FINAL PUBLISHABLE REPORT

Grant Agreement number	14SIP06			
Project short name	Siloxanes			
Project full title	Field trial of traceable online measurements of siloxanes in landfill gases			
Period covered (dates)	From	1 June 2015	To	30 November 2016
Coordinator				
Name, title, organisation	Lucy Culleton, NPL			
Tel:	+44 (0) 20 8943 6668			
Email:	lucy.culleton@npl.co.uk			
Website address	n/a			
Other partners	Protea, UK			

TABLE OF CONTENTS

1 Executive summary

Introduction

The biogas industry needs fast and reliable quantification of siloxane impurities in biogas as siloxanes form damaging silica deposits in gas processing equipment. This support for impact project (SIP) addressed this need by providing a robust assessment of the capabilities of the FTIR (Fourier Transform infrared) technology for the traceable on-line measurement of siloxane impurities in wastewater gas. These new measurement methods are being used by industrial end users and have contributed towards shaping European standard EN 16723, developed by CEN TC 408.

The Problem

There are currently no standardised methods for the measurement of siloxanes in biogas or biomethane. The current 'gold standard' methods currently employed for offline analysis are prone to introducing errors during sampling and also experience stability problems within sampling media. These errors can pose a barrier to biomethane trading if impurities are incorrectly over-reported, and a risk to biogas infrastructure caused by siloxane damage if under-reported. The development of an online FTIR (Fourier-Transform-InfraRed) analytical instrument (named 'AtmosFIR') by UK based company Protea required a traceable validation in order to demonstrate the applicability of the novel method for siloxane measurements, which is what this project set out to do.

The Solution

The project aimed to validate the FTIR instrument in both offline and online settings, and to compare the results obtained. Traceable reference gas standards produced by NPL were used to achieve this. The results of the trial were then disseminated to standardisation and industry, providing a mechanism for biogas upgraders to become aware of the benefits of online measurement, and drive advances in the biogas market.

Impact

The wider impact of the project will be through the provision and uptake of the robust method using the FTIR siloxane analyser that was developed for the accurate online analysis of siloxanes in biogas. This will result in direct cost-savings to industry and it will facilitate the expansion of the European biogas industry. This will lead to significant environmental benefits through the reduced use of fossil fuels, and societal benefits by ensuring the safe use of these 'green' gases by all European citizens.

The impact on standardisation will be achieved due to the uptake of the project's results by CEN TC 408, who have used the project results to help develop standards containing specifications for the maximum permissible levels of siloxanes (as total silicon) in biomethane for injection into gas transmission networks, or for use as a vehicle fuel. These standards (EN 16723-1 & prEN 16723-2) currently contain no fully validated standard method for the measurement of siloxanes, thus providing a direct route to impact for the work of this project via the uptake of the technology in future drafts and revisions of these standards.

2 Need for the project

A key output of the ENG01 GAS project was the development of a novel, metrologically traceable infrastructure for the measurement of siloxanes at National Measurement Institutes (NMIs). The ENG01 GAS project successfully developed a suite of novel reference gas mixtures containing four siloxanes (L2, L3, D4 & D5) in trace amounts. It also established sensitive and repeatable gas chromotography (GC) – mass spectrometry and GC – Flame Ionisation Detection methods for the measurement of these compounds.

The accurate measurement of siloxanes in biogas is needed by the rapidly-expanding European biogas industry, both for power generation and as a vehicle fuel. The siloxanes form silica deposits in gas processing equipment which are capable of causing extensive damage to equipment over time and significantly reduce efficiency. The measurement of siloxanes is crucial to operators of electricity generating plants using biogas, so that they can determine the extent that the feed gas needs to be cleaned prior to combustion.

During the project, CEN TC 408 (Natural gas and biomethane for use in transport and biomethane for injection in the natural gas grid) was working in response to the European Commission's Mandate M/475 by developing two European standards (EN 16723-1 and prEN 16723-2) which respectively specify the maximum levels of hazardous impurities that may be present in biomethane injected into the natural gas network, or used as a vehicle fuel. These two standards identify siloxanes as one of the impurities that must be measured, and set maximum permissible concentrations for these compounds. However, prior to this project there was no standard method for the measurement of siloxanes in biogas.

The industrial requirements for the measurement of siloxanes can best be met by performing online analysis to provide real-time feedback to the end-user on the concentrations of these compounds in the biogas stream.

Protea, the primary supporter of the project, have developed FTIR instruments, sometimes in combination with GC. These can perform on-line siloxane measurements, but they have lacked metrological validation prior to this project.

This project tested the implementation of an online method for measuring siloxanes through a comparison with the reference gas mixtures and lab-based methods developed in the ENG01 GAS project. It will ensure that these online measurements are valid and robust. Successful instrument validation would facilitate the uptake of the technology and be used in future drafts and revisions of the CEN TC 408 standards for biogas.

3 Objectives

The objectives of this project were:

1. To demonstrate the viability and benefits of traceable online industrial measurements of siloxanes in biogas and landfill gas (developed in EMRP project ENG01) via laboratory validations and field trials of a new measurement method, and to disseminate the findings via a relevant biogas trade journal and a biogas trade association website.
2. To incorporate the findings of the laboratory and field trials into CEN standards EN1673-1 and prEN16723-2 in order to support their wider dissemination and uptake.

4 Results

Objective 1
To demonstrate the viability and benefits of traceable online industrial measurements of siloxanes in biogas and landfill gas (developed in EMRP project ENG01) via laboratory validations and field trials of a new measurement method, and to disseminate the findings via a relevant biogas trade journal and a biogas trade association website.

4.1.1 Laboratory-based validation of the FTIR instrument (product name 'AtmosFIR')

A full lab-based validation of Protea's AtmosFIR was performed at NPL in order to assess its performance under controlled conditions. Several parameters were tested using traceable reference gas mixtures developed and validated by NPL. These being: linearity, response time, cross-interference and measurement accuracy.

The error on the full scale was within 5 % and the linearity was well within the 2 % deviation. The calculated response times were between 2-3 mins. As siloxanes are known to be reactive species which will stick to the surface of the sample path, these stabilisation times were as expected.

The detection limits of the analyser for siloxanes were calculated as noise equivalent concentrations. Ten consecutive readings were collected with nitrogen (which has no infrared response) in the gas cell. The standard deviation of the zero and the reproducibility at span level was calculated. All compounds were found to be within the required 2 % range.

The cross-interference testing was performed to test the ability of the software to differentiate between the different siloxane species. It ialso tests that the background gases in biogas (carbon dioxide and methane) do not cause false positives for siloxanes. Traceable reference gas mixtures, prepared and validated at NPL, were used for this, and the results showed that the method used was capable of differentiating between the different siloxane species and also the background gases within 3 %.

The multi-gas checks were the most important checks in the validation task, as they prove the analyser's capability to accurately quantify siloxanes in a mixture (which is as they would be in industrial biogas) and to validate the calibration of the analyser. Two multi-component siloxane gas mixtures in methane and biogas matrices were tested. All siloxane measurements were within 5 % of the NPL certified value for both mixtures (results provided in Table 1).

Results for methane matrix							
Component	**NPL Certified Concentration/ppm**	**Three Stable Readings/ppm**			**Average reading**	**Difference /ppm**	**Difference/ %**
L2 siloxane	196.87	196.7	196.2	197.13	196.86	-0.19	-0.1
L3 siloxane	14.9	14.78	14.3	14.41	14.5	-0.4	-2.71
D4 siloxane	8.49	8.22	8.33	8.2	8.25	-0.24	-2.83
D5 siloxane	3.21	3.37	3.35	3.27	3.33	0.12	3.74
Results for biogas matrix							
Component	**NPL Certified Concentration/ppm**	**Three Stable Readings/ppm**			**Average reading**	**Difference /ppm**	**Difference/ %**
L2 siloxane	204.56	204.25	204.41	202.86	203.84	-0.72	-0.35
L3 siloxane	14.4	14.45	14.44	14.53	14.47	0.07	0.51
D4 siloxane	8.7	8.56	8.69	8.55	8.6	-0.1	-1.15
D5 siloxane	3.09	3.03	3.21	3.16	3.13	0.04	1.4

Table 1: Summary of the results from the multi-gas mixture testing

4.1.2 Comparison of offline measurements

The field trial site was a waste water treatment works with a thermal hydrolysis and digestion plant to generate renewable energy. The gas from the anaerobic digestion of the waste sludge is used as a fuel for gas turbine engines. The plant has carbon beds in place to remove the siloxanes from the raw gas. Samples were collected from points before and after abatement, as in Figure 1. Four 'sulfinert' passivated sample cylinders were used to collect the samples, with NPL and Protea each receiving two samples, one from before and one from after the siloxane abatement.

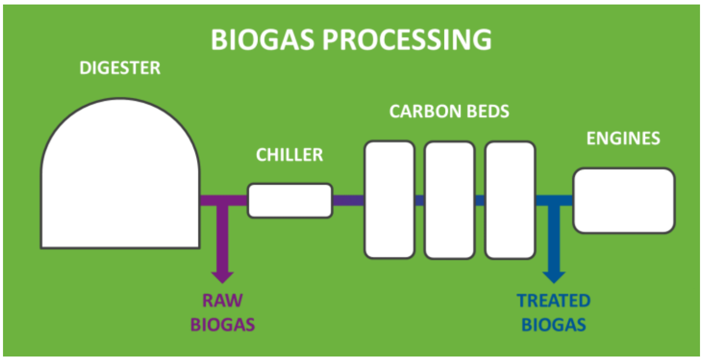
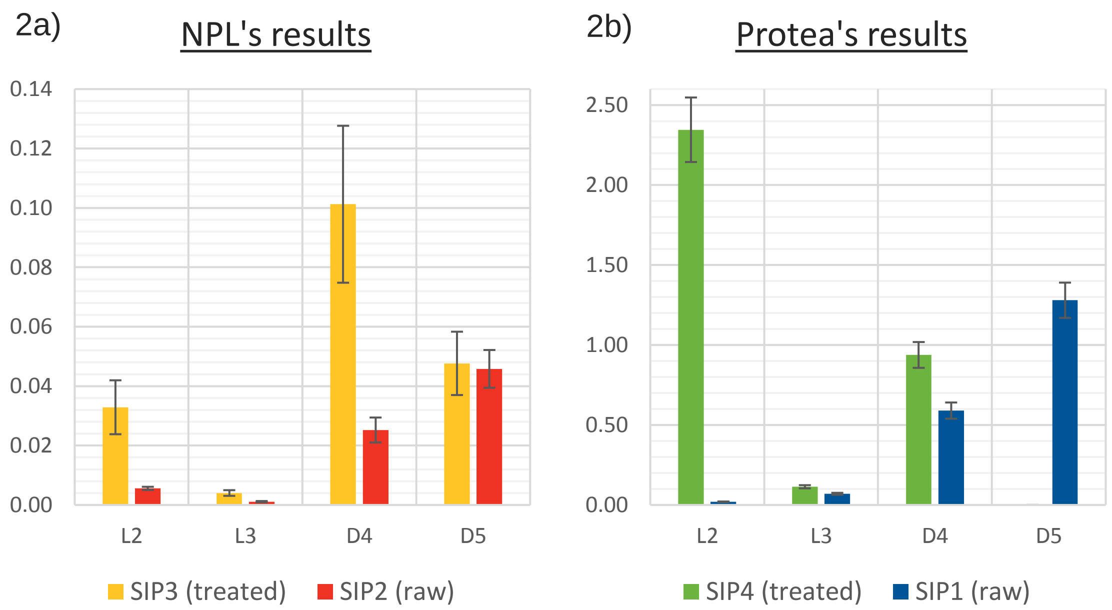


Figure 1: Plant schematic showing sampling points

The samples were collected on 27th September 2016, and analysed by NPL and Protea within a 48 hour period. The results from the offline sample analysis are presented graphically in Figures 2a and 2b, which are plotted from the values in Table 2.



Figures 2a and 2b: Offline sample analysis results comparison

	NPL RESULTS			PROTEA RESULTS		
Component	Amount fraction (µmol/mol)	k=2 uncertainty (% rel.)	k=2 uncertainty (µmol/mol)	Amount fraction (µmol/mol)	k=2 uncertainty (% rel.)	k=2 uncertainty (µmol/mol)
	Vessel ID: SIP3 (treated biogas)			**Vessel ID: SIP4 (treated biogas)**		
L2 siloxane	0.033	27.59	0.00908	2.346	8.6	0.1173
L3 siloxane	0.004	23.67	0.00095	0.114	8.6	0.0057
D4 siloxane	0.101	26.10	0.02642	0.938	8.6	0.0469
D5 siloxane	0.048	22.37	0.01066	-	-	-
	Vessel ID: SIP2 (raw biogas)			**Vessel ID: SIP1 (raw biogas)**		
L2 siloxane	0.006	9.73	0.00054	0.020	8.6	0.001
L3 siloxane	0.001	19.28	0.00021	0.070	8.6	0.0035
D4 siloxane	0.025	16.65	0.00420	0.590	8.6	0.0295
D5 siloxane	0.046	13.88	0.00636	1.280	8.6	0.064

Table 2: Offline sample analysis results

From the results it is clear that there are large differences between the reported siloxane amount fractions of Protea and NPL's analysis. There are several factors that may have contributed to this, which are discussed in turn below:

a) Although every effort was taken to minimise the amount of time between the analyses at the two labs, Protea's analysis preceded NPLs by approximately 48 hours. Short term stability studies carried out at NPL indicate that no significant decrease in stability of dry reference gas mixtures are noted in this time period for this vessel type, however industrial biogas composition stability is not known within these vessels.

b) Although sample cylinders and valves were passivated, the connecting plastic tubing did not have specialist passivation, so without appropriate purge time, it is highly possible that siloxanes were adsorbed onto the tubing walls and any untreated connections. Based on this assumption, variations in the sample purge time could cause differences in siloxane amount fractions.

c) The sample pressure within the vessels was significantly lower than what would normally be used for GC-MS/FID analysis at NPL, so the repeatability of the measurement was much poorer than what would otherwise be obtainable at higher sample pressures, causing a high measurement uncertainty for NPL. This also meant that the analysis could not be repeated to investigate the possibility of decay/interactions within the sample vessel.

4.1.3 Online measurements of siloxanes

The results of the field trial are summarised in Figure 3. The most striking observation from the results is that the total siloxane level is higher in the treated gas than in the raw gas, which is in contrast to the expected trend. This suggests that instead of removing siloxanes from the gas, the abatement process is increasing the siloxane content of the raw gas.

By looking at the trends of individual siloxanes during this time, this can be explained. The L2 concentration dropped dramatically from ~2 ppm in the treated gas to ~0ppm in the raw gas. It is this drop that is largely responsible for the fall in total siloxane. However, the D5 trend increases in the raw gas to ~1.4 ppm from zero in the treated, which is as expected.

After contacting the site, it was revealed that the carbon in the beds was overdue for replacement. Therefore, the theory is that the larger siloxanes (D5) are being trapped on the bed in place of the smaller L2, and the L2 is being released into the gas stream. Protea have seen a similar trend to this when measuring from various different points in the abatement process on a landfill site. It was found that the bed was acting like a chromatography column, with the smaller siloxanes having a shorter retention time on the media.

Gas checks using NPLs traceable reference gas standards were performed on-site at the start and end of the monitoring run. Measured amount fractions were within 5 % of the FTIR calibration for both, and the measured drift was within 3 % of initial values, which provides confidence in the siloxane concentrations measured on the sample gas.

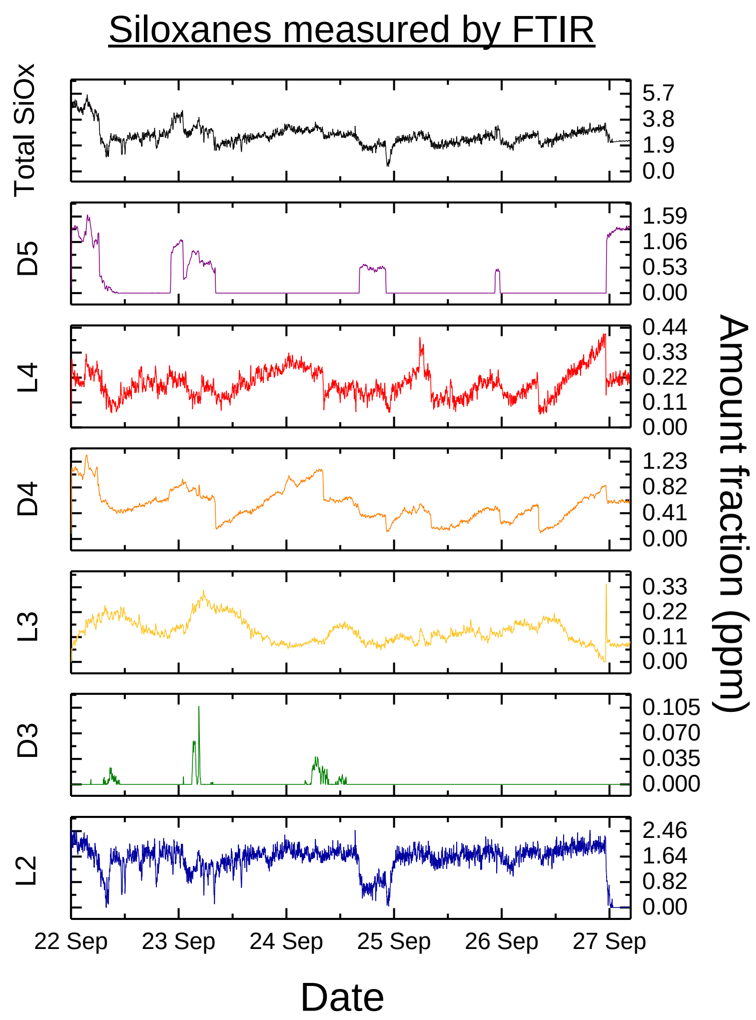


Figure 3: Trends for total and individual siloxanes plotted from the on line FTIR analysis data. Treated biogas was measured from 22-26 Sep 2016 and raw biogas from 27 Sep 2016.

The data from the check gas on site shows that the analyser performed well in-situ and gave appropriate results for the traceable reference material, this gives confidence in the subsequently measured results. The on-site analysis of the treated gas was able to reveal trends in the siloxane concentrations which fit well with what should be expected based on events on site. The data from the raw gas compared to the treated gas appeared anomalous at first, as it is in contrast to the expected trend, however this result has been observed previously and provides scope for further investigation.

4.1.4 Publication of articles

One of the project's objectives was to have articles published by industry-focused organisations. The articles described the work undertaken within the project and its outputs. The objective was achieved, as the articles were published by the following organisations:

- ADBA website (December 2016):
(http://adbioresources.org/news/solving-the-siloxane-measurement-problem)

- EBA newsletter (January 2017):
(http://european-biogas.eu/newsletter/)

- Bioenergy insight magazine article (January 2017)
(http://www.bioenergy-news.com/article_display/?volume=8&issue=1&content_item=516)

Objective 2

To incorporate the findings of the laboratory and field trials into CEN standards EN1673-1 and prEN16723-2 in order to support their wider dissemination and uptake.

4.2.1 Dissemination to CEN TC408

This objective was required in order to ensure the research and results are highlighted to standardisation bodies, in order for them to address the need for standardised methods.

The aims and results to date of the project were presented to CEN TC 408 at their meeting on 19/09/16 and a copy of the final project report was also circulated to the group. The objective was achieved as it was confirmed that the outputs of the project had contributed towards the standards, which will facilitate the wider dissemination of results to the wider European biogas community through this contribution to EN1673-1 (published 02/11/16) and prEN16723-2 (due for 2017 publication).

5 Impact

Dissemination of results

The work undertaken within the project and its outputs have been covered in articles aimed at biogas producers and end users within Europe. They were published by the following organisations:

- Anaerobic Digestion and Bioresources Association website (December 2016): http://adbioresources.org/news/solving-the-siloxane-measurement-problem
- EBA newsletter (January 2017) http://european-biogas.eu/newsletter/
- Bioenergy insight magazine article (January 2017) http://www.bioenergy-news.com/article_display/?volume=8&issue=1&content_item=516

Actual impact

The primary supporter of the project, Protea, has benefited directly from this project by robustly demonstrating the comparability of the results obtained using their FTIR siloxane analyser, against reference gas mixtures and methods from NPL. They have been able to demonstrate the practicalities of delivering fast and accurate measurements in an industrial application. This will not only provide confidence in the performance of their instrument but it will also demonstrate that the FTIR approach is a viable solution for the online process control of siloxanes in biogas. Protea have since experienced a large increase in enquiries about the product from external sources due to this exposure.

The fact that the online FTIR measurements are capable of picking up symptoms of break-through in siloxane abatement processes, such as carbon beds, is of great significance, and will have a direct benefit on upgrading gas plants if employed. Break through occurs once the carbon beds are saturated, and siloxane impurities start to 'break through'. The FTIR siloxane analyser's capability for monitoring both total and individual siloxanes in real time can be used as a tool for optimising the efficiency of the upgrading process, and predicting the optimum times for regeneration cycles and bed material replacement. This will allow for less down-time and increased efficiency within the upgrading process for gas plants.

The international metrology community will benefit from the uptake of instrumentation for the online measurement of siloxanes through an increased demand for high-accuracy traceable reference gas mixtures of siloxanes. These reference gas mixtures will be used within industry by instrument operators to perform quality control measurements of their analytical process. The work has also demonstrated the matrix independence (i.e. between pure methane and a mixed biogas composition) and therefore commutability of the siloxane reference gas mixtures, positioning NPL to be able to produce gaseous reference materials of these compounds under ISO Guide 34 (General requirements for the competence of reference material producers).

Impact on standards

The impact on standardisation will be achieved due to the uptake of the project's results by CEN TC 408, who have used the project results to help develop standards containing specifications for the maximum permissible levels of siloxanes (as total silicon) in biomethane for injection into gas transmission networks, or for use as a vehicle fuel. These standards (EN 16723-1 & prEN 16723-2) currently contain no fully validated standard method for the measurement of siloxanes, thus providing a direct route to impact for the work of this project via the uptake of the technology in future drafts and revisions of these standards.

Potential impact

The wider impact of the project will be through the provision and uptake of the robust method using the FTIR siloxane analyser that was developed for the accurate online analysis of siloxanes in biogas. This will result in direct cost-savings to industry and it will facilitate the expansion of the European biogas industry. This will lead to significant environmental benefits through the reduced use of fossil fuels, and societal benefits by ensuring the safe use of these 'green' gases by all European citizens.

Europe currently leads the world in its use and promotion of renewable energy. Decarbonisation of the energy supply is perhaps the biggest challenge in the twenty-first century and the outputs demonstrated by this project will assist the EU in moving towards alternative fuels.

6 Website address and contact details

Website address: n/a

Coordinator: Lucy Culleton, NPL, Lucy.culleton@npl.co.uk

Primary supporter: Victoria Brewster, Protea, victoria.brewster@protea.ltd.uk