On-site Monitoring of Formaldehyde in Gas Fired Turbines

Background

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 U.S. Department of Health and Human Services. As such, these sources need to be periodically monitored by emission testing firms. Gas turbine manufacturers go to great lengths in their combustion "hot section" design to minimize their formaldehyde emissions. The formaldehyde concentration levels continuously emitted from these sources are generally low, on the order of 0.1 ppmv. However, the volume of exhaust gas from gas turbines is quite large, which can cause the total mass of the pollutant to be significant.

Problem

Emission testing professionals require a technology that allows them to determine formaldehyde at or below 0.1 ppmv in the field where the gas fired turbine is located. Periodic testing follows Title V of the Clean Air Act of 1990 (operational permits) and usually occurs at 3-5 year intervals from the date of initial start-up. Formaldehyde sampling and analysis methodologies typically follow EPA Method 0011, which requires the use of collection impingers, a reacting reagent [2,4-dinitrophenylhydrazine (DNPH)], high pressure liquid chromatography and UV/Vis instrumentation. This is a very cumbersome and involved methodology to do easily and quickly on site. Due to its sampling and analytical complexity, numerous potential sources of error exist creating a need for a rugged, direct and sensitive technology which can allow for rapid detection and quantification of formaldehyde in the field.

Solution

MAX Analytical Technologies has developed a new analytical technology, MAX™, which is designed for field analysis on complex analytical samples. MAX combines the separation power of gas chromatography with the identification and quantitative analysis power of absorption spectroscopy. Prism's initial system couples a thermal desorption tube sampler/desorber to a gas chromatograph for chromatographic separation. The GC eluents then are directed into a FTIR gas analyzer for spectroscopic analysis. MAX incorporates a patent-pending technology where the eluting gases are drawn and trapped within a multiple-pass gas cell for extended measurement. The multiple-pass cell, along with spectral time averaging, can generate very low detection limits. In addition, this design allows for constant instrument-to-instrument calibrations where the GC does not affect the calibration, and the system requires only a nitrogen carrier gas.

To gain the extra sensitivity necessary for low ppb detection, a slipstream of the turbine exhaust is pulled and collected on a concentrating Thermal Desorption Tube (TDT) designed specifically for formaldehydes. The sampling time is normally in the 10 to 20-minute range but could be longer or shorter depending on the sampling method requirements.

The sample is then quickly desorbed by rapid heating of the TDT and passed to the GC. The GC can then be operated in two different modes depending on the sample matrix:

1. **Fast Mode** - Run the GC at high temperature to get the Formaldehyde through quickly and get a measurement within 10 minutes.
2. **Normal Mode** - Run through a normal GC setup to separate all the VOCs from the formaldehyde.

Reference spike testing for formaldehyde can also be achieved in the field without the need for multiple cylinders. The customer and source tester no longer need to procure and analyze all calibration cylinders, saving both time and money.

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In a typical field run, two thermal desorption tubes are attached and exposed to the input stream. One tube has been spiked with a known concentration of formaldehyde whereas the other is not spiked. After the analysis has been completed, the difference in the two concentrations is subtracted and the difference should be nearly equivalent to the amount initially spiked. Any deviation from 100% spike recovery is used to correct the overall observed concentration to a calculated initial sampled concentration. A concentrating factor, determined by the ratio of how many volumes of exhaust gas were sampled to the volume of the FTIR gas cell, is used to back out the original concentration of the formaldehyde in the exhaust stream. Since these factors can be many fold, this implies a detection much lower than what the FTIR is reporting, which can easily be in the ppb detection limit range.

Results of actual field test on a natural gas fired turbine exhaust show the raw MAX analyzed spiked and un-spiked formaldehyde levels and the resulting calculated formaldehyde concentrations after correction for recovery from the TDT (all values are in ppmv, dry corrected). The average recovery levels and the average stream concentration are presented in bold.

	Run 1	**Run 2**	**Run 3**	**Average**
Spike (ppm)	1.783	1.833	1.877	
Sample (ppm)	1.108	1.103	1.153	
Spike - Sample (ppm)	0.675	0.73	0.724	
Spike Recovery (%)	92.98%	100.55%	99.72%	**97.75 ± 4.15%**
MAX Concentration (ppm)	1.108	1.103	1.153	
Stream Concentration (ppm)	0.0736	0.0733	0.0766	
Stream Concentration [Recovery Corrected] (ppm)	**0.0792**	**0.0729**	**0.0768**	**0.0763 ± 0.003**

Rear of MAX™ analyzer showing the TDT Sample Manifold and MAX™ Desorber