A Cavity Ring-Down Spectroscopy Mercury Continuous Emission Monitor

Quarterly Technical Progress Report

For the period

Starting April 1, 2003 Ending June 30, 2003

Work Performed Under Contract:

DE-FC26-01FT41221

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Submitted To:

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Abstract:

Previous work on the detection of mercury using the cavity ring-down (CRD) technique has concentrated on the detection and characterization of the desired mercury transition. Interferent species present in flue gas emissions have been tested as well as a simulated flue gas stream. Additionally, work has been done on different mercury species such as the elemental and oxidized forms. The next phase of the effort deals with the actual sampling system. This sampling system will be responsible for acquiring a sample stream from the flue gas stack, taking it to the CRD cavity where it will be analyzed and returning the gas stream to the stack. In the process of transporting the sample gas stream every effort must be taken to minimize any losses of mercury to the walls of the sampling system as well as maintaining the mercury in its specific state (i.e. elemental, oxidized, or other mercury compounds).

SRD first evaluated a number of commercially available sampling systems. These systems ranged from a complete sampling system to a number of individual components for specific tasks. SRD engineers used some commercially available components and designed a sampling system suited to the needs of the CRD instrument. This included components such as a pyrolysis oven to convert all forms of mercury to elemental mercury, a calibration air source to ensure mirror alignment and quality of the mirror surfaces, and a pumping system to maintain the CRD cavity pressure from atmospheric pressure (760 torr) down to about 50 torr.

SRD also began evaluating methods for the CRD instrument to automatically find the center of a mercury transition. This procedure is necessary as the instrument must periodically measure the baseline losses of the cavity off of the mercury resonance and then return to the center of the transition to accurately measure the mercury concentration. This procedure is somewhat complicated due to the isotopic structure of the 254 nm mercury transition. As a result of 6 isotopes and hyperfine splittings there are 5 individual peaks that can be resolved by the CRD instrument.

SRD tested a derivative method with both simulated data and actual data taken with the CRD apparatus. Initial tests indicate that this method is successful in automatically finding the center of the mercury transitions.

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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 pyrolyzer system. The relative efficiency of the pyrolyzer for dissociating different species of mercury will be evaluated using known quantities of substances such as elemental mercury, dimethyl mercury, and mercuric chloride. The pyrolyzer 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	6/15/03
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

Results obtained during the past quarter dealt with the overall sampling system. This system will take a sample gas stream from a flue stack to the CRD cavity to be analyzed and return the gas stream back to the flue stack. The effort concentrated first, on the evaluation of commercial components for parts of the sampling system, to an entire commercial sampling system. SRD engineers then focused on the actual design of the sampling system to be used with the CRD instrument.

In addition to the sampling system design work began on developing a method for the cavity ring-down control software to automatically check the baseline absorption and return to the desired peak of mercury to perform concentration measurements.

Sampling System

Investigation of the sampling system began with the evaluation of commercially available products. A variety of these products are delineated below. Included with each product is a summary of its function as well as cost estimates, where they were available.

Apogee Scientific, Inc.

QSI (Quick Silver Inertial Separation)

\$9,250. to \$10,250.

The QSI probe system is used to extract and filter flue gas samples from coal-fired power generating plants for the purpose of determining TVM (total vapor-phase mercury) concentrations. The probe is designed to deliver these samples with minimal change to vapor-phase mercury speciation. The QSI system is mounted external to the flue gas exhaust stack and is the interface between this stack and a mercury sample processing system. Typical installation is for CEM applications.

QSI is primarily a low maintenance filter system that is both flow and temperature controlled. Principal components are an inertial separation assembly and a porous filter element. Filtering is for particles 2 μ m and above (0.5 μ m available with a concomitant increase in filter maintenance). Probe system flow rate, typically set around 10-12 acfm is managed by a closed loop flow control system. This includes a magnahelic gauge to measure pressure and is linked to a blower system that powers a pneumatic pump on the return side of the sample probe. Sample flow rate, the amount siphoned off for Hg measurement, is typically in the ≤ 4 slpm range. Flue gas not drawn off for analysis is returned to the exhaust stack. Temperature control is done in 2 zones, with the pre-filter zone set to match the flue gas temperature ($\approx 150^\circ$ C) and the post-filter section set to a slightly higher temperature (≈ 180 - 200° C). There are 3 sample ports with 1/4" Swagelok connections. One of the ports is used for sampling total Hg, one for elemental Hg, and the third for a thermocouple to monitor filter temperature. For non-isokinetic sampling, the nozzle internal to the exhaust stack is normally just a 3/4" O.D. stainless steel (SS) tube cut to the appropriate length and connected to the QSI by a Swagelok to NPT fitting. The QSI system is not normally used in an isokinetic configuration however it has been successfully adapted to this technique.

Apogee QSI systems have been installed and used at the DOE facility in Pittsburgh, Pa., at the UNDEERC/DOE facility in North Dakota, and Western Kentucky University as well as with a variety of research and CEM service providers.

Apex Instruments

Apex manufactures a variety of instruments designed to comply with EPA reference methods for isokinetic and gaseous sampling of flue gas emissions. They also sell individual components to clients fabricating their own sampling systems.

SY5-CIS Method 5 Sampling Train \$13,000.

The Method 5 Sampling Train is a complete yet portable isokinetic sampling system designed to meet EPA Method 5 requirements. It features a heated 6' sampling probe (can be ordered at any suitable length) which includes the glass lined probe itself, a Pitot type gas sampler for the manometer, probe heater and thermocouple, and can be ordered with a variety of accompanying test apparatus such as gaseous sample probes etc. This is followed by a heated sampling box, which supports a filter assembly and the appropriate set of impinger glassware. Finally there is the model 572 source sampler console which houses the temperature/thermocouple controls and power supplies, a dual manometer, sample pump, gas meter, and umbilical cable connections. The heated umbilical cord (60' plus a 15' extension), the packing/transport cases, monorail assembly, as well as a variety of support tooling is also included.

PA-4G-O2 Method 5 Probe Assembly with oversheath \$591.

Glass lined 4' probe assembly for isokinetic sampling without any attachments or support equipment.

SK-CM5 Compact Method 5 sampling system \$4270.

Includes a 6' standard heated Method 5 probe, filter assembly, unheated Teflon lined sample line, set of nozzles, and a set of stainless steel impingers along with a case.

RS-PS2-SYS PS2 RATA Sampler**\$2995.**

This is a probe designed to do gaseous (not isokinetic) sampling of flue gas emissions in CEM (Continuous Emission Monitoring) mode. It consists of a heated probe with 3 individual sampling tubes, a filter, a small console to control temperature and a magnahelic used to ensure equal flow rates from all 3 sampling tubes. There is also a 100' sample line. The system as packaged does not include pumps or impingers.

PC4-4S CEM Probe Assembly**\$245.**

This is a permanently mounted probe for use as a gaseous CEM. It includes a 4' CEM probe assembly with a sheath, heater, thermocouple, and 1/4" SS liner, mounted on a universal pipe flange reducer. The liners come in various diameters and lengths.

GNFA-2 Glass Filter Assembly + glass fiber filter**\$195. + \$46**

The glass filter housing is designed to go in-line for particulate filtering.

SFA-47 In-stack SS Filter Assembly**\$295**

This filter assembly is designed to be located immediately after the sample nozzle within the exhaust stack. It does not include a nozzle.

NS-SET Isokinetic Nozzle Set**\$427.**

A set of 7 SS nozzles (for different sample rates) used as the point source for collection of isokinetic flue gas samples. Can also be purchased in glass, Quartz and Inconel.

HSRL Self Regulating Heated Sample Line**\$25-\$28 / ft.**

A self-regulating sample line that maintains a temperature of 150° C, has a Teflon tube core, and is insulated with a braided protective sleeve. This can be ordered with more than one tube core and in a variety of tube sizes. Lengths from 10' to 100' are available.

ICS-xxx CEM Temperature Controllers**\$398 - 595**

These are one and two station temperature controllers. They can be used for thermocouple-controlled equipment or for self-regulating heated sample lines.

Clean Air Express

Clean Air Express sells and rents equipment used for CEMs and flue gas analysis. They also offer consulting and training services.

0723-100 Heated CEM Teflon Tubing**\$2878.**

A heated umbilical line for CEM applications, 100' long. It contains a 3/8" Teflon line, a 1/4" Teflon line, 2 type K thermocouple lines. This heated tubing comes in a variety of sizes and lengths with the shorter lengths costing more per foot.

O'Brien Corp.

Manufacturers of tubing bundles for a variety of applications such as stack gas analyzers, gas chromatography, water analyzers, and other scientific instrumentation.

SU-S2-T-S120/100/K15 Heated Teflon Tubing \$1850.
100'x 1/4" heated/insulated Teflon tubing with thermocouple.

SU-S2-T-S120/100/K15 Heated Teflon Tubing \$960.
40'x 1/4" heated/insulated Teflon tubing with thermocouple.

HC10-K-120 Digital Temperature Controller \$533.
Temperature controller and power supply for O'Brien heated Teflon tubing.

Clayborn

Manufacturer of electrical resistance heating tape and heated tubing assemblies.

Dekoron-Unitherm

Manufacturer of insulated tubing products and controllers. They will make custom lengths, voltage, etc.

210-4-10ft. K-115-T Series 200 Electrically Heated Hose \$742.
Outdoor heated 1/4" Teflon cored hose, 10' long with thermocouple.

210-4-30ft. K-115-T Series 200 Electrically Heated Hose \$1216.
Outdoor heated 1/4" Teflon cored hose, 30' long with thermocouple.

210-4-60ft. K-115-T Series 200 Electrically Heated Hose \$1847.
Outdoor heated 1/4" Teflon cored hose, 60' long with thermocouple.

Series 80 Controller \$387.60
Thermocouple regulated power source for heated hose.

Diebolt Co.

Designer and manufacturer of specialty hose assemblies. All hoses quoted have a single 1/4" Teflon tube core, J type thermocouple, insulation, abrasion resistant jacket, and have Swagelok end terminals. These are listed at 240VAC but can be fabricated for 115VAC. The number preceding the J is the length of the heated hose.

DTM-5-6'-J-240-Swagelok Heated Hose \$237.

DTM-5-10'-J-240-Swagelok Heated Hose \$347.

DTM-5-40'-J-240-Swagelok Heated Hose \$697.

DTM-5-60'-J-240-Swagelok Heated Hose \$997.

DTM-5-100'-J-240-Swagelok Heated Hose \$1497.

Teknocraft Inc.

This company designs and manufactures fluid control products, primarily valves.

Mini Proportional Control Valve \$392.70 (12vdc w/.125 orifice)

DC driven proportional control valve, 1/8" NPT inlet port, 6, 12, or 24 vdc, with orifice sizes .032, .062, .093, .125".

Signal Amplifier \$200.

Used to interface with computer, potentiometer, or PLC control system

Air Dimensions, Inc.

Manufacturer of specialty diaphragm type non-corrosive pumps systems used for contamination free pumping of gases and liquids.

R221-BT-AA1-M Heated Head, Teflon Coated Aluminum Diaphragm Pump \$1190.

The diaphragm pump and motor have a rated pumping speed of 27 lpm. It is heated to 200° C, operates with 115vac, and has 1/4" female NPT fittings.

From the list given above it can be seen that there are a number of possible options for the sampling system, which will integrate with the ring-down cavity. SRD has chosen to use the QGIS probe from Apogee Scientific to extract a sample gas stream from the flue gas stack. This probe has been used successfully at the DOE/NETL facility in Pittsburgh as well as a number of other facilities.

SRD engineers designed a sampling system that is suited to the needs of the CRD instrument. This includes components such as a pumping system to maintain the CRD cavity at any pressure from about 50 torr up to atmospheric pressure (760 torr). Other unique components include a pyrolysis oven and a calibration air source. Details of the system are given below.

Figure 2: Diagram of the sampling system that will be used to extract a sample gas stream from the flue gas stack, carry it through the pyrolysis oven where all the mercury species are converted to elemental mercury, move it through the cavity where the mercury concentration is determine, and return the gas stream to the stack. The major components are listed on the figure.

Shown in Fig. 2 is a diagram of the sampling system with the major components listed on the figure. The flue gas is extracted from the stack using the Quick Silver Inertial Separation (QSI) probe system from Apogee Scientific. The probe is designed to provide particulate matter free samples with minimal change to vapor-phase mercury speciation. It is important the sample be free of particulate matter in order to avoid excess scattering losses in the ring-down measurements. The sample for the CRD system is pulled from the QSI system by a vacuum pump that is located after the CRD cavity. The flow rate through the CRD system is typically between 200 and 1000 ccm. However, precise flow rates are not necessary since the CRD technique directly measures concentration instead of deriving it from a measured quantity and flow rate. Once analyzed the used flue gas is returned to the flue stack.

To ensure no mercury is removed from the flue gas sample, all gas delivery lines are heat-traced to prevent mercury adsorption to surfaces. The majority of these lines are heated Teflon tubing, which is heated to over 150°C. The pump is also Teflon coated and the CRD cell is heated with heating tape.

In order to determine the total amount of vapor phase mercury the flue gas sample is heated in a pyrolyzing oven to 1000° C to atomize any mercury species, such as mercury oxide and mercury chloride. This pyrolysis technique will convert all forms of mercury to elemental mercury.

The CRD technique is self-calibrating by tuning the laser frequency on and off the molecular absorption line. Mercury has several distinct absorption peaks, but sulfur dioxide has a flat baseline-looking response. To separate the sulfur dioxide signal from the mirror baseline and to ensure the high reflectivity of the ring-down mirrors has not been sufficiently degraded by

contaminates, a computer-controlled gas flow-valve is used to periodically switch from flue gas to calibration air or nitrogen.

A pressure gauge and thermocouple monitor the pressure and temperature of the gas inside the cell, as both are important parameters in correctly determining the concentration of mercury. In order to correct for fluctuations in these variables this information is continually relayed to the computer. Computer controlled throttling valves, before and after the CRD cell, are used to actively control the pressure and flow rate in the cavity.

The Alexandrite laser system, used to produce the desired 254 nm radiation, is fiber optically coupled into the cell with a fiber positioning system and coupling optics. The beam path is entirely enclosed to minimize the hazards of stray laser light. After passing through the cell many times the laser decay signal or ring-down signal is observed with a PMT detector. The computer collects the ring-down data, where it is used in conjunction with the pressure and temperature data to determine accurate mercury concentrations.

Ascertaining the Peak Position of the Mercury Transition

One important aspect of the CRD system will be the ability for the instrument to automatically determine the total mercury concentration. As mentioned above the CRD technique is self-calibrating, but to accomplish this the laser must change frequency to some off resonance position to measure the baseline absorptions within the cavity and then return to the mercury peak to measure the losses due to mercury. This allows the determination of the absolute concentration of mercury atoms within the sample stream without running a mercury calibration curve.

While this is one of the great advantages of the cavity ring-down technique the instrument must be able to return to the top of the mercury peak or the concentration returned could be inaccurate. This is slightly more complicated in the case of mercury because of the number of different isotopes. As a result of 6 isotopes, including hyperfine splittings, there are 5 different mercury peaks that can be resolved with the present CRD system. At lower pressures (100 torr) these 5 peaks are completely resolved. Due to pressure broadening the peaks start to overlap, as the pressure is increased to atmospheric pressure (760 torr), and the individual isotopic mercury peaks are more difficult to discern.

A possible method that can be used to determine whether the laser frequency is located at the correct position is to take the derivative of the spectrum. As the laser scans across a mercury peak the derivative will go to zero where the slope of the spectrum is zero, i.e. at the top of a peak.

To test this method out a number of data sets were simulated. These simulations included a noise level that was set at 10 % of the peak value. This value is higher than that normally observed in the CRD data for mercury concentrations greater than 1 ppb. An example of this can be seen in Fig. 3. The parameters used for this simulation were a temperature of 473 K, a mercury concentration of 1.5 ppb and a pressure of 100 torr. On this, and subsequent plots, the data is displayed as red dots, the derivative spectrum is a solid blue line, and the vertical dotted lines indicate the point at which the derivative is zero.

Figure 3: Plot of a computer generated mercury spectrum (red dots) with a simulated noise level of 10% of the peak height. The solid blue line is a plot of the derivative of the spectrum. The vertical black dotted lines show the position where the derivative crosses the zero point. The parameters used for the simulation were a temperature of 473 K, mercury concentration of 1.5 ppb, and a pressure of 100 torr.

From the plot shown in Fig. 3 it can be seen that the black vertical dotted lines pass directly through the center of the mercury peaks. This indicates that using the derivative spectrum it is possible to find the position of each of the 5 individual mercury isotopic peaks. The pressure was increased in the simulation to 400 torr. The results are shown in Fig. 4. From this figure it can be seen that indeed the 5 peaks are again correctly identified by the derivative spectrum. However, the amount of the derivative peak that crosses zero for both the first peak, located around -5 GHz, and the fourth peak, located close to 10 GHz, is somewhat less than the other three peaks. This can be accounted for by the fact that as the pressure increases and peaks become broader they become less well defined and the point at which the slope becomes zero is harder to determine.

The pressure used for the simulation was raised to atmospheric pressure (760 torr). The results of the simulated data and derivative plots are shown in Fig. 5. From this plot it can be seen that the derivative plot was only able to correctly identify three of the five peaks. The first and fourth peaks have become small shoulders on the larger peaks and are not well defined enough for the derivative to cross through zero. However, the largest peak was still easily located as was the smallest peak. The largest peak, located at 0 GHz, is due to a single isotope and has a large enough natural abundance that the peak is still well defined at higher pressures. The smallest peak, located at about 15 GHz, is separated enough in frequency that it does not blend into the larger peaks at higher pressures.

All that is needed to accurately determine the mercury concentration is a single peak. Having both the largest and smallest peaks easily identified is advantageous in that it will increase the dynamic range in which the CRD instrument will function, while the largest peak will enable the lowest concentrations to be accurately determined.

Figure 4: Plot of a computer generated mercury spectrum (red dots) with a simulated noise level of 10% of the peak height. The solid blue line is a plot of the derivative of the spectrum. The vertical black dotted lines show the position where the derivative crosses the zero point. The parameters used for the simulation were a temperature of 473 K, mercury concentration of 1.5 ppb, and a pressure of 400 torr.

Figure 5: Plot of a computer generated mercury spectrum (red dots) with a simulated noise level of 10% of the peak height. The solid blue line is a plot of the derivative of the spectrum. The vertical black dotted lines show the position where the derivative crosses the zero point. The parameters used for the simulation were a temperature of 473 K, mercury concentration of 1.5 ppb, and a pressure of 760 torr.

After obtaining the positive results with the simulated spectra the derivative method was tested on actual data obtained with the CRD instrument. Shown in Fig. 6 is a plot of CRD data taken at a temperature of 473 K, a mercury concentration of 2.2 ppb and a cavity pressure of 100 torr. Here again the derivative spectrum is plotted with a solid blue line. It can be seen from the plot that the vertical black dotted lines, indicating where the derivative crosses the zero line, are located in the center of each of the 5 different peaks.

Figure 6: Plot of actual data taken with the CRD apparatus shown in red dots. The solid blue line is a plot of the derivative of the spectrum and the black dotted vertical lines are drawn through the point where the derivative spectrum crosses zero. The experimental parameters and mercury concentration are given in the upper left corner of the plot.

Shown is Fig. 7 is a similar plot where the mercury concentration is 1.7 ppb and the cavity pressure has been raised to 450 torr. From the derivative spectrum and the vertical it can be seen that again each of the 5 peaks has been correctly identified. Similar to the simulation for 400 torr, the first and fourth peaks are less well defined and as such have a shallower zero crossing.

Figure 8 is a plot of experimental data taken with a mercury concentration of 1.7 ppb, a temperature of 473 K and a pressure of 600 torr. From the plot it can be seen that even at a pressure close to atmospheric the derivative method was able to correctly identify 4 out of 5 mercury isotopic peaks.

From both the simulated and experimental plots shown the derivative method, in the worst case, could still identify 3 mercury isotopic peaks, while for the majority of cases it could correctly identify the peak position of all 5 peaks. This is quite promising as a method for the CRD instrument to automatically correctly identify the peak positions of mercury.

Figure 7: Plot of actual data taken with the CRD apparatus shown in red dots. The solid blue line is a plot of the derivative of the spectrum and the black dotted vertical lines are drawn through the point where the derivative spectrum crosses zero. The experimental parameters and mercury concentration are given in the upper left corner of the plot.

Figure 8: Plot of actual data taken with the CRD apparatus shown in red dots. The solid blue line is a plot of the derivative of the spectrum and the black dotted vertical lines are drawn through the point where the derivative spectrum crosses zero. The experimental parameters and mercury concentration are given in the upper left corner of the plot.

Section 4: Conclusion

SRD evaluated a number of different options for a sampling system to remove a sample gas stream from a flue gas stack and take it to be analyzed by the CRD instrument. From the options it was decided that using the QGIS probe, manufactured by Apogee Scientific, would be used to extract a sample gas stream from the flue stack. SRD engineers will construct the rest of the sampling system in-house. The entire sampling system will be heat-traced to minimize losses of mercury to any of the elements contained in the sample train.

A pyrolysis oven will be used just before the sample stream enters the CRD cavity to convert all forms of mercury to elemental mercury. The CRD instrument will then determine the total mercury concentration, after which the sample stream will be returned to the stack.

In addition to work on the sampling system SRD tested a method for the CRD instrument to automatically tune the laser to the correct frequency of a mercury transition. This will be necessary, as the cavity ring-down method must first measure the baseline losses in the cavity off of a mercury resonance and then return to the center of a mercury transition to be able to accurately determine the mercury concentration.

A derivative method was tested to find the center of the mercury transitions. For both simulated and actual data the derivative method was able to accurately find the center of three out of five mercury transitions, for the worst case, and for the majority of conditions tested it was able to find five out of five. This method shows considerable promise for accurately finding the center of a mercury transition to be used to determine the absolute mercury concentration.

Future work on the CRD project will involve the construction of the proposed sampling system. The system will then be extensively tested with known concentrations of mercury in a simulated flue gas stream.

Additional work will also be done evaluating the effectiveness of the derivative method to determine the center of the mercury transition. Other methods will be evaluated and compared with the derivative method for effectiveness.

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
4/29/03	Complete evaluation of commercially available sampling system and components
5/16/03	SRD engineers design sampling system for CRD instrument
5/30/03	Develop the derivative method for automatically determining the position of a Hg peak
6/17/03	Test the derivative method on actual data

Table II: 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).
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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).