

Final Report

U.S. Department of Energy

The Development of Cavity Ringdown Spectroscopy as a Toxic
Metal Continuous Emission Monitor

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EXECUTIVE SUMMARY	3
RESEARCH OBJECTIVES.....	6
INTRODUCTION.....	6
CAVITY RINGDOWN SPECTROSCOPY (CRDS).....	6
INSTRUMENTATION:	8
RESULTS AND ACHIEVEMENTS	10
INDUCTIVELY COUPLED PLASMA-CRDS (ICP-CRDS)	10
ELECTROTHERMAL-CRDS	21
COLD VAPOR MERCURY CAVITY RINGDOWN SPECTROMETRY:.....	23
CONCLUSION	27
RELEVANCE, IMPACT, AND TECHNOLOGY TRANSFER	28
PERSONNEL SUPPORTED.....	30
PUBLICATIONS	30

LITERATURE CITED.....32

Executive Summary

We undertook an innovative program to explore the viability of using Cavity Ringdown Spectroscopy (CRDS)^{1,2} for trace analysis and monitoring of remediation processes for hazardous and radioactive wastes. Cavity ringdown spectroscopy is a measurement of the rate of absorption of a sample within a closed optical cavity rather than the standard measurement of the absorbed signal strength over a given sample path. It is a technique capable of providing ultra-sensitive absorption measurements ($< 10^{-6}$ fractional absorption) in hostile environments using commercially available easy-to-use pulsed lasers. The inherent high sensitivity stems from both the long effective sample pathlengths possible (in the tens of kilometers) and the relaxed constraints on the accuracy of the measurement of the cavity decay time (~1% accuracy yields ppm absorbance detection capability).

This project had three primary goals:

- 1) Determine the viability, through experiment and model validation, of marrying an exciting new science tool - Cavity Ringdown Spectroscopy - with standard analytical instruments, e.g. the ICP and graphite furnace.
- 2) Provide the first quantitative evaluation of cavity ringdown spectroscopy for trace analysis.
- 3) Make a significant and positive impact in support of the management and disposal of DOE radioactive, hazardous chemical, and mixed waste.

The contents of this report demonstrate the potential of cavity ringdown spectroscopy for analytical atomic spectroscopy.³⁻⁷ For example, early in this project the inherent sensitivity of CRDS for the detection of elemental mercury was again demonstrated by a scan of an empty cavity (open to the laboratory air) over the spectral region centered on the Hg 253.7 nm spectral line. This scan performed during an initial setup experiment clearly indicates not only the presence of absorption due to a weak oxygen band but also the presence of Hg (the peak at ~253.65 nm in Figure 1). This peak corresponded to Hg background level of 10 pptv and a detection limit of the order of 0.1 pptv. [The Hg was traced to a waste container holding low-level Hg waste (< 10 ppm) that was insufficiently sealed. Capping the container lowered the background Hg level in the laboratory below the detection limit.]

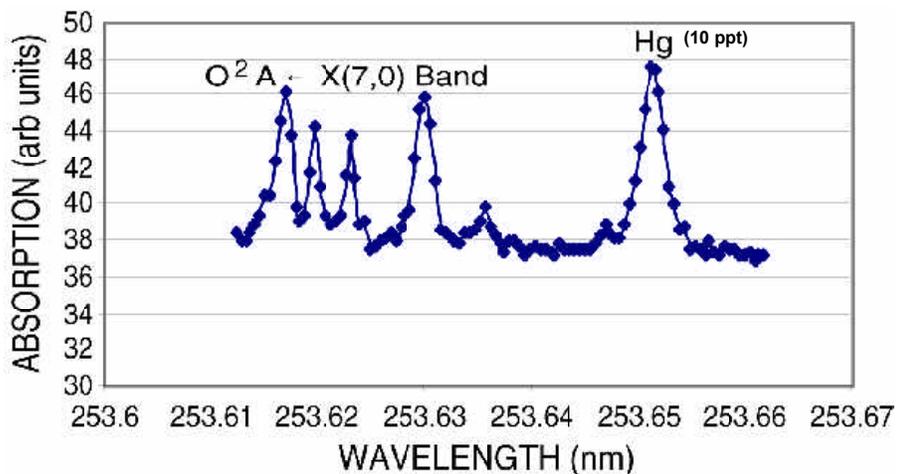


Figure 1: CRDS wavelength scan of laboratory air in an empty cavity (Determination of elemental mercury by cavity ringdown. Tao, Mazzotti, Winstead & Miller. Analyst 125, 1021 2000).

However, in general to apply this technique for trace analysis it is necessary to dissociate the compounds to be analyzed into their constituent elements. As Lundell (Ind. Eng. Chem., Anal. Ed. 5, 221 1933) succinctly put it “The rub comes in because elements never occur alone, for both man & nature frown on celibacy.” We have carried out the first experiments aimed at coupling CRDS to analytical atomization sources. Specifically, the results detailed in this report are the first to demonstrate the potential of

- 1) Inductively Coupled Plasma (ICP)-Cavity Ringdown Spectroscopy
 - 2) Electrothermal Atomization (ETA)-Cavity Ringdown Spectroscopy
- and
- 3) Cold Vapor Mercury (CV) -Cavity Ringdown Spectroscopy.

The results of this study clearly demonstrate both the robustness and sensitivity of the technique. Cavity Ringdown Spectroscopy was successfully employed in complex environments with large temperature gradients as well as rapidly changing temperatures both as an analytical tool and as a diagnostic technique. Its potential as an ultra-trace analytical elemental technique is illustrated with Cold Vapor atomization of Mercury (using an 18 cm open-ended sample cell) yielding a detection limit for of 25 ng/m³. Additional highlights achieved by this study are included below.

Selected Highlights

1. First CRDS measurements in inductively coupled plasma, graphite furnace, and cold vapor mercury sources.
2. Successful verification of initial theoretical methods for estimating CRDS sensitivity for atomic spectrometry in an ICP.

3. Demonstration of better detection limits for non-optimized graphite furnace-CRDS than for commercial graphite furnace atomic absorption spectrometers.
4. Cold Vapor-CRDS detection limit for Hg demonstrated to be orders of magnitude lower than traditional Cold Vapor atomic absorption spectrometry.
5. Demonstration of unique capabilities of CRDS for plasma diagnostics in an ICP.
6. Quantitative demonstration of isotopic resolution for CRDS coupled with an air ICP.
7. Results published in refereed journals, presented at national and international conferences, and highlighted by a major national publication (*Analytical Chemistry* 71, 660A (1999)).

Research Objectives

Introduction

Important concerns for the development and implementation of remediation processes for hazardous and radioactive wastes include characterizing the waste prior to treatment and monitoring of the efficiency of the treatment process. Central to these issues is the need for very sensitive detection of hazardous atomic and molecular species in the treatment products and offgas. Toxic metals, especially mercury, are of special note. The objective of this project, as stated in the original proposal, was/is to “provide a full evaluation of the potential of cavity ringdown spectroscopy (CRDS) as a powerful new analytical technique for elemental trace analysis.” To date we have been the first to demonstrate the potential of

- 1) Inductively Coupled Plasma (ICP)-Cavity Ringdown Spectroscopy
- 2) Electrothermal Atomization-Cavity Ringdown Spectroscopy and
- 3) Cold Vapor Mercury-Cavity Ringdown Spectroscopy.

In addition, the novel capabilities of CRDS for plasma diagnostic measurements have been demonstrated in experiments utilizing an ICP. A modified ICP torch was developed as part of the optimization of ICP-CRDS sensitivity. These efforts comprise the most complete evaluation of CRDS for atomic spectrometry to date. The results of these studies are discussed in more detail below but, first, a brief introduction to cavity ringdown spectroscopy is in order.

Cavity Ringdown Spectroscopy (CRDS)

Cavity ringdown spectroscopy (CRDS) is a novel method of carrying out ultrasensitive absorption spectroscopy. Although the use of CRDS was first reported in 1988, the technique did not achieved widespread application until the mid- to late 1990's. During that time, CRDS remained primarily a tool of the molecular spectroscopist, with its significant potential for analytical atomic use being largely overlooked. In its original form¹, CRDS is implemented by injecting and trapping a laser pulse in a stable optical cavity formed from two highly reflective mirrors (See Figure 2). The intensity of the light in the cavity decays exponentially with time at a rate determined by the round trip losses experienced by the laser pulse. This intensity decay is monitored using a photomultiplier tube (PMT) placed behind the second mirror, and the

ringdown time is usually determined by fitting the observed waveform to a single exponential function.

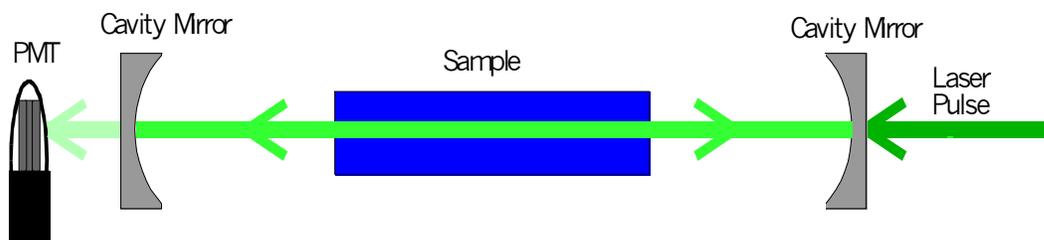


Figure 2: Basic optical configuration for cavity ringdown spectroscopy.

When the dominant losses are the mirror reflectivity and absorption from a sample species in the cavity, Equation 1 gives the time constant for the exponential decay

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

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, and c is the speed of light. As the laser wavelength is varied, the ringdown time will decrease upon tuning to an absorption wavelength of the sample (i.e. when α increases).

Alternatively, when the laser wavelength is fixed on resonance with an absorption wavelength of the sample, variations in α caused by changes in the analyte concentration are reflected in the ringdown time. Note that if the ringdown time is measured using an empty cavity (i.e. $\alpha = 0$) the reflectivity of the mirrors can be determined. Once the mirror reflectivity has been measured and a sample introduced, CRDS provides an absolute measure of the absorbance αl_s . This self-calibrating feature differentiates CRDS from other relative measurements such as laser-induced fluorescence (LIF) or resonantly enhanced multiphoton ionization (REMPI) and partly explains the rapid growth of the technique.²⁻⁷⁸ Note that the ringdown results are often presented graphically in inverse ringdown time units. As is evident from equation 1, the inverse ringdown time is proportional to the absorbance αl_s and hence the analyte concentration.

The high sensitivity of the CRDS technique stems significantly from the large number of passes the light pulse makes through the sample in the cavity. For mirrors of 99.99% reflectivity

in a 1-meter long cavity, the ringdown time is approximately 33.4 μs for an empty cavity. This is equivalent to a 10-kilometer path length traveled during the first time constant! A sample absorbance of 1×10^{-6} will decrease the ringdown time to almost 33 μs , a change of approximately 1%. Such changes in ringdown time are readily measurable in most CRDS applications. For comparison, traditional single-pass absorption spectroscopy typically detects absorbances on the order of 1×10^{-3} . Absorbance detection sensitivity in the case of CRDS; on the order of 1×10^{-8} has been demonstrated.^(6, 11, 37) Highly reflective mirrors ($R > 99.99\%$) are available for the visible and near-infrared (NIR) regions of the spectrum, with the available reflectivities dropping in the infrared (IR) and ultraviolet (UV). For the UV, mirrors of greater than 99.9% reflectivity are available down into the 200 nm range. A 1% change in ringdown time for 99.9% mirrors will still allow absorbance detection as low as 1×10^{-5} . CRDS has been successfully employed using ringdown times ranging from tenths to hundreds of microseconds, indicating the usefulness of the technique over a wide range of available mirror reflectivities.

As the results below will indicate, the simple model outlined above also neglects some other potentially important considerations. First, and foremost, to perform elemental analysis an atomization source must be used. Secondly, to achieve true single exponential behavior, the conditions for Beer's law behavior must be fulfilled.⁽⁴¹⁾ These conditions include requiring that the frequency linewidth of the laser source be narrower than the absorption linewidth. If the laser source linewidth is broader than the absorption, then only that part of the laser frequency resonant with the absorption will be attenuated. The non-resonant frequencies of the laser pulse will continue to propagate in the cavity without being absorbed, leading to distinctly non-exponential behavior.

Instrumentation:

A schematic diagram of a typical experimental system used in this work is given in Figure 3. The system consists of four primary parts, the atomization source (labeled as "Sample"), cavity, light source, and detection electronics.

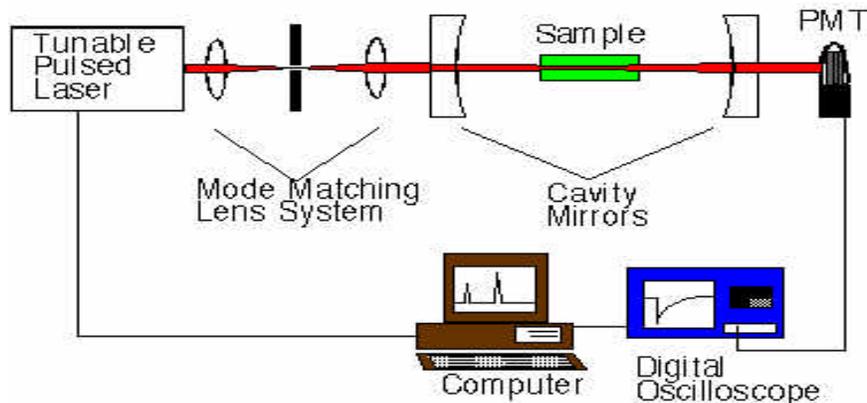


Figure 3: A schematic diagram of the typical experimental arrangement for performing cavity ringdown spectroscopy. (“Inductively Coupled Plasma Cavity Ringdown Spectrometry” by G.P. Miller and C.B. Winstead. *J. Anal. Atom. Spectrosc.* 12, 907-912 (1997).

1) Atomization Sources (Sample in figure 3 above):

- a) ICP Systems: For the majority of studies investigating ICP-cavity ringdown spectroscopy, we used a 1.6 kW, 27.12 MHz plasma system. Although, a 3.5 kW, 27.12 MHz air-ICP was used to demonstrate the techniques robustness.
- b) 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. A typical experiment went as follows: injected sample solutions were dried for 30 seconds at 120° C; ashed for 15 seconds at 300° C and atomized (wall atomization) for 3 seconds at 1400 C. The clean-up step was set at 2000° C. The argon flow was 1.5 L/min 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 dia.) were drilled in the disks to pass the laser beam.
- c) Mercury Vapor Generation: In batch mode, a 1.08 L plastic container was used as the reducing vessel. Teflon tubes of 0.75 mm diameter transported the mercury vapor from the bottle to the quartz cell. In continuous mode, a Gilson miniplus peristaltic pump was used to inject the mercury and reagent solution. A 3-meter long Teflon tube (0.75 mm OD) was used for mercury reduction and extraction. The spray chamber of a pneumatic nebulizer was used for gas/liquid separation. In continuous mode, the NaBH₄ and mercury standard solutions were pumped and merged at a “Y”

union. Argon carrier gas at a flow rate of 0.4 L/min flowed through a gas-liquid separator to carry mercury into the quartz absorption cell.

- d) **Standard AAS system:** A quartz cell of the same size as that used for CRD, but with quartz windows to seal the ends, was used as an absorption cell. A 0.5 meter echelle spectrometer with a CCD detector (Spectrum One CCD-200, Jobin Yvon-Spex) was used to detect light from a Hg lamp placed on the opposite side of the cell.

2) Laser systems: A laboratory system consisting of a Nd:YAG laser pumped tunable dye laser was used. The dye laser is capable of achieving linewidths as low as 0.04 cm^{-1} , which when frequency doubled broadens to a linewidth of approximately 0.06 cm^{-1} . The laser pulse duration is approximately 8 ns and the laser repetition rate is 20 Hz.

3) Cavity Optics: For these experiments a 56 cm long cavity was constructed from specially coated mirrors. The mirrors were plano-concave with either a 1 or 6 meter radius of curvature and were coated for maximum reflectivity at the appropriate wavelength. The laser beam was spatially filtered and mode matched into the cavity using a small homemade telescope. A narrowband interference filter was used to reject background radiation prior to the detection electronics.

4) Data acquisition: The signal from a photomultiplier tube, placed behind the second cavity mirror, was digitized by a 200 MHz digital oscilloscope and transferred by a GPIB interface to a personal computer. The decay time constant is calculated from the ringdown signal and displayed on-line. The full ringdown waveform can be saved for later analysis if desired. The time constants were processed off-line to obtain peak height and integrated absorbance values. For graphite furnace experiments, the data acquisition speed was enhanced using a fast analog-to-digital converter (100 MHz sample rate with 12-bit resolution) in place of the digital oscilloscope.

Results and Achievements

Inductively Coupled Plasma-CRDS (ICP-CRDS)

Highlights:

1. First analytical measurements in an ICP using CRDS.

2. Optimized detection sensitivity demonstrated to approach theoretical limits for both elements used as primary study targets (Hg and Pb).
3. First ICP diagnostic measurements using CRDS (Plasma temperatures, heavy particle density, and electron density distributions measured for a modified ICP torch)
4. ICP-CRDS ringdown time stability improved from typically a few percent variation in baseline ringdown times to 1% or better.
5. Results published in refereed journals and presented at national and international conferences. Additional publications in press and in preparation.

Introduction

Atmospheric pressure argon inductively coupled plasmas (ICP) remain a popular tool for analytical atomic spectrometry. Therefore it is perhaps fitting that the ICP should prove to have been the first atomization source to be coupled with CRDS.⁽²²⁾ Preliminary experiments initially performed using an old dye laser system to measure the Pb (283.3 nm) absorption line confirmed the viability of ICP-CRDS for trace analysis. Figure 3 is a measure of the relative absorbance that occurs as the dye laser is tuned across the 283.3 nm Pb line, for a blank and a 100 ppm Pb nebulized solution. Figure 3 provides an example of the relative quality of data obtainable at the start of this study.

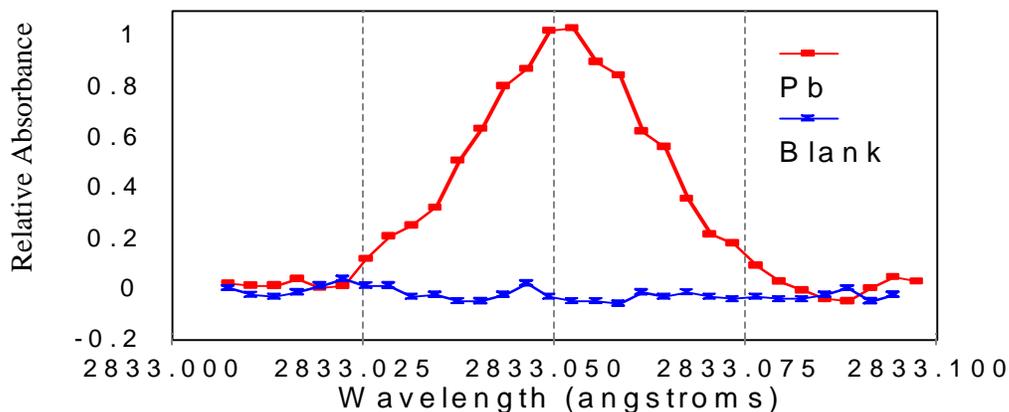


Figure 3: Early low-resolution laser scan of the lead 283 nm transition

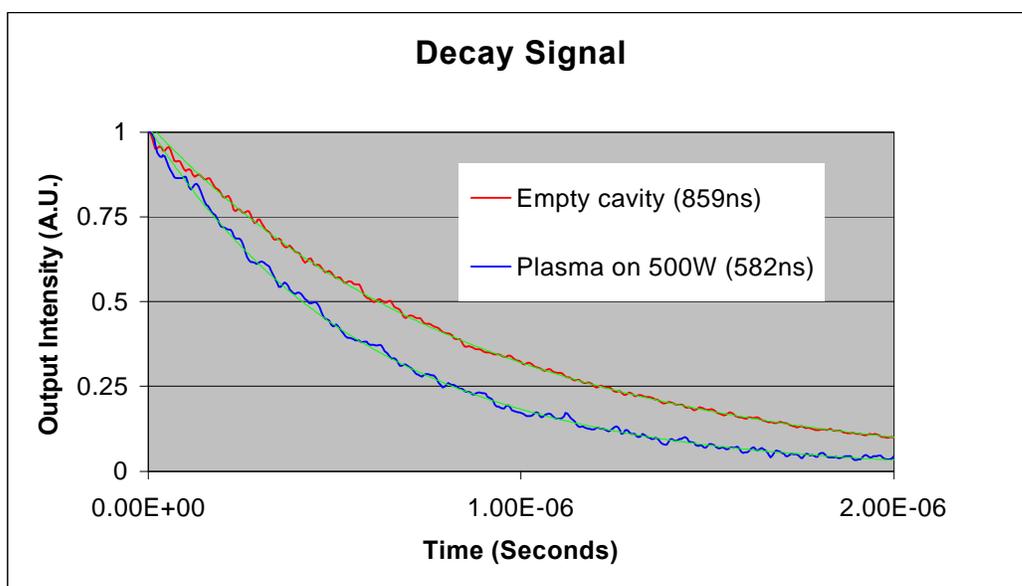
In the discussion of plasma diagnostics below, figure 7 presents updated scans of the Pb 283.3 nm line obtained under optimized conditions. To obtain the data presented in Figure 7, only 100 ppb of lead was required to generate a much better signal to noise ratio spectral scan, indicating the extreme improvement in performance achieved over the course of this study. This work also established the ground rules for performing analytical atomic cavity ringdown spectroscopy. For example, as the laser linewidth of the system used to acquire the spectrum in Figure 3 was approximately twice that of the absorption feature, the apparent absorption linewidth in Figure 3 is a combination of both the actual absorption linewidth and the laser linewidth. As mentioned above, an important consideration in being able to do quantitative ICP-CRDS is the use of a laser with a linewidth narrower than the absorption profile to be probed.⁴¹ This problem was eliminated with the use of the laser described in the instrumentation section of this report.

Loss Mechanisms in ICP-CRDS:

The necessary first concern for developing an ICP-CRDS system was interfacing the ICP and optical cavity systems. This was closely followed by the need to establish the effect on the cavity stability and ringdown time of introducing a “hot” atomization source into the cavity. Early in this study it became apparent that the simple model described earlier (Eq. 1) was incomplete. It assumes that only one factor, sample absorbance, strongly influences the sensitivity achievable in a ringdown system. This is an over-simplification. Other loss mechanisms can become significant as the operating environment changes. For example, Rayleigh scattering is much more significant for UV-CRDS than for visible or IR experiments. If we include Rayleigh scattering from air in the cavity into the ringdown time, equation (1) must be modified to

$$\mathbf{t} = \frac{d}{c[(1-R) + \mathbf{a}l_s + \mathbf{b}l]} \quad 2)$$

where β is the Rayleigh scattering attenuation coefficient for air.³⁵ β can be experimentally determined by evacuating the inside of the cavity or by successive measurements using different cavity lengths, or can be easily estimated using known scattering coefficients for air. This effect can be simply taken into account by defining an effective mirror reflectivity that is less than the true mirror performance. Early experiments indicated that the plasma itself caused unexpected levels of optical loss from the cavity, lowering system sensitivity. The introduction of the plasma into the cavity reduced the magnitude of the cavity ringdown time (Fig. 4a), even without an analyte present. A study of possible loss mechanisms and their significance in relation to the analytical properties of ICP-CRDS was performed. In an attempt to understand this behavior, we considered a number of potential mechanisms for this decrease including: Thompson scattering from electrons and photoionization of metastable argon atoms. In each of these processes, calculations indicated that the cross-section for the event is too small (by at least



an order of magnitude) to lead to the observed loss. In addition, it was found that the effect is wavelength-independent. However, as can be seen in Figure 4b, it is very dependent on input power.

Figure 4A: Ringdown transient recorded before and after ignition of the ICP at the cavity center.

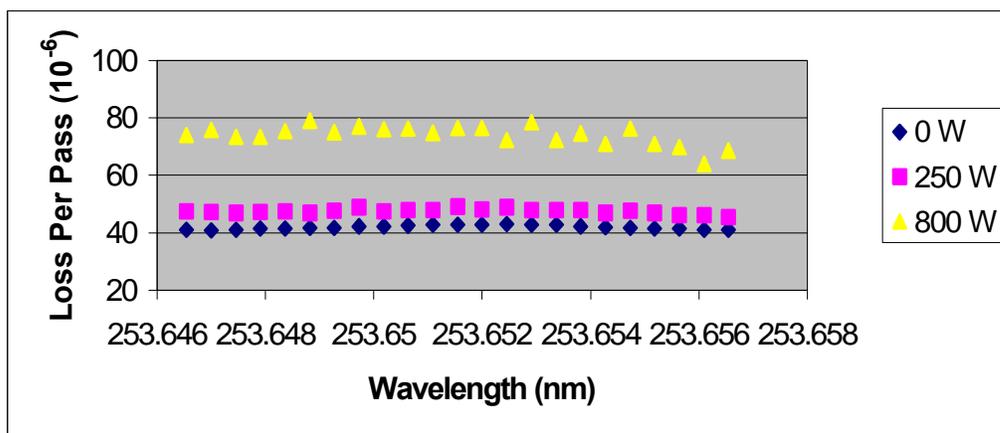


Figure 4B: The effect of ICP input power on sensitivity.

The conclusion was reached that the observed losses are due to beam steering of the laser pulse by the plasma. The cumulative effect becomes significant as an individual laser pulse makes hundreds to thousands of cavity passes. The overall effect is to reduce the effective reflectivity of the mirrors, thereby impacting the ultimate sensitivity of the technique. Under optimized conditions using a modified torch design, we were able to reduce the background loss caused by plasma insertion to negligible levels. Carrying out this optimization process was time consuming and accounted for a significant fraction of the effort devoted to ICP-CRDS. However, with the understanding gained here, ICP-CRDS performance can now be rapidly determined for any element with an optical transition accessible to our laser system.

Detection Limits:

To evaluate ICP-CRDS it was necessary to optimize the ICP as an atomization source. The optimization process, including plasma diagnostics, is outlined more in the “Plasma Diagnostics” section below. In the original proposal, a list of estimated ICP-CRDS detection limits was given to provide an estimate of the order of magnitude of performance that could realistically be expected. As we show below, using mercury as our example, the results obtained were in excellent agreement with our predictions. For those earlier estimates, we had assumed mirror reflectivity of 99.9%, sample path length of 5 mm, and ringdown stability of 1%, and a

ground population of 100%. Using these parameters an achievable detection limit for Hg was estimated to be 0.7 ppb ($0.28 \mu\text{g}/\text{m}^3$). In reality, the best we have achieved for mercury at this stage is a modified ICP torch with a sample pathlength of 3 mm, mirror reflectivity (@253.6 nm) of 99.7% and a ringdown stability of 1%. If these actual parameters are used, a Hg detection limit of approximately 6 ppb ($2.2 \mu\text{g}/\text{m}^3$) is predicted. (It should be noted that we have obtained mirrors of greater than 99.9% reflectivity at other UV wavelengths and may now be obtainable at 253 nm). The actual three standard deviation detection limit for Hg was determined to be 20 ppb, very near the theoretical prediction. Considering that the accuracy of the absorption cross-section estimate used for these calculations, based on broadening of a Lorentzian lineshape, is limited and that we assume an unrealistically high ground state population (100%) in these estimates, we believe we have effectively reached the theoretical limit achievable with the current system.

Likewise, a full system optimization was carried out using lead for comparison of measured detection limits with expected theoretical values. Lead was also used as an analyte for carrying out a significant number of novel plasma diagnostics measurements. The optimization process, including plasma diagnostic measurements, is outlined more fully below. Under optimized conditions with an effective mirror reflectivity of 99.75% and a baseline stability of 0.3%, a theoretical detection limit of 0.2 ppb is predicted. Under these same conditions, achieved with a mirror reflectivity of 99.78% which effectively dropped to 99.75% when the plasma was turned on, an experimental detection limit of 0.3 ppb was achieved. This detection limit is almost equivalent to standard ICP-mass spectrometry limits, slightly better than the best ICP-laser induced fluorescence results, and much better than standard ICP-atomic emission spectrometry.

Plasma Diagnostics:

Although the ICP is a mature technology and is widely used as both an excitation (ICP-AES) and ion source (ICP-MS), very little research has been done to use it as an atomization source.⁸⁰ A series of experiments were undertaken to study the effects that variations in sample concentration, flowrate, observation height, and input power have on the ground state populations, and thus, the sensitivity of the technique. Figure 5 is the absorption spectra of a scan from 282.5 to 286 nms of an ICP operating on argon only, the introduction of a blank solution, and one containing 100 ppb Lead. The additional spectral lines observable in the data

are due to absorption by OH radicals in the plasma. The intensity distribution of lines in the figure can be used as a measure of the plasma gas temperature. The introduction of aerosol into the plasma did not significantly change the performance. However, as can be seen from Fig. 6, input power to the plasma has a significant impact. This is explained by noting that as the input power increases so does the plasma temperature thereby exciting and ionizing the sample and depleting the ground state population. Analysis of such data allowed us to conclude that the optimum conditions for detection of lead in the ICP were a detection height of 2mm ALC at an ICP power of 200 W.

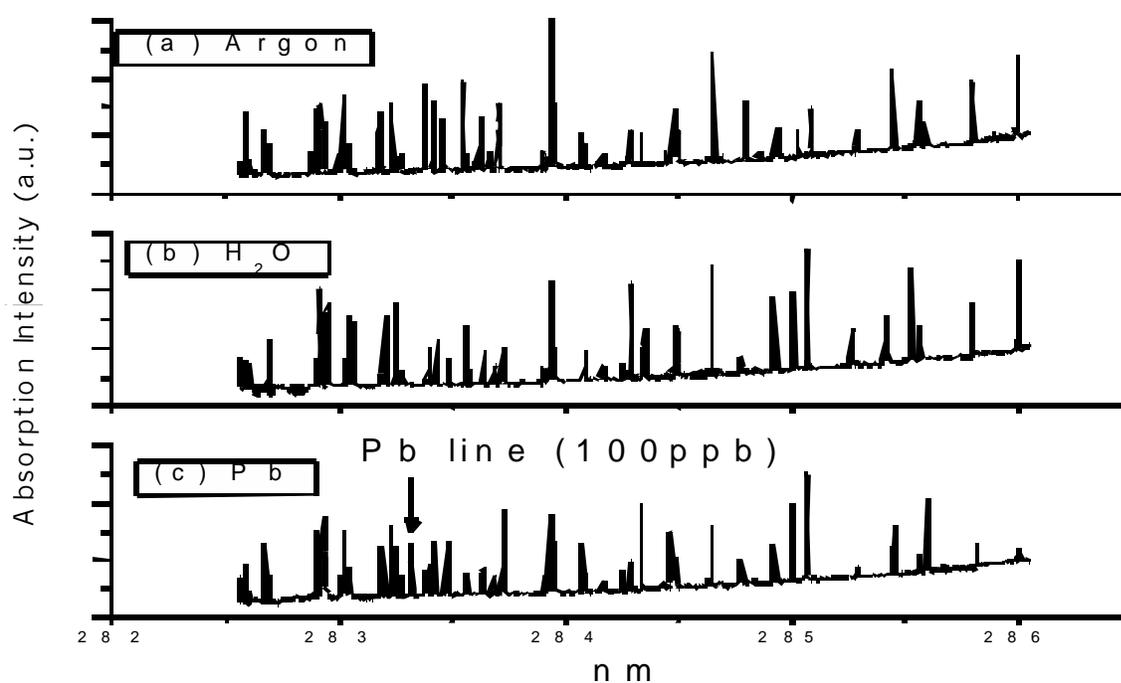


Figure 5: Absorption spectrum of an ICP obtained by CRDS a) argon only, b) argon + nebulized H_2O , c) argon + nebulized 100 ppb Pb solution.

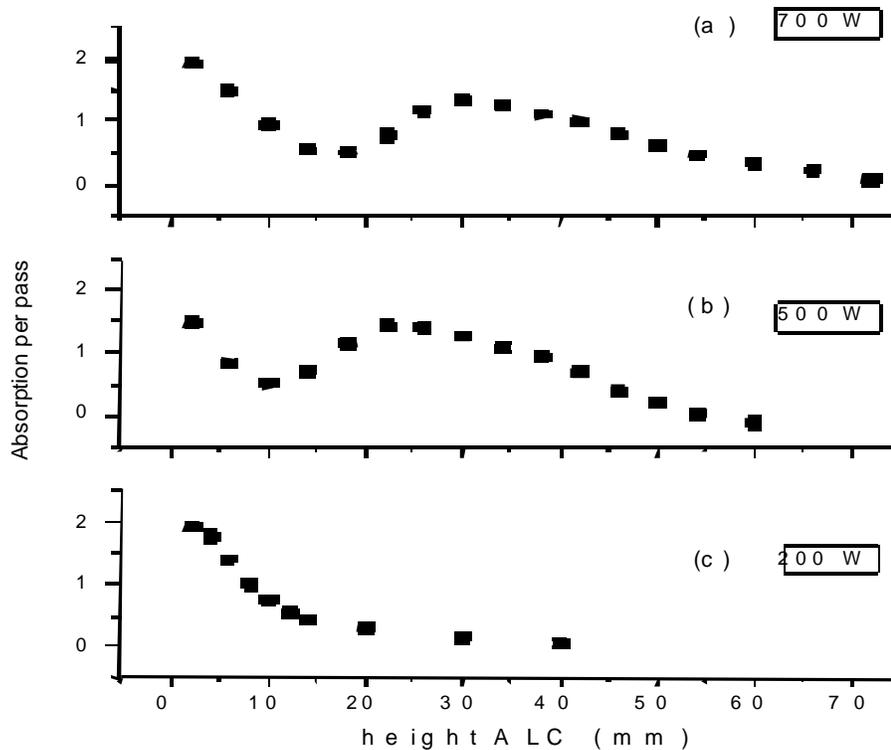


Figure 6: Variation in atomic absorption of the ground-state Lead (283 nm) with observation height in the plasma for various input powers (ALC: Above Load Coil).

CRDS is not limited to trace analysis. It also has application as a diagnostic tool. For example, to obtain the vertical and the lateral line-of-sight profiles for the gas kinetic temperature and electron density, line shape profiles versus height and lateral position were recorded at a 200 W operating power. Figure 7 shows four typical line shapes recorded through the diameter of plasma at four observation heights (2, 10, 18, and 30 mm ALC). The measured absorbance was corrected using the background absorption from a blank (no lead) solution and normalized to a 100 ng/ml concentration. The recorded line width includes both instrument and physical broadening. The former comes from the laser line width (< 0.65 pm) and the latter from Doppler and collisional broadening mechanisms, which yield Gaussian and Lorentzian line shapes, respectively. Together the various broadening mechanisms result in a Voigt line shape. Various plasma properties can be extracted through analysis of the absorption lineshapes. For example, using the Doppler component of the line shape results, a vertical temperature profile was obtained (Fig. 8). The gas kinetic temperature is approximately 2700 K when the observation height is less than 22 mm ALC, and decreases slightly to ca. 1870 K in the tail of

plasma. To our knowledge, these are the first gas kinetic temperatures obtained under such experimental conditions. A full discussion of this work is presently in press and scheduled to appear in March 2002.

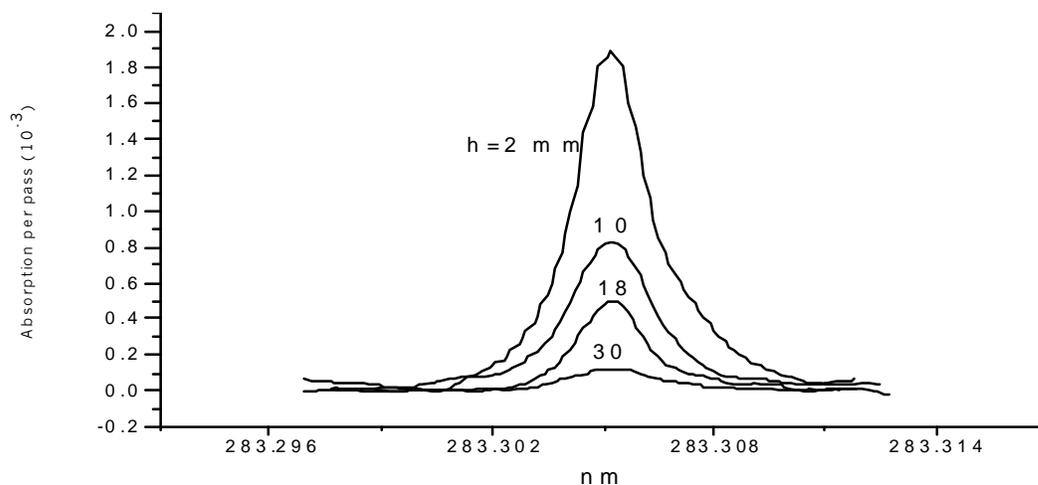


Figure 7 Variation of Pb linewidth with height above the work coil.

To explore the robustness of the technique, a high resolution scan of the mercury 253 nm spectral line produced in a 2800 W atmospheric pressure air inductively coupled plasma was obtained (see Fig. 9). Although linewidth broadening in the plasma and the laser linewidth together prevent complete resolution of the absorption lines, the experimental isotopic ratios obtained by CRDS and theoretical ratios are in excellent agreement (see Table 1). This ability of CRDS to obtain such a result under the extremely harsh conditions necessary (high power, high gas flows, complex molecular plasma) to maintain a steady-state atmospheric pressure air plasma speaks highly as to the robustness of the technique and its ability to perform under extreme conditions. A manuscript compiling all analytical results for Hg using CRDS (ICP, graphite furnace, and cold vapor) is in preparation for submission for publication.

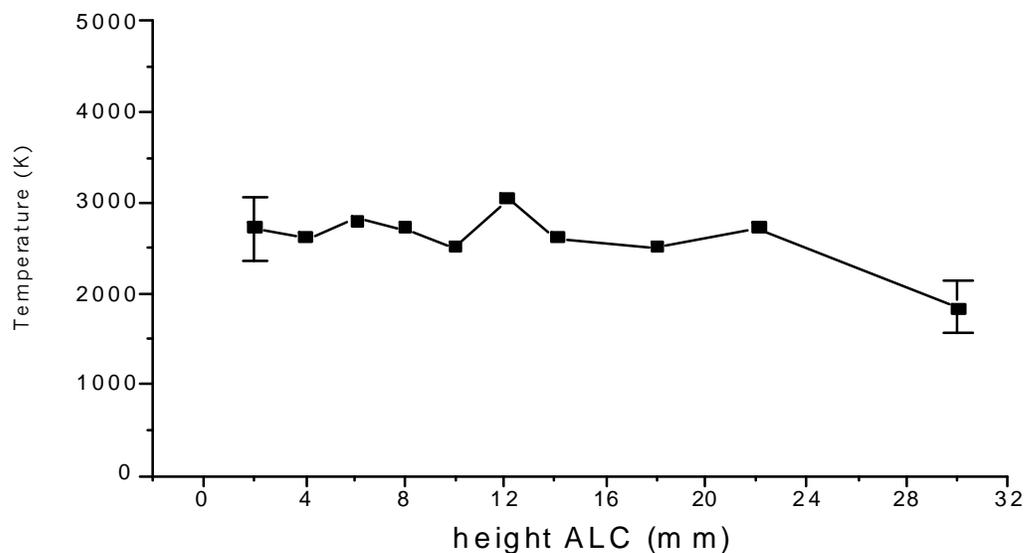


Figure 8: Gas temperature versus observation height in a 200W ICP plasma determined by CRDS.

ICP Results Summary

Once the system was optimized, the detection limit (3σ) of Hg, for example, was determined to be 20 ppb and 0.3 ppb for Pb. The sensitivity of the technique can be improved most easily with improved reflectivity mirrors. A change from 99.7% to 99.9% reflective mirrors will produce an order of magnitude reduction in detection limit. Another method for improving detection limits is increasing the sample pathlength by changing from lateral to axial viewing ICP. With this change in operating conditions, the sample length would be increased from 3 mm to an excess of 60 mm. The combination of these two factors could improve sensitivity by up to 200 times, all other factors being equal.

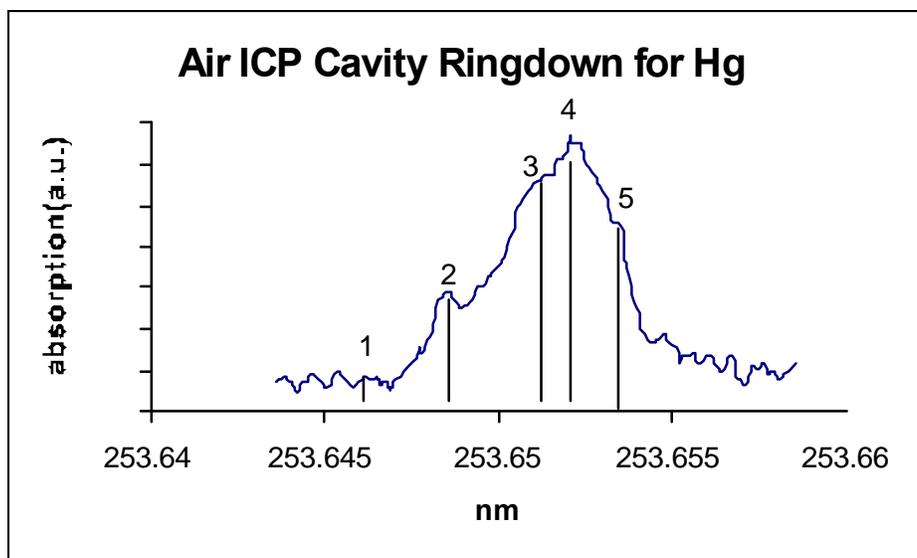


Figure 9: Cavity Ringdown high resolution spectrum of mercury in a 2800 W Air-ICP. 3-point smoothing was applied to the data before plotting. The vertical lines indicate the positions of the various mercury isotopic signatures.

Line #	Wavelength (nm)	Exp. ratio (%)	Theo. ratio (%)	Isotopic signatures
1	253.6466			$^{201}\text{c} + ^{199}\text{a}$
2	253.6498	13.9	16.6	$^{198} + ^{201}\text{b}$
3	253.6517	28.5	26.7	200
4	253.6528	34.9	34.5	202
5	253.6535	22.7	22.1	$^{204} + ^{201}\text{a}$

Table 1: Comparison of measured isotopic abundance (in Air-ICP) with the theoretical values

Electrothermal-CRDS

Highlights

1. First cavity ringdown measurement in a graphite furnace.
2. Non-optimized GF-CRDS detection limits for Hg and Pb better than commercial GF-AAS.
3. Established viability of the technique. Significant potential, but requires optimization.
4. Results published in refereed journals and presented at national and international Conferences. Analytical Communication (36, 277, 1999) was highlighted in Analytical Chemistry 71, 660A 1999.

Introduction

For this section of the study we replaced the ICP with a graphite furnace. Due to the transient nature of the atomic absorption signal in a graphite furnace, the data acquisition system that was used for the ICP-CRDS was unsuitable. Therefore, a new approach was developed for these experiments. As the typical transient signal due to atomization lasts for less than one second in a graphite furnace, it was necessary to design a fast, high-resolution data acquisition system so that integrated absorbance values could be obtained for each atomization cycle. To achieve this the signal from a photomultiplier tube, placed behind the second cavity mirror, was digitized by a 12 bit, 100 MHz sample rate analog-to-digital converter. The timing for data acquisition was determined by the software controlling the graphite furnace. An output trigger from the furnace power supply can be delayed in 0.1 second 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.

Results and Discussions

The introduction of the graphite furnace requires 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 and Mercury were selected for the initial study partly because of our previous results obtained by ICP-CRDS²² 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. Figure 9 depicts the response of $1/\tau$ (where τ 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 equation 1, $1/\tau$ is proportional to the absorbance α_{λ} . The responses for both blank and lead aqueous standards are presented. The Pb solution data for Figure 9 was obtained by manually injecting 7.5 μl of 2 ng/ml lead standard solution.

For these experiments, a linear calibration graph for absorbance vs. injected lead mass was obtained in the range of 8 to 20 pg. 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). This result is very promising, particularly considering that peak height was measured and no chemical matrix modifiers were employed. However, it is still several orders below the techniques theoretical potential.

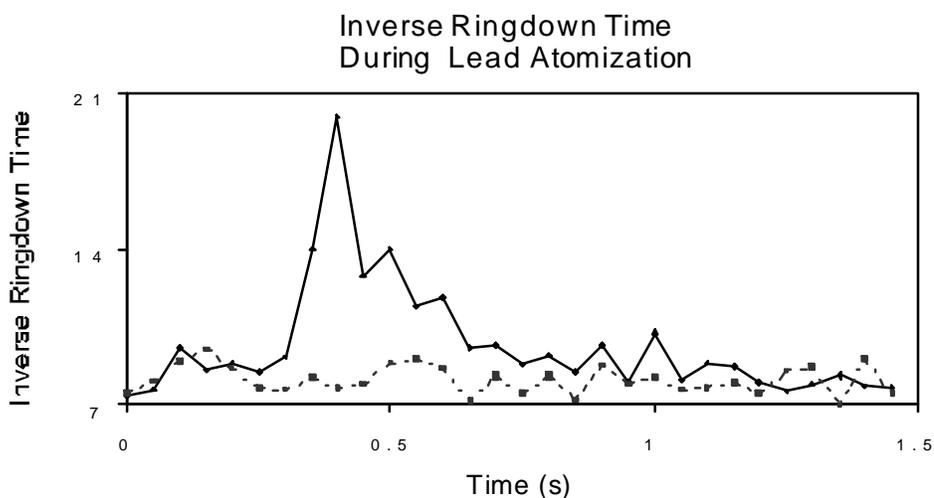


Figure 9: Analytical shape of lead atomization peak obtained from cavity ringdown time measurements.

Summary

These preliminary studies demonstrated 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, in an as yet 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 systems. For modern commercial systems, a Pb characteristic mass (the mass for which the absorbance is 4.4×10^{-3}) of approximately 5 pg is typical. For 99.9% reflective mirrors and a 1% stability in baseline ringdown times, the CRDS 3σ absorbance detection limit is 3.6×10^{-5} . Thus, by scaling the mass linearly with the absorbance, the CRDS detection limit is expected to approach 40 fg. With improvements in mirror coating technology, the absorbance limit could be one to two orders of magnitude lower; that is, 0.4 – 4 fg.

For our current system, our effective mirror reflectivity at the lead absorption wavelength is 99.86% and our baseline ringdown time variation is typically 2-3%. Continuing improvement of the ETA-CRDS technique to reach the predicted limits 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 graphite furnace is complete in well under one second while the laser repetition rate was only 20 Hz. This implies that the use of higher repetition rate lasers such as an excimer, Ti-sapphire (100-1000 Hz) or Cu vapor (2-32 kHz) lasers are needed to fully exploit the potential of the technique. Perhaps most importantly, our results for Hg in the graphite furnace now indicate a detection limit an order of magnitude improved over commercial ETA-AAS, even without the needed optimization.

Cold Vapor Mercury Cavity Ringdown Spectrometry:

Highlights:

Cold Vapor Cavity Ringdown Spectroscopy has been successfully applied to the detection of elemental Mercury. Using an absorption cell 0.18 meters in length, detection limits of 0.027 and 0.12 ng were obtained using peak area and peak height measurements respectively. For the peak area measurement, this corresponds to a gas phase concentration of less than 25 ng/m³. For comparison, using a similar absorption cell, standard AAS yielded a Hg detection limit (peak height) of 9 ng, (gas phase ~ 830 ng/m³).

Introduction

As indicated above, cavity ring down spectrometry (CRDS) has the potential to be a very sensitive spectroscopic method for trace analysis. However, what quickly became apparent was the increase in optical losses and baseline noise associated with the placement of a “hot” atomization source within the cavity.³⁵ One toxic metal of environmental importance that can be produced into an atomic form at room temperature is mercury.⁸⁷ In fact, cold vapor atomization is the standard technique used to measure trace levels of mercury. In standard atomic absorption/fluorescence mercury spectrometry, a batch reduction/trap concentration/release-by-heating procedure is often followed to convert molecular forms of mercury to the elemental state. Trapped mercury atoms are released, swept into, and through the cell in several seconds, and a transient mercury signal profile is recorded. However, the sensitivity offered by CRDS spectrometry has the potential to eliminate the need for sample concentration and allow sampling on a continuous basis under the prevailing atmosphere. No sample pre-concentration or flushing the cell was employed in the experiments reported here. This data are the first experimental results of chemical reduction/cavity ring-down spectrometric determination of mercury. Both batch and continuous mercury atom generating procedures were tested. The Hg detection limit obtained with these procedures is compared to both the theoretically predicted value and that obtained by standard atomic absorption.

Experimental Procedures

For this initial feasibility study, we follow similar lines to those reported in our earlier work on ETA-CRDS.³⁵ In this case, the graphite furnace has been replaced with a 0.18 m long absorption cell (1 cm ID). To eliminate optical losses, it was necessary to remove the quartz windows at the ends of the cell for the CRDS experiments. No attempt was made to modify the cell design so the results obtained are by no means optimum. Note: The windows were left in place for the less-sensitive AAS measurements because the increased Hg losses from the open windows reduced the signal below the measurable threshold.

Results and Discussion

As indicated earlier in the executive summary, the enhanced sensitivity of the ringdown technique became readily apparent during the initial setup of the system. An initial background

wavelength scan of the empty cavity over the spectral region centered on the Hg 253.7 nm spectral line indicated not only the presence of absorption due to a weak oxygen band but also the presence of Hg (Figure 1). As already discussed, the Hg signal was traced to an unsealed waste container in the laboratory. Once this container was removed, the Hg absorption disappeared. To quantify the technique, two approaches were used.

1) Batch mode

As described above, in this mode mercury reduction was performed in a closed container. One milliliter (ml) of a mercury standard solution and 0.2 ml of SnCl₂ solution were injected into the reaction bottle. The bottle was shaken to ensure complete mixing. The generated gas phase mercury atoms are then carried into the quartz absorption cell by argon gas. Figure 10 shows the recorded signal profile obtained for a 2 ng injection of Hg using CRDS. Both signal peak height and peak area (integration over approximately 23 data points) are linear with the injected mercury mass up to at least 3 ng, the limit of our measurements thus far. The detection limit for Hg was determined to be 0.12 ng using peak height measurement and 0.027 ng for peak area measurement. Assuming that all of the mercury is released from solution, this corresponds to sampling from a gas phase Hg concentration of 25 ng/m³ in the reaction vessel. Because of dilution from the Ar carrier gas and losses from the open windows, the actual gas phase concentration measured in the cell is somewhat reduced thereby implying that this detection limit can be improved upon. With open windows, the performance of the standard AAS system was sufficiently impacted, that direct comparisons with our initial CRDS experiments were not feasible. For comparison and following an identical procedure, but with windows installed on the absorption cell, we found that standard AAS (peak height) yielded Hg detection limit of 9 ng.

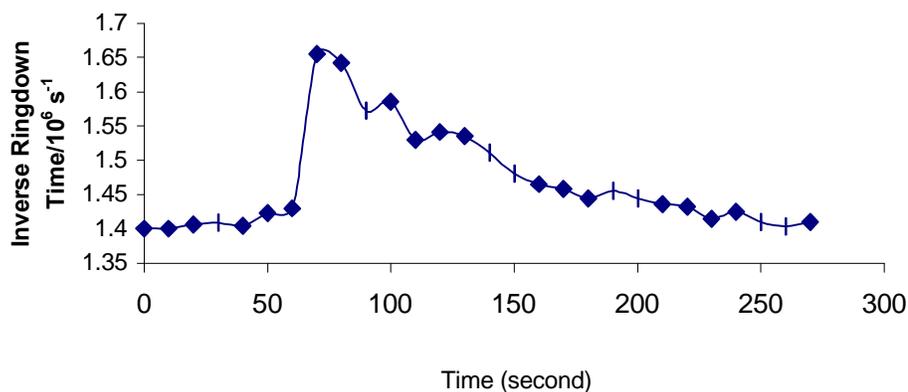


Figure 10: CRDS signal profile obtained for a 2 ng injection of Hg

2) Continuous reduction mode

In this mode mercury standard solutions and reduction reagent (0.5 % NaBH_4) solution are merged in a “Y” union prior to traveling through a long Teflon tube. When the reagent solution was mixed with acidic mercury standard solution, it decomposed and H_2 gas was formed. The H_2 gas in the tube formed bubble segments and mercury atoms were “extracted” into these H_2 gas segments. When the segments are pushed out of the Teflon tube the gas phase is separated from the solution and mercury is carried into the quartz cell with H_2 by the argon carrier gas. Figure 11 depicts signal profiles obtained using continuous mode mercury vapor generation. The background noise was found to be significantly higher than in the batch process. This was most likely due to production of H_2 gas bubbles following the decomposition of NaBH_4 . This increase in noise resulted in a detection limit of 0.12 ppb.

Summary

Using a 0.18 m absorption cell, with open ends, yielded a detection limit of 0.027 ng (25 ng/m³ gas phase in the reaction vessel) using the batch approach. Using an identical batch procedure, but an enclosed absorption cell, standard AAS yielded a Hg detection limit of 9 ng (830 ng/m³ gas phase in reaction vessel).

These preliminary results clearly demonstrate the potential of cavity ringdown spectroscopy for the detection of gas phase elemental Hg. Improved mirror reflectivities from the present 99.7% to 99.9% (@253 nm) would result in an order of magnitude improvement in detection limits. Additional

benefits would also accrue from optimizing the laser linewidth and increasing the laser repetition rate.

This is

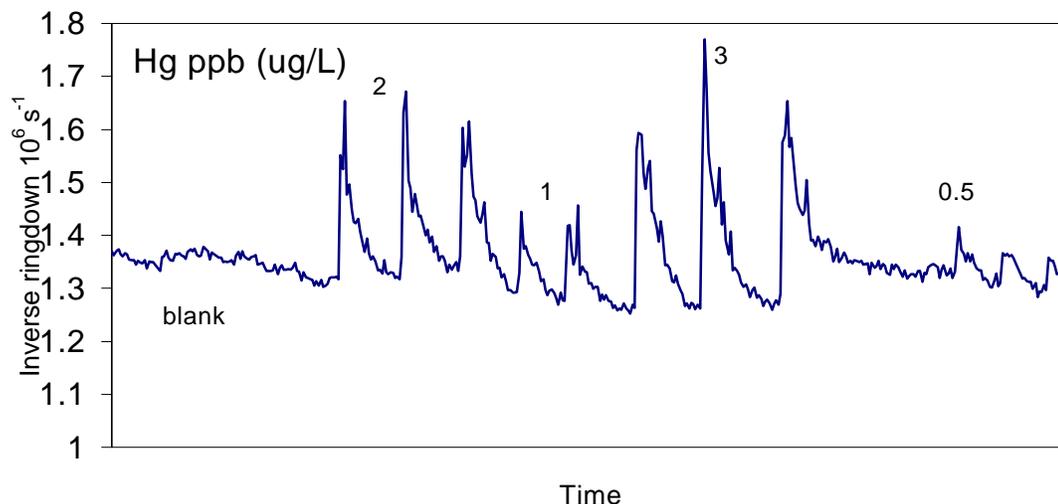


Figure 11: CRDS signal profiles obtained using continuous mode mercury vapor generation.

ignoring the simple option of increasing the absorption cell length. Of prime importance will be the design and construction of a closed absorption cell for Hg CRDS that will prevent Hg loss from the cell while protecting the surface quality of the cavity mirrors. Finally, enhanced CRDS sensitivity is not only valuable for traditional analytical applications, but may prove the solution in difficult situations such as on-line monitoring for mercury in stack emissions. The sensitivity of the technique could lead to a reduction in the complexity currently necessary for sampling from such environments. The small, robust laser systems necessary for use in such applications are currently under development by commercial laser companies.

Conclusion

The results obtained in this study are the first to demonstrate the potential of analytical atomic absorption cavity ringdown spectroscopy as an ultra-trace technique for the measurement of toxic metals. In particular, we have demonstrated

- 1) ICP-Cavity Ringdown Spectroscopy
- 2) Electrothermal Atomization-Cavity Ringdown Spectroscopy

and

3) Cold Vapor Mercury-Cavity Ringdown Spectroscopy

These experiments demonstrated that CRDS could be successfully employed in regions ranging with large temperature gradients (5000° K variations) and rapidly changing temperatures (3000° K < 1 second) as both an analytical and diagnostic technique. Sensitivity was clearly demonstrated with Cold Vapor atomization (using an 18 cm open-ended sample cell) yielding a detection limit for elemental Hg of 25 ng/m³.⁷

As can be seen from the above results, analytical applications of CRDS are just beginning to be explored. This is a new area of analytical science that is very much in its infancy. The widespread use of the technique rests at least in part on the development of laser technology. Diode lasers have been employed for CRDS of molecular species in the near-infrared. These lasers provide a small, compact light source for such measurements. Advances in nonlinear optical methods will allow diode lasers to be used at ultraviolet wavelengths for atomic absorption spectrometry. As the wavelength coverage offered by diode lasers and solid-state lasers in general continues to expand, the possibilities for constructing small, ultra-sensitive CRDS spectrometers for analytical atomic spectrometry continue to increase. For example, blue diode lasers are now commercially available. However, any inherent advantage in using cavity ringdown for atomic spectroscopy over other available techniques will be determined by the sensitivity required, the quality of the mirrors used for cavity construction, stability of the baseline ringdown time measurement, the atomization source, and the fluorescence characteristics of the element under consideration.

Relevance, Impact, and Technology Transfer

Growing concern regarding the health effect of the emission of toxic metals into the environment is driving the need for ultra-trace instruments to both monitor such emissions and to operate as process monitors to reduce or prevent the production of such wastes. The objective of the present research was to evaluate the potential of cavity ringdown spectroscopy as an ultratrace technique for the detection of such toxic metals.

Although it is clear from the results that we have established that cavity ringdown spectroscopy does have the potential to be developed into an ultra-sensitive robust technique, further development is required to fully exploit the technique. Rapid developments in laser technology will both drop the cost and complexity of the required light sources in the near

future. Once that has occurred, opportunities exist for the development of small, relatively inexpensive, highly sensitive instruments for a number of applications. The most probable application of cavity ringdown spectrometry as a toxic metal continuous emission monitor, in terms of both technical requirements and public demand, is as a mercury cavity ringdown spectrometer.

During the course of this project several postdoctoral fellows and a graduate student participated in various aspects of this work. Several of the personnel have taken positions in industry.

Personnel Supported

G. P. Miller, Principal Investigator
C. B. Winstead, Co-Principal Investigator
F. J. Mazzotti, Graduate Student
J. Mierzwa, Postdoctoral Research Fellow
Wang Chuji, Postdoctoral Research Fellow
Shiquan Tao, Postdoctoral Research Fellow

Publications

G. P. Miller and C. B. Winstead. "Inductively Coupled Plasma Cavity Ringdown Spectrometry" *J. Anal. Atom. Spectrosc.* 12, 907-912 (1997).

C. B. Winstead, F. J. Mazzotti, J. Mierzwa, and G. P. Miller. "Preliminary results for electrothermal atomization-cavity ringdown spectroscopy (ETA-CRDS)" *Anal. Commun.* 36, 277 (1999).

S. Tao, F. J. Mazzotti, C. B. Winstead, and G. P. Miller. "Determination of elemental mercury by cavity ringdown spectroscopy" *Analyst* 125, 1021 (2000).

G. P. Miller and C. B. Winstead. "Cavity Ringdown Laser Absorption Spectroscopy" pp10734-10750 *Encyclopedia of Analytical Chemistry* (Ed. R. A. Meyers) John Wiley & Sons Ltd. (2000).

D. R. Wagner, G. P. Miller and C. B. Winstead, "Infrared Cavity Ringdown Spectroscopy", in *Handbook of Vibrational Spectroscopy*, J.M. Chalmers and P.R. Griffiths (Eds), John Wiley & Sons, Ltd, Volume 1, pp. 866 – 880 (2002).

C. Wang, F. J. Mazzotti, G. P. Miller, and C. B. Winstead, "Cavity Ringdown Spectroscopy for Diagnostic and Analytical Measurements in an Inductively Coupled Plasma" *Applied Spectroscopy*. In press, currently scheduled for publication for March 2002.

Fabio J. Mazzotti, Chuji Wang, Christopher B. Winstead, and George P. Miller. "Trace Analysis for Mercury using Cavity Ringdown Spectroscopy." In preparation.

Chuji Wang, Fabio J. Mazzotti, George P. Miller and Christopher B. Winstead. "Isotopic Abundance Determination of Uranium Atom/Ions Using ICP-Cavity Ringdown Spectroscopy" In preparation.

C. Wang, F. J. Mazzotti, G. P. Miller, and C. B. Winstead, "OH Radical Measurements in an Inductively Coupled Plasma using Cavity Ringdown Spectroscopy," In preparation.

Presentations

G. P. Miller, F. J. Mazzotti, C. Wang, J. Mierzwa, and C. B. Winstead. Development of a Mercury Cavity Ringdown Spectrometer. Sensors for Industry Conference. Invited. 5-7 November, Rosemont, IL

“Recent Progress in Analytical Atomic Cavity Ringdown Spectroscopy,” G. P. Miller, C. B. Winstead, F. J. Mazzotti, S. Tao, 27th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies, September 24-28, 2000, Nashville, TN.

“Cavity Ringdown Spectroscopy for Analytical Measurements in an Inductively Coupled Plasma,” F. J. Mazzotti, C. Wang, J. Mierzwa, G. P. Miller, and C. B. Winstead, 67th Annual Southeastern Section Meeting of the American Physical Society, November 2-4, 2000, Mississippi State, MS.

“Application of Graphite Furnace-Cavity Ringdown Spectroscopy to Trace Elemental Analysis,” C. B. Winstead, F. J. Mazzotti, J. Mierzwa, G. P. Miller, 26th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies, October 24-29, 1999, Vancouver, Canada.

“Progress in Developing ICP-Cavity Ringdown Spectroscopy for Trace Elemental Analysis of Metals,” G. P. Miller, F. J. Mazzotti, J. Mierzwa, C. B. Winstead, 26th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies, October 24-29, 1999, Vancouver, Canada.

“A Discussion of the Loss Mechanisms That Can Occur in Analytical Cavity Ringdown Spectroscopy,” F. J. Mazzotti, J. Mierzwa, C. B. Winstead, and G. P. Miller, 26th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies, October 24-29, 1999, Vancouver, Canada.

“ICP-Cavity Ringdown Spectroscopy,” G. P. Miller, F. Mazzotti, J. Mierzwa and C. B. Winstead, 51st Gaseous Electronics Conference & 4th International Conference on Reactive Plasmas, October 19-23, 1998, Maui.

“Cavity Ringdown Spectroscopy and Atomic Spectrometry,” C. B. Winstead, F. Mazzotti, J. Mierzwa and G. P. Miller, The 25th Federation of Analytical Chemistry and Spectroscopy Society Conference, October 12-15, 1998, Austin, TX.

“Inductively Coupled Plasma Cavity Ringdown Spectroscopy,” F. Mazzotti, C. B. Winstead, J. Mierzwa, G. P. Miller, 1998 Southeastern Section of the American Physical Society Meeting, November 13-15, 1998, Miami, Florida.

“The Development of Cavity Ringdown Spectroscopy as a Continuous Emission Monitor for Metals,” G. P. Miller and C. B. Winstead, Environmental Management Science Program Workshop, July 27-30, 1998, Chicago, Illinois.

Literature Cited

1. A. O'Keefe and D. A. G. Deacon, "Cavity ring-down optical spectrometer for absorption measurements using pulsed laser sources" *Rev. Sci. Instrum.* 59 (12), 2544-2551 (1988).
2. A. O'Keefe, J. J. Scherer, A. L. Cooksy, R. Sheeks, J. Heath and R. J. Saykally, "Cavity ring down dye laser spectroscopy of jet-cooled metal clusters: Cu_2 Cu_3 ", *Chemical Physics Letters*, 172 (3,4), 214-218 (1990).
3. J. J. Scherer, J. B. Paul, C. P. Collier, and R. J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy and Time-of-Flight Mass Spectroscopy of Jet-cooled Copper Silicides", *J. Chem. Phys.* 102 (13), 5190-5199 (1995).
4. J. B. Paul, C. P. Collier, R. J. Saykally, J. J. Scherer, A. O'Keefe, "Direct Measurement of Water Cluster Concentrations by Infrared Cavity Ring-down Laser Absorption Spectroscopy", *J. Phys. Chem.* 101, 5211-5214 (1997).
5. R. A. Provencal, J. B. Paul, K. Roth, C. Chapo, R. N. Casaes, R. J. Saykally, G. S. Tschumper, H. F. Schaefer III, "Gas Phase Dynamics and Structure: Spectroscopy, Molecular Interactions, Scattering, and Photochemistry - Infrared cavity ringdown spectroscopy of methanol clusters: Single donor hydrogen bonding", *J. Chem. Phys.* 110 (9), 4258 (1999).
6. D. Romanini and K. K. Lehmann, "Ring-down Cavity Absorption Spectroscopy of the Very Weak HCN Overtone Bands with Six, Seven, and Eight Stretching Quanta", *J. Chem. Phys.* 99 (9), 6287-6301 (1993).
7. R. T. Jongma, M. G. H. Boogaarts, G. Meijer, "Double-Resonance Spectroscopy on Triplet States of CO", *Journal of Molecular Spectroscopy*, 165, 303-314, (1994).
8. T. G. Slanger, D. L. Huestis, P. C. Cosby, H. Naus, G. Meijer, " O_2 photoabsorption in the 40 950 - 41 300 cm^{-1} region: New Herzberg bands, new absorption lines, and improved spectroscopic data", *J. Chem. Phys.* 105 (21), 9393-9402 (1996).
9. J. J. Scherer, D. Voelkel, D. J. Rakestraw, J. B. Paul, C. P. Collier, R. J. Saykally, A. O'Keefe, "Infrared cavity ring-down laser absorption spectroscopy (IR-CRLAS)", *Chem. Phys. Lett.* 245, 273-280 (1995).
10. R. Engeln, G. Helden, G. Berden, G. Meijer, "Phase shift cavity ring down absorption spectroscopy", *Chem. Phys. Lett.* 262, 105-109 (1996).
11. D. Romanini and K. K. Lehmann, "Cavity Ringdown Overtone Spectroscopy of HCN, H^{13}CN and HC^{15}N ", *Chem. Phys.* 102 (2), 633-642 (1995).
12. D. Romanini, A. A. Kachanov, F. Stoeckel, "Cavity ring-down spectroscopy: broad band absolute absorption measurements", *Chem. Phys. Lett.* 270, 546-550, (1997).
13. Y. He, M. Hippler, M. Quack, "High-resolution cavity ring-down absorption spectroscopy of nitrous oxide and chloroform using a near-infrared cw diode laser", *Chem. Phys. Lett.* 289, 527-534 (1998).
14. D. Romanini, P. Dupre, R. Jost, "Non-linear effects by continuous wave cavity ringdown spectroscopy in jet-cooled NO_2 ", *Vibrational Spectroscopy* 19, 93-106 (1999).
15. G. Meijer, M. G. H. Boogaarts, R. T. Jongma, D. H. Parker, A. M. Wodtke, "Coherent cavity ring down spectroscopy", *Chem. Phys. Lett.* 217 (1,2), 112-116 (1994).
16. J. J. L. Spaanjaars, J. J. ter Meulen and G. Meijer, "Relative Predissociation Rates of OH ($\text{A}^2\Sigma^+$, $v'=3$) from Combined Cavity Ringdown - Laser Induced Fluorescence Measurements", *J. Chem. Phys.* 107 (7), 2242-2248 (1997).

17. J. Xie, B. A. Paldus, E. H. Wahl, J. Martin, T. G. Owano, C. H. Kruger, J. S. Harris, R. N. Zare, "Near-infrared Cavity Ringdown Spectroscopy of Water Vapor in an Atmospheric Flame", *Chemical Physics Letters*, 284 387-395 (1998).
18. X. Mercier, P. Jamette, J. F. Pauwels, P. Desgroux, "Absolute CH concentration measurements by cavity ring-down spectroscopy in an atmospheric diffusion flame", *Chemical Physics Letters* 305, 334-342, (1999).
19. A. O'Keefe, unpublished research.
20. M. Kotterer, J. Conceicao, J.P. Maier, "Cavity ringdown spectroscopy of molecular ions: $A^2\Pi_u \leftarrow X^2\Sigma_g^+$ (6-0) transition of N_2^+ ", *Chemical Physics Letters* 259, 233-236 (1996).
21. M. Kotterer, J. P. Maier, "Electronic spectrum of C_6H : $^2\Pi-X^2\Pi$ in the gas-phase detected by cavity ringdown", *Chemical Physics Letters* 266, 342-346 (1997).
22. G. P. Miller and C. B. Winstead. "Inductively Coupled Plasma Cavity Ringdown Spectrometry" *J. Anal. Atom. Spectrosc.* 12, 907-912 (1997).
23. A. Campargue, D. Romanini, N. Sadeghi, "Measurement of SiH_2 density in a discharge by intracavity laser absorption spectroscopy and CW cavity ring-down spectroscopy", *J. Phys. D: Appl. Phys.* 31, 1168-1175 (1998).
24. E. Quandt, I. Kraemer, H. F. Dobele, "Measurements of negative-ion densities by cavity ringdown spectroscopy", *Europhys. Lett.*, 45 (1), 32-37 (1998).
25. D. Romanini, L. Biennier, F. Salama, A. Kachanov, L. J. Allamandola, F. Stoeckel, "Jet-discharge cavity ring-down spectroscopy of ionized polycyclic aromatic hydrocarbons: progress in testing the PAH hypothesis for the diffuse interstellar band problem", *Chemical Physics Letters* 303, 165-170, (1999).
26. J. P.Booth, G. Cunge, L. Bienneir, D. Romanini, A. Katchanov, "Absolute Concentrations of Reactive Species in Etching Plasmas by High-Sensitivity UV Absorption Spectroscopy", *International Conference on Phenomena in Ionised Gases XXIV, Warsaw*, (1999).
27. T. Yu and M. C. Lin "Kinetics of Phenyl Reactions Studied by the Cavity Ring-down Method", *J. Am. Chem. Soc.* (115), 4371-4372 (1993).
28. T. Yu and M. C. Lin "Kinetics of the $C_6H_6 + CCl_4$ reaction in the Gas Phase: Comparison with Liquid-Phase Data", *J.Phys. Chem.* (98), 9697-9699 (1994).
29. J. Park, D. Chakraborty, D. M. Bhusari, M. C. Lin, "Kinetics of C_6H_5 Radical Reactions with Toluene and Xylenes by Cavity Ringdown Spectrometry", *J. Phys. Chem.* 103, 4002-4008 (1999).
30. D. B. Atkinson, J. W. Hudgens, "Rate Coefficients for the Propargyl Radical Self-Reaction and Oxygen Addition Reaction Measured Using Ultraviolet Cavity Ring-down Spectroscopy", *J. Phys. Chem.* 103, 4242-4252 (1999).
31. D. J. Benard, B. K. Winker, "Chemical generation of optical gain at 471 nm", *J. Appl. Phys.* 69 (5), 2805-2809 (1991).
32. Y. Huang, G. Jackson, H. S. Kim, S. Guan and A. G. Marshall, "Instrumental Configuration for Direct Measurement of Optical Absorption In Cyclotron Resonance Mass-Selected Trapped ions", *Physica Scripta*, (59), 387-391 (1995).
33. R.T. Jongma, M. G. H. Boogaarts, I. Holleman, and G. Meijer. "Trace gas detection with cavity ring down spectroscopy" *Rev. Sci. Instrum.* 66(4), 2821-2828.
34. P. Zalicki, Y. Ma, R. N. Zare, E. H. Wahl, J. R. Dadamio, T. G. Owano, C. H. Kruger, "Methyl radical measurement by cavity ring-down spectroscopy", *Chemical Physics Letters* 234, 269-274 (1995).

35. C. B. Winstead, F. J. Mazzotti, J. Mierzwa, and G. P. Miller. "Preliminary results for electrothermal atomization-cavity ringdown spectroscopy (ETA-CRDS)" *Anal. Commun.* 36, 277 (1999).
36. J. J. Scherer, J. B. Paul, A. O'Keefe, and R. J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy: History, Development, and Application to Pulsed Molecular Beams", *Chemical Reviews* 97 (1), 25-51 (1997).
37. D. Romanini, A. A. Kachanov, N. Sadeghi, and F. Stoeckel, "CW cavity ringdown spectroscopy" *Chem. Phys. Lett.* 264, 316-322 (1997).
38. J. D. Jackson, *Classical Electrodynamics*, 2nd Edition, John Wiley and Sons, New York, 1975.
39. A. D. Sappey, E. S. Hill, T. Settersten, M. A. Linne, "Fixed-frequency cavity ringdown diagnostic for atmospheric particulate matter", *Optics Letters*, 23 (12), 954-956 (1998).
40. R. L. Vander Wal, T. M. Ticich, "Cavity ringdown and laser-induced incandescence measurements of soot", *Appl. Optics* 38 (9), 1444-1451 (1999).
41. P. Zalicki, R. N. Zare, "Cavity ring-down spectroscopy for quantitative absorption measurements", *J. Chem. Phys.* 102 (7), 2708-2717 (1995).
42. S. M. Newman, I. C. Lane, A. J. Orr-Ewing, D. A. Newnham, and J. Ballard, "Integrated absorption intensity and Einstein coefficients for O_2 $a^1\Delta_g - X^3\Sigma_g^-$ (0,0) transition: A comparison of cavity ringdown and high resolution Fourier transform spectroscopy with a long-path absorption cell. *J. Chem. Phys.* 110(22), 10749-10757 (1999).
43. J. T. Hodges, J. P. Looney, R. D. van Zee, "Laser bandwidth effects in quantitative cavity ring-down spectroscopy", *Appl. Optics*, 35 (21), 4112-4116 (1996).
44. J. Martin, B. A. Paldus, P. Zalicki, E. H. Wahl, T. G. Owano, J. S. Harris Jr., C. H. Kruger, R.N. Zare, "Cavity ring-down spectroscopy with Fourier-transform-limited light pulses", *Chem. Phys. Letters* 258, 63-70 (1996).
45. K. K. Lehmann, D. Romanini, "The superposition principle and cavity ring-down spectroscopy", *J. Chem. Phys.* 105 (23), 10263-10277 (1996).
46. J. T. Hodges, J. P. Looney, R. D. van Zee, "Response of a ring-down cavity to an arbitrary excitation", *J. Chem. Phys.* 105 (23), 10278-10288 (1996).
47. A. E. Siegman, *Lasers*, University Science Books, Mill Valley, CA, (1986).
48. O. Svelto, *Principles of Lasers*, Plenum Press, New York, (1989).
49. D. C. O'Shea, W. R. Callen, and W. T. Rhodes, *Introduction to Lasers and Their Applications*, Addison-Wesley Publishing Company, Reading, MA, (1978).
50. D. Romanini, A. A. Kachanov, F. Stoeckel, "Diode laser cavity ring down spectroscopy", *Chem. Phys. Letters* 270, 538-545 (1997).
51. B. A. Paldus, J.S. Harris, Jr., J. Martin, X. Kie, R. N. Zare, "Laser diode cavity ring-down spectroscopy using acousto-optic modulator stabilization", *J. Appl. Phys.* 82 (7), 3199-3204 (1997).
52. B. A. Paldus, C. C. Harb, T. G. Spence, B. Wilke, J. Xie, J. S. Harris, R. N. Zare, "Cavity-locked ring-down spectroscopy", *J. of Appl. Phys.* 83 (8), 3991-3997 (1998).
53. M. D. Levenson, B. A. Paldus, T. G. Spence, C. C. Harb, J. S. Harris Jr., R. N. Zare, "Optical heterodyne detection in cavity ring-down spectroscopy", *Chem. Phys. Letters* 290, 335-340 (1998).
54. K. J. Schulz, W. R. Simpson, "Frequency-matched cavity ring-down spectroscopy", *Chemical Physics Letters* 297, 523-529 (1998).

55. J. W. Hahn, Y. S. Yoo, J. Y. Lee, J. W. Kim, H. W. Lee, "Cavity ringdown spectroscopy with a continuous-wave laser: calculation of coupling efficiency and a new spectrometer design", *Applied Optics*, 38 (9), 1859-1866 (1999).
56. R. Engeln, E. van den Berg, G. Meijer, L. Lin, G. M. H. Knippels, A. F. G. van der Meer, "Cavity ring down spectroscopy with a free-electron laser", *Chemical Physics Letters* 269, 293-297 (1997).
57. R. Engeln, G. Von Helden, A. J. A. van Roij, G. Meijer, "Cavity ring down spectroscopy on solid C₆₀", *Journal of Chemical Physics*, 110 (5), 2732-2733 (1999).
58. R. Engeln, G. Meijer, "A Fourier transform cavity ring down spectrometer", *Rev. Sci. Instrum.* 67 (8), 2708-2713 (1996).
59. J. J. Scherer, "Ringdown spectral photography", *Chemical Physics Letters* 292, 143-153 (1998).
60. A. O'Keefe, "Integrated cavity output analysis of ultra-weak absorption", *Chem. Phys. Lett.* 293, 331-336 (1998).
61. R. Engeln, G. Berden, R. Peeters, and G. Meijer, "Cavity enhanced absorption and cavity enhanced magnetic rotation spectroscopy", *Rev. Sci. Instrum.* 69(11), 3763-3769 (1998).
62. M. D. Wheeler, S. M. Newman, A. J. Orr-Ewing, and M. N. R. Ashfold. "Cavity ring-down spectroscopy" *J. Chem. Soc., Faraday Trans.*, 94, 337-351 (1998).
63. J. J. Scherer, J. B. Paul, C. P. Collier, A. O'Keefe, D. J. Rakestraw, and R. J. Saykally, "Cavity Ringdown Laser Spectroscopy Absorption Technique", *Spectroscopy* 11 (5), 46-50 (1996).
64. J.B. Paul and R.J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy", *Anal. Chem.* 69, 287A-292A (1997)
65. R. A. Provencal, J. B. Paul, C. N. Chapo and R. J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy", *Spectroscopy* 14 (4), 24-32 (1999).
66. J. Pearson, A. J. Orr-Ewing, M. N. R. Ashfold, and R. N. Dixon, "Spectroscopy and predissociation dynamics of the A ¹A" state of HNO", *J. Chem. Phys.* 106 (14), 5850 (1997).
67. M. D. Wheeler, A. J. Orr-Ewing, M. N. R. Ashfold, and T. Ishiwata, "Predissociation lifetimes of the A²•• = 1 state of the SH Radical Determined by Cavity Ringdown Spectroscopy", *Chemical Physics Letters*, 268, 421-428 (1997).
68. V. A. Lozovsky, I. Derzy, S. Cheskis, "Radical Concentration profiles in a low-pressure methane-air flame measured by intracavity laser absorption and cavity ring-down spectroscopy", *27th Symposium (International) on Combustion/The Combustion Institute*, 445-452, (1998).
69. V. A. Lozovsky, I. Derzy, S. Cheskis, "Nonequilibrium concentrations of the vibrationally excited OH radical in a methane flame measured by cavity ring-down spectroscopy", *Chemical Physical Letters* 284, 407-411 (1998).
70. S. Cheskis, I. Derzy, V. A. Lozovsky, A. Kachanov, D. Romanini, "Cavity ring-down spectroscopy of OH radicals in low pressure flame", *Appl. Phys., B* 66, 377-381 (1998).
71. J. J. Scherer, K. W. Aniolke, N. P. Cernansky and D. J. Rakestraw, "Determination of Methyl Radical Concentrations in a Methane/Air Flame by Infrared Cavity Ringdown Laser Absorption Spectroscopy", *J. Chem. Phys.* 107 (16), 6196-6203 (1997).
72. J. J. Scherer, D. J. Rakestraw, "Cavity Ringdown Laser Absorption Spectroscopy Detection of Formyl (HCO) Radical in a Low Pressure Flame", *Chemical Physics Letters* 265, 169-176 (1997).
73. A. McIlroy, "Direct measurement of ¹CH₂ in flames by cavity ringdown laser absorption spectroscopy", *Chemical Physics Letters* 296, 151-158 (1998).

74. X. Mercier, E. Therssen, J. F. Pauwels, P. Desgroux, "Cavity Ringdown Measurements of OH radical in Atmospheric Premixed and Diffusion Flames. A Comparison with Laser Induced Fluorescence and Direct Laser Absorption", *Chemical Physics Letters*, 299, 75-83 (1999).
75. J. J. Scherer, D. Voelkel, D. J. Rakestraw, "Infrared cavity ringdown laser absorption spectroscopy (IR-CRLAS) in low pressure flames", *Appl. Phys. B* 64, 699-705 (1997).
76. E. Quandt, H. F. Dobeles, W. G. Graham, "Measurements of negative ion densities by absorption spectroscopy", *Applied Physics Letters* 72 (19), 2394-2396 (1998).
77. A. O'Keefe and O. Lee, "Trace Gas Analysis by Pulsed Laser Absorption Spectroscopy" *Am. Lab.* 21, 19 (1989).
78. R. Vasudev, A. Usachev, W. R. Dunsford, "Detection of Toxic Compounds by Cavity Ring-Down Spectroscopy", *Environ. Sci. Technol.* 33, 1936-1939 (1999).
79. P. W. J. M. Boumans, J. J. A. M. Vrakking, "The widths and shapes of about 350 prominent lines of 65 elements emitted by an inductively coupled plasma", *Spectrochim. Acta* 41B (12), 1235-1275 (1986).
80. A. Montaser and D. W. Golightly, *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, 2nd Ed., VCH Publishers, New York (1992).
81. A. A. Radzig and B. M. Smirnov, *Reference Data on Atoms, Molecules, and Ions*, Springer-Verlag, New York, 1985.
82. D. Aeschliman and G. A. Norton, "Collection and Thermal Evolution Behaviors of Different Mercury Species Captured by Gold" *Environ. Sci. Technol.* 33, 2278 (1999).
83. *CRC Handbook of Chemistry and Physics*, ed. R. C. Weast and M. J. Astle, CRC Press, Boca Raton, FL, 1978.
84. H. G. C. Human, N. Omenetto, P. Cavalli, and G. Rossi, "Laser excited analytical atomic and ionic fluorescence in flames, furnaces, and inductively coupled plasmas – II. Fluorescence characteristics and detection limits for fourteen elements", *Spectrochim. Acta* 39B, 1345-1363, (1984).
85. J. Franzke, R. W. Fox, and L. Hollberg, "Tunable UV generation at 283 nm by frequency doubling and sum frequency mixing of two semiconductor lasers for the detection of Pb", *Spectrochim. Acta B* 53, 1951-1955, (1998).
86. J. P. Koplrow, D. A. V. Kliner, and L. Goldberg, "Development of a narrow-band, tunable, frequency-quadrupled diode laser for UV absorption spectroscopy", *App. Opt.* 37 (18), 3954-3960, (1998).
87. B. Welz and M. Sperling, *Atomic Absorption Spectrometry*, 3rd edn., WILEY-VCH, Weinheim, 1999.
88. D. B. Aeschliman and G. A. Norton, "Collection and Thermal Evolution Behaviors of Different Mercury Species Captured with Gold," *Environ. Sci. Technol.* 33, 2278 (1999).