NPL

NPL REPORT AS 77

Results of an international comparison on the analysis of real non-conventional energy gases

Lucy P Culleton
Andrew S Brown
Arul Murugan
Adriaan van der Veen
Deborah van Osselen
Paul Ziel
Jianrong Li
Dirk Tuma
Gert Schulz
Stephanie Näther
Karine Arrhenius
Daniel Kühnemuth
Jan Beránek
Judit Fuko
Mirka Vaľková

JULY 2013

Results of an international comparison on the analysis of real non-conventional energy gases

Lucy P Culleton[1], Andrew S Brown[1], Arul Murugan[1], Adriaan van der Veen[2], Deborah van Osselen[2], Paul Ziel[2], Jianrong Li[2], Dirk Tuma[3], Gert Schulz[3], Stephanie Näther[3], Karine Arrhenius[4], Daniel Kühnemuth[4], Jan Beránek[5], Judit Fuko[6], Mirka Vaľková[7]

[1] NPL (National Physical Laboratory), United Kingdom

[2] VSL (Van Swinden Laboratorium; Dutch Metrology Institute), The Netherlands

[3] BAM (Bundesanstalt für Materialforschung und-prüfung), Germany

[4] SP (Sveriges Tekniska Forskningsinstitut,), Sweeden

[5] CMI (Ceský metrologický institut), Czech Republic

[6] MKEH (Magyar Kereskedelmi Engedélyezési Hivatal), Hungary

[7] SMU (Slovenský Metrologický Ústav), Slovakia

ISSN 1754-2928

National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

Approved on behalf of NPLML by Dr. Michael Adeogun (Head of Analytical Science).

EXECUTIVE SUMMARY

This report presents the results from an international comparison of the analysis of real non-conventional gas samples. Eight laboratories participated in the task, which involved the collection and analysis of samples of real energy gases from a variety of locations in Europe. Coal mine and coal bed methane were analysed for their composition. Samples of raw and processed biogas were analysed for composition and also impurities such as hydrogen sulphide and siloxanes. The study was part of the three year EMRP project entitled ‘Characterisation of energy gases’. The results obtained by the participating laboratories are presented and discussed.

CONTENTS

1 INTRODUCTION

The requirement for a metrological infrastructure to ensure the interchangability of 'non-conventional' energy gases within existing European infrastructure[1] was the driving force behind the work undertaken in the three-year EMRP Characterisation of energy gases project EMRP ENG01 (June 2010 – May 2013).

As part of work package one of the project, standards and methods were used to perform composition and impurity measurements on samples of real energy gases collected from around Europe. The aim of this study was to compare the results obtained from different labs, and thereby provide an evaluation of the labs' capabilities and provide insight into the feasibility of different analytical methodologies for use with future measurements.

2 OPERATION OF THE COMPARISON

2.1 PARTICIPANTS

The following labs contributed towards the comparison:

- BAM  Germany
- BRML INM  Romania
- ČMI  Czech Republic
- MKEH  Hungary
- NPL  United Kingdom
- SMÚ  Slovak Republic
- SP  Sweden
- VSL  The Netherlands

Table 1 summarises the organisation of the task.

#	Sample	Obtained by	Labs performing analysis	Analytes
1	Coal Mine Methane	BAM	NPL, SMÚ, ČMI, BAM	Composition
2	Coal Bed Methane	BRML INM	NPL, SMÚ, ČMI, BAM	Composition
3	Biogas (raw)	SP	NPL, VSL, SP	Composition, H_2S & Siloxanes
4	Biogas (partially-processed)	SP	NPL, VSL, SP	Composition, H_2S & Siloxanes
5	Biogas (processed)	BAM	NPL, VSL, SP	Composition, H_2S & Siloxanes
6	Biogas (processed)	MKEH	NPL, VSL, SP	Composition, H_2S & Siloxanes

Table 1: Summary of participating labs and their contributions to the task

Based on knowledge of the typical compositions of these non-conventional energy gases, the following compounds were selected for analysis within the real samples:

Composition measurements
- methane
- ethane
- propane
- *i*-butane
- *n*-butane
- *i*-pentane
- *n*-pentane
- *n*-hexane
- oxygen
- nitrogen
- carbon dioxide
- Any other hydrocarbons

Impurity measurements
- hydrogen sulphide
- hexamethyldisiloxane (L2)
- hexamethylcyclotrisiloxane (D3)*
- octamethyltrisiloxane (L3)
- octamethylcyclotetrasiloxane (D4)
- decamethyltetrasiloxane (L4)*
- decamethylcyclopentasiloxane (D5)
- dodecamethylpentasiloxane (L5)*
- dodecamethylcyclohexasiloxane (D6)*

*To be quantified only by SP.

2.2 SAMPLES

Six different samples of real gas were collected from across Europe. The variety of mixtures was chosen to provide a range of measurement challenges. Table 2 provides information about the acquisition of each sample.

#	Sampling location	Sampling Date	Sample vessels per laboratory	Additional Information
1	Allenfeld, Saarland, Germany	18th-22nd March 2013	1 x 10L aluminium cylinder	All samples were taken before the drying step from the same site (Allenfeld) at the STEAG coal mine methane distribution grid. This allowed a maximum sample pressure of 8 bar.
2	'Uricani' Mine, 3rd layer, Romania	15th November 2012	2 x 5L steel cylinders	Sampled at very low pressure.
3	Gothenburg, Sweden	8th April 2013	3 x 1L FlexFilm bags 4 x 1L FlexFoil bags	Sampled at very low pressure.
4	Gothenburg, Sweden	8th April 2013	2 x 1L FlexFilm bags 3 x 1L FlexFoil bags	Sampled between amine scrubber and drying step, causing a higher impurity content than the fully processed gas would normally contain.
5	Gross Pankow, Brandenburg, Germany	19th October 2012	2 x 5L aluminium cylinders	Feed materials: silage from maize, grass and sugar beet crop, pig manure. Source, company: biogas plant, Bio-Erdgas Neudorf GmbH
6	Zalaegerszeg, Hungary	24th January 2013	3 x 5L aluminium cylinders	Biogas produced from anaerobic fermentation of wastewater treatment, Zalaviz Ltd.

Table 2: Sample collection details

3 MEASUREMENT METHODS AND CHALLENGES

In the six labs that performed the measurements, the analytical techniques used included GC-FID, GC-MS, GC-AED and OFCEAS. With these techniques, the labs developed their own measurement methods, as summarised in Table 3.

	Lab & measurement method					
Compound	NPL	VSL	SP	SMÚ	ČMI	BAM
CH_4, C_2H_6	GC-FID	GC-TCD	GC-TCD	GC-FID	GC-TCD	GC-TCD
C_3+ Hydrocarbons	GC-FID	GC-FID	GC-FID	GC-FID	GC-FID	GC-FID, GC-TCD
O_2, N_2, CO_2, H_2	GC-TCD	GC-TCD	GC-TCD	GC-TCD	GC-TCD	GC-TCD
H_2S	GC-MS	GC-FID, GC-AED	OFCEAS	-	-	-
Siloxanes	GC-MS	GC-MS	TD/GC-MS	-	-	-

Table 3: Summary of analytical methods (GC=Gas Chromatograph, FID=Flame Ionisation Detector, TCD=Thermal Conductivity Detector, TD=Thermal Desorption, MS=Mass Spectrometer, AED=Atomic emission detector, OFCEAS=Optical Feedback Cavity-Enhanced Absorption Spectrometry

3.1 COMPOSITION MEASUREMENT CHALLENGES

Due to the challenging nature of the samples, some of the measurements could not be approached in a routine way. In certain cases, previously developed methods had to be modified to analyse the samples.

Several factors that may have had an influence on the quality of the analyses are listed below:

- Coal mine methane samples from BAM contained a large amount of water.
- The coal bed methane samples obtained by BRML INM were taken at very low pressure, resulting in the labs receiving 5 litre cylinders at around 2 bar, which limited the number of possible analyses.
- The coal bed methane samples from BRML INM contained a large number of hydrocarbons, with species up to C_9 being identified (see Figure 1).

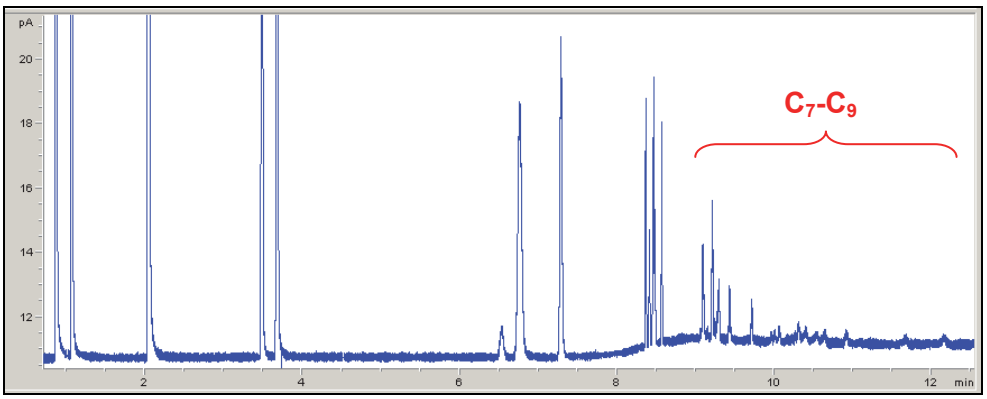

Figure 1: FID chromatogram from the analysis of a sample of real coal bed methane performed at NPL.

3.2 IMPURITY MEASUREMENT CHALLENGES

The identification and quantification of impurities in the real samples provided additional challenges. Several factors that may have had an influence on the quality of the analyses are listed below:

- The measurement of siloxanes using a GC system can have associated difficulties due to the siloxane-based stationary phase coating of capillary columns. Accurate and precise measurements require a low and repeatable amount of column bleed to be present in all repeated runs of a method.

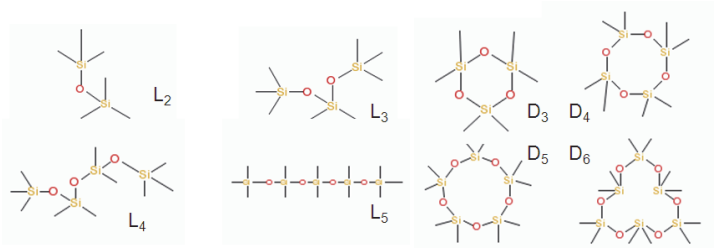

Figure 2: Structure of siloxanes measured within the study.

- Real gas 4 from Sweden was initially planned to be a sample of processed biogas, with very low levels of siloxanes. However, it was confirmed after measurements were performed that the samples had not been fully processed, and contained higher amounts of siloxanes than the raw samples (real gas 3) due to the removal of carbon dioxide without removal of siloxanes.
- Due to the nature of the materials the sample bags are composed of (described in detail below), adsorption of certain compounds to the walls posed a challenge to the analysis of the Swedish biogas samples. Two different bag materials were used for this comparison, 'FlexFoil' and 'FlexFilm' from SKC.

Overview of bag types

FlexFoil bags are designed for the analysis of highly adsorptive compounds such as hydrogen sulphide, and have been shown to achieve higher retention of adsorptive compounds than FlexFilm bags[2]. The stability of biogas-type compounds within FlexFoil bags has also been investigated by the bag manufacturer[3], with the conclusion that all components (including hydrogen sulphide impurities) remain stable for up to 2 days after sample collection.

The FlexFilm bags were originally developed to be a more economical alternative to bags made from polyvinyl fluoride. They have been shown to provide good levels of stability for the more major biogas components for at least 2 days[4]. Impurity quantification using FlexFilm is significantly less reliable than the FlexFoil bags. They are particularly unsuitable for the accurate quantification of hydrogen sulphide, due to background levels within the bags in the region of 120 µg/m^3 [5]. (Corresponding to approximately 0.08 µmol/mol under Normal Temperature and Pressure (NTP) conditions)

Based on the stability information, it was agreed that analysis should be performed within two days of the samples being obtained and synchronised across all three participating labs. This would allow for the most meaningful comparison of results, as any adsorption should in theory be present equally in across all bags of the same type.

4 RESULTS & DISCUSSION

This section presents a comparison between the results reported by each lab. All results and uncertainties are reported in mmol/mol. The x-axes contain the lab that performed the measurement, followed by the cylinder identifier. The impurity results from SP for real gases 3-6 were reported in µg/m^3 and converted to µmol/mol using normal temperature and pressure conditions (293.15 K, 101.325 kPa).

4.1 REAL GAS 1: COAL MINE METHANE (OBTAINED BY BAM)

The coal mine methane (CMM) samples were measured by NPL, SMÚ, ČMI and BAM. Table 4 presents a summary of the compounds that were detected within the samples. BAM reported a result for a combined oxygen and nitrogen amount fraction of 277.2 ± 11.09 mmol/mol, which has not been represented graphically in this section. It was generally noted by labs that the CMM samples were saturated with water, although the water content has not been quantified for this study.

	Laboratory			
Compound	NPL	SMÚ	ČMI	BAM
methane	x	x	x	x
ethane	x	x	x	x
propane	x	x	x	x
i-butane	x	x	x	x
n-butane			x	x
i-pentane		x	x	x
oxygen	x	x		x
nitrogen	x	x	x	x
carbon dioxide	x	x	x	x

Table 4: Summary of compounds reported by each lab in BAM CMM samples. Blank spaces indicate compounds that were not detected

4.1.1 Composition

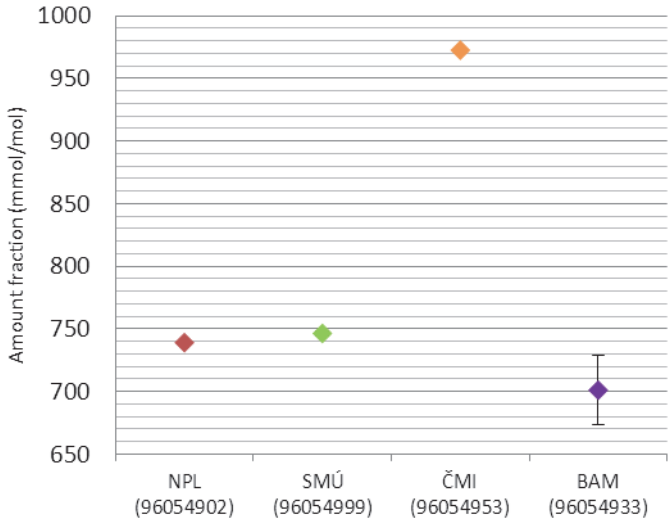

Figure 3: BAM CMM: methane

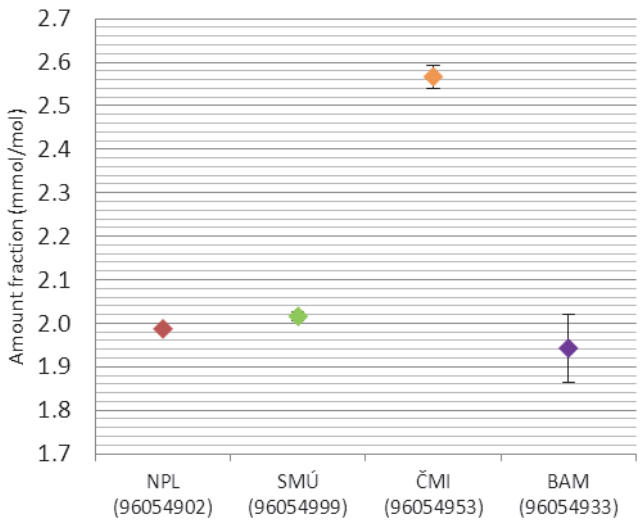

Figure 4: BAM CMM: ethane

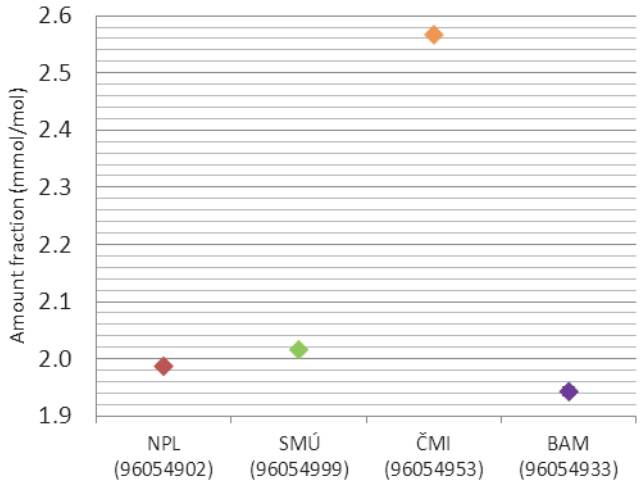

Figure 5: BAM CMM: propane

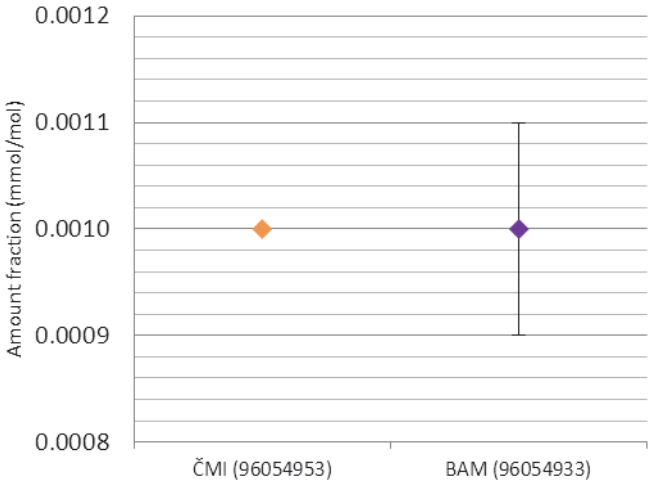

Figure 6: BAM CMM: *n*-butane (uncertainty not provided by ČMI)

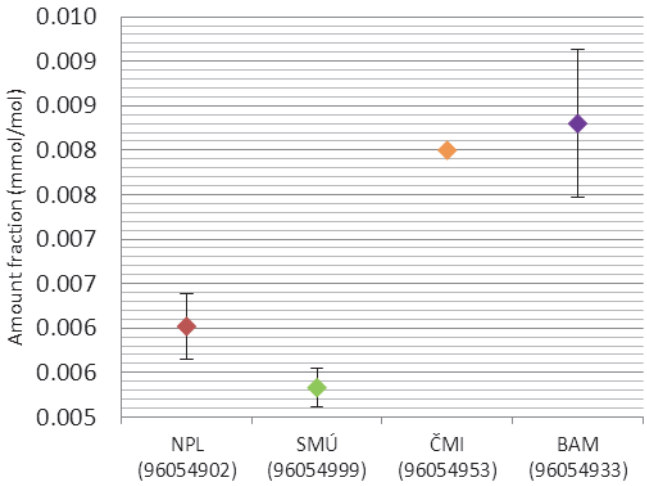

Figure 7: BAM CMM: *i*-butane (uncertainty not provided by ČMI)

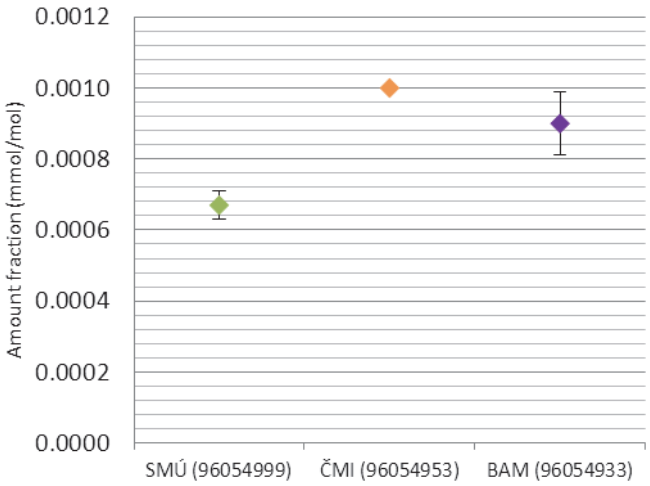

Figure 8: BAM CMM: *i*-pentane (uncertainty not provided by ČMI)

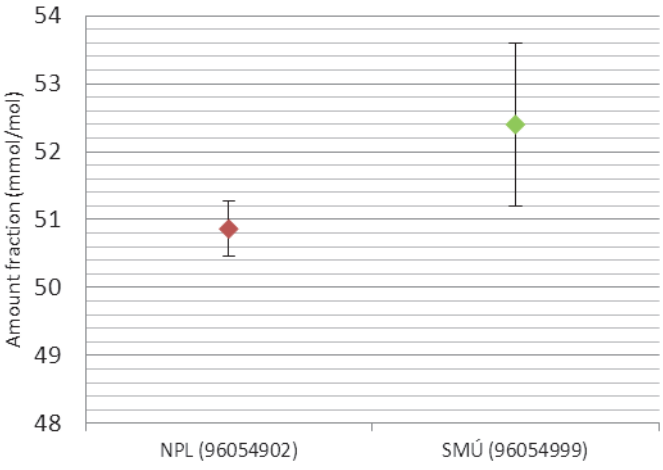

Figure 9: BAM CMM: oxygen (result not reported by ČMI)

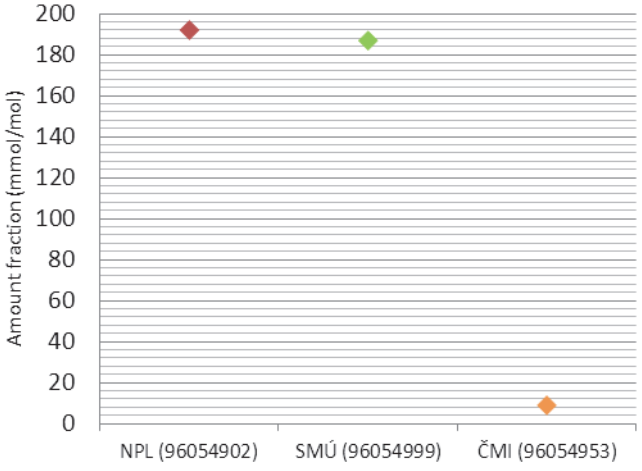

Figure 10: BAM CMM: nitrogen

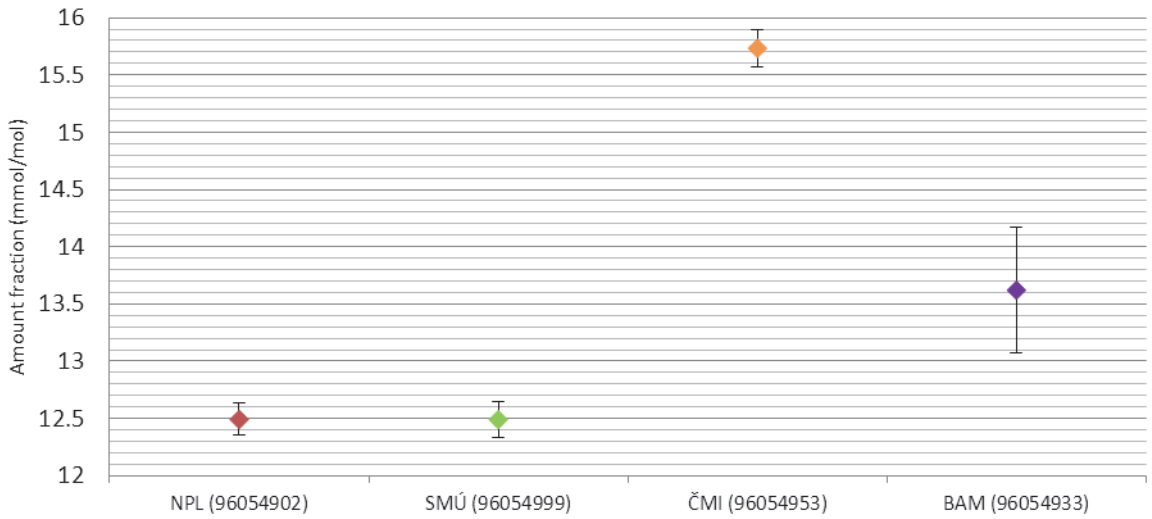

Figure 11: BAM CMM: carbon dioxide

Laboratory	Summed amount fractions
NPL	996.5
SMÚ	1000.3
ČMI	991.0
BAM	993.9

Table 5: Summation of all amount fractions reported by each lab for BAM CMM

4.1.2 Summary

The four coal mine methane mixtures have a reasonable amount of comparability over the majority of compounds. The most likely reason for the disagreements within the data is that the cylinders sent to NPL and SMÚ are likely to have incurred ingress of air during their sampling. Figure 12a and Figure 12b show how the amount fractions of methane within the three cylinders would hypothetically compare if none of the three mixtures contained any nitrogen or oxygen. Greater agreement is seen, thereby confirming the legitimacy of the air ingress assumption.

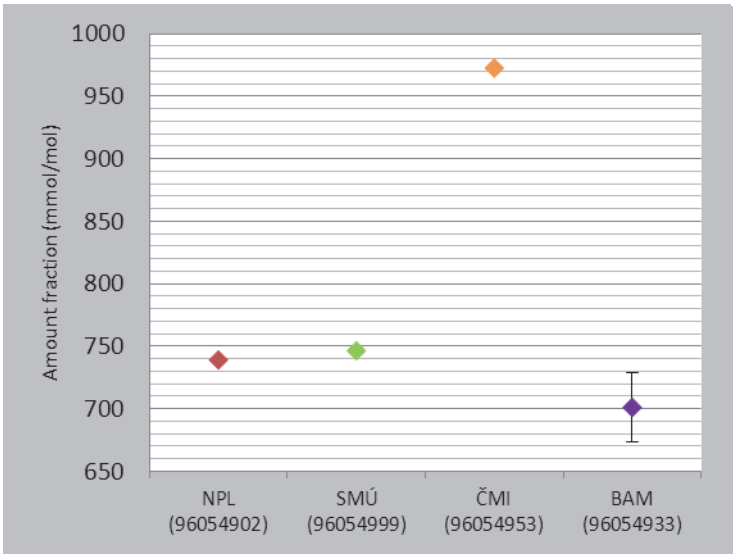

Figure 12a: BAM CMM: methane values as reported by labs

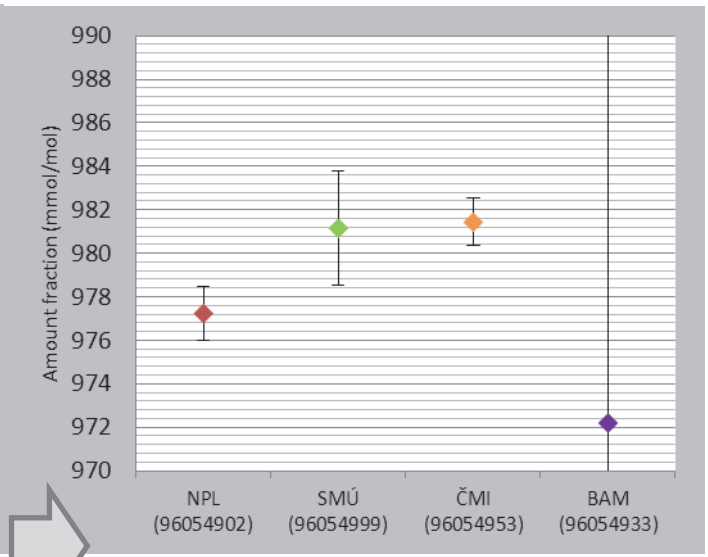

Figure 12b: BAM CMM: methane (assuming no nitrogen or oxygen in all four samples)

4.2 REAL GAS 2: COAL BED METHANE (OBTAINED BY BRML INM)

The coal bed methane samples contained a large number of C_5-C_9 hydrocarbons (as illustrated in Figure 1). Qualitative preliminary measurements performed by BRML INM revealed the presence of hydrocarbon compounds up to n-heptane. Due to the complexity of the analysis required, the majority of these species were not qualitatively or quantitatively reported within this study. Table 6 summarises the compounds detected by the labs.

	Laboratory			
Compound	**NPL**	**SMÚ**	**ČMI**	**BAM**
methane	x	x	x	x
ethane	x	x	x	x
propane	x	x	x	x
i-butane	x	x	x	x
n-butane	x	x	x	x
i-pentane	x	x	x	x
n-pentane	x	x	x	x
'other C_5'				x
n-hexane	x		x	x
n-heptane	x			
n-octane	x			
n-nonane	x			
C_6+ hydrocarbons		x		x
oxygen	x	x	x	x
nitrogen	x	x	x	x
carbon dioxide	x	x	x	x
hydrogen				x
helium				x

Table 6: Summary of compounds reported by each lab in BRML INM CBM samples

4.2.1 Composition

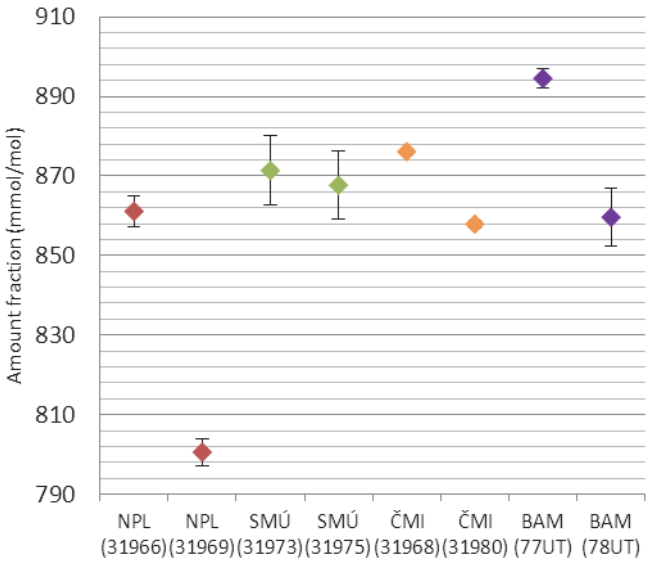

Figure 13: BRML INM CBM: methane

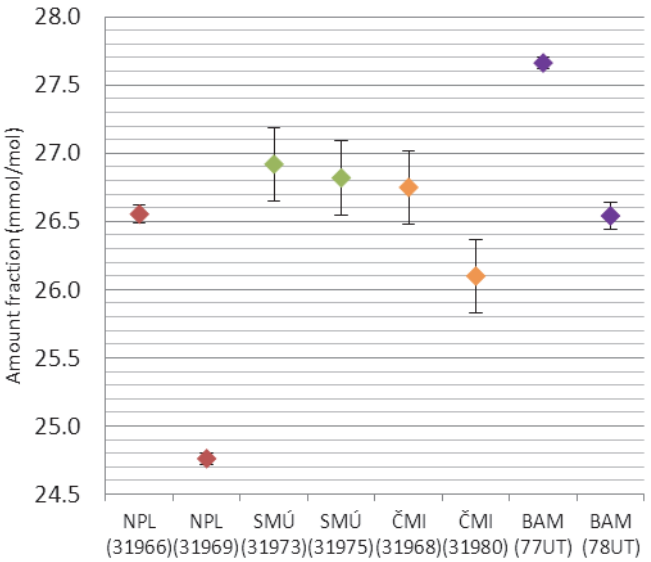

Figure 14: BRML INM CBM: ethane

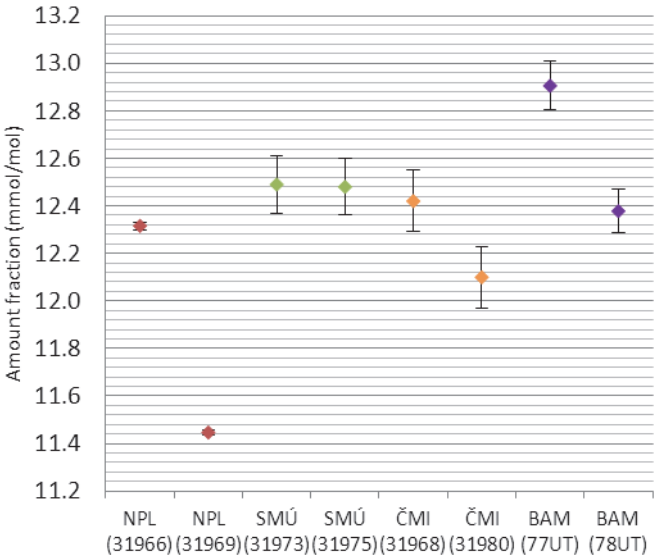

Figure 15: BRML INM CBM: propane

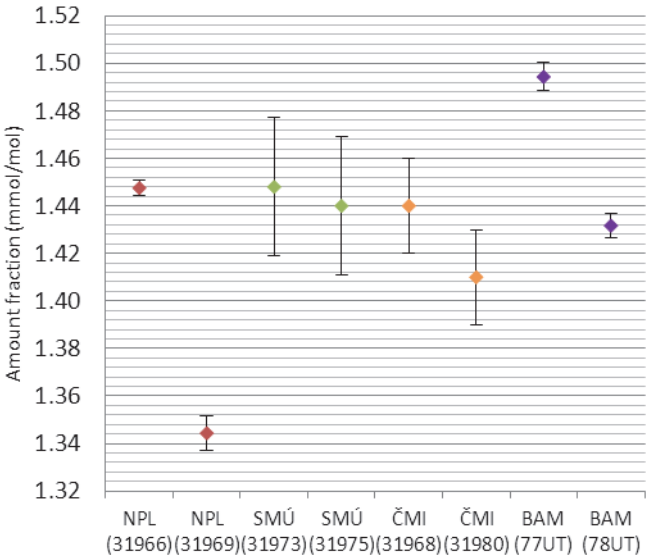

Figure 16: BRML INM CBM: *i*-butane

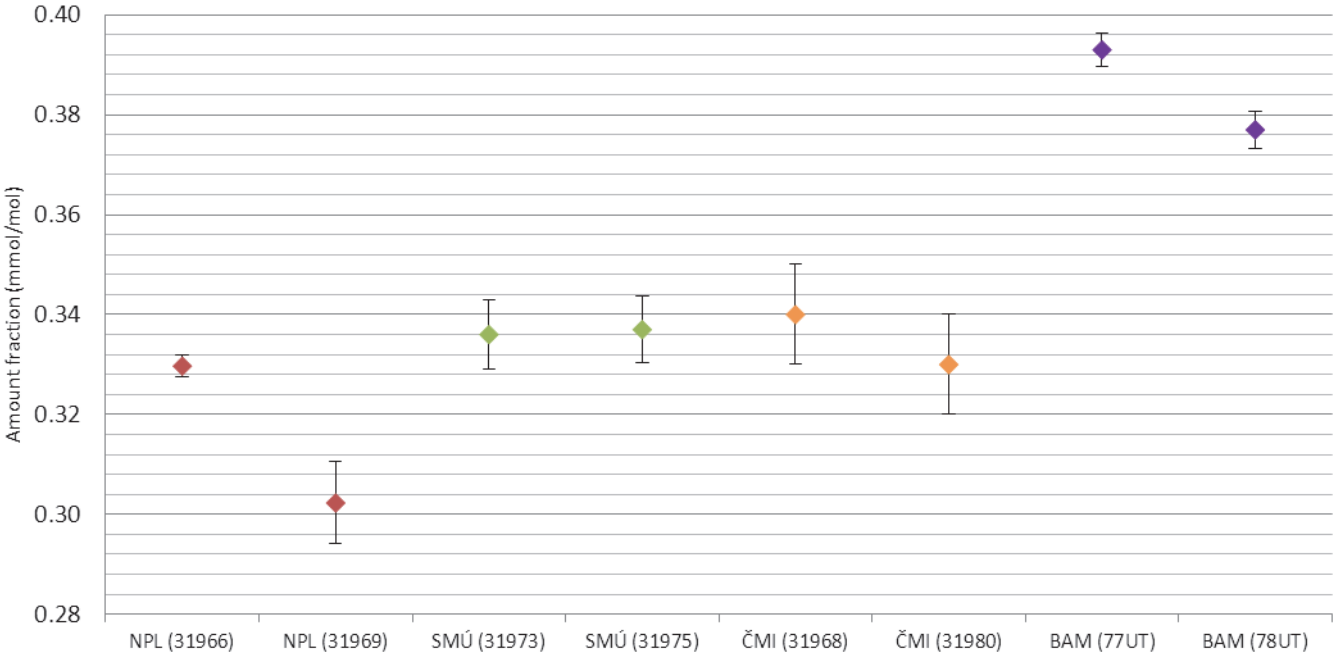

Figure 17: BRML INM CBM: *n*-pentane

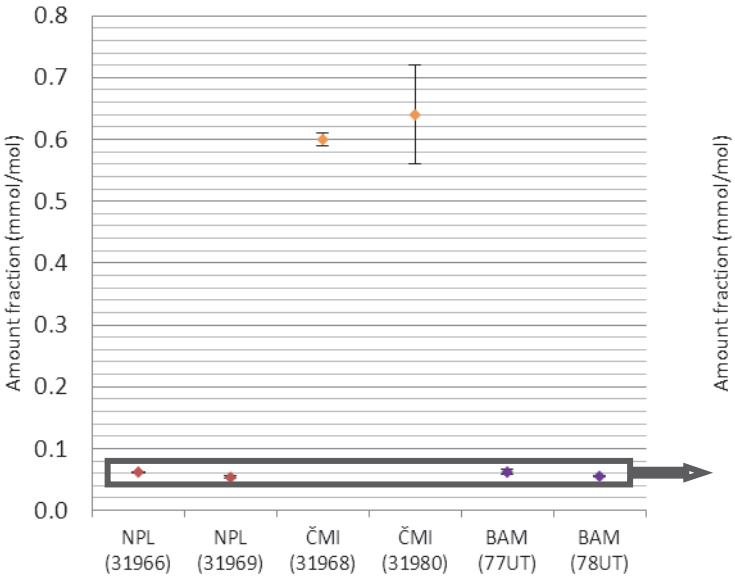

Figure 18a: BRML INM CBM: *n*-hexane

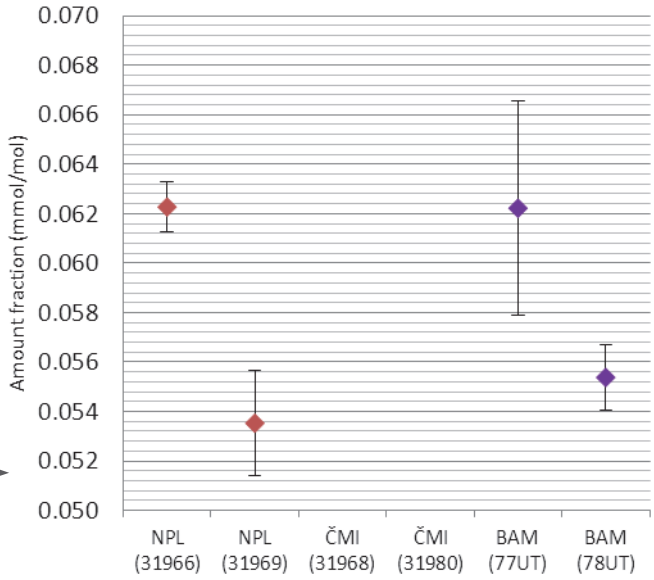

Figure 18b: BRML INM CBM: *n*-hexane (magnification)

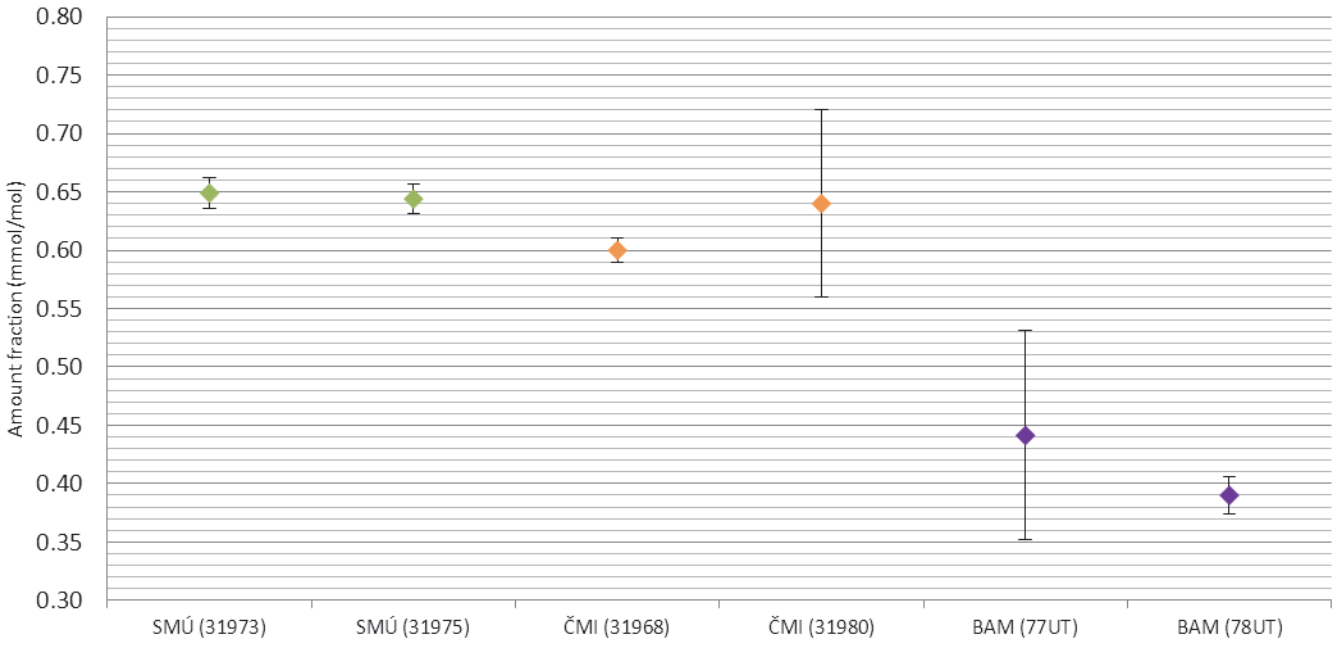

Figure 19: BRML INM CBM: C_6+ hydrocarbons (Assuming value reported by ČMI is C_6+ rather than *n*-hexane)

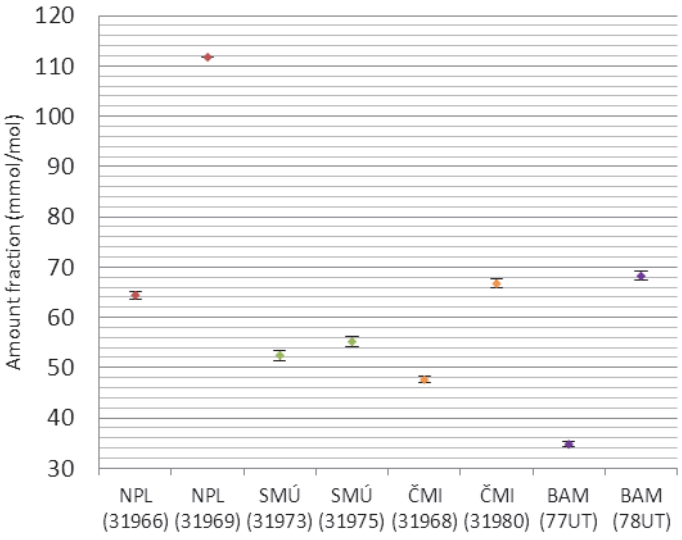

Figure 20: BRML INM CBM: nitrogen

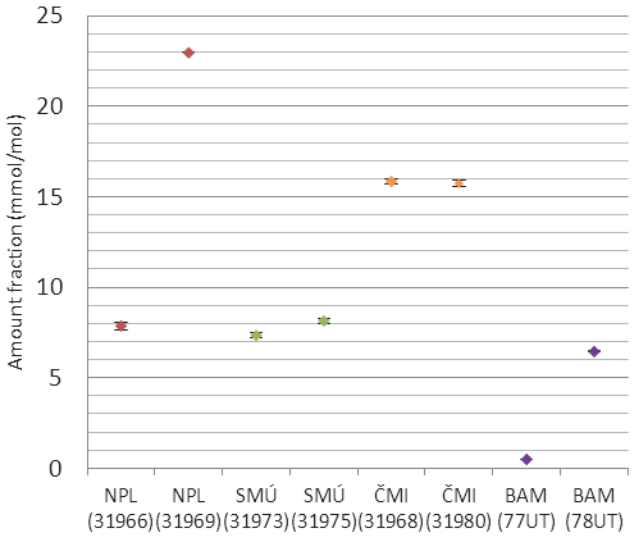

Figure 21: BRML INM CBM: oxygen

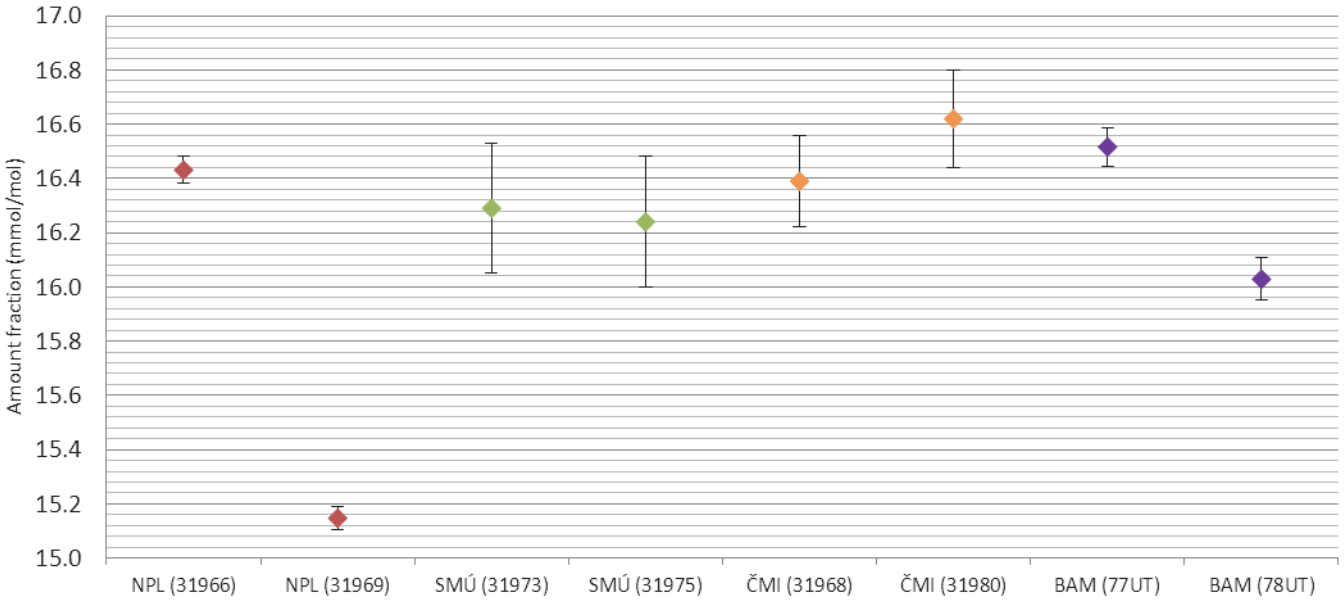

Figure 22: BRML INM CBM: carbon dioxide

Laboratory	Summed amount fractions (1st cylinder) (mmol/mol)	Summed amount fractions (2nd cylinder) (mmol/mol)
NPL	993.0	990.6
SMÚ	991.9	991.5
ČMI	1000.0	1000.0
BAM	992.1	994.3

Table 7: Summation of all amount fractions reported by each lab for BRML INM CBM

4.2.2 Summary

The CBM samples were among the most challenging within the study due to their numerous components. Clear variation can be seen between the composition of individual cylinders, particularity in the methane, oxygen and nitrogen amount fractions, which would suggest an issue with sample collection (see Figure 23a and b for evidence that methane and nitrogen amount fractions are directly correlated). The results reported as 'hexane' from ČMI were likely to have been obtained by back flushing, which explains the large differences between the other labs, as the large number of C_6-C_9 hydrocarbons will be included in these values, as can be seen in Figure 19. Another factor that could have contributed to disagreement between labs is the fact that the results from CMI were normalised, where NPL and BAM's results were not (see Table 7). However, the differences observed are likely to be largely due to the lack of homogeneity between the eight samples.

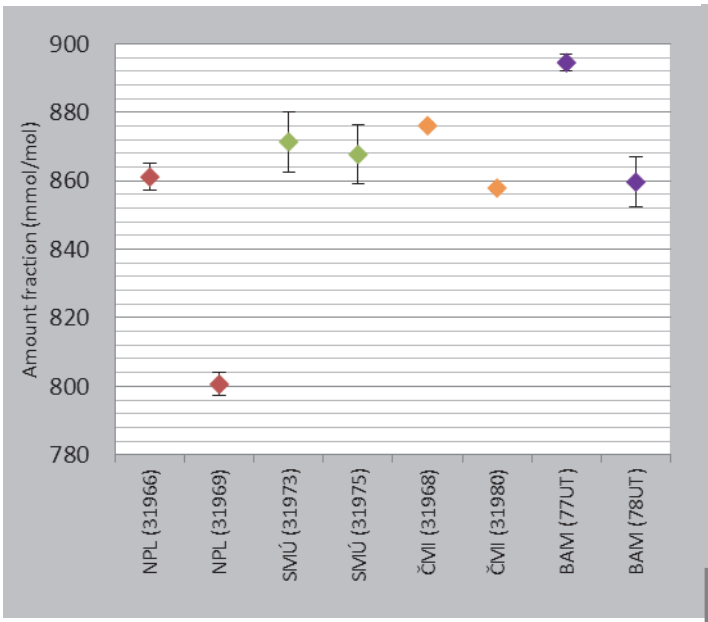

Figure 23a: BRML INM CBM: methane values as reported by labs

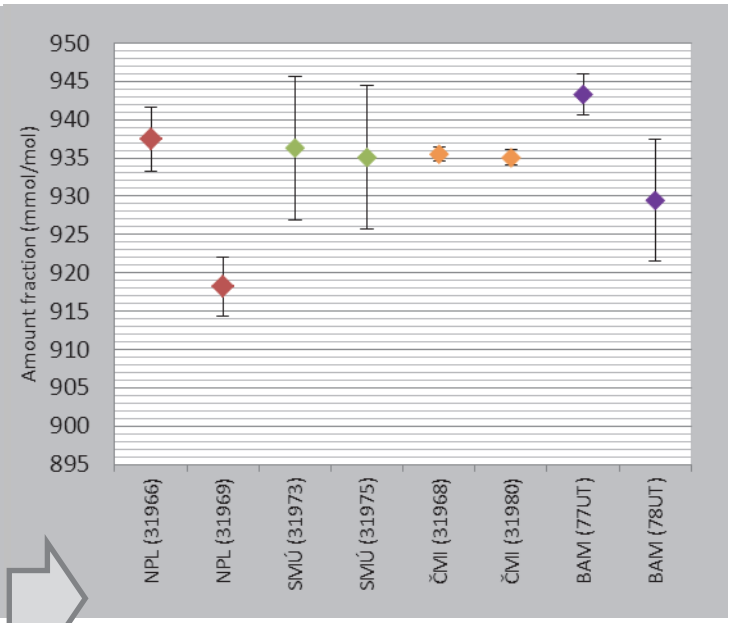

Figure 23b: BRML INM CBM: methane (assuming no nitrogen or oxygen in all eight samples)

4.3 REAL GASES 3 & 4: RAW AND PARTIALLY-PROCESSED BIOGAS (OBTAINED BY SP)

Table 8 summarises the compounds that were reported by the three labs. The composition measurements at all labs were performed within one week of the sample collection. The impurity measurements were performed within four days of the sample collection, with NPL's measurements being performed approximately 24 hours after those done at SP. VSL performed their analysis over 24 hours after NPL's.

	Laboratory					
	NPL		VSL		SP	
Compound	R	P	R	P	R	P
methane	x	x	x	x	x	x
propane	x	x				
propene	x	x				
oxygen	x	x	x	x	x	x
nitrogen	x	x	x	x	x	x
carbon dioxide	x	x	x	x	x	x
hydrogen	x	x				
hydrogen sulphide	x				x	
L2 siloxane	x	x			x	x
L3 siloxane	x	x			x	x
D4 siloxane	x	x			x	x
D5 siloxane	x	x			x	x
D3 siloxane						x
L4 siloxane					x	x

Table 8: Summary of compounds reported by each lab in both raw (R) and partially-processed (P) SP biogas samples

4.3.1 Composition

In the x axes of the following graphs, the lab names are followed by either 'R' or 'P', denoting 'raw' and 'partially-processed' respectively. For this comparison, VSL's results and uncertainties were reported un-normalised, which largely contributes to the significant differences in amount fraction when compared to the other two labs. The results from SP are the average from two bags for each raw and partially-processed samples. They stated 'negligible difference in concentrations between the two bags'. The results from NPL are the average of four partially-processed samples and the average of four raw samples.

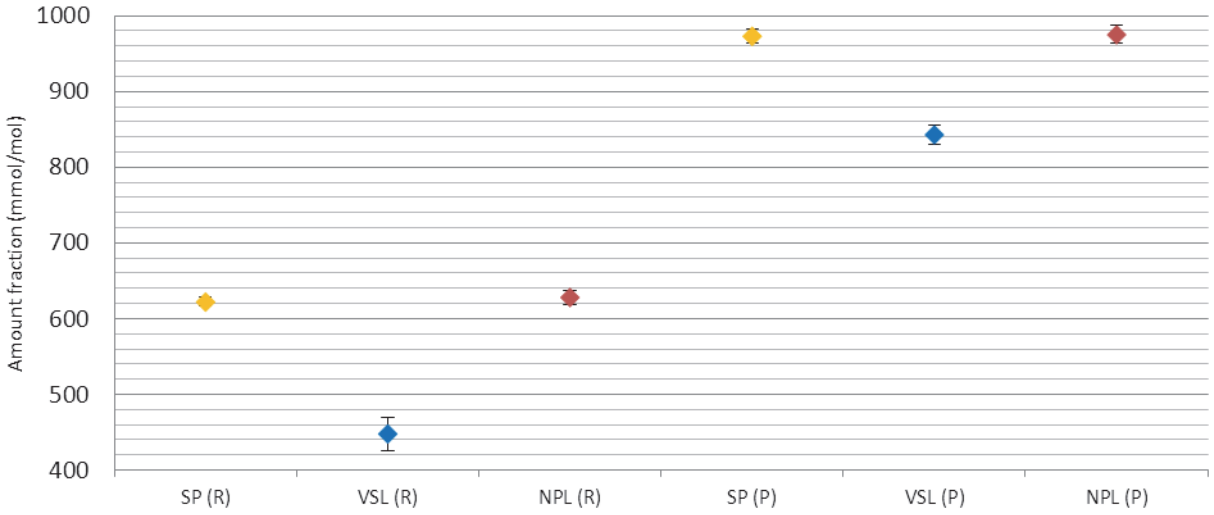

Figure 24: SP biogas: methane

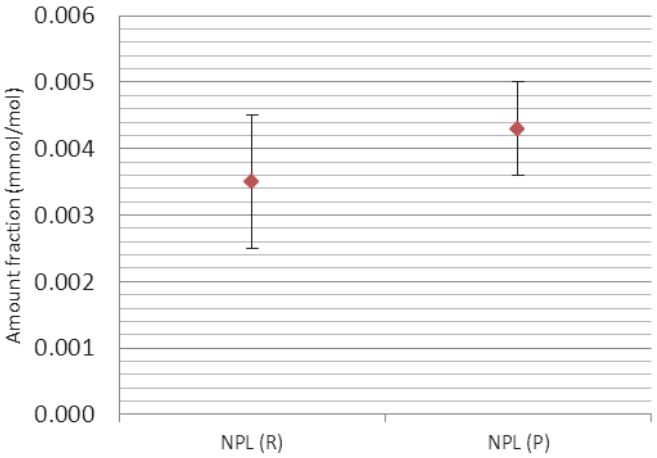

Figure 25: SP biogas: propane

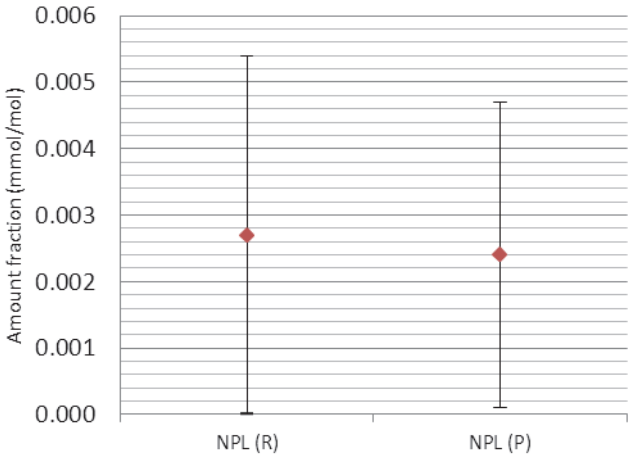

Figure 26: SP biogas: propene

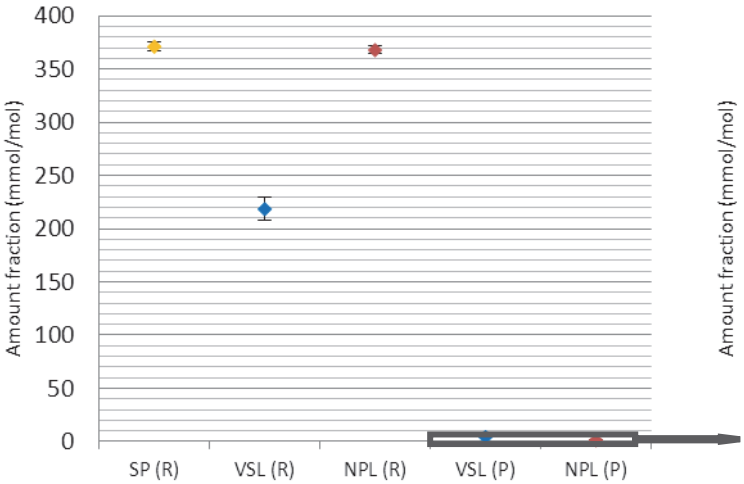

Figure 27a: SP biogas: carbon dioxide (SP reported a value for the processed gas of <1 mmol/mol)

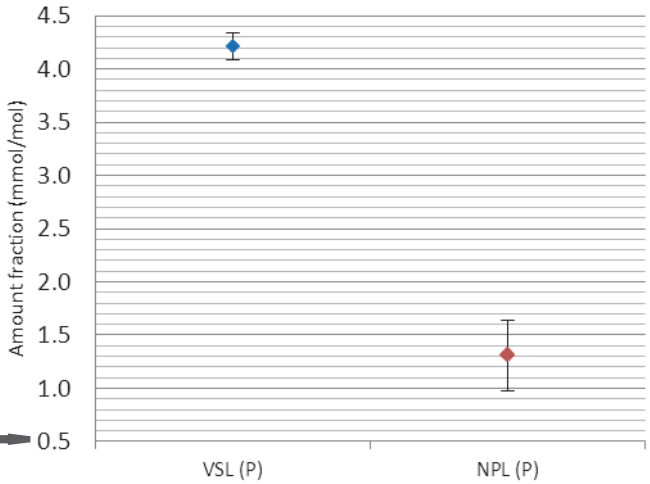

Figure 27b: SP biogas: carbon dioxide (magnification)

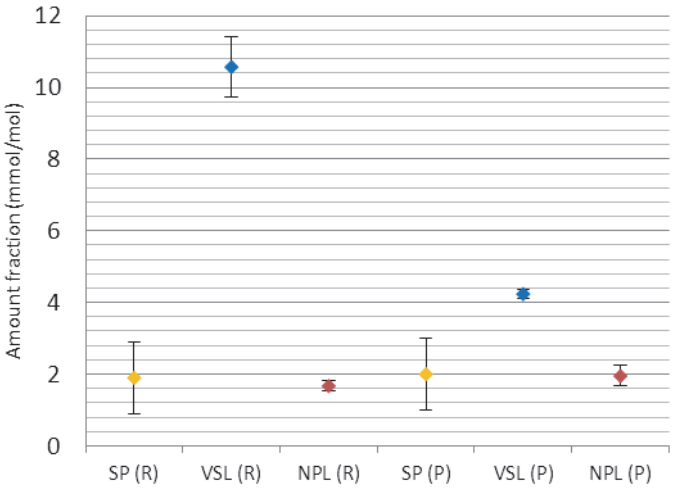

Figure 28: SP biogas: oxygen

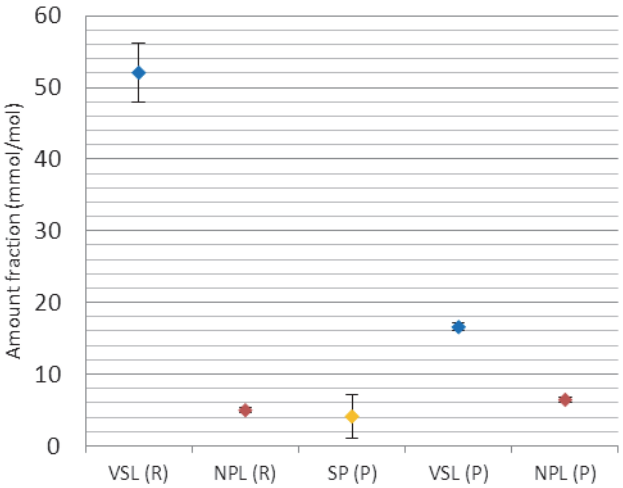

Figure 29: SP biogas: nitrogen (SP reported a value for the raw gas of <3 mmol/mol)

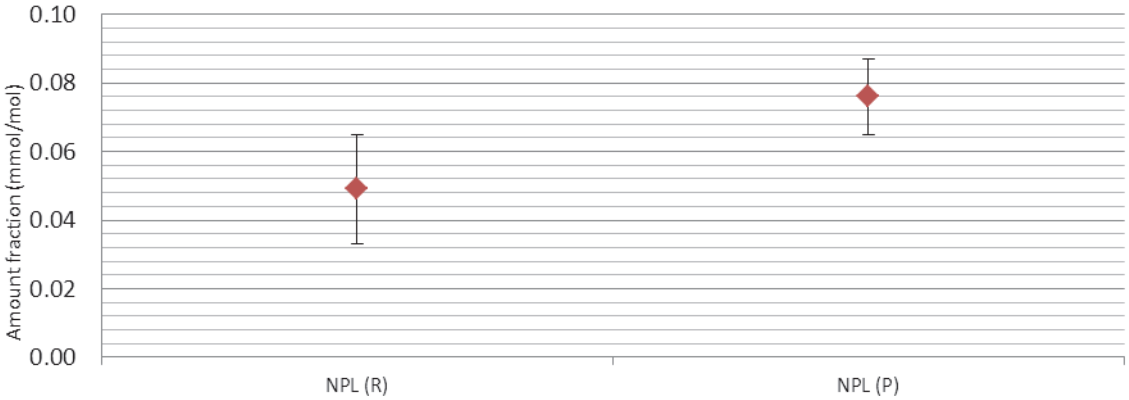

Figure 30: SP biogas: hydrogen
(SP reported results for both raw and processed biogas of <1 mmol/mol)

4.3.2 Impurities

The results from NPL are the average of repeat measurements performed on four bags for both raw and partially-processed samples. Each of SP's results is the average of two bags. VSL reported that they did not detect any siloxanes in any of the twelve samples they received. Hydrogen sulphide was neither reported by NPL nor by VSL. L5 and D6 siloxanes measured only by SP were both below the limit of detection in both types of gas (see Table **9** for all of SP's siloxane limit of detection values).

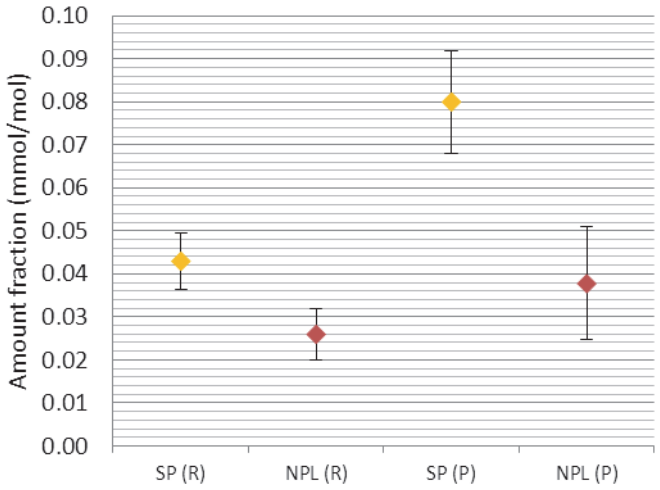

Figure 31: SP biogas: L2 siloxane

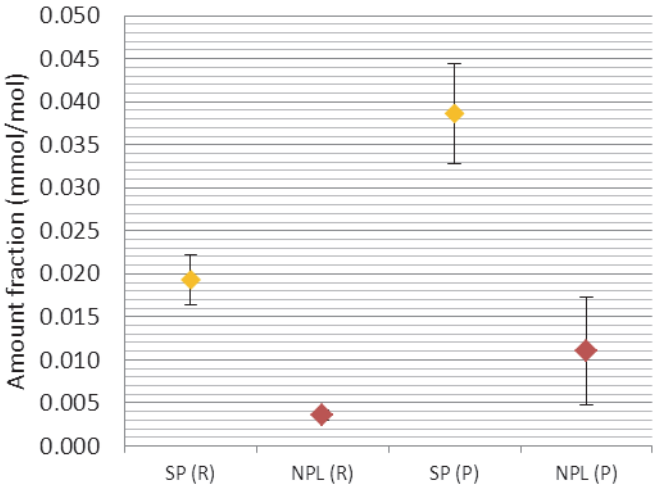

Figure 32: SP biogas: L3 siloxane

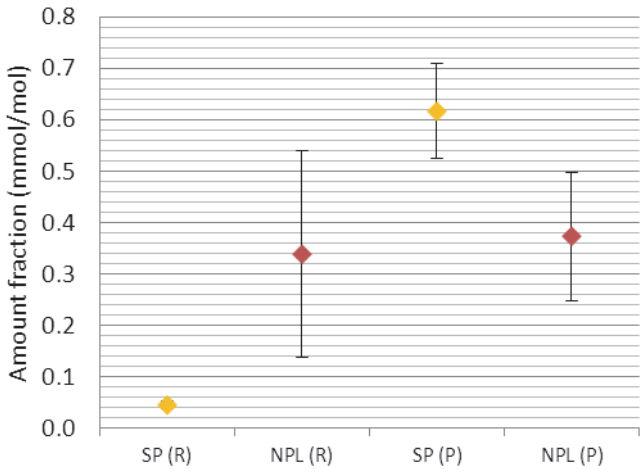

Figure 33: SP biogas: D4 siloxane

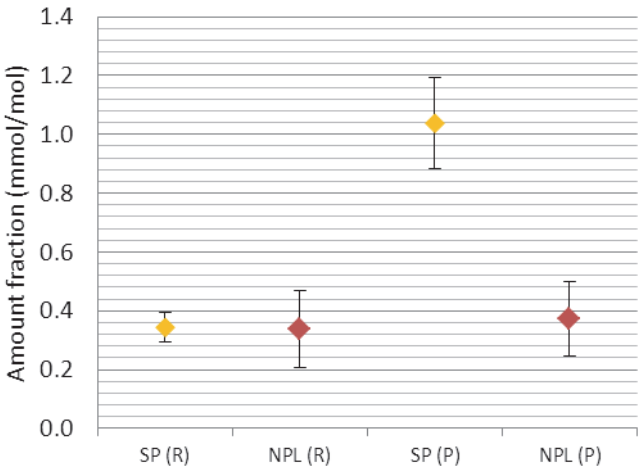

Figure 34: SP biogas: D5 siloxane

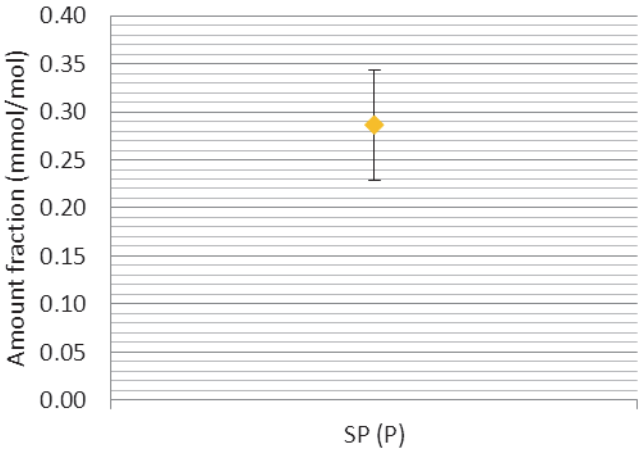

Figure 35: SP biogas: D3 siloxane
D3 in raw biogas reported as <3.24 nmol/mol

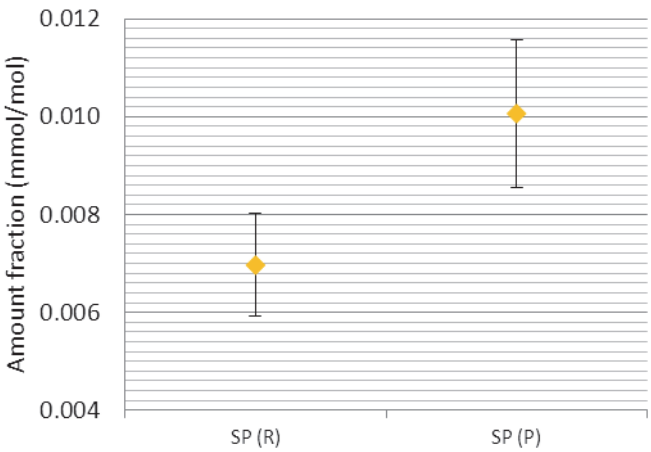

Figure 36: SP biogas: L4 siloxane

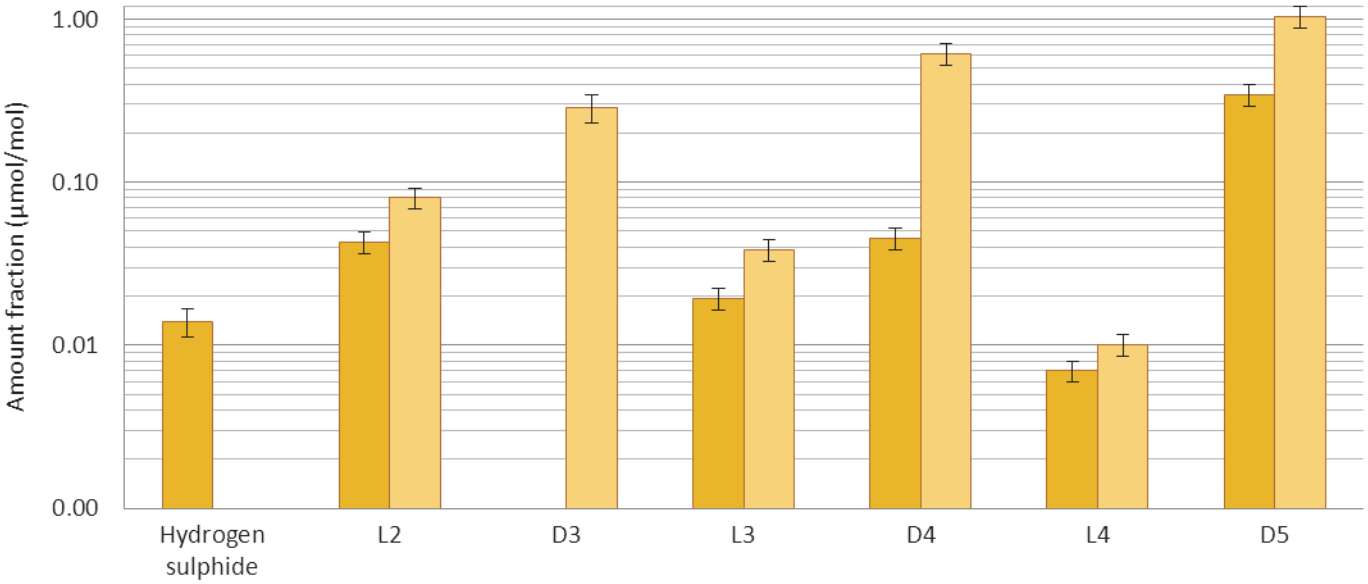

Figure 37: SP biogas: Bar chart showing a comparison of SP's TD/GC-MS results for all siloxanes and hydrogen sulphide. The left bars represent raw sample results. The right bars represent processed sample results (L5 and D6 below limit of detection in both). The absence of a bar indicates the siloxane was not detected.

Compound	Limit of detection (nmol/mol)
hydrogen sulphide	< 1.50
L2 siloxane	< 0.74
D3 siloxane	< 3.24
L3 siloxane	< 0.51
D4 siloxane	< 1.22
L4 siloxane	< 0.77
D5 siloxane	< 0.65
L5 siloxane	< 1.88
D6 siloxane	< 0.54

Table 9: Limit of detection for all impurities measured by SP

Laboratory	Summed amount fractions: raw gas (mmol/mol)	Summed amount fractions: partially processed gas (mmol/mol)
SP	995.4	981.2
VSL	728.8	868.0
NPL	1010.4	985.8

Table 10: Summation of amount fractions of all components in SP biogas reported by each lab

4.3.3 Summary

A reasonably good amount of comparability has been demonstrated for the majority of compounds in the composition measurements of the raw and partially-processed biogas samples. Propane and propene were detected at very low levels by NPL. VSL's non-normalised results contributed largely towards the dissimilarities with NPL and SP's results, which is apparent from Table 10.
Both SP and NPL reported a higher level of siloxanes in the processed gas than the raw gas. This is due to the fact that the gas was sampled part-way through the upgrading process, after the removal of carbon dioxide, but before the removal of siloxanes. This fact was not confirmed until after the analysis had been performed by the labs. The results for the amount fraction of D5 siloxane in raw biogas were in good agreement between both labs, but there is no agreement within uncertainties for the other siloxanes. This is likely due to the highly time-dependent adsorption rates of hydrogen sulphide and siloxanes to the internal surfaces of sample bags coupled with analysis at labs being separated by over 24 hours.

4.4 REAL GAS 5: PROCESSED BIOGAS (OBTAINED BY BAM)

Table 11 summarises the compounds that were reported by the three labs. TD/GC-MS measurements at SP revealed below-limit-of-detection amount fractions for all siloxanes. (See
Table **9** for all of SP's siloxane limit of detection values). None of the labs reported a value for hydrogen sulphide.

	Laboratory		
Compound	**NPL**	**VSL**	**SP**
methane	x	x	x
oxygen	x	x	x
nitrogen	x	x	x
carbon dioxide	x	x	x
hydrogen	x	x	

Table 11: Summary of all compounds reported by each lab in BAM processed biogas samples.

4.4.1 Composition

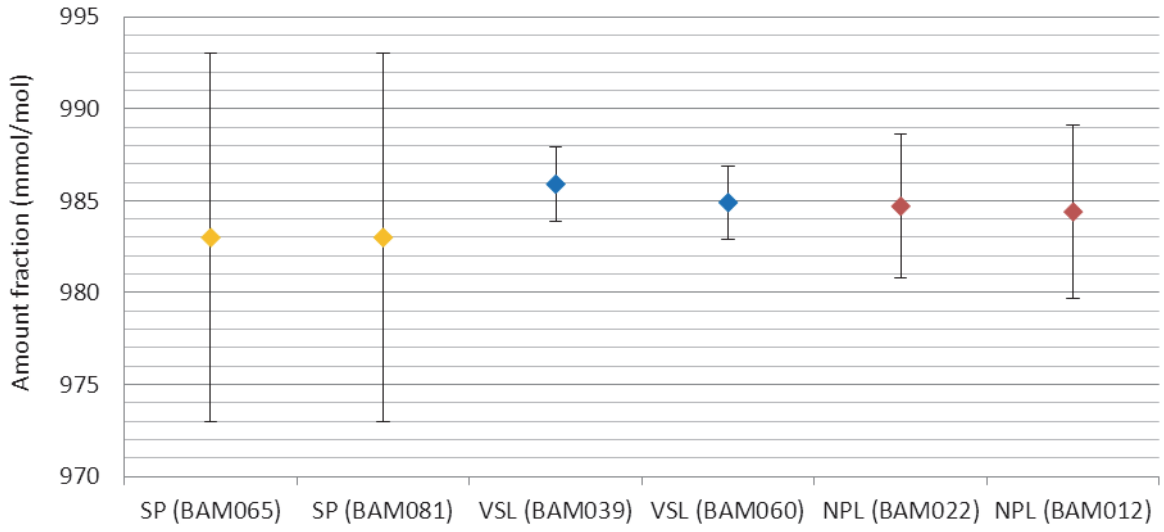

Figure 38: BAM processed biogas: methane

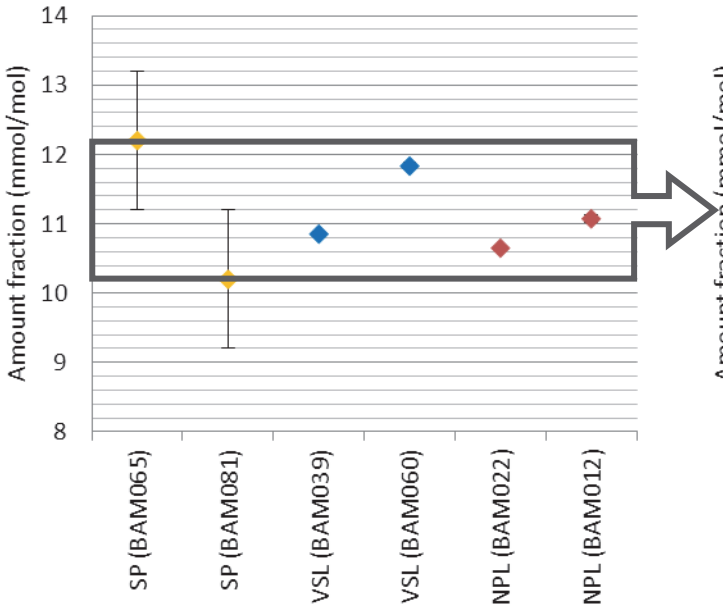

Figure 39a: BAM processed biogas: carbon dioxide

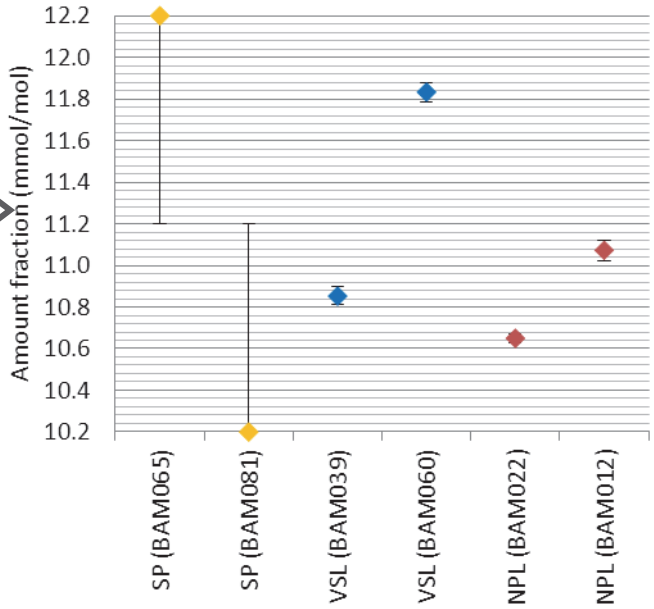

Figure 39b: BAM processed biogas: carbon dioxide (magnification)

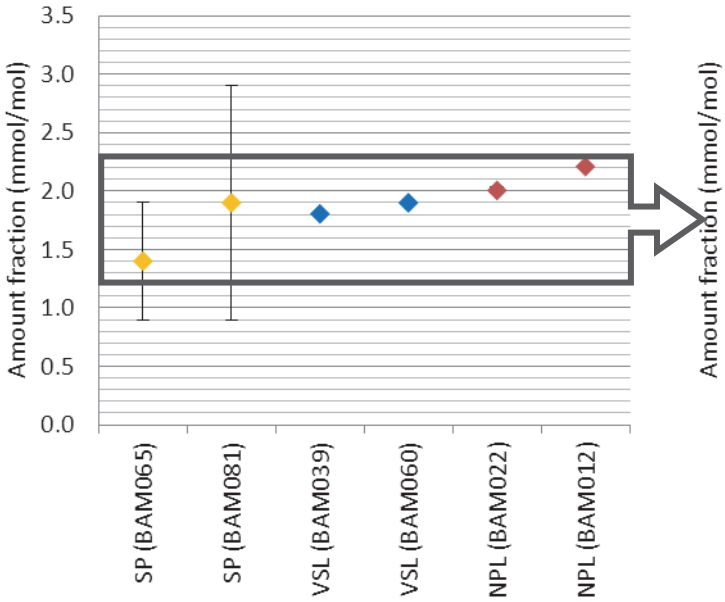

Figure 40a: BAM processed biogas: oxygen

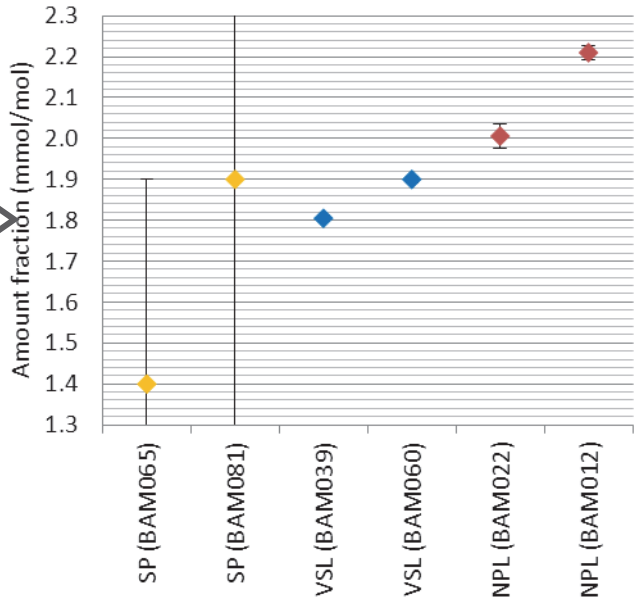

Figure 40b: BAM processed biogas: oxygen (magnification)

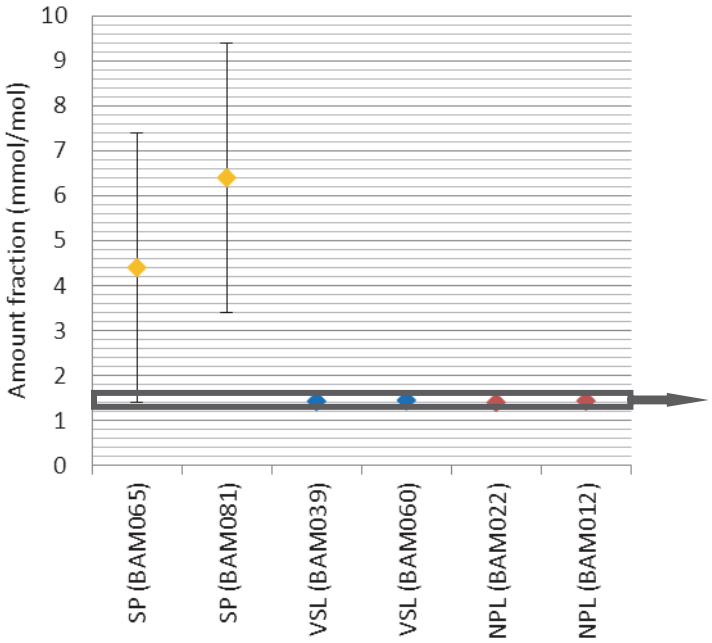

Figure 41a: BAM processed biogas: nitrogen

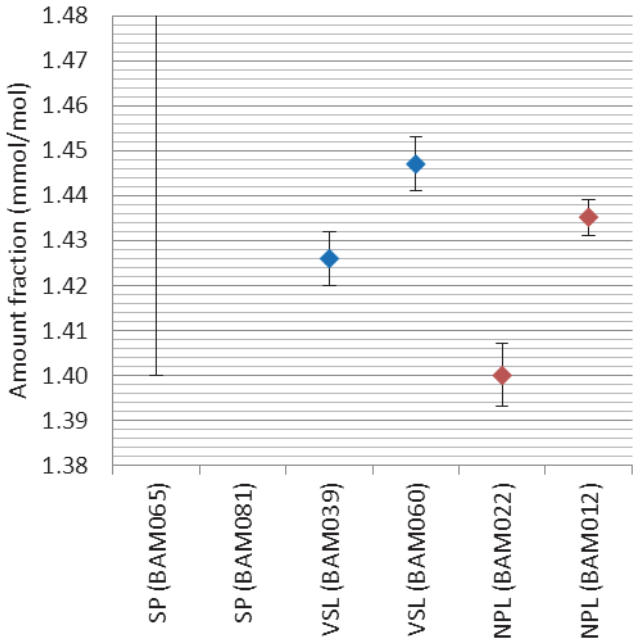

Figure 41b: BAM processed biogas: nitrogen (magnification)

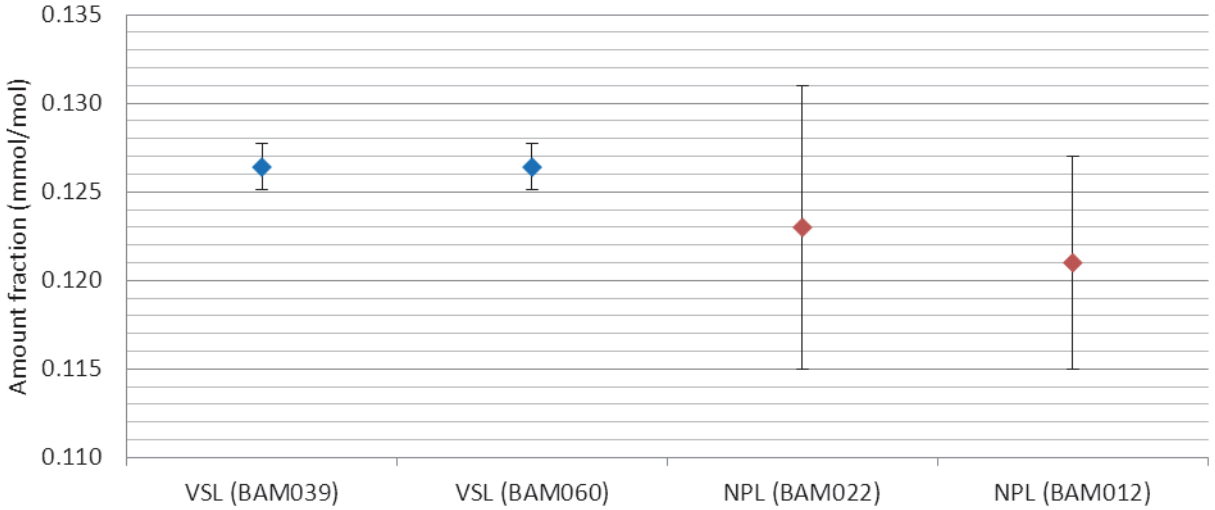

Figure 42: BAM processed biogas: hydrogen

Laboratory	Summed amount fractions (1st cylinder) (mmol/mol)	Summed amount fractions (2nd cylinder) (mmol/mol)
SP	1001.0	1001.5
VSL	1000.1	1000.2
NPL	998.9	999.2

Table 12: Summation of all amount fractions reported by each lab for BAM processed biogas

4.4.2 Summary

The reported methane amount fractions were in very good agreement across all three labs within their uncertainties, with a relative standard deviation of all 6 values of 0.12 %. The hydrogen amount fraction also agrees well between NPL and VSL. For the other compounds, the agreement is variable, but generally good. The lack of impurities found by all labs is to be expected in this type of mixture.

4.5 REAL GAS 6: PROCESSED BIOGAS (OBTAINED BY MKEH)

Table 13 summarises the compounds that were reported by the three labs. TD/GC-MS measurements at SP revealed below-limit-of-detection amount fractions for all siloxanes and hydrogen sulphide. (See
Table **9** for all of SP's limit of detection values).

	Laboratory		
Compound	**NPL**	**VSL**	**SP**
methane	x	x	x
oxygen	x	x	x
nitrogen	x	x	x
carbon dioxide	x	x	x
hydrogen	x	x	

Table 13: Summary of all compounds reported by each lab in MKEH processed biogas samples.

4.5.1 Composition

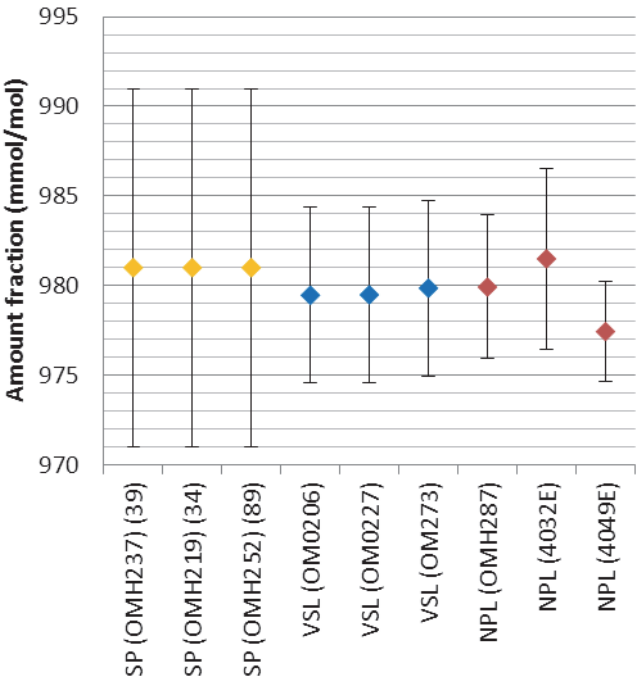

Figure 43: MKEH processed biogas: methane

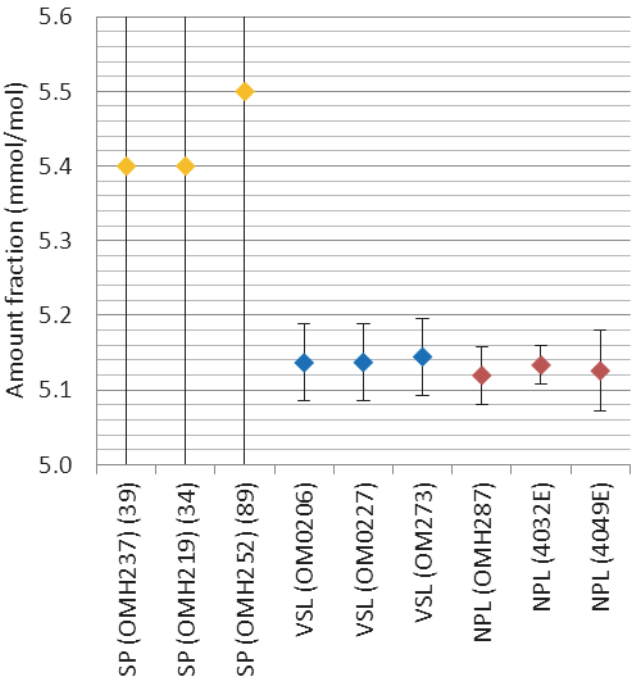

Figure 44: MKEH processed biogas: carbon dioxide (magnification) *SP uncertainty = ± 1 mmol/mol (for all 3 cylinders)

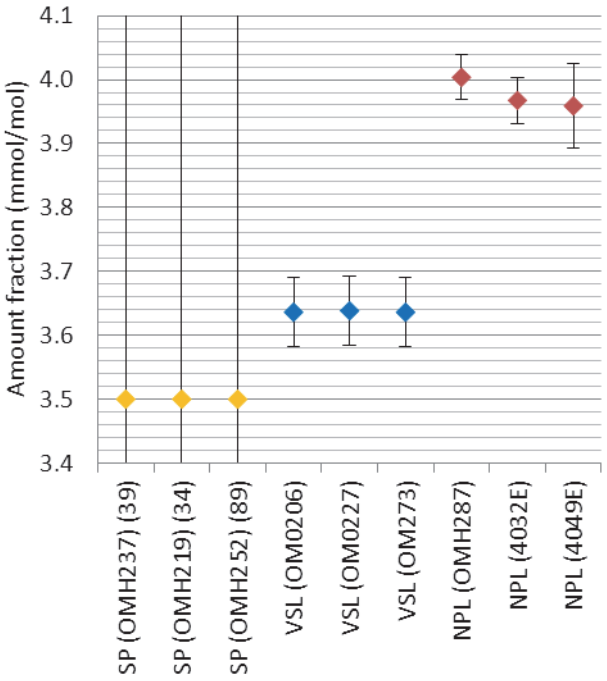

Figure 45: MKEH processed biogas: oxygen *SP uncertainty = ± 1 mmol/mol (for all 3 cylinders)

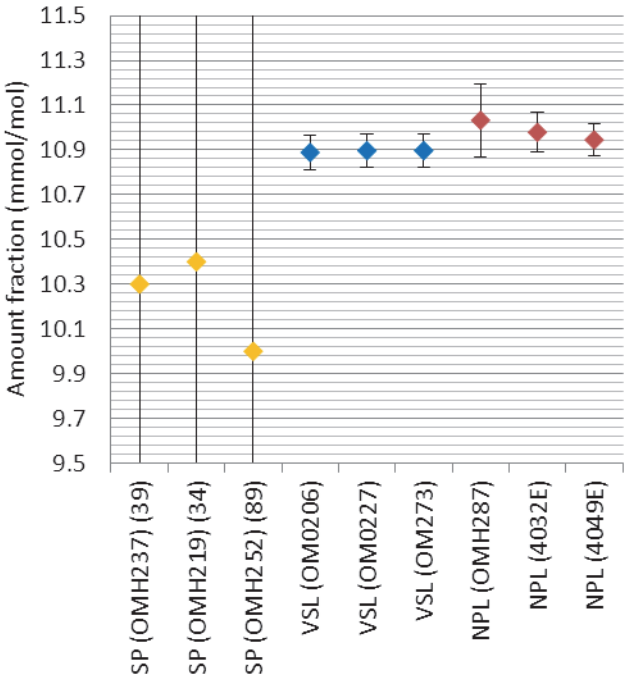

Figure 46: MKEH processed biogas: nitrogen *SP uncertainty = ± 3 mmol/mol (for all 3 cylinders)

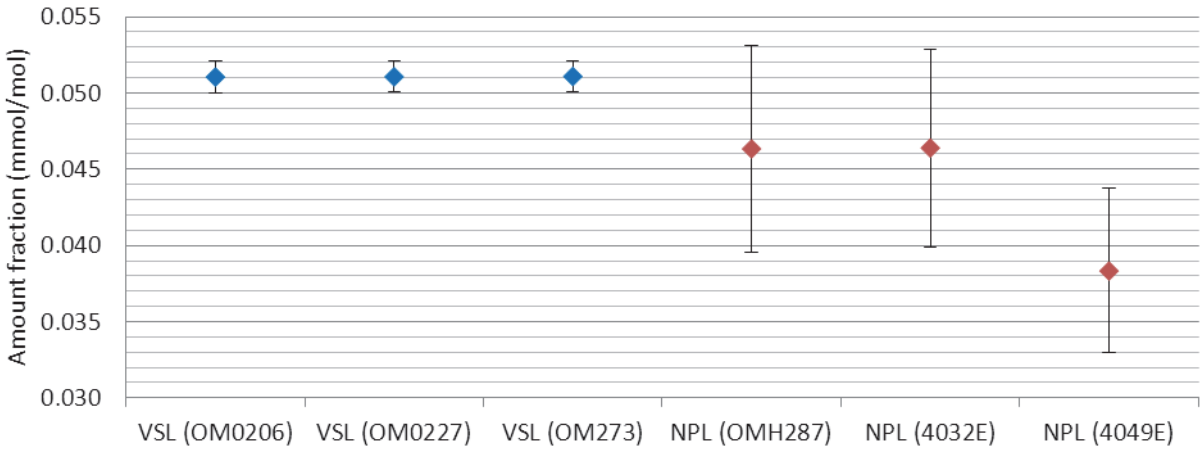

Figure 47: MKEH processed biogas: hydrogen

Laboratory	Summed amount fractions (1st cylinder) (mmol/mol)	Summed amount fractions (2nd cylinder) (mmol/mol)	Summed amount fractions (3rd cylinder) (mmol/mol)
SP	1000.2	1000.3	1000.5
VSL	999.2	999.2	999.6
NPL	1000.1	1001.6	997.5

Table 14: Summation of all amount fractions reported by each lab for MKEH processed biogas

4.5.2 Summary

Very good levels of agreement can generally be seen within uncertainties across all compounds, with the exception of oxygen. The lack of impurities found by all labs is to be expected in this type of mixture.

4.6 RESULTS SUMMARY

Table 15 provides an overview of the compounds that were detected in each sample within the study.

	Real gas number					
Compound	**1**	**2**	**3**	**4**	**5**	**6**
methane	x	x	x	x	x	x
ethane	x	x				
propane	x	x	x	x		
propene			x	x		
i-butane	x	x				
n-butane	x	x				
i-pentane	x	x				
n-pentane		x				
n-hexane		x				
n-heptane		x				
n-otcane		x				
n-nonane		x				
C_6+ hydrocarbons		x				
oxygen	x	x	x	x	x	x
nitrogen	x	x	x	x	x	x
carbon dioxide	x	x	x	x	x	x
hydrogen		x	x	x	x	x
hydrogen sulphide			x			
L2 siloxane			x	x		
L3 siloxane			x	x		
D4 siloxane			x	x		
D5 siloxane				x		
D3 siloxane			x	x		
L4 siloxane			x	x		

Table 15: Summary of compounds identified within the study.

5 CONCLUSIONS

The participating labs successfully measured the composition and impurity content of a variety of samples of challenging real non-conventional energy gases. Although good comparability was generally achieved, agreement between compounds was variable, particularly for the impurities measured in biogas sampled in sample bags. Possible reasons for the lack of comparability within the study include:

- Non-uniformity in gas sample collection methods causing sample composition to vary between cylinders. An example of which can be seen in the results from the CMM and CBM samples.
- Issues associated with performing measurements with sample bags. The main issue being highly time-dependent adsorption rates of hydrogen sulphide and siloxanes to the internal surfaces of sample bags coupled with analysis at labs being separated by over 24 hours.

The study has revealed the challenging nature of the analysis of some of these gases, and provided an insight into the capabilities of current analytical techniques used for composition and impurity quantification.

5.1 FUTURE CONSIDERATIONS BASED ON THE STUDY'S FINDINGS:

5.1.1 Composition measurements

A major issue that became apparent from the results of the study lies within the sampling of the real gases. Variable amounts of oxygen and nitrogen were found in different cylinders of nominally equivalent gas samples. To ensure accurate measurements of the composition of the gas, sampling must be carefully controlled.

5.1.2 Impurity measurements

Based on the results of this study, the use of sample bags for the accurate quantification of impurities is not recommended. Without the ability to accurately quantify the non-linear adsorption rates to bag surfaces, the data obtained from samples in sample bags will not be as reliable as samples analysed from passivated cylinders. There were also difficulties involved with sampling the low-pressure gas out of the bags for analysis, which required the use of novel methods. A more controlled form of sampling would help to improve the repeatability of the measurements.

---

[1] EC Mandate M/475 (2010) - Mandate to CEN for standards on biomethane transport and injection into natural gas pipelines

[2] "The Stability of Sulfur Compounds, Low Molecular Weight Gases, and VOCs in Five Air Sample Bag Materials" http://www.skcinc.com/instructions/1805.pdf

[3] " Stability of Biogas/Landfill Gas in FlexFoil Bags (245 Series)" http://www.skcinc.com/instructions/1796.pdf

[4] http://www.skcinc.com/instructions/SampleBagBrochure.pdf

[5] "An Evaluation of a New Film for Air Sampling Bags Used in Industrial Hygiene and Ambient Air Sampling" http://www.skcinc.com/instructions/SKC%20Bag%20Poster.pdf