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

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# Goals

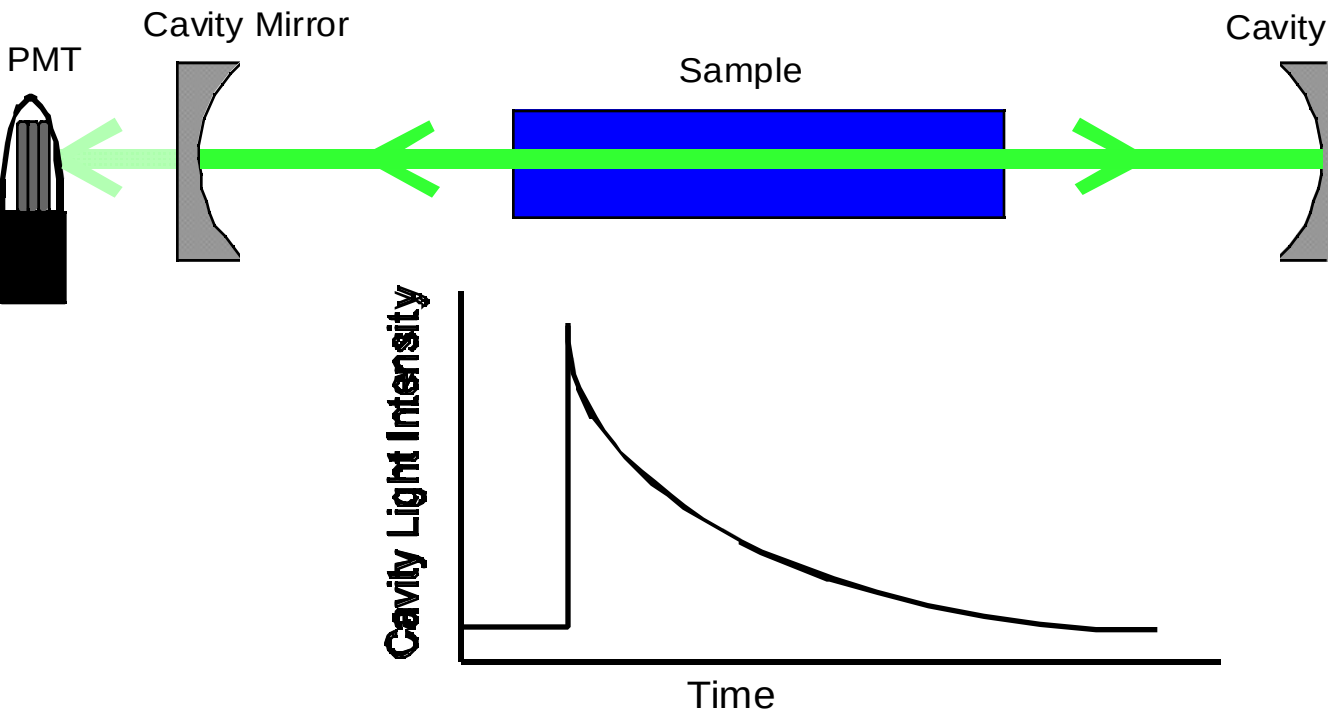
- Develop a sensitive real time monitor of environmentally important elements in industrial and waste processing off-gases
  - Heavy Metals (Hg, Pb, Cd, Cr, As, Sb, etc.)
  - Radionuclides
- Develop a new general purpose analytical tool for ultra-sensitive trace analysis

# Cavity Ringdown Spectroscopy

## “A New Analytical Approach to Trace Analysis”

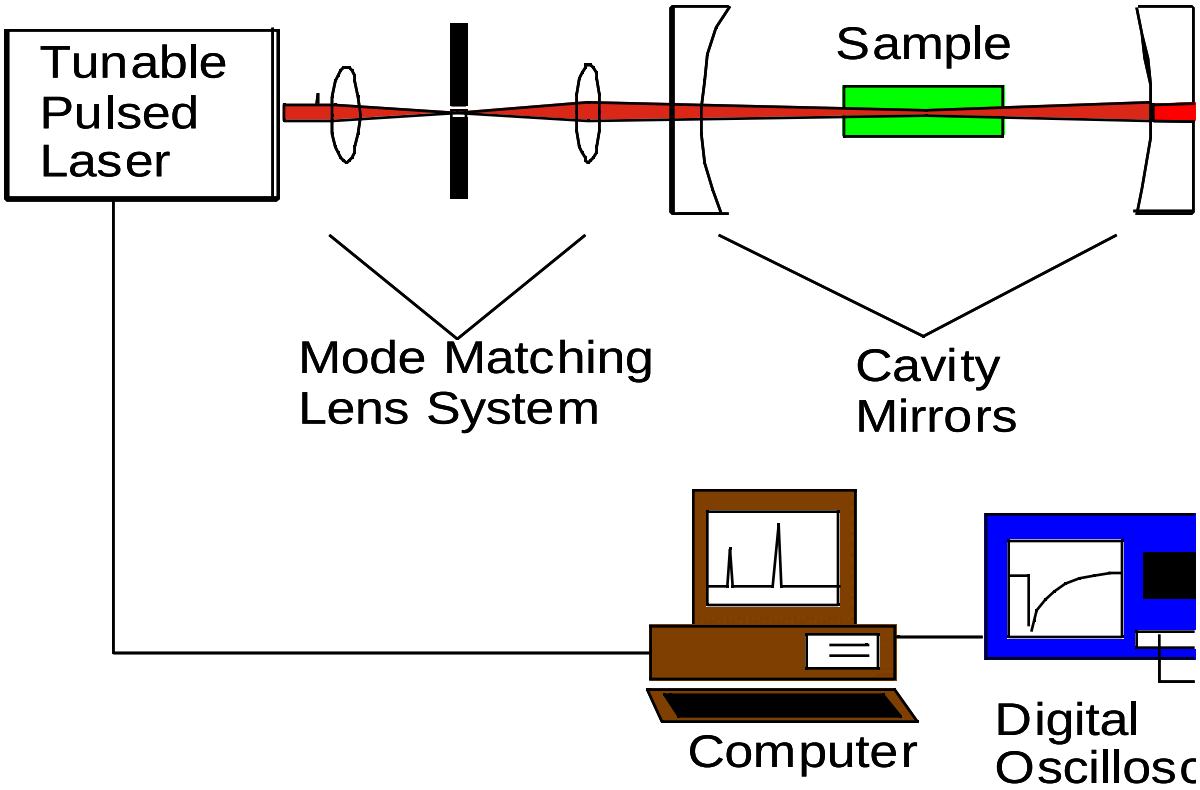
- Analytical Atomic Absorption Spectroscopy (Walsh,1955)
- Cavity Ringdown Spectroscopy (O’Keefe and Deacon, 1988)
- Analytical Cavity Ringdown Spectroscopy
  - Inductively Coupled Plasma
  - Graphite Furnace (Miller and Winstead, 1997)

# Cavity Ringdown



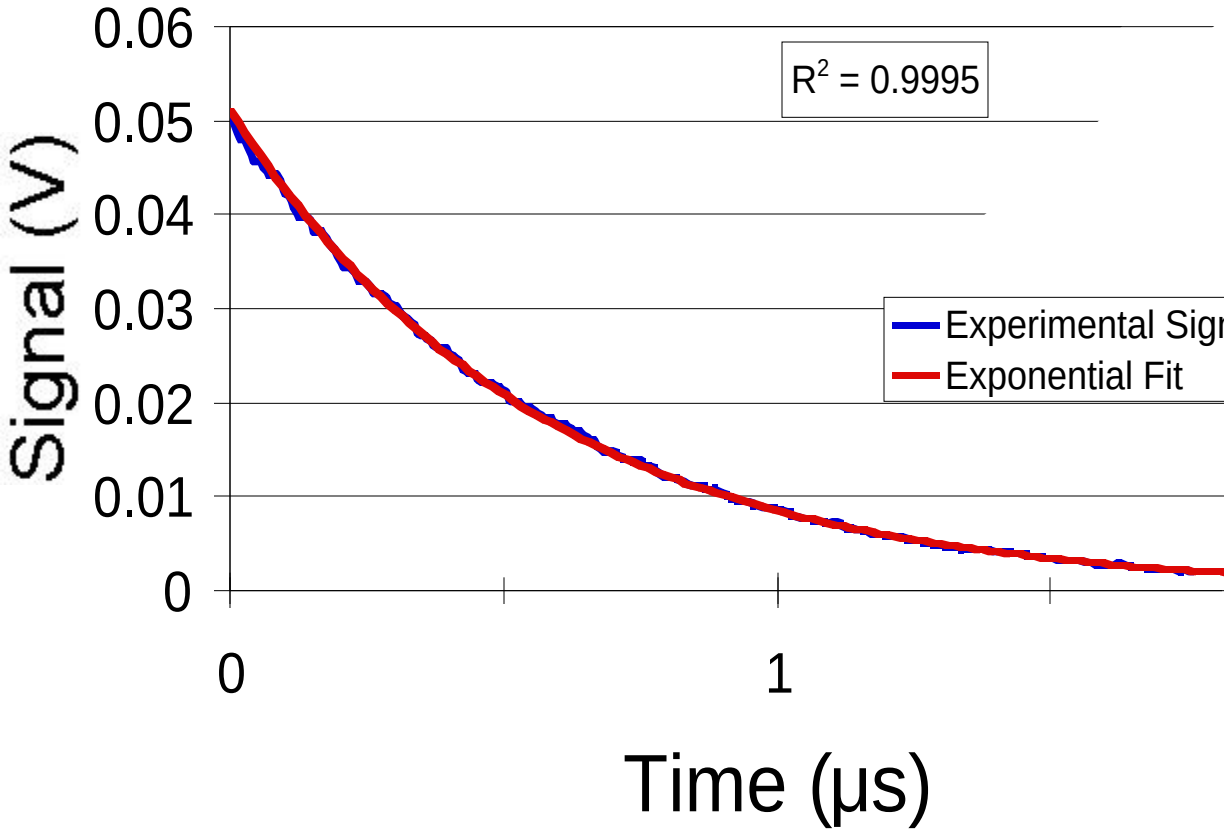

- Demonstrated Absorbance Detection per Pass: $1 \times 10^{-7}$
- Insensitive to Pulsed Laser Power Fluctuations (Enhanced UV Ca
- Effective Pathlengths can extend to several kilometers!
- Sensitivity superior to photo-acoustic spectroscopy

# Ringdown Experiment

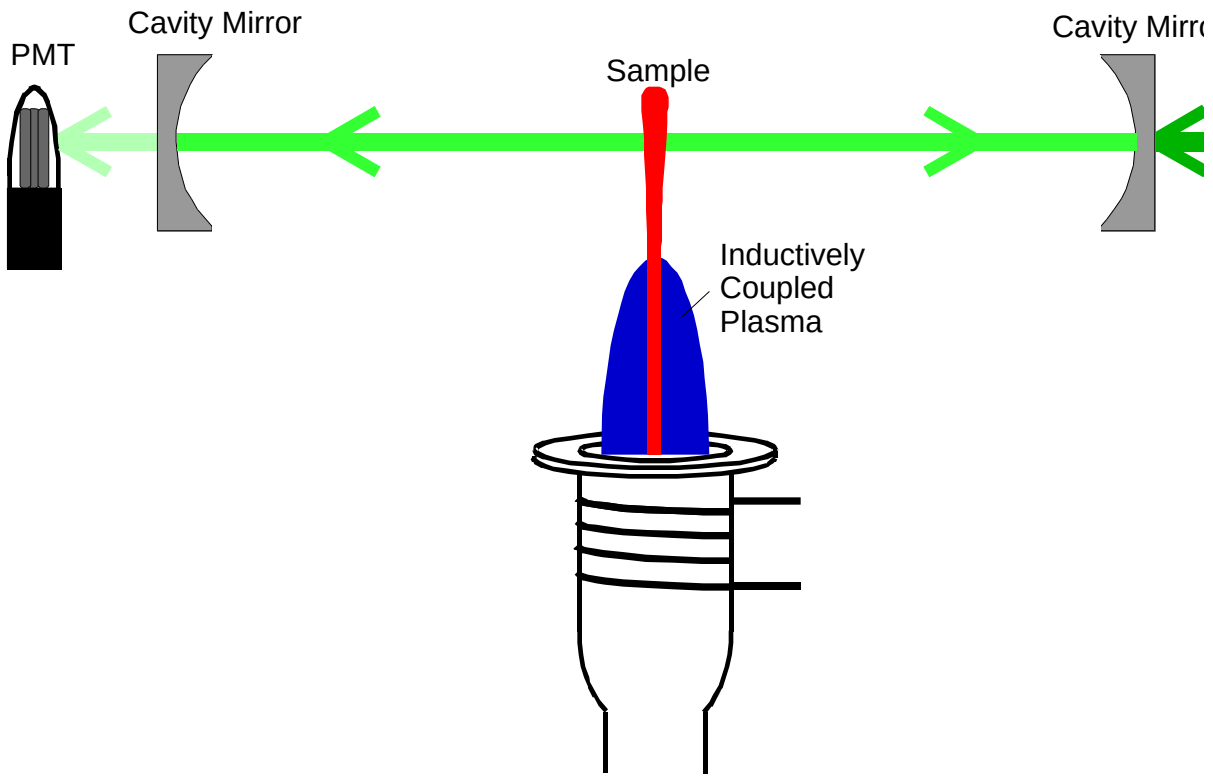


# Ringdown Signal using Mirrors Optimized for the UV

## (R = 99.6% @ 280 nm, T=560 ns)



# Inductively Coupled Plasma Cavity Ringdown Spectroscopy



# Estimating Ringdown Detection Limits

- From Absorption Spectroscopy: $I = I_0 e^{-\alpha l}$
- For typical ringdown, ($\alpha\ l_s = \sigma\ C\ l_s$) > $10^{-6}$ - $10^{-7}$
- Assuming $10^{-5}$ absorbance detection, i.e.

  $10^{-5} < \sigma\ C\ l_s$ for ICP-CRS

  $\sigma$ - Transition cross-section (Line broadened)

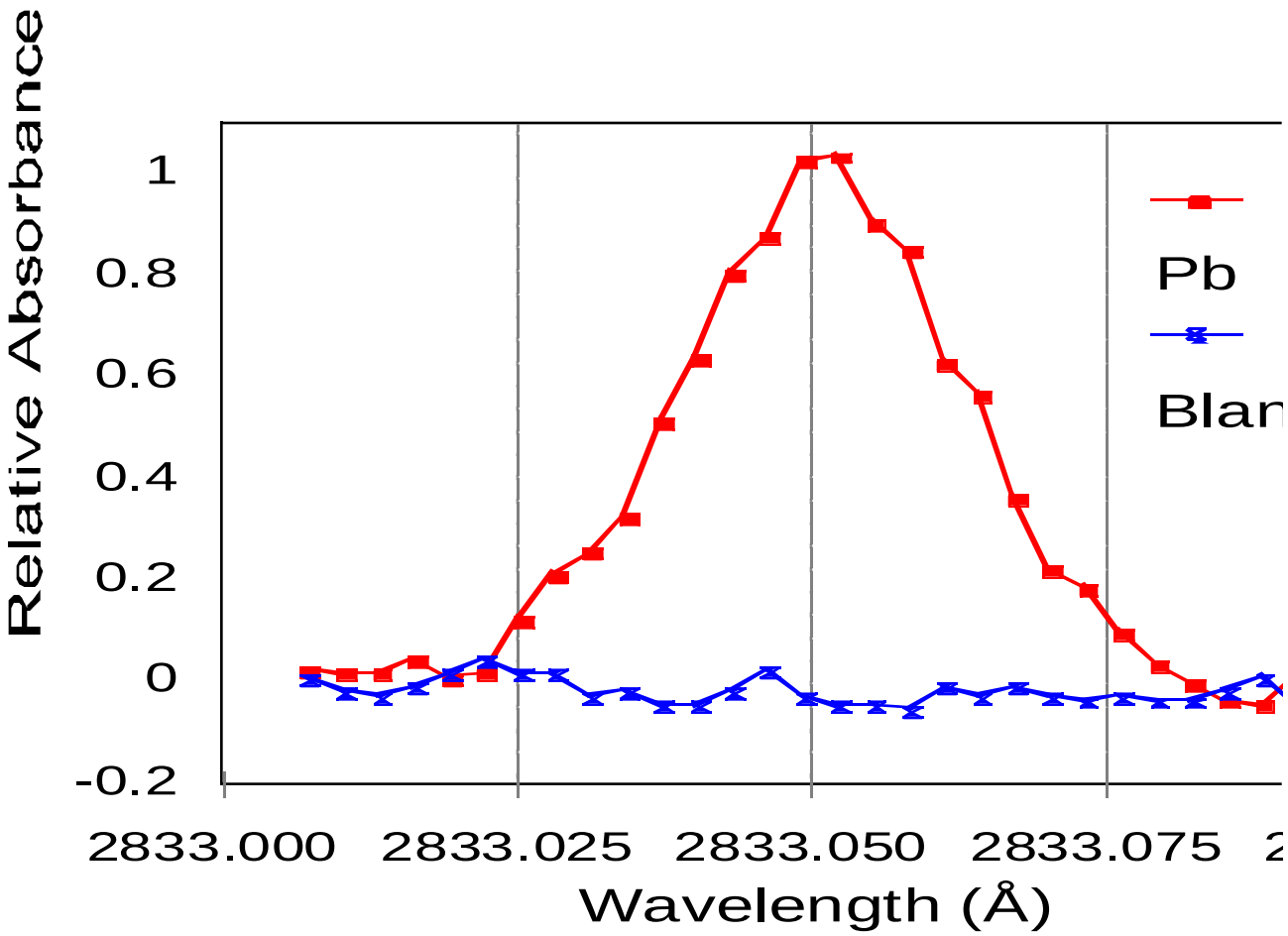
  C - Species Concentration

  $l_s$ - Pathlength through sample
- Accuracy of Time Measurement - 0.1 to 1%

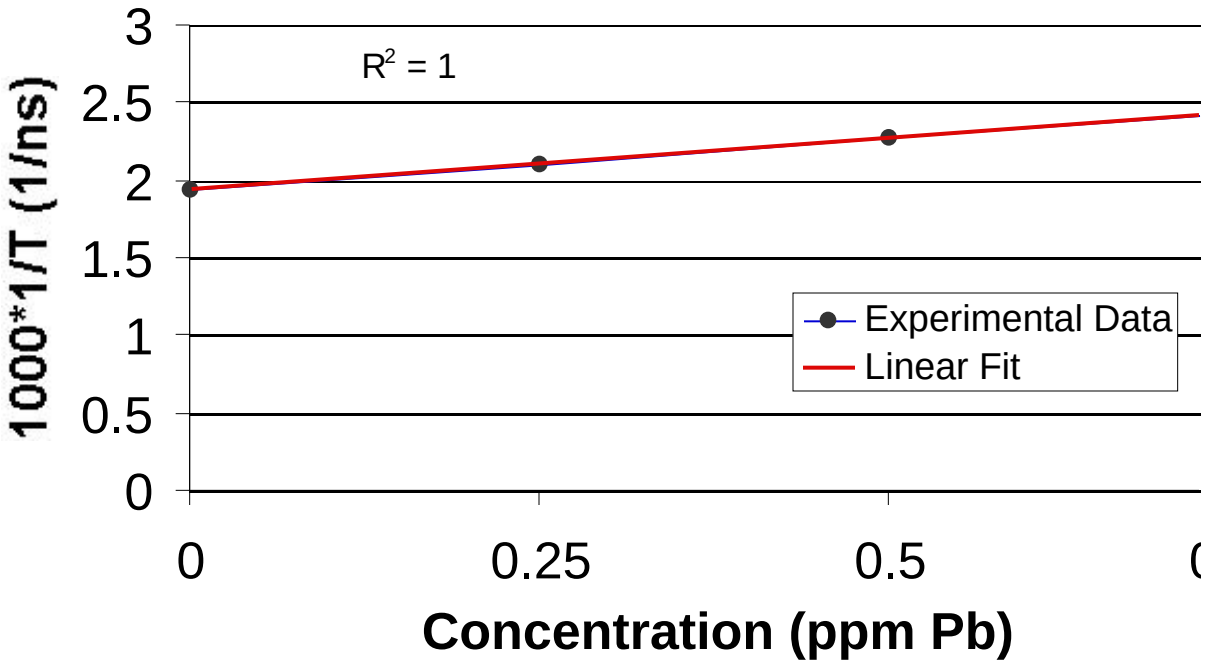
# Estimated
# ICP-CRS Detection Limits

| Element | (µg/m$^3$) | (~ppb) |
|---|---|---|
| Cd (229 nm) | 0.0008 | 0.002 |
| Hg (254 nm) | 0.28 | 0.7 |
| Pb (283 nm) | 0.016 | 0.04 |
| Sr (461 nm) | 0.00028 | 0.0007 |
| Mn (403 nm) | 0.012 | 0.03 |
| Tl (378nm) | 0.012 | 0.03 |
| Cr (425 nm) | 0.0036 | 0.009 |

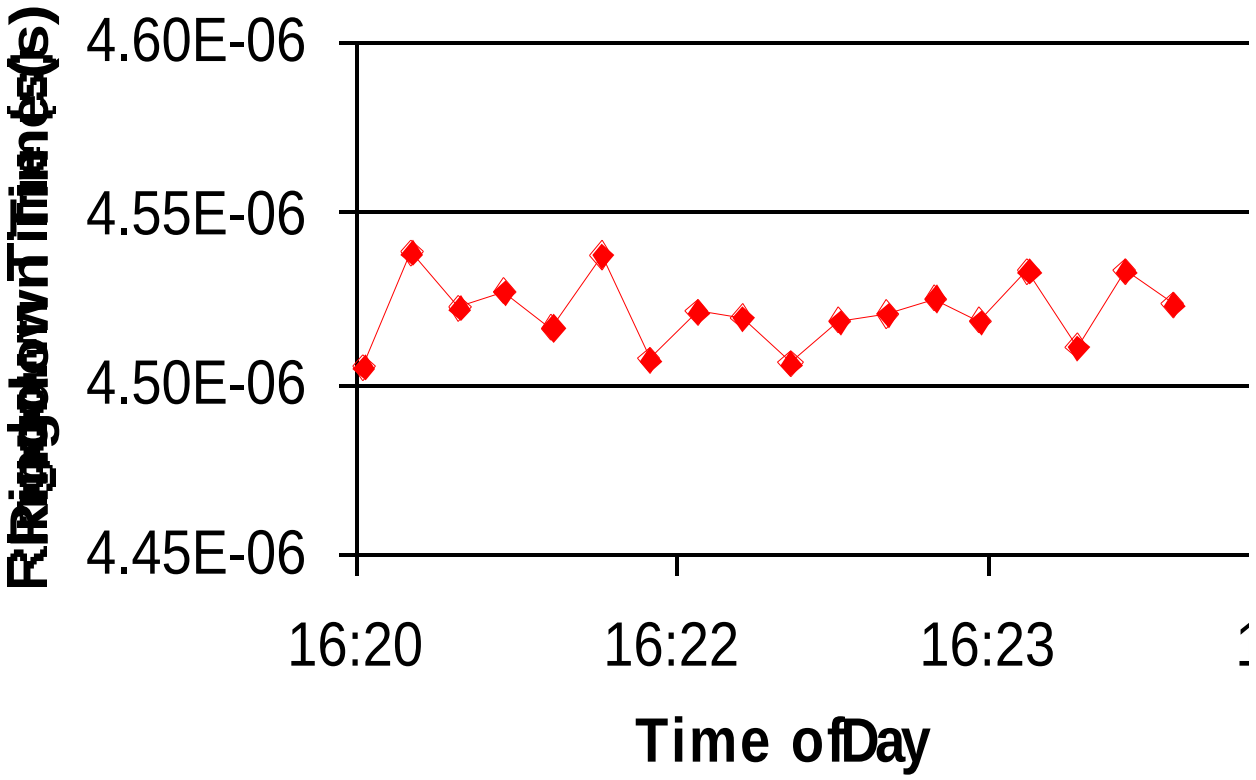
# Ringdown Detection of Lead In an ICP



# Inverse Ringdown Time versus Concentration



# Ringdown Time Stability (100 Averages)
# Standard Deviation = 0.2%



# Detection Limits

- WORK IN PROGRESS

# Path Forward

- Modify dye laser system for narrow linewidth operation
- Optimize ICP parameters (gas flows, observation height, RF power, etc.)
- Determine experimental detection limits for several heavy metals
- Graphite furnace atomization
- Air Plasma Off-Gas Emission Monitor

# Potential Applications of CRS to DOE Problems

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

# Publications & Presentations

- G. P. Miller and C. B. Winstead, Inductively-Coupled Plasma Cavity Ringdown Spectrometry. J. Anal. Atomic Spectro. 12, 907 (1997).
- G. P. Miller and C. B. Winstead, ICP-Cavity Ringdown Spectroscopy. 1997 European Winter Conference on Plasma Spectrochemistry, Gent, Belgium.
- C. B. Winstead, P. R. Jang, and G. P. Miller, “Continuous Emission Monitoring Using Cavity Ringdown Spectroscopy,” 34$^{th}$ Symposium on Engineering Aspects of Magnetohydrodynamics, Starkville, Mississippi, June 18-20, 1997.
- G. P. Miller and C. B. Winstead, Application of Cavity Ringdown to analytical analysis, FACSS Conf. Austin TX October 1998.