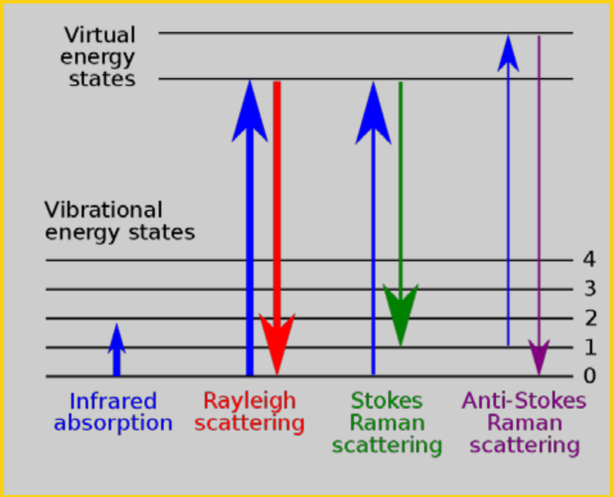
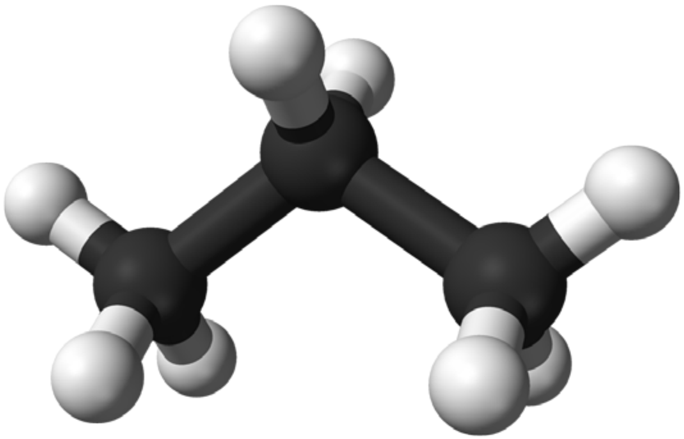
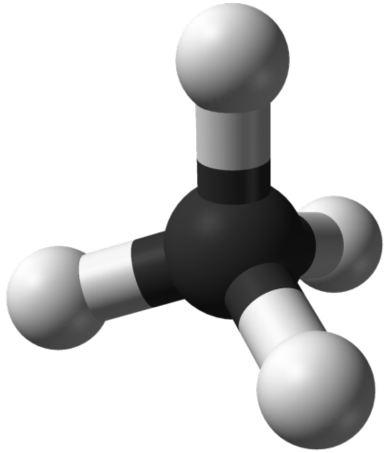
FIELD TEST OF A RAMAN APPLICATION FOR LNG

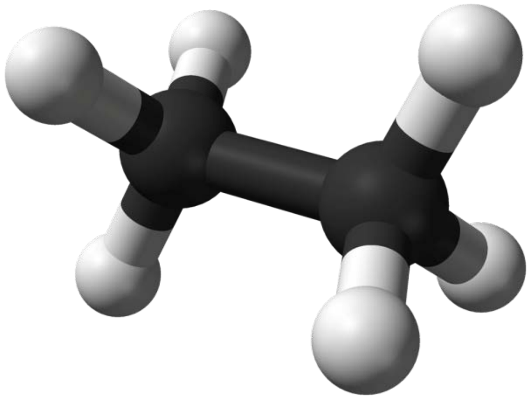


Hans van der Poort, Shell Projects and Technology
Scott W. Brians, Scientific Instruments, Inc.

RAMAN PHYSICS

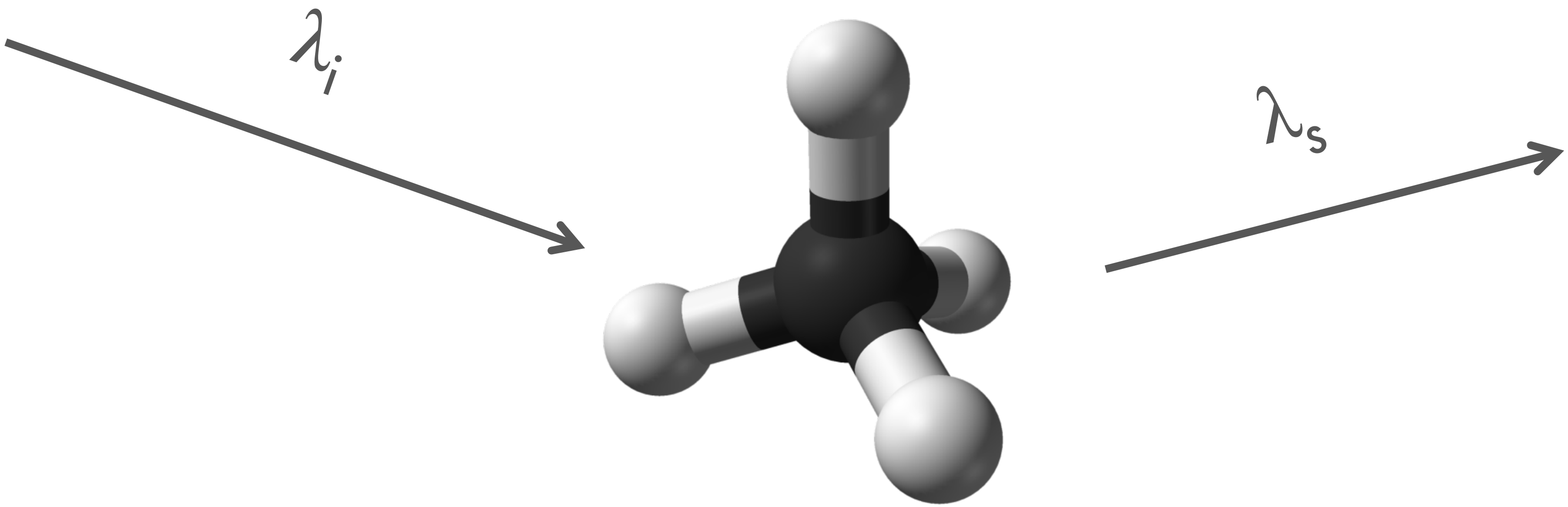






Unique

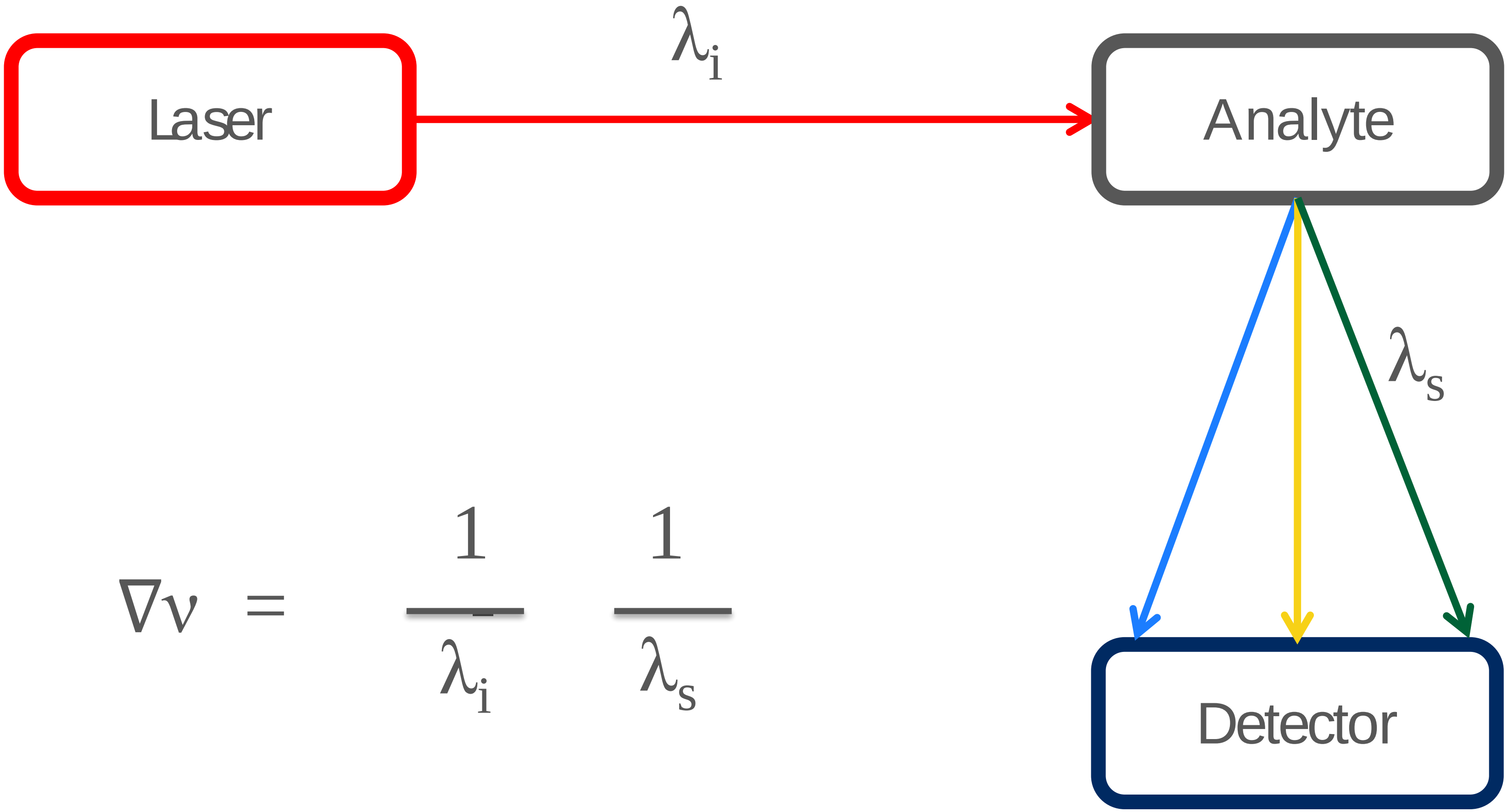
- Bonding Structure
- Vibrational Mode



Vibration

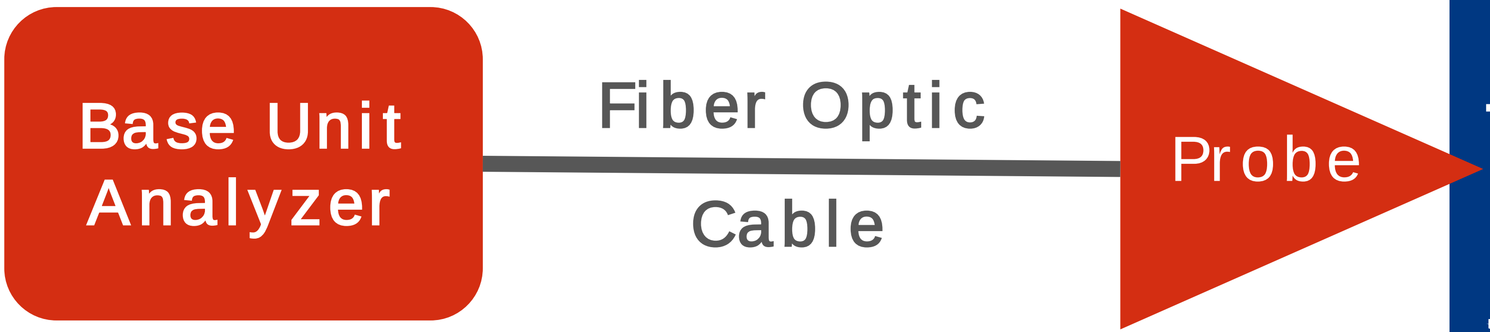
$$\nabla \nu = \frac{1}{\lambda_i} - \frac{1}{\lambda_s}$$

RAMAN SPECTROSCOPY



$$\nabla\nu = \frac{1}{\lambda_i} - \frac{1}{\lambda_s}$$

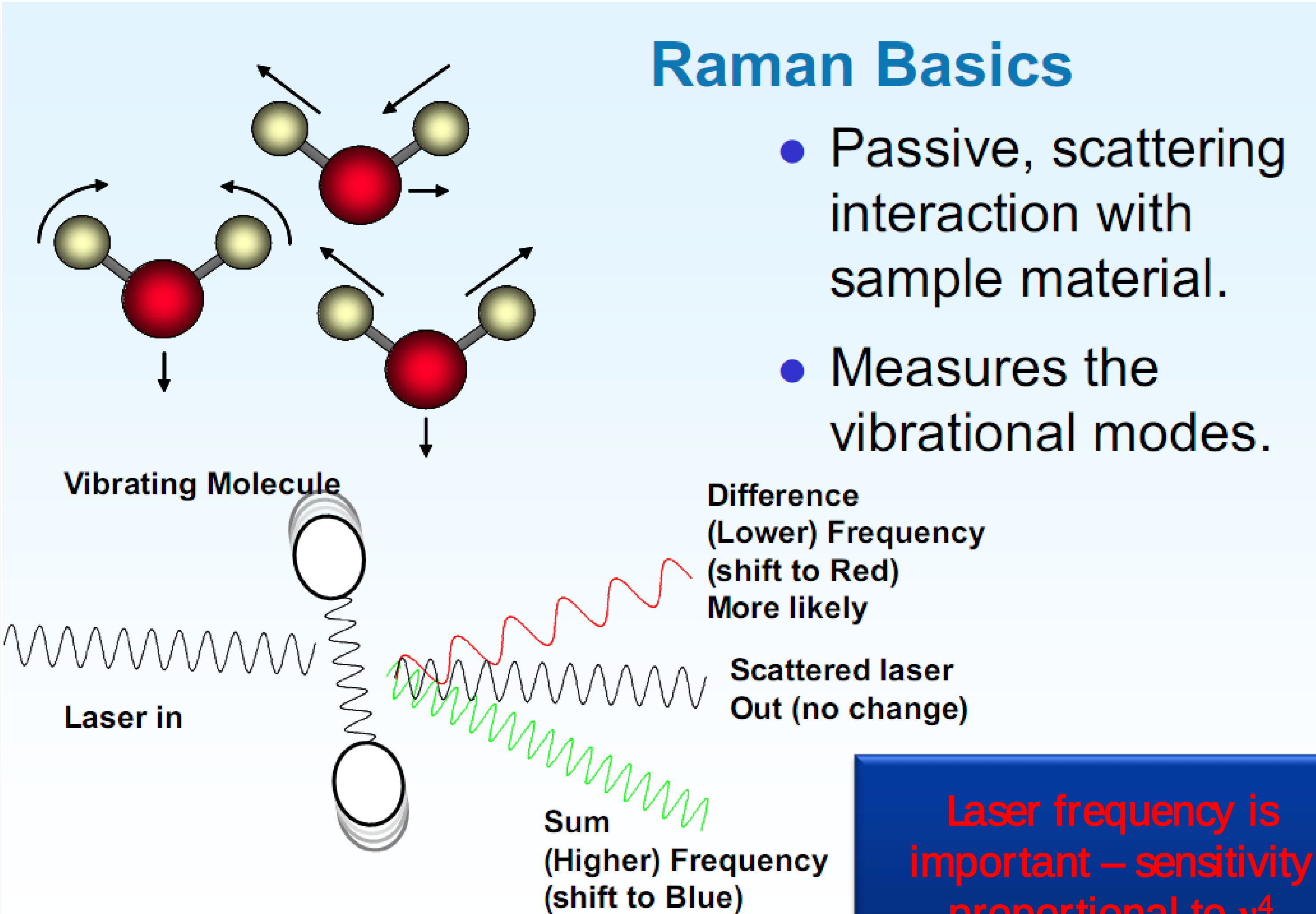
RAMAN SPECTROSCOPY EQUIPMENT



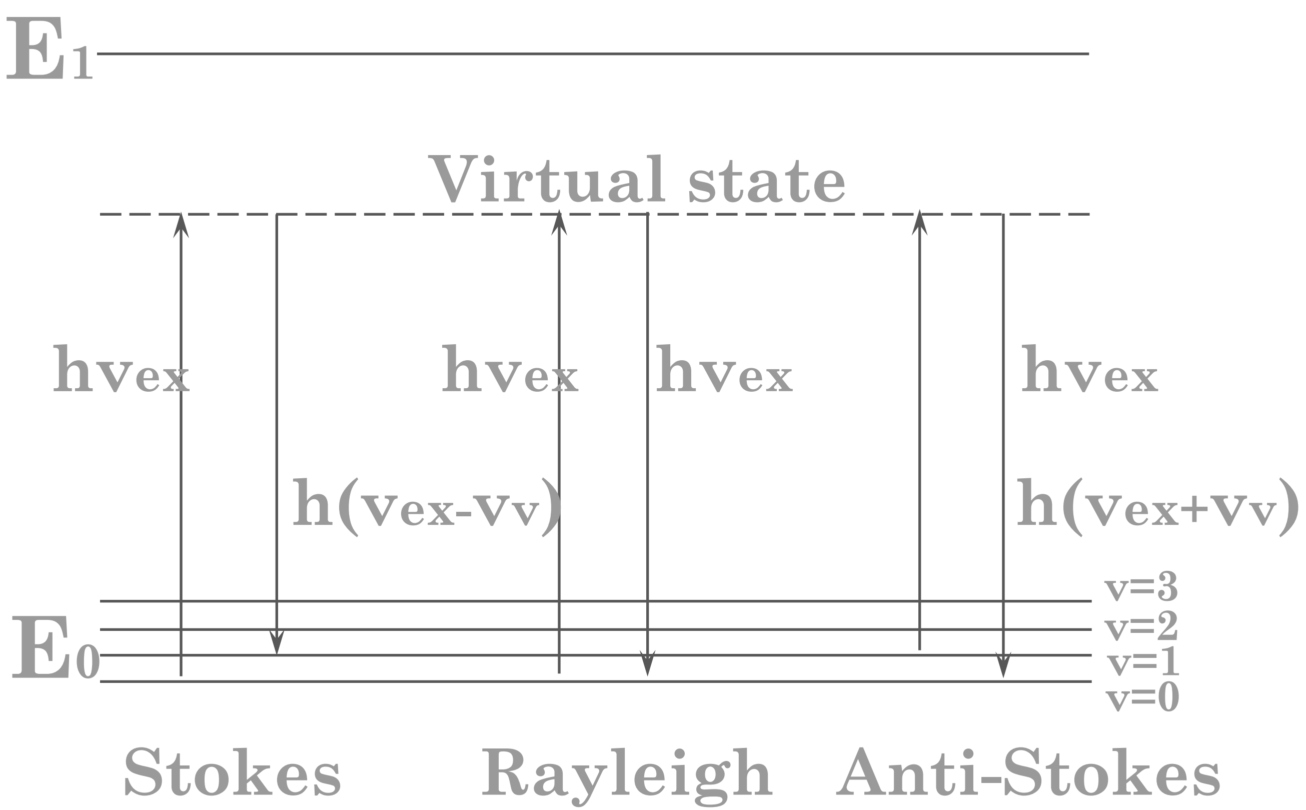
Measurement Steps

1. Laser generated at Base Unit
2. Laser guided to Probe
3. Laser enters LNG at Probe Tip
4. Raman Scattering occurs in LNG
5. Scattered Light collected by Probe
6. Scattered Light guided to Detector in Base Unit
7. Analysis of Specie and Relative Abundance

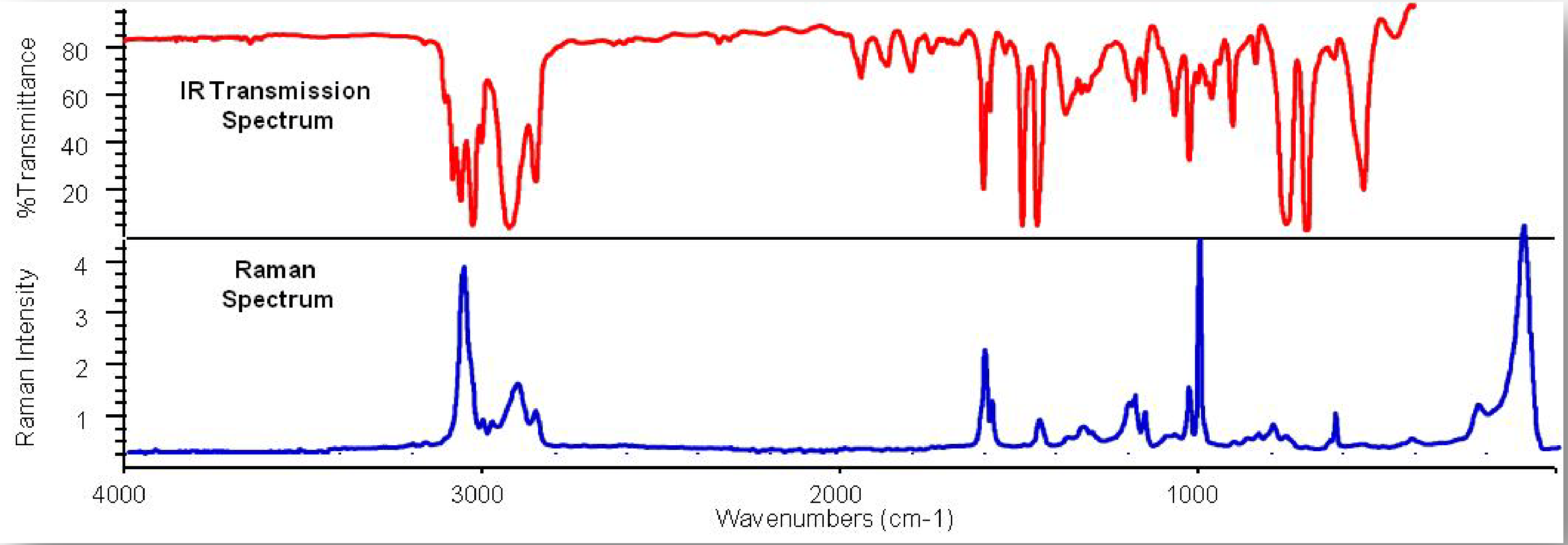
RAMAN BASICS



Laser frequency is important – sensitivity proportional to ν^4


E1
Virtual state
hvex
hvex
hvex
hvex
h(vex-vv)
h(vex+vv)
E0
v=3
v=2
v=1
v=0
Stokes
Rayleigh
Anti-Stokes

RAMAN COMPARED TO MID-IR



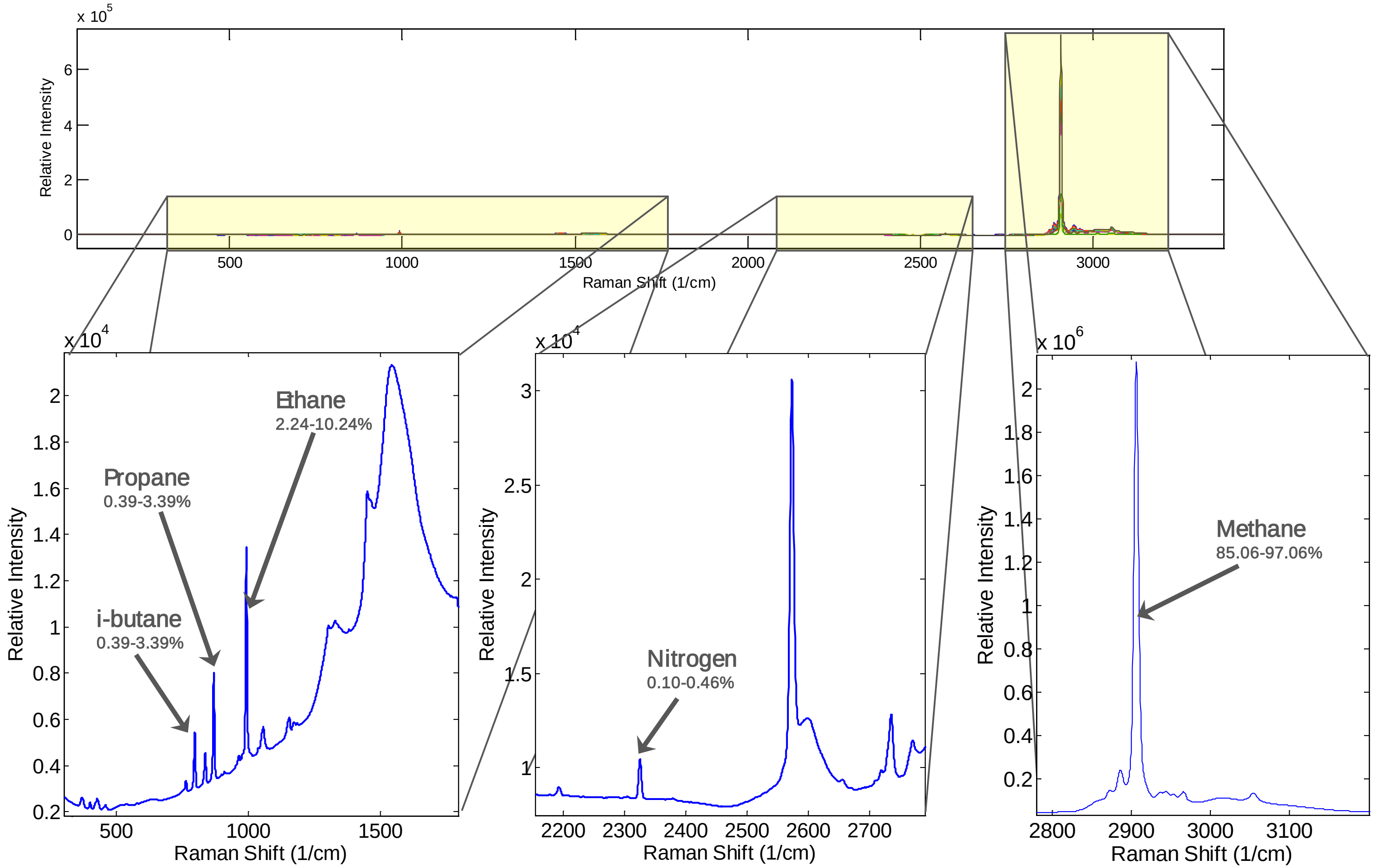
Raman spectroscopy provides information on the chemical make-up of molecules by observing the vibrational energies of the molecules.

Raman is complementary to mid-IR BUT different intensities and selectivity.

Raman spectra tend to be less cluttered than IR, much less affected by water.

The Chemical Specificity of mid-IR, but with the ease of implementation and sampling of NIR!

LNG RAMAN SPECTRUM



WHY USE RAMAN SPECTROSCOPY?

- Combines advantages of NIR and mid-IR
- Sample through common windows / containers glass, sapphire, polymer
- Utilize fiber-optics
- Direct insertion of immersion probes into process
- Fast analysis
- No sample preparation
- Aqueous Samples – easy
- Specificity for robust methods
- Univariate or multivariate calibrations
- The only? technique that can quantify diatomics without removing sample from process

TEST LOCATION

Test location at Hazira LNG Terminal in India.

History

- Started with manual sampling (2005)
- Piston sampler with GC (2008)
- Raman testing

Reason to select Hazira

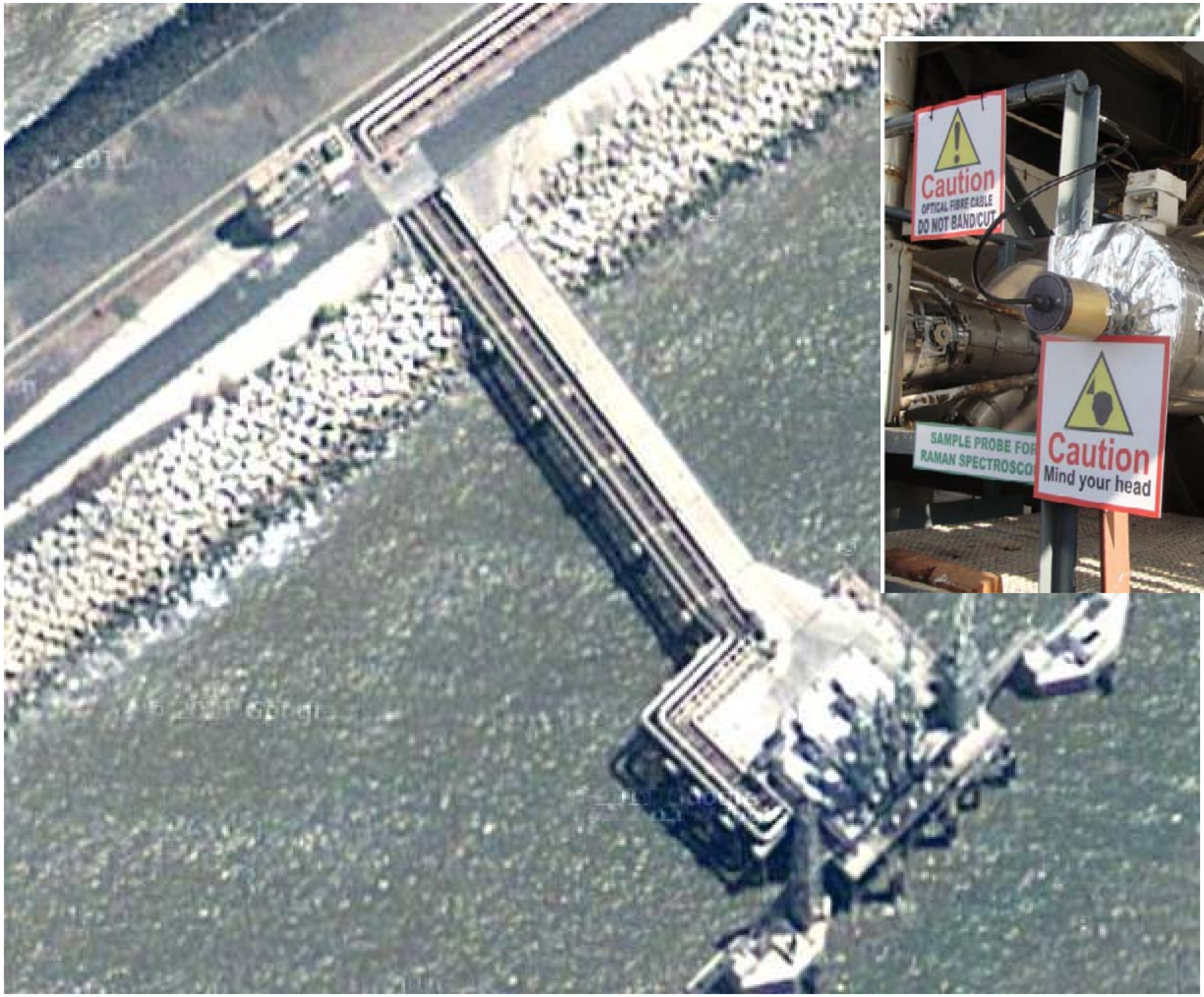
- Wide range of cargoes

INSTALLATION

The Raman spectroscope, holding the laser source is installed in the Jetty substation located over 300 meters from the sampling point.

Sample probe is installed next to the off-take for the LNG sampling system in order to be able to properly compare the results of the Raman against the online GC.

INSTALLATION



QUALITY ASSURANCE

The repeatability of the online GC was determined during the initial phase of the Raman test.

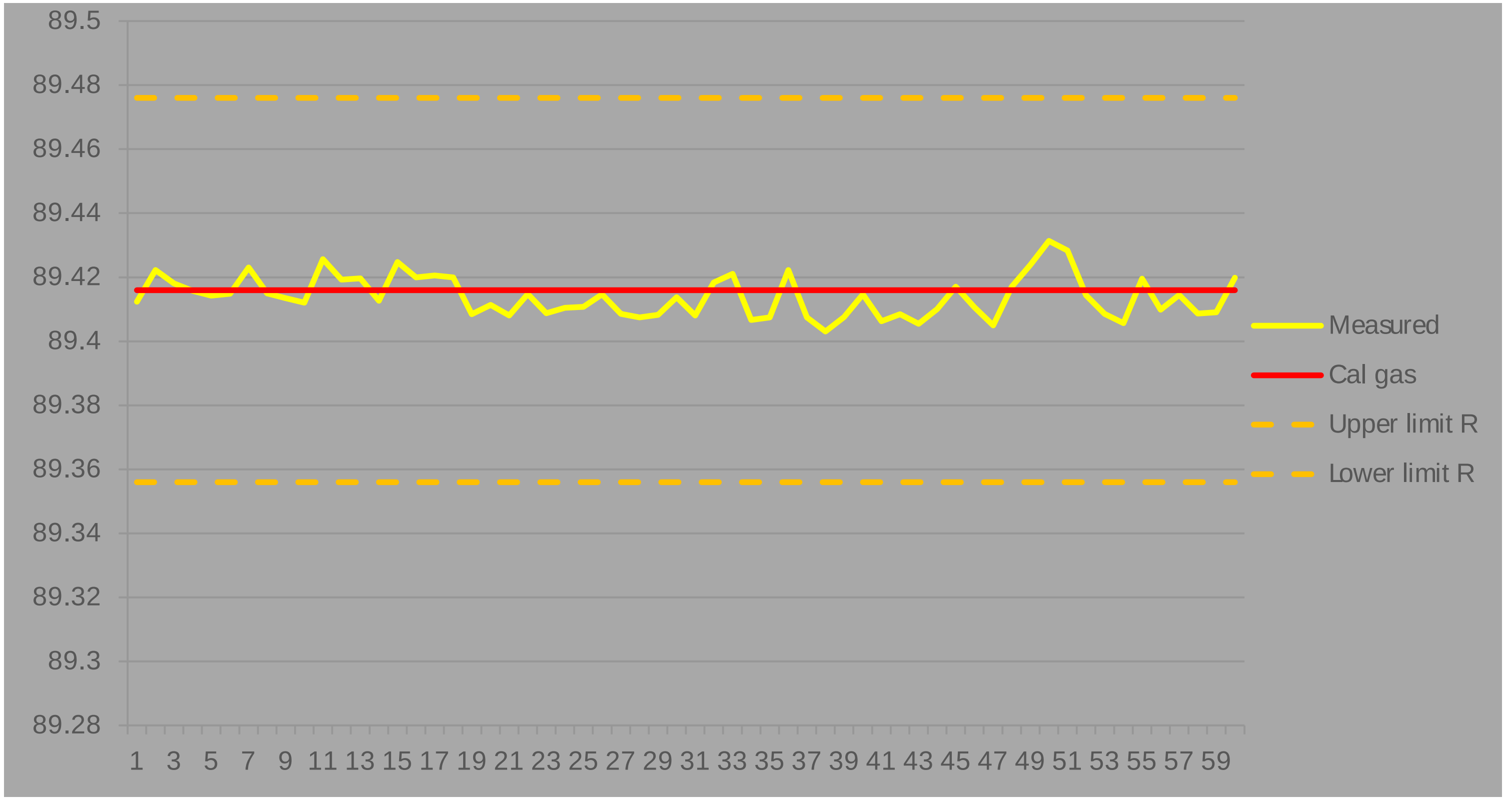
For this a certified calibration gas was analyzed 60 times with the online GC.

The repeatability was calculated using the algorithm as described in ISO 6974-5.

All repeatability's for the individual components did meet the international criteria of both ISO 6974 and GPA 2261 for all components.

QUALITY ASSURANCE

Repeatability result on Methane for online GC



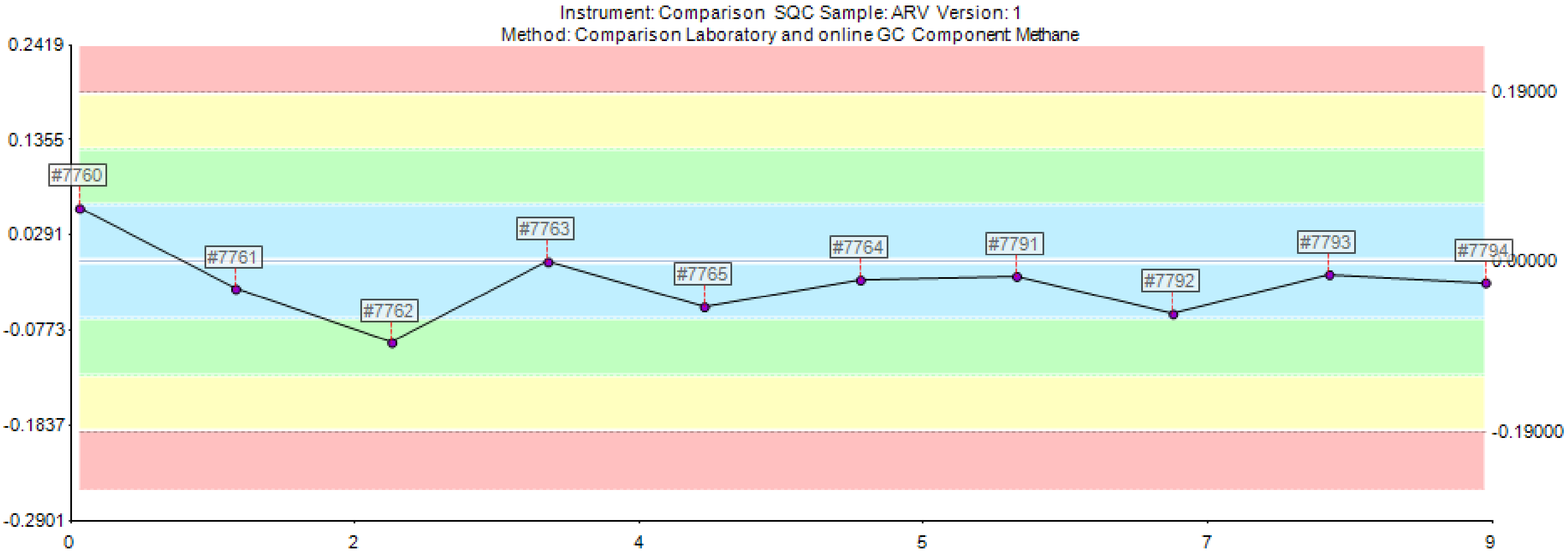
“R” is based on ISO 6974-5

QUALITY ASSURANCE

Online versus offline GC

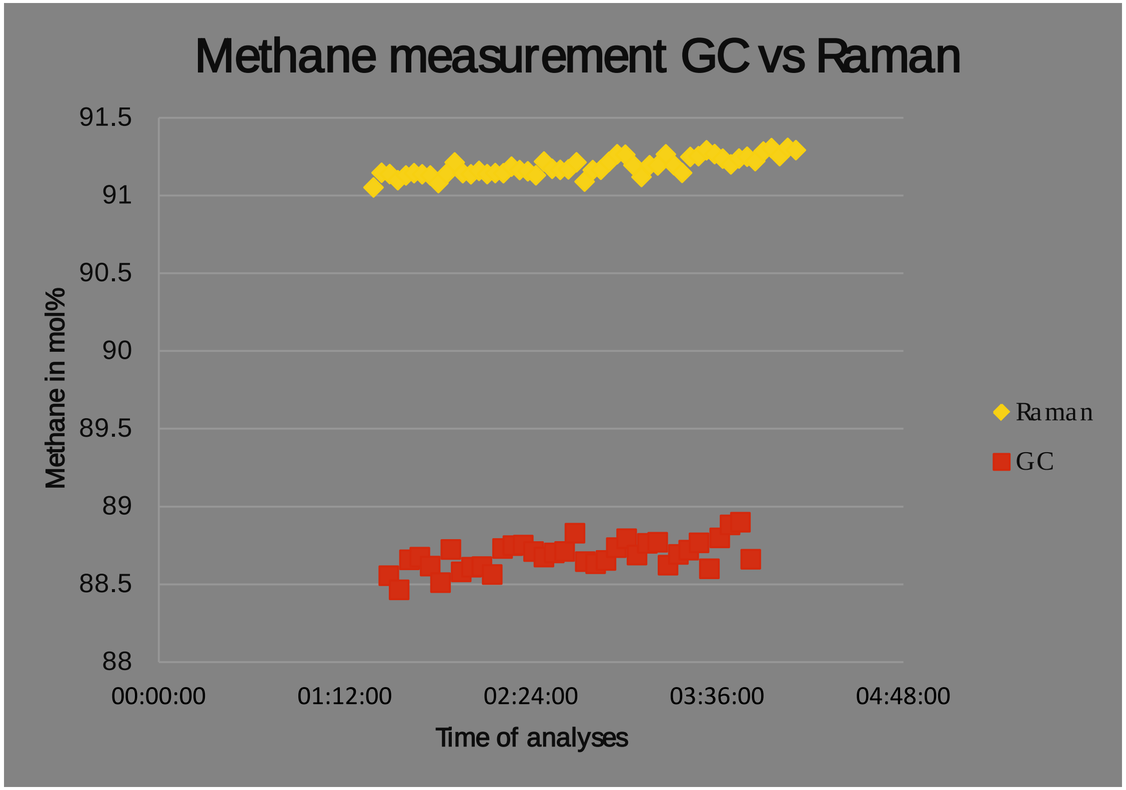
- Additionally the online and offline GC analyses results were compared
- As criteria we have used the Reproducibility of ISO 6974-3 (offline) and ISO 6974-5 (online) ($\sqrt{(0,07^2+0,18^2)}$).
- The delta plot shows that we do not have any significant difference between the laboratory and online samples.

Online compared to offline for Methane



INITIAL RESULTS OF THE RAMAN ANALYSES

The initial results of the Raman test showed a significant offset in the composition compared to the online GC analyses data.



INITIAL RESULTS OF THE RAMAN ANALYSES

Initial reasons for problems

- The vendor expected a number of reasons for the initial significant deviation of results.
  - Calibration of the fiber optics and probe.
  - Fouling on the optical windows inside the spectrograph.

INITIAL RESULTS OF THE RAMAN ANALYSES

Calibration of the fiber optics and probe

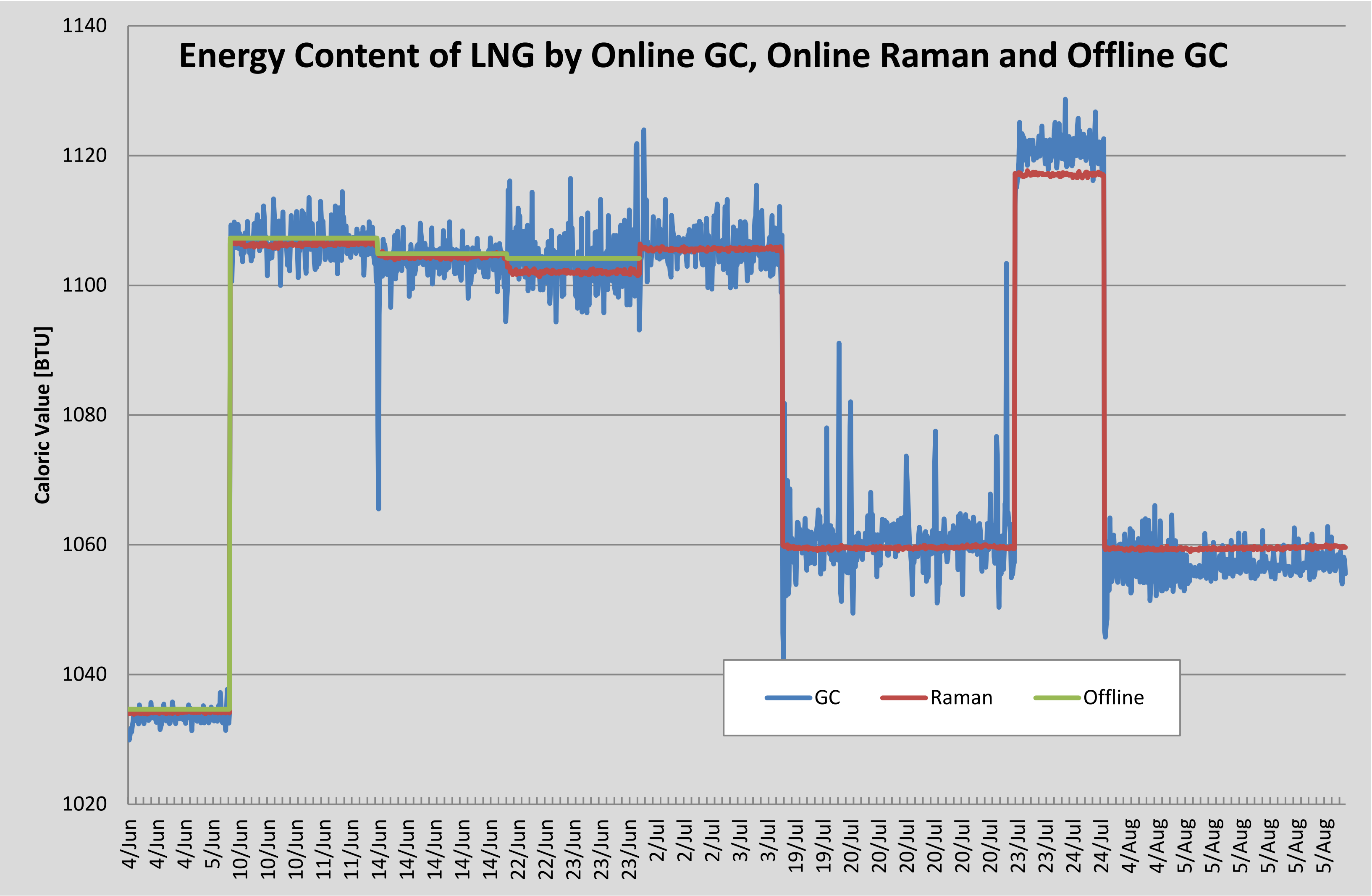
- During the initial installation of the Raman system, the vendor has to correct for any intensity losses caused by the fiber optics and the sample probe this was not properly done, an incorrect correction spectrum was used to subtract the noise of the fibers from the main Raman spectra.
- Unfortunately this was done before the raw data was saved, making it impossible to reprocess the data.

INITIAL RESULTS OF THE RAMAN ANALYSES

Fouling on the optical windows inside the spectrograph

- An epoxy resin used to fix an optical window that was installed just before the main CCD camera detector appeared to have released chemical vapors. The vapors deposited on the CCD camera. This caused the Raman peaks in the spectrum to display a slight tailing.

NEW TEST RESULTS OF RAMAN ON GHV



NEW TEST RESULTS OF RAMAN ON GHV

The new test results have demonstrated the repeatability of the Raman on the GHV to be 0.020%* relative.

Relative standard deviation for the GHV is 0.20% using the conventional method (Raman 10 times better compared to the conventional custody transfer method).

No significant deviation in bias compared to the online GC (based on t-test).

*results based on one unloading (14-6) with 166 measurements, 2 outliers removed due to GC communication failure

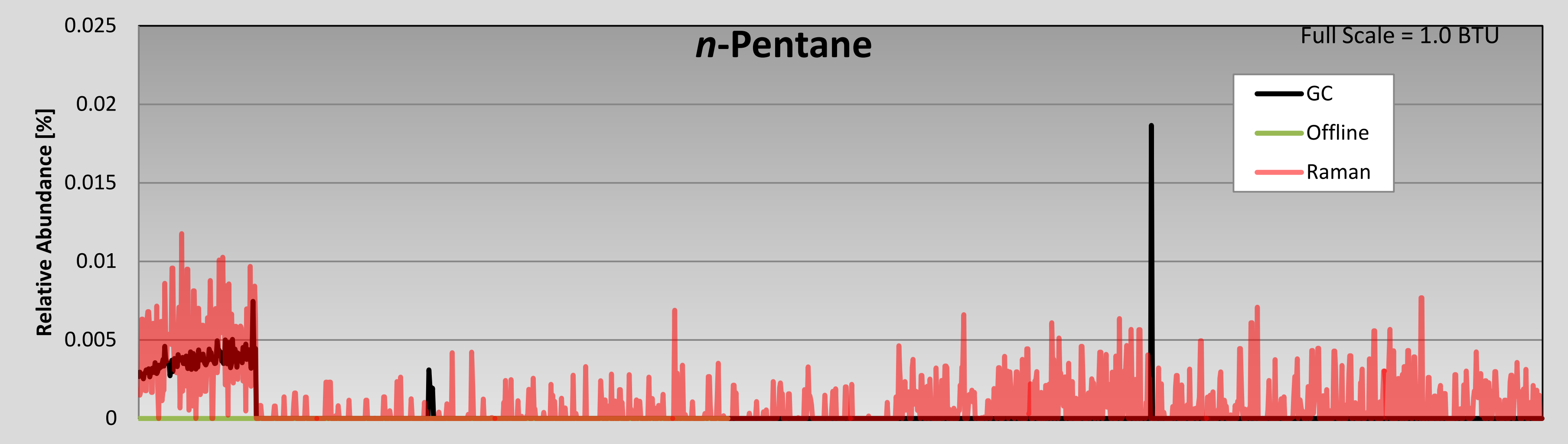
MAIN CHALLENGES STILL TO BE TAKEN

Although the tests are looking promising, the lower concentrations of the heavy hydrocarbons and nitrogen are not being detected properly .

This is due to the low concentrations (0-100ppm).

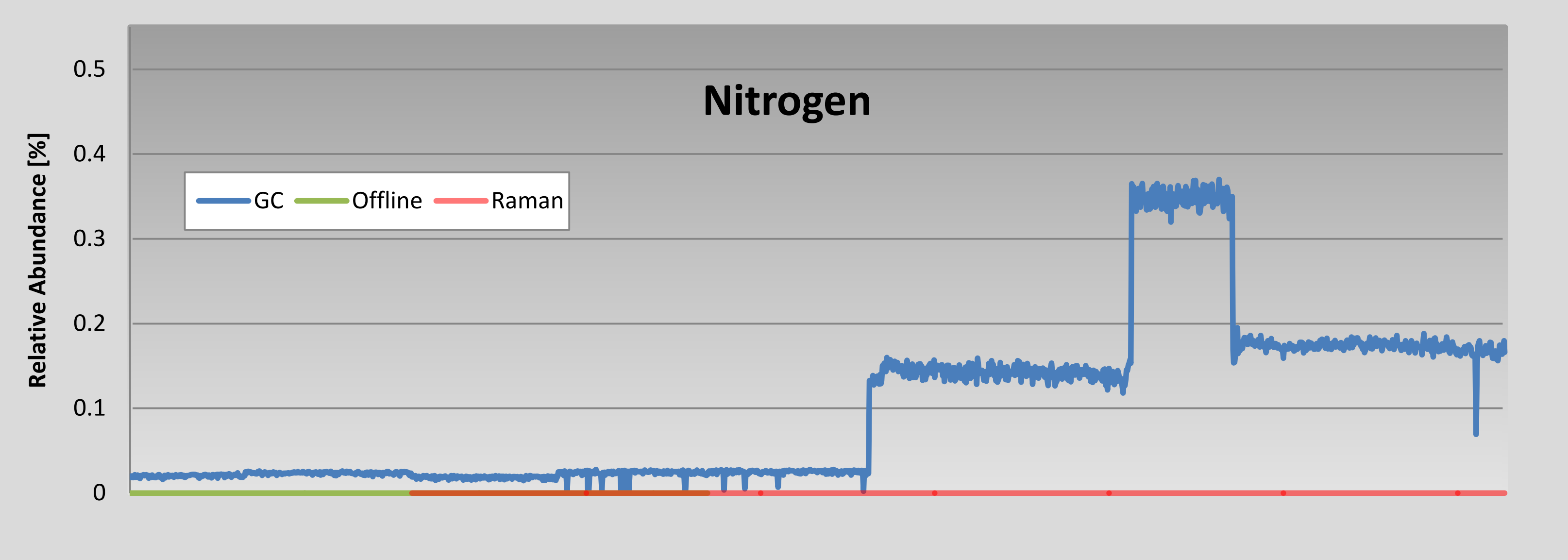
MAIN CHALLENGES STILL TO BE TAKEN

Results of C_5



MAIN CHALLENGES STILL TO BE TAKEN

Results of Nitrogen



MAIN CHALLENGES STILL TO BE TAKEN

With regards to the deviation in Nitrogen you can clearly see it is becoming more significant.

However it was expected that the GC-sampling valve was having some problems with internal leaking.

This caused a larger number of spikes in the initial data and especially showed on offset in the nitrogen.

MAIN CHALLENGES STILL TO BE TAKEN

Possible solutions

- In order to be able to more accurately detect the lower levels of heavy hydrocarbons and nitrogen, it was proposed to average the Raman data over a longer time period for these components.
- By doing this you will reduce the signal to noise ratio, improving the detection limit.

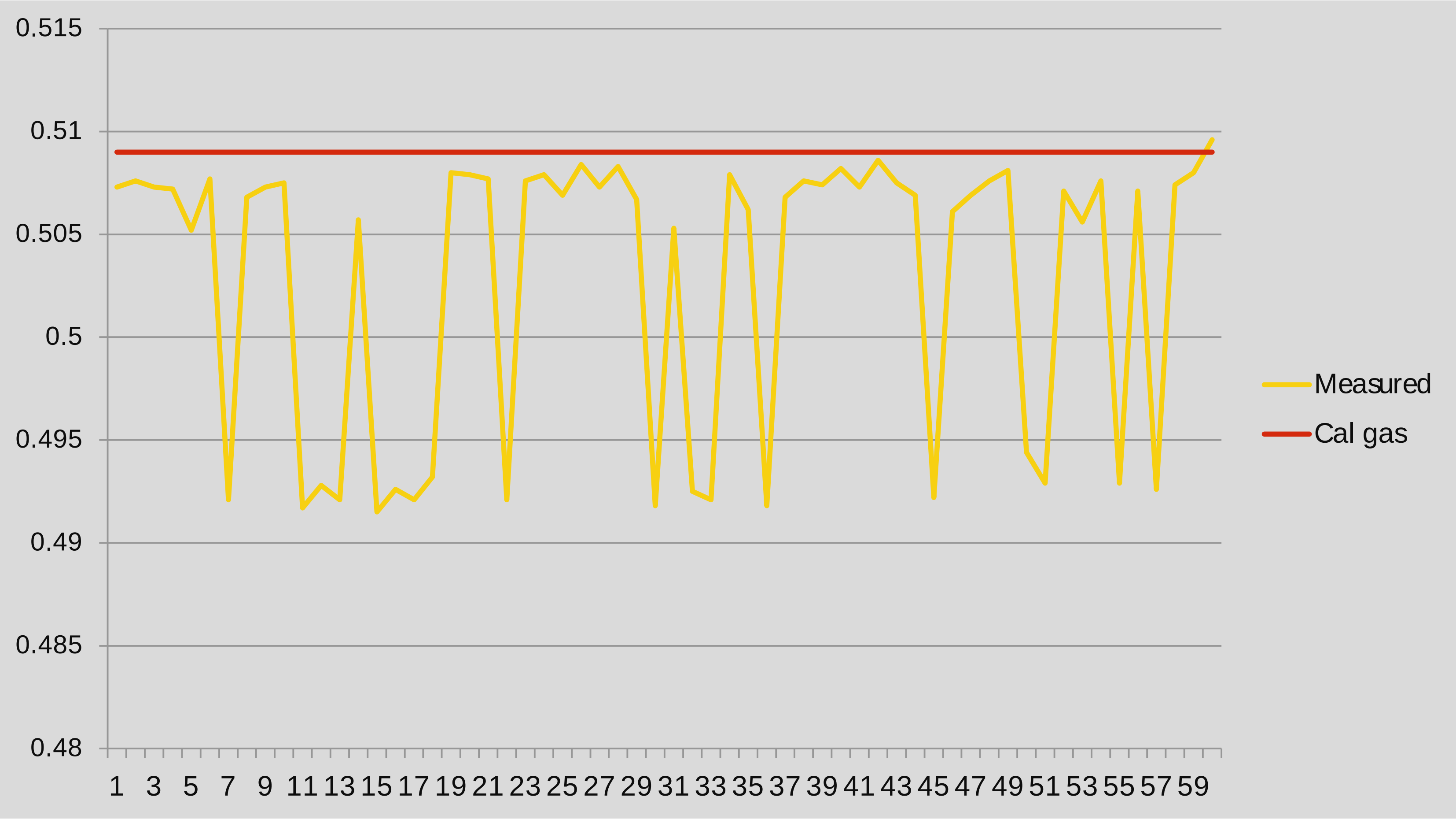
MAIN CHALLENGES STILL TO BE TAKEN

Contribution of N_2 on final heating value

- In general the deviation in the nitrogen concentrations between the online GC and the Raman system results in an average deviation in BTU of 0,99. In this the Raman measurement is always displaying a higher nitrogen content.
- However it is questionable if this is caused only by the Raman.
- Currently the average nitrogen deviation is 0,03%.

MAIN CHALLENGES STILL TO BE TAKEN

Nitrogen performance of online GC with calibration gas



CONCLUSIONS

Based on the current data, the Raman system has proven to be more stable, with a much lower repeatability compared to the conventional GC technique.

To a large extend this is because the LNG does not need to be vaporized first.

The Raman system needs specific knowledge during commissioning and start up.

Once operational little maintenance is required.

WHAT STILL NEEDS TO BE DONE

The mean time between failure has not been determined yet. This will have to be determined at a real installation over a longer period of time (3 years minimal).

Temperature stability of the measurement has not been determined. For this the analyzer will have to be installed in a different environment that will experience larger temperature swings.

FUTURE NEEDS FOR RAMAN

In order to get this technique accepted for online custody transfer, an international ISO/ ASTM/ GPA standard will have to be drafted.

Additionally the LNG industry will have to build large trust in the new technique.

Q & A