

Chemometrics

Application Note



Simplifying GC Calibration

Background

As computers came on-line four decades ago, automated quality control became practical, but we still don't take advantage of that processing capability, instead sticking with engineering heuristics and rendering most of the available data impotent for control. Chromatographic analyzers have enjoyed an intimate relationship with the computer, but we have not yet tapped into the potential of processing raw data into actionable process information. This note gives an example of using a multivariate technique to simplify the calibration requirements of an on-line chromatographic analyzer.

Chromatography and multivariate alignment

Chromatography is one of the most important monitoring tools at our disposal; it is the most direct means of measuring the chemistry in the process. A single chromatogram holds a trove of information and we can use the same multivariate tools to tap into this source. We have the option of applying multivariate algorithms to the list of peaks and their concentrations, or to the raw chromatographic trace, or both. If we process just the peak table, the approach is identical to that described above for process sensors. If we look at the raw chromatograms, we need to apply an additional multivariate step: remediation of the retention time variability.

Chemometric alignment technology using a multivariate correlation approach has been discussed for decades. Alignment technology minimizes the retention shift leading to more accurate peak identification and more reliable data. To emphasize the value of mathematical alignment, consider the following example.

In this case, the task is to monitor the molecular weight distribution for a series of motor fuels and components. The example data was drawn from the ASTM 7798 inter-laboratory study setting the standard for fast simulated distillation. The application itself is not critical to this discussion, but it is an opportunity

to study a series of well-characterized samples across a series of operators using different instruments in different labs. Figure 1 shows the procedure each of the labs followed to enable the statistical evaluation to establish this new standard.

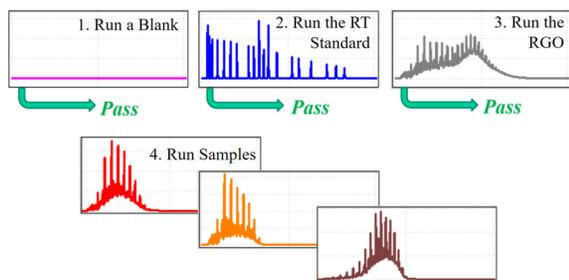


Figure 1. Laboratory procedure for simulated distillation

For any laboratory, the standard SimDist procedure is to first run a blank to insure the column is clear of carryover. If the blank passes the total area criterion, the second step is to run a retention time standard (in this case, a collection of n-paraffins). The paraffins have well known boiling points so their retention times allow us to convert the time axis of the chromatogram to temperature. If the paraffin chromatogram meets the acceptance criterion, we store these time points from the run for use later in running unknown samples. The third step is to run a well-characterized sample, in this case a reference gas oil (RGO), which has undergone countless SimDist evaluations. We then use the temperature profile set in running the paraffins, apply it to establish the x-axis of the RGO and calculate the boiling point profile. If the boiling points of the RGO match what is known about this standard within the allowed limits, we are good to run samples.

The next step is to insert the role of multivariate processing. Using the retention time adjustment mentioned earlier, it is possible to correct a current chromatogram to a historical run of the retention time standard. As long as the method is reasonably similar, that retention time standard does not need to have been run on the same instrument. This vastly simplifies the calibration of subsequent instruments. In this example, the second instrument is an on-line GC. For this, the procedure is depicted in Figure 2.

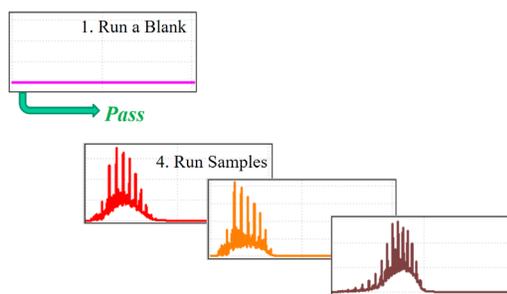


Figure 2. Using the multivariate alignment, the procedure for online analyzers does not require a calibration step.

Retention time variability can be largely eliminated from chromatography. What this means in a process is that a chromatograph can be put in place, given a file from a different (in this case laboratory) instrument, and we can use the retention time standard run on that lab instrument to correct the chromatographic traces to match an application-specific sample. In this way, we can make all instruments and process analyzers that are performing a similar task look identical. In turn, this allows true plug-and-play chromatography, where we can install or replace an on-line system with a new instrument or analyzer without running a calibration sample. This essentially means we have a universal calibration that should work in any location. At the least, the frequency with which we need to run calibration standards is significantly lower than what is currently being done.

Multivariate analysis does not stop with the retention time corrections, we can use the same PCA and PLS technology to interpret the chromatographic trace, compare the interpretation to that of the tabular output, and use the combination to ascertain the maintenance requirements and to flag, even predict, process upsets.

Conclusions

The oft-quoted statement "you can't control what you don't measure" leads easily to "the quality of your measurement dictates the quality of your control". We can further break down measurement quality into two sub-parts: 1) the precision and specificity of the measurement; and 2) the system we employ to extract the information con-

tent from these data. In the hydrocarbon processing industry, GC is a critical workhorse. In chromatography, much of the variability is solved using correlation-based multivariate alignment, giving these analyzers vastly-lower calibration requirements and giving us the opportunity for instrument interchangeability and a common interpretive base.

References

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