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The Development of Cavity Ringdown Spectroscopy as a Sensitive Continuous Emission Monitor for Metals

George P. Miller
Mississippi State University
Diagnostic Instrumentation and Analysis Laboratory
P.O. Drawer MM
320 Etheredge - Hardy Drive
Mississippi State, Mississippi 39762
Phone: 601-325-7631
E-mail: miller@dial.msstate.edu

Christopher B. Winstead
Mississippi State University
Diagnostic Instrumentation and Analysis Laboratory
P.O. Drawer MM
320 Etheredge - Hardy Drive
Mississippi State, Mississippi 39762
Phone: 601-325-2105

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Christopher B. Winstead, Mississippi State University

Research Objective

A critical need exists for the development of methods to monitor toxic metal concentrations in remediation system offgases in real-time at parts-per-billion levels or lower. Although several technology development projects are being pursued to meet the requirements of a multi-element metals continuous emission monitor (CEM), no current technique has met all the requirements of sensitivity and data quality. The use of cavity ringdown spectroscopy (CRS) as an ultra-sensitive analytical technique is a natural extension of previous atomic absorption spectroscopy methods. However, while CRS has rapidly gained popularity among the molecular spectroscopy community, the work reported here concerns the first efforts to apply this technique to analytical atomic spectroscopy. The objective of this project is to combine CRS with the well-established tools for sample atomization, the inductively coupled plasma (ICP) and graphite furnace (GF), to provide a viable technique for on-line, trace level continuous emission monitoring of species such as toxic metals and radionuclides with detection limits comparable to ICP-mass spectroscopy (ICP-MS).

Research Progress and Implications

This report summarizes our progress in the first year of a 3-year project to develop cavity ringdown spectroscopy as a sensitive, continuous emission monitor for metals. Progress has been slightly delayed by problems associated with freeing up the matching funds necessary to purchase a new narrow-linewidth dye laser and the typical problems encountered when departments move into a new building. However, these problems have been largely solved. Our new laser system has recently arrived and additional matching funds have been obtained for the purchase of a graphite furnace. This instrument is on order and will arrive in the near future. The postdoctoral and graduate positions have been filled.

Before discussing our achievements to date, a brief outline of the technique will be useful. In a typical cavity ringdown experiment, a laser pulse is injected into a stable optical cavity formed from two highly reflective dielectric mirrors and is trapped between the mirror surfaces. The light stored in the cavity decays exponentially with a time constant determined by the mirror reflectivity and the sample concentration within the cavity. The decay time is measured using a photomultiplier tube and fitted to a single exponential function which, in turn, yields the sample concentration. For the highest reflectivity mirrors available, a pulse circulating in the cavity can result in kilometers of effective pathlength. To perform elemental analysis using CRS, an atomization source (e.g. ICP & GF) is required (see ref. 1 & refs. therein).

Initial experiments have focused on ICP-CRS using a 1.6 kW, 27.12 MHz argon ICP (standard Fassel torch) equipped with an ultrasonic nebulizer. A frequency doubled Nd:YAG laser pumped tunable dye laser with pulse duration of approximately 10 ns and repetition rate of 10 Hz. The resulting laser output is of the order of 0.3 cm^{-1} linewidth. This is approximately twice the linewidth of the absorption feature, implying that the apparent absorption linewidth is a combination of both the actual absorption and the laser linewidth. As with standard absorption spectroscopy⁴, CRS absorbance measurements require the use of a linewidth narrower than the absorption line. Thus these initial results suffer from a reduced sensitivity since a significant fraction of the pulse energy remains in the cavity even after light in resonance with the atomic transition has been absorbed. This problem is eliminated with the use of the new laser system.

Various radius of curvature mirrors, coated for different wavelength ranges, have been tested for cavity construction and stability. The interface between the ICP and optical cavity systems has also been investigated especially with regard to the baseline time constant stability. The cavity has been designed and tested to minimize the fluctuations caused by the introduction of the ICP into the cavity. The stability of the technique has been studied using two very different cavity configurations. Short cavities (56 cm long) were constructed from 0.5 and 5 meter radius of curvature mirrors. Both near confocal (0.5 m) and near planar (5 m) cavity geometries were tested during ICP operation and yielded a standard deviation in baseline (no analyte) ringdown times of approximately 1%. Results obtained both with and without the ICP plasma indicate that while the ICP does not appear to have severe effects on the measured time constant stability, it does slightly reduce the magnitude of the time constant. This implies additional losses in the ICP other than absorption by analyte atoms. Research is currently underway to explain this observation. The effect of spatial filtering and mode matching optical configurations on the input laser pulse have also been evaluated.

Our trace species investigations have focused, to this point, on the detection of Pb using ICP-CRS (although we have also observed Mg and OH, Fig. 7 in Ref. 1 depicts the relative absorbance measured as the laser is tuned across the 283.3 nm Pb absorption line). The initial goal in the operation of an ICP-CRS system is the production of primarily ground state analyte atoms (i.e., similar to ICP-AFS). Full optimization, however, requires consideration of the influence of ICP torch design and operation, observation height within the ICP, gases and gas flow for the ICP torch, wavelength selection, and calibration procedures. Additional important considerations are interference effects, light scatter, sample transport, matrix effects, and spectral interferences.

With the introduction of analyte into the ICP, the ringdown time clearly drops as the solution concentration increases. However, a deviation from linearity is observed at high concentrations. While such effects are common in traditional atomic absorption spectroscopy, an additional component leading to non-linearity in our data is the linewidth of the laser. Research⁴ has found an ~8 times improvement in ringdown response with a reduction to a narrow linewidth. At lower concentrations, an excellent linear response is obtained. Our preliminary results with the old laser system indicate a ppb detection limit for Pb. While this value is still one to two orders of magnitude from theoretical values for ICP-CRS, the new laser has yet to be incorporated and significant work on system optimization remains to be completed. These early results place ICP-CRS among the most sensitive of optical analysis methods for ICPs. Continued improvements are expected, with a complete multi-parameter optimization strategy to be implemented in the future. These improvements should make ICP-CRS a viable alternative to ICP-MS in many analytical environments.

Planned Activities

The remainder of Year 1 will focus a systematic study of ICP-CRS optimization and the determination of detection limits. Parallel to this, design of the GF-CRS interface will begin. In Year 2, evaluation of the argon ICP-CRS will be completed. Preliminary experiments will begin on the viability of using air-ICP-CRS as a, for example, Hg CEM monitor. System optimization of the GF-CRS option will begin. These experiments will continue through Year 3 resulting in a complete evaluation of CRS as an analytical atomic spectroscopic tool.

Information Access

1. G. Miller and C.B. Winstead, "Inductively Coupled Plasma-Cavity Ringdown Spectroscopy," *Journal of Analytical Atomic Spectrometry* 12, 907 (1997).
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3. C.B. Winstead and G. Miller, "Detection Limits for Selected Metals by ICP-CRS" In Prep.
4. W.J. Price, *Analytical Atomic Absorption Spectroscopy*, Heyden & Son Inc., New York (1972).