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

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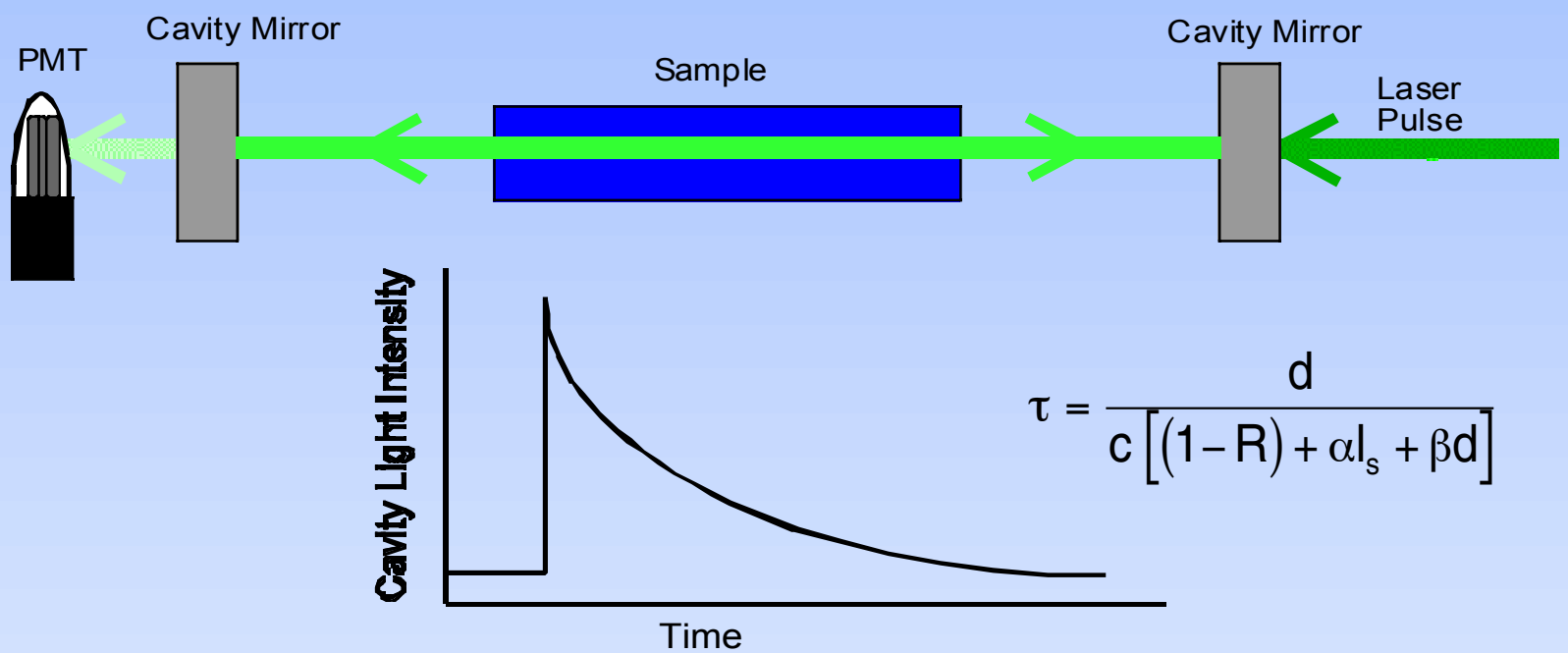
Original Goals

- Determine the viability of marrying CRDS with standard analytical instruments (e.g. ICP, graphite furnace).
- Provide the first quantitative evaluation of cavity ringdown spectroscopy for trace analysis
- Make a significant and positive impact in support of DOE's clean up efforts.

Cavity Ringdown Spectroscopy



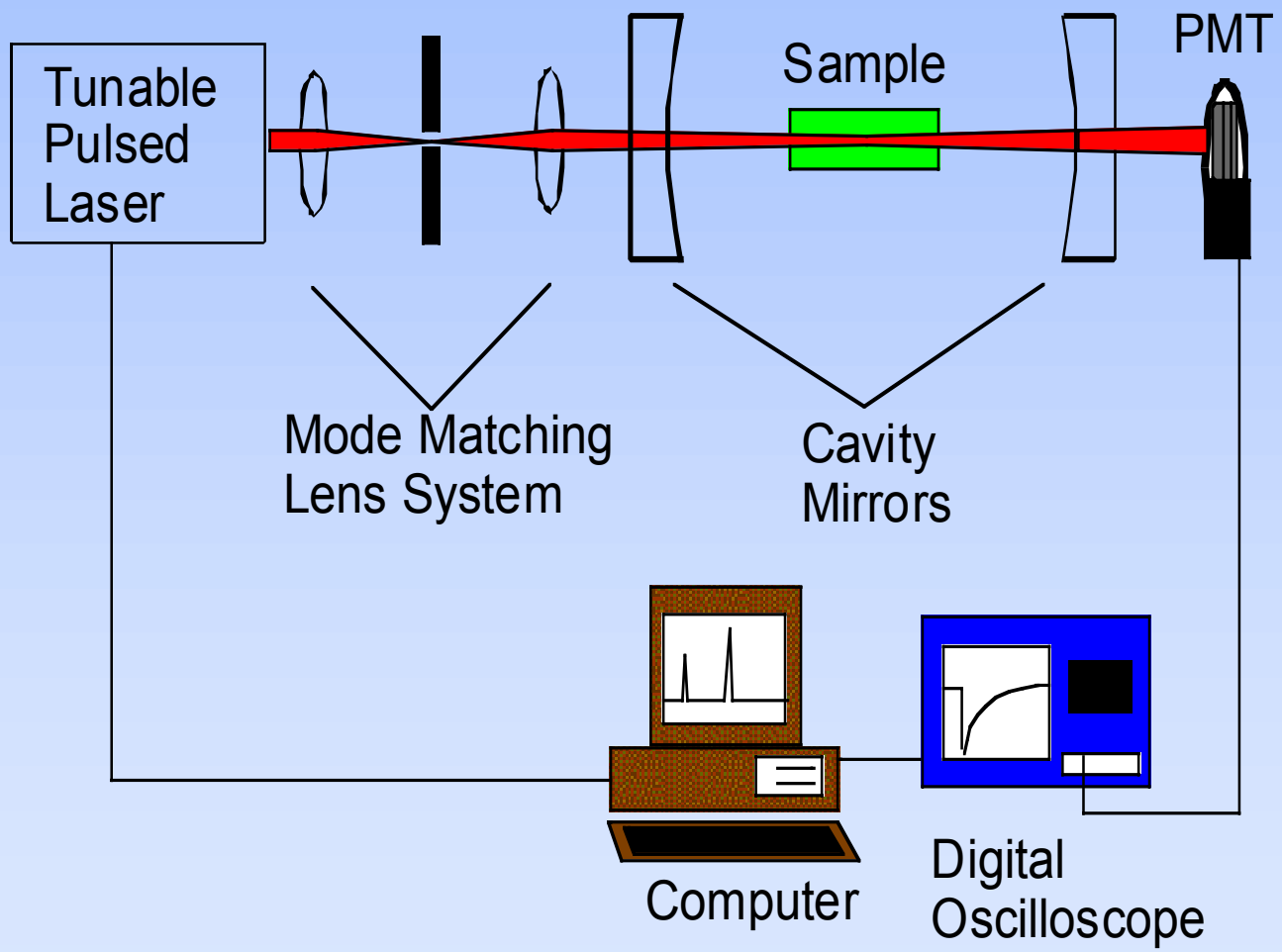
$$\tau = \frac{d}{c\left[(1-R) + \alpha l_s + \beta d\right]}$$

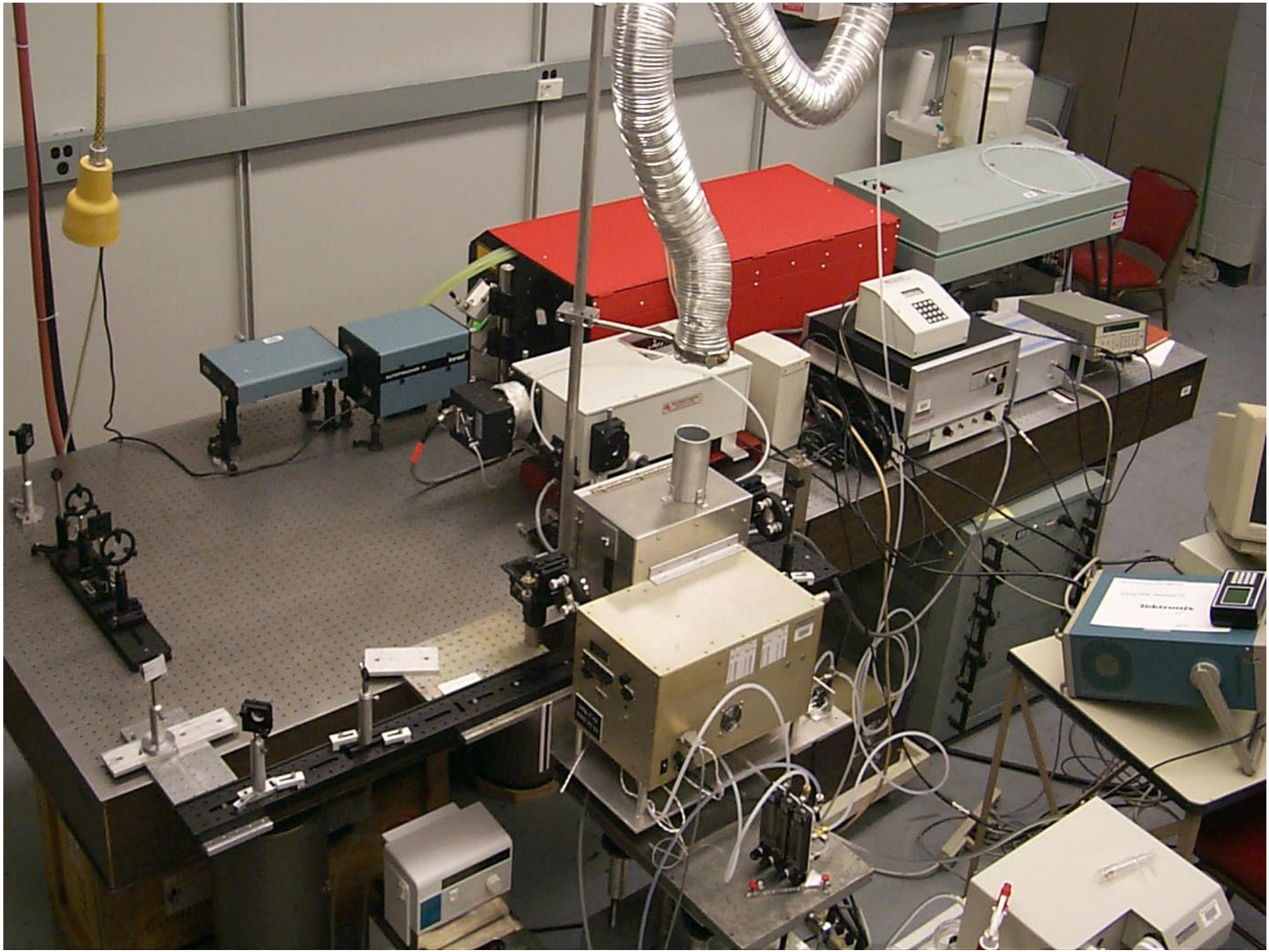
- Demonstrated Absorbance Detection per Pass: 1×10^{-7}
- Insensitive to Pulsed Laser Power Fluctuations (Enhanced UV Capability)
- Effective Pathlengths can extend to several kilometers!

Fundamentals & Limitations

- **Absolute measurement**
- **Sensitivity increases as absorption decreases**
- **Mirror reflectivity (99.97% @ 350 nm, 99.9% @ 280 nm)**
- **Sensitivity limited by accuracy of ringdown time measurement**
- **Other factors**
  - **laser & detector noise**
  - **mode competition**

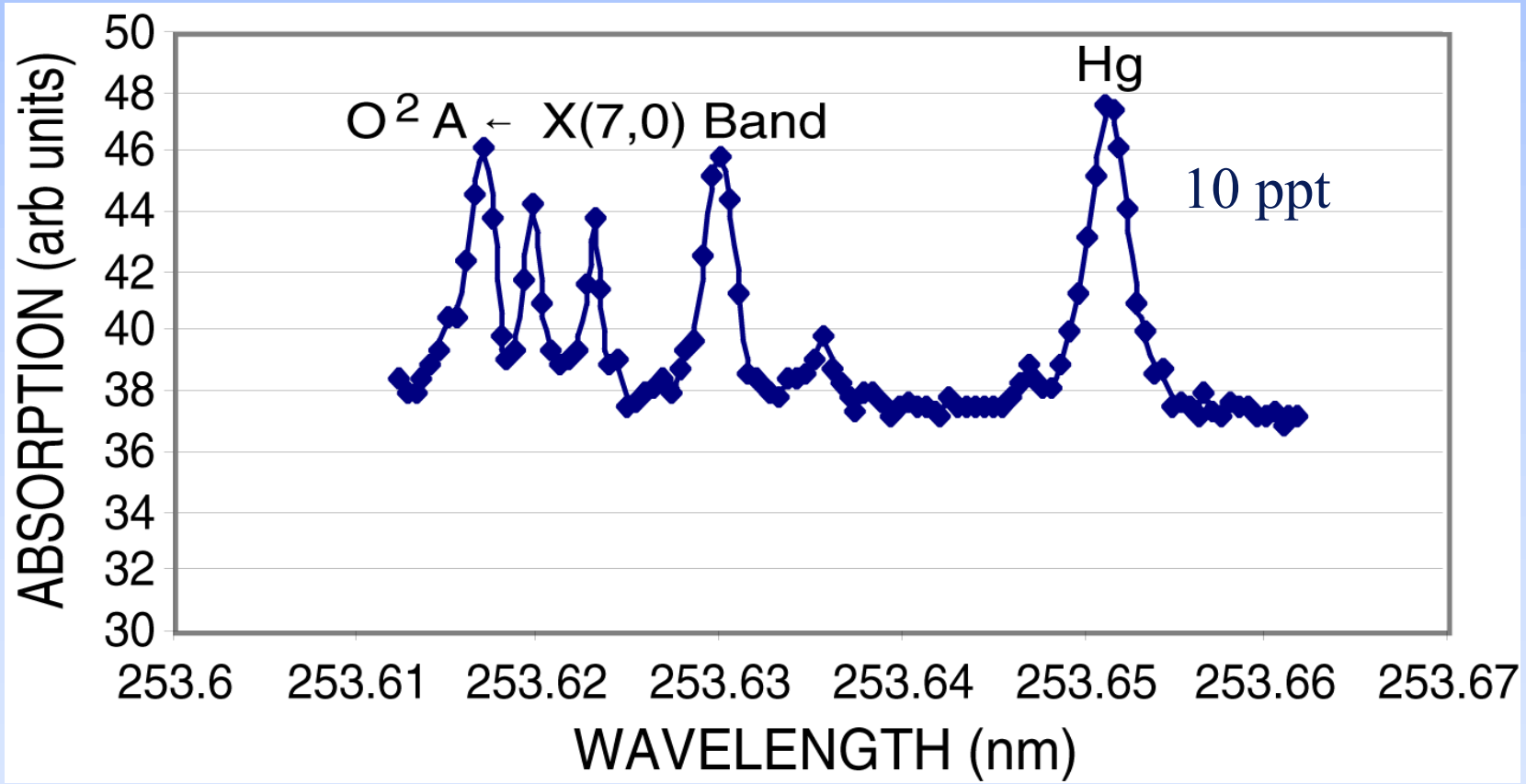
System Schematic





CRDS Scan of Laboratory Air

(Hg signal due to unsealed waste container containing ~ 10 ppm Hg sol.)

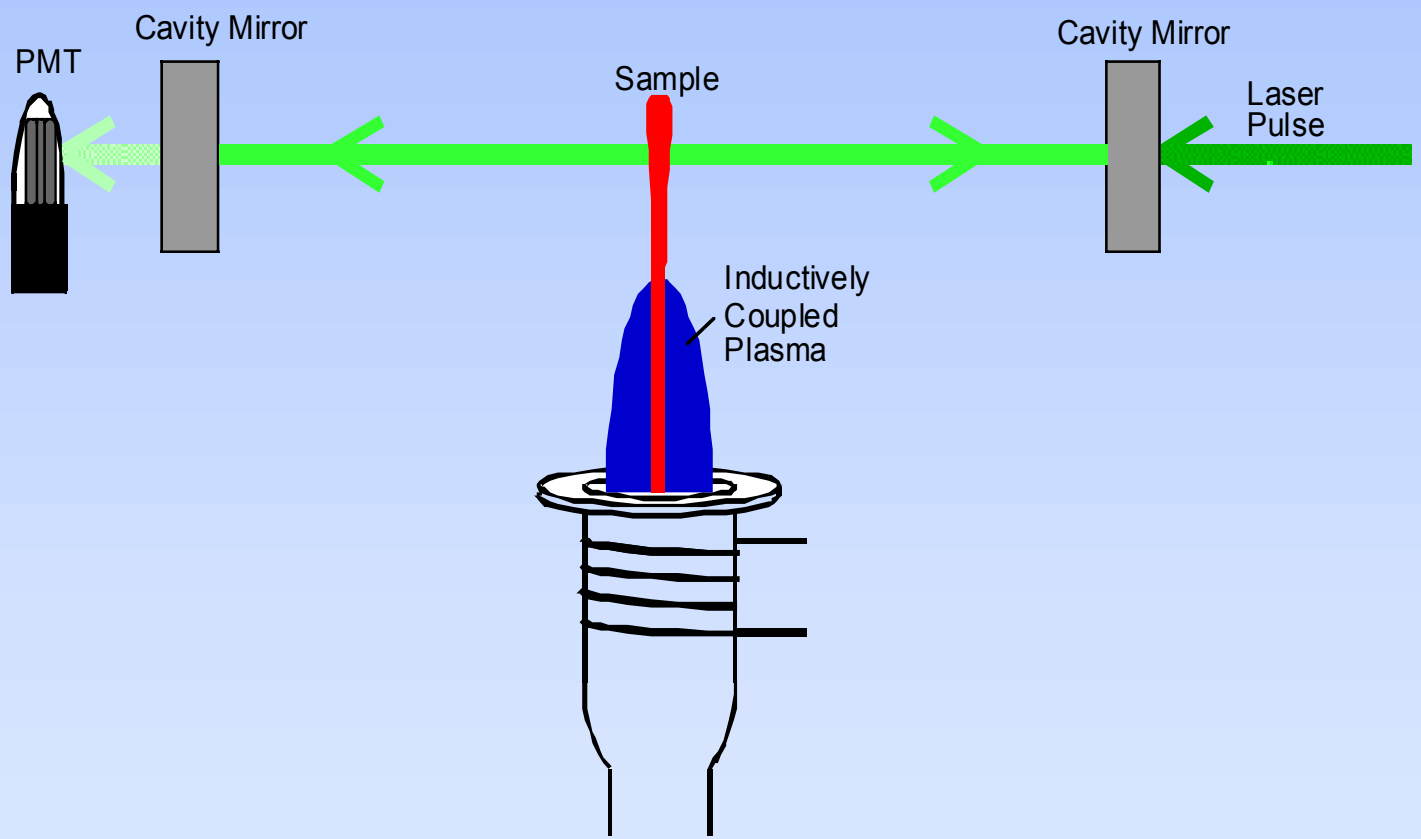


Atomization Source Required

"elements never occur alone, for nature and man both frown on celibacy" (Lundell)

- ICP
- Graphite Furnace
- Hg Cold vapor
- Etc.

Analytical Atomic Cavity Ringdown Spectroscopy - An ICP as Atomization Source



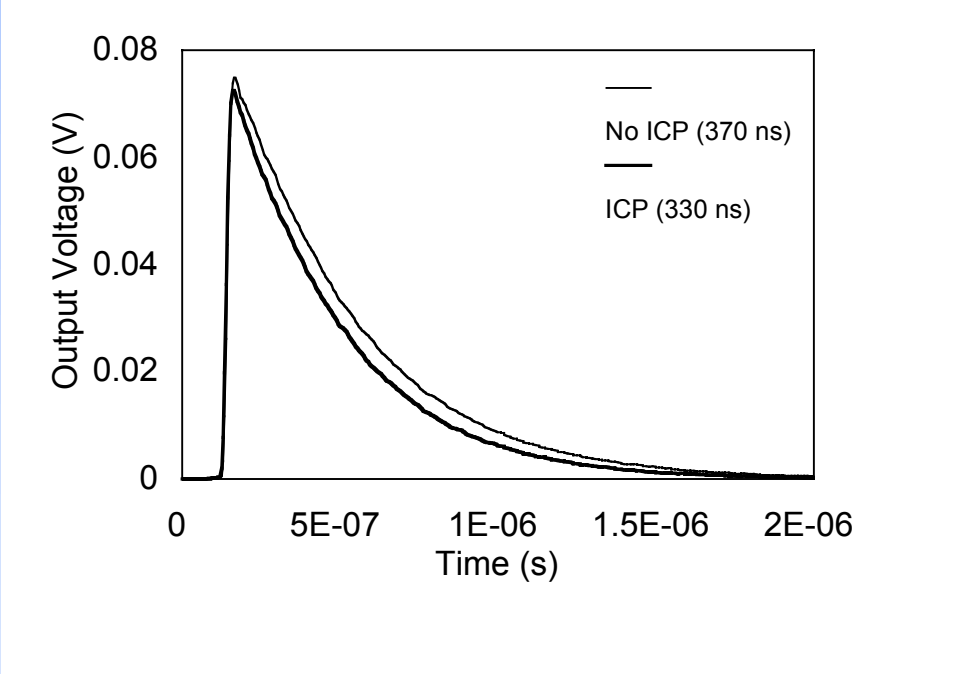
Estimated ICP-CRS Detection Limits

Element	Det. Lim. (ppb)	Det. Lim ($\mu g/m^3$)	Air-ICP DL ($\mu g/m^3$)
Cd (229 nm)	0.002	0.0008	2.5
Hg (254 nm)	0.7	0.3	20.0
Pb (283 nm)	0.04	0.015	0.9
Sr (461 nm)	0.0007	0.0003	
Mn (403 nm)	0.03	0.013	
Tl (378 nm)	0.03	0.011	
Cr (425 nm)	0.01	0.004	0.25
Cs (852 nm)	0.0006	0.0003	
Al (394 nm)	0.007	0.003	

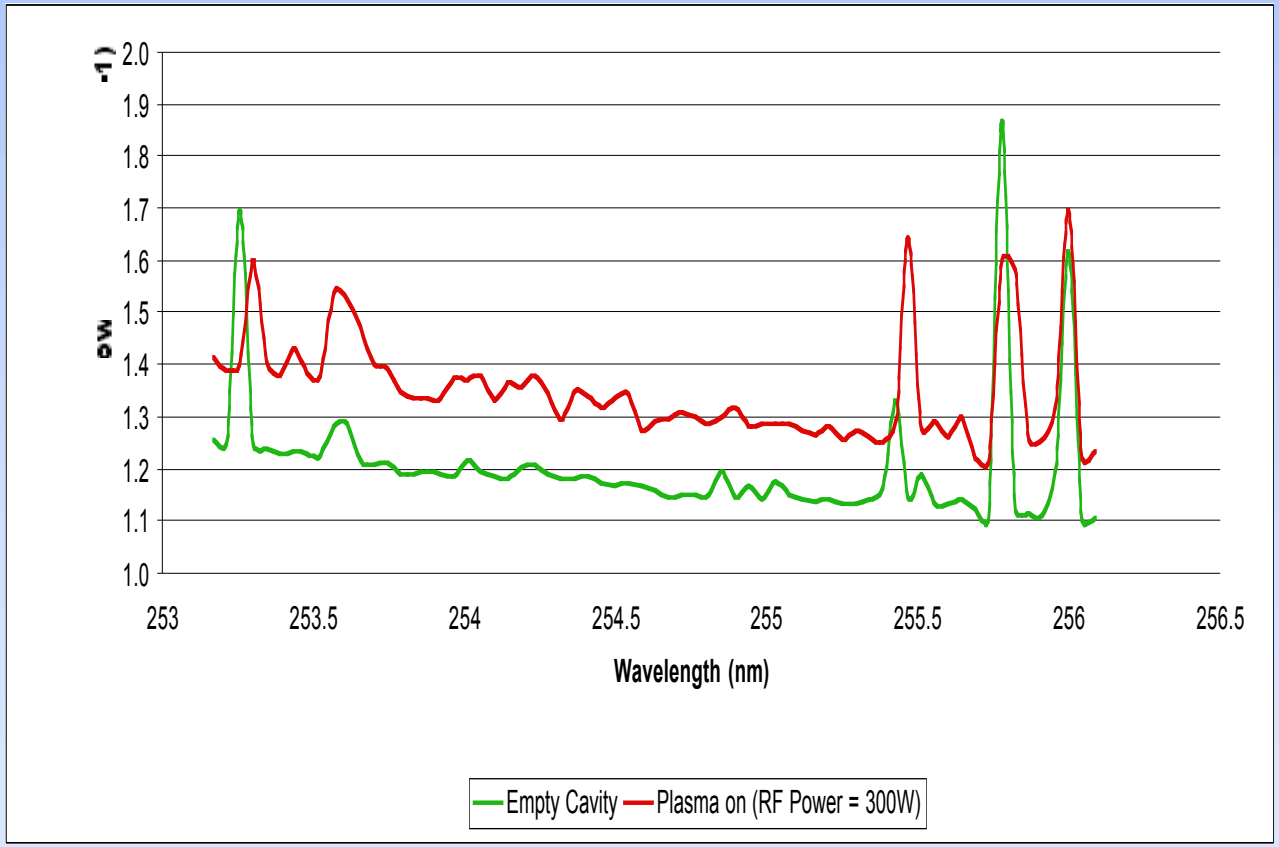
Sample pathlength = 5 mm, 1 x 10^{-5} ab/pass, 1% time accuracy

Refl 99.9%

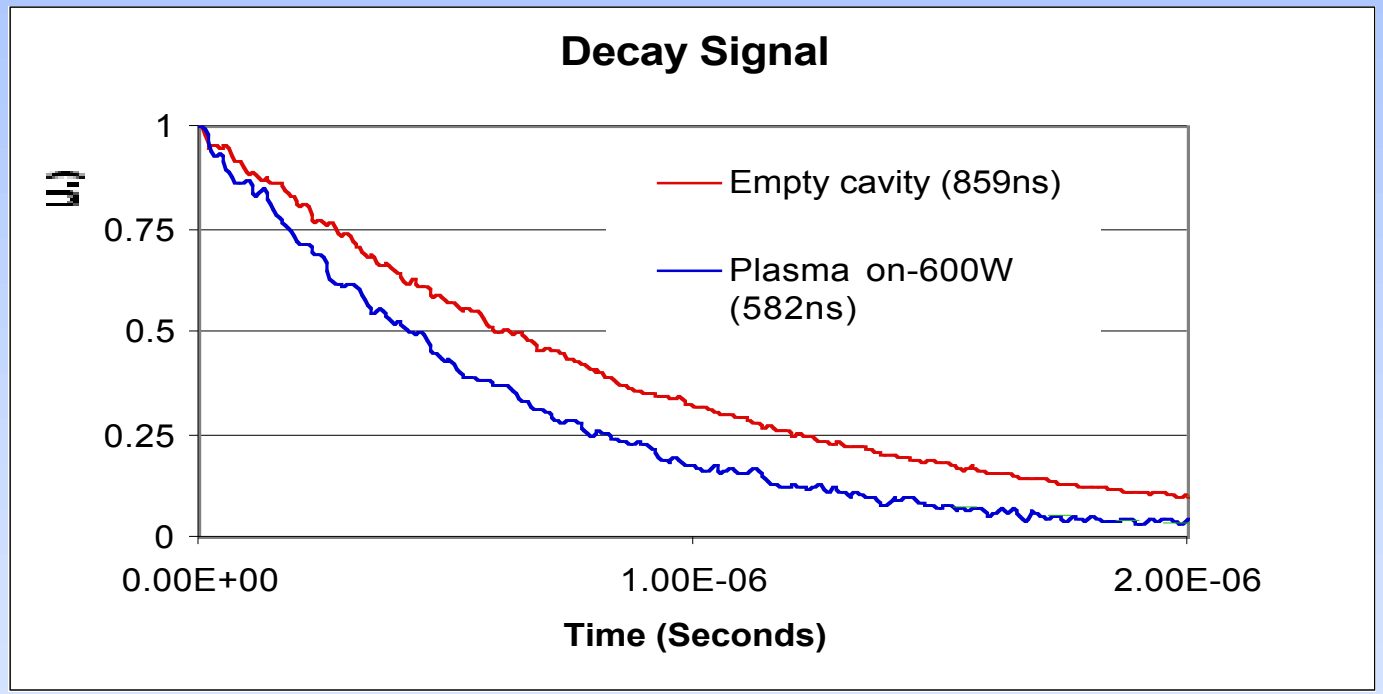
Ringdown transient recorded before & after ignition of the ICP



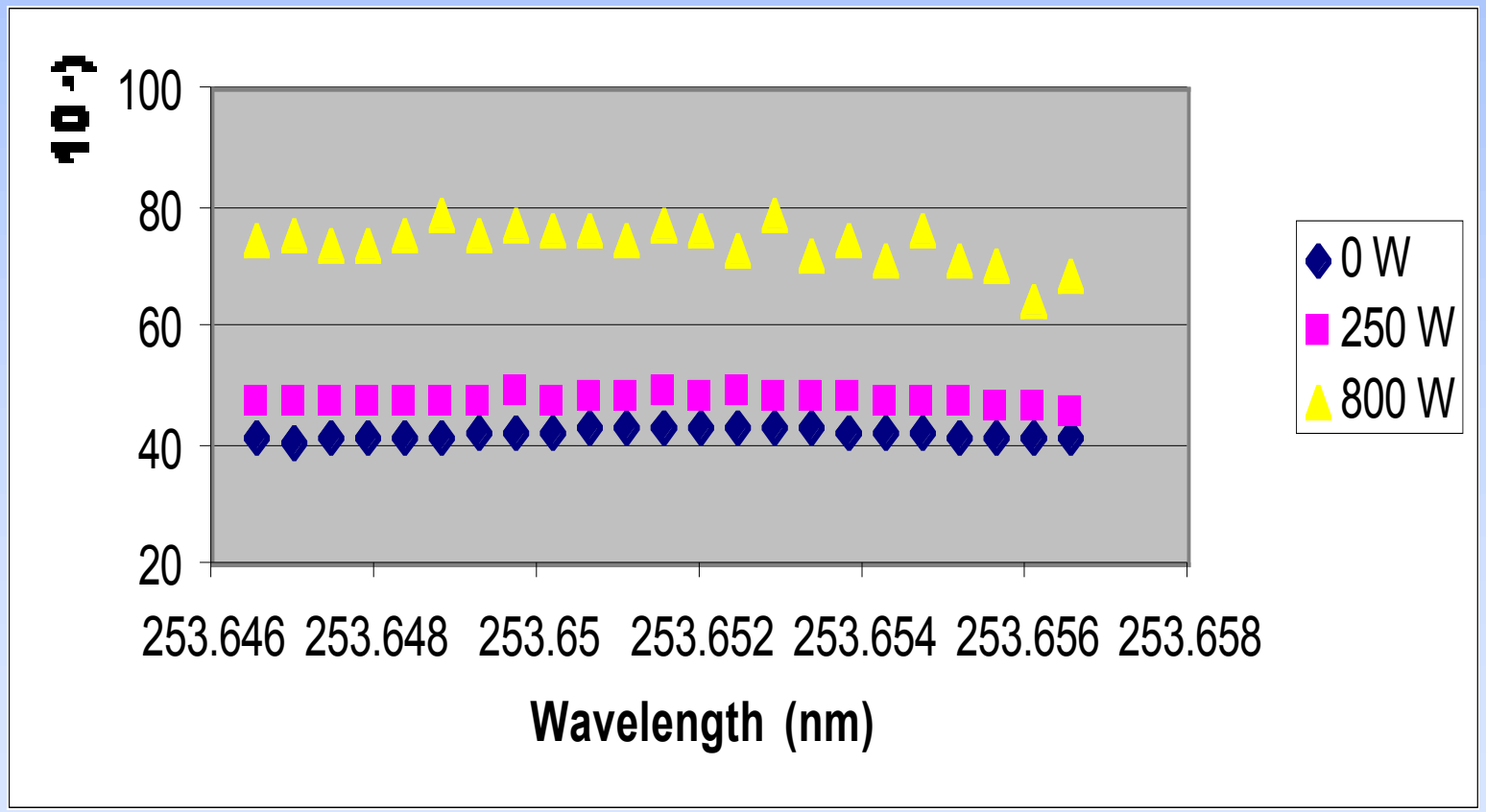
A 3 nm Spectral Scan with, & without, ICP plasma



Decay signal with and without ICP plasma



Effect of Power on the Background Losses



Sensitivity - standard low-flow torch, Mercury

- Power 800W,
  - stability=3%, DL = 600ppb
- Power 250W, 1 mm sample orifice
  - stability=1%, DL = 100ppb
- Power 250W, 3mm sample orifice,
  - stability=1% DL=20ppb,

Noting sample path length & R = 99.7%,s this result is approaching theoretical predictions

Present Status & Path Forward

- ICP parameters (torch design, gas flows, observation height, RF power, etc.)
- Achieved stability improvement from 3% to 1% with the ICP on. Further improvements underway to approach 0.1%.
- Optimizing cavity design to reduce losses
- Increase sample path length - axial, mirror reflectivity to 99.9%
- Potential 2 orders of magnitude improvement (e.g. Hg from 20 ppb to 0.2 pbb.

Graphite Furnace Atomic Absorption Spectrometry

Hollow Cathode Lamp

Graphite Furnace

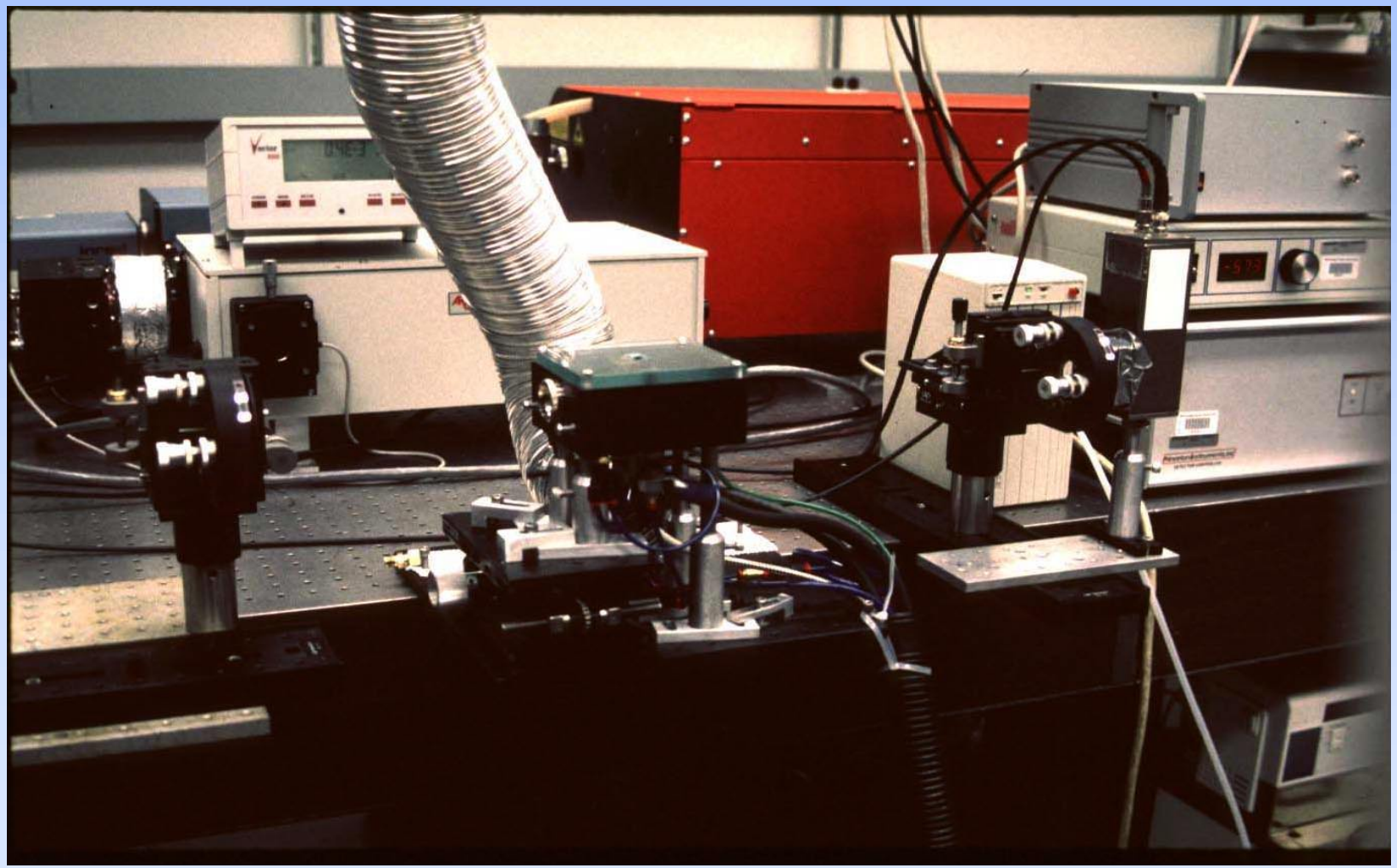
Spectrometer

- Well-established, commercially available technique
- Typical Detection Limits
  - 5.5 pg Pb, 30 pg Hg, 0.2 pg Cd, 1.5 pg Cr
- Absorbance Detection Limit (αl_s) ~10^{-3}-10^{-2}

Estimating Potential GF-CRDS Detection Limits

- Characteristic Mass for GF-AAS
  - Analyte mass for which A= $(.43\alpha l_s) = 4.4 \times 10^{-3}$
  - 5.5 pg Pb, 0.2 pg Cd, 1.5 pg Cr
- Ringdown Absorbance Detection Limit
  - R = 99.9% (UV mirrors)
  - 1% Ringdown stability
  - 3σ limit yields $(\alpha l_s) = 3.6 \times 10^{-5}$
  - Absorbance R = 99.9% (UV mirrors)
- Scale mass linearly with αl_s
  - 20 fg Pb, 0.7 fg Cd, 5 fg Cr

GF-CRDS Experiment

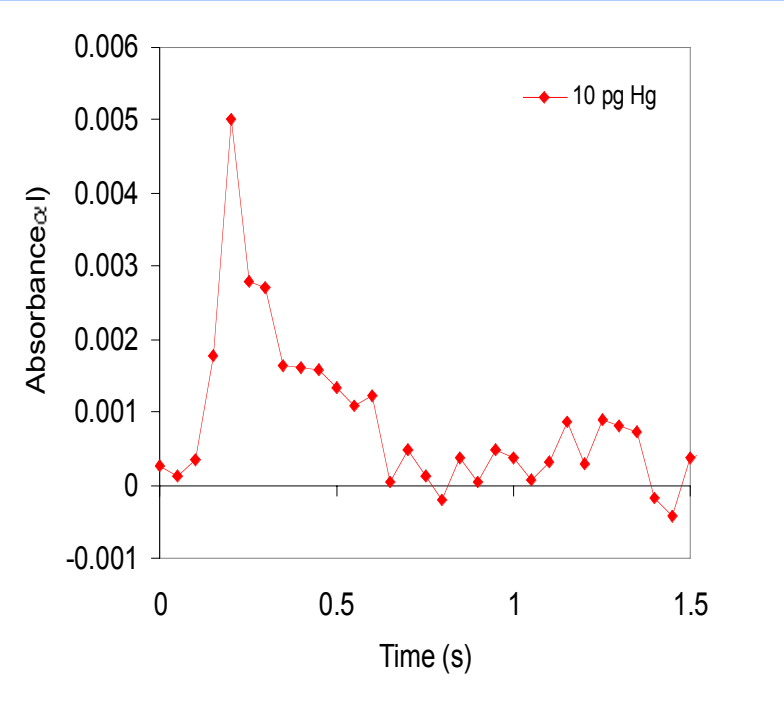


Data Acquisition System

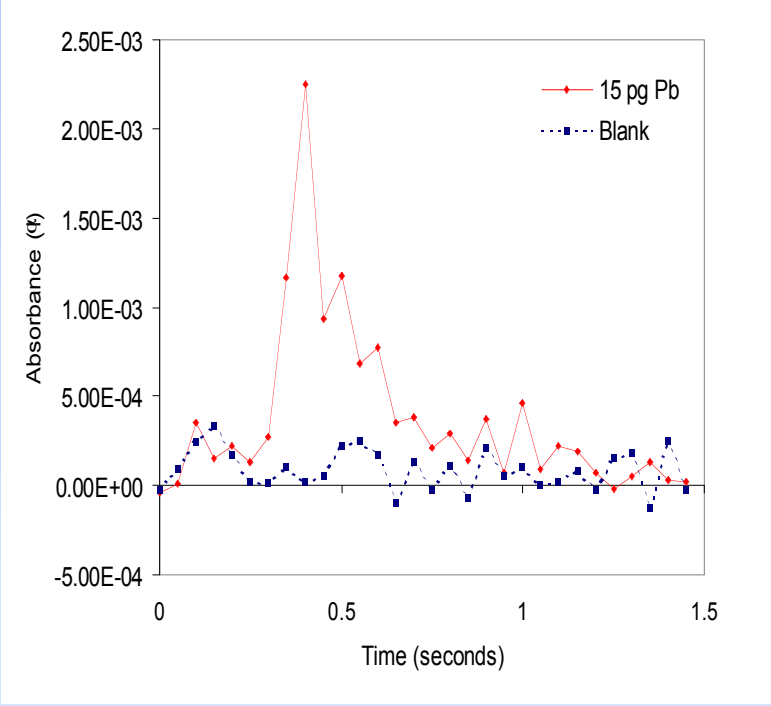
- Rapid acquisition needed
  - Atomization lasts less than one second
  - Require absorbance profile, not just average
  - Must save each ringdown waveform during atomization
- Fast A/D Converter solution
  - 100 Mhz, 12-bit digitizer
  - Operate in burst mode, every waveform saved for 4 seconds, processing follows

Hg & Pb GF Atomization

1400 °C



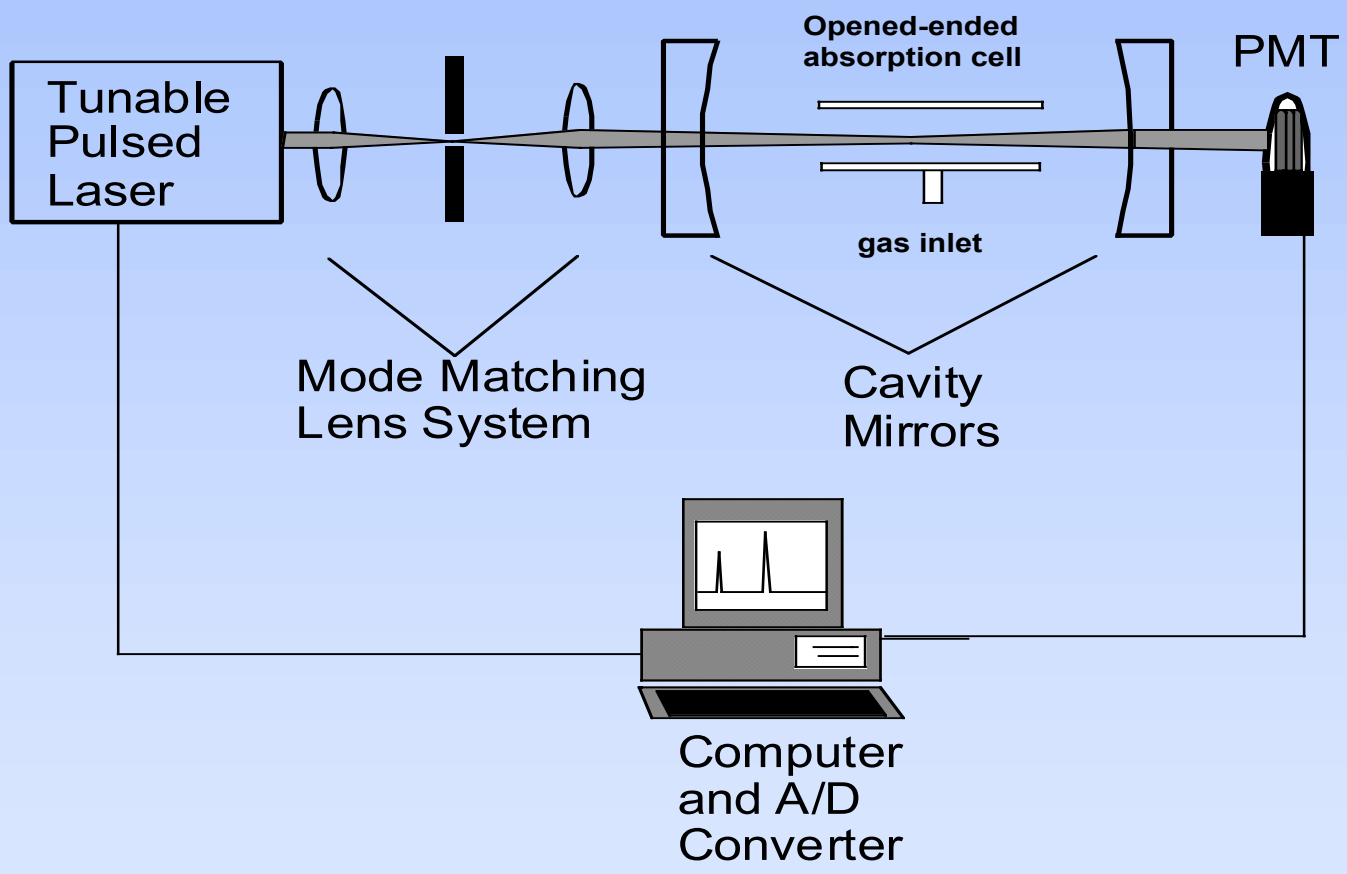
1100 °C



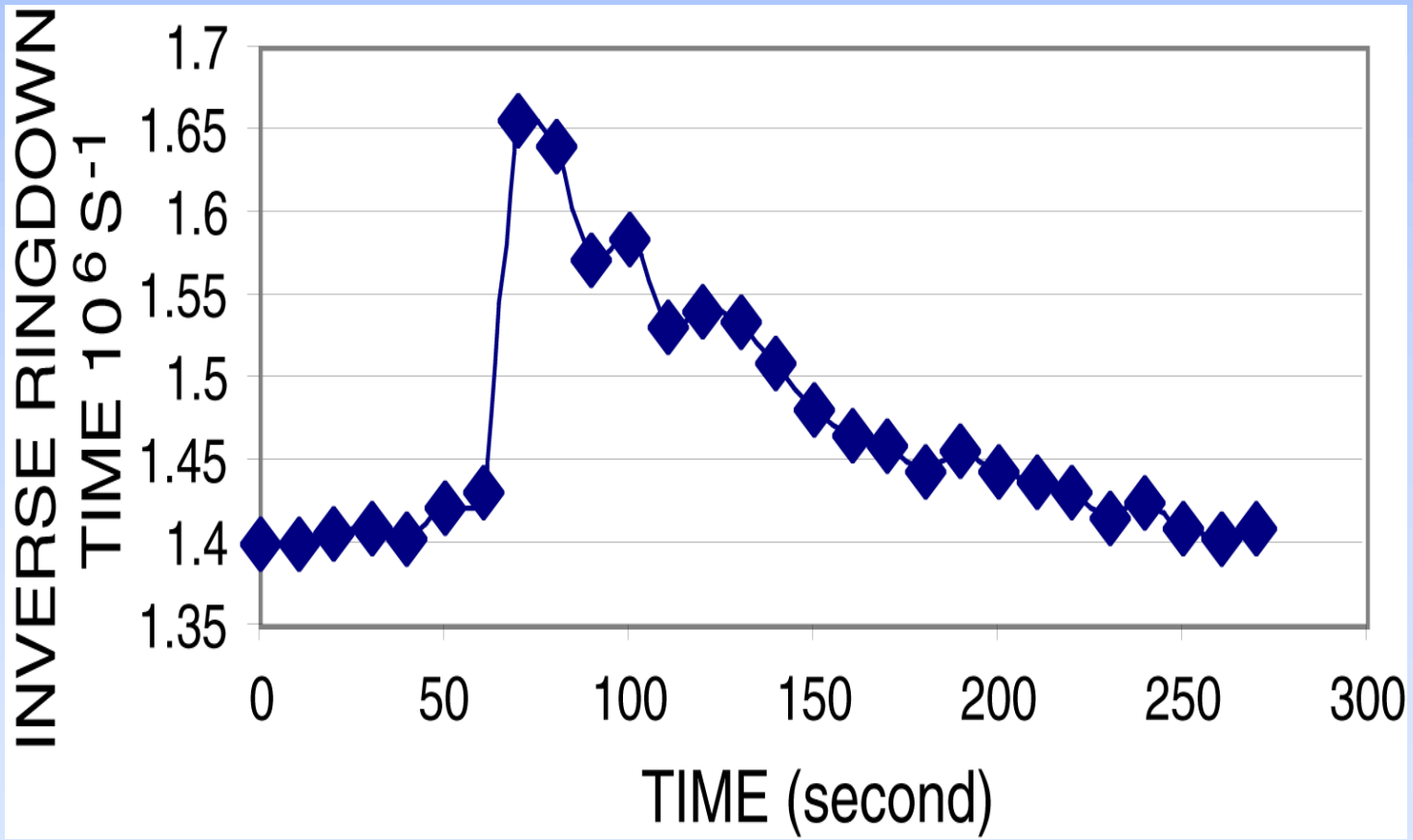
GF-CRDS Current Status

- Pb Detection Limit
  - GF-CRDS: ~ 1 pg
  - GF-AAS: 3 pg
- Hg Detection Limit
  - GF-CRDS: < 5 pg
  - GF-AAS: 30 pg
- Promising, with many improvements possible...

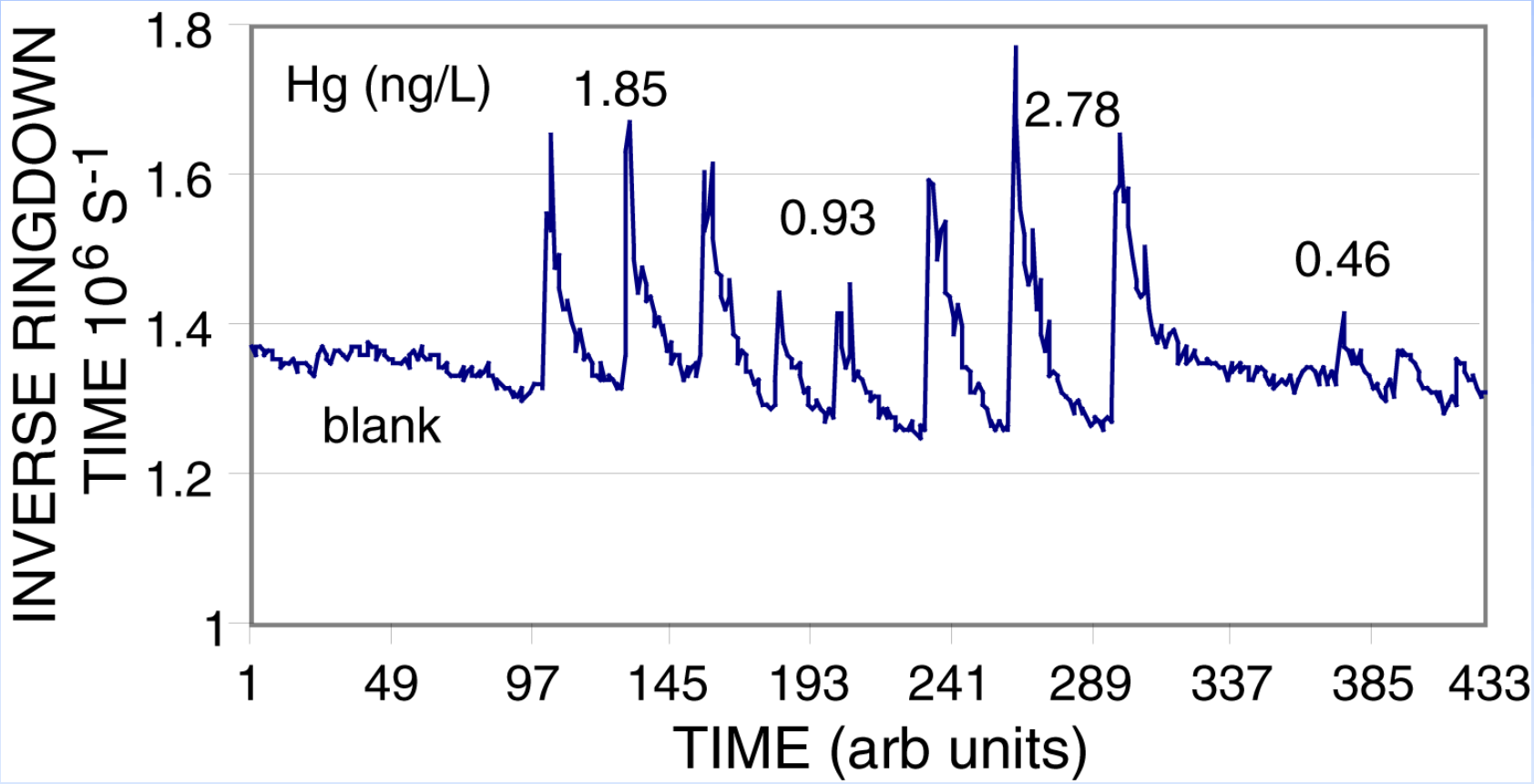
Cold Vapor Hg - CRDS



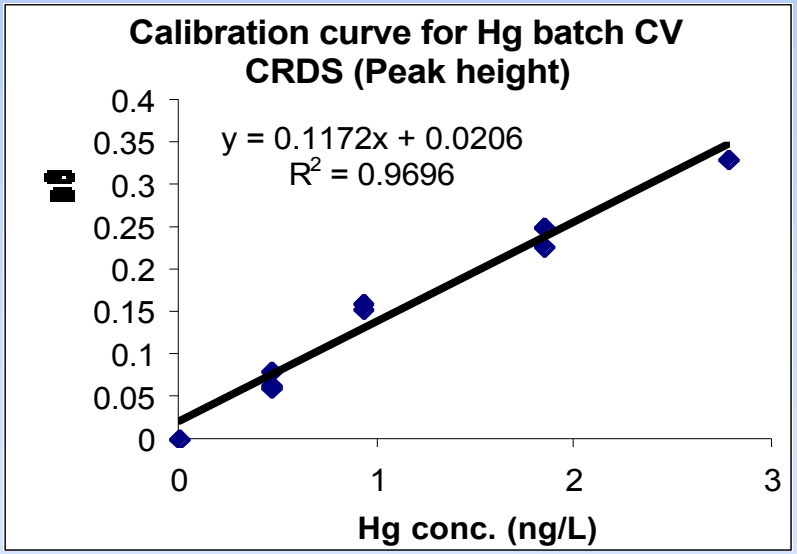
The CRDS signal profile for a 2 ng injection of Hg - Batch mode

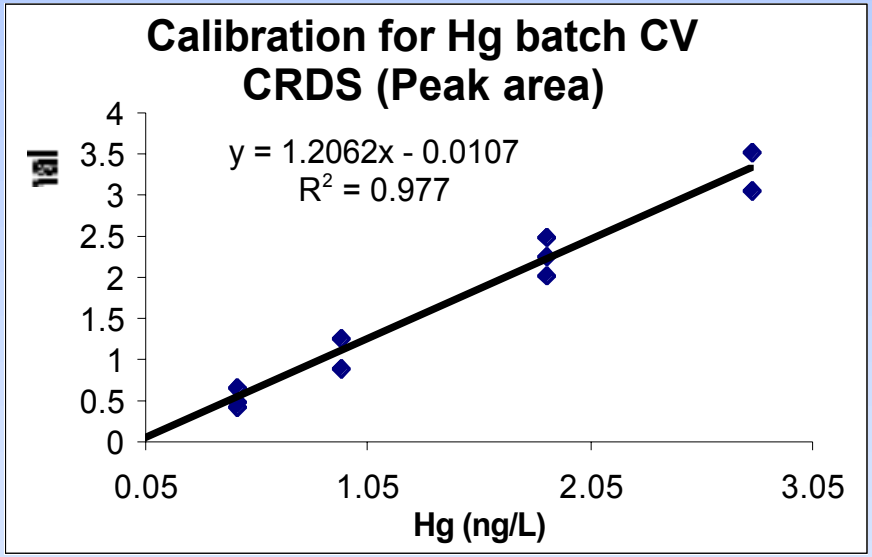


Continuous-mode Hg vapor generation signal profiles



Calibration Curves





Experimental Specifications

I) Laser system: A Nd:YAG laser pumped a tunable dye laser whose output was frequency doubled to obtain the 253.6 nm wavelength. The dye laser linewidth was approximately 0.07 cm^{-1}, which when doubled yields a final 253.6 nm linewidth of approximately 0.1 cm^{-1}. The laser pulse duration is approximately 8 ns and the laser repetition rate is 20 Hz.

II) Cavity Optics: For these experiments a 56 cm long cavity was constructed from specially coated mirrors. The mirrors were plano-concave with a 6 meter radius of curvature and were coated for maximum reflectivity at 253 nm. The reflectivity at this wavelength was approximately 99.7%. 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.

III) Data acquisition: The data acquisition system that was designed for ICP-CRDS (described in ref. 1) was used. The signal from a photomultiplier tube, placed behind the second cavity mirror, is 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 process off-line to obtain the peak height and integrated absorbance values.

Experimental Specs continued

IV) Standard AAS system: A quartz cell of the same size as used for CRD, but with quartz windows end-seals, 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.

V) Mercury Vapor Generation: In batch mode, a 1.08 L plastic bottle was used as the reducing vessel. Teflon tubes (0.75 mm OD) transported the mercury vapor from the bottle to quartz cell. In continuous mode, a peristaltic pump was used to inject the mercury and reagent solution. A 3-meter long Teflon tube was used for mercury reduction and extraction. A pneumatic nebulizer was used for gas/liquid separation. In continuous mode, the $NaBH_4$ 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.

VI) Reagents: 5% $SnCl_2$ in 10% HCl solution is made by dissolving 3.0 g $SnCl_2 \cdot 2H_2O$ in 50 ml 10% HCl for use in batch mode experiments. Solid tin beads are added to stabilize the reagent. For continuous mode generation, $NaBH_4$ solution was made by dissolving solid $NaBH_4$ in water. NaOH is added to the solution to stabilize the reagent. Mercury standard solution is made by diluting standard stock solution (1 mg/ml, with 10% HCl solution.

Comparison of Hg-CV CRDS & AAS
18 cm absorption cell

- CRDS

  Detection Limit 0.027 ng (25 ng/m^3)

- AAS

  DL = 9 ng (8.3 μg/m^3)

Note: for CRDS R = 99.7%, cell open-ended. AAS cell sealed.

Potential Applications of CRDS to DOE Problems

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

Remaining Effort & Potential Improvements

- Last 6 months
  - Air-ICP
  - Cavity losses
- Enhanced measurement repetition rate
  - Excimer or Cu vapor lasers
  - CW ringdown (e.g. diode lasers)
- Cavity and laser considerations
  - Enhanced mirror reflectivity
  - Improved time constant stability (w.r.t. index variations)
  - Reduced laser linewidths

Program Achievements To Date

- 1st results (paper accepted) using CV Hg-CRDS
  - Detection Limit 25 ng/m^3 (AAS 8.3 μg/ m^3)
- 1st published paper on ETA-CRDS
  - Work highlighted in "Analytical Chemistry"
  - Obtained lower detection limits than commercial GF-AAS
  - Demonstrated the potential of the technique
- 1st published paper on ICP-CRDS
  - Hg detection limits approaching theoretical limits
  - Ringdown stability improved to 1%. Further improvement possible
- 7 conference presentations, 5 invited seminars
- "Laser Absorption Cavity Ringdown Spectroscopy" Encyclopedia of Analytical Chemistry. Wiley & Sons, Oct 2000. Invited

Future Plans-Grant Renewal

- Develop a robust fieldable Hg-CRDS
- Continue the development of CRDS for analytical atomic analysis
- Continue to make a significant & positive impact in support of DOE's environmental efforts
- This request is supported by
  - Collaboration with Ames Laboratory
  - University matching of $185,000
  - Confidentiality agreement with Industry

Publications

- G. P. Miller and C. B. Winstead. Inductively Coupled Plasma Cavity Ringdown Spectrometry. J. Anal. Atom. Spectro. 12, 907 (1997)
- C. B. Winstead, F. J. Mazzotti, J. Mierzwa, and G. P. Miller. Preliminary results for electrothermal atomization-cavity ringdown spectroscopy (ETA-CRDS. Anal.s Commun., 36, 277 (1999). [Highlighted in Analytical Chemistry 71, 660A (1999).]
- G. P. Miller and C. B. Winstead. Cavity Ringdown Laser Absorption Spectroscopy. Encyclopedia of Analytical Chemistry, Editor R. A. Meyers. Wiley & Sons (to be published Oct 2000).
- S. Tao, F. Mazzotti, C. B. Winstead and G. P. Miller. Determination of elemental mercury by cavity ringdown spectroscopy. Analyst (accepted for publication).
- F. Mazzotti, C. B. Winstead and G. P. Miller. Loss mechanisms in ICP-Cavity ringdown Spectrometry (In preparation).
- F. Mazzotti, C. B. Winstead and G. P. Miller. A comparison of various atomization sources for elemental cavity ringdown spectroscopy. (In preparation).

Acknowledgments

- Fabio Mazzotti, Jerzy Mierzwa, Shiquan Tao, Ping-Rey Jang
- Funding
  - DOE 1997 Environmental Management Science Program DE-FG07-97ER62517