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Optimum Mixture Designs: A Pseudo-Bayesian Approach

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SUMMARY

In a mixture experiment the mean response is assumed to depend only on the relative proportion of ingredients or components present in the mixture. Scheffé (1958, 1963) first systematically considered this problem and introduced different models and designs suitable in such situations. Optimum designs for the estimation of parameters of different mixture models are available in the literature. The problem of estimating the optimum proportion of mixture components is of great practical importance. Pal and Mandal (2006) first attempted to find a solution to this problem using the trace criterion. They adopted a pseudo-Bayesian approach with invariance property of the second order moments of the optimum mixing proportions. In this paper the same criterion has been employed to find a solution to the problem, but with a pseudo-Bayesian approach, with assumed values of only the second order moments of the optimum mixing proportions.

Key word : Mixture experiments, Second order models, Non-linear function, Asymptotic efficiency, Trace criterion, Optimum designs.

1. INTRODUCTION

In a mixture experiment, the response depends on the proportions $x_1, x_2, ..., x_q$ of a number of ingredients present in the mixture satisfying $x_i \geq 0, \sum_{i=1}^{q} x_i = 1.$ Scheffé (1958, 1963) introduced canonical models of different degrees to represent the response function ς_x. He also introduced Simplex Lattice Designs and Simplex Centroid Designs for mixture experiments. Optimality of mixture designs for the estimation of parameters of the response function was considered by Kiefer (1961, 1975), Galil and Kiefer (1977), Liu and Neudecker (1995), and others. Draper and Pukelsheim (1999) established the optimality of Weighted Centroid Designs with respect to Partial Loewner Ordering (PLO) for two and three component mixtures.

The problem of estimating the optimum mixture combination in a mixture experiment is of great practical importance. In pharmaceutical research, for example, response is the potency of a new drug relative to an established one and the problem is to find the optimum proportion of the mixing substances so that the relative potency is maximized. Pal and Mandal (2006) probably first attempted to find optimum designs for the estimation of optimum mixture combination. They solved the problem under the assumption that the response function can be approximated by a second degree concave function in the mixture components. The optimum mixture combination γ came out to be a non-linear function of the unknown parameters in the response function. A pseudo-Bayesian approach was pursued where a prior distribution of γ was considered with the rather restrictive assumption of invariance property of the second order moments in respect of the mixing components. The criterion used to get the optimum design was minimization of the expected trace of $MSE(\hat{\gamma})$. Their investigation was restricted to the cases of two and three components.

Other related optimality studies confine to (i) four-component mixture design with invariance (Pal and Mandal 2007), (ii) minimax criterion (Pal and Mandal 2008) and (iii) deficiency criterion (Mandal and Pal

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2008). Most of these studies are based on the assumption of invariance of the mixing components.

In this paper, we attempt to solve the problem using the same approach as in Pal and Mandal (2006), but with a more general assumption on the second order moments of the prior distribution of γ by relaxing the assumption of invariance of the mixing components. In Section 2, we formulate and investigate the problem. In Section 3, the optimal designs are obtained for situations involving two or three mixing components.

2. THE PROBLEM AND THE PERSPECTIVES

As in Pal and Mandal (2006), we assume the response function to be quadratic concave in the components $x_1, x_2, ..., x_q$ in the factor space $\Xi = \{(x_1, x_2, ..., x_q) \mid x_i \geq 0, i = 1(1)q, \Sigma x_i = 1\}$ and to have the form

$$E(Y \mid x) = \varsigma_x = \sum_i \beta_{ii} x_i^2 + \sum_{i<j} \beta_{ij} x_i x_j$$
$$= f'(x)\beta \qquad (2.1)$$

where $x = (x_1, x_2, ..., x_q)'$

$$f(x) = (x_1^2, x_2^2, ..., x_q^2, x_1x_2, x_1x_3, ..., x_{q-1}x_q)'$$

$$\beta = (\beta_{11}, \beta_{22}, ..., \beta_{qq}, \beta_{12}, \beta_{13}, ..., \beta_{q-1,q})'$$

$f(x)$ and β being $p \times 1$ vectors with $p = \binom{q+1}{2}$.

The response function (2.1) can also be expressed in the form

$$\varsigma_x = x'Bx$$

with
$$B = \begin{pmatrix} \beta_{11} & (1/2)\beta_{12} & (1/2)\beta_{13} \ldots (1/2)\beta_{1q} \\ & \beta_{22} & (1/2)\beta_{23} \ldots (1/2)\beta_{2q} \\ \vdots & & \ldots & \vdots \\ & & \ldots & \beta_{qq} \end{pmatrix}$$

We assume that B is negative definite so that, subject to $\sum_{i=1}^{q} x_i = 1$, ς_x is maximized at $x = \gamma$, where

$$\gamma = \delta^{-1}B^{-1}1 \qquad (2.2)$$

with $\delta = 1'B^{-1}1$. We are interested in estimating the non-linear function γ given by (2.2) as accurately as possible by a proper choice of a design in Ξ. In this paper, we shall work in the framework of "approximate "or "continuous" designs.

Let ξ be an arbitrary design in Ξ and $M(\xi, \beta) = \int_{\Xi} f(x)f'(x)d\xi(x)$, the information matrix of ξ. For a given design ξ, we can estimate B by $\hat{B}$, the least squares estimator of B, and hence δ by $\hat{\delta}$. Then, replacing δ and B by $\hat{\delta}$ and $\hat{B}$ respectively in (2.2), we get an estimate of γ as

$$\hat{\gamma} = \hat{\delta}^{-1}\hat{B}^{-1}1 \qquad (2.3)$$

Under suitable regularity assumptions on error distribution, the standard ∂-method gives, for large n, an adequate approximation of the dispersion matrix of $\hat{\gamma}$ as

$$E[(\hat{\gamma} - \gamma)(\hat{\gamma} - \gamma)'] = A(\gamma)M^{-1}(\xi, \beta)A'(\gamma) \qquad (2.4)$$

where $A(\gamma)$ is a $q \times p$ matrix given by

$$A(\gamma) = \left(\frac{\partial\gamma}{\partial\beta_{11}}, \frac{\partial\gamma}{\partial\beta_{22}}, ..., \frac{\partial\gamma}{\partial\beta_{qq}}, \frac{\partial\gamma}{\partial\beta_{12}}, \frac{\partial\gamma}{\partial\beta_{13}}, ..., \frac{\partial\gamma}{\partial\beta_{q-1,q}}\right)$$

$M(\xi, \beta)$ is the information matrix of the design for the model (2.1), and $M^{-1}(\xi, \beta)$ is its generalized inverse. Here, we restrict our study to the class of non-singular information matrices, as in Pal and Mandal (2006).

It has been shown in Pal and Mandal (2006) that $A(\gamma)$ can be expressed as

$$A(\gamma) = d\begin{pmatrix} -2(q-1)\gamma_1 & 2\gamma_2 & \cdots & 2\gamma_q & \gamma_1-(q-1)\gamma_2 \cdots & \gamma_{q-1}+\gamma_q \\ 2\gamma_1 & -2(q-1)\gamma_2 \cdots & & 2\gamma_q & \gamma_2-(q-1)\gamma_1 \cdots & \gamma_{q-1}+\gamma_q \\ 2\gamma_1 & 2\gamma_2 & \cdots & 2\gamma_q & \gamma_1+\gamma_2 \;\cdots & \gamma_{q-1}+\gamma_q \\ \vdots & \vdots & & \vdots & \vdots & \vdots \\ 2\gamma_1 & 2\gamma_2 & \cdots & -2(q-1)\gamma_q & \gamma_1+\gamma_2 \;\cdots & \gamma_{q-1}+\gamma_q \\ \vdots & \vdots & \vdots & & \vdots & \vdots \\ 2\gamma_1 & 2\gamma_2 & \cdots & 2\gamma_q & \gamma_1+\gamma_2 & \cdots\gamma_{q-1}-(q-1)\gamma_q \\ 2\gamma_1 & 2\gamma_2 & \cdots & 2\gamma_q & \gamma_1+\gamma_2 & \cdots\gamma_q-(q-1)\gamma_{q-1} \end{pmatrix} \qquad (2.5)$$

where $d = [\delta q^{q-2} | B |]^{-\frac{1}{q-1}}$, |B| being the determinant of the matrix B.

Design optimality aims at minimizing some function of $A(\gamma)M^{-1}(\xi,\beta)A'(\gamma)$. Since $A(\gamma)M^{-1}(\xi,\beta)A'(\gamma)$ is singular, for comparing different designs we consider the trace criterion

$$\phi(\gamma, M(\xi)) = tr(A(\gamma)M^{-1}(\xi,\beta)A'(\gamma)) \quad (2.6)$$

It should be noted that the mixture model, in its canonical form, is linear in the parameters and, hence, the information matrix $M(\xi)$ is independent of the parameters. This means that the expression in (2.6) depends on γ only through the elements of the matrix A(γ). Of course, this is built upon the consideration that in our search for optimal design, we may and will "disregard" the common multiplying factor "d" in the expression (2.5) for the matrix $A(\gamma)$. Note that without this factor, the elements of the matrix A(γ) are linear in the γ–components and, consequently, the expression in (2.6) is quadratic in the γ-components. Therefore, assuming a prior on the first two moments of the γ-components is adequate. This is precisely what was done in Pal and Mandal (2006). We now continue along similar lines.

Pal and Mandal (2006), assumed a prior distribution of γ with $E(\gamma_i^2) = v, \; i = 1, 2, ..., q$ and $E(\gamma_i \gamma_j) = w$, $i, j = 1, 2, ..., q; \; i < j$ and minimized $E[\phi(\gamma, M(\xi))]$, expectation being taken with respect to the prior distribution of γ. We make a more general assumption on the prior moments, viz.

$$E(\gamma_i^2) = v_i, \quad i = 1, 2, ..., q$$
$$E(\gamma_i \gamma_j) = w_{ij}, \; i, j = 1, 2, ..., q; \; i < j \quad (2.7)$$

Since $\sum_{i=1}^{q} \gamma_i = 1$, v_i, w_{ij} 's must satisfy

$$\sum_i v_i + 2\sum_{i<j} w_{ij} = 1$$

Our criterion for optimal choice of design is minimizing

$$\phi(\xi) = E\,\phi(\gamma, M(\xi))$$
$$= tr(M^{-1}(\xi, \beta)E(A'(\gamma)A(\gamma)) \quad (2.8)$$

3. OPTIMUM DESIGNS

Here we find the optimum designs for different values of q.

3.1. Case of Two Components

Here

$$A(\gamma) = 2d\begin{pmatrix} -\gamma_1 & \gamma_2 & \left(\frac{1}{2}\right)(\gamma_1 - \gamma_2) \\ \gamma_1 & -\gamma_2 & \left(-\frac{1}{2}\right)(\gamma_1 - \gamma_2) \end{pmatrix} \quad (3.1)$$

with $d = [\delta | B |]^{-1}$ and $E(\gamma\gamma') = \begin{pmatrix} v_1 & w_{12} \\ & v_2 \end{pmatrix}$ (3.2)

In the case of two components, since the design can be represented by points on a straight line of length one in the two-dimensional space, the class of competing designs D can be substantially reduced by using the following theorem:

Theorem 3.1. Given any arbitrary design $\xi \in D$ with information matrix $M(\xi,\beta)$, we can always find a design $\eta \in D^* \subset D$ where D* is the class of three point designs with whole mass concentrated at the two extremes and a point in between, such that

$$M(\eta, \beta) \geq M(\xi, \beta)$$

Proof. Here the model is

$$E(Y | x) = \varsigma_x = \beta_{11}x_1^2 + \beta_{22}x_2^2 + \beta_{12}x_1x_2 \quad (3.3)$$

Since $x_1 + x_2 = 1$, we can rewrite the model as

$$\zeta_x = \beta_0^* + \beta_1^* x_1 + \beta_2^* x_1^2 \quad (3.4)$$

where $\beta^* = (\beta_0^*, \beta_1^*, \beta_2^*)'$ and $\beta = (\beta_{11}, \beta_{22}, \beta_{12})'$ are related by

$$\beta^* = P\beta \quad (3.5)$$

with $$P = \begin{pmatrix} 0 & 1 & 0 \\ 0 & -2 & 1 \\ 1 & 1 & -1 \end{pmatrix}$$

Then $$D(\hat{\beta}^*) = PD(\hat{\beta})P' \quad (3.6)$$

Let D_1 be the set of single factor designs, based on x_1. Clearly, there is a one-to-one correspondence between D_1 and D.

For any design D_1, we can write the moment matrix as $M(\xi_1, \beta^*)$, using (3.5).

Now, it is known (vide Liski *et al*. (2002)) that for any arbitrary $\xi_1 \in D_1$ with information matrix $M(\xi_1, \beta^*)$, we can find a three-point design $\eta_1 \in D_1^*$ with mass at 0, 1 and $a \in (0, 1)$ such that

$$M(\eta_1, \beta^*) \geq M(\xi_1, \beta^*)$$

in the Loewner Order Dominance sense, where D^*_1 is the class of all three-point designs.

Hence, from (3.5) and (3.6), we have that for any arbitrary two component design $\xi \in D$, there exists a three-point design $\eta \in D^*$ such that $M(\eta, \beta) \geq M(\xi, \beta)$.

This establishes the theorem.

From the theorem it is clear that, in order to find the optimal design in the two factor case, we may restrict ourselves to the class D*.

Let η denote a three-point design with masses α_1, α_2, and $1 - \alpha_1 - \alpha_2$, respectively, at the support points (1, 0), (0, 1) and (a, 1 – a). The information matrix for the design is then given by

$$M(\eta) = \begin{bmatrix} a_1 & b & c_1 \\ & a_2 & c_2 \\ & & b \end{bmatrix} \quad (3.7)$$

where

$$a_1 = \alpha_1 + a^4(1 - \alpha_1 - \alpha_2)$$

$$a_2 = \alpha_2 + (1 - a)^4(1 - \alpha_1 - \alpha_2)$$

$$c_1 = (1 - \alpha_1 - \alpha_2)\, a^3(1 - a)$$

$$c_2 = (1 - \alpha_1 - \alpha_2)a\,(1 - a)^3$$

$$b = (1 - \alpha_1 - \alpha_2)a^2\,(1 - a)^2 \quad (3.8)$$

For two-factor experiment, from (3.1)

$$E(A'(\gamma)\ A(\gamma))$$

$$= d^2 \begin{bmatrix} 8v_1 & -8w_{12} & 4(w_{12} - v_1) \\ & 8v_2 & 4(w_{12} - v_2) \\ & & 2(v_1 + v_2 - 2w_{12}) \end{bmatrix} \quad (3.9)$$

For convenience, we find the expression of the trace criterion using an alternative representation of the response function following Pal and Mandal (2007):

$$\varsigma_x = \theta_{11}x_1(x_1 - a) + \theta_{22}x_2(x_2 - (1 - a)) + \theta_{12}x_1x_2 \quad (3.10)$$

where $\theta = (\theta_{11}, \theta_{22}, \theta_{12})$ and $\beta = (\beta_{11}, \beta_{22}, \beta_{12})$ are related by

$$\beta = L\theta$$

with

$$L = \begin{bmatrix} 1-a & 0 & 0 \\ 0 & a & 0 \\ -a & -(1-a) & 1 \end{bmatrix}$$

Then

$$M(\xi, \theta) = \begin{bmatrix} \alpha_1(1-a)^4 & 0 & 0 \\ & \alpha_2 a^4 & 0 \\ & & (1-\alpha)a^2(1-a)^2 \end{bmatrix} \quad (3.11)$$

where $\alpha = \alpha_1 + \alpha_2$

Hence, $$M^{-1}(\xi, \beta) = LM^{-1}(\xi, \theta)L' \quad (3.12)$$

Therefore, we get

$$\phi(\xi) = \text{tr}\,[LM^{-1}(\xi, \theta)L'\ E(A'(\gamma)A(\gamma))]$$

$$= \text{tr}\,[M^{-1}(\xi, \theta)L'\,E(A'(\gamma)A(\gamma))L]$$

$$= \text{tr}[M^{-1}(\xi, \theta)G], \text{ say}$$

where $G = ((g_{ij})) = L'\,E(A'(\gamma)A(\gamma))L$

with
$$\begin{aligned} g_{11} &= 8(1-a)^2 v_1 + 2a^2(v_1+v_2-2w_{12}) \\ &\quad - 8a(1-a)(w_{12}-v_1) \\ g_{22} &= 8a^2 v_2 + 2(1-a)^2(v_1+v_2-2w_{12}) \\ &\quad - 8a(1-a)(w_{12}-v_2) \\ g_{33} &= 2(v_1+v_2-2w_{12}) \\ g_{12} &= -2[2a^2(w_{12}-v_2)+2(1-a)^2(w_{12}-v_1) \\ &\quad - a(1-a)(v_1+v_2-6w_{12})] \\ g_{13} &= 2[2(1-a)(w_{12}-v_1)-a(v_1+v_2-2w_{12})] \\ g_{23} &= 2[2a(w_{12}-v_2)-(1-a)(v_1+v_2-2w_{12})] \end{aligned}$$

Therefore, for given a

$$\phi(\xi) = \frac{g_{11}}{\alpha_1(1-a)^4} + \frac{g_{22}}{\alpha_2 a^4} + \frac{g_{33}}{(1-\alpha)a^2(1-a)^2} \geq \Big(\sum_i \sqrt{g_{ii}^*}\Big)^2 \tag{3.13}$$

where
$$g_{11}^* = \frac{g_{11}}{(1-a)^4}, \quad g_{22}^* = \frac{g_{22}}{a^4}, \quad g_{33}^* = \frac{g_{33}}{a^2(1-a)^2} \tag{3.14}$$

with equality in (3.13) holding for

$$\alpha_i = \alpha_i^*(a) = \frac{\sqrt{g_{ii}^*}}{\sum_j \sqrt{g_{jj}^*}} \quad i = 1,\ 2. \tag{3.15}$$

Suppose a* is the value of a minimizing $(\sum_i \sqrt{g_{ii}^*})^2$.

Then the optimal design assigns masses $\alpha_1^*(a^*)$, $\alpha_2^*(a^*)$ and $1-\alpha_1^*(a^*)-\alpha_2^*(a^*)$, respectively, at the support points (1, 0), (0, 1) and $(a^*, 1-a^*)$.

3.2 Case of Three Components

Here the model is

$$E(Y \mid x) = \varsigma_x = \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{\substack{i,j=1 \\ i<j}}^{3} \beta_{ij} x_i x_j \tag{3.16}$$

We shall assume that

$$v_1 = v_2,\ w_{13} = w_{23} \tag{3.17}$$

Then

$E(A'(\gamma)A(\gamma)) =$

$$d^2 \begin{pmatrix} 24v_1 & -12w_{12} & -6(v_1-2w_{12}) & -12w_{13} & -6(v_1-2w_{13}) & -6(w_{12}+w_{13}) \\ & 24v_1 & -6(v_1-2w_{12}) & -12w_{13} & -6(w_{12}+w_{13}) & -6(v_1-2w_{13}) \\ & & 6(2v_1-w_{12}) & -12w_{13} & -3(v_1+w_{12}-w_{13}) & -3(v_1+w_{12}-w_{13}) \\ & & & 24v_3 & -6(v_3-2w_{13}) & -6(v_3-2w_{13}) \\ & & & & 6(v_1+v_3-w_{13}) & -3(v_3+2w_{13}-2w_{12}) \\ & & & & & 6(v_1+v_3-w_{13}) \end{pmatrix}$$

where $d = [\delta q^{q-2} \mid B \mid]^{-\frac{1}{q-1}} \ [3\delta \ \mid B \mid]^{-\frac{1}{2}}$, as q = 3.

3.2.1 A heuristic search for optimum design

We note that in the invariant situation, where $v_1 = v_2 = v_3$, $w_{12} = w_{13} = w_{23}$, each component of the optimum design took three distinct values for each of the factors, two at the extremes and one in between (Pal and Mandal 2006). In the present case, the assumption in (3.17) amounts to the fact that we are treating the first two mixing components as "exchangeable". This, in its turn, presupposes that the "optimum" mixture proportion also enjoys this same property. This leads to the *heuristic* argument that it may be enough to search for an optimum design in the hyperplane manifested by the property of exchangeability of the first two components. It turns out that in such a plane, the quadratic response surface function involving all the three mixing components may be reduced to a quadratic in the third component only. Appealing to Liski *et al.* (2002), we therefore, adopt an initial design with x_3 taking the three values 0, 1 and some $a \in (0, 1)$.

Let us write

$$M^1 = \begin{pmatrix} \mu^{400} & \mu^{220} & \mu^{202} & \mu^{310} & \mu^{301} & \mu^{211} \\ & \mu^{040} & \mu^{022} & \mu^{130} & \mu^{121} & \mu^{031} \\ & & \mu^{004} & \mu^{112} & \mu^{103} & \mu^{013} \\ & & & \mu'^{220} & \mu'^{211} & \mu'^{121} \\ & & & & \mu'^{202} & \mu'^{112} \\ & & & & & \mu'^{022} \end{pmatrix}$$

Now, the criterion function introduced in (2.8) and simplified below (3.12), for any design ξ, comes out to be

$$\begin{aligned}\phi(\xi) &= 24v_1(\mu^{400}+\mu^{040})+24v_3\mu^{004}\\ &-24w_{12}\mu^{220}-24w_{13}(\mu^{202}+\mu^{022})\\ &+12(2w_{12}-v_1)(\mu^{310}+\mu^{130})\\ &+12(2w_{13}-v_1)(\mu^{301}+\mu^{031})\\ &+12(2w_{13}-v_3)(\mu^{013}+\mu^{103})\\ &-6(w_{12}+w_{13})(\mu^{211}+\mu^{121})\\ &-12w_{13}\mu^{112}+6(2v_1-w_{12})\mu'^{220}\\ &+6(v_1+v_3-w_{13})(\mu'^{202}+\mu'^{022})\\ &-3(v_1+w_{12}-w_{13})(\mu'^{211}+\mu'^{121})\\ &-6(v_3+2w_{13}-2w_{12})\mu'^{112}\end{aligned}$$

which is invariant with respect to the first two components. Further, since $\phi(\xi)$, given by (2.8), is convex with respect to the information matrix M, the optimum design will be invariant with respect to the first two components (Mandal and Pal 2008).

Hence, we propose the following class of designs with support points as indicated below:

x_1	x_2	x_3	weight
1	0	0	αW_1
0	1	0	αW_1
1/2	1/2	0	$(1-2\alpha)W_1$
0	0	1	W_2
$1-a$	0	a	$W_{3/2}$
0	$1-a$	a	$W_{3/2}$

where $0 < \alpha < ½$, $a \in (0, 1)$, $W_i > 0$, $i = 1,2,3$, $W_1 + W_2 + W_3 = 1$.

Let us denote such a design as $\xi(\alpha, a, W)$. Then, after a little algebra, the information matrix for the design comes out to be

$$M(\xi) = D\Lambda D'$$

where

$$D = d^2\begin{pmatrix}\sqrt{\alpha} & 0 & b & 0 & \frac{(1-a)^2}{\sqrt{2}} & 0\\ 0 & \sqrt{\alpha} & b & 0 & 0 & \frac{(1-a)^2}{\sqrt{2}}\\ 0 & 0 & b & 0 & 0 & 0\\ 0 & 0 & 0 & 1 & \frac{a^2}{\sqrt{2}} & \frac{a^2}{\sqrt{2}}\\ 0 & 0 & 0 & 0 & \frac{a(1-a)}{\sqrt{2}} & 0\\ 0 & 0 & 0 & 0 & 0 & \frac{a(1-a)}{\sqrt{2}}\end{pmatrix}$$

$$\Lambda = \text{Diag}\,(W_1 I_3,\ W_2,\ W_3\ I_2)$$

$$b = \sqrt{\frac{1-2\alpha}{2^4}}$$

Hence, for the design the criterion function (2.8) reduces to

$$\phi(\xi(\alpha,a,W)) = \text{tr}\Lambda^{-1}[D^{-1}E(A'(\gamma)A(\gamma))D'^{-1}]$$

$$= \frac{g^*_{11}}{W_1}+\frac{g^*_{22}}{W_2}+\frac{g^*_{33}}{W_3}$$

where

$$D^{-1}E(A'(\gamma)A(\gamma)D^{-1} = ((g_{ij}))$$

$$g^*_{11} = g_{11}+g_{22}+g_{33},\quad g^*_{22} = g_{44},\quad g^*_{33} = g_{55}+g_{66}$$

with

$$\begin{aligned}g_{11} = g_{22} &= \frac{1}{\alpha}[24v_1+6(4v_1-5w_{12})\\ &+6(v_1-w_{12}-3w_{13})\frac{1-a}{a}\\ &+6(v_1+v_3-w_{13})(\frac{1-a}{a})^2]\\ &= \frac{g^*}{2\alpha},\text{ say}\end{aligned}$$

$$g_{33} = 96\frac{(2v_1-w_{12})}{1-2\alpha} = \frac{h^*}{1-2\alpha},\ \text{say}$$

$$g_{44} = 24v_3 + 24(v_3 - 2w_{13})\frac{a}{1-a} + 6(2v_1 + v_3 - 4w_{13} + 2w_{12})\left(\frac{a}{1-a}\right)^2$$

$$g_{55} = g_{66} = 12\frac{(v_1 + v_3 - w_{13})}{a^2(1-a)^2}$$

For given a, W, $\phi(\xi(\alpha, a, W))$ is minimized at

$$\alpha = \alpha_0 = \frac{\sqrt{g^*}}{2\sqrt{g^*} + \sqrt{2h^*}}.$$

Then, at $\alpha = \alpha_0$

$$\phi(\xi(\alpha_0, a, W)) = \phi(\xi(a, W))$$

$$= \frac{g^*_{11,0}}{W_1} + \frac{g^*_{22,0}}{W_2} + \frac{g^*_{33,0}}{W_3}$$

$$\geq (\sum_i \sqrt{g^*_{ii,0}})^2 \quad (3.18)$$

where $g^*_{ii,0} = g^*_{ii}|_{\alpha=\alpha_0}$, $i = 1, 2, 3.$

Equality holds in (3.18) at $W_i = W_i(a) = \frac{\sqrt{g^*_{ii,0}}}{\sum_i \sqrt{g^*_{ii,0}}}$

i =1, 2, 3.

Hence, given a

$$\phi(\xi(\alpha, a, W)) \geq \phi(\xi(a, W(a)) = (\sum_i \sqrt{g^*_{ii,0}})^2$$

for all α, W. (3.19)

We now find optimal 'a' which minimizes the R.H.S. of (3.19). As algebraic deduction of optimal a is intractable, we have indicated the optimal value a^* of a, and hence those of α and W, for some combinations of ($v_1 = v_2$, v_3, w_{12}, $w_{13} = w_{23}$) in Table 3.1. It may be noted that this design is optimal within the class of designs

$$D_0 = \{\xi(\alpha, a, W); 0 \leq \alpha \leq 1, 0 < a < 1, Wi \geq 0, i = 1, 2, 3, W_1 + W_2 + W_3 = 1\} \quad (3.20)$$

In the following subsection we establish the optimality of the design $\xi(a^*, W(a^*))$ within the entire class.

3.2.2 Verification of optimality

For the optimal design $\xi(a^*) = \xi(a^*, W(a^*))$ in the class (3.20), let

$$\phi(\xi(a^*)) = \phi_0$$

$$M^{-1}(\xi(a^*))\, E\,(A'(\gamma)A(\gamma))M^{-1}(\xi(a^*)) = (b_{ij})$$

The matrix $M^{-1}(\xi(a^*))$ is symmetric, and since the optimum design is necessarily invariant with respect to the first two components, we get

$b_{13} = b_{23}$, $b_{14} = b_{24}$, $b_{15} = b_{26}$, $b_{16} = b_{25}$, $b_{35} = b_{36}$, $b_{45} = b_{46}$, $b_{55} = b_{66}$

We now check the optimality of the design within the entire class of competitive designs using the equivalence theorem. Kiefer (1974) established the general equivalence theorem which gives a necessary and sufficient condition for a design to be optimum in the entire class. We restate it as given in Silvey (1980).

Theorem 3.1. (Kiefer). If ϕ is concave on $\mathcal{M}$ and differentiable at $M(\xi)$, then ξ is ϕ-optimal iff

$$F\{M(\xi), f(x)f(x)'\} \leq 0 \quad (3.21)$$

for all x in the factor space $\Xi = \{(x_1, x_2, ..., x_q) \mid x_i \geq 0, i = 1(1)q, \Sigma x_i = 1\}$. Equality in (3.21) holds at the support points of ξ.

Here, $F_\phi\ \{M_1, M_2\}$ is the Fréchet derivative of the criterion function ϕ at M_1 in the direction of M_2 and $\mathcal{M}$ is the class of all moment matrices M.

In the present set-up, the theorem reduces to the following :

Theorem 3.2. A necessary and sufficient condition for. a mixture design ξ to be optimum is that

$$f(x)'\ M^{-1}(\xi)(E\ (A'A))M^{-1}(\xi)\ f(x) \leq tr\ M^{-1}(\xi)\ (E\ (A'A)) \quad (3.22)$$

holds for all x in the factor space Ξ.

(See Pal and Mandal 2007).

Equality in (3.22) holds at the support points of ξ.

For the design $\xi(a^*)$, equality at the support points (1,0,0), (0,1,0) and (0,0,1) will hold provided

$$b_{11} = b_{22} = b_{33} = \phi_0 \quad (3.23)$$

When (3.23) holds

$$f(x)' M^{-1}(\xi(a^*))(E(A'A)M^{-1}(\xi(a^*))f(x) - trM^{-1}(\xi(a^*))(E(A'A))$$
$$= x_1^2x_2^2(2b_{12} + b_{33} - 6b_{11}) + (x_1^3x_2 + x_1x_2^3)(2b_{13} - 4b_{11}) + x_3^2(x_1^2 + x_2^2)(2b_{14} + b_{55} - 6b_{11}) + x_3(x_1^3 + x_2^3)(2b_{15} - 4b_{11}) + x_3^3(x_1 + x_2)(2b_{45} - 4b_{11}) + 2x_1x_2x_3(x_1 + x_2)(b_{16} + b_{35} - 6b_{11}) + 2x_1x_2x_3^2(b_{34} + b_{56} - 6b_{11}) \quad (3.24)$$

Then, for equality at the support points (½, ½, 0), $(1 - a^*, 0, a^*)$ and $(0, 1- a^*, a^*)$, we must have

$$2b_{12} + b_{33} - 6b_{11} = -2(2b_{13} - 4b_{11}) \quad (3.25)$$

$$a^*(1-a^*)[(2b - 4b_{11})a^{*2} + (2b_{15} - 4b_{11})(1-a^*)^2 + (2b_{14} + b_{55} - 6b_{11})a^*(1-a^*)] = 0 \quad (3.26)$$

Writing, $A_1 = 2b_{45} - 4b_{11}$, $A_2 = 2b_{15} - 4b_{11}$, $A_3 = 2b_{14} + b_{55} - 6b_{11}$ and using (3.25) and (3.26) in (3.24), we get

$$f(x)'M^{-1}(\xi(a^*))(E(A'A)M^{-1}(\xi(a^*))f(x) - trM^{-1}(\xi(a^*))(E(A'A))$$
$$= x_1x_2(x_1 - x_2)^2(2b_{13} - 4b_{11}) + x_1x_3(1-x_2)^2[(A_1 + A_2 - A_3)(\frac{x_1}{1-x_2})^2 - (2A_2 - A_3)(\frac{x_1}{1-x_2}) + A_2] + x_2x_3(1-x_1)^2[(A_1 + A_2 - A_3)(\frac{x_2}{1-x_1})^2 - (2A_2 - A_3)(\frac{x_2}{1-x_1}) + A_2] + 2x_1x_2x_3[x_3(b_{34} + b_{56} - b_{16} - b_{35}) + (b_{16} + b_{35} - 6b_{11})] \quad (3.27)$$

Clearly, (3.27) equals 0 at each support point of $\xi(a^*)$.

Now, consider the quadratic form $h(y) = (A_1 + A_2 - A_3)y^2$, $-(2A_2 - A_3)y + A_2$, $0 \le y \le 1$. From (3.26), we have that $h(1-a^*) = 0$. Further, for $A_1 + A_2 - A_3 < 0$ and $A_3^2 = 4A_1A_2$, f(y) is a strictly concave function of y with maximum value 0 at $y = 1 - a^*$.

Thus, for any x in the factor space $\Xi = \{(x_1, x_2, x_3) | x_i \ge 0,\ i = 1,2,3\ \Sigma x_i = 1\}$, (3.27) is ≤ 0 under the conditions

(i) $2b_{13} - 4b_{11} < 0$
(ii) $A_1 + A_2 - A_3 < 0$ and $A_3^2 = 4A_1A_2$
(iii) $b_{34} + b_{56} - b_{16} - b_{35} < 0$, $b_{16} + b_{35} - 6b_{11} < 0$

We, therefore, get a set of sufficient conditions for a design $\xi(\alpha, a, W)$ to be optimum within the entire class of designs.

Theorem 3.3. A set of sufficient conditions for a mixture design $\xi(\alpha, a, W)$ with information matrix $M(\xi(a))$ and $M^{-1}(\xi(a^*))$ $E(A'(\gamma)A(\gamma))M^{-1}(\xi(a^*))$ $= (b_{ij})$ and value of criterion function ϕ, to be optimal within the entire class of competitive designs is as follows

(i) $b_{11} = b_{22} = b_{33} = \phi$
(ii) $2b_{13} - 4b_{11} < 0$
(iii) $A_1 + A_2 - A_3 < 0$ and $A_3^2 = 4A_1A_2$
(iv) $a = \dfrac{2A_1 - A_3}{2(A_1 + A_2 - A_3)}$
(v) $b_{34} + b_{56} - b_{16} - b_{35} < 0$, $b_{16} + b_{35} - 6b_{11} < 0$ (3.28)

where $A_1 = 2b_{45} - 4b_{11}$, $A_2 = 2b_{15} - 4b_{11}$, and

$$A_3 = 2b_{14} + b_{55} - 6b_{11}$$

Remark. In all the numerical examples considered, the optimum mixture design $\xi(a^*)$ within the subclass of designs D_0, given by (3.20), has been found to satisfy the conditions in (3.28). Thus, it appears that the optimum design within D_0 is also optimum within the entire class of competing designs.

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Table 3.1. Optimal designs and values of $f(x)'M^{-1}(\xi(a^*))(E(A'A)M^{-1}(\xi(a^*))f(x)$ at three points for different combinations of $(v_1 = v_2, v_3, w_{12}, w_{13} = w_{23})$

Parameters				Optimal				$f(x)'M^{-1}(\xi(a^*))(E(A'A))M^{-1}(\xi(a^*))f(x)$ at		
$v_1 = v_2$	v_3	w_{12}	$w_{13} = w_{23}$	a	α	W_1 W_2 W_3	Trace	$\left(\frac{1-a}{2}, \frac{1-a}{2}, a\right)$	(1/3, 1/3, 1/3)	(1/3, 2/3, 0)
0.2	0.2	0.0666	0.0666	0.5	0.2587	0.4497 0.1163 0.4340	679.645	473.4851	346.3508	516.0556
0.2	0.1	0.15	0.05	0.4863	0.2514	0.4473 0.1077 0.4450	485.4117	265.9013	215.9027	417.1758
0.2	0.1	0.12	0.065	0.4893	0.2509	0.4731 0.0949 0.4320	483.8437	245.8903	223.7324	392.3457
0.2	0.1	0.10	0.075	0.4931	0.2505	0.4905 0.0854 0.4241	480.5998	224.9987	220.0885	376.3773
0.15	0.2	0.12	0.065	0.4987	0.2501	0.4897 0.0863 0.4240	476.7452	222.6961	219.8865	375.9565
0.1	0.2	0.065	0.1175	0.5094	0.2210	0.3818 0.1229 0.4953	285.6798	50.8792	98.1190	217.1205