



D I A L

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The Application of Cavity Ringdown Spectroscopy to Trace Metal Detection

Cavity ringdown spectroscopy (CRS) is an absorption technique which differs from standard atomic absorption spectrometry in that it is a measurement of the *rate of light absorption by a sample within a closed optical cavity*. A laser pulse is introduced into an optical cavity formed from two highly reflective mirrors (see Figure 1). The light is subsequently trapped between the mirror surfaces and decays exponentially with time at a rate determined by the round trip loss experienced by the laser pulse. This ringdown time, τ , is given by

$$\tau = \frac{T_r}{2[(1 - R) + \alpha l_s]}$$

where T_r is the round trip time for the pulse in the cavity, R is the effective reflectivity of the cavity mirrors, α is the wavelength dependent absorption coefficient of a sample in the cavity, and l_s is the length of the optical path through the sample.

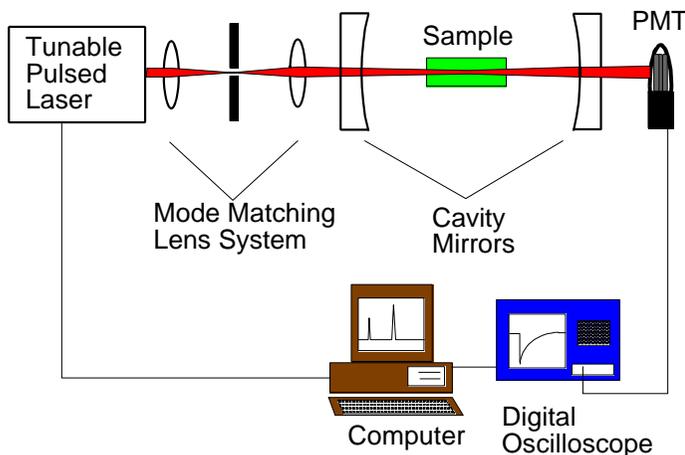


Figure 1. Schematic of experimental setup.

Figure 2 gives the actual ringdown signal obtained using our prototype CRS system. By tuning the laser wavelength through a resonance with a selected atomic or molecular absorption line, the losses in the cavity are increased (i.e. α in the equation increases). This reduces the ringdown time of the cavity and yields the sample concentration (Figure 3). Since only the ringdown time is measured, this tech-

nique is insensitive to the power fluctuations common to pulsed lasers. Due to a combination of long effective pathlengths (in the range of kilometers) and relaxed constraints on the measurement of the decay time, sensitivities superior to ICP-MS and photo-acoustic spectroscopy can be achieved.

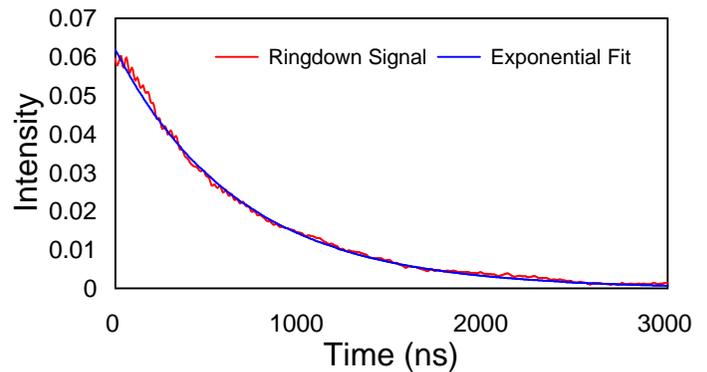


Figure 2. Cavity ringdown signal for 1-m cavity. An exponential fit yields a 676-ns time constant, corresponding to a measured average mirror reflectivity of 99.51% (99.5% specified by the manufacturer at 460 nm).

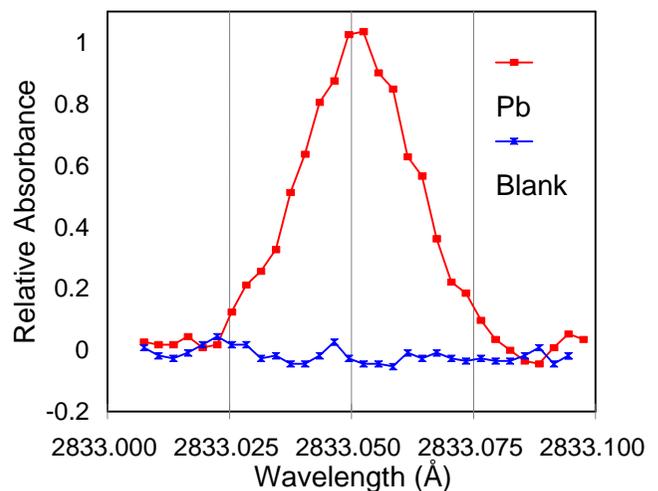


Figure 3. CRS wavelength scan for 100 ppm lead (Pb) and blank solutions nebulized into an inductively coupled plasma (ICP).

To fully utilize the potential of CRS for trace element detection, it is necessary to couple the ringdown cavity to an appropriate atomization source. To this end, DIAL is focusing on two atomization sources: the ICP and the graphite furnace (GF). The combination of these two sources with CRS holds the promise of providing powerful new techniques for atomic trace analysis. For example, ICP-CRS may one day serve as a continuous emission monitor (CEM) for off-gas analysis, while GF-CRS could provide ultra-sensitive solution and solid trace analysis.

The advantages and disadvantages of the ICP-CRS technique for trace analysis are briefly summarized below.

Advantages

- Absorption spectroscopy with the added advantages of:
 - Detection limits that could exceed those achieved by ICP-MS.
 - Sensitivity that increases as sample absorption decreases, ideal for trace analysis.
- Coupled with mature ICP and Graphite Furnace technology.

- Potentially applicable in hostile environments such as on-line monitoring of industrial processes, e.g. multi-metal CEM, Hg CEM, α -emitter monitors or radio-nuclide detectors.

To conclude, preliminary results indicate that coupling CRS to an ICP has the potential to become a valuable asset in analytical atomic spectrometry. At this preliminary stage of research, all indications are that sub-ppb detection limits are readily attainable, with sub-ppt levels possible.

Additional information about this technique can be obtained by contacting Dr. John Plodinec at:

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