## Validation of Spectroscopic Instruments for the Direct Measurement of Multi-Component Cryogenic Liquid Hydrocarbons

by

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**Doctoral Thesis** 

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#### Abstract

Opportunities exist for completely revising the way liquefied natural gas (LNG) is measured with the aim of achieving a meaningful reduction in uncertainty to below 1%, thereby providing confidence to both parties involved in custody transfer agreements. In addition, much attention has been directed toward improving the efficiency of LNG production processes by putting in place advanced control and monitoring technology. The demand for shifting to direct measurement technology stems from the inherent problems associated with sampling and vaporisation of LNG and measurement response time for mixed-refrigerant (MR) compositions. To this point, there has been no successfully developed system that allows direct measuring instruments to be validated. For the first time, the research set out in this thesis systematically evaluates the application of Raman and Infrared spectroscopy for directly measuring LNG and MR composition using a bespoke cryostat liquefier. The Raman spectrometer investigated showed acceptable performance for measuring a range of MR compositions, which was determined by comparing the differences in calculated heat capacity between the measured and reference liquid compositions. Validating the Raman spectrometer for LNG measurement was not possible due to the unavailability of the model for testing. However, an intermediate evaluation of a non-refined model showed that the Raman spectrometer was not fit for purpose for custody transfer applications. Moreover, valuable information was gained pertaining to the behaviour of multi-component mixtures at cryogenic conditions and instrument linearity, repeatability and sensitivity. In contrast, The IR spectrometer evaluated showed acceptable performance for a narrow range of compositions as indicated by an ISO 10723 evaluation, however did not meet current custody transfer benchmarks when tested over the full composition range. The data collected will contribute heavily to further developing the model and to extend its current measurement range. A rigorous testing method has been established to validate direct measuring instruments which have the capacity to considerably reduce the uncertainty in LNG composition measurement and improve the thermodynamic efficiency of LNG production processes.

#### **Publications**

#### **Proposed Journal Publications**

Walker, J.; Holland, P.; Buckley, B.; Wijayantha, U. (2017), A Monte-Carlo approach for optimizing liquefied natural gas sampling systems to prevent sample fractionation.

#### **Conference Proceedings**

Walker, J.; Holland, P.; Buckley, B.; Wijayantha, U. (2015) Advanced techniques for reducing liquefied natural gas measurement uncertainty, Midlands Energy Consortium (MEC) student conference, November 2015, Loughborough, UK.

Walker, J.; Holland, P.; Buckley, B.; Wijayantha, U. (2016), Validation of Raman spectroscopy for direct measurements of liquefied natural gas composition, *18<sup>th</sup> International conference and exhibition on liquified natural gas*, April 2016, Perth, Australia. [RSC travel bursary]

Walker, J.; Holland, P.; Buckley, B.; Wijayantha, U. (2016) The effects of composition on sub-cooling calculations used in liquefied natural gas sampling procedures, *18<sup>th</sup> International conference and exhibition on liquified natural gas*, April 2016, Perth, Australia. [RSC travel bursary]

Walker, J.; Holland, P.; Buckley, B.; Wijayantha, U. (2017), LNG Sampling and Methods for Improving Measurement Uncertainty, *Gas Analysis International Symposium*, June 2017, Rotterdam, Netherlands.

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## Symbols

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- $y_k$  amount-of-substance fraction of component i in the prepared mixture
- $M_k$  molar mass of component k
- *y<sub>i</sub>* amount-of-substance fraction i in prepared mixture
- *M<sub>i</sub>* molar mass of component i
- $m_i$  mass added of parent gas or liquid
- $m_{\Omega}$  molar mass of final mixture
- $p_{F,\Omega}$  filling pressure of final mixture
- *V<sub>cyl</sub>* volume of cylinder
- $Z_{\Omega}$  compressibility of final mixture
- R ideal gas constant
- $T_F$  filling temperature

 $x_{i,j}$  amount of substance fraction of component I in the parent gas or liquid

- c speed of light
- h Planck's constant
- IL laser intensity
- N number of scattering molecules
- v molecular vibrational frequency in Hz
- $v_L$  laser excitation frequency, in Hz
- $\mu$  reduced mass of the vibrating atoms
- k Boltzmann's constant
- T absolute temperature
- $\alpha_{a}$ ' mean value invariant of the polarizability tensor
- $\gamma_a$  anisotropy invariant of the polarizability tensor

### 1 Introduction

In response to the ever-increasing global demand for energy and irreversible changes to the climate system resulting from anthropogenic activities, the energy mix is constantly evolving politically, economically, technologically and socially. (1; 2) Natural gas has benefited greatly from the policy reforms of the energy system because of its environmental impact in replacing conventional energy producing technologies such as coal and crude oil. Natural gas use is projected to overtake coal by 2030 (figure 1.1-1) as the ageing fleet of coal-fired power plants are retrofitted for natural gas or decommissioned due to their age. (3)



Figure 1.1-1 – Actual and projected global energy use from Liquid fuels, Coal, Natural gas, Nuclear and Renewables between 1990 and 2040. Graph reconstructed from data in (3)

Currently, natural gas accounts for approximately 25% of the total energy generation mix, with coal and oil contributing around 28% and 33%, respectively. The remaining generation capacity comes from hydro, nuclear and renewable technologies. Approximately one third of natural gas reserves remain stranded and unexploited due to the lack of adequate technology. (4) The drivers for such technological progress are based on several factors, namely: an increasing energy demand, decreasing oil resources, increasing oil price, policies that favour lower green-house-gas (GHG) emitting fuels and a stop to gas-flaring regulations. Market competition is also a fundamental factor at play. More competition resulting from an increase in the number of exporters in multiple regions has allowed importing countries to maintain security of supply whilst reducing harmful emissions to the atmosphere.

On burning natural gas, the relative reduction in amounts of emissions produced per unit energy compared with coal and oil are approximately 40% and 77%, respectively. (3) New and efficient natural gas power plants emit 50% to 60% less  $CO_2$  emissions than coal. (5) In addition, fewer toxic species including sulphur oxides ( $SO_x$ )- a precursor to acid rain, nitrogen oxides ( $NO_x$ )-a precursor of smog, mercury and particulate matter are formed compared with the coal and oil-derived combustion. Therefore, natural gas is a more efficient fuel for combustion. However, assessing the overall efficiency of the natural gas supply chain from extraction to use remains a challenging topic because of the potential benefit-cancelling effects of methane leakage during extraction and transportation. Methane has a 28 times higher global warming potential (GWP) than  $CO_2$  over a 100-year period and a GWP increasing to 86 over a 20-year period. (6; 7) Estimates of methane leakage range from 1% to over 10% of total produced gas, and this range of

uncertainty makes it difficult for policy makers to make clear decisions on promoting natural gas over other fossil fuels. (8; 9; 10; 11)

There are six methods of transporting natural gas from remote locations to the global natural gas market and these include: pipeline, LNG, gas-to-liquids (GTL), gas-to-wire (GTW) HVDC, compressed natural gas (CNG) and gas-tosolids (GTS). (4) Of these, only pipeline, LNG and GTL are commercially developed and mature technologies, though there is a requirement for more research and development in the area of GTL. GTW and CNG and GTS methods are still in development with few projects sanctioned. The choice between each of the transportation technologies is dominated by the distance of gas production source to the gas market and production rates of the gas fields. Pipeline and LNG are the dominant choices for natural gas transportation since they are designed for large gas production fields. However, LNG becomes more competitive than pipeline when the distance from gas source to consumer is larger than 700km and 2000km for onshore and offshore, respectively. Long distance transport via pipeline requires costintensive equipment such as recompression facilities and large diameter pipelines. Nonetheless, pipeline still dominates the transport of natural gas from source to market with around 70% of stranded gas being transported via pipeline and 30% being transported via LNG.

Over the past two decades, LNG has gained much attention in the global natural gas market because of its evolution, flexibility and diversification. The move toward LNG is a direct result of: higher pressures felt by governments to meet the ever-increasing energy demand, geopolitical instability-particularly in the Middle East and Russia-, higher natural gas prices and the rise in import capacity from countries such as China and India who want to transition from climate-burdening technologies. Asia continues to dominate the LNG import market with over two thirds of total demand supplied to the region. (12) However, the European market continues to flourish in developing import capacity and could become a central hub for the LNG market in the future. On the other hand, future LNG forecasts are difficult to predict because of price volatility, competition with emerging technologies, large capital investments and slumps in demand due to economic recessions. Nonetheless, economies of scale have allowed the expansion of export and import capacities and new developments in LNG technology such as floating LNG (FLNG) to flourish and dominate in niche markets that need to be filled.

#### 1.1 Liquefied Natural Gas (LNG)

LNG has been the fastest growing energy source over the past 20 years with international trade increasing 6-fold from 50 mt (million tonnes) in 1990 to 290 mt in 2017. (13) LNG is a condensed form of natural gas that has been cooled to approximately 110K (-163.15°C). The process of cooling natural gas reduces its volume 600-fold making it more economically feasible to transport over longer distances and to remote locations compared with conventional natural gas transportation via pipeline. Processed LNG is predominantly 87% to 99% methane with small amounts of propane, butanes, pentanes and nitrogen. The proportion of the minor components vary with the location of extraction. Typical amount fraction ranges for each component are shown in table 1.1-1.

component	Amount fraction (%mol/mol)				
	min max				
nitrogen	0.10	1.56			
methane	79.86	99.30			
ethane	0.10	13.77			
propane	0.10	3.92			
iso-butane	0.08	1.29			
n-butane	0.08	1.05			
iso- pentane	0.03	0.15			
n-pentane	0.02	0.16			

Table 1.1-1 – Typical amount fraction ranges for LNG components (14)

### 1.1.1 LNG supply chain

The LNG supply chain is both complex and constantly evolving in response to market conditions and to meet the needs of consumers. A typical supply chain is shown in figure 1.1-2 with four key sections: (1) extraction, (2) production, (3) transportation and (4) distribution and use. First, the gas is extracted from either onshore or offshore production sites and is directed to a LNG production facility where impurities are removed and the gas is liquefied. The liquefied gas is then loaded onto large cargo tankers, followed by transportation to a regasification facility where the liquid is transformed into its gaseous state ready for distribution and use.



Figure 1.1-2- LNG supply chain

#### 1.1.2 Extraction

Extensive planning is required for the selection of gas extraction zones because it is an expensive and timely process. Decisions on drilling are based on several factors including: economic potential, risk mitigation and legal permits. There are a variety of subsurface extraction sources that can be split into two categories: conventional and unconventional. Conventional sources of natural gas may be associated with oil wells or non-associated. Unconventional sources are associated with geological formations and include: coalbed methane, tight gas sands, shale gas and gas-rich shale. Shale gas is the fasting growing natural gas source, a direct result from new developments in horizontal drilling and hydraulic fracturing allowing for previously unexploitable sources to be developed. Currently, China, Argentina, Algeria and the US are predicted to have the highest recoverable reserves at 1,115 trillion cubic feet (tcf), 802 tcf, 707 tcf and 665 tcf,

respectively. (15; 16) Once extracted, the gas is directed to the appropriate production facilities ready for processing and liquefaction.

#### **1.1.3 Production**

The production of LNG is governed by strict regulations to meet quality arrangements that aim to ensure the distributed gas is interchangeable with respect to its end use. Natural gas end uses include: appliances, gas combustion turbines, natural gas vehicle engines and non-combustion related uses such as chemical precursor manufacturing. Gas interchangeability is defined here as the ability to substitute one gaseous fuel source for another without compromising combustion performance. (17) The composition of LNG varies from the source of its extraction, resulting in differences in gas quality. The use of natural gas outside the working specification of combustion equipment can result in undesirable combustion characteristics including: unburnt hydrocarbons, an increase in emissions (SO<sub>x</sub>, NO<sub>x</sub> and CO) and a reduction in combustion efficiency. (18; 19)

Interchangeability factors include: Wobbe Index (WI)- the rate of combustion, Lift Index (LI)- flame stability, Incomplete Combustion Factor (ICF) and Soot Index (SI). Of these, the WI is the most accepted parameter worldwide, however the UK incorporates a combination of LI, SI and ICF since it provides a better understanding of combustion performance. (20) The WI is calculated by dividing the gross calorific value (GCV) of the gas with the root square of its relative density, and is related to the thermal heat rate (BTU/hour) input to the combustion equipment.

In addition to maintaining interchangeability, the distributed gas must be nontoxic, non-corrosive and have minimal potential for hydrate formation. Raw feed gas contains impurities including: hydrogen sulphide (H<sub>2</sub>S), mercaptans

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(total sulphur), CO<sub>2</sub>, mercury (Hg) and moisture (H<sub>2</sub>O) that must be removed to meet specification prior to liquefaction. Typical specification limits for H<sub>2</sub>S, CO<sub>2</sub>, Hg and H<sub>2</sub>O are less than 10-30ppmv, 2-4ppmv, 50ppmv, 0.01ppmv and 0.1ppmv, respectively. (4) Following this, the resulting dry gas is sent to a natural gas liquids (NGL) recovery unit whereby gas fractionation produces liquid petroleum gases (LPG) with high quantities of propane and butane, and other valuable products including pentanes (used in gasoline blending) and sometimes ethane. The relative proportions of these recovered products are based solely on market conditions and differences in profitability compared with LNG. A summary of the feed gas conditioning is shown in figure 1.1-3. Finally, the resultant lean gas is directed to a liquefaction unit.



Figure 1.1-3 – Feed gas conditioning process for LNG production

The liquefaction of natural gas is a complex process requiring precise modelling and engineering design. Refrigeration cycles are used to cool the gas over successive compression and expansion stages. Figure 1.1-4 illustrates the general process of a refrigeration cycle. The working fluid is usually a mixture of hydrocarbons and nitrogen and is referred to here as a mixed refrigerant (MR). The choice of MR is dependent upon the process design and gas inlet composition. The most common process designs include: Propane mixed-refrigerant process (AP-C3MR) (21; 22), duel mixed-refrigerant process (DMR) (23), mixed fluid cascade process (MFC) (24) and the AP-X process which is based on the AP-C3MR process for larger production capacities (22). These refrigeration processes differ in their use of MR composition, compression and expansion cycles, and liquefaction capacity.



Figure 1.1-4 – General LNG refrigeration process with cascade compression and expansion cycles.

The MR acts as a heat sink and removes heat from a flow of gas through a main cryogenic heat exchanger (MCHE). Prior to this, the feed gas may be pre-cooled before entering the MCHE for overall efficiency improvements. After the MR performs work on the flowing gas, it undergoes a series of compression and expansion cycles and is recycled back into the process. The efficiency of the refrigeration process is dependent upon the hot and cold

stream profiles and compressor efficiency. Highly efficient refrigeration processes have low cumulative duty between the hot and cold streams, meaning that the evaporation and condensation profiles of both the stream gas and MR are closely matching such that the energy duty between them is minimal, therefore thermal efficiency is maximised.

#### 1.1.3.1MR control and monitoring

The heat capacity of MRs is determined by the proportion of each component in the matrix since each component, for example methane, ethane and propane, has a different heat capacity. MR compositions are fine-tuned to the design of a refrigeration process such that the evaporation curve of the MR matches the cooling curve of the feed gas, ultimately leading to a higher thermodynamic efficiency. However, the MR composition may change because of a system fault, therefore the thermodynamic efficiency would be compromised. In response to mitigating such consequences, the application of an in-line direct measuring instrument could provide a level of control. Currently, the only way of measuring MR composition is by withdrawing a sample and vaporising it so that it can be measured at room temperature with a gas chromatograph. This takes on the order of several minutes. Conversely, an in-line spectroscopic instrument can make measurements on the order of seconds, a clear advantage for process operators requiring rapid response to changes in MR composition.

#### **1.1.4 Transportation**

When processed, LNG may be loaded onto trucks via a trucking bay for land transport or onto large cargo carriers via the use of a jetty for sea transport. For land transport, the use of small-scale trucks allows for additional flexibility in the distribution of gas onshore where transportation via pipeline is not viable, for example to industrial plants. For sea transport, long jetty arms are used to transfer LNG from the storage tanks to the carrier. The jetty arms are pre-cooled prior and during LNG loading to reduce boil-of-gas (BOG), which offsets heavy demurrage fees for longer docking times. Generally, loading at extended distances from the LNG storage site, for example where shallow waters prevent carriers from docking, incurs higher costs due to higher quantities of BOG generated, since the LNG travels longer distances. This BOG is recycled and cooled back to LNG temperatures, therefore requiring an extra energy input.

A cargo transporting LNG over long distances experiences a change in composition due to natural environmental heat influxes resulting from an imperfect insulation system. This process is known as 'ageing'. Heat from the environment will penetrate the storage tanks and cause the LNG inside the tank to boil. The components with the lowest boiling points evaporate preferentially resulting in a BOG rich in nitrogen and methane. The BOG is either recycled back into the liquid phase or used as a co-fuel to drive engine propulsion. BOG presents an issue for both parties involved in the fiscal transaction of LNG, since the composition of the cargo changes over the course of transport. The fiscal calculation of LNG is based on its energy value, namely a combination of GCV, density and volume. (14) Calculations of GCV and density are based on the average composition of LNG. Since the composition of the LNG changes during transportation, so does its physical properties. Hence, fair fiscal transactions are heavily dependent upon the accuracy of the measurement systems in place. An overview of the measurement infrastructure for LNG is explored in section 1.2.

The average volume of LNG carriers range from 170,000m<sup>3</sup> to 180,000m<sup>3</sup> with new designs such as the Q-Max reaching volumes of 266,000m<sup>3</sup>. (25; 4; 26)

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There are two main containment types: single-wall spheres (Moss spheres) and dual-wall membranes contributing to 40% and 50% to the total LNG fleet, respectively. (27) Both designs differ in the materials used for construction and mitigation design for structural integrity. The choice of size and type depends on the transport distance, export and import capacity, market conditions, availability and cost.

The cost of a typical LNG cargo can fluctuate depending on its sport price which can be as high as \$20 MMBTU and as low as \$2 MMBTU. This fluctuation is largely due to the link with oil prices and other volatile markets, though a large de-coupling is expected with the onset of short-term contracts and increased market competition. (28) Assuming a LNG cargo volume of 150,000 m3, the total price of an LNG cargo is approximately \$6.6 million and \$66 million for the upper and lower sport prices, respectively. Therefore, the cost of making incorrect measurements is amplified by the spot price and volume of each LNG cargo.

#### 1.1.5 Distribution and use

Once the LNG is transferred from the cargo carrier to the import facilities, it is either stored as LNG or undergoes gasification in preparation for its distribution. Before distribution, the gas must meet usability specifications in that region as described in section 1.2. If the gas is out of specification, it is often blended with other components to alter its physical properties to match the specification criteria. For example, in the UK where the WI specification is set between 47.2 MJ/Sm3 and 51.4 MJ/Sm3 with an ICF of <= 0.48, any imported gas that does not meet this specification- which is usually the case-is subject to nitrogen ballasting or a potential pipeline mixing method. (29) Nitrogen ballasting is the direct injection of nitrogen gas into the imported gas matrix resulting in lower GCV, ICF, and WI. Pipeline mixing is a more complex

process whereby imported gas is mixed with existing pipeline gas. This method is not currently used due to the required infrastructure and feasibility studies.

The BOG generated during transportation directly impacts the GCV, WI and ICF. There is a linear relationship between the nitrogen amount fraction and each physical property as demonstrated in figure 1.1-5. In figure 1.1-5, the ICF, WI and GCV are calculated from a typical LNG composition (table 1.1-2) with varying methane and nitrogen amount fractions. The ICF is more sensitive to changes in nitrogen amount fraction than both the WI and GCV as indicated by a steeper gradient. In this example case, to comply with UK import specifications, the nitrogen addition must be greater than 5%. Here, the importance of accurate measurements is partly revealed. Accurate determination of LNG composition is a prerequisite for identifying required adjustments to meet specifications. For this reason, there is a requirement for measurements during both the loading and offloading procedures to account for changes in composition, only then can contractual agreements between both parties be agreed upon.



Figure 1.1-5 – Effect of increasing nitrogen amount fraction on the WI, ICF and GCV.

	Amount fraction (%mol/mol)									
	Amount fraction (%moi/moi)									
	Mix1	Mix2	Mix3	Mix4	Mix5	Mix6	Mix7	Mix8	Mix9	Mix1
										0
nitroge n	0.50	1.00	1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00
methan	87.5	87.0	86.5	86.0	85.5	85.0	84.5	84.0	83.5	83.0
е	0	0	0	0	0	0	0	0	0	0
ethane	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
propane	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
i-butane	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
n-	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
butane										
i-	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
pentane										
n-	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
pentane										
ICF	2.28	2.09	1.90	1.71	1.52	1.33	1.14	0.95	0.76	0.58
WI	53.9	53.6	53.3	52.9	52.6	52.3	52.0	51.7	51.4	51.1
(MJ/Sm <sup>3</sup>	3	1	0	9	8	7	6	5	4	4
)										
GCV	44.1	43.9	43.7	43.5	43.3	43.1	42.9	42.7	42.6	42.4
(MJ/m³)	1	2	3	4	5	6	7	9	0	1

Table 1.1-2- LNG-type mixtures used to assess impact of nitrogen amountfraction on WI, ICF and GCV.

Another way of predicting changes in composition is to model the heat characteristics of the system to approximate vapor quality over the course of transport. However, there have been many attempts to model and predict the 'ageing' of LNG and the fact that LNG composition varies significantly from its origin, they are not always accurate. In addition to this, the underlying mechanisms of the "ageing" process are still not fully understood. More accurate models would give the operators knowledge of the cargo quality before it is unloaded thus giving them time to act on changes, if required, to comply with quality specifications.

In addition to meeting interchangeability specifications, high accuracy quality measurements are required to avoid disputes by minimising discrepancies in fiscal transactions. Currently, the only established method of obtaining such quality measurements is by using a gas chromatograph in conjunction with sampling and vaporisation system. Such a system has manifested a great deal of uncertainty due to many stages requires in combination with the issues relating to fractionation of LNG in the sampling line resulting from imperfect insulation. These issues are explored in section 1.6.3. The following section provides a complete overview of the LNG measurement infrastructure with the aim of detecting areas requiring improvement.

#### **1.2 LNG measurement Infrastructure**

The measurement of LNG is a complex process because it is a cryogenic liquid that requires both dynamic and static measurements. Measurements of volume and composition are required to determine the total energy value of the cargo. Composition measurements are a prerequisite for calculations of GCV and density. Level and pressure gauges, temperature sensors and

correction tables are used to determine total transferred volume. By combining GCV, density and volume, the total fiscal value of the LNG cargo may be deduced. A schematic representation of the LNG measurement infrastructure is illustrated in figure 1.2-1.



Figure 1.2-1 – Schematic representation of the LNG measurement infrastructure. Image based on information in (14).

The execution, accuracy and traceability of these dynamic and static measurements present a major challenge to the metrology community because of the non-standard design of infrastructure, irregular process conditions and contractual differences between each LNG transaction. The lack of international standards for custody transfer imparts a great deal of risk for the whole LNG supply chain. There are currently no international standards governing the LNG measurement process, only guidelines and recommendations through sources such as the GIIGNL. (14)

Due to the complexity of the measurement processes, the uncertainty contribution is large in comparison with other fuel measurements such as pipeline gas and oil. The uncertainty for LNG measurement has been reported as 0.78% (14); however, this is an optimistic estimation and other sources have produced realistic uncertainty budgets with an uncertainty of 1% or higher. (30; 31; 32; 33) In comparison, the typical measurement uncertainty for pipeline gas and oil is <0.8% (34; 35) and <0.25% (36), respectively.

In response to the need to reduce total LNG energy transfer uncertainty, several research programmes have initiated the transformation of metrology and infrastructure through the development of new standards and methods. The European Metrology Research Programme (EMRP) – a program of the European Association of National Metrology Institutes (EURAMET) – is the leading project organiser for these research programmes. The following section provides an overview of the aims and objections of the EMRP for LNG.

# 1.3 The European Metrology Research Programme (EMRP)

The EMRP is a consortium of NMIs that work in conjunction to deliver a specific set of deliverables that aim to bring around a reduction in overall LNG energy transfer uncertainty by one half, effectively from 1% to 0.5%. (37; 38) A reduction in uncertainty leads to several key benefits. In the social domain, the clear benefits are: more transparent trading, better functioning markets and a more stable spot price. Environmentally, the key benefit is the movement

towards using a cleaner and more sustainable fuel that promotes the policy of reduced CO2 emissions. Economically, reducing the current measurement uncertainty by half translates to a risk reduction of 150 M€/year for LNG traded in Europe and 500 M€/year for global LNG trade.

Fundamentally, the lack of traceability to the SI delays the deployment of new measurement techniques that are crucial for growth of the LNG market. The development of a sound metrological framework is the overarching aim of the EMRP for reducing the risk in fiscal transactions. Furthermore, developments in LNG metrology are crucial for the deployment of LNG as a transport fuel, which is one of the objectives of the EU clean fuel strategy. (39; 40) Specifically, the EMRP objectives are to:

- Develop traceable calibration standards for mass flow metering relating to fuel dispensing and ship loading.
- Develop a LNG reference liquefier for validating methods for measuring composition.
- Develop a method for determining Methane Number (MN) via inferential methods.
- Develop a model for accurately predicting the density of LNG at extended operating conditions.

Each research objective is itself a work package (WP) spanned over four years from 2014 to 2017. For each WP, research is disseminated through conference workshops, conference proceedings and journal publications. The following section describes the results and limitations for each work package and puts forward a justification for the work carried out in this research project.

# 1.4 Previous research into LNG measurement and reduction of measurement uncertainty

As discussed in section 1.2, three measured quantities are required to determine the energy content of LNG: volume, density and GCV. Therefore, to accomplish a reduction in total measured uncertainty, efforts must be split between these three measured quantities. The research presented here is not entirely based on the EMRP project but combines efforts from a variety of sources, specifically for uncertainty assessments and sampling methods for composition determination. Composition measurements dominate the descriptions here since a justification is required for the research undertaken in this study. Nonetheless, a full overview of each measurement area follows.

#### 1.4.1 Density Measurements

The necessity for improving methods for the determination of LNG density is based on the poor performance of equations of state (EOS) at these very low temperatures, a direct result from the lack of up-to-date experimental data. For example, the most common cubic EOS including the Peng-Robinson (PR) and the Soave Redlich-Kwong (SKR) EOS predict LNG densities with an uncertainty of 8%. (41) Newer EOS including the Revised Klosek-McKinley (RKM) EOS and the Gerg-2008 EOS predict LNG densities with an uncertainty of 0.1% and 0.5%, respectively. (42) These uncertainties are the direct result of lack of availability of accurate experimental data.

There are two main techniques that are used to measure LNG density: Pycnometer and Magnetically suspended sinker. The Pycnometer works in the temperature range 90K to123K at 1 bar with an uncertainty of 0.5%. The Magnetically suspended sinker works in the temperature range 73K to 323K
at pressures less than 350 bar with an uncertainty of 0.2%. Conversely, the uncertainties for the best methods of density measurement for pipeline gas are between 0.01% and 0.02%. (42)

A newly developed density measurement device based on the magnetically suspended sinker design provides up-to-date accurate density measurements with an uncertainty 0.044% over the temperature range 105K to 135K at pressures up to 8bar. (43) These conditions are typical of LNG storage, transport and loading procedures. An enhancement of the RSK EOS capable of predicting LNG densities in the range 100K to 135K at pressures up to 10bar- formerly restricted to saturated liquid densities- resulted from the newly available experimental data, providing an uncertainty range of between 0.1% to 0.15%. (44). Better uncertainties may be established when more experimental data is available.

#### 1.4.2 Volume measurements

The most common method for calculating LNG volume is by combining gauge tables, level gauges and trim lists. However, a great deal of uncertainty is introduced when using correction tables, choosing between types of level gauge (radar, float, capacitance) and estimating the deformation of the carrier due to the weight of the cargo. (45) The predicted uncertainty of total volume transfer using the conventional method is between 0.2 and 0.55%. (14) In response to these challenges, an alternative method has been introduced to the LNG industry that measures the flow rate in the transfer line using a flowmeter. The immediate challenges in applying such instrumentation lies with the potential two-phase flow formation due to the flow conditions being close to the saturation temperature. A pressure drop or sudden heat influx could induce bubble formation, interfering with the operation of the flow meter.

In addition, the lack of traceable standards hampers the confidence in measurement. Nevertheless, new developments in flow meter technology aim to tackle these challenges, albeit with a significant investment.

Due to the nature of LNG transfer process, pressure drops are unavoidable, therefore the use of orifice plates and turbine flow meters are unsuitable for LNG flow operations since both technologies rely on differential pressure measurements and are sensitive to flow profiles. (45; 46; 47) The main developments in LNG flow metering technology have been for Coriolis flow meters (48; 49) and ultrasonic flow meters (50; 51). Coriolis flow meters have the advantage of not requiring density calculations but do have size and pressure drop limitations, whereas an ultrasonic flowmeter does require density calculations but are not limited to pressure size or pressure drop limitations. (14) An in-depth comparison between Coriolis and ultrasonic flow metering technology is given in (47).

The lack of calibration facilities for LNG flow metering has made it difficult to bring new developments in flow metering to market. One of the aims of the EMRP for LNG is to build a mid-scale calibration facility for LNG flow measurement and this was successfully finished in 2016. The facility consists of a primary standard loop and a mid-scale loop. The primary standard loop is traceable to the SI and achieves flow rates of up to 25m<sup>3</sup>/hr. The mid-scale flow loop is traceable to the primary standard loop and is used to scale the flow rate and achieves a flow rate of up to 200m<sup>3</sup>/hr. Moreover, challenges still lie ahead since the validation of the calibration facility is uncertain due to the relatively large uncertainty of the primary flow standard (0.1%), though a reduction in uncertainty remains an objective for further work. (52)

Furthermore, an accepted standard practice for validating flowmeters for measuring LNG is yet to be established. Even though the repeatability in

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measurement (by mass) is approximately 0.125%, in line with custody transfer requirements, a meter factor is still required to achieve traceability to both mass and volume. Once established, in-line flow measurements are likely to replace conventional tank gauging techniques or supplement them as a backup system.

#### **1.4.3 Composition measurements**

The current method for measuring LNG composition requires taking a sample, vaporising it and measuring it with a gas chromatograph. This is a very challenging process since the LNG must undergo a phase transition from a cold state (110K) to a warm state (25<sup>o</sup>C) for chromatographic analysis. Consequently, the sampling system must meet the requirements specified in ISO 8943-2007 (53), ISO 10715 -2001 (54), API 14.1 -2006 (55) and BS EN 12838 – 2001 (56). All four standards cover how the LNG is sampled, conditioned and measured. The main elements of an LNG sampling include: the sampling line, vaporiser, gas homogeniser, sample cylinders, gas chromatograph and auxiliary equipment such as control valves, compressors and temperature sensors.

Firstly, LNG is sampled from a transfer line and vaporised. The vaporised liquid is either continuously fed into gas sample holders for offline analysis (continuous), or is continuously fed into a constant pressure floating piston (CP/FP) cylinder and partly directed to a GC for real time measurements (Intermittent). The choice of sampling procedure is left to the users' preference; however, the intermittent method has become more obsolete for custody transfer since it has more moving parts. (14) The vaporiser itself must have enough heat exchange capacity to fully gasify the whole sample of LNG,

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and in the case where a compressor is used to transfer the LNG, the capacity of the vaporiser must exceed that of the compressor as per ISO 8943.

The most crucial part of the sampling procedure is the state of the LNG prior to vaporisation. The transfer line must be adequately insulated to prevent as much heat influx as possible reaching the flowing liquid. A degree of subcooling is also required to distance the LNG away from its boiling point. Subcooling combined with adequate insulation should result in a homogenous liquid reaching the vaporiser. However, for systems with inadequate subcooling and insulation, the liquid will be heated prior to reaching the vaporiser, thus inducing a two-phase flow. If the heat influx is enough to boil the lighter hydrocarbons (predominantly methane) and nitrogen, fractionation will occur in the line leading up to the vaporiser. Consequently, the vaporised gas will have a different composition to the sampled liquid, therefore the measured composition will not be representative of the transfer line composition. This issue is illustrated in figure 1.4-1.



Partial fractionation

Figure 1.4-1 – Illustration of sample fractionation during LNG sampling procedures.

In addition to the pre-evaporation (fractionation) issue, the second problem is the capacity of the vaporiser to provide a whole state change from liquid to gas without partial evaporation. If the vaporiser does not provide enough heat energy to fully vaporise all components in the LNG, some heavier component residuals will remain in the vaporiser. In addition, the presence of dead volume can result in residual liquid/gas left behind. Both pre-evaporation and partial evaporation can be identified by a layer of frozen moisture- due to the cooling of ambient air- on the outside of transfer line and vaporiser. (57) However, the absence of frozen moisture does not conclude a fully operational system. To combat these issues, there are two alterations that can be made. Firstly, the sampling system can be re-designed with the aim of preventing fractionation and partial vaporization, thus providing a representative analysis. Secondly, the complete sampling and measurement system can be substituted for a direct measurement technique that measures composition directly in the liquid phase.

In response to the first alteration, several system designs have been developed. Most notably, the Opto-Periph<sup>™</sup> (58) and ASAP's Phazer<sup>™</sup> (57) shown in figure 1.4-2. The Opto-Periph utilises a vacuum insulated sampling line, whereas the Phazer pre-cools the sampling line with a 'cold box' that is continuously replenished with LNG. Both systems are relatively new designs and claim to have much better repeatability than current system set-ups, however accuracy remains an incalculable measurement. Without a traceable reference standard, the system cannot be tested for its accuracy. Since the composition of the LNG in the transfer line is unknown, there is no verification to match the measured sample against. Therefore, both systems can only be judged on the repeatability they offer, not the accuracy they are capable of.



Figure 1.4-2 – LNG sampling system designs: (A) Opta-Periph and (B) ASAPs Phazer.

In contrast, the application of direct measurement techniques offers an alternative measurement approach. The nature of laser spectroscopy offers the capability of extending the source of the laser to a desired location using fibre optics. This provides the advantage of making measurements in remote locations and in places not safe for human presence. In addition, the uncertainty associated with sampling LNG is removed since the measurement is made directly in the liquid stream. Moreover, the advantages of using laser spectroscopy is amplified with the use of multiple probes from the same instrument capable of measuring at multiple points in the transfer line or elsewhere: for example, in processes that govern LNG production, transport and distribution. This type of arrangement would bring down CAPEX and OPEX costs considerably since there would be no need to maintain a side portfolio of instruments measuring different processes.

There are currently two commercially available measurement systems: the Optograf<sup>™</sup> from Endress and Hauser Ltd. and the TFS Precisive<sup>™</sup> from MKS Instruments Ltd. The Optograf is based on Raman spectroscopy and the TFS Precisive is based on Infrared Spectroscopy (IR). For accurate compositions measurements, these systems must be calibrated with traceable reference standards close or equivalent to the composition of real LNG. If no traceability is established, there is no confidence in the performance of the instruments.

To validate such instruments, a system with the following criteria is required:

- 1. a vacuum separated chamber for storage of LNG.
- a flexible inlet for the insertion and removal of measurement probes.
- 3. a sampling line leading from the liquid to an external homogeniser.

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- a vaporiser capable of homogenous transformation of liquid to gas without pre-vaporisation and enrichment.
- 5. a thermal control to keep the LNG stable under measurement conditions.
- a system with a pressure rating of up to 10 bar to replicate LNG line conditions and to minimise vapour phase LNG.

To this point, there has been no successfully developed LNG liquefier capable of condensing reference gas mixtures and measuring a sample accurately using an analytical instrument. A summary report from EMRP WP2 confirmed an unsatisfactory system design due to system leakages. (59) One of the main aims of this work is to verify a bespoke cryostat system capable of condensing a range of traceable reference gases. By sampling and measuring the liquid, a traceability chain can be established between the liquid composition and the reference gas mixture, therefore a verification of the liquid can be realised.

Once the cryostat liquefier is verified over the full range of LNG compositions, validation of such measuring instruments can be made. Since these instruments measure directly in the liquid phase, the composition of the liquid must be determined on a case-by-case basis. It is not enough to assume the liquid composition is proportional to the reference gas composition since small changes in composition may result from vapour expelling into the headspace of the sample chamber. The determined liquid composition is to be verified against a set of criteria stated in EN12838 that specifies maximal permissible error in sampling analysis. Furthermore, the principal aim of this project is to calibrate and validate both the TFS Precisive IR spectrometer and the Optograf Raman spectrometer to determine if they are fit for purpose in custody transfer and monitoring and control applications. Moreover, this work

aims to contribute to the development of international standards and practices that will aid the deployment and commissioning of such instruments.

#### 1.5 Assessment of uncertainties

A globally accepted uncertainty for LNG energy transfer is not yet agreed. The range of uncertainties reported in literature vary from 0.34% (60) to 0.76% (14) and this is considered optimistic with sources from the EMRP speculating uncertainty values of up to 1% or higher. (61; 62; 39) This variation in uncertainty from different sources is a result of: how the uncertainty budget is calculated and propagated, availability of real data and type of instrumentation and methods used.

Each calculated physical property has several uncertainty contributions and these are summarised from the available literature in table 1.5-1. A recent study included the correlation of input quantities for an uncertainty model and combined these with real LNG tank data and available literature. (30) The study also confirmed that for the overall LNG energy transfer uncertainty, there are no significant correlations with composition and temperature. The final uncertainty budget for overall LNG energy transfer given in this study is:

- 0.19% 0.20% (k=2) for density
- 0.11% 0.12% (k=2) for GCV
- 0.21% (k=2) for volume
- 0.35% 0.36% (k=2) for total energy transfer

Component	Sources of uncertainty	Total uncertainty from different sources			
GCV	<ul> <li>Composition         <ul> <li>Calibration gas</li> <li>Sampling method</li> <li>GC uncertainty</li> </ul> </li> <li>CV of individual components</li> </ul>	0.30% (k=1) (14) 0.35% (k=3) (63) 0.15% (k=2) (60) 0.08% (k=2) (64)			
Density	<ul> <li>Composition</li> <li>Method of determination (EOS)</li> <li>Experimental data used to derive model</li> <li>Temperature</li> </ul>	0.21% (k=2) (01) 0.21% (k=1) (14) 0.16% (k=2) (60) 0.23% (k=2) (63) 0.35% (k=2) (65)			
Volume	<ul> <li>Sagging/hogging</li> <li>Temperature</li> <li>Level gauging</li> <li>Trim list</li> <li>Pressure</li> <li>Correlation</li> </ul>	0.53% (k=2) (66) 0.38% (k=2) (66) 0.31% (k=2) (60) 0.30% (k=2) (60) 0.30% (k=2) (60) 0.14% (k=2) (67)			

Table 1.5-1 – Uncertainty contributions for GCV, density and volume from available literature

In this work, the input quantities of interest are GCV and density since they both rely on measurements of composition. GCV and density are calculated via ISO 6578 (68) and ISO 6976 (69), respectively. Composition uncertainty is a product of the calibration gas uncertainty, sampling method uncertainty and uncertainty in the method of measurement (conventionally GC). By removing the need for a sampling system and applying alternative methods that measure directly in the liquid phase, the uncertainty resulting from the sampling method and measuring method may be reduced significantly. Figure 1.5-1 illustrates the potential benefits of replacing conventional LNG sampling systems with direct measurement instruments. As indicated in table 1.5-1, the current sampling method contributes 0.35% to the composition uncertainty. By replacing this sampling system, this uncertainty is removed and the

uncertainty in composition becomes dependent solely on the uncertainty of the calibration and the instrument.



Figure 1.5-1 – Illustration of the potential benefits gained by replacing existing LNG sampling systems with direct measurement technologies.

## 1.6 Project aims and Objectives

Considering the impact of reducing total LNG energy transfer uncertainty from an economic, environmental and social perspective described hitherto, this project aims to target several elements of LNG measurement with the following objectives:

 Verification of a bespoke cryostat liquefier for accurately sampling LNG composition to within the maximum permissibility criteria specified in EN12838. This verification is required to provide confidence in the condensation and measurement of LNG over a wide range of compositions. Ultimately, this system will be used to calibrate and validate spectroscopic instruments. This verification is a prerequisite for objectives 2, 3 and 4 on the premise that uncertainty of the calibration system must be sufficiently small to provide an effective calibration.

- 2. Calibration and validation of the Optograf Raman spectrometer for the measurement of MR compositions. Monitoring and controlling MR compositions during LNG production allows for improvements in thermodynamic efficiency as discussed in section 1.3.3.1. Currently, there are no validated measuring instruments capable of directly measuring MR composition. Therefore, the aim is to introduce a level of control in the MR process by applying a validated in-line instrument. This will allow operators to rapidly respond to changes in MR composition and act accordingly, to meeting design specifications.
- 3. Calibration and validation of the Optograf Raman spectrometer for the measurement of LNG-type compositions. The application of instruments that directly measure in the liquid removes the need for liquid sampling, therefore removing the uncertainty associated with the sampling process, which currently contributes approximately a third to total composition uncertainty. (14) In addition, these instruments may be used for other applications such as the monitoring of LNG composition during ship transportation and the measurement of LNG at remote locations, for example, along the loading arms during offloading. Due to the nature of laser spectroscopy, the use of multiple probes from the same instrument is not uncommon and could provide additional benefits such as those discussed in objective 2, for example, the simultaneous monitoring of different stream liquids. The best-case scenario would be an instrument capable of measuring LNG

composition at custody transfer and during transportation, and MR composition for process control and monitoring.

4. Calibration and validation of the TFS Precisive Infrared spectrometer for the measurement of LNG-type compositions. In accordance with objective 3, the testing of direct measuring instruments allows for the removal of sampling uncertainty and a potential gain in composition measurement uncertainty regarding each component and its GCV. Testing different spectroscopic technologies provides valuable insight into their advantages and disadvantages. Flexibility, accuracy, repeatability, durability, stability, selectivity and linearity are the fundamental factors that will determine the successful deployment of these instruments to the market. Cost competitiveness will also play a deciding role. One of the fundamental questions that will be heavily debated is what the level of compromise should be between accuracy and unit price. To establish this criteria, a rigorous testing procedure is required for validation prior to industrial use. Furthermore, a level playing field will be recognized which allows the direct comparison of two competing technologies.

Testing of both spectroscopic instruments in objectives 3 and 4 will contribute to the development of an international standard of which the author has been designated UK expert and committee member.

5. Identifying scope for further work. Throughout this research project, there will be opportunities to explore the scope for further work. This may be in the form of: developments in cryostat liquefier design, the use of different measuring instruments, development of models to improve the custody transfer of LNG, refinement of spectroscopic models and research into the thermodynamic properties of multicomponent fluids. Significant findings will be discussed in the further work section of the thesis.

#### 1.7 Thesis style and structure

For ease of reading and added comprehension, this thesis does not follow the standard IMRAD (Introduction, method, results and discussion) format. Rather, as with many conventional European-style theses, each chapter stands on its own. Introduction, context of the work, methodology, results and discussion sections are incorporated into each chapter. These partitions are based on the logical separations that exist between the research conducted. Chapter 2 is dedicated to the methodology used throughout the research project since a thorough description is justified due to its complexity. To this end, each chapter provides an introduction and context of the work conducted, and a brief methodology section outlining the instrumentation, methods and description of how the results were generated. A conclusion section is dedicated at the end of each chapter to summarise the key findings and explanations for ambiguous results. In closing, a conclusion chapter assimilates the major inferences resulting from each chapter and examines them in the context of the existing knowledge base. Following this, a further work chapter proposes future investigations that could widen the scope of the current work and contribute to the existing knowledge base.

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### 2 Experimental Design and Instrumentation

#### 2.1 Introduction

The design of the overall experimental process was developed throughout the project with adjustments that allowed for improved system efficiency. These improvements in efficiencies are described in *Chapter 3 - Optimisation of the cryostat liquefier*. In this chapter, we describe the final system setup that was used to acquire data for the proceeding experiments discussed in the later chapters of this thesis.

This chapter describes the interface between the individual components that make up the entire experimental system. This includes: the cryostat liquefier unit, gas chromatograph, Raman and IR spectrometers, synthetic gas mixtures, line connections, temperature and pressure monitoring/controlling equipment, and weighing balances. The following sections will describe each component individually and clarify its relationship with other components in the experimental setup.

### 2.2 Cryostat liquefier Unit

The formal definition of a cryostat (cryo meaning cold and stat meaning stable) is a system that maintains low cryogenic temperatures. (1) The cryostat used in this project is a custom-built device with the primary function of condensing multi-component hydrocarbon gases to liquids at maintained cryogenic temperatures. The cryostat is a stainless-steel construction containing various inlets, outlets and chambers whereby low temperatures liquids are maintained at constant pressure. The main function of the cryostat

is to provide a stable reference liquid that can be measured directly and sampled simultaneously without changing its chemical composition. This is fundamental to the traceability and accuracy of the experiments.

#### 2.2.1 Design

Inside the cryostat are two main chambers, the outer vacuum chamber (OVC) and inner sample chamber (SC). The OVC (Figure 1) is evacuated to below 10<sup>-6</sup> mbar to minimise heat ingress to the SC from the surrounding environment. Without the OVC the temperature of the sampling cell would not be sustained at sub-cooled conditions for the time needed for repeat measurements. The effects of vacuum pressure on the liquid nitrogen cool down efficiency and its impact on measurement stability is described in Chapter 3.

Figures 2.2-1 through to 2.2-5 show schematic representations of the cryostat unit design and its dimensions in the side-view projection and its birds-eye view projection. The sampling cell is located towards the bottom of the unit due to the gravity-fed liquid nitrogen source and the space required to insert a sampling probe. The SC itself is made from Copper because of its high thermal conductivity, equivalent to 400 W/mK, considerably higher than other metals such as stainless steel whose thermal conductivity is equal to 16 W/m K. (2) The high thermal conductivity of copper promotes faster temperature equalisation of the whole sampling cell. This is important because a temperature gradient across the SC could cause a stratification of the liquid composition, thus affecting the final measured composition. This phenomenon is discussed thoroughly in chapter 4.



Figure 2.2-1-Schematic drawing of cryostat liquefier unit in the side-view projection



Figure 2.2-2- Schematic drawing of cryostat liquefier unit in the birds-eye view projection



Figure 2.2-3- Schematic of cryostat liquefier without OVC



Figure 2.2-4- Schematic of internal heat exchanger on SC



A 1/8<sup>th</sup> inch copper tubing is connected from the 7L capacity liquid nitrogen storage tanks to the copper SC where it is wound to maximise the cooling power of the liquid Nitrogen. This will henceforth be referred to as the heat exchanger. The cool-down procedure proceeds only when both chambers are evacuated for at least 24 hours to ensure a leak-free system and to remove the risk of residual moisture in the system. The presence of moisture can affect the measurement process and can potentially block the sampling outlet port where sample is taken to the GC.

#### Figure 2.2-5-(left) Image of Cryostat liquefier, (right) close-up of cryostat components

The Raman measurement probe insert is surrounded by a polyethylene displacer that a has a very small heat conductivity and moisture permeability of 0.42 W/m K and <0.01% by % weight, respectively. [REF] The main function of this displacer is to minimise the heat transfer between the sampling cell and the external cryostat components. Inevitably there will be a

temperature difference between the sampling cell and the top of the sampling probe that is external to the cryostat. Therefore, the use of a displacer will reduce the potential for heat to dissipate, leading to an improved cooling efficiency of the heat exchanger, ultimately providing a more stable temperature profile along the sampling cell. Conversely, the IR probe design does not accommodate a displacer and therefore it is suspected that a greater heat transfer between the sampling cell and external cryostat (specifically the top end) is inevitable.

Two pressure release valves (PRV) are located at the gas inlet and sampling cell pump port where evacuation takes place. Both PRVs are set to 3 bar which is the maximum working pressure of the cryostat. Both PRVs are connected to a vent line to ensure all gas is vented in the case of a system fault. Measurements of the liquid are made overnight. Therefore, if there was a fault, for example, a sudden loss of the outer vacuum or a heat exchanger problem, the liquid would boil rapidly causing a 600-fold volumetric expansion and a rapid increase in pressure. The PRVs and venting system would allow this gas to escape safely without causing damage to the cryostat.

A pressure transmitter is attached to sampling cell pump port and monitors the cell pressure in real-time. Temperature diagnostic wiring connects PT100 electrodes that are integrated at the lower and upper sections of the sampling cell to a lakeshore 325 temperature controller where the temperature is set, controlled and recorded in real-time. Monitoring the pressure and temperature of the system is important for maintaining the stability of the reference liquid and an equilibrium that favours liquid formation over vapour or solid formation. This is fundamental to the accuracy of the composition measurement because slight changes in temperature and pressure can alter the flow rate to the GC and subsequently hinder measurement repeatability. The thermodynamics of

the system and its effect on composition equilibrium are explored in Chapter 3. An investigation into the relationship between temperature, pressure and composition supported the design of the experiments presented in chapters 4, 5, 6 and 7.

#### 2.2.2 Operation procedure

The overall process of preparing the cryostat for liquefying reference gases can be split up into four stages: (1) complete evacuation of inner sample chamber and outer vacuum chamber, (2) cooling down of the sample cell to the desired temperature, (3) introduction of the reference gas into the system via a sample inlet port and (4) monitoring and controlling the heater input and liquid nitrogen flow during the measurement process.

Firstly, a complete evacuation of the inner and outer chambers is made and this process usually takes approximately one day. High performance turbo pumps are used to ensure the lowest possible vacuum (figure 2.2-6). An Edwards V12 oil rotary pump is combined with a PT80 dry turbo pump which allows for an efficient evacuation of both the SC and OVC. The rotary pump is applied first to remove the bulk pressure, followed by the turbo pump to reach the extremely low pressures in the mbar region.





Figure 2.2-6-Shows a PT 80 DRY turbo pump (left) and an Edwards V12 oil rotary pump (right)

Secondly, liquid nitrogen is pumped through the heat exchanger using a liquid nitrogen Dewar until the 7L capacity storage tank is filled completely. The liquid nitrogen flow through the heat exchanger is controlled with needle valve which acts as a flow controller. During cool-down, the needle valve is fully opened until the set temperature is achieved. Once at the set temperature, adjustments to the applied heater power and needle valve are made to keep the temperature stable. A heating capacity between 20 % and 30 % is chosen since we want the minimise the total heat transferred to the sample chamber. Within this range, only a small flow of nitrogen is required for temperature stability. The system is rated to keep the set temperature to within 100mK. A temperature profile showing the sampling cell temperature stability to within 10mK is shown in figure 2.2-7.



Figure 2.2-7- Sample chamber temperature stability at 102K

Thirdly, primary reference gas mixtures (PRGMs) – defined here as gravimetrically prepared gaseous mixtures in accordance to ISO17025 and whose method of preparation is described in section 1.3- are transferred to the SC via a 1/16<sup>th</sup> inch stainless steel line. The mass of gas transferred is known by monitoring to loss of mass from a weighing balance. The mass of liquid required to fill the sample chamber is calculated using the following equation:

$$L_{Mass} = SC_{Volume} * L_{Density}$$

#### Equation 1.2.1

Where  $L_{Mass}$  is the predicted mass of produced liquid,  $SC_{Volume}$  is the volume of the sample chamber and  $L_{Density}$  is the density of the reference gas being condensed.

The density of the liquid is calculated using a natural gas predictive modelling suite called GasVLe. Given that the proposed LNG compositions in this study cover the expected international range, and that composition is a prerequisite for density calculations, one wold expect the density to change between compositions. The composition of 7 gases within the imported LNG ranges specified in chapter 1 is shown in table 2.2-2. The spread of density between lean and rich gases falls between 420 kg/m3 and 485 kg/m3, respectively. A 13% difference in density translates to a significant difference in volume and therefore is an important parameter for consideration during experiment design. From figure 2.2-1, the volume of the SC was estimated to be 1L. By estimating the density of each mixture, the mass of LNG required to fill 1L of space may be calculated. An example calculation is shown in table 2.2-2. A more accurate volume calculation based on the ideal gas law is demonstrated in chapter 3 of this thesis. Values shown in table 2.2-1 are to demonstrate the differences in mass required for different compositions of LNG.

	Mix 1a	Mix 2a	Mix 3a	Mix 4a	Mix 5a	Mix 6a	Mix 7a
Nitrogen	0.248	0.573	0.831	1.563	1.094	0.685	0.100
Methane	99.300	98.430	97.041	95.223	94.101	88.139	79.862
Ethane	0.100	0.220	0.511	1.185	3.129	7.128	13.769
Propane	0.098	0.226	0.411	0.766	1.261	2.122	3.920
iso- Butane	0.081	0.230	0.622	0.386	0.132	1.009	1.293
n-Butane	0.123	0.228	0.418	0.574	0.079	0.915	1.054
iso- Pentane	0.030	0.046	0.083	0.147	0.101		
n- Pentane	0.020	0.047	0.082	0.155	0.102		
Liquid Density (g/ml)	0.450	0.453	0.456	0.461	0.451	0.470	0.494
Total mass required (g/1000m l)	315.25 3	316.95 1	319.36 8	322.72 8	315.72 6	328.97 5	345.83 7

Table 2.2-1- estimated liquid mass to fill SC between rich and lean gasmixtures

When the desired mass of liquid is condensed, the gas inlet flow is stopped and the liquid nitrogen flow adjusted to compensate for the difference in heat transfer. During the first stages of gas transfer, the temperature difference between the gas and the sampling cell is large and so requires a high amount of cooling. When the gas flow is reduced or stopped, less cooling is required, hence less liquid nitrogen flow is needed to keep the system at low temperature. The system is stable and suitable for measurement when the temperature profile shows a temperature and pressure stability of 100 mK and 100 mbar, respectively.

Finally, an over-pressure of the system is made with helium gas. After the condensation process the final internal cell pressure is below 0.5 bar(a) because of the low vapour pressure of the liquid. Therefore, to force liquid through the sampling line to the GC for composition measurements, an over-pressure above 1 bar(a) is required. Helium gas is transferred via the LNG pump port such that the helium gas can settle above the liquid rather than using the gas inlet port which would cause a bubbling through the liquid and disrupt equilibrium stability. Helium gas is chosen here because it doesn't interfere with the measurement process since it is not detected on the GC when using a helium carrier gas and the liquid composition remains unchanged because of the extremely low boiling point (4.2 K) required for its liquefaction. (3)

# 2.3 Production of synthetic primary reference gas mixtures

Synthetic primary reference mixtures (PRGMs) are high quality binary or multicomponent mixtures that have been gravimetrically prepared via the procedures specified in the international standard ISO 6142- Preparation of calibration gas mixtures. (4) The gravimetric method involves transferring predetermined masses of gases and/or liquids of known composition into a gas cylinder. Due to the rigorous procedures in this method of preparation, very low uncertainties can be achieved with traceability to the SI unit of amount of substance, the Mole.

Per ISO-6142 (4), the traceability to the SI unit arises from the correct implementation of three steps:

- a) to accurately determine the masses of gases and/or liquids added
- b) conversion of masses added to amount of substance based on the chemical purity of the parent gases/liquids
- c) verification of the final mixture composition against independent reference mixtures

This section gives a brief account of the preparation method described in ISO 6142 and highlights the key points to prevent an exhaustive explanation to the

#### 2.4 Gas Chromatography

Gas chromatography is a well-known analytical technique that is widely used for analysing the constituents in natural gas, specifically with a dual FID-TCD detector setup. (5; 6; 7; 8; 9) It's versatility and robustness allows for a multitude of method developments that can be adapted to suit different matrix gases. In this work, gas chromatography is used as a reference instrument to measure the sampled liquid after it has been vaporised. A reference instrument is required to provide traceability to the initial gas mixture composition. The measured composition is mathematically combined with the gravimetric composition to give an accurate representation of the liquid composition. This transformation is discussed in detail in section 2.4.3. The result of this transformation has two fundamental uses, (1) for the development of the Raman and IR spectrometer calibration models, and (2) for the direct comparison of performance between the GC and both spectrometers in terms of accuracy and repeatability.

#### 2.4.1 Theory of gas chromatography

Due to the complexity of the measurement process in this work, a description of the theory behind each measuring instrument is warranted. Gas chromatography is a partition technique used to separate and quantify a mixture of components in a flowing 'mobile' phase onto a 'stationary' phase. Individual chemical species have a different interaction with the stationary phase because of the intermolecular forces at play. This interaction is described by a partition coefficient described by equation 2.4.1.

$$K = \frac{C_S}{C_m}$$
 Equation

2.4.1

The partition coefficient is defined here as the ratio of the component in the stationary phase ( $C_S$ ) and mobile phases ( $C_M$ ) and is dependent upon the components' physio-chemical affinity for the stationary phase. Components with different partition coefficients will elute from the column at different times before reaching the final detector. The detector generates a peak intensity which is proportional to the concentration of the component and this is combined with a time domain to create a chromatogram. The chromatogram shows Gaussian-shaped peaks that correspond to the resonance time of the components on the stationary phase, this is illustrated in figure 2.4-1.



Figure 2.4-1- Illustration of peak separation and retention time of two analytes on a GC column

The area under each peak is proportional to the concentration of the chemical species being measured. Therefore, problems can arise if there is overlapping of peaks or if peaks are close enough to affect the individual baseline allocation. The ability to resolve two adjacent peaks is fundamental to the accuracy of the peak integration and therefore the final determination of amount fraction of each measured component.

The quality of a GC system is based on the analysis time, efficiency and resolution of the chromatogram. (10) The aim of any GC optimisation is to obtain a complete analysis with resolvable peaks in the shortest time possible. To achieve this, an understanding of the chemical species and their interaction with the GC column is required. The next section will provide a description of each component in the GC system and its justification for use.

#### 2.4.2 Gas chromatograph setup

The gas chromatograph (GC) used in this work was set up to measure LNGtype gases and is configured in accordance with ISO-6974 (9). The GC is an Auto system XL from Perkin Elmer and is configured as follows. Two column configurations make up the system. Firstly, a HayeSep A 4 meter 120/140 mesh micro-packed column is interfaced with a 150uL sample loop and a thermal conductivity detector (TCD). Secondly, a HayeSep B 5 meter 100/120 mesh micro-packed column is interfaced with a 50uL sample loop and a flame ionisation detector (FID). The carrier gas is helium and the column is temperature controlled inside an oven at 180°C. A schematic representation of the GC setup is illustrated in figure 2.4-2.



Figure 2.4-2- Schematic representation of the Perkin Elmer Auto system XL GC instrument setup showing dual column and detector configurations
#### 2.4.2.1 Detector selection

TCD is a general-purpose detector and is typically used to measure nitrogen, carbon dioxide and lower molar mass hydrocarbons. Its operating principle relies upon the detected thermal conductivity change of an analyte relative to the carrier gas. (11) The variation in thermal conductivity results in a disruption of the temperature equilibrium between the filament and the carrier gas, and this causes a change in electrical current which is proportional to the concentration of the analyte being measured. All chemical species have a thermal conductivity and therefore can be measured with a TCD.

FID is the most common detector choice for gas chromatography, especially in the petroleum industry. Its working principle is based upon the ionisation of carbon species which are combusted inside a flame containing hydrogen and oxygen. The Flame provides carbon ions which are accelerated toward a collector plate on the application of voltage which in turn is measured with an ammeter. The signal measured is proportional to the concentration of chemical species. FIDs provide high sensitivity, high signal-to-noise, extremely good resolution and generally much better linearity compared with TCD. The only drawback is that it is only applicable to ionisable hydrocarbons. For this reason, a combination of TCD and FID is required for a complete analysis of non-ionisable species and ionisable hydrocarbons.

In this work, the TCD is used in two different ways. Firstly, for the analysis of LNG is it used to measure nitrogen, methane and ethane, whilst propane, n-butane, iso-butane, n-pentane, iso-pentane and neo-pentane are measured with the FID. Secondly, for the analysis of mixed refrigerant mixtures containing nitrogen, methane, ethane and propane, TCD remains the primary detector because the amount fractions of each component are sufficiently high such that they are not affected by the detectors' lower sensitivity.

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The response from both detectors is combined using the average of those components measured on both detectors and those components measured individually on each detector, effectively giving one complete analysis. This combination method is described further in section 2.4.3.

#### 2.4.2.2Carrier gas selection

The carrier gas acts as a medium for transporting the sample through the column and its flow rate is precisely controlled by an electronic pressure controller (EPC) to enable reproducibility of retention times between sample injections. (11) This is fundamental in this work because typically 96 repeat measurements are made for each gas analysis. This is due to the homogenisation and stabilisation time required when sampling the liquid composition. Typically, it takes on the order of hours to get a stable homogenous flow to the GC due to the thermodynamics of the vaporisation process. The time taken for stabilisation can be determined by the standard deviation of the measurement results. This will be described with examples in section 2.4.3.

The three main carrier gases used in gas chromatography are helium, nitrogen and hydrogen. Although, the choice of carrier gas has no influence upon the partition coefficient previously described in equation 2.4.1, the viscosity and flow rate of the carrier gas influences the analytes' distribution in the mobile and stationary phase, and consequently impacts the column efficiency and sensitivity of detection. (11) However, since nitrogen is a measured component in the gas matrix and hydrogen is a safety hazard, the choice of carrier gas in this work is helium. (12)

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#### 2.4.2.3Column Selection

The selection of a column can be categorised into five criteria: (a) column type, (b) stationary phase, (c) column internal diameter (I.D), (d) film thickness and (e) column length. (13) There are two column types, packed columns and capillary columns. In this work, packed columns are chosen over capillary columns because they can withstand a much larger flow rate between 10 and 40ml compared with 5 and 15ml. This larger flow rate is needed for natural gas type analyses due to the presence of methane as the main component which typically has a concentration above 90%. Smaller sample injections would cause a loss in peak intensity leading to the dilution of peaks corresponding to the lower amount fractions in the sample. The packed columns are made from stainless steel with a 1/8<sup>th</sup> inch I.D. and two column lengths at 4 and 5 meters.

The stationary phases used in this work are HayeSep A and HayeSep B. HayeSep stationary phases are spherical macroporous polymers with minimum bleed-leakage of polymer over time. (14) The HayeSep A is designed for separating permanent gases such as hydrogen and nitrogen and hydrocarbons up to C2. HayeSep B is designed for separating hydrocarbons and trace levels of moisture and ammonia. Accordingly, the HayeSep A is interfaced with a TCD and the HayeSep B is interfaced with a FID.

The quality of stationary phase packing directly impacts the performance of the column in terms of its separation capability. (11; 15) The Van Deemter relation (equation 2.4.2) shows that the plate height, H, an imaginary quantity is related to column efficiency and the mobile phase linear velocity  $\mu$ . The column efficiency includes three coefficients A (Equation 2.4.3), B (Equation 2.4.4), and C (Equation 2.4.5) that describe the physio-chemical behaviour of the column and experimental parameters.

$H = A + \frac{B}{\mu} + C\mu$	Equation
2.4.2	
$A=2\gamma.d_p$	Equation 2.4.3
$B = 2\gamma . D_G$	Equation 2.4.4

$$C = C_G + C_L$$
 Equation 2.4.5

The packing related term, A, includes the mobile phase flow profile to the diameter of the particles  $(d_p)$  and their uniformity and distribution  $(\gamma)$ . The mobile phase term, B, includes the diffusion of the analyte in the mobile phase  $(D_G)$  and the packing factor related to the longitudinal diffusion of the packing particle in the column. The stationary phase term, C, describes the diffusion coefficient of the solute in the mobile phase  $(C_G)$  and stationary phase  $(C_L)$ . It is clear from terms A and B that the packing properties of the stationary phase are directly related to the column efficiency and performance.

A non-uniform distribution of packing particles can cause turbulent flow paths with different lengths, ultimately resulting in band broadening. (16; 17) Band broadening is described here as the overall dispersion of a sample peak as it elutes from the column. Band broadening significantly affects chromatographic resolution, resulting in poorer baseline allocation. Quantitative analysis requires well-separated peaks with precise integration parameters.

Figure 2.4-3 shows the optimal mobile phase velocity at the lowest theoretical plate height using the Van Deemter relation. This plot demonstrates that high column efficiencies are obtained with low theoretical plate heights since this allows for more analyte separation over a fixed column length.

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Figure 2.4-3 - Van Deemter relation showing optimum mobile phase velocity at the lowest theoretical plate height

## 2.4.2.4 Sample injector

The sample injection is controlled via a 10-port valve from Valco<sup>™</sup> (figure 2.4.4). The valve has two positions it can alternate between (figure 2.4.5). The first position allows both sample loops to vent and the mobile phase to purge both columns. The second position allows the mobile phase to mix with both sample loops for injection onto both columns. The GC method is configured to switch between both positions and is aligned with the run time of each analysis.



Figure 2.4-4- Image of the Valco<sup>™</sup> ten-port switching valve



Figure 2.4-5- Illustration of valve switching to initiate twin-stream sample injections (18)

## 2.4.2.5Sample flow controller

The sample flow from the gas cylinder to the GC is controlled via an in-house made control valve known as the Vargha valve. The Vargha valve is a small mechanical device that can be used with cylinder pressures up to 200 bar. The dead volume is extremely small and therefore minimum sample purging is required. The operating principle is based upon the compression of sampling tube to sub micrometre dimensions to create a stable flow rate. Conventional dual-stage pressure regulators combined with needle valves provide poorer stability and require larger purge volumes. The Vargha valve is compared to a typical two-stage pressure regulator shown in figure 2.4.6.



Figure 2.4-6 - Vargha valve and two-stage pressure regulator

## 2.4.3 Data collection and analysis

Data collection is made via the TotalChrom<sup>™</sup> software suite. This suite allows for batch reprocessing of multiple chromatogram files. Manual integration parameters are prescribed prior to analysis. If peak shifts occur, batch reprocessing is required to apply new integration parameters to compensate for the new peak positions. The batch processing produces text files with the areas of the peaks assigned in the manual integration. The areas of each peak are extracted and imported to Microsoft Excel to be analysed. There are 144 separate analyses in total, 48 analyses for calibration and 96 analyses for liquid sampling. The calibration data is combined with the gravimetric data to give a response factor ( $R_f$ ) calculated using equation 2.4.6.  $R_f$  is then used to convert the liquid sampling data to an amount fraction. The complete data set is split into 12 runs giving 8 separate analyses for liquid sampling and 4 separate analyses for calibration. This separation makes it easier to identify errors and outliers in the analysis.

$$R_f = \frac{Peak area}{concentration}$$
 Equation

2.4.6

For ease of explanation, Table 2.4.1 shows 12 analysis runs from 1 set of calibration data. The average and % relative standard deviation (RSD) are calculated for each component. The response factors for each component are shown in table 2.4.2. Table 2.4.3 shows 12 analysis runs from liquid sampling data with average and %RSD values.

It is clear from tables 2.4.1 and 2.4.3 that the calibration data has a much lower %RSD compared with the liquid sampling data. This is expected because the sampled liquid must undergo a series of events before it reaches the GC, whereas in the calibration method the gas cylinder is directly connected to the GC sample loop. The liquid sample must first be vaporised and directed to an accumulator. Even the smallest differences in concentrations between all components can translate to significant error in analysis. If, for example, the system is not fully homogenised through mixing, differences in concentrations may occur at the liquid sampling point. The use of an accumulator can rectify this by mixing the vaporised liquid prior to sample injection, however small differences in concentrations may still arise resulting in a fluctuation of peak areas.

The average peak areas from the liquid sampling data are combined with response factors obtained from the calibration data giving a set of raw concentrations (table 2.4.4). Since Ethane and Propane are measured on both detectors, they act as bridging components. An average is taken between both calculated concentration values. Finally, the raw concentrations are normalised by scaling the unnormalised concentrations such that the sum of the new normalised concentrations equals to unity (equation 2.4.7). Normalisation provides a significant reduction in uncertainty assuming all components add up to unity, and accounts for sample size effects- a phenomenon arising from a change in the interaction of a solute with its mobile and stationary phases - which is heavily affected by ambient pressure, temperature, injection volume. (19)

$$Cn_i = \frac{Cu_i}{\sum_i^n (Cu_i)} * 100$$
 Equation

2.4.7

Where  $Cn_i$  is the normalised concentration of component i and  $Cu_i$  is the unnormalised concentration of component i.

The normalisation approach described by equation 2.4.7 only applies to gas matrices without nitrogen because it is less effective when the differences between the measured values and reference values is large. Since nitrogen has the lowest boiling point compared with the other expected components, its natural tendency towards the gas phase is greater, resulting in a larger difference between the measured and reference values. Consequently, a different normalisation approach is used whereby the measured nitrogen value is combined with the remaining gravimetric composition (see modified conc., table 2.4.5) and normalised using equation 2.4.8.

$$Cn_a = \frac{Cu_a}{\sum_i^n (Cu_a)} * 100 - C_{N2}$$
 Equation 2.4.8

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Where  $Cn_a$  is the normalised concentration of component a disregarding nitrogen,  $Cu_a$  is the unnormalised concentration of component a disregarding nitrogen and  $C_{N2}$  is the normalised raw concentration of nitrogen.

The resulting composition analysis is tested against a set of criteria based upon BS EN 12838 – Installations and equipment for liquefied natural gassuitability testing of LNG sampling systems. (20) This standard specifies maximal permissible errors (MPE) for gross calorific value (GCV), liquid density and gas density between the reference and sampled gas (table 2.4.6). The suitability testing of the cryostat sampling system is described in detail with results from 7 reference mixtures in chapter 4- Verification of synthetic LNG reference mixtures.

FID	Analysis run number	

Table 2.4-1- GC calibration peak area data from 12 analysis runs

Component	retention time	1	2	3	4	5	6	7	8	9	10	11	12	average	%RSD
ethane	0.985	577292	577493	577362	577370	577296	577525	577375	577740	576532	577009	576711	577687	577282.6	0.063
propane	1.563	238299	238371	238287	238315	238272	238365	238290	238437	237963	238466	238030	238424	238293.1	0.064
i-butane	2.532	202753	202815	202755	202770	202743	202824	202768	202874	202477	202925	202540	202874	202760	0.065
n-butane	2.931	207066	207130	207079	207102	207067	207158	207096	207229	206813	207199	206876	207206	207085	0.061
i-pentane	3.76	29953	29940	29967	29967	29932	29932	29963	29953	29913	29914	29940	29972	29945.43	0.067
TCD			1	1		1	Analysis r	un number	•		1	1	1		
Component	retention time	1	2	3	4	5	6	7	8	9	10	11	12	average	%RSD
nitrogen	0.819	30062	30064	30020	30033	30048	30053	30019	30033	30010	30010	30010	30017	30031.59	0.069
methane	0.907	1538052	1537918	1535993	1536675	1537325	1537605	1536405	1536519	1535568	1535168	1536268	1535874	1536614	0.061
ethane	1.44	186387	186422	186166	186323	186378	186437	186226	186271	186254	186261	186243	186170	186294.8	0.050
propane	2.605	66545	66519	66508	66636	66583	66597	66652	66622	66633	66592	66522	66558	66580.48	0.075

	FI	D		TCD							
Component	Amount fraction	Average peak area	Response factor	Component	Amount fraction	Average peak area	Response factor				
	%mol/mol	mV <sup>2</sup>			%mol/mol	mV <sup>2</sup>					
ethane	7.07	577282.6	81678.82	nitrogen	1.47	30031.59	20428.89				
propane	2.00	238293.1	119310.3	methane	86.73	1536614	17717.73				
i-butane	1.29	202760	156639.7	ethane	7.07	186295	26358.56				
n-butane	1.29	207085	160248.2	propane	2.00	66580	33335.97				
i-pentane	0.15	29945	199365.9								

# Table 2.4-2- Calculated response factors for TCD and FID data

					Analysis r	un number							
1	2	3	4	5	6	7	8	9	10	11	12	average	%RSD
577919	578919	577364	575807	577372	576965	575894	575211	576924	576116	575214	578591	576858.1	0.215
237551	237582	237750	237609	237127	237312	237514	237168	236862	237442	237552	237760	237435.6	0.114
201951	201921	202038	202138	201426	201469	201597	201936	200113	202011	201954	201778	201694.3	0.271
206187	206196	206180	206497	205752	205723	205989	206600	202277	206288	206345	206148	205848.5	0.561
29738	29733	29844	29807	29833	29876	29881	29758	27913	29752	29957	29916	29667.36	1.879
					Analysis r	un numbei	r		·				
1	2	3	4	5	6	7	8	9	10	11	12	average	%RSD
28526	28777	28561	28519	28481	28486	28478	28954	28497	28477	28499	28469	28560.24	0.524
1524934	1526426	1526626	1523516	1522443	1522359	1523235	1541333	1523974	1523973	1524721	1523720	1525605	0.336
186079	185518	184885	185542	185380	184800	184680	189789	184935	184681	185611	184914	185567.7	0.755
65950	66090	65987	65854	65856	65942	65901	66869	65904	65865	66041	66088	66028.98	0.420
	1 577919 237551 201951 206187 29738 29738 28526 1524934 186079 65950	1         2           577919         578919           237551         237582           201951         201921           206187         206196           29738         29733           29738         29733           2         2           2         2           2         2           2         2           2         2           2         2           1         2           28526         28777           1524934         1526426           186079         185518           65950         66090	1         2         3           577919         578919         577364           237551         237582         237750           201951         201921         202038           206187         206196         206180           29738         29733         29844           0         1         2           1         2         3           28526         28777         28561           1524934         1526426         1526626           186079         185518         184885           65950         66090         65987	1         2         3         4           577919         578919         577364         575807           237551         237582         237750         237609           201951         201921         202038         202138           206187         206196         206180         206497           29738         29733         29844         29807           29738         29733         29844         29807           1         2         3         4           28526         28777         28561         28519           1524934         1526426         1526626         1523516           186079         185518         184885         185542           65950         66090         65987         65854	1234557791957891957736457580757737223755123758223775023760923712720195120192120203820213820142620618720619620618020649720575229738297332984429807298330123452852628777285612851928481152493415264261526626152351615224431860791855181848851855421853806595066090659876585465856	1         2         3         4         5         6           577919         578919         577364         575807         577372         576965           237551         237582         237750         237609         237127         237312           201951         201921         202038         202138         201426         201469           206187         206196         206180         206497         205752         205723           29738         29733         29844         29807         29833         29876           1         20         1         206187         20818         20877         20873           29738         29733         29844         29807         29833         29876           1         2         3         4         5         6           1         2         3         4         5         6           28526         28777         28561         28519         28481         28486           1524934         1526426         1526626         1523516         1522443         1522359           186079         185518         184885         185542         185380         184800 <td< 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# Table 2.4-3- GC liquid sampled peak area data from 12 analysis runs

	Average p	eak areas		Response factor		Raw concentration (%mol/mol)					
Component	FID	TCD	Component	FID	TCD	TCD	FID	Raw conc. (%mol/mol)	Norm conc. (%mol/mol)	Grav conc. (%mol/mol)	% Diff Grav conc Norm conc.

Table 2.4-4- Normalisation method 1. Calculated concentrations and % difference from reference values

methane		152560	methane		17717.7	methane	87.506		87.506	88.1548	88.227	0.022
ethane	576858.1	185567.7	ethane	81678.8	26358.5	ethane	7.040	7.063	7.051	7.10328	7.068	0.507
propane	237435.6	66028.9	propane	119310.3	33335.9	propane	1.981	1.990	1.985	1.99972	1.997	0.145
i-butane	201694.3		i-butane	156639.7		iso-butane		1.288	1.288	1.29755	1.294	0.214
n-butane	205848.5		n-butane	160248.2		n-butane		1.285	1.285	1.29453	1.292	0.142
i-pentane	29667.36		i-pentane	199365.9		i-Pentane		0.149	0.149	0.1501	0.150	-0.192
								sum	99.26	100.00	100.00	

Table 2.4-5- Normalisation method 2. Calculated concentrations and % difference from reference values

	Raw concentration (%mol/mol)							
Component	TCD	FID	Raw conc. (%mol/mol)	Norm Raw conc. (%mol/mol)	Grav conc. (%mol/mol)	Modified conc. (%mol/mol)	Norm modified conc. (%mol/mol)	% Diff Grav conc Norm conc.
nitrogen	1.398		1.398	1.408	1.470	1.408	1.408	0.000

methane	86.106		86.106	86.746	86.727	86.727	86.782	-0.041
ethane	7.040	7.063	7.051	7.104	7.068	7.068	7.072	0.445
propane	1.981	1.990	1.985	2.000	1.997	1.997	1.999	0.082
iso-butane		1.288	1.288	1.297	1.294	1.294	1.295	0.151
n-butane		1.285	1.285	1.294	1.292	1.292	1.293	0.079
i-Pentane		0.149	0.149	0.150	0.150	0.150	0.150	-0.256
		sum	99.26	100.00	100.00	98.53	100.00	
						98.592		

# Table 2.4-6 – Example assessment of sampling process against EN12838 suitability testing criteria

	TCD	FID	Raw conc (%mol/mol)	Norm Raw Conc	Grav conc (%mol/mol)	Un-norm conc	Norm conc (%mol/mol)	k	J/kg	kg/m3	Maximal permissible
				(%mol/mol)		(%mol/mol)					error <b>(20)</b>
nitrogen	1.398		1.398	1.408	1.470	1.408	1.408				
methane	86.106		86.106	86.746	86.727	86.727	86.782				
ethane	7.040	7.063	7.051	7.104	7.068	7.068	7.072				

propane	1.981	1,990	1.985	2,000	1,997	1,997	1,999			
iso-butane		1.288	1.288	1.297	1.294	1.294	1.295			
n-butane		1.285	1.285	1.294	1.292	1.292	1.293			
i-Pentane		0.149	0.149	0.150	0.150	0.150	0.150			
		sum	99.262	100.000	99.999	98.529	100.000			
						98.592				
CV (15	/15) (kJ/k	(g)		53243.094			53244.840	1.746		9.000
Gas den	sity (kg /	m3)		0.803			0.803		0.00025	0.00030
LNG Der	nsity (kg/	m3)		494.631			494.529		0.102	0.150

### 2.5 Raman Spectroscopy

The Raman spectrometer tested in this study is an Optograf <sup>™</sup> analyser from SpectraSensors – Endress and Hauser, formally Kaiser Optical Systems, Inc. The Optograf is commercially available and has many applications in the field of chemical analysis. However, there is currently no robust and established model for the application of LNG measurement. As discussed in chapter 1, this work involves the development of an LNG model and its validation and comparison with gas chromatography. The following sections will describe the fundamentals of Raman spectroscopy, discuss the instrument configuration and explain how data is collected, collated and evaluated.

### 2.5.1 Theory of Raman spectroscopy

When light interacts with matter, the frequency of the incident light is changed per the chemical configuration of atoms and molecules (figure 2.5.1). The chemical species may absorb or scatter light via several different mechanisms, ultimately providing a chemical 'fingerprint' when the resultant light is measured. All atoms in molecules to some extent will vibrate with different vibrational frequencies. The intensity of the vibrational frequency v is determined by the spring force constant k and the reduced mass of the atoms in the molecule via equation 2.5.1. It can be deduced from equation 2.5.1 that molecules with stronger bonds and lighter atoms have a higher vibrational frequency.



# Figure 2.5-1 - illustrates the transfer of energy between a photon of light and a vibrating molecule

$$v = \frac{1}{2\pi c} \left(\frac{k}{u}\right)^{1/2}$$

Equation

2.5.1

Molecules containing atoms with different electronegativity will have either a permanent dipole (where electronegativity is distributed unevenly e.g. HCI) or an induced dipole (where electronegativity is neutralised e.g. CO2). For a molecule to be Raman active, it must be polarisable. Polarisability is the ease with which the electronic cloud of a molecule is distorted or a dipole moment is induced in an applied field. Conversely, Infrared active bands are caused by changes in dipole moment before and after equilibrium states.

Scattered light with a different wavelength to the incident light due to photonmolecule energy transfer is known as the Raman effect. This wavelength shift is unique for all molecules because it is dependent upon the molecular bonding configuration and their vibrational frequencies. Raman spectroscopy is concerned with the vibrational energy levels of molecules and their excitation and decay from virtual energy states to ground states (figure 2.5.2).



# Figure 2.5-2- Jablonski diagram showing possible optical transitions resulting from absorption, scattering and fluorescence

The Raman effect describes two mechanisms by which light can interact with matter, Stokes scattering and Anti-Stokes scattering. Both mechanisms are products of inelastic scattering, that is, there is a transfer of energy between the incident light and the scattering molecule. Conversely, when there is no transfer of energy between the photon and the molecule, the incident light is elastically scattered (Rayleigh scattering).

On the application of monochromatic incident light, scattering molecules are excited to virtual energy states with very short lifetimes. After this excitation process, the molecule undergoes a rapid decay process back to its ground electronic state containing multiple vibrational energy levels. If the molecule decays back to the vibrational state it originally started in, the light is elastically scattered (Rayleigh scattering) and there is no transfer of energy. Alternatively, if the molecule decays back to a different vibrational state, there is a transfer of energy between the photon and molecule. The transfer of energy from the photon to the molecule (Stokes-shift) is favoured over the reverse process (Anti-Stokes shift), thus providing spectra with higher intensity.

The scattered light is recorded by a detector which measures the intensity of scattered light as a function of its frequency to the incident light. The frequency shifts for Stokes and Anti-Stokes processes are symmetrical because they correspond to the energy differences between the same upper and lower energy states. However, the Stokes shift has a higher probability of taking place because in thermodynamic equilibrium the lower state will be more populated than the upper state, therefore a transition from the lower state to the upper state (Stokes) will be favoured over transitions between the

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upper states (Anti-Stokes). In most applications, stokes scattering is used. However, anti-stokes scattering may be used for specialised applications.

The Placzek equation (equation 2.5.2) describes the factors affecting Raman scattering intensity  $I_R$ . It is clear from equation 2.5.2 that  $I_R$  is proportional to the laser intensity  $I_L$  and the number of scattering molecules N.  $I_R$  is always greater at shorter wavelengths and higher temperatures which is described by the statistical term  $1 - e^{-hvlkT}$ . Also,  $I_R$  is proportional to the concentration of the sample since the number of scattering molecules is determined by the concentration. This is fundamental to the method development since it is assumed that the Raman response is linearly proportional to the concentration. Similarly, we assume a linear response with gas chromatography.

$$I_{R} = \frac{2^{4}\pi^{3}}{(45)(3^{2})c^{4}} \frac{hI_{L}N(v_{0}-v)^{4}}{uv(1-e^{-hvlkT})} [45(a_{a}')^{2} + 7(\gamma_{a}')^{2}]$$
 Equation  
2.5.2

The most common laser wavelengths for Raman spectroscopy are 532nm, 785nm and 10264nm, ranging from the visible to near-infrared. The choice between these three wavelengths is based on excitation efficiency, fluorescence, detector sensitivity and heat absorption. For this work, a 532nm is the chosen wavelength because of its clear advantages over other laser wavelengths. Since Raman signal intensity is proportional to the reciprocal of the laser wavelength to the power of 4, shorter wavelengths have higher excitation efficiencies. Although fluorescence is higher at shorter wavelengths, we don't expect to encounter any fluorescence due to the sample type. 532nm lasers provide better response for CCD detectors since it is in the visible range. The detector sensitivity diminishes at higher wavelengths, specifically at 1064nm which gives no response with a CCD above 1100nm, falling below

the nitrogen and methane excitation frequencies. Moreover, heat absorption from the laser to the sample is lower at shorter wavelengths. Since the measured samples are cryogenic liquids, a 532nm laser would minimise heat absorption at the tip of the probe leading to a more stable measurement interface. (21)

# 2.5.2 Description of Raman instrument configuration

The Optograf<sup>™</sup> contains several interconnecting components protected by a stainless-steel casing (figure 2.5.3a). Each component and its specification is described in Annex B. The optical probe which extends the laser path to the cryostat is shown in figure 2.5.3b)





Figure 2.5-3 - Optograf Raman analyser system (a) and Pilot<sup>™</sup> LNG probe inserted into cryostat (b)

A schematic diagram showing the interface between different components is shown in figure 2.5.4. A dual-path fibre optic cable connects the laser components to a probe which is inserted into the cryostat and secured with a 50mm stainless-steel flange. The probe tip is cleaned with optical cloth prior to insertion to remove any debris. Once this is achieved, the cryostat preparation described in section 2.2 can succeed.



Figure 2.5-4- schematic diagram of Raman instrument and probe set-up

## 2.5.3 Data collection and analysis

Raman peak positions for LNG are shown in table 2.5.2. The expected peak shifts for each analysis are inputted into the Raman software (Rename) prior to measurement to provide reference points.

Component	Peak shift position (cm <sup>-1</sup> )
Nitrogen	2326.0
Methane	2906.4
Ethane	993.4
Propane	869.8
iso-Butane	798.6

Table 2.5-1- Raman peak shift positions for all	I LNG components (22)
---	-----------------------

n-Butane	838.6
iso-Pentane	462.0
n-Pentane	400.0
neo-Pentane	732.0

A background spectrum is collected along with a dark spectrum for baseline subtraction required during data analysis (figure 2.5.5). A clean probe tip is required to keep the background noise to a minimum. After a small number of experiments, the background spectrum may subsequently produce more noise due to small amounts of dirt collecting at probe window. For this reason, the probe tip is cleaned after two consecutive experiments. Figure 2.5.5 illustrates the effect of probe tip cleaning on the background noise.



Figure 2.5-5 - The effect of probe tip cleaning on background noise reduction

For each experiment, a collection 30 runs with a total accumulated time of 5 minutes is recorded, giving a total measurement time of 2.5 hours. The exposure time for one accumulation is determined at the start of every experiment and is automatically calculated from the camera saturation with a test exposure. Typically, the exposure time is 15 seconds. The exposure time is divided by the total accumulation time (5 minutes) to give a total number of accumulations ((5\*60)/15 = 20 accumulations) required for each analysis. The total run time for each experiment is matched with the GC run time such that both measurements are made simultaneously. A typical LNG Raman spectrum with component labels is shown in figure 2.5.6.

Figure 2.5-6- Raman spectrum of major and minor LNG



For each gas condensation, 30 spectrums are collected. This allows for monitoring of the liquid composition as a function of time, providing a stability

assessment of the instrument itself and of the cryostat. In addition, background spectrums at both room temperature and measurement temperature are measured prior to each experiment. These are used in the development of the calibration model and for monitoring the level of background noise.

The algorithm for the calibration model was developed by an external partner in the project (Kaiser Optical Systems Inc.). The final composition determined via gas chromatography (section 2.4) is combined with the Raman data to build a calibration model for each component in the LNG matrix. The algorithm

% mol/mol

is summarised below:

- Identify baseline points. Average ± n points plus the middle point.
   Use n = 3 to give a total average of 7 points on each end of the baseline.
- 2. Subtract a linear baseline.
- 3. Identify the integration points.
- Sum the subtracted intensity data from the start to stop integration points.
- 5. Obtain response factors (as with GC, equation 2.4.6)

 Table 2.5-2- Example of processed Raman data using the real-time monitoring software

Methan	Ethane	Propane	Isobutan	Butan	lso-	n-	Nitroge	
е			е	е	pentan	Pentan	n	
					е	е		
99.289	0.103	0.099	0.082	0.135	0.027	0.019	0.246	
99.306	0.103	0.102	0.081	0.132	0.026	0.016	0.232	
99.308	0.102	0.100	0.083	0.134	0.026	0.017	0.231	
99.300	0.104	0.100	0.083	0.133	0.023	0.017	0.236	
99.306	0.104	0.100	0.082	0.132	0.026	0.018	0.231	
Ideal	Real	Specific	Wobbe	Signal				
<b>BTU Dry</b>	<b>BTU Dry</b>	Gravity	Index	Str.				
1016.04	1018.09	0.561	1358.903	79.436				
5	8							
1016.04	1018.09	0.561	1359.073	80.238				
3	6							
1016.08	1018.13	0.561	1359.109	80.517				
2	5							
1015.93	1017.98	0.561	1358.916	80.928				
6	8							
1016.07	1018.13	0.561	1359.090	81.211				
8	1							

The Optograf testing suite may be split into two sections. A utilities services suite whereby acquisition of the raw data takes place and an online testing suite for real-time measurements of composition. The former is used to collect spectra and build the calibration model and the latter is used for validating the model and collecting processed data and real-time compositions. The results from the real-time software provide a complete composition matrix, physical properties (BTU, Wobbe and specific gravity) and instrument diagnostic data.

#### 2.6 Infrared spectroscopy

The Infrared spectrometer tested in this work is a tunable filter spectrometer (TFS) supplied by MKS instruments. The TFS analyser in its 'gas analysis mode' is commercially available with a proven and tested model. However, there is currently no established model for analyzing LNG composition since the absorption characteristics of infrared light is different for dense liquids than for gaseous mediums. Also, the analyser requires a specially designed probe to be submerged into a traceable reference liquid, which hitherto has not been

achieved. As discussed in chapter 1, this work involves the development of an LNG model and its validation and comparison with gas chromatography in terms of accuracy and repeatability. The following sections will describe the fundamentals of Infrared spectroscopy, discuss the instrument configuration and explain how data is collected, collated and evaluated.

## 2.6.1 Theory of Infrared spectroscopy

Infrared spectroscopy (IR) is a form of vibrational spectroscopy that involves the absorption of incident light at different frequencies in the region 10- 14000 cm<sup>-1</sup>. (11) These frequencies correspond to the vibrational modes of the sample and at each frequency the sample will absorb incident light at different intensities. The infrared region of the electromagnetic light spectrum may be split into three portions; the near-, mid- and far-infrared, in order of decreasing energy. The differences in energy between each portion induce the excitation of different energy transitions, namely; electronic, vibrational and rotational for the near-, mid and far-infrared, respectively. The energy difference between each transition is approximately the order of one or two magnitudes from  $10^{-23}$  to  $10^{-19}$  J. The energy of these transitions is illustrated in figure 2.6-1.



Figure 2.6-1 – Available energy transitions for a molecule (23)

For a molecule to be IR active it must possess a dipole moment. A dipole moment is a non-uniform charge distribution across a molecule which may be permanent, temporary or induced depending upon the structure of the molecule and its environment. This is different to Raman spectroscopy whereby the detection of a chemical species is solely dependent upon its polarisability regardless of the presence of a dipole moment.

In general, for linear molecules with a dipole the number of degrees of freedom is equal to 3N-5, where N is the number of individual atoms in the molecule. For non-linear molecules, the number of degrees of freedom is equal to 3N-6. The number of degrees of freedom is equivalent to the number of possible vibrational modes. Since non-linear molecules have more symmetry operations, they can undergo more vibrational modes including Radial, Latitudinal, and longitudinal, both symmetrically and asymmetrically. In the case of diatomic molecules, there is only one bond and subsequently one vibrational band. Heteronuclear diatomic molecules are IR active since they

have a dipole. However, homonuclear diatomic molecules are not IR active since they do not have a dipole moment due to their symmetrical nature. This presents a problem for applications in natural gas analysis since nitrogen is present as a minor component. The possible solution for this problem is to sum all the measured components and take the difference from 100% to give a value for N<sub>2</sub>. However, a conventional mole fraction calculation requires a normalisation procedure to account for differences between repeat runs. Granted, this method is explicitly for GC analysis, though it is the most accurate way of accounting for differences between environmental changes during measurements. This issue is explored in chapter 7.

The fundamental principles of IR spectroscopy for use in quantitative analysis can be attributed to the Beer-Lambert law (equation 2.6.1) which describes the relationship between absorbance A (arb), path length L (cm), molar absorptivity  $\varepsilon$  (mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>), and concentration C (mol<sup>-1</sup> dm<sup>3</sup>). (24) From equation 2.6.1 absorbance is proportional to concentration at constant path length and molar absorptivity.

$$A = log_{10} \frac{I_o}{I} = \varepsilon cl$$
 Equation

2.6.1

#### 2.6.2 Tunable filter spectroscopy

The IR instrument used in this work utilises a new and improved method of spectral coverage using tunable filter optics. Most conventional IR analysers use multi-beam single-wavelength (MBSW) optics which only allow for a moderate spectral coverage. The issue with limited wavelength coverage is that it becomes much more difficult to differentiate or speciate similar chemical structures such as those found in hydrocarbon matrixes. This is due to the difficulty of applying chemometric models to non-linear data and additive spectra. In addition to overlapping of peaks, spectral non-linearity adds to the complexity of spectral deconvolution and application of chemometric models. (25) Spectral non-linearity is defined here as spectral changes due to different matrixes and components concentrations, peak broadening and peak shifting. With a tunable filter, a continuous spectral coverage is achieved which allows for the deconvolution of complex spectra.

# 2.6.3 Description of Infrared instrument configuration

The TFS IR analyser supplied by MKS instruments contains several interconnecting components protected by a stainless-steel casing. The fiber optic cables extend from the instrument to a measuring probe which is inserted into the cryostat (figure 2.6-2).



Figure 2.6-2 – TFS-IR analyser and experimental set-up

The TFS-IR analyser uses a Fabry-Perot interferometer consisting of highly reflective mirrors to produce an array of spectral wavelengths. The fiber optics carry the incident light to the probe measurement point and the light passes through the measuring cell. The path length of the measuring cell is 1cm. The detected light is sent back through a different optical fiber to a charge-coupled detector (CCD). Details of each component are described in Annex B. Data collection and processing is described in the following section.

#### 2.6.4 Data collection and analysis

The data collection and analysis for IR is completely different to that in Raman spectroscopy. Where Raman spectroscopy shows well-defined peaks comparable to GC, IR analysis is much more complicated due to the overlapping of spectra for each measured component. The method of spectral processing is shown in figure 2.6-3. Firstly, a background spectrum is taken at the final cooling temperature prior to the gas condensation process. An algorithm is used to combine the raw spectrum of the measured reference liquid with the background spectrum to produce a processed spectrum. The first derivative of the processed spectrum is used. Finally, an algorithm is applied to account for spectral non-linearity and to differentiate between components.



Figure 2.6-3 – TFS IR spectral processing

The TFS calibration software outputs a processed file (table 2.6.1) containing information about component mole fractions, date and time, mixture identity, physical properties including WI, GCV and Z, and some diagnostic properties of the instrument itself. The calculated mole fractions and their uncertainty for each tested mixture is applied to the testing method ISO 10723- Natural gas-performance evaluation of analytical systems. (26) This method is described thoroughly in chapter 7.

Date	Time	Note	Methane	Ethane	Propane	iso-	n-	iso-	n-	Gross	Z	SG	WI	T, deg
						Butane	Butane	Pentane	Pentane	CV				С
6/28/2017	6:48:18	Mix	99.3289	0.1527	0.1667	0.1963	0.1819	-0.0235	-0.0395	37.8258	0.998	0.5586	45.4514	40.044
	AM	17_0465_01_110K												
6/28/2017	6:48:53	Mix	99.2407	0.1126	0.1608	0.1959	0.1804	-0.0221	-0.038	37.793	0.998	0.5591	45.434	40.046
	AM	17_0465_01_110K												
6/28/2017	6:48:58	Mix	99.2594	0.1179	0.176	0.2004	0.184	-0.022	-0.0392	37.8004	0.998	0.559	45.435	40.05
	AM	17_0465_01_110K												
6/28/2017	6:49:03	Mix	99.2697	0.1342	0.1696	0.1969	0.1835	-0.0231	-0.0397	37.7993	0.998	0.5589	45.4286	40.018
	AM	17_0465_01_110K												
6/28/2017	6:49:08	Mix	99.2779	0.1472	0.1792	0.1933	0.1829	-0.0229	-0.0396	37.7908	0.998	0.5588	45.4109	39.984
	AM	17_0465_01_110K												
6/28/2017	6:49:13	Mix	99.2329	0.1041	0.1733	0.1945	0.1812	-0.0219	-0.0377	37.7889	0.998	0.5591	45.4243	39.964
	AM	17_0465_01_110K												
6/28/2017	6:49:18	Mix	99.2207	0.1114	0.1817	0.1952	0.1886	-0.0217	-0.0375	37.7878	0.998	0.5591	45.4124	39.966
	AM	17_0465_01_110K												
6/28/2017	6:49:53	Mix	99.2503	0.1262	0.1698	0.1928	0.1801	-0.0227	-0.0396	37.7857	0.998	0.5589	45.4152	39.974
	AM	17_0465_01_110K												
6/28/2017	6:49:58	Mix	99.2402	0.1226	0.1928	0.1983	0.1869	-0.0223	-0.04	37.7818	0.998	0.559	45.4035	39.968
	AM	17_0465_01_110K												
6/28/2017	6:50:03	Mix	99.2471	0.1319	0.1785	0.1922	0.1876	-0.0223	-0.0398	37.7847	0.998	0.5589	45.4083	39.97
	AM	17_0465_01_110K												

Table 2.6-1 – TFS IR processed data output
# 2.7 Experimental Overview

To summarise the overall process and the individual steps taken for a single experiment, a brief overview follows. Firstly, the primary reference gas mixture is prepared and verified in accordance with ISO-6142. The Raman/IR probe is cleaned prior to being inserted into the cryostat and secured. Both chambers of the cryostat are fully evacuated down to 10<sup>-6</sup> mbar. The cryostat is cooled down to the appropriate temperature using liquid nitrogen. The gas mixture is condensed and the system pressurised using helium. Measurements from both the GC and Raman/IR instruments are made simultaneously. The same gas mixture is used to calibrate the GC to obtain the correct response functions. The response functions are combined with the measured vaporised-liquid to provide a reference composition. A schematic representation of the overall experimental process is shown in figure 2.7-1.

Figure 2.7-1 - Schematic representation of overall experimental process



# 2.7.1 Approach to calibration and validation

For a calibration to be valid, it must cover at-least the range of what is being measured. (27) A single-point calibration assumes linearity in the response function. However, for accurate measurements, this assumption cannot be made because an instruments response may show some inherent nonlinearity or off-set. (27) Figure 2.7-2 illustrates the error that may be incurred due to a single-point calibration if the actual response function is nonlinear. To properly



Figure 2.7-2- Error in instrument response due to single point calibration

account for this error, a multi-point calibration covering the full range of expected measured parameters is required. (26) Selection of calibration and validation mixtures are discussed in chapters 5, 6 and 7 and are based on real composition ranges encountered in industry.

An instrument validation can be defined as a series of processes which validates the performance specifications published by the manufacture of the instrument. This is to ensure that the amount of error in the system will not affect the final measurement result. In this work, the precision, linearity and accuracy of composition and various calculated physical properties (GHV, Wobbe index, density etc.) of both spectroscopic instruments are evaluated and compared with the GC reference instrument.

Definitions of precision, linearity and accuracy are defined here for clarification. Linearity is an assessment of the minimum and maximum levels at which an analyte can be accurately measured. Since, we assume linearity in the response function via the Placzek relation for Raman spectroscopy and Beers law for IR spectroscopy, this will be tested via a GLS regression analysis. Precision is the degree of reproducibility among several repeat independent measurements of the same sample. It is used to measure the random error of the analytical method and this will be displayed as a standard deviation of the repeat measurements. Finally, accuracy is the closeness in agreement between the measured and true value- the true value being the reference liquid values determined via the methods described in section 2.4.3. Comparison of measured and reference composition determines the systematic error of the analytical method.

## 2.7.2 Model development and testing

The development of the calibration models was made by Kaiser optical systems Inc. for the Optograf Raman spectrometer and MKS instruments Inc. for the TFS-IR spectrometer. The data collected via both instruments was collated and sent to Kaiser and MKS for their specialist algorithm design and optimisation. Once developed, the models were installed to the instrument and validated.

### 2.8 Safety

Safety was a big consideration during the development of the overall experimental process. High pressure gases, cryogenic liquids and lasers made the bulk of safety concerns. However, with appropriate safety equipment and mitigation procedures the laboratory was made safe and prepared in the event of equipment failures.

### 2.8.1 Cryostat

The main safety risk associated with operating the cryostat includes exceeding the maximum pressure of 3 bara specified by the manufacturer. This risk is mitigated by using two pressure relief valves (one attached to the sampling port and one to the sample chamber pump port, see figure 1.2.2) set to 3 bara. The cryostat is left overnight during the measurement process, therefore, if: (a) the liquid nitrogen is depleted, (b) there is a malfunction with the heater or (c) the vacuum in the outer chamber is compromised, the relief valves would release the excess pressure caused by the rapid heating of the liquid mixture.

## 2.8.2 Cryogenic liquids

The main risks associated with handling cryogenic liquids include cold burns and asphyxiation. Liquid nitrogen expands to 695 times its original volume upon vaporisation and has no indicator such as an odorant. Unconsciousness may be induced if the volume of nitrogen is enough to reduce the oxygen content in the room to below 19.5%. LNG undergoes a similar volumetric expansion and so can induce the same effects. Ventilation systems in the laboratory are activated during experiments to release any excess gas. Adequate body protection is used during the handling of liquid nitrogen dewar.

# 2.8.3 High pressure flammable gases

Calibration gas mixtures in this work are prepared in 10L stainless steel cylinders with a pressure of up to 60 bar and are not required to be secured in or out of use. However, 50L Parent cylinders containing the pure gases to be decanted to the calibration cylinder can exceed 200 bar and therefore must be secured and capped when in and out of use. Steel toe-capped shoes and safety spectacles are equipped always when handling high pressure flammable mixtures.

#### 2.8.4 Lasers

The Optograf uses a class 3B green laser where direct vision of the beam at less than 13cm distance for more than 10 seconds is dangerous. A lock mechanism ensures the laser source does not escape the tip of the probe when the probe is being handled. No laser safety spectacles are required when handling this laser system.

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# 3 Optimising the experimental design and operation

### 3.1 Summary

The experimental method was optimised based on several modifications to the cryostat itself and with the aid of thermodynamic modelling. A restriction was applied to the sampling line from the liquid to the GC allowing for a more stable and representative gas flow. A displacer was attached to the instrument probe to minimise the headspace volume between the probe and the exhaust chamber, ensuring that the inevitable boil-off gas from the LNG is kept to a minimum to curtail changes in liquid composition. The volume of the inner cryostat space was calculated to be 1.87L and 1.33L for the instrument probe with and without the displacer, respectively. The required volume of LNG was calculated to be 1L based on the dimensions of the cryostat and the thermophysical processes occurring between the liquid-sample chamber interface. Finally, the mass of LNG required was calculated using 7mixture compositions. The difference between the minimum and maximum density was calculated to be 13.1%, therefore the mass of LNG required is calculated on a case-by-case basis.

### 3.2 Introduction

Optimising the system design was made over the course of this research. In this chapter, the main optimisations that have a significant impact on the operation efficiency of the cryostat and the method of liquefaction are explored. The experimental design was optimised through several approaches. Physical modifications to the cryostat and sampling components allowed for more stable and representative sampling from the sample liquid to the GC for analysis. Thermophysical modelling allowed for optimising the volume of LNG required to minimise the headspace above the liquid. This chapter explores the said optimisation approaches and their impact on operation efficiency and measurement.

# 3.3 The effects of outer vacuum pressure on sample chamber cool-down efficiency

The outer vacuum chamber provides a heat barrier between the sample chamber and the external environment. This heat barrier is required to promote a fast and long-lasting cooling process to maintain the stability of the cryogenic liquid. Any heat influx from the external environment will impact upon the cooling efficiency of the liquid nitrogen and might cause undesirable heating during measurements. The cooling efficiency is described here as the lowest temperature achieved, how long that temperature is maintained and how fast the system heats up naturally without any application of heat. Since at higher pressures there are more molecules available to transfer energy, it would require more work from the liquid nitrogen to achieve the same temperature than a system with fewer molecules available to transfer energy.

A study was conducted to demonstrate the impact of outer vacuum pressure on the cooling efficiency of the sample chamber. For this study, four outer vacuum pressures 1 bar, 10<sup>-3</sup> bar, 10<sup>-5</sup> bar and 10<sup>-8</sup> bar were selected and tested. For each experiment, the liquid nitrogen storage tanks were half-filled and the flow rate of liquid nitrogen was maximised by fully opening the control valve. Half-filling the liquid nitrogen storage tanks allowed for a shorter experiment time. The temperature profiles (figure 3.3.1) of the sample chamber were measured over a period of 9 hours.



Figure 3.3-1- Sample chamber cool-down efficiency as a function of outer vacuum pressure

It is clear from figure 3.3.1 that there is a significant difference in temperature profiles between all outer vacuum pressures. By comparing the temperature profiles at 1 bar and 10<sup>-8</sup> bar pressure, we see a significant difference in the lower temperature limits. At 1 bar, the lower temperature limit is 263K, compared with 185K at 10<sup>-8</sup> bar. Furthermore, the difference in natural heating is also large, where at 1 bar the temperature difference from 1.5 hours and 9 hours is 32K (295K-263K) compared with 12K (197K-185K) at 10<sup>-8</sup> bar. This evidences that a better vacuum results in a more efficiency cooling process.

Several experiments described in chapters 6,7 and 8 were repeated because of a poor vacuum during the measurement procedure. The measurement procedure ensues overnight, therefore it is required that a sufficient supply of liquid nitrogen is available to keep the liquid stable for the duration of the measurements. Since a change in temperature of the liquid would increase the flow rate of the sample to the GC, this would result in changes to the injected volume. Figure 3.3.2 demonstrates the effect that this undesirable heating and change in flow rate has on the peak areas of C1-C5 components. A temperature profile is also included to demonstrate when the sample chamber ran out of cooling capacity and started to heat up. In comparison, figure 3.3.3 demonstrates a measurement profile with good repeatability and a stable sample chamber temperature.

Tables 3.2.1 and 3.2.2 show the differences in repeatability as a relative standard deviation (%RSD) between both sets of data described in figures 3.2.2 and 3.2.3. The maximum %RSD calculated for the unstable data (table 3.2.2) was 51.7, compared with 4.38 for the stable data (table 3.2.1).

Fortunately, the loss of the outer vacuum was observed in the early stages of the experiments. The loss in outer vacuum could result from gas escaping from the sample chamber to the outer vacuum when pressurised, or a small

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leak could be present on the outer surfaces, therefore it was decided that the vacuum chamber would be evacuated after every experiment as a safeguard.



Figure 3.3-2- Measurement stability with poor repeatability of GC components C1-C5 and sample chamber temperature



Figure 3.3-3- Measurement stability with good repeatability of GC components C1-C5 and sample chamber temperature

component	average peak area	SD	%RSD		
methane	4496078.3	101162.9	2.3		
ethane	507453.5	230363.0	45.4		
propane	626627.5	319253.4	50.9		
iso-butane	89452.1	45229.7	50.6		
n-butane	167730.2	84603.6	50.4		
iso- pentane	51675.3	26690.8	51.7		

Table 3.3-1- repeatability data for unstable GC measurements for components C1-C5.

Table 3.3-2- repeatability data for stable GC measurements for components C1-C5

component	average peak area	SD	%RSD			
methane	4408068	3454.88	0.078376			
ethane	1148769	2677.713	0.233094			
propane	480167.4	1514.551	0.315421			
iso-butane	213685.1	2067.606	0.967595			
n-butane	186737.4	3013.463	1.613744			
iso- pentane	27785.58	1218.817	4.386509			

# 3.4 Modification of liquid sampling line to prevent enrichment of liquid composition

The liquid sampling port was modified such that the thermodynamics of the sampling process promoted a stable flow of gasified liquid from the sample chamber to the GC. Sampling a multi-component cryogenic liquid is a challenging process, especially when we are dealing with multiple components with different boiling points. Upon sampling, the cryogenic liquid is forced up the sampling tube and heat influx from the sampling tube itself causes vaporisation of the liquid, creating a potential multiphase flow. In a

uniform sampling tube, the flow of both phases is free to move back down the tube and enter the liquid, thus altering the liquids original composition. If a restriction (figure 3.4.1) is applied on the sample tubing, a one-way flow and a controlled vaporisation is achievable. Figure 3.4.2 illustrates the processes occurring with and without a sampling restriction.

Although this change was a minor modification, it's impact on the measurement process was significant. Initial testing showed standard deviations of peak areas to be substantially large in that they could not be used for analysis in any way. Following this problem, temperature sensors were applied just before the outlet of the sampling tube to see if there was a substantial difference between the temperature of the sampling line and liquid. The temperature exceeded the boiling point of the liquid mixture by 20-25K. This suggested that vaporisation was occurring in the sampling tube, something that was overlooked during system design. To counter this, the sampling line restriction guaranteed three key features:

- 1. Preventing back flow of vaporised liquid into the sample chamber
- 2. Stable and continuous vaporisation of liquid to gas
- 3. Homogenous vaporisation



Figure 3.4-1 – Position of sampling line modification



Figure 3.4-2- Thermophysical effects of applying a restriction to the sampling line

# 3.5 Modification of instrument probe insert

Due to the volume of headspace separating the probe from the exhaust chamber, a displacer was made to fit around the probe such that this extra volume would be significantly reduced. With this extra volume, the boil-off gas quantity – an inevitable process occurring to the low boiling point of nitrogen and higher vapour pressure of methane - of the LNG would be larger. This is problematic since the principle aim is to produce a reference liquid with an identical composition to the reference gas. Large volumes of gas in the headspace would cause the liquid composition to change even though the density of the liquid is much greater than the density of the gas.

The displacer extends the length of the probe from the top of the cryostat to just above the bottom of the probe. It is made from polyamide because it is a relatively cheap material and has high resistance to low temperatures. The internal diameter was made slightly larger than the outer diameter of the probe since under cryogenic conditions the polyamide contracts. A schematic diagram of the displacer position with reference to the cryostat is shown in figure 3.5-1.

Figure 3.5-1 – Schematic showing Raman probe with displacer polyamide insert.



# 3.5.1 Calculation of cryostat internal volume with the Raman probe with and without a displacer insert.

The schematic diagram of the cryostat shown in figure 2.2-1 (chapter 2) provides dimensions of the inner sample chamber. However, the shape of the sample chamber and the displaced volume by the instrument probes makes it troublesome to get an accurate calculation of the total internal volume (sample chamber and probe). Alternatively, the volume was estimated using the gas equation (equation 3.2.1) - which relates the pressure, P, and volume, V, to the number of moles, n, universal gas constant, R, and temperature, T, - by adding a known mass of nitrogen and measuring the resulting pressure difference. The compressibility factor, Z, is an extra term added to account for non-ideal gas behaviour and is a ratio of the molar volume of a gas to the molar volume of an ideal gas at the same temperature and pressure.

$$PV = nRTZ$$
 Equation

#### 3.2.1

The calculated total internal volume the Raman probe with and without a displacer is shown in table 3.6-1. The internal cryostat volume with the probe without a displacer was calculated to be 1.87 L compared with 1.33 L when using the Raman probe with a displacer, giving a volume difference of 0.54 L. From figure 3.6-1 shown in chapter 2, we can make a rough estimation of the SC volume using the dimensions given. The approximate width, height and calculated volume of the SC is 80 mm, 200 mm and 10<sup>6</sup> mm<sup>3</sup> or 1L, respectively. The difference in residual volume (total volume – SC volume) between with the displacer and without the displacer 0.87 L and 0.33 L, respectively.

Probe type		nitrogen					
	Before	After	total	Before	After	total	Total
	additio	addition	added	addition	addition	pressure	internal
	n (g)	(g)	(g)	(psi)	(psi)	(psi)	volume
							(L)
Raman probe	1.651	0.013	1.638	0.00	10.87	10.87	1.87
without insert							
Raman probe	1.339	0.013	1.327	0.00 12.34		12.34	1.33
with insert							

Table 3.5-1- total internal volume estimation of cryostat with Raman probe with and without a displacer insert using the ideal gas equation

The sample chamber cell is calculated to be approximately 1L in volume. Therefore, this should be the volume of LNG condensed inside the cell. If liquid is condensed above this level and passes the heat exchanger coil, there is a risk that LNG will absorb heat through the stainless-steel exhaust chamber since it has direct contact with the top end of the cryostat. If we go below this level, there will be more headspace for gaseous sample to reside, leading to changes in liquid composition. The sensitivity of the total mass of LNG to be added as a function of composition is discussed in the next section.

# 3.5.2 Calculation of LNG mass required to fill the sample chamber

The density of 7 LNG compositions covering the full global range was calculated using GasVLe gas physical property software. From table 3.7-1, the density varies significantly with as a function of composition. Those mixtures

with higher amount fractions of heavier hydrocarbon species have higher densities and this is expected since the individual density of those species is higher than methane. The difference between the minimum and maximum density is 13.1%. Therefore, the amount of liquid required to fill a volume of 1L will be calculated on a case-by-case basis.

compone nt	amount fraction (%mol/mol)										
nitrogen	0.15 0.57 0.83 1.6 1.09 0.69 0.										
methane	99.42	98.42	97.04	95.21	94.1	88.08	79.68				
ethane	0.095	0.22	0.51	1.14	3.13	7.13	13.85				
propane	0.095	0.23	0.42	0.77	1.27	2.12	3.97				
iso- butane	0.078	0.23	0.62	0.39	0.13	1.01	1.32				
n-butane	0.12	0.23	0.42	0.57	0.078	0.92	1.08				
iso- pentane	0.028	0.05	0.08	0.153	0.1	0.028	0.03				
n-pentane	0.018	0.05	0.08	0.163	0.1	0.018	0.02				
density (g/L)	449.03 46	453.90 11	461.29 52	468.21 91	468.09 34	491.73 71	516.93 77				

Table 3.5-2 – Sensitivity of required LNG mass to changes in composition

# 3.5.3 Impact of headspace volume on the loss of nitrogen to the gas phase

The mass of nitrogen lost to the headspace was estimated with 1L of LNG for a 300ml and 800ml headspace volume which is equivalent to the Raman probe with and without a displacer, respectively. Equation 3.2-1 is rearranged to calculate the number of moles of nitrogen, n, and then multiplied with the density of nitrogen at standard conditions to determine the mass of nitrogen in both volume cases. The mass of nitrogen for a 300ml and 800ml headspace volume was calculated to be 0.047g and 0.126g, respectively. In the assumption that the nitrogen mass in the liquid is approximately 10g, which is equivalent to 0.6 %mol/mol for 1L of LNG, the loss of nitrogen to the headspace with a volume of 800ml is approximately 1.2%. Conversely, the loss of nitrogen to the headspace with a volume of 300ml is approximately 0.45%. Therefore, minimising the headspace volume is critical in minimising changes in liquid composition.

### 3.6 Conclusions

The cryostat liquefaction process was optimised through several approaches, each offering improvements in efficiency and operation. The vacuum in the outer jacket of the cryostat demonstrated to significantly impact the cooling efficiency of liquid nitrogen. An extremely low vacuum pressure of 10<sup>-8</sup> mbar is required such that the liquid nitrogen flow remains constant throughout the sampling process. Higher vacuum pressures prevent the liquid nitrogen from cooling and maintaining the set temperature of the sample chamber since its depletion rate is much faster. The set temperature must be stable over the course of the measurement procedure since any small temperature change can have a significant impact on the flow rate of sampled liquid resulting from changes in liquid vapor pressure.

A physical restriction applied to the outlet of the LNG sampling line provided a homogenous and controlled vaporisation process required for repeat GC analyses. This restriction promotes a one-way flow of liquid and prevents any fractionated gas to enter the liquid phase, therefore maintaining as close as possible the original composition of the liquid. This physical alteration had the greatest impact on the success of repeat measurements. Without this restriction, an inhomogeneous and inconsistent flow would result in poor repeatability and inability to discern liquid composition data.

Finally, Using the ideal gas law, the total internal volume of the sample chamber was calculated to be 1.3 L with the Raman probe and displacer and 1.8L with the Raman probe without a displacer, giving a difference of 0.5L.

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Theoretical predictions of gas phase nitrogen showed a 1.2% and 0.45% loss of nitrogen with the Raman probe with and without a displacer, respectively. Therefore, the displacer demonstrated to be a requirement to minimise the tendency of nitrogen to reside in the headspace, and consequently minimise changes in liquid composition which is fundamental to the verification procedure described in chapter 2.

# 4 Verification of synthetic liquefied natural gas (LNG) reference mixtures

#### 4.1 Summary

The development of a LNG composition standard is part of work package 2 of the European Metrology Research Programme (EMPR) for LNG metrology. (1) The Dutch Metrology Institute (VSL) and the National Physical Laboratory (NPL) are heavily involved in delivering this project which started in 2014. However, to this point there has been no successfully developed LNG liquefier that is able condense reference gas mixtures and measure a sample accurately using an analytical instrument. A summary report for work package 2 confirmed an unsatisfactory system set-up due to leakages. (2) Nevertheless, testing is ongoing with the final aim of cross-validating the system planned in work package 2 with the cryostat system developed in this research project. In a new wave of projects proposed by the EMRP, a different approach is being adopted whereby rather than a liquefier being used, a super-critical vaporiser is being developed to allow an unbiased vaporisation process. This is to be used in conjunction with GC methods. Furthermore, this chapter demonstrates the validation of the cryostat and its sampling system for the verification of a range of synthetic LNG reference mixtures.

The cryostat sampling system was verified against a strict set of measurement criteria using seven gravimetrically prepared reference liquids. A comparison between the measured composition and gravimetric composition showed calculated physical properties GCV, gas density and liquid density to be within the maximal permissible errors specified in EN12838- suitability testing of LNG sampling systems. Values for GCV, gas density, and liquid density equalled to 1.195 kJ/kg (MPE: 9 kJ/kg),  $1.5x10^{-4}$  kg/m3 (MPE:  $3x10^{-4}$  kg/m3),  $4.9x10^{-2}$  kg/m3 (MPE: 0.15 kg/m3), respectively. In addition, the differences between the measured and corrected composition and between the gravimetric and measured composition give En values <1 indicating no statically significant differences between data sets. This demonstrates that the cryostat in combination with the measurement set-up is suitable for sampling and determining the composition of reference liquid inside the cryostat sample chamber to a high degree of accuracy.

## 4.2 Introduction

The production of reference material in terms of traceable standards requires a rigorous approach to validation and verification. (3; 4; 5; 6) This holds true for all reference materials that are used to calibrate and validate measuring instruments since they are what determine, or at least contribute to, the final accuracy and uncertainty budget. (7; 8) If a reference standard has no record of verification, then there is no confidence in its unit of measure. The reference standard should also be traceable, in that, it should be linked to a national measurement standard through an unbroken chain of comparisons with stated uncertainty, each contributing to the final uncertainty budget. (6) Without a metrological chain of traceability, any reference standard can be regarded as null and not fit-for-purpose. Therefore, it was a requirement that the liquid reference standards developed in this project be verified to ensure their accuracy and traceability. During the condensation process described in chapter 2, one cannot assume that composition of the liquid mixture is identical to the gravimetrically prepared gas mixture since there is a physical change in phase from gas to liquid. In the case of gas compositions containing nitrogen, where the boiling point differs substantially from the other components (table 4.2-1), it is inevitable that a small percentage of the total nitrogen concentration will remain in the gas phase, thus altering the final sampled liquid composition. This also holds true for methane, though to a lesser extent since its boiling point is much higher.

These unfavourable processes can be minimised by maximising the liquid volume in the sample chamber space, since there this results in less space for the gas phase to reside. However, the space in which the measurement probe and displacer is situated is not fully occupied, and given that the liquid level should be kept as close as possible to the sample chamber to prevent vaporisation due to differences in temperature between copper and steel, the condensation process will still allow for gas to reside in the headspace. These effects are illustrated in figure 4.2-1.

Table 4.2-1- boiling points of measured components methane, ethane, propane, iso-butane, n-butane, iso-pentane, n-pentane, and nitrogen at 1 bar pressure. Boiling points calculated with GasVLe ™.

Component	Boiling point (°C) 1 bar
Methane	-161.63
Ethane	-88.87
Propane	-42.66
i-Butane	-12.33
n-Butane	-0.90
i-Pentane	27.25
n-Pentane	35.34
Nitrogen	-195.92



Figure 4.2-1- demonstrates the temperature gradient of the cryostat and the air spaces most likely to accommodate undesired gas phase nitrogen and methane.

The consequence of having a partial gas phase in the sampling space causes a difference between the calibration gas mixture composition and the sampled liquid composition. This is of great significance since we require the correct liquid composition to calibrate the spectroscopic instrument. To account for this difference, we apply a correction method in the analysis of GC composition data. This method couples the measured nitrogen composition with the remaining components from the calibration gas composition, providing an accurate representation of the liquid composition. The details of this method are described thoroughly in chapter 2 section 4.4-3. Upon exploring the questions raised from the overall experimental design including; the cryostat, spectroscopic instrument, sampling system and GC, a paradox surfaced. In the current custody transfer measurement systems, LNG is sampled, vaporised and measured using a GC. However, for validating spectroscopic instruments that measure the liquid phase directly, there needs to be a confirmation of what that liquid composition is. It simply is not true to assume that the liquid composition is equivalent to the gravimetric gas composition because of the above-mentioned issues. Consequently, the performance of the cryostat vaporiser contributes heavily to the quality of the validation, since what is measured is used to develop the spectroscopic model. The paradox is broken by validating the vaporiser system against a set of established performance criteria to give confidence in the sampling process and consequently the spectroscopic model.

Considering the issues presented, the aim of this study is to determine whether the cryostat can produce liquid reference mixtures over a specified range of compositions with a high degree of accuracy. Since the sampling process in this project imitates that of a commercial LNG sampling system, whose processes are described in chapter 1, it can be evaluated in terms of error relating to the differences in measured and corrected composition and of their calculated physical properties. This includes relating the amount fraction of each component using the En ratio statistical significance test and the maximal permissible error (MPE) in gross calorific value, liquid density and gas density specified by EN12838-Installations and equipment for liquefied natural gas -Suitability testing of LNG sampling systems, described in section 4.3.2.1.

### 4.3 Experimental procedure

Seven gas mixtures were prepared and verified per the procedures described in chapter 2 section 2.3. The design of the gas mixtures was based on Shell's LNG cargo database, since this allows real expected LNG compositions to be evaluated based on a global expected composition range. For each gas condensation, the cryostat was prepared per chapter 2 section 2.2. The minimum and maximum operating temperatures for each composition were determined via thermophysical calculations using GasVLe and these are presented in the following section.

Data analysis was performed per chapter 2 section 2.4. The number of repeat runs for GC analysis was 48 for calibration and 96 for analysis of the sampled liquid composition. The data was then collated and the physical properties calculated via GasVLe for subsequent evaluation per the criteria specified in EN12838 and the EN ratio, described thoroughly in section 4.3.2.1.

For intelligibility of what data is being compared, a description follows. There are three sets of data that are used in the evaluation of the cryostat sampling system: the gravimetric composition, measured composition and corrected composition. The gravimetric composition is the content of the calibration gas mixture. The measured composition is what is measured by the GC after the liquid is sampled and homogenised and is the content of the liquid phase minus the gas lost to the headspace. The corrected composition is a modified version of the measured composition that considers the loss of nitrogen into the headspace. Figure 4.3-1 illustrates the differences between the three quantities mentioned.



Figure 4.3-1- illustration of differences between measured, corrected and gravimetric composition.

The En ratio is used to uncover any statistically significant differences between the individual components of the gravimetric composition and corrected composition, and between the measured composition and corrected composition. The MPEs specified in EN12838 are used to assess the cryostat sampling system by comparing the differences in the physical properties calculated from the measured composition (what the GC thinks is in the cryostat sample chamber) and corrected composition (the actual contents in the cryostat sample chamber).

# 4.3.1 Design of liquefied natural gas (LNG) type calibration mixtures

The design of the LNG-type calibration mixtures was based solely on Shell's LNG cargo history database (Appendix). The range of compositions determined from the database is shown in table 4.3-1. The seven designed calibration mixtures are shown in table 4.3-2. The mixture compositions considered here represents the full composition range shown in table 4.3-1. physical properties for each mixture composition including boiling point, melting point and GCV are provided in table 4.3-2.

The boiling and melting points for all seven compositions range from 107.19K to 113.35K and 82.91K to 90.20K, respectively. Therefore, the operating window within which the cryostat can be used to reduce the likelihood of forming solids and gases is between 90.20K and 107.19K. Since anything outside this range would result in solidification of the heavier hydrocarbon species or vaporisation of the lighter hydrocarbon species, this operating window should be used to minimise changes in liquid composition.

	mole fraction (%mol/mol)					
component	min	max				
nitrogen	0.10	1.56				
methane	79.86	99.30				
ethane	0.10	13.77				
propane	0.10	3.92				
iso-butane	0.08	1.29				
n-butane	0.08	1.05				
iso-	0.03	0.15				
pentane						
n-pentane	0.02	0.16				

Table 4.3-1- real LNG composition ranges determined from Shell's LNG cargo history database.

component	Mix_1V	Mix_2V	Mix_3V	Mix_4V	Mix_5V	Mix_6V	Mix_7V	
nitrogen	0.25	0.57	0.83	1.56	1.56 1.09		0.10	
methane	99.30	98.43	97.04	95.22	94.10	88.14	79.86	
ethane	0.10	0.22	0.51	1.18	3.13	3.13 7.13		
propane	0.10	0.23	0.41	0.41 0.77		1.26 2.12		
iso-butane	0.08	0.23	0.62	0.39	0.13	1.01	1.29	
n-butane	0.12	0.23	0.42	0.57 0.08		0.92	1.05	
iso- pentane	0.03	0.05	0.08 0.15		0.10	0.00	0.00	
n-pentane	0.02	0.05	0.08	0.16 0.10		0.00	0.00	
Boiling point (K)	110.84	109.95	109.26	107.19	108.66	110.20	113.35	
Melting point (K)	90.20	89.56	88.58	87.27	86.53	82.90	78.35	
GCV (MJ/m3)	38.00	38.24	38.91	39.11	39.38	42.39	45.90	

Table 4.3-2- 7 designed calibration mixtures based on real LNG composition ranges showing boiling point, melting point and GCV variation.

# 4.3.2 Evaluation criteria and statistical significance test

This section describes the evaluation criteria and statistical test used to compare the gravimetric, measured, and corrected composition data. The evaluation criteria described in EN12838 was chosen because it is an internationally recognised standard that is used for assessing 'real' LNG sampling systems in the European region. The statistical test termed the 'normalised error ratio', referred hereafter as the 'En Ratio' is used in this study to compare the measured and corrected composition directly rather than from calculated physical properties to give additional information about the data, specifically if there are statistically significant differences between individual components.

# 4.3.2.1EN12838 - Installations and equipment for liquefied natural gas - Suitability testing of LNG sampling systems

The EN12838 standard (9) is a European standard with British standard status. It specifies tests to be carried out to evaluate the suitability of LNG sampling systems to determine the composition from a sampled LNG stream, in combination with an analytical device of choice. The evaluation criteria specified in this standard incorporates provisions from ISO 6976 – Natural gas – Calculation of calorific values, density, relative density and Wobbe index from composition (10) and ISO 6578 – Refrigerated hydrocarbon liquids – Static measurement – Calculation procedure (11). Gross calorific value (GCV) and gas density ( $\rho_{NG}$ ) are calculated in accordance with ISO 6976 and LNG density ( $\rho_{LNG}$ ) is calculated in accordance with ISO 6578. All physical property calculations derived from composition are made in the GasVLe gas physical property software which follows the methods in the standards described above.

The suitability criteria shown in in table 4.3-3 gives 2 different accuracy classes for two sampling system types, continuous and discontinuous. The difference between continuous and discontinuous LNG sampling are discussed in detail in chapter 1. Broadly, they differ in the way the vaporised gas is handled after LNG is sampled. Continuous sampling stores the vaporised gas in gas holders, which is then measured offline after the completion of the sampling process. Conversely, discontinuous sampling

measures the vaporised gas during the sampling process. Since the discontinuous sampling measurement is more likely to be effected by process conditions, it is given a larger maximal permissible error in all physical properties. In this study, the maximal random error specified by the continuous process is chosen along with Class A. This is to ensure that the cryostat sampling system is subject to assessment against the most stringent criteria.

		Sampling system					
		Continuous					
Class	Physical	Maximal	Maximal				
	property	random error	random error				
	GCV in kJ/kg	9.0	54				
A	ρ <sub>NG</sub> in kg/m <sup>3</sup>	3.0 x 10 <sup>-4</sup>	18 x 10 <sup>-4</sup>				
	$\rho_{LNG}$ in kg/m <sup>3</sup>	0.15	0.9				
	GCV in kJ/kg	18	1.1 x 10 <sup>2</sup>				
В	ρ <sub>NG</sub> in kg/m <sup>3</sup>	6.0 x 10 <sup>-4</sup>	36 x 10 <sup>-4</sup>				
	ρ <sub>LNG</sub> in kg/m <sup>3</sup>	0.30	1.8				

Table 4.3-3- class A and B suitability criteria for LNG sampling systems, continuous and discontinuous sampling. (9)

### 4.3.2.2En ratio statistical test

The En ratio (equation 4.3.1) is a statistical evaluation used to compare a set of measured and reference values with the inclusion of their associated uncertainty. (12; 5; 13) It is used to identify outliers and possible failures in the measurement process. The result of the evaluation is a pass or fail, whereby a pass is subscribed if the absolute difference between the reference ( $y_{k,corr}$ ) and measured  $(y_{k,meas})$  result divided by square root sum of their uncertainties  $(u^2(y_{k,ref}), u^2(y_{k,meas}))$  is less than ±1.

$$\frac{|y_{k,ref} - y_{k,meas}|}{\sqrt{u^2(y_{k,ref}) + u^2(y_{k,meas})}} < 1$$
 equation

If the result of equation 4.3.1 is greater than 1 then one or a combination of the following reasons is valid, assuming the reference value and its associated uncertainty is correct:

1) The uncertainty is incorrect

4.3.1

- 2) The measurement is incorrect
- 3) The measurement equipment is faulty
- 4) The measurement procedure is faulty

This statistical test provides supplementary information to the evaluation criteria about how well the individual components of a measured and reference value and their uncertainties agree with each other.

# 4.4 Results and Discussion

Tables 4.4-1 – 7 display the gravimetric composition, measured composition, corrected reference composition, En numbers between the measured and corrected composition, and between the corrected and gravimetric composition for mixtures 1V to 7V. Differences in the calculated physical properties between the measured and corrected composition for mixtures 1V

to 7V are also included. The EN12838 suitability criteria is also shown in each table for side-by-side comparison.

The En ratio between the gravimetric and corrected composition is larger for nitrogen than all other species. This is expected since nitrogen has the highest potential of residing in the headspace due to its lower boiling point. Conversely, the En ratio between the measured and corrected composition is zero for nitrogen since it is the same value, but higher for all other components because the method of normalisation causes a compensation shift for components C1-C5.

The En number for the measured-corrected comparison is on average higher than the gravimetric-corrected comparison because the corrected composition uses components C1-C5 from the gravimetric composition. These differences are shown in figure 4.4-1. Furthermore, all En numbers are within the specified allowable range of  $\pm$  1 demonstrating statistical agreement between the gravimetric and corrected composition, and between the corrected and measured composition. The maximum and minimum En numbers are 0.98 and 0, respectively.

Mix_1V	gravimetric values		corrected reference values		measured values			difference	En-number		absolute difference		EN12838 suitability criteria
component	xi	U(xi)	xic	U(xic)	yi	% RSD	U(yi)	(% relative)	grav- corrected	meas- corrected	KJ/kg	kg/m3	
nitrogen	0.248	0.000	0.245	0.004	0.244	0.888	0.004	0.000	0.768	0.000			
methane	99.300	0.010	99.303	0.007	99.305	0.004	0.007	0.000	-0.210	0.316			
ethane	0.100	0.000	0.100	0.000	0.100	0.340	0.001	-0.008	-0.002	-0.410			
propane	0.098	0.000	0.098	0.001	0.098	0.727	0.001	-0.009	-0.002	-0.436			
iso-butane	0.081	0.000	0.081	0.001	0.081	0.686	0.001	-0.009	-0.002	-0.467			
n-butane	0.123	0.000	0.123	0.001	0.122	0.683	0.002	-0.007	-0.003	-0.416			
iso- pentane	0.030	0.000	0.030	0.000	0.030	0.762	0.000	-0.009	-0.002	-0.486			
n-pentane	0.020	0.000	0.020	0.000	0.020	0.747	0.000	-0.009	-0.002	-0.510			
GCV kJ/kg	55257.324		55259.879		55260.516			-0.001			0.637		9.000
Gas Density (kg/m3)	0.688		0.688		0.688							0.0001	3.0 x 10 <sup>-4</sup>
LNG Density 93K (kg/m3)	452.045		452.036		452.013							0.023	0.150

Table 4.4-1- Mix\_1V composition data, En numbers and calculated physical properties.
Mix_2V	gravimetric values		corrected reference values		measured values			difference	En-nı	ımber	abso differe	lute ence	EN12838 suitability criteria
component	xi	U(xi)	xic	U(xic)	yi	% RSD	U(yi)	(% relative)	grav- corrected	meas- corrected	KJ/kg	kg/m3	
nitrogen	0.573	0.001	0.566	0.005	0.566	0.269	0.003	0.000	0.607	0.000			
methane	98.430	0.010	98.437	0.007	98.437	0.003	0.005	0.000	-0.060	0.012			
ethane	0.220	0.000	0.220	0.001	0.221	0.309	0.001	-0.002	-0.007	-0.100			
propane	0.226	0.000	0.226	0.001	0.226	0.364	0.002	-0.005	-0.004	-0.146			
iso-butane	0.230	0.000	0.230	0.001	0.230	0.384	0.002	-0.003	-0.004	-0.102			
n-butane	0.228	0.000	0.228	0.001	0.228	0.390	0.002	-0.003	-0.004	-0.083			
iso- pentane	0.046	0.000	0.046	0.000	0.046	0.427	0.000	-0.002	-0.004	-0.069			
n-pentane	0.047	0.000	0.047	0.000	0.047	0.414	0.000	-0.001	-0.004	-0.018			
GCV kJ/kg	54861.285		54867.215		54867.688			-0.001			0.473		9.000
Gas Density (kg/m3)	0.697		0.697		0.697							0.0000	3.0 x 10 <sup>-4</sup>
LNG Density 93K (kg/m3)	456.357		456.338		456.319							0.018	0.150

Table 4.4-2- Mix\_2V composition data, En numbers and calculated physical properties.

Mix_3V	gravimetri		corrected		measured			difference	En-nı	ımber	absol	ute	EN12838
	С		reference		values						differe	nce	suitability
	values		values										criteria
component	xi	U(xi)	xic	U(xic)	yi	%	U(yi)	(%	grav-	meas-	KJ/kg	kg/m3	
						RSD		relative)	corrected	corrected			
nitrogen	0.831	0.001	0.827	0.004	0.827	0.365	0.006	0.000	0.762	0.000			
methane	97.041	0.010	97.046	0.011	97.054	0.002	0.005	0.000	-0.259	0.563			
ethane	0.511	0.001	0.511	0.002	0.508	0.170	0.002	-0.005	-0.008	-0.816			
propane	0.411	0.000	0.411	0.002	0.409	0.254	0.002	-0.004	-0.010	-0.536			
iso-butane	0.622	0.001	0.622	0.002	0.620	0.303	0.004	-0.003	-0.009	-0.455			
n-butane	0.418	0.000	0.418	0.002	0.417	0.311	0.003	-0.003	-0.010	-0.428			
iso-pentane	0.083	0.000	0.083	0.000	0.083	0.372	0.001	-0.003	-0.009	-0.326			
n-pentane	0.082	0.000	0.082	0.000	0.082	0.362	0.001	0.000	-0.011	-0.004			
GCV kJ/kg	54452.746		54456.133		54457.164			-0.002			1.031		9.000
Gas Density	0.715		0.715		0.714							0.0001	3.0 x 10-4
(kg/m3)													
LNG Density	463.796		463.785		463.743							0.042	0.150
93K													
(kg/m3)													

## Table 4.4-3- Mix\_3V composition data, En numbers and calculated physical properties.

Mix_4V	gravimetr ic values		corrected reference values		measured values			difference	En-number		absolute difference		EN12838 suitability criteria
component	xi	U(xi)	xic	U(xic)	yi	%	U(yi)	(%	grav-	meas-	KJ/kg	kg/m3	
						RSD		relative)	corrected	corrected			
nitrogen	1.563	0.002	1.564	0.003	1.563	0.180	0.006	0.000	-0.027	0.000			
methane	95.223	0.010	95.224	0.006	95.224	0.003	0.005	0.000	-0.005	-0.003			

ethane	1.185	0.001	1.185	0.003	1.187	0.225	0.005	0.005	-0.001	0.348			
propane	0.766	0.001	0.766	0.001	0.767	0.061	0.001	0.001	-0.001	0.075			
iso-butan	<b>e</b> 0.386	0.000	0.386	0.001	0.385	0.188	0.001	-0.004	-0.001	-0.283			
nMpxit8100	gravifietric	0.001	confected	0.001	measured	0.212	0.002	difference	-0. <b>£</b> 041nu	mber 254	absolute diff	erence	EN12838
iso-pentar	e values	0.000	retetence	0.001	v∕a1v <del>1€</del> s	0.323	0.001	-0.006	0.000	-0.253			suitability
n-pentan	<b>e</b> 0.155	0.000	valuses	0.000	0.155	0.290	0.001	-0.005	0.000	-0.178			criteria
componer	nt xi	U(xi)	xic	U(xic)	yi	%	U(yi)	(%	grav-	meas-	KJ/kg	kg/m3	
						RSD		relative)	corrected	corrected			
Gast Doorsi	ty 10.079248	0.001	0.128	0.004	0.028	0.380	0.008	0.000	0.075	0.000		0.0001	3.0 x 10-4
methane	94.101	0.009	94.102	0.011	94.114	0.005	0.010	0.000	-0.051	0.670			
LNETDENS	ty 47.02374	0.003	47012795	0.008	4301.2018	0.142	0.009	-0.003	-0.003	-0.614		0.027	0.150
propane	1.261	0.001	1.261	0.002	1.260	0.132	0.003	-0.001	-0.005	-0.224			
is (kg/ma)	<b>e</b> 0.132	0.000	0.132	0.000	0.132	0.177	0.000	-0.002	-0.003	-0.514			

Table 4.4-5- Mix\_5V composition data, En numbers and calculated physical properties.

n-butane	0.079	0.000	0.079	0.000	0.079	0.197	0.000	-0.003	-0.002	-0.579			
iso-	0.101	0.000	0.101	0.001	0.100	0.272	0.001	-0.006	-0.001	-0.673			
pentane													
n-pentane	0.102	0.000	0.102	0.000	0.102	0.292	0.001	-0.003	-0.002	-0.461			
GCV kJ/kg	54116.012		54116.414		54117.313			-0.002			0.898		9.000
Gas	0.728		0.728		0.728							0.0001	3.0 x 10-4
Density													
(kg/m3)													
LNG	470.374		470.373		470.331							0.042	0.150
Density													
93K													
(kg/m3)													

Table 4.4-6- Mix\_6V composition data, En numbers and calculated physical properties.

Mix_6V	gravimetric values		corrected reference values		measured values			difference	En-nu	ımber	absolute dif	ference	EN12838 suitability criteria
component	xi	U(xi)	xic	U(xic)	yi	%	U(yi)	(%	grav-	meas-	KJ/kg	kg/m3	
						RSD		relative)	corrected	corrected			
nitrogen	0.685	0.001	0.679	0.004	0.679	0.132	0.002	0.000	0.984	0.000			
methane	88.139	0.009	88.146	0.008	88.145	0.006	0.011	0.000	-0.524	-0.061			
ethane	7.128	0.007	7.128	0.007	7.130	0.089	0.013	0.000	-0.052	0.112			
propane	2.122	0.002	2.123	0.002	2.123	0.081	0.003	0.000	-0.052	0.166			
iso-butane	1.009	0.001	1.009	0.002	1.008	0.142	0.003	-0.001	-0.038	-0.258			

n-butane	0.915	0.001	0.915	0.002	0.915	0.223	0.004	-0.001	-0.029	-0.129			
GCV kJ/kg	53948.293		53953.539		53953.621			0.000			0.082		9.000
Gas	0.786		0.786		0.786							0.0000	3.0 x 10-4
MRISU	gravimetric		corrected		measured			difference	En-nı	umber	absolute dif	ference	EN12838
MR 90 LNG	gravimetric		corrected		measured			difference	En-nı	Imber	absolute dif	ference 0.002	EN12838
LNG Density	gravimetric values <sup>7</sup>		corrected reference values		measured 494ues values			difference	En-nı	Imber	absolute dif	ference 0.002	EN12838 suitability criteria

Table 4.4-7-Mix\_7V composition data, En numbers and calculated physical properties.

component	xi	U(xi)	xic	U(xic)	yi	%	U(yi)	(%	grav-	meas-	KJ/kg	kg/m3	
						RSD		relative)	corrected	corrected			
nitrogen	0.100	0.000	0.098	0.002	0.098	0.736	0.001	0.000	0.894	0.000			
methane	79.862	0.008	79.865	0.012	79.869	0.013	0.020	0.000	-0.119	0.205			
ethane	13.769	0.014	13.769	0.010	13.775	0.039	0.011	0.000	-0.028	0.122			
propane	3.920	0.004	3.920	0.004	3.917	0.068	0.005	-0.001	-0.017	-0.375			
iso-butane	1.293	0.001	1.293	0.003	1.290	0.107	0.003	-0.003	-0.005	-0.182			
n-butane	1.054	0.001	1.054	0.002	1.052	0.123	0.003	-0.003	-0.004	-0.125			
GCV kJ/kg	53886.203		53887.723		53888.918			-0.002			1.195		9.000
Gas	0.852		0.852		0.852							0.0002	3.0 x 10-4
Density													
LNG	517.862		517.858		517.808							0.050	0.150
Density													
93K													



Figure 4.4-1- En number comparison between gravimetric and corrected difference in composition and measured and corrected difference in composition.

The absolute differences in GCV, gas density and liquid density between the measured and corrected reference values are shown in tables 4.4.1-7. The minimum and maximum values for the absolute differences in GCV between measured and corrected composition are 0.082 kJ/kg and 1.195 kJ/kg, respectively. This is much lower than the MPE value of 9 kJ/kg. The same trend can be seen for gas density and liquid density predictions. The minimum and maximum values for gas density differences are 8.0x10<sup>-6</sup> kg/m3 and 1.5x10<sup>-4</sup> kg/m3, respectively, and is much lower than the MPE value of 3x10<sup>-4</sup> kg/m3. For liquid density differences, the minimum and maximum values are 2.3x10<sup>-3</sup> kg/m3 and 4.9x10<sup>-2</sup> kg/m3, respectively, and is well within the MPE value of 0.150 kg/m3. Furthermore, the absolute differences in GCV, gas density and liquid density between the measured and corrected composition are well within the MPE values defined by EN12838 in table 4.3-3. Therefore,

it can be concluded that the cryostat sampling system is suitable for determining the composition of sampled liquefied natural gas.

On comparing the measured nitrogen amount fraction with the percentage difference between measured and gravimetric nitrogen amount fraction shown in figure 4.4-2, there is a negative correlation whereby higher amount fractions correspond to smaller differences. This is not an expected outcome since at equilibrium the concentration of nitrogen should be higher in the gas phase at higher nitrogen amount fractions per Henry's law (14), which states that the amount of gas dissolved in a liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid (equation 4.4.1).

$$p_i = K_H * c_i$$
 equation

4.4.1

Where, *p* is the partial pressure of the component i above the liquid, *c* is mol fraction of component i in the liquid, and  $K_H$  is Henry's law constant.

Taking Henry's law into account and assuming a finite space for gas phase nitrogen to reside in the sample chamber headspace, we would expect to see



*Figure 4.4-2- percentage difference between measured- gravimetric nitrogen amount fraction versus measured nitrogen amount fraction.* 

a positive correlation between the measured amount fraction and the amount fraction of nitrogen residing in the headspace. However, this assumes that nitrogen has the same solubility in all liquid mixture compositions, and is not influenced by an over-pressurisation by helium during measurement. Also, it doesn't account for differences in operating conditions such as the time taken for equilibrium to be reached, the quantity of liquid produced, error in temperature and pressure measuring equipment, and the boiling point of the liquid mixture. Therefore, the assumptions made could be possible explanations for the differences in behaviour observed for nitrogen

Investigating the solubility of nitrogen in different liquid mediums was not part of the project scope, however it could have provided important information for

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improving the experimental design. A potential investigation is given in chapter 9-futher work.

Furthermore, the repeatability of the measured data suggests instability in the sampling and measurement process when compared with a typical calibration of the GC with direct gas injection from the calibration gas cylinder. Table 4.4-8 provides a comparison between the measured percentage relative standard deviation (%RSD) values for Mix\_1V to Mix\_7V and the GC calibration data set for Mix\_1V. It is clear from table 4.4-8 that there is a significant difference in repeatability between the sampled liquid analysis and calibration gas analysis.

	1							
			% RSD	in measur	ed comp	osition		
	nitrogen	methane	ethane	propane	iso-	n-	iso-	n-
					butane	butane	pentane	pentane
Mix_1V	0.888	0.004	0.340	0.727	0.686	0.683	0.762	0.747
Mix_2V	0.269	0.003	0.309	0.364	0.384	0.390	0.427	0.414
Mix_3V	0.365	0.002	0.170	0.254	0.303	0.311	0.372	0.362
Mix_4V	0.180	0.003	0.225	0.061	0.188	0.212	0.323	0.290
Mix_5V	0.380	0.005	0.142	0.132	0.177	0.197	0.272	0.292
Mix_6V	0.132	0.006	0.089	0.081	0.142	0.223		
Mix_7V	0.736	0.013	0.039	0.068	0.107	0.123		
GC calibration Mix_1V	0.07	0.01	0.03	0.10	0.08	0.07	0.13	0.12

Table 4.4-8- repeatability for Mix\_1V - 7V measured composition and Mix\_1V calibration data.

The poorest repeatability for a complete mixture analysis is seen for Mix\_1V where %RSD values range from 0.004 to 0.888. The best repeatability was seen for Mix\_6V with %RSD values ranging from 0.006 to 0.223. Overall, methane shows the best repeatability followed by ethane, propane, iso-butane, n-butane, nitrogen, iso-pentane, and n-pentane. This pattern is expected since the amount fraction range for each component follows the

same order discounting nitrogen due to the previously mentioned issues. The reason for this trend is that larger amount fractions are less influenced by GC peak area fluctuations due to sheer scale.

The repeatability of liquid sampling measurement can be attributed to three areas of the sampling process; the point of vaporisation, the liquid-gas interface, and the temperature gradient of the sample chamber. Ultimately, a stable and homogenised gas flow needs to be established to achieve a repeatable GC analysis. Changes in sample injection sizes are the main contributor to poor repeatability.

The vaporisation of liquid at the tube restriction discussed in chapter 3 section 3.4 causes small pulsations of gas flow to the GC via an intermediate homogeniser. These pulsations, however minor they are, in combination with a sample gas holder for mixing, have an impact on the flow rate of the sample to the GC. Differences in flow rate result in changes in sample size injections and subsequently different peak intensities and areas. This would most likely have the greatest impact on the repeatability of the measurements. However, sample size effects can be minimised by a mathematical procedure of normalisation described in chapter 2 section 2.4.3.

During sampling, there is a disruption to the liquid-gas equilibrium by the descending movement of the liquid layer, therefore the diffusion of gas, mainly methane and nitrogen, in and out of the liquid is constantly fluctuating. This could result in slight changes in sampled composition over the period of measurements. An over pressure with helium helps to minimise an equilibrium favouring gas formation, however it cannot wholly prevent it.

Ideally, the temperature gradient across the sample chamber should remain as uniform as possible to minimise heat convection processes. Although we

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measure the temperature of the sampling cell near the heat exchanger, we assume that the measured temperature is representative of the whole sampling cell. If we consider there may be a varying temperature profile and the presence of heat influx regions at the solid surface, this would result in convection flows of different density layers via the processes shown in figure 4.4-3.



Figure 4.4-3- free convection circulation of LNG inside a vessel. (16)

In figure 4.4-3, heat passes from the external environment to the walls of the sample chamber (1), the warmed LNG becomes lighter and rises due to density differences (2), evaporation takes place at the surface removing heat and the preferential lighter components (3), and the cooler LNG falls (4). The wall superheat, defined as the temperature difference required to facilitate heat transfer between a solid and fluid, is relatively small for LNG with values ranges between 0.01 to 0.1K and 0.1 to 1K for cold methane vapour. (15)

Therefore, only subtle changes in surface temperature would be required to promote the free convection circulation of LNG in the sample chamber.

It is possible that these small differences in temperature between the solid surface and liquid could perturb the gas-liquid equilibrium and consequently alter the liquid composition. However, with a constant cooling process during measurements and a relatively small volume for gas to occupy due to the influence of helium overpressure, it is not likely to have a huge impact on measurement repeatability. It is more likely that the vaporisation processes occurring at the sampling outlet restriction combined with the intermediate gas sample holder have the greatest impact on measurement repeatability.

## 4.5 Conclusions

In conclusion, all seven tested mixture compositions Mix\_1 to Mix\_7 have confirmed to fall within the suitability criteria specified by EN12838 with maximum values for GCV, gas density, and liquid density equal to 1.195 kJ/kg (MPE: 9 kJ/kg), 1.5x10<sup>-4</sup> kg/m3 (MPE: 3x10<sup>-4</sup> kg/m3), 4.9x10<sup>-2</sup> kg/m3 (MPE: 0.15 kg/m3), respectively. In addition, the differences between the measured and corrected composition and between the gravimetric and measured composition give En values <1, signifying no statically significant difference between composition data. This demonstrates that the sampling system of the cryostat in combination with the measurement setup is suitable for determining the composition of sampled liquid to a high degree of accuracy. Consequently, this provides confidence in the development of the spectroscopic models described in the following chapters, which are based on corrected compositions derived from combining the measured and gravimetric data.

An attempt was made to describe the behaviour of nitrogen as a function of amount fraction. An increasing amount fraction resulted in smaller differences between the measured and gravimetric compositions. Consequently, this contradicts Henry's law which predicts more vapor phase nitrogen at higher amount fractions. However, several other factors including; helium overpressure, nitrogen solubility in different compositions, temperature gradients, equilibrium time, and volume of liquid were not considered and therefore may be plausible explanations for the behaviour overserved. A potential investigation is provided in chapter 9 - Further work.

The repeatability of the liquid sampling measurement was shown to be poorer than the direct measurement from the calibration gas cylinder. %RSD values ranged between 0.002 and 0.888 for liquid sampling measurement and between 0.01 and 0.13 for direct calibration gas measurement. It was also found that a higher amount fraction equates to a lower repeatability excluding nitrogen due to its tendency to reside in the gas phase. The higher the amount fraction the less influence small changes in composition have on GC peak integration. The poorer measurement stability was mainly attributed to the thermophysical vaporisation processes occurring at the sampling outlet restriction, however heat absorption and heat convection processes in the sample chamber were explored and considered as feasible explanations, though with a lower overall contribution.

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# 5 Raman spectroscopic analysis of mixed refrigerant (MR) composition

#### 5.1 Summary

Monitoring and controlling the mixed-refrigerant (MR) composition during LNG production has gained much attention, especially in floating LNG and locations enduring extreme conditions since this can cause dramatic changes in physical properties of the MR. New developments in laser instrumentation have made such measurements possible with high-throughput, rapid analysis and high sensitivity. Developments in fibre optic technology have allowed access to remote locations where human accessibility may be limited or prohibited, for example in extreme temperature offshore locations. The ability to monitor and control MR composition remotely provides several benefits including: rapid response to changes in MR composition resulting from system errors, maintaining thermal efficiency by matching hot and cold composite curves and providing supplementary information for system optimisation. This chapter explores the application of Raman spectroscopy for measuring MR-type compositions and evaluates the impact of composition changes on heat capacity.

Analysis of the reference compositions obtained from combining GC measured data with gravimetric data showed all mixtures MR1-MR6 to be within the suitability criteria specified in EN12838, thus providing confidence in the reference values used in the development of the Raman model. The Raman model was assessed based on its accuracy and repeatability by comparing calculated heat capacity values between the reference and measured composition. The error and uncertainty for validation mixtures MR5 and MR6 was calculated to be  $7.65 \pm 1.21 \text{ J/kg/K}$  and  $30.05 \pm 6.42 \text{ J/kg/K}$ , respectively. These errors and uncertainties were considered insignificant in having an impactful change to the thermodynamic efficiency of a refrigeration process. However, further studies would be required to validate this premise and to determine measurement limits within which the error and uncertainty would be acceptable.

#### 5.2 Introduction

The production of LNG is both complex and expensive due to the strict product specifications required for gas treatment (1; 2; 3) and the energyintensive refrigeration cycles (4; 2; 5) required for liquefaction. The liquefaction plant accounts for approximately 50% of the capital cost of an LNG production facility (6), therefore the design considerations of a LNG refrigeration system are critical in providing an efficient and economic LNG production process. Numerous refrigeration processes have been developed over the past 50 years to provide cost reductions resulting from improved cycle efficiencies. There are three main types of refrigeration process; nitrogen expander process, cascade process, and mixed refrigerant (MR) process. Of these, the MR processes are the most popular due to their desirable thermodynamic properties, high cycle efficiency, reliability and simplicity of operation. (5) Several commercially available land-based LNG liquefaction processes include: Propane mixed-refrigerant process (AP-C3MR) (5; 7), duel mixed-refrigerant process (DMR) (8), mixed fluid cascade process (MFC) (9) and the AP-X process which is based on the AP-C3MR process for larger production capacities (7). An extensive review of these processes is documented in (10). Of these processes, the AP-C3MR process is the most popular because most of the current gas production fields have a low- to medium-production capacity. This technology accounts for up to 75% of total LNG production worldwide. (11; 7; 12) The DMR, PMR, and AP-X processes are based on the AP-C3MR process, however are designed to boost liquefaction capacities to between 4-12 Mtpa compared with 3-6 Mtpa for the AP-C3MR process. The MR composition used in most of these processes constitute Nitrogen and several hydrocarbons including Methane, Ethane and Propane.

In the AP-C3MR process (figure 5.2.1), the feed gas is first pre-cooled using a single component refrigerant (Propane) to around -35 °C. After this first precooling step, the feed gas is passed through a set of tube-circuits through a main cryogenic heat exchanger (MCHE) where the MR acts as the working fluid to liquefy the feed gas to around -160 °C. Through a series of compression and expansion stages, the propane and MR are re-cycled back into the cooling cycles. Propane has two main functions in this process. Firstly, it is used to pre-cool the feed gas before it enters the MCHE. Secondly, it is used to pre-cool the MR after it has undergone vaporisation and compression. The dual use of Propane and MR minimises the equipment steps required for liquefaction whilst maintaining cycle efficiency. (7)

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*Figure 5.2-1- AP-C3MR liquefaction process for LNG* The whole liquefaction process is extremely sensitive to changes in environmental conditions such as temperature and pressure. This effect is greater for offshore floating LNG facilities (FLNG) since they are subject to greater wind and wave turbulence, and mechanical stresses. An increase in temperature decreases the density and therefore reduces the heat capacity of the MR. This causes a mismatch in the hot and cold composite curves between the MR and feed gas in the MCHE, resulting in a warmer feed gas. A warmer feed gas requires more energy input to achieve the same LNG yield. Conversely, a decrease in external temperature results in an increase in heat capacity of the MR, allowing the potential for energy savings only when the MR composition is altered and matched with the feed gas composition.

LNG refrigeration process efficiency can be defined as the heating value of the feed gas minus the heating value of the MR divided by the heating value of the feed gas, assuming the feed gas composition and environmental conditions are fixed. (13) The efficiency of the refrigeration process is dependent on the efficiency of the heat exchange and the efficiency of the turbomachinery (compressors and expanders). (2) The choice of MR composition is dependent upon the feed gas composition and consequently the hot and cold composite curves of the overall heat transfer process. A mixture of Nitrogen, Methane, Ethane and Propane are the chosen because their evaporation curves are comparable to the condensation curves of natural gas. MRs are zeotropic and therefore have a gliding evaporation and condensation temperature caused by differences in volatility between the individual MR components. Therefore, monitoring the MR composition as it changes due to the gliding evaporation profile is required to determine the corrective actions required to maintaining a constant composition.

Optimisation of MR composition for LNG production is complex since there are many processes involved. Some proposed optimisations have been explored in (14; 15; 16) to improve overall system efficiency. The aim of any MR composition optimisation is to reduce overall energy consumption by minimising the cumulative duty of the hot and cold streams. A smoother temperature profile between the two streams lowers the entropy of the system, resulting in less work required by the compression shafts and decreased exergy losses from the MR. Therefore, when the MR evaporation curve matches the feed gas condensation curve there is a lower entropy system as shown by the temperature approach in figure 5.2-2.



Figure 5.2-2- Composite heat transfer process between hot (feed gas) and cold (MR) streams at 293K ambient temperature.

To illustrate the differences in evaporation curves between MR compositions, figure 5.2-3 shows a typical feed gas, Nitrogen, Propane and six MR curves. It is clear the MR evaporation curves are closer to the NG evaporation curve than for pure components Nitrogen and Propane. This demonstrates why pure components are seldom used in the MCHE for LNG liquefaction, however are still useful for pre-cooling purposes.



Figure 5.2-3 – Phase envelopes for Nitrogen, Propane, natural gas (NG) and six MRs.

The selection of MR composition is important for improving the energy and exergy efficiency of the liquefaction process. Smoother and better-matched temperature profiles of the hot and cold streams (as demonstrated in figure 5.2-2) result in a lower entropy system, hence a greater thermal efficiency. The online monitoring of MR composition has become a requirement, especially in floating liquefaction facilities (FLNG), for initiating rapid responses to changes in composition resulting from system faults, environmental fluctuations and different feed gas compositions.

MR compositions along with design specifications for different refrigeration processes tend to be kept undisclosed due to their commercial sensitivity. The MR compositions used in this work are obtained from Shell Global Solutions and represent part of their MR refrigeration process portfolio. The following sections describe the method design, calibration approach and the resulting accuracy of the Raman MR model.

## 5.3 Method design

The development of the MR model is based on the calibration principles described in chapter 1. However, the MR calibration model uses 3 fewer mixtures compared with 7 mixtures for the LNG calibration model (chapter 6) since the composition range covered is smaller and the requirements for accuracy are lower. 4 mixtures are used for building the calibration model and 2 mixtures are used to the test and validate the model. All 6 mixtures are prepared in accordance with the methods described in chapter 1. Since the MR compositions are completely different to LNG compositions in that they do not contain Butanes or Pentanes, their design was carefully considered with specific attention to the compressibility of each gas and their final mass determination, and their dew lines and J-T cooling curves.

The cryostat and Raman spectrometer were prepared per the methods described in chapter 1. After each condensation and measurement process, the cryostat was left on a vacuum overnight to remove any excess gas and moisture. In addition, the Raman probe was removed and cleaned to reset the background noise to effectively zero. This ensures comparability between each processed MR spectra.

After the first four gas condensations (MR1-MR4), the data was collated and sent to Kaiser Optical Systems Inc. for model development. Two mixtures (MR5 and MR6) were used to validate the model and to test its linearity and accuracy in comparison to the reference GC data. The next section describes the design of the mixtures and their thermodynamic characteristics.

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## 5.3.1 Design of mixtures and prediction of measurement conditions

The calibration mixtures MR1-MR4 were designed within the ranges specified in table 5.3-1. MR1-MR4 compositions (table 5.3-2) were selected to best cover this range by having two high and two low measurement points as illustrated in figure 5.3.1. This provides four measurements points for each component in the MR composition matrix. For models that only require moderate accuracy levels, this number of measurement points was considered sufficient. The testing mixtures MR5 and MR6 were designed within the MR1-MR4 composition ranges except for Nitrogen. Nitrogen was extended slightly to 21.4% (MR5) compared with 20.2 % (MR4) to test above the working range of the model. This provides a validation of how well the model performs outside its calibration range.

	Amount fraction (%mol/mol)							
Component	Minimum	Maximum						
nitrogen	1.9	20.2						
methane	34.7	71						
ethane	12.9	48.4						
propane	1.5	16.2						

Table 5.3-1- MR composition ranges for Raman spectrometer modelling

Table 5.3-2 – Designed MR compositions for model development (MR1-MR4)and validation (MR5 and MR6)

	Amount fraction (%mol/mol)										
Component	MR 1	MR 2	MR 3	MR 4	MR 5	MR 6					
nitrogen	1.9	3.9	11.1	20.2	21.4	4.5					
methane	34.7	39.1	71	66.3	63.9	38.4					
ethane	47.2	48.4	16.4	12.9	14	48					
propane	16.2	8.6	1.5	0.6	0.7	9.1					



Figure 5.3-1 – MR1-MR4 high and low composition ranges

Bubble point lines for all 6 MR mixtures are shown in figure 5.3-2. In figure 5.3-2, a comparison is made between MR1-MR6 and the 7 LNG-type mixtures specified in chapter 4 to demonstrate the differences in bubble variation. Mixtures LNG1-LNG7 show a smaller bubble point range compared with MR1-MR6. In chapter 4, the conditions of the measurement process were based on mixtures compositions LNG1-LNG7, however it is clear from figure 5.3-2 that the same conditions cannot be applied to the MR1-MR6 compositions since there bubble points are dissimilar and do not overlap. Therefore, a separate analysis is required to identify the lower and upper bounds of the measurement conditions.

Figure 5.3-3 shows bubble points and solid points for MR1-MR6 mixtures and for comparison purposes bubble points for LNG1-LNG7 at 0.5 bar, 1 bar, 1.5 bar, 2 bar, 2.5 bar and 3 bar. The bubble point variation at each pressure is wider for the MR mixtures than for the LNG mixtures. The smallest and largest bubble point variation between the MR compositions and LNG compositions is

13.70 K and 6.19 K, and 26.64 K and 7.03 K, respectively (table 5.3-3). It is clear from figure 5.3-3 that as the pressure is increased, on average the difference between the bubble points increases. The MR solid points (table 5.3-4) are less sensitive to changes in pressure because solid formation is isolated in the liquid phase and is determined by solubility. From figure 5.3-3, it can be concluded that the operating range of the cryostat during the measurement process should be between 83 K and 93 K at 2 bar. A pressure of 2 bar is chosen since it is the mid-point and minimises the risk of underpressure and over-pressure in cases where the system may undercool itself due to a heater fault or overheat itself in the sudden absence of liquid nitrogen flow.



Figure 5.3-2 – MR1-MR6 and LNG1-LNG7 bubble point lines.



Figure 5.3-3 – Bubble point variation between MR1-MR6 and LNG1-LNG7 and solid point variation between MR1-MR6 at 0.5 bar, 1 bar, 1.5 bar, 2 bar, 2.5 bar and 3 bar.

	Bubble point (K)							
Pressure	MR 1	MR 2	MR 3	MR 4	MR 5	MR 6	Range	
(Bar)								
0.5	91.42	84.33	81.19	77.61	77.05	82.70	14.37	
1.0	102.44	100.54	94.64	89.49	88.75	98.32	13.70	
1.5	109.97	100.54	94.64	89.49	88.75	98.32	21.22	
2.0	115.84	105.84	98.94	93.29	92.47	103.46	23.37	
2.5	120.74	110.33	102.55	96.48	95.61	107.82	25.13	
3.0	124.97	114.25	105.70	99.25	98.34	111.65	26.64	
	Bubble point (K)							
Pressure	LNG1	LNG2	LNG3	LNG4	LNG5	LNG6	LNG7	Range
(Bar)								
0.5	103.40	101.99	101.11	98.55	100.31	101.83	105.58	7.03
1.0	111.13	109.97	109.26	107.09	108.67	110.19	113.63	6.54
1.5	116.24	115.21	114.60	112.64	114.13	115.66	118.98	6.34
2.0	120.17	119.23	118.68	116.87	118.30	119.85	123.12	6.25
2.5	123.41	122.54	122.04	120.34	121.73	123.30	126.54	6.20
3.0	126.21	125.38	124.93	123.31	124.67	126.27	129.50	6.19

Table 5.3-3 - Bubble point predictions and range for MR1-MR6 and LNG1-LNG7 at 0.5 bar, 1 bar, 1.5 bar, 2 bar, 2.5 bar and 3 bar.

	Solid point (K)							
Pressure (Bar)	MR 1	MR 2	MR 3	MR 4	MR 5	MR 6	range	
0.5	81.09	81.73	74.96	75.00	75.71	81.65	6.77	
1.00	81.10	81.73	74.96	75.00	75.72	81.65	6.77	
1.50	81.10	81.74	74.97	75.01	75.72	81.66	6.77	
2.00	81.11	81.74	74.97	75.01	75.73	81.67	6.77	
2.50	81.11	81.75	74.98	75.02	75.73	81.67	6.77	
3.00	81.12	81.76	74.98	75.02	75.74	81.68	6.78	

Table 5.3-4- Solid point predictions and range for MR1-MR6 at 0.5 bar, 1 bar, 1.5 bar, 2 bar, 2.5 bar and 3 bar.

Another important consideration in the design of MR compositions was to determine the final preparation pressure prior to gravimetric preparations. The final preparation pressure was determined through a trial-and-error analysis by monitoring the intersection of the J-T cooling curve with the dew line for each MR mixture. The optimised J-T cooling curves and dew lines for MR1-MR6 are shown in figure 5.3-4. The maximum preparation pressures are given in table 5.3-5. From the preparation pressure, the mass added to each 10L cylinder can be deduced from equation 5.3.1.

$$m = \frac{PV}{RT} * Z * M_{MR}$$
 Equation

5.3.1



Figure 5.3-4 – Dew line and J-T cooling curve for MR1-MR6 compositions

It was anticipated that MR1, MR2, and MR6 would be problematic due to the presence of their high Propane amount fractions. Since Propane has a higher dew point than all other components, the final pressure is reduced to compensate for the J-T cooling effect. Consequently, this lowering of pressure translates to a lower mass addition. However, another quantity called the compressibility factor Z compensates for the reduction in final cylinder pressure. The compressibility is a term that relates the molar volume of a gas to that of an ideal gas at the same temperature and pressure. Since propane is more compressible than all other components, the same molar quantity of gas takes up less volume. Therefore, the total mass added at the same pressure is greater for MR mixtures containing higher amount fractions of Propane. Table 5.3-4 shows the final masses added for each MR mixture.

Component	Amount fraction (%mol/mol)							
	MR1	MR2	MR3	MR4	MR5	MR6		
nitrogen	1.90	3.90	11.10	20.20	21.40	4.50		
methane	34.70	39.10	71.00	66.30	63.90	38.40		
ethane	47.20	48.40	16.40	12.90	14.00	48.00		
propane	16.20	8.60	1.50	0.60	0.70	9.10		
Max pressure	40	52	60	60	60	52		
(Bar) at 25°C								
MW (g/mol)	27.44	25.71	20.09	20.44	20.76	25.87		
Moles (n)	16.36	16.36	16.36	16.36	16.36	16.36		
Ideal mass (g)	448.87	420.66	328.73	334.39	339.73	423.21		
Compressibility	0.72	0.78	0.91	0.93	0.93	0.78		
(Z)								
Real mass (g)	619.76	539.04	361.46	360.51	366.69	542.79		

Table 5.3-5 - Final added mass calculations for MR1-MR6 in 10L cylinders

## 5.4 Results and Discussion

In this section, a comparison is made between MR1-MR4 Raman spectra. The linearity in response for each measured component is determined by comparing the ratio of peak height to amount fraction. An evaluation of the GC composition data for each MR measurement is made to determine if the reference liquid composition falls within the suitability criteria specified in EN12838. A comparison is made between the results obtained from the Raman model and the GC reference data. Finally, the benchmark criteria set for accuracy is assessed by determining the impact on heat capacity and ultimately thermodynamic efficiency.

## 5.4.1 MR1-MR4 Raman spectra

Raman spectrums for MR1, MR2, MR3 and MR4 are shown in figures 5.4-1:4. Peak positions for nitrogen, methane, ethane and propane are illustrated in figure 5.4-5. It is clear from figures 5.4-1:4 that there are no overlapping peaks and each component can be clearly identified and integrated. Each peak of interest is approximately Gaussian-shaped (Figure 5.4-5). nitrogen shows the closest Gaussian-like characteristics attributed to its peak symmetry, whereas methane, ethane and propane are slightly left-skewed. Figure 5.4-5 shows overlapping spectrums for nitrogen, methane, ethane and propane over 30 repeat runs for MR1 to study the peak drift and laser stability between each run. The peak intensity for all components over the 30 repeat runs changes slightly, however the background spectrum taken for each repeat run compensates for this intensity drift.



Figure 5.4-1 – MR1 Raman spectrum



Figure 5.4-2 – MR2 Raman spectrum



Figure 5.4-3 – MR3 Raman spectrum



Figure 5.4-4 – MR4 Raman spectrum



Figure 5.4-5 – MR1-MR4 stacked Raman spectra with component identification



Figure 5.4-6 – nitrogen, methane, ethane and propane Raman peak drift for 30 repeat measurements.

Figure 5.4-6 shows peak shapes and intensities for each component of interest in MR1-MR4. Interestingly, the peak drift for propane changes significantly between mixtures MR1-MR4, however there is less peak drift observed for methane and minimal peak drift observed for nitrogen and ethane. This may be attributed to the amount fraction of each component measured, since methane and ethane are present in much higher quantities than nitrogen and propane. As described in chapter 2, the peak intensity is a function of the polarisability tensor. The tetrahedral geometry of methane is more polarizable than linear structures since the electron density is more easily distorted due to its highly symmetric geometry (17; 18), therefore its peak intensity is always the highest. In linear structures, more energy is required to 'energise' electrons over a further molecular distance (17). Consequently, even at similar amount fractions of methane, we observe a
significantly lower peak intensity for ethane and propane. nitrogen has fewer 'free' electrons and a strong triple bond, therefore is less polarizable overall.



Figure 5.4-7 – MR1-MR4 peak characteristics of nitrogen, methane, ethane and propane.

The linearity of the Raman instrument was determined by analysing the best fit curves via linear regression analysis. The response Intensity as a function of the amount fraction for each component is shown in Figure 5.4-8. The Pearson correlation coefficient ( $r^2$ ) values for nitrogen, methane, ethane and propane are 0.9905, 0.9968, 0.9916 and 0.9926, respectively. methane showed the best linearity with an  $r^2$  value closer to one. nitrogen showed the poorest linearity with an  $r^2$  value furthest from 1, though this may be due to the lower band of amount fractions measured. Furthermore, it can be concluded that there is a reasonable degree of linearity from the Instruments response values.



Figure 5.4-8 – Linearity of Raman response versus amount fraction for MR components nitrogen, methane, ethane and propane.

## 5.4.2 MR1-MR6 Reference composition analysis

The sampling and analysis of reference liquid composition data using GC was achieved via the methods described in chapter 1. Composition data for MR1-MR6 is shown in tables 5.4-1:6. The differences between the measured and the corrected reference liquid composition are within the 9 kJ/kg maximal permissible error specified in EN12838, which validates the use of the reference values for determining the accuracy of the Raman MR model.

There is a significant difference between the corrected and gravimetric nitrogen amount fraction in mixtures MR1, MR2 and MR6 giving percentage differences of 20.9 %, 14.7 %, 17.9 %, respectively. A repeat condensation was made for mixture MR2, of which the results were identical, to confirm that the different in nitrogen amount fraction was valid and not a result of

instrument error. One might predict that the loss of nitrogen to the headspace is due to a larger amount fraction of nitrogen in the mixture. However, the opposite is true. The lowest amount fractions show the largest ratio of vapour phase nitrogen to liquid (dissolved) phase nitrogen. This behaviour was observed in chapter 4, however for much smaller amount fractions. The reason for such behaviour was attributed to the degree of solubility of nitrogen in different matrixes. The data suggests that nitrogen is less soluble in matrixes with lower amounts of methane and higher amounts of ethane and propane since only small differences between the gravimetric and corrected reference nitrogen are observed when methane is the major matrix component.

#### Table 5.4-1- MR1 reference composition data

MR1	Compo	osition (%mc	ol/mol)			
Componen t	Gravimetri c	GC measured	Corrected reference liquid	Abs. differenc e (Ref-GC)	% Differenc e (Ref- Grav)	EN 1283 8
nitrogen	2.081	1.646	1.646	-0.434	20.875	
methane	34.479	34.315	34.632	0.152	-0.443	
ethane	47.238	47.374	47.448	0.209	-0.443	
propane	16.202	16.665	16.274	0.071	-0.443	
CV (kJ/kg)		51390.25 1	51398.92 2	8.671		9

Table 5.4-2 – MR2 reference composition data

MR2	Compo	osition (%mc	ol/mol)			
Component	Gravimetric	GC measured	Corrected reference liquid	Abs. difference (Ref-GC)	% Difference (Ref- Grav)	EN 12838
nitrogen	4.031	3.437	3.437	-0.594	14.742	
methane	38.992	39.063	39.234	0.241	-0.619	
ethane	48.416	48.880	48.716	0.299	-0.619	
propane	8.560	8.620	8.613	0.053	-0.619	
CV (kJ/kg)		50656.434	50659.227	2.793		9

MR3	Compo	osition (%mo	ol/mol)			
Component	Gravimetric	GC Corrected measured reference liquid		Abs. difference (Ref-GC)	% Difference (Ref- Grav)	EN 12838
nitrogen	11.147	10.496	10.496	-0.651	5.840	
methane	70.942	71.452	71.461	0.519	-0.732	
ethane	16.384	16.519	16.504	0.120	-0.732	
propane	1.528	1.534	1.539	0.011	-0.732	
CV (kJ/kg)		46350.367	46350.297	-0.070		9

## Table 5.4-3 – MR3 reference composition data

## Table 5.4-4 – MR4 reference composition data

MR4	Compo	osition (%mo	ol/mol)			
Component	Gravimetric	GC measured	Corrected reference liquid	Abs. difference	% Difference (Ref- Grav)	EN 12838
nitrogen	20.182	19.680	19.680	-0.502	2.487	
methane	66.108	66.602	66.524	0.415	-0.628	
ethane	13.101	13.118	13.184	0.082	-0.628	
propane	0.608	0.600	0.612	0.003	-0.628	
CV (kJ/kg)		39792.906	39797.766	4.859		9

## Table 5.4-5 – MR5 reference composition data

MR5	Compo	osition (%mo	ol/mol)			
Component	Gravimetric	GC measured	Corrected reference liquid	Abs. difference (Ref-GC)	% Difference (Ref-Grav)	EN 12838
nitrogen	21.486	20.943	20.943	-0.543	2.526	
methane	63.856	64.314	64.297	0.441	-0.691	
ethane	13.959	14.042	14.056	0.096	-0.691	
propane	0.699	0.701	0.704	0.005	-0.691	
CV (kJ/kg)		39019.266	39020.418	1.152		9.000

MR6	Compo	osition (%mo	ol/mol)			
Componen t	Gravimetri c	GC measured	Corrected reference liquid	Abs. differenc e (Ref-GC)	% Differenc e (Ref- Grav)	EN 12838
nitrogen	4.640	3.811	3.811	-0.828	17.858	
methane	38.351	38.234	38.684	0.333	-0.868	
ethane	47.922	48.709	48.338	0.416	-0.868	
propane	9.087	9.246	9.166	0.078	-0.868	
CV (kJ/kg)		50420.82 8	50428.69 1	7.863		9

Table 5.4-6 – MR6 reference composition data

Figure 5.4-9 shows the degree of correlation between the differences in nitrogen vapor lost to the headspace and matrix components methane, ethane and propane. R squared values of greater than 0.915 are observed between each component and the loss of nitrogen vapor to the headspace. This suggests that the solubility of nitrogen is highly correlated with the amount fractions of methane, ethane and propane. Consequently, higher nitrogen solubility levels are observed with higher amount fractions of methane but lower amount fractions of ethane and propane. However, this is not explicitly true since lower amount fractions of ethane and propane would inevitably give rise to higher amount fractions of methane due to normalisation. To truly understand the relationship of nitrogen solubility in different hydrocarbon matrices, an exhaustive study of many mixture combinations would be required, which is not in the scope of this work. However, it is possible to model the amount fraction of nitrogen vapour as a function of temperature in different hydrocarbon matrixes. The next section aims to correlate the thermophysical predictions with the experimental data observed here.



Figure 5.4-9 – Degree of correlation between the loss of nitrogen to the gas phase and components methane, ethane, and propane.

## 5.4.3 Comparison of experimental and modelled predictions of nitrogen vapour formation

The mixtures in this study have components with different boiling points. Consequently, the mixtures are zeotropic, in that they have a gliding temperature of evaporation and condensation. Ultimately, this results in different vapour/liquid compositions at varying temperatures. The following investigation aims to correlate the vapour/liquid compositions observed experimentally with those predicted theoretically.

The differences between gravimetric nitrogen and reference liquid nitrogen amount fractions are summarised in table 5.4-7. Nitrogen vapour phase formation for MR1-MR6 as a function of temperature at 3 different pressures is shown in figure 5.4-10. Predictions of nitrogen vapor formation were made via GasVLe gas physical property calculation software. From figure 5.4-10, there is a significant difference in nitrogen vapour formation at 1 bar, 1.5 bar and 2 bar with approximately 5K temperature difference between each pressure. It is also clear that the boiling points for nitrogen decrease as the amount fraction increases. Mixtures MR4 and MR5 show the lowest boiling points for nitrogen and this is expected since they contain the highest amount fractions of nitrogen.

Gravimetric amount fraction (%mol/mol) MR1 MR2 MR3 MR4 MR5 MR6 nitrogen 2.08 4.03 11.15 20.18 21.49 4.64 gravimetric nitrogen 1.64 3.43 10.68 19.68 20.94 3.81 reference liquid nitrogen 26.64 17.48 4.33 2.54 2.59 21.74 difference (%)

Table 5.4-7- Differences between gravimetric nitrogen and reference liquidnitrogen amount fractions for MR1-MR6.



Figure 5.4-10 – nitrogen vapour phase amount fraction for MR1-MR6 as a function of temperature at (a)1 bar, (b) 1.5 bar and (c) 2 bar.

On closer inspection of each MR vapour formation curve, one would expect MR1 to show the lowest boiling point since it has the greatest loss of nitrogen vapour to the headspace. However, MR1 has the highest boiling points at 102.5 K, 110 K and 116 K at 1 bar, 1.5 bar and 2 bar, respectively. A similar observation is made for MR6. The operation temperature and pressure of the cryostat for each mixture was 93K and 2 bar, which is far from the boiling points of MR1 and MR6 at these conditions. Therefore, it is presumed that the thermal conditions of the cryostat do not explain the difference in gravimetric nitrogen and measured nitrogen.

Furthermore, it is more likely that the solubility effects of nitrogen in different hydrocarbon matrixes is the reason for the observed nitrogen difference. However, a level of doubt could also be attributed to the accuracy of the thermodynamic model used. It is possible that the equations-of-state (EOS) used in GasVLe<sup>™</sup> version 3.4 performs inadequately at the lower limits of their modelling capability, though a large inaccuracy is not expected.

# 5.4.4 The effects of mixed-refrigerant (MR) composition on heat capacity

As discussed in section 5.2, heat capacity is one of the most important variables in the LNG refrigeration process because it determines the quantity of heat the refrigerant can remove. Heat capacity is sensitive to changes in temperature, pressure and composition. The heat composite curves of the refrigeration process are modelled prior to process operation to minimise the cumulative duty of both hot and cold fluids. The MR composition is fundamental in the modelling approach since its heat capacity dictates

cumulative duty, thus thermodynamic efficiency. Therefore, an analysis of the effects of composition on heat capacity is justified here.

Figure 5.4-11 shows the differences in heat capacity between MR1-MR6 in the temperature range 130K-280K and pressure range 1bar – 100bar. It is clear from figure 5.4-11 that each MR exhibits different heat capacities at varying temperatures and pressures. Most notably, MR1 shows the highest heat capacity of 24000 J/kg\*K at 280K in the range of 40bar to 60bar, which is approximately 75% higher than the maximum heat capacity for MR2-MR6.

There is a clear pattern between similar MR compositions showing closely matching heat capacity values. MR1 and MR2 are both similar in composition and show closely matching heat capacity curves for all temperature ranges. Additionally, MR4 and MR5 also share similar composition values and therefore have closely matching heat capacity curves, though the pattern becomes less obvious at higher temperatures, specifically at 250K and 280K. MR2 and MR6 show the closest heat capacity values since their compositions are almost identical. MR3 and MR6 show their highest heat capacity values at 130K and 60bar, and 220K and 65bar, respectively. These patterns are further illustrated in figure 5.4-12 with maximum, minimum and average heat capacity values.



Figure 5.4-11 – Heat capacity of mixtures MR1-MR6 at 130 K, 160K, 190K, 220K, 250K and 280K over the pressure range 1bar -100bar.



Figure 5.4-12 – (a) minimum, (b) maximum and (c) average heat capacity values for mixtures MR1-MR6.

Furthermore, from the data presented there is no predictable pattern that relates MR composition to heat capacity. Heat capacity values for pure components nitrogen, methane, ethane and propane over the same temperature and pressure range is shown in figure 5.4-13. Both nitrogen and methane show the highest heat capacity values at 130K and 190K, respectively as demonstrated by the peak spikes in figure 5.4-13. The heat capacity of ethane and propane is more uniform and generally increases with increasing temperature.

There is a reasonable degree of correlation between ethane and propane and a high degree of correlation between propane and temperature as shown in table 5.4-10. Table 5.4-11 shows MR2 and MR6 are more correlated to temperature than MR1, MR3, MR4 and MR5, and MR1-MR6 are weakly correlated to pressure.



Figure 5.4-13 – Heat capacity of pure components nitrogen, methane, ethane and propane at 130K, 160K, 190K, 220K, 250K and 280K covering the

#### pressure range 1-100bar.

	methane	ethane	propane	nitrogen	Р	Т
methane	1					
ethane	-0.06	1				
propane	-0.18	<mark>0.69</mark>	1			
nitrogen	0.21	-0.19	-0.36	1		
Р	0.25	0.17	-0.01	0.17	1	
Т	-0.22	0.63	<mark>0.90</mark>	-0.51	0	1

## Table 5.4-8 – Correlation matrix for pure components methane, ethane, propane and nitrogen

Table 5.4-9 – Correlation matrix for mixtures MR1-MR6

	Pressure	Temp	MR1	MR2	MR3	MR4	MR5	MR6
Pressure	1							
Temp	0	1						
MR1	0.11	0.34	1					
MR2	0.32	<mark>0.48</mark>	0.41	1				
MR3	0.43	-0.12	-0.07	0.01	1			
MR4	0.36	-0.25	-0.11	-0.08	0.65	1		
MR5	0.38	-0.26	-0.11	-0.08	<mark>0.68</mark>	<mark>0.97</mark>	1	
MR6	0.32	<mark>0.48</mark>	0.42	1.00	0.01	-0.08	-0.08	1

From figure 5.4-14, the minimum, maximum and average heat capacity of MR1 is higher than any of the pure components. In addition, the average heat capacity of MR2 and MR6 is higher than any of the pure components. This suggests that the MR mixtures differ greatly from ideal mixtures and do not follow ideal behaviour, where the ideal solution requires that the isobaric heat capacity to be equal to the amount fraction weighted sum of the individual heat capacities of each pure component, as shown in equation 5.4.1. Ideal calculations of heat capacity do not consider the effects interacting molecules have on their individual heat capacity. From a statistical point of view, to account for molecular interactions, an extra potential energy term must be included. To model the statistical parameters of these systems was not part of the project scope, though it can be concluded that the heating characteristics

of MR mixtures do not follow a clear pattern and do not resemble ideal mixtures.



Figure 5.4-14- Comparison of minimum, maximum and average isobaric heat capacity of MR1-MR6 and pure components methane, ethane, propane and nitrogen over the temperature range 130K-180K and pressure range 1-100 bar.

$$Cp = \sum_{i}^{x} x_i * Cp_i$$

Equation 5.4.1

## 5.4.5 Raman model accuracy and repeatability

The repeatability of the of measured (Raman) composition for mixtures MR5 and MR6 was calculated from 9 repeat analyses with each analysis derived from an average of 30 spectra. Tables 5.4-10 and 5.4.12 show the average composition, repeatability and error for each component in mixtures MR5 and MR6, respectively. Also included in tables 5.4-10 and 5.4-12 are the calculated heat capacities from the measured and reference composition. The Raman model was assessed based on the differences in heat capacity between the measured and reference composition since this is a crucial parameter used to determine the thermodynamic efficiency of the refrigeration process. The error in heat capacity between the measured and reference composition for MR5 and MR6 was calculated to be 7.65 J/kg/K and 30.05 J/kg/K, respectively. The uncertainty on the error was calculated by applying the standard deviation (k=2) to each component in both directions and calculating the absolute differences in heat capacity. The uncertainty for MR5 and MR6 is shown in tables 5.4-11 and 5.4-13 and was calculated to be 1.21 J/kg/K and 6.42 J/kg/K, respectively.

MR5	Amo	unt fraction (	% mol/mol)		
Averaged	methane	ethane	propane	nitrogen	
spectra					
1	64.213	14.216	0.726	20.845	
2	64.091	14.258	0.716	20.935	
3	64.202	14.224	0.718	20.856	
4	64.129	14.235	0.731	20.904	
5	64.142	14.257	0.718	20.883	
6	64.121	14.269	0.725	20.885	
7	64.15	14.243	0.715	20.893	
8	63.928	14.318	0.728	21.027	
9	64.231	14.198	0.715	20.856	Heat capacity (J/kg/K)
Average composition	64.134	14.246	0.721	20.898	2460.424
%RSD	0.141	0.245	0.867	0.266	
Reference composition	64.297	14.056	0.704	20.943	2468.071
Abs. Difference	0.163	-0.190	-0.017	0.045	7.646
% Difference	0.254	-1.352	-2.415	0.215	0.310

Table 5.4-10 – Raman model repeatability and accuracy for MR5

component	Amount fraction (%mol/mol)	Standard deviation U (k=2)	U (-)	U (+)	
methane	64.134	0.180	63.954	64.314	
ethane	14.246	0.070	14.176	14.316	
propane	0.721	0.012	0.709	0.733	
nitrogen	20.898	0.111	20.787	21.009	Abs. Difference
Heat capacity (J/kg/K)			2461.032	2459.822	1.209

Table 5.4-11 – Estimate of uncertainty on calculated heat capacity for MR5

Table 5.4-12 – Raman model repeatability and accuracy for MR6

MR6	An	nount fractio	n (% mol/mo	l)	
Averaged	methane	ethane	propane	nitrogen	
spectra					
1	39.335	47.746	9.029	3.891	
2	39.365	47.74	9.025	3.869	
3	39.485	47.642	9.004	3.869	
4	39.259	47.798	9.038	3.905	
5	39.339	47.761	9.037	3.863	
6	39.466	47.66	9.003	3.871	
7	39.5	47.628	9.014	3.858	
8	39.577	47.576	9.007	3.839	
9	39.493	47.636	8.993	3.878	Heat capacity (J/kg/K)
Average composition	39.424	47.687	9.017	3.872	3359.685
%RSD	0.103	0.075	0.016	0.019	
Reference composition	38.684	48.338	9.166	3.811	3397.738
Abs. Difference	-0.740	0.651	0.149	-0.061	38.052
% Difference	-1.913	1.347	1.626	-1.601	1.120

component	Amount fraction (%mol/mol)	Standard deviation U (k=2)	U (-)	U (+)	
methane	39.424	0.206	39.218	39.630	
ethane	47.687	0.150	47.537	47.837	
propane	9.017	0.032	8.985	9.049	
nitrogen	3.872	0.038	3.834	3.910	Abs. Difference
Heat capacity (J/kg/K)			3362.916	3356.496	6.419

Table 5.4-13 - Estimate of uncertainty on calculated heat capacity for MR6

As explored in the previous section, pressure has a significant impact on the heat capacity of the MR. For this reason, the calculations of heat capacity in tables 5.4-10:13 are based on the pressure that provides the maximum difference in heat capacity such that the maximum error and uncertainty may be determined. The maximum differences in heat capacity for MR5 and MR6 over the pressure range 1-120 bar are shown in figure 5.4-15 and 5.4-16, respectively. The pressure that determined the maximum difference in heat capacity for MR5 and MR6 was 120 bar and 100 bar, respectively.



Figure 5.4-15 – Heat capacity differences for MR5 over the pressure range 1-120bar.



Figure 5.4-16 - Heat capacity differences for MR6 over the pressure range 1-120bar.

# 5.4.6 Sensitivity of heat capacity to changes in MR composition using finite difference analysis

To determine the sensitivity of each MR component, a finite difference analysis was performed. By applying step changes in composition, the sensitivity of each component was calculated by comparing the adjusted composition with the original measured composition. The adjusted compositions shown in tables 5.4-14 and 5.4-15 are the original compositions with the added uncertainty (k=2) determined from the repeatability shown in tables 5.4-10 and 5.4-12. The sensitivity of each component to heat capacity was determined by subtracting the adjusted composition from the original composition.

Methane	Ethane	Propane	nitrogen	heat capacity Cp (J/kg/K)	new Cp - Original Cp
64.30	14.06	0.70	20.94	2304.63	
64.36	14.03	0.70	20.91	2305.29	0.66
64.25	14.12	0.70	20.93	2304.78	0.15
64.29	14.05	0.72	20.94	2304.65	0.02
64.23	14.04	0.70	21.03	2303.21	-1.42

Table 5.4-14 – Sensitivity of heat capacity to changes in MR composition for MR5

Table 5.4-15 - Sensitivity of heat capacity to changes in MR composition for MR6

Methane	Ethane	Propane	nitrogen	heat capacity Cp (J/kg/K)	new Cp - Original Cp
39.42	47.69	9.02	3.87	2783.23	
39.53	47.60	9.00	3.87	2781.65	-1.58
39.40	47.72	9.01	3.87	2783.76	0.53
39.42	47.68	9.03	3.87	2783.37	0.15
39.38	47.63	9.01	3.98	2779.87	-3.36

For both MR5 and MR6, nitrogen shows the highest sensitivity to changes in heat capacity with values of 1.42 J/kg/K and 3.36 J/kg/K, respectively. The remaining components in order of largest to smallest difference in heat capacity are methane, ethane and propane. The differences in heat capacity are relatively small, however could have a significant impact on the thermodynamic efficiency of the refrigeration process. To determine the impact of these differences on the thermodynamic efficiency of a refrigeration process was not part of this project scope. However, this may have provided useful insight into determining measurement limits that the process can work within.

## 5.5 Conclusions

In conclusion, reference values calculated from the sampled liquid composition for MR1-MR6 fell within the suitability criteria specified in EN12838, therefore is appropriate for use in the Raman model development. The maximum and minimum MPE for CV was 8.671 kJ/kg\*K and 0.070 kJ/kg\*K, respectively. Large differences between the gravimetric and reference nitrogen amount fractions were observed for MR1, MR2 and MR6 giving values of 20.9 %, 14.7 %, 17.9 %, respectively. The differences in nitrogen amount fraction between the reference and gravimetric composition were correlated with modelled predictions determined via GasVLe. The study concluded that the differences in nitrogen amount fraction amount fraction are less correlated with temperature and more impacted by the matrix composition and nitrogen solubility.

The Raman spectra for MR1-MR4 were evaluated in terms of their discernibility, reproducibility, peak characteristics and linearity. The peak characteristics for nitrogen, methane, ethane and propane were easily identified with Gaussian like properties and adequate peak separation. Analysis of 30 repeat Raman runs showed minimal peak drift, a prerequisite for a repeatable model. The linearity of the MR model was assessed by plotting peak intensity versus amount fraction, and was demonstrated to be adequate with Pearson correlation coefficients of greater than 0.99.

The effects of MR composition on heat capacity were investigated to uncover correlations between composition, temperature and pressure. There were no correlations found between composition, temperature and pressure and this was clearly identified with random patterns. An attempt was made to correlate pure component heat capacities over the same temperature and pressure range. It was found that MR1 had a higher maximum, minimum and average

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heat capacity than all pure components over the entire temperature and pressure range. In addition to this, MR2 and MR6 had higher average heat capacities than all pure components. This suggests that a combination of pure components can have a higher heat capacity than their pure constituents. To study the statistical mechanisms of such systems was not part of this study, however it is conceivable that at the molecular level, there is an extra energy potential created between molecular species that increases the heat capacity of the entire system, a phenomenon resulting from deviations from ideal behaviour.

The Raman model was assessed based on the differences in calculated heat capacity between the measured and reference composition. For mixture MR5, the heat capacity was calculated with an error of 7.65 J/kg/K and an uncertainty equal to  $\pm$  1.21 J/kg/K. For MR6, the heat capacity was calculated with an error of 30.05 J/kg/K with an uncertainty equal to  $\pm$  6.42 J/kg/K. The differences between the measured and reference heat capacity for MR5 and MR6 was calculated to be 0.3% and 1.1%, respectively. Although these differences are relatively small compared with the heat capacity of each mixture, they could have a significant impact on thermodynamic efficiency. The impact on theoretical thermodynamic efficiency has not been included in this study since it was not part of the project scope, however could have proved a useful tool in setting measurement limits within which the measurement would be acceptable.

A finite difference method was used to determine the sensitivity of heat capacity to changes in MR component amount fractions. Nitrogen had the greatest impact on heat capacity with differences between the measured composition and an altered composition reflecting the standard deviation equal to 1.42 J/kg/K and 3.36 J/kg/K for MR5 and MR6, respectively. The

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remaining components methane, ethane and propane showed smaller differences of 0.66 J/kg/K, 0.15 J/kg/K and 0.02 J/kg/K for MR5, respectively. Similarly, for MR6, the differences in heat capacity for methane, ethane and propane were calculated to be 1.58 J/kg/K, 0.53 J/kg/K and 0.15 J/kg/K, respectively. Again, these differences are relatively small, however this study demonstrates that heat capacity is not just a function of pressure, temperature and amount fraction but also of the molecular species.

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## 6 Raman Spectroscopic Analysis of Liquefied Natural Gas (LNG)

## 6.1 Summary

The direct measurement of LNG composition provides numerous benefits compared with conventional measurement techniques including: removing the need for an additional sampling system with a vaporisation step, faster response time in measurement during ship loading and off-loading and providing measurement access to remote locations using advanced fibre optics. However, the calibration and validation of such instruments requires a bespoke facility with high accuracy traceable standards. In addition to this, the principle of calibration is dissimilar to typical gas phase calibration requiring a more complex modelling approach. Raman spectroscopy is a suitable candidate for this application because of its capability in measuring all components in LNG, its high sensitivity and selectivity and its resistance to moisture interference. This chapter explores the application of Raman spectroscopy for measuring LNG-type compositions with the aim of calibrating and validating a Raman spectrometer.

Calibration of the Raman spectrometer was achieved using 8 binary mixtures containing each component in the LNG matrix with methane as the balance gas. The measurement of neo-pentane proved to be problematic due to its solidification at the temperatures required for LNG measurement. For this reason, neo-pentane was not included in any further investigation. A full validation of the Raman spectrometer was not achieved due to several shortcomings, namely insufficient data and instrument linearity issues. Instead, an interim validation using 3 multi-component mixtures allowed investigation into the model's inefficiencies. The interim validation concluded that requirements for baseline adjustment and intensity correction are a prerequisite prior to any further validation process. Finally, the interim validation showed that the current model was incapable of meeting the current UK gross calorific value (GCV) accuracy requirement for custody transfer of  $\pm 0.18$ MJ/m<sup>3</sup>.

## 6.2 Introduction

The benefits of substituting direct measuring techniques over conventional sampling methods for analysing LNG have been thoroughly discussed in chapter 1. This section aims to further clarify the points made and to put them into context with respect to measurement challenges facing said techniques. Following on from this, a full description behind the method of calibration and validation is outlined.

There are many weak links in the current methods for measurement LNG composition, namely: the potential pre-fractionation in the sampling line leading up to the vaporiser, the post-fractionation of heavier components due to inadequate vaporiser power and the lack of calibration facilities for testing the performance of vaporisers - all of which contribute heavily to the final uncertainty in total energy transferred.

The main challenge facing the deployment of direct measurement techniques is the lack of calibration facilities capable of assessing their performance. This is given top priority in the EURAMET EMRP programme, whereby a working package has been dedicated solely to the development of a calibration facility for LNG composition measurement. To this date, this working package has not been accomplished. In this work, and specifically in chapter 4, a full verification of a cryostat system is made and confirmed using the criteria specified in appropriate international standards. This provides confidence in the calibration and validation of direct measuring instruments.

The conventional method of calibrating Raman spectroscopic instruments is by using a standard such as cyclohexane. Although this provides a wavelength calibration, it does not have the capability of fully characterising the matrix of components present in LNG. For a calibration to be valid, it must cover what is being measured. However, in this case, what is being measured is a cryogenic liquid. Therefore, calibration at room temperature with the same gas composition is not feasible, and a completely new approach is required since the interaction of incident light with gases and liquids is different.

As with conventional gas chromatographic calibrations, multiple gas standards are used to obtain response functions that can be applied to unknown samples to derive their composition. The accuracy of the standards used dictates the inherent accuracy of the gas chromatograph. The same approach is applicable to Raman spectroscopy since the same principle of peak area determination is used to derive analyte identification and quantification. However, the method design at cryogenic conditions requires a complex array of data to establish an algorithm capable of distinguishing between different LNG matrixes.

At cryogenic conditions, natural gas components behave differently than at room temperature. Molecules exist in more structured arrangements since they have a lower overall kinetic energy. Since methane is the major component, it acts as a solvent for all the other components. Therefore, there

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exists a 'solvent cage' effect whereby the incident light from the Raman source must enter and exit through this solvent cage before and after it interacts with the minor components. This 'solvent cage' effect is a factor that needs to be accounted for in the final Raman model. To account for this, a maximum signal for each component is required. This is subject to the solidification point for each component at LNG temperatures. The method design is discussed in the following section.

## 6.3 Method design

The design of the calibration method does not follow the conventional multistandard approach that covers the full range of compositions as with the method outlined in chapter 5. Rather, since we are testing much lower concentrations (~200ppm) close to the Raman limit of detection (LOD), binary mixtures are used to determine the peak characteristics at each components' maximum amount fraction. This allows for better peak integration parameters to be fitted, resulting in a more accurate algorithm design. It is assumed that the Raman response is proportional to the amount fraction via the Placzek equation (equation 2.5.2) described in chapter 2. With this assumption, the main factor for consideration is the methane 'solvent cage'.

## 6.3.1 Calibration mixture design

The design of the calibration mixtures started from a trial and error analysis. The first set of proposed binary calibration mixtures are shown in table 6.3-1. The amount fraction for all components are higher than the typical LNG composition range because the maximum signal for each component is required, regardless of the amount fraction. Therefore, the aim was to maximise the amount fraction of each component whilst remaining within the limits of solidification.

			Amo	unt fractio	on (% mol	/mol)		
Component	Mix_1a	Mix_2a	Mix_3a	Mix_4a	Mix_5a	Mix_6a	Mix_7a	Mix_8a
methane	65	85	95	95	99.5	99.5	99.9	98
ethane	35							
propane		15						
iso-butane			5					
n-butane				5				
iso-pentane					0.5			
n-pentane						0.5		
neo-pentane							0.5	
nitrogen								2

Table 6.3-1 - Binary mixtures for calibration of Raman spectrometer

All mixtures were prepared and verified in accordance with the methods described in chapter 2 section 2.3. For each gas condensation, the cryostat was prepared per chapter 2 section 2.2. The operating temperatures for each composition were determined by the solidification predictions presented in the following section. Data analysis was performed per chapter 2 section 2.4. The number of repeat runs for GC analysis was 48 for calibration and 96 for analysis of the sampled liquid composition.

## 6.3.2 Solidification temperature predictions for binary calibration mixtures

The solidification temperature for each binary mixture was precited with several EOS using the GasVLe version 3.4 physical property calculation

software. Though the accuracy of these predictions for multi-component cryogenic liquid mixtures is not well known, it provides valuable insight into the correct solidification temperature required for this work.

The predicted solidification temperatures for each binary calibration mixture using several EOS are shown in table 6.3-2. KMK, RKS, LRS and SW EOS show consistent solidification temperatures for all mixtures compared with the wide range observed with the GERG, MBWR, WSVP and ISOW EOS. There are several inconsistencies, particularly between the GERG and MBWR EOS. For example, the MBWR EOS predicts a solidification temperature at 93K for Mix\_7a, whereas all other EOS predict a solidification temperature at approximately 200K.

Both iso-pentane and iso-butane show lower predicted solidification temperatures than n-pentane and n-butane. This is a direct result of the stronger molecular interaction experienced with straight chain alkanes compared with branched alkanes. Since n-pentane and n-butane remain close to the liquefaction temperature and combined with the uncertainty attributed to these predictions, it is suspected that solidification could occur and the amount fractions may need to be reduced to prevent this.

The neo-pentane binary mixture has the highest predicted solidification temperature even with an amount fraction 5 times lower than in its other isomeric forms (n-pentane and iso-pentane). For this reason, the amount fraction of neopentane was reduced from to 0.1%. Table 6.3-3 shows the differences in solidification temperature at different amount fractions of neopentane in methane from 0.5% to 0.0001%. 0.1% was the chosen amount fraction since it lays close to the LOD of the Raman analyser. The predicted solidification temperature for 0.1% neo-pentane in methane is 182K, much higher than the liquefaction temperature (<110K). Nonetheless, a compromise

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had to be made between the LOD of the Raman analyser and the solidification temperature. Furthermore, the measured liquid composition will provide evidence of solidification or stratification inside the sampling cell.

			Amo	unt fractio	on (% mol	/mol)		
Component	Mix_1a	Mix_2a	Mix_3a	Mix_4a	Mix_5a	Mix_6a	Mix_7a	Mix_8a
methane	65	85	95	95	99.5	99.5	99.9	98
ethane	35							
propane		15						
iso-butane			5					
n-butane				5				
iso-pentane					0.5			
n-pentane						0.5		
neo-pentane							0.5	
nitrogen								2
EOS	Mix_1a	Mix_2a	Mix_3a	Mix_4a	Mix_5a	Mix_6a	Mix_8a	Mix_9a
КМК	79.41	82.09	87.54	94.09	90.38	91.57	200.07	89.29
RKS	78.37	82.48	87.82	92.52	90.37	94.63	200.98	89.29
LRS	79.41	82.09	87.54	94.09	90.38	91.57	200.07	89.29
SW	73.68	84.69	89.90	90.08	92.63	92.63	200.03	91.65
GERG	79.45	87.70	91.01	106.66	95.46	111.62	93.36	92.48
MBWR	82.82	93.19	95.34	148.30	93.34	113.15	200.12	92.50
WSVP	77.31	86.11	91.25	91.37	93.46	93.47	200.17	92.55
ISOW	82.08	87.92	95.21	102.69	94.19	106.22	200.02	93.30

Table 6.3-2 – Solidification temperature predictions at 2 bar for binary calibrations mixtures using 8 equations of state (EOS)

Table 6.3-3 – Solidification temperature predictions for varying neo-pentane amount fractions in methane

component								
methane	99.50	99.60	99.70	99.80	99.90	99.99	99.99	99.99
neo-pentane	0.50	0.40	0.30	0.20	0.10	0.01	0.001	0.0001
KMK	200.07	197.42	194.11	189.64	182.47	162.22	146.12	133.55
RKS	200.98	198.36	195.10	190.68	183.60	163.58	147.65	135.07
LRS	200.07	197.42	194.11	189.64	182.47	162.22	146.12	133.55
SW	200.03	197.38	194.07	189.60	182.43	162.17	146.06	92.95
GERG	93.36	93.42	93.48	93.54	93.60	93.66	93.66	93.66

MBWR	200.10	197.45	194.14	189.66	182.49	162.20	146.05	133.42
WSVP	200.14	197.50	194.19	189.72	182.56	162.31	93.75	93.75
ISOW	200.02	197.38	194.07	189.60	182.43	162.18	146.09	133.53

## 6.3.3 Validation mixture design

The choice of validation mixtures was based on the typical range of LNG compositions shown in table 4.3-1 (chapter 4). It was decided that after the calibration model had been developed, three mixtures would be used to adjust the model where necessary prior to the final validation. Table 6.3-4 shows the three mixtures used for adjusting the calibration model. The significance of these mixtures is that they extend the typical LNG range, allowing for testing outside of the model calibration range. For the final performance testing of the model, 7 validation mixtures were chosen to reflect the typical range of LNG compositions. Table 6.3-4 shows 7 validation mixtures proposed to test the Raman model.

	Amount	fraction (%	mol/mol)		
	Mix_1b	Mix_2b	Mix_3b		
nitrogen	1.482	1.470	0.000		
methane	77.349	86.727	95.579		
ethane	14.288	7.068	0.000		
propane	4.001	1.997	4.026		
iso-butane	1.292	1.294	0.000		
n-butane	1.292	1.292	0.000		
iso-pentane	0.148	0.150	0.147		
n-pentane	0.149	0.000	0.148		
neo- pentane	0.000	0.000	0.099		

Table 6.3-4 – Adjustment mixtures for Raman calibration model

Table 6.3-5 – Validation mixtures for Raman model tes	ting
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		Ai	mount fra	action (%	mol/mol)		
component	Mix_1c	Mix_2c	Mix_3c	Mix_4c	Mix_5c	Mix_6c	Mix_7c
nitrogen	0.25	0.57	0.83	1.56	1.09	0.69	0.10
methane	99.3	98.43	97.04	95.22	94.1	88.14	79.86
ethane	0.10	0.22	0.51	1.18	3.13	7.13	13.77

propane	0.10	0.23	0.41	0.77	1.26	2.12	3.92
iso-butane	0.08	0.23	0.62	0.39	0.13	1.01	1.29
n-butane	0.12	0.23	0.42	0.57	0.08	0.92	1.05
iso-pentane	0.03	0.05	0.08	0.15	0.10	0.00	0.00
n-pentane	0.02	0.04	0.08	0.15	0.10	0.00	0.0
neo-	0.00	0.01	0.00	0.01	0.00	0.00	0.00
pentane							

## 6.4 Results and discussion

In this section, the GC reference liquid data is discussed regarding solidification temperature predictions and Raman LOD. Since we are not dealing with multi component mixtures, the suitability testing applied in chapters 4 and 5 was not applied. Rather, the emphasis is on identifying peak characteristics and the influence of the methane 'solvent cage' effect on Raman signal intensity and shift. Following this, the characteristics of the Raman spectrums are explored. Finally, issues with the final validation of the Raman model are discussed with proposals for further work.

## 6.4.1 Calibration of Optograf Raman spectrometer

Several issues arise during the development of the Raman calibration model. Blockages of the calibration gas transfer line during the condensation procedure occurred due to presence of moisture, and this led to a repeat experiment. Solidification and/or stratification occurred for n-butane and neopentane binary mixtures as indicated by the reference liquid composition data. Furthermore, problems with the Raman instrument were encountered which hindered the final testing of the calibration model.

### 6.4.1.1 Reference composition data for binary mixtures

The reference composition data for all binary mixtures are shown in tables 6.4-1 – 6.4-8. Table 6.4-9 summarises the differences in CV between the measured liquid composition and the gravimetric composition. Ethanemethane (Mix\_1a), propane-methane (Mix\_2a) and iso-butane-methane

(Mix\_3a) mixtures showed agreement between the measured liquid composition and the gravimetric composition with values of CV of less than 3.5 kJ/kg. This was expected since the predicted solidification points were on average below 90K. However, n-butane-methane (Mix\_4a) showed a 33% difference between the averaged composition derived from the measured liquid composition and the gravimetric composition. The gravimetric amount fraction for n-butane in Mix\_4a was 5%, whereas the measured liquid composition gave an average amount fraction of 3.7%. This suggests two possible causes: an asymmetric temperature profile of the sampling cell resulting in stratification of iso-butane in methane, or the predicted solidification temperatures are not accurate and a higher temperature was required (figure 6.4-1).



Figure 6.4-1 – Stratification and solidification processes

Stratification could result from a temperature-equilibrium lag since the cryogenic heat exchanger is located at the top of the sample chamber. However, since the measurements are taken overnight, the sample chamber should have adequate time to reach equilibrium, therefore solidification due to incorrect operating temperature is the most likely cause. Mix\_4a was repeated with 3% n-butane in methane (table 6.4-4) at the same temperature (98K) and the resulting measured liquid composition agreed well with the gravimetric composition. The experiment was repeated at the same conditions to ensure repeatability between condensations.

Mixtures n-pentane-methane (Mix\_5a), iso-pentane-methane (Mix\_6a) showed consistency between the measured liquid composition and gravimetric composition with CV values of 0.11 kJ/kg and 0.88 kJ/kg, respectively. Though, the difference for nitrogen was much larger than n-pentane and iso-pentane with values of 4.0%, 0.08% and 0.62% respectively. This is expected because nitrogen has a lower boiling point and therefore has a higher tendency to reside in the gas phase compared with both iso-pentane and n-pentane.

The measurement of neo-pentane in methane proved to be problematic, even when the amount fraction was initially reduced 5-fold. The amount fraction of neo-pentane in the liquid composition was calculated to be 0.5%, approximately 5 times higher than the gravimetric amount fraction. This suggests that stratification could have occurred in the sample chamber causing higher amount fractions of neo-pentane to be sampled. Though, as seen in figure 6.4-1, the temperature profile of the sample chamber (warmer towards the bottom of the cell) shows that denser amount fractions of the minor components in methane should occur towards at the top of the cell. Nevertheless, the sampling line is located towards the bottom of the cell, therefore it is less likely that stratification would be the cause of the mismatch between the sampled liquid amount fractions in the liquid could cause fluctuations in density, which would result in different measured amount

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fractions, and would also account for the high %RSD observed for repeat analyses. Furthermore, correlating the measured liquid amount fraction with the lack of identifiable peaks in the Raman spectrum for neo-pentane (figure 6.4-9) does suggest that either or both solidification and stratification have occurred.

For the purposes of this work, the importance of being able to calibrate neopentane was not given a high priority because of its trace quantities in real LNG. Consequently, its impact on calculated physical properties is negligible. Therefore, repeat experiments for neo-pentane-methane composition was not required.

### Table 6.4-1 -Reference composition data for methane-ethane binary calibration mixture

Mix_1a		GC amount fraction (%mol/mol)									
Component	Gravimetric	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Average	% Diff from
	(%mol/mol)									(%mol/mol)	gravimetric
Methane	64.9889	64.9085	64.9990	64.9828	65.1129	64.8867	64.8656	64.9400	64.9744	64.9587	-0.0450
Ethane	35.0109	35.0915	35.0010	35.0172	34.8871	35.1133	35.1344	35.0600	35.0256	35.0413	0.0835

## Table 6.4-2 - Reference composition data for methane-propane binary calibration mixture

Mix_2a		GC amount fraction (%mol/mol)									
Component	Gravimetric	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Average	% Diff from
	(%mol/mol)									(%mol/mol)	gravimetric
Methane	85.1034	85.1269	85.1168	85.1671	85.1312	85.2009	85.1427	85.1092	85.1415	85.1420	0.0453
Propane	14.8960	14.8731	14.8832	14.8329	14.8688	14.7991	14.8573	14.8908	14.8585	14.8580	-0.2600

Table 6.4-3 - Reference composition data for methane-iso-butane binary calibration mixture

Mix_3a		GC amount fraction (%mol/mol)									
Component	Gravimetric (%mol/mol)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Average (%mol/mol)	% Diff from gravimetric
Methane	94.9530	94.9349	94.9768	94.9867	94.9927	94.9980	95.0018	95.0052	95.0081	94.9956	-0.0125
iso-Butane	5.0455	5.0651	5.0232	5.0133	5.0073	5.0020	4.9982	4.9948	4.9919	5.0044	0.2660
Mix_4a				GC	amount frac	ction (%mo	l/mol)				
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Component	Gravimetric	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Average	% Diff from
	(%mol/mol)									(%mol/mol)	gravimetric
Methane	94.9969	96.8731	96.8602	96.5885	96.3098	96.1065	95.9999	95.9574	95.9344	96.2510	1.3028
n-Butane	5.0003	3.1269	3.1398	3.4115	3.6902	3.8935	4.0001	4.0426	4.0656	3.7490	-33.4476
Repeat exp.				GC	amount fra	ction (%mol/	/mol)				
Component		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Average	% Diff from gravimetric
Methane	96.9987	97.0258	97.0365	97.0367	97.0275	97.0642	97.0402	97.0185	97.0360	97.0371	0.0378
n-Butane	2.9996	2.9742	2.9635	2.9633	2.9725	2.9358	2.9598	2.9815	2.9640	2.9629	-1.2381
Confirmation exp.				GC	amount fra	ction (%mol/	/mol)				
Component		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Average	% Diff from
-										_	gravimetric
Methane	96.9987	97.1656	97.1025	97.1317	97.0613	97.0766	97.0999	97.0832	97.0853	97.0915	0.0938
n-Butane	2.9996	2.8344	2.8975	2.8683	2.9387	2.9234	2.9001	2.9168	2.9147	2.9085	-3.1318

# Table 6.4-4 - Reference composition data for methane-n-butane binary calibration mixture

Table 6.4-5 - Reference composition data for methane-n-pentane binary calibration mixture

Mix_5a		GC amount fraction (%mol/mol)									
Component	Gravimetric	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Average	% Diff from
	(%mol/mol)									(%mol/mol)	gravimetric
Methane	99.4981	99.5486	99.5173	99.4993	99.5012	99.5019	99.5096	99.5006	99.4730	99.5004	0.0003
n-Pentane	0.4999	0.4514	0.4827	0.5007	0.4988	0.4981	0.4904	0.4994	0.5270	0.4996	-0.0780

#### Table 6.4-6 - Reference composition data for methane-iso-pentane binary calibration mixture

Mix_6a		GC amount fraction (%mol/mol)							]		
Component	Gravimetric (%mol/mol)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Average (%mol/mol)	% Diff from gravimetric
Methane	99.5046	99.5005	99.5277	99.5273	99.5311	99.5033	99.4973	99.4840	99.4954	99.5095	0.0030
i-Pentane	0.4935	0.4995	0.4723	0.4727	0.4689	0.4967	0.5027	0.5160	0.5046	0.4905	-0.6178

Table 6.4-7 - Reference composition data for methane-neo-pentane binary calibration mixture

Mix_7a			GC amount fraction (%mol/mol)								
Component	Gravimetric (%mol/mol)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Average (%mol/mol)	% Diff from reference
Methane	99.9000	99.4241	99.5059	99.5009	99.5092	99.4835	99.4713	99.4594	99.4440	99.4820	-0.4207
neo-Pentane	0.0994	0.5759	0.4941	0.4991	0.4908	0.5165	0.5287	0.5406	0.5560	0.5180	80.8099

Table 6.4-8 - Reference composition data for methane-nitrogen binary calibration mixture

Mix_8a		GC amount fraction (%mol/mol)									
Component	Gravimetric (%mol/mol)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Average (%mol/mol)	% Diff from reference
Methane	98.0114	98.0882	98.0882	98.0886	98.0884	98.0889	98.0895	98.0902	98.0884	98.0889	0.0788
Nitrogen	1.9884	1.9118	1.9118	1.9114	1.9116	1.9111	1.9105	1.9098	1.9116	1.9111	-4.0486

		Amount f (%mol	fraction /mol)	CV (k	J/kg)	
		Gravimetri c	Measure d (GC)	Gravimetri c	Measure d	Abs. differenc e
Mix_1a	methane	64.988	64.959	53754.54	53753.38	-1.16
	ethane	35.012	35.041			
Mix_2a	methane	85.103	85.142	53884.16	53887.64	3.48
	propane	14.897	14.858			
Mix_3a	methane	95.008	94.996	54585.73	54583.41	-2.32
	iso-butane	4.991	5.004			
Mix_4a	methane	97.000	97.037	54967.54	54974.43	6.89
	n-butane	3.000	2.963			
Mix_5a	methane	99.500	99.500	55430.60	55430.71	0.11
	n-pentane	0.500	0.500			
Mix_6a	methane	99.506	99.509	55430.32	55431.19	0.88
	i-pentane	0.494	0.491			
Mix_7a	methane	99.901	99.482	55544.48	55418.78	-125.71
	neo- pentane	0.099	0.518			
Mix_8a	methane	98.012	98.089	53673.36	53746.31	72.95
	nitrogen	1.989	1.911			

Table 6.4-9 -Comparison of CV between gravimetric composition and measured composition for calibration mixtures Mix\_1a – Mix\_8a.

## 6.4.1.2Raman spectra for binary mixtures

30 repeat spectrums were collected for each calibration mixture to identify peak positions, peak drift and intensity changes. Peak positions for each component in Mix\_1a - Mix\_8a are shown in figure 6.4-2. Raman peak shift for each component is shown in Table 6.4-10 for a reference. Each peak is clearly distinguishable and integrateable apart from neo-pentane. The presence of a double peak for neo-pentane shown in figures 6.4-9 and 6.4-10 makes setting integration parameters difficult, especially since its peak intensity is close to the baseline noise of the instrument. Furthermore, verification of the neo-pentane-methane calibration mixture was unsuccessful, therefore a properly assigned response factor could not be realised.

Component	Peak shift position (cm <sup>-1</sup> )
nitrogen	2326.0
methane	2906.4
ethane	993.4
propane	869.8
iso-butane	798.6
n-butane	838.6
iso-pentane	462.0
n-pentane	400.0
neo-pentane	732.0

Table 6.4-10 – Raman peak shift for all components in calibration mixtures. (1)



Figure 6.4-2 – Raman spectra for Mix\_1a – Mix\_8a indicating peak locations. Laser wavelength: 523nm, accumulations: 2, exposure range: 12-16s.

30 repeat runs for individual peaks ethane, propane, iso-butane, n-butane, iso-pentane, n-pentane, neo-pentane and nitrogen are shown in figures 6.4-3 – 11. Each spectrum shows that there is minimal drift between repeat runs and minimal intensity change. Iso-pentane, n-pentane and neo-pentane show

the largest changes in peak intensity and drift due to their lower amount fractions. Upon initial investigation of each spectrum, there was no recognisable peak for neo-pentane. Only with an overlap of neo-pentane, npentane and iso-pentane spectra was it possible to distinguish unique features specific to neo-pentane and this is demonstrated in figure 6.4-10. From this overlap, we see a unique neo-pentane peak at 732nm.



Figure 6.4-3 – Raman spectrum for methane-ethane binary mixture. Laser wavelength: 523nm, accumulations: 2, exposure: 15s.



Figure 6.4-4 - Raman spectrum for methane-propane binary mixture. Laser wavelength: 523nm, accumulations: 2, exposure: 12s.



Figure 6.4-5 - Raman spectrum for methane-isobutane binary mixture. Laser wavelength: 523nm, accumulations: 2, exposure: 12s.



Figure 6.4-6 - Raman spectrum for methane-n-butane binary mixture. Laser wavelength: 523nm, accumulations: 2, exposure: 15s.



Figure 6.4-7 - Raman spectrum for methane-iso-pentane binary mixture. Laser wavelength: 523nm, accumulations: 2, exposure: 16s.



Figure 6.4-8 - Raman spectrum for methane-n-pentane binary mixture. Laser wavelength: 523nm, accumulations: 2, exposure: 12s.



*Figure 6.4-9 - Raman spectrum for methane-neo-pentane binary mixture. Laser wavelength: 523nm, accumulations: 2, exposure: 15s.* 



Figure 6.4-10 - Raman spectrum comparison for neo-, iso- and n-pentane in methane binary compositions.



Figure 6.4-11 - Raman spectrum for methane-nitrogen binary mixture. Laser wavelength: 523nm, accumulations: 2, exposure: 12s.

The data collected for each calibration mixture is combined with the calculated reference liquid composition to determine the response factors for each component. The algorithm for this model was developed by Kaiser optical systems. The model shares the same characteristics as that developed in chapter 5, except a more rigorous algorithm was required in this work to determine peak parameters and subsequently peak areas for lower amount fractions.

Moreover, during the collection of data, the Optograf instrument itself was still undergoing several additional testing procedures including: an intensity calibration, wavelength calibration and drift compensation. Up to this point, this additional testing has not proven to be successful. Consequently, a final model was not developed in time for the final validation testing stage. Nonetheless, an interim testing phase was employed to improve and fine-tune the algorithm design. The next section describes the data collected from the interim testing and outlines plans for the final validation of the Raman spectrometer.

### 6.4.2 Validation of Optograf Raman spectrometer

As discussed, the validation of the Optograf LNG model was not possible due to several shortcomings, namely: a lack of data to determine instrument drift and instrument linearity and the need for additional mixtures to fine tune the algorithm design. Also, since the Optograf is a commercial instrument, the manufacturing company are applying very cautious data modelling techniques to bring a successful model into fruition. This means that any inadequacies in the data used for modelling causes a delay in its development. Nevertheless, the following section describes data collected from an interim validation. The purpose of the interim validation is to identify errors resulting from the binary calibration mixtures due to baseline processing and artefacts and to determine adjustments to scaling factors and integration parameters if required. Three validation mixtures were chosen to reflect a broad range of compositions with low, medium and high methane and ethane amount fractions. Propane, butanes and pentanes were designed with a much lower amount fraction to test the model's linearity in response.

Composition data for all three validation mixtures are shown in tables 6.4-11:13. All mixtures show CV differences between the corrected reference liquid and measured liquid analysis to be within the suitability criteria of 9kJ/kg as specified in BS EN 12838. Large differences between the corrected reference liquid and GC measured composition are observed for all pentane components in val\_3 (2.4% - 3.0%), however these differences are smaller for val\_1 (0.35%) and val\_2 (0.67%) despite having a similar amount fraction. This suggests that the solubility of pentane is a function of composition. Since ethane is absent in val\_3 but present in val\_1 and val\_2, this component may promote pentane solubility. Therefore, it is possible that the solidification point is raised for mixtures containing ethane.

To confirm this, the solidification point was predicted for mixtures containing equal amount fractions of pentanes with increasing amount fractions of ethane. The solidification points are shown in table 6.4-14. There is a range of 9K difference (88.4K– 79.68K) between the solidification points of mixtures containing 0% ethane and 14% ethane. This supports the premise that the solubility of pentanes is a function of ethane amount fraction.

	Amount fraction	(%mol/mol)	
Component	Corrected Ref Liquid	GC measured	% Diff.
nitrogen	1.381	1.381	0.000
methane	77.428	77.390	-0.050
ethane	14.302	14.348	0.314
propane	4.005	4.007	0.043
iso-butane	1.293	1.289	-0.267
n-butane	1.293	1.289	-0.301
i-Pentane	0.148	0.148	-0.352
n-Pentane	0.149	0.148	-0.321
			Absolute Diff.
CV (kJ/kg)	52813.335	52812.675	0.660

Table 6.4-11 - Reference composition data for validation mixture val\_1

Table 6.4-12 - Reference composition data for validation mixture val\_2

	Amount fraction (	%mol/mol)	
Component	Corrected Ref Liquid	GC measured	% Diff.
nitrogen	1.398	1.398	0.000
methane	86.792	86.767	-0.029
ethane	7.073	7.103	0.417
propane	1.999	1.997	-0.072
iso-butane	1.295	1.295	-0.039
n-butane	1.293	1.291	-0.140
i-Pentane	0.150	0.149	-0.673
			Absolute Diff.
CV (kJ/kg)	53253.261	53252.684	0.574

	Amount fraction	(%mol/mol)									
Component	Corrected Ref Liquid	GC measured	% Diff.								
methane	95.579	95.550	-0.031								
propane	4.026	4.066	0.996								
neo-Pentane	0.099	0.097	-2.400								
i-Pentane	0.147	0.143	-2.678								
n-Pentane	0.148	0.144	-3.057								
			Absolute Diff.								
CV (kJ/kg)	54935.105	54932.867	2.238								

Table 6.4-13- Reference composition data for validation mixture val\_3

Table 6.4-14 – Solidification point predictions for mixtures containing

component		Α	mount	fraction (	%mol/mc	ol)	
methane	96.55	96.35	96.15	95.55	94.15	90.75	82.55
ethane	0.00	0.20	0.40	1.00	2.40	5.80	14.00
propane	3.00	3.00	3.00	3.00	3.00	3.00	3.00
iso-pentane	0.15	0.15	0.15	0.15	0.15	0.15	0.15
n-pentane	0.15	0.15	0.15	0.15	0.15	0.15	0.15
neo-pentane	0.15	0.15	0.15	0.15	0.15	0.15	0.15
EOS			Solid	ification p	oint (K)		
LRS	88.40	88.26	88.13	87.73	86.81	84.65	79.68
RKS	88.40	88.26	88.13	87.73	86.79	84.55	79.18
КМК	88.40	88.26	88.13	87.73	86.81	84.65	79.68

increasing amount fractions of ethane

An average composition for val\_1, val\_2 and val\_3 was determined from 30 repeat runs using the Raman model. A comparison between the Raman composition and reference liquid composition is shown in tables 6.4-15:17. Both iso-pentane and n-pentane were unable to be measured with the existing

Raman model because negative peak areas were assigned to their expected positions. The amount fraction of iso-pentane and n-pentane in the validation mixtures was 0.15% compared with 0.5% in the calibration mixtures (mix\_5a and mix\_6a). Therefore, the integration parameters need to be adjusted to reflect compositions less than 0.5%. This may include adjusting the lower detection interval and bringing it closer to the baseline noise. Descriptions of the peak characteristics are described in a later section.

Large differences were observed for ethane in mixtures val\_1 and val\_2 with 9% and 8% difference, respectively. The difference in methane amount fraction was poor for all validation mixtures, with differences of 1.7%, 0.6% and 6.5% for mixtures val\_1, val\_2 and val\_3, respectively. A similar conclusion can be applied to propane with differences of 6%, 11.1% and 3.2% for mixtures val\_1, val\_2 and val\_3, respectively. Neo-pentane showed the largest difference between the Raman composition and reference liquid composition with a difference of 98.3%. A contribution to these differences derives from the non-measurement of pentanes. However, the larger differences observed are less likely to be impacted from this mismeasurement and in fact are a result of a poor model formulation.

Val_1	Меа	asured (Rama	ın)	Reference liquid		
	Amount fraction (%mol/mol)	Stdev	%RSD	Amount fraction (%mol/mol)	%Diff (Raman- Ref)	
Methane	78.799	0.038	0.048	77.428	1.740	
Ethane	13.111	0.022	0.171	14.302	-9.084	
Propane	4.261	0.010	0.238	4.005	6.008	
n-butane	1.304	0.007	0.517	1.293	0.844	
iso-butane	1.266	0.006	0.487	1.293	-2.133	
i-Pentane				0.148		
n-Pentane				0.149		
nitrogen	1.258	0.011	0.913	1.381	-9.777	
sum	100.00			100.00		

Table 6.4-15 – Comparison of Raman measured values with reference liquid values for val\_1

Val_2	Measured (Raman)			Reference	liquid
	Amount fraction (%mol/mol)	Stdev	%RSD	Amount fraction (%mol/mol)	%Diff (Raman- Ref)
Methane	87.289	0.027	0.031	86.792	0.569
Ethane	6.546	0.014	0.218	7.073	-8.051
Propane	2.249	0.008	0.357	1.999	11.116
n-butane	1.335	0.005	0.367	1.295	2.996
iso-butane	1.285	0.006	0.490	1.293	-0.623
i-Pentane				0.150	
nitrogen	1.297	0.006	0.458	1.398	-7.787
sum	100.00			100.00	

Table 6.4-16 - Comparison of Raman measured values with reference liquid values for val\_2

Table 6.4-17 - Comparison of Raman measured values with reference liquid

		1/5	•	<b>D</b> <i>i</i>	
val_3	Mea	asured (Ram	an)	Reference liquid	
					I
	Amount	Stdev	%RSD	Amount	%Diff
	fraction			fraction	(Raman-
	(0/ mol/mol)			(0/mol/mol)	(I taintain Dof)
	(%1101/1101)			(%1101/1101)	Rei)
Methane	89.750	0.128	0.142	95.579	-6.495
Propane	4.163	0.013	0.304	4.026	3.291
iso-butane	0.058	0.005	8.616		
i-Pentane				0.147	
n-Pentane				0.148	
neo-	6.019	0.134	2.223	0.099	98.355
pentane					
sum	99.99			100.00	

values for val\_3

Raman spectra for val\_1, val\_2 and val\_3 is shown in figure 6.4-12. Slight differences in baseline intensity are observed, however these are corrected for when subtracting from their respective background spectra. Upon closer inspection of the neo-pentane peaks at 732nm (figure 6.4-13), the peak intensity for mixture val\_3 is approximately 4 times that of the neo-pentane binary mixture (Mix\_7a), despite having an amount fraction 5 times lower. The most likely cause of this is the solidification neo-pentane on the window of the

Raman probe. This would explain why the Raman composition prediction for neo-pentane is 60 times higher than the reference liquid composition.

Upon closer inspection of iso-pentane and n-pentane peak intervals for val\_1, val\_2 and val\_3 (figure 6.4-14), the peak characteristics are dissimilar to those seen for the binary calibration mixtures (mix\_5a and mix\_6a). For example, the iso-pentane peak at 462nm for the binary calibration mixtures shows a clear peak, whereas for val\_1 and val\_3 there is a peak at around 450nm with a slight shoulder at 462nm. This makes integration difficult, especially at detection levels close to the baseline noise. The integration routine requires a minimum level at which to start peak detection. If the level for identification of pentanes in the Raman model has a set limit, then below this limit the detection of peaks is not possible. Therefore, the model would produce negative peak areas, ultimately giving rise to negative amount fractions. To confirm this, figure 6.4-15 shows a comparison with what the model expects to see for amount fractions of 0.15% for iso-pentane and n-pentane and the actual response for mixture val\_1.



Figure 6.4-12 – Raman spectra for validation mixtures val\_1, val\_2 and val\_3.



Figure 6.4-13 – Comparison of neo-pentane Raman peaks for val\_3 and mix\_7a.



Figure 6.4-14 – Comparison of iso-pentane and n-pentane between validation mixtures and binary calibration mixtures.



Figure 6.4-15 – Comparison of Raman model prediction with actual response for 0.15% iso-pentane and 0.15% n-pentane.

Gross calorific values were calculated for both predicted Raman composition and reference liquid composition. A comparison of heating values for val\_1, val\_2 and val\_3 is shown in table 6.4-18. The smallest difference in CV was seen for Val\_2 with a difference of 0.11 MJ/m<sup>3</sup>, and this is most likely due to val\_2 having the smallest difference in methane amount fraction (0.57%). Since methane is the dominant component, it has the greatest impact on CV. The largest difference in CV was seen for Val\_3 with a difference 6.4 MJ/m<sup>3</sup>, and again this is due Val\_3 having the largest difference in methane amount fraction (6.4%). Finally, the difference in CV for val\_1 was 0.5MJ/m<sup>3</sup>.

Table 6.4-18 – Comparison of heating values for Raman composition predictions and reference liquid composition

	GCV		
Mix ID	Raman	Reference liquid	Abs. Difference
Val_1	45.66	46.15	-0.50
Val_2	42.66	42.77	-0.11
Val_3	46.94	40.51	6.43

The typical CV accuracy requirement for custody transfer in the UK is 0.18MJ/m<sup>3</sup>. (2; 3) On average, the CV differences shown in table 4.4-17 are significantly larger than this accuracy requirement. Though, val\_2 is almost half the CV accuracy requirement. Nevertheless, any instrument must perform and meet this accuracy requirement over a full range of compositions if it is to be determined fit for purpose for fiscal metering. Consequently, the estimation of amount fractions via the Raman model is unsatisfactory.

## 6.5 Conclusions

In conclusion, the reference values calculated from the sampled liquid composition for mix\_1a – mix\_6a fell within the 9 kJ/kg suitability criteria specified in EN12838. However, in mix7a and mix8a nitrogen did not meet this suitability criteria due to its higher boiling point than all other components which resulted in a 4% difference in CV between the gravimetric and measured composition. Though, since the calibration mixtures were used to build the Raman model and not test it, the emphasis of meeting this suitability criteria was given a low priority. Moreover, the differences between the gravimetric with a value of 80%. This suggested that solidification/stratification was occurring in the sample chamber, causing a lower neo-pentane amount fraction to be measured.

Several issues hindered the development of the Raman model which postponed the final validation process. Nonetheless, an interim validation proceeded with the aim of assessing the current model and to determine modifications required for optimisation. Raman measurements of both isopentane and n-pentane were unsuccessful with the model reporting negative amount fractions. Comparison of Raman spectra for all validation mixtures demonstrated that iso-pentane and n-pentane were present and had distinguishable peak characteristics. Consequently, the mismeasurement of iso-pentane and n-pentane was a result of the model algorithm not able to detect peaks at the threshold the validation components were present at and this was confirmed by comparing a theoretical response from the model to the actual response.

Neo-pentane was over-measured by 98% and the most likely cause attributed to this was solidification on the window of the Raman probe. Comparison of Raman spectra between the neo-pentane binary mixture (Mix\_7a) and the validation mixture (val\_3) confirmed this premise. The neo-pentane peak intensity for val\_3 was approximately 4 times higher than that of Mix\_7a, despite having an amount fraction of 5 times lower. Moreover, the measurement of neo-pentane at LNG temperatures does not seem practical because of its solidification potential.

Finally, the differences in CV between the predicted Raman amount fractions and reference liquid amount fractions demonstrated that the current Raman model proved to be unsatisfactory for custody transfer measurements. Although one validation mixture (Val\_2) passed the current 0.18MJ/m<sup>3</sup> requirement for measurement accuracy with a value of 0.11 MJ/m<sup>3</sup>, the remaining two mixtures Val\_1 and Val\_3 failed to meet this criterion with reported values of 0.5 MJ/m<sup>3</sup> and 6.43 MJ/m<sup>3</sup>. Nevertheless, the interim validation provided identification for model improvement, namely: the adjustment of integration parameters and a requirement for linearity testing. A final validation with 7 mixtures spanning the full range of LNG compositions is required to fully test the performance of the Raman model, and this is discussed in the further work section of this thesis.

#### 6.6 References

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# 7 Infrared Spectroscopic Analysis of Liquefied Natural Gas (LNG)

### 7.1 Summary

The benefits of replacing a conventional sampling systems with a direct measuring instrument include: faster measurement times, measurement access to remote locations or those locations not suitable for human presence and removing the need for sample conditioning which contributes heavily to the final uncertainty budget for LNG energy value determination. In this study, an Infrared (IR) spectrometer from MKS Instruments Inc. is evaluated based on ISO 10723 – Natural gas -- Performance evaluation for analytical systems (1).

Calibration of the IR spectrometer was achieved using 4 binary mixtures and 7 multi-components mixtures. An evaluation of the IR spectrometer was made with 7 multi-component mixtures covering the range of global LNG compositions. The data from this evaluation was used to model the error distributions for gross calorific value (GCV) from 10,000 hypothetical compositions. The mean error and absolute mean error plus its uncertainty was compared with industry benchmarks for maximum permissible bias (MPB) and maximum permissible error (MPE) which are set at 0.09MJ/m<sup>3</sup> and 0.18MJ/m<sup>3</sup>, respectively. The instrument performance was tested with 5 different simulations each covering difference composition ranges. The performance of the instrument was determined to be unsatisfactory over the full range of compositions for UK custody transfer, however satisfactory performance was demonstrated over a narrower testing range for simulation

5. Moreover, the instrument may provide numerous benefits for applications requiring much lower accuracy requirements such as in process control.

## 7.2 Introduction

The benefits of applying direct measurement techniques for measuring LNG composition have been thoroughly explored in chapter 1 and chapter 6. A summary of the salient points follows. The issues with conventional vaporisation and measurement by GC contribute greatly to the final uncertainty budget for LNG energy value. The introduction of direct measurement techniques allows LNG to be measured in its liquid phase without the need for vaporisation and sample conditioning, therefore the uncertainty gains to be realised, the measuring instrument must be able to perform as good as a conventional GC in terms of complying with industrial performance benchmarks.

Infrared (IR) spectroscopy is an optical-based technique that measures the absorption of light through a sample at numerous wavelengths. The benefits of IR spectroscopy include: fast measurement times and cheaper instrument components compared with Raman spectroscopy since high-stability laser sources and sensitive amplification are required to detect the weak signal Raman scattering produces. However, IR instruments are unable to measure nitrogen since an induced dipole is required which is forbidden in symmetrical molecules. Assuming a complete mixture analysis, measurement by difference is possible, though the benefits of normalisation described in chapter 2 cannot be attained. In addition, IR spectra have complex overlapping spectral lines that require complex processing tools to deconvolute, whereas Raman and GC spectra have well-defined peaks that can be easily integrated.

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The use of multiple calibration standards to determine matrix effects at LNG temperatures has been thoroughly discussed in chapter 6 with reference to a 'solvent cage' effect caused by the major component, methane. The same procedure in principle is used for calibration of the IR spectrometer in this study. Following the calibration of the IR instrument, the model will be assessed using an ISO method that determines the spread of errors over a simulated range of compositions, allowing several thousand compositions to be theoretically evaluated. The results of the evaluation will be tested against industry performance benchmarks. The following section describes the method design and principles of the ISO method.

## 7.3 Method Design

A combination of binary- and multi-component calibration mixtures were used to build the IR model. Binary mixtures were restricted to higher amount fractions including ethane, propane, iso-butane and n-butane. Binary mixtures were used to assess the response of these components in methane and to establish efficient calibration parameters. Multi-component mixtures were used to assess the correlation effects of interacting species. 11 calibration mixtures shown in table 6.3-1 were used to build the calibration model, with the final three mixtures used to adjust the model and to determine temperature effects on predicted amount fractions. 7 validation mixtures shown in table 7.3-2 were used in the ISO 10723 performance evaluation described in the following section. These mixtures represent the full range of LNG compositions available globally.

compone nt	Mix cal_ 1b	Mix cal _2 b	Mi x cal _3 b	Mix cal_ 4b	Mix cal _5b	Mix cal_6 b	Mix cal _7b	Mix cal_8b	Mix cal_ 9b	Mix cal_1 0b	Mix cal_1 1b
nitrogen					2.1 0						
methane	90	96	95	97	85. 20	76.06	92. 49	89.43	89.4 7	81.69	92.39
ethane	10				6.1 2	15.10	3.5 0	7.11	7.07	12.04	3.54
propane		4			2.0 2	6.03	2.9 7	2.01	2.04	4.02	3.01
iso- butane			5		1.9 9	1.43	0.3 2	0.69	0.69	0.99	0.32
n-butane				3	1.9 8	1.03	0.5 8	0.60	0.59	1.10	0.60
iso- pentane					0.3 0	0.20	0.1 5	0.08	0.07	0.15	0.15
n- pentane					0.3 0	0.15		0.08	0.07		

Table 7.3-1 – Calibration mixtures proposed for building of the IR model.

Table 7.3-2 – Validation mixtures proposed for 10723 performance evaluation.

Component	Val_1b	Val_2b	Val_3b	Val_4b	Val_5b	Val_6b	Val_7b
nitrogen	0.150	0.570	0.830	1.600	1.090	0.690	0.048
methane	99.420	98.420	97.040	95.210	94.100	88.080	79.680
ethane	0.095	0.220	0.510	1.140	3.130	7.130	13.850
propane	0.095	0.230	0.420	0.770	1.270	2.120	3.970
iso-butane	0.078	0.230	0.620	0.390	0.130	1.010	1.320
n-butane	0.120	0.230	0.420	0.570	0.078	0.920	1.080
iso-pentane	0.028	0.050	0.080	0.153	0.100	0.028	0.030
n-pentane	0.018	0.050	0.080	0.163	0.100	0.018	0.020

All mixtures were prepared and verified in accordance with the methods described in chapter 2 section 2.3. For each gas condensation, the cryostat was prepared per chapter 2 section 2.2. The operating temperatures for each composition were determined by the solidification predictions as those determined in chapter 5. Data analysis was performed per chapter 2 section

2.4. The number of repeat runs for GC analysis was 48 for calibration and 96 for analysis of the sampled liquid composition. The IR instrument setup and spectral processing method is described thoroughly in chapter 2 section 2.6.

Final testing of the IR instrument was achieved using an ISO 10723 performance evaluation method. (1) This method is used to determine whether an analytical system setup to measure natural gas species over a defined composition range is fit for purpose. Its versatility provides insight into an instruments performance over a large population of simulated mixture compositions within a pre-defined range. The next section describes the principle and process of how the ISO 10723 performance method was applied to the IR instrument under investigation.

#### 7.3.1 ISO 10723 performance evaluation

The ISO 10723 method applies to all analytical systems setup to measure natural gas/LNG and is a legal requirement for fiscal transfer and emissions legislation in the EU. (2) The method provides valuable information including errors and uncertainties on component amount fractions and physical properties such as CV and compression factor over many simulated mixture compositions. Therefore, instead of comparing the errors and uncertainties of several compositions, a Monte-Carlo simulation provides a comparison of several thousand generated compositions, creating a complete picture of how the instrument performs at measuring theoretically every composition available to it.

With the information gained from the performance evaluation, changes to the calibration gas and/or the instrument analysis function can be made to ensure the instrument performs better over the given composition range and within an

agreed suitability criteria. In addition, the performance evaluation provides insight into the impact of each measured component on error and uncertainty in the calculated physical properties, allowing conclusions to be drawn about the calibration gas, limit of detections (LOD) for individual components and their contribution to analytical bias.

The main advantages of employing this method include: improved confidence in fiscal metering, conforming with EU emissions legislation (3) and reducing the risk in financial transactions due to mis-measurement. (4)

#### 7.3.1.1Principle

The route to accomplishing an ISO 10723 performance evaluation is as follows:

- (a) components and their ranges are specified over which the instrument shall be evaluated.
- (b) functional descriptions of the response functions assumed by the instrument for each specified component are established. These are referred to as assumed response functions at time of calibration/evaluation. These are used to determine the amount from the measured response,  $x = G_{asm}(y)$ .
- (c) composition and uncertainty of calibration gas mixture specified is established for the proposed calibration.
- (d) a set of reference gas mixtures are designed that cover the composition range specified in a).
- (e) a multi-point calibration is performed and instrument response data collected for mixtures defined in d).
- (f) the calibration functions and analysis functions are calculated for each component using regression analysis (GLS) and the compatibility of

the functions with the calibration data set are validated. These are the true response functions,  $y=F_{true}(x)$ ,  $x = G_{true}(y)$ .

- (g) instrument errors and uncertainties are calculated for each component and/or property over the specified range using the functions and reference data in d), e), and f).
- (h) from the distribution of errors and the unbiased uncertainty estimates calculated in g), the mean error,  $\overline{E}(P)$ , and its expanded uncertainty,  $U_c\overline{E}(P)$ , is determined for each measurand and physical property.

The required performance of the instrument is specified in terms of its maximum permissible error (MPE) and maximum permissible bias (MPB). The performance of the instrument is acceptable if it satisfies the following conditions:

 $\overline{E}(P) + U_c \overline{E}(P) \leq MPE$  and

 $\overline{E}(P) \leq MPB$ 

The MPE and MPB chosen for this evaluation was 0.18MJ/m<sup>3</sup> (0.4% relative) and 0.09MJ/m<sup>3</sup> (0.2% relative), respectively. These values are based on accuracy class A specified by The International Organisation for Legal Metrology (IOML) and National Grid and are enforced by The Office of Gas and Electricity Markets (OFGEM). (5; 6; 7).

The method of obtaining functional descriptions, regression functions, error distributions and uncertainties are described in the following section.

## 7.3.1.2Method

Full descriptions and derivations of mathematical expressions described in the following method are available in (1).

- Collation of assumed response functions for each component x = G<sub>asm</sub>(y) from the instrument.
- Collation of calibration data and inspection of outliers using the Grubbs test.
- Perform a general least squares (GLS) regression analysis on the calibration data as per the methods described in ISO 6143 - Gas analysis -- Comparison methods for determining and checking the composition of calibration gas mixtures. (8)
- 4) Conduct an F-test to determine the appropriate number of polynomials. A significance test is conducted to determine whether the polynomial regression applied explains a significant amount of the variance. An Ftest statistic is generated based on equation 6.1. The F-statistic is then compared to a critical value to determine if it is fit for purpose.

$$F = df_j \frac{r_j^2 - r_i^2}{1 - r_j^2}$$
 Equation

#### 7.1

Where *i* refers to the lower order polynomial and j refers to the higher order polynomial.

- 5) Calculate response functions in both domains, yielding a calibration function ( $F_{true}(x)$ ) and analysis function ( $G_{true}(y)$ ). The calibration function is the instrument response as a function of amount fraction and the analysis function is the amount fraction as a function of the instrument response.
- 6) Validate response function using 1<sup>st</sup> 2<sup>nd</sup> and 3<sup>rd</sup> order polynomials to determine best fit. Response model is considered compatible with the calibration data set if the following condition is fulfilled for every point (j= i...p):

$$|\hat{x}_{ij} - x_{ij}| \le ku(x_{ij}) \text{ and } |\hat{y}_{ij} - y_{ij}| \le ku(y_{ij})$$

The above condition is equivalent to having the calculated response curve pass through every experimental "calibration rectangle",  $[x_{ij}+-ku_{(xij)}, y_{ij}+-ku_{(yij)}]$  based on the expanded uncertainty, U =ku with a coverage factor equal to 2.

- 7) Testing the compatibility of the calibration function, the goodness of fit Γ, defined as the maximum value of weighted differences |x̂<sub>ij</sub> x<sub>ij</sub>|/u<sub>(xij</sub>) and |ŷ<sub>ij</sub> y<sub>ij</sub>|/u<sub>(yij</sub>), between the coordinates of measured and adjusted calibration points (j= [1...p]). The function is considered admissible if Γ ≤ 2.
- Test all polynomial response models until model is compatible with calibration data set.

The true calibration function is used in combination with the instruments assumed analysis function, and the calibration gas composition and uncertainty to determine performance benchmarks in terms of error with uncertainties. Conversely, the true analysis function is used post-evaluation to update the instruments assumed response function to reduce instrument errors.

9) Once the GLS regression is optimised, the errors and uncertainties on the individual components and physical properties can be determined from a population of 10,000 simulated compositions via a Monte-Carlo method.

The mean error and its combined standard uncertainty in amount fraction and GCV is calculated from equation 6.2 and 6.3, respectively.

$$\overline{E(P)} = \frac{\sum_{i}^{i=n} E(P_i)}{N}$$
Equation  
7.2

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Where  $E(P_i)$  is the error calculated for ith of N (10,000) hypothetical compositions. Error here is defined as the difference between the actual component amount fraction (or GCV) and the predicted component amount fraction (or GCV) based on the assumed response derived from the instrument.

$$u_c(\overline{E(P)}) = \overline{u^2[E(P_l)]} + u^2(\overline{E(P)})$$
Equation
7.3

Where  $\overline{u^2[E(P_i)]}$  is the arithmetic mean of the squared standard uncertainty in error,  $u^2[E(P_i)]$ , calculated for each 10,000 hypothetical compositions and  $u^2\overline{(E(P))}$  is the squared standard uncertainty in the mean error, calculated as a variance of errors for each 10,000 hypothetical compositions.

The combined standard uncertainty,  $u_c(\overline{E(P)})$ , is multiplied with a coverage factor of 2 (providing a level of confidence equivalent to 95%) to calculate the expanded combined uncertainty,  $U_c(\overline{E(P)})$ .

These results can then be compared with the analytical requirements of the instrument to determine if the instrument is fit for purpose. The mean error is compared with the MPB and the absolute mean error plus its uncertainty (mean error + combined uncertainty on mean error) is compared with the MPE. A visual representation illustrating these comparisons for a methane error distribution is shown in figures 7.3-1:4. Figure 7.3-1 shows the error and associated uncertainty (error bars) for 4 mixture compositions. Once this calculation is performed for 10,000 simulated mixture compositions, the mean errors are combined as shown in figure 7.3-2. The mean error is compared with the maximum permissible bias (MPB) as shown in figure 7.3-3. Following this, the absolute mean error plus its uncertainty is compared with the maximum permissible error (MPE) as shown in figure 7.3-4.



Figure 7.3-1 – Error and associated uncertainty for four mixture compositions



Figure 7.3-2- Error and associated uncertainty for 10,000 simulated mixture compositions



Figure 7.3-3 – Comparison of mean error with maximum permissible bias (MPB)



Figure 7.3-4 – Comparison of uncertainty on the mean error with the maximum permissible error (MPE)

## 7.4 Results and Discussion

This section is split into two parts. The first part describes experimental findings from the calibration of the IR spectrometer including the effects of different temperatures and a direct comparison of gross calorific value (GCV) between the IR measured composition and the GC liquid reference composition. The second part describes the results from the ISO 10723 performance evaluation with the addition of four alterations of the simulation to uncover any potential benefits of increasing the limit of detection (LOD) of the heavier hydrocarbon components and limiting the range over which the instrument measures.

### 7.4.1 Calibration of IR spectrometer

The calibration of the IR spectrometer was made using the mixtures shown in table 7.3-1. Reference composition analysis for all calibration mixtures is shown in tables 7.4-1:11. All mixtures shows good analytical agreement and verified to be within the specified EN12838 maximum permissible error criteria, with minimum and maximum differences in CV of 0.109 kJ/kg and 8.758 kJ/kg, respectively. For mixtures not containing nitrogen, a comparison of CV was made between the GC measured average composition and the gravimetric composition as specified by the methods described in chapter 2 section 2.4.3. For mixtures containing nitrogen, the corrected reference composition obtained through the methods described in chapter 2 section 2.4.3 was compared with the measured GC average composition.

Mix cal_1b	Amount (%mol		
component	GC average	Grav	Abs. Diff
methane	90.005	90.003	
ethane	9.995	9.997	
CV (kJ/kg)	54950.684	54950.574	0.109

Table 7.4-1- Verification of liquid composition for mix cal\_1b.

Table 7.4-2- Verification of liquid composition for mix cal\_2b.

Mix cal_2b	Amount (%mol		
component	GC average	Abs. Diff	
methane	96.036	96.012	
Propane	3.964	3.988	
CV (kJ/kg)	55044.551	55041.539	3.012

Table 7.4-3- Verification of liquid composition for mix cal\_3b.

Mix cal_3b	Amount (%mol		
component	GC average	Grav	Abs. Diff
methane	97.025	97.005	
n-butane	2.975	2.994	
CV (kJ/kg)	54975.938	54968.645	3.516

Table 7.4-4- Verification of liquid composition for mix cal\_4b.

Mix cal_4b	Amount (%mol		
component	GC average	Grav	Abs. Diff
methane	95.055	95.017	
iso-butane	4.945	4.982	
CV (kJ/kg)	54593.816	54587.320	6.496

Mix cal_5b	Amount fr (%mol/r		
component	GC average	Ref. Liquid	Abs. Diff
nitrogen	2.099	2.099	
methane	85.196	85.242	
ethane	6.123	6.206	
propane	2.016	1.926	
iso-butane	1.987	1.975	
n-butane	1.981	1.967	
i-Pentane	0.298	0.296	
n-Pentane	0.301	0.289	
CV (kJ/kg)	52487.305	52496.063	8.758

Table 7.4-5- Verification of liquid composition for mix cal\_5b.

Table 7.4-6- Verification of liquid composition for mix cal\_6b.

Mix cal_6b	Amount fr (%mol/r		
component	GC average	Grav	Abs. Diff
methane	76.061	75.925	
ethane	15.102	15.181	
propane	6.029	6.049	
iso-butane	1.429	1.459	
n-butane	1.031	1.031	
i-Pentane	0.201	0.201	
n-Pentane	0.153	0.153	
CV (kJ/kg)	53643.723	53634.945	8.777

Table 7.4-7- Verification of liquid composition for mix cal\_7b.

Mix cal_7b	Amount fr (%mol/r		
component	GC average	Grav	Abs. Diff
methane	92.376	92.386	
ethane	3.556	3.538	
propane	3.007	3.010	
iso-butane	0.320	0.321	
n-butane	0.596	0.599	
i-Pentane	0.145	0.146	
CV (kJ/kg)	54751.051	54750.789	0.262
Mix cal_8b	Amount fr (%mol/r		
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component	GC average	Grav	Abs. Diff
methane	89.427	89.449	
ethane	7.108	7.099	
propane	2.012	2.020	
iso-butane	0.688	0.688	
n-butane	0.602	0.594	
i-Pentane	0.080	0.073	
n-Pentane	0.083	0.078	
CV (kJ/kg)	54603.469	54607.281	3.813

Table 7.4-8- Verification of liquid composition for mix cal\_8b.

Table 7.4-9- Verification of liquid composition for mix cal\_9b.

Mix cal_9b	Amount fr (%mol/r		
component	GC average	Abs. Diff	
methane	ethane 89.435 89.467		
ethane	7.106	7.066	
propane	2.038	2.038	
iso-butane	0.689	0.691	
n-butane	0.589	0.591	
i-Pentane	0.072	0.072	
n-Pentane	0.070	0.075	
CV (kJ/kg)	54607.320	54607.844	0.523

Table 7.4-10- Verification of liquid composition for mix cal\_10b.

Mix cal_10b	Amount fraction		
component	GC average	Abs. Diff	
methane	81.623		
ethane	12.117		
propane	4.025	4.019	
iso-butane	0.991 0.995		
n-butane	1.099		
i-Pentane	0.146	0.150	
CV (kJ/kg)	54034.590	54036.445	1.855

Mix cal_11b	Amount fraction		
component	GC average	Abs. Diff	
methane	92.376		
ethane	3.556		
propane	3.007		
iso-butane	0.320	0.321	
n-butane	0.596	0.599	
i-Pentane	0.145	0.146	
CV (kJ/kg)	54751.051	54750.789	0.262

Table 7.4-11- Verification of liquid composition for mix cal\_11b.

#### 7.4.1.1IR spectral analysis

Data collected from the IR spectrometer was sent to MKS Instruments Inc. for data processing and algorithm design. Raw beams for calibration mixtures cal\_1b to cal\_8b are shown in figure 7.4-1-a. An example processing of beams obtained for mix cal\_8b is shown in figure 7.4-1-b. A logarithmic approach is used to convert the raw beams to spectral beams fit for processing, and this is achieved through combination with the zero background spectra. From figure 7.4-1, it is evident that the IR spectra are more complex to deconvolute than typical GC and Raman spectra that show well defined peak characteristics. For this reason, very complex algorithms are required for complete deconvolution from determination of peak areas to calculation of amount fractions. Consequently, the development of the algorithm and conversion of raw data to amount fractions was performed by MKS instruments Ltd.



Figure 7.4-1 – (a) IR raw beams for mix cal\_1b:8b and (b) example data processing for mix cal\_8b.

One of the major concerns during the initial planning of this study was the fact that nitrogen cannot be detected via IR absorption spectroscopy. The issue with this is that the data cannot be normalised (as with GC and Raman spectroscopy) since the nitrogen must be determined by difference. Normalisation provides a way of eliminating non-linearity resulting from sample size effects, therefore providing much better instrument repeatability. Without this tool at hand, there is no guarantee that the results can be systematically improved. Nonetheless, an algorithm design combined with the appropriate calibration data was realised.

As mentioned previously, the final three calibration mixtures (mix cal\_9b, mix cal\_10b, mix cal\_11b) were used for model alterations and temperature studies. The repeatability of these three mixtures at 110K is shown in table 7.4-12.

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	Mix cal_9b						
component	average composition (%mol/mol)	Std. dev.	%RSD				
methane	89.612	0.054	0.060				
ethane	7.983	0.150	1.882				
propane	2.637	0.022	0.846				
iso-butane	0.637	0.013	2.086				
n-butane	0.611	0.009	1.406				
iso-pentane	0.113	0.014	12.075				
n-pentane	0.067	0.007	10.007				
	M	lix cal_10b					
component	average composition (%mol/mol)	Std. dev.	%RSD				
methane	81.365	0.032	0.040				
ethane	12.208	0.053	0.436				
propane	4.440	0.013	0.299				
iso-butane	0.929	0.007	0.763				
n-butane	1.107	0.008	0.696				
iso-pentane	0.224	0.006	2.599				
n-pentane	0.169	0.004	2.127				
	M	lix cal_10b					
component	average composition (%mol/mol)	Std. dev.	%RSD				
methane	91.950	0.038	0.041				
ethane	3.759	0.115	3.065				
propane	3.194	0.006	0.195				
iso-butane	0.321	0.009	2.763				
n-butane	0.569	0.008	1.406				
iso-pentane	0.084	0.011	12.896				
n-pentane	-0.001	0.005	-523.992				

Table 7.4-12 – Repeatability of measured amount fractions for mix cal\_9b, mix cal\_10b and mix cal\_11b at 110K.

Methane performs the best with repeatability values ranging between 0.040 and 0.060%RSD. This is expected since methane is the major component in all three mixtures. A similar pattern should exist for ethane; however, this is not the case and ethane shows poorer repeatability than propane and in some cases a similar repeatability with iso-butane, despite iso-butane having an amount fraction 10-fold lower in all three mixtures. The higher repeatability for ethane could be due to the algorithm design and the impact from external influences such as temperature fluctuations, however temperature effects are likely to have an equal effect on all components. Though, this is not necessarily true if the raw signal from the instrument has a different sensitivity for different wavelengths. This can be tested by comparing the relative differences between measured composition and reference composition over a range of temperatures. The next section explores the sensitivity of temperature on composition.

#### 7.4.1.2Effects of temperature on composition

The effects of varying temperature on composition was investigated to see if a temperature sensitivity parameter was required for modelling purposes. Changes in composition as a function of temperature is predicted because the density of the liquid sample is extremely sensitive to temperature as shown in table 7.4-13. Liquid densities were calculated from the GasVLe physical properties software. A lower temperature results in a higher density and consequently more interacting molecules over the same path length (1mm). A 7% difference is observed between the liquid density at 95K and 120K for all mixtures. Therefore, there are 7% more molecules per unit volume at 95K than at 120K. This is where the method of normalisation could have be used to eliminate sample size effects assuming a linear response over the full range of compositions. However, due to an incomplete sample analysis (nitrogen by balance), the method of normalisation cannot be applied.

	liquid density (kg/m3)						
temperature (K)	mix cal_9b	mix cal_10b	mix cal_11b				
95	490.10	515.29	479.38				
100	483.61	508.96	472.81				
105	477.01	502.54	466.11				
110	470.29	496.02	459.28				
115	463.42	489.38	452.28				
120	456.39	482.61	445.11				

Table 7.4-13 – Liquid density at 95K, 100K, 105K, 110K, 115k and 120K for mixes cal 9b, cal 10b and cal 11b.

Figures 7.4-2:4 show amount fraction and % differences from reference amount fractions as a function of temperature for methane, ethane and propane for mix cal\_9b, mix cal\_10b and mix cal\_11b. These three components were chosen because they make up at least 97% of total composition and therefore have the most significant impact on final measurement error. The % differences shown represent those differences between the measured amount fraction and the GC reference amount fraction.



Figure -7.4-2- Methane amount fraction and % difference between measured and reference amount fraction as a function of temperature for mix cal\_9b, mix cal\_10b and mix cal\_11b.



Figure 7.4-3 - Ethane amount fraction and % difference between measured and reference amount fraction as a function of temperature for mix cal\_9b, mix cal\_10b and mix cal\_11b.



Figure 7.4-4- Propane amount fraction and % difference between measured and reference amount fraction as a function of temperature for mix cal\_9b, mix cal\_10b and mix cal\_11b.

Figure 7.4-2 shows % differences in methane to be within 2% of the reference composition. Conversely, ethane shows % differences to be within 12.5% of the reference composition as shown in figure 7.4-3. This difference is higher than what was measured for methane and this is expected since it is present at much lower amount fractions and smaller peaks are generally less repeatable. If this premise was true, then we would expect propane to show an even larger range of differences because of its lower amount fractions. Figure 7.4-4 shows % differences between measured composition and reference composition for propane to be within 20%, significantly higher than that found for both ethane and methane. Therefore, lower amount fractions are more susceptible to changes in temperature.

Furthermore, it is a clear that a temperature sensitivity correction is required if the model is to be successful in environments which are more susceptible to changes in temperature. In this work, the instrument model uses calibration data at 110K and this can be seen from figures 7.4-2:4 as the % differences between the IR measured and the GC reference liquid composition are the smallest. 110K was the chosen calibration temperature because it represents the temperature of most LNG cargos and import facilities.

#### 7.4.2 Validation of IR spectrometer

Validation of the IR spectrometer was made with 7 validation mixtures shown in table 7.3-2 spanning the full range of global LNG compositions. Prior this, a calibration with one mixture was made after the model was finalised to replicate a true calibration during installation. The validation was made at 110K to match the temperature at which the calibration model data was based upon. This section is split up into two parts. Firstly, a direct comparison of composition and GCV between the IR measured composition and GCdetermined reference composition is presented. Following this, the results from the ISO17023 are discussed.

#### 7.4.2.1 Direct comparison of composition and CV

A comparison of composition and GCV is shown for mixtures cal\_1c and val\_1b:7b in tables 7.4-14:21. On first observation, one can see a clear pattern of larger differences in composition in descending order of composition from methane to n-pentane. Methane shows the smallest difference in composition with a range from 0.03% to 1.61%. The largest differences are seen for iso-pentane and n-pentane with values ranging from 68% to 1300%, respectively. However, since both components are present in the lowest amount fractions, they have minimal impact on reported GCV. The measurement of ethane is shown to problematic with amount fractions below 0.25% giving rise to differences in the range between 125% and 360%. Negative amount fractions were reported for ethane, iso-pentane and n-pentane in mixtures val\_1b and val\_2b, therefore there is a requirement for a built-in auto-zero to prevent the model from reporting negative amount fractions.

Mix cal_1c	IR values			GC reference		
	yi	%RSD	U (yi) k=2	X <sub>REF</sub>	Difference (x <sub>REF</sub> - yj)	% Difference (x <sub>REF</sub> - yi)
methane	85.875	0.052	0.089	85.900	0.025	-0.03
ethane	8.302	0.259	0.043	8.638	0.336	-4.05
propane	3.309	0.542	0.035	3.482	0.174	-5.25
iso-butane	1.187	0.487	0.011	1.229	0.042	-3.52
n-butane	0.564	0.625	0.007	0.488	-0.076	13.47
iso-pentane	0.074	2.681	0.003	0.148	0.074	-100.93
n-pentane	0.042	2.208	0.001	0.116	0.074	-175.18

Table 7.4-14- Comparison of IR measured composition and GC-reference composition for mix cal\_1c.

CV (MJ/m3)	43.684		43.979	0.295	
15/15					

Mix Val_1b	IR values		Corrected reference			
	yi	%RSD	U (yi) k=2	X <sub>REF</sub>	Difference (x <sub>REF</sub> - xj)	% Difference (x <sub>REF</sub> - yi)
nitrogen	0.828	3.133	0.052	0.144	-0.684	82.60
methane	99.190	0.033	0.065	99.433	0.243	-0.24
ethane	-0.140	14.429	0.040	0.098	0.238	170.17
propane	-0.172	9.576	0.033	0.091	0.263	152.77
iso-butane	0.196	1.839	0.007	0.075	-0.122	62.01
n-butane	0.167	2.963	0.010	0.115	-0.052	31.27
iso- pentane	-0.024	4.680	0.002	0.027	0.051	210.30
n-pentane	-0.046	2.805	0.003	0.018	0.064	138.31
CV (MJ/m3) 15/15	37.775			38.017	0.242	

Table 7.4-15- Comparison of IR measured composition and GC-referencecomposition for mix val\_1b.

Table 7.4-16- Comparison of IR measured composition and GC-reference
composition for mix val_2b.

Mix Val_2b	IR values			GC reference		
	yi	%RSD	U (yi) k=2	X <sub>REF</sub>	Difference (x <sub>REF</sub> - xj)	% Difference (x <sub>REF</sub> - yi)
nitrogen	0.595	2.087	0.025	0.558	-0.037	6.27
methane	98.678	0.028	0.056	98.462	-0.216	0.22
ethane	-0.083	24.089	0.040	0.216	0.299	360.76
propane	0.145	3.874	0.011	0.227	0.082	-56.27
iso-butane	0.295	1.543	0.009	0.219	-0.076	25.65
n-butane	0.377	1.514	0.011	0.223	-0.154	40.81
iso-pentane	0.008	9.760	0.001	0.046	0.039	-508.52
n-pentane	-0.015	5.764	0.002	0.048	0.064	412.86
CV (MJ/m3) 15/15	38.215			38.241	0.026	

Mix Val_3b	IR values			GC reference		
	yi	%RSD	U (yi) k=2	X <sub>REF</sub>	Difference (x <sub>REF</sub> - xj)	% Difference (x <sub>REF</sub> - yi)
nitrogen	0.899	2.060	0.037	0.728	-0.171	19.02
methane	97.346	0.032	0.061	97.192	-0.154	0.16
ethane	0.229	7.707	0.035	0.515	0.286	-125.11
propane	0.177	3.128	0.011	0.410	0.232	-131.18
iso-butane	0.681	0.521	0.007	0.592	-0.089	13.09
n-butane	0.642	0.602	0.008	0.408	-0.234	36.51
iso-pentane	0.020	3.887	0.002	0.077	0.058	-294.21
n-pentane	0.006	23.529	0.003	0.078	0.073	-1229.87
CV (MJ/m3) 15/15	38.755			38.906	0.151	

Table 7.4-17- Comparison of IR measured composition and GC-referencecomposition for mix val\_3b.

Table 7.4-18- Comparison of IR measured composition and GC-referencecomposition for mix val\_4b.

Mix Val_4b	I	R values		GC reference		
	yi	%RSD	U (yi) k=2	X <sub>REF</sub>	Difference (x <sub>REF</sub> - yj)	% Difference (x <sub>REF</sub> - yi)
nitrogen	1.278	1.026	0.026	1.331	0.053	-4.13
methane	95.576	0.027	0.051	95.493	-0.083	0.09
ethane	1.064	.064 1.343 0.		1.149	0.085	-7.96
propane	0.557	1.114	0.012	0.765	0.208	-37.33
iso-butane	0.473	0.465	0.004	0.386	-0.087	18.49
n-butane	0.955	0.331	0.006	0.567	-0.388	40.62
iso-pentane	0.047	1.461	0.001	0.149	0.102	-215.69
n-pentane	0.049	2.005	0.002	0.160	0.111	-226.96
CV (MJ/m3) 15/15	39.234			39.194	0.041	

Mix Val_5b	I	R values		GC reference		
	yi	%RS D	U (yi) k=2	X <sub>REF</sub>	Difference (x <sub>REF</sub> - yj)	% Difference (x <sub>REF</sub> - yi)
nitrogen	0.962	1.926	0.037	0.989	0.027	-2.81
methane	94.341	0.034	0.065	94.031	-0.310	0.33
ethane	3.112	0.680	0.042	3.325	0.213	-6.85
propane	1.013	0.863	0.017	1.251	0.238	-23.48
iso-butane	0.189	1.513	0.006	0.129	-0.061	31.98
n-butane	0.329	1.630	0.011	0.077	-0.252	76.56
iso-pentane	0.020	4.801	0.002	0.099	0.079	-396.76
n-pentane	0.034	3.504	0.002	0.099	0.065	-189.61
CV (MJ/m3) 15/15	39.381			39.464	0.083	

Table 7.4-19- Comparison of IR measured composition and GC-referencecomposition for mix val\_5b.

Table 7.4-20- Comparison of IR measured composition and GC-referencecomposition for mix val\_6b.

Mix val 6b	I	R values		GC reference		
	yi	%RS D	U (yi) k=2	X <sub>REF</sub>	Differenc e (x <sub>REF</sub> - yj)	% Difference (x <sub>REF</sub> - yi)
nitrogen	0.368	3.471	0.026	0.562	0.194	-52.88
methane	88.580	0.025	0.044	88.156	-0.424	0.48
ethane	6.883	0.253	0.035	7.238	0.355	-5.16
propane	2.100	0.376	0.016	2.092	-0.008	0.39
iso- butane	0.893	0.330	0.006	0.999	0.106	-11.92
n-butane	0.982	0.478	0.009	0.906	-0.076	7.69
iso- pentane	0.100	0.689	0.001	0.028	-0.072	72.43
n- pentane	0.094	1.099	0.002	0.018	-0.076	80.80
CV (MJ/m3) 15/15	42.609			42.490	0.119	

Mix val_7b	I	R values		GC reference		
	yi	%RSD	U (yi) k=2	X <sub>REF</sub>	Difference (x <sub>REF</sub> - yj)	% Difference (x <sub>REF</sub> - yi)
nitrogen	-0.575	-3.042	0.035	0.042	0.616	107.25
methane	81.089	0.048	0.078	79.780	-1.309	1.61
ethane	12.777	0.214	0.055	13.869	1.093	-8.55
propane	4.212	0.286	0.024	3.898	-0.314	7.46
iso-butane	1.229	0.327	0.008	1.295	0.066	-5.34
n-butane	1.071	0.564	0.012	1.067	-0.004	0.34
iso- pentane	0.132	0.624	0.002	0.029	-0.103	78.01
n-pentane	0.064	1.943	0.003	0.020	-0.044	68.90
CV (MJ/m3) 15/15	45.955			46.007	0.052	

Table 7.4-21- Comparison of IR measured composition and GC-reference composition for mix val\_7b.

The measurement of nitrogen was very problematic because of its calculation by difference. When the remaining components mis-measure by even a small amount, this adds to the error in measured nitrogen amount fraction. For example, in mix val\_1b methane was underestimated by 0.2 %mol/mol and ethane, propane, iso-pentane and n-pentane reported negative amount fractions. Hence, the prediction of nitrogen by difference was significantly larger than the reference composition (0.828 %mol/mol compared with 0.144 %mol/mol). This is a clear weakness of the model, especially with amount fractions greater than 0.5% since they have a large impact on GCV. A built-in auto-zero method would prevent negative amount fractions from being reported and improve this. Though, closer estimation of all amount fractions would result in a better prediction for nitrogen amount fraction.

The accuracy requirement for GCV-determining instruments was recently relaxed by OFGEM (The Office of Gas and Electricity Markets) from 0.14MJ/m3 to 0.2MJ/m3. (6) This relaxation was implemented to allow and

encourage the development of alternative technologies for their penetration into the market.

All but two of the testing mixtures (cal\_1c and val\_1b) pass this criterion with minimum and maximum values of 0.026 MJ/m3 and 0.151 MJ/m3, respectively. However, differences in error are not the only consideration during the testing of such instruments. Repeatability is also an important consideration because it determines the uncertainty on the error. Without a statement of uncertainty, there is no confidence in the measurement itself. The uncertainties expressed in tables 7.4-14:21 are those only attributed to the standard deviation of the measurement itself. A true uncertainty would require incorporating uncertainty from the calibration mixture and other sources. However, for the purposes of this comparison, only the composition and CV were of importance. The following section explores the errors, uncertainties and biases through a simulated experiment design which allows for theoretically all compositions to be tested based on the current model.

#### 7.4.2.2ISO 10723 performance evaluation

The principle, methods and benefits of an ISO 10723 evaluation have been discussed in section 7.3.1. This section discusses the results from such an evaluation using the data generated from the 7 validation mixtures described in section 7.4.2.1. Calibration functions comparing measured amount fraction to actual (reference) amount fraction are shown in figure 7.4-5. The ideal relationship between the true and measured response is linear, however polynomial functions are applied when required. Both methane and ethane show linear relationships. All other components are non-linear except for isopentane and n-pentane which show non-contiguous behaviour toward the lower end amount fractions. Similarly, nitrogen provides a linear relationship but the spread of data suggests a poor degree of relation between amount

fraction and response. Nonetheless, all data was included in the Monte-Carlo simulation.



Figure 7.4-5 – Calibration functions derived from reference composition and measured composition

10,000 mixtures were simulated based on the range of validation compositions used. For each composition, the mean error and its associated uncertainty in GCV and component-related error is calculated. The minimum, maximum and average error and uncertainty is shown in table 7.4-22 and table 7.4-23. Two uncertainty values are shown. The uncertainty U(P) is the uncertainty derived from the calibration gas and instrument repeatability, whereas the uncertainty on the bias (B(P)) considers the spread of error in addition to the uncertainty of the calibration gas and instrument repeatability.

The mean error was determined to be 0.314MJ/m<sup>3</sup> compared with the MPB limit of 0.09MJ/m<sup>3</sup>. The absolute mean error plus its uncertainty was calculated to be 0.834MJ/m<sup>3</sup> compared to the MPE limit of 0.18MJ/m<sup>3</sup>. Both MPE and MPB limits have been significantly exceeded, therefore the instrument performance over the proposed composition range can be considered unacceptable.

One of the biggest contributors to these large errors is the mismeasurement of nitrogen. From table 7.4-23, the relative difference between the mean error (0.36MJ/m<sup>3</sup>) and the mean composition range (0.75MJ/m<sup>3</sup>) is larger for nitrogen than any other component. The reason for this is that the IR instrument determines nitrogen amount fraction by difference, therefore any mis-measurement in the other components is factored into this calculation. For example, the instrument response for iso-pentane and n-pentane can be considered as a random since there is no relationship between actual amount fraction and instrument response. Therefore, the mis-measurement resulting from these poor calibration functions results in a significant error in nitrogen amount fraction. Also, nitrogen has a larger influence on total GCV than the heavier components because of its larger difference in GCV relative to methane.

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property	rar	nge	errors				bias				
	P,min	P,max	E(P),min	E(P),mean	E(P),max	U(P),min	U(P),mean	U(P),max		B(P)	
GCV (MJ.m-3)	40.839	48.019	-0.456	0.314	1.085	0.022	0.027	0.034	0.314	±	0.520
%			-1.064%	0.713%	2.499%	0.053%	0.061%	0.075%			

Table 7.4-23- min, max and mean error, bias and uncertainty in component amount fraction for 10,000 simulated mixture compositions from the full data set.

component	calibration gas	rar (% mc	nge ol/mol)		errors			uncertainties			bias		
		x,min x,max		ax E(x),min E(x),mean E(x),max U(x),min U(x),mean U(x),m		U(x),max	B(x) (9	%mol/	'mol)				
nitrogen	0.000	0.048	1.585	-0.641	0.366	1.623	0.000	0.000	0.000	0.366	±	0.708	
methane	85.889	79.766	97.967	-0.923	-0.216	0.468	0.046	0.056	0.073	-0.216	±	0.636	
ethane	8.630	0.100	13.843	-0.286	0.001	0.185	0.042	0.053	0.071	0.001	±	0.268	
propane	3.501	0.094	3.928	-0.271	-0.169	0.133	0.013	0.015	0.020	-0.169	±	0.213	
iso-butane	1.237	0.078	1.312	-0.026	0.051	0.132	0.006	0.008	0.011	0.051	±	0.119	
n-butane	0.491	0.078	1.081	-0.458	-0.095	0.054	0.006	0.009	0.010	-0.095	±	0.304	
iso-pentane	0.150	0.028	0.152	-0.003	0.070	0.143	0.008	0.008	0.009	0.070	±	0.085	
n-pentane	0.103	0.018	0.163	-0.065	-0.009	0.046	0.008	0.012	0.019	-0.009	±	0.065	

An error distribution for methane is shown in figure 7.4-6. It is clear there is a large bias in the positive direction, therefore on average the GCV is overestimated. The error distribution is scattered uniformly across the full range of composition which shows that the performance of the instrument is the same regardless of the measured methane amount.





Figure 7.4-6 – Methane error distribution for 10,000 simulated mixtures over the full composition range.

The calibration functions shown in figure 7.4-5 demonstrate that there is high degree of non-linearity in the lower amount fractions of iso-butane, n-butane, iso-pentane and n-pentane. Therefore, a separate study was set up to investigate the impact of increasing the limit of detection (LOD) for these four components. The LOD for iso-butane and n-butane was set to 0.2 MJ/m<sup>3</sup> and the LOD for iso-pentane and n-pentane was set to 0.04MJ/m<sup>3</sup>. 10,000 hypothetical mixtures were run through the ISO10723 simulation and the resulting errors and uncertainties are reported in table 7.4-24 and 7.4-25. The

mean error in GCV decreased by one half from 0.314 MJ/m<sup>3</sup> to 0.149 MJ/m<sup>3</sup>, however the uncertainty on the bias (mean error) decreased by only 0.009 MJ/m<sup>3</sup> from 0.520 MJ/m<sup>3</sup> to 0.511 MJ/m<sup>3</sup>. For this simulation, the mean error calculated to be 0.149 MJ/m<sup>3</sup> exceeds the MPB limit of 0.09 MJ/m<sup>3</sup> and absolute mean error plus its uncertainty was calculated to be 0.660 MJ/m<sup>3</sup>, exceeding the MPE limit of 0.18MJ/m<sup>3</sup>. Therefore, under the proposed LOD, the instrument performance over the full composition range is considered unacceptable.

Figure 7.4-7 illustrates the changes observed in the error distribution and bias for methane. In comparison to figure 7.4-6, there is less bias and this is indicated by the more even spread of errors around the zero line. However, the actual range of errors has effectively been unaltered. Again, the error distribution is scattered uniformly across the full range of composition which shows that the performance of the instrument is the same regardless of the measured methane amount. E(CV<sub>sup</sub>) / MJ.m<sup>-3</sup>



Figure 7.4-7- Methane error distribution for 10,000 simulated mixture compositions over LOD-altered data range.

Table 7.4-24- min, max and me	an error, bias and uncertai	nty in GCV for	<sup>.</sup> 10.000 simulated mixture	e compositions from the	LOD-altered data set.
,	,		,		

property	rar	nge	errors		uncertainties			bias			
	P,min	P,max	E(P),min	E(P),min E(P),mean		U(P),min	U(P),mean	U(P),max	B(P)		
GCV (MJ.m-3)	40.175	48.169	-0.734	0.149	0.938	0.016	0.023	0.029	0.149	±	0.511
%			-1.678%	0.340%	2.152%	0.038%	0.053%	0.063%			

 Table 7.4-25- min, max and mean error, bias and uncertainty in component amount fraction for 10,000 simulated mixture compositions from the

 LOD-altered data set.

component	calibration	rang	je (%	errors				uncertaintie	S	bias		
	gas	mol/	'mol)									
		x,min	x,max	E(x),min	E(x),mean	E(x),max	U(x),min	U(x),mean	U(x),max	B(x) (%mo	ol/m	ol)
nitrogen	0.000	0.048	1.585	-0.526	0.515	1.877	0.000	0.000	0.000	0.515	±	0.707
methane	85.889	79.733	98.105	-0.934	-0.213	0.471	0.044	0.055	0.072	-0.213	±	0.634
ethane	8.630	0.098	13.843	-0.286	0.002	0.185	0.042	0.053	0.071	0.002	±	0.268
propane	3.501	0.094	3.928	-0.271	-0.168	0.133	0.013	0.015	0.020	-0.168	±	0.213
iso-butane	1.237	0.078	1.312	-0.200	0.031	0.136	0.000	0.008	0.011	0.031	±	0.166
n-butane	0.491	0.078	1.081	-0.475	-0.125	0.019	0.000	0.008	0.010	-0.125	±	0.278
iso-pentane	0.150	0.028	0.152	-0.040	-0.018	0.001	0.000	0.005	0.007	-0.018	±	0.018
n-pentane	0.103	0.018	0.163	-0.128	-0.025	0.010	0.000	0.007	0.011	-0.025	±	0.072

Surprisingly, the mean error for nitrogen increased from 0.366 MJ/m<sup>3</sup> to 0.515 MJ/m<sup>3</sup> despite the mean and range of errors decreasing for iso-butane, nbutane, iso-pentane and n-pentane. Therefore, the mismeasurement of these components cannot be the only reason for the poor calculation of nitrogen by difference discussed hitherto. The next section explores the impact of applying narrower composition ranges and more suitable calibration gases to the final error and uncertainty in GCV.

# 7.4.2.3ISO 10723 Testing for specific import/export terminal composition ranges

An ISO 10723 simulation was performed for the composition ranges provided from three import terminals shown in table 4.4-26. The data for each import terminal was provided by Shell Global Solutions Ltd. For each simulation, the typical composition was used as the effective calibration gas since it is a mid-range composition. It is expected that the terminal with the narrowest composition range will perform best in terms of overall error in GCV and component related error. This is because the assumed response curve derived from the calibration gas will have a higher likelihood of matching the actual response curve for a narrower range compared with wider range. The wider the range of compositions, the higher the likelihood the assumed response curve will deviate from the actual response. This effect is illustrated in figure 7.4-8. Figure 7.4-8 demonstrates that for a narrower testing range, the accumulated errors due to differences between the measured amount fraction and the true amount fraction are smaller than those accumulated errors resulting from a wider testing range.

	omount	Terminal 1	nol/mol)							
Component	amount fraction (%mol/mol)									
Component	IVIIII	IVIAX	i ypicai							
nitrogon	0.020	1 150	0.210							
mothana	0.020	07.440	0.310							
othono	2 270	97.440	90.000							
Propapo	2.270	2 410	3.730							
iso-butano	0.020	0.720	2.040							
n-butane	0.000	0.720	0.000							
iso-pontano	0.000	0.000	0.000							
n-pontano	0.000	0.000	0.020							
n-pentane	0.000	U.UZU	0.000							
	amount	fraction (%	ol/mol)							
Component	Min	Max	Typical							
component	IVIIII	Ινίαλ	comp							
nitrogen	0.000	0.550	0 140							
methane	88 870	97 710	92 942							
ethane	2 030	10 550	5 575							
nronane	0.020	2 280	1 079							
iso-butane	0.020	0.320	0.152							
n-butane	0.000	0.280	0.102							
iso-pentane	0.000	0.170	0.003							
n-pentane	0.000	0.060	0.003							
n pontano	0.000	Terminal 3	0.000							
	amount	fraction (%r	nol/mol)							
Component	Min	Max	Typical							
			comp							
nitrogen	0.060	0.660	0.324							
methane	88.920	93.040	90.572							
ethane	4.210	6.680	5.819							
propane	1.910	2.590	2.225							
iso-butane	0.270	0.740	0.506							
n-butane	0.220	0.720	0.533							
iso-pontano	0.000	0.050	0.021							
150-pentane										

### Table 7.4-26 – Minimum, maximum and typical composition ranges for three import terminals.



Figure 7.4-8- Illustration of the differences in accumulated error between a narrow testing range and a wider testing range.

The mean error and its associated uncertainty calculated from 10,000 hypothetical compositions for each terminal is shown in tables 7.4-27:29. Terminal 1 gives a mean error of 0.0295 MJ/m<sup>3</sup> and an absolute mean error plus its uncertainty equal to 0.2742 MJ/m<sup>3</sup>. In this case the mean error is within the MPB limit of 0.09MJ/m<sup>3</sup>, however the absolute mean error plus its uncertainty exceeds the MPE limit of 0.18 MJ/m<sup>3</sup>. For terminal 2, the mean error and the absolute mean error plus its uncertainty was calculated to be - 0.126 MJ/m<sup>3</sup> and -0.356 MJ/m<sup>3</sup>, respectively. Consequently, terminal 2 failed to meet both MPB and MPE criteria. Finally, for terminal 3, the mean error and the absolute mean error plus its uncertainty was calculated to be 0.004 MJ/m<sup>3</sup> and 0.135 MJ/m<sup>3</sup>, respectively. As predicted, terminal 3 performed best with its narrower composition range compared with terminal 1 and terminal 2, and fell within both the MPE and MPB criteria.

Table 7.4-27- min, max and mean error, bias and uncertainty in GCV for 10,000 simulated mixture compositions based terminal 1.

property	rar	nge	errors				;	bias			
	P,min	P,max	E(P),min	E(P),mean	E(P),max	U(P),min	U(P),mean	U(P),max	B(P)	0	0
calorific value (superior) (MJ m-3)	38.343	43.354	-0.3067	0.0295	0.4016	0.0207	0.0359	0.0551	0.0295	±	0.2446
%			-0.720%	0.072%	0.986%	0.053%	0.088%	0.132%			

Table 7.4-28- min, max and mean error, bias and uncertainty in GCV for 10,000 simulated mixture compositions based terminal 2.

property	range		errors			uncertainties			bias		
	P,min	P,max	E(P),min	E(P),mean	E(P),max	U(P),min	U(P),mean	U(P),max	B(P)	0	0
calorific value (superior) (MJ.m-3)	38.325	41.853	-0.440	-0.126	0.250	0.016	0.035	0.053	-0.126	±	0.230
%			-1.070%	-0.312%	0.623%	0.042%	0.086%	0.128%			

Table 7.4-29- min, max and mean error, bias and uncertainty in GCV for 10,000 simulated mixture compositions based terminal 3.

property	range		errors			uncertainties			bias		
	P,min	P,max	E(P),min	E(P),mean	E(P),max	U(P),min	U(P),mean	U(P),max	B(P)	0	0
calorific value	40.450	42.135	-0.204	0.004	0.180	0.023	0.029	0.037	0.004	±	0.131
(superior) (MJ.m-3)											
%			-0.490%	0.011%	0.441%	0.057%	0.071%	0.088%			

Error distributions for methane from terminal 1, 2 and 3 simulations are shown in figures 7.4-9:11. Data from terminal 1 shows a relatively even error distribution around the zero line, however there is a subtle positive trend with increasing amount fraction. The smallest errors are seen for amount fractions greater than 94 %mol/mol. A similar trend is seen in figure 7.4-10 for terminal 2, however the error distribution is disproportionately negative demonstrated by the zero-line reference. Therefore, for terminal 2 the instrument model would, on average, underestimate the GCV over the expected composition range. Data from terminal 3 shows the most even distribution of errors around the zero-line for methane. Therefore, on average, the instrument model would neither overestimate nor underestimate the measurement of GCV for compositions equivalent to terminal 3.



E(CV<sub>sup</sub>) / MJ.m<sup>-3</sup>

Figure 7.4-9 - Methane error distribution from 10,000 simulated mixture compositions for Terminal 1 data.

E(CV<sub>sup</sub>) / MJ.m<sup>-3</sup>



Figure 7.4-10- Methane error distribution from 10,000 simulated mixture compositions for Terminal 2 data.



Figure 7.4-11- Methane error distribution from 10,000 simulated mixture compositions for Terminal 3 data.

Overall, applying specific and smaller composition ranges with representative calibration gases does significantly reduce the mean error and its associated combined standard uncertainty in GCV. In all three terminal cases, the MPB limit of 0.2 MJ/m3 was achieved. However, the MPE limit of 0.02 MJ/m3 was not realised in any of the terminal cases due to the large uncertainties associated with the mean error. The improvement in mean error and combined standard uncertainty was associated with the fact that the composition ranges applied were much narrower than in the original simulation. This was illustrated in figure 7.4-8 as a comparison between the accumulation of errors between a wider composition range and a narrower composition range.

#### 7.5 Conclusions

In conclusion, all calibration and validation mixtures were successfully verified against the EN12838 maximum permissibility criteria, providing confidence in their use. Since nitrogen cannot be measured by IR spectroscopy, this was an initial concern since no normalisation method could be used to improve instrument repeatability. However, the repeatability of the data showed to be satisfactory and equivalent to typical GC measurement repeatability.

The Density of LNG varies by approximately 7% over the temperature range 95K to 120K, therefore the effects of temperature on IR measured composition was studied to determine if a temperature correction parameter was required. The major LNG components methane, ethane and propane showed significant differences between the IR measured composition and the GC reference liquid composition. The IR measured composition was within 2%, 12.5% and 20% of the GC reference liquid composition for methane, ethane and propane, respectively. This confirmed the need for a temperature correction if the instrument is to be used in environments where there is an

expected difference between the calibration temperature and usage temperature.

Following the 7-mixture validation, a comparison of the IR measured composition with the GC reference liquid showed small differences for methane and significantly large differences for iso-pentane and n-pentane. The influence of the both iso-pentane and n-pentane on GCV is insignificant at these very low amount fractions, therefore their accuracy was not considered impactful. Amount fractions of ethane below 0.25% showed to be problematic with differences between IR and GC measured composition covering the range of between 125% and 360%. Reporting of negative amount fractions was also observed for ethane, iso-pentane and n-pentane for mixtures val\_1b and val\_2b, and since nitrogen is calculated by difference, the negatively reported amount fractions will contribute to the its mismeasurement. Therefore, an auto-zero is required to be built into the model to prevent negative amount fractions being reported and to minimise the impact on the calculation of nitrogen.

The first ISO 10723 performance evaluation was made using the complete data set over the full range of LNG compositions. The mean error was determined to be 0.314MJ/m<sup>3</sup> compared with the MPB limit of 0.09MJ/m<sup>3</sup>. The absolute mean error plus its uncertainty was calculated to be 0.834MJ/m<sup>3</sup> compared to the MPE limit of 0.18MJ/m<sup>3</sup>. Therefore, the instrument performance over the full composition range was considered unacceptable with reference to OFGEM limits. The heavier components iso-pentane, n-pentane, iso-butane and n-butane showed a heavy degree of non-linearity toward the lower end amount fractions. Therefore, an ISO 10723 performance evaluation with set limits for LOD for each component was made to help remove the impact from the observed non-linearity. Although the mean error

decreased by almost one half, the uncertainty on bias changed by approximately 0.009MJ/m3. So, there was an improvement in the model's performance, though the OFGEM performance limits were exceeded, rendering the performance of the model unacceptable.

Several 10723 performance evaluations were made on narrower composition ranges based on three existing LNG terminals. A significant reduction in mean error was achieved for all three terminals and the MPB limit was achieved in all three cases with mean error values falling below 0.09MJ/m<sup>3</sup>. However, the uncertainty on the mean error satisfied the MPE specification limit of 0.18MJ/m<sup>3</sup> in only one of the three cases. The best performing evaluation was that with terminal 3 which shows the narrowest composition range. The reason for this is that the accumulation of errors between the measured and true composition is reduced when the range of compositions is smaller.

Moreover, the performance of the IR spectrometer was determined to be unsatisfactory in terms of complying with the current accuracy requirements for UK custody transfer over the full range of compositions. However, when applying specific and narrower composition ranges, the instrument demonstrated satisfactory performance. Moreover, there is much scope for model improvement including: the introduction of a temperature correction, reducing the non-linearity of heavier components towards the lower-end amount fractions, using additional calibration mixtures to model mid-range amount fractions and improving the prediction of nitrogen amount fraction with an automatic zero when negative amount fractions are calculated.

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#### 8 Conclusions

This chapter provides a summary of the main conclusions drawn from each results chapter and aims to provide context with reference to the project aims and objectives specified in chapter 1. Following this, and in accordance with objective 5, a further work section will propose potential studies that could prove to be useful in further developing the research undertaken in this project.

### 8.1 Objective 1 – verification of cryostat liquefaction system

The first objective of this work was to validate the cryostat liquefaction system over the full range of typical LNG compositions to provide confidence in its use for testing direct measuring instruments. The verification was made by comparing sampled liquid compositions with the reference calibration gas compositions and testing the results against the specification criteria in EN12838 with the addition of the En-ratio statistical significance test. Meeting this objective was a prerequisite for the studies conducted in chapters 5, 6 and 7. The verification was made with the strictest benchmark criteria on the premise that the calibration device must be a 'sharper' tool than the instrument under investigation. The results from 7 LNG compositions covering the full

range fell within the said criteria, therefore validating the cryostat sampling system.

The cryostat liquefier used in this work is the only known device that can reliably and representatively sample multi-component liquid compositions. An investigation on the European Metrology Research Programme (EMRP) for LNG metrology revealed several failed attempts to replicate such a system due to system leakages and design flaws. However, the research groups from the National Physical Laboratory (NPL) and the Dutch Metrology Institute (VSL) responsible for delivering this work package have found a different way of assessing vaporiser systems and cross-validating direct measuring instruments by sampling an unknown stream of LNG. However, with this design approach vaporisers can only be assessed on their repeatability since an accuracy assessment would require knowledge of the LNG composition prior to vaporisation. Therefore, this method of assessment adds an extra dimension of uncertainty which is eliminated in the method developed in this work because the original composition is known and has a traceability chain to the SI unit of amount of substance.

### 8.2 Objective 2 – Validation of Raman spectrometer for

#### measuring mixed refrigerant (MR) composition

The second objective of this work was to calibrate and validate an Optograf<sup>™</sup> Raman spectrometer for measuring mixed-refrigerant (MR) composition. The direct measurement of MR composition in LNG refrigeration processes provides numerous benefits including; fast measurement times, quicker responses to unexpected changes in composition and the in-line monitoring of composition over time. Perhaps the biggest benefit is that the model may be used in conjunction with other models such that multiple processes can be monitored simultaneously, therefore having one instrument that measures all.

The validation of the MR model demonstrated to be successful with relatively small differences observed in measured and reference compositions. The impact of these differences was assessed by comparing the theoretical heat capacities calculated from the measured and reference composition. Heat capacity was the chosen physical property because it has a direct influence on the hot and cold composite curves in the refrigeration process. Minimising the work done by the MR by closely matching the hot and cold composite curves results in an improvement in thermodynamic efficiency because less work is required by the compressors and expanders when recycling the 'used' MR.

The impact of the measured differences in heat capacity on thermodynamic efficiency was not part of the project scope, however could have provided conclusive evidence on accuracy requirements of the system. Nevertheless, it was proposed that the relatively small differences (0.3% - 1%) in heat capacity between the measured and reference composition would not significantly impact the thermodynamic efficiency of a LNG refrigeration process, therefore rendering the performance of Raman instrument suitable for MR measurement.

# 8.3 Objective 3 – Validation of Raman spectrometer for measuring liquefied natural gas (LNG) composition

The third objective of this work was to calibrate and validate an Optograf<sup>™</sup> Raman spectrometer for measuring LNG-type compositions. The replacement of the current LNG sampling systems with characteristic vaporiser and GC configurations by direct measurement instruments could provide numerous benefits. Firstly, the uncertainty associated with LNG sampling and vaporisation (approx. 0.3%) is eliminated. Of the total LNG energy measurement uncertainty (best estimate = 1%), this uncertainty elimination equates to one third. Secondly, the use of fibre optic cables allows remote access to locations where sampling and GC systems are not suitable or where human safety is a concern. Thirdly, a lower operation cost is incurred because of a lesser equipment requirement and there is no need for offline analysis - which is sometimes a mandatory requirement in custody transfer contracts. Lastly, the use of multiple optical fibres to measure different processes means a 'one instrument measures all' arrangement can be achieved.

This objective was more difficult than objective 2 because of the requirement to measure lower amount fractions of pentanes down to 1000ppm and the fact that there is a UK accuracy gross calorific value (GCV) requirement of 0.18 MJ/m<sup>3</sup> for custody transfer. Delays with model development from the external partner Kaiser Optical Systems Inc. meant that a validation of the model could not proceed. However, an interim validation using three mixtures provided useful information on requirements for model improvements such as baseline adjustment, intensity calibration and additional linearity testing. The three interim validation mixtures were also used to compare the model's accuracy against the accuracy requirements for custody transfer. The difference in GCV between the measured and reference composition fell within the UK accuracy requirement of 0.18 MJ/m3 for one out of the three mixtures. To fully validate the model, a wide range of mixtures would be needed to assess the accuracy over the full range of LNG compositions. In addition to this, an ISO 10723 evaluation could provide useful information on calibration gas design and instrument bias and uncertainties. This is discussed in the further work section of this chapter.
# 8.4 Objective 4 - Validation of Infrared spectrometer for measuring liquefied natural gas (LNG) composition

The fourth objective was to calibrate and validate a TFS-IR Precisive<sup>™</sup> spectrometer for measuring LNG-type compositions. As mentioned in objective 4, the benefits of replacing conventional sampling systems with direct measuring instruments are numerous. However, these benefits can only be realised if the instrument can perform as good as the currently used GC analytical systems. Flexibility, stability, durability, linearity, accuracy and repeatability are the fundamental factors that are considered when new instruments are deployed into the market, therefore rigorous testing is required to determine if they are fit for purpose.

The TFS-IT Precisive<sup>™</sup> model developed from several calibration mixtures was tested using the ISO 10723 performance evaluation method. This method provided information on errors and uncertainties in GCV from several thousand theoretically simulated mixtures in 5 different simulations. The average errors and uncertainties in GCV was compared with the current UK custody transfer specifications for maximal permissible error (MPE) and maximal permissible bias (MPB) of 0.18 MJ/m3 and 0.09 MJ/m3, respectively. The first two simulations considered the full composition range and a limit-of-detection (LOD)- adjusted range. In both simulations, the MPE and MPB were exceeded. The final three simulations considered narrower composition ranges from three active terminals. Only the terminal 3 simulation with the narrowest composition range fell within the MPE and MPB specification. This suggested that the model is only applicable to narrow composition ranges. This is a realistic expectation because in current industrial configurations for natural gas analysis the measuring instrument is never subject to the full

composition range but a narrower range from which the imported gas will fall within.

Furthermore, there is much scope for improving the current model including: reducing the non-linearity of the heavier hydrocarbon species pentane and butane toward the lower-end amount fractions, introducing a temperature correction for when the measured LNG temperature may deviate from the calibration temperature, applying additional calibration data in the mid-range composition and improving the prediction of nitrogen amount fraction by applying an automatic zero for when negative amount fractions are recorded.

# 8.5 Objective 5 – Developing scope for further work

The fifth objective aimed to uncover exploratory work to enhance the findings in this project. Since this is not explicitly part of the research project itself, the main findings relating to this objective will be discussed in the further work section of this thesis.

# 8.6 General remarks

The method of directly measuring LNG has not yet been standardised, that is, there are no standard guidelines, specifications or requirements to help deploy such technologies to market. Standardisation provides a means of cooperation between experts, users and governments to maximise the quality, reproducibility, repeatability, compatibility and safety of new technologies. This work has contributed heavily to the development of new standards for LNG measurement and the author has been appointed UK expert for the committee responsible for delivering a standard for LNG composition measurement by sensor technology. This standard aims to establish a level playing field over which similar technologies can be compared and to provide crucial information to users, developers and non-experts in the field. Furthermore, the

introduction of such standards provides confidence and guidance in the deployment of these new technologies.

# 9 Further work

Throughout the research project, the potential for further work was revealed as the challenges relating to LNG measurement became clearer and better understood. This included:

- The need for thermodynamic modelling to better understand the thermophysical processes occurring at cryogenic temperatures. Consequently, with experimental data, validation of equations of state (EOS) for predicting vapour, solid and liquid equilibrium can be explored.
- Additional experiments for confirmation of uncertain conclusions such as the behaviour of nitrogen in different liquid matrices.
- Amendments to the cryostat design to accommodate higher pressures to reflect those of real LNG transfer lines.
- Density measurements using indirect techniques.
- Methods for optimisation of LNG sampling procedures.

The following sections explores these ideas and discusses the potential benefits of undergoing such further work.

## 9.1 Thermodynamic modelling

The thermodynamic modelling undertaken in this research project was solely based on GasVLe version 3.4. Although this software is frequently used in the oil and gas industry, its performance for LNG-type conditions is not very well understood. There is no doubt that the EOS used are applicable to LNG, however the performance at the extreme limits of LNG are questionable – as was seen with the attempt at predicting solidification in chapter 6. The use of more sophisticated software to understand these thermophysical processes would provide much more insight into the physical conditions at these very low temperatures. This research has uncovered many potential areas of research with respect to thermodynamic modelling since experimental data can confirm theoretical predictions with validation.

## 9.2 Cryostat design and operation

The original cryostat design was limited to a maximum internal pressure rating of 3 bar because of the design limitations with vacuum systems. An ideal design would be able to accommodate a pressure equal 9 bar which is equivalent to the pressure in LNG transfer lines. Although this pressure difference would have little impact on the experiments undertaken in this research, it could have provided additional evidence of pressure effects and the potential to investigate other areas of research including LNG subcooling and solidification. In addition, for triple point measurements where a solid, liquid and gas phase exists, a solid sampler could help understand the proportion of these three phases, therefore validating old experimental data and providing new insight into the transport properties of cryogenic liquids. Another modification could include the use of larger volumes of LNG required for validating vaporisers. The volume of LNG in the current cryostat design is limited to 1L. Typical vaporiser flow rates are hundreds of L of gas/hr. For example, the OptaPeriph<sup>™</sup> and Phazer<sup>™</sup> vaporisers described in chapter one can accommodate flow rates of up to 1200 litres of gas per hour. (1) The density of LNG is approximately 600 times that of natural gas, therefore the current volume of the sample chamber (1L) would only provide 600L of gas, enough for around 30 minutes of testing. This is inadequate since purging of the sampling lines and vaporiser, along with repeat analysis would be required. Validation of vaporisers could only be achieved If this volume could be increased by at least a factor of 10. Major changes to the cryostat design would be required to achieve this. Furthermore, this method of validation would provide significant benefits because the current way of assessment vaporisers relies on an unknown LNG composition combined with the repeatability of GC measurements, therefore accuracy statements cannot be established.

#### 9.3 Additional experiments

In chapter 5, the solubility of nitrogen was discussed with reference to difference compositions. Due to the limited number of experiments performed, a complete hypothesis of nitrogen solubility was not given. To understand fully the behaviour of nitrogen, many experiments would need to be performed with incremental changes of liquid composition. Following this, a finite difference analysis could help develop a strong hypothesis as to why nitrogen behaves the way it does in different liquid compositions. Theoretical predictions using GasVLe did not agree well with experimental data, however they did provide guidelines on approximate temperatures to expect nitrogen phase changes.

Upon development of the Raman LNG model – which was not established in the timeframe of this research- 7 additional mixtures would be required to fully validate the model to test its performance against custody transfer benchmarks specified in (2; 3). Furthermore, an ISO 10723 (4) performance evaluation could help tweak model analysis functions by studying the distribution of errors and uncertainties over several thousand theoretical compositions – as was done with the Precisive IR spectrometer in chapter 7.

#### 9.4 Density measurements

The cryostat was developed to accommodate many different instruments with varying probe designs. LNG energy is calculated on the combination of volume, density and composition. There are potential investigations in to the indirect determination of density using a range of techniques including speed-of-sound and ultrasonic technology. The current method of determining LNG density relies on measurement of temperature and composition. Therefore, a direct measurement could help reduce these uncertainties by eliminating uncertainties derived from sampling, vaporisation and temperature data. Moreover, this could help validate EOS for correctly predicting the density of LNG at these very low temperatures.

Another important research area is the validation of EOS used to predict density over a wide temperature and pressure range. A primary density standard has been developed as part of the European Metrology Research Programme (EMRP) which utilises a single-sinker densimeter design. (5) The design allows a chamber filled with LNG to be weighed magnetically. Combining this with the volume of the cell, the density may be determined. However, this design limits the capability of introducing different probes since the weighing balance must be positioned directly above the sample cell. Moreover, if such a densimeter could be combined with the design of the cryostat in this research project, both validation of EOS and of indirect measurement techniques could be made.

### 9.5 Methods for optimising LNG sampling procedures

LNG sampling is a complex process because a vaporised sample of liquid is required at ambient temperature and pressure prior to GC analysis. In addition, the LNG must transfer through the two-phase region from liquid to gas. With this transfer, there is potential for fractionation resulting from imperfect insulation around the sampling line and improper performance of vaporisers. A method for optimising LNG sampling systems could help maintain sub-cooled LNG to prevent sample fractionation in LNG sampling lines. By theoretically calculating the subcooling on a case-by-case basis and determining the heat influx from the sampling system characteristics, the LNG can be kept subcooled prior to vaporisation and eliminate the chance of sample fractionation. This method would provide significant benefits to process designers and operators.

The guidelines set out in ISO 8943 (6) for LNG sampling do not provide the reader with adequate information for predicting LNG sub-cooling and heat influx characteristics due to poor example scenarios. A more thorough investigation into the impact of composition on sub-cooling degree is required to fully understand the process. The research paper in the proposed publications section of this thesis puts forward a method that utilises a Monte-Carlo method for predicting fractionation characteristics over a simulated range of compositions, thus providing insight into areas where the LNG sampling system may fail. With this information, the sampling system may be optimised by changing system parameters to either increase sub-cooling capacity or/and decrease heat influx to prevent sample fractionation.

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# Annex A- Production and verification of primary reference gas mixtures (PRGMs)

# A.1 Mixture feasibility

Firstly, the feasibility of the gas mixture composition is considered. For hydrocarbon mixtures, there are no chemical species that could react with each other or with the internal surfaces of the cylinder, therefore the stability of the mixture does not remain a risk. The final filling pressure of the gas cylinder is another consideration due to the potential liquefaction upon expansion. When a gas is freely expanded from a high pressure to a low pressure without the transfer of heat to the surrounding environment, it may undergo a phase change from gas to liquid due to a change in temperature. (1) This is called the Joule-Thomson effect and it is a key parameter in the preparation of synthetic hydrocarbon gas mixtures, especially when the composition homogeneity is of great importance.

Calculations of the Joule-Thomson cooling curve are required for this study because of the potential phase change from gas to liquid. During the condensation stage discussed in section 2.2.3, a phase change from gas to liquid at the cylinder valve would result in a reference liquid with a different composition to the reference cylinder. This is because not all the gas is transferred from the cylinder to the SC. Therefore, the minimum dew point pressure of the mixture composition is calculated at the working temperature, and this is usually set to between 15 °C and 25 °C.

Figure 8 shows Joule-Thomson cooling curves for a typical natural gas mixture at 50 bar and 60 bar with respect to its Dewline at 15°C working temperature. The overlap between of the Joule-Thomson line at 60 bar and the Dewline results in a phase change from gas to liquid, whereas the Joule-Thomson line at 50 bar does not cross the Dewline, therefore no phase change from gas to liquid occurs. For all mixture preparations in this research project, the Joule-Thomson cooling curve was calculated and included in the final calculations of target masses.



# A.2 Purity analysis

The calculation of the purity of parent gases and liquids is a critical step in the preparation of primary reference gas mixtures. Impurities found in the parent gases contribute to the final composition matrix and therefore is a prerequisite for target mass estimation. Significant impurities are minimised by selecting high grade parent gases and liquids. The output of the purity analysis contains all impurities and their associated uncertainties. The purity analysis is included in the target mass calculation. An example purity analysis for a propane parent mixture is shown in table A.2-1. The uncertainties determined in the purity analysis are also included in the final calculation of target mass uncertainties.

Component	Amount (% mol/mol)	Uncertainty (kg/kmol)
Propane	99.99935	0.00011
neo-Pentane	0.00014	0.00001
Nitrogen	0.00010	0.00006
Propylene	0.00010	0.00006
Water	0.00010	0.00006
iso-Butane	0.00006	0.00001
Oxygen	0.00005	0.00003
Carbon Dioxide	0.00005	0.00003
n-Butane	0.00004	0.00001

Table A.2-1	- Example	purity	analysis	for 5.0 grade	Propane
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Table A.2-1 shows all impurities in the propane parent mixture to be less than 15ppm. The target gas mixture containing any of the said impurities as major components will be adjusted to include the amount of impurity. The remaining impurities that are not major components in the target gas mixture are listed as impurities in the final amount fraction calculation.

## A.3 Calculation of target masses

Target masses are the masses of pure components to be added to the target cylinder. All target masses are calculated using equation A.1 and A.2.

$$m_j = rac{y_k * M_k}{\sum_{i=1}^q y_i * M_i} * m_\Omega$$
 Equation

A.1

Where  $m_{\Omega}$  is calculated from

$$m_{\Omega} = \frac{p_{F,\Omega} * V_{cyl}}{Z_{\Omega} * R * T_F} * \sum_{i=1}^{q} y_i M_i$$
 Equation

A.2

Target masses are calculated by compensating for the purity of the parent being used and applying an additional factor called the compressibility factor. The compressibility factor ( $Z_{\Omega}$ ) is the ratio of the actual volume of n moles of gas to that of an ideal gas under the same conditions. (2)  $Z_{\Omega}$  is a function of gas composition and is calculated using the GasVLe software suite. An example target mass calculation before and after  $Z_{\Omega}$  is applied is shown in table A.3-1.

# Table A.3-1- Example target masses with corrected z factor and impurity contributions

	Target m (uncorrected purit	asses for parent y)	Target ma (corrected fo mixtur	asses or parent es)
Component	ideal mass (g)	mass / Ζ <sub>Ω</sub> required (g)	ideal mass (g)	mass / Z <sub>Ω</sub> required (g)
Methane	21.519	24.130	303.178	339.962
Ethane	27.049	30.331	21.519	24.130
Propane	303.178	339.961	27.046	30.328
iso-Butane	3.862	4.331	3.863	4.332
n-Butane	7.131	7.996	7.133	7.999
iso-Pentane	2.213	2.481	2.224	2.494
total mass	364.952	409.230	364.964	409.244
			$Z_{\Omega}$ factor	0.8918

After the target masses are calculated, the correct procedure for addition is

# Table A.3-2 Example final target mixture amount fraction with impurities and associated uncertainties

Component name	Amount fraction (% mol/mol)	Uncertainty (% mol/mol)
selected. The methods of addit	ion are described in	detail in section 2.3.4. The
method of addition is based	on the mass of su	ostance to be added. For
example, an addition of 4g of	f propane to a gas	cylinder would require an
intermediate smaller filling loop	o. The direct addition	of 4g of propane from the
parent cylinder to the final gas	cylinder would jeopa	rdise the uncertainty of the
final mixture composition beca	ause the resolution of	of weighing balance would
not be sufficient to give a low	v uncertainty. Instea	ad, 4g of propane can be
transferred from the parent cyli	inder to a small filling	g loop. This method allows
the filling loop to be weighed	on a high-resolution	n weighing balance before
and after its addition to the	final gas cylinder,	providing a much lower
measurement uncertainty. Unc	certainty calculations	are discussed in section
2.3.5.		

Methane	92.39135	0.002107
Ethane	3.523679	0.001724
Propane	3.016356	0.001246
iso-Butane	0.324474	8.61E-05
n-Butane	0.594729	0.000246
iso-Pentane	0.148499	4.61E-05
Nitrogen	8.3E-05	3.57E-05
Oxygen	2.11E-05	7.68E-06
Water	3.42E-05	6.44E-06
Carbon Dioxide	3.27E-06	2.68E-06
neo-Pentane	7.9E-05	7.51E-06
Propylene	3.02E-06	3.48E-06
Sulphur	4.6E-07	3.91E-07
n-Pentane	0.000692	3.44E-05
sum	100	

After all the mass additions are made, the amount fractions of each component in the final mixture is calculated using equation A.3 to produce a table of normalised components (table 2.3-3).

Compo nent	Meth ane	Etha ne	Liq Prop ane	Liq iso- Butane	Liq n- Butan e	i- Penta ne	n- Penta ne	Nitro gen
$y_k = \frac{\sum_{j=1}^r \sum_{j=1}^r \sum_{j=1$	$=1\left(\frac{x_{k,j}}{\sum_{i=1}^{q} x}\right)$ $=1\left(\frac{m}{\sum_{i=1}^{q} x}\right)$	$\frac{m_j}{m_i}$					E	quation

A.3

# A.4 Method of preparation

Two types of method addition were used for preparing gas mixtures in this research project. The main difference between the two methods is the use of an intermediate filling loop. These filling loops are made in-house and are of a stainless-steel construction with a pressure rating of 200 bar. The volume of each filling loop and the maximum mass addition of each LNG component to the filling loops is shown in table A.4-1. The appropriate filling loop is chosen based on the target mass required and composition.

density (g/L)	0.66	1.28	580.0 0	551.00	601.2 6	614.4 8	620.99	1.15
loop		Ma	ximum n	hass that c	an be ad	lded to lo	op (g)	
size								
(cm3)							-	
2	0.20	0.38	1.16	1.10	1.20	1.23	1.24	0.34
3	0.30	0.58	1.74	1.65	1.80	1.84	1.86	0.52
4	0.39	0.77	2.32	2.20	2.41	2.46	2.48	0.69
5	0.49	0.96	2.90	2.76	3.01	3.07	3.10	0.86
16	1.58	3.08	9.28	8.82	9.62	9.83	9.94	2.75
20	1.97	3.85	11.60	11.02	12.03	12.29	12.42	3.44
45	4.43	8.65	26.10	24.80	27.06	27.65	27.94	7.73
200	19.71	38.4	116.0	110.20	120.2	122.9	124.20	34.36
		6	0		5	0		

Table A.4-1 – filling loop maximum mass for each component

There are two methods of mass addition to the target cylinder. Method 1 describes component mass additions from parent cylinder to target cylinder. Method 2 describes component additions to the target cylinder via an intermediate filling loop.

Method 1 involves:

- 1. Evacuation of target cylinder if first component is being added.
- 2. Target cylinder is weighed on a Mettler balance with a 26kg capacity and a 10 mg resolution.
- Purging of connecting lines between parent cylinder and target cylinder to prevent contamination. The target cylinder is then placed on a balance and the balance is zeroed. The transfer is initiated by opening the target cylinder.
- The target cylinder is weighed after the addition. The difference between weighing before and after addition is the total mass added.

Method 2 involves:

- Evacuation of the filling loop and cylinder (if first component being added) to below 10-6 mbar.
- Filling of loop with parent gas. The loop is cooled to maximise transfer.
- Weighing of the filling loop using a Mettler series balance with a 10mg resolution.
- The loop is then connected to the cylinder via a three-way valve. The space between the loop and the cylinder is evacuated and then the addition is made.
- 5. The loop is weighed once again and the difference between the first weighing is taken as the mass added to the target cylinder).

# A.5 Calculation of preparation uncertainty

The uncertainty for the mass addition of each component to the final parent cylinder is evaluated. This evaluation considers all sources of uncertainty including:

- The accuracy of the weighing balance including its linearity and calibration
- The repeatability of balance
- Buoyancy effects arising from the displacement of air around the weighing plate
- Moisture and dust absorption on the outer cylinder surface
- Errors resulting from the loss of material during mass transfer

The uncertainty associated with the amount fraction determined from gravimetry  $u^2(y_{k,grav})$  is calculated via the application of the law of propagation of uncertainties (Equation A.4).

$$u^{2}(y_{k,grav}) = \sum_{i=1}^{q} \left(\frac{\delta y_{k}}{\delta M_{i}}\right)^{2} x u^{2}(M_{i}) + \sum_{j=1}^{r} \left(\frac{\delta y_{k}}{\delta m_{i}}\right)^{2} x u^{2}(m_{j}) + \sum_{j=1}^{r} \sum_{i=1}^{q} \left(\frac{\delta y_{k}}{\delta x_{i,j}}\right)^{2} x u^{2}(x_{i,j})$$
Equation

A.4

The expressions for the sensitivity coefficients  $\left(\frac{\delta y_k}{\delta M_i}\right)$ ,  $\left(\frac{\delta y_k}{\delta m_i}\right)$  and  $\left(\frac{\delta y_k}{\delta x_{i,j}}\right)$  and their derivations are described in (3).

Uncertainties resulting from the stability of the gas mixture over time is also considered. The stability of the gas mixture is quantified by a drift rate of amount fraction of component k via equation 2.3.5. The drift rate is determined on a case-by-case basis because different mixtures exhibit different reactivity. Saturated hydrocarbons and permanent gases (N2, Ar, Xe) can be considered as unconditionally stable compared with reactive gases (NO<sub>2</sub>) and therefore a stability assessment is only required to a small extent.

$$y_k^t = y_k^0 - b_k * t_d$$
 Equation  
A.5

Furthermore, the gravimetric uncertainty  $u^2(y_{k,grav})$  is combined with the uncertainty resulting from stability  $u^2(y_{k,stab})$  to calculate the preparation uncertainty  $u^2(y_{k,prep})$  (equation 2.3.6). In this work, the time between gas mixture preparation, verification and use is short and therefore the uncertainties derived from stability are considered negligible.

$$u^{2}(y_{k,prep}) = \sqrt{u^{2}(y_{k,grav}) + u^{2}(y_{k,stab})}$$
 Equation

A.6

# A.6 Verification of calibration gas mixtures

The gravimetric composition of the gas mixture is experimentally verified against reference standards to ensure consistency between the composition of the sampled gas from the cylinder and the gas mixture composition calculated from gravimetry. The composition of the gas mixture can only be considered traceable to the SI unit of amount-of-substance when a verification is made. The gas mixture is considered verified if equation A.7 is satisfied:

$$\left| y_{k,prep} - y_{k,ver} \right| \le 2 * \sqrt{u^2 \left( y_{k,prep} \right) + u^2 \left( y_{k,ver} \right)}$$
Equation  
A.7

Alternatively, the En-ratio may be used such that the result from equation A.8 is less than 1.

$$\frac{|y_{k,prep} - y_{k,ver}|}{\sqrt{u^2(y_{k,prep}) + u^2(y_{k,ver})}} < 1$$
 Equation

A.8

An example of both verification calculations is shown in table A.6-1.

Production gravimetry	Analytical calibration	Criterion	

compone nt	Y <sub>k,prep</sub>	U(y <sub>k,pre</sub> p)	Y <sub>k,ver</sub>	U(y <sub>k,ve</sub> r)	Y <sub>k,pre</sub> p <sup>-</sup> Y <sub>k,ver</sub> 	2*√(U(y <sub>k,prep</sub> )+ U(y <sub>k,ver</sub> ))	criterio n passed	<i>En</i> numb er
ethane	3.5383	0.0016	3.5356	0.0088	0.002 7	0.0180	yes	0.30
propane	3.0097	0.0011	3.0144	0.0093	0.004 7	0.0187	yes	-0.51
methane	92.385 5	0.0019	92.385 3	0.0176	0.000 2	0.0354	yes	0.01
iso- butane	0.3210	0.0001	0.3203	0.0011	0.000 7	0.0021	yes	0.66
n-butane	0.5987	0.0002	0.5988	0.0018	0.000 1	0.0037	yes	-0.07
iso- pentane	0.1459	0.0000	0.1455	0.0008	0.000 4	0.0017	yes	0.47

If equations A.7 or A.8 are not satisfied, then the verification is considered unsatisfactory and the calibration gas mixture is remade.

# A.7 References

1. Perry, Robert H. and Green, Don W. Perry's Chemical Engineers' Handbook, Eighth Edition. s.l. : AccessEngineering, 2008.

2. An efficient correlation for calculating compressibility factor of natural gases. N. Azizi, R. Behbahani, M. A. Isazadeh. 6, Ahwaz : Elsevier, 2010, Vol. 19.

3. British Standards Institute . *ISO* 6142-1 Gas analysis - Preparation of calibration gas mixtures Part1: Gravimetric method for Class I mixtures. London : s.n., 2015. ISBN 978 0 580 76273 4.

# Annex B – Raman and Infrared instrument configurations

Table B-1 – Specification of Raman Optograf spectrometer

Component	Description	Specification
Laser	Generates monochromatic light used to excite the sample	Wavelength: 532nm Power: 400mW Source: nd:YAG laser , flash pump/diode
Detection Unit	Spectrograph: separates Raman shifted photons by wavelength CCD: charge-coupled detector. Silicon based 2D array with light-sensitive pixels Spectrum standard: light source with characteristic spectrum used to calibrate detector and map the scattered wavelength to CCD pixel coordinates Raman shift standard: A sample with known spectral characteristics used to calculate wavelength of the detector module and provide spectral drift correction.	Spectrograph: spectral range: $\leq 150 \geq 3500 \text{ cm}^{-1}$ spectral resolution: $\leq 7 \text{ cm}^{-1}$ spectral thermal stability: $\leq 0.1 \text{ cm}^{-1}/^{\circ}\text{C}$ band shift optical throughput: Numerical aperture of spectrograph matched with fibre (f1.8) notch filter: $\geq 8$ optical density at laser wavelength $\geq 80\%$ transmission at wavenumbers $\geq 200 \text{ cm}^{-1}$ <b>CCD:</b> Quantum efficiency: $> 40\%$ at centre range Spectral range: $\geq 4\%$ quantum efficiency between 400 -1050nm Dynamic range: $\geq 50,000$ electron quantum well efficiency Read noise: $\leq 10$ electrons Dark count: $\leq 0.5$ electrons/pixel/second <b>Spectrum standard</b> : neon source light <b>Raman shift standard</b> : cyclohexane
Fibre-Optic cable	Medium for transporting light to and from the sample. Laser light and scattered light travel through separate fibres.	Fibre length = 2.5m Dual-channel fibres
Sample probe	Pilot <sup>™</sup> probe. A protective casing for the optical fibre that is inserted into the cryostat.	Pressure rated: 3000 psi at probe tip Temperature rated: -196 to 150 °C 316 Stainless steel High purity sapphire window
Computer control system and user interface	Provides an interface between the software, CCD, detection system, diagnostics and system monitoring.	Windows 7
Software	Kaiser acquisition	Version 2.7.1
Outer protective case	Provides protection for the internal components	Dimensions: 45.72 cm w x 83.44 cm h x 25.4 cm d 316 painted steel explosion proof for industrial environments

# Table B-2 – Specification of Precisive Infrared spectrometer

Component	Description	Specification
Laser	Broadband light source. Black body emitter.	Wavelength: 532nm Power: 400mW Source: nd:YAG laser , flash pump/diode
Detection Unit	Single-element photo- detector.	indium gallium arsenide (InGaAs)
Fibre-Optic cable	Mediumfortransportinglighttoand from the sample.LaserlightandLaserlightlightismeasuredonareverse path.	Fibre length = 1m Dual-channel fibres
Sample probe	Development probe. A protective casing for the optical fibre that is inserted into the cryostat.	Pressure rated: 3000 psi at probe tip Temperature rated: -196 to 150 °C 316 Stainless steel Measuring cell: 1 cm path length.
Computer control system and user interface	Provides an interface between the software, CCD, detection system, diagnostics and system monitoring.	Windows 7
Software	HMI TFS	Version 2.15
Outer protective case	Provides protection for the internal components	Dimensions: 45.72 cm w x 83.44 cm h x 25.4 cm d 316 painted steel explosion proof for industrial environments