2.8 Process Monitoring and Control: Ammonia Measurements in Offgases

Technology Need

Ammonia is released during the sluicing removal of Hanford tank wastes and processing of high-level wastes in the Savannah River Site (SRS) Defense Waste Processing Facility (DWPF) offgases. On-line measurements of ammonia are needed to provide operational control, enhance worker safety, and to assure that the release of ammonia will not exceed regulatory limits. Several commercially available techniques have been tested; however, none of these have been proven to be sufficiently robust to monitor ammonia reliably in the presence of high moisture contents typical of both Hanford and SRS operations.

Technology Description

In support of the Tank Focus Area, this project is developing and applying tunable-diode-laser (TDL) absorption spectroscopy as a continuous monitor for ammonia in offgases from SRS and Hanford tank wastes. This technology is also applicable to monitoring offgases in thermal treatment processes that are utilized in the MWFA.

The robust instrument developed by this project will provide on-line ammonia detection that is (1) sensitive, (2) stable, (3) capable of operation at high temperatures in a radiation environment, and (4) not affected by the presence of high concentrations of water vapor and carbon dioxide in the offgas stream.

The method detects gaseous ammonia using optical absorption by vibrational transitions in molecular overtone and combination modes at wavelengths near 1.55 micrometers. The sensitivity of the near-infrared TDL to ammonia is greatly enhanced by a proprietary method involving high-frequency modulation of the laser beam and phase-sensitive detection. The ultra-high resolution characteristics of the TDL source permit the separation of ammonia absorption features from nearby spectral lines, due to either water vapor or carbon dioxide. This is a very large advantage when compared with lower resolution optical techniques, such as ultraviolet absorption spectroscopy, Fourier transform infrared spectroscopy, or nondispersive infrared analysis.

Diode lasers are extremely compact, robust, solid-state devices. Their development by the semiconductor industry allows them to be manufactured by mass production methods, thus greatly reducing the cost of individual diode lasers. Operation in the near-infrared wavelength region permits direct coupling of the laser output into optical fibers, which facilitates transmission of the laser beam and alignment with the off-gas stream or extractive sampling volume. This feature also permits the location of laser and electronic modules

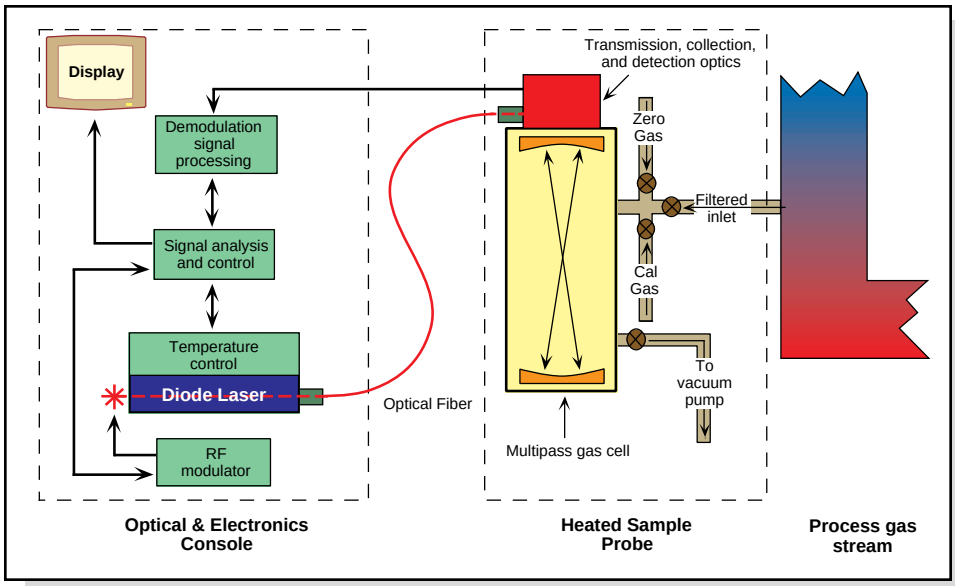

Figure 2.8-1 Experimental layout for the real-time ammonia monitor based on tunable diode laser spectroscopy.

at a safe distance from toxic, hazardous, or radioactive sources. A schematic diagram shown in Figure 2.8-1 illustrates the characteristics of the TDL-based monitor.

Benefits

The benefits of near-infrared TDL instrumentation for ammonia monitoring in waste tank treatment are numerous: (1) unambiguous identification of ammonia, even in high moisture and carbon dioxide environments; (2) rapid data acquisition and analysis for process control and demonstration of regulatory compliance; (3) low-cost optical and electronic hardware; (4) physically robust components; and (5) possibility of remote sampling. Real-time analysis for process control can reduce downtime for cleaning by increasing operational efficiency. It can also reduce the time required for regulatory compliance checking and permitting.

Collaboration/Technology Transfer

Throughout this project, we are working closely with Spectrum Diagnostix (SDx). SDx is currently commercializing an instrument for ammonia detection based on TDL spectroscopy for application in the commercial power-generation industry. We are conducting the research and development necessary to adapt this technology for DOE waste management processes, and to facilitate its rapid commercialization.

Accomplishments

- SDx tested a TDL ammonia monitor on a continuous basis at three commercial electric power generation plants during FY95. Continuous monitoring of ammonia was done in conjunction with the operation of NOx suppression hardware on gas streams saturated with water vapor and with high concentrations of carbon dioxide. Results demonstrated sub-ppm sensitivity that compares well with independent wet chemical analysis.
- During FY95 we were supported by the Mixed Waste Focus Area in an effort to develop a TDL-based monitor for volatile organic compounds (VOCs). During this period we measured near-infrared survey spectra and ultrahigh-resolution TDL absorption spectra in the 1.65-μm wavelength region for a number of small inorganic molecules and VOCs. For a TDL-based VOC monitor, we estimate good sensitivity for methane, chloromethane, dichloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, and vinyl chloride, in addition to ammonia.
- We have established technical contacts at SRS and made plans for initial testing of the TDL-based ammonia monitor on their pilot-scale facility while the construction of the DWPF is completed. Laboratory tests are underway to evaluate potential interference from major species in the process offgas.

TTP Information

Process Monitoring and Control: Ammonia Measurements in Offgases technology development activities are funded under the following technical task plan (TTP):

TTP No. AL36C216 "Process Monitoring and Control: Ammonia Measurements in Offgases"

Contacts

Dr. David K. Ottesen
Principal Investigator
Materials Chemistry Department
Sandia National Laboratories
P.O. Box 969, MS-9403
Livermore, CA 94551-0969
(510) 294-3567

Dr. Sarah W. Allendorf
Principal Investigator
Combustion Research Department
Sandia National Laboratories
P.O. Box 969, MS-9052
Livermore, CA 94551-0969
(510) 294-3379
swallen@sandia.gov

Allendorf, S.W., D.K. Ottesen, and M.B. Frish. "Tunable Diode Lasers: A New Tool for Continuous Emissions Monitoring and Process Control in Thermal Treatment Processes," P*roceedings for the* I*nternational* I*ncineration* C*onference*, Seattle, WA, pp. 137-140 (1995).

Allendorf, S.W., and D.K. Ottesen. "Continuous Monitoring of VOCs Using Tunable Diode Lasers," FY95 Final Report, DOE's EM-50 Mixed Waste Focus Area (1995).