

Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors

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Introduction

- **Project Goal** – develop a fundamental understanding of Hg “re-emissions” from wet FGD systems
 - Seen as FGD outlet Hg^0 concentration > inlet Hg^0
 - Apparent reduction of Hg^{+2} removed in FGD absorber
 - Limits overall Hg removal by FGD system
- **Technical Approach** – conduct kinetics experiments, kinetics modeling, and bench-scale wet FGD model validation tests
- **Expected Benefits** – the ability to predict FGD re-emissions, and optimize FGD conditions to minimize or eliminate

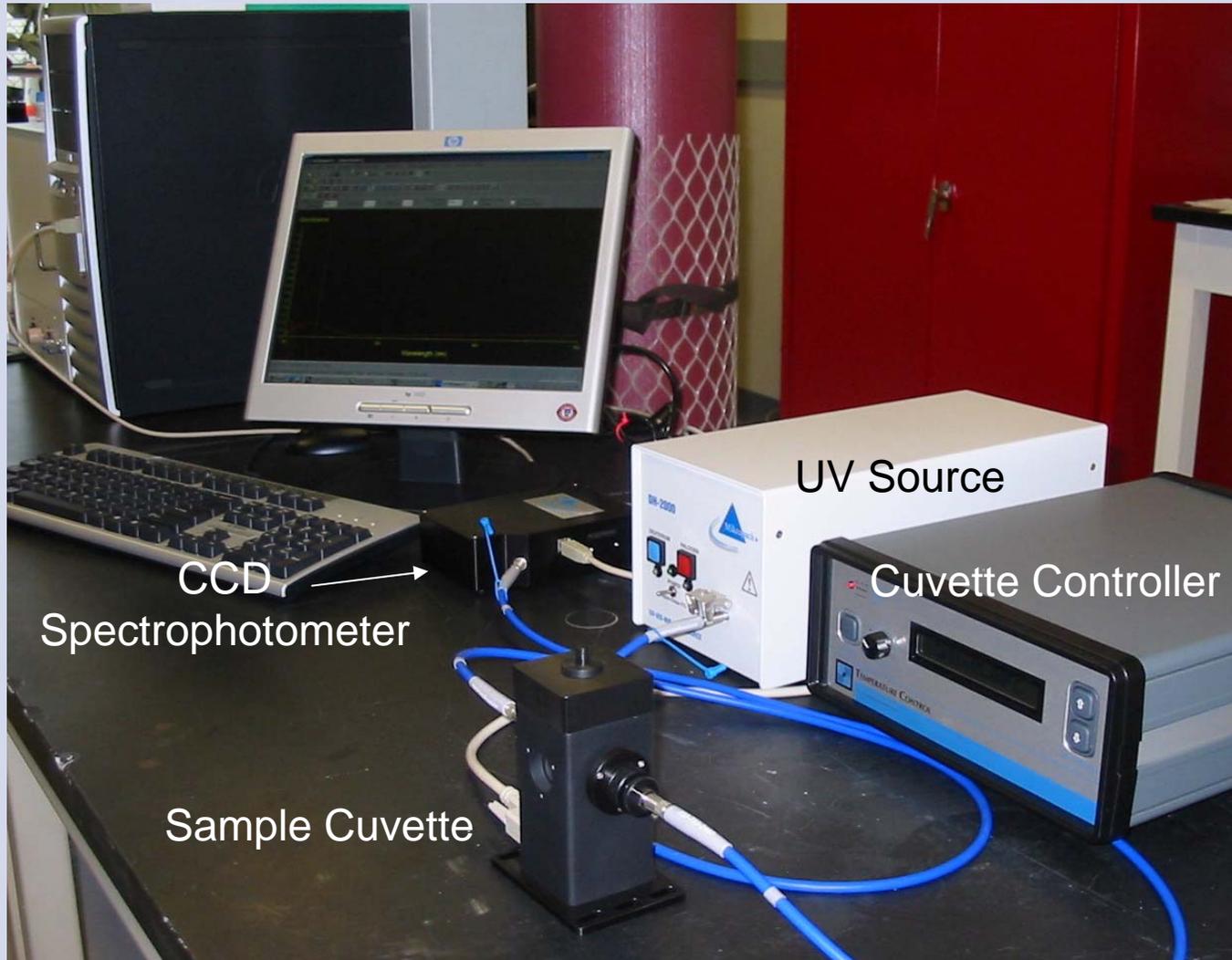
Main Project Elements

- Measure kinetics using both spectroscopy of the Hg-Sulfite complex reactants, and production / stripping of Hg^0
- Extend reaction conditions to include presence of chloride, thiosulfate, additives and into the FGD pH region
- Construct a kinetics model which describes the results
- Test the model using the URS bench scale FGD

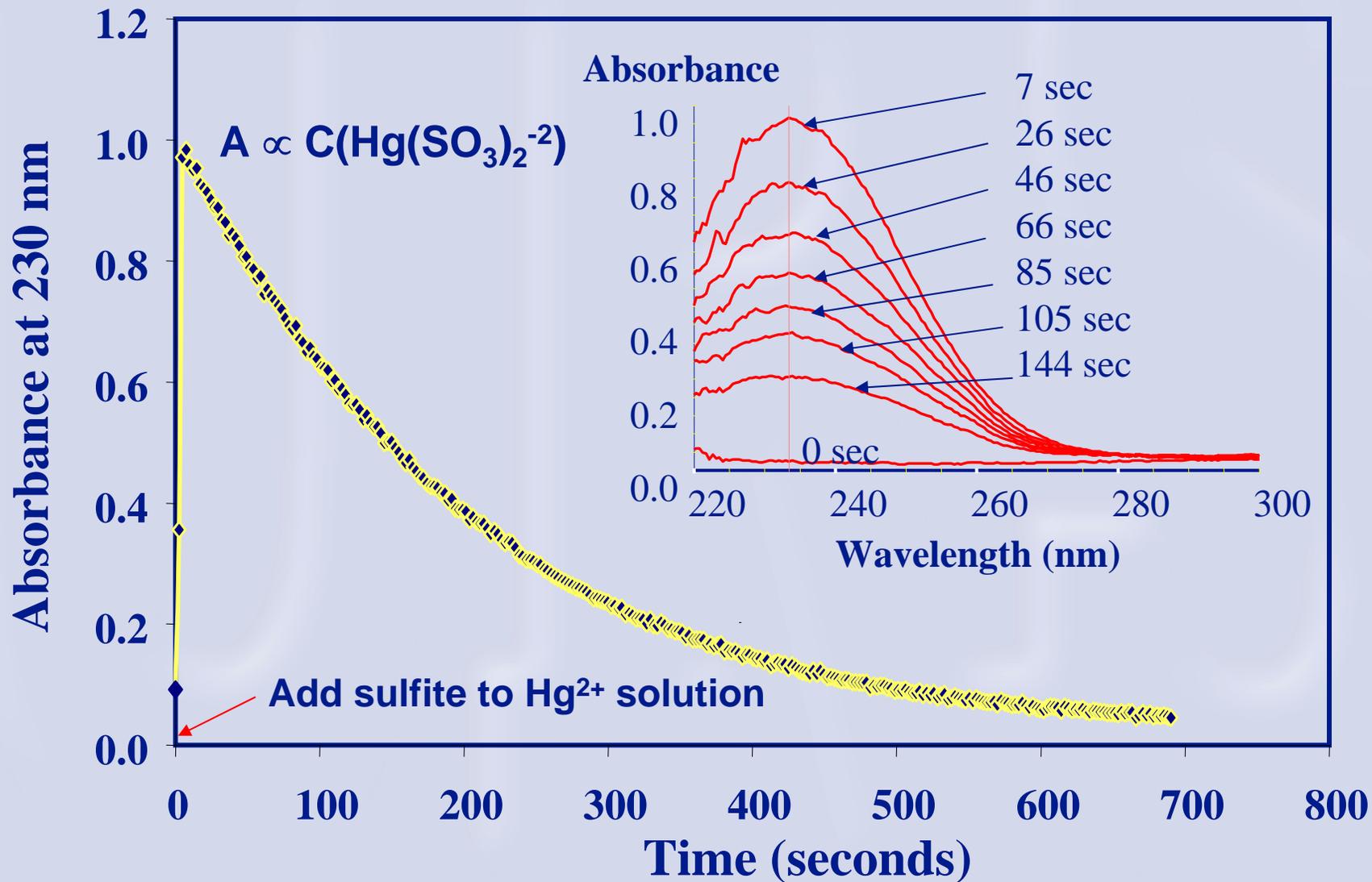
Main Chemical Reactions for Hg Emission without Chloride

- Overall reaction:
 - $\text{Hg}^{+2} + \text{HSO}_3^- + \text{H}_2\text{O} \rightarrow \text{Hg}^0\uparrow + \text{SO}_4^{-2} + 3 \text{H}^+$
- Main pathway is through mercuric-sulfite complexes:
 - $\text{Hg}^{+2} + \text{SO}_3^{-2} \leftrightarrow \text{HgSO}_3$
 - $\text{HgSO}_3 + \text{SO}_3^{-2} \leftrightarrow \text{Hg}(\text{SO}_3)_2^{-2}$
- Equilibrium favors $\text{Hg}(\text{SO}_3)_2^{-2}$ in presence of excess sulfite
- But only HgSO_3 decomposes to give reduction of Hg^{+2} :
 - $\text{HgSO}_3 + \text{H}_2\text{O} \rightarrow \text{Hg}^0\uparrow + \text{SO}_4^{-2} + 2 \text{H}^+$

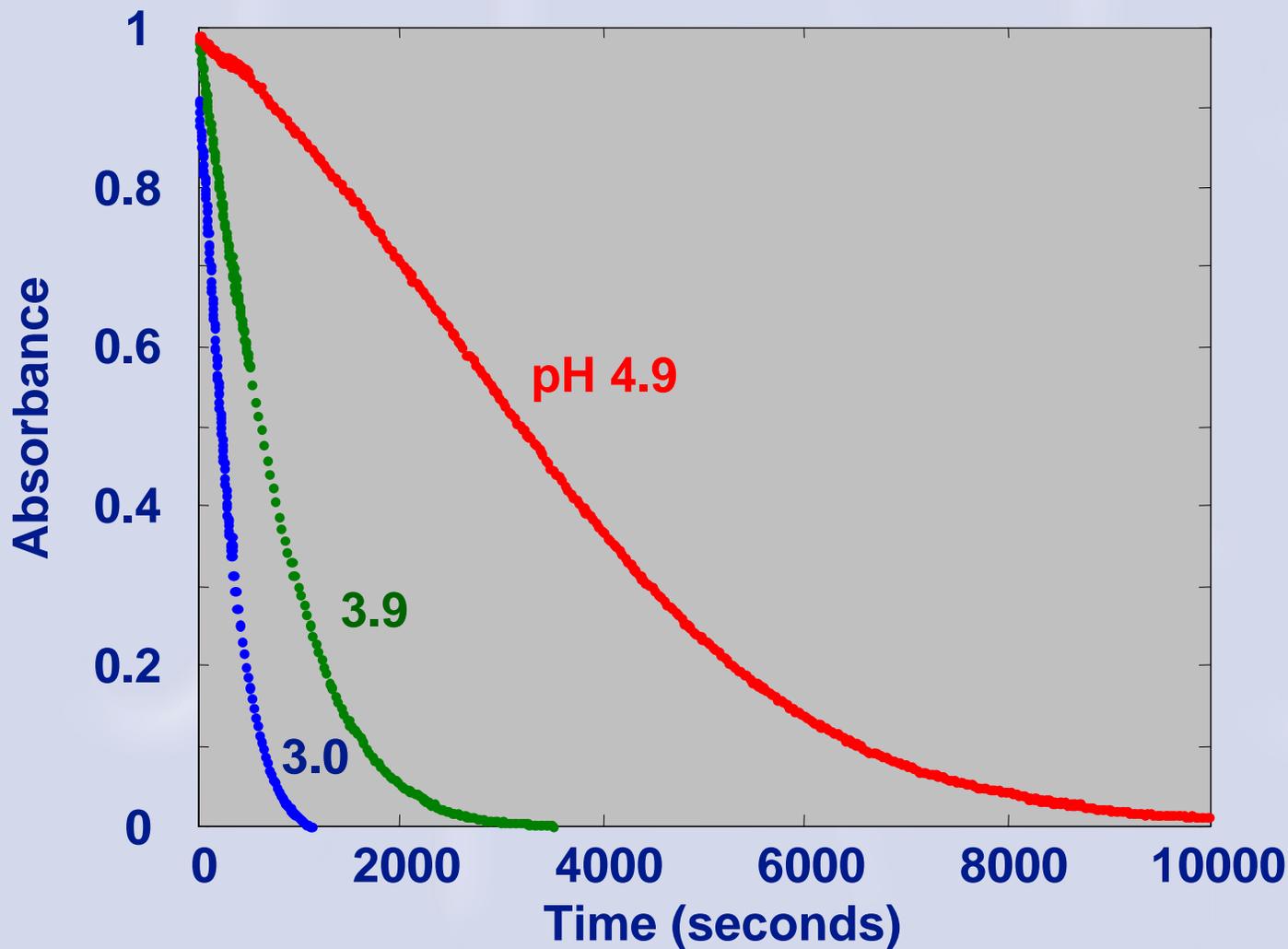
URS UV/Visible Spectrophotometer



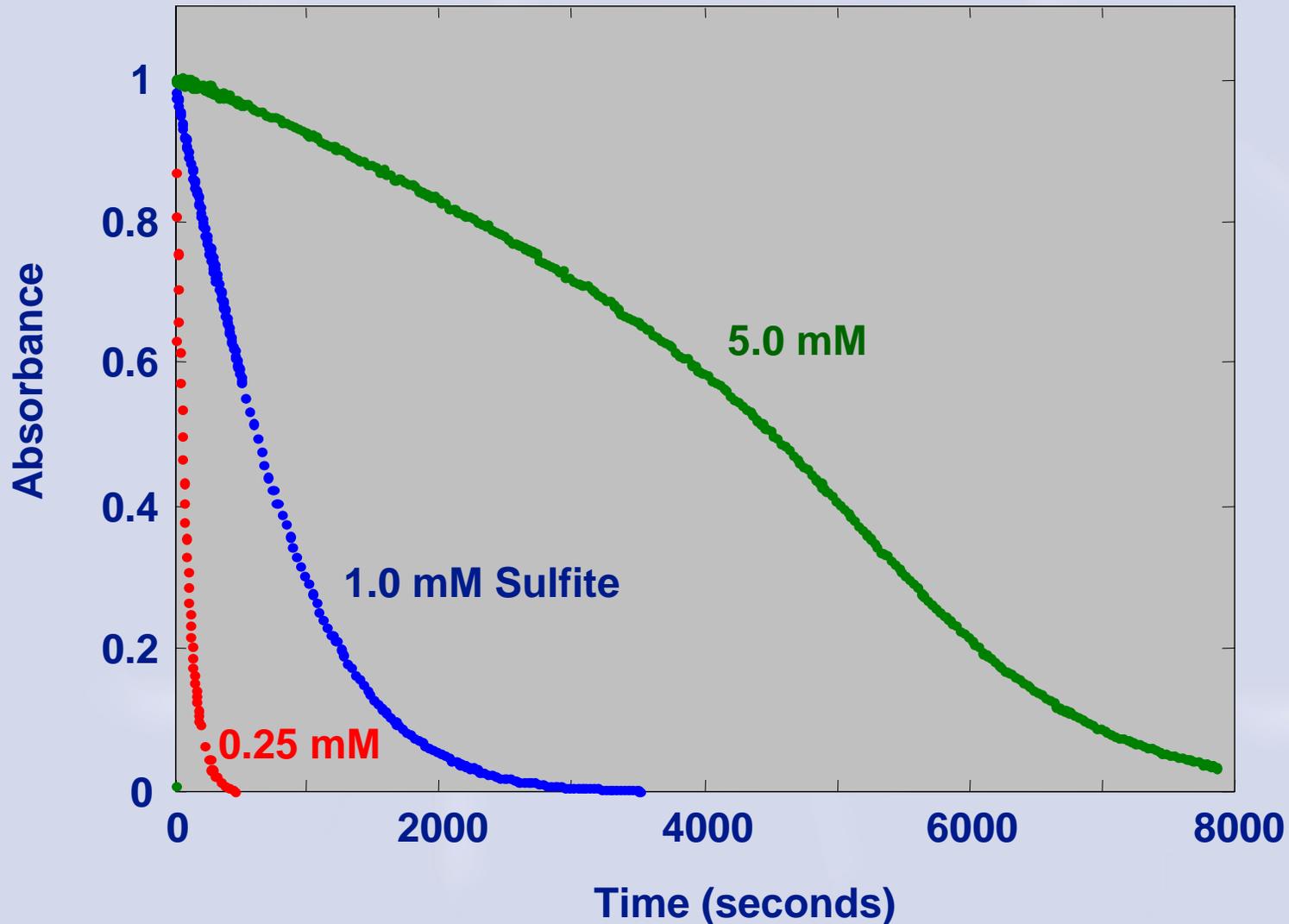
Example Spectra and Rate Curve



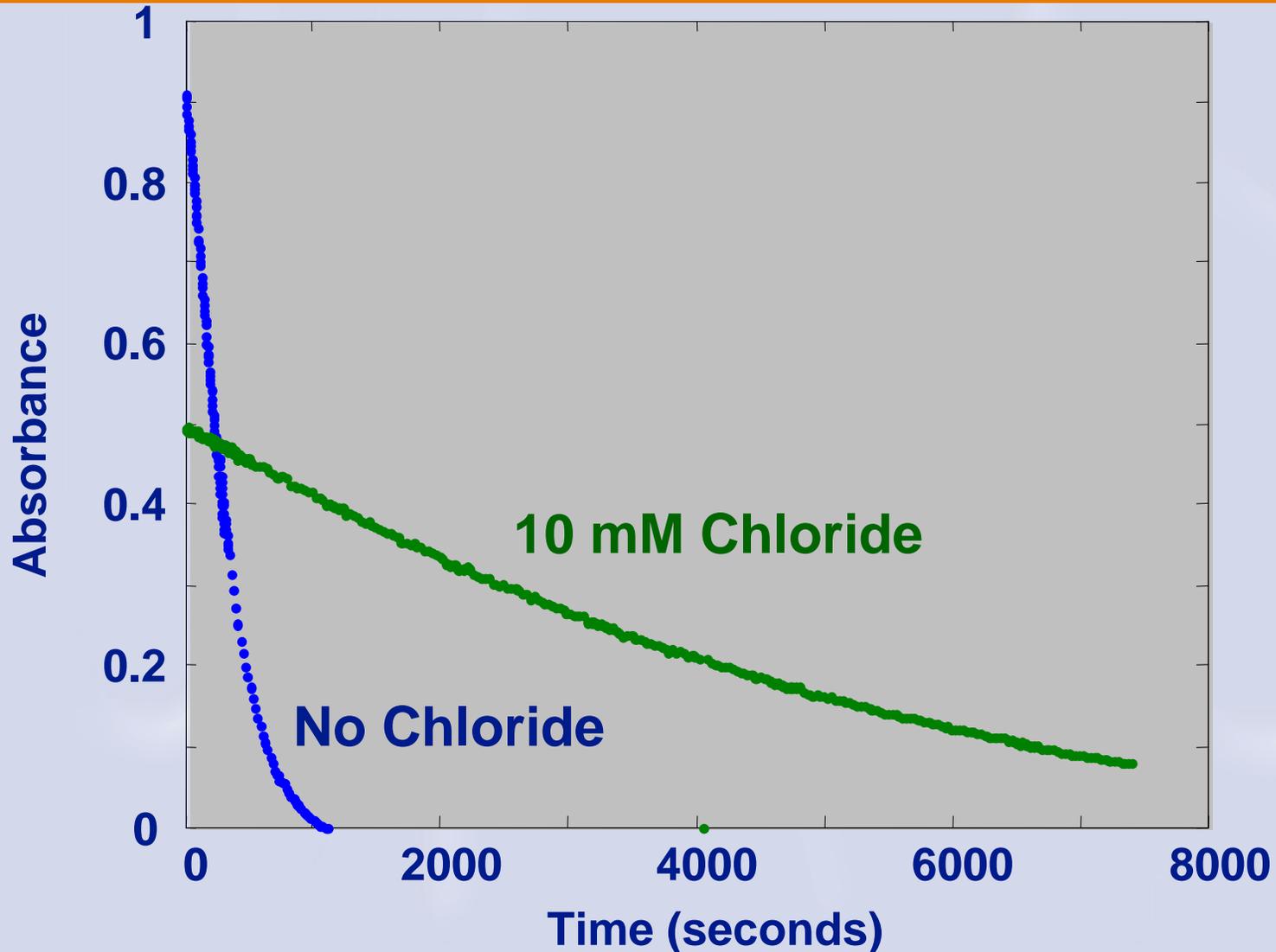
Effect of pH on Rate Curves without Chloride. 1.0 mM sulfite, 55° C, 40 microM Hg(II)



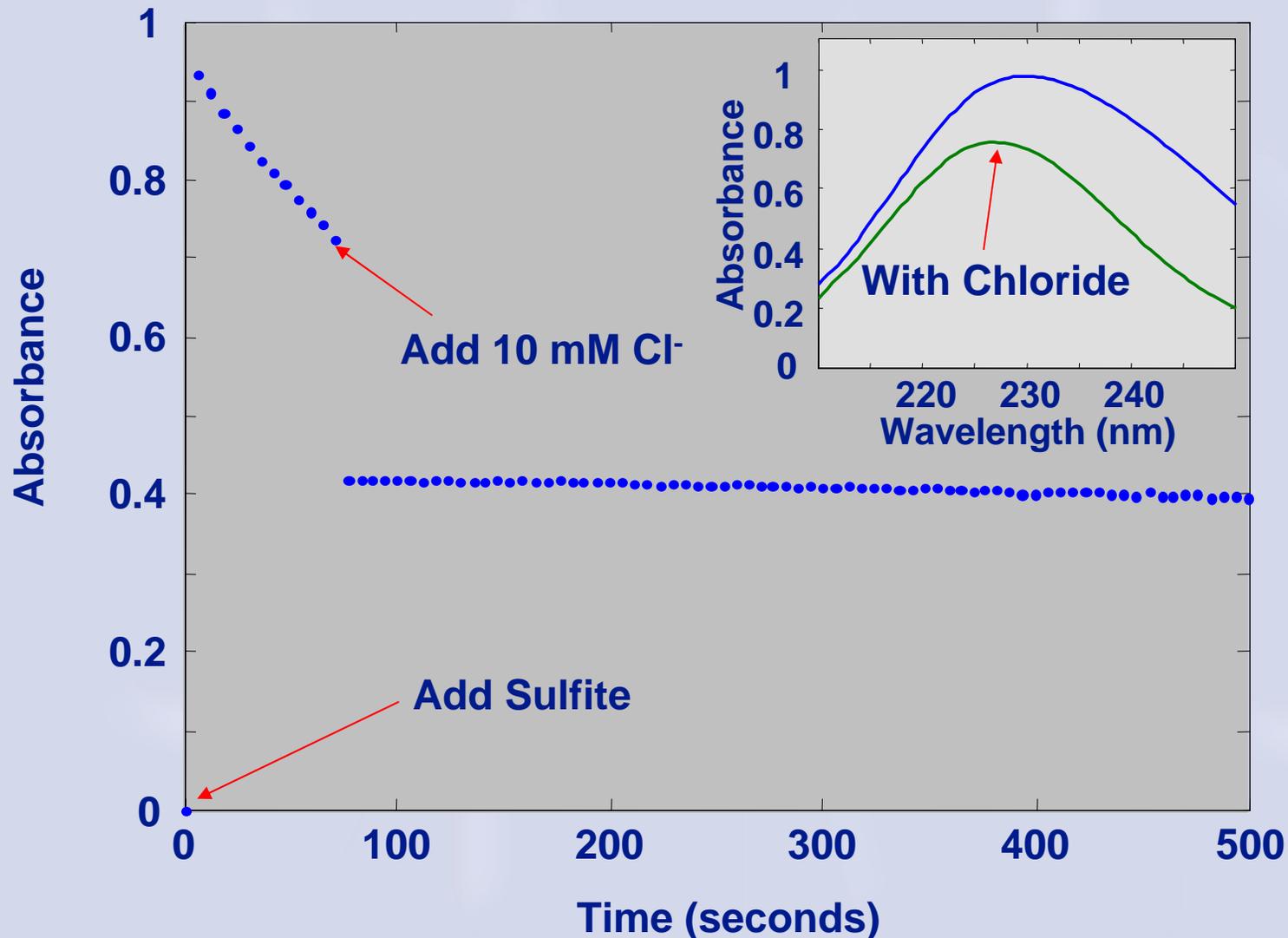
Effect of sulfite on rate curves without chloride; pH 3.9



Effect of Chloride on Rate Curve at pH 3.0 and 1.0 mM Sulfite



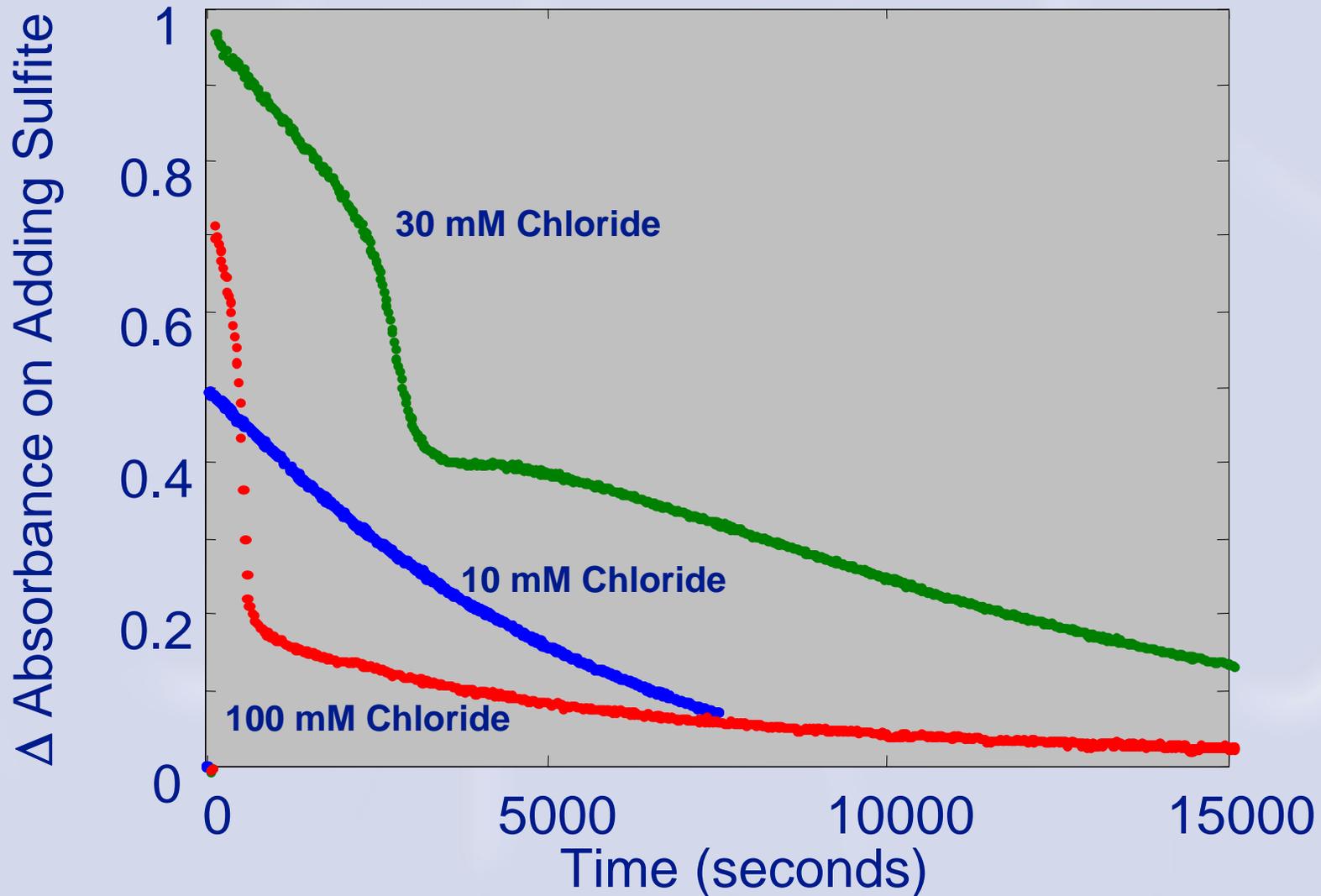
Adding chloride during the run; pH 3.0; 1.0 mM sulfite



Reaction Mechanism Observations

- Chloride evidently causes a change of mechanism - new intermediate, ClHgSO_3^-
- But also observe complex “composite” reaction behavior without chloride
- “Slow” reaction conditions tend to give complex response such as a large increase in reaction rate after an initial “induction time”
- Several factors affecting this behavior are under investigation

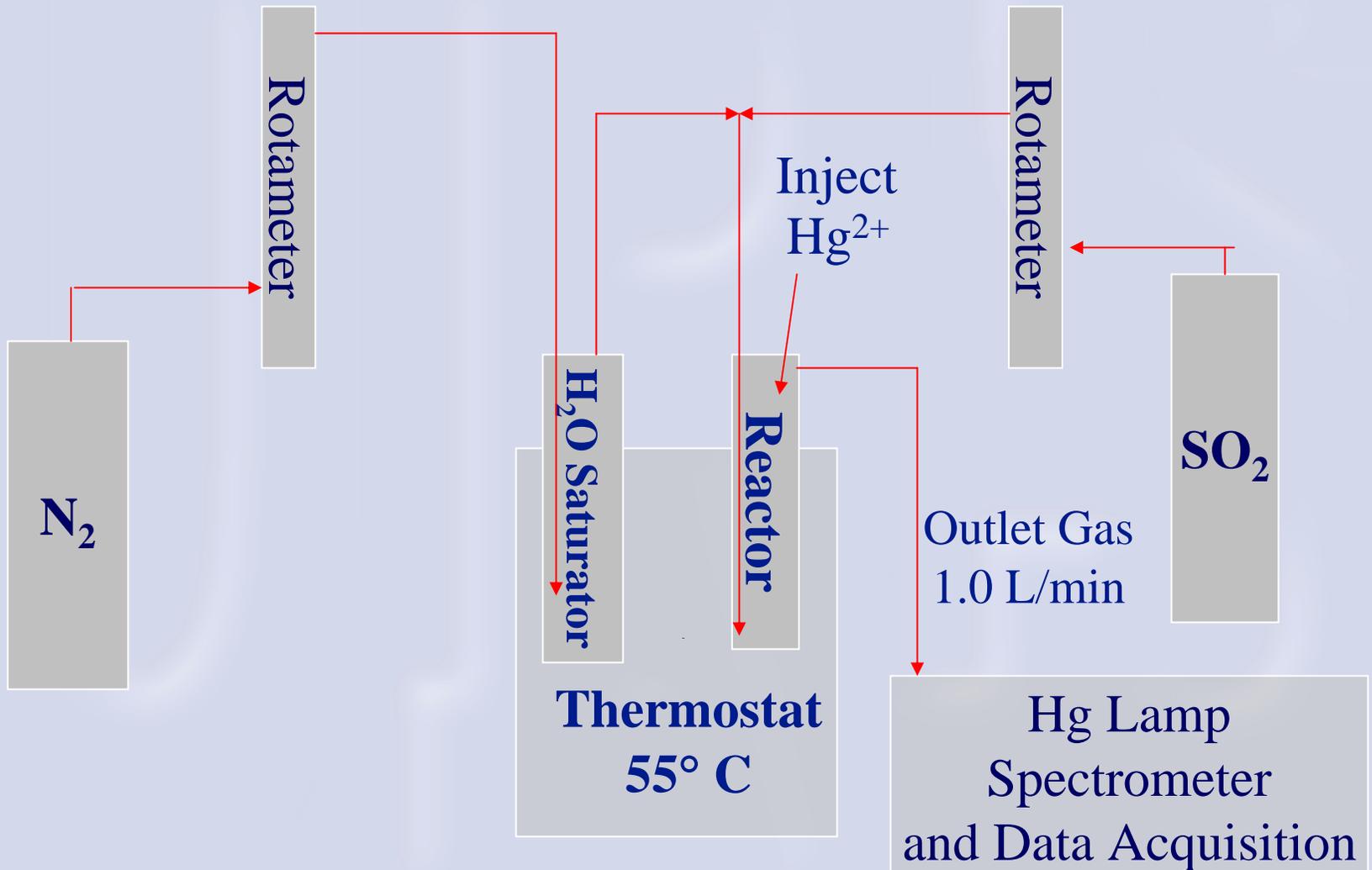
Induction Time Behavior in Chloride Solutions



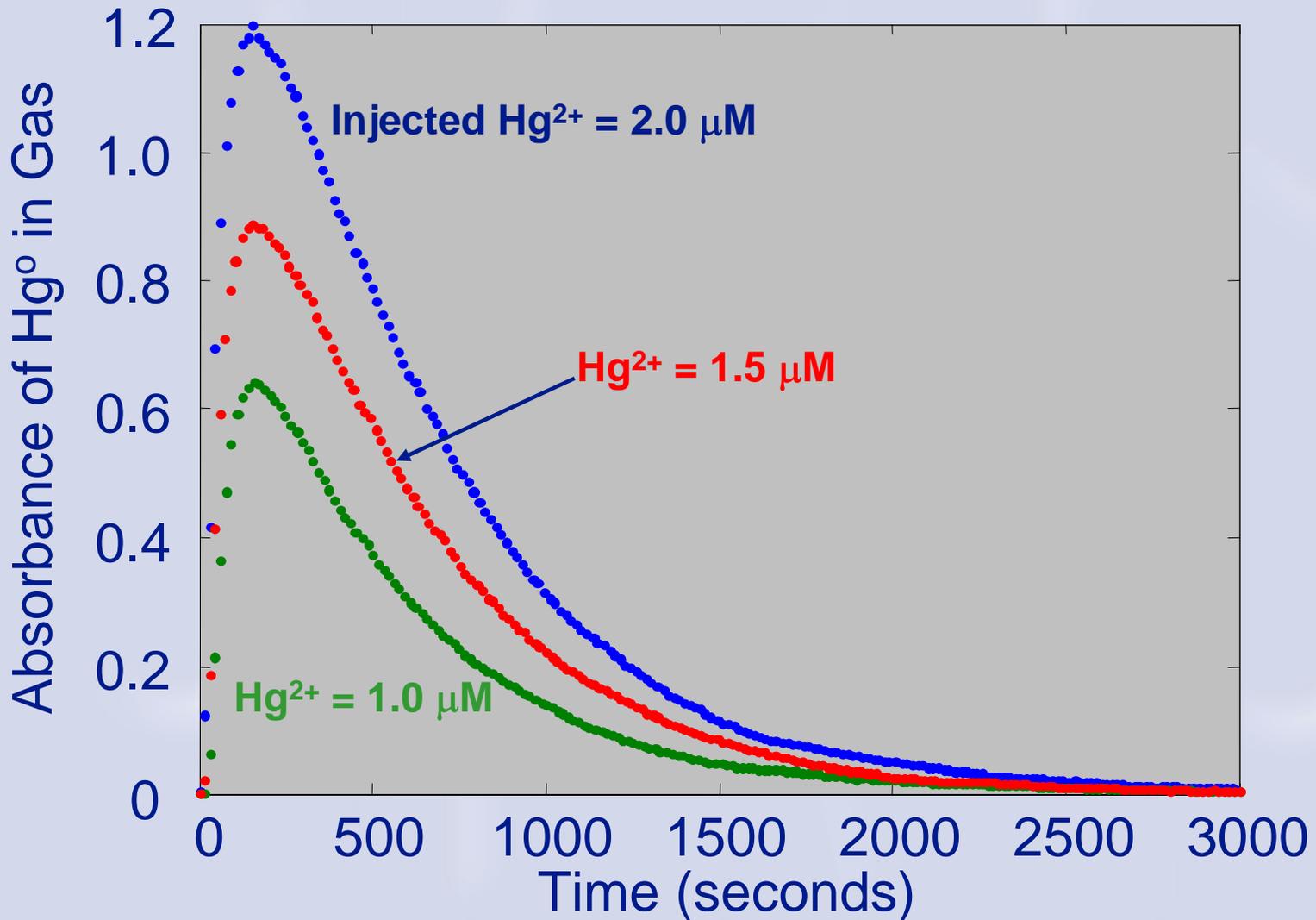
Stripping Method for Measuring Hg^0 Emissions from Test Solutions

- Continuously measures Hg^0 in gas phase as it is emitted following Hg^{++} injection and stripping from reactor
- Able to use low “FGD levels” of Hg^{++} in reactor: 0.5 – 2 micromolar
- Getting close material balances on Hg^{++} added, Hg^0 measured in gas phase, and Hg left in liquid (which is usually negligible)
- Exponential decay rates are independent of initial Hg^{2+} concentration, matching spectroscopic results

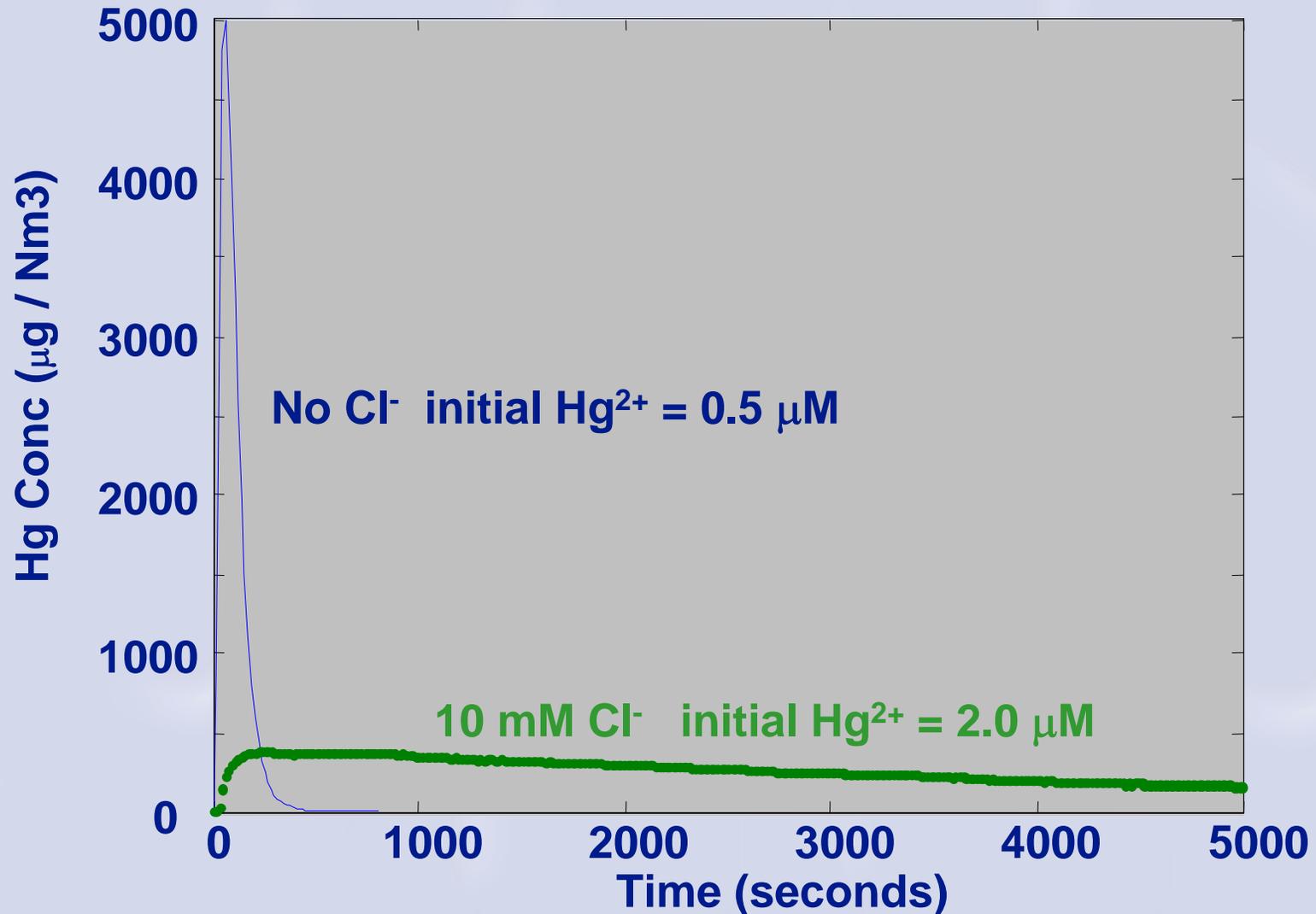
Hg⁰ Stripping Kinetics Apparatus



Stripping Runs at Different Initial Hg^{2+} Concentrations



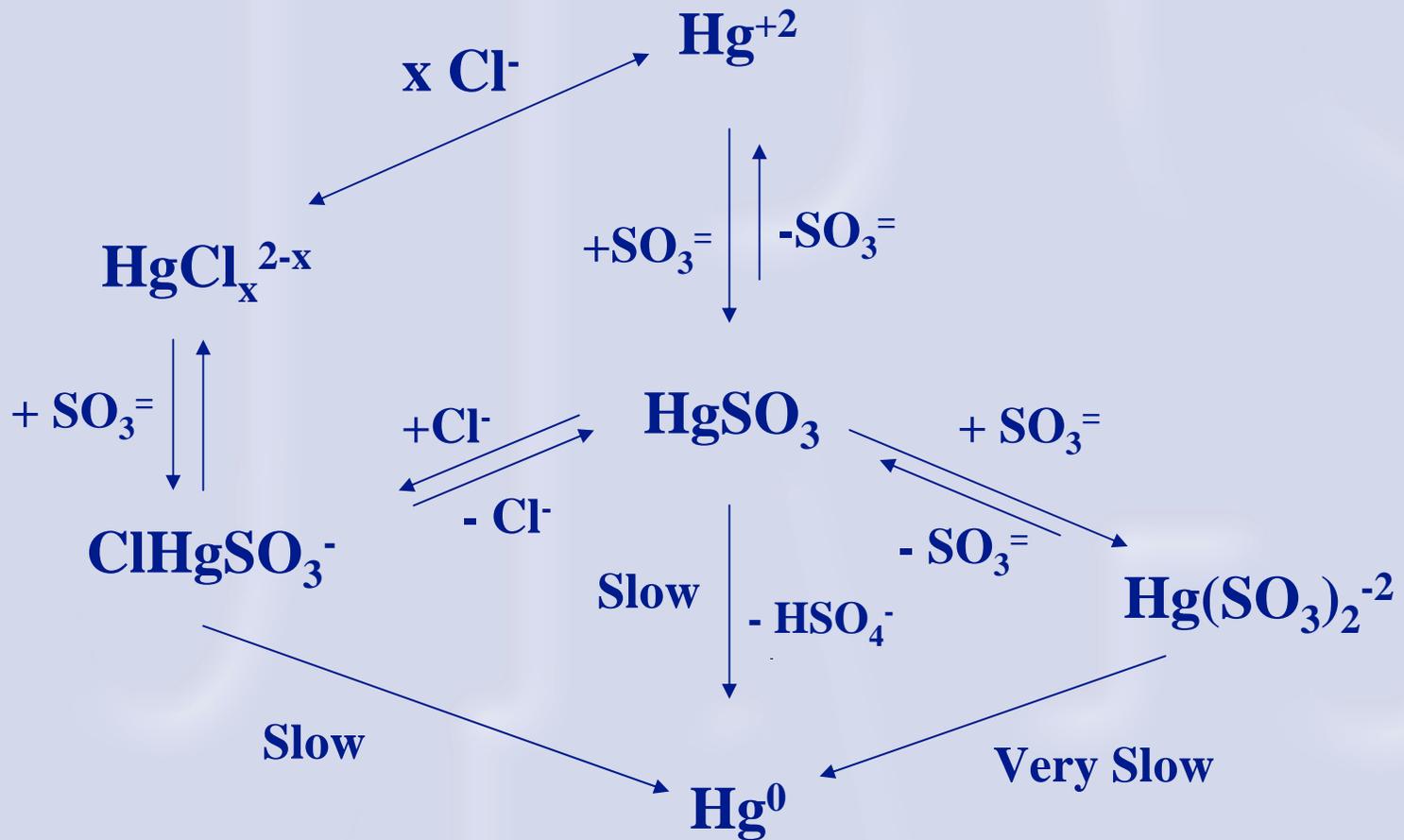
Effect of Chloride on Hg⁰ Stripping Kinetics



Kinetics Modeling

- URS modeling software maintains database of reactions, rate constants, and reaction conditions - initial concentrations, pH, temperature
- Calculates concentration-time profiles for all chemical species and intermediates
- Develop model by comparing experimental and calculated results while varying rate parameters until results match experiment over a wide range of conditions

Major Reaction Pathways



Project Status and Conclusions

- Developed experimental methods for following reactants and products independently
- Determining effects of pH, sulfite, temperature, ionic strength, and other "FGD" components on reaction rates
- Chloride has major effects on reaction rates and mechanism
- New reaction intermediates proposed; in process of constructing model using these mechanisms