Chemometrics

Application Brief

Monitoring Fugitive Hydrocarbons

Demonstration of the Pirouette® multivariate pattern recognition technology in a downstream application

Summary

The use of pattern recognition technology to screen samples collected from test wells can give results in 10% of the time for 10% of the cost. Analyses can be done with in-house instruments or farmed out to a contract lab. The advantage is better control over product-reclaiming operations and the ability to monitor fugitive hydrocarbons (and take remediation steps) in a more time-effective manner. These data can be posted in real time to a centralized server and managed centrally.

We worked with employees from a refinery operation to develop a rapid means of evaluating test well samples taken from a refinery site. These well locations are plotted on a map of the facility at the bottom. Samples are collected to evaluate the extent and timing of spills or leakage from the facility and determine if the groundwater is at risk.

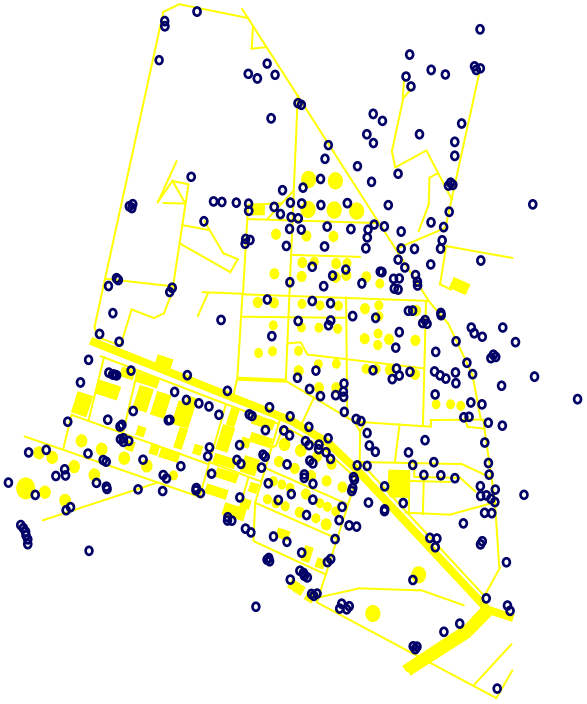

Figure 1. Refinery test well locations

Currently, analysis is done by gas chromatography at a cost of about $180 per sample and a turnaround time of 4 to 6 months.

We processed 278 samples from the refinery, ranging from pure hydrocarbon product to pure water using a commercial headspace mass spectrometer (the Gerstel ChemSensor based on the Agilent 5973 mass spectrometer). Compared to the standard gas chromatography, the assessments are made much more quickly, approximately 12 samples per hour compared to less than one per hour for the GC method.

In addition, the headspace samples require no sample preparation, the collection does not need to differentiate between water and oil samples, and the samples do not have to be either measured or weighed into the collection (headspace) vials.

The samples run in this experiment required roughly one minute apiece for the operator to prepare and approximately 5 minutes for the instrument to process. Burdened cost per analysis is estimated to be $20 per sample.

The headspace results are processed by Pirouette pattern recognition software as shown in Figure 2. We use the algorithms to identify oils, contaminated water (shown in green) and uncontaminated water (blue). The clusters of green water points represent different contaminants (e.g., BTEX, gasoline, crude). The chemical composition of the oils (aromatic versus aliphatic content) as well as the specific water contamination are interpreted automatically as part of the analysis, without the need for manual review.

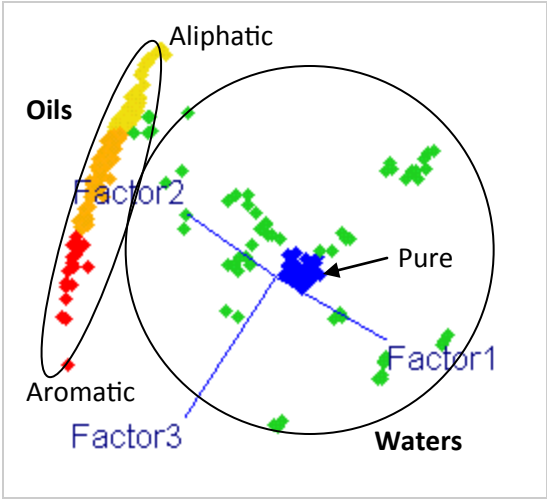

Figure 2. PCA scores of well samples

Even though the samples were not weighed, the quantitation is good enough for most purposes (within 5-10%). With MTBE (due to a unique ion), we can give results that span four orders of magnitude (e.g., 5 ppb to 60 ppm) and use that information to isolate the source of tank leakage.

A similar need exists today for screening soils around transfer facilities and gas stations.