



## Calibration of Sensor Technology Using Traceable LNG Reference Mixtures

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Date: 25<sup>th</sup> October 2018

LNG3 Workshop, Aberdeen

Dr Joey Walker

EngD - EffecTech/Loughborough University – Validation of spectroscopic instruments for the direct measurement of multi-component cryogenic liquid hydrocarbons

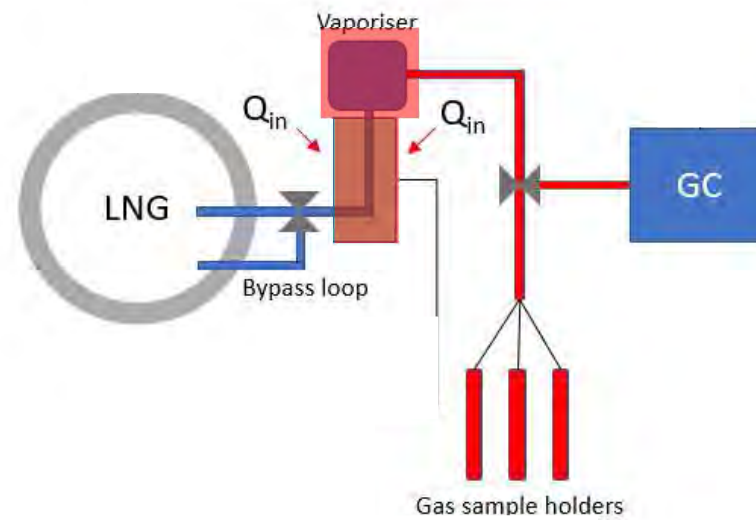
LNG research project started in 2013 at EffecTech labs

Currently employed by EffecTech Ltd  
Technical Support Engineer

## What prompted the development of direct LNG measurement?

Sampling concerns  
Vaporiser concerns

Faster measurement  
More accurate  
Dynamic process control



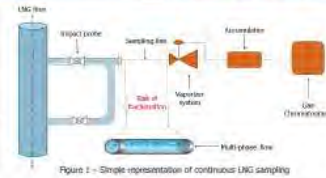
# The Effects of Composition on Sub-cooling Calculations Used in LNG Sampling Procedures

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Errors in Gas Measurement

## 1. BACKGROUND

- LNG composition measurements are necessary for the calculation of CV and density used in the determination of energy content of LNG cargo.
- The current universal method for measuring LNG composition involves the conversion from liquid to gas via an evaporator process. The resulting gas sample is measured with a gas chromatograph.
- If enough heat is absorbed through sampling lines during LNG sampling, inhomogeneous boiling of components due to their different boiling points will result in unrepresentative sampling, ultimately leading to financial discrepancies.
- The international standard ISO 8943 [1] provides guidelines on sound methods for intermittent and continuous sampling of LNG. The standard gives detailed equations for calculating sub-cooling enthalpies for predicting sample fractionation, however this does not take into account the composition of the LNG being sampled.
- This work demonstrates the effects of LNG composition on sub-cooling enthalpies and shows how a bespoke Monte-Carlo simulation can evaluate an LNG sampling system's operational conditions where fractionation and enrichment will not occur.



## 2. STUDY - COMPOSITION EFFECTS ON SUB-COOLING ENTHALPY

### Important definitions

- Sub-cooling enthalpy – the amount of heat energy required to raise a unit mass of LNG to its bubble point.
- Enthalpy of absorption – the amount of heat energy absorbed through sampling lines leading up to vaporization (Figure 1).
- Fractionation – if enthalpy of absorption is higher than enthalpy of sub-cooling.
- Question – Could a LNG sampling system provide a fractionation free expansion process over a wide range of typical LNG compositions?

### Investigation:

- Using the Gascalc™ property calculation software, we investigated the effects different LNG compositions have on final calculations of sub-cooling enthalpies (table 1 and 2).
- Vapor-liquid envelopes illustrate the difference in bubble points for different LNG compositions (Figure 3).
- The effects of this bubble point variation are shown in table 3. Due to the differences in bubble point and heat capacity for each LNG composition, the resulting sub-cooling enthalpies are different.

$$Q = \frac{m(T_a - T_b)}{h_e - h_l} + m h_l$$

$$\dot{Q} = \frac{q + 340q}{P}$$

Figure 1 – ISO 8943 heat balance equation [1].

- Using ISO 8943 equations (Figure 2), we can calculate the heat absorption enthalpy based on the design and environment of the sampling system.
- A Monte-Carlo approach was taken such that sub-cooling and absorption enthalpies can be calculated from an entire range of parameters and compositions. With this, we can reveal LNG compositions that are susceptible to fractionation.
- An example simulation is shown in section 3 along with the configuration of computations.

## 3. MONTE CARLO SIMULATION - DIAGNOSTIC TOOL FOR SYSTEM OPTIMISATION

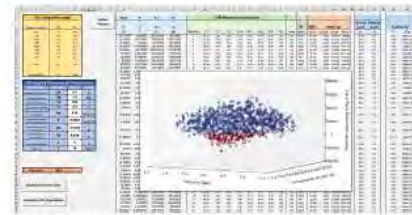


Figure 4 – Monte Carlo simulation running in Excel 2013.

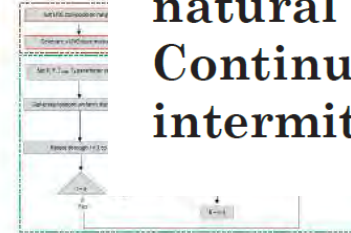


Figure 5 – Process flow for the Monte Carlo simulation.

## 4. CONCLUSIONS

- Initial studies showed a large variance in bubble point and heat capacity between different LNG compositions.
- This led to the development of a Monte Carlo simulation capable of assessing a LNG sampling system's susceptibility to fractionation.
- This tool has the capability of optimising LNG sampling operational conditions to achieve a fractionation-free measurement process.

## 5. REFERENCES

- [1] – ISO 8943 - Refrigerated light hydrocarbon fluids - intermittent and continuous sampling

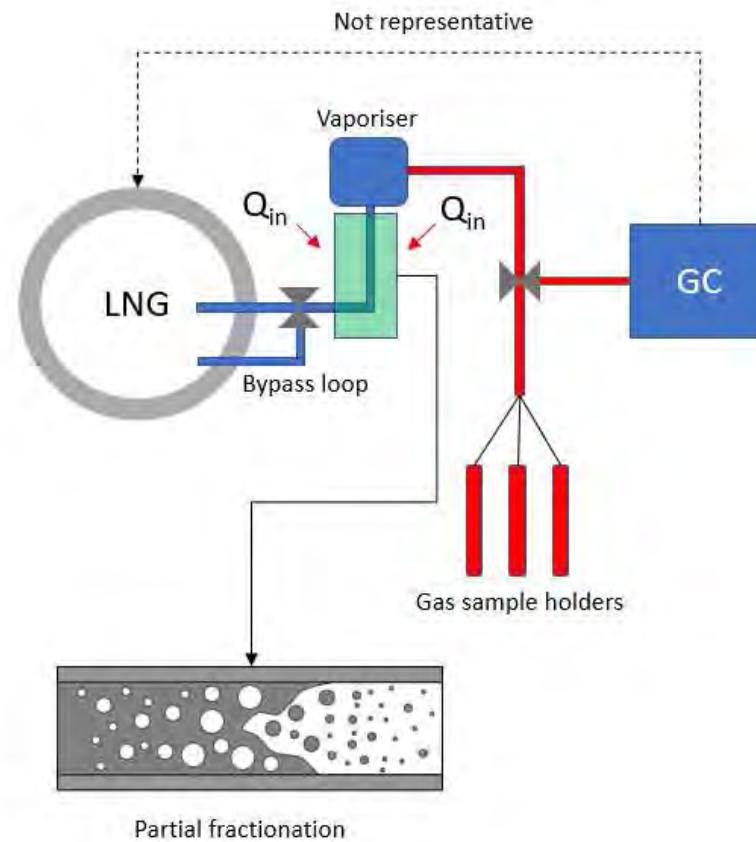
## 6. ACKNOWLEDGEMENTS

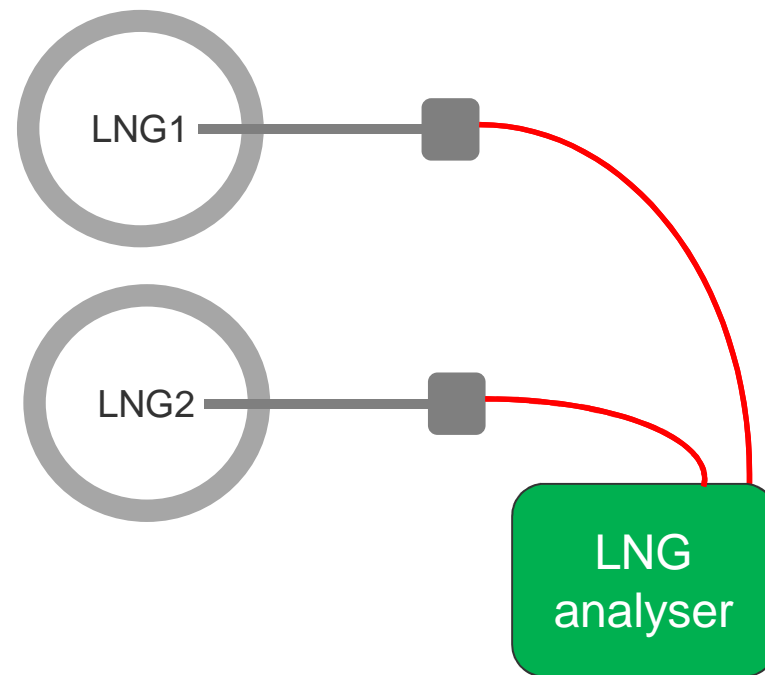
I would like to thank the ASC for funding my trip to LNG 18.

## BRITISH STANDARD

BS ISO 8943:2007

# Refrigerated light hydrocarbon fluids — Sampling of liquefied natural gas — Continuous and intermittent methods





## How do we calibrate LNG analyzers?

gas?

cyclohexane standard?

Calibration standard and medium should  
be the same as what is being measured!



# Production of LNG reference standards

## Optimal system:

- 1) efficient gas to liquid conversion
- 2) temperature control and stability
- 3) space for a LNG probe
- 4) ability to sample and measure LNG directly for verification
- 5) minimal headspace

## Initial questions:

How much gas to condense?

What temperature to condense/measure?

Sampling method?

Cooling medium?

LNG range?

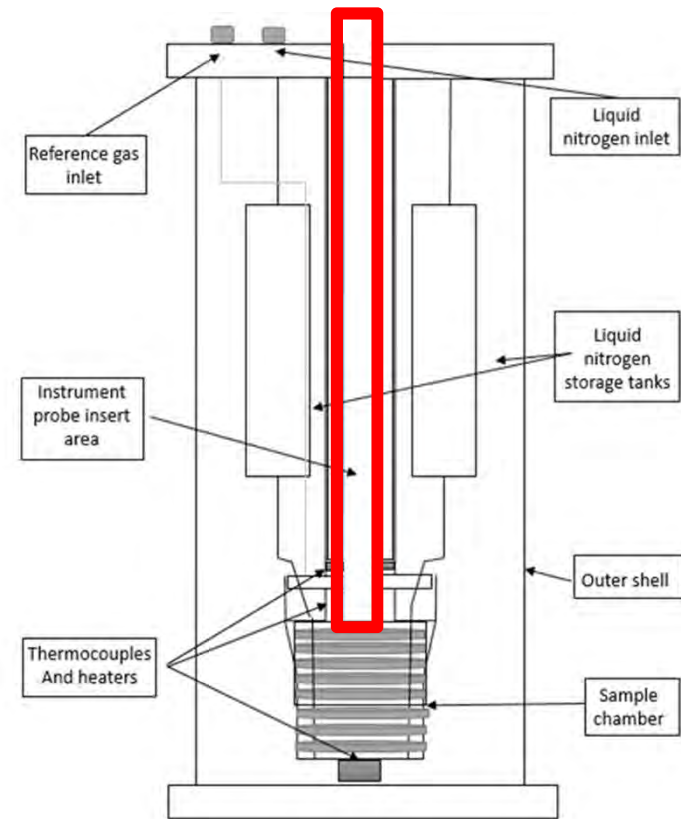
Lower/upper limits?

How to evaluate such a system?



## Cryostat at EffecTech

- Liquid nitrogen as cooling medium. 7 litre storage tank.
- 3 bar maximum working pressure
- Stainless steel/ copper cell construction
- Space for different probes (50mm diameter max).



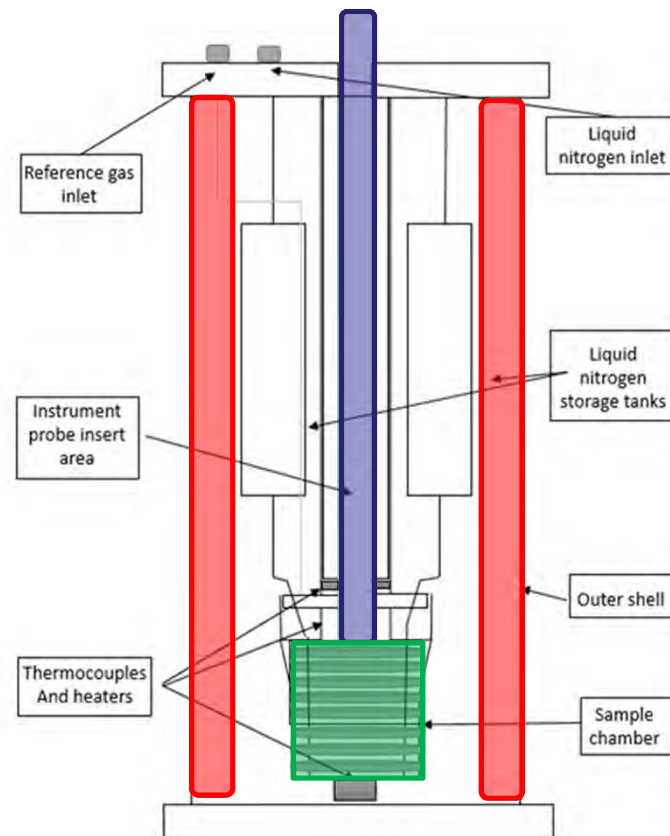
## 1. Preparation

1. Insert measurement probe

2. Evacuate outer chamber

3. Evacuate sample chamber

$10^{-6}$  mbar

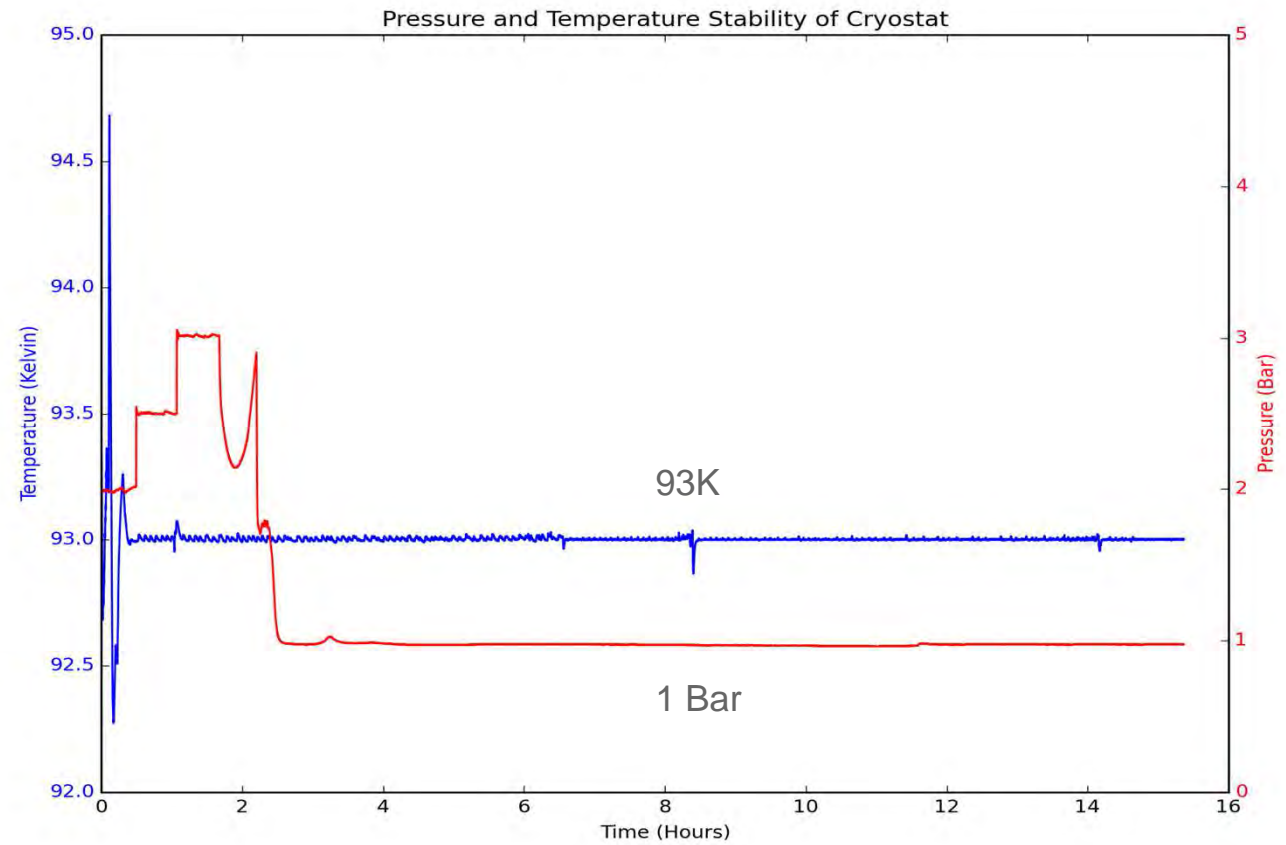


## 2. Condensati

1. Initial cool-down  
using liquid N<sub>2</sub>

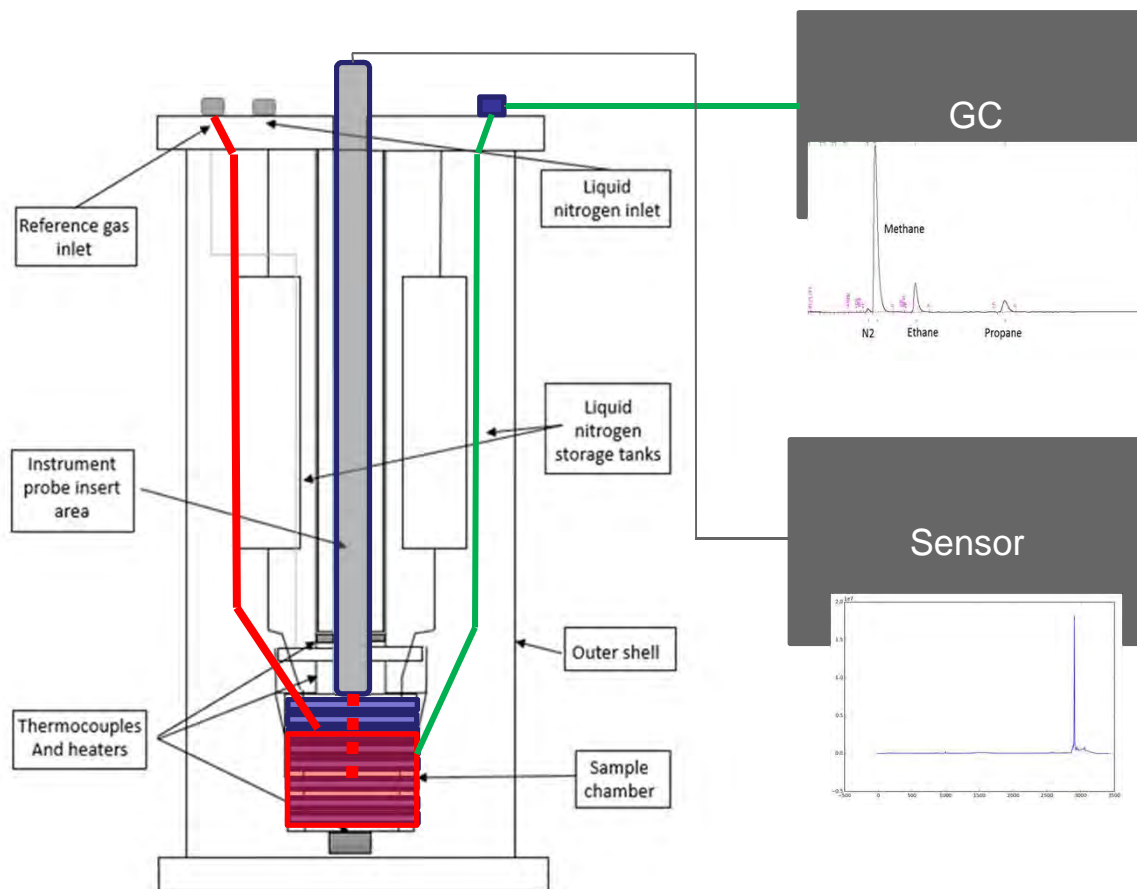
2. Addition of PRGM

3. Thermal control



### 3. Measurement

1. Connect sample lines to Gas chromatograph
2. Pressurise the system with helium
3. Open outlet and measure with GC and sensor instantaneously





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# Thermophysical predictions

## Boiling point

What temperature to condense at?

component	Amount fraction (%mol/mol)			
	MIX 1	MIX 2	MIX 3	MIX 4
nitrogen	0.6001	0.1494	1.1657	0.04096
methane	93.0700	98.4376	92.6334	86.848
ethane	5.4810	0.09604	2.7762	10.649
propane	0.6791	0.09362	3.0278	2.0024
iso-butane	0.0597	0.6269	0.13067	0.2059
n-butane	0.0800	0.4297	0.0694	0.24349
iso-pentane	0.0201	0.08232	0.09861	0.004691
n-pentane	0.0101	0.08418	0.0985	0.005378

	Pressure (bar)			
	1	1.5	2	2.5
<b>MIX 1</b>				
Temperature (LRS, K)	110.31	115.65	119.75	123.13
Temperature (RKS, K)	110.65	116.00	120.11	123.49
Temperature (GERG, K)	110.17	115.62	119.81	123.25
<b>MIX 2</b>				
Temperature (LRS, K)	111.22	116.34	120.29	123.54
Temperature (RKS, K)	111.56	116.69	120.65	123.91
Temperature (GERG, K)	111.18	116.40	120.42	123.73
<b>MIX 3</b>				
Temperature (LRS, K)	108.43	113.93	118.14	121.60
Temperature (RKS, K)	108.76	114.28	118.49	121.95
Temperature (GERG, K)	108.16	113.80	118.10	121.63
<b>MIX 4</b>				
Temperature (LRS, K)	112.90	118.15	122.21	125.56
Temperature (RKS, K)	113.27	118.53	122.60	125.96
Temperature (GERG, K)	112.86	118.22	122.35	125.77

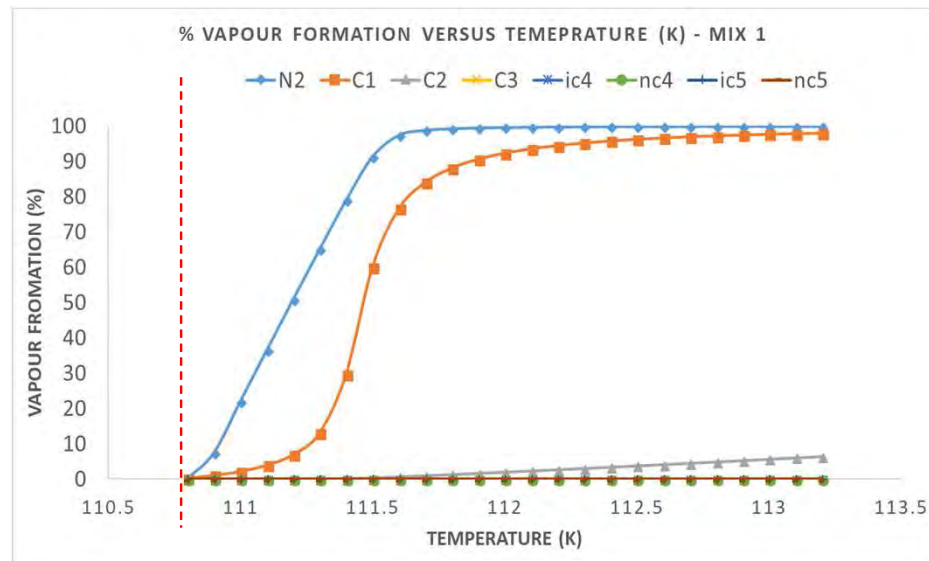
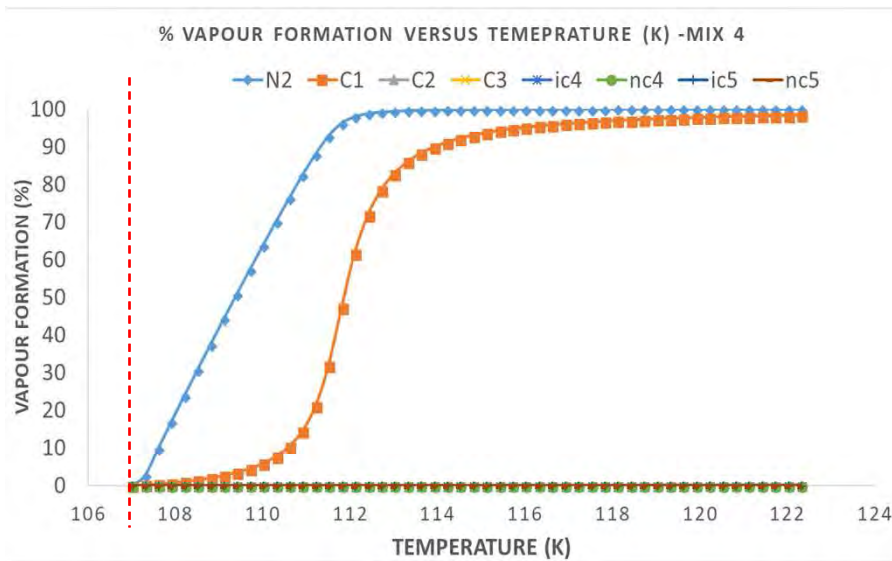
## Thermophysical predictions

How much gas to add?

component	Amount fraction (%mol/mol)			
	MIX 1	MIX 2	MIX 3	MIX 4
nitrogen	0.60	0.15	1.17	0.04
methane	93.07	98.44	92.63	86.85
ethane	5.48	0.10	2.78	10.65
propane	0.68	0.09	3.03	2.00
iso-butane	0.06	0.63	0.13	0.21
n-butane	0.08	0.43	0.07	0.24
iso-pentane	0.02	0.08	0.10	0.00
n-pentane	0.01	0.08	0.10	0.01
LNG density (g/L)	470.55	459.10	478.48	490.54

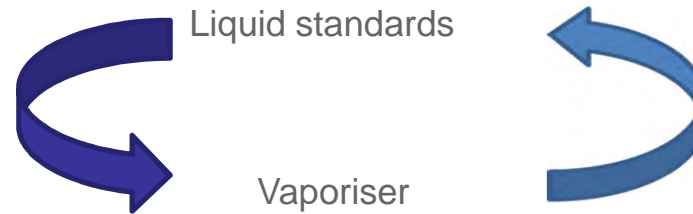
# Thermophysical predictions

Predicting vapour phase amount of nitrogen and methane



## Paradox

- The project was conceived to develop liquid reference standards as there was some concern over vaporiser issues.
- Liquid standards being validated using a GC & vaporiser



## Paradox

- The project was soon
- Liquid state

BRITISH STANDARD

**Installations and  
equipment for liquefied  
natural gas —  
Suitability testing of  
LNG sampling systems**

- Validate paradox

BS EN  
12838:2000

is there



## Vaporiser suitability criteria

Values for mass CV, gas density and LNG density taken from Table 1 of EN 12838

Class	Physical property	Typical value	Continuous sampling	
			Maximal random error	Maximal systematic error
A	CV in kJ/kg	53948	9.0	Not significant
	Gas density kg/m <sup>3</sup>	.7858	3.0*10 <sup>-4</sup>	
	LNG density kg/m <sup>3</sup>	494.76	0.15	
B	CV in kJ/kg	53948	18	11
	Gas density kg/m <sup>3</sup>	.7858	6.0*10 <sup>-4</sup>	5.0*10 <sup>-4</sup>
	LNG density kg/m <sup>3</sup>	494.76	0.30	0.20



## $E_n$ Number

- Agreement between measured and reference values is quantified through the  $E_n$  number, which divides the difference in values by the combined uncertainty

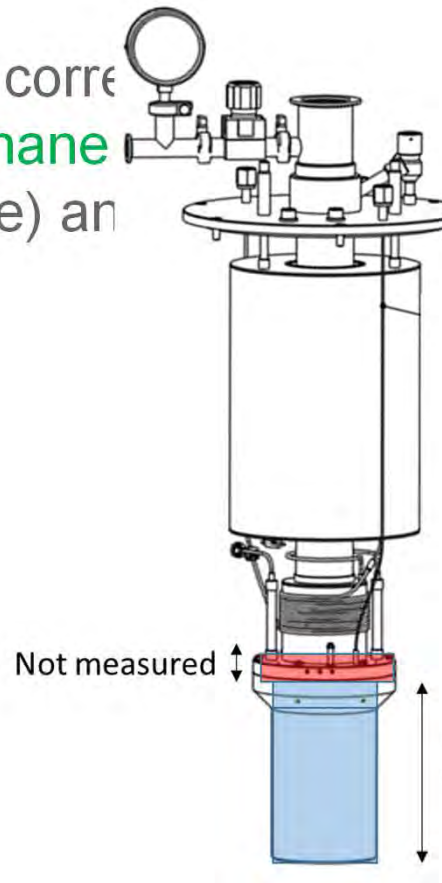
$$E_n = \frac{meas - Ref}{\sqrt{U_{meas}^2 + U_{Ref}^2}}$$

- An  $E_n$  value of 1 or less shows that the measured and reference values are in statistical agreement



## Nitrogen and methane correction

- The correction factors (measured methane value) and



values use the **measured nitrogen and methane** as En ratio consistent with PRGM and are normalised to 100%





**Slide 24**

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**JW1**

Diagram to illustrate  $2$  and  $c_1$  in headspace above liquid ... more with higher amount fractions of  $n_2$

Joey Walker, 06/06/2018

## Example results for one reference liquid composition

mix #4R	gravimetric values		measured (GC) values		Modified values	corrected reference values		difference	difference	difference	EN128 38
component	$x_i$	$U(x_i)$	$y_i$	$U(y_i)$	$y_{im}$	$x_{ic}$	$U(x_{ic})$	(% relative)	KJ/kg	kg/m <sup>3</sup>	criteria
nitrogen	1.5635	0.0015	1.5638	0.0257	1.5638	1.5638	0.0129	0.0000			
methane	95.2233	0.0095	95.2232	0.1834	95.2232	95.2232	0.0918	0.0000			
ethane	1.1849	0.0011	1.1907	0.0141	1.1849	1.1851	0.0092	0.0049			
propane	0.7660	0.0008	0.7667	0.0081	0.7660	0.7661	0.0041	0.0009			
iso-butane	0.3855	0.0004	0.3838	0.0051	0.3855	0.3856	0.0031	-0.0044			
n-butane	0.5740	0.0006	0.5713	0.0090	0.5740	0.5741	0.0052	-0.0046			
iso-pentane	0.1469	0.0002	0.1459	0.0032	0.1469	0.1469	0.0018	-0.0063			
n-pentane	0.1552	0.0002	0.1545	0.0036	0.1552	0.1552	0.0019	-0.0046			
GCV (15/15)	53699.87		53700.28			53699.51			0.757813		9
Gas Density	0.728388		0.728316			0.728390				-0.0001	3.00E-04
LNG Density 93K	470.3735		470.3477			470.374715				-0.0270	0.15

$$\text{Corr} = \frac{\text{Grav value}}{100 - (\text{sum}(c_2 - c_5))} \times 100 - \text{sum}(\text{nitrogen} + \text{methane})$$

# EffecTech scope of accreditation (UKAS)

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

**Uttoxeter**

Assessment Manager: D43 Page 12 of 14



## Upcoming research projects:

1. Testing of densitometers using ultrasonic technology
2. Odorising LNG
3. new design to expand application range



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Thank you for listening