Advantages Of Continuous Siloxanes Measurements

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Renewable natural gas (RNG), also known as biomethane, is a carbon-neutral fuel that can be used as an alternative to fossil natural gas. RNG is produced by upgrading biogas to meet defined quality standards, after which it may be distributed via the existing gas grid or sold as an alternative fuel source in the form of compressed natural gas for vehicles. As a result of various government incentives, federal renewable fuel requirements and an increase in public demand to reduce greenhouse gas emissions, RNG production has expanded in recent years and is projected to grow substantially.

The gas used to create RNG is derived from methanogenic decomposition of organic materials such as landfill waste, sewage sludge, crop waste, manure and food waste. This raw biogas generally contains 45-65 percent methane, with varying concentrations of moisture, particulate, O2, N2, VOCs, H2S and siloxanes, depending on the source feedstock. Raw biogas must go through a series of treatment stages before it is suitable for biogas applications and another series of treatment stages to produce RNG.

Typically, a carbon-based adsorbent material is used to remove siloxanes from a raw gas stream. By continuously measuring the siloxanes' concentration in the gas, the supplier can reduce the frequency of material replacement by waiting for the concentration to reach 90 percent of its quality standard limit (0.09 mg/m3).

Recently, utilities have started requiring RNG suppliers to ensure their siloxanes are below a certain concentration before the gas can be injected into a distribution system. Two examples are PG&E's Rule 21 and SoCalGas' Rule 30. Both set 0.1 mg Si/m3 for the "lower action level" and 0.01 mg Si/m3 for the "trigger level" of siloxanes in RNG. These levels are used to define specific frequencies and testing requirements for biomethane derived from various sources.

Until recently, no standardized protocol existed for dependable measurement of the 0.1 mg Si/m3 specification. To address this, ASTM Method D8230-19 was recently created. It lists gas chromatography — atomic emission detector (GC-AED), gas chromatography — mass spectrometry (GC-MS), and inductively coupled plasma mass spectrometry (ICP-MS) as suitable methods for laboratory analysis of samples collected from biogas/RNG production facilities. Although a small number of commercial labs have started reporting limits that can meet the requirements described in rules 21 and 30, most cannot.

In addition to the difficulty of accurately measuring siloxanes, there are also problems with the common methods of sample collection. With Tedlar bags or passivated stainless steel canisters, less volatile siloxanes like D4 and D5 — the majority of siloxanes in landfill and digester gas — may adhere to the interior, leading to low-measurement bias. In addition, siloxane recoveries can degrade rapidly in Tedlar bags, which is why ASTM D8230- 19 requires analysis within 72 hours. Finally, some Tedlar bags may contain silicone-based lubricants in the valve stem, leading to high-measurement bias.

While sorbent traps have the potential to be the ideal sampling method, the ASTM method calls for sample extraction using methylene chloride, but there are concerns regarding matrix interferences from the extraction solvent and the sorbent material itself. A user-friendly sampling technique and thermal desorption method for siloxane sorbent traps is now being developed and will be presented to the ASTM D03 committee for inclusion in D8230-19.

Given these challenges, the future is a continuous online analyzer. An analyzer utilizing gas chromatography coupled with an ion mobility spectrometer (GC-IMS) applies two dimensions of separation to the constituent compounds, providing excellent sensitivity for every siloxane species, and reporting speciated and total siloxane measurement data without matrix interferences.

With the GC-IMS, a biogas or RNG supplier will be able to comply with utility interconnection rules while also optimizing scrubber material replacement.

For more information, visit www.ohiolumex.com/bic-siloxanes.