



*Kevin C. Galbreath
Principal Investigator*

DEVELOPMENT OF A LASER ABSORPTION CONTINUOUS MERCURY MONITOR

Key Personnel: Kevin C. Galbreath (EERC), Blaise A. Mibeck (EERC), Michael J. Wuitschick (EERC), Grant E. Dunham (EERC), and Jeffrey S. Thompson (EERC)

Project Description

Effective mercury control technologies are being developed but will not be implemented until technical issues surrounding mercury continuous emission monitors (CEMs) are resolved. Currently available CEMs 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 (Hg^0) can be potentially developed for use in the presence of common flue gas constituents and dust. Experiments are planned to demonstrate the validity of using a diode laser-based measurement of Hg^0 in flue gas. Two techniques will be combined: two-photon absorption and frequency modulation spectroscopy.

Goal

The primary goal of this project is to develop a method for measuring Hg^0 in coal combustion flue gas based on 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.

Rationale

The method proposed for separating interferences from the mercury signal involves two well-established techniques. At temperatures normally encountered, Hg^0 is found in its lowest electronics state (the ground state). A series of two photons is used to measure mercury by absorption. The second photon separates the mercury measurement from interference such as SO_2 . A frequency modulation scheme is then used to isolate the mercury signal from other sources of interference (scattering).

Approach

An ultraviolet (UV) lamp provides the first photon, filtered to emit a narrow band of light centered on 253.7 nm. A tunable external-cavity diode laser will provide the second photon. Bauer et al. [1] have successfully developed a two-photon laser-induced fluorescence technique to measure Hg^0 in air for eddy correlation studies where high sensitivity and fast response are essential. Based on this work, the following combination of transitions will be used: 61S0 | 63P1 (253.7 nm) followed by 63P1 | 71S0 (407.8 nm).

Bauer's work used two pump lasers to produce 253.7 and 407.8 nm using a frequency-doubled dye laser and optical parametric oscillator, respectively. The method developed under this project calls for a UV lamp and tunable diode laser system to induce the two absorptions in order to reduce the complexity of the instrumentation. This will allow application of this method outside the laboratory.

Progress

A lab room was prepared and major equipment was purchased, including a Toptica tunable laser diode system and an Ando optical spectrum analyzer. Both of these have been assembled and tested. Procedures for adjusting the output frequency of the laser have been exercised. A detector utilizing an OPT101 monolithic photo-diode/trans-impedance amplifier has been assembled and tested. A holder for the UV lamp was assembled from Swage-Lok fittings to facilitate purging the lamp with nitrogen.

Status

Present activity includes operating and testing a LeCroy digital storage oscilloscope for collecting signal waveforms for computer processing. A lens arrangement is needed to focus the light from the UV lamp. Testing of the lock-in amplifier that came with the laser system is necessary. After this, the setup described in Task 1 of the project will be used to test this technique on a closed cell containing mercury vapor. Once this is successful, the project will move into Task 2, evaluating the measurement technique at low mercury concentrations and in the presence of other gases.

Quality Assurance/Quality Control

The Energy & Environmental Research Center (EERC) is committed to delivering consistent and high-quality research that meets our clients' needs and expectations. An organizationwide quality management system is in effect that governs all programs within the organization. This project is required to be in compliance with the Quality Manual and any project-specific quality assurance (QA) procedures, thus ensuring that any requirements relating to quality and compliance with applicable regulations, codes, and protocols are adequately fulfilled. The EERC Quality Assurance Manager implements and oversees all aspects of QA/quality control (QC) for all research, development, and demonstration projects and will review the QA/QC components of this project. The EERC maintains a wide range of analytical and testing laboratories that follow nationally recognized or approved standards and methods put forth by the U.S. Environmental Protection Agency, the American Society for Testing and Materials, the National Institute of Standards and Technology, and other agencies.

Quality objectives for this project include verification of measurements performed with the apparatus. This will be accomplished with the use of zero air measurements, background measurements (with the laser blocked), etc. As the project progresses, comparison with other mercury analyzers will become routine. Data collection will take place using a digital storage oscilloscope to acquire the output of a lock-in amplifier. Data will be compared to the data from other mercury monitors, the parameters of the dilution system for generating Hg^0 , and the past performance of the experimental apparatus.

Potential Users/Technology Transfer

This work will become the basis for a CEM design. Interest in this technique for use in field applications is expected. Diode laser-based instruments for field use are becoming more prevalent.

References

1. Bauer, D. ; Campuzano-Jost, P.; Hynes, A.J. Rapid, Ultra-Sensitive Detection of Gas Phase Elemental Mercury under Atmospheric Conditions Using Sequential Two-Photon Laser Induced Fluorescence. *Journal of Environmental Monitoring* **2002**, 4, 339–343.