Biodiesel Analysis Utilising Alternating Current Small-Signal Impedance Spectroscopy - The i-SPEC™ Q 100 Handheld Analyser

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Alternative fuels, especially ethanol and biodiesel, are rapidly gaining momentum to reduce US and EU dependence on traditional motor vehicle fuels, to improve air quality, and to reduce the carbon footprint. Biodiesel use is accelerating faster than any other fuel due to its use of non-food feedstocks (animal fat and used vegetable oil) and the minimal need to alter diesel engines or fuel delivery infrastructure when using biodiesel. William Thurmond, author of Biodiesel 2020 International (http://www.emerging-markets.com/biodiesel/), says: "A fundamental transition in global fuel production is now happening. In the year 2007, there were only 20 oil producing nations supplying the needs of over 200 nations. By the year 2010, more than 200 nations will become biodiesel producing nations and suppliers. The world is entering a new era of participation by emerging market nations in global green energy production for transport fuels."

Fuel quality is the key issue faced by any biodiesel producer or distributor. Fuel is transported through numerous channels before it gets to the consumer, creating many points along the supply chain at which fuel quality may be compromised. Fuel quality can deteriorate as it is introduced, stored, diluted, or further distributed and sold. Problems in fuel quality can result in clogged filters and injectors, rough engine operation and wear, ruined fuel injection pumps, crank case oil deterioration and long-term engine damage.

The Paradigm i-SPEC™ Q-100:

Paradigm Sensors' i-SPEC™ Q-100 handheld biodiesel analyser can be used by anyone from the biodiesel plant throughout the distribution chain. This analyser uses Impedance Spectroscopy (IS), which has demonstrated excellent correlation to traditional reference methods (Dr. R. Hirthe, AOCS paper 2008), to test the quality and percent of biodiesel blends. The i-SPEC™ can simultaneously measure the blend percent and original total glycerin in B100 used for blends above 5% within minutes, and also tests for total glycerin (TG), methanol and acid number in finished B100 samples. This mobile testing unit is extremely easy to use and provides results within minutes.

These results are quantitative for blend percent within 1-2% and for total glycerin to 0.07%. The determination for methanol and Acid Number is within or out of spec. No interpretations are necessary, nor are subjective observations used to evaluate results.

The Use of Impedance Spectroscopy in Materials Characterisation

The use of AC impedance measurements to characterise the electrical properties of materials systems provides an alternate means of measuring composition, as well as critical physio-chemical attributes. This methodology (see *Figure 2)* has been successfully applied to a variety of fluids, including multiple parameter determinations for biodiesel fuel.

Figure 1. Paradigm Sensors' i-SPEC™ Q-100 Handheld Biodiesel Analyser with Cartridge. The 1 ml sample to be tested is inserted into the single-use cartridge, which is then inserted into the unit.

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 included a variety of B100 fluids from multiple feedstocks, as well as a range of blends from 1-99% derived from commercially available petroleum diesel fuels. Multivariate regression analysis was utilised to develop temperature compensated correlations between IS derived variables and 1) Blend Concentration (ASTM D7371); 2) Total Glycerin Concentration (ASTM 6584); 3) Methanol Concentration (EN 4110); and 4) Acid Number (ASTM 664).

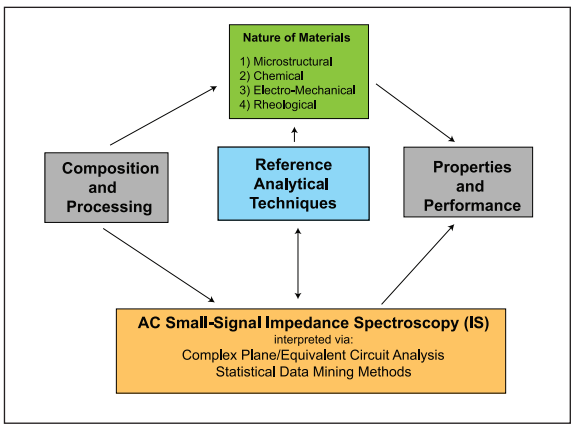

Figure 2. IS as a Materials Characterisation Tool.

The reference methods used to evaluate IS capabilities are as follows:

Blend Concentration (2-99%)
- Mid Infrared Spectroscopy (ASTM 7371)

Total Glycerin (0.03 - 0.7 %)
- Gas Chromatography (ASTM 6584)
- SafTest

Methanol (0.02 – 0.9 %)
- Gas Chromatography (EN 14110)
- Mid Infrared Spectroscopy

Acid Number (0.2 – 3.5)
- Titration (ASTM 664)
- SaFTest

Blend Concentration Correlation of the IR Reference Standard to IS

Established in 2007, the reference standard (ASTM D7371) for Bxx blend concentration incorporates the use of mid–infrared spectroscopy. This standard utilises the region of the IR spectra that reflects the amount of Fatty Acid Methyl Ester (FAME) 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 data.

Figure 3 demonstrates that blend concentration determined from IS measurements is very well correlated (r^2= 0.998) with that found using the ASTM FTIR standard. Upper and lower 95% prediction limits for IS blend concentration are also shown. The error in the IS derived values is within the stated lab-to-lab reproducibility of the ASTM standard, which is on the order of 1.6 volume % at the B20 level.

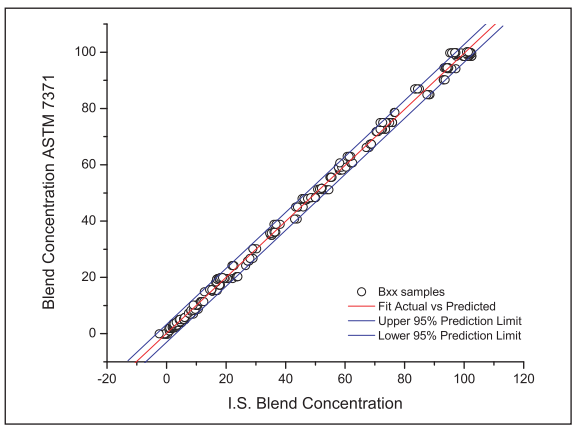

Figure 3. Blend Concentration ASTM 7371 versus IS Blend Concentration

Correlation of the Total Glycerin (TG) Concentration Reference Standard Method to the IS Spectroscopic Data

The reference standard (ASTM D6584) for biodiesel total glycerin concentration utilises gas chromatography for the quantitative detection of glycerol (free), mono, di and triglyceride species (bound glycerides). Evaluation of B100 samples via this standard technique has been employed at Paradigm Sensors and an external reference analytical laboratory in order 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 IS 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.

Figure 4 illustrates that total glycerin content determined from IS measurements is very well correlated (r^2= .93) with that found using the ASTM D6584 - GC standard. The upper and lower prediction limits of 95% confidence for IS predicted TG concentrations are also shown. These errors in the IS 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 %).

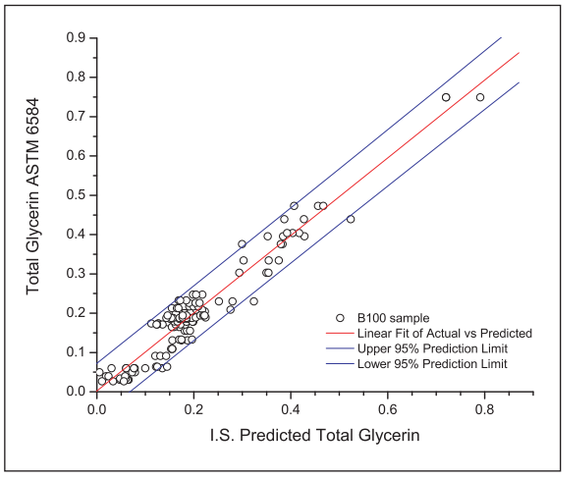

Figure 4. Total Glycerin ASTM 6584 versus IS Predicted Total Glycerin

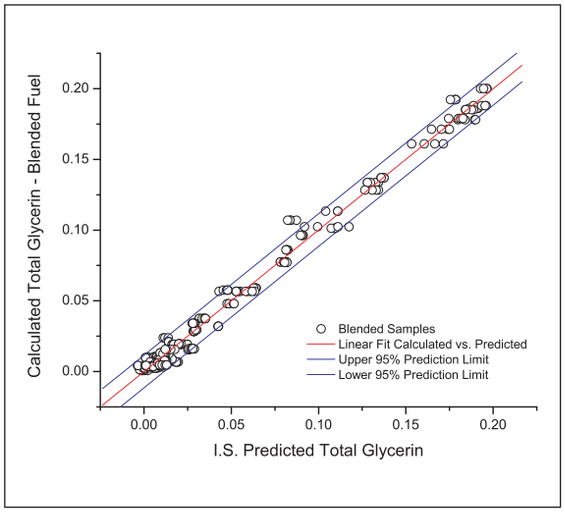

Figure 5. Calculated Total Glycerin in Blends vs IS Predicted Total Glycerin

Figure 5 reveals that total glycerin can also be determined in Bxx blends via IS when 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 (above 5%).

Biodiesel Methanol Concentration Reference Standard Correlation to IS Spectroscopic Results Using GC/IR Model Calculations

The reference standard (EN 14110) for biodiesel methanol concentration utilises 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 utilised 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. 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).

Figure 6 depicts the correlation obtained for methanol content as determined from IS measurements with respect to the values calculated from the calibrated EN GC standard/mid-IR method. This correlation is capable of determining whether a given sample is above or below the ASTM specification limit of 0.2 volume%, and is suitable for "pass/fail" evaluation of B100 biodiesel methanol concentration.

Acid Number Correlation to IS Spectroscopic Results

The reference standard (ASTM D664) for biodiesel acid number utilises potentiometric titration for the determination of acid number. Evaluation of B100 samples via this technique and SaFTest has been employed both at Paradigm Sensors, as well as an external analytical laboratory, to establish reference acid number values (mg KOH/g) for subsequent correlation to I.S. data.

IS measurements were then correlated to the ASTM reference method values, as is shown in *Figure 7*. This correlation is capable of determining whether a given sample is above or below the ASTM specification limit of 0.5, and is suitable for "pass/fail" evaluation of B100 biodiesel acid number.

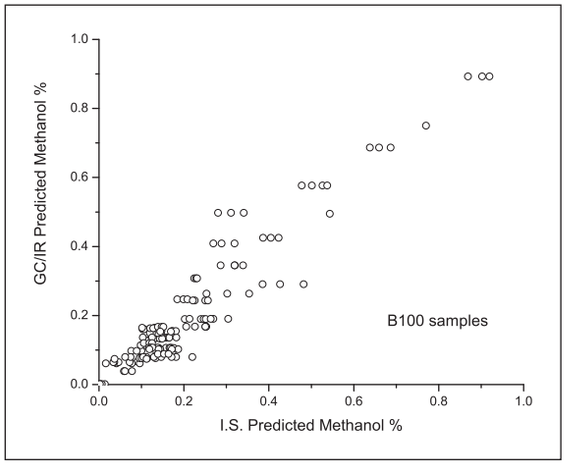

Figure 6. GC/IR versus IS Estimated Methanol Concentration – B100

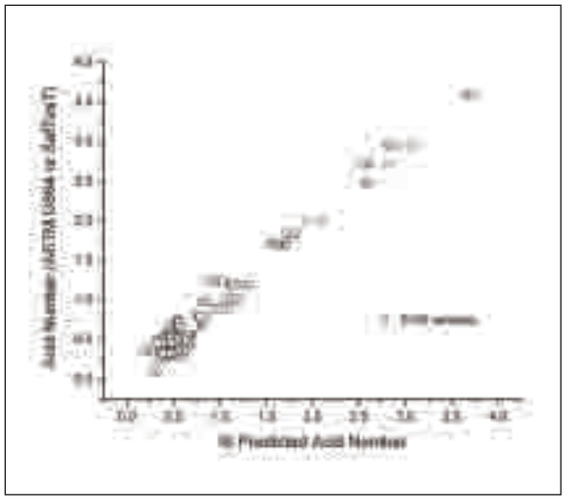

Figure 7. Acid Number D664 versus IS Predicted Acid Number

Conclusion

The i-SPEC™ Q-100 is able to determine blend concentration in blends from 2 - 99% and total glycerin in B100 from 0.03 - 0.5%. Pass/Fail determinations of methanol and acid number enable those in the biofuel industry to rapidly assess fuel quality and the presence of contamination, both at the plant and throughout the distribution chain. The reliablity and ease of use of the i-SPEC make it an essential analyser for those interested in assuring the quality of biodiesel produced and distributed in today's market.