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Making use of mixture design to optimize olive oil – a case study excerpted from *Formulation Simplified*¹

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Olive oil, an important commodity of the Mediterranean region and a main ingredient of their world-renowned diet (see sidebar), must meet stringent European guidelines to achieve the coveted status of “extra virgin.” Oils made from single cultivars (a particular variety of the olive tree) will at times fall into the lower “virgin” category due to seasonal variation. Then it becomes advantageous to blend in one or more superior oils based on a mixture design for optimal formulation. For example, a team of formulators² experimented on four Croatian olive oils – Buza, Bianchera (pronounced “be an kay ra”), Leccino (pronounced “la chee no”) and Karbonaca – to achieve an overall sensory rating of at least 6.5 on a 9-point hedonic scale, thus easily exceeding the cut off for “extra virgin” (5.5 considered to be “virgin”). The ratings were done by ten assessors trained on fundamental tastes (sweet, salt, sour and bitter) and defects of virgin olive oils, such as rancidity.



Figure 1: Mediterranean olive oil

We’ve adapted the original study a bit to simplify it and make it more educational, while capturing the essence of how these formulators made use of mixture design and what they discovered as a result.

| # | Point Type | A: Buza | B: Bianchera | C: Leccino | D: Karbonaca | Sensory Rating |
|----|--------------|------------|-----------------|---------------|-----------------|-------------------|
| 1 | Vertex | 1 | 0 | 0 | 0 | 6.98 |
| 2 | " | 1 | 0 | 0 | 0 | 6.84 |
| 3 | Vertex | 0 | 1 | 0 | 0 | 6.49 |
| 4 | " | 0 | 1 | 0 | 0 | 6.45 |
| 5 | Vertex | 0 | 0 | 1 | 0 | 7.25 |
| 6 | " | 0 | 0 | 1 | 0 | 7.30 |
| 7 | Vertex | 0 | 0 | 0 | 1 | 5.88 |
| 8 | " | 0 | 0 | 0 | 1 | 5.95 |
| 9 | Third Edge | 0.667 | 0.333 | 0 | 0 | 7.38 |
| 10 | Third Edge | 0.333 | 0.667 | 0 | 0 | 7.12 |
| 11 | Third Edge | 0.667 | 0 | 0.333 | 0 | 6.87 |
| 12 | Third Edge | 0 | 0.667 | 0.333 | 0 | 6.84 |
| 13 | Third Edge | 0.333 | 0 | 0.667 | 0 | 6.95 |
| 14 | Third Edge | 0 | 0.333 | 0.667 | 0 | 7.17 |
| 15 | Third Edge | 0.667 | 0 | 0 | 0.333 | 7.36 |
| 16 | Third Edge | 0 | 0.667 | 0 | 0.333 | 7.14 |
| 17 | Third Edge | 0 | 0 | 0.667 | 0.333 | 7.50 |
| 18 | Third Edge | 0.333 | 0 | 0 | 0.667 | 7.16 |
| 19 | Third Edge | 0 | 0.333 | 0 | 0.667 | 6.95 |
| 20 | Third Edge | 0 | 0 | 0.333 | 0.667 | 7.00 |
| 21 | Triple Blend | 0.333 | 0.333 | 0.333 | 0 | 7.56 |
| 22 | Triple Blend | 0.333 | 0.333 | 0 | 0.333 | 7.53 |
| 23 | Triple Blend | 0.333 | 0 | 0.333 | 0.333 | 7.29 |
| 24 | Triple Blend | 0 | 0.333 | 0.333 | 0.333 | 7.28 |
| 25 | Axial CB | 0.625 | 0.125 | 0.125 | 0.125 | 7.41 |
| 26 | Axial CB | 0.125 | 0.625 | 0.125 | 0.125 | 7.37 |
| 27 | Axial CB | 0.125 | 0.125 | 0.625 | 0.125 | 7.50 |
| 28 | Axial CB | 0.125 | 0.125 | 0.125 | 0.625 | 7.19 |
| 29 | Centroid | 0.25 | 0.25 | 0.25 | 0.25 | 7.58 |
| 30 | " | 0.25 | 0.25 | 0.25 | 0.25 | 7.55 |

Table 1: ASL design for blending four olive oils and their sensory results

The assessors can discern very tiny differences in sensory attributes that may depend on subtle non-linear blending of two or more oils. Therefore, the four component ($q = 4$) simplex lattice is set up to the third degree ($m = 3$). That produces 20 unique blends. To augment this lattice, the formulators add 4 axial check blends and the overall centroid. They then specify that the four vertices (chosen for their high leverage) and centroid be replicated (for added pure error measure) at random intervals. (Always randomize!) Assume that the formulators use a 1 liter blender to mix the oils – 30 blends in total after the augmentation. This ASL (augmented simplex lattice) design and the end results for overall sensory ratings are shown in Table 1. (Note that, for

the sake of simplicity, the one-third and two-third levels are rounded to 0.333 and 0.667; respectively – thus adding to the total of 1.)

The chosen model is a reduced special cubic:

$$\begin{aligned} \text{Sensory Rating} = & 6.91 A + 6.47 B + 7.29 C + 5.93 D \\ & + 2.51 AB - 0.91 AC + 3.70 AD + 0.54 BC + 3.75 BD + 2.78 CD + 11.65 ABC \end{aligned}$$

The presence of the ABC non-linear blending term supports the choice of a third-degree lattice design. The other three special-cubic terms (ABD, ACD, BCD) were insignificant ($p > 0.1$) so we chose to remove them from the final model. Rather than laboriously dissecting the model by its remaining terms, let's focus on the response surface graphics: The pictures will tell the story.

Unfortunately, now that we've gone to the third dimension the imaging gets trickier – only three out of the four components can be depicted on a contour plot, for example. This complication provides the perfect opportunity to present the “trace” plot – a way to view the relative effects of any number of components. A trace plot for the olive-oil mixture experiment is shown in Figure 2.

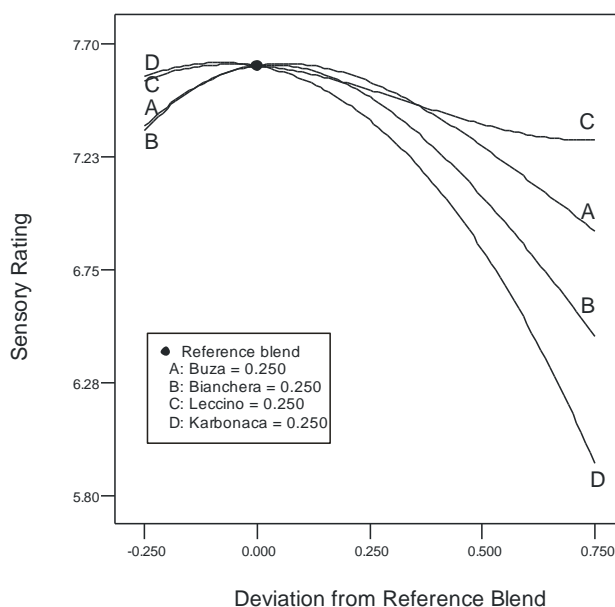


Figure 2: Trace plot for olive-oil mixture experiment

The traces are drawn from the overall centroid – all components at equal volume within the 1-liter vessel. This is called the “reference blend.” Each component alone is then mathematically varied while holding all others in constant proportion. This reveals that the sensory evaluation falls off dramatically as the Karbonaca oil (D) is increased relative to the three alternatives.

To give you a better feel for how the trace plot is produced, consider the simpler case of only three components. Figure 3 shows the paths of the three traces.

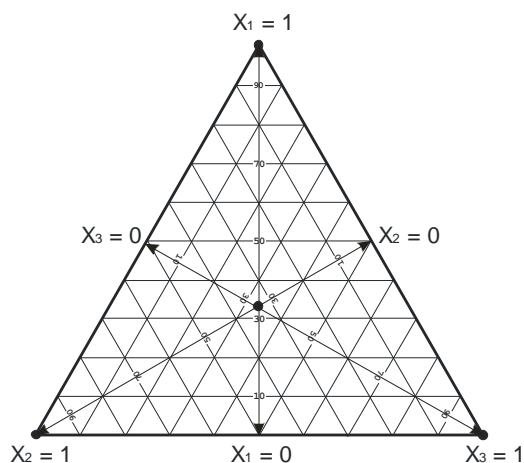
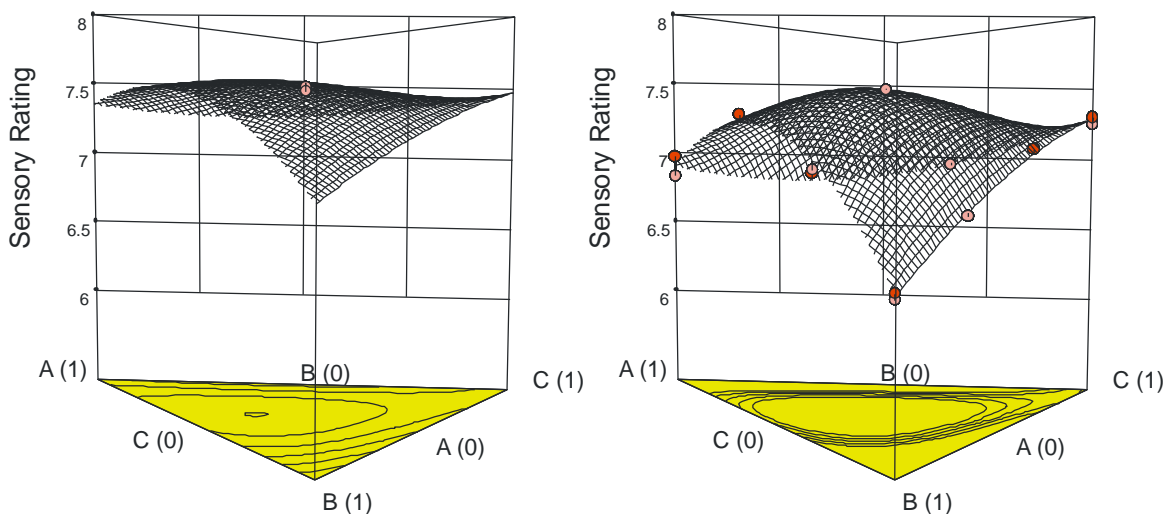


Figure 3: Traces for three components only

The trace for x_1 starts at the overall centroid where it amounts to one-third of the three-component blend. The other two components are also at one-third, thus their ratio is one-to-one. Tracing x_1 from the centroid down to the base of the ternary diagram reduces the amount of this individual component to zero. At this point the amounts of the other two components become one half each – thus their ratio remains one-to-one. In fact, if you pick any point along any of the three traces, the other two components remain at constant proportions! Try working this out for yourself – it will be good practice for reading off coordinates on the ternary diagram.

Now that we've been provided with clues on the non-linear blending behavior of the four olive oils, it seems sensible to study the response surfaces of the three good components 'sliced' at varying levels of the inferior fourth component. For example, Figures 4a and 4b show the sensory results at the overall centroid (all components, including D, at 0.25 concentration) versus no Karbonaca oil ($D = 0$). If anything, it's the Bianchera (B) oil that creates the greatest effect on taste – very noticeably on these slices with D held fixed at two specific levels (0 and 0.25).



Figures 4a and 4b: Sensory results at the overall centroid versus no Karbonaca oil ($D = 0$)

These response surface graphs are very illuminating! It appears as if the complete four-part blend at the centroid, shown on the left (Figure 4a), will be most robust to variations in olive oil

concentrations and deliver a superior sensory rating for the most part. A more comprehensive computer-aided search of the entire tetrahedral formulation space produced the optimal blend (best tasting) depicted in Figure 5:

- A. 0.333 Buza
- B. 0.299 Bianchera
- C. 0.189 Leccino
- D. 0.179 Karbonaca

This is predicted to produce a sensory rating of 7.63 – higher than any of the actual test results. However, any such prediction must be subject to verification.

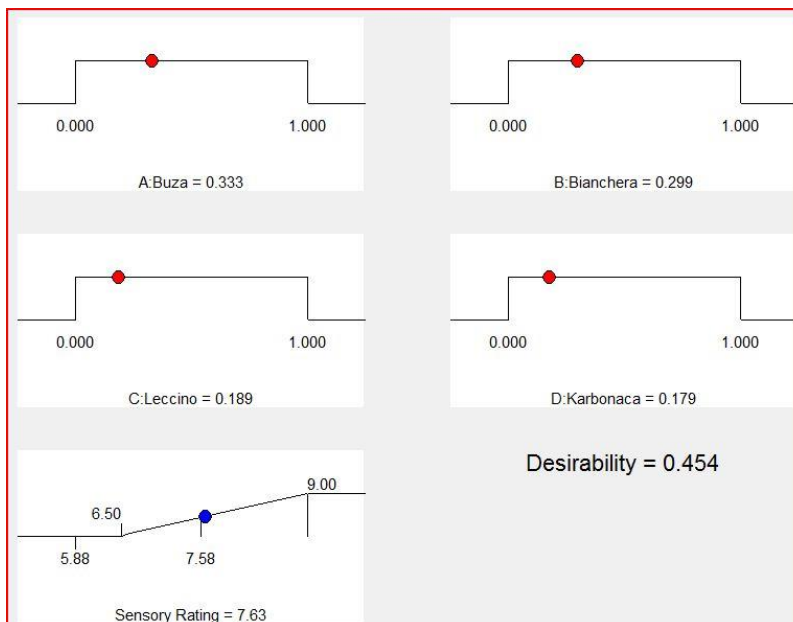


Figure 5: Most desirable blend via computer-aided numerical search

The upward ramp for the sensory response shows how a rating below 6.5 will be completely undesirable, whereas a rating of 9 represents the peak of desirability (prima!). The predicted optimum falls 0.454 up the scale from zero to one on desirability. This may be the best the blenders can do with these particular varieties. A sensory outcome of 9 on the hedonic scale remains in the province of the gods who enjoy only the best of the best.

Figure 6 flags the attainable optimal blend of these four olive oils. It displays the prediction interval (7.51 to 7.76) based on 95 percent confidence. Ideally the verification blend will be rated by the sensory panel within this range. A result outside of the prediction interval would cast doubt on the validity of the model.

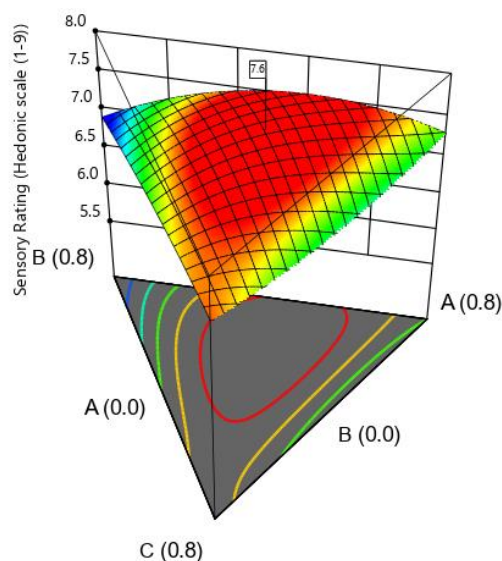


Figure 6: Most desirable blend flagged on contour plot (D sliced at 0.179)

Remember that these plots are derived from the Scheffé-polynomial predictive-model fitted to the actual experimental data and validated statistically. However, only by producing a confirmatory blend and subjecting it to sensory evaluation will this be verified for all practical purposes.

The optimum sensory comes from a blend that goes light on the Karbonaca oil. But what if this inferior oil can be bought very cheaply? Then a blend with it being maximized could be made at a sensory just good enough to pass the panel at Extra Virgin level. This might be worth a try!

By employing mixture design these sophisticated olive oil formulators obtained “a knowledge of the whole experimental dominion with the advantage to be able to find various mixtures bearing the same qualities.” Furthermore, “in this way, despite the presence of external limits such as olive oil availability or other economic aspects, a variety of optimal blends can be selected according to market preference.”

– Mark, Pat & Martin

References

1. Anderson, M. J., Whitcomb, P. J. and M. A. Bezener. *Formulation Simplified: Finding the Sweet Spot through Design and Analysis of Experiments with Mixtures*, 2018, Chapter 3, pp. 62-70. New York, NY. Productivity Press.
2. Vojnovic, D., et al. “Experimental Mixture Design to Ameliorate the Sensory Quality Evaluation of Extra Virgin Oils. *Chemometrics and Intelligent Laboratory Systems*, 1995, Vol. 27, pp. 205-210.