Chemometrics

Application Note

Analysis of Oil Mixtures in Margarine

Abstract

The production of margarine involves the precise mixing of fats from a variety of sources. This combination of ingredients is critical for a variety of reasons. Foremost is the need to achieve a consistent product but clearly cost of ingredients plays a critical role. Another dimension to the control equation is the relative proportions of saturated, unsaturated and trans fats which drive health concerns and truth in labeling laws. Added to this environment are source changes such as batch to batch variation in the ingredients, changes in suppliers and the fact that product consistency needs to span many factories.

In the case described in this note, margarine is produced in five factories in the United States and dozens more spread throughout the world. Four ingredient fat mixtures are combined in the manufacturing process and tight tolerances are in effect including comparing one factory's output with another. This note outlines the steps required to evaluate the quality of the final product and determine the relative proportion of the ingredient oils. If a mixing problem is detected, the cause can be simultaneously identified. The products used are LineUp™ to eliminate the retention time variation and Pirouette® for the product quality evaluation and unmixing.

The samples were processed by melting the margarine, saponifying and esterifying the oil fraction. Figure 1 shows the resulting chromatograms for each of four ingredient oils.

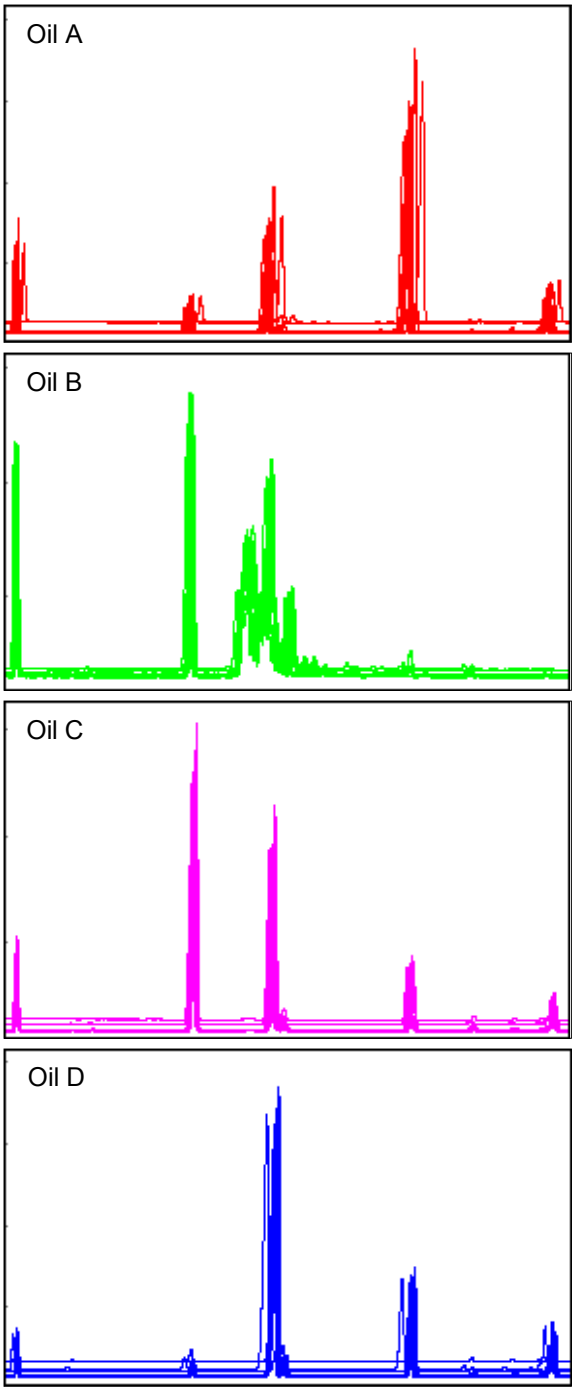

Figure 1: Replicate chromatograms for each of the four ingredient oils prior to alignment

Oils from different sources show significant differences in composition. There is also variability among the samples within any single ingredient type due to retention time variation and baseline offset in the chromatographic run.

We can correct for the retention time variation using the LineUp alignment software. The elution profile is adjusted to conform to a standard run automatically as part of the GC post-run processing. Results of the alignment for the tallest peak in Oil D are shown in Figure 2.

Even though the peaks are not symmetrical, the peaks can be adjusted to more-closely match a standard oil run. The LineUp algorithm does not match the apex of peaks, but rather fits the overall peak shape as closely as possible. In the case of symmetrical peaks, the retention apices will coincide.

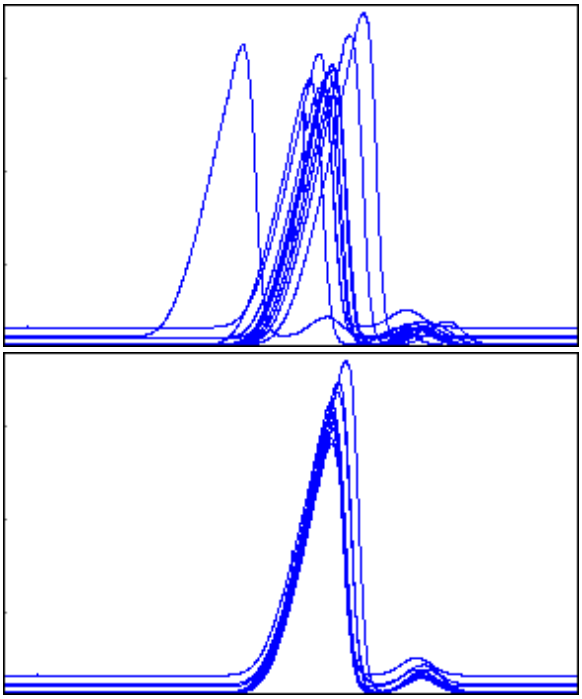

Figure 2: Zooming in on the tallest peak in ingredient D before (top) and after (bottom) alignment

Once the chromatograms are processed to remove retention time instability, the data can be used to determine the oil concentrations in the factory mixtures.

First a principal component analysis (PCA) was run to insure that the ingredient oils are distinguishable from one another and that the intra-group variability is within acceptable limits. The PCA results are in Figure 3.

The ingredient oils are distinct from one-another and describe a tetrahedron in the scores plot. Oil C (the green points at the far left in the plot) are very consistent, but the other oils show some variability of relative abundance from run to run.

Because of the variability in the data, we chose the median oils of each of the four ingredient sets and used those samples to represent the oil groups. The corresponding peak height table of these oils was then processed using alternating least squares (ALS) in Pirouette to build a predictive model.

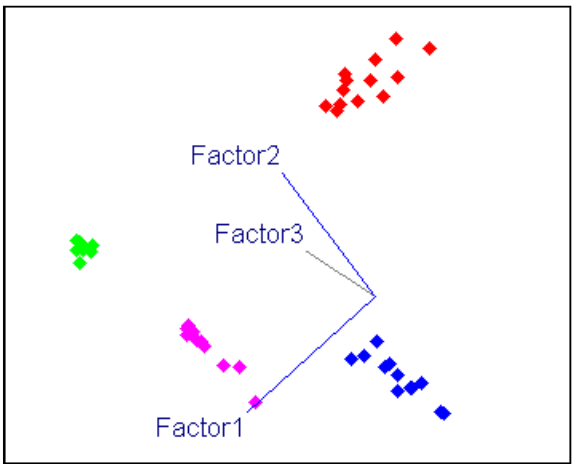

Figure 3: PCA scores plot for the aligned ingredient oils

The oil chromatograms from each of the two factories are shown in Figure 4.

Twelve samples from Factory 1 and eight samples from Factory 2 are in this display and were processed using ALS. The resulting estimates of the concentrations are listed in the following table along with the target composition of oils for both factories.

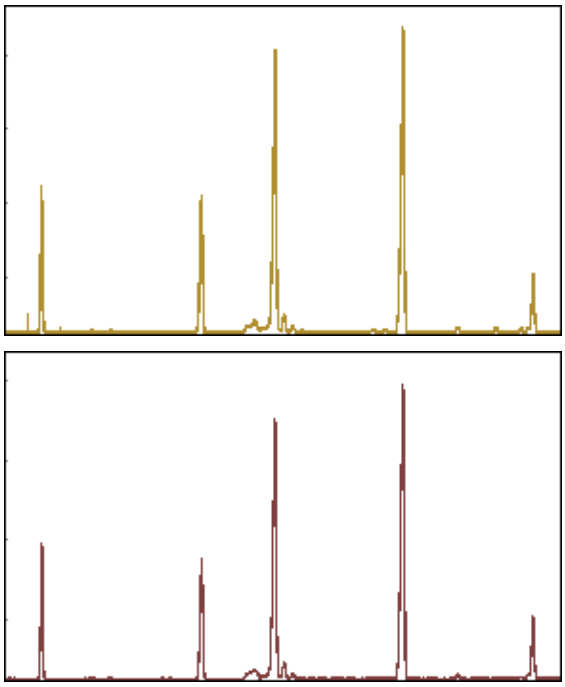

Figure 4: Aligned and normalized chromatograms overlaying 12 samples from Factory 1 (top) and 8 from Factory 2 (bottom)

For the samples tested here, the composition determined by Pirouette matches the expectation. There is some variability in the data that is within the operating norm. It appears that Factory 2 uses more of ingredient oil A on average than would be expected in Factory 1. Factory 2's output is also more consistent from batch to batch within the confines of these data.

We can project the factory data back onto the PCA scores plot of the ingredients. This projection is shown in Figure 5, which can be thought of as a three-dimensional tetrahedral concentration grid. The factory samples fall near the top of the view, nearest the Ingredient A samples (in red) because over 50% of the product is composed of Oil A.

Table 1: Result of Pirouette unmixing of the margarine samples

Sample	Ingredient A	Ingredient B	Ingredient C	Ingredient D
Target Composition	53	10	17	20
Factory 1-1	52.31	10.13	16.88	20.67
Factory 1-2	52.76	11.16	16.36	19.64
Factory 1-3	52.07	11.28	16.41	19.97
Factory 1-4	51.64	10.17	16.62	21.42
Factory 1-5	52.66	9.90	17.03	20.22
Factory 1-6	53.11	9.99	17.02	19.73
Factory 1-7	52.49	11.31	16.07	19.86
Factory 1-8	53.44	9.80	17.24	19.40
Factory 1-9	58.26	9.92	15.23	16.82
Factory 1-10	53.06	8.90	16.57	20.66
Factory 1-11	54.67	10.52	15.47	19.74
Factory 1-12	56.09	11.28	14.48	18.37
Factory 1-13	55.02	10.22	15.66	19.46
Factory 2-1	56.59	9.75	15.61	18.16
Factory 2-2	56.82	9.52	15.78	17.91
Factory 2-3	56.99	9.54	15.66	17.90
Factory 2-4	56.40	9.65	15.76	18.28
Factory 2-5	57.35	8.99	16.77	16.75
Factory 2-6	58.02	9.43	16.35	16.08
Factory 2-7	58.43	9.05	16.05	16.35
Factory 2-8	57.94	9.07	15.97	17.12

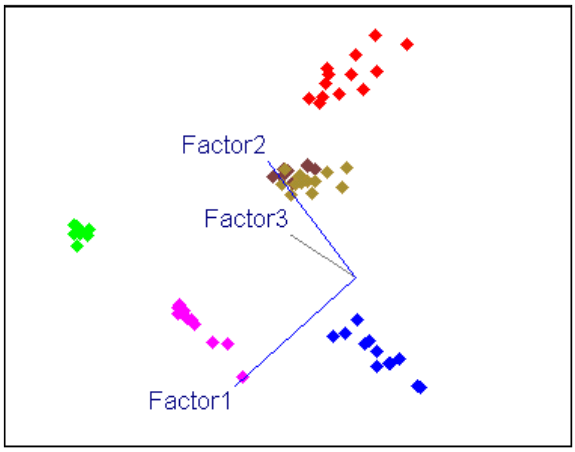

Figure 5: PCA scores including the factory samples

Other applications of benefit to the producer derive from these results. For example,

- Future factory margarine samples could be compared to the current collection of samples to test for product consistency. Samples that fall outside of an expected confidence region could be flagged for further evaluation.
- Similarly, ingredient oils can be tested on delivery to insure they conform to an acceptable composition based on a metric that simultaneously accounts for all of the compounds present. Alternatively, this analysis could be required of the supplier; the factory would know if the ingredient were acceptable prior to receiving goods.
- If any of the supplied ingredients change in relative composition, the ALS mixture analysis routine can identify the new mixing proportions required to keep the same fat distribution in the product margarine.
- If a competitor is known to blend product from a similar set of source oils, the ALS model could be used to reveal that product's composition.