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SEQUENTIAL EXPERIMENTAL DESIGN FOR PARAMETER ESTIMATION: ANALYSIS OF RELATIVE DEVIATIONS

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Abstract—The equations used to design experiments for parameter estimation are modified to take relative uncertainties in model parameters into consideration. It is shown that parameter-oriented design criteria (SC, SSC, βTC) are slightly changed by this relative formulation, while prediction-oriented design criteria (VC, SVC, YTC) remain the same. It is also shown that parameters obtained using the relative method are generally associated with the smallest relative uncertainties and have a more uniform distribution of relative deviations. The relative β-trace design criterion seems to be the best criterion for sequential experimental design for parameter estimation among those criteria analysed.

INTRODUCTION

In a previous paper, Pinto *et al.* (1990) presented a general view of the area of sequential experimental design for parameter estimation. In this work they introduced two novel strategies and analysed the performance of six different design criteria when applied to three different problems. The criteria studied were the simple volume (SVC), the volume (VC), the simple shape (SSC), the shape (SC), the β-trace (βTC) and the y-trace (YTC) design criteria. According to the results obtained and to the analysis performed, the authors concluded that the β-trace design criterion was the best among them. Pinto *et al.* (1990) showed in particular that most of the time the use of simple design criteria cannot be justified, because they lead to less significant parameters and are computationally equivalent to the others. The authors also showed that prediction-oriented methods, such as the volume and y-trace design criteria, may lead to worse model predictions since parameter estimates may be obtained with significant bias.

The main objective of this paper is to reformulate the general approach to the parameter estimation problem presented by Bard (1974) in terms of the relative uncertainties in the model parameters and to verify the results presented by Pinto *et al.* (1990) under these new conditions. It is shown that parameter-oriented design criteria, such as the shape and β-shape design criteria, are slightly changed by the relative formulation while prediction-oriented design criteria remain the same.

THEORY

Let

$$\mathbf{y} = \mathbf{f}(\mathbf{x}, \boldsymbol{\beta}) \tag{1}$$

be the functional relationship between the output variables, y_i $(i = 1, \ldots, n)$ and the input variables x_u $(u = 1, \ldots, m)$ and a set of parameters β_q $(q = 1, \ldots, p)$, where $\mathbf{y}$, $\mathbf{x}$, and $\boldsymbol{\beta}$ are respectively n-dimensional, m-dimensional and p-dimensional real vectors and $\mathbf{f}$ is an n-dimensional vector of real smooth functions.

Let $G_{\beta_j}(\hat{\boldsymbol{\beta}}_j, \mathbf{V}_j)$ be a Gaussian distribution that represents the present knowledge of $\boldsymbol{\beta}$, after j experiments. If l additional experiments are now performed and if $G_{\varepsilon_k}(\mathbf{0}, \mathbf{V}_{\varepsilon_k})$ is a normal distribution that represents experimental deviations $\boldsymbol{\varepsilon}_k$, where $\boldsymbol{\varepsilon}_k$ is given by

$$\boldsymbol{\varepsilon}_k = \mathbf{y}_k - \mathbf{f}(\mathbf{x}_k, \hat{\boldsymbol{\beta}}_j) \tag{2}$$

and $\mathbf{x}_k$ and $\mathbf{y}_k$ are measured in the kth experiment $(k = j + 1, \ldots, j + l)$, then the new Gaussian distribution G_β associated with the parameter vector $\boldsymbol{\beta}$ will be $G_{\beta_{j+l}}(\hat{\boldsymbol{\beta}}_{j+l}, \hat{\mathbf{V}}_{j+l})$, where $\hat{\mathbf{V}}_{j+l}$ is the posterior covariance matrix of parameter, approximated by (Bard, 1974)

$$\hat{\mathbf{V}}_{j+l} \cong \left[\sum_{k=j+1}^{j+l} \mathbf{B}_k^T \mathbf{V}_{\varepsilon_k}^{-1} \mathbf{B}_k + \mathbf{V}_j^{-1} \right]^{-1} \tag{3}$$

where $\mathbf{B}_k = [b_{iq}]$ is the sensitivity matrix evaluated at $\mathbf{x} = \mathbf{x}_k$ and $\boldsymbol{\beta} = \hat{\boldsymbol{\beta}}_j$, with

$$b_{iq} = \frac{\partial f_i}{\partial \beta_q}. \tag{4}$$

Therefore, we may write

$$\hat{\mathbf{V}}_{j+l} = \hat{\mathbf{V}}_{j+l}(\mathbf{x}_{j+1}, \ldots, \mathbf{x}_{j+l}). \tag{5}$$

The posterior covariance matrix $\hat{\mathbf{V}}_{j+l}$ is symmetric, positive-definite and can be associated with the hyperellipsoid in the parameter space

$$|(\boldsymbol{\beta} - \hat{\boldsymbol{\beta}}_{j+l})^T \hat{\mathbf{V}}_{j+l}^{-1} (\boldsymbol{\beta} - \hat{\boldsymbol{\beta}}_{j+l})| \leqslant z \tag{6}$$

where z depends on the number of degrees of freedom, the confidence level and the experimental error (Bard, 1974). This region in the parameter space is the joint confidence region—the greater this region, the smaller the confidence in the estimated parameters.

The basic idea of Box and Lucas (1959) and Box and Hunter (1965) was to perform the l experiments that would minimize the volume of the hyperellipsoid

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defined by eq. (6). Defining

$$\boldsymbol{\Pi} = \begin{bmatrix} \mathbf{V}_{\varepsilon_{j+1}} & \mathbf{0} & \cdots & \mathbf{0} \\ \mathbf{0} & \mathbf{V}_{\varepsilon_{j+2}} & \cdots & \mathbf{0} \\ \vdots & \vdots & & \\ \mathbf{0} & \mathbf{0} & \cdots & \mathbf{V}_{\varepsilon_{j+l}} \end{bmatrix} \tag{7}$$

and

$$\mathbf{B}' = \begin{bmatrix} \mathbf{B}_{j+1} \\ \mathbf{B}_{j+2} \\ \vdots \\ \mathbf{B}_{j+l} \end{bmatrix} \tag{8}$$

Bard (1974) shows that it is equivalent to carrying out the l experiments that either

(a) maximize $\det(\mathbf{B}'^T\boldsymbol{\Pi}^{-1}\mathbf{B}' + \mathbf{V}_j^{-1})$, or
(b) maximize $\det(\boldsymbol{\Pi} + \mathbf{B}'\mathbf{V}_j\mathbf{B}'^T)$.

This is the volume design criterion. With additional assumptions (Pinto *et al.*, 1990), it can be concluded that the best set of l experiments is that which maximizes $\det \mathbf{B}'^T\mathbf{B}'$. This is the simple volume design criterion.

Hosten (1974) proposed that the chosen set of experiments should minimize the largest eigenvalue of $\hat{\mathbf{V}}_{j+l}$, so that the confidence region would be as round as possible. If $\hat{\mathbf{V}}_{j+l}$ is calculated from eq. (3), this criterion will be called the shape design criterion. If the eigenvalues are computed from the matrix $\mathbf{B}'^T\mathbf{B}'$, according to Hosten's original scheme, it will be called the simple shape design criterion.

Pinto *et al.* (1990) proposed that the best set of experiments should be that which maximizes the sum of the eigenvalues of $\hat{\mathbf{V}}_{j+l}$. Since it is equivalent to maximizing the trace of $\hat{\mathbf{V}}_{j+l}$, it was called the β-trace design criterion. They also showed that maximization of the sum of the eigenvalues of $\mathbf{B}'\mathbf{V}_j\mathbf{B}'^T$, so that the set of output variables is placed in the least known region of the output space, could be computationally advantageous and equivalent to the VC. This criterion was called the y-trace design criterion.

Equation (6) can be rewritten as

$$|(\boldsymbol{\beta} - \hat{\boldsymbol{\beta}}_{j+l})^T\mathbf{P}_{j+l}^{-1}\mathbf{P}_{j+l}\hat{\mathbf{V}}_{j+l}^{-1}\mathbf{P}_{j+l}\mathbf{P}_{j+l}^{-1}(\boldsymbol{\beta} - \hat{\boldsymbol{\beta}}_{j+l})| \leqslant z \tag{9}$$

where $\mathbf{P}_{j+l}$ is a diagonal matrix of parameters defined by

$$\mathbf{P}_{j+l} = \operatorname{diag}(\hat{\beta}_1, \hat{\beta}_2, \ldots, \hat{\beta}_p)_{j+l}. \tag{10}$$

Equation (9) can be cast in the form

$$|\mathbf{r}_{j+l}^T\hat{\mathbf{R}}_{j+l}^{-1}\mathbf{r}_{j+l}| \leqslant z \tag{11}$$

where

$$\mathbf{r}_{j+l} = \mathbf{P}_{j+l}^{-1}(\boldsymbol{\beta} - \hat{\boldsymbol{\beta}}_{j+l}) \tag{12}$$

and

$$\hat{\mathbf{R}}_{j+l} = \mathbf{P}_{j+l}^{-1}\hat{\mathbf{V}}_{j+l}\mathbf{P}_{j+l}^{-1}. \tag{13}$$

The matrix $\hat{\mathbf{R}}_{j+l}$ is the posterior relative covariance matrix of parameters and its elements are the relative covariances, given by

$$\hat{\mathbf{R}}_{j+l} = [\mathscr{R}_{iq}]_{j+l}$$

$$\mathscr{R}_{iq} = \frac{v_{iq}}{\hat{\beta}_i\hat{\beta}_q}, \quad i, q = 1, \ldots, p \tag{14}$$

and v_{iq} is the covariance between the ith and qth parameters after $j + l$ experiments.

The vector $\mathbf{r}_{j+l}$ is a vector of relative deviations or relative uncertainties in the parameters of the model. Its elements are given by

$$\mathbf{r}_{j+l} = [r_q]_{j+l}$$

$$r_q = \frac{\beta_q - \hat{\beta}_q}{\hat{\beta}_q}, \quad q = 1, \ldots, p. \tag{15}$$

Therefore, there exists a hyperellipsoid in the space of relative deviations that represents the present knowledge of the parameters. It can be obtained from the original hyperellipsoid in the parameter space after some proper transformations, according to eqs (9)–(15). The new hyperellipsoid is centered at the origin and can be completely different from the original one.

Combining eqs (3) and (13), an approximation of $\hat{\mathbf{R}}_{j+l}$ can be written as

$$\hat{\mathbf{R}}_{j+l} \cong \mathbf{P}_{j+l}^{-1}\left[\sum_{k=j+1}^{j+l} \mathbf{B}_k^T\mathbf{V}_{\varepsilon_k}^{-1}\mathbf{B}_k + \mathbf{V}_j^{-1}\right]^{-1}\mathbf{P}_{j+l}^{-1}, \tag{16}$$

Equation (16) can be rearranged to yield

$$\hat{\mathbf{R}}_{j+l} \cong \left[\sum_{k=j+1}^{j+l} (\mathbf{P}_{j+l}\mathbf{B}_k^T\mathbf{V}_{\varepsilon_k}^{-1}\mathbf{B}_k\mathbf{P}_{j+l}) + \mathbf{P}_{j+l}\mathbf{V}_j^{-1}\mathbf{P}_{j+l}\right]^{-1} \tag{17}$$

$$\hat{\mathbf{R}}_{j+l} \cong \left[\sum_{k=j+1}^{j+l} \mathbf{S}_k^T\mathbf{V}_{\varepsilon_k}^{-1}\mathbf{S}_k + \mathbf{R}_j^{-1}\right]^{-1} \tag{18}$$

where

$$\mathbf{S}_k = \mathbf{B}_k\mathbf{P}_{j+l} \cong \mathbf{B}_k\mathbf{P}_j. \tag{19}$$

The approximation used in eqs (18) and (19) implies that the elements of the matrix $\mathbf{P}$ are $(\beta_q)_j$. Equation (18) is very similar to eq. (3), where $\mathbf{V}$ was replaced by $\mathbf{R}$ and $\mathbf{B}$ by $\mathbf{S}$. $\mathbf{S}_k = [s_{iq}]$ is the matrix of relative sensitivities computed at $\mathbf{x} = \mathbf{x}_k$ and $\boldsymbol{\beta} = \hat{\boldsymbol{\beta}}_j$, with

$$s_{iq} = \frac{\partial f_i}{\partial \beta_q}\beta_q = \frac{\partial f_i}{\partial r_q}, \quad i = 1, \ldots, n \quad q = 1, \ldots, p. \tag{20}$$

According to eq. (20), it can be said that $\mathbf{S}_k$ carries much more information about the model parameters than does $\mathbf{B}_k$, since relative sensitivities may be compared to each other no matter how large or how small the parameters are.

It is now proposed that $\hat{\mathbf{R}}_{j+1}$ and eq. (18) be used to design experiments for parameter estimation instead of $\hat{\mathbf{V}}_{j+1}$ and eq. (3), since it seems more reasonable to obtain parameters with equivalent relative uncertainties than with equivalent absolute uncertainties. For example, the set of parameters (0.1 ± 0.04, 1.0 ± 0.4) may be considered better evaluated than the set (0.1 ± 0.2, 1.0 ± 0.2) most of the time. The six different design criteria presented before will be used to analyse this proposal.

PRELIMINARY ANALYSIS

It can easily be shown that if the model parameters have approximately the same value the results obtained will be the same, no matter which method, "absolute" [eq. (3)] or "relative" [eq. (18)], is used. The same cannot be said when the magnitude of at least one of the parameters is different from the magnitudes of the others [see Appendix]. Thus, the relative method may be considered to be a proper correction of the absolute method to take into account that the uncertainties of parameters with different magnitudes cannot be compared directly.

If the relative method is used and the VC is chosen as the proper criterion, it can be written that

$$\det \hat{\mathbf{R}}_{j+1} = \det \mathbf{P}_{j+1}^{-1} \det \hat{\mathbf{V}}_{j+1} \det \mathbf{P}_{j+1}^{-1}. \tag{21}$$

However, $\det \mathbf{P}_{j+1}^{-1}$ can be computed from

$$\det \mathbf{P}_{j+1}^{-1} \cong \det \mathbf{P}_j^{-1} = \prod_{q=1}^{p} \left[\frac{1}{\hat{\beta}_q}\right]_j \tag{22}$$

and it does not depend on the experimental condition that is being analysed. Thus, if the VC is to be used, it does not matter which method is chosen to design the experiments for parameter estimation. Likewise, the same can be said about the SVC.

If one chooses the relative method and the YTC, we can write

$$\begin{aligned} \operatorname{tr}(\mathbf{S}_{j+1}\mathbf{R}_j\mathbf{S}_{j+1}^T) &\cong \operatorname{tr}(\mathbf{B}_{j+1}\mathbf{P}_j\mathbf{P}_j^{-1}\mathbf{V}_j\mathbf{P}_j^{-1}\mathbf{P}_j^T\mathbf{B}_{j+1}^T) \\ &= \operatorname{tr}(\mathbf{B}_{j+1}\mathbf{V}_j\mathbf{B}_{j+1}^T). \end{aligned} \tag{23}$$

Thus, if the YTC is to be used, it does not matter which method is chosen to design the experiments for parameter estimation.

From the last two paragraphs it can be concluded that prediction-oriented design criteria cannot be modified to take relative uncertainties in parameters into consideration. This result could already be expected because the main concern of prediction-oriented criteria is to give good predictions and not to provide well-evaluated parameters.

The behaviour of parameter-oriented design criteria is quite different. For example, if the βTC is to be used, we can write

$$\operatorname{tr} \hat{\mathbf{R}}_{j+1} = \operatorname{tr}(\mathbf{P}_{j+1}^{-1}\hat{\mathbf{V}}_{j+1}\mathbf{P}_{j+1}^{-1}) = \sum_{q=1}^{p} \frac{v_{qq}}{[\hat{\beta}_q^2]_j}. \tag{24}$$

So, the minimization of $\operatorname{tr} \hat{\mathbf{R}}_{j+1}$ is an operation completely different from the minimization of $\operatorname{tr} \hat{\mathbf{V}}_{j+1}$. Depending on the differences of magnitude among the parameters, the minimization of $\operatorname{tr} \hat{\mathbf{R}}_{j+1}$ can lead to experimentation in a region of the experimental grid far from that chosen by the minimization of $\operatorname{tr} \hat{\mathbf{V}}_{j+1}$. The same can be said about the SC and the SSC. Therefore, whenever parameter-oriented design criteria are used, it must be clearly stated which method was chosen for the experimental design.

EXPERIMENTS AND RESULTS

Three examples are presented below. The first example is a simulation prepared to show the main differences between the absolute and relative methods, the second is a study of the solubility of VCM (vinyl chloride) in PVC (polyvinyl chloride) and the third is a classical study of the dehydrogenation of ethanol.

A general version of the algorithm presented by Anderson *et al.* (1978) was used for parameter estimation. A slight modification of the algorithm presented by Law and Bailey (1963) was used to assure convergence.

Example 1

Let a mathematical model be represented by

$$\begin{aligned} y_1 &= \beta_1/x_1 \\ y_2 &= \beta_2 x_1. \end{aligned} \tag{25}$$

Supposing that this system is homoscedastic and that errors are normally distributed with standard deviations equal to $\sigma_1 = 0.025$ and $\sigma_2 = 0.25$ and with zero mean value, a set of three experiments was generated for $\beta_1 = 1.00$ and $\beta_2 = 10.0$ (see Table 1) using the appropriate Statgraf subroutine.

Using these experimental data, the following results can be obtained:

$$\begin{aligned} &\beta_1 = 1.017 \pm 0.04 \quad (95\%) \\ &\beta_2 = 9.973 \pm 0.40 \quad (95\%) \\ &\mathbf{V}_3 = \begin{bmatrix} 3.784022 \times 10^{-4} & 0 \\ 0 & 3.784022 \times 10^{-2} \end{bmatrix}. \end{aligned} \tag{26}$$

It can be seen that the absolute uncertainty associated with β_2 is much larger than that associated with β_1. However, it cannot be concluded that β_1 is better evaluated than β_2 because the relative deviations are equal to 4% in both cases.

Based on the experimental grid shown in Table 2, five different criteria were used to design two new experiments for parameter estimation with the absolute and relative methods. The results obtained are presented in Tables 3 and 4. The SVC was not

Table 1. Initial set of experiments, example 1

x_1	y_1	y_2
0.5000	2.0494	5.0198
1.0000	1.0055	10.1141
2.0000	0.4719	19.8662

analysed because it is not sensitive to changes in the value of x_1, since

$$\det \mathbf{B}^T\mathbf{B} = 1 \tag{27}$$

$$\det \mathbf{S}^T\mathbf{S} = \beta_1^2\beta_2^2. \tag{28}$$

Example 2

Following Berens (1975), the solubility of VCM in PVC can be represented by

$$\ln\frac{P_{VCM}}{P_{sat}} = \ln(1 - v_2) + v_2 + \chi v_2^2 \tag{29}$$

$$v_2 = 1\Big/\left(1 + \frac{1000\rho_2}{\rho_1}S_N\right) \tag{30}$$

$$S_H = \frac{S^* P_{VCM}}{b' + P_{VCM}} \tag{31}$$

$$S = S_N + S_H \tag{32}$$

$$S^* = \exp\left(\frac{\Delta E}{RT} + \frac{\Delta S}{R}\right) \tag{33}$$

where P_{VCM} and P_{sat} are, respectively, the partial pressure and the saturation pressure of VCM at the temperature T, v_2 is the polymer volume fraction in the VCM-swollen PVC phase, ρ_1 and ρ_2 are, respectively, the densities of monomer and polymer in the polymeric phase, S_N and S_H are contributions from different processes to S, the global solubility of VCM in PVC, and χ, b' and S^* are model parameters, the latter being temperature dependent.

Table 2. Experimental grid, example 1

x_1	y_1	y_2
0.1000	10.0147	0.7483
0.2500	3.9832	2.5074
0.5000	1.9719	5.4336
0.7500	1.3222	7.7467
1.0000	1.0291	10.1396
1.3333	0.7981	13.1940
2.0000	0.4919	20.1519
4.0000	0.2366	39.5177
10.0000	0.0676	100.5524

Using eqs (29)–(33) and the experimental data presented by Berens (1975), the four unknown parameters (χ, b', ΔE, ΔS) were estimated. To evaluate the parameters, four different design criteria were used, with both the relative and the absolute methods. Only the SVC and the SSC were not used since the matrix $\mathbf{B}^T\mathbf{B}$ is singular everywhere, as can easily be shown.

The first five experiments of all different sequences were the same to provide a common starting point of analysis (Table 5). The sequences of experiments that resulted from the application of each design criterion are presented in Table 6. The parameters evaluated after each sequence of experiments and the relative uncertainties are presented in Table 7. Table 8 shows the predictive capacity of each set of parameters when all the experiments presented by Berens were analysed. The evolution of relative uncertainties in the parameters is presented in Fig. 1.

Temperature and solubility were chosen as the independent variables to accelerate the computational work. Although this choice does not agree with the real experimental procedure, it does not modify any of the general results and conclusions presented here.

Example 3

Experimental data on the dehydrogenation of ethanol, i.e.

$$\underset{A}{CH_3CH_2OH} \rightarrow \underset{R}{CH_3CHO} + \underset{S}{H_2} \tag{34}$$

Table 3. Experiments designed for parameter estimation, example 1

	Method of analysis			
	Absolute		Relative	
Criterion	4th exp.	5th exp.	4th exp.	5th exp.
βTC	$x_1 = 10$	$x_1 = 10$	$x_1 = 10$	$x_1 = 0.10$
SC	10	10	1.00	1.00
VC	10	0.10	10	0.10
YTC	10	10	10	10
SSC	1.00	1.00	0.25	0.25

Table 4. Results obtained after carrying out 5 experiments, example 1

Criterion	β_1 (95%)	Rel. error	β_2 (95%)	Rel. error
Rel. SC. Abs. SSC	1.0205 ± 0.022	2.2%	10.0187 ± 0.22	2.2%
YTC, Abs. βTC Abs. SC	1.0159 ± 0.034	3.4%	10.0531 ± 0.055	0.55%
VC, rel. βTC	1.0022 ± 0.008	0.8%	10.0509 ± 0.08	0.8%
Rel. SSC	0.9988 ± 0.012	1.2%	9.9740 ± 0.32	3.2%

in the presence of water vapour presented by Franckaertz (1963) and Franckaertz and Froment (1964) are analysed in this example.

Table 5. Initial set of experiments, example 2

Experiments		
T (K)	P_{VCM}/P_{sat}	S
303	0.78	135
313	0.38	53
323	0.025	5.50
333	0.95	225
343	0.060	6.85

As the reactor was approximately a PFR, the total conversion could be written as

$$x_T = \int_0^W \frac{r}{F_{AO}} d\omega \tag{35}$$

with

$$r = \frac{k[P_A - (P_R P_S/K)]}{(1 + K_A P_A + K_R P_R)^2} \tag{36}$$

and

$$K = \exp\left(\frac{-14{,}159.9}{T} + 25.2681\right) \tag{37}$$

where P_i are the partial pressures, K_i are the adsorp-

Table 6. Sequences of experiments obtained with each design criterion, example 2

Experiments		βTC, SC (abs.)	βTC, SC (rel.)	VC	YTC
1	S	45	45	45	45
	T	303	303	303	303
	P_{VCM}/P_{sat}	0.20	0.20	0.20	0.20
2	S	7.7	4.4	8.25	55
	T	343	323	323	303
	P_{VCM}/P_{sat}	0.070	0.016	0.050	0.27
3	S	7.2	202	8	162
	T	343	333	343	333
	P_{VCM}/P_{sat}	0.065	0.90	0.077	0.84
4	S	98	8	55	75
	T	303	343	303	303
	P_{VCM}/P_{sat}	0.64	0.077	0.27	0.48
5	S	75	2.8	162	202
	T	303	323	333	333
	P_{VCM}/P_{sat}	0.48	0.008	0.84	0.90

Table 7. Parameter estimates and relative uncertainties, example 2

Criterion	χ (95%)	b' (95%)	ΔE (95%)	ΔS (95%)
βTC, SC (Abs.)	1.066 ± 0.089 (8.3%)	0.235 ± 0.209 (88.9%)	12,299 ± 1,324 (10.8%)	− 33.88 ± 4.40 (13.0%)
βTC, SC (Rel.)	1.010 ± 0.070 (6.9%)	0.157 ± 0.131 (83.4%)	13,843 ± 2,029 (14.7%)	− 39.04 ± 6.56 (16.8%)
VC	1.012 ± 0.086 (8.5%)	0.255 ± 0.286 (112.2%)	14,118 ± 2,340 (16.6%)	− 39.71 ± 7.88 (19.8%)
YTC	1.004 ± 0.072 (7.2%)	0.205 ± 0.233 (113.7%)	13,235 ± 2,505 (18.9%)	− 36.98 ± 8.37 (22.6%)

Table 8. Predictive capacity of model parameters, example 2

Criterion	$\lvert\overline{\Delta x}\rvert$†	$\overline{\Delta x^2}$	$\lvert\Delta x\%\rvert$	Max Δx	Max $\Delta x\%$
βTC, SC (abs.)	0.023	0.031	8.0%	0.077	11.6%
βTC, SC (rel.)	0.017	0.023	7.4%	0.075	10.9%
VC	0.016	0.023	7.3%	0.071	11.1%
YTC	0.017	0.024	8.8%	0.074	13.6%

†$x \equiv P_{VCM}/P_{sat}$.

tion constants, k is the rate constant and T is measured in Kelvin.

The procedure used to estimate the parameters was similar to that presented by Pinto *et al.* (1990). The parameters k, K_A and K_R were evaluated at 225°C, 250°C and 275°C and afterwards they were expressed in accordance with the Arrhenius equation. At each temperature, the βTC and the SC, both with the relative method, were used to simulate a sequential experimental design for parameter estimation. As in the previous paper, the SSC was not used since the matrix $\mathbf{B}^T\mathbf{B}$ was singular everywhere. The results obtained for sets of eight experiments are presented in Tables 9–15. The sequences of experiments obtained are presented in Tables 10 and 11. The parameters evaluated are shown in Tables 12 and 13. Tables 14 and 15 show the predictive capacity of each set of parameters, when all experiments carried out by

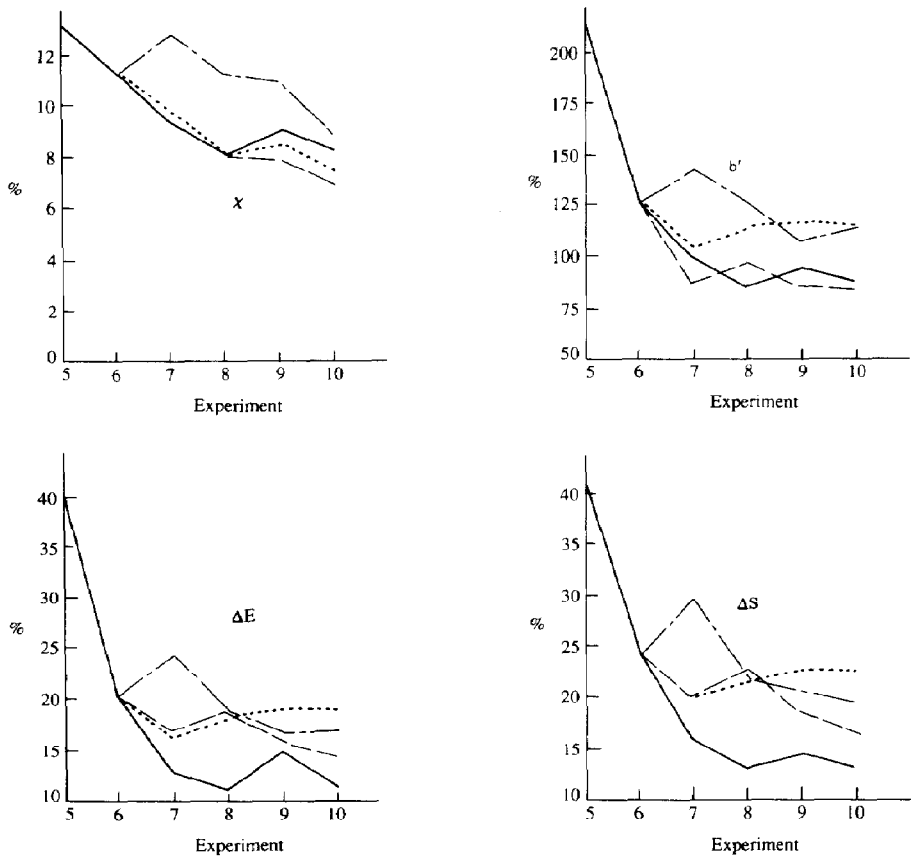

Fig. 1. Evolution of relative uncertainties. Legend: (———) βTC, SC (abs.); (– – –) βTC, SC (rel.); (. . . .) YTC; (— · — · —) VC.

Table 9. Initial set of experiments, example 3

Temperature	W/F_{AO}	P	X_A	X_W	X_R	x_T
	1.60	7	0.865	0.135	0.0	0.066
	0.80	4	0.865	0.135	0.0	0.083
225°C	0.40	3	0.865	0.135	0.0	0.055
	1.00	1	0.865	0.135	0.0	0.118
	1.60	7	0.865	0.135	0.0	0.149
	0.80	4	0.865	0.135	0.0	0.157
250°C	0.40	3	0.865	0.135	0.0	0.108
	1.00	1	0.865	0.135	0.0	0.218
	1.60	7	0.865	0.135	0.0	0.254
	0.80	4	0.865	0.135	0.0	0.262
275°C	0.40	3	0.865	0.135	0.0	0.200
	1.00	1	0.865	0.135	0.0	0.362

Table 10. Sequence of experiments obtained with relative βTC, example 3

Temperature	W/F_{AO}	P	X_A	X_W	X_R	x_T
	0.20	1	0.865	0.135	0.000	0.035
	1.00	1	0.672	0.145	0.183	0.048
225°C	0.40	1	0.865	0.135	0.000	0.060
	1.00	7	0.865	0.135	0.000	0.065
	1.00	1	0.672	0.145	0.183	0.123
	0.40	1	0.865	0.135	0.000	0.111
250°C	0.85	3	0.796	0.158	0.046	0.147
	0.60	1	0.865	0.135	0.000	0.152
	0.20	1	0.865	0.135	0.000	0.118
	4.22	1	0.865	0.135	0.000	0.590
275°C	0.40	1	0.865	0.135	0.000	0.196
	0.20	10	0.865	0.135	0.000	0.100

Table 11. Sequence of experiments obtained with relative SC, example 3

Temperature	W/F_{AO}	P	X_A	X_W	X_R	x_T
	0.40	1	0.865	0.135	0.000	0.060
	0.80	3	0.796	0.158	0.046	0.068
225°C	0.85	3	0.796	0.158	0.046	0.072
	1.00	1	0.672	0.145	0.183	0.048
	1.60	3	0.865	0.135	0.000	0.202
	0.20	1	0.865	0.135	0.000	0.065
250°C	1.00	1	0.672	0.145	0.183	0.123
	0.60	1	0.865	0.135	0.000	0.152
	1.60	3	0.865	0.135	0.000	0.352
	0.20	3	0.865	0.135	0.000	0.140
275°C	0.60	1	0.796	0.158	0.046	0.243
	4.54	1	0.865	0.135	0.000	0.600

Table 12. Parameter estimates, example 3

Temperature	k (95%)	K_A (95%)	K_R (95%)	Criterion
225°C	0.58 ± 0.24	0.71 ± 0.28	6.15 ± 3.31	βTC (rel.)
	0.48 ± 0.22	0.61 ± 0.31	4.60 ± 2.76	SC (rel.)
250°C	0.90 ± 0.12	0.54 ± 0.10	3.03 ± 0.64	βTC (rel.)
	1.03 ± 0.28	0.60 ± 0.18	3.86 ± 2.72	SC (rel.)
275°C	1.77 ± 0.40	0.43 ± 0.13	3.05 ± 1.03	βTC (rel.)
	2.33 ± 0.50	0.48 ± 0.11	4.15 ± 1.02	SC (rel.)

Table 13. Parameter estimates according to Arrhenius equation, example 3

Parameter	ΔE (cal/mol)	ΔS (cal/mol K)	Criterion
$k^\dagger$	13,323	25.41	βTC (rel.)
	17,898	34.32	SC (rel.)
K_A	− 5,478	− 11.66	βTC (rel.)
	− 2,382	− 5.71	SC (rel.)
K_R	− 9,484	− 15.50	βTC (rel.)
	− 1,252	0.46	SC (rel.)

$^\dagger k = \exp(-\Delta E/RT + \Delta S/R)$.

Table 14. Predictive capacity of model parameters without using Arrhenius equation, example 3

Temperature	Criterion	$\lvert\overline{\Delta x_T}\rvert$	$\overline{\Delta x_T^2}$	$\lvert\overline{\Delta x_T}\rvert$%	Max $\lvert\Delta x_T\rvert$	Max $\lvert\Delta x_T\rvert$%
225°C	βTC (rel.)	0.009	0.010	4.5%	0.030	6.1%
	SC (rel.)	0.007	0.010	3.7%	0.030	5.4%
250°C	βTC (rel.)	0.008	0.010	6.5%	0.030	8.4%
	SC (rel.)	0.007	0.009	7.3%	0.027	9.7%
275°C	βTC (rel.)	0.005	0.007	10.5%	0.018	14.4%
	SC (rel.)	0.005	0.007	9.7%	0.021	12.8%

Table 15. Predictive capacity of model parameters on using Arrhenius equation, example 3

$\lvert\overline{\Delta x_T}\rvert$	$\overline{\Delta x_T^2}$	$\lvert\overline{\Delta x_T}\rvert$%	Max $\lvert\Delta x_T\rvert$	Max $\lvert\Delta x_T\rvert$%	Criterion
0.009	0.010	8.8%	0.028	19.0%	βTC (rel.)
0.007	0.008	7.2%	0.028	14.7%	SC (rel.)

Table 16. Relative uncertainties in model parameters, example 3

	Relative uncertainty			
Temperature	k	K_A	K_R	Criterion
225°C	56%	55%	56%	VC, YTC
	92%	47%	149%	SVC
	44%	47%	58%	SC, βTC (abs.)
	41%	40%	54%	βTC (rel.)
	46%	51%	60%	SC (rel.)
250°C	16%	15%	24%	VC, YTC
	42%	32%	83%	SVC
	14%	16%	21%	SC, βTC (abs.)
	13%	19%	21%	βTC (rel.)
	27%	36%	71%	SC (rel.)
275°C	22%	31%	33%	VC, YTC
	27%	30%	59%	SVC
	21%	40%	26%	SC, βTC (abs.)
	22%	30%	34%	βTC (rel.)
	22%	23%	25%	SC (rel.)

Franckaertz were analysed. Table 16 shows the relative uncertainties in each parameter obtained with the application of the different design criteria analysed, including those studied by Pinto *et al.* (1990).

DISCUSSION

The main objective of example 1 was to show that the absolute method may be inadequate to design experiments for parameter evaluation, since the relative uncertainties associated with the final estimates can be quite different. It can be seen from Table 4 that the best parameter estimates were obtained with the VC and the relative βTC, when final relative deviations were not only similar but also very small. However, these relative deviations for β_2 were larger than those given by the YTC, the absolute βTC and the absolute SC, showing that the concept of best solution is not unique.

Example 2 was a practical application of sequential experimental design to a thermodynamic study. As can be seen from Table 6, the relative βTC and the relative SC provided the widest exploitation of the experimental grid, selecting experiments leading to both high and low amounts of VCM in PVC. Table 7 and Fig. 1 show that the parameter estimates given by the βTC and the SC, both absolute and relative, may be considered better than those given by VC and YTC, since they are associated with the smallest relative uncertainties. Particularly for b', the parameter which could not be properly evaluated and so could be considered as a good test for the criteria, the relative βTC and the relative SC gave the best results.

As can be seen from Table 8, the predictive capacity of all different sets of parameters may be considered similar, although the results provided by the absolute βTC and the absolute SC were a little poorer than the

others. This result could be expected because those criteria are parameter oriented. It must be stressed, on the other hand, that the relative βTC and the relative SC led to predictions as good as those given by the prediction-oriented criteria.

Example 3 was an application of sequential experimental design to a kinetic study and can be considered a continuation of the work of Pinto *et al.* (1990), who analysed the absolute method. Both the relative βTC and the relative SC provided a good exploitation of the experimental grid, selecting experiments at different pressures, with different feed composition and residence times, as it can be seen in Tables 10 and 11. Comparing the results in Tables 12–15 with those presented by Pinto *et al.* (1990), it can be seen that the predictive capacity of the new sets of parameters may be considered equivalent to that observed before in Pinto *et al.* (1990). However, with the use of the relative βTC, the relative uncertainties associated with the parameter estimates were generally smaller than those presented in the previous paper. The results are summarized in Table 16.

CONCLUSION

According to the results presented, the relative method may be effectively used to design experiments for parameter estimation. The parameters so obtained are expected to be associated with the smallest relative uncertainties (when compared with those obtained with the absolute method) and to have a more uniform distribution of relative deviations (when the parameters are compared with each other).

It can also be seen that the relative β-trace design criterion led almost always to the best set of parameter estimates. This result is in accordance with the analysis presented in a previous work by Pinto *et al.* (1990), where these authors show that trace design criteria should be advantageous.

It is important to notice that the use of parameter-oriented design criteria did not prejudice the predictive capacity of the models studied as already pointed out in the previous work.

For all these reasons, the relative β-trace design criterion seems to be the best criterion for sequential experimental design for parameter estimation among those criteria analysed.

NOTATION

b' parameter of Langmuir isotherm
$\mathbf{B}$ sensitivity matrix
$\mathbf{B}'$ matrix defined by eq. (8)
$\mathbf{f}$ vector of smooth real functions
F_{AO} feed rate of ethanol, mol/h
G_ε Gaussian distribution associated with experiments
G_β Gaussian distribution associated with the parameters
k kinetic constant, mol/(h g cat atm)
K_i adsorption constant of i, atm^{-1}
K equilibrium constant, atm
m number of input variables
n number of output variables
p number of parameters
P pressure, atm
P_i partial pressure of i, atm
$\mathbf{P}$ diagonal matrix of parameters
P_{VCM} partial pressure of VCM
P_{sat} saturation pressure of VCM
r rate of reaction, mol/(h g cat)
$\mathbf{r}$ vector of relative deviations of parameters
r_q relative deviation between the parameters
$\mathbf{R}$ relative covariance matrix of parameters
$\hat{\mathbf{R}}$ posterior relative covariance matrix of parameters
$\mathscr{R}_{iq}$ relative covariance between the parameters
S global solubility of VCM in PVC, mg VCM/g PVC
S_N contribution of the normal dissolution process
S_H contribution of the hole-filling process
$\mathbf{S}$ matrix of relative sensitivities
S^* parameter of Langmuir isotherm
T absolute temperature, K
v_2 polymer volume fraction
v_{iq} covariance between the parameters
$\mathbf{V}$ covariance marix of parameters
$\hat{\mathbf{V}}$ posterior covariance matrix of parameters
$\mathbf{V}_\varepsilon$ covariance matrix of output variables
$\mathbf{x}$ vector of input variables
x_T total conversion of ethanol
X_i molar fraction of i
W mass of catalyst, g
$\mathbf{y}$ vector of output variables

Greek letters

$\boldsymbol{\beta}$ vector of parameters
Δx difference between measured and calculated values
$\boldsymbol{\varepsilon}$ vector of experimental deviations
$\boldsymbol{\lambda}$ vector of eigenvalues
$\boldsymbol{\Pi}$ matrix defined by eq. (7)
ρ_1 density of monomer in the polymeric phase
ρ_2 density of polymer in the polymeric phase
χ polymer–solvent interaction parameter

Subscripts

A ethanol
R ethanal
S hydrogen
W water

Superscripts

T transpose
$\hat{}$ estimate

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APPENDIX

According to eq. (13)

$$\hat{\mathbf{R}}_{j+1} = \mathbf{P}_{j+1}^{-1}\hat{\mathbf{V}}_{j+1}\mathbf{P}_{j+1}^{-1}. \tag{A1}$$

So, if parameters are approximately the same we may write

$$\mathbf{P}_{j+1} = \beta\,\mathrm{diag}\,(1_1, 1_2, \ldots, 1_p) \tag{A2}$$

Therefore,

$$\hat{\mathbf{R}}_{j+1} = \frac{1}{\beta^2}\hat{\mathbf{V}}_{j+1} \tag{A3}$$

and

$$\mathrm{tr}\,\hat{\mathbf{R}}_{j+1} = \frac{1}{\beta^2}\,\mathrm{tr}\,\hat{\mathbf{V}}_{j+1} \tag{A4}$$

$$\det\hat{\mathbf{R}}_{j+1} = \left(\frac{1}{\beta^2}\right)^p \det\hat{V}_{j+1} \tag{A5}$$

$$\lambda_{R_i} = \frac{1}{\beta^2}\lambda_{V_i}, \qquad i = 1, \ldots, p. \tag{A6}$$

As β is a constant, the results are the same no matter which method or which criterion is used to design the experiments.