

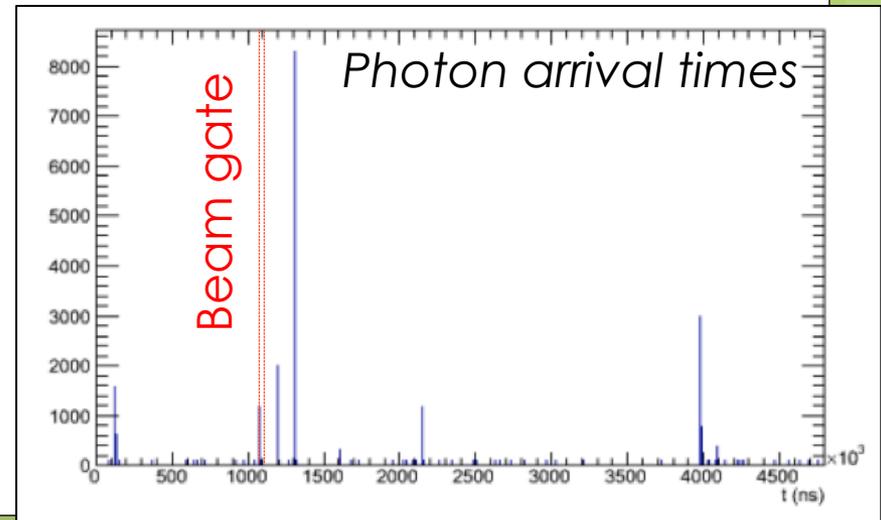
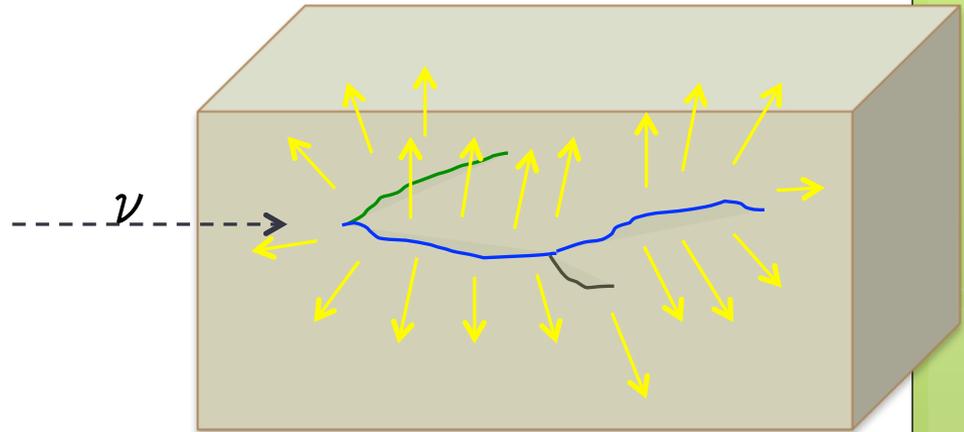
Degradation Mechanisms of TPB Coatings

Ben Jones, MIT

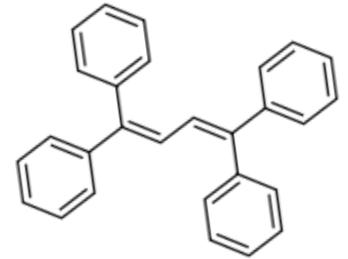
*Advances in Neutrino Technology,
May 2013*

Argon Scintillation Light

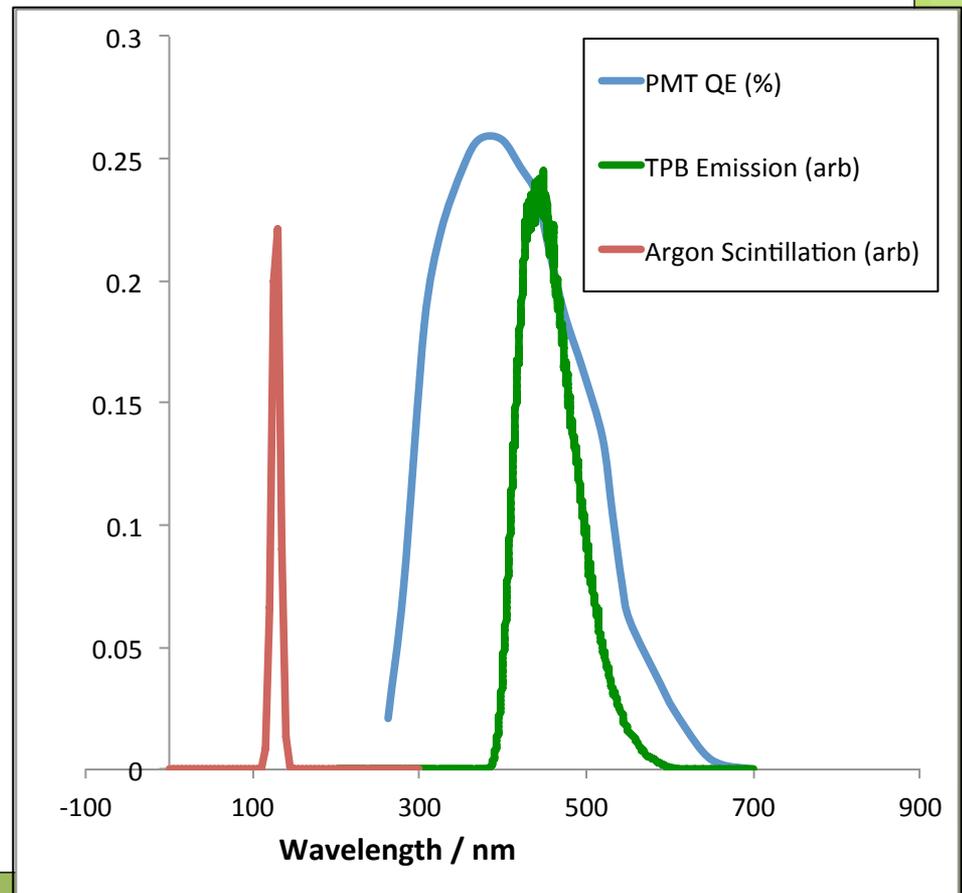
- Energy deposits in liquid argon produce copious scintillation light
- The photon yield is tens of thousands of γ / MeV at 128nm
- Argon is highly transparent to its own scintillation
- Light travels much faster than charge
- Thus scintillation detection gives an excellent tool for obtaining timing information in neutrino detectors



Tetraphenyl Butadiene

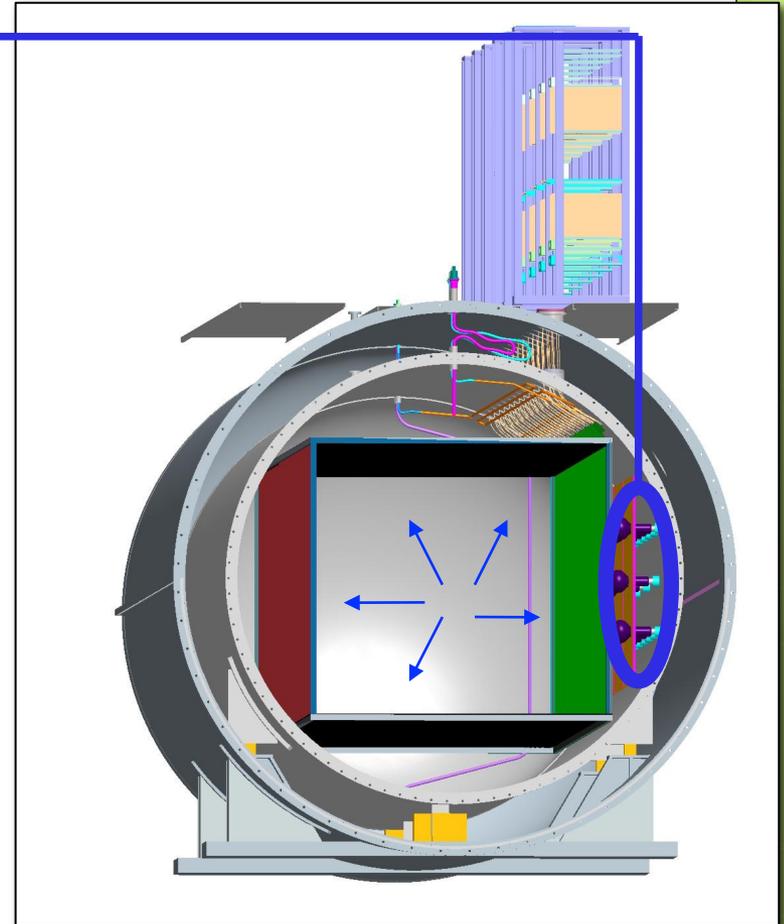
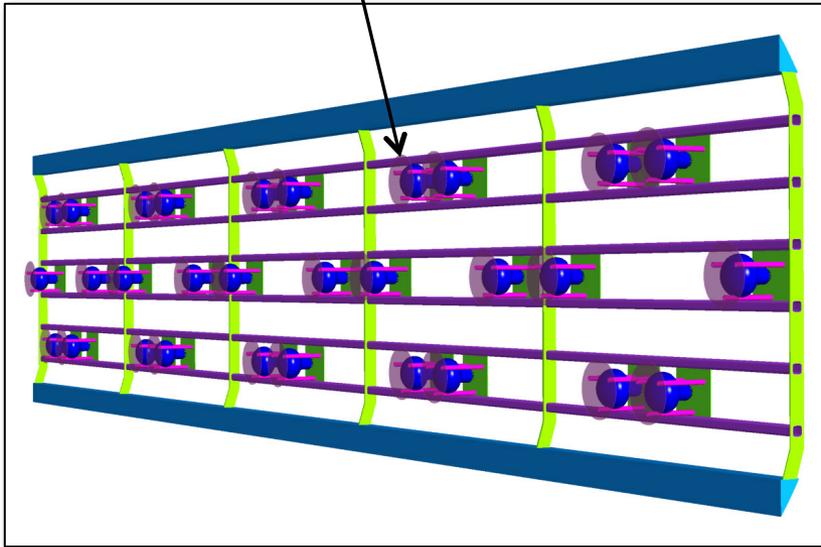


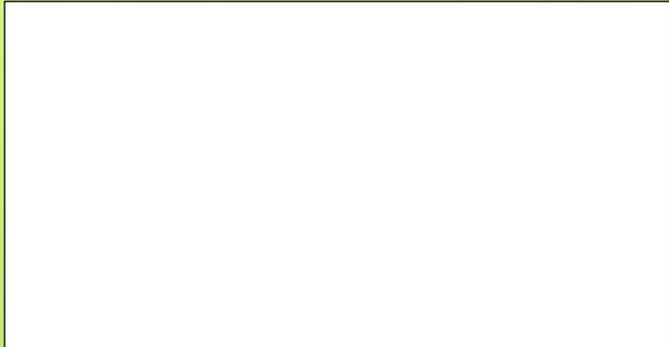
- 128 nm light will not penetrate, glass, air, acrylic, etc.
- This is a problem for the design of optical liquid argon detectors.
- Common solution is to use a fluorescent chemical like tetraphenyl butadiene (TPB)
- TPB absorbs 128nm light and emits it in the visible.



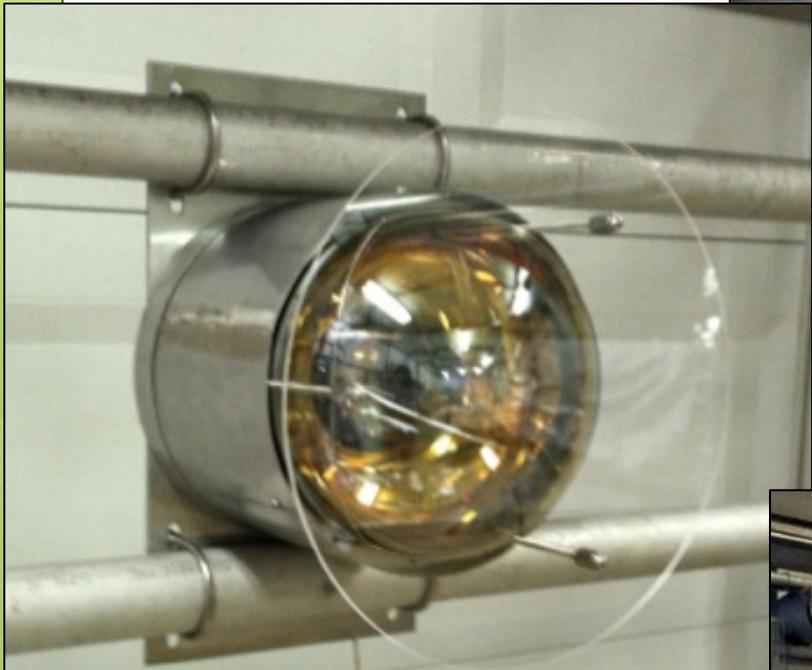
MicroBooNE Optical System

Cryogenic photomultiplier tube (PMT) assemblies





Handsome grad student in the recently opened cryostat



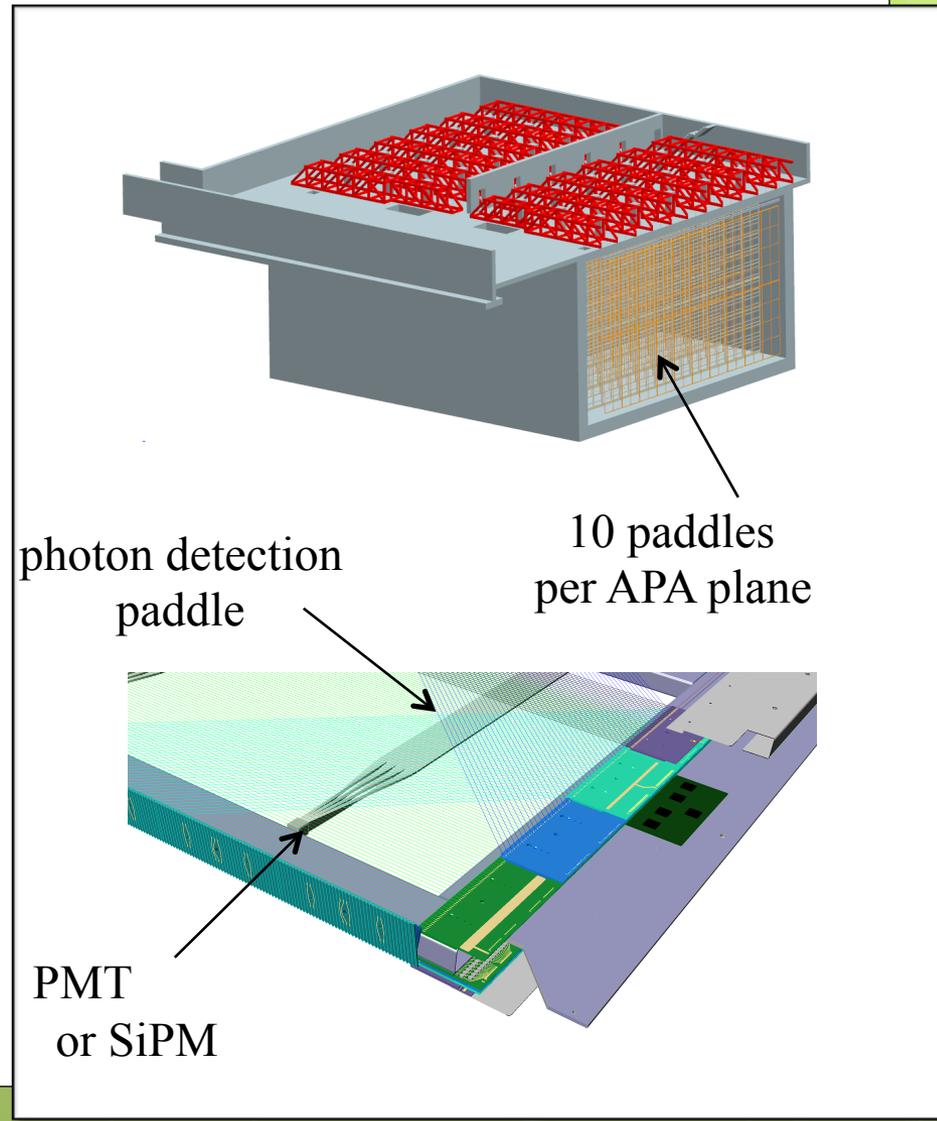
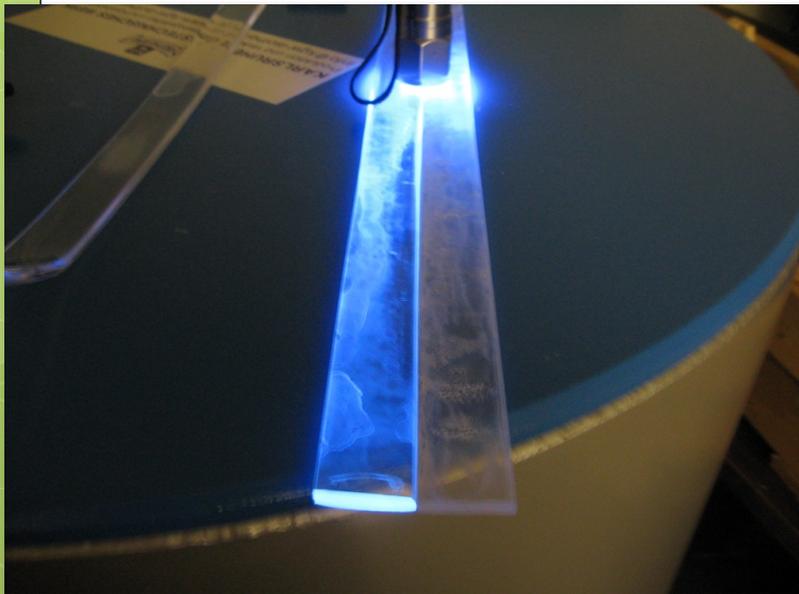
First mounted optical assembly



PMT rack installation test

LBNE Optical System

Long light guiding acrylic bars between wireplanes



photon detection paddle

10 paddles per APA plane

PMT or SiPM

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)



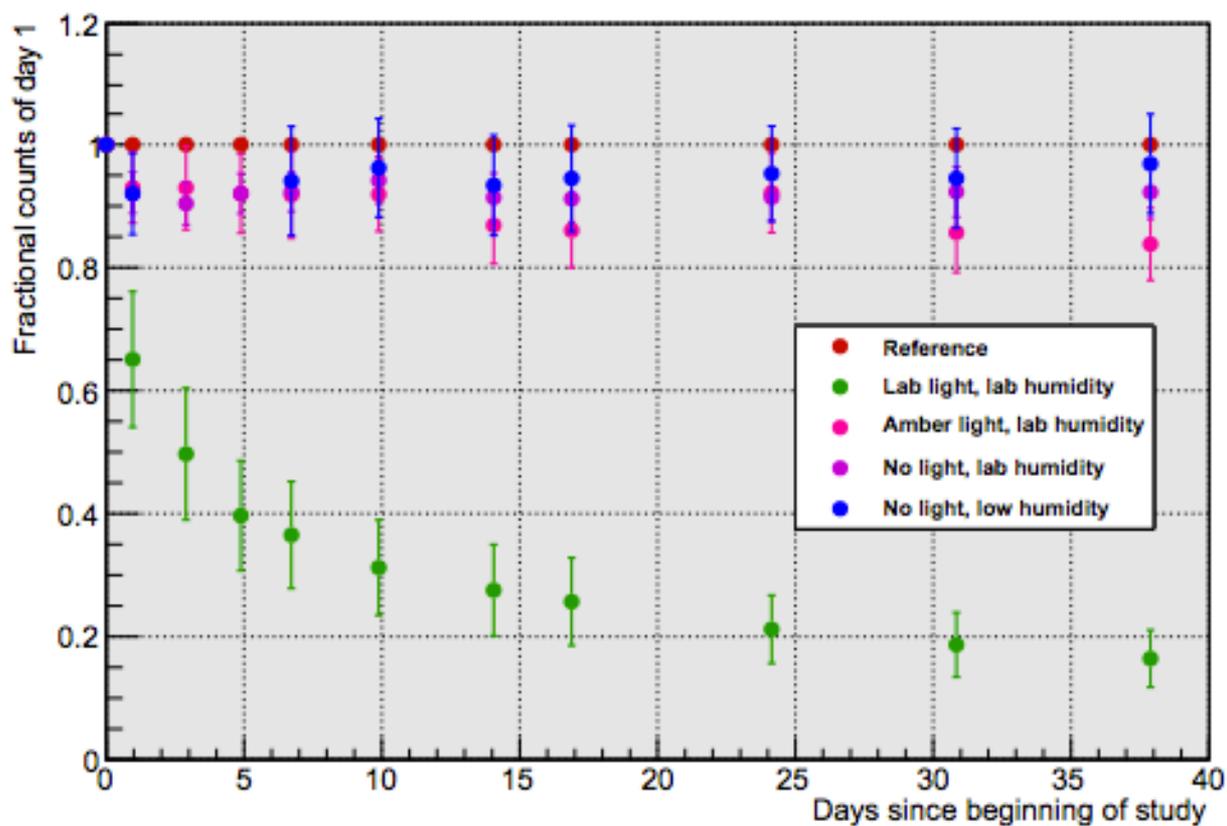
Figure 4: Left: Toluene and 99% TPB mixture exposed to light for three days. The initially clear mixture became yellow-green. Right: Powdered 99% pure TPB exposed to the SOLUX lamp for five days. The initially white powder became yellow.

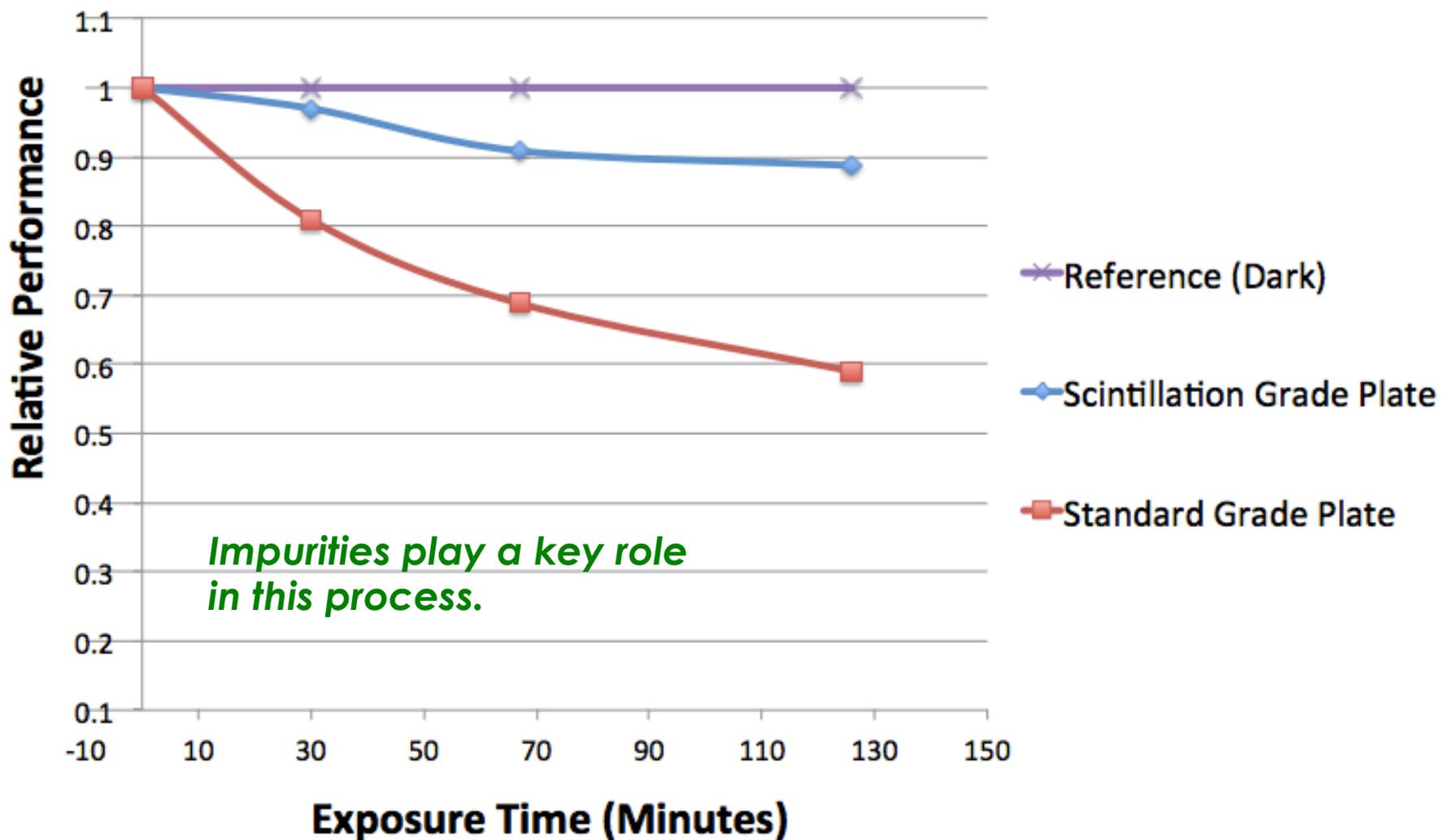
Environmental effects on TPB wavelength-shifting coatings

C.S. Chiu, C. Ignarra,¹ L. Bugel, H. Chen, J.M. Conrad, B.J.P. Jones, T. Katori and I. Moul

Journal of Instrumentation > Volume 7 > July 2012

C S Chiu et al 2012 JINST7 P07007 doi:10.1088/1748-0221/7/07/P07007





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

B.J.P. Jones,^{a,1} J.K. VanGemert,^b J.M. Conrad^a and A. Pla-Dalmau^b

^a*Massachusetts Institute of Technology,*

77 Massachusetts Avenue, Cambridge, MA 02139, United States of America

^b*Fermi National Accelerator Laboratory,*

PO Box 500, Batavia, IL 60510, United States of America

E-mail: bjpjones@mit.edu

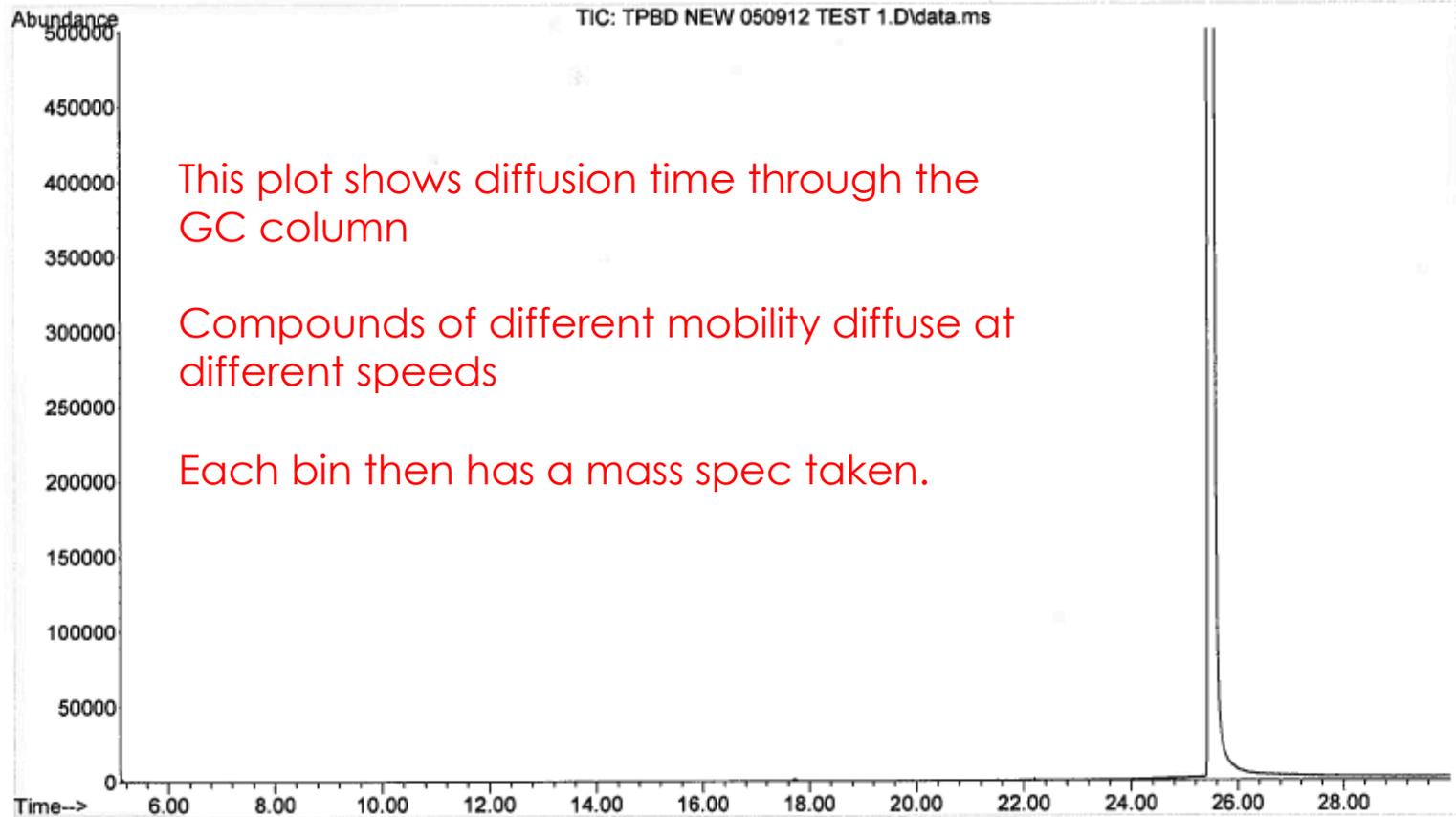
GCMS Studies

- Gas chromatography to separate ions of different mobility, followed by mass spectrometry
- In all cases, TPB peak is by far the dominant GC peak
- Impurities are visible to the GCMS at ppm levels.



WHITE TPB

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

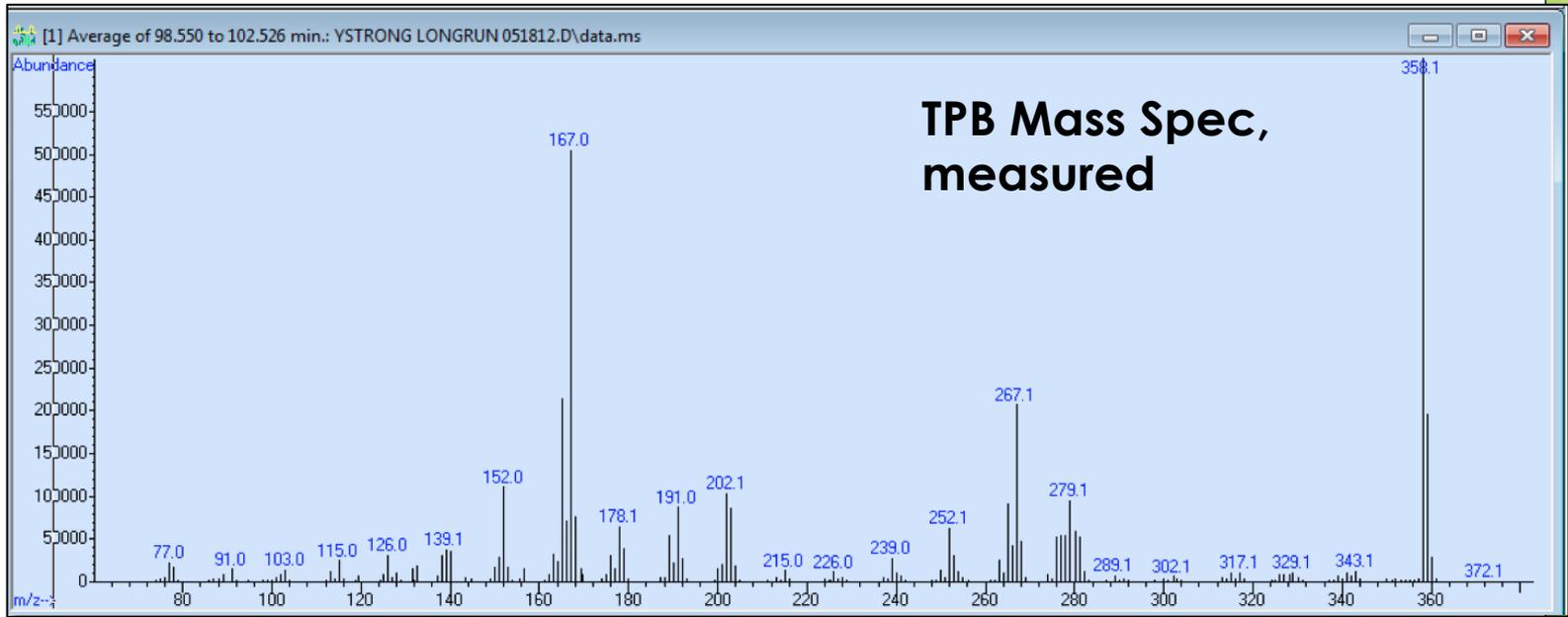
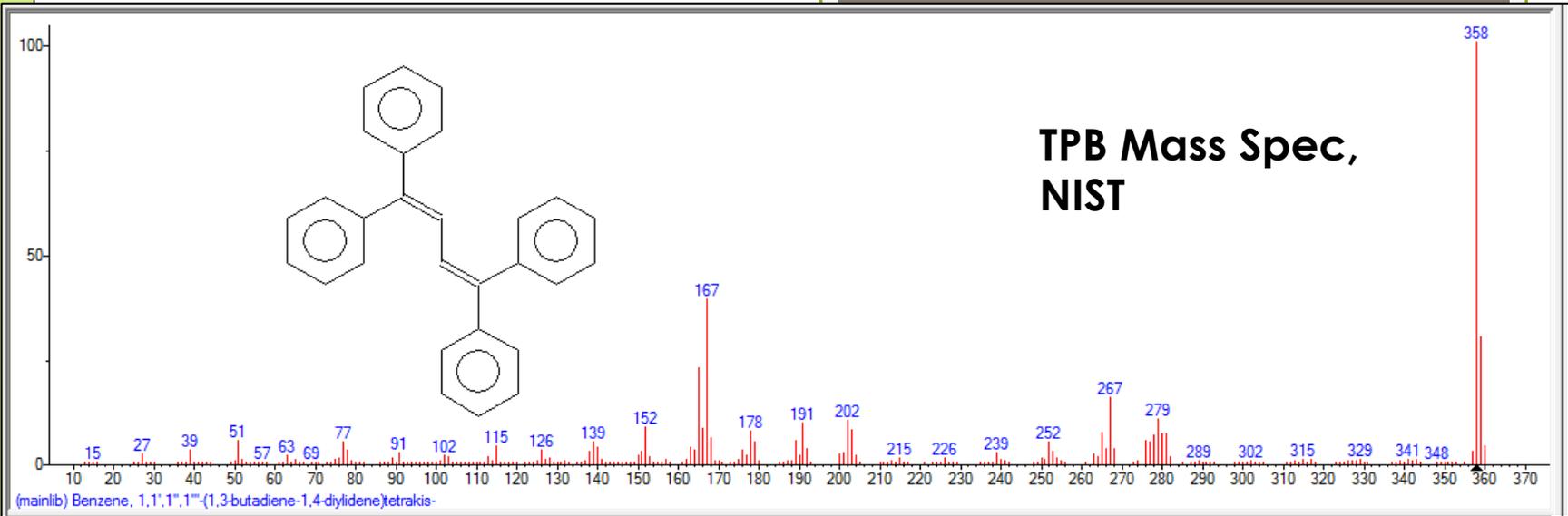


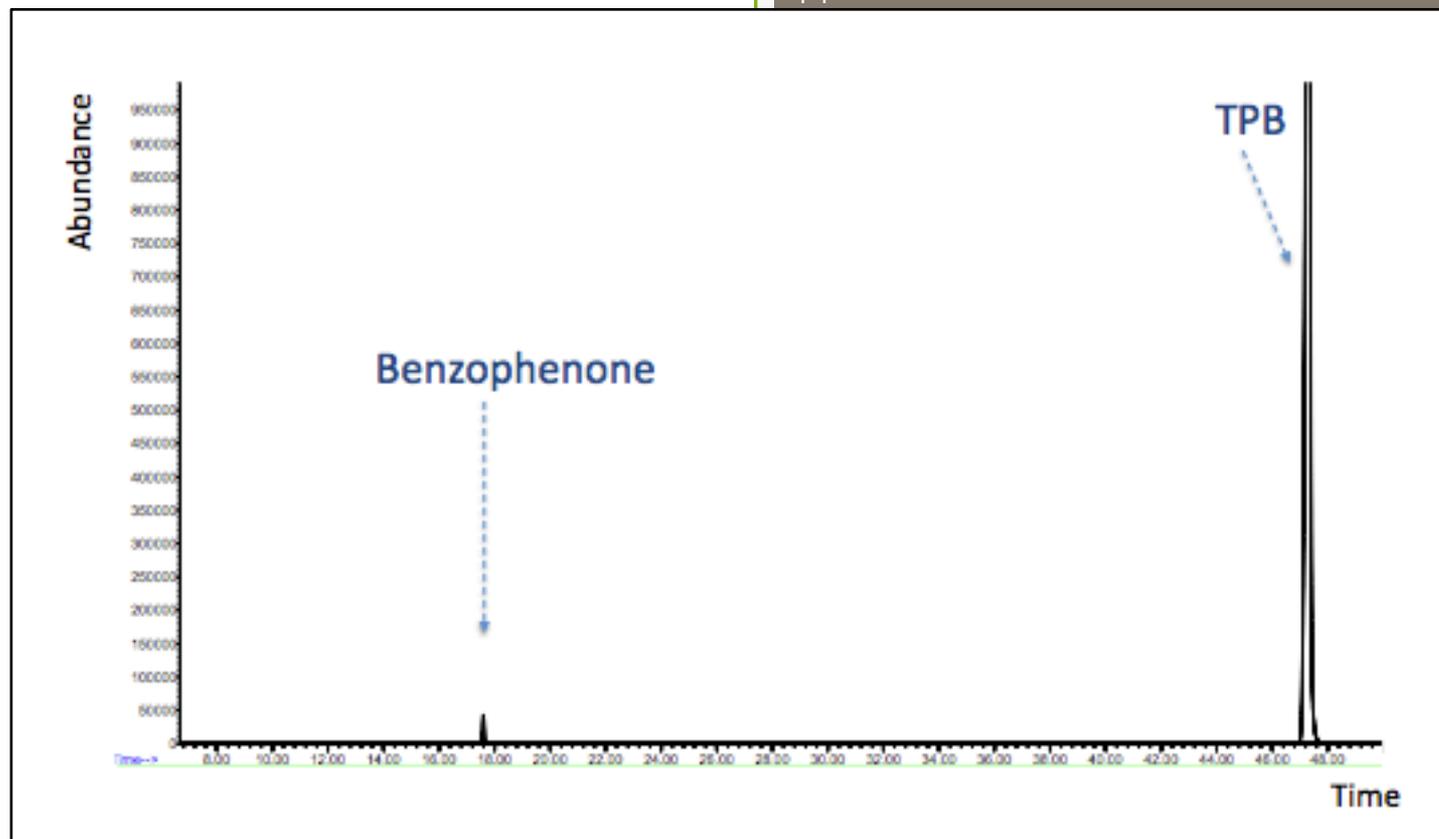
This plot shows diffusion time through the GC column

Compounds of different mobility diffuse at different speeds

Each bin then has a mass spec taken.

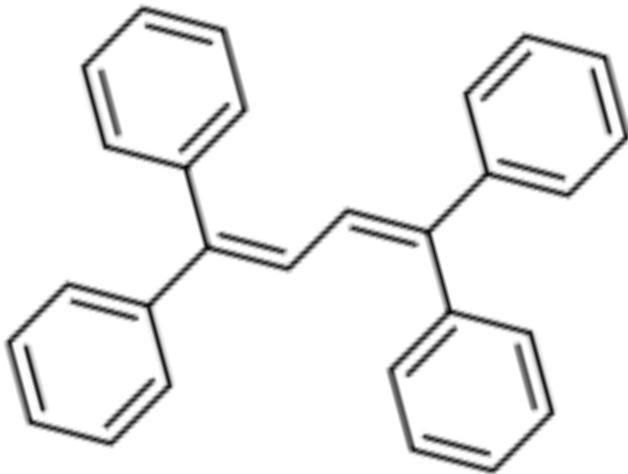
Diffusion Time ->



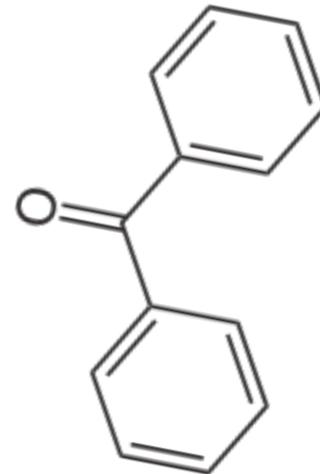


Sample	Benzophenone / TPB Peak Ratio
Scintillation Grade (Unexposed, White)	4.13×10^{-6}
Standard Grade (Unexposed, White)	8.43×10^{-6}
Standard Grade (Exposed, Yellow)	1.82×10^{-5}

TPB

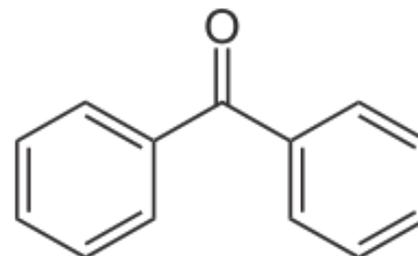


Benzophenone



Benzophenone

One of the only sensible oxidation products of TPB



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.

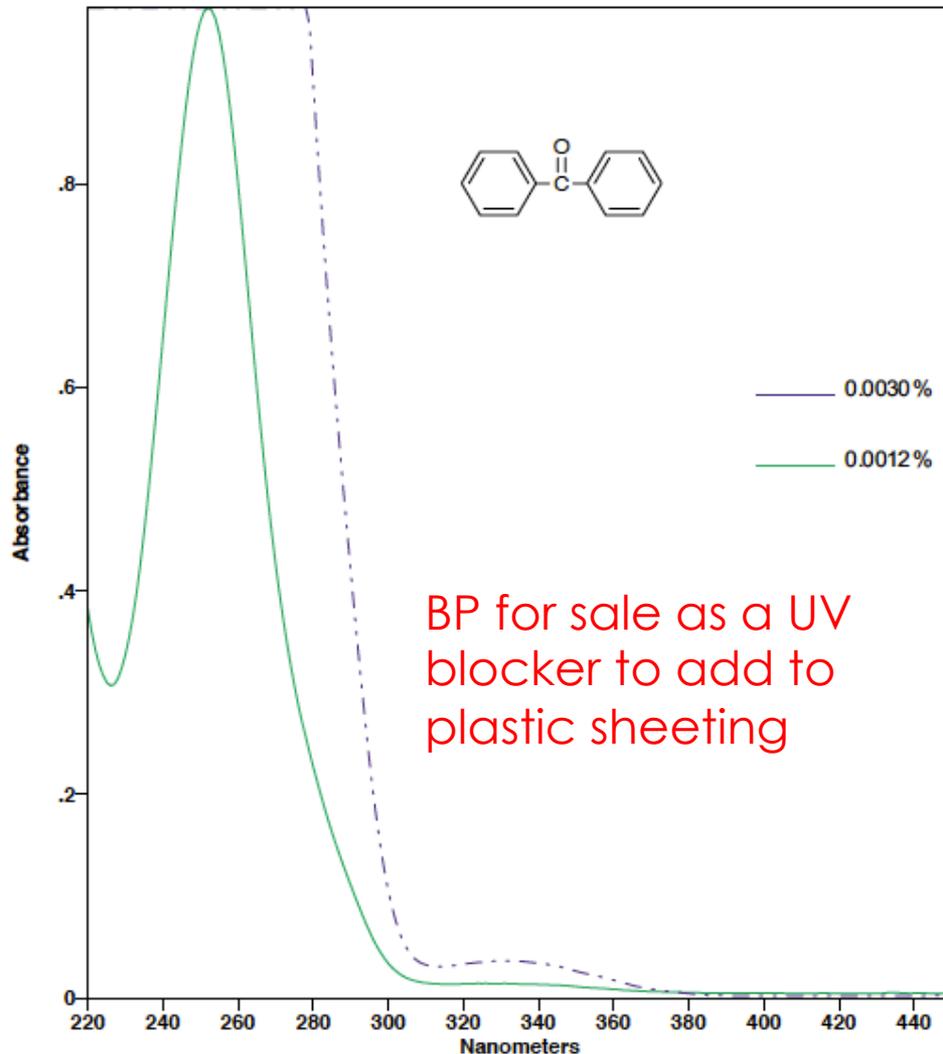
In biological applications, benzophenones have been used extensively as photophysical probes to identify and map peptide–protein interactions^[1].

See also

[\[edit\]](#)

- [Sunscreen](#)

B930-0 Benzophenone, 99%



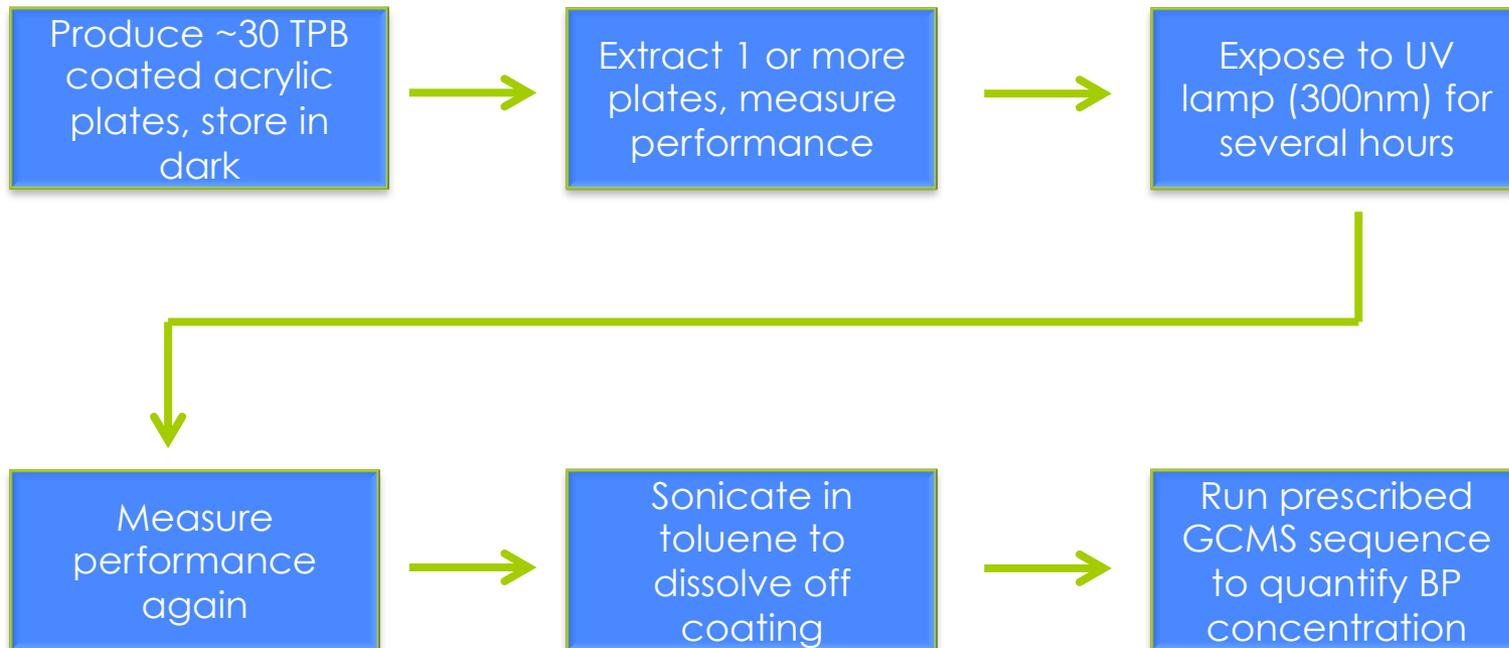
Photoinitiators: Classification

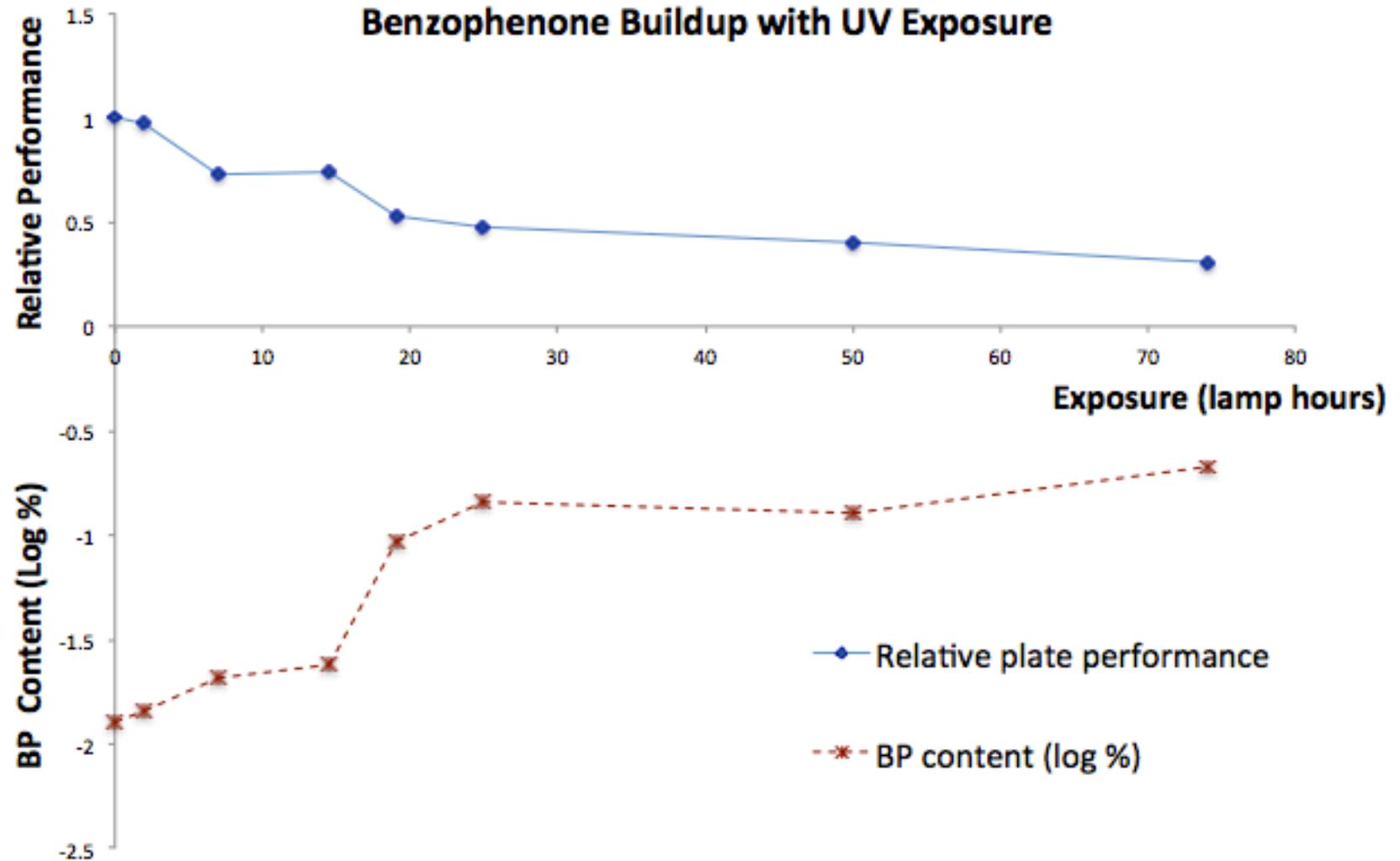
A photoinitiator is a compound especially added to a formulation to convert absorbed light energy, UV or visible light, into chemical energy in the form of initiating species, viz., free radicals or cations. Based on the mechanism by which initiating radicals are formed, photoinitiators are generally divided into two classes:

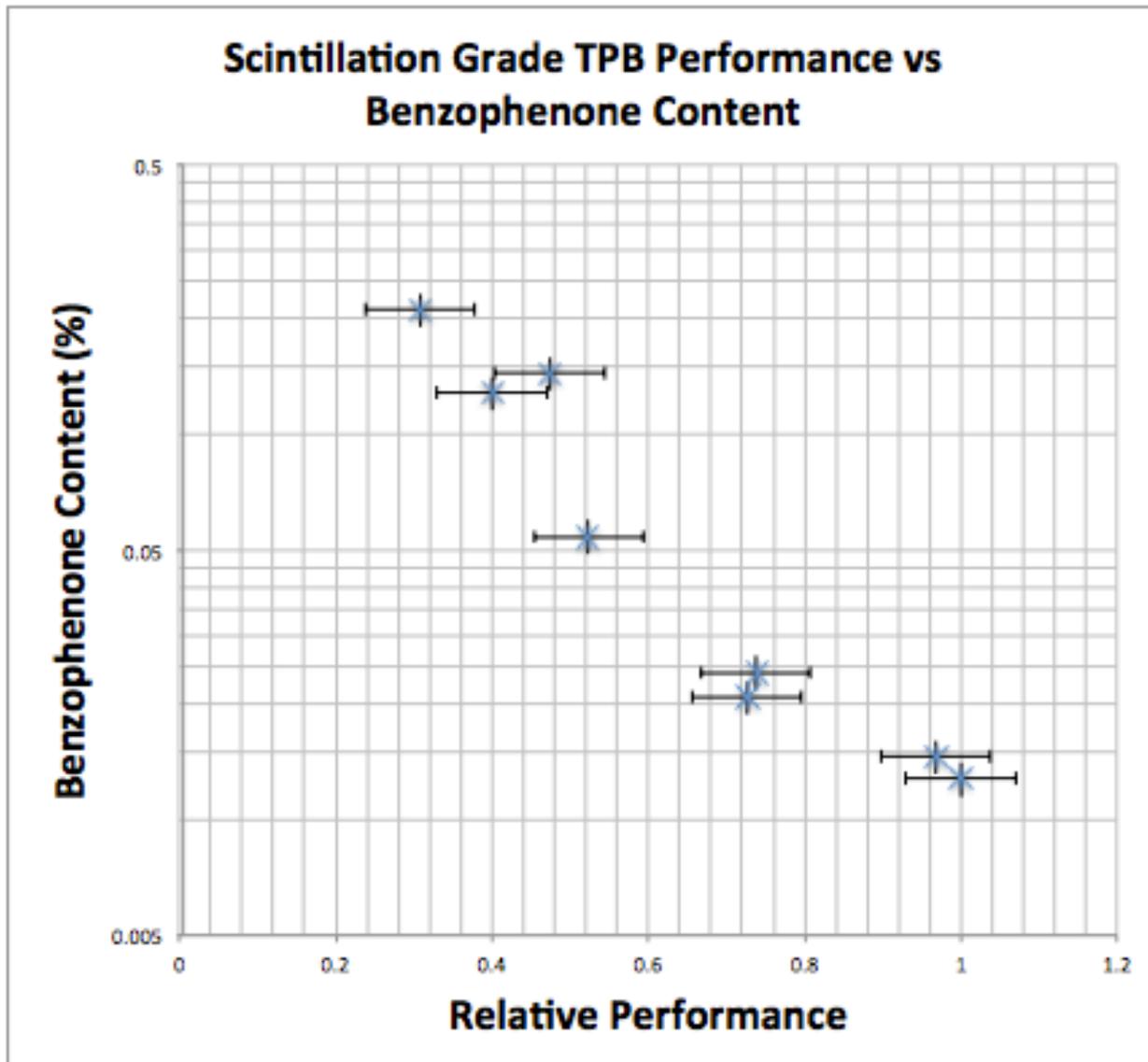
- Type I photoinitiators undergo a unimolecular bond cleavage upon irradiation to yield free radicals.
- Type II photoinitiators undergo a bimolecular reaction where the excited state of the photoinitiator interacts with a second molecule (a coinitiator) to generate free radicals.

UV photoinitiators of both Type I and Type II are available. However, visible light photoinitiators belong almost exclusively to the Type II class of photoinitiators. Table I summarizes the various classes of available Type I and Type II photoinitiators and their common applications.

Systematic BP buildup study



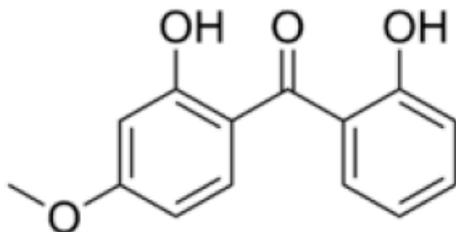




Yellowing?

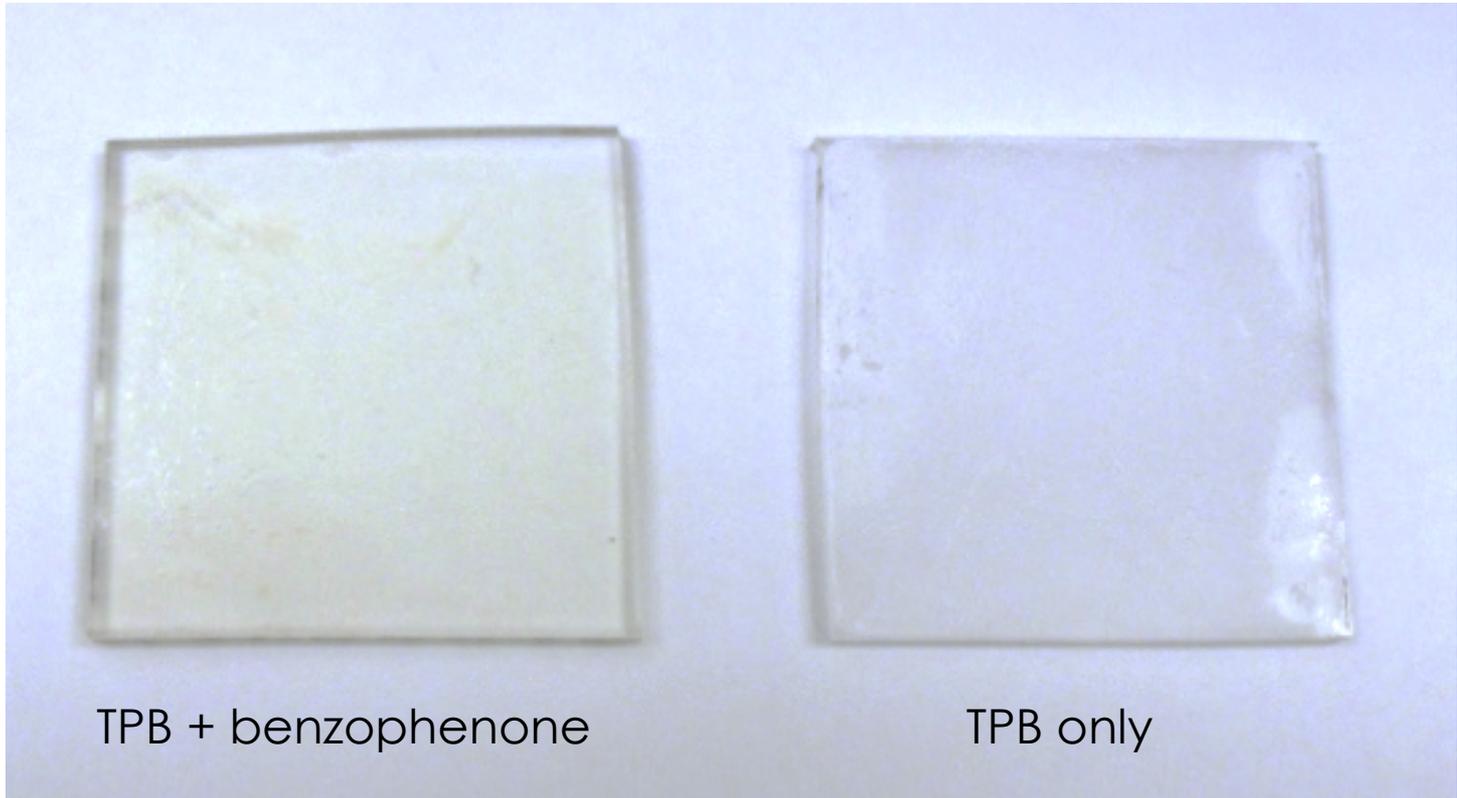
- BP is not yellow- so decay to BP does not explain yellowing in itself.
- Many of its simple derivatives are yellow, however.
- Possibly a second stage after BP production, to produce yellow BP derivatives?

Both of these very yellow and very UV blocking...



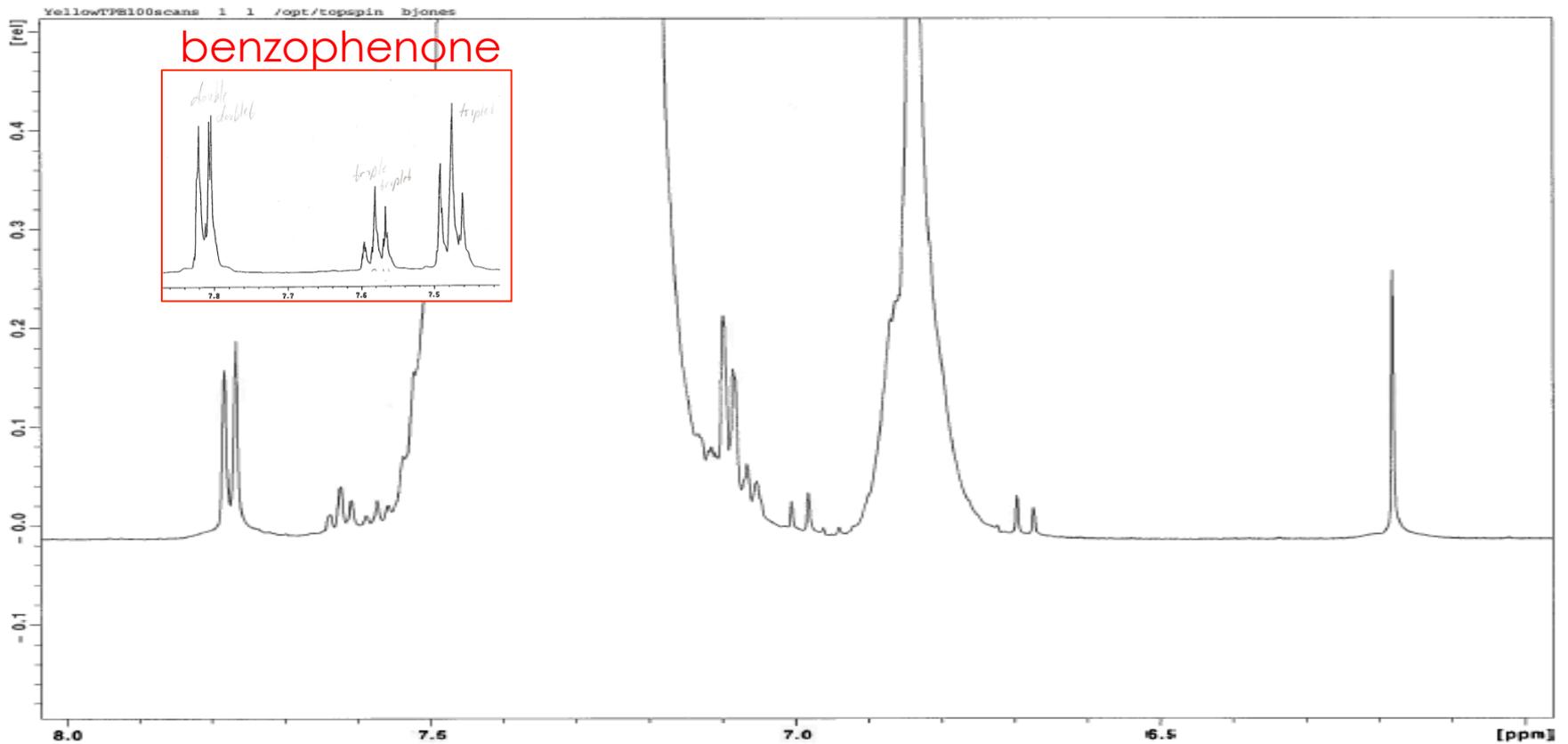

The image is a product advertisement for Uchem. It features a large yellow crystalline product on the left and a brown cylindrical container with a lid on the right. The text "uchem.en.alibaba.com" is overlaid on the product. Below the product is the chemical structure of 4-methoxy-2,6-dihydroxyacetophenone. At the bottom left are the ANAB and BSI certification logos. At the bottom right is the Uchem logo and the website address "www.uchem.com.cn".

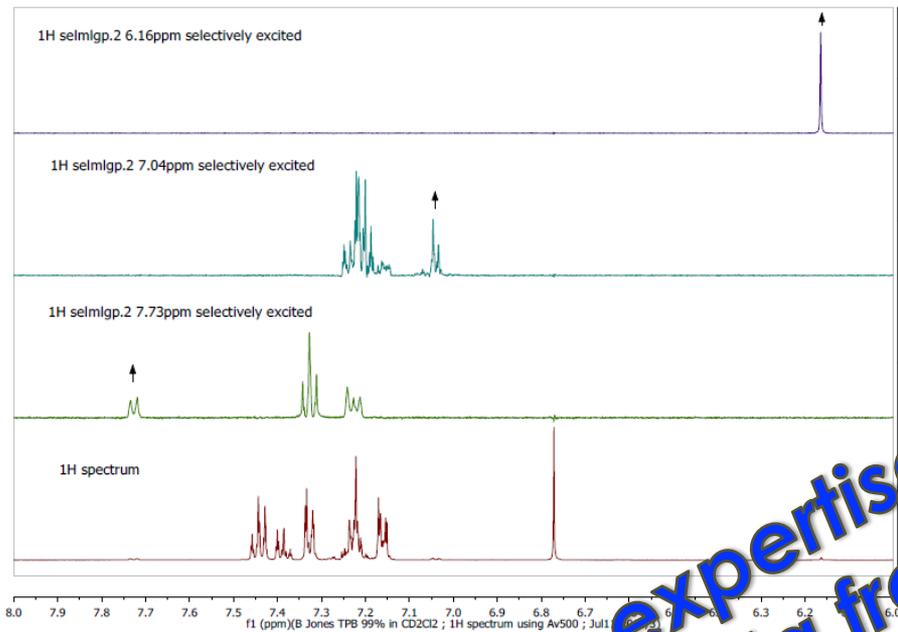
Impact of Added BP on Yellowing



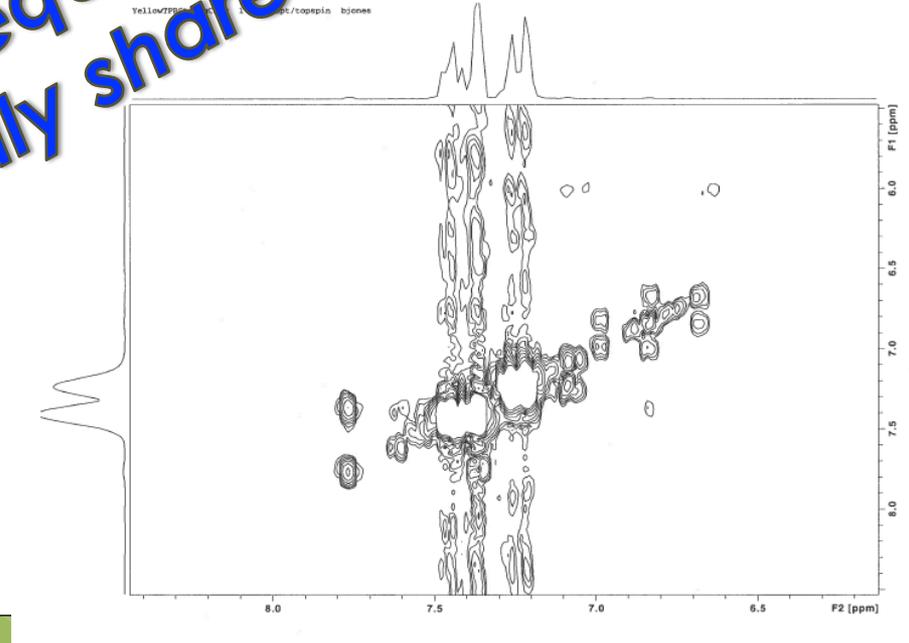
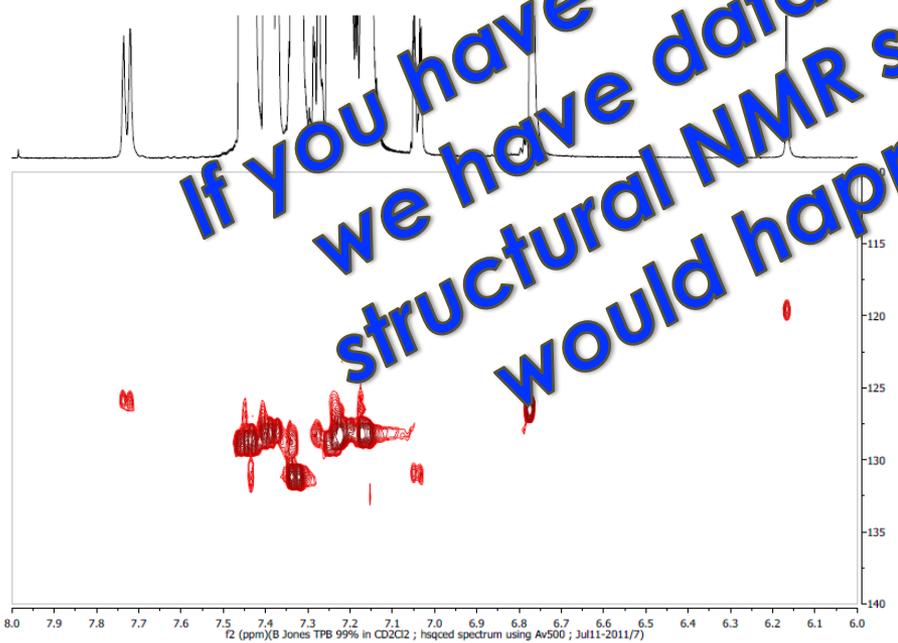
This observation supports the interpretation on the previous slide...

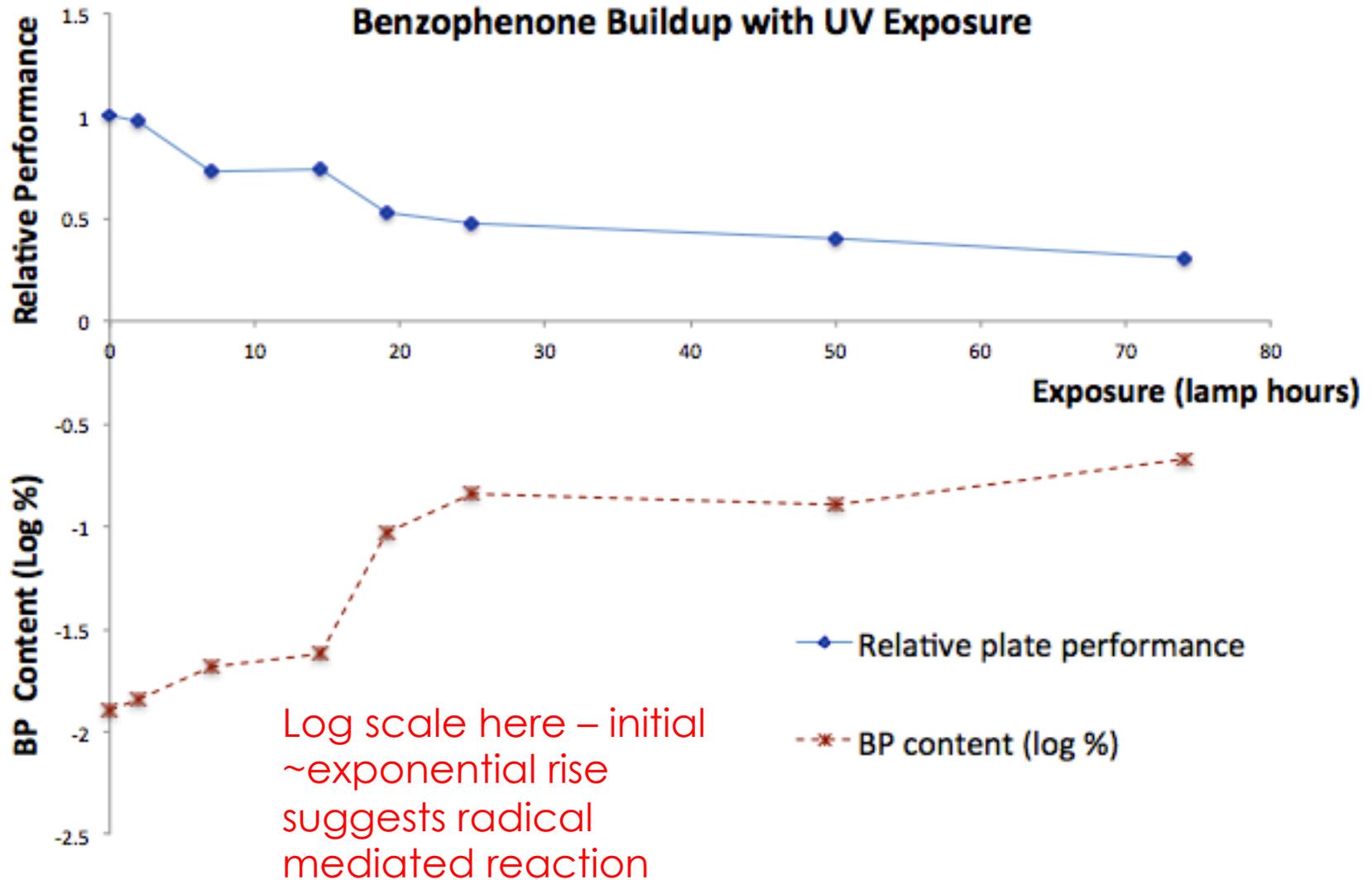
Hints at the Next Stage?





If you have expertise / care about this, we have data from many different structural NMR sequences which we would happily share with you!



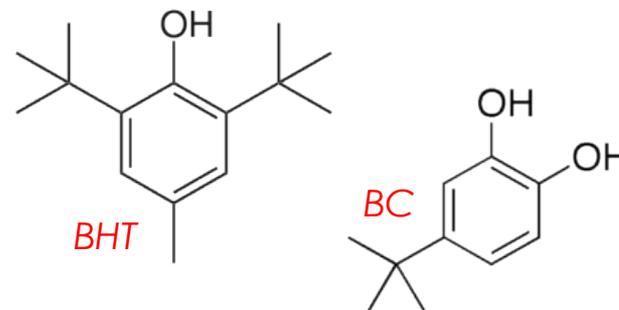


Terminating Radical Reactions

- Can we show more conclusively that this is a radical reaction? And can we stop it?
- Radical mediated decomposition is common in UV polymer degradation.
- Chain terminators sometimes added to end the radical chain reaction prematurely and protect polymers.

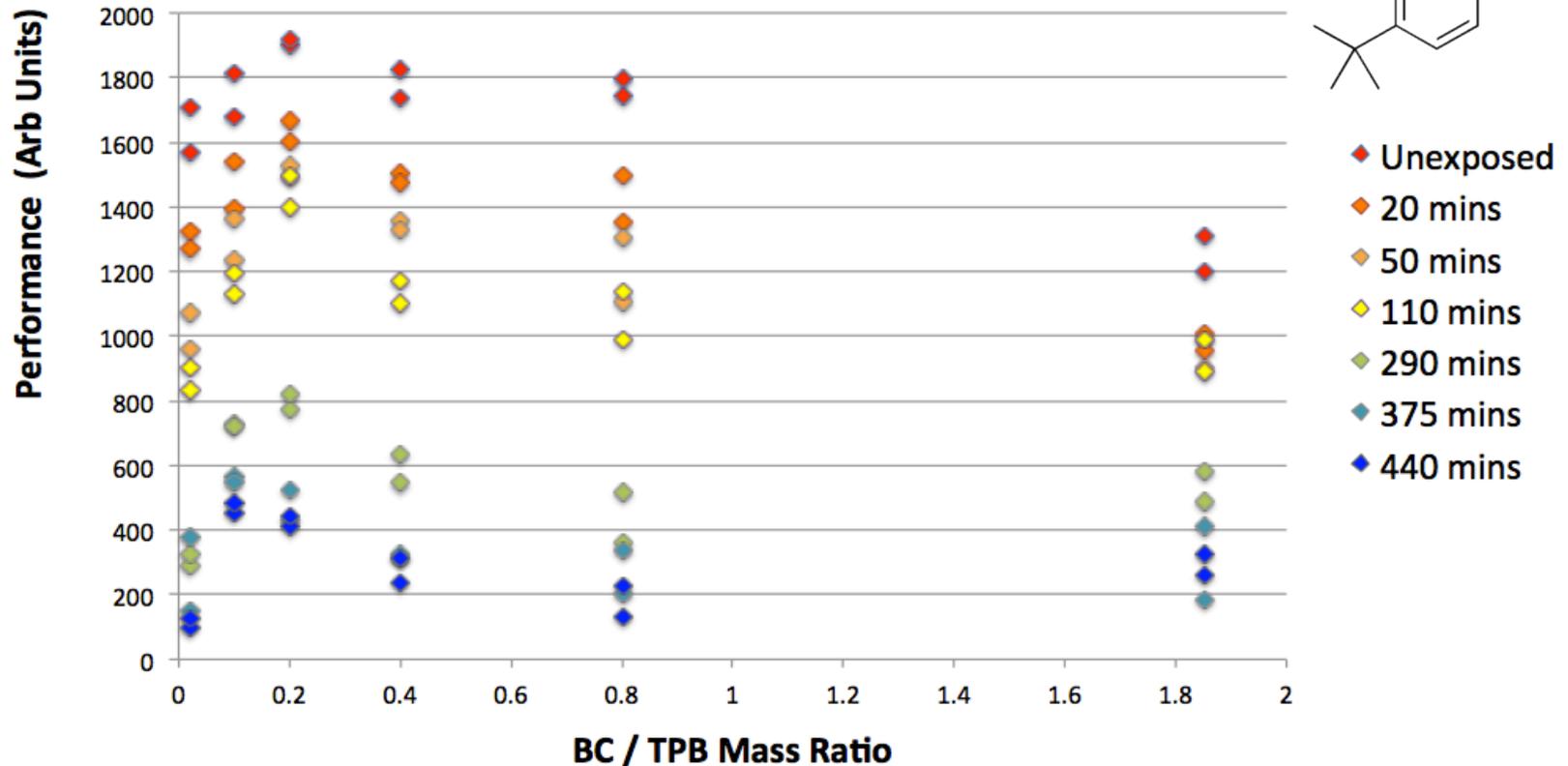
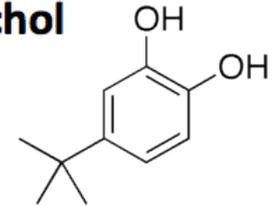
- We tried two common radical eaters:

- Butylhydroxytoluene (BHT)
- 4-tert Butylcatechol (BC)



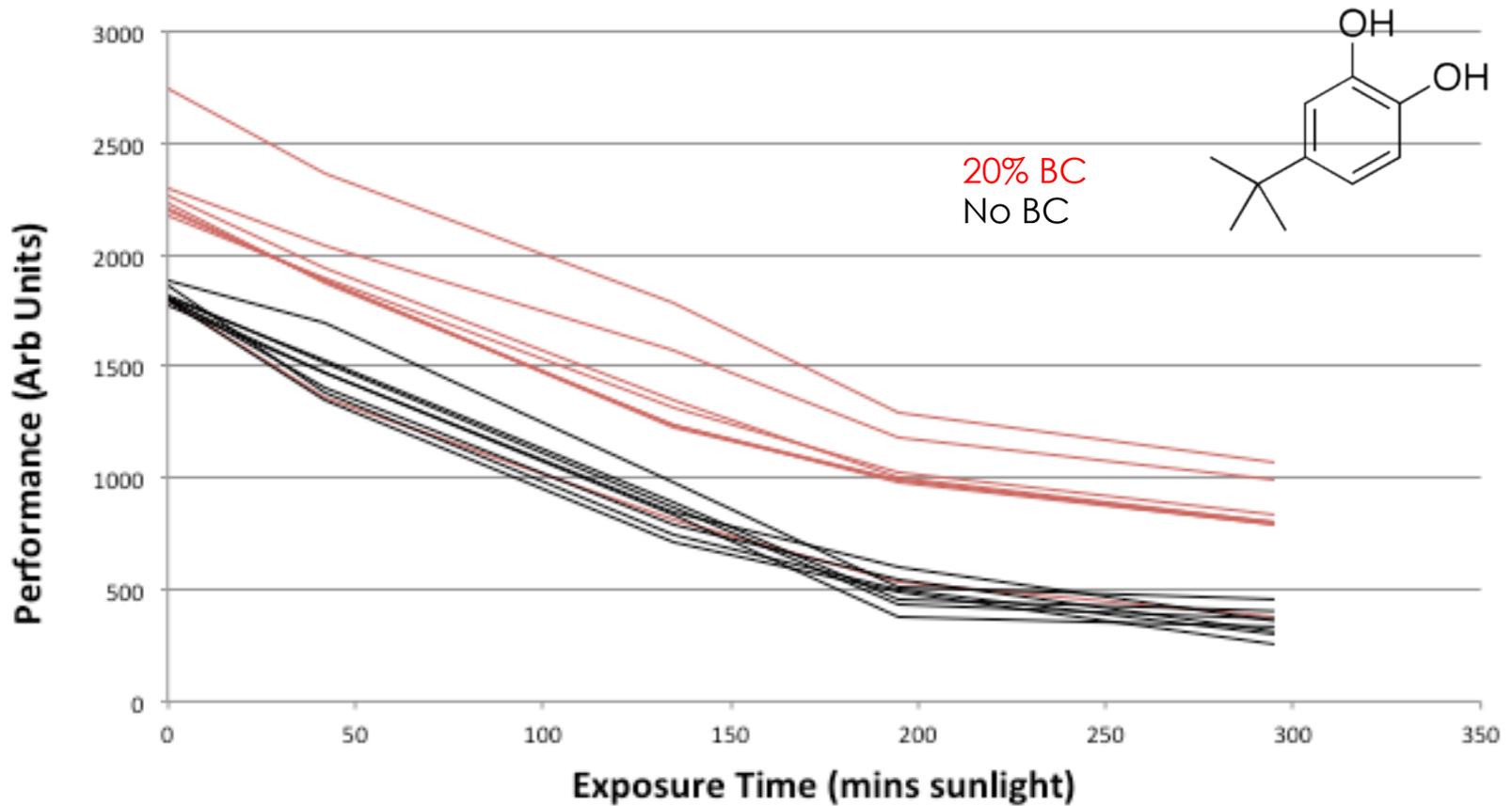
- If they slow down this reaction, confirmation that we see a radical mediated photo-oxidation.

Degradation of Plates with Different 4-Tert Butylcatechol Concentrations



- Best improvement in initial performance for 20% BC by mass
- Best improvement in lifetime for 10% BC by mass

Performance of Improved Lightguide Coating



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.
- Yellowing also connected to BP, likely production of derivatives in a second stage reaction – precise decay products not identified, but hints seen in NMR.
- Coatings can be stabilized by removing radicals – maybe someone can suggest “the killer compound”...