Ultra-Sensitive Elemental and Isotope Measurements with Compact Plasma Source Cavity Ring-Down Spectroscopy (CPS-CRDS)

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Research Objective

The proposed research is to develop a new class of instruments for actinide isotopes and hazardous element analysis through coupling highly sensitive cavity ring-down spectroscopy to a compact microwave plasma source. The research work will combine advantages of CRDS measurement with a low power, low flow rate, tubing-type microwave plasma source to reach breakthrough sensitivity for elemental analysis and unique capability of isotope measurement. The project has several primary goals: 1). Explore the feasibility of marrying CRDS with a new microwave plasma source; 2). Provide quantitative evaluation of CMP-CRDS for ultratrace elemental and actinide isotope analysis; 3). Approach a breakthrough detection limit of ca. 10^{-13} g/ml or so, which are orders of magnitude better than currently available best values; 4). Demonstrate the capability of CMP-CRDS technology for isobaric measurements, such as ^{238}U and ^{238}Pu isotopes. 5). Design and assemble the first compact, field portable CMP-CRDS instrument with a high-resolution diode laser for DOE/EM on-site demonstration. With all these unique capabilities and sensitivities, we expect CMP-CRDS will bring a revolutionary change in instrument design and development, and will have great impact and play critical roles in supporting DOE's missions in environmental remediation, environmental emission control, waste management and characterization, and decontamination and decommissioning. The ultimate goals of the proposed project are to contribute to environmental management activities that would decrease risk for the public and workers, increase worker productivity with on-site analysis, and tremendously reduce DOE/EM operating costs.

Research Progress and Implications

As of statement, this report summarizes the work from 10/01/2004 to 09/30/2005 for the third year of a three-year project. Major achievements are attributed to the following aspects described below.

(1) **Uranium Emission Spectra with a Low Power Microwave Plasma Source**

The present work for the first time uses a low power microwave plasma source to generate uranium spectrum for transition study and emission measurements. With a 200 watts power and low gas flow rate, we have successfully obtained distinct uranium peaks in a wavelength range examined from 320 to 430 nm. Temperature influence on the uranium behavior in the plasma source are discussed, and the intensity of the spectral lines obtained with this low power source are systematically compared with the results reported in literature, which was obtained with high power plasma sources. Several new uranium spectral lines were identified within the wavelength range tested. Concentration effects are studied and the calibration curves are made for some strong spectral lines. The detection limits of uranium are also estimated to be at a level of sub-ppm. The research establishes a method to effectively generate uranium atoms and ions at a low power and low gas flow rate, which should be useful for uranium fundamental characteristic studies and uranium on-site monitoring work.

(2) **Blue Diode Laser-MIP CRDS of Uranium:**

Uranium is one of the most important elements/isotopes. Purpose of this task is to develop a portable uranium detector using diode laser plasma cavity ringdown system. Isotopic measurements of uranium using an ICP-CRDS have been demonstrated by using the bulky, expensive, and impractical pulsed laser system. In order to develop a portable instrument, this pulsed laser source must be replaced with a compact, inexpensive laser source. Uranium has abundant UV transition lines, of which 409 and 424 nm lines are widely used for isotopic measurements due to their large transition strengths and isotopic shifts. An external cavity diode laser with wavelength output at 409 nm is commercially available. Such a laser source has been purchased and tested. The ringdown system using this blue diode laser source has been quantitatively evaluated by measuring NO_2 absorption under atmospheric condition. A good ringdown baseline stability of 0.4% was obtained with this new external laser system. The ICP plasma source was modified and incorporated with the ringdown system for the generation of uranium atoms/ions. This experimental arrangement is intentionally designed for a direct comparison of uranium measurements with different laser source (pulsed and cw lasers) but with the same plasma source. After testing the ICP-diode laser system, the ringdown system will be upgraded using MIP-diode laser configuration for uranium and its isotopic measurements. The new system with the MIP-diode laser configuration is under construction.

(3) **Development of Alternative Plasma Sources for Cavity Ringdown Measurements of Mercury**

We have been exploring innovative technologies for elemental and hyperfine structure measurements using Cavity Ringdown Spectroscopy (CRDS) combined with various plasma sources. A laboratory CRDS system utilizing a tunable dye laser is employed in this work for demonstrating the feasibility of the technology. An in-house fabricated sampling system is used to generate aerosols from solution samples and introduce the aerosols into the ringdown path. The ringdown signals are monitored using a photomultiplier tube (PMT) and recorded using a digital oscilloscope interfaced to a computer. Several microwave plasma discharge devices are tested for mercury CRDS measurement. Various discharge tubes have been designed and tested to reduce background interference and increase the sample path-length while still controlling any turbulence generated from the plasma gas flow. Significant background reduction has been achieved with the implementation of the newly designed tube-shaped plasma devices, which has resulted in a detection limit of 0.4 ng/ml for mercury with the plasma source CRDS. The calibration curve obtained in this work readily show that linearity over two orders of magnitude can be obtained with plasma-CRDS for mercury detection. In this work, the hyperfine structure of mercury at the experimental plasma temperatures is clearly identified.

(4) **Cavity Ringdown Measurements of Mercury and its Hyperfine Structures at 254 nm in an Atmospheric Microwave Plasma: Spectral Interference and Analytical Performance**

The plasma-cavity ringdown spectroscopic (Plasma-CRDS) technique has been demonstrated as a powerful tool for elemental and isotopic measurements in recent studies. This work reports the first application of plasma-CRDS to measurements of elemental mercury and its stable isotopes at the 254 nm transition under atmospheric conditions. A microwave-induced plasma (MIP) operating at 80–100 W is used to generate Hg atoms from standard $HgCl_2$ solutions diluted by 2% nitric acid solvent. It is found that a background absorption, attributed to the overlap of two broadened rovibrational transitions $R_{21}(21)$ and $P_1(15)$ of the OH A-X (3-0) band located at 253.65 nm, generates significant spectral interference with the absorption peak of Hg at 254 nm. With an optimized operating condition, including plasma powers, gas flow rates, and laser beam positions in the plasma, the detection sensitivity of Hg is determined to be 9.1 ng ml^{-1} in aqueous solution, equivalently 221 pptv in the gas phase; this detection limit is approximately 2-fold higher than the theoretical detection limit, 126 pptv, which was estimated by using the parameters of the instrument system and the calculated absorption cross-section, 2.64×10^{-14} cm^2 $atom^{-1}$, of the transition under atmospheric plasma conditions. High-resolution spectral scans show a clear contour of the stable isotopes of the 254 nm transition. The technical challenges encountered and the potential for further development of the Hg analyzer using the MIP-CRDS technique are discussed.

(5) **Real-Time Measurements of Elemental Mercury Naturally Ecaporated from Contaminated Soil Using Cavity Ringdown Spectroscopy**

In an effort to develop a real-time, portable, sensitive mercury monitor, we are exploring the feasibility of directly detecting mercury in contaminated soil samples as well as mercury-spiked solutions at atmospheric conditions using Cavity Ringdown Spectroscopy (CRDS). In these experiments, the frequency doubled output of a tunable dye laser that was pumped by a Nd:YAG laser was used to probe the mercury line at 253.65 nm. The wavelength of the laser output was verified and continuously monitored by a wavemeter The 56 cm long cavity was constructed from two high reflectivity, plano-concave mirrors which are specially coated for maximum reflectivity at the wavelength range explored. The effective ringdown time at 254 nm is >99.67%. Mercury exhibits an intense absorption line at 253.65 nm, and an initial ambient background scan of this wavelength region indicated the presence of a weak oxygen band, $O_2A \leftarrow X$ (7,0). For a 56 cm cavity displaying 0.3% baseline stability and an absorption cross-section equal to 3.3 x 10^{-14}

cm^2/molecule, the estimated theoretical detection limit for this system, based on the 3σ criteria, is 0.6 ppt.

We have demonstrated the feasibility of utilizing CRDS to directly detect mercury vapor evaporating from contaminated soil and mercury-doped solution samples under atmospheric conditions. The sensitivity of this system (~ pptv for contaminated soils and mercury-doped solutions) is sufficient for accurate determination of the presence of mercury in such environments. Additional research is being conducted in our lab to further explore mercury detection of other contaminated substances, such as plants, utilizing CRDS. Future developments will focus on the construction of a portable, real-time Hg/ Hg-isotope monitor that is capable of accurately detecting trace amounts of mercury in soil, water, plants, and air.

Planned Activities

In this report period, significant progresses are made and research activities are on schedule. The R & D towards field deployable instrumentation using this technique has been vigorously processing in our laboratories. Future developments will focus on following major aspects:

(1) A technical challenge was encountered in the testing the tube-shape MIP-CRDS system. The plasma gas turbulence has a significant impact on the ringdown performance, such as the influence on the ringdown baseline stability. The plasma design will be modified in the future work.

(2) A diode laser-MIP configuration will be developed for uranium and its isotopic measurements.

(3) Mercury hyperfine structures at 254 nm will be further investigated under low pressure condition.

Information Access:

- Yixiang Duan, Chuji Wang; Susan T. Scherrer; and Christopher B. Winstead, "Development of Alternative Plasma Sources for Cavity Ring-Down Measurements of Mercury", *Anal. Chem.*, **77**, 4883, 2005.
- Chuji Wang, Susan T. Scherrer; Yixiang Duan; and Christopher B. Winstead, "Cavity Ringdown Measurements of Mercury and Its Hyperfine Structures at 254 nm in an Atmospheric Microwave Plasma: Spectral Interference and Analytical Performance", *J. Anal. Atom. Spectrom.*, **20**, 638, 2005. (Hot Article).
- Yixiang Duan; Susan T. Scherrer; Sudip P. Koirala; Chuji Wang; and Christopher B. Winstead, "Uranium emission spectra with a low power microwave plasma source", *Analytica Chimica Acta*, **532**, 47-54 (2005).
- Chuji Wang, Koirala, Sudip P.; Scherrer, Susan T.; Duan, Yixiang; Winstead, Christopher B. "Diode Laser Microwave Induced Plasma Cavity Ringdown

Spectrometer: Performance and Perspective," Rev. Sci. Instrum. **75**, 1305-1313 (2004).

- Wang, Chuji; Mazzotti, Fabio J.; Koirala, Sudip P.; Winstead, Christopher B.; Miller, George P. "Measurements of OH Radicals in a Low-Power Atmospheric Inductively Coupled Plasma by Cavity Ringdown Spectroscopy," Appl. Spectrosc. **58**(6), 734-740 (2004).
- Chuji Wang, Christopher B. Winstead, Yixiang Duan, Susan. T. Scherrer, Sudip P. Koirala, Ping-Rey Jang, George P. Miller, and Fabio J. Mazzotti, *"Plasma Cavity Ringdown Spectrometer for Elemental and Isotopic Measurements: Past, Present, and Future"*, ACS 2004, Anaheim, CA, Mar. 2004.
- Sudip P. Koirala, S. T. Scherrer, Chuji Wang, Yixiang Duan, and Christopher B. Winstead, "Elemental and Isotopic Measures Using Plasma Diode Laser Ringdown Spectroscopy", FACSS 2003, Oct. Ft. Lauderdale, FL. USA.
- Yixiang Duan, Chuji Wang, Susan. T. Scherrer, Sudip P. Koirala, Christopher B. Winstead, *Exploration of plasma source cavity ring-down spectroscopy for elemental and isotopic measurements: performance and perspective*, invited talk presented in Annual ACS meeting, American Chemical Society**,** Anaheim, CA, March 28 – April 1, 2004.
- Yixiang Duan, Chuji Wang, Christopher B. Winstead, *Exploration of Plasma Source Cavity Ring-Down Spectroscopy for Highly Sensitive Elemental and Isotope Measurements*, AIP Conference Proceedings, 2003, v.673, p399. 3rd Topical Conference on Plutonium and Actinides, July 6 - 10, 2003, Albuquerque, NM.
- Yixiang Duan, Chuji Wang, and C. B. Winstead, "Exploration of microwave plasma source cavity ring-down spectroscopy for highly sensitive elemental measurements", *Anal. Chem.*, **75**, 2105 (2003).

Optional Additional Information

(http://emsp.osti.gov)

Optional Proprietary Information

- The paper entitled "Cavity Ringdown Measurements of Mercury and Its Hyperfine Structures at 254 nm in an Atmospheric Microwave Plasma: Spectral Interference and Analytical Performance" (*J. Analytical Atomic Spectrometry,* **20**, (2005)) has identified as "Hot Article" by Royal Society Chemistry.
- Method and Apparatus for Elemental and Isotope Measurements and Diagnostics—Microwave Induced Plasma-Cavity Ring-Down Spectroscopy, Chuji Wang, Christopher B Winstead, and Yixiang Duan, Patent pending # 10/367,806.