# **Mixture Designs based on Hadamard Matrices**

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#### **Abstract**

Prescott (2000) constructed orthogonally blocked mixture designs using projection of augmented pair designs. Singh (2003) constructed optimal orthogonally blocked designs for the Darroch and Waller quadratic model in three and four components. In this paper, mixture designs have been constructed by projecting screening designs based on Hadamard matrices. The constructed designs have been further compared on the basis of uniformity and G efficiency criteria. Orthogonal blocking of the constructed mixture designs has also been presented.

Key words: Mixture Experiments, Scheffé's Model, Darroch and Waller Model, Hadamard Matrices, Projection Designs, Quantitative Screening Designs, Measures of Uniformity, G efficiency, Orthogonal Blocking.

#### 1. Introduction

Mixture experiments are characterized by the fact that the response(y) depends on the relative proportion of each component x<sub>i</sub> satisfying

$$0 \le x_i \le 1, i = 1, 2, ..., m \text{ and } x_1 + x_{2+} ... + x_m = 1$$
 (1.1)

and not on the total amount of the mixture. These constraints define a (m-1) dimensional simplex. Scheffé (1958, 1963) introduced models and designs for experiments with mixtures. The linear and quadratic models given by Scheffé (195 8) are as follows:

$$E(Y) = \sum_{i=1}^{m} \beta_i x_i \tag{1.2}$$

$$E(Y) = \sum_{i=1}^{m} \beta_i x_i$$

$$E(Y) = \sum_{i=1}^{m} \beta_i x_i + \sum_{i < j=1}^{m} \beta_{ij} x_i x_j$$
(1.2)
(1.3)

Scheffé (1963) introduced process variables for these experiments. John (1984) discussed the need of blocking for mixture experiments in the presence of process variables and constructed orthogonal block designs using Latin squares. Singh (2003) used the Darroch and Waller quadratic model to construct optimal orthogonal designs in two blocks for three and four components. Aggarwal et al (2008) used F-squares as a basis for the Darroch and Waller quadratic mixture model to construct optimal orthogonal designs in two blocks for four components. The quadratic model given by Darroch and Waller (1985) for mixture experiments is

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$$E(Y) = \sum_{i=1}^{m} \beta_i x_i + \sum_{i=1}^{m} \beta_{ii} x_i^2$$
 (1.4)

This model is additive in the mixture components, in the sense that it is a sum of separate functions  $x_1, x_2, ..., x_m$ . When mixture components  $x_1, x_2, ..., x_m$  vary but the sums  $x_1 + x_2 + .... + x_s$  and  $x_{s+1} + x_{s+2} + .... + x_m$  ( $1 \le s \le m$ )are fixed, the total effect of the expected response is the sum of the effects of varying  $x_1, x_2, ..., x_s$  and  $x_{s+1}, x_{s+2}, ..., x_m$  separately. Such models are suitable for the designs of industrial products where mixture components have additive effects on the response function. An example where the Darroch and Waller quadratic model was more suitable than Scheffé's quadratic model was discussed by Chan (1998: p.361) in the design of a solder plate used in surface- mount technology in electronic manufacturing.

A detailed bibliography of mixture designs is available at IASRI site at http://iasri.res.in/design/mixture/mixture/Bibliography.htm.

In this paper, we have used Hadamard matrices to construct screening designs and then projected them to obtain mixture designs. These designs have been compared for various values of n for their uniformity and design criteria. Section 2 contains Hadamard matrices and their applications. In Section 3, we have discussed the mixture designs obtained through projection of Quantitative Screening Designs(QSDs). Section 4 compares these designs on the basis of uniformity measures. In Section 5 we have compared these designs on the basis of G- efficiency criteria. In Section 6, we have presented orthogonal blocking of these projected designs. Section 7 gives the conclusion.

## 2. Hadamard Matrices

A square matrix  $\mathbf{H}_n$  of order n whose entries are +1 or -1 is called a Hadamard matrix of order n provided that its rows are pair wise orthogonal, in other words,  $\mathbf{H}_n$  is such that

$$\mathbf{H}_{n}\mathbf{H}'_{n}=n\mathbf{I}=\mathbf{H}'_{n}\mathbf{H}_{n} \tag{2.1}$$

Hadamard matrices were first studied by Sylvester (1867) who observed that if  $\mathbf{H}$  is a Hadamard matrix, then

$$\begin{bmatrix} H & H \\ H & -H \end{bmatrix}$$

is also a Hadamard matrix. He also claimed that there is a Hadamard matrix of order 2<sup>t</sup> for all non-negative t. The matrices of order 2<sup>t</sup> constructed using Sylvester's techniques are usually referred to as Sylvester-Hadamard matrices. Apart from Sylvester's techniques, there are several other systematic ways of constructing such matrices. Lists of those techniques can be found in Hedayat et al. (1999) and the listing of the matrices can be found in Seberry (2004) and Sloane (2004). For comprehensive review and methods of construction of Hadamard matrices, one may refer to Gupta et al.( 2007) and for online generation, may refer to http://iasri.res.in/design/WebHadamard/WebHadamard.htm.

Two Hadamard matrices are essentially the same if one can be obtained from the other by a permutation of the rows, or of the columns, or by negating certain rows, or columns. Two Hadamard matrices are called equivalent if one can be obtained from the other

by a sequence of these operations. The number of non equivalent Hadamard matrices of order n is known only for  $n \le 32$ . The number of non equivalent Hadamard matrices of order 1, 2, 4, 8, 12, 16, 20, 24, 28, 32 is respectively 1, 1, 1, 1, 1, 5, 3, 60, 487, 13710027.

# 2.1 Applications of Hadamard Matrices

Hadamard matrices have a very wide variety of application in modern communications and statistics. Hadamard matrices constructed using Sylvester's techniques are used in engineering applications including communication systems and digital image processing.

The application of Hadamard matrices in the construction of weighing designs, group divisible designs, optimal resolution 3 designs, Youden designs, factorial designs and orthogonal arrays has been discovered recently.

Hadamard matrices are intimately connected to factorial experiments in which each factor is at two levels. Plackett and Burman (1946) utilized Hadamard matrices for the construction of optimum multi factorial experiments. Other statisticians have used Hadamard matrices for a number of experiments under different optimality criteria. Applications of Hadamard matrices in the area of optimal regression theory have been noticed recently by workers in the field of optimal design theory.

Hadamard matrices have recently been found useful in spectrometry and pattern recognition in the construction of masks. These applications can be found in Tai, Harwit and Sloane (1975) and Decker (1973).

# 3. Projection of Quantitative Screening Designs (QSDs) based on Hadamard Matrices

Georgiou et al (2013) have proposed a new concept of three level QSDs from weighing matrices. Let  $\mathbf{W} = \mathbf{W}(n, k)$  be a weighing matrix of order n and weight k. Set

$$QD = \begin{bmatrix} \mathbf{W} \\ \mathbf{0}_{sxn} \\ -\mathbf{W} \end{bmatrix}$$
(3.1)

Where  $O_{sxn}$  is an  $s \times n$  zero matrix (the centre points). Then QD is a three-level screening design with 2n+s design points. The columns of the design matrix QD are orthogonal to each other. We have used Hadamard matrices  $H_m$  instead of weighing matrices and s=1 to obtain QSDs with 2m+1 design points.

Box and Hau (2001), Prescott (2000, 2004), Aggarwal and Singh (2003) discussed the projection of an unconstrained design **D** into a constrained mixture simplex. Given an unconstrained design **D**, we need a projection matrix **P**, to project **D** into a mixture space to get the design matrix  $\mathbf{X} = \alpha \mathbf{DP} + \frac{1}{m} \mathbf{J}_{2m+1,m}$ , satisfying the constraints in (1.1) where  $\mathbf{J}_{2m+1,m}$  is an 2m+1x m matrix of 1's and  $\alpha$  is a scaling constant needed to ensure that all design points lie within the mixture simplex. The elements of the constrained region  $\mathbf{DP}$  are defined as  $d_{P,iu} = \frac{(x_{iu}-x_{ou})}{\alpha r_i}$  for u=1, 2,...,2m+1, i=1,2,...m, where  $\mathbf{x}$  is any point,  $\mathbf{x}_0$  is some reference point and  $\mathbf{r}_i$ 's determine the direction of projection. Equation (1.1) implies that we must have  $d'_{P,u}\mathbf{R} = 0$ , where  $\mathbf{R} = (r_1, r_2, ..., r_m)'$  and  $d_{p,u}$  is the  $u^{th}$  row of  $\mathbf{DP}$ . Then the

projection matrix P=I-R  $(R'R)^{-1}R'$  with R'=(1, 1, ..., 1). Prescott (2000) illustrated projection of central composite response surface designs into constrained mixture simplexes. Aggarwal and Singh (2003) projected three level response surface designs to construct mixture designs for 3 to 5 mixture components.

We have used various Hadamard matrices to obtain mixture designs by projection of QSDs. We considered these designs to fit models given in (1.2), (1.3) and (1.4). The model given in (1.3) required at least m(m+1)/2 design points to estimate the parameters whereas the Darroch and Waller quadratic model given in (1.4) can be fitted using 2m design points. In this paper, we restrict ourselves to designs containing (2m+1) design points only. The constructed designs are compared on the basis of uniformity and optimality criteria for Scheffé linear model and the Darroch and Waller quadratic model.

As an example consider the following Hadamard matrix of order 4

which are projected to get a mixture design.

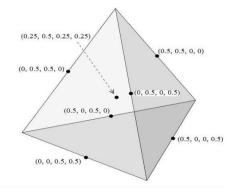
The design matrix obtained by taking  $\alpha = \frac{1}{4}$  is as follows:

$$\mathbf{X} = \begin{bmatrix} 0.2500 & 0.2500 & 0.2500 & 0.2500 \\ 0.5000 & 0.5000 & 0.0000 & 0.0000 \\ 0.5000 & 0.0000 & 0.5000 & 0.0000 \\ 0.5000 & 0.0000 & 0.0000 & 0.5000 \\ 0.2500 & 0.2500 & 0.2500 & 0.2500 \\ 0.2500 & 0.2500 & 0.2500 & 0.2500 \\ 0.0000 & 0.0000 & 0.5000 & 0.5000 \\ 0.0000 & 0.5000 & 0.5000 & 0.5000 \\ 0.0000 & 0.5000 & 0.5000 & 0.0000 \end{bmatrix}$$

$$(3.2)$$

The design points in X given in (3.2) are displayed in Figure 1, where the centre run (0.25 0.25 0.25 0.25) is replicated thrice.

Figure 1: Design points of the projected design given in (3.2)



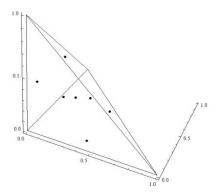
The design matrix obtained by taking  $\alpha = \frac{1}{5}$  is as follows:

$$\mathbf{X} = \begin{bmatrix} 0.2500 & 0.2500 & 0.2500 & 0.2500 \\ 0.4500 & 0.4500 & 0.0500 & 0.0500 \\ 0.4500 & 0.0500 & 0.4500 & 0.0500 \\ 0.4500 & 0.0500 & 0.0500 & 0.4500 \\ 0.2500 & 0.2500 & 0.2500 & 0.2500 \\ 0.2500 & 0.2500 & 0.2500 & 0.2500 \\ 0.0500 & 0.0500 & 0.4500 & 0.4500 \\ 0.0500 & 0.4500 & 0.0500 & 0.4500 \\ 0.0500 & 0.4500 & 0.4500 & 0.0500 \end{bmatrix}$$

$$(3.3)$$

The design points in X given in (3.3) are displayed in Figure 2 where the centre run (0.25 0.25 0.25) is replicated thrice.

Figure 2: Design points of the projected design given in (3.3)



We have used Hadamard matrices for m varying from 4 to 32 to construct mixture designs with  $\alpha = \frac{1}{m}$  and  $\alpha = \frac{1}{m+1}$ . After projecting these QSDs we obtain the required mixture designs containing 2m+1 design points for various values of m. These designs are available with the authors. It is interesting to note that for a particular value of m, more than one Hadamard matrices exist, but the mixture designs constructed by projecting the QSDs based on these matrices are all the same.

# 4. Uniformity Measures

A Uniform Design seeks design points that are uniformly scattered on the domain (see Fang, Lin, Winker and Zhang(2000)). Warnock (1972)gave an analytical formula for calculating the  $L_2$  discrepancy which is a measurement of uniformity. Hickernell (1998) pointed out some disadvantages in the formula. To overcome these, he proposed three new measures of uniformity, namely, the Centered  $L_2$  discrepancy ( $CL_2$ ), Symmetric  $L_2$  discrepancy ( $CL_2$ ) and modified  $CL_2$  discrepancy ( $CL_2$ ). Hickernell(1998) gave an analytical expression for the above three as follows:

$$(CL_{2}(P_{n}))^{2} = \left(\frac{13}{12}\right)^{s} - \frac{2}{n} \sum_{k=1}^{n} \prod_{j=1}^{s} \left(1 + \frac{1}{2}|x_{kj} - 0.5| - \frac{1}{2}|x_{kj} - 0.5|^{2}\right)$$

$$+ \frac{1}{n^{2}} \sum_{k=1}^{n} \sum_{j=1}^{n} \prod_{i=1}^{s} \left(1 + \frac{1}{2}|x_{ki} - 0.5| + \frac{1}{2}|x_{ji} - 0.5| - \frac{1}{2}|x_{ki} - x_{ji}|\right)$$

$$(SL_{2}(P_{n}))^{2} = \left(\frac{4}{3}\right)^{s} - \frac{2}{n} \sum_{k=1}^{n} \prod_{j=1}^{s} \left(1 + 2x_{kj} - 2x_{kj}^{2}\right) + \frac{2^{s}}{n^{2}} \sum_{k=1}^{n} \sum_{j=1}^{n} \prod_{i=1}^{s} \left(1 - |x_{ki} - x_{ji}|\right)$$

$$(ML_{2}(P_{n}))^{2} = \left(\frac{4}{3}\right)^{s} - \frac{2^{1-s}}{n} \sum_{k=1}^{n} \prod_{j=1}^{s} \left(3 - x_{ki}^{2}\right) + \frac{1}{n^{2}} \sum_{k=1}^{n} \sum_{j=1}^{n} \prod_{i=1}^{s} \left[2 - max(x_{ki} - x_{ji})\right]$$

where  $P_n$  is a set of n design points for s factors.

We compiled uniformity measures for the various designs obtained in Section 3. The results are given in Table 1a.

Table 1a: Discrepancy measures for mixture designs based on  $H_m$ , m varying from 4 to 32 with  $\alpha = \frac{1}{m}$ .

			<u>m</u>			
S.No.	m	No. of Hadamard matrices used to construct mixture designs	$CL_2$	$ML_2$	$SL_2$	
1	4	1	0.6142	1.2379	2.0615	
2	8	1	2.4650	8.9039	9.8312	
3	12	1	6.3632	40.8943	38.8861	
4	16	5*	14.9750	170.8800	154.7159	
5	20	3*	34.2487	693.8280	617.2743	
6	24	4*	77.5736	2790.7	2469.4	
7	28	4*	175.0859	11188.0	9881.5	
8	32	$2^*$	394.6331	44803.0	39543.0	

Table 1b: Discrepancy measures for mixture designs based on  $H_m$ , m varying from 4 to 32 with  $\alpha = \frac{1}{m+1}$ 

S.No.	m	No. of Hadamard matrices used to construct mixture designs	$CL_2$	$ML_2$	$SL_2$
1	4	1	0.6218	1.3290	2.2227
2	8	1	2.5338	9.0881	10.3670
3	12	1	6.4938	41.3666	40.4265
4	16	5*	15.1407	172.2685	159.2459
5	20	3*	34.5458	698.2477	632.5255
6	24	4*	78.1282	2.805E+03	2.52E+03
7	28	4*	176.1530	1.123E+04	1.006E+04
8	32	2*	396.7308	4.498E+04	4.015E+04

<sup>\*</sup> All designs had the same uniformity values

As m increases from 4 to 32, the variation increases in the discrepancy measures  $CL_2$ ,  $ML_2$  and  $SL_2$  in Table 1a and Table 1b.

On comparing the values for the discrepancy measures between Table 1a and Table 1b, it is observed that all measures of Table 1a are better than those of Table 1b. That is,  $CL_2$  value in Table 1a for a particular design with  $\alpha = \frac{1}{m}$  is better than that of the corresponding design with  $\alpha = \frac{1}{m+1}$ . A similar pattern is observed for the rest of the values in Table 1a and Table 1b.

Thus uniformity is affected by the values of m and  $\alpha$ . The smaller the value of m, better is the uniformity. Discrepancy measures for designs projected using  $\alpha = \frac{1}{m}$  are better than the designs projected using  $\alpha = \frac{1}{m+1}$ .

# 5. Design Criteria

Several popular design criteria are available for the evaluation of a proposed experimental design. A systematic study of the specification of optimum experimental designs was undertaken by Kiefer (1959,1961) in a series of papers, where he introduced various design criteria (D,A,E,L,M), discussed interrelations amongst these and established the optimality property of some well-known designs for some particular problems.

A design is said to be D-optimal if  $D = |(\mathbf{X}'\mathbf{X})^{-1}|$  is minimized, A-optimal if  $A = tr(\mathbf{X}'\mathbf{X})^{-1}$  is minimized and G-optimal if  $G = max.[diag.(\mathbf{X}(\mathbf{X}'\mathbf{X})^{-1}\mathbf{X}')]$  is minimized, where  $\mathbf{X}$  is the extended design matrix corresponding to the model under consideration.

Moreover, G-efficiency criterion, defined as  $100X \frac{p}{(GXN_d)}$ , where p is the number of factors and  $N_d$  is the number of design points, is commonly used for mixture designs. It refers to minimizing the maximum variance of the prediction over the experimental region. Wheeler (1972) suggested that any design with G efficiency of 50% or more can be considered as an efficient design. Tabulated below are the G and G-efficiency values for the mixture designs based on the Hadamard matrices  $H_m$ , with m varying from 4 to 32 for Scheffé's linear model.

Table 2a: G and G-efficiency values for mixture designs based on  $H_m$ , m varying from 4 to 32, for Scheffé's Linear Model

		,		Scheffé's Linear Model				
S. No.	m	No. of Hadamard matrices used to construct	$p, N_d$	α =	$=\frac{1}{m}$	$\alpha = \frac{1}{m+1}$		
		mixture designs		G	G-efficiency (%)	G	G-efficiency (%)	
-	4		4.0	0.6100	` ,	0.6100	` ′	
1	4	1	4, 9	0.6100	73	0.6100	73	
2	8	1	8, 17	0.5588	84	0.5588	84	
3	12	1	12, 25	0.5400	89	0.5400	89	
4	16	5*	16, 33	0.5303	91	0.5303	91	
5	20	3*	20, 41	0.5244	93	0,5244	93	
6	24	4*	24, 49	0.5204	94	0.5204	94	
7	28	4*	28, 57	0.5175	95	0.5175	95	
8	32	2*	32, 65	0.5154	96	0.5154	96	

<sup>\*</sup> All designs had the same G values

The G values are identical for  $\alpha = \frac{1}{m}$  and  $\alpha = \frac{1}{m+1}$ . As the value of m increases the G efficiency improves. From Table 2a, we notice that all the mixture designs constructed have G efficiency greater than 50%. Hence the designs in Section 3 are all G efficient for fitting Scheffé's linear model. The designs constructed in Section 3 by projecting a QSD based on Hadamard matrices of order m contain 2m+1 points. Hence these designs can be used for fitting a Darroch and Waller quadratic model with p = 2m parameters.

In Table 2b, we have given the values for the best or optimal design for different m by G- optimality criterion. Also tabulated are the corresponding G- efficiency of the best designs.

Table 2b: G and G- efficiency values for mixture designs based on  $H_m$ , m varying from 4 to 32, Darroch and Waller Quadratic Model

		No. of Hadamard matrices used to		Darroch and Waller Quadratic Model					
S. No.	m			$\alpha = \frac{1}{m}$		$\alpha = \frac{1}{m+1}$			
	construct mixture designs	$p, N_d$	G	G-efficiency (%)	G	G-efficiency (%)			
1	4	1	8, 9	1.5	59	1.4647	61		
2	8	1	16, 17	1.5156	62	7.2596	13		
3	12	1	24, 25	1.8090	53	1.4841	65		
4	16	5	32, 33	0.6519	149	0.6337	153		
5	20	3	40, 41	1.7063	57	0.9554	102		
6	24	4	48, 49	1.4851	66	1.1307	87		
7	28	4	56, 57	0.6586	149	0.8185	120		
8	32	2	64, 65	1.2954	76	0.8735	113		

The G efficiency values of almost all the designs, except for the case m=8 when  $\alpha = \frac{1}{m+1}$ , are greater than 50%. Hence, the designs constructed in Section 3 are efficient designs.

# 6. Orthogonal blocking in Mixture Experiments

Block designs for mixture experiments are group of mixture blends where each group or block is assumed to differ from other groups or blocks by an additive constant. A design is said to block orthogonally with respect to the blending properties of the components if the estimates of the blending properties in the fitted model are uncorrelated with and are unaffected in the presence of block effects.

Orthogonally blocked mixture designs have been studied by Nigam (1970, 1976) and John(1984). John (1984) gave simplified conditions for estimation of the parameters of Scheffé's quadratic model in the presence of block effects and constructed orthogonally blocked designs for mixture experiments using Latin squares. Cornell (2002, pp 438-454) gives an excellent review of block designs for mixture experiments.

Let N mixture blends (not necessarily all distinct) be arranged in t blocks such that the  $w^{th}$  block contains  $n_w$  blends and  $n_1 + n_2 + \ldots + n_t = N$ . Let  $\gamma_w$  represent the effect of the  $w^{th}$  block, then the Darroch and Waller quadratic model with block terms is

$$E(y_u) = \sum_{i=1}^{m} \beta_i x_{ui} + \sum_{i=1}^{m} \beta_{ii} x_{ui}^2 + \sum_{w=1}^{t} \gamma_w Z_{uw} ; u = 1, 2, ..., N$$
 (6.1)

where  $Z_{uw}$  is a dummy block variable that equals 1 if the  $u^{th}$  blend is in the  $w^{th}$  block and 0 otherwise.

Singh (2003) suggested the following conditions for orthogonal blocking of blends for the Darroch and Waller quadratic model:

$$\sum_{u=1}^{n_{w}} x_{ui} = c_{i}$$

$$\sum_{u=1}^{n_{w}} x_{ui}^{2} = c_{ii} \quad \forall \ w = 1, 2, ..., t \ and \ i = 1, 2, ..., m$$
(6.2)

where  $c_i$ 's and  $c_{ii}$ 's are constants.

As an illustration, we consider the design matrix **X** obtained by projecting a QSD based on  $\mathbf{H}_8$  with  $\alpha = \frac{1}{8}$ 

$$\mathbf{X} = \begin{bmatrix} \mathbf{0.125} & 0.125 &$$

This design satisfies the conditions for orthogonal blocking given in (6.2).

$$\sum_{u=1}^{n_w} x_{ui} = 2.125, \quad \sum_{u=1}^{n_w} x_{ui}^2 = 0.484375 \quad \forall i = 1, 2, ..., m$$
 (6.3)

All projected designs with different value of  $\alpha$  are particular cases when  $c_i = 2.125$  for all i.

Permuting the columns in the mixture design X we can construct 8! designs. All these designs satisfy (6.3). Therefore, we obtain 8! orthogonal blocks satisfying (6.3).

## 7. Conclusion

This paper uses Hadamard matrices to construct QSDs which are projected to obtained unconstrained mixture experiments. Hadamard matrices have not been used in this way earlier for this purpose. The number of design points in the constructed designs has been kept to 2m+1 where m is the number of components in the mixture. This makes the constructed designs appropriate for estimating all the parameters of Scheffé's linear model as well as the reduced Darroch and Waller quadratic model.

In this paper, we have noticed that uniformity and efficiency are both affected by the values of m. Uniformity measures for designs obtained through projection using  $\alpha = \frac{1}{m}$  are better than those designs using  $\alpha = \frac{1}{m+1}$ . The designs constructed in Section 3 are G efficient. As illustrated, orthogonally blocked mixture designs can be constructed using Hadamard matrices for the Darroch and Waller quadratic model.

Although the focus of this paper is on construction of unconstrained mixture designs based on Hadamard matrices, we can use the projection of Hadamard matrices for constructing designs for constrained mixture experiments, as well. The important area of orthogonal block designs for constrained mixture regions is also an open problem.

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