

ON-LINE FT-IR ANALYSIS OF FOSSIL-FUEL FIRED POWER PLANTS

C.M. Nelson, K.S. Knight, M.A. Serio, P.R. Solomon, and M.A. Halter*
Advanced Fuel Research, Inc.
87 Church Street
East Hartford, CT 06108
*Graseby STI
P.O. Box 2470
Waldron, AR 72958

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ABSTRACT

This paper describes the test of a prototype FT-IR CEM system at a full scale power plant. Initial tests were done in an extractive mode over a one week period and measured SO₂ levels were compared to levels measured by an existing CEM system. The system was able to report concentrations of six different gas species simultaneously, and IR spectra were periodically saved for future analysis and measurement of other gas species concentrations. Subsequent tests will involve a comparison of simultaneous in-situ and extractive measurements with FT-IR based CEM systems and a long duration (one-month) evaluation of the extractive system.

INTRODUCTION

The use of an FT-IR based continuous emission monitoring (CEM) instrument for a fossil-fuel fired power plant offers several advantages: 1) it can be used in either an in-situ (emission/transmission) or extractive (transmission) mode; 2) FT-IR transmission spectroscopy can measure concentrations for multiple gas species which significantly reduces the cost and complexity of the measurement system; 3) FT-IR emission/transmission spectroscopy allows the determination of concentration and temperature information on gases and number density, size, temperature and composition information on particles; 4) FT-IR transmission spectroscopy can provide concentration measurements on species which are difficult to provide by other on-line techniques (e.g. NH₃, H₂SO₄). Although FT-IR is an established multicomponent sensor technology, the use of FT-IR for CEM systems is still under development [1]. FT-IR has been used for both in situ and extractive monitoring of coal combustion, pulp and paper mills, and hazardous waste incinerators [2,3,4,5]. This paper describes extractive FT-IR measurements were performed at Cogentrix of Richmond, Richmond, VA.

RESULTS AND DISCUSSION

Description of Test Site - The first field test was conducted from May 24-27, 1993 at the Cogentrix Coal-Fired cogeneration plant in Richmond VA. The plant consists of eight spreader stoker-fired boilers rated at 300k lbm/hr. Two boilers are joined to one turbine with a maximum expected generator output of 55 MW each. The plant also supplies process steam for a nearby chemical production facility. The Cogentrix power plant uses a urea injection system to control NO_x and reduce SO₂, and also uses lime spray drying and additional capture in the baghouse resulting in 90% reduction in SO_x emissions.

Samples were extracted from the process after urea injection, but prior to particulate collection or SO₂ removal, with the STI Dilution Probe (Graseby/STI, Waldron, AR). The majority of samples were obtained with a dry basis probe (a heat exchanger is used to condense water prior to sample dilution), although some samples were obtained with a wet basis probe (no heat exchanger), and sampling was performed with and without a glass fiber filter. The process gas was diluted ≈20:1 with instrument air (CO₂-free, dry air) before being transferred to a 5.6 m effective path-length gas cell through a 100' long, 1/4" PTFE transfer line. Figure 1 is a schematic of the sampling probe and monitoring system. The FT-IR spectrometer was a Bomem MB100 equipped with a liquid N₂ cooled, MCT detector. All spectra were obtained with 1 cm⁻¹ spectral resolution, and the cell temperature and pressure were maintained at 30° C and 1 atm respectively. Pure component spectra were measured in the laboratory for CO₂ (from 424.1 to 50000 ppm), CO (from 0.56 to 10000 ppm), NO (0.85 ppm), and SO₂ (0.85 ppm) under similar conditions. Theoretical, high resolution (< 0.0625 cm⁻¹) spectra were

generated from the HITRAN Optical Spectroscopy Database using USF HITRAN-PC (University of South Florida Research Foundation, Tampa, FL) for CO₂ (from 12.5 ppm to 1250 ppm), H₂O (from 100 to 10000 ppm), NH₃ (from 0.125 to 12.5 ppm), HCl (from 0.25 to 25 ppm), NO (from 1 to 100 ppm), and SO₂ (from 1 to 100 ppm). The high resolution spectra were deresolved to 1 cm⁻¹ using a triangle apodization function to approximate the instrument line shape for the Bomem MB100 spectrometer.

Gas Analysis - Prior to analyzing gases extracted through the dilution probe, a calibration gas (a mixture of 251 ppm NO, 635 ppm SO₂, 205 ppm CO, and 5% CO₂ in N₂) was measured directly and also measured after being diluted 20:1 with N₂, to verify the optical pathlength and gas flow meters, respectively. The optical pathlength was measured as 5.6 ± 0.1 m. The same calibration standard was used to measure the dilution ratio for the STI probe. The ratio was determined to be ≈20:1. For continuous measurements, single beam spectra were recorded at ≈1 min intervals (25 full scans at 1 cm⁻¹), absorbance spectra were calculated based on a previously recorded reference spectrum, gas concentrations were determined using a modified principal component regression, and concentration vs. time was reported for six gas species.

The FT-IR based continuous monitor measured process gas concentrations for approximately three hours from 18:00 hours to 21:00 hours on May 25, 1993. Figures 2 and 3 compare CO₂ and SO₂ levels, respectively, as measured by the FT-IR system to those measured by the existing CEM. The FT-IR-based CO₂ levels were calculated using a laboratory measured CO₂ spectrum as the reference and a previously determined calibration curve. The existing process monitor does not measure CO₂ directly, but the CO₂ concentration can be inferred from the process stoichiometry and the measured O₂ concentration. The FT-IR-based SO₂ levels were calculated using a HITRAN-PC generated reference, while the existing CEM uses a fluorescence measurement. The reported values for the existing CEM system are 15 min averages for the period in question, while the FT-IR data represent 1 min averages. Calibrations based upon laboratory pure-component spectra and upon theoretically generated pure component spectra worked equally well for calculating process concentrations. The periodic spikes in the concentration measurements correspond to blow-back periods, periods when instrument air is forced back through the probe and through the heat exchanger to remove particulates and condensed H₂O. The timing of blow-backs could be varied from 15 min to 1 hour or could be controlled manually. In future tests, the timing will be controlled by the FT-IR system computer.

Trace Gases - The FT-IR system was also able to detect CO and NO at levels of 72 and 150 ppm, respectively. The 20:1 dilution in the probe resulted in single digit ppm concentrations in the gas cell for these species. The current continuous analysis software was not able to accurately quantify these gases due to baseline anomalies and interference by remaining water (even with the heat exchanger, residual water levels approached 1000 ppm in the cell, partly from incomplete drying of the instrument air used for dilution). This problem is being addressed in software which is under development.

Because of the urea injection, ammonia is expected to be present in the effluent in addition to the standard combustion gases expected from coal. Sulfur dioxide and ammonia react in hot combustion gases to form particulates. This precipitation is both temperature and moisture sensitive, and can cause difficulties when trying to measure SO₂ and NH₃ in an extracted gas stream [1]. The concentration of NH₃ was first measured from a calibration standard (25.4 ppm NH₃ in N₂) that was injected through the dilution probe. All of the gas lines leading to the probe were pressurized with the calibration gas for 8 hours prior to the experiment to condition the lines. Without prior conditioning, NH₃ continues to permeate the teflon tubing and accurate NH₃ concentrations are not obtained. When the calibration gas was injected through the filter, no detectable NH₃ (<0.1 ppm) made it through the probe into the gas cell after 20 min. It is possible that residual water in the glass filter and heat exchanger was absorbing the NH₃. If the calibration gas was allowed to bypass the glass fiber filter and the heat exchanger, the NH₃ concentration in the gas cell increased to > 1 ppm (vs. 1.27 ppm expected).

Figure 4 presents the NH₃ concentration vs. time over a one hour time period. After 1 min of time elapsed, 25.4 ppm NH₃ was injected into the dilution probe (with the filter removed, and heat exchanger bypassed). The continuous FT-IR monitor measured an increase in NH₃ concentration to 10 ppm where it leveled off. At 16 minutes, instrument air was forced through the probe, and the extraction was switched from cal gas to process gas. After an initial increase in NH₃ concentration that corresponded to the blow-back, the NH₃ concentration

dropped to zero. After 15 min, the process was switched back to the NH₃ calibration standard, but the NH₃ levels in the cell did not recover during the duration of the analysis. A second series of experiments was performed with a 47 ppm NH₃ standard with similar results. Preliminary measurements with the cal gas reported increasing levels of NH₃. Upon switching to the process gas, the level of NH₃ dropped to zero and ≈ 1 hour of cal gas flow was required before NH₃ levels returned to normal. During process gas sampling, a powdery substance quickly coats the inside of the sample probe and, if the filter is removed, the lines leading to the educator assembly. This substance is probably a combination of ammonium sulfates, sulfites, and ash. It is possible that the moist particulates which line the tubing after sampling process gas continue to absorb NH₃ from the calibration standards until saturated. This absorption would account for the extremely long lag times required for NH₃ from the calibration standard to reach the FT-IR system after sampling process gas.

Similar experiments were performed with HCl calibration standards. Although HCl was easily detected during dilution experiments performed directly into the gas cell, when the HCl calibration standard (≈ 50 ppm HCl in N₂) was injected through the wet-basis probe (no heat exchanger) with filter, the HCl concentration increased to ≈ 1 ppm in the gas cell after prolonged flow (> 20 min). It is possible that moisture trapped in the filter from the ambient air was absorbing some of the HCl. Upon switching to process gas, no HCl was detected in the cell (< 0.2 ppm) and upon switching back to the calibration gas, no HCl was detected after 60 min. Again, it is possible that moisture and particulates from the process stream are collecting in the filter and tubing and absorbing/reacting with the HCl. Removal of the glass fiber filter did not increase the level of HCl measured in the process.

FUTURE PLANS

The objective of this work is to develop in situ and extractive FT-IR monitors for emission monitoring and process control. Future field work will address some of the problems discovered during extractive measurements of NH₃ and HCl, and will include in situ monitoring as well.

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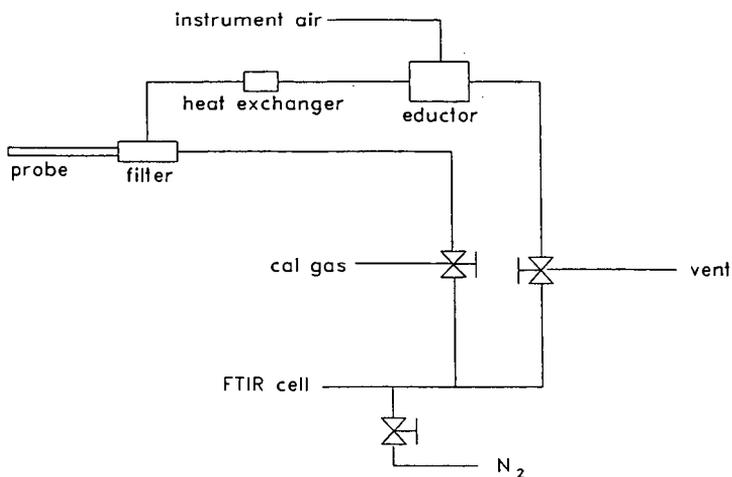


Figure 1. Schematic flow diagram for dilution probe.

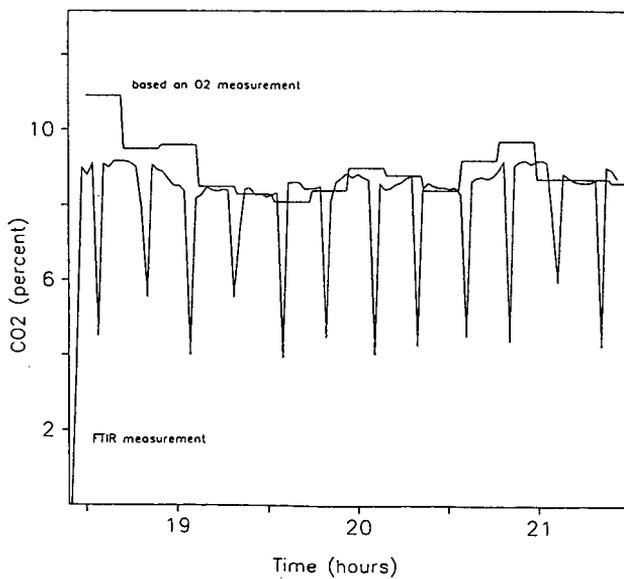


Figure 2. Comparison of CO₂ concentrations as measured by continuous FTIR system and as inferred from O₂ measurements.

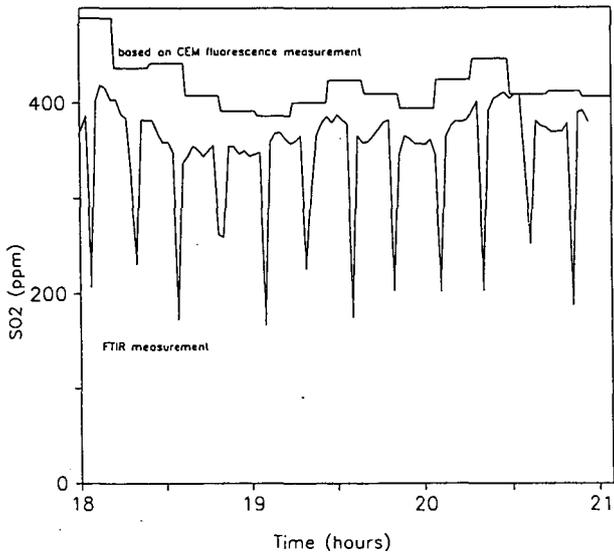


Figure 3. Comparison of SO₂ concentrations as measured by continuous FTIR system and as measured by existing fluorescence monitor.

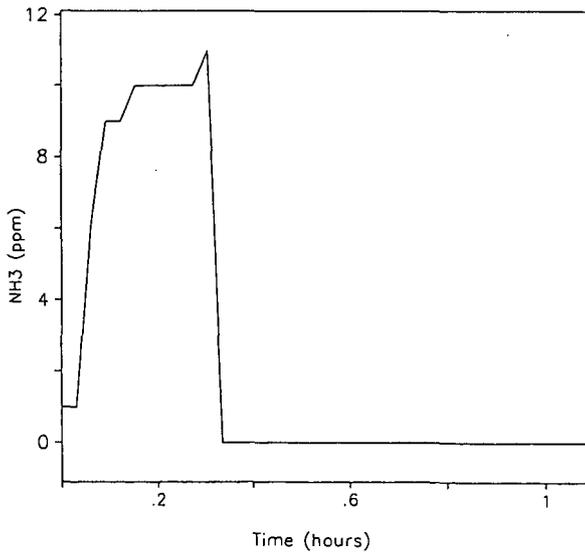


Figure 4. Continuous NH₃ measurements during cycling of standard calibration gas and process gas streams.