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Development of Inexpensive Continuous Emission Monitors for Feedback Control of Combustion Devices that Minimize Greenhouse Gases, Toxic Emissions, and Ozone Damaging Products

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Abstract

This is the final report of a three-year, Laboratory Directed Research and Development project at the Los Alamos National Laboratory. Combustion is the major cause of poor urban air quality, of depletion of the ozone layer, and a major source of the greenhouse gas, carbon dioxide. Careful control of combustor conditions is important for minimizing the effects of combustion on our environment. We have developed sensitive, inexpensive continuous emission monitors that will assist in direct feedback of turbine power systems and provide assurance to the public and the operators of the facilities that their facility emissions lie within the accepted bounds. These include a robust solid-state Fourier transform spectrometer for rapid gas analysis, based on the use of ferroelectric liquid crystal technology, and an infrared helium-neon probe for real time measurement of combustor air-to-fuel ratios.

Background and Rationale

There is little doubt that combustion is the major cause of poor urban air quality, of depletion of the ozone layer, and a major source of the greenhouse gas, carbon dioxide. Furthermore, there is little doubt that global combustion activity is increasing. The increase is not so much driven by world population increase, but due to emerging nations increasing their use of energy. It is possible that these increasing demands for energy can be met with greatly reduced impact on the global environment. Taking China as an example, they have much coal and are faced with the prospect of burning the coal in a conventional steam Rankine-cycle power plant or they could use more recent technology of gas turbines using gasified coal. Placement of a gas-turbine combined-cycle power plant can have twice the efficiency of a simple-cycle steam plant using the same amount of fuel. Simply stated, the

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gas-turbine cycle can produce twice as much electrical energy for the same amount of CO₂ greenhouse gas. Furthermore, the oxides of nitrogen (NO_x) emitted from gas turbines are 10 times smaller than comparable coal fired plants. There is a global incentive for the best equipment to be installed everywhere. A common feature of the best equipment is the need for continuous feedback control. A key ingredient to feedback control is the need for sensors. The less expensive these sensors become, the more likely they will be used and thus the more likely that the most advanced, least polluting, highest efficiency power equipment will be installed worldwide.

Beyond generation of power, combustion is used for destruction of a wide variety of potentially harmful compounds (even freons!). In today's climate of environmental awareness it has become increasingly evident that continuous analysis of stack gases is necessary to comply with the public's demands for assurance of nontoxic emissions. In the past, facility approval from the Environmental Protection Agency (EPA) consisted of running the proposed system under normal conditions and measuring the amount of toxic species present using well defined sampling trains. After passing of such tests, the facilities were required to monitor CO concentrations at fifteen minute intervals, with the premise that CO production would be a measure of the 'inefficiency' of the combustor. Subsequent changes would then be made to the stack input to bring the level of CO back to 'safe operating' levels if it were found to deviate from normal concentration levels. In fact, due to the complexity of the kinetic processes giving rise to stack emission, it may not be possible to rely on such a correlation for minimization of hazardous emissions.

In an effort to address all of the above concerns, we undertook to research and develop sensitive, inexpensive continuous emission monitors (CEMs) based on the optical properties of the expected gas-phase hazardous materials. We expect that these types of sensors will assist in direct feedback of turbine power systems and provide assurance to the public and the operators of the facilities that their facility emissions lie within the accepted bounds. Moreover, part of the project has been to foster collaboration between Los Alamos National Laboratory (LANL) and the University of California-Berkeley (UC-Berkeley) campus.

Importance to LANL's Science and Technology Base and National R&D Needs

The development of "clean" power for the American people and the world has been one of the principal missions of the Department of Energy since its inception. Los Alamos has contributed in many ways, from experimenting with inertial confinement fusion to experiments conducted on saltwater ponds for collecting solar energy. Recently, the

Laboratory partnered in the development of fuel cells that will become onboard generators in new automotive systems. The research presented here supports the Country's increasing desire for energy by providing diagnostics that help minimize pollution and maximize electrical generator/combustor systems. We take advantage of the strong spectroscopic capability of the Laboratory, brought here by the need for isotope separation in the late 1970s, and apply it to the problems of the 1990s.

Scientific Approach and Accomplishments

Our project consisted of three related tasks with slightly different impacts on science and technology in environmental chemistry. These tasks and accomplishments in each are described in the next sections.

Inexpensive Solid State NO_x detector

The present widely accepted NO_x detector is based on chemiluminescence of NO₂ generated from the reaction of ozone with NO. The instrument cost (\$15,000) is considered prohibitively expensive for most combustion sites. There is need for a less expensive alternative, one that is based in the spirit of the ubiquitous home 'smoke alarm' which does a remarkable job for about \$20. We proposed development of an inexpensive NO_x monitor using anticipated blue diode lasers and/or light-emitting diodes (LEDs). The technical impact of a NO_x detector that costs less than \$1,000 is enormous. The market is large and there would, no doubt, be a wide variety of companies that would seek patent agreements. It is easy to imagine that 1,000 of these units could be sold each year.

The instrument proposed was an improvement over the ubiquitous chemiluminescence NO_x analyzer (from TECO Inc.) that reacts ozone with NO to produce NO₂^{*}, which then fluoresces in the 800 nm region. The fluorescence is detected by (expensive) extended-red multi-alkali photomultiplier tubes. We generated NO₂^{*} from NO₂ by absorption of light from a blue laser diode. Ozone (or perhaps a catalyst) is still needed to convert NO to NO₂. With the ozone reaction, each NO produces one photon [times a low quantum efficiency], whereas with the blue laser pump, many thousands of photons are anticipated (multiple excitation of each molecule) [times the same low quantum efficiency]. Thus there will be more light to detect and/or lower concentrations of NO₂ will be detected.

The detector, a photomultiplier tube, can be replaced by the new, less expensive technology of avalanche photodiodes (APD). The proposed system is entirely solid state, using fiber optics to route the light. The system is therefore rugged, compact, and inexpensive. Initially, we determined sensitivities using conventional laser technology that we then tried to translate to the expected performance from blue diodes. We did not

achieve the expected sensitivity, and as a result, our efforts focused primarily on the next two efforts.

Fourier-Transform Solid-State Spectrometer

This new device is both an improved scientific tool and a marketable instrument that will measure a wide variety of species simultaneously. It is well known that infrared and UV-VIS spectroscopies are suitable for detecting volatile molecular species found in effluents associated with weapon production as well as those found in industrial stack emissions. The use of Fourier transform spectroscopy (FTS) is one method of choice for this application. Unfortunately, the instruments are fairly expensive, \$30,000 to \$100,000 depending on the optical resolution and bells and whistles attached. More importantly, FTS instruments are sensitive to optical alignment, have moving parts, and are not easily adapted to rough service. We propose a new scheme that will provide many of the advantages of FTS instruments, but in addition will be inexpensive (\$10,000 to \$20,000) and easily adapted to rough service. The instrument could be used for unattended monitoring or would be well suited for airborne deployment.

Light from an infrared or visible source (Nernst glower, Globar, tungsten ribbon lamp) is collimated, polarized and sent through a dispersing element after which it intersects a multielement liquid crystal display (LCD) mask capable of transmitting polarization - dependent fractions of the light (Figure 1). The mask consists of discrete rectangular elements that transmit a specific polarization of light, depending on the applied voltage. These masks can have a variable number of elements depending on the resolution one wishes to attain. The number of elements, or channels, will ultimately be limited by the amount of digital signal processing (DSP) memory available. The transmitted light is then passed through a second dispersing element of the opposite direction as the first to bring all of the light back into a collimated beam (these elements could be holographic gratings). Half of the transmitted light is passed through the sample and imaged onto one InSb, Si, photomultiplier, or pyroelectric detector. The other half of the transmitted light is imaged onto a second detector to act as a reference beam.

The LCD elements are switched from one polarization to the other in a sinusoidal manner, *with each element operating at a different frequency*. This results in a time-dependent intensity falling on the detector for each of the i elements. The resulting time-dependent signal on the detector can then be written as a sum of sines, with the amplitude of each sine function corresponding to the intensity of light at that frequency. The resultant waveform is then sampled digitally with an oscilloscope. The waveforms are fast Fourier transformed on a DSP board or computer with the amplitude of the frequency component, ω_i (of sine i) equal to the intensity of light falling on the detector from the i_{th} LCD element.

The two amplitudes (sample and reference) are then ratioed and the natural log taken for a measure of the absorbance at that wavelength.

Shown in Figure 2 are two time-dependent traces observed with an LCD mask striped into a 1x4 array with the bottom trace the reference and the top trace the sample: a Corning 2-64 color filter that transmits only the red portion of the light placed prior to the phototube. As seen in the figure, the fully modulated (reference) spectrum shows complex beating of the four frequencies against each other, while the red-light-only spectrum (sample) shows the characteristic frequency at which the red portion of the spectrum is modulated. Additionally, the sample trace shows that we are presently using a square wave for modulation, a result of our directly addressing the mask and our use of digital communications. Future designs will use analog driving potentials coupled to phase-locked loops, yielding as pure as possible sine waves to keep all the energy in the fundamental and not move it into the harmonics composing the square wave.

Shown in Figure 3a are spectra taken with a standard diode array UV-VIS spectrometer (Hewlett-Packard). Also shown are Gaussian fits to the bandpass transmission of each of the four 1x16 element segments (the transmission is not Gaussian; we use them only for pedagogical purposes). Shown in Figure 3b are the resultant amplitudes of the carrier frequencies for each band and for the filters studied. As observed in the figure, the relative intensities of the four peaks in the spectral domain exhibit the expected behavior for each of the filters examined. For example, looking at just the red transmission filter (small dashed line), we observe that the intensities of all the spectral elements except that containing the red color are zero. In the future, we expect to integrate the areas under each peak in the frequency domain, and ratio these areas (sample/reference) to obtain the quantitative absorption in each band.

The device is a solid state instrument and can be made robust. By modulating the LCD elements we will obtain the sensitivity of lock-in amplification. We expect to realize large increases in sensitivity over traditional dual-beam spectrometers. Furthermore, we will obtain much of the Fellgett advantage by sampling an entire portion of the spectrum. How large the spectral window is will be dictated by resolution and the number of elements used in the LCD mask. The upper limit for the number of elements will be controlled by the Shannon Sampling Theorem and the memory available on the DSP board used both to sample and transform our data.

Inexpensive HeNe IR Laser for Monitoring of Hydrocarbon Emission

During the first year of the project, it occurred to us that the He-Ne infrared (IR) laser could be a valuable diagnostic for determination of emissions from combustion devices in general and toxic incinerators in particular. The IR emission from the He-Ne

laser at wavelength of 3.3922348 microns has a fortuitous overlap with absorption bands of most hydrocarbons. Documented example hydrocarbons that absorb at this wavelength are methane, ethane, propane, gasoline, diesel, ethanol, dimethyl-ether, and many others. NONE of these hydrocarbons should be emitted from an incinerator. Thus, absorption of the IR laser beam as it traverses the exhaust duct of an incinerator or other combustion device becomes an inexpensive diagnostic that warns of potentially unsafe, inefficient operating conditions. Furthermore, when combined with the red beam of a laser diode, we can discriminate between absorption from hydrocarbons (IR only) and from droplets and particulates that will effect both beams.

Early in the project, we purchased an IR He-Ne laser (wavelength at 3.39 microns) and a related detector for the IR wavelength. Shown in Figure 4 is an example geometry of the probe as it is presently used. The application allowed the observation of pressure oscillations in a combustor observed as time-varying air-to-fuel ratios (AFRs). This was accomplished as follows: The probe produced a time series of air-to-fuel ratios. By applying the Fourier transform to the time series we determined the power spectrum of the AFR. We discovered several preferred frequencies in combustion chambers. This finding is most exciting to the gas turbine researchers since pressure dynamics are a serious problem that limit the operational envelope of the combustor. As a result, there is even more interest in this probe.

Recently, we have evolved the IR He-Ne air-to-fuel device from gas turbines to spark engines by modifying a spark plug to accept two IR transmitting optical fibers. The IR He-Ne light passes through one fiber in the spark plug center electrode. Light exits this fiber and crosses the spark gap where it reflects back from the polished ground electrode to a return fiber optic. The absorption of the laser beam by hydrocarbons in the gap gives the air-to-fuel ratio in the gap, which is where most of the interest is.

More than one gas turbine manufacturer has asked to buy the IR He-Ne probe. We presented the idea to several laser high-tech companies. Since the parts cost \$5,000 we were told that the finished product would sell for six times as much, i. e. \$30,000, a 'reasonable price' according to the gas turbine companies. All looked good until we guessed the market to be 5 to 10 a year; the laser company lost interest. We are now in the mode of taking the IR He-Ne laser probe to the various gas turbines companies for one- to two-week research campaigns. We have done experiments at Solar Turbines (San Diego, CA) and at General Electric Gas Turbines (Schenectady, NY), and we are in discussions with Pratt and Whitney (and related, with UTRC). We have made one visit to Westinghouse in Florida and we are having discussions with ABB in Virginia and with

Siemens in Germany. In short, nearly all manufacturers of gas turbines have recognized our probe as a tool they would like to have.

Publications

1. Funk, D. and Moore, D. "Fourier-transform Spectroscopy using Liquid-crystal Technology," *Optics Letters*, **22**(23), 1799-1801, 1997.
2. Mongia, R., Tomita, E., Hsu, F., Talbot, L. and Dibble, R., "Use of an Optical Probe for Time-Resolved *In Situ* Measurement of Local Air-to-Fuel Ratio and Extent of Fuel Mixing with Applications to Low No_x Emissions in Premixed Gas Turbines," Twenty-sixth Symposium (International) on Combustion, **26**, 2749, 1996.
3. Mongia, R., Dibble, R., Lovett, J., and Yamazaki, A., "Measurement Of Air-Fuel Ratio Fluctuations Caused By Combustor Driven Oscillations," Western States Section of the Combustion Institute, October, 1997.

Figure 1. A schematic of the present experimental layout. Light from a tungsten lamp is collimated and run through a subtractive double spectrometer. The dispersed radiation is intersected with the 1x4 element mask and with each spectral component encoded with a different frequency, and the time-dependent output observed with a photomultiplier tube.

Figure 2. Raw output of the phototubes as a function of time. The top trace is the time-dependent signal transmitted through a red filter; only one of the stripes in the mask is transmitting light and only a signal frequency is detected. The bottom trace is the time-dependent signal of the full output from the mask (no filters); the four carriers exhibit the expected beating behavior.

a)

b)

Figure 3. (a) The dashed lines are the spectra of each of the filters used: red (-----); orange (— — — — —); yellow(— · — · — · —); blue (· · · · ·). The solid lines are Gaussian fits to the spectral windows of each pixel in the mask. (b) The Fourier transformed output; the dashes are for the same filters as in (a). Note that the relative intensities of the frequency peaks follow what is expected from the overlap of the filters and the Gaussian transmission functions.

Figure 4. Schematic of optical probe. A small probe volume is created by the gap between the infrared transmitting fiber optics. Light from a $3.39\text{ }\mu\text{m}$ He-Ne laser is focused into one of the fiber optics.