EffecTech
Specialists in Gas Measurement

Evaluation of a Raman spectrometer for the measurement of Fluxys LNG

Report

prepared for the client
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Our reference: 15/1068
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Author: Dr Paul Holland

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Approvals

EffecTech		
Name	Signature	Date
Dr Paul Holland		22 December 2015

Shell Global Solutions International BV		
Name	Signature	Date
Martin van der Veer		

Reference Documents

Title	Ref	Rev	Date	Source
ISO 6142 *Gas analysis – Preparation of calibration gas mixtures - Gravimetric method*	[1]		2001	ISO Central Secretariat
ISO 17025 *General requirements for the competence of testing and calibration laboratories*	[2]		2005	ISO Central Secretariat
ISO 6143 *Gas analysis - determination of composition and checking of calibration gas mixtures - comparison methods*	[3]		2001	ISO Central Secretariat

Document History

Issue	Date	Author(s)	Comments
1	22 December 2015	Dr Paul Holland	***Report (for approval)***
2	24 February 2016	Dr Paul Holland	***Issue of report following comments from Martin van der Veer***
3	17 March 2016	Dr Paul Holland	***Inclusion of adjusted Raman results from Kaiser***

Executive Summary

Evaluation of a RXN2 Raman spectrometer using a single point LNG reference liquid showed that the determination of the heating value of the reference LNG liquid using the spectrometer was better than 9.9 kJ/kg (0.45 BTU).

Introduction

SGSI commissioned EffecTech to produce a Primary Reference Gas Mixture (PRGM) and use this to produce a high quality cryogenic reference LNG composition in the EffecTech cryostat. The mixture was based on the composition measured at the Fluxys terminal in Belgium. This reference LNG mixture was then used to evaluate the performance of the Raman spectrometer when measuring a typical Fluxys composition.

The PRGM was prepared at a higher pressure than normal as the remaining gas; following condensation; would be shipped in a cylinder to the Fluxys terminal and be used to calibrate the on-line gas chromatograph at site. By knowing the expected performance of the Raman spectrometer and comparing the analytical results from the spectrometer with the gas chromatograph, errors in the vaporisation process could be evaluated.

Results

Production of a reference LNG mixture in the laboratory

A cryogenic liquid reference LNG composition was generated using primary reference gas mixtures (PRGMs) contained at high pressure in cylinders. The required gas compositions were prepared gravimetrically In accordance with international standard ISO 6142 [1]. Once the primary standards were produced, they were verified analytically using traceable reference gases from the National Physical Laboratory (NPL). Verification was performed using EffecTech's in-house technical method, based on ISO 6143 [3], which is accredited to ISO 17025 [2] by the United Kingdom Accreditation Service (UKAS). This verification bestows international traceability to the mole, the SI unit of amount of substance, to the primary standards.

The reference gas was transferred into a purpose build cryostat where the gas was cooled to below the dewpoint of the gas mixture using liquid nitrogen at 77K. Table 1 shows the composition of the gas used in the evaluation of the Raman spectrometer. Annex A shows the ISO 17025 calibration certificate.

Table 1. PRGM composition

mix 15/1068/01	gravimetric values (%mol/mol)	
D328619	xi	U(xi)
nitrogen	0.5981	0.0014
methane	92.8920	0.0110
ethane	5.6370	0.0140
propane	0.7029	0.0032
iso-butane	0.0604	0.0004
n-butane	0.0777	0.0006
iso-pentane	0.0211	0.0002
n-pentane	0.0100	0.0002

Validation of cryogenic liquid reference LNG mixtures using gas chromatography

Cryogenic LNG produced inside the cryostat was sampled using a 1/16" stainless steel tube. The small internal diameter tube samples liquid from the LNG cell where it has been produced and exits the cryostat through the vacuum jacket and out of the top of the cryostat and into a small capacity accumulator. The flow of re-gasified LNG is controlled using a proprietary Vargha^{TM} valve. The re-gasified liquid leaves the accumulator and enters the gas sampling valve in the GC.

The sampling arrangement also allows some of the primary standard gas directly from the cylinder to flow into the GC sampling system. This facilitates a direct calibration of the GC with the nominally identical reference gas. The calibration is a simple point to point calibration of the re-gasified LNG at the same composition.

Many precautions have been taken to ensure the sampling system and cryostat design will reduce significant differences between the vapour and cryogenic liquid compositions.

Table 2 shows a summary of the 96 GC measurements from the re-gasified LNG.

Table 2. GC measurements

	GC RESULTS (Measurements from liquid port)									
	run 1	run 2	run 3	run 4	run 5	run 6	run 7	run 8	**GC Avg.**	**%RSD**
nitrogen	0.5711	0.5710	0.5705	0.5707	0.5702	0.5698	0.5698	0.5698	**0.5703**	**0.0982**
methane	92.933	92.932	92.939	92.926	92.924	92.940	92.939	92.938	**92.934**	**0.007**
ethane	5.631	5.632	5.627	5.640	5.644	5.627	5.628	5.629	**5.632**	**0.113**
propane	0.699	0.701	0.699	0.698	0.698	0.698	0.699	0.699	**0.699**	**0.118**
iso-butane	0.059	0.059	0.059	0.059	0.059	0.059	0.059	0.059	**0.059**	**0.266**
n-butane	0.076	0.076	0.076	0.076	0.076	0.076	0.076	0.076	**0.076**	**0.228**
iso-pentane	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	**0.020**	**0.226**
n-pentane	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	**0.010**	**0.607**

Due to the presence of nitrogen in the LNG reference liquid, the final reference composition is modified to reflect the loss of nitrogen from the liquid as the LNG temperature is above the boiling point of nitrogen, typically 98K. Table 3 shows the resulting reference liquid composition.

Table 3. Determination of reference liquid composition

mix 15/1068/01	PRGM		Measured (GC)		**LNG reference values**		En-number	difference (%mol/mol)
D328619	xi	U(xi)	yi	U(yi)	**xic**	**U(xic)**	meas-corrected	measured-PRGM
nitrogen	0.5981	0.0014	0.5703	0.0127	**0.5703**	**0.0278**	0.00	-0.0278
methane	92.8923	0.0110	92.9339	0.0127	**92.9183**	**0.1350**	0.07	0.0416
ethane	5.6374	0.0140	5.6321	0.0016	**5.6390**	**0.0432**	-0.40	-0.0053
propane	0.7029	0.0032	0.6989	0.0003	**0.7031**	**0.0061**	-0.70	-0.0040
iso-butane	0.0604	0.0004	0.0591	0.0003	**0.0604**	**0.0013**	-0.97	-0.0013
n-butane	0.0777	0.0006	0.0757	0.0001	**0.0777**	**0.0021**	-0.98	-0.0020
iso-pentane	0.0211	0.0002	0.0203	0.0001	**0.0211**	**0.0008**	-0.95	-0.0008
n-pentane	0.0100	0.0002	0.0096	0.0011	**0.0100**	**0.0005**	-0.99	-0.0004
CV (kJ/kg)	54544.3		54570.9		54569.1			**-1.8**
Gas Density (kg/m3)	0.72816		0.72786		**0.72804**			**0.00018**

The difference in the gross calorific value (GCV) between the reference gas and the re-gasified LNG is 1.8 kJ/kg.

Assessment of the accuracy of the Raman spectrometer

The Raman spectrometer was used to measure the LNG reference liquid and more than 170 measurements of the LNG were made. Table 4 shows a comparison of the reference LNG composition and the analytical data from the Raman spectrometer.

Table 4. Shows a comparison of the reference LNG and analytical data from the Raman spectrometer

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

The data shows that there was some differences in the analytical results compared to the reference LNG, however the differences in the calculated calorific value was 9.9 kJ/kg (0.45 BTU) which is considered acceptable for fiscal purposes.

The uncertainty for the Raman measurements U(yi) was calculated simply as twice the standard deviation of the repeat measurements for each component. No calibration uncertainties, nor linearity components are included in the uncertainty estimation and hence U(yi) is significantly underestimated.

Conclusions

Comparison of the primary reference gas mixture composition and that measured by the GC following regasification of the LNG was satisfactory providing evidence that the LNG composition was very close to the reference gas composition. Presence of nitrogen in the headspace of the cryostat gave consistently negative results in the LNG liquid which was expected and corrected for.

Comparison of the LNG reference composition and the Raman spectrometer showed some absolute deviations, particularly for the butanes, but on the whole, the overall error in the calculated physical properties were small.

Annex A – ISO 17025 Calibration certificate of PRGM

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CERTIFICATE OF CALIBRATION

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

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

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ilac-MRA
UKAS CALIBRATION
0590

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

Composition

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

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

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