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Assessment of LNG Sampling Systems and Recommendations

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1 INTRODUCTION

The work described in this paper is part of the European Metrology Research Programme (EMRP) project for Liquefied Natural Gas (LNG) which is jointly funded by the European Commission and participating countries within Euramet and the European Union. The objective of this project is to improve the uncertainty associated with the calculation of LNG energy transfer by developing new techniques and methods. This will be achieved by looking at the complete LNG custody transfer process including volume and composition measurements along with density and gross calorific value calculations. Detailed description of all work packages is found in the project website [1]. The work described in this paper falls under Work Package 3 of the project.

Currently, the calculations of the density and the gross calorific value of the LNG transferred are made on the basis of the average composition of the LNG. This composition is obtained from LNG sampling and subsequent chromatographic analysis.

The sampling stage is the most important point of the LNG measurement sequence. The sampling procedure must be consistent throughout the whole operation to ensure representative results. Unrepresentative samples are responsible for the majority of errors that occur in the energy transferred calculation.

Sampling of LNG must be completed at both the loading and unloading terminals to take account of the ‘ageing’ phenomenon. This ‘ageing’ process occurs over time due to the effects of ‘boil-off’. The boil-off gas is when the lighter components of LNG vaporise and exit the tank. When this occurs, the composition and thus the properties of the LNG will change. This change occurs naturally over time and has a significant consequence on the gross calorific value and density of the transferred LNG and thus its value.

The accuracy of LNG composition obtained from sampling will have direct influence on the accuracy of calculated density and gross calorific value and subsequently the accuracy of LNG energy transferred. The LNG shipment value is often in the range of €40 - €50 million. A small error in the determination of the gross calorific value and density of the LNG has a significant financial impact on the exporter/importer. An error of 1% in energy transferred equates to €400,000 - €500,000 in misallocation during custody transfer.

Therefore one of the main work packages of the EMRP project focuses on LNG sampling systems and looks at the current sampling technologies used in the LNG custody transfer measurements. Information was gathered on continuous and intermittent sampling systems, LNG vaporisation systems, practices in Middle East (LNG production plants), European countries and North America (LNG receiving terminals). Information also gathered on retention of samples during LNG loading or unloading and on the uncertainty associated with measured composition. This was achieved by visiting two LNG terminals, one in Spain (Cartagena LNG Import Terminal**)** and the other in the USA (Sabine Pass LNG Terminal**)**. Information from other sites (Isle of Grain LNG import terminal, UK and RasGas LNG export terminal, Qatar) was collected by emailing a detailed survey form. The main objective of this survey is to review sampling and vaporisation practices in different parts of the world. More information on all these sites can be found in the detailed report [2].

The gathered information enabled detailed assessment of current LNG sampling systems, highlighting associated issues and challenges, providing an overview of uncertainty in measured gas composition and finally making recommendations for improvement where applicable.

2 CURRENT STATE OF THE ART

LNG is currently traded in the form of energy transferred based on measurement of the volume in the ship's tanks, measurement of composition from sampling and subsequent calculations of density and gross calorific value from the measured composition. This also requires measurement of energy of displaced gas and where applicable the energy of boil-off gas consumed by the ship's engine. Reference [3] describes fully how LNG energy transferred is determined.

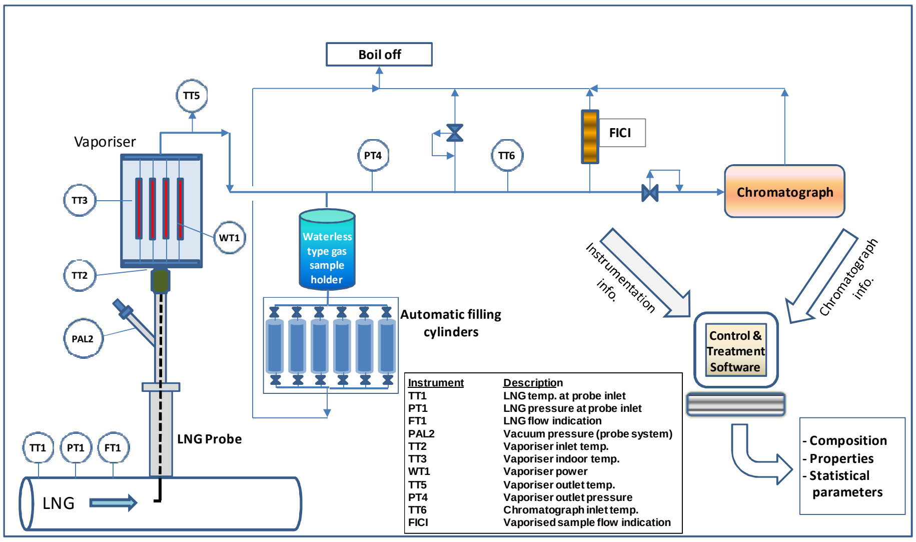
In order to determine the composition of the LNG it is first necessary to condition the fluid sampled from its initial state, liquid at low temperature, to a final state, gas at ambient temperature, without partial vaporisation or loss of components. The conditioned vapour sample is then analysed by gas chromatography.

The LNG industry has gained significant experience with LNG sampling and therefore developed new equipment as well as improved sampling procedures. The spot (discontinuous) sampling system has become almost obsolete for custody transfer measurements and the GIIGNL handbook recommends use of this system as a back-up system in case of failure of the main system or for impurity analyses only.

The sampling processes currently used in the LNG industry are mainly of two types; continuous and intermittent as defined in ISO 8943 [4]. The intermittent sampling is also referred to as discontinuous sampling in other publications such as the EN 12838 standard [5] and the current GIIGNL handbook [3].

LNG sampling systems always sample and vaporise LNG on a continuous basis and the terms continuous and intermittent sampling are related to the analysis of gas phase, that is, after vaporisation of the sampled liquid stream. The continuous sampling system sample vaporised LNG at constant flowrate while the intermittent system samples at predetermined intervals. An example of continuous sampling system is shown in Figure 1 [6].

It was observed that some of the continuous sampling systems witnessed on visited sites deviate slightly from those described in ISO 8943 by having a direct feed of conditioned gas sample from the accumulator and mixing vessel to gas chromatograph or in other cases directly from vaporiser to gas chromatograph as shown in Figure 1. The gas containers (or cylinders) are filled either manually or automatically during the whole duration of stable sampling. The purging of the system is performed by running the sample through the system (including gas containers in some cases) for a specified period of time.



Instrument	Description
TT1	LNG temp. at probe inlet
PT1	LNG pressure at probe inlet
FT1	LNG flow indication
PAL2	Vacuum pressure (probe system)
TT2	Vaporiser inlet temp.
TT3	Vaporiser indoor temp.
WT1	Vaporiser power
TT5	Vaporiser outlet temp.
PT4	Vaporiser outlet pressure
TT6	Chromatograph inlet temp.
FICI	Vaporised sample flow indication

Figure 1 Example of continuous LNG sampling system [6]

2.1 Sampling System Requirements

The current requirements of LNG sampling systems for achieving representative sampling and accurate compositional analysis of vaporised LNG are described in [7] as follows.

- The LNG sampling system must meet or exceed the following:
    - ISO 8943-2007, Refrigerated light hydrocarbon fluids- Sampling of liquefied natural gas– Continuous and intermittent methods [4].
    - ISO 10715-2001- Natural gas sampling guidelines [8]
    - BS EN ISO 12838-2001 Installations and equipment for liquefied natural gas- suitability testing of LNG sampling systems (section 8) [5].
    - API 14.1 (2006)- Collecting and Handling of Natural Gas Samples for Custody Transfer.
- The system must automatically collect samples over the duration of a batch providing an 'averaged' sample of the pipeline contents and eliminating the risk of biased manual samples.
- The system must be suitable for sampling a complete LNG batch in a loading cycle when LNG is stable in the liquid phase. The sampling system must be unaffected by any changes in line pressure for main line flow rates.
- The system must extract three samples as specified in ISO 8943:2007 to provide redundancy and enable validation of reproducibility and sampler performance.
- The automated system must be designed to minimise the risk of operator errors and ensure a representative sample is provided for analysis.
- The system must provide a method to fully purge all interconnecting process lines to prevent contamination from atmosphere and previous sample.
- When an on-line gas chromatograph is used, the sample conditioning system must have a capability to provide a stable homogenous vaporised gas feed to the chromatograph. It must include a facility to extract manual samples at specific points throughout the batch.
- In the case of intermittent sampling system, the system must be able to take samples at sufficient frequency and configured to re-pressurise the gas samples

into constant pressure containers with a sampler discharge pressure up to 150 bar. Samples must be maintained above the dew point to prevent any condensation.

- The system must be configurable for any duration of sample period and sample volume, providing the flexibility to match the sampling to future quality requirements.
- The system must be simple to maintain.

The main elements of LNG sampling system are briefly described below with main focus on achieving representative sampling.

3 MAIN COMPONETS OF LNG SAMPLING SYSTEM

3.1 Sampling Probe and Piping to Vaporiser

The first point of LNG sampling system is the sampling probe (see Figure 1). The sampling probe is installed at a right angle to the axis of the LNG transfer line. In the case of multiple transfer lines, the sample probe is located downstream of the manifold, if one exists, otherwise, each line will be provided with a sampling point [4].

The sampling probe must be installed at a point on the transfer line where the degree of subcooling is high. Subcooling must be maintained when the sample is transferred through the sampling probe in order to prevent formation of bubbles or vaporisation of LNG. This is normally achieved by careful insulation of the probe to minimise ambient heat gain through the probe. The degree of subcooling at sampling point is ascertained by observation of the temperature and pressure of the LNG at that point (Figure 1) and comparing the observed temperature with the boiling point temperature calculated from LNG pressure and composition.

Sampling probes are normally constructed from stainless steel due to its robustness and ability to handle extreme temperatures. ISO 10715 [8] specifies that the sampling probe must be equipped with a shut-off valve.

Vacuum insulated sampling probe with a mechanism to monitor and maintain the vacuum (e.g. 1.10 to 4 torr) and fitted with a cryogenic valve remotely shut-off by an actuator is an effective way to draw a representative sample. Often the sampling probe is fully assembled with LNG sample pipe to vaporiser and supplied as one unit. An example of this type of probe with a vacuum insulated sampling pipe that connects directly to the vaporiser is shown in Figure 2 [9].

Figure 2 Vacuum insulated LNG sampling probe with connection line to vaporiser [9]

Detailed description of all the elements making the sampling probe shown in Figure 2 is found in [9].

Figure 3 shows an example of sampling probe, with vacuum jacket insulation (right), installed on an LNG transfer line in an import terminal compared with another probe with inefficient insulation resulting in ice formation (left).

Figure 3 LNG sampling probes with effective (right) and less effective (left) insulation [Courtesy of Enagas]

It is important that the liquid sample line, between the sampling probe and the LNG vaporiser, have a short length, small inside diameter (e.g., 2 mm) and provided with efficient insulation so that the LNG is kept in a sub-cooled condition until it reaches the vaporiser. The design of this line must take in consideration all possible unloading conditions. Calculation of the maximum length of the liquid sample line between the probe and the vaporiser is given in ISO 8943 [4].

3.2 Sample Vaporiser and Control Devices

ISO 8943 specifies the following requirements for LNG sample vaporiser:

- “The heat exchange capacity of the LNG sample vaporiser shall be sufficient to gasify the whole volume of LNG which is being withdrawn for sampling”.
- “The sample vaporiser shall be so constructed that the heavier components of the LNG shall not remain in the vaporiser”.
- “Where a compressor transferring vaporised LNG is provided, the maximum gasifying capacity (heat input) of the LNG sample vaporiser shall be greater than the capacity of the compressor”.

From the above it is clear that the vaporiser must be designed carefully in order to avoid fractionation, especially if the gas sample is directly taken for analysis. To that effect heating to a sufficiently high temperature, e.g. 50℃ or greater, is required to ensure immediate vaporisation of even the heaviest trace components.

Vaporisers are normally electrically based but other types using water heated by steam or by steam directly are available. More details are given in [3].

An example of electrically heated vaporisers (using heated rods) is shown in Figure 4 [10].

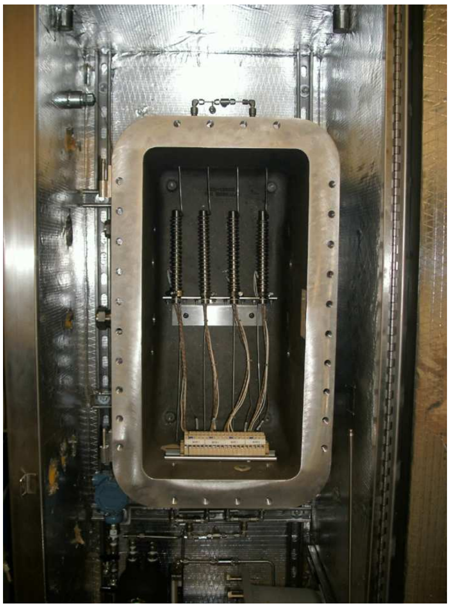


Figure 4 Electrically heated vaporiser with four heating rods [10]

The condition of vaporised LNG must be controlled; firstly in order to monitor the sample vaporisation condition and secondly in order to protect the equipment used. Control devices are required before inlet to vaporiser, within the vaporiser and at vaporiser outlet. These devices are described in detail in [3 and 4].

On vaporiser inlet, a check valve (prevents back flow of vaporised components), restriction orifice (to achieve flash vaporisation), needle valve (to control LNG or gas flow), sample filter, isolation valves and bypass system (for maintenance) are installed.

To control conditions within the vaporiser, a temperature regulator, thermometer, thermostats and control of the power supply of the transformer or of the (submerged) resistance heating element are installed.

On vaporiser outlet, a pressure regulator (controls LNG flow to vaporiser independently of LNG transfer pipe pressure), anti-pulsation vessel or mixing accumulator, impingement chamber, Flow meters and / or flow limiters, pressure instruments, temperature detection switches and safety valves are installed. Other safety measures must be taken to meet requirements for operation in hazardous conditions.

3.3 Gas Sample Collection (Sample Holder and Sample Containers)

There are two types of gas sample holders; water-seal type or waterless type. These can hold gas volume between 500 and 1000 litres and designed to store a representative portion of the vaporised LNG during the transfer operation. A sampling holder of constant pressure floating piston (CF/FP) type is also available and typically designed to accumulate 25 litres sample volume. A gas compressor is normally used to deliver small portions of vaporised LNG into the CP/FP container.

The characteristics of the gas contained in these holders after completion of sampling operation is aimed to be a well mixed sample that is representative of the LNG loaded or unloaded.

ISO 8943 provides technical specifications of gas sample containers used in continuous and intermittent sampling systems and provides a description of the filling and cleaning procedure.

Figure 5 shows a picture of typical sample containers used in continuous sampling system.

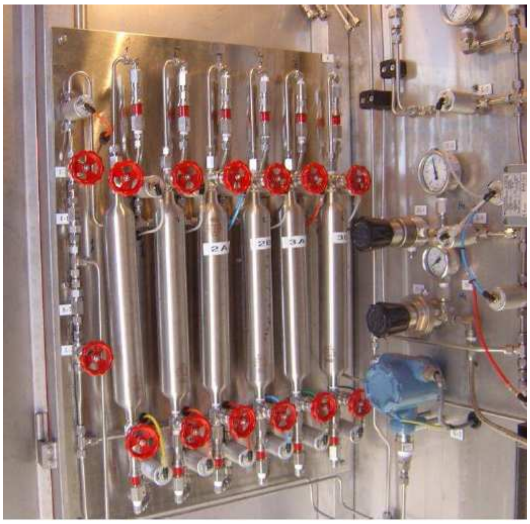


Figure 5 Example of gas sample containers [Courtesy of Enagas]

3.4 Gas Analysis System

The next step after collection of vaporised LNG sample is to analyse this sample in order to determine its composition. The current practice is to perform the analysis by gas chromatography. Gas analysis by Raman Spectroscopy is also available where the composition of LNG is measured directly in the LNG transfer line but this method still in the development and verification stage.

The energy content (gross calorific value) of loaded/unloaded LNG is determined from the gas composition. A direct energy content measurement by e.g. calorimeter is less precise and also will not give the compositional information needed for calculating other properties such as density or Wobbe index. The gross calorific value and density are both required for the LNG energy transfer calculations in the LNG custody transfer trade.

Detailed description of gas chromatography can be found in; ISO 6974, Energy Institute IP 377, ASTM D 1945 and GPA 2261.

3.5 Data Acquisition and Processing System

A dedicated data acquisition system is installed in order to monitor and control the sample condition from the point of collection to the point of analysis, process the analysed data, apply data consistency checks and filter the data to provide a final reliable measurement of LNG composition. This system normally consists of the following main hardware and software elements:

- **Remote data collection unit**: collects data from all instruments, control devices and gas chromatograph and sends it to the computer system for analysis and treatment.

- **Software application for communication**: facilitates communications between the remote control unit and computer to visualise and store the data acquired from the remote unit.
- **Alarms software and database**: insure all parameters operate within predefined limits.
- **Software for data processing and treatment:** process the data and eliminate LNG compositions produced during unstable periods (i.e. outside predefined limits).

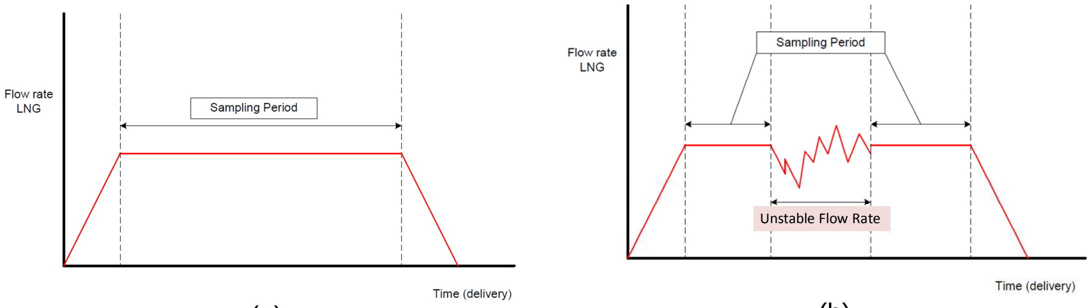
After performing this data processing step, a subset of acceptable LNG compositions is available for further treatment. The purpose of data treatment is to obtain, from a statistical point of view, a consistent result that best reflects the quality of the discharged LNG. The data treatment is achieved by firstly applying a statistical test called “GRUBBS test” for each LNG component as detailed in ISO 5725-1, secondly calculate the average composition of the LNG and finally normalise the LNG composition. This will results in a final LNG molar composition from which the relevant LNG properties such as density, gross calorific value and Wobbe index can be calculated.

4 SAMPLING PROCEDURE

4.1 LNG Flowrate

Sampling of LNG must take place continuously throughout the sampling period at a constant LNG transfer flow rate regardless of whether the sampling method is continuous or intermittent [4]. For example, in Figure 1 the flow monitoring device (FT1) is used for this purpose.

In this process the initial period corresponding to the starting of transfer pumps is excluded until the full flow rate is established. Similarly the final period corresponding to stopping of transfer pumps is also excluded, Figure 6(a).



(a) (b)

Figure 6 LNG sampling period

When significant changes in pressure or flow rate occur in the transfer line, Figure 6(b), the sampling must be suspended temporarily. Sampling can only be conducted during stable unloading/loading flow rate.

4.2 Sample Condition from Probe Inlet to Vaporiser Inlet

The sampling probe must be installed at a point in the LNG transfer line where the LNG is under sub-cooled condition. The degree of subcooling is ascertained by comparing the LNG temperature at the sampling point (TT1) with the LNG boiling point calculated at pressure (PT1), Figure 1. The calculation of boiling point also requires knowledge of LNG composition. If the LNG temperature in the transfer line is lower than the boiling point then the sampled LNG is under sub-cooled condition.

Figure 7 (top part) shows natural gas liquid-vapour equilibrium curve for an example of LNG from Qatar. For LNG to be in sub-cooled condition, it has to be on the left hand side of the liquid-vapour equilibrium curve. The LNG condition during the unloading operation is normally within the zoomed area shown by the dotted line.

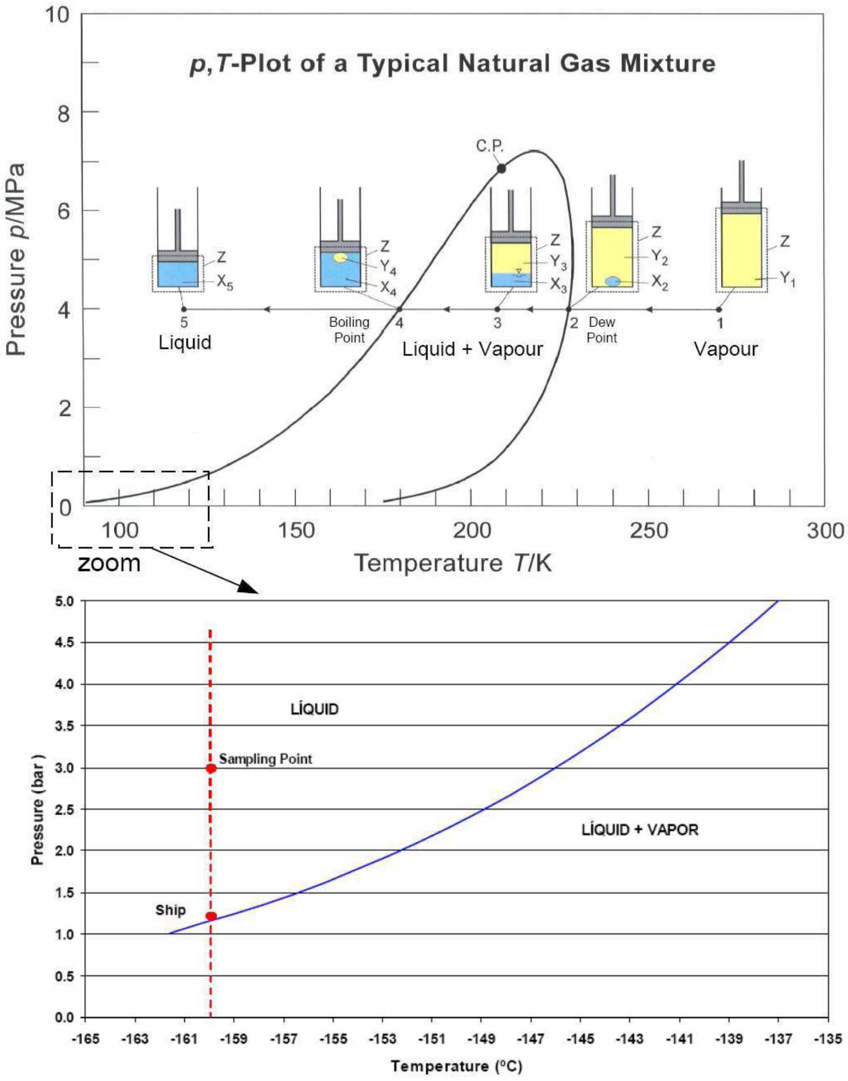


Figure 7 Natural gas liquid-vapour equilibrium curve [6]

The zoomed area in Figure 7 (bottom part) shows the condition of LNG in the ship's tanks where the pressure is close to ambient value and LNG is very close to the saturation line (boiling point). When LNG unloading pumps start the pressure increases (in this example) to about 3 bar resulting in increase in LNG boiling point (from -160°C to about -146°C). If for example the unloaded LNG temperature is -160°C then there will be subcooling of about 14°C.

In the LNG sample probe and transfer line to vaporiser, any ambient heat gain or pressure variation may result in LNG partial vaporisation. In the case of ambient heat gain, two main factors play major role in this process, the first is the degree of sub-cooling that is available and the second is the quality of insulation used for the probe and sampling line to vaporiser. In order to maintain the LNG sample in sub-cooled condition before entering the vaporiser it is essential to use an efficient insulation such as vacuum jacketing to minimise the heat ingress into the system. The degree of subcooling is a parameter that has to be monitored continuously and an alarm must be set when the LNG temperature in the line is closely approaching the boiling point.

If boiling takes place in the probe and sampling line then the collected LNG sample entering the vaporiser may not be representative of LNG unloaded due to a preferential vaporisation of components with lowest boiling point such as nitrogen and methane.

To illustrate how the condition of LNG is changing from the point of sampling to vaporiser inlet, the following example for LNG unloading case is given as shown in Figure 8. Note that this case is different from the one shown in Figure 7.

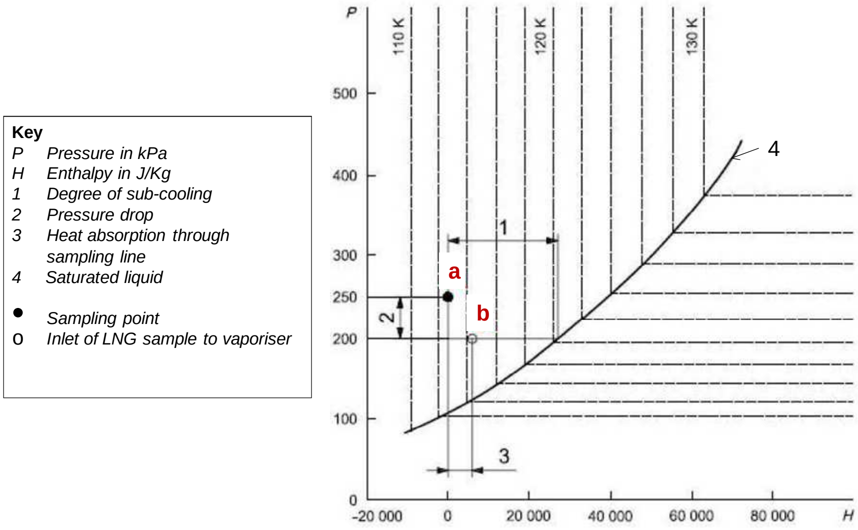


Figure 8 LNG pressure enthalpy diagram

During the unloading period, an LNG sample is taken at point “a” of Figure 8 from the LNG transfer line. The LNG is at sub-cooled condition which means that the whole substance is in liquid state. Through the probe and sample line, a pressure drop together with a warming due to heat absorption will occur resulting in change of sample state from point “a” to point “b”. In this example it can be seen that the enthalpy change is less than sub-cooling degree and therefore the LNG will remain in sub-cooled liquid state before entering the vaporiser. As indicated above this condition has to be monitored continuously. Representative sampling with minimum subcooling of 0.5^{o} K is achievable according to [11].

4.3 Sample Vaporisation Process

The LNG sample entering the vaporiser must be completely vaporised before being analysed in a gas chromatograph device. In particular heavy components of the LNG must not remain in the vaporiser.

Figure 9 shows the pressure / temperature diagram of natural gas. It is important to note that this figure is for illustration of the vaporisation process in particular point 1. This point in fact represents point b in Figure 8.

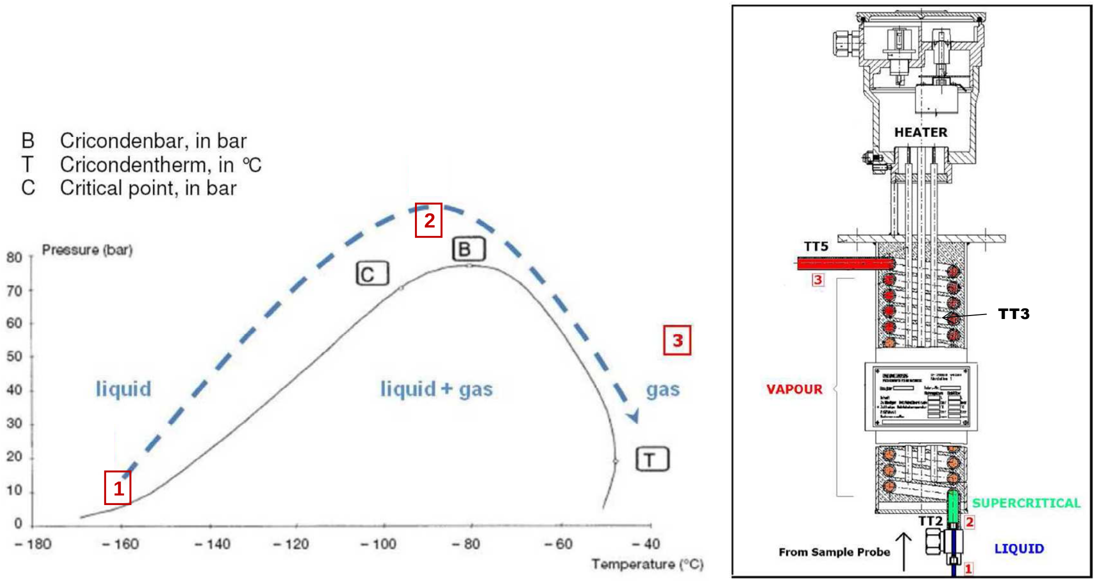


Figure 9 LNG vaporisation path [6]

The objective is to transform LNG from liquid to gas state in supercritical conditions at a pressure higher than the Cricondenbar point (i.e. higher than 75 bar) so that the LNG sample goes directly (flash) into the desired gas state without fractionation. Such transformation is represented in the Figure 9 (left) by the dotted line.

Within the vaporiser the following processes are taking place, Figure 9:

- When LNG sample enters the vaporiser at the condition described in Figure 9 (point 1), it first passes through a restriction device such as a small volume pressure relief valve to allow LNG to flash into natural gas in supercritical state (illustrated in green colour in Figure 9 (right)).
- The process of LNG flashing will result in higher pressure and temperature of around 80 bar and -100°C (point 2 in Fig. 9).
- In the vaporiser, the flashed LNG will enter heated environment (e.g. heating rod or coil) and the gas sample temperature at the vaporiser outlet (point 3) will be controlled to obtain gas sample temperature > 20°C.

For the example given in Figure 1, the measured vaporiser parameters (TT2, TT3, WT1, TT5 and PT4, FIC1) will be monitored in order to control this process of vaporisation. The LNG inlet temperature (TT2) ensures that the liquid is sub-cooled and can be flashed. The outlet temperature and pressure (TT5 and PT4) ensures that gas leaving the vaporiser is at the correct condition for analysis by chromatography. The electrical power (WT1) ensures that the vaporiser is at the right power. Finally the gas flow from vaporiser (FIC1) indicates that the LNG flow to be vaporised is at the required rate. These parameters are monitored by the alarm software.

4.4 Purging and Filling Process

As indicated in section 2.1, the LNG sampling system must provide a method to fully purge all interconnecting process lines to prevent contamination from atmosphere and previous sample. An example showing complete purging process can be found in [9].

The number of required purging cycles for sample containers is defined in annex D (sampling by fill and empty method) of ISO 10715 [8] according to the final pressure in the gas cylinder, see Table 1.

Table 1
Number of purge cycles for sampling by fill and empty method [8]

Final Pressure in cylinder, MPa	Number of purge cycles
0.1 to 0.2	13
0.2 to 0.4	8
0.4 to 0.6	6
0.6 to 1	5
1 to 3.5	4
≥ 34	3

The "LNG Measurement Study" of N.B.S. [11] has shown that the sample containers initially containing air should be purged and filled at least 14 times to remove all the air from these containers. If continuous purging is adopted, the sample container must be purged the equivalent of 14 or more purge and fill cycles. The purge gas throughput is estimated by monitoring the pressure, flow rate and time.

For intermittent sampling the purging and filling of sample containers (CP/FP) apply different procedures. According to [4], these containers need to be cleaned and purged by helium gas, take a sample of helium present in the container and run lab analysis for trace amounts of hydrocarbon or impurities. If hydrocarbons remain present after extensive purging, a solvent cleaning may be required.

4.5 Data Processing and Treatment

At the end of LNG unloading process, analysis report is normally completed as described in [3]. The main output of this report is LNG composition.

As indicated above, the data provided by gas chromatography must be processed and treated in order to eliminate LNG compositions produced by analyses in a period of time during which some operating parameters were outside their preset limits. The valid data will be then treated by applying the "GRUBBS statistical test", calculate the average composition of the LNG and normalise the final LNG composition.

An example of how the data is processed and treated is fully described in [6 and 2].

5 UNCERTAINTY IN SAMPLING AND GAS ANALYSIS

Detailed information on the estimate of uncertainty of measured composition of LNG from sampling appears to be limited to the NBS study [11] and ISO 6974-2 [12]. The latter focuses only on the uncertainty of composition measured by gas chromatography. The GIIGNL manual [3] also refers to the NBS study for estimation of uncertainty in measured composition and uncertainty in calculated LNG density and calorific value.

In this work the focus is placed on the total uncertainty in measured gas composition. The uncertainty in the gross calorific value and density are covered in separate work within the EMRP project as part of estimate of overall uncertainty in measured LNG energy transferred [13].

The uncertainty in the measured LNG composition can be considered to be composed of two main elements. The first is from the sampling and vaporisation system and its operating conditions and the second is from gas analysis by chromatography.

The first element (sampling system and its operating conditions) has been investigated in detail by the NBS study [11]. In this study, the lack of field performance information and data meant that the approach taken for estimating the uncertainties was based on assumed conditions at a typical LNG import terminal. In this case the estimate of total uncertainty is composed of an allocation for known sources of systematic error plus random error. The study considered many factors which could affect the precision and accuracy of the composition of samples withdrawn from a flowing LNG stream. Precision is defined as the closeness with which the results of independent replicate measurements agree and usually quantified by the estimated standard deviation. This will be referred to as “repeatability” hereafter. Accuracy denotes the closeness of computations or estimates to the exact or true value.

The factors considered in the NBS study covered:-

- Three probe designs
- Two vaporiser designs
- The following operating variables:
  - Flow rate of the liquid stream in the transfer line,
  - Flow rate through the sampling system,
  - Amount of subcooling,
  - Temperature of LNG,
  - Pressure drop (between sampling probe inlet and vaporiser inlet)
  - Time-averaging the sample,
  - Vaporiser outlet temperature, and
  - Composition, particularly the effect of pentane and higher hydrocarbons

The effect of above listed factors on sampling repeatability and accuracy is grouped below:-

- Variables affecting both sampling repeatability and accuracy:
  - Heat leak to liquid sample line.

- Variables affecting sampling repeatability but not accuracy:
  - Sampling flowrate,
  - Vaporiser design,
  - Time-averaging the vaporised sample,
  - Sample rate transients,
  - Sampling probe design.

- Variables not affecting sampling repeatability and accuracy:
  - Temperature and pressure at the sampling point,
  - Degree of subcooling
  - Flow rate past the sampling point,
  - Pressure drop (between sampling probe inlet and vaporiser inlet)
  - Composition of the liquid being sampled.

There is no mention in the NBS study what would be the total uncertainty associated with the factors related to the sampling system only (i.e. the first element of uncertainty indicated above).

The uncertainty associated with the second element (i.e. gas analysis) is reported by the NBS study. The estimate of total uncertainty given below for this element is composed of an allocation for known sources of systematic error plus random error [11].

The random error for the gas analysis process is estimated to be ±0.02% and expanded to ±0.06% using a coverage factor of 3 to achieve confidence level of 99.7%. This value represents the maximum value obtained from over 100 measurements of three or more repetitive analyses employing a properly operating gas chromatograph with programmable integrator system.

The known sources of systematic error are the uncertainty in the composition of calibration gas which is estimated as ±0.03%. This represents the uncertainty in the weighing process used to prepare the calibration gas mixtures. Great care must be taken to assure the purity of the components of the calibration gas in order to maintain this uncertainty value.

From above, the total uncertainty in gas analysis is worked out from the sum of random error and known sources of systematic error (i.e. 0.09%) rather than from the root mean square (RMS) of these values. This means that the estimate of this uncertainty is conservative. The value worked out from the RMS is 0.067%.

It can be concluded based on the above study that the uncertainty in gas analysis should be within ±0.09%.

The GIIGNL handbook [3] indicates by reference to the NBS study [11] that the uncertainty in measured LNG composition due sampling and analysis is ±0.3% (this includes the ±0.09% indicated above). However, close examination of reference [11] revealed no mention of this but in several sections, it was stated that "*the total uncertainty of a single measurement in sampling and analysing LNG mixtures can be less than ±0.3 percent in the computed calorific value*". Therefore the ±0.3 refers to the uncertainty in calculated calorific value and not in the gas sampling and analysis only. However, the only additional parameter that contributes to the uncertainty of calculated LNG gross calorific value is the gross calorific value of the components used in the mixture which is given by [11] as ±0.04%. Since this uncertainty is very small, it can be concluded that the uncertainty associated with gas sampling and analysis is ±0.30% (using a coverage factor of 3 to achieve confidence level of 99.7%). This uncertainty should be lower when a coverage factor of 2 is used to achieve confidence level of 95%.

6 SUMMARY AND RECOMMENDATIONS

6.1 Selection of Sampling System

When selecting LNG sampling system, it is extremely important to adhere to the requirements listed in section 2.1. It appears that the continuous LNG sampling system uses less equipment with moving parts than the intermittent sampling system and the purging process of sample containers may be less involved, however the use of CP/FP containers (fixed pressure containers) minimises atmospheric or cross batch contamination and ensure that the sample is stored at the correct process conditions.

Some of the continuous sampling systems witnessed on visited sites deviate slightly from those given in ISO 8943 by having a direct feed of gas sample from the accumulator and mixing vessel to gas chromatograph or if an accumulator is not used then the gas sample leaving vaporiser is fed directly to the gas chromatograph and to gas sample holder (e.g. Figure 1). The gas containers are filled either manually or automatically from the accumulator or sample holder during the whole duration of stable sampling. For example the first cylinder is filled one hour after start of stable sampling conditions, the second half way through sampling duration and the third before stopping the LNG pumps.

In conclusion, provided that the LNG sampling requirements indicated above are fulfilled, the choice of sampling system type (continuous or intermittent) is left to user preference.

6.2 Sampling Probe and Sample Line to Vaporiser

To achieve representative sampling, the LNG flow through the sampling probe and sampling line to vaporiser must be maintained in liquid phase. This can be achieved by:-

- Installing the probe at a point on the transfer line where the degree of subcooling is high. The probe access point is normally located on the top of horizontal pipe and this appears to be the current practice [3]. The probe tip should be at least 0.3D away from the tube wall (where D is the tube diameter) and preferably at the centre of the pipe. However, the NBS study [11] indicates that use of side tap probe mounted horizontally with the probe flush with the wall of the LNG pipe produced best results in that study. It is recommended to avoid this arrangement due to possible effect of a boundary layer at the surface of the main pipe, which can lead to samples of the LNG that are not representative.
- The probe inner diameter should be as small as feasible and reference [11] recommends the diameter to be less than 0.25 in (6.4 mm).
- The LNG subcooling must be maintained through the probe and sample line to vaporiser to prevent LNG boiling. This can be achieved by using efficient insulator that minimises ambient heat gain and withstands atmospheric conditions. Experience has shown that use of vacuum jacketed insulation is ideal and therefore recommended for use. However this option will be more expensive than other types of insulation and the vacuum level has to be monitored.
- The length and diameter of the sample line to vaporiser should be designed according to ISO 8943. A tube diameter of 2 or 3 mm is commonly used.
- If length of sample line to vaporiser is greater than the design length, it is recommended to install two temperature instruments and one pressure instrument. The first temperature instrument is at probe exit and the second at vaporiser inlet to monitor LNG temperature. The use of pressure instrument and second temperature instrument are required to evaluate the degree of subcooling which is dependent on LNG composition. The second temperature instrument will also provide indication on the gradual loss of vacuum when vacuum jacketing is used for insulation. This temperature in addition to formation of ice around piping indicate significant loss of vacuum.
- Other considerations:
  The probe must be constructed from stainless steel material designed to withstand the temperature and pressure and equipped with automatic shut-off valve. The piping to vaporiser must be equipped with pressure relief devices set at the correct relief pressure in case of LNG boiling.

6.3 Vaporiser and Control Devices

The vaporiser must be designed to meet the requirements of ISO 8943. The main requirement is to vaporise the LNG from liquid to gas phase directly without going through the 2-phase region. Therefore LNG flashing and subsequently heating to a sufficiently high temperature, i.e. 50℃ or greater , is required to ensure immediate vaporisation of even the heaviest trace components.

It is not recommended to use open tubular atmospheric vaporisers in which the heat comes from the ambient air as these devices will not guarantee LNG vaporisation with no fractionation.

Laboratory results [11] indicated that a small diameter tube vaporiser was better than a vaporiser with a large cross sectional area. Both steam and electrically heated vaporisers produced comparable results.

Experience has shown that some types of electrical vaporisers fed from the bottom of vaporiser may not achieve complete vaporisation, but when LNG is fed from the top and flow to vaporiser is carefully restricted, flash vaporisation with no fractionation can be achieved and gas temperature leaving the vaporiser can be controlled at the desired temperature.

In order to achieve the controlled vaporisation process described in section 4.3, control devices must installed at vaporiser inlet, within vaporiser and at vaporiser outlet as described in section 3.2.

6.4 Sample Condition

The main parameter that must be controlled when the liquid sample flows through the probe and sample line to vaporiser is degree of subcooling. The NBS study [11] indicates that representative sampling can be achieved with subcooling as low as 0.5^{o} K. However this should be considered as the minimum value.

The main parameters that must be controlled when the gas sample leaves the vaporiser are; temperature, pressure, sample homogeneity and flowrate.

The gas sample temperature is controlled by combination of heat regulation device and temperature instruments. The vaporiser electrical power is also monitored in order to achieve this. Reference [11] recommends gas sample temperature leaving the vaporiser in the range of (27^{o}C to 38^{o}C) and this must be maintained (e.g. by use of heated sample line) to prevent condensates in particular water vapour condensation. There is no advantage in having the vaporiser outlet temperature above 38^{o}C.

Both pressure and flowrate regulation are used in order to control the LNG flow to be vaporised independently of pressure or flow rate in the main LNG transfer pipe. In general, reference [11] recommends to maintain the sample flowrate above 1200 l(n)/h and the sample pressure greater than 1.4 bar to provide sufficient gas sample pressure for purging and filling of sampling containers.

An anti-pulsation vessel (or a mixing accumulator) is also used to absorb the pressure pulses and to maintain gas homogeneity. The minimum residence time necessary to obtain representative results depends on the sampling system. Residence times of 20 to 120 seconds gave good results in the NBS study [11].

Flow meters and/or flow limiters are also required to control the maximum sample flowrate.

In addition to pressure and temperature instrumentation pressure and temperature interlock systems are required for auto-shut-off the main LNG isolation valve if the gas sample temperature at vaporiser outlet drops to the application set point or if pressure at vaporiser outlet exceeds set pressure.

6.5 Purging Process

In order to prevent contamination of newly sampled LNG by the previous sample or by presence of air in the system, it is extremely important to perform through purging of the sampling system. The purging of sampling system is performed according to ISO 8943 [4] and ISO 10715 [8]. The information given in ISO 10715 is relevant to natural gas sampling rather that LNG sampling and therefore care must be taken when following this standard for purging process. The information given in ISO 8943 lack details on purging process and gives only very brief guidance.

For purging the sample containers, the NBS study [11] have shown that the sample containers initially containing air should be purged and filled at least 14 times to remove all the air from these containers. If continuous purging is adopted, the sample container must be purged the equivalent of 14 or more purge and fill cycles. The purge gas throughput is estimated by monitoring the pressure, flow rate and time to achieve this requirement.

An automated process for both continuous and intermittent sampling systems is recommended except when CP/FP sample containers are used, these must be manually cleaned as detailed in section B4 of ISO 8943.

6.6 Data Processing and Treatment

After achieving stable sampling conditions, the composition of the conditioned sample is measured by a gas chromatograph. Before producing the analysis report which is required after completion of LNG unloading process, the data provided by gas chromatography must be processed and treated in order to eliminate LNG compositions produced by analyses in a period of time during which some operating parameters were outside their preset limits. The valid data will be then treated by applying the “GRUBBS statistical test”, calculate the average composition of the LNG and then normalise the final LNG composition.

During this process the data acquisition system must incorporates software for monitoring the sampling conditions (and when necessary raise an alarm) and software for data processing and treatment.

The monitoring software checks that each measured parameter is operating within its limits, otherwise an alarm will be triggered and this means that the LNG composition data must not be taken into account for processing and treatment.

The data processing and treatment software eliminates LNG compositions produced by analyses in a period of time during which some operating parameters were outside their preset limits.

6.7 Uncertainty in Sampling and Gas Analysis

During this study, it was found that the information available on the uncertainty associated with the LNG sampling and vaporisation is limited to the NBS study [11] which has been reported in 1985. Although all the parameters contributing the uncertainty associated with sampling and vaporisations were explored and their effects were summarised, a figure on expected overall uncertainty in sampling and vaporisation is not given directly. However the uncertainty in gas composition associated with gas analysis by chromatography has been detailed and given as ±0.09% (using a coverage factor of 3 to achieve confidence level of 99.7%).

In the NBS study it is stated that “*the total uncertainty of a single measurement in sampling and analysing LNG mixtures can be less than ±0.3 percent in the* *computed calorific value*". This covers the uncertainties in sampling and vaporisation, gas analysis as well as the uncertainty in gross calorific value of the components used in the calibration gas mixture which is given by [11] as ±0.04%. Since the latter uncertainty is very small (i.e. only ±0.04%), it can be concluded that the overall uncertainty in sampling and analysis can be achieved within ±0.30% (using a coverage factor of 3 to achieve confidence level of 99.7%). It appears that this value is currently accepted by the LNG industry as it is indicated in the GIIGNL hand book [3] and uses a high value for confidence level.

A breakdown of all uncertainty elements associated with sampling and analysis as well as the uncertainty in the density and gross calorific value is covered in separate work [13] as part of estimate of overall uncertainty in measured LNG energy transferred.

6.8 ISO 8943:2007

From the above review and assessment of LNG sampling systems, it appears that a practical guidance document on sampling system design and operation is required. The ISO 8943 provides general guidelines and requirements that must be met to achieve representative sampling of LNG but lacks detailed information and examples on operating conditions and limits of the main parameters. It is understood that some parameters will depend on the design of the system and its associated elements but providing practical examples of typical LNG sampling systems recently installed at an import and export terminals and range of operating parameters within which representative sampling can be achieved would be extremely helpful. Some of these shortfalls are addressed by the GIIGNL handbook [3] but this document is neither a standard nor a specification and therefore an enhancement to ISO 8943 is recommended.

The following are proposed to enhance ISO8943:

- More examples of continuous and intermittent sampling systems are required. Current LNG sampling systems in operation deviates from those in the standard and cause confusion whether the system can be described as continuous or intermittent. The standard defines both continuous and intermittent systems but during the survey conducted in this work it was observed that a system which has direct feed to a gas chromatograph is being regarded as intermittent by one visited site although the sampling, vaporisation and analysis are continuous. This is simply caused by showing direct feed of sample from vaporiser to analyser in the ISO 8943 example of the intermittent sampling system only (Figure 3 of ISO8943).
- Recommendations on inner diameter of probe and sampling line to vaporiser.
- The selection of insulation type for probe and sampling line to vaporiser is left to the user. Despite cost implications, it is highly recommended to indicate that vacuum insulation should be considered first, in particular when subcooling degree is low, as it provides best insulation efficiency and withstands weather conditions when compared to traditional insulation materials. However the vacuum level must be monitored and maintained.
- More information on type of vaporisers used and advantages and disadvantages of each type. Typical recent examples would be helpful.

- More guidance on sampling procedure is required, the following questions are raised:
  - What is the minimum degree of subcooling that should be maintained before sample enters vaporiser?
  - What is the minimum/maximum sample pressure? Typical examples
  - What is the minimum/maximum sample flowrate? Typical examples
  - What is the criterion for achieving complete purging process? More details required on how purging is conducted, the number of purge cycles required for each element of the system (in particular sample containers). If continuous purging is adopted, for how long the purging should be carried out? Typical examples for purging would be helpful.
  - For how long the water-seal-type gas sample holder should be subjected to bubbling and what is the criterion for achieving complete purging.

It would be beneficial to take the above suggestions in consideration in the next update of ISO8943:2007.

6.9 Development of Reference Standard for LNG Composition Measurement

A traceable reference standard for measurement of LNG composition with defined low uncertainty does not exist yet.

Such a standard is required for two reasons:

1- To benchmark current and newly developed LNG sampling systems,
2- Conversion of primary mass flow measurement to volumetric flow measurement with sufficiently low uncertainty through traceable calculation of LNG density from composition.

A draft proposal has been put forward by VSL supported by industry and national authorities to develop such a reference system within a newly developed LNG mid-scale (200 m^3/hr) flow meter calibration facility. The work involves detail design of the mid-scale system and LNG composition measurement standard (currently put as an option for approval) based on experience from industry using the most up to date techniques for sampling and composition analysis.

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