Publishable Summary for 14SIP06 Siloxanes
Field trial of traceable online measurements of siloxanes in landfill gases

Overview
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.

Need
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.

Objectives
The objectives of this project were:

1. To demonstrate the viability and benefits of traceable online industrial measurements of siloxanes in biogas (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 draft standards prEN1673-1 and prEN16723-2 in order to support their wider dissemination and uptake.

Results

To demonstrate the viability and benefits of traceable online industrial measurements of siloxanes in biogas (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.

This objective was needed in order to ensure the project provides real world impact, with meaningful results that can be disseminated to biogas upgarders and users, as currently traceable instrument validation of this type is not commonplace.

Laboratory based validation

The laboratory-based validation of the FTIR instrument was performed at NPL using the traceable reference gas mixtures and GC methods developed in the ENG01 GAS project. The results demonstrated that the FTIR instrument developed by Protea is capable of measuring the amounts of a variety of linear and cyclic siloxanes in both methane and biogas matrices. The FTIR instrument is capable of performing traceable measurements to a defined level of uncertainty of 5 %, which is acceptable for requirements within the biogas measurement field.

Offline measurements

Offline analysis of samples was performed by NPL and Protea from a wastewater site. NPL used the validated tests from the ENG01 project and Protea used their FTIR instrument. Unexpectedly large differences were observed between the reported siloxane amounts by Protea and NPL. Several factors may have contributed to this. The main factor contributing to the large difference in the results was thought to be low sample pressure (close to atmospheric) of the sample gas, however other variables such as the lack of a standardised sampling procedure may have affected the results.

The offline comparison proved that offline analysis of siloxanes in industrial biogas can be highly challenging. Making an accurate comparison between two independent measurement methods requires standardised, robust and reliable sampling procedures, which are as yet not available. Additionally the effects of sample pressure on lab based analytical methods should be fully understood in order to obtain reliable analytical results. This work has highlighted the importance of using the existing standardised sampling methods for offline measurements.

Online measurements

The Protea FTIR analyser was used for online measurements, which were capable of capturing trends in the varying siloxane concentration over time. There were cyclical patterns in the D4 siloxane concentrations related to the carbon bed regeneration cycles. These measurements demonstrated the value of regular, online measurements compared to one-off tests.

A striking result was apparent when the measurement stream was switched from treated to raw biogas. The total siloxane reading of the raw gas was lower than in the treated gas, indicating that the abatement process was not functioning appropriately. The site confirmed that the beds were overdue for replacement, which serves as a potential explanation of this result. This was a useful example of the information that could be captured by the online measurement technique.

Based on the results of this project, it is apparent that online measurement has several advantages over more common methods which take ‘grab-samples’ for offline analysis. Online methods mitigate a lot of sampling issues and highlight rise and fall trends that offline methods may miss. This potentially allows greater control over the upgrading process for plant. Though online techniques are on average more expensive than offline methods, there is potential for this to be offset by the benefits that process optimisation could bring.

To incorporate the findings of the laboratory and field trials into CEN draft standards prEN1673-1 and prEN16723-2 in order to support their wider dissemination and uptake.

This objective was necessary in order to ensure the research and results are highlighted to standardisation bodies such as (CEN TC 408), in order for them to address the need for standardised sampling and test methods for siloxanes.

The project was 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. CEN TC 408 have confirmed that the outputs of the project (i.e. a recommended measurement technique) have contributed towards the standards, which will facilitate the wider dissemination of results to the wider European biogas community. The updated standard for biogas EN1673-1 was published 02/11/16, and prEN16723-2 for automotive fuel is due for publication in 2017.

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.

Project start date and duration:	01 June 2015, 18 months	
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