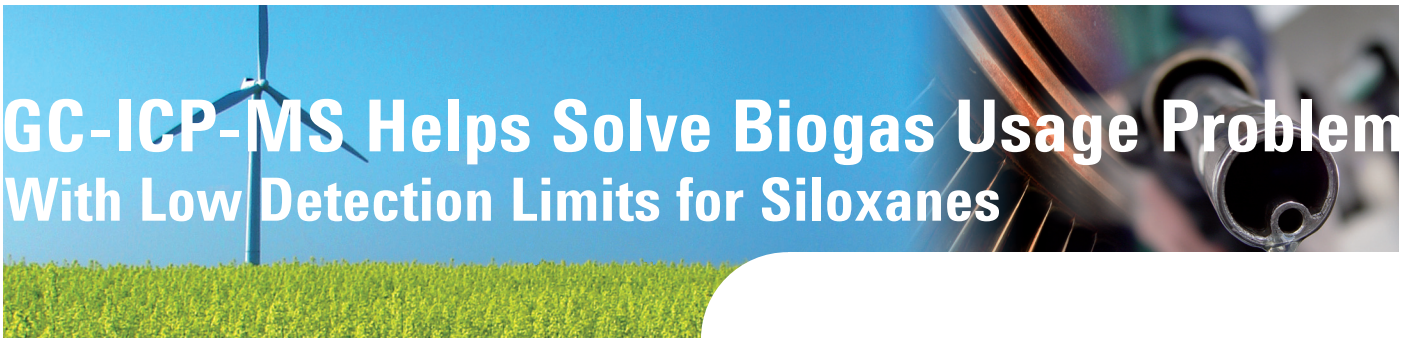

GC-ICP-MS Helps Solve Biogas Usage Problem With Low Detection Limits for Siloxanes

Introduction

Biogas is the term used to describe the mixture of methane, carbon dioxide, nitrogen and other components resulting from the anaerobic fermentation of a variety of biodegradable materials including animal waste, domestic sewage sludge and municipal landfill waste. Because of its methane content (40-75%), biogas can be used as a substitute for natural gas and is commonly used at wastewater treatment plants and landfills for heating, electricity generation, and vehicle fuel. However, as a waste byproduct, it may also include undesirable components including volatile sulfur and halogen containing compounds, as well as volatile silicon compounds (siloxanes).

Upon combustion, the sulfur and halogen compounds can form corrosive acids and the siloxanes can form abrasive silicon dioxide (silica). Silicon dioxide is particularly problematic because it accumulates within process equipment, such as boilers, and both reciprocating and turbine engines, causing premature wear and eventual failure. For this reason, levels of volatile siloxanes must be carefully monitored and controlled when biogas is used to fuel expensive machinery.

Analysis of Volatile Siloxanes

Traditionally siloxanes in biogas have been measured using gas chromatography mass spectrometry (GC/MS) with detection limits ranging from 0.02 to 1 ppmv (parts per million by volume) depending on the specific method. However, as engine technology has shifted from fairly robust reciprocating engine usage to cleaner burning microturbine usage, the tolerance to siloxanes has decreased to the point where better analytical sensitivity is required.

GC-ICP-MS

GC coupled to inductively coupled plasma-MS (GC-ICP-MS) was evaluated for sensitivity, ease of use and robustness for siloxanes analysis. While Si analysis can be challenging by ICP-MS, the Agilent GC interface uses a dry plasma for very high temperature and efficient ionization and significantly reduced interferences from oxygen and nitrogen based polyatomics. Utilizing the Octopole Reaction System (ORS) collision/reaction cell of the Agilent 7500ce ICP-MS in hydrogen reaction mode further reduces the N_2 background on Si to insignificant levels, resulting in superior sensitivity for siloxane analysis.

Results

Eight siloxanes, each at approximately 45 ppb (µg/L) in methanol, were analyzed using the Agilent 6890/7500ce GC-ICP-MS system. Total run time was less than 10 minutes and detection limits based on twice the peak-peak signal to noise were < 1 pg per compound. When converted to concentrations in biogas, assuming standard sample collection techniques, the resulting detection limits ranged from 0.03 - 0.07 ppbv (parts per billion by volume), which is 100x lower than the most stringent engine manufacturers requirements and more than 500x more sensitive than the lowest reported GC/MS detection limit.

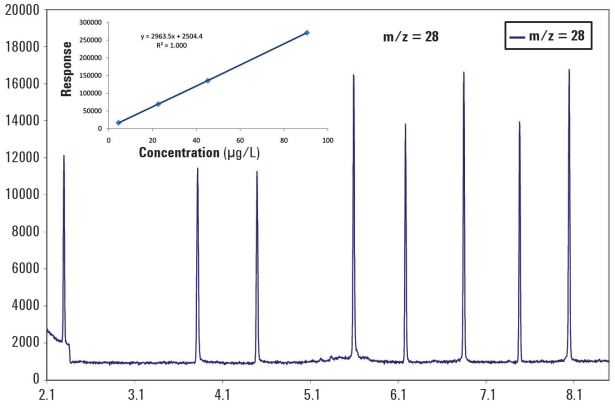

Figure 1. Chromatogram of eight siloxanes at approximately 45 ppb (µg/L) each in methanol analyzed using GC-ICP-MS. Inset: Calibration curve of dodecamethylpentasiloxane from 4.5 to 90.45 ppb

Furthermore, since ICP-MS is capable of compound independent calibration, the unavailability of standards for some compounds is not a problem. Accurate quantification of any volatile Si containing compound can be based on the response of a single standard compound.

The calibration curve inset of Figure 1 was generated using dodecamethylpentasiloxane from 4.5 to 90.45 ppb with excellent linearity (r^2 = 1.000). When a standard at 4520 ppb was analyzed against this curve, the calculated concentration was 4244 ppb (94% recovery) indicating that the method was linear up to 50 times higher than the highest calibration point.

Conclusions

Volatile siloxanes pose increasingly significant problems for biogas use at wastewater treatment plants and landfills. As a result, process equipment manufacturers are imposing stricter limits on acceptable concentrations of Si in biogas. In some cases, these limits cannot be reliably measured using the currently used methodologies.

Agilent GC-ICP-MS can easily achieve the desired detection limits, with excellent linearity, reproducibility and ease of use.

More Information www.agilent.com/chem/icpms

www.agilent.com/chem/icpms

Agilent Technologies