



# Preliminary results for electrothermal atomization-cavity ringdown spectroscopy (ETA-CRDS)

C. B. Winstead, F. J. Mazzotti, J. Mierzwa and G. P. Miller\*

Diagnostic Instrumentation and Analysis Laboratory, Mississippi State University, 205 Research Blvd., Starkville, MS 39759, USA. E-mail: miller@dia.msstate.edu

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We report the first experimental results using electrothermal atomization-cavity ringdown spectroscopy for trace elemental analysis. Lead aqueous standard solutions were analyzed using graphite furnace-cavity ringdown spectroscopy and a preliminary detection limit of approximately 1 pg was obtained for peak height absorption measurements. No chemical matrix modifiers were used. These preliminary results together with an estimate of theoretical detection limits suggest that the coupling of ETA and CRDS has the potential to become a valuable new technique in analytical atomic spectrometry.

## Aim of investigation

Since its introduction in 1988,<sup>1</sup> cavity ringdown spectroscopy (CRDS) has rapidly developed into a widely used technique for sensitive spectroscopic applications.<sup>2–7</sup> However, to date there has been only one reported use of CRDS for trace atomic spectrometry.<sup>8</sup> In that earlier study, we reported our initial efforts to apply CRDS for elemental analysis in an inductively coupled plasma (ICP). While the development of the ICP-CRDS is continuing, we have recently begun an evaluation of CRDS using a graphite furnace as the electrothermal atomization source. Preliminary results, given below, indicate that GF-CRDS has the potential to significantly enhance the sensitivity of electrothermal atomization systems.

A full discussion of CRDS can be found in several recent review articles (and the references therein),<sup>2</sup> and thus the technique will only be briefly summarized here. CRDS is based upon the measurement of the rate of light absorption in a closed optical cavity rather than a measurement of the quantity of light absorbed. As depicted in Fig. 1, a laser pulse from a tunable pulsed laser is injected into a stable optical cavity through one of the cavity mirrors. As the cavity is constructed from highly

reflective mirrors, only a fraction of the laser pulse energy is transmitted into the cavity through the mirror. 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. A photomultiplier tube placed behind the second cavity mirror monitors the intensity of light trapped within the cavity. The decay time is obtained by fitting the observed decay waveform to a single exponential function.

For electrothermal atomization experiments, the primary loss mechanisms governing the decay time of the cavity are mirror reflectivity losses, atomic absorption in the graphite furnace, and Rayleigh scattering from air in the cavity. The decay time is given approximately by

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

where  $d$  is the cavity length,  $R$  is the reflectivity of the cavity mirrors,  $\alpha$  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),  $\beta$  is the wavelength-dependent Rayleigh scattering attenuation coefficient, and  $c$  is the speed of light. When the laser wavelength is fixed on resonance with an atomic absorption line, variations in  $\alpha$  caused by changes in the analyte concentration are reflected in the ringdown time. As the concentration of analyte increases (*i.e.*,  $\alpha$  increases), the ringdown time constant decreases. Mirror reflectivity,  $R$ , is found by measuring the ringdown time with no sample analyte ( $\alpha$  is zero), and including the calculated value for  $\beta$ .<sup>9</sup> Thus, in principle, a measurement for the ringdown time will yield an absolute measurement for  $\alpha$ , since all other parameters in eqn. (1) are known.

With the use of highly reflective mirrors, it is possible to achieve thousands of passes through the sample resulting in a significant increase in sensitivity. An additional benefit in using ringdown is that it is an absorption technique. For example, 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 occurs 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. Pulsed lasers, in general, are characterized by shot-to-shot power fluctuations that normally preclude their use in sensitive absorption measurements. However, since the decay time (rather than the absorbed intensity) is measured, ringdown is effectively insensitive to these fluctuations. Pulsed lasers are currently desirable for atomic spectrometry due to their ability to provide tunable ultraviolet radiation.

However, the ultimate benefit of using cavity ringdown for atomic spectrometry rather than other techniques, such as LEAFS, will be determined by the stability of the baseline ringdown time-constant measurement, the quality of mirrors used for cavity construction, and the particular element under study. High quality mirrors ( $R \approx 0.999$ ) are available at wavelengths down to almost 200 nm. For such mirrors, a baseline stability of 1% in ringdown time measurement is all that is required to achieve minimum detectable per pass

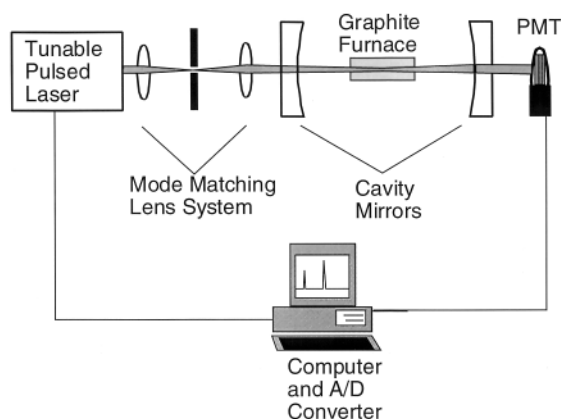


Fig. 1 Basic experimental configuration for graphite furnace-cavity ringdown spectroscopy.

absorbances ( $\alpha_s$ ) of 36 parts per million (based on a  $3\sigma$  criterion).

## Experimental procedures

For this initial feasibility study we follow similar lines to those reported in our earlier work on ICP-CRDS.<sup>8</sup> In this case, the ICP has been replaced with a graphite furnace. A schematic diagram of the experimental setup is presented in Fig. 1. The individual experimental specifications are as follows:

(I) Electrothermal atomizer: A transversely heated graphite furnace (GF 110, Aurora Instruments, Canada) was used. Aqueous standard solutions were pipetted manually using an Eppendorf type micropipette. Injected sample solutions were dried for 30 s at 120 °C; ashed for 15 s at 300 °C and atomized (wall atomization) for 3 s at 1400 °C. The clean-up step was set at 2000 °C. Maximum heating prior to the atomization step was applied. The argon flow was 1.5 l min<sup>-1</sup> except for the atomization step, when the gas flow was stopped. To eliminate optical loss from the furnace housing windows, the windows were removed and replaced with metal disks. Small holes (~5 mm id) were drilled in the disks to pass the laser beam.

(II) Laser system: An Nd:YAG laser was used to pump a tunable dye laser. The dye laser output was frequency doubled to obtain ultraviolet laser wavelengths. The dye laser output has a specified linewidth of 0.04 cm<sup>-1</sup>, which when doubled yields a final ultraviolet linewidth of approximately 0.06 cm<sup>-1</sup>. The laser pulse duration is approximately 8 ns and the laser repetition rate is 20 Hz.

(III) Cavity optics: For these experiments a 55 cm long cavity was constructed from specially coated mirrors. The mirrors were plano-concave with a 6 m radius of curvature and were coated for maximum reflectivity at 280 nm. The reflectivity at the 283 nm wavelength used for these experiments was approximately 99.9%. The laser beam was spatially filtered and mode matched into the cavity using a small homemade beam-expander. A narrowband interference filter was used to reject background radiation prior to the detection electronics.

(IV) Data acquisition: Due to the transient nature of the atomic absorption signal in a graphite furnace, the data acquisition system that was designed for ICP-CRDS (described in ref. 8) was inappropriate. Therefore, a new approach, still under development, was employed for these experiments. Since the typical transient signal due to lead atomization lasts for less than one second, to save every waveform during the atomization process it was necessary to design a fast, high-resolution data acquisition system so that integrated absorbance values can be obtained for each atomization cycle. The signal from a photomultiplier tube, placed behind the second cavity mirror, is digitized by a 12 bit, 100 MHz sample rate analog-to-digital converter. The timing for data acquisition is determined by the software controlling the graphite furnace. An output trigger from the furnace power supply can be delayed in 0.1 s intervals from the start of atomization. Following this preset delay, the output trigger causes approximately four seconds (80 waveforms) of ringdown data to be acquired. These waveforms were processed off-line to obtain the peak maximum and integrated absorbance values.

(V) Reagents: A stock solution of lead (1000 µg ml<sup>-1</sup>) from High Purity Standards (Charleston, SC, USA) was used together with trace analysis-grade nitric acid from Fisher Scientific (Pittsburgh, PA, USA) and high purity deionized water (Millipore) was used to prepare all standard solutions. These solutions were prepared by a sequential dilution of lead 1000 µg ml<sup>-1</sup> stock solution with either 2% nitric acid or deionized water.

## Results and discussion

The introduction of the graphite furnace required simply that the furnace be firmly mounted within the cavity and that the laser

beam pass through the center of the graphite tube. Introduction of test samples followed standard ETA-AAS methods. Lead was chosen for the initial study partly because of our previous results obtained by ICP-CRDS<sup>8</sup> and partly due to the fact that its 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.

Fig. 2 depicts the response of  $1/\tau$  (where  $\tau$  is the ringdown time constant) at 283.3 nm as a function of the data acquisition time following the start of the atomization step. As is clear from eqn. (1),  $1/\tau$  is proportional to the absorbance  $\alpha_s$ . The responses for both a blank and lead aqueous standard are presented. The data for Fig. 2 was obtained by injecting 7.5 µl of 2 ng ml<sup>-1</sup> lead standard solution. A linear calibration graph for absorbance vs. injected lead mass was obtained over the range 8 to 20 pg and a limit of detection of approximately 1 pg was obtained based on the  $3\sigma$  criterion and twelve individual blank measurements. This detection limit is slightly better than the typical detection limit usually obtainable in electrothermal atomic absorption spectrometry (ETA-AAS), particularly considering that peak height was measured and no chemical matrix modifiers were employed.

## Conclusions

These preliminary results suggest that the coupling of ETA and CRDS has the potential to become a valuable new technique in analytical atomic spectrometry. The detection limits that have been demonstrated, with a clearly non-optimum experimental system, compare favorably to commercial ETA-AAS systems that have been continuously optimized over many years. The theoretical detection limits possible with ETA-CRDS may be easily estimated by comparison with standard ETA-AAS system. For modern commercial systems, a Pb characteristic mass (the mass for which the absorbance is  $4.4 \times 10^{-3}$ ) of approximately 5 pg is typical.<sup>10</sup> For 99.9% reflective mirrors and a 1% stability in baseline ringdown times, the CRDS  $3\sigma$  absorbance detection limit is  $3.6 \times 10^{-5}$ . Thus, by scaling the mass linearly with the absorbance, the CRDS detection limit is expected to be approximately 40 fg. For our current system, our effective mirror reflectivity is 99.86% and our baseline ringdown time variation is typically 2–3%. With improvements in mirror coating technology, the absorbance limit could be one to two orders of magnitude lower (as is already the case for visible and near-infrared CRDS systems).

Continuing improvement of the ETA-CRDS technique to reach the predicted limits includes optimization of the laser linewidth,<sup>11</sup> 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 graphite furnace is complete in well under one second

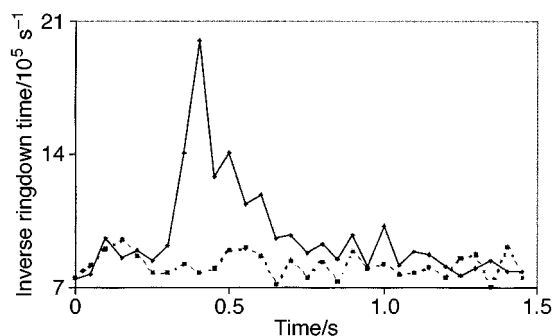


Fig. 2 Analytical shape of lead atomization peak obtained from cavity ringdown time measurements.

while the laser repetition rate was only 20 Hz. This implies that significant benefit would accrue from the use of higher repetition rate lasers such as an excimer (100–1000 Hz) or Cu vapor (2–32 kHz) lasers. Future research will also investigate elements of lower volatility and reduced fluorescence yield (such as the actinides), where the advantages of ETA-CRDS would be more evident (at least, at this stage of technology development).

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 (*e.g.* refs. 12–14) and provide a small, compact light source for CRDS measurements. Such systems are also capable of very high data acquisition rates. In addition, frequency-doubled diode lasers have been employed at ultraviolet wavelengths for atomic absorption spectrometry (but not CRDS) for a few selected elements (*e.g.* refs. 15 and 16). 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.

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