A Cavity Ring-Down Spectroscopy Mercury Continuous Emission Monitor

Quarterly Technical Progress Report

**For the period
Starting January 1, 2003 Ending March 31, 2003**

Work Performed Under Contract:

DE-FC26-01FT41221

Submitted By:

**Sensor Research and Development Corporation
17 Godfrey Road
Orono, Maine 04473**

Christopher C. Carter, Ph.D.

Phone Number: 207/866-0100 x239

Fax Number: 207/866-2055

Submitted To:

**U. S. Department of Energy/National Energy Technology Laboratory
Morgantown Energy Technology Center
Morgantown, West Virginia
COR: Susan Maley**

Disclaimer:

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The view and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Abstract:

Accurate reporting of mercury concentration requires a detailed model that includes experimental parameters that vary, such as: pressure, temperature, concentration, absorption cross-section, and isotopic structure etc. During this quarter a theoretical model has been developed to model the 253.7 nm mercury transition. In addition, while testing the interferent species SO_2 , SRD was able to determine the absorption cross-section experimentally and add this to the theoretical model. Assuming that the baseline losses are due to the mirror reflectivity and SO_2 , SRD can now determine the concentrations of both mercury and SO_2 from the data taken.

For the CRD instrument to perform as a continuous emission monitor it will be required to monitor mercury concentrations over extended periods of time. The stability of monitoring mercury concentrations over time with the CRD apparatus was tested during the past quarter. During a test which monitored the mercury concentration every 2 seconds it was found that the standard deviation, of a signal from about 1.25 ppb Hg, was only 30 ppt.

SRD continued interferent gas testing during this past quarter. This included creating a simulated flue gas composed of the gases tested individually by SRD. The detection limits for mercury, although dependent on the concentration of SO_2 in the simulated gas matrix, remained well below the ppb range. It was determined that for the gases tested the only measurable changes in the baseline level occurred for SO_2 and mercury.

Speciation studies continued with mercury chloride (HgCl_2). This included checking for spectral speciation with both Hg and HgCl_2 present in the CRD cavity. There was no observable spectral shift. Also a pyrolysis oven was incorporated into the gas delivery system both for tests with HgCl_2 as well as atomization of the entire gas stream. The pyrolysis tests conducted have been inconclusive thus far.

Table of Contents

DISCLAIMER:	1
ABSTRACT:	2
SECTION 1: INTRODUCTION	4
SECTION 2: EXPERIMENTAL	5
SECTION 3: RESULTS AND DISCUSSION	7
CROSS-SECTION CALCULATIONS	7
STABILITY OF MONITORING MERCURY CONCENTRATIONS	12
FLUE GAS INTERFERENTS	13
MERCURY CHLORIDE AND SPECIATION	18
SECTION 4: CONCLUSION	21
SECTION 5: REFERENCES	23

Section 1: Introduction

The objective of this project is an innovative science-driven technology program to develop a prototype instrument that exploits the full potential of Cavity Ring-Down spectroscopy (CRD) as a powerful new analytical technique for the detection of ultra-trace levels of mercury.

The core effort focuses on the optimization and evaluation of a laboratory CRD spectrometer for gaseous mercury detection. Detection limits, calibration and appropriate analytical procedures will be established. The impact of individual interferent gases expected in flue gas emissions from advanced power plants will be determined. Upon testing of the individual gases a simulated flue gas steam consisting of a mixture of all expected flue gas components will be tested to determine combined interferences as well as mercury detection limits. While the primary concern of this project is the determination of the total mercury content of flue gas emissions, approaches to determine mercury speciation will also be investigated. A sampling interface will be designed, built, and integrated into the CRD spectrometer to provide a continuous sample stream from the flue gas stack to the cavity of the CRD instrument.

A summary of the major tasks involved in the project is described below:

Task 1: Mercury (Hg) CRD System Development. Design and construct CRD system for optimum mercury detection.

Task 2: Software Modification. Modify an existing LabView software package to analyze the data and control the 50 Hz laser and sampling system.

Task 3: Hg-CRD System Optimization. Determine the optimum operating conditions of the spectrometer, establish the sensitivity of the technique in terms of detection limits, and evaluate the effect of typical interferents. Develop and test a mercury speciation system to insure detection of total mercury concentration.

Task 4: Sampling Interface. Design and build the sampling system for delivery of sample gas to and from the mercury speciation system.

Task 5: Integration of Sampling System. Combine sampling system and spectrometer and determine impact, if any, on the instruments performance.

Task 6: Formalize Hg-CRD Analytical Procedures. Establish and formalize operating parameters and calibration procedures to provide validation of the results to meet the requirements necessary to allow comparison of the instrument performance with either EPA Reference 29 or the Ontario Hydro methods.

Task 7: Reporting

Prepare publications and presentations, as appropriate, to disseminate results. Formalize and document operating and calibration procedures and submit a final report.

Section 2: Experimental

The experimental technique that will be used for this project is Cavity Ring-Down spectroscopy (CRD). CRD is a sensitive absorption technique that was first developed by O'Keefe and Deacon in 1988.¹ This technique injected a pulse of light into a stable optical cavity formed by two highly reflecting mirrors. The light reflects back and forth in the cavity giving extremely long effective pathlengths. Using mirrors with a reflectivity of 99.99% and a 1-meter long cavity it is possible to achieve an effective pathlength of 10 kilometers, during the first 1/e time of the decay of the ring-down signal. As the light reflects back and forth in the cavity a small amount of light is transmitted through the end mirror of the cavity to a photon detector, such as a photomultiplier tube. The light exiting the cavity decays exponentially with time at a rate determined by round trip loss mechanisms within the cavity. The measured time constant for the exponential decay of light is called the "ring-down time" of the cavity. The dominant loss mechanism for an empty cavity is the mirror transmission. However, if a sample species, which absorbs light at a particular wavelength, is placed within the cavity the ring-down time will decrease from that of the empty cavity at that particular wavelength. The ring-down time is given by

$$\tau = \frac{l_c}{c[(1 - R) + \alpha_s l_s + \alpha_b l_c]} \quad (1)$$

where, l_c is the cavity length, c is the speed of light, R is the reflectivity of the mirrors, α_s is the absorption coefficient of the sample species of interest, l_s is the pathlength through the sample, and α_b is the absorption coefficient for various background losses. Background losses, which are all include in the last term of the denominator of eq. 1, can include scattering losses due to Mie or Rayleigh scattering or absorptions due to other components in the sample gas stream. Once the empty cavity losses and any other background losses have been determined, CRD spectroscopy provides an absolute measure of the concentration of the absorbing sample of interest within the cavity. This self-calibrating feature differentiates CRD from other highly sensitive laser-based methods such as laser induced fluorescence (LIF) or resonantly enhanced multiphoton ionization (REMPI).²

The laser source that will be used for the project is a pulsed Alexandrite laser. This is a solid-state laser that runs at 50 Hz, will produce pulse energies of >0.5 mJ/pulse at 254 nm, and has a fundamental laser linewidth of about 10 GHz. A diode seed laser is used with the system to bring the fundamental linewidth down to approximately 60 MHz, which results in a laser linewidth of about 180 MHz at 254 nm. This laser pulse will be spatially filtered and mode matched to the particular ring-down cavity that will be used. Initial results indicate a cavity length of about 65 cm is optimum for the CRD setup using specially coated plano-concave mirrors with a 6 m radius of curvature. The actual absorption cell that will be used for the mercury detection will be placed between the highly reflecting mirrors.

The design of the CRD absorption cell will have an inlet for the sample containing mercury and exit for a continuous flow. The design is such that a low flow of inert gas can be sent over the face of the highly reflecting mirrors to insure no degradation of the mirror surface, due to deposited contaminants, and hence a decrease in the ring-down time resulting in a decrease of the sensitivity of the CRD instrument. A diagram of the absorption cavity is shown in Fig. 1. From the figure it can be seen that the flow of sample flue gas will enter the cavity near the end and be exhausted from the center of the cavity to maintain the gas flow away from the mirror surfaces.

Figure 1: Diagram of sampling cavity (not done to scale) placed between the two highly reflecting mirrors

The data acquisition system will take the output of a photomultiplier tube and send it to a fast analog-to-digital 12-bit, 100 MHz card. A LabView program will be written for control of the laser system, data acquisition, and signal processing. The program will calculate the decay time of the ring-down curve, compare it with that for the empty cavity, and determine the absolute concentration of mercury in the absorption cell at any time.

A mercury vapor generation system will be used to generate known amounts of mercury for testing as well as a periodic calibration check of the CRD instrument. The vapor generation system will consist of a temperature-controlled dynacalibrator with a mercury permeation tube of a known permeation rate. Additional verification of the mercury concentration delivered to the CRD instrument will be done using an Atomic Fluorescence Spectrometer (AFS). The AFS is calibrated using a gold trap with injections of mercury vapor from the headspace of a container held at a known constant temperature.

Mercury speciation studies will begin by using a pyrolizer system. The relative efficiency of the pyrolizer for dissociating different species of mercury will be evaluated using known quantities of substances such as elemental mercury, dimethyl mercury, and mercuric chloride. The pyrolizer should allow the detection of the total amount of mercury in a sample stream by dissociating any mercury compounds. Further speciation studies will look at the possibility of spectrally differentiating compounds containing mercury from elemental mercury. An initial study into the spectral separation of mercury and mercury chloride concluded that there may have been a slight spectral shift but they were unable to resolve the small frequency shift with their laser system.³ The diode seeded Alexandrite system utilized for this project has a spectral resolution over 20 times narrower than the above-mentioned study. This increase in resolution may well allow us to spectrally separate elemental mercury from compounds of mercury.

Table I lists the major milestones and their planned completion dates for the project.

Milestone Description	Baseline	Actual
1. Finalize CRD design	3/31/02	3/31/02
2. Integration of LabView software for data acquisition	3/31/02	4/23/02
3. Hg-CRD system optimization, including approaches to speciation	3/15/04	Ongoing
4. Sample interface design	6/15/03	Initiated
5. Integrate sample system with CRD and determine combined performance	3/15/04	
6. Formalize Hg-CRD analytical procedures	3/15/04	
7. Reporting	5/15/04	

Table I: Project milestones and completion dates.

Section 3: Results and Discussion

The results obtained this quarter proceeded along a couple of fronts. One dealt with the theoretical prediction of the observed mercury transition, another with the stability of monitoring mercury concentrations over time. Also the work with flue gas interferences was continued, as well as the effort on mercury chloride and speciation.

Cross-section calculations

In order to determine absolute concentrations an accurate model is needed that includes all the experimental parameters: pressure and temperature of the sample gas, molecular absorption cross-sections, naturally occurring isotopic ratios, and resonance frequency positions.

From CRD the absorption coefficient α is found experimentally by measuring the decay time and knowing the reflectivity of the mirrors and the length of the cavity used at a given frequency (see Eq. 1). To find the number of molecules N , and hence the concentration, the absorption coefficient is related to the absorption cross-section by $\alpha = N\sigma$. It is well known that the absorption cross-section of a particular atom or molecule at frequency, ν , is given by

$$\sigma(\nu - \nu_0) = \frac{g_k}{g_i} \frac{A\lambda^2}{8\pi n^2} \cdot g(\nu - \nu_0)$$

where ν_0 is the resonance frequency, g_k and g_i are the degeneracies of the upper and lower energy levels respectively, A is the Einstein coefficient, λ is the wavelength, n is the index of refraction, and $g(\nu - \nu_0)$ is the molecular line-shape function which is dependent upon pressure and temperature.

In order to simplify the calculations an integrated cross-section is defined as

$$S = \int_0^\infty \sigma(\nu - \nu_0) d\nu$$

which reduces to

$$S = \frac{g_k}{g_i} \frac{A\lambda^2}{8\pi n^2 c}$$

A factor of the speed of light c is included in order to express S in its more common units. Notice S does not contain the line-shape function, as the integrated function is equal to 1 by definition, making it independent of pressure and temperature. This fact makes the integrated cross-section an ideal number to use as a reference value and it is commonly found in papers and reference resources, including the Hitran⁴ database. Unfortunately, for mercury it is not directly given in any of the references found so far. However, the degeneracy and Einstein coefficient for mercury can be found in the CRC Handbook of Chemistry and Physics⁵ and published journals⁶:

$$g_k = 3$$

$$g_i = 1$$

$$A = 8.00 \times 10^6 \text{ s}^{-1}$$

$$\lambda = 253.652 \text{ nm}$$

$$n = 1.00$$

Using these values $S = 2.05 \times 10^{-14} \text{ cm}^{-1}/(\text{cm}^{-2} \cdot \text{molecule})$.

In order to determine the concentration the line-shape function must be evaluated. Being able to evaluate this function at various pressures and temperatures is necessary in order to make the model flexible and to determine the best test conditions. For example, decreasing the pressure from atmosphere to 100 torr reduces the molecular linewidth by a factor of 4.5 and allows the five separable isotopic lines to be resolved. It also reduces the absorption strength by a factor of 2.5.

The linewidth of a particular transition is due to contributions from a number of different mechanisms that can be broken down into two categories: homogeneous and inhomogeneous line broadening. Line broadening due to collisions, or so-called pressure broadening, is an example of the former, while Doppler broadening is an example of the latter. These are the two dominant broadening mechanisms that will be considered here. Homogeneous broadening due to the radiative lifetime of the mercury transition is orders of magnitude smaller than the other two effects and will be neglected.

At low pressures, Doppler broadening, caused by the distribution in molecular speed, is dominant. The line shape function is given by

$$g(\nu - \nu_0) = \left(\frac{4 \ln 2}{\pi} \right)^{\frac{1}{2}} \frac{1}{\Delta \nu_D} e^{-4 \ln 2 \left(\frac{\nu - \nu_0}{\Delta \nu_D} \right)^2}.$$

This Gaussian function has a full-width half-maximum (FWHM) Doppler-broadened linewidth given by $\Delta \nu_D = 7.1 \times 10^7 \nu \sqrt{\frac{T}{M}}$, where M is the molecular mass and T is the temperature in Kelvin.

At high pressures, collisional or pressure broadening, dominates. In this case the line shape function is given by

$$g(\nu - \nu_0) = \frac{\Delta \nu_{coll}}{2\pi \left[(\nu - \nu_0)^2 + \left(\frac{\Delta \nu_{coll}}{2} \right)^2 \right]}.$$

This Lorentzian function has a collisionally broadened linewidth given by $\Delta \nu_{coll} = 8.996 \cdot P \cdot \left(\frac{273}{T} \right)^{1/2}$ MHz. The factor, 8.996 MHz/torr, was determined empirically for mercury in a nitrogen atmosphere by Jacobs and Warrington.⁷

For intermediate pressures a convolution of the two line shapes is necessary since the Doppler broadened molecules will also be collision broadened. This ‘Voigt’ function is expressed as

$$g(\nu - \nu_0) = \int_{-\infty}^{\infty} g_{coll}(\nu'_0 - \nu_0) g_D(\nu - \nu'_0) d\nu'_0$$

Fortunately, this ‘Voigt’ function can be approximated⁸ with minimal error. The resulting cross-section approximation is given by the following equations:

$$\sigma_V(\nu) = \sigma_V(\nu_0) \left\{ (1-x)e^{-(4 \ln 2)y^2} + \frac{x}{1+4y^2} + .016(1-x)x \left[e^{-0.4y^{2.25}} - \frac{10}{10+y^{2.25}} \right] \right\}$$

$$x = \frac{\Delta \nu_{coll}}{\Delta \nu_V} \quad \sigma_V(\nu_0) = \frac{S}{\Delta \nu_V (1.065 + 0.447x + .058x^2)}$$

$$y = \frac{|\nu - \nu_0|}{\Delta \nu_V} \quad \Delta \nu_V = 0.5346\Delta \nu_{coll} + (.2166\Delta \nu_{coll}^2 + \Delta \nu_D^2)^{\frac{1}{2}}$$

Notice at low pressures the value of x goes to zero and at high pressure it goes to one, making $\sigma_V(\nu_0)$ approach the values given in the low and high-pressure scenarios, given above, where no approximation is used.

Using the known relative line positions⁹ and integrated cross-sections for the different isotopes a complete spectral model for mercury has been established. With the correct values of integrated cross-section and collision broadened linewidth this same model can be used for any molecule, including the oxygen transition bands found near mercury transitions.

Shown in Fig. 2 is a plot of the oxygen transition observed near the 253.7 nm transition of mercury. Along with the assignment of the various lines to their respective electronic state is a theoretical plot using the model described above. It can be seen that the agreement between the theoretical plot and the experimental data is excellent. There is a slight frequency shift of the last line in the plot between the theoretical and experimental plots due to the non-linear behavior of the applied voltage and frequency of the diode seed laser. The agreement achieved provides validation of the theoretical model.

The plot shown in Figs. 3 and 4 is a scan over the 253.7 nm transition of mercury. The data taken for Fig. 3 was obtained at a cavity pressure of 760 torr and a temperature of 200° C with a mercury concentration of about 1.2 ppb. The data taken for Fig. 4 was also obtained with a cavity temperature of 200° C, but the pressure was reduced to 100 torr, and the mercury concentration used was ~75 ppt. From the two figures it can be seen that the agreement between the CRD data and the data obtained from the theoretical model is excellent.

Figures 2 – 4 demonstrate the versatility and accuracy of the model. The model accurately predicts the correct concentrations with changes in both pressure and temperature. In addition the model is flexible enough to use with other molecular species as well as mercury.

Figure 2: Scan of the oxygen transition originating from the ground $X^3\Sigma_g^-$ electronic state and terminating on one of 3 excited electronic states labeled on the plot. The absorption cross-section, σ , for the various transitions is given in cm^2 . The experimental plot is shown in red while a theoretical plot is shown in blue. The 65 cm cell contained 400 torr of oxygen and was held at room temperature.

Figure 3: Scan of the 253.652 nm transition of atomic mercury. The pressure in the 38 cm CRD cavity was 760 torr, the temperature was held at 473 K, and the mercury concentration was about 1.2 ppb. The full-width half-maximum of the mercury line is approximately 22.5 GHz due to the isotopic structure of mercury (see text) combined with pressure broadening.

Figure 4: Scan of ~ 75 ppt of mercury with the 38 cm cavity held at a pressure of 100 torr and temperature of 473 K, showing the resolved isotopic structure of atomic mercury. The plot in blue (with dots) is the experimental data while the plot in red is the theoretical prediction. Due to the hyperfine splitting some of the peaks contain more than one single line resulting in 5 lines from 6 different isotopomers.

Figure 5: A plot of the mercury concentration determined by the cavity ring-down instrument compared with the mercury concentration determined by the atomic fluorescence spectrometer (AFS).

Further verification of the theoretical model used to calculate mercury concentrations is demonstrated in Fig. 5. This plot is a comparison of the mercury concentration obtained from the permeation oven using the AFS and the concentration obtained from the CRD data using the above-described model. The solid red line in the figure is the concentration obtained from the calibrated AFS. The dotted red lines indicating the error associated with the mercury concentration are only due to fluctuations in the temperature of the oven and do not take into account sources of error associated with the AFS measurement itself. The black points on the plot indicate the CRD data and its associated data. From the plot it can be seen that the agreement between the two is very good. Only one CRD data point, out of 14 total, lies outside the error limits.

Stability of Monitoring Mercury Concentrations

The prime function of the CRD instrument will be to continuously monitor the concentration of mercury in a flue gas stream. To this end, SRD has tested the stability of monitoring mercury concentration over time with the CRD instrument under a variety of conditions. These conditions include using various pressures and temperatures. The pressure of the cavity is important as the linewidth of the various mercury isotopic transitions decreases significantly in going from 760 torr to 100 torr. Any frequency drift of the diode seed laser over time will accentuate apparent fluctuations in the mercury concentration, as the linewidth of the mercury transition gets narrower.

Shown in Fig. 6 is a plot of total cavity losses versus time. During this test the CRD cavity was kept at a pressure of 760 torr and a temperature of 200° C. The mercury being delivered from the permeation oven was maintained at a concentration of about 1.25 ppb in air. The data points shown in Fig. 6 were obtained every 2 seconds over a period of 25 min.

From Fig. 6 it can be seen that the concentration of mercury monitored by the Hg-CRD CEM varies only slightly over the 25-minute time span of the test. The standard deviation of the fluctuations over time was about 750 ppm total cavity losses. These losses correspond to a standard deviation in the mercury concentration of about 30 ppt. The permeation oven is temperature controlled to $\pm 1^\circ$ C. SRD has performed a number of tests to determine the relationship between the temperature of the permeation oven and the mercury concentration. From this data it has been determined that fluctuations of $\pm 1^\circ$ C would result in fluctuations of the mercury concentration of ± 10 ppt, assuming that the temperature within the oven has equilibrated.

While it appears that there are fluctuations above and beyond those attributable to just temperature changes of the permeation oven, they are relatively small. There are a number of possible sources, other than the permeation oven, of this variation over time. The fluctuations may be due to a slight frequency drift of the output wavelength of the diode seed laser over time, they may be due to shot-to-shot fluctuations of the laser system itself, or possibly fluctuations of the temperature and pressure at which the cavity was maintained.

SRD will continue to test the CRD instrument for stability of monitoring the mercury concentration over time. This effort will continue throughout the entire project.

Figure 6: Plot of the cavity losses versus time. The data was taken with the 38 cm cavity that was held at atmospheric pressure (760 torr) and the temperature of the cavity was held at 473 K. The concentration of mercury from the permeation oven was kept at 1.25 ppb in air. A data point was acquired every 2 seconds. The standard deviation of the plot is about 750 ppm loss, which corresponds to a mercury concentration of about 30 ppt.

Flue Gas Interferents

With the detection limits of mercury down in the low ppt range the next step was to determine any background absorptions or interferences caused by other constituents of flue gas emissions from coal-fired power plants. Table II lists the untreated flue gas components from a power plant burning low sulfur eastern bituminous coal. The total mercury concentration listed is in the ppb range, which is well above our present detection limits. From the list the component of greatest concern, in terms of an UV absorption technique, is SO₂.

Sulfur Dioxide is known to absorb in the same region of the ultra-violet as mercury. The absorption cross-section for SO₂ has been estimated³ to be on the order of 10⁻¹⁹ cm². While this cross-section is 5 orders of magnitude smaller than that of mercury, the concentration of SO₂ in flue gas, from Table II, is approximately 5-6 orders of magnitude higher than typical levels of mercury. Presently used commercial CEM's based on atomic emission, atomic fluorescence, or atomic absorption require the removal of SO₂, and other flue gas constituents, before an accurate determination of the mercury concentration can be made. SRD has shown previously the detection of mercury in a gas stream with relatively high concentrations of SO₂.

The addition of SO₂ to the CRD cavity has an immediate effect on the baseline level of the CRD spectrum. There is an observable increase in the base absorption losses of the cavity, dependent on the SO₂ concentration. However, the absorption loss level is constant over the frequency range used to observe the mercury transitions. The absorption is also unstructured indicating that there would be no possibility of observing a peak of SO₂ rather than mercury.

Species	Volume
H ₂ O	5 – 7 %
O ₂	3 – 4 %
CO ₂	15 – 16 %
Total Hg	1 ppb
CO	20 ppm
Hydrocarbons	10 ppm
HCl	100 ppm
SO ₂	800 ppm
SO ₃	10 ppm
NO _x	500 ppm
N ₂	Balance

Table II: Typical untreated flue gas composition from a power plant burning low sulfur eastern bituminous coal.¹⁰

In an effort to incorporate SO₂ concentrations into the theoretical model, SRD performed some additional tests. Shown in Fig. 7 is a plot of the absorption losses versus concentration of SO₂. The point on the left side of the plot, shown in Fig. 7 at 0 ppm, corresponds to baseline losses of an empty cavity with no SO₂ present in the cell. The rest of the points correspond to concentrations ranging from 100 to 2500 ppm. This range of concentrations is generally greater than the output from coal-fired power plants. The higher concentrations tested were about 1 million times the concentration levels of mercury to be detected (low ppb).

It is encouraging that the plot of losses versus concentration is linear. This is a good indication that we are not observing any saturation effects or non-Beer-Lambert law behavior, both of which could substantially inhibit our ability to accurately determine mercury concentrations with relatively high background absorptions. It should also be noted that the exponential decays used to determine the absorption due to SO₂, while the time constant decreased, was still fit very well to a single exponential. Again this is also important for accurate determination of the mercury concentration.

From the information obtained, to produce the plot for Fig. 7, SRD was able to experimentally determine the absorption cross-section of SO₂ in the wavelength region adjacent to the UV mercury transition. The concentration of SO₂ was determined from a certified cylinder and mass flow controllers, which were used to accurately measure the gas flow. SRD independently checked the concentration of SO₂ from the cylinder using a gas chromatograph and the results agreed with the certified value. The experimentally determined value of the absorption cross-section of SO₂ by SRD was approximately $1.45 \times 10^{-19} \text{ cm}^2$. This value agrees quite well with the experimentally determined value by Spuler and co-workers.³ They determined the SO₂ cross-section to be $1.2 \times 10^{-19} \text{ cm}^2$.

This experimentally determined cross-section has been incorporated into the theoretical model, which can now be used to determine both the mercury concentration and the SO₂ concentration. This assumes that the losses in the cavity are due to only mercury, SO₂, and the high reflectivity mirrors.

Figure 7: Baseline absorption losses versus SO₂ concentration. From this plot the absorption cross-section for SO₂ can be determined.

Shown in Fig. 8 is a plot of the mercury isotopic structure observed in the presence of SO₂. This scan was done with the 65 cm cavity held at a pressure of 100 torr and a temperature of 200° C. The concentration of mercury used for this scan was approximately 1.2 ppb while the concentration of SO₂ used was about 2175 parts-per-million by volume (ppm). This is a difference in concentration of close to 2 million times. While the background absorption level is higher than previously observed with no SO₂, from the plot it can be seen that the CRD instrument was able to easily detect mercury. The amount of mercury in the gas stream was close to the same concentration levels in the untreated flue gas, in the presence of SO₂ at a concentration almost 3 times that reported for the particular untreated flue gas given in Table II. These results are very promising for the development of the CRD spectrometer without the need for extensive sample pre-treatment as is needed for most mercury CEM monitors on the market today.

Figure 8 includes both the experimental plot, shown in blue, and the theoretically predicted mercury spectrum, shown in red. The calculated spectrum was done as described in the section, *Cross-Section Calculations*, above with an addition to the baseline losses to include losses from SO₂. From the figure it can be seen that the agreement between the experimental and theoretically predicted results is very good. The limit of detection of mercury, in the presence of SO₂, is dependent on the SO₂ concentration. For example, a SO₂ concentration of 1000 ppm, above that for the untreated flue gas given in Table II, the limit of detection was determined to be about 150 ppt. This limit of detection is far below the mercury concentration expected in the flue gas stream.

Figure 8: A plot of the losses in the 65 cm cavity versus relative frequency. The cavity was held at a pressure of 100 torr and a temperature of 473 K. Clearly seen are the 5 mercury peaks above the SO_2 background absorption. The concentration of mercury is ~ 1.2 ppb while that for SO_2 is about 2175 ppm. The plot includes the experimental data (blue), and the theoretical plot (red) including both the mercury and SO_2 concentrations, and losses from the mirrors.

While it is important to be able to determine the baseline losses due to additional absorbing species, the real question remains; can the CRD instrument accurately determine low levels of mercury in the presence of these background gases?

SRD had previously demonstrated detection of mercury within a matrix of SO_2 with the 65 cm cell. As the 65 cm cavity had been replaced with the 40 cm cavity the detection of mercury within SO_2 needed to be verified. Figure 9 is a plot of cavity losses versus relative frequency using the 40 cm cavity. The data shown in the plot was taken with a flow through the cavity of ~ 1700 ppm SO_2 and ~ 1.5 ppb mercury. This corresponds to a mercury concentration over 1,000,000 times less than SO_2 . The cell was maintained at a pressure of 50 torr to fully resolve the individual mercury isotopic peaks and the temperature was held at 200°C . From the plot it can be seen that the baseline noise level, with a background of SO_2 , is somewhat, but not significantly, noisier than that observed with an empty cavity. It can also be seen that the CRD instrument was able to detect the low concentration level of mercury with a relatively good signal to noise ratio in the shorter 40 cm cavity. From the observed signal it can be seen that the detection limits for mercury are clearly at the sub-ppb level.

In addition to the experimental data shown in Fig. 9, there is also a theoretical plot included. The theoretical plot includes losses due to the mirrors, a specific concentration of mercury, and a specific concentration of SO_2 . From the figure it can be seen that the theoretically determined plot agrees extremely well with the experimental data. This gives us additional confidence in our ability to determine accurate concentrations of mercury even in the presence of strongly absorbing species, which raise the baseline level of the background. If the background absorption is due primarily to SO_2 the CRD instrument can also determine the concentration of SO_2 at the same time as the mercury concentration.

Figure 9: Scan over the atomic mercury isotopic structure with the 38 cm cavity held at a pressure of 50 torr and a temperature of 473 K. The flow of gas contained ~1.5 ppb mercury and ~1700 ppm SO₂. The blue plot is the experimental data and the red plot is the theoretically predicted mercury spectrum.

There are a number of other molecular species that are present in flue gas emissions (see Table II). SRD has tested a number of these additional gases previously. These include carbon monoxide (CO), carbon dioxide (CO₂), nitric oxide (NO), and nitrogen dioxide (NO₂). All of these gases tested were very similar to water. None of the gases absorbed any measurable amount of UV radiation near the mercury transition. The baseline level remained similar to that of the empty cavity. These results are also very encouraging for the ability of CRD to detect sub-ppb levels of mercury even within a complex background of gases such as those present in flue gas emissions.

Subsequent to the completion of tests on each individual flue gas component SRD used a gas-mixing manifold to combine a number of the gases and create a ‘simulated’ flue gas mixture to test the CRD instrument. The gases and concentrations included in the mixture were: 1000 ppm SO₂, 285 ppm CO, 285 ppm CO₂, 70 ppm NO, 70 ppm NO₂, 1.5 ppb Hg, and the gas stream was passed through a water bubbler to elevate the concentration of water in the sample stream. This sample stream was sent to the CRD cavity where the pressure was maintained at a constant 100 torr and the temperature at 200° C. The results are shown in Fig. 10. The figure has two plots included on it; the first is the experimental plot obtained from the ring-down time, and the second is a theoretical plot for a concentration of mercury of about 1.5 ppb and a concentration of SO₂ of 1000 ppm. From the figure it can be seen that there is excellent agreement with the peak heights and widths. The frequencies are slightly shifted due to the non-linear response of the scanning diode laser to the applied voltage. There has only been a linear conversion of the voltage to frequency.

Figure 10: Plot of mercury contained in a 'simulated' flue gas. Components of the gas stream are listed on the figure. The cavity pressure was maintained at 100 torr and the temperature was held at 473 K. The red line is the experimentally determined losses and the blue line is the theoretical prediction for a mercury concentration of 1.5 ppb and a SO_2 concentration of 1000 ppm. The slight offset in frequency is due to non-linear scanning of the diode seed laser with the applied voltage.

Mercury Chloride and Speciation

The aim of this project is to be able to determine the total mercury content in a flue gas stream. Mercury can be in many different forms including compounds containing mercury. One method for determining the total mercury content is to atomize the incoming gas stream to ensure all the mercury is in its elemental form, $\text{Hg}^{(0)}$. SRD has chosen to approach this process using the method of pyrolysis. Pyrolysis has a number of advantages over other methods. It is a relatively easy and inexpensive method of atomizing a stream of gas. Other methods such as using a graphite-furnace involve placing the atomization source within the cavity thus significantly decreasing the pathlength available to the species of interest and hence the detection limits attainable with CRD, given the direct relationship between sensitivity and pathlength. Also, methods involving complicated atomization sources will severely hamper the development of a CRD instrument capable of autonomous operation.

SRD has incorporated a Lindberg/Blue model TF55030A oven capable of heating the sample gas stream to 1100° C. This will provide enough energy to atomize molecular species in the gas stream. As well as atomizing all mercury compounds to elemental mercury the oven can also atomize interfering species such as SO_2 . While some of the SO_2 will recombine, pyrolyzing the entire gas stream may lower any background absorption losses, as none of the atomic species or other reaction products should absorb in the same spectral region of the UV as mercury.

Initial tests with the pyrolyzing oven set to 800° C did not show any definitive results. There was no observable decrease of the background absorption indicating that either the SO_2 is just recombining or is not pyrolyzing.

While the initial results were inconclusive there may be a number of reasons for this: first, the glass beads initially used within the quartz tube, to increase heating throughout the sample, limited the operation of the oven to about 800° C; second, the resident time may not have been long enough to pyrolyze the gas stream; and third, after exiting from the oven there could be recombination or reactions to produce additional species. The addition of quartz beads or chips will allow the temperature to be elevated to the oven limit of 1100° C. A previous report¹¹ of atomizing a gas stream with mercury species indicates a temperature of 1000° C should be sufficient for pyrolysis. Adjusting the flow rate can be done to ensue enough resident time in the oven for full pyrolysis. Minimizing the distance from the oven to the CRD cavity and heating any tubing between the two can reduce the chances for reaction and/or recombination.

Aside from determining the total mercury concentration there is a great deal of interest in an instrument capable of mercury speciation. In particular the ability to determine the amount of elemental mercury, $\text{Hg}^{(0)}$, from the oxidized form, $\text{Hg}^{(+2)}$, is highly desirable. The binding energy of mercury with other atoms or molecules is generally very weak. This suggests that there may only be a small spectral perturbation to the atomic mercury transition in mercury compounds. It has been reported that a small spectral shift may have been observed for mercury chloride (HgCl_2) relative to the atomic mercury transition. The resolution of this experiment, done by Spuler and co-workers,³ was approximately 3.3 GHz (0.11 cm^{-1}), which was not spectrally narrow enough to resolve the isotopic structure of the mercury transition or definitively establish a spectral shift of the mercury chloride peak relative to the atomic mercury transition. However, the resolution of the CRD instrument at SRD is approximately 0.18 GHz (0.006 cm^{-1}) in the UV, which is clearly narrow enough to resolve the isotopic structure and may be narrow enough to observe a spectral shift between HgCl_2 and atomic mercury. If the shift is great enough it may be possible to determine absolute concentrations of mercury compounds and atomic mercury as well as the total mercury content of a sample.

SRD had previously observed absorptions due to HgCl_2 that were in the same region as those belonging to atomic mercury. The next step was to add elemental mercury at the same time to establish if there was any spectral separation between the two species. Figure 11 is a plot of the losses in the cavity with $\sim 1 \text{ ppb}$ HgCl_2 and $\sim 1.5 \text{ ppb}$ $\text{Hg}^{(0)}$. The two gas streams were mixed together just prior to the CRD cavity inlets. The HgCl_2 gas stream had heated Teflon tubing from the dynacalibrator permeation oven to the CRD cavity and was maintained at a temperature of about 200° C.

Prior to the combined experiment each species was introduced individually into the CRD cavity to determine the individual losses due to the HgCl_2 and $\text{Hg}^{(0)}$. Included in the figure is a theoretical plot that assumes a combined mercury concentration of $\sim 2.5 \text{ ppb}$. From the figure it can be seen that the theoretical plot agrees very well with the experimental plot for the total concentration. An assumption made in the theoretical plot is that the absorption cross-section for HgCl_2 is the same as that for elemental mercury. The agreement between the theoretical predictions and those obtained from the permeation rate are good, which gives this assumption some validation.

It can also be seen that there is no observable spectral separation between the two mercury species. This could be due to a couple of reasons; the first is that any spectral shift of the HgCl_2 is too small to be observed with the CRD instrument, or the second possibility is that the HgCl_2 has broken down to elemental mercury. The former of the two possibilities seems relatively unlikely while the latter seems to be a much more probable result, although the good agreement between the theoretically predicted spectrum, the permeation rate of the HgCl_2 permeation tube, and the experimentally determined spectrum would indicate that all of the HgCl_2 would have to have decomposed.

Speciation studies will continue. This will include efforts to spectrally separate HgCl_2 from elemental Hg. Spectral separation would be the most desirable method, as this would lead to unambiguous assignment of the two different mercury species. The selectivity inherent in a laser-based method such as CRD would be able to exploit any spectral separation and individually quantify the two species.

Figure 11: Plot of the total amount of mercury determined from both HgCl_2 and elemental mercury. The 38 cm cell was held at a pressure of 100 torr and temperature of 473 K. The concentration of each was: 1 ppb HgCl_2 , and 1.5 ppb Hg. The total concentration used in the theoretical plot (red) was 2.5 ppb Hg.

Section 4: Conclusion

SRD has developed a theoretical model for predicting the 253.7 nm mercury transition. The model is very flexible and takes into account a number of experimental parameters that may vary during the measurement of mercury concentrations, such as: temperature and pressure of the CRD cavity, absorption cross-section, mirror reflectivity, and certain interferent species. SRD was able to experimentally determine the absorption cross-section of SO₂ and incorporate these results into the model. Presently the CRD instrument can determine both the concentrations of SO₂ and mercury, assuming that losses in the cavity are only due to the mirrors, mercury, and SO₂.

The ability of the CRD instrument to measure mercury concentrations over time was investigated. Measurements were done at 2-second intervals for 25 minutes. A mercury permeation tube held at constant temperature in an oven was the source of mercury used for the test. It was found that for a concentration of ~1.25 ppb mercury in air the standard deviation of the measurement was around 30 ppt, or about 2 %. This result does not take into account changes in the mercury concentration due to fluctuations in the permeation oven temperature.

The effect of flue gas interferents continued to be tested during the past quarter. SRD had previously tested a number of flue gas constituents individually. These species included: SO₂, H₂O, CO₂, CO, NO₂, and NO. The only species that absorbed any measurable amount of UV radiation, in the region near the mercury transition, was SO₂. SRD constructed a gas manifold to create a simulated flue gas stream for the CRD instrument. The results obtained with the simulated flue gas was similar to that obtained with just SO₂ and mercury. The detection limits are dependent on the amount of SO₂, but as an example, the detection limits determined for mercury in the presence of 1000 ppm SO₂ was about 150 ppt, well below that expected in an actual flue gas stream from a coal-fired power plant.

SRD continued work on the speciation of elemental mercury (Hg⁽⁰⁾) and oxidized mercury (Hg⁽²⁺⁾). A dynacalibrator containing a HgCl₂ permeation tube was used along with the elemental mercury permeation oven source. Tests were conducted with both sources flowing into the CRD cavity. No spectral separation was observed even at lower pressures where the isotopic structure of the mercury transition is resolved. The model predicted that the combined absorption of the two species was equivalent to the two individual sources, although the model does assume that the absorption cross-section is the same for both species.

SRD incorporated a pyrolysis oven into the CRD instrument as an atomization source for the sample gas stream. Initial results were inconclusive. There could be a number of reasons for this result although the most likely is that the temperature of the oven was limited to about 800° C due to the composition of the glass beads used within the pyrolysis tube. Replacing these beads with quartz beads or chips will allow the oven to be heated to its maximum temperature of 1100° C.

SRD will continue to work on both speciation and pyrolysis during the next quarter. In addition, work will begin on the design of the sampling system to be integrated into the CRD instrument that will allow continuous sampling of a flue gas stream. A variety of commercial sampling systems will be evaluated as well as a number of in-house designs.

A chronological listing of significant events and accomplishments is given in Table III. This is a continuous list from the project inception through the present report.

Date	Description
10/01	Acquired and setup Alexandrite PAL ring laser system
10/01	Acquired high reflectivity mirrors needed for CRD cavity
10/01	Installed fast digitizing card for data acquisition
12/18/01	Setup CRD cavity
12/27/01	Produced 253.7 nm light from laser system needed for mercury detection
12/31/01	Coupled light into cavity and detected ring-down signal
1/21/02	Calculated needed mode matching optics for the cavity and inserted into optical setup
2/8/02	Checked 'long' term stability of CRD cavity and laser system alignment
3/5/02	Determined empty cavity parameters
3/21/02	Integrated data acquisition program for CRD data
3/29/02	Prepared system for mercury delivery
4/12/02	Incorporated mercury permeation tube gas delivery system to CRD instrument
4/23/02	Integration of software control for scanning of the laser system
5/17/02	Detection of weak oxygen lines with the cell filled to atmospheric pressure with air
6/6/02	Integration of an Atomic Fluorescence system to verify mercury delivery and concentrations
6/18/02	Optimization of optics and laser parameters using 400 torr of Oxygen
7/9/02	Installed Iodine cell for absolute calibration of the Alexandrite laser system
8/15/02	Calibrated Atomic Fluorescence system and confirmed delivery of mercury to CRD cavity
8/21/02	Calibrated Alexandrite laser system in the spectral region of the mercury transition
9/12/02	Detected mercury in the CRD cavity
9/27/02	Early detection limits in the low parts per trillion (ppt) range
10/17/02	Tested various cavity lengths and switched from a 64.5 cm to 38 cm cavity
10/30/02	Able to detect sub-ppb levels of Hg in presence of high concentration of SO ₂
11/7/02	Tested CO, CO ₂ , NO, NO ₂ , and did not observe any background interferences
11/13/02	Not able to observe any change in baseline level with high concentration of water vapor
12/11/02	Installed pyrolysis oven for atomization of sample gas stream
12/18/02	Integrated dynacalibrator into CRD system for delivery of mercury chloride
12/20/02	Observed mercury signal due to mercury chloride
1/13/03	Theoretically modeled mercury and oxygen absorption lines
1/23/03	Constructed simulated flue gas delivery system
2/5/03	Optimized laser power injected into cavity for best signal-to-noise
2/14/03	Based on the model added a thermocouple inside the CRD cavity
2/21/03	CRD detection of HgCl ₂ and Hg in the presence of multiple flue gas components
2/28/03	Completed initial pyrolysis tests of HgCl ₂ , Hg, and simulated flue gas
3/11/03	Determined SO ₂ absorption cross-section
3/20/03	Tested dynamic range of the CRD instrument
3/28/03	Checked long term laser frequency drift to determine stability

Table III: Chronological listing of significant events.

Section 5: References

1. A. O'Keefe and D. A. G. Deacon, "Cavity ring-down optical spectrometer for absorption measurements using pulsed laser sources" *Rev. Sci. Instrum.* **59** (12), 2544-2551 (1988).
2. G. Berden, R. Peeters, and G. Meijer, "Cavity ring-down spectroscopy: Experimental schemes and applications" *Int. Rev. Phys. Chem.* **19** (4), 565-607 (2000).
3. S. Spuler, M. Linne, A. Sappey, and S. Snyder, "Development of a cavity ring-down laser absorption spectrometer for detection of trace levels of mercury" *Appl. Opt.* **39** (15), 2480-2486 (2000).
4. L. S. Rothnam, and J. Schroeder, "The HITRAN (2000) Molecular Spectroscopic Database and JHAWKS (2001)", Cambridge, MA.
5. D. R. Linde, Handbook of Chemistry and Physics, 80th ed. (CRC Press, Boca Raton, Fla., 1999).
6. G.C. King and A. Adams, "An accurate determination of the lifetime of the 6^3P state in mercury using a new electron-photon delayed coincidence apparatus," *J. Phys. B: Atom. molec. Phys.* **7**, 1712-1718 (1974).
7. J. P. Jacobs and R. B. Warrington, "Measurement of pressure broadening and shift for Hg 254 nm line by N_2 ," *Bul. Am. Phys. Soc.* **44**, Part I, 729-730 (1999). Presented at the American Physical Society Centennial Meeting, Atlanta, GA.
8. E.E. Whiting, "An empirical approximation to the Voigt profile," *J. Quant. Spectrosc. Radiat. Transfer* **8**, 1379-1384 (1968).
9. W. G. Schweitzer, Jr., "Hyperfine structure and isotope shifts in the 2537 – Å line of mercury by a new interferometric method" *J. Opt. Soc. Amer.* **53** (9), 1055-1072 (1963).
10. E. J. Granite, Paper 12-1, Pittsburgh Coal Conference, Sept. 2002.
11. D. P. Baldwin, S. J. Bajic, D. E. Eckels, and D. S. Zamzow, "Testing of continuous sampling Air-ICP and mercury systems as continuous emissions monitors at the Diagnostic Instrumentation and Analysis Laboratory" Ames Laboratory-USDOE, *Report IS-5144*, (2001).