

Biodiesel Analysis Utilizing AC Small-Signal Impedance Spectroscopy

R.W. Hirthe, PhD and C.J. Koehler, PhD

Paradigm Sensors, LLC

The use of AC impedance measurements to characterize the electrical properties of materials systems provides an alternate means of measuring composition, as well as critical physio-chemical attributes. This methodology has been successfully applied to a variety of fluids, including multiple parameter determinations for biodiesel fuel.

Correlation of IS Data to ASTM Physio-Chemical Parameter Values

The acquisition of electrical impedance data over approximately five decades of AC frequency (employing a proprietary measurement probe configuration) was performed on a substantial population of samples over a defined temperature range (10 - 45° C). The samples investigated include both a variety of B100 fluids (multiple feedstocks), as well as a range of blends from 1-100% derived from commercially available petroleum diesel fuels. Multivariate regression analysis was utilized to develop temperature compensated correlations between I.S. derived variables and 1) blend concentration (ASTM D7371), 2) Total Glycerin concentration (ASTM 6584), and 3) Methanol Concentration (EN 4110).

Blend Concentration Reference Standard

As established in 2007, the reference standard (ASTM D7371) for Bxx blend concentration incorporates the use of mid-infrared spectroscopy. This standard utilizes the region of the IR spectra that reflects the amount of FAME (Fatty Acid Methyl Ester) present in a given blended sample, as well as other regions where absorbance is derived from biodiesel, in a model calibrated from known blend concentrations. Evaluation of samples via this technique has been employed at Paradigm Sensors, LLC, to establish baseline blend concentration values, (volume %), for subsequent correlation to impedance spectral (I.S.) data.

I.S. Blend Concentration Evaluation

Figure 1 illustrates that blend concentration determined from I.S. measurements is very well correlated ($r^2 = 0.998$) with that found using the ASTM FTIR standard. Upper and lower 95% prediction limits for I.S. blend concentration are also shown. The error in the I.S. derived values is within the stated lab-to-lab reproducibility of the ASTM standard, which is on the order 1.6 volume % at the B20 level.

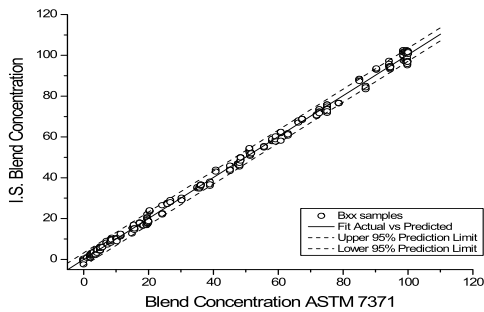


Figure 1. I.S. Estimated vs Specified Biodiesel Blend Concentration Total Glycerin Concentration Reference Standard

The reference standard (ASTM D6584) for biodiesel total glycerin concentration utilizes gas chromatography (GC) for the quantitative detection of glycerol (free), mono, di, & triglyceride species (bound glycerides). Evaluation of B100 samples via this standard technique has been employed both at Paradigm Sensors, as well as an external reference analytical laboratory, to establish a series of samples to be used as references of known total glycerin values (mass %). These reference samples are used for subsequent correlation to the I.S. data.

The fuels investigated include a variety of B100 source fluids (multiple feedstocks), including those in and out-of-specification (ASTM D6751) for total glycerin concentration, as well as a statistical cross-section of biodiesel/petroleum diesel blends.

I.S. Total Glycerin Concentration Evaluation

Figure 2 illustrates that total glycerin content determined from I.S. measurements is well correlated ($r^2 = .93$) with that found using the ASTM D6584 - GC standard. The upper and lower prediction limits of 95% confidence for I.S. predicted TG concentrations are also shown. These errors in the I.S. derived values are within the stated reproducibility of the ASTM standard (the latter is on the order of 50% at the specification limit of 0.24 mass %, and increases to 75% at 0.05 mass %).

Figure 3 reveals that total glycerin can also be determined in Bxx blends via I.S., where the blend TG values are calculated from ASTM D6584 - GC standard measurement of the respective B100 blend stocks. This allows an equivalent B100 blend stock value to be estimated for Bxx samples when blend concentration is also determined (B5 and above).

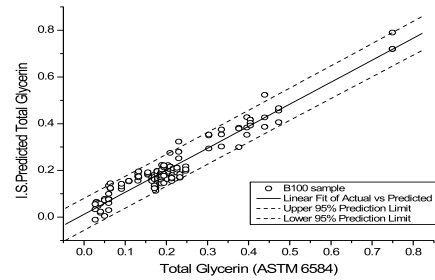


Figure 2. I.S. Predicted vs Specified Total Glycerin Concentration - B100 Fuels

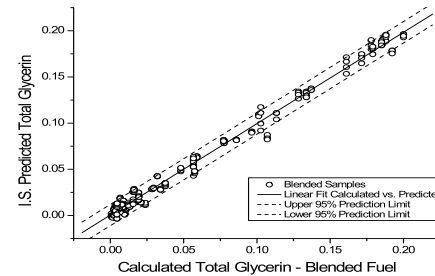


Figure 3. I.S. Predicted versus Calculated Total Glycerin Concentration - Blended Fuels

Biodiesel Methanol Concentration Reference Standard

The reference standard (EN 14110) for biodiesel methanol concentration utilizes head space gas chromatography (GC) for the quantitative detection of methanol. Evaluation of B100 samples per this standard was conducted by an external reference laboratory to establish known methanol values (mass %). These data were then utilized to calibrate a mid-IR spectroscopy model for determining methanol concentration, based upon the 1035 cm-1 peak height (indicative of the presence of methanol) obtained from a 0.2 mm transmission cell, per Figure 4. The fuels investigated were B100 media derived from multiple feedstocks, both in and out-of-specification (ASTM D6751) for methanol concentration (0.2 mass % limit).

I.S. Methanol Concentration Evaluation

Figure 5 depicts the correlation between methanol content determined from I.S. measurements with respect to the values calculated from the calibrated EN GC standard/mid-IR model. This correlation is capable of accurately determining whether a given sample was above or below the ASTM specification limit of 0.2 mass %, and is suitable for "pass/fail" evaluation of B100 biodiesel methanol concentration.

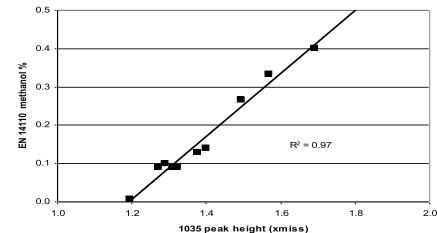


Figure 4. IR 1035 Peak Height cm-1 vs EN 14110 Methanol Concentration - B100 Fuels

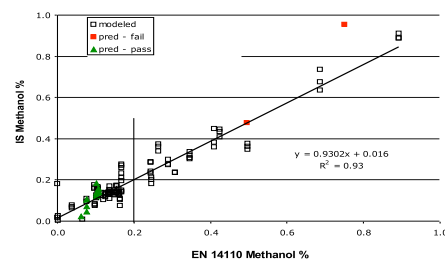


Figure 5. I.S. Estimated vs IR Derived Methanol Concentration - B100 Fuels