Real-time formaldehyde monitoring from natural gas-fired turbines

Natural gas-fired turbine engines are a source of formaldehyde which has been recognized as a known human carcinogen by the International Agency for Research on Cancer as well as the US Department of Health and Human Services. As such, regulations require gas-fired turbine engines to be periodically monitored by emission testing firms.

The US Environmental Protection Agency (EPA) Stationary Combustion Turbine Regulation (40 CFR Part 63 Subpart YYYYY) requires this type of turbine to limit formaldehyde emissions to 91 ppbvd or less at 15% O₂. Gas turbine manufacturers go to great lengths in their combustion “hot section” design to minimize formaldehyde emissions, and the formaldehyde concentration levels continuously emitted from these sources are generally low (around 0.1 ppmv). However, the volume of exhaust gas from gas turbines is quite large, and that exhaust can cause the total mass of the pollutant to be significant enough to pose a hazard to human health.

Measurement challenge
Source testing professionals require an analytical technology that can measure < 91 ppbv formaldehyde precisely from a natural gas-fired turbine in real-time. FTIR gas analyzers following EPA Method 320 in some configurations can reach this low level, but the analyzers often don’t have the precision to accurately measure formaldehyde emission. EPA Method 0011 is also utilized, and it requires the use of collection impingers, a derivatizing reagent [2,4-dinitrophenylhydrazine (DNPH)], followed by high pressure liquid chromatography (HPLC) with UV-Vis detection which lacks precision and is also not a real-time measurement. This application needs a real-time analysis methodology with single digit ppb detection limits to be efficient.

Solution
The Thermo Scientific™ MAX-iR™ FTIR Gas Analyzer with an optical enhancement called Thermo Scientific™ StarBoost™ Technology can meet this challenge. StarBoost technology significantly increases the sensitivity, detector linearity and dynamic range of the FTIR gas analyzer. This breakthrough technology allows for single digit ppbv detection of hazardous air pollutants (HAPs), such as formaldehyde, in real-time.

A MAX-iR analyzer with StarBoost technology employs a longpass optical filter that allows the measurement of compounds from 1,900 – 3,300 cm⁻¹. This filter system can simultaneously measure hydrocarbons and other oxygenates including CO, CO₂, CH₄, and H₂O.

In addition to the MAX-iR analyzer with StarBoost technology, a novel technique exists for zeroing the analyzer using stack emissions. The Thermo Scientific™ MAX-OXT Thermal Oxidizer Module selectively removes the target analyte from the sample matrix without reducing the concentration of atmospheric interferences such as H₂O, CH₄, and CO₂. This allows for the collection of an interference spectrum which can be added to the regression in real time to improve the IR residual and formaldehyde data quality. Even if the interference spectrum is not used in the regression is the MAX-OXT module is a powerful tool for data validation.
Figure 1: Formaldehyde measurements collected in the field from a natural-gas fired turbine engine.

Experimental
To demonstrate the ability of the MAX-iR analyzer with StarBoost technology to measure formaldehyde emissions, data was collected from a natural gas-fired turbine. Data were periodically zeroed using the MAX-OXT module. When switching between MAX-OXT oxidation and sample gas, the response time is <15 seconds at 5LPM sample flow, allowing for rapid detection of formaldehyde. Results from the field test are shown in Figure 1.

The plot in the upper left panel shows the concentration of formaldehyde (in ppb) during the data collection period. For the selected sample spectrum, indicated by the green hashed line, the formaldehyde concentration was 13.98 ppb. This application utilized a MAX-OXT module to periodically remove the formaldehyde from the sample and collect interference spectra, as shown in the concentration plot. When these spectra are added to the regression matrix, the formaldehyde concentration can be easily validated down to 10 ppb. This technique minimizes bias in the formaldehyde measurement due to spectral interference, which is critical for accurately measuring compounds on a 10-ppb scale.

The standard deviation on the formaldehyde measurement was 1.37 ppb, meaning the minimum detection limit for this test was 4.11 ppb. At a concentration of 13.98 ppb, the formaldehyde is visible in the regression reconstruction.

Conclusion
This note shows that the MAX-iR analyzer with optional StarBoost technology can measure low ppb levels of formaldehyde from gas-fired turbine engines. The ease of sampling and data flow allow for increased efficiency for this measurement compared with EPA Method 0011. Whereas it previously could take hours for a result, it now can be performed in minutes, saving the source tester time, aggravation and money. In addition, the heightened precision of the enhanced analyzer assures the tester and the client that the result will truly reflect the actual formaldehyde levels sampled during the test.