International Journal of Statistical Sciences *ISSN 1683-5603*
Vol.24(1), March, 2024, pp 1-14
DOI: https://doi.org/10.3329/ijss.v24i1.71866

Optimum Designs for Optimum Mixtures: An Informative Review

Manisha Pal

Department of Statistics,
St. Xavier's University, Kolkata, India
Email: manishapal2@gmail.com

[Received January 17, 2024; Accepted February 27, 2024]

Abstract

In a mixture experiment, the measured response is assumed to depend only on the relative proportions of ingredients or components present in the mixture. Scheffe´ (1958) first systematically considered this problem, and introduced different models and suitable designs. Optimum designs for the estimation of parameters in various mixture models are available in the literature. However, in a mixture experiment, interest is likely to be more on the optimum mixing proportions of the ingredients being used. In this exposition, we take the readers on a journey through the optimum designs developed for estimating the optimum mixture combination as accurately as possible under various mixture models.

Keywords and Phrases: Mixture experiments; second-order models; non-linear function; asymptotic efficiency; weighted centroid designs; optimum designs.

AMS Classification: 62K99, 62J05.

1. Introduction

Mixture experiments are commonly observed in chemical, pharmaceutical and food industries, as well as in other industrial segments, like agriculture, biomedical, horticulture, to name a few. Here the response depends on the proportions $x_1, x_2, \ldots, x_q$ of the q ingredients/components in the mixture, and these proportions satisfy the conditions:

$$x_i \geq 0, i = 1,2, \ldots, q, \quad \sum_{i=1}^{q} x_i = 1.$$

The experimental region containing the q components may be geometrically represented by the interior and boundaries (vertices, edges, faces, etc) of a regular (q - 1)-dimensional simplex. The vertices represent mixtures consisting of single components and the interior points denote combinations of all the components.

Scheffe´ (1958) introduced models in canonical forms of degrees one to three to represent the response function. Of these, the most commonly used model is the quadratic model given by

$$\eta_{\boldsymbol{x}} = \sum_{i=1}^{q} \beta_i x_i + \sum_{\substack{i,j=1 \\ i<j}}^{q} \beta_{ij} x_i x_j. \tag{1.1}$$

Scheffe´ (1958, 1963) also introduced the simplex lattice designs and the simplex centroid designs appropriate in such situations. Several authors investigated the problem of identifying optimal designs for estimation of the parameters of Scheffe´s mixture models. Noteworthy are the works of Kiefer (1961), Farell et al. (1967), Atwood (1969), Galil and Kiefer (1977), Liu and Neudecker (1997), to name a few. Later, other models were also introduced, like the log-contrast model by Aitchison and Bacon-Schone (1984) and the additive quadratic mixture model proposed by Darroch and Waller (1985). Optimum designs for parameter estimation of these models have also been addressed (cf. Chan, 1992; Chan et al., 1998; Chan and Guan, 2001; Huang and Huang, 2009a, 2009b).

Though estimation of the optimum mixture combination is of great importance to the experimenter, optimal designs for the same were addressed as late as in 2006! It may be noted that the problem has been addressed for quantitative multi-factor experiment for the first time by Box and Wilson (1951), followed by a number of contributions in the area [cf. Mandal (1982), Silvey (1980), Chatterjee and Mandal (1981), Mandal (1986), Mandal and Heiligers (1992), Fedorov and Müller (1997), Cheng et al. (2001), Melas et al. (2003)]. However, the difference in mixture experiment and the ordinary response surface problem is owing to the constraint $\sum_{i=1}^{q} x_i = 1$. In this paper we discuss the development of the methodology associated with the problem. In Sections 2- 4., we bring forward optimal designs under different mixture models. We concentrate only on the cases where the mixing proportions are not subject to any constraint other than the natural ones.

2. Optimum Design for Optimum Mixture under Scheffé's Quadratic Mixture Model

Pal and Mandal (2006) were the first to study optimum design for estimating the optimum mixture combination that maximizes the mean response in Scheffé's quadratic mixture model (1.1). They assumed the response function to be concave and that there exists a finite maximum in the interior of the experimental region

$$\Xi = \{\boldsymbol{x} = (x_1, x_2, \ldots, x_q)' | x_i \geq 0, i = 1,2, \ldots, q, \quad \sum_{i=1}^{q} x_i = 1\}. \tag{2.1}$$

Because of the constraint $\sum_{i=1}^{q} x_i = 1$, the model (1.1) can be re-written as

$$\eta_{\boldsymbol{x}} = \sum_{i=1}^{q} \beta_{ii} x_i^2 + \sum_{\substack{i,j=1 \\ i<j}}^{q} \beta_{ij} x_i x_j = \boldsymbol{x}' B \boldsymbol{x}, \tag{2.2}$$

where $B = ((1 + \delta_{ij})\beta_{ij}/2)$, with $\delta_{ij} = 1$ if $i = j$, and $\delta_{ij} = 0$ if $i \neq j$.

The optimum mixture combination $\boldsymbol{x} = \boldsymbol{\gamma} = (\gamma_1, \gamma_2, \ldots, \gamma_q)'$,say, is given by

$$\boldsymbol{\gamma} = \delta^{-1} B^{-1} \mathbf{1}_q,$$

where $\mathbf{1}_q$ is a unit vector of order $q \times 1$, and $\delta = \mathbf{1}_q' B^{-1} \mathbf{1}_q$.

Based on a continuous design ξ, if $\hat{\beta}_{ij}'$s be the estimates of the unknown parameters β_{ij}'s, a plugged-in estimate of $\boldsymbol{\gamma}$ is obtained as $\hat{\boldsymbol{\gamma}} = \hat{\delta}^{-1} \hat{B}^{-1} \mathbf{1}_q$, with large sample dispersion matrix $A(\boldsymbol{\gamma}) M(\xi)^{-1} A(\boldsymbol{\gamma})'$, where $M(\xi)$ is the information (moment) matrix of ξ for estimating β_{ij}'s, and

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

After some algebraic manipulation, interestingly the elements of $A(\boldsymbol{\gamma})$ are expressible as linear functions of γ_is as given below:

$$A(\boldsymbol{\gamma}) = \begin{bmatrix} -2(q-1)\gamma_1 & 2\gamma_2 & \ldots & \gamma_1-(q-1)\gamma_2 & \ldots & \gamma_{q-1}+\gamma_q \\ 2\gamma_1 & -2(q-1)\gamma_2 & \ldots & \gamma_1-(q-1)\gamma_2 & \ldots & \gamma_{q-1}+\gamma_q \\ 2\gamma_1 & 2\gamma_2 & \ldots & \gamma_1+\gamma_2 & \ldots & \gamma_{q-1}+\gamma_q \\ \ldots\ldots & \ldots\ldots & & \ldots\ldots & & \ldots\ldots \\ 2\gamma_1 & 2\gamma_2 & \ldots & \gamma_1+\gamma_2 & \ldots & \gamma_{q-1}-2(q-1)\gamma_q \\ 2\gamma_1 & 2\gamma_2 & \ldots & \gamma_1+\gamma_2 & \ldots & \gamma_q-2(q-1)\gamma_{q-1} \end{bmatrix}$$

Now any measure of accuracy for estimating $\boldsymbol{\gamma}$ depends on the dispersion matrix $A(\boldsymbol{\gamma})M(\xi)^{-1}A(\boldsymbol{\gamma})'$, and, in view of the expression of $A(\boldsymbol{\gamma})$ above, it is quite evident that it will be a function of the unknown parameters β_{ij}'s through γ_i's!

Pal and Mandal (2006) pursued a pseudo-Bayesian approach to resolve the matter. Since the elements of the dispersion matrix come out to be quadratic functions of γ_i's, without considering any prior distribution of $\boldsymbol{\gamma}$, they assumed that the apriori second order moments of γ_i's are known. Further, they argued that under the condition that nothing is known about the relative influence of the different components on the response, one can take $\varepsilon(\gamma_i^2)$ to be same across all i's and also the product moments $\varepsilon(\gamma_i\gamma_j)$ to be equal for all $i < j$, that is,

$$\varepsilon(\gamma_i^2) = v, \text{ for } i = 1(1)q, \ \varepsilon(\gamma_i\gamma_j) = w, \text{ for } i = 1(1)q, i < j, \tag{2.3}$$

where, because of the restriction $\boldsymbol{\gamma}'\mathbf{1}_q = 1$, v and w are related through the equation $qv + 2\binom{q}{2}w = 1$, with $v, w > 0$ and $\frac{1}{q^2} < v < \frac{1}{q}$.

2.1 Trace Criterion

Because of the restriction $\boldsymbol{\gamma}'\mathbf{1}_q = 1$, the dispersion matrix $A(\boldsymbol{\gamma})M(\xi)^{-1}A(\boldsymbol{\gamma})'$ comes out to be a singular matrix. Pal and Mandal (2006), therefore, took the criterion for comparison of designs as the expectation of the trace of the dispersion matrix with respect to the prior:

$$\varphi(\xi) = \text{Trace } \varepsilon[A(\boldsymbol{\gamma})M(\xi)^{-1}A(\boldsymbol{\gamma})'] = \text{Trace } [M(\xi)^{-1} \ \varepsilon\{A(\boldsymbol{\gamma})'A(\boldsymbol{\gamma})\}]. \tag{2.4}$$

This is a linear optimality criterion (cf. Fedorov, 1971), and the optimal design minimizes φ. Making use of the invariance property of the problem, and using the result of Draper and Pukelsheim (1999), they restricted to the class of weighted centroid designs (WCDs) to find the optimal design.

Pal and Mandal (2006) derived the optimal designs for the cases of two- and three-component mixtures, which came out as:

(a) For q =2, the optimal design is

$$\xi_{opt} = \begin{Bmatrix} (1.0) & (0,1) & \left(\frac{1}{2},\frac{1}{2}\right) \\ \alpha & \alpha & (1-\alpha) \end{Bmatrix},$$

where $\alpha = \frac{\sqrt{s}}{\sqrt{s}+\sqrt{t}}$, $s = 2(4v-1) + \frac{1}{2}, t = 2(4v-1)$, v being given by (2.3).

This is a (2,2) – simplex lattice design

(b) For q =3, the optimal design has support points at $(1.0,0), (0,1,0), (0,0,1)$, each with mass $\alpha_1/3$, $\left(\frac{1}{2},\frac{1}{2},0\right)$, $\left(\frac{1}{2},0,\frac{1}{2}\right)$, $\left(0,\frac{1}{2},\frac{1}{2}\right)$, each with mass $\alpha_2/3$, and $\left(\frac{1}{3},\frac{1}{3},\frac{1}{3}\right)$ with mass $(1-\alpha_1-\alpha_2)$, where α_1 and α_2 are functions of v, but cannot be obtained in closed form.

The following table extracted from Pal and Mandal (2006) shows the values of α_1 and α_2 for some given values of v:

v	α_1	α_2
0.12	0.2565	0.7434
0.16	0.3285	0.6715
0.20	0.3492	0.6508
0.24	0.3589	0.6411
0.30	0.3670	0.6330

It is easy to note from the table that the mass of the support point $\left(\frac{1}{3},\frac{1}{3},\frac{1}{3}\right)$ is almost zero. So, the authors conjectured that the optimum design for q = 3 is a (3, 2)-simplex lattice design.

2.2 Use of Equivalence Theorem

In a subsequent paper in 2007, Pal and Mandal ventured to confirm that the optimal designs are (q, 2) - simplex lattice designs via Kiefer's (1974) Equivalence Theorem. For the problem considered, the Equivalence Theorem reduces to the following [after writing the model in the form $\eta_{\boldsymbol{x}} = f(\boldsymbol{x})'\boldsymbol{\beta}$]:

A necessary and sufficient condition for a mixture design ξ to be trace-optimal is that

$$f(\boldsymbol{x})'M^{-1}(\xi)[\varepsilon\{A(\boldsymbol{\gamma})'A(\boldsymbol{\gamma})\}]M^{-1}(\xi)f(\boldsymbol{x}) \leq Trace[M(\xi)^{-1}\ \varepsilon\{A(\boldsymbol{\gamma})'A(\boldsymbol{\gamma})\}], \qquad (2.5)$$

for all $\boldsymbol{x} \in \Xi$, where equality holds at the support points of ξ.

For easy algebraic manipulation, the authors wrote the quadratic model (2.2) as

$$\eta_{\boldsymbol{x}} = \sum_{i=1}^{q} \theta_{ii} x_i \left(x_i - \frac{1}{2}\right) + \sum_{\substack{i,j=1 \\ i<j}}^{q} \theta_{ij} x_i x_j, \qquad (2.6)$$

where the parameters $\boldsymbol{\theta}$ and $\boldsymbol{\beta}$ bear a relation of the form $\boldsymbol{\theta} = P\boldsymbol{\beta}$, with

$$P = \begin{bmatrix} 2I_q & 0 \\ R & I_{\binom{q}{2}} \end{bmatrix}, \quad R = \begin{bmatrix} 1 & 1 & 0 & \dots & 0 & 0 \\ 1 & 0 & 1 & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 1 & 0 & 0 & \dots & 0 & 1 \\ 0 & 1 & 1 & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 1 & 0 & \dots & 0 & 1 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & 1 & 1 \end{bmatrix}.$$

This facilitates in finding the information matrix of a design ξ for estimating $\boldsymbol{\beta}$ using the information matrix of ξ for estimating $\boldsymbol{\theta}$.

Taking clue from their earlier paper, Pal and Mandal (2007) concentrated on the class of (q, 2)-simplex lattice designs, and proved, using Equivalence Theorem, the following results for the cases of 3- and 4- component mixture models:

Result 2.1: *In a three-component mixture model, a* (3,2)-*simplex lattice design with total mass at the extreme points given by* $\alpha = \frac{\sqrt{11v-10w}}{\sqrt{11v-10w}+4\sqrt{2v-w}}$ *is optimal among all competing designs, for given prior moments v and w.*

Result 2.2: *In a four-component mixture model, a* (4,2)-*simplex lattice design with total mass at the extreme points given by* $\alpha = \frac{\sqrt{v-w}}{\sqrt{v-w}+2\sqrt{3v-w}}$ *is optimal among all competing designs, for given prior moments v and w.*

2.3 Case of Unequal Prior Moments

Mandal et al. (2008) relaxed the assumption of equality of the expectations of γ_i^2's and that of $(\gamma_i\gamma_j)$'s and took a more general assumption on the prior moments as follows:

$$\varepsilon(\gamma_i^2) = v_i, \text{ for } i = 1(1)q,\ \varepsilon(\gamma_i\gamma_j) = w_{ij}, \text{ for } i = 1(1)q, i < j,$$

where, because of the restriction $\boldsymbol{\gamma}'\mathbf{1}_q = 1$, v_i's and w_{ij}'s, satisfy

$$\sum_{i=1}^{q} v_i + \sum_{i<j} w_{ij} = 1.$$

For the case of two-component mixture, they showed that for any arbitrary design ξ there exists a three point design η with support points (1,0), (0,1) and (a, 1 - a), $a \in (0,1)$, such that $M(\xi) \leq M(\eta)$, where $M(.)$ denotes the information matrix of a design for estimating $\boldsymbol{\beta}$. Hence, the optimal design will be a three-point design of the form as above.

To obtain the trace criterion $\varphi(\xi)$, Mandal et al. (2008) used an alternative representation of the response model following (2.6) for the sake of convenience:

$$\eta_{\boldsymbol{x}} = \theta_{11}x_1(x_1 - a) + \theta_{22}x_2\big(x_2 - (1-a)\big) + \theta_{12}x_1x_2.$$

This leads to the relation $\boldsymbol{\beta} = L\boldsymbol{\theta}$, where $L = \begin{pmatrix} 1-a & 0 & 0 \\ 0 & a & 0 \\ -a & -(1-a) & 1 \end{pmatrix}$, and the criterion function comes out to be

$$\begin{aligned}\varphi(\xi) &= Trace[LM(\xi;\theta)^{-1}L'\varepsilon\{A(\boldsymbol{\gamma})'A(\boldsymbol{\gamma})\}] \\ &= Trace[M(\xi;\theta)^{-1}G],\end{aligned}$$

where $G = L'\varepsilon\{A(\boldsymbol{\gamma})'A(\boldsymbol{\gamma})\}L = (g_{ij})$, say, has its elements as linear functions of the prior moments. For given a, the lower bound to $\varphi(\xi)$ is given by $(\sum_{i=1}^{3} g_{ii}^{*}(a))^2$, where

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

the expressions of g_{ii}'s being

$$\begin{aligned}g_{11} &= 8(1-a)^2v_1 + 2a^2(v_1 + v_2 - 2w_{12}) - 8a(1-a)(w_{12} - v_1) \\ g_{22} &= 8a^2v_1 + 2(1-a)^2(v_1 + v_2 - 2w_{12}) - 8a(1-a)(w_{12} - v_2) \\ g_{33} &= 2(v_1 + v_2 - 2w_{12}).\end{aligned}$$

The optimal value of a is obtained by minimizing $(\sum_{i=1}^{3} g_{ii}^{*}(a))^2$, and the optimal masses at the support points (1,0), (0, 1) and (a, (1-a)) are obtained respectively as

$$\alpha_1 = \frac{\sqrt{g_{11}^*}}{\sum_{i=1}^{3} g_{ii}^*},\ \alpha_2 = \frac{\sqrt{g_{22}^*}}{\sum_{i=1}^{3} g_{ii}^*},\ \text{and } (1-\alpha_1-\ \alpha_2).$$

In the case of three-component mixture, Mandal et al. (2008) considered the simplified situation where $v_1 = v_2$ and $w_{13} = w_{23}$. This amounts to considering the first two components of the mixture as "exchangeable". This, in turn, presupposes that the optimum mixture combination also enjoys the same property. Hence, it leads to the heuristic argument that it may be sufficient to search for the optimum design on the hyperplane manifested by the property of exchangeability between the first two components. As such, on such a plane, the quadratic response function based on three components reduces to a quadratic function on the third component. So, appealing to Liski et al. (2002), one can take an initial design with x_3 taking the values 0, 1 and some $a \in (0, 1)$.

Further, for any design ξ, the authors showed that under the assumptions made, the criterion function $\varphi(\xi)$ is invariant with respect to the first two components. Also, as $\varphi(\xi)$ is convex with respect to the information matrix $M(\xi)$, the optimum design will be invariant with respect to the first two components. Hence, the authors defined a sub-class of designs $\mathcal{D} = \{\xi(a, \alpha, \boldsymbol{w})\}$, where a design $\xi(a, \alpha, \boldsymbol{w})$ has the support points and masses as follows:

x_1	x_2	x_3	Mass
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
a	0	1-a	$w_3/2$
0	a	1-a	$w_3/2$

Here, $\alpha < \frac{1}{2},\ a \in (0,1), w_i \geq 0, i = 1(1)3, \sum_{i=1}^{3} w_i = 1.$

For a design $\xi\ (a, \alpha, \boldsymbol{w})$, let $M(\xi)$ denote the information matrix, and $M(\xi)^{-1}\ \varepsilon\{A(\gamma)'A(\gamma)\}M(\xi)^{-1} = (b_{ij})$. Further, let ϕ denote the value of the criterion function. Based on the Equivalence Theorem, the authors proved the following theorem which gives the sufficient conditions under which the design ξ is optimum within the class of all competing designs.

Theorem 2.1: *A set of sufficient conditions for a mixture design* $\xi \equiv \xi(a, \alpha, \boldsymbol{w})$ *to be optimal within the entire class of competing designs is*:

(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) $a = \frac{2A_1 - A_3}{2(A_1 + A_2 - A_3)}$

(v) $b_{34} + b_{56} - b_{16} - b_{35} < 0, b_{16} + b_{35} - 6b_{11} < 0,$

where $A_1 = 3b_{45} - 4b_{11},\ A_2 = 2b_{15} - 4b_{11},\ A_3 = 2b_{14} + b_{55} - 6b_{11}$.

Extensive numerical computation showed that the optimal mixture design in the sub-class $\mathcal{D}$ satisfies all the conditions stated in Theorem 2.1. Thus, the authors conjectured that the optimal design in $\mathcal{D}$ is also optimal within the class of all competing designs.

2.3 Deficiency Criterion

For the Scheffe's quadratic mixture model, Mandal and Pal (2008) used a modification of the deficiency criterion due to Chatterjee and Mandal (1981) as a measure for comparing the performance of competing designs for estimating the optimum mixing proportions.

If $\hat{\boldsymbol{\gamma}}$ be an estimate of the optimum mixture combination $\boldsymbol{\gamma}$, and $\eta_{\hat{\gamma}}$ denotes the corresponding estimate of the maximum expected response, the deficiency in using $\hat{\boldsymbol{\gamma}}$ as an estimate of $\boldsymbol{\gamma}$ is given by

$$\psi(\gamma, \hat{\gamma}) = \eta_{\boldsymbol{\gamma}} - \eta_{\hat{\gamma}} = \delta^{-1} - \hat{\boldsymbol{\gamma}}' B \hat{\boldsymbol{\gamma}},$$

where $\delta = \mathbf{1}_q' B^{-1} \mathbf{1}_q$, and B is defined in (2.2).

So, the mean deficiency is given by

$$E[\psi(\gamma, \hat{\gamma})] = \delta^{-1} - E[\hat{\boldsymbol{\gamma}}' B \hat{\boldsymbol{\gamma}}],$$

which should be minimum, or $E[\hat{\boldsymbol{\gamma}}' B \hat{\boldsymbol{\gamma}}]$ maximum, for the optimal design. However, as $E[\hat{\boldsymbol{\gamma}}' B \hat{\boldsymbol{\gamma}}]$ depends on the unknown $\boldsymbol{\gamma}$ and the elements of B, Mandal and Pal (2008) assumed a prior on $\boldsymbol{\gamma}$ given by (2.3), and a prior on $B^* = -B$, with

$$\boldsymbol{\mathcal{E}}_{B^*|\gamma}[B^*] = Diag(a_1, a_2, \ldots, a_q) + b \mathbf{1}_q \mathbf{1}_q',$$

which is assumed to be independent of $\boldsymbol{\gamma}$. They considered minimization of

$$\boldsymbol{\mathcal{E}} E[\hat{\boldsymbol{\gamma}}' B^* \hat{\boldsymbol{\gamma}}] = \boldsymbol{\mathcal{E}}[Trace\{B^* E(\hat{\boldsymbol{\gamma}}\hat{\boldsymbol{\gamma}}')\}],$$

where $\boldsymbol{\mathcal{E}}$ denotes the expectation with respect to the prior of $\boldsymbol{\gamma}$ and B.

Noting that $B^* E(\hat{\boldsymbol{\gamma}}\hat{\boldsymbol{\gamma}}')$ can be expressed as $B^* \boldsymbol{\gamma}' \boldsymbol{\gamma} + B^* A(\gamma) M(\xi)^{-1} A(\gamma)'$, and that $B^* \boldsymbol{\gamma}' \boldsymbol{\gamma}$ is independent of the design, the authors modified the criterion function as

$$\varphi(\xi) = Trace\,[\boldsymbol{\mathcal{E}}\{B^* E(A(\gamma) M(\xi)^{-1} A(\gamma)')\}],$$

which reduces to $\varphi(\xi) = Trace[M(\xi)^{-1} G]$, where $G = \boldsymbol{\mathcal{E}}_{\gamma} \boldsymbol{\mathcal{E}}_{B^*|\gamma}[A(\gamma)' B^* A(\gamma)]$.

The authors showed that in the case of two- component mixture, the criterion function is invariant with respect to the two components, and the optimal design is a weighted centroid design as obtained using the trace optimality criterion in sub-section 2.1. It is noteworthy that the design does not depend on the choices of a_1 and a_2.

In the case of three-component mixture, the authors considered two cases, viz., (i) all a_i's equal, and (ii) $a_1 = a_2$. In the former case, the optimal design is a (3,2)-simplex lattice design as given by result 2.1. Thus, it does not depend on the common value of a_i's. In case (ii), it is shown that the optimum design is necessarily invariant with respect to the first two components. Keeping this in mind, and the fact that in case (i), irrespective of the common value of a_i's, the support points of the optimal design are at (1,0,0), (0,1,0), (0,0,1), (½, ½, 0), (½,0, ½), (0, ½,½,), Mandal and Pal (2008) restricted to the sub-class of designs $\mathcal{D}^*$ having the same support points and with masses respectively α_1, α_2, α_3, α_{12}, α_{13}, α_{23}, where $\alpha_1 = \alpha_2$, $\alpha_{13} = \alpha_{23}$. Then, using the alternative representation (2.6) of the response function, the optimal design in $\mathcal{D}^*$ has been obtained to have the masses

$$\alpha_i = \frac{\sqrt{g_{ii}}}{\sqrt{\sum_{j=1}^{6} g_{jj}}}, \text{for } i = 1,3;\ \alpha_{12} = \frac{\sqrt{g_{44}}}{\sqrt{\sum_{j=1}^{6} g_{jj}}},\ \alpha_{13} = \frac{\sqrt{g_{55}}}{\sqrt{\sum_{j=1}^{6} g_{jj}}},$$

where $G = (g_{ij})$, with

$$g_{11} = g_{22} = 4v(5a_1 + a_3);\ \ g_{33} = 4v(2a_1 + 4a_3);$$

$$g_{44} = 2v(5a_1 + a_3) - 2w(4a_1 - a_3);\ \ g_{55} = (7a_1 + 5a_3) - 2w(a_1 + 2a_3) = g_{66}.$$

Verification of the optimality of the above design in the whole class of competing designs using the Equivalence Theorem is algebraically intractable. Mandal and Pal (2008) examined the same numerically at several points of the experimental region, and showed that while equality holds at the support points, strict inequality (less-than type) prevails at other points. They conjectured that in the general case of q-component mixture, the optimal design is also likely to be a $(q, 2)$ – simplex design, even for arbitrary $a_i{}'$s.

3. Optimum Design for Optimum Mixture under Darroch-Waller Quadratic Mixture Model

An additive quadratic mixture model was introduced by Darroch and Waller (1985) for the case of three-component model. They investigated the optimal design for the estimation of the model parameters. In the general case of q - component mixture, the model would be given by

$$\eta_x = \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q} \beta_{ii} x_i (1 - x_i). \tag{3.1}$$

Scheffé's quadratic mixture model and the above model are equivalent for $q = 3$. However, in the case of $q = 2$, the parameters of the Darroch-Waller model are not uniquely estimable. For $q \geq 4$, (3.1) is a particular case of Scheffé's model with the parameters being subject to a system of linear constraints. The additive model (3.1) is often found to fit data well. Optimal designs for estimation of the parameters for $q \geq 4$ have been studied by Chan et al. (1998).

Pal et al. (2017) attempted to find the optimal design for estimating the optimum mixture combination in model (3.1). To do so, they rewrote the model in the form $\eta_x = \boldsymbol{x}' B \boldsymbol{x}$, taking help of the natural constraint $\sum_{i=1}^{q} x_i = 1$, and assumed that B is negative definite. The optimal mixture combination maximizing the mean response then, as before, comes out to be $\boldsymbol{\gamma} = \delta^{-1} B^{-1} \mathbf{1}_q$, with the symbols having the same meaning. Then, proceeding as in Pal and Mandal (2006), and using the same argument for assuming $\varepsilon(\gamma_i^2) = v$, for $i = 1(1)q$, $\varepsilon(\gamma_i \gamma_j) = w$, for $i = 1(1)q, i < j$, Pal et al. (2017) established the following theorem for finding an A-optimal design, using the criterion function $\varphi(\xi) = Trace[M(\xi)^{-1} \varepsilon\{ A(\boldsymbol{\gamma})' A(\boldsymbol{\gamma})\}]$, where $A(\boldsymbol{\gamma})$ is defined as before:

Theorem 3.1: *The barycentres of the experimental region are the possible support points of the A-optimal design.*

As a weighted centroid design (WCD) comprises of all the barycentres of the experimental region, the above theorem restricts the search for the optimum design within the sub-class of WCDs.

Suppose for a WCD ξ, $w_r^{(q)}$ is the mass at each of the barycentres of depth (r – 1), $1 \le r \le q$. Let $\xi_{1,i}^{(q)}$ denote a WCD with $w_r^{(q)} = 0$ for all $r \neq 1$, i, where $i \in \{2, 3,\dots, q\}$, and let $\xi_{1,i,j}^{(q)}$ denote a WCD with $w_r^{(q)} = 0$ for all $r \neq 1, i, j$, where $i, j \in \{2, 3,\dots, q\}$, $i < j$. Pal et al. (2017) showed the within the sub-class of designs of the form $\xi_{1,i}^{(q)}$, for $2 \le i \le q$, the optimal values of the masses are:

$$w_1^{(q)} = w_{10}^{(q)} = \frac{\sqrt{d_{1i}}}{\sqrt{\binom{q}{1}}\left(\sqrt{\binom{q}{1}d_{1i}}+\sqrt{\binom{q}{i}d_{2i}}\right)}, w_i^{(q)} = w_{i0}^{(q)} = \frac{\sqrt{d_{2i}}}{\sqrt{\binom{q}{i}}\left(\sqrt{\binom{q}{1}d_{1i}}+\sqrt{\binom{q}{i}d_{2i}}\right)},$$

where $d_{1i} = q^2(q-1) + \frac{4i}{i-1}q^2(q-1)\left(\frac{1}{q}-\frac{1}{2}\right) + 4\left(\frac{i}{i-1}\right)^2 aq$

$$d_{2i} = \left[\frac{4i^4 a}{(i-1)^2}q - \frac{4i^3}{(i-1)(q-1)}q(a-b+bq)\right] / \binom{q-2}{i-1}$$

$$a = q(q-1)[v + (\tfrac{1}{4}-\tfrac{1}{q})], b = q[w + (\tfrac{1}{4}-\tfrac{1}{q})].$$

They, thereafter, established the following results with the help of the Equivalence Theorem:

Result 3.1: *For q = 3, the design $\xi_{1,2}^{(3)}$ with $w_1^{(3)} = w_{10}^{(3)}$ and $w_2^{(3)} = w_{20}^{(3)}$ is A-optimal for $v \in (\frac{1}{9}, \frac{1}{3})$.*

Result 3.2: *For q = 4, the design $\xi_{1,2}^{(4)}$ with $w_1^{(4)} = w_{10}^{(4)}$ and $w_1^{(4)} = w_{10}^{(4)}$ is A-optimal provided $v < v_0$, where v_0 rounded off to seven places of decimal is 0.1975663.*

Through numerical computation, Pal et al (2017) showed that for q = 4 and $v \ge v_0$ the optimal design belongs to the sub-class of designs $\xi_{1,2,3}^{(4)}$, and that for q = 5 the optimal design belongs to the sub-class of designs $\xi_{1,2,3}^{(5)}$.

The following table is an excerpt from Pal et al (2017) showing the optimal designs for q = 4, 5 for some values of v.

q	v	$\binom{q}{1}w_1$	$\binom{q}{2}w_2$	$\binom{q}{3}w_3$
4	0.08	0.2168	0.7832	0
	0.15	0.3210	0.6790	0
	0.20	0.3419	0.6566	0.0015
	0.24	0.3484	0.6308	0.0208
5	0.06	0.1999	0.6403	0.1598
	0.10	0.2502	0.4184	0.3314
	0.16	0.2710	0.2392	0.4898

4. Optimum Design for Optimum Mixture Under Log Contrast Model

Aitchison and Bacon-Shone (1984) proposed the quadratic log-contrast model given by

$$\eta_x = \sum_{i=1}^{q-1} \beta_i \log(x_i/x_q) + \sum_{\substack{i,j=1 \\ i<j}}^{q-1} \beta_{ij} \log(x_i/x_q)\log(x_i/x_q). \quad (4.1)$$

The advantage of the log-contrast model over other mixture models is that while in Scheffe's model and Darroch-Waller model the mixing proportions $x_i{}'$s can be varied subject to the restriction $\sum_{i=1}^{q} x_i = 1$, in the log-contrast model $z_i = \log(\frac{x_i}{x_q})$ can be varied independently. Further, the polynomial forms in $z_i{}'$s can be full in the sense of including all terms of appropriate degrees as against Scheffe's polynomial models which require the omission of certain terms to ensure identifiability.

D-optimal design for parameter estimation in the log-contrast model has been studied by Chan (1992) under the experimental region

$$\Xi_\delta = \{(x_1, x_2, \dots, x_q) \in \text{rel.int.}\Xi: \delta \leq \frac{x_i}{x_q} \leq \frac{1}{\delta}, i = 1(1)(q-1)\}, \delta \in (0,1). \quad (4.2)$$

Pal and Mandal (2012) ventured to investigate the optimum design for estimating the optimum mixture by restricting to the experimental region (4.2). They transformed the model in terms of $t = -\log(\frac{x_i}{x_q})$, which takes the form

$$\eta_{\boldsymbol{x}} \equiv \eta_{\boldsymbol{t}} = \theta_0 + \sum_{i=1}^{q-1} \theta_i t_i + \sum_{i,j=1}^{q-1} \theta_{ij} t_i t_j = \theta_0 + \sum_{i=1}^{q-1} \theta_i t_i + \boldsymbol{t}'\Delta\boldsymbol{t}, \quad (4.3)$$

where $\theta_0 = \beta_0$, $\theta_i = \beta_i(-\log\delta), 1 \leq i \leq (q-1)$, $\theta_{ij} = \beta_{ij}(\log\delta)^2, 1 \leq i,j \leq (q-1)$, $\boldsymbol{t} = (t_1, t_2, \dots, t_{q-1})'$, and $\Delta = ((1+\delta_{ij})\theta_{ij}/2)$, with $\delta_{ij} = 1$ if $i = j$, and $\delta_{ij} = 0$ if $i \neq j.$).
The experimental region for $\boldsymbol{t}$, therefore, comes out to be

$$\mathcal{T} = \{\boldsymbol{t} = (t_1, t_2, \dots, t_{q-1})' \in [-1,1]^{q-1}: t_i - t_j \in [-1,1], \text{for } 1 \leq i,j \leq q-1\}.$$

It is assumed that Δ is negative definite, and that $\eta_{\boldsymbol{t}}$ is maximized at an interior point of the experimental region $\mathcal{T}$. Clearly, $\eta_{\boldsymbol{t}}$ is maximized at $\boldsymbol{\rho} = \frac{1}{2}\Delta^{-1}\boldsymbol{\theta}$, where $\boldsymbol{\theta} = (\theta_1, \theta_2, \dots, \theta_{q-1})$, and, from the inverse transformation $\boldsymbol{t} \rightarrow \boldsymbol{x}$, one can find the mixing proportions $\boldsymbol{x} = \boldsymbol{\gamma}$ that maximizes $\eta_{\boldsymbol{x}}$.

As before, for a continuous design ξ, the large sample dispersion matrix of the estimate $\hat{\boldsymbol{\rho}}$ of $\boldsymbol{\rho}$ comes out to be $A(\boldsymbol{\rho})M(\xi)^{-1}A(\boldsymbol{\rho})'$, where $M(\xi)$ is the information matrix of ξ and $A(\boldsymbol{\rho})$ is the matrix of partial derivatives of the components of $\boldsymbol{\rho}$ with respect to the model parameters. The authors showed that $A(\boldsymbol{\rho}) = -\Delta^{-1}A^*(\boldsymbol{\rho})$, where the elements of $A^*(\boldsymbol{\rho})$ are constants (0 or ½) or linear functions of $\boldsymbol{\rho}$, as given below:

$$A^*(\boldsymbol{\rho}) = \begin{bmatrix} 0 & \frac{1}{2} & 0 \dots 0 & \rho_1 & 0 \dots 0 & \frac{\rho_2}{2} & \frac{\rho_3}{2} \dots 0 \\ 0 & 0 & \frac{1}{2} \dots 0 & 0 & \rho_2 \dots 0 & \frac{\rho_1}{2} & 0 \dots 0 \\ & & & & \dots & & \\ 0 & 0 & 0 \dots 0 & 0 & 0 \dots 0 & 0 & 0 \dots \frac{\rho_{q-1}}{2} \\ 0 & 0 & 0 \dots \frac{1}{2} & 0 & 0 \dots \rho_{q-1} & 0 & 0 \dots \frac{\rho_{q-2}}{2} \end{bmatrix}.$$

The D-optimality criterion selects the optimum design by minimizing Det. $[A(\boldsymbol{\rho})M(\xi)^{-1}A(\boldsymbol{\rho})']$. However, as the determinant depends on the unknown parameters of (4.3) through $\boldsymbol{\rho}$, Pal and Mandal (2012) took recourse to the pseudo-Bayesian approach of Pal and Mandal (2006) whereby, under the assumption of no information about the relative importance of the mixing components, it is assumed that the prior moments $\varepsilon(\gamma_i^2)$ are all equal for $i = 1(1)q$, and $\varepsilon(\gamma_i\gamma_j)$ are all equal for $i,j = 1(1)q, i < j$. Because of the constraint $\sum_{i=1}^{q} x_i = 1$, this gives $\varepsilon(\rho_i) = 0$, $\varepsilon(\rho_i^2) = v$, for $i = 1(1)(q-1)$, and $\varepsilon(\rho_i\rho_j) = w$, for $i,j = 1(1)(q-1), i < j$, where $v \in (0, 1)$, $w \in (-1, 1)$, and $v > w$. These prior moments are assumed to be known. Using this information, the D-optimum design is obtained by minimizing

$$\varphi_D(\xi) = \text{Det.}\{\mathcal{E}[A(\boldsymbol{\rho})M(\xi)^{-1}A(\boldsymbol{\rho})']\},$$

or, by maximizing $\varphi_D^*(\xi) = -\log\varphi_D(\xi)$.

Noting that $\varphi_D^*(\xi)$ has the properties of invariance and concavity, Pal and Mandal (2012) restricted to the sub-class $\mathcal{D}_C$ of invariant designs given by

$$\mathcal{D}_C = \{\tau | \tau = \alpha_0\tau_0 + \alpha_1\tau_1 + \cdots + \alpha_{q-1}\tau_{q-1}, 0 \le \alpha_i \le 1, i = 0(1)(q-1), \textstyle\sum_{i=0}^{q-1}\alpha_i = 1\},$$

where for each *i*, the design τ_i is given by

$$\tau_i = \left\{\boldsymbol{t} \leftrightarrow \overbrace{1,1,\ldots,1}^{i}, \overbrace{0,0,\ldots,0}^{q-i-1}, \boldsymbol{t} \leftrightarrow \overbrace{-1,-1,\ldots,-1}^{i}, \overbrace{0,0,\ldots,0}^{q-i-1}\right\},$$

where $\boldsymbol{t} \leftrightarrow \boldsymbol{r}$ means $\boldsymbol{t} = P\boldsymbol{r}$, *P* being some $(q-1)\times(q-1)$ permutation matrix, and the mass at each support point is $1/2\binom{q-1}{i}$.

The D-optimal design within $\mathcal{D}_C$ is then obtained by maximizing $\varphi_D^*(\tau)$ with respect to α_i's. subject to $0 \le \alpha_i \le 1, i = 0(1)(q-1), \sum_{i=0}^{q-1}\alpha_i = 1$. The optimality or otherwise of the design thus obtained within the whole class of competing designs is verified using Kiefer's Equivalence Theorem, which, in this case, reduces to the following [after writing the model in the form $\eta_{\boldsymbol{t}} = f(\boldsymbol{t})'\boldsymbol{\theta}$] :

A necessary and sufficient condition for a design ξ to be D-optimal is that

$$\textit{Trace}\ \mathcal{E}\{A^*(\boldsymbol{\rho})M(\xi)^{-1}f(\boldsymbol{t})f'(\boldsymbol{t})M(\xi)^{-1}A^*(\boldsymbol{\rho})\}(\mathcal{E}\{A^*(\boldsymbol{\rho})M^{-1}(\xi)A^*(\boldsymbol{\rho})'\})^{-1} \le q-1$$

for all $\boldsymbol{t} \in \mathcal{T}$, where equality holds at the support points of ξ.

To find the optimal design in the experimental region Ξ_δ, the authors used the notation $\boldsymbol{x} \sim (k_1, k_2, \ldots, k_q)$ to define

$$x = \frac{(k_1,k_2,\ldots,k_q)'}{||(k_1,k_2,\ldots,k_q)||},$$

where $\delta \le \frac{k_i}{k_j} \le \frac{1}{\delta}, i,j = 1(1)q, \delta\epsilon(0,1)$, and || || denotes the L_1 norm, and the notation $\boldsymbol{x} \overset{\boldsymbol{q-1}}{\longleftrightarrow} (k_{P(1)}, k_{P(2)}, \ldots, k_{P(q-1)}, k_q)$, for all permutation *P* of {1,2,…,*q*-1}. For example, if *q* = 3, $\boldsymbol{x} \sim (1,\delta,1)$ means $\boldsymbol{x} = (\frac{1}{2+\delta}, \frac{\delta}{2+\delta}, \frac{1}{2+\delta})$, and $\boldsymbol{x} \overset{\boldsymbol{2}}{\leftrightarrow} (1, \delta, 1)$ means $\boldsymbol{x} \in \{\boldsymbol{x} \in \Xi_\delta : \boldsymbol{x} \sim (1,\delta,1) \text{ or } \boldsymbol{x} \sim (\delta,1,1)\}$.

Then, the design τ_i on the experimental region $\mathcal{T}$ corresponds to the design ξ_i on the experimental region Ξ_δ, given by (2.1), where

$$\xi_i = \left\{\boldsymbol{x} \overset{\boldsymbol{q-1}}{\longleftrightarrow} \overbrace{1,1,\ldots,1}^{i}, \overbrace{\delta,\delta,\ldots,\delta}^{q-i-1}, \delta, \boldsymbol{x} \overset{\boldsymbol{q-1}}{\longleftrightarrow} \overbrace{\delta,\delta,\ldots,\delta}^{i}, \overbrace{1,1,\ldots,1}^{q-i-1}, 1\right\},$$

and the mass at each support point is $1/2\binom{q-1}{i}$.

For the case of *q* = 2, the optimal design, therefore, assigns mass $\alpha/2$ at each of the support points $(\frac{\delta}{1+\delta}, \frac{1}{1+\delta})$ and $(\frac{1}{1+\delta}, \frac{\delta}{1+\delta})$, and mass 1 - α at the centroid (1/2 ,1/2), where $\alpha = \frac{\sqrt{v+1/4}}{\sqrt{v}+\sqrt{v+1/4}}$. For *q* > 2, owing to the presence of the apriori moments (*v*, *w*), the verification of the optimality of a design using Equivalence Theorem is rather involved. Pal and Mandal (2012) therefore, numerically checked the conditions of the theorem using innumerable points from the experimental region for *q*

= 3,4,5. The tables below are taken from Pal and Mandal (2012), and show the optimal masses assigned to $\tau_i{}'$s for some combinations of (v, w), when q = 3,4,5:

q =3

v	w	α_0	α_1	α_2
0.1	0.05	0.2265	0.5157	0.2578
0.2	0.10	0.2572	0.4952	0.2476
0.3	0.15	0.2712	0.4859	0.2429
0.4	0.15	0.2805	0.4874	0.2321
0.6	0.23	0.2483	0.5063	0.2454

q =4

v	w	α_0	α_1	α_2	α_3
0.1	0.07	0.1327	0.3747	0.3624	0.1302
0.2	0.10	0.1630	0.3870	0.3210	0.1290
0.4	0.15	0.1782	0.3934	0.3058	0.1226
0.6	0.40	0.1787	0.3775	0.3061	0.1377
0.8	.25	0.1857	0.3966	0.2995	0.1182

q =5

v	w	α_0	α_1	α_2	α_3	α_4
0.1	0.05	0.0897	0.2942	0.3255	0.2170	0.0736
0.3	0.10	0.1102	0.3153	0.3063	0.1966	0.0716
0.4	0.20	0.1116	0.3111	0.2997	0.1998	0.0778
0.6	0.40	0.1124	0.3037	0.2937	0.2061	0.0841
0.8	0.25	0.1173	0.3201	0.3004	0.1914	0.0708

Acknowledgement

The author acknowledges with thanks the fruitful comments of the referee, which helped to improve the presentation of the paper.

References

[1] Aitchison, J., and Bacon-Shone, J. (1984): Log contrast models for experiments with mixtures. Biometrika 71:323–330.

[2] Atwood, C. L. (1969): Optimal and efficient designs of experiments. Ann. Math. Statist. 40:1570–1602.

[3] Box, G. E. P. and Wilson, K. B. (1951): On the Experimental Attainment of Optimum Conditions. Journal of the Royal Statistical Society Series B, 13, 1-45.

[4] Chan, L. Y. (1992): D-optimal design for a quadratic log contrast model for experiments with mixtures. Communications in Statistics-Theory and Methods 21(10):2909–2930.

[5] Chan, L.Y. and Guan, Y.N. and Zhang, C. (1998): A-optimal design for an additive quadratic mixture model. Statistica Sinica, 8:979-990.

[6] Chan, L. Y. and Guan, Y. N. (2001): A- and D-optimal designs for a log contrast model for experiments with mixtures. Journal of Applied Statistics 28(5):537–546.

[7] Chatterjee, S. K. and Mandal, N. K. (1981): Response surface designs for estimating the optimal point. Calcutta Statistical Association Bulletin 30:145-169.

[8] Cheng, R. C. H., Melas, V. B. and Pepelyshev, A. N. (2001): Optimal designs for the evaluation of an extremum point. In, Atkinson, Anthony, Bogacka, Barbara and Zhigljavsky, Anatoly A. (eds.) Optimum Design 2000. (Nonconvex Optimization and Its Applications, 51) Dordrecht, The Netherlands. Kluwer, pp. 15-24.

[9] Darroch, J. N. and Waller, J. (1985): Additivity and interaction in three-component experiments with mixtures. Biometrika, 72(1):153–163.

[10] Draper, N. R. and Pukelsheim, F. (1999): Kiefer ordering of simplex designs for first and second degree mixture models. Journal of Statistical Planning & Inference 79:325–348.

[11] Farrel, R. H., Kiefer, J.C., and Walbran, A. (1967): Optimum multivariate design. In: Le-Cam, L. M., Neyman, J. (Eds.), Proceedings Fifth Berkeley Symposium on Mathematical Statistics and Probability (Vol. 1, 113–138), Berkeley C.A., 1965 & 1966.

[12] Fedorov, V. V. (1971): The designs of experiments for linear optimality criteria, Theory of Probability and its Applications, 1971, Volume 16, Issue 1, Pages 189–195.

[13] Fedorov, V. V. and Müller, W. G. (1997): Another view on optimal design for estimating the point of extremum in quadratic regression. Metrika, 46: 147–157.

[14] Galil, Z., Kiefer, J. (1977): Comparison of simplex designs for quadratic mixture models. Technometrics 19:445–453.

[15] Huang, M.-N.L., Huang, M.-K. (2009a): ϕ_p-optimal designs for a linear log contrast model for experiments with mixtures. Metrika 70(2):239–256.

[16] Huang, M.-K., Huang, M.-N.L. (2009b): Ds-optimality designs for quadratic log contrast model for experiments with mixtures. Communications in Statistics-Theory and Methods 38:1607–1621.

[17] Kiefer, J. (1961): Optimum designs in regression problems, II. Ann. Math. Statist. 32, 298-325.

[18] Kiefer, J. (1974): General equivalence theory for optimum designs (approximate theory). Annals of Statistics 2:849–879.

[19] Liski, Erkki P., Mandal, Nripes K., Shah, Kirti R. and Sinha, Bikas K. (2002): Topics in Optimal Design. Lecture Notes in Statistics Volume 163. Springer Nature.

[20] Liu, S., Neudecker, H. (1997): Experiments with mixtures: optimal allocation for Becker's models. Metrika 45:53–66.

[21] Mandal, N. K. (1982): D-optimal designs for estimating the optimum point in a multifactor experiment. Calcutta Statistical Association Bulletin 31:105–130.

[22] Mandal, N. K. (1986): D-optimal designs for estimating the optimum point in a multiresponse experiment. Calcutta Statistical Association Bulletin 35:37-49.

[23] Mandal, N. K., and Heiligers, B. (1992): Minimax designs for estimating the optimum point in a quadratic response surface. Journal of Statistical Planning and Inference 31:235–244.

[24] Mandal, N. K. and Pal, M. (2008): Optimum mixture design using deficiency criterion. Communications in Statistics – Theory and Methods, 37:565-575.

[25] Mandal, N. K., Pal, M., Sinha, B. K., Das, P. (2008): Optimum mixture designs: A pseudo-Bayesian approach. Journal of the Indian Society of Agricultural Statistics (special volume in memory of Prof. K. Kishen) 62(2):174–182.

[26] Melas, V. B., Pepelyshev, A. N. and Cheng, R. C. H., (2003): Designs for estimating an extremal point of quadratic regression models in a hyperball. Metrika, 58: 193–208.

[27] Pal, M., Mandal, N. K. (2006): Optimum designs for optimum mixtures. Statistics and Probability Letters 76:1369–1379.

[28] Pal, M. and Mandal, N. K. (2007): Optimum mixture design via Equivalence Theorem. Journal of Combinatorics, Information & System Sciences, 32:107-126.

[29] Pal, M. and Mandal, N. K. (2012): D-optimal designs for optimum mixture in a quadratic log-contrast model. Communications in Statistics – Simulation and Computation, 41:253-264.

[30] Pal, M., Mandal, N. K. and Aggarwal, M.N. (2017): A-optimal designs for optimum mixture in an additive quadratic mixture model. Statistics, 51(2): 265-276.

[31] Scheffé, H. (1958): Experiments with mixtures. Journal of the Royal Statistical Society B 20:344–360.

[32] Scheffé, H. (1963): Simplex – centroid design for experiments with mixtures. Journal of the Royal Statistical Society B 25:235–263.

[33] Silvey, S. D. (1980): Optimal Designs. London: Chapman Hall.