Raman vs. FTIR Process Analyzers for In-Line Blending Use

Ara Barsamian
Refinery Automation Institute, LLC
Jabarsa@refautom.com: Tel: +1-973-644-2270

This paper was provoked by recent interest in using Raman and other spectroscopic methods for certifying in-line blends, particularly after ASTM sponsored a working group in D02 [1] to work on practices (e.g. using generalized calibrations for direct match technique) that would be acceptable to FTC (for certifying octanes) and other US government agencies.

Bottom line: spectroscopic methods work, but they are highly dependent on the quality of modeling and design of spectrometers…

1. Background

Turbulent economic times are pressing refiners to increase profits to simply stay in business. We feel acutely this pressure in gasoline and diesel blending since we make an easy target for news media and politicians readily pointing fingers at us to escape public wrath for their incompetence and bias against the oil industry.

Well, how do we increase profits? By lowering production costs (something alien to US Congress).

We do this "magic" by implementing well-established and proven techniques, such as in-line blend property control (1965) to insure we meet specs as close as possible to legal limits, and equally important, that we can certify in-line blends "on the fly" using on-line analyzers (1965 – first in-line blend release based on knock engines!).

In US, where we typically produce about 100 to 150kbpd of various grades of gasoline (a big "sea" of gasoline worth a couple of billions a year to the refinery), stopping the blending process because of analyzer failure is usually not acceptable because you might miss a shipment (waiting tanker demurrage, missing your pipeline parcel injection time slot), and you never hear the end of it from planning and economics, traders, "instant experts", your boss signing your paycheck, aso…

The first generation of on-line analyzers were electro-mechanical contraptions, like CFR knock engines (1929), Reid Vapor Pressure analyzers, D86 Distillation, etc., one for each property to certify for releasing the blend to "sales". As one can imagine, the costs piled up, not just the initial acquisition cost, but also maintenance costs, spares, training…and each technology used different design, parts, method of operation and maintenance, a mixture of mechanical, electrical and electronic parts…enough to drive the blending people crazy.

In the 1970's refiners were looking desperately for more reliable and cheaper technology for on line analysis, and this how the spectroscopic methods were "born" with Ashland's pioneering effort with "Infra-Tane"[TM] octane analyzer using NIR spectroscopy, and then we had a "booming" field with every oil major developing its own proprietary method.

2. Spectroscopic Analysis Methods

Today we use three different spectroscopic techniques for on-line gasoline analysis

- Near Infra Red (NIR), Mid-IR
- Raman
- Nuclear Magnetic Resonance (NMR); also known as Magnetic Resonance Analyzer (MRA)

Of these three methods, we will look at the first two because they turned out to be easier to implement and use. Nevertheless, all are INFERENTIAL type of measurements relying on models to predict properties based on spectral analysis.

The proliferation of "optical" spectroscopic methods for in-line blend property measurements, e.g. IR, NIR, Mid-IR, and Raman type of spectroscopic techniques produced various confusing claims that "method A is better than method B", thus it would be useful to briefly review their basic functionality and usefulness for blending. All these methods are available in direct spectra (so-called dispersive) or Fourier Transformed (FT) spectra measurement technique, IR or FTIR.

Issues to consider are reliability and robustness of property predictions, ease of developing and implementing property prediction models, and field equipment reliability and cost.

2.1 Basics of Raman and FT-IR Spectroscopy

There are two classes of spectroscopic measurement: DISPERSIVE (Fig. 1) and Fourier-Transformed (FT) which apply to both IR/NIR and Raman (Fig 2).

A dispersive method simple involves passing a light (reflected or through a sample) through a spectrograph and then a multi-channel detector to determine the spectra. In the FT method, we combine the direct light and the reflected light through a Michelson interferometer; the resulting interferogram is FT-transformed to get the spectra.
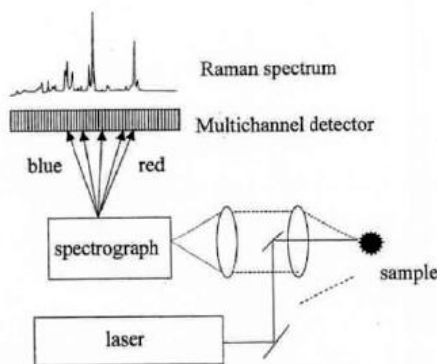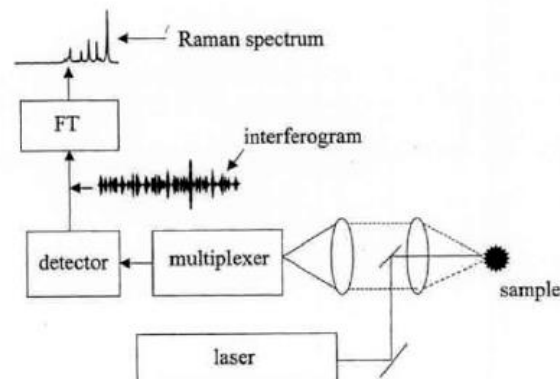
Fig. 1 Dispersive Raman Spectrometer[2]   Fig. 2 FT-type Spectrometer[2]

2.1.1 Raman Basics

Raman method illuminates a sample with a <u>monochromatic light</u> from a laser; the illuminated sample material gives off light of a different color (Raman shifted light, which means a different wavelength or color, see Fig. 3). The Raman effect light has specific spectral peaks which indicate specific composition, and the peak intensity indicates the concentration.

It is a linear process, which means that models to predict properties of interest are simpler to build and more robust than IR methods (MIR, NIR, FT-IR).

On the other hand, the sample also fluoresces (like a chest X-ray phosphor screen) and also the primary illuminating beam "punches thru" the sample. This requires careful filtering out of these spurious lights. The actual Raman shift light is very weak, which means that special measures have to be taken to "intensify" it so it can have enough "strength" (S/N ratio) to be measured.

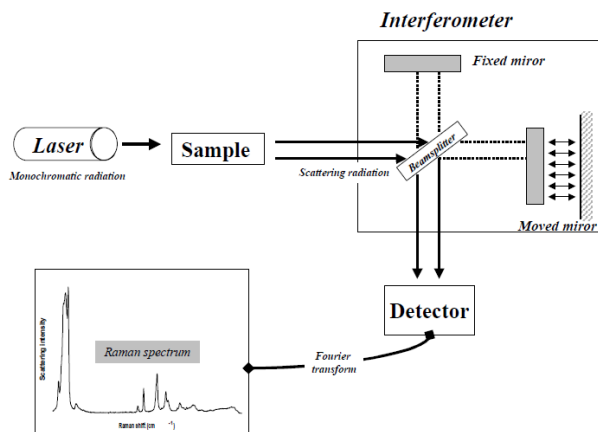The Raman spectrum is illustrated in Fig. 6.
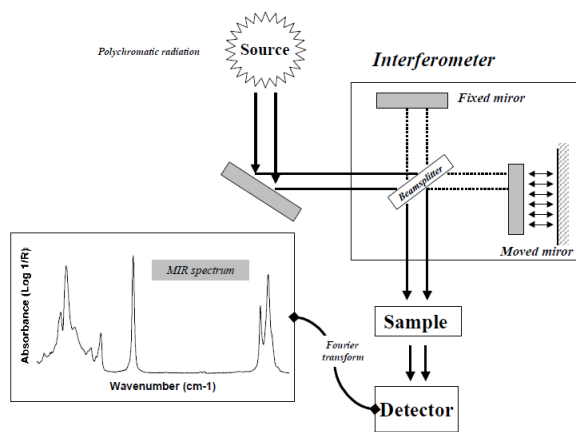
Fig. 3 FT Raman Spectrometer[3]   **Fig. 4 FTIR Spectrometer[3]**

2.1.2 FT-IR Basics

The FTIR method illuminates a sample with a <u>multispectral light</u> and measures the absorbance attenuation of the beam of light at various wavelengths as it passes through the sample (Fig. 4). The challenge here is that some of the compositional spectral lines overlap, so they are partially SUPERIMPOSED (and look "smeared"), thus one cannot accurately separate individual component spectral lines and peak intensities, and this makes the prediction model and the type of chemometric tool used much more complicated.

2.1.3 Property Prediction Modeling Basics and Practices

All spectroscopic methods require a mathematical model that ties the "spectra" to a "property", e.g. octane.

The mathematical tools to build these property prediction models use "Chemometrics" which combines math with statistics, e.g. PLS (partial least squares), PCA (principal component analysis), etc.

In theory, the Raman spectral lines being linear with composition concentration would require fewer samples and make it easier, faster, and cheaper to develop, but that is not always the case. The samples needed to build a robust and reasonably accurate model are specified in the ASTM E1655 practice "Modeling Bible" [5], and there are no short-cuts.
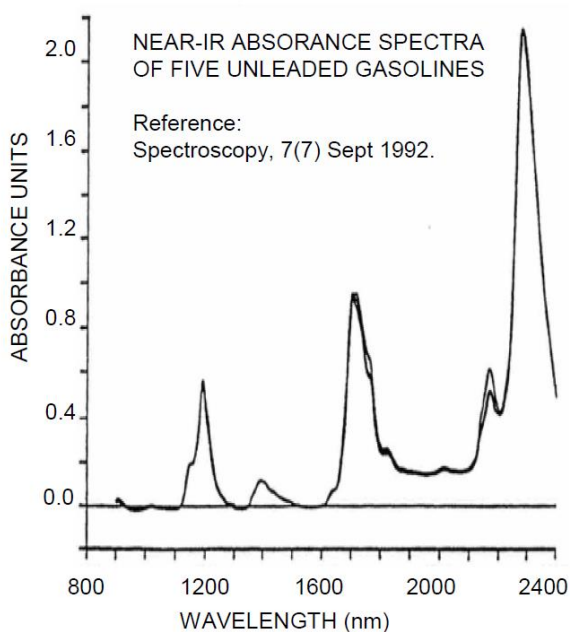
Fig. 5 FTIR Spectrum[4]   Fig. 6 Raman Spectrum[4]
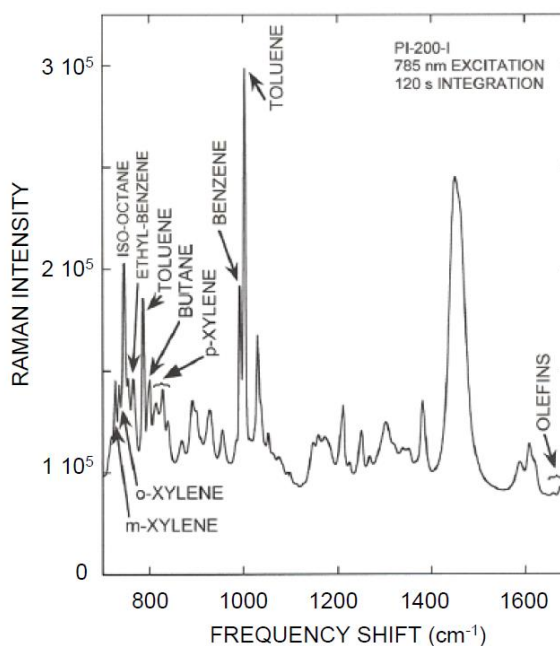
Established industrial practice is to use a Lab analyzer to build property prediction models which are then transferred to on-line analyzer(s) on the in-line blender header; this process is referred to as "**Calibration Transfer**".

For example, a successful calibration transfer produces model prediction differences between a Lab analyzer and a field on-line analyzer much closer than ASTM repeatability of the test method, e.g. octanes should agree within 1 standard deviation, or about 0.1 ON. To be able to do this is very demanding of the precision of optical system design, manufacturing tolerances, and thermal stability of the spectrometers, which is not always the case.

Mechanically, a model is built using fuel sample spectra measured by the Lab analyzer which is then correlated to actual properties measured using accepted conventional analysis methods, e.g. ASTM D2885 for octanes.

2.1.4. Enhanced Capability Through Fourier Transform (FT) Techniques

It is important to understand that Fourier Transform (FT) techniques apply to both IR, NIR, Mid-IR, and Raman type of spectroscopic instruments.

Applying FT techniques improves the "sharpness" of the spectra and increases the signal to noise (S/N) ratio allowing to "see" very weak spectral lines (thus lower concentrations). The FT technique is a bit more complicated, the spectrometer and/or interferometer are a bit more complex than a simple dispersive grating and thus potentially more expensive.

What is Fourier Transform (FT)?

A FT-type instrument works in two steps:

1. first collects an Interferogram (combination of direct polychromatic reference light beam with the transmitted light beam spectrum through the sample using a Michelson interferometer (like in High School elementary physics class)
2. second, it uses "Fast Fourier Transform Algorithm" mathematics to convert an interferogram (which looks like a shapeless blob) into a frequency-domain spectra identifying hydrocarbon components (like a hologram). The resulting spectrum has a much higher resolution (better discerning closely spaced spectral lines, and thus composition) and a higher signal to noise ratio (higher sensitivity detecting low concentrations).

The benefits of using FT type instruments justify the more parts, and higher cost when compared with the ordinary "dispersive" type instruments like straight NIR or Raman.

3. Raman Vs. FT(IR, mid-IR, NIR)

Before briefly comparing Raman with IR/FTIR technology, one needs to put things in perspective: there are over 20,000 NIR/FTIR instruments in the field vs. less than 2000 Raman instruments. Most of the instruments are used in pharmaceutical and foodstuff industry, not refining. Theoretical advantages do not always translate into actual experience; in **refining the experience was mixed**, so it is good practice to thoroughly investigate technologies before using them!

Raman **Theoretical** Advantages

- Property prediction model is easier to make, and more robust than NIR

- o Chemical and molecular information is rich with high specificity (well defined spectral lines) compared with NIR
- o Raman spectral bands are usually sharper and interference weaker than NIR, making data analysis easier
- No interference from water
- No sample conditioning required
- Probe is Temperature insensitive if swings are less than 10 deg C/hr

Disadvantages

- Raman spectrograph and Raman laser more complicated than FTIR
- Spectrometer optical path requires tight temperature control (a must)
- Calibration transfer between instruments is very sensitive to spectrometer temperature control
- Laser aging impacts accuracy
- Smaller number of Raman instruments in the field than FTIR
- Small number of companies selling Raman for blending applications and support
- Life-Cycle-Cost and initial price of equipment could be higher, although the cost of modeling could theoretically be lower

4. Conclusion

What is the best spectroscopic technique for in-line blend property measurement? Remember to put things in perspective:

- That we have to deal with ASTM precision of measurement, don't expect zero errors, but use the ASTM reproducibility (or repeatability for in-line measurements) as a guideline
- Property prediction model development takes know-how (like ASTM E1655) [5], not brute-force feeding of each blend result in the prediction model
- The "goodness" of a spectroscopic method is defined against ASTM precision numbers, and ASTM performance measurement practices (like ASTM D6122) [6], not claims in a magazine article
- If you use wrong methodology for building the model, it will never work right
- Modeling requires interaction between planning, Lab, blending, and vendor chemometrician
- Quality of spectroscope design is crucial for accuracy and usable calibration transfer
- Expensive does not mean guaranteed success
- Vendor proven experience in fuel blending application and high quality equipment and design is key to success
- Always buy with "process performance guarantees" demonstrated over a minimum of 6 months (no fiddling with the model); the extra x% you pay will repay in a matter of weeks…and happy end users

There are no short cuts or "magic". The best way to decide what is best for a specific application is to rent one for about six to nine months to gain experience by using it preferably, in parallel with conventional in-line blender measurements.

During the site testing, spend 2 to 3 months to build and check models; the next 6 months is to check robustness of models (a model should be insensitive to crude changes, to seasonal grade variation, and minor process upsets, e.g. reformer octane). If the "finished" model requires any adjustments in 6 months (assuming no major process changes or significant new components), you have a poor model…most likely because of not following the steps in the ASTM E1655 practice…

If the results during this "post-finished model" site evaluation are positive, buy it.

5. Acknowledgement

References:

[1] Mertens, D., "ASTM D02-WK38018 Draft: Standard Test Method for Spectroscopic Determination of Properties of Spark Ignition Fuels Using Direct Match Comparison Technique", (June 2012)

[2] McCreery, R.L., "Raman Spectroscopy for Chemical Analysis", 3rd ed., Wiley, NY(2000)

[3] Baeten, V., Dardenne, P., "Spectroscopy: Developments in Instrumentation and Analysis", Grasas y Aceites, p.55, V53, 1, 2002

[4] Smith, L., "Process Instruments Inc. Application Brochure", p.4 (2013)

[5] ASTM E-1655 "Standard Practices for Infrared Multivariate Quantitative Analysis", (2005)

[6] ASTM D-6122 "Practice for Validation of Performance of Multivariate Online, and Laboratory Infrared Spectrophotometer Based Analyzer Systems Analysis", (2013)