Sci. Annales, Fac. Phys. & Mathem., Univ. Thessaloniki, **15**, 213, (1975)

EXPERIMENTS WITH MIXTURES
ANOTHER EXTENTION OF THE MODIFICATION TO THE SIMPLEX - CENTROID DESIGN

by

Dr. EVANGELOS KONSTANTELOS

(University of Thessaloniki, Greece)

(Introduced by Prof. G. Georganopoulos)

(Received 8.10.75)

Abstract : *In this paper, the modification to the Simplex-Centroid design introduced by D. Lambrakis (*1966) *and applied to a polynomial up to 3rd degree is extended to a polynomial of 4th degree.*

I. Introduction

Sceffé (1963) introduced and developed the Simplex—Centroid Design. The main features of this design, in a q-component mixture in which the proportions $x_1, x_2, \ldots, x_q$ of the components are in the simplex

(1.1) $$\sum_{i=1}^{q} x_i = 1, \qquad x_i \geq 0,$$

are the centroid polynomial

(1.2) $$u = \sum_{i=1}^{q} a_i x_i + \sum_{1 \leq i < j \leq q} a_{ij} x_i x_j + \sum_{1 \leq i < j < k \leq q} a_{ijk} x_i x_j x_k + \ldots +$$

$$+ \sum_{1 \leq i1 < i2 < \cdots < in \leq q} a_{i1i2 \cdots in} x_{i1} x_{i2} \ldots x_{in}$$

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

as a regression function, and the mixture of one, two, three, ..., q components with equal proportions. These mixtures are to be used to esti mate the coefficients in the polynomial (1.2). The purpose of this design is the empirical prediction of the response to any mixture of the components when the response depends only on the proportions of the components present but not on the total amount of the mixture.

Lambrakis (1966) introduced the idea of a modification to this design. In this modification the mixtures of one component, pure mixtu res, are replaced by mixtures of q — 1 components of equal proportions, (q — 1) — nary mixtures and the mixtures of two components are replaced by mixtures of q — 2 components of equal proportions, (q — 2) — nary mixtures. He gave results for the cubic case. This case remains unpublished in his Ph. D. Thesis, Department of Statistics, University of Aberdeen, 1966.

In this paper the above mentioned modification is extended to the quartic case.

2. QUARTIC CASE

The centroid polynomial of fourth degree is

$$(2.1) \qquad u = \sum_{1 \leq i \leq q} a_i x_i + \sum_{1 \leq i < j \leq q} a_{ij} x_i x_j + \sum_{1 \leq i < j < k \leq q} a_{ijk} x_i x_j x_k +$$

$$+ \sum_{1 \leq i < j < k < l \leq q} a_{ijkl} x_i x_j x_k x_l \,.$$

The mixtures to be used to estimate the coefficients in (2.1) are q (q — 1) — nary g_i $(1 \leq i \leq q)$ with proportions

$$x_1 = x_2 = \ldots = x_{i-1} = x_{i+1} = \ldots = x_q = \frac{1}{(q-1)},\ x_r = 0,\ \text{for } r = i$$

$\binom{q}{2}$ (q — 2) — nary f_{ij} $(1 \leq i < j \leq q)$ with proportions

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

$$x_1 = x_2 = \ldots = x_{i-1} = x_{i+1} = \ldots = x_q = \frac{1}{(q-2)}, \; x_r = 0, \text{ for } r = i, j$$

$\binom{q}{3}$ ternary $w_{ijk}(1 \leqq i < j < k \leqq q)$ with proportions

$$x_i = x_j = x_k = \frac{1}{3} \;, \quad x_r = 0, \text{ for } r \neq i,j,k$$

$\binom{q}{4}$ quartenary $v_{ijkl}(1 \leqq i < j < k < l \leqq q)$ with proportions

$$x_i = x_j = x_k = x_l = \frac{1}{4} \;, \quad x_r = 0, \text{ for } r \neq i,j,k,l$$

Taking $r_{\bar{i}}$, $r_{\bar{ij}}$, r_{jjk}, r_{ijkl} observations for $g_{\bar{i}}$, $f_{\bar{ij}}$, w_{ijk}, v_{ijkl} respectively and substituting their observed means $\hat{g}_{\bar{i}}$, $\hat{f}_{\bar{ij}}$, $\hat{w}_{ijk}$, $\hat{v}_{ijkl}$ into (2.1) we have the system of the normal equations

$$(2.2) \quad \hat{w}_{ijk} = \frac{1}{3} (\hat{a}_i + \hat{a}_j + \hat{a}_k) + \frac{1}{9} (\hat{a}_{ij} + \hat{a}_{ik} + \hat{a}_{jk}) + \frac{1}{27} \hat{a}_{ijk}$$

$$(2.3) \quad \hat{v}_{ijkl} = \frac{1}{4} (\hat{a}_i + \hat{a}_j + \hat{a}_k + \hat{a}_l) + \frac{1}{4^2} (\hat{a}_{ij} + \hat{a}_{ik} + \hat{a}_{il} + \hat{a}_{jk} +$$

$$+ \hat{a}_{jl} + \hat{a}_{kl}) + \frac{1}{4^3} (\hat{a}_{ijk} + \hat{a}_{ijl} + \hat{a}_{ikl} + \hat{a}_{jkl}) + \frac{1}{4^4} (\hat{a}_{ijkl})$$

$$(2.4) \quad \hat{g}_{\bar{i}} = \frac{1}{(q-1)} \sum_{r \neq i} \hat{a}_r + \frac{1}{(q-1)^2} \sum_{r,s \neq i} \hat{a}_{rs} +$$

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

$$+ \frac{1}{(q-1)^3} \sum_{r,s,t \neq i} \hat{a}_{rst} + \frac{1}{(q-1)^4} \sum_{r,s,t,v \neq i} \hat{a}_{rstv}$$

$$(2.5) \quad \hat{f}_{\overline{ij}} = \frac{1}{(q-2)} \sum_{r,s \neq i,j} \hat{a}_{rs} + \frac{1}{(q-2)^2} \sum_{r,s \neq i,j} \hat{a}_{ij} +$$

$$+ \frac{1}{(q-2)^3} \sum_{r,s,t \neq i} \hat{a}_{rst} + \frac{1}{(q-2)^4} \sum_{r,s,t,v \neq i} \hat{a}_{rstv}$$

Solving the system above, of normal equations, we obtain the least squares estimates of the coefficients

$$(2.6) \quad \hat{a}_i = \Sigma\, \hat{a}_r - \sum_{r \neq i} \hat{a}_r$$

$$(2.7) \quad \hat{a}_{ij} = \left(\sum \hat{a}_{rs} + \sum_{r,s \neq i,j} \hat{a}_{rs} \right) - \left(\sum_{r,s \neq i} \hat{a}_{rs} + \sum_{r,s \neq j} \hat{a}_{rs} \right)$$

$$(2.8) \quad \hat{a}_{ijk} = \left(\sum \hat{a}_{rst} + \sum_{r,s,t \neq i,j} \hat{a}_{rst} + \sum_{r,s,t \neq j,k} \hat{a}_{rst} + \sum_{r,s,t \neq i,k} \hat{a}_{rst} \right) -$$

$$- \left(\sum_{r,s,t \neq i} \hat{a}_{rst} + \sum_{r,s,t \neq j} \hat{a}_{rst} + \sum_{r,s,t \neq k} \hat{a}_{rst} + \sum_{r,s,t \neq i,j,k} \hat{a}_{rst} \right)$$

$$(2.9) \quad \hat{a}_{ijkl} = 4^4 \hat{v}_{ijkl} - 4^4 \left(\frac{1}{4} (\hat{a}_i + \hat{a}_j + \hat{a}_k + \hat{a}_l) + \frac{1}{4^2} (\hat{a}_{ij} + \hat{a}_{lk} + \right.$$

$$\left. + \hat{a}_{il} + \hat{a}_{jk} + \hat{a}_{jl} + \hat{a}_{kl}) + \frac{1}{4^3} (\hat{a}_{ijk} + \hat{a}_{ijl} + \hat{a}_{ikl} + \hat{a}_{jkl} \right)$$

For more details see appendix A.

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

APPENDIX A

Solution of the System (2.2) — (2.5)

Equation (2.4) is actually a system of q equations. If we write down explicitly all these equations, we observe that each element

$\hat{a}_r (1 \leqq r \leqq q)$ appears in the system $\frac{q\binom{q-1}{1}}{\binom{q}{1}} = q - 1$ times

$\hat{a}_{rs} (1 \leqq r < s \leqq q)$ " " " " $\frac{q\binom{q-1}{2}}{\binom{q}{2}} = q - 2$ "

$\hat{a}_{rst} (1 \leqq r < s < t \leqq q)$ " " " " $\frac{q\binom{q-1}{3}}{\binom{q}{3}} = q - 3$ "

$\hat{a}_{rstv} (1 \leqq r < s < t < v \leqq q)$ " " " " $\frac{q\binom{q-1}{4}}{\binom{q}{4}} = q - 4$ "

If we add all the equations mentioned above, we have

$$\text{(A.I)} \quad \sum \hat{g} = \sum \hat{a}_r + \frac{(q-2)}{(q-1)^2} \sum \hat{a}_{rs} + \frac{(q-3)}{(q-1)^3} \sum \hat{a}_{rst} + \frac{(q-4)}{(q-1)^4} \sum \hat{a}_{rstv} .$$

Equation (2.5) is actually a system of $\binom{q}{q-2} = \binom{q}{2}$ equations

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

If we write all of them, we observe that each element

$\hat{a}_r (1 \leqq r \leqq q)$ appears in the system $\dfrac{\binom{q}{2}\binom{q-2}{1}}{\binom{q}{1}} = \dfrac{(q-1)(q-2)}{2}$ times

each $\hat{a}_{rs} (1 \leqq r < s \leqq q)$ appears in the system $\dfrac{\binom{q}{2}\binom{q-2}{2}}{\binom{q}{2}} =$

$$= \frac{(q-2)(q-3)}{2} \text{ times}$$

each $\hat{a}_{rst} (1 \leqq r < s < t \leqq q)$ appears in the system $\dfrac{\binom{q}{2}\binom{q-2}{3}}{\binom{q}{3}} =$

$$= \frac{(q-3)(q-4)}{2} \text{ times}$$

each $\hat{a}_{rstv} (1 \leqq r < s < t < v \leqq q)$ appears in the system $\dfrac{\binom{q}{2}\binom{q-2}{4}}{\binom{q}{4}}$

$$= \frac{(q-4)(q-5)}{2} \text{ times}$$

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

If we add all these equations, we have the following new equation

$$(A.2) \qquad \sum \hat{f} = \frac{(q-1)}{2} \sum \hat{a}_r + \frac{(q-3)}{2(q-2)} \sum \hat{a}_{rs} +$$

$$+ \frac{(q-3)(q-4)}{2(q-2)^3} \sum \hat{a}_{rst} + \frac{q-4)(q-5)}{2(q-2)^4} \sum \hat{a}_{rstv}$$

From (2.5) we can form a system of $(q-1)$ equations where the left side of each equation is a mixture of $q-2$ components of equal proportions and no containing one component $x_i (1 \leqq i \leqq q)$.

If we write all these equations we observe that each of the elements

$\hat{a}_r (r \neq i)$ appears in the system $\dfrac{(q-1)\binom{q-2}{1}}{\binom{q-1}{1}} = q-2$ times

$\hat{a}_{rs} (r,s \neq i)$ " " " " $\dfrac{(q-1)\binom{q-2}{2}}{\binom{q-1}{2}} = q-3$ times

$\hat{a}_{rst} (r,s,t \neq i)$ " " " " $\dfrac{(q-1)\binom{q-2}{3}}{\binom{q-1}{3}} = q-4$ times

$\hat{a}_{rstv} (r,s,t,v \neq i)$ " " " $\dfrac{(q-1)\binom{q-2}{4}}{\binom{q-1}{4}} = q-5$ times

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

If we add all these equations we have the following equation

$$(A.3)\ \sum \hat{f}_{\bar{i}} = \sum_{r \neq i} \hat{a}_r + \frac{(q-3)}{(q-2)^2} \sum_{r \neq s \neq i} \hat{a}_{rs} + \frac{(q-4)}{(q-3)^3} \sum_{r \neq s \neq t \neq i} \hat{a}_{rst} +$$

$$+ \frac{(q-5)}{(q-2)^4} \sum_{r \neq s \neq t \neq v \neq i} \hat{a}_{rstv}$$

Equation (2.2) is actually a system of $\binom{q}{3}$ equations. If we write all these equations we observe that each element

$\hat{a}(1 \leqq r \leqq q)$ appears in the system $\dfrac{3\binom{q}{3}}{\binom{q}{1}} = \dfrac{(q-1)(q-2)}{2}$ times

$\hat{a}_{rs}(1 \leqq r < s \leqq q)$ " " " " $\dfrac{3\binom{q}{3}}{\binom{q}{2}} = q - 2$ times

$\hat{a}_{rst}(1 \leqq r \leqq q)$ " " " " once

If we add all these equations we get the equation

$$(A.4)\ \sum \hat{w} = \frac{(q-1)(q-2)}{6} \sum \hat{a}_r + \frac{(q-2)}{9} \sum \hat{a}_{rs} + \frac{1}{27} \sum \hat{a}_{rst}$$

Thinking the same way, from (2.3) follows the equation

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

$$(A.5)\quad \sum \hat{v} = \frac{(q-1)(q-2)(q-3)}{24}\sum \hat{a}_r + \frac{(q-2)(q-3)}{32}\sum \hat{a}_{rs} +$$

$$+ \frac{(q-3)}{64}\sum \hat{a}_{rst} + \frac{1}{256}\sum \hat{a}_{rstv}.$$

In my thesis for the Dr's degree, appendix E, p. 50, University of Thessaloniki, Greece it is derived the equation

$$(A.6)\quad \sum \hat{v}_{\bar{i}} = \frac{(q-2)(q-3)(q-4)}{24}\sum_{r\neq i} \hat{a}_r + \frac{(q-3(q-4)}{32}\sum_{r,s\neq i} \hat{a}_{rs}$$

$$+ \frac{(q-4)}{64}\sum_{r,s,t\neq i} \hat{a}_{rst} + \frac{1}{256}\sum_{r,s,t,v\neq i} \hat{a}_{rstv}.$$

Solution of the system of the equations (A.1), (A.2), (A.4), (A.5) gives us $\Sigma\hat{a}_r$, $\Sigma\hat{a}_{rs}$, $\Sigma\hat{a}_{rst}$, $\Sigma\hat{a}_{rstv}$.

Where the solution of (2.4), (A.3), (A,6) and

$$(A.7)\sum \hat{w}_{\bar{i}} = \frac{(q-2)(q-3)}{6}\sum_{r\neq i} \hat{a}_r + \frac{(q-3)}{9}\sum_{r,s\neq i} \hat{a}_{rs} + \frac{1}{27}\sum_{r,s,t\neq i} \hat{a}_{rst}$$

which follows from (2.2) gives $\sum_{r\neq i} \hat{a}_r$, $\sum_{r,s\neq i} \hat{a}_{rs}$, $\sum_{r,s,t\neq i} \hat{a}_{rst}$, $\sum_{r,s,t,v\neq i} \hat{a}_{rstv}$

Thus we have (2.6) — (2.9).

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

REFERENCES

GORMAN J. W. AND HINMAN J.E. (1962), "Simplex Lattice Designs for Multicomponent Systems". Research and development Department, American Oil Company, Whiting, Indiana, pp. 464-465.

LAMBRAKIS D. P., "Designs for Experiments with Mixtures". Thesis for the Degree of Doctor of Philosophy, University of Aberteen, 1966.

LAMBBAKIS D. P. (1968), "Experiments with Mixtures. A generalization of the Simplex - Lattice Designs", The Journal of the Royal Statistical Society, Series B (Metbological), V. 30, No. 1, pp. 123-136.

QUENOUILLE, M. H. (1959), "Experiments with Mixtures", J. R. Statist. Soc., Series B, V. 21, pp. 201-202.

SCHEFFE H. (1957), "Experiments with Mixtures", University of California, Berkeley, pp. 455-456.

SCEFFE H. (1963), "The Simplex - Centreid Design for Experients with Mixtures (Read at Methods Meeting of the Society).

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

ΠΕΡΙΛΗΨΙΣ

ΠΕΙΡΑΜΑΤΑ ΕΠΙ ΤΩΝ ΜΙΓΜΑΤΩΝ ΜΙΑ ΑΛΛΗ ΕΠΕΚΤΑΣΙΣ ΤΗΣ ΤΡΟΠΟΠΟΙΗΣΕΩΣ ΕΙΣ ΤΟ ΣΥΜΠΛΕΚΤΙΚΟΝ - ΚΕΝΤΡΙΚΟΝ ΜΟΝΤΕΛΛΟΝ

Ὑπὸ

ΕΥΑΓΓΕΛΟΥ ΚΩΝΣΤΑΝΤΕΛΟΥ

Τὸ 1966 ὁ καθηγητὴς Δ. Λαμπράκης ἐτροποποίησεν τὴν μέθοδον τῆς κατασκευῆς τοῦ μοντέλου Sceffé τοῦ ὁποίου τὰ κύρια χαρακτηριστικὰ εἶναι τὸ κεντρικὸν πολυώνυμον ὡς συναρτήσεως παλινδρομήσεως καὶ τὸ simplex εἰς τὸ ὁποῖον ὑπόκεινται αἱ μεταβληταί.

Εἰς τὸ μοντέλον Scheffé, διὰ τὸν προσδιορισμὸν τῶν ἐκτιμήσεων τῶν συντελεστῶν τοῦ πολυωνύμου ἐχρησιμοποιήθησαν τὰ καλούμενα καθαρὰ μίγματα (ἑκάστη τῶν γνωστῶν οὐσιῶν αἱ ὁποῖαι ὑπεισέρχονται διὰ νὰ ἀποτελέσουν τὸ μίγμα). Ὁ Λαμπράκης ἀντικατέστησε τὰ καθαρὰ μίγματα διὰ μιγμάτων τῶν q - 1 οὐσιῶν (q ὁ ἀριθμὸς τῶν χρησιμοποιουμένων οὐσιῶν) καὶ τὰ μίγματα τῶν δύο οὐσιῶν διὰ μιγμάτων τῶν q - 2. Ἐπέτυχεν ἀποτελέσματα διὰ τὴν περίπτωσιν ὅπου ἡ συνάρτησις παλινδρομήσεως εἶναι τὸ κεντρικὸν πολυώνυμον 3ου βαθμοῦ.

Εἰς τὴν παροῦσαν ἐργασίαν τὰ προαναφερθέντα ἀποτελέσματα ἐπεκτείνονται εἰς τὴν περίπτωσιν ὅπου ἡ συνάρτησις παλινδρομήσεως εἶναι πολυώνυμον 4ου βαθμοῦ.

Τὸ κύριον μέρος τῆς ἐργασίας αὐτῆς εἶναι ὁ σχηματισμὸς τοῦ συστήματος τῶν κανονικῶν ἐξισώσεων καὶ ἡ ἐπίλυσίς του.

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.