# Final Technical Report

## DOE Grant #: DE-FC26-04NT42311

## DEVELOPMENT OF NEW OPTICAL SENSORS FOR MEASUREMENTS OF MERCURY CONCENTRATIONS, SPECIATION, AND CHEMISTRY

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# 1. DISCLAIMER

## 2. ABSTRACT

A diode-laser-based ultraviolet absorption sensor for elemental mercury was developed and applied for measurements in a high-temperature flow reactor and in the exhaust stream of a coal-fired combustor. The final version of the sensor incorporates a 375-nm single-mode laser and a 784-nm distributed feedback (DFB) laser. The output of these lasers is sum-frequency mixed in a non-linear beta-barium borate crystal to generate a 254-nm beam. By tuning the frequency of the DFB laser, the ultraviolet beam frequency is tuned across the transition frequency of mercury at 253.7-nm. The tuning range is large enough that an off-resonant baseline was clearly visible on both sides of the Hg transition. Because of this large tuning range, the effects of broadband absorption can be effectively eliminated during data analysis. Broadband absorption is a major concern for lamp-based mercury sensor, and the sample to be monitored must be chemically treated prior to analysis to remove species such as $SO_2$ that absorb near 253.7 nm. No pretreatment is required when our diode-laser-based sensor is used for elemental mercury measurements. Our laser sensor measurements were compared to measurements from a commercial mercury analyzer (CMA), and were generally in good agreement except that the in-situ diode-laser-based sensor measurements tended to give somewhat higher concentrations than the CMA measurements, presumably due to absorption of elemental mercury in the sampling lines needed for the CMA measurements. At Texas A&M University, the homogeneous oxidation of elemental mercury was studied using a high-temperature flow reactor.

## 3. TABLE OF CONTENTS

# 4. INTRODUCTION

A diode-laser-based ultraviolet absorption sensor for elemental mercury was developed and applied for measurements in a high-temperature flow reactor and in the exhaust stream of a coal-fired combustor. The final version of the sensor incorporates a 375-nm single-mode laser and a 784-nm distributed feedback (DFB) laser. The output of these lasers is sum-frequency mixed in a non-linear beta-barium borate crystal to generate a 254-nm beam. By tuning the frequency of the DFB laser, the ultraviolet beam frequency is tuned across the transition frequency of mercury at 253.7-nm. The tuning range is large enough that an off-resonant baseline was clearly visible on both sides of the Hg transition. Because of this large tuning range, the effects of broadband absorption can be effectively eliminated during data analysis. Broadband absorption is a major concern for lamp-based mercury sensor, and the sample to be monitored must be chemically treated prior to analysis to remove species such as $SO_2$ that absorb near 253.7 nm. No pretreatment is required when our diode-laser-based sensor is used for elemental mercury measurements. Our laser sensor measurements were compared to measurements from a commercial mercury analyzer (CMA), and were generally in good agreement except that the in-situ diode-laser-based sensor measurements tended to give somewhat higher concentrations than the CMA measurements, presumably due to absorption of elemental mercury in the sampling lines needed for the CMA measurements. At Texas A&M, the homogeneous oxidation of elemental mercury was studied using a high-temperature flow reactor.

# 5. RESULTS

### Diode-Laser Based Sensor for Elemental Mercury

The development of the diode-laser-based sensor and its application are described in detail in two archival journal articles:

T. N. Anderson, J. K. Magnuson, and R. P. Lucht, "Diode-Laser-Based Sensor for Ultraviolet Absorption Measurements of Atomic Mercury," *Applied Physics B* 87, 341-353 (2007).

Jesse K. Magnuson, Thomas N. Anderson, Robert P. Lucht, Udayasarathy A. Vijayasarathy, Hyukjin Oh, Kalyan Annamalai, and Jerald A. Caton, "Application of a Diode-Laser-Based Ultraviolet Absorption Sensor for *in situ* Measurements of Atomic Mercury in Coal Combustion Exhaust," *Energy and Fuels* **22**, 3029-3036 (2008).

These archival articles are attached at the end of the document.

### Measurements of Elemental Mercury during Homogeneous Oxidations

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The work reported here is based on supporting the development of new optical sensors for measurements of atomic mercury (Hg) and mercury chloride (HgCl) in exhaust streams. These sensors use optical absorption. The atomic mercury sensor takes advantage of new developments in commercial diode laser systems and offers high accuracy and sensitivity.

These sensors represent a new class of diode-laser-based sensors which perform optical absorption measurements in the ultraviolet or in the mid-infrared spectral regions. Frequency conversion techniques are employed to enable the use of well-developed lasers that emit in the visible and/or near-infrared. In the case of Hg, sum-frequency-mixing (SFM) is used to produce laser radiation at 253.7 nm in the ultraviolet region of the spectrum. In the case of HgCl, the direct output of a blue external cavity diode laser (ECDL) is used. As described below, the sensors were tested in a flow reactor at Texas A&M University.

The sensors for atomic Hg, total Hg, and HgCl were used in a well-controlled flow reactor at Texas A&M for measurements of mercury chemistry in simulated high-temperature combustion exhaust gas seeded with controlled amounts of species of interest in controlling mercury speciation. The residence time, temperature, and composition of the simulated exhaust gas in the flow reactor was varied systematically to develop fundamental understanding of the mercury chemistry and for comparison with numerical models of the chemical kinetics of mercury speciation.

Optical sensors are inherently well-suited for implementation in the harsh environment characteristic of fossil fuel power plants. Application of optical sensors at specific locations in the power plant requires optical access and a means of preventing window fouling, but the sensor itself need not survive the harsh conditions interior to the combustor or boiler.

## Experimental Facility

***System Overview***. The experimental apparatus shown in Figure 1 is composed of four distinct systems: (1) source of simulated flue gas, (2) a mercury generation system, (3) a flow reactor (or electrical heating furnace), and (4) a mercury measurement system. The simulated flue gas mixes with Hg vapor emitted from the Hg generator, and the flue gas passes through the flow reactor. The mercury vapor monitor measured the concentrations of the elemental mercury ($Hg^0$). Tygon tubes were used between the systems. Each of these systems is described in the following section.

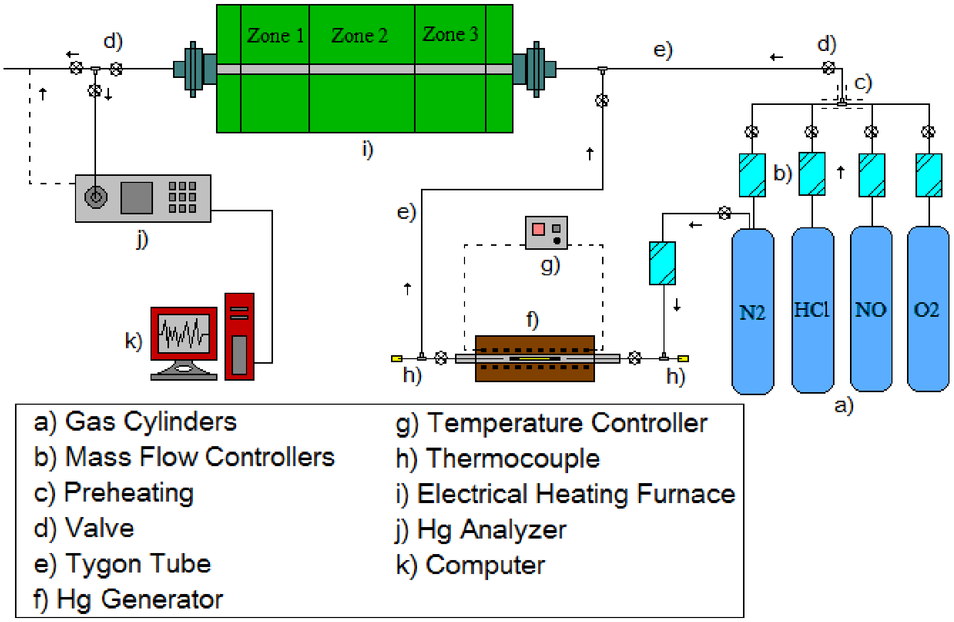

Figure 1. Schematic of the experimental apparatus used to perform Hg oxidation.

***Simulated Flue Gas***. To simulate actual exhaust gases, various gases were used from standard gas cylinders. The total balance of the simulated flue gas in the system was $N_2$. Gas species were well-mixed after passing through mass flow controllers (MFC). The simulated gas stream (the mixture of HCl, NO, and $O_2$ in balance $N_2$) entered into a long quartz-tube inside the flow reactor. The additional pure $N_2$ ($Hg^0$ carrier gas) entered into a short quartz-tube inside the mercury generation system.

***Mercury Generation System***. The Hg generator contained a certified $Hg^0$ permeation tube. The $Hg^0$ permeation tube was placed in the short quartz-tube. A flexible electric heating tape was wrapped around the short quartz-tube. The quartz-tube was covered by insulation fibers, and sealed into an aluminum box. A temperature controller was used to keep the temperature inside the quartz-tube constant. The temperature of the $Hg^0$ carrier $N_2$ was measured at each end of the permeation tube. The mercury vapor was mixed with the main gas stream before the entrance of the flow reactor.

***Flow Reactor***. The simulated gas mixture flowing through the reactor was heated to reach the desired temperatures by a three-zone furnace which was designed for obtaining laminar flow. Zones 2 and 3 were heated for the entire experiments. The long quartz-tube supported by clamps and clamps holders were located in the center of the quartz-tube reactor. With the reactor temperature up to a maximum of 1200ºC, the gas temperature reached the desired temperature. The temperature at the furnace exit was typically below 300ºC, and the temperature decreased below 30ºC at the measurement port.

***Mercury Measurement System***. Mercury concentrations were measured by mercury vapor monitor at the ambient temperature. The system was capable of monitoring elemental mercury ($Hg^0$) in the gas stream every second. The gas stream enters an optical cell where ultra violet light of wavelength 253.7 nm is made to pass through and light absorption takes place depending on the concentration of mercury present. The absorption of light at this wavelength is a direct indication of mercury concentration in the gas stream which is displayed instantaneously at the screen and is recorded at a workstation computer.

## Results and Discussions

### *Effects of HCl*

It was found that the $Hg^0$ concentration in the flue gas without HCl (only pure $N_2$) did not change up to 1200ºC of the reactor temperatures. Hg oxidation in the presence of HCl in the gas stream (pure $N_2$) was investigated. In Figure 2, Hg oxidations with various HCl concentrations (0 – 150 ppm) at 700ºC in 700 SCCM of the total flow rate are presented. The extent of Hg oxidation is listed in Table 1 in the presence of various HCl concentrations for two different total flow rates at 700ºC. The different RTs were estimated because of different flow rates. About 17% and 14% Hg oxidations were found with 90 ppm HCl, and about 30% Hg oxidation was measured for HCl concentrations from 110 to 150 ppm. The meaningful Hg oxidation occurred in the presence of 90 ppm HCl or higher, and the 90 ppm represented about $1.1 \times 10^{-8}$ moles of HCl in the heating region of the flow reactor for both cases by considering different RTs and total flow rates. The result is very similar to the results obtained by Ghorishi et al. [1]; the gas-phase Hg oxidation by HCl took place at temperatures higher than 700ºC with HCl in the range of 100 to 200 ppm.

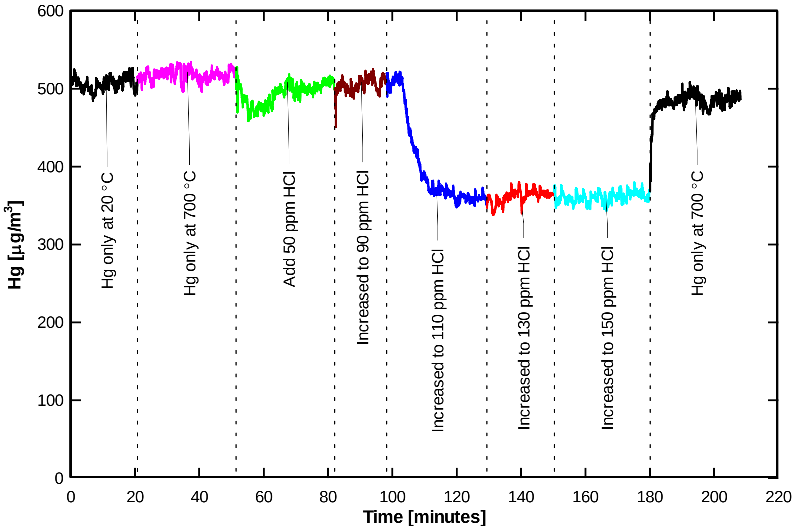

Figure 2. Hg oxidation with HCl concentrations (0 – 150 ppm) at 700ºC in 700 SCCM of the total flow rate.

Table 1. Hg oxidation by HCl at 700ºC.

| 700 SCCM (0.26 *s* RT) | | 1100 SCCM (0.16 *s* RT) | |
|---|---|---|---|
| HCl | Hg Oxidation | HCl | Hg Oxidation |
| 0 ppm | 0.0% | 0 ppm | 0.0% |
| 50 ppm | 0.4% | 30 ppm | 0.0% |
| 90 ppm | 14.2% | 50 ppm | 0.0% |
| 110 ppm | 29.1% | 70 ppm | 0.0% |
| 130 ppm | 28.7% | 90 ppm | 17.3% |
| 150 ppm | 29.9% | - | - |

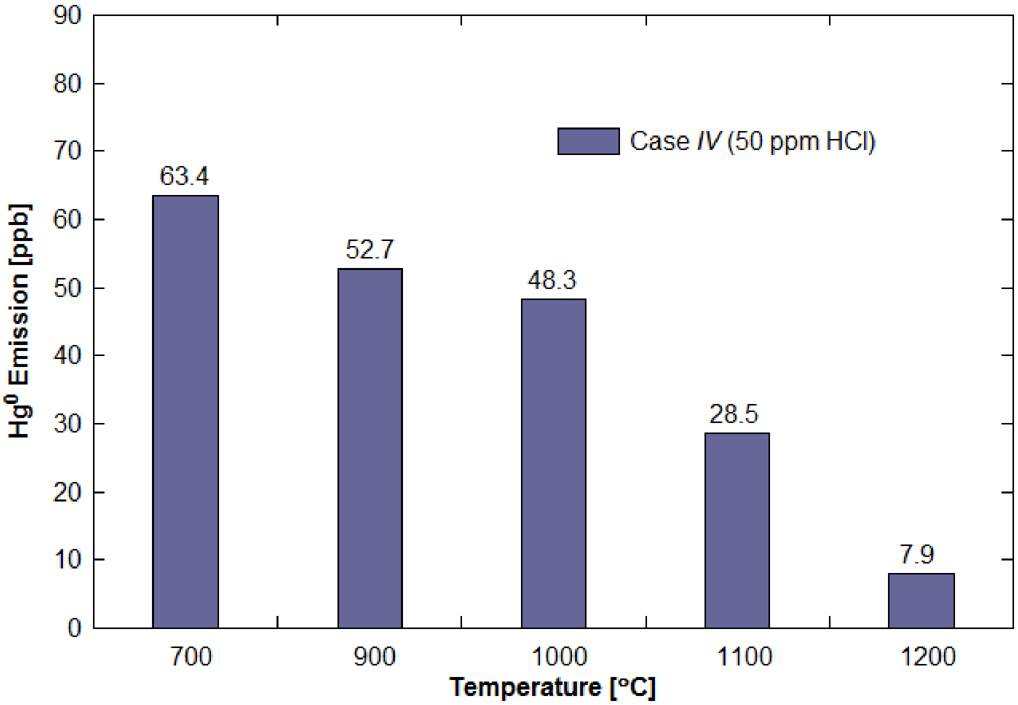

Figure 3. Hg emissions in the presence of 50 ppm HCl for the RT of 0.16 s and the flow rate of 1100 SCCM.

Figure 3 shows Hg emissions in the presence of HCl for reactor temperatures from 700 to 1200ºC, the RT of 0.16 *s*, and the flow rate of 1100 SCCM. The temperature had a strong effect on Hg oxidation. Though no oxidation occurred below 700ºC, the Hg emissions decreased with an increase in the temperature higher than 700ºC, thus, more Hg oxidation took place at higher temperatures. In general, $HgCl_2$ is a dominant oxidized form of Hg, thus the possible mechanisms of Hg oxidation are considered as reactions (1) to (6).

$$Hg^{o} + HCl \rightarrow HgCl + H \tag{1}$$

$$HgCl + HCl \rightarrow HgCl_2 + H \tag{2}$$

$$Hg^{o} + Cl \rightarrow HgCl \tag{3}$$

$$Hg^{o} + Cl_2 \rightarrow HgCl + Cl \tag{4}$$

$$HgCl + Cl \rightarrow HgCl_2 \tag{5}$$

$$HgCl + Cl_2 \rightarrow HgCl_2 + Cl \tag{6}$$

### *Effects of NO and/or $O_2$ in the presence of HCl*

The effects on Hg oxidation in the presence of HCl and NO in the gas stream were studied for the RT of 0.16 *s* and the flow rate of 1100 SCCM. In the Table 2, the concentration of NO varied from 0 to 300 ppm with 50 ppm HCl at 700ºC, and the results showed about 31 to 35% Hg oxidation were measured between 50 and 300 ppm NO. However, little inhibition or no major change in Hg oxidation was observed with an increase of the NO concentration. It was suggested that the first addition of NO in the system significantly promoted Hg oxidation; however, the further increase of NO concentrations showed minor effects.

The effects of $O_2$ on Hg oxidation in the presence of HCl in the gas stream were studied for the RT of 0.16 *s* and the flow rate of 1100 SCCM. The results in Table 2 presents about 34% Hg oxidation was found by the addition of 1% $O_2$ at 700ºC. The Hg oxidation increased with an increase in the $O_2$ concentration. Hall et al. [2] reported Hg oxidation results by the addition of HCl concentrations in the presence of $O_2$ at 500ºC. Their results showed about 30% oxidation with 50 ppm HCl and 10% $O_2$ at 500ºC. The current results showed about 40% oxidation in the presence of 50 ppm HCl and 5% $O_2$ at 700ºC. The result in the current study showed higher Hg oxidation with lower $O_2$ concentration and higher temperature than the result obtained by Hall et al. The difference was mainly caused by the temperature effect.

Hg emissions were also measured for temperatures from 25 to 1200ºC in the cases with HCl + NO and HCl + $O_2$. The reactor temperature had a great influence on Hg oxidation. The Hg oxidation increased with an increase of the temperature.

Table 2. Hg oxidation for HCl + NO and HCl + $O_2$ at 700ºC.

| NO | Hg Oxidation | $O_2$ | Hg Oxidation |
|---|---|---|---|
| 0 ppm | 0.0% | 0 % | 0.0% |
| 50 ppm | 35.1% | 1 % | 34.2% |
| 100 ppm | 31.6% | 3 % | 38.3% |
| 200 ppm | 32.2% | 5 % | 40.1% |
| 300 ppm | 31.3% | - | - |

The study of Hg oxidation in the presence of HCl, NO and $O_2$ was performed for the RT of 0.16 s and the flow rate of 1100 SCCM. According to the current results, the NO addition inhibited the Hg oxidation at all temperatures while $O_2$ promoted the Hg oxidation. The addition of $O_2$ lowered the reaction temperature. At 1200ºC, the results in all cases in the presence of HCl showed very high Hg oxidations between 86% and 97%.

***Effects of Residence Time***

The effects of the residence time on Hg oxidation were studied as a function of the reactor temperature with the flow rate of 1100 SCCM. The longer residence time promoted the Hg oxidation because it provided longer periods for the reactions among gas components.

***Effects of Catalyst***

In addition to homogeneous Hg oxidations, the reductions of Hg emissions in heterogeneous reactions were also examined using a VWT catalyst. In the beginning of the tests, the effect of Hg capture by the catalyst was observed, and it resulted in approximately 60 to 70% of the baseline concentration of $Hg^0$ was captured and stored. The VWT catalyst promoted the Hg oxidation and shifted the effective temperature lower than the homogeneous cases.

**References**

[1] S. B. Ghorishi, C. W. Lee, W. S. Jozewicz, J. D. Kilgroe, *Environmental Engineering Science* 22 (2) (2005) 221-231.
[2] B. Hall, P. Schager, O. Lindqvist, *Water, Air, and Soil Pollution* 56 (1991) 3-14.

## 6. MILESTONES NOT MET

All milestones were met for the project.

## 7. COST AND SCHEDULE STATUS

The budget has been expended.

## 8. SIGNIFICANT ACCOMPLISHMENTS

A diode-laser-based ultraviolet absorption sensor was successfully demonstrated for both *in situ* and extractive sampling atomic mercury measurements in a laboratory scale 29.3 $kW_t$ (100,000 BTU/hr) coal combustor and *in situ* measurements in a flow reactor at Texas A&M University. Laser sensor measurements were compared to measurements from a commercial mercury analyzer (CMA). A 375-nm single-mode laser and a 784-nm distributed feedback (DFB) laser are sum-frequency mixed in a non-linear beta-barium borate crystal to generate a 254-nm beam. By tuning the frequency of the DFB laser, the ultraviolet beam frequency was tuned across the transition frequency of mercury at 253.7-nm. The tuning range was large enough that an off-resonant baseline was clearly visible on both sides of the Hg transition. No pretreatment is required for elemental mercury measurements, and the effects of broadband absorption can be effectively eliminated during data analysis.

Extractive sampling was demonstrated to improve the detection limit of the sensor and to demonstrate the feasibility of total mercury concentration measurements in the future through extractive sampling. Significant variation in the atomic mercury concentration of coal-combustion exhaust was observed over short time periods during our *in situ* measurements. The sensor detection limits for *in situ* and extractive sampling are 0.3 and 0.1 parts per billion over a one meter path length, respectively.

## 9. ACTUAL OR ANTICIPATED PROBLEMS

None.

## 10. TECHNOLOGY TRANSFER ACTIVITIES

No technology transfer activities occurred during the reporting period.

## 11. JOURNAL AND CONFERENCE PAPERS

The mercury sensor and its application for measurements in the exhaust stream of a coal-fired combustor and in a flow reactor are described in the two archival journal articles below:

T. N. Anderson, J. K. Magnuson, and R. P. Lucht, “Diode-Laser-Based Sensor for Ultraviolet Absorption Measurements of Atomic Mercury,” *Applied Physics B* 87, 341-353 (2007).

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