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DEVELOPMENT OF A LASER-BASED MERCURY CONTINUOUS EMISSION MONITOR

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Project Description

Effective mercury control technologies are being developed but will not be implemented until technical issues surrounding continuous mercury monitors (CMMs) are resolved (1). Currently available CMMs are too complex in their implementation to be in regular service. Because of recent advances in laser diode technology, an improved absorption technique for measuring trace concentrations of elemental mercury can be developed for use in the presence of common flue gas constituents and dust. Experiments will be performed to investigate the validity of using a diode laser-based measurement of elemental mercury in flue gas. Combining two-photon absorption and frequency modulation spectroscopy to separate mercury from interferences will be explored.

Goal

The primary goal of this project is to develop a method for measuring elemental mercury in flue gas-based two-photon absorption and frequency modulation spectroscopy using a tunable diode laser system. This method will be evaluated for its performance: precision, accuracy and minimal detection limit (MDL).

To accomplish this goal, a system has been assembled to perform controlled spectroscopic measurements on elemental mercury.

Rationale

The concept being explored in this project involves separating the mercury measurement from interferences by inducing two successive transitions in mercury. The second transition is caused by a tunable diode laser and its effects, either the absorption of laser light or the fluorescence from a higher electronic state, are measured. 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 tunable across 404 to 409 nm can be used to cause one of either two secondary transitions. Compounds like NO₂ and SO₂ will not be mistaken for mercury in this 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 than visible light).

Approach

An ultraviolet lamp provides the first photon, filtered to emit a narrow band of light centered on 253.65 nm. A tunable external cavity diode laser will provide the second photon. The diode laser system is capable of operating at frequencies between 404 and 409 nm. Two multiphoton paths were chosen for this investigation. Path A is based on the research of Bauer et al. and has been successfully developed into a two-photon laser-induced fluorescence (LIF) technique to measure elemental mercury in air for eddy correlation studies where high sensitivity and fast response are essential (2). Elemental mercury in the S_0 state is excited to the P_1 state with 253.65 nm light from a mercury electrode-less discharge lamp. A laser tuned to 407.784 nm excites the mercury from the P_1 state to the $7sS_0$ state. This transition is followed by decay to the $7sS_1$ state and then fluorescence of a 546.07-nm photon bringing the mercury atom to the P_0 state. Bauer's research used two pump lasers to produce 253.65 and 407.784 nm using a frequency-doubled dye laser and optical parametric oscillator (OPO), respectively. Our research plan called for a UV lamp and tunable diode laser system to induce the two absorptions in order to reduce the complexity of the instrumentation.

Path B involves exciting the mercury to the P_1 state via a 253.7-nm photon from the lamp, followed by a collisional decay to the P_2 state. The laser tuned to 404.66 nm would then excite the mercury to the $7sS_0$ state. Paths A and B are depicted in Figure 1.

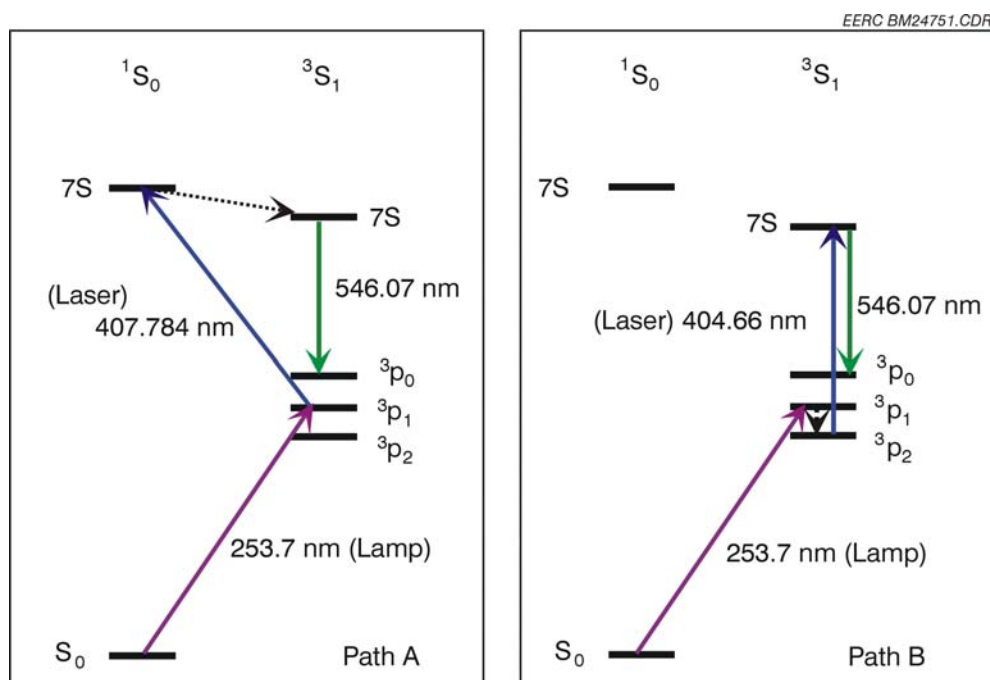


Figure 1. Multiphoton transitions being considered for laser-based mercury measurement.

Experimental Apparatus

To test whether it is possible to induce two-photon absorption in mercury using a tunable diode laser and a mercury electrodeless discharge lamp, an apparatus was assembled consisting of a square cross-sectioned quartz flow through cell. The light from a UV lamp was focused onto this cell, and filtered to only allow the 253.7-nm light to enter the cell. The laser light, used for effecting the second transition, was propagated through the cell from the opposite direction of the lamp. One side window of the quartz cell allowed light to be collected by an imaging spectrometer. The other window faced the open entrance slit of a monochromator mounted to the face of a photomultiplier tube (PMT). The imaging spectrometer allows the collection and monitoring of scattered lamp and laser light. It is also hoped that this instrument will allow the recording of the fluorescence at 546 nm (see Figure 2).

The monochromator is tuned to 546 nm by looking through the exit slit at light from a low-power mercury lamp illuminating the entrance slit. The PMT consists of a built-in preamplifier and power supplies for the preamplifier and PMT. The output of the PMT is a voltage brought to a combination low-pass filter amplifier and then observed with an oscilloscope. To collect this signal, a data logger is used.

Mercury from a permeation source is monitored by a Nippon DM-6B mercury analyzer and sent to a carbon trap before being dumped to the atmosphere. Before the carbon trap, a stream is pulled through the quartz cell. With this arrangement, concentrations between 0 and 600 $\mu\text{g}/\text{m}^3$ can be simulated by changing the dilution at the exit of the permeation source. Refer to Figure 3.

The laser is tuned to within 0.5 nm using the procedure outlined in the manual. To tune the laser within 1 pm (0.001 nm), the laser diode temperature and current are adjusted while the output of the laser wavelength meter (Coherent Wave Master) is monitored. The laser wavelength is monitored and recorded during all experiments.

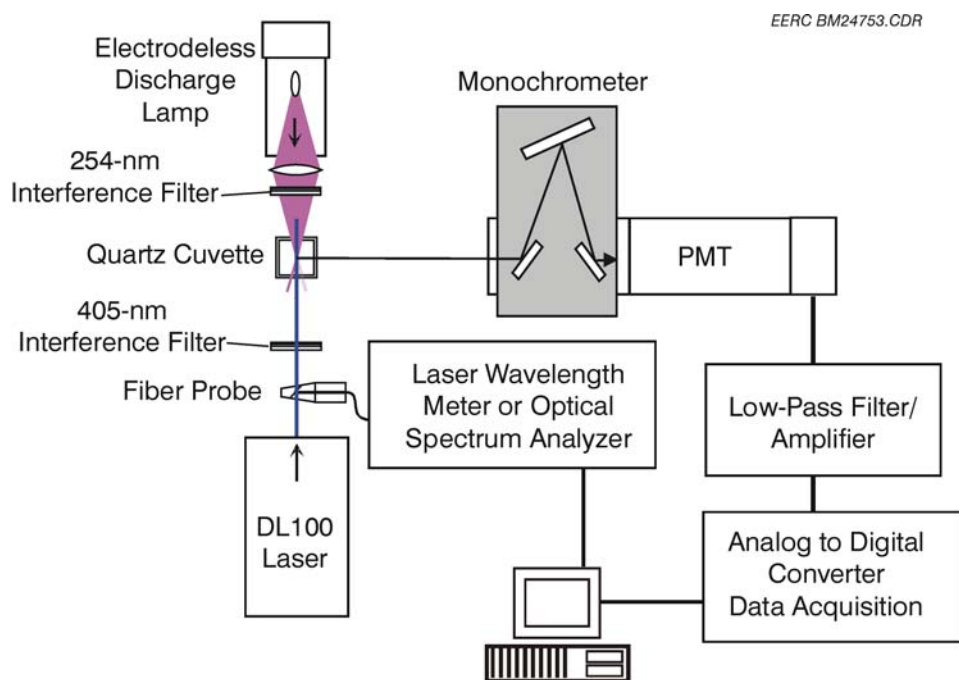


Figure 2. Experimental arrangement for studying two-photon induced fluorescence.

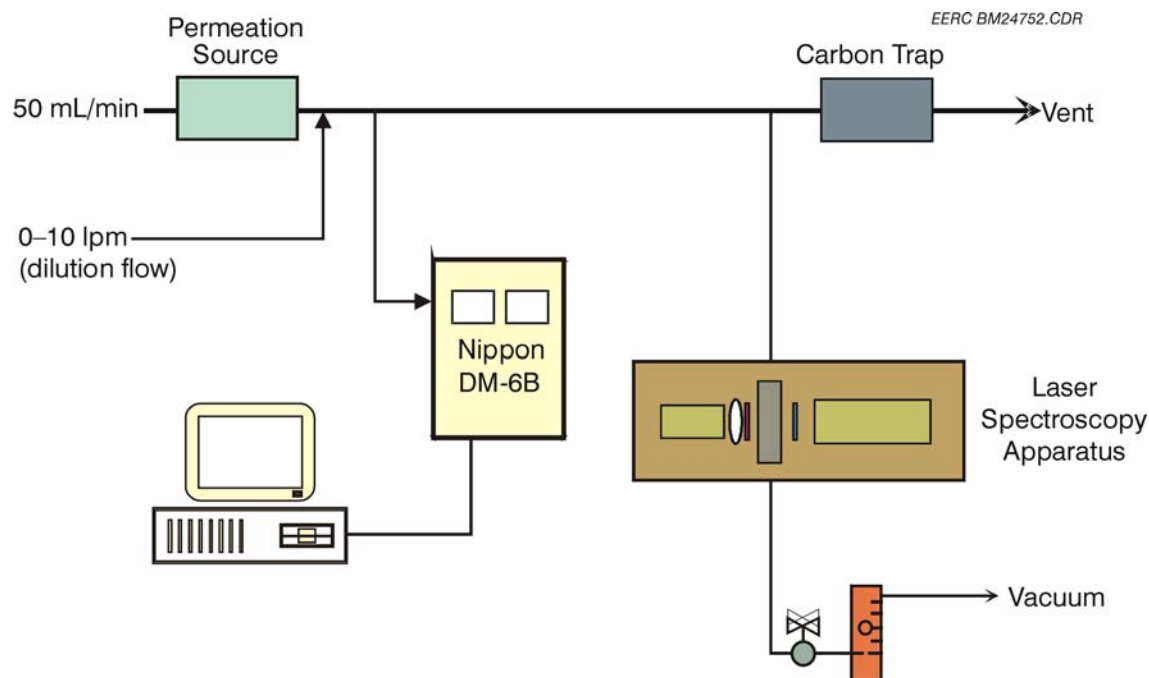


Figure 3. Arrangement for monitoring and delivering mercury to the experimental apparatus.

Initial Results

To test the apparatus, experiments were performed in which only the lamp was used to fluoresce mercury at various concentrations. The monochromator was tuned to around 254 nm, and the concentration of mercury was varied by changing the dilution flow into the sample stream. Figures 4 and 5 show how the PMT signal and mercury concentration are related.

To demonstrate the concept of two-photon induced fluorescence, the monochromator was tuned to 546 nm using the procedure described above. The laser was tuned to 407.784 nm and propagated in the opposite direction to the lamp beam. To verify that two-photon absorption was taking place, the laser and lamp beams were blocked individually. In each case, the fluorescence signal disappeared (i.e., the PMT signal dropped to background levels, shown in Figure 6). The data presented in Figure 7 show the mercury concentration versus PMT signal.

Progress

The apparatus assembled has been used to observe two-photon induced fluorescence on mercury in argon using the multiphoton path used by Bauer's group (Path A). Concentrations above $100 \mu\text{g}/\text{m}^3$ were difficult to simulate. Improvements to the PMT signal amplification and lamp collimation are necessary. These issues will be resolved before continuing.

Path B

After enough data are gathered evaluating the apparatus when using multiphoton Path A, the laser will be tuned to 404.66 nm and the experiment performed again. These two methods will then be

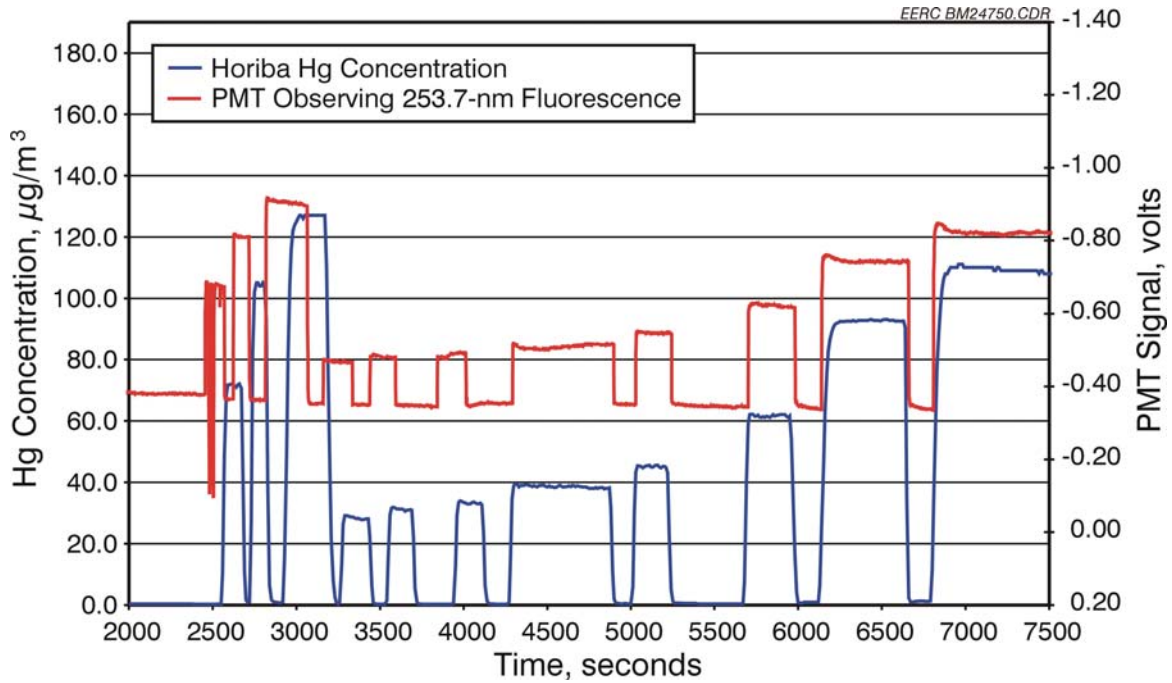


Figure 4. Comparison of PMT signal data with mercury concentration.

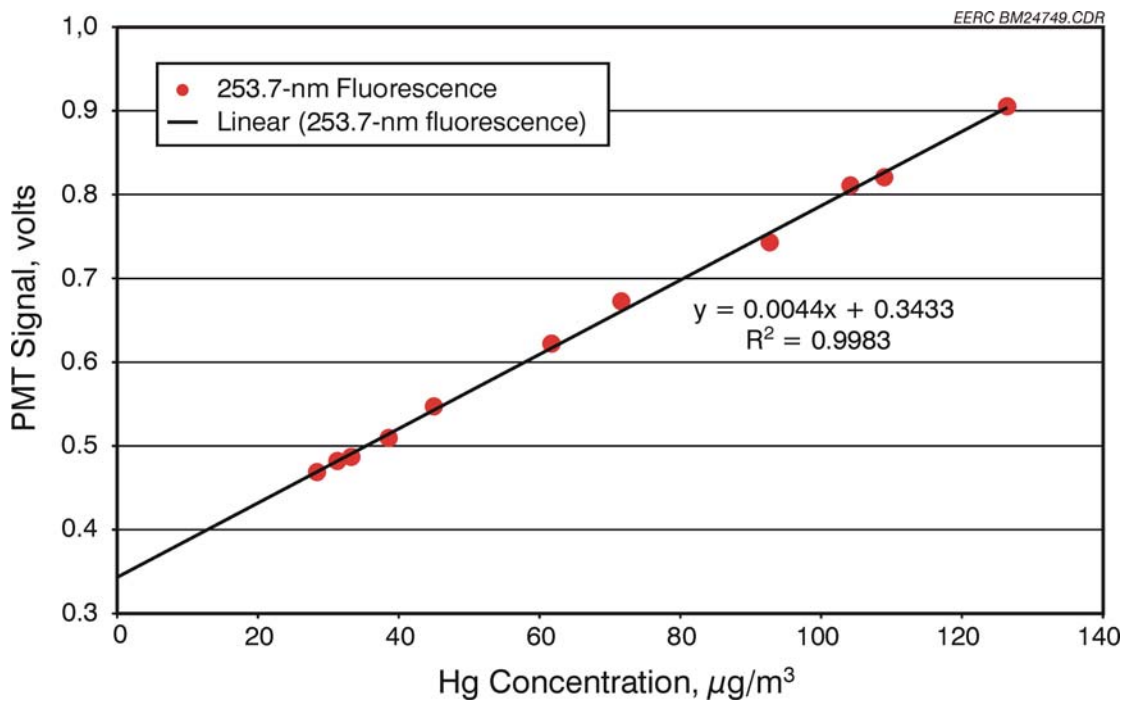


Figure 5. Fluorescence signal at 253.7 nm versus mercury concentration.

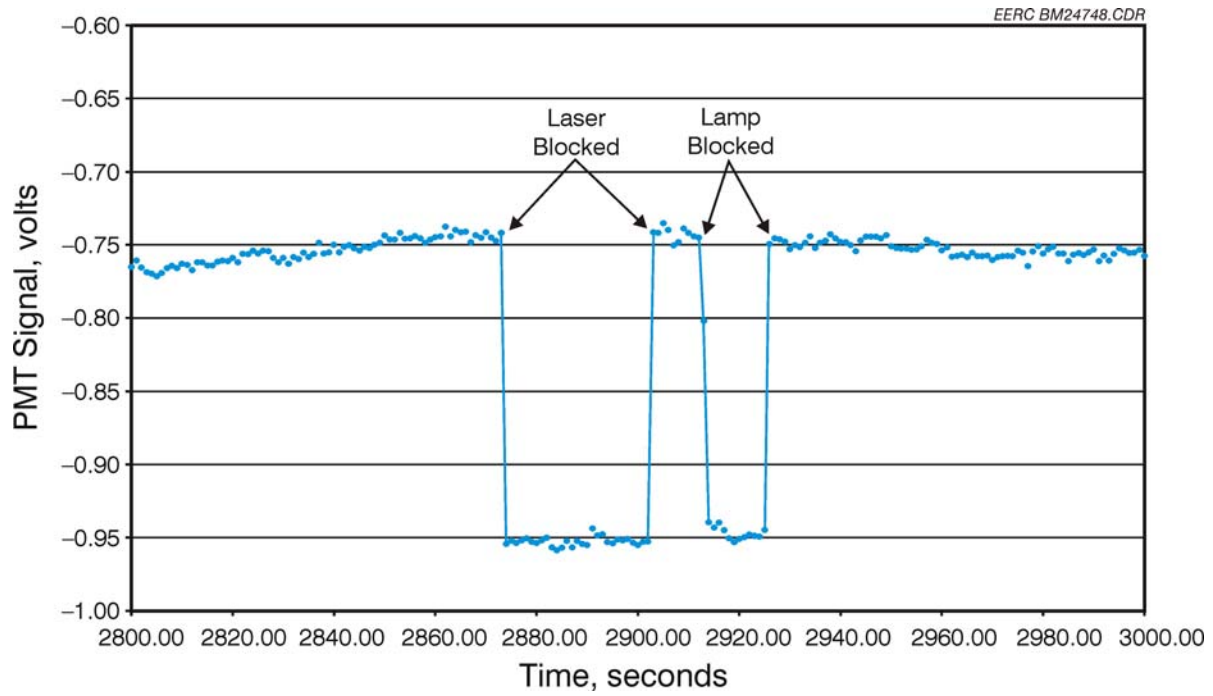


Figure 6. Proof that the signal produced is due to two-photon absorption.

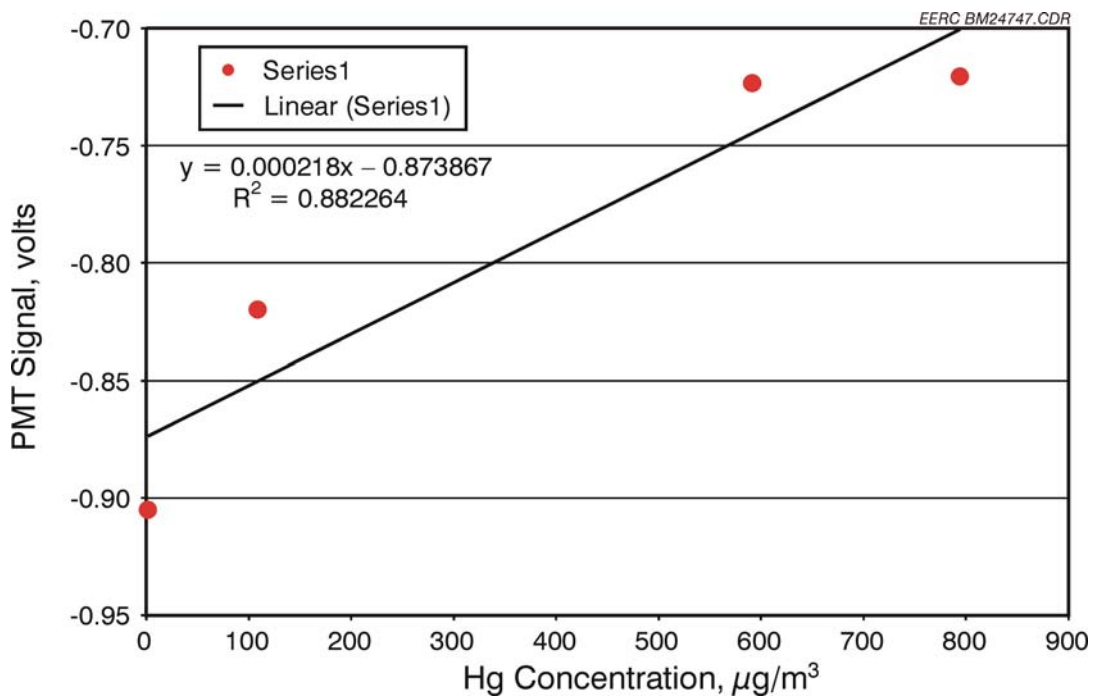


Figure 7. Fluorescence signal at 546 nm versus concentration for the laser tuned to 407.784 nm.

compared directly to each other for the following information: signal linearity with mercury concentration and brightness of the fluorescence at 546 nm.

Laser Absorption Spectroscopy

An attempt will be made to perform laser absorption spectroscopy using the data gathered so far.

Quality Assurance/Quality Control

At this time, modification of the apparatus and more preliminary data are needed before determining whether or not a minimal detection limit for these techniques is possible. The laser is being tuned to standard transition wavelengths (3) using the procedures outlined in the laser and wavelength meter manuals.

Status

This research is ongoing.

Potential Users/Technology Transfer

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

References

1. Thompson, J.S.; Laudal, D.L.; Chu, P.; Roberson, R.; Brockett, L. Use of Continuous Emission Monitors for Mercury at Coal-Fired Utilities. Presented at the 19th Annual Pittsburg Coal Conference, Pittsburgh, PA, Sept 23–27 2003.
 2. Bauer, D.; D'Ottone, L.; Campuzano-Jost, P.; Hynes, A.J. Gas Phase Elemental Mercury: A Comparison of LIF Detection Techniques and Study of the Kinetics of Reaction with Hydroxyl Radical. *Journal of Photochemistry and Photobiology A: Chemistry* **2003**, *147*, 247–257.
 3. Sansonetti, C.J.; Salit, M.L.; Reader, J. Wavelengths of Spectral Lines in Mercury Pencil Lamps. *Applied Optics* **1996**, *35* (1).
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