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Block Designs for Mixture Experiments

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Summary

One of the desirabilities of any response surface design is that it should lend itself to blocking. Arrangement of design points into several blocks help reduction in experimental error and consequently provide efficient estimates of the regression parameters β of a response surface model. In this paper the problem of orthogonal blocking of mixture designs and method of estimating the parameters of the model are discussed. A method of blocking symmetric simplex designs and another method using orthogonal arrays of strength 2 are presented.

Key words : Experiments with mixtures, orthogonal blocking, orthogonal arrays, symmetric simplex designs.

Introduction

Experiments in which the compositional variables are proportions of different components and the response due to any combination depends on the proportions of the components present in the combination but not on their amounts are called experiments with mixtures. Each combination is a mixture of q components. If x_{ij} denotes the proportion of the j^{th} components in the i^{th} combination, then,

$$0 \le x_{ij} \le 1 , \sum_{j=1}^{q} x_{ij} = 1, \qquad i = 1, 2, \ldots, N \tag{1.1}$$

Due to the constraints (1.1) the factor space is a regular (q–1) dimensional simplex and designs for exploration of such factor spaces are called simplex designs. Simplex lattice, simplex centroid designs (Scheffe' [9] [10]) and symmetric simplex designs (Murty and Das [4]) are examples of simplex designs. Let D = (x_{ij}) be the N_{xq} design matrix for the study of response surfaces with N mixture combinations. According to Box and Hunter [1] one of the requirements of any response surface design is that it should lend itself to blocking. When the design points are arranged in blocks and the response at i^{th} mixture combination occurring in the m^{th} block is denoted as y_{im}, a first order model for the response surface will be of the form

$$y_{im} = \sum_{j=1}^{q} \beta_j x_{ij} + \alpha_m + \varepsilon_{im} \tag{1.2}$$

where β_j is the effect of the j^{th} mixture component in the i^{th} combination α_m is the m^{th} block effect and ε_{im} is the random error associated with y_{im}.

Arrangement of the design points in blocks in general facilitates reduction in experimental error by providing separate estimates of block effects $\underline{\alpha}' = (\alpha_1, \alpha_2, \ldots, \alpha_b)$, with a consequent increase in efficiency of the estimates of the regression parameters $\underline{\beta}' = (\beta_1, \beta_2, \ldots, \beta_q)$ and the estimated response. Also, intrablock comparisons of the estimated responses become more efficient than inter block comparisons. This fact would become important and valuable when blocking is made on the basis of some physical or experimental conditions. The arrangement of the N design points in b blocks $(B_1, B_2, \ldots, B_b)$ such that $\underline{\beta}$ and $\underline{\alpha}$ can be estimated with $\text{cov}(\hat{\underline{\beta}}, \hat{\underline{\alpha}}) = 0$, is known as orthogonal blocking. Otherwise it is called non orthogonal blocking.

In this paper the problem of estimating regression parameters $\underline{\beta}$ and block parameters $\underline{\alpha}$ such that $\text{cov}(\hat{\underline{\beta}}, \hat{\underline{\alpha}}) = 0$ is discussed. A method of blocking symmetric simplex designs and a method using orthogonal arrays of strength 2 are presented.

2. *Fitting of Response Surface Models*

A general linear model representing the response surface may be written as

$$Y = X\underline{\beta} + \underline{\varepsilon} \tag{2.1}$$

where

$Y = (y_1, y_2, \ldots, y_N)'$ is a vector of N observations at the N design points,

X : (Nxn) matrix of coefficients of the regression parameters,

$\underline{\beta}$: (nxl) vector of regression parameters,

$\underline{\varepsilon}$: (Nxl) vector of random errors following $N(0, \sigma^2 I)$

The least squares estimate of $\underline{\beta}$ is given by

$$\hat{\underline{\beta}} = (X'X)^{-1} X'Y \tag{2.2}$$

$$V(\hat{\underline{\beta}}) = (X'X)^{-1}\sigma^2, \text{ and} \tag{2.3}$$

$$\hat{\sigma}^2 = \frac{(Y - X\hat{\underline{\beta}})'(Y - X\hat{\underline{\beta}})}{N - n} \tag{2.4}$$

We assume that the first and second order canonical polynomials of Scheffe' [9] are appropriate for representing the response surface. Then a first order model has $X = X_1 = D$, $n = q$ and is written as

$$E(y_i) = \sum_{j=1}^{q} \beta_j x_{ij} \tag{2.5}$$

For a second order model, $X = [X_1 : X_2]$, $n = \frac{q(q+1)}{2}$, the $\binom{q}{2}$ additional columns X_{jk} $(j < k)$ of X_2 arising due to the product terms $(x_{ij}x_{ik})$, $(i = 1, 2, \ldots, N)$. The model then is written as

$$E(y_i) = \sum_{j=1}^{q} \beta_j x_{ij} + \sum_{j<k=1}^{q} \beta_{jk} x_{ij} x_{ik} \tag{2.6}$$

Suppose the N design points are arranged in b blocks $(B_1, B_2, \ldots B_b)$ in such a way that a point occurs at most once in any block, the m^{th} block B_m containing n_m design points, $\sum_{m=1}^{b} n_m = N$.

Define the matrix Z such that

$$Z_{im} = 1 \qquad \text{if } x_{ij} \in B_m, \ j = 1, 2, \ldots, q \tag{2.7}$$

$$= 0 \text{ otherwise}$$

The matrix Z of order Nxb (b<N) is then the incidence matrix of the design. It may be noted that

$$X_1 J_{q1} = J_{N1} \quad \text{and } ZJ_{b1} = J_{N1} \tag{2.8}$$

where J is a vector with all its elements one. Also the rank of Z is b. Incorporating the block effects $\underline{\alpha}$, the model (2.1) can be written as

$$Y = X\underline{\beta} + Z\underline{\alpha} + \varepsilon \tag{2.9}$$

where Y, X, $\underline{\beta}$, Z, $\underline{\alpha}$ and ε are as defined in (1.2), (2.1) and (2.7). The normal equations for estimating the parameters are given by

$$\begin{bmatrix} X'X & X'Z \\ Z'X & Z'Z \end{bmatrix} \begin{bmatrix} \hat{\underline{\beta}} \\ \hat{\underline{\alpha}} \end{bmatrix} = \begin{bmatrix} X'Y \\ Z'Y \end{bmatrix} \tag{2.10}$$

In view of (2.8), the coefficient matrix on the l.h.s. of (2.10) has rank less than (n + b) and is therefore singular. In order to solve the normal equations in such a case one method is to impose restrictions on the parameters. The actual number of the required restrictions depend upon the rank of the coefficient matrix. For example, when a first order model is considered, $X = X_1$, $n = q$ the rank of the coefficient matrix is $q + b - 1$. Therefore, only one restriction on the parameters is required to obtain their estimates. We suggest below two sets of restrictions, namely,

$$\text{(i)} \qquad Z'X\hat{\underline{\beta}} = 0 \tag{2.11}$$

$$\text{or} \quad \text{(ii)} \qquad X'Z\hat{\underline{\alpha}} = 0 \tag{2.12}$$

(2.11) involves b restrictions on $\hat{\underline{\beta}}$ whereas (2.12) involves n restrictions on $\hat{\underline{\alpha}}$. By a suitable arrangement of the design points into blocks it is possible to reduce (2.11) or (2.12) to the required number of restrictions as will be seen later. The estimates of the parameters are derived below under each of the above restrictions (2.11) and (2.12) separately.

(a) $Z' X \hat{\underline{\beta}} = o$ Under this case the normal equations (2.10) reduce to

$$X' X \hat{\underline{\beta}} + X' Z \hat{\underline{\alpha}} = X' Y \quad (2.13)$$

$$Z' Z \hat{\underline{\alpha}} = Z' Y \quad (2.14)$$

From (2.14) $\hat{\underline{\alpha}} = (Z' Z)^{-1} Z' Y$ (2.15)

Substituting (2.15) in (2.13) and simplying, we get the adjusted

$$\hat{\underline{\beta}} = (X' X)^{-1} X' \ (1 - M)Y, \text{ where } M = Z(Z' Z)^{-1} Z' \quad (2.16)$$

It can be seen that $\hat{\underline{\alpha}}$ and $\hat{\underline{\beta}}$ are unbiased, and

$$V(\hat{\underline{\alpha}}) = (Z' Z)^{-1} \sigma^2$$

$$V(\hat{\underline{\beta}}) = (X' X)^{-1} X' (1 - M) X(X' X)^{-1} \sigma^2 \quad (2.17)$$

Also, $Cov(\hat{\underline{\alpha}}, \hat{\underline{\beta}}) = 0$, as it should be.

(b) $X' Z\hat{\underline{\alpha}} = 0$: Under this case, as in the above, the unbiased estimates of $\underline{\beta}$ and $\underline{\alpha}$ are given by

$$\hat{\underline{\beta}} = (X' X)^{-1} X' Y \quad (2.18)$$

$$\hat{\underline{\alpha}} = (Z' Z)^{-1} Z' (1 - P)Y, \text{ where } P = X(X' X)^{-1} X' \quad (2.19)$$

Further

$$V(\hat{\underline{\beta}}) = (X' X)^{-1} \sigma^2$$

$$V(\hat{\underline{\alpha}}) = (Z' Z)^{-1} Z' (I - P) Z(Z' Z)^{-1} \sigma^2 \quad (2.20)$$

and $Cov(\hat{\underline{\alpha}}, \hat{\underline{\beta}}) = 0$

Remark : (2.16) and (2.19) can be considered as the adjusted estimates whereas (2.15) and (2.18) as unadjusted estimates.

It can be seen that the two sets of restrictions (2.11) an (2.12) not only provided unbiased estimates of the parameters but also estimates $\underline{\hat{\beta}}$ and $\underline{\hat{\alpha}}$ have turned out to be orthogonal since $Cov(\underline{\hat{\alpha}}, \underline{\hat{\beta}}) = O$. We investigate below the nature of the restrictions in terms of the composition of the matrices X and Z.

(a) Considering $Z' X \underline{\hat{\beta}} = O$, we can write

$$Z' X = \begin{bmatrix} C_1^{(1)}, & C_2^{(1)}, & \ldots & C_q^{(1)} & C_{12}^{(1)} & \ldots & C_{q-1,q}^{(1)} \\ C_1^{(2)}, & C_2^{(2)}, & \ldots & C_q^{(2)} & C_{12}^{(2)} & \ldots & C_{q-1,q}^{(2)} \\ \cdots & & & & & & \cdots \\ \cdots & & & & & & \cdots \\ C_1^{(b)}, & C_2^{(b)}, & \ldots & C_q^{(b)} & C_{12}^{(b)} & \ldots & C_{q-1,q}^{(b)} \end{bmatrix} \qquad (2.21)$$

where $C_j^{(m)} = \sum_{i \varepsilon B_m} x_{ij}$, $\quad j = 1, 2, \ldots, q.$

and $C_{jk}^{(m)} = \sum_{i \varepsilon B_m} x_{ij} x_{ik}$, $\quad j<k = 1, 2, \ldots, q, \quad m = 1, 2, \ldots b.$

Then the conditions $Z' X \hat{\beta} = O$ reduces to

$$\sum_{j=1}^{q} C_j^{(m)} \hat{\beta}_j = 0 \qquad (2.22)$$

for a first order model,

and

$$\sum_{j=1}^{q} C_j^{(m)} \hat{\beta}_j + \sum_{j<k=1}^{q} C_{jk}^{(m)} \hat{\beta}_{jk} = 0 \qquad (2.23)$$

for a second order model

In particular when a first order model is fitted using symmetric simplex design, the b restrictions of (2.22) can be reduced to a single restriction, arranging the design points of the symmetric simplex design into blocks such that

$$\sum_{i \varepsilon B_m} x_{ij} = C_j^{(m)} = a_1^{(m)} \quad j = 1, 2, \ldots, q \qquad (2.24)$$

In this case the only restriction is $\sum_{j=1}^{q} \hat{\beta}_j = 0$. Whereas when a second order model is fitted using symmetric simplex design, arranging the design points into blocks such that

$$a_1^{(m)} \neq a_1^{(m')} \text{ and } \quad a_2^{(m)} \neq a_2^{(m')} \tag{2.25}$$

for some $m \neq m'$

where $a_2^{(m)} = \sum_{i \in B_m} x_{ij} x_{ik} = C_{jk}^{(m)} \qquad j < k = 1, 2, \ldots, q.$

lead to atleast two distinct restrictions.

These are termed as "blocking conditions" by Nigam [5]. Thus, it can be seen that the conditions $Z' X\hat{\underline{\beta}} = 0$ provide a general set of restrictions, which lead to orthogonal estimates of $\underline{\beta}$ and $\underline{\alpha}$ of which (2.24) and (2.25), also obtained by Nigam [5] are particular cases applicable only in case of symmetric simplex designs.

(b) Now consider $X' Z \hat{\underline{\alpha}} = 0$. Using a symmetric simplex design in blocks satisfying (2.25) we have from (2.21) a set of $\frac{q\,(q+1)}{2}$ restrictions in which the first q restrictions which are identical are given by

$$\sum_{m=1}^{b} a_1^{(m)} \hat{\alpha}_m = 0 \tag{2.26}$$

and the next $\binom{q}{2}$ restrictions which are also identical are given by

$$\sum_{m=1}^{b} a_2^{(m)} \hat{\alpha}_m = 0 \tag{2.27}$$

Thus $X' Z \hat{\alpha} = 0$ lead to two sets of restrictions (2.26) and (2.27) on

$\underline{\hat{\alpha}}$. (2.26) is equivalent to $\sum_{m=1}^{b} n_m \hat{\alpha}_m = 0$ and (2.27) is equivalent to $\sum_{m=1}^{b} n_m (1-d_m) \hat{\alpha}_m = 0$ where $d_m = \sum_{j=1}^{q} x_{ij}^2$, $i \varepsilon B_m$. For a first order model (2.26) is the only restriction on $\hat{\alpha}$ where as for a second order model both (2.26) and (2.27) should hold but not (2.26) alone as suggested by Singh, Pratap and Dass [11]. Here again $X' Z \underline{\hat{\alpha}} = 0$ provide the general set of restrictions, for all types of design including symmetric simplex designs.

2.1 *Variance of estimated response :*

From (2.17) and (2.20) we have

$$D(\underline{\hat{\beta}}) = (X' X)^{-1} X' (I - M) X (X' X)^{-1} \sigma^2$$

$$D(\underline{\hat{\alpha}}) = (Z' Z)^{-1} Z' (I - P) Z (Z' Z)^{-1} \sigma^2$$

The estimated response at the i^{th} combination in the m^{th} block, assuming first order model is given by

$$\hat{y}_{im} = \sum_{j=1}^{q} \hat{\beta}_j x_{ij} + \hat{\alpha}_m \tag{2.28}$$

A simple contrast between the estimated responses at i^{th} and i'^{th} combinations of the same m block is given by

$$(\hat{y}_{im} - \hat{y}'_{im}) = \sum_{j=1}^{q} \hat{\beta}_j (x_{ij} - x_{i'j}) \tag{2.29}$$

and its variance is

$$V(\hat{y}_{im} - \hat{y}_{i'm}) = \sum_{j=1}^{q} (x_{ij} - x_{i'j})^2 V(\hat{\beta}_j) + 2 \sum_{j<k} (x_{ij} - x_{i'j}) (x_{ik} - x_{i'k}) \operatorname{cov}(\hat{\beta}_j, \hat{\beta}_k) \tag{2.30}$$

In particular, for a symmetric simplex design arranged in blocks satisfying (2.25), it can be found, for the adjusted $\hat{\underline{\beta}}$'s, that $V(\hat{\beta}_j) = \frac{q-1}{q(a-b)}\sigma^2$ and $Cov(\hat{\beta}_j, \hat{\beta}_k) = -\frac{1}{q}\frac{\sigma^2}{a-b}$

where $a = \sum_{i=1}^{N} x_{ij}^2$, $j = 1, 2, \ldots, q$ and $b = \sum_{i=1}^{N} x_{ij} x_{ik'}$,
$j < k = 1, 2, \ldots, q$.

then $V(\hat{y}_{im} - \hat{y}_{i'm})$

$$= \frac{q-1}{q(a-b)}\sigma^2 \sum_{j=1}^{q} (x_{ij} - x_{i'j})^2 - 2\frac{\sigma^2}{q(a-b)} \sum_{j<k=1}^{q} (x_{ij} - x_{i'j})(x_{ik} - x_{i'k}) \qquad (2.31)$$

3. *Analysts*

When the design points are arranged in b blocks the analysis of variance of the data in the presence of block effects is given below.

The regression sum of squares with (n+b-1) degrees of freedom is given by either

(i) $\hat{\underline{\beta}}' Q + Y' MY$

(ii) $Y' PY + \hat{\underline{\alpha}}' R$ (3.1)

where $Q = X'(I-M)Y$, $R = Z'(I-P)Y$.

$\hat{\underline{\beta}}' Q$ represents the sum of squares (s.s) due to $\hat{\underline{\beta}}$'s (adjusted) with (n–1) degrees of freedom and $(Y' MY - \frac{G^2}{N})$ gives the s.s due to blocks unadjusted with (b–1) degrees of freedom. Similarly $\hat{\underline{\alpha}}' R$ represents the s.s due to blocks (adjusted) with (b–1) degrees of freedom and $(Y' PY - \frac{G^2}{N})$ give the s.s due to $\hat{\underline{\beta}}$'s unadjusted with (n–1) degrees of freedom, $\frac{G^2}{N}$ is the correction factor. The ANOVA table showing the proper s.s for testing $H_o : \underline{\beta} = O$ against $H_o' : \underline{\beta} \neq 0$ and for testing $H_1 : \alpha = O$ against $H_1' : \underline{\alpha} \neq 0$ is given below.

A N O V A Table

Under $Z'X\hat{\underline{\beta}} = 0$					Under $X'Z\hat{\underline{\alpha}} = 0$		
Source	d.f	s.s	mss	F	s.s	mss	F
Due to $\hat{\underline{\beta}}$	n–1	$\hat{\underline{\beta}}'Q$ (adjusted)	s_β^2	$\frac{s_\beta^2}{s_e^2}$	$Y'PY - \frac{G^2}{N}$ (unadjusted)		
Due to $\hat{\underline{\alpha}}$	b–1	$Y'MY - \frac{G^2}{N}$ (unadjusted)			$\hat{\underline{\alpha}}'R$ (adjusted)	s_α^2	$\frac{s_\alpha^2}{s_e^2}$
Error	N–n–b+1	By subtraction	s_e^2		By subtraction		
Total	N–1	$Y'Y - \frac{G^2}{N}$					

4. *Symmetric Simplex Designs in Blocks*

Murty and Das [4] introduced symmetric simplex designs for mixture experiments. The i^{th} design point $(x_{i1}, x_{i2}, \ldots, x_{iq})$ in which d of the x_{ij} $(j = 1, 2, \ldots, q)$ are non zero quantities is called d^{th} order mixture and is denoted by S_d. Further, let d_1 of the x_{ij} of S_d be each equal to $q_1, \ldots, d_h$ of the x_{ij} of S_d be each equal to q_h, so that $\sum_{k=1}^{h} d_k = d$ and $\sum_{k=1}^{h} q_k d_k = 1$. All the d^{th} order mixtures obtainable by permutation of different proportions in the mixture over the q components is called a group and is denoted by G_d. A symmetric simplex design for experiments with mixtures consists of some or all the groups G_d $(d = 1, 2, \ldots, q)$.

Since every group G_d of the symmetric simplex design satisfies (2.25), we have the following theorem.

Theorem 4.1 : Every group G_d of order $(d = 1, 2, \ldots, q)$ of a symmetric simplex design constitutes a block of the mixture design.

5. *Blocking Mixture Designs Using Orthogonal Arrays*

A (N, r, s) array is an r x N matrix with entries from a set of s elements.

For a given selection of d rows, we denote by $n(i_1, i_2, \ldots, i_d)$ the number of times the column vector $(i_1, i_2, \ldots, i_d)$ occurs in the dxN submatrix specified by the selected rows.

Definition 5.1 : A (N,r,s) array is said to be an orthogonal array of strength d if

$$n(i_1, i_2, \ldots, i_d) = \lambda, \text{ constant.}$$

for all possible combinations $i_1, i_2, \ldots, i_d \varepsilon$ s and for any selection of d rows. Such an array is denoted by (N, r, s, d). The constant λ is called the index of the orthogonal array.

Definition 5.2 : A(N, r, s) array is said to balanced array of strength d if $n(i_1, i_2, \ldots, i_d)$ is constant for all permutations of $i_1, i_2, \ldots, i_d$ and for any selection of d rows.

Definition 5.3 : A(N, r, s) array is said to be a semibalanced array of strength d if for any selection of d rows.

(i) $n(i_1, i_2, \ldots, i_d) = O$ if any two i_j are equal and

(ii) $$\sum_p n(i_1, i_2, \ldots, i_d) = \lambda$$

where p represents summation over all permutations of distinct elements $i_1, i_2, \ldots, i_d$.

Lemma 5.1 : When q is a prime or a prime power, an orthogonal array $[q^2, q+1, q, 2]$ can be constructed using the elements of GF(q). (Raghavarao [6]).

Lemma 5.2 : Let q be an odd prime or an odd prime power.

Then $(\frac{q(q-1)}{2}, q, q, 2)$ semi balanced array exists.

Lemma 5.3 : For odd prime number q, the (q−1) mutually orthogonal latin squares can be partitioned into sets of $\frac{q-1}{2}$ latin squares each such that the $\frac{q(q-1)}{2}$ pairs of the q elements occurs exactly once in any two colummed sub-matrix of an array formed by $\frac{q(q-1)}{2}$ rows of array of the two sets. (Murty [3]).

Suppose we have q distinct proportions $p_1, p_2, \ldots, p_q$ which are such that $p_j \geq 0$ and $\sum_{j=1}^{q} p_j = 1$ (q is a prime number or a prime power). A mixture combination of the q components can be formed by the q distinct proportions. The proportion x_j of the j^{th} component can assume any of the $p_1, p_2, \ldots, p_q$ values. For example $(p_1, p_2, \ldots, p_q)$ is one mixture combination and $(p_2, p_1, \ldots, p_q)$ is another mixture combination and so on. Thus we have q! distinct mixture combinations which constitute the mixture design D. Since q is prime or prime power there exists a GF(q) with elements $\alpha_0, \alpha_1, \ldots, \alpha_{q-1}$. According to Lemma 5.1 an orthogonal array OA[q^2, q+1, q, 2] also exists with elements belonging of GF(q). Then by a one to one correspondence of the elements of GF(q)with $p_1, p_2, \ldots, p_q$ in the orthogonal array OA(q^2, q+1, q, 2) and by deleting the entire first row and the first q columns we obtain a balanced array [q(q–1), q, q, 2]. Each column of this array represents a mixture combination in q components and the entire array of q(q–1) columns can be regarded as a block consisting of q(q–1) mixture combinations. Further it is possible to have (q-2)! distinct such balanced arrays by permuting any (q–2) rows of the array. Therefore we have (q–2)! distinct blocks each of size q(q–1) for the mixture design D.

Hence the following theorem.

Theorem 5.1 : If the number of components constituting a mixture is q, q being a prime number or a prime power, and a mixture combination in the q components can be a constituted by distinct proportions $p_1, p_2, \ldots, p_q$ which are such that $p_j \geq 0$ and $\sum_{j=1}^{q} p_j = 1$ then the mixture design of q! combinations can be arranged in (q–2)! blocks each of size q(q–1) using orthogonal array [q^2, q+1, q, 2].

By lemma 5.3 we have the following corrolary.

Corrolary 1: When q is odd and all the proportions $p_1, p_2, \ldots, p_q$ are distinct, the mixture design D can be arranged in 2(q–2)! blocks each of size $\frac{q(q-1)}{2}$.

Example 5.1. Let q=4 and all the proportions p_1, p_2, p_3, p_4 are distinct $p_j \geq 0$ and $p_1 + p_2 + p_3 + p_4 = 1$: Then the mixture design consists of 24 combination given by

	p_1	p_2	p_3	p_4	p_2	p_3	p_1	p_4
	p_1	p_2	p_4	p_3	p_2	p_1	p_4	p_3
	p_1	p_3	p_4	p_2	p_2	p_1	p_3	p_4
	p_1	p_3	p_2	p_4	p_2	p_4	p_1	p_3
	p_1	p_4	p_2	p_3	p_2	p_4	p_3	p_1
D =	p_1	p_4	p_3	p_2	p_3	p_1	p_2	p_4
	p_2	p_3	p_4	p_1	p_3	p_1	p_4	p_2
	p_3	p_2	p_4	p_1	p_4	p_1	p_3	p_2
	p_3	p_2	p_1	p_4	p_4	p_2	p_3	p_1
	p_3	p_4	p_1	p_2	p_4	p_2	p_1	p_3
	p_3	p_4	p_2	p_1	p_4	p_3	p_1	p_2
	p_4	p_1	p_2	p_3	p_4	p_3	p_2	p_1

Consider the elements of GF(2^2) namely 0, 1, α, α^2, the two orthogonal arrays (16, 5, 4, 2) are given by

OA_1 :

0	0	0	0	1	1	1	1	α	α	α	α	α^2	α^2	α^2	α^2
0	1	α	α^2	0	1	α	α^2	0	1	α	α^2	0	1	α	α^2
0	1	α	α^2	1	0	α^2	α	α	α^2	0	1	α^2	α	1	0
0	1	α	α^2	α	α^2	0	1	α^2	α	1	0	1	0	α^2	α
0	1	α	α^2	α^2	α	1	0	1	0	α^2	α	α	α^2	0	1

OA_2 :

0	0	0	0	1	1	1	1	α^2	α^2	α^2	α^2	α	α	α	α
0	1	α^2	α	0	1	α^2	α	0	1	α^2	α	0	1	α^2	α
0	1	α^2	α	1	0	α	α^2	α^2	α	0	1	α	α^2	1	0
0	1	α^2	α	α^2	α	0	1	α	α^2	1	0	1	0	α	α^2
0	1	α^2	α	α	α	α^2	1	0	1	0	α	α^2	α^2	0	1

The arrays obtained by deleting the first row and the first four columns of OA_1 and OA_2 and writing p_1, p_2, p_3, p_4 for O, 1, α, α^2 respectively, the two blocks each consisting of 12 combinations of a four component mixture design are given below. Each column is a mixture combination.

Block 1 :

p_1	p_2	p_3	p_4	p_1	p_2	p_3	p_4	p_1	p_2	p_3	p_4
p_2	p_1	p_4	p_3	p_3	p_4	p_1	p_2	p_4	p_3	p_2	p_1
p_3	p_4	p_1	p_2	p_4	p_3	p_2	p_1	p_2	p_1	p_4	p_3
p_4	p_3	p_2	p_1	p_2	p_1	p_4	p_3	p_3	p_4	p_1	p_2

Block 2 :

p_1	p_2	p_4	p_3	p_1	p_2	p_4	p_3	p_1	p_2	p_4	p_3
p_2	p_1	p_3	p_4	p_4	p_3	p_1	p_2	p_3	p_4	p_2	p_1
p_4	p_3	p_1	p_2	p_3	p_4	p_2	p_1	p_2	p_1	p_3	p_4
p_3	p_4	p_2	p_1	p_2	p_1	p_3	p_4	p_4	p_3	p_1	p_2

The mixture design D of this example is a symmetric simplex design which is arranged in two blocks. By including one additional combination say centroid $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ in one of the blocks (say block 2) it can be easily seen that the blocking conditions (2.25) are satisfied. Further, the block sizes are

$$n_1 = 12 \text{ and } n_2 = 13$$

Let $Y' = (y_1, y_2, \ldots, y_{25})'$ be the vector of observations taken at the 25 design points and a first order model (2.28) is fitted. Then the least squares estimates of the parameters $\underline{\beta}$ and $\underline{\alpha}$ under the restriction $\sum_{j=1}^{4} \hat{\beta}_j = 0$, using (2.16) are given by

$$\hat{\underline{\beta}} = (X'X)^{-1} X'(I - m)Y$$

where X : 25 x 4 design matrix of mixture combinations

$$(X'X)^{-1} : \qquad (c, d), \ 4 \times 4 \text{ matrix with } c = \frac{4(a + 2b)}{25(a - b)}$$

as diagonal element, $d = \dfrac{-4b}{25(a-b)}$ as off diagonal element in which

$$a = 6\sum_{1}^{4} p_i^2 + \frac{1}{16}, \quad b = 4\sum_{i<j=1}^{4} p_i p_j + \frac{1}{16}$$

z : 25x2 block matrix given by

$$\begin{bmatrix} E_{12,1} & 0 \\ 0 & E_{13,1} \end{bmatrix}$$

M : $$Z(Z'Z)^{-1}Z' = \begin{bmatrix} \dfrac{E_{12,12}}{12} & 0 \\ 0 & \dfrac{E_{13,13}}{13} \end{bmatrix}$$

in which E is a matrix with all its elements

$$\hat{\underline{\alpha}} = (Z'Z)^{-1} Z'Y = \begin{bmatrix} \bar{y}^{(1)} \\ \cdots \\ \bar{y}^{(2)} \end{bmatrix}$$

where $\bar{y}^{(m)}$ is the mean of the observations in the m^{th} block, (m = 1, 2)

The variance-covariance matrix of adjusted $\hat{\underline{\beta}}$'s is

$$D(\hat{\underline{\beta}}) = \frac{1}{4(a-b)}[4I - E]\sigma^2$$

Variance of simple contrast between estimated responses at any two (say 1st and 2nd) points of the same block (say block is given by

$$V(\hat{y}_{11} - \hat{y}_{21}) = \frac{2\sigma^2}{a-b}[(p_1 - p_2)^2 + (p_3 - p_4)^2]$$

Similar results under the restriction $\sum_{m=1}^{2} n_m \alpha_m$ can also be derived.

Analysis of variance table for testing hypothesis $H_0 : \underline{\beta} = O$ against $H_0' : \underline{\beta} \neq 0$ is given below

ANOVA Table

	df	S.S	m.s.s	F
Due to $\hat{\beta}$'s (adjusted)	3	$\hat{\underline{\beta}}'\ \underline{Q}$	s_β^2	$\frac{s_\beta^2}{s_e^2}$ $F_{3,20}$
Due to $\hat{\alpha}$'s (unadjusted)	1	$Y'MY - \frac{q^2}{25}$		
Error	20	By subtraction s_e^2		
Total	24	$Y'Y - \frac{G^2}{25}$		

where $Q = X'(I - M)Y,\ G = \sum_{i=1}^{25} y_i$

Remark : By including atleast one additional design point like centroid to one of the blocks the blocking conditions (2.25) are satisfied. More number of centroids also could be included to increase the efficiency to a desired level, if cost constraints are not involved.

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REFERENCES

[1] Box, G.E.P and Hunter, J.S., 1957. Multifactor experimental Designs for exploring response surfaces, *Ann. Math. Stat.*, **28**, 195- 241.

[2] John, P.W.M., 1971. Statistical Design and Analysis of Experiments. Macmillan Co., New York.

[3] Murty, J.S., 1966. Problems of construction and analysis of designs of experiments. Ph.D. thesis, Delhi University.

[4] Murty, J.S. and Das, M.N., 1968. Design and analysis of Experiments with mixtures. *Ann. Math. Stat.*, **39**, 1517-1539.

[6] Raghavarao, D., 1971. Constructions and combinational problems in design of experiments. Wiley, New York.

[7] Ramachandra Murthy, M.S., 1980. Some studies on Design and analysis of experiments with mixture. Unpublished Ph.D. thesis, Osmania University.

[8] Rao, C.R., 1973. A survey of combinatorial theory. Edited by J.N. Srivastava, North Holland, 349-359.

[9] Scheffe', H., 1958. Experiments with mixtures. *J.R. Stat. Soc., B* **20** 344-360.

[10] Scheffe', H., 1963. The simplex centroid design for experiments with mixtures. *J.R. Stat. Soc., B* **25**, 235-265.

[11] Singh, S.P., Pratap, M. and Das, M.N., 1982. Analysis of mixture experiments in presence of block effects. *Sankhya*, **44**, B, 270-277.