the lowest available pressure. When the criterion defined in Eq. (23) was used, the selected experimental condition was x equal to 5.00 bar; that is, the highest allowed pressure. The difference is amazing and the use of the posterior

Table 3
Designed experiment in Example 2 with Eq. (6) (Run 4-Eq6) and Eq. (23) (Run 4-Eq23)

Run	x (bar)	y (mol kg^{-1})	D
4-Eq6	0.05	0.26	4.365
4-Eq23	5.00	2.60	10.05

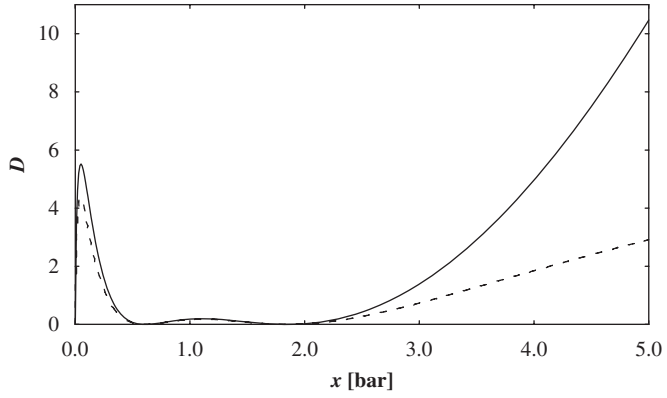

Fig. 2. Discriminant values calculated with (full line) and without (dashed line) the posterior covariance matrix of parameter estimates in Example 2.

covariance matrix of parameter estimates for model discrimination changes completely the notion about the best experimental condition. In Table 3 one can see the new selected experimental condition, the generated experimental response and the value of the discriminant at the selected experimental condition. One can observe that the discriminant value D obtained when the posterior covariance matrix is used is much higher, showing its higher discrimination power.

Fig. 2 shows both discriminant values as functions of the experimental condition. Fig. 2 shows that the maximum discriminant values are placed at different experimental conditions and that discriminant values calculated with the posterior covariance matrix of parameter estimates are always higher, due to the smaller prediction variances after execution of the new experimental condition. This effect is illustrated in Figs. 3 and 4.

By comparing Figs. 3 and 4, one can observe the decrease of the variances of model predictions for both models when the posterior covariance matrix of parameters is considered. According to Fig. 3, the variances of model predictions are high and it is possible to observe differences between model responses only when x values are close to 0. When the posterior covariance matrix of model parameters is considered, a different scenario is unveiled, as shown in Fig. 4. The prediction errors become smaller and significant differences appear at high x-values. Therefore, it becomes possible to discriminate between the models in this region. As a matter of fact, even in the region of small x-values, the prediction errors become smaller and the discriminant is higher, as also shown in Fig. 2.

After "execution" of the new experimental condition, selected in accordance to each criterion, the parameter estimates are obtained as presented in Table 4. Although, the discrimination between the two rival models was attained in both cases, since Model 1 reaches relative probabilities that are higher than 97.5 % in both cases, the parameter errors are smaller when the posterior covariance matrix of parameter is used in the design. It is interesting to observe that model discrimination is better and that model parameters are better for both models when the covariance matrix of parameter estimates is considered. Therefore, the use of Eq. (23) allows for simultaneous improvement of model discrimination and parameter estimation, as pursued by many researches in the field.

Fig. 5 shows the determinants of the posterior covariance matrixes of the parameter estimates for both models as func-

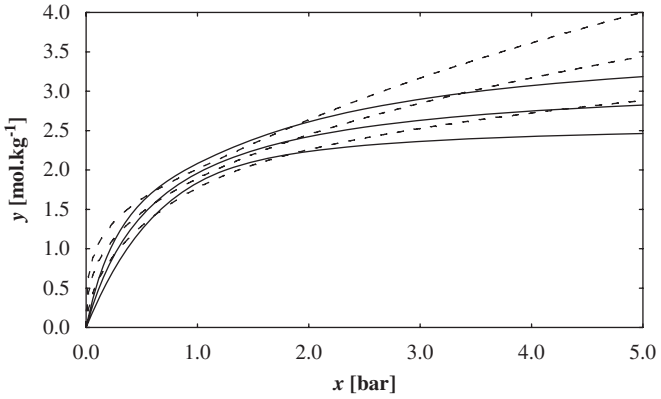

Fig. 3. Predictions and confidence intervals for Model 1 (full line) and Model 2 (dashed line) in Example 2, without considering the posterior covariance matrix.

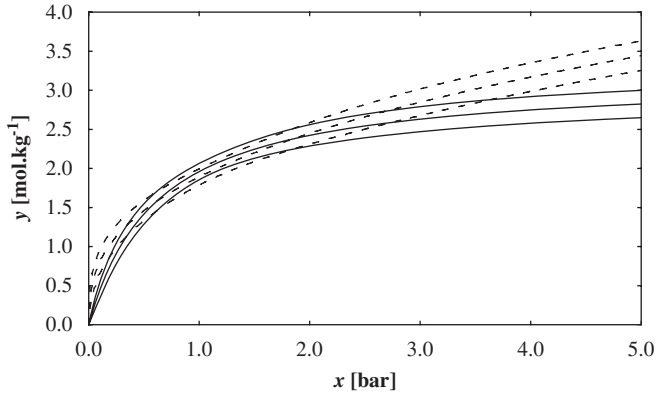

Fig. 4. Predictions and confidence intervals for Model 1 (full line) and Model 2 (dashed line) in Example 2, considering the posterior covariance matrix.

Table 4
Parameter estimation results after one designed experiment in Example 2, using Eqs. (6) and (23)

Model	F_m	P_m	$\theta_{m,1} \pm \Delta\theta_{m,1}$	$\theta_{m,2} \pm \Delta\theta_{m,2}$
1-Eq6	0.182	98.2	3.157 ± 0.268	1.642 ± 0.387
1-Eq23	1.294	99.2	2.935 ± 0.131	1.978 ± 0.339
2-Eq6	8.165	1.8	1.832 ± 0.056	0.464 ± 0.044
2-E23	10.84	0.8	1.880 ± 0.058	0.232 ± 0.028

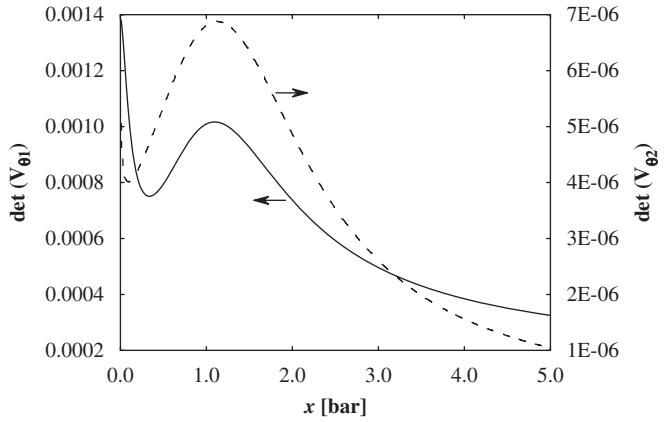

Fig. 5. Value of the determinant of the posterior covariance matrix of parameters for Model 1 (full line) and Model 2 (dashed line) in Example 2.

Table 5
Designed experiments with two criteria (Eqs. (6) and (23)) in Example 2 and determinant of the covariance matrix of parameter estimates of Model 1

Exp.	Eq. (6)		Eq. (23)	
	x (bar)	det($\mathbf{V}_\theta$)	x (bar)	det($\mathbf{V}_\theta$)
3	–	1.39	–	1.39
4	0.05	1.26	5.00	0.54
5	5.00	0.36	0.05	0.51
6	0.05	0.34	0.05	0.42
7	0.05	0.32	0.05	0.36
8	1.20	0.25	1.15	0.29
9	0.05	0.23	5.00	0.16
10	5.00	0.15	1.30	0.13

tions of experimental condition. Since this determinant is proportional to the volume of the confidence region of model parameters (Bard, 1974), a smaller determinant is equivalent to a smaller confidence region of the model parameters. As Fig. 5 shows, the minimum value of the determinant for both models is achieved when x is equal to 5.0 bar, the same experimental condition selected when the posterior covariance matrix of parameter estimates is used during the model discrimination procedures, as proposed in this work.

It was shown in this simple example that the use of the posterior covariance matrix of the parameter estimates for calculation of the prediction variances used for model discrimination increases the discriminant power and simultaneously leads to more precise model parameters.

In order to illustrate the sequence of designed experiments obtained with the analyzed criteria, seven additional experiments are designed and performed, as given in Table 5. It must be clear, though, that model discrimination is attained after execution of a single additional experiment, which means that the additional six experiments are not really needed for selection of the best model.

After execution of two additional experiments, both experimental designs lead to essentially the same results (although the proposed criterion selects the best model first). This shows that, when the variances of parameter estimates attain low levels, model discrimination depends only on the differences between model responses, as the variance of model predictions is not changed significantly with the additional experiments. Consequently, the proposed example shows that the new proposed design criterion allows for simultaneous model discrimination and minimization of the variances of the parameter estimate, as precise parameter estimates allow for more effective model discrimination.

3.3. Example 3: discrimination of kinetic models for the water-gas shift reaction

This example comprises the discrimination among kinetic models for the water-gas shift reaction (WGSR). Several kinetic models for the WGSR can be found in the literature and Schwaab et al. (2006) studied the discrimination among 13 different models. In order to show results obtained with the new discrimination procedure proposed here, five kinetic models were selected and are shown in the following equations:

Model 1:

$$r = \frac{k p_{CO} p_{H_2O}(1-\beta)}{(1+K_{CO}p_{CO}+K_{H_2O}p_{H_2O}+K_{CO_2}p_{CO_2}+K_{H_2}p_{H_2})^2}, \tag{35a}$$

Model 2:

$$r = \frac{k p_{CO} p_{H_2O}(1-\beta)}{1+K_{CO}p_{CO}+K_{H_2O}p_{H_2O}+K_{CO_2}p_{CO_2}+K_{H_2}p_{H_2}}, \tag{35b}$$

Model 3:

$$r = \frac{k p_{CO}\sqrt{p_{H_2O}}(1-\beta)}{1+K_{CO}p_{CO}+K_{H_2O}p_{H_2O}+K_{CO_2}p_{CO_2}+K_{H_2}p_{H_2}}, \tag{35c}$$

Model 4:

$$r = \frac{k_1 k_2 p_{CO} p_{H_2O}(1-\beta)}{k_1 p_{CO} + k_2 p_{H_2O} + k_3 p_{CO_2}}, \tag{35d}$$

Model 5:

$$r = \frac{k_1 k_2 p_{CO} p_{H_2O}(1-\beta)}{k_1 p_{CO} + k_2 p_{H_2O} + k_3 p_{CO_2} + k_4 p_{H_2}}, \tag{35e}$$

where r is the reaction rate in mol g^{-1} s^{-1}, p_i is the partial pressure of component i in atm, k's and K's are the model parameters and β is a measure of the equilibrium state, defined as

$$\beta = \frac{p_{CO_2} p_{H_2}}{p_{CO} p_{H_2O} K_{eq}} \tag{36}$$

and the equilibrium constant K_{eq} is defined as:

$$K_{eq} = \exp(4577.8/T - 4.33). \tag{37}$$

This example regards the discriminations of multiple models, which depend on multiple inputs and multiple parameters.

Model 1 was assumed to be the true model and the parameter values were $k = 0.352$ mol g^{-1} s^{-1} atm^{-2}, $K_{CO} = 2.726$ atm^{-1}, $K_{H_2O} = 0.559$ atm^{-1}, $K_{CO_2} = 1.532$ atm^{-1} and $K_{H_2} = 1.459$ atm^{-1} (Amadeo and Laborde, 1995). The reaction rates calculated with Model 1 were corrupted with a random

Table 6
Preliminary experiments in Example 3

Run	p_{CO}	p_{H_2O}	p_{CO_2}	p_{H_2}	r (10^3)
1	0.25	0.25	0.25	0.25	3.6908
2	0.25	0.25	0.50	0.50	1.8486
3	0.25	0.50	0.25	0.50	4.9220
4	0.25	0.50	0.50	0.25	4.3712
5	0.50	0.25	0.25	0.50	2.9268
6	0.50	0.25	0.50	0.25	4.3868
7	0.50	0.50	0.25	0.25	6.3938
8	0.50	0.50	0.50	0.50	4.2412

Table 7
Designed experiments in Example 3 with Eq. (19)

Exp.	p_{CO}	p_{H_2O}	p_{CO_2}	p_{H_2}	r (10^3)	$D(m,n)$
9	1.00	1.00	0.85	1.00	6.527	6.908 (1,4)
10	0.10	0.25	0.05	0.05	3.347	5.285 (1,2)
11	1.00	0.15	1.00	0.90	1.739	0.534 (1,3)
12	0.05	1.00	0.05	0.05	4.240	0.598 (1,3)
13	0.35	0.95	0.20	0.25	11.40	1.677 (1,3)
14	1.00	0.15	0.25	0.40	3.171	3.055 (1,3)
15	1.00	1.00	0.75	0.55	10.31	4.498 (1,5)
16	0.15	1.00	0.05	1.00	5.919	9.955 (1,4)
17	0.35	0.90	0.25	0.05	14.34	2.672 (1,3)

normal deviation with a variance of 1×10^{-6}. Preliminary experiments were defined as given in Table 6 and follow a fractional $2^{\{4-1\}}$ factorial design.

The sequentially designed experiments were selected from a discrete experimental grid, where each variable (p_{CO}, p_{H_2O}, p_{CO_2} and p_{H_2}) was allowed to vary from 0.05 to 1.00, in steps of 0.05. The specific design criterion was evaluated at every point within the discrete experimental grid and for every pair of models. The new selected experimental condition was the one where the analyzed design criterion achieved its highest value for a particular pair of models.

Initially, the experiments were designed with the criterion that does not take into account the posterior covariance matrix of parameter estimates, defined in Eq. (19), using a Z value of 1. The designed experiments and the simulated experimental values for the reaction rate are presented in Table 7 where the value of $D(m,n)$ is also shown. ($D(m,n)$ is the discriminant value between models m and n without the use of model probabilities, calculated in accordance with Eq. (6).) According to Buzzi-Ferraris and coworkers (1983, 1984, 1990), $D(m,n)$ can be used as an indication of the discrimination feasibility after execution of the new selected experimental condition.

The evolution of model probabilities along the experimental design is shown in Fig. 6. One can see that after execution of eight preliminary experiments, all rival models have similar probabilities (that is, similar performances). However, after design of nine additional experiments Model 1 is selected as the best one. It is also given in Table 7 that the value of $D(m,n)$ becomes smaller than 1 after the design of experiments 11 and 12. According to Buzzi-Ferraris and coworkers (1983, 1984, 1990), the discrimination procedure should be halted at this point, because model discrimination would not be possible. However, the procedure was continued and the model discrimination was achieved. Actually, model discrimination was achieved because the $D(m,n)$ values presented in Table 7 are too pessimistic and do not consider that model parameters are improved after execution of the new designed experiment.

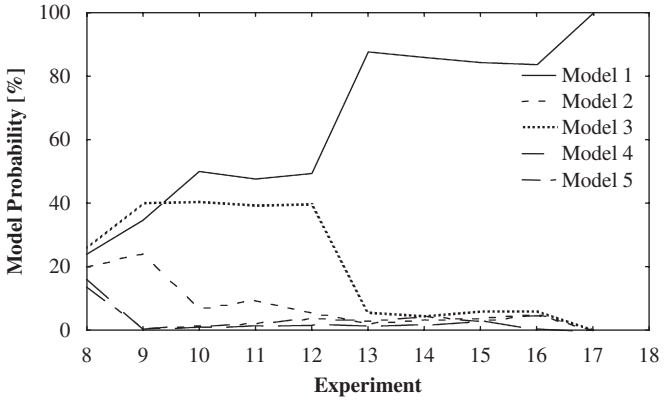

Fig. 6. Evolution of model probabilities along the experimental design in Example 3 with Eq. (14).

Table 8
Designed experiments in Example 3 with Eq. (23)

Exp.	p_{CO}	p_{H_2O}	p_{CO_2}	p_{H_2}	r (10^3)	$D(m,n)$
9	0.20	0.65	0.05	0.10	9.564	2.649×10^8 (1,3)
10	0.05	0.45	0.10	0.10	2.846	1.559×10^7 (1,2)
11	0.05	0.95	0.20	0.05	4.789	1.022×10^6 (1,3)
12	0.05	1.00	0.05	0.05	5.822	36.24 (1,3)
13	0.25	1.00	0.05	1.00	6.172	33.79 (3,4)
14	1.00	1.00	0.05	0.05	16.15	12.50 (1,5)
15	1.00	1.00	1.00	1.00	5.589	6.639 (1,5)
16	0.05	0.10	0.05	0.10	0.357	1836 (1,2)
17	0.30	1.00	0.25	0.05	14.22	6.512 (1,3)

Fig. 6 shows that the probabilities of Models 1 and 3 become much higher than the remaining ones after the 10th experiment. For this reason, Table 7 implies that the following designed experiments were selected almost always for discrimination between Models 1 and 3, the most probable ones.

Starting from the preliminary experiments, Table 8 presents the sequence of designed experiments when the posterior covariance matrix of parameter estimates is taken into account, as defined in Eq. (23), with the parameter Z set to 1. The designed experiments, the simulated experimental values for the reaction rate and the values of $D(m,n)$ are also given in Table 8. Fig. 7 shows the evolution of model probabilities along the experimental design.

Using the new criterion, the discrimination was achieved after design of nine additional experiments, as shown previously for the traditional criterion (Fig. 6). However, as given in Table 8, the values of $D(m,n)$ are much higher than the values given in Table 7. Besides, $D(m,n)$ never becomes lower than 1, indicating unequivocally that model discrimination is indeed

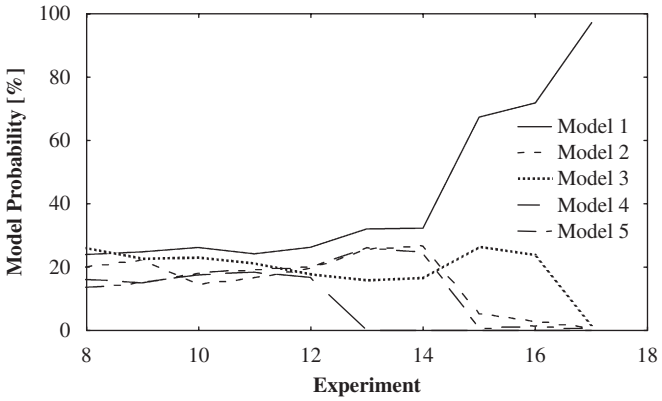

Fig. 7. Evolution of model probabilities along the experimental design in Example 3 with Eq. (23).

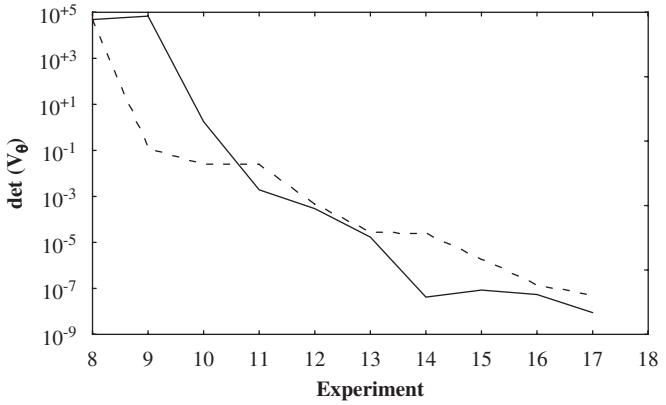

Fig. 8. Determinant of the covariance matrix of parameter estimates for Model 1 along the experimental design in Example 3 with Eq. (19) (dashed line) and Eq. (23) (full line).

possible. It is interesting to observe in Fig. 7 that the model probabilities remain comparable until execution of experiment 14, with the exception of Model 4 that assumes a probability of 0 after experiment 13 (one should observe in Table 8 that experiment 13 was designed for discrimination between Models 3 and 4). After execution of experiments 15 and 16, Models 2 and 5 were eliminated. With one more experiment, Model 3 was eliminated and Model 1 was selected as the best one, as it might already be expected.

It is important to observe that Eqs. (19) and (23) lead to completely different experimental designs. Only experiment 12 of Table 7 and experiment 12 of Table 8 are present in both designs; the remaining ones are different. This clearly indicates that the proposed procedures are not similar and lead to different designs. Figs. 6 and 7 also show that the evolution of model probabilities can also be very different in both cases. One may be tempted to consider Fig. 6 to be better than Fig. 7, as model probabilities vary faster in Fig. 6. However, one should observe that discrimination would be halted unsuccessfully after experiment 9 in Fig. 6, because of the unrealistic low values of the discriminant after selection of experiment 10. Besides, one should consider that Fig. 7 reflects the fact that models can be improved after inclusion of new experimental data, which is the reason why the new procedure is being proposed here.

Besides the increase of the discrimination power, it is also important to analyze the confidence in the model parameters and the effect of taking into consideration the posterior covariance matrix of parameter estimates along the experimental design. The values of the determinant of the covariance matrix of parameter estimates are plotted as a function of the number of experiments in Fig. 8 for both criteria. One must observe that the determinant of the covariance matrix of parameter estimates is proportional to the volume of the confidence region of the parameter estimates and can also be used as a criterion for experimental design to obtain precise parameter estimates (Box and Lucas, 1959; Bard, 1974). As shown in Fig. 8, when the posterior covariance matrix of parameter estimates is considered for model discrimination, after 17 experiments the confidence in the model parameters is about 1 order of magnitude better than obtained with the traditional design. As one can observe in Fig. 8, parameters obtained with the new proposed procedure are better along most of the experimental trajectory. This result shows the capability for model discrimination and precise parameter estimation of the design proposed in this work.

4. Conclusion

Design criteria used to formulate experimental design for discrimination among rival models normally neglect the fact that the variances of model parameters decrease when additional experiments are included in the experimental data set. For this reason, the variances of model predictions are overestimated and the discriminant power is underestimated. It was shown here through simple examples that the posterior covariance matrix of parameter estimates should be taken into consideration during the design of experiments for model discrimination. Besides leading to more realistic estimation of model prediction errors and of the discrimination power, the new procedure leads to simultaneous improvement of the variances of the parameter estimates along the experimental design, as reduction of the variances of the parameter estimates also contribute to the increase of the model discrimination power.

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