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A Release of Internal Original Research Documents

Authored
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Dec 2017 – Jun 2018

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5 SUBJECT NOTEBOOK

180
SHEETS

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10.5 IN x 8 IN

LAB NOTEBOOK

VOL XXII

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Item#77186

0 26229 77186 6

Volume 22

Dec 2017
to
Jun 2018

Dec 21 2017

In Quartzsite, AZ for a spell...

I am looking @ the critical frequency, the maximum usable frequency etc.

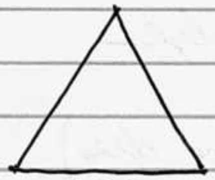
Boulder CO is listed as the nearest ionogram source.
The CF, (or plasma freq) is currently listed as ~2.5MHz. Then has dropped from ~3.3MHz ~1 hr ago.

The MUF is a function of distance (& about 6 other variables). For vertically incident waves, the MUF is the same as the critical frequency).

We are interested in the case of propagation from Quartzsite to Sacramento CA area.

Disregarding curvature.

Very good propagation take place @ ~3.5 MHz @ ~2310.



~627mi
≅1000 km

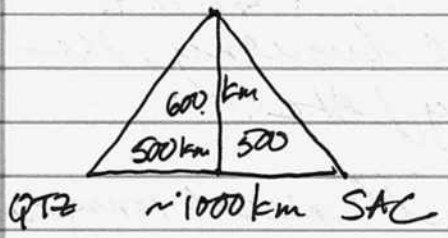
~1900 CT
today.

From real time data.

dist (km)	MUF (MHz)
0	~2.5
100	3.1
200	3.1
400	3.2
600	3.4
800	3.7
1000	4.1
1500	5.2
3000	7.9

I expect this will drop a little more as time progresses tonight.

It looks like the F_2 layer is now @ ~600 km = 370 mi



$\tan\alpha = \frac{600}{500}$ $\alpha = \tan^{-1}\left(\frac{600}{500}\right)$

$= 50.$°

Which you notice is rather close to exactly what the sloping radials of your antenna are at.

This suggests the sloping radials (esp the upper portion) might be instrumental in affecting how the antenna is working.

—

Next it would be interesting to look @ 40 meters during the day too to see if it matches Bakersfield area.

These frequencies are helpful to visualize

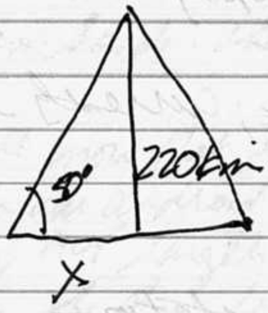
CF Critical frequency (plasma freq)
MUF Maximum usable freq
LUF Lowest usable freq

CF is measured directly w/ an ionosonde.
MUF & LUF are calculated quantities (quite complex w/ multiple variables).

Page 3

Sure enough, the F_2 layer seems to have dropped now @ 1945 CT to ~ 515 km.
The MUF has dropped from 4.1 MHz to 4.0 MHz @ 1000 km.
This is making sense. I think you can likely predict the antenna behavior.

We can already project ahead for the Bakersfield question. The height of the F_1 layer during the day is ~ 220 km.
Lets assume the takeoff angle of 50°



$$\tan 50^\circ = \frac{220\text{km}}{X}$$

$$X = \frac{220}{\tan 50^\circ} \cong 185\text{km}$$

$$2X \cong 370\text{km} = 225\text{mi}$$

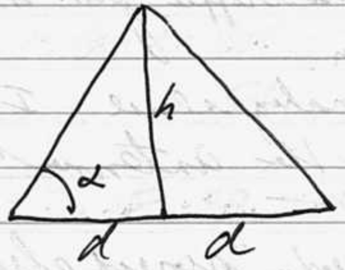
Map Quest: Dist from Quartzsite to Tehachapi.
It is 320 miles distant. This is drive distance)
Now, this is not too bad considering all unknowns @! Straight line is less.

Straight line is 260 miles

This is quite excellent. I believe the strategy and method will work.

I believe that I can make a very reasonable estimate of the optimum signal distance for my antenna.

The geometry is ~



Curvature disregarded @ this level

D = 2d

h is current F layer height
F_1 (day) (~ ~~225 km~~) (300km)
F_2 (night) (~ 600km)

α is antenna takeoff angle, currently estimated @ ~50°

d is midpoint distance
D is distance to prospective station
Highest population center @ dist D is most likely contact point.

h can be collected from the ionosonde graph.

How to convert from the MUF to the F_1 or F_2 layer? Even on an approximate level?
The Global Ionospheric Radio Observatory shows the data
(www.hamwaves.com)

MUF is a function of distance, it is not a single number.

Page 5

But remember F_2 by night, F_1 by day, no real choice in the matter

The most useful or practical data seems to be:

1. The height of the F_1 & F_2 layer (estimates are already available @ ~300 & ~600 km)

2. Your takeoff angle is recently stable @ ~ 50°

3. Next you must decide on a proper frequency to select. It needs to fall in between the MUF & LUF. Remember it is constrained by the ham bands themselves, however (eg 80m, 40m).

We all now that the optimum freq is ~ 4MHz.
(from our android software app)
This MUF largely has to do w/ the sun.
During the day it is 40 or 20 meters.
At night it is 80 m.

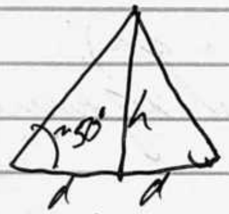
We have very good agreement between model & reality

This gives us the ability to predict our range w/ the antenna.

@2100CT now: but?

$F_1 \cong$ 275 km (stronger) (day)

Current $F_2 \cong$ 530 km (weaker) (night)



$$\tan\alpha = \frac{h}{d}$$

$$D = 2d \quad \text{or} \quad d = \frac{D}{2}$$

This means two zones are probable:

$$\text{so } \tan\alpha = \frac{2h}{D} \qquad D = \frac{2h}{\tan 50^\circ}$$

F_1: h = 275 km

D ≅ 450 km
≅ 280 mi

NIGHTTIME
(Sacramento is ~1000 km)

F_2: 530 km
(~~[illegible]~~ map) 4.3" in
D ≅ 1050 km
≅ ~~800~~ mi, 650 mi

Quartzsite to Idaho Falls Straight Line Distance ≅ 690 mi (~1.8" on map)

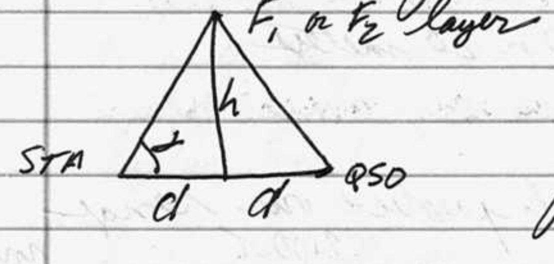
Dec 22 2017

The CF Critical Frequency (Plasma Frequency)
MUF Maximum Usable Frequency
LF Lowest Usable Frequency

are each important topics. In addition, even though the MUF is a function of more than 6 variables (the least of which may the curvature), it can actually be approximated quite well by a simple geometric relationship:

$$MUF \cong \frac{CF}{\sin(\text{Vertical Incidence Angle})}$$

In our case, the vertical incidence angle appears to be on the order of ~50°.



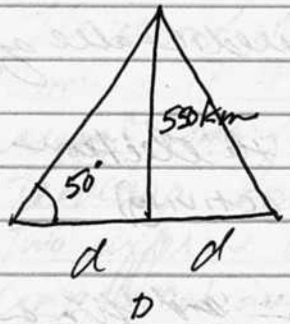
Vertical incidence angle does not approach zero because of the earths curvature.
Min angle $F_2 \geq \sim 19°$
$F_1 \geq 11°$

There appears also to be a optimum (eg @ ~ 90%) level operating frequency w/in the android software that has been acquired.

You also have gained access to an ionosonde from Boulder CO - you can see the difficulty of getting access to this instrumentation locally.

Lets look @ the current situation w.r.t. 40 meters @ ~1600CT from Boulder CO info.

Currently the CF is ~ 5.2 MHz
@ 1000 km, the MUF is 8.4 MHz which puts us w/in 40 meter range. The F2 layer center appears to be @ ~ 550 km.



$$\tan 50^\circ = \frac{550\,\text{km}}{d} \qquad d = 460\ \text{km}$$

$$D \cong 920\ \text{km}$$

So this is right within range.

This tells us that 40 m is very suitable to use right now.

We also know that current MUF for our antenna configuration is $\sim \frac{5.2}{\sin 50^\circ} = 6.79\,\text{MHz}$ which is also quite close to 40 m.

It is an interesting loop of computation.

Now lets see what android software depicts.

Page 8

Holiday season - MUF is not provided.
We need to use the 90% level, 50% is pretty worthless.
$\phi \cong 32° N$
$\lambda \cong -115W$

90% optimum operating frequency w/ software is indeed shown as a strong 7.0. MHz
We can see off the east coast of the US it has dropped to ~ 5.0 because of sun setting and in Europe (in darkness) it has dropped to ~ 3.0 MHz.

So you can see that this is a quite predictable affair and that all starts from the

1. Critical frequency (depends upon the electron density (ie sunspot activity)

and

2. The height of the F_1 & F_2 layers and from a practical standpoint the F_2 layer (the higher one) would seem to be the most important as far as distance communication goes.

You can see now why it is so difficult to acquire DX contacts under the current solar conditions, hence the development of sophisticated modes such as FT8 - WSJT.

Dec 23 2017 Page 9

Two events of interest w/ propagation & Communication last night.

1. I made it to Post Falls ID w/ 12 watts. Digital. This is quite the accomplishment. This is Pat N7UVH, who was running 50 watts. The signal reports were on the order of 569 to 579. Acceptable and amazing @ the same time. This will be of interest to look @ w.r.t. F_1 & F_2 layers. Time ~ 2300CT & on ~ 3580 kHz.

2. The second observation is that a signal on 80 meters SSB comes in @ +40dB SSB on 80 also, however the signal came from Bakersfield area. This matches the Tehachapi signal on 40 meters @ midday.
Two different bands, one night, one day w/ favorable communications to the same general location. Look @ the potential equivalency of ~~co~~ CF & MUF & F_1 & F_2 layers w.r.t. night and day propagation.
CF @ day $\cong$ 7 MHz   CF @ night $\cong$ 3.5 MHz
D = Quartzsite to ~ Bakersfield in both cases.

3. We also found an article that provides the following [illegible]:

LUF $\cong$ 0.25 CF   These could be useful as a
MUF $\cong$ 0.85 CF   starting point.

We also know, w/ greater certainty that $\text{MUF} \cong \frac{\text{CF}}{\sin(\text{Vertical Incidence})}$

or $\text{MUF} = \frac{\text{CF}}{\cos(\text{Elevation Angle})}$

How all of this work relates to CI research is through the Critical Frequency (plasma frequency) and how this is likely subject to change from the aerosol operations.

The problem is access to data. Ionosonde data is very limited in availability and there is no local access unless you happen to live in Boulder CO.

It has certainly been noticed that aerosol operations have produced a noticeable change (ie massive improvement) in HF propagation. This is in accord w/ the postulate, as well as being supported by field ion counts of increased electron density.

The answer to this question is likely found w/ repeat field msmts of ion counts. We do have the means w/ the ion counter instrument @ the lab.

We now have a series of relationships @ hand.

Of greatest suspect are the linear approximations to the MUF & LUF.

We have, therefore

CF = field measurement (ideally)
likely can be estimated from sunspot - geographic location & date models).

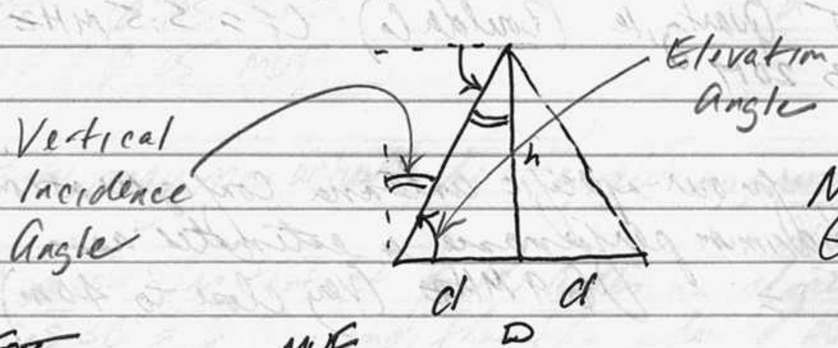
Error Found

$$\text{MUF} \cong \frac{\sout{\text{Vit}}\ \text{CF}}{\sin(\text{Vertical Incidence Angle})}$$

$$\text{MUF} \cong \frac{\text{CF}}{\sin\ \cancel{\cos}(\text{Elevation Angle})}$$

Most practical

Use! Sin not cos



Neglecting Curvature

Caution

$$\overset{\text{FOT}}{\cancel{\text{MUF}}} \cong 0.85\ \overset{\text{MUF}}{\cancel{\text{CF}}}$$
$$\text{LUF} \cong 0.25\ \text{CF}$$

Use caution w/ these.

FOT = Freq. of Optimum Traffic

I do not accept these latter approximations very easily. We know that MUF is a function of distance and that it increases w/ distance between the stations. It is not just a coefficient of the CF.

We also notice that I was using the vertical - elevation angles in reverse. Elevation angle is more practical.

We are close to 45° w/ our antenna slopers so we had no major consequence w/ the accidental reversal. But there is no further need to repeat this.

Now I have measured the slopers of the antenna design:

	Elevation Angle
Sloper 1	40°
2	30°
3	40°

$\overline{X} = 36.7° \cong 37°$

$\cos 37° \cong 0.80$

1115 CT Quartzite (Boulder Co) CF ≅ 5.5 MHz
Dec 23 2017

Therefore, for our specific antenna configuration, the maximum performance is estimated as

$\frac{5.5}{0.8} = 6.9$ MHz (Very close to 40m)

This is theoretically the ~~MUF~~ FOT, not the optimum operating frequency.

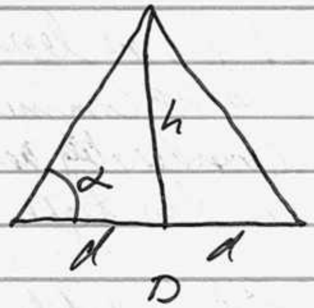
The linear estimate given as MUF =

OK, we have some adjustments to the relationships that we have identified. Time to reset.

CF = field measurement (ideally)
(possible model approach)

Sin

$$\text{MUF} \cong \frac{\text{CF}}{\cancel{\text{Cos}}\ \text{Sin}(\text{elev } \overset{(\alpha)}{\text{angle}})}$$



$\text{FOT} \cong 0.85\ \text{MUF}$
$\text{LUF} \cong 0.25\ \text{MUF}$

(These may now actually be acceptable approximations)

We know also that α for the antenna slopers ≅ 38° ($\cos 38° \cong 0.8$) and that this should determine the maximum performance of the particular antenna).

Now, what would likely seem to affect performance the most is the actual current height of the F_1 & F_2 layers. We also see that these seem to actually be reasonably stable.

$F_1 \cong 215$ km (at least so far this is what
$F_2 \cong 600$ km we see).

Another source shows an estimate of
$F_1 \cong 250$ km
$F_2 \cong 475$ km

So, we are not too bad w/ the current estimates based on actual ionosonde data.

Actually, additional important information and definitions are:
Daytime:
F_1 : 150 - 250 km
F_2 : 250 - 400 km (peak @ ~ 300 km)

Next, we learn that daytime F_1 is not important to HF communications. This simplifies matters considerably as now we know that our focus in day light is F_2 @ ~ 300km.

This establishes daytime geometry.

At night, F_2 shifts upward a bit. The overall average is best estimated for night @ ~ 330km (but it can vary between (200 - 400 km)

Now, what is really becoming interesting is the data from the actual ionogram.

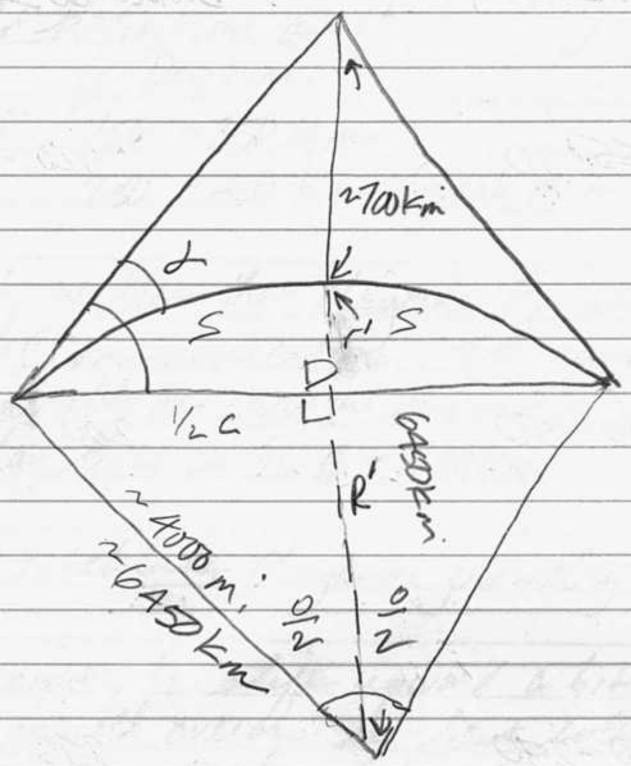
First, the D layer should be between 55-90 km.

There is no D layer visible here. The ~~D~~ lowest layer first visible ranges between 125 - 175 km.

We are seeing a major ~~soo~~ issue (discrepancy) here w/ the altitudes of the various layers.

	Layer:	ARRL (km)	Boulder Co Ionogram (km)
	D:		
Day		55-90	120-160
Night			
	E:		
Day		90-150	200 - 275?
Night			
	F_1		
Day		150-250	275 - 480?
Night			
	F_2		
Day.		250 - 400	500 - 700+ (~800?)
Night			

These numbers depart radically from expectations. Data indicates that the ionosphere's layers have been shifted substantially in their positions. This has major implications w.r.t. surveillance and energy systems developments and applications.



$2S = R\theta$

Need Chord-Arc Relationship $C = 2R\sin\frac{\theta}{2}$ (?)
from the old surveying days

$$\sin\left(\frac{\theta}{2}\right) = \frac{\left(\frac{C}{2}\right)}{R}$$

$$\frac{C}{2} = R \cdot \sin\frac{\theta}{2}$$

$$C = 2R\sin\left(\frac{\theta}{2}\right)$$ Yes, easy enough.

$$(R)^2 = \left(\frac{C}{2}\right)^2 + R'^2$$

$$(R)^2 = \left(R\cdot\sin\left(\frac{\theta}{2}\right)\right)^2 + R'^2 \quad \Rightarrow R'^2 = R^2 - \left(R\cdot\sin\left(\frac{\theta}{2}\right)\right)^2$$

$$R' = \left[-\left(R\cdot\sin\left(\frac{\theta}{2}\right)\right)^2 + R^2\right]^{1/2}$$

$R' + r' = R$ or $r' = R - R'$

Therefore

$$r' = R - \left[-\left(R\cdot\sin\left(\frac{\theta}{2}\right)\right)^2 + R^2\right]^{1/2}$$ R is known.

$2S = R\cdot\theta$ Theta is <u>in</u> radians here!

therefore $\theta = \frac{2S}{R}$ and $\frac{\theta}{2} = \frac{2S}{R\cdot 2} = \frac{S}{R}$ the angle here is <u>in radians</u>.

Therefore

$$r' = R - \left[-\left(R\cdot\sin\left(\frac{S}{R}\right)\right)^2 + R^2\right]^{1/2}$$ R is known. we only need to pick S.

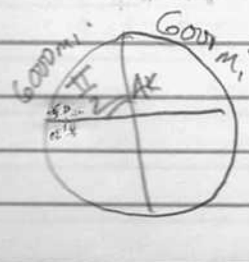
Let $S = 4000$ mi, for example. $\cong 6450$ km.

$r' = 2965$ km. So this is highly significant. $\cong 1838$ mi

if $S = 4000$ mi, then $2S = 8000$ mi, 1/3 of globe circumference.

What if $S = 6000$ mi (1/4 of earth circumference) $\cong 9677$ km

$r' \cong 6000$ km. $= 3717$ mi Why not 4000 mi? OK, we have it



$S = R\theta$ This matches OK

$S = 6450\left(\frac{\pi}{2}\right) = 10130\text{ km} \cong 6280$ mi

$$C = 2R\sin\left(\frac{\theta}{2}\right) \qquad \left(\frac{2\pi}{2}\right) = \pi$$

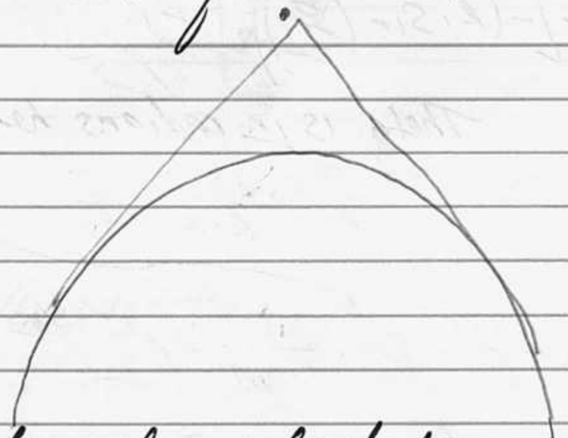
$$C \cong 2(6450)\overset{\sin}{}\left(\frac{\pi}{2}\right) =$$

$$C \cong 2(6450)(1) = 12900\,\text{km} \cong 8000\ \text{mi}$$

OK.

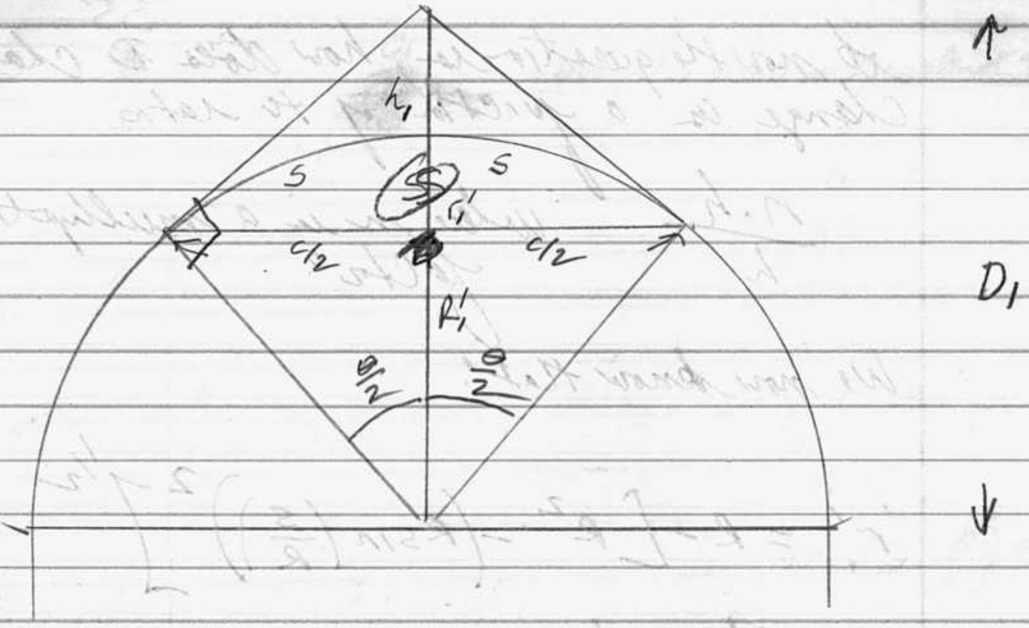
Ok, we have everything.
Once we have ~, which we do, the geometry is defined.

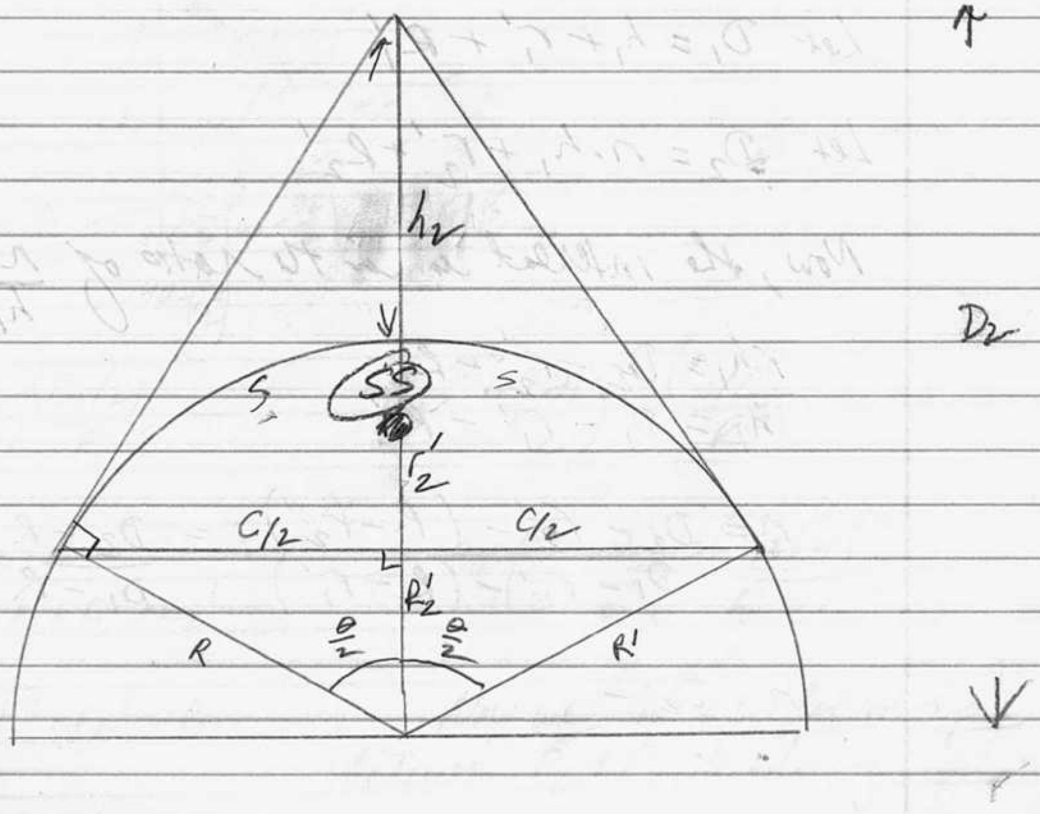
The question now is, what h is required to see the other side of the world?



Or in other words, what distance can be spanned by increasing the F2 layer from 300 to 800 km?

Page 19





So now the question is, how does SS change change as a function of the ratio

$\frac{n \cdot h}{h}$ where n is a multiplicative factor?

We now know that:

$$r' = R - \left[R^2 - \left(R\sin\left(\frac{s}{R}\right)\right)^2\right]^{1/2}$$

Now, the question is:

How does s vary with respect to n???

Let $D_1 = h_1 + r_1' + R_1'$

Let $D_2 = n \cdot h_1 + r_2' + R_2'$

Now, the interest is in the ratio of $\frac{nh_1}{h_1}$

$$\frac{nh_1}{h_1} = \frac{D_2 - r_2' - R_2'}{D_1 - r_1' - R_1'}$$

or $$n = \frac{D_2 - r_2' - (R - r_2')}{D_1 - r_1' - (R - r_1')} = \frac{D_2 - R}{D_1 - R}$$

$n = D_2 -$

What matters here is the ratio $\frac{\frac{C_2}{2}}{\frac{C_1}{2}}$ since this determines S.

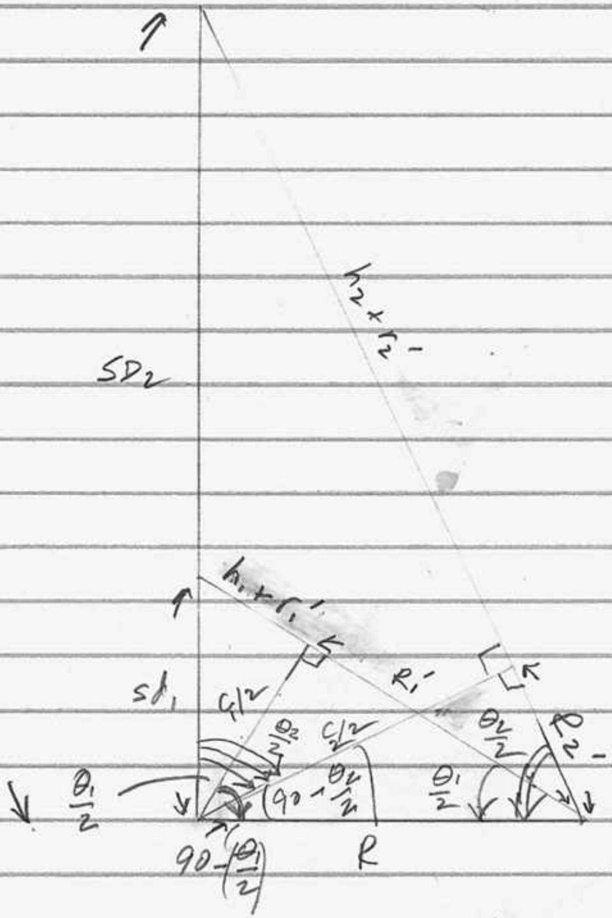
but this ratio is equivalent to $\frac{C_2}{C_1}$.

$\frac{o}{h}$ sin

$\frac{a}{h}$ cos

$\frac{o}{a}$ tan

$90-\left(90-\frac{\theta}{2}\right)=\frac{\theta}{2}$



$\sin\frac{\theta_1}{2}=\frac{(C_1/2)}{R_1}$

$\sin\left(\frac{\theta_1}{2}\right)=\frac{(C_1/2)}{R}$

so

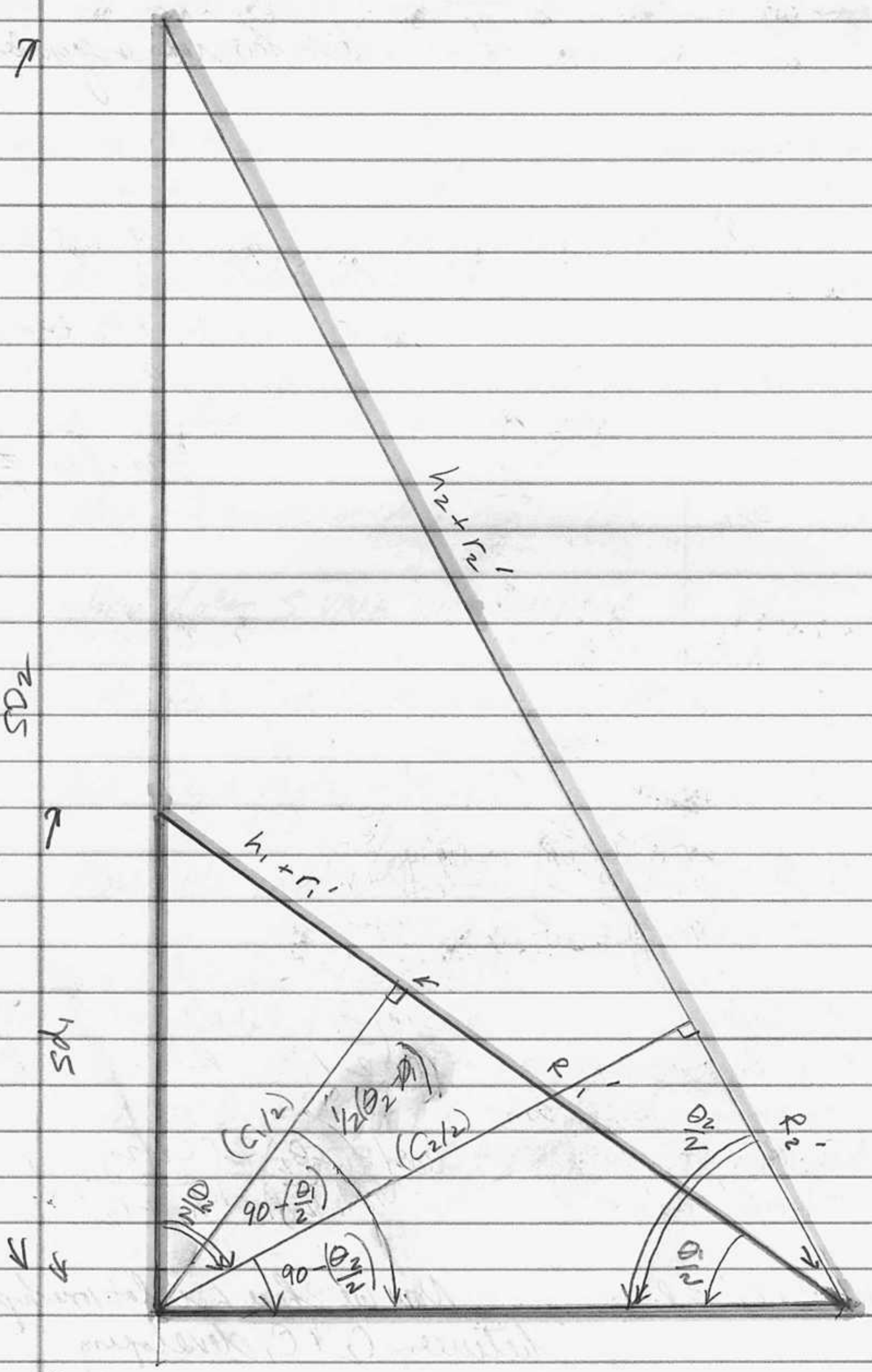
$\cos\frac{\theta_2}{2}=\frac{R}{h_2+r_2'+R_2'}$

$\cos\left(\frac{\theta_1}{2}+\frac{\theta_2}{2}\right)=\frac{(C_2/2)}{h_2+r_2'}$

but $r_2'+R_2'=R$

Now we have a relationship between C_2 & C_1 developing

Page 22



Page 23

$$\left(90-\frac{\theta_1}{2}\right)-\left(90-\frac{\theta_2}{2}\right) = 90-\frac{\theta_1}{2}-90+\frac{\theta_2}{2} = \frac{\theta_2}{2}-\frac{\theta_1}{2}$$

$$=\tfrac{1}{2}(\theta_2-\varphi_1)$$

$$\tan\left(\frac{\theta_2}{2}\right)=\frac{(C_2/2)}{R_2'}=\frac{(C_2/2)}{(R-r_2')} \quad \text{or } (C_2/2)=(R-r_2')\tan\left(\frac{\theta_2}{2}\right)$$

$$\text{or } C_2=2(R-r_2')\tan\left(\frac{\theta_2}{2}\right)$$

$$\tan\left(\frac{\theta_1}{2}\right)=\frac{(C_1/2)}{r_1'}=\frac{(C_1/2)}{(R-r_1')} \quad \text{so } C_1=2(R-r_1')\tan\left(\frac{\theta_1}{2}\right)$$

Now we have an expression for C_2/C_1:

$$\frac{C_2}{C_1}=\frac{(R-r_2')\tan\left(\frac{\theta_2}{2}\right)}{(R-r_1')\tan\left(\frac{\theta_1}{2}\right)}$$

1 radian ≈ 57.3°

and we know that

$$r_2'=R-\left[R^2-\left(R\sin\left(\frac{\theta_2}{2}\right)\right)^2\right]^{1/2}$$

$$r_1'=R-\left[R^2-\left(R\sin\left(\frac{\theta_1}{2}\right)\right)^2\right]^{1/2}$$

so

$$\frac{C_2}{C_1}=\frac{\left[R^2-\left(R\sin\left(\frac{\theta_2}{2}\right)\right)^2\right]^{1/2}}{\left[R^2-\left(R\sin\left(\frac{\theta_1}{2}\right)\right)^2\right]^{1/2}}\cdot\frac{\tan\left(\frac{\theta_2}{2}\right)}{\tan\left(\frac{\theta_1}{2}\right)}$$

let $\theta_2 = 2$ radians

$\theta_1 = 1$ radian

$R = 6450$ km

$$\frac{.62}{.47}=1.32$$

$$\frac{1.904E3}{3.092E3} \quad (2)$$

let $R=1$

$$\frac{5427}{3092}=1.76$$

so R matters

$$\frac{C_2}{C_1}=1.76$$

This needs to be plotted to find the maximum.

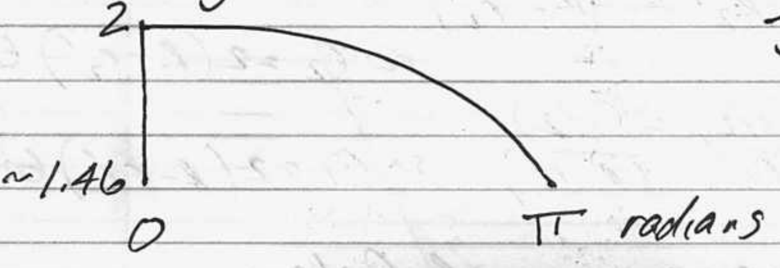
Page 24

Ionospheric Shift Investigation

The graph of the function has some interest. We are on the watch for errors. It shows a monotonic gradual decrease (non-linear)

@ $\theta = 0$, $C_2/C_1 = n$.
But logically, should equal 1.0?

eg in $n=2$



Does this seem reasonable? No....
We have now set $\frac{\theta}{2}$ fixed @ 1 radian (ie $\frac{1}{2}$)
Now we let $\frac{\theta}{2}$ vary from 1 to 2 $\frac{1}{2}$ to $\frac{2}{2}$
@ this leads to the expected results
@ ~~π~~ x = 1 radian vs ½ radian
the C_2/C_1 ratio is 1.76
exactly as computed before.

When θ goes to 3, $C_2/C_1 = 2.08$

So there are diminishing returns.

There is a slope break @ ~ 2.34

and 2.34(300 km) = 700 km.

Exactly what is happening with the data!

Page 25

You need the derivative of this curve.
Look for the slope break.
We show the slope plotted now.

@ X	y'	y''	Integral from 1.0 to	
1.04	0.91	-.3	1.04 = -.04	1%
1.17	0.87	-.3	-.18	5%
1.30	.83	-.3	-.34	10%
1.43	.79	-.3	-.51	15%
1.56	.74	-.4	-.70	21%
1.69	.69	-.4	-.89	27%
1.82	.64	-.4	-1.10	33%
1.95	.59	-.4	-1.32	.40%
2.08	.53	-.4	-1.55	46%
2.21	.47	-.5	-1.79	54%
2.34	.41	-.5	-2.03	61%
2.47	.34	-.5	-2.29	69%
2.60	.28	-.5	→ -2.55	76%
2.73	.21	-.5	-2.80	84%
2.86	.15	-.5	-3.08	92%
2.99	.08	-.5	3.34	100%

Max X possible is π radians.

The linear regression of y' shows a maximum achievement @ ~ 2.7 radians.
This is $\frac{2.7}{3.14}$ = 86% of the 1/2 circumference of the earth.

Jan 05 2017

Some interesting observations tonight.
160 m propagation - digital communication to Brookings OR went extremely well tonight.

BUT - unexpectedly.

Lets look @ critical frequency.

@ 0030 CT the critical freq (plasma freq) is listed @ ~ 2.75 MHz.
Notice this match the F_2 layer @ ~ 300 km height.

But again, notice the layer @ ~ 600 km.

We made good communications down to 5 watts tonight - a 15 watts was as stable as can be.

Next: the distance from Quartzsite AZ to Brookings OR straight line ≅ 1282 Km.

Now lets investigate the expected propagation -

$$\text{MUF} \cong \frac{\text{CF}}{\cos(\text{elev. angle})} \qquad \text{FOT} \cong 0.85\ \text{MUF}$$

$$\text{LUF} \cong 0.25\ \text{MUF}$$

$$D = \frac{2h}{\tan\alpha} \qquad \text{Avg elev angle } (\alpha) \cong 37^\circ$$

Linear Approximation applied.

Which D is closer?

F_2 ~~or "G"~~ $\qquad\qquad$ F_2^* or "G"

$D \cong 2\frac{(300 km)}{\tan(37°)} = 796 km$ $\qquad$ $D = 2\frac{(600 km)}{\tan 37°} = 1600 km$

Now, realize we are ~ 2½ hrs later than the actual QSO. This means the layer may have been a little lower.

A better estimate for the layer elevation might be.

$F_2 \cong 260 km$
$F_2^* \cong 525 km$

$D(F_2)$ $\qquad\qquad$ $D(F_2^*)$ or $D(\text{"G"})$

$= 2\frac{(260)}{\tan 37°} \cong 690 km$ (~428 mi) $\qquad$ $2\frac{(525 km)}{\tan 37} = 1393 km$ (~864 mi)

and guess which calculation is closer to the actual distance of propagation?

The proposed, and unknown "G" layer"

1393 km vs actual 1282 km — Obviously much closer. The further substantiates the behavior of the proposed "G" layer
also 2½ hrs late w/ QSO

vs

690 Km vs actual 1282 km

Very intriguing.

$$MUF \cong \frac{2.75\ \text{MHz}}{\cos(37^\circ)}\ (@\ 0030) = 3.4\ \text{MHz}$$

$$FOT = .85\,(3.4\ \text{MHz}) = 2.9\ \text{MHz}.$$

This says that 3.8 MHz really would not have been the best tonight (and it was not) and that 1.8 MHz would have been better, which it was.

Looking @ the MUF from Boulder @ the time of propagation is valuable to estimate the best band & expected distance of propagation.

Now the CF is up to 3.15 MHz. And notice that 80 m is sounding much better. This makes perfect sense.

This propagation experiment was especially interesting tonight. QRP on 160 m 1400 km from Quartzsite AZ to Brookings OR.

Notice the ionosphere is stated to extend to 650 km.

But F_2 is expected to be between 250-400 which is exactly what ARRL Handbook p 19.1 shows and says.

Page 29

So even though the ionosphere technically may extend to 650 km but the concentration of electrons is not expected to be high @ 600 km.

This is the issue.

Jan 11 2018 Quartzsite AZ

I lost resonance on the 160 meter antenna. Possibly because of rain?

Antenna study today.

Variables
  1. Variable coil at base of vertical?
  2. Addition of coil to any of wires?
  3. Check connections for oxidation?

Tuner is theoretically able to manage 1.8-30 MHz. We have the problem @ 1.8-2.0 MHz - 160 meters

Start w/ coil @ base of vertical
  Option 1: CB stick (~27MHz)
  Option 2: 20 m stick (~14MHz - no whip included)

The CB stick provides ~~initial~~ partial resonance @ ~3.7 MHz. Now lets swap to the ham stick for 20m: SWR = 4.33

The 20 m stick lowers the resonance point to 2.2 MHz w/ SWR 1.87.

This would seem to be in close range and would appear to be superior for seeking out 160 meters.

Next we combine both segments, 20m stick
& CB stick,
Our best resonance is @ ~3.1 @ ~3.5 SWR.
Notice this is the approximate mid point, it
is not lower on the band.

20m. stick should be better for 160m
CB stick should be better for 80m.

Now we have added the coil to the 72' foot wire end.
Resonance is now 1.43 @ 2.36 MHz.
So it raised the resonance point a little.

Resonance @ 2.2 MHz is now 2.7SWR so it
did raise the resonance point.

Next we place the coil @ the 52' point w/in
the long wire (72'), ie, in mid stream.

The resonance point is now 2.2 MHz w/ SWR of 1.8
So it ever so slightly decreased the resonant point
but not by any significant amount.

The ant will still not in any way tune up on 160m.

Next I have added the coil to the end of the 60' wire.
(Still no tuning on 160m)
This has almost the identical effect of adding the
coil to the end of the 72' wire. Resonance is now
1.60 @ 2.34 MHz. No significant difference
there.

Now I clip the coil onto the end of the 40' wire.

Resonance seems to be unstable and, if anything, seems to be matching the other wire effects. Thus it does not seem to matter which wire the coil is added to.

Yes, we did not have good contact. We have an SWR of 1.55 @ 2.4MHz.

		SWR	MHz	Resonance
	72'	1.43	2.36	
	60'	1.60	2.34	
	40'	1.55	2.4	
midstream	52'	1.8	2.2	

There is, therefore no real significance w/ adding the coil to any of the wires

No Coil added.	72', 60', 40'	1.87	2.2MHz

Next remove the 12' ft segment. This means we have 60', 60', 40'

60, 60, 40 1.4 2.5

This dropped the SWR a lot, but also raised the resonance point some.

We found resonance on 160 meters!!!
Now I lost it again.

Not sure why we lose it, but we do.
Now 60, 60, 40 & CB stick.

We get resonance again on 80 meters @ ~ 3.7 MHz
w/ SWR = 3.1

There seems to be no negative impact from shortening
the wire to 60, 60, 40. The transmitter & CB
stick behave the same.

CB stick seems to remain better for 80 m.
I can not seem to get the resonance point of
160 m to drop enough to bring it into range.

Back to same stick & add segment to 40'
Have added coil & 12' wire segment.
We have SWR of 1.3 @ 2.5 MHz, slightly lower.
Still does not tune on 160 m.

Next I took off the coil. I have an SWR of
~~1.2~~ 1.3~~0~~ @ 2.5 MHz. Coil is making no difference.
This configuration is the lowest even seen
antenna thus far.

I have resonance @ 1983 KHz! High end
of band
Inductance = K
Transmitter ≅ 0.2
Antenna ≅ 1.0

But I lost it again.

For now I am settling on

	SWR	MHz
2 60' lengths	3.4	3.7 MHz
1 40 length.	~3.0	7.1

These is not bad! W/ the CB Stick

Cannot however, pick up 160 meters. Not the 20 meter stick!

Jan 12
~~Dec 13~~ 2018

I have added 50' segments to the primary 40' segments of the antenna. This now gives three segments of 90' in addition to the vertical section.

Partial resonance came in @ 1.8MHz @ SWR ≅ 9.0 (<10). This is a favorable sign. This is using the 20m hamstick.

Unfortunately, the antenna will still not tune @ 160 meters. I believe the limitation is coming from the tuner, not the antenna.

Inductance for 80m tuning can now drop to H setting instead of I.

I would require a separate antenna to test the idea of the tuner problem.

—

The antenna has worked quite well today on 40 meters to the Jefferson Noon Net.

Jan 13 2018. Page 36

I have removed two 50' segments from the antenna.

The tuning settings remain identical on 40 meters regardless of this change.

The first partial resonance came in on 40 meters @ 7.1 MHz @ SWR of 9.5
Actually 7240 KHz @ SWR 8.8
Therefore the antenna is closer to resonance on 40 meters than 160.

Lets work out the calculations.

20m stick:

$$\frac{1}{4}\text{ wave} = \frac{0.5\,(468)}{14.2\text{ MHz}} = 16.5\text{ ft}$$

subtract 4.5 ft whip = 16.5 - 4.5 = ~~9~~ 12 ft
Vertical is ~ 32' high physically.

The vertical section electrically is

32' - (4.5' (coiled ham stick)) + 12' (electrical equiv. of ham stick)

* = 39.5 ft ≅ 40' electrical vertical equiv. w/ hamstick

Now we have 40' + 40' + 90' slopers = Σ 170'

Total electrical length ≅ 170' + 40' = 210 ft

1/2 wave resonance estimated $\cong \frac{468 \text{ ft}}{210 \text{ ft}} = 2.3$ MHz.

1/4 wave resonance $\cong .5 \frac{(468)}{210} = 1.1$ MHz

Full wave: $2\frac{(468)}{210 \text{ ft}} = 4.5$ MHz. This is closest match

Now, if we take average of slopers: $\frac{40+40+90}{3} = \cancel{110}\ 57'$

4.8 MHz

$\frac{\cancel{2}(468)}{40+57'} = \cancel{8.2}$ MHz. ~~This is reasonably close.~~

What if we chose weighted average: ~~$\frac{2(40)+1(90)}{3} =$~~

This suggests avg of slopers may come closer to indicating the resonance point.

If we had 3 40' segments, $\bar{x} = 40'$.

40 (vertical segment) $+ \overline{40}$ (slopers) $\Rightarrow 80'$

$\frac{468}{40' + \overline{40}'} = \cancel{11.1 \text{ MHz}}\ 5.85$ MHz.

Ok, we have identified a essentially perfect linear relationship with respect to the antenna total length and the resonant frequency.

The three data points are as follows

Total antenna length: (using 20m hamstick)	Lowest SWR
40' (hamstick+vertical) + 3(90') = 310'	1.8 MHz Still high, however (~9.5)
40' (hamstick vertical) + ~~80'~~ 40'+40'+90' = 210'	7.2 MHz (~8.5 SWR)
40' (hamstick vertical) + 40'+40'+40' = 160'	10.1 MHz (~1.5 SWR)

$$\text{Resonant Freq}^{\text{MHz}} \simeq -.055 \cdot \text{Total Length} + 18.866$$

$r^2 = 0.9997$

$$\text{Total Length} \simeq -18.13 \cdot \left(\begin{array}{c}\text{Resonant}\\ \text{Freq MHz}\end{array}\right) + 342.09$$

$r^2 = 0.9997$

1.9 MHz w/ 2 coils

Therefore Total Length for a 160 m antenna @ 1.8 MHz
are

160m (MHz): $TL = -18.13(1.8\,MHz) + 342.09$

$= 310'$ as shown.

We have the relationship identified. It is of interest that the $40' + 3(40)'$ is also resonant @ 2.8 MHz

* This could definitely be an advantage for 80m.

We are also interested in the wavelength ratio of resonance
eg.

full wavelength length for 7.2MHz is $\frac{2(468)'}{7.2\,MHz} = 130'$

Our antenna is 210' $\ni \frac{210}{130} = 1.62 \cdot \lambda$

$= 1\frac{5}{8}$ wavelengths for 40m.

for $\overset{160}{80}$m. We would need 894' Total length (Each Slope = 285')

for 30m. $= \underline{1.72\,\lambda}$

If SWR is higher on the high end of the band than the low end then the antenna is too long.
We have a fortunate sequence of resonance occurring w/ the tuner near 1.8 MHz.
Add a short segment of wire to see the effect.

I have done it!

I now have 160 meters w/ a tunable antenna.

I now have a perfect 1.1 SWR @ 10.5 MHz

and I have tunable w/ the tuner 160m!

The entire range of bands should now be operative.

The solution was to add 2 coils at the end of separate 40' sloper segments. About 1/3 of each sloper is now on a 2" coil form.

What is our ratio of the wavelength for 160m?

Antenna is ~ 40' (vertical) + 35' + 35' + 40' $\cong$ 150'

λ for 160m $= \frac{2(468)}{\sim 1.85\text{ MHz}} = 506$ ft

$\frac{150}{506} \cong 0.30$ wavelength. $\cong$ 1/4 wavelength

Now for 30 m which also has a low SWR our ratio is:

Total length $\cong$ 160' λ of 30 m = $\frac{2(468)}{10.1} \cong$ 93'

$\frac{160'}{93'} = 1.72\lambda$

This may well be equatable to a $1\frac{5}{8}$ wavelength antenna w/some loss of efficiency.

The 40 m ratio is 1.62 which is indeed $1\frac{5}{8}$ wavelength.

Verticals are commonly $\frac{1}{4}$ & $\frac{5}{8}$ wavelengths.

—

Technically, if I want to improve matters I add one 50' segment to bring in resonance @ 7.2 MHz & also improve 80 meters. I am not sure how important this is, however, but it might help.

—

I have learned a great deal about the performance & resonance behavior of this antenna.

For 80 m & 40 meters, (2) 40' sections and (1) 90' section will be required.

For 160 m you will actually only use the 40' sections w/ the tuning coils added and it will flip to a $\frac{1}{4}$ wavelength mode.

2(90') sections are probably best for 80 m but it will be extra trouble.

The behavior of resonance w/ total length of 1 5/8 wavelength is unexpected but quite real.

We therefore have two modes of operation ~1 5/8 λ for ~~160 m~~ 80-40λ-30 m and 1/4 λ wavelength for 160 m w/ tuning coils.

You can compromise as well, and conditions will dictate how much of a compromise there will be.

Current CF is: ~6MHz 5 MHz
Boulder station gives: 5.96 MHz.

$$MUF \cong \frac{5.5\text{ MHz}}{\cos 37^\circ} \text{ @ 1500 CT} = 6.9\text{ MHz}$$

$$FOT = .85(6.9\text{ MHz}) = 5.8\text{ MHz}$$

This is why 40m is so marginal right now.

$$h \cong 325\text{ km} \quad D \cong \frac{2h}{\tan 37^\circ} = 862\text{ km} = 535\text{ mi.}$$

but not reachable on 40 m well.

It is noted that I could not reach the 40m net w/out adding the longer 50' section to create 1 90' ft section.

The NCS which heard me is in Twin Falls ID.
~~K7~~ A7CM "DOC"

Sure enough Twin Falls looks to be closest to ~535 mi.
So everything is matching quite well.

The steeper part of the sloper (eg $\alpha \doteq 50°$ or so) will favor propagation toward the shorter distances.

—

A question is, even though you would like 160 m to work, how practical is it to change the antenna configuration to achieve it?
The 40 m configuration seems to be the best compromise antenna.

For 80 m we would (or should) add another 50' section. Not essential but helpful.

Jan 14 2018

I would like to look at the question of 0.30λ vs 0.25λ.

Single wavelength for 160 m is ~ 506'

$\Delta = .05\lambda$ $\quad .05(506') = 25'$

You do not have any uncertainties of measurement of this magnitude. Therefore the antenna is only approximately 1/4 wavelength.
For now, we will assume a resonant freq occurs @ only approximately 0.30λ vs 0.25λ

Interesting observation on the tuner capability. With 2 tuning coils we can tune between 1.8 & 1913 KHz. The tuning capability of the radio can be added to that of the conventional tuner to increase the range from 1.8 to 1870 KHz to 1.8 to 1913 KHz - enough to make an important difference for SSB activity.

It is best to use the conventional tuner for tuning but for final adjustment use the SWR meter or the radio's for final tuner reading. Do keep it less than 2.0. SWR on radio is very handy.

Resonance center is ~ 1850 KHz ± ~ 40 KHz to hold SWR < 2.0. Not a bad choice.

Jan 15 2018

I now have an antenna that is resonant on 160m and tunable across the band.

To raise resonance freq: add more turns on loading coils
To lower resonance freq: remove turns from loading coil.

Three coils on 3 slopers allow for tuning across the entire band. The two tuners (MFJ & Yaesu) can be stacked up on each other.

The band will therefore perform from 160m to 20m w/out a problem.
Performance can be enhanced by adding a 50' wire to the sloper of choice.

We now have $\sim 40' + 3(40) - 3(5') = 145'$
Our approximate resonant freq is:

$$-.055(145) + 18.666 = 10.69 \text{ MHz}$$

This is a fairly decent choice between ~4 & 14 MHz
Midpoint is 9 MHz.
This is out of the ham bands so we need software to determine.

If you add a 50' segment, the resonance pt is

$$\sim -.055(195) + 18.666 = \underline{7.94 \text{ MHz}}$$

Which is better for 40 & 80m.
but it is tunable across the entire range
2 (50') segments: $\cong -.055(245') + 18.67 = 5.2 \text{ MHz}$
(better for 80m)

Page 46

Another extraordinary QSO tonight on 160 meters. Digital 15 watts w/ reliable communication to Brookings OR. Time ≅ 1 hr, no losses.

CF @ ~~18~~ 0615UCT (0015CT) is 2.3 MHz.

Error

~~CF~~ = $\text{MUF} = \dfrac{CF}{\underline{\underline{\sin}}\ \cancel{\cos}\,\alpha}$ $\alpha \cong 37°$

Actually steeper, so closer to 45°.

$\text{MUF} \cong 3.25\ \text{MHz}$

Use sin. not cos!

$\text{FOT} = .85\,(3.25) = \underline{\underline{2.76\ \text{MHz}}}$

80 m performance was poor & the FOT predicts that result.

$D = \dfrac{2h}{\tan\alpha}$ two options: $h_1 = 325\ \text{km}$

$h_2 = 550\text{-}600\ \text{km}$

$D_1 = 650\ \text{km} = 403\ \text{mi}$

$D_2 = 1150\ \text{km} = 713\ \text{mi}$

Dist from Quartzsite to Brookings OR: 798 mi

Guess which is closer again? D_2, ie, h_2. Which, by conventional sourcing

h_2 should not exist. ???

I got the antenna analyzer software working again via the Windows Compatibility Checker. Not sure what settings it actually used or saved, but it is working now!

2 Points of resonance: ~ 8MHz & 16MHz.

		SWR
We have two points @ ~8MHz:	7.7 MHz	3.0
	8.4 MHz	2.0

Would be nice to get points @ 7 & 14 MHz but that would require adding more wire.

We estimated 7.94 MHz vs actual 8.4 MHz. Not bad @ all.

actually lowest calculated SWR = 2.0 @ 8.4 OK.

Different results now: ~2MHz & ~10 MHz
This actually makes more sense.

2.90MHz   Laptop battery is out.

1.16 SWR @ 2.95 MHz
1.54 SWR @ 11.125 MHz

@11.125 MHz this means that the effective length of the antenna is now:

$-18.13(11.125\ \text{MHz}) + 342.1\ \text{ft} = 140.4\ \text{ft}$

Your estimated length was ~~140'~~. 145'. Very close!

How much wire would need to be added to bring resonance to 7.2 MHz?

$-18.13(7.2) + 342.1 = 211.6$ ft

$$\begin{array}{r} 211.6 \\ -\,145 \\ \hline =\ 66.6 \end{array}$$ ft additional.

This would mean that we add one 50' segment plus one 17' segment. We have a 20'. Therefore if we add 70', we'll have

$-.055(145+70) + 18.87 = 7.04$ MHz.

Certainly not bad.

Add $\left.\begin{array}{l}\text{1 50' segment}\\ \text{1 20' segment.}\end{array}\right\} \Rightarrow 7.04$ MHz

If you only add 1 50' segment, we will have

$-.055(145+50) + 18.87 = 8.14$ MHz

Therefore only

Jan 18 2018

I have achieved 160m w/out the tuning coils. The coils were complicating the installation and compromising the structural integrity.

Resonance has been achieved w/ 3 (60') slopers + the vertical segment ≅ 180 + 40' ≅ 220' ft.

160m wavelength ≅ 2 (460) ≅ ~~243' ft~~ = 506'
~~3.85MHz~~ 3. 1.85MHz

220 / 506 ≅ 0.435 λ

It simply appears to be sufficiently close to ½ wavelength to be w/in the range of the MFJ tuner or @ high end (of ~~3.95MHz~~ 1.95MHz) MFJ + Yaesu FT450D tuner.

The model predicts a resonant frequency @~

MHz -.055 (~220') + 18.67 ≅ 6.57 MHz.

Measure w/analyzer:

Actual resonance occurs @ 9.61MHz (~30m) @~1.8MHz

This is higher than expected but still very usable.

This suggests that each installation may have its own unique resonance relationship (presumably linear).

Jan 22 2018

The antenna is working superbly & performing unusually well. If I can hear most any station @ S5 or higher I seem to be able to work with them in all cases w/ lower power (12-30 watts).

Lets measure SWR and look @ the wavelength relationship.

Ant is resonant @ 2.41 MHz @ SWR = ~~2.16~~ ≤2.00

Ok, what wavelength is this?

$$\lambda = \frac{2(468)}{f_r\,(\text{MHz})} = \frac{2(468)}{2.41\ \text{MHz}} = 388'$$

Our wire is ~40' + 3(60) = 220'

$\frac{220}{388}$ ~~$\frac{388}{220}$ = 1.76λ = 1 3/4 wavelength.~~

0.57λ = Close to 5/8 vertical

We have seen this before.

What would be 1/4 wavelength?

$$4\left(\tfrac{1}{4}\right)220 = 880' = \frac{468(2)}{880} = 1.06\ \text{MHz}$$

If we were to remove 20' segment we have

$\sim 40' + 3(40) \cong 160'$

$2\frac{(468')}{160'}(1.75\lambda) = \overset{3.6\text{ MHz}}{\cancel{10.2}}\text{ MHz}$ which is also what we have seen before.

For 1/4 wavelength resonance: ~~4(46~~ $\frac{2(468)}{4(160')} = 1.46\text{ MHz}$.

This is why 30' segment brought resonance into 160m range

Our regression equation is:

Total length $\cong -18.13\,(\text{Resonant freq in MHz}) + 342.09$

or

Resonant freq $\cong -.055 \cdot \text{Total length} + 18.866$

Therefore total length estimate $\cong$

$-18.13(2.40\text{ MHz}) + 342.09 = 299'$

This will need to be reexamined @ some point.

This is off a fair amount from the measured 220' actual length. I have no explanation for this.

For 160m: $\frac{2(468)(.625)}{1.8\text{ MHz}} \cong 325'$

40m: $\frac{2(468').625}{7.1\text{ MHz}} = 82.4$

$\frac{82.4-40}{3} = 14'$

Radial slopers are therefore $\frac{(325-40)}{3} = 95$ feet would be required for a resonant 3/8 wave 160m antenna.

Next we look @ 5/8 wave for 2m against the CB band.

CB ≅ 27.2 MHz
2m ≅ 146 MHz

$(\tfrac{1}{2}\lambda)\ f_r = \dfrac{468}{f(MHz)}$ or $f_r(2\lambda) = \dfrac{2(468)}{f(MHz)}$

and $\tfrac{5}{8}\ f_r = \dfrac{2(468)(.625)}{f(MHz)}$

for 2 meters $= \dfrac{2(468)(.625)}{\cancel{27}\ 146MHz} = 4.01'$

for CB: $\tfrac{1}{4}$ wave $= \dfrac{0.25(468)}{27.2MHz} = 4.3'$

Therefore a CB antenna shortened by ~ 3.5" Will make a 5/8 wave 2 meter vertical. But it is not <u>resonant</u> and requires a coil but a CB antenna has one.

But this is only in theory & it would <u>not</u> be resonant.

Jan 28 2018

Some recent assessments on the antenna.

When the 27MHz (CB) stick is being used the antenna is resonant @ 3.7MHz (80m) and 7.4MHz (40m).

Use of the 20 meter hamstick lowered the resonance point from 3.7MHz to 2.4MHz.

When you added a 50' coil to one of the slopers it did not significantly change the resonance point, but it did generally broaden the curve.

I have reestablished resonance on 160 meter w/ the use of two loaded coils, 50' each, one on each end of a sloper.

The use of three loading coils actually caused a deterioration in SWR. Best performance is with two.

Feb 02 2018

A major 160 m resonance project today. Our goal is to see if we can bypass the tuner since it seems to be unable to handle it.

We will have a higher interest in 1/4 & 5/8 vertical antenna resonant points & any that show up w/in the investigation.

Scenario 1:
20 meter stick + 3(~40') segments + vertical segment.
Resonance ≅ 2900 KHz.
We can assume an arbitrary total length & look @ it from a differential viewpoint.
There is a smooth broad peak from approx 2.7-3.1 MHz.

Now let's change to the whip alone.
Scenario 2:
Whip segment + 3(~40') + vertical segment.
For some reason, I did not envision this scenario in the past sessions but it is valuable to eliminate any coil inclusion.
This has bumped up resonance to ~ 3.75 MHz
With a range of ~ 3.45 – 3.9 MHz.
This is a fine 80 m ant as it stands.

Scenario 3:
CB whip + 3(~40' segments) + vertical segment.
Resonance is now @ ~4.15 MHz.
Very intriguing that it increased the resonance point rather than settling in between the results from the 20m stick & whip section only. This was unexpected.

Nevertheless, our first and primary reference point is with the use of the whip alone - no coils.

$f_r = \frac{2(468)}{3.75 \text{ MHz}} = 249.6'$ for a full wavelength ant.

Actual estimated length is ~32' + 3(40) = 152'
$\frac{152}{249.6} = .61\lambda$ $\quad\quad 5/8\,\lambda = 0.625\lambda$

This says that our reference point of resonance is most likely to be a 5/8 wave vertical

This may cause a problem. What is the length of a 5/8 160 m antenna? $\frac{2(468)(.625)}{1.8\text{MHz}} = 325'$

We already have ~152'. 325' - 152' = 173' needed
Each sloper would be an additional 58'.

Lets see if the relationship holds: (It did not so far in the past, you only made it to ~2.2 MHz.

I have added 1 (13') segment: But w/the CB Stick!
It is now resonant @ ~ 4.05 MHz.
~~It was~~ resonant @ ~~3.75~~ MHz. 4.15 MHz
~~This is therefore not what I expected~~. OK, a minor effect.

~~Now lets add another segment of~~

You need to work w/the whip as the reference.

Scenario 4:
Whip + Vertical segment + 13' + 3(~40'):
Resonance @ ~ 3.4 MHz w/ range of 3.3 - 3.6 MHz.

Scenario 5:
20 Ham Stick + 3(~40') + 13' + Vertical segment
~2.7 MHz w/ range of 2.6 - 2.8.

Notice very little difference here.

Scenario 6:
20 Ham Stick + 2(13') + 3(~40) + Vertical Segment:
~2.7 MHz.
Notice that it is not going any lower.

Scenario 7:
Whip + 2(13') + 3(~40') + Vertical Segment:
~ 3.3 MHz.
Therefore it is clearly not linear.

Scenario 8:
CB Stick + 2(13') + 3(~40') + Vertical Segment:

Lets look @ whip scenarios alone.
Lets call the whip + vertical segment + (3)(~40') segments as a reference length called TL.

Length	Resonant Freq (MHz)	Full Wave Resonance λ
TL (~152')	3.75	~~249.6'~~ 250'
TL + 13'	3.4	275'
TL + 26'	3.3	284'

Linear estimate is sufficient @ this point.

λ_r ~~Resonant Freq~~ $\cong -74.5 \cdot \underset{\text{Resonant Freq}}{f_r} + 529.1$ $\quad r^2 \cong .998$

$\lambda_r \cong 395'$ for 160m.

Assume we have TL = 152' ∴ 395 − 152 = 243' 243/3 = 81'
This means that 81' slopers would need to be added and this assumes the relationship is linear. This will never work.

We must now consider shifting from a 5/8 λ scenario to a 1/4 λ scenario. Look @ CB whip data.

Length	Resonant Freq	Full Wave λ	1/4 wave λ
TL w/CB	4.15 MHz	226'	
TL w/CB + 13'	4.05 MHz	231'	
TL w/CB + 26'	3.95 MHz	237'	

Next look @ 20 meter stick data

	Resonant f_r (MHz)	λ	¼ Resonance
TL + 20m	2.9 (MHz)	323'	
TL+13 +20m	2.7	347'	
TL+26' +20m	2.7	347'	

Notice it does not drop any lower.
We will assume 5/8 resonance is achieved @ 2.9MHz.

$$\frac{\text{1/4 resonance}}{\text{5/8 resonance}} = 0.40 \text{ factor}$$

This means our resonance for ¼ wave would be achieved @ ~ .40 (323') = 129.2'

So we have $\frac{2.9 \text{ MHz}}{129.2'} = \frac{1.8 \text{ MHz}}{x}$ $x = 80'$

But our actual length of wire for TL is ~ $(12' + 32' - 4) + 3(\sim 40) = 160'$

So this is actually ~ $\frac{160}{323} = 0.495\lambda$

Which is almost exactly a ½ wave phenomenon

Now for 160m, full wavelength is ~ $\frac{2(468)}{1.8 MHz}$ = 520'

1/2 wave = 260'

We have ~ ~~323'~~ 152'

Therefore this suggests 260 − 152 = 108 108/3 = 36'

This suggests if we add 3(~36' lengths) we may achieve resonance on 160 m.

This raises some questions. We now have evidence of 1/4, 1/2 & 5/8 resonance points being achieved @ various occasions. We want the antenna as short as possible. We already see we'll have 80 m w/ the whip alone + 3(40' segments).

Let's back up. We have good 80 m resonance w/ three 40' segments. ~3.75 MHz.

$\frac{2(468)}{3.75} \cong 250'$ Actual length estimates

~32' + 3(40) = 152'

$\frac{152'}{250'} = 0.61 \cong$ 5/8 wavelength.

Therefore if we used on 160 m we have an ~ 0.30λ. This means an adjustment of 0.05 wavelength is all that is required. This is nevertheless ~25' on 160 m. This is about exactly what we found w/ our coils.

OK, we see some net results here.

We are in very good shape up through 80 meters. 160m is a no go w/out considerable complications or exploring an alternate tuner.

The whip + vertical + 3 (~40') slopers is adequate for 80m. Tuning w/ the tuner is much broader than w/ the radio alone. We notice that inductance on the tuner is @ a higher setting w/ the use of the whip than w/ the coil section. (It is now required)

The region of coverage for the antenna may have changed from use of the shorter configuration. Intermountain area coverage appears to be stronger now vs the California region from the longer configuration.

Feb 20, 2018

Because of high winds (50-55mph) I have constructed an alternate antenna w/a simpler and lower profile.

It was done by complete instinct, whim and with an ARRL conceptual diagram.

The astounding fact is that the antenna, as constructed from scratch, is immediately resonant on ideal portions of 80 & 40 meters.

This is an amazing serendipitous act.

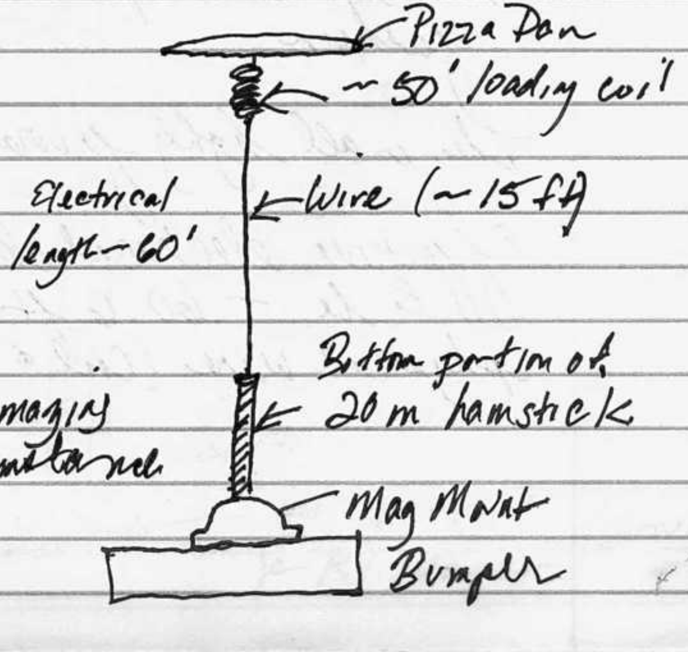
80m: SWR = 1.18 @ 3860 kHz
<2. to 1 from 3820-3900 kHz.

This antenna has a high Q factor.

40m: SWR 1.21 @ 7320 kHz
<2 to 1 from 7100 — 7500 KHz.

General drawing
(Total length ~20')
Wire and loading coil are attached to a 20' extendible mast (painters pole).

This appears to be an amazing achievement by circumstance esp. suited to mobile applications.



Lets compute the estimated wavelength fraction for 80m:

Coil ~ 50'

Hamstick section: $\frac{468(.5)}{\sim 14.2\ \text{MHz}} = 16.5'$ - Missing 4.5' Whip

$\cong$ 12 ft.

Straight wire ~ 15'

$\Sigma = 50 + 12 + 15 \cong 77'$

Wavelength for 80m $\cong \frac{2(468)}{3.86\ \text{MHz}} = 242.5'$

$\frac{77'}{242.5'} = 0.32$ wavelength.

Therefore our best estimate is that a $\frac{1}{4}$ wavelength ant for 80m has been created and a $\frac{1}{2}$ wave for 40 m has been created, both in a vertical fashion.

These are all highly favorable.

Effective electrical length is estimated to be ~.60.6 ft vs the estimated physical wire (coil & non coiled) of ~77'.

Page 63

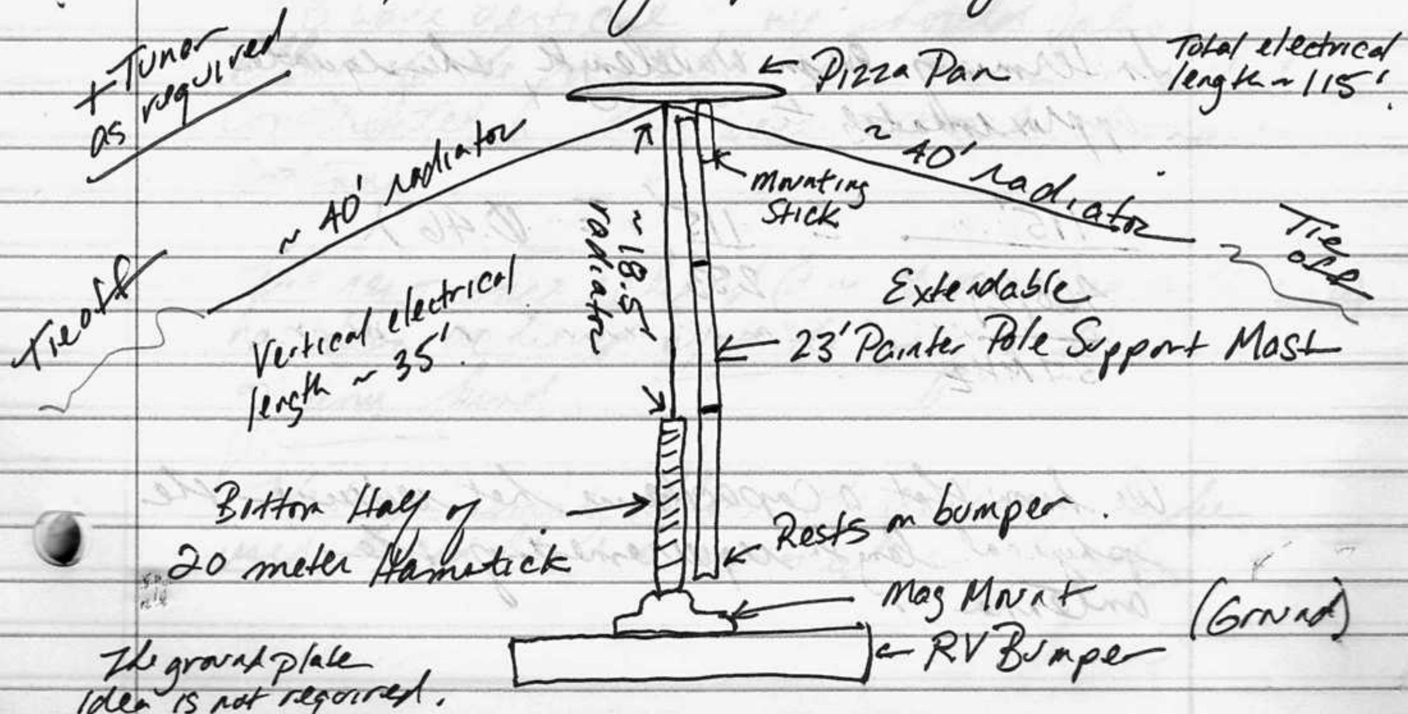
Feb 26 2018. Advanced Antenna Development.

Difficulties w/ grounding and performance eventually developed w/ the modified low foot print antenna. Experiments w/ a grounding plate have also been unsatisfactory and productive.

We have, in the process, arrived @ a compromise in size & foot print that seems to be still very efficient. It also happens to be finely resonant on 80 meters @ ~~3900KHz~~ with a 1.00 SWR of ~~1.28~~. Quite fine ~~3720~~ 3700 KHz.

SWR < 2.0 from ~~3630~~ - 3560 - 3850.

This is a marvelous achievement, broad band resonance on 80 m w/a relatively small footprint mobile antenna that is easily erected. This new, smaller foot print design is:



The ground plate idea is not required.

The electrical length of the vertical antenna is ~ 30'.

Bottom half of 20 meter hamstick :

$\frac{468(.5)}{14.2 \text{ MHz}} \cong 16.5$ ft

$16.5 - 4.5$ ft whip $\cong 12'$

Painter Pole Mast $\cong 23'$

$23' - 4.5$ bottom of 20 m. Hamstick $\cong 18.5'$

$18.5' + 16.5' \cong 35'$ good. a little higher than expected.

Total length $\cong 35' + 2(\sim 40'$ radiators$) \cong 115'$ electrical w/ a capacitance hat from pizza pan and 40' radiators and a base loaded hamstick (20m) coil.

In terms of 80 m wavelength, the equation approximates to:

$$\frac{115'}{\frac{468(2)}{3.7\text{ MHz}}} \cong \frac{115'}{253} \cong 0.46\lambda$$

We know that a capacitance hat reduces the physical length requirements of the antenna.

This can be on the order of a factor of 2.
Since we clearly have exceeded a 1/4 wave vertical I suspect we have a 5/8 wave vertical ant (0.625λ) that has been reduced in physical length to ~ 1/2 wavelength ant.

Question: Is there commonly a 1/2 wave resonant vertical antenna?

Yes, so they definitely exist, and are quite viable as an antenna. A major advantage is that it does not require a ground plane. This may be why tuning is actually easier w/ the mag mount than it was w/ the ground plate attached.

So although we anticipate that a fair amount of capacitance has been added consistent w/ the physical length reduction of a 5/8 wave vertical, we should also allow for the possibility that we have indeed constructed a half wave vertical resonant antenna.

The resonance achieved @ ~ 0.46λ (ie ~ 1/2 wave) has been achieved w/out the use of a tuner of any kind.

The tuner simply allows the antenna to be used broadband or on multiple bands all said and done, there appears to be a very:

1. Effective antenna
2. relatively modest footprint & adaptable to varying field conditions
3. Quickly and easily erected.
4. Resistant to fairly high winds (estimate up to 50 - 60 mph
5. Convenient for portable operation

—

Three radiators no longer appear to be required. 40' radiators are a very convenient length to work with.

—

all Radiators are bolted to the pizza plate.

—

My best guess, also based upon previous analyses w/ 5/8 λ resonance achieved, is that we have a 5/8 vertical antenna resonance & gain achieved on 80 m.

Feb 28 2018

The current antenna, in its more practical form, has performed quite well yesterday.

Daytime SSB transmission to UT was received well w/ a strong signal station.

More importantly, the test to the NW from SE AZ to SW OR HF digital net did succeed. There are significant mountains nearly that interfere w/ the path.

1. My normal 15 watts (essentially QRP) did not succeed. This is hardly a surprise w/ the smaller ant & smaller footprint & intervening mountains.

2. 30 watts did succeed quite well. This is more power than I prefer to use but it is still quite low by normal standards.

The performance of this antenna is quite promising both at transmit & receive. Setup is quick & easy. Footprint is small and it will accomodate quite strong winds.

Two stations in Calgary BC have also been received quite strongly (80m & 15m) and I believe that I would make successful contact w/ SSB w/ 35 watts.

Mar 01 2018 - Cochise Stronghold, AZ

It was observed that the propagation on 80m tonight was unusually local (esp Texas, etc) This is quite different from recent nights where propagation to Boston, MA, Ohio, Arkansas etc was quite prominent.

A glance at the ionosonde showed two interesting features:

1. The ionosonde originates from Elgin AFB tonight, not Boulder, CO as has been in the past.

2. The electron density was especially low, [illegible] primarily in a single layer. This fits the conventional description of the nighttime layer formation & altitude, but this is in stark contrast to what has been observed in the research of a high altitude, doublet layer.

Lets look @ the ionosonde. Currently it is 0130CT Mar 02 2018.

It should also be mentioned that aerosol operations seem to have been non-existent in this area over the past several days.

The ionosonde from Elgin continues to show a single, lower layer.

The base of the layer has an altitude of ~300 km.
The critical freq is stated as 3.7 MHz.

Lets review our propagation relations:

CF = field measurement.

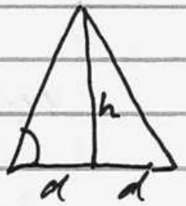
$$\text{MUF} = \text{CF} / \text{Cos(elev. angle)}$$

$$\text{FOT} \cong 0.85 \cdot \text{MUF} \cong \frac{.85 \cdot \text{CF}}{\cos \alpha} \cong \frac{.85(3.7\,\text{MHz})}{\cos 40^\circ} = 4.1\ \text{MHz}$$

Our current antenna has two radiators @ ~ 40° elevation angle.

This shows why 40 meters is certainly dead.

$$D \cong \frac{2h}{\tan\alpha} \cong \frac{2(300\,\text{km})}{\tan 40^\circ} \cong 715\ \text{km} \cong \underline{440\ \text{mi}}$$



This matches exactly what is going on with propagation centred on Texas.
Distance to Texas Ft Worth ~ 500 mi.
Distance to Laramie / Cheyenne about the same (another strong station heard).
High mountains to Far West are blocking path to the W.

Linear approxs are usually adequate.

The singular, lower ionosphere layer matches perfectly the observed propagation.

Clearly "short path". The observation further confirms the research regarding potential manipulation of the ionospheric layers.
Need additional propagation observations.

We also notice that on the global CF map (hamgsl.com)

that the path of propagation w/ CF of 3-4 MHz is oriented E/W.

This path is also blocked to the north (circa UTAH latitude) by a lower CF zone of 2-3 MHz.

Both of these factors:

1. optimum distance
2. CF global (esp US) map

indicate favored propagation to the East w/ a FOT slightly higher than 80 m and propagation should be fairly poor for 3.9 MHz, which it is.

3. Mountain topography to the west explain the lack of propagation to the East.

Texas is indeed the most probable target of propagation and observation support the conclusion exactly.

April 05 2018

The Ionosphere Research Project is in better position to proceed now.

We have some good tools in place.

1. 6 Books have come in, 4 on ionosphere physics & propagation, two on antenna design.
2. Some useful software tools & methods are now in place
    1. MUF propagation model for the globe w/ iso lines that show the direction of the gradient.
    2. A path propagation modeler (S/N Ratio & MUF provided for 24 hrs)
    3. Real time solar data input into the model
    4. WebSDR to remove noise noise of local QTH
    5. A reasonable base ham station set up w/ a "tri-inverted vee" design, ie 3 radiators.
    6. Propagation reporting stations, eg PSK reporter

We notice tremendous variations in the ionograms. The feature catching our attention the most is the presence of multiple hops, up to extreme altitudes. This would imply an extremely electron dense ionosphere. Up to 4 hops have been seen.

Tonight (0140MST on April 05 2018) we have an ionogram that has developed into a two hop scenario. There has been a slow and gradual development through the day and notice that it now in the midnight hour a 40 m has now opened up better than earlier in the day.

We notice that propagation is very good to the eastern US tonight approx 1600 miles distance on 40 m.

MUF @ Monticello is ~ 3.2 MHz and eastern US MUF is ~ 2.6 MHz
Avg MUF ≅ 2.9 MHz.

Lets review a original computation method. Assume a planar version.
Critical freq is listed currently (at Boulder Co) @ ~ 3.2 MHz

The path propagation software estimates a path MUF of ~ 9.6 MHz right now. We are using 40 m @ ~ 7.2 MHz w/ good propagation reports apparent, both w/ SSB observation & PSK reports feed back.

We notice that this MUF prediction of 9.6 MHz agrees very well w/ the Boulder estimate of 3000 km MUF of 9.3 MHz.

Recall that the MUF is always a function of the path length.

Some of our equations & computation methods are:

CF = Critical Frequency = Field measurement (taken from Ionogram) currently ~3.15 MHz.

Now we also have   Also: FOT ≅ 0.85 MUF

$$MUF \cong \frac{CF}{\cos(\text{elev angle})}.$$

LUF ≅ 0.25 MUF

Notice our MUF @ Monticello is 3.2 MHz and this matches the CF observed @ Boulder. This implies an elevation angle of 0.

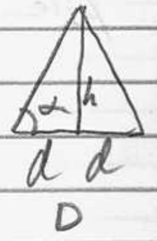
Also notice the height of the F_2 layer @ Boulder is stated as ~ 295 km.

DXatlas predicts the height of F_2 @ Monticello is ~ 325 km and on the eastern US ≅ 320 km. Lets use ~310 km as our best estimate for now.

MUF(3000) means the MUF @ 3000 km.

Our distance to the eastern US area tonight is ~1600 miles.

Our planar distance relationship is ~ $D = \frac{2h}{\tan\alpha}$



Lets look @ α estimate:

$$\alpha = \tan^{-1}\left(\frac{2h}{D}\right) = \tan^{-1}\left(\frac{2(310\text{ km})}{(1600\text{ mi}/.62)}\right) = \underline{13.6^\circ}$$

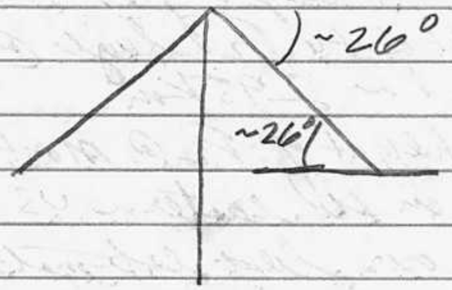
However, my antenna design does not support a ∠ of 13.6°.

So what if we regard this as a double hop?

Then our ∠ estimate is:

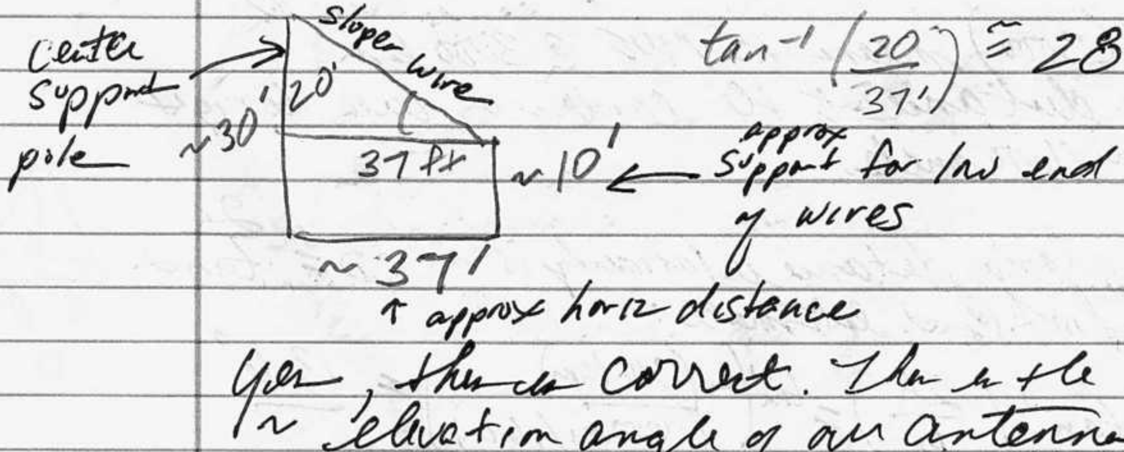
$$\alpha \cong \tan^{-1}\left(\frac{2.310\,km}{[.5\,(1600\,mi)/.62]}\right) =$$

$\alpha = 26°$ and this is much more realistic.



There is a much closer coincidence to our antenna design.

Antenna slope estimated @ ~27°



$$\tan^{-1}\left(\frac{20'}{37'}\right) \cong 28.4°$$

Yes, this is correct. This is the ~ elevation angle of our antenna.

Recall, however, that multiple hops increase the attenuation, and this will lead to diminishing returns. Making 2 hops w/ such low power being used is remarkable in its own right.

What we are seeing, therefore, is that the ionosphere is sometimes supporting a double hop, even w/ very low levels of power. The samples are especially dense electron count. It largely explains the propagation patterns that are being observed.

It also shows why propagation earlier in the day was so poor, as there were no dry, ionized, strong layers in the ionosphere.

The question is centering around the extreme variation in the electron density of the ionosphere that is being observed, even in times of the lowest activity solar cycle (sunspot number = 0!) in decades.

There is a strong case here that the ionosphere is being altered on a regular basis and that HF propagation can be used to monitor those changes. The broad variation defies normal & natural expectations @ these times.

You need to research the archives on the prevalence & frequency of multihops upon historical ionograms.

Logically you can make the case here as to what is happening.

We are seeing a double hop tonight.

Page 76

Also, why would the election density increase so much @ nighttime hours without the sun's energy?

Well, if it was artificially induced it would ~~make a~~ provide a strong reason for the change.

Tucson Conf topics:

1. Ionosphere research?

2. Supplement review?

3. Legacy project?

1. The direction of the isoline is also an interesting topic of propagation prediction.

2. Angle of the slope may well predict the ~~and~~ distance reached

3. Multihop appear to be a critically identified factor

error in sin vs cos

We now estimate the antenna slope @ ~27°C

$$MUF \cong \frac{CF}{\sin \cancel{\cos}\alpha} =$$

However we are given the MUF so we can use:

$$CF \cong MUF \cdot \overset{\cancel{\cos}}{\sin}\alpha \cong 2.9\,MHz \cdot \cos 27^\circ$$

(average path to eastern US)

$$CF = 2.6\,MHz \text{ @ Mid path}$$

$$MUF \cong \frac{2.6\,MHz}{\cos 27^\circ} = 2.9\,MHz \text{ (Mid path)}$$

$$\text{Single hop: } D = \frac{2h}{\tan(\alpha)} = \frac{2(310\,km)}{\tan(27)} = 1215\,km$$

Double hop $\cong$ 2450 km $\cong$ 1510 miles

Which is exactly what we are seeing, also generally parallel to the isolines!

$$\cos\overset{\text{given}}{\alpha} = \frac{CF}{MUF \text{ given}} \Rightarrow \frac{\cos\alpha}{\tan\alpha} = \frac{CF \cdot D}{MUF \cdot 2h}$$

$$\tan\overset{\text{given}}{\alpha} = \frac{2h \text{ given}}{D} \quad \text{or } D = \frac{\cos\alpha \cdot MUF \cdot 2h}{\tan\alpha \cdot CF}$$

$$\text{but } CF = MUF \cdot \cos\alpha \quad \text{so } D = \frac{\cancel{\cos\alpha} \cdot \cancel{MUF} \cdot 2h}{\tan\alpha\ \cancel{MUF} \cdot \cancel{\cos\alpha}}$$

Very important

$$\text{or } \boxed{\text{Single hop } D} \cong \frac{2h}{\tan\alpha}$$

which is what we already know.

h in km, D in km., Convert to miles w/ 0.62 factor

It seems like our propagation prediction will take on the following sequence:

1. Determine average path $\overline{MUF}$

2. Determine FOT $\cong$ 0.85 $\overline{MUF}$

3. Acquire the height of the F_2 layer and inspect its density in the Ionogram.

4. Estimate Single hop $D = \frac{2h}{\tan\alpha}$

Where α is defined by the design of our antenna (ie, takeoff angle).

5. Apply double hops as observed.

6. Ask how a higher freq can sometimes be used, especially when the density of the electron profile increases?

??

Increasing the electron density is allowing a higher MUF to be used.

Doubling the density might simply allow doubling of the MUF.

So what if we have the relation:

1. $MUF \cong \frac{n^2 \cdot CF}{\cos\alpha}$ where n equals the no of hops shown on the ionogram?

2. $FOT \cong 0.85(n)^2(MUF)$ (disregarding attenuation).

eg $FOT = 0.85(2)^2\ 2.9\,MHz$ = ~~4.93 MHz~~ 9.9 MHz

≅ 5 MHz.

Why did the prop predicted path show a MUF of ~ 9.6 MHz?

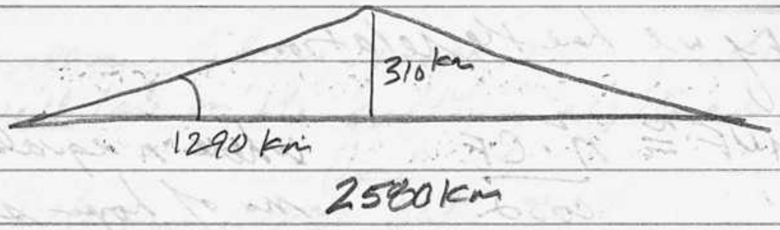
3. $D = \frac{2h \cdot (n)}{\tan\alpha}$ h = F2 height in km (α defined by antenna, currently approx 27°)

~~Single~~ n Hop ≅ Distance

Convert to miles

??? These relations seem more in accord w/ reality but we need to know how the path MUF is determined Why so high @ ~ 9.6 MHz to East Coast?

Page 80



$\tan\alpha = \frac{310}{1290}$ $\alpha = 13.5°$

this angle is not the same as the antenna take off angle.

2.9 MHz

Need to look into how reflection affects the MUF.

It appears to vary as a inverse function of sine or tan θ, not cosine θ.

Skipping a stone

April 05 2016 - 2355 (almost Apr 06 2016)

Tonight we have a MUF of only 2.9 MHz.
The second hop F2 layer is very weak.
The ht of F2 is ~ 320 km.

Propagation on 40 m is much weaker ~~tonight~~ and 80 m propagation seems to be improved over last night. This is in correspondence w/ predictions of propagation that are developing.

Notice also that the isolines are oriented more N-S than last night. We also observe that the one station heard best on 40 m tonight was from Canada; this is also in correspondence with developing propagation hypotheses.

I would anticipate that propagation is exactly as it appears to be tonight.

Single hop computation:

$$D \cong \frac{2h}{\tan\alpha} = \frac{2\,(320\,km)}{\tan 27^\circ} = 1256\,km \cong 780\,mi$$

This places target location ~ northern MO (in conjunction w/ isoline hypotheses).

The propagation prediction program projects (HAMCAP) current optimum short path signal @ ~ 6 MHz, which is considerably above the path MUF @ ~ 3 MHz so no propagation is expected (or observed) to occur tonight.

Hamcap also predicts a global propagation map from the home qth. This looks to be especially valuable.

It also shows the SNR anticipated to all locations on the globe. This is especially valuable and interesting.

It shows a SNR of 0dB or even < 0dB in the path to the north of us. It shows favored SNR out in the Pacific Ocean @ ~ 145W longitude.
(But this prediction was for the 20 meter band)!
You can select the band, eg 80 meters and such and it shows a much shorter zone of favorable propagation

—

For Hamcap, the yellow rectangles on the chart view show the favored time of best propagation for each band.

We can predict very poor conditions for 40 m tonight. Recall that MUF is currently ~ 2.0 MHz. Clearly our best option is 80 m. and there is one strong signal on 80 m. Unfortunately our antenna is performing very poorly ~~f~~ on 80 meters by high noise. 80 m is currently largely unusable.

Page 83

My signal is audible on 80 meters to N. UT.
Also to Morro Bay CA
In both cases, very weak, but audible.

To Sedona AZ, the signal was not audible. NOT TRUE W/DIGITAL

WebSDRs are located in
N. UT
Morro Bay CA
Sedona AZ

My signal was clearly audible to Sedona AZ on digital & visible. It looks fine

My digital signal to N. UT was very clear, visible and audible w/ 30 watts

Morro Bay digital signal looks a somewhat weak @ 30W.

The situation is that my 80m antenna appears to be performing as a suitable NVIS antenna but not as a distance antenna.

Question: Could you somehow use your existing portable antenna by adding a coil and ground connector?

I am making it to Morro Bay CA on 35 watts digital. Not strong, but it is audible.

3700-3800 is only possible voice sector.
SSB 50 watts went nowhere.

Web SDR is odd.

3625 shows up in 2 segments of the display ie, an overlap exists.

Problem is one band segment shows the signal on 3625, the other does not.
Why?

—

You really want to improve the 80 m antenna.
80 m require SDR to even hear any of what is out there.
Except 3700 – 3800 has some hope for strong SSB stations

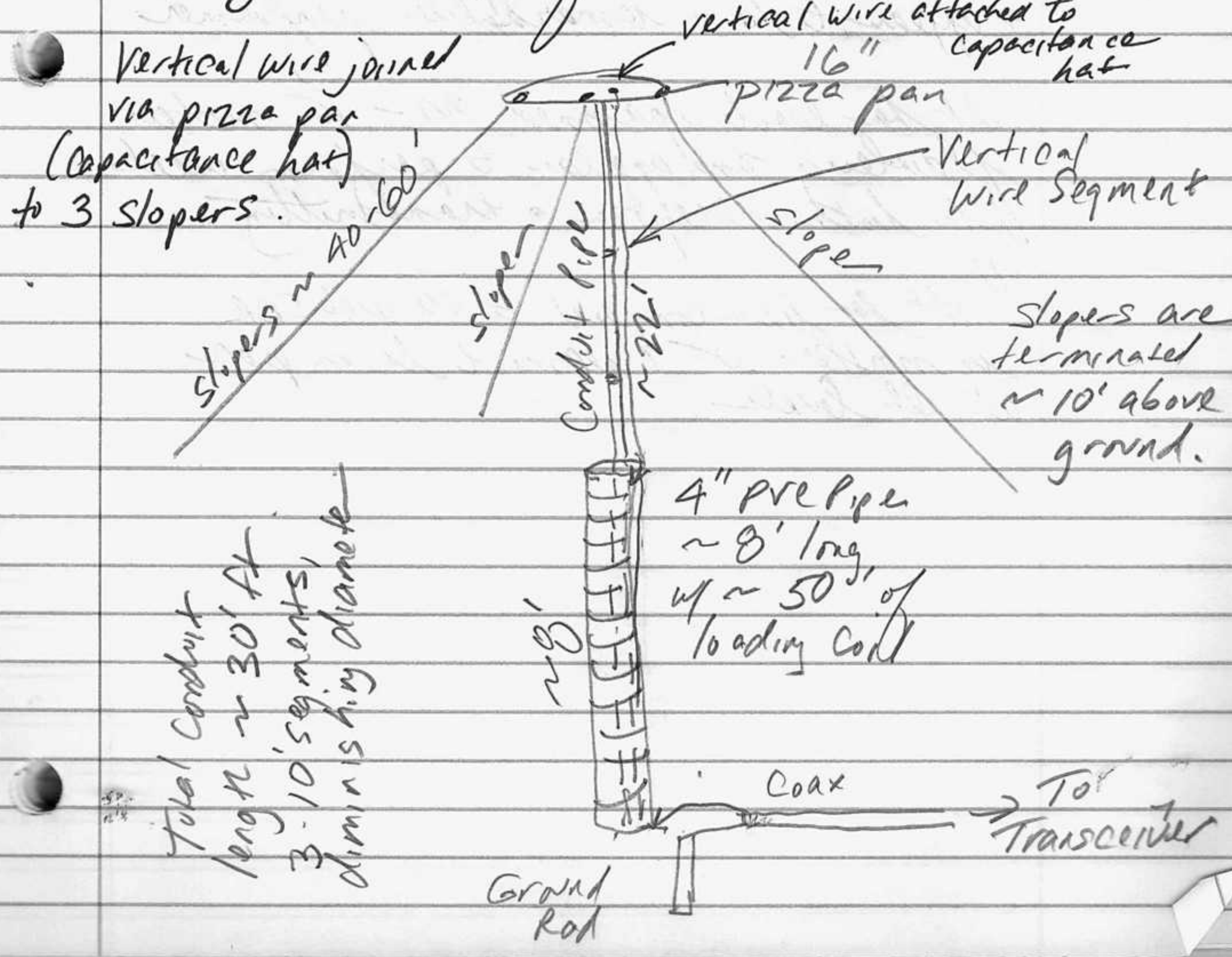
Apr 06 2018

I have most certainly developed a very effective, original & custom antenna.

It could be described as a "base loaded vertical coupled with a tri element sloping array w/a capacitance hat".

I have basically replicated the portable antenna that was developed over the last 1 1/2 years, but @ a larger scale for a base station.

The general design for the base station ant is.



The antenna does not require a ground radial system. A simple ground rod has been used for the ground system

This antenna seems to combine the features of a vertical antenna (eg low takeoff angle) w/ the benefits of dipole - inverted vee features. It tunes easily to 80m & w/ a beefier tuner it should also tune on 160m.

This antenna is a unique development & appears to be a remarkable performer.

It has easily spanned 80 - 15 meters flawlessly and appears to perform well for both reception & transmitting.

It has been compared to the WebSDR in northern VT & seems to be on par at all levels.

Page 87

Now, here is what we have to analyze.

The current CF is ~ 3.4 MHz
Direct listening of a superior antenna shows us that we can easily receive higher than the freq, as well as TXMIT.

For instance you have spanned signals on 80m, 40m & 15m since the antenna was set up only this afternoon.

You would like to have a model for predicting the phenomenon.

April 07 2018

Observations today:
1. Propagation is poor, by all measures

2. CF @ 1345 MDT is 5.5 (normal)

3. Path seems to be N-S (Tucson, Idaho)
vs E-W.

4. Ionogram shows no hops.
D layer absorption visible
E layer visible
F_2 layer distinct & visible
F_2 extraordinary visible
F_2 true ht ~ 215 km.

Appears to be normal & mediocre conditions

Now the CF high point is over N. South America. It has moved westward from the morning hours.

It has shifted to W. of Hawaii by 2130 MDT. Major movement here!

Notice isolines for CF are oriented E-W so observe for pattern in path orientation

Notice the CF increases to the S. (Tucson direction). The isolines are decreasing to the N.

IMPORTANT CONCLUSION
TAKES PLACE HERE.

I shall be looking into historical data.
What are the years for the lows of the 2 previous solar cycles?

Last low was 2009 (Jan-Feb)
Previous low was approx 1996.8

Take data for 8 weeks near low of cycles (preferably @ same station, but Boulder was not operational in 1996. Take data @ 1500 MST (2100 UTC) on 1st, 7th, 14th, 21st, 28th and @ 0300 MST (0900 UTC) if available.

The work has solidified:

I can now make the case, based upon field data observation (ionogram archives) that the ionosphere has indeed been artificially altered.

The state of charge w/in it has been dramatically increased.
The analysis of Ionosonde data from Millstone Hill during the solar minimums of 1996, 2009 & the current environment will make this fact evident.

Basically we have an F2 nighttime layer (ie 24/7 military purposes) at all times now.
* Geoengineering IN ITS FULLEST CAPACITY

2130 MDT :

We note that the peak CF (critical frequency) is now located W. of Hawaii.
There is a move from S-America – Africa w/in a half day!

Major shifts in the "topography" of the CF take place here.

---

* We now have the evidence, based on unique observational data, that the nature of the ionosphere has indeed been changed over the last 22 years.

I would like to work on the question of how the frequency of propagation increase over the CF — a higher frequency propagate on a slant.

But how to estimate the magnitude of this increase?

Each S unit is equivalent to a 6dB change in signal strength.

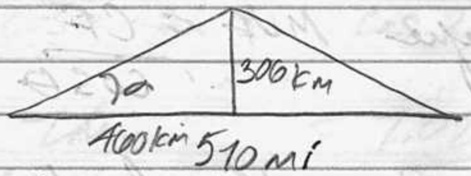
This should be approx a 4 fold increase in power. But by a chart we find each S unit represents a doubling of the voltage of the signal received.

Values from the chart

	Received Voltage	
S1	0.20 uV	
S3	0.19 uV	
S5	3.2 uV	
S7	13 uV	
S9	50 uV	— the reference value.
S9 + 20	500 uV	

HamCap seems to have a reasonably accurate prediction of the SNR (signal to noise ratio). I am still not sure what the elevation term refers to.

$MUF \cong \frac{CF}{\cos\alpha}$



$\alpha = 34^0$

$MUF \cong \frac{3.87}{\sin \cancel{\cos} 34^\circ} = \cancel{4.67}$ 6.9 MHz

OK this matches the HamCap prediction.

$1.6449\sigma =$

$1\sigma = 68^{03}$

$\sim 0.68\sigma = 7.2 \quad \Rightarrow \sigma \cong 13.53 \qquad E_{50} = 7.2$

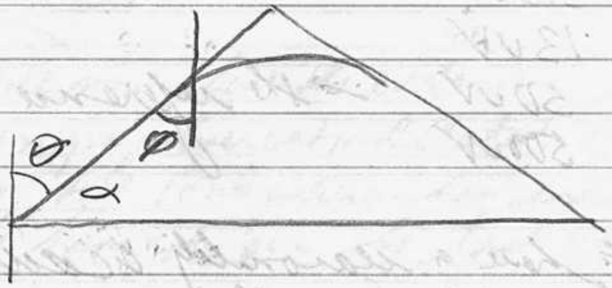
OK, I see the problem. We must use the sin, not cos.

Error
Cos to Sin
$\Longrightarrow$

50% MUF is worthless to me.
How do I convert from 50% MUF to 90% MUF

Ok, I have identified an error in my formulation of the MUF from the CF.

If we look @ Kenneth Davies book we see the geometry is:



The critical frequency is measured w.r.t. the vertical (zenith), not the horizon.

Therefore $MUF = \frac{CF}{\cos\theta} = \frac{CF}{\sin\alpha}$

where α is the elevation angle

This is what we are calculating or measuring

OK, we now know how the MUF for a path is actually calculated.

$MUF = \frac{CF}{\sin \alpha}$ $\quad \alpha$ = elevation angle

& $FOT \cong 0.85\ MUF$ $\quad$ and $D = \frac{2h}{\tan \alpha}$
$LUF = 0.25\ MUF$ $\quad$ remain correct.

$\sin \alpha = \frac{CF}{MUF}$ $\quad \frac{o}{h}$ $\quad \frac{o}{h} \frac{a}{o} = \frac{a}{h} = \cos$

$\Rightarrow$

$\tan \alpha = \frac{2h}{D}$ $\quad \frac{o}{a}$

Therefore

$\cos \alpha = \frac{CF}{MUF} \cdot \frac{\cancel{d} D}{2h}$

newly developed more comprehensive relationship.

$$\boxed{\text{Therefore: } MUF = \frac{CF \cdot \cancel{d} D}{\cos \alpha \cdot 2h}}$$

$\frac{3.87 \cdot 920\,km}{\cos 34° \,(2 \cdot 306)}$

This is interesting. This will be a more exact formula (planar).

$= \underline{\underline{7.02\,MHz}}$

New relationship: (planar)

$$\boxed{MUF \cong \frac{CF \cdot D}{\cos \alpha \cdot 2h}}$$

or approximate: $\boxed{MUF = \frac{CF}{\sin \alpha}}$

$FOT \cong .85 \cdot MUF$

The elevation angle given in HAMCAP is our α (taken from HAMCAP)

This is perfect.
CF is also given }
D is also given } taken from DXAtlas.
h is also given }

Therefore we can directly compute FOT between 2 points any time we want and compare to ionograms or direct listening to bands that are open on the WebSDR (closest).

$$\text{So FOT} \cong \frac{0.85 \cdot CF \cdot D(\text{miles}) \cdot .62}{\cos\alpha \cdot 2h\,(\text{km})}$$

or

Simplified Equation

$$\boxed{\text{FOT} \cong \frac{0.53 \cdot CF \cdot \overset{(\text{midpoint})}{D}(\text{miles})}{2 \cdot h \cdot \cos\alpha}}$$

Example: to Boston now @ 2330 MDT. (2330)

$$\text{FOT} \cong \frac{0.53 \cdot 3.14 \cdot 2041(\text{mi})}{2 \cdot 324\,(\text{km}) \cos 18^\circ} = \underline{5.51\ \text{MHz}}$$

HAMCAP Computes 7 MHz @ 50% level.

I believe our equation is likely to be more realistic

FOT to Brookings is: (@ 2045 MDT)

$$FOT = \frac{0.53\ CF \cdot D(mi)}{2 \cdot h(km) \cdot \cos\alpha} = \frac{0.53\,(4.56)\,(827)}{2\,(280)\cos 48^\circ} = 5.3\ \text{MHz}$$

3.581 MHz should still work.
Depending upon Ionogram

Tonight I am hearing Boston & Hawaii on the 40m band, a very long path.

Hawaii reception appears to be a double hop.
HAMCap shows 50% MUF @ 11.5 MHz
We estimate 0.75 (11.5) = 8.6 MHz
HamCap also shows 2F2 → this means a double hop
Elev angle is 15°. Our elev angle is ~ 27°.
These further substantiate the double hop to Hawaii
Listening to 7195.00 kHz. [redacted] DD/BE
FK also hearing station forom Caledonia (New)
[redacted]

[redacted] is "Paradise Contesters", Keeau, Hawaii (Hilo)

New Caledonia is about 7000 miles away! This suggests 4 hops! It was indeed very weak.
Receiving 1500 watts with 4 hops is quite different than transmitting w/ 60 or 50 watts!

New Caledonia is right on the gray line right now. Hawaii is well into darkness now.

The peak CFs are following the sun.

The Ionogram shows' that a double hop is in place.

Now, your FOT computation assume a single hop. But this will not always be the case, especially w/ DX stations.

If it is a double hop scenario, your elevation angle will actually be twice (approx) what the single hop computation will be.

Example: Hawaii is now being received. You are on 40 meters. Ionogram also suggests that double hop is available.

Let's run through the computation.

$$\text{FOT} \cong \frac{0.53 \cdot CF \cdot D}{2h\cos\alpha} = \frac{0.53\,(4.22)\,(3075\,\text{mi})}{2\,(338\,\text{km})\cos(12^\circ)}$$

(single)

Now:

1. We know that the angle of our radiator is ~27°. You can run the computation w/ that angle & see what difference it causes.

2. You see that HAMCAP shows 2F2. Check on this - it may well mean double hop.

$\text{FOT}\,(\text{singlehop}, \alpha = 12^\circ) = 10.40$ MHz

This is a bit high for the time of night.

Also note that HamCap lists 50% MUF @ 11.5 MHz.
I would drop this to .75(11.5) = 8.6 MHz.

However, a double hop computation is

$$FOT_{(double)} = \frac{.53(4.22)\overset{1537km}{\cancel{3075}}km}{2(338km)\cdot\cos(24^\circ)} = \cancel{11.1\,MHz}$$

$\underline{\underline{5.6\,MHz}}$

This is much more reasonable.

Notice the HI station has now disappeared after ~2hrs on the air.

Hamcap adjusts the elevation angle automatically for one hop vs multiple hops. 2F2 is indeed 2 hops. It has even gone to 3F2.

Another discovery: HAMCAP will overlay the Global map onto DXAtlas, Cursor within DXAtlas will give output w/in the Hamcap window. The more that I use this program, the more that I like it and discover new features.
This was accomplished w/in settings of HAMCAP.

April 08 2018

A nevertheless, instructive day in propagation behavior today.

The bands, across the board, exhibited very poor propagation throughout almost the entire day today.

This made it difficult to establish any references upon transmission.

You also discovered a problem in the connection w/in the antenna and it required a repair, Propagation will need to improve to establish the reference value for the antenna.

Another big problem is the town background noise here in Monticello. Camp is a dream for ham radio, town presents many challenges. This is an increasing problem across the board that many hams now speak of. We are living in an electromagnetic soup these days, and the soup is that much thicker in town these days.

Noise cancelling devices may now be essential.

April 09 2018

The approximation of $MUF \cong \frac{CF}{\sin\alpha}$

Can be used to great advantage.
HamCap give an elevation angle that is not exactly intuitive but is explaining propagation results very well.

4 Three location analysis : Current CF $\cong$ 5 MHz

	HamCap Elevation α	~ MUF (5MHz/sinα)
Reno	63°	5.6 MHz
Sacramento	56°	6.0 MHz
Tucson	31°	9.7 MHz
Central WA	43°	7.3 MHz

Operating on 40 m @ 7185.5. The simple MUF computation agrees extremely well w/ the observed propagation conditions from the Early Bird Net today.

Tucson appeared ~~best~~ best.
WA & Sacramento were mediocre
Reno was the worst.

The topography of the SNR plot matters a great deal and at [illegible] point is not intuitive @ the local level of 40 m coverage. The high that follows the sun across the globe is.

The lower the elevation angle (not determined by distance alone!) the higher the MUF.

So how is the elevation angle determined? It is not just a function of distance & F_2 height.

The notch filter is advantageous to birdies & carriers.

It looks like we would like the MUF to be above the CF by a couple MHz if possible

Apr 09 2018

The antenna that I have made is resonant across the entire 160m band. This is quite remarkable.

Freq	SWR
1990 kHz	1.03
1800 kHz	1.94

Also close to resonance on 15 meter.

My wire are basically longer than they need to be. We should probably choose 80, 60 or 40 meter as our reference point.

Rough estimate of total wire length.

~30' on Coil

(27-8) = 19 on mast

$[8.2(5.5)]/\cos 27^\circ \cong 51'$

$7.7(5.5)/\cos 27^\circ \cong 47'$

$10(5.5)/\cos 27^\circ \cong 62$

$2\left(\frac{468}{1.990\text{MHz}}\right) = 470'$

$\Sigma = 209'$

$\frac{209}{470} = .445$

We therefore have ~~got~~ close to a half wave vertical or a half wave dipole.

Lets adjust to 80 meter first.

The antenna is perfectly resonant on 160m.

KX9

$\frac{468}{3.5\ \text{MHz}} = 134'$ vs 209

$\Delta = 75'$

75'/3 wire = 25 feet trimmed
on each wire.

suggest we start w/ 20' ft trimmed.

Now resonant @ 2100 kHz,
up to 2300 KHz is < 2.0

I removed 15' 4"

$\frac{\Delta f}{15.33'} = \sim 2200\ \text{kHz} - 1990\ \text{kHz}$

$= \frac{210\ \text{kHz}}{15.33}$

Now two 15' segments have been
removed. SWR < 2.0 @ 2400 kHz

Change is small.

Now 3 segments have been removed (~45').

Now <2.0 SWR @ 2570 MHz.
Could be removed further?

Shows SWR ~ 5.5 across 40 meter now
~5.5 close to 20 meter

This might be a good compromise. Let's get the antenna analyzer software running.

Ok, I was able to get the SARK program working. Curiously, it has 3 Lower SWR points

Near 2.5 MHz — Not actually too far from
5.6 MHz — 80m
14.4 MHz — 40m
20m

This seems very workable.

This seems to be a rather amazing antenna.
20 meters is completely resonant
40 & 80 are reasonably close - tuner will make up difference.
Numerous regions of resonance from 1.8 - 60 MHz.

April 10 2018

It is an interesting observation that 20 meters is sometimes relatively open even when 40m is almost completely shut down.

Hamcap propagation modelling (based upon VOCAP) agrees w/ this observation.

HAMCAP SNR propagation modeling is becoming increasingly interesting to study. It is somewhat akin to a topographic map w/ relief that changes on an hourly/daily basis.

What happens there is not a simple affair. There is a great deal of change to be observed along any radial or concentric circle.

Understanding the basic model/theory of VOCAP would be beneficial, as the SNR plot would be more easily interpreted. Very big change between 7 & 20 meters, for example.

Also I observe that my antenna reception can vary quite a bit from the N. Utah SDR. In some ways worse, in some ways better. Background noise here is the main problem now, however. It is difficult to compare, for now.

Page 105

Lets look @ Houston propagation, for the time being, on ~~40~~ 20m. Hapcap estimates SNR @ +45dB. ~~Very good~~ propagation should be decent, ~ ~~S6~~. S7.5
1 S unit = ~~8 dB~~ 6 dB.

Next look @ our model: 2330 UCT or 1725 MDT

$$MUF \cong \frac{CF}{\sin\alpha} = \frac{5.4\text{ MHz}}{\sin 7^\circ} = 44\text{ MHz}$$
(midpoint)

$$FOT = \frac{0.53\,CF \cdot D}{2h\cos\alpha} = \frac{.53(5.4\text{ MHz})(980\text{ mi})}{2 \cdot 264 \cdot \cos 7^\circ}$$

$$= 5.35\text{ MHz}$$

obviously there are signif difference between these two results and neither one agrees well w/ the MUF prediction of 15.6 MHz (which incidentally seems quite close to reality). .85(15.6) = 13.3 MHz. Just shy of 20 metres.

Clearly VOCAP is superior here.

If you can only double electron density will it make a signif difference in propagation results :

April 11 2018 Critical Frequency Analysis

Let's start looking @ some of the stats of the solar minimums : FoF_2

			1996		2009		2018	
			Sep-Oct		Jan - Feb		Feb - Apr	
			0900 UGT	2100	0900	2100	0900	2100
1	Sep	05	0	3.96	0	4.78	2.42	5.05
2		07	0	3.98	2.75	4.50	2.50	4.97
3		14	0	4.82	3.37	4.57	2.60	5.40
4		21	0	0	2.78	4.61	2.78	5.11
5	~~Oct~~	28	0	0	2,37	4.38	2.95	5.79
6	Oct	01	0	5.48	2,05	4.52	2.52	5.09
7		07	2.56	5.31	2.52	4.57	2.45	5.55
8		14	2.71	5.78	2.78	4.95	2.60	4.85
9		21	1.97	6.16	2.75	5.22	2.48	5.36
10		28	2.32	6.18	3.80	4.80	3.10	4.80
		$\bar{x}$	0.96	4,17	2.52	4.68	2.64	5.20
		σ	1.18	2.21	0,96	0.29	0.22	0.30
		σ_s	1.25	2.33	1,01	0.26	0.23	0.32
Group #			1A	2A	1B	2B	1C	2C

We have:

1. High statistical difference between
   Night 1996 — Night 2009
   Night 1996 — Night 2018
   Day 2009 — Day 2018

2. Modest statistical difference between:
   Day 1996 — Day 2018

T Test Results: One Tail

0900 UTC: Night hours

1A ↔ 1B $t = -3.0734$
$p = .003275$
Result significant @ < 0.01 99.613 %

1A ↔ 1C $t = -4.18702$
$p = .000277$
Result significant @ $p < .01$ 99.972 %

1B ↔ 1C $t = -0.36589$
$p = .359356$ 64.1 %

2100 UTC: Afternoon hours

2A ↔ 2B $t = -0.68912$
$p = 0.249769$ 75.0 %

2A ↔ 2C $t = -1.38463$
$p = .091546$ 93.8 %

2B ↔ 2C $t = -4.00183$
$p = .000418$ 99.95 %

Therefore:
1. Nighttime differences are dramatic in all respects
2. Daytime differences have gradually & consistently increased from 1996 - 2018

EZNEC Antenna Simulator program
is actually very easy to use or setup.

The radiation pattern of my antenna is
exactly as I would expect it to be.

It does get interesting on 20 m with the
complex layer of lobes that overlap.
80 m, because of its proximity to
ground.

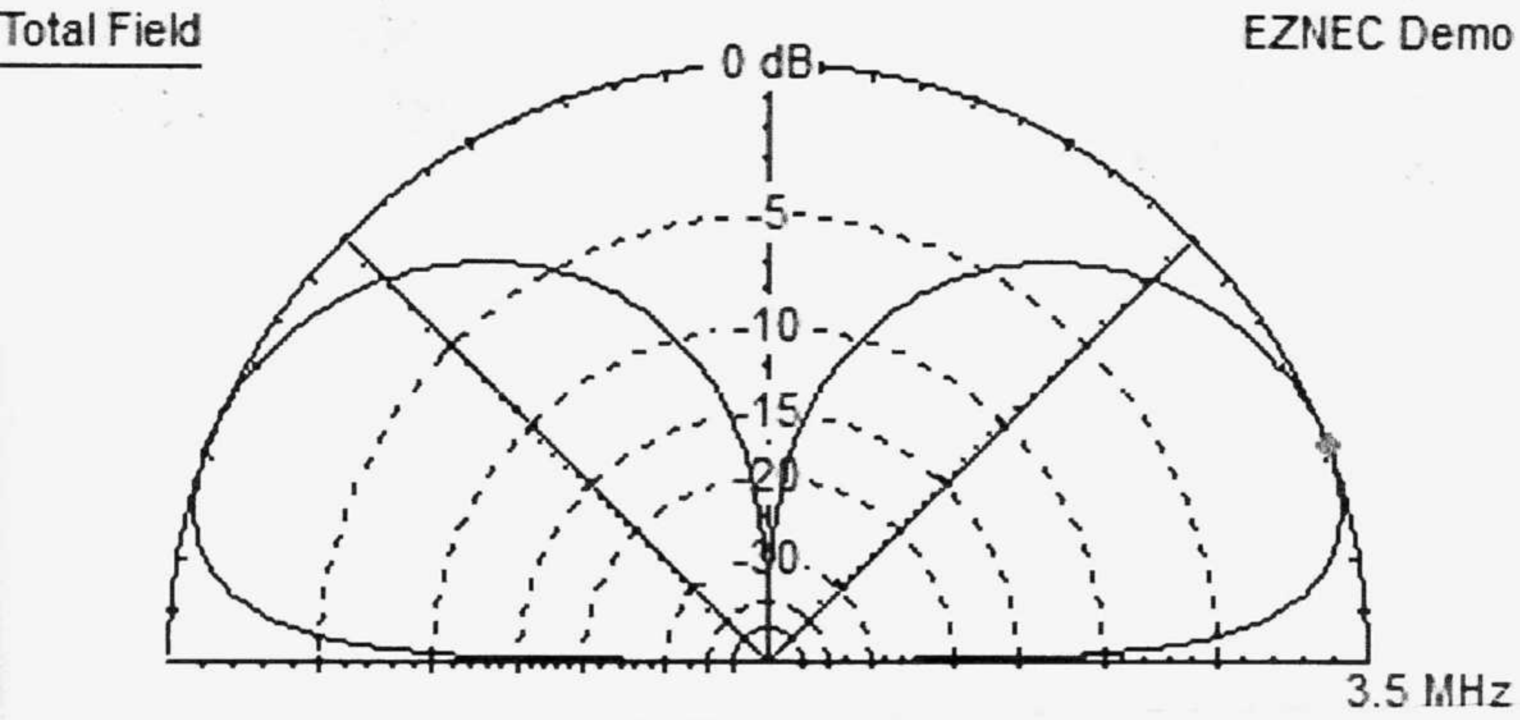
Properly placing the source of transmission
@ the bottom of the antenna has
changed things much to the better.
It looks like an excellent radiation pattern.

Max radiation is between the wires, not
along or broadside to the wire orientation

Electron Density is proportional to the
square of the Critical Frequency.

This is a good design. you are essentially increasing your power by a factor of 2 right where you need it instead of radiating it vertically.

mbrella Antenna - Radiators approx 40 ft. Vertical ~45' w/coil



```
Elevation Plot                          Cursor Elev    21.0 deg.
Azimuth Angle      0.0 deg.             Gain           2.93 dBi
Outer Ring         2.93 dBi                            0.0 dBmax

Slice Max Gain     2.93 dBi @ Elev Angle = 21.0 deg.
Beamwidth          47.2 deg.; -3dB @ 5.1, 52.3 deg.
Sidelobe Gain      2.93 dBi @ Elev Angle = 159.0 deg.
Front/Sidelobe     0.0 dB
```

A dipole has a dBi of 2.15 $\Rightarrow$ Pwr gain = ≈1.6 broadside only

$dB = 10\log(P1/P2)$

$\log(P_1/P_2) = \frac{dB}{10}$

$P1/P2 = 10^{dB/10}$

$\Rightarrow 10^{.293} = \underline{\underline{1.96}} \simeq 2.0$

in all directions

April 13 2018

The background noise in Monticello makes HF operation almost impossible. It is a severe situation.

A noise Canceling circuit/device is currently (MFJ 1026) under testing. It did not appear to produce any results from following the stated instructions.

I, however, seem to have made some significant progress by some modifications to the process. I want to record those steps in hopes that the process can be duplicated.

1. The test is conducted on 40 meters
2. The new antenna tuner also required an adjustment of a slightly bent capacitor plate. It seems to be OK now and is working on 80 (set on D) & 40m (set on H).
3. The primary HF rig has the pre-amp off.
4. The noise canceller has the pre-amp on (this means the internal whip antenna is being used).
5. I have added ~ 15' of wire clipped to the top of a CB antenna to enhance the signal reception of the auxiliary antenna.

6. In the final adjustments, the

   1. T/R Delay is set fully clockwise
   2. Antenna Auxiliary Gain is fully Counterclockwise,
   3. The Pre Amp is on
   4. The freq. switch is set too high.
   5. The Phase dial is set to mid-point (5) but for some reason does not seem to matter.
   6. The Phase switch is set to normal
   7. The main antenna gain is set to 1.5.
   8. The Yaesu DNR is set to ~ midpoint
   9. Notch filter is on as required.
   10. Yaesu IPO (pre-amp is off)
   11. RF gain is set to ~ 1 o'clock position.

Even though this does appear to follow the instructions given, it seems to be working extraordinarily well. You have dropped a background noise of S4.5 down to 0. This makes all the difference in the world in the ability to receive signals. With the Yaesu pre-amp off almost all signals will end up falling between 0 - 4.5 S units.

From all the above the station set up is obviously more complex. However, noise reduction appears to be dramatic and I am able to hear some very weak stations even when the band does not seem to be open in any fashion.

On 80m, S9 +10 is dropping to S4.5. That is 5+ S units.

80 m still leaves much to be desired but there may still be hope w/ S7-S9 signals.

The Ionogram looks especially weak tonight.

The tuner seems to be able to hold its position on the transmitter. SWR can be brought in w/ antenna switch alone.

Secondly, the noise canceler does not seem to need to be changed in any significant way.

We:

1. Turn the main antenna gain as low as possible that still picks up a signal.

2. Carefully adjust phase for a minimal dip / deviation. 1 bar on meter seems to be adequate for detection.

Page 113

The main factor that seems to be affecting reduction of the noise level is the reduction of gain on the input antenna signal.

Phase adjustments seem to have a negligible or small effect thus far.

This suggests that we have a very high gain antenna @ hand. Recall in the field that you are almost always able to hear ALL stations w/in any net. This may be an expression of the same characteristic except for in town any noise is too much noise.

April 15 2018

Nighttime propagation on 40 m is much quieter and therefore gain can be increased (on the antenna (~ from 1.5 to 2.5)

A useful chapter (from Springer Geophysics) has been acquired & perused.

Some stations simply do come into northern UT that do not come into southeastern UT. (esp on 40 m)
The SDR location is, in fact, 300 miles away so this is significant w/in the 40 m context.

One example is station from Hawaii came in very strong on N. UT SDR, it did not register here locally.

The SDR disrupted the USB port communication for digital HF. Swapping ports and resetting sound card has resolved the problem, at least temporarily. You may need a better hub.

CF is extremely low tonight, 2.6 MHz. This raises difficulties for 40 m operation.

T/R delay set @ midpoint now.

Conclusions : Major success w/ noise reduction on 80 m.

Not True! I Cannot seem to reduce the background noise sufficiently to acquire SSB on 80 meters.

I have acquired an 80 meter signal!
Phase ~~step~~ dial was very sensitive, and produced a peak signal @ position 9
Phase switch is in normal position. Read instructions very carefully.
Auxiliary antenna is in 5 position to match the main signal antenna.
You work the auxiliary gain and the phase dial together to maximize the voice signal.
You really do need a voice signal to work with. Then when the SDR helps a lot.

The noise blanker also has some effect.

I have extracted an 80 m signal! But you did need to know where a signal was to succeed. This is a fascinating process, it does work.

The settings on 80 m signal currently are

1026: 1. T/R delay fully clockwise 2. Pre-amp on
3. Auxiliary Gain ~ 4.6 4. Frequency gain is high
5. Phase is @ Position 9. Phase switch is invert.
10. Main Ant Gain is @ 9.0

Yaesu: 1. Contour on light accent 2. DNR @ midpoint 3. PreAmp is OFF
4. Noise Blanker is on 5. RF Gain ~ 0.6 counterclockwise

We can increase DNR & raise contour magnitude if we would like to.

Minor band position changes require only very small change in the phase or auxilary antenna change.

Once you get the settings working do not adjust the main antenna gain or you will undo your work.

Changing the tuning of the antenna has lost much of the benefits. You must tune the antenna first & leave it alone.

I am guessing you need an S9 signal to succeed w/ this. Or at least a reasonably strong signal

Interesting: Another approach to finding the null was to
1. Match the main signal @ the lower first match
2. Set phase position to maximum
3. Turn up main antenna gain slowly and you also found the null.

This seemed to be another approach that works.

In this mode, the null is found by

1. Leaving the aux. gain alone (eg Position #3)
2. Leaving the phase alone (eg Position 10, fully clockwise)
3. Adjusting the main antenna gain until you hear the null (in this case, quite clearly near position #4).

This method has worked extremely well

It is very easy to find the full null position using the main antenna gain.
I have reduced an S9 noise level to an ~~S5~~ S3.5 to S4. This is great.
Make sure the Yaesu RF gain is wide open when seeking the null. This means you can receive signals ≥ S5 now on 80 m.

Method is key.

0. TUNING TO FREQ MUST OCCUR FIRST.
1. Auxiliary antenna set upon first match to primary signal
2. Phase control full clockwise
3. Find null (w/ Main antenna gain in mid position.
4. Set Yaesu) 3/4 DNR, high contour accent, PreAmp On, Noise Blanker on, RF gain reduced to maximum level possible

I am very pleased w/ the method developed and the results.

April 16 2018

Noise reduction on 40 meters:

Difficult, not as effective, but I still made it. General setup.

1. 2nd external antenna had to be hooked up to pre-amp on noise reducer.
2. Pre Amp switch on
3. Auxiliary antenna gain 0.5
4. Phase 2.5
5. Phase switch normal
6. Main antenna gain ~~2.5~~ 1.5-2.5

Yaesu:

1. PreAmp on
2. Notch required in this case
3. DNR 0.6 out of 1.0
4. Signal weak so RF gain back only 1/2

Conditions again extremely poor but I have succeeded.

—

Now let's repeat.

Main antenna gain only affect the overall strength of the signal, it does not affect the null.

What is ~~[illegible]~~ having the most effect in nulling is the auxiliary antenna gain, which is set almost @ 0 - set @ 0.3!
Very little room for adjustment, but also very sensitive.

—

Great accomplishment: I now have the offline SDR on the computer coupled with the HF receiver using the same antenna w/ an antenna switch. This now means that both receivers see the same signal w/ phased noise reduction. Very valuable as the SDR offers many advantages for reception. It can be considered as a "pan adaptor" ie, panoramic view of the band w/ identical reception signal available to both the offline SDR & the HF rig. The online SDR is another backup alternative that can be viewed in real time as a pan adapter in combination w/ the HF Rig.

—

There is an interesting conflict in propagation today. The ionogram is completely devoid and does not have even a critical frequency measured @ ~1300 MDT in Monticello Ut. However, VOACAP/HamCap predicts very good propagation over the western states. In practice, I make it to Bakersfield CA on 50 watts w/ a strong report received. In further conflict I can hear very poorly in general. SDR on web is my primary method of reception on 40m. A very mixed day of propagation conditions.

April 17 2018

I have successfully replicated reduction of background noise on 80m reception. The band is now usable and this is an important accomplishment since it is a mainstay of HF communications during this segment of the solar cycle.

No access to 80m communication represents a real hardship to communications & further research, especially those that involve the hours of darkness.

40m:

2S unit reduction thus far.

Maybe 2-4 S unit reduction

This is significant

The question of noise reduction on 40 m remains unresolved. At this point it does not appear achievable in a manner similar to that accomplished w/ 80m. I will continue working w/ this. Thus far 40 m represents a compromise band in terms of signal strengths and background noise.

Next, a very important question has emerged between the status of UV levels historically, and their relationship to the ionosphere.

I have already established that it is essentially a certainty that the ionosphere has been significantly altered over the past 22 years.

UV Analysis

The critical frequency has been increased systematically by increasing the electron density of the ionosphere. The change is highly significant statistically speaking.

Here is the question:

What does the UV data show over the same time period?

Another observation is that as the last two solar cycles have become weaker, one would expect, if anything, for the critical frequency to Decrease, not increase.

Now that the CF has increased, one might expect the UV levels to decrease. Is this the case? Anecdotal reports suggest otherwise. Let's try to find this data.

Also relationship to ozone levels
Ozone is produced by UV radiation, but it is a reciprocating, or reversible reaction.

Ok, I have found some historical UV data.

Page 122

~ 10% Increase per decade

The best way to look for any trend change here may be to analyze the number days per year UV is ≥ high reading(s).

Let's look @ the UV data for two location @ 3 different times

No. of days Index ≥ High

New York   Los Angeles

1996 $59+81+0=140$ $57+122+14$ 193

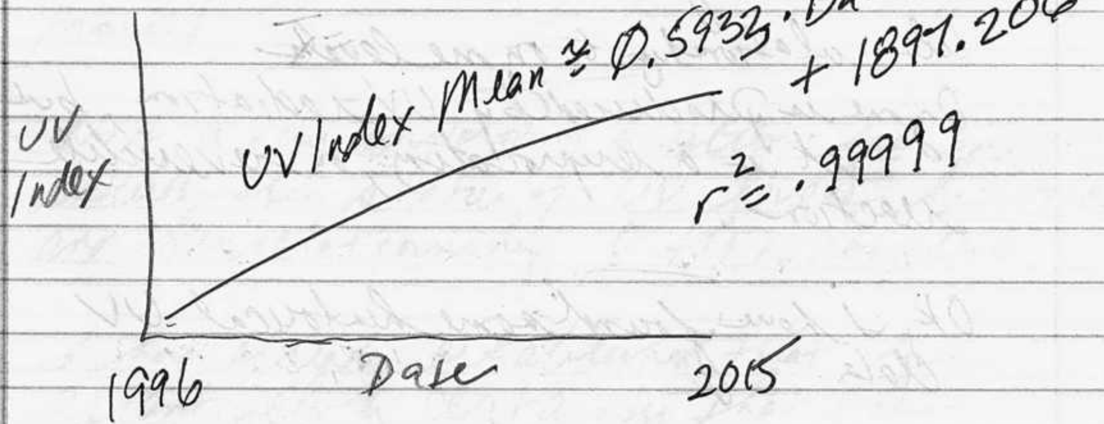
$x = 166.5$

2009 $51+111+0=162$ $57+96+62=215$

$\bar{x}=188.5$

(latest available) 2015 $62+110+0=172$ $44+110+71=225$

198.5



UV Index Mean ≈ $0.5933 \cdot \text{Date} + 1891.206$

$r^2 = .99999$

This is valid.

Regression Analysis of UV Data is Valid.

T test on UV Data is not verified as valid @ this point.

t test between:

Date	$\bar{X}$ UV Index
1996	166.5
2009	188.5
2015	198.5

Careful here

?????

leads to significance @ <.00001 = 99.999%

Let's think about the test that you are running. In the case of Critical Frequency analysis, you are inputting raw data in groups of 10!

	1996	2009	2018
Night Observations	$n=10$ 1A	$n=10$ 1B	$n=10$ 1C
Day Observations	$n=10$ 2A	$n=10$ 2B	$n=10$ 2C

You did not input the date into the analysis; only the raw data.

In the case of UV, we have

	1996	2009	2005
UV Index Days ≥ High	$n=1$ $\bar{X}_1$	$n=1$ $\bar{X}_2$	$n=1$ $\bar{X}_3$

In the case of CF analyses, we looked for differences between any two groups of either night or day data for all years.

In the case of UV analyses, we basically only have one "treatment", ie, the year, and we are comparing differences between the means.

We have very high statistical differences taking place in both cases.

We do not have enough corresponding data between CF analyses & UV analyses to determine level of correlation since we have

CF Analysis	UV Analysis
1996	1996
2009	2009
2018	2015

Now, another way of looking @ the CF data is also by order

In terms of UV analysis, what we have are essentially three data points (means) that span time.

In the case of CF analysis, we have much more extensive data to be looking @.

What we can infer, however, is this:

1. CF is increasing over time @ the extreme low point of the solar cycle.

(1) Possible explanations:
   1. Increased solar activity & therefore increased UV activity and therefore increased ionization and therefore increased electron density. But recall this is occurring even though the sun activity is actually decreasing over the last 3 cycles so there is a contradiction. Also the data is being collected @ the extreme lows of the solar cycle when solar activity is @ an absolute minimum.

(2) Injecting ionizable particulates into the atmosphere. This explanation does fit the observed data & evidence

We can also infer, in a general sense, that UV radiation is increasing towards the earth from 1996 - 2015.

We do not have evidence that this is occurring @ the level of the ionosphere based on the analysis of the CF scenarios discussed.

So now it is logical to look @ data for ozone over the same period.

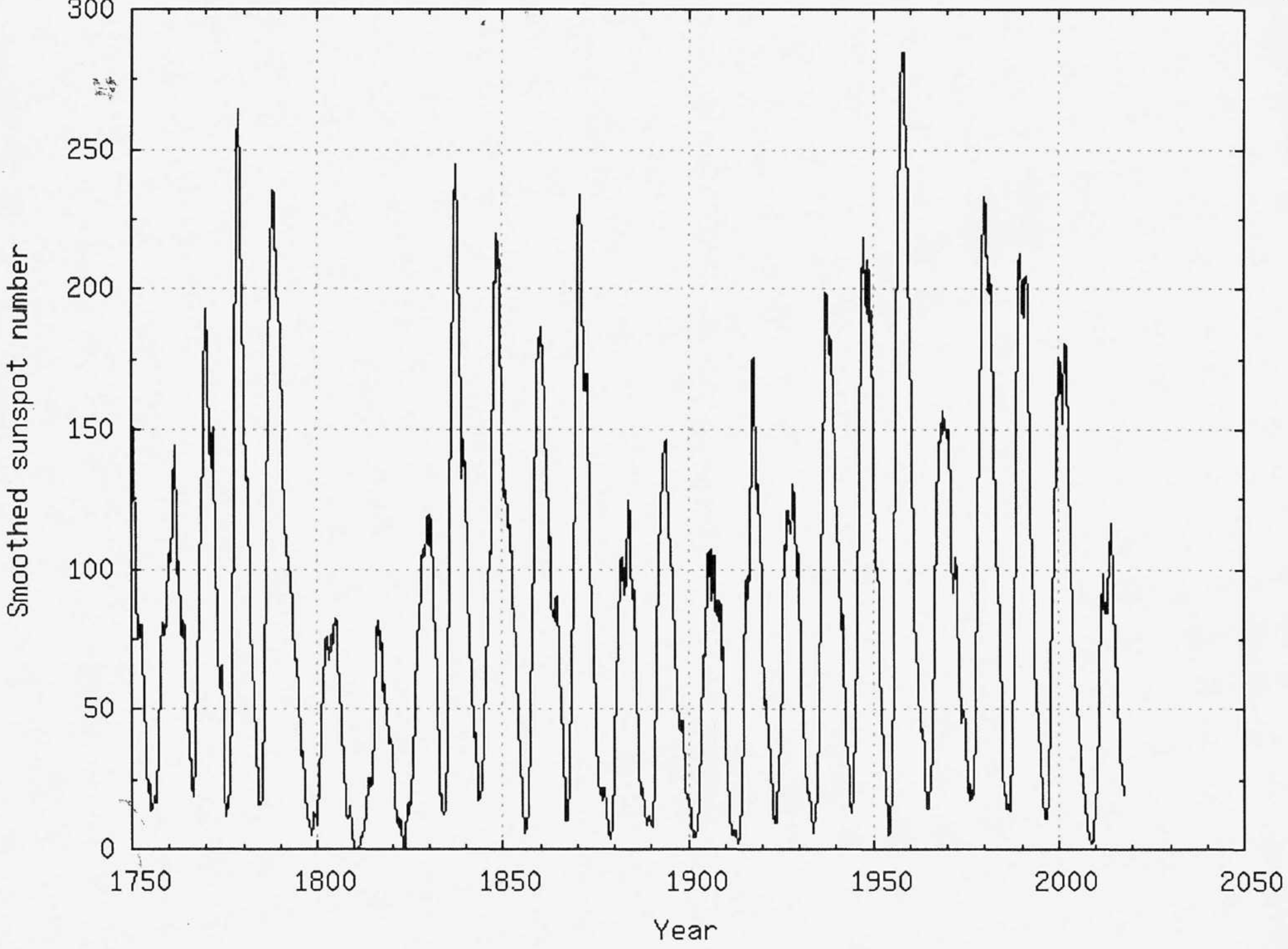
The ozone layer is the second level of protection from UV radiation. If UV radiation is increasing, it is hypothesized to be occurring within losses (damage) from the ozone, NOT the ionosphere.

Therefore, next we are to look @ data for the ozone layer:

1. Ionosphere
2. UV Radiation
3. Ozone layer

Relationships & Pattern Analyses 1996-2018

Solar Cycles - Source Australia.jpg



A Composite, Consistent Picture of
3 Fundamental Geophysical Components:

Ozone Analysis:
1. Ionosphere changes
2. UV Radiation (Surface) Changes
3. The state of the ozone layer

Examination shows that the "Ozone Hole" is not a problem.

The data speaks clearly. Maybe it was a problem, maybe not (CFC, legislation, etc).

But it is not a problem now. Your "authorities" of NOAA & Nat'l Geographic also say as much now.

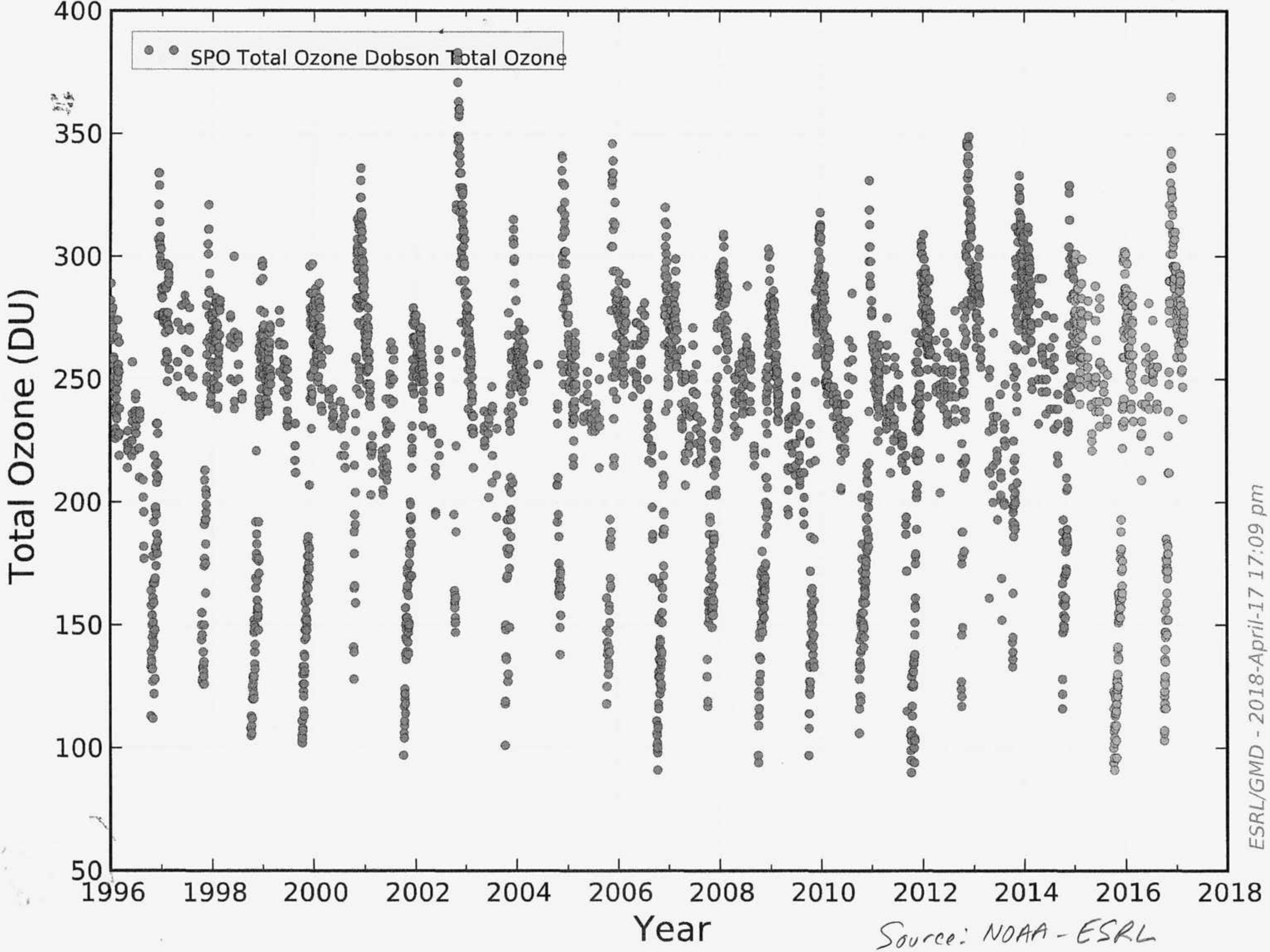
We therefore have

1. An increasingly charged ionosphere
2. An increasing level of UV radiation @ U.S.A sites — UV index is based upon UVA (315-400 nm)
3. A stabilized ozone layer

guess why? aerosols, haze & thin clouds

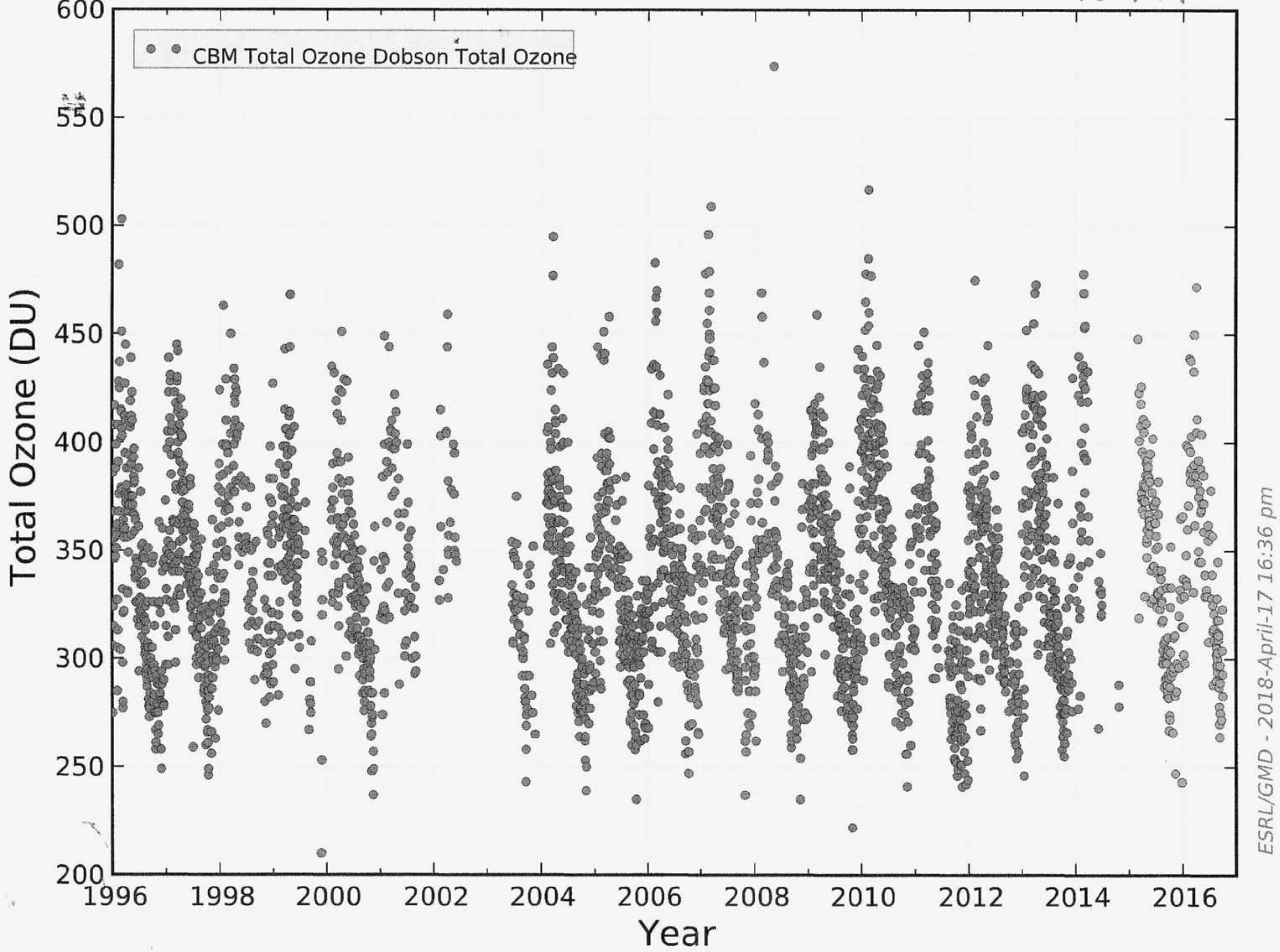
Now it is turning toward interpretation of the composite picture.

South Pole, Antarctica, United States (SPO)



Source: NOAA - ESRL

Caribou, Maine, United States (CBM)



NATIONAL GEOGRAPHIC

https://news.nationalgeographic.com/2016/06/antarctic-ozone-hole-healing-fingerprints.html

Remember the Ozone Hole? Now There's Proof It's Healing.

Scientists find evidence that the hole is finally shrinking, thanks to the phasing out of harmful chemicals 30 years ago.

PUBLISHED JUNE 30, 2016

After three decades of observation, scientists have finally found the first fingerprints of healing in the notorious Southern Hemisphere ozone hole.

In 1974, Mario Molina and Sherwood Rowland, two chemists at the University of California, Irvine, published an article in *Nature* detailing the threats to the ozone layer from chlorofluorocarbon (CFC) gases. At the

Page 130

April 18 2018

Noise Cancellation via phasing does work better and more consistently w/ use of the external antenna.

The HF tuner can be used to extend the range of acceptable SWR w/out disturbing the noise cancellation achievement.

Propagation on 40 m is now even exceptionally difficult during daytime hours. Sundown hours, plus or minus a couple on each side, appear to be most favorable 40 m propagation hours.

80 m digital works well @ night w/ noise reduction

What you have learned, with respect to noise cancellation, is that on 80 m you are dealing w/ a complete noise overload situation. Your best result, and it is phenomenal, is that you have been able to reduce a noise background of S9 + 40dB to an S2 level. To do this, the whip is fully collapsed, the antenna inputs are at almost complete minimum, and the phase is @ absolute maximum. The phase switch is normal.

This shows you that you are @ the maximum limits of the instrument design.
Successful nulls are achieved w/ both the auxiliary & the main antenna gains.
This is a remarkable achievement.

40 m (& 20m) appear to be an entirely different situation. I am not sure if much can be done to improve those yet. The result may depend upon band conditions as well.

Actually we have similar results w/ similar settings on 40 meters also. Low end static (S≤3) is primarily what is removed. Strong signals do not require the noise reduction.

April 20 2018 Page 132

Ionogram interpretation. Also to look @ the legend in more detail. Extremely poor propagation conditions accompany this ionogram. Taken @ ~1000 MST. @ 1100 MST there is no msmt for foF2 – it has deteriorated even further.

Units of the relationship between N & CF are important. Davies on p 390 is very weak & unclear on this matter. He gives

$$N = 1.24E10 \, (f_oF_2)^2 \text{ electrons per cubic meter}$$

URSI publication 1978 is much more clear on the matter & relationship:

One place calls it f_oF_2, another fN, I call it CF. In all cases we are speaking of the critical freq. The units of CF are in MHz.

N is measured in electrons per cubic meter.

So what we have is

$$N = 1.24E10 \, (CF)^2 \quad \text{leads to}$$

$$\frac{e}{m^3} = a \cdot (\text{MHz})^2 \Rightarrow \frac{e}{m^3} = 1.24E10 \cdot \left(\frac{\text{cycles}}{\text{sec} \cdot E10}\right)^2$$

This means $\left(\frac{\text{cycles}}{\text{sec} \cdot E10}\right)^2 \cdot \left[\underbrace{\left(\frac{\text{sec} \cdot E10}{\text{cycles}}\right)^2 \cdot \frac{e}{m^3}}_{\uparrow \text{ units of } a} \right] = \frac{e}{m^3}$

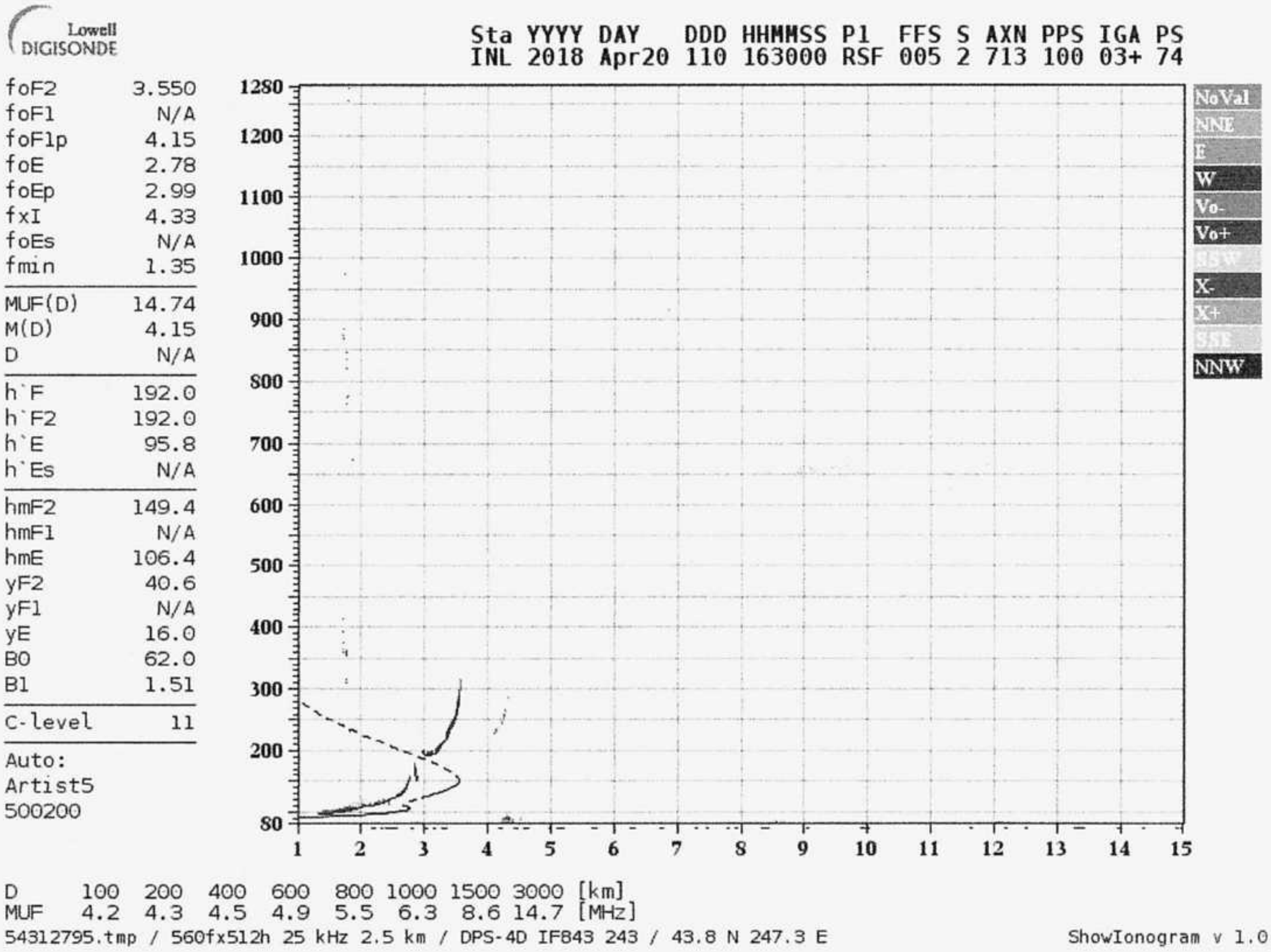


Figure 1: Real-time ionogram near your IP address location

Source: Global Ionospheric Radio Observatory (GIRO) DIDBase[1]

Legend

OK, this tells us that the coefficient "a",
ie 1.24E10

must be defined in terms of the units

$\frac{e}{m^3 \cdot MHz^2}$ This is a coefficient that has been developed to make a simple relationship available.

This was apparently developed by experimental observation, just like the coefficient of gravity, etc.

Therefore we are left with a simple relationship

$N = 1.24E10\ (CF)^2$

↑ electrons per cubic meter units

↑ MHz units

how many cm^3 in a m^3? $(100)^3 = 1E6$

Therefore

$N = 1.24E4\ (CF)^2$

electrons per cm^3

↑ MHz

This is the most practical form of the relationship.

so lets plot this out a bit

CF (MHz)	N (e/cm³)	Multiplicative Factor
1	1.2E4	1
3	1.1E5	~10 (actually 9.2)
7	6.1E5	~50
14	2.4E6	~200
28	9.7E6	~800

So we know less than 1% of the mass of the ionosphere was electrically charged. If we double the CF therefore we quadruple the electron density.

Therefore, a small change goes a very long way.

We see that our mean CF in 1996 was ~ 1.0 MHz @ nighttime.

But we see in 2009 to 2018 it is at ~2.5

Therefore our electron density, at night is expected to have increased by approx $(2.5)^2 \cong \underline{6}$ times. This is quite radical to consider changing from 1% to 6% w.r.t. the mass charge level, and correspondingly, the electron density level.

Note daytime factor is $\sim \left[\left[(4.68+5.20)/2\right]/4.2\right]^2 = 1.4$

Which is exactly what we are seeing. Nighttime propagation appears to be enhanced (from field observations) much more than daytime propagation.

THIS MEANS 24/7 COVERAGE NOW

THIS IS EXACTLY WHAT IS OBSERVED.

Now we are in a position to understand
the modern version of the "Woodpecker"

which is almost certainly based in
North America, if not more specifically
the U.S.

since we now hear the scanning
interference @ high S levels

ON THE 80 M BAND!

at night.

traditionally interpreted to be suitable
for relatively close range communication
@ night.

Notice the frequent declaration @ night by
amateurs / "oh the band has gone long
again".

The observations also match what must
be multihop operation because of frequent
propagation from S. Arizona / to
Brookings / OR w/ only 5-15 watts
on multiple occasions w/ digital modes
(eg MFSK, not JT65, not FT8) at night.

Therefore a

1. 6x enhancement during night hours
2. 1.5 enhancement during daylight hours.

Now lets look @ the UV index a bit. How is the scale generated, is it linear or exponential

UV index is essentially $= C_1 \cdot \frac{a_1 \cdot a_2}{25}$

Somewhat arbitrary again, as usual.

NY & LA are both @ sea level, so a_1 (which is an elevation factor) can be taken as 1.0. C_1 is fixed as a weighting factor of combining wavelengths (UV C has dominant influence, UV-A is not even measured). = 280
so we are left with

$UV = 11.2 \cdot a_2$ a_2 is a cloud factor.
Now normally a higher UV index means that there are fewer clouds. But we also know that high clouds, aerosols & haze generally increase the levels of UV radiation. So how is that effect measured and how is it incorporated into the current reporting of the UV index.

The classic interpretation here would be
higher UV index means more sun
But this presents contradictions w/ haze, "high thin clouds" & aerosols actually increase the UV ~~levels~~ levels

I do not know how the computation of the index has been altered by the knowledge of aerosol scattering, but it is known that this can be a significant influence.

Diffusion & scattering by aerosols & thin clouds are two main factors that will account for an increase in UV @ surface levels. Reflectivity of surface (albedo) is an additional factor.

April 22 2010

Additional observations on noise cancellation:

We know now that the primary noise source is the DSL modem. It is catastrophic on 80m. Very poor DSL modem design w/ no shielding whatsoever. But the main problem is identified.

What we ~~learned~~ learn is that an inductive relationship between the external antenna and the whip antenna of the noise canceller is a very effective way of tuning out the noise. Direct connection of the ~~and~~ external antenna to the noise canceller overloads the system. But inductive transfer of the energy from the external auxiliary antenna works extremely well. It has become quite a sophisticated process to reduce the noise by a phased antenna comparison process, but I do love it.

It is, by far, most effective on 80 m but 40 m also is successful to some degree. Working both the auxiliary antenna connected to a tuner in combination w/ the noise canceller is ~~very~~ very effective but also a rather complex adjustment to find & make.

Tucson Presentation May 12 2018

Potential Topics:

1. Ionosphere - UV - Ozone
2. Agricultural
3. Morgellons - Pukin
4. Legacy Project
5. Global Validation

April 25 2018

I am now starting to look @ the reactance of the portable antenna for the first time w/ the antenna analyzer.

Eventually I will compare the portable antenna to the base antenna. We know that the portable ant is working exceptionally well.

Our first observation is that when we increase inductance in the tuner, the resonant point shifts to the left from the tuned point of 7185 kHz 6050 kHz. The SWR also increased from ~1.5 to ~2.4. The before behavior of SWR, X (total reactance) & total impedance (Z) has shifted to the left toward a lower frequency.

When we decrease inductance in the tuner it shifts resonance to the right to ~ 9000 kHz. The behavior of the curve is displaced smoothly to the right (increased freq) and the min SWR remains @ ~1.5.

These are very sensible operations & concur w/ expected behavior. Increasing the inductance lengthens the antenna & therefore lowers the resonant freq & visa versa.

Now, let's go back t resonance @ 7185 kHz.

I am wondering how you determine the radiation resistance, or efficiency of an antenna. This is obviously a critical computation.

Ok, we are back @ resonance.
Cont. Capacitance is set @ ~ 4.2 on tuner.
Let's increase t ~4.5. on tuner.

This shifts the resonance point t ~ 7490 kHz
and the SWR ~~increases~~ decreases t ~1.26.
RL (dB) is now @ 18.8 dB.
Total ~~resistance in~~ impedance has increased
to ~~≈ 837 Ω~~ ~863 Ω @ 7670 kHz.

Go back t resonance @ 7185 kHz (approx)
Ok, what happens here is that
RL(dB) ≅ 13.0 dB and the total Z ≅ 720 Ω
@ ~0732 kHz.

Now back t capacitance @ ~4.5 on tuner. Ok, we have repeated the results.

Now, what exactly is RL in dB?
Everything says we would like a high number
@ the resonant point.

With the increased capacitance, we see:

1. A lower SWR achieved (at the resonant freq!)
2. A higher resonant frequency.
3. a higher total impedance above the resonant point.
4. Resonce always occur @ ~ 60 ~ 75 Ω
RG-58 coax is stated to have a resistance of 75 Ω, as I recall.

Now we will go the opposite direction and reduce capacitance on the ant to ~3.5 on the tuner.

Ok, here we have the resonant point @ 6620 KHz. The resonance in SWR ≅ 2.10 so it is higher. RL dB ≅ 9.0 so it is ~ 1/2 of RL (dB) w/ the increased capacitance. This is undoubtedly very significant. In addition, total impedance reach ~ 674 Ω @ 6750 KHz.

So lowered capacitance on the antenna.

1. Increased the SWR @ the resonant freq.
2. A significantly lower dB @ the lower resonant freq.
3. A lower resonant frequency.

your material for interpretation is very nice here.

1. What is RL (dB)?
2. You can certainly see the basis for a tuned antenna here, built into the design, esp w/ a tuning capacitor.
3. What happens if you were to retune the antenna @ the lower capacitance level (ie, by adjusting the transmitter capacitance instead of the antenna capacitance, using the tuner). Would it bring the SWR & the RL(dB) values back to the types of values achieved by adding antenna capacitance?
4. How do you know when you have a good antenna? If you start to figure out the consequences on one band (eg 40m) then how do you have any idea what is going to happen on 80 m? What about compromise results of trying to accomodate both bands?

Let's work a little bit w/ item #3
Lets tune the antenna holding the capacitance and the inductance & only changing the transmitter capacitance.

Ok, here is some of the answer:

1. First off, you must retune @ 7105 because the 6620 KHz area is outside the ham band.

2. Secondly, changing the transmitter capacitance had much less effect than changing the ant. Cap. It was important to achieve a tuned ant, but the ant. cap. was far more influential.

This tells me that changing the capacitance of the antenna has far more influence than anything else and that it significantly affects the:

1. Resonant frequency achieved
2. The SWR achieved (ie, optimization)
3. The RL (dB) value (maximization of) which undoubtedly seems especially important.

Now to work on an antenna, you probably need to select a favored band.

We see that increasing the capacitance of the ~~antem~~ antenna ~~som~~ seemed to have improved the performance of the antenna in all respects (ie lower SWR and higher RL dB) but it did so @ the expense of being @ a higher frequency.

Now, you are after getting this increased performance @ a lower frequency.

Now, how do you do this.?

We know that a lower freq can be achieved normally w/ an increased inductor or increased length, but @ what cost in performance?!

Remember, the increased capacitance is attempting to cancel out inductive reactance that already exists. It seems to me that we might want to decrease the inductance (of the whip antenna) that we already are ~~using~~ using?!

Ok, I have now reduced the inductance on the whip antenna by replacing the coil of the whip.

Let's evaluate the influence of doing so.

Little difference noticed by received audio.
Now let's look @ the analyzer.

Here is what we have w/ the reduced inductance
@ the base of the antenna.

Resonant freq chosen ≅ 7204

Actual data: SWR
1. Min resonance @ 7190 = 1.64
2. RL(dB) @ 12.1 dB

Max resistance achieved as 653Ω @ 7360.

Formerly w/ the coil we had:

1. Min Resonance @ 7105 (close enough) @ 1.5
2. RL = 13 dB
3. I do not have the value for Max resistance.

This suggests the increased inductance helps a little bit but increased capicatance helps a whole lot more.

Increase capacitance from 4.2 to 4.4:
We show:
1. Min SWR @ 7330 kHz of 1.5
2. RL = 14.3 dB
3 Max resistance of 706Ω @ 7520

Increase Capicatance to 4.6:
1. Min SWR of 1.23 @ 7530 KHz
2. RL = 19.7 dB
3. Max R of 827Ω @ 7130 kHz

We have ½ wave on 80m, not 40m.

So clearly increased capacitance is improving the performance of the antenna @ the higher frequency. So the question is, how can you lower the frequency of optimum performance.

We have full wave on 40m.

Changing the inductance (ie decreasing it) at the base of the antenna seems to have very little effect.

for ½ wave!

So it seems to me the way of lowering the resonant frequency will be to increase the length of the antenna. Let's try it.

$$(\tfrac{1}{2})\,l = \frac{468}{f_0} = 460 \cdot f_0^{-1}$$

This adjustment method did work!

$$\Delta l = 468 f_0^{-2}\,\Delta f_0$$

current resonant frequency

desired resonant frequency

$$\Delta l = \frac{468}{7.530^2}\,\Delta\underset{\text{actually}}{\underset{(7.2-7.530)}{(7.530 - 7.200)}} = \cancel{2.72\text{ ft}}$$

So we lengthen by ~ 3 ft.

Note! (not ½ wave!)

A mistake: Actually two mistakes. It is a full wave on 40m & you forgot the coefficient of −2! So

$$\Delta l = -2\frac{(2)\,468}{7.530^2}\,\Delta(-0.33\,\text{MHz}) = +10.9 \cong \boxed{+11.0'}$$

Note

Surprisingly close! 12' fixed it. See next page!

I have lengthened the antenna by ~ 3ft.
It has ~~s~~ no significant effect.

Min SWR = 1.69 @ 7195 kHz
RL(dB) = 11.8dB

Total R however did increase significantly to
a max of 905Ω @ 7370 kHz.

~~So it~~ We have retuned w/ the tuner and
~~Oops~~ it had no significant change whatsoever.
Lets add a longer segment.

OK we did it!!! Note/ See mistakes(s)!
this is why it is 12', not 3'!!

I have added about a 12' segment of wire.
I now have, when tuned up on the tuner @ 7200kHz

1. A min of SWR of 1.29 @ 7200KHz!

2. Max RL of 18.0dB @ 7200kHz!

Max R of ~~≥~~ 916 Ω @ 7370 ~~k~~ MHz!

OK then has achieved the desired result.

I have accomplished exactly what I intended to do.

Now, what happens when we add the 20 m coil back into the antenna instead of the whip?

You are seeing that even with the use of a tuner, your antenna still needs to optimized for a particular band and frequency.

With the ~~whip~~ coil added, the ant is still perfectly tuned @ 7200. This made no difference.

Here are the results w/ the coil back in:

Very poor results:

Min SWR of 3.84 @ 7.100 MHz
RL dB = 4.6 dB

Max R of ~31 @ 7360.

This is terrible!!!!

Back to whip.

Page
151

40 m only! 80 may be entirely different

No, we have a mistake of some kind.

Ok something happened w/ the antenna analyzer. Had to reset it & now it is back.

Ok, place the coil back into the circuit. I get almost exactly the same thing. RL (dB) is even a little less & SWR is a little higher.

The coil is not helping.

Capacitance info from the radiator is!

If increasing capacitance on the tuner helps the antenna then increase the wires. If the opposite, shorten the wires.

Maximize the RL (dB) and minimize the SWR!

This is great work today. The ant must be tuned to even the tuner. The physical configuration of the antenna still dramatically affects RL (dB) and the min SWR attainable.

My next question is:

What performance is now achievable on 80m?

80 meter is showing very good performance. The 20 m coil is once again not needed.

at ~3900 kHz w/ the ant tuned (adjusted now for 40 m performance) we have

SWR = 1.49 @ 3930] these are
RL(dB) = 14.1] good values.

Now tune to 3850.

Notice you have a very narrow bandwidth of good performance, ~40 kHz.

Min SWR = 2.01 @ 3890,
RL(dB) max only = 9.2 not great.

so these are not so good.

What about @ 3581?

First, lets go @ 3950.
We have

Min SWR of 1.60 @ 3980
RL (dB) " = 12.7 not bad

It is not tuning well on 80 m @ 50 watts

80 m is sort of messed up @ 3581.
Even though tuner says it is tuned. I
Cannot get a good reading from the
antenna analyzer.

It says the reactance is down to zero
but the SWR is still high?

OK, a huge lesson here, 80 m
require the COIL!!!

With the coil on 3581 we have

SWR min = 1.62 @ 3610] OK
RL (dB) = ~~[illegible]~~ 12.5 dB] good readings

Then now begs the question, what is happening on 3900, 3850 & 3950 w/ the coil?

~~The Coil Stats~~

The coil works perfectly on 3900.
We have:

Min SWR @ 1.18 @ 3910
RL (dB) = 21.7 dB   great results

It looks really good.

We now know what to do:

1. The coil must be used on 80 meters.
2. The coil can not be used on 40 meters
3. The length of the antenna has been adjusted and it works on both.

We have close to 1/2 wavelength on 80 m.
16' + 15 vertical
~~~35'~~ 40   Σ = ~~121'~~ 131'
~~~55'~~ 60

And we have close to a full wavelength on 40 m.

The house antenna probably has a problem.

Coil is about 20' + (30-8) $\cong$ 42 vertical
~ 35'
~ 40'
~ <u>40'</u>
$\Sigma = 157 \cong 160'$

The antenna is probably about 30' too long.
I bet you can <u>remove</u> the coil.

I now know what R_L (dB) is.
It is the "Return loss in dB".
Return loss is related to both the standing wave ratio and the reflection coefficient.

Smaller return loss is "bad" and means less energy is going into our antenna
This means, in converse, that a large return loss is good, and means that more energy is going into our antenna
Performance @ a R.L. of ≤ 9 dB may be unsatisfactory. This is exactly what I am seeing.

What you are seeing is that even though the antenna shows an SWR of 1:1, the antenna analyzer does not show such perfection and it is much more dependent upon the actual physical structure of the antenna.

Return loss is somehow a more * comprehensive parameter to assess antenna performance than SWR is.

How is return loss calculated?

RL(dB) = f(SWR $\underline{\underline{\&}}$ Reflection Coefficient)

↑ What is this?

The antenna analyzer shows you how effectively capacitive & inductive reactances are balancing one another. SWR does not show you this. The RL (dB) is a parameter which shows this very effectively.

The other thing you notice is that the SWR measured w/ the antenna analyzer is not exactly the same as the tuner shows. The antenna analyzer seems to be far more effective and sensitive in measurement. I wonder why this is.

Page 157

It is true, Reflection Loss (in dB) is a much more sensitive parameter of antenna performance than SWR is.

May 13 2018.

The presentation in Tucson on May 12 2018 has been given. On the route back to Monticello tonight.

Let's revisit the CDB secreted protein a bit and use basic IR analysis via Pavia. We are also going to use shape & intensity.

Our peaks are @:

3263 NH = 3500 (base) OH = 3600 (base)
med (med)

2916

1632

~1422

1018

Start w/ 3263. We know it is an amide but how do we know this?

Base values (p A19) present the first clue.
NH @ 3500 (base value)
OH @ 3600 (base value)

May 14 2018
What is the amide?

Pavia in Intro to Organic Laboratory Techniques Appendix 3 really does have a great intro to IR.

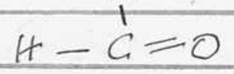
Introductory segments that are highly valuable:
1. Base values p A19
2. Primary bond regions in mid IR p A16
3. CH modes of vibration (graphically!) p A18
4. Simplified Correlation Table p A19
5. One page approach to IR interpretation p A20
6. A more detailed analysis of each functional group A21-A31

This assumes that you know the functional groups. These are not tabulated in Pavia's book.

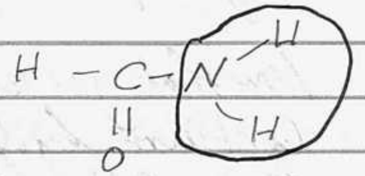
You have them on the phone & numerous sources.

An amide contains O-C-N ↙ This is more memorable

* So actually it IS a Carbonyl group attached to an NH group



So assume we have NH_2:



This is indeed, therefore, the simplest amide that can be constructed.

So Indeed this is the simplest way to attach on a Carbonyl group.

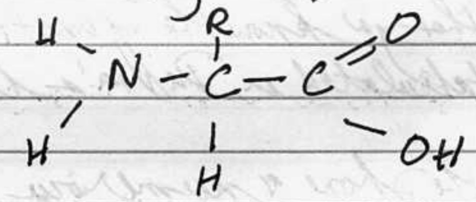
This is called "formamide".

So how does an amine within a protein relate to an amide?

Your notes of Dec 11 2017 (Volume 21) definitely tell & show the story.

The peptide bond that holds amino acids together is an amide functional group.

Remember an amine is only NH.
An amino acid will need to have more added (eg acid)
ie

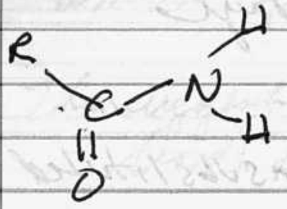


Remember this disassociates in real life.

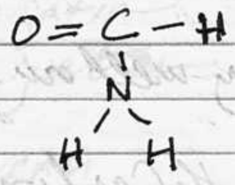
So an amide is simply taking a carbonyl group and adding it to the amine group.

Now that you understand that an amide contains hydrogen bonds and similarity to an OH bond, this is why the peak is apparently occurring near 3500 cm^{-1}. It is an interesting case as it does not fit the traditional IR OH interpretation however.

A traditional method of presenting an amide is



but we see that all that is actually required is to add a carbonyl group to an amine, ie



ie, Start w/ NH3 add a carbonyl & then fill in the minimum structure

Very interesting notes on p 270 of Vol 21 @ bottom where

Amide I come from C=O (~70-85%)
Amide II Comes from N-H (~40-60%) & C-N (~18-40%)

Amide A & B resonate from amide II
Amide III & IV apparently a lot more complicated

I do still find it curious that our amide is @ 3263 and such a major peak.

The amine group is actually driving this but the carbonyl is definitely causing a shift & apparent broadening of the peak

It is now that we can progress to Pavia p A31 on the amide group.

Recall that we have a peak @ ~ 1632
We relate this now to the Carbonyl
aspect.

Pavia has the monosubstituted or unsubstituted
NH stretch at 3100 - 3500.

This matches very well our peak @ 3263.

However, Pavia has the Carbonyl stretch @
1640 - 1670 cm^{-1}. We see that we are
slightly outside of that and definitely
not in the central range.

So it will be curious to learn what is
causing that shifting in the carbonyl.

Avram is our preferred source here.

Our range is 1631 - 1634 cm on the IR plot.
What does AVRAM say about this?

But before we do this, look @ Pavia on Carbonyls!

Pavia indicates that we should ~~have~~ more
likely have a case of increased conjugation
as well as decreased ring strain
(page A29).

He also shows that we are oriented toward the amides (pA20)

This suggests that we have an amide (ie peptide bond) that includes

1. increased conjugation (eg aromatic)
2. decreased ring strain

Now we can go to AVRAM.
Now even AVRAM gives us a range of 1650-2000 cm^{-1}!
So even this is outside the range where our peak is @ 1631-1634.

Avram amides start on p 439

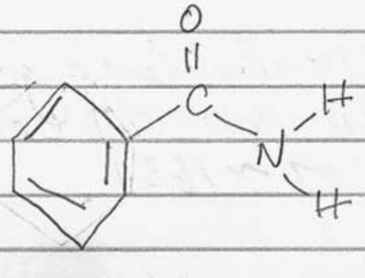
Amide I bands can go as low as 1623
Amide II band can go as low as 1605
so we are definitely in range.

In fact, benzamide is @ 1631.

This is a perfect match in all ways mentioned above, ie conjugation, etc.

Benzamide is $C_6H_5CONH_2$
slightly soluble in water + soluble in many organic solvents.

Therefore the amide group is attached to a benzene ring.



May 15 2018

I can see that I actually did a very good job of IR analyses of the CDB protein in Dec of 2017 and that the conclusion of a ferridoxin protein is quite sound.

However, lets build this process up again from the fundamentals of IR interpretation. It also does seem, however, that some very detailed analysis of protein IR absorptions, from several different detailed research papers was required to reach the conclusions of Dec 2018. The chart on the following page is one such example, where contradictions between the text of an article and its included table were also noted in previous notes. I wish to avoid the specialized information for the time being and look @ the IR picture from a more fundamental viewpoint.

most definitely

We do notice, however, looking ahead that we have fine matches w/ the table listed for Amide A (3250-3300 cm^{-1}) w/ our value of 3263-3269 region.

We also have a match w/ amide B of 3090 cm^{-1} in table w/ our shoulder showing up @ ~3080.

We also have a good match w/ Amide I w/ 1600-1700 cm^{-1} in table w/ our value of ~1631.

Amide IR Table : BioProcess International Jun 2006

Page
165 A

[illegible] spectroscopic data (5–10).

The relationship between amide I band position and type of secondary structure is best recognized by analyzing IR spectra of simple homopolypeptides that fold into well-defined and often homogeneous (purely alpha-helical or beta-sheet) structures. By contrast with such homopolypeptides, proteins usually fold into complex three-dimensional structures that include a variety of domains containing polypeptide segments folded into different types of secondary structures. Because each conformational entity contributes to the molecule's IR spectrum, observed amide I band contours are complex composites. They consist of many overlapping component bands that represent different structural elements, e.g., alpha helices, beta sheets, turns, and nonordered or irregular structures (Figure 2). A fundamental difficulty encountered in analyzing such composite band contours arises from the fact that the width of each contributing component band is usually greater than the separation between the maxima of adjacent peaks (Figure 2). So individual bands cannot be resolved and/or identified in the broad contours of experimentally measured spectra. Extraction of structural information encoded in those IR bands requires extensive mathematical analysis of experimental data.

In analyzing the amide I band, we must consider that some absorptions arising from buffer components may absorb between 1600 and 1700 cm^{-1}, thus perturbing analysis of the amide I protein absorptions. The most common interference is an absorption band of water in that region, but contributions of amino acid side chain absorptions must also be considered (11).

[illegible] hydrogen–deuterium exchange in proteins, providing information on subtle structural changes in protein secondary structure. Some authors have also used amide III band data to derive information with respect to protein secondary structure (7, 13, 14).

Figure 1 represents exemplarily different protein IR spectra obtained in transmission at protein concentrations of ~10 mg/mL in pure water at 25 °C. As can be deduced from the shape of the amide I absorption, secondary structural elements are different for these proteins. Hemoglobin shows a more or less symmetrical amide I absorption, whereas a broad amide I absorption is observed for alpha-lactalbumin and alcohol dehydrogenase. Such differences in overall amide I band shape come from different amounts of secondary structural elements in a protein structure.

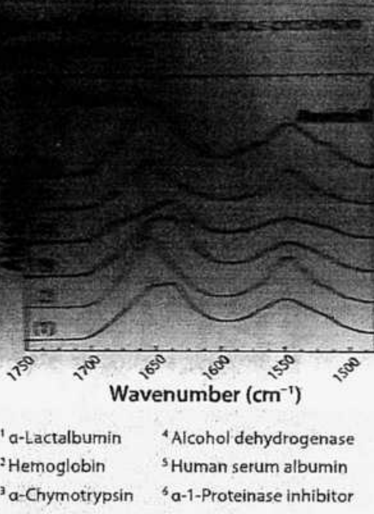


Table 1: Band assignments of the main infrared active vibrations of biomolecules

Frequency Range (cm^{-1})	Assignment
3490 and 3280	Asymmetric and symmetric H–O–H stretching
3250–3300	Amide A (N–H stretch in resonance with amide II overtone)
3080	Amide B
3010	=C–H stretching of alkenes
2957	Asymmetric CH_3 stretching
2920	Asymmetric CH_2 stretching
2872	Symmetric CH_3 stretching
2851	Symmetric CH_2 stretching
1738	C=O stretch
1600–1700	Amide I (mainly C=O strech)
1645	H–O–H bending
1480–1575	Amide II (N–H bend in plane and C–N stretch)
1468	CH_2 scissoring
~1395	C=O stretch of COO^-
1378	CH_3 symmetric bend
1343	CH_2 wagging
1230–1330	Amide III (N-H bend in plane and C-N stretch)
1240	Asymmetric PO_2^- stretch
1170	Ester C–O asymmetric stretch
1080	Symmetric PO_2^- stretch
1047	C–OP stretch
980	Choline asymmetric stretch
625–770	Amide IV (mainly O=C-N deformation)
720	CH_2 rocking

ANALYSIS AND APPLICATIONS

Within the 1600–1700 cm^{-1} IR spectral range, where the amide I absorption is detected, regions have been identified as being sensitive to particular secondary structural conformation. The "Band Assignments" box summarizes these structure sensitive regions within the amide I band. Hydrogen–deuterium exchange among amide hydrogen atoms causes a difference in band positions from those characteristically recorded in H_2O and D_2O.

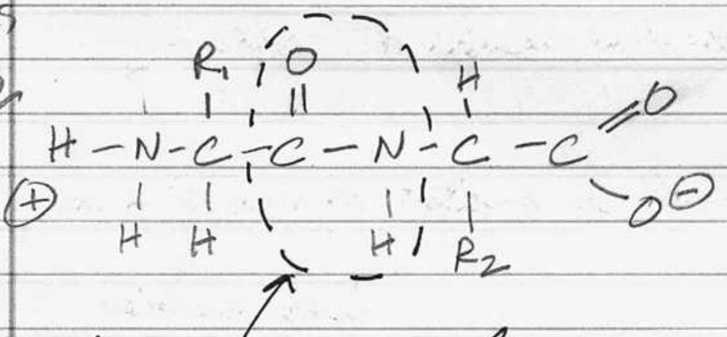
Characterizing Protein Structure: Extraction of single-subcomponent bands is achieved using curve-fitting approaches to assign each subcomponent to a particular protein secondary structure. The principle of such procedures is to resolve an original protein structure into individual bands that fit its overall spectrum. To estimate the range and positions of discrete subcomponent absorption bands, band-narrowing techniques are applied. Based on this

We also have two shoulders in the region of $1480-1575\ cm^{-1}$ w/in the table that correspond to the Amide II vibrations.

This tells us that we know we have the protein and the amide functional group.

Now if we go back to the struc structure of the peptide bond as described on Dec 11 2007

N only has 3 bonds



This is the peptide bond

The amide functional group

But we understand that an amide is actually simply the addition of a carbonyl group (C=O) added to an amine (NH is all that is required for an amine),

That this is exactly what we have.

Now the question arises what might we know about the nature of the R group(s)?

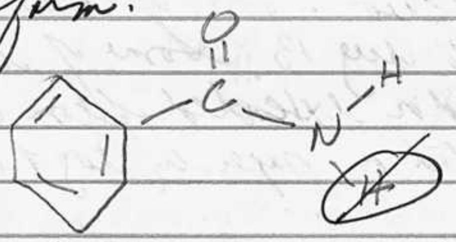
Now our notes of May 14 almost certainly come into play as we studied general characteristics of Pavia & Avram.

Pavia told us that we are most likely to have
1. increased conjugation (as in a benzene ring or something similar.

2. Decreased ring strain (as in a cyclic ring for example)

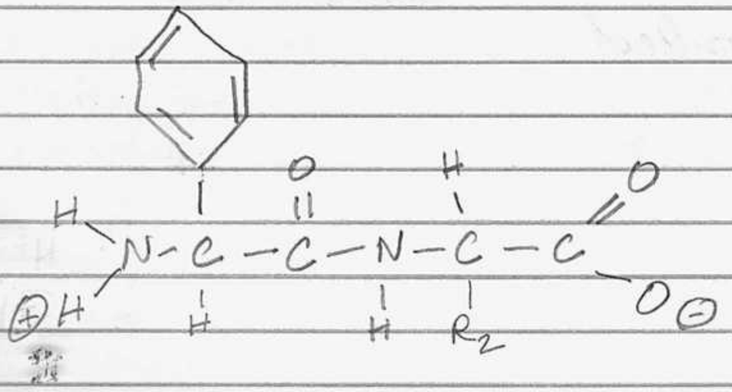
and Avram told us that we have a match w/ benzamide w/ the 1631 cm^{-1} peak.

So all analyses are indeed pointing to a structure of the form:



benzamide

or as closely as possible to this.
This means if we construct:



Then we are looking for a "R" group (amino acid of this structure)

or possibly a cyclic ring?

As I recall, we have done some rather extensive evaluation of potential amino acids to comprise the protein.

Two features come to mind.
1. Acidic
2. Aromatic or cyclic
3. Recall that NIR analyses suggest ArOH, ArCH
4. Water solubility indicates OH

On Aug 13 2017 I posted a paper on numerous attributes of the protein that have been identified. The work therefore took place prior to Aug 13. Some of it may have been repeated or extended from Aug & Dec 2017. Edits noted on paper in Aug & Oct 2017

We see an entry on July 29 2017 that indicates

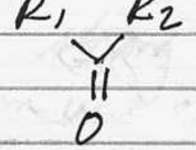
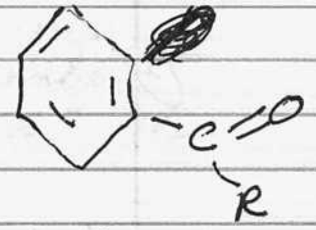
Proline — are the primary
Tryptophan — Candidates.
& Glutamic Acid

& see some amazing gas chromatography work (GC)
Completed on Jul 23 2017. Volume 20.

We are clearly working with
1. Amides
2. Aromatic ketones } as candidates

We need to review Vol 19 notes also.
Our GC peak of 3.93 min. - paper pyrolysis & CDB Charged protein pyrolysis & trapping of peaks into IR instrument.

We are most certainly scrutinizing both amides & aromatic ketone.

A ketone is  An aromatic ketone is therefore 

Altogether we have the following cyclic n aromatic amino acids:

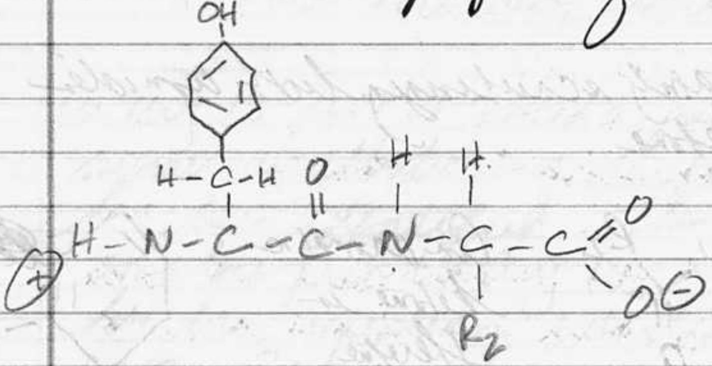
Cyclic	Aromatic
Proline	Phenylalanine
Tryptophan	Tryptophan
Histidine	* Tyrosine ArOH e ArCH

The acidic amino acids are

aspartate
glutamate

Tyrosine is a very strong candidate as it satisfies the NIR data of ArOH & ArCH as well as being of polar character.

This leads to a proposal of



CDB core structural proposal - Phase I analysis.

Next, we look for the effects of tyrosine disruption.
And we look into the acidity of glutamate & most likely it is proposed as R_2.

Also look into IR plot of tyrosine

Tyrosine is involved in neurotransmission, dopamine, cognitive function, mood

Also important w/ the thyroid. Hypothyroidism is a Candidate here.

Also involved in synthetic protein production.

Tyrosine is obviously a nice topic for investigation & there are certainly Consistent disruption symptoms to investigate.

—

No IR Capability right now but UV or electrochemistry Could be useful. Consider Colorimetric, organic tests as well.

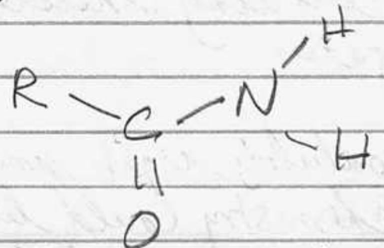
Tyrosine is a strong IR absorber. Remember Comment on use of KCl plate in IR? ie - Very high IR absorption noted.

May 19 2018

I continue to study the IR spectrum of the protein. Four additional IR books have arrived and they look very useful.

IR Pal is a good start but it hardly is the whole story. It managed 3269 as either a phenol or carboxylic acid. We know in actuality it is Amide A & B.

An amide is:



Recall a carbonyl attached to an amide, so IR Pal really does fail me here. We found the amide solution by looking @ individual research papers. The fact that absorption is above the alkene & hydrogen bonding might be tipoff that you need to look harder. It also by separate tests that you know you are dealing w/ a protein

Now what did Pavia say? On the most rudimentary level of IR interpretation, how would you suspect that you have a protein or an amide here?

Formerly I only had two practical Correlative IR interpretation books, Koj. & Avram. I now have some additional useful sources.

Sidebar: CEC ECG following a week+
(???) anxiety, panic, unstable angina episode during
week of ~ 05/08/18. afte stabilizing ECG is normal.

ID:
DOB: 1/19/1953 (65 yr)
Gender: Male

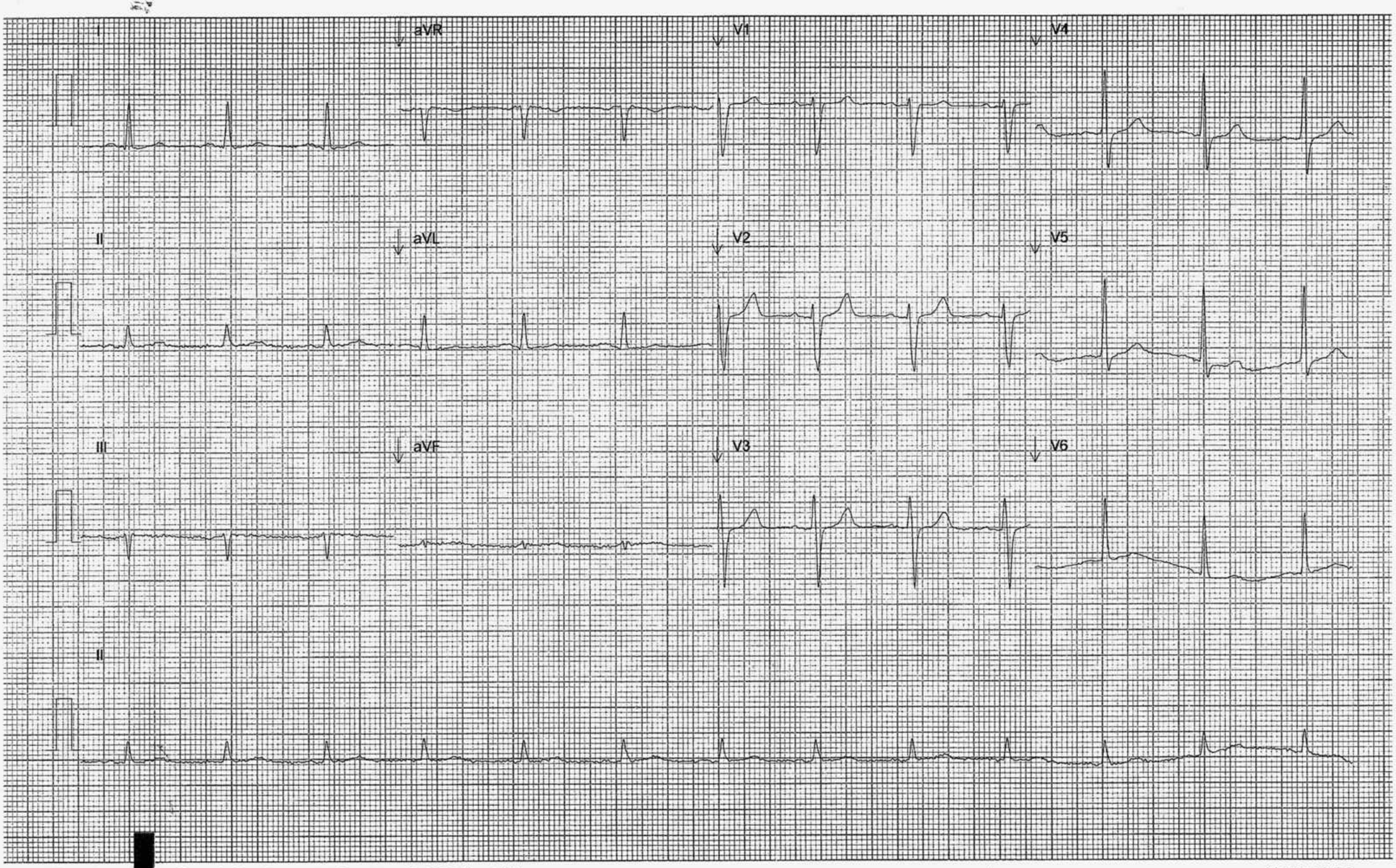
Name:

P/PR:	128/166 ms
QRS:	104 ms
QT/QTc:	378/430 ms
P/QRS/T Axis:	-14/8/57 deg
Heart Rate:	78 BPM

Normal ECG

Unconfirmed Report

Page 173A



25 mm/s [redacted] 10 mm/mV Frequency Response [0.5-35] Hz 60 Hz

1

Version 2.5.0

Now let's go back to Pavia and see what he says & determine how we get tipped off that we are dealing w/ amides and a protein.

Now Pavia has a general approach.

1. He asked first and above all, do we have a Carbonyl?

And the answer is Yes!. This is a really big deal as a Carbonyl has major implications in its own right.
It was because of significant absorption between 1600-1820. We are @ ~1631 cm^{-1}! So close to the edge but still in range.

2. Next Pavia does something else very important. He uses the Carbonyl group as a major separator between the following two sets;

C=O Carbonyl Present	No C=O No Carbonyl present
1. Acids	1. Alcohols or Phenols
2. Amides	2. Amines
3. Esters	3. Ethers
4. Anhydrides	
5. Aldehydes	
6. Ketones	

This was our tipoff. Since we have a carbonyl we progress through Pavia w/ his six groups. Pavia really does have a high level plan that already is paving the way.

1. The acid did not work. Broad absorption 2500-3300. We do not have it.

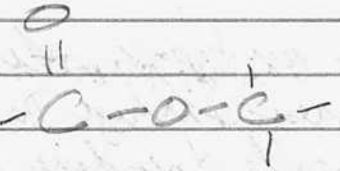
2. Amides? Do we have NH?
Well, even w/ Conleys p 88 generalized chart we already see that we are confined to either OH or NH in the 3269 region. But we already know that we do not have OH (we are shifted from 2500-3300 and we are not that broad. So we already know that our main group is not likely OH. This means that it already says we are dealing w/ NH. Now Conley has NH from 3000-3800, Pavia gives us the peak @ ~3500. We are @ ~3269, We also notice shoulders @ ~3200 & 3300. This suggests increased NH activity here. We already have signs of an amide here.

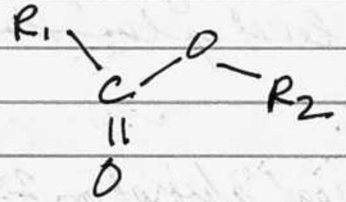
3. Keep working w/ Pavia. He is onto Esters next. This requires C-O, 1300-1000. We do have some activity @ 1211 & 1018. 1018 is a very major peak.

Conley gives C-O range from 1300-900. So Esters do remain a candidate here.

Page 176

What is an ester?





An ester is a Carbonyl attached to a C-O bond.

So I therefore place esters in the candidate list, along w/ amides.

4. Next, Pavia asks for anhydrides. These require two Carbonyl absorptions near 1810 & 1760.
This does not match at all.

5. Next, Pavia asks for aldehydes. Need 2850 & 2750 on the side of CH absorptions. We do not have it.

6. Pavia now asks for ketones. This means all previous candidates have failed.

But they have not failed

Our primary target list is therefore

1. Amides
2. Esters

We would next work w/ Pavia in greater detail on these two groups.

Now, and only now, are we justified in moving on.

We can see that IR Pal really caused us some problems, confusion & unnecessary grief here for many years. Pavia has a real sense of logic & order here.

Now for amides.

1. Pavia has C=O stretch @ 1610-1640.

We are slightly outside of this but conjugation and ring size are mentioned here, same as Avram did.

We suspect therefore some effect from conjugation & ring size & we are to learn about this.

2. Pavia next mentions a monosubstituted or unsubstituted NH stretch from 3100-3500.

Unsubstituted has two bands w/in 3100-3500 and we do <u>not have</u> this.

We therefore already suspect:

1. Conjugation effects
2. Ring size effects
3. Monosubstitution or unsubstitution on NH, whatever that refers to.

3. Pavia then mentions NH bending @ 1640-1550 and we definitely have this @ ~1631 cm^{-1}.

Therefore from Pavia we already anticipate an amide compound with:

1. Conjugation effects
2. Ring size effects
3. NH mono/substitution or unsubstitution
4. NH bending.

These are important additions to the amide structure that are to be explored further.

Next let us examine the ester candidate from Pavia.

Now, the ester candidate did not work because the carbonyl group required a stretch absorption @ ~ 1735 cm^{-1}!

We definitely do not have that. This means that our peak (very strong) @ 1018 cm^{-1}

(even though it is the range of 1300 - 1000 cm^{-1} as specified by Pavia, the ester candidate DOES NOT SUCCEED because of the failure of the primary ester carbonyl peak @ ~ 1735.

We therefore have double confirmation of the azide w/ the additional properties that we have something else very significant @ 1018 - a major absorption that did not fit the ester.

We know that we have additional test methods down the road that also help us, especially

1. NIR
2. Electrochemical
3. Colorimetric tests
4. pH

But for now, there is heightened interest in the 1018 absorption. We have tentatively identified sulfate groups but lets see if we arrive there again.

IR Pal suggests phosphine - P-H and phosphate esters but we already know that esters can not work. We normally do not consider inorganic but we may well be lead that way. Charring the protein might help here to determine if we have organics but we already know that this can cause serious health effects from the pyrolysis experiments.

So we have an issue here. Very significant absorption but it may not fit organics.

Chemistry Toolbox is suggesting

not really here ~~Sulfur~~, Silica or Phosphorus Compounds

Ester did not work.

~~Sil~~ Silane	Si-O-C	1110-1000
Phosphoester	P-O-C	1090-920
Phosphonic Acid	P-O	1040-910

I wonder where we pulled sulfates from?

An ester is a C-O bond.
We have failed the "normal ester" with anticipated Carbonyl @ ~1735.

So we have an issue here.
VERY SIGNIFICANT absorption @ 1018.

SDBS is indeed coming up w/ sulfate compounds using the 1018 peak alone.

Lets add the 1121 cm^{-1} peak w/ the 1018 cm^{-1}
Condition +/- 10 cm^{-1}, transmission < 50.
4 out of 7 top compounds are indeed sulfates.

hydroxylamine sulfate is top candidate
One compound does show iron sulfate

From colors, we are certain to have iron.

Hydroxyl amine sulfate is an interesting compound:

$NH_2-OH \cdot \frac{1}{2} H_2SO_4$ ie sulfuric acid combined w/ amine & OH group.

We are seeing that we are indeed being led to
* an iron-sulfur protein, exactly as we had determined earlier.

Iron from color & known composition
Sulfur from 1018 peak
Protein from amides

Lets look @ the sulfate & iron w/ chemical or colorimetric testing. This has been done previously but finding the notes will be difficult.

OK, we definitely have a sensitive chemical test for sulfates based upon the use of BaCl & HCl from our water testing kit.

It has been applied to a very weak solution of $FeSO_4$ w/ great success, whereby a white precipitate is formed.

absolutely positive proof of the iron-sulfur
nature of the CDB Protein today (ferredoxin)
May 20 2018 Next we look @ health impacts.

We have a definite Chemical test for sulfates available. Let's apply it to the protein.
Result:
It takes a few seconds for the reaction to develop but

* the protein definitely passes the test for the existence of SULFATES when the protein is diluted in water.

This shows the success of the IR spectrum interpretation.

* We also have an absolutely positive test for the existence of the Fe+2 ion in a dilute protein solution.

* This means that our IR interpretation of having ~~an~~ an iron-sulfur protein is absolutely correct.

Good work.

* From here on you can continue to try and ascertain amino acids in play but based upon the IR work a pH analysis

* Tyrosine & glutamic acid are very strong candidates.

May 25 2018

We are now looking @ the IR spectrum of the environmental filament w/ a fresh eye. Especially via the big picture flowchart of Pavia.

First off, we do have a carbonyl. This is the first primary division.

Our carbonyl is @ 1624 cm^{-1}. (range = 1820-1600).
Because of the carbonyl
We now examine the amides. Everything is saying that we have an amide in almost identical fashion to that of the protein

	Amide A Proposition	Amide I Proposition
Protein	~3266 cm^{-1}	1631 cm^{-1}
Env. Filament	~3356 cm^{-1}	~~1624 cm^{-1}~~ 1635 cm^{-1}

Lets examine this more closely. We do have a difference on the amide prospect of ~100 cm^{-1}. Using Pavia:

Now amines are listed as 3500-3300 cm^{-1}
Amides range from 3100 cm^{-1} to 3500 cm^{-1}.

So we are well w/in range. The amide (NH stretch) conclusion is well supported. Pavia also looks for NH bending from 1640-1550 cm^{-1}!
We are @ ~ 1635 cm^{-1}. We are therefore in range but notice we are on the left boundary.
But we were before as well.

Our overall conclusion is strongly justified. We can examine this in more detail when the overall view is completed.

Next we have something important going on. With the env. filament sample that was digested by Catalysis ($FeSO_4 + H_2O_2$ discovery of method of breaking down the filament)

we have the appearance of a cyanate group. This is significant.
Our peak is @~2066 cm^{-1}.

The peak does not show up w/ Microwave NaOH digestion; this is a lesson on how important the sample preparation method can be.
Fe^{+2} and H_2O_2 are definitely available w/in the body. High H_2O_2 production could be a very troublesome signal to look for.

* Side topic: What causes increased H_2O_2 production w/in the body?

IR Pal gives 2066 cm^{-1} as $R-N=C=S$

Time to pull out AVRAM reference also.

Aliphatic From AVRAM p411 we have Aromatic
~2140 cm⁻¹ 1. R-S-C≡N Thiocyanate ~~2140~~ 2160-2175 cm⁻¹
1990-2140 2. R-N=C=S ~~Aliphatic~~ Isothiocyanate 2040-2130
$\bar{x}$=2065 $\bar{x}$=2085

They say, w/ absorption @ 2066 we clearly have an iso thiocyanate compound.

It also strongly indicates that it is an alyphatic form vs an aromatic form.

* The presence of an isothiocyanate w/in the filament is a very important finding. It concurs w/ other body fluid spectra that show the presence of this group.

It is also significant that the group was found only through a specific and unusual catalytic digestion using $FeSO_4$ & H_2O_2.

Conley book p117 concurs exactly w/ the information given above.

Therefore we have amides (protein) w/ a thiocyanate compound within

Next we have a definite peak,
sometimes double:
@
1366 cm^{-1}, 1374 cm^{-1} $\bar{x} = 1370\ cm^{-1}$.

Now for grins, start w/ IR Pal;
a few choices. He gives

alkanes & sulfates.
We do not have alkane so that leaves
sulfates.

Now back to Pavia, as we recall our
preliminary examination suggests either
nitro and/or sulfate groups.

Recall also that one of our samples removed
the salt plate interference from NaOH - HCl
neutralization after NaOH digestion. This
was a good move, as that spectrum provides
strong signature @ 1554 & 1374 cm^{-1}.

~~Pa~~ IR Pal @ 1554 says Nitroso N=O

This is concurring w/ Pavia.
It is also dead center in the band for IR Pal
of 1500 to 1600 cm^{-1}.

So lets go back to Pavia to see where the nitro and sulfate groups came from.

Pavia
1. Carbonyl group was present.
2. This led to amides upon Section 2

This advanced us to Sec 4.
This did not satisfy other than the indication of an aromatic ring, but this does not match since there is no CH activity

This advances us to Sec 5 Triple bonds
No activity there.

Next we go to nitro groups
Requires 1600 - 1500 strong absorption
We have it.
1390 - 1330 strong absorption.
We have it (at least moderate).

We therefore satisfy all preliminaries for the nitro group w/ the use of Pavia.

Last group of hydrocarbons fail.

Thus far we have, therefore, to a high level of certainty:

1. Amides (protein)
2. Isothiocyanates
3. Nitro group.

In addition, we do see another strong peak (actually double) centered @ ~ $1015\ cm^{-1}$.

One possibility here w/ Pavia is an ester but it is on the edge of the band (1300-1000). It also is termed a medium intensity absorption but ours is strong.

We must recall our protein that had a positive ID w/ sulfates and the peak (very strong like here) was @ $1016\ cm^{-1}$!

Everything we have says sulfate group again. (Inorganic)

Certainly we know the filament is extremely difficult to break down and we can strongly infer disulfide bonds here.

How did you find the group before?
If Pal does not show it.

We know esters can not work because it require a carbonyl absorption near 1735 cm^{-1} which we do not have.

It came from the use of the SDBS database from Japan. Sulfates show up very strongly there. We see that we found another source (at this point it is fair to be thinking of inorganics because of the Pavic failure).

I do see that we found another source somewhere, it must have been an inorganic correlation chart.

It look like you are dealing w/ the S=O bond
But where was the condensed correlation chart for inorganics that I used?

Conley p 184 w/ Chart on p 193 certainly nails it in combination w/ SDBS.
Best estimate here is HSO_4^-.

Conley does have our ~~best se~~ chart so far.

FOUND IT. Parker p482 Inorganic Ion Chart.
Sulfur & Phosphorus (i.e. sulfates & phosphates are both candidates there.

Our best analysis is, therefore

1. Amides (protein)

2. Isothiocyanate Group

3. Nitro Group

4. Sulfur groups (specifically $S_2O_3^{2-}$
seems to be a likely choice.
(Presumably this is a disulfide bond?)

These functional groups comprise the core constituency of the Environmental Filament.

These are also very important findings.

* You now have the core essence of

1. The CDB generated protein:
(protein, iron, sulfur) - ferredoxin

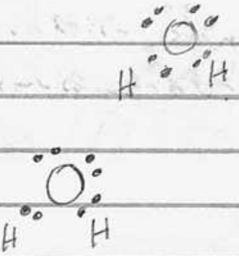
* 2. The Environmental Filament:
(protein, Isothiocyanate, Nitro, Sulfur)

This is good work: Next? HEPA filter

May 26 2018

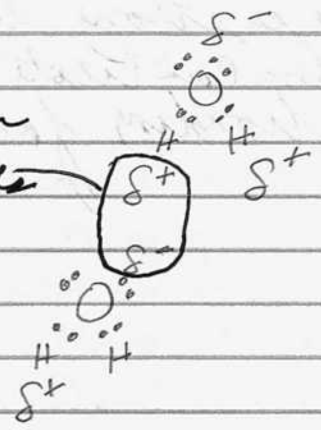
I am interested in this hydrogen bonding process. This issue rears its importance repeatedly, and it came up twice now in the IR interpretations of spectra.

Brian Smith introduced this in Spectroscopy magazine Jan 2018. Hydrogen bonding results from intermolecular interaction. Water is a great example. Brian Smith shows a diagram. Raymond also shows a picture on p108 in Lewis Diagram style - let's start w/that.



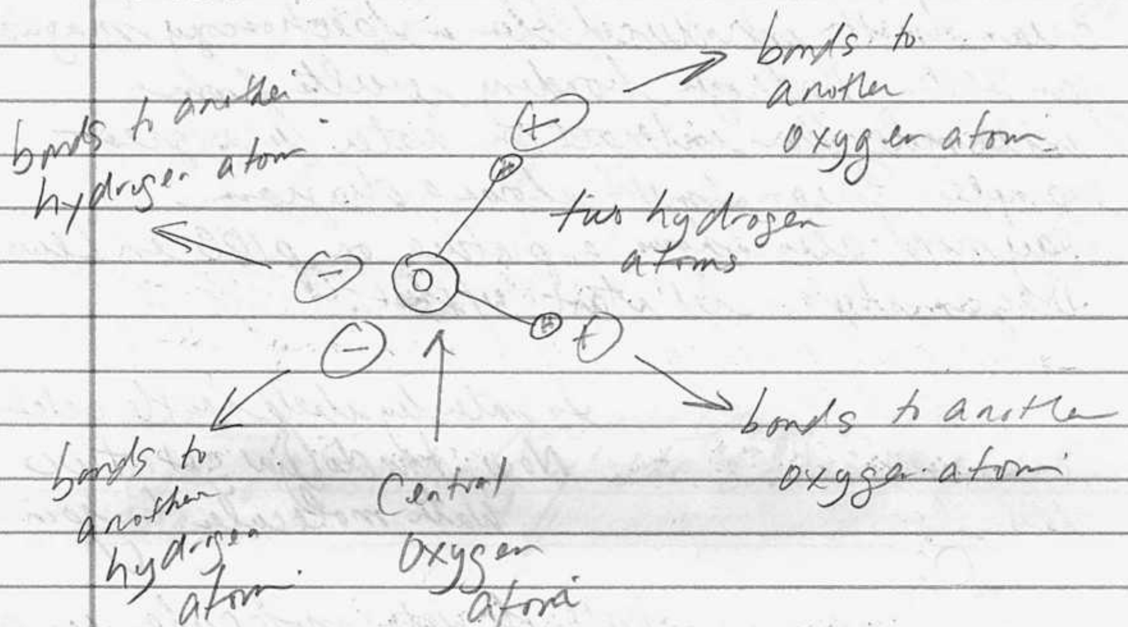
So water by itself has the octet. Now, how do you get two water molecules to join

Well, the water molecule is polar. This is because oxygen is more electronegative than H. This causes partial charges to exist w/in the molecule.



This attraction is what causes the bond.

Each water molecule can hydrogen bond w/ 4 other water molecule so they combined bonding actually ends up being a rather powerful force. It explains why it takes so much heat to boil water



So an individual hydrogen bond may not be so strong but the multiplicity of them can create a very powerful bonding force.

May 27 2018

On to the next set. These will be both rainfall & HEPA extracts. On first glance, they appear to have strong similarities. The rainfall was extracted via xylene & the HEP via ethanol. Evaporation of the solvent was used in both cases w/ the residual film left on ATR.

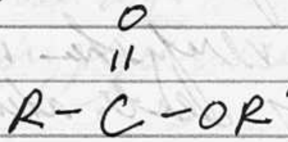
Let's start w/ rainfall.

First question: Do we have a carbonyl? (Pavia) The answer is yes & then is the first significant division. Our carbonyl is @ 1736 cm^{-1}!

From Pavia pA28 this is most definitely an ester (1735 cm^{-1}).

So this is significant - what is the structure and what types of compounds are esters? Also what are expected environmental sources?

Esters are



$$R-\overset{\overset{O}{\|}}{C}-OR'$$

We show no deviation in absorption to either right (conjugation in the R part) or to the left (conjugation in the R' part with the O) so we do not anticipate any significant conjugation in either part.

Now Pavia seems to show a contradiction.

The 1735 cm^{-1} (ie, 1736) absorption is listed as a C=O stretch.

However he also refers to a C=O stretch w/ two additional bands to be expected, one stronger than the other, between 1300-1000 cm^{-1}. We actually do seem to have these (and more).

The problem is that w/in the example spectrum given (methyl benzoate) he designates these bands to a C-O bond, not a C=O bond. I believe this is what he intended since

1. a difference is expected w/ a different assignment
2. The C-O bond is the other essential core element of the ester structure.

We will, however, verify this w/ a more detailed study of ester absorption.

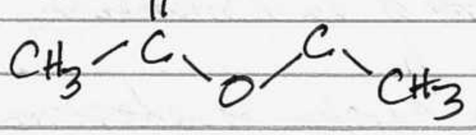
My next biggest question is, however:

Since we know we absolutely do have an ester, what are the properties of an ester?
What are the environmental or biological implications of an ester?

Page 195

Crippen
14
75
100
103
110
129
138
188
178
180
* 190
* 191
171
228
229
254
266

Ethyl acetate is one example of an ester.



They are formed from reactions between an acid and an alcohol.
They have sweet fruit smells w/ low molecular mass
The lower the molecular mass, the stronger the odor.

Phosphoesters form the backbone of DNA molecules
Esters are utilized in the assembly of polyesters;
Polyesters are a part of forming plastics.

There are two tests (one is colorimetric) for the presence of an ester in Roberts - Experimental Organic Chemistry p 712. These tests are feasible. One reagent required will be hydroxylamine.

Polymers, polyamides have associations w/ esters. Esters are involved with odors + perfumes, beeswax, fruit smells, triglycerides, additionally.

"When ~~you combine~~ an organic acid, such as a fatty acid, is joined end to end w/ an alcohol, the result is an ester.

There are several aspects of esters in Cripper's book on the Identification of Organic Compounds

p 178, 191, 266, 171, 110, 138, 14, 180, 191, 266, 190, 228
229, 254, 188, 129, 190, 191, 100, 103, , 75

Crippen's objective is identification
but lets look @ some of his comments.

Refractive index as a function of retention
in GC occurs on p 103.
Density of esters vs retention volume on p110.

Preparing esters for injection into GC on p191.

Also the colorimetric test for esters,
called the "Hydroxamate Test"
is described on p191 (similar to color test previously)
requires:

1. Hydroxylamine hydrochloride in methanol
2. Potassium hydroxide in methanol.
3. Hydrochloric acid.
4. Ferric chloride

This is a feasible test, however, not required @ this point since IR proves existence conclusively.

So what we see from this is a verification of a colorimetric test available as well as potential involvement w/ gas chromatography (GC).

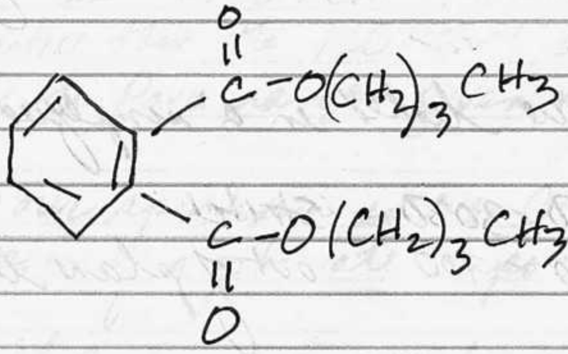
On to McMurray, he has a full section devoted to Esters (21.6) starting on p 789.

Early mentions:

1. Ethyl acetate (an ester) is a commonly used solvent
2. Dialkyl phthalates are used as plasticizers to keep polymers from becoming brittle.

Remember that our earlier work brought out a strong interest in phthalates?

Here is an example (appears we combine aromatics, esters, and hydrocarbon chains).



We already know from the IR spectrum that we most certainly have the hydrocarbon chains. Keep an eye for the aromatic quite promptly please.

Saponification is also involved w/ esters.
This is the process of ester hydrolysis.

The boiling of animal fat w/ base
to make soap is saponification.

<u>Fats</u> <u>have</u> ester linkages.

From the second book by McMurray:

"You may be aware that there is current
concern about possible toxicity of phthlates
@ high concentrations..."

We obviously need to look at the property of
aromatics.

Aromatics are listed in a simplified table as:

C-H : 3150 - 3050 stretch
1000 - 700 out of plane bend

C=C 1600 - 1400

Pavia also has:
medium to strong absorptions in 1650 - 1450 cm^{-1}
often imply an aromatic ring.
Confirm the above by consulting the CH
region.

Well, we most certainly have absorption @ 1454 cm^{-1} and this does correlate w/ the CH presence @ 2195 cm^{-1} & 2850 cm^{-1}.

This combination will be examined closely. SDBS can be of interest here also, using

2915, 2850, 1736, 1454.
Lets see what it shows ,

We have a single match of a phthlate compound in SDBS database w/ peaks of 2915, 2850, 1736 & 1454 cm^{-1}. So it can indeed happen. This particular compound is butenyl hydrogen phthlate. The main peak in the "aromatic zone" is ~ 1287 cm^{-1}, however (vs our 1454). But notice that the 1287 cm^{-1} would be even outside the Pavia range given of 1650 - 1450 cm^{-1}!

Therefore our spectrum is even closer to the expectation of a phthlate compound.

I shall continue to investigate the aromatic functional group here as we seem to be in range.

Out of curiosity, what is the spectrum of benzene? or methyl acetate, for example?

June 01 2018.

Continuing w/ the rainfall extraction spectrum. Our interest @ this point is the peak @ 1454 cm^{-1}.

We already know that we have alkanes.
We also know we have an ester.
We suspect we have an aromatic.
The combination produces a phthlate, a plasticizer!

Let's work on the aromatic issue

A most general way to start is w/ Koji & Pavia.

Pavia lists aromatics actually in 3 different places:

3150-3050	The C-H bond
1600-1400	The C=C bond.
1650-1450	~~Double bonds or aromatic~~ Often implies an aromatic ring.

We satisfy 2 of these 3 conditions.
We do not, however show the 3150 to 3050.

Caution, however. This sample is a xylene extract. We also have an extraction into alcohol, and there are some major differences.

Take one spectrum & one situation @ a time.

So leaving the C-H aromatic bond alone for now.
We move on w/ 1454 cm^{-1}.
IRSpecCheck
~~Spectra mate~~ gives us a benzene ring (1450-1600)
Notice however that it does list a C-H alkane
@ 1470 cm^{-1}. This is a fair amount of difference
but it still should be considered.

Spectramate Pro gives us the following:

1454 cm^{-1} is a $R-OCH_3$ peak, belonging to a saturated alkyl.

So we do indeed have some uncertainties here.
We have another peak @ ~1050 (double peak) & 798.
Spectramate: 1050 ⇒ $R=C-O-C$
belong to an ether.
798 ⇒ $C-O-C$
IRSpecCheck: 1050 ⇒ C-F Alkyl Halide
798 ⇒ Benzene Ring.

This is obviously fairly complex & uncertain.
Stick to the basics for now.

Pavic says aromatic.
However Pavic also said alkane – VERY CLEARLY.
Notice Pavic said near to 1450 for alkane.

This therefore is the most obvious candidate.

Next we look @ Koji for the big picture.
We have either
Alkane or Aromatic
(1400-1470) (1600-1450)
(CH_2, CH_3)

So which of the two? Alkanes are the most obvious.

Koji says that an aromatic has a signal @ 3030, 1600-1500 & < 900.

We do not have this.
Alkanes are still the strongest candidate here

Here is what I notice.
Koji gives 1450 as an alkane.

June 02 2018

Continuing w/ rainfall extraction spectrum - xylene extraction

Since aromatics have a C=C resonance bond
it only make sense that they would need to show
up above 3000, which is for the alkenes.

Notice in Parker p 104 he gives a listing for ~1455
as a C-H group, specifically a
"alicyclic - CH_2"
That is interesting as it certainly a match.
What exactly is this?

I am looking for a high level bond chart
Pavia has one on p A16 but the wavenumbers
are not detailed enough.

Conley has one - very good - on p88.

The primary references are now:

Books:

Pavia - Primary Flow Chart
Avram - Great Detail General Bond Chart ~~Great Correlation Chart~~
Conley - ~~Correlation Chart~~ & Great Detail
Koji - Mid Level-Detail
Parker - Great Correlation Chart

Software:

IRPal
SpectraMate
IR Spec
SDBS

We see that there are a lot of options for the 1454 peak, however the big picture is that

1. The broad Chart (p 88) Conley focus is indeed CH bending.

2. Koji emphasis is also CH but he does show edge overlap w/ aromatics.

3. Pavia mentions that aromatics can occupy 1650 - 1450 (we are on the very edge of this) but he emphatically states that we must check the CH region to accept this. Aromatics exist above 3000 cm-1 AND WE DO NOT HAVE THIS W/in the xylene extraction. The alcohol rainfall extraction will come later and that is a different story.

For right now, it is only the xylene (non polar) extraction that we are speaking of.

Therefore, the big picture already says that we do not have an aromatic in the xylene extraction. This is important as it reduces the phthalate consideration for the time being.

So lets recall our supplementary consideration list:

1. Davis does not really help us now.
2. Koji is big on the CH factor
3. Conley p88 Bond Chart is strong on CH bonding.
4. Parker p104 Correlation Chart is
incredibly specific w/ an alicylic CH_2 @ ~1455 cm^{-1};
you cannot get a better match than that.
5. IR Spec (app) gives us a CH alkane @ ~1470
6. Spectra mate (app) gives us an R-OCH_3, a
"saturated alkyl" - the first time
we are bringing a CO bond into the picture
- this appears anomalous @ this stage.
7. What does IR Pal say?
IR Pal gives the same result: either alkanes (RCH_2CH_3) or
aromatics. Additional alkane corroboration to be found @
1350-1380 & @ 722 cm^{-1}. Alkanes remain @ strongest candidate
8. What does SDBS (Japan) say, assuming we
use 2915, 2850, 1736 & 1454 ?
(Use +/-5 cm^{-1}, T<30%)

The SDBS matches (we have reduced to a set of 6 matches)
are extremely interesting. We are definitely on the right
track and the consideration of aromatics is
indeed allowable.

However, starting w/ IR Pal, additional corroboration
of alkanes @ (1350-1380) cm^{-1} & ~722 cm^{-1}
are not supported — this is also of interest.

The question of aromatics seems largely focused on the question (or lack of absorption) above 3000 cm^{-1}.

However, we notice that with the SDBS matches 2 out of 6 of the matches, even though they DO contain aromatics, DO NOT show very strong, or any absorption above 3000 cm^{-1}.
This is especially intriguing so aromatics are not necessarily off the table.

Let's look @ SDBS groups that show up:

SDBS#	Groups Found:
1	Ester, NH, cyclic ring, alkanes, aromatic
2	Aromatic, Ester
3	Aromatic, alkane, Ester (looks like a phthlate)
4	alkane, aromatic, S=O, NH, cyclic, N-O
5	aromatic, alkane, Ester
6	Cyclic, N, alkane

Our tally on this, therefore, is: (SDBS)

			Sorted
Ester	4	5	Aromatic
N	3	5	Alkane
Cyclic	3	4	Ester
Alkane	5	3	Cyclic
Aromatic	5	3	N
Sulfur	1	1	S

Sorted we have exactly the correct functional group targets, and aromatics are surprisingly strong:

We should therefore, still strongly consider
1. Aromatics, Alkane, Esters & Cyclic

which we clearly are. We will continue to attempt to differentiate on the probability.

Note that it also is quite true that the vast majority of the SDBS matches do indeed show some level of absorption above 3000 cm^{-1}. This tends to continue to reduce but not eliminate the strength of the aromatic candidate.

Certainly one question coming up is whether or not we have an alternative chemical, colorimetric or spectral (UV-NIR?) test for an aromatic ?

Ok, good news. We may have chemical tests available for aromatics, etc.
But even more simply, it looks like we can likely use UV.
Benzene has absorption @ ~ 255 nm.
Source: Thomas - Open Learning, p64, UV-VIS book
This should be doable.

I think we need to work that route.
In the meantime, let's explore Parker p104 "alicyclic CH_2".

Alicyclic compounds refer to saturated & unsaturated aliphatic compounds in which some of the carbon atoms are in a ring, but not benzene or aromatic.

Alternative nomenclature is:
cycloalkanes
~~Cycloparrafins~~ (sp) Cycloparaffins
napthenes

The general formula is C_nH_{2n}.

Cycloalkanes occur naturally in crude oil and a variety of fuels.

This all makes perfect sense and this does exist as a candidate.

You will need to differentiate on the question w/ a further test.

So ~~as~~ our primary candidates are:

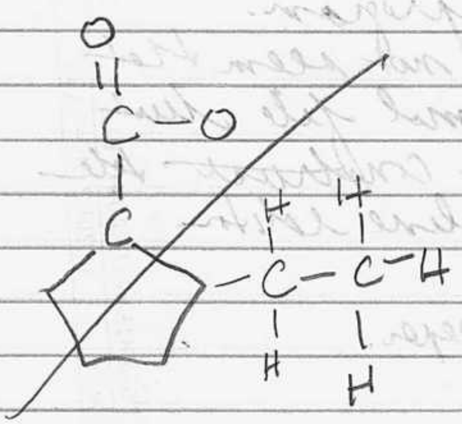
1. alkanes, Ester, Aromatic (phthlates)

2. alkanes, Ester, Cyclic Hydrocarbon

I wonder what type of compounds are representative of the second category.

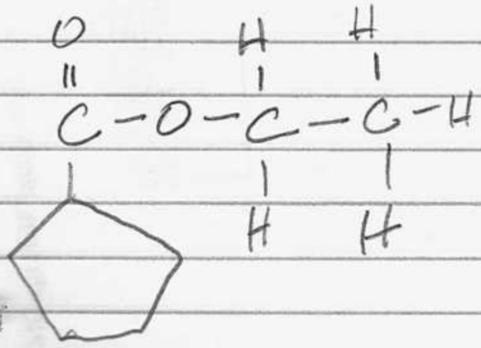
I think we need to construct it and run a chemical search.

Molview is a great online program.



The nearest match to the candidate compound is cyclopentylpropionic acid

However, we have no signs of an acid or OH group. Change this.



This compound is

ethyl cyclopentanecarboxylate

also known as
ethyl ester
ethyl cyclopentyl methanoate

Molview is an online program.

It will allow to

1. Easily construct a compound
2. Easily create a 3d model
3 Allow you to save a mol file
4. Allow to create the smiles format
5. Do search of exact or similar compounds very easily.

This is a very capable program.
Unfortunately it does not seem that you can import a mol file but it is very easy to con~~struct~~ the compound in the online editor

This program is a keeper.

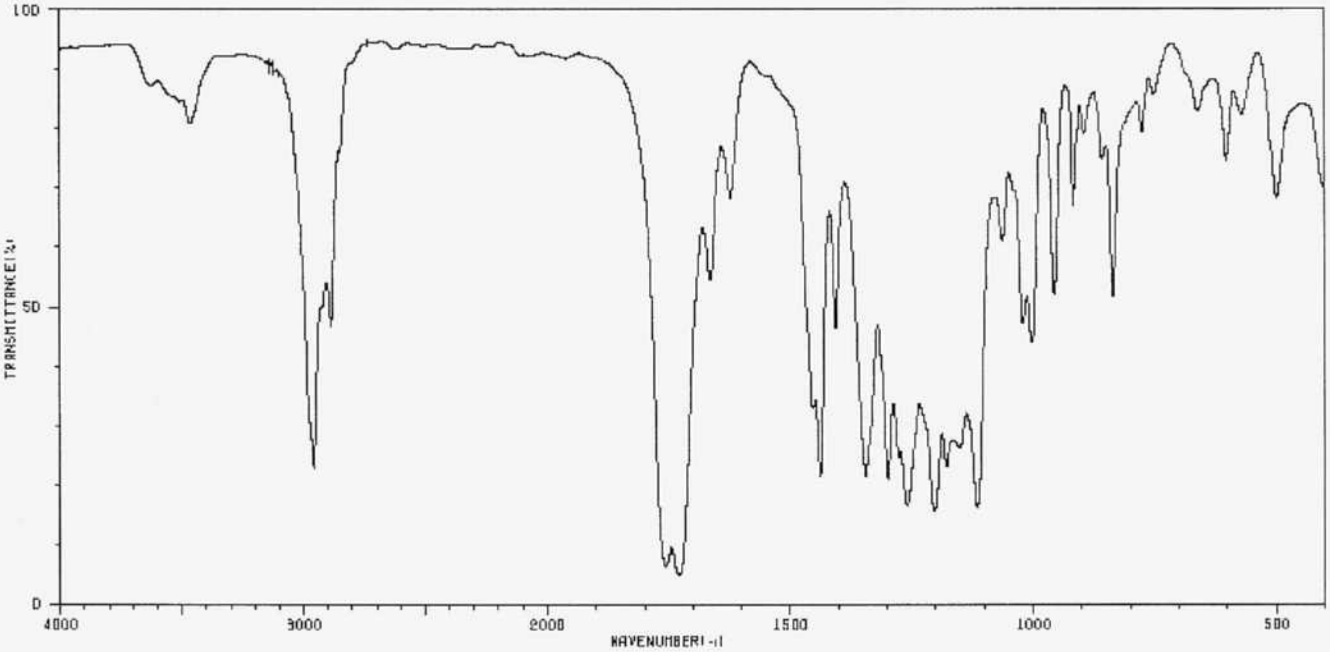
IR Candidate Investigation - SDBG - Japan

Page 211A

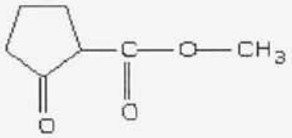
HIT-NO=3085 | SCORE= ( ) | SDBS-NO=5732 | IR-NIDA-58299 : LIQUID FILM

METHYL 2-OXOCYCLOPENTANECARBOXYLATE

$C_7H_{10}O_3$



3466	77	1464	31	1178	22	1002	42	776	77
2957	21	1438	20	1166	26	956	50	752	81
2887	44	1408	44	1151	25	917	64	662	79
1766	6	1346	20	1114	16	903	81	607	77
1728	4	1299	20	1062	58	895	77	602	72
1664	52	1259	16	1021	44	857	72	570	79
1622	66	1204	14	1013	60	836	48	498	66



Carrying On...

Our closest match w/ the SDBS database looks surprisingly good.

Our peaks are @ 2915, 2850, 1736, 1454, broad activity from 1250 - 1000, & 798 cm^{-1}.

Our candidate has peaks @
2957, 2881, ~1750, 1438
broad activity from 1350-1100, & 836 cm^{-1}.

This is quite good from a massive database search. Functional groups represented in the SDBS candidate are

1. Pentane cyclic ring
2. Hydrocarbons
3. Ester group

] Definitely conforms w/ our target functional groups.

4. It does have an additional C=O bond on the pentane ring.

We also examine the spectrum of pentane & the spectrum is simple, w/ peaks @
2968, 2871, 1466 & 896 cm^{-1}
No ester, of course, so no absorption ~ 1736 cm^{-1}.

This further supports the pentane cyclic group existence.

In addition, when we look @ Avram for cyclopentane (p 145)

she shows peak absorption @ 1455 cm^{-1}.

This is a strong supporter of the pentane functional group.

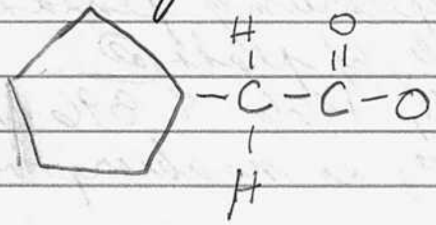
We have a strong case for the existence of a pentane cyclic ring w/ an ester attached.

If we examine 2915 & 2850 cm^{-1} more closely we have:

The CH_2 group w/ 2853 & 2926
vs our 2850 & 2915

as opposed to a CH_3 group @ 2872 & 2962 cm^{-1}.

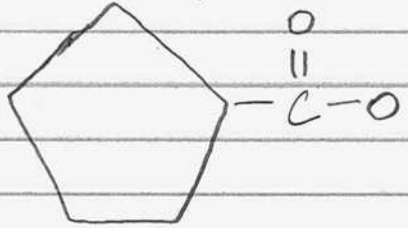
This would therefore suggest a minimal structure of



No CH_3 group is required @ this point

Let's go back to MolView.

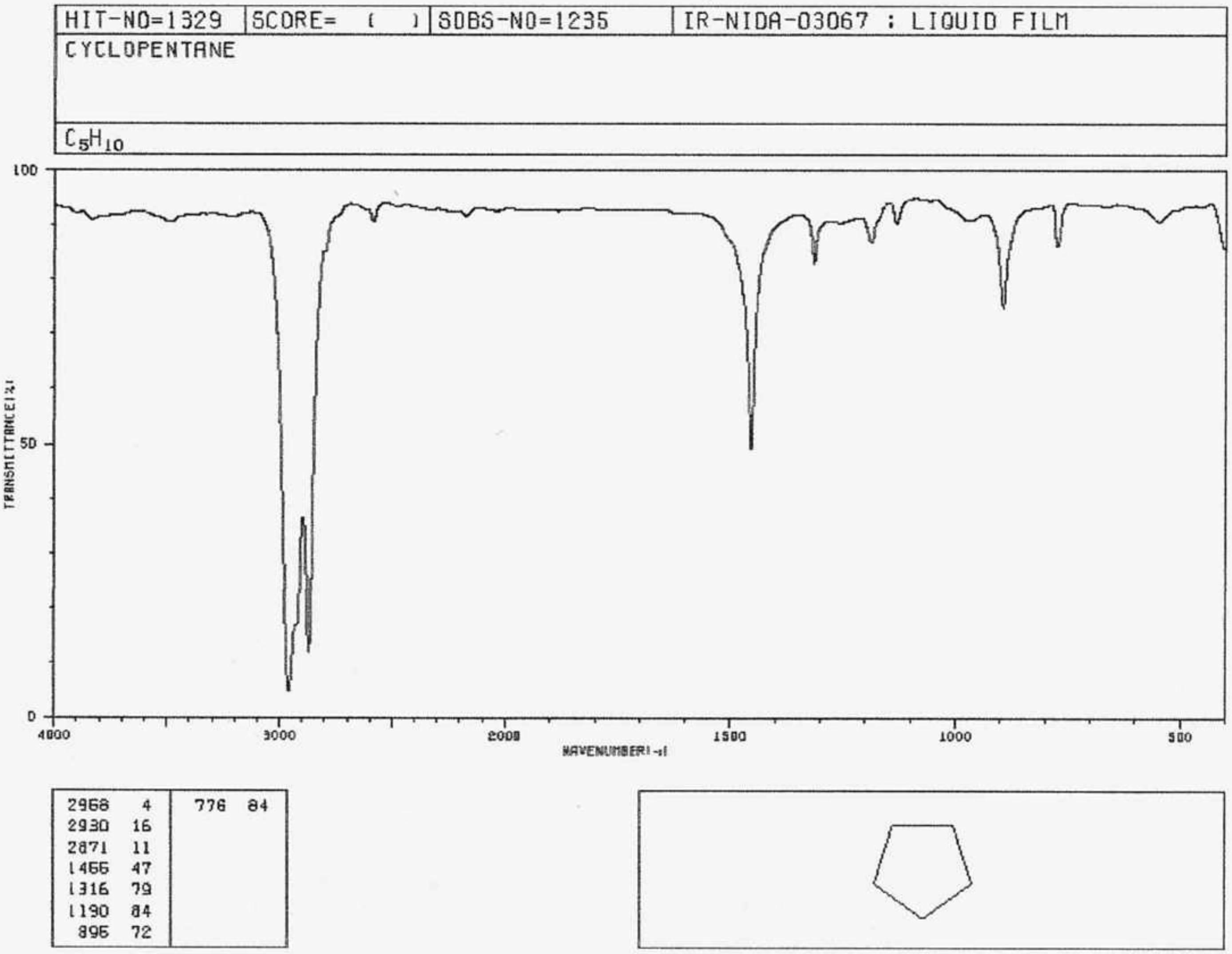
But conceivably the CH_2 groups could also be represented w/in the pentane, so it may also be possible to reduce it to:



However, this leads to an OH group. Not acceptable.

This also satisfies our conditions thus far. The fact that this was extracted via xylene (highly non polar) will also need to be kept in mind.

Page 215



HIT-NO=1329 | SCORE= ( ) | SDBS-NO=1235 | IR-NIDA-03067 : LIQUID FILM

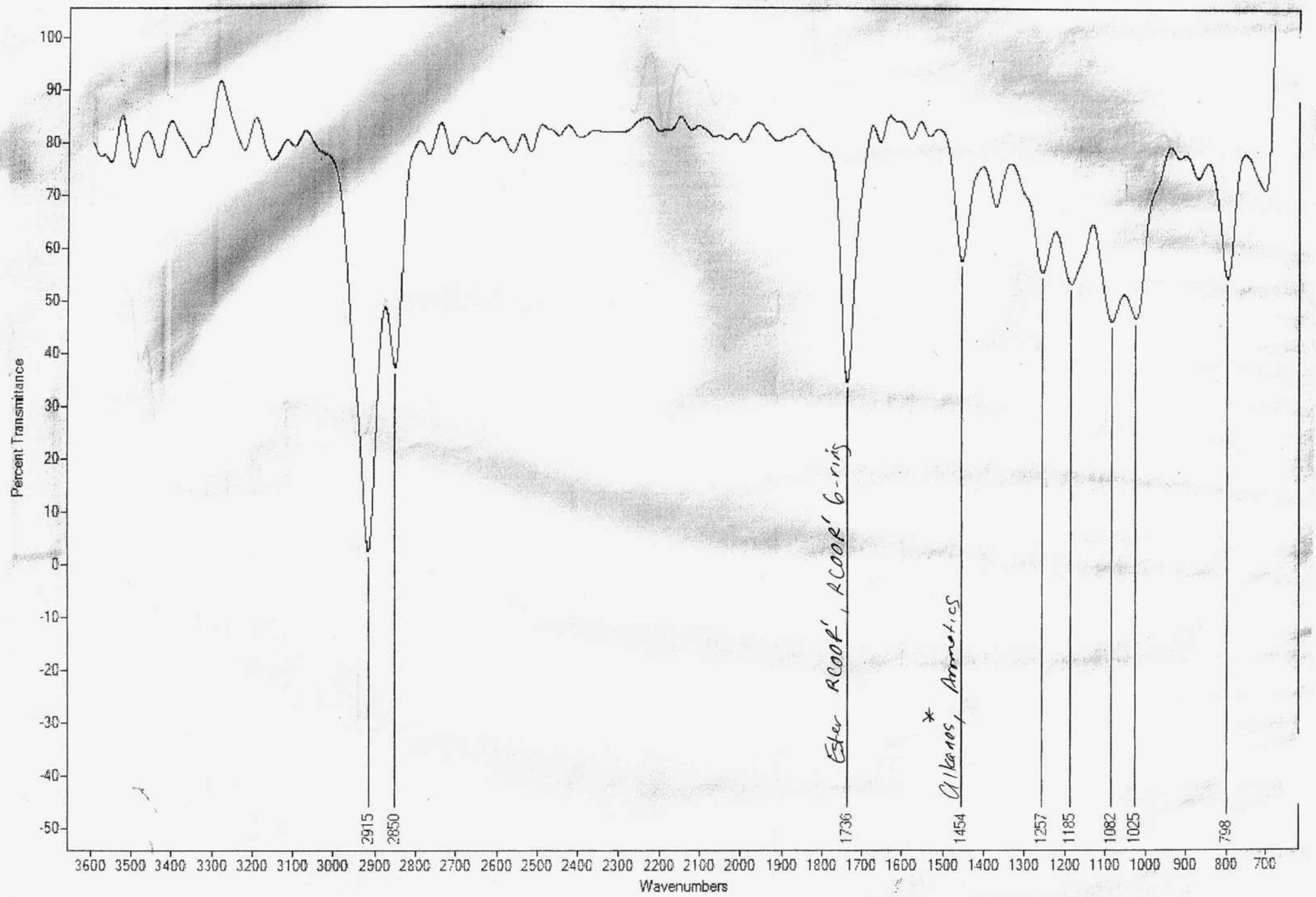
CYCLOPENTANE

C_5H_{10}

2968	4	776	84
2930	16		
2871	11		
1466	47		
1316	79		
1190	84		
896	72		

Reference spectrum of cyclo pentane alone

Rainfall Xylene Extraction Evaporated Clean Average Nov 22 2017 - 03.JPEG

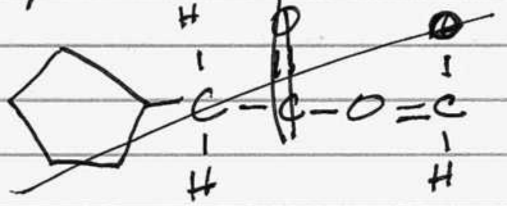


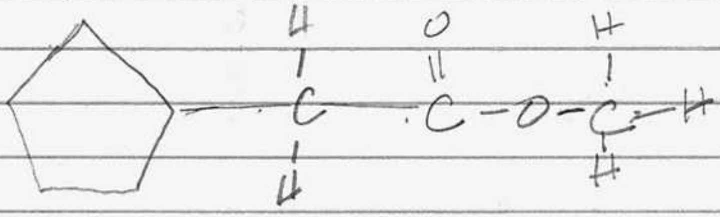
June 03 2018

Back to Molview w/ the simplified structure,

The simplest structure results in an OH group. This is not acceptable.

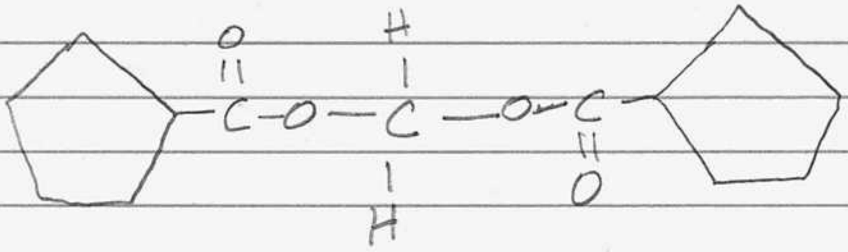
Revert to





try this

There is a difficulty here w/ not including a terminal CH_3 group. What about symmetry?



This avoids the CH_3 terminal group.

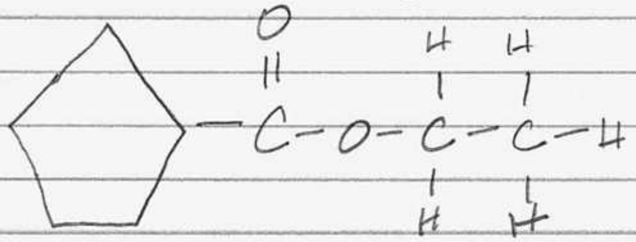
There is no match found for this compound.

Lets add the CH_3 terminal group for now.

The match for this is methylcyclopentyl acetate
NO SDBS matches.

Our closest match is

Ethyl Cyclopentanecarboxylate.



This is the same functionally.

Try SDBS search.
Guess what? My closest match is exactly what I had acquired before.

Methyl 2 Oxocyclopentanecarboxylate
And we see that the spectrum is actually quite good. Let's review it again more closely.

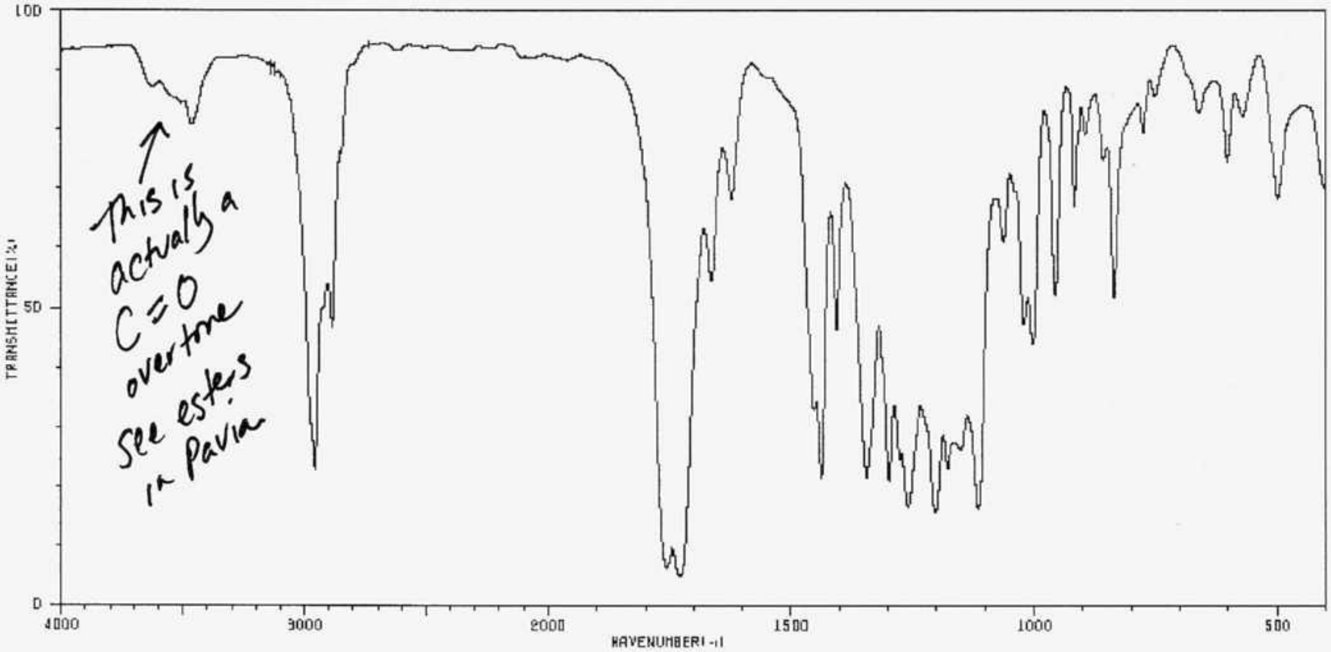
We are essentially trying to reverse engineer a spectrum here. I would say we have done quite well.

Page 219

HIT-NO=3085	SCORE= ( )	SDBS-NO=5732	IR-NIDA-58299 : LIQUID FILM

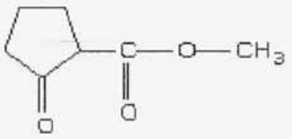
METHYL 2-OXOCYCLOPENTANECARBOXYLATE

$C_7H_{10}O_3$



This is actually a C=O overtone See esters in Pavia

3466	77	1464	31	1178	22	1002	42	776	77
2867	44	1408	44	1151	25	917	64	662	79
2957	21	1438	20	1166	26	956	50	752	81
1766	6	1346	20	1114	16	903	81	607	77
1728	4	1299	20	1062	58	895	77	602	72
1664	52	1259	16	1021	44	857	72	570	79
1622	66	1204	14	1013	60	836	48	498	66



We see, therefore, that we are definitely drawn to the class of compounds, characterized by

1. Hydrocarbons (aliphatic)
2. Hydrocarbons (cyclic)
3 Esters

Now, lets look @ the active fingerprint region.
We have a lot of activity from 1250-1000 cm^{-1}.
Candidate plot (methyl oxy cyclopentane carboxylate)
also has a lot of activity, in that case
1350-1100.
We are shifted, therefore approx 100 cm^{-1} lower.

Lets start w/ the bond region. Then use p 88 Conley.

This is either C-O stretching or C-N stretching.
We already have a case for asymmetric C-O stretching
and we can see that it takes place w/in the
candidate spectrum, which has no N w/in it.
Therefore the case for CO stretching already existent
and identified does appear sufficient.

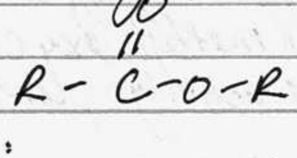
Our strongest peak is @ ~ 1050.

IR Pal: Esters run from 1320-1000 cm^{-1}.
This is again, a sufficient match.

Pavia also talks about esters in the fingerprint region.

He states they have C=O absorption (notice Conley p 88 says C-O absorption) from 1300 - 1000 cm^{-1}.

This is our second level confirmation of the ester.

The ester is 

$R-\overset{\overset{O}{\|}}{C}-O-R'$

Now Pavia says:

1. Conjugation in R moves absorption to the right
2. Conjugation in the R' part moves absorption to the left
3. Ring strain (lactones) moves absorption to the left.

I can't say that we are particularly shifted either way, we occupy the entire region as well as does the candidate spectrum.

All information continues to affirm our candidate identification in the class of compounds

1. Hydrocarbon (aliphatic)
2. Hydrocarbon (ring)
3. Ester

Page 222

So what about Carboxylates? What are they?

A carboxylate is a salt OR ester of a Carboxylic acid.

Carboxylate salts have the form M(RCOO)n where M is a metal

We do not have this known

We do have this.

Carboxylate esters have the general formula RCOOR' where R & R' are organic groups, & not hydrogen.

So now our emphasis is upon Carboxylate esters.

Now if we end up becoming involved w/ organophosphates (These are esters of phosphoric acid) then we do have a significant issue to contend with. We are not there yet.

Recall that this study thus far is of a highly non-polar extraction. We are going to have a polar extraction that is going to add another entire dimension to the problem of rainfall extraction(s).

For now, we can let this sit, but before this, let's look @ the 797-798 absorption. It is strong and repeating in the non-polar extraction.

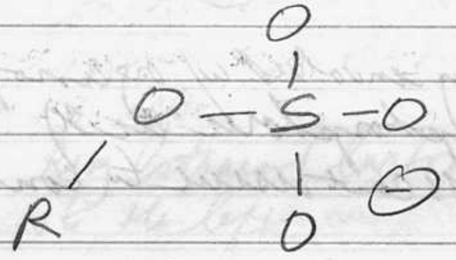
We are given a strong match due to a SULFATE ESTER. (900-700 cm^{-1}) dead center in the band. This is the only reasonable match w/ IR QAL.

This could now be an important additional Clue.

S-OR. ester in addition to
CH_2
Pentane
Ester

So what exactly is a sulfure ester.

The topic here is that of a "sulfate ester".



or $R-O-SO_3^{\ominus}$

Many organisms use natural sulfate ester reactions for metabolic purposes or for the biosynthesis of sulfur compounds required for life.

June 04 2018.

Let's continue w/ this sulfate ester prospect.
Our peak is @ 798 cm^{-1}.
IR Pal offers a definite read, in the center of the range (900-700 cm^{-1}) of a sulfate ester.

IR Pal does not really offer anything reasonable for us here.
Spectra mate offers a 3 membered aromatic
IR Pal also offers an aromatic.
We can not completely dismiss this, but the case for it is not nearly as strong.
Look up benzene spectrum.

Koji only covers the aromatics as well, no inorganics it seems. The aromatic band in this region is quite broad, 900-690 cm^{-1}.

Avram is going to have a full chapter on organosulfur compounds - great.
Avram does not cover inorganics in general, however, eg, phosphates.

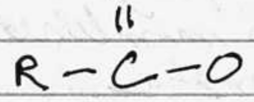
Parker's chart only runs from 1500-900 cm^{-1} on p480

The case for the sulfate ester is not yet sufficiently strong to warrant its inclusion in the structure @ this point.

It may be true that we do not have mutual corroboration now beyond the IR Pal reference. It is also more difficult to know what the structure actually is.

What IR Pal gives us is "S-OR ester"

An ester is



$R-\overset{O}{\overset{\|}{C}}-O$

Not quitting yet.

What exactly is an S-OR ester?

Encyclopedia Brittanica gives us some information that is helpful.
An example of a "S-OR" ester is given, ie

"RC(S)OR'" is thionoate ester
and a specific example of a thionoate ester is:

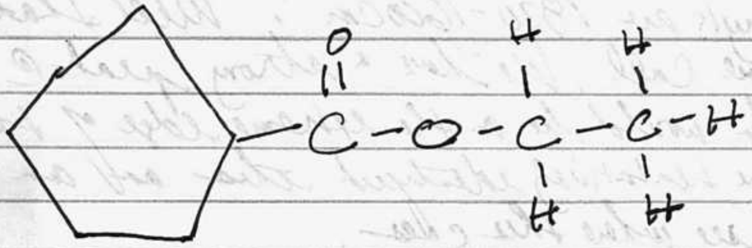
thionoacetic acid methyl ester.

Notice that our cyclopentane carboxylate IR spectrum also has absorption ~ 860 cm^{-1}. This is not all that removed from our 798 cm^{-1}.

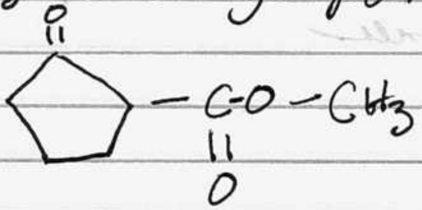
For now, we must settle on what we have w/ higher level of corroboration.

With the xylene (non-polar) extraction we are therefore left reliably with:

1. Hydrocarbons
2. Cyclic pentane presumed
3. Ester



is a reasonable model to proffer.
Ethyl cyclopentane carboxylate
and the closest match found is
methyl 2 oxocyclopentane carboxylate



We now move on to the ~~no~~ polar extraction (alcohol) which we see is quite different.

The polar extraction of the conc. rainfall into alcohol is an entirely different story. Quite a fair amount of activity here

First off, do we have a carbonyl group, via Pavia?

Carbonyls are 1820-1600 cm^{-1}. Well that is a close call. We have a strong peak @ 1595 cm^{-1} so this would be on the extreme edge of the range. We have tentatively identified this as an amine – let's see where this goes.

Key list @ or surrounding 1595 cm^{-1}

1. Aromatics (1450–1600)
2. RNH_2, $ArNH_2$ (1560–1640)
3. Aromatic amines
4. NO_2
5. N=O

Well it almost certainly looks like we are dealing w/ amines or nitrogen compounds here.

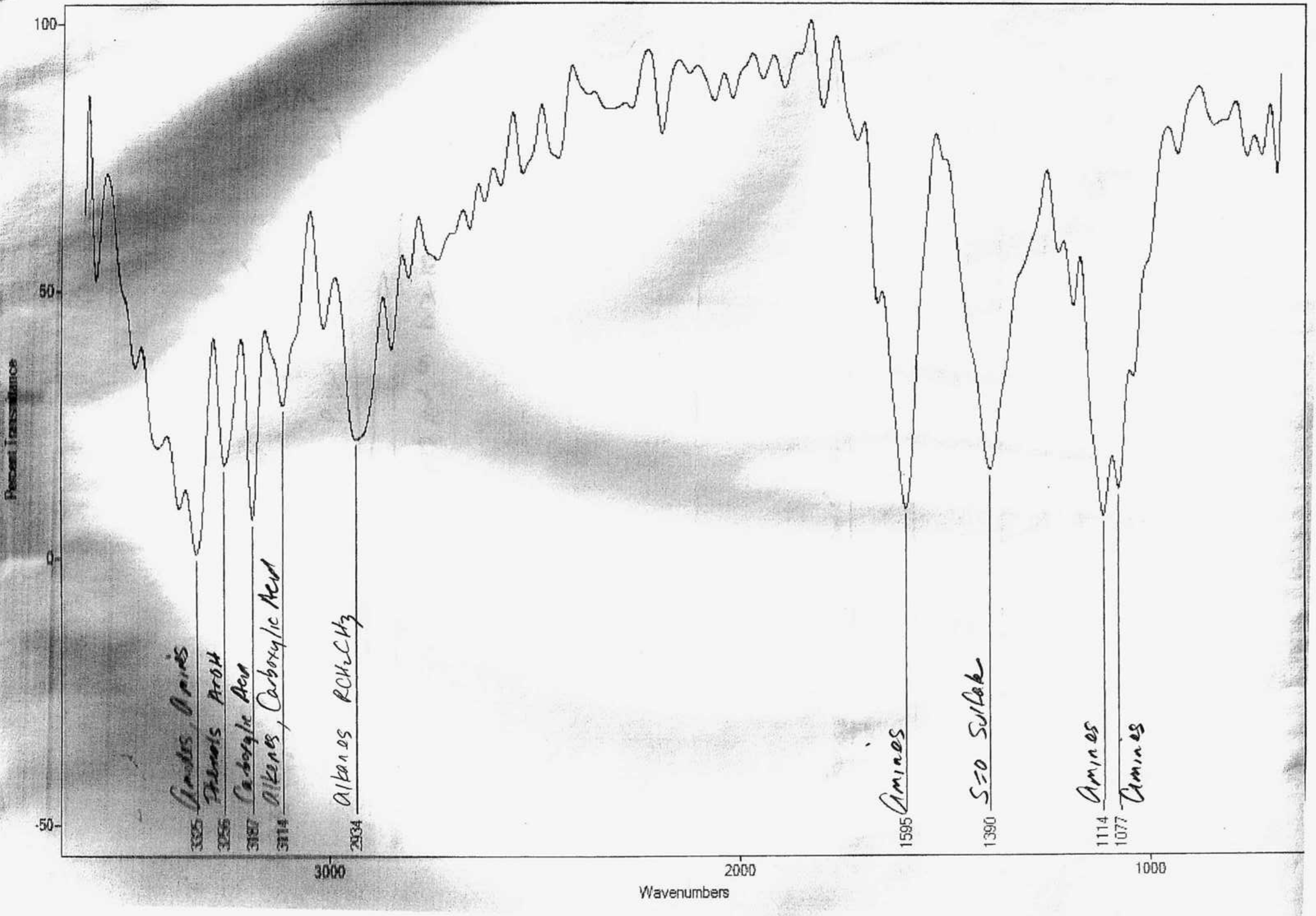
From the bond chart, Conley, p 88 the most likely bond band involved is indeed NH.

At this point, I will propose a negative on the carbonyl existence and act in favor of nitrogen compounds. However the carbonyl will not be eliminated completely from consideration.

Rainfall Concentrate – Polar Extraction (Ethanol)

Extraction into Alcohol Evaporated Avg Nov 23 2017 - 03.JPEG

Page 228A



Continuing w/ Pavia, assuming no Carbonyl @ the time, we are next to look for alcohols or phenols, amines, or ethers.

1. Alcohols or Phenols.
I see no singular broad absorption > 3000 so OH looks to be negative. Let's go further

OH just does not work.
a) No hydrogen bonding (dilute solutions) has a sharp peak @ 3650-3600 cm^{-1}.
Not present.

b) hydrogen bonding (3500-3200) broad absorption and skewed to the right.
See example of alcohol in Pavia on p A25.
We do not have it.

Alcohols & Phenols fail in a big way here.

2. Next we start looking @ amines..
We have a good example of an amine on p A27 in Pavia.

We have strong absorption @ 3325 cm^{-1}!

This is very much in the range of amines (3500 - 3300) cm^{-1} by Pavia.

We already have strong evidence of an amine @ this stage.

We also satisfy Pavia w/ N-H scissoring @ 1595 cm^{-1} (range is 1640 - 1560 cm^{-1}).

We now have 2nd level corroboration @ a high level for the existence of an amine w/in the polar extraction from conc. rainfall. This is significant!

We obviously also have alkanes present.

Let's investigate ethers also per Pavia.

Incidentally, Koji also affirms amines by:

~~1450-1600~~ 1560 - 1640 ($\bar{x}$ = 1600) cm^{-1} as RNH_2 & $ArNH_2$
also NO_2 1500 - 1650
$N=O$ 1480 - 1680

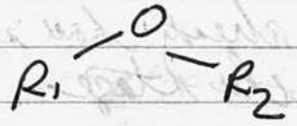
so we clearly have nitrogen based compounds.

Jun 06 2010

Continuing w/the polar extraction.

Extending the flow chart of Pavia, what do ethers require?

Incidentally, an ether is:



Basically a conventional oxygen bond.

Guess what, Pavia has a bond table also on pA19. This is a very useful complement to Conley p88.

With Pavia on ethers, we look for:

1. A prominent C-O stretch @ 1300-1000
2. No C=O bond] if present, these imply
3. No O-H bond] an alcohol or an ester.

We do have one strong band @ 1114-1077
— a ~~b~~ double peak.

We already know we do not have the C=O carbonyl bond and we know that we do not have the OH bond.

Therefore the additional constraints are satisfied. Therefore we continue to explore the prospect of an ether.

We have tentatively identified the band (double band) as being an amine group.

We need to
1. substantiate any finding previously suggested.
2. In the process, settle if we are dealing w/an amine, an ether, or something entirely different.

IRspec gives:
1. An amine (1020-1230) cm^{-1}
   It is the only reasonable choice

IR spec also says that an ether would be expected to occur @ # 1120 cm^{-1}

Spectra Mate
1. Actually gives us an ether! So how is that for conflict? (for 1114 cm^{-1}).
2. For (1017 cm^{-1}), Spectramate gives us a C-O-C structure, calling it a 5 membered oxane. (Notice the structure is an ether).

Therefore we definitely have some conflict here,

Let's look @ Parker Table p 102-106.

1070-1150 ($\bar{x}$=1110) is given as an aliphatic ether C-O-C
1100-1150 ($\bar{x}$=1125) is given as a benzoic or phthalic ester
~~1100-1150 ($\bar{x}$=1125)~~ C-O
1100-1150 ($\bar{x}$=1125) is given as a S=O
~1120 is given as a C=S ie -NH-(C=S) thioamide

We therefore have quite a few choices given by Parker.

Let's look @ Parker for 1077 also.

$\bar{x} = 1060$ 1030 - 1090 P-O-C phosphoric ester.
1070 - 1150 C-O-C aliphatic ether.
1020 - 1090

Since there is no carbonyl we know that we cannot have an ester.

We can see that an aliphatic ether can and does remain on the table here. Notice that only IR spec is given on the amine at this point.

What does IR Pal do here?

also Koji: 1114 & 1077
Koji gives thio ketone (S=O)

Koji definitely gives us aliphatic amines from (1030-1230) cm^{-1}.

Therefore aliphatic amines & ethers do remain on the table as well as a sulfur compound, IR Pal for 1114 & 1077

1. Strongest centered candidate is an ether (1150-1070) x=1110 vs our 1114. intensity is strong.

2. Amines are widespread from 1030 to 1230 of medium intensity.

Look @ examples & you should be able to discern between these candidates.

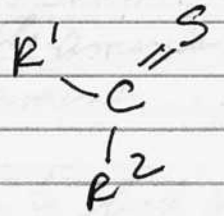
Amines require corroboration from IR Pal @

3500-3300 by Pavia! 3405 - 3395
3505 - 3495
yes 1640 - 1560
1230 - 1030
910 - 665

How many of these do we have? 2 out of 4

Also IR Pal gives a thiocarbonyl - (ie C=S) but what is this? As we know we do not have the carbonyl.

Thiocarbonyls are also called thioketones. Their structure is



Notice there is no C=O involved even though the carbonyl term is used.

Since it is a double peak here
it seems that we could easily have an
amine and an ether?

Check for correlation of bands on amines.

Jun 01 2018

Increasingly I suspect we have both an amine and an ether w/our double peak @ 1114 & 1017.

If we choose an amine, we require additional corroborating absorption.
We have it.

By Pavia, absorption will additionally be required at 3500 - 3300. We have it.

By Pavia, absorption will additionally be required @ 1640-1560. We have it.

By ~~Pavia~~ IR Pal, we will require additional absorption @ 1030-1230. Also the absorption is widespread of moderate intensity. In addition to the fact that we have a double peak (indicative of both amine & ether) notice the numerous shoulders from ~ 1000-1250. Sufficient grounds for acceptance of an amine @ either 1114 or 1017 does exist.

Notice also, however that we are dead centre in the band for an ether (1070-1150) @ our 1114 cm⁻¹! This would indicate the ether band is fairly narrow and sharp. This is why the amines would most likely be coupled w/ the amine.

What is required next is to look @ illustrative examples of both ethers and amines w/in this region.

From Koji, Problem 27, we can see that
the ether absorption is indeed quite strong.
Koji give the range as 1030 - 1150 cm^{-1}
The center of the range is 1090 cm^{-1}
We are @ 1077 or 1114, either way is
reasonable.

The case for the ether remains strong.

Now let's look @ representative amines.

Koji, Problem 32 shows an amine w/absorption
@ 1012 - This is a C-N absorption, not N-H!
He gives the range as 1030-1230.
The absorption is not nearly so strong.
We have absorption @ 1077.

My interpretation is, therefore, that we
do have ether absorption (strong) @ 1114 cm^{-1}
coupled w/amine absorption @ 1077 along
w/ shoulders in the range of 1030-1230.

Conclusion thus far w/ the polar extract

1. Amines
2. Alkanes
3. Ether

Now our remaining question is the strong absorption @ 1380, tentatively identified as a sulfate. Let's revisit earlier work on sulfate detection.

Prior absorption determined for sulfur was during examination of the env. filament with absorption @ 1018 cm^{-1} described in May 19 2018 notes. Chemical test also proved positive for sulfates.

This is hardly the same case. IR pal may have suggested sulfur bonds, we will see.

What we do have is absorption @ 1390 cm^{-1}, and it is strong.

Let's start w/ Parker's correlation chart p102-106
Well indeed, sulfur is a candidate here

	1360 - 1390	C-H	medium
*	1330 - 1420	S=O	strong.
	1325 - 1440	C-C	medium
*	1350 - 1440	S=O	strong

Of the cases, the strong S=O is the only one that fits the bill.

As far as inorganic ions go, Parker shows the CO_3^{2-} Carbonate ion, but notice this is only w/ a high pH. (~ > 10). We do not have this pH in our rain sample. S=O bond remains a target.

Page 239

Using Koji next,

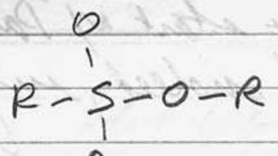
our strongest candidate is again a sulfur group. Koji shows SO_2 ~~from 1340~~ 1310-1440 ($\bar{x}$ = 1375) We have 1390 cm-1 very well centered.

There do not seem to be any other strong candidate from Koji.

There is now 2nd level corroboration of a sulfur group @ 1390 cm-1.

Koji gives two Sulfur candidates:

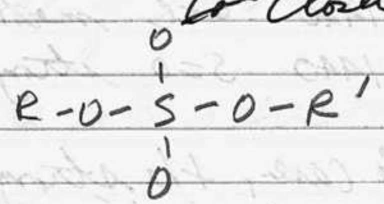
1420-1330 ($\bar{x}$ = 1375 cm-1)
$R-SO_2-OR'$
"Sulfonate"


$R-S(=O)(=O)-O-R'$

1440-1350 ($\bar{x}$ = 1395 cm-1)
$R-O-SO_2-OR'$

This is a closer match

Sulfate (notice the SO_4)


$R-O-S(=O)(=O)-O-R'$

Originally our previous call was indeed a sulfate (most likely from Pavia).

1. Amine
2. Ester
3. Sulfate
4 Alkane

Polar extraction

Koji gives an example of sulfur absorption w/ Problem 00.

The absorption is indeed strong.

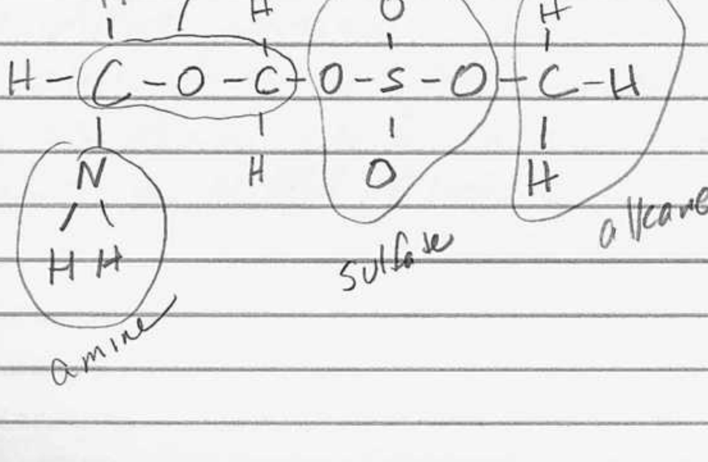
We notice that for the sulfates, additional absorption is expected from 1150 / 1230.
If we look closely, we do have this. Notice the two shoulder peaks in this range.

Conley also mentions sulfur absorption in the same general range the Koji states.

Our case for the sulfate group is sufficiently strong.

Our polar rainfall extraction is now expected to consist of

1. alkanes CH_2, CH_3
2. Amine NH or NH_2
3. Ether R-O-R
4. Sulfate $R-O-\overset{O}{\underset{O}{S}}-O-R'$



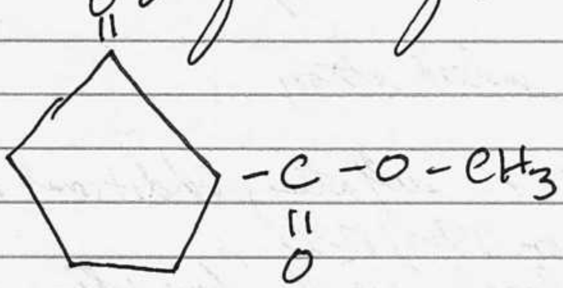
What type of compound is this?

Page 241

Non polar extraction

Also recall from the non polar rainfall extract we found the following:

Ester
Hydrocarbons



We have already identified the type of compound class as of ethyl cyclopentane Carboxylate.

Molview is not identifying a name for the polar extracted Compound.

Database search results:

Molview comes up w/ no candidates whatsoever in matching the structure or even similarly in structure.

SDBS (massive Japanese database) w/ conditions attached, ie.

Sulfur required.
5+ Oxygen required
1+ Nitrogen required
Transmittance ≤ 80%
Cm^{-1} ± 10 error

Only one candidate satisfies the search, including the presence of a sulfate group. It appears to be a very complex structure but indeed the spectrum matches quite well on the peaks of

3325 2934 1595 1390 1114 cm^{-1}.

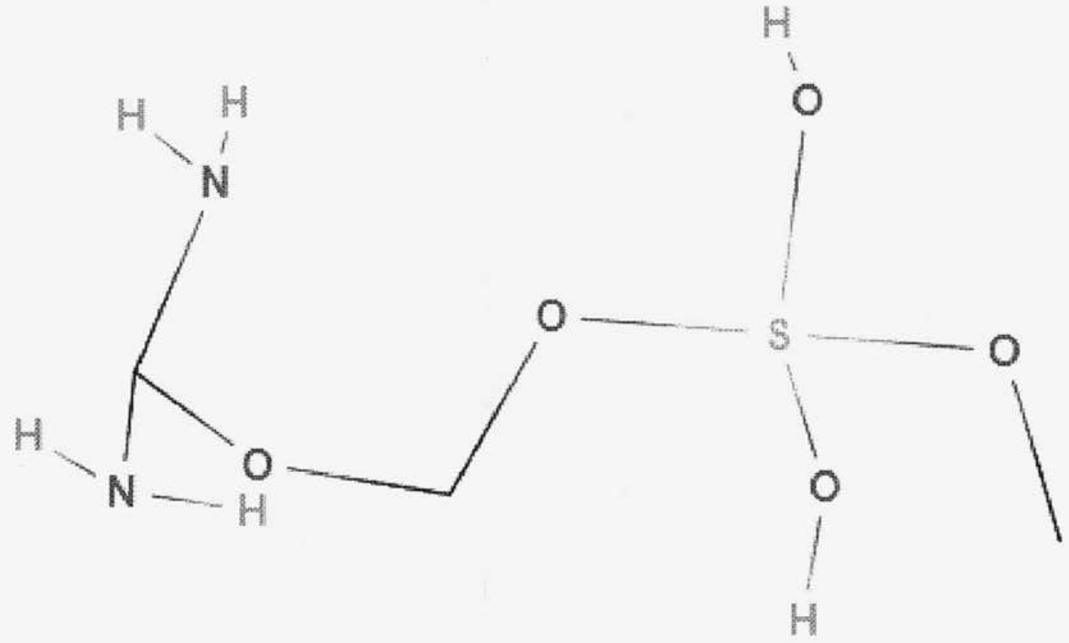
HydroxyProplylAmino Oxo Cycloheptatrienyl Toluenesulfonate

Candidate structure and SDBS best (singular) match shown on following pages. Interpretation of the health effects or toxicity of the non-polar extraction will obviously be a handful.

Rainfall Extract

Non Polar Candidate Structure

Rainfall Polar Extraction Candidate Structure based upon IR spectral interpretation



Rainfall Extract

Page 244

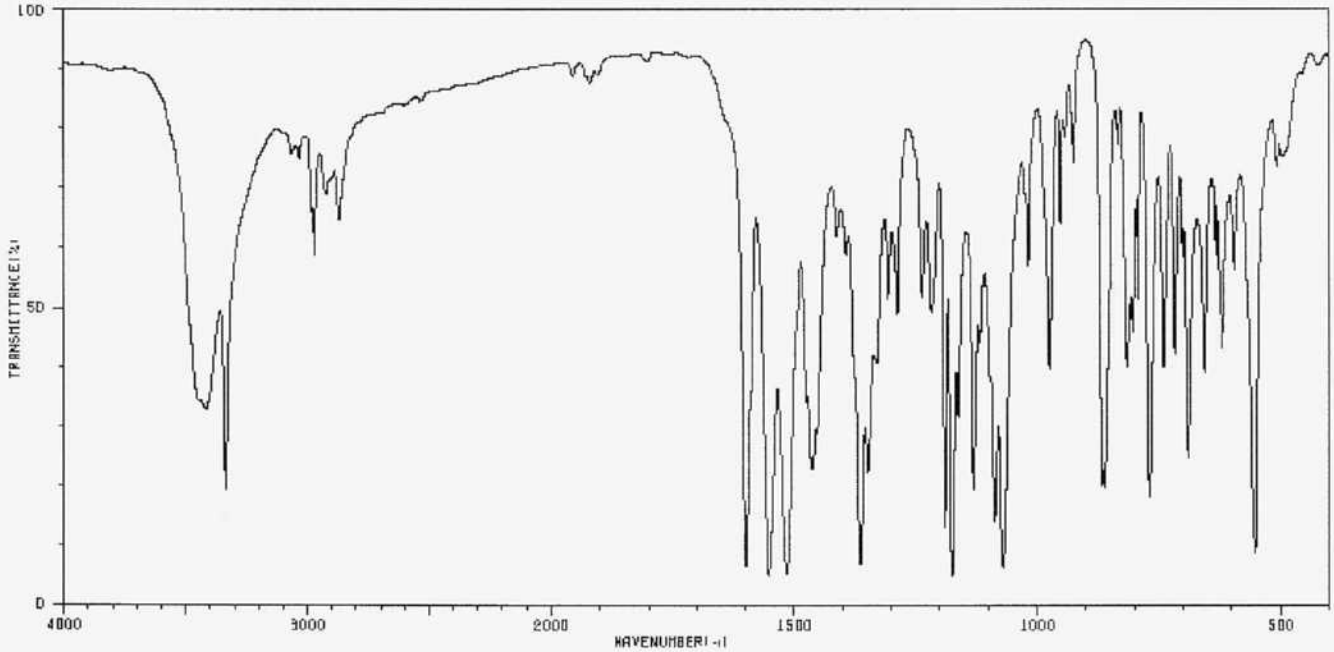
Non Polar SDBS Best Match (w/conditions)

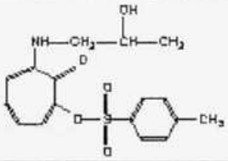
Page 244 A

HIT-NO=16268	SCORE= ( )	SDBS-NO=30633	IR-NIDA-44968 : KBR DISC

6-(2-HYDROXYPROPYLAMINO)-7-OXO-1.3.5-CYCLOHEPTATRIENYL P-TOLUENESULFONATE

$C_{17}H_{19}NO_5S$



3447	33	1462	21	1218	47	1070	6	770	17	
3433	33	1453	27	1190	12	975	38	741	38	
3417	31	1364	6	1174	4	866	19	716	41	
3336	18	1349	21	1163	30	860	18	690	23	
1599	6	1330	39	1130	18	814	38	657	37	
1552	4	1307	49	1116	42	804	44	621	42	
1516	6	1289	47	1087	13	792	48	562	8	

IR Interpretation Summary
to Date:

We have, therefore, completed IR interpretations
with no prior assumptions of

1. The environmental filament
    1. Amides
    2. Isothiocyanate Group
    3. Nitro Group
    4. Sufur Group $S_2O_3^-$

2. The CDB Generated Protein
    1. Amides (Protein
    2. Iron (Fe 2+)
    3. Sulfates (SO_4)
    4. (Ferrodoxin Protein)

3. Rainfall Extract (Non-Polar):
    1. Hydrocarbons (aliphatic)
    2. Hydrocarbons (Cyclic)
    3. Ester (Note sulfate ester merits Consideration)

4. Rainfall extract (Polar)
    1. Alkanes
    2. Amines
    3. Ether
    4. Sulfates
    5. Notice SDBS Best Match w/ Sulfate Esters)

5. HEPA - alkanes, cyclic, aldehyde, thiocarbonyl

Jun 08 2018

Next we go on to the HEPA polar extraction into ethanol.

Before doing so, we should mention:

1. Two additional spectra have been gathered:
   a) sample sent from skin solids collected (appears to be protein based)
   b) two urine samples frozen/refrigerated for approximately 6 months. Remarkable CDB culture growth has taken place.

2. Remarkable CDB culture growth w/in two urine samples stored in frozen or refrigerated state for approx 6 mos. They show
   1. Development of the blue colored circular forms photographed earlier w/in advanced culture growths.
   2. Massive CDB production
   3. Occassional filament production w/in one of the samples
   4. Geometric (ie rectangular packing / linear arrangements of CDB enclosed w/in a membrane) structural forms of encapsulated CDB. It has an artificial or design appearance. The "Circuit" analogy is indeed under consideration there.

disregard this peak. See notes for Jun 10 2018

Should also be dismissed. See spectra Jun 10.

Now on to the HEPA polar extraction.
We have peaks @
2911, 2850, 1723, 1445, 1371, 1142 & 1100 cm^{-1}.

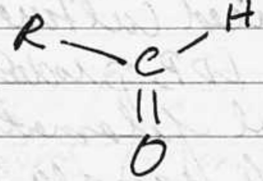
1st Question: Do we have a Carbonyl?

1. Absolutely. Strong @ 1723. C=O

In Pavia, on the Carbonyls, 1725 is the aldehyde. (Figure IR.15 on p A28).

Pavia also mentions —CHO absorption @ 2850 cm^{-1} and we have it also. We know, therefore, that we positively have an aldehyde.

So what is an aldehyde?



Simplest example is that R becomes CH_3.

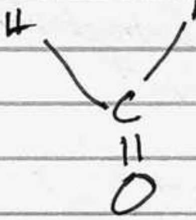
Now from the 2911 peak we already know that we have alkanes.

Aldehydes are fairly simple in their structure, one of the R groups is a hydrogen. On the other side, anything goes.

What are characteristics of aldehydes?

Here is the first item of importance. The fact that a molecule is "simple" or complex in structure means nothing w.r.t. toxicity or health effects.

The simplest aldehyde, for example, is formaldehyde. Here, instead of one hydrogen, we have two. i.e. the R group of the aldehyde is nothing more than another hydrogen.



formaldehyde

and yet, look @ the toxicity of formaldehyde.

Aldehydes are easy to oxidize. They are highly polar. Small aldehydes are highly soluble. Found in many fragrances, such as vanilla, camphor, and bleu cheese. They are a part of many hormones. As usual, it looks like "anything goes" so this means that you need to know more.

Let's continue w/the spectrum.

Our next peak is @ 1445.

Start w/ Parker, he has about the best table listing going.

wide weak -N=N- azo group (1400-1450)

Strong C-O Carboxylate $-COO^-$ (1400-1460)
Strong — C-H alicyclic $-CH_2$ ~1455

Did we have ~1445 in prior spectra?

In our HEPA polar extraction we have 2 similar peaks

Rainfall Non Polar Extraction	HEPA Polar Extraction
1736 cm^{-1}	1723 cm^{-1}
1454 cm^{-1} (Non Polar!) Extraction	1445 cm^{-1} (Polar Extraction)

In our notes of June 02 2018 we assigned the 1455 cm^{-1} to the alicyclic group (pentane ring).

That might apply here also but recall it is @ a specific wavenumber, ie 1455 (not 1445) and no range is given.

& there is hardly fixed. Lets continue to descreminate.

Koji's best and only real representation
is CH_3, CH_2, $-CH_2-CO$ T1(1)
with a range of 1400 - 1410. T1(2)
T1(14-16)

you have to wonder if this
* Could have been overlooked in the rainfall
non-polar extraction?

It is possible that it would have to be in error
by 5 cm^{-1} or also be @ the extreme edge of
the alkane (aliphatic) absorption bands.

This absorption remains a bit unclear
@ this point.

Actually Koji does mention cyclic hydrocarbons
in the remarks section of Alkane
He says
1445 cm^{-1} = cyclopentane (We are indeed
closest here).

1450 cm^{-1} = cyclohexane.

Notice Koji & Avram differ!!!

	Cyclopentane	Cylcohexane
Koji	1445 cm^{-1}	1450 cm^{-1}
Avram	1455 cm^{-1}	1450 cm^{-1}

→ resolve
this Conflict!

Wavelength
Conversion
Chart
Parker
p 560

Page 251

Bond Tables:
Pavia : Page A19
Conley : Page 88

Correlation Table :
Parker Pages 102-106
Inorganic Ions (Fingerprint Region) Parker p 482

Notice Parker does not help matters.
He generalizes & says
". ~~acyclic~~ alicyclic hydrocarbons are at "~ 1455 cm^{-1})

So he does not elemenate the confusion.

Either way, we know that between 1445 & 1455 cm^{-1} we are very likely dealing w/ a cyclic hydrocarbon, either pentane or hexane.

That is narrowed in fairly well.

Azo group is expected to center @ ~1425
Carboxylate is expected to center @ ~ 1430

Both are less likely but they still require full examination.

A cyclic candidate remains a strong prospect.

Continuing the examination, 1454 cm^{-1} is a strong absorption so that further diminishes the likelihood of the azo group.

C-O bonds are listed by Pavia in Bond Table p A19 as being from 1300-1000 cm^{-1}.

C-O bonds are listed by Conley bond table p 88 as between 1300-900 cm^{-1}.

We now examine the carboxylate group further. First off, there is listed as a C-O bond.

So clearly the carboxylate absorption is occurring well outside the stated range of the C-O bond.

So what, again, exactly is the carboxylate group?

? IR Spec check misses the carboxylate entering @ 1454.
? Spectramate lists 1454cm^{-1} as a R-OCH_3, belonging to a saturated alkyl group.

The carboxylate group (-COOH) is a functional group common to all carboxylic acids.

A carboxylate is a common name for all salts that carboxylic acids yield by reacting w/ hydroxides, carbonates, bicarbonates and other alkaline reagents.

So no wonder you are confused, are you talking about the group or the salt? How do you know.

June 09 2018

I have worked out the noise reduction issue w/ the phased antenna device. The findings are:

1. The noise is primarily local (ie, this building, modem, etc) and therefore only the internal whip antenna along w/ the preamp is more than sufficient.

2. The easiest method found to reduce the noise is to reduce the signal completely from the main antenna. Secondly increase the gain of the auxiliary (phasing) antenna only slightly to introduce the local noise into the HF reception. Next adjust the phase (or visaversa) to null out the noise to the best degree possible. This is being accomplished w/ the phase switch in the normal position. Lastly, increase the main ant gain to the necessary level to bring in the signal. RF gain of the HF rig can then be reduced to further reduce the noise level. This method is working quite well & makes perfect sense.

There is no need for the external antenna this is not where the noise is primarily coming from.

Jun 10 2018

An interesting session of urine analyses by IR. I have compared fresh urine samples from two individuals w/ refrigerated / frozen 6 mos. culture that developed in urine from the same individuals.

The urine cultures have been photographed under the microscope. The cultures are significant and dramatic in some respects.

What is of interest is that the IR spectra between the two does show some differences but they are reasonably subtle. Best demonstrated by difference spectra which we have recorded and will analyze later.

The lesson here is that important changes can occur visually and yet they might not readily reflect in an obvious way in the IR spectra. The spectra of urine seems to be mostly dominated by the existence of urea.

The differences, though ~~subtle~~ subtle, are to be examined later. The culture growth, although significant and apparent, does not readily reflect itself in the spectra, at least via ATR methods. Digestion of the CDB/ protein is most likely required

Now lets go back to the HEPA polar extract.

I have repeated the polar (methanol) HEPA extraction and I achieve essentially the same results.

* The only difference is that the 1371 cm^{-1} peak ~~is~~ now to be discarded. The magnitude is not significant in the current run. We have for comparison:

$\bar{x}$	Original ~~Polar~~ Extraction	Current Repeat
✓2920	2911 cm^{-1}	2930
✓2855	2850	2861
✓1729	1723	1735
✓1454	1445	1463
1103 cm^{-1}	1100	1106

These are the only peaks that will be used in the polar interpretation of the HEPA filter.

Now curiosly enough, we have performed a prelemary non polar extraction using xylene.

We see below that the results are very similar below, but we do see two differences.

1. The addition of an absorption peak @ 1521 cm^{-1}
2. The shift of at absorption peak from 1103 cm^{-1} to 1161 cm^{-1}.

Xylene (Non Polar) Extraction Results

2925

2861

1736

1521 new peak is stronger here than original

1462

1161 A shift occurs here w/ primary peak.

We now return to the question of the Carboxylate/azo groups @ $\sim 1455\ cm^{-1}$!

Curiously enough, we have an entire article devoted specifically to the Carboxylate group in Spectroscopy magazine May 2018.

This is most fortunate, as we can now definitely determine that we do <u>NOT</u> have a carboxylate group.

Brian Smith, author tells us that we must have <u>STRONG</u> absorption peaks at both
1650 - 1540
& 1450 - 1360

<u>In addition</u>

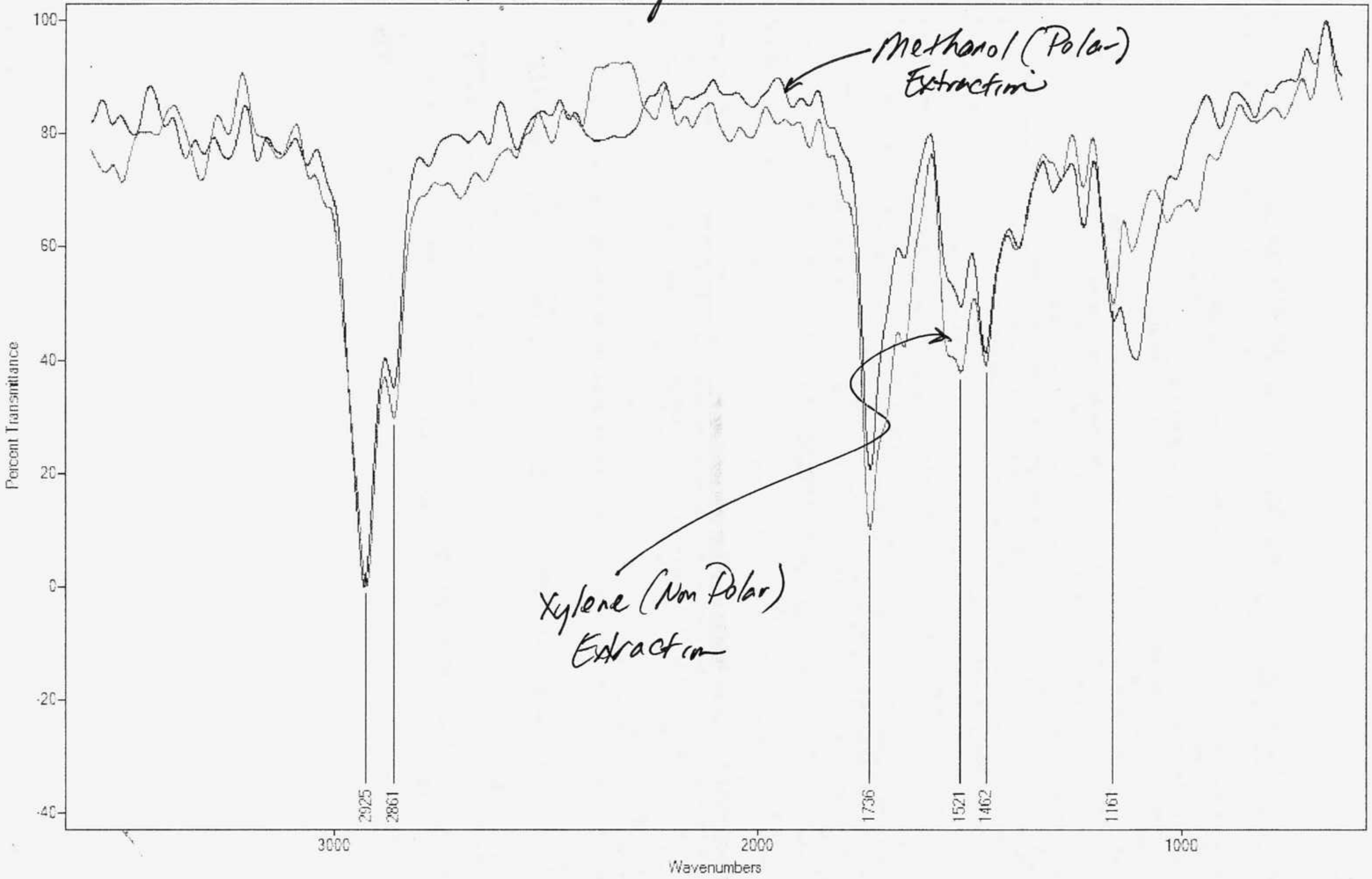
Because "Carboxylates contain neither a C=O bond nor a C-O bond, they WILL NOT contain a carbonyl stretching peak around $1700\ cm^{-1}$ or a C-O stretch between $1300 - 1000\ cm^{-1}$!

We do not meet these conditions. We do not have especially strong absorption at the two bands above, our 1455 is actually even outside 1450 - 1360, and we most definitely have a carbonyl identified as an aldehyde.

HEDA Non Polar & Polar Extractions Compared

HEPA Preliminary Non Polar Extraction ATR Xylene Jun 10 2018 - 01 spc: 06/10/2018 17:57:33 title

HEPA: Non Polar & Polar Extractions Compared



Methanol (Polar) Extraction

Xylene (Non Polar) Extraction

printed on 06/10/2018 18:14:48

This now forces us to push to the top of our list the alicyclic compound C-H as most strongly suspected in the analyses as well as identification of w/in the rainfall extract.

We now have

1. alkane

2. aldehyde

3. Cyclic Compound

Assigned for the HEPA filter polar (methanol) extraction.

These are rather firm assignments @ this point.

Our remaining points of examination are

1. A significant absorption @ 1103 cm^{-1} in the polar extraction (methanol)

2. An apparent shift in the peak to 1161 in the non-polar extraction (xylene)

3. A new peak (actually amplified from the non-polar extraction) @ ~ 1521 cm^{-1}!

Lets go to work w/ these remainders, Beyond the Pavia big picture approach, and the broad table approach, the Parker correlation table seems to be the easiest & most efficient place to start.

From Conley Bond table p88
1103 cm^{-1} can arise from either:

C-O stretching
C-N stretching
C-C stretching.

The C-O stretch case has already been diminished to some degree by Brian Smith's previous comments.

Parker's Candidates are:

Str	C-F	monofluoro derivative	1000-1110
Str	C=S	-NH-(C=S)- thioamide	~1120
Str	C-O-C	aliphatic ether	1010-1150
Str	C-O	benzoic ester	1100-1150
Str	S=O	R_2SO_2 sulfone	1100-1150

Of these, the sulfone appears to be the most likely candidate. We do not have an ester or an ether, we have an aldehyde.

We do not have evidence of an amide (amine w/ a carbonyl attached). It is of interest that sulfur is mentioned however.

The sulfur group remains as our best prospect thus far.

Sulfur has also previously been assigned in 3 out of 4 previous sample analyses, ie

1. The environmental filament
$S_2O_3^-$ (sulfur group)

2. CDB Secreted Protein
SO_4 sulfate
confirmed chemically also.

3. Polar Rainfall Extraction
Sulfates

4. Recall even the remaining sample has a note that a "sulfate ester" merits consideration.

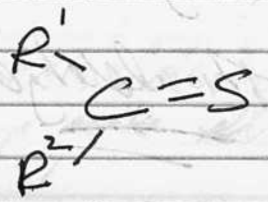
The case for sulfur presentation is indeed strong.

Lets look @ some of the sources

IR Pal lists a C=S thiocarbonyl as a Candidate. Strong absorption (matches). Range 1050-1200 matches.

Other candidates of halides, alcohols, ethers, amines, esters, carboxylic acids, Si-R have no known basis @ this time
Notice a P=O bond is mentioned 'this exists therefore as a neutral candidate.

We also know that we do have a carbonyl group, so what is a thiocarbonyl?



"Thiocarbonyl"
"Thioketone"

These are also known as thioketones
Ketones are $R_2C=O$
Thioketones are $R_2C=S$

Notice even though the name says "carbonyl" there IS NO C=O bond in this compound.

Guess what, however? The thiocarbonyl functional group ($R_2C=S$), "analogous to the carbonyl group" [BUT ALSO NOTE THAT IT IS NOT THE CARBONYL GROUP, only "analogous"] is found in THIOALDEHYDES and thioketones.

So guess what is on the short list here for now:

1. Sulfone group (Parker)

$S=O$ R_2SO_2 sulfone

2. "Thiocarbonyl" groups (IRPal)

$R_2C=S$ (Notice no carbonyl!
"analogous to a carbonyl group"

and found in thioaldehydes.

Avram & Conley will be consulted here.

In Koji, our strongest 2 candidates are:

Table 11 (6)   1. Thioketones (1200–1040 cm^{-1})
Table 11 (8-11)   2. $S=O$
Table 11 (12-16)   3. SO_2 ~~(1300~~ ~~1310–1440~~)
(1120–1230)

but item #3 here in Koji, apparently require corroboration w/ absorption @ (1300–1440) and we do not have this.

We are also looking @ the shift in absorption from 1103 cm^{-1} (polar extraction) to 1161 cm^{-1} in the non polar extraction. We would like to satisfy both extractions if we can.

Thioketones, Thioaldehydes do this (1200-1040).

Koji's additional candidates of alcohols, phenols, ethers, ethers, amines, ketones, esters, halides did not work also as in IRPal.

The case for thioaldehydes continues to develop quite strongly.

Look @ Koji's table entries:

The SO bonds in Koji Table 11 (p 54) do not work.
What does work is the C=S bond in Table 11, entry #6 (1200 - 1050 strong). Also, absorption is influenced by substituents, ring strain.

I assess, rather strongly also, that we are very likely to have a thioaldehyde here.

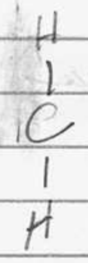
Time now for AVRAM.

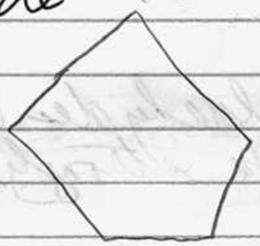
AVRAM has an entry for thioketones.
She does not appear to cover thioaldehydes.

Next to SDBS.

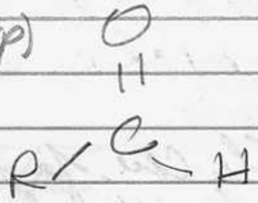
No direct entry there.
It appears to me that we have

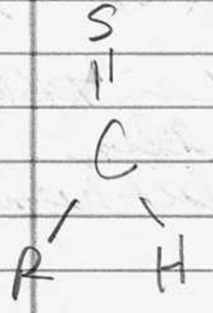
1. CH_2
2. Cyclic Structure
3. Aldehyde
4. Thioaldehyde (Thial group)





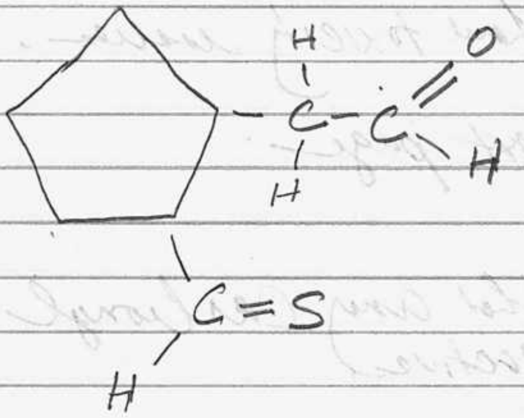
Cyclic Structure





Thial group
Thiocarbonyl group
$R_2C=S$

Now we Combine these groups



We look @ these in MOLVIEW
and use SDBS w/ peaks @

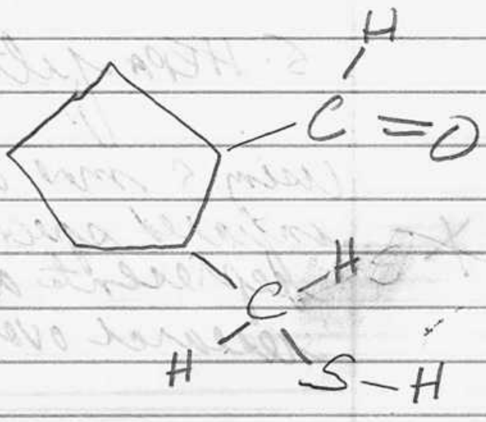
2920 2855 1729 1454 ~1130 ±10, 15

require sulfur
& Carbons
O

We have no simplified match w/ SDBS.
In Molview, our closest (and only) similar match is

Sulfanyl methyl cyclopentane carbaldehyde

Doesn't look too bad!



IMPORTANT SUMMARY STATEMENT:

We see that aldehyde

do indeed have toxicity issues.

See article next page.

—

Recall also that any carbonyl group is reactive.

—

The analyses of the previous set of environmental samples:

1. The environmental filament
2. The CDB generated protein
3. Rainfall extraction (Non-Polar)
4. Rainfall extraction (Polar)
5. HEPA filter (polar & non polar extractions)

* using a more directed & thoughtful infrared spectroscopy interpretation methods represents a milestone in CI research over the last 20 years.

CHEMICAL RESEARCH IN TOXICOLOGY

ACS Publications

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Chem Res Toxicol. 2014 Jul 21; 27(7): 1081–1091.
Published online 2014 Jun 9. doi: 10.1021/tx5001046

PMCID: PMC4106693
PMID: 24911545

Molecular Mechanisms of Aldehyde Toxicity: A Chemical Perspective

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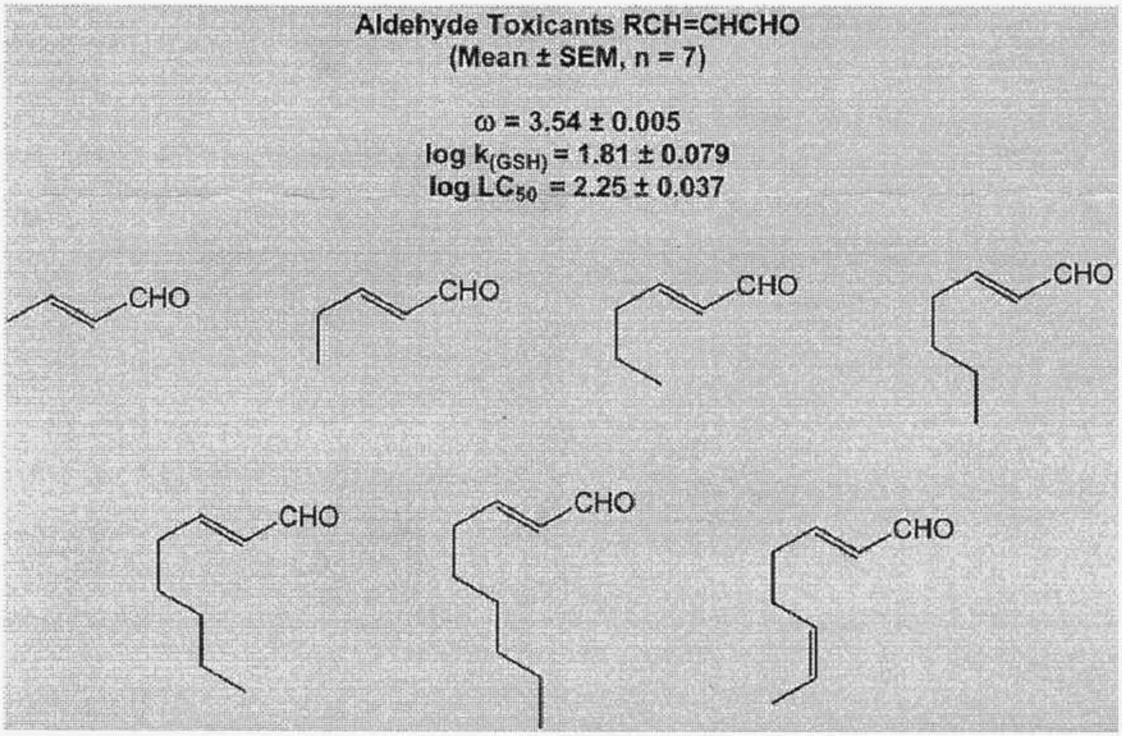
Received 2014 Mar 20

Abstract

Go to:



Aldehydes are electrophilic compounds to which humans are pervasively exposed. Despite a significant health risk due to exposure, the mechanisms of aldehyde toxicity are poorly understood. This ambiguity is likely due to the structural diversity of aldehyde derivatives and corresponding differences in chemical reactions and biological targets. To gain mechanistic insight, we have used parameters based on the hard and soft, acids and bases (HSAB) theory to profile the different aldehyde subclasses with respect to electronic character (softness, hardness), electrophilic reactivity (electrophilic index), and

Page 268A

biological nucleophilic targets. Our analyses indicate that short chain aldehydes and longer chain saturated alkanals are hard electrophiles that cause toxicity by forming adducts with hard biological nucleophiles, e.g., primary nitrogen groups on lysine residues. In contrast, α,β-unsaturated carbonyl derivatives, alkenals, and the α-oxoaldehydes are soft electrophiles that preferentially react with soft nucleophilic thiolate groups on cysteine residues. The aldehydes can therefore be grouped into subclasses according to common electronic characteristics (softness/hardness) and molecular mechanisms of toxicity. As we will discuss, the toxic potencies of these subgroups are generally related to corresponding electrophilicities. For some aldehydes, however, predictions of toxicity based on electrophilicity are less accurate due to inherent physicochemical variables that limit target accessibility, e.g., steric hindrance and solubility. The unsaturated aldehydes are also members of the conjugated type-2 alkene chemical class that includes α,β-unsaturated amide, ketone, and ester derivatives. Type-2 alkenes are electrophiles of varying softness and electrophilicity that share a common mechanism of toxicity. Therefore, exposure to an environmental mixture of unsaturated carbonyl derivatives could cause "type-2 alkene toxicity" through additive interactions. Finally, we propose that environmentally derived aldehydes can accelerate diseases by interacting with endogenous aldehydes generated during oxidative stress. This review provides a basis for understanding aldehyde mechanisms and environmental toxicity through the context of electronic structure, electrophilicity, and nucleophile target selectivity.

Introduction

Go to:

Aldehydes are a large class of electrophilic carbonyl compounds that have at least one hydrogen atom substituent on the carbonyl carbon atom (Table 1). Chemicals in this family can be divided into subclasses based on corresponding structures that incorporate additional functional moieties: (1) short chain, unhindered aldehydes, formaldehyde, acetaldehyde; (2) long chain alkanals, nonanal; (3) aromatic aldehydes, benzaldehyde, vanillin; (4) α,β-unsaturated aldehydes that include numerous subclasses,aromatic alkenals, short and long chain alkenals, and hydroxy or oxoalkenals; and (5) α-oxoaldehydes, glyoxal and glycolaldehyde.[1,2] Aldehydes present in the environment are derived from both natural and anthropogenic sources.[1–5] For example, formaldehyde and acetaldehyde are normal dietary constituents and pervasive environmental contaminants due to their broad natural sources and high-volume use in a variety of industrial and manufacturing processes (Table 1). α,β-Unsaturated aldehyde derivatives such as acrolein and crotonaldehyde (Table 1) are significant components of air pollution due to petrochemical combustion[5–7] and smoke from cigarette, wood, and coal combustion.[4,8,9] Many aldehydes are contaminants of the U.S. water supply, and more than 300 unsaturated aldehydes (e.g., crotonaldehyde, citral, and cinnamaldehyde) are natural constituents of various foods (e.g., cheese, fish, and potatoes). Aldehyde derivatives are produced during the cooking of fats, oils, and sugars; e.g., 2-pentenal, acrolein, 2,4-nonadienal,[2,3,10] and low concentrations of α,β-unsaturated aldehydes are used for flavor enhancement in the food and beverage industries, e.g., *trans*-2-hexenal.[11] On the sole basis of dietary consumption, it is estimated that the daily α,β-unsaturated aldehyde burden in humans is 5.0 mg/kg-body weight.[12,13] Human exposure to aldehydes can also occur through the formation of reactive intermediates during drug metabolism, e.g., metabolism of the chemotherapeutic agent cyclophosphamide to acrolein.[14]

Table 1

Classification and Hardness/Softness Values for Selected Aldehdyes[a]

Jan 12 2016

Our listing of cross Connections includes:

1. Env. Filament
   1. Digestion] sample prep
   2. Catalytic] methods

2. Rainfall
   1. Polar extraction
   2. Non Polar extraction

3. HEPA filter
   1. Polar extraction
   2. Non Polar extraction

Coupled with:

1. Skin
2. Blood
3. Saliva
4. Ear Wax
5. Urine
6. Hair

Core Finding Here

Page 270

June 13 2018

Here is an important finding that ~~has~~ has taken place. This development has occurred over a period of several years, essentially when the infrared (IR) instrument came on board.

The issue is the existence of a thiocyanate group/compound that has surfaced amongst a broad spectrum of sample types. The functional group is not present at all times in all samples but it occurs frequently enough to establish well founded concern.

The sample types now include (but not necessarily limited to):

cm^{-1}

1. A reference of lit for sodium thiocyanate (2064 cm^{-1})
2. Cross domain bacteria (CDB) Pyrolysis (2174, 2113)
3. CDB Viscous Protein (Culture secreted protein) (2133)
4. Earlier blood sample (Jul 2015) (2118)
5. 2nd blood sample - separate individual (Aug 2015) 2014
6. Rainfall Concentrate - Aug 2016 (2069)
7. Ear wax sample (2018) (2186)
8. Saliva (2054)
7. The "Environmental Filament" (2066)
8. Human Hair (2060)
9. Skin foliation sample from individual that directly presents the "Morgellons" skin symptoms (verified filament existence upon skin sample using microscopy) (2061)

The infrared plots for each of the samples verifying the thiocyanate functional group appear as attached (9 plot types).

It is quite certain that this functional group / structure SHOULD NOT BE THERE at this level of distribution.

This is an absolutely core finding of the Morgellons research.

There are undoubtedly significant health impacts, monumental in fact.

These plots make the case for the existence of this problem.

—

There may well be other sample types demonstrating this problem; this is just the collection to date.

—

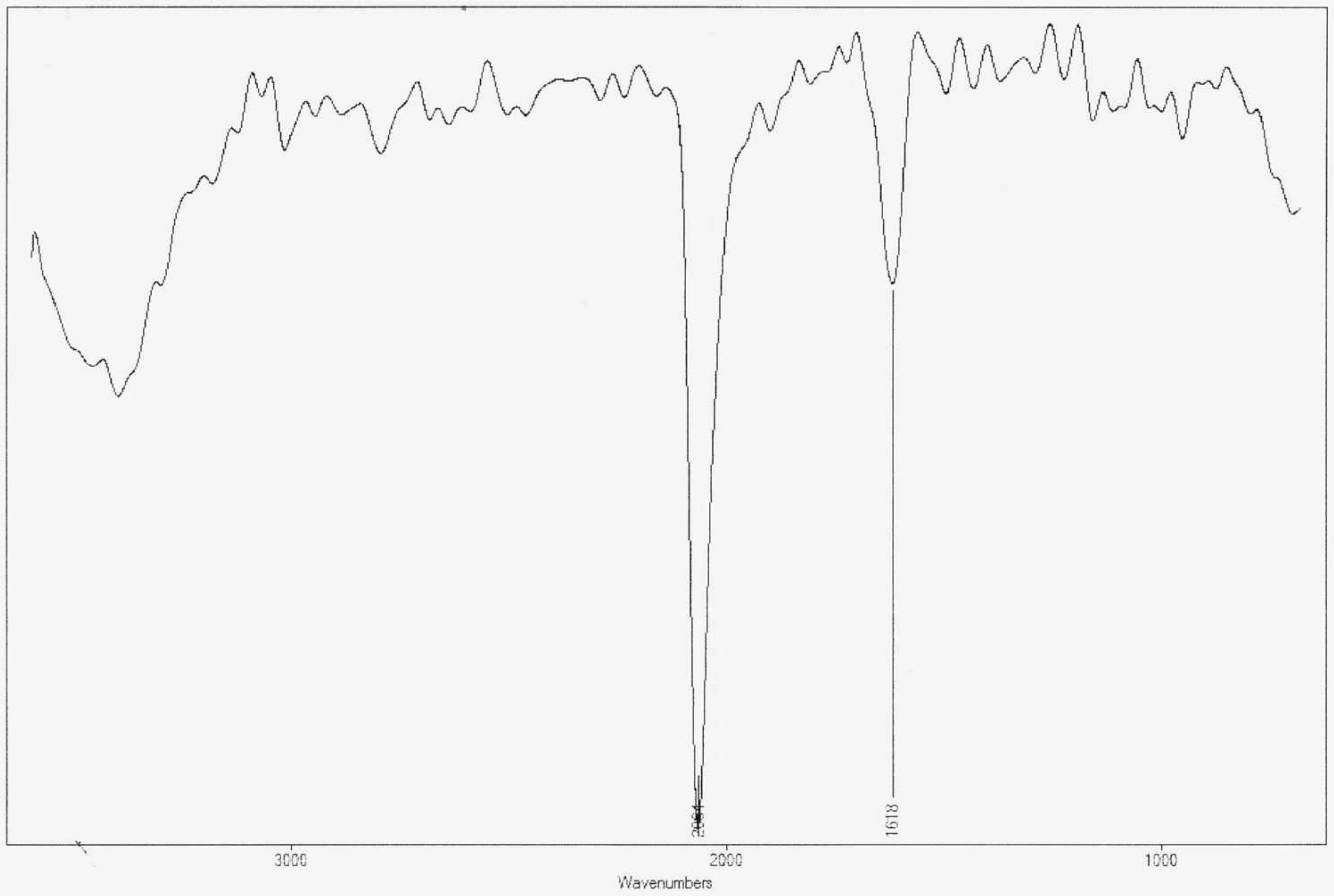
It is especially interesting that pyrolysis of the CDB itself, without any further culturing, processing or separation demonstrates the existence of the thiocyanate group.

~~Cor~~ Core Finding : Page 272

Thiocyanate Group Presence - Wide Distribution

Sodium Thiocyanate Solution Evaporated ATR Dec 04 2017 - 01.spc: 12/05/2017 02:26:38 title

Page 272A



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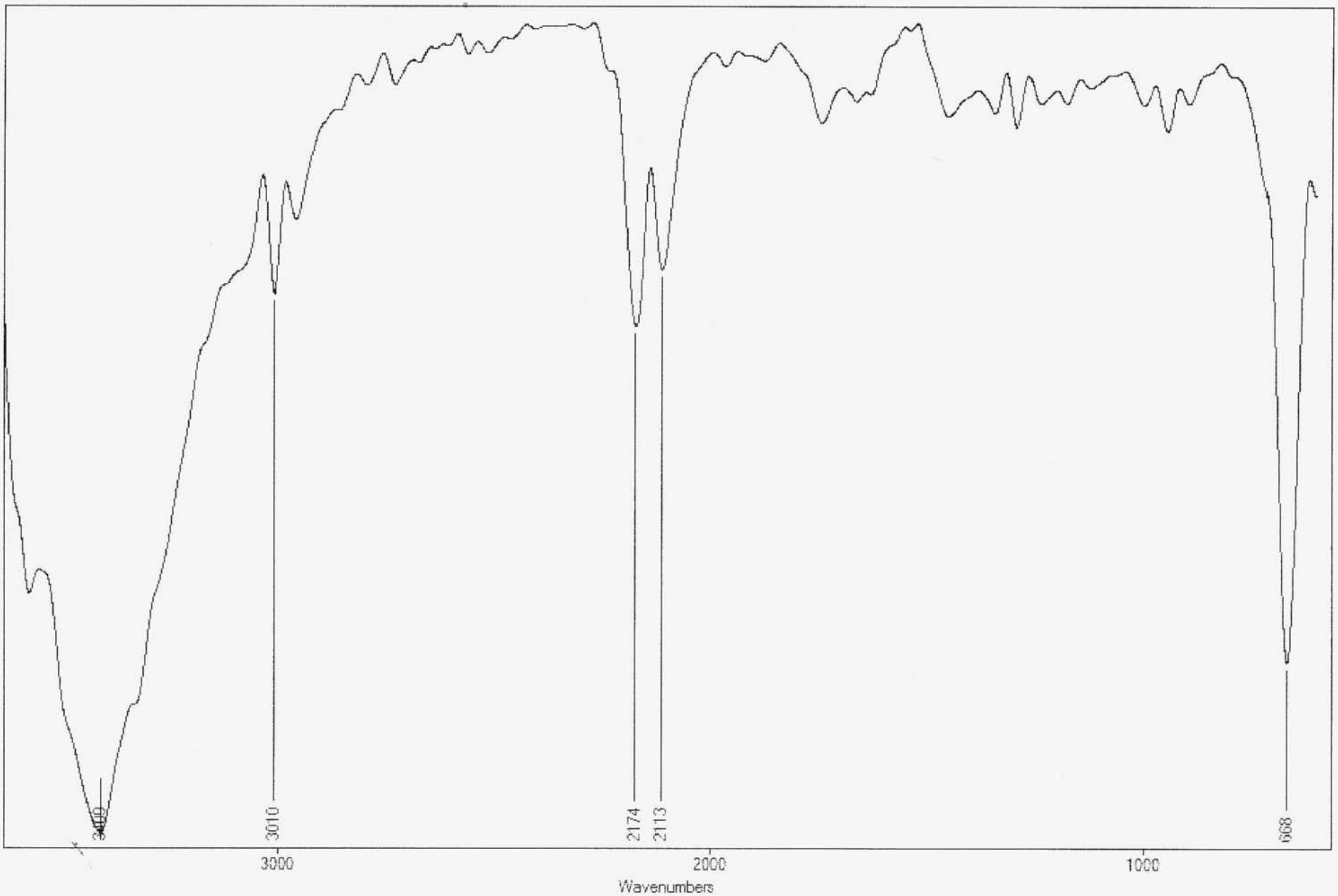
CDB Protein Pyrolysis Jul 06 2016 - 02.spc: 07/07/2016 02:12:53 title

Page 272 B



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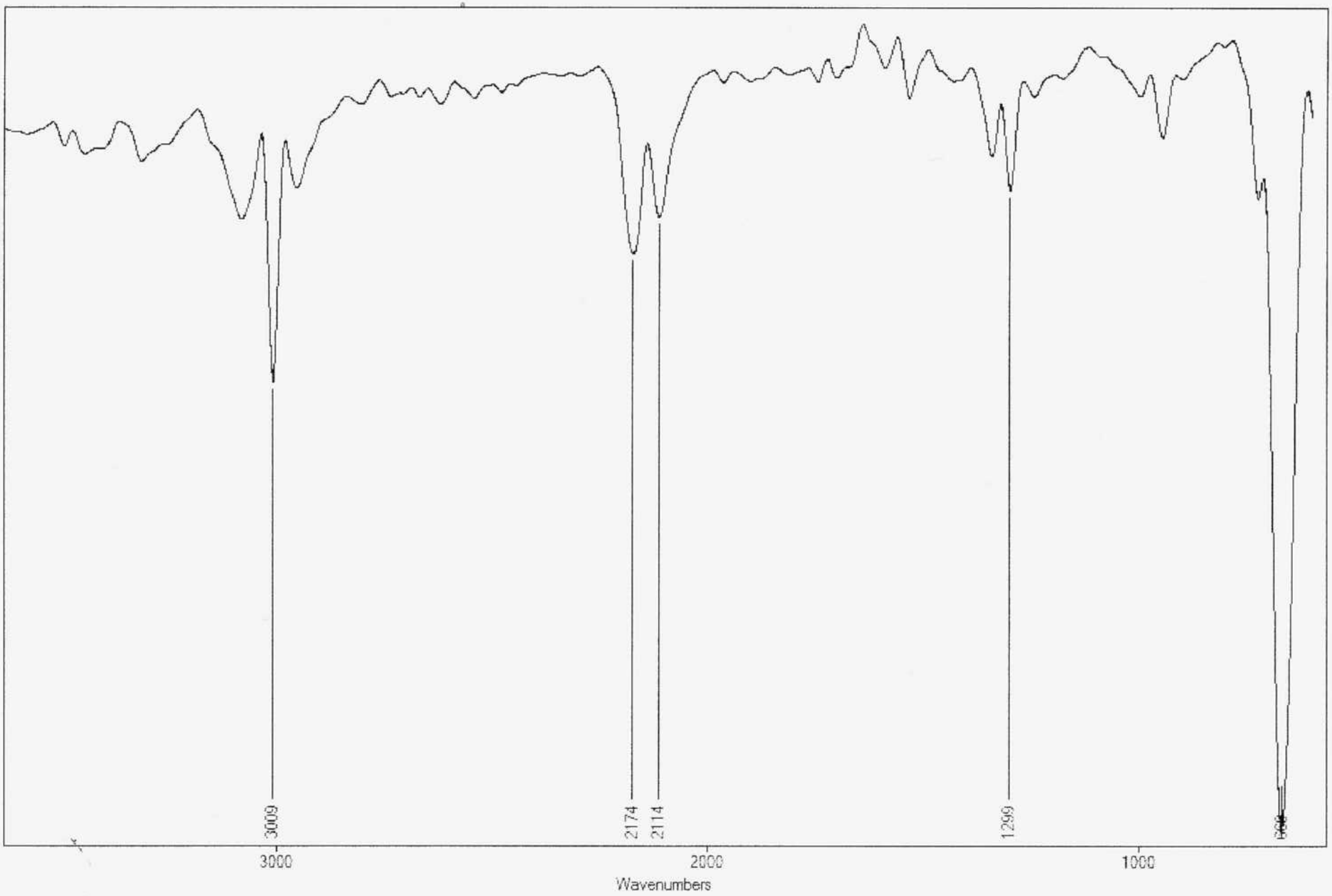
CDB Pyrolysis Jul 07 2016 - 05.spc: 07/06/2016 19:29:51 title

Page 272C



eFTIR

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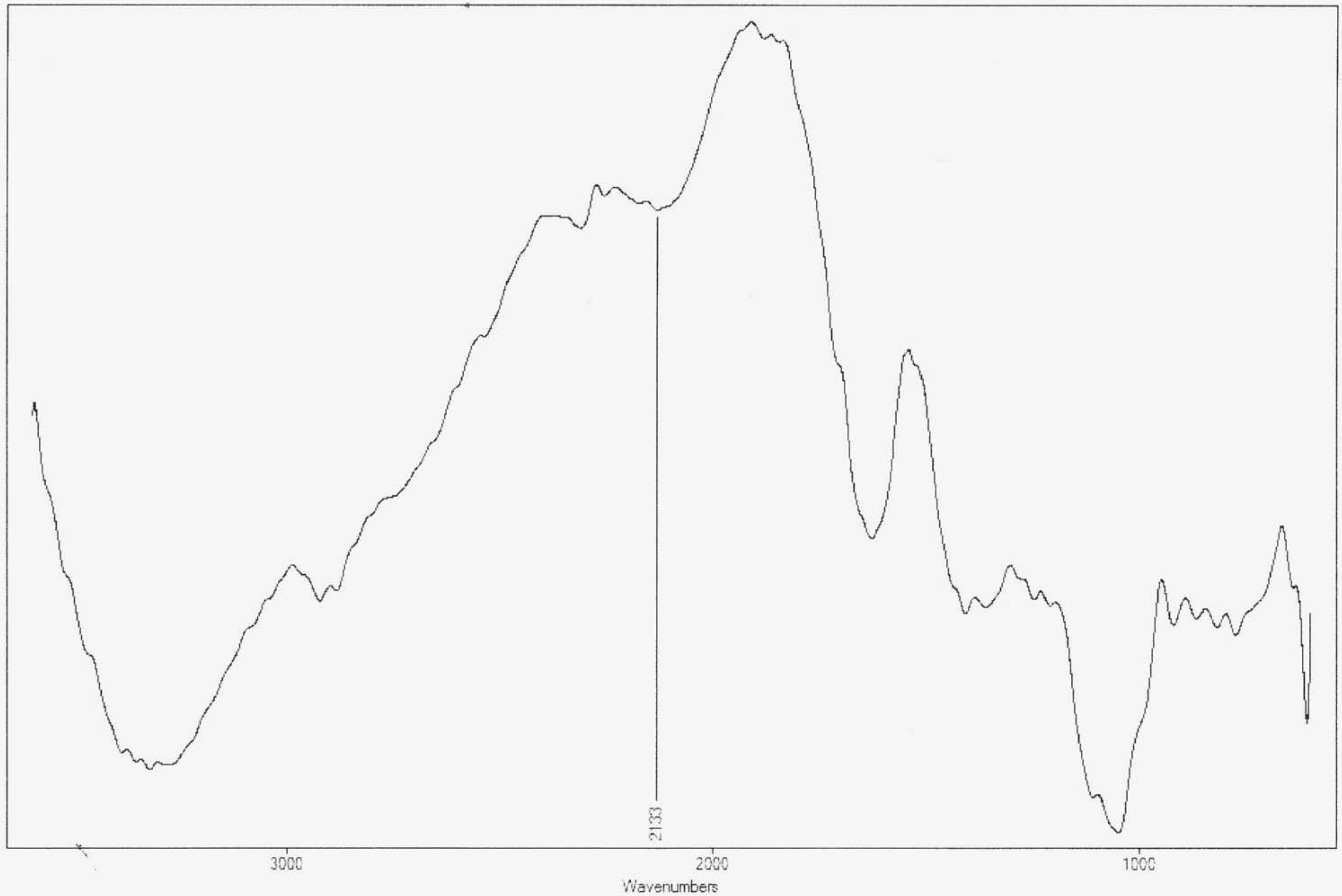
CDB Viscous Protein Jul 31 2017 - 01.spc: Synthetic spectrum by averaging. See audit trail for details.



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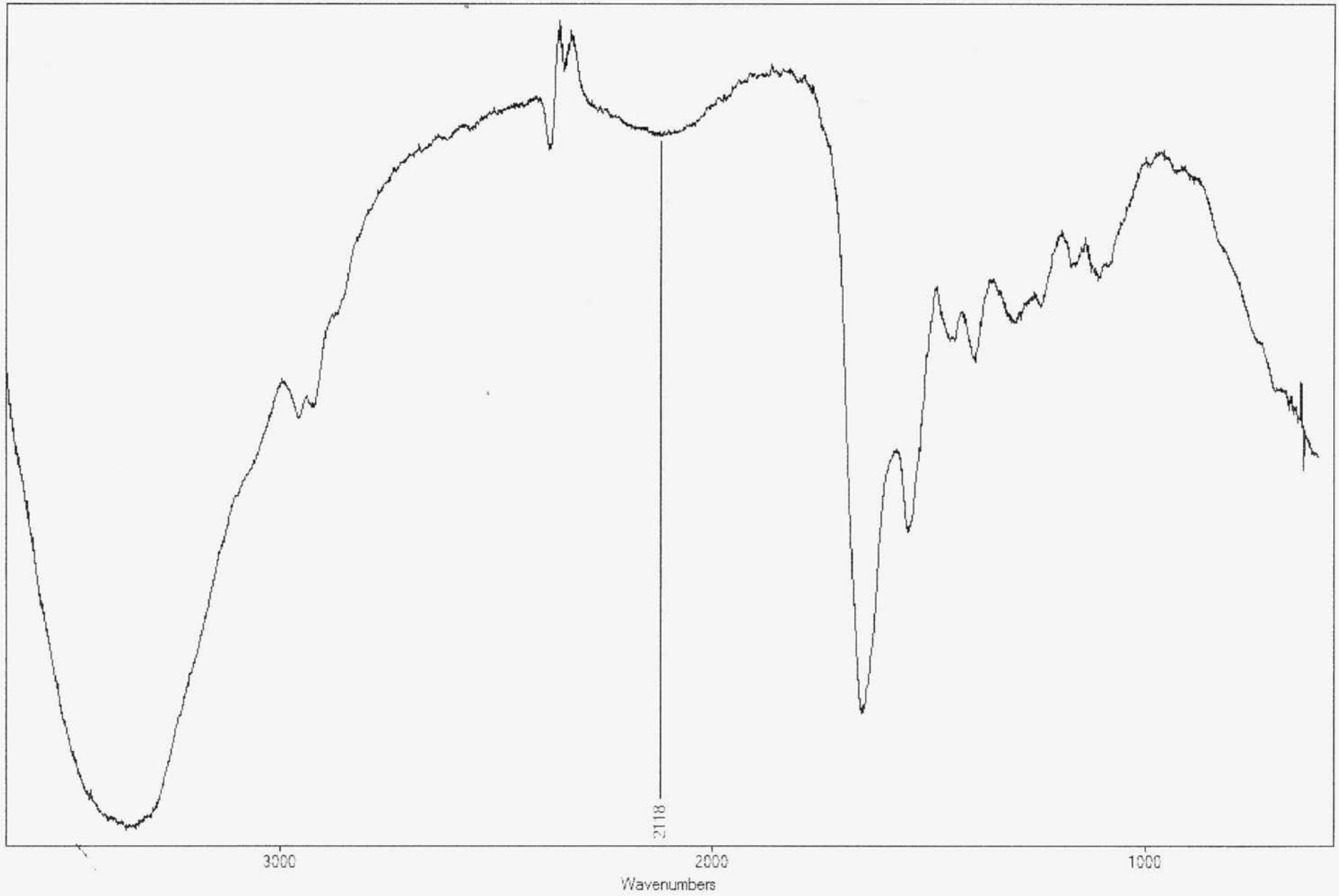
Blood CEC Average Jul 05 2015 - 01.spc: Synthetic spectrum by averaging. See audit trail for details.

Page 272E

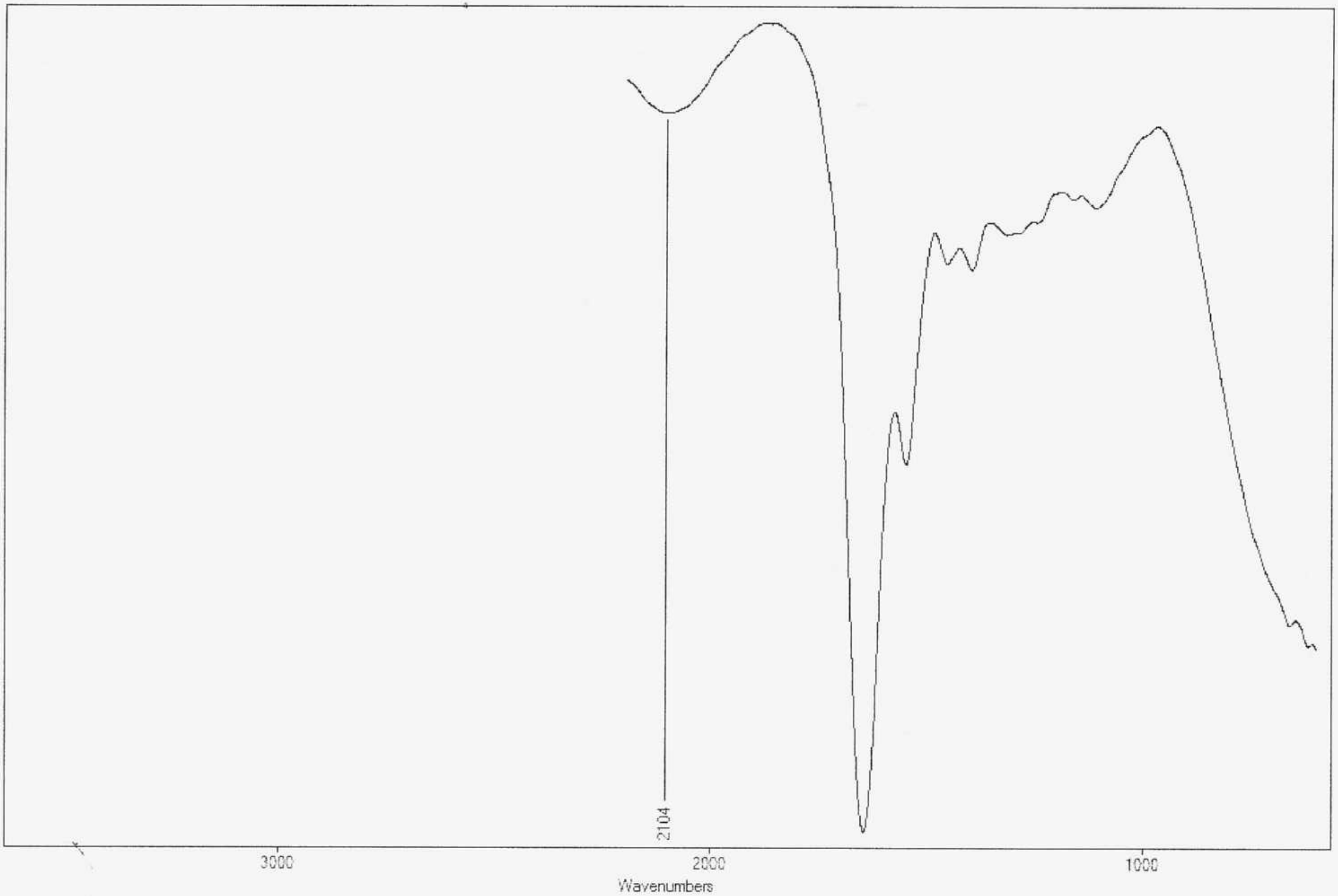


eFTIR

printed on 06/12/2018 16:16:51

Blood Katie Serum Dominant KCl Aug 05 2015 - 01.spc: 08/05/2015 18:51:15 title

Page 272 F



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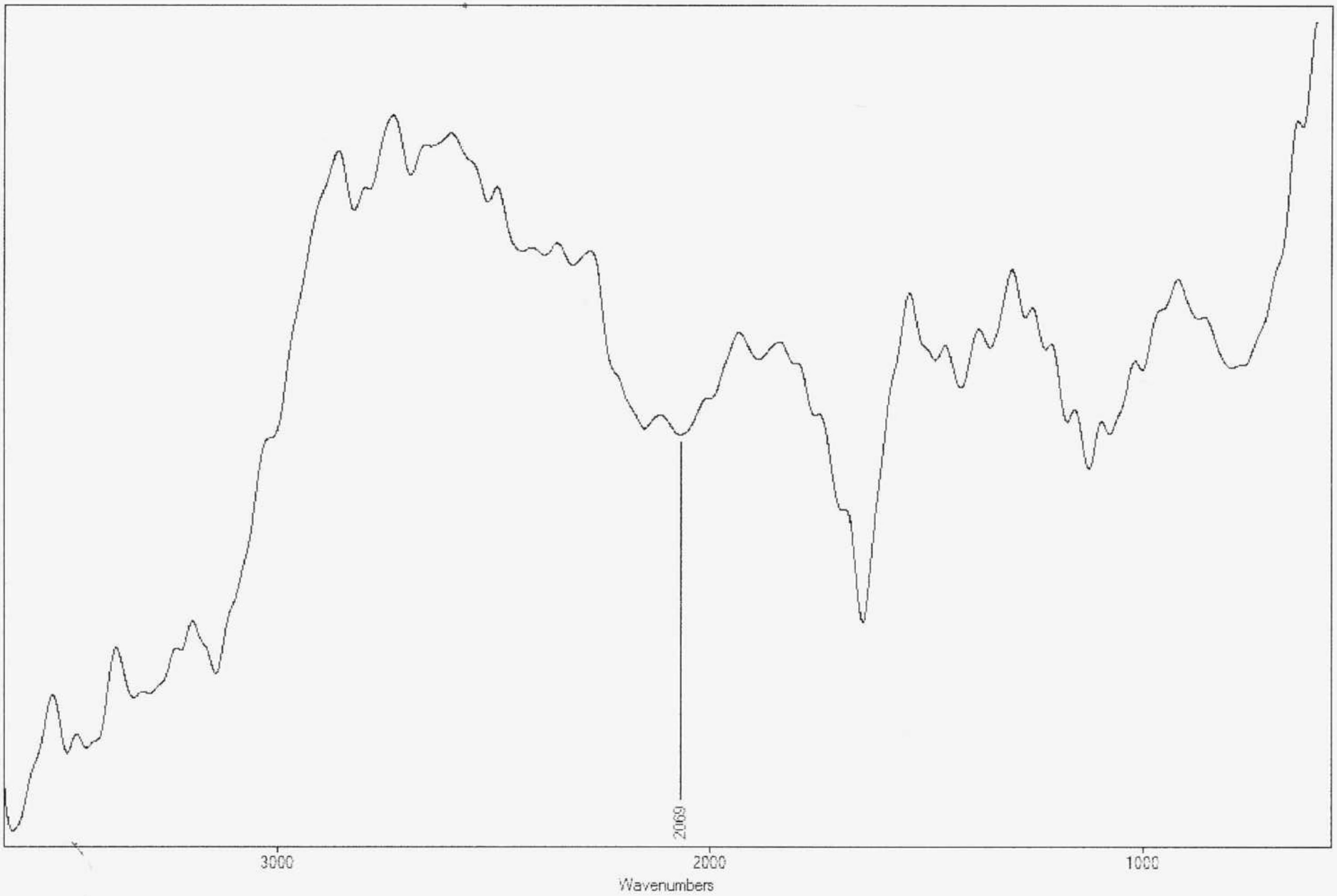
Rainfall Concentrate Distillation Average Aug 09 2016 - 05.spc: Synthetic spectrum by averaging. See audit trail for details.

Page 272G



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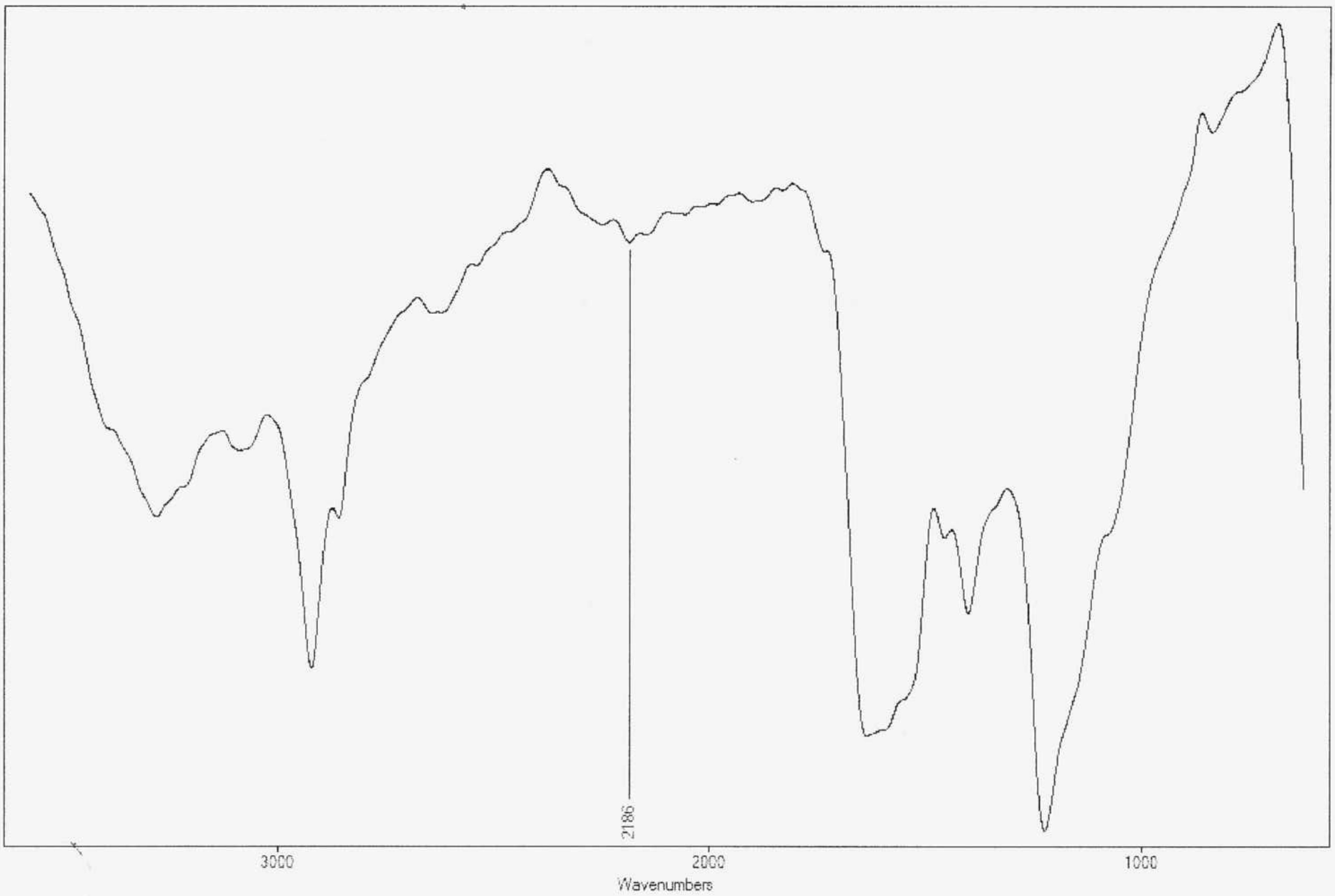
Ear Wax Avg Jun 08 2018 - 03.spc: Synthetic spectrum by averaging. See audit trail for details.



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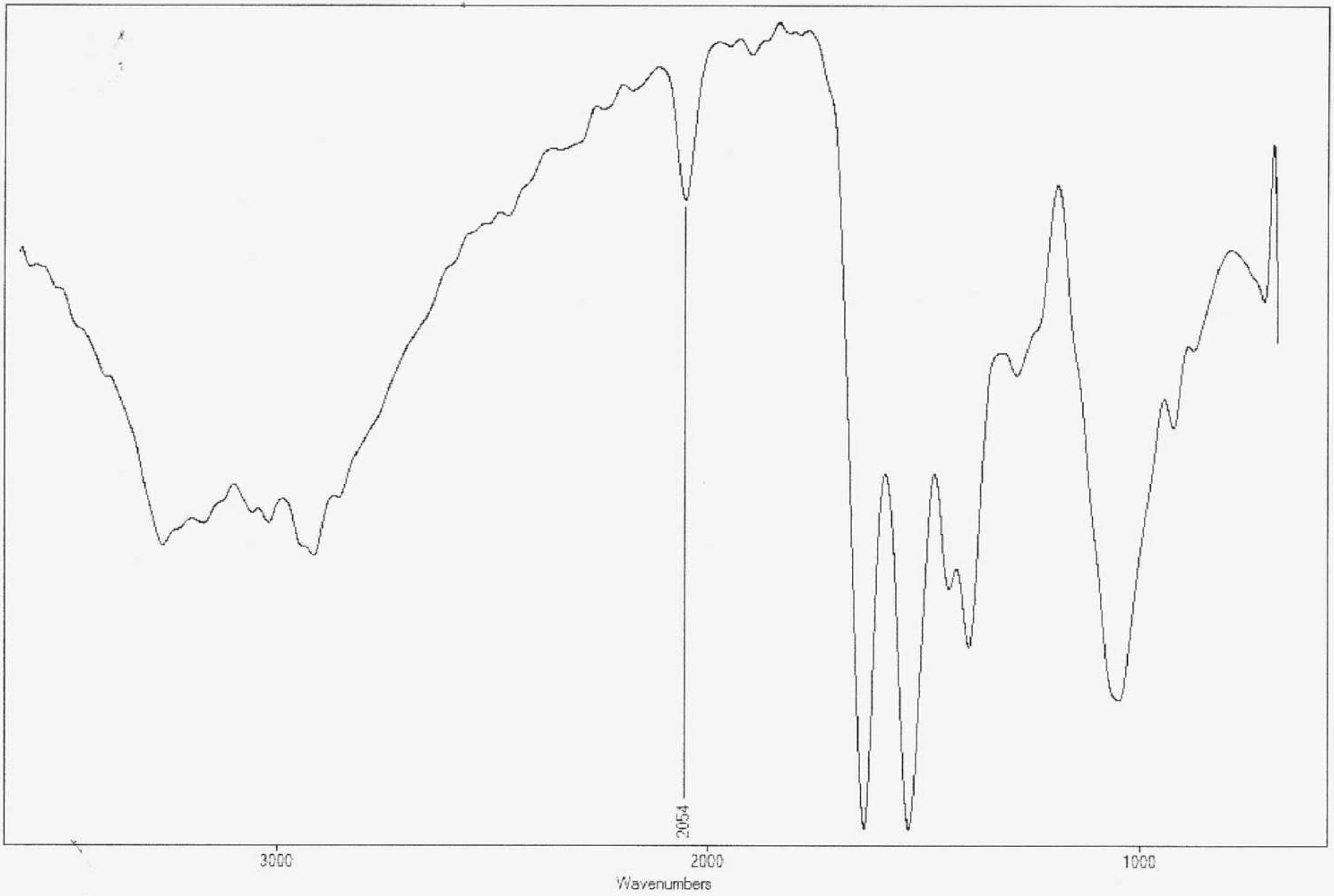
Saliva Carol ATR Dec 04 2017 - 01.spc: Synthetic spectrum by averaging. See audit trail for details.

Page 272 I



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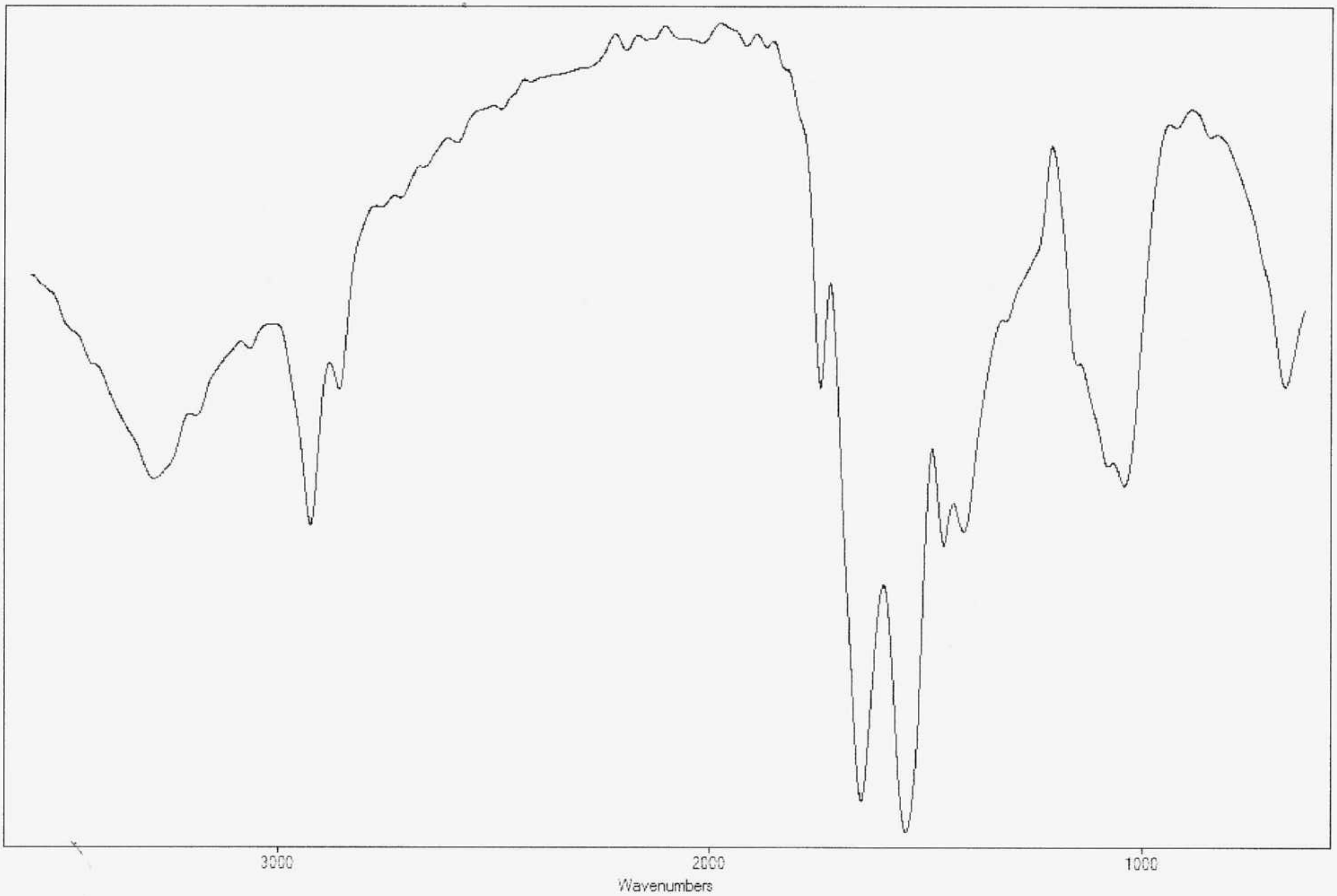
Saliva CEC ATR Jun 12 2018 - 01.spc: Synthetic spectrum by averaging. See audit trail for details.



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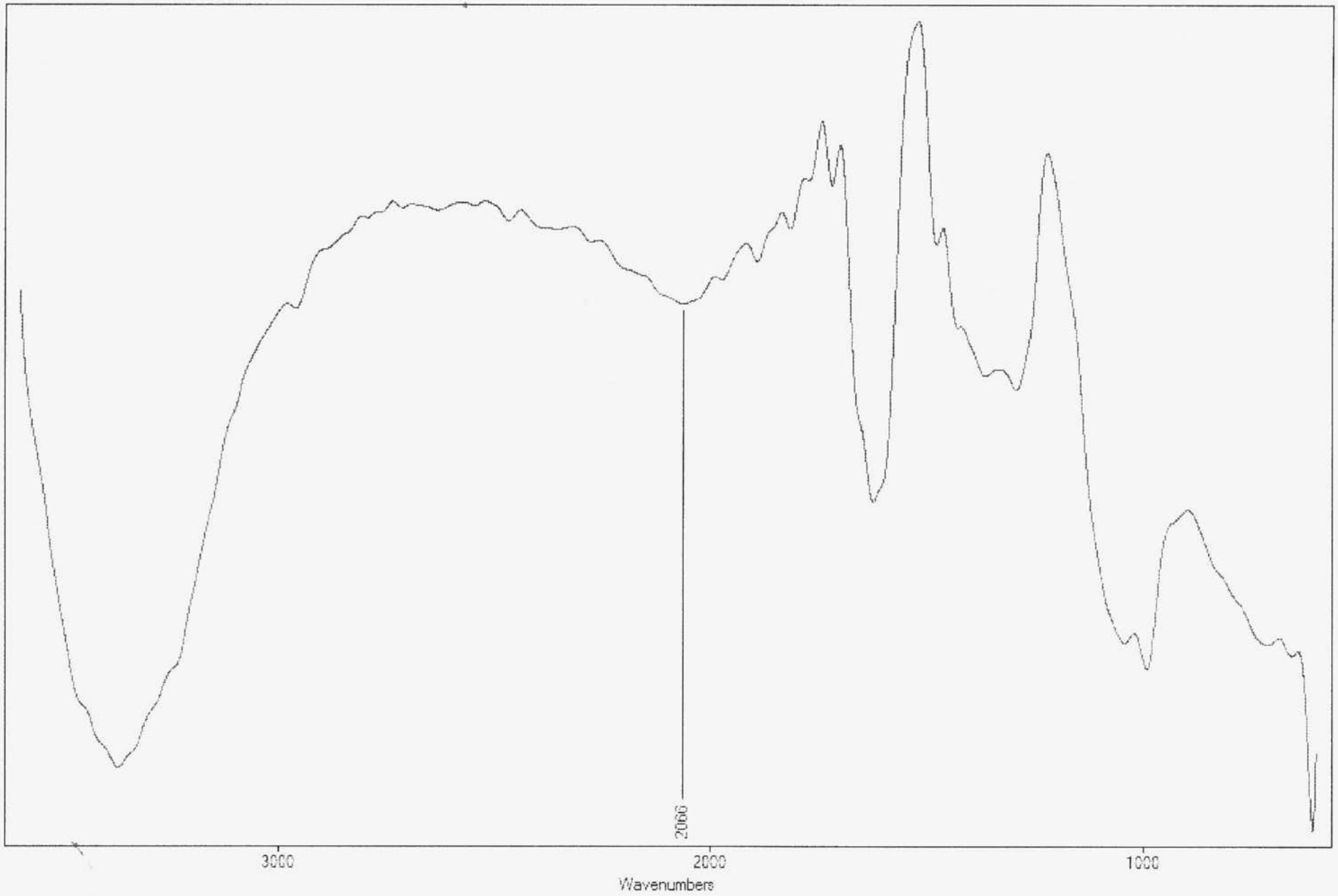
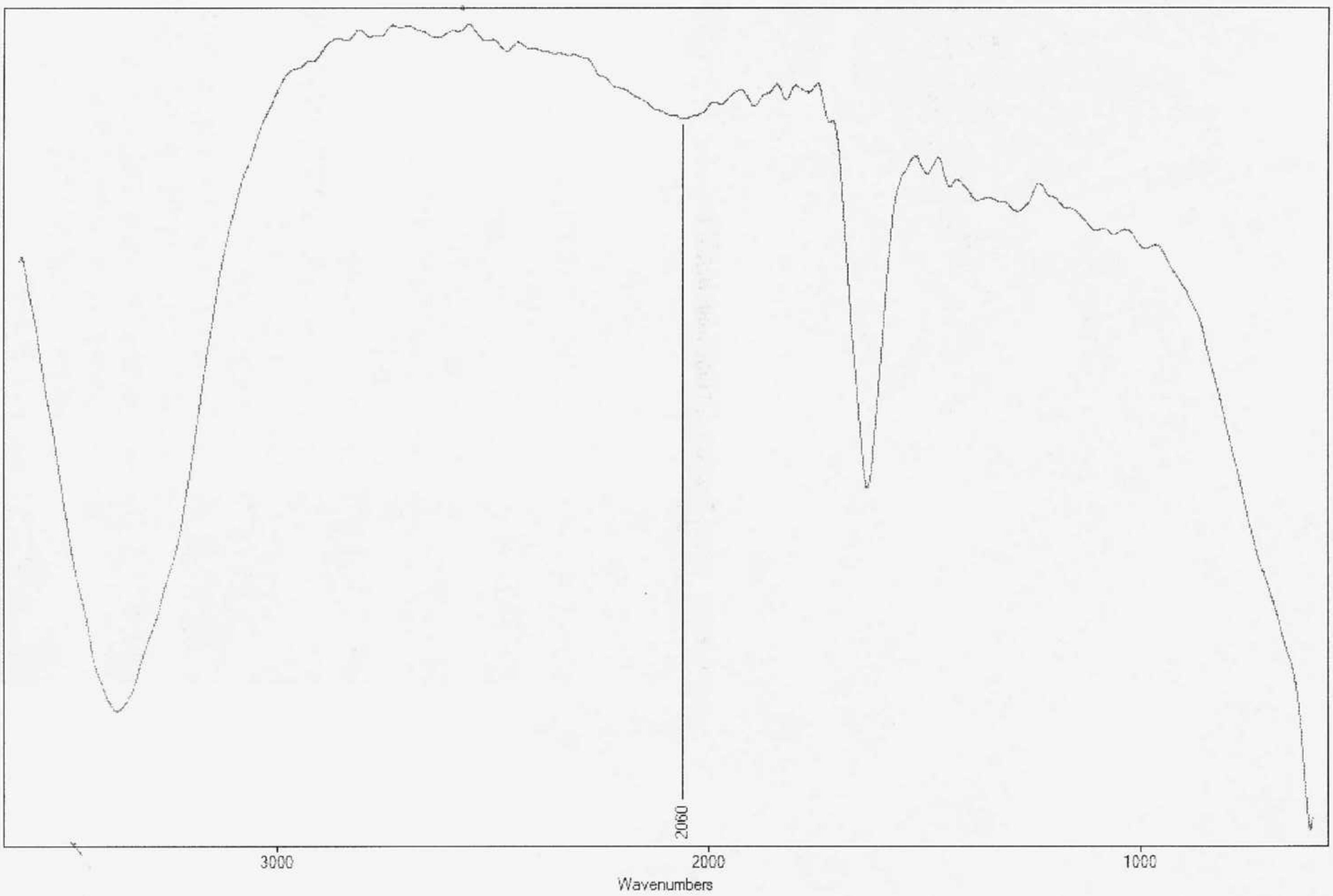
Environmental Filament ATR KCl Average Digestion-Catalysis Aug 28 2017 - 02.spc: Synthetic spectrum by averaging. See audit trail for details.



printed on 06/12/2018 16:02:55

Hair Microwave Digestion NaOH Carol Aug 30 2017 - 01.spc: Synthetic spectrum by averaging. See audit trail for details.



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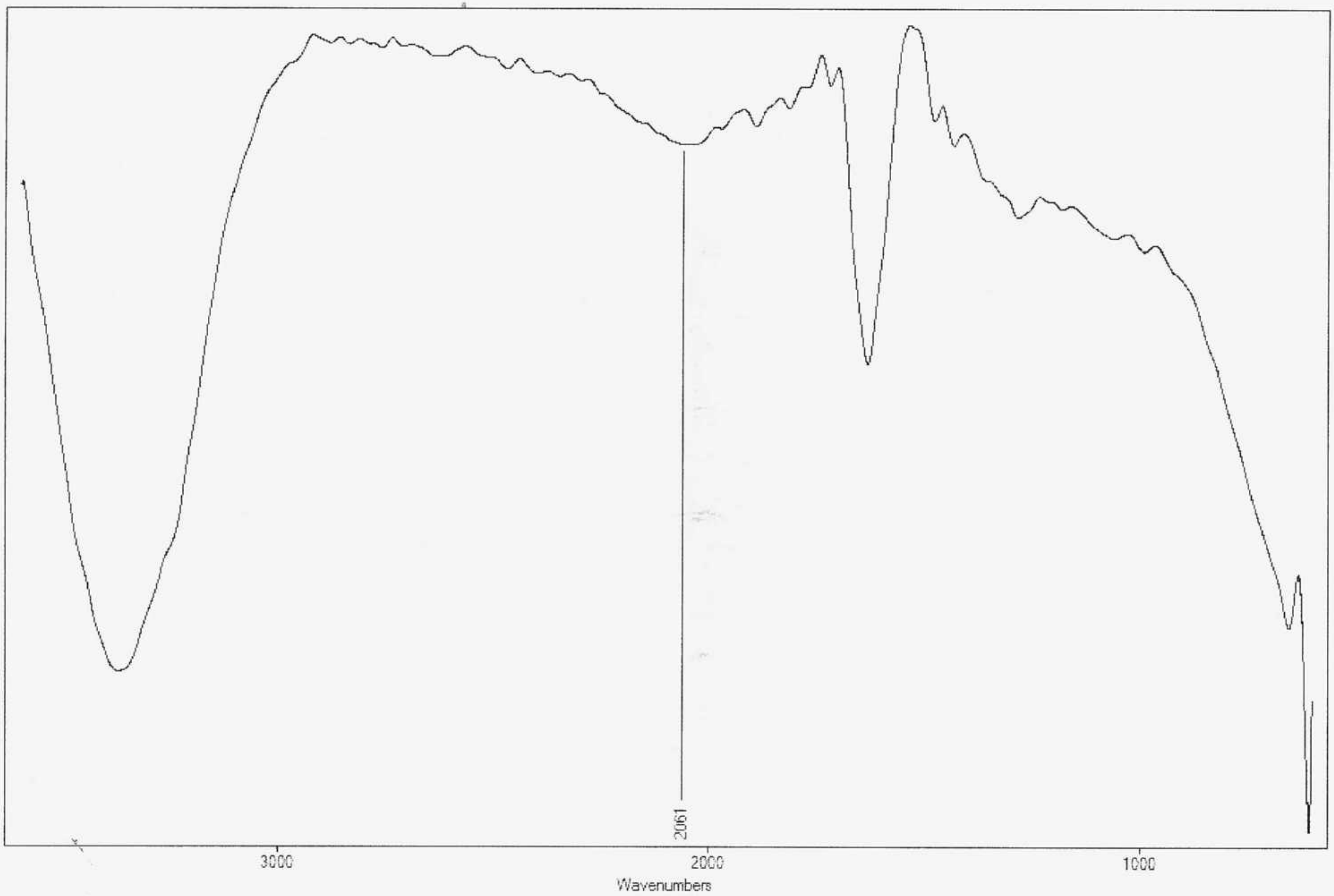
Skin Foliation NaOH Microwave ATR Aug 28 2017 - 01.spc: Synthetic spectrum by averaging. See audit trail for details.



eFTIR

printed on 06/12/2018 15:58:24

Please,

Please be advised of earlier work that demonstrates the potential significant hazards of pyrolysis examination.

(i.e. ~~B~~ the swollen neck issue that arose as a ~~se~~ result of pyrolysis of the CDB secreted protein.)

Pyrolysis of the CDB and the inherent protein(s) must be handled w/ great caution and respect. The thiocyanate presence is very likely related to or causative of the problem.

I wish to repeat, under more highly controlled, pyrolysis of the CDB alone

Jun 14 2018 Page 274

The IR plots on the following page prove, from a second independent run, of the existence of a thiocyanate groups within the CDB in their native state.

The CDB sample here results from a carefully conducted culturing process.

The method is one of pyrolysis; heating is to ~ 400°C. Gas Cell IR analysis.

The large dominant absorption peak @ ~~26~~ 2361 cm^{-1} is CO_2.

Notice, as in the plots presented within the notes of Jan 13 2018 that ~~ab~~ thiocyanate (or related compounds) is a

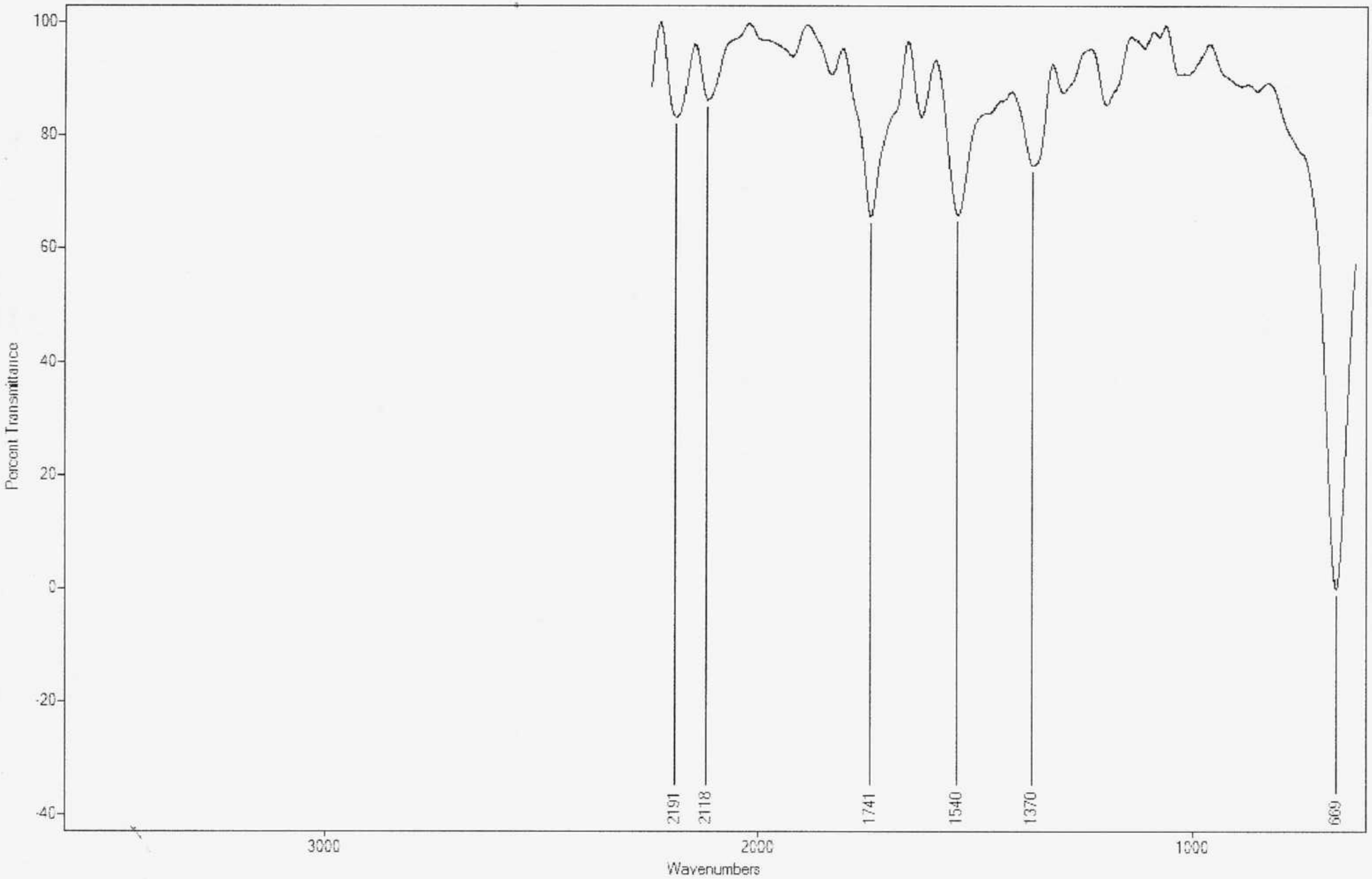
Double absorption peak, @ ~2191 cm^{-1} & ~2118 cm^{-1}.

Interpretation of these peaks in greater detail will occur @ a later point.

The double peak absorption appears to be a reasonably distinct chemical signature.

Notice the peak @ 669 cm^{-1} is especially strong along w/ the CO_2 peak.

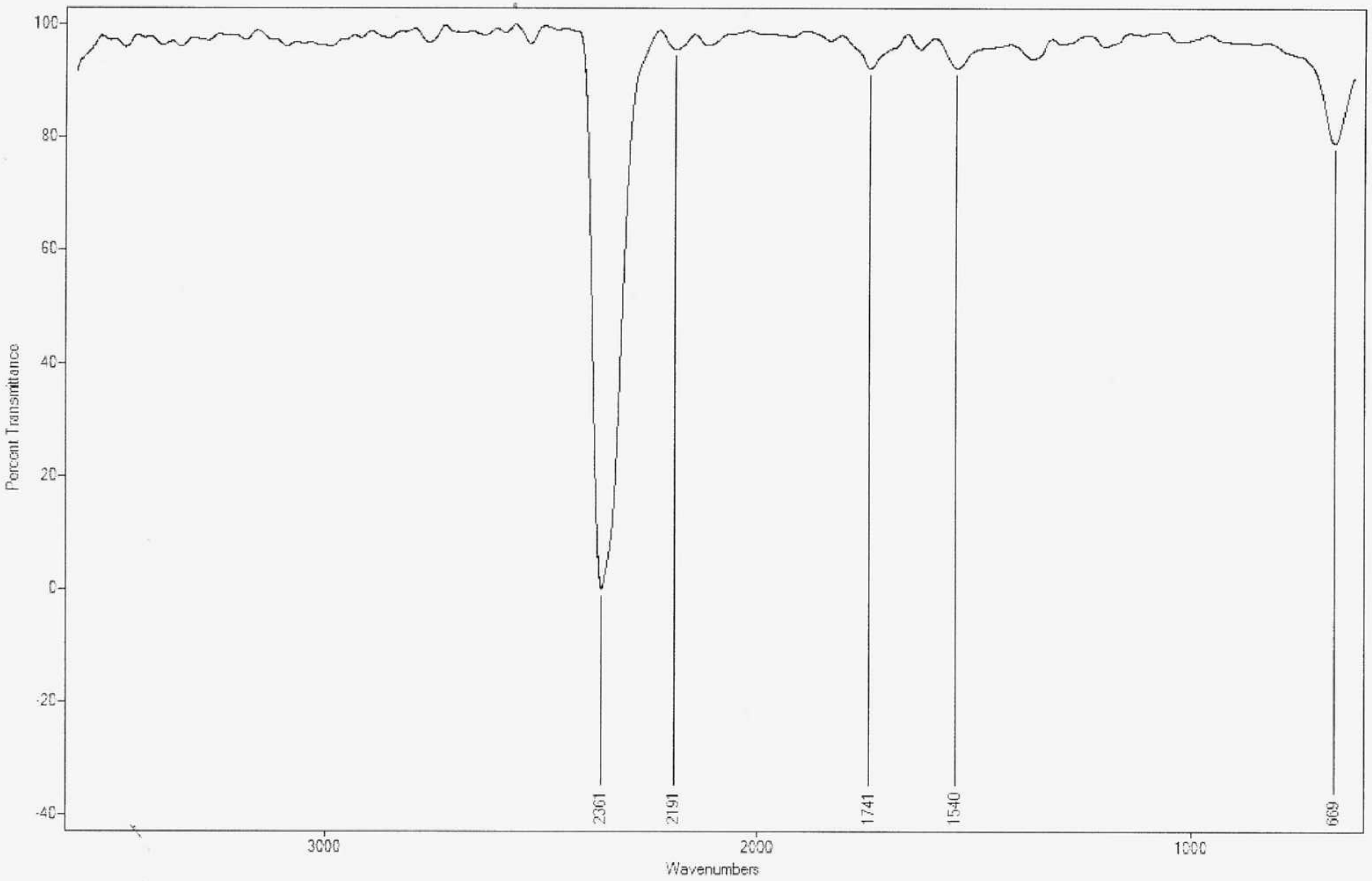
CDB Pyrolysis Gas Cell 2253-600 Jun 14 2018 -02.spc: Synthetic spectrum by averaging. See audit trail for details.



printed on 06/14/2018 17:25:58

CDB Pyrolysis Gas Cell 3600-600 Jun 14 2018 -01.spc: Synthetic spectrum by averaging. See audit trail for details.

Page 275 A



eFTIR

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Notice that w/ a SDBS (Japan) database search, the top two matching candidates are

1. Ethyl isothiocyanate

2. Propyl isothiocyanate

This is under conditions of use of the 2191 cm-1 and 2118 cm-1 peaks alone with T ≤ 50% and error ± 10 cm-1.

Notice also that within the 8 candidates matching the above search parameters,

7 out of 8 of the compounds are

isothiocyanate compounds.

We most definitely have the functional group/structure/compound identified.

See the search result on the next page.

SDBS Search Results: 1 - 8 out of 8 hits

Sort by: Molecular Weight Ascending Order Search

SDBS No	Molecular Formula	Molecular Weight	MS	CNMR	HNMR	IR	Raman	ESR	Compound Name
4221	C3H5NS	87.2	N	N	N	Y	N	N	ethyl isothiocyanate
21756	C4H7NS	101.2	Y	Y	Y	Y	N	N	propyl isothiocyanate
13721	C7H4FNS	153.2	Y	N	N	Y	N	N	p-fluorophenyl isothiocyanate
25259	C11H14N2	174.2	N	N	N	Y	N	N	N-tert-butyl-N'-phenylcarbodiimide
17186	C7H4N2O2S	180.2	Y	Y	Y	Y	N	N	p-nitrophenyl isothiocyanate
22587	C8H4N2S2	192.3	Y	Y	Y	Y	N	N	p-phenylene diisothiocyanate
19711	C11H15NS	193.3	Y	Y	Y	Y	N	N	1-adamantyl isothiocyanate
16780	C9H9NO2S	195.2	Y	Y	Y	Y	N	N	3,4-dimethoxyphenyl isothiocyanate

Return to Search

Jan 15 2010

Working on some calibration runs on the IR ATR configuration & w/ gas chromatography (GC).

The IR instrument has been repaired (fortunately!) but there is some loss of energy over time, which is expected.

The ATR crystal & gas cell show enough attenuation that increasing the gain of the instrument is now an option. Background ATR & gas cell spectra are now being collected under a gain of 10. It appears this can be accomplished w/out clipping & that we are in range. This is great. Signal looks quite good.

Actually, there is some fairly minor clipping taking place @ 866 cm^{-1} but it can be accomodated fairly easily. It can be ignored or removed @ well.

I am also generating a background ~~cell~~ spectrum for the gas cell w/ gain of 10. There is no clipping of any kind & this will be the preferred route since the attenuation is the greatest w/ the gas cell (2 KCl discs).

You notice there is some dust on the mirrors of the ATR. Some of this has now been removed and an updated background spectrum attained. It did make some difference.

There are two points of clipping now w/ this additional cleaning.

This is not desirable and therefore the gain of 10 WILL NOT BE USED for the ATR. Remove the background spectrum.

We see that a signal strength of 10+ is more than sufficient to collect a suitable spectrum. If the signal strength falls to approx 5 then it is appropriate to increase the gain by a factor of 10, as in the gas cell.

The ATR crystal is actually reaching a max gain of ~ ~~20~~ 21 which is more than adequate.

The gas cell, on the other hand, is attenuated enough that it can benefit from using a gain of 10.

Combustion analyzer question: (via GC-TCD)

If you have the % of CO_2 & H_2O in a combustive process, can you determine the empirical formula of the compound?

eg sugar combustion, human breath, etc.

Human breath is a mixture so the question does not exactly apply but for hypothetical purposes, let us assume that it is a compound to investigate the question.

In our human breath example, we have

Case I		Case II	Case III
39.50%	O_2-N_2	39.71%	Assume Excess O_2-N_2
0.98	CO_2	0.98%	1.63%
~~0.52~~ 59.00	H_2O	59.31%	98.37%
0.52	Argon		
Full Breath		Null Argon	CO_2 & H_2O only.

—

Also, we have learned that a column temperature of 120°C. This allows separation of the CO_2 peak, as well as argon as well as H_2O vapor. N_2O_2 combine as a single peak. This is great.

I believe this problem can be solved.

We start w/ the assumption that we do have complete combustion.

The general model is

$$C_xH_yO_z + \overset{\text{Excess}}{O_2} \rightarrow \overset{1\text{mol}}{\underset{.037\text{ moles}}{CO_2}} + \overset{\sim 148\text{ moles}}{\underset{5.46\text{ moles}}{H_2O}}$$

We must have complete combustion to produce a viable result.

Our case is $CO_2 = 1.63\%$
$H_2O = 98.37\%$

Approach is to
1. Find the mass of C from CO_2
2. Find the mass of H from H_2O
3. Find the mass of O by subtraction.

Since we have % values (ie, relative mass) we will assume a mass of the product

Assume we have 100 gms of product.
Then we have 1.63 gms of CO_2
98.37 gms of H_2O

Page 282

The molecular wt of CO_2 is 44.01 gms/mol

The molecular wt of C is 12.01 gms/mol
Therefore the ratio of C is $\frac{12.01}{44.01} = 27.3\%$

Therefore we have 0.273 (1.63 gms CO_2) = 0.445 gms C of product.

The molecular wt of H_2O is 18.015 gms/mol

The ratio of H is: $(0.5)\left(\frac{2.016\text{gms}}{18.015}\right)(98.31) = 5.504$ ~~.056 gms~~ gms H

This means that we have $100 - (.445 + 5.504) = 94.051$ gms O

Therefore we have (assuming a pure compound)

	~~Ratio~~	Moles	Ratio
~~H~~ C: .445 gms/(12.011)	~~1~~	= .037	1
H: 5.504 gms/(1.008)	~~12.37~~	= 5.46	147.6
O: 94.051 gms/(16.0)	~~211.35~~	5.88	158.9

So our hypothetical compound is ~~$C_1H_{12.4}O_{211.4}$~~

And therefore we see that human breath $C_1H_{148}O_{159}$ is almost entirely O_2 (disregarding the nitrogen presence) Since H is in form of H_2O it is C_1

which does make perfect sense.

Our model

Page 283

Let's work thru the example problem and see if we achieve the same answers;

Given:

$14.77g$ of $C_xH_yO_z$

Result: Produce 43.26 gms CO_2
12.40 gms H_2O

or:

$_2$ 77.7 gms or in our case 77.7% CO_2 Assume
22.3 gms 22.3% H_2O 100 gms product

C: therefore we have $\frac{12.01}{44.01}(77.7gms) =$

$= (0.273)(77.7gms) = 21.20 gms\ C$
$(= 1.76 moles)$

H: and $\left(\frac{1}{2}\right)\left(\frac{2.016}{18.015}\right)(22.3gms) =$

$= .056(22.3gms) = 1.248 gms\ H$
$(= 1.24 moles)$

O: The O in the sample is therefore

$100 - (21.20 + 1.25) = 77.55$ gms
$(= 4.85$ moles$)$

	Ratio
or H: 1.24 moles	1
C: 1.76 moles	1.42
O: 4.85 moles	3.91

or a. $HC_{1.42}O_{3.91}$

Now, in the example given, the actual amount of original organic compound is 14.77 gms. We assumed 100 gms.

Therefore, scaling our results, we have:

C: $\left(\frac{14.77}{100}\right)(21.20 gms\ C) = 3.13 gms = 0.26$ moles C

H: $\frac{14.77}{100}(1.248 gms\ H) = 0.184 gms = 0.183$ moles H

O $.1477(77.55 gms\ O) = 11.454 gms = 0.716$ moles O

	Moles	Ratio
H	.183	1
C	0.26	1.42
O	.716	3.91

We get $C_{1.42}H_1O_{3.91}$?

Actual is: $C_{10}H_{14}O$

Actual amounts are 11.81 gms C
1.388 gms H
1.57 gms O

and we are quite wrong so we are to regroup!

Ok, we have a problem, lets sort it out.

Lets start by assuming we have the 14.77 gms of original product. We wish to translate the problem into our percentage model as we go.

Our ratio of original product is 1.797 to 1

Page 285

14.77 gms original compound.

$\rightarrow$ 43.26 gms CO_2
$\rightarrow$ 12.40 gms H_2O } These numbers do not add up to 14.77 because they are new compounds

CO_2: 43.26 gms Actual Carbon is 11.81 gms

$$\frac{43.26 \text{ gms}}{44.01 \text{ gms/mol}} = 0.983 \text{ mole } CO_2$$
(not actually needed)

Carbon mass ratio is 0.273(43.26 gms) = 11.81 gms OK

In our case, assuming a 100 gm original pure sample we have

~~100 gm~~ 77.72 gms CO_2 = 77.7 % CO_2
22.28 gms H_2O 22.3 % H_2O

We are OK to here.
Our actual Carbon content is $\frac{12.011}{44.01}$ (77.7 gms) = 21.21 gms C

Stop here. Do not convert this to moles!

His sample has 11.80 gms. (21.21 / 1.797)
Our is 21.21 gms.

OK, we produce 22.3 gms of H_2O
The amount of H_2 is $\left(\frac{4}{4}\right)\left(2\left(\frac{1.008}{18.015}\right)\right)(22.3) = 2.496$ gms H_2

OK, we have this correct also.
He has $\frac{2.496 \text{ gms}}{1.797}$ = 1.389 gms H_2

We now have: $\Sigma = 14.77$gms

US: His problem

21.21gms C 11.80gms C

2.496gms H~~2~~ (not H_2!) 1.389 gms H (not H_2!)

wrong. ~~100-(21.21+2.496)= 76.30gms O~~ ~~42.46gms O~~

Ok, our Oxygen computation is completely wrong.

Ok, here is the problem. The computation of oxygen w/in the sample REQUIRES that the mass of the original sample (NOT THE PRODUCTS!!!) be known. We do not have this! Therefore we can not determine the amount of oxygen present with this method. We may be able to determine another method.

We can work on the CH ratio, assuming no oxygen present for the time being.

11.80gms C = 11.80/12.011 gms/mol = 0.982 moles C
1.389gms H = 1.389/1.008gms/mol = 1.378moles H

Therefore we have $C_1 H_{1.40}$ or $C_{10}H_{14}$

Very good, we now have it. We must ignore Oxygen for now.

Page 287

Now let's go back to the human breath:

We have $CO_2 = 1.63\%$
$H_2O = 98.37\%$

Assume product mass is 100 gms.

Therefore mass of $CO_2 = 1.63$ gms
mass of $H_2O = 98.37$ gms

mass of C is $\frac{12.001 \text{ gms/mol}}{44.01 \text{ gms/mol}}(1.63 \text{ gms}) = 0.444 \text{ gms}$

mass of H is $\frac{(2)(1.008) \text{ gms/mol}}{18.015 \text{ gms/mol}}(98.31 \text{ gms}) = 11.008 \text{ gms}$

moles of C: $\frac{.444 \text{ gms}}{12.001 \text{ gms/mol}} = .037$ moles

moles of H: $\frac{11.008}{1.008 \text{ gms/mol}} = 10.921$ moles

So we have $C_{.037} H_{10.921}$ or $C_1 H_{295}$

Now, I think that there is an alternate method to determine the oxygen content.

Within the CO_2, we have 72.7% of the mass ~~is of O_2~~ ~~of O_2~~ of CO_2 is O_2

Within the H_2O, we know that 88.81% of the H_2O is $\underline{O}$.

We can use this to our advantage.

Going back to the original problem,

We now know that the mass of oxygen derived from the CO_2 is:

$$2\left(\frac{16.00}{44.01}\right) = .727 \quad \cancel{7} \quad .727(43.26\text{gms}) = 31.455\text{gms } O$$

^ in our case (100gm sample) = 56.52gms

We also know that the mass of oxygen derived from the H_2O is: $\frac{16.00}{18.015} = 0.888(12.40\text{gms}) = 11.013\text{gms}$

^ in our case (100gms) = 1.797(11.013) = 19.79gms

We therefore know that his sample has a total oxygen mass of (31.455gms + 11.013gms) = 42.468gms.

We know that the mass of O in his sample is therefore 43.26 − 42.468 = 0.792gms

$\Rightarrow$

He gets 1.57gms. We are off by the factor of 2! Why?

We are on the right track & the method will work.

Page 289

$C_xH_yO_z \Rightarrow \overset{\text{Does Equal}}{\cancel{\ \ }}$ C + H + O

The no. of grams of the Original compound		grams	grams	gram
14.71 grams Compound	$\rightarrow$	11.81 grams of Carbon	1.388 gms of Hydrogen	1.57 gms of Oxygen

---

We can therefore solve our problem indirectly via a 2 step process with Oxygen. We do not know why we are off by a factor of 0.792 gms in the problem, the method does appear to be sound.

Let's resume w/our problem

$C_xH_yO_z \xrightarrow{\text{reaction}} C + H + O$

grams = grams grams grams

We know we have CO_2 1.63% H_2O 98.37% Assume 100gms of product.

Therefore we have 1.63 gms CO_2
98.37 gms H_2O

C ratio is $\frac{12.001}{44.01} = 0.273$ & $.273(1.63) = 0.444$ gms C

H ratio is $2\frac{(1.008)}{18.015} = .112(98.37) = 11.008$ gms H

But this means we have $100 - (.444 + 11.008) = 88.548$ gms O
You do not need to break it down in parts.

Ratios: C 1 ~ ~~C_4 H_{100} O~~ $\underline{\underline{CH_{25}O_{200}}}$
H 24.8
O 199.4

This is our answer. If human breath (held in balloon) was a single compound, then it has roughly 4 times as much Oxygen as H. It is therefore mostly oxygen considering that we ignore nitrogen as a passive carrier.

OK, we are ready for sugar analysis now.

Then assume the model
$C_xH_yO_z \rightarrow CO_2 + H_2O$ is correct.

There may not be any O attached.
Sucrose is $C_{12}H_{22}O_{11}$ so here we go.

I have made 3 runs w/ table sugar for a combustion test.

It seems apparent that the runs are too variable to allow for accurate CHO analyses.
But I shall complete it as an exercise nonetheless.
You also see that the H_2O peak is massive compared to the CO_2 peak so some form of calibration (ie response factor) will be required regardless of the accuracy problem.

Here is our data:

$\bar{X}$	Area %:	Trial #1	#2	#3
2.44%	CO_2	1.00%	~~5.41~~ 5.82%	0.50%
97.56%	H_2O	99.00%	~~88~~ 94.18%	99.50%

Assume 100 gms of product:

CO_2 = 2.44 gms
H_2O = 97.56 gms

Mass ~~Mole~~ fraction of C: $\frac{12.001}{44.01} = 0.273$

$0.273 (2.44 \text{ gms}) = .665 \text{ gms}$

$\frac{.665 \text{ gms Carbon}}{12.001 \text{ gms/mole}} = .055$ moles Carbon

We know, for reference that sucrose is $C_{12}H_{22}O_{11}$

H fraction $= \frac{2(1.008)}{18.015} = .112$

$.112(97.56\text{gms}) = 10.92\text{gms H}$

$\frac{10.92\text{gms}}{1.008} = 10.831$ mole H

$22/12 = \overset{1.833}{\cancel{2.00}}$

So if carbon is .055 mole then H needs to be ~~0.11 moles~~ .101 moles but we have 10.831

Factor $= \frac{10.831}{.101} = \cancel{98.46}\ 107.2$

For some reason, the response of H_2O to the column is ~100 times greater than it should be (~~98.5~~ 107.2)

Therefore the adjustment is $H_2O = \frac{97.56\text{gms}}{107.2\ \cancel{98.5}} = \overset{0.91}{\cancel{0.99\text{gms}}}$ H_2O

Mass ~~Mole~~ fraction $= \frac{2(1.008)}{18.015}\left(\cancel{0.99\text{gms}}\ 0.91\text{gms}\right) = \cancel{0.111\text{gms}}\ .102\text{gms}$

$\frac{\overset{.102}{\cancel{.111\text{gms}}}}{1.008\text{gms/mol}} = \overset{.101}{\cancel{0.110}}$ moles

So C: .055 moles
H: ~~.110~~ moles
.101

Ratio
1
~~2~~ 1.84

$C_1H_{1.84}$
~~C_1H_2~~ is the ratio which is correct.

$X_1 + \dfrac{X_2}{\cancel{98.5}\ 107.2} + X_3$, Actually $X_1 + X_2\left(\overset{107.2}{\cancel{98.5}}\right) + X_3 = 100$

~~25 + 60 + 15~~ = 100 H_2O response factor

Oxygen $0.665\text{ gms} + \overset{.91}{\cancel{0.99}}\text{ gms}\left(\overset{107.2}{\cancel{98.5}}\right) + 2X = 100$

$X = \cancel{1.82}$ gms $\overset{.892}{\cancel{0.91}}$ gms

~~Mass fraction: H8~~ Mole = $\dfrac{\overset{.892}{\overset{\cancel{0.91}}{\cancel{1.82\text{ gms}}}}}{16\text{ gms/mol}} = .\overset{.056}{\overset{\cancel{.057}}{\overset{\cancel{.114}}{\cancel{114\text{ gms}}}}}$ mole

So we have

C: .055 moles

H: ~~0.110~~ .101

O: ~~0.114~~ mole

~~0.057~~ .056 (This actually should be .050)

Ratio:

C : 1   ⇒ $C_1H_2O_1$

H : ~~2~~ ~~1.83~~ 1.84

O : ~~1.04~~ 1.02 and then do correct for C_{12}

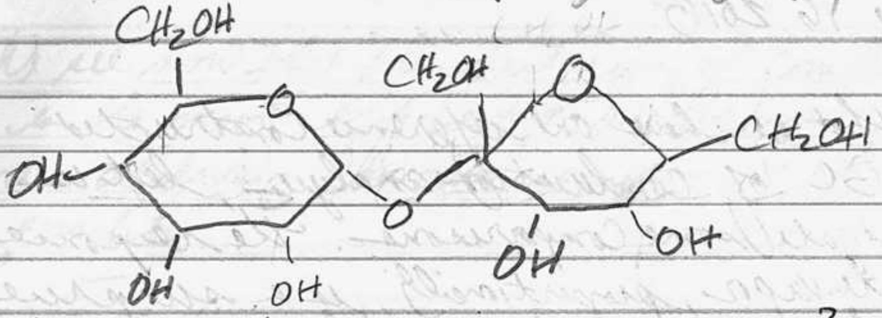
$C_1H_{1.84}O_1$

$C_6H_{11}O_6$

Fairly close
It should actually be

$C_1H_{1.84}O_{.917}$

Page 294



What is the Lewis diagram for sucrose?

This is rather amazing, Notice all the OH groups.
Notice the cyclic structures

June 16 2018

Now that we have one reference constructed by GC of combustion analyses, let us investigate some comparisons. The response of water vapor, proportionally, is a surprise @ this point! Also variability in the combustion process does appear to be a difficulty. The method may end up being unreliable or unusable. We shall see.

I am attempting to standardize, to the degree possible a combustion chamber. The changes do hold some progress. I am using sucrose as the reference.

A glass tube w/ ~~gas +~~ glass inlets now comprise the chamber w/ cork seals.
I have achieved the highest CO_2 reading in the scale thus far. I also have additional peaks showing up. Air from an aquarium pump is being injected into the chamber to enhance combustion.

We have a very clear run coming out on the GC now.

The glass tube has been slightly bent to form a reservoir for the compound.

We see now that the first run of combustion is the most efficient & productive. Every run deserves its own sample if at all possible.

—

Additional lessons:

Use plenty of heat and retrieve the first main burst of compression. You now have the CO_2 peak up to about 24 - a dramatic improvement over the earlier trials. You are also starting to see greater stability w/ the results. You even have a tail now on the CO_2 as it is combining w/ an additional peak.

—

We still have some instability.
Need a CO_2 reference

—

I have established a good stand alone reference for CO_2 w/ use of vinegar & baking soda. Peak has a magnitude of ~300 mV so it is reliable. Notice that there is some tailing w/ this strong peak.

I had some contamination from acetone which now can be recognized.

O_2-N_2 peak @ ~ 0.633 min]
CO_2 peak @ ~ 0.896 min.] 120°C
Argon @ ~ 2.14 m]

Let's look @ the sucrose data:

Trial	CO_2	H_2O
01	.51mV	14.74mV
02	10.21	13.20
03	1.14	11.82
04	16.32	8.18
05	10.98	7.51
06	12.46	38.88
07	9.19	32.07
08	14.53	44.08
09	Not usable - acetone contamination	
10		

The usable data is from trials 6, 7, 8. It is here that our combustion methods stabilized. You must be very careful about introducing any acetone contamination from cleaning the needle.

Let's compute areas on these three trials.

Let's assume our compound has O, C, H

Page 298

% Areas , Sucrose $C_{12}H_{22}O_{11}$

Trial	CO_2	H_2O
6	0.62%	99.38%
7	0.84%	99.16%
8	0.70%	99.30%

$\bar{x} = 0.72\%$ $\bar{x} = 99.28\%$

Let's Calibrate the solution.

Assume 100 grams of product

$CO_2 = \overset{0.72}{\cancel{0.62}}$ grams

$\frac{12.001}{44.01} = .273$ H_2O 99.28 grams

Carbon fraction = 0.273 ⇒ .273(0.72 gms) = 0.197 gms

Moles C = $\frac{.197}{12.001}$ = .016 moles

H fraction : $\frac{2(1.008)}{18.105} = 0.111 \Rightarrow .111(99.28\text{ gms}) = 11.055$ gms

$\frac{11.055\text{ gms}}{1.008} = 10.967$ moles.

However, it should be $\left(\frac{22}{\underset{12}{\cancel{11}}}\right)(.016\text{ moles}) = \overset{.029}{\cancel{.032}}\text{ m}$

So reduction factor for H_2O is $10.967/.029 = \underline{\underline{378.17}}$

For Oxygen

C

$x + y(378.17) + z = 100$ gms

~~.016~~ + ~~.029(348.17)~~ + z = 100 gms ~~z =~~

~~.197~~ 11.055 gms ~~.015~~ = 100 gms z = 88.75 gms

~~.016~~

.197 gms

We need to defer the O question for now.

* We are to divide the water peak area by 378.2 and then so normalize the values so they add up to 1

In our case, we had

$CO_2 = .72\%$ $H_2O = 99.28\%$

$\div 378.2 = 0.263\%$

Now lets normalize these

$X\,(0.72 + .263) = 100$

* $X = 101.73$ Normalization factor

* $CO_2 = 73.25\%$

$H_2O = 26.75\%$

OK Try again

Carbon $0.273\,(73.25\text{ gms}) = 20.0\text{ gms} = 1.667$ moles

H $.111\,(26.75\text{ gms}) = 2.969\text{ gms} = 2.946$ moles

Normalized

$C = 1$ or $C_1H_{1.77}$ Vs 1.83 not bad

$H = 1.77$

OK, good ✓

We could therefore estimate $C_1H_{1.8}$

Which is not bad @ all.

You need to determine the molecular weight in order to determine the molecular formula. This could be involved.

However, you might have a method in place now to at least determine the CH ratio. This is a good start

Deficiencies:

1. We do not know how to handle oxygen yet
2. We do not know the molecular wt yet.

This is where the osmometer might come in.

We need to test the CH ratio on another material now. Also the combustion process must be stable.

Sugar is not a hydrocarbon, it is a Carbohydrate. Carbohydrates have oxygen, hydrocarbons do not. Furthermore Carbohydrates HAVE ~~Twice~~ half as many oxygen atoms as hydrogen eg Sucrose $C_{12}H_{22}O_{11}$.

Now we have $C_1H_{1.8}$ We therefore know the compound is unsaturated. It is therefore likely to have O. We know therefore that a likely formula will be

$C_1H_{1.8}O_{0.9}$ or $\underline{\underline{C_{12}H_{22}O_{11}}}$

Which is true.

Let's work thru the example problem and see if we achieve the same answers:

Given:

14.77g of $C_xH_yO_z$

Result: Produce 43.26 gms CO_2
12.40 gms H_2O

or:
CO_2 77.7 gms
H_2O 22.3 gms

or in our case 77.7% CO_2
22.3% H_2O

Assume 100 gms product

C: therefore we have $\frac{12.01}{44.01}$ (77.7gms) =

= (0.273)(77.7gms) = 21.20gms C
(= 1.76 moles)

H: and $\left(\frac{1}{2}\right)\left(\frac{2.016}{18.015}\right)$ (22.3gms) =

= .056(22.3gms) = 1.248 gms H
(= 1.24 moles)

O: The O in the sample is therefore
100 − (21.20 + 1.25) = 77.55 gms
(= 4.85 moles)

	Ratio
or H: 1.24 moles	1
C: 1.76 moles	1.42
O: 4.85 moles	3.91

or a $HC_{1.42}O_{3.91}$

So this is very interesting. You can therefore deduce

1. That the compound likely has oxygen
2. If you can presume a carbohydrate you can determine the likely number of O atoms.

Now lets revisit our problem of oxygen.

We have

$C_xH_yO_z \Rightarrow CO_2 + H_2O$

grams = C grams + H grams + O grams

We determined that we had

C : .197 grams

H : 11.055 grams / 378.2 = (response factor)

CO_2 O mass fraction $= 2\frac{(16.0)}{44.01} = 0.73$

and 0.73 (0.72 gms) = 0.53 gms.

~~mole~~ mass fraction

H_2O O mass fraction $\frac{12.001}{18.015} = .666$

and $.666\left(\frac{11.055}{378.2}\right) = .019$ gms

So our total O is 0.53 + .019 gms = 0.55 gms O

$= \frac{.55 \text{ gms}}{16 \text{ gms/mol}} = .034$ moles

So we had

C : .016 moles
H : .029 moles
O : .034 mole

Ratio
C: 1
H: 1.81
O: ~~0.411~~ 2.125
Actual is 0.92 ✓ ??? $\frac{1}{2}(2.125)$
= 1.06
Which is much close but why?

So we have
$C_1H_{1.01}O_{1.06}$?

But there is a problem that exists here. We are off by a factor of 2, and I think that we have seen this before.

Generally we are looking pretty good.
You must try another known.

Starch is $(C_6H_{10}O_5)_n$
Let's try it next.

Jun 14 2018

Today we are working w/ starch combustion. Much has been learned to increase & develop stability in the results.

My greatest concern here is that the response factors of water and CO_2 are not constant across different compounds.

Even though stability w/ a particular compound may be achievable, it may not carry over w/ the response factors to a different compound.

The response factor of H_2O in starch seems completely different w/ starch compared to sugar.

This is a big problem and may negate the process.

Lessons learned:
1. Smaller combustion sample gives better results.
2. Collect during most intense combustion
3. No second burning of sample
4. Clean tube & prepare new sample for each trial.
5. Clean needle, syringe have a finite lifespan
6. Avoid acetone to degree possible, only clean needle to level required.
7. Turn the fume hood on!
8. Keeping the outlet tube is more beneficial than trying to keep the needle clean.

I think that sugar must have a lot of water in it. Let's test this.

Watch glass mass:	59.69 gms	Time 13:30
With sugar added	62.30 gms	Heat @ ~ 100°C
Mass of sugar	2.61 gms	

A very peculiar event occurred. On my fourth run w/ starch, I got no H_2O peak for the GC. How can this be?

We see that Pavia (Intro to Organic Laboratory Techniques) has a fantastic Chapter on Identification of Unknown Organic substances. *

The Chapter ranks equally w/ the Crippen book. These are both invaluable sources.

Our second pass w/ a Clean needle w/ starch sample produce NO WATER peak of substance. This is important. It means that your tube was contaminated.

We therefore have a situation..

Sugar combustion produces a massive amount of water, a large peak w/ significant trailing.

Starch produced a contaminated peak for some time (with residual water). Now starch produces no water but does produce a very clear and stable CO_2 peak.

What are you supposed to do w/ this? I have no idea how to interpret no water vapor being produced via combustion.

Pavia talks about a simple general ignition test - a sooty flame is indicative of a high carbon/-hydrogen ratio.

Ok, we have definitely reached some stumbling blocks here.

—

Sugars and starches are both carbohydrates. Starches are polysaccharides, ie, chains of sugar molecules linked together.

We do not know why starch and sugar combustion produces such a marked difference in the TCD gas chromatography analyses!

It may also be that what you have created is a process somewhere in between pyrolysis and combustion, and this can confuse matters further.

You definitely do not understand why the starch does not produce a water peak, which has been verified w/ a clean needle.

Interpretation of the chromatogram differences of sugar and starch combustion / pyrolysis certainly does present some challenges.

—

OK, let's think about our agenda. The proposed combustion process, although interesting, does not appear to be viable for CHO ratio analyses. This is unfortunate.

—

An upshot is that you did discover a great chapter by Davian on organic substance identity, carbon.

Let's think about this a little more.

We seem to have reasonably stable readings for CO_2.

We should be able to get the value as a %.

We also have an O_2 meter.

$C_xH_yO_z \rightarrow CO_2 + H_2O$

If I measure CO_2 & O_2, how can I get H? I do not see what I can. I also do not have the mass of the original sample, which is a problem.

O_2 does not help me since it is provided in excess during combustion.

Certainly what you can do is get an estimate of carbon content.

OK, we do not leave completely open ended. We can leave w/ a % carbon estimate of the exhaust from combustion. This can give us relative carbon content.

For example, with our clean syringe starch runs, we have

	Trial 1 %	Trial 2 %	$\bar{X}$
O_2 N_2	83.2	75.4	79.3 %
CO_2	14.3	21.4	17.8 %
Unknown	0.41	1.17	0.8 %
Argon	2.11	2.03	2.07 %
H_2O	0?	0	0
CO_2 Carbon Content	3.90	5.85	4.8 %

We know that room air is ~ 400 PPM. = 4E-4 %
So 5% is still very significant.

What was sucrose? What is charcoal?
Interestingly enough, what is the actual mass C ratio of starch?

$C_6H_{10}O_5$ Guess what the mass ratio of C is?

~~6.6% You are surprisingly close!~~
~~This is not bad, and~~
~~still useful.~~

44.4%

Actual:
C : 44.4%
H : 6.2%
O : 49.3%

We are off by a factor of ~9.2.

What is sucrose compared to our analyses?
$C_{12}H_{22}O_{11}$

C: 42.1%
H: 6.5%
O: 51.4%

Our sucrose analyses is rather variable, but the mean carbon content (CO_2) estimate is 1.75%

This is hardly any good as it should be reasonably close to [illegible].

There are some problems here no matter how it shakes out.
I have my doubts about the value of this process.

The nostril crystal received was analyzed tonight under the microscope & IR. This crystal required 40 min on KOH 5M microwave digestion to break down.

Under the microscope, very active & developed Morgellons growth evident. Reasonably large (~20-30 microns) encapsulating cellular structures. Massive CDB presence. Numerous filaments present.

Important Notes on this page

Difficult to make it with the sample to IR ATR but I did. Decent spectrum obtained. Closest match is the environmental filament, also microwave digested Aug 2017

KOH neutralized w/ HCl to form a KCl plate on the ATR. It worked admirably.

* Major issues have surfaced in the lab over the last couple of weeks:

1. Isothiocyanate presence directly w/in the CDB

2. Isothiocyanate presence across a spectrum of sample types, both biological & environmental

3. The match of a sno nostril crystal to that of the env. filament, as well as the skin folicle. Massive correspondence in spectra & chemical signature is now established across a wide spectrum of samples, both environmental & biological.

4. The appearance of "geometrically encased" CDB w/in urine samples, both fresh and culture aged.

5. The more accurate interpretation methods now established for IR spectra.

Jun 19 2019

You have several (many) additional spectra that have been obtained.

You can continue your systematic approach to further characterize the various samples

These include: (or we should say prior to this, we have completed: (See Notes 06/07/18)

1. The environmental filament
2. The CDB generated protein
3. Rainfall extract
   1. Polar
   2. Non Polar
4. HEPA filter
   1. Polar
   2. Non Polar

In addition, potential research papers include

1. Summary view of IR spectra results underway
2. Isothiocyanate
3. CDB geometric formations (design, order, structure)

4. ~~3.~~ Crystal examination (nostril) Comparison w/ Env Filament IR ATR

These papers are all rather profound in what they show.

Now, let's organize some of the spectra that have
been collected. Definitely our most valuable instrument.

2018 Starch (academic primarily)] but still of interest
2018 Sucrose (academic primarily)] and value.

2018 CBB pyrolysis - high interest, thiocyanate apparent
2018 Ear wax - moderate interest, partially academic,
but one sample does show isothiocyanate

2017 Skin foliation - high interest, simple spectrum,
already known to strongly match nostril crystal,
isothiocyanate also strongly present.

CBB Headspace gas analysis - Higher interest
2017
2018 Hair Digestion - lower interest, no isothiocyanate
2018 Dried blood - lower interest, no isothiocyanate
2018 Urine fresh - lower interest
2018 Urine - subtraction of aged (altered) from fresh sample.
Two spectra set. Of moderate interest.
Also Comparison to SDBS Urea sample.
Two sets of two spectra here. One set appears
vastly superior to analyze here.
Apparently the female sample. - Moderate interest

2018 The shower sample - protein appears likely -
moderate interest
Floating & sediment samples

2018 Nostril Crystal - Digested - High Interest
2018 CBB Viscous Protein - High Interest

Thiocyanate toxicity is a major issue.
It can effect
1. The liver
2. The thyroid
3. Can result in tinnitus

But major conflicting statements exist:
Oregon State Univ - Linus Pauling Institute
says:
"No serious adverse effects of isothiocyanates in humans have been reported"

Wow - what a conflict there —

"Isothiocyanates act on the thyroid mainly by their rapid conversion to thiocyanate."
" They also react spontaneously w/ amino groups ... also to produce an anti-thyroid effect.

It makes sense that the double bonds of isothiocyanates would be more reactive

Thiocyanate	Isothiocyanates
$R-S-C\equiv N$	$R-N=C=S$

Thiocyanate is "analogus" to the cyanate ion $[OCN]^-$
wherein oxygen is replaced by sulfur $[SCN]^-$

Now lets organize the spectra into three
levels: high interest, medium & low.

High	Medium	Low
CDB Pyrolysis	CDB Headspace	Starch
Skin Foliation	Urine Subtraction	Sucrose
Nostril Crystal	Shower Sample	Earwax
CDB Viscous Protein		Hair Digestion
		Dried blood
		Fresh Urine

Let's start, therefore, with CDB pyrolysis.
Our attention will be on the fingerprint region.
Our peaks are @
2191 & 2118 double peak cm^{-1}
1741
1540
1310
669

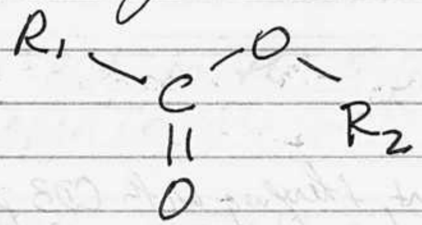
Start with 1741 cm^{-1}
This does indeed match the Carbonyl.
The closest Carbonyl group here is that
of the ester.

The strongest Candidate from Parker's table
will be

1735 - 1745 saturated ester
~1740 lactone

A saturated ester is definitely the target here.

An ester is:



Animal & vegetable fats and oils are
just big complicated esters.

An ester can be made from an acid &
an alcohol.

Let's move on. We know that we have the
150 thiocyanate group.

Next is 1540. From Pavia overview, nitro groups w/ absorption @ 1600-1500 & 1390-1300 are candidates. N=O

$R-NO_2$ fits the bill so far.

Parker has 1580-1520 of C=N

This matches very well R-N=C=S of isothiocyanate. The match from Parker is right on track.

Now for 1370.
Our strongest candidates from Parker are:

Sulfuric ester (1440-1350) S=O bond
$(RO)_2SO_2$

or

Sulfonic ester (1420-1330) S=O bond,
$ROSO_2R'$

These seem to be reasonable candidates.

Calibration of the microscope:

(100x)
8000x !!

$\frac{80\text{ mm}}{\cancel{20\text{ um}}\ 10\text{ um}}$ or $\frac{80E-3\text{ m}}{\cancel{20E-6\text{ m}}\ 10E-6\text{m}} = \frac{\overset{E-3m}{\cancel{1mm}}}{x}$ $x = \cancel{4000}$

yes, 8000x exactly as previously determined.
Good.

$8000\left(\frac{40}{100}\right) = 3200$ (40x)

$8000\left(\frac{10}{100}\right) = 800$ (10x)

$8000\left(\frac{4}{100}\right) = 320$

Series:
300, 800, 3000, 8000

Jun 27 2018

On Abajo Mtn. Continuing w/ spectra interpretation.

Our list examined thus far includes:
(see notes on Jun 10 2018)

1.
1. The Environmental Filament
2. The CDB generated protein
3. Rainfall extraction
   polar & non-polar
4. HEPA filter
   polar & non-polar

Furthermore, we categorized a series of collected spectra into high, medium & low priorities.

Our set of high priority includes:

1. CDB pyrolysis
   We must recall that pyrolysis by nature means that we are dealing w/ fragmented compounds, and not the original structures).

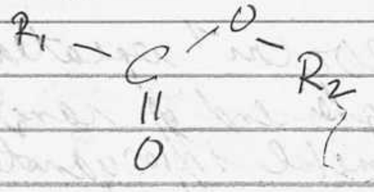
2. Skin foliation

3. Nostril crystal

4. CDB viscous protein (already examined as item #2 above).

Now, we have already started w/ the CDB pyrolyses on Jan 19. Recall that these, by nature, are fragmented - do not try to construct a combined compound unless ya understand that it is hypothetical.

Started w/ 1741 cm⁻¹. Our assignment is to a saturated ester.



We have the double peak @ 2191 & 2118 cm⁻¹.

There was a shift to the left for 2191 cm⁻¹!
Avram gives the ranges for
Thiocyanates: 2140 - 2175 ← 2118 2191 →
Isothiocyanates: 1990 - 2140 2118 ok 2191 →?
$R-N=C=S$ ($\bar{x}$ = 2015)

Notice also, however, that Avram states $N\equiv C$ 2100 - 2200.
We have also found sources that indicate combination of iso thiocyanates w/ metallic ions shifts the ranges

From Science Direct article Spectrochimica Acta
Vol 22 Issue 6 June 1966, Clark:
"For tetrahedral complexes of a given metal, the C=S stretching frequencies are higher (40-65 cm⁻¹) than for octahedral complexes
[2015 + ~52 cm⁻¹ = 2067 cm⁻¹] but what are the octahedral complexes at?

Another paper states

"The infrared spectra of a series of metal (hexaisothiocyanate ions have been recorded over the range 2200 - 70 cm^{-1}!

Linkage isomerism is the topic of research.

2200 cm^{-1} repeatedly shows up as the higher end of range examination for metal thiocyanate complexes

This remains our strongest candidate for the shift or higher on the second peak.

Notice also that Avram mentions (p471) that w/ aliphatic isothiocyanates that

"often the bands are split or have shoulders".

We definitely appear to have a split band.

The assignment remains here

al certainly
* A transition metal (most likely iron)
isothiocyanate complex

ADDITIONAL NOTE: (Jun 28 2018) Parker clearly gives the 2200-2000 range to cyanide, thiocyanate & cyanate.

Now let's return to the absorption @ 1540 cm^{-1}, which we already have tentatively reviewed.

Parker has $C=N$ from 1520 – 1580 ($\bar{x} = 1540 cm^{-1}$)
This is certainly right on track w/ corroboration of ~~$R-S-C=N$~~ $R-N=C=S$

This is the most direct assignment to be made.

However also note that Pavia gives us
NO_2 w/ 1600 – 1500 & 1390 – 1300
& we must note that we do indeed have both of these w/ 1540 cm^{-1} & 1370 cm^{-1} absorption.

See if further discernment is available, if not, hold $C=N$ assignment but attempt to explain the 1370 cm^{-1} absorption in the process.

What is the strength of the absorptions?

Parker lists 1520-1580 ($C=N$) as medium strength
He also adds comment of pyrimidines, which we are not familiar with.

Notice that Parker gives us NO_2 from 1600 – 1650.
(Not 1500-1600). This does not match.
Peak absorption is listed as strong.

Also Parker gives us NO_2 @ 1250 – 1300, not 1300 – 1390 so this is not matching either.
Peak absorption is listed as strong.

We therefore see, what appears to be a level of contradiction or lack of corroboration between Parker & Pavia.

In the interest of minimal complexity of corroboration, I will hold assignment to C=N @ this time.

However, this requires continued evaluation of the 1370 cm^{-1} absorption.

Parker appears to be an excellent source of sufficient detail in all respects. Let us start there & ask what Parker offers for 1370 cm^{-1} absorption.

Sulfuric ester (1440 - 1350) $\bar{x}$ = 1395 cm^{-1}

Sulfonic ester (1420 - 1330) $\bar{x}$ = 1370 cm^{-1}
$ROSO_2R'$

Of the two, the sulfonic ester seems to be the stronger candidate. We also have already established an ester, and we therefore have further corroboration.

We also have sulfur known, so this is also corroborating.

Our last peak, which is unusually strong is c. 669. cm^{-1}. Since the instrument has recently been maintained & calibrated, in no way can this peak be dismissed. It is significant.

What does Parker hold here?
He offers ~~a very definite~~ two choices, neither exact:

~690 C-H   We have 669 cm^{-1}.
~650 C-Br

Our simplest choice is clearly CH: cis RHC=CHR' however this would indicate an alkene, and we have no evidence of an alkene thus far (ie absorption >3000 cm^{-1}). & this would seem to leave serious doubts on this. Now for other sources.

Pavia tells us that halides can be difficult to determine. Koji gives the same info:

1000 - 670 C=C-H
900 - 690 aromatics
800 - 600 C-Cl

] The strongest of these remains C-Cl as we actually do have skewed absorption toward 600 cm^{-1}.

Additional sources:
Spectra mate also gives the same alkene match, but we have no evidence of an alkene, so this remains unsupported
$RCH=CHR$ (CIS)

IR Spec gives
Alkyl Halide C-Cl 800-600 cm^{-1}
strong absorption

and an alkene.

The alkyl halide continues to win favor.

~~the~~ Chemistry Toolbox
Shows a Thiol C-S from 550-710

Halide C-Br 550-700
Alkynes 600-700.

The alkenes, alkynes our are out.
Halide is a strong candidate
Thiol is an interesting appearance.

From AVRAM, p292 the location of the C-S bond is essentially correct
CH_3-S 685-705 (slightly off)
RCH_2-S 630-660

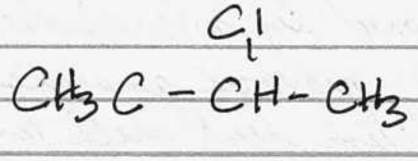
but she says they are weak. Our absorption is hardly weak.

Summary of CDB Pyrolysis IR Spectrum:

Our best match continues to be w/ the halogen, specifically chlorine.

Avram shows Cl to be 600-800 cm^{-1}.
The other halogens do not match this.

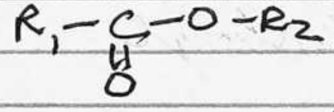
In addition, she gives a very specific halide form @ 667 cm^{-1} (vs our 669)



$CH_3C(Cl)-CH-CH_3$

This truly seems to be our best choice. The question is, what is the source of the chlorine in the culture? Is it the tap water that is treated w/ chlorine? Apparently so.

Either way, this is our best assignment +

1. An ester  $R_1-C(=O)-O-R_2$

2. A sulfonic ester $ROSO_2R'$ (Diagram?)

3. Iron-Isothiocyanate Complex (Problematic

4. An alkyl halide of chlorine (Problematic)
A test for this would be valuable.

Ok, on to the next high priority spectrum. The one is the nostril crystal which has been digested in KOH ~ 45 min 5M KOH. Also recorded under the microscope, rather amazing complexity.

We also already know that our closest IR spectrum match was with the env. filament sample (also prepared by microwave digestion). We will not look @ previous analyses of the Env. filament spectrum but will assume the problem from scratch.

Almost always begin w/ Pavia. Do we have a carbonyl or not?

We have a strong peak @ 1662 cm^{-1}!
Carbonyls run from 1600-1820 so yes we have a carbonyl.

From Pavia it looks like our most likely carbonyl candidate is the amide (~1690 Pavia).

We certainly may already be looking @ a protein ☺

For amides, we also look @ ~3500. We have double absorption peak @ 3360 & 3298.

We most certainly have sufficient grounds to consider the amide group.

With Pavia, we examine amides in greater detail. He has

stretch	C=O	@	~1670 - 1640 cm^{-1}	We have 1622 cm^{-1}
stretch	N-H	@	3500 - 3100	We have 3360 & 3298
bend	N-H	@	1640 - 1550	We have 1622 cm^{-1}

We match quite well w/ the amide. Notice we have a shift (w/ the C=O stretch, conjugation & ring size are mentioned as factors. I recall that we have identified cyclic structure in the past so we will look into that.

Notice also we have the double NH peak.

Before proceeding further, I would like to bring Kendall (Applied Infrared Spectroscopy) general overview methods into the analysis as well. This is anticipated to be a complement to Pavia for the general overview. This is Chapter 5 p 166.

Kendall first mentions the importance of sample history (and prep). The fact that the sample has color (reddish) is not to be ignored also.

Kendall's Chapter is insightful but not so orderly or well organized as Pavia. More leisurely & extended study of Kendall will be required.

Parker definitely supports the amide assignment.
He lists:

	$\bar{X}$			We have
C=O	1645	1670 - 1620	primary amide (strong) stretch	1622
N-H	1635	1650 - 1620	primary amide (strong) deformation	1622
N-H	1605	1620 - 1590	primary amide (strong) deformation	1622

$\bar{X}$ = 1628 cm^{-1}

Before we get too far along, please note that the CDB pyrolysis spectrum (of previous analyses) is available on the following page. There was no significant absorption on this particular gas cell run above 2191 cm^{-1}.

We have a definite assignment of the 1622 cm^{-1} & the (3360, 3298) cm^{-1} pair to an amide.

This means, once again, that we almost certainly have a protein involved.

Our next absorption is @ 1906 cm^{-1}.

Parker gives no result here.

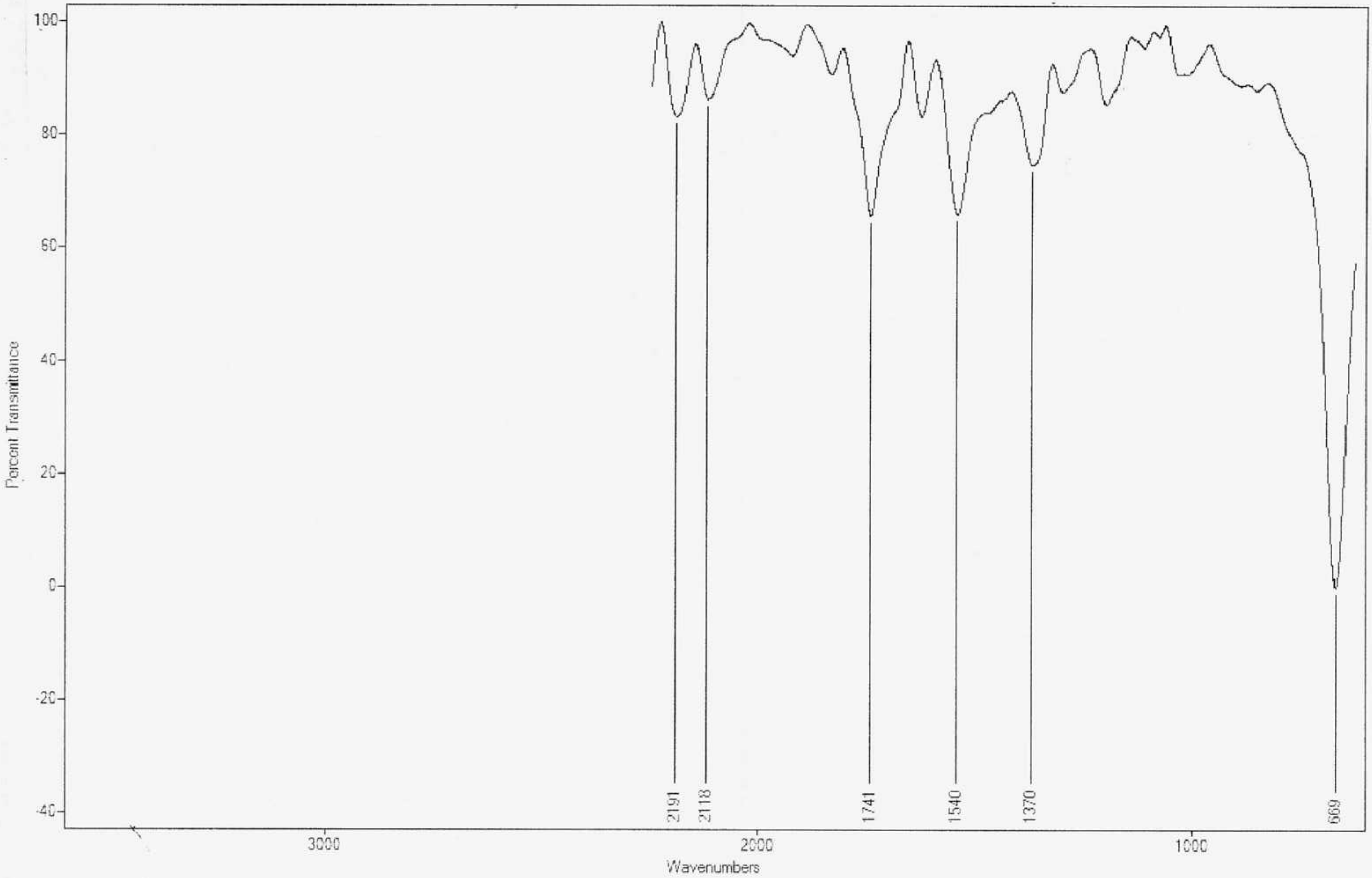
We must now also consider inorganics.

Before we forget: CDB Pyrolysis

CDB Pyrolysis Gas Cell 2253-600 Jun 14 2018 -02.spc: Synthetic spectrum by averaging. See audit trail for details.

Page
328A

High



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Jun 28 2018

We have an unknown @ 1906 cm-1. Parker offers no candidates here. InOrganics are under consideration.

It is of interest that Koji lists an entry of 1800 - 2200 of $>C=N^{+}-H$ on Table 7, Item 12.

Koji also lists aromatics from 1660 - 2000 but this would seem unlikely because of lack of absorption in 2900 - 3100 cm-1 HC region.

Since we know we do have the thiocyanate compound (looking ahead) in the sample let us investigate Koji a bit further on this.

The entry of Koji on this range (1800 - 2200) is actually for an unsaturated aromatic amine. It is also referred to specifically as the Immonium band. This appears unlikely because of expected presence of several absorption peaks in this region. An interesting case here.

OK, we have found a rather obscure reference for 1906 cm-1.

"A high resolution study has been carried out on cyanogens . . .

HNCC (3562, 2205, $\underline{\underline{1906 cm^{-1}}}$)

This strongly suggests that we have a cyanogen. (Note: thiocyanate will be present also)

Our source here is "Spectroscopic Properties of Inorganic & Organometallic Compounds", p 29, Google books, by G. Davidson.

Cyanogen is a colorless toxic gas w/ the formula $(CN)_2$. It is a pseudo halogen. Certain derivatives of cyanogen are also called "cyanogen" even though they only contain only one CN group.

(Such as HNCC, for example). (or NCBr, for e.g.)

Recall our mention of "pseudo halide" in our research paper.

It may be best to refer to this compound as a "cyanogen derivative" therefore, to avoid confusion w/ the more specific cyanogen.

This is a significant finding, we now have our second cyanide derivative that has been identified. This time from a human biological sample (crystals). (embedded w/in skin). Furthermore, the crystal, upon suitable digestion, shows the entire array of microbial growth identical w/ that developed from the cultures.

$HNCC(CN)_2$ Dicyanketenimine HNCC – cyanogen derivative

"The chemistry of pseudohalides" is a topic of research here.

HNCN is cyanomidyl

Notice HN is actually an amine. What we have here, therefore is an amine attached to ~~cyanide~~ / what a combination that reeks of a cyanogen radical.

On we go to 21B. We know that is the isothiocyanate, most likely complexed. Enough said for now.

Our next peak of significance is 1022 cm^{-1}.

This speaks strongly of sulfur.

Parker gives 1050-1022 as S=O (stretch)

>S=O   sulfoxide

There are no realistic alternatives seen @ this time.
This has been assigned previously, to my recollection.

Next, we have strong absorbance @ ~649 cm^{-1}.

This is back to our halides.
In fact, Parker specifically gives ~650 cm
as C-Br (stretch) Brom. derivatives.
This corresponds well w/ the HNCC chemistry
already noticed in the reference to amine-
cyanogen chemistry.

This is a rather cohesive picture ~~starting to~~ that
has emerged in this particular spectrum.

We have several small peaks @ 1291, 1236 & 1176.
We have Parker (1200-1305) cm^{-1} w/ secondary
amides - Amide III band. I will maintain
the assignment to amides @ this point.

This completes the initial interpretation
of the "embedded crystal"
(ie "skin-embedded crystal" spectrum
(Nostril-crystal sample received).

Summary:

1. Amides - protein
2. Cyanogen derivative
3. Isothiocyanate
4. Alkyl halide

A rather potent combination, it would seem.

We must also recall that our closest
IR spectral match, from our entire
* library, commercial as well as self-collected,
is that of the environmental filament
sample(s), also microwave digested.

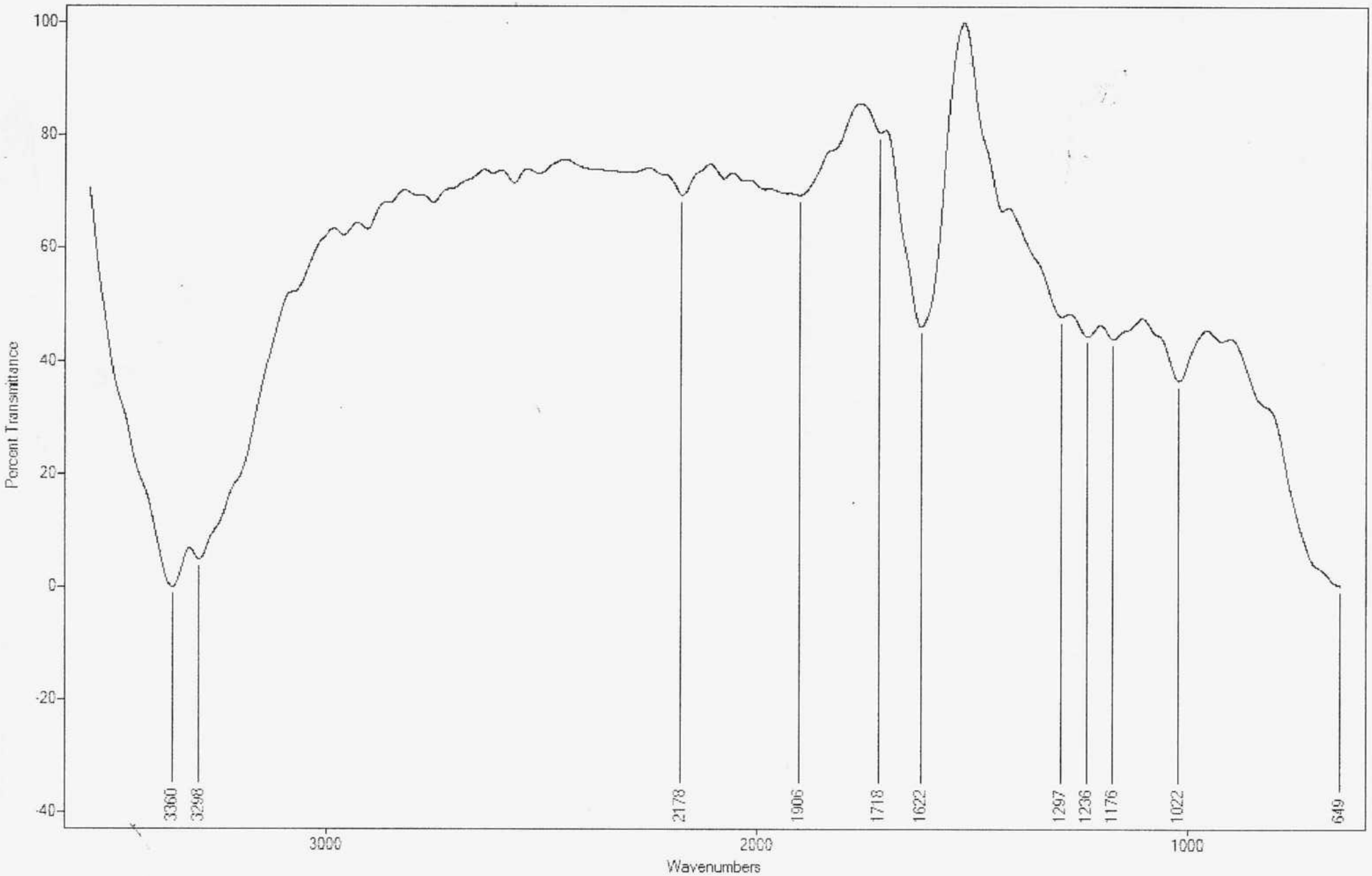
Embedded skin crystal spectrum
(Nose sample)

Page 334

High

Page
334A

Nostril Crystal ATR KOH-HCL Digestion CA Jun 18 2018 - 01.spc: Synthetic spectrum by averaging. See audit trail for details.



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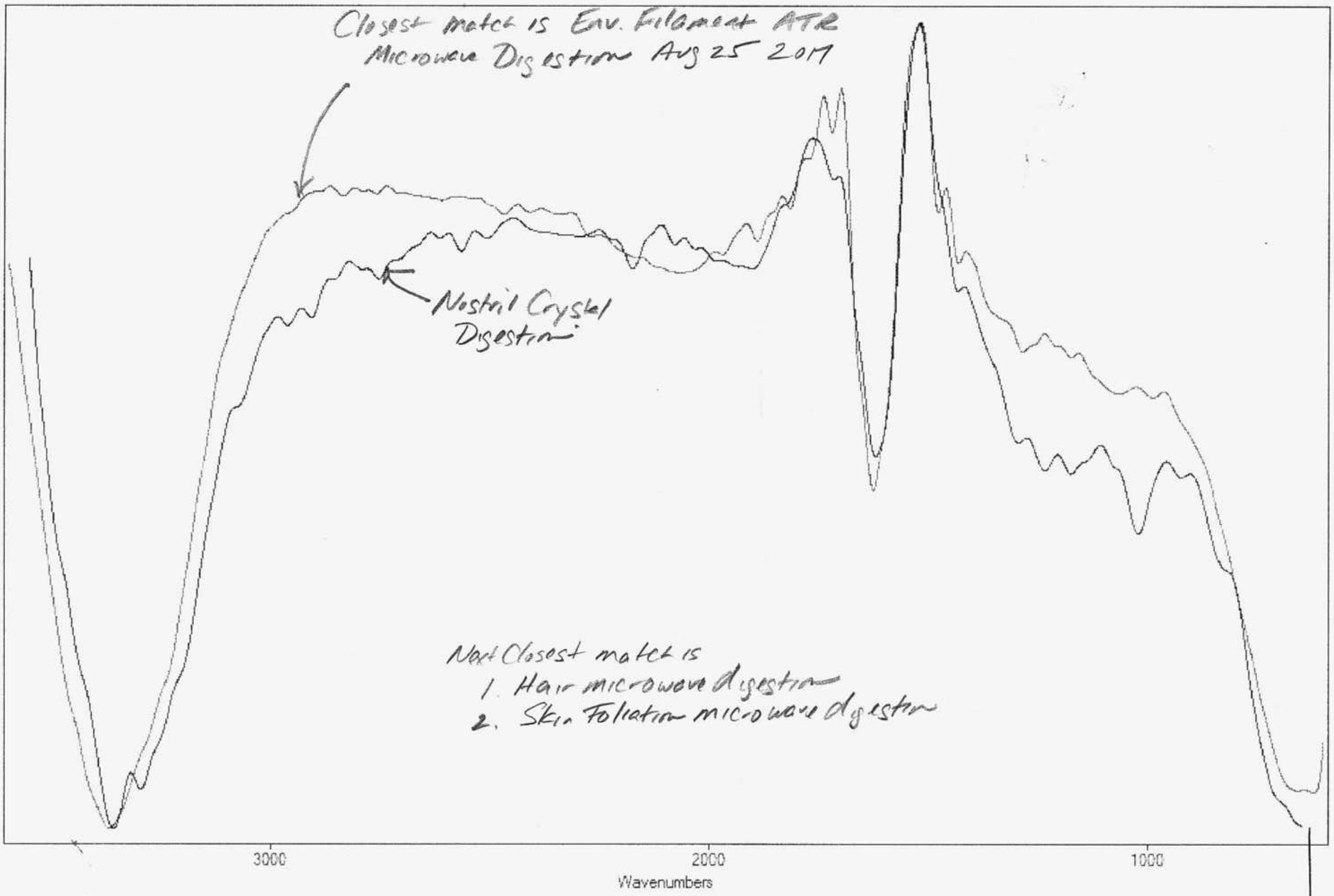
Nostril Crystal ATR KOH-HCL Digestion CA Jun 18 2018 - 01.spc: Synthetic spectrum by averaging. See audit trail for details.



Closest match is Env. Filament ATR
Microwave Digestion Aug 25 2017

Nostril Crystal
Digestion

Next Closest match is
1. Hair microwave digestion
2. Skin Foliation microwave digestion

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The final spectrum of high priority, at least currently, is the CDB viscous protein. Notice that on May 13 we also examined a CDB viscous protein sample by IR.

Currently, I do not know the date of that sample that was analyzed, but we had absorption peaks @:

3263 2916 1632 ~1422 1018
✓ ✓ ✓ ✓

Our conclusion, w/ extended analyses, is that we most definitely have an

iron-sulfur protein. (see May 20 conclusions)
We also have some candidate amino acids identified.

—

Now we have a repeat and more recent spectrum taken. Here are our peaks now:
(this is w/ the recently maintained + calibrated IR instrument.)

✓
3298 2968 2934 2897 1650 1519 1418 1025
✓ ✓ ✓ ✓ ✓
770 625

Let's go to work w/ this.

Start, as will now be customary, with the carbonyl question. (Pavia)

Carbonyls are from 1600 - 1820. We are @ 1650.

We therefore have a carbonyl.

Once again, our strongest candidate, from Pavia is the amide.

From Pavia, amide range is 1640 - 1670 cm⁻¹.
We therefore have an C=O stretch.
We also require a N-H stretch from 3100 - 3500 cm⁻¹
We have it @ 3298.
N-H bending can occur around 1640 - 1550.

We have these conditions satisfied. We have an amide.

Next we go to the 1025 peak. SDBS was used here to arrive @ the sulfate group candidate. From colors we also surmised iron. Chemical tests confirmed both. Fe^{+2} SO_4

This alone makes the case for an iron-sulfur protein.

Now w/ the HC peaks ~ 2900 - 3000 the hydrocarbons are perfectly in keeping w/ a protein assessment.

At this point we have matched our previous assessment.

However, we still have four additional peaks that we may consider

1418 (strong)
625 (strong)
1519 (medium)
770 (shoulder)

We see that the 1418 peak also has shoulder w/in it. We therefore expect more than one contribution to the absorption. From Parker:

1	med	1418 - 1400	amide (primary)
~~2~~	~~str~~	1420 - 1330	$ROSO_2R'$ sulfonic ester
~~3~~	~~weak~~	1420 - 1406	$C=CH_2$
~~4~~	~~med~~	1440 - 1325	aliphatic aldehyde
~~5~~	~~str~~	1440 - 1350	sulfuric ester
~~6~~	~~weak~~	1440 - 1395	carboxylic acid
~~7~~	weak	1450 - 1400	azo
8	str	1460 - 1400	carboxylate

Many or most of these can be eliminated w/ care. 1418 is not a weak absorption. It is questionable whether it is even medium.

But weak absorptions are eliminated first
\# 3 $C=CH_2$ also no alkene present
\# 6 Carboxylic ~~ac~~ acid
\# 7 azo

Amide is already satisfied & therefore maintained.

Esters absorb near 1735 and we do not have that so esters are out.
Aldehydes absorb @ ~1725 & ~2850 & 2750.
We have neither so aldehydes are out.
This reduces our candidate list to.

1. Amides
2 Carboxylates

We have one great article on Carboxylates in the Spectroscopy magazine. (May 2018)

Carboxylate peaks are very strong & sharply defined @
1650 - 1450 We do not have it.
1450 - 1360 We have a peak here but it is not sharply defined.

The assignment remains, therefore, as an amide and we remain as a Non-sulfur protein.

Next is 625 cm^{-1}.

There is no alternative seen here. Parker shows this to be the alkyl halide. C-Br remains as the most likely! CH bond requires an alkene and we do not have this.

CDB Viscous Protein Assessment.

This definitely adds a new twist to the interpretation of the CDB viscous protein, as it brings an alkyl halide into the iron-sulfur protein complex. Bromine remains as the strongest candidate.

In the process we notice that an amine salt, either NH_3^+ or NH_2^+ is most likely indicated @ the weak 770 absorption (based upon Parker).

Our remaining question is the 1519 peak.

Parker here clearly gives us an amide.

1570-1515 secondary amide Amide II band (solid)

1550-1510 secondary amide

This concludes our fundamental & preliminary IR spectral interpretation of the CDB viscous protein. We now modify our former assessment, slightly but importantly, to

* An iron-sulfur protein in conjunction w/ an alkyl halide.

This concludes the immediate high priority IR spectral interpretations, for the moment.

Skin Foliation sample in next volume (23) will be added
to the high priority list.

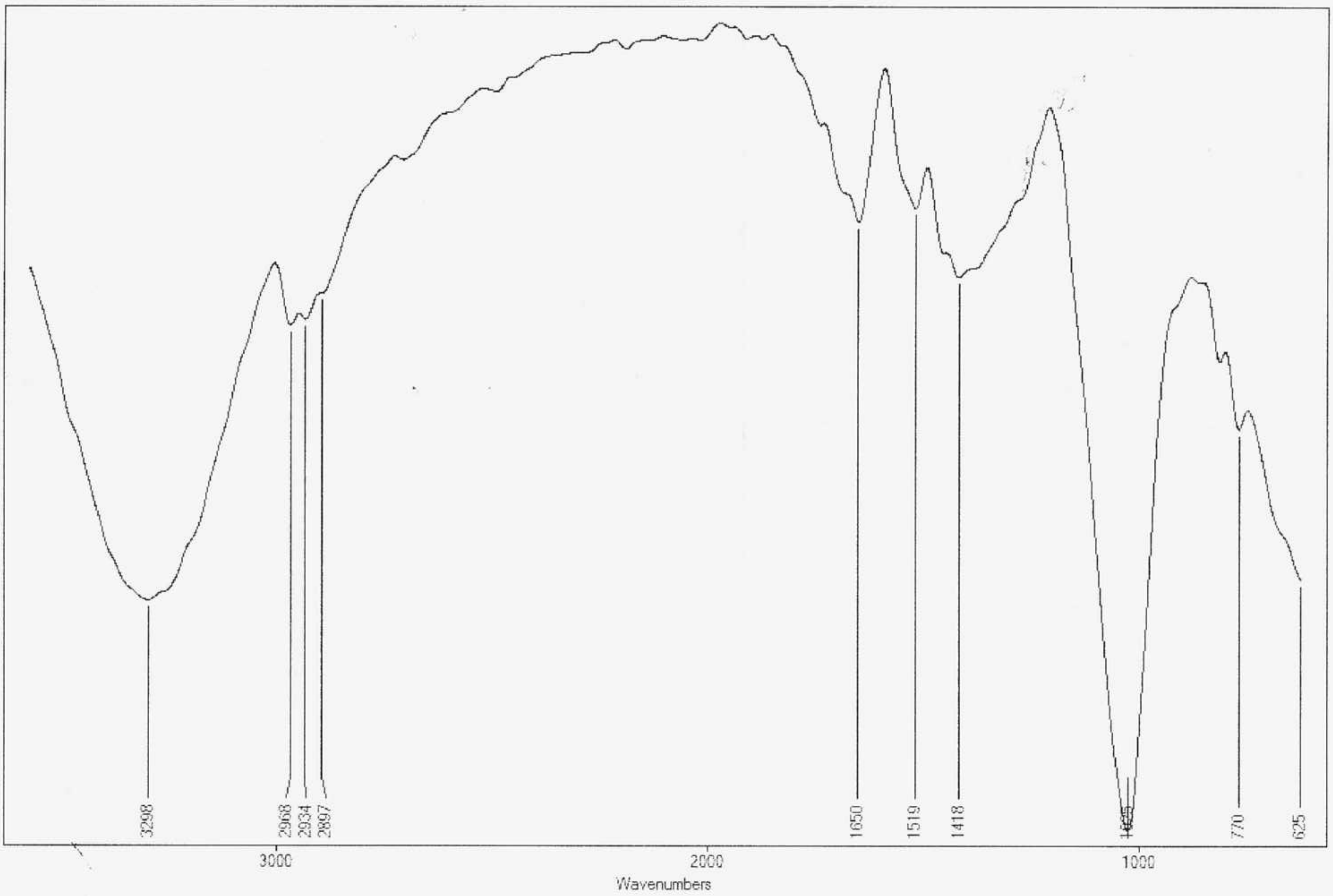
CDB Viscous Protein - IR - Most Current Assessment.

PAGE 340

CDB Viscous Protein ATR Jun 12 2018 - 01.spc: Synthetic spectrum by averaging. See audit trail for details.

Page
340A

High



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