

Application Note — On-Line Monitoring of Caustic & Carbonate with a ChemView® Photometer

Purpose: To simultaneously measure caustic (NaOH) and sodium carbonate in aqueous process streams, particularly at low (<2%) caustic concentrations, using a ChemView® NIR photometer and fiber optic probe.

Background: The dominance of water in the NIR hampers the measurement of caustic. Nevertheless, there are several successful reports of using full-spectrum FT-NIRs and discrete wavelength photometers for moderate caustic concentrations. Watson and Baughman (*Spectroscopy*, 2(1) 44-48 (1984)) summarized a typical approach using the spectral region from 1700 to 2300 nm and narrow optical cells of <1 mm. Their calibration (shown at top right) is a caustic calibration used when other species are present, such as carbonate and Na₂S. Our lower range of interest is circled on their calibration.

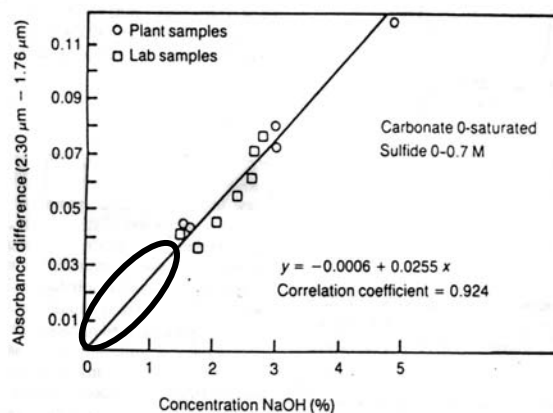
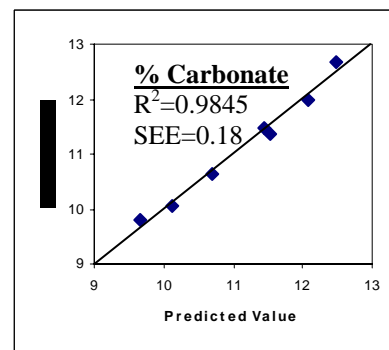
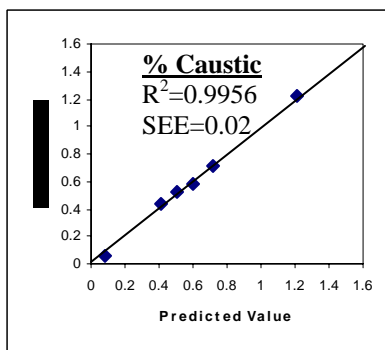


Figure 5. Plot of absorbance difference at 2.30 and 1.76 μm versus percent of equivalent NaOH. Samples contained NaOH, Na₂CO₃, and Na₂S; % NaOH calculated assuming Na₂S was hydrolyzed.

Approach: We used the same procedure as described in our recent article (*Spectroscopy*, 15(2) 40-46 (2000)). Samples were thermostated in a sample cell at 35 °C and analyzed with our PS-2 diode array spectrophotometer. A partial least-squares (PLS) analysis of the spectral calibration set was performed using Galactic Industries' PLSPlus/IQ for GRAMS/32 in the PS-2. This analysis revealed that several analyzing wavelengths were required in addition to a reference wavelength for both measurements. A ChemView® photometer was configured with those wavelengths. The samples were re-run in the ChemView® and their absorbances were recorded. Our OutlierDetect™ program for Microsoft Excel™ was then used to automatically determine the MLR coefficients and outlier parameters (Mahalanobis Distance [M] and Sum of Squares [Q]).

Results: The resulting MLR calibrations are shown middle right. Months of on-line data have demonstrated the linearity of the caustic calibration with a precision of better than ± 0.1. We have extended this approach to another customer's sample set in the 1-10% caustic range with an R²=0.9938 and an SEE of ± 0.47. It is pointed out that temperature conditioning of the sample in the slip stream to better than 2 °C is important, primarily for caustic.



ChemView® has the capability to correct the calibration for wider temperature fluctuations using the measured sample temperature from an RTD sensor. Nevertheless, this places demands on the sampling system containing the fiber optic probe. Due to the likely need of cleaning the sapphire windows in the probe with HCl, we recommend a probe with a Hastelloy® body, sapphire windows and epdm primary o-rings seals.

Conclusions: Our multiple wavelength ChemView® photometer has the sensitivity and stability to measure low levels of caustic in the presence of carbonate. This has been successfully demonstrated on-line. Dynamic outlier detection helps to assure the quality of the analyses in real time.