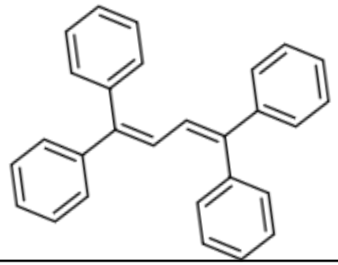
Degradation Mechanisms of TPB Coatings

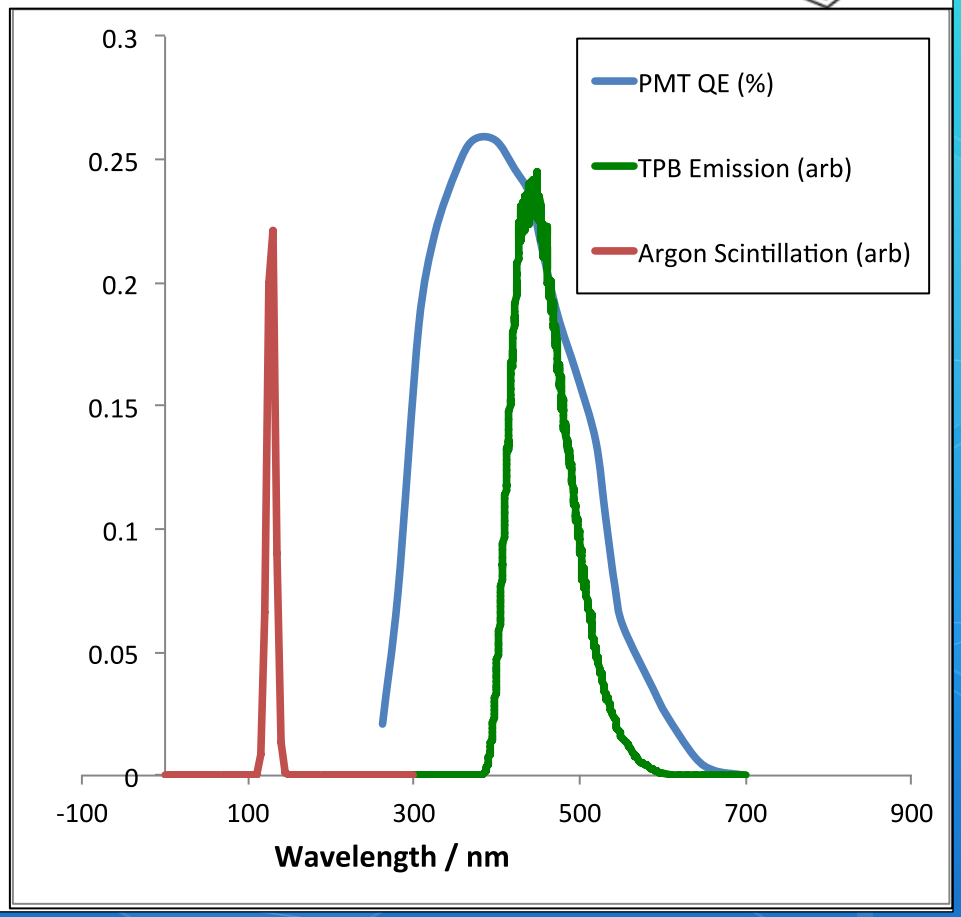
Jennifer VanGemert, FNAL

LIght Detection In Noble Elements, May 2013

Tetraphenyl Butadiene



- High absorption coefficient at 128nm
- Emission spectrum maximum near 450nm
- Emits 1.3 photons for each incident photon
- Fragile pure coating strengthened with toluene/polystyrene mixture

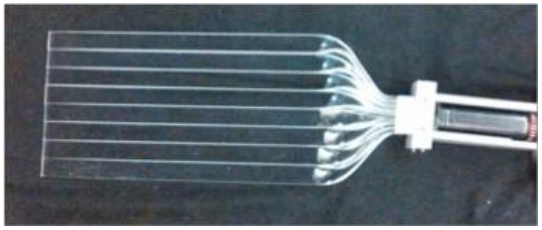


Coating Styles

- Coatings brush coated onto plates, TPB embedded in polystyrene for mechanical robustness

- "Rough" Coating
  - Designed for maximum WLS efficiency (TPB crystalizes on surface)
  - Used in MicroBooNE PMT assembly
  - 3 coats of 50% TPB and 50% PS in toluene solution

- "Smooth" Coating
  - Designed for smooth optical surface for light guiding
  - Used in paddle / lightguide detectors
  - 1 coat of 25% TPB in PS in Toluene solution



arXiv.org > physics > arXiv:1001.4214

Physics > Instrumentation and Detectors

A Study of the Fluorescence Response of Tetraphenyl-butadiene

R. Jerry, L. Winslow, L. Bugel, J.M. Conrad

(Submitted on 24 Jan 2010)

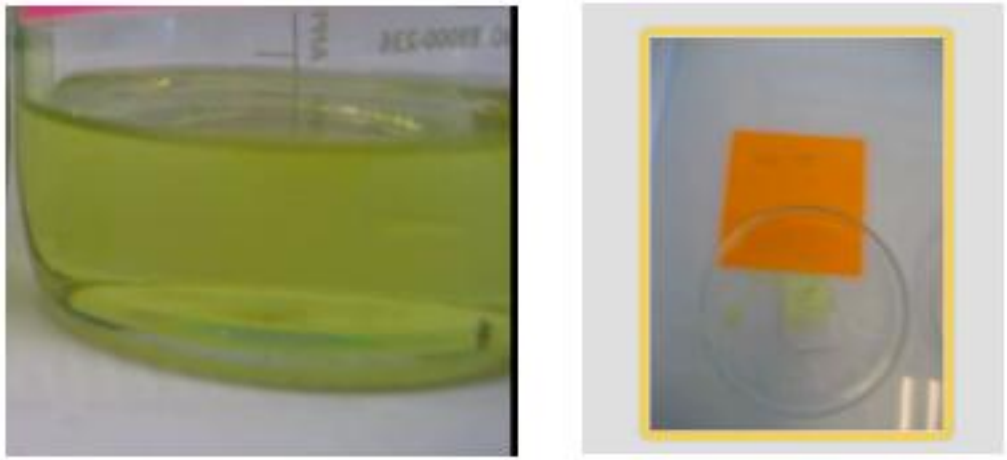


Figure 4: Left: Toluene and 99% TPB mixture exposed to light for three days. The initially clear mixture became yellow-green. Right: Powdered 99% pure TPB exposed to the SOLUX lamp for five days. The initially white powder became yellow.

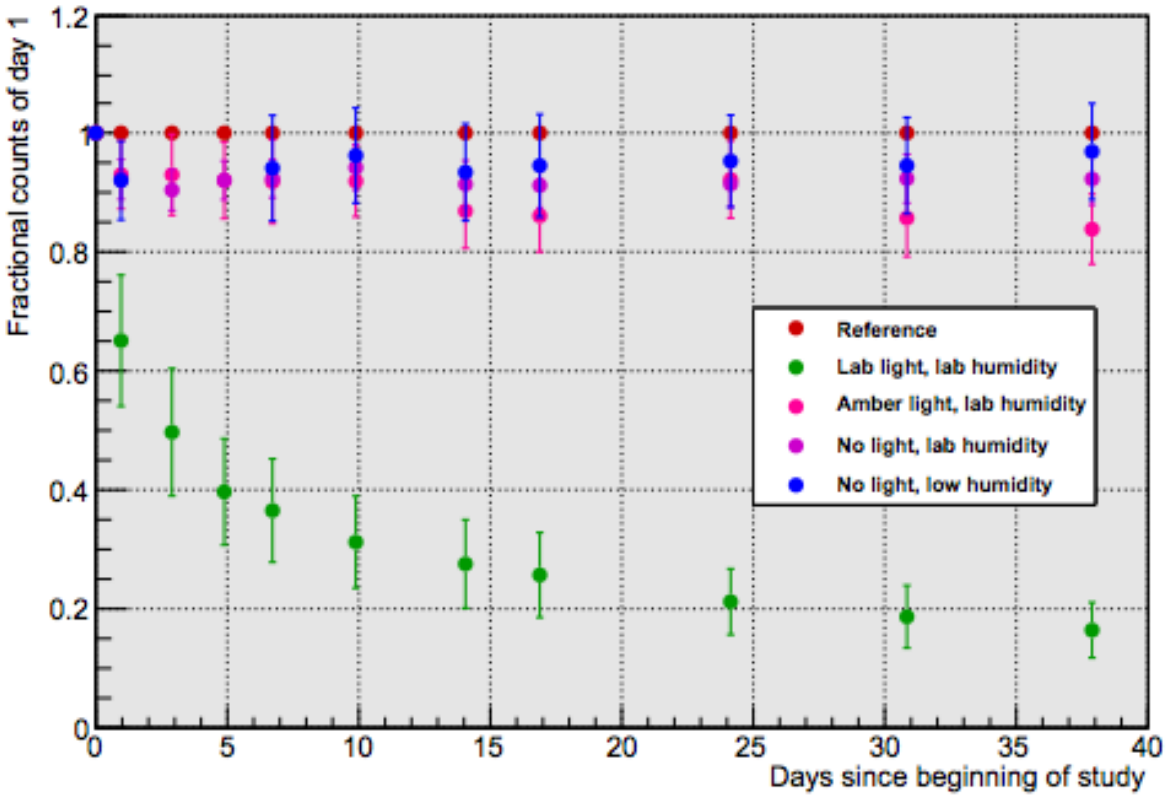
arXiv.org > physics > arXiv:1204.5762

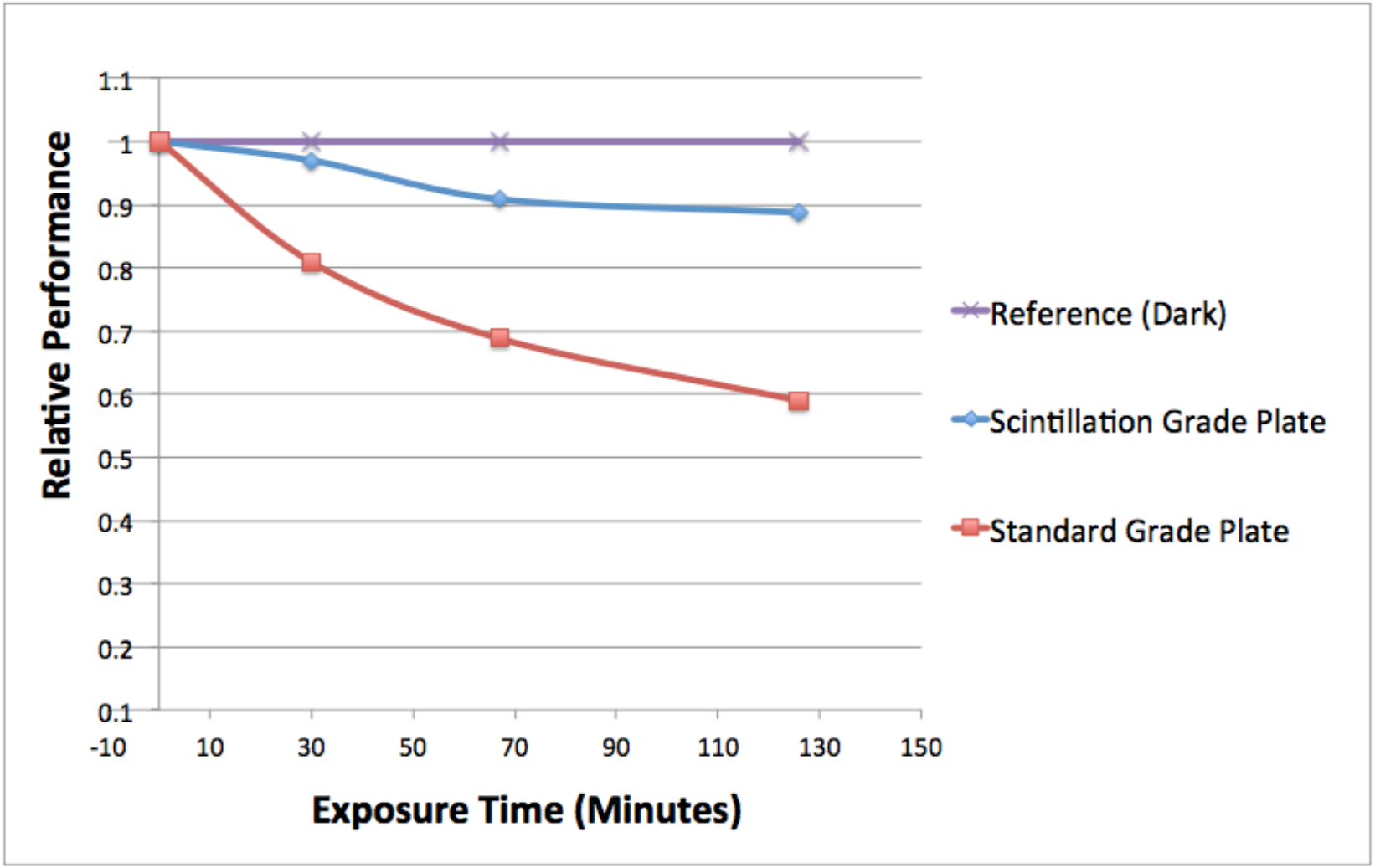
Physics > Instrumentation and Detectors

Environmental Effects on TPB Wavelength-Shifting Coatings

C.S. Chiu, C. Ignarra, L. Bugel, H. Chen, J.M. Conrad, B.J.P. Jones, T. Katori, I. Moult

(Submitted on 25 Apr 2012)




Relative Performance
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
-10
10
30
50
70
90
110
130
150
Exposure Time (Minutes)
Reference (Dark)
Scintillation Grade Plate
Standard Grade Plate

This Talk:

Journal of Instrumentation > Volume 8 > January 2013
B J P Jones *et al* 2013 *JINST* **8** P01013 doi:10.1088/1748-0221/8/01/P01013

Photodegradation mechanisms of tetraphenyl butadiene coatings for liquid argon detectors

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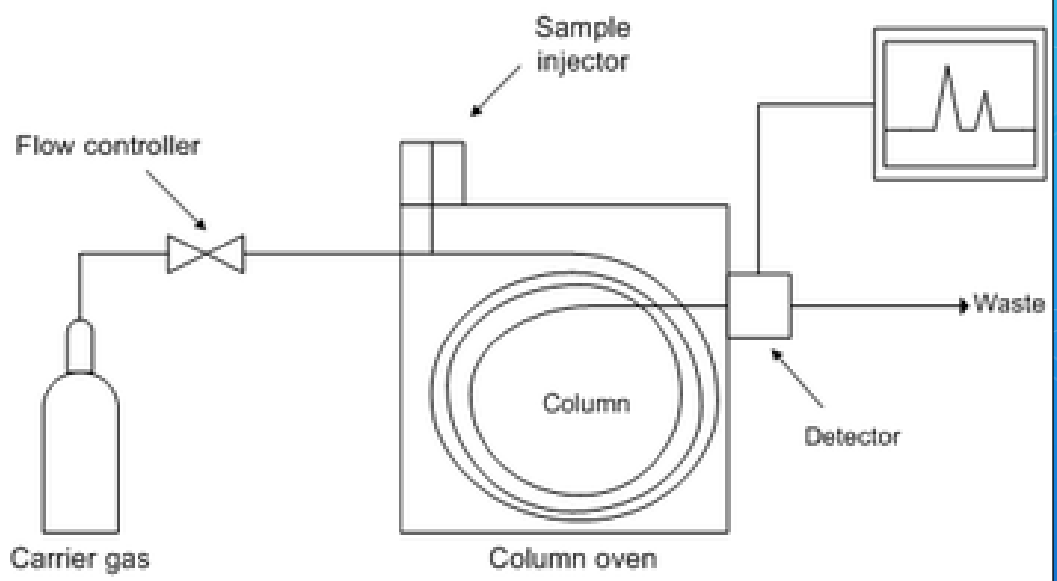
GCMS Studies

- Gas chromatography to separate compounds of different mobility, followed by mass spectrometry
- Impurities are visible to the GCMS at ppm levels.

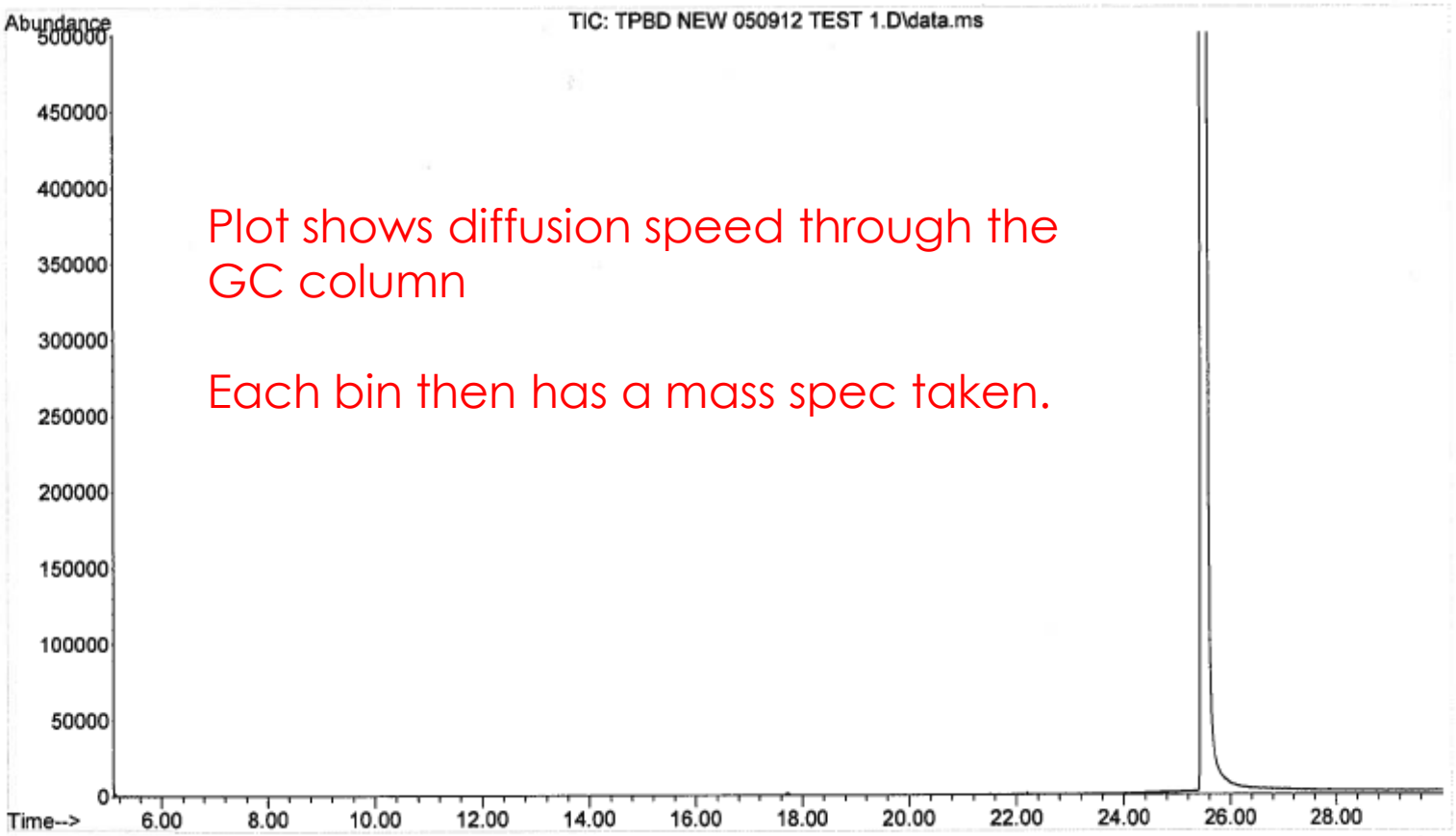
GCMS

- GC vaporizes sample
- Compounds in sample separate as they pass through chromatographic column
- MS ionizes compounds
- Sample mass spectrum compared to known spectra



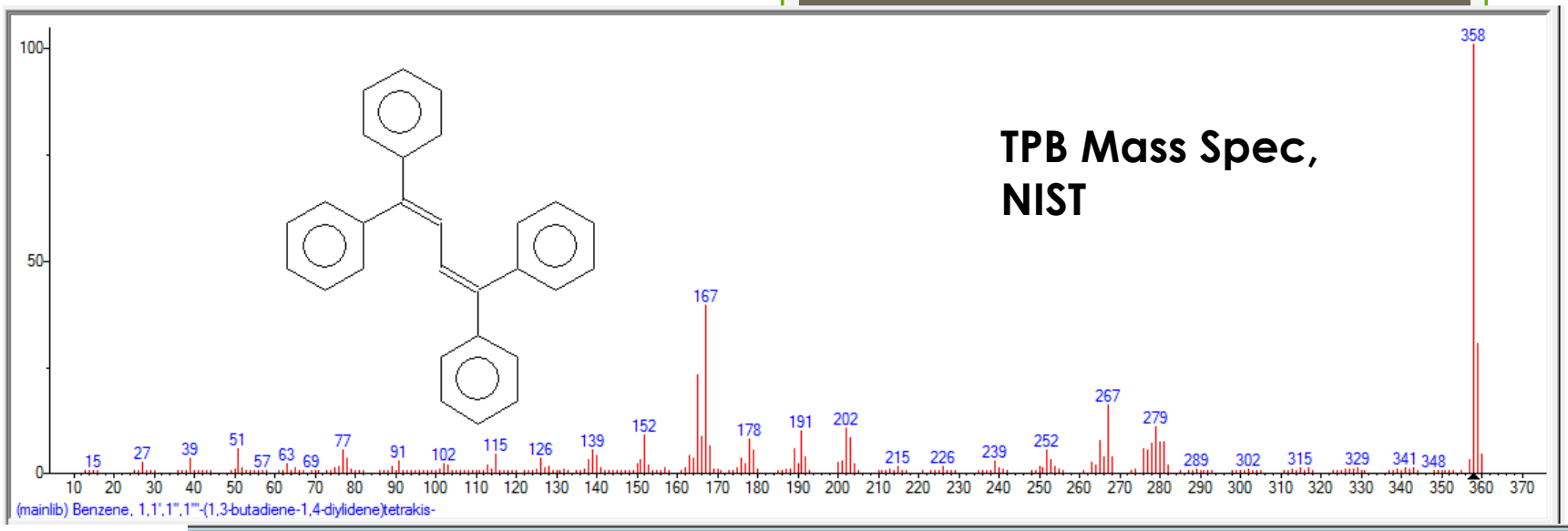
WHITE TPB

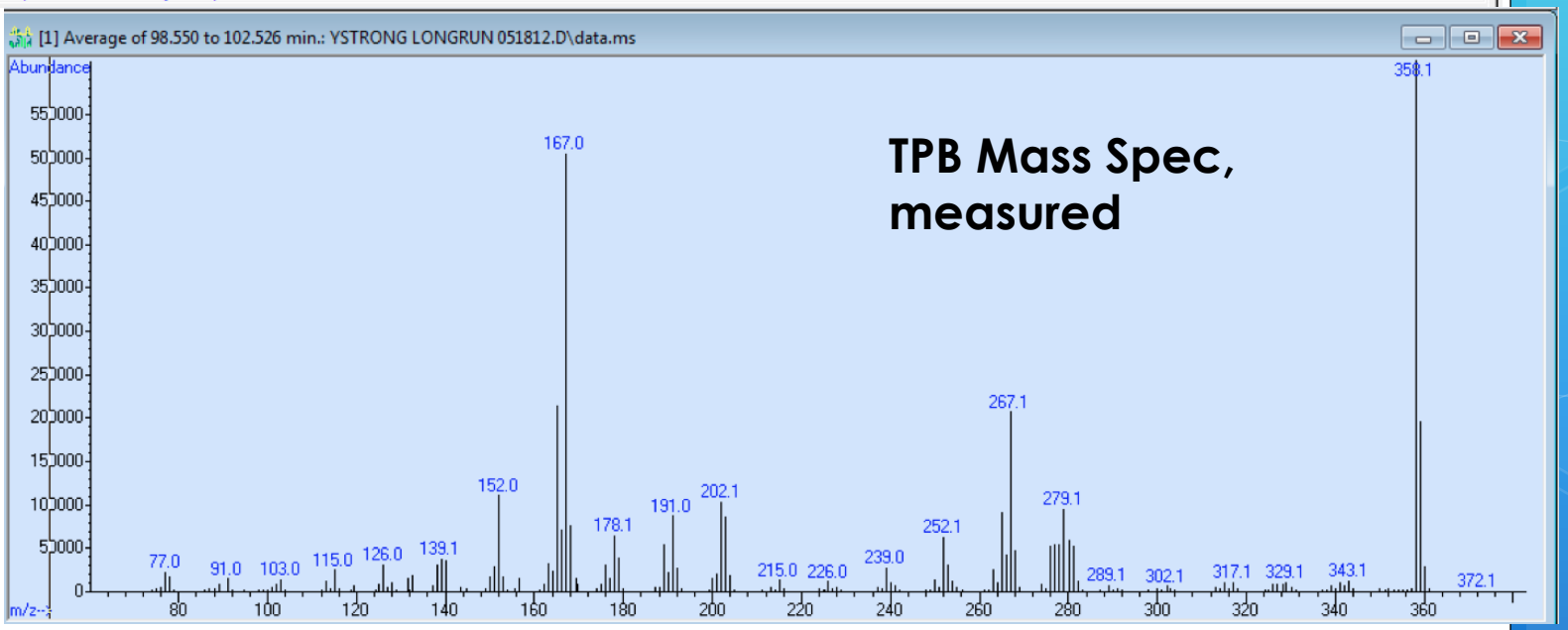
```
File        :C:\msdchem\1\data\BenTPBD\TPBD NEW 050912 TEST 1.D
Operator    :
Acquired    :  9 May 2012  11:36     using AcqMethod TBPD.M
Instrument  :    GCMSD
Sample Name:
Misc Info   :
Vial Number: 1
```

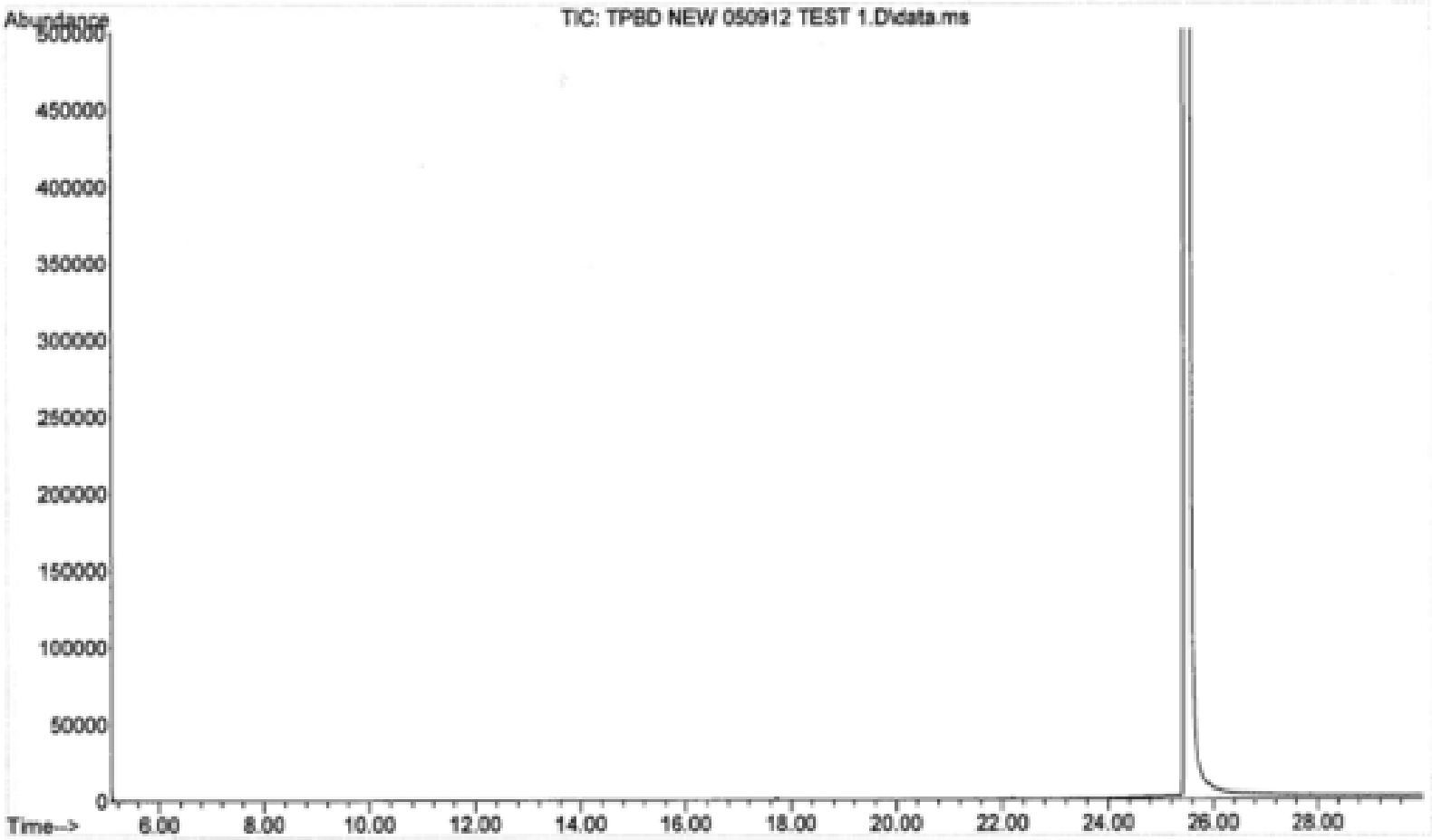


Plot shows diffusion speed through the GC column

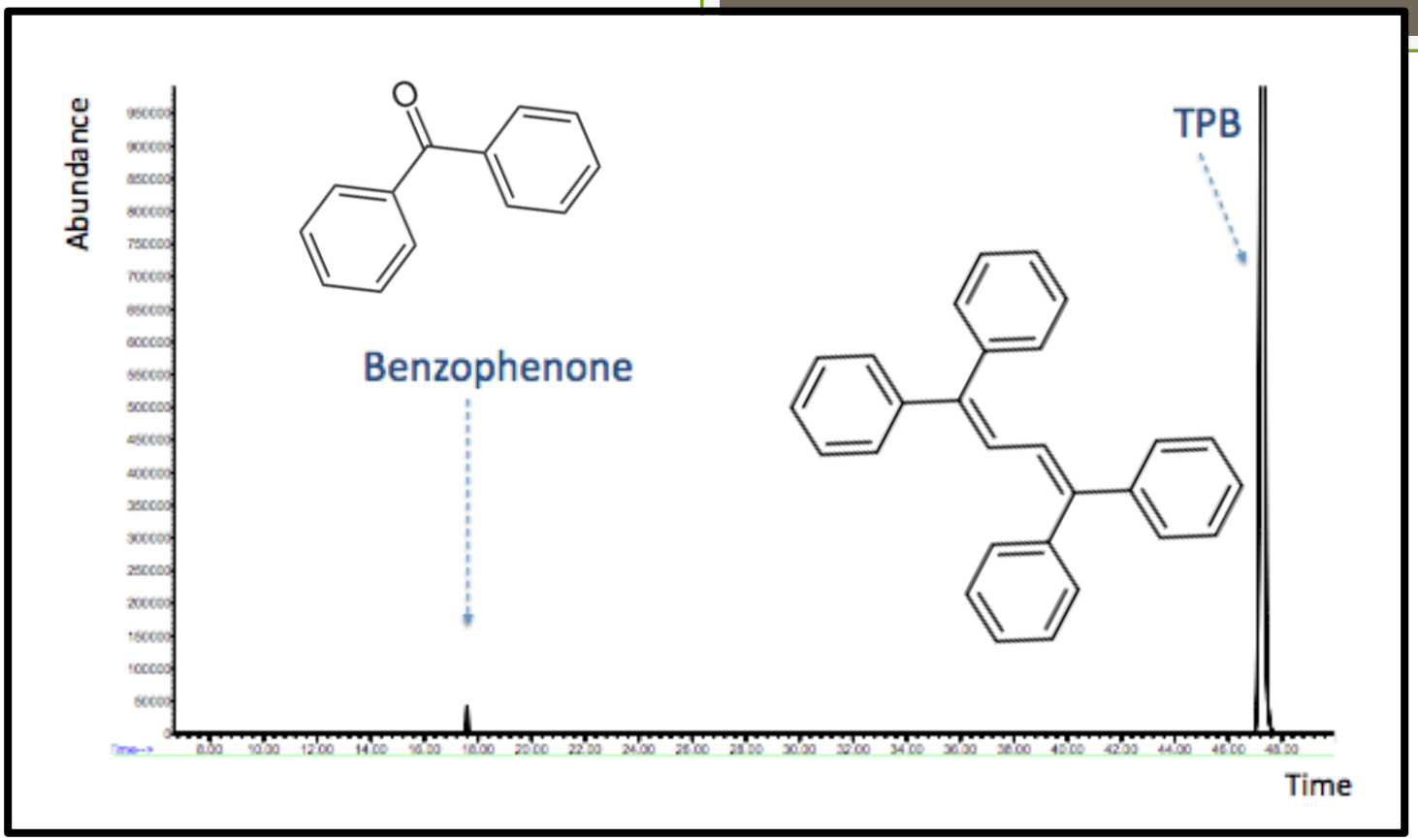
Each bin then has a mass spec taken.


TPB Mass Spec, NIST
(mainlib) Benzene, 1,1',1",1'"-(1,3-butadiene-1,4-diylidene)tetrakis-


[1] Average of 98.550 to 102.526 min.: YSTRONG LONGRUN 051812.D\data.ms
Abundance
m/z
TPB Mass Spec, measured



Remember this?



Sample	Benzophenone / TPB Peak Ratio
Scintillation Grade (Unexposed, White)	4.13×10^{-6}
Standard Grade (Unexposed, White)	8.43×10^{-6}
Standard Grade (Exposed, Yellow)	1.82×10^{-5}

Benzophenone

Wikipedia says:

Uses

[edit]

Benzophenone can be used as a photo initiator in UV-curing applications such as inks, imaging, and clear coatings in the printing industry. Benzophenone prevents ultraviolet (UV) light from damaging scents and colors in products such as perfumes and soaps. It can also be added to the plastic packaging as a UV blocker. Its use allows manufacturers to package the product in clear glass or plastic. Without it, opaque or dark packaging would be required.

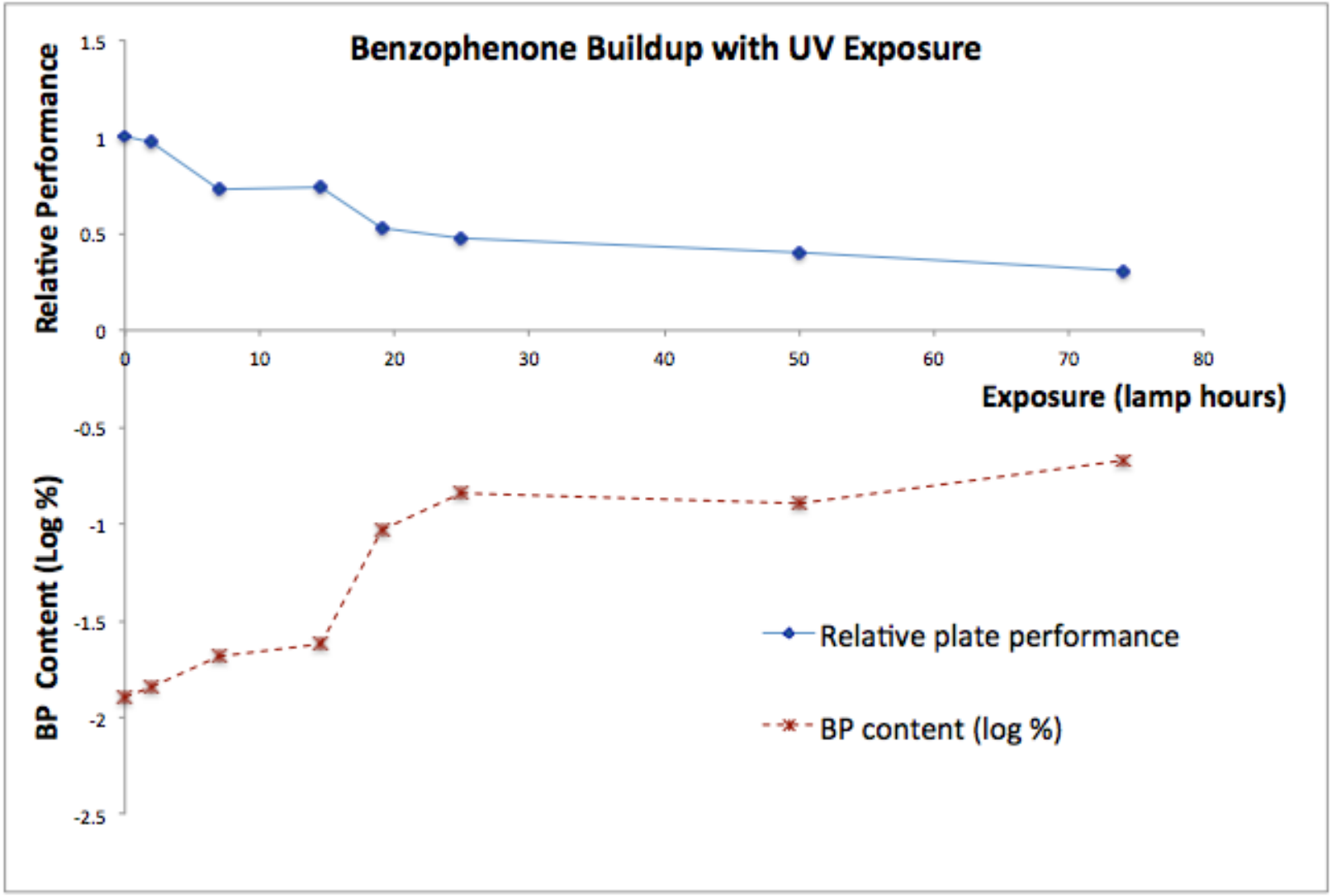
In biological applications, benzophenones have been used extensively as photophysical probes to identify and map peptide–protein interactions[1] .

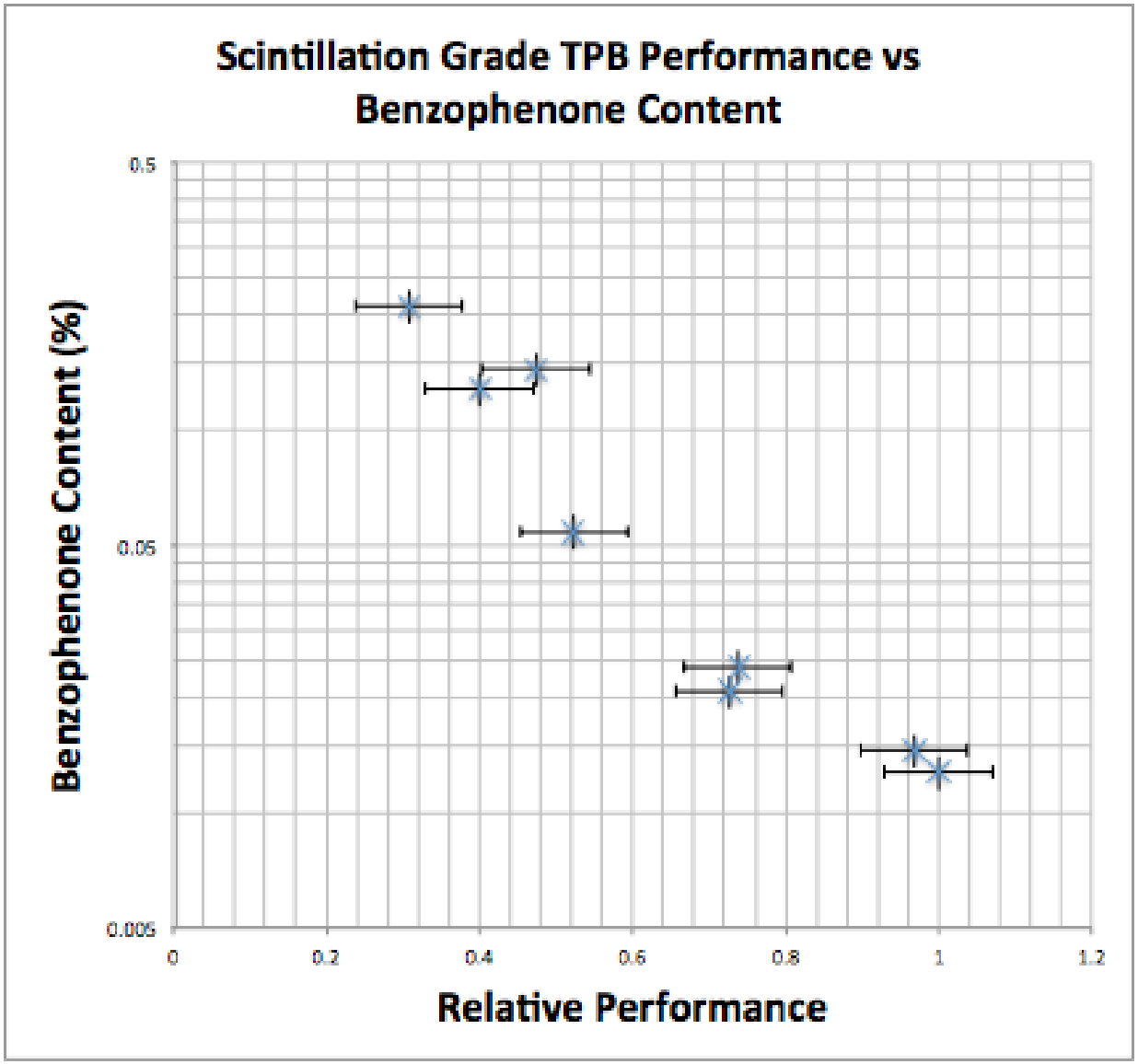
What is a photoinitiator?

A photoinitiator is a compound that undergoes a photoreaction on absorption of light, producing reactive species. These are capable of initiating or catalyzing chemical reactions that result in significant changes in the solubility and physical properties of suitable formulations. Hence, the photoinitiator is a compound that can transform the physical energy of light into suitable chemical energy in the form of reactive intermediates.

Controlled Study:

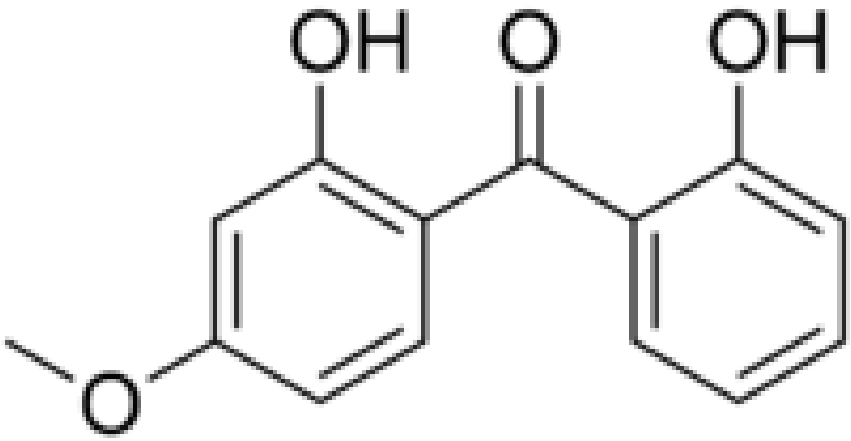
- Produce ~30 TPB coated plates
- Measure WLS performance of each before degradation
- Degrade under a UV lamp (300nm)
- After some exposure time, measure WLS performance again
- Dissolve off coating with toluene bath with sonicator
- Quantify benzophenone relative to TPB
- Fresh solvent run between each sample to minimize cross contamination


Benzophenone Buildup with UV Exposure
Relative Performance
1.5
1
0.5
0
0
10
20
30
40
50
60
70
80
Exposure (lamp hours)
BP Content (Log %)
-0.5
-1
-1.5
-2
-2.5
Relative plate performance
BP content (log %)

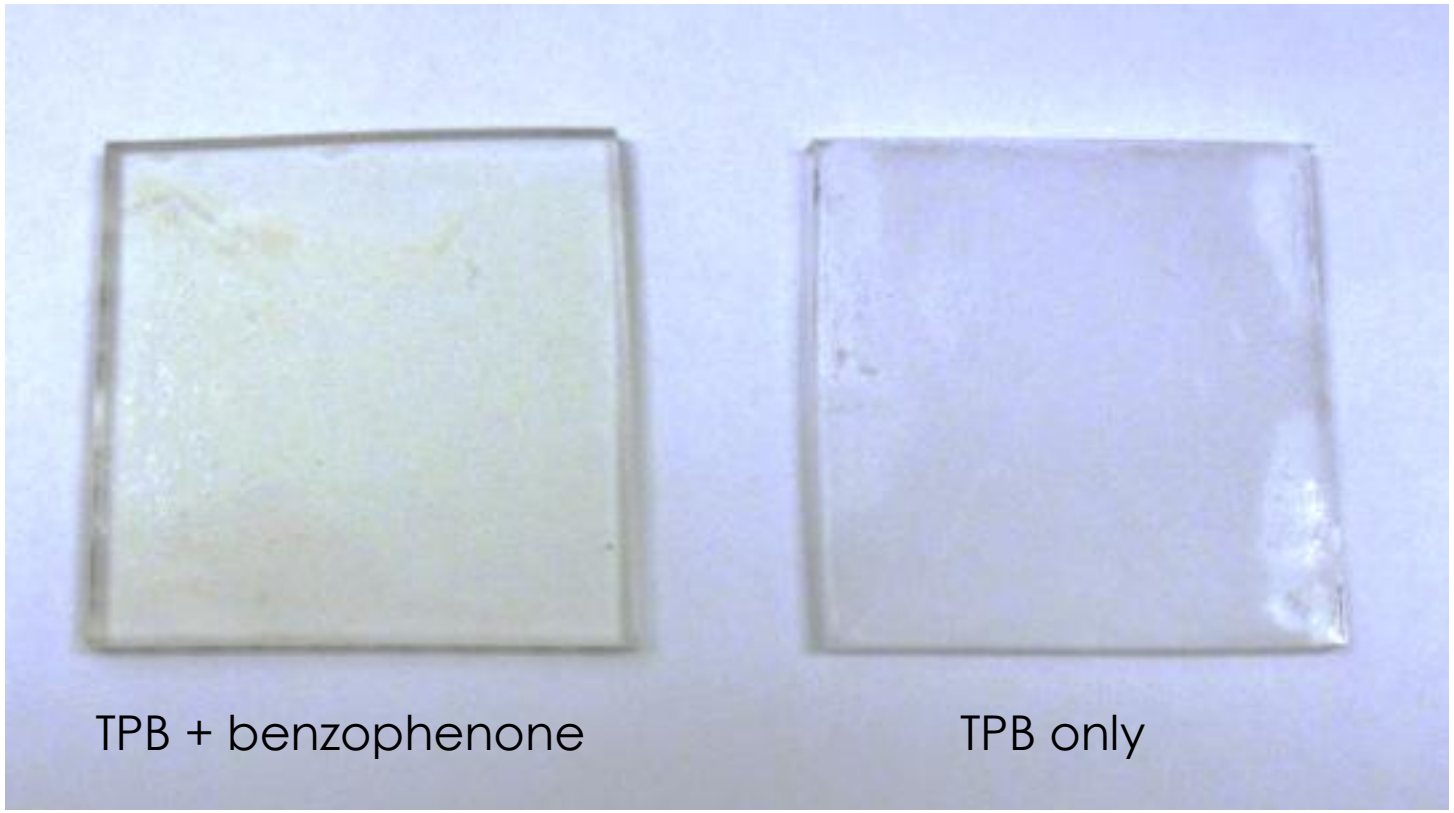

Scintillation Grade TPB Performance vs Benzophenone Content
Benzophenone Content (%)
0.5
0.05
0.005
0
0.2
0.4
0.6
0.8
1
1.2
Relative Performance

So where is the yellow?

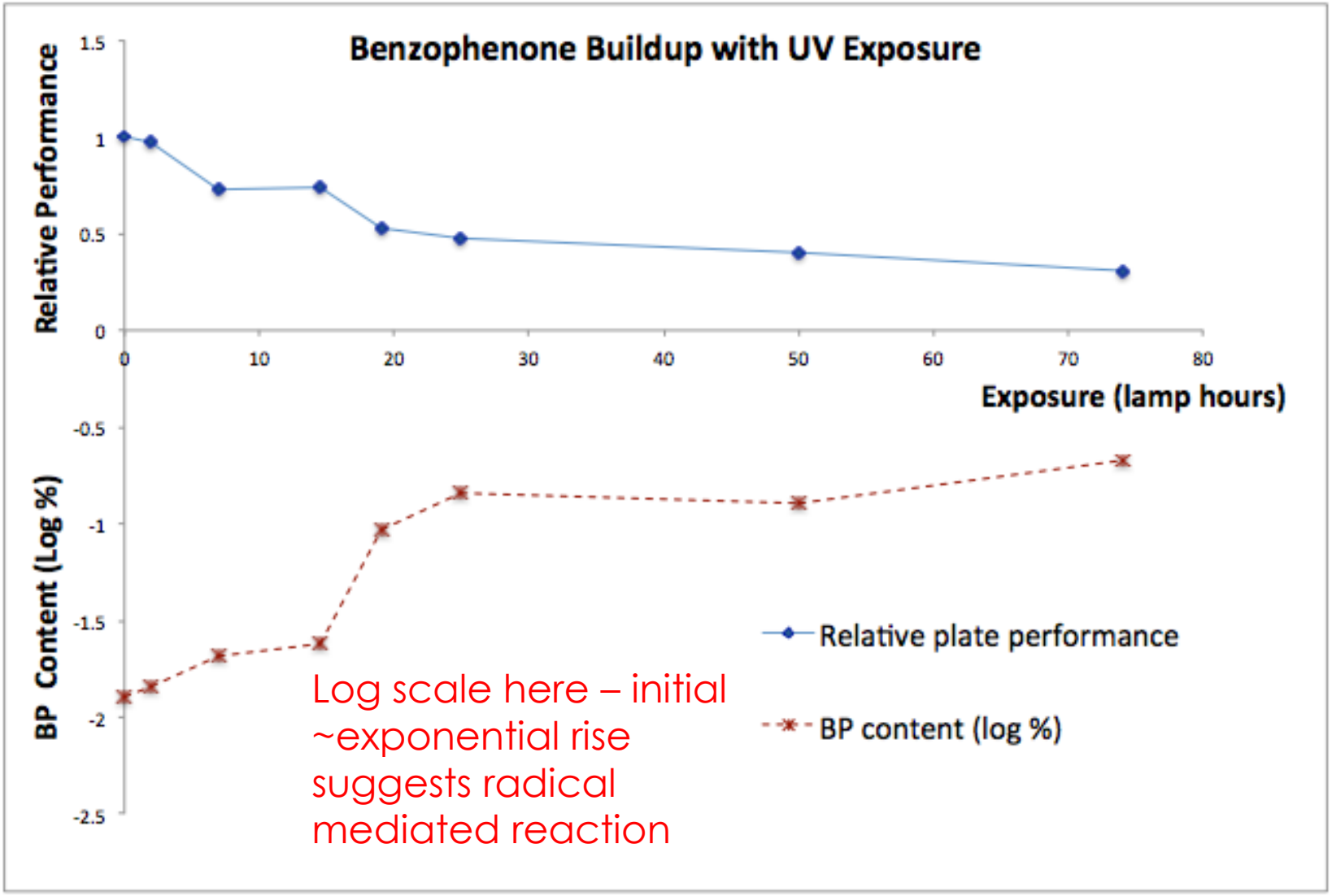
- BP is white, not yellow
- However, many of its simple derivatives are yellow
- Possibly a second stage after BP production, to produce yellow BP derivatives?



Impact of Added BP on Yellowing



This observation supports the interpretation on the previous slide…



Log scale here – initial ~exponential rise suggests radical mediated reaction

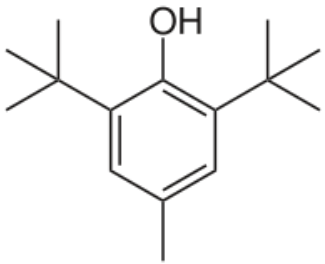
Hypothesis

- Photo-initiated radical mediated reaction turns TPB into benzophenone
- Second stage reaction turns benzophenone into various derivatives.

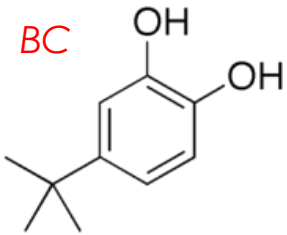
Terminating Radical Reactions

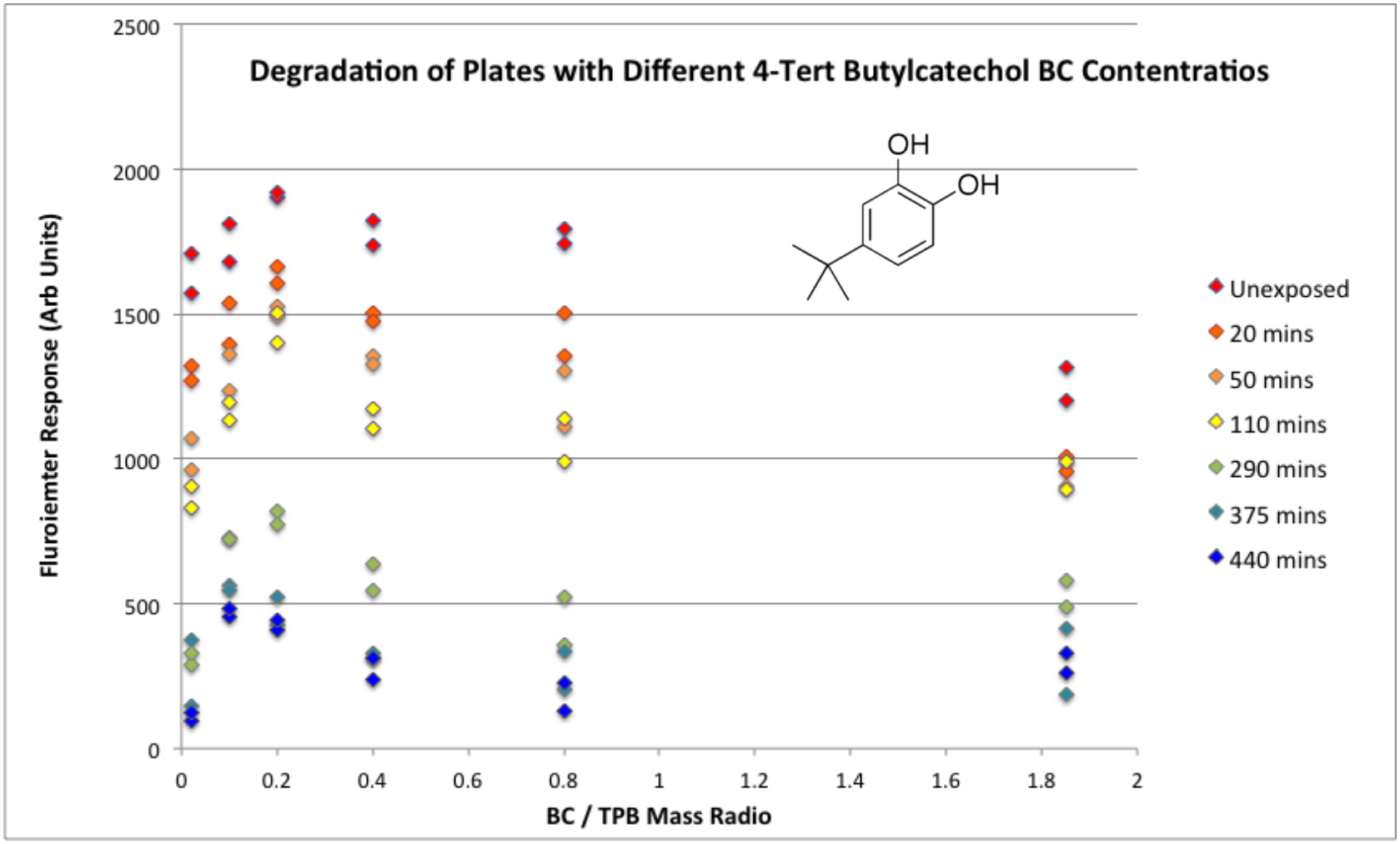
- Compounds exist which are used to terminate these reactions
- Stopping the reaction prevents further degradation
- We tried two common radical eaters:
  - Butylhydroxytoluene (BHT)
  - 4-tert Butylcatechol (BC)
- If they slow down this reaction, confirmation that we see a radical mediated photo-oxidation.

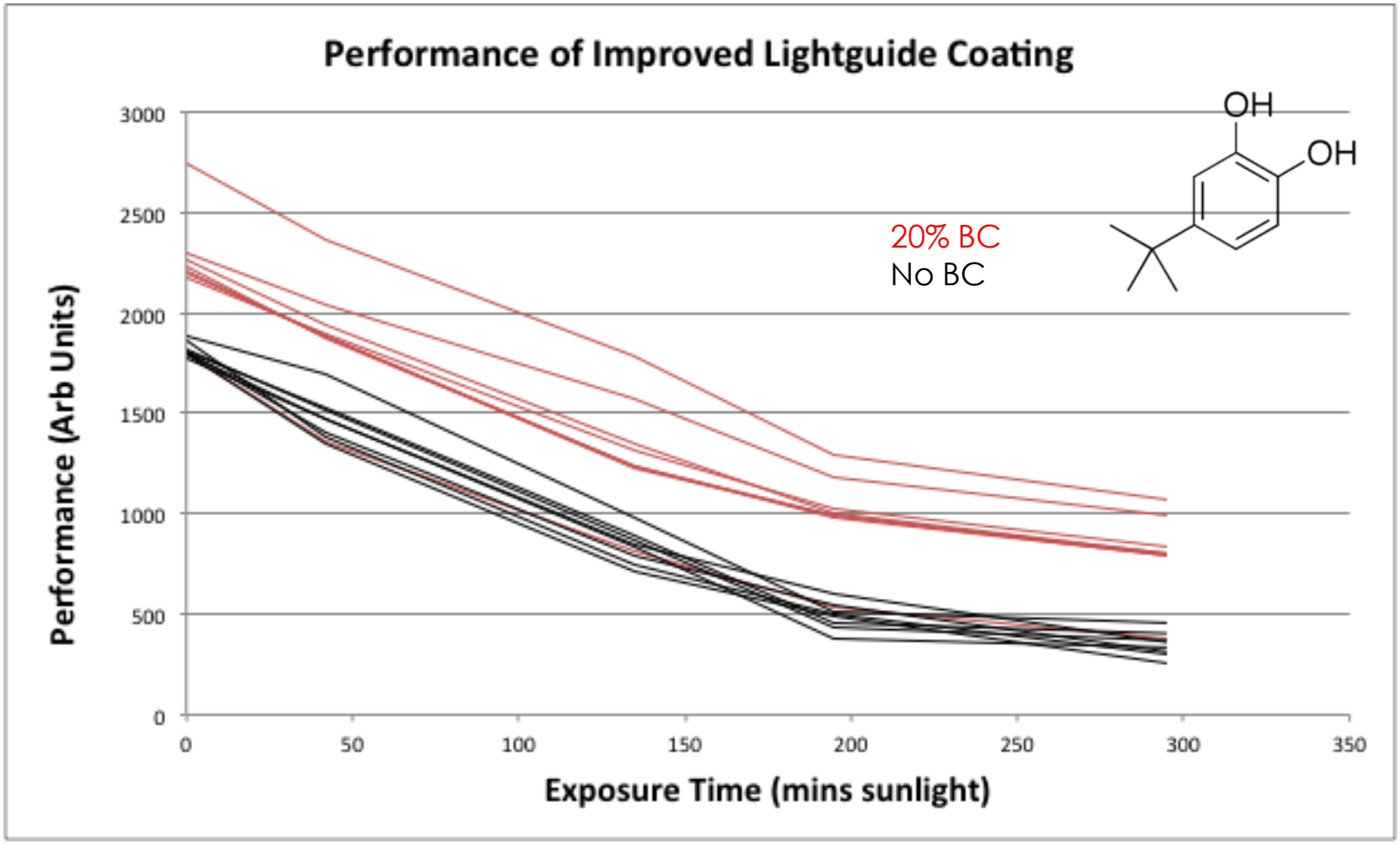
BHT



BC




Degradation of Plates with Different 4-Tert Butylcatechol BC Contentratios
Fluroiemter Response (Arb Units)
2500
2000
1500
1000
500
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
BC / TPB Mass Radio
OH
OH
Unexposed
20 mins
50 mins
110 mins
290 mins
375 mins
440 mins


Performance of Improved Lightguide Coating
Performance (Arb Units)
3000
2500
2000
1500
1000
500
0
0
50
100
150
200
250
300
350
Exposure Time (mins sunlight)
20% BC
No BC
OH
OH

Conclusions

- We have identified an impurity, benzophenone, which is a known UV blocker and photo-initiator, which builds up with UV exposure in TPB
- Rate of buildup indicates radical mediated photo-oxidation, this was confirmed by stabilizer tests
- We can improve coatings by 20% and significantly stabilize them with 4-tert butylcatechol.
- Yellow also connected to BP, likely production of derivatives in a second stage reaction.
- Investigations of other radical removing stabilizers are ongoing – maybe we can find an even better one!

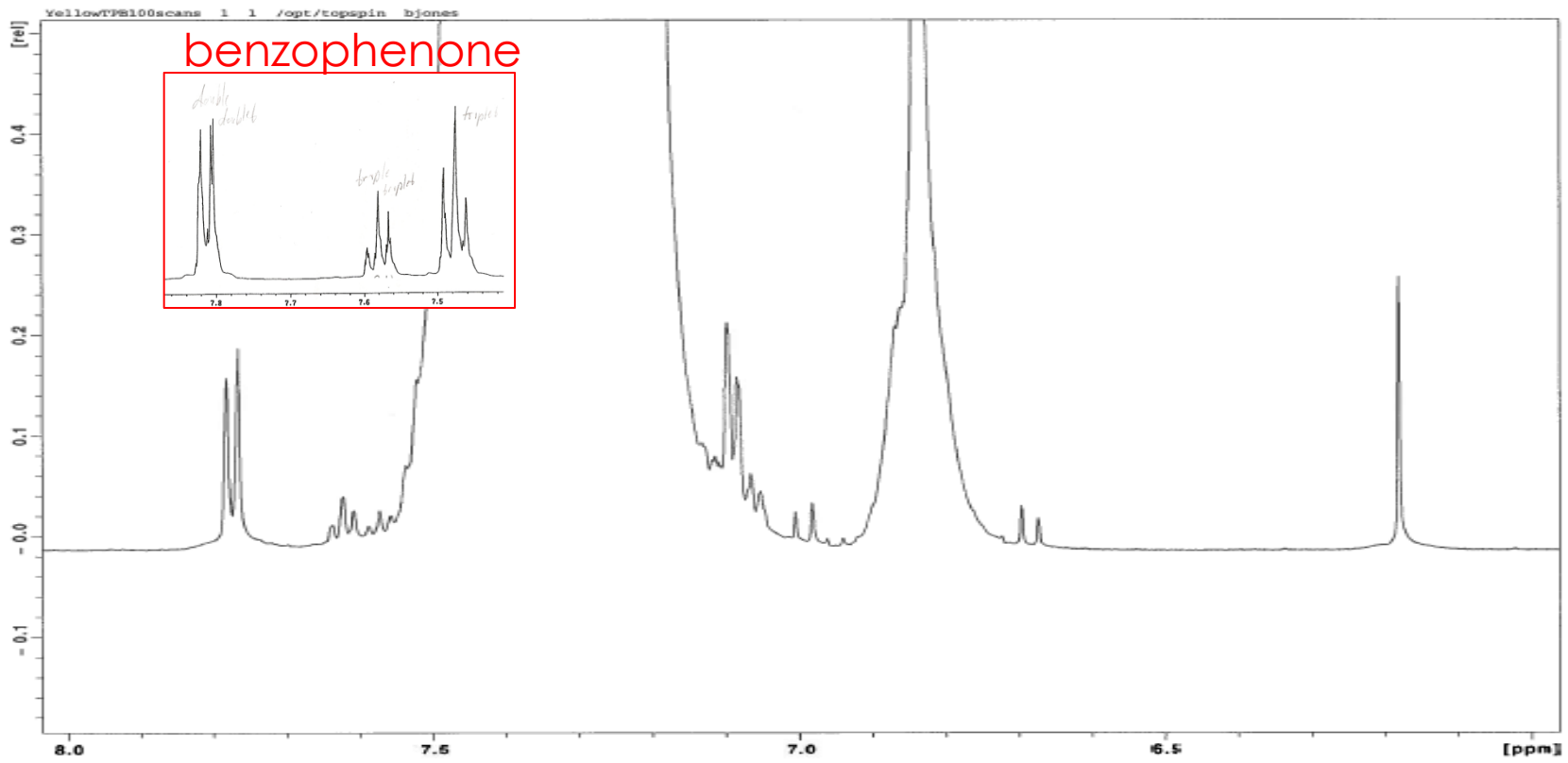
BACKUP SLIDES

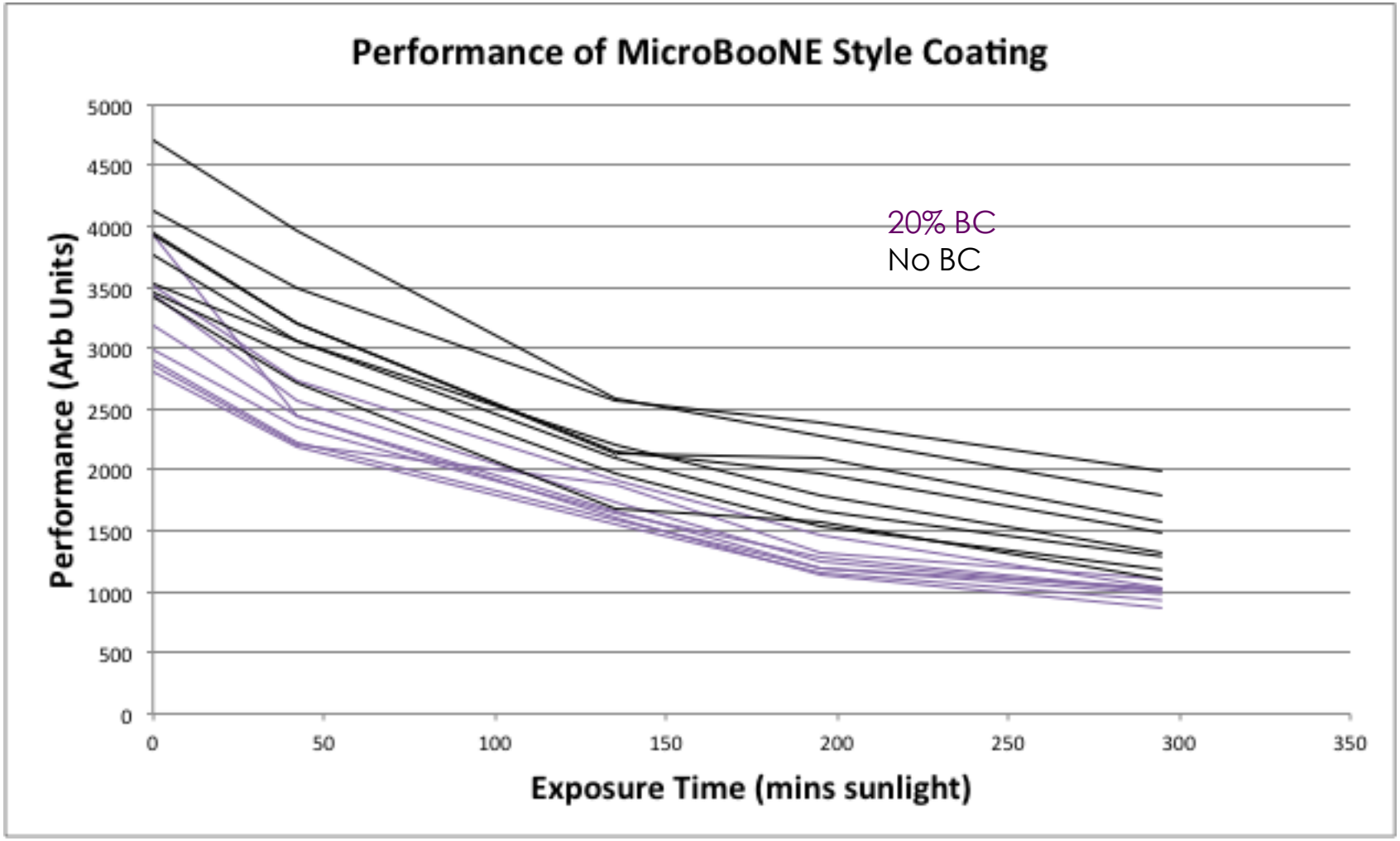
Contact Information

- If you have further questions not answered in this talk or workshop, feel free to contact me at:

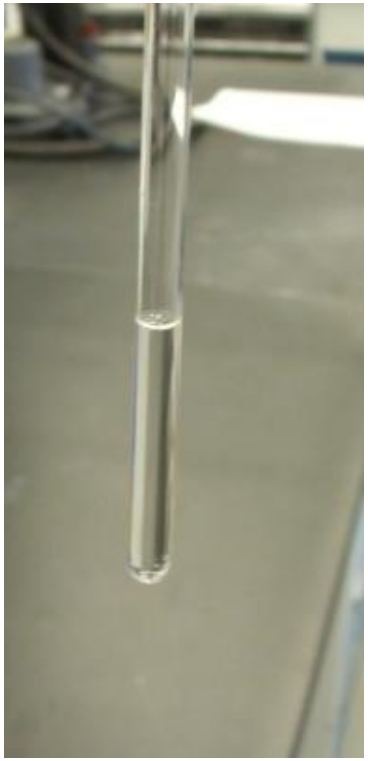
jennifer.thompson618@gmail.com

Compare NMR

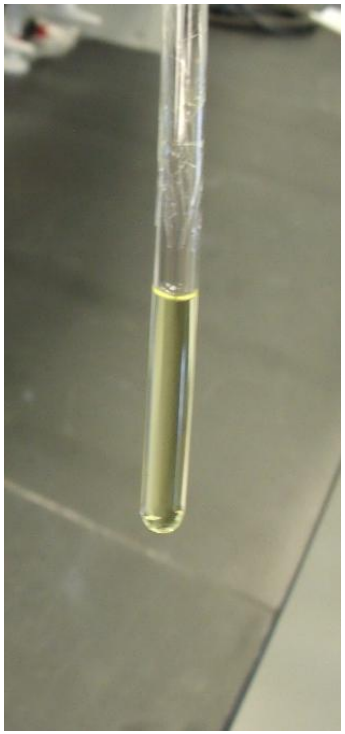

YellowTPB100scans 1 1 /opt/topspin bjones
benzophenone
double doublet
triplet
triple triplet
[rel]
0.4
0.3
0.2
0.1
-0.0
-0.1
8.0
7.5
7.0
6.5
[ppm]


Performance of MicroBooNE Style Coating
Performance (Arb Units)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
50
100
150
200
250
300
350
Exposure Time (mins sunlight)
20% BC
No BC

Yellowing in DHCL3 Solution



Scint



White Standard

YellowStandard