

Application Note — Chemical Outlier Detection with a ChemView® Filter Photometer

Process Analytical Systems

Introduction

Optical Solutions, Inc. has introduced a new option for its ChemView® process photometers - OutlierDetect™. It provides chemical outlier detection with most multiple linear regression (MLR) calibrations in which more than one wavelength predicts a chemical variable.

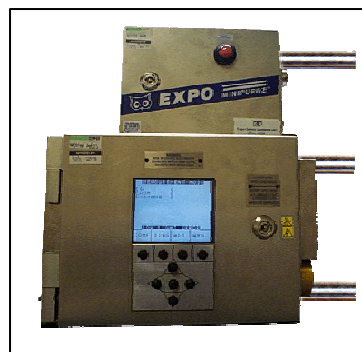
Outlier detection provides a means to assess the “quality” of the predicted answer in real-time based upon the absorbance variations in the calibration model. It attempts to warn you when the current sample does not “fit” the calibration model. Because this is unique for photometers, worldwide patent applications have been applied for OutlierDetect™.

Outlier Detection

OutlierDetect™ is similar to the outlier detection methods commonly used in full-spectrum analyzers, such as FT-NIRs. It addresses one of the fundamental criticisms levied against the use of photometers for process control, which is that the predicted answers are less reliable, because the photometer does not account for the presence of a contaminant at wavelengths other than the ones used to predict a result.

Chemometrics

Determining the reliability of an analytical measurement when performing on-line chemical analysis is as important as making the measurement itself. Chemometric models such as Multiple Linear Regression (MLR), Principal Component Analysis (PCA) and Partial Least Squares (PLS) are routinely used to calibrate on-line analyzers, particularly near Infrared (NIR) process spectrophotometers. The success of these models depends on the quality of the sample spectra used in the predictions. How does one determine when chemometric models are failing and the analytical results are incorrect? Two instances when this can happen are when a sample falls outside the range of calibration conditions covered in a chemometric model or when an unmodeled interference occurs and biases a measurement.



ChemView in Class 1, Div 2, Z-Purged Enclosure

Every analytical instrument or method can be classified according to the type of data that it provides. Instruments that provide a single data point, like a pH meter or single wavelength filter photometer, are classified as zero-order instruments because the single number that they provide is a zero-order tensor. It is not possible to detect when interference occurs on a zero-order instrument. First-order instruments include spectrometers, chromatographs and arrays of zero-order sensors. Because of the nature of the full spectrum data generated by most process NIR spectrophotometers they are classified as first-order instruments.

Among the advantages of using a first-order instrument is the ability to detect when a chemometric model fails or an interference occurs. These “upsets” can be detected through a variety of descriptive statistics that can be calculated from the spectrum. Two important descriptive statistics are the sum of square error Q and the Mahalanobis distance M . Reporting these statistics with the analytical measurement gives a measure of the confidence in the result. Generally, low values for any of these “reliability” statistics mean a good result. To indicate when there are problems, it is necessary to determine limits that indicate when a spectrum no longer fits the model and the result is in error. It is possible that confidence limits can be calculated for Q and M to indicate when a model fails and the value predicted by a model is suspect.

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MLR and Outlier Detection in ChemView®

Once a calibration requires more than a single wavelength (i.e. a linear regression), it falls into the same category as a full spectrum analysis. Once multiple wavelengths are used, it becomes a first-order problem. Thus, a photometer using four wavelengths is fundamentally no different from a spectrophotometer analyzing 1000 contiguous wavelengths. As is demonstrated below, the same type of outlier statistics used in the full-spectrum analyzer can now be used in the ChemView® photometer.

For example, assume that sample temperature variation is included in the calibration model by analyzing each sample over the full range of temperatures expected in the process. In this case, it is NOT necessary to know the temperature. Its effect is included in the various measured absorbances. If the temperature of a sample measured on-line increases beyond the largest temperature used in the calibration model, one of two outliers of OutlierDetect, M , may increase and exceed its limit. When this happens, a 4-20 mA analog output may be set to read to 22 mA, signifying a questionable answer to the control computer, and suggesting that a "grab" sample be collected for laboratory analysis. Additionally, a separate "answer" can be assigned for that outlier parameter in ChemView® for continuous trending. In this way, one can react before an outlier limit is triggered.

Alternatively, perhaps a contaminant enters the sample. Even though it may not occur exactly at all wavelengths used by the ChemView®, it may still have an effect on those absorbances. In this case, the second of the two outliers, Q , may increase and exceed its limit. When that happens, the 4-20 mA analog output may be set to 2 mA, for example, signifying a questionable answer to the control computer, and again suggesting that a sample be collected. In this way, M and Q statistics can be evaluated on-line in real time.

Thus, the 4-20 mA analog output signal from a ChemView® can be used to inform which outlier has been activated. The ChemView already uses this approach to indicate system problems, such as lamp failure, probe fouling or breakage of optical fibers, where the analog output is set to read 0 mA. These diagnostic capabilities allow process photometers to become "SMART" sensors.

Step-by-Step Example of MLR Calibration and Outlier Detection

1. Selecting ChemView® Wavelengths from PLS

As an example, a small sample system is analyzed over a range of temperatures. The goal is to model the effect of temperature into the MLR model WITHOUT measuring the sample temperature on-line.

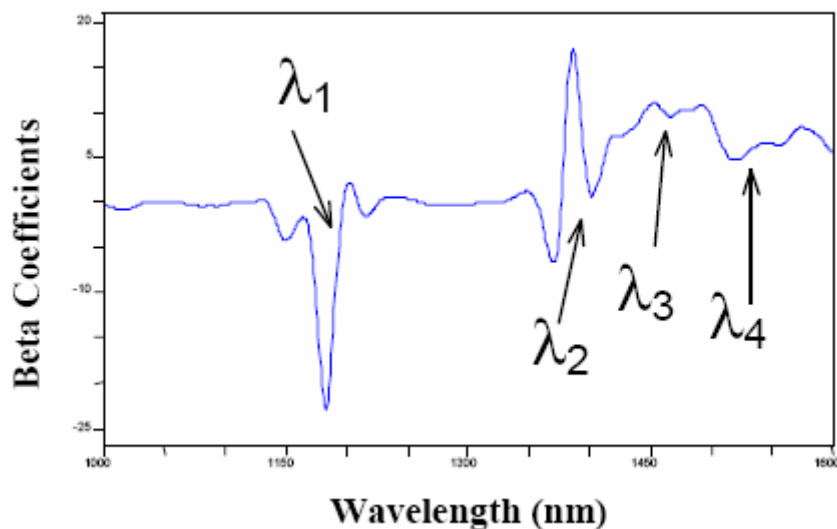
The Optical Solutions' PS-2 portable NIR diode array spectrophotometer (or equivalent) is used to measure the complete NIR spectrum of each sample in a quartz cuvette in an Optical Solutions' HeaterCell™ fiber optic accessory at several temperatures.

A PLS (Partial Least Squares) model of the data is then developed. The PS-2 employs Galactic Industries' PLSPlus/IQ™ in GRAMS™, although any one of a number of commercial software packages may be used. Principal components adequately describe the data using the PRESS plot (Predicted Error Sum of Squares) generated by the software. PRESS indicates that a 4-factor PLS model adequately describes the data.

Next, the BETA Coefficients are examined and four wavelengths are selected, one from each of the four regions that contribute most strongly to the 4-factor model. These BETA Coefficients show the weighting that the 4-factor model places at each wavelength.

This procedure is typically done in a feasibility study by Optical Solutions with the PS-2 on customer-supplied samples provided prior to the purchase of a ChemView® photometer. In this system, these four wavelengths have been selected from the beta coefficient plot as shown on the next page.

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In essence, PLS is used to determine the “dimensionality” of the problem, providing importance guidance for selecting wavelengths in the subsequent MLR calibration. Those with MLR experience know how spurious wavelength selection can occur. PLS provides a systematic means to help select those wavelengths.

2. Configuring the ChemView®

A ChemView® is then configured with the wavelengths selected above using appropriate filters and detectors.

3. Repeating the Measurements with ChemView®

The calibration samples are now re-analyzed with the ChemView®, preferably using the fibers and probe that will be installed into the process. This accounts for possible small changes between the wavelengths and absorbances measured in ChemView® and those determined in the PS-2 or other spectrophotometer. It should be noted, however, that there has been very good success transferring calibrations from cuvettes in a HeaterCell attached to the ChemView® to a process probe. This provides the advantage of using small sample volumes of only a few ml, controlling sample temperature in HeaterCell (which is hard to do in a probe) and minimizing contamination among samples (avoiding various “dead” spaces in probes without large volumes of samples to “flush” the probe).

First the probe or sample cell connected to ChemView® is zeroed so that all absorbances read zero mAU. This is critical for success. Then the samples are analyzed with the ChemView® over the temperature range specified and the absorbances recorded at each of the wavelengths.

4. MLR Analysis

An MLR model can be easily generated from the data obtained from the readings of the four wavelengths at the various temperatures. Optical Solutions now optionally provides OutlierDetect™, an add-in for Microsoft® Excel 97! that computes the MLR model and all *M* and *Q* matrices and limits required for outlier detection by ChemView®. It performs PCA in Excel 97! This program is used in our factory calibration because it also provides the MLR coefficients

5. Enter the MLR Coefficients into ChemView®

Subroutines in the software of the ChemView® allow the values calculated by OutlierDetect™ to be entered to set up the calibration and the *M* and *Q* statistics which the program has determined using PCA. The software also allows the limits and alarms to be set up for the two statistics.

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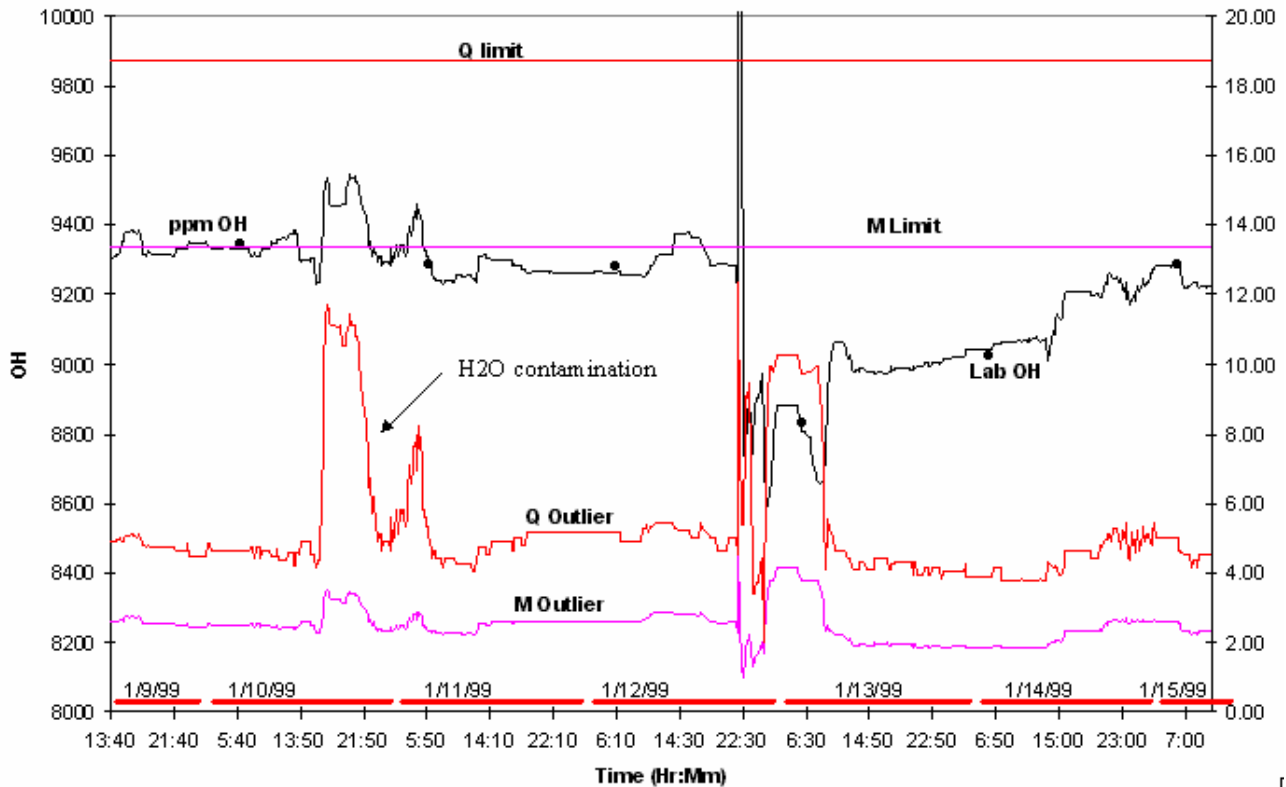
CASE STUDY: SiOH in Silicone Dilution Tank Including Sample Temperature Variation

The following trend data, obtained from an actual process over a period of five days, demonstrate the ability of OutlierDetect™ to monitor variations in the process.

- Measured ppm OH (left vertical axis) from the ChemView® (black line). Lab Values (black dot).
- *M* Outlier Statistic (right vertical axis) shown by violet line (acceptable if below about 13.5). *M* can be thought of as how far the sample is from the mean of points projected on a linear regression line.
- *Q* Outlier Statistic (right vertical axis) shown by red line (acceptable below 18.5). *Q* can be thought of as how far the sample is above or below that regression line. It appears to be a more sensitive outlier statistic than *M*.

Regions of rapid outlier increases on 1/10/99 and 1/13/99 reflect molecular water ingress into the mixing tank. Note that molecular water was NOT included in the model. Nevertheless, these excursions did not exceed the outlier limits, as supported by the agreement between the ChemView® OH analyses and the lab analyses from grab samples. The large change on 1/12/99 is from switching source tanks.

This ChemView® has been on-line since November 1998 with no down time. It replaced a top-of-the-line, scanning-grating fiber optic process spectrophotometer for ¼ its price.



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Conclusions

ChemView® with OutlierDetect™ brings process photometry to a new level of confidence, which breaks the barrier of plant-level acceptance at an affordable price. No moving parts means nearly maintenance-free operation. Many of the more complex applications traditionally thought to require an FT-NIR can in fact be done with this powerful, compact analyzer.

Our OutlierDetect™ Excel® program makes calibration as easy as entering a column for the chemical variable, and columns for the absorbances at each wavelength taken from the ChemView®. A click of the mouse creates several worksheets with the MLR coefficients and M and Q matrices and limits. Entering these into the appropriate screens in a ChemView® prepares it for installation. The program will also indicate any calibration samples that may be outliers so that they may be removed and the system recalibrated. This is as simple as removing a row from the spreadsheet and clicking a re-compute button. Similarly adding rows to the spreadsheet from grab sample analyses is a simple way to evolve the calibration over time from changing conditions, such as raw material supplies.