# Alcohol Oxidation by Metallic Benzoquinone Complexes

Joey Easterling

Randy F. Johnston, Ph.D.

1050 Union University Dr. Jackson, TN, 38305

# Introduction

Linck and Taube discovered that p-benzoquinones and chromium oxidized ethanol.


Linck, R.G.; Taube, H. *J. Am. Chem. Soc.* **1963**, 85, 2187-2189.

# Further Study

A later, in depth study on the reaction of chloranilic acid, chromium, and ethanol provides some very important information:

- Two chromium atoms per benzoquinone atom are, in fact, necessary for alcohol oxidation
- The reduced chromium and chloranilic acid complex is a semiquinone bridged polynuclear complex

Holwerda, R.A. Johnston, R. F. *Inorg. Chem.* **1985**, 24, 153-159.


2+

# Objectives

What kind of alcohols are more easily oxidized?

Which benzoquinones are more effective oxidizing agents?

How will changing the metal effect the reaction?

# Solutions Analyzed

Seventeen alcohols of differing characteristics were used.

Two p-benzoquinones were used, Chloranilic acid and Bromanilic acid.

Two metals were used, chromium (III) and aluminum.

# Solution Preparation

Enough benzoquinone to identify carbonyl compounds with GCMS. At least 2.5-1 metal moles per benzoquinone moles.

Four solutions per alcohol:

1. Chromium and chloranilic acid
2. Chromium and bromanilic acid
3. 1-1 Chromium and chloranilic acid in excess of aluminum
4. Aluminum and chloranilic acid

Chloranilic Acid and Chromium

Chloranilic Acid and Aluminum

Bromanilic Acid and Chromium

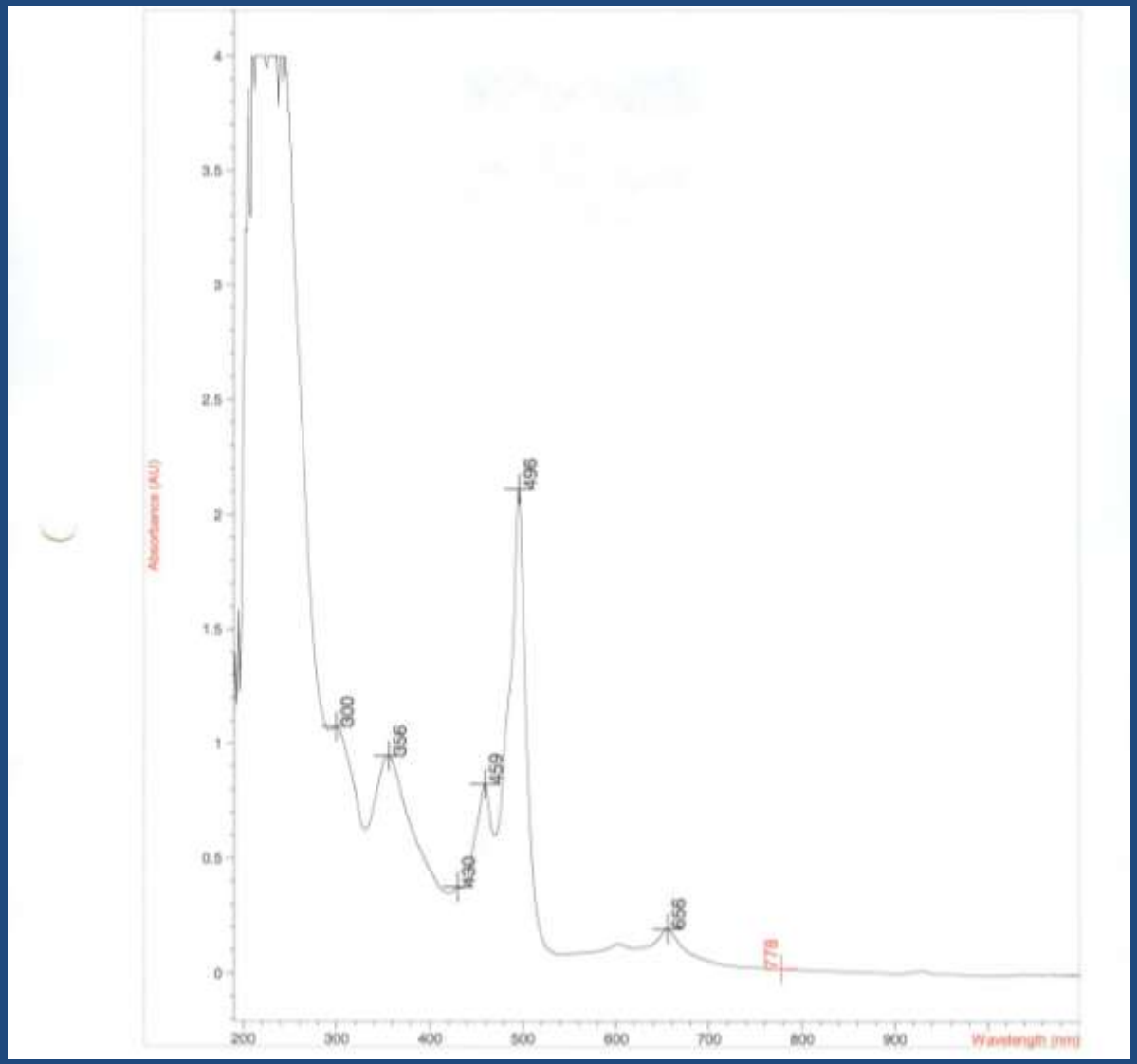
Chloranilic Acid, Chromium, and Aluminum

# Methods of Analysis

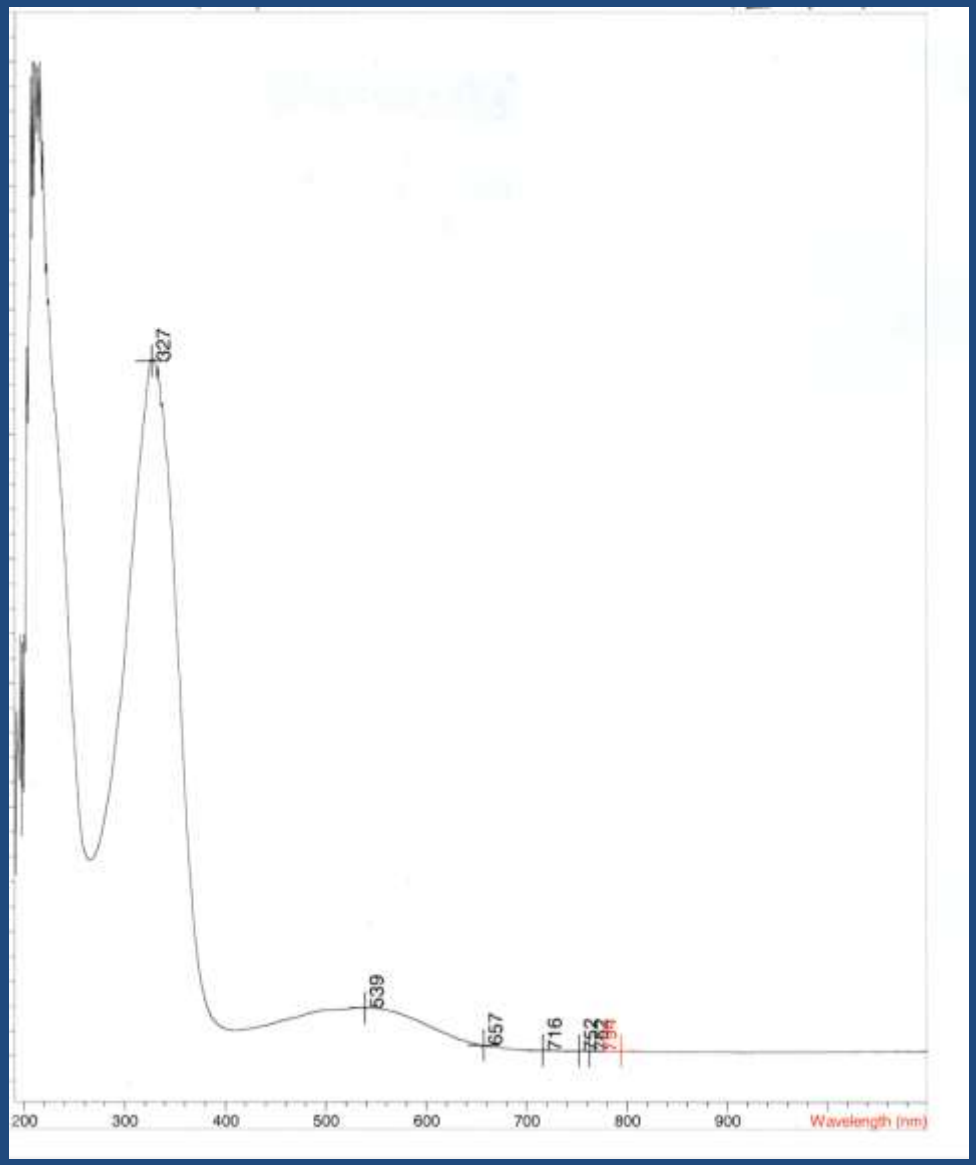
Two principle methods of analysis were used:

- UV-vis spectroscopy to identify reduced benzoquinone
- Gas chromatography and mass spectroscopy to identify oxidized alcohol

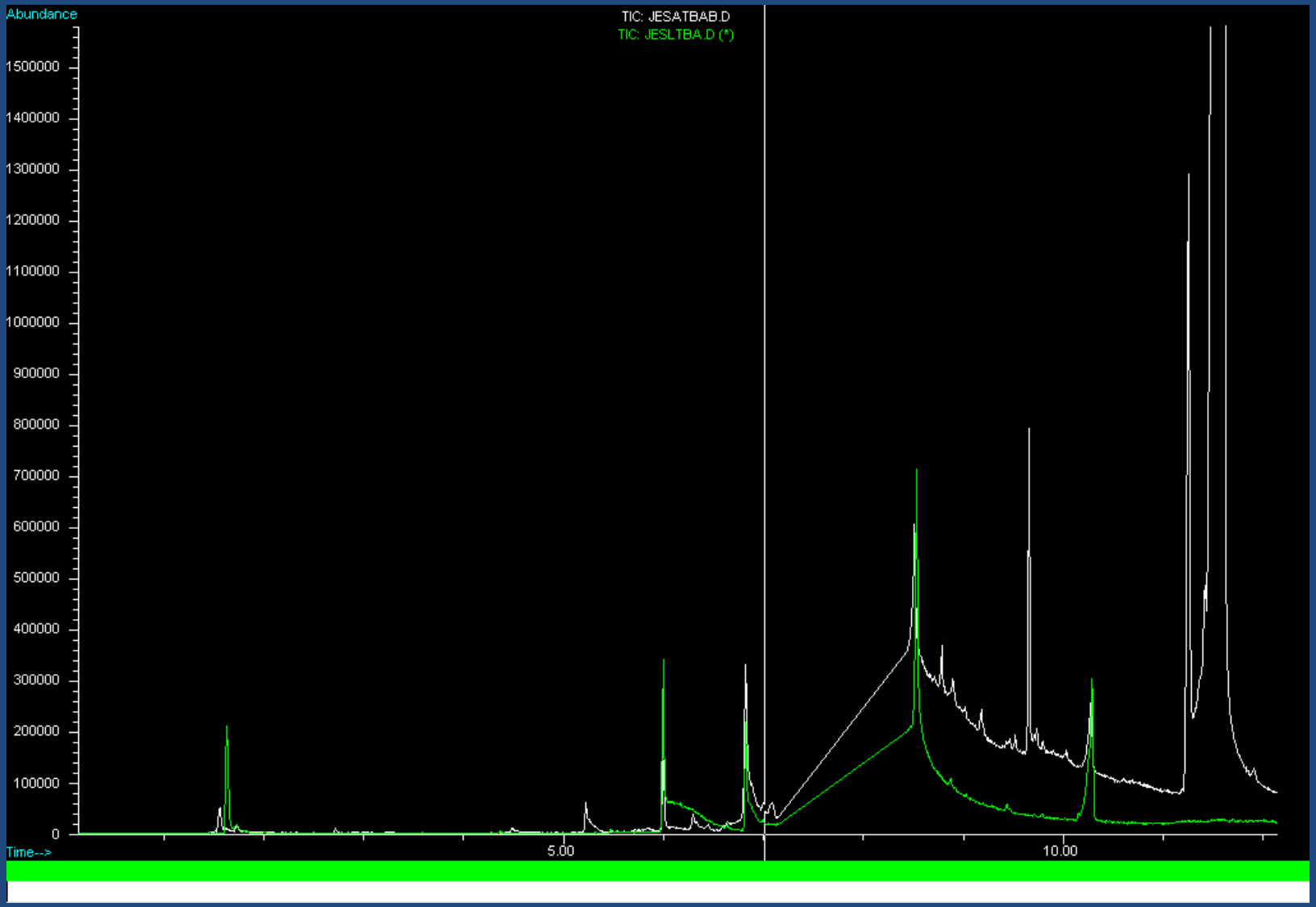
# The Reduced 2-1 Complex Spectrum



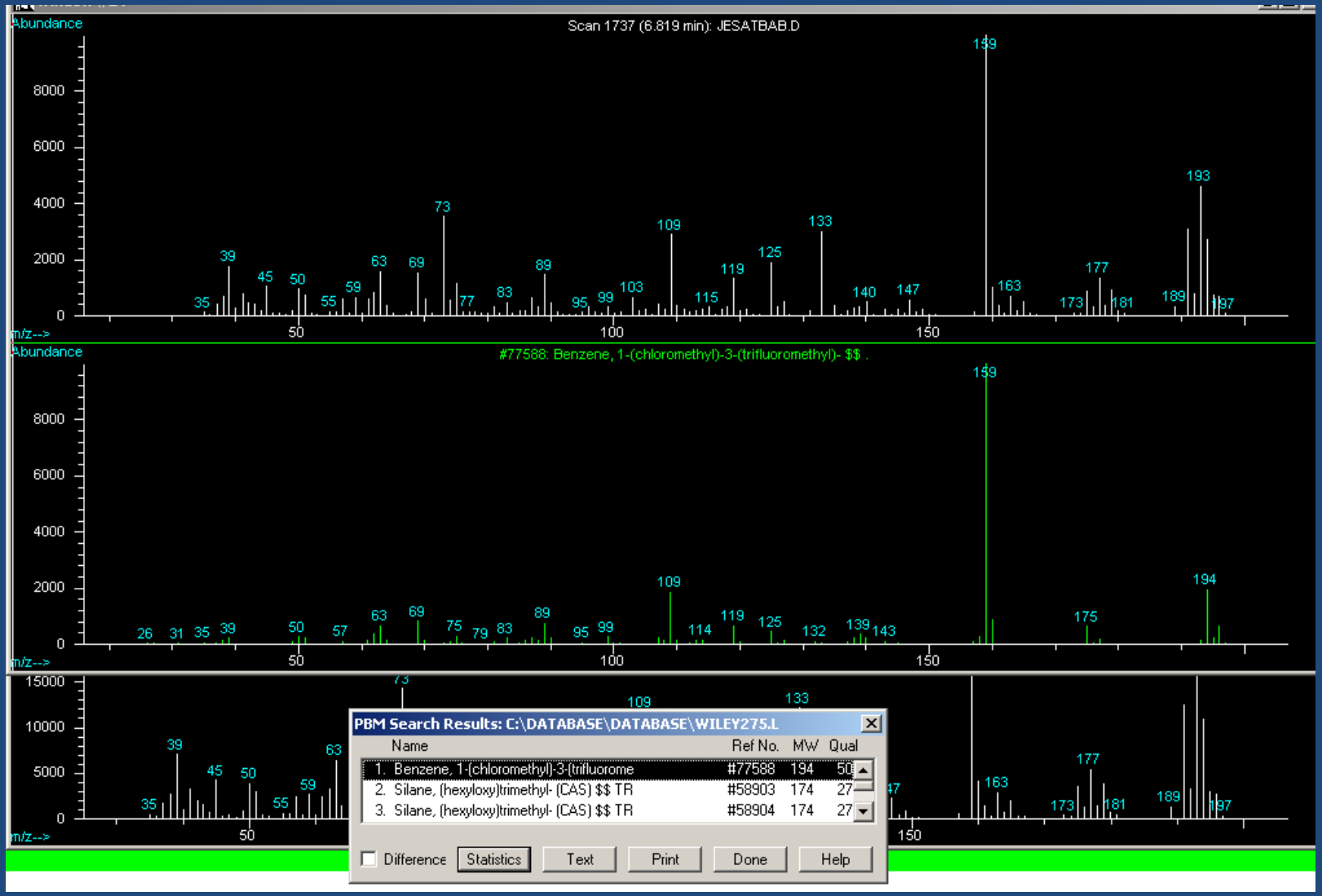
# The 1-1 Complex Spectrum



# Using Gas Chromatography

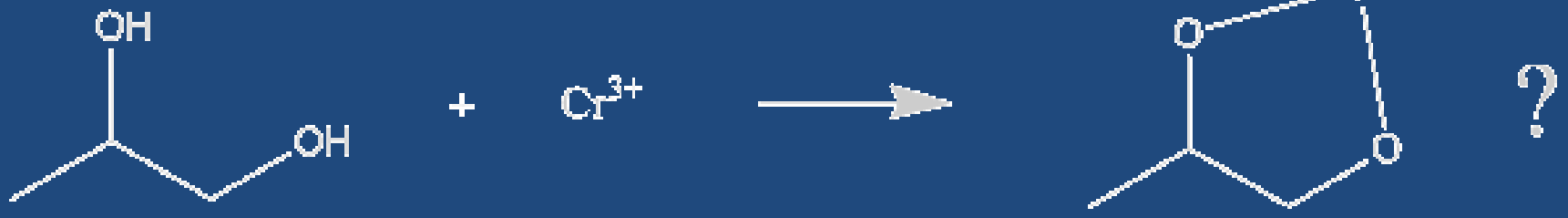


# Using Mass Spectroscopy



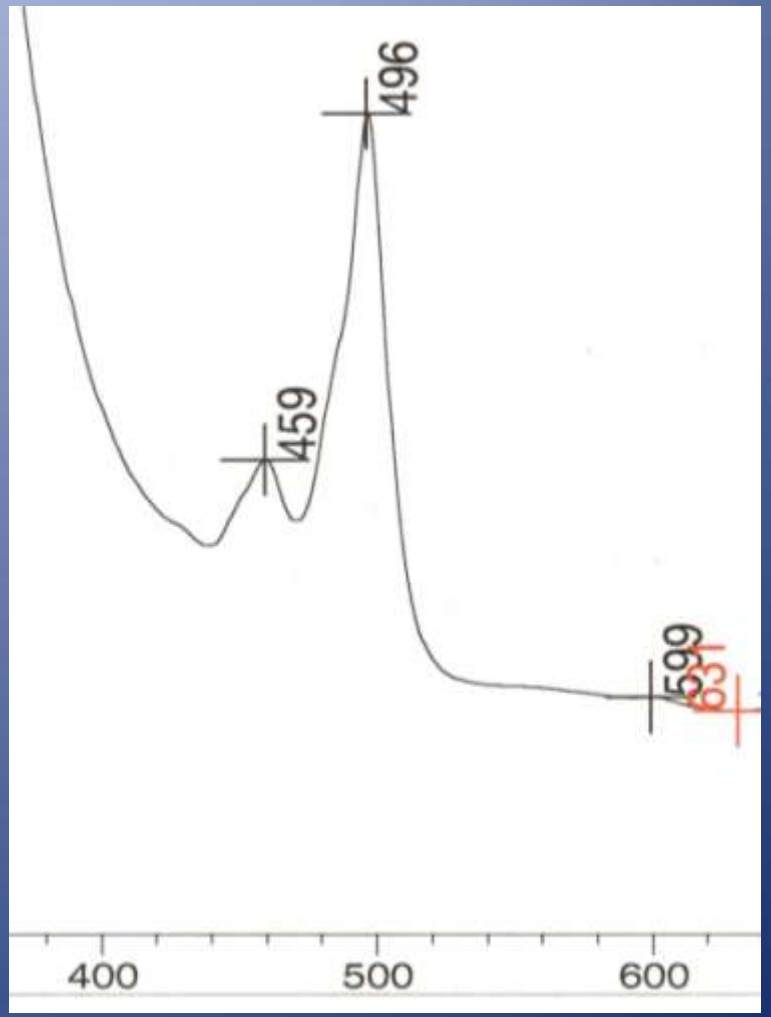
# Results: $Cr^{3+}$ and C.A.

| Alcohol | GCMS | UV-Vis |
|---|---|---|
| Benzyl Alcohol | X | X |
| 1-Butanol | X | X |
| 2-Butanol | X | X |
| 2-Butene-1,4-diol | | X |
| 3-Butene-1-ol | | X |
| 2-Butyn-1-ol | X | X |
| 2-Bromoethanol | | |
| Ethanolamine | | |
| Methanol | | X |
| 2-Methoxyethanol | | X |
| 2-Chloroethanol | X | X |
| Ethanol | X | X |
| 1-Propanol | X | X |
| 2-Propanol | | X |
| 1,2-Propanediol | | |
| 1,3-Propanediol | | |
| 4-(Trifluoromethyl)-benzyl alcohol | X | X |


OH
OH
+
$Cr^{3+}$
O
O
?

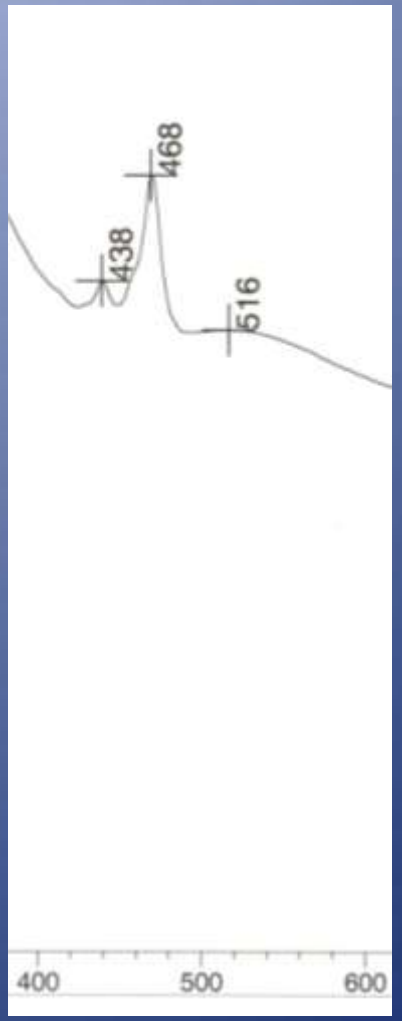
# Results: Which Metal?

- Chromium was much more effective than the other two metal combinations
- Chromium and aluminum were more effective than aluminum alone



# Results: Which Metal?

Aluminum was least effective, but some solutions' UV-visible spectra still contained sharp peaks



# Results: Which Benzoquinone?

Chloranilic acid was the better oxidizing agent; more solutions contained oxidized alcohol and more UV-visible spectra contained sharp peaks.

# Alcohol Dehydration

Most solutions contained a dehydrated product of the alcohol.

Ex: 


- Required metal
- Independent of benzoquinone
- Independent of time

# Future Work

Stoichiometry

- Is the reaction cyclic?
- Does aluminum react in the same way as chromium?

GCMS analysis using a derivatization method

Investigation of the dehydration of alcohol catalyzed by $Cr^{3+}$