Process Insights
Premium Insights Into Process

GuidedWave

Application Note:

Hydroxyl and Acid Numbers in Resin Melts with a ClearView® db Photometer

Purpose

To measure hydroxyl and acid numbers on-line in resin melts to determine end-of-reaction across different products with a ClearView db photometer and fiber optic probe.

Approach

NIR spectra were taken at 245 °C in a 1 cm cuvette using a M412 spectrometer. The data was analyzed with the chemometric method of partial least-squares (PLS). This guides wavelength selection for the ClearView db photometer. Multiple linear regression (MLR) is then used for calibration. It is possible to select enough wavelengths to obtain a reasonable fit with MLR. The ClearView db photometer is configured with the selected wavelengths, the samples are run and the MLR model is calibrated for on-line use.

Two Cases

Here are two representative cases using samples from different manufacturers. Each set of samples spans several products. The products in the first set are spectrally similar and require fewer wavelengths to calibrate than the second set.

The following describes our systematic approach to these different sample sets.

Simplest Case Spectral Results

The resulting spectra (Figure 1) are shown at right for several different resin products. C-H overtones are present in the 1700 and 1200 nm regions. There is little difference in the C-H regions among these similar samples. Hydroxyl has a strong peak at about 1410 and a weaker peak at 2020 nm. Samples with high hydroxyl number have low acid numbers, and vice versa.

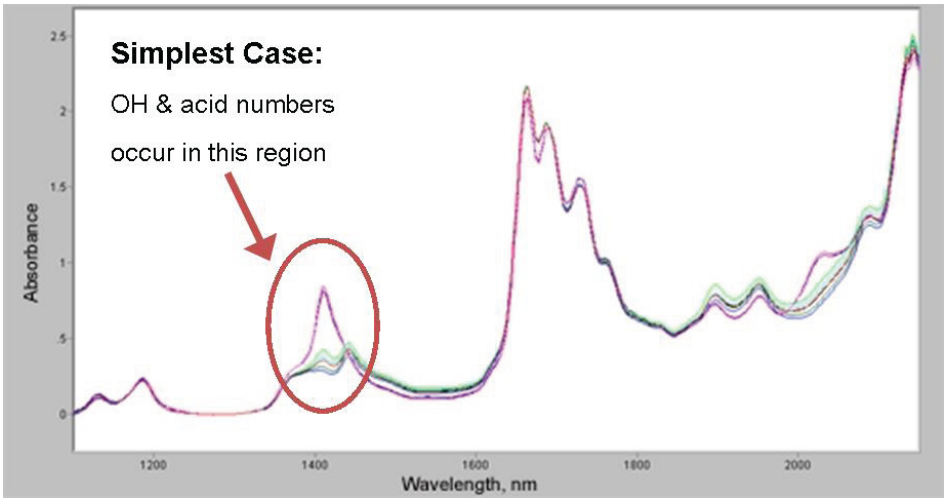

Figure 1

Zpurge Unit
Class I, Division 2

ExProof Unit
Class I, Division 1

General Purpose Unit

ClearView db Enclosure Options

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PLS Analysis

The first row of graphs in Figure 2 is for hydroxyl number from PLS analysis. The left most graph shows that the PLS model converges in 1 factor (X axis), meaning that there is generally one dominant wavelength region contributing most of the information for hydroxyl number.

The middle graph is the actual vs. predicted plot for the 1-factor model and in the rightmost graph are the beta coefficients. Beta coefficients are multiplied by the absorbances at each wavelength and summed to a hydroxyl number. They show the dominant wavelength at 1412 nm, and a less significant wavelength at 2000 nm (both are related to hydroxyl number).

Based upon these results, the absorbances at 1412 and 1440 nm were chosen, and Excel™ used to compute the regression coefficients. The reference wavelength, chosen in a region with no activity related to these parameters, was 1280 nm.The ClearView db will compute the absorbance at 1412 nm relative to 1280 nm. The observed vs. predicted MLR plots for both parameters are shown in Figure 3 along with some of the statistical results.

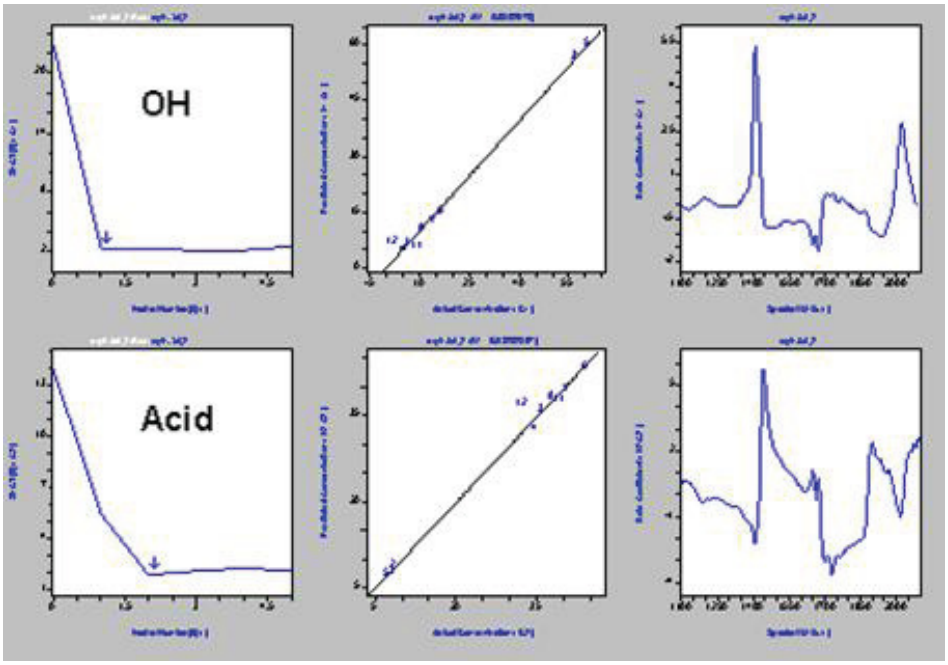

Figure 2

Regression	Hydroxyl Number	Acid Number
R Square	0.99345	0.9953
Standard Error	2.15	1.69
Observatons	9	9
NIR Wavelengths	1412	1412,1440

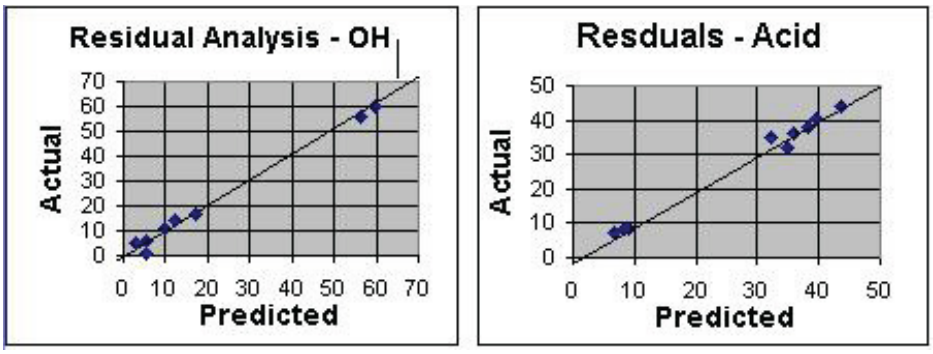

Figure 3 MLR Calibration from Laboratory Spectral Data

Process Insights
Premium Insights Into Process
GuidedWave
+1 916-638-4944 phone
+1 916-635-8458 fax
gwinfo@guided-wave.com
a Process Insights Brand

Literature: 3019-13-11

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General Case:

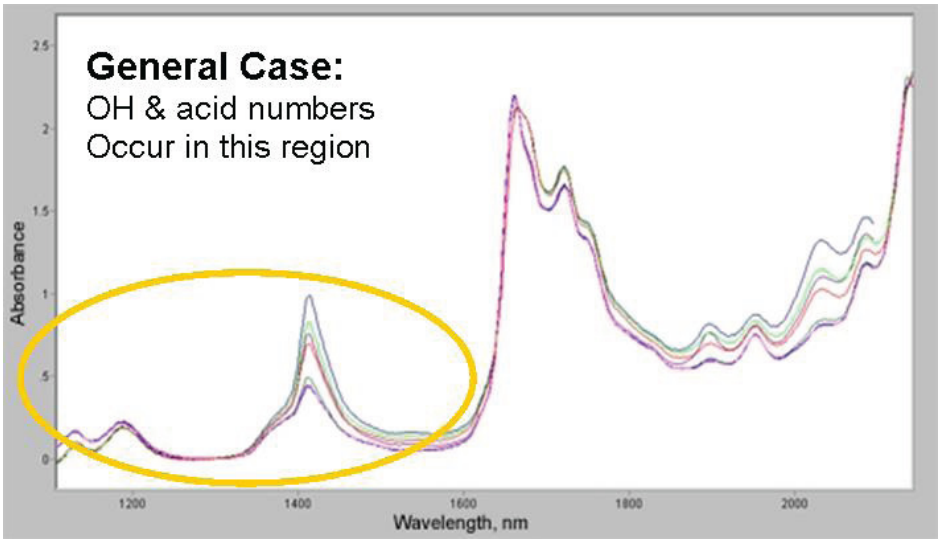

Figure 4

Spectral Results

This set of samples shows the strong effect of hydroxyl variations in the 1400 and 2000 nm regions, similar to that presented above. However, the C-H regions near 1200 and 1700 nm exhibit more structure here. In particular, different product types show stronger differences near 1150 nm, a region that indicates a more unsaturated character.

PLS Analysis

As before, the PLS analysis of these samples at 245 °C indicates that only one wavelength is required for hydroxyl number, shown in Figure 5 (top row of graphs).

Acid Number (lower row of graphs) converges in 3 PLS factors, rather than 2, as in the simpler case. As before, the beta coefficient plot shows the negative contribution from hydroxyl near 1412 nm and positive contribution near 1440 nm. However, this plot also shows a strong positive contribution near 1150 nm and a weaker negative contribution near 1620 nm. These reflect the additional complexity across product types in this sample set. The resulting laboratory regressions for this data set resulted in SEE (standard error of estimate) values for hydroxyl and acid number of 1.3 and 0.4, respectively.

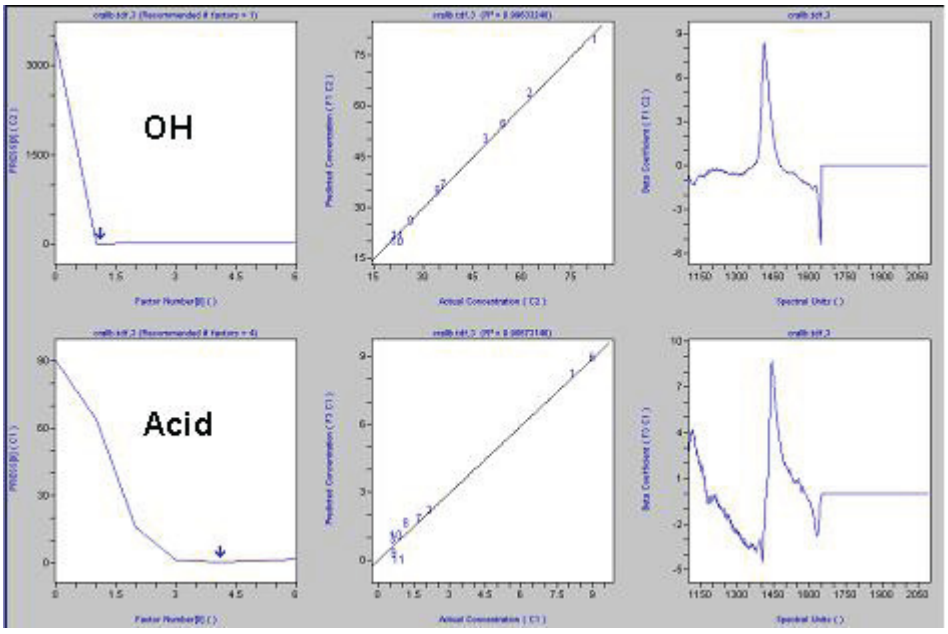

Figure 5

Application Note:

Hydroxyl and Acid Numbers in Resin Melts with a ClearView® db Photometer

Progression to On-Line

Samples are then re-run in a ClearView db. Absorbances are exported into a Microsoft® Excel™ spreadsheet and the regression coefficients determined. The ClearView db is shipped with this "preliminary" factory calibration. It can be tested on-line for a few weeks and, if necessary, the model may be improved by recording the absorbances from the ClearView db, determining the hydroxyl and acid numbers on grab samples taken to the laboratory, and computing new regression coefficients. The result of this on-line upgrade process is shown above for hydroxyl number for this data set using a ClearView db connected to a fiber optic transmission probe inserted directly into the reactor at 245 °C. The resulting SEE was 1.9, or about 2% full-scale

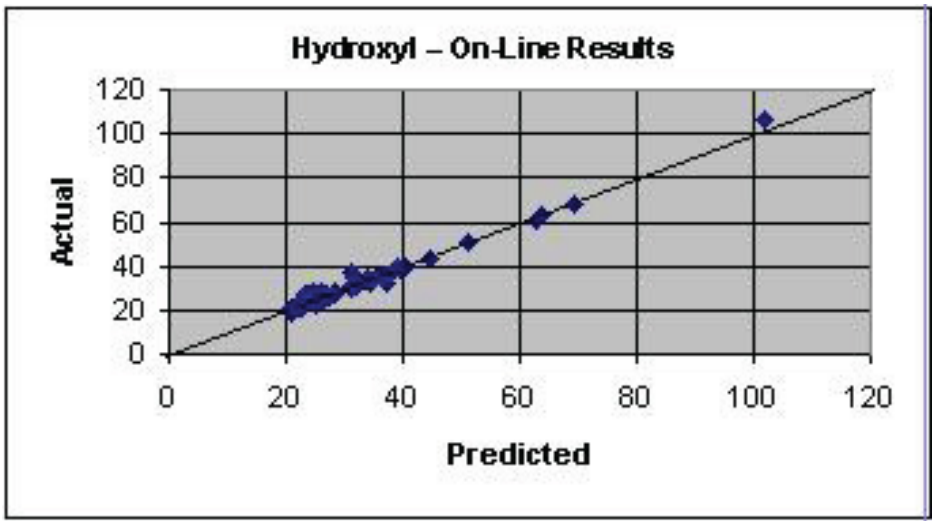

Figure 6

Conclusion

These data indicate that when only acid value and hydroxyl number are required for the determination of end-of-reaction, a ClearView db filter photometer is all that is required. Although it was found that the same calibrations could be used among the different products in both sample sets described, this may not always be the case. The ClearView db photometer is capable of monitoring multiple calibrations at the same time, for cases when different products require different calibrations. In fact, ppm water and yellow color (ie APHA) calibrations could also be added and these values measured simultaneously. The ClearView db can accommodate one or two sample points.

If your chemistry changes over time or you need to predict several other properties, such as crosslinking, etc., it may be better to select a Guided Wave spectrometer. The Model 412 spectrometer is also capable of automated outlier detection.

In summary, for single or dual point measurements in systems our low-cost ClearView db photometer can provide measurement of both parameters. For more complex chemistries, or more than 2 sample points choose a Model 412 spectrometer.

Feasibility Testing

We can perform a feasibility study with your samples to assist you in determining the most cost-effective solution for your application. In many cases, you may already have spectral data taken with other spectrometers in your company. We can import these spectra into our multivariate analysis software, perform the above calculations and provide the necessary guidance.

ClearView db	Model 412
	
1-2 sample points	Up to 12 sample points
Hydroxyl and Acid Numbers in chemically simpler systems requiring up to 5 analytical wavelengths and a reference wavelength	Complex Chemistries
No outlier detection	Outlier Detections