Underpinning green energy use: Traceable measurements of total silicon in biogas

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A green energy future is fast becoming a reality, as sustainable energy targets set by European governments drive advances in science on a daily basis. As part of a European biogas research project, the UKs National Physical Laboratory (NPL) is helping to provide a foundation to underpin quality control in the introduction of biogas into European natural gas networks.

Biogas is produced when organic matter is broken down anaerobically. The raw materials come from many different sources, such as manure, waste water, plant material, and municipal waste.

One significant hurdle that the biogas economy has had to overcome is implementing ways to manage the diverse impurity content. The wide range of production routes by their nature, will produce biogas of varying composition. Impurity management is a critical part of the upgrading process, as without the correct quality control procedures, the effects downstream can be financially and environmentally damaging.

Figure 1: An anaerobic digestion plant in rural Germany

In particular, the presence of siloxanes within biogas can cause irreversible damage to gas processing equipment, as abrasive silicon dioxide deposits are formed during combustion. The fouling of thermocouples and oxygen sensors are also a problem when siloxanes are present in the gas, causing feedback errors.

Siloxanes are a relatively new impurity found in biogas, as their use within personal care products has gradually increased over the last few decades. They are now commonly added to products such as cleaning agents, deodorants and cosmetics to improve their consistency and performance.

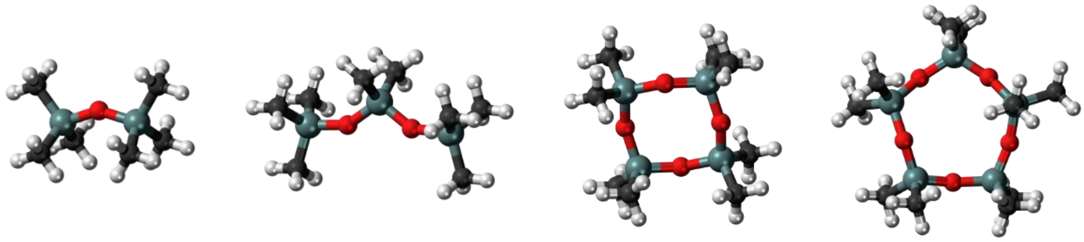

Figure 2: Molecular structure of L2, L3, D4 and D5 siloxanes (C: black, H: white, O: red, Si: teal)

Once disposed of, these products become effluents in waste water and become part of municipal waste. Due to their volatility, the siloxanes become entrained with the biogas during the digestion stage, and must be removed to below a certain level before the biogas can be used to produce energy. This 'total silicon' limit level varies by application, and the values themselves are still under scrutiny.

TC 408
prEN 16723-1
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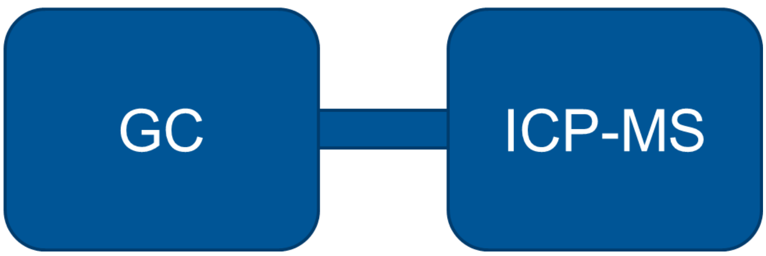
Within Europe, two draft standards are currently under development that will specify the maximum allowable total silicon content of biogas for entry to grid. Once legislation is in place, it will need to be upheld by a metrological infrastructure that is traceable back to the SI to provide confidence in gas quality regulation. The EMRP metrology for biogas project will address this need.

There are several methods available for the quantification of total silicon that are currently used in the field. However the need for a more accurate and traceable method has driven research work on total silicon measurements at NPL. The Gas and Particle Metrology Group are currently setting up a facility that will measure the total silicon content of a biogas sample with high accuracy, with a limit of detection goal in the low nmol/mol level. The analytical equipment consists of a gas chromatograph (GC), coupled to an Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The unique analytical procedure will concentrate all of the siloxane molecules within a gas sample, by separating off the major biogas components using chromatography. The siloxanes are then transferred as a single packet onto the ICP-MS, which is a highly sensitive detector, capable of measuring the total silicon content



Relative isotopic abundances are monitored, to confirm the presence of silicon. Potential interferents such as nitrogen are completely removed by the GC, allowing lower detection limits to be achieved than what is otherwise possible, by using the Silicon 28 signal.

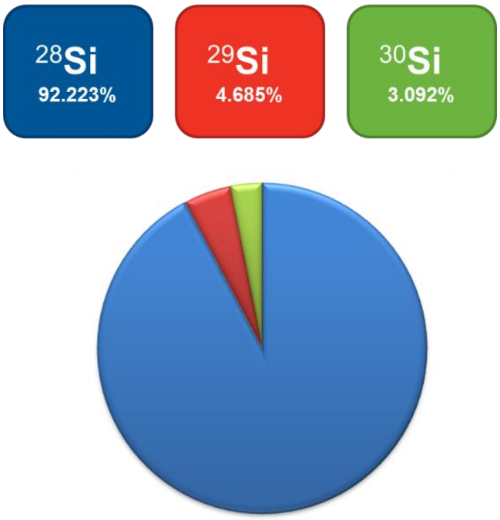


Figure 3: Relative isotopic abundances of silicon

This technique will be validated using NPL's suite of high-accuracy siloxane reference gas standards. These traceable standards are prepared via sequential high-accuracy weighings of each mixture component, and then put through a homogenisation process. The individual component amount fractions are then validated using Gas Chromatography Mass Spectrometry (GC-MS). The reference standards contain L2, L3, D4 and D5 siloxanes at ppb amount fractions, which were chosen to meet future industrial requirements.

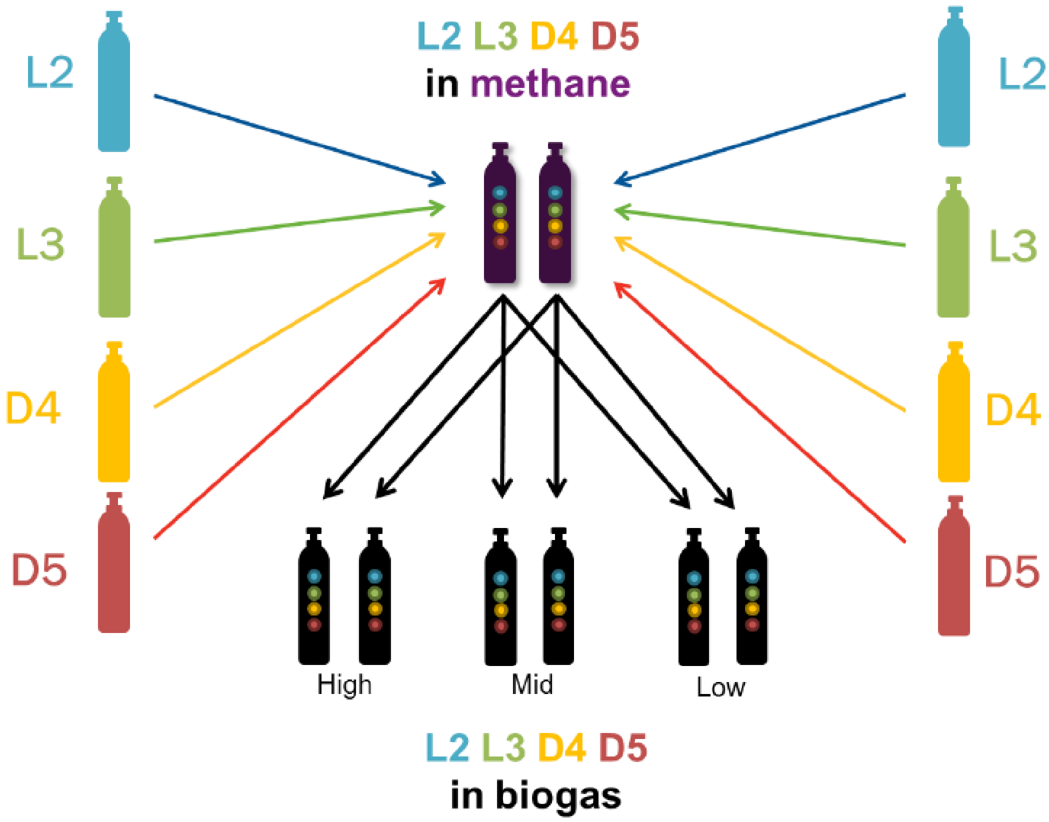


Figure 4: A preparation route for ppb-level multi-component siloxane reference standards. Mixtures are always produced in pairs from different parent materials to allow validation at every stage of the process.

Over the last 5 years, NPL has successfully developed the capability to prepare a variety of high-accuracy siloxane Primary Reference Gas Mixtures (PRGMs) in a range of matrix gases such as nitrogen, methane and biogas. For more information, see our **dedicated biogas webpage**.

Once validated in 2016, the GC-ICP-MS total silicon method will provide an important contribution to a reliable and traceable measurement infrastructure for total silicon in biogas.

Research funding provided by the European Metrology Research Programme and the UK Government National Measurement & Regulation Office's Chemistry and Biology Knowledge Base Programme

EMRP
European Metrology Research Programme
Programme of EURAMET

The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

National Measurement & Regulation Office