Chemometrics

Application Brief

Detailed Hydrocarbon Analysis

Demonstration of the LineUp™ alignment technology in downstream applications

Summary

- An automated alignment technology that does not require internal standards has been integrated into DHA
- Alignment in combination with pattern recognition eliminates the need to manually review chromatograms
- The result is cost-effective and can work with existing laboratory or near-line instrument systems
- The development leads the way to performing reliable DHA chromatography on-line
- The identical approach is expected to impact other chromatographic analyses (both HPLC and GC)
- Global chromatographic databases for common applications are possible

Gas chromatography in a refinery setting needs to analyze multiple fuel types each with hundreds or thousands of compounds. One common GC procedure is detailed hydrocarbon analysis (DHA). In this example, DHA is employed to evaluate gasolines and their ingredient fractions, including naphthas, alkylates and reformates. DHA has been employed in refinery laboratories as a quality measure for many years and is a control method required in Canada.

Several limitations in the past have prevented DHA from being effectively integrated into the engineering controls on site. The first issue is the fact that the GC instrument is not perfectly consistent in its separation of the constituents of gasoline. Consequently, the software that produces the DHA values cannot insure that the report reflects the true state. Thus, the results must be reviewed in order to insure accuracy. Not only is this a drain on time, but the quality of this manual step is a function of the availability, experience and skill of the interpreter. The procedure as it is performed in most lab settings, where two QC checks are used, is diagrammed on the right.

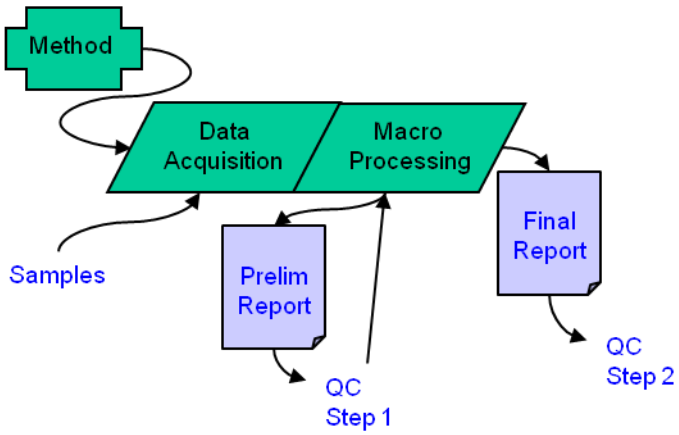

Figure 1. Current procedure showing two QC steps that can be eliminated

Retention time variability causes misidentifications which, in turn, force processing of samples to be interrupted. A preliminary report is then created for review by at least one analyst. Corrections are made by adjusting the peak table ***of the standard***, the sample is reprocessed and a new report is produced. Note that the change in the standard report table causes this table, at least temporarily, to be out-of-sync with the standard chromatogram. In a process such as this, quality of the QC depends on experience of the reviewer and is less conducive to distributed analysis.

A solution was developed in conjunction with several industry labs. This solution is a software system to correct the retention time shift that causes inconsistency in GC analysis, feeds this corrected raw data into the DHA reporting system, and automatically interprets the output report as a final quality check. It is important to note that this software setup is now commercially available and supported for laboratory use (*www.analytical-controls.com*). Migration to use in individual refinery labs or configuration as an on-line measurement is not expected to pose technical difficulties, and will result in a significantly faster turnaround of the QC values and allow better process information for line engineers.

Evaluation of this software process was attempted with a data set consisting of 75 samples equally distributed among alkylates, naphthas and reformates. The DHA system first identifies the sample type (naphtha, reformate, etc.) and uses that information to choose the appropriate alignment standard. During the check-out process, several naphtha samples were mislabeled as reformates because they were collected on entry to the reformate splitter. These ‘reformates” were correctly assigned to the naphtha group, aligned and processed successfully.

Using multivariate correlation, chromatographic alignment is achieved by adjusting for variation in column loading, column aging and changes in flow. The solution produces an improvement in reproducibility that can be seen below. The adjustment is completely automated for the Agilent ChemStation and any system employing Agilent’s EZChrom Elite, which spans both laboratory and process GCs.

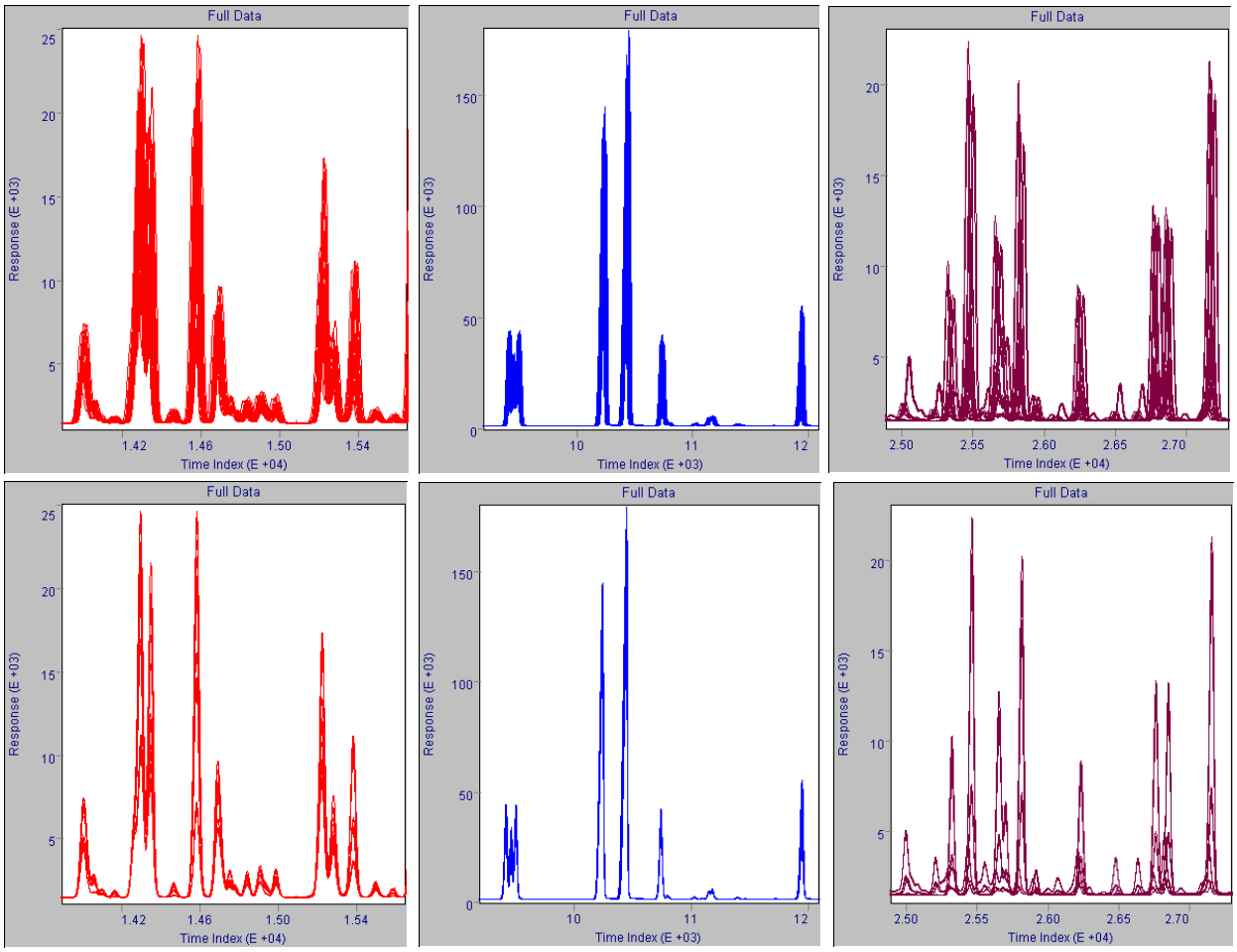

Figure 2. An overlay of 25 consecutive naphtha (red), alkylate (blue) and reformate (brown) runs prior to alignment (top) and after alignment (bottom)

Changing this hands-on analysis to a fully automated procedure eliminates preliminary reports and automates the heretofore manual QC steps. The pattern recognition solution:

- is cost-effective, automated, and does not require a change in the existing instrument hardware and software
- aligns the chromatogram to remove retention changes and feeds the aligned chromatogram into the DHA reporting software
- helps identify system failures (instrument-caused or process upset)

Business Model: An automated alignment technology has been integrated into routine DHA analysis. Applying the same tools to other laboratories for this analysis would result in immediate cost savings. Further, this process of alignment in combination with pattern recognition may eliminate the need to review chromatograms in most routine analyses. Ideally, this analysis should be performed on-line and incorporated into the information stream coursing through the DCS. With alignment plus objective, automated identification, efficient mining of a global chromatographic database is achievable.