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THE D-OPTIMAL DESIGN OF BLOCKED AND SPLIT-PLOT EXPERIMENTS WITH MIXTURE COMPONENTS

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Abstract

So far, the optimal design of blocked and split-plot experiments involving mixture components has received scant attention. In this paper, an easy method to construct efficient blocked mixture experiments in the presence of fixed and/or random blocks is presented. The method can be used when qualitative variables are involved in a mixture experiment as well. It is also shown that orthogonally blocked mixture experiments are highly inefficient compared to $\mathcal{D}$-optimal designs. Finally, the design of a split-plot mixture experiment with process variables is discussed.

Keywords: fixed and random blocks, minimum support design, mixture experiment, orthogonal blocking, process variables, qualitative variables, split-plot experiment

1 Introduction

The orthogonal design of blocked mixture experiments has received a considerable amount of attention in the literature. Orthogonally blocked experiments allow the mixture component effects to be estimated independently from the block effects. The conditions for orthogonal blocking are derived by Nigam (1976) and John (1984). Several examples of such designs are given in Cornell (2002). Draper et al. (1993) find orthogonally blocked mixture designs for experiments with four components and two blocks, while Prescott et al. (1993, 1997) consider designs with five components. Prescott and Draper (1998) derive orthogonally blocked designs for experiments with three and four constrained components. Prescott (2000) shows how orthogonally blocked response surface designs can be projected onto a constrained design region in order to obtain an orthogonally blocked mixture design. Mixture designs that are not orthogonally blocked are derived by Donev (1989), who presents a method that allows an easy construction of blocked mixture designs.

In all of these references, only the case of a single blocking variable that is treated as fixed was investigated. In some experimental situations, there is however more than one blocking variable. Typical examples of blocking factors are the vendor supplying the raw material, the shift or personnel running the experiments, the laboratory performing the experiments, or the day on which the runs are carried out. Clearly, some of these blocking variables should be treated as random. Other complications in many practical experiments are that the block sizes are small and that constraints are imposed on the proportions of the mixture components, so that designing orthogonally blocked experiments is often impossible. The purpose of this paper is to propose a few other approaches to design blocked mixture experiments in such situations. Firstly, the simple design construction method presented by Donev (1989) will be extended to the case of a blocking variable that is treated as random and to the case of more than one blocking variable. This method allows an easy construction of efficient blocked mixture experiments. Secondly, the algorithmic approach will be investigated for designing blocked mixture experiments in complicated situations. In addition, the trade-off between orthogonally blocked designs and designs obtained by the algorithmic approach will be discussed, as well as the design of mixture experiments involving qualitative variables.

The design of mixture experiments involving process variables will be the focus in the second part of this paper. Cornell (1988) points out that this type of experiment is often conducted as a split-plot experiment. Kowalski et al. (2002) propose a couple of new designs while considering a new model form. In many practical situations where constraints are imposed on the mixture component proportions or the whole plot sizes are dictated by the experimental situation, these designs will however be infeasible so that an algorithmic approach is needed.

2 Motivating examples

Draper at al. (1993) describe an experiment involving four varieties of wheat. The purpose of the experiment, which was conducted at the Technical Services Department of Spillers Milling Limited in Cambridge, England, was to find mixtures of different varieties of flour with good bread-making abilities. In the experiment, four flours, each derived from a different variety of wheat, were mixed into doughs in various proportions. The doughs were baked into bread and the response measured was the specific volume, expressed in ml/100g, of the bread. Good flours produce loaves of high specific volume. Because the loaves were baked consecutively, the experiment was blocked to reduce the possible effects of within-day time effects. In the paper, orthogonally blocked designs with two blocks are presented for block sizes 7, 9, 10 and 13. The experiment actually conducted is displayed in Table 1. It consisted of two different blocks of size 9, both of which were duplicated. In Section 4.3, we will compute an alternative design for this example and compare both design options.

Table 1: Orthogonally blocked design used for the bread baking experiment.

Block 1					Block 2				
Run	x_1	x_2	x_3	x_4	Run	x_1	x_2	x_3	x_4
1	0.00	0.25	0.00	0.75	1	0.00	0.75	0.00	0.25
2	0.25	0.00	0.75	0.00	2	0.25	0.00	0.75	0.00
3	0.00	0.75	0.00	0.25	3	0.00	0.25	0.00	0.75
4	0.75	0.00	0.25	0.00	4	0.75	0.00	0.25	0.00
5	0.00	0.75	0.25	0.00	5	0.00	0.00	0.25	0.75
6	0.25	0.00	0.00	0.75	6	0.25	0.75	0.00	0.00
7	0.00	0.00	0.75	0.25	7	0.00	0.25	0.75	0.00
8	0.75	0.25	0.00	0.00	8	0.75	0.00	0.00	0.25
9	0.25	0.25	0.25	0.25	9	0.25	0.25	0.25	0.25

Kowalski et al. (2002) introduce a 28-run split-plot experiment with seven runs of size four for estimating a model in three mixture variables s_1, s_2 and s_3 and two process variables w_1 and w_2. The experiment is taken from Cornell (2002). It involves producing vinyl for automobile seat covers. The three mixture components in the experiment are plasticisers and the two process variables are rate of extrusion and temperature of drying. As many mixture experiments involving process variables, this experiment was carried out as a split-plot experiment. The levels of the process variables were held constant during four consecutive runs in which several different mixtures were tested. The design proposed by Kowalski et al. (2002) for this problem is displayed in Table 2. Two levels were used for each process variable. For the mixture components, the points of the second order lattice design were used, as well as the centroid of the simplex. The experiment was carried out by randomly selecting a combination of the levels of the process variables and running all blends at this combination. Next, another combination of the process variable levels is randomly chosen and all blends are run at this combination. This procedure was repeated until all combinations of the process variables had been performed. The experiment was therefore conducted in a split-plot format. The process variables are the whole plot factors of the experiment, whereas the mixture components are the sub-plot factors. In Section 6.2, we will compute $\mathcal{D}$-optimal designs for this experiment assuming unconstrained and constrained design regions. We will also investigate the impact of including center points in the design.

3 Mixture experiments

Mixture experiments involve blending of two or more ingredients or components. In this type of experiment, the quality of the end product depends on the relative proportions of the components in the mixture. If we denote by q the number of components in the mixture and by x_i ($i = 1, 2, \ldots, q$) the proportion contributed by the ith component, the

Table 2: Design proposed by Kowalski et al. (2002) for the vinyl thickness experiment.

Whole plot	s_1	s_2	s_3	w_1	w_2
1	1.00	0.00	0.00	-1	1
1	0.00	1.00	0.00	-1	1
1	0.00	0.00	1.00	-1	1
1	0.33	0.33	0.33	-1	1
2	1.00	0.00	0.00	1	-1
2	0.00	1.00	0.00	1	-1
2	0.00	0.00	1.00	1	-1
2	0.33	0.33	0.33	1	-1
3	0.50	0.50	0.00	1	1
3	0.50	0.00	0.50	1	1
3	0.00	0.50	0.50	1	1
3	0.33	0.33	0.33	1	1
4	0.50	0.50	0.00	-1	-1
4	0.50	0.00	0.50	-1	-1
4	0.00	0.50	0.50	-1	-1
4	0.33	0.33	0.33	-1	-1
5	0.33	0.33	0.33	0	0
5	0.33	0.33	0.33	0	0
5	0.33	0.33	0.33	0	0
5	0.33	0.33	0.33	0	0
6	0.33	0.33	0.33	0	0
6	0.33	0.33	0.33	0	0
6	0.33	0.33	0.33	0	0
6	0.33	0.33	0.33	0	0
7	0.33	0.33	0.33	0	0
7	0.33	0.33	0.33	0	0
7	0.33	0.33	0.33	0	0
7	0.33	0.33	0.33	0	0

following constraints apply to the mixture component proportions:

$$0 \leq x_i \leq 1, \tag{1}$$

and

$$\sum_{i=1}^{q} x_i = 1. \tag{2}$$

The experimental region defined by these constraints is a $(q-1)$-dimensional simplex. A two-dimensional simplex is an equilateral triangle and a three-dimensional simplex is a tetrahedron.

Often, additional constraints are imposed on the design region. Typically, some of the constraints can be specified as

$$l_i \leq x_i \leq u_i, \qquad i = 1, 2, \ldots, q, \tag{3}$$

where l_i and u_i represent the minimum and maximum proportions allowed for ingredient i. The resulting design region is in general an irregular simplex. In some specific cases however, the design region is again a regular simplex. Such situations occur if all u_i are one or if all l_i are zero and the sum of the $(q-1)$ largest upper bounds u_i is less than or equal to unity. In these cases, the use of pseudo-components allows the experimenter to use the standard results for unconstrained mixture experiments, i.e. for mixture experiments where no other constraints than (1) and (2) are active. An introduction to the use of pseudo-components is given in Cornell (2002). As an illustration of an irregular design region, we will use an example introduced by Piepel et al. (2002) throughout the paper. The hexagonal mixture region in the example is defined by $0.18 \leq x_1 \leq 0.80$, $0.00 \leq x_2 \leq 0.50$ and $0.0 \leq x_3 \leq 0.60$.

In the paper, we will concentrate on Scheffé models for modelling the response y of a mixture experiment. The first order Scheffé model is given by

$$y = \sum_{i=1}^{q} \beta_i x_i + \varepsilon.$$

The second order Scheffé model is given by

$$y = \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q-1} \sum_{j=i+1}^{q} \beta_{ij} x_i x_j + \varepsilon,$$

and the special cubic model can be written as

$$y = \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q-1} \sum_{j=i+1}^{q} \beta_{ij} x_i x_j + \sum_{i=1}^{q-2} \sum_{j=i+1}^{q-1} \sum_{k=j+1}^{q} \beta_{ijk} x_i x_j x_k + \varepsilon.$$

In matrix notation, these models can be written as

$$\mathbf{y} = \mathbf{X}\boldsymbol{\beta} + \boldsymbol{\varepsilon},$$

where $\mathbf{y}$ is the vector of the responses of the n observations, $\mathbf{X}$ is the $n \times p$ extended design matrix corresponding to the mixture components, $\boldsymbol{\beta}$ represents the p effects of the mixture variables and $\boldsymbol{\varepsilon}$ is the vector of random errors.

4 Blocked experiments

In this section, we will investigate the design of blocked experiments. Initially, we will restrict our attention to the case of minimum support designs, i.e. to designs where the number of support points is equal to the number of parameters. Next, we will consider the more general case where the number of distinct design points is allowed to be larger. Firstly, however, we will describe the statistical model corresponding to a blocked mixture experiment.

4.1 The statistical model

In a general setting with both fixed and random blocking variables, the statistical model corresponding to a blocked mixture experiment can be written as

$$\begin{aligned} \mathbf{y} &= \mathbf{X}\boldsymbol{\beta} + \mathbf{C}\boldsymbol{\gamma} + \mathbf{Z}\boldsymbol{\delta} + \boldsymbol{\varepsilon}, \\ &= \mathbf{F}\boldsymbol{\xi} + \mathbf{Z}\boldsymbol{\delta} + \boldsymbol{\varepsilon}, \end{aligned} \tag{4}$$

where $\mathbf{X}$ is the $n \times p$ extended design matrix corresponding to the components of the mixture, $\mathbf{C}$ is the design matrix corresponding to the indicator variables for the fixed blocks, $\mathbf{Z}$ is the design matrix corresponding to the indicator variables for the random blocks, and $\mathbf{F} = [\,\mathbf{X}\;\mathbf{C}\,]$. The vectors $\boldsymbol{\beta}$, $\boldsymbol{\gamma}$, $\boldsymbol{\delta}$ and $\boldsymbol{\varepsilon}$ represent the effects of the mixture variables, the fixed block effects, the random block effects and the random errors, respectively. Finally, $\boldsymbol{\xi}' = [\,\boldsymbol{\beta}'\;\boldsymbol{\gamma}'\,]$. We will denote the number of fixed and random blocking variables by B_F and B_R respectively, the number of elements in $\boldsymbol{\gamma}$ and $\boldsymbol{\delta}$ by b_F and b_R respectively, and assume that $\boldsymbol{\varepsilon} \sim N(\mathbf{0}_n, \sigma_\varepsilon^2 \mathbf{I}_n)$, that $\boldsymbol{\delta} \sim N(\mathbf{0}_{b_R}, \mathbf{G})$, where

$$\mathrm{var}(\boldsymbol{\delta}) = \mathbf{G} = \mathrm{diag}(\sigma_1^2, \ldots, \sigma_1^2, \sigma_2^2, \ldots, \sigma_2^2, \ldots, \sigma_{B_R}^2, \ldots, \sigma_{B_R}^2),$$

and that $\mathrm{cov}(\boldsymbol{\varepsilon}, \boldsymbol{\delta}) = \mathbf{0}_{n \times b_R}$. As a result,

$$\mathrm{var}(\mathbf{y}) = \mathbf{V} = \mathbf{Z}\mathbf{G}\mathbf{Z}' + \sigma_\varepsilon^2 \mathbf{I}_n.$$

In the case where all blocking variables are treated as fixed, we have that $\mathbf{V} = \sigma_\varepsilon^2 \mathbf{I}_n$. If there is one blocking variable that is treated as random, then $\mathbf{V}$ is block diagonal.

Since the component proportions of the mixture sum to one, a condition for the identifiability of model (4) has to be implied. For simplicity, we shall assume that the number of columns of $\mathbf{C}$ is $\sum_{i=1}^{B_F}(b_i - 1)$, where b_i represents is the number of levels of the ith fixed blocking variable. This can be accomplished by dropping one indicator variable and the corresponding element of γ for each blocking variable that is treated as fixed.

When the random error terms as well as the random block effects are normally distributed, the maximum likelihood estimator of the unknown fixed model parameter $\boldsymbol{\xi}$ in (4) is the generalized least squares estimator

$$\hat{\boldsymbol{\xi}} = (\mathbf{F}'\mathbf{V}^{-1}\mathbf{F})^{-1}\mathbf{F}'\mathbf{V}^{-1}\mathbf{y}.$$

We shall be concerned with the computation of designs that allow an efficient estimation of the mixture component effects $\boldsymbol{\beta}$. In order to find such designs, we will use the $\mathcal{D}$-optimality criterion. As a result, we will compute designs that maximize $|\mathbf{X}'\mathbf{V}^{-1}\mathbf{X} - \mathbf{X}'\mathbf{V}^{-1}\mathbf{Z}(\mathbf{Z}'\mathbf{V}^{-1}\mathbf{Z})^{-1}\mathbf{Z}'\mathbf{V}^{-1}\mathbf{X}|$, which is equivalent to maximizing the determinant of the information matrix $\mathbf{F}'\mathbf{V}^{-1}\mathbf{F}$ on the fixed effects $\boldsymbol{\xi}$ if the blocking structure is dictated by the experimental situation. When B_R random blocking variables are involved in the experiment, the $\mathcal{D}$-optimal design depends on the ratios $\eta_1 = \sigma_1^2/\sigma_\varepsilon^2$, $\eta_2 = \sigma_2^2/\sigma_\varepsilon^2$, $\ldots$, $\eta_{B_R} = \sigma_{B_R}^2/\sigma_\varepsilon^2$ through $\mathbf{V}$. In order to compare two designs with design matrices $\mathbf{F}_1$ and $\mathbf{F}_2$, we will report the relative efficiencies $\{|\mathbf{F}_1'\mathbf{V}^{-1}\mathbf{F}_1|/|\mathbf{F}_2'\mathbf{V}^{-1}\mathbf{F}_2|\}^{1/p}$.

4.2 Minimum support designs

A minimum support design is a design for which the number of distinct design points is equal to p. If we denote by $\mathbf{X}$ an $n \times p$ extended design matrix, the information matrix of a design with minimum support can be written as

$$\mathbf{X}'\mathbf{X} = \mathbf{X}_m'\mathbf{W}\mathbf{X}_m, \tag{5}$$

where $\mathbf{X}_m$ is a $p \times p$ matrix with rows equal to the Scheffé polynomial expansions of the p distinct design points, $\mathbf{W} = \mathrm{diag}[\, n_1 \; n_2 \; \ldots \; n_p]$, and n_i represents the number of replicates of the ith design point. Using this result, we find that

$$\mathbf{X}_m(\mathbf{X}'\mathbf{X})^{-1}\mathbf{X}_m' = \mathbf{X}_m(\mathbf{X}_m'\mathbf{W}\mathbf{X}_m)^{-1}\mathbf{X}_m' = \mathbf{X}_m\mathbf{X}_m^{-1}\mathbf{W}^{-1}(\mathbf{X}_m')^{-1}\mathbf{X}_m' = \mathbf{W}^{-1}. \tag{6}$$

This result, which does not depend on the choice of the design points, implies that, in the absence of blocking variables, the prediction variance in a design point is proportional to the inverse of its number of replicates and that the covariance between the predictions in two distinct design points is zero. This result will be used extensively in the sequel of this section. It was also used by Donev (1989) who showed that, when there is one fixed blocking variable acting at b levels, $|\mathbf{F}'\mathbf{F}| = |\mathbf{X}'\mathbf{X}| \times |\mathbf{R}|$, where

$$\mathbf{R} = \begin{bmatrix} r_1 - \sum_{i\in R_1} n_i^{-1} & -\sum_{i\in R_{12}} n_i^{-1} & \cdots & -\sum_{i\in R_{1,b-1}} n_i^{-1} \\ -\sum_{i\in R_{12}} n_i^{-1} & r_2 - \sum_{i\in R_2} n_i^{-1} & \cdots & -\sum_{i\in R_{2,b-1}} n_i^{-1} \\ \vdots & \vdots & \ddots & \vdots \\ -\sum_{i\in R_{1,b-1}} n_i^{-1} & -\sum_{i\in R_{2,b-1}} n_i^{-1} & \cdots & r_{b-1} - \sum_{i\in R_{b-1}} n_i^{-1} \end{bmatrix} \tag{7}$$

is a matrix which only depends on the assignment of the design points to the blocks. In this expression, which is valid only if no points are replicated within a block, r_i $(i = 1, 2, \ldots, b)$ is the number of points in the ith block that appear more than once in the entire design. The set of these points is denoted by R_i, and the set of points the ith and the jth block have in common is denoted by R_{ij} $(i, j = 1, 2, \ldots, b)$. Using this result, a $\mathcal{D}$-optimal minimum support design in the presence of one fixed blocking variable can easily be constructed in two steps:

1. Choose the p distinct design points and replicate them as evenly as possible in order to obtain a minimum support design with n observations that maximizes $|\mathbf{X}'\mathbf{X}|$. Which design points are replicated most is unimportant.

2. Spread the replicated design points as evenly as possible over the blocks and avoid replicating points within a block. The assignment of the non-replicated design points to the blocks does not affect the $\mathcal{D}$-optimality criterion value.

Usually, there are several options for the assignment in step 2 that lead to the same $\mathcal{D}$-criterion value. A similar result can be derived for the situation in which there is one random blocking variable. This is a consequence of the following theorem which is proven in Appendix A.

Theorem 1 *The determinant of the information matrix of a blocked experiment with minimum support and one blocking variable that has b levels and is treated as random is given by $\sigma_\varepsilon^{-2p}|\mathbf{X}'\mathbf{X}|\,|\mathbf{S}|\,|\mathbf{C}|$, where*

$$\mathbf{S} = \begin{bmatrix} \frac{\sigma_\varepsilon^2}{\sigma_1^2} + r_1 - \sum_{i\in R_1} n_i^{-1} & -\sum_{i\in R_{12}} n_i^{-1} & \cdots & -\sum_{i\in R_{1b}} n_i^{-1} \\ -\sum_{i\in R_{12}} n_i^{-1} & \frac{\sigma_\varepsilon^2}{\sigma_1^2} + r_2 - \sum_{i\in R_2} n_i^{-1} & \cdots & -\sum_{i\in R_{2b}} n_i^{-1} \\ \vdots & \vdots & \ddots & \vdots \\ -\sum_{i\in R_{1b}} n_i^{-1} & -\sum_{i\in R_{2b}} n_i^{-1} & \cdots & \frac{\sigma_\varepsilon^2}{\sigma_1^2} + r_b - \sum_{i\in R_b} n_i^{-1} \end{bmatrix},$$

$$\mathbf{C} = \begin{bmatrix} \frac{\eta_1}{1+k_1\eta_1} & 0 & \cdots & 0 \\ 0 & \frac{\eta_1}{1+k_2\eta_1} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \frac{\eta_1}{1+k_b\eta_1} \end{bmatrix},$$

$\eta_1 = \sigma_1^2/\sigma_\varepsilon^2$ and $k_1, k_2, \ldots, k_b$ represent the block sizes.

This result extends the result of Donev (1989). This is because the structure of S is identical to that of $\mathbf{R}$ when $\eta_1 \to \infty$. The theorem implies that, as in the case of one fixed blocking variable, a minimum support design in the presence of one random blocking variable can be constructed in two independent stages.

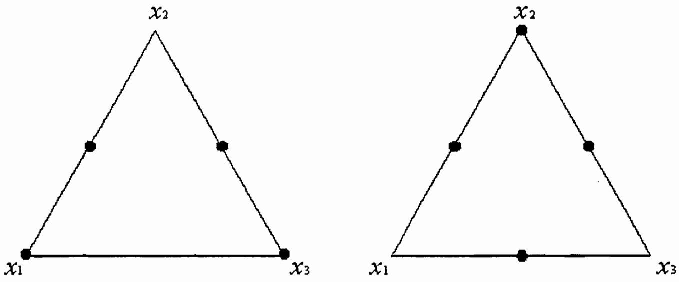


Figure 1: Graphical representation of a $\mathcal{D}$-optimal minimum support design with two blocks of size four for estimating a second order Scheffé polynomial in three mixture components.

Suppose, for example, that an experiment with eight runs has to be designed for estimating a second order Scheffé polynomial in three mixture variables and that there are two blocks of size four. The determinant $|\mathbf{X}'\mathbf{X}|$ can then be maximized by choosing the six points of the second order simplex lattice design and duplicating any two of the points. This yields $|\mathbf{X}'\mathbf{X}| = 0.000977$. Next, one instance of the duplicated points is assigned to the first block and the other is assigned to the second block. Finally, two of the four non-replicated points are assigned to one block and the remaining points are assigned to the other. One possible design obtained in this way is displayed in Figure 1. This design is a $\mathcal{D}$-optimal minimum support design no matter whether the blocking variable is treated as random or fixed. In a similar fashion, a $\mathcal{D}$-optimal minimum support design can be constructed for the constrained design region introduced in Section 3. In order to determine six points for estimating a second order Scheffé model, a search was performed over a 118-point grid consisting of the vertices of the design region, the centroids of order one, the overall centroid, and all points the proportions of which are multiples of 0.05 and that satisfy the constraints. The best points found are five of the six vertices of the design region and the overall centroid. The proportions corresponding to these design points are displayed in Table 3. In Figure 2, these points are used to construct a $\mathcal{D}$-optimal minimum support design.

As it is shown in Appendix B, the theorem of Donev (1989) can also be extended to the situation where more than one fixed blocking variable is involved in the experiment. The result in Theorem 1 can be extended to the situation where there is more than one random blocking variable, provided the block sizes are equal. This is shown in Appendix C.

Theorem 2 *The determinant of the information matrix of a blocked mixture experiment with minimum support and two or more blocking variables that are treated as fixed is proportional to the product of the determinant* $|\mathbf{X}'\mathbf{X}|$ *and a determinant that depends only on the assignment of the points to the blocks.*

Table 3: $\mathcal{D}$-optimal points for constructing a $\mathcal{D}$-optimal minimum support design on a constrained design.

x_1	x_2	x_3
0.180	0.220	0.600
0.180	0.500	0.320
0.400	0.000	0.600
0.477	0.237	0.287
0.500	0.500	0.000
0.800	0.000	0.200

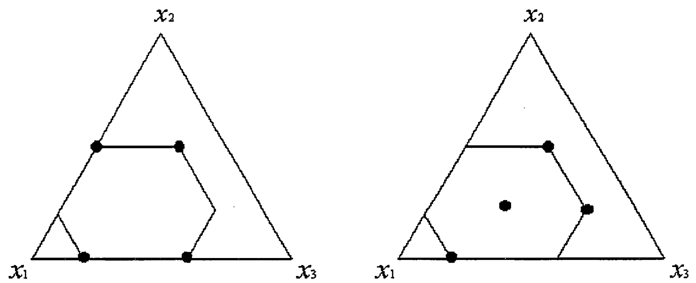


Figure 2: Graphical representation of a $\mathcal{D}$-optimal minimum support design on a constrained design region with two blocks of size four for estimating a second order Scheffé polynomial in three mixture components.

Theorem 3 *The determinant of the information matrix of a blocked mixture experiment with minimum support, equal block sizes and two or more blocking variables that are treated as random is proportional to the product of the determinant* $|\mathbf{X}'\mathbf{X}|$ *and a determinant that depends only on the assignment of the points to the blocks.*

These theorems imply that constructing $\mathcal{D}$-optimal minimum support designs can still be done in two stages when more than one blocking variable is involved in the experiment. In assigning the replicated design points to the blocks, it should be avoided that points are replicated at a given level of one of the blocking variables. Firstly, $|\mathbf{X}'\mathbf{X}|$ is maximized, and next, the best possible assignment is determined. Suppose, for example, that a mixture experiment involving two blocking variables has to be designed for estimating a second order Scheffé polynomial model. Suppose also that each blocking variable acts at two levels and that each block contains two observations. As a result, the experiment consists of eight observations. The $\mathcal{D}$-optimal design points for a minimum support design are given by the six points of the second order simplex lattice design, two of which are duplicated. The best assignment is obtained by assigning one of the duplicated design points to every block. Two designs obtained in this way are given in Figure 3. The two designs are optimal for this problem in case of fixed block effects as well as in case of random block effects. This small example shows that the non-replicated points can be assigned to any block without affecting the design criterion value.

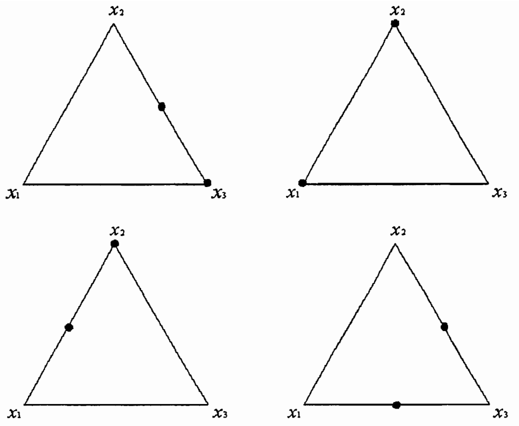
An example of the construction of $\mathcal{D}$-optimal minimum support designs with unequal block sizes for estimating a second order Scheffé model in four components is given in Figure 4. Unequal block sizes may be needed when, for instance, different numbers of machines are used every day or different numbers of laboratory assistants are available. The 16-point design in Figure 4 has four blocks of size three and two blocks of size two. It was designed for a situation in which there is one blocking variable acting at three levels and another acting at two levels. The ten distinct points of the design are the ten points of the second order simplex lattice design. The midpoints of the six edges were duplicated in order to obtain 16 design points. The duplicated points were assigned to the blocks first so that each block contains two edge midpoints. No edge midpoints occur more than once at the same level of any of the blocking variables. Finally, a corner point is assigned to each of the blocks that should have three observations.

4.3 General case

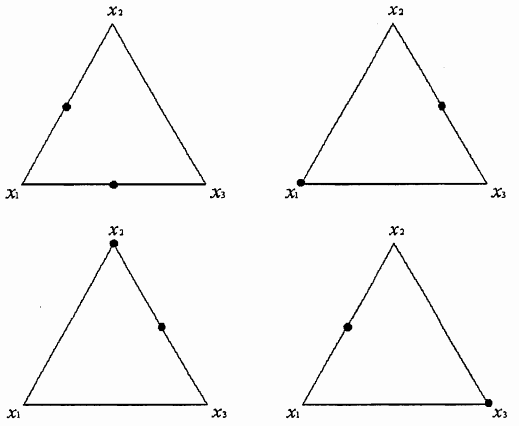
For the examples shown, the construction of $\mathcal{D}$-optimal minimum support designs is easy. However, the problem rapidly becomes complicated when the design region is constrained when more than one blocking variable acting at more than two levels is involved. If the design region is constrained, it may become hard to find a good set of design points. This was already illustrated by the design in Figure 2. For problems with relatively large blocks and/or relatively large numbers of levels for the blocking variables, finding the best possible assignment will also become less easy. In such cases, an algorithmic approach will be needed. In that case, one might as well consider moving away from the minimum support designs and consider using more than p distinct design points. The algorithmic approach is also helpful when the design region is irregular.

Atkinson and Donev (1992) (see page 162) already indicated that moving away from minimum support designs destroys the properties that facilitate the construction of designs in blocks and that this complication might yield a negligible or no increase in efficiency. It turns out that for some blocked mixture experiments the potential gain is larger. The design displayed in Table 4 is for example 8.26% better in terms of $\mathcal{D}$-efficiency than the minimum support designs in Figure 3 when the blocks are treated as fixed. The design was obtained by using the algorithm of Goos et al. (2002) and a grid of 231 equally spaced candidates on the design region. The proportions of the candidates were multiples of 0.05. It can be seen from Table 4 that, apart from the corner points, all design points lie on the edges of the design region.

The design in Table 4 can also be found when the block effects are treated as random, for example when $\eta_1 = \eta_2 = 5$. In that case, the design is 7.32% more efficient than the



(a)



(b)

Figure 3: Alternative $\mathcal{D}$-optimal minimum support designs with two blocking variables acting at two levels for estimating a quadratic Scheffé polynomial in three components.

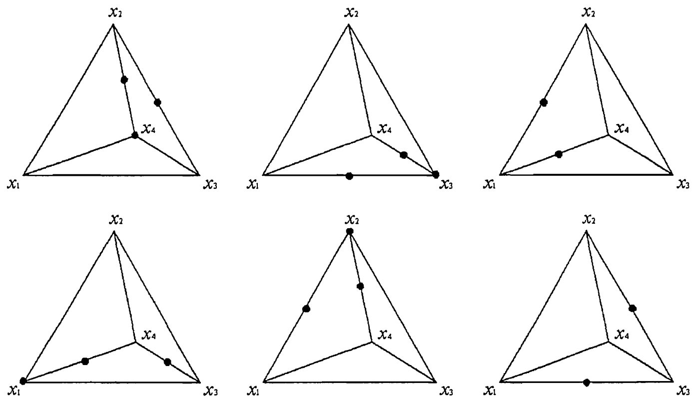


Figure 4: Graphical representation of a $\mathcal{D}$-optimal minimum support design with two blocking variables and unequal block sizes for estimating a quadratic Scheffé polynomial.

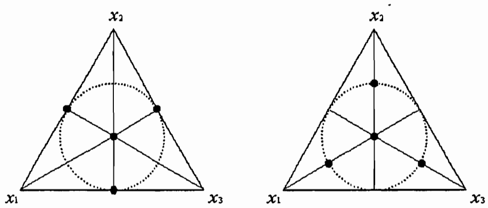
Table 4: $\mathcal{D}$-optimal design with blocks of size two for an experiment with two blocking variables acting at two levels.

		Blocking variable 1					
		Level 1			Level 2		
		x_1	x_2	x_3	x_1	x_2	x_3
Blocking variable 2	Level 1	0.70	0.30	0.00	0.00	0.00	1.00
		0.50	0.00	0.50	0.00	0.65	0.35
	Level 2	0.00	0.35	0.65	0.45	0.55	0.00
		0.00	1.00	0.00	1.00	0.00	0.00

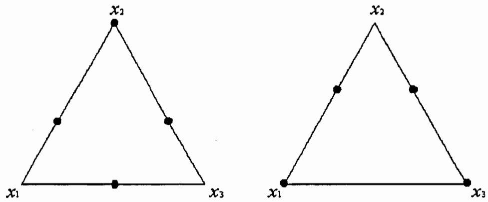
minimum support designs in Figure 3. When three observations per block are available, then no improvement can be realized by using the 231-point grid as the set of candidates. When four observations per block are available, a negligible improvement is possible. If the block effects are fixed, an improvement of 3.18% in the $\mathcal{D}$-criterion value is possible if the design points on the edges are moved in the direction of one of the vertices for the four component design in Figure 4. Similar improvements can be realized when the block effects are treated as random and η_1 and η_2 are not too small.

4.4 Orthogonality versus efficiency

An alternative method to design blocked mixture experiments is to construct an orthogonally blocked mixture experiment. The advantage of an orthogonally blocked design is that the mixture component effects can be estimated independently of the block effects. The conditions for orthogonal blocking were derived by Nigam (1976) and John (1984).



(a) Orthogonally blocked design



(b) $\mathcal{D}$-optimal design

Figure 5: Graphical representation of two three-component mixture designs with two blocks of size four for estimating a second order Scheffé polynomial.

For an experiment to be orthogonally blocked, the average level of the columns of $\mathbf{X}$ must be the same in every block. One approach to produce designs for mixture experiments in orthogonal blocks is described by Prescott (2000). He shows how projecting well-known orthogonally blocked response surface designs onto a constrained design region yields an orthogonally blocked mixture design. An example of such a design for three components x_1, x_2 and x_3 is provided in Figure 5a. The design points are also displayed in the left panel of Table 5. This design with two blocks of size four was obtained by projecting the eight points of a 2^3 factorial design onto the simplex.

The $\mathcal{D}$-optimal design in Figure 5b was obtained using the algorithm of Goos et al. (2002) and the set of 231 candidate points described earlier. If the block effects are treated as fixed, the relative $\mathcal{D}$-efficiency of the $\mathcal{D}$-optimal design with respect to the orthogonally blocked design amounts to 3.33. This means that the $\mathcal{D}$-optimal design is more than three times as efficient. A drawback of this design is that it is not orthogonally blocked. This drawback is, however, outweighed by the enormous increase in $\mathcal{D}$-efficiency. The minimum support design displayed in Figure 1 and in the right panel of Table 5 is 3.11% less efficient than the $\mathcal{D}$-optimal design but it is still more than three times as efficient

Table 5: Three-component mixture designs with two blocks of size four for estimating a quadratic Scheffé polynomial.

	Prescott			$\mathcal{D}$-optimal			Min. support		
Block	x_1	x_2	x_3	x_1	x_2	x_3	x_1	x_2	x_3
1	2/3	1/6	1/6	0.6	0.4	0	0.5	0.5	0
1	1/6	2/3	1/6	0.5	0	0.5	0.5	0	0.5
1	1/6	1/6	2/3	0	1	0	0	0	1
1	1/3	1/3	1/3	0	0.4	0.6	0	0.5	0.5
2	1/2	1/2	0	0.4	0.6	0	1	0	0
2	1/2	0	1/2	0	0.6	0.4	0	1	0
2	0	1/2	1/2	1	0	0	0.5	0	0.5
2	1/3	1/3	1/3	0	0	1	0	0.5	0.5

Table 6: $\mathcal{D}$-optimal design used for the bread baking experiment.

Block 1					Block 2				
Run	x_1	x_2	x_3	x_4	Run	x_1	x_2	x_3	x_4
1	0.45	0.55	0.00	0.00	1	0.55	0.45	0.00	0.00
2	0.00	0.50	0.50	0.00	2	0.00	0.00	1.00	0.00
3	0.50	0.00	0.00	0.50	3	0.50	0.00	0.00	0.50
4	0.00	0.50	0.00	0.50	4	0.00	1.00	0.00	0.00
5	0.00	0.00	0.50	0.50	5	0.00	0.00	0.00	1.00
6	0.50	0.00	0.50	0.00	6	0.00	0.00	0.50	0.50
7	0.00	0.00	1.00	0.00	7	0.50	0.00	0.50	0.00
8	1.00	0.00	0.00	0.00	8	0.00	0.50	0.00	0.50
9	0.00	0.00	0.00	1.00	9	0.00	0.50	0.50	0.00

as the orthogonally blocked design. Similar efficiency gains are obtained when the blocks are treated as random.

Another illustration of the poor performance of orthogonally blocked mixture experiments in terms of $\mathcal{D}$-efficiency is provided by the bread baking experiment introduced in Section 2. An orthogonally blocked design with two blocks of size nine is given in Table 1. A $\mathcal{D}$-optimal design for the same problem is displayed in Table 6. Contrary to the orthogonally blocked design, the $\mathcal{D}$-optimal design has observations at the corners of the design region and at or close to the midpoints of the edges. When the blocks are treated as fixed, the $\mathcal{D}$-optimal design is 70.07% better in terms of $\mathcal{D}$-efficiency. Again, this shows that orthogonality is extremely expensive in terms of efficiency.

The $\mathcal{D}$-optimal designs are not orthogonally blocked. However, for the $\mathcal{D}$-optimal design in Table 6 the orthogonality condition is satisfied for eight of the ten mixture component terms in the second order model. The two terms for which the condition is not satisfied are those in x_1 and x_2. For the minimum support design in Table 5, the orthogonality condition is satisfied for three of the six terms in the mixture model, one of which is a term involving a linear effect. For the $\mathcal{D}$-optimal design in the same table, the orthogonality condition is satisfied for two of the interaction terms only.

In this section, it was shown that orthogonally blocked mixture designs may perform poorly in terms of $\mathcal{D}$-efficiency. However, $\mathcal{D}$-optimal designs perform reasonably well in terms of orthogonality, especially when the block sizes are not too small. $\mathcal{D}$-optimal designs typically satisfy the orthogonality condition for most mixture component interaction terms and some of the linear terms. The number of terms for which the orthogonality condition is satisfied increases with the block sizes. This is also true for $\mathcal{D}$-optimal minimum support designs.

5 Qualitative experimental variables

The problem of designing a blocked mixture experiment with fixed block effects is strongly related to that of designing an experiment involving both qualitative and mixture variables. For both situations, the model (4) can be used since both blocks and levels of qualitative variables are represented by dummy variables. However, the effects of the blocking variables are usually considered as nuisance in a blocked mixture experiment, i.e. they are not of primary interest to the experimenter. The main reason for including the block effects in the model is to reduce the residual variance. If qualitative experimental variables are involved in an experiment, estimating their effects is as important as estimating the mixture component effects. Another difference between both problems is that, in blocked experiments the numbers of runs at each level of the blocking variables are often dictated by the experimental situation whereas usually no such constraints are imposed if an experiment involves qualitative variables that are of primary interest to the researcher. It is clear that, in the latter situation, other design options become available.

Reconsider for example the minimum support designs in Figure 3. These designs are $\mathcal{D}$-optimal minimum support designs for an experiment involving three mixture components and two qualitative variables acting at two levels. It turns out, however, that the unbalanced design in Figure 6 is equally good in terms of $\mathcal{D}$-efficiency if the interest is in estimating the mixture component effects and the effects of the blocking variables. The unbalanced design in Figure 6 and the balanced designs in Figure 3 only differ in the assignment of the non-replicated design points. Similarly, the design in Figure 7 is equivalent to the design in Figure 4. The optimality of the unbalanced designs is important for situations in which running experiments at certain levels of the qualitative variables is more difficult or more costly than at others. Of course, a design with one observation at some combinations of levels of the qualitative variables, like that in Figure 6 might not be liked by a practitioner. Such a situation is however unlikely to occur in practice as the total number of observations will usually be larger.

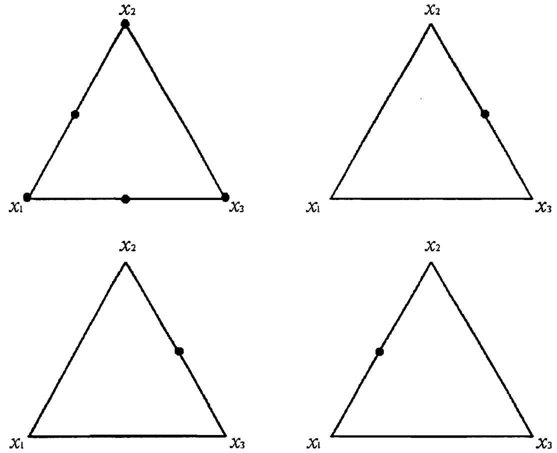


Figure 6: Alternative $\mathcal{D}$-optimal minimum support design with two qualitative variables acting at two levels for estimating a quadratic Scheffé polynomial in three components.

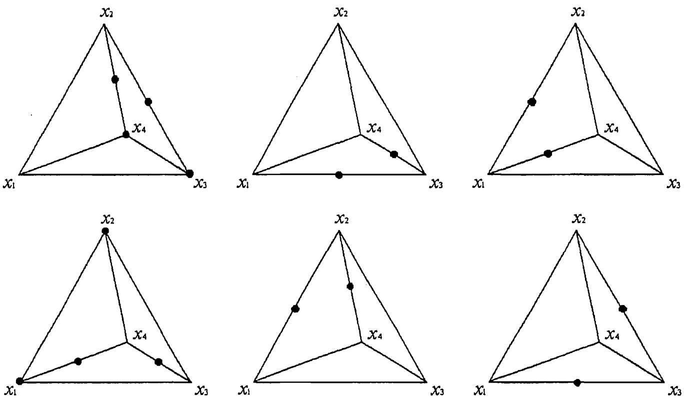


Figure 7: Alternative $\mathcal{D}$-optimal minimum support design with two blocking variables for estimating a quadratic Scheffé polynomial in four components.

6 Split-plot experiments

Many industrial mixture experiments involve process variables. As Cornell (1988) pointed out, a great number of them are carried out in a split-plot format. In this section, we will first describe the statistical model corresponding to this type of experiment. Next, the usual approaches to designing mixture experiments with process variables are discussed and the algorithmic approach is presented as an alternative. Finally, we will apply the algorithmic approach to the vinyl thickness experiment introduced in Section 2.

6.1 Statistical model and design

The hard-to-change factors in a split-plot experiment are usually called whole plot variables and can be denoted by $w_1, w_2, \ldots, w_{m_w}$ or simply by $\mathbf{w}$. The remaining $m_s = m - m_w$ variables are referred to as the sub-plot variables $s_1, s_2, \ldots, s_{m_s}$ or $\mathbf{s}$. In the vinyl thickness example, there are two whole plot variables and three sub-plot variables. The whole plot variables are the process variables rate of extrusion (w_1) and temperature of drying (w_2), whereas the sub-plot variables are the three mixture variables (s_1, s_2 and s_3).

The jth observation ($j = 1, 2, \ldots, k_i$) within the ith whole plot ($i = 1, 2, \ldots, b$) of a split-plot experiment can be written as

$$y_{ij} = \mathbf{f}'(\mathbf{w}_i, \mathbf{s}_{ij})\boldsymbol{\beta} + \gamma_i + \varepsilon_{ij}, \tag{8}$$

where $\mathbf{f}'(\mathbf{w}_i, \mathbf{s}_{ij})$ represents the expansion of the whole plot variables and the sub-plot variables, the $p \times 1$ vector $\boldsymbol{\beta}$ contains the p model parameters, γ_i is the random effect of the ith whole plot or the ith whole plot error, and ε_{ij} is the sub-plot error. We will assume that the split-plot model is estimable. For that purpose, a model containing linear terms in all mixture components should not contain an intercept.

In matrix notation, the model corresponding to a split-plot design is written as

$$\mathbf{Y} = \mathbf{X}\boldsymbol{\beta} + \mathbf{Z}\boldsymbol{\gamma} + \boldsymbol{\varepsilon},$$

where $\mathbf{X}$ represents the $n \times p$ design matrix containing the settings of both the whole plot variables $\mathbf{w}$ and the sub-plot variables $\mathbf{s}$. The matrix $\mathbf{Z}$ is a $n \times b$ matrix of zeroes and ones assigning the n observations to the b whole plots. The random effects of the b whole plots are contained within the b-dimensional vector $\boldsymbol{\gamma}$, and the random errors are contained within the n-dimensional vector $\boldsymbol{\varepsilon}$. It is assumed that $\boldsymbol{\varepsilon} \sim N(\mathbf{0}_n, \sigma_\varepsilon^2 \mathbf{I}_n)$, $\boldsymbol{\gamma} \sim N(\mathbf{0}_b, \sigma_\gamma^2 \mathbf{I}_b)$ and $\text{cov}(\boldsymbol{\varepsilon}, \boldsymbol{\gamma}) = \mathbf{0}_{n \times b}$. Under these assumptions, the variance-covariance matrix of the observations $\text{var}(\mathbf{y})$ can be written as

$$\mathbf{V} = \sigma_\varepsilon^2 (\mathbf{I}_n + \eta \mathbf{Z}\mathbf{Z}'),$$

where $\eta = \sigma_\gamma^2 / \sigma_\varepsilon^2$ is a measure for the extent to which observations within the same whole plot are correlated. The larger η, the more the observations within a whole plot are correlated.

Under normality, the maximum likelihood estimate of the unknown model parameter $\boldsymbol{\beta}$ in (8) is the generalized least squares estimate. As a result, the unknown model parameters $\boldsymbol{\beta}$ are estimated by

$$\hat{\boldsymbol{\beta}} = (\mathbf{X}'\mathbf{V}^{-1}\mathbf{X})^{-1}\mathbf{X}'\mathbf{V}^{-1}\mathbf{y},$$

and their information matrix is given by $\mathbf{X}'\mathbf{V}^{-1}\mathbf{X}$. A $\mathcal{D}$-optimal split-plot design maximizes the determinant of this matrix taking into account the restrictions imposed by the practical situation. In order to compare two designs with design matrices $\mathbf{X}_1$ and $\mathbf{X}_2$, we will report the relative efficiencies $\{|\mathbf{X}_1'\mathbf{V}^{-1}\mathbf{X}_1|/|\mathbf{X}_2'\mathbf{V}^{-1}\mathbf{X}_2|\}^{1/p}$.

In many cases, mixture experiments involving process variables are designed by combining simplex lattice designs for the mixture components and factorial arrangements for the process variables. This way of constructing a design is very simple but it leads to large experiments. Smaller designs, as for example the one in Table 2, are proposed by Kowalski et al. (2002).

In a split-plot experiment, the number of observations within each whole plot is usually dictated by the experimental situation. Typical examples of constraints on the number of observations in a whole plot are the size of a furnace or the number of runs that can be performed on one day. It is clear that the design in Figure 2 is a design option when the whole plot sizes are equal to four, for example because four runs can be performed on one day if the rate of extrusion and temperature of drying are kept fixed, and when the design region is unconstrained. For example, if five or six observations would be available per whole plot, then one or two center points could be added to each whole plot without destroying the balance of the design. In terms of design efficiency, this would however not be the best thing to do.

We propose to use an algorithmic approach to design mixture experiments involving process variables because this method is flexible enough to cope with any whole plot sizes as well as with constrained design regions. In addition, it enables the experimenter to take into account the split-plot nature of the experiment. Goos and Vandebroek (2002) developed an algorithm to generate $\mathcal{D}$-optimal split-plot designs with given numbers of whole plots and sub-plots. We have applied their algorithm to the vinyl thickness experiment. The resulting designs are compared to the design proposed by Kowalski et al. (2002) in the remainder of this section. The effects of including center points in the design and of constraining the design region are investigated as well.

6.2 The vinyl thickness experiment

In order to compute alternative designs for the vinyl thickness experiment, we have used the algorithm of Goos and Vandebroek (2002) which computes $\mathcal{D}$-optimal split-plot designs for given numbers of observations, whole plots and sub-plots. The model assumed is given by

$$y_{ij} = \sum_{k=1}^{3} \beta_k s_{k,ij} + \sum_{k=1}^{2} \sum_{l=k+1}^{3} \beta_{kl} s_{k,ij} s_{l,ij} + \alpha w_{1,i} w_{2,i} + \sum_{k=1}^{3} \sum_{l=1}^{2} \delta_{kl} s_{k,ij} w_{l,i} + \gamma_i + \varepsilon_{ij}.$$

This model combines the second order mixture model

$$y = \sum_{i=1}^{3} \beta_i s_i + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} s_i s_j$$

and the main-effects plus interactions model

$$y = \alpha_0 + \alpha_1 w_1 + \alpha_2 w_2 + \alpha_3 w_1 w_2.$$

More details on this type of model can be found in Kowalski et al. (2000, 2002).

The set of candidate design points consisted of all combinations of the six points of the second order simplex lattice design and the centroid for the three mixture components and the 2^2 factorial design for the two process variables. This produced a set of 7×4 candidate points. The $\mathcal{D}$-optimal design for this problem is displayed in Table 7. This design is optimal for a wide range of η-values including the estimated values obtained by Kowalski et al. (2002) and Goos (2002).

The $\mathcal{D}$-efficiency of the design in Table 7 is much larger than that of the design in Table 2. This is true for any value of η. For example, the $\mathcal{D}$-optimal design is 2.08 times better in terms of $\mathcal{D}$-efficiency than the design in Table 2 when $\eta = 1$. In addition, the average variance of the parameter estimates is 40% smaller. The $\mathcal{D}$-optimal design is therefore 67% better in terms of $\mathcal{A}$-efficiency. The average prediction variance over the design region is 44% smaller, so that the $\mathcal{D}$-optimal design is 78% better in terms of $\mathcal{V}$-efficiency. Finally, the maximum prediction variance is 55% smaller, yielding an improvement of 81% in $\mathcal{G}$-efficiency. Similar figures were obtained for other values of η. However, as opposed to the design proposed by Kowalski et al. (2002), the $\mathcal{D}$-optimal design does not have replicates of the center point and it does not allow the estimation of the pure whole plot error variance or the pure sub-plot error variance. In order to find out the effect of adding center points on the efficiency of the design for the vinyl thickness experiment, we have computed $\mathcal{D}$-optimal designs with 4, 8 and 12 center points. The resulting designs are displayed in Table 8.

The inclusion of center points leads to a smaller $\mathcal{D}$-efficiency. When $\eta = 1$ and four center points are included, the design obtained is 80% more efficient than that of Kowalski et al (2002). When 12 center points are included, a gain of 27% can be achieved. An overview of the improvements in efficiency is given in Table 9. From the table, it can be seen that the designs found using the algorithm of Goos and Vandebroek (2002) outperform the design of Kowalski et al. (2002) in terms of $\mathcal{D}$-optimality, $\mathcal{V}$-optimality and $\mathcal{G}$-optimality.

Table 7: $\mathcal{D}$-optimal design for the vinyl thickness experiment.

Whole plot	s_1	s_2	s_3	w_1	w_2
1	0.00	1.00	0.00	-1	-1
1	1.00	0.00	0.00	-1	-1
1	0.00	0.00	1.00	-1	-1
1	0.50	0.00	0.50	-1	-1
2	0.50	0.50	0.00	-1	-1
2	0.00	0.00	1.00	-1	-1
2	0.00	0.50	0.50	-1	-1
2	1.00	0.00	0.00	-1	-1
3	1.00	0.00	0.00	-1	1
3	0.00	0.00	1.00	-1	1
3	0.00	1.00	0.00	-1	1
3	0.00	0.50	0.50	-1	1
4	0.50	0.50	0.00	1	-1
4	0.00	0.00	1.00	1	-1
4	0.00	1.00	0.00	1	-1
4	1.00	0.00	0.00	1	-1
5	0.00	1.00	0.00	1	-1
5	0.00	0.50	0.50	1	-1
5	0.50	0.00	0.50	1	-1
5	1.00	0.00	0.00	1	-1
6	0.00	0.50	0.50	1	1
6	0.00	0.00	1.00	1	1
6	1.00	0.00	0.00	1	1
6	0.00	1.00	0.00	1	1
7	0.50	0.50	0.00	1	1
7	0.00	0.00	1.00	1	1
7	0.00	1.00	0.00	1	1
7	0.50	0.00	0.50	1	1

Table 8: $\mathcal{D}$-optimal designs with 4, 8 and 12 center points for the vinyl thickness experiment.

Whole	4 center points					8 center points					12 center points				
plot	x_1	x_2	x_3	z_1	z_2	x_1	x_2	x_3	z_1	z_2	x_1	x_2	x_3	z_1	z_2
1	0.00	0.50	0.50	-1	-1	0.00	0.00	1.00	-1	-1	0.00	1.00	0.00	-1	-1
1	0.00	1.00	0.00	-1	-1	0.00	1.00	0.00	-1	-1	0.00	0.00	1.00	-1	-1
1	1.00	0.00	0.00	-1	-1	1.00	0.00	0.00	-1	-1	1.00	0.00	0.00	-1	-1
1	0.00	0.00	1.00	-1	-1	0.50	0.50	0.00	-1	-1	0.00	0.50	0.50	-1	-1
2	1.00	0.00	0.00	-1	1	0.00	1.00	0.00	-1	1	0.50	0.00	0.50	-1	1
2	0.50	0.50	0.00	-1	1	0.00	0.00	1.00	-1	1	1.00	0.00	0.00	-1	1
2	0.00	0.00	1.00	-1	1	1.00	0.00	0.00	-1	1	0.00	1.00	0.00	-1	1
2	0.00	1.00	0.00	-1	1	0.00	0.50	0.50	-1	1	0.00	0.00	1.00	-1	1
3	0.00	0.50	0.50	-1	1	0.50	0.00	0.50	1	-1	0.50	0.00	0.50	1	-1
3	0.50	0.00	0.50	-1	1	1.00	0.00	0.00	1	-1	0.00	0.00	1.00	1	-1
3	0.50	0.50	0.00	-1	1	0.50	0.50	0.00	1	-1	1.00	0.00	0.00	1	-1
3	0.00	1.00	0.00	-1	1	0.00	0.50	0.50	1	-1	0.00	1.00	0.00	1	-1
4	0.00	0.00	1.00	1	-1	1.00	0.00	0.00	1	-1	0.50	0.50	0.00	1	1
4	0.50	0.00	0.50	1	-1	0.50	0.00	0.50	1	-1	0.00	1.00	0.00	1	1
4	1.00	0.00	0.00	1	-1	0.00	1.00	0.00	1	-1	0.00	0.00	1.00	1	1
4	0.00	1.00	0.00	1	-1	0.00	0.00	1.00	1	-1	1.00	0.00	0.00	1	1
5	0.00	0.50	0.50	1	1	0.50	0.50	0.00	1	1	0.33	0.33	0.33	0	0
5	0.50	0.50	0.00	1	1	0.00	1.00	0.00	1	1	0.33	0.33	0.33	0	0
5	0.00	0.00	1.00	1	1	0.00	0.00	1.00	1	1	0.33	0.33	0.33	0	0
5	1.00	0.00	0.00	1	1	1.00	0.00	0.00	1	1	0.33	0.33	0.33	0	0
6	0.00	1.00	0.00	1	1	0.33	0.33	0.33	0	0	0.33	0.33	0.33	0	0
6	0.00	0.00	1.00	1	1	0.33	0.33	0.33	0	0	0.33	0.33	0.33	0	0
6	1.00	0.00	0.00	1	1	0.33	0.33	0.33	0	0	0.33	0.33	0.33	0	0
6	0.50	0.00	0.50	1	1	0.33	0.33	0.33	0	0	0.33	0.33	0.33	0	0
7	0.33	0.33	0.33	0	0	0.33	0.33	0.33	0	0	0.33	0.33	0.33	0	0
7	0.33	0.33	0.33	0	0	0.33	0.33	0.33	0	0	0.33	0.33	0.33	0	0
7	0.33	0.33	0.33	0	0	0.33	0.33	0.33	0	0	0.33	0.33	0.33	0	0
7	0.33	0.33	0.33	0	0	0.33	0.33	0.33	0	0	0.33	0.33	0.33	0	0

Table 9: Relative efficiencies of the design options for the vinyl thickness experiment.

	$\eta = 1$				$\eta = 10$			
	D	A	V	G	D	A	V	G
$\mathcal{D}$-optimal	2.08	1.67	1.78	1.81	2.09	1.61	1.42	1.04
4 center points	1.80	1.52	1.64	1.92	1.79	1.42	1.28	1.12
8 center points	1.54	1.23	1.40	1.77	1.52	1.15	1.15	1.14
12 center points	1.27	0.77	1.14	1.23	1.24	0.79	1.03	1.07
Kowalski et al. (2002)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

In terms of $\mathcal{A}$-optimality, the design with 12 center points is worse than the benchmark design, but the others are all considerably better. If the experimenter requires an independent estimate of the variances of the experimental errors, an alternative approach to that taken by Kowalski et al. (2002) is to spread the replications over as many design points as possible. This way the efficiency of the design would be higher.

The approach presented here is particularly useful when constraints are imposed on the mixture components. It does not only allow us to generate an optimum design under certain constraints but also to evaluate the robustness of the design in the case of departures from them. For example, the design in Table 10 is $\mathcal{D}$-optimal for η-values in the neighborhood of one when the constraints introduced in Section 3 apply. It was obtained using a 52-point candidate set obtained by combining the vertices, the edge midpoints and the overall centroid for the mixture region with a 2^2 design for the process variables.

7 Discussion

Orthogonality is a useful feature of an experimental design. Two-level factorials designs can be divided in orthogonal blocks without loss of efficiency, while the loss in the case of blocking response surface designs is modest. However, our results show that when orthogonality is required for studying the properties of a mixture, it comes at a considerably higher cost in terms of the precision of the model parameters than in other cases. Often orthogonality is even unattainable because of constraints on the mixture components, the block sizes and the total number of observations. It can be lost as a result of missing observations or inaccurate setting of the component levels. There are also many situations where the experimenter needs to investigate the effect of other variables, such as process controls, or to address complications with the block structure, such as those occurring in split-plot experiments. The requirement of orthogonality then becomes a secondary issue.

The approach to blocking experiments with mixtures described here is free from all these limitations and ensures $\mathcal{D}$-optimality of the blocked experimental designs. It provides valuable flexibility to select the number of blocks and the number of observations in them, and to specify the nature of the blocking variables generating the blocks. It is also

Table 10: $\mathcal{D}$-optimal design for the vinyl thickness experiment assuming a constrained design region.

Whole plot	s_1	s_2	s_3	w_1	w_2
1	0.24	0.48	0.29	-1	-1
1	0.20	0.80	0.00	-1	-1
1	0.00	0.40	0.60	-1	-1
1	0.50	0.18	0.32	-1	-1
2	0.50	0.50	0.00	-1	-1
2	0.00	0.40	0.60	-1	-1
2	0.22	0.18	0.60	-1	-1
2	0.00	0.80	0.20	-1	-1
3	0.20	0.80	0.00	-1	1
3	0.00	0.40	0.60	-1	1
3	0.50	0.18	0.32	-1	1
3	0.50	0.50	0.00	-1	1
4	0.24	0.48	0.29	-1	1
4	0.00	0.80	0.20	-1	1
4	0.50	0.50	0.00	-1	1
4	0.22	0.18	0.60	-1	1
5	0.50	0.18	0.32	1	-1
5	0.00	0.80	0.20	1	-1
5	0.22	0.18	0.60	1	-1
5	0.50	0.50	0.00	1	-1
6	0.24	0.48	0.29	1	1
6	0.00	0.40	0.60	1	1
6	0.20	0.80	0.00	1	1
6	0.50	0.18	0.32	1	1
7	0.00	0.40	0.60	1	1
7	0.50	0.50	0.00	1	1
7	0.00	0.80	0.20	1	1
7	0.22	0.18	0.60	1	1

possible to establish the optimum block sizes. Our computational results have shown that choosing equal block sizes is not always optimal.

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Appendix A. Proof of Theorem 1

The information matrix of an experiment with one random blocking variable is

$$
\begin{aligned}
\mathbf{M} &= \mathbf{X}'\mathbf{V}^{-1}\mathbf{X}, \\
&= \frac{1}{\sigma_\varepsilon^2}\left\{\mathbf{X}'\mathbf{X} - \begin{bmatrix}\mathbf{X}_1'\mathbf{1}_{k_1} & \mathbf{X}_2'\mathbf{1}_{k_2} & \cdots & \mathbf{X}_b'\mathbf{1}_{k_b}\end{bmatrix} \begin{bmatrix} \frac{\eta_1}{1+k_1\eta_1} & 0 & \dots & 0 \\ 0 & \frac{\eta_1}{1+k_2\eta_1} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \frac{\eta_1}{1+k_b\eta_1} \end{bmatrix} \begin{bmatrix} \mathbf{1}_{k_1}'\mathbf{X}_1 \\ \mathbf{1}_{k_2}'\mathbf{X}_2 \\ \vdots \\ \mathbf{1}_{k_b}'\mathbf{X}_b \end{bmatrix}\right\}, \\
&= \frac{1}{\sigma_\varepsilon^2}\left\{\mathbf{X}'\mathbf{X} - \begin{bmatrix}\mathbf{X}_1'\mathbf{1}_{k_1} & \mathbf{X}_2'\mathbf{1}_{k_2} & \cdots & \mathbf{X}_b'\mathbf{1}_{k_b}\end{bmatrix} \mathbf{C} \begin{bmatrix} \mathbf{1}_{k_1}'\mathbf{X}_1 \\ \mathbf{1}_{k_2}'\mathbf{X}_2 \\ \vdots \\ \mathbf{1}_{k_b}'\mathbf{X}_b \end{bmatrix}\right\},
\end{aligned}
\tag{9}
$$

where k_i is the number of observations in the ith block and $\eta_1 = \sigma_1^2/\sigma_\varepsilon^2$.
Using Harville's (1997) Theorem 18.1.1, we have that

$$
|\mathbf{M}| = \sigma_\varepsilon^{-2p}|\mathbf{X}'\mathbf{X}|\,|\mathbf{C}|\left|\mathbf{C}^{-1} - \begin{bmatrix} \mathbf{1}_{k_1}'\mathbf{X}_1 \\ \mathbf{1}_{k_2}'\mathbf{X}_2 \\ \vdots \\ \mathbf{1}_{k_b}'\mathbf{X}_b \end{bmatrix} (\mathbf{X}'\mathbf{X})^{-1} \begin{bmatrix}\mathbf{X}_1'\mathbf{1}_{k_1} & \mathbf{X}_2'\mathbf{1}_{k_2} & \cdots & \mathbf{X}_b'\mathbf{1}_{k_b}\end{bmatrix}\right|,
$$

where

$$
\mathbf{C}^{-1} = \begin{bmatrix} \frac{1}{\eta_1}+k_1 & 0 & \dots & 0 \\ 0 & \frac{1}{\eta_1}+k_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \frac{1}{\eta_1}+k_b \end{bmatrix}.
$$

Using Equation (6), we have that $\mathbf{1}_{k_i}'\mathbf{X}_i(\mathbf{X}'\mathbf{X})^{-1}\mathbf{X}_i'\mathbf{1}_{k_i} = k_i - r_i + \sum_{i\in R_i} n_i^{-1}$ and that $\mathbf{1}_{k_i}'\mathbf{X}_i(\mathbf{X}'\mathbf{X})^{-1}\mathbf{X}_j'\mathbf{1}_{k_j} = \sum_{i\in R_{ij}} n_i^{-1}$ if no design points are replicated within a block. The definitions of r_i, n_i, R_i and R_{ij} can be found in Section 4.2.

Appendix B. Proof of Theorem 2

Firstly, suppose that there are two blocking variables acting at b_1 and b_2 levels respectively and that they are both treated as fixed. Denote by $\mathbf{X}_{ij}$ the part of the design matrix $\mathbf{X}$ corresponding to the ith level of the first blocking variable and the jth level of the second blocking variable, and by n_{ij} the corresponding number of runs so that $\sum_{i=1}^{b_1}\sum_{j=1}^{b_2} n_{ij} = n$. The $n \times (p + b_1 + b_2 - 2)$ design matrix for all the fixed effects can then be written as

$$\mathbf{F} = \begin{bmatrix}
\mathbf{X}_{11} & \mathbf{1}_{n_{11}} & \mathbf{0}_{n_{11}} & \cdots & \mathbf{0}_{n_{11}} & \mathbf{1}_{n_{11}} & \mathbf{0}_{n_{11}} & \cdots & \mathbf{0}_{n_{11}} \\
\mathbf{X}_{12} & \mathbf{1}_{n_{12}} & \mathbf{0}_{n_{11}} & \cdots & \mathbf{0}_{n_{12}} & \mathbf{0}_{n_{12}} & \mathbf{1}_{n_{12}} & \cdots & \mathbf{0}_{n_{12}} \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\
\mathbf{X}_{1b_2} & \mathbf{1}_{n_{1b_2}} & \mathbf{0}_{n_{11}} & \cdots & \mathbf{0}_{n_{1b_2}} & \mathbf{0}_{n_{1b_2}} & \mathbf{0}_{n_{1b_2}} & \cdots & \mathbf{0}_{n_{1b_2}} \\
\mathbf{X}_{21} & \mathbf{0}_{n_{21}} & \mathbf{1}_{n_{21}} & \cdots & \mathbf{0}_{n_{21}} & \mathbf{1}_{n_{21}} & \mathbf{0}_{n_{21}} & \cdots & \mathbf{0}_{n_{12}} \\
\mathbf{X}_{22} & \mathbf{0}_{n_{22}} & \mathbf{1}_{n_{22}} & \cdots & \mathbf{0}_{n_{22}} & \mathbf{0}_{n_{22}} & \mathbf{1}_{n_{22}} & \cdots & \mathbf{0}_{n_{22}} \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\
\mathbf{X}_{2b_2} & \mathbf{0}_{n_{2b_2}} & \mathbf{1}_{n_{2b_2}} & \cdots & \mathbf{0}_{n_{2b_2}} & \mathbf{0}_{n_{2b_2}} & \mathbf{0}_{n_{2b_2}} & \cdots & \mathbf{0}_{n_{2b_2}} \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\
\mathbf{X}_{b_1-1,1} & \mathbf{0}_{n_{b_1-1,1}} & \mathbf{0}_{n_{b_1-1,1}} & \cdots & \mathbf{1}_{n_{b_1-1,1}} & \mathbf{1}_{n_{b_1-1,1}} & \mathbf{0}_{n_{b_1-1,1}} & \cdots & \mathbf{0}_{n_{b_1-1,1}} \\
\mathbf{X}_{b_1-1,2} & \mathbf{0}_{n_{b_1-1,2}} & \mathbf{0}_{n_{b_1-1,2}} & \cdots & \mathbf{1}_{n_{b_1-1,2}} & \mathbf{0}_{n_{b_1-1,2}} & \mathbf{1}_{n_{b_1-1,2}} & \cdots & \mathbf{0}_{n_{b_1-1,2}} \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\
\mathbf{X}_{b_1-1,b_2} & \mathbf{0}_{n_{b_1-1,b_2}} & \mathbf{0}_{n_{b_1-1,b_2}} & \cdots & \mathbf{1}_{n_{b_1-1,b_2}} & \mathbf{0}_{n_{b_1-1,b_2}} & \mathbf{0}_{n_{b_1-1,b_2}} & \cdots & \mathbf{0}_{n_{b_1-1,b_2}} \\
\mathbf{X}_{b_1 1} & \mathbf{0}_{n_{b_1 1}} & \mathbf{0}_{n_{b_1 1}} & \cdots & \mathbf{0}_{n_{b_1 1}} & \mathbf{1}_{n_{b_1 1}} & \mathbf{0}_{n_{b_1 1}} & \cdots & \mathbf{0}_{n_{b_1 1}} \\
\mathbf{X}_{b_1 2} & \mathbf{0}_{n_{b_1 2}} & \mathbf{0}_{n_{b_1 2}} & \cdots & \mathbf{0}_{n_{b_1 2}} & \mathbf{0}_{n_{b_1 2}} & \mathbf{1}_{n_{b_1 2}} & \cdots & \mathbf{0}_{n_{b_1 2}} \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\
\mathbf{X}_{b_1 b_2} & \mathbf{0}_{n_{b_1 b_2}} & \mathbf{0}_{n_{b_1 b_2}} & \cdots & \mathbf{0}_{n_{b_1 b_2}} & \mathbf{0}_{n_{b_1 b_2}} & \mathbf{0}_{n_{b_1 b_2}} & \cdots & \mathbf{0}_{n_{b_1 b_2}}
\end{bmatrix}.$$

Denoting $\mathbf{X}'_{i.} = \begin{bmatrix}\mathbf{X}'_{i1} & \mathbf{X}'_{i2} & \cdots & \mathbf{X}'_{ib_2}\end{bmatrix}$, $\mathbf{X}'_{.j} = \begin{bmatrix}\mathbf{X}'_{1j} & \mathbf{X}'_{2j} & \cdots & \mathbf{X}'_{b_2 j}\end{bmatrix}$, and by $n_{i.}$ and $n_{.j}$ the number of rows of $\mathbf{X}_{i.}$ and $\mathbf{X}_{.j}$, the information matrix on the unknown fixed effects can be written as

$$\mathbf{F}'\mathbf{F} = \begin{bmatrix}
\mathbf{X}'\mathbf{X} & \mathbf{X}'_{1.}\mathbf{1}_{n_{1.}} & \cdots & \mathbf{X}'_{b_1,1.}\mathbf{1}_{n_{b_1-1,.}} & \mathbf{X}'_{.1}\mathbf{1}_{n_{.1}} & \cdots & \mathbf{X}'_{.,b_2-1}\mathbf{1}_{n_{.,b_2-1}} \\
\mathbf{1}'_{n_{1.}}\mathbf{X}_{1.} & n_{1.} & \cdots & 0 & n_{11} & \cdots & n_{1,b_2-1} \\
\mathbf{1}'_{n_{2.}}\mathbf{X}_{2.} & 0 & \cdots & 0 & n_{21} & \cdots & n_{2,b_2-1} \\
\vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\
\mathbf{1}_{n_{b_1-1,.}}\mathbf{X}_{b_1,1.} & 0 & \cdots & n_{b_1-1,.} & n_{b_1-1,1} & \cdots & n_{b_1-1,b_2-1} \\
\mathbf{1}'_{n_{.1}}\mathbf{X}_{.1} & n_{11} & \cdots & n_{b_1-1,1} & n_{.1} & \cdots & 0 \\
\mathbf{1}'_{n_{.2}}\mathbf{X}_{.2} & n_{12} & \cdots & n_{b_1-1,2} & 0 & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\
\mathbf{1}_{n_{.,b_2-1}}\mathbf{X}_{.,b_2-1} & n_{1,b_2-1} & \cdots & n_{b_1-1,b_2-1} & 0 & \cdots & n_{.,b_2-1,.}
\end{bmatrix},$$

the determinant of which is equal to

$$|\mathbf{F}'\mathbf{F}| = |\mathbf{X}'\mathbf{X}|\ |\mathbf{N} - \mathbf{L}(\mathbf{X}'\mathbf{X})^{-1}\mathbf{L}'|,$$

where

$$\mathbf{N} = \begin{bmatrix} n_{1.} & \cdots & 0 & n_{11} & \cdots & n_{1,b_2-1} \\ 0 & \cdots & 0 & n_{21} & \cdots & n_{2,b_2-1} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ 0 & \cdots & n_{b_1-1,.} & n_{b_1-1,1} & \cdots & n_{b_1-1,b_2-1} \\ n_{11} & \cdots & n_{b_1-1,1} & n_{.1} & \cdots & 0 \\ n_{12} & \cdots & n_{b_1-1,2} & 0 & \cdots & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ n_{1,b_2-1} & \cdots & n_{b_1-1,b_2-1} & 0 & \cdots & n_{.,b_2-1,.} \end{bmatrix},$$

and

$$\mathbf{L}' = \begin{bmatrix} \mathbf{X}'_{1.}\mathbf{1}_{n_{1.}} & \cdots & \mathbf{X}'_{b_1,1.}\mathbf{1}_{n_{b_1-1,.}} & \mathbf{X}'_{.1}\mathbf{1}_{n_{.1}} & \cdots & \mathbf{X}'_{.,b_2-1}\mathbf{1}_{n_{.,b_2-1}} \end{bmatrix}.$$

Using (6), it is easy to see that the matrix product $\mathbf{L}(\mathbf{X}'\mathbf{X})^{-1}\mathbf{L}'$ only depends on the assignment of the design points to the blocks and not on their factor levels. As a result, the determinant of the information matrix can be split in two parts: one that depends on the design points and one that only depends on the assignment. A proof for more than two blocking variables that are treated as fixed can be constructed in the same way.

Appendix C. Proof of Theorem 3

Now suppose that there are B_R blocking variables acting at $b_1, b_2, \ldots, b_{B_R}$ levels, that the blocking variables are treated as random and that the block sizes are equal. Using the results of Donev and Goos (2002), it can be seen that the information matrix is given by

$$\begin{aligned} \mathbf{M} &= \frac{1}{\sigma_\varepsilon^2}\Big\{\mathbf{X}'\mathbf{X} - \sum_{i=1}^{B_R}\sum_{j=1}^{b_i} c_i(\mathbf{X}'_{ij}\mathbf{1}_{a_i})(\mathbf{1}'_{a_i}\mathbf{X}_{ij}) + d(\mathbf{X}'\mathbf{1}_n)(\mathbf{1}'_n\mathbf{X})\Big\}, \\ &= \frac{1}{\sigma_\varepsilon^2}\left\{\mathbf{X}'\mathbf{X} - \begin{bmatrix}\mathbf{X}'_{11}\mathbf{1}_{a_1} & \cdots & \mathbf{X}'_{Bb_B}\mathbf{1}_{a_B} & \mathbf{X}'\mathbf{1}_n\end{bmatrix} \begin{bmatrix} c_1 & 0 & \cdots & 0 \\ \vdots & \ddots & \vdots & \vdots \\ 0 & \cdots & c_B & 0 \\ 0 & \cdots & 0 & -d \end{bmatrix} \begin{bmatrix} \mathbf{X}'_{11}\mathbf{1}_{a_1} \\ \vdots \\ \mathbf{X}'_{Bb_B}\mathbf{1}_{a_B} \\ \mathbf{X}'\mathbf{1}_n \end{bmatrix}\right\}, \end{aligned}$$

where $a_i = n/b_i$, and c_i $(i = 1, 2, \ldots, B_R)$ and d are constants that depend on the block size, the numbers of levels of the blocking variables and the variance components only. This matrix is similar to (9), so that its determinant can be written as a product of two determinants that are independent of each other.

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