A Comparison of Aqueous PCE and TCE Degradation using Persulfate with: Lime; NaOH; or Straight Up

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Overview

- Background
- Activation
- Experiments
- Conclusions

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%)

Catalyzed or Activated Oxidant Adds More Energy

- $S_2O_8^{2-}$ + energy (heat, light, Me^+, pH???) $\longrightarrow$ $2SO4\bullet^-$

- Sulfate Radical has lots of energy, electrons ready to react.

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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.

Oxidation Potential

- Hydroxyl radical $\bullet OH$ 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

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Good Things About Persulfate

- Pretty safe to handle
- Pretty soluble in water (~ 36 wt %)
- Powerful oxidant
- Even more powerful when converted to sulfate radicals

Persulfate Issues

- Produces acid as it is converted to sulfate (one mol persulfate: 2 mols H^+)
- Many successes, some problem sites – lack of activation?
- Recommended activation high pH (base activation) between pH 10.5 and 12 S.U.

Test persulfate with base in comparison with no base

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Achieving and Maintaining pH in Subsurface

- Base Demand
  - Soil and groundwater
    - Empirically determined
  - Persulfate decomposition
    - Stoichiometry 2:1(3.4 lbs NaOH : 10 lbs $Na_2S_2O_8$) or 1:1 (3.1 lbs Ca(OH)2 : 10 lbs $Na_2S_2O_{8)}$
- Commonly Used
  - $Ca(OH)_2$: at solubility pH = 12.3
  - NaOH : pH 14

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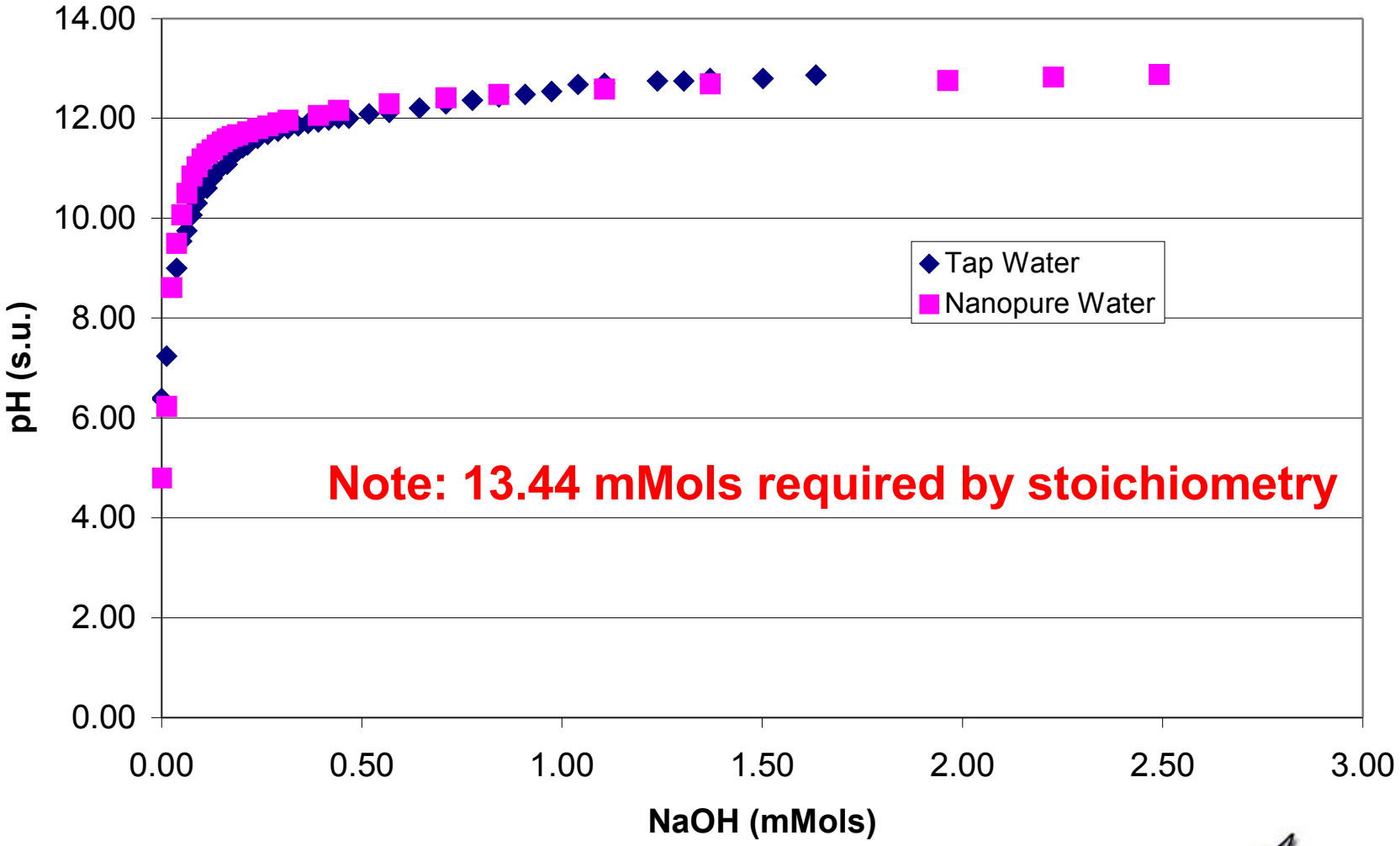
Titration: 20 g/l Sodium Persulfate
(1.6 g in 80 mL = 6.72 mMols)



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Test Conditions

- Performed in di water; 20 ml per vial
- Target Chemicals:
  - TCE 10 mg/l (0.076 mM)
  - PCE 10 mg/l (0.060 mM)
- Persulfate:
  - No base
    - 125 mg/l (0.525mM); 250 mg/l
  - Ca (OH)2 – Exceed stoichiometric demand (>6x)
    - 125 mg/l; 250 mg/l
  - NaOH – Equal or Exceed stoichiometric demand (≥1x)
    - 125 mg/l; 250 mg/l

Test Conditions cont.

- Separate 40 ml vials filled with 20 ml fluid with mininert gas tight valves.
- Maintained in 30C water bath
- Three replicates of each condition
  - Each set 9 vials plus TCE/PCE controls
- Analyses:
  - Ion Pair chromatography: Cl^-, $SO4^{2-}$, $S2O8^{2-}$
  - GC Headspace: TCE, PCE

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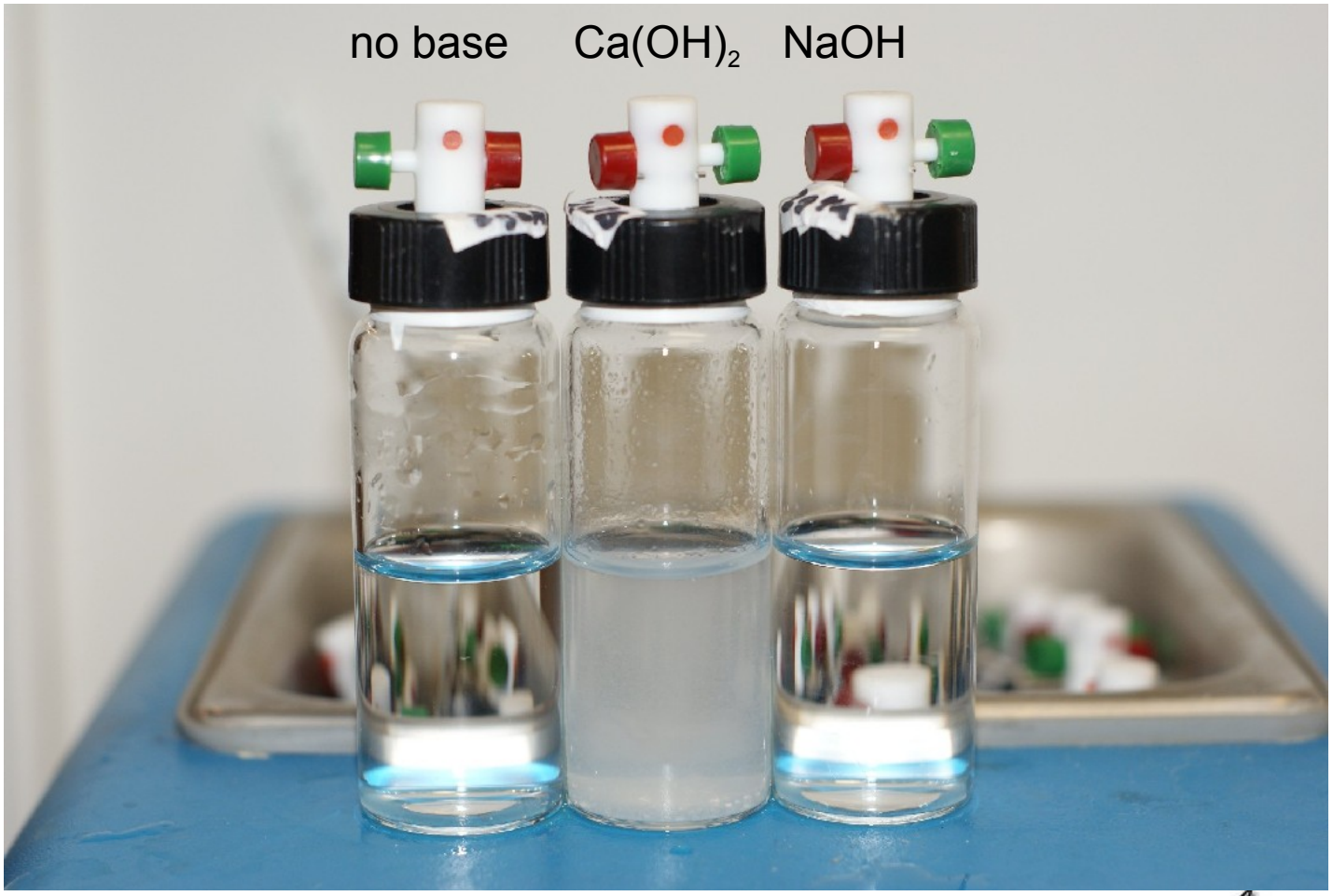
Reactor vials with Mininert Push-Button Valve



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Waterbath

Vials are constantly heated at 30°C

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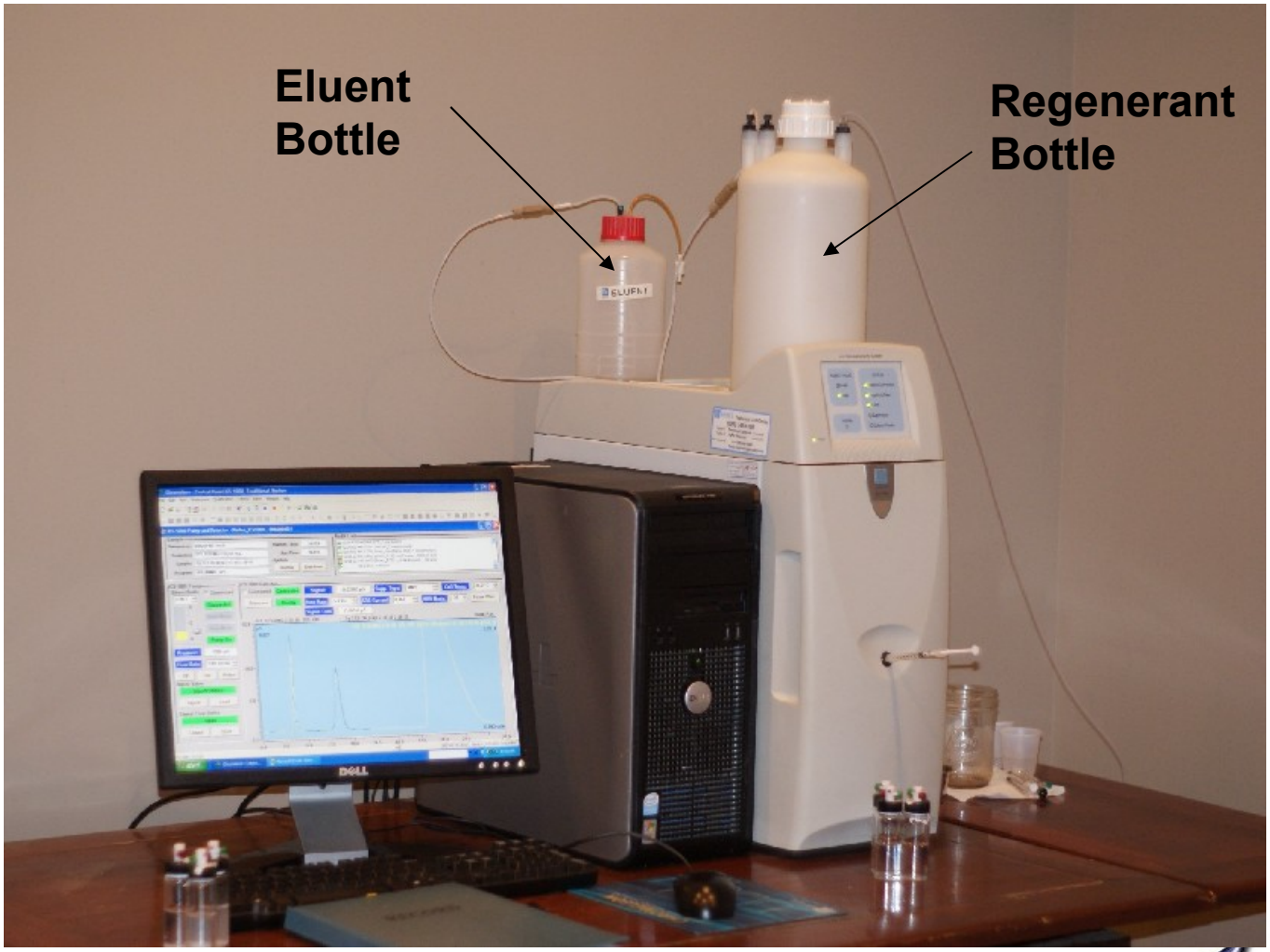
Ion Pair Chromatography

(Weiss, 1995; Rossabi et al, 2008)

- 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 0-2000 mg/l.

Ion Chromatograph Setup with Workstation



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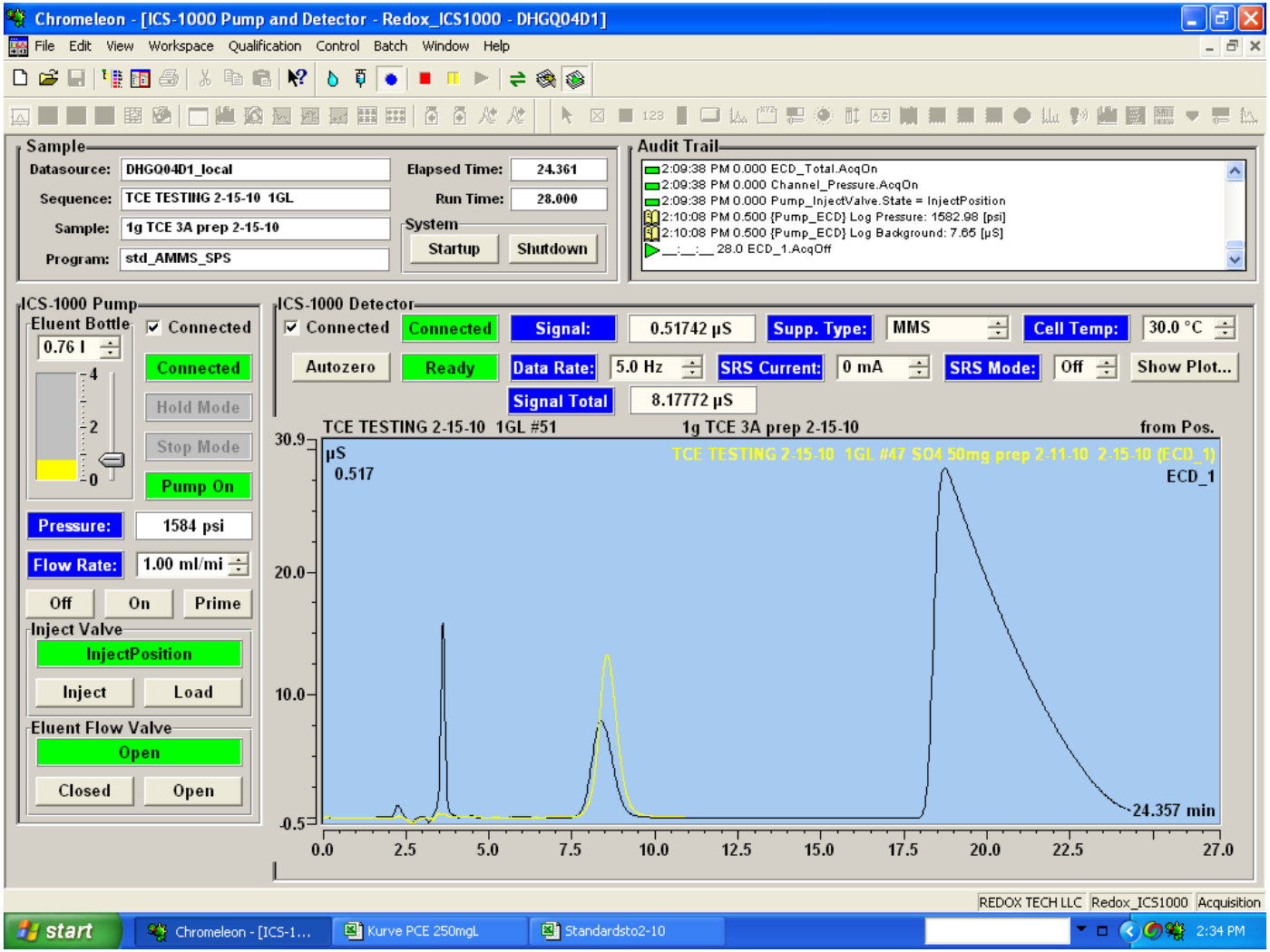
Ion Chromatograph – Chromeleon Desktop



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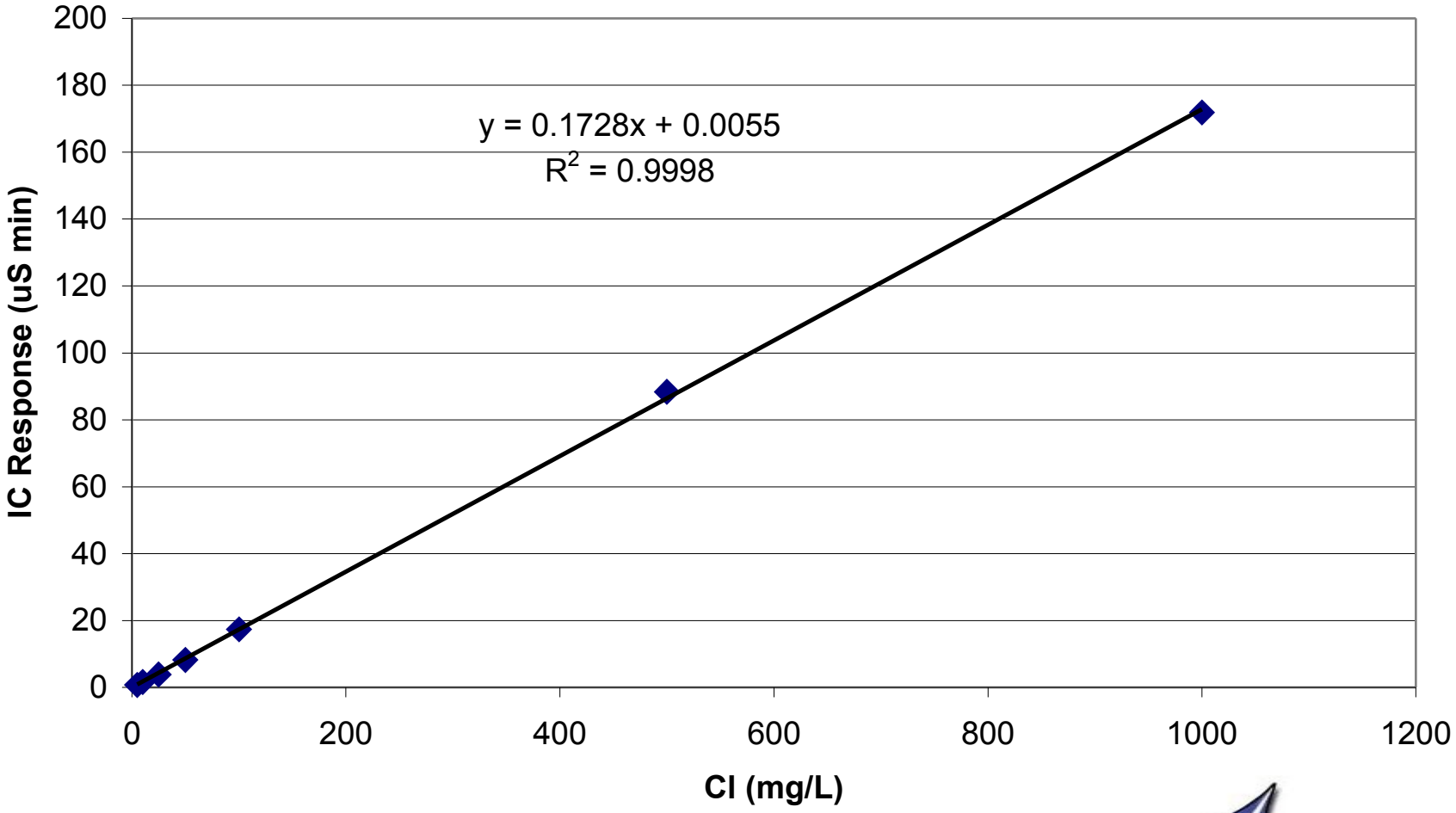
Ion Pair Chromatography SO4 Standard Curve
Average of 4 months data



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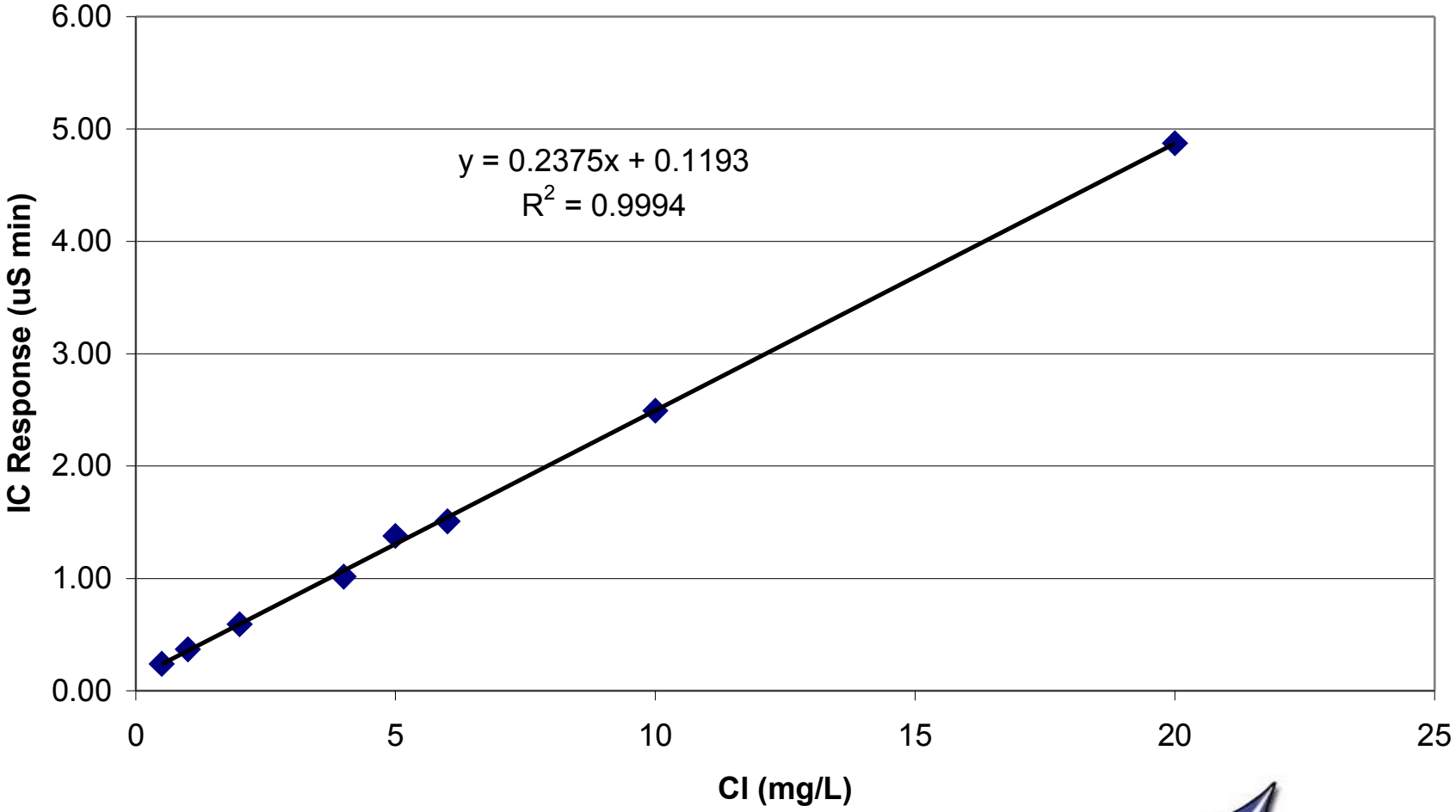
Ion Pair Chromatography Cl Standard Curve
Average of 4 months data



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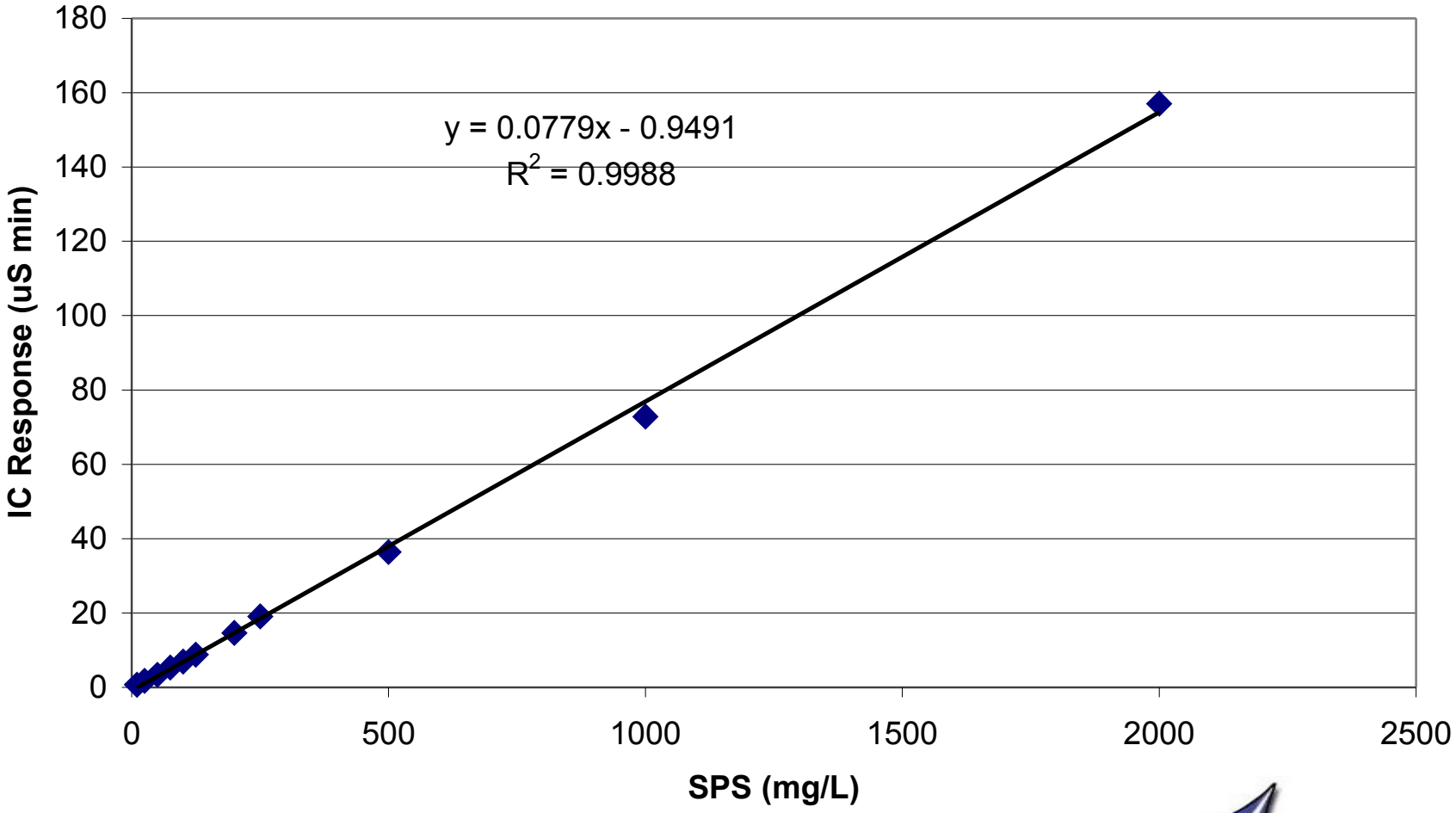
Ion Pair Chromatography SPS Standard Curve
Average of 4 months data



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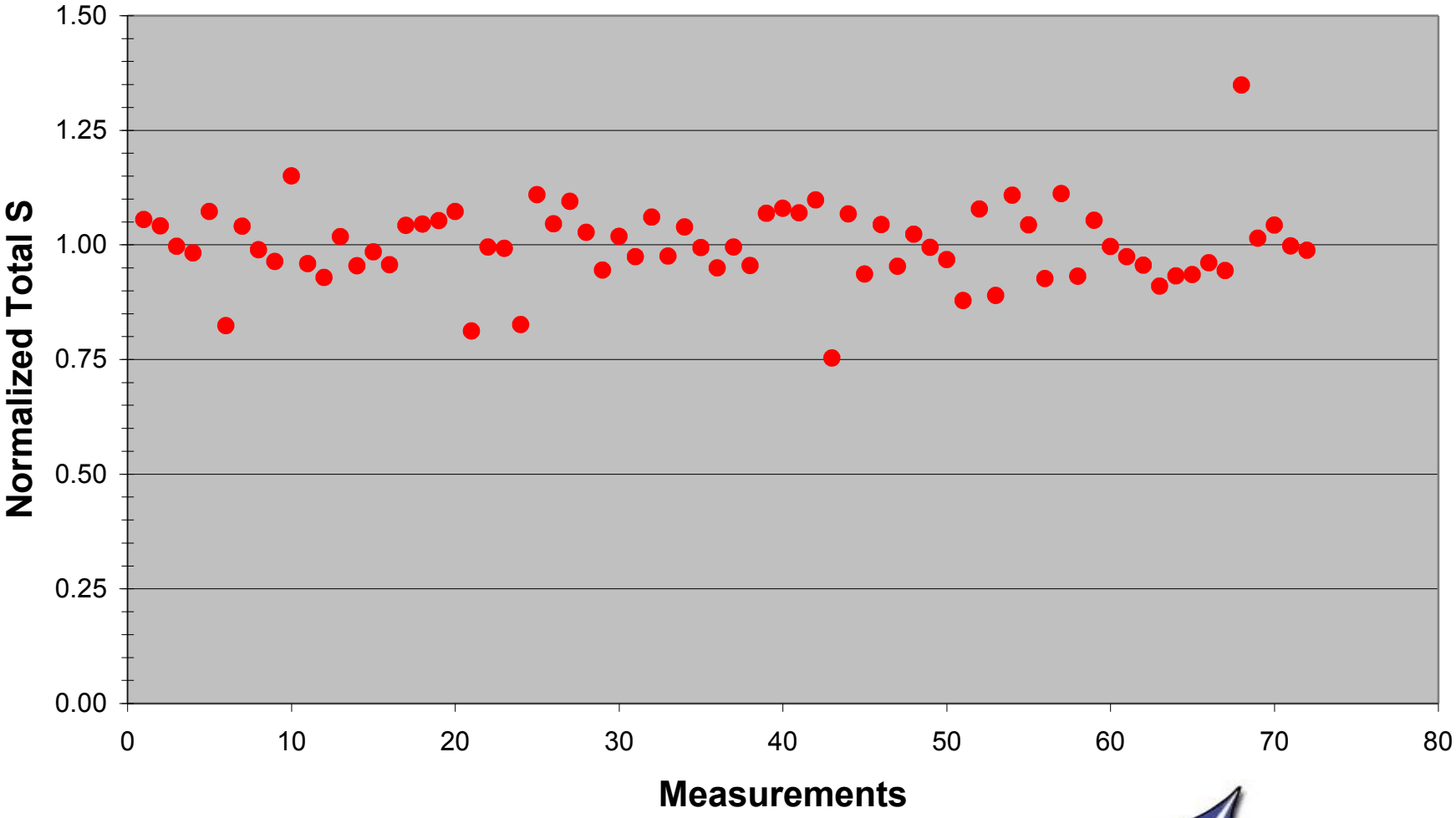
Normalized Total Sulfur
(persulfate + sulfate)



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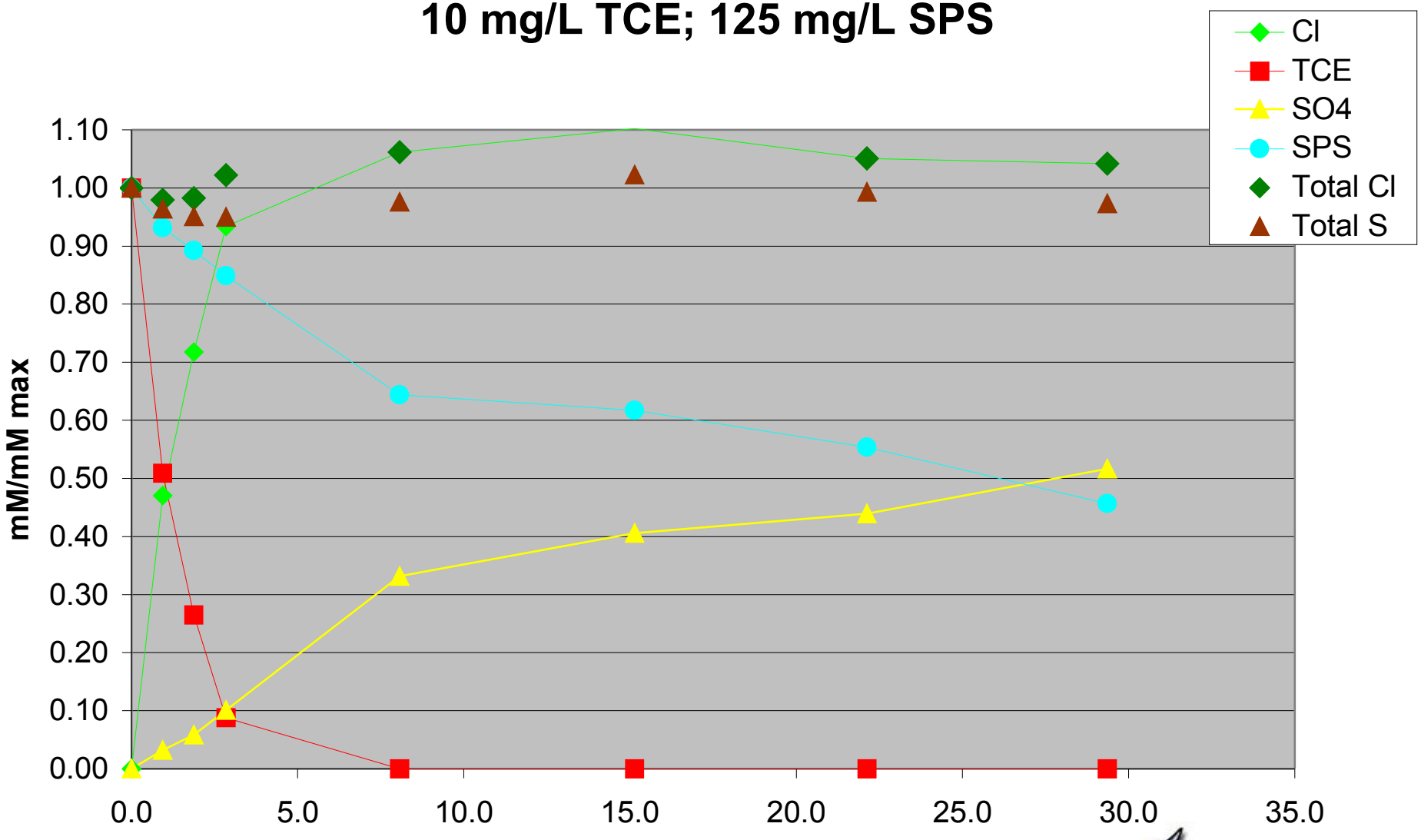
Assumptions

- Sulfate radical is more reactive (faster reaction rates) and has a shorter lifetime (4 sec - ITRC) than non-radical species.
  - Measured rxn rates of sulfate radical on the order of 10^7 or 10^8 moles per second Dogliotti and Hayon, 1967
- So if more radicals are being made:
  - SPS goes away faster
  - PCE or TCE goes away faster
  - Cl increases faster
  - SO4 increases faster

Normalized Concentrations - No Base
10 mg/L TCE; 125 mg/L SPS



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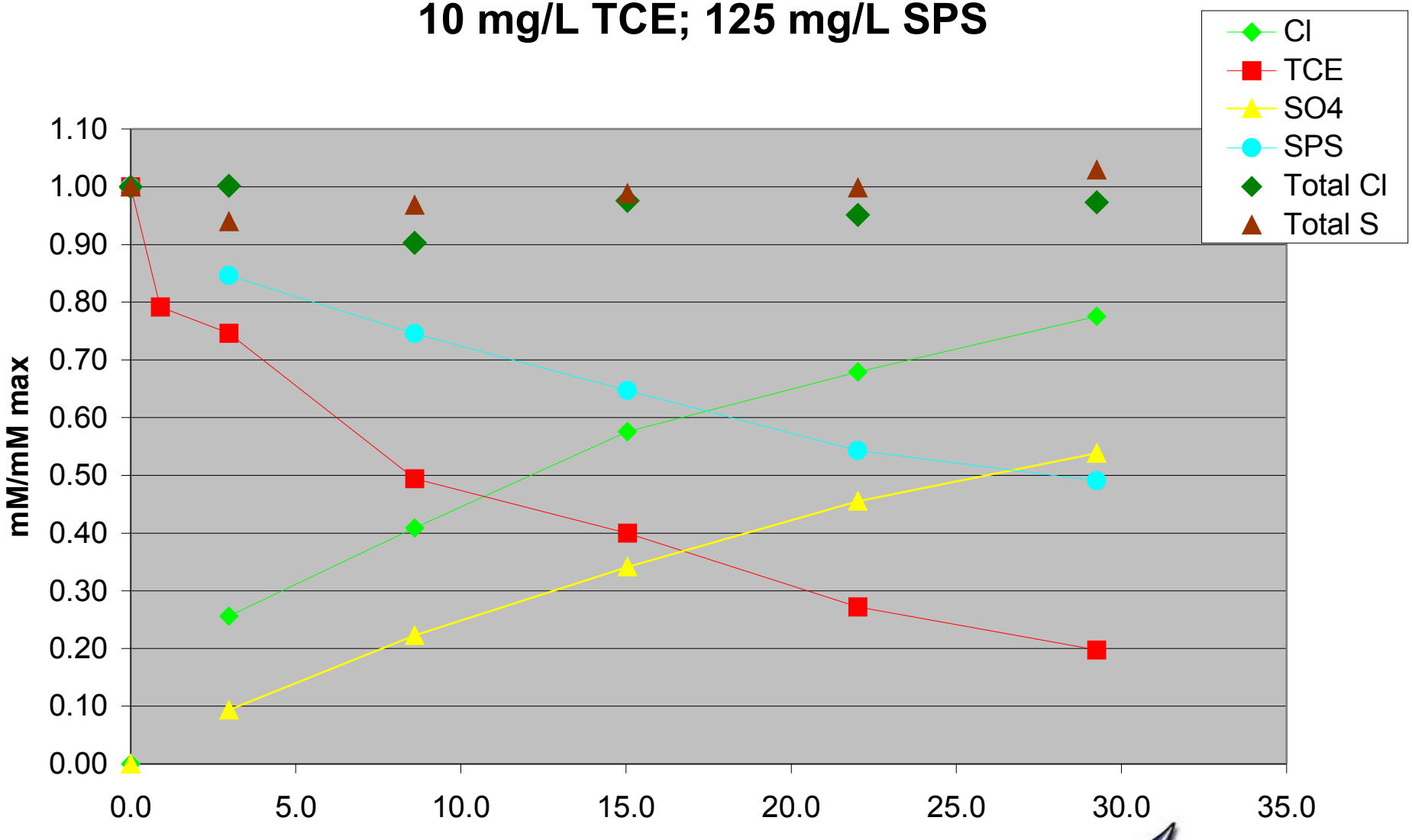
Normalized Concentrations - Lime
10 mg/L TCE; 125 mg/L SPS



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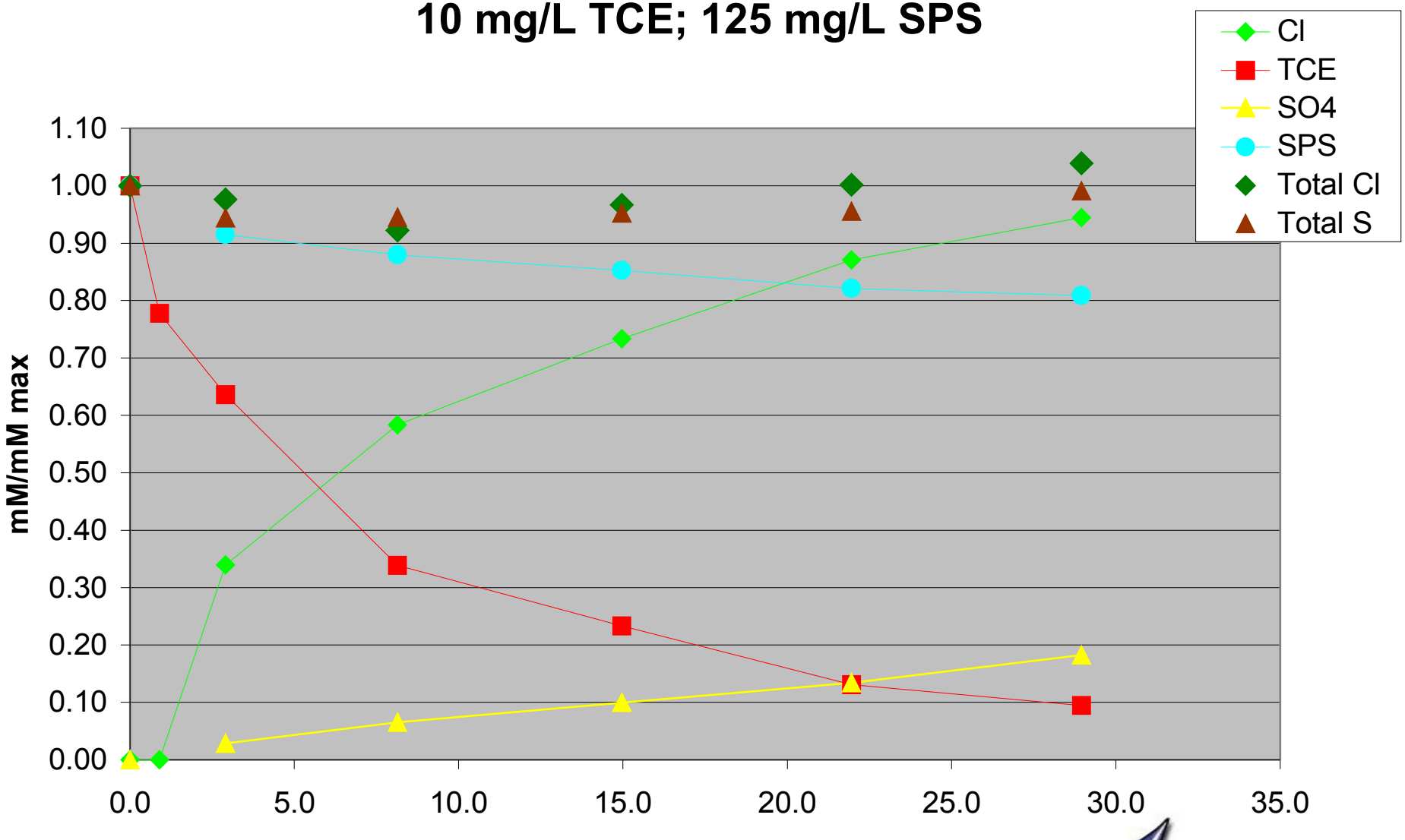
Normalized Concentrations - NaOH
10 mg/L TCE; 125 mg/L SPS



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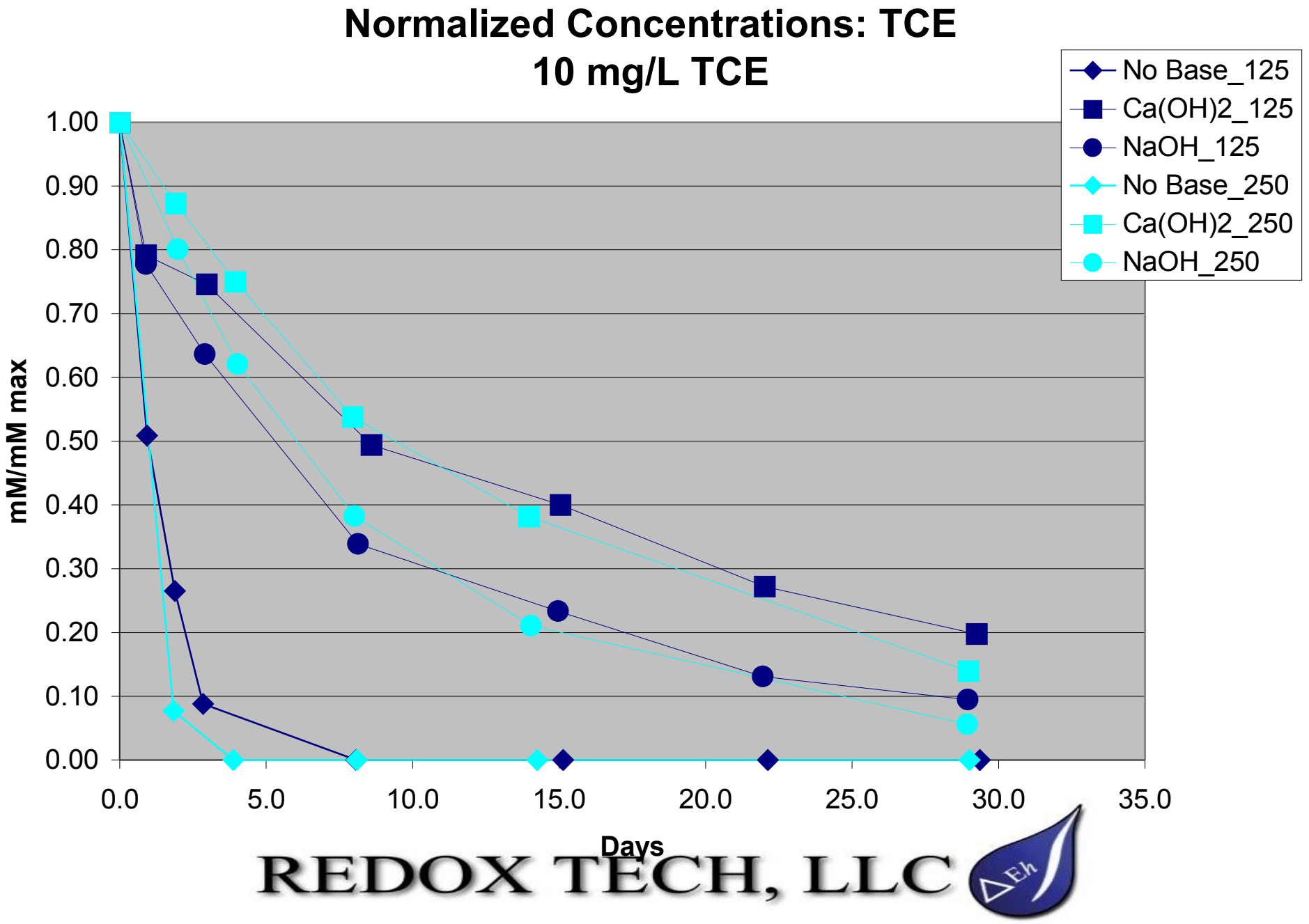

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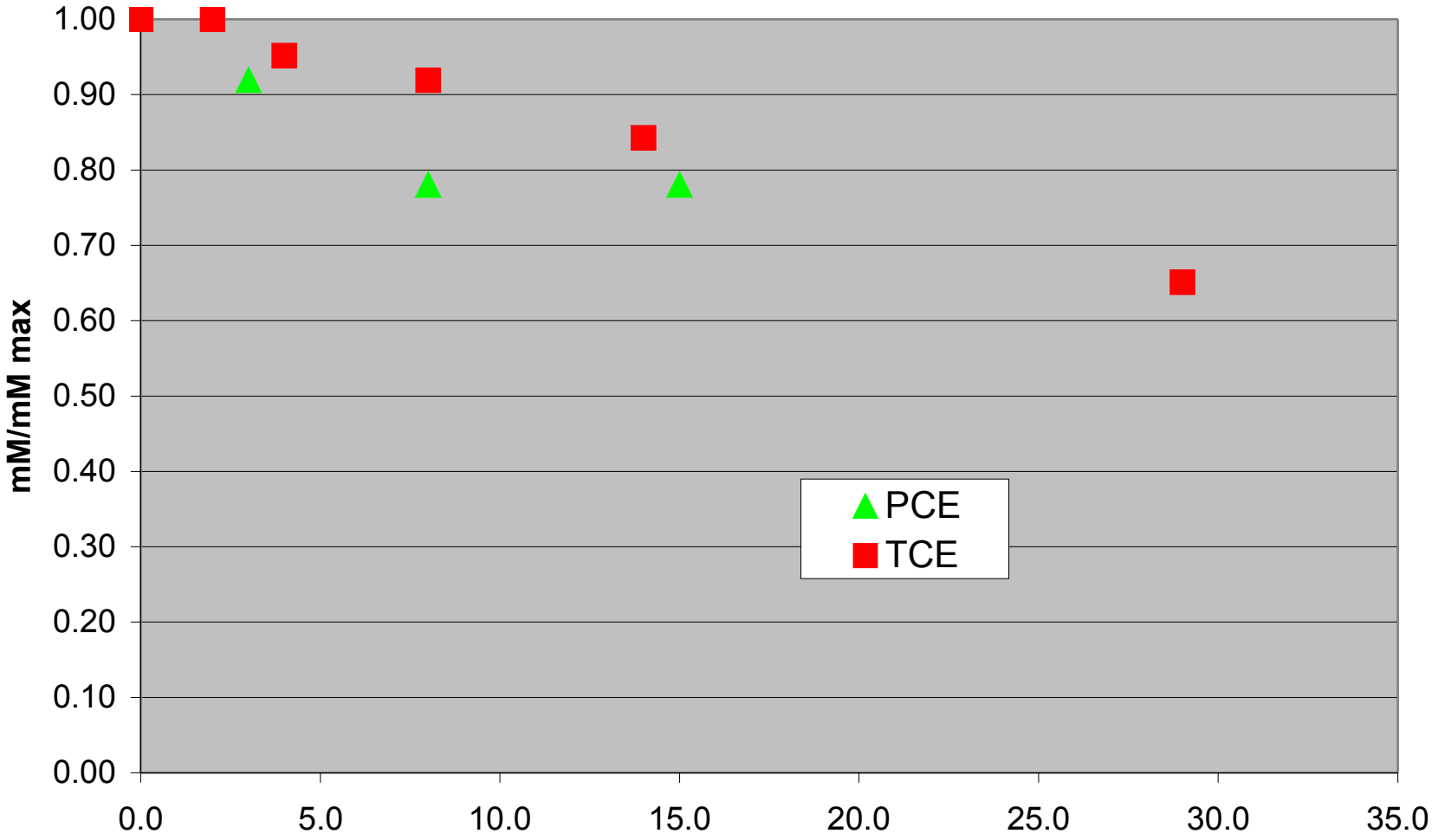
Normalized Concentrations: Control TCE/PCE



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Theoretical oxidation stoichiometry of PCE and TCE

PCE: $C_2Cl_4 + O_2 + 2H_2O \Rightarrow 2CO_2 + 4H^+ + 4Cl^-$

2 moles SPS per 1 mole PCE

TCE: $2C_2HCl_3 + 3O_2 + 2H_2O \Rightarrow 4CO_2 + 6H^+ + 6Cl^-$

3 moles SPS per 1 mole TCE

Or $3Na_2S_2O_8 + C_2HCl_3 + 4H_2O \Rightarrow 2CO_2 + 9H^+ + 3Cl^- + 6Na^+ + 6SO_4^{2-}$

per ITRC 2005

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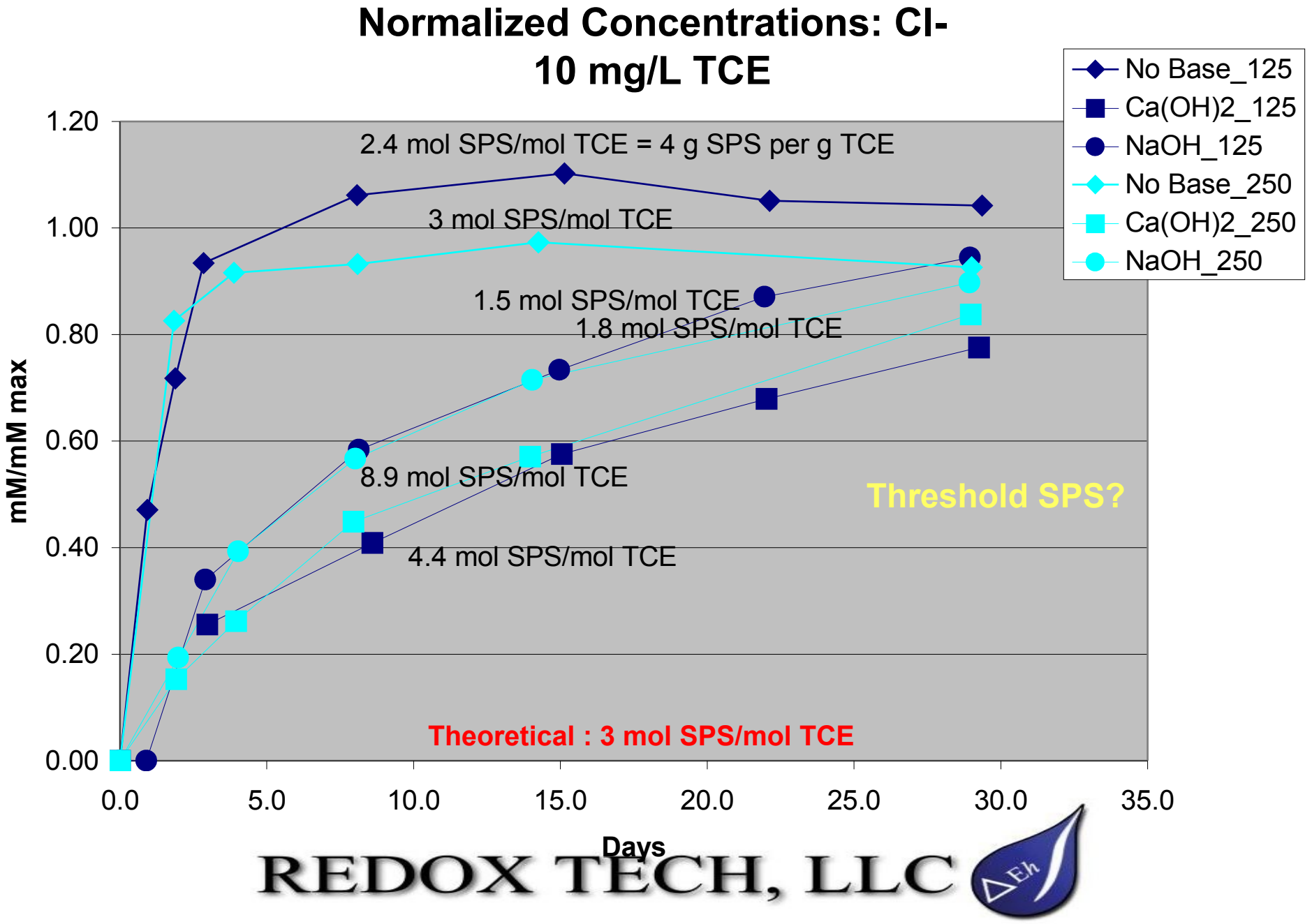

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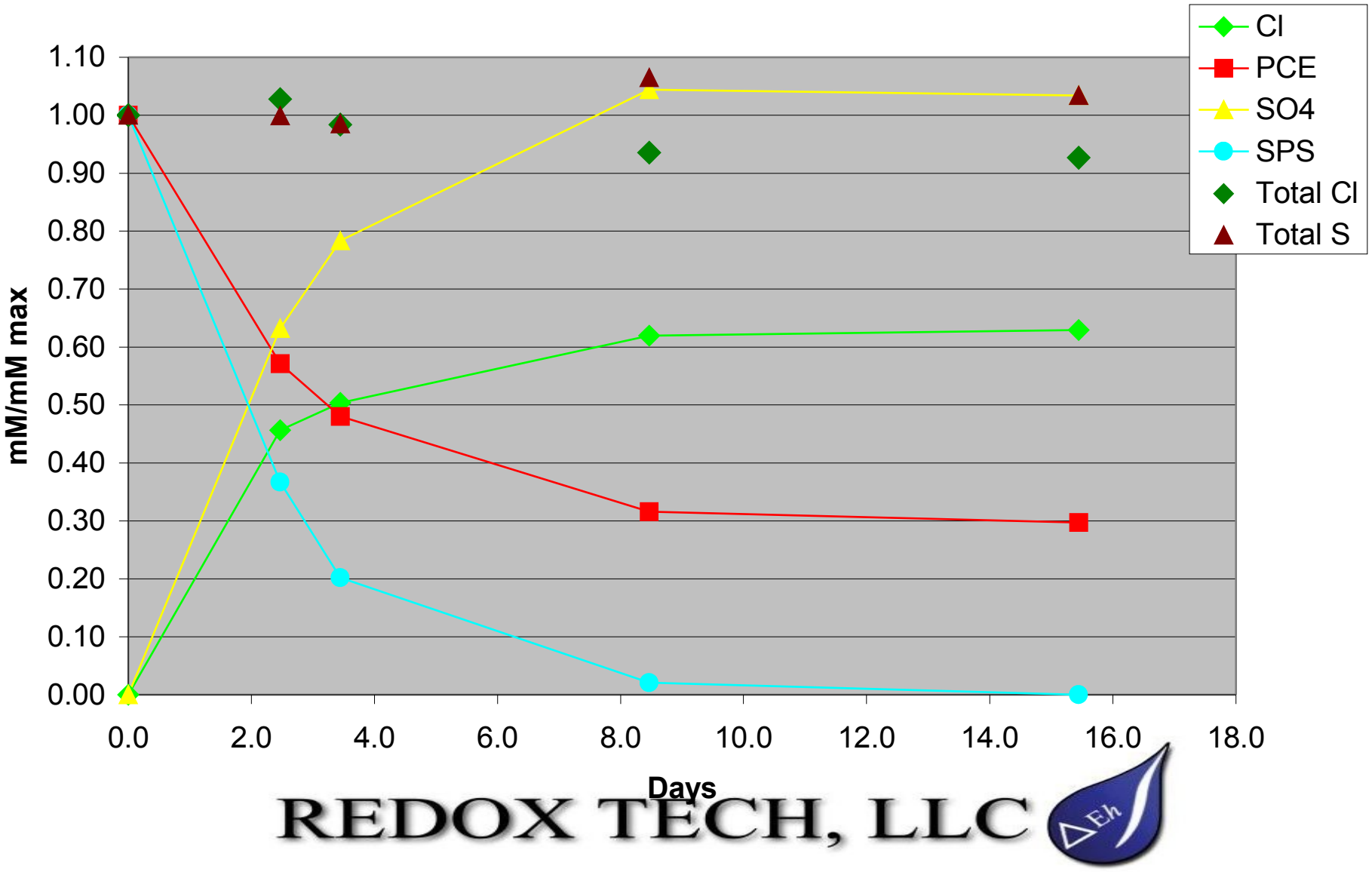
Normalized Concentrations - No Base
10 mg/L PCE; 250 mg/L SPS



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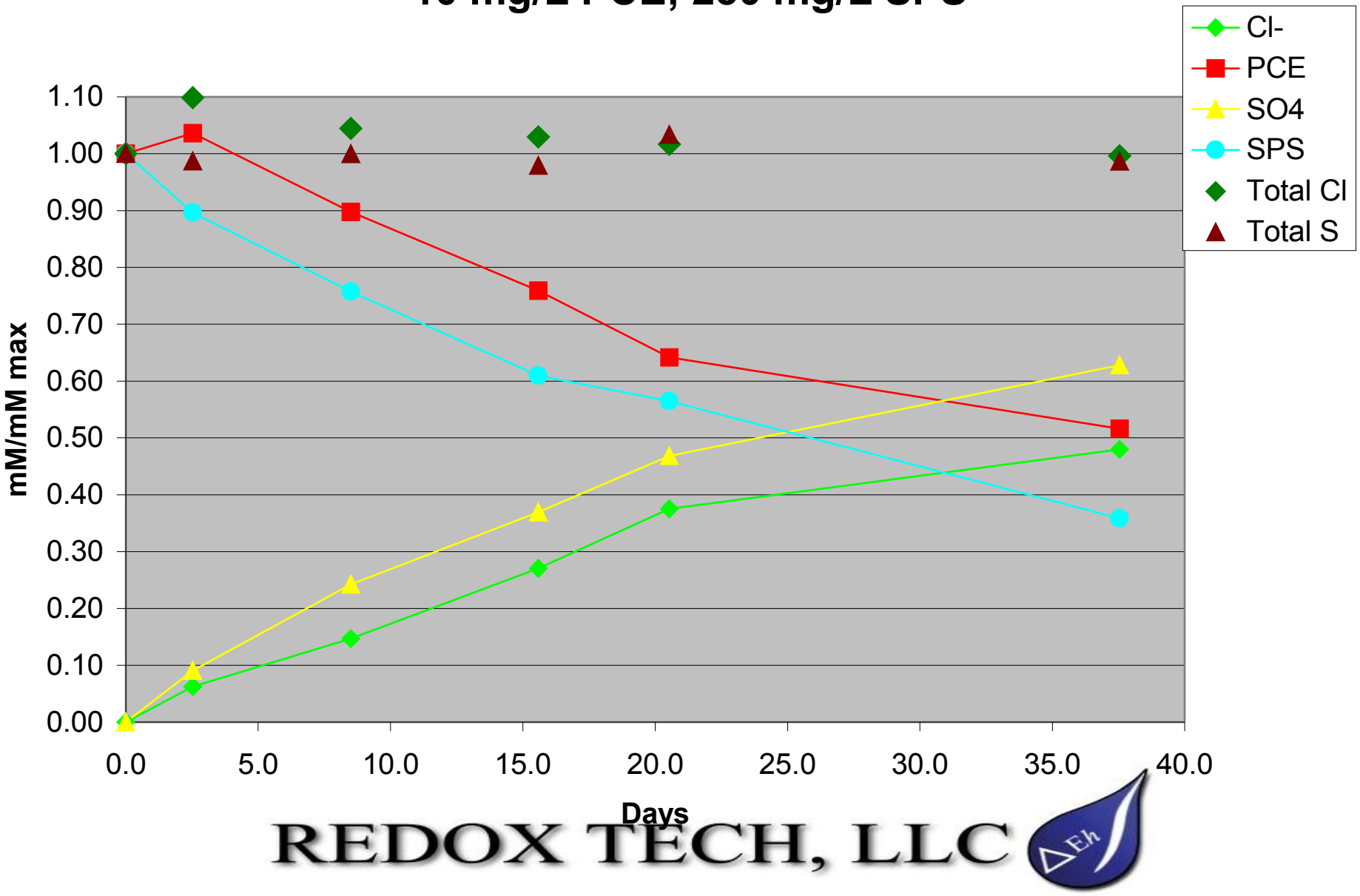
Normalized Concentrations - Lime
10 mg/L PCE; 250 mg/L SPS



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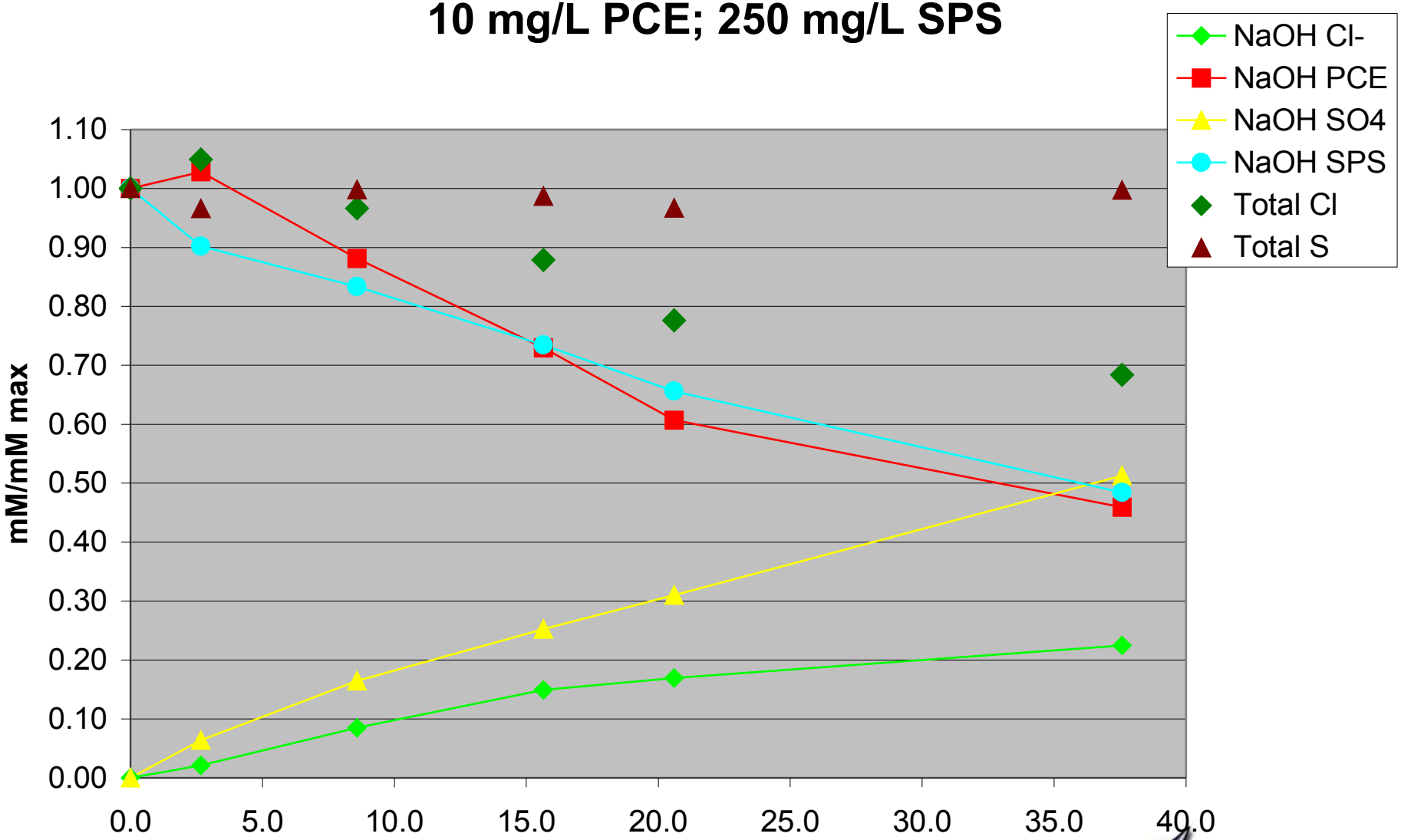
Normalized Concentrations - NaOH
10 mg/L PCE; 250 mg/L SPS



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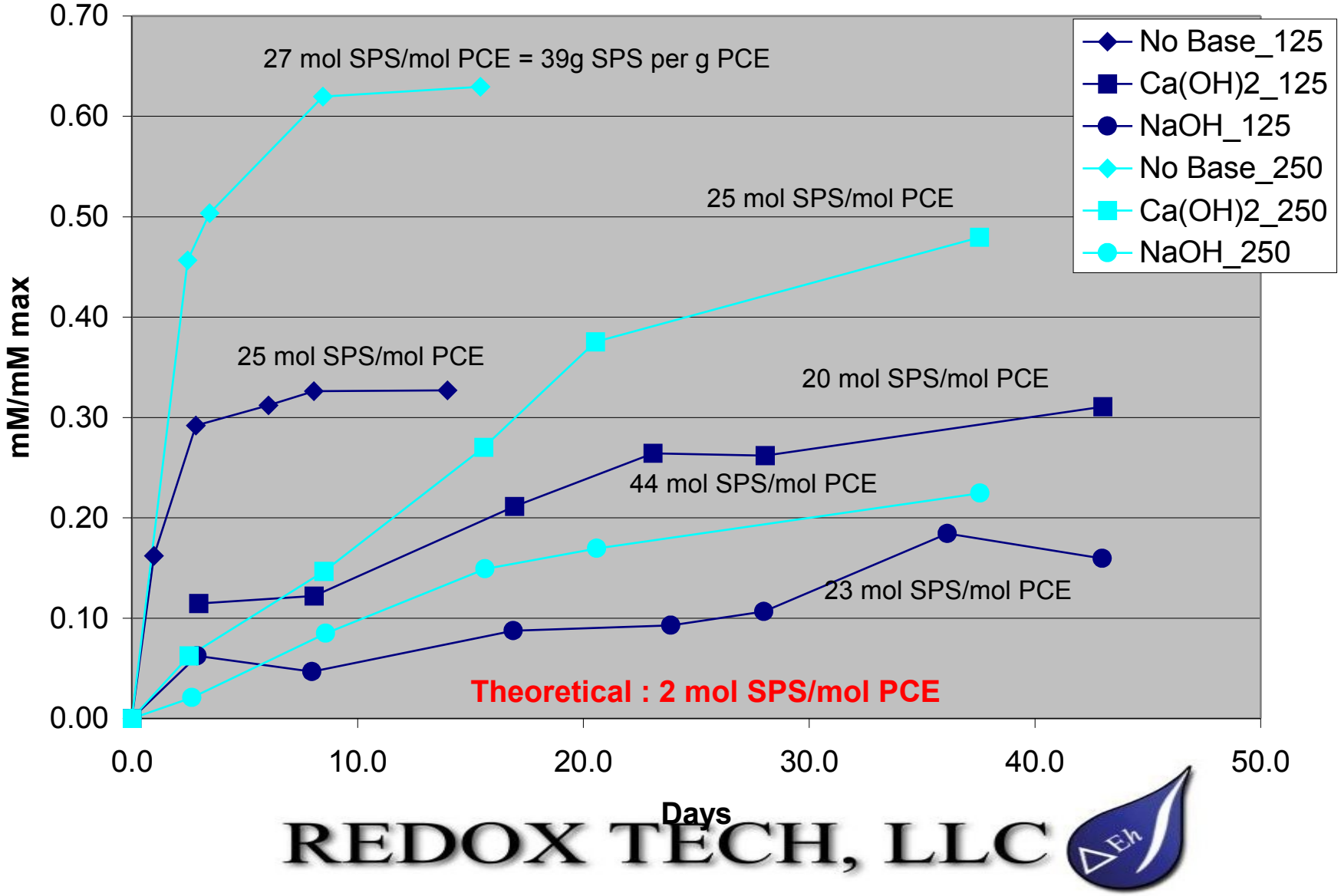
Normalized Concentrations: Cl-
10 mg/L PCE



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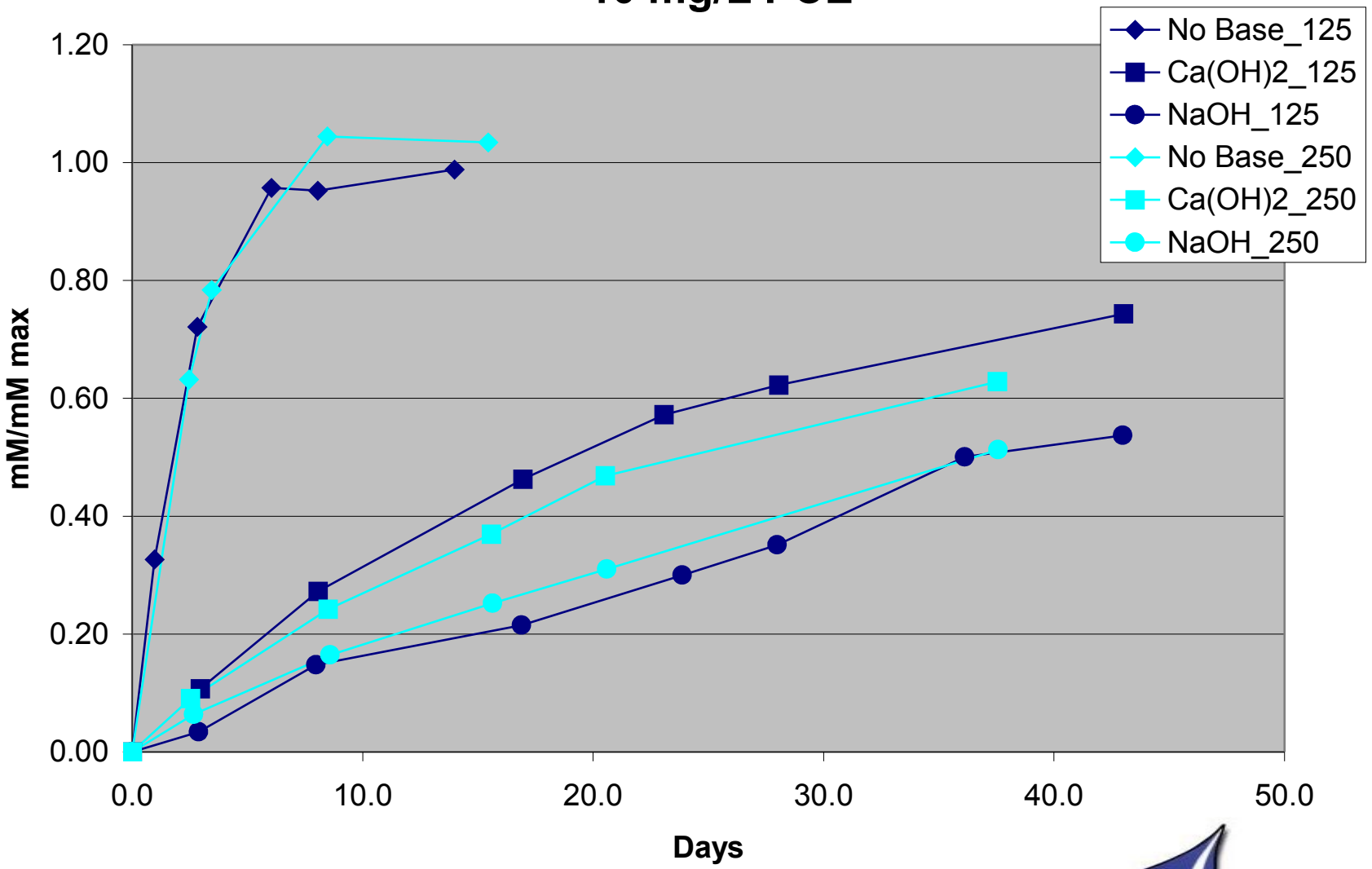
Normalized Concentrations: SO4
10 mg/L PCE



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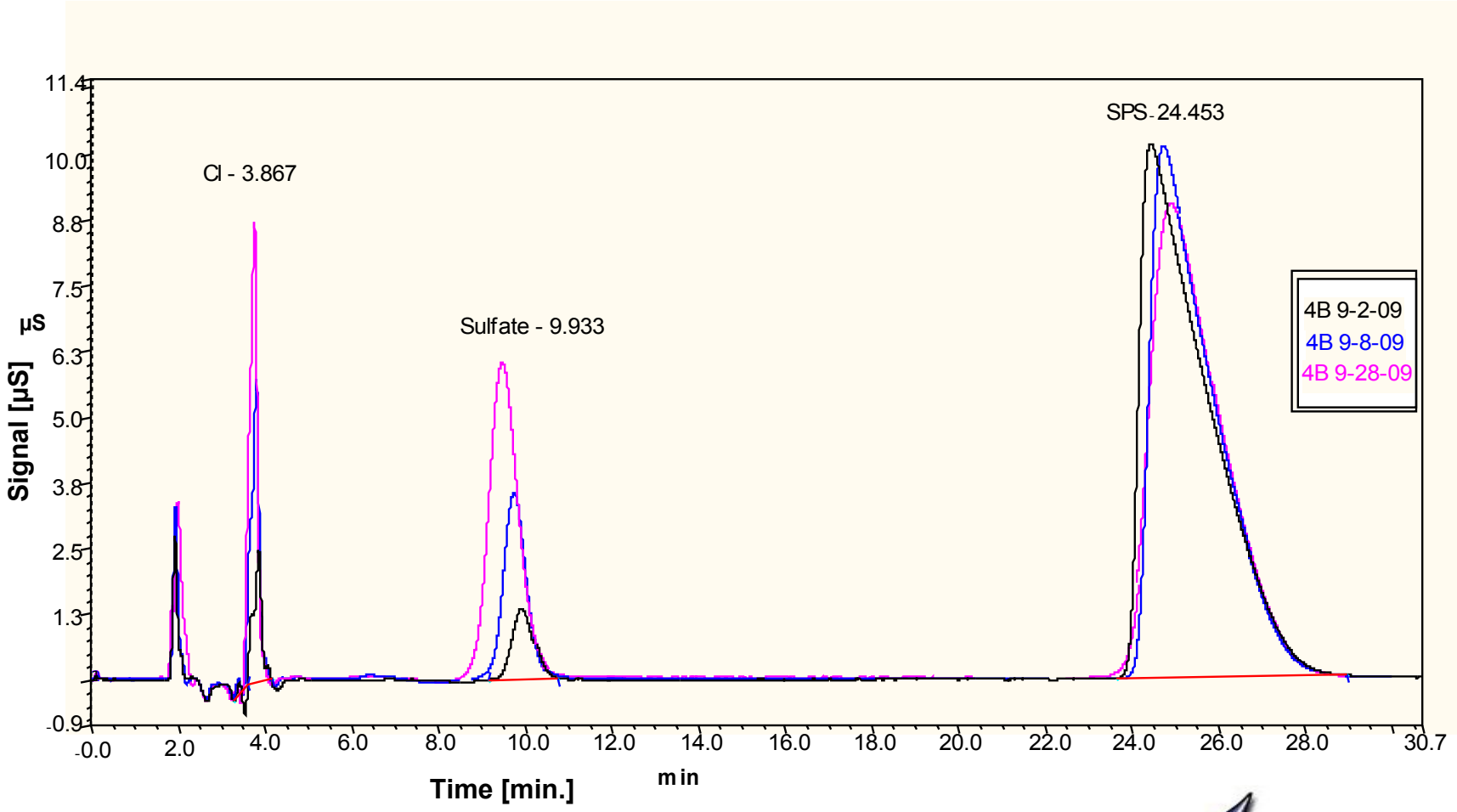
IC Chromatogram for three different times

9/2/09 (Day3), 9/8/09 (Day9), 9/29/09 (Day29)
for Chloride, Sulfate, and Sodium Persulfate
10mg/L TCE treated with 250mg/L SPS and NaOH



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Conclusions

- High pH (NaOH and Ca(OH)2) does not activate persulfate in aqueous solution.
- Persulfate degrades PCE and TCE faster without base.
- Persulfate molar requirement for degradation of PCE is higher than simple theoretical.
- Persulfate chemistry is not simple.

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