

Characterizing Products from a Refinery by GC and Principal Components Analysis

L. Scott Ramos and Brian Rohrback
Infometrix, Inc., Bothell, WA, USA



Spectroscopy

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Abstract

In a refinery, there can be no waste; everything that comes into the facility has to be made into a product. Some products such as gasoline go directly to the consumer, while others are prepared as intermediates for other product blends. Of course, quality control of these products is critical. Gas chromatography is one of the traditional tools utilized to evaluate product composition. This case study shows how performing multivariate analysis on chromatographic profiles can be a reliable method for product characterization.

Methods

Samples from three product streams were analyzed using gas chromatography. These included five replicate analyses of each of five different samples of alkylate, crude naphtha, and reformate product.

Retention time variability is known to influence the outcome of multivariate analysis; therefore, the chromatograms were aligned using LineUp™ (Infometrix, Inc.) prior to subsequent analysis. A KnowItAll® database was created from the 75 aligned chromatograms. During data import, the chromatograms were filtered to 20% of the original data density resulting in profiles that contained 10,948 data points each.

The entire chromatographic profiles were subjected to principal component analysis (PCA) using the AnalyzeIt™ MVP utility in the KnowItAll Informatics System. The data were first pre-treated by normalization to minimize the effect of sample size, then pre-processed by mean-centering. Because these were neat samples, no solvent peak was present, so it was not necessary to remove the solvent region from the analysis.

Results

PCA scores are shown in Figure 1, color coded by product type. As expected, the replicate alkylate and naphtha samples cluster together in cohesive groups because the profiles for each product are very similar.

However, the reformate samples (in blue) did not cluster into a single group, rather they were grouped into several clusters. It appears from the plot that one group of reformates may be

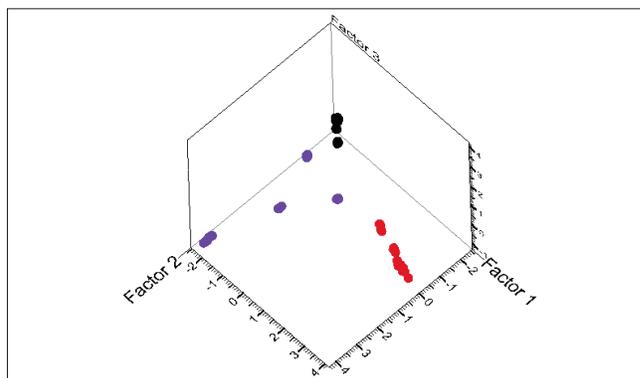


Fig. 1. PCA scores of refinery products • = alkylates, • = naphthas, • = reformates).

more closely related to the alkylates and another to the naphthas. By selecting points in the scores plot, the corresponding profiles are overlaid in a separate plot window pane. Accordingly, one each of the reformates and naphthas samples were selected, and their chromatograms exhibited some similarity, but many peaks are not in common.

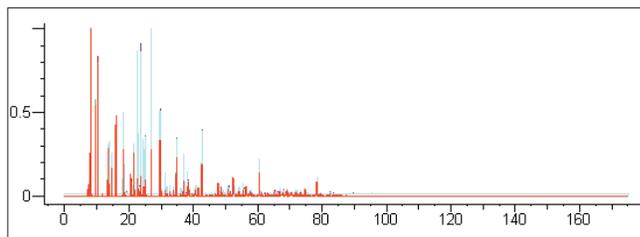


Fig. 2. Overlaid chromatographic profiles of a naphtha and a reformate sample chromatogram.

On the other hand, profiles of the neighboring subgroup of reformat samples do not resemble those of the alkylates, as shown in Figure 3.

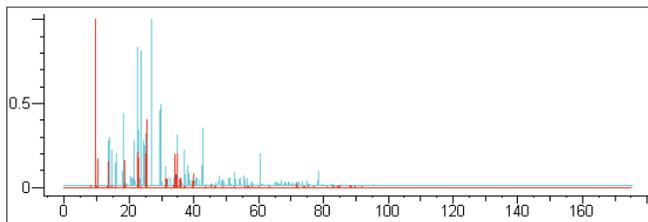


Fig. 3. Overlaid chromatographic profiles of an alkylate and a reformat sample chromatogram.

The question to ask is: what, then, are the materials in the group designated as reformates and how are they different? The 25 samples in the five reformat subgroups were highlighted, and transferred to KnowItAll's Minelt™ application, which retained only the selected group as a hit list. This select list was then sent back into the KnowItAll Analyzelt™ MVP application as a new database subset.

The same analysis conditions were set, and a new PCA was generated (see Figure 4). This time the scores show clearly that the five reformat samples are not comprised of the same material. Two of the subgroups appear to cluster together; the others do not.

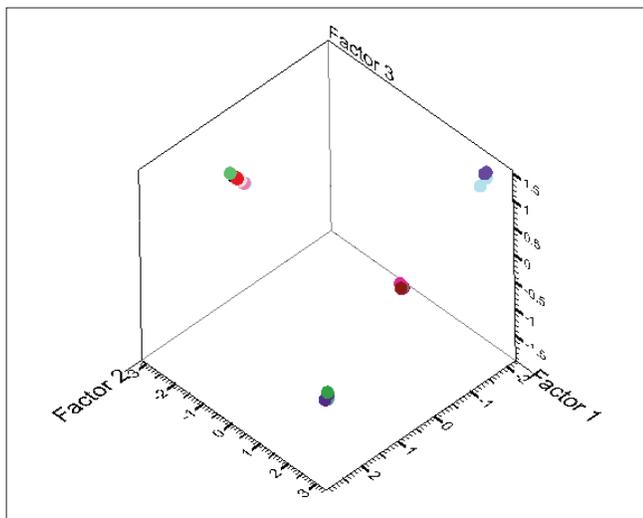


Fig. 4. Four subgroups of reformat samples are exhibited in PCA scores plot.

For example, Figure 5 shows a comparison of the chromatograms from the two groups at the top of the plot.

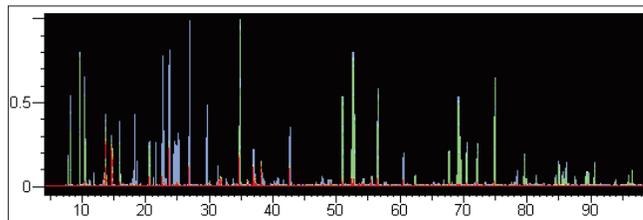


Fig. 5. Overlap density profiles of two reformat sample clusters.

In this overlap density heatmap, the red-shaded trace at the bottom of the plot shows the regions of the chromatograms of greatest similarity between the two groups while the blue and green traces show those regions of the two groups that are relatively unique to the corresponding group. Because the red area of the heatmap is minimal, we infer that the two groups are dissimilar.

Conclusions

Combining the capabilities of a chromatographic database with principal component analysis gives the user the capability of evaluating trends and groupings in a set of chromatograms without resorting to tedious side-by-side comparisons. In addition, the overlap density heatmap is a means for rapidly identifying portions of the chromatograms that either differentiate or are common to a collection of samples. The speed with which a large database can be mined for relevant information is also greatly accelerated by this process.

Acknowledgement

The data and background for this application note were supplied by Elizabeth Harvey of Chevron Corporation, Richmond, CA.



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