1.4.3	Report on the LN2 tests with the LDV standard	**CESAME**	Report	Jan 2016	D1.4.1, D1.4.2
1.4.4	Report on the flow simulations with the geometry of the LDV standard	**CESAME,** CMI	Report	May 2016	D1.4.1
1.4.5	Particle size characterisation of the LNG and its dependence on source	**CESAME**	Dataset	May 2016	D1.4.1
1.4.6	Confirmation of the completion of the LNG tests for validating the LDV standard	**CESAME**, VSL	Email	Feb 2017	D1.4.1 D1.4.2
1.4.7	Report uncertainty calculations for the LDV standard	**CESAME**, JV	Report	Mar 2017	D1.4.1 D1.4.2, D1.4.6

C2 WP2: LNG Composition Measurements

*(**NPL**, CMI, SP, VSL, Shell, REG(RUB))*

Start month: Jun 2014, end month: Jan 2017

Accurate and traceable measurement of liquefied natural gas (LNG) composition is essential in order to accurately calculate physical properties used in the trade and transport of the energy gas. As the LNG share of the European energy budget grows, the financial implications of more accurate and reliable composition measurement also grows becoming much more impactful.

Due to physical state of LNG, the accurate measurement of LNG composition for trade / transport is significantly more challenging than that of gaseous natural gas (NG). This work package will investigate some of the issues and challenges associated with accurate composition measurement of bulk LNG. Information gathered from the previous EMRP JRP in this area will be used to assess the current 'state of the art' equipment used in industry and find where it can be improved.

The most accurate method to measure NG composition is by GC, and International Standards (the ISO 6974 series) exist for this. However in the case of LNG, the sampling of a liquefied gas into a homogenous gaseous state for analysis by GC is highly challenging – preferential sampling of one phase may occur, resulting in discrimination of the sample. Industrial measurements of LNG composition are currently being tested on-line by Raman spectroscopy in LNG pipelines but this is considered an unproven technology. Calculations to determine calorific value and density are based on gasified LNG which is analysed via GC in a similar way to NG. The aim of this work package is to investigate the issues in this area in two ways:

1 Methods to sample and vaporise LNG in a representative and homogeneous fashion will be developed in Task 2.2, while Task 2.1 will involve making an accurate, lab-based sampling and analysis reference method to test and calibrate commercially available systems.

2 Raman spectroscopy methods for composition analysis will be validated and compared with the results gained by those of GC methods in Task 2.3.

The effects of long-term storage (in terms of effect on LNG composition) will also be investigated in Task 2.4

Accuracy in the area of LNG composition analysis is currently a concern and no international intercomparisons have been performed on LNG composition analysis. This work package aims to produce a standard that will cover high accuracy sampling and measurement of LNG.

The work of this technical work package will lead to the submission for publication of at least two peer reviewed paper. These papers are included in WP5 as D5.1.7, however the resource is included in this WP.

C2.a Description of Work

Task 2.1: LNG composition reference standard (VSL, NPL, SP, Shell)

(Start Jun 2014, end Nov 2016)

The aim of this task is to design, build and validate a reference standard for validating/qualifying LNG sampling and composition measurement systems. Conceptually the reference standard will consist of a liquid sampling and vaporisation unit and a gas chromatograph. The design of the sampler and vaporiser will be optimised to minimise errors and with the possibility for uncertainty validations. The target measurement uncertainty for the sampler and vaporiser combination is 0.2 % on calorific value. The target measurement uncertainty for the GC will be 0.1 % on calorific value. The reference standard will be integrated in the LNG flow calibration facility from Task 1.1. The LNG composition reference standard developed in Task 2.1 will be integrated in the mid-scale LNG flow standard in Task 1.2 and used to compare it with a commercial sampler, vaporiser and GC also integrated in the mid-scale LNG flow standard (D1.2.4).

Description of activities:

- VSL with input from Shell will complete a literature study to gain an overview of what is available for the scope of the Task 2.1. As part of this activity a set of LNG mixtures will be defined, for use in the validation of a reference standard for validating/qualifying LNG sampling and composition measurement systems. This work will be recorded in a document. (VSL, Shell) (D2.1.1)
- VSL with support from SP, NPL and Shell will produce a basic design for a system for measuring representative LNG composition, based on the literature study in the previous activity (D2.1.1) and input from the JRP Advisory Group (D5.1.1). The validation approaches required will be taken into account, as well as safety requirements and an equipment list will be prepared and the specifications determined. Finally, a basic design diagram will be delivered and a cost-estimation will be made based on the equipment list quotations. (VSL, SP, NPL, Shell) (D2.1.2)
- Using the basic design D2.1.2 as input, VSL with support from SP, NPL, Shell will produce a detailed design report for the LNG composition reference standard. In the detailed design, the equipment list will be updated, detailed specifications will be made and requests for quotations will be sent to suppliers. This activity will be supported with calculations, knowledge and simulations. Based on the detailed design, an updated equipment list and detailed cost-estimation will be worked out and a final investment decision will be made. (VSL, SP, NPL, Shell) (D2.1.3)
- VSL will construct the LNG composition reference standard based on the detailed design report from the previous activity. Purchase orders will be sent to the selected suppliers and the execution of the activity will require careful planning of material delivery times and safety requirements. (VSL) (D2.1.4)
- VSL together with NPL and SP will validate the LNG composition reference standard (D2.1.4). A preliminary validation program will be documented as part of the basic design (D2.1.2) and this will be used to create a detailed validation program, in parallel with the detailed design (D2.1.3) and the construction of the LNG composition reference standard phase (D2.1.4). LNG gas mixtures will be prepared using input from D2.1.1 and certified for validating the LNG gas samples obtained from the LNG composition reference standard. The validation program will consist of a laboratory validation, using the liquefier designed in D2.3.4, and an ‘in-field’ validation following integration of the LNG composition reference standard in the in the mid-scale LNG flow standard D1.2.4. A report on the results of the laboratory and ‘in-field’ validation for the LNG composition reference standard will be produced using input from D2.3.6. (VSL, NPL, SP) (D2.1.5, D2.1.6)
- VSL together with NPL and SP will complete an uncertainty analysis based on the results of the previous activity and produce an uncertainty budget for the LNG composition reference standard. The target uncertainty for the reference sampler and vaporiser is 0.2 % and for the GC 0.1 %. (VSL, NPL, SP) (D2.1.7)
- VSL with input from NPL, SP and Shell will write a final report on the results of the task and the validation of a reference standard for validating/qualifying LNG sampling and composition measurement systems (D2.1.8).

Major facilities to be used: none

Task 2.2: Improved Sampling Techniques for LNG (SP, CMI)

(Start Jun 2014, end Jan 2017)

The aim of this task is to develop a sampling line to sample LNG (discontinuous sampling for point sampling). A major concern within the LNG transportation and trading industry is that it is very difficult to obtain a representative homogenised sample of LNG. This has knock-on effects in the ability to measure the calorific value, density etc. of the gas, as knowing whether the gas being transferred has the same calorific value as the gas further upstream has huge financial implications.

In the sampling line, the LNG shall be vaporised in order to sample gasified LNG. The system may require a vaporiser, control devices and sampling devices. Examples of places where the sampling system is needed are public fuelling stations that are not equipped with a sampling line.

Description of activities:

- SP will research into the correct point in which to take samples of LNG, as part this SP will hold discussions with the JRP Advisory Group (D5.1.1). A report on the sampling points for LNG sampling will be produced. (SP) (D2.2.1)
- Based on the results of D2.2.1, SP with input from CMI will then design a sampling line system for LNG sampling. It is expected that the system may need to include a vaporiser, control devices and sampling devices. (SP, CMI) (D2.2.2)
- Using the design from the previous activity, SP will then manufacture the sampling line system for LNG sampling. (SP) (D2.2.3)
- Using the sampling line system D2.2.3, SP will then take at least 5 LNG samples, at 2 different locations, at existing facilities such as public fuelling stations not equipped with a sampling line. The facilities (public fuelling stations) will be located in the south of Sweden (e.g. Gothenburg, Jonkoping or Lidkoping). The LNG samples will then be quantitatively analysed for composition and the sampling line system will be compared with existing techniques. A report on the results of the task and the construction and performance of the sampling line system for LNG sampling will be produced. (SP) (D2.2.4, D2.2.5)

Major facilities to be used:

Stig Center (SP)

Task 2.3: Validation of Raman Systems (NPL, VSL, REG(RUB), CMI, Shell)

(Start Jun 2014, end Jan 2017)

The aim of this task is to perform a robust validation of a Raman spectroscopy system used to perform measurements of LNG composition. A novel liquefier / measurement cell system will be developed as part of the task, which will be used to force high-accuracy LNG reference gases into the liquid phase in order to validate the Raman measurements. These measurements will then be compared to the composition analysis of LNG standards in the gaseous phase by GC, and cross-validated by performing measurements at other participating laboratories.

There are several challenges to overcome throughout this task. The liquefier system to be developed needs to be able to liquefy the natural gas whilst ensuring homogeneity, and must be able to operate at pressures of up to 80 bar and temperatures of below -130 °C. An additional complication is that the Raman spectroscopy laser will provide some heating of the LNG, which may result in a partial re-gasification (and therefore discrimination) of the sample. Also, the window of the measurement cell must be strong enough to withstand the elevated pressure of the LNG, but thin enough for the laser to be able to measure the composition of the LNG accurately. Some of these issues will be simulated prior to testing.

Online LNG composition measurement systems can use Raman spectroscopy if the accuracy of this method can be proved to be comparable to that of the state-of-the art LNG composition measurements. Raman Spectroscopy however has the additional advantage that the measurement can be taken as the LNG is flowing within the pipework in a liquid phase, hence, eliminating any discrimination caused in sampling/gasification process. This task aims to validate whether these measurements are indeed comparable.

Description of activities:

- NPL will produce a report on current designs of Raman LNG measurement cells and the use of Raman spectroscopy systems to measure LNG composition. This will include discussions with REG(RUB) who has previously developed plans for similar systems. NPL with support from REG(RUB) will use the information from the previous activity to design a liquefier/measurement cell for the Raman spectroscopy measurement of LNG composition. (NPL, REG(RUB)) (D2.3.1, D2.3.2).
- CMI will perform computer simulations of the LNG cooling/heating and the phase changes associated with the design (D2.3.2) for the liquefier/measurement cell for the Raman spectroscopy measurement of LNG composition. (CMI) (D2.3.3)
- Using the design in D2.3.2 and the results of the simulations in D2.3.3, NPL will construct a liquefier/measurement cell for the Raman spectroscopy measurement of LNG composition. (NPL) (D2.3.4)
- An initial validation of the liquefier/measurement cell (D2.3.4) will be performed by NPL in two ways. Firstly, using cyclohexane as a reference for the measurement of liquid hydrocarbons as per ASTM standard E1840. This can be performed using a lab-based Raman spectrometer at NPL. Secondly, using typical LNG composition standards. The standards will be prepared gravimetrically at NPL and the Raman analysis results will be compared to gravimetric data and GC analysis results. These tests will assess the repeatability and accuracy of the liquefier/measurement cell for the Raman spectroscopy measurement of LNG composition, and will be performed using a Raman spectrometer similar to those used in industry. (NPL) (D2.3.5, D2.3.6)
- The liquefier/measurement cell for the Raman spectroscopy measurement of LNG composition D2.3.4, will be used by NPL with support from Shell to validate a commercial LNG Raman spectrometer used in the LNG industry, such as that in use at Shell or the National Grid in the UK. (NPL, Shell) (D2.3.7)
- Further cross-validation of the liquefier/measurement cell for the Raman spectroscopy measurement of LNG composition D2.3.4, will then be performed by NPL, with support from VSL and Shell, using different LNG standards. Following this D2.3.4 will be shipped to VSL to compare it with the LNG composition reference standard (D2.1.4) as part of D2.1.6. The target uncertainty for the comparison is 0.2 %. As part of the validation, the system will also be validated at a commercial LNG site (e.g. the National Grid) and a report will be produced on the results of this. (NPL, VSL, Shell) (D2.3.8)
- Using input from D2.3.1- D2.3.8, NPL together with VSL will write a report on the results of the Task and the validation of a Raman spectroscopy system for performing measurements of LNG composition. (NPL, VSL) (D2.3.9)

Major facilities to be used:

Gas chromatograph with TCD and FID detectors (NPL)

LNG standard preparation facilities (NPL, VSL)

Task 2.4: Ageing Effects at LNG Storage and Filling Stations (SP)

(Start Jun 2014, end Jul 2016)

Long-term storage (i.e. several days up to a month) of LNG is very desirable due to the significant increase in the amount of substance that is able to be stored in a smaller volume/facility in comparison to gas phase natural gas. However, due to the fact that this is a relatively new process (cryogenically cooled natural gas) the effects of such storage on the composition of LNG are currently not well documented. It is well known that the composition of LNG may change during storage as boil-off gases are released, but what is less well known is how fast these composition changes occur and how to avoid the release of boil-off gases.

The aim of this task is therefore, to determine the ageing effects for LNG stored in tanks at filling stations. This will be achieved by analysing LNG composition after the filling of a storage tank in defined conditions (e.g. every day, at the start of the day the tank is filled). Other points of interest for stakeholders are the effects on fuel composition when filling the tank with fuels at different temperatures or with different qualities. Therefore, stakeholder input from the JRP Advisory Group will be sought.

Description of activities:

- Samples of LNG will be taken daily by SP from a selected storage facility in Sweden. The samples will be taken using the most reliable sampling technique available and the technique will stay constant throughout the testing. SP will use input from the JRP Advisory Group (D5.1.1) on the choice of the sampling technique and subsequent analysis of the samples. (SP) (D2.4.1)
- The LNG samples obtained in D2.4.1 will be analysed by SP, using GC/TCD and GC/FID, to measure the composition of the LNG samples and determine any ageing effects on the stored LNG. (SP) (D2.4.2)
- SP will analyse the results from D2.4.2, in particular for the LNG composition of samples versus the time since fuelling. From the results of this SP will produce a report on the long-term storage and ageing effects on LNG. (D2.4.3)

Major facilities to be used:

Stig Center (SP)

C2.b Labour Resources for WP2

	1- VSL	2- CESAME	3- CMI	4- FORCE	5- INRIM	6- JV	7- NPL	8- PTB	9- SP	10- Shell	11- REG(RUB)	12- REG(TUBS)	TOTAL
WP2	10.1		5.5				19.5		6.0	1.0	0.5		42.6

C2.c Summary of Deliverables for WP2

Deliverable number	Deliverable description	Participants (Lead in bold)	Deliverable type	Delivery date	Dependent on
2.1.1	Definition of a set of LNG mixtures to be used in the validation of a reference standard for validating/qualifying LNG sampling and composition measurement systems	**VSL**, Shell	Document	Jul 2014	
2.1.2	Basic design of a system for measuring representative LNG composition	**VSL**, SP, NPL, Shell	Design	Oct 2014	D2.1.1, D5.1.1
2.1.3	Report on detailed design report for the LNG composition reference standard	**VSL**, SP, NPL, Shell	Report	Jan 2015	D2.1.2
2.1.4	LNG composition reference standard constructed	**VSL**	Facility	Aug 2015	D2.1.3,
2.1.5	Certified LNG gas mixtures validated	**VSL**, NPL, SP	Samples	Sep 2015	D2.1.1
2.1.6	Report on the laboratory and 'in-field' validation of the LNG composition reference standard	**VSL**, NPL, SP	Report	Jun 2016	D1.2.4, D2.1.2, D2.1.3, D2.1.4, D2.1.5, D2.3.4, D2.3.6

2.1.7	Uncertainty budget for the LNG composition reference standard	**VSL**, NPL, SP	Uncertainty budget	Jul 2016	D2.1.6
2.1.8	Report on the validation of a reference standard for validating/qualifying LNG sampling and composition measurement systems	**VSL**, NPL, SP, Shell	Report	Nov 2016	D2.1.1 to D2.1.7
2.2.1	Report on the sampling points for LNG sampling	**SP**	Report	Aug 2014	D5.1.1
2.2.2	Design of sampling line system for LNG sampling	**SP**, CMI	Design	Mar 2015	D2.2.1
2.2.3	Sampling line system for LNG sampling manufactured	**SP**	Devices	Nov 2015	D2.2.2
2.2.4	LNG sampling results from the sampling line system for LNG sampling	**SP**	Datasets	Jul 2016	D2.2.3
2.2.5	Report on the construction and performance of the sampling line system for LNG sampling	**SP**	Report	Jan 2017	D2.2.1 to D2.2.4
2.3.1	Report on current designs of Raman LNG measurement cells and the use of Raman spectroscopy systems to measure LNG composition	**NPL**	Report	Jul 2014	
2.3.2 (REG(RUB) D1)	Design of the liquefier/measurement cell for the Raman spectroscopy measurement of LNG composition	**NPL,** REG(RUB)	Design	Dec 2014	D2.3.1
2.3.3	Simulation of the LNG cooling/heating and the phase changes associated with the design D2.3.2	**CMI**	Datasets	Feb 2015	D2.3.2
2.3.4	Liquefier/ measurement cell for the Raman spectroscopy measurement of LNG composition	**NPL**	Equipment	Aug 2015	D2.3.2, D2.3.3
2.3.5	LNG calibration standards for D2.3.4	**NPL**	Calibration standards	Nov 2015	D2.3.4
2.3.6	Initial validation of D2.3.4	**NPL**	Datasets	Mar 2016	D2.3.4, D2.3.5
2.3.7	Test results from D2.3.4 using an industrial Raman spectrometer	**NPL,** Shell	Datasets	Apr 2016	D2.3.4
2.3.8	Report on the validation of D2.3.4 at a commercial LNG site	**NPL**, VSL, Shell	Report	Apr 2016	D2.3.4
2.3.9	Report on the validation of a Raman spectroscopy system for performing measurements of LNG composition	**NPL,** VSL	Report	Jan 2017	D2.3.1 to D2.3.8
2.4.1	Samples of LNG taken from storage facility	**SP**	Samples	Nov 2014, May 2015, Jan 2016	D5.1.1
2.4.2	Analysis of the LNG samples D2.4.1 using GC/TCD and GC/FID	**SP**	Datasets	May 2016	D2.4.1
2.4.3	Report on the long-term storage and ageing effects on LNG	**SP**	Report	Jul 2016	D2.4.2