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Process Monitoring and Control: Ammonia Measurements in Off-gases

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Process Monitoring and Control: Ammonia Measurements in Off-gases

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ABSTRACT

This interim report describes technical progress in the development of a laser-based, real-time optical monitor for ammonia in off-gas streams from defense waste processing applications at the Savannah River Site (SRS). An optimized monitor has been fabricated by Spectrum Diagnostix using a tunable diode laser operating in the 1.55- μm wavelength region. Instrument detection limits of 2-3 ppm for ammonia are demonstrated that are more than adequate for the SRS required sensitivity of 10 ppm. Laboratory research at Sandia revealed a lack of interference at the operating wavelength by other molecular species that might be present in the SRS off-gas stream.

Initial tests of the ammonia monitor by Sandia were conducted at SRS using a bench-scale processing system for surrogate defense waste sludges. The results of these experiments confirmed that ammonia concentrations issuing from the ammonia-scrubber section of the bench-scale reactor were below the design limit of 10 ppm. We also found that no other molecular species in the off-gas produced observable false-positive readings from the monitor.

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INTRODUCTION

This document reports progress in the development and field testing of an optimized continuous emission monitor for ammonia in the off-gases from defense waste processing operations at the Savannah River Site (SRS), and completes milestones 36C216D1 and E1 of Technical Task Plan AL3-6-C2-16.

The development of this monitor has been funded by DOE / EM-50 through the Characterization, Monitoring and Sensing Technology crosscutting program (CMST) for the Tanks Focus Area (TFA). Sandia National Laboratories (SNL / CA) has led the technical development of the project, working closely with a small commercial instrument manufacturer, Spectrum Diagnostix (SDx), who is currently commercializing an instrument for ammonia detection based on tunable diode laser (TDL) spectroscopy for use in the commercial power generation industry.

The application for TDL technology in the current project is the continuous monitoring of ammonia in the effluent from the Defense Waste Processing Facility (DWPF) process at SRS. Ammonia is released during the processing of high-level wastes in this facility, and on-line measurements are needed to provide continuous assurance of appropriate ammonia scrubber operation. Excess ammonia in the off-gas exiting the scrubber presents a potential operational problem due to condensation of solid ammonium salts in the downstream section of the processing facility. Consequently, a highly sensitive method is required to detect ammonia concentrations in the post-scrubber off-gas above 10-ppm. In order to respond to possible incipient scrubber breakthrough events in a timely fashion, the ammonia monitor must also possess a time response of 10-seconds, or less.

During the performance of this project, SRS provides both bench-scale and pilot-scale facilities for processing surrogate defense waste sludges. These experimental facilities are used to design and evaluate processing methods at the full-scale DWPF for the wide range of waste materials to be treated at SRS. Following initial laboratory evaluations of the TDL monitor at Sandia, experiments will be performed at SRS using the bench and pilot scale facilities to integrate this monitoring technology into the SRS waste processing engineering protocols.

Sandia's role in this project is to assess the technical feasibility of the near-infrared TDL spectroscopic method for ammonia detection in defense waste processing applications. Since the instrument developed by SDx is configured for ammonia detection in atmospheres produced by commercial power-generation, significant technical issues remain to be addressed with respect to potential interfering species and resulting sensitivities when this method is applied to an off-gas stream from processed defense waste.

SDx provides the commercial laser-based ammonia monitor for this project and supports the installation, personnel training, and operation of the monitor at SRS. In addition, if potential difficulties are discovered in the application of this method to off-gas ammonia detection, SDx will work with both Sandia and SRS to find and implement engineering solutions.

Several commercially available monitoring techniques have been tested, however none have proven to be sufficiently robust to monitor reliably the required low ammonia concentrations in the presence of high moisture contents typical of the SRS operation on the near-real-time scale required. The development of a TDL-based ammonia monitor addresses the Tanks Focus Area (TFA) need for a robust, on-line method for ammonia detection. The technique is sensitive, stable,

capable of operation at high temperatures in a mild radiation environment, and not affected by the presence of high concentrations of water vapor and carbon dioxide in the off-gas stream.

TDLs are extremely compact, robust solid-state devices. 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 at a safe distance from toxic, hazardous, or radioactive sources.

Key intermediate steps in the development and application of this technology are: (1) preliminary laboratory R&D at SNL/CA to demonstrate technical feasibility; (2) acquisition and optimization of the monitor hardware and software; (3) on-site testing of the monitor for a bench-scale surrogate sludge processing operation at SRS; and (4) interfacing and testing the ammonia monitor with a pilot-scale surrogate sludge processing facility at SRS.

The first three activities have been largely completed during FY96 and will be discussed in this report. A new pilot-scale sludge processing facility at SRS has been approved and is expected to be on line early in CY97. Testing an optimized ammonia monitor with a multi-probe measurement system on this pilot-scale facility will form the focus of our work in FY97. Successful completion of our technical task plan in FY97 will lead to a transfer of this monitoring technology to SRS, and its incorporation into the DWPF by SRS.

Under support from EM-50, laboratory work at SNL/CA was conducted using existing prototype TDL monitors to determine the feasibility of this technology for ammonia monitoring in the off-gas streams characteristic of defense waste processing streams at SRS. In particular, we searched for possible interference effects that could result from the large variety of gas-phase species produced during the complex series of sludge processing reactions.

Following favorable laboratory results, a dedicated ammonia monitor was purchased from SDx during FY96. Only minor changes from its commercially available format were required to optimize it for the initial tests, and the hardware was installed for field testing at a bench-scale reactor at SRS. In these tests the instrument was interfaced with the effluent from a bench-scale off-gas generation system in which a simulated DWPF sludge was processed. Two complete sludge processing cycles were observed over the course of several days with the ammonia monitor.

The initial test results were very promising and indicated ammonia concentrations in the gas stream below the detectability limit of the monitor at all times ($\pm 2-3$ ppm). This detection level is consistent with anticipated instrument performance. It also meets the SRS ammonia sensitivity (detectability of <10 ppm) and time response (<10 seconds) requirements for the sludge processing output stream following the ammonia scrubber. Furthermore, no interferences were observed in the monitor operation due to other molecules present in the gas stream.

An additional experiment was performed to assess the ammonia monitor sensitivity along with the effectiveness of the bench-scale system ammonia scrubber. Although we continued to observe no interferences in the monitor operation, the deliberate injection of ammonia-containing purge gas into the complex process-flow substantially altered the standard bench-scale system operation, and no conclusive results were obtained. Frequent calibration checks of the monitor during both sludge processing cycles and the ammonia scrubber experiment demonstrated conclusively that the monitor was responding to the presence of ammonia above its lower detection limit ($\pm 2-3$ ppm).

Construction of the new SRS pilot-scale facility will permit interfacing the TDL-based ammonia monitor in a manner that avoids upsetting gas flow rates and pressures encountered in the bench-scale experiments, and will be the ideal venue for completing these tests. During FY97, the monitor will be installed and tested at the pilot-scale facility of the DWPF for continuous ammonia monitoring, including training facility personnel in its operation. The successful conclusion of this project will result in the transfer of the ammonia monitor to SRS for incorporation into the DWPF for permanent use.

BACKGROUND

The choice of a TDL-based monitor for ammonia detection in this project was based on an extensive comparison with other analytical methods and an independent review committee constituted by DOE / EM. A TDL-based monitor detects ammonia in real-time using optical absorption by vibrational transitions in overtone and combination modes at wavelengths near 1.55 micrometers [1-4]. Near-infrared distributed-feedback diode-lasers emit extremely narrow, single-mode radiation that can be tuned without mode hops across ammonia absorption lines by varying injection current or device temperature near room-temperature. The sensitivity of the near-infrared TDL method to these species is greatly enhanced by high-frequency modulation of the laser beam and phase-sensitive detection. The ultrahigh resolution characteristics of the TDL source permit the separation of ammonia absorption features from nearby spectral lines due to other infrared absorbing gas-phase species.

Traditional methods for ammonia analysis based on sample extraction and wet chemistry are unsuitable for the SRS application due to both inordinate manpower requirements and slow time response. An optical method based on ammonia detection in the ultraviolet region was attempted and rejected by SRS due to poor sensitivity and interference with other absorbing species. An alternative optical method for ammonia detection based on infrared absorption in the 10.6- μm wavelength region has been developed using a line-tunable CO_2 laser source. A commercial instrument based on this approach is available, but was judged to be less suitable for the SRS application for two principal reasons: (1) the limited number of CO_2 laser lines coincident with ammonia vibrational transitions makes this approach more vulnerable to interferences from other absorbing species in the off-gas when compared to a continuously tunable TDL source; and (2) the requirement for close-coupling the CO_2 laser output beam with the measurement volume is a distinct disadvantage for the radioactive environment of the DWPF in contrast with a fiber-optically coupled TDL monitor that can be located at a safe distance from toxic, hazardous, or radioactive sources. Finally, the ultrahigh spectral resolution characteristics of a TDL-based monitor renders this method superior to lower resolution optical techniques such as Fourier transform infrared (FTIR) spectroscopy, or non-dispersive infrared (NDIR) analysis [5], for sample streams containing large concentrations of water vapor and carbon dioxide.

Spectrum Diagnostix, the commercial supplier of the "SpectraScan" near-infrared TDL ammonia monitor, has tested this device on a continuous basis at three commercial electric power generation plants during FY95. A general equipment layout of the monitor for real-time measurements using a multi-pass extractive gas cell is shown in Figure 1.

Figure 1. Experimental layout of a continuous, real-time TDL-based ammonia monitor in an extractive sampling multipass gas-cell configuration.

Continuous monitoring of ammonia was done in conjunction with the operation of NO_x suppression hardware on gas streams saturated with water vapor and with high concentrations of carbon dioxide. Results demonstrated ppm sensitivity that compares well with independent wet chemical analysis. Figure 2 demonstrates the results obtained during one series of field trials, when the selective non-catalytic reduction (SNCR) system was functioning erratically. The response of the TDL-based CEM compares favorably with the labor-intensive wet-chemical measurements that were also performed during these field tests. It is apparent that the wide variation in ammonia slip cannot be followed in real-time by the wet-chemical sampling technique, while the continuous nature of the TDL technique does reveal ammonia fluctuations with a response time of less than 10 seconds.

In order to extend this technology to ammonia monitoring for DOE / EM waste processing applications, two different approaches to off-gas measurement are possible: extractive and in-situ modes. In this work we use the extractive method employing a multipass gas cell at temperatures above 200°C in order to avoid the formation of condensable particulate material. This approach lends itself well to accurate, reproducible instrument calibration and ease of optical alignment. In addition, reducing the total pressure within the sampling cell to 200-torr narrows the molecular absorption lines sufficiently that spectral interference from water vapor and carbon dioxide is eliminated.

In-situ measurements, although possible, are more difficult to quantify since no direct calibration along the measurement line-of-sight is possible. Despite the very narrow linewidth of tunable diode laser sources, measured intensities of ammonia lines are affected by spectral overlap with water vapor and carbon dioxide absorption lines at ambient pressure due to collisional broadening of the

Figure 2. Field results of SDx "SpectraScan" ammonia monitor recorded during testing of SNCR system at Salem Harbor Power Station.

molecular absorption lines under these conditions. In-situ measurements must also take into account the effects of both temperature and pressure on ammonia absorption line shapes.

We are actively pursuing in-situ line-of-sight TDL absorption methods for real-time monitoring of major gas-phase species in other process-control applications. However, the combination of ambient pressure, relatively low temperature, high concentrations of CO_2 and H_2O , and the low target concentration of ammonia in the SRS off-gas matrix severely limits the accuracy and sensitivity of an in-situ line-of-sight measurement for this specific application. The virtue of minimal sample handling by using in-situ techniques may be severely compromised, and was thus rejected as the off-gas sampling method of choice.

LABORATORY RESEARCH AND DEVELOPMENT

A laboratory feasibility study was conducted in order to begin adapting a commercial TDL-based ammonia monitor for combustion environments to the needs of DOE / EM waste processing applications. Of major concern was the possible presence of additional gas-phase molecules in the Savannah River Site off-gas streams that possess absorption lines overlapping significantly with the selected ammonia-monitoring line near $1.55\text{-}\mu\text{m}$ wavelength. Although many of the potential interfering species were eliminated as problems during the commercial development of the monitor by SDx (CO_2 , H_2O , NO , NO_2), several additional species were known to be present in the waste processing off-gas. Most critical are the smaller molecular species that possess absorption line widths of less than 0.1 cm^{-1} at a temperature of 200°C and pressure of 200 torr. In particular, we

examined the absorption spectrum of N_2O and formic acid in the $1.55\text{ }\mu\text{m}$ wavelength region to test for possible interference.

These absorption spectra were evaluated using prototype TDL spectrometers obtained from SDx and equipped with a distributed-feedback diode-laser module with a nominal cw-output power of 5-mW. The laser is temperature stabilized using a Melles-Griot thermoelectric cryostat module, and coarse wavelength tuning is obtained by adjusting and equilibrating the laser-diode temperature. The total available temperature tuning range for this device is on the order of 4 nm (18 cm^{-1}). High-resolution wavelength tuning of the diode laser is done by varying the diode injection current using either internal or external function generators. Reasonably linear wavelength output scans with input drive current are obtained over a few tenths of wavenumbers by this method, and are used to map out the shape of the gas-phase absorption lines under study.

A "triangular ramp" function of drive current is most commonly used. Since the laser output from the diode increases with increasing drive current, a characteristic triangular output amplitude is obtained that simplifies the calibration of a spectral wavelength scale. Typical ramp scanning frequencies of 100 to 1000 Hz are used in this work. Superimposed on this linear tuning function is a high-frequency, 1-MHz sine wave with independently variable amplitude. The detected laser signal following absorption by the gas-phase is analyzed at the second harmonic 2-MHz frequency to provide high-sensitivity phase detection and wideband noise rejection. This process is key to the very low detection limits afforded by TDL-based instrumentation (<1 part in 10^5 absorbance).

Finally, a 256-kHz analog/digital data acquisition system is used to collect the spectral information using precision delay generators to synchronize the computer sampling time with the TDL tuning function. The data acquisition system and its software were constructed at Sandia, and permit the flexible time-averaging of both direct absorption and second-harmonic absorption signals, their manipulation and their storage.

This laboratory approach to TDL spectroscopy is quite distinct from the intended operation of the ammonia monitor in the commercial SDx instrument. The ammonia monitor is constructed with a second high-frequency modulation at 10 kHz, and is constrained to be wavelength-locked to the desired ammonia absorption line using a proprietary process. Modulation amplitudes of the 10-kHz and 1-MHz frequencies are optimized for ammonia absorption line widths at 200 torr and 200°C , and the absorbed laser light signal is doubly demodulated at the second harmonics of both frequencies. Additional signal processing results in a DC signal output with a time constant of 1-Hz proportional to ammonia absorption. Straightforward calibration with a certified span gas of ammonia in nitrogen is then used to quantitatively extract ammonia concentration for the unknown sample.

One can readily appreciate that this monitoring method depends critically on a precise knowledge of the absorbing species in the immediate wavelength region of the desired ammonia absorption line. Should additional absorption lines appear due to new and unexpected molecular species, the effects on the DC signal output would be very difficult to discriminate against absorption by varying concentrations of ammonia. For this reason, a laboratory study using a spectroscopic method was crucial to characterize the wavelength region immediately surrounding the selected analytical ammonia transition.

For this work we used a Herriott multi-pass gas cell with an effective absorbing pathlength of 20 meters. Controlled gas atmospheres are admitted to the cell at pressures from 2 to 760 torr, and for this study were maintained at ambient temperature. In Fig. 3 we present the absorption spectrum of

ammonia at 1040-ppm in nitrogen at a pressure of 20 torr (dashed curve). The single strong absorption feature is the desired analytical transition used by the SDx ammonia monitor. The distinctive second-derivative lineshape is due to signal processing by the lock-in amplifier at the 1-MHz modulation frequency.

The solid curve in Fig. 3 is a spectrum measured in the same gas cell with 20 torr of pure N_2O . The total tuning range of this diode laser with respect to the central ammonia absorption line is approximately $\pm 0.15 \text{ nm}$ ($\pm 0.6 \text{ cm}^{-1}$). The addition of pure N_2O to the gas cell produces two strong and two weak absorption features, well removed from the desired ammonia absorption line. The excellent spectral separation of these lines indicates that nitrous oxide will not be an interfering species for ammonia monitoring at Savannah River. Further immunity from interference is conferred by the artificially high concentration of pure N_2O added to the cell compared to expected transient concentrations on the order of hundreds of ppm.

Characterization of sludge-processing off-gases at Savannah River has also revealed occasional production of formic acid at concentrations up to 100 ppm. This small, asymmetric gas-phase molecule may have a very rich, complex absorption line spectrum in the $1.55\text{-}\mu\text{m}$ region due to both O-H and C-H overtone vibrations, and could lead to interference with the target ammonia monitoring line. Quantitative investigation was hampered by a lack of certified gas mixture standards, and in order to proceed, we initiated laboratory studies using the equilibrium gas-phase overpressure from pure formic acid.

Figure 3. Long-pass gas-cell measurements of 1040 ppm NH_3 diluted in N_2 (dashed curve) and pure N_2O (solid curve), both recorded at 20-torr cell pressure.

Approximately 3 torr of formic acid vapor were transferred to our 20-m multipass gas cell for examination. Nitrogen was then introduced to bring the total cell pressure up to 20 torr, and the spectral results are presented in Fig. 4 as the solid curve. For comparison, the dashed curve shows the absorption spectrum of 1024-ppm ammonia in nitrogen, also at a pressure of 20 torr.

The formic acid absorption spectrum is very rich, and shows the presence of two small transitions on either side of the ammonia line. Further pressure broadening of these absorption lines will occur at the normal operating cell pressure of 200 torr, and will almost certainly cause some spectral overlap of the two formic acid absorption lines with the ammonia absorption line. The effect will be negligible, however, due to the relative concentrations of the components shown in Figure 4.

To estimate the upper limit of this interference, we first note that the noise-equivalent detection limit for the ammonia monitor as configured for SRS is ± 2.5 ppm, corresponding to a detected signal level of 5 mV. The formic acid absorption line strengths in Figure 4 can be converted to the expected maximum concentration of 100 ppm, using a linear relation between detected signal level and gas concentration. For the stronger formic acid transition located at -0.05 cm^{-1} relative to the ammonia absorption line, we calculate a maximum signal strength of less than 1 mV. Any interference at the ammonia line center will be far less than this value, and will be undetectable.

Figure 4. Long-pass gas-cell measurements of 1040 ppm NH_3 in N_2 (dashed curve) and 15% formic acid in N_2 (solid curve), both recorded at 20-torr cell pressure.

No other small molecular species have been identified as potential interferents for a TDL-based ammonia monitor. Larger molecular species (primarily complex mixtures of volatile organic compounds, VOCs) are expected to be present in the off-gases at varying concentrations. However, previous work at Sandia [5] has shown that the wavelength modulation technique used in TDL-based monitors is extremely effective at discriminating against spectral interference caused by broad-band absorption of all but the smallest VOCs.

In spite of the positive results from our feasibility studies, it is possible that unknown molecular species with either narrow or broad band absorptions may interfere with the performance of the ammonia monitor, as it is currently configured. Our investigations lead us to believe that any such interference will be small, if not entirely negligible. However, this remains to be demonstrated in FY97 at Savannah River by ammonia monitoring during sludge surrogate processing, which will include direct comparisons of the TDL-derived data with concurrent independent ammonia analyses.

To complete our survey of possible small molecular interferents for ammonia monitoring, we are beginning an investigation of the absorption spectra of gas-phase nitric acid, a common reagent in the Savannah River sludge treatment process. We anticipate that sample introduction will be similar to the studies on formic acid, although considerably more complex and time consuming. Spectral characterization of nitric acid in the 1.55- μm region will be completed early in FY97.

AMMONIA MONITOR ACQUISITION AND OPTIMIZATION

The very favorable results of our laboratory work encouraged us to accelerate the project schedule for monitor hardware acquisition. In view of the lack of interfering species for the optical measurement, the current SDx commercial ammonia monitor format was purchased with a consequent large savings in research and development time that would have been necessary to identify an alternative analytical absorption line for ammonia.

Ammonia Monitor Hardware

An optical console was purchased containing a 1.55- μm TDL unit capable of temperature and injection current tuning. Output from the laser is directly coupled into a fiber optic, and subsequently split to four output ports, capable of measuring ammonia concentrations simultaneously at four remote locations. Four signal processing units are incorporated into the optical console to demodulate, process, and amplify the TDL signals at the four measurement locations. For the experiments conducted in FY96, only a single fiber optic output channel was used, as described below.

A fifth fiber optic element directs a small amount of the 1.55- μm laser light to a reference gas cell containing an ammonia / air mixture. An independent detector and signal processing electronics assembly are used in conjunction with this cell to measure a constant ammonia absorption signal. Laser tuning parameters are continuously adjusted under software control to ensure that the emitted laser wavelength is precisely centered on the desired ammonia absorption line center for all measurement locations.

Other components of the optical console are on-board microprocessors for data acquisition, analysis, storage and control functions. Ammonia concentrations are presented in real-time at a selectable rate up to 1-Hz, and stored on hard disk for archival purposes. Precision waveform generators are used for producing dual high-frequency TDL modulation functions at 10 kHz and 1 MHz. Finally, a variety of power supplies, solid-state relays, and heater controllers are used to power the console and external measurement probe modules.

Ammonia Measurement Probe

A single ammonia measurement probe was also acquired from SDx early in FY97. This unit consists of an insulated, temperature- and pressure-controlled Herriott multi-pass gas cell with an effective 10-m absorbing pathlength. A standard operating pressure of 0.25 atm is provided by restricting the cell input line and pumping on the cell output with a vaneless-bellows vacuum pump. Constant temperature control is maintained with solid-state heaters controlled by the optical console.

Laser light at 1.55- μ m wavelength is transmitted from the optical console to the measurement probe via single-mode optical fibers. With these fibers, the optical console and measurement probe can be separated by as much as 1 km. Modulated detector signals from the probe are returned to the optical console via coaxial cable for demodulation and processing. Substantial phase shifts may occur in these signals as a result, and these are compensated by adjustments in the signal processing modules at the optical console for each independent detector.

The available dynamic range for ammonia monitoring has proved to be about 500:1 for current SDx hardware. Practical upper and lower concentration limits range between 50,000 and 2.5 ppm, and are selectable by a combination of optical pathlength adjustment, detector gain and high-frequency modulation amplitude characteristics. Stated accuracy is $\pm 10\%$ of the reading or the minimum sensitivity, whichever is greater.

In addition to the sample inlet and vacuum-pumped outlet, the measurement probe is plumbed with inlets for the introduction of calibration gases. Separate vacuum lines are provided for a zero gas (typically nitrogen) and a span gas (typically ammonia in nitrogen at a nominal concentration of 50 ppm). All three inlet lines and the outlet line are controlled by electrically operated valves that can be operated either manually or by the monitor microprocessor software.

The commercial form of the SDx ammonia monitor includes a heavy-duty, insertable probe for gas extraction in a highly particulate-laden combustion gas. The probe is equipped with a sintered stainless steel tip for particulate removal. In order to periodically remove accumulated soot and ash from the probe tip, the cell inlet valve is closed, and a separate gas-line containing high-pressure purge gas (dry air) is activated backward through the probe tip.

Since the initial testing of the ammonia monitor was to be done on a clean gas-flow at the Savannah River bench scale reactor, the measurement probe was modified by removing a sintered metal filter for particle trapping. This allowed the low-volume gas stream from the bench-scale reactor to be directly introduced to the multi-pass gas cell sampling volume for maximum sensitivity and time-response.

Future measurements on gas flows generated by pilot-scale reactors will contain particulates, and will require the presence of an optimized particle removal system, since the accumulation of particles in the gas-cell rapidly degrades monitor performance primarily by coating the two cell

spherical mirrors. Furthermore, particle accumulation on the optical surfaces can also promote heterogeneous reactions that may lead to corrosion or oxidation of the mirrors, with attendant degradation in performance.

Ammonia Monitor Software

Control of the monitor mechanical, electrical and optical functions is provided by software through a resident microprocessor in the optical console. Communications with the user is through an alphanumeric keypad and 4-line LCD display panel. Additional electrical output signals are available through a front panel connector for diagnostic and trouble-shooting functions. Process control outputs are available through several solid-state relays, a 4-20 mA signal line, or an RS-232 signal line. Twenty-four hours of accumulated monitor data can also be downloaded to an external computer for additional analysis or archival.

The current commercial form of the SDx ammonia monitor software has proved to be adequate for initial bench-scale testing at Savannah River, as discussed below. This discussion will center on those portions of the software package that are critical for analysis of the TDL optical data and that may require future modification for defense waste processing applications.

As mentioned above, the monitor software is responsible for maintaining the TDL output wavelength at line center of the desired ammonia absorption line via an independent reference gas cell. Other supervisory functions include maintenance of constant measurement probe temperature, monitoring probe pressure, running probe calibration procedures on an automated predetermined schedule, and monitoring and setting predetermined alarm conditions for process control applications.

The data analysis software uses doubly demodulated and processed detector signals from the ammonia measurement probes as input. As described earlier, these electrical signals are typically 0 to 2.5 VDC in amplitude with a time constant of 1 Hz. Quantification is achieved by running a calibration gas routine, typically once daily. Zero levels are set by flowing pure nitrogen through the measurement probe, and, if necessary, a constant DC offset is determined to produce a software zero value.

Span gas is flowed through the probe for a user-selectable period of several minutes (either under automatic or manual control). After a constant analyzer signal output is obtained, the system software queries the user for the span gas ammonia concentration, and a simple linear algorithm computes monitor sensitivity in terms of ppm ammonia per millivolt of DC output signal. These constants are then used to analyze and report ammonia concentrations during real-time monitoring of sample flow conditions.

The software also computes a rolling average of the 1-Hz measured concentrations. The interval of the rolling average is selectable by the user, but is typically updated on the order of once every two minutes. The rolling average data are stored in a log file that can be easily downloaded daily. Additional data processing of the real-time data is available through current and output voltage lines if necessary.

The current data analysis software is therefore extremely straightforward and robust. Variations in laser power in the gas cell (due to particulate attenuation or dirty optics) are broad-band in nature, and do not affect the accuracy of the ammonia concentration data in the same way that interfering gas-phase absorptions do. Drops in total laser power within a defined range can be accounted for

by a software normalization routine. These variations are continuously monitored by the software system, and an alarm notifies the user when the total laser power falls below the acceptable normalization range.

As stated earlier, the success of the method for defense waste processing applications depends critically on the absence of optically interfering gas-phase species in the probe measurement volume. Spectral overlap due to additional absorption line structure on a constant or transient basis will invalidate the linear algorithm used to calculate ammonia concentrations from the processed TDL absorption signal. The critical requirement of a well-characterized spectral "landscape" in the 1.55- μm region during ammonia monitoring was a key focus of our work during FY96 and will continue to be vital to the success of this project at Savannah River during pilot-scale testing in FY97.

At present we do not believe any significant change in the software algorithm or support functions will be necessary to perform pilot-scale testing of the monitor in FY97. Extensive cross-comparisons of the TDL monitor data with independent ammonia analyses will be acquired to reveal the magnitude of any possible optical interference in the operation of the monitor, and to suggest modifications in the monitor hardware and software to eliminate its effect.

AMMONIA MONITOR BENCH-SCALE TESTING

A dedicated ammonia monitor was delivered to Savannah River during FY96 as part of the first year of the Technical Task Plan. The ammonia monitor was installed by SDx and Sandia personnel, and was configured for a maximum ammonia concentration of 500 ppm, and a noise equivalent detection limit of ± 2.5 ppm. The instrument was used to monitor ammonia concentrations in order to demonstrate the feasibility of the method.

Sludge Processing Tests

Two separate tests were monitored during June and August in which a surrogate sludge was processed in a bench-scale reactor over a period of two days per test. The off-gas was entrained in a nitrogen purge, and the entire gas stream was passed from the reactor through an intermediate reservoir that acted as a buffer volume to prevent pressure transients from affecting the sludge reactor. A slip-stream was extracted from the reservoir and passed through the monitor's gas sampling cell using an input valve to limit the flow through the gas cell. A vaneless vacuum pump was used to maintain cell pressure at a constant value of 0.25 atm and to exhaust the gas to a fume hood.

The ammonia monitor was calibrated before each test using zero and span gases as described above. The ammonia concentration was consistently found to be less than 10 ppm for both tests as shown in Figures 5 and 6, except for the injection of a nominal 50-ppm NH_3 span gas at the beginning of the test run on June 4. This is apparent as the sharp spike at the beginning of the data collection in Figure 5, and demonstrates the sensitivity of the monitor to ammonia.

Although the calibration procedure is designed to set an instrumental "zero" level using nitrogen as the zero gas, instabilities produced by phenomena such as ambient temperature drift and residual ammonia from prior measurements can result in a reading off-set from zero. This is the case in both Figures 5 and 6, with average positive zero off-sets of 1.7 and 1.9 ppm, respectively.

Figure 5. Ammonia monitor output during sludge processing test of June 4-6, 1996.

If we evaluate the variation of the monitor signal for these two data sets (excluding the calibration spike at the beginning of the run in Figure 5), we find 1-sigma standard deviations of ± 1.6 and 2.3 ppm for the June 4-6 and August 13-15 tests, respectively. These results are in good agreement with the instrument specification of ± 2.5 ppm for equivalent noise, and imply that ammonia concentrations were not detected by the monitor at levels statistically greater than the instrumental noise response for the two bench-scale processing cycles. This is consistent with normal operation of the two water-cooled condensers and an ammonia scrubber system in the sludge processing reactor.

The experimental data also show that the variation in measured concentration is characterized by a long time constant. High-frequency noise is virtually undetectable for the June 4-6 data, and is prominent only for two short periods during the August test. The precise cause for long-term variation in measured concentration is not known at this time, and will be studied during tests in FY97.

The data from these two tests do not demonstrate the detection of ammonia, as expected, during normal operation of the Savannah River sludge processing cycles. The rapid response of the monitor to a 50-ppm ammonia span gas, and the lack of a detectable ammonia signal above the instrument noise level in the off-gas following the ammonia scrubber, are encouraging results. Furthermore, the lack of detectable signals also substantiates the ability of the TDL-based monitor to discriminate against possible interfering absorbers in the off-gas stream.

Figure 6. Ammonia monitor output during sludge processing test of August 13-15, 1996.

Ammonia Scrubber Experiment

An additional experiment was performed by Sandia and Savannah River personnel during August using the bench-scale sludge processing reactor described above. A certified ammonia-nitrogen gas mixture was introduced into the sludge processing vessel following the conclusion of a bench-scale test run. The gas flow passed through the reactor system into the reservoir buffer volume, and a slip stream was extracted for continuous analysis by the ammonia monitor.

The goal of the experiment was to monitor ammonia concentration in this simulated off-gas with the reactor ammonia scrubber turned on and off. By this method we hoped to assess the effectiveness of the scrubber design, and monitor possible "ammonia break-through" when the scrubber capacity was sufficiently reduced.

In practice, no ammonia was detected in the simulated off-gas using ammonia span gases of 50-ppm and 1,000-ppm concentrations. Visible color changes in the hot, refluxing sludge indicated that significant absorption of ammonia from the purge gas was taking place in the sludge processing vessel. Introduction of the ammonia span gas was then attempted at various points in the reactor downstream from the sludge processing vessel. Additional ammonia absorption occurred in the ammonia scrubber and two water-cooled condensers before and after the scrubber. Furthermore, introduction of the ammonia span gas at points downstream from the sludge processing vessel upset the gas flow through the reactor system.

In conclusion, no satisfactory introduction point was found for the ammonia span gas that successfully tested the performance of the ammonia scrubber component while avoiding an upset of the required gas flow through the bench-scale sludge reactor system. These effects were aggravated by the low flow-rate of off-gas through the bench-scale system and the consequent requirement of a buffer volume in conjunction with the ammonia monitor extractive gas cell. Future experiments are being planned to address the issue of ammonia scrubber effectiveness, and will use the higher capacity pilot-scale reactor currently under design at SRS (see below).

CONCLUSIONS

Work in this project during FY96 has demonstrated a real-time monitor for low-ppm ammonia measurements in DOE defense waste processing off-gas streams using a near-infrared tunable-diode-laser-based instrument. The measured instrumental sensitivity of ± 2.5 ppm for ammonia with a time response of less than 10 seconds meets requirements for detecting ammonia breakthrough in the ammonia-scrubber system of the Defense Waste Processing Facility at DOE's Savannah River Site.

Laboratory research and development show a lack of interference from other potential absorbing gas-phase species in the 1.55- μm wavelength range for this ultra-high spectral resolution method. These results are confirmed by bench-scale tests at SRS in which defense waste sludge surrogates were processed, and the off-gas monitored by the TDL-based monitor for ammonia. During these tests, no false-positive results were recorded due to interfering gas-phase species.

Ammonia was not detected above the instrumental noise-level, as expected, for two bench-scale sludge processing cycles. Calibration of the monitor before and after processing cycles demonstrated that the monitor was responding properly to a calibrated ammonia mixture. Any real variations in the off-gas ammonia concentration may have been masked by the large volume of nitrogen purge gas used to stabilize the gas flow through the bench-scale sludge processing reactor. Attempts to study ammonia scrubber effectiveness by passing a simulated off-gas containing ammonia through the reactor were not successful due to upset conditions produced in the small, bench-scale reactor system.

FUTURE PLANS

Further tests of the TDL-based ammonia monitor for ammonia scrubber efficiency during sludge processing will be performed in FY97. These experiments will be conducted on a pilot-scale sludge processing facility now under construction at Savannah River. The sludge batch size of this facility is 25-50 gallons, and its scale is 1/240 that of the Defense Waste Processing Facility. The much larger flow rates associated with the pilot-scale reactor should minimize the difficulties encountered in our experiments at the bench scale.

A second extractive gas-cell measurement probe will be incorporated into the ammonia monitor system, and will be situated in the sludge reactor system prior to the ammonia scrubber. This probe will be configured for high ammonia gas concentrations (up to 50,000 ppm), and will be used in conjunction with the low-concentration probe located downstream from the ammonia scrubber to quantitatively assess scrubber performance.

The successful completion of this project at the pilot-scale will result in a transfer of the TDL-based monitor technology to Savannah River for incorporation into the full-scale Defense Waste Processing Facility.

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