New NMR Applications for Old Spectroscopic Techniques:

Detection of Lignin-Quinone Structures by ^{31}P-NMR

Michael Zawadzki, Arthur Ragauskas

Overview

- Goals
- Lignin-Chromophores
- Quinone Analysis: Trimethylphosphite Chemistry
- Quinone Contents of Pulps
- Bleaching Chemistry
- Conclusion

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Goals

- Understand Brightness Development & Brightness Ceiling Formation

- Determine Lignin Structures which Negatively Impact Brightness Development

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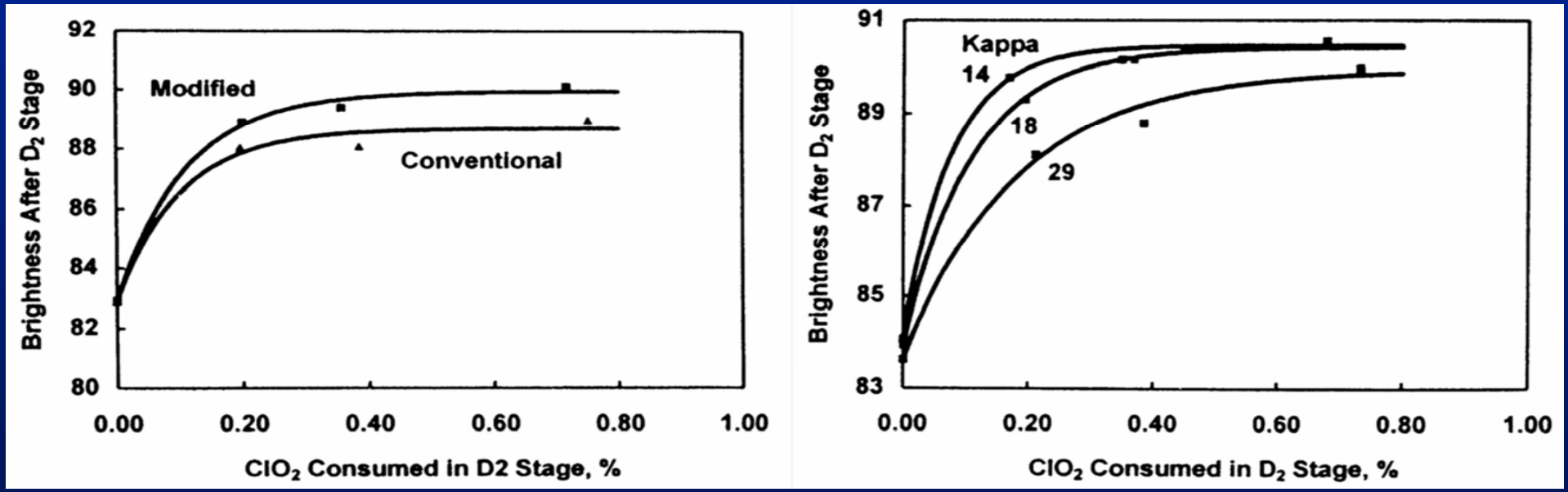
Lignin Structure May Impact Brightness Development



McDonough, TAPPI Pulping Conference 1996

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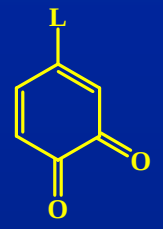
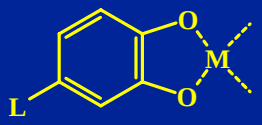
Possible Chromophoric Structures

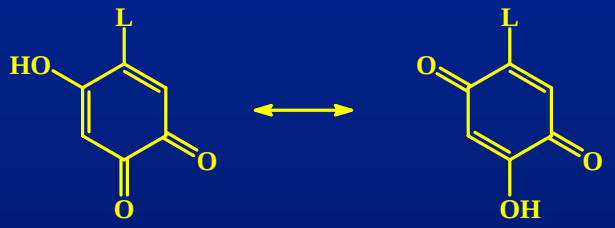


Ortho-Quinone

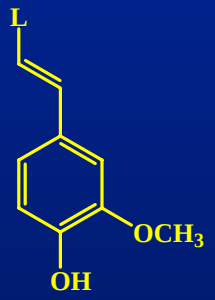
Para-Quinone



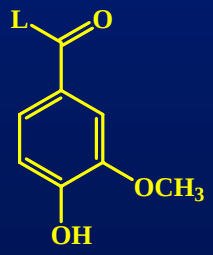
Catechol-Metal Complex



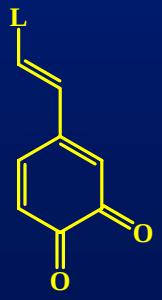
Hydroxy-Quinone



Stilbene or Enol Ether



Alpha-Carbonyl



Stilbene-Quinone

(Conjugated Carbonyl, Aromatic, Furan Derivatives)

Carbohydrate Derived

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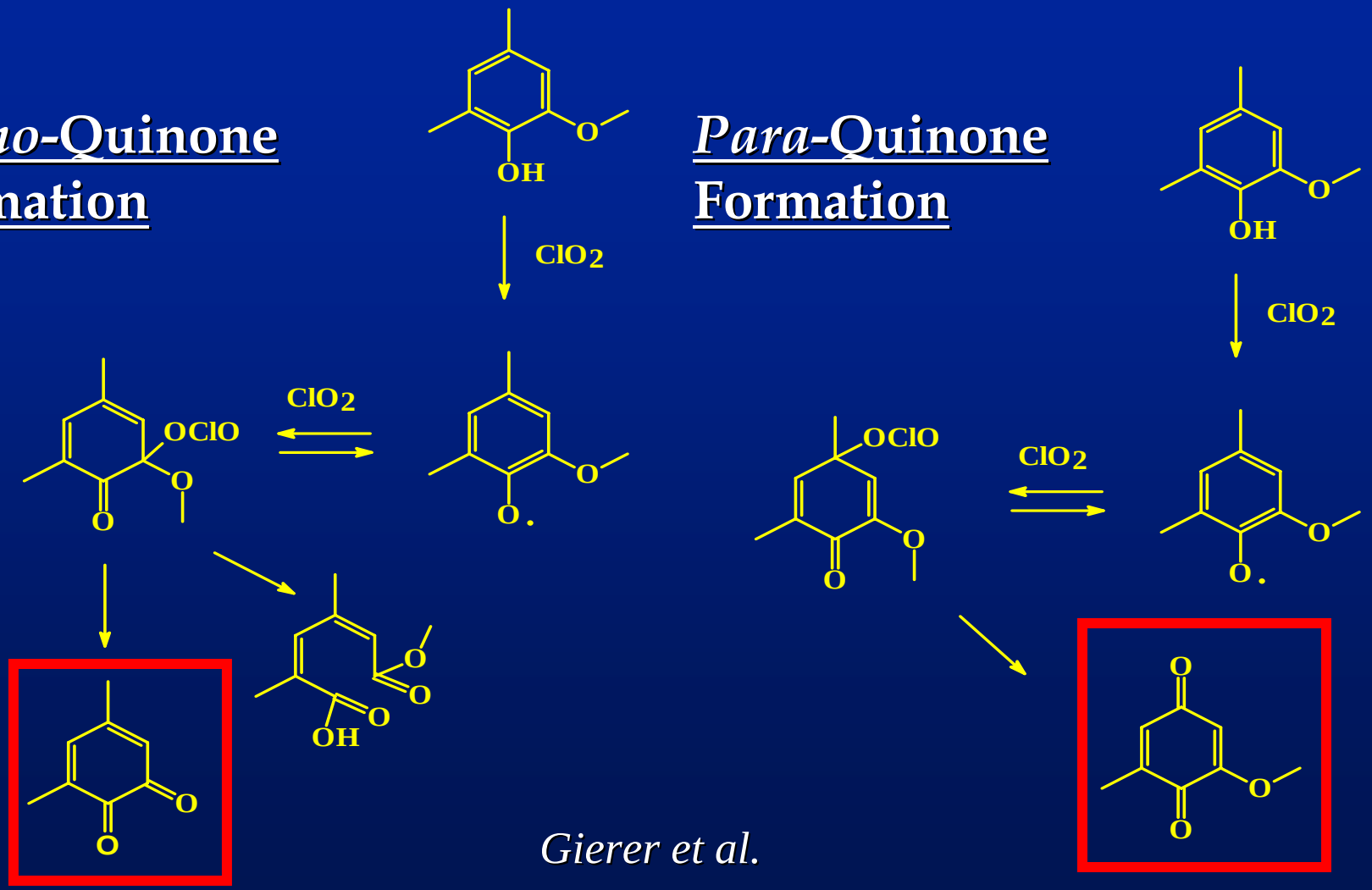
Chlorine Dioxide Bleaching Chemistry



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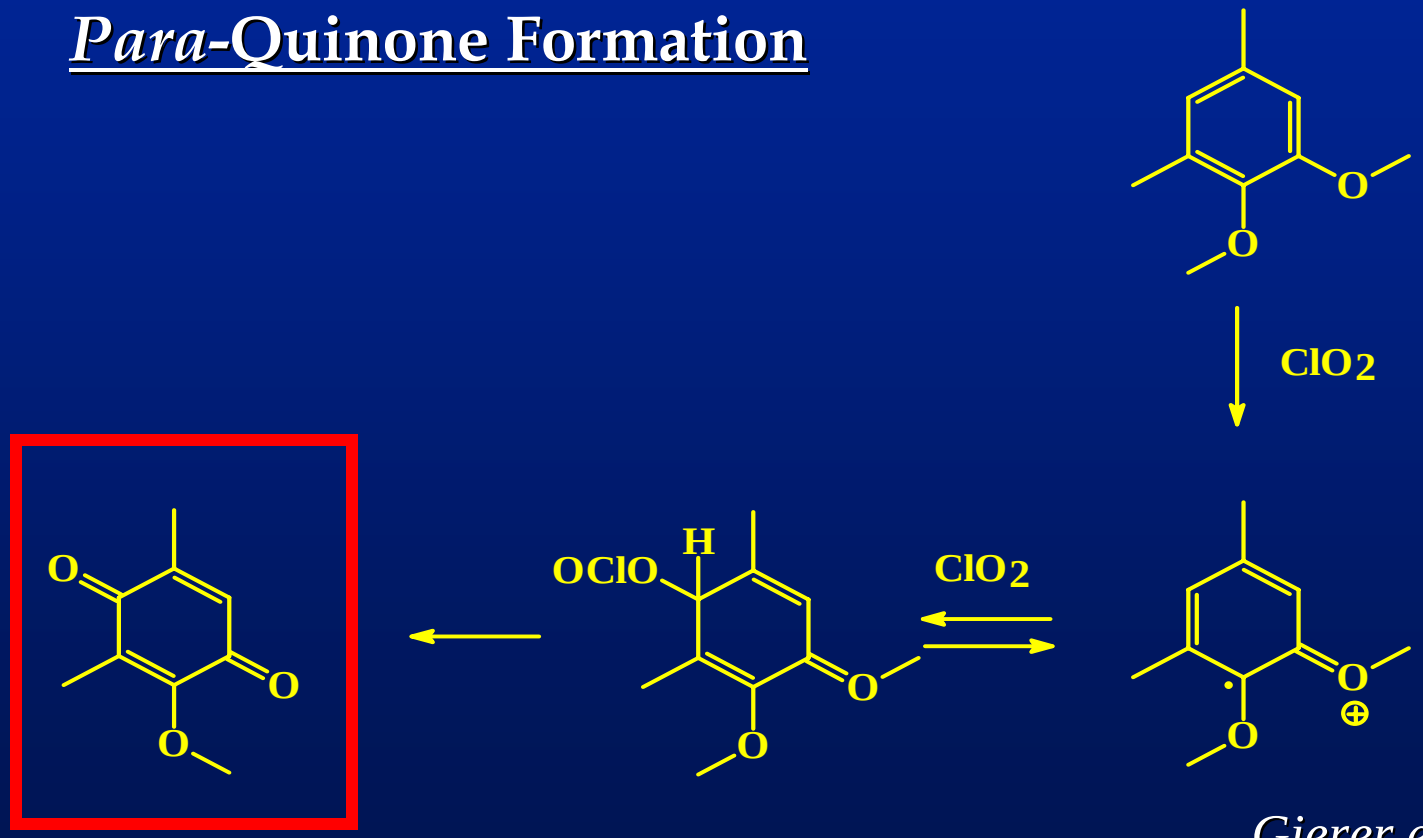
Chlorine Dioxide Bleaching Chemistry

Para-Quinone Formation



Gierer et al.

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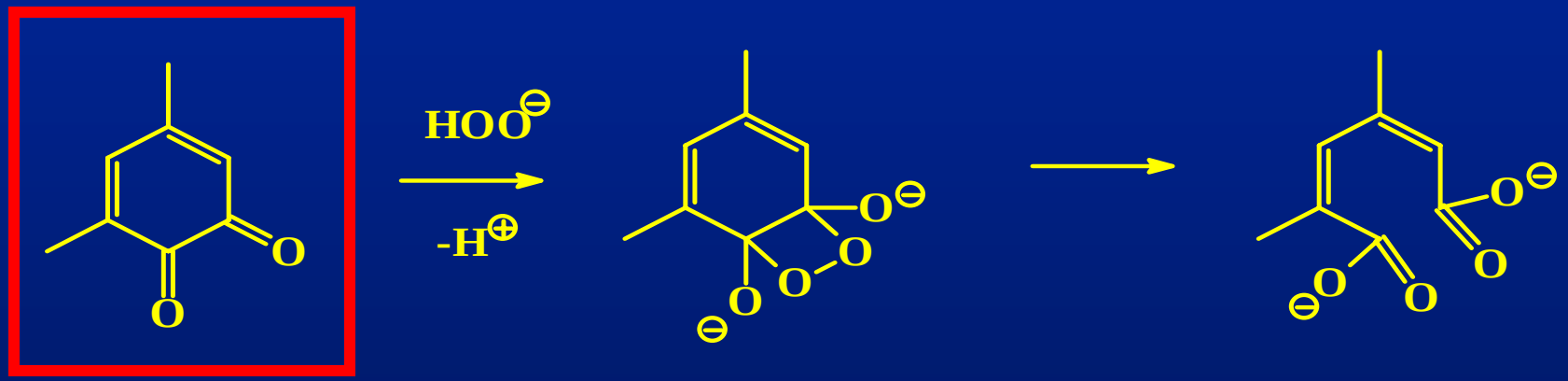
Hydrogen Peroxide Chemistry: Quinone Degradation



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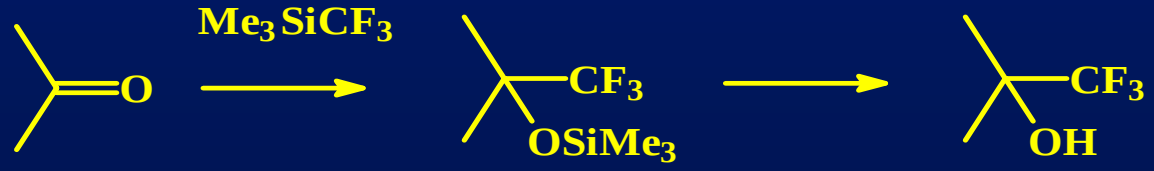
Quinone Analysis Methods

- **Reduction (Zakis *et al.*)**

- **Aryl-hydrazine (Sevillano *et al.*)**

- **Ruppert's Reagent (Ahvazi *et al.*)**



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Quinone Analysis Methods

- **Phenylenediamine (Zhu *et al.*)**

- **Trialkylphosphite (Konya and Scaiano)**

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Method Selected for this Study: Trimethylphosphite & ^{31}P-NMR

- **Chemistry: Ramirez**
- **Mechanical Pulp: Lebo & Argyropoulos**
- **Recent Lignin Application: Zawadzki, Argyropoulos**
- **Model Compounds: Medvecz, Gellerstedt, Argyropoulos, Zawadzki**

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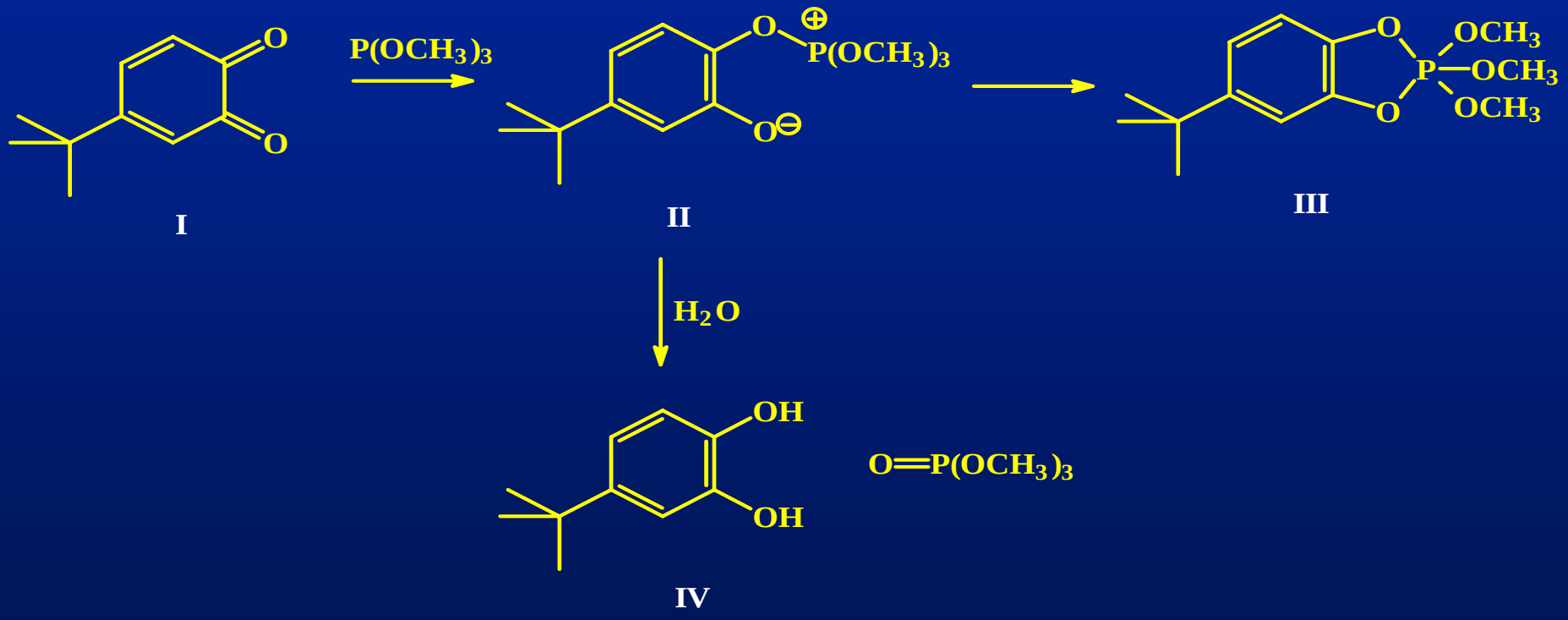
Trimethylphosphite Chemistry:
Reaction with Ortho-Quinone Structures



Ramirez et al., Sidky et al., & Medvecz

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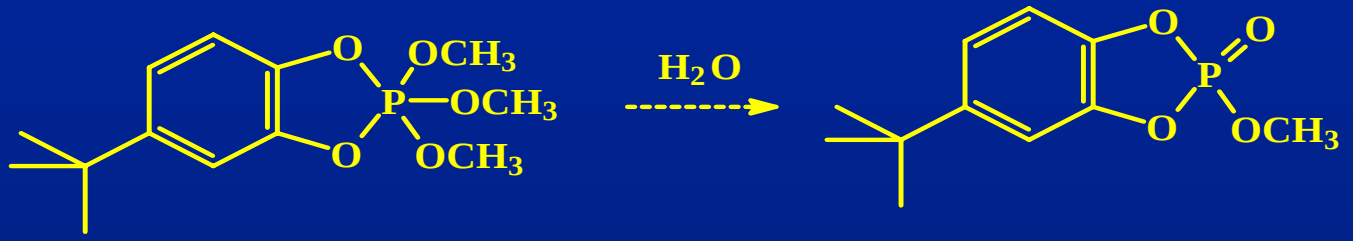
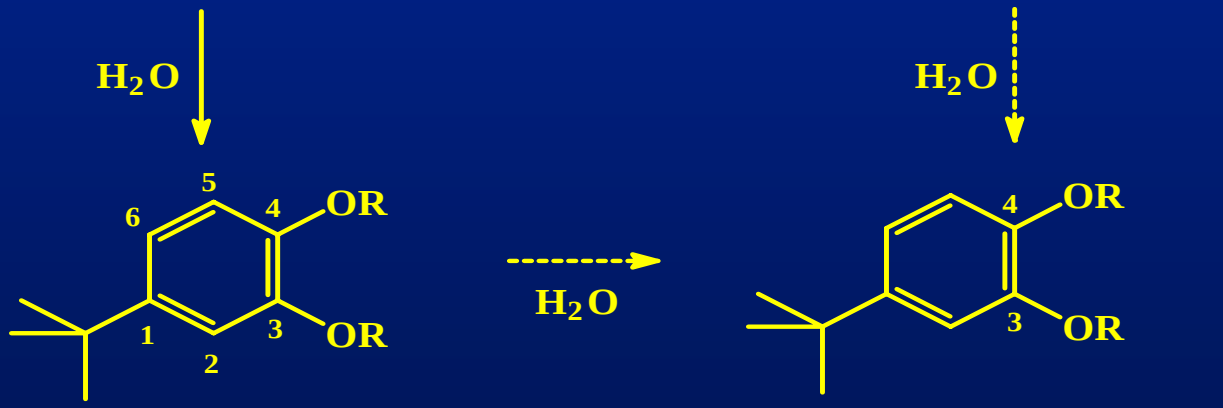
Trimethylphosphite Chemistry:
Benzodioxaphospholene Hydrolysis



II (-45.4 ppm) **III**



R = $PO(OCH_3)_2$ or H **R = $PO(OCH_3)(OH)$ or H**

IV a,b (-2.3, -2.6 ppm) **V a,b**

Ramirez et al.

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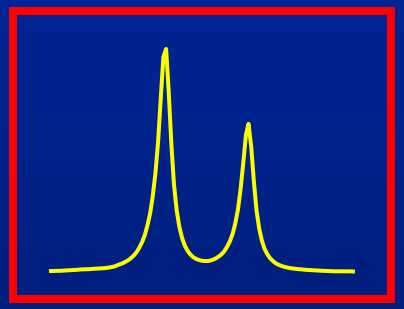
^{31}P-NMR spectrum:

4-tert-Butyl-1,2-Benzoquinone
(1) Trimethylphosphite (2) Hydrolysis



-2.3 & -2.6 ppm

Quinone Adduct

Internal Standard

0 -5 -10 -15 ppm

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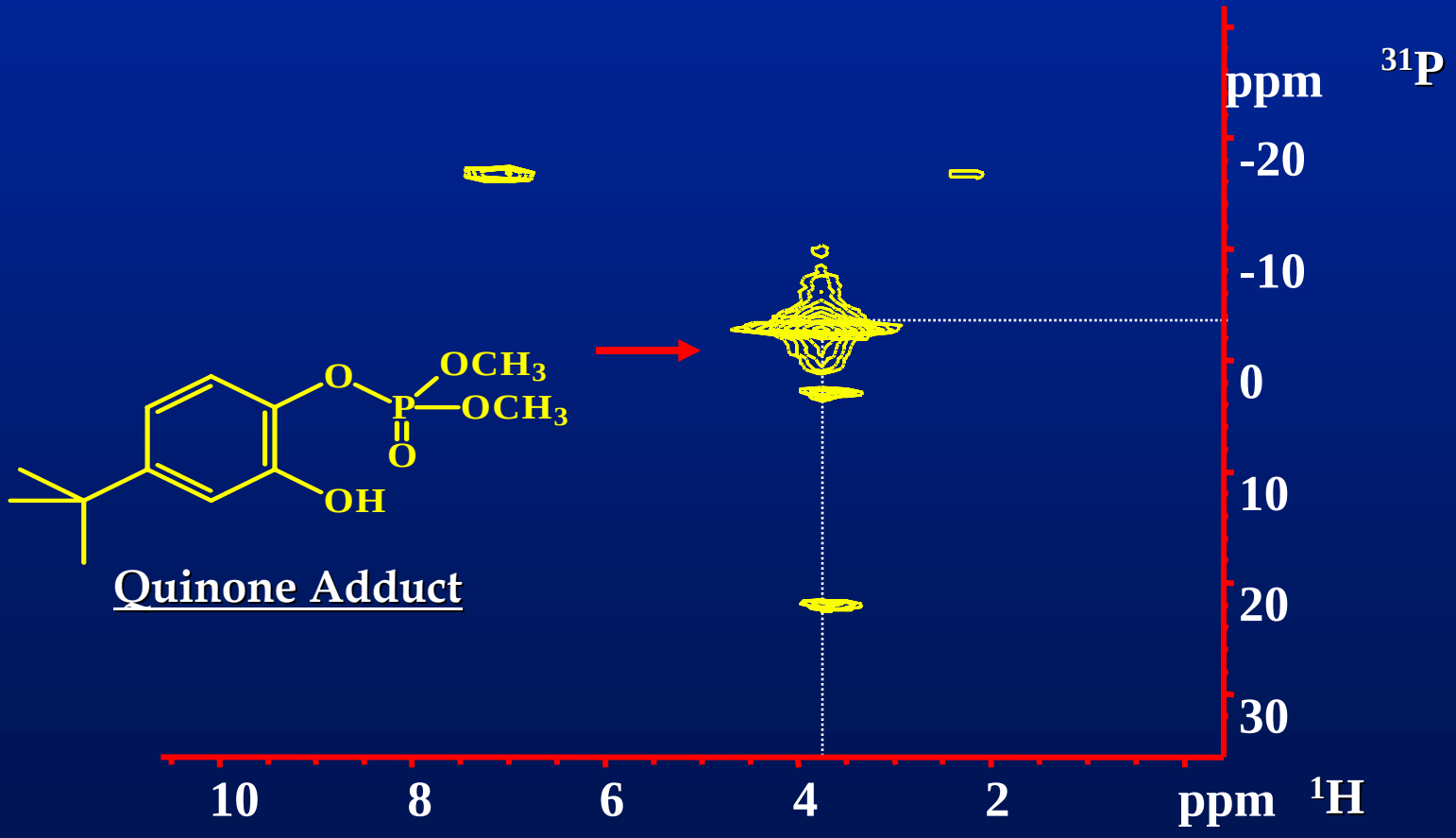
^{31}P-^{1}H COLOC spectrum:

4-tert-Butyl-1,2-Benzoquinone

(1) Trimethylphosphite (2) Hydrolysis



Quinone Adduct

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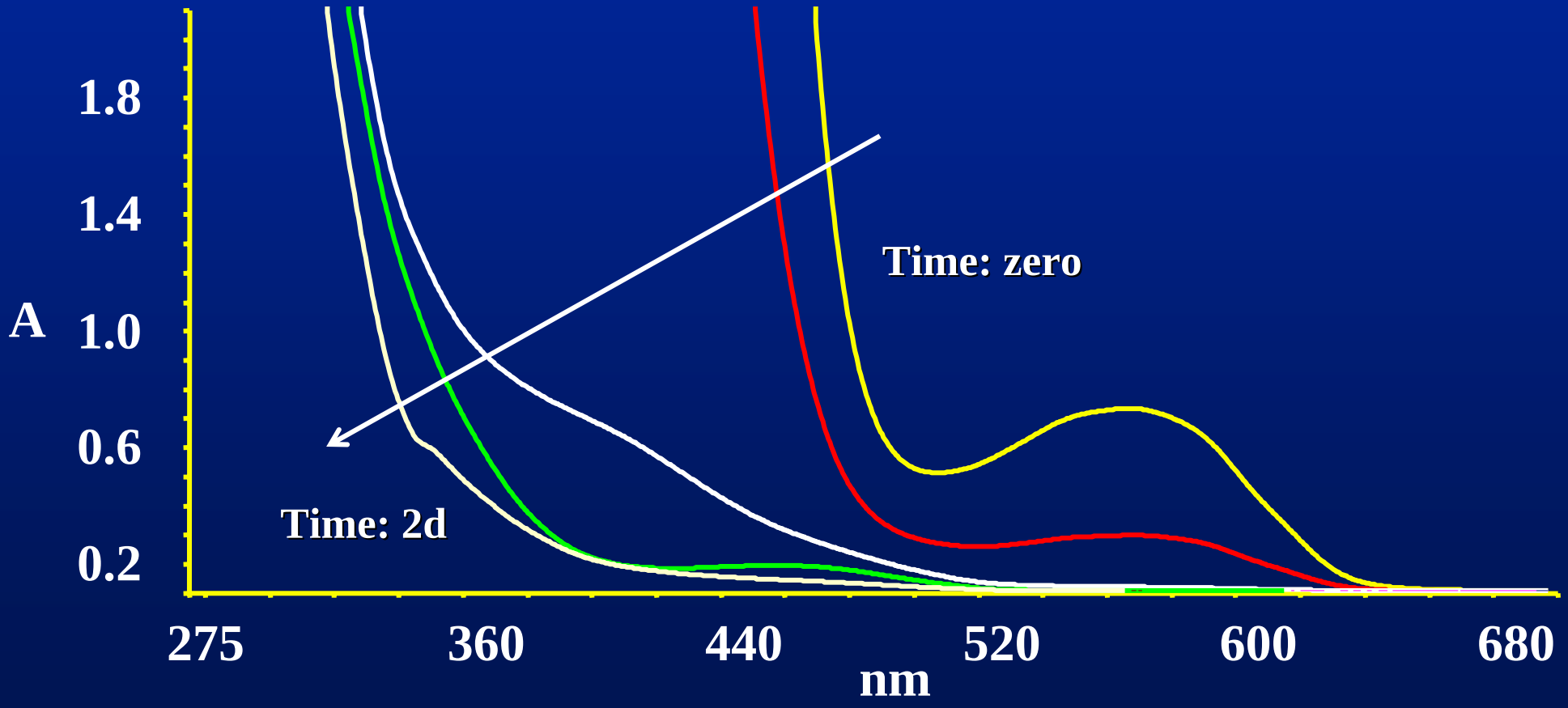
Trimethylphosphite Reaction with 4-t-Butyl-1,2-Benzoquinone monitored by Visible Spectroscopy



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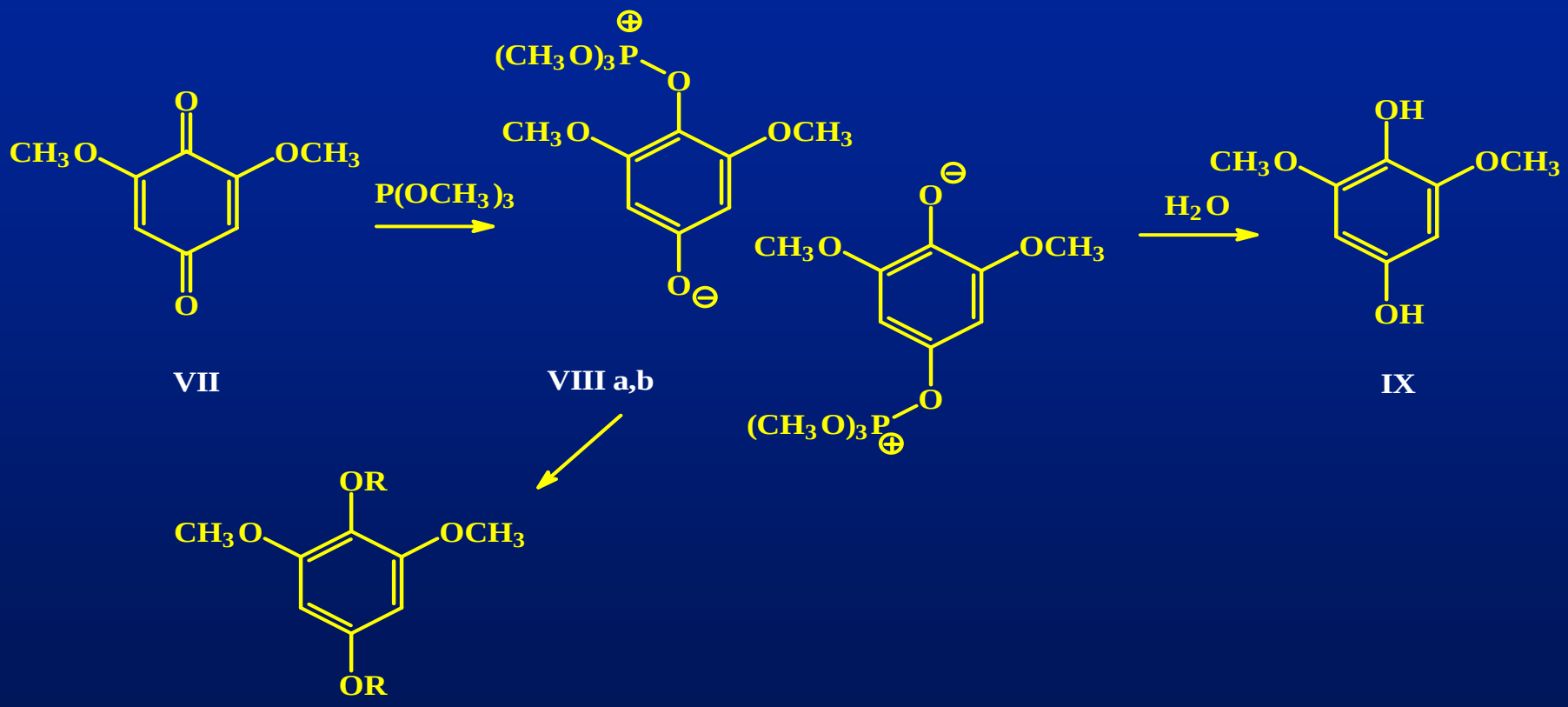
Trimethylphosphite Chemistry:
Reaction with Para-Quinone Structures



VII **VIII a,b** **IX**

R = $PO(OCH_3)_2$ or CH_3 or H

IX a,b (-1.6, -1.7 ppm)

Ramirez et al., Sidky et al.

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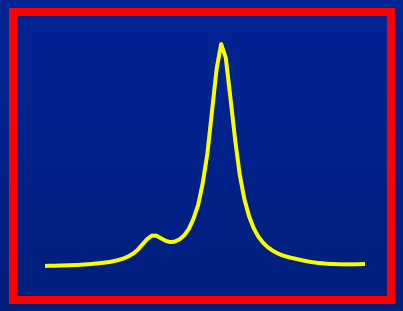
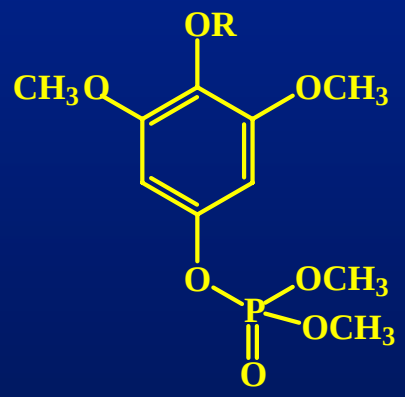
^{31}P-NMR spectrum:

2,6-Dimethoxy-1,4-Benzoquinone
(1) Trimethylphosphite (2) Water Addition



-2.3 & -2.6 ppm

Quinone Adduct



Internal Standard

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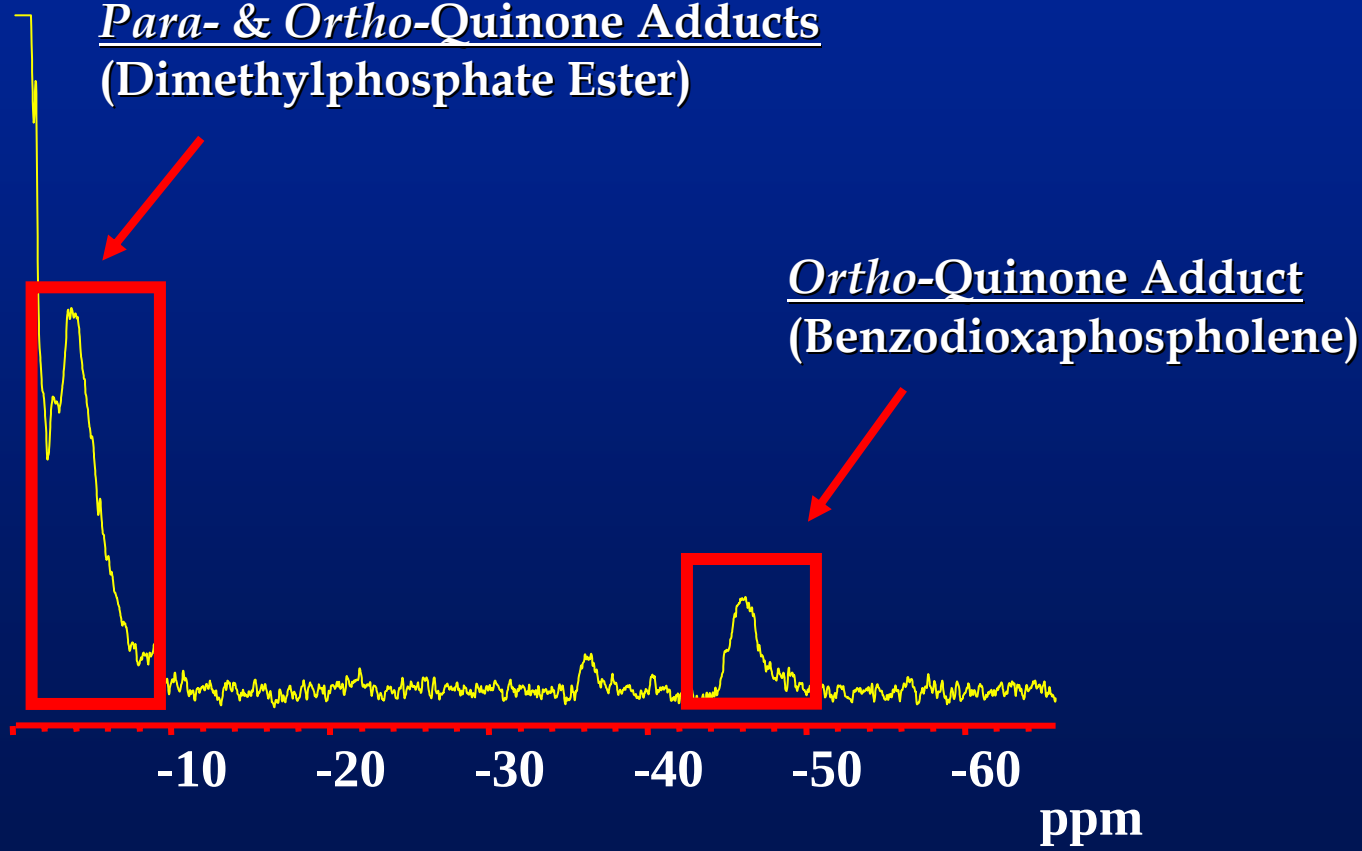
^{31}P-NMR Spectrum:
Trimethylphosphite Treated Effluent Lignin



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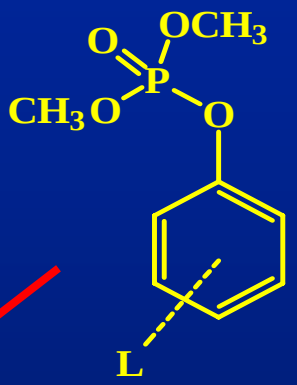
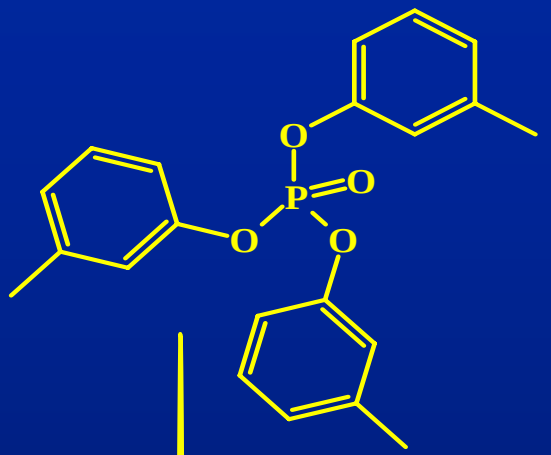
^{31}P-NMR Spectrum:

(1) Trimethylphosphite (2) Hydrolysis





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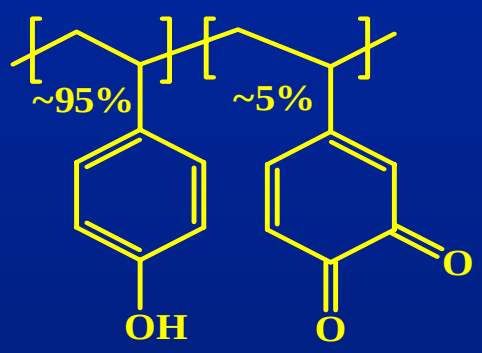
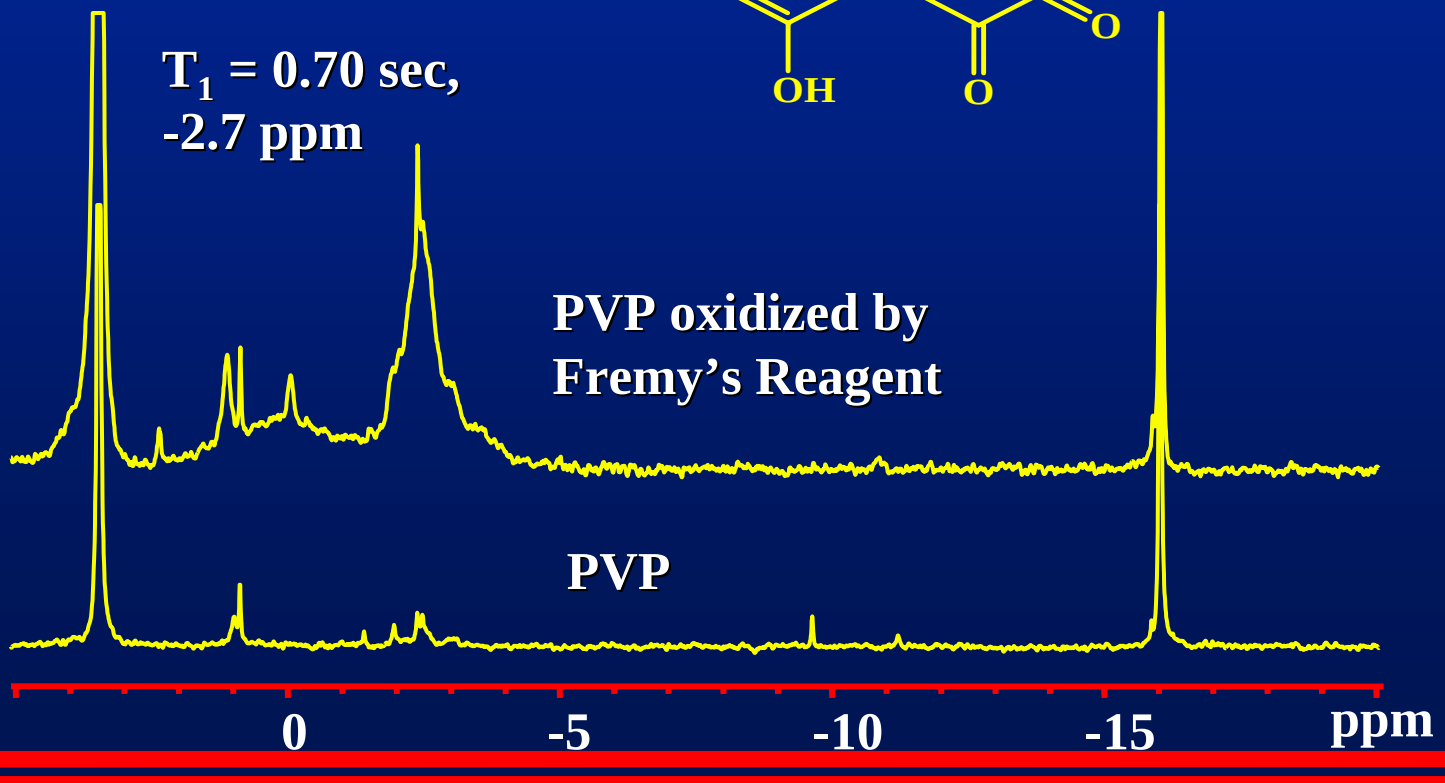
^{31}P-NMR Spectrum:

Quinone Structures Detected in Oxidized Poly(4-vinylphenol)





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Chromophore contents of ECF Pulps

- **Residual Lignins Isolated from:**
  DE*D
  where, E* = EAr, E, EO, EP, EOP
  (EAr means E with Air Excluded)

- **Brightness & Visible Spectrum**
- **Quinone Contents**

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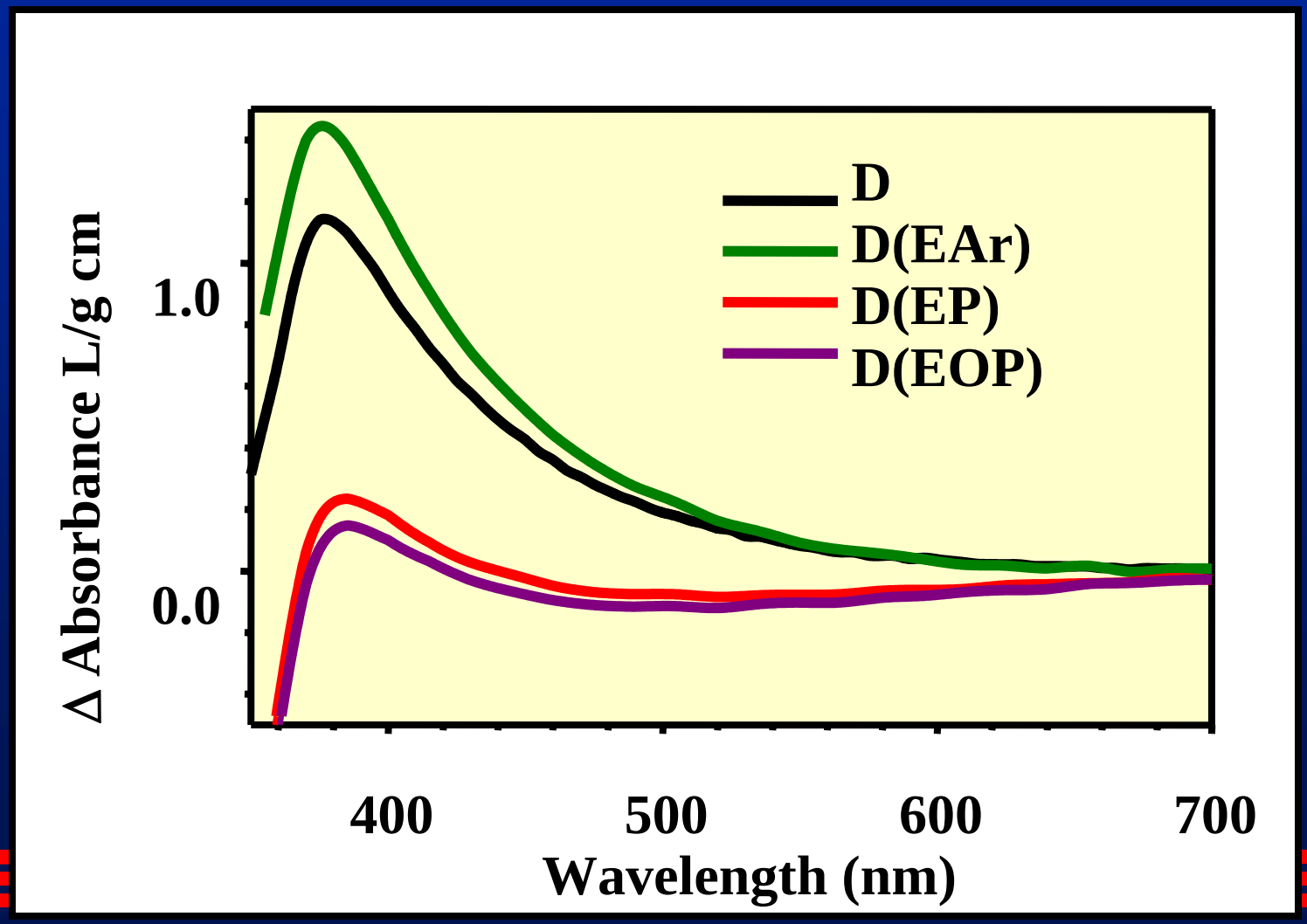
Visible Absorbance Difference Spectra:
DE - BS Residual Lignin Value)*



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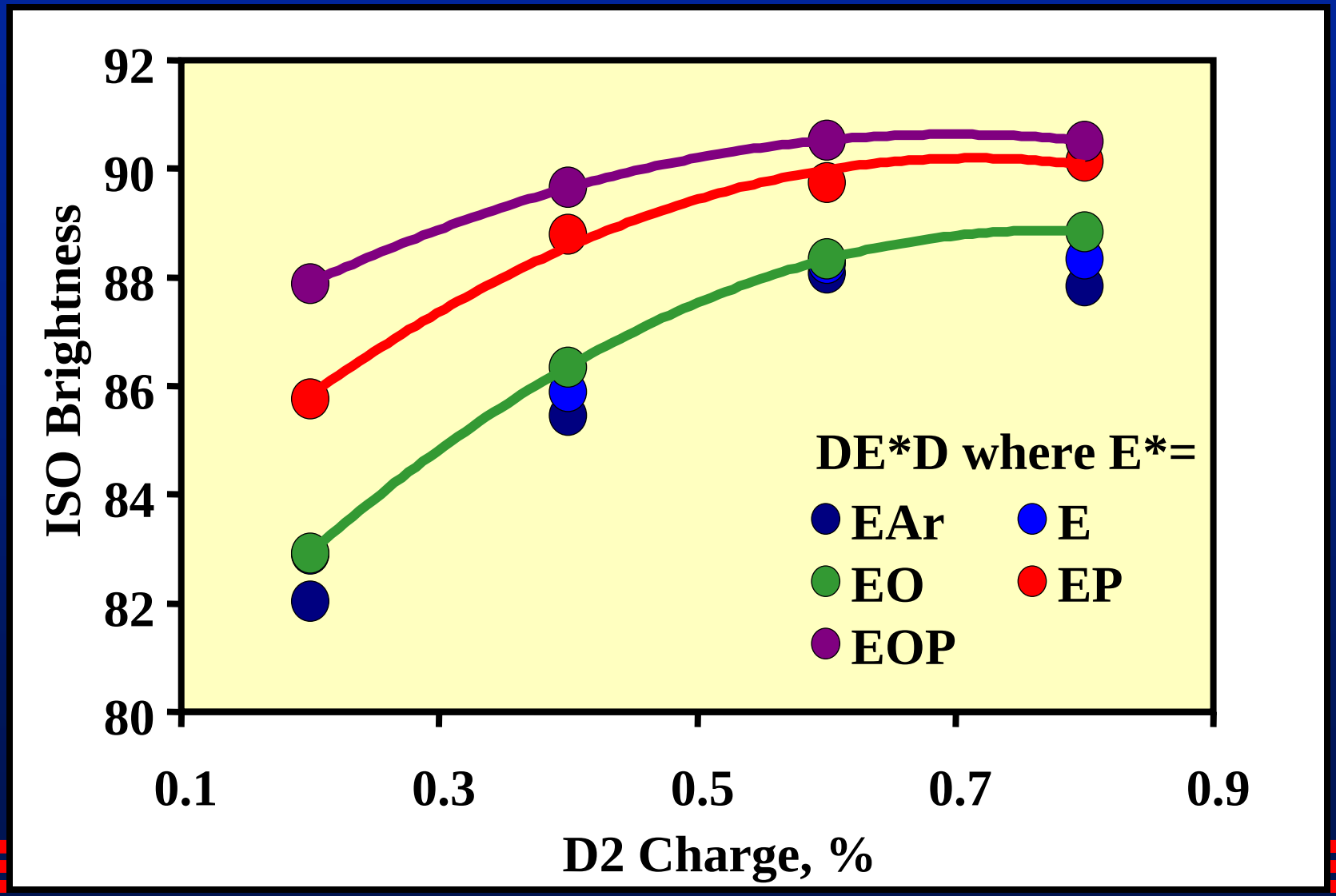
D_2 Brightness Ceiling Data



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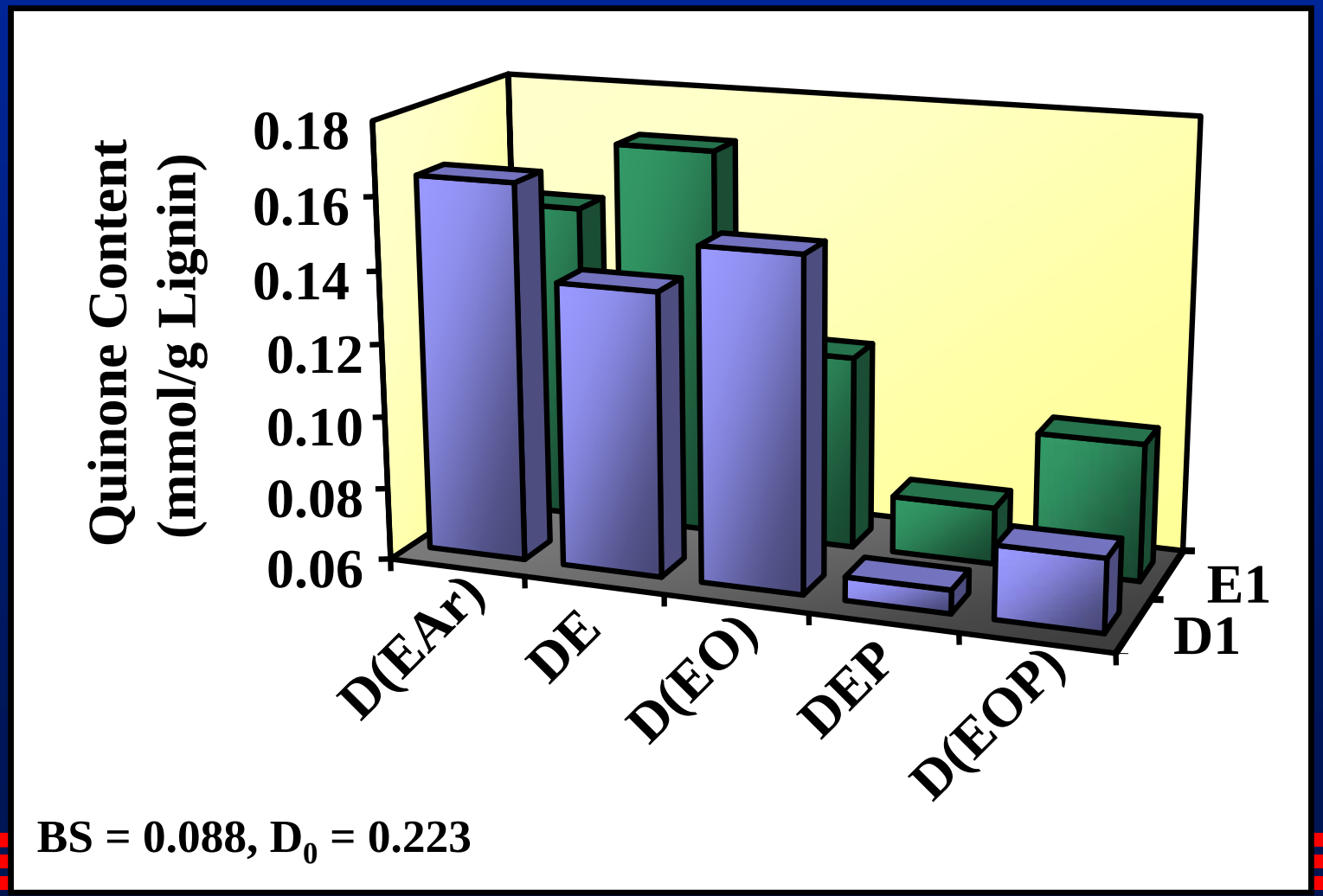
Quinone Contents: E_1 & D_1 Residual Lignins



BS = 0.088, D_0 = 0.223

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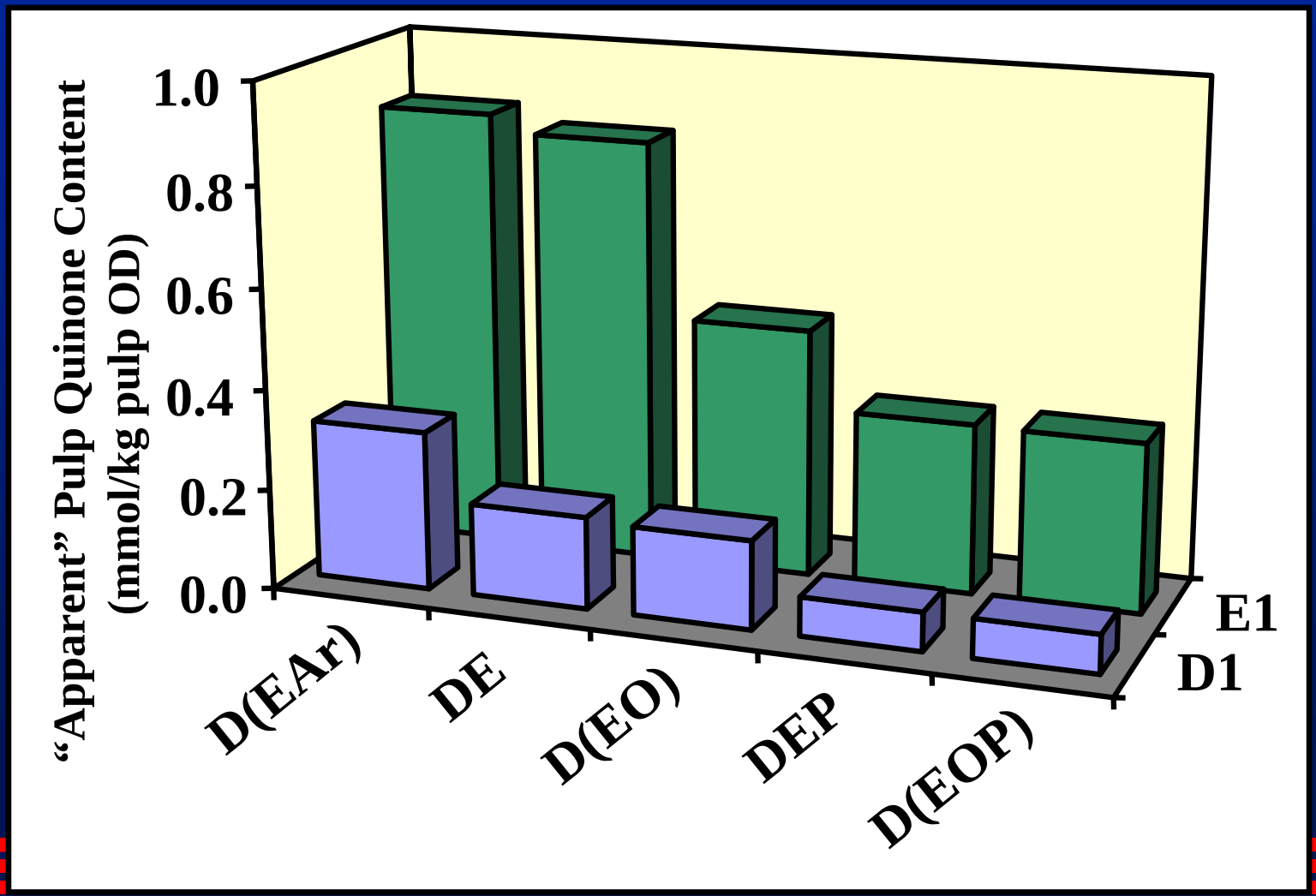
"Apparent" Pulp Quinone Contents: E1 & D1 Stages



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Conclusions

- **Trimethylphosphite/^{31}P-NMR is Useful For Quinone Detection**
- ***Ortho*- and *Para*-Quinone Structures Form Dimethylphosphate Adducts**
- **Bleaching: Chlorine Dioxide Enriches Lignin-Quinone Content**
- **Bleaching: Alkali and Peroxide Decrease the Quinone Content**

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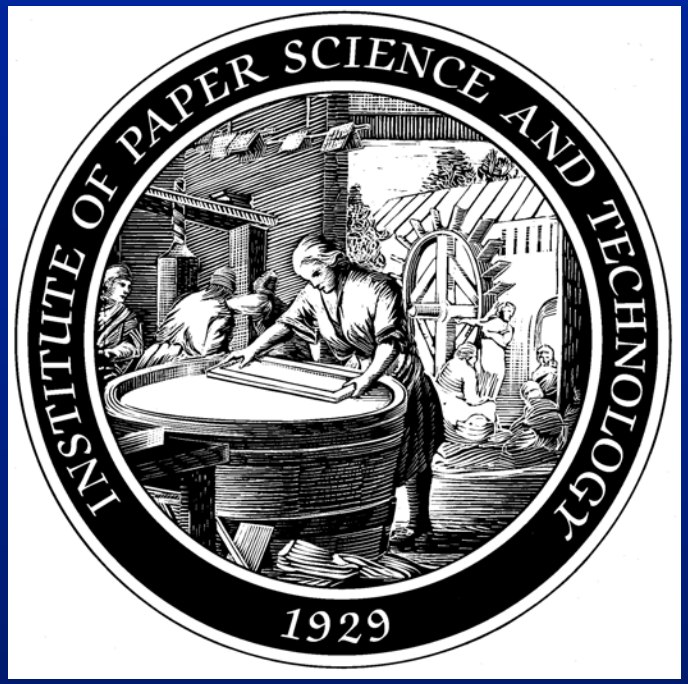

Acknowledgements

IPST Member Companies

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