Project ID: **60070**

Project Title: **The Development of Cavity Ringdown Spectroscopy as a Sensitive Continuous Emission Monitor for Metals**

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RESEARCH OBJECTIVE

The aim of this study is to evaluate cavity ringdown spectroscopy (CRDS) as an ultra-sensitive technique for trace analysis of metals. Potential applications of CRDS meeting the Department of Energy needs include:

>   Mercury Continuous Emission Monitor
>   Multi-Metal Emissions Monitor
>   Radionuclide Detector and Monitor

CRDS is based upon the measurement of the rate of light absorption in a closed optical cavity. A laser pulse is injected into a stable optical cavity through one of the cavity mirrors. This light pulse is trapped between the mirror surfaces and decays exponentially over time at a rate determined by the round trip losses within the cavity. When used for trace analysis, the primary loss mechanisms governing the decay time are mirror reflectivity losses, atomic absorption from the sample, and Rayleigh scattering from air in the cavity. The decay time is given by

$$\tau = \frac{d}{c\left[(1-R) + \alpha l_s + \beta d\right]} \qquad (1)$$

where d is the cavity length, R is the reflectivity of the cavity mirrors, α is the familiar Beer's Law absorption coefficient of a sample in the cavity, l_s is the length of the optical path through the sample (i.e., approximately the graphite furnace length), β is the wavelength-dependent Rayleigh scattering attenuation coefficient, and c is the speed of light.

Thus, variations in α caused by changes in the sample concentration are reflected in the ringdown time. As the sample concentration increases (i.e., α increases), the ringdown time decreases yielding an _absolute_ measurement for α. With the use of suitable mirrors, it is possible to achieve thousands of passes through the sample resulting in a significant increase in sensitivity. An additional benefit is that it is not subject to collisional quenching, the branching of fluorescence emission into multiple transitions, and the ability to detect only a fraction of the fluorescence photons that occur in laser-excited atomic fluorescence (LEAFS). One other advantage of the ringdown technique is the ability to use pulsed UV tunable lasers for atomic absorption spectroscopy.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work 18 months into a 3-year project. Last year's report focused on the initial results using an ICP as the atomization source. While the development of the ICP-CRDS is continuing, the need for repairs of the ICP system permitted us to begin an evaluation of CRDS using a graphite furnace as the atomization source. It is these results that we will focus on in this report. The introduction of the graphite furnace into the cavity requires simply that the furnace be firmly mounted within the cavity and that the laser beam pass through the center of
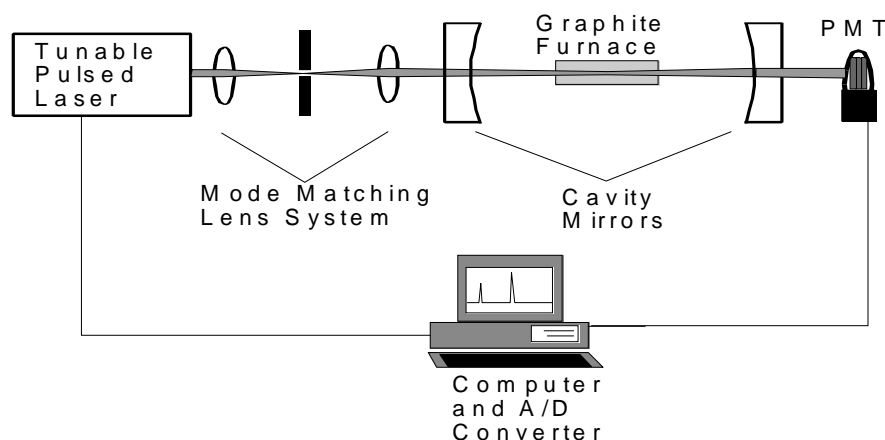

Figure 1: Schematic Diagram of ETA-CRDS System

the graphite tube. Introduction of test samples followed standard electrothermal atomization atomic absorption spectroscopy (ETA-AAS) methods.

Mercury and Lead were chosen for the initial study partly because of the need for mercury monitoring within DOE and partly due to the fact that their volatility would present a challenge to the technique.   Preliminary experiments used the Pb 283.3 nm absorption line to confirm the viability of ETA-CRDS for trace analysis. This Pb absorption line was chosen, rather than the stronger 217.0 nm absorption, for convenience with the laser system and cavity mirrors. The Pb solution data for Figure 2 was obtained by injecting 7.5 µl of 2 ng/ml lead standard solution for each heating cycle. As is clear from equation 1, $1/\tau$ is proportional to the absorbance αl_S.

The first experimental data, using ETA-CRDS, indicates that this technique has the potential to significantly enhance the sensivity of electrothermal atomization systems. Preliminary results for mercury and lead standard solutions gave detection limits of approximately 2.8 and 1 pg respectively were obtained for peak height absorption measurements. No chemical matrix modifiers were used. These detection limits, obtained in a clearly non-optimum experimental setup, compare favorably to commercial GF-AAS systems (Hg DL ~30 pg) that have undergone continuously optimization over many years. Additional experiments to measure a detection limit for Hg using a Hg-hydride cold vapor system as the Hg source are in progress.

Continuing improvement of the ETA-CRDS technique includes optimization of the laser linewidth, cavity stability during the furnace atomization sequence, data acquisition rate and timing, and the operation of the graphite furnace itself.   For example, the atomization of lead within the GF is complete in well under one second while the laser repetition rate was only 20 Hz. This implies that the results obtained in this study would greatly benefit from the use of higher repetition rate lasers such as an excimer (100-1000 Hz) or Cu vapor (2-32 kHz) lasers. Finally, in a glance to the future, it is important to note that CRDS has been carried out in other "non-traditional" configurations.   Diode lasers have been employed for CRDS of molecular species at near-infrared wavelengths, and provide a small, compact light source for CRDS measurements. In addition, frequency-doubled diode lasers have been employed at ultraviolet wavelengths for atomic absorption spectrometry (but not CRDS) for a few selected elements. As the wavelength coverage offered by diode lasers and solid state lasers in general continues to grow, the possibilities for constructing small, ultra-sensitive CRDS spectrometers for analytical atomic spectrometry continue to increase.
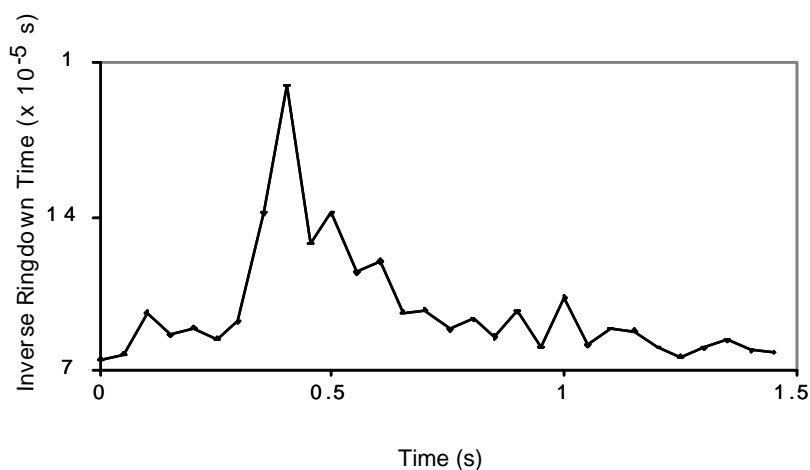
Figure 2: $1/\tau$ (where τ is the ringdown time constant) at 283.3 nm as a function of the data acquisition time following the vaporization of a 7.5 μl of 2 ng/ml Pb solution.

PLANNED ACTIVITIES

It is our intention to return our focus to the ICP-CRDS system. Work on optimizing the ICP-CRDS cavity design will be completed within the next couple of months. Several new ICP torches, designed and built to increase sample path and maximize atomization, will also be evaluated and detection limits for various metals established. In addition, the potential for this technique to detect and monitor transuranic elements will be evaluated. With respect to the GF-CRDS, future research will investigate elements of lower volatility and reduced fluorescence yield (such as the actinides), where the advantages of ETA-CRDS (at this stage of technology development) and the needs of DOE are most evident

INFORMATION ACCESS

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