Ion Chromatography for Persulfate and Total Oxidant Demand Analyses

J. Rossabi

B. Fasolt

REDOX TECH, LLC

Overview

- History Persulfate (Things you may know)
- In Situ Chemical Oxidation, Free Radicals, and TODs (Things you probably know)
- Analytical Methods (Things to think about)
- Features
- Data (Things I worry about)
- Summary and Future Work

History Persulfate (peroxydisulfate $S_2O_8^{2-}$)

- Prior to 1940s - Like many oxidizers (e.g., hydrogen peroxide) used initially for laundry and other bleaching. (ammonium, potassium, sodium)
- 1950s – Used as an initiator for polymers (e.g., teflon, PVC, polystyrene, neoprene)
- 1970s - Metal Etching (printed circuit boards, etc.)
- Other (cosmetics, chemical prep, photog.)
- Environmental (~10%)

Oxidation

- Taking electrons away from a molecule oxidizes it.
- May make the molecule more stable or less stable and susceptible to further oxidation.
- $C^{(-IV)}H_4 \rightarrow$ (VCl, DCE, TCE, PCE, etc.) $\longrightarrow C^{(IV)}O_2$
- May need to add energy to system
- Oxidants add energy to system

Catalyzed Oxidant Adds More Energy

- $S_2O_8^{2-}$ + energy (heat, light, etc.) ⟶ 2SO4●$^-$
- Sulfate Radical has lots of energy, electrons ready to react.

Radicals

- Can produce other radicals including organic radicals:
- $SO_4\bullet^- + H_2O \longrightarrow HSO_4^- + \bullet OH$
- $SO_4\bullet^- + CH_3OH \longrightarrow HSO_4^- + CH_2\bullet OH$

From Bartlett and Cotman, 1949.

REDOX TECH, LLC

Oxidation Potential

- Hydroxyl radical ●OH 2.7V
- Sulfate radical $SO_4 \bullet^-$ 2.6V
- Ozone O_3 2.2V
- Persulfate anion $S_2O_8^-$ 2.1V
- Hydrogen peroxide H_2O_2 1.8V
- Permanganate ion MnO_4^- 1.7V
- Peroxymonosulfate anion HSO_5^- 1.4V

REDOX TECH, LLC

Mineralization of Benzene

- 15:1 mol/mol (46:1 g/g) of persulfate to benzene
- For 20m x 10m x 5m contaminated volume, @1 mg/l benzene (0.35 porosity):
- Therefore need 16 kg persulfate to oxidize contaminant (or 0.01 g oxidant/kg soil)…
- **but contaminant doesn't usually produce the majority of the oxidant demand**

REDOX TECH, LLC

Total Oxidant Demand Tests

- Add oxidant to representative soil/groundwater, measure how much is consumed in time.
- Majority of oxidant demand in subsurface is from rocks (reduced minerals) aqueous or solid phase
- Rest from organic contaminant and natural organic material and self-demand
- Note: NAPL and large amounts of NOM may produce very large demand.

Generalized TOD Results

Geochem Status	Occurrence	Range of TOD (g/kg)
Low metals	Limestone or clean sand	<0.1 to 0.5
Low NOM	Limestone or clean sand	<0.1 to 0.5
Oxic	Elevated dissolved O_2	<0.1 to 1.0
Mildly reducing	Elevated ferrous iron	<0.1 to 2.0
Moderately reducing	Depressed nitrate but elevated sulfate	<0.1 to 5.0
Strongly reducing	Elevated methane or ethene (CVOCs)	<0.1 to 15.0

From Haselow et al., *Remediation*, Autumn 2003.

REDOX TECH, LLC

Analytical Methods

- Permanganate is usually pretty easy – color change (watch out for muddy waters).
- Persulfate – add something to react with oxidant, colorimetric methods:
  - Good stuff, has worked for around a century… for all prior persulfate applications.

Analytical Methods (brief digression)

- Specific to analyte of interest and consistent response
  - Environmental matrices are complicated, interfering compounds likely.
- Repeatable correlative response to quantity
- Appropriate dynamic range (sensitivity)
- Reasonable cost

Specificity

- Best methods probe molecular components and their unique characteristics.
  - Some spectroscopies – IR, Raman, AA, ESR, etc.
- Next best – nearly unique properties (sorption - relative BP, electronegativity, etc.)
  - Chromatography (gas, liquid)
- Acceptable in controlled situations – broad properties (energy absorption, redox rxns)

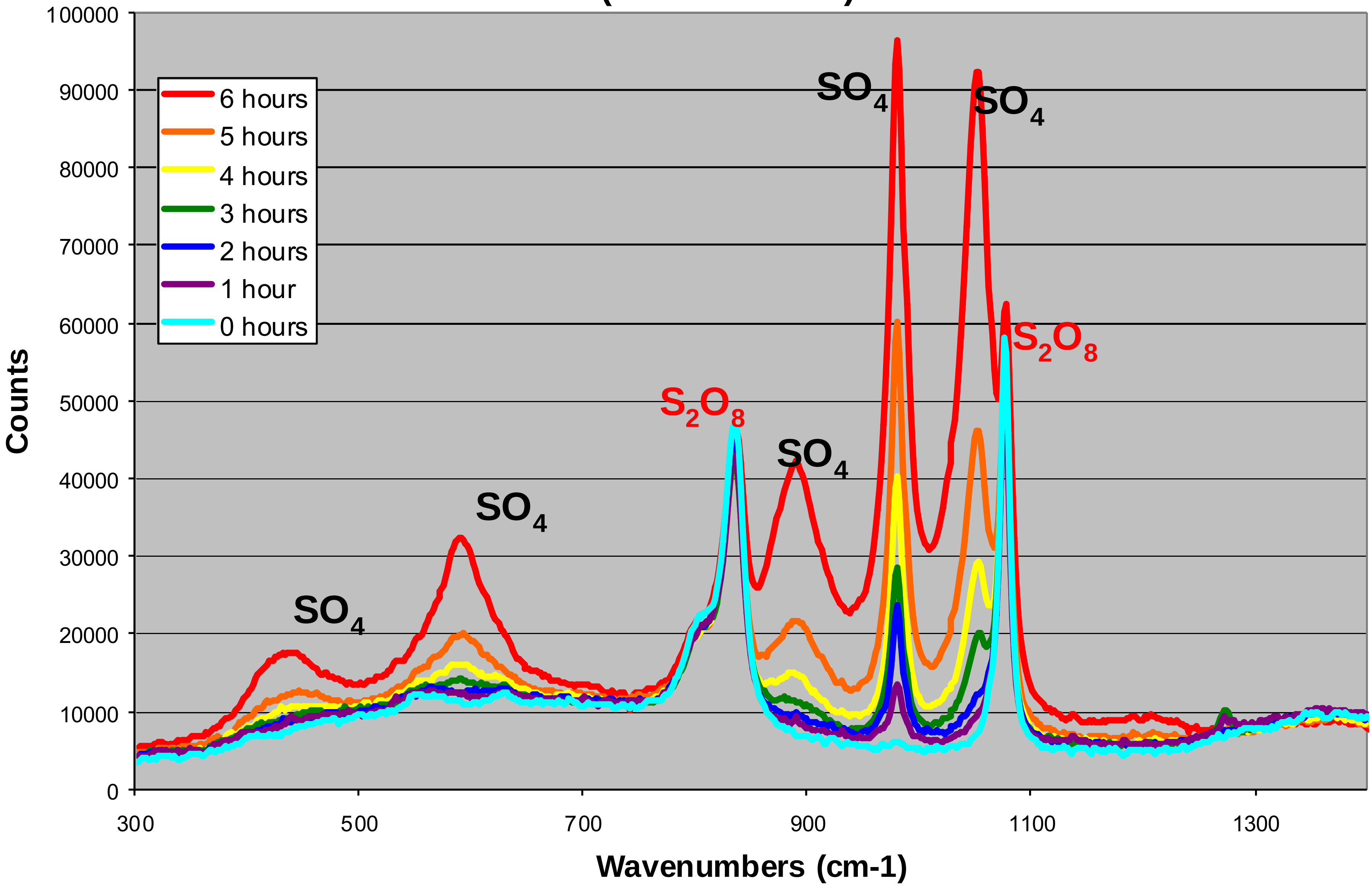
ESR or EPR (tech geek dream)

- Electron Spin Resonance (ESR) or Electron Paramagnetic Resonance (EPR)
- Probe molecules, atoms for unpaired electrons (radicals) spin > 0
- Like nuclear magnetic resonance only use GHz (microwave) RF energy absorbance rather than MHz energy
- A bit expensive.

Raman Spectroscopy (less expensive, but still get to use lasers)

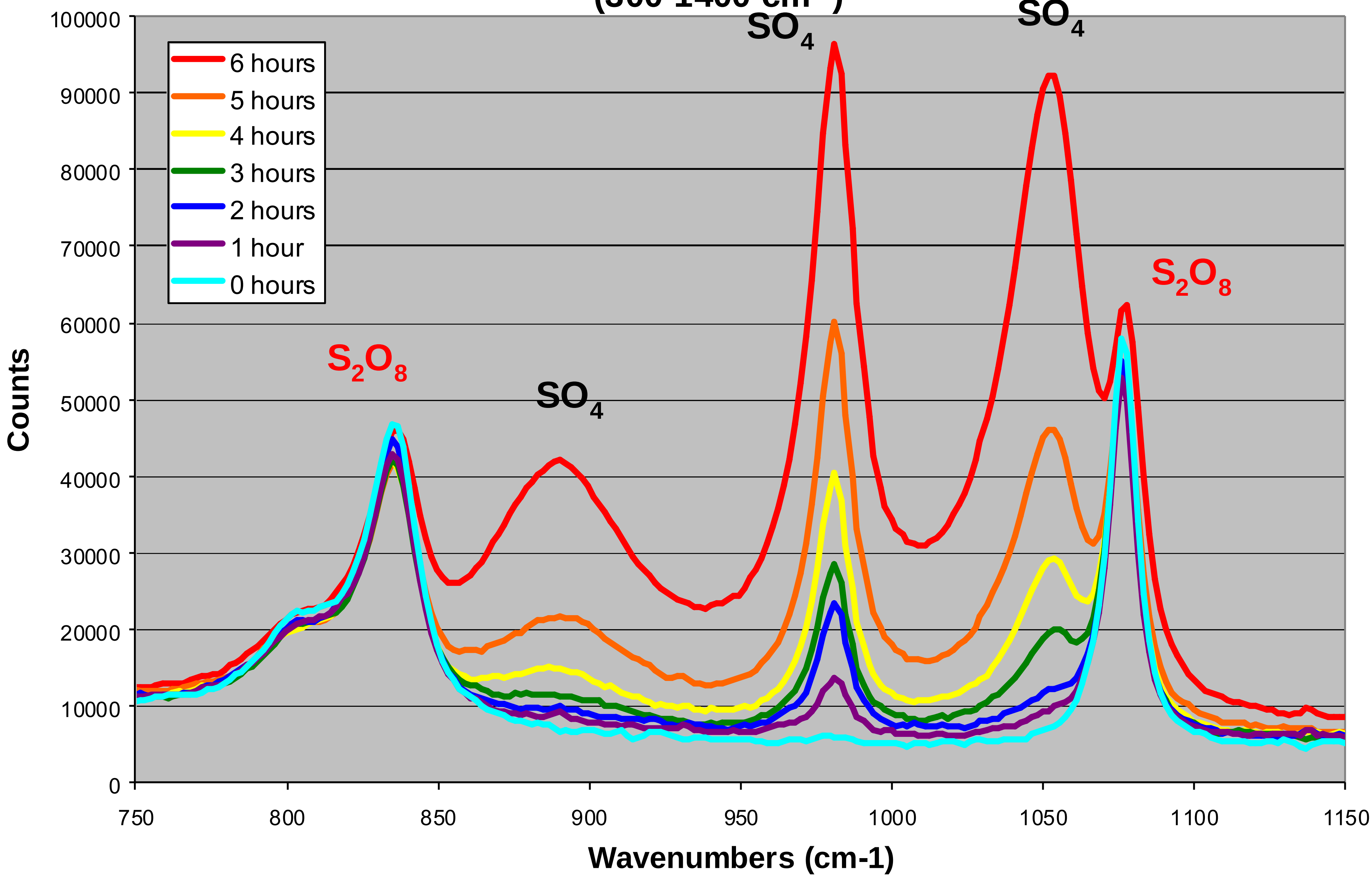
- Vibrational energy of bonds
- Specific and consistent response
- Reasonable cost – simple, fast non-invasive measurement
- Reasonable sensitivity
- Unfortunately: Inconsistent response to quantity.
- Maybe resonance effects
- IR spectroscopy may work better.
- Maybe use sulfate response.

Raman Spectra 5 wt % Solution Heat Time Series
(300-1400 cm^{-1})



REDOX TECH, LLC

Raman Spectra 5 wt % Solution Heat Time Series
(300-1400 cm^{-1})



REDOX TECH, LLC

Persulfate TOD/Measurements

- Ferric Thiocyanate
- Ferrous ammonium sulfate hexahydrate plus KPerm back titration
- IC for sulfate
- Ion Pair Chromatography

REDOX TECH, LLC

Ferric Thiocyanate Method

- Colorimetry method used by CHEMetrics kits and many labs, often with spectrophotometer.
- Excess ferrous iron, ammonium thiocyanate mixed into acidic solution containing persulfate.
- Persulfate oxidizes ferrous to form ferric thiocyanate- develops red-orange color proportional to original persulfate concentration.
- Interferences: ferric iron, any substance that can oxidize iron to ferric or (e.g., ozone, H2O2), Cu2+, peracetic acid.
- Measurement range 0-70 mg/l.

FASH/$KMnO_4$ Titration

- Assume persulfate in sample and add a known excess of ferrous iron (ferrous ammonium sulfate hexahydrate or FASH).
- Persulfate consumed by oxidizing some of ferrous to ferric in acidic solution.
- Remaining ferrous is oxidized by permanganate titration.
- Persulfate back calculated by known quantity of FASH added and permanganate titration.
- Interferences: ferrous iron, any substance that can oxidize FASH to ferric (e.g., ozone, H_2O_2).

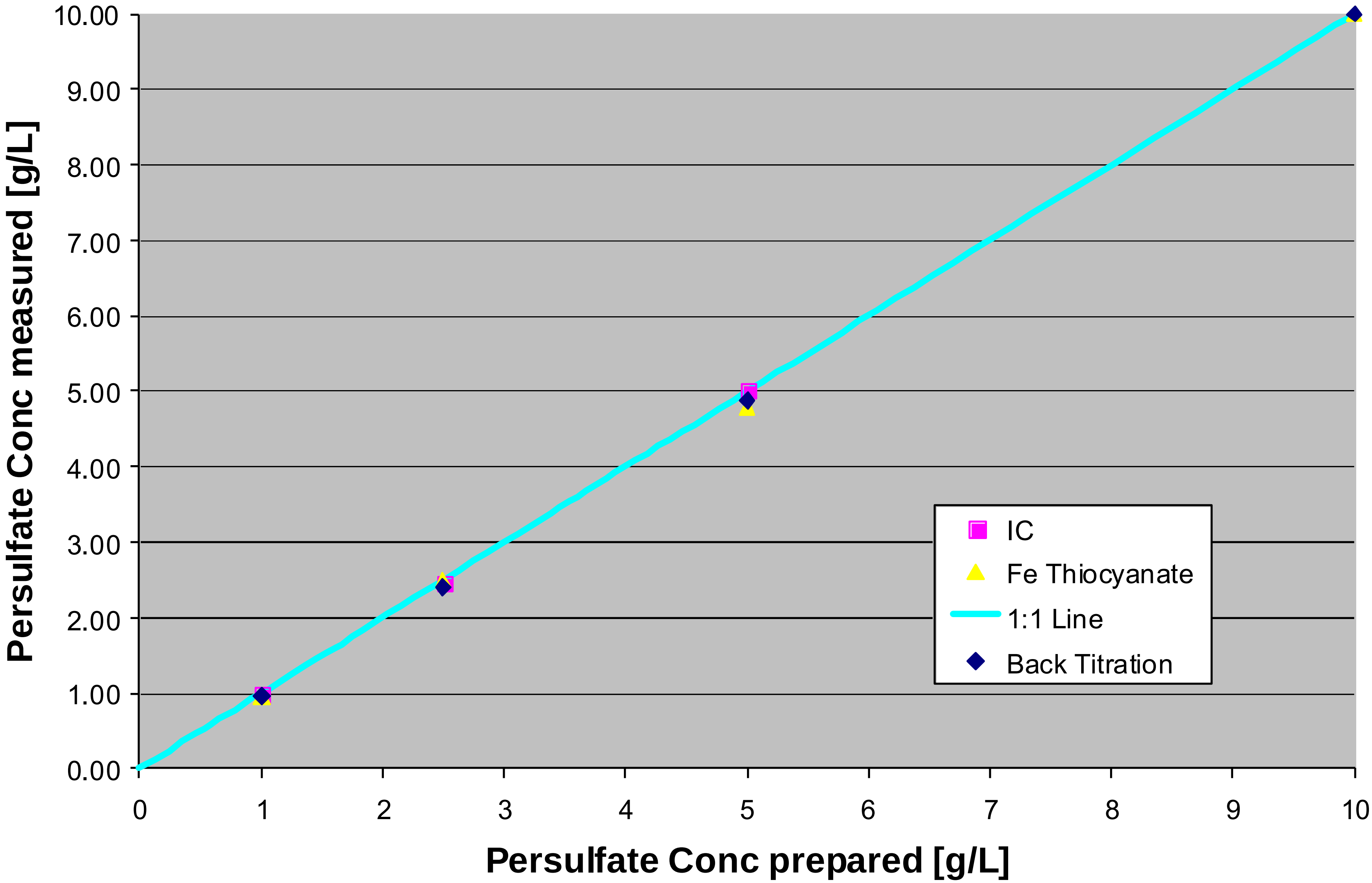
Ion Pair Chromatography
(after Weiss, 1995)

- A lipophilic mobile phase (e.g., TBAOH) interacts with target solute ion (e.g., sulfate, persulfate, etc.) and is retained on non-polar column.
- Either the lipophile complexes with the solute and then reversibly sorbs to the stationary phase on the column, or
- Lipophile adsorbs to stationary phase making it an ion exchange medium to react with solute, or
- Both. Sometimes organic modifiers are added to shorten retention times by competitive sorption.
- Measurement range 0-500 mg/l.

Theoretical Methods Comparison

- Ferric thiocyanate
  - The more ferric in or added to system, the higher the persulfate concentration. Should be OK in water.
- FASH, KPerm backtitration
  - The more species present that can consume KPerm (additional Fe(II) or Fe (0)), the lower the persulfate concentration. Should be OK for TOD testing.
- IC
  - Specifically measures persulfate and sulfate based on sorption and desorption to column and conductivity.

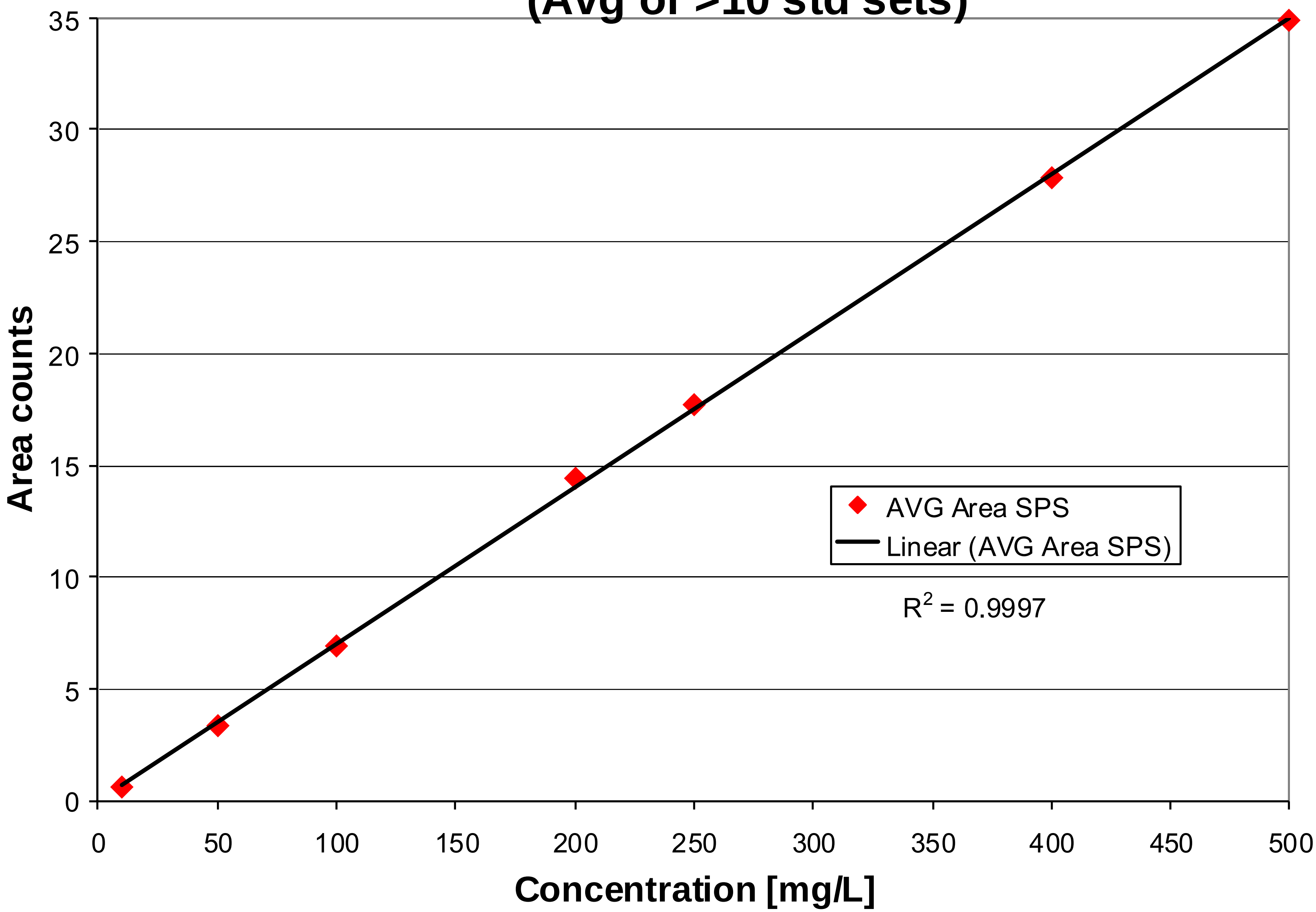
Standards Comparison



REDOX TECH, LLC

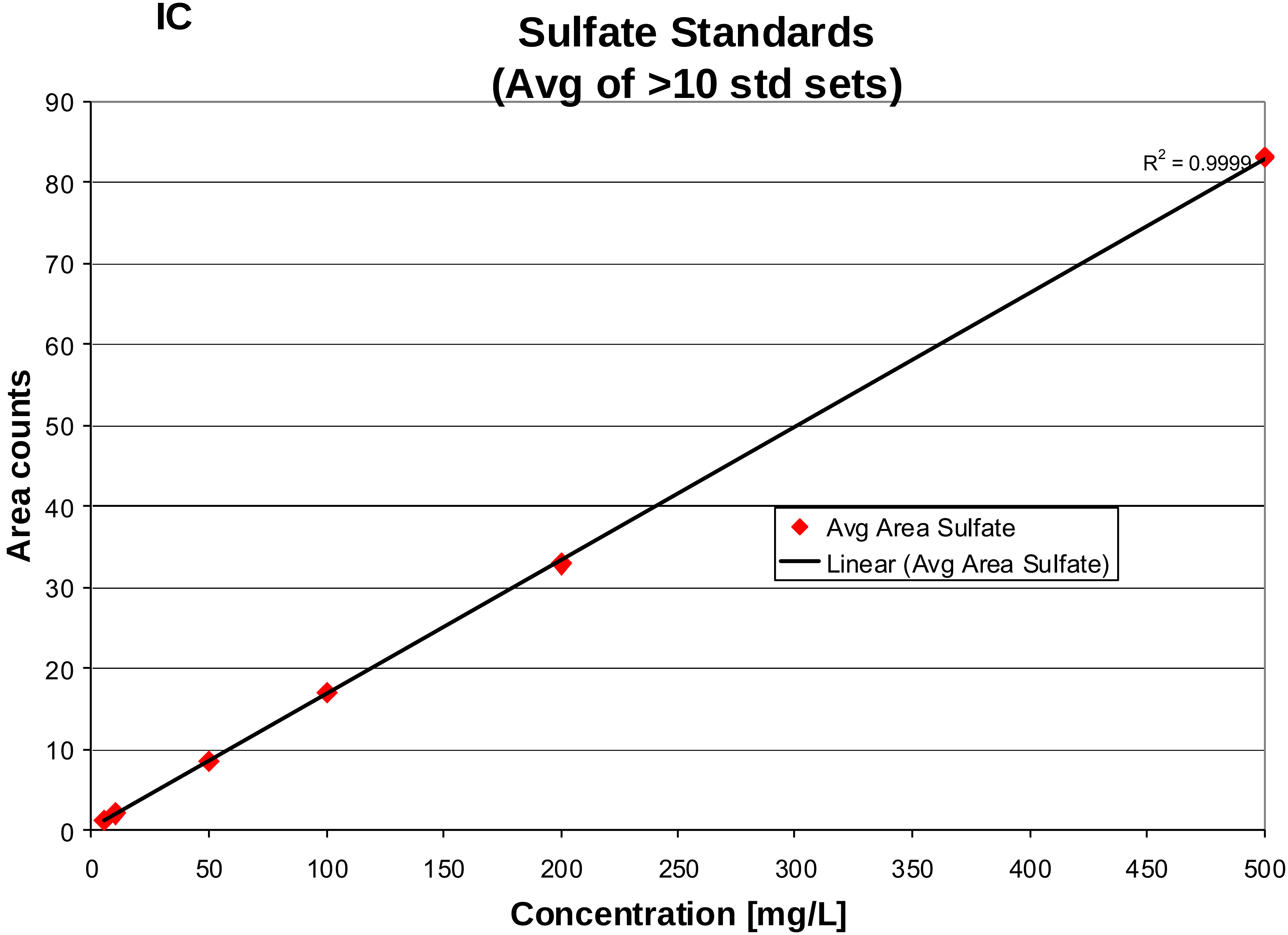
IC

Sodium Persulfate Standards (Avg of >10 std sets)



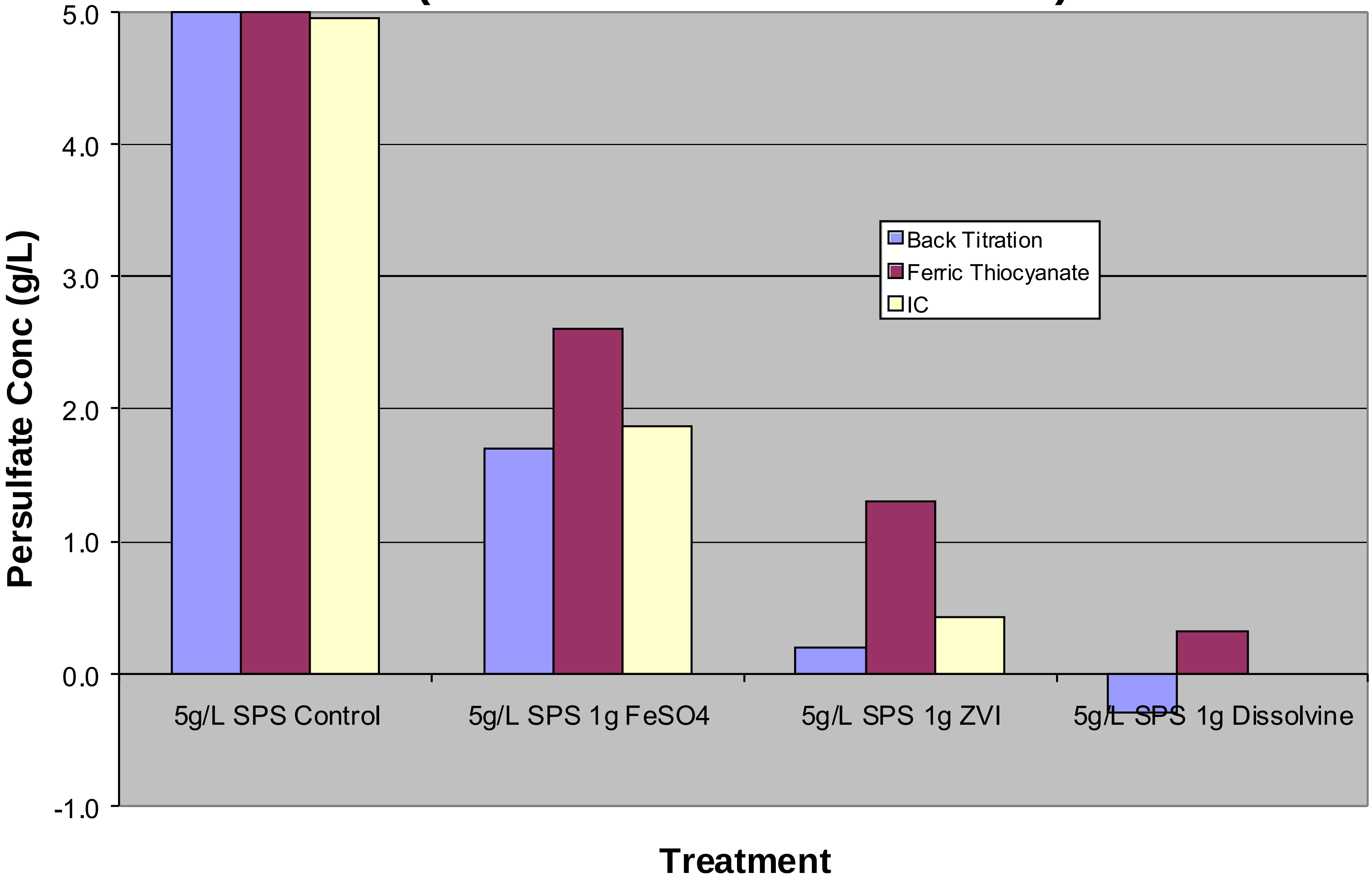
REDOX TECH, LLC

IC



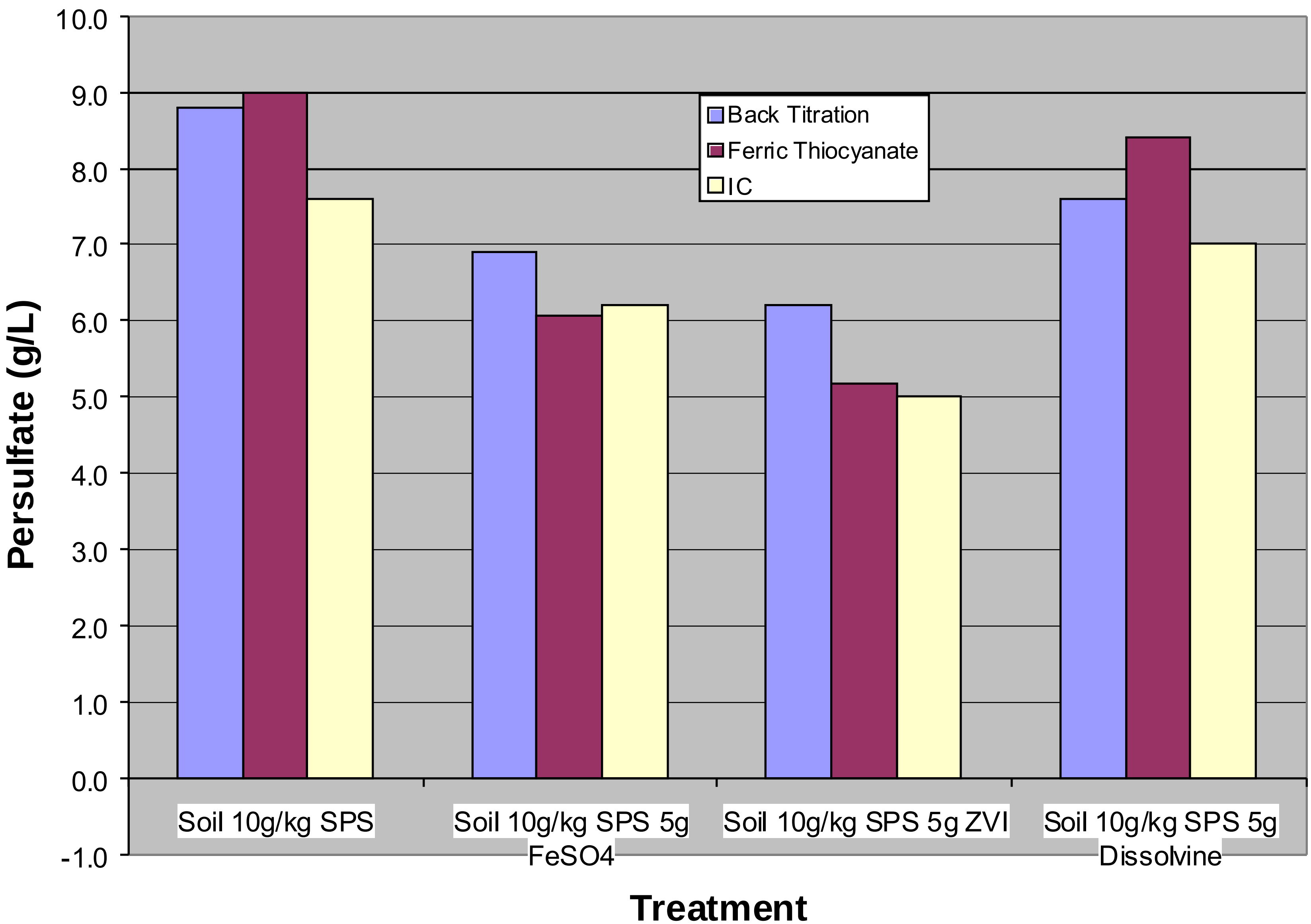
REDOX TECH, LLC

Measurement Method Comparison (Heated Persulfate in DI Water)



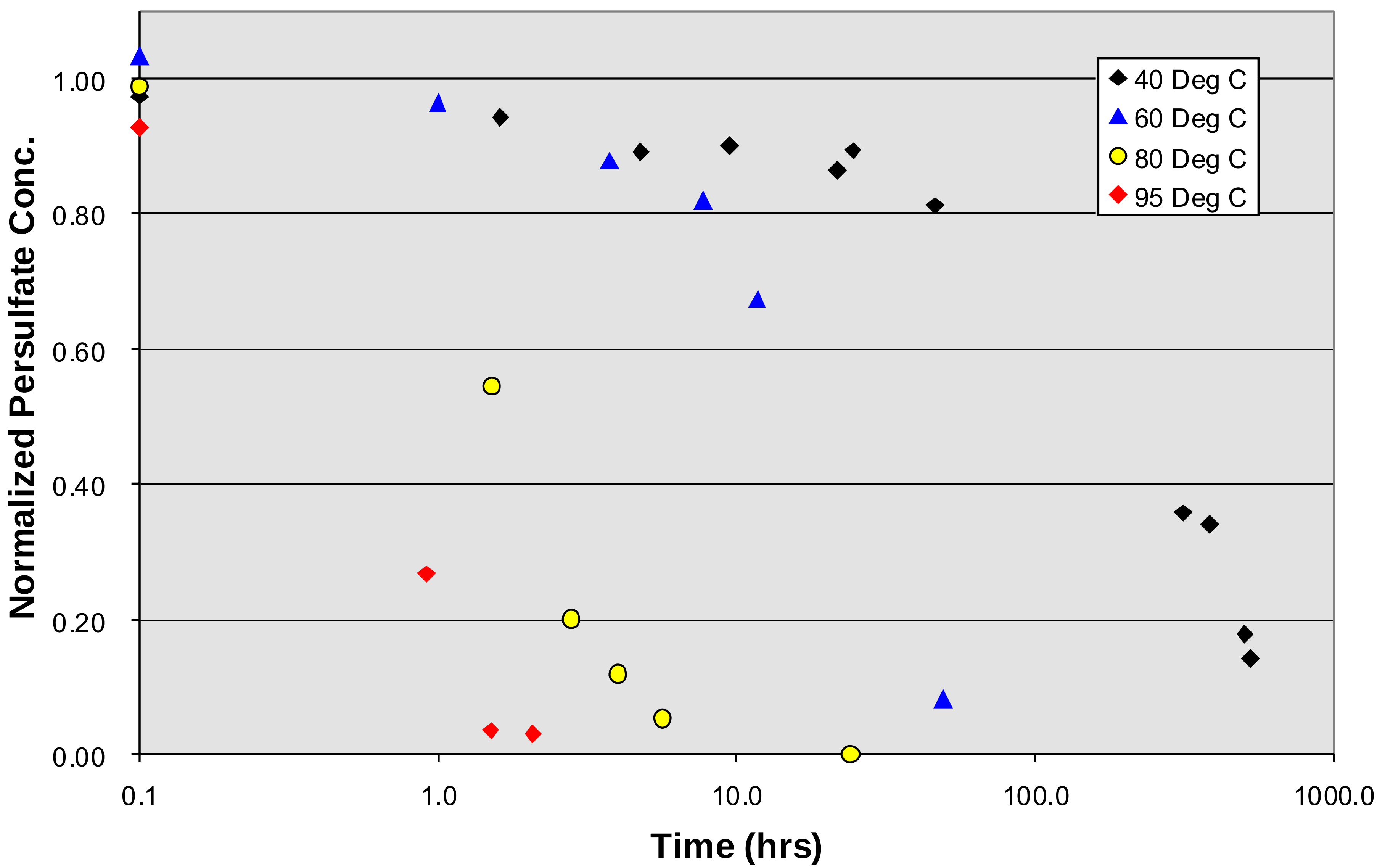
REDOX TECH, LLC

Methods Comparison Soil



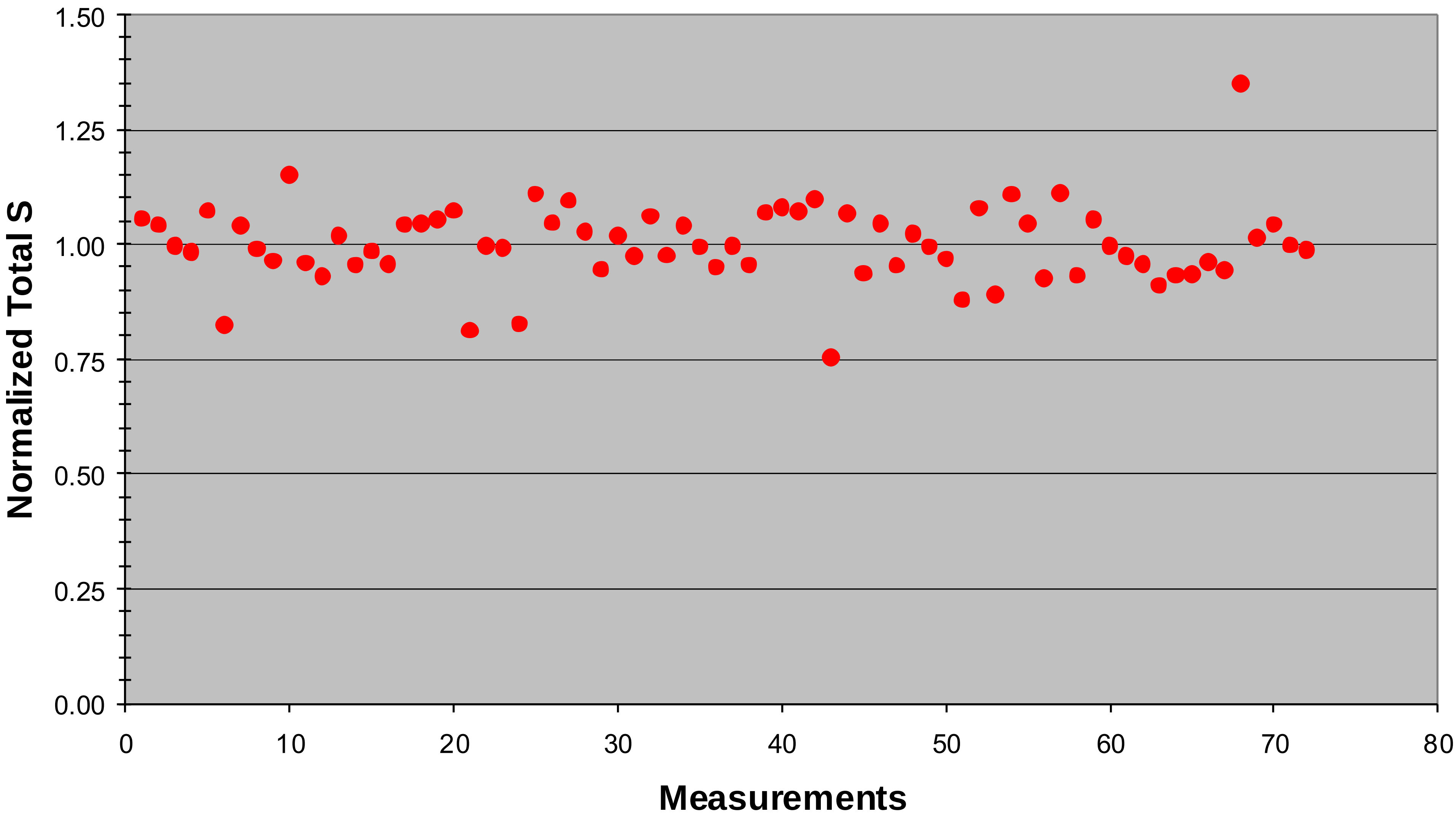
REDOX TECH, LLC

Persulfate Auto-oxidation in DI Water



REDOX TECH, LLC

Normalized Total Sulfur
(persulfate + sulfate)



REDOX TECH, LLC

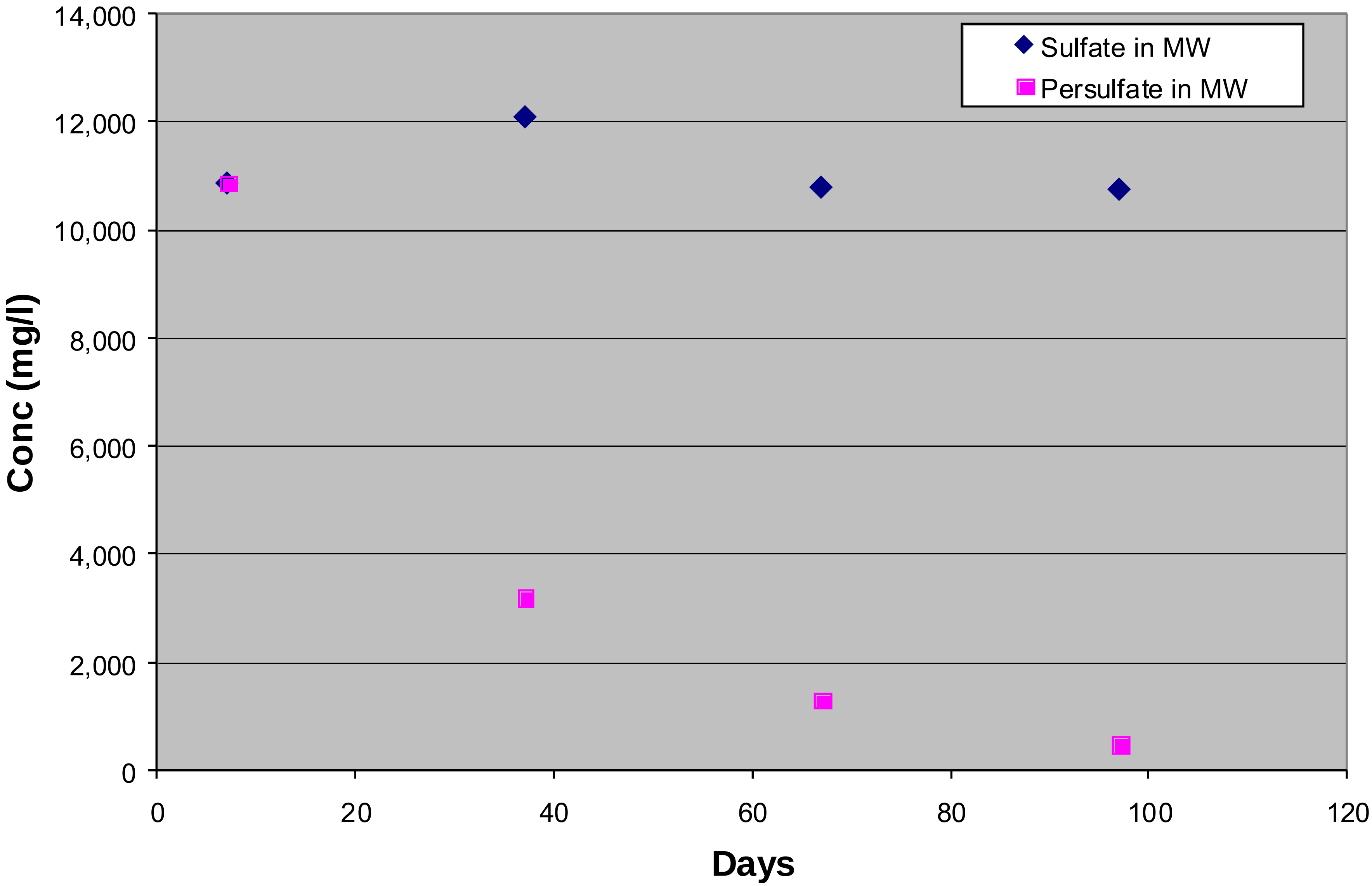
Persulfate Anecdotes

- California Site in fractured rock
  - 5/07: Inj 222 g/l
  - 10/07: IC 46.5 g/l - 99.98% TCE removal

California Groundwater with persulfate 5 months after injection.

- Initial persulfate Conc = 46.5 g/l, 1 week treatment time.
- Added NaOH: Conc = 44.4 g/l
- Added zvi: Conc = 11.4 g/l
- Fe3 EDTA: Conc = 22.5 g/l
- FeSO4: Conc = 39.9 g/l

Field Application of Persulfate



REDOX TECH, LLC

Summary 1

- Different measurement results with iron.
- Not great for tracking persulfate, but ferrous methods OK for dosing calcs (10-40% off).
- Sulfur is conserved between persulfate and sulfate.
  - Myriad sulfate measurement techniques will work well when you know how much you've added (e.g., TOD, treatability tests).
- Non specific methods not accurate for persulfate in unknown system.

Summary 2

- Limited Dynamic Range of all methods at concentrations of interest – need to dilute samples (possible errors).
- Color change methods cheaper.
- Color change subjective in colored water.

REDOX TECH, LLC

Need more research/application paradox.

- Understand mechanism, intermediate products, effective catalysts, etc.
- Maurice Hilleman died 4/11/2005
  - Developed vaccines for mumps, measles, rubella chicken pox, bacterial meningitis, flu, hepatitis B.
  - "…don't know a damn thing about how they (vaccines) work…in the old days we used to solve problems without having to understand them."