

U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY



A CAVITY RING-DOWN SPECTROSCOPY MERCURY CONTINUOUS EMISSION MONITOR

Description

Sensor Research & Development Corporation (SRD) is carrying out an innovative science-driven technology program to develop an 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. This will be accomplished within the complex gas matrix found in the emissions from coal-fired power plants. Present Continuous Emission Monitors (CEMs) often require extensive sample pretreatment prior to mercury analysis and are only semi-continuous at best. SRD is using the sensitive and selective CRD technique for the analysis of mercury without extensive pretreatment to provide a true real-time continuous measurement of the mercury concentration within a flue gas stream.

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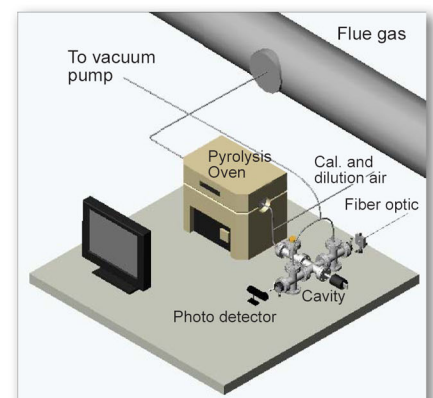
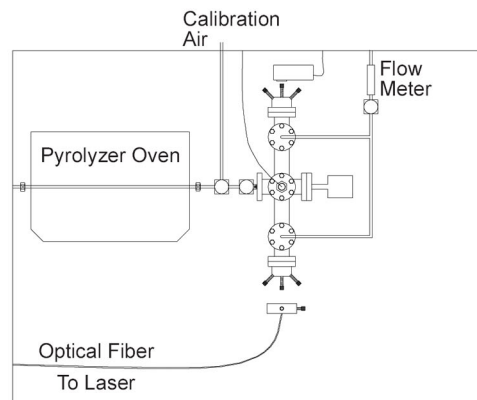
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Advantages of the CRD technique:

- Real-time continuous measurements;
- Self-calibrating technique, no calibration curves needed;
- Narrow band laser source inherently very selective; and
- Small sample cavity can produce extremely long effective pathlengths leading to greater sensitivity and detection limits

The CRD technique will be used for the absolute determination of the total amount of gaseous mercury present within the flue gas stream. In addition to this goal, the possibility of optically speciating oxidized and elemental mercury and determining the concentrations is being investigated.



Figures 1 and 2: Schematic drawing and 3-D image of the breadboard CRD instrument



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PROJECT COST

DOE Share

\$840,134

SRD Share

\$213,987

Total Cost

\$1,054,121

PROJECT DURATION

10/01/2001 -05/15/2004

WEBSITES

www.netl.doe.gov/coal

Accomplishments

A cavity for the CRD detection of mercury has been built and extensively tested. A schematic drawing and 3-D image of the breadboard CRD instrument is illustrated in Figures 1 and 2. Each constituent of flue gas has been tested individually, and a sample flue gas stream for the detection of mercury within this complex gas matrix has been tested. Sulfur dioxide (SO₂) in flue gas can be a problem for most CEM detectors as it absorbs radiation in the same region of the ultra-violet as mercury. SRD has been able to detect low mercury concentrations in the presence of high concentrations of SO₂. Indeed, a byproduct of the absorption by SO₂ at this wavelength is that the CRD instrument is able to determine the sulfur dioxide concentration as well as the mercury concentration. This can be seen in the graph, which shows a laser scan over the various isotopic peaks of the mercury transition. This was done in a simulated flue gas stream that contained 1000 parts-per-million (ppm) SO₂ and less than 2 parts-per-billion (ppb) mercury. The theoretical model developed by SRD calculates the mercury concentration from the losses determined in the cavity for any given temperature and pressure, which is constantly monitored within the cavity. The theoretical model used to produce the plot also includes calculating the concentration of SO₂ contained within the sample gas stream.

Some of the accomplishments of the project to date are:

- Low parts-per-trillion by volume (ppt) detection of mercury in air;
- Detected mercury (ppt range) in the presence of sulfur dioxide (up to 3000 ppm) and within a simulated flue gas stream;
- Accurate determination of total mercury concentration with a mixture of oxidized and elemental mercury; and
- Constructed prototype cavity for mercury detection and in the process of integrating the required sampling system in preparation for a pilot scale field test at NETL's facility in Pittsburgh.

The benefits of using the CRD technique is that it is not only selective and highly sensitive for mercury detection, but it can be a true real-time and continuous monitor of total mercury concentration without extensive pretreatment. Additional benefits potentially include the optical speciation of the elemental and oxidized forms of mercury.

Laser frequency scan of the CRD cavity over the mercury transition near 253.7 nm. A continuous flow of simulated flue gas (constituents and experimental conditions are given on the plot) was present in the cavity. The isotopic structure of the mercury transition is clearly seen from the data (blue plot), which has excellent agreement with the calculated theoretical model (red plot). The total cavity losses are directly proportional to the mercury concentration.

