

# **CARNICOM INSTITUTE LEGACY PROJECT**

A Release of Internal Original Research Documents

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## **Laboratory Notes Series: Volume 13**

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Chemistry Vol XIII



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Chemistry (and...) Vol XIII

FEB 2016

Feb 15, 2016

We are working w/ a developed diff eq via Lomen

$$\frac{dT}{dt} \approx -.014T + 4.76 \quad \text{NO! IT}$$

$$\text{IS } \frac{dT}{dt} = -.14T + 4.76$$

We are having some difficulty getting an explicit solution that gives up Lomen. We have a decent numerical solution. Central difference do appear to be superior to forward difference. Castro is handling the needed operations well.

We believe that a solution should be of the form

$$\frac{1}{-.014} \ln |-.014T + 4.76| + C_1 = t$$

We could try to plot this as is?

$$\ln |-.014T + 4.76| = (t - C_1) \cdot .014$$

$$|-.014T + 4.76| = e^{-.014(t - C_1)}$$

$$|-.014T + 4.76| = e^{-.014t - C_1}$$

$$4.76 = .014T + e^{-.014t - C_1}$$

$$.014T = 4.76 + C_1 e^{-.014t}$$

$$T = 340 + C_1 e^{-.014t}$$

$$\text{When } t = 0, T = 32.78 \Rightarrow C_1 = -30722$$



Guess what! I see the problem!

Page  
2

It is  $-0.14$  not  $-0.014$ !!!!

$$T = 340 - 307.22e^{-0.014t}$$

$$t=0, T=32.78$$

$$t=10, T=72.92$$

No still a problem. Why?  
We have reached the solution twice now.

$$e^{5-2t} = e^5 \cdot e^{-2t}$$

$$= .37$$

$$= e^5 \cdot e^{-2t}$$

NO

$$\text{let } x=3$$

$$e^5 \cdot e^{-2t}$$

$$= .37$$

YES

YES

but  $e^5$  is a constant.

Try it back to the primitive form

$$C_1 = \frac{1}{.014} \ln(-.014T + 4.76) + t$$

$$T = 32.78$$

$$t=0$$

$$C_1 = 104.20$$

IT IS  $-0.14$ !!  
not  $.014$ !

Something must  
be wrong with  
this.

$$\ln(-.014T + 4.76) = (C_1 - t) \cdot .014$$

$$\ln(-.014T + 4.76) = .014(104.20 - t)$$

$$\ln(-.014T + 4.76) = 1.46 - .014t$$

$$-.014T + 4.76 = e^{(1.46 - .014t)}$$

$$-.014T = e^{(1.46 - .014t)} - 4.76$$

$$.014T = 4.76 - e^{(1.46 - .014t)}$$

$$T = 4.76 - \frac{e^{(1.46 - .014t)}}{.014}$$

$$T = 32.43 \text{ @ } t=0$$

$$T = 72.61$$

$$t=10$$

NO

Not Luv

Why?

Why does this keep happening?

Page 3

I see what's likely the major problem.  
Ragroup: The coefficient is  $-0.14$  not  $-0.014$ !  
So now again.

$$-\frac{1}{0.14} \ln |-.14T + 4.76| + C_1 = t$$

$$-\ln |-.14T + 4.76| = (t - C_1) 0.14$$

$$\ln |-.14T + 4.76| = (C_1 - t) 0.14$$

$$-.14T + 4.76 = e^{.14(C_1 - t)}$$

$$-.14T = e^{.14C_1} \cdot e^{-t} - 4.76$$

$$\cancel{.14T} = \cancel{4.76} + C_1 e^{-t}$$

$$-.14T = C_1 \cdot e^{-t} - 4.76$$

$$.14T = 4.76 + C_1 e^{-t}$$

$$T = \frac{4.76 + C_1 e^{-t}}{.14}$$

When  $t=0$ ,  $T=32.78$

$$4.76 + C_1 e^{-t} = T(.14)$$

$$C_1 e^{-t} = T(.14) - 4.76$$

$$C_1 \cdot e^0 = T(.14) - 4.76$$

$$C_1 = T(.14) - 4.76$$

$$C_1 = 32.78(.14) - 4.76 = \\ = 4.59 - 4.76 = -.17$$

So now we have:

$$T = \frac{4.76 - .17e^{-t}}{.14}$$

This is a perfectly valid solution, all to well.

When  $t=10$ ,  $T=?$  34.0

OK, now you have it.

The actual answer is 33.70

So it is off some, but it is finally the correct solution!

Let's see at  $t=20$   $T = 34.0$  excellent.

So we do see the limiting value being approached.

That's great.

Now revisit the equilibrium point and phase diagram the actual diff eq is:

$$\frac{dT}{dt} = -.14T + 4.76$$

$$\text{Set } -.14T + 4.76 = 0$$

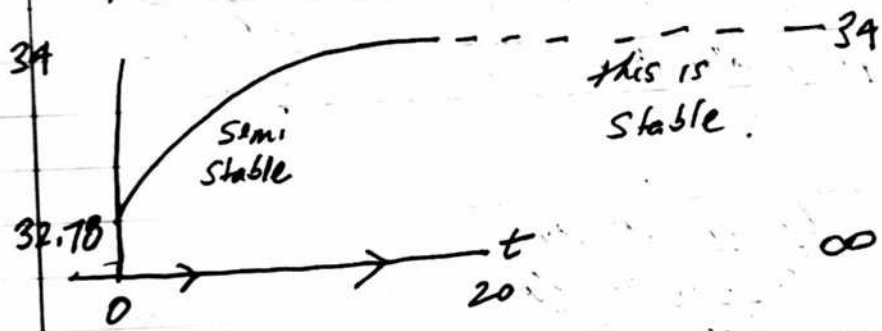
$$-.14T = -4.76$$

$$.14T = 4.76$$

$$T = 34^{\circ}\text{C}$$

This is super.

Now can we draw the phase diagram.



This is where the finger and the probe reach an equilibrium temperature.

So you can see here that you do not always need "exponential harmonics".

1. IF a standard regression does not work
2. and IF you are willing to explore differential relationships, which you now should be willing to do, you may well be able to discover a relationship that will meet standard linear regressions
3. and THEN you may well be able to come up with an explicit or closed solution which is extremely powerful!

This is fantastic knowledge and now open up differential relationships and investigation to you, which you have wanted your whole life!

You did find an diff. relationship, probably one of the best ones to ever befall mankind, and now you understand more deeply how you went about it.

The relationship you discovered is simply more complex than a linear form but the idea was the same and your solution immediately powerful.

# Page 6

We now get to move on and we can now always be on such a search any quest in life and the fruits of it are boundless.

Lomen's book really is fantastic. He has opened up DQ's in a very real sense.

Now we can move on to the next example: Kenya. We can see that an exponential regression works very well,  $r^2 = 0.995$ .

So to think we probably would not have to go any further. But what if it did not? Then we need to explore differentiated relationships.

Our regression equation is  $y = 2.546E-29e^{.035x}$ .

Interesting that coefficient is successful and down to  $E-29$ .

Now, he leads us a certain direction, but let's try it ourselves first. (How can Export and Import easily).

So investigating relationships, we do indeed see a relationship (it appears quadratic between  $P$  and  $\frac{dP}{dt}$ ). We have a very strong linear relationship here.

List 2  
List 3

$$\begin{array}{l} X \text{ is } P \\ Y \text{ is } \frac{dP}{dt} \end{array} \quad \text{So } \frac{dP}{dt} = 0.275P - .87 \quad r^2 = .999$$

So this is the relationship you are looking for. You will definitely have another closed solution here.

There is now the question of  $\frac{dP}{dt}$  and  $f(t)$ ?

Not linear  
Quadratic yes.  
So we could go further.



# Page 7

So if you think about it, even if you discover a quadratic relationship in  $t$  it means the solution will be cubic which will be a lousy form.  
So strive for the simplest relationship possible.

On we go. Assume that we do not know that exponential regression is highly successful w/ the raw data.  
Be aware that we are using back differences.

$$\frac{dP}{dt} \approx 0.275P - .07$$

$$\frac{dP}{.275P - .07} = dt$$

$$\int \frac{dv}{v} = \ln|v| + C$$

$$v = .275P - .07$$

$$dv = .275$$

$$\frac{1}{.275} \int \frac{.275 dP}{(.275P - .07)} = \int dt$$

$$\frac{1}{.275} \ln|.275P - .07| + C = t$$

$$\ln|.275P - .07| = (t - C) \cdot .275$$

$$|.275P - .07| = e^{.275(t-C)}$$

$$= e^{.275t} \cdot e^{-C}$$

$$.275P - .07 = C_1 e^{.275t}$$

$$.275P = .07 + C_1 e^{.275t}$$

Page 8

the term is way too high. why?

$$P \approx 0.87 + C_1 e^{\frac{.275t}{K}}$$

and/or then we are way too low.

when  $t=1950$ ,  $P=6.265$

$$C_1 e^{.275t} = P(.275) - .87$$

$$C_1 = \frac{P(.275) - .87}{e^{.275(1950)}}$$

$$C_1 = 1.097E-233$$

$$\text{so } P = 0.87 + \frac{1.097E-233 e^{.275t}}{.275}$$

let  $t=1951975$   $P=3002$  Not working!

Try when  $t=0$ ,  $P=6.265$

$$C_1 = \frac{P(.275) - .87}{1} \quad C_1 = .853$$

$$P = .87 + \frac{.853 e^{.275t}}{.275}$$

let  $t=25$   
 $P=3005$  No

Something is very wrong again.  
Let's figure it out.

You had  $x$  &  $y$  reversed. No I did NOT.

It is

$$\frac{dP}{dt} = 3.626P + 3.169$$

$$r^2 = .999$$

$\frac{dP}{dt}$  is list 3

P is list 2

We want

$$\frac{dP}{dt} = f(P)$$

list 3 <sup>y</sup> list 2 <sup>x</sup>

But indeed we have

$$\frac{dP}{dt} \approx 0.275P - .07$$

$$r \approx .999$$

eg when  $P = 8.33$ ,  $\frac{dP}{dt} = 1.42$  test. yd, ok.

Could it be back difference giving the problem?  
Test the numerical solution next.

Ok, there is a problem. This solution is  
rising far too quickly.

so something is seriously wrong.



Let's work out central difference and see how it behaves.

x	x*	y	$\Delta_c$	$\frac{\Delta y}{\Delta t}$ (2)	$\frac{\Delta y}{\Delta t}$ (3)	t
1950	0	6.265			P	
1955	5	7.189	.2067	.2067	7.189	5
1960	10	8.332	<del>.8560</del> .256	.2560	8.332	10
1965	15	9.749	.3166	.3166	9.749	15
1970	20	11.498	.3992	.3992	11.498	20
1975	25	13.741	.5134	.5134	13.741	25
1980	30	16.632	.6612	.6612	16.632	30
1985	35	20.353	.8498	.8498	20.353	35
1990	40	25.130				

Central difference DQ

$$\frac{\Delta y}{\Delta t} \approx .0492P - .157 \quad \text{and this is totally different.}$$

I think you had your columns reversed.  $r^2 = .999$

This is a very good numerical solution

Now I see, you forgot to divide by 5! Yes, big mistake.

Forward Difference Equation

$$\frac{\Delta y}{\Delta t} = .055P - .174 \quad r^2 = .999$$

This is a fairly poor solution.

So now you have two equations to judge error.

You must keep track of columns & time up are properly.

Notice that  $\frac{\Delta y}{\Delta t}$  implicitly had to write it.

From this, we can now see twice that central differences are far superior, it makes sense as they are symmetrical.

Page 11

Now we can proceed to a closed solution  
as we know we have something good to  
work with now.

$$\frac{dP}{dt} \approx .0492P - .157$$

$$\frac{dP}{.0492P - .157} \approx dt$$

$$u = .0492P - .157$$

$$du = .0492$$

$$\int \frac{du}{u} = \ln|u| + c$$

$$\frac{1}{.0492} \int \frac{.0492P}{.0492P - .157} dP = \int dt$$

$$\frac{1}{.0492} \ln|.0492P - .157| + C_1 = t$$

$$\ln|.0492P - .157| = (t - C_1) \cdot .0492$$

$$.0492P - .157 = e^{(t - C_1) \cdot .0492}$$

$$.0492P - .157 = C_1 e^{t \cdot (.0492)}$$

$$.0492P = .157 + C_1 e^{t \cdot (.0492)}$$

$$P = \frac{.157 + C_1 e^{t \cdot (.0492)}}{.0492}$$

$$C_1 = \frac{.0492P - .157}{e^t}$$

$$\text{When } t=0, P=6.265 \Rightarrow C_1 = .151$$

So our equation is

$$P = \frac{.157 + .151 e^{t(.0492)}}{.0492}$$

Something is still very wrong. It is OK now.  
I forgot to carry the .0492 in the exponential term.

We do have an excellent solution.

Lomen took a different route, which was actually necessary, but it points out that it will not always be a linear differential relationship and so you will just have to see what it takes to solve it. Exp harmonics can always be used but if you use them you can probably just fit the data itself.

OK, we have done well. Two diff eqs have been developed and solved for both numerically and explicitly, using raw data. You also learned the value of central difference data.

To apply the method We should need a case that does not match regression. This should be a prerequisite.

It looks like we have a very good one with the AIDS data by Lomen on p157

Logistic is the only one that looks close but the Mean square error is still way too high.

Let's first see why the logistic and if the logistic should be rejected.

$$y = \frac{159861.2}{1 + 166.11 e^{-.1998 Qtr}}$$

$$Mse = 190,115$$

Mse seems especially high compared to graph.

The solution is actually quite good. It is mostly on the low end of the curve but that is actually quite respectable and usable. Let's look for alternatives, however.

List 4	List 5	List 6
X	Y	dy/dx

y'  
y'

Plot 6 against 4 (x)

Plot 6 against 5 (y)

$\frac{dA}{dt} = f(x)$  is not linear

Logistic does indeed look the best.  
So there is a case for this.

$\frac{dA}{dt} = f(y)$  is not very linear also.  
not logarithmic

Power regression is quite decent.  
Quadratic is actually excellent.

So we actually have 2 candidates

$$\frac{dA}{dt} = f(y)$$

$f(y)$  is quadratic  $r^2 = .999$   
 $y = ax^2 + bx + c$   $Mse = 6528?$

$$\frac{dA}{dt} = f(y)$$

$f(y)$  is power  $r^2 = .998$   
 $y = 1.5099x^{.7703}$   $Mse = 2.26E-3$

The power law looks quite appealing  $A = \text{no. of deaths}$

$$\frac{dA}{dt} \approx 1.5099A^{.7703}$$

This seems to be a separable form.

$$\frac{dA}{1.5099A^{.7703}} = dt \quad \text{so}$$

$$u = Ax^b$$

$$du = bAx^{b-1}$$

on integral form:

$$\int \frac{1}{Ax^b} dx$$

$$\frac{1}{Ax^b} = \frac{1}{A} x^{-b}$$

Test this w/ Casio  $\int = \frac{-b}{a} x^{-(b+1)} = \frac{-b}{ax^{b+1}}$

Casio integration can handle coefficients! Very smart!  
 The integral is:

$$\frac{-x^{-b+1}}{a \cdot (b-1)} \approx \frac{-A^{-.7703+1}}{1.5099(.7703-1)} + C_1 = t$$

or

$$\frac{-A^{.2217}}{-.3347} + C_1 = t$$

$$\text{or } C_1 = t - \frac{A^{.2217}}{.3347}$$

when  $t=1$   
 $A=559$

$$A^{.2217} = (t - C_1)(.3347)$$

$$\text{so } C_1 = -11.146$$

$$y^{1/5} = x$$

$$\text{let } y = 2$$

$$2^{1/5} = 1.149$$

$$(2^{1/5})^5 = 1.149^5$$

$$2 \stackrel{?}{=} 2 \quad \text{yes}$$

so the proposal is

$$A = \left[ (t + 11.146)(.3347) \right]^{4.511} \quad \text{or } A = 7.173E-3$$

$$t=10, A=6820$$

$$t=20, A=39125$$

an alternate simple form is:

$$A = (7.173E-3) (t + 11.146)^{4.511} \approx 7.2E-3 (t + 11.15)^{4.5}$$

[this is superb] [this is decent]

Aids  
Death  
Model

This is a wonderful equation, it is elegant, it is stable, and models the data beautifully.

This is a beautiful application of developing an explicit equation from a developed differential equation.



So a differential equation can give insight into the relationships within data that may not be obvious. Furthermore it is examining CHANGES within that data to uncover these hidden relationships.

Many times you will probably be able to come up with a closed form for the equation, and that is needed so that you will be able to integrate the approximation that we develop for the differential relationship.

You can also see where partial DPs come from. Here we would have

$$z = f(x, y)$$

and you would have to develop a relationship, in a differential form, that involve both  $x$  and  $y$ .

It looks like we next should learn about linear differential equations. They appear in real life in many occasions.

A RC Circuit, which is going to come up w/ electrical impedance spectroscopy (EIS) is:

$$a \cdot \frac{dy}{dt} + \frac{y}{b} = E(t)$$

Con numerical form:  $\frac{dy}{dt} = \frac{E(t) - \frac{y}{b}}{a}$

$y$  = Charge  
 $t$  = time

$$a = R = 10 \Omega$$

$$b = C = .01 F$$

$$E(t) = 12$$

$$y_0 = 5 \text{ Coulombs}$$

$$t_0 = 0$$

so an RC circuit is a perfect example of a linear first order diff eq.



$$a \frac{dy}{dx} + by = f(x) \quad \text{this is the form of a 1st order linear diff eq.}$$

for kicks, let's rearrange this.

$$\frac{dy}{dx} = \frac{f(x) - by}{a} \quad \text{this is another form for the same thing. Notice this is a non-autonomous diff eq.}$$

the format is described as "the left hand side is a linear combination of  $y$  and its derivative"

It is linear because  $\frac{dy}{dx}$  is first order &  $y$  is linear

so this makes it a linear combination of  $y$  and its derivative.

Now your format is also interesting to observe (which Casio will need to be able to graph

$$y' = \frac{f(x) - by}{a} \quad \text{or} \quad y' = \frac{1}{a} (f(x) - by)$$

this is the same equation as  $ay' + by = f(x)$

and the same here.



Here are three forms of the same equation.  
There is certainly no guarantee that you would be able to recognize any or all of the forms so you certainly need to know the definition.

Another big question is how would you ever derive or recognize the form as existing within data?  
I don't know how you would ever recognize it.

Let's see if any problems are listed for data sets.  
I tend to doubt it.

Now we see that the actual form is

$$\boxed{y' + p(x)y = q(x)}$$

← This is even more general.

This could also be written in the form:  $y' = q(x) - p(x)y$ . This is called the "forcing function".

So think about this.

$\frac{dy}{dx}$  is a function of  $x$ , but then another function of  $x$ , & sometimes  $y$ .  
What a curious situation to recognize.

Another way:

$$\boxed{\frac{dy}{dt} = f(t) - g(t)y}$$

2 different functions of  $t$   
as well as a product  
with  $y$ .

This is probably the most practical to try and remember.

sure enough, there are no data sets given. All problems are given equations known for certain situations. I suspect that they are very difficult to draw out of any raw data. There must be a long history to have developed these equations.

So now the question is, would you like to try to work through the type of equation? It is the method that requires an "integrity factor".

I am actually more curious how you would even develop such an equation.

It is not exactly a simple method to solve these, at least not yet. You would get into a cookbook procedure from Schram's DPs but differentiated from that recognition and development of the linear form to me as the real issue.

We are moving to Loren p223.

This is fascinating already. "Deniso & Chad" Casio plots this fine.

This is a coupled set of first order differential equations.

A Personal Relationship equation, no less.

So this is really quite amazing. The time we have two DEPENDENT Variables, or entities to be studying instead of one.

Denise's affection

Chad's affection

and

Chad's

Denise's affection

$$\frac{dx}{dt} = ay$$

$$\frac{dy}{dt} = -bx$$

Who even thought that you could model "affection" with a differential equation, and one of such a simple nature, no less.

"the romantic attraction of two individuals all suited to each other"

"x" is Denise's affection for Chad

"y" is Chad's affection for Denise

x is not Denise

y is not Chad

x & y are "affections", i.e. an emotion is being modelled here by a variable. x & y are not "things" and they are not people, these are emotions and we are looking @ the change in emotion here as they are affected by another person's emotion.

So this really opens up the consideration of what can be modelled with a differential equation. maybe modelling an emotion is simply. It may not need to be precise, only an estimate of how something changes may be sufficient. In this case it is simply two linear relationships.

## Page 21

We have indeed plotted this.

Phase line plot is a circle.

Time dependent plot is a sin wave.

You have also learned that Camo can handle a system of diff eqs. This is great!

Now what is really interesting is how Lomen's opening paragraph is explaining exactly where we are headed. We now have 2 first order DQS. But two 1st order DQS are equivalent to one 2nd order DQ! And that's what he is saying, that there is a continuous identity between these two versions of the same thing.

He also explains how someone would come up with a second order equation, which you could not understand before. It's the reverse process of breaking down a second order equation into two first order equations.

Lomen's book is really opening up your eyes to DQS.

if

$$x' = y \text{ and } y' = -2x$$

$$\text{then } y' = x'' \text{ so } x'' = -2x \text{ or } x'' + 2x = 0.$$

Notice what is happening here.

Converting two separate first order equations into one second order equation

Look what happens here.

Due to this change, we were dealing w/ 2 different "affections". Now we are dealing with only one persons affection, but @ the second order level. So what is happening here is that implicit within the second order relationship of one persons affection we actually have the second person affection integrated, even though you cannot see it. So now you understand what second order animal means. Second order actually means two singles, & 3rd order means 3 singles, etc. That is perfectly and hardly obvious.



Feb 21 2016

Very good things are happening.

1. Voltammetry is now alive and well w/ the Palmsens 3. This is going to be amazing.
2. Oxidation-reduction is a great topic to learn about. Chang Book Ch 19 p 614+ (and spontaneity of reactions) is going to be really interesting.  
Also Chang Ch 4 p 91 is also great.
  1. Precipitation
  2. Acid Base
  3. Redox reactions
 } Most Chemical reactions!
3. Our work on Differential Equations is also fascinating. The heck. Lomen is the ticket here. You have even entered into:
  1. Social science! (which you never would have expected)
  2. Systems of differential equations (very cool!)
  3. Interplay of high order, esp 2<sup>nd</sup> order, and systems of 1<sup>st</sup> order equations.
4. You have two papers on tap
  1. Exotic Technology
  2. Exponential Harmonics intro.

5. Other paper on top
1. Call ya Citizen Science
  2. Analysis of R PM 2.5 Data
6. Ham radi. study  
Better keep them above  
Complex numbers will help you in both  
Electrical Impedance Spectroscopy and  
Ham.

Now, a last question for today is:

1. How can you tell if something is being oxidized or reduced in a voltammetry experiment?



Today we also study the Pine Voltammetry Book.

Carrying out a redox process in an electrochemical cell is the fundamental idea.

Current control regulate how fast  
something happens

Control by voltage determine to what extent  
it happens.

You control one @ a time, and you can only  
control one @ a time. Control by voltage  
is voltammetry. Galvanostatic methods  
control the current. Voltammetry is  
more common.

We hold concern on what is happening @  
the WORKING electrode. That is what is  
most important for now.

Highly  
Highly

Positive potentials generally oxidize analytes.  
Negative potentials generally reduce analytes.

The magnitude of the current flowing through  
the electrode is proportional to the concentration.

We have a law of diffusion, generally of the  
form  
$$i = k \cdot \frac{dc}{dx}$$
 where  $C$  is the concentration

The  
Diffusion  
Limited  
Current.



Looks like a differential eq here, does it not?  
The equation involves current and the concentration gradient.

Most of the voltammetry methods vary because of how the concentration gradient is created and managed.

3 Type of methods

1. Potse

2. Sweep

3. Hydrodynamic

Actually:

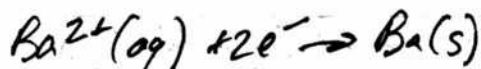
1. Sweep (General behavior)

2. Pulse (quantitative info)

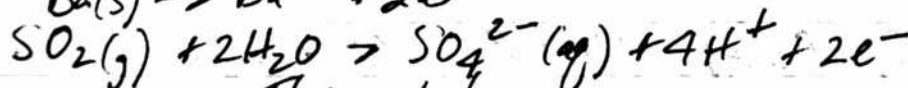
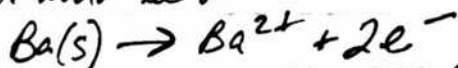
3. Hydrodynamic

KCl or strong acids (~1M) can be used as electrolytes if needed.

We should be in a position to determine what it takes to create  $\text{BaSO}_4$ :

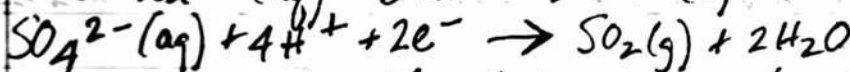
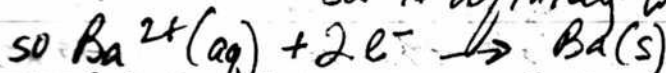


we would need



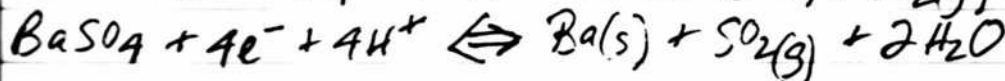
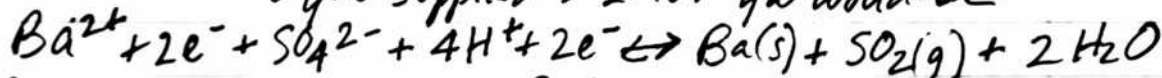
This would be spontaneous

but it definitely was not.



definitely not spontaneous, but if

you supplied  $> 2.70\text{V}$  you would have:



This says that it was possible if you were in 1M solution.

+2.90V

-1.20

$E = 2.70\text{V}$

-2.90V

+1.20V

$= -2.70\text{V}$

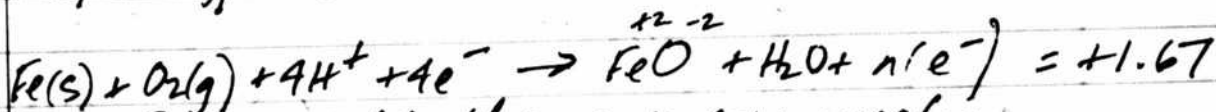
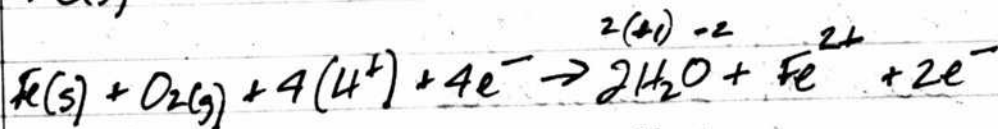
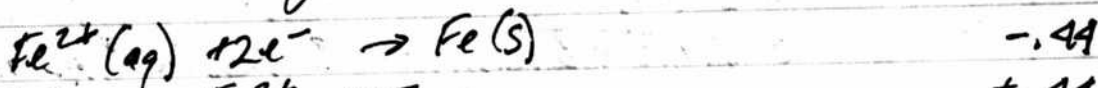
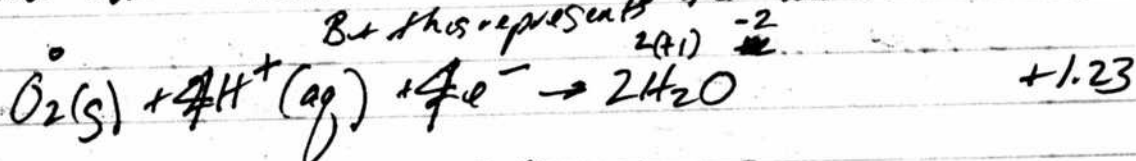
I have everything in my graphs to determine what is spontaneous or not.

Measuring redox reaction is really interesting.

What if you place some iron ( $\text{Fe}^{2+}$ ) in water?  
Will it oxidize?  
What about a nail?

But this represents the formation of water.

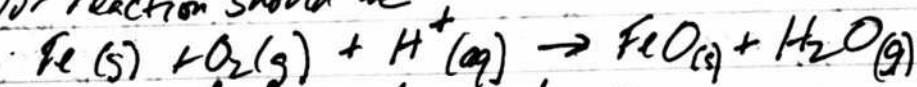
oxygen becomes  
oxidized here



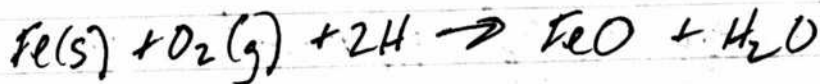
So this is definitely a spontaneous reaction.

Electrons will cancel out in a redox reaction.

Our reaction should be

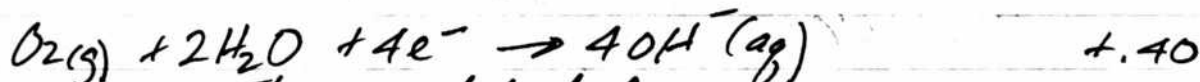


And our balanced reaction is



Well this is interesting, it seems like you have shown that this is a spontaneous reaction.

The reaction actually likely involved is:

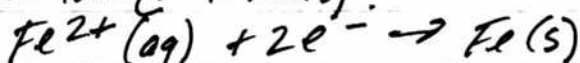


This is indeed balanced.

We also know that water dissociates to some degree

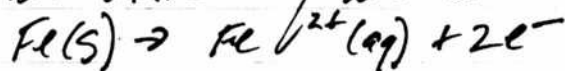


Now look at iron(s).



this is the reduction -.44

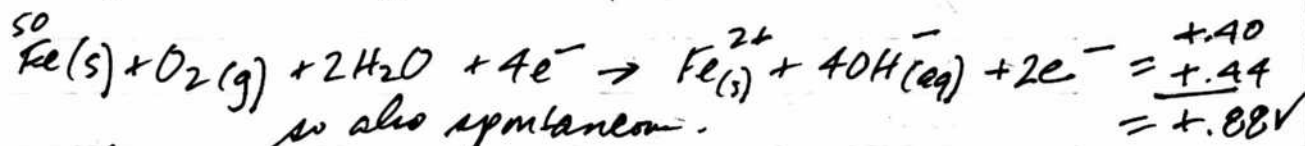
The oxidation of iron is



of iron.

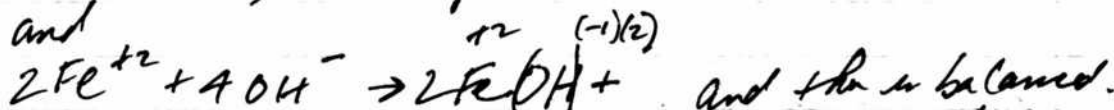
= +.44V

unbalanced



so also spontaneous.

and



so it says iron in water will form ferrous hydroxide and will occur spontaneously.

Actually it does, it forms a hydrated complex.

Iron run.  $FeSO_4$

Derivative

Measure w/ derivative:

-.45	-.57
-.41	-.49
-.22	-.41
+.26	-.15

+0.15

$Cu^{2+}$  being reduced to  $Cu^+$

+0.41

$Fe^{2+}$  being reduced to  $Fe$  Fe being oxidized to  $Fe^{2+}$

-.35

$Cu$  being oxidized to  $Cu^{2+}$

$CuSO_4$  Derivative w/ HCl

Measure w/ derivative

+0.72V

+0.34V

$Cu^{2+}$  being reduced to  $Cu$

-.54V

-.39V

-.26V

+0.24V

Let's look @ plots & derivatives

H<sub>2</sub>O w/HCl Blue  
 $y'$   
 $+ .20$   $.44$

$\phi .51$

FeSO<sub>4</sub> Red  
 $y'$   
 $- .44$   $y$   
 $- .14$   $\phi .17$   
 $+ .22$   $- .07$   
 $- .52$

CuSO<sub>4</sub> Green  
 $+ \phi .17$  this is  
 $- \phi .31$   $y$

Sulfate is  $\phi .2\phi$

Why do these vary so much?

FeSO<sub>4</sub> has peaks @  $y'$   
 $- .43$   
 $- .40$   
 $- .16$   
 $+ .21$

CuSO<sub>4</sub> has peaks @  $y'$   
 $- .55$   
 $- .40$  this is  $y'$   
 $- .26$   
 $+ .24$

Now, what exactly is our analysis here?  
 What is the level of contamination on the electrodes?  
 What is the level of contamination in the bottles?

Reduction of  $Fe^{+2}$  to  $Fe$  is  $-.44$

You may have contamination of  $FeSO_4$  in the  $H_2O$ .

Sulfate ion is  $\phi$   $\sqrt{20}$  for  $SO_4^{2-}$

$Fe^{+2}$  reduction to  $Fe$  is  $-.44$

$+.44$  would indicate oxidation to  $Fe^{+2}$

$+.20$  indicates the oxidation of the sulfate ion.

Iron shows  $\bar{X} = -41.5$  vs  $44$  maybe

$\bar{X} = 18.5$  vs  $20$  for sulfate, maybe.

$CuSO_4$  is varying to much. Why?

$+1.17$   $-.55$

$+1.26$   $-.40$

$-.31$

$-.26$

$+1.17$

$+1.24$

What gives here?

Should be  $.34$   
 $.15$

$-.30$   
 $+1.17$

$-.71$   
 $-.17$

$y'$

$\log y$

$-.17$   
 $-.46$   
 $+1.27$

# Page 31

I think that next we need to go for  
purity of sample and no contamination

Fe has values of .71  
.44

Is HCl Complicating  
the picture?

Cu has values of .39  
.15

So<sub>2</sub> has a value of 0.20

We record values of  
0.20 Iron  
.44 Iron  
.14 Iron  
.22

I think that you need to work on the  
Contamination issue.

Now the confusion continues.

We have to lab report on Fe<sup>2+</sup> to Fe<sup>3+</sup>

It is in WPS and the file is called art-xy-com

He gives E<sub>0</sub> as 0.227 vs literature of .225

But no graph! again!

He also gives  $\Delta E_p = E_{pa} - E_{pc} = .268 - .159 = .109$   
~~.059~~ He finds.  $\frac{.109}{.059} = 1.85$

So he is just plain wrong.  $1.85 \approx 2$

but he claims  $\Delta = .144$  and  $n \approx 1$

He is all wet.



Feb 23 2017

1. Today I want to research the voltammetry saturation in more detail. I am unable to extract the details of computation and graphs that I require.

OK, I finally have some hard data.

$E_p = .230 \text{ mV}$       I get  $E_0 = 0.26 \text{ V}$   
 $E_p = 294 \text{ mV}$       his  $\Delta E_p = .064 \text{ V} = 64 \text{ mV}$  (not bad).

This is from the CV-50! Bioanalytical Systems!

The  $\Delta \gamma .059$  is quite theoretical and probably seldom achieved.

We also notice that a curve is shown w/  $E = .225 \text{ V}$

So no-one is explaining the redox potential table vs measured values. It appears that we are clearly w/  $1/2$  vs full value.

It is time to collect real data again.

We must establish additional water as a reference. Fresh water.

Feb 23 Measurements

	4'	24	4'
FeSO <sub>4</sub>	$\frac{1}{2}$ (.21)	.42	.098
	.46		.36
	-.01		

CuSO <sub>4</sub>	-.25		-.31
	.17	.34	-.36
	-.47		.098
			-.51
			-.49

FeSO<sub>4</sub> + CuSO<sub>4</sub>



Notice on the Log y Chart where we have  
Iron & Copper superimposed.

The Iron appears to be orange  
The Copper is black.

Now if we look @ y:

The Iron has a peak @ .21 8.46 and @ - .01  
The Copper is very distinctive.  
Let's study Iron alone first.

We have found another plot of Iron. It has  
my Shape but numbers are @  $\sim +.65$  and  $-.38$   
 $X = \phi.52$  no idea what this means.  
BAS is giving  $+ .23$  and  $+ .299 \approx .26$

With the derivatives, we have 2 clustering  
needs:

$\sim + \phi.12$  and

I do not understand the plots.

Again

FeSO<sub>4</sub>:

$q$ : .22 fwd  
 .46 fwd  
 -.002 rev

$q'$ : .098  $\log q$ : .22  
 .37 -.36  
 .25  
 -.006

CuSO<sub>4</sub>

$q$  -.25 fwd  
 .19 fwd  
 -.47 rev

$q'$  -.31  $\log q$ : .24  
 -.36 -.35  
 -.51  
 +.009

Ok, we have good images now of FeSO<sub>4</sub>, FeSO<sub>4</sub>', CuSO<sub>4</sub> and CuSO<sub>4</sub>'.

Let's start up Fe. We see that it is not symmetrical. The tells us that the material is probably not pure or solely FeSO<sub>4</sub>. The two primary peaks are generally symmetrical but they are widely separated from one another, far more than 0.059V.

Now we do know that a small peak measure m @ 0.46 V but the main peak measure @ 0.4 + 0.22V

Since we are starting @ -1.0V

Maybe we do next to look @ the baseline.

Ok, think about this:

If the graph was of the form.



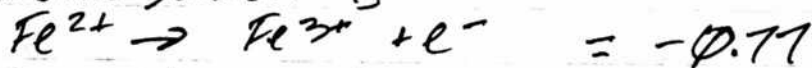
Then they would be separated by 0.054V (or essentially the same) and that would be the value. There would be no doubling of anything involved. It would be the average of the two potentials that are slightly offset from one another.

Does it matter that you start @ -1.0V

$$-1.0V + 0.22 = -.78V$$

Is it not curious that  $Fe^{3+} + e^- \rightarrow Fe^{2+} = +0.77$ ?

The oxidation reaction is



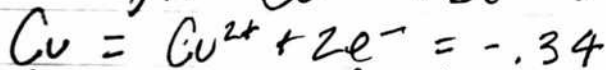
So this could represent iron perfectly.

In reverse, it went from +.15 to ~~-.15~~  $\Delta = .35$  so this is not so good.

Now let's look @ Copper.

It went from -0.6 to -0.25  
 $\Delta = -.35$

Reduction of Copper



Notice the similarity of this to Copper.

The potential difference is from a starting point, not from 0.00!

You started @ an arbitrary potential.

Let's test this w/ a joint solution.

Start @ -1.0 V

First step = -.175

$\Delta = 0.82 \text{ V}$  vs .34

Second step = 0.3 V

$\Delta = 1.3 \text{ V}$  vs .77  
 $\Delta = 0.48$

$$\begin{array}{r} .77 \\ - .34 \\ \hline = .43 \end{array}$$

.43 vs .48 is not bad.

It might be w/ two metal you must only be able to see the difference in oxidation, not the actual value.

Now let's look @ derivative.

The <sup>peaks</sup> derivatives tell you where the slope is the greatest, not where the original peaks are.  
They mean nothing in terms of peaks.

When you start the CV seems to be a critical no. not where you end.

$$\begin{matrix} (F_1) & (1.77) \\ OM_1 & = C_1 \end{matrix}$$

$$\begin{matrix} C_2 & (1.34) \\ OM_2 & = C_2 \end{matrix}$$

$2OM_1 - 2OM_2 \approx C_2 - C_1$  approximate only an approximate observation that is of interest.  
This is an interesting observation

$$\left. \begin{aligned} SO \quad OM_1 + OM_2 &= C_1 + C_2 \quad \text{is also true?} \\ 2OM_1 - 2OM_2 &= C_2 - C_1 \quad \text{approximately?} \end{aligned} \right\}$$

We may be on to something. When you start measuring, the difference might be very important.

That about your previous work up to CV27.  
You measured  $\Delta$  between the min & max regardless of where you started from.

This is the same idea as what you are doing here. Now you are just measuring voltage on the horizontal axis instead of proportional current on the vertical axis w.r.t. time on to CV27.

I think you have figured it out.

Remember you superimposed the graphs?  
Let's look at the combined solution again.

Notice that we went from

-1.0 to -0.2 this  $\Delta = 0.8$   
 then a quite close to -0.77 +.77  
 And then we go from? Iron & Silver are  
 How? Candidates. Guess who wins?  
 Iron!

It then goes from -0.18 to 0.3

$$\Delta = 0.48$$

So this actually can work.

$$OM_1 + OM_2 = 0.48$$

We know  $OM_1 = 0.8$  (actually 0.77)

0.8  $\cdot 77$   
 $\cdot 77 + OM_2 = 0.48$

①  $OM_2 \approx .48 - .77 = -.29$  Cu is closest

vs actual +.34  
 Nothing else is really ever close

+ .34



Feb 24 2016

Page 40

The trigger point ~~will~~ may be under the peak  
w/ respect to the zero current point.

Eg FeSO<sub>4</sub> Limits -1 to +1

Current  
Zero crossing  $\phi$  -0.57 V      Reverse:  $\phi$  @ .54 V  
Peak  $\phi$  +1.23  
 $\Sigma = \phi$  .90 V

FeSO<sub>4</sub> Limits -0.8 to +0.8

The zero crossing idea does not work.

Eg  $\phi$  @ -0.43  
Peak  $\phi$  +0.20

$|E| = .63$  This does not work.

The other idea is the peak as determined by  
the derivative.

We have oxidation @ 0.22

If  $\Delta E = 1/2 E$ , then  $E = +0.44 V$

this is equivalent to  $Fe(s) \rightarrow Fe^{2+} + 2e^-$   
and that is right on.

But it is not 0.77 for  $Fe^{+2}$  to  $Fe^{+3}$ .

What I am looking @ is not  $Fe^{+2}$  or  $Fe^{+3}$ .

So now let's look @  $E$ .

$\phi$  is 0.15 or 0.34

Zero crossing is -0.22

When you start plot @  $E_1 = 0$ , the zero crossing is 0.21 same

I cannot figure out how to get the potential of redox.

A statement is:

for reversible. 
$$E = \frac{(E_a + E_c)}{2} = E^{1/2}$$

for irreversible

$E^{1/2}$  = the potential at which the value of the current is  $1/2$  of the peak current.  
 After finding the peak current and divide by 2 you will have to locate it manually.

Note

For iron, we may be able to take it directly  
 $.22(2) = .44$  This is for  $Fe^{+2} \rightarrow Fe(s) + 2e^-$

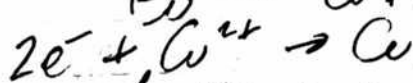
Quasi reversible?

for Cu: Cu is .015 or .034

We measure ~ .018

$.018(2) = .036$  So not too bad

This is for



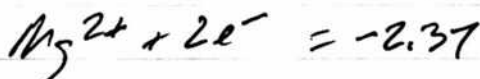
So this is possible.

Quasi reversible?

Page 42

Magnesium has slope break occurring @

-4.3



+4.0

I do not know how to interpret my graph.  
We get



Found one paper, they talk about film deposits  
and such and not at all about a normal  
selective potential. Cyclic voltammetry to  
me seems highly problematic, as it seems highly  
variable. No rhyme or reason so far  
How can we get  $dI/dE$ ?

Is it a case of running your own voltammogram  
just like  $dI/dE$ ? or  $dI/dE$ ?

This may not be as bad as you think.

It is interesting that you seem to have double  
values for both Al & Mg. Why?

For Mg, we have a slope break @ -4.3 & 4.4  
No idea why but  $1/2 \times -2.4$  and  $2.2$

Is it only a coincidence that Mg has a redox  
of 2.4? Why would there be an integer relationship?

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Al also has a major slope break @  
 $+3.4V$

Divide by 2 and we get 1.7  
Al has a redox potential of 1.7

Is this coincidence?

Why would there be a factor of 2 with  
Al & Mg?

Notice also on Al that the cyclic  
crosses over itself @ 7.6  
Is this a coincidence also?

Magnesium crosses over itself @  $\sim 2.8$

Mg has a redox of 2.4.  
Is there also coincidence?

A crossover, say at Carbon means  
metal deposition.

The area under the reverse peak corresponds  
to the amt of material deposited at  
the electrode.

It is odd that it likely means that  
surface processes are involved.

Instrumental Methods in Electrochemistry  
D. Pletcher

From Raven:

In most cases the reference electrode should be as close as possible to the working electrode.

Feb 27 2016

Today we collected more data from

Lithium

Potassium

Bleach

Hydrogen Peroxide

City of Rocks Camp water

Ammonium Nitrate

in addition to what we already have of

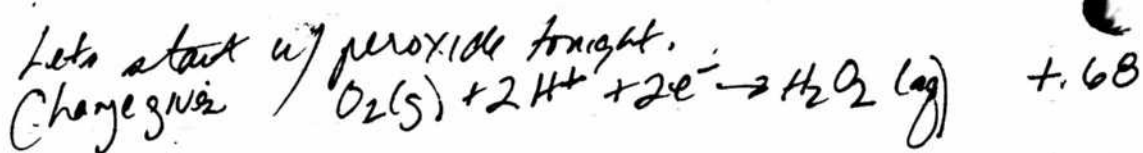
Iron

Magnesium

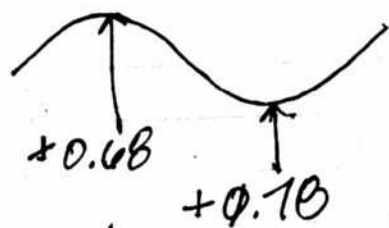
Aluminum

Copper

Let's start w/ peroxide tonight.



Now we see we have a peak @  $\Phi.68$   
and the a great, however



we have a local max  
of  $+0.68$  and a local  
min of  $+0.78$

How would you know on the lower curve that  
 ~~$+0.68$~~   $+0.68$  is our target instead of  
 ~~$+0.78$~~   $+0.78$ ?



There's a lot going on w/ the peroxide sample.

We also have a local min @ -2.9

A local max @ -3.2

Also a slope break @ -1.5 on the upside.

The -2.9 to -3.2 certainly indicate a Gap I or II element. Is the form contamination?  
Why would it be there?

A slope break @ -1.5 matches Manganese  
or Gold, silver  
Nothing here exactly makes sense, does it?

So we have some age openers here, esp with the local min/max situation.

Back to Camp water &  $H_2O_2$  show activity around 30. It seems most likely that we would be dealing w/ something like Calcium here. Remember pH & conductivity of the Camp water, ~10.5 & ~7000. These are high values.

Ammonium nitrate for a local min @ +0.63

-1 Ca 2.90-2.87  
 Rank of slope  
 Ba - 2.90  
 1. Li - 3.05 - 1.5 Sr - 2.89  
 2. K - 2.93  
 maybe. Wh else?

Distinction between metal is very subtle but possible.

Consider running all these metals

@ high resolution from -2 to -4

Sodium I -2.93 -2.71  
 Lithium I -3.05

Potassium I -2.93

Barium II -2.90

Calcium II -2.87

Strontium II -2.89

1. Can we distinguish between Group I & II

The slope is steeper steeper in all cases  
 between Group II & Group I  
 That is pretty cool.

Notice that Camp water slope is much less  
 shallow. It does not really match either  
 Group I or II. This makes you wonder if it  
 contains any of them.

Feb 28 2016

Page 48

Potentiometry is also interesting, even though it is generally a simple process. Conductivity alone was also important. Conductivity can be used for titration. It can also be used for redox. It is also used in Chromatography.

I got a reaction under two conditions.

1.  $H_2O + HCl + Salt + Bleach$   
measured immediately after bleach.
2. By introducing current into the solution.

We will study potentiometry further.

Let's go back to metals focusing on small differences.

1. NaCl Very strong local min  
It occurs on the ~~very~~ zero run.  
We got -2.72 vs -2.71 theoretical.  
This is superb.

We also have a strong local min @ +0.58  
What is this?

This is manganese. What is this about?

0.58 vs 0.59 theoretical.

$MnO_4^-$  or  $MnO_2$ ? Why? How?

It looks to be iodine! 0.53 vs 0.58 theoretical  
This is a great example of selectivity.

Now in more detail:

A window approach did not work for NACI.  
We apparently have to flip the switch  
to an equally opposite voltage.

Begin 0.0V  
E Vertex<sub>1</sub> +4.0  
E Vertex<sub>2</sub> -4.0

We are picking it up again @  $\approx 2.69V$   
vs theoretical  $\approx 2.71$  which is  
fine, but it's weak.

Also, No Iodine is being picked up now.  
What is the difference caused by?

Try E begin = 0.0  
E Vertex<sub>1</sub> = -4.0  
E Vertex<sub>2</sub> = +4.0

(This has been the  
most common route.)

Upon repeating this, the dramatic result  
has been lost. We do have a crossover (the  
mean deposition) in the region but the  
exact pt is very hard to discern. So the  
resolution and identification is being lost over time.

The Crossover point also seems to be migrating  
closer to zero.

Now let's clean the worky electrode.

That did nothing. It made the signal even weaker than before.

Adding more salt did not work either. Iodine region again. Flipping the voltage picked up the iodine again.

So flipping the voltage picked up <sup>local min</sup> peaks again but they have migrated toward a positive voltage. Why?

Iodine peaks now @ .8 instead of .58.

So now we add acid again.

And flip the voltage. We get a strong crossover but it still is shifted to the right.

2.48 crossover instead of 2.71

So something change and gets shifted.

Second scan to 2.6

2.6 + 3.1 Average?

Flipping the voltage seems to be helping.

Now I peak at +0.69 vs 0.58

No peak at 2.66 so now vs 2.71

so we are getting it back w/ more sharp peaks.

We need to have a reset that forces the starting voltage to be far away.

It looks like that power is

$$E_{begin} = 0$$

$$E_1 = +4.0V$$

$$E_2 = -4.0V$$

but it still may require flipping.



Page 51

The CV curves are different going from

-4.0V vs +4.0V  
to +4.0V to -4.0V

It looks like the latter route is preferable  
and is the only one that gives us our results.

But we picked up Na again on the second  
pass even w/ using -4.0V to +4.0V  
We also pick up Fe again but at  $\Phi$  90V.  
So it's a characteristic.  
Na is @ 2.8 which is OK.

We are indeed learning subtleties.

We have +0.19 (which is iron?)

So the first pass was the best. Why?

1. Flipping the voltage

and

2. Running from +4.0 to -4.0V  
seems to produce the best results  
w/  $E_{\text{begin}} = \Phi$ .



A first run.  $+4.0$  to  $-4.0V$   $E_0 = 0$

$H_2O + HCl + NaCl$

1. We picked up a minor peak at  $+0.40$  then in the electrolysis of water.
2. We also picked up 2.73 right away.
3. We did not pick up  $I_2$  does
4. We also picked up 2.73 on the high end.

As she worked perfectly. We have positively identified Na but it had to be on a first run

Now for Barium:

Not easy.

We are trying a window function to save time.

Running

E Condition 3.5

t Condition 5

E Deposit 3.5

t Condition 5

E begin -3

$E_1 = -2$

$E_2 = -4$

Page 53

We notice that the slope gets "rough"  
@  $\sim 3.0$

Also the derivative shows this as  
a series of many peaks.

Feb 29 2016

## Stripping Chronopotentiometry Investigation

I have succeeded!

Perfect identification of Na!

Settings are

E Condition  $\emptyset$ t Condition  $\emptyset$ 

E deposition 2.0V

t Deposition 10s

Sample is

Water

HCl

NaCl

t equilibration 1 sec

E End 3V

Stripping Current  $1.0 \times 1 \text{ nA}$ 

Measurement time 5 sec

We pick up a perfect peak @ 2.70 vs  
theoretical 2.71

It moved to 2.58 after weighting. fixed it

You do not want any voltage overload.

Barium came out coming @ 2.6

Which is wrong. Actual is 2.90

Let's work on Calibrated Variables

Old	New
X	Y
100	80
80	70
60	40
40	30
30	25
10	10
5	5

Linear regression is not too bad

$$Y = .80X + 0.15$$

$$r^2 = .978$$

$$New = .80(Old) + 0.15$$

Logistic looks even a little better

$$Y = \frac{100.4}{1 + 12.83e^{-.04X}}$$

$$New = \frac{100.4}{1 + 12.83e^{-.04(Old)}}$$

$$MSE = 19$$

Mar 01 2016

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## Chronopotentiometry Shipping CS.

We start from scratch today w/

1. Clean electrode
2.  $H_2O$ ,  $HCl$  &  $AlSO_4$

We get a clear and definite peak @ 2.45

Condition:

$$E_{condition} = -3.0V$$

$$t = 5s$$

$t$  equilibrate 5s

$$E_{end} = 4V$$

$$Current = 1\mu A$$

$$MS_{start} \text{ time} = 10sec$$

Magnitude of peak is 94  
so the signal is quite  
strong.

What does the mean  $Al$  redox is  $-1.66V$

$Al$  is only @ +3 & 0 so there should be  
nothing else involved.

$$2.45$$

$$\frac{-1.66}{2.45}$$

$$\Delta = 0.79? \quad \text{Silver is } 0.80, Fe^{+3} = .77, Zn \text{ is } .76$$

and the hydrolysis of water is  $-.83$

So the last one does catch our interest.

Try plain water &  $AlSO_4$

I get no signal w/ water &  $AlSO_4$ .

Acids & metals react.  
 Does this cause a problem.

We used peroxide and we also got a strong spike.  $t + u @ 2.78$

$H_2O_2$  w/  $AlSO_4$  peak is 2.78 close  
 $HCl$  w/  $Al_2SO_4$  peak is 2.72

Essentially the same result.

1.66 Nothing really matches this.  
 $2.75$   
 $\Delta = 1.09$

I am not sure what is going on w/  $AlSO_4$   
 but it definitely is repeatable.

2.65  
 2.66  
 2.72

We now have 2 peaks  
 2.4 & 2.58

Best value seen is 2.54  
 $2.54$  Dissociation of water  
 $- 1.66$  is 0.88

$\Delta = 0.88$

$2.54$   
 $- 0.83$   
 $= 1.71$

+ 1.66 is the  
 oxidizing Al.



Do some metals oxidize more easily?

Does aluminum oxidize easily?  
What about Na, Ba?

Aluminum oxidizes within a few seconds  
when exposed to air.

Ease of oxidation

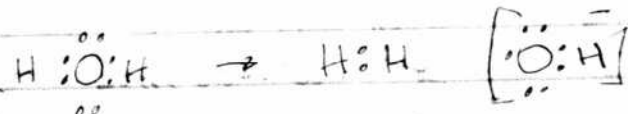
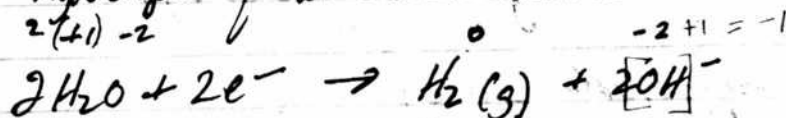
K  
Na, Ca  
Mg  
Al  
Zn  
Pb  
Cu  
I-  
Br-  
Cl-  
F-

So a lesson might be  
if it does not match  
anything on the table  
it might be competing  
with oxygen?

Notice there is no Zn on  
the table and yet  
you know what you have  
aluminum.

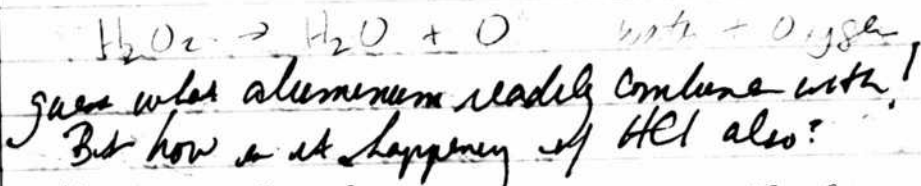
Try OCP!  
Open Circuit Potential!

Hydrolysis of water

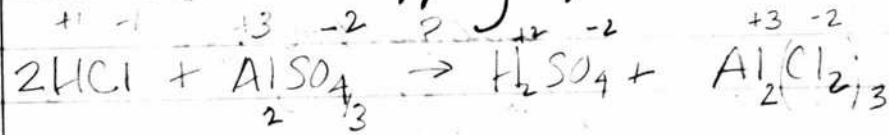


This is therefore making the water more alkaline?

What is the reaction of peroxide w/ water?



But how is it happening w/ HCl also?



Is this true?  
Balance

# Ba<sup>2+</sup> identification.

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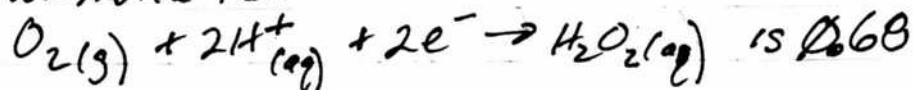
Now we are testing barium

With H<sub>2</sub>O<sub>2</sub> we are getting a very strong peak @ 3.67V

The actual potential of Ba<sup>2+</sup> is 2.90V

$$\begin{array}{r} 3.64 \\ - 2.90 \\ \hline \Delta = 0.74 \end{array}$$

We notice that



I am not sure how to interpret the result yet

Dissociation of water is 0.03?

It is, however, a perfect looking curve.

Now I have a 3.74

$$\begin{array}{r} 3.74 \\ - 2.90 \\ \hline \end{array}$$

$\Delta = 0.84$  and this does not match dissociation.

3.44

3.60

3.74

3.69

3.71

3.68

3.69

$$\Sigma = 3.685$$

10A

1nA

nA

10mA

10mA

nA

3.685

- 0.03

$$= 2.86 \approx 2.9$$

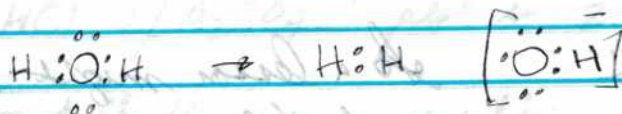
3.77

Actual value is 2.9

so this is quite good.

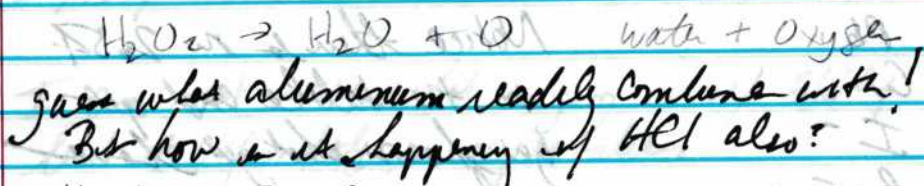
We may have something here.

Hydrolysis of water



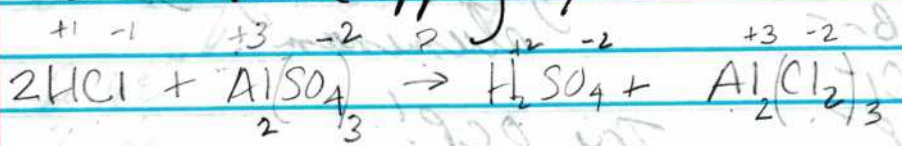
This is why making the water more alkaline?

What is the reaction of peroxide w/ water?



But how is it happening w/ HCl also?

Is this true?  
Balance



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I believe your measurements early in the  
game with clean electrodes are the best.

It seems to drift w/ the passage of time.

Now working w/  $\text{H}_2\text{SO}_4$  again

We measure

3.49

Acid works,  $\text{H}_2\text{O}_2$  does not.

We measure

2.57

Double peak: 2.459 2.50

2.47

2.37

2.33

$\bar{x} = 2.45$

2.45

- .83

= 1.62

vs 1.66 for Alamar

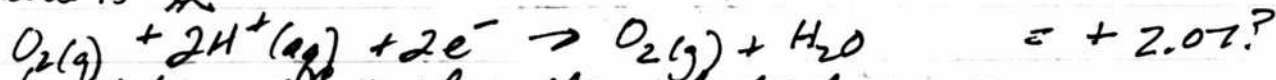


Mar-02 2016

Control w/  $H_2O$ ,  $HCl$ 

We have a reading of 2.15

I do not know why?

There is ~~the~~

We did not think that there should be anything.

2.25

2.24

We definitely have a signal. I am not sure why.

2.31

Repeat Control - Is there contamination here.

2nd Control

E Condition -3.0V  $\rightarrow$  2.75E Cond. +3.0V  $\rightarrow$  2.52

So Condition Voltage is having an effect.

This is undesirable.

No Conditioning, no deposition. = 2.67

This means it starts @ zero, which means you cannot have a window without affecting it.

E dep = -1  $\rightarrow$  2.72 Very clean slope curve but minimal signal strength.

The issue seems to be the signal strength!

C It measures only D.O.F

You can see signal to the 100 when you get it right.

Notice from this that Conditioning may affect the results to some degree.



With iron, something unusual maybe  
happening.

We have peak @ 3.52  
but also @ 3.94  
 $\Delta = 0.42$

And Iron is 0.44 Coincidence?  
But now I am not repeating this?

Measurement time of 2 is producing an  
entirely different result than measurement time of 5

Something unusual is happening  
we get a sharp slope disruption @

3.52 and a peak @ 3.94

$$\begin{array}{r} 3.94 \\ - 3.52 \\ \hline = .42 \text{ again} \end{array}$$

and it is right on edge  
of graph.

$$X = \underline{.455} \text{ vs } 0.44$$

$$\begin{array}{r} 3.42 + 3.91 \\ - 3.91 \\ \hline 3.42 \\ - 3.42 \\ \hline 0.49 \end{array}$$

Two peaks are showing up.

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This is a case of deposition not appear?

Now something else is happening.

We have an emergence of signal @ 1.30

1.30

- .83

$\Delta = 0.47$  Is this coincidence.

Notice the signal is very weak on all of these,

0.21 we have a signal emerging  $(2)(.21) = 0.42?$

The magnitude is changing dramatically.

The value is settling in @ 2.91

???

Condition and Deposition may have brought up an emergence here.

2.93	signal peak	1.5	Condition
- 2.56	signal start	1.5	Deposition
<u>      </u>			
.37			

2.90	1.5
- 2.47	1.10
<u>      </u>	
= .43	

Something is happening here @ 2.91 Why?

2.91	primary peak	} but still a very weak signal.
- 2.51	signal emergence (small peak)	
<u>      </u>		
$\Delta = .42$		

$$\begin{array}{r} 2.93 \text{ peak signal} \\ - 2.49 \text{ start of signal} \\ \hline \Delta = 0.44 \end{array} \left. \begin{array}{l} \text{small signal} \\ \text{overall.} \end{array} \right\}$$

pre The is now repeated under conditions:  
 CS 1, 5  
 1, 10  
 0, 4, 1, 5

The lesson here is that you seem best to use CV & SC together.

CV gives  $1/2$  @  $\approx 0.22 \pm .44$   
 and

SC gives an unusual pattern of a  $\Delta$  of .44  
 This is peculiar it seems to me.

CV Ba gives activity @ 3.1 approximates

SC  $3.60 - .63 = 2.9$  Actual

This was an unexpected result with  
 Mon today.

The difference seemed to be important.  
 A difference of two peaks @ a small  
 magnitude.

We are going to need to be careful.  
You must now repeat

Ba

Al

Fe

You will need to sort these all out again.  
In one case you arbitrarily subtract 0.83  
In the other case you look @ a difference of  
small peaks with a small signal.  
This is questionable.

Back to Square One. Ba, Al, Fe

CV first:

-3.3V are targets  
-1.6V

-3.3V remain  
-1.6V target

CV Settings are

Pre 0,0,0,0

CV 0,0,-4,4,0.01,0.5,2

We got +2.94 peak

1.75 start of peak

low signal.

SC Settings:

0,0,0,0

0,4,1.0A,5

We are unable to reproduce results of Nov 01/2016

Be:

1 set 2.95  
but notice I was getting set with  
now earlier today.

2.95

2.91

2.94

2.93

2.93

$\bar{X} = 2.94$

Mag = 60  
60

Settngs

Pre 0, 0, 0, 0

SC 5, 5, 10A, 5

S. we  
set CV: 2.94

CS: 2.94

Actual 2.90

S. the machine Be but what happen w/  
Al & Ir?

Al:

Now Al:

We have 2.91 peak  
& starts @ 1.67

???

vs 1.66 theoretical

2.91

2.84

2.83

2.84

2.88

2.91

1.67

1.55

1.32

1.37

1.50

1.52

$\Delta$

1.24

1.29

1.51

2.98

1.58

[0, 0, 0, 0]  
[0, 5, 10A, 1]

Start of

Signal

1.67

1.59

1.58

1.62

1.59

1.57

CV: have peaks  
@ 1.55  
& 3.56

$\bar{X} = 1.59$

vs 1.66  
theoretical

It seem like we are getting something but we do not know if the difference is method

1. Ba : straight ready of single peak
2. Al : begins of signal
3. Fe :  $\Delta$  of signal

Fe Nav

CV: We have a target @ +0.44

We needed to decrease the scan rate to pick this up. It was coming up fairly empty otherwise

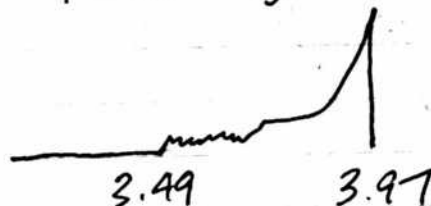
0, 0, 0, 0

0, 0, -2, 2, .01, 0.1, 2

SC: We pick up a  $\Delta$  of 0.48 only with great persistence.

0, 0, 30

0, 4, 1 nA, 4





What is happening here is that

Barium may be the easiest

Al may be in between

and Fe is the hardest to detect.

1E

6-12

6 mil

9 billion

12 trillion

It seems we need both CV & SC, 15 quadrillion  
to identify targets & to home in.

Why do we need 3 methods?

+2.94

1. Ba - a straight reading

CV

CS

2.94 2.94

+1.66

2. Al - beginning of the signal

1.55

1.59

+1.44

3. Fe - change in the signal  
(had to steer it way to the right). 44 m. 40

But why 3 different SC methods required?

$$(2.5E-6)^3 \cdot 2 = 3.125E-17 \text{ m}^3$$

1

Now we work w/ Mg.

We get a CV peak of 2.18  
only on the first pass.

We have a slope break of 2.32  
Only the first pass seems necessary.

2.51 has a slope break.

Nothing is showing up here.  
One of the electrodes was spilt internally!

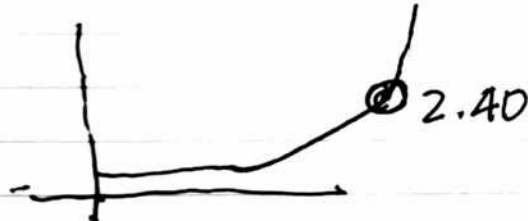
We do pick up 2.34 on CV @ scan rate of 0.1  
It is weak

Stripping gives 2.45 1st run  
2.51  
2.54  
2.55

We have an important slope break that is taking  
place in SC when the peak is developing  
and revealed by decreasing the scan rate to  
2 sec & zooming in. The slope break occurs

@ 2.40 this looks to be on target

esp. when matched w/ CV.



these 2 things  
seem to be  
important

-3.5	0.5
5.4	1.0 A, 2

2.37 2nd run

The conditioning terms seemed to be important. Deposition was not

$[-3, 25]$  for Conditioning makes a difference.  
It reveals the slope break.

Notice that Conditioning value is near theoretical value.

$[-3, 10]$  smooths it out even more,

$[-3, 20]$  smooths it out even more.

5-10 sec. does seem sufficient

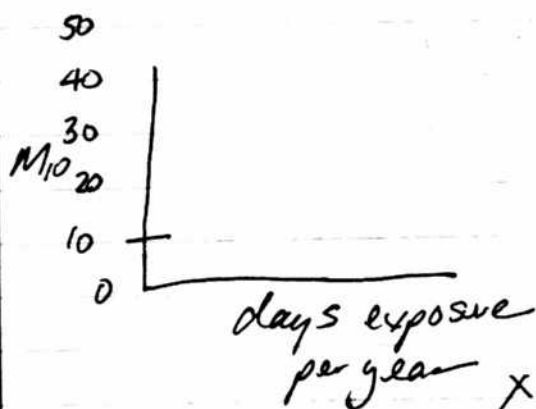
2 sec. reveals it even more

On successive rounds, where the signal starts at the point  
there is also what happened w/ aluminum.

Mar 04 2016

We have a mortality model.

$$M_{10} \approx .007 \text{ days} + .48 \ln(\text{days}) + 1.65$$



$$Z = \frac{PM}{10} (.007 \text{ days} + .48 \ln(\text{days}) + 1.65)$$

$$\text{Mortality} \% \approx \frac{PM}{10} (.007 \text{ days} + .48 \ln(\text{days}) + 1.65)$$

Now get  
Visibility in terms of PM:

We can now develop an estimate of  
PM as a function of visibility.

PM = X

visibility = Y

1st level power regression is

$$V = 76.6 \cdot PM^{-.49}$$

$$r = 0.50$$

$$\text{or } PM \approx 34.1 \cdot Vis^{-.51}$$

$$r = -.50$$

Now lets use this to refine the model.

<del>PM</del> X	Y
PM	Visibility Est
0	110
<del>12.5</del>	<del>90</del> 90
15	80
10	60
12	55
20	45
30	30
40	25
50	20
60	15
70	12
80	11
90	10
100	8
500	1.001

$$\text{Visibility Est} = \cancel{90 \cdot \text{PM}^{.474}} \quad 90e^{-.027 \text{PM}}$$

$$\text{PM} \approx 28.4 e^{-.073 \cdot \text{Visibility}}$$

$$\text{PM} \approx 300 e^{-.073 \cdot \text{Visibility}}$$

This is not a bad model.

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Therefore we now have an adjusted mortality model of

$$Mortality \% \approx \frac{300e^{-.013 \cdot Visibility}}{10} (.001 \text{ days} + .48 \ln(\text{days}) + 1.65)$$

$$M \% \approx 300e^{-.013 \cdot Visibility} (.001 \text{ days} + .48 \ln(\text{days}) + 1.65)$$

and

$$M \% \approx \frac{PM}{10} (.001 \text{ days} + .48 \ln(\text{days}) + 1.65)$$

$X = \text{days}$  (0-100) days  
 $Y = \text{Visibility}$  (0-110) mi  
 $Z = M \%$

No,  $Z$  is way too high here. OK we have, off by factor of 10

$X = 4.17$  no of days exposed  
 $Y = 32.1$  Visibility  
 6.8% OK then  $Z = 6.8\%$  increase in mortality.

Still might be a little high.



The model now assumes 24hr exposure  
but we realize that is not the case.

Our paper indicates that the real exposure  
is approx 20 for 5 hrs?

$$\text{We had a mean of } \sim \frac{20 \text{ PM } 2.5}{19 - 8.5} = \frac{x}{24}$$

$$x = \frac{20}{10.5 \text{ hrs}} = 20 \cdot \frac{10.5}{24 \text{ hrs}} = 8.75 \approx 9 \text{ parts}$$

So we need to diminish our peak of ~  
60 by a factor of

$$\frac{9}{60} = \underline{\underline{0.15}}$$

So now our model is:

$$M^{\text{no}} = \frac{300}{10} (0.15)^{0.001 \text{ days} + .40 \ln(\text{days}) + 1.65}$$

Now it is too low. We really only want to reduce  
our number by

$$\frac{(19 - 8.5) \text{ hrs}}{24 \text{ hrs}} = 0.44 \quad \text{not } 0.15$$

the compensator for the solar exposure time

then to looky find about:

$$M_{\% \text{ increase}} \approx \frac{300(.44)}{10} e^{-.013 \text{ Visits}} (.001 \text{ days} + .40 \ln(\text{days} + 1) + 1.65)$$

$$M_{\% \text{ increase}} \approx 13.2 e^{-.013 \text{ Visits}} (.001 \text{ days} + .40 \ln(\text{days} + 1) + 1.65)$$

Mar 05 2016

We are learning about some very important patterns when electrochemical observations and methods, assuming graphite electrodes in aqueous solution.

1. All methods explored thus far have value, and the best results incorporate a synthesis of each method. Thus far, the includes:

1. Linear voltammetry
2. Cyclic voltammetry
3. Chronopotentiometric stripping

1. Linear Voltammetry has some real advantages. It is definitely the simplest method. The method seems to be to inspect carefully for perturbations of slope - all seem to be a far cry from the reversible reaction textbook examples.

2. You can progress to CV. CV gives the big picture but it seems difficult to separate out between various influences. Also it does not seem to repeat exactly and you are still learning about that variance.

3. CS then a very intriguing but also sometimes very difficult to sort out.  
So far you see:

1. Direct readout w/ no problem
2. The rest of the signal taken precedence
3. And, in a very unusual situation w/ the a difference between a displaced peak and ascent.

Group 1 & 2 seem to be of the first kind  $\pm 3V$   
 All seems to be of the second kind  $\pm 1.7V$   
 Fe seems to be of the third kind.  $\pm .44V$

I have no idea what is creating this variance.

You are seeing certain patterns now. You still have a long way to go but one of the main lessons is that all 3 methods have various advantages & interpretation. You need to put all 3 together & step through. Later on we will investigate various electrode but for now learn as much as you can from graphite.

It looks like Normal Pulse may be next on the list.

Major success has taken place w/ the normal pulse method! (NP)

Mar 08 2016

A focus now is NP: Normal Pulse Voltammetry.

We are starting by attempting to establish reference with distilled water & distilled water w/ HCl and with subtracting a blank.

Our first is with water only.  
We show a peak of  $-1.61$

The only thing that matches this is  $\text{Ce}^{3+}$

And then Pt is closer.

We do not expect to see this in distilled water.  
Now let's add acid HCl

Also note that it gives a strong voltage overload. We moved the electrodes closer and it seems to have changed things.

Moving the electrode does change the signal some.  
The electrodes closer together does look more stable.

Our number w/ water alone are  $-2.35$   
 $+1.55$

Adding acid knocked out the voltage overload issue.

There is no problem here.

Water gives current in VA

Water + HCl give current in mA

Totally different animals.

We believe we want to use acid but we could allow for ester.

I have learned how to form and subtract a blank. This is critical.

We are getting +1.87

2.08

1.40

1.0

1.36

Closest Close

1.48

No signal

1.00

$[-1, 3]$

$[0, 3]$

$[-2, 3]$

$[-3, 3]$

$[-2, 2]$

$[-1.8, 1.0]$

$[1, 2]$

$[1, 2]$

$(.01, .01, .5)$

$(.001, .001, .1)$

The smaller the window, the more smaller the resolution seem to be.

The pulse does seem to be moving all over the place.

Closest

1.60

$[-2, 2]$

$.01, .02, .2$

±1

Close

1.52

$[-1.7, +1.7]$

$.01, .01, .5$



Notice the hierarchy window seem to give the best results.  $\sim +1.52$

Best results with A1 seem to occur with

1. Tightly bracketed window  $[-1.7, 1.7]$  volts
2. (.01, .01, .5) settings
3.  $t$  equilibration does not seem critical

Blank does not seem to be a huge advantage  
esp. as you look @ derivatives

$$\begin{aligned} [-3.3] &\rightarrow +.98 \\ [-2.23] &\rightarrow +1.36 \\ [-1.8, 1.8] &\rightarrow +1.41 \\ [-1.7, 1.7] &\rightarrow +1.51 \\ [-1.6, 1.6] &\rightarrow +1.56 \end{aligned}$$

This may be very important.

Notice how it appears to be approaching a limiting value of  $\sim +1.6$   
theoretical  $\sim +1.66$

# Page 82

Now, if you tighten the window between 1 & 2.

$[1, 2]$	.01, .01, .5	does not work
$[1, 2]$	.005, .005, .1	no
$[1, 2]$	.005, .005, .2	no
$[1, 2]$	.005, .005, .3	no

I do not have the signal.

Back to

$$[-1.67, 1.67] \text{ } (.01, .01, .5) \rightarrow 1.37 \text{ not so good}$$

$$[1.6, 1.4] \rightarrow 1.43$$

Conditions to  $-4.0V @ 10 \text{ sec}$  brought it to 1.52

It looks like you have a limiting value of  $\sim 1.50$

Which is found by bracketing the value to  $[-1.5, 1.5]$   
w/  $(.01, .01, .5)$

Knowing the S can rate to P.A decreases to 1.34, not good  
And you cannot go to .6

The limits seem to be more sensitive than I would like. But I do seem to have something of some type of repeatable strategy.

I believe we capture b.k. hydrolysis of water  
and Al

limit  $\rightarrow 1.20 \quad 1.08$

$\Delta = -.15$

n/1.52/limit

$\rightarrow 1.42 [-1.6, +1.6]$

$\Delta = -.24$

Is it possible that we have a  $\Delta$  of  $-.20$ ?

We have shifted the limit to the right with:

$$t \begin{bmatrix} 15 \\ -1.7 \\ +1.7 \\ .010 \\ .010 \\ \emptyset.5 \end{bmatrix}$$

$\rightarrow +1.64$

use greater sensitivity here  
use greater sensitivity here

$$\begin{bmatrix} 45 \\ -1.0 \\ +1.0 \\ .010 \\ .010 \end{bmatrix}$$

$\rightarrow 1.63$

It does look like a limiting value  
is reached w/ judicious selection  
of the window

Let's try mercury again.

I am settling in @  $\pm 2.2$  V theoretical is 2.80

Now  $\pm 2.3$

Now  $\pm 2.4$

E Step should probably never be  $< 0.05$

True seems to be to

(readable)

1. Get E Step as low as possible

2. E pulse as high as possible

3. Scan rate as low as possible To keep the scan rate as high as possible under the above conditions (only for time sake)

Up to  $\pm 2.5$

I now have a dip @  $\pm 2.35$  Very good:

with  $\left[ \begin{array}{c} 15 \\ -3 \\ +3 \\ .04 \\ 0.15 \\ 0.1 \end{array} \right] \epsilon$

Scan rate

= Minor dip @  $2.07$

It takes a lot of slow & careful work to push it to the right to find the limit.

Range is  $\pm 3.1$

Derivative is right @ 2.91 vs 2.90

You cannot get any better than this

The high activity metals are much slower  
and require much more patience by and  
repeated.

I lost it @ Scan rate = .09

You shimming in the 3 variables:

Estep (as low as possible for resolution)  
t-pulse (as large as possible to shift to right)  
Scan rate (whatever you can tolerate  
in terms of resolution)

It is  
what  
ever  
works

And you bracket the voltage symmetrically

There is more than one combination of values that  
can work. It is a three way.

What does it mean when the current max's at?

It means the current was not as high enough!

I lost it on a second round to repeat.

Stopped @ 2.4  
It will be tricky.

Now Mon.

We have 2 rough peaks.  
 $+0.22$  and  $1.6$

$1.6$  is strong?  
 We are not picky up  $0.44$ ?  
 $1.36$  is very strong.

We have something @  $-0.54$ ?

No, we are picky up  $-1.75$

Now you move it to the left as  
 Since <sup>for as possible</sup> it is a reduction

We get  $-0.78$  @  $[10, -1, +1, .01, .004, .5]$

Now we have a strong peak to the right. (positive)  
 Move it to the right

Actually we have a strong peak @  $+0.29$   
 w/  $[-2, 2, .01, .004, .5]$

$1.6$  @  $[-2, 2, .01, .01, .5]$

$1.66$  @  $[-2, 2, .01, .015, .3]$



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With scan, I have an interesting  
symmetry that has taken place  
w/ Clean electrode in a clean solution  
 $\text{HCl} + \text{K}_2\text{SO}_4$

I have a small peak @  $-0.79$   
and a strong peak @  $+0.79$   
with  $[10, -1, +1, .01, .015, 0.3]$

Is there a coincidence or is it not  
on both sides?

With a change of pulse from  $.015$  to  $.014$   
It changed from  $-0.79$  to  $-0.81$   
 $+0.79$  to  $+0.61$

It looks like I have symmetry.

this is  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$

Bracket the window with the minimum  
number.

Now Camp water:

We have peak @ -1.35 & -.25

Now -1.40 & -.25

-1.26 & -.30

Maybe you do one @ a time.

-1.34 & -.44  
Chromium? Iron?

We get Chromium & Iron.

We also seen to have peak @

Manganese

Chromium & Manganese

Iron & ~~Salt~~ Calcium,

Aluminum.

Therefore we have  
Iron, Calcium

Chromium, Manganese, Aluminum

+1.17	&	2.46
1.18	&	2.56
1.20		2.62
1.20		2.66
1.20		2.72
1.2		2.79
1.22		2.83

-1.66

New looky @ wine

$$[-3, 3] \rightarrow +1.4$$

$$[0, 2] \rightarrow .42 \text{ to } .46 \quad \bar{x} = .44$$

This is iron.

$$[-2, 2] \rightarrow -1.4 \quad \& \quad .14 \rightarrow .34 \rightarrow .60$$

$$\rightarrow 1.3$$

$$+1.27 \rightarrow 1.64$$

$$+ \begin{matrix} 1.64 \\ 1.64 \end{matrix} \text{ Strong likelihood of Alun.}$$

-1.34 seems to be Chromium & Chlorine  
 -1.35  
 -1.34 is Chlorine

+

Method is to put the scan rate as low as you can comfortably tolerate and treat pulse as high as you can given the scan rate  
 E step looks like it can hold @ essentially a constant.

We have, in urine: In Urine:

+ .44	Iron
+ 1.64	Alum
- 1.36	Chlorine
+ 2.81	Calcium or Sodium

In Saliva

We found nitrates-nitrites p. 90!

and yes, human saliva has a lot of them

Mar 11 2016

We are now going to start working w/ concentrations.  
We will only use filtered water even though  
it will take more work.

TDS of filtered water is: 426  
which is actually quite high.

TDS of unfiltered water is so there is = 455  
no significant difference there.

Let's run profiles of each. It does  
not seem like it needs HCl.

NaCl has a molecular weight of 58.44 gms/mol  
So a

1 molar solution is 58.44 gms/liter.

.1 " " " 5.84

.01 " " .584 gms/ml let's use this.

We have Na@ 2.68 (bottom of peak)  
vs theoretical 2.71. This looks  
very good with

[10, -2, 3.0, .01, .0162, 0.3]

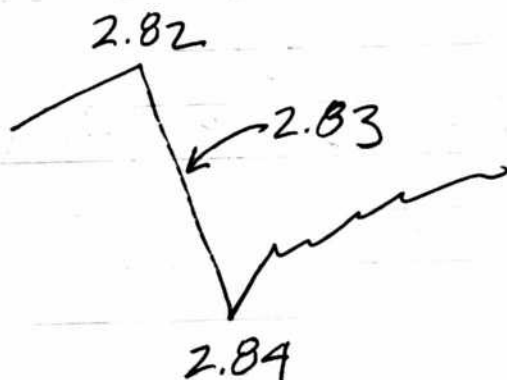
2.73@ vs 2.71

[10, -2, -3.0, .01, .0163, 0.3]

2.75@

[10, -2, -3.0, .01, .0164, 0.3]

2.70 @ .0165 (t pulse)  
 2.83 @ .0166 this is max reached.  
 Now lets look @ peak in more detail  
 see since Ca is 2.87 and this is not Ca.  
 We must split hairs.



So nothing is perfect here. But if we look where  
 our range is when everything settled in, we have

$\left. \begin{array}{l} 2.68 \\ 2.73 \\ 2.75 \\ 2.70 \\ 2.83 \end{array} \right\} \bar{x} = 2.75$  vs 2.71 theoretical Na  
 vs 2.87 for Ca

Lesson here is that it may be hard to not settle for  
 the average in our final range vs the absolute  
 max to the last digit.

It may be that t pulse to 3 digits is  
 sufficient.

This max in this case is 0.016 (t pulse)  
 and this leads to 2.68 and this certainly  
 settles to Na. Quite good work.



We also see that we can load a blank within the same range and it works great

The derivative plot is even more dramatic.  
A very good sharp peak.

Now lets look @ concentration.  
The derivative measure @  $-8.74E3 \text{ VA/dE}$

So now is when we want to work w/  
Concentration.

We have saved some DP curve @  $N = .01M$

Now we have  $\frac{10 \text{ ml}}{500 \text{ ml}} = .02$  of the original solution

$$\text{so } .02(.01M) = \underline{2E-4 M}$$

and  $2E-4 M (58.44 \text{ gms/liter}) = .012 \text{ gms/liter}$

$$\frac{.012 \text{ gms}}{1000 \text{ gms}} = \frac{12 \text{ gms}}{1000000} = 12 \text{ PPM}$$

Original magnitude of OP was

Molar Concentration Y

Magnitude X

.01M (584 PPM)  
2E-4M (12 PPM)  
2E-6M (.117 PPM)

.156 mA = 156 uA  
.125 mA 125 uA  
.118 mA 118 uA

Power: PPM  $\approx 8.853E-57$  uA <sup>26.89</sup>

r = .93 mse = 4.6

or PPM  $\approx 16.30$  uA - 1969.3 mse = 5386 r = .99

This is best.

Now we have diluted the second sample to 10 ml / 1000 ml  
so we have

$$\left(\frac{10 \text{ ml}}{1000 \text{ ml}}\right) (2E-4 \text{ M}) = 2E-6 \text{ M} = 2E-6 \left(\frac{58.44 \text{ gms}}{1000 \text{ ml}}\right) = \frac{1.17E-4}{1000 \text{ ml}}$$

$$\frac{1.17E-4 \text{ gms}}{1000 \text{ ml}} = \frac{X}{1,000,000} \quad X = .117 \text{ PPM}$$

$$.01 \left(\frac{58.44 \text{ gms}}{1000 \text{ ml}}\right) = \frac{.584 \text{ gms}}{1000 \text{ ml}} = \frac{X}{1000000} \quad X = 584 \text{ PPM}$$

If we use only the 1st two points we get

PPM  $\approx 2.03E-36$  uA <sup>17.536</sup>

~~This is actually?  
probably better  
to use.~~

Maybe not.

The more data points the better.

I have therefore done it.

I have determined the concentration of salt (Na) in water.

This is superb work.

I have a range of approx 600 PPM to 0.2 PPM of measurement which is superb.

My dilution series (of NaCl)

- |    |   |  | PPM   |
|----|---|--|-------|
| a) | 0.6 gms / 1000 ml                       | = 0.01M                                | = 584 |
| b) | $\left(\frac{10}{500}\right) \times a$  | Need an intermediate here<br>= $2E-4M$ | 12    |
| c) | $\left(\frac{10}{1000}\right) \times b$ | = $2E-6M$                              | .117  |

Now, a factor to consider is that the mass  
 22.99gms Composition of Na is 39.34% of the total NaCl mass  
 35.45gms Cl is 60.66% " " " "

So this changes your interpretation?

Instead of 0.6 gms of NaCl, what we really have is  
 $.3934 (0.6) \text{ gms} = 0.236 \text{ gms}$

but this is still a  $\frac{0.236 \text{ gms}}{22.99 \text{ gms}} = 0.01M$  solution of Na<sup>+</sup>.

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$$\text{and } \frac{236 \text{ gms}}{1000 \text{ ml}} = \frac{236 \text{ gms}}{1 \text{ Eb ml}} = 236 \text{ PPM Na}^+$$

So the book is that your PPM number are wrong.

Your number should actually be

UA	PPM	PPM
156	$.3934(584) = 230$	$= 230,000 \text{ PPB}$
125	$.3934(12) = 4.72$	$= 4720 \text{ PPB}$
118	$.3934(.117) = .05$	$(= 50 \text{ PPB!})$

So the adjusted power regression is:

$$\text{PPM} \approx 9.96 \text{E-}57 \text{UA}^{26.68} \quad \text{MSE} = 4.71$$

It appears to be very good work and a very reasonable regression equation.

And it is for  $\text{Na}^+$  now.  
 $\text{Cl}^-$  is not involved. You are measuring only  $\text{Na}^+$ .

$$1^{\text{st}} \quad y = ax^b$$

$$y' = b \cdot a x^{b-1}$$

$$b \neq 1$$

$$2^{\text{nd}} \quad y = ax^1$$

$$y' = a$$

they therefore assume the slope is a constant but we know that it is not.

Range is 60 to 0.2 PPM Al Calibration Curve

You probably have an effective range of 300 PPM to 0.2 PPM

This was a perfect curve

with this curve.

Ma-12 2016 Sat

$$PPM \approx 4.347E-97UA$$

48.715

$$r^2 = .9999$$

$$MSE = 2.705E-4$$

Today we are going to develop a concentration curve for Al.

We will use  $Al_2(SO_4)_3 \cdot [x(10)] H_2O$  MW = ~~594~~ 522.31

1M solution = ~~594~~ 522.31 gms/liter

.01M = 5.22 gms

.001M = .522 gms / 1000 ml

Al Mass % = 10.33%

A MW of Al is 26.92 g/mole

PPM

Y

Concentration x

Current

SA

.001M

$\bar{x} = 103.2$

103.2 uA

+ @ 1.38V

2.2

4E-5M

$\bar{x} = 96.6$

96.2 uA, 96.9

+ 1.31V, 1.40V

0.2

4E-6M

$\bar{x} = 92.0$

92.9, 96.0, 91, 92.2

1.44, 1.20, 1.47

$$\text{Next we have } \frac{20ml}{500ml} (.001M) = 4E-5M$$

$$\text{for } .001M \quad .1033 \left( \frac{.522 gms}{1000 ml} \right) = \frac{.0539 gms}{1000 ml} = \frac{53.9 gms}{1E6} \approx 54 PPM$$

$$\text{for } 4E-5M \quad .1033 \left( \frac{.0209 gms}{1000 ml} \right) = \frac{2.16E-3 gms}{1000 ml} = \frac{2.16}{1E6} \approx 2.2 PPM$$

$$\text{Next we have } \left( \frac{50ml}{500ml} \right) (4E-5M) = 4E-6M$$



Notes on Concentration determination:

1. You seem to need to play the same game. You adjust the  $t$  pulse to the highest value you can under the slowest scan rate that you can comfortably accommodate.
2. The dial in method has some similarities to normal pulse where you dial in.
3. It seems that for very low concentrations you can tweak it to pull the max out of it, i.e., slow the scan rate and fine tune the  $t$  pulse to detect the slight peak better.

So now a question is Can we determine the aluminum in tea or in your urine

Now, using the calibration curve, we find no aluminum in either black tea or dilute urine. But there definitely does seem to be a high activity level metal in urine, of Na, Ca, K, etc.

Now we are trying to measure pure  $AlSO_4$  in water. We may have a peak of 99.3 uA @ 1.75V

Unknown Concentration Trial

This means 8 PPM

This is not unreasonable.

The curve actually looks to be in perfect form.  
Unknown Concentration

✓  
1.40

UA  
95.5  
No Pulse

PPM

Parameter  $t_{pulse}$

$[10, .5, 2, .01, .01, .03, .01]$   
 $[10, .5, 2, .01, .1, .04, .01]$

So you do not always get a pulse if  $t_{pulse}$  is too high!

1.47

94.1

1.47

97.1 weak

94.2

93.4

1.51

94.0 (weak)

1.51

93.9

$[10, .5, 2, .01, .1, .03, .1]$   
 $[10, .5, 2, .01, .1, .02, .1]$

$t_{pulse} = .032$   
 $= .028$

$[10, .1, 2, .01, .1, .03, .1]$

So a lesson here is that we lose  $t_{pulse}$  if it is too high or too low.

$$\bar{X} = (94.1 + 94.2 + 93.4 + 94.0 + 93.9 + 95.5) / 6$$

$$= 94.2 \text{ UA}$$

$$\text{PPM} \approx 4.347 \times 10^{-9} \text{ UA}^{48.715} \Rightarrow 0.64 \text{ PPM}$$

There was a dusting of the small metal spatula  
in approx 50 ml of  $\text{H}_2\text{O}$  and only 10% of  
this is actually Aluminum. So this is  
quite good work.  
Black tea is not wacky.

So now we go back to tea:

Black Tea aluminum levels: ~~estimated~~  
from NIH article

$$\frac{2 \mu\text{g}}{\text{ml}} = \frac{2000 \text{ mg}}{1000 \text{ ml}} = \frac{2 \times 10^{-3} \text{ g}}{1000} \quad \frac{2 \text{ ppm}}{1 \text{ g}}$$

So it may well be that we are drinking  
tea @ a concentration of 2 ppm.

There is not entirely to be dismissed.

Now the next test is w/ a 2<sup>nd</sup> unknown  
Al concentration.

We read 100.5 @  $x = +1.39 \text{ V}$

We added substantially more  $\text{AlSO}_4$  to the  
solution. This gives us a  
 $\text{ppm} = 14.92 \approx 15 \text{ ppm}$ .

This is not unreasonable but it seemed like  
it might be higher than that.

So 100.5  
98.5

102

109.5 @  $t_{\text{pulse}} = 1.42$

OK, we are getting variations with respect to  $t_{pulse}$

$t_{pulse}$	VA	V	
.01	109.5, 109	1.42, 1.39	
.02	100.4, 100.7	1.45, 1.41	barely visible
.03	97.2	1.40	barely visible
.04	95.9	1.49	
.05	96.2	1.50	

Settings are  $[10, .5, 1.8, .01, \overset{\uparrow}{t_{pulse}}, 0.1]$

$t_{pulse}$	VA	V
.008	111.8	1.43
.006	113.4	1.42
.004	117	1.42
.002	No Pulse Visible	
.003	120	1.42

So we see that we need to maximize the peak w/  $t_{pulse}$ .

This leads to a concentration of 84,237 PPM or 84 PPT (thousand)

This is not impossible since it is a concentration

But there is a lesson here. You must optimize the peak. The settings used here are  $[10, .5, 1.8, .01, .1, .003, .1]$

The says to me that the calibration must be repeated to maximize the currents

You are also not sure if you can change the settings. Let's try this.

Question: Can you change the settings midstream and get the same results?

Shifting the scan rate & shifting the V value but the current is staying the same.

OK, the results indicate that you cannot go changing the value midstream.

Holding original value we get

$$V_A = 101.5 \quad V = 1.46$$

the is right in range of our original value & looks reasonable.

This results in

$$4.341 \times 10^{-9} \times 101.5^{48.715} = 24.2 \text{ PPM}$$

and the fits perfectly with the original sample.



Now we know we have a very good signal curve.  
Let's recall them.

.001 M Specs are  $[10, .5, 1.5, .01, .1, .025, 0.2]$  <sup>t pulse</sup>  
4E-5M Specs are <sup>the same!</sup>  
4E-6M Specs are  $[10, .5, 1.5, .01, .1, .04, .1]$

We have what appear to be very good curves.  
We have some variation introduced into the 4E-6 curve, and apparently it enhanced variability.  
I do not think that this caused any problem.  
Since you tightened up the window, you decreased the scan rate. This allowed you to increase the t pulse from .025 to .04. This all seems legitimate to me.

Let's use these slightly modified parameters to see how it affects the results. We get, using 4E-6 specs:  
A current of 94.5  $\mu A$  for our unknown solution  $H_2O$ . We know that this is too low.  
WAY TOO LOW!

This tells us that we cannot change the rules of the game midstream. 94.5 again.

We cannot do this. We must hold the conditions steady. Revert to .001M & 4E-5M Specs.

We get  $V_{H_2} = 101$ , same as before.

This means our calibration curve actually has an error in it.



The says to me that we should redevelop our concentration curve using only the first two values when the SPECS were held constant.

this leads to a new curve of

(UA)	(PPM)
X	Y
103.2 UA	54 PPM
96.6 UA	2.2 PPM

$$\text{So PPM} \approx 1.646E-96 \text{ UA}^{48.427}$$

This does not look too far off from the original in this case, but it is still enough to change the condition. This leads to unknown solution #2 having a concentration of

$$\begin{aligned} \text{PPM} &\approx 1.646E-96 (101.25)^{48.427} \\ &= 21.5 \text{ PPM} \end{aligned}$$

In this case, almost identical results but you cannot count on that.

There is a big lesson here, and that is that you can not go changing the condition of calibration. You must leave the speed the same for each calibration sample.

Another lesson: 20 PPM of AI is easily visible.

2 PPM is probably not.

Let's work our equation backwards:

$$UA \approx 95.04 \text{ PPM}^{.0206} \quad \text{eg PPM} = 0.2, UA \approx 91.9 \text{ UA}$$

looks very good.

The matches we work very well. We may be able to get away with what we did of slightly changing the speed but it does not seem like it is good practice.

Another lesson is that you want to maximize the peak for each calibration with the pulse.

Now, the next thing going on is that you have some kind of large spike going on @  $\sim 0.5$  V. What is this?

NP shows that there is a component @  $-0.69$  V

There may well be what you are picking up in DP:?

This matches the hydrolysis of water very well.  
 $= +0.68$  V

We have another @  $+0.24$   
 $+0.29$  moving to right  
 $+0.36$   
 $+0.39$

This also seems to be water reaction:  
 $O_2 + 2H_2O + 4e^- \rightarrow 4OH^- = +0.40$   
 This is more likely than Cd.

Both of these are very weak peaks in NP.

Now, for an application.  
When you run your AI Calibration on black tea,  
it comes up with no AI.

Clearly something is happening in black tea  
but it does not seem to be AI.

Roughly @ .16V & @  $\Phi$ .70V  
There are actually 3 peaks on the plus side alone  
in black tea using DP  
.004, .80 & 1.00 No Alum is showing up?

In black tea, we are getting sulfate.  
We measure +  $\Phi$ .19 NP  
Theoretical +  $\Phi$ .20

We also get the Concentration peak in DP.

It looks very difficult but I seem to have the  
sulfate DP peak @ .013V.  
Also a very sharp peak.

Mar 13 2016

Let us continue w/ Concentration investigation.  
We will now look @ Pulsed Amperometry  
in addition to Differential Pulse.

We are using H<sub>2</sub>SO<sub>4</sub>.

First solution is again .001M (0.52 gms/1000 ml)

In PA we have

#6 [10, 1, 0, .001, dc, 10] and a peak at 28.0 uA

#7 [10, 1, .1, .001, dc, 10] 37.3 uA  
look slike our best curve.

#8 [10, 1, .2, .001, dc, 10] 24.8 uA

But peak is varying with scenario #7

Measurements are:

37.3

26.4

23.6

25.9

26.7

25.0

23.8

$\bar{x} = 25.2$

Solution #2  
 $\left(\frac{50 \text{ ml}}{1000 \text{ ml}}\right) \cdot .001 \text{ M} = 5 \text{E-5 M}$

.001M

32.9, 27.4, 25.4, 25.3, 25.3

5E-5M

There is nothing here.  
It has stabilized @ the same point.

Up to, however, have some activity @

2.10 mA @ 9.1 secs

w/ [10, 3, .004, .001, dc, 20]

2.20 minor peak

2.13

2.18 definite peak [10, 3, .003, .001, dc, 20]

2.18 (also a second peak @ 2.19)  
no peak

w/ [10, 3.5, .003, .001, dc, 20]  
we get

2.95 & 2.99 peaks.  
They are fairly prominent.

2.93 2.98

2.995 3 peaks

w/ [10, 3, .002, .001, dc, 30] we get 2.10

to show a reproducible and the E pulse seems to affect  
the magnitude of the peak to some degree  
smaller E pulse seems to increase magnitude

Interestingly we get

[10, 3.0, .002, .003, dc, 30]

we get a quite strong peak now @ 2.20.

Nothing on repeat.

2.16 mA @ 15.4 sec

2.11 @ [10, 3, .002, .01, dc, 30]

magnitude decreased.

↑ E pulse may be too high



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We get a good strong peak of 2.88 @ 18.1 sec  
with [10, 3.5, .002, .005, dc, 30]

Did not repeat. (small peak @ 2.87 OK)

2.83 large & 2.85 smaller.

2.77 & 2.85  
2.85 highest peak.

---

Now for .001 M

No peak.

Small peak @ 3.57 mA @ 23.3 secs.  
3.60 but it is a small peak

We have a first definite peak with  
[10, 3.5, .001, .002, dc, 50]

of 3.78 @ 38.6 sec

Notice that we increased the time span  
and decreased E pulse & t pulse.

Next No peak.

Now we are up to 4.17 V?

4.13 @ 46.1 sec.

Indeed it does seem to peak @

4.16 mA @ 44.4 sec (a broad but definite peak)  
w [10, 3.5, .001, .002, dc, 60]

You also did move the electrode a little closer.  
This may have improved peak formation.

4.19 w/ 60 sec period.

4.22 w/ 100 secs. seems to keep rising some.

4.23 w/ 120 secs.

OK, w/ 150 secs we pull out an even broader peak  
@ 4.42 very definite, very broad @ 127 sec.

4.29 but may not have peaked.

4.41 @ 133 sec. Very broad major peak.  
[10, 3.5, .001, .002, dc, 200]

4.47 may not be fully developed.

4.25 @ 271 secs.

4.50 good strong peak @ 325 sec s.

We are now reversing the charge @ -3.5V  
to see how it affects things.

Hypothesis is that it will reduce the time  
required when reversed again.

Recall that everything that we are  
doing here is in water alone.  
No HCl.

This is because the sample water has plenty  
of conductivity already.

Indeed after two runs it did seem to "undo"  
an accumulation.

We do seem to be peaking @ 4.46 @ only 209 sec  
so indeed the idea seems to be working.

Peak is @ 4.50 @ 311 sec.

So this is similar.

Our peak moments are therefore

4.61 @ 133 sec

4.56 @ 325 sec

4.50 @ 311 sec

$$\left. \begin{array}{l} 4.61 @ 133 \text{ sec} \\ 4.56 @ 325 \text{ sec} \\ 4.50 @ 311 \text{ sec} \end{array} \right\} \bar{x} = \underline{\underline{4.56}} \text{ for } .001 M$$

Now back to SE-SM:

Time does not seem to be critical, it changes  
on deposition or accumulation changes. What  
seems to matter is the peak current reached.  
Reversal can stabilize or renew the system  
it does seem.

Proposed is also that more concentrated  
solutions require more time to peak out  
and that  $E_{pulse}$  &  $T_{pulse}$  seem to need to  
be set quite low.

you might not be able to change Epulse & Tpulse.  
 It may affect the results.  
 It may be that you can only change the time window.

3.35  $\mu$  limiting current right now for 5E-5M  
 [10, 3.5, .001, .002, dc, 250]

3.34 @

3.36 @ 118 sec. a definite peak succession.

3.36 reached twice now. Multiple 3.36 peaks.  
 time was not exhausted here.

3.33

$$\bar{X} = 3.35 \text{ mA}$$

50

$$\begin{array}{ll} .001 \text{ M} & 4.56 \text{ mA} \\ 5\text{E}-5 \text{ M} & 3.35 \text{ mA} \end{array} \quad \begin{array}{l} (.001)(522.31 \mu\text{S}/\text{mA})(.1033) = .0539 \mu\text{S} \\ (5\text{E}-5)(522.31)(.1033) = 2.70\text{E}-3 \mu\text{S} \end{array}$$

$$\frac{.0539 \mu\text{S Al}}{1000 \text{ ml}} = \frac{53.9 \mu\text{S}}{1000 \text{ ml}} \approx 54 \text{ PPM}$$

$$\frac{2.70\text{E}-3 \mu\text{S Al}}{1000 \text{ ml}} = 2.7 \text{ PPM}$$

50

TDS  
 Conductivity  
 500  
 410  
 420

X	Y
4.56 mA	54 PPM
3.35 mA	2.7 PPM
3.14 mA	.05 PPM

$$y = 2.141\text{E}-5 \text{ mA} \quad 9.715$$

$$\text{PPM} \approx 2.14\text{E}-5 \cdot \text{MA} \quad 9.715$$

$$\left(\frac{10}{500}\right) 5\text{E}-5 \text{ M} = 1\text{E}-6 \text{ M} = .05 \text{ PPM}$$

3.2 mA

3.15 mA

3.14 mA 15.884

$$\text{PPM} \approx 2.442\text{E}-9 \text{ MA} \quad r^2 = .82$$

Therefore

Normal Pulse seems excellent for identification

Pulsed Amperometric Detection seems excellent for Concentration.

Differentiated Pulse also seems good for Concentration.

Linear Sweep is good for preliminary analysis

Cyclic Voltammetry is good for well rounded picture and for spectral signature

Four out of 7 Voltammetric techniques have now been investigated.

What remains is:

1. Square wave volt.
2. AC Voltammetry
3. Stripping Chronopotentiometry

Two out of 8 Time functions have been investigated:

1. Amperometric Detection
2. Pulsed Amperometric Detection

Several methods remain

EIS is a total open door to us.

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Now we have an unknown solution of  $\text{AlSO}_4$ .

You third sample used different water (filtered)  
and it has used the same Depth.  
Back to original.

$$\text{PPM} \approx 2.14 \times 10^{-5} \text{ mA} \quad 9.715$$

We now measure 3.05  $\Rightarrow \text{PPM} \approx 1.08 \text{ PPM}$ .  
Seem reasonable.

Repeated measurements.



Mar 15 2016

Exotic Technology of Paper

$$\frac{2.25}{1.05 \text{ cm}} = \frac{5}{5 \text{ mi}} = \frac{22.5}{10 \text{ mi}}$$

x 1.53 mi

$$\frac{4 \text{ mi}}{1 \text{ cm}} = \frac{2 \text{ mi}}{1.3 \text{ cm}} \quad \frac{5 \text{ mi}}{3.25} \quad \frac{10 \text{ mi}}{6.5}$$

$$11.5 + 6.5 = 18 \text{ cm}$$

$$18 \text{ cm} (1.53 \text{ mi}) \approx 27\frac{1}{2} \text{ mi.}$$

S75E  
of Gila Bend.

Mon 15, 2016

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Let's revise MW of  $\text{FeSO}_4$  -  
It should be  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 278.02$

$$\text{Fe} = 5.08\%$$

$$\text{Al}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O} = 522.31$$
$$\text{Al} = 10.33\%$$

$$1\text{M } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 278.02 \text{ gms/ml}$$

$$.001\text{M} = .28 \text{ gms/liter}$$

$$\begin{array}{r} .28 \\ .52 \\ \hline .80 \end{array}$$

$$1\text{M } \text{Al}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O} = 522.31$$

$$.001\text{M} = .52 \text{ gms/liter}$$

Combine this into 1 liter of distilled water.

Conductivity of this solution is 260 TDS.  
~~seems~~ like it should be sufficient

$$\text{We have } \frac{10}{1000} (.001\text{M}) = 1\text{E-5M} \quad \text{Conductivity} = 10\text{TDS}$$

$$\text{and } \frac{10}{500} (1\text{E-5M}) = 2\text{E-7M} \quad \text{TDS} = 1.0$$

Therefore Conductivity is not sufficient. Must add HCl.  
One drop to each sample.

I identify it as 1st.

(smaller) (larger)  
we have peaks @ -1.58 and -1.28  
that are above of both reduction.

Maximum to left.

There may also be a small peak @ -1.71

[10, 3, 3, .01, .01, .5]  
We set -1.71 immediately  
with [10, -1, 0, .01, .01, .5]

this was immediate and simple.

seems to be the peak before descent that is  
the reference point.

-1.46 maximum to left.

-1.54

-1.53

-1.47

-1.41

-1.48

-1.58

-1.52

-1.53

-1.56

-1.57

-1.57

-1.71

There was a lot of stuff to sniff  
out. We ended up lowering everything  
to almost minimum values. The -1.71  
peak did not come up until you dropped  
down the EStep to .001, let alone  
to rise.

-1.59 [10, -2, -1, .001, .001, .1]

This suggests there is something happening @  
-1.5B indeed, in addition to something at  
-1.71 of Al.

-1.72 & -1.60  
-1.73 & -1.61  $\bar{x} = 1.67$   
-1.73 & -1.61

So this is interesting. Nothing else seems close  
yet you do not have a single peak. You  
have a double peak.  
Notice the mean is essentially spot on.

We do wonder if there is an alternate form  
of detection.

Linear sweep came up w/ -1.75 immediately  
Al is plain missed.

AC Voltammetry looks like a very good tool  
for ID.

Linear Sweep - Basic	] Identification Methods - All useful
Cyclic Voltm. - Basic	
NP - maximize required but good	
AC Voltammetry - looks quite powerful	

Chronoamperometry & Differential Pulse  
seem best for concentration so far.

AC Voltammetry gives -1.71 story & -1.77  
if you look carefully for minimums.

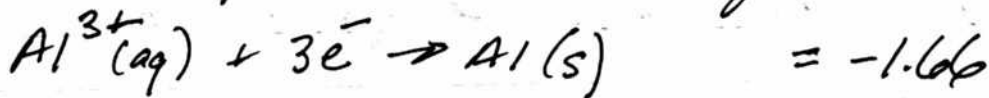
Settings [10, -2, 0, .01, .25, .05, 20 Hz]  
 I believe AC Voltammetry is  
 telling us a great deal.

1. We have a small reductive peak @ -1.89  
 that is very close to Cobalt.

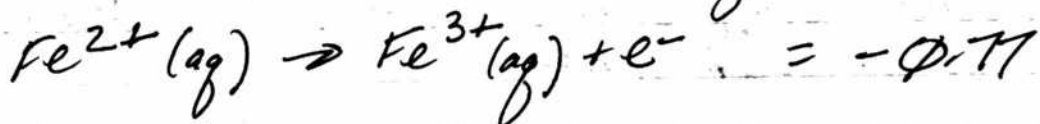
I believe we have the oxidation of Cobalt as



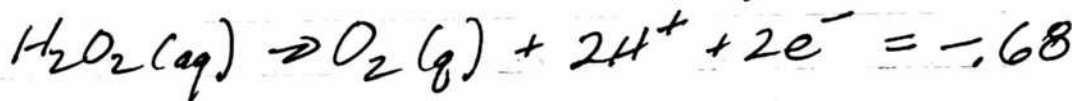
2. Next, we have a broad strong min @ -1.70  
 that corresponds to the reduction of Al, as



3. We have a local min @ -1.77  
 this corresponds to the oxidation of Iron, as



4) Lastly, you have a broad min @ -1.68.  
 This corresponds to the oxidation of peroxide



The better you know AC Voltammetry  
 tells you a great deal about identification.

## AC Voltammetry - Very promising

1/2 make you wonder if you can use at your  
Concentration also

AlSO<sub>4</sub> 691  
-1.70V 684 uA  
.001M

Fe 818  
-1.77V 700 uA

It appears that the method needs to stabilize  
@ the neg. Now we have

$[-2, 15, -2, 15]$   $[10, -2, 0, .01, .25, .05, 20]$

We are getting superb results again.

-1.80 Co  
-1.70 Al  
-1.78 Fe  
-1.68 H<sub>2</sub>O<sub>2</sub>

Let's try  $1E-5$  M in HCl (note HCl is required!)  
We are starting to pick them both up but only after  
several runs.

$1E-5$  -1.80 <sup>miss</sup> Cobalt 436 uA -1.78 493

Notice that you might have Co instead of Al  
and yet it is very similar in magnitude to Al.

-1.72 474 -1.82 520

It keeps getting better and better with more runs.

They are separately better now.

-1.65 486

-1.84 537

-1.70 497

-1.84 542

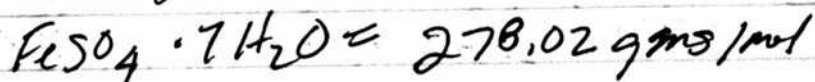
1.88



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Now got  $2E-7 M$

But before the solve PPM



$$.001 M = .278 \text{ gms/l}$$

$$(.0508) (.278 \text{ gms/l}) = \frac{.014 \text{ gms}}{1000 \text{ ml}} = \frac{14}{1000}$$

$= 14 \text{ PPM}$  No wonder you are having a hard time

for  $1E-5 M$ :

$$1E-5 M (278.02) = 2.78E-3 \text{ gms/l}$$
$$(.0508) (2.78E-3) = \frac{1.41E-4}{1000 \text{ ml}} = \frac{0.14}{1000}$$

$$= 0.14 \text{ PPM}$$

No wonder it is so hard. It is easy  
At 1500.

This is sufficient to form the precipitate.

$$\text{Now by } 2E-7 M = 2.8E-3 \text{ PPM} = 3 \text{ PPB}$$

AC Voltammetry. Good but here  
S.D. is 1+.

Iron is still very much detectable here.  
Cobalt also seems to be detected.  
But Al looks very questionable.

The current measurements also seem to  
have reached a limiting value and is no  
longer useful. As a matter of fact, the  
current is higher than the  $1E-5$  solution  
which makes no sense.

In retrospect, you could have made the solution  
more concentrated.

So we must leave concentrated in out of the  
picture @  $\leq 1$  PPM. This is reasonable.  
You do, however, have superb detection going on  
here but you cannot really measure this  
concentration any more.

For Al, we have

$$.001 M = (.1033) (1E-3) 522.31 \text{ gms/mol} = \frac{.054 \text{ gms}}{L} = 54 \text{ PPM}$$

$$\text{for } 1E-5 M, \text{ PPM} = .54$$

$$\text{for } 2E-7 M, \text{ PPM} = .010 \text{ PPM} = 10 \text{ PPB}$$

You would have two separate regression lines,  
one for Fe & one for Al!

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Once again, after statistical we are  
doing very well with detection.

Unfortunately the current is elevated  
so it is not useful.

Maybe the acid concentration here  
is making a difference?

A lesson here.

\* You must add exactly the same amount  
of supporting electrolyte in each solution!

You are, however, getting superb detection.

You have not proven that you can determine  
concentration with this method yet.

Note:  $AlSO_4$  formed a precipitate  
with the Camp water. It does not  
do so w/ distilled water. Problem

What is the precipitate?

# Then go ACV work (AC Voltammetry)

Mar 16 2016.

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Let's go again w/ AC Voltammetry  
.001M  $FeSO_4$  &  $AlSO_4$

1E-5M

2E-7M

Conductivity: (TDS)

1115

970

976

The time we will exert greater control over the supporting electrolyte concentration, 100 mL, 1 drop HCl!  
Marvelous plot under concentration.

DOT	E	Co	I/A	AlSO <sub>4</sub>	PPM	FeSO <sub>4</sub>	PPM	E <sup>x</sup>	I
	-1.			E	I	E	I		
.001M	-1.82	372		-1.70	365	5A		-1.70	494
	-1.74	359		-1.66	358			-1.69	488
				-1.66	337			-1.76	474
				-1.70	358			-1.84	538
								-1.43	599

It looks like the slope break is more important than the minimum that are being reached?

-1.66 371

-1.68 400 398

-1.79 527

-1.77 534

OK, you have some really nice curves showing up.

You control the number of points w/ EStep.

Try to have ~250-300 points for a 3 V range.

Keep the scan rate as low as you comfortably can.

Current settings are

[ -2, 15, -2, 15 ] [ 10, -2, 0, .008, .25, .02, 20 ]

you lost the -0.44 additional mV but you now you need to let this go.

It's intriguing that it creates minimums instead of maximums. Is this because of reduction?

.001M:

$\bar{x} = -1.68, 36A$

-1.76, 509

Pasc 127

Now lets go to 1E-5M.

	AlSO <sub>4</sub>	PPM	FeSO <sub>4</sub>	PPM
1E-5M	-1.74 473	.54	-0.89 522	.14
	-1.73 503		-0.91 536	
	-1.71 409		-0.90 525	
	-1.67 493		-0.89 527	
	-1.65 <del>493</del> 498		-0.88 514	

The zero crossings on the derivative plots  
will give you the E<sub>1/2</sub> values very well.

It looks like we can increase the scan rate  
to a reasonable level w/out changing the  
results in a highly significant fashion.  
We have a continual compromise of size & value.

$\bar{X} =$  1.70 493      -0.89 523

2E-7	-1.78 471	.01	-0.86 497	2.8E3
	-1.95 458		-0.87 503	
	-1.75 439		-0.87 475	
			470	

Concentration @ this level is not detectable.  
Species remains identifiable.  
This is @ 100 PPB      2.8 PPB  
Not Feasible

Therefore our concentration curve must be based upon .001M & 1E-5M only.

In retrospect you need to make the first solution more concentrated. Our solutions are

	X	Y		
AlSO <sub>4</sub>	IUA	PPM	AlSO <sub>4</sub> :	-15.181
.001M	364	54	PPM = 4.092E40 UA	
1E-5M	493	.54		

	X	Y		
FeSO <sub>4</sub>	IUA	PPM	FeSO <sub>4</sub> :	-169.723
.001M	509	14	PPM = 3.45E460 UA	
1E-5M	523	.14		

eg if Al UA = 300, PPM = 1015  
UA = 520, PPM = 0.24

Let's try it w/ an unknown mixture of FeSO<sub>4</sub> & AlSO<sub>4</sub>

Also 100ml w/ 1 drop HCl Unknown			
AlSO <sub>4</sub>		FeSO <sub>4</sub>	
-1.88	408	-1.85	448
-1.85	329	-1.84	399

Our problem is that our original solution was not concentrated enough.

But you are on the right track. You want to be within the range.



You need to make a more concentrated solution

$.01$   
 $1E-4$   
 $2E-6$

These are more reasonable ranges

$AlSO_4:$   
 $FeSO_4: .01(278.02) = \frac{2.78}{1000ml} = \frac{.289ms}{100ml}$

$.01(522.31) = \frac{5.2239ms}{1000ml} = \frac{.529ms}{100ml} = \frac{1.569ms}{300ml}$

$AlSO_4:$   
 $1E-4(522.31) = \frac{.0529ms}{1000ml}$

$\frac{x}{500} = .01 \quad x =$

$\frac{10}{1000 \times 500} = .02 \Rightarrow .02(1E-4M) = 2E-6$

$AlSO_4$   ~~$FeSO_4$~~   $FeSO_4$   
 So .01M : .529ms / 100 ml  $\phi$  .289ms

$1E-4M : .0529ms / 1000 ml$

$2E-6M : \left( \frac{20}{500} \right) (1E-4) = 2E-6M$

Did you add acid?

So I do not have enough distilled water for  
this. So I improvise.

$\Sigma = .80$  .01M .529ms/100ml  $\text{FeSO}_4$  .289ms/100ml

So your biggest problem was that you did not have  
a sufficiently concentrated control solution.

I also do not think you should be changing your conditions

	(E) $\text{AlSO}_4$ (I)	(E) $\text{FeSO}_4$ (I) UA
.01M	-1.42 356	-.88 437
	-1.40 324	-.91 406
	-1.43 302	-.85 381
	-1.43 283	-.75 377

There is not looking right. Did I add acid?

I do not have the look of the.

Next we learn that the frequency changes the curve.

A high frequency produces the curve

This means that you cannot change the  
conditions.

ACV may not be the best method for concentration.

Also if it is too concentrated it does not identify  
the value properly.

.01M	-1.60 322	-.94 409
------	-----------	----------

OK, big discovery. If you condition and deposit far left of the start range it makes the process dramatically more sensitive. You had lost everything.

$[-3, 15, -3, 15]$   $[10, -2, -0.5, .007, .25, .03, 20]$

AlSO4

FeSO4

-3	-1.74	636	-.80	1045
-3	-1.68	600	-.82	969
-3	-1.71	534	-.84	880
-4	-1.83	721	-.80	1170
-4	-1.71	840	-.78	1155
-4	-1.75	845	-.78	1140

Notice that higher condition & deposition raised the currents level. You are probably seeing the highest current level that you can.

-1.77 876 - .77 1148

Use EStep to control the no. of points.

Eac always has a max of 0.25 and it seems best then ya!

Scan rate you go as low as you can comfortably tolerate. It looks like 20Hz is about right for the freq.

I flipped the electrode and it changed everything?

Now I have resharpened the electrodes on both sides.

The results are entirely different now. File #08

I have flipped all electrodes as well.

OK, flipping each electrode over to make sure  
 it's clear has changed things dramatically.

-2      -1.55    829      -1.68    283  
 using  $[-2, 10, 2, 10]$   $[10, -2, -1.5, .007, .25, .03, 20]$

-2      -1.56    847      -1.68    283  
 -3      -1.60    715      -1.71    298

So now is behaving very differently now, a very sharp drop.

-3 20Hz    -1.58    758      -1.69    317  
 -3 30Hz    -1.64    880      -1.67    386 (raised to 30 Hz)  
 -3 20Hz    -1.62    900      -1.65    351

It is a nice looking curve. Fe is entirely different.  
 $[-3, 10, -3, 10]$   $[10, -2, -1.5, .007, .25, .03, 20]$

-1.61    875      -1.68    350  
 -1.62    884      -1.66    365

PPM      PPM  
 .01M 540 X=1.62    885      -1.66    363      140

HCl added!  
Now we are using second solution,  
which is .001 M

		PPM			PPM
	-1.66	353	54	-1.73	192
	-1.60	343		-1.73	188
	-1.61	335		-1.73	182
.001 M	$\bar{X} = -1.62$	344.0 A		-1.73	187

Now for 1E-5 M HCl added.

		PPM			PPM
-3	-1.88	<del>320</del> 315	+54	-1.85	146
	-1.88	343		-1.78	144
	-1.91	340		-1.78	144

Borderline Detection.

Model  
580  
5.6  
5.0

Therefore AlSO<sub>4</sub>

.01 M 540 PPM  
1E-3 M 54 PPM  
1E-5 M .54 PPM

Model FeSO<sub>4</sub>

22A 140 PPM 363  
3 14 PPM 187  
33AUA .5 114 PPM 144

6.689  
7.064

PPM =  $2.02E-12$  UA 4.906  
MSE = 9.95  
 $r^2 = .60$

AlSO<sub>4</sub>  
Calibration  
Curve

Maybe not to bad

FeSO<sub>4</sub>  
Calibration  
Curve

PPM =  $1.689E-15$  UA  
MSE = 4.14  
 $r^2 = .82$

There are some real nuances here w/ AEC.

1. The electrodes must be clean and not overused in any one session.
2. The electrodes must stabilize over several runs.
3. The peaks are increasingly difficult to identify as the concentration gets weak.
4. You should not need to change the settings very much.
5. AEC is indeed a sensitive method however.

OK, in retrospect, the calibration curve is not good enough.

It is an approximation, but it is too rough.

You are going to have to develop better calibration curves using a different method.



Now looking @ the Urene.

1. Urene is way too concentrated to use straight. I have diluted by a factor of at least 10 w/ distilled water.

2. Urene has plenty of conductivity, even diluted ~ 450 TDS.

I do not get a signal w/ my current spec. That is not true just seems very weak.

We have 2-3 peaks:

-1.48	-1.33	-1.33	-1.30
-.74	-.79	-.69	-.70
+.88	.83	.85	+1.96
			+3.06
-1.30	[-3.5, 10, -3.5, 10] [10, -3.2, 3.2, .02, .25, .1]		
-.70			[.98]
.97	-1.27	-1.31	-1.31
+2.73	-.67	-.69	-.71
+2.78	+1.13	1.10	+1.20
+3.00	2.93	2.85	
	2.81	2.92	
	2.96	3.01	
			Co
			H <sub>2</sub> O <sub>2</sub>
			Mn
			U <sub>3</sub>
			Zn
			SO <sub>4</sub>
			AsCl <sub>3</sub>
			Ni
			Br, Mn
			Mg
			Na
			Cr

File 08 has a lot of detail

[-3.1, 10, -3.1, 10]	[10, -3.1, .01, .25, .05, 20]	+2.77 K
		+2.86
		+2.93

NP identify first by maximizing.  
Then is when we need to maximize.

NP we have -1.52 and -1.37 w/ [10, -2, 0, .01, .01, .5]

-1.53	-1.39	
-1.54	-1.40	-.15
-1.55	-1.41	-.19
-1.55	-1.42	-.25
-1.56	-1.43	-.30
-1.57	-1.43	-.33

These are maximized.

$\text{NiO}_2$  +1.59  
 $\text{Co, NH}_3, \text{Br}$  +1.42 to 1.45  
 $\text{Cu} = +1.34$   
 $\text{Fe CN}_6$  +.36  
 $\text{PbSO}_4$  -.35  
 $\text{Zr}$  -1.45

+1.28    0.13    0.14    .15    +.20  
 +1.40    +1.54    +1.63    +1.82    +2.26  
 +1.46

.24     $\text{Ni?}, \text{AgCl}$   
 2.46     $\text{Mg}$  2.37

~~1.15~~  
~~2.54~~    This is matching ACV!    Good, then look to the maximums  
 1.16  
 2.59    Max

Ok, some interesting things going on here.

ACV and DP look seem to have value and unique qualities for identification.

There is not a one to one correspondence and they may both reveal diff components in a mixture.

With ACV we believe that Conditions or deposition immediately beyond the window are helpful.

We know that Estep primarily controls the no of points (estimate 300 for  $n=0$  to 3).  
Eac step @ max of 0.25 seems to be a preferred constant. Also the 20 Hz seems to be able to hold a constant.

The only thing left change is the scan rate and slower is not always better.

There was a big difference in sensitivity between

$E_{step} = .02$   
Scan rate = .1

and  $E_{step} = .01$   
Scan rate = .5

is better

$E_{step}$  should be = .01 because you need ~ 300pts / 3V.

So the only thing to actually change is the scan rate to a higher scan rate reveals more data.

Urine Analysis - Detection  
 File 08 picked up a slew of pts.

-1.83	Co, Be	1.82, 1.85
-1.26	MnO <sub>2</sub> in O <sub>2</sub> -H <sub>2</sub> O, Mn	1.23, 1.23
-0.81	Ag, Fe, Hg, H <sub>2</sub> O	.80, .71, .05, .83
+0.24 weak	SO <sub>4</sub> , AgCl, Ni	.20, .22, .25
+0.64 weak	H <sub>2</sub> O <sub>2</sub>	.68
+1.12	Mn, Br	1.18, 1.07
+2.36	Mg	2.37
+2.49	Mg	2.37
+2.65	Na	2.71
+2.75	Na	2.71
+2.91	K	2.93
+3.09 (maybe)	NH <sub>3</sub>	3.09

The rest of course, a huge and yet possible list.

NP Capture:

-1.57	NiO <sub>2</sub>	1.59
-1.43	Co, NH <sub>3</sub> , Br	1.42 to 1.45
-0.60	<del>-1.47</del> <del>-1.33</del> <del>-1.59</del> MnO <sub>4</sub> , MnO <sub>2</sub>	+0.59, ---
+0.24	SO <sub>4</sub> , AgCl, Ni	
+1.16	Mn, Br	
2.46	? Mg	2.37
2.59	Na	

Cobalt is not highly toxic.  
It is a catalyst in bit B-12

P45 Nasa POF

Co	11	2
Mn	111	3
Be	1	1
O <sub>2</sub> - H <sub>2</sub> O	111	3
Ag	111	3
Fe	11	2
Hg	1	1
SO <sub>4</sub>	<del>111</del> 11	2
Ni	<del>111</del> 11	2
Br	11	2
Mg	111	3
Na	111	3
K	1	1
NH <sub>3</sub>	11	2
Cu	1	1
Pb	1	1

3: Mn, O<sub>2</sub>-H<sub>2</sub>O, Ag, ~~SO<sub>4</sub>~~, ~~Na~~, Mg, Na

2: Co, Fe, Br, NH<sub>3</sub>, SO<sub>4</sub>, Ni

1: Be, Hg, K, ~~Ag~~, ~~Pb~~

Expected components that we are likely to have found are  
 1.  $Mg$ ,  $Na$ ,  $NH_3$ ,  $SO_4$  &  $K$ .

The leading prospect is that of manganese

Measured:  
 $Mn$  OCCW @ +1.23 then  $MnO_2$  which may not exist.  
                     0.59                      +.64 - .56  
                     1.18                      +1.12, +1.16

So there does remain a possibility.  
 We then need to have  $Mn$  by itself or develop a  
 qualitative test for  $Mn$ .



There are some very definitive points  
seen w/in NP. Maximized in detail.

-1.57

-1.60

for E70, you need to increase t pulse (shift right)  
for E20 you need to decrease t pulse (shift left)  
in order to maximize the shift

+1.20

+2.13

+1.18

+2.43

Vary the range  
and the scan rate  
also become of great  
importance ultimately  
beyond t pulse  
you must go through all these.

Ordered

~~#57~~  
-1.57  
-1.60  
+1.20  
1.18  
2.13  
2.43

There are all very definite.

Al (-1.66) MnO<sub>4</sub> (+1.51) Ce (+1.61)  
MnO<sub>4</sub> (+1.59)  
SO<sub>4</sub> (+0.20)  
Mn (-1.18)  
O<sub>2</sub>, H<sub>2</sub>O (+2.07)  
M<sub>2</sub> (-2.37)

This  
looks  
like some  
solid  
work

They seem to be more definitive than ACV.

So manganese seems to be strong.  
Also Magnesium,  
Also sulfates.

Source of manganese in the urine?

ACV seems a little more vague but let's try it again.

ACV also gives some definite results

+2.92	K (-2.93)
+2.86	Ca (-2.86)
+2.82	Ca?
+2.59	?
+2.40	Mg (-2.40)
+1.46	??? Chlorine in water?
-0.25	Ni (-0.25) SO <sub>4</sub> (+0.20)
-0.79	Fe (+0.77)
-1.06	Br (+1.07)

Acceptable:  
Mg, Ca, K  
SO<sub>4</sub><sup>2-</sup>

Now the candidate list is:

Manganese } Maybe not OK

Magnesium  
Potassium  
Calcium } OK

Iron } Maybe not OK?  
Bromine  
Sulfate } OK

Targets:  
Manganese  
Iron  
Bromine  
Chlorine  
or Bromine

+1.46 } ? BrO<sub>3</sub> or ClO<sub>3</sub>  
1.44 1.47

Mar 10 2016

The sample types now on tap are

1. Camp water
2. blood
3. blood
4. alternate urine

First: Camp Water: ACV &amp; NP TDS = 300

ACV AC Voltammetry

We do like overall default settings of

[-3.1, 10, -3.1, 10] [10, -3.1, 3.1, .01, .25, .05, 20]

TDS of 300 means that it is sufficiently conductive.  
 This may help w/ bleach or hydrogen detection.

Q1:

-1.42 Cl  
 -.32 Cu, PbSO<sub>4</sub>  
 +1.52 MnO<sub>4</sub>  
 +2.63 Na

Cl = +1.36  
 Pb -.31 Cu +.34  
 MnO<sub>4</sub> +1.51  
 Na -2.71

Recall that we take minimum w/ ACV.  
 The overall graph looks very clean.

Q2:

-3.05? +.53  
 -1.96  
 -1.50  
 -.86  
 -.31

Ø3:

-2.82 -2.78  
-1.60  
-.83  
-.57  
+.55  
+1.86  
+2.92

Ø4:

-2.68 -2.75  
-1.58 -1.54  
-.98 -1.01  
-.46 -.46  
.58 .53  
1.25 1.23  
2.38 2.38  
2.93 2.93

Ø5:  
higher resolution?

-2.97 weak  
-2.32 weak  
-1.61  
-.61  
+.31  
+1.66  
+2.59  
+2.67

Ø6:

-2.87  
-2.52  
-1.67  
-.80  
-.39  
+.32  
+1.65  
+2.49  
+2.94

Ø7:

-2.87 FI?  
-2.53 Asa?  
-1.65 Al  
-.78 Fe  
-.39 O<sub>2</sub> and  
+.69 O<sub>2</sub>  
+1.78 H<sub>2</sub>O<sub>2</sub>  
+2.51 Asa?  
+3.00 K

File #1 was created by  
subtracting a quadratic  
from left, center, right  
points and a high  
resolution curve  
[-3.1, 10, -3.1, 10] [10, -3.1, 3.1, .008, .25,  
.04, 20.0]  
all points selected are minimums  
selected from the difference  
curve.

This plot appears to be superb

It appears to be a very workable set.

Now let's see if we can zero in on a window  
and get the same results. With window [-3.1, 0]  
you really do not get the same results.

There is some overlap but for some reason the  
plot looks better.

Maybe ACV should be symmetrical?

The camp water is giving some interesting results.

Do we have  $Fl$ ,  $K$ , or both?  
What is this  $-2.53$  and  $+2.59$  that shows up?  
 $\bar{X} = 2.56$ ?

Do we have  $Al$   
Do we have  $Cl$

$Br$  or  $Cl$  is in range  $1.44$  to  $1.47$   
We do not seem to have this.

So now we go to NP

The higher the scan rate, the lower the + pulse

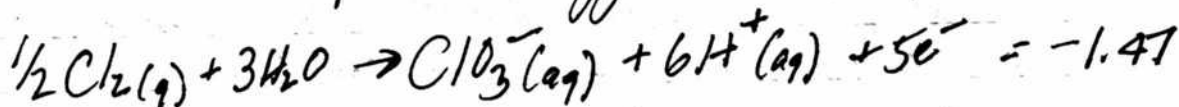
(1)	(2)	(3)	
$-1.55$	$-1.62$	$-1.65$	V. weak $Al$
	$-1.42$	$-1.46$	V. weak $Br$ or $Cl$

(4)	(5)	(6)	(7)	These
$-1.63$	$-1.65$	$-1.66$	$-1.66$	are final
$-1.40$	$-1.42$	$-1.43$	$-1.44$	tight for a value.

$[-2, -1]$   
 $\pm .02$

$-1.66$  is  $Al$   $Al^{3+} + 3e^- \rightarrow Al(s)$   
 $-1.44$  is  $Br$  or  $Cl$   $Br^-(aq) + 3H_2O \rightarrow BrO_3^- + 6H^+ + 6e^-$   
 $= -1.44$

$Cl$  is  $1.47$  you could be off but it does not seem so.



So they are putting  $ClO_3^-$  into the water.

-2.27 picked up [-3, -2] solid point.

First, set E step to get the right no. of pts.  
Start w/ a scan rate of 0.4 to 0.5

for ELO, set pulse as low as possible & maximize to left  
for E70, set pulse as high as possible to max. to right.

Then get scan rate as fast as possible under the  
above circumstances.

-0.75  
-0.74

We have Fe.

This means Iron is being oxidized.  
 $Fe^{2+} \rightarrow Fe^{3+}(aq) + e^{-}$

They require some very fine tuning to get the last value.  
It looks to me like you should not adjust  
the scan rate so much, pulse seems to be  
the critical factor.

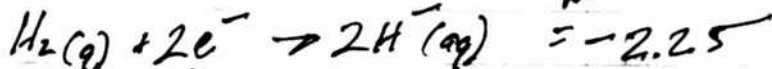
pulse commonly needs to go out 4 digits to maximize  
-0.75 vs -0.77 actual zero.

so this shows that you can easily be off  $\pm 0.02$   
even under good circumstances.

that means 1.41 can easily be 1.46  
which is closest to Cl for Chlorine.

We have  
Al  
Iron  
Cl

H meas -2.27



so there are  $H^{-}$  ions in the water.

notice it is minus  
instead of a plus?  
what is this?



Now we have flipped the corner and  
we have 0.16

Cu, Sr, or SO<sub>4</sub>

+0.18

+0.19

+0.20

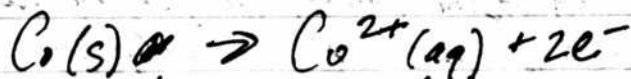
+0.21

+0.22

+0.24

+0.27

+0.28 done This is Cobalt



this means that it is being oxidized.

So now:

Al reduced

Fe oxidized

Cl reduced

H reduced

Co oxidized.

Now [1,2]

1. Always at Estep to adequate n.
2. Default pulse should be ~.01
3. Adjust scan rate

We now pick up +1.22

+1.25

+1.26

+1.27

looks fixed.

fixed.

could be  $O_2$ . = 1.23

but could be  $NH_4^+$  ~ Mn

1.24

1.23

So now:

Al (v)

1.66

/meas/ 1.66 theoretical

Fe (o)

.75

.77

Cl (r)

1.44

1.47

H (r)

2.27

2.25

Co (o)

0.28

0.28

$O_2$ , Mn or  $NH_4$

1.27

1.23-1.24

Now 2.98 picked up by extending range from 0 to 3.

[2-3] did not pick it up. Neither did [1.5 to 3].

So there is just some trial & error here no matter what you do.

Scan rate should be between  
(0.3 & 0.5 it seems)

2.95

2.96

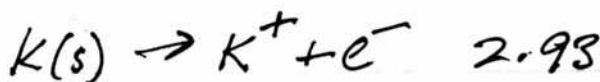
2.98

2.98

find

Closest is K@ +2.93

Li is 3.04



Our best candidates are therefore:

	meas	theoretical
Al (r)	1.66	1.66
Fe (o)	.75	.77
Cl (r)	1.44	1.47
H (r)	2.27	2.25
Co (o)	<u>0.28</u> Flawed?	0.28
O <sub>2</sub> , Mn or NH <sub>4</sub>	1.27	1.23-1.24
K (o)	2.98	2.93

AC-V gave us an an investigatory template.

- ✓ -2.07
- ✓ -1.66
- ✓ -.78
- ✓ -.39
- ✓ +.69
- ✓ 1.65
- ✓ 2.51?
- ✓ 3.00

The net result is that it seems to give us target area to investigate but that is all.

It seems that NP is the only method established to identify unique and repeatable numbers.

Mar 19 2016

Model for Pollution, Concentration &amp; Mortality

$$M_{10} \text{ model is } M_{10} \approx .007 \text{ days} + 0.40 \ln(\text{days}) + 1.65$$

$$\text{Therefore } M_{10}^{\text{PM2.5}} = \left( \frac{\text{PM2.5}}{10} \right) (.007 \text{ days} + 0.40 \ln(\text{days}) + 1.65)$$

y

This should be all that you need.

$$x = 0 \text{ to } 100 = \text{days}$$

$$y = 0 \text{ to } 80 \text{ PM2.5}$$

This paper is done. Very good

OK, back to camp water tank analysis.  
I want to look for correlation between AC-V  
and NP voltammetry.

So AC-V seems to be a useful overall guide  
but not specific enough as NPV is.

Now we go to filtered camp water.

Question: How effective is the water filter?

# Filtered Camp Water Analysis

1. Conductivity of camp water is 410 TDS.  
TDS of original water is 300 so there  
is nothing to indicate improvement.  
No HCl is needed.

Preliminary:

-1.27V

+1.18V

[-3, +3]

[-3, 0]

-1.27

0.27

Slowed?

Indicates that there is  
a lot of broken acting  
between -3 and -2.2.

Remember to measure to pulses for E<sub>0</sub>  
max to E<sub>70</sub>.

Try to keep scan rate between 0.3 and 0.5.

[-3, -2] Come out clean.

[-2, -1]

-1.34

-1.31

-1.38

-1.40

+1.04

-1.40

Closes to Cl or Br

By increasing scan rate to 0.5  
we picked up an Al peak @ -1.65

So now we have

-1.40  
-1.65

We are also picking up weak sig @ 1.79 Not definite enough

-0.72 Scan rate .5  
-0.72 .4  
-0.72, -0.73 .3

-1.40  
-1.65  
-0.72  
-0.73

Now we have 0.22 There is to method

+0.23  
+0.30  
+0.33  
+0.36  
+0.38

Procedure is to

1. Set Scan rate ~ 0.4
2. Set EStep to suitable n  
i.e. ~ 150 pts/Volt
3. Max (E70) or min (E70)  
miller type

Now the +0.38

term is very interesting.

It notes the case for

using AC-V if there is any doubt since AC-V  
is what originally uncovered this.

Notice we have the .27 w/ the overall scan and  
the result may indeed have been flawed!  
Maybe we need the detail of 1 Volt Windows!  
I think the 0.27 result is flawed.

Notice it was also -0.39 — then a further  
confirmation this is the valid result.

So now we have

-1.40  
-1.65  
-0.73  
+0.38

Reversible?

(-0.40) (+0.40)  
This can be either  $\text{CO}$  or  $\text{O}_2$



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Crucial Discovery.  
NP method outlined Below  
(It is iterative).

We now have

~~-1.43~~ -1.43

-1.65

-0.73

+0.38 (maybe always did,  $O_2$  or Cd)

+1.23 (maybe preliminary AC-V) NP

+1.25

+1.29

+1.32

+1.34

+1.37

+1.46

+1.46

You have just uncovered a  
very important procedural error.  
The scan rate must be  
lowered to a min on  
certain occasions to actually  
maximize.

The NP procedure is now

1. Set the scan rate midway to start (eg 0.3)
2. Set EStep to  $\sim 150$  pts/Volt
3. if  $E < 0$ , maximize  $t_{pulse}$   
if  $E > 0$ , maximize  $t_{pulse}$
4. Adjust scan rate and repeat Step 3  
until max or min is again achieved

The method is essential. You missed the  
influence that the scan rate  
SOMETIMES (not always) has.  
This should lead to greater correlation  
between AC-V and NP voltametry.

We need to:

1. Investigate the  $\phi.38$  a little deeper.  
Cd or  $O_2$   
Let's make a run w/ distilled water.
2. We need to revert back to <sup>on</sup> filtered water  
w/ refined methods for NP.  
~~Attempt~~ to reduce the list.
3. Then we need to move on to blood  
w/ refined NP methods
4. Then we go back to urine.

Distilled water has a TDS of 15.  
This is not sufficient. Try it w/ & without HCl.

Distilled water w/ w/ HCl gives a very low  
current value. This makes sense.

Nothing shows up between  $[-1, 0]$  and  $[0, 1]$

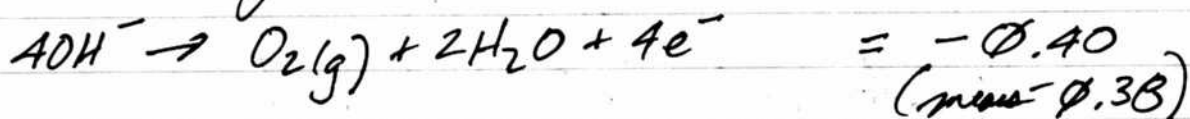
Now w/ HCl added the TDS is: 140

Now we have a definite strong signal @  $-\phi.38$ !

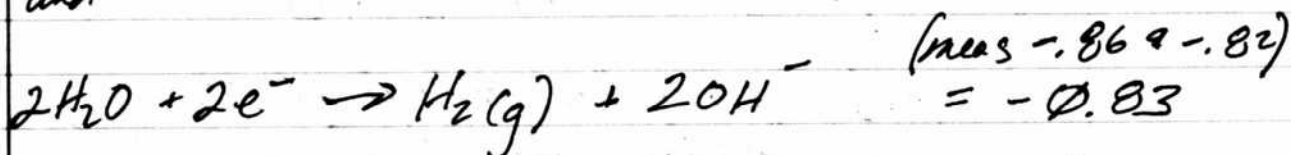
We also have additional  
weaker signals @  $-\phi.86$  and  $-.82$

all of these can be refined.

These points definitely correspond to interactions with water which we must now always be on guard for.



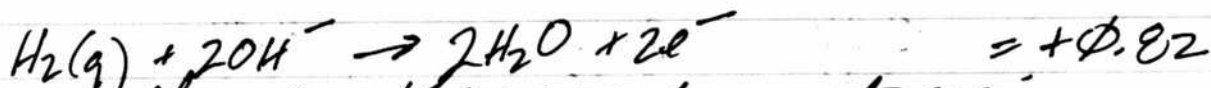
and



So we have the production of hydrogen & oxygen gas!  
And this is the electrolysis of water.  
So you must always watch out for this as a background signal.

Now look for [0,1]

I also get +0.82 which is



And this means that we are forming water again when I flipped the voltage direction.

Now I work with [-2,-1]

and I immediately pick up -1.45 which is Cl!  
from the HCl dissociation. This is perfect.

Now to Blood CEC.

Blood in water has a TDS of 3. Suggests.  
Added HCl. Water for 0.38 & 1.05

Very sharp peak @ +0.62 [-3, 3]  
Weak peak @ -1.32 [-3, 3]

[-4, -2] We may have something @ -2.72

[-3, -2] Ascending peak @ -2.94, -2.95  
We believe that this is now just as  
important as a descending peak.

Now we are also picking up a -2.84

-2.85  
-2.83

-2.91  
-3.00  
-2.96  
-2.97

-3.16  
-3.11  
-3.19  
-3.10

-3.32  
-3.40  
-3.42  
-3.34  
-3.34  
-3.41

-3.06  
-3.04

-3.75  
-3.80  
-3.96  
-3.92  
-3.88  
-3.93

~~-4.39~~  
-4.40

Two to Four Clusters possible

$\bar{X} = 3.89$   
 $\bar{X} = 3.38$   
?  $\bar{X} = 3.14$   
?  $\bar{X} = 2.94$

Potassium

Next we clean the electrode. It is observed that the  
working electrode has become very active.

4.16 -3.81  
3.67 -4.36  
Nothing -4.38  
4.22 -4.39  
-4.33  
-4.31  
-4.05

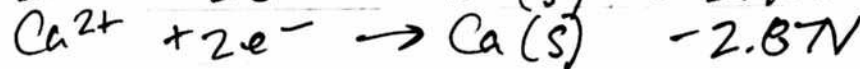
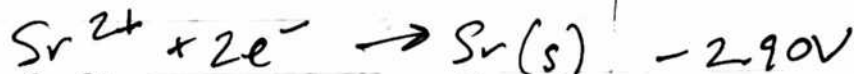
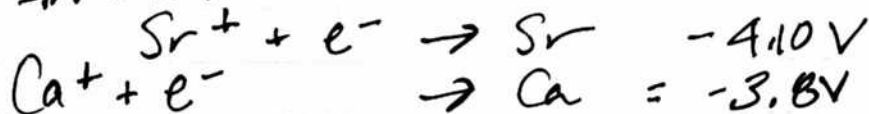
4.34, 3.89, 3.38, 3.14, 2.94

There seem to be potential pockets  
of activity. I do not know  
if anything this active this can.

Reduction potential of  $As^-$  is the highest  
reducing potential known in biology  
 $As$  is chlorophyll

$NADH$  has the highest reduction potential of all  
biological molecules of a cell. Therefore  
it is one of the most potent biological  
antioxidants.

Strontium reduction is  $-4.10V$



Strontium  
&  
Calcium  
are being  
reduced  
here



# The Modified NP Protocol

Mar 20 2016

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1. The NP Voltammetry Protocol has been modified. It is painless, repeatable and accurate.

The method is:

1. Set scan rate @ 0.3 for default
2. Set Estep to ~ 150 pts/Volt,  
higher if more detail is required.
- 3. If E < 0 minimize tpulse for E  
If E > 0 maximize tpulse for E
4. Adjust scan rate to Continue & Complete  
maximization or minimization.  
Repeat steps 3 & 4

AC-Voltammetry can be used to Corroborate NP  
if required.



Mar 20 2016 (Continuing)

1. We have some very interesting things going on with blood. How do we explain 4 Volts?
2. We now want to refine our previous sampling unfettered with a view w/ the new NPV protocol.
3. Then we continue w/ blood.

For <sup>Camp</sup> Water, we now have

Unfettered

✓ 1.66	Al(r)
✓ .75	Fe(o)
✓ 1.44	Cl(r)
2.27	H(r)
0.20 (adj to 0.30?)	?
1.27 (adj?)	O <sub>2</sub> , Mn, NH <sub>4</sub> ?
2.98	K(o)

Filtered

✓ 1.65	Cl
✓ 1.43	At Cl
✓ .73	Fe
0.38	O <sub>2</sub>
✓ 1.46	Cl
.82-.86	H <sub>2</sub>

Agreements:

1.66 vs 1.65  
1.44 vs 1.43 vs 1.40  
.75 vs .73  
.20 vs .30?

Disagreements

.20 vs .30  
2.27 vs nothing H(r)  
1.27 vs nothing O<sub>2</sub>, Mn, NH<sub>4</sub>  
2.98 vs nothing K

So now we have:

- 1.40 (Confirm this w/ new info on NY protocol)
- 1.65
- 0.73
- +0.38
- +1.46, 1.41, 1.40 it is.

Nothing shown from [2-3].

Now let's repeat -1.40?

I think the scan rate iteration is related to current levels.  
I think it is more relevant w/ low current levels.

Now -1.41

tpulse can not be less than .001

-1.42

-1.43

This is min.

The revised method applies @ all time. It is more sensitive in low current situation, but it also applies in ALL cases. The iteration is required.

So we now have

Cl.  
Cl  
from

Cd or O<sub>2</sub>  
Cl

- 1.43
- 1.65
- 0.73
- +0.38
- +1.46

vs 1.66

0.75

1.44

2.27

0.38 (adjusted)

1.27

2.98

Now let's go back to unfilt water

Anticipate	$[-3.1, 2]$	$[-2, -1]$	
$\approx 2.80$			
-1.91	-2.74	-1.86	-1.52
-1.52	-2.72	-1.87	-1.53
-12.52	-2.71	-1.88	-1.58
	-2.68	-1.88	-1.57
	-2.69		

If you raise the scan rate, you must decrease  $t_{pbc}$

$$\bar{x} = 2.71 \text{ is Na}$$

So now:

2.71  
1.82, 1.05  
1.51

$\approx 2.71$   
-1.87  
-1.55

Na

Be, not Al? or Co?

Mn

$$\bar{x} = 1.87$$

$$\bar{x} = 1.55$$

So what happens to Al & Cl 1.65 <sup>and</sup> vs 1.43?  
Maybe it will occur on the positive side?

We picked up a lot of activity with a 1 V window  
@  $[10, -2, -1, 0.006, 0.01, 0.3]$

-1.83

-1.68

-1.65

Aluminum shows up now

-1.23 (Notice not -1.55)

Notice we worked w/ 1.23 before and it went to 1.46, which meant Chloride.

So now it's picking up Al & Cl.

The next thing is that it looks like you need to work each one individually. The looks to be a sensitive setting so save it for the template.

We immediately picked up

-2.69

-1.07

-1.52

+2.13

Not too bad, but everything requires fine tuning.

Now let's center in on windows.

Very strong exploratory settings appear to be [10, left, right, .006, .01, .3]

-2.65

-2.69

-2.63

first.

Max reached so this holds from initial scan

Now for [-2, -1]

(.01)

-1.79

-1.66

-1.62

-1.22

(.008)

-1.81

-1.69

-1.66

-1.33

So there is a lot of activity here. Now maximize each one.

(.006)

-1.84

lost it

lost it

-1.41

(.004)

-1.86

lost

lost

-1.49

(.002)

-1.88

-1.56

(.001)

-1.89

-1.62

-1.60

.01

-1.69

-1.65

-1.65

This is very interesting. It looks like the -1.22  
essentially merged w/ the -1.62

Cursorry  
Review  
was  
quite soon.

Our cursorry remeasure

-2.80

-1.91

-1.52

+2.52

And we all now we have settled on

-2.69

-1.89

-1.65

into range [-3, -1] This is quite interesting  
on the data does seem solid.

This would be

-2.71 Na vs 2.69

-1.89 Be or Co -1.85 n + 1.82

-1.65 Al vs -1.66 Al.

Now for [-1, 0]

But before we go to this realize you  
did not vary the scan rate.

Would this have made a difference?

I am not sure. Epitaxial variation did  
pick up the Al.

Continuing: [-1, 0] lots of activity again

(.01)	(.008)	(.006)	(.004)	(.002)	(.001)
-.90	-.91	-.92	-.93	Lost	
-.86	-.86	-.89	-.91	Lost	
-.41	-.45	-.55	-.64	-.70	-.74

So this is getting real interesting. Not everything maximizes @ the same rate.

It actually seems like you can fix  $E_{step}$  @ .005  
It also seems that you can fix the scan rate of 0.3  
These are both very stable and useful values.

It seems like you only need to slowly vary  $E_{pulse}$  to effect minimization or maximization.  
Notice that close double peaks may well merge into a single value. Notice that other values can migrate a great distance (e.g. 0.3V!) and might even merge w/ a double peak.  
You can lose a point also so you need to be able to recover by reversing the pulse "push" toward max or minimization.

So now we have:

-2.69	Na
-1.89	Be or Co?
-1.65	Al
-.92	Hg
-.74	Fe

What a powerhouse!

This is all on the reduction side alone.

Now to oxidation: [0,1]  
+ .43, .44

[1,2]	+1.46
+1.26	+1.47
+1.31	+1.48
+1.33	+1.49
+1.35	(+1.49) max
+1.40	
+1.41	

So now we have:

-2.69	Na
-1.89	Be or Co
-1.65	Al
-.92	Hg
-.74	Fe
+ .44	Fe
+1.49	???
	(Mn) Gold not possible



Now [2,3]

Nothing shown up here.  
Wrong

+3.36  
Nothing from 2.5 to 3.5  
but 3.42 from [2, 3.5] why  
3.44 (2,4)  
3.44

If scan rate is higher, pulse gate lower.  
If scan rate is lower, pulse gate higher

So now we have:

Unfiltered

-2.69

-1.89

-1.65

-.92

-.74

+1.44

+1.49

+3.44

Na

Be or Co

Al

Hg

Fe

Fe

Mn or Cl

This is a big unknown?

1.66 Al

.73 Fe

1.43-1.46 mg, Cl

Unfiltered  
(NP  
work)

Now back to ~~distill~~ filtered water.

Template [-3,3] sig

-2.32 It is highly questionable how she correlate to  
 -1.36 the unfiltered water [-3,3] template results.  
 +1.22

[-3,-2]

Mg is -2.37

-2.31 -2.45

-2.39 -2.46

-2.42 -2.46

-2.43 -2.46

How can this be? How can you  
 identify Na on the unfiltered  
 run and Mg on the filtered  
 run? The makes no sense.

The scan rate is having no effect here. We end up  
 @ -2.46 no matter how we vary.  
 There is a major point of comparison.

2.69 vs 2.46 is the diff between Na & Mg  
 And right now you say that you cannot separate them.  
 What does AC-V say?

Conductivity of the sample is sufficient here in  
 both cases.

Well, looking @ AC-V I am not sure it clarifies  
 anything they get, but the minimums or changes there are at:

Only  
 AC-V  
 work

~~-2.68 (very weak)~~

-2.65 (very weak)

-2.07

-1.72

-1.72

+1.65

+1.41

+2.68

+2.90

Notice the fairly  
 high level of  
 correlation there  
 with the unfiltered  
 water.

of filtered water

AC-V seems to show some correlation support for the NP work on unfiltered water.

But it is hardly exact.

Secondly, the NP work for filtered is deviating somewhat. We move from

NP	- 2.69 Unfiltered	] Why this change?
NP	- 2.46 Filtered	

AC-V seems to very mildly support the NP of the unfiltered water but does not seem to do as well w/ the filtered water.

They seem that they should be the same. No is not Mg.

Just maybe, I cannot separate @ this level?

Next:	-1.56	-1.20	
	-1.59	-1.28	
	-1.63	-1.34	
	-1.65	-1.37	
	-1.67	-1.40	
max	-1.69	-1.43	values

So now we have

Unfiltered vs ~~Un~~Filtered  
 -2.46 -2.69 no -1.89  
 -1.69 -1.65  
 -1.43

In general, but not always, the best results are coming in w/ the slowest scan rate.

X	Unfiltered		Filtered
-2.58	-2.69	Na-Mg	-2.46
-1.67	-1.89	Be-C	None
-1.67	-1.65	Al	-1.69
-.91	-.92	Hg	-.90
-.73	-.74	Fe	-.72
+1.44	+1.44	Fe	+1.44
	+1.49	Mn-Cl	+1.41
	+3.44		None

-.90 (Hg) in Filtered almost undetectable.

Only slight variation in t-pulse revealed it.

Very small change in t-pulse revealed slight Hg on one trial - it did not repeat.

Picking up  $\phi.17$  [1,2]  
 +.23  
 +.29  
 +.30  
 .35  
 +.36  
 +.44 perfect max  
 1.20 +1.40  
 1.20 +1.41  
 +1.28  
 +1.36  
 +1.31

Note

A very important discovery.

Relaxing EStep from .005 to .006 or .007 allowed a further maximization - a critical difference took place here.

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# Water Filter Effectiveness Final Results

lastly [2-3.1]

Nothing

We now have a valid comparison

$\bar{x}$	Unfiltered	Candidate	Filtered	most likely
-2.58	-2.69	Na or Mg	-2.46	Na
	-1.89	Be <del>or</del> Co	None	Co
-1.67	-1.65	Al	-1.69	Al
-1.91	-.92	Hg	(As per test) -1.43	very weak Cl
-1.73	-.74	Fe	-.90	Hg very weak
+1.44	+1.44	Fe	-1.72	Fe
+1.45 vs 1.41	+1.49	Mn or Cl	+1.44	Fe
	+3.44	Unknown	+1.41	Cl

# How to chelate metal from the blood?

Mar 20, 2016

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Now we go back to blood w/ the new Protocol.

AC-V Candidates:

-2.78  
-2.67  
-2.54  
-1.41  
-.68  
-.49  
.40  
1.41  
2.40

-2.75  
-2.42  
-1.64  
-.43  
+.63  
+2.35

-3.15  
-2.56  
-.45  
.58  
1.27

Cyclic

-3.71  
-2.92  
-2.28

[-4, -3]

NP

-.10  
-1.33

-3.74  
-3.39  
-3.61

-3.88  
-3.72  
-3.66  
-3.37  
-3.47  
-3.28  
-3.41  
-3.73  
-3.31  
-3.65  
-3.78  
-3.08  
-3.45  
-3.92  
-3.22

[-4, -3]

-3.92  
-3.76  
-3.70  
-3.62  
-3.13

Appears to have high activity

[-3, -2]

-2.84  
-2.54

[-2, -1]

-1.50  
-1.09  
-1.66  
-1.50 (double)  
-1.15

Al  
-1.65  
Mn -1.52  
Mn -1.20  
-1.21

-1.63, -1.65  
Derivative  
1.24 is pretty  
tense up  
nicely.

Al, Mn, Fe, I, etc



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The derivative is picking up the spikes very well

$[-1, 0]$	$[0, 1]$	$[1, 2]$	$[2, 3]$
-0.80	+0.24	+1.17	<del>2.76</del> 2.47
		+1.16	2.75
Fe	HgCl <sub>2</sub>		
		Mn	
		n	
		Cl	

Blood Candidates are (NP)

-3-9 Vol/Hs (-3.92 to -3.13)

-2.84

-2.54

-1.65

Al

- wacky line

-1.52

Mn or Cl

-1.22

Mn

-0.80

Fe

+0.24

HgCl<sub>2</sub>?

+1.17

Mn or Cl

(2.47, 2.75)?

Mar 21 2016

Mission of CE

Environmental & Health  
Ethics

1. The issue of geoengineering & biotechnology. including its harmful effects  
This is the systematic and deliberate alteration of the atmosphere, biology, and ultimately to control it by

Engineers design  
The application of technology to alter a system and control

2. Ideal future

Everyone recognizes they have to a. everyone  
has the responsibility to safeguard the welfare  
of the planet and that they actively assume  
that role. Also that they think beyond  
their own immediate lifespan, and that  
they ensure the welfare of successive generations

2.2.2

2.1

3. Education, but also participation and action.  
Should be the entire global pop.  
Then live depend upon it.

2.3

2.3

2.4

4. Global power structures, can include governments  
and corporations, anyone with power.

2.5

It is a means of control. It provides for  
profit, dependency & servitude of the masses

3. First is to stop it while we take stock.

CRISPR is a great example

All disciplines in (1) are to be involved

Mar 21 2016  
Manganese research

surface water median contain  $\frac{16 \text{E-6 gms}}{1000 \text{ ml}} = \frac{x}{1 \text{E6 ml}}$   
 $x = 16 \text{E-3 ppm} = \underline{16 \text{ PPB}}$

Ground water: 5 to 150 PPB

Particulate matter is primary source of excess exposure.  $\text{Mn}$  is ubiquitous in drinking water.

Normal ranges: 4-15 PPB in blood  
 1-8 PPB in urine  
 .4 to .85 PPB in serum.

Accumulate in the brain.

$\text{Mn}$  is normally eliminated from the body through bile.

Accumulate in blood and eventually the brain.

> 0.2 PPM in drinking water may lead to neurological effects in children.

0.3 PPM in drinking water - high infant mortality  
 so it can easily become problematic.

"A Clash in Evidence"

Chelation  
 A Call for Action Since  
 No. 1

Ma-24 2016

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We have some interesting work taking place here.  
We are looking @ background noise &  
a blank reference spectra.

We have distilled water & He1 only.  
We have a main peak @  $\sim +1$  that  
drifted off to  $> 3.1V$  after about 6 runs  
and no idea what was going on why.  
We also have some additional minor activity  
that is taking place @  $\sim -1.9V$  &  $-0.7V$ .  
We are going to try and subtract them out  
w/ the blank work.

I waited 3 minutes & it reappeared.  
Next time it disappeared again to  $> 3.1V$   
reappeared.

I think you need a blank for each  
sector run; it changes.

We are now experiments w/ applying the blanks.  
[-3,3]

-2.24  
+0.10

I do not see  
the blanks helping at?

The blank current is close to zero so I am  
not sure it means anything.

[3,3]

-2.69  
-1.68  
-1.36  
+0.28

No blank  
Corr

[-3,-2]

-2.79

No blank  
Corr

[-2,-1]

-1.62  
-1.36

Maybe blank  
Corr @  
-1.63

[-1,0]

-1.71

No blank  
Corr

[0,1]

+0.18  
No Corr

[1,2]

1.95  
No Corr

[2,3]

Nothing

Original blood test. we get (1<sup>st</sup> run)

-2.84  
-2.54  
-1.65  
-1.52  
-1.22  
-.80  
.24  
1.17

~~-2.69~~ -2.79

-1.62

-1.36

-1.71

+1.18

+1.95

Now rework our set today w/ maxime.

$[-3.3]$

-2.70

-2.68

-2.88

-2.90] Strontium or Barium?

-2.95

-2.95

+2.88

$\bar{X} = -2.93$

K is -2.925

Potassium is a much stronger  
but than Be or Sr.

$[-2, -1]$

-1.59

-1.61

-1.64

-1.68  
-1.69  
-1.66  
-1.73

$\bar{X} = 1.69$

Al is my  
real candidate

1.66

-1.34

-1.40

-1.44

-1.50  
-1.49  
-1.44  
-1.54

1.49

Mn

1.51

So far

K -2.93

Al -1.69

Mn -1.49

Actual

-2.92

-1.66

-1.51



$[-1, 0]$

-1.82

-1.82

-1.86

-1.89

-1.91

-1.91 (weak)

Hg

-1.19  
~~-1.82~~ (strong)  
-1.20

Mo, Hg Br  
strong signal

$[0, 1]$

.12

.15

.19

.20

Mo, Hg Br

$[1, 2]$

1.89

+1.13

+1.96

1.16

+1.96

+1.17

(strong)

+1.17

↑

Mn

this goes  
beyond 2p

$[2, 3]$

2.07 (slope breaks)

+2.08

+2.02

2.70?  
Na

Best estimate

$$(1.96 + 1.96 + 2.07 + 2.08 + 2.02) / 5 = \underline{\underline{2.02}}$$

Al Fluoride?

AlF<sub>6</sub> = 2.07 Nothing else seem to be close

Leads to:

K  
Al  
Mn  
Hg  
Hg Br  
AlF<sub>6</sub>

seem pretty definite.

No iron picked up? Why?

Mar 25 2016

Blood Again

This time w/ 50ml container and smaller electrodes.

[-3,3] [-3,-2]

- 2.77	-2.06	-2.45
- 1.80	-2.08	-2.46
- 1.63	-2.13	-2.48
+ .009	-2.26	-2.50
+ 1.73	-2.29	also
	-2.36	-2.15 weak
	-2.40	-2.50
	-2.44	-2.15 weak

Scan rate can  
go very low i.e..01 instead of  
.1 to 0.5The very slow scan rate is picking up some  
real detail

-2.77 (very weak)	(only occasional)
-2.50 strong	-2.51 -2.48
-2.16 weak	-2.18 -2.17

They are all definite.

Ce or La  $\bar{X} = -2.77$  weak Na is still most probable  
 -2.50 strong Possibly Fluoride (2.65)  
 -2.17  $\text{AlF}_6$  is closest (-2.07)

Notice on previous run we have a +2.02  
 w/ conclusion of  $\text{AlF}_6$  (notice mean  $\leq 2.10$   
 vs actual 2.07)

$[-2, -1]$

-1.63   -1.64   -1.69  
 -1.45   -1.46  
 -1.34   -1.36

This activity is a little hard to separate.  
 Let's break it up.

$[-2, -1.6]$

$[-1.6, 1]$

-1.63  
 -1.65 clearly aluminum.

-1.51   -1.45   -1.46  
 -1.24   -1.25   -1.28  
           -1.18   -1.20

So we have

-1.63   Al  
 -1.46   MnO<sub>2</sub> (1.51)  
 -1.28   Mn?  
 -1.20   Mn (1.18)

$[-1.4, -1]$

-1.32   -1.34   -1.34  
 -1.11   -1.20   -1.19  
 -1.02

Zeroing in on the window seems to be giving  
 better data and elements are becoming  
 double peaks. This tight analysis indicates

-1.63   Al (1.66)  
 -1.34   Cl (1.36)  
 -1.19   Mn (1.18)

Now to  $[-1, 0]$

We are learning  
 something here.

-0.84   -0.76   -0.76  
 -0.51   -0.26   -0.66  
           -0.003

It is not just the maximum value.

It is the maximum value given that  
the measurements of pulse & scan rate  
are @ their "maximum extraction of information"

- .77 Fe (.77)  
- .66 Ti Br ??? This is new.  
- .003 H<sup>+</sup>

Now [0, 1]

+ .007 H<sup>+</sup>  
+ .30 HgCl<sub>2</sub> (.27) Ti (-.34) .46  
.91 Hg (.92) .94

.36 It seems like the method is,  
.94 given a certain scan rate, to  
set the pulse to the highest that  
can be tolerated (for positive values)  
.44 .51 .59 .63 .70 .71 .77  
.97 .98 .99 1.00 1.04 1.06 1.10

Then change everything.

.77 = Fe (.77)  
1.10 = Bromine (1.065) No real competitor.

The pulse is away from the Hg.

So now

-2.77	Na (2.71) ~ F1 (2.65)	
-2.50	Ce, La, ~ F1 (2.65)	
-2.17	Al F16 (-2.07)	
-1.63	Al (1.66)	
-1.34	Cl (1.34)	
-1.19	Mn (1.18)	
-.77	Fe (.77)	
-.66	Tl Br -.66	<u>Thallium</u>
-.003	H <sup>+</sup> 0	
+ .007	H <sup>+</sup> 0	
.77	Fe (.77)	
1.10	Br 1.065	
+1.23 +1.47	Mn 1.51	
1.65	Al 1.66	

[1,2]

1.23  
1.42  
+1.46  
+1.47

With a slower scan rate, 30.1, there is a definite maximum peak value that is attained. Then the value will actually start to decrease.

It appears that you have much more sensitivity in your data.

[1.5, 3]

+1.78

Then electrode seem to represent a major improvement.

Some repetition  
 $[-3, -2]$

Method: Vary the scan rate & maximize.

-2.40  
 -2.59  
 -2.86

-2.86   -2.89   -2.96   -2.94  
 -2.66   -2.74   -2.72   -2.70  
 -2.38   -2.49   -2.61  
                   -2.33

-2.94    $[-3, -2.6]$   
 -2.77  
 -2.53

-2.95 } Clear Signal  
 -2.76 }  
 -2.56 Weak but visible

-2.95   K (-2.93)  
 -2.77   Na (-2.71)  
 -2.53   F1 (+2.65)

$[-2.8, 2.5]$

$$\bar{X} = 2.65 = F1 (2.65)$$

-2.68

-2.72

-2.65  
 -2.67   F1

By tightening a window,  
 you can really zero in on a pt & you have  
 much greater flexibility to maximize  
 (eg Vly slow scan rate = .01)  
 quite high to pulse = 0.1 this is high!

You also see now that the dips are your  
 target point.



some repetition

$[-3, -2]$

Method: Vary the scan rate & maximize.

-2.40

-2.59

-2.86

-2.86

-2.89

-2.96

-2.94

-2.66

-2.74

-2.72

-2.70

-2.38

-2.49

-2.61

-2.33

-2.94

$[-3, -2.6]$

-2.77

-2.53

-2.95

-2.76

} Clear Signal

-2.56 Weak but visible

-2.95

K (-2.93)

-2.77

Na (-2.71)

-2.53

F1 (+2.65)

$[-2.8, 2.5]$

-2.68

-2.72

-2.65

-2.67

F1

$\bar{X} = 2.65 = F1 (2.65)$

By tightening a window,  
you can really zoom in on a pt & you have  
much greater flexibility to maximize  
(eg. Vary slow scan rate = .01)  
quite high to pulse = 0.1 this is high!

You also see now that the dips are your  
bigger point.

So now we know that we have

-2.95	K	(-2.93)
-2.66	Fl	(-2.65)
-2.17	AlF <sub>6</sub>	(-2.07)
-1.63	Al	(-1.66)
-1.34	Cl	(+1.36)
-1.19	Mn	(1.18)
-.77	Fe	(.77)
-.66	TlBr	(-.66)
-.003	H <sup>+</sup>	(0)
+0.07	H <sup>+</sup>	(0)
0.77	Fe	(.77)
1.10	Br	1.065
1.47	Mn	1.57
1.65	Al	1.66

Thallium Bromide?

Mar-26 2016

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Repeat Blood Trial Scan Rate  $\emptyset.1 - \emptyset.4$

$[-3, 3]$	$[-3, -2]$		$(\emptyset.3, .005)$
			$[-3, -2]$
-1.91	-2.92 v.wk	-2.13	-2.97
-.005	-2.03	-2.97 v.wk	-2.94
$\emptyset.24$	-2.95	-2.93 v.wk	-2.86
+1.82	-2.03	-2.07	-2.50
	-2.04		-2.01
	-2.12		
	-2.12		

A very slow scan (.005) & high pulse ( $\emptyset.3$ ) brings a lot of detail into the solution but it is also very slow.

It is better to tighten the window for specific targets when you are doing this.

So now

$(\emptyset.3, .005)$   
 $[-3, -2.6]$

Slow Scan, High Pulse Detects this.

-2.95	-2.94 v.wk	-2.98	-2.97
-2.83	-2.84 v. strong	-2.95	-2.86
-2.68	-2.81 strong	-2.85	-2.82
	-2.75	-2.67	-2.71
			-2.64

We therefore have:

-2.95, -2.94, -2.98, -2.95, -2.97  
 -2.83, -2.84, -2.81, -2.85, -2.86, -2.82  
 -2.68, -2.67, -2.71, -2.64

$$\bar{Y} = -2.96$$

$$\bar{X} = -2.84$$

$$X = -2.68$$

The comparison very well to the full previous set, but we pick up an additional -2.84

Mean	Prospect	Act
-2.95.5	K	-2.925
-2.84	Ca	-2.87
-2.67	(F)Na	-2.65, -2.71

Now for [-2.6, 2.07]

(.008, .3) -2.05

~~-2.05~~

(.01, .2) -2.10

~~-2.10~~

(.012, .2) -2.12

(.014, .1) -2.16

(.02, .1) -2.19

(.025, .1) -2.20

Final the comparison well to -2.17

Mean	Prospect	Actual
-2.965.5	K	-2.925
-2.84	Ca	-2.87
-2.687	F	-2.65
-2.185	AlF <sub>6</sub>	-2.07

The closest match to the remains AlF<sub>6</sub> @ -2.07 especially given that we indicate F.

Now  $[-2, -1]$  Electrochemical Board Profile

$[-2, -1]$

$(.008, .3)$   $(.006, .4)$   $(.012, .2)$   $(.025, .1)$

$-1.48$   $-1.88, -1.83$   $-1.46$   $-1.40$   
 $-1.02$   $-1.53$   $-1.31$   $-1.23$   
 $-1.16$   $-1.91, -1.87$  v.wk

The window makes a difference in allowable settings.  
 We have some clusters

$-1.4$  and also some very weak activity  $\sim -1.90$   
 $-1.2$  So break up into windows.

$[-2, -1.8]$

$(.008, .3)$   $-1.90$   
 $(.006, .4)$   $-1.96, -1.88, -1.83$

$(.004, .5)$   $-1.81$  strong

$(.012, .2)$   $-1.97, -1.90$

$(.07, .02)$   $-1.97, -1.96, -1.93$   
 $-1.83, -1.80$  (stronger)

$$\bar{x} = 1.95$$

$$\bar{x} = 1.82$$

So there are weak signals but we have

Possible Co then @  $1.82$  this is a match.

$-1.95$  does not have a great match. The closest is Th. @  $-1.90$

This is Thorium. This is radioactive.

There is a very weak signal.

So current status:

Mean	Prospect	Actual
-2.955	K	-2.925
-2.04	Ca	-2.07
-2.67	Fl	-2.65
-2.185	AlF <sub>6</sub>	-2.07
-1.95	Thorium?	-1.98 v. weak
-1.02	Co	-1.02 weak

Now

[ -1.8, 1 ]		
(.008, .3)	-1.57, -1.41 (strong)	
(.006, .4)	-1.60, -1.43	
(.004, .5)	-1.66, -1.54, -1.27	
(.012, .2)	-1.56, -1.31	
(.02, .1)	-1.53, -1.32, -1.23	
(.025, .1)	-1.53, -1.31, -1.19	
(.025, .1)	-1.53, -1.31 weak, -1.19 weak	
(.004, .5)	-1.66, -1.55, -1.28	

Note

What we learn here is that some items are picked up with to fast a scan & low pulse.

Other items are picked up w/ a slow scan & high pulse. This is all very important, because now we see what has

-1.66	Al (1.66)
-1.54	Mn (1.51)
-1.31	Cl (1.36) ~ Cr (1.33)
-1.19 - 1.23	<del>Co, Mn</del> (1.23) ~ Mn (1.10)



Very important comments on  
NP Protocol here.

There is another nuance here.

Note

Whatever scan-pulse combination maximizes  
or minimizes the value is the correct one.

There is in addition to the fact that some compounds  
are found w/ a fast scan - slow pulse  
and that others are found w/ a slow scan - fast pulse

So now we have

Mean	Prospect	Actual	Notes
-2.955	K	~2.925	
-2.84	Ca	~2.87	
-2.67	Fl	~2.65	
-2.185	AlFe <sub>6</sub>	~2.07	
-1.95	Th?	~1.90	
-1.82	Co	~1.82	
-1.66	Al	1.66	
-1.54	Mn	1.51	
-1.31	Cl or Cr	1.36 ~ 1.33	
-1.19	Mn	1.18	

Ok, you have a definite protocol in place.  
Your methods are repeatable.

Now let's go to  $[0, 1]$

We  
missed  
[-1, 0]!

2E-3  
2.4E-3  
2.5E-3

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,002

2.0E-3

[0,1] We realize now that Scan Rate \*  $t_{pulse} \leq 2.5E-3$

(.008, .3) .22, .64, .94, .79 (weak)

(.006, .4) .27, .77

(.004, .5) .21, .72

(.012, .2) + .009, + .44, .92

(.025, .1) + .14, + .58, + 0.97

(.050, .05) + .75

Remember that different scan rates - pulse level combinations detect different components.

We seem to have several groupings here.

LP-HS

[.009, .14] OK  
[.22, .21, .27]  
[.58, .64, .44]  
[.79, .72, .77, .75]  
[.94, .97]

up to 5 different groupings.

Let's break into windows.

[0, 0.3]

(.008, .3) + .007

(.005, .4) .004, 0.27

(.002, .2) + .10 max.

(.025, .1) + .16

scan	$S_0$	$t_{pulse}$
.5		.004
.4		.005
.3		.008
.2		.012
.1		.025
.05		.050
.02		.10

So we have one signal @ 0.16 Cu, Sn, Hg, Ag, Sn

We also have a separate signal @ 0.27

(.005, .4) 0.27

(.004, .5) 0.21

(.008, .3) Not detectable.

(.005, .4) .27

(.006, .38) 0.32

(0.0065, .36) + 0.34 both detectable.

~ + 0.33 is estimated value.

Cu, Ti (weak), Vm

What has happened here is that we have some  
very weak signals that have been introduced  
between  $[0, .3]$  as now

Mean	Properties	Actual
-2.955	K	2.925
-2.84	Ca	2.87
-2.67	Fl	2.65
-2.185	Al <sub>2</sub> O <sub>3</sub>	2.07
-1.95	Th?	1.90
-1.82	Co	1.82
-1.66	Al	1.66
-1.54	Mn	1.51
-1.31	Cl or Cr	1.36 or 1.33
-1.19	Mn	1.18

add  $[-1, 0]$

+0.16 <sup>fin</sup> Cu, Sn, Hg, Ag, Sn  
+0.33 <sup>fin</sup> Cu, Ti, Or

Now we continue

$[0.3 - 0.6]$

(.3, .008) <sup>(wk)</sup> .34, <sup>(sk)</sup> .53, .59 (v.wk)  
(.2, .012) <sup>(wk)</sup> .36, <sup>(sk)</sup> .59 stronger now.  
(.1, .025) .39, lost it  
(.0, .025) .40, lost it

So we pick it up again w/  $[\phi.3 - \phi.1]$

$[\phi.3 - \phi.1]$

$(.1, .025) + .40, +.67$

So now our projected set is

+  $\phi.16$  Cu, Sn, Hg, Ag, Sn

+  $\phi.40$

+  $\phi.67$

But we actually have 2 more sets. +  $\phi.33$  and +  $\phi.40$

$\bar{X} = + \phi.365$

It is of interest that  $\text{Fe}(\text{CN})_6$  is +  $\phi.37$

$\phi.67$  remains questionable.

But we also have

$(.05, .05)$   $\phi.46$

So we actually have prospects now of

+  $\phi.16$   $(.1, .025)$

+  $\phi.33$   $(.3, .008)$

+  $\phi.46$   $(.05, .05)$

+  $\phi.67$   $(.1, .025)$

Yes, we pick up  $\phi.16$  and  $\phi.65$  @  $(.1, .025)$

We pick up  $\phi.54$  @  $(.05, .05)$

We pick up  $\phi.44$  @  $(\phi.3, .008)$

We sort of got lost here between  $[0, 1]$   
and we forgot  $[-1, 0]$  in the meantime.

It looks like one of the lessons is to not  
chase the very weak signals and signals.  
The is an effect of diminishing returns,  
especially at the point.

So let's return to  $[-1, 0]$  and focus  
on the stronger signals.

There is a question developing as to whether the optimum  
value corresponds to the maximum signal  
peak or the maximum potential reached.  
You can test that on a known signal as  
AI or FE when you get to it.

Work on the bigger peaks first  
 $[-1, 0]$

$$\Delta = 4.6$$

(.3, .008)    -.80    -.49    -.003  
These are indeed the likely stronger signals.

(.4, .006)    -.80    -.56  
 $\Delta = 0.1$

(.2, .012)

Waker?

We are going to test the optimum value for Fe @ +0.77

(.5, .004)	-.69	$\Delta = 31.8 \text{ uA} - 31.3 = 0.5 \text{ uA}$
(.4, .006)	-.78	$\Delta = 2.74 - 2.96 = 0.22 \text{ uA}$
* (.3, .008)	-.77	$\Delta = 1.9 \text{ uA} + 5.4 = 7.3 \text{ uA}$
Here we have a nice definite peak.		
(.2, .012)	-.68	$\Delta = 3.8 - 3.0 = 0.8 \text{ uA}$
.1, .025	-.66	$\Delta = \dots < 0.5 \text{ uA}$

It clearly it looks like the optimum value is when we have the largest peak. The way it may not correspond to the maximum. We will see. In the case it did, but the most strength peak seems to be the biggest answer here.

So now

K, Ca, Fe, Al, Fe, Th, Co, Al, Mn, Cl or Cr, Mn  
we add

Mean  
\* -0.77

Purpose  
Fe

Ac. level -  
0.77

Now we have another strong peak @ -0.002V  
This should be H<sup>+</sup>.

(.1, .025)	-.002	H <sup>+</sup>
(.2, .012)	Lost H <sup>+</sup>	
(.05, .05)	Lost H <sup>+</sup>	

So

-0.77

-0.002

Fe

H<sup>+</sup>

0.77

0.



Another @ -.91

(.05, .05) -.91  $\Delta=3$

(.1, .025) -.91  $\Delta=3$

(.2, .012) -.94  $\Delta=4$

\* (.3, .006) -.95  $\Delta=4$  a/s - .80, -.50

(.4, .006) -.95 getting weaker

peaks @ -.80 & -.50 have been lost mostly

So the signal strength has a maximum strength

and this is what you want.

So now

-.77 Fe

-.002 H+

-.95 H

.77

$\emptyset$

$\emptyset.92$

Now @ -  $\emptyset.51$  we have a sharp peak but

it is momentary, so this confirms matters

(.3, .006) -.51 momentary sharp.  $\Delta=4$

(.35, .007) lost it.

(.25, .006) -.52  $\Delta=1$

(.25, .009) -.46  $\Delta=\emptyset$

( $\emptyset.26$ , .0096) -.40  $\Delta=2$

We actually have a nice sharp peak here.

This indicates our last value.

(.27, .0092) -.43  $\Delta=2$

Very clear peak.

(Iron also happens to be very good here)

(.28, .0089) -.44  $\Delta=2$

good peak.

ve  
2.5E-3  
Scan rate

Max

ve  
2.5E-3

So instead of being momentarily sharp, when you deal with the exact no. via  $(2.5E-3 / \text{Scan Rate})$  you can get to peak to maximize its signal.

So now

-2.955	K
-2.84	Ca
-2.67	Fl
-2.185	AlFe
<del>-1.95</del>	<del>Th?</del> This is so weak as to be questionable
-1.82	Co
-1.66	Al
-1.54	Mn
<del>-1.27</del>	<del>Cl to Cr?</del> TL?
-1.19	Mn
-0.002	H
-0.44	Fe
-0.77	Fe
-0.95	Hg

lets work on ambiguity w/ the new knowledge.

(3, .008) -1.96 but very weak.

(4, .006) pretty much lost

(2, .012) not clear

Increase resolution w/ step

(.002) (2, .005) lost but -1.83 comes in strong (Co on Cl?)

-1.95 gets knocked out. Not definite.

-1.83 is definite. This seems to hold.

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Test -1.31

$[-1.5, -1.0]$

<del>(.003,</del>		
$(\phi.3, .005, .003, n=164)$	-1.29	$\Delta=2$
$(\phi.3, .005, .003)$	-1.27	
$(.2, .007, .003)$	-1.22	$\Delta=1.5$
$(\phi.28, .0053, .003)$	-1.26	$\Delta=2$

$$\bar{X} = 1.26 + 1.27 + 1.29 \Rightarrow 1.27$$

Or  $\bar{C}^2$ ? Closest is TL (1.25)

Strangely enough, we had another reading of TL with  $+\phi.33$ ?

Now we go back to  $[0, 1]$

~~.004~~ (.3, .008,  $n=190$ ) .002, +.20, .72 (strong)  
 $\Delta=5$

(.4, .006, 190) .82

$\Delta=3$

(.3, .012, 190) .91

$\Delta=2$

(.32, .0078, 190) .90

$\Delta=2$

→ (.28, .0089, 190)  $\phi$ .92

$\Delta=2.1$

(.26, .0096, 190)  $\phi$ .93

$\Delta=2.2$

(.24, .0104, 190)  $\phi$ .94

$\Delta=2.4$

\* (.22, .0113, 190)  $\phi$ .95

$\Delta=4.5$

Peak here

(.20, .0125, 190) .95

$\Delta=4.1$

Now

-2.955

K

-2.84

Ca

-2.67

Fl

-2.185

AlFe

-1.82

Co

ok

-1.66

Al

ok

-1.54

Mn

-1.27

Tl?

-1.19

Mn

-1.95 ~~0.02~~

Hs

-1.71

Fe

-1.44

Fe

-1.002

H+

+0.17 ~~0.02~~?

Fe

+0.95

He

+1.35

Cl

Ok, you are really  
 falling into line here.

(1.36)

We must investigate  $\phi.54$   
to see if we already have the maximum.

(.3, .000) +.53  
(.2, .0125) .54  
(.1, .025) .62  
(.05, .05) .77

$\Delta = 1$   
 $\Delta = 2.0$   
 $\Delta = 3.5$  } do not  
 $\Delta = 3.4$  } split here

This is it.

Then tell you that every peak is unique and  
that it must be solved separately.

Next is [1, 2]

Peak  
(.3, .000) +1.15  
(.2, .0125) +1.35  
(.1, .025) +1.38  
+1.35 Cl- (1.36)

$\Delta = 2.1$   
 $\Delta = 2.7$   
 $\Delta = 2.4$

[2, 3]

(.3, .000) +2.88  
(.4, .006) +2.72  
(.2, .012) 2.58

$\Delta = 160 \text{ uA}$   
 $\Delta = 118 \text{ uA}$   
very small

Ca is 2.87  
(.34, .0073)

Actually we have 3 peaks now that's flat at.  
+2.44  
+2.60  
+2.78

(.126, .0096) 2.52  $\Delta$   $\Delta$   $\approx$  160 also.  
 Is this is confusing.

I am not sure that you can use this last point.

Let's start looking @ concentration again

$$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 278.02 \text{ gms/ml}$$

$$\text{Fe} = 5.08\% \text{ of total MW}$$

$$.1\text{M} = .0508(278.02 \text{ gms/ml}) = 14.12 \text{ gms}$$

$$.01\text{M} = \frac{.14 \text{ gms}}{1000 \text{ ml}} = \frac{.14 \text{ gms}}{1000 \text{ ml}}$$

Conductivity of .01M is 122 TDS.

How do we want to handle conductivity?

If you place it within the original solution, they still get diluted and conductivity will decrease. It seems you need to add it to the sample container each time.

Let's try NP first to make sure we have a signal. First, we have a very interesting NP graph -3 to 3.

Small peak @ -.85 but massive peak @ .40  
 Reflection takes place @ -.44



FeSO<sub>4</sub> Concentration Investigation

[-3,3] HCl (1 drop) added to each sample.

(0.3, .008) 0.44 goes crazy on derivative.

So this is sample 1 say detection of FeSO<sub>4</sub>  
@ +0.44V.

Nothing else is needed here.

$$I = 2405 \text{ uA} \quad 2405 \text{ uA} \quad 14.1 \text{ PPM}$$

Can we accomplish concentration from here.  
We want

$$\cancel{.0001 \text{ M}} \cdot .001 \text{ M} = 1 \text{E}-3$$

$$\frac{50}{500} = .1 \quad \frac{25}{500} \cdot \frac{5}{500} = .01 \quad \frac{50}{450+50} = .1$$

$$\frac{.14 \text{ gms}}{100 \text{ ml}} = \frac{14 \text{ gms}}{100 \text{ ml}} = 14 \text{ PPM} \quad \text{or } \frac{100}{900+100} = .1 = 1.4 \text{ PPM}$$

$$I = \cancel{308.6 \text{ uA}} \quad 3086 \text{ uA}?$$

Now for ~~.0000~~ .001M

$$\frac{50}{500} = \frac{50}{450+50} = .1 \quad \text{and } .1(.001 \text{ M}) = 1 \text{E}-4 \text{ M}$$

$$= 0.14 \text{ PPM} = 140 \text{ PPB}$$

$$I = 1274 \text{ uA}$$

$$r^2 = 0.95$$

$$\text{PPM} = 4.997 \text{E}-6 \text{ uA} \quad 1.4889$$

If  $VA = 100$ , then  $PPM = 4.75E-3 = 4.75 PPB$

These all seem very feasible.

Now let's look @ a window of  $[0, 1]$

$[0, 1]$  @  $(.3, .000)$

.14 PPM

25.2  $\mu A$  @  $\Phi.44V$

Bottom of Peak

(26.9  $\mu A$  @  $\Phi.51V$ )

1.4 PPM

20.2  $\mu A$  @  $\Phi.44$

(26.4  $\mu A$  @  $\Phi.51V$ )

14 PPM

17.7  $\mu A$  @  $\Phi.44V$

(26.4  $\mu A$  @  $\Phi.60V$ )

$r^2 = \Phi.979$

$PPM = 2.082E-17 VA^{12.765}$

$MSE = \Phi.22$

30  $\mu A = 149.2 PPM$

10  $\mu A = 1.212E-4 PPM = \Phi.12 PPB$

These all look very reasonable.

It seems to me that we have a good calibration curve for  $Fe^{+2}$  related to  $Fe$ .

Now, it seems to me that we could test below, at least approximately.

It looks to me like NP can be used for both identification and concentration.

I think it is better to use a narrow window.

I believe you must take readings until they stabilize.

14 PPM	<del>19.40A</del>	19.0	19.0	19.0	$\bar{X} = 19.00A$
1.4 PPM	20.2				
.14 PPM	<del>19.40A</del>	18.7			

That did not work! You must find a different method.

DP: Best results so far with a ratio of  $\frac{E_{pulse}}{E_{pulse}} = \frac{.1}{.005} = 20$

[10, -1.5, 1.5, .01, .1, .005, .1]

14 PPM Slope =  $\phi @ -0.005V \rightarrow -0.05V$   
 $-0.046V$   
 $= 1267 \mu A$

PPM = 1.4 we get 1242 hardly any difference

PM - 0.14 we get 1213

We do, however, get very good results  
 $r^2 = 0.998$   $MSE = .025$

PPM =  $6.92E-327 \mu A$  105.4783

This is actually a very good curve

I have a solute w/ SW for FeSO<sub>4</sub>

How do you know what is with the data

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Believe it or not, the results appear  
very reasonable.

If you have more than one peak, you must  
have more than one component?

It would be nice if NP would work  
since you know what is what there  
but can not see the impossible.

Try again (P. 4, .006) Measure  $+ .43$   
 ~~$- .38$~~   $[-1, 1]$

14	29.15 VA	
1.4	<del>2924</del> 2923	35.7 VA
.14 PPM	<del>2914</del> VA	32.6 VA

Electrode broke and everything changed.

THIS DOES NOT WORK. (NA)

Now look square wave.

It has a new pulse @  $+ .65$   
with  $[10, -1, 1, .05, .01, 20]$

Momentary pulse @  $- .02$  w/  $[10, -1, 1, .005, .01, 30]$

Same  
wave

14.1 PPM	@ $.65V$	2.95 VA
1.41 PPM	$.65$	2.63 VA
.141 PPM	$.65$	2.32 VA

OK  
I have  
something.  
Measure  
near  
spike

w/  $[10, 0.1, .005, .04, 30]$

$r^2 = .9994$

MSE =  $6.87E-3$

PPM =  $1.3506E-8$  VA

19.1568

Blood Sample ~ 4 drops in 35 ml

3.18 uA

$$= \underline{\underline{56.9 \text{ PPM}}}$$

$$4 \text{ drops @ } .05 \text{ ml} = 0.20 \text{ ml}$$

$$\frac{0.20 \text{ ml}}{35 \text{ ml}}$$

$$\text{Ratio } \gamma \sim \frac{35 \text{ ml}}{0.20 \text{ ml}} = 175$$

so expected PPM of blood of  $\text{Fe}^{+2}$  is

$$175(56.9 \text{ PPM}) = 9957.5 \text{ PPM}$$

$\approx 10 \text{ PPT}$  parts per thousand

What is the iron content of blood?

$$\frac{9957.5}{1\text{E6}} = \frac{x}{1\text{E2}} \quad x = .996 = 1.0$$

so we estimate 1% of blood is iron in  $\text{Fe}^{+2}$  form.

Note, actual value is ~ 0.075 %

off here by a factor of  
about 13. Not too bad

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I am displaying square wave again. Definitely activity.  
E Step can be used to slow things down without  
any effect upon system.

Typical settings are

[10, -3, 3, .005, .04, 30]

Lots of activity w/ FeSO<sub>4</sub> here.

[-3, 3]

-2.30

-1.16

+1.77

Mg?

Mn?

Fe

} Why are these here.  
This is ours.

[-2, 2] Lots of interesting activity.

Spikes @ -1.31

-1.12 maj min

-.66 maj min

+1.23

But notice a <sup>max</sup> maj peak @ -0.80 and -1.10

-1.79 maj peak. This is it. [10, -20, .005, .04, 30]  
[-1.5, 0] did not work.



We have found one great example of the value of conditioning.

The best window to operate in  $[-1.5, 0]$

but something about having the electrode conditioned to  $-2V$  (min?) is important.

Otherwise you lose the negative peak @  $-0.82$  that you are looking for.

So Condition @  $-2V$  for 10 sec and it brings out the peak beautifully.

Conditioning @  $-2V$  works but @  $-3$  and @  $-1.5$  does not work either.

Maybe Condition  $-1/2V$  left of the observed window?

Conditioning appears to be very important in SW.

	E	I
.01 M	$-0.82V$	<del>768.1 uA</del>
	$-0.83$	667.6
	$-0.82$	652.8
	$-0.82$	664.4
	$-0.83$	652.0
		$\bar{x} = 659.2$

So power spectrum is  
 $PPM = 3.3E-10 \cdot VA$   
 $r^2 = .91$   $MSE = .94$

3.7978

The model is  
 for spectrum.

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.001M	V	PPM
-	.89V	<del>307.8</del>
-	.87V	286.0
-	.87	279
-	.83V	283.5
-	.87	215.0
	$\bar{X} =$	280.9

.0001M	V	PPM
-	.83V	<del>229.9</del>
-	.83	223
-	.84	220
-	.84	216
-	.84	213
	$\bar{X} =$	218

- but OK  
 (hang detector)

FRESH BLOOD WAS INDEED REQUIRED.

Blood [REDACTED] Nothing visible. Use fresh blood?

V	PPM
- .83	<del>160.5</del>
- .83	153.2
- .83	151.1
	$\bar{X} = 152.1$

So  $PPM \approx .064$  PPM  
 $\approx 64$  PPB very good.

Peak no longer detectable after 3rd run

X	Y	Power
I	PPM	model
659.2	14.1	(16.8)
280.9	1.41	(.66)
218	.141	(.25)

This is indeed linear.  $r^2 = .997$   
 $MSE = .30$

$PPM = .0323 VA - 7.261$   
 But this is not really correct since  
 $PPM = 0 @ I \approx 225 VA$   
 which is obviously not true.

Now that we have an estimate of the  
~~let~~ now in dilute blood, let's estimate  
 raw blood.

Estimate 10 drops of .02 ml  
 so estimate .2 ml of blood in 35 ml H<sub>2</sub>O

$$\text{Dilution factor} = \frac{35}{.2} = 175$$

Surprisingly  
 good  
 estimate

so .064 ppm (175) = 11.2 ppm in raw blood.

actual is  
 supposed to be 1.0

$$\frac{11.2 \text{ ppm}}{156} = \frac{x}{100} \quad x = 1.12 \times 10^{-3} \text{ or } .00000112$$

Your  
 dilution  
 may be  
 off

estimate of blood is that .001% of it is  
 in the fet<sup>2</sup> state.

How much blood in the human body? (actual 3.5-gal)  
 let's say there is 7 liters. (Note it is closer to 5 liters)  
 $(1.12 \times 10^{-5})(7)(1000 \text{ gms}) = .078 \text{ gms} = \underline{78 \text{ mg}}$

error.

I suspect this is too low. Dilution factor should be near  
 I suspect the dilution factor is way too low.  
 Maybe more like 500.

$$(.064 \text{ ppm})(500) = 32 \text{ ppm}$$

$$\frac{32}{156} = \frac{x}{100} \quad x = 3.2 \times 10^{-3} \text{ new estimate of } \text{Hb} \text{ in raw blood.}$$

Assume 4 1/2 liters.

$$(3.2 \times 10^{-5})(4.5)(1000 \text{ gms}) = .144 \text{ gms} \approx \underline{150 \text{ mg}} \text{ in blood?}$$

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The investigation will now be of uric acid. We have a detection factor of

10 ml  $H_2O$   
1 ml Uric acid

Now we run the template from -3 to +3 V.

We have increased the resolution - down to  $\Delta$  step .002 when allowable.

[-3, -2]

(.005, .001, 0.5)

Notice Al seems to need a high scan rate.

-2.04  $AlF_6^{3-}$  (2.01)

$\Delta = 7.37$

(.005, .001, 0.5) -2.05  $AlF_6^{3-}$  (2.01)  
no other real competitor.

(.005, .001, 0.4) -2.11

$\Delta = 7.99$

(.005, .006, 0.4) -2.04

$\bar{X} = -2.06$

Actual -2.07

no  $AlF_6^{3-}$  is a prime candidate.

[-2, -1]

(.3, .008, .005) -1.76 -1.43

(.4, .006, .005) -1.79 -1.57

\* (.5, .004, .005) <sup>2.04</sup> -1.83 -1.64 (.36)

(.5, .005, .005) -1.80 -1.55

(.5, .003) (1.83) -1.87 -1.73 (.47)

Use max  $\Delta$  analysis chosen

-1.83

$(-1.64 + -1.73)/2 = -1.68$

So now we have

Meas	Prospect	Actual
-2.06	AlFe <sup>3+</sup>	-2.07
-1.83	Co	+1.82
-1.68	Al	-1.66

~~[-2, -1]~~ [-1, 0]

	$\Delta$		
(.3, .000)	-.60	(0.39)	(.41) $\bar{X} = 0.40$
(.4, .006)	-.66	(.22)	(.25)
(.5, .004)	-.79	(.42)	(.30) $\bar{X} = 0.40$

This presents a quandary. The max  $\Delta$  theory is not worthy here.

So the logic would be if the  $\Delta$  peak is the same choose the maximum  $\Delta$ . This selects -.79 then is iron.

So we now have

Meas	Prospect	Actual
-2.06	AlFe <sup>3+</sup>	-2.07
-1.83	Co	+1.82
-1.68	Al	-1.66
-.79	Fe	+1.77
+1.10	H <del>or</del> H <sub>2</sub> I	0.0, (HCl)
+1.48	Fe	-.44
<del>+1.36</del> +1.37	Cl	+1.36 (HCl)

[0,1]

(.3, .008) +,003  
 (.4, .006) .05  
 (.5, .004)  
 (.2, .0125) .05  
 (.1, .025) .09  
 (.1, .025) .10

+ .27  
 + .25  
 .17  
 0.39  
 0.48  
 0.48

[1,2]

(.3, .008) 1.13  
 (.4, .006) 1.16 0.3  
 (.5, .004) 1.13  
 (.2, .0125) 1.24  
 (.1, .025) 1.32 (.23)  
 (.05, .05) 1.37

1.95  
 72.0  
 72.0  
 72 (1.33) (1.36)  
 72 Cr, Cl

So there is a big question. The max peak edie  $\Delta$  may not be worthy.  
 It looks like the max value still holds.

[2,3]

So the urene profile is

(.3, .008) Nothing  
 (.4, .006) "  
 (.5, .004) "  
 (.2, .0125) "  
 (.1, .025) "  
 (.05, .05) "

Meas	Prospect	Actual
-2.06	AlF <sub>6</sub> <sup>3-</sup>	-2.07
-1.83	Co	+1.82
-1.68	Al	-1.66
-1.79	Fe	+1.77
+1.48	Fe	-1.44



Blood: 20 ml H<sub>2</sub>O, few drops blood  
w/HCl

[-3, -2]

(.2, .0125) -2.03, -2.00  
(.1, .025) -2.03, -2.02

Meas	Prospect	Actual
-2.03	AlF <sub>3</sub> <sup>-</sup>	-2.07

[-2, -1]

(.3, .008)	-1.80	-1.62	-1.55
(.4, .006)	-1.85	-1.68	-1.62
	-1.88	-1.64	
(.5, .004)	-1.91	-1.72	-1.26
	-1.93	-1.74	-1.27, -1.31
	Th? Co	Al	Cl -1.31
	$\bar{x} = -1.86$	-1.67	-1.34,
	Co = +1.82	Al = -1.66	Cl = +1.36

(.5, .0039)

-1.34  
-1.35

So

Meas	Prospect	Actual
-2.03	AlF <sub>3</sub> <sup>-</sup>	-2.07
-1.86	Co	+1.82
-1.67	Al	-1.66
-1.35	Cl	+1.36

$[-1, 0]$

(.3, .008)	-.87	-.09
	-.88	-.09
(.4, .006)	-.90	-.17
	-.90	-.17
(.5, .004)	-.94	-.41
	-.94	-.42
(.5, .0038)	-.94	-.45
	-.94	-.45
	Hg (+.92)	Fe (-.44)

So,

Meas

-2.03

-1.86

-1.67

-1.35

-.94

-.45

Prospect

AlF<sub>3</sub>

Co

Al

Cl

Hg

Fe

Actual

-2.07

+1.82

-1.66

+1.36

+0.92

-.44

$[0, 1]$

(.3, .008)

(.4, .006)

(.5, .004)

(.4, .006)

~~(.4, .0062)~~

.4, .0062

+1.05

+1.04

+1.04

+1.37

+1.40

+1.34

+1.45

+1.46

+1.48

$\bar{X} = +1.41$

Now:

Meas	Prospect	Actual
-2.03	AlF <sub>3</sub> <sup>-</sup>	-2.07
-1.86	Co	+1.82
-1.67	Al	-1.66
-1.35	Cl	+1.36
-.94	H <sub>2</sub>	+1.92
-.45	Fe	-.44
+0.04	H	0.0
+1.47	Fe	-.44

[1,2]

(.3, .008)	+1.21	
(.4, .006)	+1.30	
(.5, .004)	+1.31	
(.5, .005)	+1.33	Cl +1.36

So

Meas	Prospect	Actual
-2.03	AlF <sub>3</sub> <sup>-</sup>	-2.07
-1.86	Co	+1.82
-1.67	Al	-1.66
-1.35	(Cl)	+1.36
-.94	H <sub>2</sub>	+1.92
-.45	Fe	-.44
+0.04	(H)	0.0
+1.47	Fe	-.44
+1.33	(Cl)	+1.36
2.71	Fl or Na ?	+2.68, 2.71

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[2,3]

(.3, .008)	+2.77	
(.4, .006)	+2.73	
(.5, .004)	+2.72	
(.2, .0125)	2.71	Fl or Na
(.3, .008)		

We appear to have very repeatable & sensitive methods in place.

I am using 1 ml of urine in 20 ml of  $H_2O$ .  
I am using likely 0.1 - 0.2 ml of blood in 20 ml  $H_2O$ .  
You need to run blanks on distilled water.

Mar 29 2016

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1. Today was a good day of accomplishment.  
The full draft of a Chart of Evidence  
is now available.

2. With respect to electrochemistry.

1. What does the simple mode of  
potentiometry measure? What are  
its applications?

2. What about measuring distilled water?

3. What about my blood again?

4. What about the camp water?

5. What about a mix of concentrations?

What are some other topics of interest?

1. What about renewing her radio study?
2. What about APKS?
3. How about other fun items?
4. What about the Chemistry simulator?
5. What about the biology experiments?
6. What about all of my new voltammetry work?
7. What about history books?
8. What about differential equations?
9. What about the chemistry set?



Mar 29 2016

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Tonight we continue w/ reference Calibration work.

Our sample is distilled water w/ HCl.  
We start w/ 20 ml  $H_2O$  + 1 drop HCl  
[-3,3] gave serious overload results, so therefore  
the current is way too high.  
It came in too high @  $+1.5V$ ; +1.4V

Let's dilute this by a factor of 2 to see if  
it affects it as we know that it is  
close to zero current w/ no acid added.

I have diluted it by a factor of  $\sim 4$ .  
This has worked perfectly. This  
tells us that our amount of acid added  
is way too strong. So we must use  
about 1 drop of HCl per 100 ml  $H_2O$   
which is what we were trying originally.  
This is a first important discovery.

Let's measure the conductivity of these 2 solutions

1 drop HCl / 20 ml = 5900 TDS. Absurd level.  
1 drop HCl / 100 ml = 233 TDS. Fantastic.

So this is the first mandiscovery.  
You must be w/ a range. It is still  
too high on my second level.

So if you exceed the current range you must dilute.

$[-3, 3]$  Apts seen:  $-2.08$   $-2.23$   $-1.96$   $-1.42$   
So can't that a bit interesting already?

$[-3, -2]$   
(.3, .008)  $-2.07$  (Ca?)  
(.4, .008)  $-2.89$   
(.5, .004)  $-2.95$   
(.5, .0038)  $-2.94$   
(.5, .003)  $-2.93$   
(.5, .005)  $-2.93$

This indicates K in  
the distilled water.  
(K) mean  $-2.94$  actual  $-2.93$   
 $I = -1.3 \text{ mA}$   
Fairly high.  
Not a moderate range.

There is another weak signal @  $\sim -2.27 \text{ V}$   
Ag may also be there as a weak signal (actual  $-2.37 \text{ V}$ )

$[-2, -1]$   
(.3, .008)  $-1.63$   
(.4, .006)  $-1.68$   
(.5, .005)  $-1.70$   
 $I = +0.25 \text{ mA}$

Al?  
 $I = +0.25 \text{ mA}$   
moderate I

appears at least definitely smaller

$-1.92$   
(could be the  $\text{Th}$ , Co issue)  
 $I = -1.10 \text{ mA}$   
weak I

So we now see that we do have background noise  
and just maybe the water is not as pure as  
you think!

We need to learn to automate the process w/ a script but we, more importantly, need to consider a blanky process.

The blank would vary according to race setting.

I can see now that blanky is going to be very important.

What is truly how well he goes

1. Control of Concentration on the blanky solution

2. The reading requires optimization & the mean a different blank for every reading.

The next important thing serve you to be 5 man needs

.3, .008  
.4, .006  
.5, .005  
.2, .0125  
.1, .025

The mean 5 blanks

~~w/ a sufficient~~

What the mean ~~there~~ is that the blank  
becomes the actual sample until you can  
measure the supporting electrolyte accurately.

We could create our own electrolyte w/  
~~3 drops HCl~~  
1 drop HCl in 100 ml of distilled H<sub>2</sub>O.  
Then we know what we have.

We have now made a background electrolyte  
of 1 drop HCl in 500 ml of distilled water.  
It yields a  $\sigma$  of  $\sim 80$  HOS.  
The source almost perfect.  
This will now be our background electrolyte.

Now we have a control in place.  
Use 20 ml of control background electrolyte.  
Record a blank under these circumstances  
(Actually all 5 conditions)  
(.3, .000)  
(.4, .006)  
(.5, .005)  
(.2, .0125)  
(.1, .025)

Now, I did not help matters by misnaming  
all my file but I do have them.

My series starts @ -03

So let's identify the final set:

(.3, .008) ✓

3	$[-3, -2]$	-2.41, -2.43 - (2.23)
5	$[-2, -1]$	-1.41 repeated and superseded.
7	$[-1, 0]$	-1.52
9	$[0, 1]$	0.20
11	$[1, 2]$	None
13	$[2, 3]$	None

(.4, .006)

$[-3, -2]$

-2.41 is gone.

-2.17

(.2, .0125)

$[-3, -2]$

-2.41 is gone

-2.21

(.1, .0125)

$[-3, -2]$

(2.22)

(-2.23)

$H_2$  is -2.23  
and  $Fe^{3+}$  is +2.20  
 $Fe^{3+} \rightarrow FeO_4$

We have an issue here w/  $-0.54$  reached.

$Ga^{3+}$  is  $-0.53$

Uranium is  $-0.52$

Lead is  $-0.50$

Titanium is  $-0.56$

Iodine is a match

@  $+0.53 +0.54$

$(.4, .006)$

$[-2, -1] -1.38$

$(.2, .0125) -1.29$

$[-2, -1]$

so  $-1.41$  appears to be the max.

Best candidates are

$N_2H_5 +1.42$

$Co^{3+} +1.42$

$Cl_2(g) +1.36$

You can show blanks after loading by unclipping & rechecking.

Repeat:

$(.3, .008) [-2, -1] -1.36$

So now we have  $-1.36$  as best estimate.

$Cl^-$  is  $+1.36$

perfect match.

Next:

$(.4, .006) [-1, 0]$

$(.5, .005) [-1, 0]$

$(.2, .0125) [-1, 0]$

$-0.54$

$-0.54$

$-0.44$

1rm

This raises an important question.

Now, this is interesting. Notice the slower scan seems to be giving the best result.  $-0.44$  makes

some  $-0.54$  does not

$(.1, .0425) [-1, 0] -0.35$

still holds.

So no, max value



Last is  $+\phi.20$

$(.3, .008) [0, 1] + \phi.23$   
 $(.4, .006) [0, 1] + \phi.28$   
 $(.5, .005) [0, 1] + \phi.29$

Co is  $-\phi.28$

The new seems the most likely  
 w/ this added.

We have [REDACTED] Blood Mar 29 2016

Meas	Pr. spect	Actual
-2.225	H <sub>2</sub>	-2.23
-1.37	Fe <sup>3+</sup> $\rightarrow$ FeO <sub>4</sub>	+2.20
	Cl <sup>-</sup>	+1.36
-1.54	Iodine?	+1.53, +1.54
$+\phi.29$	Chalk	$-\phi.28$

There is a very interesting result.

The gives an actual different portrait  
 than working without a background removal.

But if your background has HCl in it,  
why would you then detect  $H^+$  or  $Cl^-$   
unless it were in higher concentration?

The suggestion you may collect he picks up

Iron  
Chloride  
Iodine  
Cobalt

??

You will be able to acquire metal salts  
of inorganic to test, excluding by on Eby.

You should be able to detect the oxidation  
of iron kinetically.

$$1 dm^3 = 0.1 m^3$$

$$\frac{1 mmol}{dm^3}$$

$$\frac{1E-3 moles}{0.1 m^3} = 1E-3 moles$$

$$\frac{1E-3 moles}{1E5 cm^3} = \frac{1E-5 moles}{liter}$$

$$10 cm = 1/10 m$$

$$(10 cm)^3 = 1000 cm^3 = 1 liter$$

$$1 m^3 = (100 cm)^3 = 1E6 cm^3$$

$$.1 m^3 = 1E5 cm^3$$

$$\frac{mmols (1E-2)}{dm^3} = \frac{moles}{liter}$$

Deise Voit can go as low as  
 $\frac{1E-8 moles}{liter}$

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Now if something has a molar wt of  $\frac{1 \text{ gm}}{\text{mole}}$   
 the  $1\text{E-}5 \text{ gms}$  can be detected  
 with w/ normal voltammetry.

$$\text{Ans } \frac{1\text{E-}5 \text{ gms}}{\text{liter}} = \frac{1\text{E-}2 \text{ gms}}{1\text{E}6 \text{ gms}} = 1\text{E-}2 \text{ PPM}$$

or .01 PPM which is already extraordinarily low.

If the MW = 16 then you can detect to .16 PPM  
 Not true! 56

We know with Fe this is about ~~200~~ gms/mol  
 so  $(200)(.01) \text{ PPM} = 2 \text{ PPM}$  .56 PPM  
 So

So normal can detect to about 8 PPM of Fe.

$$0.5 \text{ PPM} = 500 \text{ PPB}$$

As long as we can reduce this  
 by an order of magnitude this would get us  
 to about 50 PPB which is sufficient for  
 many cases.

However dropping down to 5 PPB is much  
 more agreeable and I think this is quite  
 close.

# Normal & Pulse Voltammetry Expected Detection Limits.

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So Normal Voltammetry has a detection level of  
approximate  
Molecular Wgt ( $\cdot 01 \text{ PPM}$ )

So Normal Voltammetry Detection  $\approx$  Mol. Wgt  $\times (\cdot 01 \text{ PPM})$   
Eq Fe =  $56(\cdot 01) \text{ PPM} \approx 0.56 \text{ PPM} = 56 \text{ PPB}$   
Pulse Voltammetry can theoretically at times  
reduce the factor by  $10^{-5}$  so theoretically  
we have

$$\begin{aligned}\text{Normal Pulse Detection Limit} &= \text{Mol. Wgt} (\cdot 01 \text{ PPM}) (10^{-5}) \\ &= \text{Mol. Wgt} \times 1000 \text{ PPM} \\ &= \text{Mol Wgt} = \underline{\underline{1 \text{ PPB}}}\end{aligned}$$

or for Iron:  
 $(56)(1 \text{ PPB}) \approx 56 \text{ PPB}$

I think that we proved exactly the detection level ourselves.

So  
Normal  $\approx$  MW ( $\cdot 01 \text{ PPM}$ ) eg Fe  $\approx 0.5 \text{ PPM}$   
Detection  
Limit

Pulse V.  $\approx$  MW (1 PPB) Fe  $\approx 50 \text{ PPB}$   
Detection  
Limit in  
PPB  
Diff. Pulse achieved  
exactly this.