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

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Project Goals

- Explore the feasibility of marrying CRDS with new microwave plasma sources;
- Provide quantitative evaluation of CMP-CRDS for ultratrace elemental and isotope analysis;
- Approach a breakthrough detection limit, which are orders of magnitude better than currently available best values;
- Demonstrate the capability of CMP-CRDS for isobaric measurements, such as ^{238}U and ^{238}Pu isotopes;
- Design and assemble the first compact, field portable CMP-CRDS with a high-resolution diode laser.

Related DOE Needs

Major DOE sites:

- Hanford
- Idaho National Engineering and Environmental Laboratory (INEEL)
- Nevada Test Site (NTS)
- Oak Ridge Reservation (ORR)
- Rocky Flats Environmental Technology Site
- Savannah River Site (SRS).

DOE Site Specific Need

Need Number

Real-time Field Instrumentation for Characterization and Monitoring Soils and Groundwater.
(**ID-6.1.02**)

Continuous Emissions Monitor for Offgas Analysis
(**ID-2.1.18**)

Cost Effective, In Situ Remediation in the Vadose Zone of One or More of the Following Radionuclides: Uranium, Plutonium, Cesium, Cobalt, and Strontium
(**RL-SS12**)

Improved, Real-Time Field Screening During Excavation for Radionuclides with Emphasis on the Following: Uranium, Plutonium, Strontium-90, and Technetium
(**RL-SS14**)

Improved, In Situ Characterization to Determine the Extent of Soil Contamination of One or More of the Following Radionuclides: Uranium, Plutonium, C
(**RL-SS16**)

Improved, Real-Time, In-Situ Detection of Hexavalent Chromium in Groundwater
(**RL-SS06**)

Real-Time Beryllium Air Monitoring
(**RL-DD16**)

Continuous Emissions Monitors for Offgas Analysis
(**ID-S.1.02**)

Real-time Field Instrumentation for Characterization and Monitoring Soils and Groundwater.
(**ID-S.1.04**)

Long-Term Groundwater Monitoring
(**CH-SS04-99**)

Real-Time Monitoring of Plutonium and Americium in Sewage Treatment Plant Influent
(**RF-ER11**)

Metals Monitoring of Gaseous Emissions
(**ORWM-13**)

On-Site Quantitation of Plutonium and Americium in Soil and Concrete Ruble from D&D Projects
(**AI-09-01-13-DD**)

Mobile Analysis Methods for Hazardous Metals in TRU Waste
(**AI-09-01-05-MW**)

Plutonium Materials Characterization/Testing
(**AL-09-01-35-NM**)

Current Technologies for Elemental and Isotope Measurement, ICP-MS

Advantages of ICP-MS:

- Fast response to various samples with high throughput;
- Good accuracy;
- Multiple function capability (elements and isotopes).

Limitations of ICP-MS:

- Needs a rather high power (~2000W) and significant plasma gas (~15 L/min);
- Detection system needs to maintain a high vacuum with a considerable pumping when coupled with an atmospheric pressure plasma source;
- ICP-MS hardly field portable, and almost impossible to move around frequently;
- ICP-MS has various interferences, such as isobaric interference, which prevent its use for isotopes with same or similar masses (i.e., ^{238}Pu and ^{238}U);

Current Technologies for Radioactive Alpha Emitter Measurement, ASC

Advantages of Alpha Scintillation Counting (ASC):

- ASC can provide ultra-high sensitivity for alpha emitters;
- Can resolve isotopes with same mass through distinguishing alpha particle energy levels;

Limitations of ASC:

- ASC technology has serious limitations in practical use;
- It is very time-consuming (the total turn around time is about two weeks);
- Preparation of an alpha counting source is a tedious procedure, may take weeks through co-precipitation, solvent extraction, or ion exchange;
- Is labor intensive and generates significant amount of secondary waste;
- ASC may also require long counting time in order to detect isotopes with low disintegration energies.
- ASC can only used for alpha emitters, no multiple functions.

Technical Background of CRDS

- **CRDS, a laser absorption technique introduced by O'Keefe and Deacon*;**
- **Is based upon a significantly different principle from traditional absorption spectroscopy methods;**
- **In CRDS, absorption is measured via a change in the decay time for light trapped in an optical cavity rather than a change in intensity;**
- **Absolute absorption measurement;**
- **Performance of the technique is relatively insensitive to laser fluctuation noise;**
- **Capable of providing ultra-sensitive measurement of 10^{-7} fractional absorbance;**
- **Effective pathlength can be extended to several kilometers!**

*A. O'Keefe and D. A. G. Deacon, Rev. Sci. Instrum. 59 (12), 2544-2551 (1988).

Principle of the CRDS Measurement

In a simple case of a low-pressure gas uniformly filling the cavity, the cavity loss originates from the mirrors and absorption of the sample based on the Beer-Lambert law. The time constant of the exponential decay or ring-down lifetime is given by:

$$\tau = \frac{d}{c(1 - R + \sigma(\nu)nd)}$$

The term $\sigma(\nu)nd$ represents a single-pass absorbance of the sample in the cavity and is recognized as the exponent from the Beer-Lambert law.

With a plasma source as an atomization cell, the absorption sample only fills a fraction of the cavity length. Additional losses due to plasma scattering and the air in the open cavity can be simply incorporated by substituting a lower effective reflectivity R_{eff} for R in the equation by measuring the ring-down time with (τ) and without (τ_0) an analyte (blank).

$$\text{Absorbance} = \frac{d}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$$

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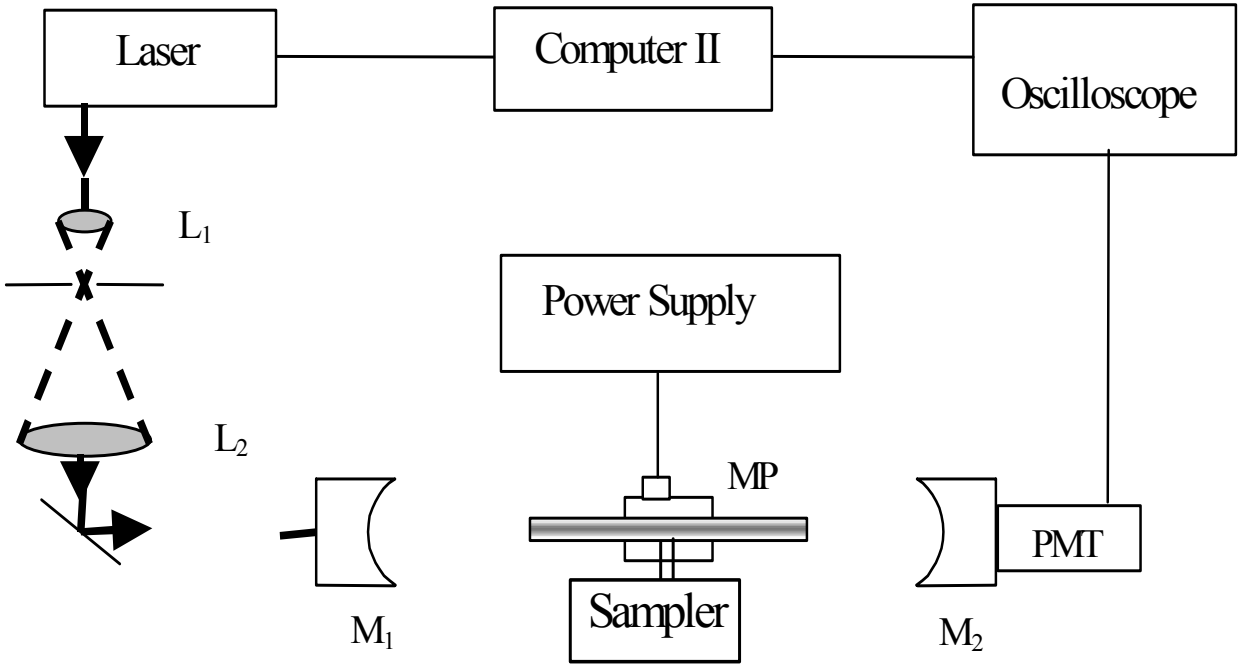
Advantages of Microwave Plasma Source for AAS Measurement

- Capable of working with various gases, including argon, helium, nitrogen and even air;
- Can be sustained at fairly low power (more than ten times lower than ICP source);
- Need only minimal gas for maintaining the plasma (about ten times lower than ICP source);
- Simplicity and low cost for instrument construction and maintenance;
- Can be designed in various shapes (like tubular shape) with extended absorption path length;
- Easily field portable.

Schematic Diagram of Experimental Setup



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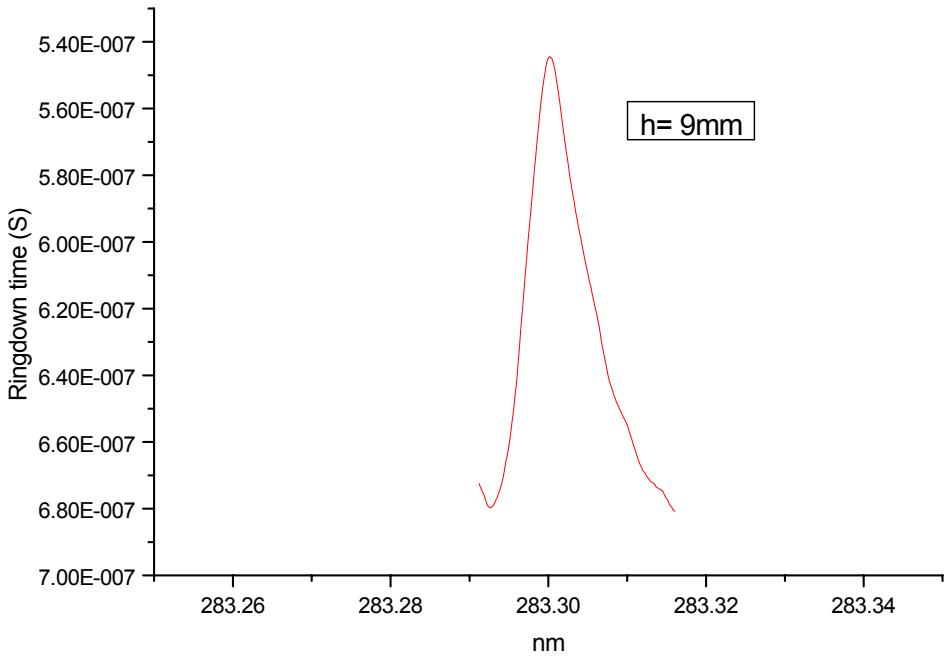
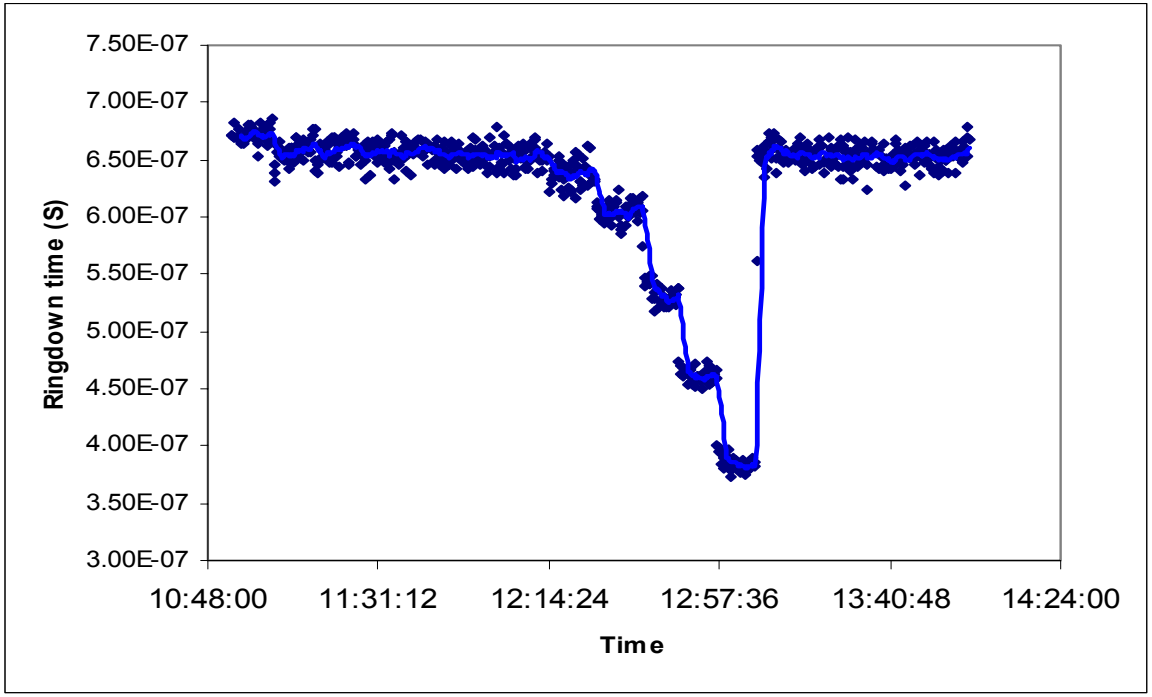
Plasma Source (MPT) Used for CRDS Measurement at the Initial Step

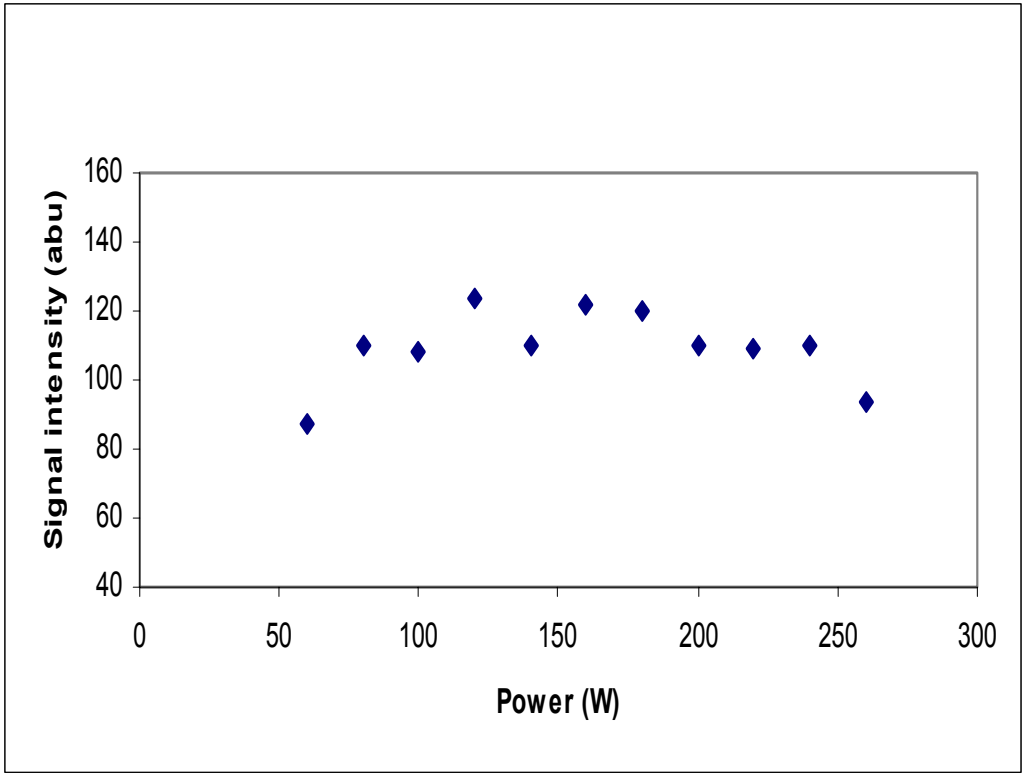
Spectral Line Profile of Lead at 283.30 nm



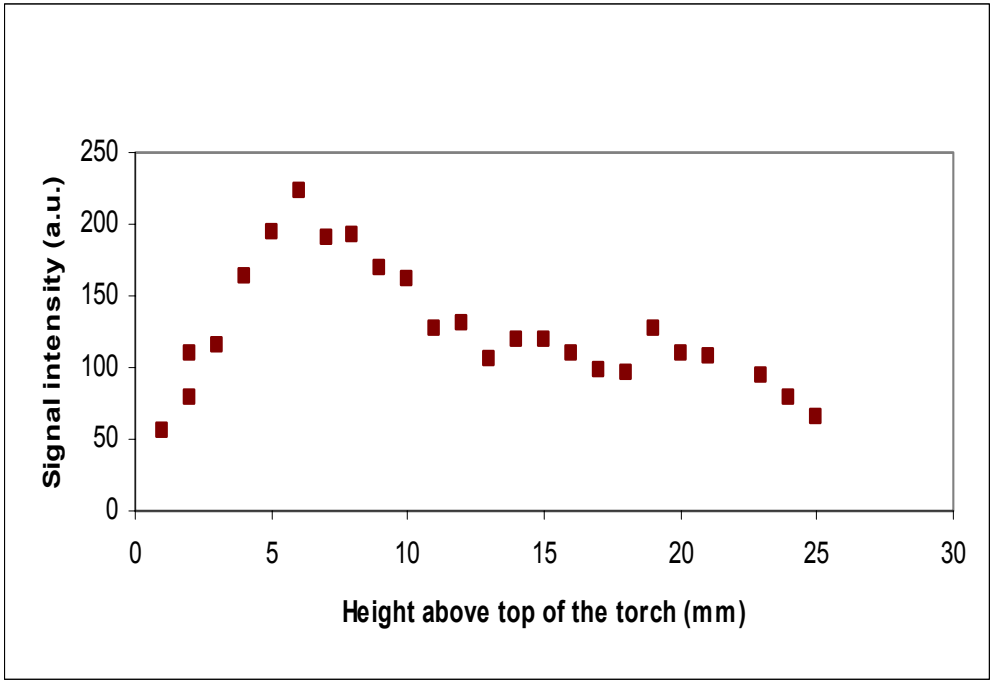
Sample Concentration v.s. Ringdown Time



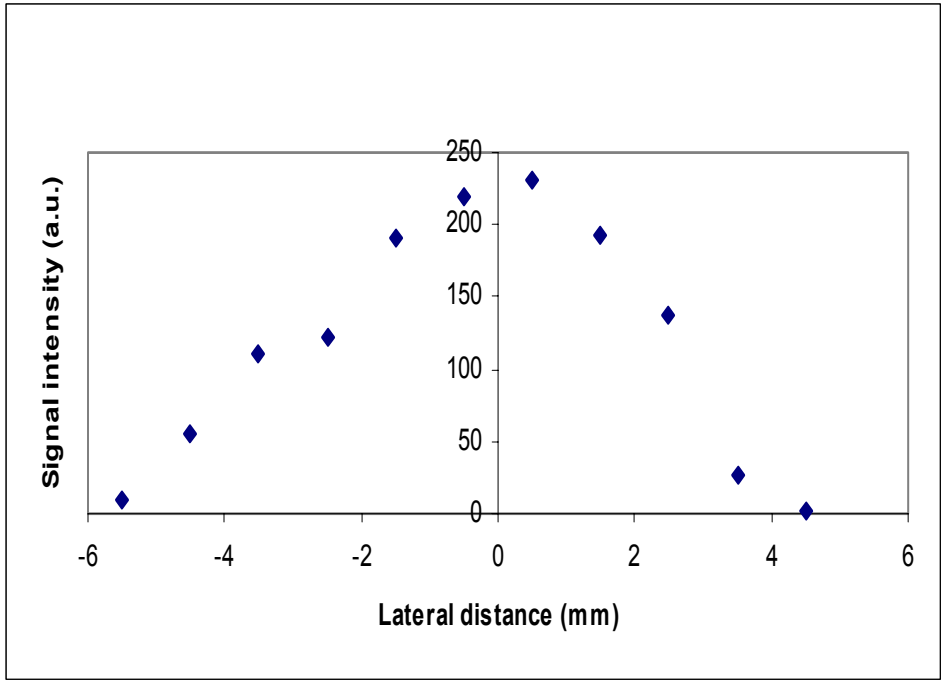
Microwave Power Dependence



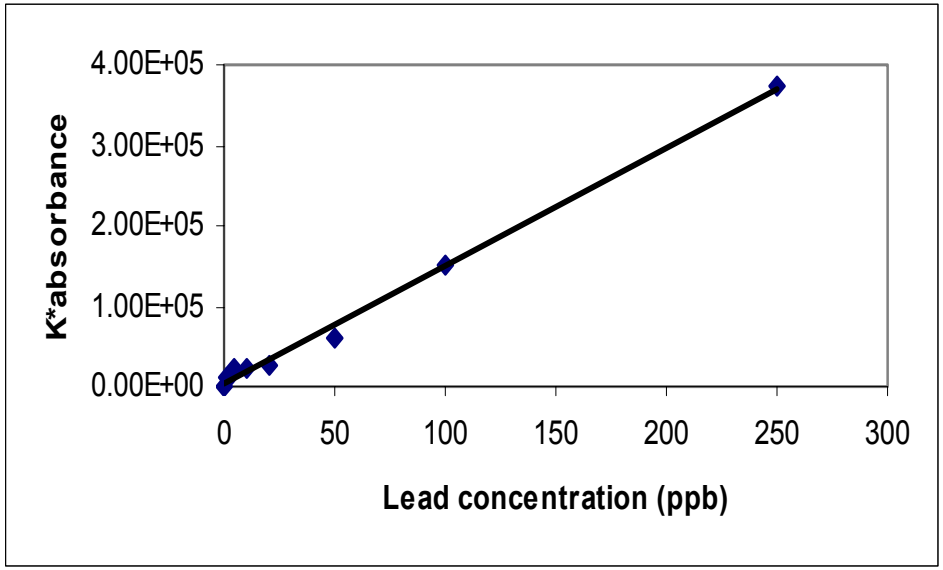
Vertical Profile of the Plasma Source



Lateral Profile of the Plasma Source



Calibration Curve and Linear Testing



Expected Advantages of the Proposed work

- **High sensitivity;**
- **Field portable;**
- **Multiple capabilities for both elemental and isotope measurements;**
- **Applicable to isobaric measurements such as ^{238}U and ^{238}Pu isotopes;**
- **Fast response with high sample throughput;**
- **Low construction and maintenance costs;**
- **Ease of operation.**

Potential Impacts and Benefits for DOE EM Sites

- Significant reduction of sample turn around time through on-site analysis – save time!
- Instant results for site workers –efficient work!
- Reduction of analytical cost – save money;
- Provide unique feature – new capability!
- Reduction of instrument and maintenance cost;
- Fast identification of isobaric isotopes such as ^{238}U and ^{238}Pu.

Technical Plans and Future Work

- Test various elements with pulsed dye laser system with MPT plasma source;
- Design a compact, tubular plasma source for CRDS measurement;
- Use single mode diode laser to couple with microwave plasma source;
- Test alternative wavelength ranges for readily available high quality mirrors;
- Design and build a field portable instrument.