HyFMet Data Update

Objective: Measurement of free HF in LCP

Principal of Operation

A colorimetric reaction between an indicator and sample is quantified by absorbance spectroscopy. The absorbance measurements are correlated to concentration by comparison to three standards that span the specification range: Low, Target, and High. An unknown sample's concentration is calculated by extrapolation from the absorbances of two of the standards that bracket the unknown's concentration, one run before and the other after the unknown.

Sequence of Operation

1) Calibration – The three standards are run and validated for absolute absorbance values, linearity, slope, intercept, and deviation.

2) Initialization - The target standard is run, repeated, and checked for deviation.

3) Measure Unknown – The result determines which standard to run next. If the unknown's absorbance is greater than the target's (lower in concentration) the low standard is run. If the unknown's absorbance is lower (higher in concentration) the high standard is run.

4) Measure Standard - The unknown's concentration is calculated from the two standards.

5) Repeat - The unknown is run again followed by the appropriate standard.

Background

Sequential Injection Analysis is a sensitive technique. Combined with automation, this instrument allows a level of real-time concentration monitoring and control previously unavailable. The precision required for this particular application required some modifications to the existing instrument to achieve the desired sensitivity. The most significant of these improvements is reaction temperature control. Currently the system is using a prototype temperature control system.

Future

1) Correlate standards with existing analytics. A "Gold Standard" needs to be produced and rigorously analyzed with existing methods. It will then be used for the QA of the production lots.

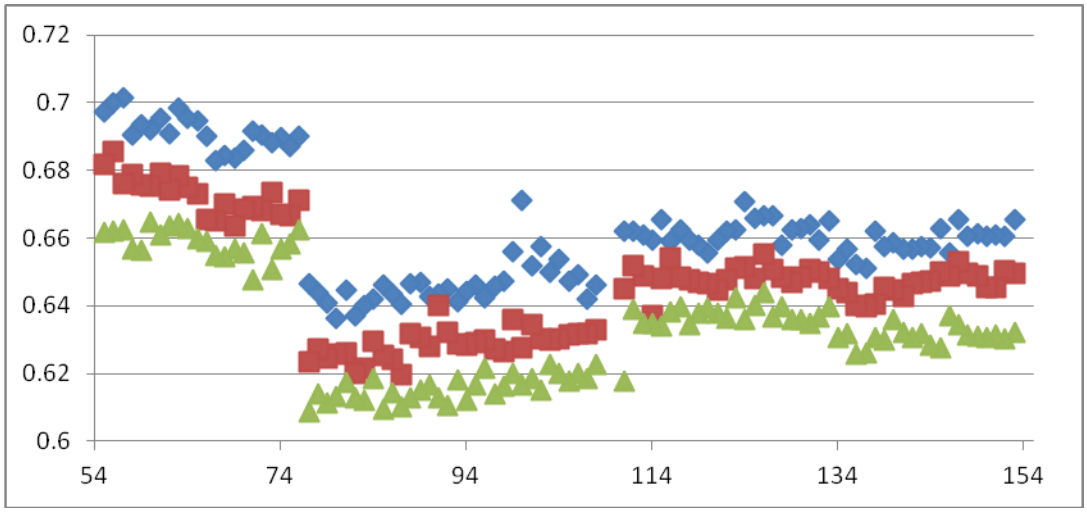
2) Development of process data. Comparison of instrument results to process metrics such as etch rate and bath life.

3) Determine application and interface criteria. The system can be configured to monitor or control blending, for tank or loop monitoring, to run bottle samples, or all of the above.

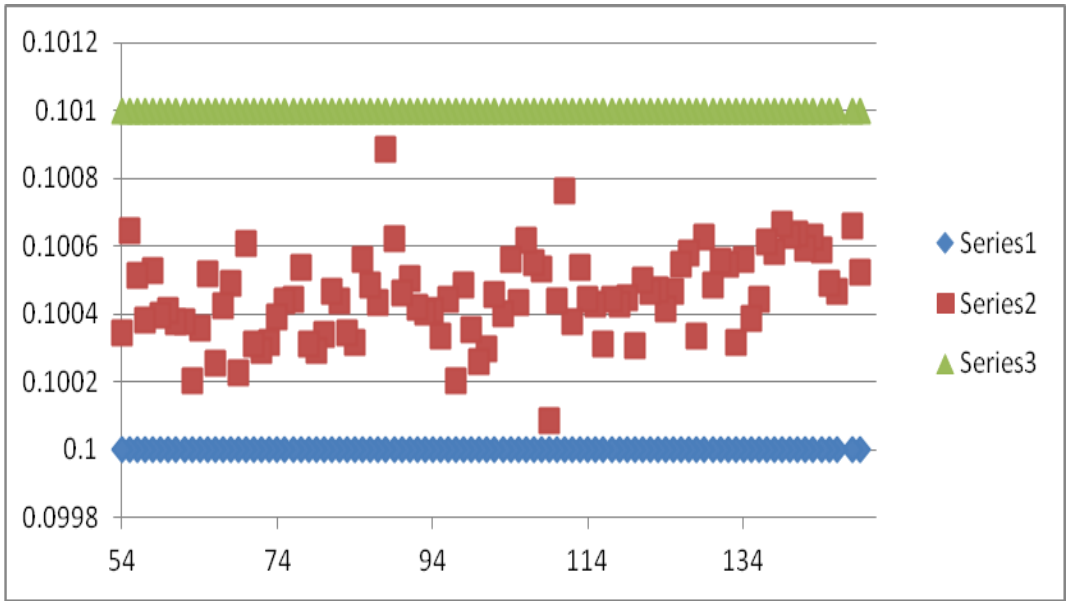
Data

Below is a summary of data generated during the development of this application. It encompasses an evolution of both the protocol and mechanical configuration. Data was acquired in sets of Low, Target, and High, usually repeated 11 times to make a run. 200 mL of LCP was spiked with 10 and 20 uL of 10% HF to create the Target and High standards.

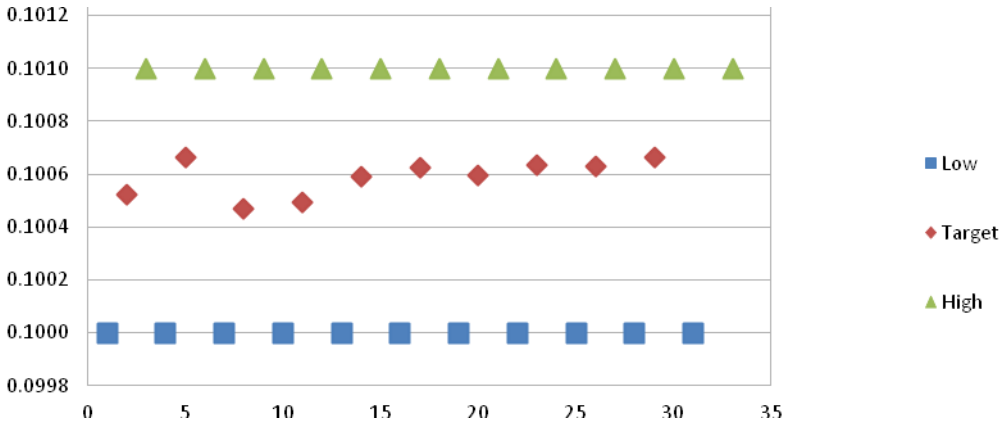
Raw Data: The last 100 absorbance data points, the shifts are from reagent lot changes.



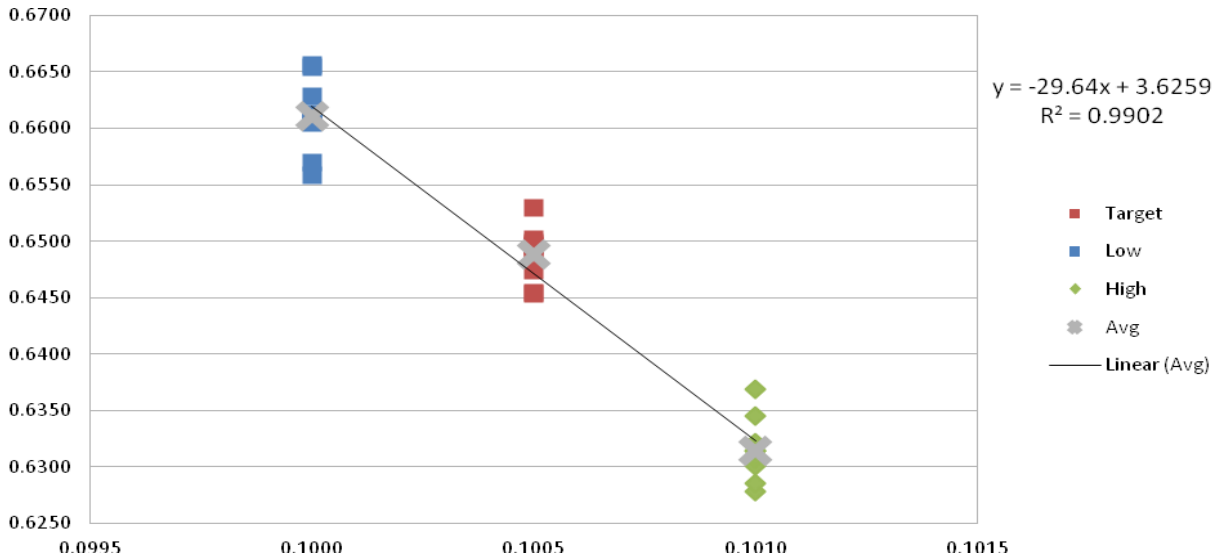
The same data is normalized to the adjacent low and high standards. The target is plotted as an unknown, predicted in % HF.



A typical recent run of 10 sets of low, target, and high, normalized to the low and high.



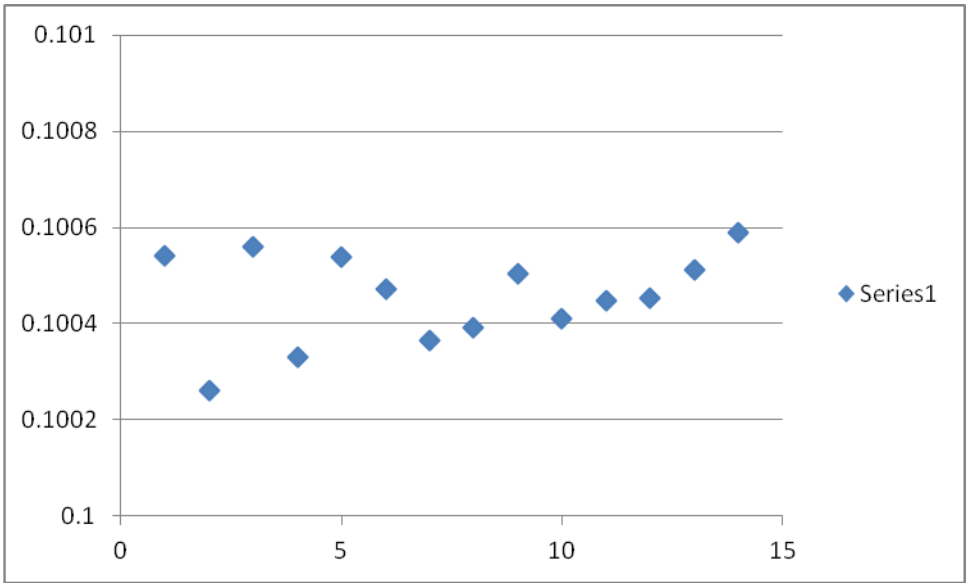
This run's quantitative summary. Each sample type is averaged and a least squares fit is applied (Excel Linest function). The Average and Std Dev are of the target data above and are expressed in % HF.



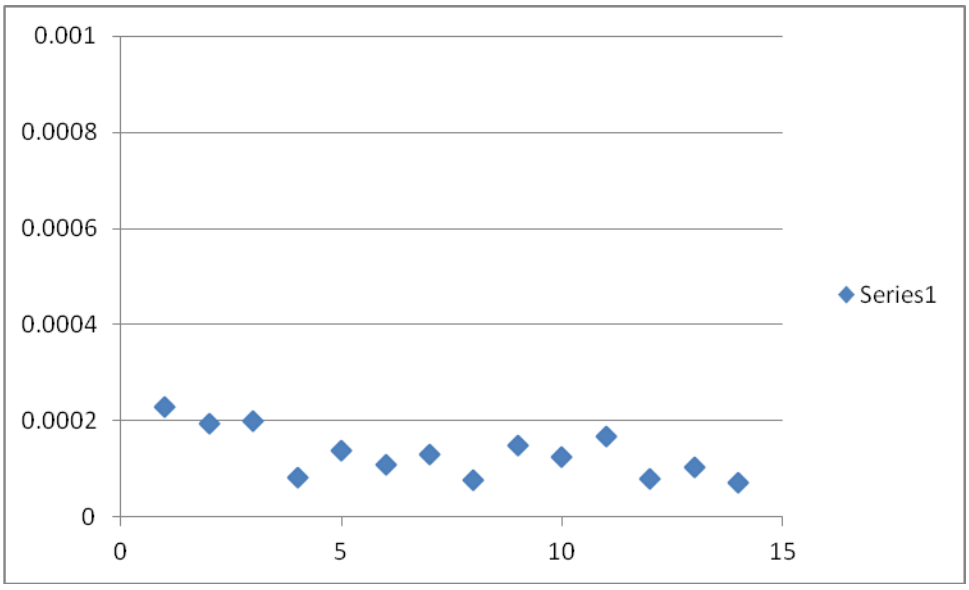
	Slope	Intercept
	-29.64	3.62593333
	2.95603338	0.29708381
R2 ->	0.99015164	0.00209023
	100.539734	1
	0.00043926	4.3691E-06

Average	0.100588
Std Dev	0.000070

The averages of 14 recent runs are expressed in % HF, each run is 10 sets of Low, Target, High.

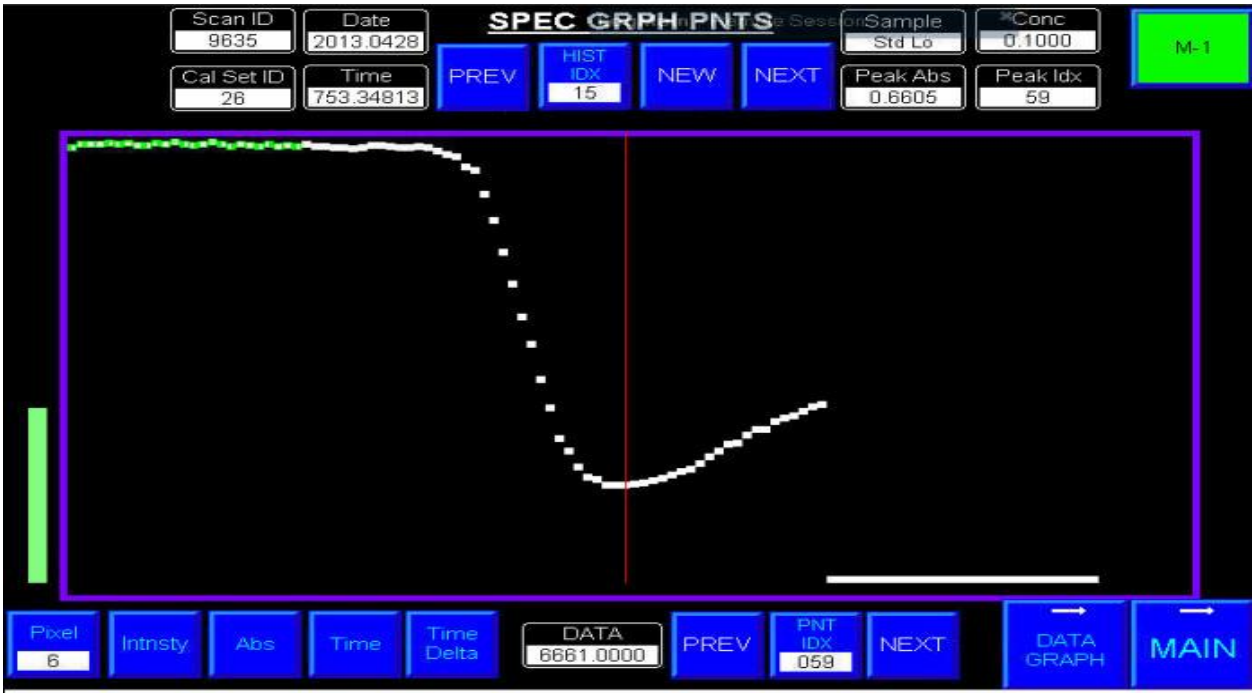


The standard deviations of the above runs are expressed in % HF.

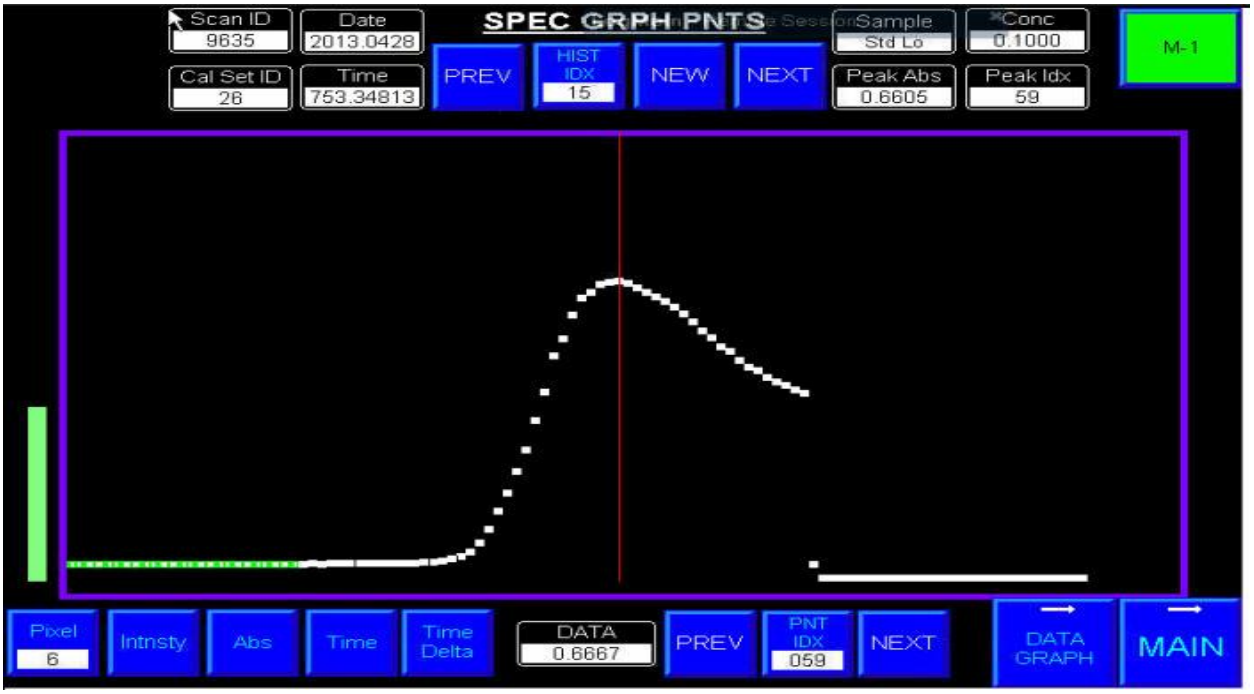


The Process

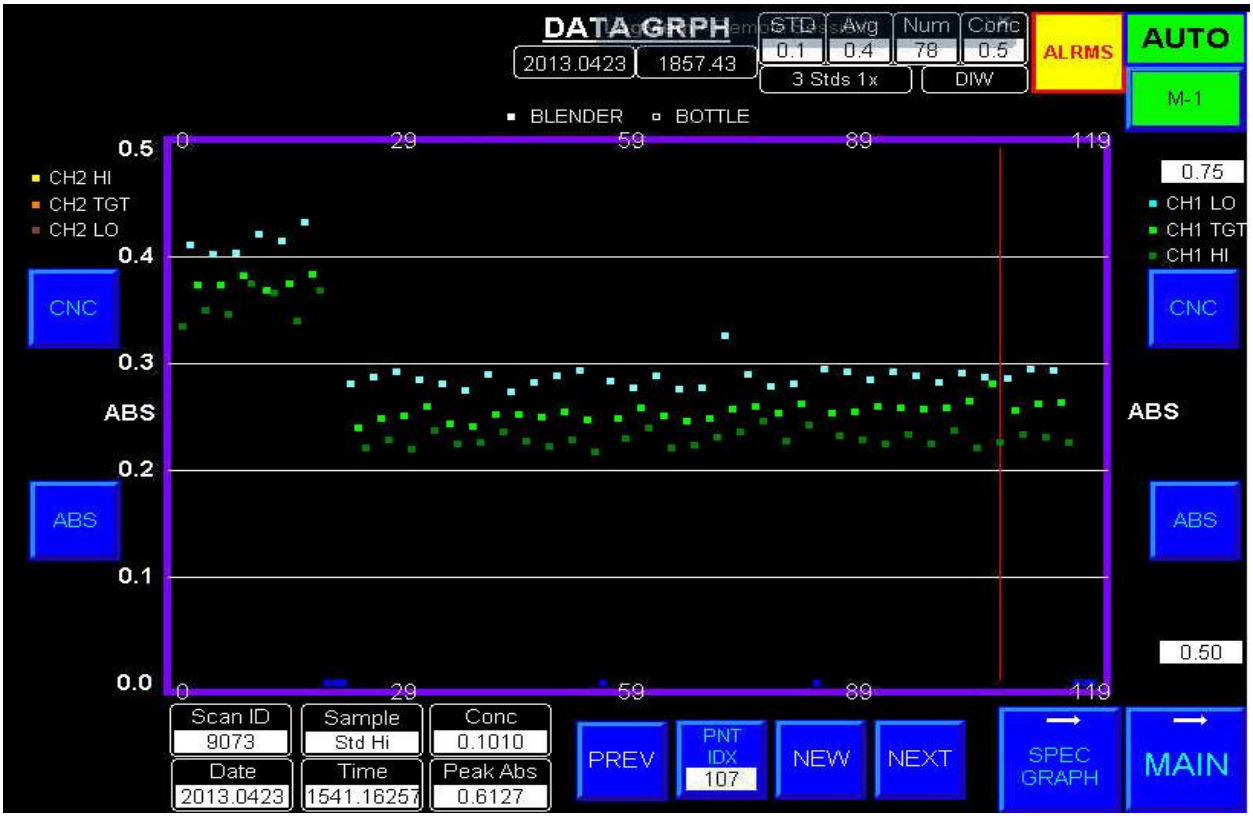
A precision micro syringe pump aspirates volumes of sample and indicator into a holding coil, and then dispenses it through a flow cell. A spectrometer monitors the mixture as it flows by, producing a graph of light intensity over time. The green data points are used as the reference light intensity for the calculation of absorbance.



The data is converted into absorbance.



The maximum absorbance value (indicated by the scooter above) is proportional to the concentration of the chemical. The last 120 samples' absorance maximums are plotted here.



The system is available as either a process instrument designed for 24/7 automated process monitoring and control, or as a bench-top instrument. The sample results can be reported via an Ethernet/IP (Allen Bradley Compact Logix PLC), a hardware interface (4-20mA / Dry Contact), or local printer.