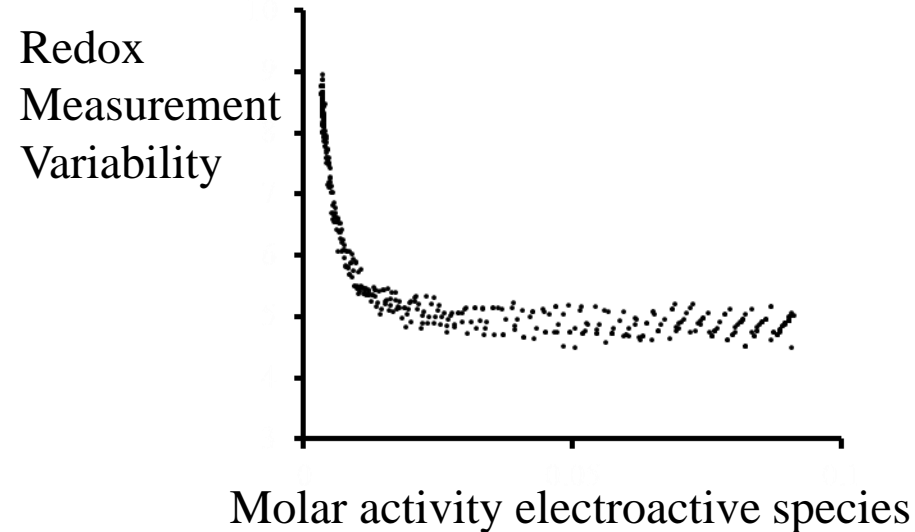


# Concentration dependence

## A new understanding regarding the validity of **redox measurements** in the soil environment

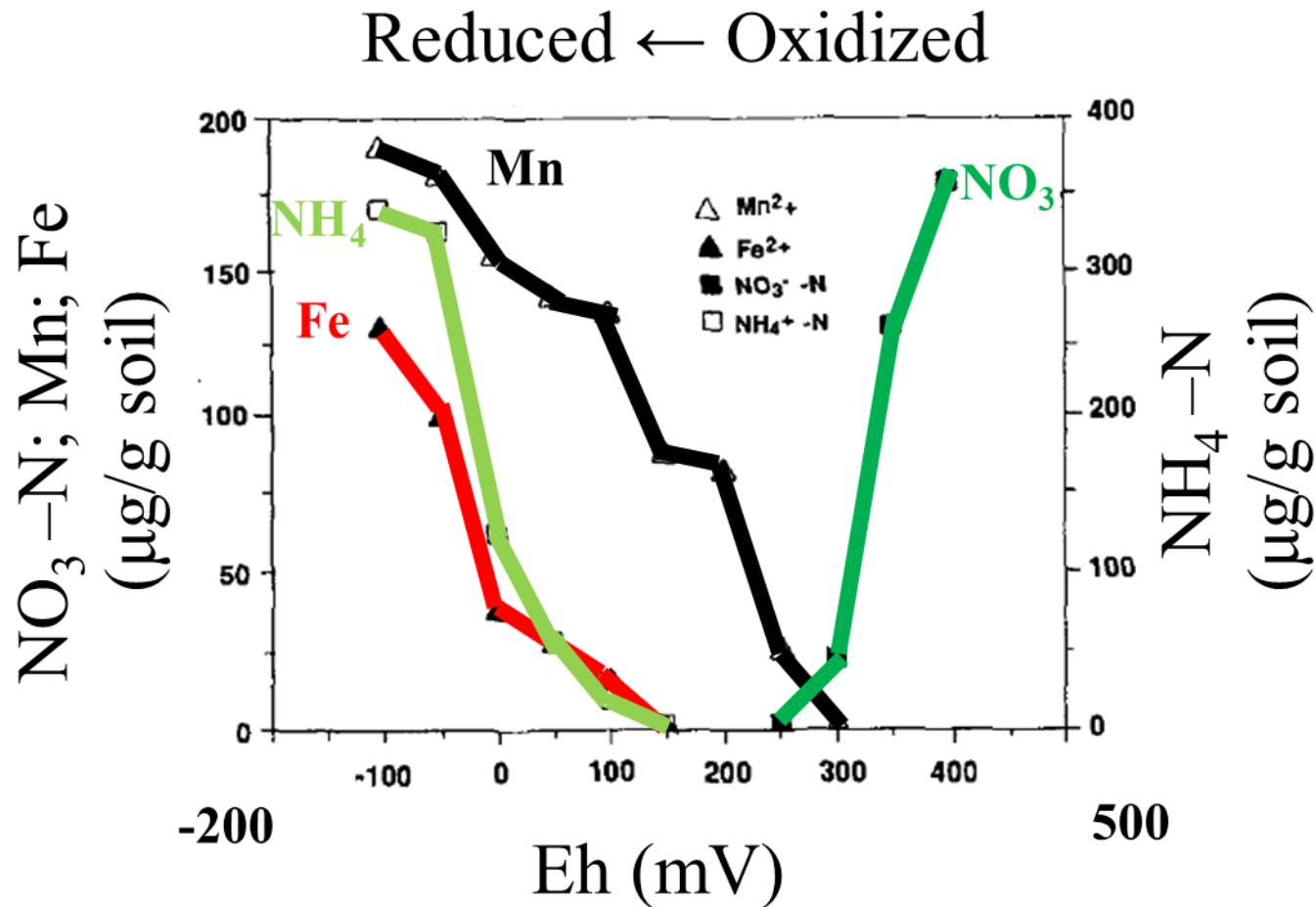


David Yalin and Moshe Shenker

The Hebrew University of Jerusalem Israel

# Background

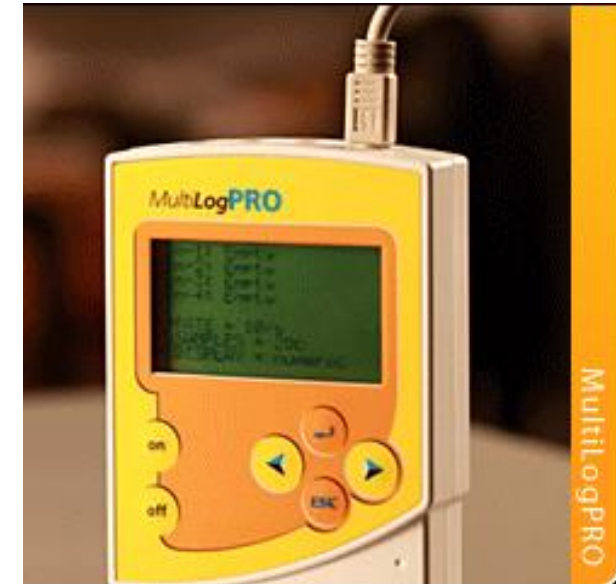
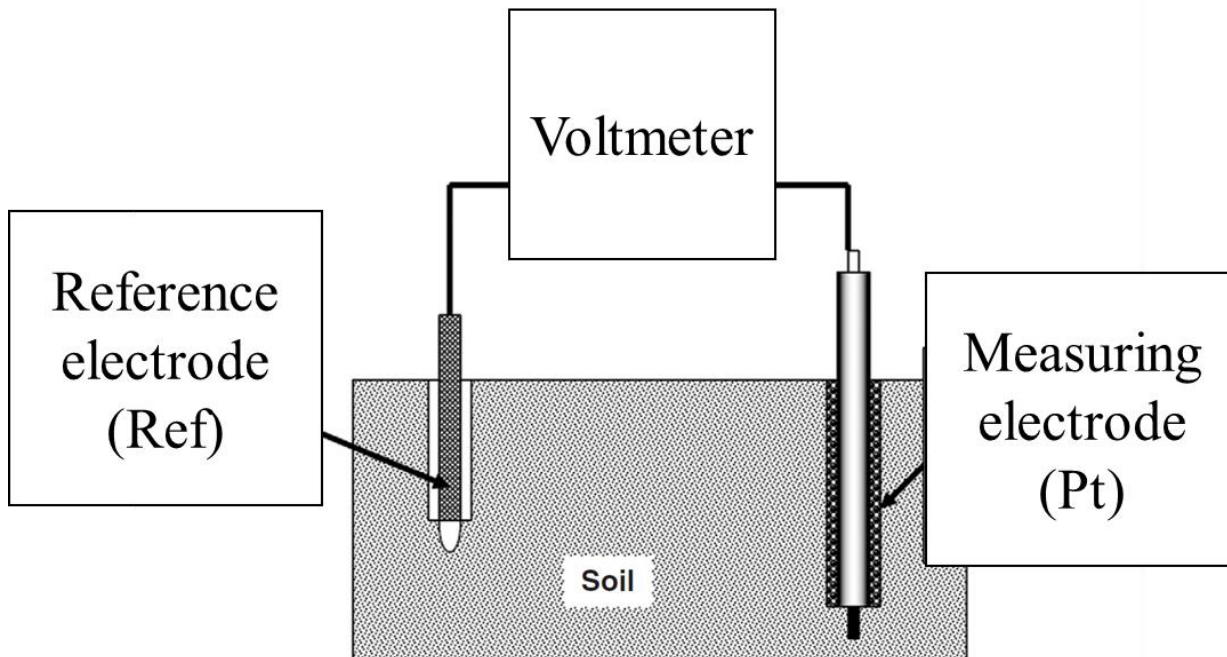
Redox potential is a biogeochemical master variable



# Background

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## How we measure redox potential

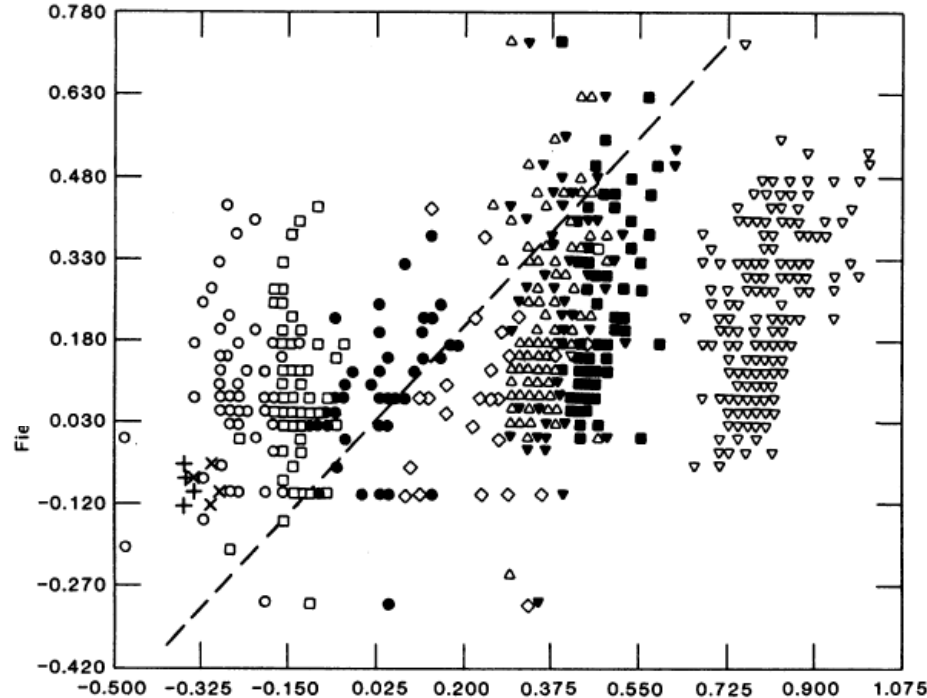


# Background

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## Electrode readings don't match solution composition

Field  
measured  
Eh (mV)



Eh computed from redox couples (mV)

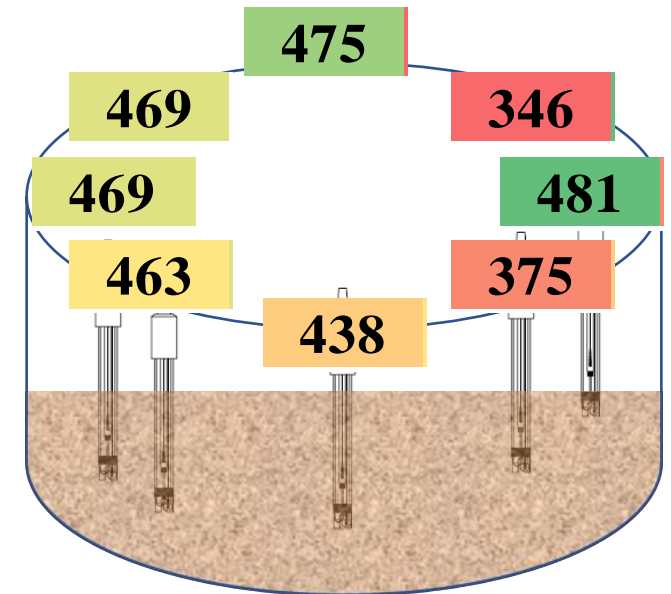
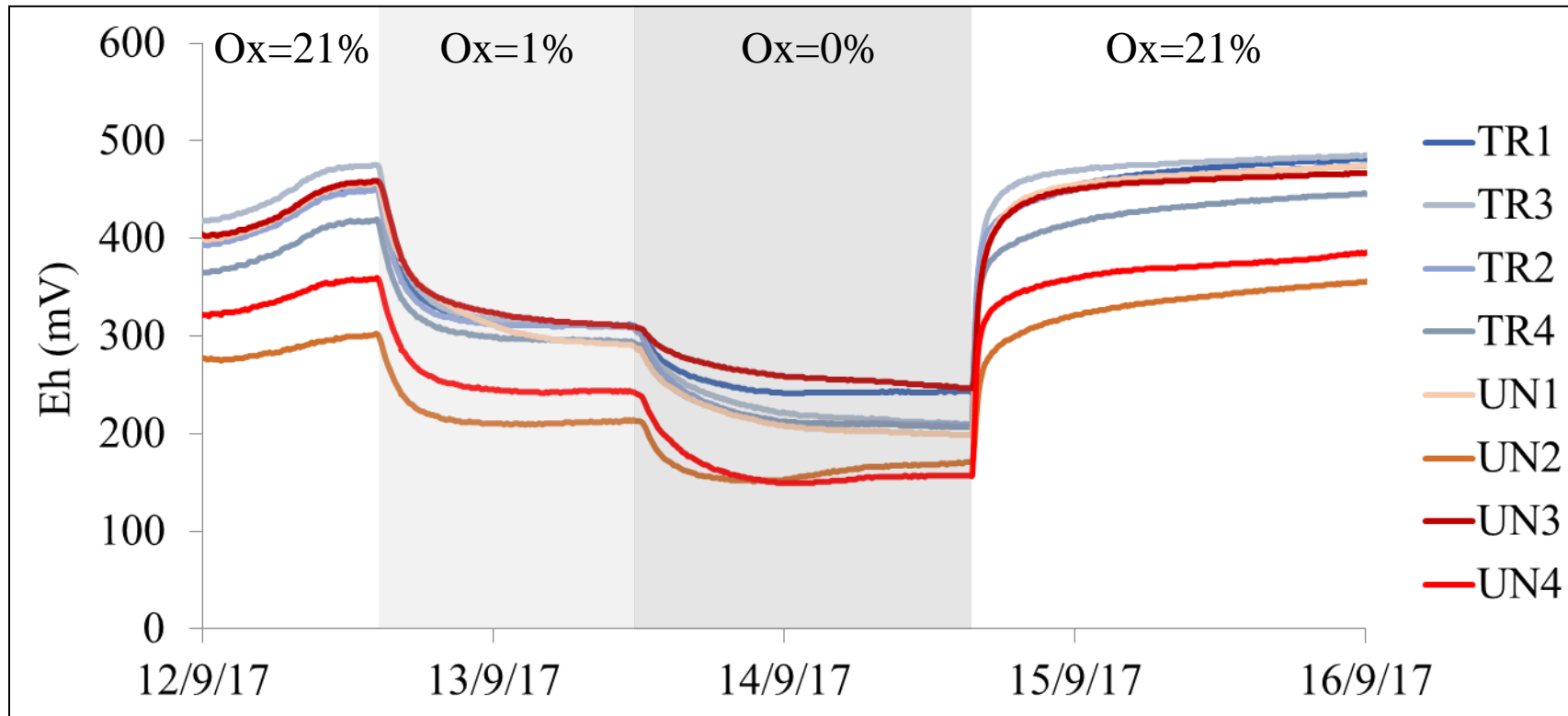
**“Measured values of EH obtained... have only a qualitative significance in soil solutions”**

The chemistry of soils 2<sup>nd</sup> ed.

Sposito, 2008

# Background

## Redox variability in a soil slurry incubation



# Research questions

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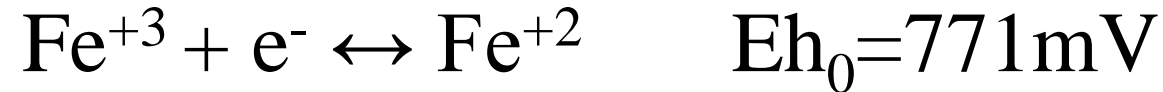
- Is the variability a sign of electrode malfunctions?
- What is causing the variability?
- Can the variability be corrected



# Methods

---

## Back to basics - one electroactive couple incubation



$$\text{Eh} = 771 - \log \left( \frac{\text{Fe}^{+2}}{\text{Fe}^{+3}} \right)$$

## Treatments

- Measuring devices
- Fe concentration
- pH
- Ionic strength

# Methods

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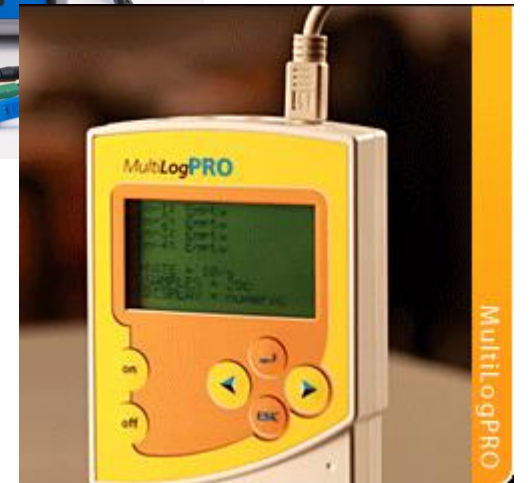
8 electrodes



External robust reference



High impedance potentiostat and data logger

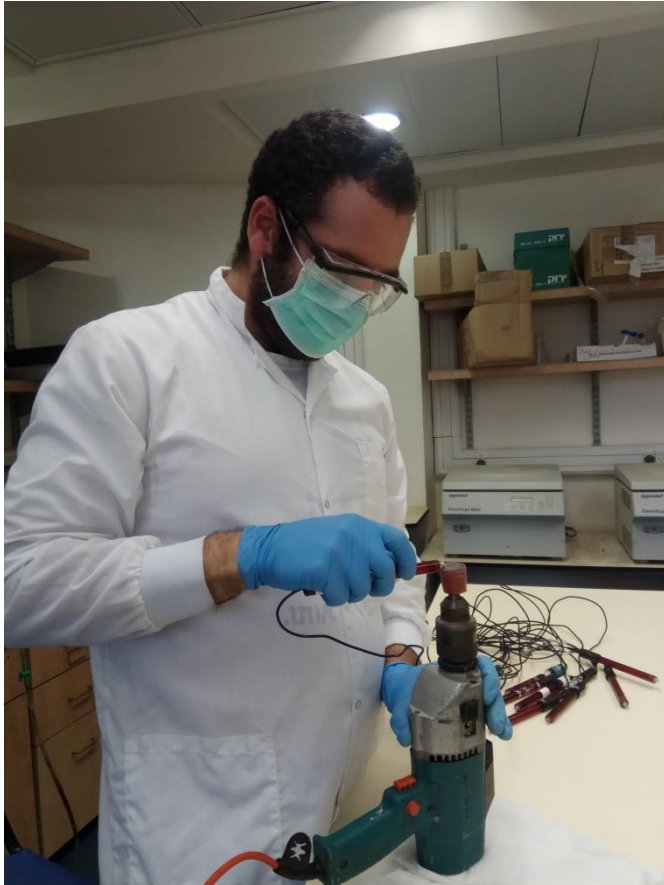




# Methods

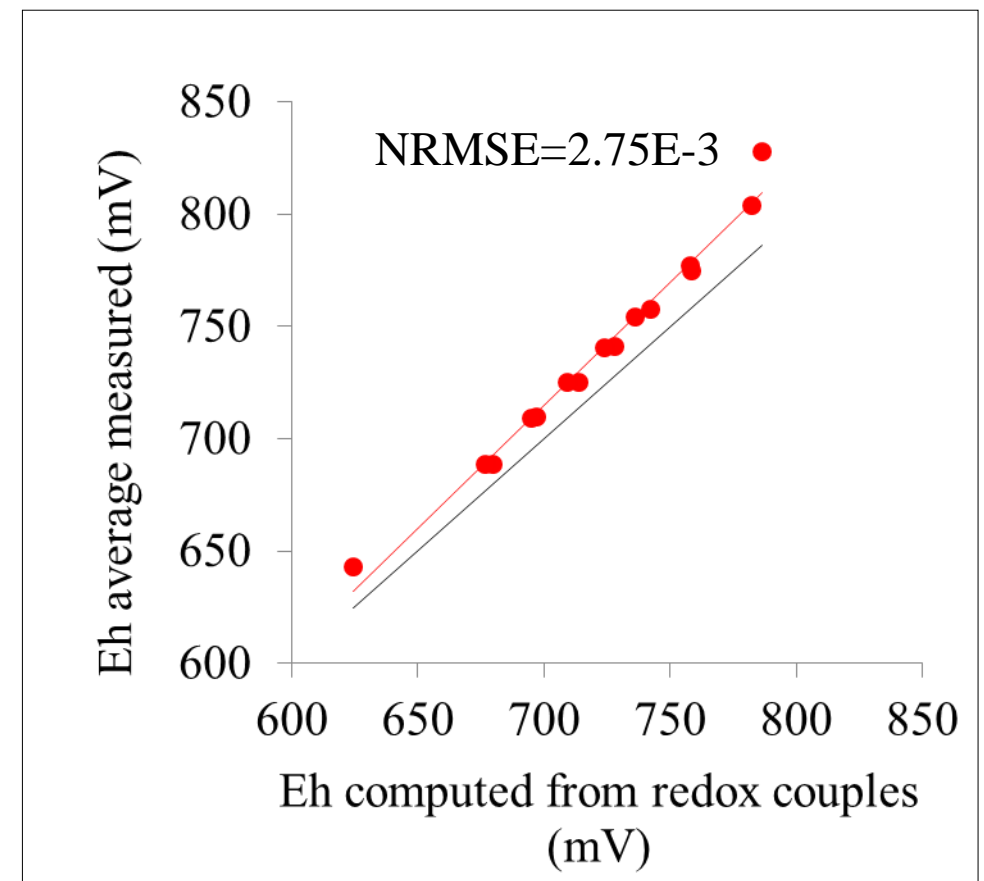
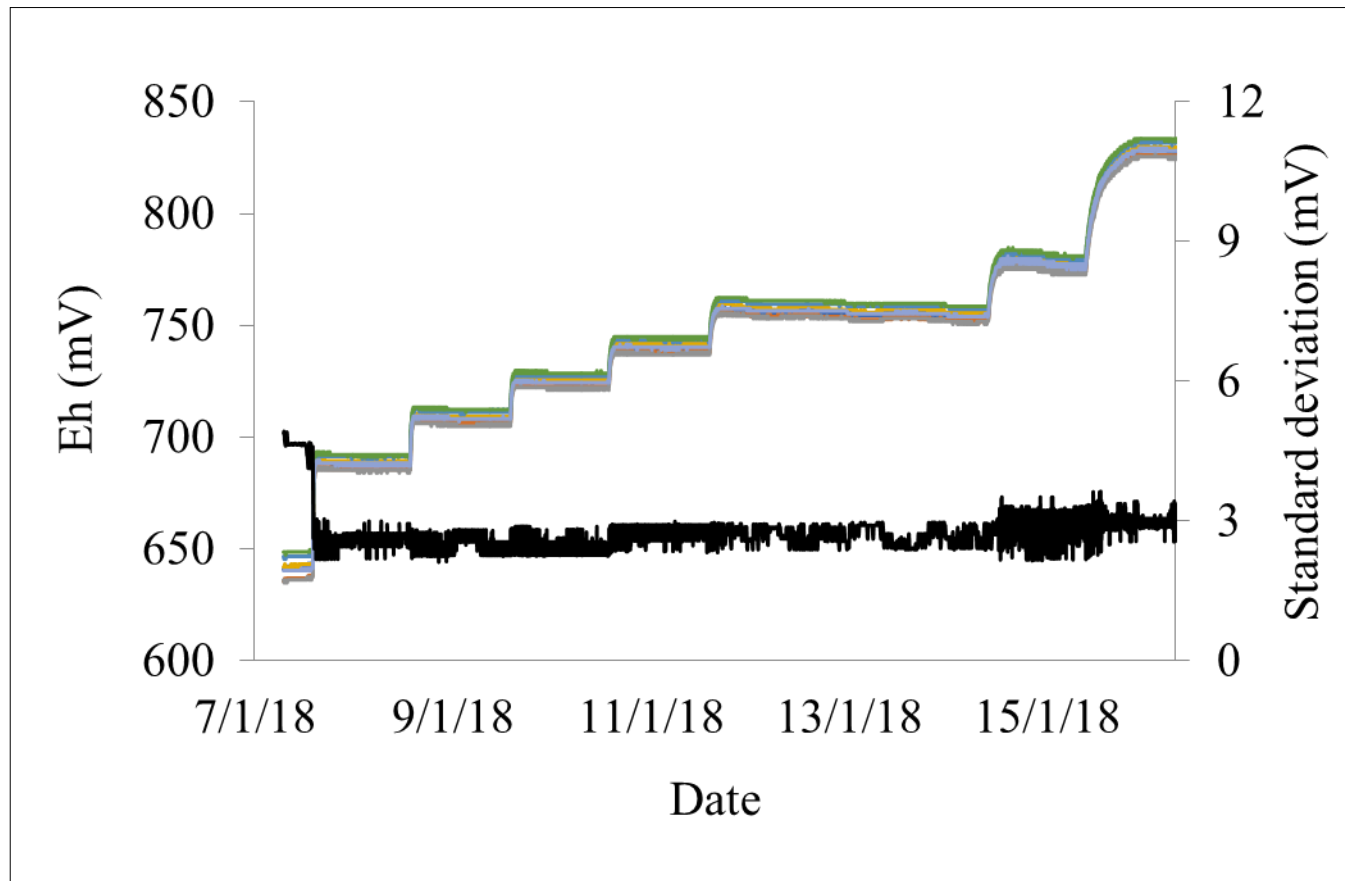
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## Electrode preparation and calibration



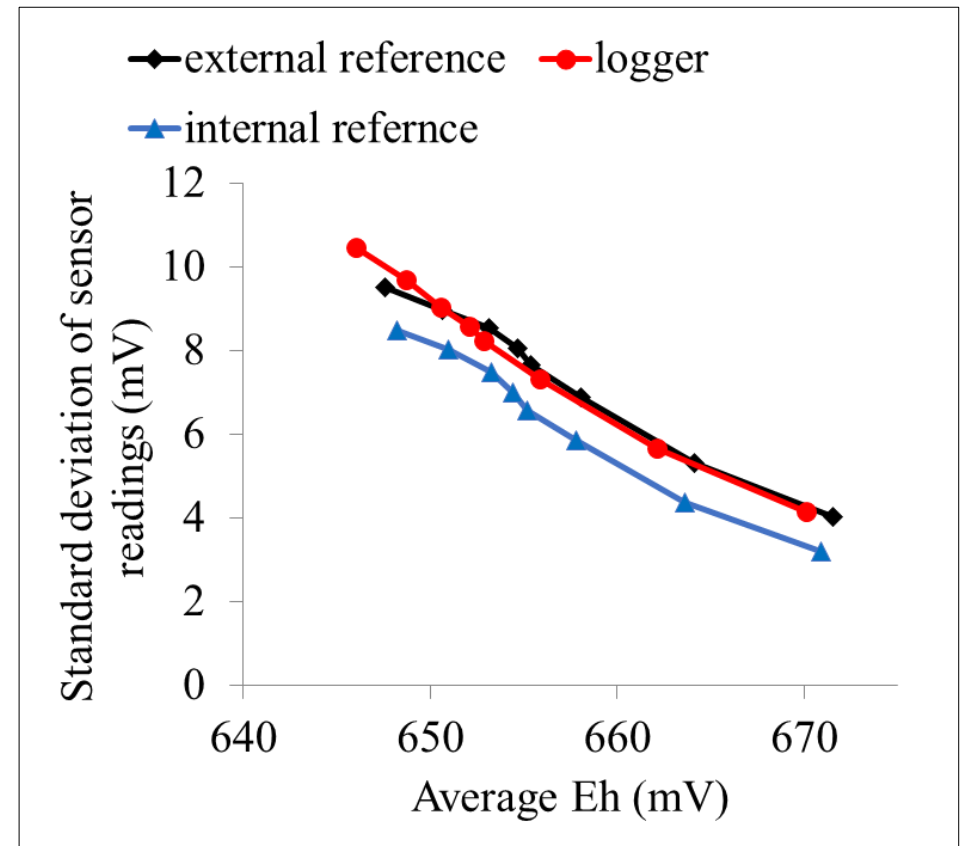
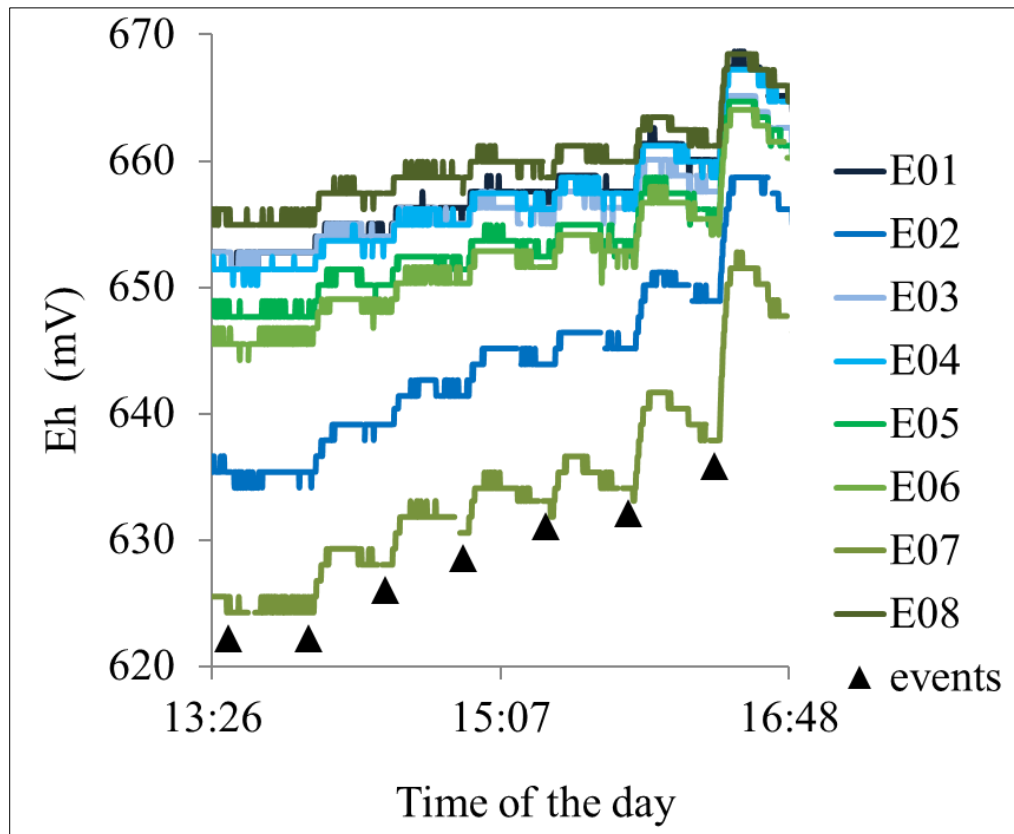
# Results

“High”  $\text{Fe}^{+2}$  concentration ( $30\mu\text{M}$ ) oxidation with  $\text{H}_2\text{O}_2$ ;  $\text{pH}=2.7$



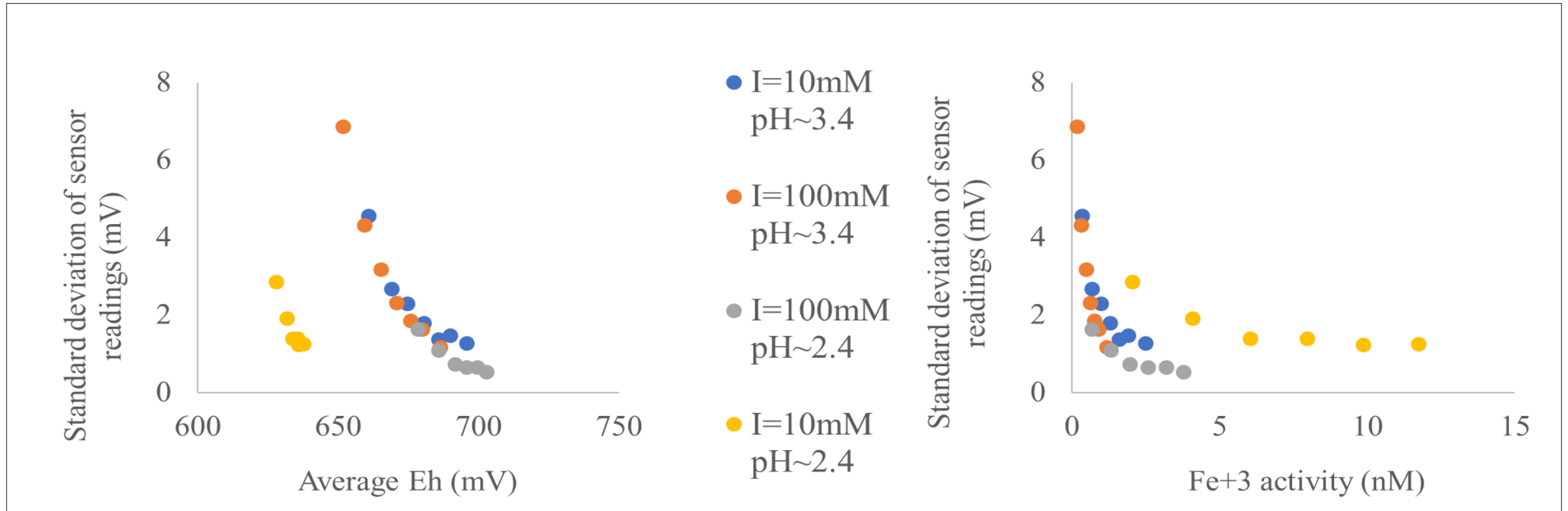
# Results

“Low”  $\text{Fe}^{2+}$  concentration ( $0.5\mu\text{M}$ ) oxidation with  $\text{Fe}^{3+}$ ; pH=3.3



# Results

“Low”  $\text{Fe}^{+2}$  concentration ( $0.5\mu\text{M}$ ) oxidation with  $\text{Fe}^{+3}$ ; Different pHs and Ionic strengths.  $\text{Fe}^{+3}$  activity calculated by added



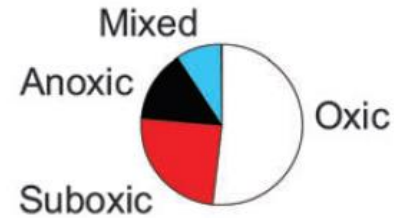
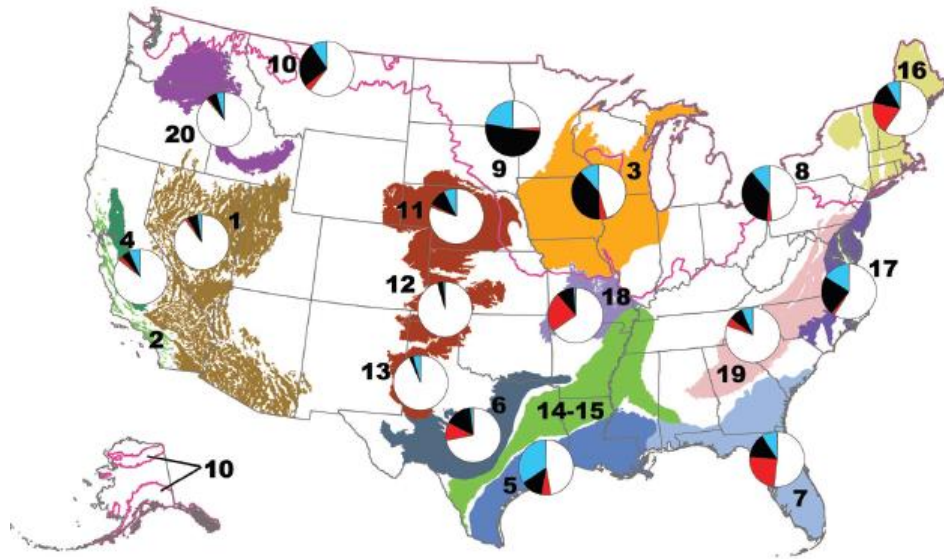
# Discussion

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The concept of limit of quantification in spectroscopic methods  
" Sufficient analyte concentration must be present to produce an analytical signal that can reliably be distinguished from 'analytical **noise**', the signal produced in the absence of analyte. " (Shrivastava and Gupta 2011)

# Discussion

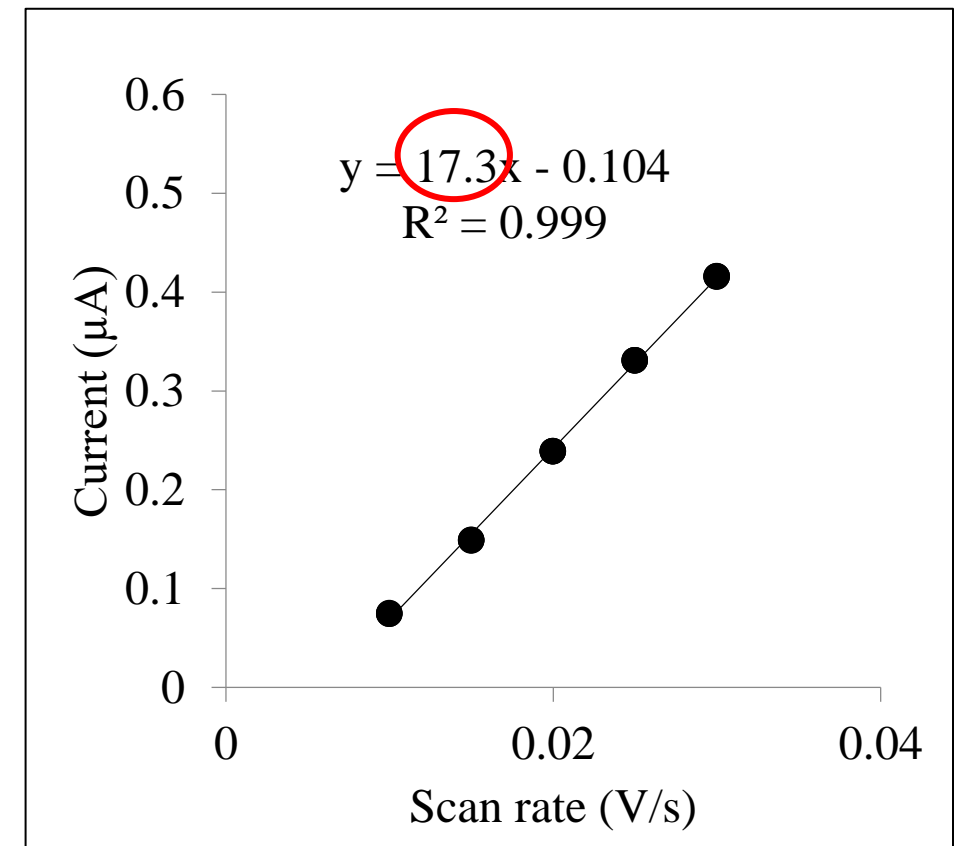
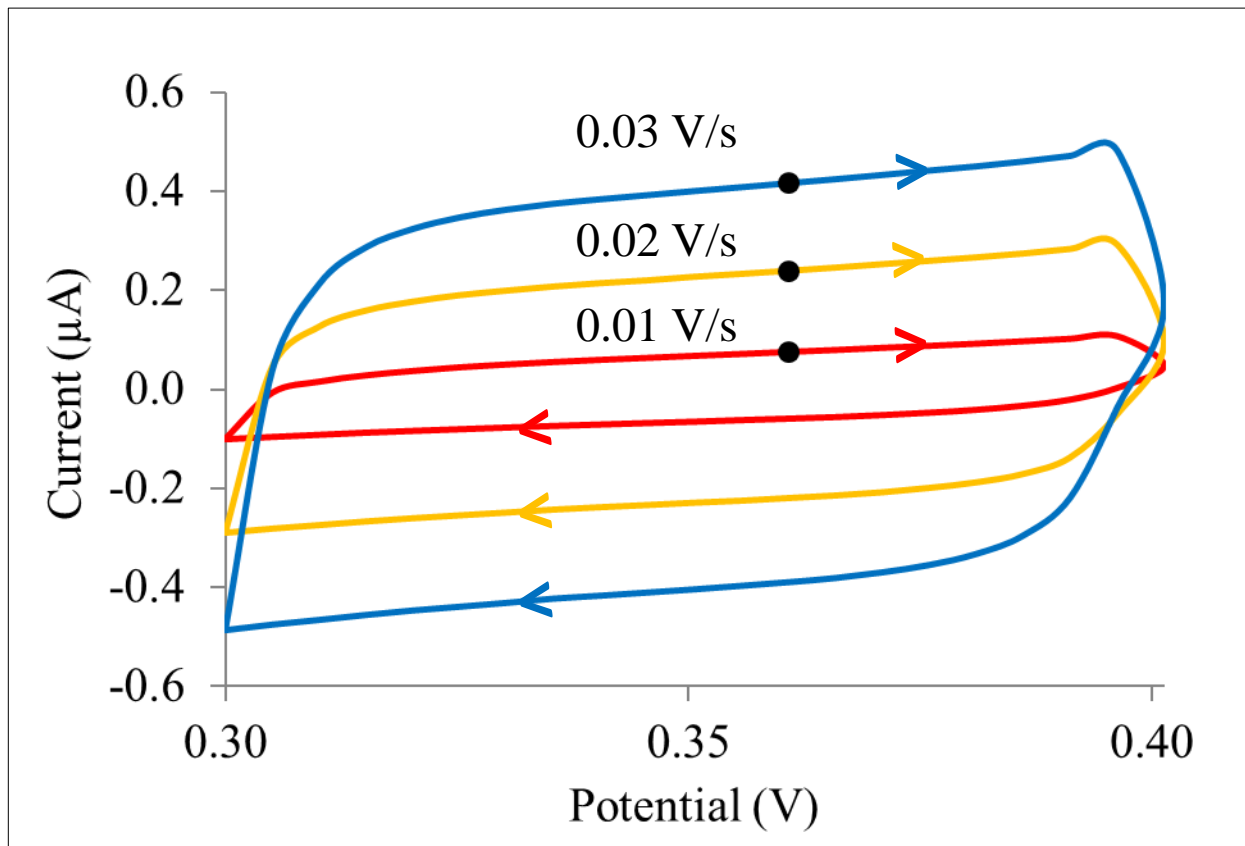
## Examining results in view of the new insight



DO <sub>2</sub> (mg/L)	NO <sub>3</sub> -N (mg/L)	Mn <sup>+2</sup> (μg/L)	SO <sub>4</sub> <sup>-2</sup> (mg/L)	Fe+2 (μM)
0.1	0.71	60	7.6	0.02
0.1	0	40	40	0.36
0.1	0.05	1	0.4	0.43
0.1	0.02	64	5.2	0.61
0.1	0.6	10	0.2	3.58
0.1	0.06	172	0.12	28.8
0.1	3.9	174	4.1	269

# Discussion

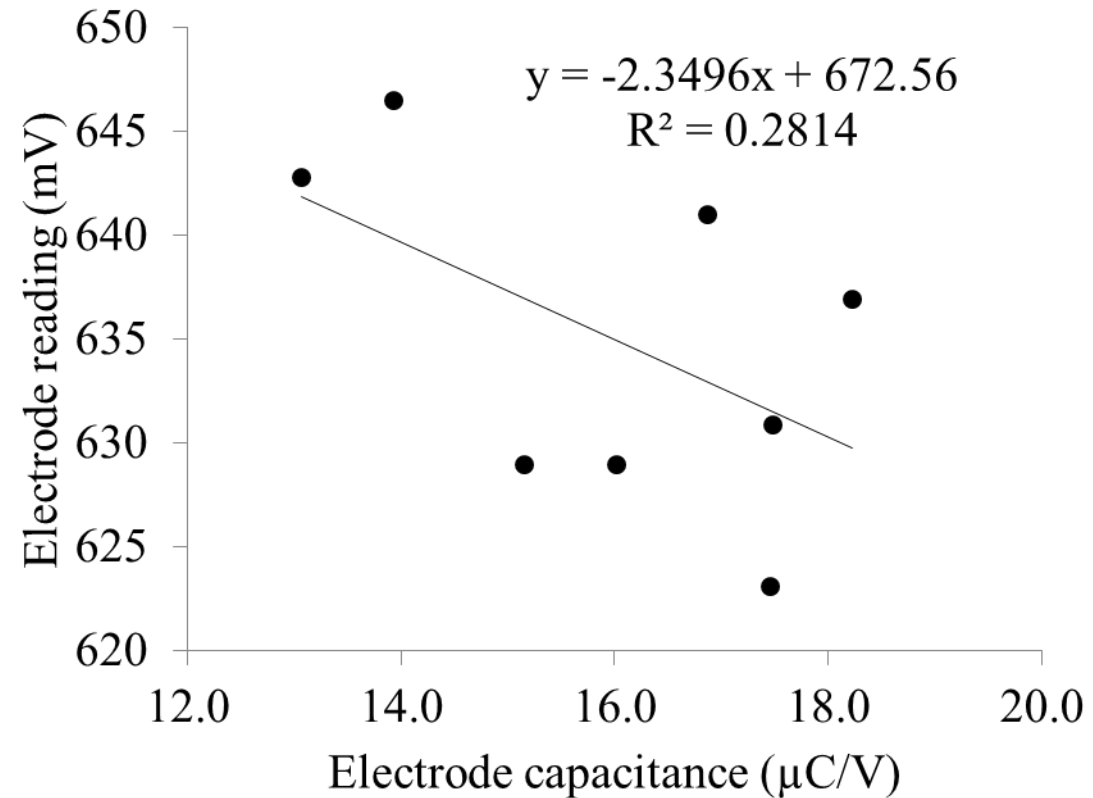
## Electrode surface measurement using Cyclic Voltammetry



# Discussion

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## Capacitance vs. readings in Fe solutions





# Conclusions

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- Pt electrodes gave different Eh values in a homogeneous solution
- In Fe solutions the variability increased dramatically as Eh dropped below a critical value
- The differences in critical Eh values seem to point towards  $\text{Fe}^{+3}$  molar activity as the underlying critical effector
- In short term experiments device issues (reference electrodes and lack of calibration) did not pose a problem

## Take home message

**Redox electrodes have a concentration above which they are more reliable**

# Thank you

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To the crowd

Moshe Shenker



Daniel Mandler



The engineering team

