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Raman for LNG composition measurement

GERG performance evaluation on a Raman application against LNG custody transfer limits.

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Endress+Hauser Optical Analysis - for making their Raman instrument available and provide technical support on the hardware and modelling throughout the testing period.

GERG - for adopting this as a workstream in their workplans and organizing a steering committee.

Executive summary

This report is sharing the results and conclusions of the performance evaluation for Raman technology based on the latest LNG model developed by the Raman manufacturer. The testing contained verification against certified LNG standards at a metrology laboratory and field testing against a traditional LNG custody transfer measurement at the LNG terminal of Fluxys LNG in Zeebrugge, Belgium.

For transparency, a GERG (The European Gas Research Group) steering committee was formed to provide LNG producers, operators, traders and buyers with the opportunity to review and provide input to the testing and review test results.

Raman measurement is an optical technology using laser light, at a specific frequency, to excite molecules in a fluid and measure the optical scattering of inelastic bands over a wavelength range. Different molecules (components) will appear at different wavelengths. Subsequently, chemometric application modelling is used to model the amount of scattered light at the specific wavelengths to individual component amounts.

The Raman instrument consists of a probe, fibre optic cable and an electronics unit. The probe can be inserted directly into the liquid LNG, eliminating the need of complex bespoke LNG vaporizer systems and the efforts to maintain them. Also, the stabilization time is very short, which is beneficial for use in small size LNG cargoes applicable to the downstream LNG businesses such as bunkering and breakbulk applications.

The test was performed to determine if Raman technology can measure the Liquified Natural Gas (LNG) composition and calculate the physical properties for energy calculation at a precision suitable for LNG custody transfer. For this, the results are compared with Fluxys LNG's LNG custody transfer quality measurement system which is quality controlled by their laboratory and designed to meet the performance criteria in the GIIGNL Custody Transfer Handbook version 6.0.

After the initial field test demonstrated LNG temperature related biases, the Raman analyser was returned to Effectech where certified LNG standards, prepared under their UKAS accreditation, were used to add temperature correction to the model over the temperature range from 93 to 117K.

From the final testing we conclude that the Raman analyser, with an additional verification on a high accuracy certified- LNG standard, meets the fiscal criteria below:

- The Raman measurement capability meets the mass based GHV uncertainty limit of 0.07% as stated in the GIIGNL Custody Transfer Handbook version 6.0
- For the mass and volume based GHV measurement, no significant bias was found between the Raman and the traditional LNG vaporizer/GC measurement according evaluation done according the En method from ISO-17043 with results shown in figure 1 below.

En Evaluation between Raman analyser and Fluxys LNG vaporizer/GC according ISO 17043												
Test Cargo nr.	T15	T16	T17	T18	T19	T20	T21	T22	T23	T24	T25	T26
GHV_vol	0.19786	0.02242	0.09786	0.04151	0.20608	0.31176	0.24657	0.09437	0.30936	0.45828	0.12012	0.08301
GHV_mass	0.98428	0.5426	0.61301	0.78687	0.71394	0.62491	0.73219	0.28972	0.71575	0.35835	0.09579	0.94408
En Limit	1	1	1	1	1	1	1	1	1	1	1	1

Figure 1 Performance evaluation based on En-method and uncertainties within custody transfer limits

- As shown in figure 2. The Raman analyser demonstrated a superior repeatability compared to the GC/Vaporizer during loading/discharge.

Repeatability performance based at 2 times the pooled standard deviation over all evaluated cargoes												
	Methane %mole	Ethane %mole	Propane %mole	I Butane %mole	N Butane %mole	I Pentane %mole	N Pentane %mole	Nitrogen %mole	GHV_v MJ/m3	GHV_v %MV	GHV_m MJ/kg	GHV_m %MV
Rep. Limit_GIIGNL CTH 6.0										0.2		0.07
Repeatability_GC	0.072	0.056	0.014	0.005	0.005	0.00030	0.0002	0.008	0.029	0.074	0.009	0.016
Rep. Limits ASTM D7940-14	0.06	0.06	0.06	0.02	0.02	0.012	0.012	0.02		0.05		
Repeatability Raman	0.051	0.042	0.009	0.003	0.003	0.00004	0.0016	0.011	0.019	0.048	0.011	0.020

Figure 2 Repeatability performance against international standards criteria

Further testing results demonstrated that:

- During the test runs the Raman analyser met the test requirements of 99% availability, the analyser showed no drift and performed without alarms or maintenance intervention for the full test period.
- The Raman analyser demonstrated a much faster response to process changes, making it especially suitable for measuring small and medium sized cargoes were loading lines are not kept under cryogenic conditions outside loading/discharge operations.
- The maximum measurement uncertainty for volumetric based GHV of the Raman analyser met the manufacturers claim for the Raman unit under test of ± 0.112 MJ/m³ (± 3 BTU/SCF) using the manufacturers standard calibration practice with the optical calibration tool, without requiring additional validation on a certified LNG.
- Occasional component biases were found outside the significance limit for:
    - Nitrogen at or below 0.1%mole due to modelling limitations in the lowest part of the range specifically to Nitrogen and,
    - Ethane due to normalization effects between the main components Methane and Ethane. Where a larger bias developed by the Raman in Methane will cause Ethane to compensate the opposite way due to normalization.

En Evaluation between Raman analyser and Fluxys LNG vaporizer/GC according ISO 17043									
Test Cargo nr.	Methane	Ethane	Propane	I Butane	N Butane	I Pentane	N Pentane	Nitrogen	En Limit
	En	En	En	En	En	En	En	En	En
T15	0.5044	0.1696	0.2131	0.0791	0.3749	0.4534	0.0142	1.0530	1.0000
T16	0.1693	0.5831	0.2603	0.1578	0.6470	0.3112	0.0931	0.6598	1.0000
T17	0.0493	0.4071	0.0980	0.2248	0.7217	0.2913	0.0659	0.7795	1.0000
T18	0.2207	0.0804	0.1475	0.0396	0.1959	0.1522	0.0248	0.9622	1.0000
T19	0.2247	0.1839	0.0250	0.2343	0.7357	0.3134	0.0912	0.7693	1.0000
T20	0.3135	0.0233	0.0248	0.2752	0.7544	0.2980	0.0778	0.6114	1.0000
T21	0.2757	0.1390	0.0035	0.2808	0.7758	0.2827	0.0881	0.7635	1.0000
T22	0.2282	0.2060	0.1529	0.0544	0.1109	0.0233	0.0238	0.3238	1.0000
T23	0.3000	0.0639	0.0116	0.2928	0.7084	0.3904	0.0968	0.6321	1.0000
T24	0.5288	1.0395	0.1152	0.1253	0.0244	0.0001	0.0198	0.5928	1.0000
T25	0.6045	1.0462	0.4427	0.0041	0.6099	0.7595	0.0823	0.2405	1.0000
T26	0.4786	0.1894	0.1604	0.0971	0.3280	0.0825	0.0373	1.0679	1.0000

Figure 3 Statistical agreement testing for individual components based on calculated uncertainties

- Principally, the uncertainty limits that can be achieved for a well-engineered and maintained GC/Vaporizer system can be tighter than that of a Raman analyser system. However, the required OPEX and technical expertise necessary to a to outperform the Raman analyser system is extensive.

Overall, the performance test successfully proved that the results can be used to proceed with international standards bodies for including Raman technology into international standards for LNG custody and for the manufacturer to continue MID certification of the Raman instrument.

Contents

1. Definitions

1.1. Abbreviations

ASTM	American Society for Testing and Materials
CCD	Charge-Coupled Device
CTH	Custody Transfer Handbook
DCS	Distributed Control System
EU	European Union
E+H	Endress + Hauser Optical Systems
FO	Fibre Optics
GC	Gas Chromatograph
GERG	Gas European Research Group
GHV	Gross Heating Value
GIIGNL	Groupe International des Importateurs de Gaz Naturel Liquéfié (International Group of Liquefied Natural Gas Importers)
ISO	International Standards Organization
LNG	Liquefied Natural Gas
MID	Measuring Instrument Directive
MV	Measured Value
NDA	Non-Disclosure Agreement
OPEX	Operating Expenditure
PRGM	Primary Reference Gas Mixture
SGSI	Shell Global Solutions International B.V.
UKAS	United Kingdom Accreditation Service

1.2. Specific Definitions

Repeatability	Closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement. Known as the dispersion characteristic of instrument results and for this document taken as the standard deviation of each measured component at k=2.
Precision	The sum of all uncertainties in the measurement chain for the measurement and characterizes the dispersion of the values that could reasonably be attributed to the measurand.

	It is understood that the result of the measurement is the best estimate of the value of the measurand, and that all components of uncertainty, including those arising from the systematic effects, such as components associated with corrections and reference standards, contribute to the dispersion.
Bias	Results whereby the measured value of the measurement differs from the true underlying quantitative value.
Accuracy	Bias determined between the measured and the reference value including the repeatability identified for each component in the mixture.
MID Certificate	An EU type examination certificate issued by a notified body in accordance with module B or H1 in the Measuring Instruments Directive.
Uncertainty	The range of possible values within which the true value of the measurement lies. Often accompanied with a level of confidence. Where standard uncertainty is at 1 sigma or 67% confidence level and expanded uncertainty is at 2 sigma or 95% confidence level
GIIGNL CTH	The GIIGNL LNG Custody Transfer Handbook reflects GIIGNL's understanding of best current practice at the time of publication. The purpose of this handbook is to serve as a reference manual to assist readers to understand the procedures and equipment available and used by the members of GIIGNL to determine the energy quantity of LNG transferred between LNG ships or LNG trucks and LNG terminals. It is neither a standard nor a specification.
UKAS	The UK's national accreditation body recognised by the British government to assess the competence of organisations that provide certification, testing, inspection, and calibration services. It evaluates these conformity assessment bodies and then accredits them where they are found to meet relevant internationally specified standards.

2. Introduction

Conventional LNG terminals use gas chromatography to measure LNG composition using a sample handling arrangement that includes a bespoke LNG vaporizer compliant to requirements stated in ISO 8943. For LNG loading/unloading these LNG vaporizer systems are working in a narrow operating window, close to the bubble point where insulation and flow rates need to be checked frequently. Also, they require considerable stabilization time after start-up and stable flow and pressure to be able to produce precise measurements.

Traditional measurement technology for LNG custody transfer is based on vaporizing the LNG and measure the composition in the gas phase using a gas chromatograph application built in accordance with the international standards stated in the contract.

The vaporization of LNG has always been challenging as the LNG transferred is close to boiling point, with a preferential boil off risk for lighter components. To prevent these risks impacting the measurement accuracy, strict design requirements and maintenance need to be in place.

In recent years Raman spectroscopy has been identified as a promising technology to determine the LNG composition directly in the cryogenic process liquid.

The main benefits expected from the Raman technology are:

- Reduced complexity for integrating the measurement in the LNG process.
- Reduced OPEX
    - Raman replaced both the LNG vaporizer and the GC. (less hardware to be maintained)
    - No high purity carrier gases required
    - No longer requires tuning of vaporizer to suit the loading conditions. (deviations in Pressure, Temperature and Flowrate.)
- Composition measurement fully traceable to the mole.
- Faster measurement stability after cooldown, enabling reliable quality measurement for applications with small cargo transfers, such as downstream LNG and bunkering applications. (No extensive cooldown and stabilization time (≥30 min) for the LNG vaporizer is required.)

After initially exploring the suitability of utilizing Raman technology for composition analysis directly into Liquefied Natural Gas (LNG), Kaiser Optical Systems Inc. started the development of the Raman Analyser's model for LNG by cooperating with some export terminals. Most of these tests involved installing a Raman probe in series with an existing traditional measurement device. One limitation of these evaluations in developing a robust analysis model was the limited compositional changes of LNG and differences in performance between the traditional vaporiser/GC installations.

In tests done with Shell Global Solutions Inc. it was found that there is potential as reliability was good, but some gaps were identified in the analytical performance and traceability. This was flagged as one of the key areas for improvement.

To overcome these limitations, E+H turned to Effectech who have developed a bespoke cryostat to condense a PRGM into a Certified LNG mixture ensuring traceability to the mole under their ISO 17025 certification. This allowed E+H to further improve their model hereby covering the full LNG composition range.

This resulted in E+H having a commercial Raman analyser including a validated model based on certified LNG standards with a known uncertainty and traceability to the mole.

These capabilities made it possible to consider Raman measurements for custody transfer applications and a project was launched to test the Raman performance in the field at an LNG terminal.

The project was started between Shell Global Solutions International, E+H and Fluxys LNG. However, to provide maximum transparency to the LNG business a GERG steering committee was formed and led by Shell Global Solutions International with Fluxys LNG maintaining the contact and reporting to the GERG. The following companies participated in the steering group; *Enagás, Gas Natural Fenosa, TotalEnergies S.E., GRTgaz RICE, Tokyo Gas Co. Ltd., Equinor and Exelerate Energy*.

2.1. LNG composition range

In the initial model development stage, the component ranges were reviewed by Shell based on their cargo history database containing LNG composition information of loading and discharge sites all over the world.

For the GERG testing, the composition ranges used for the method development were reviewed against the GERG's LNG composition database and the individual composition ranges as per figure 4 were included in the test scope.

Although components like CO2 and O2 can be measured using Raman technology, the amount present in LNG is below the lower detection limit and are therefore excluded from the scope.

These values can be included by using relative response factors. However, the values obtained shall be considered non-fiscal and for information only.

component	minimum	maximum
	(%mol/mol)	
nitrogen	0	1.3
methane	87.2	99.7
ethane	0.1	11.0
propane	0.1	4.5
iso-butane	0.08	1.3
n-butane	0.08	1.1
iso-pentane	0.03	0.15
n-pentane	0.02	0.15

Figure 4 LNG composition range

3. Raman test objectives and scope

The objective of this test was to demonstrate that Raman technology can be used to provide reliable, accurate and precise composition measurement directly from LNG in the liquid phase.

For this an RXN type Raman analyser with the LNG composition model was used to perform a field test to assess if the Raman system can perform reliably under the varying conditions in the field.

This report includes the results of the field testing that prove the performance of the Raman analyser is within the minimum requirements as agreed upon between all companies participating in the GERG evaluation project. Also, it shares the experiences with respect to installation and maintenance of the Raman analyser, to maintain the required performance level and uptime.

This report can be used by regulators, operators, industry bodies and companies as a technical basis to consider Raman technology as a measurement in LNG custody transfer applications. Also, it is to act as a guide on the minimum performance criteria and application testing for manufacturers that want to include a Raman application for LNG custody transfer applications.

From discussions within the GERG, Fluxys LNG Belgium volunteered to host the Raman field test at their LNG receiving and regasification terminal in Zeebrugge, Belgium.
A 3-way test agreement was executed between Fluxys LNG, E+H and Shell Global Solutions International, where:

- E+H will supply a Raman analyser for installation on site and the required maintenance and modelling support.
- Fluxys LNG will install the Raman analyser in their LNG discharge line and collect the measuring data of both the Raman and their installed GC/Vaporizer system available for the individual LNG cargo loadings.
- Shell Global Solution International will do the project management and based on their previous Raman development experience, perform the evaluation of the measurement data and reporting.
- The progress, results and findings will be reported to the GERG steering committee for feedback to ensure Industry objectives are met.

Following a recommendation from the GERG steering committee, an engagement with a 3rd party surveyor was scheduled, sharing the measurement data, to understand their approach for assessing this new technology.

The outcome of the field test for the Raman analyser with LNG application:

- Shall provide insight in the closeness of agreement between a Raman analyser and a traditional LNG measurement using an LNG vaporiser and online gas chromatography.
- Provide insight in the installation requirements for a Raman probe.
- Gives an understanding on the maintenance and operational requirements for a Raman analyser compared to traditional LNG measurements.

3.1. Evaluation criteria

The evaluation of the Raman analyser is performed against a well-maintained traditional measurement system of a GC and LNG vaporizer.

For each LNG discharge cargo, the results (cargo mean values) of both the Raman analyser and the installed traditional method (GC/LNG vaporiser) are evaluated

The performance limits are taken from the GIIGNL CHT 6.0 based on:

a) Meting measurement uncertainty for mass based GHV
b) Meting repeatability limits for volumetric GHV
c) For Raman, additionally, repeatability against ASTM D7940-14 is checked

To provide a complete overview of the measurement behaviour the below non fiscal evaluations are performed.

d) Availability of the Raman analyser
e) Performance of the Raman analyser against the manufacturer's performance claims
f) Closeness of agreement between the measurement components.

3.2. Criteria of success

For the performance testing of the Raman analyser the following criteria of success were defined for LNG Custody transfer:

3.2.1. Uncertainty for mass based GHV

The uncertainty, at 95% confidence level, of the Fluxys LNG's existing GC/Vaporizer for custody transfer and the Raman analyser shall be equal or better than ± 0.07% of the calculated mass based GHV as stated in the GIIGNL custody transfer handbook version 6.0.

3.2.2. Repeatability for Volumetric GHV

Both measurements shall meet the repeatability performance limit in GIIGNL CTH version 6.0 stating the volumetric GHV at 95% confidence level, shall be within 0.2%MV for GC/Vaporizer.

3.2.3. Repeatability

For the Raman analyser also, the performance stated in ASTM D7940-14 as per table in figure 5. Where the precision is taken as 2 times the Std. Deviation.

ASTM D7940-14 Performance limits	Raman Methane	Raman Ethane	Raman Propane	Raman I_Butane	Raman N_Butane	Raman I_Pentane	Raman N_Pentane	Raman Nitrogen	Raman GHV_vol	GHV_v	Raman GHV_mass	GHV_m
	%mole	%mole	%mole	%mole	%mole	%mole	%mole	%mole	MJ/m3	%MV	MJ/kg	%MV
Mean	94.491	3.796	0.931	0.297	0.246	0.011	0.007	0.22	39.699		55.089	
St Dev Limit [u]	0.03	0.03	0.03	0.01	0.01	0.006	0.006	0.01				
Precision [U] (K=2)	0.060	0.060	0.060	0.020	0.020	0.012	0.012	0.020	0.020	0.05	0.028	0.05

Figure 5 Evaluation limits for precision as per ASTM D7940-14

From engagement with a 3rd party surveyor feedback was received that as a default they would look for an available international standard to evaluate the Raman technology during a custody transfer loading. For Raman currently the ASTM D7940-14 was the referred standard by the surveyor as the only available standard for this purpose.

To provide the best possible insight in the measurement behaviours for the Raman analyser compared to a traditional GC/Vaporizer measurement the following evaluations were also included.

3.2.4. Availability

Raman analyser availability of 99% during the testing period and when required by operations. Start of the testing period shall be after completion of commissioning and start-up.

3.2.5. Measurement uncertainty

The Raman analyser meet the manufacturers claim of determining the volumetric GHV within the precision limit of ± 0.112 MJ/Sm³ (± 3 BTU/SCF).

3.2.6. Analyzer measurement comparison

For each cargo loading/discharge the closeness of agreement between the Raman and GC/Vaporiser mean values are evaluated for each component as well as the GHV.

Evaluation is done according the En number method described in the ISO 17043:2010 – Conformity assessment – General requirements for proficiency testing Annex B.

According this procedure, the deviation between the two values is statistically insignificant when the deviation between the cargo mean values does not exceed the combined uncertainty of the online GC/Vaporizer and the Raman analysers. The En number is calculated using the formula:

$$En = \frac{(X_{GC} - X_{Raman})}{\sqrt{(Ux_{GC}{}^2 + Ux_{Raman}{}^2)}}$$

Where:

- X_{GC} = The reading from the Fluxys LNG GC/Vaporizer instrument
- U_{XGC} = The uncertainty calculated for the Fluxys LNG GC/Vaporizer instrument
- X_{Raman} = The reading from the Raman instrument
- U_{XRaman} = The uncertainty calculated for the Raman instrument

For uncertainty the values at 95% confidence level are used.

If the En number is ≤ 1 the difference between the measurement results of the GC/vaporizer and the Raman analyser is considered not significant.

3.3. Online LNG Vaporizer/GC uncertainty

The process gas chromatograph used for this evaluation is controlled under Fluxys LNG internal verification procedures and fully complies with industry standard procedures for LNG custody transfer.

The uncertainty calculation is based on methods described in the GIIGNL Custody Transfer Handbook version 6.0 and for the evaluation based on:

3.3.1. The certified calibration gas

The PRGM, prepared under ISO 17025 accreditation, to prepare the certified LNG for the Raman validation at Effectech is shipped to Fluxys LNG for calibrating their online GC.

Full certificate is attached to this document under appendix 4.

component	amount fraction (% mol/mol)
nitrogen	0.5981 ± 0.0014
ethane	5.637 ± 0.014
methane	92.892 ± 0.011
propane	0.7029 ± 0.0032
iso-butane	0.06038 ± 0.00042
n-butane	0.07770 ± 0.00064
iso-pentane	0.02109 ± 0.00016
n-pentane	0.01003 ± 0.00017

3.3.2. The GC/LNG vaporizer limit as per GIIGNL

For the LNG vaporizer the limit of 0.3% of volumetric GHV at k=3 from the GIIGNL CTH is used to determine the performance limit. As we are determining the data at a 95% confidence level (k=2) a limit of 0.2% of the volumetric GHV is used.

A Monte Carlo simulation is used to determine the precision limit for the individual components that make the GHV's 0.2% precision. The Monte Carlo simulation randomly varies all the components over each component's uncertainty limit determined according the ISO-6974-5 uncertainty calculation and calculates the GHV from the composition according ISO-6976. The variation is increased according an equal percentage for each component until the limit value of 0.2% for GHV is matched.

See example for the calibration gas composition in figure 6 below.

LNG vaporiser/GC performance limits	Mole based calculation [%mole] / [15/15/1.01325]								[MJ/m3]	[MJ/kg]	
	Methane	Ethane	Propane	I Butane	N Butane	I Pentane	N Pentane	Nitrogen	GHV	GHV	
%Mole	92.8920	5.6370	0.7029	0.0604	0.0777	0.0211	0.0100	0.5981	39.796	54.499	
GHV uncert limit (K=2)									0.20	0.08	% MV
Std Dev	0.058	0.029	0.017	0.009	0.010	0.007	0.006	0.016	0.039	0.015	
Precision [U] (K=2)	0.116	0.057	0.034	0.018	0.020	0.014	0.012	0.033	0.078	0.042	

Figure 6 Combined Vaporizer/GC precision limits

The GC/Vaporizer performance limit is calculated from the root mean square of the PRGM and Monte Carlo simulation. The limit values will vary with composition hence a performance limit is calculated for each of the evaluated cargoes. An example is shown in figure 7 below.

GC/Vaporizer performance limits using MC calculation										
EU	Methane %mole	Ethane %mole	Propane %mole	I Butane %mole	N Butane %mole	I Pentane %mole	N Pentane %mole	Nitrogen %mole	GHV MJ/m3	GHV MJ/kg
Composition	92.8920	5.6370	0.7029	0.0604	0.0777	0.0211	0.0100	0.5981	39.7971	54.4994
Uxi_PGRM	0.0110	0.0140	0.0032	0.0004	0.0006	0.0002	0.0002	0.0014	0.0210	0.0120
Uxi_GC/Vap	0.116	0.057	0.034	0.019	0.020	0.014	0.012	0.033	0.078	0.048
Uxi	**0.116**	**0.059**	**0.034**	**0.019**	**0.020**	**0.014**	**0.012**	**0.033**	**0.081**	**0.049**

Figure 7 Combined PRGM & GC/Vaporizer uncertainty limits

3.4. Raman analyser uncertainty

This is the calculated performance envelope for the Raman analyser including the optical calibration and LNG model that is used as the performance limit.

3.4.1. Introduction

As the Raman application for LNG composition measurement is new, an uncertainty calculation had to be developed under this project. This uncertainty is set up as a method uncertainty considering; multiple Raman instruments (model transfer), multiple optical calibration tools (HCA White Light calibrator) and multiple users.

For final expanded uncertainties a coverage factor k=2 is applied to maintain a 95% level of confidence.

The Uncertainty from this calculation will cover all Raman instruments using the LNG composition measurement application.

3.4.2. Determining the method uncertainty

For the assessing the instrument precision, the instrument measurement chain is evaluated. From this assessment the below uncertainty contributors are identified:

a. Raman instrument uncertainties
    - *Including uncertainties from LNG certified reference fluids used for modelling.*
b. Measurement uncertainties based on repeatability of the individual components during operation. (installation factor)

As a first step we have evaluated each of the individual contributors and determined their individual precision. After determining the individual contributors, the overall uncertainty is calculated based on root mean square method.

3.4.3. Raman instrument internal uncertainties

The Raman instrument is and optical device that uses laser light at a specific wavelength to induce vibration of inelastic bands (Raman scattering) causing a frequency shift relative to the laser wavelength and unique to a molecule. The number of photons at the specific molecule wavelength are collected using a CCD camera and correlated/modelled to a concentration of the individual components.

For our application calculations as per ISO-6976 are used calculate the properties like Mole weight and Gross Heating Value.

For the Raman instrument the below uncertainty contributors have been determined for the method precision:

a. Internal optical calibration incl. Probe and Fibre optic cable.
b. Modelling uncertainties for each of the individual measurement components.
c. Temperature compensation for the Raman model
d. Metrology laboratory UKAS uncertainties for Certified LNG liquids
e. Uncertainties of ISO-6976 method used for calculations of properties.

We considered instrument electronics uncertainty negligible in relation to the uncertainty of the optical calibration source and modelling chemometrics.

Since a some of the individual contributors are related to each other[1], the root mean square method will cause the precision to be overestimated. Therefore, the overall precision for the Raman instrument itself is determined using a Monte Carlo simulation.

In this Monte Carlo simulation, the overall precision range for each of the individual contributors is used to calculate the overall instrument precision for the individual components. The individual component variations are included in the ISO-6976 calculation for Mole Weight and Gross Heating Value. The standard deviation from the simulation results is calculated and the Uncertainty is taken as 2 times the standard deviation. (Assuming 95% Confidence level)

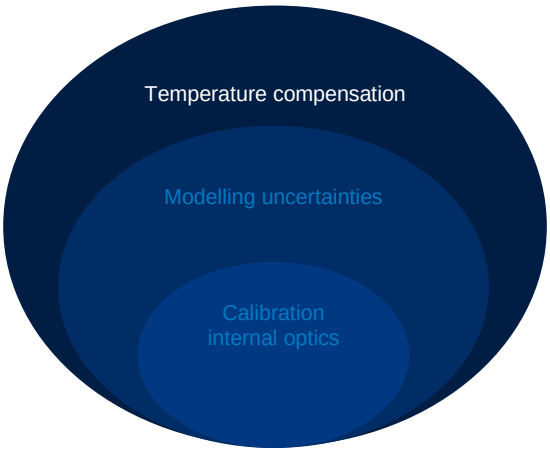


Figure 8 Related uncertainties

Internal optics calibration incl. probe and fibre optic cable

To set-up the Raman instrument the manufacturers procedure requires an internal optics calibration incl. probe and fibre optic cable to set the full optical path and detector to a fixed intensity. This step compensates for transmission losses due to individual component variations and allows for models to be transferred across instruments.

Calibration is done using a calibration tool based on a white light source (HCA lamp) with a NIST traceable relative uncertainty over the full spectrum as shown in Figure 9. From this graph, the relative error for the measuring value can be determined for each based on the measured component's Raman wavelength shift.

The HCA White Light calibrator NIST traceable uncertainty limits shown are to cover all calibrators supplied by the manufacturer, making it a relevant contributor to the method precision.

With this relative error the absolute uncertainty limits are calculated from the actual composition and used as an input in the Monte Carlo simulation.

[1] *Core model uncertainty is contributing to temperature compensation uncertainty and probe calibration uncertainty is contributing to both core model and temperature compensation uncertainty*

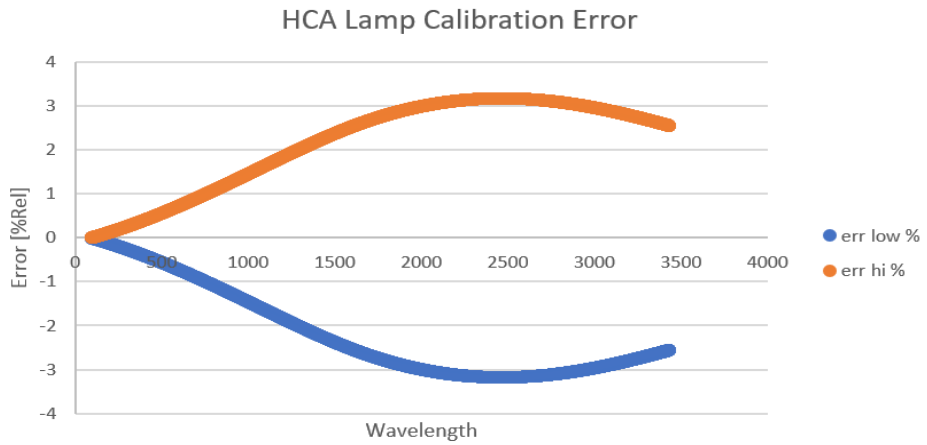


Figure 9 Typical relative error HCA Lamp

Modelling uncertainties

The application model precision is determined by Endress+Hauser Optical Systems based on the evaluation of five LNG certified reference fluids, covering the full measurement range for each of the individual components in LNG, at the model reference temperature of 113K (No LNG temperature correction applied).

The uncertainty for each of the five compositions using the formula described in ISO-6142-1 Chapter 11. Although originally developed to determine the analytical uncertainty of a gravimetric standard it fits our objective very well as this calculation considers, the uncertainty of the calibration gas mixture, the repeatability of the instrument and the bias between the instrument and the standard.

component	Mix1	Mix2	Mix3	Mix4	Mix5		min	max
nitrogen	0.040	0.050	1.050	0.570	0.300		0.040	1.050
methane	87.000	98.170	90.500	92.918	92.870		87.000	98.170
ethane	10.500	1.300	4.210	5.639	4.500		1.300	10.500
propane	2.000	0.160	3.000	0.703	1.750		0.160	3.000
iso-butane	0.210	0.100	0.400	0.060	0.300		0.060	0.400
n-butane	0.240	0.120	0.600	0.078	0.250		0.078	0.600
iso-pentane	0.005	0.060	0.120	0.021	0.020		0.005	0.120
n-pentane	0.005	0.040	0.120	0.010	0.010		0.005	0.120
sum	100.00	100.00	100.00	100.00	100.00			

Figure 10 LNG compositions for testing Raman performance

$$Uc_{mix(n)} = \frac{1}{2} * \sqrt{U\_certLNG(n)^2 + u\_Raman(n)^2 + (x_{certLNG(n)} - y_{Raman(n)})^2}$$

The mean and standard deviation at each of the compositions is determined over at least twenty measurement.

The overall result is calculated by using root mean square of the five uncertainties calculated and applying a k-factor of 2 to come to the expanded uncertainty at a 95% confidence level.

The expanded uncertainty result is used as the upper and lower limit for modelling the overall instrument uncertainty in the Monte Carlo simulation.

Core model uncertainty								
%mole	Methane	Ethane	Propane	I butane	N butane	I pentane	N pentane	Nitrogen
uncertainty	0.0681	0.0507	0.0170	0.0108	0.0101	0.0173	0.0098	0.0109
Uncertainty (k=2)	**0.1363**	**0.1013**	**0.0339**	**0.0215**	**0.0202**	**0.0346**	**0.0196**	**0.0217**

Temperature compensation uncertainties

The uncertainty introduced by the temperature compensation is determined based on the evaluation of the same five LNG certified reference fluids as used in for the core model, except for this the individual runs are done at five LNG temperatures from 93 to 117K with 5K steps.

The uncertainty for each of the five compositions using the formula described in ISO-6142-1 Chapter 11. Although originally developed to determine the analytical uncertainty of a gravimetric standard it fits our objective very well as this calculation considers, the uncertainty of the calibration gas mixture, the repeatability of the instrument and the bias between the instrument and the standard.

$$Uc_{mix(n)} = \frac{1}{2} * \sqrt{U\_certLNG(n)^2 + u\_Raman(n)^2 + (x_{certLNG(n)} - y_{Raman(n)})^2}$$

The mean and standard deviation at each of the compositions is determined over all the full temperature range with at least twenty measurement at each temperature.

The overall result is calculated by using root mean square of the five uncertainties calculated and applying a k-factor of 2 to come to the expanded uncertainty at a 95% confidence level.

The expanded uncertainty result is used as the upper and lower limit for modelling the overall instrument uncertainty in the Monte Carlo simulation.

Temperature corrected model Uncertainty								
%mole	Methane	Ethane	Propane	I Butane	N Butane	I Pentane	N Pentane	Nitrogen
uncertainty	0.1000	0.0593	0.0220	0.0113	0.0124	0.0200	0.0071	0.0099
Uncertainty (k=2)	**0.1999**	**0.1187**	**0.0440**	**0.0227**	**0.0249**	**0.0400**	**0.0142**	**0.0197**

Monte Carlo Simulation of correlated uncertainties

Due to the nature of the individual Precisions calculated for each of the contributors, a rectangular distribution must be used. For this reason, the precisions for each of the contributors is randomly variated in the Monte Carlo simulation for each measured component. After the variation, normalization is applied to ensure the full composition equals a 100%.

The precision results for the individual components, volumetric GHV and Mole Weight (MW) are used as the Raman instrument uncertainty in the overall uncertainty calculations. The weight GHV is calculated from the gas density (calculated from MW) and volumetric GHV (as per ISO-6976 method for calculating GHV mass.)

3.4.4. Uncertainty from ISO-6976

The properties, Volumetric Gross Heating Value, Mole Weight and Mass based Gross Heating Value are calculated from the composition using the method described in ISO-6976.

Just as the composition has uncertainty also the properties of the individual components have an uncertainty. These property uncertainties are calculated using the relevant tables in ISO-6976-2016 and included in the overall uncertainty calculation for the Gross Heating Value.

3.4.5. Repeatability at final installation

As installation in the field adds to the uncertainty also the precision of the instrument after final installation must be considered as a part of the uncertainty calculation.

The uncertainty calculation shows the precision for the installation done at the Fluxys LNG site for the test. For this the repeatability of each cargo was calculated. From the individual repeatability's a pooled standard deviation is calculated using the formula:

$$Pooled\ Uc_{AllCargo} = \sqrt{\frac{U_{Cargo1}^2 * (N_{meas_{cargo1}} - 1) + U_{Cargo2}^2 * (N_{meas_{cargo2}} - 1) + U_{CargoN}^2 * (N_{meaN} - 1)}{\left(N_{meas_{cargo1}} - 1\right) + \left(N_{meas_{cargo2}} - 1\right) + \left(N_{meas_{cargoN}} - 1\right)}}$$

The cargoes are measured during the various seasons of the year and at different LNG temperatures and pressures.

The repeatability will differ per site as it is subject to many factors such as ambient temperature and installation factors. For this reason, it is configured as a manual input in the calculation sheet.

Raman repeatability over cargoes under test													
Test Cargo nr.	Instrument	Methane %mole	Raman Ethane %mole	Propane %mole	I_Butane %mole	N_Butane %mole	I_Pentane %mole	N_Pentane %mole	Nitrogen %mole	GHV_vol MJ/m3	Raman GHV_v %MV	GHV_mass MJ/kg	GHV_m %MV
Total	Uxi_Raman	0.051	0.042	0.009	0.003	0.003	0.000	0.002	0.011	0.019	0.048	0.011	0.020
	Pooled St Dev Raman	0.025	0.021	0.004	0.001	0.001	0.000	0.001	0.006	0.010	0.024	0.005	0.010

3.4.6. Overall Method Uncertainty

For determination of the overall precision the contributors described in the previous chapters are summed using sum of square method. Results for the overall method uncertainty are composition dependent; a typical result is shown in the figure 11 below.

			Mole based calculation [%mole] / [15/15/1.01325]								[MJ/m3]	[MJ/kg]	
Description	K	Source	Methane	Ethane	Propane	I Butane	N Butane	I Pentane	N Pentane	Nitrogen	GHV	GHV	
LNG composition		User*1	92.8920	5.6370	0.7029	0.0604	0.0777	0.0211	0.0100	0.5981	39.628	54.538	
Raman uncertainty	1	GERG trial*2	0.1365	0.1124	0.0207	0.0091	0.0093	0.0137	0.0064	0.0172	0.043	0.024	
Repeatability	1	GERG trial*3	0.0251	0.0206	0.0044	0.0014	0.0013	0.0000	0.0008	0.0059	0.009	0.006	
LNG cert std Unc	1	GERG trial*4											
LNG val Raman bias		GERG trial*5											
GHV std uncertainty	1	ISO6976;2016									0.008	0.011	
uncertainty [u]	1	Sum SQRT	0.1388	0.1143	0.0211	0.0092	0.0094	0.0137	0.0064	0.0182	0.0449	0.0273	
Uncertainty [U])	2	Sum SQRT	**0.2776**	**0.2285**	**0.0423**	**0.0183**	**0.0189**	**0.0275**	**0.0128**	**0.0365**	**0.090**	**0.055**	
GHV relative uncertainty	2										0.23	0.10	% MV

Figure 11: Overall uncertainty of the Raman analyser

Notes	
1	Manually enter your LNG composition
2	Raman uncertainty takes into account the errors in; Optics calibration, Core model and Temperature correction as well as Metrology laboratory Uncertainty under UKAS accreditation *Optics is from NIST traceable light source. Core model and temperature correction are determine under Raman trials under GERG*
3	Repeatability used is originated from the GERG trial test data from LNG cargo loadings to include installation effects in the uncertainty calculation. *If clients have historical data on record for their Raman installation they are able to manually enter this.*
4	Manually enter the uncertainty of the Certified LNG std used for verification from the validation report. *Default blank if no validation on a certified LNG standard is done at a metrology laboratory to use optical calibration tool method uncertainty. Values included are from validation on Certified LNG peformed at metrology laboratory to improve uncertainty for optical calibration tool.*
5	Manually enter the deviation between the certified LNG standard and the Raman measurement from the validation report. *Default blank if no validation on a certified LNG standard is done at a metrology laboratory to use optical calibration tool method uncertainty. Values included are from validation on Certified LNG peformed at metrology laboratory to improve uncertainty for optical calibration tool.*

3.4.7. Raman instrument specific uncertainty

The method uncertainty is applicable for all instruments and applying the standard calibration procedure from the manufacturer as done for all Raman instruments.

However, for custody transfer an additional verification using a high accuracy certified LNG at an accredited metrology laboratory can be done on the Raman analyser. With this, the standard NIST overall uncertainty from the White Light calibrator can be replaced with the much lower uncertainty determined during the verification on the certified LNG mixture.

The procedure for this validation is set as per below:

f. At the metrology laboratory first a white light calibration is performed to set the proper light intensity.
g. After this the Raman analyser is validated in a cryostat on a high accuracy Certified LNG reference liquid under an accredited procedure.
h. The validation allows users to replace the NIST overall uncertainty from the White Light calibrator with the uncertainty of the validation performed on the Certified LNG reference liquid (bias and calibration liquid uncertainty).

The advantage of this procedure is that it provides a correlation between the HCA white light calibrator and the certified LNG reference liquid which allows sites to verify the optical calibration in the field using the HCA white light calibrator instead of having to organize a certified LNG reference liquid.

This correlation is valid for the validity period of the White Light Calibration tool which is 500 burning hours and an indication of the burning hours left is available in the calibration tool software.

Typically, the manufacturer recommends returning the HCA tool to their calibration facility every two years to verify if the uncertainty is met.

Instrument specific uncertainty for the performance test.

For the Fluxys LNG performance testing a validation was performed after completing the optical calibration.

The Raman probe was installed in the cryostat and verified against the certified LNG standard to verify the analyser performance based on its current optical calibration. The validation results for the Raman analyser at a single LNG temperature are shown in the below table.

mix 15/1068/01	LNG reference values		Measured (Raman)		**difference**
D328619	xic	U(xic)	yi	U(yi)	**Raman-LNG Ref**
nitrogen	0.5703	0.0285	0.5641	0.0064	**-0.0062**
methane	92.9183	0.0425	92.9390	0.0148	**0.0207**
ethane	5.6390	0.0088	5.6607	0.0108	**0.0217**
propane	0.7031	0.0043	0.6942	0.0024	**-0.0089**
iso-butane	0.0604	0.0013	0.0391	0.0018	**-0.0213**
n-butane	0.0777	0.0020	0.0624	0.0012	**-0.0153**
iso-pentane	0.0211	0.0008	0.0293	0.0022	**0.0082**
n-pentane	0.0100	0.0007	0.0112	0.0012	**0.0012**
CV (kJ/kg)	54569.1		54579.0		**9.9**
CV (BTU/rcf)	1064.14		1063.69		**-0.45**
Gas Density (kg/m3)	0.7280		0.7276		**-0.0004**

Figure 12 Raman validation results on a certified LNG mixture

The uncertainty for the Raman measurements U(yi) was calculated simply as twice the standard deviation of the repeat measurements for each component.

From the validation the deviation between the LNG standard and the Raman analyser under test was obtained against their respective uncertainties.

When replacing the uncertainty of the HCA calibration tool with the uncertainties of the validation the below figure 13 instrument specific uncertainty is calculated.

			Mole based calculation [%mole] / [15/15/1.01325]								[MJ/m3]	[MJ/kg]	
Description	**K**	**Source**	**Methane**	**Ethane**	**Propane**	**I Butane**	**N Butane**	**I Pentane**	**N Pentane**	**Nitrogen**	**GHV**	**GHV**	
LNG composition		**User[*1]**	92.8920	5.6370	0.7029	0.0604	0.0777	0.0211	0.0100	0.5981	39.627	54.539	
Raman uncertainty	**1**	**GERG trial[*2]**	0.0496	0.0433	0.0158	0.0090	0.0093	0.0138	0.0063	0.0084	0.026	0.015	
Repeatability	**1**	**GERG trial[*3]**	0.0251	0.0206	0.0044	0.0014	0.0013	0.0000	0.0008	0.0059	0.009	0.006	
LNG cert std Unc	**1**	**GERG trial[*4]**	0.0213	0.0044	0.0022	0.0007	0.0010	0.0004	0.0004	0.0143	0.003	0.001	
LNG val Raman bias		**GERG trial[*5]**	0.0074	0.0108	0.0012	0.0009	0.0006	0.0011	0.0005	0.0032	0.001	0.001	
GHV std uncertainty	**1**	**ISO6976;2016**									0.008	0.011	
uncertainty [u]	**1**	**Sum SQRT**	0.0600	0.0494	0.0166	0.0092	0.0094	0.0138	0.0064	0.0178	0.0287	0.0195	
Uncertainty [U])	**2**	**Sum SQRT**	**0.1199**	**0.0987**	**0.0333**	**0.0184**	**0.0188**	**0.0276**	**0.0128**	**0.0357**	**0.057**	**0.039**	
GHV relative uncertainty	**2**										0.14	0.07	% MV

Figure 13 Raman instrument specific uncertainty

These uncertainty results are used to evaluate the Raman instrument during the testing at Fluxys LNG. An excel calculation sheet for the uncertainty calculation is included as Appendix 5.

4. Hardware arrangement

This chapter describes the Raman field trial set-up for the instruments under test, how they are validated and how they are hooked up to the main LNG discharge line.

The field test was performed at the Fluxys LNG regassification terminal in Zeebrugge, Belgium.

4.1. Equipment under test

The equipment under test includes:

- The Raman instrument of the type RXN-3 using a 785nm laser, a Pilot-E probe suitable for insertion in the main LNG line and 300meter Fibre Optic cable made available by Kaiser Optical Systems Inc. Technical brochures are attached to this report under Appendix 1
- LNG vaporiser (Cegelec) and online gas chromatograph (Agilent AGI3000) used for LNG custody transfer by Fluxys LNG.
- Separate online analyser (Agilent AGI3000) was put in parallel with the Fluxys custody transfer gas chromatograph and calibrated per Fluxys LNG's custody transfer requirements using a Primary Reference Gas Mixture fully under ISO-17025 accreditation.
- Fluxys LNG laboratory gas chromatograph results from a separate LNG sampler are to be used for initial spot checks.

Fluxys LNG custody transfer measurement is frequently audited by independent surveyor as well as LNG suppliers and found compliant with ISO 8943; 2007. Fluxys LNG's Gas chromatograph performance verified by Fluxys LNG's laboratory.

Primary Reference Gas Mixture certificates used for calibration of the gas chromatographs are attached to this report under Appendix 4.

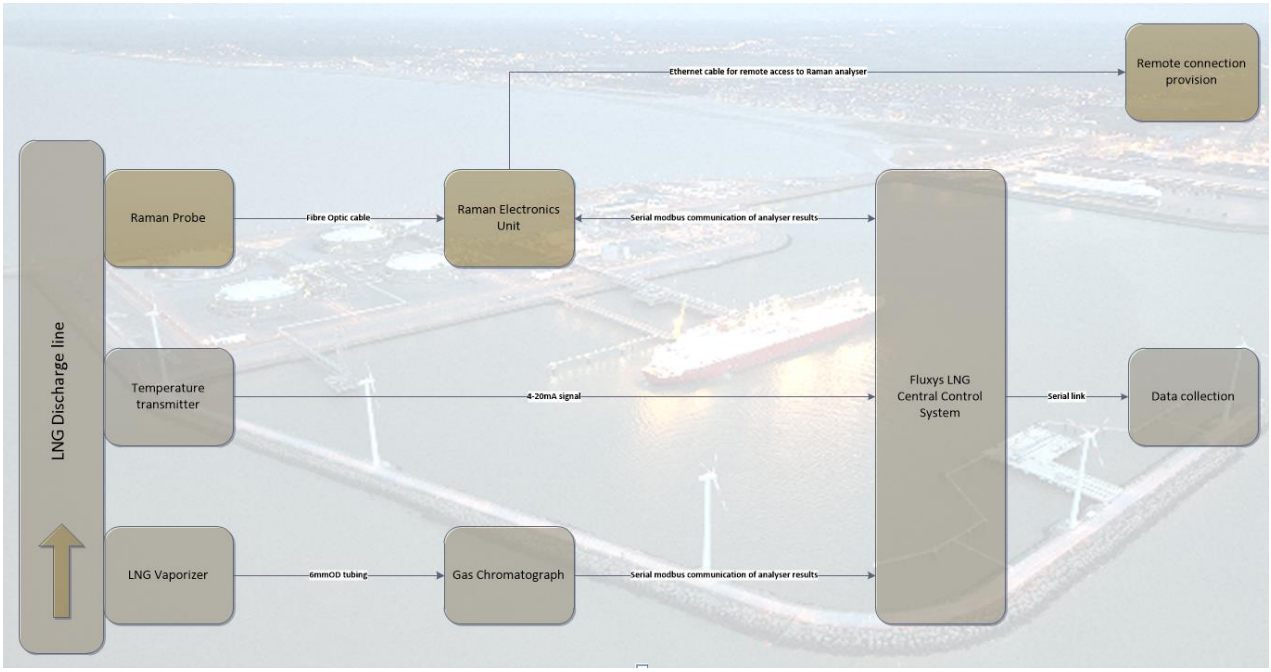


Figure 14 Block diagram measurement arrangement

5. Site installation and testing

The performance test followed the steps as described in the next paragraphs, in chronological order.

5.1. Raman analyser performance checks

As per the agreement E+H has made its RXN Raman analyser available for the field trial. As this is generic hardware, the LNG composition measurement application model was installed on the analyser by the E+H application engineer.

To make sure the Raman instrument and application are working within the limits, the Raman analyser FO cable and measuring probe were sent to the Effectech metrology laboratory for a validation run on a certified LNG standard. For this validation, the composition was matched closely to the average LNG composition discharged at Fluxys LNG as per Chapter 3.3.7 of this report.

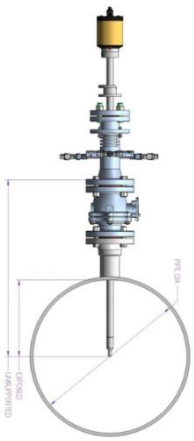
A detailed description of the Effectech cryostat and validation report is included in Appendix 2.

5.2. Installation, Commissioning & Start-up

For the field trial the E+H commissioning engineer came to the installation site to assist Fluxys LNG maintenance staff on the installation and commissioning of the Raman analyser.

Installation

The Raman analyser is installed on a spare 3"-300# process connection on top of the LNG discharge line. Measurement location is at a low point in the LNG discharge line to ensure line is completely filled with LNG.



The probe is directly inserted in the main process line using a "Lubricator body" designed for use in cryogenic conditions, which enables the user to insert and retract the probe during operations.

The Raman probe tip insertion in the main process line is generally limited to remain in the outer 0.25 ID of the main line to avoid excessive stress on the probe.

It is highly recommended to have the vendor perform a vortex shedding calculation according international standards (e.g. ASME-PTC.19.3) when determining the final length of the probe.

From the jetty, the Raman analyser take-off location is about 300 meters downstream of the LNG vaporiser used to feed gas to the gas chromatograph used in LNG custody transfer.

For the temperature measurement the PT-100 temperature element located about 100 meters upstream the Raman probe in the LNG discharge line is used as temperature input for the Raman model. If implemented for the purpose of temperature correction the temperature probe shall be a class-A PT-100 calibrated for a cryogenic temperature range.

The electronic units for both the gas chromatographs and the Raman analyser are in the same analyser house.

The analyser house is a climate-controlled building fitted with safeguarding measures to safely allow flammable gases to be measured.

The Raman analyser is connected to the Fluxys LNG's central control system through a serial connection based on a Modbus TCP/IP serial connection.

An ethernet connection is provided to allow E+H to login to the Raman electronics unit remotely when access is granted by the Fluxys LNG maintenance team.

5.2.1. Commissioning & Start-up

Raman optical calibration

Before the validation on any process fluid mixture can be started, the Raman analyser, FO cable and probe need to be connected to allow for a light intensity calibration.

This calibration corrects for any transmission losses that are introduced by slight manufacturing tolerances on the instrument, the Fiber Optic cable (including cable length) and the Raman probe.

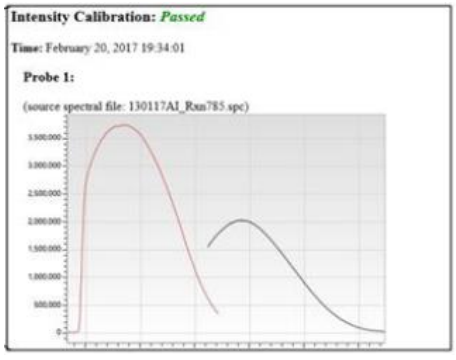
To set these values correctly, the following three internal calibrations must be executed:

- A spectrometer wavelength calibration
- A laser wavelength calibration
- A full spectrograph intensity calibration

A spectrometer wavelength calibration is executed by calibrating against a set of neon atomic emission wavelengths.

A laser wavelength calibration is executed by calibrating against a fixed shift from a diamond installed as a calibration standard in the Raman analyser.

The full spectrograph intensity calibration is performed by using a white light source with a known intensity over the wavelength range of the detector having a NIST traceable uncertainty over the full wavelength range considering multiple calibrators.



The white light spectrum file is supplied with the calibration unit and must be loaded as a calibration file in the Raman analyser. This will be used to correct the optical response from the system under test.

The full calibration and verification report can be saved locally as a *.pdf file and viewed on the analyser screen as well as accessed remotely using the analyser maintenance software.

For full details on optical validation/calibration of the Raman analyser we refer to ASTM D7940-2014.

After this a full system verification was performed on a surrogate fluid with a known Raman response at the key peaks of interest and for subsequent derived property calculations. After verifying that the Raman response is within the set limits, the probe was installed into the LNG discharge line.

To keep the analyser stable during operation, at factory set predetermined intervals, the automatic calibration function of the Raman analyser[1)] will compare the current instrument response to calibration specifications and will recalibrate the spectrograph wavelength against a Neon source and laser wavelength against a diamond shift if this is out of spec.

During start-up the performance of the Raman analyser was monitored on LNG by means of the Raman signal intensity. The signal intensity should not be more than 80% to avoid overloading the optical detector. For the Raman system at Fluxys LNG the signal intensity was 56% which is matching the values shown during the validation at the Effectech test laboratory. The signal intensity value does not impact the metrology provided by the analyser. The recommended operating range is between 20% and 70%.

With this the Raman analyser is fully operational and ready for the field trial.

No further preventive or corrective maintenance was performed on the Raman analyser during the performance run.

*1) Wavelength calibrations are validated automatically typically every hour and calibrated when deviations are above threshold values to ensure measurement results are not influenced by the instruments optical arrangement and instrument temperature fluctuations. Other than this, no preventive maintenance was done on the Raman analyser during the evaluation period.

6. Performance testing

During the data collection period in total 7 performance runs where done where after each performance runs corrections were made either in the model or in the data communication. The 7th performance run was the final run.

One of the main findings was that in order to meet the tight performance criteria required for custody transfer an LNG temperature compensation was required which was developed under this test program.

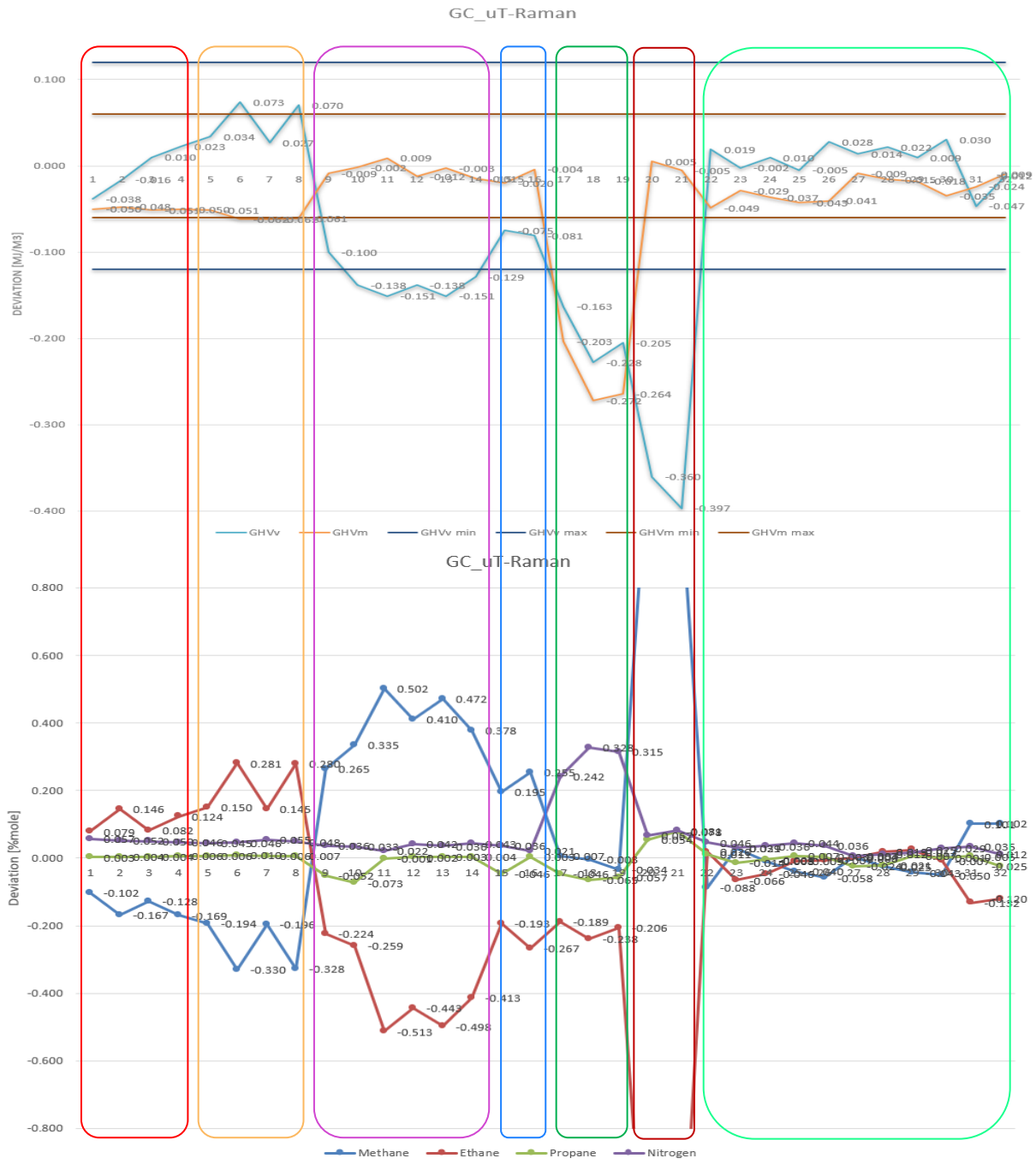


Figure 15 Different performance runs at Fluxys LNG

The boxes in the graphs of figure 15 indicate the different performance runs done over time to come to the final model resulting in meeting the performance specifications.

- Red box is the initial performance run at stable LNG temperature of 113K.
- Yellow box is the performance run at varying LNG temperatures between 113 to 117K.
- Magenta box is the first performance run on the new model with temperature compensation included. (*Temperature on wrong serial communication address*)
- Blue box performance run with temperature reading connected but temperature model compensation not working. (*kept referring to fixed temperature of 113K*)
- Dark green box performance run after correcting temperature reading for the model compensation. (*values kept referring to fixed temperature of 113K)*
- Brown box performance run with temperature measurement live and correction working but with temperature reading set in °C instead of Kelvin.
- Light green box final performance run with temperature correction working correcting

6.1.1. Raman temperature compensation.

During the first test run at Fluxys LNG a variation in the performance was found during different runs. Although the results would meet the requirements for an online analyser for process control they were outside the limits set for custody transfer.

During a detailed investigation it was found that the root cause was due to changes in LNG temperature. With the unit at Effectech it was decided that E+H would add temperature compensation to the model.

The temperature range for the compensation was determined together with the GERG steering committee considering both traditional and the downstream LNG applications as well as the LNG composition range based on GIIGNL cargo data.

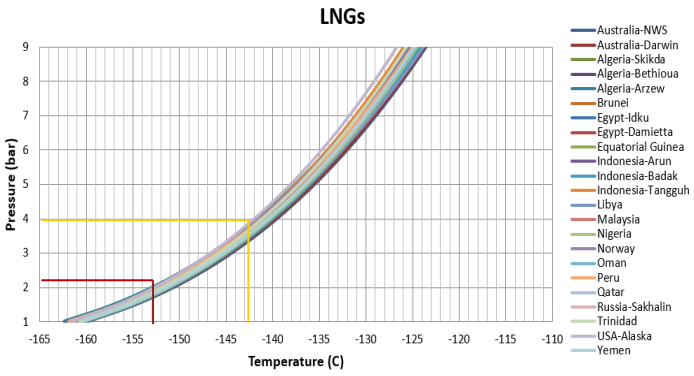


Figure 16 LNG temperature compensation range (courtesy of Enagás)

LNG cargo loading for retail LNG and bunkering is determined at 3-4 bara at a maximum.

From bubble curve calculation based on GIIGNL cargo data shown in figure 16, the temperature range for LNG custody transfer is -163 to -143°C (110 – 130K).

Due to a design pressure limitation on the cryostat of 3 bara and having to take a margin to avoid being too close to the bubble point the current model is developed over the temperature range of -180 to -156°C (93 – 117K). Due to the limited a linearity in the temperature correction the analyser should be able to cover temperatures up to 130K but caution is advised on extrapolating on the corrections across the min/max temperature values.

After E+H added the temperature compensation a model verification was performed. To test the model including the temperature compensation the GERG steering committee proposed five (5) certified LNG mixtures covering the range of LNG compositions based on the GIIGNL cargo data. These LNG mixtures are checked over a temperature range achievable with the cryostat.

component	Mix1	Mix2	Mix3	Mix4	Mix5		min	max
nitrogen	0.040	0.050	1.050	0.570	0.300		0.040	1.050
methane	87.000	98.170	90.500	92.918	92.870		87.000	98.170
ethane	10.500	1.300	4.210	5.639	4.500		1.300	10.500
propane	2.000	0.160	3.000	0.703	1.750		0.160	3.000
iso-butane	0.210	0.100	0.400	0.060	0.300		0.060	0.400
n-butane	0.240	0.120	0.600	0.078	0.250		0.078	0.600
iso-pentane	0.005	0.060	0.120	0.021	0.020		0.005	0.120
n-pentane	0.005	0.040	0.120	0.010	0.010		0.005	0.120
sum	100.00	100.00	100.00	100.00	100.00			

Figure 17 LNG compositions for testing Raman performance

This also provided the opportunity to evaluate the Raman analyser performance on a wide range of compositions which, due to the limited variations at Fluxys LNG, could not be done during the field trial.

It was agreed with E+H to do an initial test on Mixtures 1 and 4 and evaluate the performance allowing E+H to make final modifications. Mixtures 2, 3 and 5 are used to evaluate the performance on the final model.

After the first validation using mixture 5, it was found that a programming error in the TC model was causing a significant bias in the temperature causing invalid readings.

The error was corrected and the validation was continued with the other two gasmixtures. As this would include a formal validation for releasing the analyzer back to Fluxys LNG it was decided to prepare a sixth mix with a similar composition as mix 5 and include this in the evaluation.

The test is considered successful when the validation is within the set limit values from the uncertainty model for both composition and GHV.

For GHV, the results of the tests are shown in two graphs (Figure 18 and 19). The Detailed composition data is attached under appendix 3 Raman temperature compensation testing. The compositions differ slightly from the requested composition in figure 17 as a result from blending tolerances.

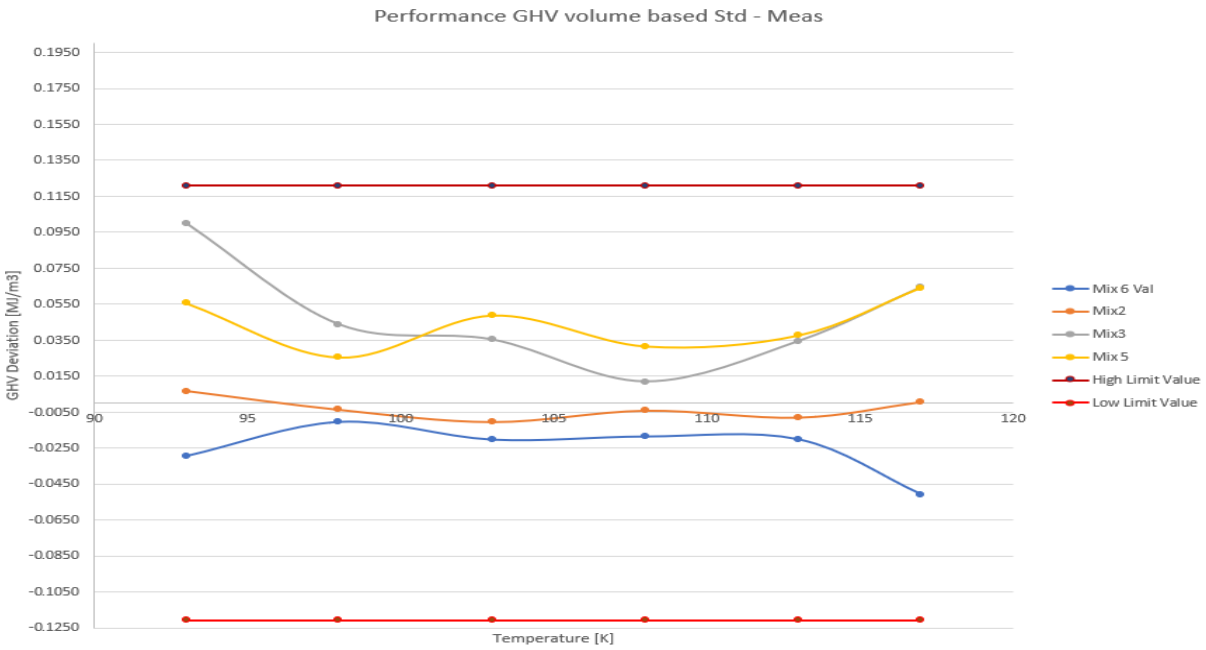


Figure 18 Performance GHV vol with TC

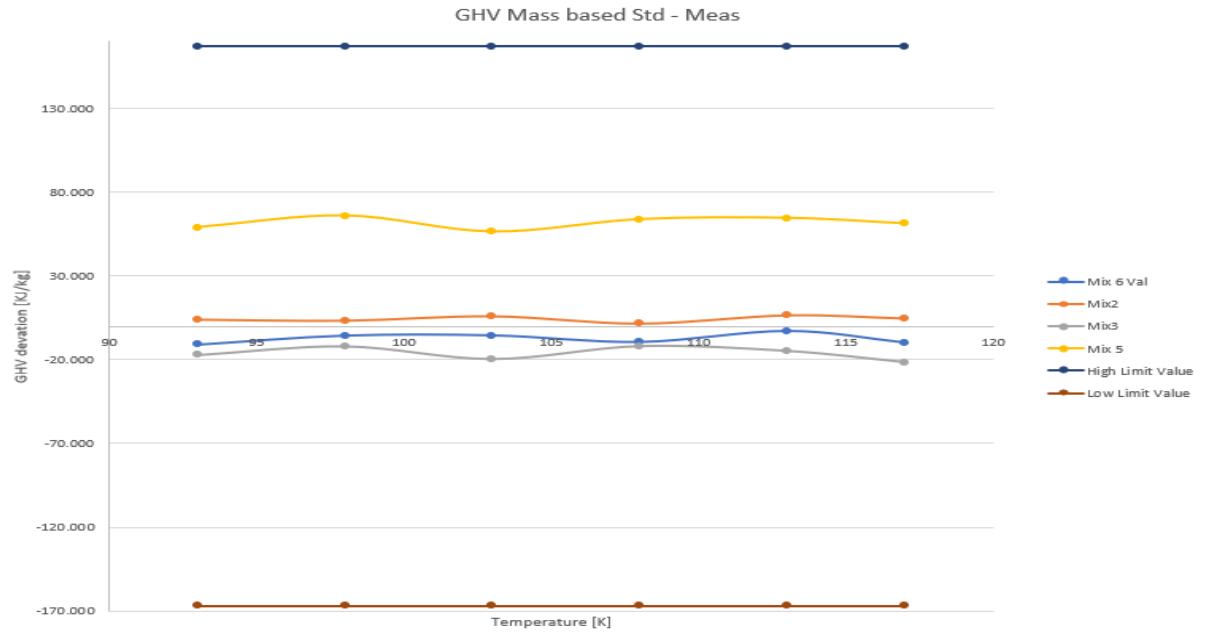


Figure 19 Performance GHV mass with TC

6.1.2. Hardware performance.

Over the test period, the analyser hardware performed very reliably with the following remarks:

- October 2019 a hardware failure occurred on the power board; the manufacturer replaced the power board after which the measurement could continue requiring only the internal optical calibration cycles.
- For the field test, the Raman instrument was fitted with a temporary software licence. As the testing period was longer as initially planned, the licence expired stopping the instrument. After the licence was re-activated the measurement could continue without requiring any additional calibrations. For this, the manufacturer was allowed access to the Raman unit to extend the temporary license for the instrument software. This feature can be used by the vendor to provide remote support to customers
- The Raman analyser's automatic internal calibration cycle for the optics proved very efficient causing the analyser to run drift free for whole trial period. The first period of was one and a half (1.5) year of drift free operation with a second period of one (1) year. In between the analyser was taken out to perform additional model testing at the test laboratory.

Preventive maintenance

Although during the test the Raman analyser did not require any maintenance, for long term operations the following preventive maintenance is to be considered.

- Replacing the Neon calibration board every four (4) years. After replacing the board an internal optical validation shall be performed.
- Replace the Laser every four (4) years. After replacing the laser, a full intensity calibration needs to be performed which would require the probe to be taken out of the process.
- Typically, the manufacturer recommends returning the HCA tool to their calibration facility every two years to verify if the uncertainty is met.

The typical advised life cycle of the Raman analyser's Neon calibration board and the laser unit is estimated at 5 years.

Typically, the time required for these maintenance actions is less than a working day. With taking out the probe and warming up would be the most time-consuming part.

A typical verification procedure from purchase to commissioning and operation is provided in appendix 7. The procedures are based on lessons learned in the Raman field trial and are included as a handout to LNG sites, terminals, and barges. It is at each owner's discretion to tune the maintenance program to their individual requirements including the necessary verification steps to make sure the measurement is installed with a traceable reference.

6.1.3. Final performance run

The final performance run was done from January 2020 till August 2020 and the evaluation includes 12 LNG cargoes.

During this performance run no maintenance or validation was performed on the Raman analyser. In an effort to present most realistic data, we choose not to apply filtering of measurement data (outlier removal) on the individual cargo runs.

The individual cargo evaluations against both the method uncertainty and the instrument specific performance limits are included under appendix 6.

The uncertainty limit shown for the GC is the performance limit values where Uxi_GC/Vap values reflect 0.2%MV and LNG density is 0.45% as per the GIIGNL CTH version 6.0 and is identical for both tables.

For the LNG density is included for completeness and is evaluated against the uncertainty limit stated in GIIGNL

For the Raman analyser two different uncertainties are used:

- For figure 20, the Raman method uncertainty reflects the uncertainty that is calculated based on the manufactures procedure and using optical calibration tool.
- In figure 21, the Raman instrument uncertainty reflects the uncertainty calculated taking the results from the validation with the certified LNG standard instead of the optical calibration tool uncertainty.

Composition			Evaluation online metering GC						Evaluation Raman in LNG line				Evaluation ISO 17043 En		
LNG Temp	116K		As Left T15 GC_uT				GIIGNL		Raman Method Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi MC_model	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		95.607	0.011	0.1170	0.1175			95.694	0.2007			-0.087	0.37	Pass
Ethane	%mole		3.769	0.014	0.0520	0.0538			3.750	0.1736			0.019	0.11	Pass
Propane	%mole		0.378	0.0032	0.0291	0.0293			0.367	0.0413			0.010	0.21	Pass
I Butane	%mole		0.087	0.0004	0.0200	0.0201			0.085	0.0197			0.002	0.08	Pass
N Butane	%mole		0.073	0.0006	0.0191	0.0191			0.063	0.0197			0.010	0.37	Pass
I Pentane	%mole		0.010	0.0002	0.0116	0.0116			0.000	0.0175			0.010	0.46	Pass
N Pentane	%mole		0.005	0.0002	0.0098	0.0098			0.005	0.0100			0.000	0.01	Pass
Nitrogen	%mole		0.071	0.0014	0.0193	0.0193			0.026	0.0258			0.046	1.42	Bias
GHV	MJ/m3		39.111	0.021	0.0750	0.0779	0.20		39.092	0.0744	0.19		0.019	0.17	Pass
GHV	MJ/kg		55.169	0.01200	0.0270	0.0295	0.05		55.219	0.0431	0.08		-0.050	0.96	Pass
LNG Dens	kg/m3		433.637			1.9514	0.45		433.208	1.9494	0.45		0.429	0.16	Pass

Figure 20 Evaluation based on GIIGNL limits and Raman acc. standard manufacturer optical calibration procedure

Composition			Evaluation online metering GC						Evaluation Raman in LNG line				Evaluation ISO 17043 En		
LNG Temp	116K		As Left T15 GC_uT				GIIGNL		Raman Instr Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		95.607	0.011	0.1170	0.1175			95.694	0.1262			-0.087	0.50	Pass
Ethane	%mole		3.769	0.014	0.0520	0.0538			3.750	0.0994			0.019	0.17	Pass
Propane	%mole		0.378	0.0032	0.0291	0.0293			0.367	0.0391			0.010	0.21	Pass
I Butane	%mole		0.087	0.0004	0.0200	0.0201			0.085	0.0195			0.002	0.08	Pass
N Butane	%mole		0.073	0.0006	0.0191	0.0191			0.063	0.0196			0.010	0.37	Pass
I Pentane	%mole		0.010	0.0002	0.0116	0.0116			0.000	0.0177			0.010	0.45	Pass
N Pentane	%mole		0.005	0.0002	0.0098	0.0098			0.005	0.0101			0.000	0.01	Pass
Nitrogen	%mole		0.071	0.0014	0.0193	0.0193			0.026	0.0388			0.046	1.05	Bias
GHV	MJ/m3		39.111	0.021	0.0750	0.0779	0.20		39.092	0.0539	0.14		0.019	0.20	Pass
GHV	MJ/kg		55.169	0.0120	0.0270	0.0295	0.05		55.219	0.0413	0.07		-0.050	0.98	Pass
LNG Dens	kg/m3		433.637			1.9514	0.45		433.208	1.9494	0.45		0.429	0.16	Pass

Figure 21 Evaluation based on GIIGNL limits and Raman uncertainty using certified LNG std.

An instrument specific evaluation Figure 22 is added to demonstrate the maximum measurement capability of each measurement set-up. For this evaluation the site repeatability data on the GC/Vaporizer is used instead of the GIIGNL limits. For the Raman the site-specific data developed under this test program is used.

Composition			Evaluation online metering GC						Evaluation Raman in LNG line				Evaluation ISO 17043 En		
LNG Temp	116K		As Left T15 GC_uT				GIIGNL		Raman Instr Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo Repeat	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		95.607	0.011	0.0506	0.0518			95.694	0.1262			-0.087	0.64	Pass
Ethane	%mole		3.769	0.014	0.0371	0.0397			3.750	0.0994			0.019	0.18	Pass
Propane	%mole		0.378	0.0032	0.0087	0.0093			0.367	0.0391			0.010	0.26	Pass
I Butane	%mole		0.087	0.0004	0.0034	0.0035			0.085	0.0195			0.002	0.11	Pass
N Butane	%mole		0.073	0.0006	0.0034	0.0035			0.063	0.0196			0.010	0.52	Pass
I Pentane	%mole		0.010	0.0002	0.0007	0.0007			0.000	0.0177			0.010	0.54	Pass
N Pentane	%mole		0.005	0.0002	0.0004	0.0004			0.005	0.0101			0.000	0.02	Pass
Nitrogen	%mole		0.071	0.0014	0.0030	0.0033			0.026	0.0388			0.046	1.17	Bias
GHV	MJ/m3		39.111	0.021	0.0210	0.0297	0.08		39.092	0.0539	0.14		0.019	0.30	Pass
GHV	MJ/kg		55.169	0.0120	0.0050	0.0130	0.02		55.219	0.0413	0.07		-0.050	1.15	Bias
LNG Dens	kg/m3		433.637			1.9514	0.45		433.208	1.9494	0.45		0.429	0.16	Pass

Figure 22 Evaluation based on GC/Vaporizer cargo limits and Raman uncertainty using certified LNG std.

For the tables below, the first table shows the En comparison results that is used to verify if the difference between the readings is significant if compared to the uncertainty limits.

The second table gives a numerical presentation of the main components used in the custody transfer process with their limit values. The limit values are calculated by using the root mean square of the GC /Vaporizer and Raman maximum allowed uncertainties.

Again, for the Raman instrument both the method uncertainty and the uncertainty using a certified LNG standard are shown respectively in figures 23 and 24. The figure 25 is the site-specific repeatability used for the GC/Vaporizer as well as the Raman instrument.

En Evaluation between Raman analyser and Fluxys LNG vaporizer/GC according ISO 17043												
Test Cargo nr.	Methane	Ethane	Propane	I Butane	N Butane	I Pentane	N Pentane	Nitrogen	GHV_vol	GHV_mass	LNG Dens	En Limit
	En	En	En	En	En	En	En	En	En	En	En	En
T15	0.3740	0.1054	0.2059	0.0788	0.3738	0.4561	0.0142	1.4167	0.1740	0.9567	0.1556	1.0000
T16	0.1118	0.3631	0.2160	0.1505	0.6273	0.3082	0.0930	0.8171	0.0182	0.4981	0.0374	1.0000
T17	0.0323	0.2505	0.0815	0.2138	0.7004	0.2962	0.0663	0.9802	0.0788	0.5668	0.0883	1.0000
T18	0.1670	0.0494	0.1455	0.0397	0.1963	0.1543	0.0248	1.2478	0.0372	0.7643	0.0717	1.0000
T19	0.1468	0.1113	0.0208	0.2253	0.7171	0.3132	0.0915	0.9667	0.1680	0.6579	0.1496	1.0000
T20	0.2087	0.0147	0.0207	0.2627	0.7364	0.3017	0.0778	0.7507	0.2561	0.5770	0.3737	1.0000
T21	0.1826	0.0866	0.0030	0.2676	0.7533	0.2832	0.0886	0.9418	0.2013	0.6735	0.1376	1.0000
T22	0.1381	0.0964	0.1532	0.0548	0.1108	0.0231	0.0243	0.3529	0.0790	0.2622	0.0622	1.0000
T23	0.1996	0.0396	0.0098	0.2801	0.6871	0.3958	0.0981	0.7860	0.2545	0.6608	0.1442	1.0000
T24	0.3296	0.4861	0.1155	0.1249	0.0249	0.0001	0.0199	0.6691	0.3777	0.3304	0.0942	1.0000
T25	0.3193	0.5177	0.3410	0.0040	0.5870	0.7616	0.0830	0.2411	0.0914	0.0790	0.0348	1.0000
T26	0.2721	0.0821	0.1576	0.0964	0.3263	0.0834	0.0375	1.4043	0.0646	0.8902	0.1262	1.0000

Figure 23 Cargo evaluation results for standard manufacturer optical calibration procedure

En Evaluation between Raman analyser and Fluxys LNG vaporizer/GC according ISO 17043												
Test Cargo nr.	Methane	Ethane	Propane	I Butane	N Butane	I Pentane	N Pentane	Nitrogen	GHV_vol	GHV_mass	LNG Dens	En Limit
	En	En	En	En	En	En	En	En	En	En	En	En
T15	0.5044	0.1696	0.2131	0.0791	0.3749	0.4534	0.0142	1.0530	0.1979	0.9843	0.1556	1.0000
T16	0.1693	0.5831	0.2603	0.1578	0.6470	0.3112	0.0931	0.6598	0.0224	0.5426	0.0374	1.0000
T17	0.0493	0.4071	0.0980	0.2248	0.7217	0.2913	0.0659	0.7795	0.0979	0.6130	0.0883	1.0000
T18	0.2207	0.0804	0.1475	0.0396	0.1959	0.1522	0.0248	0.9622	0.0415	0.7869	0.0717	1.0000
T19	0.2247	0.1839	0.0250	0.2343	0.7357	0.3134	0.0912	0.7693	0.2061	0.7139	0.1496	1.0000
T20	0.3135	0.0233	0.0248	0.2752	0.7544	0.2980	0.0778	0.6114	0.3118	0.6249	0.3737	1.0000
T21	0.2757	0.1390	0.0035	0.2808	0.7758	0.2827	0.0881	0.7635	0.2466	0.7322	0.1376	1.0000
T22	0.2282	0.2060	0.1529	0.0544	0.1109	0.0233	0.0238	0.3238	0.0944	0.2897	0.0622	1.0000
T23	0.3000	0.0639	0.0116	0.2928	0.7084	0.3904	0.0968	0.6321	0.3094	0.7157	0.1442	1.0000
T24	0.5288	1.0395	0.1152	0.1253	0.0244	0.0001	0.0198	0.5928	0.4583	0.3584	0.0942	1.0000
T25	0.6045	1.0462	0.4427	0.0041	0.6099	0.7595	0.0823	0.2405	0.1201	0.0958	0.0348	1.0000
T26	0.4786	0.1894	0.1604	0.0971	0.3280	0.0825	0.0373	1.0679	0.0830	0.9441	0.1262	1.0000

Figure 24 Cargo evaluation results Raman uncertainty using certified LNG std.

En Evaluation between Raman analyser and Fluxys LNG vaporizer/GC according ISO 17043												
Test Cargo nr.	Methane	Ethane	Propane	I Butane	N Butane	I Pentane	N Pentane	Nitrogen	GHV_vol	GHV_mass	LNG Dens	En Limit
	En	En	En	En	En	En	En	En	En	En	En	En
T15	0.6376	0.1791	0.2589	0.1116	0.5163	0.5417	0.0197	1.1721	0.3045	1.1542	0.1556	1.0000
T16	0.2132	0.6207	0.3404	0.2627	1.0454	0.3609	0.1314	0.7835	0.0367	0.6892	0.0374	1.0000
T17	0.0623	0.4352	0.1268	0.3760	1.1656	0.3362	0.0911	0.9169	0.1604	0.7741	0.0883	1.0000
T18	0.2767	0.0811	0.1775	0.0526	0.2575	0.1740	0.0353	1.1200	0.0626	0.9736	0.0717	1.0000
T19	0.2692	0.1858	0.0314	0.3774	1.1682	0.3626	0.1281	0.8987	0.3123	0.9035	0.1496	1.0000
T20	0.3745	0.0244	0.0302	0.4220	1.1255	0.3456	0.1094	0.7249	0.4656	0.7982	0.3737	1.0000
T21	0.2650	0.1179	0.0039	0.4263	1.1688	0.3252	0.1224	0.8941	0.3165	0.8958	0.1376	1.0000
T22	0.3142	0.2286	0.1772	0.0676	0.1372	0.0248	0.0260	0.4341	0.1517	0.4253	0.0622	1.0000
T23	0.3882	0.0694	0.0152	0.4817	1.1387	0.4585	0.1379	0.7476	0.5099	0.9247	0.1442	1.0000
T24	0.7506	1.2017	0.1326	0.1264	0.0258	0.0001	0.0208	0.7298	0.7511	0.4838	0.0942	1.0000
T25	0.5871	0.8639	0.5274	0.0061	0.9701	0.9535	0.1170	0.2971	0.1543	0.1295	0.0348	1.0000
T26	0.4966	0.1517	0.1914	0.1394	0.4689	0.0904	0.0470	1.2205	0.1180	1.1313	0.1262	1.0000

Figure 25 Cargo evaluation results on Site repeatability instead of GIIGNL limits

Repeatability

Comparing the results between the Raman analyser and the existing measurement system has been done using the uncertainty limits. The repeatability is used to review the measurement performance of the individual instruments during the cargo loadings.

Raman repeatability over cargoes under test													
Test Cargo nr.	Instrument	Raman Methane %mole	Raman Ethane %mole	Raman Propane %mole	Raman I_Butane %mole	Raman N_Butane %mole	Raman I_Pentane %mole	Raman N_Pentane %mole	Raman Nitrogen %mole	Raman GHV_vol MJ/m3	Raman GHV_v %MV	Raman GHV_mass MJ/kg	Raman GHV_m %MV
T15	Raman	0.019	0.014	0.004	0.002	0.001	0.000	0.002	0.007	0.008	0.019	0.006	0.011
T16	Raman	0.040	0.030	0.007	0.003	0.002	0.000	0.002	0.007	0.016	0.039	0.007	0.013
T17	Raman	0.040	0.028	0.010	0.003	0.003	0.000	0.002	0.007	0.017	0.043	0.008	0.015
T18	Raman	0.056	0.046	0.008	0.003	0.003	0.000	0.002	0.008	0.023	0.059	0.007	0.013
T19	Raman	0.045	0.033	0.009	0.003	0.002	0.000	0.002	0.014	0.019	0.047	0.012	0.023
T20	Raman	0.047	0.032	0.009	0.003	0.003	0.000	0.002	0.008	0.019	0.047	0.009	0.016
T21	Raman	0.028	0.018	0.005	0.002	0.002	0.000	0.002	0.008	0.009	0.024	0.008	0.015
T22	Raman	0.048	0.036	0.011	0.003	0.002	0.000	0.001	0.011	0.017	0.043	0.011	0.019
T23	Raman	0.039	0.029	0.008	0.003	0.003	0.000	0.002	0.012	0.019	0.049	0.010	0.018
T24	Raman	0.045	0.039	0.002	0.002	0.000	0.000	0.001	0.018	0.013	0.032	0.017	0.030
T25	Raman	0.069	0.051	0.011	0.002	0.003	0.000	0.002	0.023	0.024	0.061	0.022	0.040
T26	Raman	0.092	0.090	0.011	0.003	0.003	0.000	0.001	0.008	0.029	0.074	0.009	0.017
Total	**Rep_Raman (k=2)**	**0.051**	**0.042**	**0.009**	**0.003**	**0.003**	**0.000**	**0.002**	**0.011**	**0.019**	**0.048**	**0.011**	**0.020**
	Pooled St Dev Raman	**0.025**	**0.021**	**0.004**	**0.001**	**0.001**	**0.000**	**0.001**	**0.006**	**0.010**	**0.024**	**0.005**	**0.010**
GIIGNL Performance limits	**Precision [U] (K=2)**	0.113	0.050	0.035	0.027	0.025	0.012	0.010	0.025		**0.2**		**0.07**
ASTM D7940-14 Performance limits	**Mean all Cargoes**	**94.491**	**3.796**	**0.931**	**0.297**	**0.246**	**0.011**	**0.007**	**0.22**	**39.699**		**55.089**	
	St Dev Limit [u]	0.03	0.03	0.03	0.01	0.01	0.006	0.006	0.01				
	Precision [U] (K=2)	**0.060**	**0.060**	**0.060**	**0.020**	**0.020**	**0.012**	**0.012**	**0.020**		**0.05**		

Figure 26 Repeatability for the Raman instrument

GC repeatability over cargoes under test													
Test Cargo nr.	Instrument	GC Methane %mole	GC Ethane %mole	GC Propane %mole	GC I_Butane %mole	GC N_Butane %mole	GC I_Pentane %mole	GC N_Pentane %mole	GC Nitrogen %mole	GC GHV_vol MJ/m3	GC GHV_v %MV	GC GHV_mass MJ/kg	GC GHV_m %MV
T15	GC/Vaporizer	0.0506	0.0371	0.0087	0.0034	0.0034	0.0007	0.0004	0.0030	0.0210	0.0530	0.0050	0.0110
T16	GC/Vaporizer	0.0476	0.0329	0.0111	0.0044	0.0047	0.0002	0.0002	0.0039	0.0200	0.0510	0.0057	0.0100
T17	GC/Vaporizer	0.0466	0.0315	0.0126	0.0043	0.0047	0.0002	0.0002	0.0035	0.0200	0.0500	0.0055	0.0100
T18	GC/Vaporizer	0.0697	0.0566	0.0093	0.0032	0.0033	0.0003	0.0002	0.0048	0.0270	0.0680	0.0060	0.0110
T19	GC/Vaporizer	0.0669	0.0484	0.0156	0.0056	0.0057	0.0002	0.0002	0.0066	0.0310	0.0790	0.0050	0.0100
T20	GC/Vaporizer	0.0690	0.0394	0.0208	0.0099	0.0102	0.0004	0.0002	0.0063	0.0360	0.0900	0.0087	0.0160
T21	GC/Vaporizer	0.1234	0.0862	0.0272	0.0098	0.0095	0.0003	0.0002	0.0077	0.0520	0.1300	0.0122	0.0220
T22	GC/Vaporizer	0.0536	0.0470	0.0116	0.0029	0.0026	0.0001	0.0002	0.0078	0.0220	0.0550	0.0069	0.0130
T23	GC/Vaporizer	0.0389	0.0262	0.0101	0.0042	0.0045	0.0003	0.0002	0.0057	0.0190	0.0480	0.0059	0.0100
T24	GC/Vaporizer	0.0513	0.0398	0.0006	0.0000	0.0001	0.0000	0.0000	0.0185	0.0150	0.0380	0.0180	0.0320
T25	GC/Vaporizer	0.1223	0.0965	0.0256	0.0029	0.0075	0.0005	0.0001	0.0132	0.0510	0.1280	0.0110	0.0200
T26	GC/Vaporizer	0.1147	0.1080	0.0127	0.0040	0.0041	0.0001	0.0001	0.0037	0.0380	0.0950	0.0075	0.0140
Total	**Rep_GC (k=2)**	**0.072**	**0.056**	**0.014**	**0.005**	**0.005**	**0.0003**	**0.0002**	**0.008**	**0.029**	**0.074**	**0.009**	**0.016**
	Pooled St Dev GC	**0.036**	**0.028**	**0.007**	**0.003**	**0.003**	**0.0001**	**0.0001**	**0.004**	**0.015**	**0.037**	**0.004**	**0.008**
GIIGNL Performance limits	**Precision [U] (K=2)**	0.113	0.050	0.035	0.027	0.025	0.012	0.010	0.025		**0.2**		**0.07**

Figure 27 Repeatability for the GC/Vaporizer

6.1.4. Validation after testing

After completing the Raman analyser is shipped back to the metrology laboratory to do final verification to make sure the Raman analyser performance is in line with the validation done before starting the field trial at Fluxys LNG. The test is considered successful when the validation is within the set limit values from the uncertainty model for both composition and GHV as shown in chapter 3.

Raman analyser repair

During unpacking of the Raman analyser at the metrology laboratory it was found damaged during the transport and during power up it became apparent that both the laser module was damaged beyond repair and the cooling system required repair and coolant filling.

The manufacturer shipped the parts and repairs were made by the metrology laboratory staff with virtual presence of the manufacturer by video link and remote connection to the Raman analyser. The below repairs and verification were executed:

1) The laser module of the Rxn3 was replaced Friday, January 29, 2021
2) Coolant for the liquid cooling system was added to the reservoir on January 29, 2021.
3) A remote support session was conducted on February 2, 2021 with the following executed:
    a. Logged into the system and backed up all log and .ini files, and took screenshots of the laser control settings and LNG configuration parameters to keep a baseline
    b. Connected HCA calibration tool to the Pilot probe and performed a system wavelength calibration, following the standard operating procedure.
    c. Performed a throughput (intensity) calibration using the NIST-traceable white light source of the HCA following the standard operating procedure.
    d. Added Cyclohexane to a sample cell connected to the probe and performed a laser wavelength calibration, following the standard operating procedure.
    e. The Raman analyser was set to the cyclohexane verification program, which is for collecting results for Methane, Ethane and Wobbe Index which are evaluated against predetermined limits.
4) On February 3rd, 2021, two (2) cyclohexane surrogate verifications were run on the system and passed the verification testing.

The surrogate verification results, as well as one done on November 17, 2015, were compared and shown to be within the accepted tolerance values as shown in the table below.

Method ID	Results			Temperature	Methane [%mole]		Ethane [%mole]		Wobbe Index [BTU]	
	Methane	Ethane	Wobbe Index	[K]	Target Low	Target High	Target Low	Target High	Target Low	Target High
RXN Cyclo LNG Surrogate 10/1/2018 3:14:29 PM	89.49	4.96	1428.79	298	89.2	89.6	4.9	5.2	1427	1432
RXN Cyclo LNG Surrogate 10/1/2018 3:14:29 PM	89.36	5.00	1430.08	298	89.2	89.6	4.9	5.2	1427	1432
RXN Cyclo LNG Surrogate 10/1/2018 3:14:29 PM	89.53	4.92	1428.92	298	89.2	89.6	4.9	5.2	1427	1432

Method ID	Results			Temperature	Methane [%mole]		Ethane [%mole]		Wobbe Index [BTU]	
	Methane	Ethane	Wobbe Index	[K]	Target Low	Target High	Target Low	Target High	Target Low	Target High
RXN Cyclo LNG Surrogate Before white light 3/2/2021 17:49	89.45	4.97	1427.92	298.00	89.20	89.60	4.90	5.20	1427	1432
RXN Cyclo LNG Surrogate Before white light 3/2/2021 17:58	89.43	4.98	1428.15	298.00	89.20	89.60	4.90	5.20	1427	1432
RXN Cyclo LNG Surrogate After white light 3/8/2021 15:11	89.44	4.98	1428.16	298.00	89.20	89.60	4.90	5.20	1427	1432
RXN Cyclo LNG Surrogate After white light 3/8/2021 15:15	89.40	4.99	1426.55	298.00	89.20	89.60	4.90	5.20	1427	1432

Figure 28 Raman spectral verification on cyclo-hexane surrogate fluid

Raman final validation run

With the Raman analyser repaired, the final validation was performed as per the metrology laboratories UKAS accredited procedure identical to the previous testing. A similar composition like Mix 6 val as was prepared for the final verification run.

The PRGM was condensed and with the uncertainty of the Certified LNG standard calculated the Raman analyser final verification was performed.

Component	Analytically verified primary reference gas mixture		Analytically verified LNG composition		Difference
	Amount fraction (%mol/mol)	Uncertainty (%mol/mol) k=2	Amount fraction (%mol/mol)	Uncertainty (%mol/mol) k=2	
nitrogen	0.28978	0.00069	0.28453	0.00678	
methane	92.871	0.0068	92.89822	0.03500	
ethane	4.5201	0.0087	4.50562	0.01225	
propane	1.7419	0.0028	1.73632	0.00410	
iso-butane	0.29945	0.00056	0.29849	0.00175	
n-butane	0.24822	0.00048	0.24742	0.00162	
iso-pentane	0.01951	0.0001	0.01945	0.00030	
n-pentane	0.00997	0.00009	0.00994	0.00025	
sum	100.000		100.000		
CV (kJ/kg)	54685.316		54691.770		6.453
CV 15/15 (MJ/m3)	40.448		40.441		0.007

Figure 29 PRGM Mix 20_1430_02 Certified LNG

Results on the final performance run are included in figure 30. Additionally, the final performance graphs on the results, collected over the full temperature range, are included in the performance sheet provided for the validation before the start of the field trial in figures 31 and 32 to provide a good comparison on the performance before and after the field trial.

Raman TC –Final verification after field testing Mix 20_1430_02

	93	Deviation Ref-Meas	98	Deviation Ref-Meas	103	Deviation Ref-Meas	108	Deviation Ref-Meas	113	Deviation Ref-Meas	117	Deviation Ref-Meas
methane	93.165	-0.267	93.049	-0.151	92.996	-0.098	92.963	-0.065	92.873	0.026	92.875	0.023
ethane	4.173	0.333	4.343	0.163	4.410	0.096	4.471	0.034	4.534	-0.029	4.534	-0.028
propane	1.790	-0.053	1.750	-0.014	1.730	0.007	1.725	0.011	1.747	-0.010	1.744	-0.008
iso-butane	0.295	0.003	0.298	0.000	0.295	0.004	0.300	-0.001	0.307	-0.008	0.305	-0.007
n-butane	0.222	0.026	0.222	0.025	0.224	0.024	0.228	0.019	0.226	0.021	0.229	0.018
iso-pentane	0.003	0.016	0.001	0.019	0.006	0.013	0.001	0.019	0.002	0.018	0.000	0.019
n-pentane	0.008	0.002	0.017	-0.007	0.017	-0.008	0.017	-0.007	0.020	-0.010	0.015	-0.005
nitrogen	0.345	-0.060	0.320	-0.036	0.322	-0.038	0.294	-0.010	0.292	-0.008	0.298	-0.014
sum	100.000		100.000		100.000		100.000		100.000		100.000	
CV 15/15 (MJ/m3)	40.207	0.137	40.257	0.087	40.270	0.074	40.297	0.047	40.335	0.009	40.325	0.019
CV (kJ/kg)	54671.729	18.3512	54673.444	16.6357	54668.917	21.1625	54690.755	-0.6755	54684.697	5.3829	54681.221	8.8588

Figure 30 Performance results during final verification

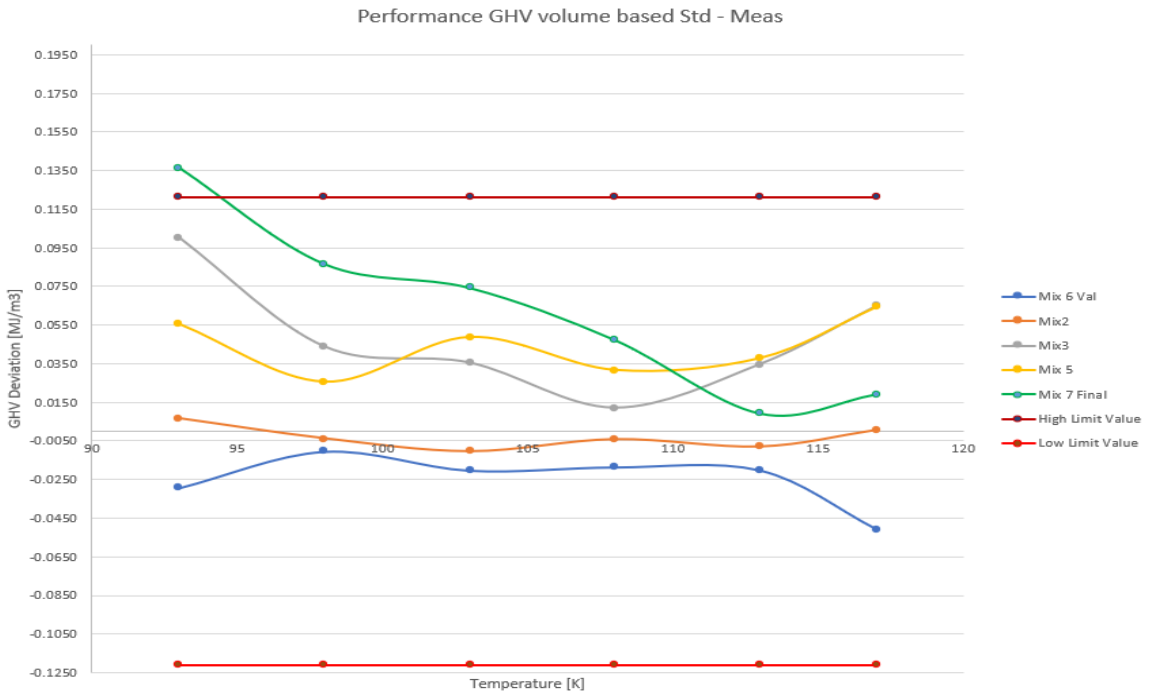


Figure 31 Performance GHV vol with TC and final validation Mix 7 included

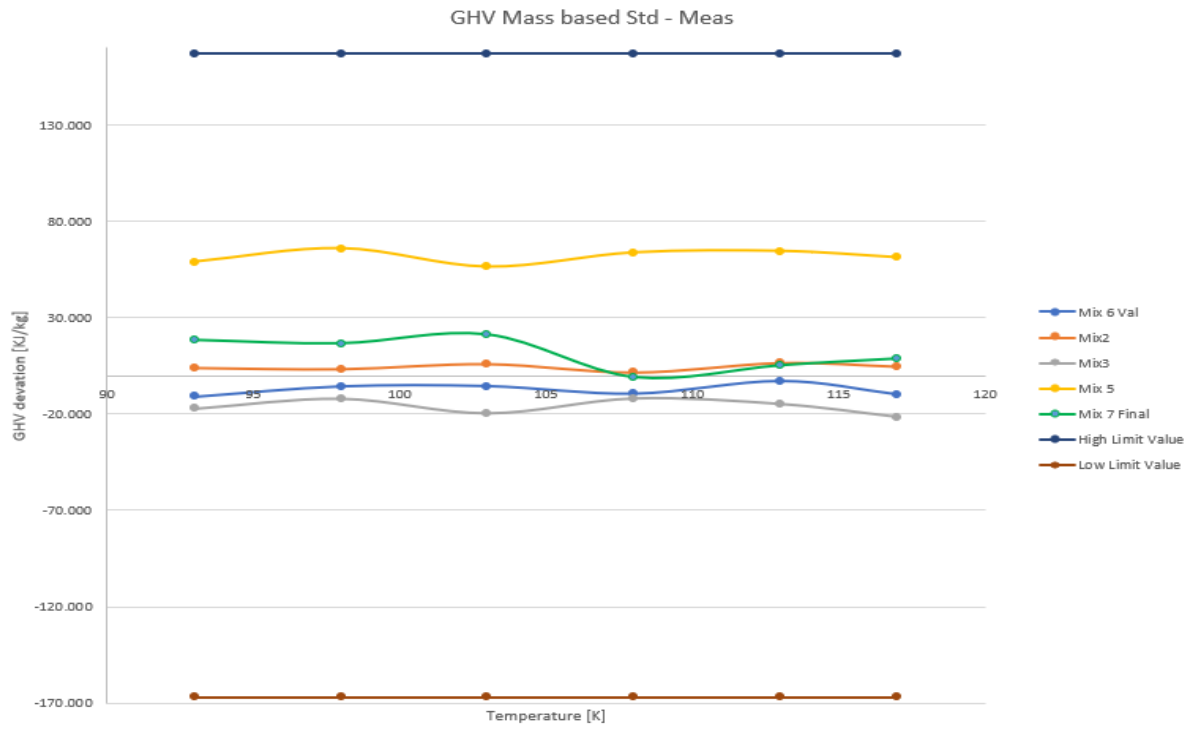


Figure 32 Performance GHV mass with TC and final validation Mix 7 included

7. Test results and conclusions

7.1. Conclusions

Overall, the duration of the field trial was from July 2017 through August 2020. During this trial several measurement sessions were done. Learnings from the initial sessions were used to improve the model. At the end a final performance trial was done from January 2020 until August 2020.

The Raman analyser performance, when verified against a certified high accuracy LNG standard, meets the GIIGNL CTH version 6.0 performance criteria for LNG custody transfer and measurements were in close agreement with a well-maintained traditional LNG custody transfer measurement.

Demonstrated by outperforming one of the best-in-class GC/Vaporizers on repeatability, the Raman analyser proved to be a reliable instrument, more robust to process changes while requiring no maintenance for the full testing period.

Principally, the uncertainty limits that can be achieved for a well-engineered and maintained GC/Vaporizer system can be tighter than that of a Raman analyser system. However, the required OPEX and technical expertise necessary to a to outperform the Raman analyser system is extensive.

7.1.1. Evaluation against custody transfer performance limits.

Measurement Uncertainty

- The uncertainty of the cargo mean values shall be within the mass based GHV performance limit of 0.07%MV as stated in the GIIGNL Custody Transfer Handbook version 6.0.
    - When an additional validation is performed using a certified LNG at a metrology laboratory, the uncertainty of the Raman analyser meets the 0.07%MV.
    - The method uncertainty for the Raman analyser based on the manufacturers standard practice of using only the optical calibration tool is found to be just outside the 0.07%MV, performance limit.
- No significant deviation was found between the mass based GHV values of the Raman analyser and the GC/Vaporizer. Evaluation is done using the En method with both GC/Vaporizer and the Raman uncertainty limits being within the custody transfer performance limit.

Measurement repeatability

- Both measurements shall meet the repeatability performance limit in GIIGNL CTH version 6.0 stating the volumetric GHV shall be within 0.2%MV for GC/Vaporizer.
    - The Raman analyser demonstrated a superior repeatability compared to the GC/Vaporizer during loading/discharge.
- For the Raman analyser an evaluation according ASTM D7940-14 was added based on feedback from 3rd party surveyor evaluation.
    - Based on the repeatability over the total number of cargoes evaluated, the ASTM performance limits were met as per table in figure 33.

Repeatability performance based at 2 times the pooled standard deviation over all evaluated cargoes												
	Methane %mole	Ethane %mole	Propane %mole	I Butane %mole	N Butane %mole	I Pentane %mole	N Pentane %mole	Nitrogen %mole	GHV_v MJ/m3	GHV_v %MV	GHV_m MJ/kg	GHV_m %MV
Rep. Limit_GIIGNL CTH 6.0										0.2		0.07
Repeatability_GC	0.072	0.056	0.014	0.005	0.005	0.00030	0.0002	0.008	0.029	0.074	0.009	0.016
Rep. Limits ASTM D7940-14	0.06	0.06	0.06	0.02	0.02	0.012	0.012	0.02		0.05		
Repeatability Raman	0.051	0.042	0.009	0.003	0.003	0.00004	0.0016	0.011	0.019	0.048	0.011	0.020

Figure 33 Repeatability performance over total cargo's

- Several the individual cargoes did not meet the performance limits. However, after closer evaluation against the GC/Vaporizer component repeatability, it was found that the cargoes failing the ASTM repeatability also did not pass the GC/Vaporizer repeatability limits which demonstrates that these performance issues were caused by external process influences during the loading.
- Detailed performance data is shown in the tables of Figures 34 and 35.

GC repeatability over cargoes under test														
Test Cargo nr.	Instrument	GC Methane %mole	GC Ethane %mole	GC Propane %mole	GC I_Butane %mole	GC N_Butane %mole	GC I_Pentane %mole	GC N_Pentane %mole	GC Nitrogen %mole	GC GHV_vol MJ/m3	GC GHV_v %MV	GC GHV_mass MJ/kg	GC GHV_m %MV
T15	GC/Vaporizer	0.0506	0.0371	0.0087	0.0034	0.0034	0.0007	0.0004	0.0030	0.0210	0.0530	0.0050	0.0110
T16	GC/Vaporizer	0.0476	0.0329	0.0111	0.0044	0.0047	0.0002	0.0002	0.0039	0.0200	0.0510	0.0057	0.0100
T17	GC/Vaporizer	0.0466	0.0315	0.0126	0.0043	0.0047	0.0002	0.0002	0.0035	0.0200	0.0500	0.0055	0.0100
T18	GC/Vaporizer	0.0697	0.0566	0.0093	0.0032	0.0033	0.0003	0.0002	0.0048	0.0270	0.0680	0.0060	0.0110
T19	GC/Vaporizer	0.0669	0.0484	0.0156	0.0056	0.0057	0.0002	0.0002	0.0066	0.0310	0.0790	0.0050	0.0100
T20	GC/Vaporizer	0.0690	0.0394	0.0208	0.0099	0.0102	0.0004	0.0002	0.0063	0.0360	0.0900	0.0087	0.0160
T21	GC/Vaporizer	0.1234	0.0862	0.0272	0.0098	0.0095	0.0003	0.0002	0.0077	0.0520	0.1300	0.0122	0.0220
T22	GC/Vaporizer	0.0536	0.0470	0.0116	0.0029	0.0026	0.0001	0.0002	0.0078	0.0220	0.0550	0.0069	0.0130
T23	GC/Vaporizer	0.0389	0.0262	0.0101	0.0042	0.0045	0.0003	0.0002	0.0057	0.0190	0.0480	0.0059	0.0100
T24	GC/Vaporizer	0.0513	0.0398	0.0006	0.0000	0.0001	0.0000	0.0000	0.0185	0.0150	0.0380	0.0180	0.0320
T25	GC/Vaporizer	0.1223	0.0965	0.0256	0.0029	0.0075	0.0005	0.0001	0.0132	0.0510	0.1280	0.0110	0.0200
T26	GC/Vaporizer	0.1147	0.1080	0.0127	0.0040	0.0041	0.0001	0.0001	0.0037	0.0380	0.0950	0.0075	0.0140
Total	Rep_GC (k=2)	0.072	0.056	0.014	0.005	0.005	0.0003	0.0002	0.008	0.029	0.074	0.009	0.016
GIIGNL Performance limits	Precision [U] (K=2)	0.113	0.050	0.035	0.027	0.025	0.012	0.010	0.025		0.2		0.07

Figure 34 Repeatability data for the GC/Vaporizer against GIIGNL CTH performance limits.

Raman repeatability over cargoes under test													
Test Cargo nr.	Instrument	Raman Methane %mole	Raman Ethane %mole	Raman Propane %mole	Raman I_Butane %mole	Raman N_Butane %mole	Raman I_Pentane %mole	Raman N_Pentane %mole	Raman Nitrogen %mole	Raman GHV_vol MJ/m3	Raman GHV_v %MV	Raman GHV_mass MJ/kg	Raman GHV_m %MV
T15	Raman	0.019	0.014	0.004	0.002	0.001	0.000	0.002	0.007	0.008	0.019	0.006	0.011
T16	Raman	0.040	0.030	0.007	0.003	0.002	0.000	0.002	0.007	0.016	0.039	0.007	0.013
T17	Raman	0.040	0.028	0.010	0.003	0.003	0.000	0.002	0.007	0.017	0.043	0.008	0.015
T18	Raman	0.056	0.046	0.008	0.003	0.003	0.000	0.002	0.008	0.023	0.053	0.007	0.013
T19	Raman	0.045	0.033	0.009	0.003	0.002	0.000	0.002	0.014	0.019	0.047	0.012	0.023
T20	Raman	0.047	0.032	0.009	0.003	0.003	0.000	0.002	0.008	0.019	0.047	0.009	0.016
T21	Raman	0.028	0.018	0.005	0.002	0.002	0.000	0.002	0.008	0.009	0.024	0.008	0.015
T22	Raman	0.048	0.036	0.011	0.003	0.002	0.000	0.001	0.011	0.017	0.043	0.011	0.019
T23	Raman	0.039	0.029	0.008	0.003	0.003	0.000	0.002	0.012	0.019	0.049	0.010	0.018
T24	Raman	0.045	0.039	0.002	0.002	0.000	0.000	0.001	0.018	0.013	0.032	0.017	0.030
T25	Raman	0.069	0.051	0.011	0.002	0.003	0.000	0.002	0.023	0.024	0.061	0.022	0.040
T26	Raman	0.092	0.090	0.011	0.003	0.003	0.000	0.001	0.008	0.029	0.074	0.009	0.017
Total	Rep_Raman (k=2)	0.051	0.042	0.009	0.003	0.003	0.000	0.002	0.011	0.019	0.048	0.011	0.020
ASTM D7940-14 Performance limits	Mean all Cargoes	94.491	3.796	0.931	0.297	0.246	0.011	0.007	0.22	39.699		55.089	
	St Dev Limit [u]	0.03	0.03	0.03	0.01	0.01	0.006	0.006	0.01				
	Precision [U] (K=2)	0.060	0.060	0.060	0.020	0.020	0.012	0.012	0.020		0.05		

Figure 35 Repeatability data for the Raman analyser against ASTM D7940-14 performance limits

7.1.2. Detailed evaluation based on available measurement data from for the test.

Availability

- Raman analyser availability shall be 99%.
    - The Raman analyser met the test requirements of 99% availability, the analyser showed no drift and performed without alarms or maintenance intervention for the full test period.

The Raman analyser demonstrated a much faster response to process changes, making it especially suitable for measuring small and medium size cargoes were loading lines are not kept under cryogenic conditions outside loading/discharge operations.

Manufacturer's performance claim

- The maximum measurement uncertainty for volumetric based GHV of the Raman analyser shall meet the manufacturers claim of ± 0.112 MJ/m³ (± 3 BTU) *(equivalent to 0.08 – 0.10%MV).*
    - The manufactures claim was met using the manufacturers standard practice of using the optical calibration tool, without requiring additional validation on a certified LNG.

Measurement Closeness of Agreement Evaluation

This evaluation was performed against the custody transfer uncertainty limits established for both the Raman and the GC/Vaporizer and being within the performance limits for LNG custody transfer. The results are shown in table in figure 36 below.

En Evaluation between Raman analyser and Fluxys LNG vaporizer/GC according ISO 17043												
Test Cargo nr.	Methane	Ethane	Propane	I Butane	N Butane	I Pentane	N Pentane	Nitrogen	GHV_vol	GHV_mass	LNG Dens	En Limit
	En	En	En	En	En	En	En	En	En	En	En	En
T15	0.5044	0.1696	0.2131	0.0791	0.3749	0.4534	0.0142	1.0530	0.1979	0.9843	0.1556	1.0000
T16	0.1693	0.5831	0.2603	0.1578	0.6470	0.3112	0.0931	0.6598	0.0224	0.5426	0.0374	1.0000
T17	0.0493	0.4071	0.0980	0.2248	0.7217	0.2913	0.0659	0.7795	0.0979	0.6130	0.0883	1.0000
T18	0.2207	0.0804	0.1475	0.0396	0.1959	0.1522	0.0248	0.9622	0.0415	0.7869	0.0717	1.0000
T19	0.2247	0.1839	0.0250	0.2343	0.7357	0.3134	0.0912	0.7693	0.2061	0.7139	0.1496	1.0000
T20	0.3135	0.0233	0.0248	0.2752	0.7544	0.2980	0.0778	0.6114	0.0000	0.0055	0.3737	1.0000
T21	0.2757	0.1390	0.0035	0.2808	0.7758	0.2827	0.0881	0.7635	0.2466	0.7322	0.1376	1.0000
T22	0.2282	0.2060	0.1529	0.0544	0.1109	0.0233	0.0238	0.3238	0.0944	0.2897	0.0622	1.0000
T23	0.3000	0.0639	0.0116	0.2928	0.7084	0.3904	0.0968	0.6321	0.3094	0.7157	0.1442	1.0000
T24	0.5288	1.0395	0.1152	0.1253	0.0244	0.0001	0.0198	0.5928	0.4583	0.3584	0.0942	1.0000
T25	0.6045	1.0462	0.4427	0.0041	0.6099	0.7595	0.0823	0.2405	0.1201	0.0958	0.0348	1.0000
T26	0.4786	0.1894	0.1604	0.0971	0.3280	0.0825	0.0373	1.0679	0.0830	0.9441	0.1262	1.0000

Figure 36 11Closeness of agreement for all components on individual cargoes.

Measuring components

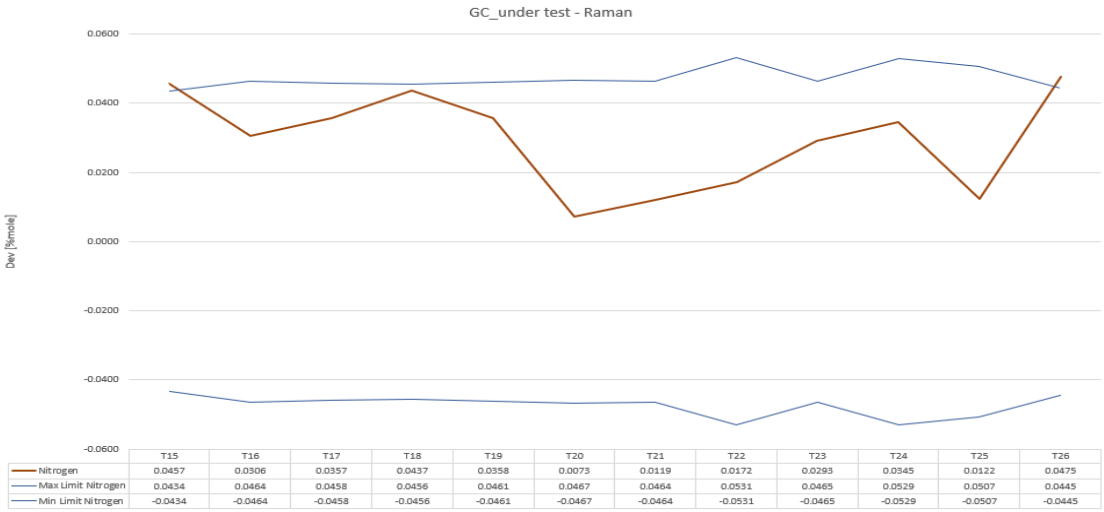
For the individual components occasional biases appeared for Nitrogen and Ethane.

Nitrogen evaluation

From the evaluation it was found that at or below 0.1%mole the bias between the measurements is causing the Nitrogen to be outside the significant limits.

This bias is a result from physical limitations in the cryostat and nitrogen volatility during the modelling over the full nitrogen and LNG temperature range. Also, in being the most volatile component nitrogen is the most vulnerable to preferential boil off in the vaporizers.

The combination of these conditions caused the nitrogen bias to be out of the significance limits. However, the impact on the GHV is not significant as the actual bias is still very small and is presenting itself at concentrations at or below 0.1%mole of nitrogen only.



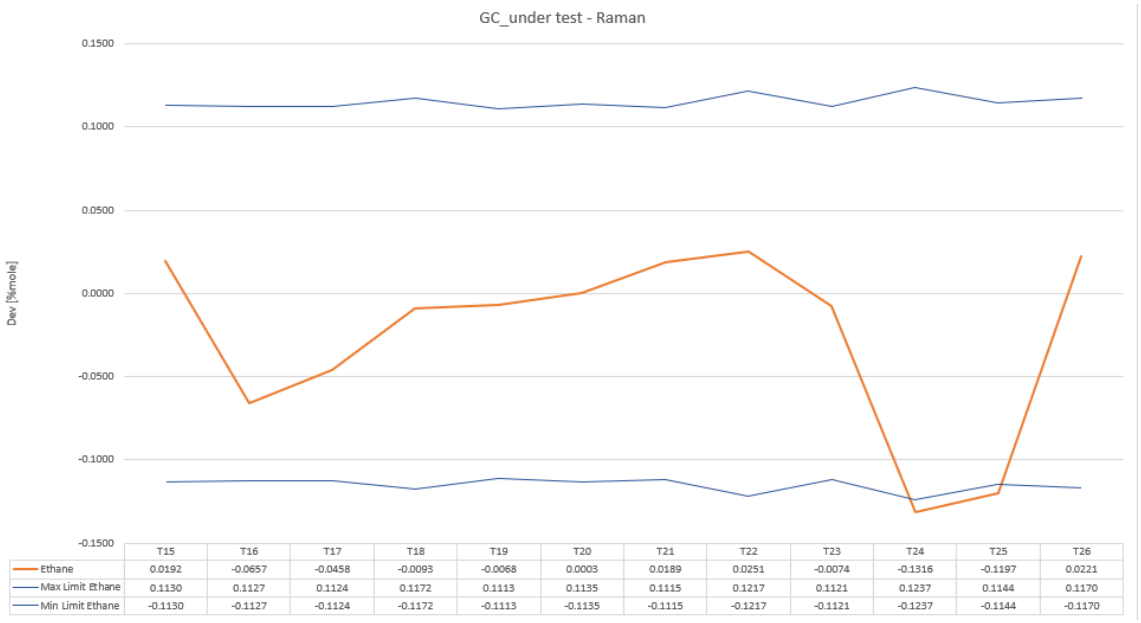
	T15	T16	T17	T18	T19	T20	T21	T22	T23	T24	T25	T26
Nitrogen	0.0457	0.0306	0.0357	0.0437	0.0358	0.0073	0.0119	0.0172	0.0293	0.0345	0.0122	0.0475
Max Limit Nitrogen	0.0434	0.0464	0.0458	0.0456	0.0461	0.0467	0.0464	0.0531	0.0465	0.0529	0.0507	0.0445
Min Limit Nitrogen	-0.0434	-0.0464	-0.0458	-0.0456	-0.0461	-0.0467	-0.0464	-0.0531	-0.0465	-0.0529	-0.0507	-0.0445

Figure 37 Closeness of agreement for Nitrogen measurements

Ethane evaluation

For cargoes T24 and T25 the Ethane showed a bias just outside the significance limits. The bias was observed for both Methane and Ethane and appearing in opposite direction due to normalization which is inherently build in the method of the Raman analyser. With methane being the dominant component, the bias was still within the significance limits. However, for Ethane being at a much lower value this was not.

Normalization is an inherent part of the method for the Raman analyser. Although the deviation for ethane is outside the limit it was not causing a significant bias in GHV.



	T15	T16	T17	T18	T19	T20	T21	T22	T23	T24	T25	T26
Ethane	0.0192	-0.0657	-0.0458	-0.0093	-0.0068	0.0003	0.0189	0.0251	-0.0074	-0.1316	-0.1197	0.0221
Max Limit Ethane	0.1130	0.1127	0.1124	0.1172	0.1113	0.1135	0.1115	0.1217	0.1121	0.1237	0.1144	0.1170
Min Limit Ethane	-0.1130	-0.1127	-0.1124	-0.1172	-0.1113	-0.1135	-0.1115	-0.1217	-0.1121	-0.1237	-0.1144	-0.1170

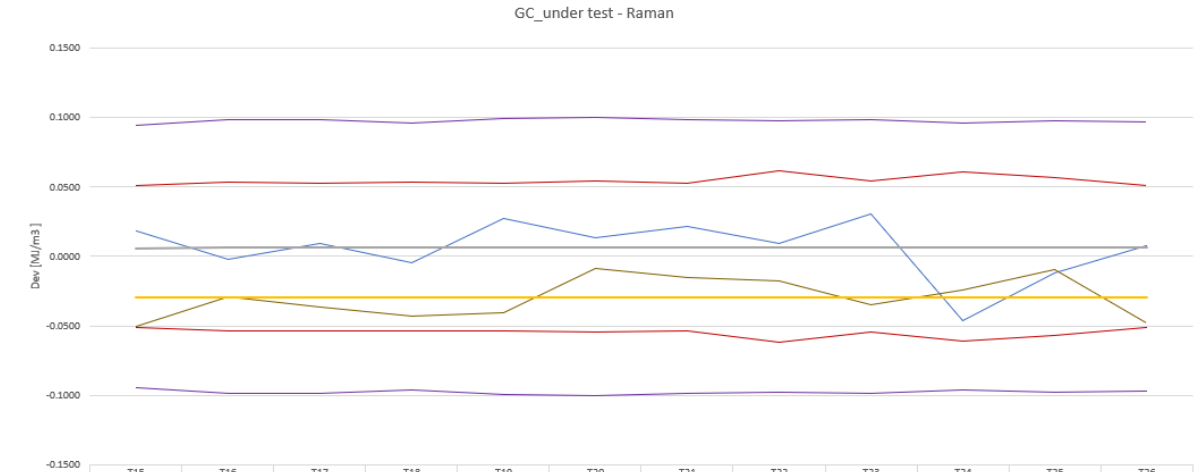
Figure 38 Closeness of agreement for Ethane measurements

Physical Properties

When evaluated against the GIIGNL performance limits for LNG custody transfer, no significant deviations on GHV and LNG density between Raman and Fluxys LNG's existing measurement were found.

GHV

The absolute bias between the two measurement systems, for both volumetric and mass based GHV individually, was within ± 50kJ, which would be considered a very good measurement agreement for LNG custody transfer measurements.



	T15	T16	T17	T18	T19	T20	T21	T22	T23	T24	T25	T26
GHV_vol	0.0187	-0.0022	0.0097	-0.0048	0.0277	0.0138	0.0217	0.0093	0.0304	-0.0466	-0.0118	0.0081
GHV_mass	-0.0500	-0.0290	-0.0366	-0.0426	-0.0405	-0.0087	-0.0154	-0.0180	-0.0350	-0.0240	-0.0095	-0.0480
AVG_vol	0.0062	0.0062	0.0062	0.0062	0.0062	0.0062	0.0062	0.0062	0.0062	0.0062	0.0062	0.0062
AVG_mass	-0.0298	-0.0298	-0.0298	-0.0298	-0.0298	-0.0298	-0.0298	-0.0298	-0.0298	-0.0298	-0.0298	-0.0298
Max Limit GHV_vol	0.0947	0.0990	0.0991	0.0964	0.0996	0.1007	0.0991	0.0982	0.0991	0.0966	0.0982	0.0974
Min Limit GHV_vol	-0.0947	-0.0990	-0.0991	-0.0964	-0.0996	-0.1007	-0.0991	-0.0982	-0.0991	-0.0966	-0.0982	-0.0974
Max Limit GHV_mass	0.0508	0.0535	0.0532	0.0534	0.0532	0.0545	0.0532	0.0621	0.0545	0.0614	0.0571	0.0508
Min Limit GHV_mass	-0.0508	-0.0535	-0.0532	-0.0534	-0.0532	-0.0545	-0.0532	-0.0621	-0.0545	-0.0614	-0.0571	-0.0508

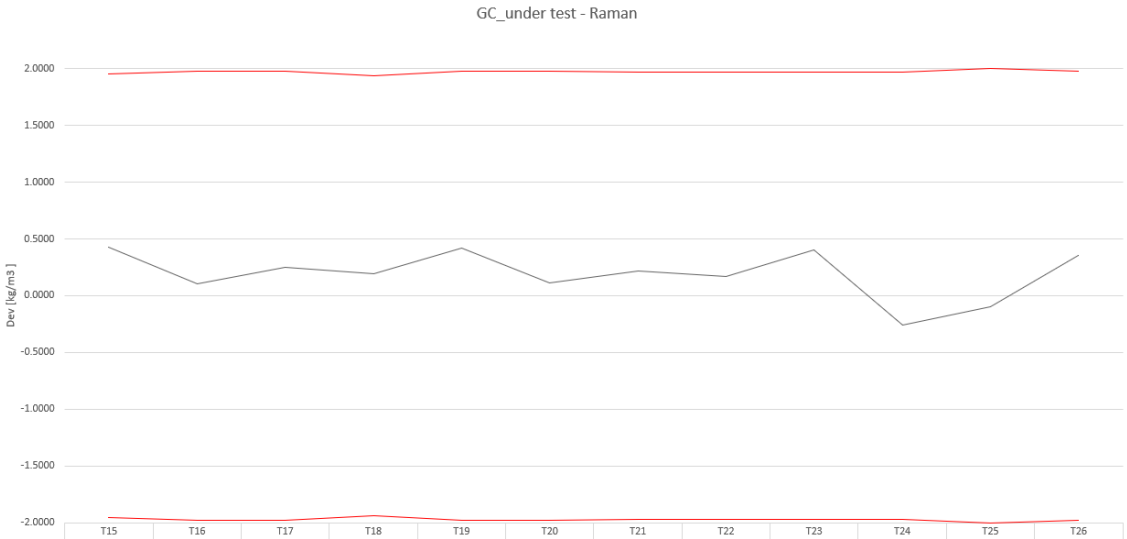
Figure 39 Closeness of agreement for GHV mass and volumetric

LNG Density

For the evaluation the composition data of both the GC/Vaporizer and the Raman analyser are used to calculate the individual LNG densities according the Revised Klosek-McKinley method. To mitigate uncertainties the same LNG temperature measurement is used for both the Raman temperature compensation and the LNG density calculation.

The for the uncertainty of the LNG density we took the GIIGNL CTH 6.0 uncertainty of 0.23% relative to the calculated value at k=1. For our evaluation we multiplied this by 2 to come meet the 95% confidence level k=2 in line with the other evaluations.

As per the below results are in close agreement and within ± 0.5 kg/m^3.



	T15	T16	T17	T18	T19	T20	T21	T22	T23	T24	T25	T26
LNG Dens	0.4292	0.1046	0.2472	0.1962	0.4186	0.1141	0.2200	0.1732	0.4021	-0.2620	-0.0984	0.3532
Max Limit LNG Dens	1.9494	1.9783	1.9787	1.9333	1.9773	1.9792	1.9720	1.9695	1.9705	1.9668	2.0004	1.9779
Min Limit LNG Dens	-1.9494	-1.9783	-1.9787	-1.9333	-1.9773	-1.9792	-1.9720	-1.9695	-1.9705	-1.9668	-2.0004	-1.9779

Figure 40 Closeness of agreement LNG Density

7.2. Recommendations

From the experiences gained during both the development of the Raman model and the field testing the following would be considered an improvement to the measurement performance:

- For installation it is recommended to avoid installing the Raman probe in the top part of the process piping. A piping nozzle either at the 3 or 9 o'clock position in a horizontal line with a minimum straight length of 5D upstream and 2D downstream the probe would be recommended.
  Both a cryogenic bypass loop design using impact probes or a bespoke cryogenic retractable device, that can be ordered with the Raman probe, could be installed to implement the Raman probe into the process. Detailed design is subject to the owner's preference and site Management of Change procedures.
- It is recommended for the manufacturer to add a temperature measurement in the Raman probe to measure the LNG temperature. This makes it possible to perform the LNG validation including temperature compensation and process measurements with the same temperature measurement.
  If a separate temperature element is required, it is recommended to have the temperature measurement calibrated on the cryogenic temperature range.
- Adding restrictions in user access for modifying parameters and a parameter change report for the critical application and validation parameters would be considered a requirement to enhance the integrity of the application for use in custody transfer.

When the model verification on a certified LNG standard fluid is included in the requirements it is strongly recommended for clients to purchase a dedicated white light calibrator with the Raman instrument to enable them to claim better uncertainty.

- The white light calibrator is used to calibrate the optical path to the required signal strength, before verifying the Raman analyser on a certified LNG.
- The verification on a certified LNG is allows for transferring the improved uncertainty to the white light calibration instrument.
- The identical white light calibrator must be used in the field to set the signal strength to be able to use the uncertainty of certified LNG standard verification in the uncertainty calculation.
  This maintains valid for the lifetime of the calibration tool's light bulb (certificate validity) which is set at 500 hours by the manufacturer. *(*E+H *recommends sending the calibrator back to their workshop every two years, for validation.)*

MID Certification

Based on the performance during the test run Endress+Hauser have started a project with a Notified Body in metrology to obtain MID certification for their RXN Raman instrument. For the MID certification the GERG steering team agreed to share the performance data this project collected as supporting evidence in the certification project.

MID certification is an instrument specific process and will be performed under NDA between Endress+Hauser and the selected Metrology Institute with the authority to provide MID certification.

APPENDIX 1. RAMAN TECHNOLOGY DESCRIPTION

A.1.1. Raman Spectroscopy – A Tutorial by Endress+Hauser©

Raman spectroscopy is a form of vibrational spectroscopy, much like infrared (IR) spectroscopy. However, whereas IR bands arise from a change in the dipole moment of a molecule due to an interaction of light with the molecule, Raman bands arise from a change in the polarizability of the molecule due to the same interaction.
This means that these observed bands (corresponding to specific energy transitions) arise from specific molecular vibrations. When the energies of these transitions are plotted as a spectrum, they can be used to identify the molecule as they provide a "molecular fingerprint" of the molecule being observed.
Certain vibrations that are allowed in Raman are forbidden in IR, whereas other vibrations may be observed by both techniques although at significantly different intensities, thus these techniques can be thought of as complementary.
Since the discovery of the Raman effect in 1928 by C.V. Raman and K.S. Krishnan, Raman spectroscopy has become an established and practical method of chemical analysis and characterization applicable to many different chemical species.

A brief look at Raman scattering theory

The Raman Effect and Normal Raman Scattering.

When light is scattered from a molecule, most photons are elastically scattered. The scattered photons have the same energy (frequency), and therefore wavelength, as the incident photons. However, a small fraction of light (approximately 1 in 107 photons) is scattered at optical frequencies different from, and usually lower than, the frequency of the incident photons. The process leading to this inelastic scatter is termed the Raman effect. Raman scattering can occur with a change in vibrational, rotational, or electronic energy of a molecule. Chemists are concerned primarily with the vibrational Raman effect, and thus in this tutorial we use the term Raman effect to mean vibrational Raman effect only.

The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of a vibration of the scattering molecule. A plot of intensity of scattered light versus energy difference is a Raman spectrum.

The Scattering Process

When a beam of light is impinged upon a molecule, photons are absorbed by the material and scattered. Most of these scattered photons have exactly the same wavelength as the incident photons and are known as *Rayleigh scatter*. In the scattering process, the incident photon excites an electron into a higher "virtual" energy level (or *virtual state*) and then the electron decays back to a lower level, emitting a scattered photon. In Rayleigh scattering, the electron decays back to the same level from which it started and thus, Rayleigh scattering is often referred to as a form of elastic scatter. The process of Rayleigh scattering is visualized in Figure 1.1.

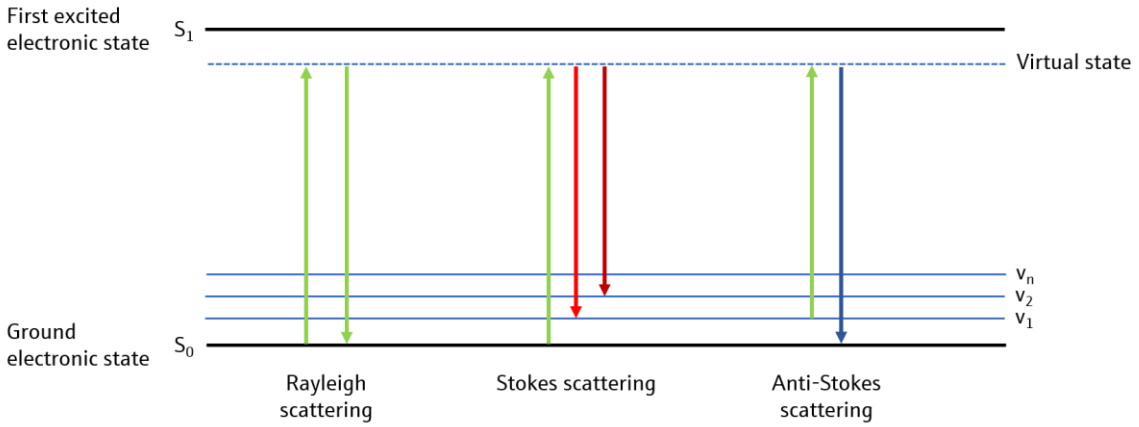


Figure 1.1. Energy level diagram for scattering processes. Left: Rayleigh scattering, Center: Stokes Raman scattering and Right: anti-Stokes Raman scattering.

The Raman effect arises when a photon is incident on a molecule and interacts with the electric dipole of the molecule. It is a form of electronic (more accurately, vibronic) spectroscopy, although the spectrum contains vibrational frequencies. In classical terms, the interaction can be viewed as a perturbation of the molecule's electric field. In quantum mechanical terms, the scattering can be described as an excitation to a virtual state lower in energy than a real electronic transition with nearly coincident de-excitation and a change in vibrational energy. The virtual state description of scattering is shown in Figure 1.1a. In the Raman effect, the electron excited in the scattering process decays to a different level than that where it started which is termed inelastic scattering.

The energy difference between the incident and scattered photons is represented by the arrows of different lengths in Figure 1.1a. Numerically, the energy difference between the initial and final vibrational levels, or Raman shift in wave numbers (cm-1), is calculated through equation 1 in which λ incident and λ scattered are the wavelengths (in nm) of the incident and Raman scattered photons, respectively.

$$\bar{\nu} = \left(\frac{1}{\lambda_{incident}} - \frac{1}{\lambda_{scattered}}\right) \times 10^7$$

The vibrational energy is ultimately dissipated as heat. Because of the low intensity of Raman scattering, the heat dissipation does not cause a measurable temperature to rise in a material.

At room temperature, the thermal population of vibrational excited states is low, although not zero. Therefore, the initial state is the ground state and the scattered photon will have lower energy (longer wavelength) than the exciting photon. This Stokes shifted scatter is what is usually observed in Raman spectroscopy. Figure 1.1 (centre) depicts Raman Stokes scattering.

A small fraction of the molecules are in vibrationally excited states. Raman scattering from vibrationally excited molecules leaves the molecule in the ground state. The scattered photon appears at higher energy, as shown in Figure 1.1 (right). At room temperature, the anti-Stokes-shifted Raman spectrum is always weaker than the Stokes-shifted spectrum, and since the Stokes and anti-Stokes spectra contain the same frequency information, most Raman experiments look at Stokes-shifted scatter only.

Vibrational Energies

The energy of a vibrational mode depends on molecular structure and environment. Atomic mass, bond order, molecular substituents, molecular geometry and hydrogen bonding all effect the vibrational force constant which, in turn, dictates the vibrational energy. For example, the stretching frequency of a phosphorus-phosphorus bond ranges from 460 to 610 to 775 cm-1 for the single, double and triple bonded moieties, respectively.[1] Much effort has been devoted to the estimation

or measurement of force constants. For small molecules, and even for some extended structures such as peptides, reasonably accurate calculations of vibrational frequencies are possible with commercially available software.

Vibrational Raman spectroscopy is not limited to intramolecular vibrations. Crystal lattice vibrations and other motions of extended solids are Raman-active. Their spectra are important in such fields as polymers and semiconductors. In the gas phase, rotational structure is resolvable on vibrational transitions. The resulting vibration/rotation spectra are widely used to study combustion and gas phase reactions generally. Vibrational Raman spectroscopy in this broad sense is an extraordinarily versatile probe into a wide range of phenomena ranging across disciplines from physical biochemistry to materials science.

Raman Selection Rules and Intensities

A simple classical electromagnetic field description of Raman spectroscopy can be used to explain many of the important features of Raman band intensities. The dipole moment, **P**, induced in a molecule by an external electric field, **E**, is proportional to the field as shown in equation 2.

$$P = \alpha E$$

The proportionality constant α is the polarizability of the molecule. The polarizability measures the ease with which the electron cloud around a molecule can be distorted. The induced dipole emits or scatters light at the optical frequency of the incident light wave.

Raman scattering occurs because a molecular vibration can change the polarizability.

The change is described by the polarizability derivative, where **Q** is the normal coordinate of the vibration. The selection rule for a Raman-active vibration, that there be a change in polarizability during the vibration, is given in equation 3.

$$\frac{\delta \alpha}{\delta Q} \neq 0$$

The Raman selection rule is analogous to the more familiar selection rule for an infrared-active vibration, which states that there must be a net change in permanent dipole moment during the vibration. From group theory it is straightforward to show that if a molecule has a center of symmetry, vibrations which are Raman-active will be silent in the infrared, and vice versa.

Scattering intensity is proportional to the square of the induced dipole moment, that is to the square of the polarizability derivative.

If a vibration does not greatly change the polarizability, then the polarizability derivative will be near zero, and the intensity of the Raman band will be low. The vibrations of a highly polar moiety, such as the O-H bond, are usually weak. An external electric field cannot induce a large change in the dipole moment and stretching or bending the bond does not change this.

Typical strong Raman scatterers are moieties with distributed electron clouds, such as carbon-carbon double bonds. The pi-electron cloud of the double bond is easily distorted in an external electric field. Bending or stretching the bond changes the distribution of electron density substantially, and causes a large change in induced dipole moment.

Chemists generally prefer a quantum-mechanical approach to Raman scattering theory, which relates scattering frequencies and intensities to vibrational and electronic energy states of the molecule. The standard perturbation theory treatment assumes that the frequency of the incident light is low compared to the frequency of the first electronic excited state. The small changes in the ground state wave function are described in terms of the sum of all possible excited vibronic states of the molecule.

Polarization Effects

Raman scatter is partially polarized, even for molecules in a gas or liquid, where the individual molecules are randomly oriented. The effect is most easily seen with an exciting source which is plane polarized. In isotropic media polarization arises because the induced electric dipole has components which vary spatially with respect to the coordinates of the molecule. Polarized Raman experiments can be a power tool in studying the mechanism of orientation and the final structure of polymeric films and fibres as well as in the characterization of single crystals.

A.1.2. Raman product information


DS Kaiser RXN4.pdf


Kaiser Raman Analyzer Brochure.p


Kaiser Raman Probes Brochure.pd


Fiber Optic Cables for Raman Spectros


DS Pilot Probe.pdf

APPENDIX 2. ACCREDITED LNG CRYOSTAT FOR CERTIFIED LNG MIXTURES.

LIQUEFIED NATURAL GAS (LNG) ANALYSERS
Calibration of LNG analysers using reference liquid mixtures

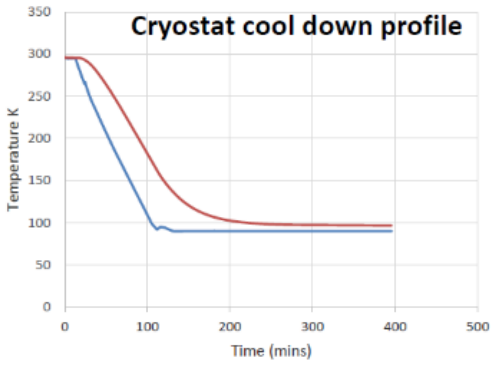
LNG ANALYSERS	amount fraction (% mol/mol)	amount fraction (% mol/mol)	In-house method TM024/UT
nitrogen	0.1 to 1.8	0.10 % relative + 0.0065	Calibration of analysers used for direct measurement of liquefied natural gas (LNG) using cryogenically prepared reference liquid mixures
methane	79 to 100	0.035	
ethane	0.1 to 4 4 to 14	0.30 % relative + 0.001 0.05 % relative + 0.01	
propane	0.1 to 4	0.15 % relative + 0.0015	
iso-butane	0.02 to 1.3	0.25 % relative + 0.001	
n-butane	0.02 to 1.3	0.25 % relative + 0.001	
iso-pentane	0.01 to 0.16	0.50 % relative + 0.0002	
n-pentane	0.01 to 0.16	0.50 % relative + 0.0002	

UKAS CALIBRATION
0590

Liquid reference LNG mixtures were produced by condensing primary reference gas mixtures (PRGMs) contained at high pressure in cylinders. The required LNG compositions were first prepared as gas compositions gravimetrically in cylinders by weighing pure components into the cylinder in accordance with international standard ISO 6142-1:2015 – Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures.

Once the primary standards were prepared, they are rolled to homogenise the mixture then verified analytically using in house traceable reference gases. Verification was performed using EffecTech's in-house technical method, based on ISO 6143:2001 – Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures, which is accredited to ISO 17025 by the United Kingdom Accreditation Service (UKAS). This verification bestows international traceability to the mole, the SI unit of amount of substance, upon the primary standard gas mixtures.

Once the gravimetric compositions of the reference gases were verified, the cylinders were relocated to the cryogenic facility where the gas was liquefied in a bespoke cryostat. The cryostat consists of a copper cell with an approximate volume of 1 litre which is cooled using liquid nitrogen through heat exchangers. The gas was transferred by mass into the pre-cooled sample cell using liquid nitrogen as the refrigerant. The gas is cooled to below its dewpoint to form a cryogenic liquid mixture inside the cryostat.



In practice, a typical condensation temperature of 93K was used which was low enough to condense the methane and nitrogen, with only negligible amounts of nitrogen and methane in the vapour phase. The condensation temperature of the cryostat was controlled using small resistive heaters

attached to the LNG cell and heat exchanger coupled with an adjustable flow of liquid nitrogen through the heat exchanger of the sample cell.

Once the LNG temperature is determined to be stable, the liquid LNG is sampled, vaporised and measured with a gas chromatograph. The calculated amount fraction of the liquid LNG is compared with that of the analytically verified gas phase composition prior to the condensation step. The En number is used to demonstrate agreement between the measured values and uncertainties. Calculation of the reference value uncertainties was performed in accordance with that proposed in the recent revision ISO/DIS 6142-1.

A convenient and internationally accepted method of demonstrating agreement between two measurements with their uncertainties is using the En number. If the result of a measurement of a reference material produces an En number less than 1 then there is agreement between the measurement and reference material. If the En number is greater than 1 then there is a statistically significant difference between measured and reference value.

$$E_n = \frac{meas - Ref}{\sqrt{U_{meas}^2 + U_{Ref}^2}}$$

Where:

- Meas is the average measured value and U_{meas} is the uncertainty (k=2) of the measured value and
- Ref is the reference value and U_{Ref} is the uncertainty (k=2) of the reference value.

The maximum difference between the gross calorific values (GCV) of the reference gas and Liquefied LNG is 0.016 % relative (0.007 MJ.m-3).

In addition, the E_n numbers for the comparison of gravimetric amount fractions and corrected amount fractions for all seven mixtures is less than 1 showing they are statistically identical. E_n numbers for the comparison of measured and corrected amount fractions for all seven mixtures is less than 1, showing also that they are statistically identical.

Typical evaluation sheet for verification of the Certified LNG reference mixture.

mix #1	gravimetric values		corrected reference values		measured (GC)			difference	En-number	En-number	difference	difference	difference
D 108638	xi	U(xi)	xi_c	$U(xi_c)$	yi	% RSD	U(yi)	(% relative)	grav-corrected	meas-corrected	MJ/m-3	KJ/kg	kg/m3
nitrogen	0.2478	0.0005	0.2451	0.0035	0.2451	0.88	0.0043	0.000%	0.76	0.00			
methane	99.2997	0.0099	99.3026	0.0125	99.3063	0.004	0.0076	0.004%	-0.18	0.26			
ethane	0.0998	0.0001	0.0998	0.0011	0.0989	0.81	0.0016	-0.810%	0.00	-0.41			
propane	0.0983	0.0001	0.0983	0.0012	0.0974	0.82	0.0016	-0.884%	0.00	-0.44			
iso-butane	0.0813	0.0001	0.0813	0.0009	0.0806	0.74	0.0012	-0.871%	0.00	-0.47			
n-butane	0.1225	0.0001	0.1225	0.0013	0.1217	0.72	0.0017	-0.727%	0.00	-0.42			
iso-pentane	0.0303	0.0001	0.0303	0.0004	0.0300	0.72	0.0004	-0.891%	0.00	-0.48			
n-pentane	0.0201	0.0001	0.0201	0.0002	0.0199	0.70	0.0003	-0.923%	0.00	-0.51			
GCV (15/15)	38.0011		38.0022		37.9996			-0.007%			-0.003	-3.766	
Gas Density	0.68771		0.68770		0.68764								-0.00005
LNG Density 93K	452.045		452.036		452.013								-0.023

A.2.1. Cryostat product information and validation report

EffecTech LNG Leaflet.pdf

15_1068 Report_Rev3.pdf

APPENDIX 3. RAMAN TC MODEL VALIDATION RESULTS

These are the results from the validation of the Raman LNG custody transfer model including temperature correction over the range of 93 to 117K.

- The blue headers are the preparation of the Certified LNG standards
- The green headers are the validation results from the performance runs.

Mix2

Mix 17_1118_08 Liquid composition

Component	Gravimetric Amount fraction %mol/mol	Reference Liq Amount fraction %mol/mol	Uncertainty (corrected)	
N2	0.2514	0.2577	0.0068	0.00338
c1	97.9626	97.9689	0.0350	0.0175
c2	1.3078	1.2987	0.0106	0.00532
c3	0.1589	0.1578	0.0022	0.00109
ic4	0.1006	0.0999	0.0019	0.00095
nc4	0.1186	0.1177	0.0022	0.00109
ic5	0.0597	0.0593	0.0010	0.00052
nc5	0.0403	0.0400	0.0007	0.00035
sum	100	100		
			difference	EN12838
CV (MJ/m3)	38.4405	38.4482	0.0077	
CV (kJ/kg)	55147.3203	55152.0000	-4.6797	9
gas density	0.6971	0.6971	-0.0001	0.15
liquid density	0.0395951	0.0395996	0.0000	0.0003

Raman TC - Reprocessed data

Component	93	Deviation Ref-Meas	98	Deviation Ref-Meas	103	Deviation Ref-Meas	108	Deviation Ref-Meas	113	Deviation Ref-Meas	117	Deviation Ref-Meas
N2	0.256	0.001	0.253	0.004	0.254	0.004	0.251	0.006	0.255	0.002	0.254	0.004
c1	97.957	0.012	97.943	0.026	97.934	0.035	97.960	0.009	97.950	0.019	97.975	-0.006
c2	1.321	-0.022	1.331	-0.032	1.333	-0.035	1.314	-0.015	1.315	-0.016	1.294	0.004
c3	0.154	0.004	0.154	0.004	0.154	0.004	0.151	0.007	0.152	0.006	0.150	0.007
ic4	0.098	0.002	0.098	0.001	0.099	0.001	0.097	0.002	0.098	0.002	0.097	0.003
nc4	0.118	0.000	0.119	-0.001	0.119	-0.002	0.118	-0.001	0.120	-0.002	0.119	-0.001
ic5	0.053	0.007	0.056	0.003	0.060	0.000	0.061	-0.002	0.063	-0.004	0.062	-0.003
nc5	0.044	-0.004	0.046	-0.005	0.047	-0.007	0.048	-0.007	0.048	-0.008	0.047	-0.007
sum	100.000		100.000		100.000		100.000		100.000		100.000	
CV (kJ/kg)	55148.08		55148.74		55146.03		55150.52		55145.45		55147.42	
diff from liquid	3.920		3.260		5.970		1.480		6.550		4.580	
CV(MJ/m3)	38.441		38.452		38.459		38.452		38.456		38.448	
diff from liquid	0.0067		-0.0037		-0.0105		-0.0042		-0.0081		0.0006	

Mix3

Mix 17_1118_09 Liquid composition

Component	Gravimetric Amount fraction %mol/mol	Reference Liq Amount fraction %mol/mol	Uncertainty (corrected)	
N2	1.0574	1.0538	0.0076	0.00378
c1	90.4760	90.5074	0.0350	0.0175
c2	4.2078	4.1940	0.0146	0.00731
c3	3.0238	3.0139	0.0258	0.01288
ic4	0.3975	0.3962	0.0026	0.0013
nc4	0.5947	0.5927	0.0033	0.00167
ic5	0.1202	0.1198	0.0011	0.00055
nc5	0.1226	0.1222	0.0014	0.0007
sum	100	100		
			difference	EN12838
CV (MJ/m3)	41.4009	41.4128	0.0119	
CV (kJ/kg)	53782.3945	53777.0508	5.3438	9
gas density	0.7698	0.7701	-0.0003	0.15
liquid density	0.04371128	0.04372808	0.0000	0.0003

Raman TC - Reprocessed data

Component	93	Deviation Ref-Meas	98	Deviation Ref-Meas	103	Deviation Ref-Meas	108	Deviation Ref-Meas	113	Deviation Ref-Meas	117	Deviation Ref-Meas
N2	1.056	-0.003	1.052	0.001	1.043	0.011	1.047	0.007	1.046	0.007	1.046	0.008
c1	90.636	-0.129	90.536	-0.029	90.536	-0.029	90.500	0.007	90.568	-0.061	90.649	-0.142
c2	4.130	0.064	4.191	0.003	4.208	-0.014	4.211	-0.017	4.161	0.033	4.092	0.102
c3	3.020	-0.007	3.034	-0.020	3.018	-0.004	3.033	-0.019	3.016	-0.002	3.011	0.003
ic4	0.379	0.017	0.382	0.014	0.381	0.015	0.382	0.015	0.380	0.016	0.377	0.019
nc4	0.573	0.020	0.581	0.011	0.580	0.012	0.584	0.009	0.584	0.008	0.583	0.009
ic5	0.086	0.034	0.095	0.025	0.098	0.022	0.103	0.017	0.105	0.015	0.104	0.016
nc5	0.119	0.004	0.128	-0.006	0.135	-0.013	0.140	-0.018	0.139	-0.017	0.138	-0.016
sum	100.000		100.000		100.000		100.000		100.000		100.000	
CV (kJ/kg)	53794.33		53789.04		53796.67		53788.85		53791.77		53798.55	
diff from liquid	-17.279		-11.989		-19.619		-11.799		-14.719		-21.499	
CV(MJ/m3)	41.313		41.369		41.377		41.401		41.378		41.348	
diff from liquid	0.1003		0.0438		0.0354		0.0121		0.0346		0.0647	

Mix 5

Mix 17_1118_11 Liquid composition

Component	Gravimetric Amount fraction %mol/mol	Reference Liq Amount fraction %mol/mol	Uncertainty (corrected)	
N2	0.2293	0.2281	0.0067	
c1	92.873	92.9400	0.0690	
c2	4.516	4.5189	0.0291	
c3	1.7311	1.7322	0.0124	
ic4	0.29823	0.2984	0.0068	
nc4	0.25196	0.2521	0.0073	
ic5	0.02015	0.0202	0.0011	
nc5	0.0101	0.0101	0.0006	
sum	100	100		
			difference	EN12838
CV (MJ/m3)	40.4691	40.4687	0.0004	
CV (kJ/kg)	54740.5078	54739.2656	1.2422	9
gas density	0.7393	0.7393	0.0000	0.15
liquid density	0.04198502	0.0419856	0.0000	0.0003

Raman TC- Reprocessed data

Component	93	Deviation Ref-Meas	98	Deviation Ref-Meas	103	Deviation Ref-Meas	108	Deviation Ref-Meas	113	Deviation Ref-Meas	117	Deviation Ref-Meas
N2	0.302	-0.074	0.303	-0.075	0.298	-0.070	0.301	-0.073	0.305	-0.076	0.306	-0.078
c1	92.869	0.071	92.785	0.155	92.849	0.091	92.806	0.134	92.823	0.117	92.900	0.040
c2	4.549	-0.030	4.618	-0.099	4.583	-0.064	4.604	-0.085	4.579	-0.060	4.511	0.008
c3	1.740	-0.008	1.748	-0.016	1.729	0.003	1.743	-0.011	1.747	-0.015	1.741	-0.008
ic4	0.287	0.011	0.290	0.009	0.287	0.011	0.290	0.009	0.291	0.008	0.289	0.010
nc4	0.242	0.010	0.245	0.007	0.243	0.009	0.245	0.008	0.244	0.008	0.243	0.009
ic5	0.002	0.018	0.002	0.019	0.001	0.019	0.001	0.019	0.001	0.019	0.001	0.019
nc5	0.009	0.001	0.009	0.001	0.010	0.000	0.010	0.000	0.010	0.000	0.010	0.001
sum	100.000		100.000		100.000		100.000		100.000		100.000	
CV (kJ/kg)	54680.33		54673.37		54682.89		54675.55		54674.8		54678.08	
diff from liquid	58.936		65.896		56.376		63.716		64.466		61.186	
CV(MJ/m3)	40.413		40.443		40.420		40.437		40.431		40.404	
diff from liquid	0.0555		0.0255		0.0487		0.0316		0.0377		0.0642	

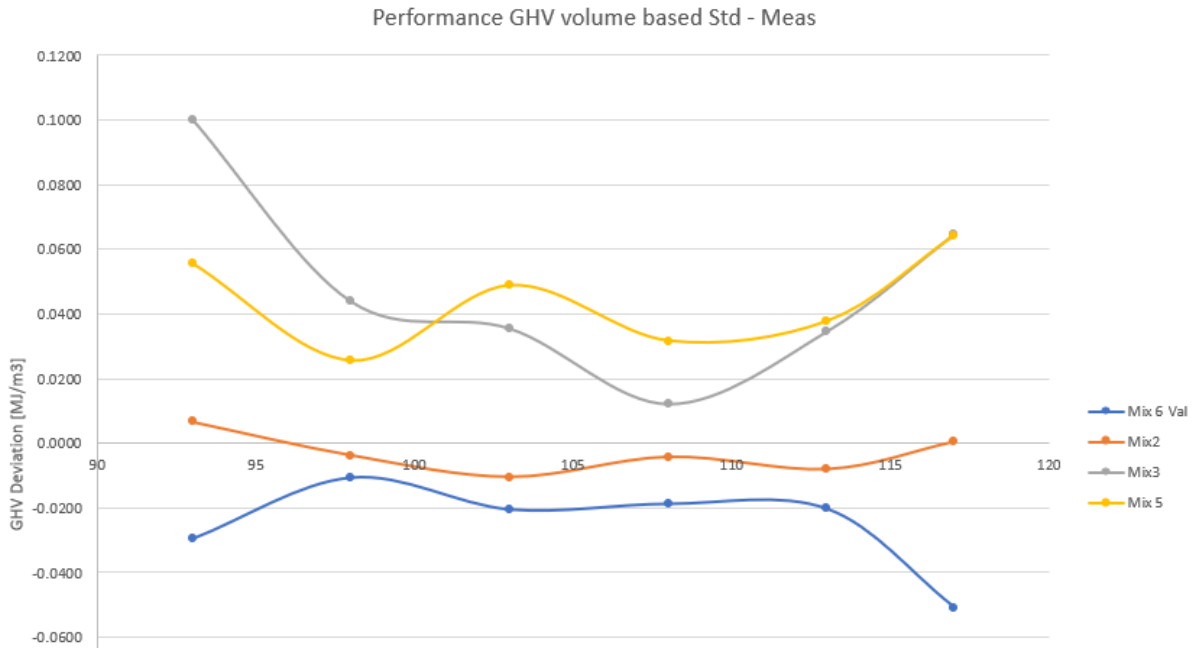
Mix 6 Val

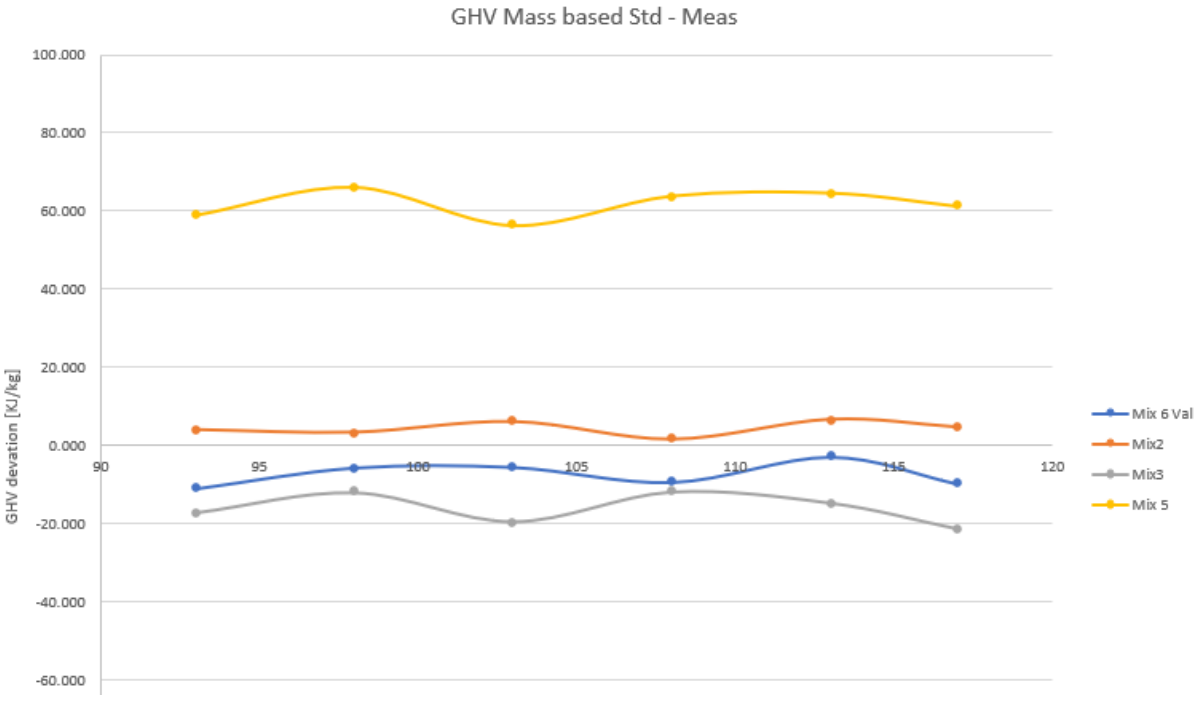
Mix 18_1242_01 Liquid composition

Component	Gravimetric Amount fraction %mol/mol	Reference Liq Amount fraction %mol/mol	Uncertainty %mol/mol	
N2	0.291	0.293	0.007	
c1	92.779	92.788	0.035	
c2	4.524	4.516	0.014	
c3	1.827	1.824	0.005	
ic4	0.301	0.300	0.002	
nc4	0.249	0.248	0.003	
ic5	0.020	0.020	0.000	
nc5	0.010	0.010	0.000	
sum	100.000	100.000		
			difference	EN12838
CV (MJ/m3)	40.4932	40.4988	0.0056	
CV (kJ/kg)	54672.4570	54673.2617	-0.8047	9
gas density	0.7407	0.7407	-0.0001	0.15
liquid density	0.04206218	0.04206732	0.0000	0.0003

Raman TC2 directly from Raman analyser

Component	93	Deviation Ref-Meas	98	Deviation Ref-Meas	103	Deviation Ref-Meas	108	Deviation Ref-Meas	113	Deviation Ref-Meas	117	Deviation Ref-Meas
N2	0.287	0.007	0.288	0.005	0.291	0.003	0.286	0.007	0.293	0.000	0.293	0.000
c1	92.804	-0.015	92.743	0.045	92.764	0.025	92.770	0.018	92.770	0.018	92.861	-0.073
c2	4.535	-0.019	4.589	-0.073	4.577	-0.061	4.571	-0.055	4.555	-0.039	4.478	0.038
c3	1.836	-0.012	1.836	-0.012	1.825	-0.001	1.829	-0.005	1.837	-0.013	1.828	-0.004
ic4	0.290	0.010	0.292	0.008	0.292	0.008	0.292	0.008	0.293	0.007	0.291	0.009
nc4	0.238	0.010	0.241	0.008	0.241	0.008	0.241	0.008	0.241	0.007	0.239	0.009
ic5	0.001	0.019	0.002	0.018	0.002	0.018	0.002	0.018	0.002	0.018	0.001	0.019
nc5	0.009	0.001	0.009	0.001	0.010	0.000	0.010	0.000	0.009	0.000	0.009	0.001
sum	100.000		100.000		100.000		100.000		100.000		100.000	
CV (kJ/kg)	54684.2656		54679.0313		54678.875		54682.6602		54676.3203		54683.043	
diff from ref liquid	-11.004		-5.770		-5.613		-9.398		-3.059		-9.781	
CV(MJ/m3)	40.469		40.488		40.478		40.480		40.479		40.448	
diff from ref liquid	-0.0295		-0.0105		-0.0204		-0.0186		-0.0202		-0.0508	


Performance GHV volume based Std - Meas
GHV Deviation [MJ/m3]
0.1200
0.1000
0.0800
0.0600
0.0400
0.0200
0.0000
-0.0200
-0.0400
-0.0600
90
95
100
105
110
115
120
Mix 6 Val
Mix2
Mix3
Mix 5


GHV Mass based Std - Meas
GHV devation [KJ/kg]
100.000
80.000
60.000
40.000
20.000
0.000
-20.000
-40.000
-60.000
90
95
100
105
110
115
120
Mix 6 Val
Mix2
Mix3
Mix 5

APPENDIX 4. GC PRGM AND VALIDATION REPORT

Page 1 of 1

CERTIFICATE OF CALIBRATION

Approved signatory
Name: **Dr Gavin Squire**
Signature:

Issued by: **EffecTech**
Date of Issue: **18 December 2015** Certificate No.: **15/1068/01**

EffecTech
Specialists in Gas Measurement

Dove House
Dove Fields
Uttoxeter
Staffordshire ST14 8HU
United Kingdom www.effectech.co.uk

ilac-MRA
UKAS CALIBRATION
0590

Customer	:	Shell Global Solutions International BV Kessler Park 1, 2288 GS Rijswijk, Zuid-Holland, Netherlands
Customer reference	:	PO No. 4550126157
Cylinder number	:	D328619
Destination	:	Fluxys Belgium SA Kaai 615 Henri-Victor Wolvenstraat 3, B-8380 Zeebrugge, Belgium
Date of calibration	:	04 December 2015
Description	:	Primary Reference Gas Mixture (PRGM) for use in natural gas and LNG calibration

Composition

component	amount fraction (%mol/mol)
nitrogen	0.5981 ± 0.0014
ethane	5.637 ± 0.014
methane	92.892 ± 0.011
propane	0.7029 ± 0.0032
iso-butane	0.06038 ± 0.00042
n-butane	0.07770 ± 0.00064
iso-pentane	0.02109 ± 0.00016
n-pentane	0.01003 ± 0.00017

Contents pressure at calibration	:	80 bar
Cylinder size	:	10 litres (water capacity)
Cylinder material	:	aluminium
Valve outlet connection	:	BS341 - No.4
Recommended minimum usage pressure	:	3 bar
Recommended minimum storage/usage temperature	:	0°C

Mixture prepared and certified by high precision gravimetry and verified analytically by EffecTech technical methods and in accordance with ISO 6142-1:2015 - *Gas Analysis — Preparation of Calibration Gas Mixtures — Part 1: Gravimetric Method for Class I Mixtures*
To re-order this calibration gas mixture contact EffecTech quoting certificate number 15/1068/01.
telephone : +44(0)1889 569229, fax : +44(0)1889 569220, email : sales@effectech.co.uk
EffecTech is accredited by UKAS to ISO/IEC 17025 : 2005 to undertake the calibration presented in this certificate. The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor *k*=2, providing a level of confidence of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

Typical field verification by Fluxys LNG laboratory on the GC under test as part of their internal verification program.

Fluxys Laboratory
Industrielaan 17 - Boulevard industriel 17
B-1070 Brussel - Bruxelles
Tel. +32 (0)2 282 7811 - Fax. +32 (0)2 282 7799

Place : Terminal
Time : 13/05/2016 12:07:13
Analyst : WH
Software Revision : 7.33
File : H:\Kalibratiefiles\Chrom_9_Backup Raman\9_160513_E.CDF

Instrument : Agilent AGI3000
Serial Number: CHROM9
Number Measurements: 10
Calibration gas Bottle : Effectech

Chromatograph Calibration Report

Instrument Method Settings

Setting	Column A	Column B
Temperature [DegC]	65	80
Run Time [s]	180	180
Detector Filament	On	On
Detector Autozero	Off	Off
Detector Sensitivity	High	Low
Inject Time [ms]	30	30
Sample Time [s]	Continuous	Continuous

Integration Method Settings

Setting	Column A	Column B
Integration Start [s]	0.00	0.00
Integration Stop [s]	180.00	180.00
Sensitivity	High0	High0
Smoothing	Normal	High
Detector Limit [V]	0.15	12.00
Max. Area Ratio	1.00e-005	1.00e-005
Peak Broadening Nominal Time[s]	19.00	19.00
Front Coefficient	0.70	0.70
Rear Coefficient	0.70	0.70
Baseline Fit R-square	0.95	0.95
Retention Fit R-square	0.85	0.85

Response Factors

	N2	C1	CO2	C2	C3	iC4	nC4	iC5	nC5
Old RF0	-	-	-	-	-	-	-	-	-
New RF0	-	-	-	-	-	-	-	-	-
Diff RF0 [%]	-	-	-	-	-	-	-	-	-
Old RF1	114.771	157.670	-	92.656	23.469	20.327	19.927	17.819	17.170
New RF1	115.159	157.953	-	92.846	23.504	20.353	19.947	17.879	17.252
Diff RF1 [%]	0.338	0.179	-	0.205	0.148	0.125	0.104	0.335	0.476

General Calibration Data

Number of calibration gases: 1
Number of control gases: 0

for Fluxys

FLUXYS LNG NV
LNG TERMINAL
HENRI-VICTOR WOLVENSSTRAAT 3
KAAI 615
8380 ZEEBRUGGE

Signatures

Chromatograph Calibration Report

Place : Terminal
Time : 13/05/2016 12:07:13
Analyst : WH
Software Revision : 7.33
File : H:\Kalibratiefiles\Chrom_9_Backup Raman\9_160513_E.CDF

Instrument : Agilent AGI3000
Serial Number: CHROM9
Number Measurements: 10
Calibration gas Bottle : Effectech

Calibration Gas Composition

	N2	C1	CO2	C2	C3	iC4	nC4	iC5	nC5	ESTD Total	GCV	Ron
	0.5981	92.8927		5.6370	0.7029	0.0604	0.0777	0.0211	0.0100	100.00	41874	0.76853

Detailed Measurement Results

	N2	C1	CO2	C2	C3	iC4	nC4	iC5	nC5	ESTD Total	GCV	Ron
1	0.5973	92.8946		5.6357	0.7031	0.0605	0.0777	0.0211	0.0099	99.81	41874	0.76852
2	0.5974	92.8938		5.6365	0.7031	0.0604	0.0777	0.0211	0.0100	99.83	41874	0.76852
3	0.5974	92.8949		5.6351	0.7034	0.0604	0.0778	0.0210	0.0100	99.82	41874	0.76852
4	0.5972	92.8954		5.6349	0.7033	0.0604	0.0778	0.0211	0.0100	99.80	41874	0.76852
5	0.5974	92.8951		5.6351	0.7031	0.0604	0.0778	0.0210	0.0101	99.83	41874	0.76852
6	0.5971	92.8933		5.6370	0.7032	0.0604	0.0778	0.0211	0.0100	99.82	41875	0.76853
7	0.5970	92.8957		5.6354	0.7028	0.0604	0.0777	0.0210	0.0100	99.82	41874	0.76851
8	0.5971	92.8947		5.6359	0.7032	0.0604	0.0778	0.0210	0.0100	99.81	41874	0.76852
9	0.5969	92.8957		5.6350	0.7030	0.0604	0.0778	0.0211	0.0100	99.83	41874	0.76851
10	0.5970	92.8944		5.6363	0.7031	0.0604	0.0778	0.0211	0.0100	99.81	41875	0.76852
Avg	0.5972	92.8948	-	5.6357	0.7031	0.0604	0.0778	0.0211	0.0100	99.82	41874	0.76852
StDev	0.0002	0.0008	-	0.0007	0.0001	0.0000	0.0000	0.0000	0.0000	0.0081	0.28	0.00001
RSTD [%]	0.033	0.001	-	0.013	0.021	0.039	0.033	0.208	0.355	0.008	0.001	0.001
Max-Min	0.0005	0.0024	-	0.0021	0.0005	0.0001	0.0001	0.0001	0.0001	0.02	0.9	0.00002
outliers	0	0	-	0	1	1	0	0	0	0	1	0
trend	2	0	-	0	0	0	0	0	0	0	0	0

Retention times

	N2	C1	CO2	C2	C3	iC4	nC4	iC5	nC5
Old	16.06	16.60	-	26.12	18.13	22.00	25.08	35.67	40.91
New	16.07	16.61	-	26.14	18.12	21.99	25.07	35.65	40.89

APPENDIX 5. RAMAN UNCERTAINTY CALCULATION.

Uncertainty%20eval
uation%20Raman%2

APPENDIX 6. TEST RESULTS CLOSENESS OF AGREEMENT GC/VAPORIZER AND RAMAN

Below are the results from the final performance test runt which took place from January 2020 until August 2020. The evaluation is done as per the procedures described in this report.

Performance test data for measurements under test

For each of the cargoes, the following data is shown.

a. Evaluation based on GIIGNL method uncertainty limits for GC/Vaporizer and Raman uncertainty limits using manufacturers standard calibration procedure only.
b. Evaluation based on GIIGNL method uncertainty limits for GC/Vaporizer and Raman uncertainty limits using manufacturers standard calibration procedure and additional verification on a Certified LNG standard fluid.
c. Evaluation based on Cargo repeatability data for the GC/Vaporizer and Raman uncertainty limits using manufacturers standard calibration procedure and additional verification on a Certified LNG standard fluid.

For the tables the colours indicate the following:
The green background indicates that the value is above the minimum threshold.
The yellow background indicates that the value is below the minimum threshold.
The amber background indicates that a bias is detected for a value above the minimum threshold.

A.6.1. Individual cargo evaluation results

Cargo evaluation T15 a.

LNG Temp	116K		As Left T15 GC_uT				GIIGNL		Raman Method Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman Manuf_std	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		95.607	0.011	0.1170	0.1175			95.694	0.2007			-0.087	0.37	Pass
Ethane	%mole		3.769	0.014	0.0520	0.0538			3.750	0.1736			0.019	0.11	Pass
Propane	%mole		0.378	0.0032	0.0291	0.0293			0.367	0.0413			0.010	0.21	Pass
I Butane	%mole		0.087	0.0004	0.0200	0.0201			0.085	0.0197			0.002	0.08	Pass
N Butane	%mole		0.073	0.0006	0.0191	0.0191			0.063	0.0197			0.010	0.37	Pass
I Pentane	%mole		0.010	0.0002	0.0116	0.0116			0.000	0.0175			0.010	0.46	Pass
N Pentane	%mole		0.005	0.0002	0.0098	0.0098			0.005	0.0100			0.000	0.01	Pass
Nitrogen	%mole		0.071	0.0014	0.0193	0.0193			0.026	0.0258			0.046	1.42	Bias
GHV	MJ/m3		39.111	0.021	0.0750	0.0779	0.20		39.092	0.0744	0.19		0.019	0.17	Pass
GHV	MJ/kg		55.169	0.01200	0.0270	0.0295	0.05		55.219	0.0431	0.08		-0.050	0.96	Pass
LNG Dens	kg/m3		433.637			1.9514	0.45		433.208	1.9494	0.45		0.429	0.16	Pass

Cargo evaluation T15 b.

LNG Temp	116K		As Left T15 GC_uT				GIIGNL		Raman Instr Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman LNG val	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		95.607	0.011	0.1170	0.1175			95.694	0.1262			-0.087	0.50	Pass
Ethane	%mole		3.769	0.014	0.0520	0.0538			3.750	0.0994			0.019	0.17	Pass
Propane	%mole		0.378	0.0032	0.0291	0.0293			0.367	0.0391			0.010	0.21	Pass
I Butane	%mole		0.087	0.0004	0.0200	0.0201			0.085	0.0195			0.002	0.08	Pass
N Butane	%mole		0.073	0.0006	0.0191	0.0191			0.063	0.0196			0.010	0.37	Pass
I Pentane	%mole		0.010	0.0002	0.0116	0.0116			0.000	0.0177			0.010	0.45	Pass
N Pentane	%mole		0.005	0.0002	0.0098	0.0098			0.005	0.0101			0.000	0.01	Pass
Nitrogen	%mole		0.071	0.0014	0.0193	0.0193			0.026	0.0388			0.046	1.05	Bias
GHV	MJ/m3		39.111	0.021	0.0750	0.0779	0.20		39.092	0.0539	0.14		0.019	0.20	Pass
GHV	MJ/kg		55.169	0.0120	0.0270	0.0295	0.05		55.219	0.0413	0.07		-0.050	0.98	Pass
LNG Dens	kg/m3		433.637			1.9514	0.45		433.208	1.9494	0.45		0.429	0.16	Pass

Cargo evaluation T15 c.

LNG Temp	116K		As Left T15 GC_uT				GIIGNL		Raman Instr Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo Repeat	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		95.607	0.011	0.0506	0.0518			95.694	0.1262			-0.087	0.64	Pass
Ethane	%mole		3.769	0.014	0.0371	0.0397			3.750	0.0994			0.019	0.18	Pass
Propane	%mole		0.378	0.0032	0.0087	0.0093			0.367	0.0391			0.010	0.26	Pass
I Butane	%mole		0.087	0.0004	0.0034	0.0035			0.085	0.0195			0.002	0.11	Pass
N Butane	%mole		0.073	0.0006	0.0034	0.0035			0.063	0.0196			0.010	0.52	Pass
I Pentane	%mole		0.010	0.0002	0.0007	0.0007			0.000	0.0177			0.010	0.54	Pass
N Pentane	%mole		0.005	0.0002	0.0004	0.0004			0.005	0.0101			0.000	0.02	Pass
Nitrogen	%mole		0.071	0.0014	0.0030	0.0033			0.026	0.0388			0.046	1.17	Bias
GHV	MJ/m3		39.111	0.021	0.0210	0.0297	0.08		39.092	0.0539	0.14		0.019	0.30	Pass
GHV	MJ/kg		55.169	0.0120	0.0050	0.0130	0.02		55.219	0.0413	0.07		-0.050	1.15	Bias
LNG Dens	kg/m3		433.637			1.9514	0.45		433.208	1.9494	0.45		0.429	0.16	Pass

Cargo evaluation T16 a.

LNG Temp	113K		As Left T16 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman Manuf_std	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.564	0.011	0.1138	0.1143			94.536	0.2309			0.029	0.11	Pass
Ethane	%mole		3.717	0.014	0.0507	0.0526			3.783	0.1732			-0.066	0.36	Pass
Propane	%mole		0.930	0.0032	0.0357	0.0359			0.943	0.0524			-0.014	0.22	Pass
I Butane	%mole		0.290	0.0004	0.0270	0.0270			0.285	0.0221			0.005	0.15	Pass
N Butane	%mole		0.260	0.0006	0.0261	0.0261			0.238	0.0213			0.021	0.63	Pass
I Pentane	%mole		0.006	0.0002	0.0103	0.0103			0.000	0.0178			0.006	0.31	Pass
N Pentane	%mole		0.003	0.0002	0.0083	0.0083			0.002	0.0084			0.001	0.09	Pass
Nitrogen	%mole		0.230	0.0014	0.0253	0.0254			0.199	0.0276			0.031	0.82	Pass
GHV	MJ/m3		39.668	0.021	0.0809	0.0836	0.21		39.670	0.0887	0.22		-0.002	0.02	Pass
GHV	MJ/kg		54.886	0.01200	0.0335	0.0356	0.06		54.915	0.0462	0.08		-0.029	0.50	Pass
LNG Dens	kg/m3		439.736			1.9788	0.45		439.631	1.9783	0.45		0.105	0.04	Pass

Cargo evaluation T16 b.

LNG Temp	113K		As Left T16 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman LNG val	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.564	0.011	0.1138	0.1143			94.536	0.1259			0.029	0.17	Pass
Ethane	%mole		3.717	0.014	0.0507	0.0526			3.783	0.0996			-0.066	0.58	Pass
Propane	%mole		0.930	0.0032	0.0357	0.0359			0.943	0.0386			-0.014	0.26	Pass
I Butane	%mole		0.290	0.0004	0.0270	0.0270			0.285	0.0195			0.005	0.16	Pass
N Butane	%mole		0.260	0.0006	0.0261	0.0261			0.238	0.0196			0.021	0.65	Pass
I Pentane	%mole		0.006	0.0002	0.0103	0.0103			0.000	0.0176			0.006	0.31	Pass
N Pentane	%mole		0.003	0.0002	0.0083	0.0083			0.002	0.0083			0.001	0.09	Pass
Nitrogen	%mole		0.230	0.0014	0.0253	0.0254			0.199	0.0388			0.031	0.66	Pass
GHV	MJ/m3		39.668	0.021	0.0809	0.0836	0.21		39.670	0.0530	0.13		-0.002	0.02	Pass
GHV	MJ/kg		54.886	0.01200	0.0335	0.0356	0.06		54.915	0.0400	0.07		-0.029	0.54	Pass
LNG Dens	kg/m3		439.736			1.9788	0.45		439.631	1.9783	0.45		0.105	0.04	Pass

Cargo evaluation T16 c.

LNG Temp	113K		As Left T16 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo Repeat	Uxi	Rel unc. [%MV]		Mean	Uxi	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.564	0.011	0.0476	0.0489			94.536	0.1259			0.029	0.21	Pass
Ethane	%mole		3.717	0.014	0.0329	0.0358			3.783	0.0996			-0.066	0.62	Pass
Propane	%mole		0.930	0.0032	0.0111	0.0115			0.943	0.0386			-0.014	0.34	Pass
I Butane	%mole		0.290	0.0004	0.0044	0.0044			0.285	0.0195			0.005	0.26	Pass
N Butane	%mole		0.260	0.0006	0.0047	0.0048			0.238	0.0196			0.021	1.05	Bias
I Pentane	%mole		0.006	0.0002	0.0002	0.0003			0.000	0.0176			0.006	0.36	Pass
N Pentane	%mole		0.003	0.0002	0.0002	0.0003			0.002	0.0083			0.001	0.13	Pass
Nitrogen	%mole		0.230	0.0014	0.0039	0.0042			0.199	0.0388			0.031	0.78	Pass
GHV	MJ/m3		39.668	0.021	0.0200	0.0290	0.07		39.670	0.0530	0.13		-0.002	0.04	Pass
GHV	MJ/kg		54.886	0.01200	0.0057	0.0133	0.02		54.915	0.0400	0.07		-0.029	0.69	Pass
LNG Dens	kg/m3		439.736			1.9788	0.45		439.631	1.9783	0.45		0.105	0.04	Pass

Cargo evaluation T17 a.

LNG Temp	114K		As Left T17 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman Manuf_std	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.504	0.011	0.1136	0.1141			94.513	0.2328			-0.008	0.03	Pass
Ethane	%mole		3.787	0.014	0.0507	0.0526			3.832	0.1749			-0.046	0.25	Pass
Propane	%mole		0.948	0.0032	0.0359	0.0360			0.953	0.0524			-0.005	0.08	Pass
I Butane	%mole		0.292	0.0004	0.0269	0.0269			0.285	0.0221			0.007	0.21	Pass
N Butane	%mole		0.264	0.0006	0.0262	0.0262			0.240	0.0214			0.024	0.70	Pass
I Pentane	%mole		0.006	0.0002	0.0102	0.0102			0.000	0.0173			0.006	0.30	Pass
N Pentane	%mole		0.003	0.0002	0.0082	0.0082			0.002	0.0085			0.001	0.07	Pass
Nitrogen	%mole		0.197	0.0014	0.0244	0.0244			0.161	0.0271			0.036	0.98	Pass
GHV	MJ/m3		39.715	0.021	0.0810	0.0837	0.21		39.705	0.0901	0.23		0.010	0.08	Pass
GHV	MJ/kg		54.908	0.01200	0.0330	0.0351	0.06		54.941	0.0456	0.08		-0.033	0.57	Pass
LNG Dens	kg/m3		439.964			1.9798	0.45		439.717	1.9787	0.45		0.247	0.09	Pass

Cargo evaluation T17 b.

LNG Temp	114K		As Left T17 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman LNG val	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.504	0.011	0.1136	0.1141			94.513	0.1257			-0.008	0.05	Pass
Ethane	%mole		3.787	0.014	0.0507	0.0526			3.832	0.0993			-0.046	0.41	Pass
Propane	%mole		0.948	0.0032	0.0359	0.0360			0.953	0.0388			-0.005	0.10	Pass
I Butane	%mole		0.292	0.0004	0.0269	0.0269			0.285	0.0193			0.007	0.22	Pass
N Butane	%mole		0.264	0.0006	0.0262	0.0262			0.240	0.0197			0.024	0.72	Pass
I Pentane	%mole		0.006	0.0002	0.0102	0.0102			0.000	0.0177			0.006	0.29	Pass
N Pentane	%mole		0.003	0.0002	0.0082	0.0082			0.002	0.0086			0.001	0.07	Pass
Nitrogen	%mole		0.197	0.0014	0.0244	0.0244			0.161	0.0388			0.036	0.78	Pass
GHV	MJ/m3		39.715	0.021	0.0810	0.0837	0.21		39.705	0.0530	0.13		0.010	0.10	Pass
GHV	MJ/kg		54.908	0.01200	0.0330	0.0351	0.06		54.941	0.0400	0.07		-0.033	0.61	Pass
LNG Dens	kg/m3		439.964			1.9798	0.45		439.717	1.9787	0.45		0.247	0.09	Pass

Cargo evaluation T17 c.

LNG Temp	114K		As Left T17 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo Repeat	Uxi	Rel unc. [%MV]		Mean	Uxi	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.504	0.011	0.0466	0.0479			94.513	0.1257			-0.008	0.06	Pass
Ethane	%mole		3.787	0.014	0.0315	0.0345			3.832	0.0993			-0.046	0.44	Pass
Propane	%mole		0.948	0.0032	0.0126	0.0130			0.953	0.0388			-0.005	0.13	Pass
I Butane	%mole		0.292	0.0004	0.0043	0.0043			0.285	0.0193			0.007	0.38	Pass
N Butane	%mole		0.264	0.0006	0.0047	0.0048			0.240	0.0197			0.024	1.17	Bias
I Pentane	%mole		0.006	0.0002	0.0002	0.0003			0.000	0.0177			0.006	0.34	Pass
N Pentane	%mole		0.003	0.0002	0.0002	0.0003			0.002	0.0086			0.001	0.09	Pass
Nitrogen	%mole		0.197	0.0014	0.0035	0.0038			0.161	0.0388			0.036	0.92	Pass
GHV	MJ/m3		39.715	0.021	0.0200	0.0290	0.07		39.705	0.0530	0.13		0.010	0.16	Pass
GHV	MJ/kg		54.908	0.01200	0.0057	0.0133	0.02		54.941	0.0400	0.07		-0.033	0.77	Pass
LNG Dens	kg/m3		439.964			1.9798	0.45		439.717	1.9787	0.45		0.247	0.09	Pass

Cargo evaluation T18 a.

LNG Temp	116K		As Left T18 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman Manuf_std	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		95.571	0.011	0.1301	0.1306			95.612	0.2023			-0.040	0.17	Pass
Ethane	%mole		4.027	0.014	0.0587	0.0604			4.037	0.1810			-0.009	0.05	Pass
Propane	%mole		0.222	0.0032	0.0285	0.0287			0.214	0.0398			0.007	0.15	Pass
I Butane	%mole		0.036	0.0004	0.0177	0.0177			0.037	0.0196			-0.001	0.04	Pass
N Butane	%mole		0.033	0.0006	0.0173	0.0173			0.028	0.0196			0.005	0.20	Pass
I Pentane	%mole		0.003	0.0002	0.0098	0.0098			0.000	0.0174			0.003	0.15	Pass
N Pentane	%mole		0.002	0.0002	0.0085	0.0085			0.001	0.0083			0.000	0.02	Pass
Nitrogen	%mole		0.105	0.0014	0.0239	0.0239			0.062	0.0258			0.044	1.25	Bias
GHV	MJ/m3		38.997	0.021	0.0770	0.0798	0.20		39.001	0.0722	0.19		-0.004	0.04	Pass
GHV	MJ/kg		55.163	0.01200	0.0320	0.0342	0.06		55.205	0.0430	0.08		-0.042	0.76	Pass
LNG Dens	kg/m3		429.826			1.9342	0.45		429.629	1.9333	0.45		0.196	0.07	Pass

Cargo evaluation T18 b.

LNG Temp	116K		As Left T18 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman LNG val	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		95.571	0.011	0.1301	0.1306			95.612	0.1271			-0.040	0.22	Pass
Ethane	%mole		4.027	0.014	0.0587	0.0604			4.037	0.1004			-0.009	0.08	Pass
Propane	%mole		0.222	0.0032	0.0285	0.0287			0.214	0.0390			0.007	0.15	Pass
I Butane	%mole		0.036	0.0004	0.0177	0.0177			0.037	0.0197			-0.001	0.04	Pass
N Butane	%mole		0.033	0.0006	0.0173	0.0173			0.028	0.0197			0.005	0.20	Pass
I Pentane	%mole		0.003	0.0002	0.0098	0.0098			0.000	0.0177			0.003	0.15	Pass
N Pentane	%mole		0.002	0.0002	0.0085	0.0085			0.001	0.0084			0.000	0.02	Pass
Nitrogen	%mole		0.105	0.0014	0.0239	0.0239			0.062	0.0389			0.044	0.96	Pass
GHV	MJ/m3		38.997	0.021	0.0770	0.0798	0.20		39.001	0.0540	0.14		-0.004	0.04	Pass
GHV	MJ/kg		55.163	0.01200	0.0320	0.0342	0.06		55.205	0.0410	0.07		-0.042	0.79	Pass
LNG Dens	kg/m3		429.826			1.9342	0.45		429.629	1.9333	0.45		0.196	0.07	Pass

Cargo evaluation T18 c.

LNG Temp	116K		As Left T18 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo Repeat	Uxi	Rel unc. [%MV]		Mean	Uxi	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		95.571	0.011	0.0697	0.0706			95.612	0.1271			-0.040	0.28	Pass
Ethane	%mole		4.027	0.014	0.0566	0.0583			4.037	0.1004			-0.009	0.08	Pass
Propane	%mole		0.222	0.0032	0.0093	0.0099			0.214	0.0390			0.007	0.18	Pass
I Butane	%mole		0.036	0.0004	0.0032	0.0032			0.037	0.0197			-0.001	0.05	Pass
N Butane	%mole		0.033	0.0006	0.0033	0.0033			0.028	0.0197			0.005	0.26	Pass
I Pentane	%mole		0.003	0.0002	0.0003	0.0004			0.000	0.0177			0.003	0.17	Pass
N Pentane	%mole		0.002	0.0002	0.0002	0.0003			0.001	0.0084			0.000	0.04	Pass
Nitrogen	%mole		0.105	0.0014	0.0048	0.0050			0.062	0.0389			0.044	1.12	Bias
GHV	MJ/m3		38.997	0.021	0.0270	0.0342	0.09		39.001	0.0540	0.14		-0.004	0.06	Pass
GHV	MJ/kg		55.163	0.01200	0.0060	0.0134	0.02		55.205	0.0410	0.07		-0.042	0.97	Pass
LNG Dens	kg/m3		429.826			1.9342	0.45		429.629	1.9333	0.45		0.196	0.07	Pass

Cargo evaluation T19 a.

LNG Temp	114K		As Left T19 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman Manuf_std	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.510	0.011	0.1150	0.1155			94.548	0.2329			-0.038	0.15	Pass
Ethane	%mole		3.757	0.014	0.0509	0.0528			3.777	0.1761			-0.020	0.11	Pass
Propane	%mole		0.947	0.0032	0.0357	0.0359			0.948	0.0524			-0.001	0.02	Pass
I Butane	%mole		0.292	0.0004	0.0265	0.0265			0.284	0.0219			0.008	0.23	Pass
N Butane	%mole		0.263	0.0006	0.0259	0.0259			0.239	0.0210			0.024	0.72	Pass
I Pentane	%mole		0.006	0.0002	0.0103	0.0103			0.000	0.0176			0.006	0.31	Pass
N Pentane	%mole		0.003	0.0002	0.0083	0.0083			0.002	0.0084			0.001	0.09	Pass
Nitrogen	%mole		0.223	0.0014	0.0247	0.0248			0.187	0.0271			0.035	0.97	Pass
GHV	MJ/m3		39.695	0.021	0.0810	0.0837	0.21		39.675	0.0890	0.22		0.021	0.17	Pass
GHV	MJ/kg		54.883	0.01200	0.0330	0.0351	0.06		54.921	0.0459	0.08		-0.038	0.66	Pass
LNG Dens	kg/m3		439.811			1.9792	0.45		439.393	1.9773	0.45		0.419	0.15	Pass

Cargo evaluation T19 b.

LNG Temp	114K		As Left T19 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman LNG val	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.510	0.011	0.1150	0.1155			94.548	0.1245			-0.038	0.22	Pass
Ethane	%mole		3.757	0.014	0.0509	0.0528			3.777	0.0980			-0.020	0.18	Pass
Propane	%mole		0.947	0.0032	0.0357	0.0359			0.948	0.0390			-0.001	0.02	Pass
I Butane	%mole		0.292	0.0004	0.0265	0.0265			0.284	0.0197			0.008	0.23	Pass
N Butane	%mole		0.263	0.0006	0.0259	0.0259			0.239	0.0197			0.024	0.74	Pass
I Pentane	%mole		0.006	0.0002	0.0103	0.0103			0.000	0.0176			0.006	0.31	Pass
N Pentane	%mole		0.003	0.0002	0.0083	0.0083			0.002	0.0084			0.001	0.09	Pass
Nitrogen	%mole		0.223	0.0014	0.0247	0.0248			0.187	0.0389			0.035	0.77	Pass
GHV	MJ/m3		39.695	0.021	0.0810	0.0837	0.21		39.675	0.0540	0.14		0.021	0.21	Pass
GHV	MJ/kg		54.883	0.01200	0.0330	0.0351	0.06		54.921	0.0400	0.07		-0.038	0.71	Pass
LNG Dens	kg/m3		439.811			1.9792	0.45		439.393	1.9773	0.45		0.419	0.15	Pass

Cargo evaluation T19 c.

LNG Temp	114K		As Left T19 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo Repeat	Uxi	Rel unc. [%MV]		Mean	Uxi	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.510	0.011	0.0669	0.0678			94.548	0.1245			-0.038	0.27	Pass
Ethane	%mole		3.757	0.014	0.0484	0.0504			3.777	0.0980			-0.020	0.19	Pass
Propane	%mole		0.947	0.0032	0.0156	0.0159			0.948	0.0390			-0.001	0.03	Pass
I Butane	%mole		0.292	0.0004	0.0056	0.0057			0.284	0.0197			0.008	0.38	Pass
N Butane	%mole		0.263	0.0006	0.0057	0.0057			0.239	0.0197			0.024	1.17	Bias
I Pentane	%mole		0.006	0.0002	0.0002	0.0003			0.000	0.0176			0.006	0.36	Pass
N Pentane	%mole		0.003	0.0002	0.0002	0.0003			0.002	0.0084			0.001	0.13	Pass
Nitrogen	%mole		0.223	0.0014	0.0066	0.0068			0.187	0.0389			0.035	0.90	Pass
GHV	MJ/m3		39.695	0.021	0.0310	0.0374	0.09		39.675	0.0540	0.14		0.021	0.31	Pass
GHV	MJ/kg		54.883	0.01200	0.0050	0.0130	0.02		54.921	0.0400	0.07		-0.038	0.90	Pass
LNG Dens	kg/m3		439.811			1.9792	0.45		439.393	1.9773	0.45		0.419	0.15	Pass

Cargo evaluation T20 a.

LNG Temp	114K		As Left T20 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman Manuf_std	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.435	0.011	0.1165	0.1170			94.489	0.2297			-0.054	0.21	Pass
Ethane	%mole		3.791	0.014	0.0518	0.0537			3.794	0.1721			-0.003	0.01	Pass
Propane	%mole		0.966	0.0032	0.0369	0.0370			0.964	0.0529			0.001	0.02	Pass
I Butane	%mole		0.295	0.0004	0.0273	0.0273			0.286	0.0222			0.009	0.26	Pass
N Butane	%mole		0.267	0.0006	0.0266	0.0266			0.242	0.0211			0.025	0.74	Pass
I Pentane	%mole		0.006	0.0002	0.0104	0.0104			0.000	0.0173			0.006	0.30	Pass
N Pentane	%mole		0.003	0.0002	0.0084	0.0084			0.002	0.0084			0.001	0.08	Pass
Nitrogen	%mole		0.237	0.0014	0.0259	0.0259			0.208	0.0278			0.029	0.75	Pass
GHV	MJ/m3		39.717	0.021	0.0810	0.0837	0.20		39.685	0.0896	0.23		0.031	0.26	Pass
GHV	MJ/kg		54.865	0.01200	0.0350	0.0370	0.07		54.899	0.0460	0.08		-0.034	0.58	Pass
LNG Dens	kg/m3		438.788			1.9745	0.45		439.833	1.9792	0.45		-1.045	0.37	Pass

Cargo evaluation T20 b.

LNG Temp	114K		As Left T20 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman LNG val	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.435	0.011	0.1165	0.1170			94.489	0.1256			-0.054	0.31	Pass
Ethane	%mole		3.791	0.014	0.0518	0.0537			3.794	0.1000			-0.003	0.02	Pass
Propane	%mole		0.966	0.0032	0.0369	0.0370			0.964	0.0389			0.001	0.02	Pass
I Butane	%mole		0.295	0.0004	0.0273	0.0273			0.286	0.0195			0.009	0.28	Pass
N Butane	%mole		0.267	0.0006	0.0266	0.0266			0.242	0.0197			0.025	0.75	Pass
I Pentane	%mole		0.006	0.0002	0.0104	0.0104			0.000	0.0176			0.006	0.30	Pass
N Pentane	%mole		0.003	0.0002	0.0084	0.0084			0.002	0.0084			0.001	0.08	Pass
Nitrogen	%mole		0.237	0.0014	0.0259	0.0259			0.208	0.0389			0.029	0.61	Pass
GHV	MJ/m3		39.717	0.021	0.0830	0.0856	0.22		39.685	0.0530	0.13		0.031	0.31	Pass
GHV	MJ/kg		54.865	0.01200	0.0350	0.0370	0.07		54.899	0.0400	0.07		-0.034	0.62	Pass
LNG Dens	kg/m3		438.788			1.9745	0.45		439.833	1.9792	0.45		-1.045	0.37	Pass

Cargo evaluation T20 c.

LNG Temp	114K		As Left T20 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo Repeat	Uxi	Rel unc. [%MV]		Mean	Uxi	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.435	0.011	0.0690	0.0698			94.489	0.1256			-0.054	0.37	Pass
Ethane	%mole		3.791	0.014	0.0394	0.0418			3.794	0.1000			-0.003	0.02	Pass
Propane	%mole		0.966	0.0032	0.0208	0.0210			0.964	0.0389			0.001	0.03	Pass
I Butane	%mole		0.295	0.0004	0.0099	0.0099			0.286	0.0195			0.009	0.42	Pass
N Butane	%mole		0.267	0.0006	0.0102	0.0102			0.242	0.0197			0.025	1.13	Bias
I Pentane	%mole		0.006	0.0002	0.0004	0.0004			0.000	0.0176			0.006	0.35	Pass
N Pentane	%mole		0.003	0.0002	0.0002	0.0003			0.002	0.0084			0.001	0.11	Pass
Nitrogen	%mole		0.237	0.0014	0.0063	0.0064			0.208	0.0389			0.029	0.72	Pass
GHV	MJ/m3		39.717	0.021	0.0360	0.0417	0.10		39.685	0.0530	0.13		0.031	0.47	Pass
GHV	MJ/kg		54.865	0.01200	0.0087	0.0148	0.03		54.899	0.0400	0.07		-0.034	0.80	Pass
LNG Dens	kg/m3		438.788			1.9745	0.45		439.833	1.9792	0.45		-1.045	0.37	Pass

Cargo evaluation T21 a.

LNG Temp	115K		As Left T21 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman Manuf_std	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.488	0.011	0.1135	0.1141			94.535	0.2282			-0.047	0.18	Pass
Ethane	%mole		3.746	0.014	0.0507	0.0526			3.762	0.1710			-0.015	0.09	Pass
Propane	%mole		0.959	0.0032	0.0360	0.0361			0.959	0.0515			0.000	0.00	Pass
I Butane	%mole		0.293	0.0004	0.0267	0.0267			0.284	0.0221			0.009	0.27	Pass
N Butane	%mole		0.266	0.0006	0.0263	0.0263			0.241	0.0212			0.025	0.75	Pass
I Pentane	%mole		0.006	0.0002	0.0101	0.0101			0.000	0.0177			0.006	0.28	Pass
N Pentane	%mole		0.002	0.0002	0.0081	0.0081			0.001	0.0083			0.001	0.09	Pass
Nitrogen	%mole		0.239	0.0014	0.0253	0.0254			0.204	0.0277			0.035	0.94	Pass
GHV	MJ/m3		39.696	0.021	0.0810	0.0837	0.21		39.671	0.0879	0.22		0.024	0.20	Pass
GHV	MJ/kg		54.871	0.01200	0.0330	0.0351	0.06		54.910	0.0460	0.08		-0.039	0.67	Pass
LNG Dens	kg/m3		438.605			1.9737	0.45		438.221	1.9720	0.45		0.384	0.14	Pass

Cargo evaluation T21 b.

LNG Temp	115K		As Left T21 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman LNG val	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.488	0.011	0.1135	0.1141			94.535	0.1247			-0.047	0.28	Pass
Ethane	%mole		3.746	0.014	0.0507	0.0526			3.762	0.0983			-0.015	0.14	Pass
Propane	%mole		0.959	0.0032	0.0360	0.0361			0.959	0.0391			0.000	0.00	Pass
I Butane	%mole		0.293	0.0004	0.0267	0.0267			0.284	0.0194			0.009	0.28	Pass
N Butane	%mole		0.266	0.0006	0.0263	0.0263			0.241	0.0196			0.025	0.78	Pass
I Pentane	%mole		0.006	0.0002	0.0101	0.0101			0.000	0.0177			0.006	0.28	Pass
N Pentane	%mole		0.002	0.0002	0.0081	0.0081			0.001	0.0084			0.001	0.09	Pass
Nitrogen	%mole		0.239	0.0014	0.0253	0.0254			0.204	0.0388			0.035	0.76	Pass
GHV	MJ/m3		39.696	0.021	0.0810	0.0837	0.21		39.671	0.0530	0.13		0.024	0.25	Pass
GHV	MJ/kg		54.871	0.01200	0.0330	0.0351	0.06		54.910	0.0400	0.07		-0.039	0.73	Pass
LNG Dens	kg/m3		438.605			1.9737	0.45		438.221	1.9720	0.45		0.384	0.14	Pass

Cargo evaluation T21 c.

LNG Temp	115K		As Left T21 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo Repeat	Uxi	Rel unc. [%MV]		Mean	Uxi	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.488	0.011	0.1234	0.1239			94.535	0.1247			-0.047	0.27	Pass
Ethane	%mole		3.746	0.014	0.0862	0.0873			3.762	0.0983			-0.015	0.12	Pass
Propane	%mole		0.959	0.0032	0.0272	0.0274			0.959	0.0391			0.000	0.00	Pass
I Butane	%mole		0.293	0.0004	0.0098	0.0098			0.284	0.0194			0.009	0.43	Pass
N Butane	%mole		0.266	0.0006	0.0095	0.0095			0.241	0.0196			0.025	1.17	Bias
I Pentane	%mole		0.006	0.0002	0.0003	0.0004			0.000	0.0177			0.006	0.33	Pass
N Pentane	%mole		0.002	0.0002	0.0002	0.0003			0.001	0.0084			0.001	0.12	Pass
Nitrogen	%mole		0.239	0.0014	0.0077	0.0078			0.204	0.0388			0.035	0.89	Pass
GHV	MJ/m3		39.696	0.021	0.0520	0.0561	0.14		39.671	0.0530	0.13		0.024	0.32	Pass
GHV	MJ/kg		54.871	0.01200	0.0122	0.0171	0.03		54.910	0.0400	0.07		-0.039	0.90	Pass
LNG Dens	kg/m3		438.605			1.9737	0.45		438.221	1.9720	0.45		0.384	0.14	Pass

Cargo evaluation T22 a.

LNG Temp	115K		As Left T22 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman Manuf_std	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		93.209	0.011	0.1394	0.1398			93.252	0.2761			-0.043	0.14	Pass
Ethane	%mole		6.215	0.014	0.0707	0.0721			6.190	0.2499			0.025	0.10	Pass
Propane	%mole		0.123	0.0032	0.0267	0.0268			0.116	0.0391			0.007	0.15	Pass
I Butane	%mole		0.013	0.0004	0.0150	0.0150			0.014	0.0195			-0.001	0.05	Pass
N Butane	%mole		0.011	0.0006	0.0146	0.0146			0.009	0.0196			0.003	0.11	Pass
I Pentane	%mole		0.000	0.0002	0.0065	0.0066			0.000	0.0177			0.000	0.02	Pass
N Pentane	%mole		0.000	0.0002	0.0037	0.0037			0.000	0.0080			0.000	0.02	Pass
Nitrogen	%mole		0.428	0.0014	0.0362	0.0363			0.411	0.0326			0.017	0.35	Pass
GHV	MJ/m3		39.397	0.021	0.0800	0.0827	0.21		39.388	0.0833	0.21		0.009	0.08	Pass
GHV	MJ/kg		54.762	0.01200	0.0460	0.0475	0.09		54.780	0.0495	0.09		-0.018	0.26	Pass
LNG Dens	kg/m3		437.845			1.9703	0.45		437.672	1.9695	0.45		0.173	0.06	Pass

Cargo evaluation T22 b.

LNG Temp	115K		As Left T22 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman LNG val	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		93.209	0.011	0.1394	0.1398			93.252	0.1245			-0.043	0.23	Pass
Ethane	%mole		6.215	0.014	0.0707	0.0721			6.190	0.0981			0.025	0.21	Pass
Propane	%mole		0.123	0.0032	0.0267	0.0268			0.116	0.0392			0.007	0.15	Pass
I Butane	%mole		0.013	0.0004	0.0150	0.0150			0.014	0.0197			-0.001	0.05	Pass
N Butane	%mole		0.011	0.0006	0.0146	0.0146			0.009	0.0196			0.003	0.11	Pass
I Pentane	%mole		0.000	0.0002	0.0065	0.0066			0.000	0.0176			0.000	0.02	Pass
N Pentane	%mole		0.000	0.0002	0.0037	0.0037			0.000	0.0083			0.000	0.02	Pass
Nitrogen	%mole		0.428	0.0014	0.0362	0.0363			0.411	0.0388			0.017	0.32	Pass
GHV	MJ/m3		39.397	0.021	0.0800	0.0827	0.21		39.388	0.0530	0.13		0.009	0.09	Pass
GHV	MJ/kg		54.762	0.01200	0.0460	0.0475	0.09		54.780	0.0400	0.07		-0.018	0.29	Pass
LNG Dens	kg/m3		437.845			1.9703	0.45		437.672	1.9695	0.45		0.173	0.06	Pass

Cargo evaluation T22 c.

LNG Temp	115K		As Left T22 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo Repeat	Uxi	Rel unc. [%MV]		Mean	Uxi	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		93.209	0.011	0.0536	0.0547			93.252	0.1245			-0.043	0.31	Pass
Ethane	%mole		6.215	0.014	0.0470	0.0490			6.190	0.0981			0.025	0.23	Pass
Propane	%mole		0.123	0.0032	0.0116	0.0120			0.116	0.0392			0.007	0.18	Pass
I Butane	%mole		0.013	0.0004	0.0029	0.0029			0.014	0.0197			-0.001	0.07	Pass
N Butane	%mole		0.011	0.0006	0.0026	0.0027			0.009	0.0196			0.003	0.14	Pass
I Pentane	%mole		0.000	0.0002	0.0001	0.0002			0.000	0.0176			0.000	0.02	Pass
N Pentane	%mole		0.000	0.0002	0.0002	0.0003			0.000	0.0083			0.000	0.03	Pass
Nitrogen	%mole		0.428	0.0014	0.0078	0.0079			0.411	0.0388			0.017	0.43	Pass
GHV	MJ/m3		39.397	0.021	0.0220	0.0304	0.08		39.388	0.0530	0.13		0.009	0.15	Pass
GHV	MJ/kg		54.762	0.01200	0.0069	0.0138	0.03		54.780	0.0400	0.07		-0.018	0.43	Pass
LNG Dens	kg/m3		437.845			1.9703	0.45		437.672	1.9695	0.45		0.173	0.06	Pass

Cargo evaluation T23 a.

LNG Temp	114K		As Left T23 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman Manuf_std	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.544	0.011	0.1145	0.1150			94.595	0.2276			-0.051	0.20	Pass
Ethane	%mole		3.758	0.014	0.0510	0.0529			3.765	0.1727			-0.007	0.04	Pass
Propane	%mole		0.910	0.0032	0.0356	0.0357			0.909	0.0513			0.001	0.01	Pass
I Butane	%mole		0.290	0.0004	0.0267	0.0267			0.280	0.0221			0.010	0.28	Pass
N Butane	%mole		0.254	0.0006	0.0259	0.0259			0.230	0.0214			0.023	0.69	Pass
I Pentane	%mole		0.008	0.0002	0.0110	0.0110			0.000	0.0175			0.008	0.40	Pass
N Pentane	%mole		0.004	0.0002	0.0090	0.0090			0.002	0.0086			0.001	0.10	Pass
Nitrogen	%mole		0.234	0.0014	0.0255	0.0255			0.204	0.0273			0.029	0.79	Pass
GHV	MJ/m3		39.664	0.021	0.0810	0.0837	0.21		39.633	0.0866	0.22		0.031	0.25	Pass
GHV	MJ/kg		54.879	0.01200	0.0350	0.0370	0.07		54.918	0.0460	0.08		-0.039	0.66	Pass
LNG Dens	kg/m3		438.284			1.9723	0.45		437.882	1.9705	0.45		0.402	0.14	Pass

Cargo evaluation T23 b.

LNG Temp	114K		As Left T23 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman LNG val	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.544	0.011	0.1145	0.1150			94.595	0.1247			-0.051	0.30	Pass
Ethane	%mole		3.758	0.014	0.0510	0.0529			3.765	0.0989			-0.007	0.06	Pass
Propane	%mole		0.910	0.0032	0.0356	0.0357			0.909	0.0390			0.001	0.01	Pass
I Butane	%mole		0.290	0.0004	0.0267	0.0267			0.280	0.0197			0.010	0.29	Pass
N Butane	%mole		0.254	0.0006	0.0259	0.0259			0.230	0.0198			0.023	0.71	Pass
I Pentane	%mole		0.008	0.0002	0.0110	0.0110			0.000	0.0179			0.008	0.39	Pass
N Pentane	%mole		0.004	0.0002	0.0090	0.0090			0.002	0.0088			0.001	0.10	Pass
Nitrogen	%mole		0.234	0.0014	0.0255	0.0255			0.204	0.0389			0.029	0.63	Pass
GHV	MJ/m3		39.664	0.021	0.0810	0.0837	0.21		39.633	0.0530	0.13		0.031	0.31	Pass
GHV	MJ/kg		54.879	0.01200	0.0350	0.0370	0.07		54.918	0.0400	0.07		-0.039	0.72	Pass
LNG Dens	kg/m3		438.284			1.9723	0.45		437.882	1.9705	0.45		0.402	0.14	Pass

Cargo evaluation T23 c.

LNG Temp	114K		As Left T23 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo Repeat	Uxi	Rel unc. [%MV]		Mean	Uxi	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		94.544	0.011	0.0389	0.0404			94.595	0.1247			-0.051	0.39	Pass
Ethane	%mole		3.758	0.014	0.0262	0.0297			3.765	0.0989			-0.007	0.07	Pass
Propane	%mole		0.910	0.0032	0.0101	0.0106			0.909	0.0390			0.001	0.02	Pass
I Butane	%mole		0.290	0.0004	0.0042	0.0042			0.280	0.0197			0.010	0.48	Pass
N Butane	%mole		0.254	0.0006	0.0045	0.0045			0.230	0.0198			0.023	1.14	Bias
I Pentane	%mole		0.008	0.0002	0.0003	0.0003			0.000	0.0179			0.008	0.46	Pass
N Pentane	%mole		0.004	0.0002	0.0002	0.0003			0.002	0.0088			0.001	0.14	Pass
Nitrogen	%mole		0.234	0.0014	0.0057	0.0059			0.204	0.0389			0.029	0.75	Pass
GHV	MJ/m3		39.664	0.021	0.0190	0.0283	0.07		39.633	0.0530	0.13		0.031	0.51	Pass
GHV	MJ/kg		54.879	0.01200	0.0059	0.0134	0.02		54.918	0.0400	0.07		-0.039	0.92	Pass
LNG Dens	kg/m3		438.284			1.9723	0.45		437.882	1.9705	0.45		0.402	0.14	Pass

Cargo evaluation T24 a.

LNG Temp	113K		As Left T24 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman Manuf_std	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		93.469	0.011	0.1462	0.1466			93.367	0.2726			0.102	0.33	Pass
Ethane	%mole		6.134	0.014	0.0737	0.0750			6.263	0.2536			-0.129	0.49	Pass
Propane	%mole		0.054	0.0032	0.0225	0.0227			0.049	0.0391			0.005	0.12	Pass
I Butane	%mole		0.000	0.0004	0.0026	0.0027			0.002	0.0195			-0.002	0.12	Pass
N Butane	%mole		0.001	0.0006	0.0071	0.0071			0.000	0.0195			0.001	0.02	Pass
I Pentane	%mole		0.000	0.0002	0.0016	0.0017			0.000	0.0177			0.000	0.00	Pass
N Pentane	%mole		0.000	0.0002	0.0026	0.0027			0.000	0.0082			0.000	0.02	Pass
Nitrogen	%mole		0.343	0.0014	0.0360	0.0360			0.312	0.0300			0.031	0.67	Pass
GHV	MJ/m3		39.348	0.021	0.0780	0.0808	0.21		39.392	0.0849	0.22		-0.044	0.38	Pass
GHV	MJ/kg		54.853	0.01200	0.0450	0.0466	0.08		54.875	0.0476	0.09		-0.022	0.33	Pass
LNG Dens	kg/m3		436.814			1.9657	0.45		437.076	1.9668	0.45		-0.262	0.09	Pass

Cargo evaluation T24 b.

LNG Temp	113K		As Left T24 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman LNG val	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		93.469	0.011	0.1462	0.1466			93.367	0.1254			0.102	0.53	Pass
Ethane	%mole		6.134	0.014	0.0737	0.0750			6.263	0.0983			-0.129	1.04	Bias
Propane	%mole		0.054	0.0032	0.0225	0.0227			0.049	0.0393			0.005	0.12	Pass
I Butane	%mole		0.000	0.0004	0.0026	0.0027			0.002	0.0195			-0.002	0.13	Pass
N Butane	%mole		0.001	0.0006	0.0071	0.0071			0.000	0.0200			0.001	0.02	Pass
I Pentane	%mole		0.000	0.0002	0.0016	0.0017			0.000	0.0179			0.000	0.00	Pass
N Pentane	%mole		0.000	0.0002	0.0026	0.0027			0.000	0.0082			0.000	0.02	Pass
Nitrogen	%mole		0.343	0.0014	0.0360	0.0360			0.312	0.0388			0.031	0.59	Pass
GHV	MJ/m3		39.348	0.021	0.0780	0.0808	0.21		39.392	0.0530	0.13		-0.044	0.46	Pass
GHV	MJ/kg		54.853	0.01200	0.0450	0.0466	0.08		54.875	0.0400	0.07		-0.022	0.36	Pass
LNG Dens	kg/m3		436.814			1.9657	0.45		437.076	1.9668	0.45		-0.262	0.09	Pass

Cargo evaluation T24 c.

LNG Temp	113K		As Left T24 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo Repeat	Uxi	Rel unc. [%MV]		Mean	Uxi	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		93.469	0.011	0.0513	0.0524			93.367	0.1254			0.102	0.75	Pass
Ethane	%mole		6.134	0.014	0.0398	0.0422			6.263	0.0983			-0.129	1.20	Bias
Propane	%mole		0.054	0.0032	0.0006	0.0032			0.049	0.0393			0.005	0.13	Pass
I Butane	%mole		0.000	0.0004	0.0000	0.0004			0.002	0.0195			-0.002	0.13	Pass
N Butane	%mole		0.001	0.0006	0.0001	0.0006			0.000	0.0200			0.001	0.03	Pass
I Pentane	%mole		0.000	0.0002	0.0000	0.0002			0.000	0.0179			0.000	0.00	Pass
N Pentane	%mole		0.000	0.0002	0.0000	0.0002			0.000	0.0082			0.000	0.02	Pass
Nitrogen	%mole		0.343	0.0014	0.0185	0.0186			0.312	0.0388			0.031	0.73	Pass
GHV	MJ/m3		39.348	0.021	0.0150	0.0258	0.07		39.392	0.0530	0.13		-0.044	0.75	Pass
GHV	MJ/kg		54.853	0.01200	0.0180	0.0216	0.04		54.875	0.0400	0.07		-0.022	0.48	Pass
LNG Dens	kg/m3		436.814			1.9657	0.45		437.076	1.9668	0.45		-0.262	0.09	Pass

Cargo evaluation T25 a.

LNG Temp	113K		As Left T25 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman Manuf_std	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		92.444	0.011	0.1150	0.1155			92.342	0.2983			0.102	0.32	Pass
Ethane	%mole		5.298	0.014	0.0567	0.0584			5.418	0.2238			-0.120	0.52	Pass
Propane	%mole		1.242	0.0032	0.0396	0.0397			1.266	0.0601			-0.025	0.34	Pass
I Butane	%mole		0.118	0.0004	0.0218	0.0218			0.118	0.0198			0.000	0.00	Pass
N Butane	%mole		0.291	0.0006	0.0272	0.0272			0.270	0.0219			0.020	0.59	Pass
I Pentane	%mole		0.017	0.0002	0.0135	0.0135			0.000	0.0176			0.017	0.76	Pass
N Pentane	%mole		0.003	0.0002	0.0087	0.0087			0.002	0.0085			0.001	0.08	Pass
Nitrogen	%mole		0.587	0.0014	0.0326	0.0326			0.575	0.0387			0.012	0.24	Pass
GHV	MJ/m3		40.051	0.021	0.0800	0.0827	0.21		40.063	0.0991	0.25		-0.012	0.09	Pass
GHV	MJ/kg		54.464	0.01200	0.0400	0.0418	0.08		54.469	0.0553	0.10		-0.005	0.08	Pass
LNG Dens	kg/m3		444.445			2.0000	0.45		444.544	2.0004	0.45		-0.098	0.03	Pass

Cargo evaluation T25 b.

LNG Temp	113K		As Left T25 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman LNG val	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		92.444	0.011	0.1150	0.1155			92.342	0.1233			0.102	0.60	Pass
Ethane	%mole		5.298	0.014	0.0567	0.0584			5.418	0.0984			-0.120	1.05	Bias
Propane	%mole		1.242	0.0032	0.0396	0.0397			1.266	0.0388			-0.025	0.44	Pass
I Butane	%mole		0.118	0.0004	0.0218	0.0218			0.118	0.0193			0.000	0.00	Pass
N Butane	%mole		0.291	0.0006	0.0272	0.0272			0.270	0.0197			0.020	0.61	Pass
I Pentane	%mole		0.017	0.0002	0.0135	0.0135			0.000	0.0177			0.017	0.76	Pass
N Pentane	%mole		0.003	0.0002	0.0087	0.0087			0.002	0.0086			0.001	0.08	Pass
Nitrogen	%mole		0.587	0.0014	0.0326	0.0326			0.575	0.0389			0.012	0.24	Pass
GHV	MJ/m3		40.051	0.021	0.0800	0.0827	0.21		40.063	0.0530	0.13		-0.012	0.12	Pass
GHV	MJ/kg		54.464	0.01200	0.0400	0.0418	0.08		54.469	0.0390	0.07		-0.005	0.10	Pass
LNG Dens	kg/m3		444.445			2.0000	0.45		444.544	2.0004	0.45		-0.098	0.03	Pass

Cargo evaluation T25 c.

LNG Temp	113K		As Left T25 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo Repeat	Uxi	Rel unc. [%MV]		Mean	Uxi	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		92.444	0.011	0.1223	0.1228			92.342	0.1233			0.102	0.59	Pass
Ethane	%mole		5.298	0.014	0.0965	0.0975			5.418	0.0984			-0.120	0.86	Pass
Propane	%mole		1.242	0.0032	0.0256	0.0258			1.266	0.0388			-0.025	0.53	Pass
I Butane	%mole		0.118	0.0004	0.0029	0.0029			0.118	0.0193			0.000	0.01	Pass
N Butane	%mole		0.291	0.0006	0.0075	0.0075			0.270	0.0197			0.020	0.97	Pass
I Pentane	%mole		0.017	0.0002	0.0005	0.0006			0.000	0.0177			0.017	0.95	Pass
N Pentane	%mole		0.003	0.0002	0.0001	0.0002			0.002	0.0086			0.001	0.12	Pass
Nitrogen	%mole		0.587	0.0014	0.0132	0.0133			0.575	0.0389			0.012	0.30	Pass
GHV	MJ/m3		40.051	0.021	0.0510	0.0552	0.14		40.063	0.0530	0.13		-0.012	0.15	Pass
GHV	MJ/kg		54.464	0.01200	0.0110	0.0163	0.03		54.469	0.0390	0.07		-0.005	0.13	Pass
LNG Dens	kg/m3		444.445			2.0000	0.45		444.544	2.0004	0.45		-0.098	0.03	Pass

Cargo evaluation T26 a.

LNG Temp	117K		As Left T26 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman Manuf_std	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		92.823	0.011	0.1239	0.1244			92.908	0.2833			-0.084	0.27	Pass
Ethane	%mole		6.619	0.014	0.0636	0.0651			6.596	0.2617			0.022	0.08	Pass
Propane	%mole		0.311	0.0032	0.0297	0.0299			0.303	0.0402			0.008	0.16	Pass
I Butane	%mole		0.077	0.0004	0.0209	0.0209			0.074	0.0197			0.003	0.10	Pass
N Butane	%mole		0.076	0.0006	0.0209	0.0209			0.066	0.0198			0.009	0.33	Pass
I Pentane	%mole		0.002	0.0002	0.0079	0.0079			0.000	0.0175			0.002	0.08	Pass
N Pentane	%mole		0.001	0.0002	0.0062	0.0062			0.000	0.0081			0.000	0.04	Pass
Nitrogen	%mole		0.092	0.0014	0.0219	0.0219			0.045	0.0258			0.048	1.40	Bias
GHV	MJ/m3		39.854	0.021	0.0790	0.0817	0.21		39.846	0.0947	0.24		0.008	0.06	Pass
GHV	MJ/kg		54.991	0.01200	0.0290	0.0314	0.06		55.039	0.0438	0.08		-0.048	0.89	Pass
LNG Dens	kg/m3		439.884			1.9795	0.45		439.531	1.9779	0.45		0.353	0.13	Pass

Cargo evaluation T26 b.

LNG Temp	117K		As Left T26 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo GIIGNL	Uxi	Rel unc. [%MV]		Mean	Uxi_Raman LNG val	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		92.823	0.011	0.1239	0.1244			92.908	0.1244			-0.084	0.48	Pass
Ethane	%mole		6.619	0.014	0.0636	0.0651			6.596	0.0972			0.022	0.19	Pass
Propane	%mole		0.311	0.0032	0.0297	0.0299			0.303	0.0391			0.008	0.16	Pass
I Butane	%mole		0.077	0.0004	0.0209	0.0209			0.074	0.0195			0.003	0.10	Pass
N Butane	%mole		0.076	0.0006	0.0209	0.0209			0.066	0.0196			0.009	0.33	Pass
I Pentane	%mole		0.002	0.0002	0.0079	0.0079			0.000	0.0178			0.002	0.08	Pass
N Pentane	%mole		0.001	0.0002	0.0062	0.0062			0.000	0.0082			0.000	0.04	Pass
Nitrogen	%mole		0.092	0.0014	0.0219	0.0219			0.045	0.0387			0.048	1.07	Bias
GHV	MJ/m3		39.854	0.021	0.0790	0.0817	0.21		39.846	0.0530	0.13		0.008	0.08	Pass
GHV	MJ/kg		54.991	0.01200	0.0290	0.0314	0.06		55.039	0.0400	0.07		-0.048	0.94	Pass
LNG Dens	kg/m3		439.884			1.9795	0.45		439.531	1.9779	0.45		0.353	0.13	Pass

Cargo evaluation T26 c.

LNG Temp	117K		As Left T26 GC_uT				GIIGNL		Raman Unc.		GIIGNL		GC_uT-Raman		
	EU		Mean	Uxi_PGRM	Uxi_GC/Vap Cargo Repeat	Uxi	Rel unc. [%MV]		Mean	Uxi	Rel unc. [%MV]		Diff	En	Evaluation
Methane	%mole		92.823	0.011	0.1147	0.1152			92.908	0.1244			-0.084	0.50	Pass
Ethane	%mole		6.619	0.014	0.1080	0.1090			6.596	0.0972			0.022	0.15	Pass
Propane	%mole		0.311	0.0032	0.0127	0.0131			0.303	0.0391			0.008	0.19	Pass
I Butane	%mole		0.077	0.0004	0.0040	0.0040			0.074	0.0195			0.003	0.14	Pass
N Butane	%mole		0.076	0.0006	0.0041	0.0042			0.066	0.0196			0.009	0.47	Pass
I Pentane	%mole		0.002	0.0002	0.0001	0.0002			0.000	0.0178			0.002	0.09	Pass
N Pentane	%mole		0.001	0.0002	0.0001	0.0002			0.000	0.0082			0.000	0.05	Pass
Nitrogen	%mole		0.092	0.0014	0.0037	0.0040			0.045	0.0387			0.048	1.22	Bias
GHV	MJ/m3		39.854	0.021	0.0380	0.0434	0.11		39.846	0.0530	0.13		0.008	0.12	Pass
GHV	MJ/kg		54.991	0.01200	0.0075	0.0142	0.03		55.039	0.0400	0.07		-0.048	1.13	Bias
LNG Dens	kg/m3		439.884			1.9795	0.45		439.531	1.9779	0.45		0.353	0.13	Pass

A.6.2. En results according ISO 17043

All cargoes a.

En Evaluation between Raman analyser and Fluxys LNG vaporizer/GC according ISO 17043												
Test Cargo nr.	Methane	Ethane	Propane	I Butane	N Butane	I Pentane	N Pentane	Nitrogen	GHV_vol	GHV_mass	LNG Dens	En Limit
	En	En	En	En	En	En	En	En	En	En	En	En
T15	0.3740	0.1054	0.2059	0.0788	0.3738	0.4561	0.0142	1.4167	0.1740	0.9567	0.1556	1.0000
T16	0.1118	0.3631	0.2160	0.1505	0.6273	0.3082	0.0930	0.8171	0.0182	0.4981	0.0374	1.0000
T17	0.0323	0.2505	0.0815	0.2138	0.7004	0.2962	0.0663	0.9802	0.0788	0.5668	0.0883	1.0000
T18	0.1670	0.0494	0.1455	0.0397	0.1963	0.1543	0.0248	1.2478	0.0372	0.7643	0.0717	1.0000
T19	0.1468	0.1113	0.0208	0.2253	0.7171	0.3132	0.0915	0.9667	0.1680	0.6579	0.1496	1.0000
T20	0.2087	0.0147	0.0207	0.2627	0.7364	0.3017	0.0778	0.7507	0.2561	0.5770	0.3737	1.0000
T21	0.1826	0.0866	0.0030	0.2676	0.7533	0.2832	0.0886	0.9418	0.2013	0.6735	0.1376	1.0000
T22	0.1381	0.0964	0.1532	0.0548	0.1108	0.0231	0.0243	0.3529	0.0790	0.2622	0.0622	1.0000
T23	0.1996	0.0396	0.0098	0.2801	0.6871	0.3958	0.0981	0.7860	0.2545	0.6608	0.1442	1.0000
T24	0.3296	0.4861	0.1155	0.1249	0.0249	0.0001	0.0199	0.6691	0.3777	0.3304	0.0942	1.0000
T25	0.3193	0.5177	0.3410	0.0040	0.5870	0.7616	0.0830	0.2411	0.0914	0.0790	0.0348	1.0000
T26	0.2721	0.0821	0.1576	0.0964	0.3263	0.0834	0.0375	1.4043	0.0646	0.8902	0.1262	1.0000

All cargoes b.

En Evaluation between Raman analyser and Fluxys LNG vaporizer/GC according ISO 17043												
Test Cargo nr.	Methane	Ethane	Propane	I Butane	N Butane	I Pentane	N Pentane	Nitrogen	GHV_vol	GHV_mass	LNG Dens	En Limit
	En	En	En	En	En	En	En	En	En	En	En	En
T15	0.5044	0.1696	0.2131	0.0791	0.3749	0.4534	0.0142	1.0530	0.1979	0.9843	0.1556	1.0000
T16	0.1693	0.5831	0.2603	0.1578	0.6470	0.3112	0.0931	0.6598	0.0224	0.5426	0.0374	1.0000
T17	0.0493	0.4071	0.0980	0.2248	0.7217	0.2913	0.0659	0.7795	0.0979	0.6130	0.0883	1.0000
T18	0.2207	0.0804	0.1475	0.0396	0.1959	0.1522	0.0248	0.9622	0.0415	0.7869	0.0717	1.0000
T19	0.2247	0.1839	0.0250	0.2343	0.7357	0.3134	0.0912	0.7693	0.2061	0.7139	0.1496	1.0000
T20	0.3135	0.0233	0.0248	0.2752	0.7544	0.2980	0.0778	0.6114	0.3118	0.6249	0.3737	1.0000
T21	0.2757	0.1390	0.0035	0.2808	0.7758	0.2827	0.0881	0.7635	0.2466	0.7322	0.1376	1.0000
T22	0.2282	0.2060	0.1529	0.0544	0.1109	0.0233	0.0238	0.3238	0.0944	0.2897	0.0622	1.0000
T23	0.3000	0.0639	0.0116	0.2928	0.7084	0.3904	0.0968	0.6321	0.3094	0.7157	0.1442	1.0000
T24	0.5288	1.0395	0.1152	0.1253	0.0244	0.0001	0.0198	0.5928	0.4583	0.3584	0.0942	1.0000
T25	0.6045	1.0462	0.4427	0.0041	0.6099	0.7595	0.0823	0.2405	0.1201	0.0958	0.0348	1.0000
T26	0.4786	0.1894	0.1604	0.0971	0.3280	0.0825	0.0373	1.0679	0.0830	0.9441	0.1262	1.0000

All cargoes c.

En Evaluation between Raman analyser and Fluxys LNG vaporizer/GC according ISO 17043												
Test Cargo nr.	Methane	Ethane	Propane	I Butane	N Butane	I Pentane	N Pentane	Nitrogen	GHV_vol	GHV_mass	LNG Dens	En Limit
	En	En	En	En	En	En	En	En	En	En	En	En
T15	0.6376	0.1791	0.2589	0.1116	0.5163	0.5417	0.0197	1.1721	0.3045	1.1542	0.1556	1.0000
T16	0.2132	0.6207	0.3404	0.2627	1.0454	0.3609	0.1314	0.7835	0.0367	0.6892	0.0374	1.0000
T17	0.0623	0.4352	0.1268	0.3760	1.1656	0.3362	0.0911	0.9169	0.1604	0.7741	0.0883	1.0000
T18	0.2767	0.0811	0.1775	0.0526	0.2575	0.1740	0.0353	1.1200	0.0626	0.9736	0.0717	1.0000
T19	0.2692	0.1858	0.0314	0.3774	1.1682	0.3626	0.1281	0.8987	0.3123	0.9035	0.1496	1.0000
T20	0.3745	0.0244	0.0302	0.4220	1.1255	0.3456	0.1094	0.7249	0.4656	0.7982	0.3737	1.0000
T21	0.2650	0.1179	0.0039	0.4263	1.1688	0.3252	0.1224	0.8941	0.3165	0.8958	0.1376	1.0000
T22	0.3142	0.2286	0.1772	0.0676	0.1372	0.0248	0.0260	0.4341	0.1517	0.4253	0.0622	1.0000
T23	0.3882	0.0694	0.0152	0.4817	1.1387	0.4585	0.1379	0.7476	0.5099	0.9247	0.1442	1.0000
T24	0.7506	1.2017	0.1326	0.1264	0.0258	0.0001	0.0208	0.7298	0.7511	0.4838	0.0942	1.0000
T25	0.5871	0.8639	0.5274	0.0061	0.9701	0.9535	0.1170	0.2971	0.1543	0.1295	0.0348	1.0000
T26	0.4966	0.1517	0.1914	0.1394	0.4689	0.0904	0.0470	1.2205	0.1180	1.1313	0.1262	1.0000

A.6.3. Precision results

Raman repeatability over cargoes under test													
Test Cargo nr.	Instrument	Raman Methane %mole	Raman Ethane %mole	Raman Propane %mole	Raman I_Butane %mole	Raman N_Butane %mole	Raman I_Pentane %mole	Raman N_Pentane %mole	Raman Nitrogen %mole	Raman GHV_vol MJ/m3	Raman GHV_v %MV	Raman GHV_mass MJ/kg	Raman GHV_m %MV
T15	Raman	0.019	0.014	0.004	0.002	0.001	0.000	0.002	0.007	0.008	0.019	0.006	0.011
T16	Raman	0.040	0.030	0.007	0.003	0.002	0.000	0.002	0.007	0.016	0.039	0.007	0.013
T17	Raman	0.040	0.028	0.010	0.003	0.003	0.000	0.002	0.007	0.017	0.043	0.008	0.015
T18	Raman	0.056	0.046	0.008	0.003	0.003	0.000	0.002	0.008	0.023	0.059	0.007	0.013
T19	Raman	0.045	0.033	0.009	0.003	0.002	0.000	0.002	0.014	0.019	0.047	0.012	0.023
T20	Raman	0.047	0.032	0.009	0.003	0.003	0.000	0.002	0.008	0.019	0.047	0.009	0.016
T21	Raman	0.028	0.018	0.005	0.002	0.002	0.000	0.002	0.008	0.009	0.024	0.008	0.015
T22	Raman	0.048	0.036	0.011	0.003	0.002	0.000	0.001	0.011	0.017	0.043	0.011	0.019
T23	Raman	0.039	0.029	0.008	0.003	0.003	0.000	0.002	0.012	0.019	0.049	0.010	0.018
T24	Raman	0.045	0.039	0.002	0.002	0.000	0.000	0.001	0.018	0.013	0.032	0.017	0.030
T25	Raman	0.069	0.051	0.011	0.002	0.003	0.000	0.002	0.023	0.024	0.061	0.022	0.040
T26	Raman	0.092	0.090	0.011	0.003	0.003	0.000	0.001	0.008	0.029	0.074	0.009	0.017
Total	Rep_Raman (k=2)	**0.051**	**0.042**	**0.009**	**0.003**	**0.003**	**0.000**	**0.002**	**0.011**	**0.019**	**0.048**	**0.011**	**0.020**
	Pooled St Dev Raman	**0.025**	**0.021**	**0.004**	**0.001**	**0.001**	**0.000**	**0.001**	**0.006**	**0.010**	**0.024**	**0.005**	**0.010**
GIIGNL Performance limits	Precision [U] (K=2)	0.113	0.050	0.035	0.027	0.025	0.012	0.010	0.025		**0.2**		**0.07**
ASTM D7940-14 Performance limits	Mean all Cargoes	**94.491**	**3.796**	**0.931**	**0.297**	**0.246**	**0.011**	**0.007**	**0.22**	**39.699**		**55.089**	
	St Dev Limit [u]	0.03	0.03	0.03	0.01	0.01	0.006	0.006	0.01				
	Precision [U] (K=2)	**0.060**	**0.060**	**0.060**	**0.020**	**0.020**	**0.012**	**0.012**	**0.020**		**0.05**		

GC repeatability over cargoes under test													
Test Cargo nr.	Instrument	GC Methane %mole	GC Ethane %mole	GC Propane %mole	GC I_Butane %mole	GC N_Butane %mole	GC I_Pentane %mole	GC N_Pentane %mole	GC Nitrogen %mole	GC GHV_vol MJ/m3	GC GHV_v %MV	GC GHV_mass MJ/kg	GC GHV_m %MV
T15	GC/Vaporizer	0.0506	0.0371	0.0087	0.0034	0.0034	0.0007	0.0004	0.0030	0.0210	0.0530	0.0050	0.0110
T16	GC/Vaporizer	0.0476	0.0329	0.0111	0.0044	0.0047	0.0002	0.0002	0.0039	0.0200	0.0510	0.0057	0.0100
T17	GC/Vaporizer	0.0466	0.0315	0.0126	0.0043	0.0047	0.0002	0.0002	0.0035	0.0200	0.0500	0.0055	0.0100
T18	GC/Vaporizer	0.0697	0.0566	0.0093	0.0032	0.0033	0.0003	0.0002	0.0048	0.0270	0.0680	0.0060	0.0110
T19	GC/Vaporizer	0.0669	0.0484	0.0156	0.0056	0.0057	0.0002	0.0002	0.0066	0.0310	0.0790	0.0050	0.0100
T20	GC/Vaporizer	0.0690	0.0394	0.0208	0.0093	0.0102	0.0004	0.0002	0.0063	0.0360	0.0900	0.0087	0.0160
T21	GC/Vaporizer	0.1234	0.0862	0.0272	0.0098	0.0095	0.0003	0.0002	0.0077	0.0520	0.1300	0.0122	0.0220
T22	GC/Vaporizer	0.0536	0.0470	0.0116	0.0023	0.0026	0.0001	0.0002	0.0078	0.0220	0.0550	0.0069	0.0130
T23	GC/Vaporizer	0.0389	0.0262	0.0101	0.0042	0.0045	0.0003	0.0002	0.0057	0.0190	0.0480	0.0059	0.0100
T24	GC/Vaporizer	0.0513	0.0398	0.0006	0.0000	0.0001	0.0000	0.0000	0.0185	0.0150	0.0380	0.0180	0.0320
T25	GC/Vaporizer	0.1223	0.0965	0.0256	0.0029	0.0075	0.0005	0.0001	0.0132	0.0510	0.1280	0.0110	0.0200
T26	GC/Vaporizer	0.1147	0.1080	0.0127	0.0040	0.0041	0.0001	0.0001	0.0037	0.0380	0.0950	0.0075	0.0140
Total	Rep_GC (k=2)	**0.072**	**0.056**	**0.014**	**0.005**	**0.005**	**0.0003**	**0.0002**	**0.008**	**0.029**	**0.074**	**0.009**	**0.016**
	Pooled St Dev GC	**0.036**	**0.028**	**0.007**	**0.003**	**0.003**	**0.0001**	**0.0001**	**0.004**	**0.015**	**0.037**	**0.004**	**0.008**
GIIGNL Performance limits	Precision [U] (K=2)	0.113	0.050	0.035	0.027	0.025	0.012	0.010	0.025		**0.2**		**0.07**

APPENDIX 7. RAMAN VERFICATION AND MAINTENANCE

Calibration, Verification and Testing

Currently ASTM D7940-14 is the only standard covering LNG analysis using Raman spectroscopy and as such will be used by 3rd party surveyor companies to validate the performance in case no further agreements exist between parties on LNG custody transfer.

Based on learnings from the GERG validation work, an enhanced testing plan is recommended for each deployment in Shell LNG bunkering custody transfer applications and is described below.

The main differences with the standard manufacturers test plan are the inclusions of reference LNG verification to verify the application parameters and temperature compensation model are included correctly and white light calibration at factory acceptance testing.

In House Testing (IHT)

The In-House Testing consists of the vendor's standard internal quality assurance, inspection, set-up and functional testing activities. These tests involve the vendor only and test results shall be documented and included in the vendor's documentation package. The In House Testing is typically not witnessed by the owner or a 3rd party.

Factory Acceptance Testing

The FAT should consist of the following items and should be witnessed by the owner and/or a 3rd party surveyor assigned by the owner:

- Vendor's standard FAT activities
- Reference LNG verification: This is a verification of the analyser electronics unit to assess the temperature compensation and measurement application performance against a certified reference LNG mixture. The test shall be executed in a cryostat at an accredited laboratory. Verification against a single LNG mixture is enough, but the verification should cover the range of LNG temperatures from 93-117K.
  Currently Effectech in the UK is the only accredited facility, but it is feasible to schedule cryostat verification together with the other factory acceptance tests. This is an analyser application verification only and any probe and fibre cable can be used.
- White light calibration: White light calibration is described in ASTM D7940 and involves using a NIST traceable white light source to calibrate the wavelength response of the complete assembly (probe, fibre cable and analyser). This must be performed with the analyser, probe and cable used for the measurement to disconnect installation and fabrication effects from the measurement performance.

Commissioning & Site Acceptance Testing (SAT) at final location

Shipyard commissioning and site testing activities should consist of the following items and should be witnessed by the owner and a 3rd party surveyor:

- Vendor's standard installation checks and tests.
- Integrated testing between the analyser and other systems such as the CTMS to test and confirm the communications setup and configuration. This test should be performed with representatives from each system vendor and the engineering integrator present.
- White light calibration should be performed again on board the vessel and, as per ASTM D7940, is ideally done as part of the final functional check during gas trials or first operation to minimise the possibility for alteration prior to introduction of LNG shortly after. The probe will be removed from the line and this test should be done before first loading. ***Once completed the FO shall remain connected, removal of the fibre optic connections will void the calibration.***
- Wavelength and Intensity check results shall be verified. Both checks shall be performed automatically at set intervals and results shall indicate PASS. To ensure internal optical alignment is unchanged and within the instrument's performance limits.
- A surrogate fluid test using a small fluid sample with similar spectra to LNG, usually cyclohexane, which can be used to generate analyser readings and test the communication interfaces.

Commissioning & SAT at Gas Trials or 1st Operation

Shipyard commissioning and site testing activities should consist of the following items and should be witnessed by the owner and a 3rd party surveyor. Tests should be completed in the order listed here.

- Wavelength and Intensity check results shall be verified. Both checks are performed automatically by the instrument at set intervals to ensure internal optical alignment is unchanged and within the instrument's performance limits and results shall indicate PASS.
- White light calibration should be performed on board the vessel and, as per ASTM D7940, is ideally done as part of the final functional check during gas trials or first operation to minimise the possibility for alteration prior to introduction of LNG shortly after. The probe will be removed from the line and this test should be done before first loading.
  Once completed the FO shall remain connected, removal of the fibre optic connections will void the calibration.
- A surrogate fluid test should then be performed while the probe is still removed to verify the analyser response. The probe can be reinserted into the pipe on completion of this test.
- The final step is to review LNG composition measurements and CTMS and BDN interfaces during first operation. Raman analyser measurements can be compared against loading terminal composition measurements.

In Service Verification, Maintenance & Calibration

At present the following activities are recommended after the bunker vessel enters service:

- Wavelength and Intensity check results shall be verified during each vessel loading at the loading terminal. Both checks are performed automatically by the instrument at set intervals to ensure internal optical alignment is unchanged and within the instrument's performance limits and results shall indicate PASS.
- Review LNG loading composition measurements and CTMS and BDN interfaces Raman analyser measurements results can be compared against loading terminal composition measurements. ***It is recommended to track the deviation between the Raman and the load port results for each component in a control chart as a performance record.***
- A surrogate fluid test is recommended every 2 years to verify the analyser. Note that this requires the probe to be removed from the pipe.
- Planned maintenance can be scheduled during vessel dockings (every 4 years). This is to include replacement of the analyser laser board and neon board and electronics overhaul.
- White lite calibration and Reference LNG verification should be performed after planned maintenance. This is a verification of the analyser electronics unit to assess the temperature compensation and measurement application performance against a certified reference LNG mixture. The test shall be executed in a cryostat at an accredited laboratory. Verification against a single LNG mixture is enough, but the verification should cover the range of LNG temperatures from 93-120K.

References

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5. **ISO 17043:2010** – Conformity assessment – General requirements for proficiency testing
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Bibliographic information

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