

A Cavity Ringdown Spectroscopy Mercury Continuous Emission Monitor

Quarterly Technical Progress Report

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Abstract:

Work on the Cavity Ring-Down (CRD) mercury spectrometer this past quarter concentrated on the actual detection of mercury and the beginning of flue gas interference testing. After obtaining the initial mercury signal detection was done at various pressures and concentrations. The Alexandrite laser system used for the CRD spectrometer has a narrow enough linewidth to spectrally resolve the isotopic structure of mercury. This includes both isotopic frequency shifts as well as hyperfine splittings due to a couple of the odd isotopes of mercury. Initial flue gas interference testing concentrated on SO₂, which is expected to cause the greatest interference with mercury detection due to its absorption of ultra-violet light in the same region as that of the mercury atomic line.

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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 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.

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. 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 cross section 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 ring-down cavity that will be used. Preliminary results indicate a cavity length of 56 cm is optimum for 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.

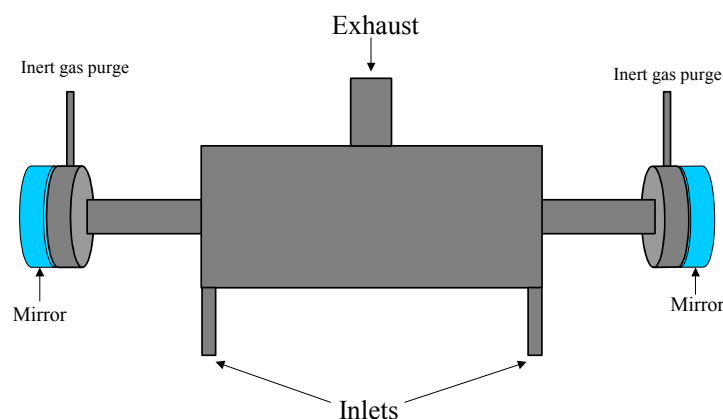


Figure 1: Diagram of sampling cavity (not done to scale) placed between the two highly reflecting mirrors

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 (AF) spectrometer. The AF spectrometer is calibrated using a gold trap with injections of mercury 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.

Table I: Project milestones and completion dates.

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. Establish baseline properties of CRD spectrometer	3/31/02	3/31/02
4. Characterize and optimize Hg detection	12/31/02	
5. Evaluate approaches to Hg speciation	9/30/03	
6. Construct sampling system for on-line CRD	9/30/03	
7. Integrate sampling system with CRD spectrometer	3/15/04	
8. Establish calibration procedure and operational parameters	3/15/04	

Section 3: Results and Discussion

During this phase of the project a custom built Iodine cell was incorporated into the CRD setup for absolute wavelength calibration of the Alexandrite laser system. The iodine cell is an enclosed glass cylinder approximately 15 cm in length and 2.5 cm in diameter. A few crystals of Iodine were placed in the cell; it was evacuated and then sealed. The molecular Iodine atlas, in the spectral region of the fundamental wavelength of the Alexandrite laser, requires that the cell be heated to about 250 C. The cell was heated to this temperature in an oven. The fundamental wavelength, used to obtain the ultra-violet light needed for the mercury atomic transition, is in the region of 761 nm. This beam was put through the cell and the absorption of light measured with a silicon photodiode (Thor Labs. PD155).

After a calibration of the Alexandrite system was performed the absolute quantum number assignment could be made for the previously observed transitions of oxygen. This weak, electronic dipole forbidden transition is shown below in Fig. 2. From the figure it can be seen that we actually observe transitions to three different excited electronic states. These have been labeled in the figure. The absorption cross section for these individual transitions ranges from 10^{-24} to 10^{-23} cm^2 . The cross section for these weak transitions can be compared to the mercury cross section which is on the order of 10^{-14} cm^2 or 10^{10} times stronger than these observed oxygen transitions.

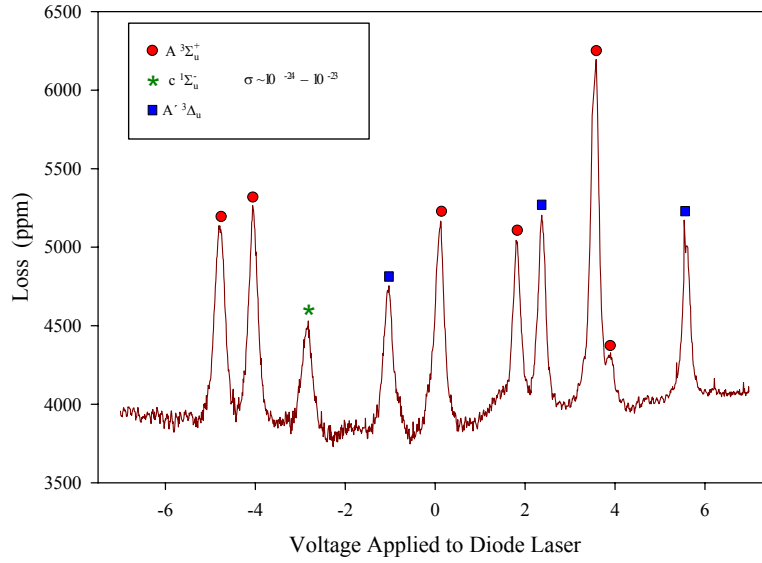


Figure 2: Scan of the oxygen transition originating from the ground $X^3\Sigma_g^-$ electronic state and terminating on one of 3 excited electronic states labeled on the plot. The absorption cross section, σ , for the various transitions is given in cm^2 .

After the system had been calibrated the Alexandrite laser was tuned to the spectral region around the 253.652 nm transition of atomic mercury. Mercury was sent to the cavity in known quantities using a temperature controlled mercury permeation tube delivery system. The amount of mercury entering the cell was verified using an Atomic Fluorescence Spectrometer (Brooks Rand Model III). This was done at the exit of the temperature controlled system as well as the entrance and exit of the CRD cavity to ensure that there were no mercury losses incurred in the delivery system.

The CRD cavity was kept at atmospheric pressure (760 torr) and the diode laser was scanned over the mercury transition. The resulting plot is shown in Fig. 3. The scale shown at the bottom of the plot is the voltage applied to the diode seed laser. The scale corresponds to approximately 18 GHz per volt. The mercury concentration used was approximately 1.5 parts per billion by volume (ppbv). From the plot it can be seen that there is more than one individual line that makes up the observed structure. This can be seen by the shoulders present in the spectrum as well as multiple peaks observed near the maximum of the observed peak. Mercury has 7 naturally occurring isotopes. The individual isotopes should exhibit a slight isotopic shift relative to each other. The linewidth of the diode seeded Alexandrite laser system should be spectrally narrow enough (~ 180 MHz) to resolve the isotopic structure of mercury. Table II below lists all the naturally occurring isotopes of mercury.

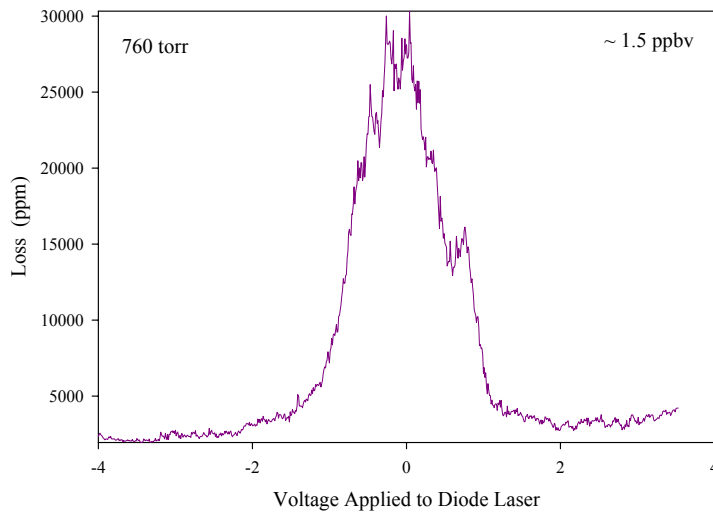


Figure 3: Scan of the 253.652 nm transition of atomic mercury. The pressure in the CRD cavity was 760 torr and the mercury concentration was about 1.5 ppbv. The full-width half-maximum of the mercury line is approximately 22.5 GHz due to the isotopic structure of mercury (see text) combined with pressure broadening.

Table II: Isotopic abundances of all naturally occurring isotopes of mercury.⁴

Isotope	Natural Abundance (%)
196	0.15(1)
198	9.97(8)
199 (I=1/2)	16.87(10)
200	23.10(16)
201 (I=3/2)	13.18(8)
202	29.86(20)
204	6.87(4)

Included in the table is the value of the nuclear spin for the odd isotopomers. The various isotopes each have individual spectral shifts. In addition, the hyperfine interaction causes the odd isotopomers to split as well as shift. Schweitzer was able to experimentally measure the individual isotopic shifts as well as the hyperfine splittings.⁵ Shown in Fig. 4 is a schematic plot of the isotopic shifts and hyperfine splittings for the various isotopes of mercury as noted on the plot. Included on the top right side of the plot are a couple of lines indicating the spectral linewidth of a single isotopic line of mercury for 760 torr and 100 torr cavity pressure. For a pressure of 760 torr the linewidth is dominated by pressure broadening while at 100 torr both Doppler broadening and pressure broadening components are comparable. From the indicated linewidths we would not expect to resolve isotopic structure at 760 torr but at 100 torr we expect to resolve 5 isotopic components. These 5 isotopic components have 2 that are due to individual isotopes and 3 that are a combination of transitions due to the hyperfine splittings.

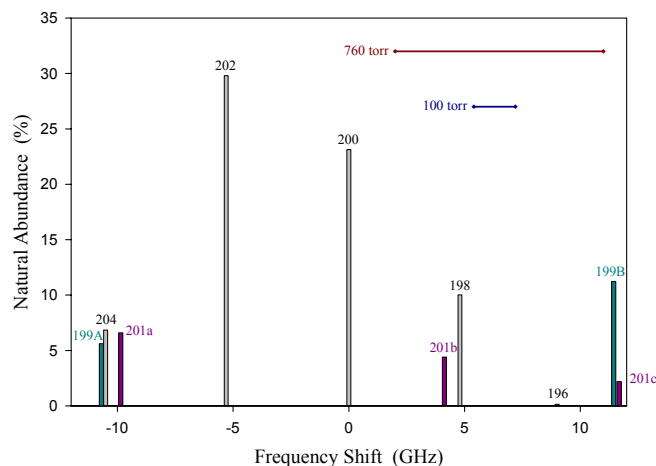


Figure 4: Schematic plot of the isotopic shifts and hyperfine splittings of the various isotopes of mercury. Also indicated in the plot is the expected linewidth for a single isotopomer line at 760 and 100 torr cavity pressure.

Indeed, if the pressure within the CRD cavity is decreased to 100 torr we are able to resolve these 5 lines due to the isotopic and hyperfine structure. A plot of the resulting scan is shown in Fig. 5. The concentration of mercury used for this particular scan is approximately 250 parts per trillion by volume (pptv). From this plot it can be seen that the detection limits for atomic mercury are in the low pptv range. The bars shown under each line are the calculated natural abundances for the five different lines. From the plot it can be seen that the observed intensity agrees very well with the predicted intensities from the naturally occurring isotopes of mercury.

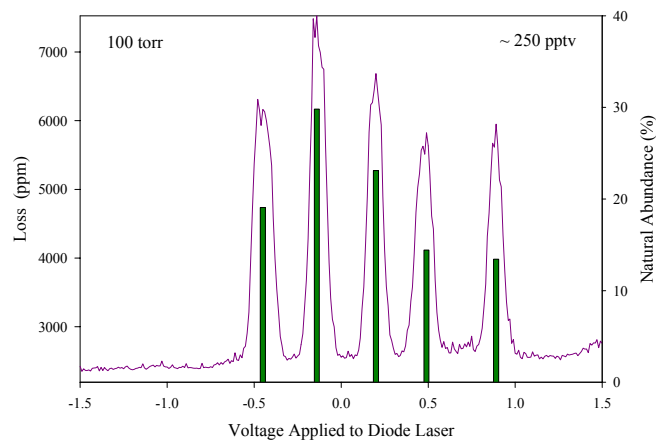


Figure 5: Scan of ~250 pptv of mercury at a cavity pressure of 100 torr showing the resolved isotopic structure of atomic mercury. The bars are the predicted natural abundances for each resolved isotopic peak. Due to the hyperfine splitting some of the peaks contain more than one single line resulting in 5 lines from 7 different isotopomers.

With the detection limits of mercury down in the low pptv range the next step is to determine any background absorptions or interferences caused by other constituents of flue gas emissions from coal-fired power plants. Table III lists the untreated flue gas components from a power plant burning low sulfur eastern bituminous coal. The total mercury concentration listed is in the ppbv range, which is well above our present detection limits. From the list the component of greatest concern, in terms of an 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 III, is approximately 5-6 orders of magnitude higher than typical levels of mercury.

Table III: Typical untreated flue gas composition from a power plant burning low sulfur eastern bituminous coal.⁶

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

Shown in Fig. 6 is a plot of the mercury isotopic structure observed in the presence of SO₂. The concentration of mercury used for this scan was approximately 1.5 ppbv while the concentration of SO₂ used was about 3000 ppmv. This is a difference in concentration of 2 million times. While the background absorption level is much higher than previously observed with no SO₂ from the plot it can be seen that we are able to easily detect mercury in the presence of SO₂ at a concentration over three times that reported for the particular untreated flue gas given in Table III. 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 detectors on the market today.

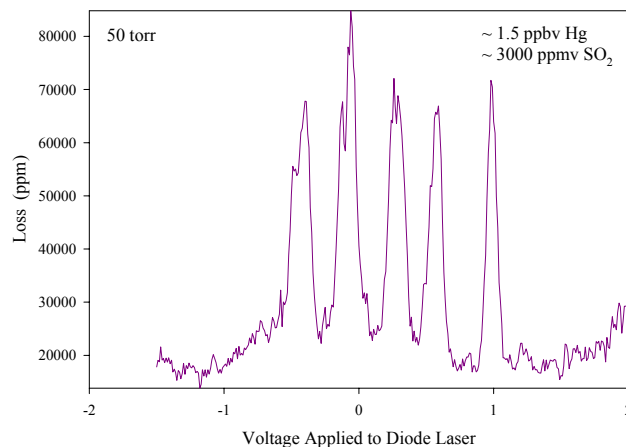


Figure 6: Scan over the atomic mercury isotopic structure with the cavity held at a pressure of 50 torr. The flow of gas contained ~ 1.5 ppbv mercury and ~ 3000 ppmv SO_2 .

Section 4: Conclusion

The Alexandrite laser system's wavelength was calibrated using a molecular iodine absorption cell. With the system calibrated the laser was tuned to the region of the 253.652 nm line of atomic mercury. Mercury was detected in the CRD cell at atmospheric pressure. The pressure in the cell was decreased to reduce the amount of pressure broadening. At lower cell pressures we were able to spectrally resolve structure of the atomic mercury line due to both isotopic shifts and hyperfine splittings. Early detection limits of the CRD spectrometer are in the low pptv range.

After determining detection limits for the CRD instrument for atomic mercury in air the next step in the project was to test for possible interferences due to other constituents contained in flue gas emissions. Initial tests have been done with Sulfur Dioxide, as SO_2 is known to absorb ultra-violet radiation in the same region as the mercury transition. Preliminary results show that with relatively high concentrations of SO_2 (over three times that found in untreated flue gas) we were still able to easily detect mercury at a concentration of approximately 1.5 ppbv, which is on the same order as the amount of mercury found in flue gas emissions.

This result is particularly encouraging as it opens the possibility of taking samples of flue gas straight to the CRD spectrometer without the need of extensive sample pre-treatment. Most of the presently available mercury analysis equipment require extensive pre-treatment of the flue gas to remove most components before the mercury content can be obtained.

Work will continue for the next quarter on checking interferences or background absorptions due to other constituents in flue gas emissions. Each component of flue gas will be checked individually first and then a sample flue gas stream using all of the gases will be used to check the mercury detection limits as well as the best operational parameters to use with this type of gas mixture to optimize the accuracy and level of mercury detection. Following work on the flue gas components work will begin on speciation. The first phase of which will be to test a pyrolysis oven to atomize compounds in the gas stream to determine the

total mercury concentration. The next phase will be to check if we are able to spectrally separate elemental mercury from mercury compounds.

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

Table IV: Chronological listing of significant events.

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 nm light from laser system needed for mercury detection
12/31/01	Coupled light into cavity and detected ringdown 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 (pptv) range

Section 5: References

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