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Authored
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TOP GRADE

Chemistry Vol XIV

150 5 Subject

Perforated Sheets • 10-1/2 x 8" • 26.7 x 20.3 cm

NOTEBOOK

College Ruled

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Chemistry Vol XIV

Mar 2016

Mar 30 2016 Electrochemistry on Top

Many exciting topics ahead.

1. Autosave files
2 Script file
3. Baseline again (possible auto save)

4. There may be a fair amount of contamination in any water, including distilled?

5. The question is Al + Fe in combination in distilled. Will the Al show up above background noise?

6. Multiple concentration determination is next on the horizon – differential pulse.

7. What is actually happening w/ blood?
Is it H^+ + Cl^- or is it Fe → FeOH and add. Cl^-?
This can form the basis for use of an alternative electrolyte, such as (NaOH) or KOH.

8. We have done some very good work w/ blank incorporation. Now we apply this to a Fe + Al mixture.

9. Why do you have such a big difference w.r.t. Fe in blood w/ & w/out blanking? What about the concentration levels of Fe in blood w/ DP determined w/o prominent peak in your $FeSO_4$ reference solution.

10. What about regular potentiometry?
Can I use the Palmsens essentially as a voltmeter?
What is OCP and how do I measure it?
Palmsens talks about this on p 26.

You also have overlay graphs as an option. This means that you do not need to save every file separately. Maximization and minimization can be done w/a single session.

Autosave is covered on p28. This will also be very helpful. You can specify a file prefix name. The numbering looks like it may be off w/ single digits used, however.

You can add your own -0, or -1, -2 etc as a pre prefix and get 9 files @ a crack.

PLO has potentiometry.
Our regular chemistry set has an electrochemistry section.

OCP is the potential when the current (This would be an additional introduced current) introduced is zero.

Let's try this.

Page 2

I think that the microchemistry kit is an ideal way of laying down the experiment before we start looking at this in more detail. We are given

$Zn(s) + Cu^{+2}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + Cu(s)$

We know that Zn is oxidized here
We know that Cu is reduced.
Question: Is the reaction spontaneous?
Question: What physical set up is required to make
the reaction happen?

Zn donates electrons so it is negative and is the anode (away)

$Zn(s) \rightarrow Zn^{2+} + 2e^{-}$ +0.76 (oxidation loses electrons)

$2e^{-} + Cu^{2+}(aq) \rightarrow \rightarrow Cu(s)$ +0.34 (reduction gains electrons)
(Cu lands on its feet) (cathode) Copper is positive because it wants electrodes.
the right side of the equation is where the result takes place.
$E = 0.76 + 0.34 = +1.10V$ The reaction should be spontaneous.

But now, how to measure it? You can not measure w/ one electrode. For the reaction to actually take place you should only have to place a strip of zn metal into a $CuSO_4$ solution and it will create Cu metal and zinc ions. This is fascinating, is it not? But again, what physical set up is required to measure it.

So a salt bridge is a concentrated electrolyte that does not react with either of the original 2 solutions.

He is going to use sodium acetate as the salt bridge. The salt ~~bridge~~ bridge has some similarity to the supporting electrolyte in electrochemistry.

What if you used HCl? Would it react with any of the salt solutions

~~$CuSO_4$~~ $Cu(NO_3)_2$ + HCl? $CuCl_2$?
$Zn(NO_3)_2$ + HCl? $ZnCl_2$?
probably it would react.

Ok, to the very basics.
We have made a potato clock (potato slices)
Not only that but we have wired two in series to generate 1.6Volts. The metals used are zinc & copper. Theoretical voltage is 1.10V for one cell or 2.2V for series in two

Now this construction is solving the very question you were asking about the physical setup. We need to separate the metals so that we can get access to the current.

This is what the salt bridge idea is about. The salt bridge is the potato

S lets say you put a zinc electrode
in the potato and the Cu electrode
in the potato. How do you know which one
is oxidized. and which one is reduced?

Answer: Two ways:

1. With a voltmeter, positive and negative readings
will determine the cathode and the anode.
Cathode is positive terminal (accepts electrons) This is reduction
Anode is negative (a source of electrons) this means it loses
electron, so oxidation takes place here

The other way will be the activity series.

Let's deal w/ cathode & anode first.
In our potato clock, positive voltage is read when
the red (positive terminal) is connected to copper
and negative (black) is connected to zinc.
This means copper is the cathode, this means it accepts
electrons, and therefore Cu should be being reduced.
On the other hand, the anode is zinc, the anode is a
source of electrons, and therefore electrons should be
lost here, and therefore oxidation is taking place
here with zinc.
So now test it with the reaction.

From the given reaction:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Zinc is being oxidized.] This is exactly right,
Cu is being reduced] as you determined!

(Anodes) (negative) are a source of electrons, therefore they
can be lost here, therefore oxidation takes place here.

Notice when you use a potato you are skipping using the salt form of the metal ie there is no Cu salt or zinc salt. So how it working?

Let's look @ reduction potentials

Cu^{2+} has a reduction potential of +.34V
Zn^{2+} has a reduction potential of -.76V

Copper therefore has a much higher reduction potential (ie, the potential to be reduced)
So this is how we know Cu is going to be reduced.
If Cu is going to be reduced, it is going to gain electrons and therefore it will be the cathode (cat lands on positive feet).
and sure enough, that is exactly the case.

So the metal w/ the higher reduction potential will be the metal that is willing to accept more electrons, and it will therefore be the cathode, or the positive terminal in the cell.

Ok, we have done well today.

Oxidation & Reduction further understood
Electron sink & Electron sources now distinguished
Cathodes & Anodes & where they come from and
how to determine which is which.
Reduction table and how to tell which is the
anode & the cathode.
The role of a salt bridge
How a potato can act as a salt bridge.
The problem of not being able to use one electrode
to measure.
The benefit of providing a wire to serve as a
conduit for the electrons & how to tap into it.
with a meter or a load of some kind.
What potential means in terms of "work"

Read Thompson:

Next is an acid cell instead of a potato cell.
It seems like the same idea.
We have magnesium & zinc electrodes in HCl
instead of a potato. Here we do not have a
semi permeable membrane (or a salt bridge)
and he is not explaining anything about that deficiency

What he is doing is measuring the current flow
as a function of distance between the electrodes.
We presume current will decrease w.r.t. distance.

I tried this experiment but I do not have
the proper set up for it yet.

We have galvanic cells and voltaic cells.

I think we could create the voltaic cell easily.

Cu & $CuSO_4$
Mg & $MgSO_4$
paper salt bridge

(in series
We now measure the potato clock w/
Palmsens potentiometry.
We measure -4.6V
I do not know why is it always - 4+ volts
even when we flip the electrodes?

Now for Potentiometry w/ Palmsens.

It works great
We get -3.2V approx. I am not sure
why it is always negative.

Since this is a function of time, it is like having
a logging voltmeter. A question is why
the OCP and Non OCP measurements are
essentially the same.

Also I am only using 2 electrodes since
I do not see why I need more.

Now looking @ NP again.
Something very strange has happened.
The electrodes are acting completely differently
w/ very sharp pulses now.
I added HNO_3, H_2O_2, HCl on previous trials
just to play around. It may have changed
something dramatically. Might be good, don't know
The blanks are all very close now.
We have peaks @ ~
[-3,3]
-2.00
-1.67
-.19
+.16
+2.81

Are these real?
They are very distinct now.

Blood Analysis w/ Blanks Applied
[-3,-2] (.3,.008) -2.32
[-2,-1] -1.95, -1.59
[-1,0] -.69
[0,1] Nothing
[1,2] Nothing

(.4,.006)
[-3,-2] -2.02

[-3,-2]
(.4,.006) -2.02
(.5,.005) -2.12
(.2,.0125) -2.23
(.1,.025) -2.23

Same exactly as yesterday w/ altered electrodes.

Now for (-2, -1)

[-2, -1]

(.3, .008)	-1.92	-1.53
(.4, .006)	-1.94	-1.55
(.5, .005)	-1.94	-1.57
(.2, .0125)	-1.94	-1.51
(.1, .025)	-1.94	-1.45

So we have

Vs -2.225, -1.37, -.54, .29

-2.23	H_2 (-2.23)	$Fe^{3+} + 4H_2O \rightarrow FeO_4^{2-}$ (2.20)
-1.94	Cf^{3+} (-1.94)	Li^{3+} (-1.96)
-1.57	Ni^{2+} (1.59)	

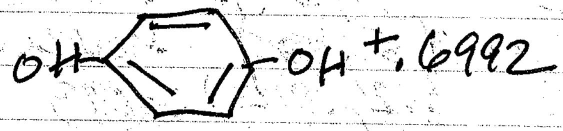
These do seem that likely.

Now

[-1, 0]

(.1, .025)	-.56	-2.23	1. Fe^{3+}
(.2, .0125)	-.63	-1.94	2. Li^{3+}
(.3, .008)	-.67	-1.57	3. Ni^{2+}
(.4, .006)	-.69	-.69	4. H_2O_2 or Aromatic
(.5, .005)	-.69	Ag?	

-.69 H_2O_2 (0.70)



Mar 31 2016 This does seem reasonable

Some very important lessons have been learned.
Blanks must be captured and prepared immediately prior to sampling.
Blanks must cover only the area of examination.
HNO_3 does affect, and appears to clean the electrode.
Blood does change color (oxidizes w/ time).

Segment Blank Analysis (Fresh) (Prior to Oxidation)
(.3, .008)
[-3, -2] nothing
[-2, -1] -1.54 shifts to -1.30
[-1, 0] -.11 shifts to -.61 Confusing here
[0, 1] 0.18
[1, 2] 1.60
[2, 3] None

Page 11

Now for post-oxidation
(.3, .090)
[-3, -2] nothing, no change

[-2, -1] Change do occur here. It was -1.54
We now have two new @ ~~-1.86~~ -1.81 + ~~-1.28~~ -1.29
Co (+1.82) Tl (+1.25)
Br (+1.85) Mn (1.23)

[-1, 0] -.61, ~~-.56~~, ~~-.54~~, -.59, -.59, -.61 $\bar{X}$ = .60
Mn is + 0.59

Br + Mn are best targets thus far.
[0, 1] +0.25, +.32, +.34, +.36, +.35, +.35, +.42, .48, +.49
.42
~~Interesting~~ Big difference takes place between (0.2, .0125) + (0.1, .025)
$\bar{X}$ = +.45.4 almost certainly Fe .42 .49

So Post Oxidation

Br
Mn
Fe are best targets.

now [1,2] +1.55 +1.72 also +1.22
+1.23 +1.76
+1.24 +1.84
1.24 +1.06
+1.27 +1.77
+1.29 +1.70
Tl = +1.25
Mn = +1.23

Consistently Tl [illegible] coming closer but Mn remains a strong target because of
-1.29, +1.27 and -.60
(all of these speak of Mn
+1.23 +1.23 +.59

1.86 Co is +1.82
So we also have
-1.87 and +1.86
so Co is very strong candidate @
+1.82 +1.82

So we have a good case for

Br
Mn
Fe
~~Co~~

Post Oxidation.

Low
[2,3] Nothing

Okay we have learned a lot

1. Blanks immediately prior and post oxidation
   (Time is a factor then.

2. Segments of sampling must correspond to blanks
   Overlaps & variations are helpful.
   It may not be the most extreme value.
   You may have error ± 0.04

3. "Cleaning" electrodes might make some difference.

4. Probably only one blank @ mid range (.3, .000) is required.

5. Inspect carefully, multiple passes & averaging
   will give the best results.

6. Sampling is also very likely a function of time.

Now we are headed toward concentration of a mixture along with identification of the component.

We will use:

.01M $FeSO_4 \cdot 7H_2O$ = ~~.14gms/1000ml~~

.01M $Al_2(SO_4)_3 \cdot xH_2O$

$.7H_2O$

1M $FeSO_4$ = 278.02 gms/mol   Fe = 20.09%

(1 Mol Fe, 27 moles total)

1M $AlSO_4 \cdot 10H_2O$ = ~~303.20~~ 522.31 gms/mol   Al = 8.90%

(1 mol Al, 36 moles total)

So, do you want to make a .01M solution of $FeSO_4$ or a .01M of Fe? I think Fe.

We know if we have 1M of $FeSO_4 \cdot 7H_2O$ we have a lot of moles but we still only have 1M of $FeSO_4$ contained within.

So a .01M solution of $FeSO_4 \cdot 7H_2O$ = 2.78 gms/1000ml.

now of this, .2009(2.78 gms) is 0.56 gms is Fe but you still need 2.78 gms to get .01M of Fe in the solution.

~~So we would try~~

What we really need is .001M to start.

.001M $FeSO_4 \cdot 7H_2O$ = $\frac{0.28 \text{ gms}}{1000 \text{ ml}}$

of this .2009(.28) = .056 gms is actually Fe

so $\frac{.056 \text{gms Fe}}{1000 \text{ml}} = \frac{56}{1E6}$ = 56 PPM

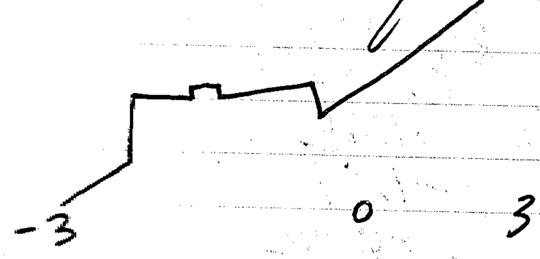
And this is too low. We need .01M for 560PPM

~~So~~ should therefore use
560 PPM = ~~2.8~~ 2.18 gms but we do not have that much
5.6 PPM to spare.
.5 PPM We use .001M $FeSO_4$ = 56PPM (0.28gms)

Now for Al:
MW = 522.31
.001M = .52gms/1000 ml

of this .0890(.52gms) = .046gms is Al
so $\frac{.046}{1000\text{ ml}} = \frac{46\text{ PPM}}{1E6}$
We Use .001M $AlSO_4$ = 46 PPM (.52gms)

Now we have learned what happens to the electrodes. IF you put them in very weak acid HNO_3 and subject them to 1 mA for 120sec twice then the electrodes will change dramatically to the geometric form. I have no idea why and I am not sure if the HNO_3 is even required.



So now we know what happened yesterday. I have no idea what it means, what causes it or whether it is useful. It certainly a modified electrode but it certainly reveals up to 4 definite points of interest.

Now, the peaks that are now so symmetric are likely very interesting as they are occurring in distilled water of HCl.

(.3, .008)
[-3,3]

-2.31 These points are probably of interest.
-1.79
-1.61
-.46

So now the question is, how do these shift towards maximums?

(.4, .006) overlay
-2.48
-1.77
-1.59
-.39

(.2, .0125)
-2.49
-1.75
-1.56
-.004

(.5, .005) overlay
-2.25
-1.76
-1.61
-.45

(.1, .025)
-2.49
-1.72
-1.57
+0.22

$\bar{x}$ = -2.49 Hf (-2.50) Th (-2.48) This is a problem?
-1.79 Co (+1.82)
-1.61 Ti (-1.63) Ce (1.61)
-.46 Fe (-.44)

Page 16

The electrode subjected to weak HNO_3 w/ 1mA for 120 sec twice show some very puzzling behavior.

Two pks are very unusual & unexpected.

Two points match the blood sample Co & Fe, but not really if you notice.
Blood gave an +.48, not a -.46
So this is not a match.

Blood gave a -1.87 not a -1.79
This is too much for error.
Co = +1.82 actual
Br = +1.85 actual

We read in blood -1.87 and +1.86
This is much closer to Bromine in both cases.
And is the more likely choice.

The case for Cobalt in blood is not strong.

Ok we have learned some more very important items

1. The water itself has some contaminants @ approx

-2.12 That have nothing to do w/ the
-.93 electrodes.
-.40

The geometric pulses come from the water itself. With no supporting electrolyte (ie HCl) they are weaker in magnitude but still very much there.

One thing from this you learn is do not use a supporting electrolyte unless you have to. Checking the conductivity of your sample is a very good pre-check on simplifying contaminants which are already in the water.

So blood needs it, but $FeSO_4$ & $AlSO_4$ will not.
Ok, this is a good lesson.

Now go on to a joint solution of .001 M $FeSO_4$ and .001 M $AlSO_4$.
Use 20 ml. No supporting electrolyte.
Check the conductivity in a final solution.

TDS = 158 perfect.

We are now working w/ $FeSO_4$ + $AlSO_4$

We have a background blank of H_2O.
We can see clearly that it does have some Al, n H.

But in our .001M Mix, we see two clear strong peaks:

-104uA -1.67V] Can't get any better than that Al (-1.66)
-451uA -.74V] ← These are the targets. Fe (+.77)

So what is happening is
$Al^{3+} + 3e^- \rightarrow Al$ Al is being reduced
$Fe^{2+} \Rightarrow Fe^{3+} + e^-$ Fe is being oxidized.

Ok, these are beautiful solution and the reaction is taking place when you introduce a potential.
We notice we have another peak @ ~ -1.43 (1.40 - 1.45)
much smaller but nevertheless distinct.

Let's work on the concentration since we have it in place.
We do have two peaks immediately
-.47 and 1.08 w/[20, -3, 3, .01, .01, .005, .1]
-.43 and 1.13
(Fe) (Al)

56.7uA Al did not work w/ these settings
[20, .5, -1, 0, .01, 0.1, .02, .1]

We do pick up Al @ ~ +0.15

So it does look like we have a way of picking up both peaks now.

Range seems to be $[-1, 0.5]$

$[-0.5, 0.5]$

It looks like you can pick up both peaks from -.5 to +.5

PPM	Fe	Al	PPM
56	63.3	62.6	46
5.6	15.7	14.9	4.6

this does not look real good.

take 10 ml, add 90

$\left(\frac{10}{10+90}\right) = 0.1$

62.2

Page 20

It looks like it is best for scaling E take
once peak separates
range for ~~Al~~ is [-.5,0]
range for Al is [(0.4]

	[-.5,0] Fe	PPM	[0,.4] Al		PPM
1E-3 .001M	62.4 uA	56	57.0	X=.11	46
1E-4 .0001M	16.1 uA	5.6	15.2		4.6
1E-5 .00001M	4.95 uA	.56	4.44		.46
1E-6 ~~1E-5~~M	1.68 uA	.056 (56PPB)	1.62	(46PPB)	.046
	x	~~x~~y	x		y

Now determine regression and Minimum Detectable Level by pulse voltammetry.

$r^2 = 0.997$! $r^2 = 0.996$
Mse = .035 Mse = .047
PPM(Fe) = ~~.024~~ .0237 uA $^{1.9100}$ PPM(Al) = .02166 uA $^{1.9260}$

This is marvelous work. Down to ~.05 PPM or ~ 50 PPB

Now for MDL w/ NP Voltammetry.

You have them (very faint, but you have them) @ 1E-5M!
First, if concentrations are strong (eg .001M) the targets are easy to spot, this time @ -1.67 (Al) & -.74 (Fe)
(-1.66 act) (-.77 act)

If the concentration is weak, it takes a keen eye to spot. but it is there.

Fe is detectable, Al is detectable but E value is off for some reason to ~ -1.30 vs -1.67?
See next page

You are simply not picking up the Al @ 1E-5M.

You are picking up the other small peak that you identified @ ~ -1.43V. You do not know what this is.

We are seeing therefore that there is indeed value in concentrating a sample

It will make the work more reliable if there is sufficient sample size to do this.

Even though Al is there and you can even detect the amount of it properly you cannot detect it @ the 1E-5 level w/ NP to know that you should be measuring for it.

Try to concentrate the sample.
Only add supporting electrolyte if required!
Always use a blank to compare to!

When you have a double peak, the average may be the best.

We are not picking up Al @ 1E-4M
The points out difficulties.

It appears your solution must be foul.

Certainly they are no longer being picked up?

We have discovered something very important.
* Conditioning the electrode w/ potentiometry introducing a current of 1 mA for 120 sec twice dramatically increases the sensitivity of the electrode.

Now trying 10 mA for 120 sec twice.
It does ~~seem~~ to increase the activity, a cleaning effect.
You probably do it until the curve comes out reasonably flat.

It does look like conditioning the electrode in this manner may increase the sensitivity however it still did not pick up Al @ 1E-6M,
I ran out of battery, could not test further

Page 24

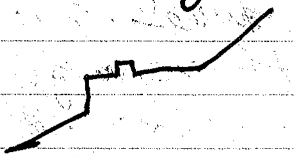
Apr 01 2016

Tonight we are investigating potentiometry and the conditioning of the electrodes w/ 1mA for 120 secs.

We are doing this w/ "pure" distilled water @ this stage, no HCl added.

We will examine the effect of the conditioning upon our NP blank of H_2O also

Ok, it behaved exactly as we anticipated with the geometric form.



So this can now be adopted as a reference quite easily.

We immediately pick up
-1.68
-.69
+2.14
good strong signals.

Square Wave Voltammeter [redacted]

Page 25

		-2.00V Al?	~~+1.60~~ Al?	+.68V Fe?	
1E-3	.001M Al (-2.00)	278.1UA	293.1 (1.60)	348.9 (+.68)	56
~~1E-4~~ 1E-4	.0001M Al (-1.46)	97.4	100.6 (1.50)	103.1 (.79)	5.6
1E-5	.46 (~-1.75)	32.6	28.8 (1.64)	30.1 (~.75)	.56
1E-6	.046 -2.00	16.7	16.9 (~1.65)	~~16.9~~ 14.7	.056
		r^2 = .990 Mse = .136	r^2 = .977 Mse = .302	r^2 = .969 Mse = .115	

This is square wave voltammetry Concentration ~~Determination~~
Notice that the method seems to be a bit more
sensitive as evidenced by the range accomplished
ie max 300uA for SW vs ~60uA for DP
The curve for DP was a better fit but the
increased range likely offers greater discernment
And we appear to have close to 10 times sensitivity
@ the 1E-6 (level) ie ~16uA vs 1.7uA.

So square wave seems to win in both cases
However, in both cases it seems you need it
to be almost 5PPM to even detect it.
Notice that @ .5PPM we appear to see reduction
of Al and oxidation of Fe.

All cases must be preceded by detection and
identification w/ NP.

Page 26

If you already know that something is there you can determine concentration down to 50 PPB or so or even less

But and it is a big but!

You must know that it is there and detect it easily @ concentrations of 5-50 PPM before you can proceed to assume that it is there.

But also note all high concentration in SW that all concentration points appear to be minimums. Is this true?

-2.00 V Al?
+.74 V Fe?
+1.61 V Al?

There are still some uncertainties here
It looks like [-2, 2] gave a better window.

Min peaks @	[-2,1]
-1.56 (Al?)	-1.54 V Al (?)
+.64 (Fe?)	+.64 V Fe (?)
	is even better

So provide a window of what you need to get best curve.

You now have some very good SW Voltammetry Concentration work in place w/ Calibration curves for $FeSO_4$ + $AlSO_4$ solution Concentration.

You can test this further now by varying the concentration. You could put a .001M $FeSO_4$ and a .003M $AlSO_4$ solution together and see how these SW peaks change.

NP Trace Identification
DP Trace Concentration
SW Trace Concentration (may be more sensitive)
Potentiometry w/ Induced Current: Condition electrode & monitor reaction changes.

Page 28

Let's briefly look @ Camp Water
Villa Nueva State Park

Potentiometry
1mA 120secs

1. First condition the electrode
1mA current for 120secs (twice)

NP

2. Form blank w/ reference solution (eg H_2O)
or (H_2O w/ HCl)

(.3, .008)

	[-3, -2]	None
Co, Mn	[-2, -1]	-1.84, -1.47, -1.30
Fe	[-1, 0]	-.70
Mn	[0, 1]	0.19
Mn	[1, 2]	1.12
Mg	[2, 3]	2.37

3. Maximize or minimize

Page 29

A very valuable analyse of identifying the ~~reducer~~ reducer, the oxidizer, what IS reduced, and what IS oxidized.

Apr 03 2016

The reducer IS oxidized.
The oxidizer is reduced.

Let's continue to clarify the relationship of oxidants, oxidizers, oxidizing agents to that of reductants, reducers and reducing agents, per the discussion in the textbook of Electrochemistry p193 by Iqbal (India book)

He says that "Oxidants are usually chemical substances with elements in high oxidation numbers (eg ~~AA~~ MnO_4^-, H_2O_2, $Cr_2O_7^{2-}$, CrO_3 etc)

Let's look @ them a little closer.
Take the first simple example he gives on p195

[illegible]

$$\overset{0}{Fe} + \overset{+2}{Cu}\overset{-2}{SO_4} \rightarrow \overset{+2}{Fe}\overset{-2}{SO_4} + \overset{0}{Cu}$$

the oxidizer IS reduced
the reducing agent IS oxidized.

[illegible]

Therefore in this case we know that Fe IS oxidized (lost electrons and therefore become more positive) and that Cu IS reduced (gained electrons and became more negative) ~~reducing~~ reducer ~~so in this case, the oxidizing agent~~, or ~~oxidizer~~ is Copper, ~~and notice indeed that it does have the higher oxidation state to begin with. Copper is reduced here so this means that~~ Fe.

Oxidizing agents are reduced.
Reducing agents are oxidized.

So Copper is the oxidizing "agent" or oxidizer (Cu does have the higher oxidation number)
Fe is the reducing "agent" or reducer.
Fe does have the lower oxidation number)

This is a very helpful way to see things. You can memorize but you can also figure it out if you need to.

The oxidizer steals electrons, leaving something which has had electrons stolen from it. (oxidized)

The reducer "leaves" something that has been reduced.
The oxidizer leaves something that has been oxidized.

This is a nice way to think of things logical and internally consistent.

The reducer donates electrons, leaving something which has had electrons gained (ie, reduced)

Page 30

I really like the way of thinking more.
It is logical and internally consistent.

The reducer leaves something that IS reduced.
(or results in something)

The oxidizer leaves something that has been oxidized.
(or results in something)

And the "something" is something different from what you started with, i.e., the oxidizer or the reducer.

You have to look @ the reaction.
Both Fe & Cu are metals with common +2 oxidation states, but they can both act as either reducer or oxidizer.

The oxidation states before and after are what is key.

The oxidizer usually has the higher oxidation state before the reaction, and the lower oxidation state after the reaction (i.e. it is "reduced".)

The oxidizer is reduced
The reducer is oxidized.

The reducer usually has a lower oxidation state before the reaction and a higher oxidation state after (i.e, it is oxidized).

Page 31

This is a very valuable lesson & session.

It should help you to look @ reactions in a different way.

Remember, most reactions are

[illegible] 1. Acid - base] electrochemistry can actually be used for all these types! not just two!
[illegible]metry 2. precipitation
[illegible] [illegible]metry 3 redox

A precipitation reaction would be great to see.
What is something that would form a precipitate,
that you have with you?

Let's predict and form a precipitate.

Strontium, Barium sulfate are insoluble.
Ca, Mg hydroxides are insoluble, also Cu & Fe
oxides are insoluble

Try Mg OH, Completely successful. ~~4~~ 6
~~3~~ ~~5~~

1. First, we will condition the electrodes ~~2~~ times
1mA, 120 secs in distilled water.
Notice that it never entirely stabilizes and that
it also never exactly repeats.

2. Now let's look @ NP -3 to 3V.

3. Now let's go back to potentiometry.

Page 32

4. We now Continue w/ potentiometry.
Our goal is to monitor a precipitation reaction.

5. ~~Lets go to POT w/ 3 drops KOH added after rotating t.~~

5. Lets go to POT w/ H2O with <u>no</u> <u>current</u> now.
This is what is standard of course.

6. The results here are very nice. Close to ~~zoo~~ zero.
But not zero, which is also interesting.
About 0 - 30 mV on average.
We can also see activity on the electrodes
7. Now lets add 2 ~~1~~ drops KOH,
no current
The POT is still Close to zero, ~ -22 mV.

8. Now lets add a little MgSO4. ?!!?
and let's set time for 5 min = <u>300 secs</u>

Lets look @ the reaction a bit in the meantime.

$MgSO_4 + NaOH \rightarrow MgOH +$ ~~$NaSO_4$~~ ? probably soluble

$MgSO_4 \rightarrow Mg^{+2} + SO_4^{-2}$
$NaOH \rightarrow Na^+ + OH^-$

$\overset{+2}{Mg}\overset{-2}{SO_4} + \overset{+1}{Na}\overset{-1}{OH} \rightarrow Mg^{+2} + SO_4^{-2} + Na^+ + OH^-$

$\rightarrow \overset{+2}{Mg}SO_4^{-2} + Na^{+1} + OH^{-1}$

Wrong! Nothing is oxidized or reduced here!

This is a precipitation reaction alright, but it is displacement and not redox.

The stuff might be useful but no idea how to interpret anything yet.
Lets go ahead & stir it now after 800 secs.

Upon stirring, the potential shot up sharply and is now equalizing.

9. Now lets add current 1mA for 600 secs

Lets look @ $CuSO_4$ + $FeSO_4$

$\overset{+2}{Cu}\overset{-2}{SO_4} \rightarrow Cu^{+2} + SO_4^{2-}$ once again, this is not
$FeSO_4 \rightarrow Fe^{+2} + SO_4^{-2}$ oxidation or reduction.

You must have something change oxidation state to involve oxidation or reduction. Precipitation does not necessarily do this.
Notice that there is no visible reaction here.
So I am not sure that you really can do anything here electrochemically.

Precipitation does not necessarily involve electron transfer.

But you have made an error.
It forms $Mg(OH)_2$

Let's go again...

$MgSO_4 \rightarrow Mg^{+2} + SO_4^{-2}$

$NaOH \rightarrow Na^{+1} + OH^{-1}$

$MgSO_4 + NaOH \rightarrow \overset{+2}{Mg}(OH)_2^{-1(2)} + Na_2SO_4^{-2}$

Can't you still monitor this formation?

Notice that it reaches a potential of +1.56V
when I is 1mA
2.81V when I = 10mA
.65V when I = 1uA

I	V
1E-3A	1.56V
10E-3A	2.81V
1E-6A	.65V
1E-9A	.57.60V

There is a relationship here but it is hardly standard.

Now let's go the other way. Hold the current constant and change the concentration.

Page 35

Now a Calibrated $FeSO_4$ solution.

PPM	Distilled H_2O	2.83 V
56	1E-3M $FeSO_4$	1.09V, 1.80V, 1.73
5.6	1E-4M $FeSO_4$	2.29V
.56	1E-5M $FeSO_4$	2.64, 2.66
.056	1E6M $FeSO_4$	3,10V
.0056	1E-7M $FeSO_4$	+ 3.24
.00056	1E-8M $FeSO_4$	Not detectable does not approach a limity value

all of these approach a limity value

$r^2 = .966$ quite good w/5 Concentrations.

$$PPM = 2453386\ Volts^{-16.109}$$

Notice higher concentration decrease the potential.
$Mse = 0.6V$

This is quite phenomenal work.
We are at 5.6 PPB.

The catch is we cannot detect it @ this level yet, only determine the concentration knowing that it already is there. This is problematic.

How can we get the detection level down?

Measuring @ -0.77, Deposition @ a positive voltage did affect the curve but you have also lost -.77V.
I seem to be getting it. I am getting a more accurate result with a longer positive deposition.

Investigation of .001M $FeSO_4$
Deposition is having an effect

I got perfect results eg (-0.76)
with
[1, 10, 1, 60] [10, -1, 0, .005, .008, 0.3]

so deposition and/or conditioning does seem to make a difference

Notice deposition is taking place @ a positive
voltage but we are seeking -0.77V

Cost it @ (0.4, .006)
(.2, .0125) Very modest, no better

Notice the solution has turned color.
It ~~is~~ now oxidized. It is yellow brown,
Maybe this is making it harder ??

Deposition is having an effect
0 Volts is switching it from -.77 to -.44V

Deposition is simply not required
for the time. With very careful work
& Can detect to a few PPM (eg 5)

but not PPB.

[redacted] [redacted]

Many good things learned today.

I can determine concentration to PPB.
I can identify components to PPM.

Potentiometry w/ current is a simple powerful method to concentration determination.
A particular concentration approaches a limiting value over time.

Precipitation does not necessarily involve redox in any way. There is not necessarily any change in the oxidation ~~state~~.

Precipitation reactions are still intriguing but I am not sure what you can do with it w.r.t. electrochemistry yet.

Apr 07 2016 Ionic Foot Bath

Initial Testing: pH & TDS

Mixed [redacted]			Tap H2O + Salt	40 min Control	[redacted] Mixed
9.1	9.2	pH	9.1	9.4	9.5
945 ppm	851 ppm	TDS	1110 ppm	872 ppm	820 ppm

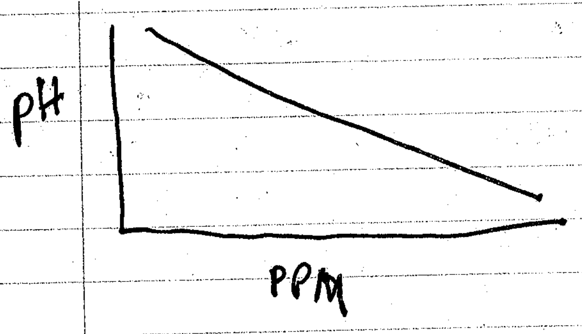
	greatest effect	least effect	2nd greatest effect
n	0	50	100

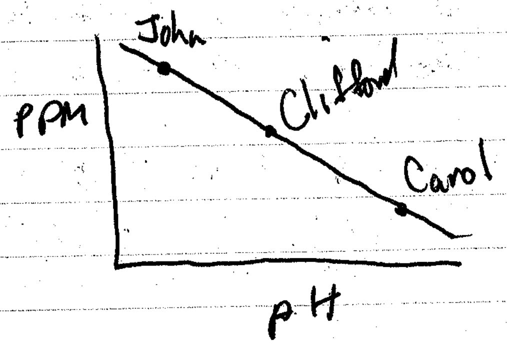
	40 min Control	[redacted]		
pH	9.4	9.1	9.2	9.5
Δ		-0.3 (0)	-0.2 (25)	+0.1 (100)
TDS ppm	872	945 0	851 75	820 100
		+73 (~~100~~)	-21 (~~25~~)	-52 (~~0~~)

PPM ≅ -229pH + 3001.7 ~~pH~~ $r^2 = 0.62$

~~pH ≅ -2.70E-3 + 11.66~~

pH ≅ -2.70E-3 · PPM + 11.66 $r^2 = 0.62$





Page 39

Normalized

Range of pH = 0.4
Range of PPM = 125

Normalize to 100

5min Control   Hot Tap H_2O

9.4   9.0

921 ppm   137 ppm

$\log 10 = 1$
$\log 100 = 2$
$\log 1000 = 3$

$10^{.3} = 2.0$
acidity varies by a factor of 2

$10 = 10^1$
$100 = 10^2$
$1000 = 10^3$

$y = \log_{10}(x)$

$10^0 = 1$

$\bar{x} = 9.3$ $\sigma_s = 0.18$

$x = 872$ $\sigma_s = 53.1$

1. The higher the pH, the lower the PPM

2. The higher the PPM, the lower the pH

1. So, what do these results mean?
2. What happens when you use electrolysis for a salt?

Δ acidity

pH: $10^{.3} = 2.0 = 100\%$ effect
$10^{.2} = 1.6 = 60\%$
$10^{.1} = 1.26 = 26\% = -26\%$

So +100%
+60%
−26%

[redacted]

PPM 945 = +8.4%
851 = −2.4%
820 −6.0%

[redacted]

Page 40

Interesting relationships

$\%\,\text{Change in Acidity} \approx 7.59\,\%\,\text{TDS}_{\text{ppm}}\,\text{Change} + 44.7$

$r^2 =$ ~~[illegible]~~ 0.70 $\quad r = 0.80$

$\%\,\text{Change in Acidity} = \left(10^{|\text{pH} - \text{Control pH}|} - 1\right) \cdot 100$

$\%\,\text{Change in TDS}_{\text{ppm}} = \frac{\text{TDS} - \text{Control}}{100}\,\text{pH}$

The higher the salt content post-op
the higher the acidity of the solution.

April 09 2016

The blood information from net:

3.5-4.0 gms in body
1.0 to 1.5 mg perday

loss is thru urine, sweat, body waste
4.7 to 5.5 liters volume
~1050 gms/liter
Water has a density of 1000 kg/m^3

$$\frac{3.75\ \text{gms}}{\text{ml}\ 5000\ \cancel{\text{liters}}\ \cancel{\text{gms}}} = \frac{x}{100} \qquad x = .075\ \% = .00075$$

$$\frac{.075}{100} = \frac{750\ \text{ppm}}{1E6}$$

The "swap-out" amount is

$$\frac{1.25E\text{-}6\ \text{gms}}{5000\ \text{ml}} = \frac{x}{100} \qquad x = 2.5E\text{-}8\ \% = 2.5E\text{-}10$$

$$\frac{1.25E\text{-}6\ \text{gms}}{5000\ \text{gms(ml)}} = \frac{x}{1E6} \qquad x = 2.5E\text{-}4\ \text{PPM} = \underline{\underline{0.25\ \text{PPB}}}$$

Now lets say we took a ml of blood & diluted it.
What would we expect

$$\frac{3.75\ \text{gms Fe}}{5000\ \text{ml}} = \frac{X}{.1\ \text{ml}} \qquad X = \frac{7.5E\text{-}\overset{5}{\cancel{4}}\ \text{gms}}{.1\ \text{ml}}$$

Page 42

Now we assume we dilute it up to 20 ml

Ratio of dilution is $\frac{\overset{ml}{20 - .1\,ml}}{.1\,ml} = 199$

So our actual concentration is — but this is diluted

$\frac{7.5E\text{-}5\,gms}{20\,ml} = \frac{x}{1E6}$ $x = 3.75$ PPM

This is very reasonable.

$\frac{7.5E\text{-}5\,gms}{20\,ml} = \frac{x}{100\,ml}$ $x = 3.75E\text{-}4\,\%$

$= .000375\,\%$

So not diluted, raw blood estimate is

$3.75(199) = 746$ PPM $\cong$ 750 PPM

This is the raw amount of Fe^{+2} in raw blood

We should be measuring about 4 PPM in 20 ml H_2O with 0.1 ml (not very much) blood.

The work is tying in w/ Lab Notebook Vol 13

Blood is actually high in Fe^{+2} iron, ~ 750 PPM

Our measurements @ this point, even w/ dilution, appear to be much too low.

Another source is saying the concentration of iron in blood is 0.8 to 1.8 ppm (???)

Another says in serum it's

$$\frac{50-175\ \text{ug}}{0.1\ \text{liter}} \sim \frac{\overset{\sim 112}{\cancel{175}}\text{E-6 gms}}{\cancel{0.1\ \text{lit}}\ 100\ \text{ml}} = \frac{X}{1\text{E}6}$$

$X = 1.12$ PPM?

These are in range. very close. 750 PPM must be way off.

Serum

The reference range is indeed $\frac{55-160\ \text{ug}}{\text{dL}}$ men

$\frac{40-155\ \text{ug}}{\text{dL}}$ women

April 09 2016

We have some conflicting information on the amount of iron in blood.

We have sources which say
3.5 - 4.0 gms Fe in body
1.0 to 1.5 ug "swap" per day
Blood loss 4.7 to 5.5 liters
~ 1050 gms / liter
Water = 1000 kg/m^3

Now we also have 2 sources that say the conc. of iron in blood is
0.8 to 1.8 PPM $\bar{x} = 1.3$

Another says $\frac{50-175\ ug}{0.1\ l} \Rightarrow \frac{50E\text{-}6\ gms}{0.1\ l} = \frac{x}{1\ l}$ ~~1E6~~ (blood)
$\bar{x} = \frac{5E\text{-}4\ gms}{1000\ ml} = \frac{0.5}{1E6} \Rightarrow$ 0.5PPM - 1.75PPM $\bar{x} = 1.2$
Another says $\frac{55-160\ ug}{0.1\ l}$

So $\bar{x}$ blood concentration of Fe is ~ 1.2 PPM

So what is in the blood is apparently entirely different from what is in the body vs the blood.

$\frac{3.75\ gms}{70E3\ gms} = \frac{x}{1E6\ gms}$ $x = 54$ PPM

This says that there is a lot more iron in the body than in the blood. Is this reasonable?

Now the 1.2 PPM is just about the limit of my detection range.

If you dilute it further, that would make it harder. So plotting these does not make sense here.

April 10 2016

We know that electrolysis can produce precipitates. We have seen it w/ $BaSO_4$ and we see it w/ the salt bath.
I do not yet know when you know that it will happen but let's take $BaSO_4$ as a example.

$$Ba^{+2} + SO_4^{-2} \rightarrow \overset{+2}{Ba}\overset{-2}{SO_4}$$

Notice that there is no oxidation or reduction taking place here. Only displacement.

But what if you had elemental barium in place

$$Ba_{(s)} + \overset{+2}{X}\overset{-2}{SO_4} \xrightarrow{elect} Ba^{+2} + X^{+2} + SO_4^{-2}$$

so here Ba is being oxidized.
Sulfur is being ionized?

so it oxidizes very easily. $Ba_{(s)} \rightarrow Ba^{2+} + 2e^-$ (+2.90V)

But then means that you would not find it in elemental form.

$$\overset{+2}{Ba}(\overset{2(-1)}{OH})_2 + X\overset{-2}{SO_4} \rightarrow BaSO_4$$

You could certainly test this out.
You have
$Ba(OH_2)$
You have $MgSO_4$
What if you combine under electrolysis?

We also have $AlSO_4$

Under what conditions, though, can electrolysis produce a precipitate?
When the results of a redox reaction produce ions that form an insoluble precipitate.

~~$M_1^{n} X_k^{-n \cdot k}$~~ eg $M^{+2}X_2^{-1}$ eg $Ba^{+2}(OH)^{-1(2)}$

$M_1^{n} X_z^{-k(z)} \xrightarrow{elect} M_1^{n+p} +$

$M_1 = Ba$
$n = 2$
$X = OH$
$k = 1$
$z = 2$

eg Ba is always +2 however.
Mg is always +2.

$$MgSO_4 + Ba(OH)_2 \underset{\text{elect required?}}{\overset{?}{\rightarrow}} BaSO_4 + Mg(OH)_2$$

What if you had electrolysis req?

$$MgSO_4 + Ba(OH)_2 \rightarrow BaSO_4 + Mg^{+2} + 2(OH)^-$$

$BaSO_4$ is definitely insoluble. Then seems like it would work.

[redacted]

Something is being produced @ the anode.
Let's figure out what this means?

Anode (negative), (away)
is a source of excess electrons.
It is therefore an electron donor

Cathode (positive) electron deficient.

Oxidation lose electron
Reduction gain electrons.

Therefore reduction takes place @ the cathode (positive)
& Oxidation takes place @ the anode.

This means that we have oxidation taking place @ the anode. Therefore

$M^{n} \rightarrow M^{n+p}$

but it seems like what is happening is that a precipitate is forming instead.
Al is always +3.

We see @ the cathode that the graphite electrode is being destroyed. This means that it is being reduced.

$M^{n+p} \rightarrow M^{n}$ ~~Graphite~~ Carbon has 2 oxidation states
+2 & +4

This suggests that Carbon @ the graphite Cathode is being reduced from ~~a~~ +4 to a +2 state.

~~+4~~ -2(2)　　+2 -2
CO_2　　　CO

~~A~~ what kind of state is Oxygen in between +4 vs +2?

Graphite is the most stable carbon form.
Its enthalpy of formation is therefore zero.

We notice now that the anode is being coated!

We seriously believe that ~~it~~ is an oxide.
A question now is it BaO or MgO???
It is probably BaO but how do you know?
Is the material that is white falling to the bottom the same thing?

Question: does oxidation always involve a change in electron? We remember reading NO, not always!

This must be electroplating.

Redox by definition involves the transfer of electron.
We do not know that there is any transfer taking place here.

We have a definite coating. What is it made of?

Page 50

Now think about what is happening with the water

$2H_2O \rightarrow 2H_2 + O_2$

cathode ~~anode?~~ ↑ ~~cathode?~~ anode

@ the anode we have

$2H_2O(l) \rightarrow O_2(g) + 4H^+_{(aq)} + 4e^-$

so hydrogen is being oxidized here.

@ the Cathode:

$H^+(aq) + e^- \rightarrow .5\ H_2(g)$

or

$2H^+(aq) + 2e^- \rightarrow H_2(g)$

Net reaction

$2H_2O \rightarrow 2H_2(g) + O_2(g)$

cathode anode

This is really interesting.

The electrolyses of $MgSO_4$ & $BaOH_2$ are entirely different from one another

$MgSO_4$ in H_2O
Very reactive. MgO forms on anode.
Graphite Cathode gets obliterated.

$BaOH_2$
does not dissolve well in H_2O. Very slow to little reaction. Add HCl: A vigorous reaction ensues but no deposits on electrodes. Graphite Cathode seems unaffected even to the point of "healing" itself. $BaOH_2$ seems to dissolve easily under electrolysis. No deposits.

Now I add $AlSO_4$ to $Ba(OH)_2$ + HCl solution.

No obvious reaction w/ the $AlSO_4$ added.
The solution remains cloudy

Pack up for now.

April 12 2016

Assessment:

1. Basic electrolysis is fascinating in its own right.

   Each salt is behaving in a different way.

   1. Magnesium Sulfate $MgSO_4$
   2. $Ba(OH)_2$
   3. $AlSO_4$

1.) $MgSO_4$ readily forms an oxide layer on the anode.

2.) $Ba(OH_2)$ did not interact very noticeably but w/ added HCl a strong reaction occurred. It seems to dissolve much more readily

3.) $AlSO_4$ slowly appears to be making an oxide

A important issue is whether a reaction occurs or not, and if so why. Heat of formation seems to be the focal point.

2. It is fascinating in its own right on each metallic salt & its variations. NaCl does not form the metal form - why?

3. We need to study thermodynamics.

3. Next, we Continue w/ Palmsens.

We have now been introduced to

1. Voltammetry (Basic Intro)
2. Cyclic voltammetry (Detection & Behavior)
3. Normal pulse voltammetry (Detection)
4. Differential pulse (conc)
5. Potentiometry (w/ & w/out current) (conc)
6. Chronopotentiometry (Conc.)

We have looked @:

1. Distilled water
2. Distilled water w/ HCl
3. Camp water
4. Filtered camp water
5. Blood
6. Saliva
7. References & Blanks
8. Calibrated Solution $FeSO_4$
9. Calibrated Solution $AlSO_4$
10. Calibrated Solution of $FeSO_4$ + $AlSO_4$
11. Basic electrolysis
    Redox vs decomposition.
    Electrolysis is not always redox!

12. Ion bath water
    (TDS & pH)
    Seek: reference vs post-op
13. River water @ Cochise Stronghold?

Let's look @

1. NaCl
2. $MgSO_4$
3. $Ba(OH)_2$
3. $AlSO_4$

Let us also look @ thermodynamics of these salts and their oxides.

We start w/ salt!

We understand spontaneity of redox reaction reasonably well. A positive Eo is required ~~for reduction pot~~ considering both oxidation & reduction.

Chang has a very short section on electrochemistry p632.

He ~~does have~~ has a key statement on spontaneity, eg the electrolysis of water is NOT spontaneous p633.
$\Delta G^\circ = 474$ KJ free energy change is high.

The standard electrode potential is directly related to Gibb's free energy ΔG.

Iqbal p141 shows how important electrolysis is. It is a major & important operation.

now back to this direct relationship

Gibbs free energy = f (Standard Electrode Potential)

Notice that NaCl is not producing any solid product. This will be a great example.

The energy relationship is going to be:

$\Delta G^\circ = -nFE^\circ_{cell}$

Let's look @ NaCl in H_2O

(2)(+1) -2 0

$2H_2O_{(aq)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$ hydrogen SRP (reduction) -.83

~~$O_{2(g)} + 2H^+_{(aq)} + 2e^- \rightarrow$~~

2(2)(+1) 2(-2) +1 -2

$O_{2(g)} + 2H_2O + 4e^- \rightarrow 4OH^-$ oxygen (reduction) +.40

Now we know that oxygen is produced @ the anode
(Oxidation takes place @ the anode).
This means the cell potential for oxygen should be -.40
We know that hydrogen is produced @ the cathode.
Reduction takes place @ the anode.
Therefore the cell potential for H_2 should be -.83

Net potential is -1.23. Now because this is so largely negative, we know from Chang that it is far from a spontaneous process.
We should be able to determine the energy required further.
It looks like n = 4
So $\Delta G^\circ = (-4)(96,500)(-1.23) = 474780$ ~~Joto~~ Joules
$= +474.8$ KJ Correct!!

This is great. a high value indicates that it is not spontaneous!

To make the process happen, we would have to supply in excess of $+1.23V$!

This is great to understand. This is really cool. Now we understand why electrolysis does not occur spontaneously. Not only that, we know how much voltage we need to apply to make it happen. That is actually a lot of energy that it requires to split water.

Now lets look @ salt.
When we add NaCl to water, what happens
(with electricity!)

~~we have~~

reduction H_2 ~~$\overset{2(+1)\ -2}{2H_2O_{(aq)}} + 2e^- \rightarrow \overset{0}{H_2}(g) + 2OH^-_{(aq)}$~~ $-.83$

It is simpler than this. We now have a net reaction for hydrolysis of

$H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $-1.23V$

This is all we need to determine ΔG° !!! $= nFE_0$
If we add salt, what happens?
$NaCl \rightarrow Na^+ + Cl^-$
no oxidation or reduction takes place.
What we have is ionization.

So now it seems like the question is what happens with:

$O_2 + 4H^+ + 4e^- + Na^+ + Cl^- \xrightarrow[+1.23V]{}$?

Does $Na^+ + O_2$ form NaO?
apparently not. Why not?

$Na^+ + e^- \rightarrow Na^0 \quad = -2.71V$

So to get oxygen and H_2 to begin with we needed
+1.23 V.
To even reduce Na^+ we need another +2.71 V
So we could not even begin to think about it
unless we have (1.23)+(2.71) = 3.94 Volts
but what would it take to form NaO?
Why is there no such thing
$Na^{+1} + O_2^0 \overset{?}{=} NaO$ no. Why?

There appear to be no Group 1 Oxides.
$Na^{+1} + O_2^0 \rightarrow$ apparently nada
$Na^+ + O_2^-$ (needs to be combined w/ something → apparently nada

So this brings up the question as to what makes an
oxide.
It seems to be: $\overset{+2}{Ca}$, $\overset{+2}{Mg}$, $\overset{+2}{Sr}$, $\overset{+2}{Ba}$, $\overset{+2}{Fe}$, $\overset{+2}{Cu}$, $\overset{+2}{Zn}$,
$\underset{+2}{Pb\,II}$, $\underset{+2}{Hg(1)}$, $\underset{+1}{Ag}$

This seems to be your answer, doesn't it.

So the upshot here,
is whatever you put into water that
is being decomposed, it will need to
react w/ either oxygen ~~or H~~ to form
an oxide.

Group I elements form hydroxides
not oxides.

Na might form sodium hydroxide
So why doesn't this happen.

Remember what we have is

$H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Notice that we are not given OH from
this electrolysis of water.
So this might be one reason. You have to
have OH to begin with.

Now let's try to see why MgO does form.
We know that

$H_2O \rightarrow O_2 + 4H^+ + 4e^-$: $-1.23V$

~~$MgSO_4 + O_2$~~

Before we do this, let's learn more about
why salt does not have a reaction.

Oxidation takes place @ the anode.
Reduction take place at the cathode

Page
59

Ok, we do have NaCl @ a basic level from the PDF called "electrolysis".

We know we have
$H_2O \rightarrow O_2 + 4H^+ + 4e^-$
and
$NaCl \rightarrow Na^+ + Cl^-$

He says we have Na^+, Cl^-, H^+ and OH^- present. We know that water does dissociate to some degree but I am not sure how these would be the dominate components for reaction. But proceeding.

This is not relevent here.
We call ~~the + terminal~~ the cathode but in Europe they ~~flip that convention~~.

NO
So I think we would change his phrase on p5 to read "The positive ions are attracted to the negative ~~anode~~
So let's proceed w/ this. (vs his "cathode")

He says Na^+ & H^+ are both trying to get to the anode. Hydrogen is preferred. Let's see why.

Hydrogen reduction is:
$2H_2O(aq) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ −0.83V
but wait, we know reduction is taking place @ the cathode. This whole terminology thing gets interesting.

~~Change~~ Chang p 135 defines anode as the electrode at which oxidation occurs.
Cathode is defined as the electrode where reduction occurs.

Hydrogen gas is indeed produced @ the cathode and hydrogen is reduced there. So this is all fine in this respect.

Lets discuss his language. He says "The positive ions are attracted to the negative "cathode").

Now he says hydrogen gas is produced so we know that we are clearly w/ the cathode. So this is all Ok

But he calls the cathode "positive" and we call it negative. So this is the difference and it does imply that the article was written in Europe.

The lesson here is be very careful w/ the use of the terms "positive" and negative. It is much better to use the terms anode (oxidation) and cathode (reduction) if there is any point of confusion

So this helps now.
We see that the discussion is definitely focusing on the cathode & hydrogen reduction.
So this is why he is comparing Na^+ & H^+.

Now we know that the reduction potential for H_2 production is -.83V

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \quad (-0.83V)$$

Now we Can go to ~~Cl~~ Na^+.

The reduction of Na^+ is as follows:

$Na^+(aq) + e^- \rightarrow Na(s)$ $= -2.71V$

So this is why he is saying that hydrogen is reduced before Na is! And this is why you do not see and Na^0 produced.! All of the water would have to disappear first.

Now he goes to oxidation.
Oxidation happens @ the anode.
Oxidation is an increase in oxidation state.
The production of oxygen increases the oxidation state, so we have:

$4OH^-(aq) \rightarrow \overset{0}{O_2}(g) + 2H_2O + 4e^-$ is $-0.40V$

But we have $Na^+ + Cl^- + H^+ + OH^-$
so what does it take to oxidize Cl?

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $-1.36V$

He says that when concentrated the chloride ions preferentially lose electrons to hydroxide ions.

But what we also see then is that

$4OH^- \rightarrow H_2O + O_2 + 4e^-$ $-0.40V$

$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow SO_2(g) + 2H_2O$ $= +0.20$

or

$SO_2(g) + 2H_2O \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$ $= -0.20V$

You do not understand this yet.
You do not know whether chlorine gas or oxygen gas is produced when NaCl is subjected to electrolysis

Cl:

reduced $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ +1.36

oxidized $2Cl^-_{(aq)} \rightarrow Cl_2(g) + 2e^-$ −1.36V

$4OH^-(aq) \rightarrow O_{2(g)} + 2H_2O + 4e^-$ −.40V

+3.05 (Li) has a higher oxidation potential than K (2.93)
so lithium oxidizes before K.

Therefore by the same reasoning, oxygen should be produced before Cl_2 gas is.

This seems to make sense.

This says to me that H_2 & O_2 should be produced even if you add some salt to water.

But we have a reference that says that the products of electrolysis of aqueous NaCl are H_2 & Cl_2

So we are wrong.
There is something called the electrochemical series

	Cations	Reduction Potential		Anions	Reduction Potential	Ox Pot
	K^+	-2.93	These are discharged last (takes more energy)	SO_4^{2-}		
*	Na^+	~~-2.87~~ -2.71		NO_3^-		
	Ca^{2+}	-2.87		CO_3^{2-}		
	Mg^{2+}	-2.37		OH^-		
	Al^{3+}	-1.66		Cl^-	+1.36	-1.36
	Zn^{2+}	-.76	O_2 is in here →	Br^-	+1.07	-1.07
	Fe^{2+}	-.44		S^{2-}	~~+.53~~	
*	Sn^{2+}	-.14	see Chang p. 634	I^-	+.53	-.53
*	Pb^{2+}	-.13				
	H^+	0			These are "discharged" first	
	Cu^{2+}	.15	these are "discharged" first			
	Ag^+	+.80				

Notice that these correlate to some degree by the reduction potential but it is not absolute

The electrochemical series is its own important reference.

Notice the lower numbers are "discharged" first

Electrolysis - 1 is the best paper.

So the electrochemical series, i.e., observation trumps theory here. I assume there is a very complete "electrochemical series" table

Page 64

The following is for pure water:

A couple of reference points:

The electrode potential to reduce hydrogen is $-0.83V$

The electrode potential to oxidize oxygen is $-0.40V$

$4OH^-_{(aq)} \rightarrow O^{\circ}_{2(g)} + 2H_2O + 4e$ $= -0.40V$

$2H_2O + 2e^- \rightarrow H^{\circ}_{2(g)} + 2OH^-_{(aq)}$ $= -0.83V$

Net reaction:

$H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Next, we are learning what happens when you place salt NaCl in water and introduce a current.

Positive ions compete, and negative ions compete.

Cations	Anions
H^+ & Na^+	OH^- & Cl^-

These compete.

The electrochemical series helps us.
Ions lower on the list, are "discharged"
before those higher on the list.

Note: Chang. P634

I was exactly right. There is a point of confusion.
And it has been labled as "overvoltage"
Chang describes the situation in some detail.

I was exactly right.
We know the electrolysis of water as:

$H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$ as $-1.23V$

and $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ as $-1.36V$

The lower voltages are "discharged" first.
Therefore it is perfectly logical that O_2 should be
produced before Cl_2.

But! Guess what! Experiment shows that it is NOT!
There is NO explanation why but it is called
OVERVOLTAGE. How is that for a trick?
This would be a great problem to solve.

He says the "overvoltage" for ~~Oxygen~~ Oxygen is
quite high.

So now I understand better what is happening w/ plain salt water and even it ends up being more complicated than you might think.

Now we have observed

$NaCl$
$MgSO_4$
$Ba(OH)_2$
$AlSO_4$

What we try to learn in each case is what is happening @ each electrode.

I think that the case of $MgSO_4$ is the next case of interest. Why and how do we get an oxide and can it be predicted?

Competition of Ions & Electrochemical Series are of interest.

Rain Water - Hyde Park - Apr 13 2016

Sample comes from ice sheet on top of weathered smooth and clean ~~woden~~ wooden tv table. Water is filtered w/ Coffee filter.

	Control Distilled Water (Comm)
TDS = 19 PPM.	0.00 PPM
pH = 7.0	~~6.8~~ ~~6.7~~ 6.8

Next is electrolysis.
No significant reaction in original sample.
1 drop HCl (conc.) added to ~ 20 ml.

April 13 - Voltammetry on SF Rainwater

Distilled water shows activity @

[-3,3]
(.008, .3) -2.20, -.84, -.32

SF Rain No HCl shows activity @
(.008, .3) -2.73, -1.40, -1.25, -.82

The -.82 seems noticeably stronger than w/ distilled water.

Tentative suggestions would be

Na	-2.71
Cl	+1.36
H_2O	1.23
Fe?	+.77

[-3,-2]

(.008, .3)	-2.72	
(.3, .006)	-2.76	←
(.5, .005)	-2.75	
(.2, .0125)	-2.72	
(.1, .025)	-2.70	

Na remains the strongest candidate.
Also consider

F	2.65
Ca	2.87
Mg	2.70
$Mg(OH)_2$	2.69

[-2, -1]	
(.3, .008)	-1.09
(.4, .006)	-1.13
(.5, .005)	-1.18
(.2, .0125)	-1.19
(.1, .025)	-1.20

Now we have missed the peak @ -1.39

Candidates there are
① Ti (1.37)
Cl (1.36)

Pt (1.20)
H_2O (1.23)
Mn (1.18)
V (1.18)
② TiO (1.23)
Zn (1.20)
$Fe(CN)_6$ (-1.16)

[-1, 0]	Str	Wk	Str
(.3, .008)	-.88,	-.67,	-.20
(.4, .006)	-.88,	gone,	-.22
(.5, .005)	-.88,	-.68	-.21
(.2, .0125)	-.88	-.67	-.17
(.1, .025)	-.88	-.67	-.14

③ -.88: TiO -0.89
-.68 U -.66
Hydroquinone .70
H_2O_2, O_2, H^+ .70

~~.20~~
④ -.22 HgBr (.21)
Mo (.20)
Ty TiO (.19)

[0, 1]
(.3, .008) +.61
(.4, .006) +.62
(.5, .006) +.63
(.2, .0125) +.70 } Strong peaks ???
(.1, .025) +.75 }

$\bar{X}$ = .66 Zn −.76
Cr −.74
$\bar{X}$ of Strong Peaks Ti .72
⑤ = .72 Hydroquinone .70

[1, 2]
(.3, .008) Nothing
(.4, .006) +1.34
(.5, .005) +1.36

Ti (1.37)

[2, 3] Ar
(.3, .008) Nothing
(.4, .006) Nothing
(.5, .005) Nothing

We have extremely strong evidence of Titanium. What does this mean?
Extremely high index of refraction, optical dispersion
Excellent reflector of infrared.

[illegible] we make a run w/ Conditioned electrodes. Next we stabilize run @ [-3,3] w/ (.3, .008)
after almost 5 runs it stabilizes.
No acid added; it does not seem necessary

[-3,3]
(.3, .008) -2.48, -2.49, -2.48
(.4, .006) -2.49
(.5, .005) -2.52, -2.54, -2.57, -2.58, -2.59
(.2, .0125) -2.58

Candidates:
F (2.65)
La (2.52)

Current mean = (2.59 + 2.76)/2
= 2.68
Closest match is Fluoride?

* $Mg(OH)_2$ is -2.69 This is Closest match

[-2,-1]
(.3, .008) -1.06, -1.10, -1.18, -1.22, -1.32
-1.36, -1.34, -1.34
also a minor peak @ -1.20, -1.23, -1.23
We have a definite double peak here.
(.4, .006) -1.27 and -1.16 wrong direction
(.2, .0125) -1.27 & -1.15
-1.32 & -1.20
-1.33 & -1.22

So we
* have peak @ -1.34 Ti^{3+} (1.37) TiO (-1.31)
-1.23 Ti_2O_3 (-1.23)

[-1, 0]

(.3, .008) Triple Peak	-.68	-.56	-.24
	-.68	-.56	-.23
(.4, .006)	-.69	-.56	-.25
	-.69	-.57	-.26
(.2, .0125)	Wrong direction		

-.69 Hydroquinone (.70) Or -.66
O_2, H^+, H_2O_2 (.70)

-.57 TiO_2 (-.56)

-.26 V^3 (.26)
Ni (-.25)
GeO (.26) (-.29)
U (.27)

[0, 1]

(.3, .008) (+.24) (.29) (.31) (.32) (.33)
(.34) (.34)
(.4, .006) (.34)
(.2, .0125) (.36) (.36) (.40) (.40)

.40 Cd (-.40)
GeO (-.37)
O_2, H_2O, OH (+.40)

[1, 2]

(.3, .008) Nothing , Nothing
(.4, .006) " "
(.5, .005) " "
(.2, .0125) " "
(.1, .025) " "

[2, 3]

(.3, .008) Nothing
(.4, .006) "
.2, .0125 "

Apr 14 2016

1. [redacted] paper clarification
2. Lidar - Titanium - surveillance
3. Traffic of papers

A Climate Engineering Introduction
to Media and the Uninformed

Titanium reflects infrared
powders / CO_2 & H_2O
lidar surveillance

lidar 3 dimensional mapping of the
elements of the atmospherics &
pollutants
surfaces
infrared

The receiver of a lidar system detects
the light waves scattered back to the receiver
by objects in the path of the photons of the
laser emission of the transmitter.

Light is absorbed @ different wavelengths
@ different altitudes.

single photon detection

Works in darkness & light; penetrate foliage

Uses VIS, UV & IR
SINGLE MOLECULE DETECTION

Titanium dioxide exhibits excellent light scattering and infrared reflectance due to its high refractive index. (~2.5)

Optimum scattering @ 500 - 500 nm = .5 um

TiO_2 hydrophilic loving water. water will form a sheet

Any organic chemical will undergo decomposition to CO_2 & H_2O.

The subject is photocatalysis - Science Watch
Nobel prize territory

Benzene

$C_6H_6 \rightarrow 6CO_2 + 3H_2O$

Apr 15 2016

Ionic foot Bath Study.

Control indicates activity @

-1.84V Co? Br
-1.82 (1.82) (1.85)
-1.63V Al? -1.66
-1.64

-.94, -.96 Mn (.95)

-1.42, -1.41 Co (1.42)

.007, .008

.70 .77, .79, .80 Fe (.77)

+1.04, 1.08, +1.08 Br? (1.087)

+1.54 +1.63 +1.67 Al

Nothing from +2.0 to +3.0

Summary: Co, Al, Mn, Fe, Br?

[redacted]

-1.79 -1.73 -1.70 Match

-1.66 -1.57 -1.54 Match

-1.27 -1.03 -1.00 Match

-1.42?

-.96 Match

-.11 ~~Match~~ ?

.007, .007 Match

.71, .75, .77 Match

1.58, 1.65, +1.69 Match

+1.07, +1.08 Match

Nothing from 2 to 3

April 16 2016

Controls & Blood Analyses.

Tonight we are working further w/ controls & then blood.
First, we see that conditioning the electrodes seems to be really important. You do this w/ potentiometry and introduced current of 1mA for 120secs until it stabilizes.

Next we evaluate a distilled H_2O - acid control. We are seeing that all controls must also be run until they stabilize and they do. The H_2O-H_2SO_4 (now weak w/ 1 syringe drop) took several iterations to stabilize.

The end profile is quite different from the initial profile.

It also has changed from sitting for a while also.
It has to run 5 or 6 times to stabilize

We are settling in @:

-2.80 (this is varying between -2.6 & 3.0
-1.59 Al? Ti? (1.63) Al (1.66)
Ti (1.23, 1.31) -1.28 Cl_2 (1.36) 1.23 is Hydrolysis of Water
+.34 ~~Ti?~~

We notice something however.
The slope follows its usual course @ V=0.

-2.59		
-1.63	Ti (1.63)	Al (1.66)
-1.37	Cl_2 (1.36)	
.003	(H)	

So we could have hydrogen formation, Chlorine formation, hydrolysis of water (all makes sense) and either Ti or Al in distilled water and an unknown from -2.6 to 3.0V.

Now put in second control w/ acid.

We get the same result

-2.70	Unknown
-1.65	likely Al?
-1.41	likely Cl_2
0.00	likely H_2

Now add blood. Picked up -.47 immediately.
Now for more detail.

[3,-2]

-2.58 (same as Control)

[-2,-1]

Cr or Co -1.73 -1.76 -1.78 -1.79 } maximized

Ti or Al -1.54 -1.59 -1.62 -1.63 } @ .5, (.005)

= [-1,0]

TiO -.82, -.85, -.87 Max. @ (.5, .005)

TiO is -.89

He is 0.92

[0,1]

.007 (H?)

0.69, 0.79, 0.82, 0.85, .86, .87,

Very large peak .88, .89, .89, .90

Maximized @ (.3, .008)

Sure looks like TiO is showing up.

[1,2]

+1.42, +1.51, 1.57, 1.60, 1.62, 1.65, 1.66

+1.08, +1.09, 1.10, 1.11, 1.12

+1.67, 1.68, 1.69, 1.70

max @ (.3, .008)

1.12 Could be Mn (1.18) (weak)

1.70 appears to be Al (1.66) (strong)

[2,3] Nothing

[-3,3]

Very interesting here.

When the blood was first put in
you picked up -0.49 to begin with

Now that the iron has oxidized from sitting for
a while, you are picking up ~~-.77~~ -0.76

Two things:

1. You are only picking this up in the range of [-3,3]
and width maximizing.

2. This also indicates a change in ~~state~~ in
the solution

3. The peaks are strong, which indicates high
concentration.

We see that it is changing as we run it from
[-3,3]
It is headed back to -.44
This seems to be more unstable.

$Fe^{2+} + 2e^- \rightarrow Fe$ -0.44
$Fe^{2+} \rightarrow Fe^{3+} + e^-$ +0.77

The work tonight, they're, indicates

1. something on the high end, -2.6 to 3.0

	Meas	Actual
2. Vr or Co	-1.79	
3. Ti or Al	-1.63	Ti (1.63) (Al 1.66)
4. TiO	-.87	(-.89)
5. TiO	.90	(-.89)
6. Mn	1.12	(1.18)
7. Al	1.70	(1.66)

[redacted]

[redacted]

April 16, 2016

There are signs of titanium showing up in rainwater and potentially blood as well.

Your controls are getting better.

There remains the question of stabalization vs maximization. It almost seems like stabalization is more influential. We will continue to test this.

The difference between Al & Ti redox is very slight. We are going to need a second test.

We may have to make several tests to determine error. We need titanium salts

Ebay has Cobalt Chloride
Titanium dioxide
Manganese
Nitric Acid
Mercury Salts
Manganese Sulfate is really inexpensive

usage

Alpha Chemicals on Ebay looks like the place to go. There are many powder items on this site.

April 18 2016

Continuing to refine and calibrate the methods, especially the removal of any background spectrum.

In addition, we are carefully examining the relationship between maximization, stabilization of the signal as coupled w/ conditioned electrodes.

It is suspected that stability outranks maximization.

Lets work with control solutions again.

We are also examining how concentration may be determined w/ NP voltammetry.

The titanium - aluminum question is an intriguing one. Can you separate these?

We are also studying carefully the background spectrum of

1. H_2O distilled
2. H_2O distilled w/ small amount HCl added.
3. I am trying to avoid supporting electrolytes if possible.

We start by looking @ plain H_2O.
& first we look @ stabilization & magnitude.

There is a dynamic stabilization process that is taking place, & it happens w/out any supporting electrolyte.

It seems to keep migrating. We are now up to, after 10 curves

-1.77V	+1.86
+1.90V	+1.90
(10)	(20)

It finally regressed on curve no. 17.

It is very interesting that the two values have essentially stabilized @ the same point ~1.88V

This is not anything common. And yet, something is obviously happening here.

Now, if i waited a while it jumped back all the way from +1.86 to 1.71 !!!

So delay between runs may also be a factor
We notice a cluster @ ~-1.78 and ~+1.75.

Wait again & we get -1.70 again.

Page 86

We are now also picking up an additional minor signal @

−0.56
and −0.17

If we wait a bit between passes we are now getting identical results.

−1.69
−,56
−,18
+1.68

We see, therefore, that waiting between passes brings stabilization.

Now what happens if you stir?
−1.63
−,57
−.20
+1.57

Now wait after stirring	No further stir, but wait.
−1.68	−1.68
−,58	−,57
−,20	−,20
+1,59	+1.60

Next:

-1.67
-.58
-.20
+1.61

Notice that the 2 peaks are almost identical in size.

Are actually -1.67 and +1.61 actually the same then?

$\bar{X}$ = <u>1.64</u>

Next, after waiting.

-1.66
-.56
-.18
+1.63

The values are definitely stabilizing.

$\bar{X}$ (1.66 + 1.63) = 164.5

-1.67
-.56
-.18
+1.64

x (1.67, 1.64) = 165.5 $\cong$ 166

Al is best candidate

~~TC~~ TlCl -.56
CuI -0.18

Long break for the day:

We have learned that conditioning the electrodes (1mA, 120secs in H_2O) dramatically improves their response & sensitivity, with no question.

Now back to a fresh run on H_2O

We really are not getting the same results. Instead we are getting @

-1.51
-.61 these are all quite different.
-.30
+1.26

Now lets try fresh water.

-1.71 -1.69 -1.72 -1.76 -1.79
-.45 -.54
-.12
+1.96 -1.82 +1.79 +1.78

Or is 1.80? -1.82 -1.66 Stir, wait 1 minute -1.84

+1.75 +1.70 +1.70

~~+1.10~~

There is indeed more variance than I would like to see here. Now lets add HCl.

HCl added now.

-1.69 It changed from 0.1-0.2mA
-1.22 to 0-20mA
-1.54

-1.80 -1.76 -1.76 -1.76
-.92 -1.04 -1.55 -1.55
2.64 1.91 -1.09 -1.11
+1.91 +1.72

-1.75 [-2,-1]
-1.56 -1.68 -1.66 Al
-1.16 -1.55 -1.54 $H_2O_2 \rightarrow H_2O$?
+1.50 -1.26 -1.25 H_2O?

These values have come in very stable.

Make a pass on 24hr old H_2O w/ HCl

It can be obviously seen that the electrode require conditioning. Do this first. Very poor initial signal.

Conditioning: 3 Passes 120sec 1.0mA
Very clean stabilization takes place

Now go to NP [-3,3]

-2.12 Now lets match carefully
-1.69 w/ segments.
-.94

[-3, -2]

-2.15 , -2.14

We seem to have a little noise here. We seem to have a parallel displacement.

[-3, -2] -2.14
[-2, -1] -1.94 these appear to be the same (strong) origin but displaced.

~~-1.67~~ -1.67 (narrow peak)
-1.71

The -1.94 did not repeat on the second trial. This is good.

Let's work w/the range of [-3, -2] [-2, -1] together.

[-3, -2] [-2, -1]
-2.15 -1.95 (notice repeat again)
-1.68
-1.96
-1.68

So try:
[-3, -1]
-2.19 , -1.70
-2.19 , -1.69
-2.20 , -1.69
,

-2.20 : Pm, Tm, Dy, Ac?
$Fe^{3+} \rightarrow FeO_4^{2-}$?
-1.69 matches Al fine.

Page 92

Now, this was 24 hr water.
How does this compare to fresh water?

Electrodes are still conditioned and show a sensitive response.

[3,3] w/ 1 drop HCl, fresh H_2O

-2.13, -1.68, -1.52, -.56
-2.27, -1.72, -1.54 -.48
-2.33, -1.70, -1.51 -.42
2 min wait -2.10, -1.73 -1.05 gone +2.81

Notice the variance here.
maybe stir & then 1 min?

-1.92, -1.77, -1.45 +.75
Stir, 1 min -1.89, -1.52 +0.26
Stir, 1 min -1.89 -1.58 +0.08
Stir, 1 min -2.94, -1.89, -1.62 -.24
Stir, 1 min -2.09, -1.90 -1.67 -.38

Ca Th Al Ti
Stir, 1 min -2.72 -1.91 -1.68 -.48
Stir, 1 min -2.68 -1.91 -1.69 -.54 Seem to be stabilizing
Stir, 1 min -2.61 -1.92 -1.72 -.60

Notice the moving target on ~-2.7
Stir, 1 min -2.51 -1.92 -1.74 -.63 Still moving

This part is not good. A moving target.

Remember Iron changed meditation

Distilled Water 1 syring drop HCl

[-3, -0]

Stir, 1'	-2.50	-1.93	-1.76	-.75	
Stir, 1'	-2.45	-1.94	-1.77	-.81	
Stir, 1'	-2.39	-1.94	-1.79	-.86	
	Mg	Th	U	Ti	
Stir, 1'	-2.38	-1.96	-1.82	-.93	Still moving
Stir 2'	-2.38	-1.96	-1.82	-.92 $^{.925}$	stable!
	(-2.37)	(-1.90)	(-1.80)	(-.89)	
	Mg^{2+}	Th^{4+}	U^{3+}	TiO^{2+}	
Apeak	12.92 mA	1.06mA	1.0mA	4.98mA	

These values may well be proportional to concentrations

[0, -3] backwards! Proceed until msmst Δ ≤ ~~0.01~~ 0.02V? & then take avg

Stir, 2'	None	None	None	-1.0
Stir, 2'				-.93
Stir, 2'				-.90 → $\boxed{-0.89}$
Stir 2'				-.88
Stir, 2'				-.86
Stir, 2'				-.84
Stir, 2'				-.82
Stir				-.80

If we adopt criterion that ΔV ≤ 0.02V then

$\overline{X} = (.925 + .89)/2 = -\underline{\underline{0.91}}$ vs theoretical $-\underline{0.89}$

We therefore have a check on TiO_2^{2+}.

You have learned that you can
& should go backwards

[0,3]

Page 94

+0.51
+0.80
+0.86
+0.84
⇒ 0.85

$\bar{X} = (.925 + .89 + .85)/3 = \underline{0.89}$ vs $\underline{0.89}$

Good work. $\sigma_s = \underline{0.04}$

When the solution (H_2O + HCl) sits for several hrs, the value appears to change. The 0.85 point above now measures 0.65

I have no idea why.

Lets go back to fresh water again w/2 drop HCl

[0,3] You started w/this instead of [-3,0]

[0,1] .69
[0,3] 0.29 2.51
[0,3] 0.19 +1.81

1. Order of investigation?
2. Condition of electrodes?

[0,3] 0.15 +1.62
[0,3] 0.13 +1.39
[0,3] 0.11 +1.28
[0,3] 0.11 +1.27 stabilizes

TiO_2^{+2} H_2O (1.23) formation of water.
(0.10) Tl (1.75)

Page 95

Now, [3,0]

+2.0	+1.32	1.10	.60
2.0	+1.30	1.10	.64
Voltage Overload	+1.29	1.11	.68
	+1.27	+1.11	+.71
	Stable	Stable	not stable
	+1.26	1.10	.74
			.76
			.77 Stable

$(127.5 + 128)/2 = 127.75 = \underline{\underline{128}}$

H_2O (+1.23)
Tl .(1.25)

Could we just have the formation of water here?

Is it possible that the centre of the band is our position? $(1.26 + 0.77)/2 = 1.02$

Is it an accident that we have a sharp peak @ 1.10?

$\bar{X} = 1.06$?

Br = 1.065 Is this possible?

You probably need $FeSO_4$ as an example.

[-3,0]	Small		
-2.16	-1.81	-1.18	
-2.14	-1.84	-1.27	
-2.16	-1.86	-1.29	Stable
-2.15	-1.85	-1.28	[-3,0]
-2.37	-1.82	+1.26	[3,0]
		+1.27	[0,3]
$\bar{X} = 2.00$	-1.835		

We also have
0.11
1.10
0.77
0.89

$\bar{X} = 1.27$ What if these are just water?

Distilled Water 2d results

From a Conservative point of view, the analysis could require multiple hits to confirm. This may restrict the results to reversible reactions.

If this is the case, we have

$-1.28\ [-3,0]$
$+1.26\ [3,0]$
$+1.27\ [0,3]$

$\overline{X} = 1.27$ Since $\sigma_s = .04$ @ this stage
we could assume $X \geq 1.23$ & $X \leq 1.31$

The most Conservative approach says that there the formation of H_2O (+1.23)

instead of the presence of Tl @ 1.25.
this would make sense.

We also have a multiple hit however @
0.11 TiO_2^{2+}
& 0.89 TiO_2^{2+}] so this does make TiO_2^{2+} a Candidate.

1.10 remains unidentified
0.77 remains unconfirmed as Fe (.77)
−1.82 " " " Cr (1.80)

Out of curiosity, does your reading change w.r.t. Conditioning of electrodes?

The NP method as now.

1. Condition electrodes
2. Stabilization Δ = ~~#2~~ 0.03
3. Reversal Runs
4. Multiple hits for Confirmation.
5. Water effect & supporting electrolyte effects
6. Small peaks mean

Ok, let's go to rainwater again. No HCl added.
Apr 13 2016 Sample:

Be sure to determine peaks.

[-3,3]

	-1.25	-.45	-.18	+1.44
Stir 1'	-1.40	-.66	-.38	+1.16
stir 1'	-1.51	-.76	-.49	+1.06
stir 2'	-1.58	-.82	-.55	+1.02
" 2'	-1.62	-.86	-.60	+0.94
" 2'	-1.66	-.90	-.64	+0.91
" 2'	-1.69	-.93	-.67	+.88
2'	-1.69	-.95	-.70	+.77

Have
-1.63 Al(-1.66)
-0.91 Hg,TiO2
(.92, .89)

Stable ~~Stable~~
-1.69 -.94
Al ~~Hg~~
(-1.66) (+.92)
(-.89)
~~TiO2~~+

-1.66	[-.98 small	-.75]	+.65
-1.62	-1.01 x=.90	-.79	+0.49
-1.63	-1.03 x=.92	-.82	+0.44
-1.63	-1.05	-.84	+0.40

−1.70 −.93 (mid) +.50

(1.70 + 1.63)/2 = −1.66 Al

(.90 + .92 + .93)/3 = 0.92 Hg (.92) TiO_2 (.89)

.37 still decreasing.

.31] stable?

Stationary 0.29]

Notice we had a cluster near.

Δ = .03 .44, .40, .37 $\overline{X} = .40$ Ti^{+2} (.37)

.25 decreasing.

.30

We seem to be showing stability @

(.31, .29, .30) ⇛ $\overline{X} = .30$ UO (.33)

Tl (.34)

0.31

Definite stability @

(.31, .29, .30, .31) ⇛ $\overline{X} = 0.30$ UO (0.33)

Tl (0.34)

We therefore have prospect of

Actmsd	Actual	Δpeak
−1.66	Al (1.66)	0.93 mA
−.92	Hg (.92) or TiO_2 (.89)	0.06 mA
−.30	UO (0.33) or Tl (0.34)	0.17 mA

Now for [3, -3]
[small peak]

+.70		+ 0.29		−.67	
+1.08		+.61		−.48	
+1.17		+.72		−.33	
+1.20		+.77		−.20	
+1.23		+.82		−.12	~~Stable~~ ⇒ −0.13
+1.28	Stable	+.85		−.19	
+1.28		+.90	Stable	+.004	Stable
+1.33		+ 0.91		−.006	
~~1.31~~		TiO_2		H^+	
1.31		.94		+.008	

We will therefore accept

Δ

+1.28 H_2O (1.23)
+.905 TiO_2 (.89) .05 mA
0.00 H^+ (0.00)

This now places our list as

−1.66 (Al)
± 0.91 (TiO_2) (2 hits)
−.30 (UO (0.33)) or Tl (0.34)
0.00 H^+] water dynamics.
+1.28 H_2O]

Now from [-3,0]

		[small peak]	
Stir, 2'	-1.96	-.51	
	-2.00	-.51	
	-2.03	-.84	-.45
	-2.00	-.92	-.58
	-1.83	-.85 mid	
	-1.72	-.89 mid	
	-1.64	-.95 mid	
	-1.66	-.94 mid	
	stable	mod stable	
	$\bar{X}=-1.65$	$\bar{X}=-0.90$	

We therefore now have:

Actual		Δ
-1.66	-1.66 Al (2 hits)	.9mA
-0.89	-.90 TiO_2^{2+} (3 hits)	.06mA
.33 & .34	-.30 UO or Tl (1 hit)	.03mA

[0,-3]

-0.29	-1.48
-0.20	-1.51
-0.21	-1.51
stable	stable

Actual	We now have		
-1.66	±1.66 Al (~~2~~ 3 hits)		
-.89	±.90 TiO_2^{2+} (3 hits)		
33 & .34	±.29 UO or Tl (2 hits)		
1 hit 1.51	-1.51 ~~unidentified.~~	MnO_4^-	~~Discard~~ Prospect
2 hits 1.33	±1.34	$Cr_2O_7^{2-}$ (2 hits)	0.7mA

Ⓢ = stable

Page 102

Apr 20 2016

Now lets work w/ the Apr 16 Sample.

1. Conditioned the electrodes 6 times @ 120 secs @ 5mA.

2. TDS reading of Apr 16 sample is: 8PPM
pH is 7.2pH

[-3,3]

[Small peak]

Stir, 2'	-2.40	-.63	0.0+2.55	
	-2.56	-.70	0.00	+2.65
	Ⓢ -2.58	-.76	-.18	+2.53
	-2.54	-.82	-.25	+2.41
	-2.58	-.86	-.31	+2.28
	-2.60	-.89	-.36	+2.20
	-2.50	-.92	-.42	+2.13
instability introduced	-2.44	Ⓢ1 -.93	-.50	+1.86
	Ⓢ2 -2.44	-.95	Ⓢ1 -.51	+1.80
notice instability introduced	-2,24	-,96	-.57	+1.61
	-2.13	-.97	-.60	+1.48
$\bar{x}$=2.38	Ⓢ3 -2.13	-.98	-.61	+1.43
	-2.18	-.98	-.61	Ⓢ +1.46
	-2.25	-.97	-.58	+1.57
	-2.14	-.91	-.60	+1.47
		$\bar{x}$=0.78		Could be Cr & Mn interaction

There appears to be some instability in the system. The point of interest appears to be @ the point the slope approaches being linear

Mn?

-.78

Best estimate are -2.38, -.~~89,~~ .42, +1.50

TDS = 12 PPM

Page 101

[0,3]	Δ		Δ
+1.06			
+1.30	24	MW	
+1.43	13	27	9mA
+1.51	8	79.9	.05
+1.56	5	270	.03
+1.61	5	216	~1
+1.65	4	119	~d
+1.66	1		9mA
Stable			

Final List for
Ap-13 2016
Snowfall Sample

Lit	Meas.		
-1.66	±1.66	Al	3 hits
-.89	±.90	TiO_2^{2+}	3 hits
.33 & .34	±0.29	VO_2 or Tl	2 hits
-1.33	±1.34	$Cr_2O_7^{2-}$	2 hits
-1.51	-1.51	MnO_4^-	1 hit

[3,0]	[Small peak]	
+1.30	+.82 mid	
+1.31	+.90	
+1.32	+.93	
stable		
H_2O?		
$Cr_2O_7^{2-}$? (1.33)		
+1.34	+.96	
+1.37	+.98	+0.09
+1.38	.99	+0.11
stable	stable	stable

Tl = Thallium
Very dense

$.1X + 1X + .05X + .03X + 9X = 12PPM$

$X(.1 + 1 + .05 + .03 + 9) = 12$

$X = 1.1$

Al	Ti	V	Cr	
4.8	.08	.16 so	4.2	2.3 Mn

ppm?

$x(27(.9) + 80(.05) + 270(.03) + 216(1) + 119(1)) = 12$

$x = .0197$

$\bar{X} = 1.375$ $\bar{X} = .97$

Question: Can we determine concentration by NP ΔP?

It looks like $\Delta = .03$ is sufficient since there w/in $\sigma_S = 0.04$

But this is a very sloppy set. Now for [3, -3]

	[Small peak]	[Small peak]	
+.97	+.36	-1.07	
+1.29	.65	-.80	
+1.30	+.65	-.80	
Cr (Strong)	[Small Peak]	~~II~~ medium	
+1.33	+.74	-.61	
Ⓢ +1.33	+.80	-.39	-2.39
+1.35	+.85	-.32	Ⓢ -2.36
+1.38	Ⓢ .88	Ⓢ -.29	-2.28

The reverse run has made everything clear. We have

		$\Delta\varphi$
2.37	Mg (-2.38, +2.36) 2 hits	1.3 mA
.89	TiO_2 (0.89)	~~.7 mA~~ .05 mA
1.33	$Cr_2O_7^{2-}$ (+1.33)	.7 mA
.33	VO or Tl (-0.29)	.15 mA
1.51	Mn (~1.50)	.7 mA

No aluminum, but magnesium

$$x(\underset{Mg}{\overset{1.2}{1.3(24)}} + \underset{Ti}{\overset{.16}{.05(80)}} + \underset{Cr}{\overset{5.9}{.7(216)}} + \underset{VO}{\overset{1.6}{.15(270)}} + \underset{Mn}{\overset{3.2}{.7(119)}}) = 12$$

$x = .039$

	Al	Mg	Ti	Cr	V	Mn	
	4.8	1.2	.08	4.2	.16	2.3	~ PPM
			.16	5.9	1.6	3.2	
x	4.8	1.2	.12	5.0	0.9	2.8	
	2	4	6	1	5	3	Rank

Ranked
Cr
Al
Mn
Mg
V
Ti

[-3,0]   Notice we have a small hump @ -.79

@ -2.55	-.63	
-2.74	-.78	
-2.57	-.86	-.33
(S) -2.57	(S) -.90	-.41
-2.29	-.91	-.49
-2.07	-.92	-.56
-2.03	-.94	(S) -.59

instability

Work in progress

$\frac{764E-6\ gms}{1000\ ml} = \frac{764E-6\ gms}{1000\ gms} = \frac{764E-3\ gms}{1E6\ gms}$

.008 ~~PPT~~ PPM = .01 PPM

$\frac{764E-6\ gms}{1000\ gms} = \frac{.8\ PPM}{\cancel{100\ 1E6\ gms}}$ Al

764E-3

$\frac{milligram}{liter}$

Ba .7 PPM

$\frac{36E-6}{1000\ ml} = \frac{36E-3}{1E6\ ml}$ .04 PPM

$\frac{15.43E-3\ gms}{1000} = \frac{15.4}{1E6}$

April 30 2016

Can the electrodes ~~[illegible]~~ be the same material?

We see from a google books reference that the reference & counter (auxiliary) electrodes are normally made using the same material (this is in reference to a 2 electrode system)

We also have from Palmsense screen printed electrodes that the working and counter electrodes are usually the same material.

This provides an argument that the materials can be the same.

Distilled water is its own topic.
It varies tremendously depending upon what part of the country it is purchased in.
SW US: Wal Mart - Come from City Water in Texas.
Did not measure not clean @ all. Distillation only
N. US. Come from Denver Artesian Spring
Distillation, Microfiltration & Ozonation.
TDS = 0.00
This is the Denver water.

	Texas	Denver
TDS	0.00	0.00
pH	6.9	~~7.3~~ 7.2

See next page for voltammetry results

With NP Voltammetry, the results between TX & CO does vary.

TX water does seem to be more active.

There does appear to be a benefit in getting the most pure distilled water possible.

We notice the pH is also varying.

One lesson is that it is much better to avoid using a supporting electrolyte if @ all possible.

It definitely introduces a strong signal into the measurement which will need to be sorted out, compared, or ~~subtracted~~

If the water has any conductivity @ all your instrument seems more than capable of picking it up.

You can study the TX & Co curves carefully to look for any differences.

We notice that the TX water ~~may be~~ is more more acidic.

$$\frac{10\,ug}{12\,ml} = \frac{10E{-}6\,gm}{12\,gms\ H_2O} = \frac{x\ \ .8\,PPM}{1E6\,gms\ H_2O}$$

$$X = 1\,PPM$$

1 single Commercial NaCl grain in ~ 12 ml of H_2O corresponds to ~14 PPM TDS

We estimated that 1 grain weigh 10 ug and then leads to a concentration estimate of 0.8PPM. but ~~is~~ a actually 14 PPM so

$\frac{14}{.8} = 17.5$ and $17.5(10\,ug) = 175\,ug$

$175E{-}6\,gms\,(x) = 1E{-}3\,gms \qquad x = 6.$

May 05 2016

Strontium Spectrometer Test.

We measure	Actual	Δ	Intensity ~~208~~
603 nm	597	= +6	200
583 nm	586	-3	200

Actual values are: 597 = +6
586 = -3
$\bar{x} = +1.5$

This is quite good.
K & Ca do not compete.
These were the only other color that were even close.

Note Barium Chloride & Barium hydroxide do not appear to be soluble

[redacted]

OUTLINE OF PROJECTS

May 07 2016 Wallace ID

We are definitely back in the lab again after an absence of close to 6 months.
So this is a very big deal and it is time for a major regrouping.

[redacted]

2. We have samples of varying types that have come in and you have invited them and welcomed them.

✓ 3. We are switching computers to some degree
Black Acer Windows 8 may stay in the lab since it is already set for electrochemical work.
You need another wireless mouse

[redacted]

✓ 6. Get Palmsens set up on silver ACER

7. Electrochemistry & oscilloscope software is now setup on the silver Acer. This is good.
Electrochemistry can start w/ the Palmsens
I need the vice

Page 110

8. You have several rainfall samples to work through now.

   1. The original Wallace sample
   2. Two samples from Santa Fe
   3. Beulah snow sample
   4. Beulah tap water
   5. Distilled water from Texas
   6. Distilled water from Denver.

9. Spectroscopic work w/ elements
   & Wallace rainfall sample
   & spectral analysis software.

10. HEPA filter analysis

11. Recovery on all infra red work
    the environmental filament project
    proteins
    lipids
    All papers need to be regrouped & resorted

12. Gas Chromatography
    Reacquaintance

13. IR Hair Analysis, Pyrolysis

14. Electrochemistry of CDB

[redacted] sample might be interesting.

16. % Carbon content analysis

17. Gel Electrophoresis - DNA

18. Protein molecular weight

19. Lipid molecular weight

20. Protein electrophoresis

21. Radiation msmt

22. New pH meters? What actually is ORP?

23. Visible light spectrometry vs Emission Spectrometry.

24. Environmental sampling & kits in more detail
    Soil Kit   Chemical Composition of the soil
    Water Kits

25. Pig Dissection

26. Aromatic Oil Study

27. Rife Machine Study - this can go on road

28 COB Environmental Stress Study

29. Original Potentiometer.
Test & Compare.

30. Chemlab installed on CT lab machine.

31. Fuel Cell Analyzer COB vs yeast

32 Acid Base Chemistry - Titration
Electrochemistry.

Distilled water came out w/ an ORP
of a minimum of ~~80~~ 145

No significant difference

Page 13

Purchase pH meter ORP
v
TDS
T°

Lets get the Beulah Snow Water Sample Started
in Concentration

1 qt jars dry w/ a lid are 460.5 gms.
1 qt jar dry w/out a lid is ~~440 gms~~ 441 gms

Jar # 1 = ~~1254~~ gms w/ water & jar 1266 gms (no lid)

Jar # 2 = 1262 gms

Jar # 3 = 1263 gms

Jar # 4 = 1292 gms

Jar # 5 = 1269 gms

Water was stored in distilled water plastic jugs approximately 2 weeks

Jar # 6 = 1304 gms

254/280 H_2O:

$\bar{X}$:		Beaker 1	Beaker 2	~~Beaker 3 Discard?~~	Beaker ~~3~~ 4
7.5	pH	7.5	7.5	~~7.1~~	7.5
130 mV	ORP mV	126	~~110~~ ~~106~~ 124	~~140~~	139
3 PPM	TDS PPM	4	3	~~10~~	001
5 uS	σ uS	7	5	~~29~~	004
23.2°C	IOR	0.00	0.00	~~0.00~~	0.00

Slow Steady drop seems best.

Page 114

May require warming up.

Would you like to try UV analyzer also?

.02 Setting @ ~~.002~~	Distilled Start End	Beak 1	Beak 2	Beak 3	Beak 4
254 nm	-1.5/-21	19 ~~80~~	19	27	20
Again 254 nm	-0.5/-28 0 5	20	7	0.0	-5
$\bar{X}$ = 19.4		20 ~~25.5~~	21 ~~18~~	21 ~~17~~	23 ~~17~~

y	x
0	-.5
5	-28

It seems like we have some significant drift.

~~280 nm~~ Our average is 21.2

What we are seeing is that the original reading is OK. But then it drifts most likely as a function of time.

0.01 254 nm	Dist	#1	#2	#3	#4
t = 0	-2.2	46	42	46	36
t	-13 ($3^m 30^s$)	($1^m 0^s$)	($1^m 30^s$)	($2^m 0^s$)	($2^m 45^s$)
Correction	t=0 +2.2 t=3.5 +15.2	+6	+8	10	12

OK, we see we do have drift but we can correct for it

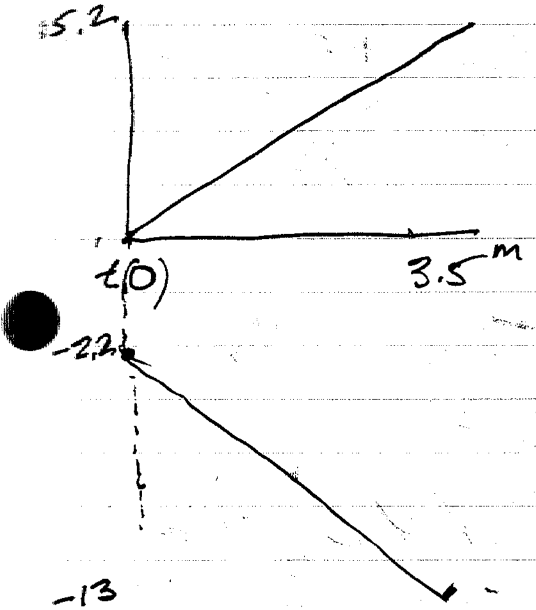
Time Corrected 254nm	0	+52	+50	+56	+48

Now, we have chosen to discard beaker #3.

Method is to flush through and then pump slowly a drop(?) at a time & take stable reading along w/ time record to correct for drift.

Drift factor

		Map to
$t=0$	-2.2	0
$t=3.5^m$	-13	15.2



$y = ax + 2.2$
when $x = 3.5$ $y = 15.2$

when $x=0$, $y = +2.2$
$y = 3.71t + 2.2$ $r^2=1$
when $x = 3.5$, $y = 15.2$

Then:

t	(254)(y)
0	2.2
3.5	15.2

This worked superbly.
Our mean is therefore $(52+50+48)/3 = 50$
Our actual reading is $50(.01) = 5$ because of a scaling but scaling is only a relative factor.

Page 116

We can now proceed to 280 nm.

Setting = 0.01	Dist	#1	#2	~~#3~~	#4
Value	-2.0	38	35	~~40~~	36
t	0	1m	1m 30s	~~2m 15s~~	3m

-4 @ 3m 45s.

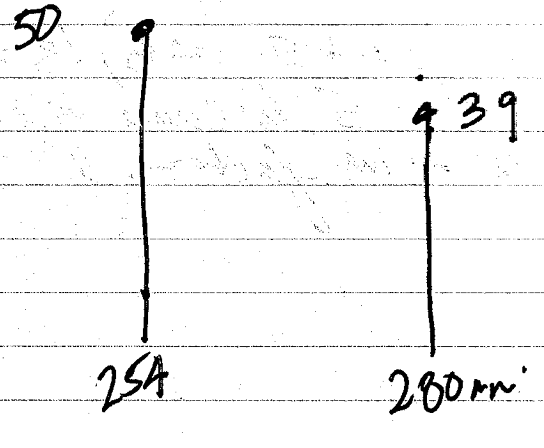
So there is almost no error here.
Correction is therefore

		+2	+2.5	+3	+3.5
Corrected Values are therefore	0	40	37.5	~~43~~	39.5

Disregard beaker #3
Our mean value is therefore

$$(40 + 37.5 + 39.5)/3 = 39$$

Our 254/280 ratio is therefore $\frac{50}{39} = \underline{\underline{1.28}}$



This is called

Specific UV absorbance (SUVA)
and
Estimation of Concentration of Dissolved Organic Matter.

ORP is a measure of a chemical species to acquire electrons and therefore be reduced.

The higher the ORP, the greater the number of oxidizing agents.

Low pH water has more oxidizing agents (+ORP)
High pH water has more reducing agents (−ORP)

ORP of most tap water is +150 - 600 mV and so is an oxidizing agent.

pH & ORP are not tied to one another.

A positive redox potential indicates ability to accept electrons.

ORP of distilled water is ~~tap~~ 145
no significant difference.

May 08 2016

Let's regroup for today.

[redacted]

We learn that Absorbance from the Gilson is determined by:

$$\text{Absorbance} = \text{Sensitivity} \cdot \frac{\text{Digital Reading}}{100}$$

Example: Reading is 50
Sensitivity is 0.01

So

$$\text{Absorbance} = .01\left(\frac{50}{100}\right) = \overset{.005}{5E{-3}}$$

Dissolved ~~Carbon~~ Aromatic Organic Content (DOC) relationship has been developed. (Allgeier & Summers 1995)

$$\frac{UV_{254}}{\text{meter}} \simeq 4.679 \cdot \underset{\substack{(\text{mg/liter})\\ \text{ie PPM}}}{DOC} - 5.243 \qquad R^2 = 0.93$$

or more importantly:

$$\underset{\substack{\text{mg/liter}\\ (\text{ie, PPM})}}{DOC} = \frac{UV_{254}\,m^{-1} + 5.243}{4.679}$$

Note that $UV_{254}\,m^{-1} = UV_{254}\,cm^{-1} \cdot 100$

So an absorbance of

$$\frac{.005}{cm} = \frac{0.5}{meter}$$

In our case of CO rainwater, we therefore have

$$DOC. \cong \frac{(.005)(100) + 5.243}{4.679} \cong 1.2\ PPM$$

Barely, if at all, above the noise floor of the linear regression.

Now, to refine the method, I think that it would be beneficial to develop a standard with phenol.

Let's assume we want 20 PPM.
Solution is stated to be 95% pure.
Therefore we need $\frac{20}{.95} = 21\ PPM$.

$$21\ PPM \Rightarrow \frac{21\ ml}{1E6\ ml} = \frac{x}{500\ ml} \qquad x = .0105\ ml = 10.5\ ul$$

So we develop a 95% phenol control with:

$$\frac{10.5\ ul\ phenol}{500\ ml\ H_2O}$$

We have $\frac{\overset{(15+8\,ul)}{23\ ul}(.95)}{510\ ml} = \frac{X}{1E6}$

$X = 43\ PPM$

Now for the phenol test
Calibrate to distilled water

	Distilled	Phenol #1 (43 PPM) estimated
Abs	-0.1	10
t	+ 0s	1m

0.0 @ 2m ok.

$$Abs = .5\left(\frac{10}{100}\right) = .05$$

$$DOC = \frac{.05(100) + 5.24}{4.68} = \underline{\underline{2.2\ PPM}}$$

Seems like it should be higher than this.

This suggests what we have in the ~~so~~ snowmelt may not be insignificant.

Our absorbance is only 10 times greater than what we measured yesterday.

.05 Absorbance w/ 23ul 95% Phenol in 510 ml

vs

.005 " w/ Rainwater.

This suggests the rainwater may have the equivalent of

$$\frac{2.3\,ul}{510\,ml} = \frac{x}{1E6\,ml} \qquad x = .0045\,ul = \frac{4.5\,ml}{1E6}$$

This suggests we may have ~ 4.5 PPM
DOC in the snowwater.
This is not insignificant esp. since it
is potentially of the aromatic variety.

Sens= 0.1 Let's go to 100 ul in 500 ml H_2O.

	Distilled	Phenol #2
Abs	-.6	197
t	0^m	1^m15^s
Abs	+1.0	
t	2^m30^s	

No significant drift.
We now have two data points.

$$Abs = 0.1\left(\frac{197}{100}\right) = .197 \approx 0.20$$

$$\text{Ratio of absorbances} = \frac{\overset{.197}{\cancel{0.20}}}{.05} = \cancel{4}\ 3.94 \approx \frac{0.20}{.05} = 4.0$$

$$\text{Ratio of Concentrations} = \frac{100\,ul}{23\,ul} = 4.35$$

This shows a respectable linear relationship w/
Absorbance vs Concentration.

Absorbance	Concentration
.05	$\frac{23\,ul}{510\,ml}(.95) = \frac{x}{1E6}$ $x = 43$ PPM
.20	$\frac{100\,ul}{500\,ml}(.95) = \frac{x}{1E6}$ $x = 190$ PPM

Linear ~~Regression~~ results: Page 122

PPM ≃ 980 (Absorbance) −6

If absorbance = .005 , PPM = −1

this leads to a Concentration of essentially zero.

We can rework this w/ concentrated snowfall.

However, if we do assume a linear relationship w/ Absorbance, we have two values to use.

$\frac{.005}{.05}$ (43 PPM) = 4.30 PPM

$\frac{.005}{.20}$ (190 PPM) = 4.75 PPM

And this seems to be the more realistic of the two methods. Linear extrapolation is likely subject to greater error. The two ratios give a consistent result. The mean value is 4.5PPM

This is indeed our best estimate.
We can further check this work by
providing a control @ ~ 5PPM.

$\frac{5ml}{1E6ml} = \frac{X}{500ml}$ X = .0025 ml = 2.5 ul

We can only measure to 10 ul.
Therefore we must use.

4(500ml) = 2000ml. w/ 10ul of phenol.

This can be done.
We now have a 5PPM solution of phenol.
Set sensitivity to 0.01
$\sigma = 0.01$

	Distilled	Phenol #3	Distilled
Abs	-2.0	+112	-7
t	0^m	2^m	3.5^m

Minor drift error. $\Delta = -5$
$(2/3.5)(5) =$

Adjusted value = +115
So
Abs = $.01\left(\frac{115}{100}\right)$ = .012 @ 5PPM(.95) = 4.8PPM

We now have 3 points of reference

Abs	PPM
.012	4.8
~~.005~~	
.05	43
.20	190

Regression:

$PPM = 983.7A - 6.4$ $r^2 = .99990$

@ $A = .005$ $PPM = -1.5 \Rightarrow 0$.

By ratio method
$$\left(\frac{.005}{.012}\right)(4.8) = \boxed{2.00\ PPM}$$
We know that something exists because of calibration

Power Solution:
$$PPM = 1743.4 \cdot Abs^{1.3086}$$ $r^2 = .990$

Our best analysis leads to an estimate of DOC w/in the rain of 2.0 PPM as determined by the ratio method.

We can see that Absorbance is definitely a strong linear relationship.

We also know that the value is not zero from Calibration work w/ distilled water.

The ratio method is therefore preferred for small concentration value.

$$\frac{50}{115}\overset{\text{Calibrated}}{\underset{\text{Solution}}{\left(\begin{matrix}4.8\\ \text{PPM}\end{matrix}\right)}} = 2.2\,\text{PPM} \cong 2.0\,\text{PPM}$$

Now what are the implications of this?

It will need to be investigated w/ respect to all other rainfall / snowfall solution.

Summary w.r.t. Co snow sample: While not a shining bill of clean health, the snow melt does fall within expected range of DOC.

Comparison w/ known measurements.

$1\text{ mole} = \frac{12\text{ gms.}}{1000\text{ ml}} = 1M\text{ solution}$

$1uM = \frac{12E\text{-}6\text{ gms}}{1000\text{ ml}} = \frac{12E\text{-}3\text{ gms}}{1E6} = 12\text{ PPM}$

The values seem way too high.
DOC flux is a [illegible] term.

DOC can be used to estimate the influence of "global warming" as well.

Also tied in w/ the acid rain situation

The pursuit of the identification of organics within a snowfall melt has led to some interesting situations:

1. The sample itself may be w/in reasonable limits

2. However, the result is tied in w/ the investigation of global warming issue

3. As well as acidification issues

I think that the DOC (Dissolved Organic Carbon) issue carries forward w/ the examination of additional samples.

We now have three reference values. Actually we have 4.

Abs	PPM
0	0
.012	4.8
.05	43
.20	190

4 pt linear solution is PPM = 996.59 Abs − 3.86
$r^2 = .999$

@ Abs = .005, PPM = 1.1 PPM ≃ 1.0 PPM

Therefore we have two varying approaches. The mutual solution for the two cases is that

PPM of CO snow sample ≃ 1-2 PPM of Dissolved Organic Carbon.

This is not a high number under any known circumstances.

[redacted]

May 09 2016   0200

I think that our next move is to look@ the DOC of the ID rain sample concentrate from Nov 2015.

On Nov02 we have some notes on concentration. (Vol XI) Aug 2015 — Nov 30

When we were left w/ #10 & #11 jars we apparently had ~200ml left in each jar. Our final concentration was a factor of ~16.01.

We only have a portion of jar #11 left but the concentration factor should be the same. Let's measure DOC.

Absorbance should be ~ 0.05

$\text{Abs} = \sigma \frac{(\text{Digital Readout})}{100} \cong .05$

So let readout $\cong$ 100.

$\sigma = \frac{.05 \cdot 100}{100} = .05$ set σ to 0.05

$\boxed{\sigma = 0.1 \quad \text{Reading} = 134}$

No significant drift

$t=0$, $l = -0.5$

$t=1^m$, $l =$ ~~+1.0~~ +0.5

We have our result.

An important determination to follow here.

Abs of Nov 10 Rainfall sample Concentrate is:

$$Abs = \frac{(0.1)(134)}{100} = 0.134.$$

Now with Concentration factor of 16.81 we have

$$\frac{0.134}{16.81} = .008$$

This leads to a PPM estimate of

$$PPM_{IDAHO} \simeq 996.59(.008) - 3.86 = 4.1 \simeq 4.0 \text{ PPM}.$$

This now leads to an expected range of
<u>2-4 PPM</u> for two separate precipitation
samples across 6 months of time
separated by approx 850 miles (direct line)

Adjust to fractional mass.

Let's think about where we are.

1. CO sample is concentrating nicely.

2. Method for DOC has been developed. The far implication beyond those originally conceived.

Let's look @ the carbon mass ratio:

C_6H_6O Molar Mass is 94.1 gms/mol

The mass % of C is 76.6%

We therefore have another adjustment factor to consider.

There are now two:
1. 95%
2. 76.6%

Our combined adjustment factor is therefore

$$(.95)(.766) = \underline{0.73}$$

We therefore will apply this factor in our DOC measurements.

DOC Finalized Regression

Page 131

Our adjusted DOC regression is therefore now:

Abs	PPM	Therefore
0	0	
.012	3.7	$PPM \cong 742.75 \cdot Abs - 2.98$
.05	33	or
.20	146	$PPM \cong 742.8 \cdot Abs - 3.0$

We also have the direct ratio method available.
Eg, with regression, we have for $Abs = .005$, $PPM = 0.7$
with ratio, we have $(.005/.012)(3.7) = 1.5$

Mean value = 1.1 PPM ≅ 1.0 PPM
This says that our minimum detectable level for DOC is ~ 1.0 PPM.

It is possible that it could be slightly less, but there is no need for it @ this point.

Our ~~CO sample~~ ID now Sample therefore rates as:

$PPM_{Idaho} = 742.8(.008) - 3.0 = 2.9 \cong 3.0\ PPM$

6 month, 850 mile separation.
This leads to a mean value of ~2 PPM.
There is not known to be any due cause for alarm.

It is of interest to revisit the Nov ID sample for

TDS
σ
ORP
pH

The Nov ID Concentrated sample
Comes in @: Conc. factor = 16.81

Colorado Sample		Concentrated	Original Estimates
3PPM	TDS	188 PPM	11.2 PPM
5uS	σ	366uS	21.8uS
+130mV	ORP	+082mV	
7.5	pH $\bar{x}$=8.5 ~~8.8~~ ~~8.2~~ (revised!)		7.5
1PPM	DOC	48.7PPM	3.0PPM
0.00	IOR	0.1	0.00
↑		↑	↑
CO Original		IDAHO Concentrated	IDAHO Original Est.

What we see here is that the ID sample appears to contain 3-4 times the level of dissolved materials that the CO sample does. This tells us that you cannot expect samples to remain constant & that you must consider the range.

Emission Spectrometry may be falling into place now.
Have Tripod. NaCl Trial.

We have a strong line @ w/ Sodium.
-2 587 w SP125 Actual 589 (1000)
-4 585 w/ Star

Let's check w/ software.

I need the Ebook uninstalled

Strontium ~~605~~ @ 590.

actual? 597 582
Sr I Sr II

(597.01) (581.9)

Why does NIST not show this data?
Nothing close.

We also have the edit of 2 documents today
SGG & Europe

Page 134

CO Sample CF = 22.98

May 10 2016 Tuesday.

The Co snow melt sample is now ready!

Weight of a dry jar with lid is: 190gms

Weight of the Co sample is: 408 gms Gross

The net weight of the Co sample is therefore:

$$\begin{array}{r} 408 \\ -\ 190 \\ \hline =\ 218\text{gms.} \end{array}$$

The original sample was.

1 1266 − 441 = 825
2 1262 − 441 = 821
3 1263 − 441 = 822
4 1292 − 441 = 851
5 1269 − 441 = 828
6 1309 − 441 = 863
Σ = 5010

Our remainder is $\frac{218}{5010} = .0435$

or a Concentration ratio of 22.98 times.

The ID sample has a Concentration factor of 16.81 times.

[illegible] Let's start measuring base parameters of the CO sample:

Original		Concentrate	Revised Original (22.98)
3ppm	TDS	~~Concentrate~~ 16	3.3 ~~Original (22.98)~~ ≅ 3 OK
5uS	σ	~~127~~ 126	.5.5uS ≅ 5uS OK
7.5	pH	8.5	
+130mV	ORP	+103 mV	
0.00	IOR	0.0	

We see ~~an~~ a very close match w/ the pH of the Idaho sample. We can see that the dissolved salts seem to be @ ~ 1/3 to 1/4 of the ID sample.

Next: DOC

σ = ~~.02~~ .05

	Abs	CO Concentrate	CO orig.
t=0	-1.0	158	
t=	+4		

Therefore subtract 2 from reading. = 156

$$Abs = .05\left(\frac{156}{100}\right) = .078$$

Now divide by 22.98

$$\frac{.078}{22.98} = \underline{\underline{.0034}}$$

Therefore ↓

$$PPM = 742.8(.0034) - 3.0$$

$$\underline{\underline{PPM}} = -0.41 = \underline{\underline{0}}$$

Therefore

The CO sample has an estimated DOC PPM of 0–1 PPM. or ≤ 1PPM

The 1D sample has an estimated DOC PPM of 3 PPM.

These appear to be low by any standard a measure and the greatest interest is therefore in the

1. pH
2. Dissolved salt Content
3. Trace metals
4. Organics and biologicals
5. Organophosphates and pesticides

The "Carbon footprint" does not appear to be a major issue of concern @ this time.

Now, let's collect the same data on the 2 SF samples!

Page 137

SF ~~04/16~~ 04/13
Snow Sample

Als not use

TDS 13 PPM
σ 27 uS
pH 7.2
ORP +157 mV

Remember DOC make solution more acidic?

We may have contamination in this sample from the table.

DOC:
$\sigma = 0.1$
Msmt = 45

$\text{Abs} = 0.1\frac{(45)}{100} = $ ~~.0045~~ .045

PPM = 742.8(~~.0045~~ .045) − 3.0 = ~~0.34~~ 30 PPM
PPM ≤ ~~2 PPM~~ 30 PPM

What has happened here.

SF Snow 04/16
TDS 6 PPM
σ 12 uS
pH 7.4
ORP +161 mV

DOC: $\sigma = .02$
meas 31
t=0, measured = −1
t=1m mgmt = −8, add 4

$\text{Abs} = .02\frac{(42)}{100} = .0084$

PPM $\tilde{=}$ 3 PPM

Page 138

Repeat on 04/13 SF Snow

This was the sample from the table. We have a high DOC value. This is the most likely sample to be Contaminated from the wooden table.

Repeat from the original jar:

TDS 20 PPM
σ 42US
pH 6.3
ORP +113mV

DOC σ = 0.1
msmt 84 error = 0

$$Abs = \frac{(0.1)84}{100} = .084$$

$$PPM = 742.8(.084) - 3.0 = 59\ PPM$$

So clearly there is something different and apparently some significant organic contamination in sample #3. This was the sample that drained from the wooden table. This sample will be discarded but it is an interesting case of sensitivity to organic contamination.

do not use

The SF sample 04/13 can be investigated for curiosity sake but I may or may not have the time for this.

Summary results: 4 samples.

		TDS	σ	pH	ORP	DOC
(SNOW)	SF 04/16	6PPM	12 uS	7.4	+161 mV	3PPM
(22.98)	CO (SNOW)	3PPM	5 uS	7.5	+130 mV	1 PPM
(6.81)	1D	11 PPM	22 uS	7.5 / 8.2 (conc)	+82 mV (Conc.)	3PPM
	$\bar{X}$	7PPM	13 uS	7.5	+124 mV	2PPM

Assessment:

1. ~ 7PPM of dissolved solids (eg, metallic salts, ionic salts are best candidates)
   2 PPM of Al^{+3} is a significant deviation from "natural water"
2. Alkaline nature, hydroxide present, explore relationship between oxide & hydroxide
3. ~~Very~~ Relatively low dissolved organic carbon.
4. Organics & biologicals known to be present (from 1D analyses)
5. Organophosphates, Neonicotinoids, Pesticides are candidates.

SF 04/13 sample is disregarded due to probable contamination

May 11 2016

Time for Electrochemistry. ID sample
~~Concentration~~ Remember to reverse 9 bracket

2^{m} Stir [-3,3] -2.12, -1.72, -.73
-2.13, -1.74, -.72
Very stable results.

[3,-3] +2.94, +1.39, +0.20
+2.93, +1.85, +1.38, +0.21

[-3,0] -2.22, -1.85, -.93
-2.17, -1.76, -.70
-2.16 -1.77 -.72

[3,0] +1.90, +1.39, +0.13
+2.82, +1.83, +1.40, +.36
+2.94, +1.86, +1.39, +.27

Major peaks appear to be @

+2.92 +1.85 +1.40 +.25
-.78 -1.77, -2.16 -2.7(?)

May 12 2016 Page 141

Entrance of 1D sample

Lets look @ some mean value starts to emerge.

2.94
2.93
2.94

$\bar{x}$ = 2.94

K is 2.93
F_2 is 2.87

1.74 Co is 1.82
1.85 ~~[illegible]~~ V is 1.80
1.85
1.76
1.77
1.83
1.86
1.90

$\bar{x}$ = 1.82

1.39 Ti is 1.37
1.38
1.40
1.39

$\bar{x}$ = 1.39

0.20 TiO is .19
0.21
0.13
0.36
0.27

$\bar{x}$ = 0.23 ?

-.73
-.72
-.70
-.72

$\bar{x}$ = 0.72 ?

2.12
2.13
2.17
2.16

$\bar{x}$ = 2.14 ?

From abreviated table:

|2.94|: ~~rs~~ K is -2.92
Ba is -2.90

|1.82|: V is -1.80
Co is +1.82

|1.39|: Cl is +1.36

|.72| : Cr is -.74

|2.14| AlF6 is -2.07

NP Idaho Sample (.005, .008, .3)

[-3,3] -2.24 -1.84 -1.68 -.48
-2.26 -1.85 -1.69 -.49
-2.26 -1.85 -1.68 -.50

[3,-3] +1.86 +1.40 +1.24 -.009 -2.58
+2.82 +1.85 +1.43 +1.28 ~~+.10~~ -2.30

y' gives very nice pulses: @
+2.81 +1.86 +1.43 +1.28 +.01 -2.27
this looks like a very clean method.
+1.86 is a very strong pulse.

[3,-3]
y' +2.82 +1.84 +1.42 +1.27 +.10 -2.20
y' +2.80 +1.86 +1.42 +1.27 +.08 -2.21
y' +2.82 +1.87 +1.43 +1.27 +.10 -2.21
Very stable results here.

-m [-3,3]
~~-2.28 -1.91 -1.77 -.12 +1.23~~
-2.24 -1.84 -1.69 -.50 +1.67
-2.24 -1.84 -1.68 -.47 +1.77
-2.24 -1.84 -1.69 -.48 +1.77

Sr is -2.90
$Sr(OH)_2$ is -2.88

We have a clear set of values from [-3,3]:

-2.24	+1.84	-1.69	-.50
-2.24	+1.86	-1.68	-.47
-2.24	+1.87	-1.69	-.48
-2.20	-1.84	+1.67	-.48
-2.21	-1.84	-1.68	-.49
-2.21	-1.84	-1.69	-.50
		-1.68	
$\bar{X}$=2.22	$\bar{X}$=±1.85	$\bar{X}$=±1.68	$\bar{X}$=-0.49
Non Reversible Indicated	Reversible Indicated	Reversible Indicated.	Non Reversible Indicated

+1.24	+.10	+2.82	+1.40
+1.28	+.10	+2.81	+1.43
+1.27	+.08	+2.82	+1.43
+1.27		+2.80	+1.42
+1.27		+2.82	+1.42
			+1.43
$\bar{X}$= +1.27	$\bar{X}$= +.09	$\bar{X}$=+2.81	$\bar{X}$= +1.42
Non Reversible Indicated.	Non Reversible Indicated	Non Reversible Indicated	Non Reversible Ind.

Page 144

Therefore, the first candidates are -

n

6 ± 1.85
8 ± 1.68] Reversible Indicated.

Al (-1.66)

Abbreviated Chart
Co(+1.82) U(-1.80)
Be(-1.85) Np(-1.86)
Th(-1.90)

6 -2.22
6 -0.49] Non Reversible Indicated

No good match
Fe(-.44) Cr(-.41)
Ga(-.53) Cu(+.52)

~~3 +.09~~
~~5 +1.24~~
~~5 +1.27~~
~~5 +2.81~~

3 +.09
5 +1.27
6 +1.42
5 +2.81] Non Reversible Indicated

No good match

?
TiO (+.10)
VO (+.05)
Tl (+1.25) O_2 (+1.23)
Ca (-2.87)

More complete Chart:

Sr(-1.79) U(-1.80) H_2PO_2 (-1.82) (Interesting)
Ti (-1.63) (Al (-1.66)

H_2 (-2.23) Fe^{3+} (+2.20)
SO_2 (+0.50) U(-.52) H_3PO_3 (-.50) TiO_2(-.56)

Fe_3O_4 (+.09)
NH_4(+.11) CO_2 (-.11) PH_3(-.11) PH_3(-.06) Fe^{3+}(-.04) TiO(+.19) ?

Tl (+1.25) O_2 (+1.23) Ti (-1.23) TiO (-1.31)
Ti (~~+1.37~~ -1.37) CoO_2 (+1.42)
Fl (+2.87) Ra(-2.80) Ca(-2.87) $SiOH_2$(-2.88)

Counts: * Proximity:

Page 146

Recondition electrodes a narrow range

Str, 2m

[-3,0]

-2.28	-1.91	-1.76	-.63
-2.28	-1.90	-1.75	-.61
-2.28	-1.89	-1.75	-.62

[0,-3].

-2.51	-.20
-2.49	-.19
-2.48	-.18
-2.48	-.19

yes, these are additional readings.

How exactly is this interpreted.
Do we have a repeat of -2.22 vs -2.28
and ±1.85 vs -1.89

and then new species @
-1.75, -.62, -2.48 and -.19?

Notice that $\bar{x}$ (1.85 and 1.68) = 1.76
Is this coincidental?

Let's see if we can shift these curves or not.

(.008,.3) [-3,0] Restarting, guess what, now we get

4'

-2.22	-1.85	-1.67	-.55
-2.22	-1.84	-1.69	-.55
-2.21	-1.84	-1.69	-.58
-2.21	-1.84	-1.70	-.61

Still Moving.

So think about this. We actually reproduced our original results from [-3,3] & [3,-3] but only after repeating the alternating cycle twice. We have essentially exact results however: -0.49 has shifted to -0.55

Notice the close matches of $\sigma = 0.04$

-2.22 Fe^{3+} (2.20) H_2 (-2.23)
-1.845 H_2PO_2 (-1.82) V(-1.80)
-1.68 Al (-1.66)

And then the difference from

-0.49 to -0.56 (TiO_2 (-.56))

~~10~~ We now have
10 (6(-2.22) + 2(-2.22) + 2(-2.21)) /10 = -2.22
11 (8(-1.68) + -1.67 + 2(-1.69) + -1.70) /11 = -1.68
9 (6(-1.85) + 3(-1.84)) / 9 = -1.85

10 (6(-.49) -.55 -.55 -.58 -.61)/10 = -.52

-2.22 Fe^{3+} (2.20) H_2 (-2.23)
-1.85 H_2PO_2 (-1.82) V(-1.80)
-1.68 Al (-1.66)
-.52 SO_2 (.50) V(-.52) H_3PO_3 (-.50) TiO_2 (-.56)

Notice that alternating cycle were required.
Derivative is very clear

Do not run in derivative mode!

Page 148

Recondition electrode a tighter range:

[0,3]

	Strong peak	
+.23	+2.51	+2.80
+.21	+2.49	+2.79
+.22	+2.54	+2.84
+.23	+2.54	+2.85

[3,0]

	Strong peak			
+2.80	+1.82	+1.38	+1.22	+.09
+2.79	+1.84	+1.40	+1.24	+.06
+2.80	+1.84	+1.39	+1.24	+.05

We therefore have a clear set of signals showing up.

	Non	Rev	Non		Rev	
	+2.82	−2.51	−2.24	−2.21	−1.84	−1.91
	+2.81	−2.49	−2.26	−2.21	−1.85	−1.90
	+2.82	−2.48	−2.26		−1.85	−1.89
	+2.80	−2.48	−2.24		+1.86	−1.85
	+2.82	+2.51	−2.24		+1.84	−1.84
	+2.80	+2.49	−2.24		+1.86	−1.84
	+2.79	+2.54	−2.28		+1.87	−1.82
	+2.80	+2.54	−2.28		−1.84	+1.82
2.80	~~+2.94~~		−2.28		−1.84	+1.84
2.79	~~+2.93~~		−2.22		−1.84	+1.84
2.84	+2.82		−2.22			
2.85	~~+2.94~~					
	$\bar{X}$ = ~~[illegible]~~ +2.81	Strong peak $\bar{X}$ = ±2.50	$\bar{X}$ = −2.24		Strong peak $\bar{X}$ = ±1.85	
	σ = ~~.06~~ .02	σ = .02	σ = .03		σ = .02	
	n = ~~[illegible]~~ 13	n = 8	n = 12		n = 20	

Rev		Nm	Nm		
-1.68	-1.69	+1.40	+1.24	-.48	-.63
-1.69	-1.69	+1.43	+1.28	-.49	-.61
-1.68	-1.70	+1.42	+1.28	-.50	-.62
-1.69	+1.67	+1.42	+1.27	-.50	-.55
-1.68		+1.42	+1.27	-.41	-.55
-1.69		+1.38	+1.27	-.48	-.58
-1.76		+1.40		-.61	
-1.75		+1.39			
-1.75					
-1.67					

$\bar{X} = \pm 1.70$
$\sigma = .03$
$n = 14$

$\bar{X} = \overset{+}{1.41}$
$\sigma = .02$
$n = 8$

$\bar{X} = \overset{+}{1.27}$
$\sigma = .01$
$n = 6$

$\bar{X} = .50$
$\sigma = .13$
$n = 13$

.10	+.20
.08	+.21
.10	+.13
-.20	+.27
-.19	
-.18	
-.19	
+.20	
+.13	

$\bar{X} = \pm .17$
$\sigma = .05$
$n = 13$

Avg $\sigma = .037$ $\bar{X} = \pm .04$

$1.6449\,\bar{\sigma} = \pm .06$

Pase 150

			Abbreviated	Full
Nor	+2.81	σ ≈ .02	None ~~[.33] Ca (−2.87)~~ ~~[.25] Sr (−2.89)~~ [.22] Ba (−2.90)	$Sr(OH)_2$ −2.88 [.28] Sr (−2.89) [.25] Ca (−2.87) [.33] F_2 (+2.87) [.33]
Rev Strong	± 2.50	σ ≈ .02	None	Th (−2.48) [1.0] Hf (−2.50) [∞]
Nor	−2.24	σ ≈ .03	None	H_2 (−2.23) [3.0] FeO_4 (+2.20) [.75]
Rev Strong	± 1.85	σ ≈ .02	Be (−1.85) ∞ Uran (−1.80) [.40] Np (−1.86) [2.0] Th (−1.90) [0.4] ~~Co (+1.82) [.67]~~	Co (+1.82) [.67] BrO_3 (+1.85) [∞]
Rev	± 1.70	σ ≈ .03	~~Al (−1.66) [.75]~~ ~~Ti (−1.63) [.43]~~ V (−1.80) [.30]	MnO_2 +1.70 [.30] Al (+1.66) [.75] Ti (−1.63) [.43]
Nor	+1.41	σ ≈ .02	Cl (+1.36) [.40] Cr (+1.33) [.28]	Ti (−1.37) [.50] Co (+1.42) [2.0] HBrO (+1.45) [.50]

$n^2 \cdot w_i$ · abundance
× likelihood.

Abbrev.

[illegible] +1.27 $\sigma = .01$ ~~Tl(+1.25) [.50]~~ TiO(-1.31) [.25]
~~O_2(+1.23) [.25]~~ O_2(+1.23) [.25]
Cr(+1.33) [.17] Mn(1.23) [.28]
Tl(+1.25) [.5]

[illegible] -.50 $\sigma = .13$ TlCl(-.56) [2.17]
[6.5] C(+.52) [13] H_3PO_2(-.51)
[∞] SO_2(+.50) H_3PO_3(-.50) [∞]
[6.5] U(-.52)

Rew ± .17 $\sigma = .05$
Sn(+.15) [2.5]
TiO(0.1)? [0.5]
UO(+.05) [.42]
Sn(-.14) [1.67]

[1.25] Sn(-.13) [2.50] Sn(+.15)
O_2(-.13) [1.25]
SO_4(+.17) [∞]
TiO(+.19) [2.5]
UO(+.16) [5.0]

Now, how to assess the most probable.

Small $\left(\frac{\Delta}{\sigma}\right)$ mean more weight

No of incidence means more wgt.

large $\left(\frac{\Delta}{\sigma}\right)$ mean less weight

or $\frac{\sigma}{\Delta}$ as a direct weight

Page 152

Next we tally the elements:

n							~~Σw_i~~	Σw_i
1	Ca	.33						.33
2	Sr	.25	.28					.53
1	Ba	.22						.22
1	F	.33						.33
2	Th	1.0	0.4					1.40
1	Hf	∞	10				10	∞
1	H	3.0						3.0
1	Fe	.75						.75
1	Be	∞					10	∞
→ ~~2~~	~~U~~	~~.40~~	~~6.5~~					~~6.95~~
1	Np	2.0						2.0
2	Co	.67	2.0					2.67
2	Br	∞	.50				10.5	∞
1	Al	.75						.75
5	Ti	.43	.50	.25	.5	2.5		4.18
→ ~~3~~ 5	V	.30	.42	5.0	.40	6.5		~~5.72~~ 12.62
2	Mn	.30	.25					.55
1	Cl	.40						.40
2	Cr	.28	.17					.45
2	Tl	.50	2.17					2.67
2	O	.25	1.25					1.50
1	C	6.5						6.5
2	S	∞	∞				20	∞
2	P	13	∞				23	∞
4	Sn	2.5	1.67	1.25	2.50			7.92

Page 153

$n^2 w_i$	$n^2 \ln(\Sigma w_i)$	$\ln(n^2 \cdot \Sigma w_i)$		
.33	-1.11	-1.11	8	
2.12	-1.27	.75	45	
.22	-1.51	-1.51	0	
.33	-1.11	-1.11	8	
5.6		1.72	64	Th
~~∞~~ 10		2.30	~~52~~ 76	Hf
3.0		1.10	52	H
.75		-.29	24	
~~∞~~ 10		2.30	76	Be
13.9		2.63	83	U
2.0		.69	44	
5.34		1.67	63	
~~∞~~ 10.5		2.35	77	B
.75		-.29	24	
20.9		3.04	91	Ti
~~51.48~~ 63.1		4.14 ~~3.94~~	113 ~~109~~	U
2.2		.79	46	
.40		-.92	12	
.90		-.10	28	
10.68		2.37	77	Tl
3.0		1.10	52	O
6.5		1.87	67	C
~~∞~~ 20		3.0	90	S
~~∞~~ 23		3.14	93	P
31.68		3.46	100	Sn

min = -1.51 0

max = 3.46 100

$y \stackrel{?}{=} 20.12x + 30.38$

$\stackrel{?}{=} 20x + 30$

4 ml tube

[-3,3]
-2.51 -1.45 -1.33 -1.30 -1.02 +1.42 +2.71

Condition (recall we changed electrode)
Make sure solution is the same depth.

It looks like it can work

~~-2.06 -.91 -.79 -.49 +1.75~~
-2.77 -1.08 -.90 -.48 +2.27
-2.56 -1.14 -.98 -.61 +2.04
-2.50 -1.20 -1.06 -.73 +1.82
-2.53 -1.23 -1.09 -.74 +1.93
-2.50 -1.28 -1.14 -.82 +1.78
-2.51 -1.33 -1.20 -.87 +1.70
-2.52 -1.36 -1.23 -.92 +1.65

It seems to be having a harder time stabilizing than in a larger volume.
It seems to be there now but it took a long time.

Back to 15 ml:
-1.44 -1.24 -.76 +2.62
-1.49 -1.28 -.79 +2.61
-1.52 -1.32 -.81 +2.59

[3,-3]
-2.59 -.09 +.26 +1.17 +2.86
-2.41 +.39 +.66 +.77 +1.77
-2.81 +.52 +.83 +.97 +2.10
-2.94 +.57 +.90 1.04 +2.23
-2.75 +.63 +.95 +1.08 +2.27
-2.74 ~~+1.10~~ .66 +.97 ~~+.66~~ 1.10 2.27

Notice how the values are reversing & stabilizing.

Now back

[-3,3]

-.64 -.39 -.31 +.27

-.81 -.56 -.47 +.14

-.94 -.70 -.62 -.40

It may be that conditioned electrodes in a small tube give the best & immediate result.

Condition @ ~~+4 & -4~~ 3.5 3.5 for 120 secs before run.

You might need to condition only once on each end.

+3.5V for 120 secs

[-3,3] Conditioning, no equilibration

-1.42 -.26 +.14 +2.34

+3.5 for 60 secs.

-1.52 -.29 -.16 +.14 +2.42

+3.5 for 60 secs.

x=.155

-1.53 -.28 -.15 +.17 +2.50

+3.5 for 60 secs.

-1.55 -.28 -.15 +.18 +2.53

no extended equilibration now required

Notice how quickly this converge. All values ≤ 0.03

-3.5V for 60 secs

[3, -3]

-1.48 +.25 +.49 +1.12 +2.96

Conditioning No early equilibration

-3.5 for 60 secs.

(strong) -1.64 -.08 +.32 +.96 +2.86

-3.5 for 60secs

-1.72 -.12 -.003 +.24 +.89 +2.78

-3.5 for 60secs

-1.52 +.21 .45 1.11

-1.47 .29 .53 1.19

-1.43 .32 .57 1.23

Lost this pt after equilibration

equilibrating caused this reversal.

Page 156

Equilibration time appear to be important in getting stable results. (20sec Changed things)

We have a clean set that seem to be evolving

		Abbr.
✓	+/- 1.42	None
✓		
	+/- 0.29	Co (.20) Vo (.33)
✓	+/- 0.155 , ± 0.19 $\tilde{\bar{X}} \approx .17$	Unknown?
	2.53 or 2.65?	Fl (2.65)
	.57	U (.61)
	1.23	O_2
	2.03	AlF (-2.01)

Now repeat +3.5 60secs Condition 20secs.
[-3,3] equilibration

	-2.12	-.44	-.25	+.12	+2.62
	-2.04	-.39	-.24	+.15	+2.62
$\Delta \leq .03$	-2.03	-.37	-.20	+.18	+2.64

Fluoride? Need straight electrolyte also.
Uranium?
Aluminum?

May 13 2016 Friday.

11.24
1D Concentration Factor.

I think that it is now time to dilute the 1D water sample. It is currently under a dilution factor of 16.81 (presumed).

Weight of small jar w/out lid is: 176 gms
w/ lid is 190 gms.

Weight of current remaining 1D sample w/out lid is: 283 gms.
We therefore now have (283-176) = 107 gms = 107 ml of 1D sample remaining @ 16.81 Concentration.
Lets add about 50 ml to the solution. (distilled Denver)
This will bring the current weight to ~ 283+50 = 333 gms.
Actual wt is 336 gms.
We therefore added 336-283 gms = 53 ml.

We therefore now have 107 ml + 53 ml = 160 ml.
The concentration factor is now.

$$\frac{107}{160}(16.81) = .6687(16.81) = \underline{\underline{11.24}}$$

This is our new concentration factor.

We have improved things dramatically.
I have reduced the sample size to 4 ml.
Very good.

Electrolysis of 1D sample is in full swing.
This is a very good thing.

Page 158

Ok back to NP. We have seen that we can incorporate conditioning into the NP process. We also see the benefits of reversing the reaction.

The first strategy of conditioning is a voltage above the end pt, eg +3.5V for 60 secs when the range is [-3,3].
Vice versa.
We may try to reverse this.

We also see that a period of equilibration affects the results. This is going to be explored in some detail. The 4 ml approach does seem to be working very well.

3.5V @ 60sec, Eq = 20secs.
[-3.2, 3.2]

We can see that electrodes are not conditioned. The results are far inferior.

-2.05   -.38   -.20   +.15   +2.67   +2.77

Notice that we get identical results to yesterday. This is very good.

y' -2.05   -.37   -.19   +.18   +2.70 $\Delta \le .03$
y' -2.04   -.37   -.18   +.18   +2.72
STRONG   STRONG

We essentially have the same results as yesterday. GOOD.
Now reverse.

$\bar{X}$ -2.05   -.37   -.19   +.18   +2.70

-3.5V @ 60sec Eq = 20sec
~~[3, -3]~~ [3.2, -3.2]

+1.40	+.76	+.52	-1.22	
+1.42	+.77	+.53	-1.24	Δ ≤ .03
+1.44	+.78	+.54	-1.22	
$\bar{x}$ = +1.42	+.77	+.53	-1.23	

This is fascinating that we are getting very stable results immediately. Why - what are the factors?

1. Sitting overnight in the electrolyte tube?
2. 3.2V range instead of 3V?
3. 3.5 Conditioning vs 3.2 V range?

It is incredible, these seem like very reliable numbers.

		Abb		Full
~~+2.70~~	+2.70	F(+2.65)	Na(-2.71)	
~~-2.05~~	-2.05	AlF_6(-2.07)		
~~+1.44~~	+1.42	None		
~~-1.22~~	-1.23	O_2 H_2O(+1.23)		
~~+.77~~	+.77	$Fe^{3+} \rightarrow Fe^{2+}$(+.77)		
	+.53	I_2(+.54)	Ga(-.53)	
	-.37	Fe(CN_6) (+.36)		
	±.185	CuI(.185)		

0 Component Prospective

Pase 160

Now lets tighten the range.
Set Condition = +0.5V 60sec
[-3.2, 0]

-.60			
-2.51	-.72	-.11	
-2.50	-.79	-.59	-.21
STRONG			
-2.53	-.84	-.64	-.27

Notice how this is drifting again.

-2.58	-.94	-.75	-.38

It looks to me like you want to avoid overloads during equilibration.

-2.61	-1.00	-.83	-.47

Now @ V=+0.1V, ~~20sec~~, 60sec, Eq 20sec

-2.65	-1.06	-.89	-.54

The value has stopped the overload.

	-2.62	-1.10	-.94	-.60
	-2.66	-1.14	-.98	-.64
time break	-2.64	-1.16	-1.01	-.68
	-2.71	-1.25	-1.07 weak	-.75
Δ ≤ .03	-2.71	-1.25	-1.09	-.76
	~~reversible~~ Stable results positive slope peak (indicates reduction?)	positive peak	Bromine (1.06?) an addition negative peak, very weak	reversible you are oxidizing Fe2+ here. (negative Slope peak) negative peak

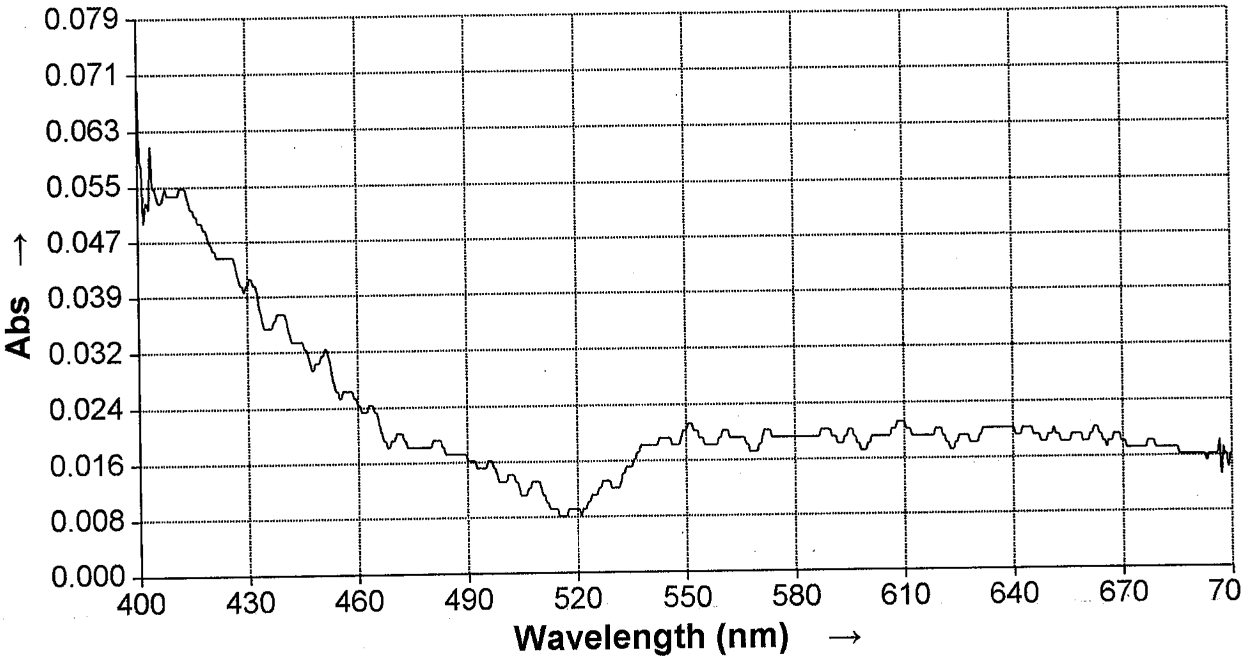
Reduction is a positive value.

~~reduction?~~ oxidation?	~~reduction?~~ Oxidation?	~~oxidation~~ reduction?	~~oxidation?~~ reduction?

SPECTRONIC 200

Scan report

Spectrum of :	ID Rain	Analysis date :	13 - May - 2016
Analyzed by :	CI	Analysis time :	2:46:41 PM
Channel # :	1	Print date :	13 - May - 2016
		Print time :	2:48:31 PM

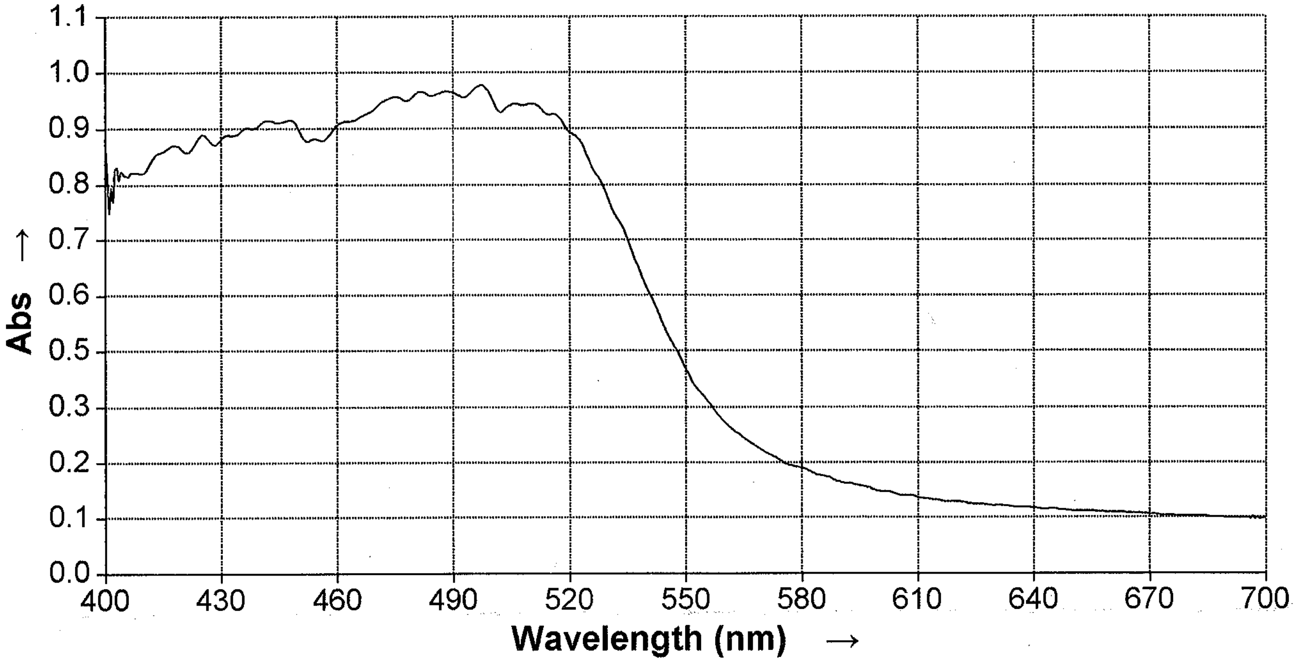


Page 161 B

SPECTRONIC 200

Scan report

Spectrum of :	Fe +2 Reagent	Analysis date :	13 - May - 2016
Analyzed by :	CI	Analysis time :	2:46:01 PM
Channel # :	0	Print date :	13 - May - 2016
		Print time :	2:48:52 PM



Now run V= -3.3V for 60sec, t=20 Eq.
then [0, -3.2]

	-2.98	-1.02	-.75	-.04
	Negative P Peak Reduction?	Negative Peak Reduction?	Positive Peak Oxidation?	Positive Peak Oxidation?
~~Δ~~ ≤ .04	-3.02	-1.05	-.78	-.08
Drift	-3.03	-1.09	-.82	-.20
	-3.08	-1.11	-.84	-.10
Δ ≤ .03	-3.09	-1.11	-.84	-.13
	Strong			Strong

Values accepted are:

-3.02	-1.05	-.78	-.08
addition Li (-3.04)?	match	match	

Our list now includes:

Li, Al, Br, Fe?

- strong -3.02
- Strong ±2.705
- Strong -2.05
- +1.42
- -1.24
- ~~-.7~~ -1.07
- +/-.77
- +.53] notice this midpoint = 0.45 Fe?
- -.37]
- ±.18

Page 163

Next run right segment. V= +3.3 60sec Eq = 20sec
then [0, 3.2]

You can run prelimenary prob until it stabilizes.

+.41 +.65 +2.41
Δ≤.03 +.42 +.66 +2.42
+.42 +.66 +2.40
2.37 is AlF6?
+Slope -Slope -~~2.40~~ slope

High voltage during
conditioning might
induce drift

V= +3.1 @60S Eq = 30sec
[0, 3.0]
+.33 +.60 +2.44
+.32 +.60 +2.53

Notice how this
is drifting
again.

You are seeking to
learn to avoid drift.

V= -0.1 @ 60S Eq = 30S
[0, 3.0]
.008 +.43 +2.71

This picked Fe & F up.
You are therefore beneath
the starting point, not
above the end point.

You lost it.
I got it largely back by
moving V to 1.0V.
+.12 +.42 +2.63
We used 3.2V@20sec -0.2@20 dep Eq = 10
+.17 +.48 +2.75
+.22 +.54 +2.83
Δ≤.03 +.24 +.56 +2.82 Stability achieved.
+.24 +.56 +2.82 High Stability.
+.23 +.58 +2.91 Lost it.
.23 .60 +2.89

Page 164

We have high stability achieved with:

Cond +3.2V @ 20sec. Dep -0.2 @ 20sec. Eq 10sec
[0, 3.0]

But we lost it again?
Then regained it?

Reverse to
-0.2 @ 20, +3.2 @ 20s Eq 10
[3.0, 0]

We had a problem w/ Palmsens.
Reran the test program & it worked fine.
I reset the electrodes & made a fresh sample.

strong
+1.85 +1.21 +1.00 a very clean signal
$\Delta \leq 0.3$ +1.86 +1.21 +.98 Perfectly clean signal

We tested the 1.85 on May 11. Very sharp signal.
+1.80 +1.21 +.97

Now +3.2 @ 20, -0.2 @ 20, 10
[0, 3.0]

strong
+.27 +.40 +.69 +2.83
+.25 +.39 +.68 +2.88
$\Delta < .03$ +.24 +.39 +.69 +2.91

Perfectly reproducible stable results??

You cannot run it in derivative mode.

go to +0.2 @ 20, -32 @ 20 Eq 10
[-30, 0]

~~+.21~~ You are having a major coincidence w/ the methods of May 11. The result seems to be substantially different than the result of today. Could both be true.

Revert now to the methods of May 11. Note
[-3,3] +3.0 @ 20s, Eq 10

[illegible].03 -2.34 -.32 +.42 Steady

[-3,3] 0.0 @ 20s Eq 10 Notice the symmetry

-.51 -.27 -.20 +.34
-.59 -.34 -.27 +.28
-.73 -.48 -.41 +.13
-.78 +2.88

Break for dinner. Electrodes require reconditioning.
It seems like electrode conditioning may still be valuable

-.11 +.46
-.37 +.41 Seems to be going
-.53 +.26 every way.
-.62 +.18
-.72 -.47 -.39 +.10
-.75 -.53 -.46 +.01
-.81 -.59 -.51 -.03

I believe this is the iron couple

Maybe Ga

Page 166

Sequentially Step thru Cond'l Firing Voltage & then Reverse

Cnd @ -3.0sec Eq @ 10sec
[-3,3]

-2.56 -1.71 -1.39
-2.66 -1.77 -1.42 +.79
Δ≤ 0.3 -2.69 -1.78 -1.42 +.80

C@ -2.0
[-3,3]
-1.79 -1.43 +.88
-1.74(+) -1.39(-) +1.00(+Strong)
-1.76(+) -1.38 +1.16
-1.72 -1.35 +1.13 +2.94
-1.74 -1.37 +1.11

C@ -1.0 [-3,3]

Notice the drifting taking place

You are picky in the high end

-1.74 -1.36 +1.21 +2.90
-1.74 -1.63 -1.32 +1.35 +2.91
-1.70 -1.58 -1.24 +1.56 +2.93
-1.76 -1.63 -1.30 +1.45 +3.06
-1.76 -1.62 -1.26 +1.48 +3.05
+1.52 +3.06

When it drifts it is time to leave it.

C@ 0.0 [-3,3]
+1.66 2.94
2.95
T1 (~~[illegible]~~ .37) 2.95

Data is moving to the right

$\frac{n}{\sigma}$

Page 167

It looks like the conditioning value is crucial to uncovering redox pts. Pick up each pt as it stabilizes.

?	(+)	(−)				
−2.66	−1.77	−1.39	−1.63	~~+3.06~~	+2.94	+2.95
−2.69	−1.78	−1.42	~~−1.58~~	~~+3.05~~	+2.90	+2.94
	−1.79	−1.42	−1.63	~~+3.06~~	+2.91	+2.90
	−1.74	−1.43	−1.62	~~+2.94~~	+2.93	
	−1.76	−1.39	−1.64	~~+2.95~~	+2.94	
	−1.72	−1.38		~~+2.95~~	+2.95	
	−1.74	−1.35		~~+3.07~~		
		−1.37				
		−1.37				
		−1.40	−1.63			
$\bar{x}$ −2.68	−1.76	−1.39	~~−1.62~~	~~+3.00~~	+2.93	
σ .02	.02	.02 ~~.03~~	.01 ~~.02~~	~~.06~~	.02	
2	7	10 ~~8~~	4	~~6~~	9	
w ~~7.1~~ 10	~~13.2~~ 35	~~9.4~~ ~~24~~ 50	~~20~~ 40		45	

This is valid

Yes, OK we have it.

+3.06	−2.27
+3.05	−2.28
+3.06	−2.30
+3.07	−2.18
+3.08	−2.13
+3.04	−2.15
	−2.22
	−2.22
x 3.06	−2.22
σ .01	.06
n 6	8
w 60	13

So our ranks are

	l	σ	wt		
Li	+3.06	.01	60		1
Sr, U	−1.76	.02	35	H_2O_2	3
Ti	−1.39	~~.03~~ .02	~~27~~ 50	(Full)	4
Al, Ti	−1.62	.02	~~20~~ 40		5
K	+2.93	.02	45	role	2
Mg?	−2.22	.06	13		7
* F	−2.68	.02	10		8
* Fe	−.46	.02	15		6
−.48	.24	.03	7		9

−.46	.22
−.43	.26
x: −.46	$\bar{x}$ = .24
σ .02	σ = .03
n 3	n = 2
wt 15	wt = 7

OK, we seem to have our set

Page 168

-1, 0, +1

C@ +1.0: seem to be subject to a lot more error.

[-3,3]

+3.39

Does not seem like a good set.

Suspect we should use -3, -2, +2, +3

C@ +2.0

[-3,3]

-2.18	-.62	~~+2.90~~	~~+3.08~~
-2.27		2.94	~~+3.04~~
-2.28		2.90	
-2.30			

C@ +3.0

[-3,3]

-2.13	-.48	+.22	3.08
-2.15	-.46	+.26	3.04
-2.22	-.43		
-2.22			

Page 169

add these two to previous page

Now for reverse

C @ +3.0 @ 30s   Eq 10sec

[+3.2, -3.2]

	-.85	+.93	+1.15	+1.77
	-.93	+.94	+1.21	+1.77
-3.02	-.64	+1.00	+1.22	+1.92
				+1.86
-3.08	-.72	+1.00	+1.25	~~+1.89~~ +1.90
B<.03 -3.07	-.68	+1.03	+1.25	+1.89

add   add

C $\overset{+}{=}$ 2.0 @ 30S

[+3.2, -3.2]

-3.03	-.61	+1.03	+1.24	+1.89	Thorium is
-3.06	-.63	+1.04	+1.28	+1.90	1.90
+3.13	-.76	+1.03	+1.27	+1.92	
3.13	-.82	1.00	+1.25	+1.93	

Skir +1, 0, -1

?

x = 1.90

σ = .02

n = 6

wt = 30

C = -2.0 @ 30S   strong

[+3.2, -3.2	-1.37	add	+.81	+1.13
	-1.40			+1.15
Dufty	-1.48		+.83	

C = -3.0 @ 30S   Strong

-1.64

but could be

x = 1.26   Ti, O (-1.23) O_2, H_2O (+1.23)

or, // σ = .02

n = 6

wt = 30

These two get added

May 14 2016 Co Brown Sample (Filtered)

Now let's move on to the Co sample.
B4 I recall that you have an unidentified
redox peak @ 1.90 σ=.02 n=6
From earlier work, the peak was @ 1.85.
Thorium (Th) is 1.90? Then one remains
unknown.

Start @ C = −3.0V @ 30secs. Eq = 10
[−3.2, +3.2]

Then took 15 curves & then, it has finally
stabilized @:

	−1.79	−1.62	−1.56	−1.09	
Strong	−1.83	−1.63	−1.57	−1.02	
Δ≤.03	−1.86	−1.65	−1.59	−1.04	n=18 Curves
	−1.84	−1.64	−1.58	−1.04	Very stable now
$\bar{x}$	−1.84	−1.64	−1.58	−1.03	
σ	.02	.01	.01	.02	
n	3	3	3	3	
	U, Th?	Al (−1.66)	Ti (−1.63)	Br (+1.065)	

Notice we had the −1.8 very strongly from May 12
n=6 and here we have it again.

Noticed we have a −1.76 U is −1.80
a −1.84 midpoint.
and a −1.90 Th is −1.90

[redacted]

-3, -2, $\overset{?}{0}$, 2, 3

Page 171

Now C = -2.0V @ 30secs Eq = 10
[-3.2, 3.2]

-1.84 -1.64 -1.57 -1.04 Stable after 5 Curves.

Identical results to previous run but it took 5 curve to stabilize. We therefore have

-1.83	-1.63	-1.57	-1.02
-1.86	-1.65	-1.59	-1.04
-1.84	-1.64	-1.58	-1.04
-1.84	-1.64	-1.57	-1.04

$\bar{x}$
σ
n

U = -1.80 Al(-1.66) Ti(-1.63) Br(1.065)
Th = -1.90

Now C = +2.0 @ 30secs Eq = 10
-.84 -.49 -.39 +.48
Strongly suggestive of iron.

-.81	-.47	-.35	+.52
-.81	-.45	-.33	+.56

Iron

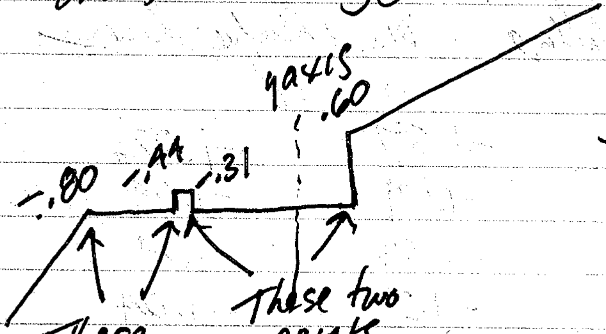
-.80 -.44 -.31 +.60 let this go.
Stable Unstable

$\bar{x}$ = -.81 -.46 This is an iron
σ = .01 .02 Couple.
n = 3 3

± 0.04 is what you are watching for.

Notice that increasing the Conditioning voltage shifts the graph to the right
And vice versa.

Notice the pattern of stability on one side and instability on the other side



These two points reach stability as plots shifting to the right (Conditioned voltage also shifted to right

These two points continue to be unstable and continue to shift to the right.

This is a pattern to watch for esp in conjunction w/ shifting Conditioning voltage.

One lesson is that the Conditioning voltage affects what is detected.

Incidentally the CO scan also shows positive for Fe #2. Very weak but it is detectable.

In other words, keep an eye for partial stability, esp w/ a small flat peak in between.

To be fair, test CO for F also. We see no sign.

Now C= + 3.0V for 30 secs , Eq = 10

(valid -2.93)   -.64   +.51   stable n=2
Strong   v. weak   v. weak

But now after this stability, it look like it is shifting to the L1 point.

A new point of stability has been reached

-3.14   -.60   +.65
v. weak   v. weak

Then is a very interesting case. The plot converged at a stable point as it shifted to the right. Then upon reaching the stable point (ie -2.93)

-3.16   -.60   .72

it then started destabilizing.

This shows you that you must observe the shifting patterns closely & carefully & identify points of stability and instability.

Very good lessons here.

Now we reverse.

Page 174

$C = +3.0V - 30sec$ $Eq = 10$
[3.2 to -3.2]

	hydrogen?	oxygen?		Diversity	
n=2	+2.26 strong	+1.20 weak	+.82 weak	—	
	2.27 strong n=4	+1.21 weak	.81 weak	Div ~2.1	-2.93 n=2 -2.93 n=3
	+2.27 strong n=5	+1.21 weak	+.81 weak	-2.25 strong reversible	-2.94 n=4

1. So we hv a strong reversible @ ±2.26 This matches previous.
2. A strong @ ~2.93 which we know is actual and ~~repeats~~ repeats.
3. Another weak indicator of Uran @ +.81
4. And an unknown but hinted @ repeatable @ 1.21 (but this is very weak). ~~[illegible]~~

1.23 region could be O_2 or TiO

need to separate.

Page 175

Now C= +2.0 for 30 secs Eq =10
[3.2 to -3.2]

We seem to be getting the same results, with ~~most~~ instability again @ ~2.1.
H_2 is -2.23 so this could be the point of instability. We proposed it could be Mg but this is not very reasonable. It seems it is much more likely that you have H_2 involved over Mg.
You also seem to be showing the reaction for O_2 @ 1.23. so 1.23 & 2.23 may be hydrolysis issue.

We will let this go. I see no new information coming in except for above, what a very insightful.

Now C= -2.0
[3.2 to -3.2]

+1.11	+.97	+.93	+.56	Stable n=2
+1.12	+.96	+.92	+.51	
Strong	weak	weak	moderate	
+1.13	+.97	+1.93	+.53	

Now C= -3.0 [3.2 to -3.2]

+2.94	+.99 !	+.84	+.81	+.44 +.42
	Strong +1.03	weak	weak	hold this.
		Skip for now		iron

hold this. +1.01 Strong

What is this?

This is important. It is a strong signal.

Br is 1.06

Page 176

~~Now C = -3.0~~ No flat's pts

~~[-3.2 to -3.2]~~

Ok, we have data now for two concentrated urine samples. It is now time to analyze the data.

We could so but it is probably better to regroup w/ these two concentrated samples.

To be complete and fair you need to test the Co sample for fluoride.

I have done so and Co fails the test as is anticipated.
All data is consistent.

We have done some very important work this week. All appearances are that you have some very good data. You now need to organize and collect it.

You could proceed to the other two samples from Santa Fe but I am not sure how critical it is now. You have learned the most critical information that you needed. You could work on qualitative ~~tests~~ to verify results further but these should be based upon some doubt.

You need to think clearly about getting the information organized, the level of verification, and the writing of the paper.

Also confirmation w/ the other two samples is helpful (you certainly can concentrate it now also!) as well as an understanding of concentration effects & limitations.

But it also would be nice to take a little break. You have worked very hard during this week and you have learned how to control and regulate the voltammetry w/ great reproducibility as well as an understanding of errors involved.

What really is of interest to you now is to see if you can digest the environmental filament! Microwave, H_2O_2, ~~FeO_2~~ $FeSO_4$?

Santa Fe
04/16 Sample
Concentration Factor = <u>4.18</u>

May 15 2016

OK, let's see where we are.
Foam testing is in order. We can also work
on one SF sample.
You can write a paper
Call tonight also @ 1800.

You are looking @ the filament w/ electrochemistry.

But let's evaporate SF 04/116 sample.
Dry Jar weighs 434 gms.

Wet jar weighs ~~1072~~ 1073
This should have ~~630~~ ml of water 639
Condense this ~ 25 ml
Remaining Volume = 153 ml. Concentration Factor = <u>4.18</u>

Ferrous iron w/ hydrogen peroxide <u>IS</u> Fenton's reagent.
It is used to <u>oxidize</u> contaminants in waste water
Can be used to destroy some organic compounds.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot + OH^-$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\cdot + H^+$$

"The exact mechanisms of the redox cycle are uncertain"

Page 179 A

Fenton's reagent

From Wikipedia, the free encyclopedia

Fenton's reagent is a solution of hydrogen peroxide with ferrous iron as a catalyst that is used to oxidize contaminants or waste waters. Fenton's reagent can be used to destroy organic compounds such as trichloroethylene (TCE) and tetrachloroethylene (perchloroethylene, PCE). It was developed in the 1890s by Henry John Horstman Fenton as an analytical reagent.[1]

Contents

Overview

Iron(II) is oxidized by hydrogen peroxide to iron(III), forming a hydroxyl radical and a hydroxide ion in the process. Iron(III) is then reduced back to iron(II) by another molecule of hydrogen peroxide, forming a hydroperoxyl radical and a proton. The net effect is a disproportionation of hydrogen peroxide to create two different oxygen-radical species, with water ($H^+ + OH^-$) as a byproduct.

(1) $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-$
(2) $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+$

The free radicals generated by this process then engage in secondary reactions. For example, the hydroxyl is a powerful, non-selective oxidant. Oxidation of an organic compound by Fenton's reagent is rapid and exothermic and results in the oxidation of contaminants to primarily carbon dioxide and water.[2]

Reaction (1) was suggested by Haber and Weiss in the 1930s as part of what would become the Haber–Weiss reaction.[3] Iron(II) sulfate is typically used as the iron catalyst. The exact mechanisms of the redox cycle are uncertain, and non-OH• oxidizing mechanisms of organic compounds have also been suggested. Therefore, it may be appropriate to broadly discuss *Fenton chemistry* rather than a specific *Fenton reaction*.

In the electro-Fenton process, hydrogen peroxide is produced *in situ* from the electrochemical reduction of oxygen.[4]

Fenton's reagent is also used in organic synthesis for the hydroxylation of arenes in a radical substitution reaction such as the classical conversion of benzene into phenol.

(3) $C_6H_6 + FeSO_4 + H_2O_2 \rightarrow C_6H_5OH$

A recent hydroxylation example involves the oxidation of barbituric acid to alloxane.[5] Another application of the reagent in organic synthesis is in coupling reactions of alkanes. As an example *tert*-butanol is dimerized with Fenton's reagent and sulfuric acid to 2,5-dimethyl-2,5-hexanediol.[6]

Biomedical applications

The Fenton reaction has importance in biology because it involves the creation of free radicals by chemicals that are present in vivo. Transition-metal ions such as iron and copper donate or accept free electrons via intracellular reactions and help in creating free radicals. Most intracellular iron is in ferric (+3 ion) form and must be reduced to the ferrous (+2) form to take part in Fenton reaction. Since superoxide ions and transition metals act in a synergistic manner in the creation of free radical damage, iron supplementation must not be done in patients with any active infections or in general any diseases.[7]

References

1. Fenton H.J.H. (1894). "Oxidation of tartaric acid in presence of iron". *J. Chem. Soc., Trans.* **65** (65): 899–911. doi:10.1039/ct8946500899.
2. http://geocleanse.com/fentonsreagent.asp
3. Haber, F. and Weiss, J. (1932). "Über die Katalyse des Hydroperoxydes". *Naturwissenschaften* **20** (51): 948–950. doi:10.1007/BF0150471.
4. Juan Casado,Jordi Fornaguera,Maria I. Galan (January 2005). "Mineralization of Aromatics in Water by Sunlight-Assisted Electro-Fenton Technology in a Pilot Reactor". *Environ. Sci. Technol.* **39** (6): 1843–47. doi:10.1021/es0498787. PMID 15819245.
5. Brömme HJ, Mörke W, Peschke E (November 2002). "Transformation of barbituric acid into alloxan by hydroxyl radicals: interaction with melatonin and with other hydroxyl radical scavengers". *J. Pineal Res.* **33** (4): 239–47. doi:10.1034/j.1600-079X.2002.02936.x. PMID 12390507.
6. E. L. Jenner (1973). "α,α,α',α'-Tetramethyltetramethylene glycol". *Org. Synth.*; *Coll. Vol.* **5**, p. 1026
7. Robbins and Cotran (2008). *Pathologic Basis of Disease - 7th edition*. Elsevier. p. 16. ISBN 9780808923022.

Further reading

- Goldstein Sara, Meyerstein Dan, and Czapski Gidon (1993). "The Fenton reagents". *Free Radical Biology and Medicine* **15** (4): 435–445. doi:10.1016/0891-5849(93)90043-T. PMID 8225025.
- K. Barbusiński (2009) (http://tchie.uni.opole.pl/freeECE/S_16_3/Barbusinski_16(3).pdf) *Ecological Chemistry and Engineering* vol 16 no 3 pp 347–358 "Fenton Reaction - Controversy concerning the chemistry"

External links

- USGS definition (http://toxics.usgs.gov/definitions/fentons_reagent.html)
- Reference Library Peroxide Applications (http://www.h2o2.com/applications/industrialwastewater/fentonsreagent.html)
- Companies that use Fenton's Reagent for chemical remediation: ORIN (http://www.orinrt.com)

Retrieved from "https://en.wikipedia.org/w/index.php?title=Fenton%27s_reagent&oldid=705910330"

Page 180

$Fe^{2+}(aq) + H_2O_2 \rightarrow Fe^{3+}(aq) + H_2O(l)$

not balanced

$2Fe^{2+}(aq) + H_2O_2(l) + 2H^+(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(l)$

balanced.

You have learned some important part ~~of~~ the reaction.

1. High temps may not be an asset
2. Low pH is required
3. Iron concentration can be very ~~small~~ low.
4. High pH will turn the iron to $Fe(OH)_3$ - ferric!

1. Temperature should be approx 30°C
2. pH should be ~4.5 (3-6)
3. Iron concentration does not need to be high.

1 drop = .06 ml = 60 ul

3-15 ppm is OK as a minimum.

Lets say you want 50ppm

What is our concentration in 1 M solution?

1M Solution $\frac{278gms}{1000ml} = \frac{x}{60ml}$ x = 16.7gms This is very high.

But iron is 20.1% by mass. Therefore $1M = \frac{55.9gms (Fe)}{1000ml}$

~~In 60ul we have~~

~~$\frac{60E-6}{1000}(55.9gms) = 3.35E-6gms =$~~ 3.35 ugms.

We also have $\frac{(16.7gms)}{60ml}(.201) = \frac{3.36gms}{60ml}$

In one drop we therefore have $\frac{.06\ ml}{60\ ml}$ (3.36 gms) = 3.36E-3 gms per drop

So let's say we add this to 5 ml.

$\frac{3.36E\text{-}3\ gms}{5\ ml} = \frac{x}{1E6\ ml}$ x = 672 PPM

Since you only need about 50 PPM, you can dilute by a factor of 13.
We can therefore use
~ 1 drop of 1M $FeSO_4 \cdot 7H_2O$
50 ml of water to be safely above our level.

We can, therefore, now produce Fenton's reagent.

1. Bring ~200 ml H_2O to pH 4.5
2. add

I think what you will do is
1. Get 50 ml of H_2O_2
2. add HCl to bring pH to 4.5 (3-6)
3. Add 1 drop of 1M $FeSO_4$.

No, this is way too strong (1 drop 7M HCl should work)

Use 1 drop 1M HCl maximum!

This is the right way to make Fenton's reagent.
Not the mess that I make.
Redo the electrochemistry of this solution a the base with no heat or microwave added.

Page 182

NP Test w/ Filament.

Under weak Fenton's, no reaction is observed compared to potential Magnesium result from yesterday (heated in microwave, more reaction).

Now heat for $\overset{+1}{5}$ min in microwave.
5 min + 1 min.

We notice that there does seem to be a little more foam produced in the filament sample run.

The clothespin arcs so you must remove that. This almost destroyed the sample.
It is too much heat. 2 min looks to be ok.

The heating appears to have changed the color of the precipitate from rust colored to pure white, however

There is, however, some change starting to occur.

There is a shift occurring

We know now that the clothespin arrangement can apparently take 3 min of heating w/ microwave @ level 1, or at least 3 separate segments of 1 min each.

2 min is probably much safer and adequate -

Page 183

Condition on Control C = -3.0 @ 30^s, Eq = 10^s [-3.2, 3.2] Mild Filament w/Heat

-1.09 -.75 -.64 +.16 -.94 -.70 -.64 -.11 +3.04

Filament added but no heat results in: -.96 -.73 -.67 -.12 +2.87

-1.00 -.72 -.64 -.01 -1.00 -.73 -.66 -.10 +2.90

Δ<.03 -.98 -.73 -.67 -.09 +2.92

It ~~is~~ also destroying the electrode more readily w/the sample.

The sample appears to be introducing two new peaks:

~~-.96~~	-.12	+2.87	weak signals.
~~-1.00~~	-.10	+2.90	
~~-.98~~	-.09	+2.92	So Ms
$\bar{x}$	-.10	+2.90	Ti 3 hits
σ	.015	.025	Ba, Sr (in Grp in II)
n	3	n=3	

-2.92 (K)

+2.90 (Ba) -2.87 (Ca) -2.89 (Sr) K(-2.92)

0.1 (TiO) We can see the changes in the file.

Now let's go back to the control.
Let's recondition the electrode and do this again.
We will also heat up the control for 1 min @ low power.
to equate things further. 2 min Conditioning.

matches w/out heat
w/or w/out Filament

Control again

Hot (Greater Heat)
Filament again

n=2 -1.00 -.76 -.66 -.01 -.88 -.72 ~~-.30~~ +3.00
~~-.33~~ -.34

This is a big difference.

Stability also achieved

Page 184

The working electrode is being destroyed in the solution (Control w/ mild heat).

We now see from the control unit that the heat combined with filament is what is producing the new peaks @ -.10 and +2.90.

So the heat is critical but it must be very mild. 3 min max @ power level 1.

The electrode is visibly being destroyed in the process.

Peaks just starting after 6 trials
Hot acid IS what is destroying the electrode

We are seeing the -.10 peak coming in very slightly after 11 trials post heated filament. Nothing @ 2.90

I believe that heat is critical to the process.

You can have NO Clothespin in the microwave ever, not even for 1 min.

2 min max @ Power 1 for 4 ml of solution in cut off test tube

Page 185

Ok, we have the solution to the problem.
that acid is required.

We are not positive iron is required but we
believe that it almost certainly is.

What we have therefore is
1. Extreme oxidation
2. Temperature elevated
3. Acid environment.
4. Electrolysis.

That is certainly one strong combination.

ie hydroxyl radical

We have an interesting situation.
We may have different metals being released @ different temperatures.

1. With one method (high pH, high iron) we have an indication of magnesium low temperature being released.
2. Under moderate temperatures we may have Ti @ Ba (Sr, Ca or K) being released.
3. Under even higher temperatures we have stability @

-.88 strong TiO (-.89)
-.72 weak Iron (.77)
-.34 ~~-.33~~ moderate Ti (-.37)
3.00 weak Ba, Sr or Group I or II elements

We have 3 hits on TiO

We have learned a lot w/ this test:

We can see that heat, acid, oxidation capacity, & pH & electrolyte are each apparently a factor in bringing the reaction to fruition.

We could do the test again, but in the limited time available it may be best to reverse the direction.

Our candidates thus far are:
1. Magnesium
2. Titanium
3. Ba, Sr, Ca or Grp I or II element.

We have also learned how to manage the microwave better.
1. No clothespins <u>ever</u>.
2. Heat a maximum of 2 minutes 30sec w/4 ml of solution in a holding vase. (Plastic cup w/in glass dessert cup) Save your clothespin position w/ a pen or small test tube
3. Acid will destroy the electrode.

We actually have 4 combinations of events

C= ~~+3.0~~ -3.0 [-3.2 to +3.2]
C= +3.0 [-3.2 to 3.2]
C= -3.0 [3.2 to -3.2]
C= +3.0 [3.2 to -3.2]

that will need to be considered.

Next let's use C=+3.0 [-3.2 to 3.2]
There does not appear to be any difference in the control
Now let's work on the filament then. Three trials
including Curves 1-34 & 1-35.

Generally the same result as before but we have a very clear higher peak @ 2.76 now.
So it did make a difference here.
Our measurements are:

-.84 -.67 -.63 -.25 +2.56 n=3

So we do have a more defined peak on the high end.
We also have a new entry @ -.25
not sure what this means.
As the temperature cools, the points are shifting ~~to the right.~~
-.91 -.69 -.64 -.18 +2.72 Interesting.
So what are the real values & how do you know?

-.14 +2.73
-.12 +2.77
-.00 +2.77

They were so pointing out that there is a temperature relationship in potential msmts. It is a "standard" table so temperature can skew the results.

-.05 +2.84

The temperature relationship may be more important than you imagined.

Page 188

You are seeing now that drift in temperature could be an important factor

We are now going to start controlling the heater
Exploring temperature 46°C now.

Electrolysis is very active w/ the increasing temperature.

Now @ 60°C

nothing else near this.
We have a very strong peak @ -.86 (very stable)
Another moderate @ -0.18 (which seem to be moving to the left)

Now 69°C
-.84 -.21
-.24
-.26

Now 80°C
-.81 -.30

~~As temperature increases, voltage decrease~~ (maybe)

SF 04/16 Snow Sample
Concentration Factor = 4.18

Page 189

[illegible] @ Curve 152
Ile - 09 seem to be the issue.

Our readings are
−.80 (very strong) [illegible] [illegible] −.27
we have lost the peak @ 2.9+

It really did not seem to matter if you went +3.0
or −3.0 for Conditioning,
but reversing to [3.2, −3.2] made a big difference
Now we are running @
C= −3.0 [3.2, −3.2]

We picked up +2.85 right away. +.36 also w/T=80°C

So we have a moderate peak @ +.36 which matches
−.37 right away.

80°C +2.85 Strong +.36 moderate
+2.83 +.38
53°C 2.88 Ti(−.37) .39 We had
46°C +2.88 +.41 2.90
30°C +2.80 .41 2.84
$\bar{x}$ = .39 2.83
2.88

Best Candidates are
+2.89 and (.39+.34)/2 = 0.36

Ba and Ti

May 16 2016

Important findings are taking place wrt rainwater and the environmental filament, but the information remains unorganized and not in any form for presentation.

[redacted]

You have many projects for the lab. You are going to have to pick a/choose what is most important for the lab setting.

Ok we have worked the Twitter scene, hashtags are very simple. Some effort must be put into social media on a regular basis to help distribute the work.

What are the priorities for today?

1. Magnesium detection in filament.
2. What about DNA exploration?
3. Molecular weight of lipids?

We have projects & then we have projects that require the lab.

Projects of Interest | Projects of Interest that Require the Lab

2 Molecular wt of Lipids →
1 DNA Studies → ①
2 DNA Production →
1 Env. Filament Study → ①
    Electrochemistry, Microwave → ①
    IR → ①
2 Protein Studies →
2 Hair Analysis
    Pyrolysis →
    IR Gas →
    GC →
1 Rainfall Studies → ①
    Microscope → ①
    Electrochemistry
    IR →
2 HEPA Filter Analysis
    Microscope →
    Electrochemistry
    IR , DOC (UV) →
1 IR Recovery → ①
    Regroup Papers → ①
    Reprint Papers → ①
    Recover Hard Notes → ①
    Recover Topics → ①
1 Electrophoresis → (Possible in field?)
    Edvotek Labs → ①
    CDB DNA → ①
    Proteins → ①
    Lab Experiments → ①
3 Pig Dissection
3 Soil, Water Experiment Kits

Projects of Interest   Projects of Interest that Require Lab

3 "Rile Machine" & Cultures → (maybe in field?)

2 Gas Chromatography Explorations →

3 Emission Spectrometry

[redacted] book   ①

2 Carbon Content Analysis →

2 CDB Environmental Stress Study →

3 Fuel Cell Analysis & CDB → (Maybe in field?)

3 Acid Base Chemistry Explorations →

1. Supplies needed
    Titanium
    Chlorine & Bromine
    Manganese
    Cobalt

Equipment that Can Go on Road

1. Delmsens (Env Filament, Rainball?, Culture, Proteins, Lipids, etc)
2. pH, Conductivity & TDS meter
3. "Rile machine"
4. PM 2.5 meter
5. Biology kit
6. Chemistry kit
7. Soil Kit
8. Small Microscope
9. Refractometer?
10. Dissection kit & Pig
11. VIS spectroscope Emission

[redacted] boat!

13. ChemLab on Computer
14. Trifield meter
15. Voltage Cell

Ok the work & settings are now listed to a large degree. Now you need to rank it, prioritize it, & organize it. Distinction between travel mode & lab mode can be helpful.

Ok, this has helped a lot. We can now give some priority to projects, including those that require the boat or are of such importance that the lab equipment is not the overriding factor.

High Priority Projects ①
(CI Lab Facilities may or may not be required)

DNA Studies
- Edvotek Labs
- Electrophoresis
- COB DNA
- DNA Prep & Staining
- Protein Analysis & Studies

Environmental Filament Study
- Electrochemistry - Trace Metal Analysis
- Microwave Requirements
- IR

Rainfall Studies
- IDaho 1
- Idaho 2
- Colorado 1
- Santa Fe 1

Electrochemistry, Infra Red, Microscope,
Cultures, Biologicals, Halogens, Organophosphates

IR Recovery
- Organize damaged papers
- Reprint Copies
- Transfer Notes or Photocopy
- Reprint selected & important work

Projects Prioritized

Electrophoresis
  - Edvotek Labs
  - CDB Dna
  - Proteins

[redacted]

Hair Analysis - pyrolysis
GC aquaintance

CDB Lipids & Proteins

Page 196

Mid Level Priority Projects ②

Molecular Weight of Lipids - new method

DNA Production

Protein Studies (maybe #1)

Hair Analysis
    Cyanide
    Pyrolysis
    Electrolysis
    IR Gas
    GC

HEPA Filter analysis
    Electrochemistry
    IR
    Microcsopy
    UV DOC

Gas Chromatography Explorations

Carbon Content Analysis

Page 197

COS Environmental Stress Study

Chromatography Combined w/ Electrochemistry, UV Detection

NIR Examinations

Lower (but not low) Level Priorities ③

Pig Dissection

Soil, Water Experiment Kits

Pufe Machines & Cultures

Emission Spectrometry Trials

Fuel Cell Analysis & COB

Acid Base Chemistry Explorations

High Iron Content

Heavily Microwaved Filament Sample

Ok This was very important to get this organized.
We can pick one off @ a time.
I think we need to examine the magnesium
and ask how the material was prepared & what
cause the difference.

Lets work on the magnesium issue w/ the filament.
Try to pick up everything from your processed sample
including Ti, Fe?, Mg, Ca. This would be
a late sample.

Testing if there is a difference between C=-3.0 & C=3.0
yes there is.

Curves 0 & ~~3~~2 ⇒ C = -3.0 [-3.2, 3.2] set 1
1 & 3 = C= +3.0 [-3.2, 3.2] set 2
and there is definitely a difference.

Now

set 3 Curves ~~3~~ 4 C = -3.0 [-3.2, 3.2] Big
5 C = -3.0 [3.2, -3.2] Difference

set 4 Curve 6 C = +3.0 [-3.2, 3.2]
Curve 7 7 C = +3.0 [3.2, -3.2]

Matches
0&2✓ 1&3✓ 2&4✓ ~~3&7~~ ~~4&7~~
0&4✓ 1&6✓ ~~2&0~~ 3&6 ~~4&0~~

5&7 ~~6&7~~ ~~7&5~~

1-3-6 0-2-4 5-7

Matching sets

1 C = +3.0 [-3.2, 3.2]
3 C = +3.0 [-3.2, 3.2]
6 C = +3.0 [-3.2, 3.2]

0 C = -3.0 [-3.2, 3.2]
2 C = -3.0 [-3.2, 3.2]
4 C = -3.0 [-3.2, 3.2]

5 C = -3.0 [3.2, -3.2]
7 C = +3.0 [3.2, -3.2]

The three ~~Combination of matching~~ distinct entities are

1,3,6 +3.0 [-3.2, 3.2]

0,2,4 -3.0 [-3.2, 3.2]

5,7 +/- 3.0 [3.2, -3.2]

+3.0 [3.2, -3.2]

-3.0 [+3.2, -3.2]

C+3 UP ↗ C-3 UP ↗ C+3 ~~or~~ DN OR C-3 DN ↙

Cases:

Page 201

Curve			
8	C=+3	[3.2, -3.2]	these match
9	C=-3	[3.2, -3.2]	
10	+3	[-3.2, 3.2]	different
11	-3.0	[-3.2, 3.2]	different

So we have 3 sets to make up one trial:

C= +3 or -3 [3.2, -3.2] It does not matter which C

C= +3.0 [-3.2, 3.2]
C= -3.0 [-3.2, 3.2]

So

C=+3.0 ↗ C3UP

C=~~+3.0~~ -3.0 ↗ C-3UP

C=+ or -3.0 ↙ C+3 DN or C-3 DN

These will be the future terminology

Very interesting. I could never have predicted this.

You have 3 unique cases to work out.

This is now very interesting work. Demanding also.
Our fuel is -02. Looks superb.

Page 202

Rainfall Interruption:

We have the second half of the 102 rain sample.
Empty quart jar weighs 441gms

2nd jar weighs 848gms

We therefore have in jar 848-441= 407gms

Now condense

We also have 109 gms(ml) in the first jar.
Since the Concentration Factor is 2
We will combine & weigh the final product.

Total available: 407 + 109gms = 516gms.
We can easily condense this to 50ml if we would like to, but @ least 100 ml.

Remainder = 169 ml

so Concentration Factor is currently

$\frac{516}{169} \approx \underline{\underline{3.05}}$

Page 203

Both Env. Filament MW2 sample high via Fenton
we have come up w/ a good method to compare
against control.
The three case are run and labeled by category
until they stabilize w/ a control if required.
The same is done for the sample. Nomenclature is

Case I C+3UP Control C+3UP Sample
Case II C-3UP Control vs C-3~~DN~~(UP) Sample
Case III C-3DN Control C-3DN Sample
C3+3DN is available also

Each case is compared, control against sample
a difference observed.

Case I C=+3 UP Difference only:
Control

Sample

Case I -2.80 ~~-2.76~~ ~~+1.49~~ ~~+1.44~~ +1.44
Ca

It is best to look @ all 3 controls combined and just look @ difference.

Strong ~~-1.1~~ Strong
HBrO (1.45)
Ca(2.81) Ti(-1.31)
F(2.87)

Case II
-2.02 ~~-1.14~~ -1.92
weak weak

Case III
-2.47 -1.63
Ce? (-2.48) Strong Ti
Mg (-2.37)

High Iron Content Microwave

Let's measure again

Case I C+3 UP [-3.2, 3.2]
Case II C-3 UP [-3.2, 3.2]
Case III C-3 DN [3.2, -3.2]

You did not place acid in this sample.
Method was H_2O_2
2-3 drops $FeSO_4$
Microwave 5min @ Power Level 1

2nd Sample uses: H_2O_2 50ml
2 3 drops $FeSO_4$
2-3 Drops Conc. HCl

then we decanted 4 ml sample & added filament & heated in microwave repeatedly ~ 2 min, Electrodes showed damage from heat & electrolyte.

Difference from control occur @
Most Common Oxidation State is +4, This is +3.
Ti(-1.37)
-1.20 +1.33 +1.83
Mn(-1.18) Cr(+1.33) Co(1.83) Be(-1.85)
This is quite a bit different from last time

Control has strong peaks @
-2.80 -2.25 +1.95
Ca(-2.87) [illegible]
Mg(-2.37)

Is there any possibility you have the tubes crossed

Page 205

If all is correct, your numbers received are.

-2.80	Ca (-2.87)	Zn is -.76
-1.63	Ti (-1.63)	
+1.44	Ti (-1.37)	
-2.41	Mg (-2.37)	
-1.20	Mn (~~-1.20~~) (-1.18)	
-1.33	Ti (-1.37)	
+1.83	Br (1.85)?	

Lab Rank is from

Ca	(-2.87)
Mg	(-2.37)
K	-2.92
~~Na~~ Ti	-1.63
Mn	~~-1.20~~ -1.18

Yesterday we had

+2.90	Ca, K
-.10	Ti
-.88	TiO

Why did we not repeat on the trials?
Increase strength of sample. Added 100 ml of sample.

Page 206

Increased concentration of sample

Diff peaks are now
+2.69 -2.55 -.29 +1.34

None of them makes any sense.
Yesterdays data does, todays does not

Apparently we need to go to
1. Straight Fenton's
2. Acid (pH 4)
3. Heat

May 17 2016 Env. Filament.

We were not able to duplicate results yesterday.
We will start again.
Let's use H_2SO_4 & Fenton's Light & mild microwave.
pH 4.
Recall that Fenton's is already acidic by
Composition. H_2O_2 50 ml
$FeSO_4$ 1 drop
pH should be 4 but it is 2.3.
Notice rim stays white however.
We will place the 4 ml Fenton vial in the
microwave without the filament for 5 min.
All measmt will be done @ room temperature
Let's get Control in place w/ Fenton's alone
Case I, Case II, Case III run.
Case 1 +3 [-3.2, 3.2] } they are the same this time!
Case 2 -3 [-3.2, 3.2] } they look very clean. Minimal Activity
Case 3 -3 [3.2, -3.2] Very clean signals.

Good news is that the sample processing looks very good.
Heated up vial w/ Fentons (acidic) for 5 min
Placed in filament in hot vial after heating and it
is bubbling nicely.

Now for the filament vial, which has been
cooling down.

Case 2: We also have a shift taking place here.
As the vial is cooling down the electrolyzer activity is decreasing.
But we also have 2 shifts
The method seems to be very slowly working.
Something is occurring @ -.84 also that is disappearing after plot completion
This is TiO (-.84)
-1.13 -.87 -.21 + 3.05 are all new
We are starting to reproduce the work now.

Case 3 Looks to be very minor change. The vial is cooling down and activity is decreasing again

Reheat again for 2m 30s

Save the work of the last session and it starts a new group for you.

Cover the 4ml vial holder w/ a 250 ml beaker beaker.

Reheated

Case 1 Temp spike occurring @ -.78 (you have caught it)

Case 2 Very strong shift now.

Case 3 Very little difference here.

Now heat again.

Page 210

Heat is definitely affecting the extraction (to benefit) but you must be very careful. If you overheat you will lose the contents of the vial and destroy the entire run. 2^{m} 30^{s} is definitely the max segment. You should be able to hold the vial but not squeeze it of a temperature. The filament constituents solubilize under mild heat and appear to be being cleaned of insolubles attached.

Reheated Series (3)

Case 1

Case 2 Temp spike @ -1.12, -1.09

Case 3

Idaho 2 Rain Sample 05/15/16

Now measures 239 gms
Original wt 176 gms
$\Delta = 63$ ml

Original volume was 516 ml
The Concentration factor is therefore now.

$\frac{516}{63} = 8.19$ CF Idaho 2 05/15/16

The Demise of Rainwater
The photo has been posted.

Page 212

Env. Filament - Continued.
Time to make an analysis:
File is -06.mux on May 17 2016

Br(1.06)
Case 1: -1.07(1) -.80*(2) -.36(1)
-.99(2) -.86(1) -.30(2)* +2.66

-.82 -.77 -.33 +2.66
Fe Ti(-.37) F?

-1.30*(1)
Case 2: -1.14(2) -.44 +2.98
Fe K(2.92)

Case 3 +2.38
Mg
(2.37)

My List

K
F
Mg
Fe
Ti
Br

Results are Good.

Page 213

Let's take poss 1 first prior to heating
That really does not make much sense.
Heating session #3 shows the greatest deviation

Case 1

~~+2.73~~ Not found

-1.01 -.86 -.80 -.30 +2.73

Br(-1.06) ~~Ti~~ ~~Zn~~(-.89) Zn Ti(-.37) F(2.65) Ca(2.81)

TiO (-.76) or Fe(.77)

Heating #3 Case 2:

-1.30 -.43 +2.98

Mn(-1.18) Fe (.44) K(2.92)

Case 3:

+2.39

Mg(2.37)

Heat 2 Case #1

-.82 +2.69

-1.00 -.77 -.36

Case #2

?

-1.26 -.54 +2.93

Case #3

-2.64 Run Ca, F tests. +2.36 ~~+2.24~~

→ The test strips positive

Averages

(+2.98 + 2.93)/2 = +2.96 Ca(2.87) K(2.92)

(+2.65, -2.64)/2 = +/- 2.64 F(2.65)

(+2.39, +2.36)/2 = +2.37 Mg (2.37)

(-.30, -.36)/2 = -.33 Ti (-.37)

-.43 = -.43 Fe (.44)

(-.80, -.77)/2 = -.78 Fe (.77)

(-.86, -.82)/2 = -.84 TiO (-.89)

(-1.01, -1.00)/2 = -1.03 Br (-1.06)

(-1.30, -1.26)/2 = -1.28 Mn (-1.18)

No Ca identified

Page 214

(1) You have enough information to write the metals aspect of the Env. Filament Project

There will be several phases to the project:

1. Metals & supporting info
2. ~~Microscopy~~ IR work
3. Microscopy
4. The final paper

(2) You also have your first handle on rain metal analysis. You will do it again and compare the results.

(3) Also do the metal analyses on the Env. Fil again

What will be your next topic?
Molecular wt of liquids through alternative

$PV = nRT$

$MW = \frac{dRT}{P}$ $d =$ density $V = \frac{nRT}{P}$

$d = \frac{m}{V}$ or $V = \frac{m}{d}$ so $\frac{m}{d} = \frac{nRT}{P}$

so $m = \frac{\text{dens.} \cdot n \cdot RT}{P}$ so $\frac{\text{mass}}{n} = \frac{dRT}{P}$

Page 215

This means $MW \overset{?}{=} \frac{mass}{n}$

Test this.

Assume Oxygen is $\frac{16\ gms}{mole}$ if $n = 1$ then mass = $\frac{16\ gms}{mole}$ = MW of Oxygen.

$MW = \frac{dRT}{P}$

Vegetable Oil should work.

Dumas method is causing some problems. It needs to be highly volatile w/ a low boiling point to work. Xylene, a predominately liquid, has a high boiling point. You are going to need to go to the other method.

May 18 2016

[redacted]

Now we have our information in order. Software & Computer Info. transfer has been the name of the game, but everything is in place now. We download game Chemistry from Great Course and we should be OK.

Now two goals for today.

1. Env Filament in watch glass
2. DNA Prep!

We have used:
   1. Mild heat (microwave & tungsten)
   2. Filament
   3. Fairly generous $FeSO_4$
   4. HCl Concentrated

We have extracted about 1 ml of the remaining solution, diluted it to 4 ml and will now neutralize

Page 217

Case 1 We had a massive current overload.
I have diluted to 1kg
We have a problem of some kind.

Something is throwing the Palmsens into a tizzy when the current is too high. We have ~~too~~ to reset w/ the test sensor.

I am now using only 30-60 ul So whatever I have in solution is really really strong. Added to distilled water.

Case 1 Fe
-2.24 -1.90 -1.75 -.74
Strong

Separate testing shows that the solution is indeed very conductive and very acidic.

Case 2 Al Ti(.33?)
-2.00 -1.67 -.27 all strong.

Case 3

~~+1.20~~
+.30 +.97 +1.06 +1.32 +2.08

We have a lot of new numbers here.
They're all very uncertainty.

~~-2.24~~ -.74 +2.88
~~-2.00~~ -.27
-1.90 +.30
-1.75 +.97
-1.67 ~~+1.32~~

Need a Control!
There is all questionable on this page

Page 218

Maybe you need to work on a control that is better here

H_2O_2 $FeSO_4$ a HCl
60 ul in 4 ml H_2O distilled
This looks to be important.

Cases
Save the file after each case, no just after each sample
we have pts @

-2.20	-2.05	-1.32	+.54	+.87	+.99
Str	Str	Mod	Weak	Weak	Moderate

The filament seem to be entirely different than the Control but they both have peaks.

	-1.93		~1.76					
-2.16	-1.96	-1.90	-1.81	-1.71	-1.08	-.66	+.43	+1.06
	weak		weak					

Now there are definite points of distinction

+1.06 Matches w/ Bromine
+.43 matches w/ Iron
-1.08 Matches w/ Bromine

.66 matches w/ TlBr (Thallium Bromide?)

FeO_4^{2-} matches w/ -2.16 (2.18)

Page 219 These are results.

Env Filament Project - ~~Metals~~ Inorganics Analysis.
So now we have:

+2.96
+/- 2.64
+2.37
$\pm \left[\left(2(1.03) + 1.06 \right) + 1.08 \right] / 4 = \pm 1.05$
-1.28
-.84
-.78
-.43 + .43 = +/- .43
- .33

-.66	Hydroquinone?
+2.96	K(2.92) Ca(2.87)
+/-2.64	F(2.65)
+2.37	Mg(2.37)
+/-1.05	Br(1.06)
-1.28	Mn(-1.18)?
-.84	TiO (-.89)
-.78	Fe(.77)
+/-.43	Fe(.44)
-.33	Ti(.37)
-1.89	BrO_4^- (1.85)
-1.71	Al (1.66)

I also had a spike @
Case 1. We have a definite first small peak of ~~1.89~~.
When we move from left to right / we believe it's 1st peak.
Therefore we have

-1.89 & -.66
~~Thorium?~~ ~~F&Br?~~
~~Case 2~~: Hydroquinone?
BrO_4^- 0.70
(is 1.85)

Case 2
We repeat -1.90.

It appears that both methods of processing the filament, microwave and watch glass, have been useful & productive.

I uncover 3 other candidates, F, Br, & Hydroquinone.

Page 220 Important notes

Momentous occasion:
It has taken close to 20 years but this week I have finally learned to break into the environmental filament. Both for metals analyses and for organics.

1. H_2O_2 & $FeSO_4$ & Acid (HCl) and heat to access the metals for voltammetry

2. KOH-NaOH solution applied to filament in watch glass. Microwave @ lowest power for only a few seconds. The material will burst open completely and create a paste. Env. filament absorbs microwave on the exterior and infrared on the interior.

3. Excellent voltammetry results obtained from method 1.

4. Superb IR spectra obtained from method 2.

Page 208

Filament vial is cooling down. Now subject to NR.

Case I is producing no change yet.
Case II A very small change may be taking place here after 6 runs.
Case III A minor difference in place.

We will now heat the vial again for 2^m30^s.
There may be a time factor involved here.
Also we wonder if Sensor's needs to be made fresh

The heating for 2½ minutes w/ a heater core seems to have worked perfectly.

Case I. Repeated. We are starting to see a difference now. We have a new peak @ +0.82 and another is shifting near the zero point. Heating and time do appear to make a difference. The sample continues to show signs of bubbling. We are starting to see a difference. The solution in the vial also seems to be showing increased activity. We definitely have a shift of some type taking place. The working electrode is now getting more active.

May 19 2016 Page 221

I have my Davis Organic Chemistry Course back!
It looks great!

Dumas Trial w/ Lard:

Wgt of flask, wire, & foil:
55.71 gms, .72 (tare each time)
.70 .72
.71 .70
.71 .71
.71 .71

Lipids are ~~starts~~ to boil @. No.
BP is ≥ 170°C!
≥ 180°C!
≥ 187°C
≥ 190°C

$\bar{x} = \bar{X} = .71$ $\sigma_s = 6.67E-3$

190°C is maximum temperature reachable with hotplate.
We must put to higher temp w/ safety container on stove
Let's assume a case of $\Delta W = .02$ gms.
and a volume of ~~150 ml?~~ 140 ml

We can see that the lipids did darken some so it did have some kind of effect. But they did not boil

$d = \frac{M}{V} = \frac{.02 \text{ gms}}{\cancel{130 \text{ ml}}\ 140} = \frac{x}{1 \text{ ml}}$ $x = .0001\cancel{54}\,43$ gms/ml
= .~~154~~ gms/L
.143 gms/L

$MW = \frac{d \cdot RT}{P}$ $R = .08206$ L atm/mol K
$T = 190 + 273 = 463$
$P = 1.0197$ atm or 1.00
P here ≅ 0.90

hypothetical <6.5 gms
MW = ~~.055~~ 6.49 gms/mole way too low.

1 hPA = 100 pascals

Page 222

So 1013 hPA = 101300 pascals

3000' elev

Your value is way too low.

$\cong$ 908.1 hPa

~~48~~ demo example is 498 ml

Ours is 140.

so $\frac{140}{498} = .281$

he has 5 gms of weight! per liter

let's assume we .5 gms instead

$\frac{.5 \text{ gms}}{140 \text{ ml}} = \frac{x}{1 \text{ ml}}$ $x = .0035 \frac{\text{gms}}{\text{ml}} = 3.5 \frac{\text{gms}}{\text{liter}}$

So $MW = (3.5)\left(\frac{.08206}{.9}\right)(463) = \underline{\underline{140}}$

Xylene has a molecular weight of $\underline{106}$

so this type of number is very reasonable.

We would need to measure ~ 0.5 gms of vapor.

We think that our final measurement

will be $\leq$ 55.9

This does not bode well for the

molecular weight. It would therefore

be very low but of a very high boiling point.

Volatile oils can indeed have a molecular

weight from 43 to 70

<43 gas

43 – 70 volatiles

70 – 150 black oils but may go to 190 – 210

>210 are heavy oils.

Page 223

We already measured density, refractive index, etc

Almond oil has a MW of ~ 106 C_7H_6O

Your possibility is that the oil was slowly driven off to a fraction of the original but was not brought to boiling quickly enough.

Imagine we had ~~0.8~~ 0.3 gms @ 220°C

It is definitely not xylene under these conditions

$\frac{.3\text{gms}}{140\text{ml}}$ = ~~.214~~ 2.14 gms/liter

~~.214~~ $\frac{2.14(.08206)(493)}{.9}$ = 108 gms/mole

These are all very reasonable.

Determine MW of xylene tomorrow also.
Get temp higher.

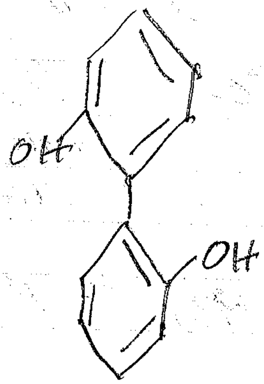
Our rainwater is now 533 gms − 441 gms
= 92 gms.
We want about 1/2 of this

May 19 2016

CDB Lipids IR Plot. Let's go to work.

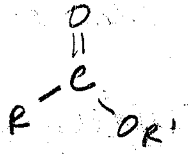
3463 Avram p 279 gives a strong indication of a dimer phenol

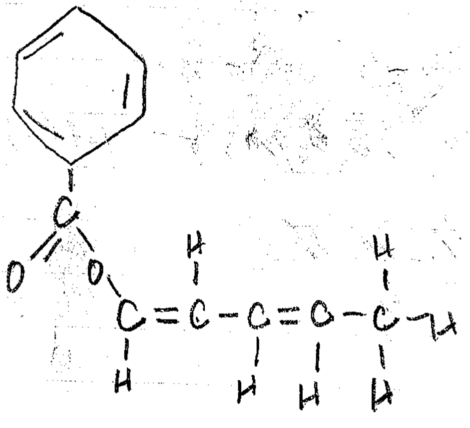
No longer



6(12) = 72
× 2 = 144
+ 32
2
178 is high

An ester is

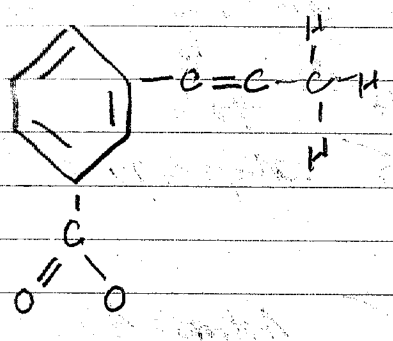


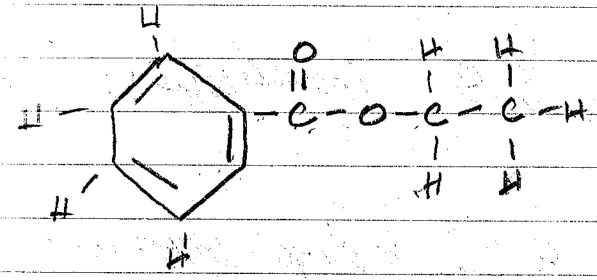


12(12)

Conjugated diene
ester
aromatic

Page 225





$6(12) + 3(12) = 108$

$2(16) = 32$

5

$\Sigma = 145$

$+ 4$

$\Sigma = 149$

This is in range.

Our estimate was 135 gms/mole

but it goes up to 160 gms/mole

We have a very dark oil now.

mol file created

~~$C_9H_{16}O_2$~~ MW= ~~156.22~~ 150.17 $C_9H_{10}O_2$

NIST Structure Search - no molec

EMolecules found something: Ethyl ~~Benzoate~~ Benzoate

PubChem ID is 7165

Chlorine & Bromine Tests on Rainwater. Also pH & Total Alkalinity

CF			PPM Cl	PPM Br	pH	Total Alkalinity
11.24	11/15	Idaho 1	0	0	7.5	10drops = 100 = 100ppm $CaCO_3$
22.98	04/16	CO 1	0	0	7.5	4drops = 40 = 40PPM $CaCO_3$
8.19	05/15	Idaho 2	0 PPM	0 PPM	6.8	Insufficient Sample
4.18	04/16	SF, NM	0 PPM	0 PPM	8.2	6 drops = 60 = 60PPM
17.13	05/15	ID 3				

Total Alkalinity (TA), is a measure of "alkali" (not to be confused w/"alkaline") in the form of

1. Carbonates
2. bicarbonates
3. and hydroxides present in the water.

It is a measure of water's resistance to change in pH (ie, the buffering capacity).

An amount of total alkalinity in the range of 100-200 PPM will stabilize the pH in a stream.

We are not referring to if a liquid is acid or alkaline.

Rainwater is usually less than 10 PPM.

CDB Liquids MW Estimate

Ok, let's try DUMAS method again to CDB liquids

55.62	.64
.63	.65
.64	.64
.62	.64
.63	.64

$\bar{x} = 55.64$

BP ≥ 233°C. Vapor now visible

We can tell that a small portion of xylene is likely present from brief activity @ 144°C

~~55.79~~ Estimate 235°C = 508°K

55.90
.88
.89
.89

$x = 55.89$ $\Delta = 55.64 - 55.89 = 0.25$

Vol = 184 - 54 = 130 ml (close estimate)

$\frac{0.25 \text{ gms}}{130 \text{ ml}} = 1.923$ gms/liter

$$\frac{1.923(.08206)(508°K)}{.9} \simeq 89.6 \simeq \underline{90} \text{ MW Estimate}$$

We had 160 based upon Colligative properties. This is a broad spread. $\bar{x} = \sim 125$ gms/mole

Best estimate to date

We could do Dumas again.
It is not too hard.
We can use differences in IR to determine structure.

Reference weights

55.61 (Hot) 55.70 (Cold) ??

55.65
.68
.65
.66
.64

$\bar{x} = 55.65$

Raise to ~~25~~ 235°C quickly

55.96
55.96

So now we have
$\frac{0.31}{130\ \text{ml}} = 2.38\ \text{gms/liter}$

$MW = 2.38\left(\frac{.08206}{.9}\right)(508) = \underline{\underline{110}}$

~~BP should be 138°~~

So we now have 2 methods.

160 gms/mole (Colligative method)
110 gms/mole (Dumas method)

$\bar{X} = 135 \frac{gms}{mole}$ best estimate of CDB lipids MW

We should use our remaining oil for IR analysis

This will be much more pure. Notice the dark color?

~~do do we heat a~~ mixture?
~~You heat~~ first

May 20 2016

1. Determine if CF has a body of work available.

(1) Thermal ion flow over polar cap may have some relevance.

(2) DNA - ELF propagation
Experiments lack concrete experimentation

(3) Geomagnetic storms - mitochondria damage

[redacted]

1. Rainfall tests organized

2. Distillation of liquid & IR?

We should be able to back out the pH of a concentrate.

definition of pOH = $-\log[OH^-]$

So $8.5 = -\log(OH)$

~~$-10^{8.5} = OH$~~

Page 231

~~Conc.~~ pOH.

$\text{Conc pH} = -\log\left(\frac{OH^*}{CF}\right)$

so

$-\text{Conc pH} = \log\left(\frac{OH^*}{CF}\right)$

$10^{-\text{Conc pH}} = \frac{OH^*}{CF}$

$CF \cdot 10^{-\text{Conc pH}} = OH^*$

so log CF

$pH^* = pH - \log(CF)$

$-\text{Conc pH} = \log\left(\frac{OH^*}{CF}\right)$

$-\text{Conc. pH} = \log(OH^*) - \log(CF)$

~~$10^{-\text{Conc pH}}$~~ =

$abs = \left(\frac{\text{Digital Reading}}{10}\right)(\text{Sensitivity}$

if Concentration is 10
pH changes by factor 1

~~if pH change by 11.01~~
if Conc is 11.01
then pH changes by
1.07

if Conc factor is 3.2
pH changes by .5

$\ln\left(\frac{a}{b}\right) = \ln(a) - \ln(b)$

?

$= \cancel{\ln(a) - \ln(b)}$

1.08
.60

$\log\left(\frac{12}{4}\right) = .48$

1.08

Page 232

We have some interesting work w/ rainfall samples. With 5 concentrated samples we now have

		$\bar{X}$	σ	
n=5	pH	7.1	0.3	✓
	σ	21 μS	12 uS	
	TDS (PPM) ~~(Inorganic)~~	9 Inorganic	4	✓
	Dissolve Organic Carbon (PPM)	6 Organic	8	✓
Total Dissolved PPM	~~TDS Inorganic & Organic~~	15 PPM	11	✓
TDS	~~TDS Organic~~ Ratio	71%	17%	✓
R	DOC Ratio	29%	17%	✓

Page 233

Expected Values.

5.6

~0.5

~1.0

~1.5

Davis - Org Chem Lec 2

"Enthalpy" <u>is equivalent</u> to <u>heat</u>.

It is <u>the same thing</u>! Just another word.

"Entropy" is <u>randomness</u> (also called disorder)

Gibbs ~~Free~~ Free Energy = Heat [Enthalpy] (H) − Temperature (T) * Randomness [Entropy] (S)

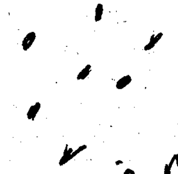
Take the difference of two equations (measurements)

$$\Delta G = \Delta H - T \cdot \Delta S$$

Heat is not temperature. Heat will be the accumulation of temperature over time.

more like:

Gibbs Free Energy = $\int$ Temp − Temp *



ie, not produced, apparently ("heat is released")

applied to:

Propane + Oxygen → CO_2 + H_2O + Heat + Randomness

Page 235

When a system releases heat, the overall heat decreases, and therefore the heat term (enthalpy) is negative.

Increasing randomness (ie more heat causes things to bounce around more)

Spontaneous reaction means that the energy of the products is lower.

1. releasing heat
2 increasing spontaneity

The "Octet Rule" should really be known as The Full Shell energy Rule

He is telling why electronegativity is increasing in the periodic table as we move from left to right. It is because the elements are accumulating more positive charge (i.e, MORE PROTONS!)

This makes sense and nobody would just say this before.

Electronegativity also increases as you go up the periodic table. Why?

" Because the electron clouds are becoming smaller, screening the nucleus from the outermost electrons the least. "

Now that is an interesting phrase to visualize.

Page 236

Fluorine is the example he gives

1. 9 protons, most within the 2nd row.
2. Small electron clouds mean that the nucleus can more readily attract electrons.

The bonding discussion by Dave is absolutely engaging. Visualization and animation are crucial to understanding here.

Now start the metals analyses of Raimunda.
Control well be distilled water from Denver.
3 Conditioning trials prior to Control run.
Control: Three matching runs.

Case 1 +3 [-3.2, 3.2]
Case 2 -3 [-3.2, 3.2]
Case 3 -3 [3.2, -3.2]

Takes a long time to stabilize. ~10 trials for each Case
Condition each sample 3 times the same way. W/ tap sample

Idaho 01 Case 1
Case 2
Case 3

Complete. Readings @

Very important

-2.56 -2.09 -.64 +.65 +1.78

Minor readings @

-1.64 ~~1.39~~ -1.45 -1.34 -.12 +.99 +1.20

double peak!
Al & Ti

$\bar{X} = 1.40$
Ti (1.37)

CO_2?
(.11)

NO?

Page 238

May 22 2016

[redacted]

2. Continue to Condense rain sample
   Combine two samples.

3. Study NP results

✓ 4. Alphabetical CDC Index Copy

5. Go to next rain sample

6. Distillation of CDB?

7. CDB Spectrum study Avagadro Construction
   Chemsketch properties, SMILES, and search.

8. DNA prep?

[redacted]

Let's work out the concentration issue.
If you have an original concentration of a volume

100 ml @ CF = 3.0
50 ml @ CF = 1.0
What is final concentration and volume?

$$= \frac{100(3.0) + 50(1.0)}{150} = 2.33$$

Yes, it is simply a weighted average.
So in our case we have 1D of 05 w/ a current concentration of:

Current wgt is ~~600~~ ~~606~~ 604
Original wgt is 441
Current volume is 167 ml
Original volume was 1143 - 441 = 702 ml
Therefore the current concentration factor is 167/702 = .238
or inversely: 4.20.
We therefore have ~~167~~ ml with a CF of 4.20.
165 163

Let's go get additional rain that has been collected
Our 2nd portion of the sample weighs: 874 w/nt lid.
Volume of 2nd portion is therefore 874 - 441 = 433 ml
If we combine we therefore have

$$\frac{163\text{ml}(4.20) + 433(1.00)}{596\text{ml total}} = \underline{1.875\text{ CF}}$$

So our net sample now has a volume of 596 ml w/ CF = 1.875

Check work 1035 gms - 441 gms = 594 gms vs 596 very good.
(new wt)

We will choose 595 ml @ CF = 1.875

Page 240

Ok, I have finally found some redox software that works! Much better!

Let's start working through ID 01 sample:

Disussion:
-2.56

Very strong peak @ -2.56

Notice we had strong peak here w/ Control also. This indicates something is happening w/ water itself since there should not be any major contaminants w/in the distilled sample. This means that we look for O & H relationships then question oxidation or reduction.

The variance of data is from -2.50 to -2.56 we can analyze an avg of -2.53.

There are no positive voltage entries here. Positive values are oxidizing agents, ie they are the stealers of electrons. Notice Fluorine & Oxygen @ the top of the list. Notice also Fe +3 (Fenton's Reagent is used in here).

This means that we are looking for a reducing agent, something that gives electrons.

Notice how so many are from Group I & II. Given what, they have electrons to give.

Page 241

Now in our case (remember that H & O should be involved) by itself, and there is nothing.
Our closest candidate is Sc, Scandium, it has an oxidation state of +3. How could this exist in the control solution? This makes no sense.
W/ an average of -2.53 our candidates are
No (-2.5) $\Delta = .03$
La (-2.52) $\Delta = .01$ → This is our closest.
Ac (-2.6) $\Delta = .07$
Sc (-2.6) $\Delta = .07$

If La were involved it would be a reduction of La^{+3}
$La^{+3} + 3e^- \rightarrow La$ (-2.52)
This is radioactive, however. This does not seem likely.

Sr-90 is a "radioactive isotope"
Ce-137
Iodine 131
But remember that our stable value is @ -2.56
and Sc reacts here.

So we have no basis for it, but our closest match is $Sc(OH)_3$

$Sc(OH_3)$ is not soluble in water, however.
It is soluble in acids. This does not fit. (But this is the metal!)

Sc is particularly prone to hydrolysis.

The halides ScX_3 $X = Cl, Br,$ or I
are very soluble in water.

Page 242

$Sc(OH)_3$ is a gelatinous white material which precipitates out in a ~~alk~~ alkaline environment. This is not happening.

We have a problem here.
+/- .645 is our next problem
It is reversible.

I is .62

Sb SbO is +.68 SbO_2^- is -.67
Sb_2O_3 is +.69

Sb^{+3} is the normal oxidation state.
Sb is antimony.

Sb not detected in the filament.
Sb_2O_3 dissolve in aqueous solution
Antimony trioxide.

This does seem like a candidate

We may have, as candidate.
(1) Aluminum (5) ~~Carbonat~~ Carbonate ~ 10PPM
(2) Titanium (4) Magnesium Carbonate
(3) Sb Antimony

~~Scandium?~~ No
Did Not Pass Test Stop — 1 Nitrates? – ~~Noxtime~~? ~~Nitrous Oxide~~
F?

Page 243

This is for ID 01! Sample

Carbonates.

OK, we have a very important result.

The carbonates are leaching out @ ~ 100 PPM.
Our concentrate is 11.24
This means that we are clearly at ~ 10 PPM
carbonates

Big News Here

So what type of carbonate is soluble in H_2O?

Ca or Mg?

$MgCO_3$ is soluble in water .1 - 1 gm/100 ml
$CaCO_3$ is v almost < 0.1 gm ml

It is magnesium carbonate

This is what is happening.
Mg -2.37 } $\bar{x} = 2.52$
-2.68

We read this

Our mean result of all ~~these~~ values is 2.
2.50
2.52
2.56
$\bar{x} = 2.53$

We appear to have the mean of Mg^{2+} and $Mg(OH)$

Deduced by solubility of carbonates

$Mg(OH)_2$ is only slightly soluble.

2.09 ±
± .64 ± -.99 are the remains ~~memories~~ unknowns
Apparently ↑
Sb ? ~~Actually this is the last~~ remaining unknowns
Antimony.

Water solubility of $Mg(OH)_2$ is 12mg/L (i.e. 12PPM)

It appears as though alkaline solution has either precipitated out w/something or filaments may be now visible now

Condense this carefully & examine under microscope

Note

We have an important reaction that has taken place.

When we

1. Add acid
2. Add base
3. Heat the rainwater

We get a pink color!

What has happened here?

We have 2 important peaks that showed up here in VIS spectroscopy

360.5 nm
364 nm
Possible Activity also @ 965 nm.

Something is going on here. ID 01 rain sample. Take a couple ml. Add HCl. Then you added $NaOH$. Then you heated. It formed a precipitate, or something?

The first time it formed a pink color, but the $NaOH$ had set quite a bit longer.

The precipitate is repeatable. The pink color is not.

May 22 (cont)

Now the Co sample

✓Case 1 +3 [-3.2, 3.2]

✓Case 2 -3 [-3.2, 3.2]

Case 3 -3 [3.2, -3.2]

We have

		U?	Mn?			
-2.90	-1.66	-1.39	-1.16	+.54	+1.32	+2.91
Ba	Al	~~Ba~~?				Ba

The combined set is now:

Ba	Mg(X)		Al	Ti	U? ~~Ba~~		Sb?	
-2.90	-2.56	-2.09	-1.66	-1.63	-1.39	-1.16	-.64	-.12
S	S	S	W	W	W	W	M	W

	Sb?					Ba
+.54	+.66	0.99	+1.20	+1.32	+1.78	+2.91
W	M	W	W	W	M	S

Continuing w/ the Sr sample: Case 1, 2, 3 ✓✓✓

Difference between the three curves can never be more than .02 V.

Now 1D02 Case 1, 2, 3 ✓✓✓

Interesting observation w/ delay. Data goes away & then comes back in. This means you must be steady & that time is a factor. Δ ≤ .02

1003: Case 1, 2, 3 ✓

We are now going to combine two concentrated sample.

Portion 1

Original Vol = 595

Curr Vol = 511 - 441 = 70 ml

$CF_2 = 595/70 = 8.50$

But $CF_1 = 1.875$

Therefore $CF_3 = 8.5(1.875) = 15.94$

Portion 2

1084 ~~1085~~ gms - 441 gms
= 643 ml

Org Vol = 706 ml

CF = 1.098

Current Volume = 643 ml

We therefore have Portion 1 @

CF = 15.94

Vol = 70 ml

If we now combine, what we will:

$$\overline{CF} = \frac{15.94(70\,ml) + 1.098(643\,ml)}{(70+643)} \cancel{15.94 + 1.098} = \underline{\underline{2.56}}$$

or

$$\frac{70\,ml(15.94) + 643(1.098)}{70+643} = 2.56 \quad CF_4$$

and Vol = 713 ml

May 23 2016

As you see, the water testing can become quite complex.

1. Trace metal analysis
2. Basic tests pH, TOC, DOC

Writing these all up

3. Then you have organics to consider & ~~that~~ takes more work to separate. Can we use a solvent? It needs a boiling point higher than water?

4. Acid base chemistry is leading to precipitation. What does this lead to? 2-4 micron spheres?

5. You have your entire water testing kit. You already learned about Carbonate from this. Why do Carbonates increase pH?

So this project could go on all summer. You have other things also to accomplish.

Other Priority Topics:

[redacted]

2. You have to write up the rainfall work or it does not help anyone.

3. Highest Priority Projects (but many others are still high)

   1. DNA work
   2. Env. Filament Work
   3. CDB & Protein Work & Lipids
   4. Rainfall Studies Complete
   5. IR Recovery
   6. Electrophoresis
   7. [redacted] Book
   8. Hair Analysis, Pyrolysis
   9. GC Skill Development

Reset the 1D 02 sample.

We currently have 472 gms w/jar
− 441 jar
31 ml sample

It definitely has a lot of color to it.
We had 713 ml
Our CF is now 713/31 = ~~21~~ 23.00
however we had an existing CF of 2.56.
Our CF* is therefore 23.00(2.56) = 58.88
And it certainly shows the color from it.

Our next, and most likely final addition is
863 ~~ml~~ w/jar gms
− 441 gms
422 gms = $\underline{422\ \text{ml}}$ of CF = 1
Therefore if we mix we have

$$\frac{\overset{\text{ml}}{422}(\overset{\text{CF}}{1.00}) + \overset{\text{ml}}{31}(\overset{\text{CF}}{58.88})}{422 + 31} = \underline{4.96}\ \text{CF}$$

w/a volume of 453 ml

This is current status.
Check on work: 893 − 441 = 452 ml ✓ OK
This is 1D 05

$\sigma = .013\,V = 13\,mV$
$n = 15$

Page 251

Our list of Elements in Therefore	n	Δ	weight n/σ
Ba	1	~~.005 0~~	~~200 ∞~~
Sr	1	.015	67
Sc	1	.04	~~25~~
Mg	1	.02	~~50~~
Sc	1	.01	2/.025 = 80
Al	1	.01	100
Ti	1	0	~~∞~~
Mn	1	.04	25
Zr	1	.02	50
Ti	1	.01	~~2/.005 = 400~~
Ga	1	.01	2/.01 = 200
	1	.01	
	1	.04	3/.02 = 150
Ti	1	.01	3/.007 = 429
Mg	1	.02	2(.02) = 100
Ba	1	.01	2/.005 = 400

Page 252

Our metals ranked therefore are

Scale to 100		Log	Score		Scalelogs	*
100	Ti	2.63	429	-1.63, -1.31, -1.23	100	100
93	Ba	2.60	400	~~Ba~~ +/- 2.90	99	82
35	Ga	2.18	~~200~~ 150	-.56, ±.65	83	69
23	Al	2.00	100	-1.66	76	63
23	Mg	2.00	100	-2.68, -2.37	76	38
	~~Sr~~		~~67~~		75%	
19	Sc	1.90	80	-2.60, -2.08	72	36
16	Sr	1.83	67	-2.89	70	58
12	Zr	1.70	50	-1.43	65	43
6	Mn	1.40	25	-1.56	53	9

What is needed next is to weight the score by the number of samples that record the metal.

Page 253

	1001 # of Samples	C001	SF	1002	1003	Σ
[illegible]	11	1		1	11	6
[illegible]	1	11	1	1		5
45	11	1		1	1	5
380	1	1	1	1	1	5
228			1	1	1	3
216	11				1	3
350	1	11	1	1		5
240	1		1	1	1	4
53				1		1

Page 254

Now we have a new ranking

Ti	100
Ba	82
Ga	69
Al	63
Sr	58
Zr	43
Mg	38
Sc	36
Mn	9

Our formula was $\text{Score} = C \cdot \overset{\log}{\left(\frac{N \cdot n}{\sigma}\right)}$

$$\text{Score} = C \cdot \log\left(\frac{N \cdot n}{\sigma}\right)$$

N = total no of matching peaks
n = no of matches within a sample
C such that $\text{Score}_{max} = 100$

We could reorder to

- Ti
- Ba
- Al
- Sr
- Ga
- Mg
- Zr
- Sc

- Ti
- Al
- Ba
- Sr
- Mg
- Ga
- Sc
- Zr

Let's determine volume & Conc. factor of 1D05 sample.

Small jar wt = 109 gms
now 297 gms
Δ = 108 ml

But originally it was 453 ml
so the initial CF is 453/108 = 4.19
However the embedded CF of the sample is 4.96
Therefore the current CF is 4.19 (4.96) = 20.78

Therefore 1D 05: Volume = 108 ml
CF = 20.78

May 24 2016

1. Completing supplemental tests on rain sample would be beneficial
Then go back to your water quality testing, you also have your water quality test kit from lab aids.

2. We have an unexpected surprise w.r.t. precipitation w/in the rain water. It appears biological.

3. Why do carbonates increase pH?

Additional priorities:
1. DNA work
2. Env. Filament
3. CDB, Protein & lipid work
   Lipid Distillation
4. Complete rainfall studies
5. IR Recovery
6. Electrophoresis
[redacted] book
8. Hair analysis, pyrolysis
9. GC skill development
10. Davis, Organic Chemistry

Page 257

2040 ~~5~~1 7.5 80 120

For ease of processing we will now combine all samples into one container po lid

	Item	¥ CF	Tot Wt	Container	Vol ml
1	1D01	11.24	266 −	176	= 90
2	Co01	22.98	315 −	round bevel 176	= 139
3	SF01	4.18	287 −	(more square) −189 bevel	= 98
4	1D02	8.19	228 −	~~189~~ 190	= 38
5	1D03	17.13	171 −	141	= 30
6	1D04	6.45	210 −	190	= 20
7	1D05	20.78	265 −	190	= 75
					Σ = 490

$$CF_{Combined} = \frac{90(11.24)+139(22.98)+98(4.18)+38(8.19)+30(17.13)+20(6.45)+75(20.78)}{490}$$

check check $= \frac{7128.08}{490} = \underline{\underline{14.55}}$

Current Volume Meas = ~~9~~ 928 − 441 = $\underline{481}$ checks OK

Page 258

We have done well, we have a supplemental section on organics to prepare.

sulfates all
phosphates 2 out of 5
nitrates 1 out of 5
Carbonates high value.

We have a spreadsheet w/ the results to report.

Now we can conduct qualitative lab-aid tests

On ammonia we are getting a positive result. It actually looks pretty strong.

These came out clear which did help.

Our ~~calibration test is not at~~ all successful
You ~~can determine the~~ concentration of this colorimetrically. You added vinegar instead of ammonia. It is a very sensitive ~~test~~. It come out brilliant orange with a concentration of ~~8~~ 10E-6 l / 5E-3 l   1 in 500

Dilution of 2000 times is 1 in 1 million

You can indeed solve for this colorimetrically.

Therefore ammonia is positive result

Page 259

1. Ammonia test complete. - Positive results.
2. pH test. Green pH ≅ 8.0

pH can be alkaline from numerous influence
1. Carbonates
2. hydroxides - metals & ammonia
3. ammonia NH_3 → ammonium hydroxide

[redacted]

3. Chlorine test is negative.

?

4. Chromium & Chromate test is negative,
Actually there is the slightest tinge of
purple in the solution after a few minutes.
Then please revisit.
Put on spectroscope.
Passes on spectroscope @ trace level!

5. Cyanide test is not entirely clean.
We also have a slight tinge of purple. Passes on spectrometer @ trace level

6. Iron test also very pale but appears positive. Spectroscope here also.

7. Nitrate test is positive

8. Phosphate test is positive. This can also be managed spectroscopically.

Page 260

9. Silica Test is highly positive

10. Sulfide test fails
[Sulfate test passes].

UV & NIR spectra run
UV 254 & UV 200 determined

+ Ammonia
Rain + Ninhydrin + NH_3 + heat = yellow color
Maybe less required?
What is causing this?

NH_3, Ninhydrin & Heat are all that is required to produce the color result. No rainwater is required.

This is not useful, therefore.

You most likely need IR.

Alchol vs Alcohol + Water

Evaporation Rate?

Eosin Test?

Page 253

	ID01	Co0	SF	ID02	ID03	Σ
	No of samples					
600	~~00~~ 11	1		1	11	6
445	1	11	1	1		5
415	11	1		1	1	5
380	1	1	1	1	1	5
228			1	1	1	3
216	11				1	3
350	1	11	1	1		5
240	1		1	1	1	4
53				1		1

May 25 2016

1. You have another arsenal to be added to the Defense of Rainfall paper. It is a strong combination. It needs to be written.

2. You started to branch off into organics yesterday and also looking @ near UV and near IR & combining 254/280 UV data for a better UV picture. I have no idea how you interpret a full UV spectra, however.

3. You have an unexpected rain - ammonia reaction.

4. You want to watch Davis organic chem.

5. Working IR w/ aqueous samples is definitely a challenge but very rewarding.

6. Alcohol + Water vs evaporation test? This is important.

You have your list:
1. DNA work
2. Env. Filament
3. CDB, Protein & Lipids work, Lipids distillation?
4. Complete rainfall studies
5. IR recovery
6. Electrophoresis

[redacted]

8. Hair analysis, pyrolysis
9. GC skill development
10. Davis, organic chemistry.

There was no discernible difference in the evaporation rate between H_2O and a 50-50 mix of ethanol a water.

How can this be??

Rain:

1. Evaporation
2. Extraction
3. Eosin

Continue alcohol w/ water mix evaporation test.

The rainwater solution, after settling for a day is less productive of filament material. The bottom sediment material however, is highly productive.
Do not heat it too high, about 80°C max.
Maybe 2 drops acid
5 drops NaOH

[redacted]

May 26 2016

Method of producing biologicals (filaments w/ proteins)

1. Concentrate rainwater 15-20x

2. Sample from sediment on bottom (there is more production but water alone is possible)

3. Apply acid (HCl to solution) - modest strength
   Shake & wait - time undetermined.
4. Apply NaOH about 2-3x that of acid.

5. Heat - about 60-80°C appears best

6. Centrifuge & isolate filamentous material

7. Record under scope @ 2000 - 5000x.
   Eosin stain appears to be beneficial?

Today we would like to get this same material under IR.
Use sediment plain & then heated w/ HCl & NaOH.

Add examples of positive test results.

[redacted]

We have a decent IR plot from the rainwater residual by:
1. Heat Treat w/ Acid (HCl)
2. Treat w/ NaOH
3. Evaporate & Powder (Filament notable)
4. Nujol required to pull out IR.

I have definitely come up with a method to isolate the filament from the general environment via rainfall.

1. Concentrate rain 15-20X

2. Collect sediment

3. ~~Evaporate~~. Add HCl 1st, then NaOH (2 to 1 acid)

4. Evaporate under 60°C

5. IR analysis shows strong phosphorus & nitrogen content

6. Visual analysis:
    1. Low power – see obvious filament network
    2. Filaments w/ proteins visible.

Consider impact of microwave.

Yes, this is the method. 1 drop, 2 drops NaOH
Extremely low power, ~2 minutes.
Actual microwave time is about 15 sec total
Absorbs microwave dramatically. Reacts identically to environmental filament.

Page 265

Diethylene Glycol

melty point?
-10°C no go

[redacted]

1. Dissolve in water w/ some effort. It make some suds, Dissolve in a wide range of solvents, includy acetone, alcohol & Xylene.

2. pH is approximately 7.1.

3. Is insoluble in
HCl, H_2SO_4 & NaOH

How do you interpret this?

4. Is soluble in Acetic Acid 28%

5. No odor

6. Index of refraction Brix is 67.9 = 1.456

7. Get boiling point. Starting near ~~145°C~~ ~155 degC

8. Electrochemistry? Pyrolysis?

9. Conductivity is 148 uS, so it has ions present.

10. No strong odor.

11. Flammable? ~~Seem to have a yellow flame.~~
Definitely not flammable, even with alcohol added.
Yes it does burn nicely when heated up w/ a torch
A yellow flame.

[redacted]

BP revisited. >165°C   > 370°F

>182   > 360°F

> 385°F

First sign of activity @ 182°C   390°F

Some bubble @ surface top

400°F

405°F

184°C   410°F

Bubbles increasing

More bubbles   415°F

425°F

435°F

187°C = 360°C   445°F

It is clearly boiling @ 184°C -187°C

Best estimate = 186°C

>189°C

It changes the more you heat the substance & it cools. You need to do it fast now.

You really should be using an
It turns dark as it oxidizes.
then is no longer the same.

Page 267

Wax is a much better medium for high boiling points. Boiling point = 370°C

Ok, all from scratch, nice and clean in wax. This is the way to do it. Also put probe directly in the tube if possible.

°C	°F	
114	310	
123	335	
127	340	
133	350	
138	360	
146	360	
146	370	
156	375	Wax is vaporizing?
156	385	
166	390	
168	415	1st bubble
166	430	
168	445	
184	452	
187 bubbles starting		
	500°	
187°C max	525	
	530°C	

Wax seem to produce quite a bit of steam.

It looks much cleaner than last. But why did vol of container increase by 50 ml 25 ml?

Just like water it reaches a maximum steady value. I wonder how much pressure change the value.

Page 268

Now for melting point..

16.1° first sign of melting
on perimeter

16.5 working inward

17.0 getting more clear.

17.5 really interior probe
18°C getting more clear in center

18.5 clear

Best estimate is 18°C

meas 1.456 error = .022

Dimethyl Sulfoxide 1.478 actual

we got 1.456

Saturated CH

$C_2H_6O_1S_1$ C_2H_6OS

BP = 189°C

IOR 1.453

$C_6H_{18}S_1$

Dibutyl Sulfide

melting point -80°C?

Density = .84

2-Amino-1-Hexanol

3 Candidates meas	186°	18°	1.456 ~1.46
	BP	MP	IOR
	Actual	Actual	Actual ~1.48
$(CH_3)_2.SO$ Dimethyl Sulfoxide	189°	19°C	~~1.478~~ 1.479
Dibutyl Sulfide	189°C	-80°C	1.453
2 Amino 1 Hexanol	190°	29°	1.452

Pressure Change → 3° is quite reasonable.

[redacted]

Subject: Mystery substance
From: Clifford E Carnicom [redacted]
Date: 5/27/2016 15:47

[redacted]

I have taken some time to revisit your problem since I did not have it before leaving for the SW, it was a mad dash in those last few hours.

I have a match on the mystery substance now, on five accounts:

1. Boiling point

2. Melting point

3. Index of Refraction

4. Solubility characteristics

5. Infrared spectrum

and the leading candidate is :

Dimethyl sulfoxide

https://en.wikipedia.org/wiki/Dimethyl_sulfoxide

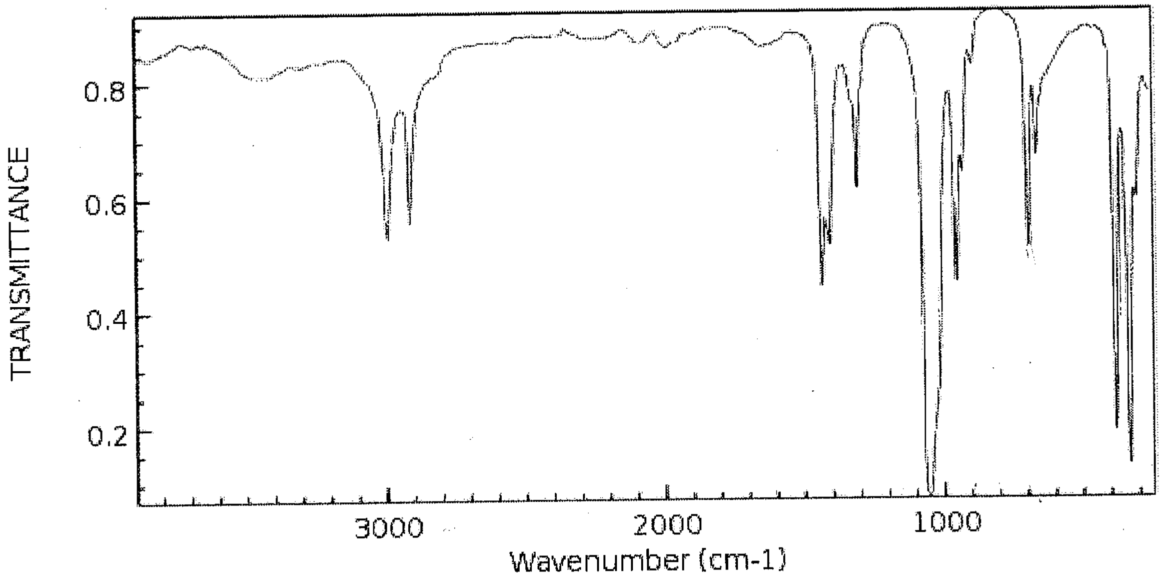
I am rather confident of the results, as it has been approached from several different angles. It also appears to be a very interesting substance. See how the properties fit on your end. I might even be able to use it here, as solubility characteristics are very unusual.

Holler if you have an interest, and I will go over the details with you. I enjoyed the problem also as increasingly it is the type of situation that I am encountering, where I know nothing and need to find out something. It has always been the case, but your material was a great example to work with.

Best to you, from Clifford

Page 269 B

SULFOXIDE, DIMETHYL
INFRARED SPECTRUM

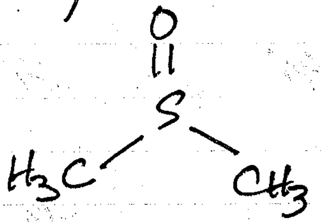


NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

May 27 2016

I have done some very good work today.
I have successfully identified the unknown mystery substance [redacted]

It is dimethyl sulfoxide



Sulfur usually makes 2 bonds
but sometimes it can make 6!
Here it made 4. How interesting.

OK, let's regroup.

IR machine is overloading sometimes. This means reduce the sample. This has already helped but crystals are dramatically attenuating the signal. I suggest

1. Increasing gain setting
2. Reducing the amount of sample dramatically

Both of these influences should help in the proper direction. Let's test it.

We are doing some testing w/ gain.
Background of double cell w/ gain 10 has also been made.

Also reducing sample to 10 ul!

Conclusion: Little material is required!

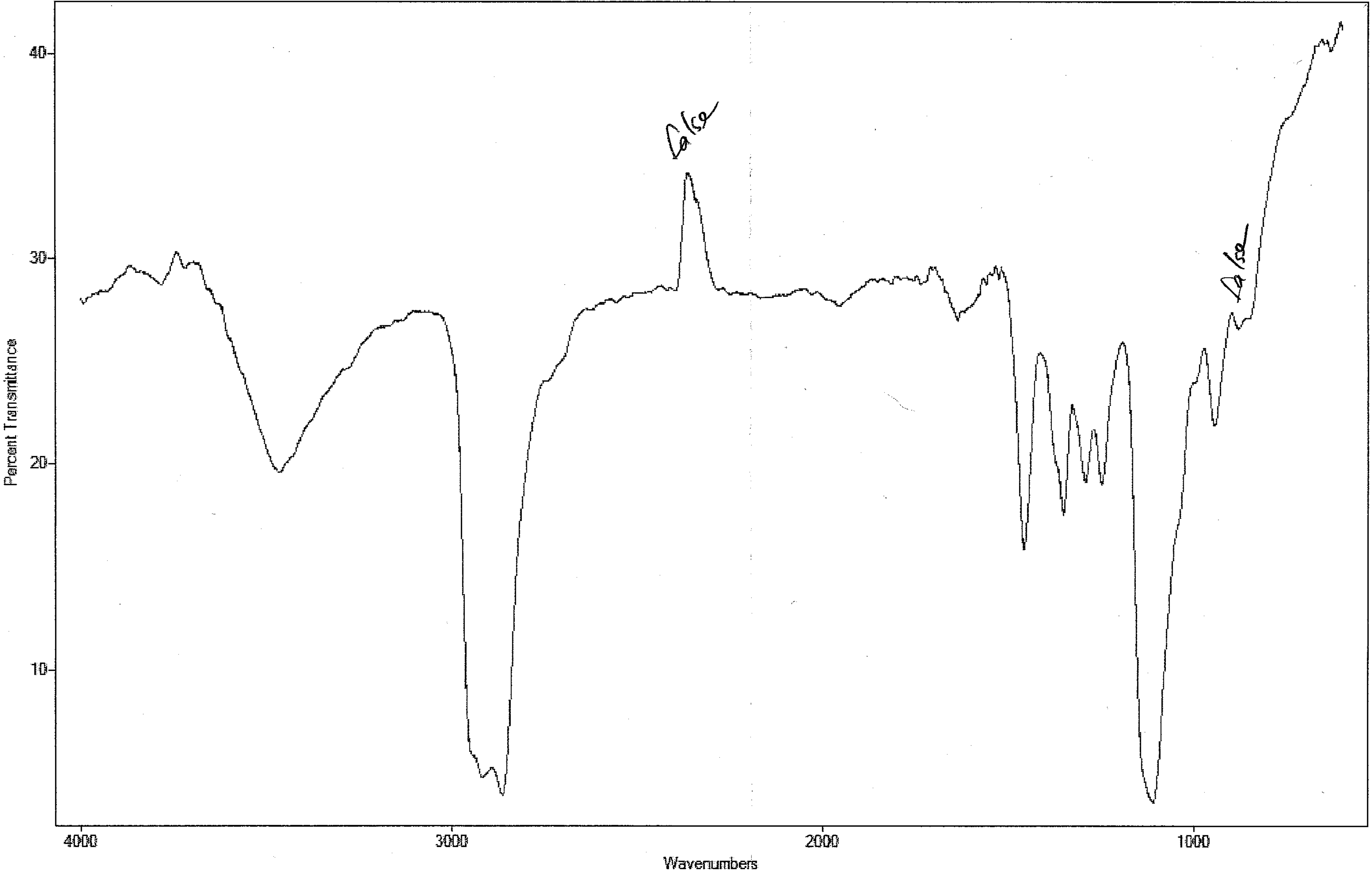
1. Very little material is required eg 10ul
   More is not necessarily ~~little~~ better.
2. Background gain 01 & sample gain 01 is usually sufficient.
3. If the signal is very weak, Background gain 10 and sample 10 might be
   But you need to be very careful with false signals from the background esp @ ~868.
4. Gain & sample must be matched.
5. You might get clipping up top w/ background 10 & Gain 10.

6 A rerun and comparison of both extractions might be helpful.

Background Gain 01 Sample Gain 01 Sample Size 10ul - May 27 2016 - 03.spc: 05/27/2016 16:50:02 title

Page 272 A

Background01
Sample 01



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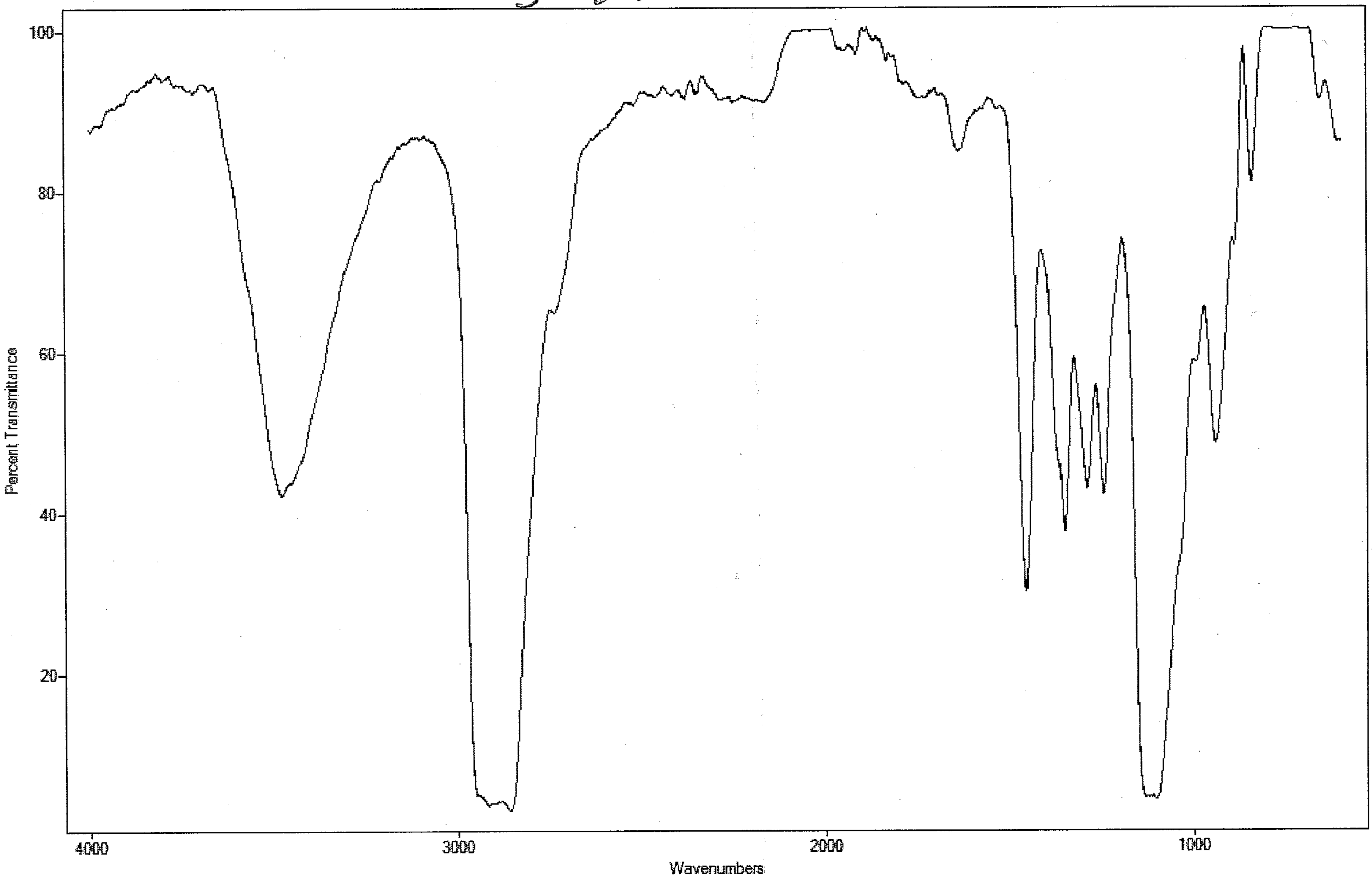
Background Gain 10 Sample Gain 10 Sample Size 10ul - May 27 2016 - 01.spc: 05/27/2016 16:37:58 title

Page 272B

Backgrund 10
Sample 10



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