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An Application of Mixture Design: A Case Study on Blending of Olive Oils by Design-Expert

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Abstract: For quality control, raw material, semi-finished, and finished product analysis in chemistry, biochemistry, food, and environmental sciences, well-designed experimental strategies are needed to perform all experimental studies at minimum cost and under optimum conditions. The steps in the experimental strategies essentially constitute the experimental procedure followed, and here the aim is to select a model for the experimental procedure, to determine the number of experiments and experimental factor limitations for each run, to identify the correlation between experimental results and factors, and to optimise the experimental factors. The response surface methodology as an experimental design method also reduces the number of experiments required for multi-factor trials for optimisation. Mixture design, a special type of response surface function, is a very effective method for determining the proportions of components or variables in a mixture. A three-component mixture is represented by a triangle, *which* is a two-dimensional cross-section of a three-dimensional space represented by a cube representing the region *where* the proportions of the three components are added up to 100%. The points within this triangle or blend area represent possible blends, *where*: three corners correspond to single components, points along the edges to binary mixtures, the dots in the triangle to triad mixtures, and the centre of the triangle to an equal mix of all three components. Several common designs can be considered as ways to determine the logical number and arrangement of points in a simplex, the most well-known being the Simplex Centroid and Simplex Lattice patterns. This study focused on an experimental design application for fourteen blends of olive oils from four cultivars A–D mixed in the design presented together with a taste panel score for each blend and statistical evaluation of the results for mixture design applications. The higher the score is the better the taste of the olive oil. Here, the mixture design chosen for optimising blending ratios was Simplex-Lattice, and DesignExpert 7.3 software was used for statistical analysis. Comparing of calculated correlation coefficients of the response surface function and its parameters, and function constants, it could be understood that as the correlation coefficient would be 0.21 for used linear terms only, adding quadratic terms into the function increases it to 0.92 drastically.

Keywords: Olive oil; blending; mixture design; response surface

1. Introduction

Today, studies in many fields such as chemistry, biochemistry, food, and environmental sciences are carried out experimentally in laboratories for quality control, raw material, and product analysis required for semi-finished and finished products. Well-designed experimental strategies are needed to perform these experimental studies at minimum cost and in optimum conditions. This is only possible

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with experimental design, which is based on applying statistical methods to experimental process factors. The steps in the experimental strategies essentially constitute the experimental procedure followed, and here the aim is to select a model for the experimental procedure, to determine the number of experiments and experimental factor limitations for each run, to identify the correlation between experimental results and factors, and to optimise the experimental factors. The response surface methodology also reduces the number of experimental trials required for multi-factor experiments. Therefore, the function for the response surface can be expressed in some linear or nonlinear models. Mixture design, a special type of response surface function, is a very effective method of determining the proportions of variables or components of a mixture. It is frequently encountered in industries like paint, food, glass, ceramic, frits, polymers, etc. In chemistry, a mixture refers to any combination of the substances *that* make up it, *while* statisticians define it as a factor set *whose* sum is constant. For example, ingredients in a solvent system in HPLC or a product such as food or paint are considered a mixture, and each ingredient can be specified as a part, and the total varies from 1% to 100%. The response may be the separation constant for a foodstuff test, *while* the conductivity may be the response of a molten salt mixture or oil blending.

Most chemists represent their experimental conditions in mixture space, *corresponding* to all possible allowed proportions of components that add up to 100 %. For example, a three-component mixture can be represented by a triangle (Figure 1), *which* is a two-dimensional cross-section of a three-dimensional space, represented by a cube, showing the allowed region *in which* the proportions of the three components add up to 100 %. Points within this triangle or mixture space represent possible mixtures or blends:

- the three corners correspond to single components.
- points along the edges correspond to binary mixtures.
- points inside the triangle correspond to ternary mixtures.
- the centre of the triangle corresponds to an equal mixture of all three components.
- all points within the triangle are physically allowable blends.

As the number of components increases, so does the dimensionality of the mixture space. Physically meaningful mixtures can be represented as points in this space:

- for two components the mixture space is simply a straight line.
- for three components it is a triangle.
- for four components it is a tetrahedron.

Each object is pictured in Figure 2 and is called a *simplex* – the simplest possible object in the space of a given dimensionality: the dimensionality is one less than the number of factors or components in a mixture. Hence, a tetrahedron (three dimensions) represents a four-component mixture. A number of common designs can be envisaged as ways of determining a sensible number and arrangement of points within the simplex. Most known are Simplex Centroid and Simplex Lattice models.

Simplex centroid designs are probably the most widespread. For k factors, they involve performing a $2k-1$ experiment, i.e., for four factors, 15 experiments are performed. It involves all possible combinations of the proportions 1, 1/2 to $1/k$ and is best illustrated by an example. A three-factor design consists of

- three single-factor combinations.
- three binary combinations.
- one ternary combination.

Just as previously, a model and design matrix can be obtained. However, the nature of the model for the response surface requires some detailed thought. Consider trying to estimate a model of the form

$$y = c_0 + c_1x_1 + c_2x_2 + c_3x_3 + c_{11}x_1^2 + c_{22}x_2^2 + c_{33}x_3^2 + c_{12}x_1x_2 + c_{13}x_1x_3 + c_{23}x_2x_3 \qquad [1]$$

Calculation of the coefficients in a mathematical model based on another minimisation process, the sum of the differences between the responses from the model and their experimental values, called the least squares method. The written optimisation function for the response surface is as follows [1,2 and 3].

$$J = \sqrt{\sum_{i=1}^{n} d_i^{\,2}} = \sqrt{\sum_{i=1} (y_{i-\text{experim}} - y_{i-calcul})2} \rightarrow Min \qquad [2]$$

One of the application areas of mixture designs is the blending of oil olives. Olive oil is extracted from the olive tree *Olea europaea* L. fruits and consumed directly. An 'olive oil blend' most commonly refers to a blend of canola, soybean, or various types of olive oil mixed with olive oil in a specific ratio. These blends can be made up of any type of oil mixed with any particular olive oil grade [4].

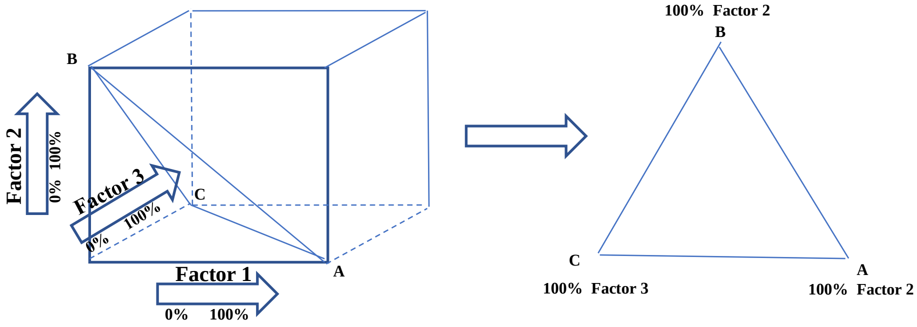


Figure 1. Three-component mixture space

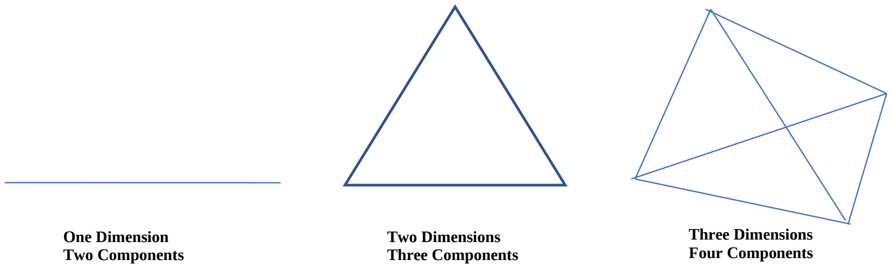


Figure 2. Simplex in one, two, and three dimensions

This study focused on an experimental design application for fourteen blends of olive oils from four cultivars A–D mixed in the design presented together with a taste panel score for each blend in Table 1 and statistical evaluation of the results for mixture design applications. The higher the score, the better the taste of the olive oil. Here, the mixture design chosen for optimising blending ratios was Simplex-Lattice, and Design Expert 700 software was used for statistical analysis [1 and 5].

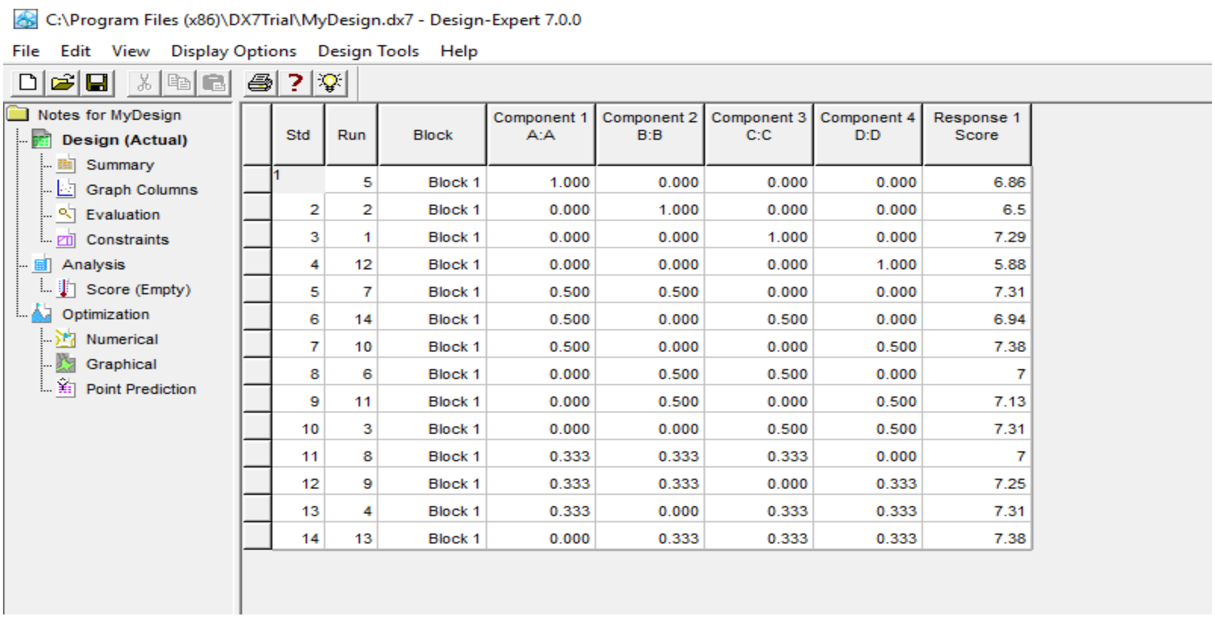
2. Materials and Methods

The first step of the design is to code the factors defined as mixing ratios, and it is always important to choose reasonable physical values for each factor. The central point of each factor is assumed to be between 0 and 1, and the design is asymmetrical around it. In the case of the mixture Simplex-Lattice design model, the four factors are the mixing ratios of the olive oil cultivars, namely (1) A, (2) B, (3) C, and (4) D, and the response of the design is the test score of the blended olive oil samples depending on the mixing ratio of each base olive oil samples in the range of 5-10. Here, the total number of experiments (N=14). Design Expert 700 software menu steps were followed to optimise the mixing parameters of olive oil blending Simplex-Lattice design [5].

The results of the experiments are given in Figure 3. In the experiments, the value of 1 corresponds to the upper limit and 0 to the lower limit, supported by pseudo-components [1]. After the model selection, Figure 4 defined the process factor limits. First, the process factors with responses were measured experimentally, and all parameters were transformed into design form by the software, and then statistical evaluation was carried out.

Table 1. Test panel score for each blend

A	B	C	D	Score
1	0	0	0	6.86
0	1	0	0	6.50
0	0	1	0	7.29
0	0	0	1	5.88
0.5	0.5	0	0	7.31
0.5	0	0.5	0	6.94
0.5	0	0	0.5	7.38
0	0.5	0.5	0	7.00
0	0.5	0	0.5	7.13
0	0	0.5	0.5	7.31
0.333	0.333	0.333	0	7i56
0.333	0.333	0	0.333	7.25
0.333	0	0.333	0.333	7.31
0	0.333	0.333	0.333	7.38



Std	Run	Block	Component 1 A:A	Component 2 B:B	Component 3 C:C	Component 4 D:D	Response 1 Score
1	5	Block 1	1.000	0.000	0.000	0.000	6.86
2	2	Block 1	0.000	1.000	0.000	0.000	6.5
3	1	Block 1	0.000	0.000	1.000	0.000	7.29
4	12	Block 1	0.000	0.000	0.000	1.000	5.88
5	7	Block 1	0.500	0.500	0.000	0.000	7.31
6	14	Block 1	0.500	0.000	0.500	0.000	6.94
7	10	Block 1	0.500	0.000	0.000	0.500	7.38
8	6	Block 1	0.000	0.500	0.500	0.000	7
9	11	Block 1	0.000	0.500	0.000	0.500	7.13
10	3	Block 1	0.000	0.000	0.500	0.500	7.31
11	8	Block 1	0.333	0.333	0.333	0.000	7
12	9	Block 1	0.333	0.333	0.000	0.333	7.25
13	4	Block 1	0.333	0.000	0.333	0.333	7.31
14	13	Block 1	0.000	0.333	0.333	0.333	7.38

Figure 3. Design Expert 7.0.0 Mixture Design – Simplex Lattice design page interface menus, the introduction of all experimental data

3. Results and Discussion

Calculated correlation coefficients of the response surface function and its parameters, and function constants, one by one were given in Table 2. Examining Table 2, it could be understood *that* as the correlation coefficient would be 0.21 for used linear terms only, adding quadratic terms into the function increases to 0.92 drastically. Simulation of response surface function with linear and quadratic terms for optimisation was given in Figure 5a and Figure 5b, respectively.

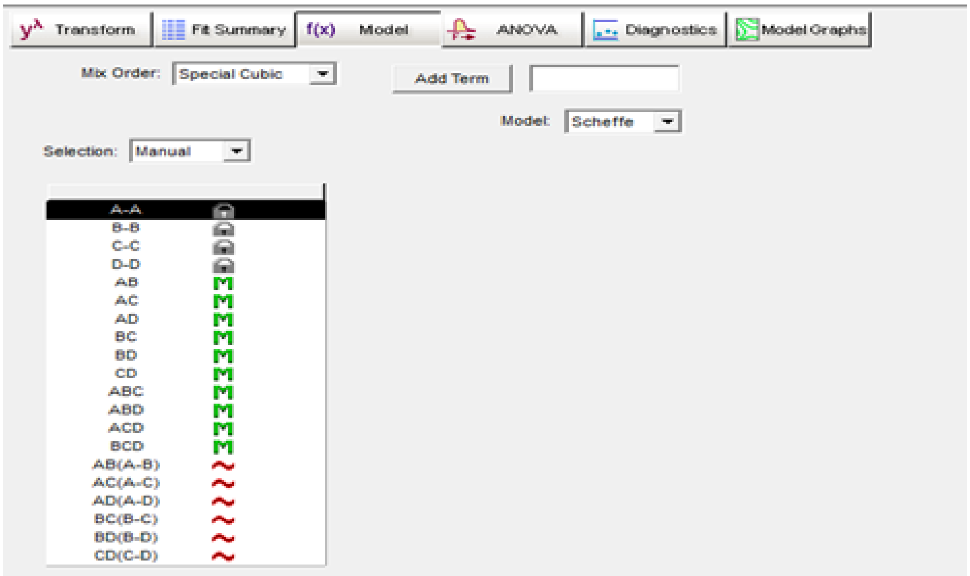


Figure 4. Design Expert 7.0.0 Mixture Design – Simplex Lattice design page interface menus, model selection for evaluation of all experimental data

Table 2. Model Summary Statistics of DesignExpert 7.3

Source	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**	
Linear	0.44	0.2141	-0.0217	-1.4707	6.17	
Quadratic	0.22	0.9228	0.7490	-1.5166	6.28	Suggest

Final Equation in Terms of Real/Actual Components:

$$R1 = +6.86 * A + 6.49 * B + 7.26 * C + 5.91 * D + 2.65 * A * B - 0.078 * A * C + 3.48 * A * D + 1.04 * B * C + 3.36 * B * D + 2.83 * C * D$$

4. Conclusion

Several common designs can be considered as ways to determine the logical number and arrangement of points in a simplex, the most well-known being the Simplex Centroid and Simplex Lattice patterns. This study focused on an experimental design application for fourteen blends of olive oils from four cultivars A–D mixed in the design presented together with a taste panel score for each blend and statistical evaluation of the results for mixture design applications. Naturally, the higher the score, the better the olive oil taste. Here, the mixture design chosen for optimising blending ratios was Simplex-Lattice, and Design Expert 700 software was used for statistical analysis.

In the case of the mixture Simplex-Lattice design model, the four factors are the mixing ratios of the olive oil cultivars, namely (1) A, (2) B, (3) C, and (4) D, and the response of the design is the test score of the blended olive oil samples depending on the mixing ratio of each base olive oil samples in the range of 5-10. Here, the total number of experiments (N=14). DesignExpert 7.3 software menu steps were followed to optimise mixing parameters of olive oil blending Simplex-Lattice design. In the experiments, the value of 1 corresponds to the upper limit and 0 to the lower limit, supported by pseudo-components.

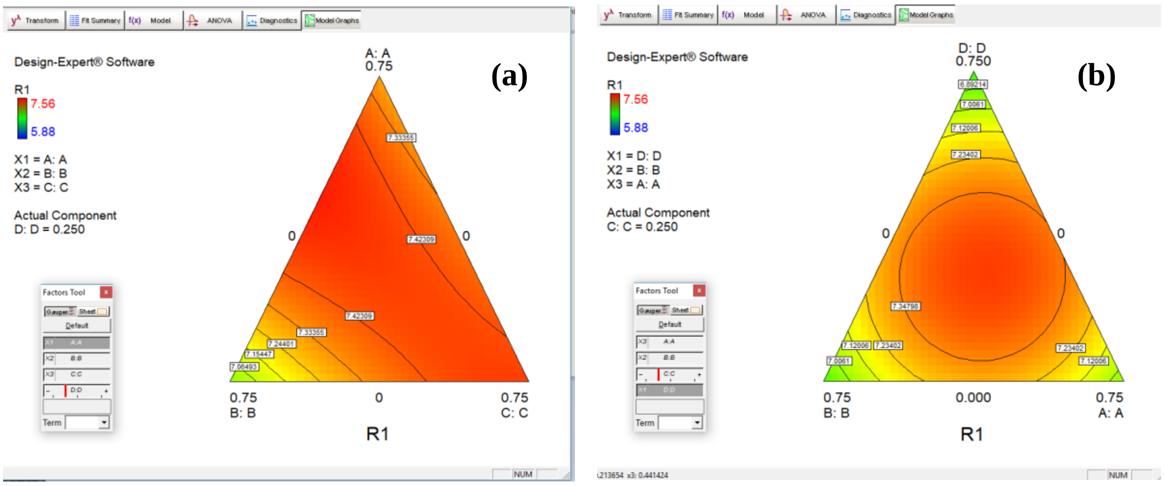


Figure 5. (a) Simulation of response surface function with quadratic terms (Factor A, B, and C) **(b)** Simulation of response surface function with quadratic terms (Factor A, B, and D)

After the model selection, the process factor limits were defined, the process factors with responses were measured experimentally, and all parameters were transformed into design form by the software. Then, a statistical evaluation was carried out. Comparing of calculated correlation coefficients of the response surface function and its parameters, and function constants, it could be understood that as the correlation coefficient would be 0.21 for used linear terms only, adding quadratic terms into the function increases it to 0.92 drastically,

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