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 06/01/2003 to 05/31/2004 for the second year of a three-year project. Major achievements are attributed to following six aspects described below. Due to the limited length of the report, plenty of experimental data and figures are presented in Optional Additional Information in http://emsp.osti.gov.

(1) **The improved instrument configuration--diode laser MIP-CRDS:** One of the major goals of the plasma-CRDS project is to develop a new generation, field deployable, cost-effective instrument for monitoring DoE contaminated sites and environmental management processes. In an effort to improve the portability and reduce the cost of the system construction and operation, we have modified our apparatus to include a compact microwave plasma source and a continuous wave diode laser. A novel technique for controlling the continuous wave laser to couple the ringdown cavity has been developed and implemented

through a standard power combiner instead of acouto-optic modulator or cavity modulation. To test the system performance, strontium were introduced into the plasma by an in-house fabricated sampling device combined with an ultrasonic nebulizer. SrOH radicals were generated in the plasma and detected using both a pulsed laser system and a diode laser via a narrow band transition near 680 nm. The experimental results obtained using both light sources are compared for system characterization. The ringdown baseline noise and the detection limit for Sr are determined for the current experimental configuration. The results indicate that a plasma-CRDS instrument using diode lasers and a compact microwave plasma can serve as a small, portable, and sensitive analytical tool.

(2) **Design and Fabrication of tube-shaped linear MIP sources:** Initial research was started with a microwave plasma source called microwave plasma torch (MPT), which was used as an atomization cell for ring-down measurement. The advantages of the MPT plasma source include low power, low gas flow rate, good stability, and ease of handle. However, since the MPT plasma takes a toroidal shape, it has significant limitation in plasma absorption path length. To overcome this limitation and enhance the system performance, we have designed and developed new tubing-shaped linear plasma sources with various absorption geometries, particularly T-shaped and L-shaped discharge tubes. Through optimization of the discharge tube diameter and various geometries, we have obtained a very stable linear plasma source with an absorption path-length over 80 mm to 100 mm at a power level of about 120 W (see photos in http://emsp.osti.gov). Currently, we are working on coupling this new plasma source to cavity ring-down measurement and to examine the system performance.

(3) **Uranium emission in a low power microwave plasma source:** In order to design field portable instruments, plasma sources with functions of low power, low gas flow rates, and high tolerance are particularly attractive to us. However, there are few references that reported uranium measurement using microwave plasma source even with a high power. One of the major motivations of this work is to systematically evaluate whether such a low power microwave plasma source can be used as an effective atomization/ionization cell for uranium cavity ringdown measurements. To our best knowledge, this is the first time to report uranium emission measurements using a low power microwave plasma source. This work also provides a solid foundation for our further research for uranium cavity ringdown measurement. Please see the related publication for details of this work.

(4) **Mercury measurement in MIP-CRDS with a pulsed light source:** Sensitive, real-time, on-site measurements of mercury have a significant impact on environmental monitoring and analytical chemistry. Ringdown measurements of mercury using a low power microwave induced plasma source cavity ringdown spectroscopy under atmospheric conditions are performed with the transition line of 254 nm, where the UV laser radiation is provided by the frequency doubling of a dye laser pumped by an Nd:YAG laser. The spectral background interference was extensively studied in the UV spectral region, where a high-resolution ringdown spectrum of the forbidden transitions in Hertzberg band I $A^3\Sigma_u^+ \leftarrow X^3\Sigma_g^-$ of O_2 was obtained. Ringdown measurements of such O_2 band under low-pressure conditions were reported previously, however, there is no report on the ringdown spectrum at atmospheric pressure. Influences of the plasma parameters such as power, flow rates, and plasma locations on the background interference are explored. The estimated detection limit of

mercury is in sub-ppb levels and it is expected to be further improved by utilizing the newly-fabricated tube-shaped linear plasma source.

(5) **Preliminary instrument design of plasma ringdown spectrometer:** Parallel to the science-driven study of the MIP-CRDS system, the engineering efforts are now focused on the preliminary instrument design. The system is a standalone unit with a laptop located on the top of the instrument for data processing and display of spectrum. The plasma source and ringdown cavity are located in the second floor of the platform. The first floor houses the sample introduction package and two 4-liter plasma supporting gas cylinders. The laser is introduced into the ringdown cavity through a section of single mode optical fiber. The current modulation and the laser wavelength scan are controlled by the computer which has a wireless internet access.

(6) **Blue diode laser-MIP CRDS of Uranium:** Uranium is one of the most important elements/isotopes. Isotopic measurements of uranium using an ICP-CRDS have been demonstrated. In order to develop a portable instrument, the bulky, expensive, and impractical pulsed laser system 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 and 424 nm was ordered; and the laser performance at 409 nm was extensively tested. The system was ready for uranium and its isotopic measurements.

Planned Activities

In this reported 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) Finalize the development of the low cost, compact, linear-shaped MIP source with an elongated absorption path-length, and diagnose chemical and physical properties of the new plasma source.
(2) Utilize diode lasers as the light source, e.g. external cavity diode lasers operating at 409 nm and 424 nm for isotopic measurements of uranium.
(3) Improve the sampling system performance, including efficiency and gas tolerance.
(4) Study of chemical matrix effects on the measurement accuracy and repeatability as well as selectivity (simulation testing on the real site samples).
(5) Preliminary design of the instrument frame and blueprint.

Clearly, hurdles always exist ahead. However, these hurdles will definitely be overcome with the experience gained from our many years dedicated efforts in this area. We believe that a new generation of plasma cavity ringdown spectrometer for elemental and isotopic measurements will be available within the next few years.

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Optional Additional Information

(Submitted in http://emsp.osti.gov)

Optional Proprietary Information

- 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.