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DEVELOPMENT OF A LASER–BASED MERCURY CONTINUOUS EMISSION MONITOR

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Project Description

The focus of this project, investigating a two-photon laser-induced mercury measurement technique, was prompted by recent advances in ultraviolet (UV) and near-UV laser diode technology and the need for more reliable mercury measurement techniques for applications in fossil fuel combustion systems. Initial investigations have tested two excitation schemes, and parameters include laser excitation wavelengths, monitored emission wavelengths as well as control of quenching by choice of carrier gas (argon or nitrogen). Data from several experiments show how these parameters affect the detection limit of such a technique.

Goal

To develop a two-photon laser-induced measurement of elemental mercury. Starting with the proof of concept, this project set about acquiring the instrumentation for building an apparatus for carrying out these laser spectroscopy experiments.

Rationale

Mercury measurements in air or flue gas typically use the interaction with 253.67-nm light from a mercury lamp to induce fluorescence at the same excitation wavelength. This is problematic when NO_2 or SO_2 are present as these compounds have broad absorptions in the UV. Techniques such as modulating the lamp wavelength and separating the mercury using gold amalgamation have been used with varying degrees of success. A laser spectroscopic technique for separating these interferences could be a valuable tool for conducting in situ transport and kinetics experiments.

To separate the mercury measurement from interferences, two successive transitions in mercury were effected. The second transition is caused by a laser that induces the mercury to fluorescence. The first transition is effected by a lamp, filtered to emit 253.7-nm light, and induces mercury to the first excited state. A diode laser is used to cause one of either two secondary transitions. Compounds like NO_2 and SO_2 will not be mistaken for mercury in the measurement scheme because the two transitions will screen out the effects of these common interferences. Added to this is the benefit that the measurement takes place in the visible region of the spectrum (UV is more strongly scattered by air then visible light).

For the study presented here, two excitation schemes were chosen for experimenting with two-photon laser-induced fluorescence spectroscopy of mercury, Figure 1. Mercury behaves in the following way for each path.

Path A: At normal sample temperatures (ambient to 500°F) the majority of mercury atoms in a given sample will exist in the ground state; this is represented by the notation Hg^0 $^1S_0$. Upon interacting with a photon of wavelength 253.65 nm, the atom may absorb the photon and increase in energy to the $6p^3P_1$ state. In a gas comprising mostly a noble gas (like helium or argon), the $6p^3P_1$ state will eventually decay and a 253.65-nm photon will be spontaneously emitted. In Figure 1, Path A shows second excitation occurring when a photon of wavelength 407.78 nm from the laser is absorbed by the $6p^3P_1$ mercury atom, raising it to the $7s^1S_0$ state. This new state is coupled with the $7s^3S_1$ state and, after a collision, will be quenched to this new state. After some time, this atom will decay to the $6p^3P_0$ state and, with this decay, will spontaneously emit a photon of wavelength 546.07 nm.

Path B: Mercury in the ground state, $^1S_0$, is excited to the $6p^3P_1$ state were it is quenched to the $6p^3P_2$ state. This quenching is promoted by gases such as nitrogen and oxygen. From the $6p^3P_2$ state, the mercury atom can absorb a photon of wavelength 404.66 nm, rising in energy to the $7s^3S_1$ state where it will decay to the $6p^3P_0$ state while emitting a photon around 546.07 nm in wavelength.

Each path has advantages and disadvantages that dictate how each could be used. For instance, Path A is limited to use in argon or helium carrier gases because quenching would populate the $6p^3P_2$ state, preventing the second absorption needed for the measurement. Path B similarly requires this

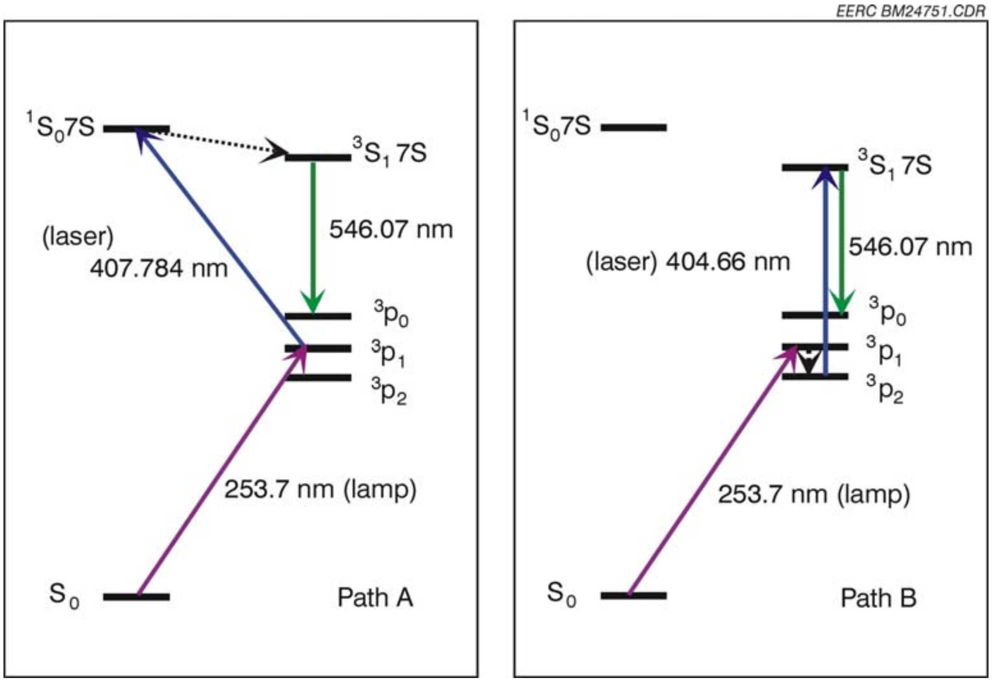

Figure 1. Schematic representation of electronic states important to this study.

quenching, limiting its effectiveness when quenching gases like oxygen and nitrogen are present. In each case, fluorescence at 546.07 nm occurs. It is also possible for mercury in the $7s^3S_1$ state to decay to the $6p^3P_1$ state, emitting a 435.84-nm photon.

Approach

The experimental apparatus assembled for this project consists of two light sources: a high-powered mercury electrodeless discharge lamp (EDL) and a gallium nitride diode laser (Figure 2).

The mercury EDL uses a coil and radiofrequency source to excite the mercury in a completely sealed quartz ampoule. The strongest transition, which emits light around 253.67 nm is approximately 100 watts. This is passed through an interference filter that transmits 254-nm light and has a band pass of approximately 10 nm. The mirrored side of the interference filter is directed toward the lamp. In an effort to increase the power delivered to the volume of the sample probed by the laser, the lamp light is concentrated using a converging quartz lens. Another arrangement has been used that excludes the lens and simply places the lamp and filter close to the sample chamber.

For this project, a diode laser in a grating-stabilized external cavity of the Littrow type was purchased from Toptica (DL100L). This diode laser (Toptica DL100) uses a gallium nitride diode which has a free-running wavelength around 406 nm at 20°C. In the external cavity, the diode laser can be tuned from around 404.0 nm to about 409.0 nm with a peak power of about 35 mW. Typical powers used during this project were between 15 and 25 mW.

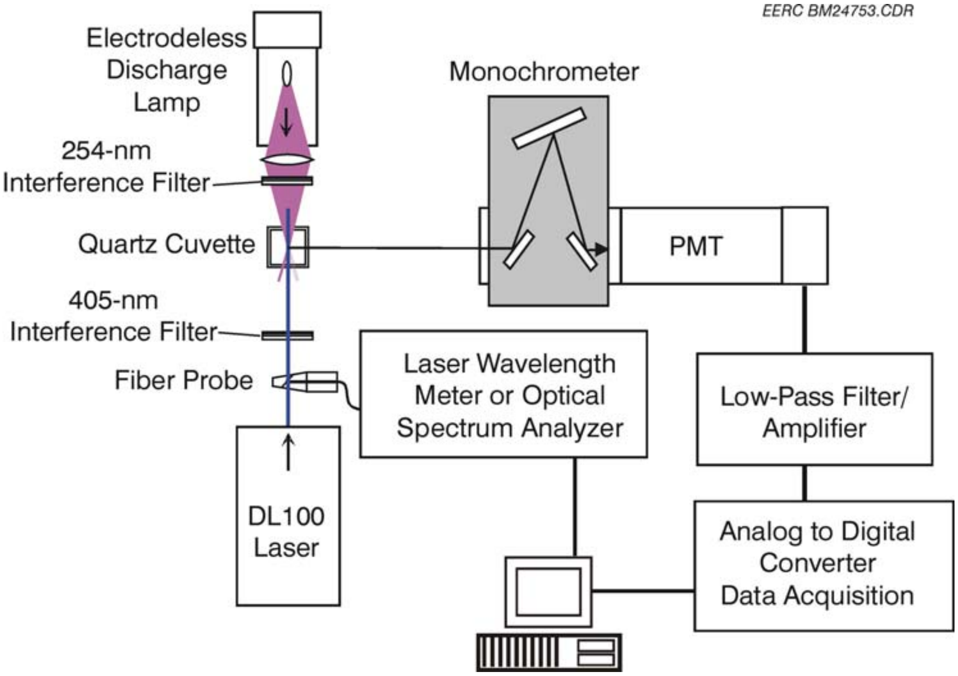

Figure 2. Experimental apparatus used to study two-photon laser-induced fluorescence in mercury.

A portion of the laser beam is sampled by a fiber optic probe coupled to a wavelength meter (Coherent Wavemaster). The wavelength meter has a 1-pm (1×10^{-12}meter) accuracy. The remainder of the beam can be sent to an optical spectrum analyzer for measuring the spectral characteristics of the beam (power, spurious signals, coherence). When the laser is tuned, the wavelength is monitored while the beam is directed into the sample chamber (Figure 3). The laser beam propagates in the opposite direction of the lamp. The region in which the two beams interact is within a quartz flow through cuvette (2.5 cm × 1 cm × 1 cm) which has four polished windows. The sample stream is a slip taken off the gas exiting a permeation source of mercury vapor. Argon and nitrogen gas have been used as carriers in various experiments.

The laser is tuned and monitored before experiments are performed. During experiments, data are collected from the wavelength meter.

One window of the quartz cuvette is placed near the slit of a monochrometer. A photomultiplier tube is coupled to the exit slit of this monochrometer and is used to detect a fluorescence signal. The monochrometer allows the filtering of scattered lamp and laser light while passing through, at a high efficiency, the fluorescence signal of interest.

The photomultiplier tube has a built-in preamplifier stage. The signal is amplified and measured with an analog to digital converter (Fluke Hydralogger), and the values are recorded with a computer.

A Nippon Instruments Corporation DM-6B mercury analyzer was used to monitor the mercury concentration in the sample stream (Figure 4). Calibration of this instrument was performed using the procedures described in the manual. After data are collected, the signal from the experimental apparatus and mercury analyzer are associated with each other using the time stamps in the data files. Excel is used to plot the photomultiplier tube (PMT) signal with respect to mercury concentration.

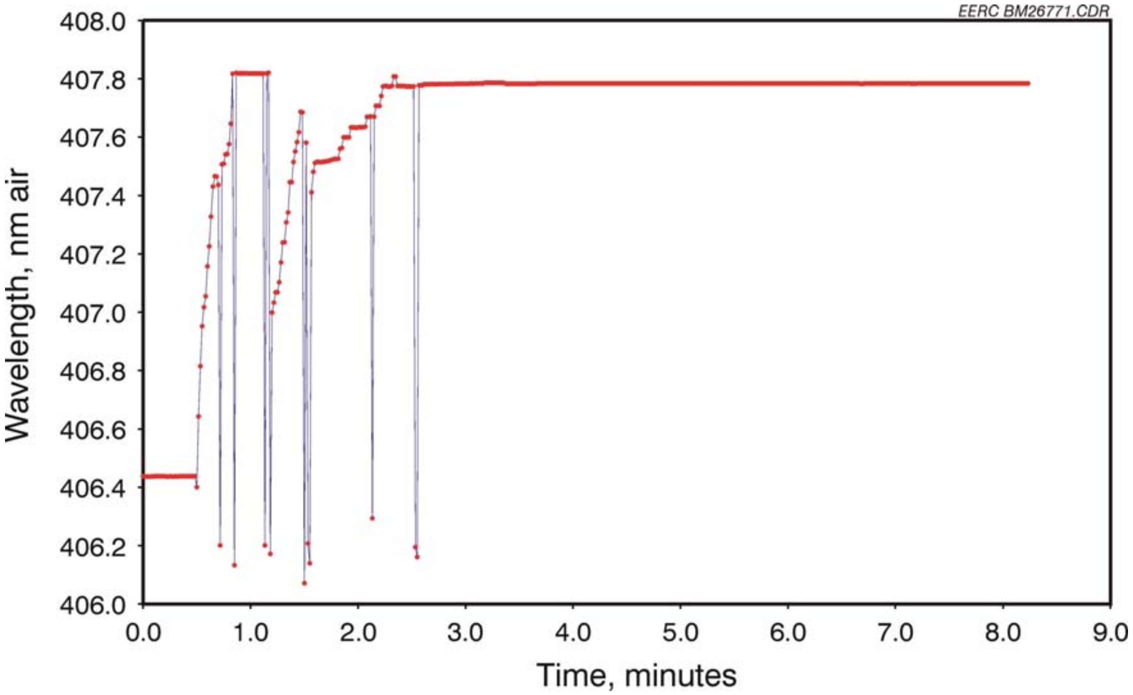

Figure 3. Example data from laser wavelength monitor during a tuning procedure.

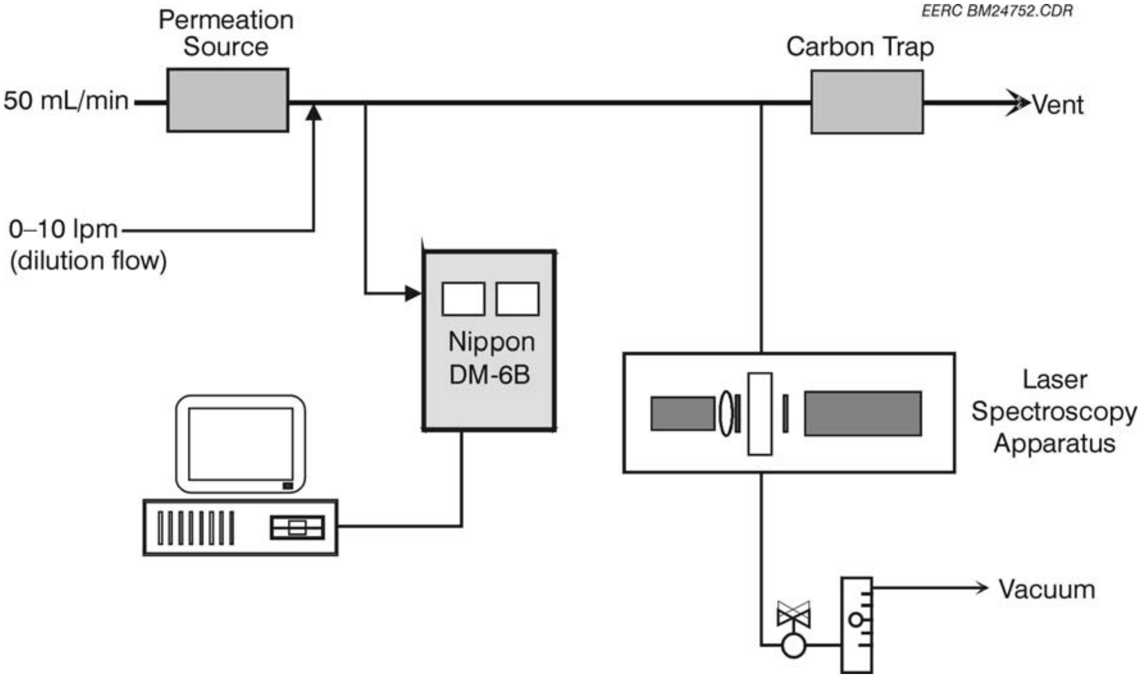

Figure 4. Experimental apparatus for testing the laser spectroscopy apparatus.

Progress

Table 1 lists the tests performed with the apparatus.

Table 1. Summary of Experiments Conducted

Test	Carrier Gas	Excitation Wavelength, nm	Fluorescence Wavelength, nm	Detection Limit, µg/m^3
1	Argon	404.66	546.01	>1000
2[a]	Nitrogen	404.66	546.01	116
3[b]	Argon	407.78	546.01	226
4	Nitrogen	407.78	546.01	>1000
5[c]	Argon	253.67	253.67	2.6
6	Nitrogen	253.67	253.67	32.5

[a] See Figures 5 and 6.
[b] See Figures 7 and 8.
[c] See Figure 9.

Data collected with these experimental conditions are displayed in Figures 3 and 6. The detection limit, in µg/m^3, is computed using the slope, m, and intercept, b, of the regression and the average standard deviation, σ_{ave} in the formula:

$$DL = \frac{3 \times \sigma_{ave} - b}{m}$$

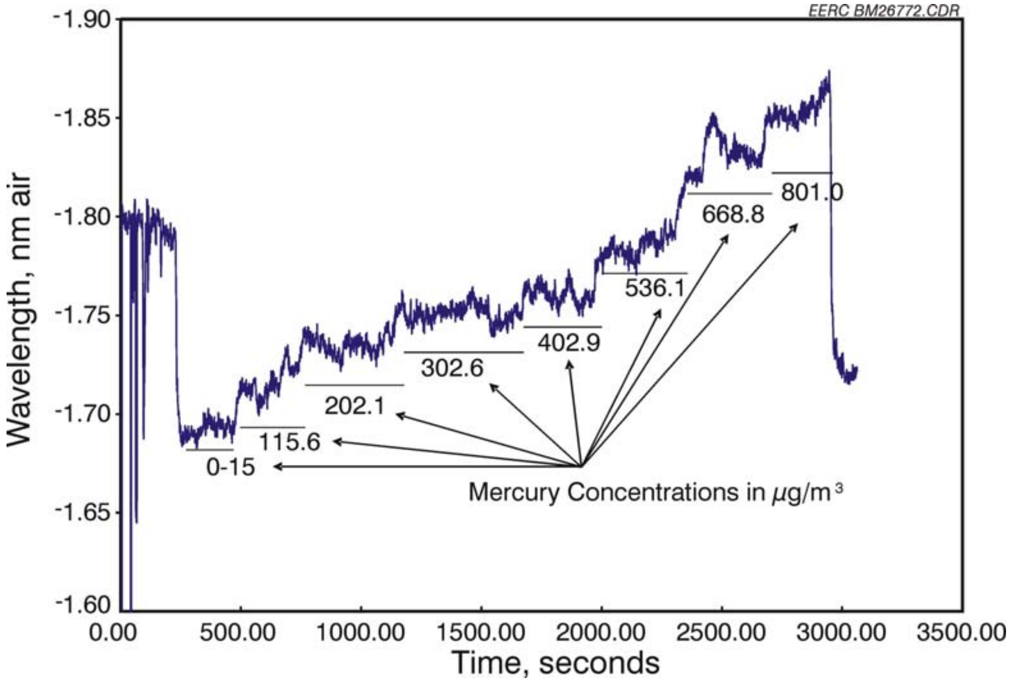

Figure 5. PMT signal versus time for experiment Test 2: Path B in nitrogen gas.

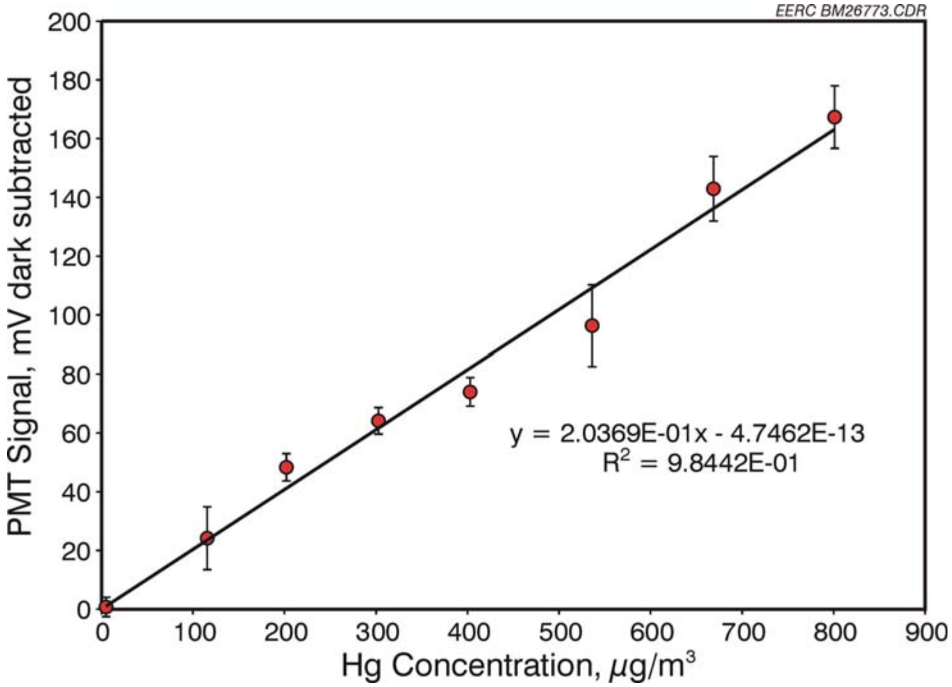

Figure 6. Laser-induced fluorescence (LIF) signal versus Hg concentration using 404.66 nm excitation and a nitrogen carrier (Test 2). The detection limit for mercury in this experiment is 116 µg/m^3.

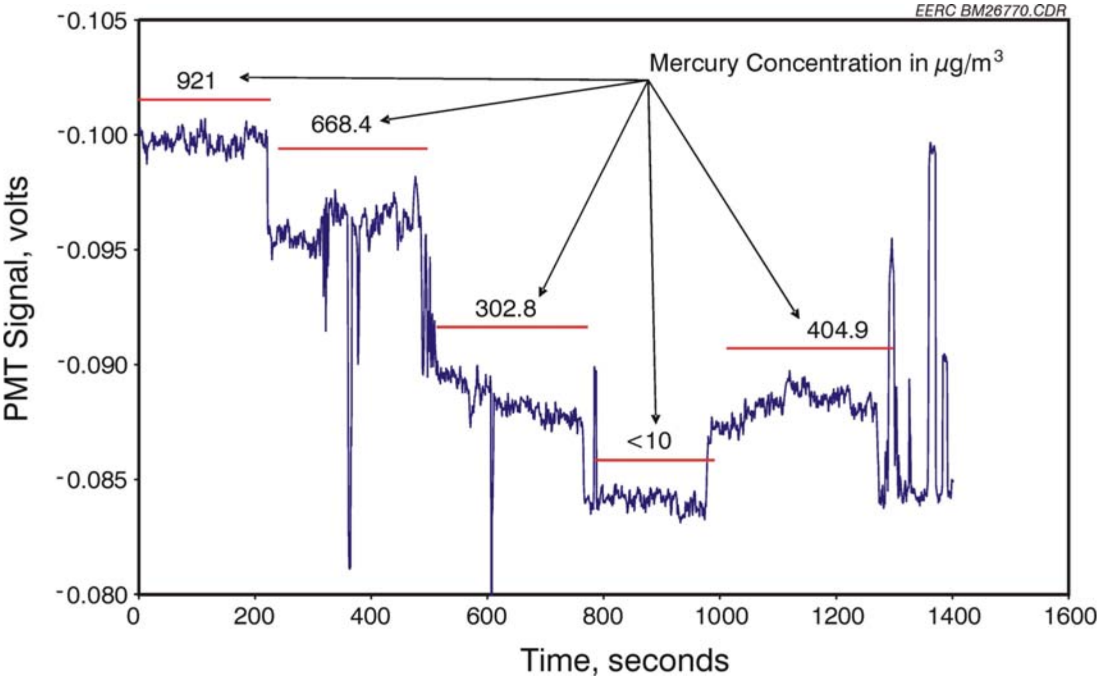

Figure 7. PMT signal versus time for experiment Test 3: Path A in argon gas.

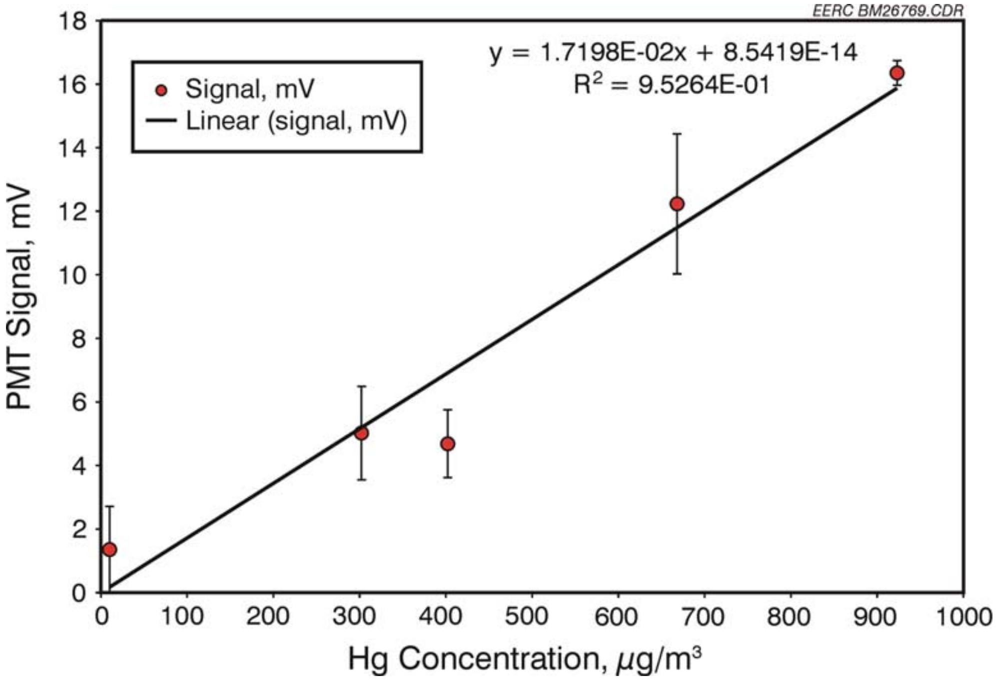

Figure 8. LIF versus Hg concentration using 407.78 nm excitation and an argon carrier gas. The detection limit calculated from this experiment is 226 µg/m^3.

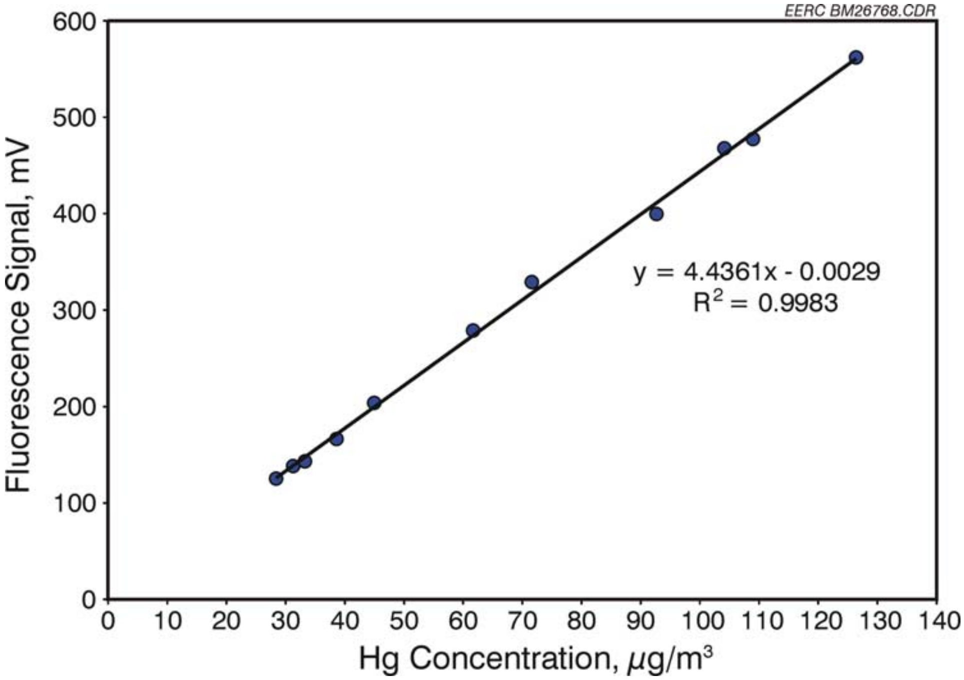

Figure 9. Fluorescence signal versus mercury concentration using 253.67 nm excitation (Test 5). Detection limit calculated to be 2.6 µg/m^3.

Quality Assurance/Quality Control (QA/QC)

QA/QC design for this project includes the following issues:

1. The precise measurement of laser wavelength to facilitate tuning required by the experiment.

2. Conditioning and acquisition of analog signals such as the signal from the PMT used to measure the strength of the fluorescence.

3. Relate the signal produced by the experiment to a mercury concentration by appropriately measuring said concentration.

The requirement for precision in laser wavelength measurement was determined to be 1 pm (picometer) or less. This determination took into account the spectral width of the laser and the spectral width of the atomic transition being effected by the laser, allowing for Doppler and pressure broadening. Because an absolute measurement of fluorescence intensity is not within the technical scope of this initial study, it was only necessary to condition the PMT signal by measuring and subtracting the dark background signal from the signal during data collection. This was accomplished using a light-tight shutter between the PMT and monochrometer. Before data collection, equipment was allowed enough warm-up time to ensure stable operation during tests. During each test, a detection limit was obtained that ranged from between 2.6 and 226 µg/m^3. The detection limit of the Nippon DM-6B being used for this study is many times lower (0.1 µg/m^3). Calibration and maintenance of the mercury continuous emission monitor (CEM) were performed in accordance with the practices devised by the Nippon Instrument Corporation.

Status

This research is nearly complete.

Potential Users/Technology Transfer

Instrumentation developed in this area could impact research requiring small, low-power measurement techniques for high speed mercury determination.

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