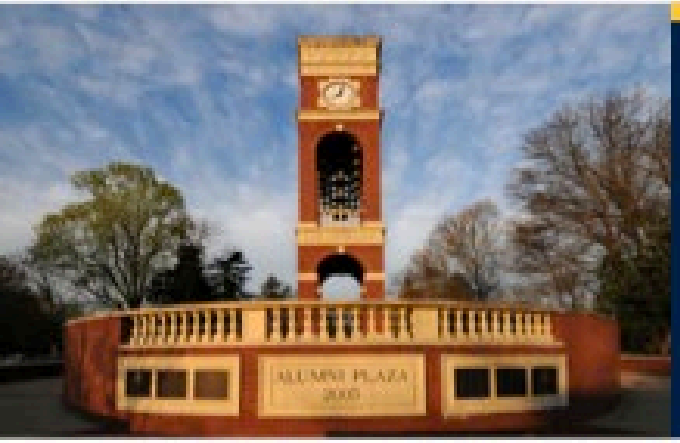
Apr 6th, 1:00 PM - 2:40 PM

Amine and Pesticide Detection with Phthalocyanines

Kyle Bittner

SCOTT Dane Dr
East Tennessee State University

EAST TENNESSEE STATE UNIVERSITY



AMINE AND PESTICIDE DETECTION AND REMOVAL WITH PHTHALOCYANINES

Presented by
Kyle Bittner
April 2022

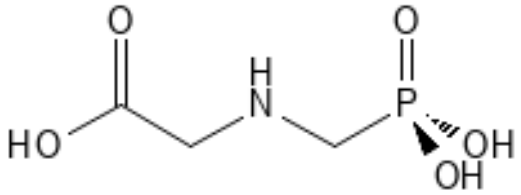
OUTLINE

- INTRODUCTION
- RESEARCH GOALS
- EXPERIMENTAL
- FeTSPc
- DIBUTYLAMINE
- REMOVAL
- GLYPHOSATE
- CONCLUSIONS
- FUTURE WORK

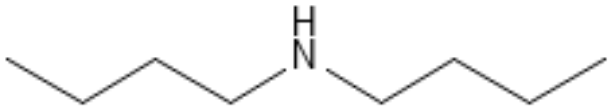
INTRODUCTION

- Types of **Pesticides** and their uses?
  - **Herbicides** – Developed to target and kill plants
  - **Insecticides** – Developed to target and kill insects
  - **Rodenticides** – Developed to target and kill rodents
  - **Fungicides** – Developed to target and kill fungi

- What are pesticides?
- Glyphosate (Roundup active ingredient)
  - Amine, Carboxylic Acid, Phosphonate



- Dibutylamine (DBA)
  - Amine
  - Not a pesticide



PESTICIDE CONSIDERATIONS

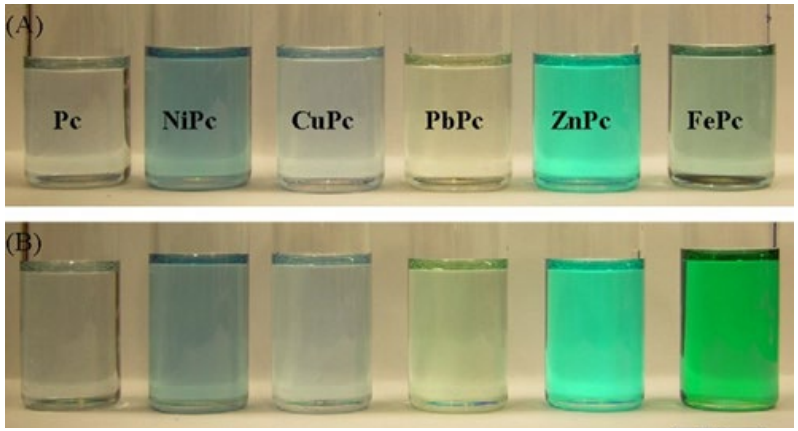
- Increasing household use
- Increasing agricultural use
- increasing introduction into the environment from runoff
- Although acute and chronic health affects are still being examined, Glyphosate has a maximum contamination level (MCL) of 700 ppb (0.7 ppm)
- Pesticide detection, quantification, and removal is an ongoing area of research

RESEARCH GOALS

- Evaluate water soluble iron phthalocyanine (FePc) interactions with amines and pesticides
- Develop an analytical method for quantification and remediation of amines and pesticides
- Evaluate amine and pesticide removal with FeTSPc

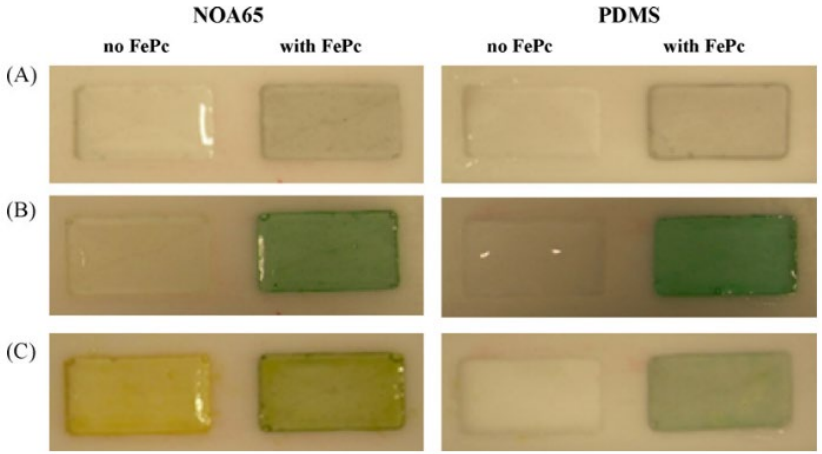
WHY FePc?

L. Sutarlie and K.-L. Yang (2008)



Various MPc's in toluene solution (50µM) showing colorimetric responses

(A) before
(B) after addition of 5mmol hexylamine

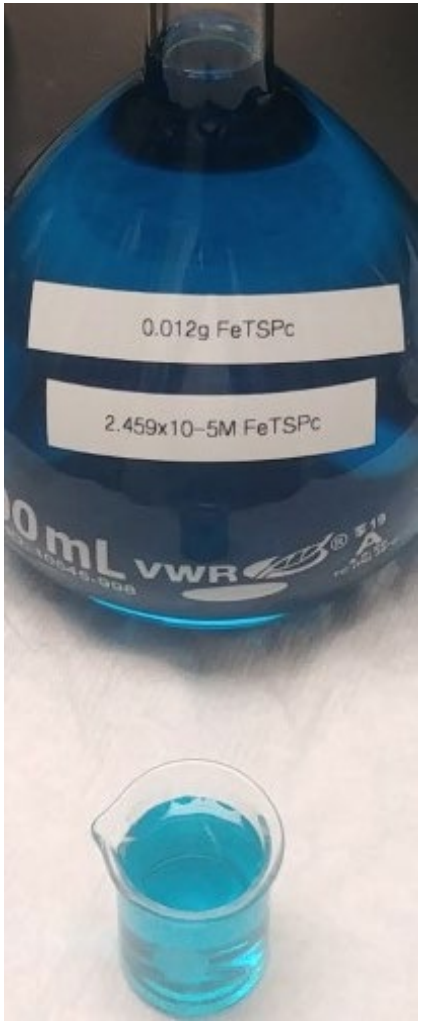


Norland Optical Adhesive 65 (NOA65) & Poly(dimethylsiloxane) (PDMS) with or without FePc (0.03%, w/w)
(A) stored in clean air
(B) exposed to 11,600ppmv hexylamine vapor
(C) exposed to 15,000ppmv ethylenediamine vapor.

Reprinted with permission Sutarlie, L.; Yang, K.-L., Colorimetric responses of transparent polymers doped with metal phthalocyanine for detecting vaporous amines. *Sensors and Actuators B: Chemical* ***2008, 134 (2), 1000-1004.***

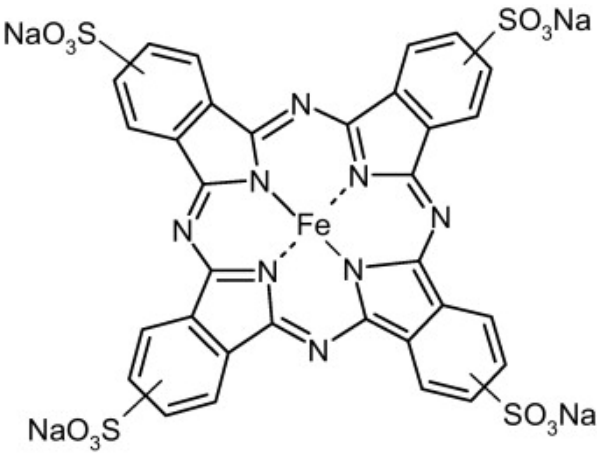
EXPERIMENTAL

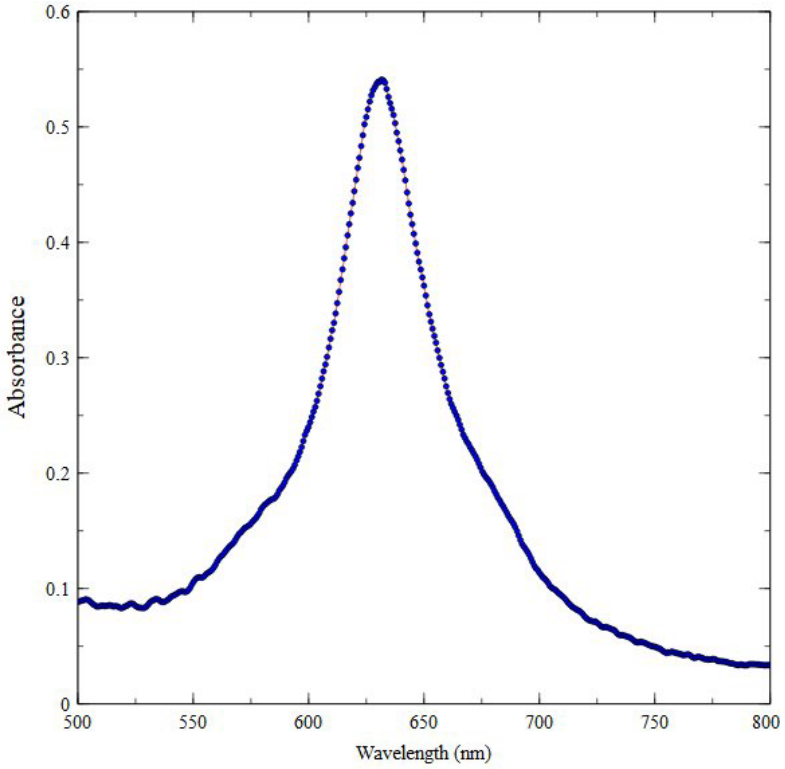
- Color – Visible Region
- Absorbance Range
  500 - 800 nm
- Vernier Spectro-Vis
- 10 – 20 mg in 500 mL



FeTSPc

- Iron(II) tetrasolpho-phthalocyanine (FeTSPc)
- MPc with iron center
- Sulfonated for water solubility
- Absorbance peak at 632 nm

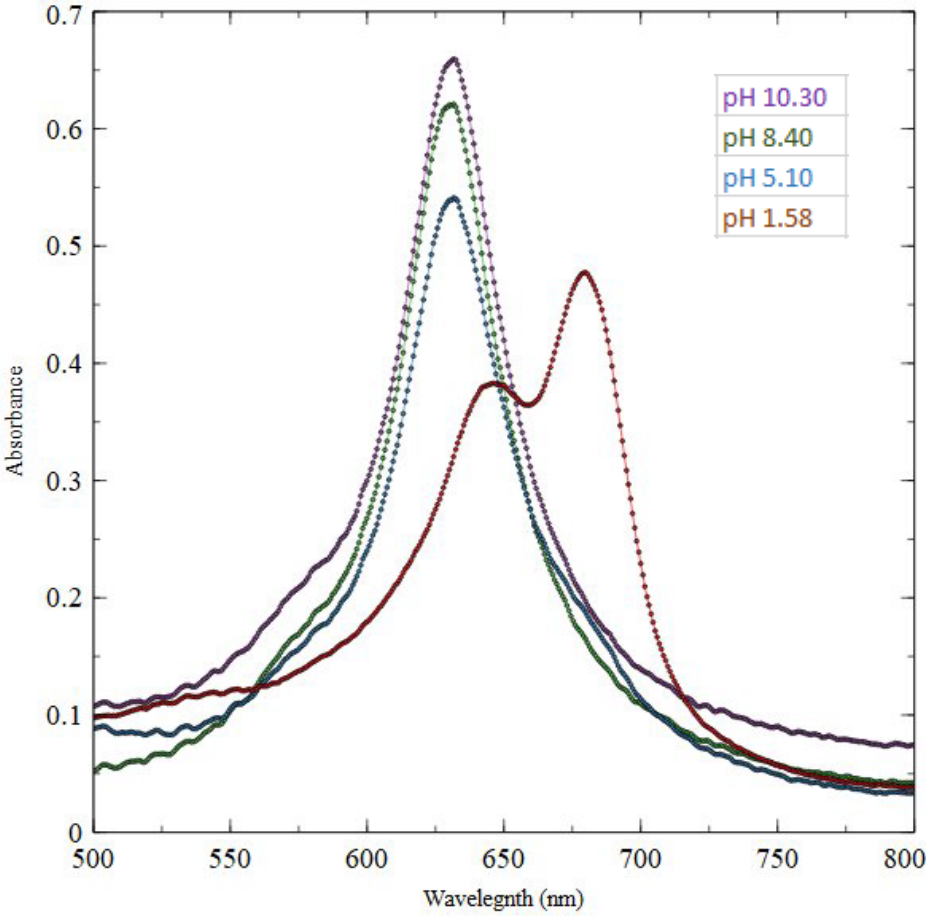




FeTSPc Absorbance Spectrum

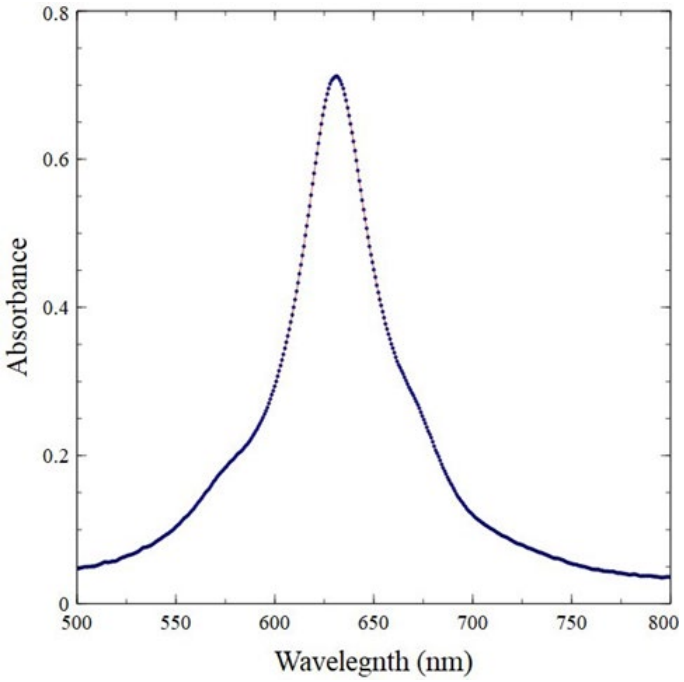
$A = 23{,}174\ (L\ mol^{-1}\ cm^{-1}) \times (1\ cm)\ C\ (mol\ L^{-1}) + 0.0433 \rightarrow R^2 = 0.9955$

pH DEPENDENCE

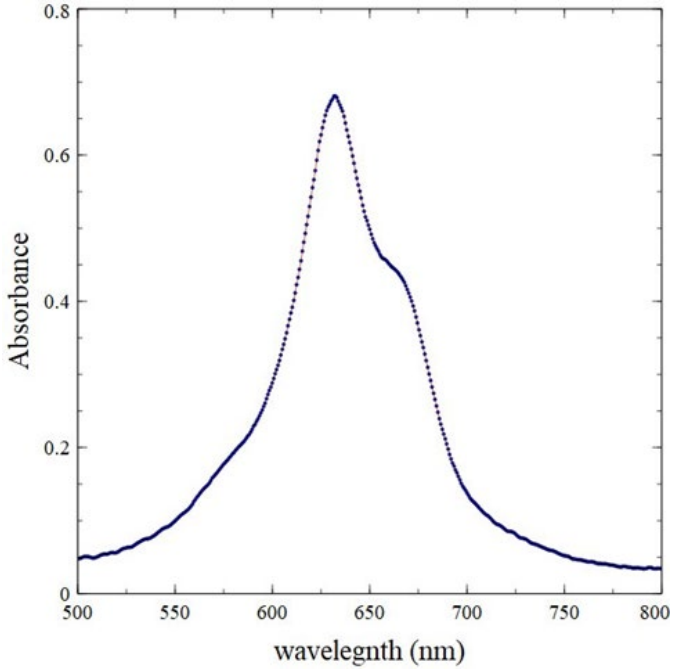


- Initial pH 5.10
- Added 2.06 M acetic acid dropwise to obtain a steady pH of 1.58
- Added sodium hydroxide solid to reach two steady pH levels of 8.40 and 10.30
- Prepared phosphate buffer
  - Added 0.53 g of Na_2HPO_4 to 400 mL of water
  - Added HCl dropwise until reaching a steady pH of 8.19

INTRODUCTION OF DBA



Buffered FeTSPc Spectrum

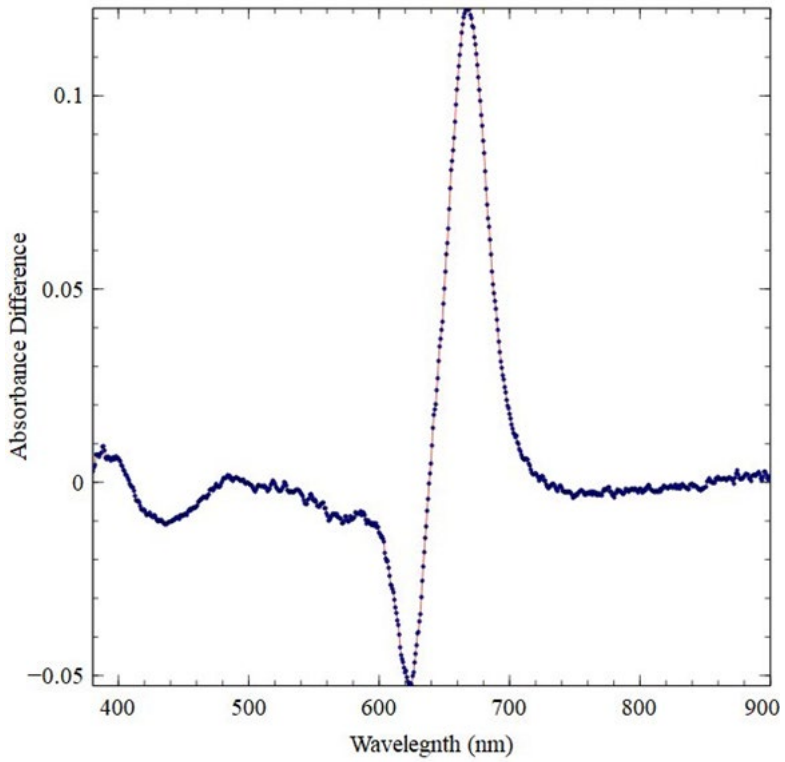


Buffered FeTSPc with 200 ppm DBA

Sample Preparation for DBA testing

FeTSPc Stock (mL)	Phosphate Buffer (mL)	500 ppm DBA (mL)	DI Water (mL)	DBA Concentration in Sample (ppm)
2.50	0.50	2.00	0.00	200
2.50	0.50	0.00	2.00	0

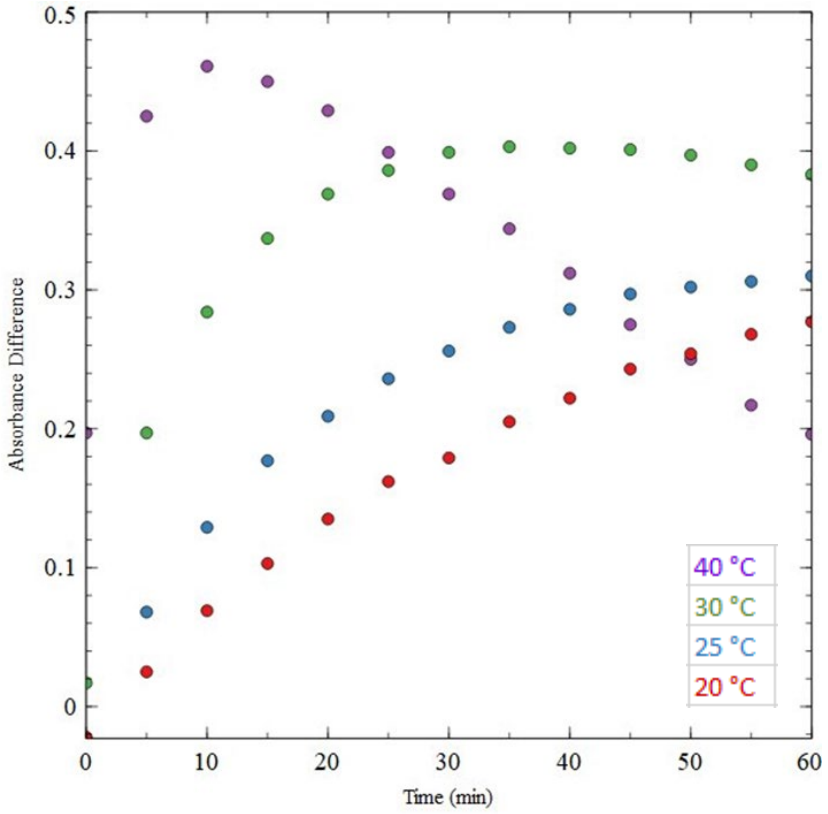
SPECTRAL DIFFERENCE



Spectrum difference between 0 and 200 ppm DBA

- 0 ppm DBA spectrum subtracted from 200 ppm spectrum
- Decrease in peak absorbance at 632 nm
- Absorbance increase at 667 nm
- Target wavelength for DBA analysis

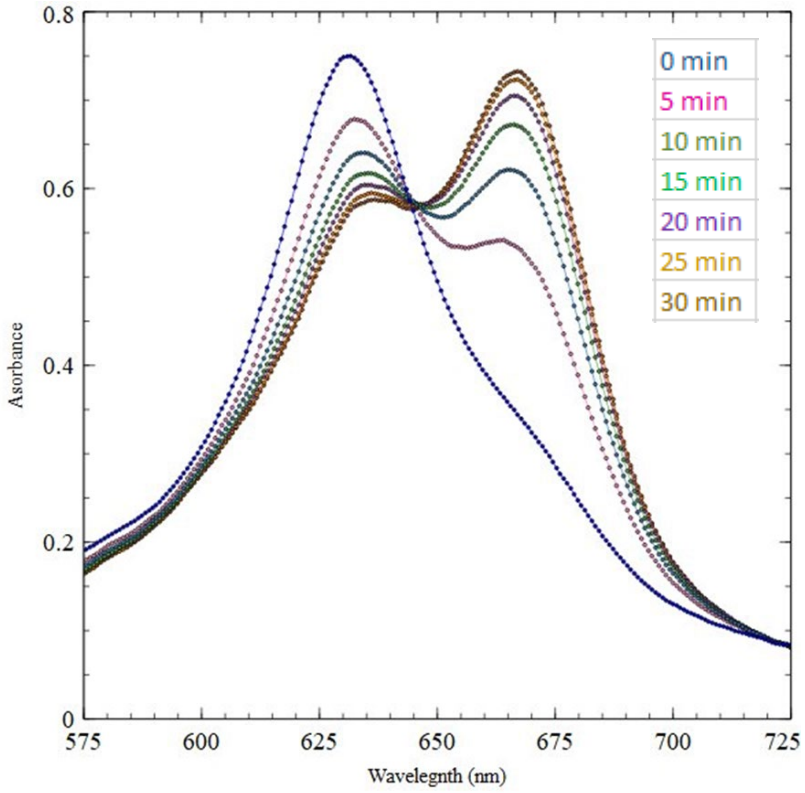
FeTSPc/DBA vs TEMPERATURE



FeTSPc Interaction with 800 ppm DBA vs Time and Temperature

- Higher temperatures correspond to faster. absorbance response
- Peaked after 10 min at 40° C followed by an absorbance. decline possibly due to fast complex formation then slow dimer formation.
- Plateau at 30° C between 30 and 60 min.
- 30° C and 40 min best suited for analysis.

FURTHER INVESTIGATION CONT'D



FeTSPc Interaction with DBA
(30 min at 30 °C)

- FeTSPc peak at 632 nm diminishes
- Formation of a new peak at 667 nm
- Rate of change is reduced over time
- Rate of change is minimal between 25 and 30 min

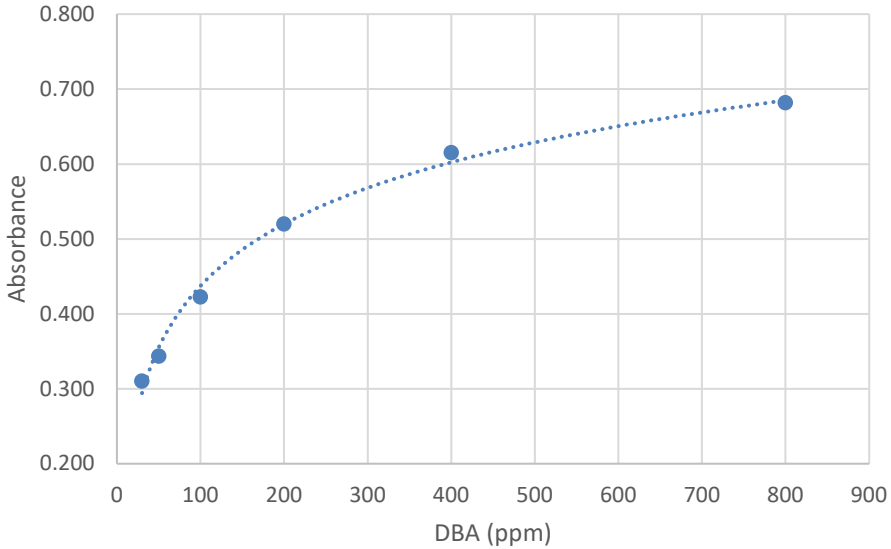
ANALYTICAL METHOD

DBA	Absorbance @ 667 nm				
ppm	Sample 1	Sample 2	Sample 3	Average	STD DEV
30	0.310	0.310	0.311	0.310	0.00057
50	0.369	0.328	0.333	0.343	0.02236
100	0.466	0.423	0.379	0.423	0.04350
200	0.576	0.491	0.493	0.520	0.04850
400	0.679	0.581	0.586	0.615	0.05519
800	0.748	0.649	0.648	0.682	0.05744

- Six concentrations were analyzed
- Three samples at each concentration
- Range 30 to 800 ppm DBA
- Prepared in a 100 mL round bottom flask in temperature controlled water bath
- Mixed periodically by hand

- $Y = 0.199\ln(x) - 0.1107$
- $R^2 = 0.9929$

- DL = 55 ppm (99% CI)



FeTSPc / DBA Calibration Curve (40 min at 30° C)

PREPARATION OF FeTSPc RESIN

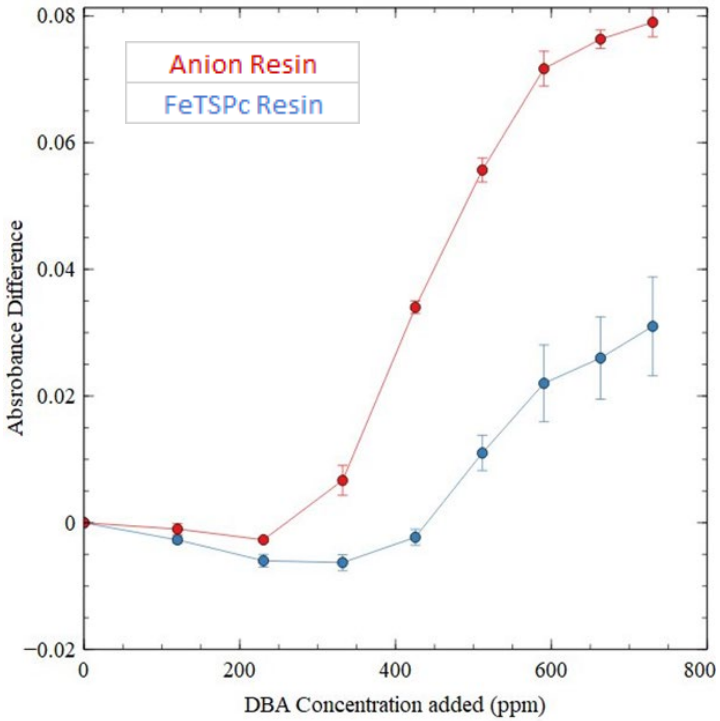
- Dowex 1x8, 100-200 mesh, anion exchange resin.
- FeTSPc resin was prepared by adding 14.047 grams resin to a 1000 mL beaker.
- Added 500 mL of FeTSPc solution twice in a consecutive manner. The initial and final absorbances were recorded.
- Absorbances values and ε were used to calculate that 4.245 µmoles of FeTSPC were supported per gram of resin.

Time	Absorbance
0	1.835
15	0.428
30	0.318
45	0.259
60	0.203
Decant / Refill	
0	1.331
30	0.806
60	0.668
Decant / Wash / Dry	

DBA REMOVAL

- 1 g of FeTSPc treated and untreated resin in 50.0 mL of DI water (x 3 trials)
- Extracted 4.00 mL of sample → Returned 4.00 mL of 1,500 ppm DBA → Stirred 10 minutes → Let settle for 3 minutes → Measure absorbance
- Repeated

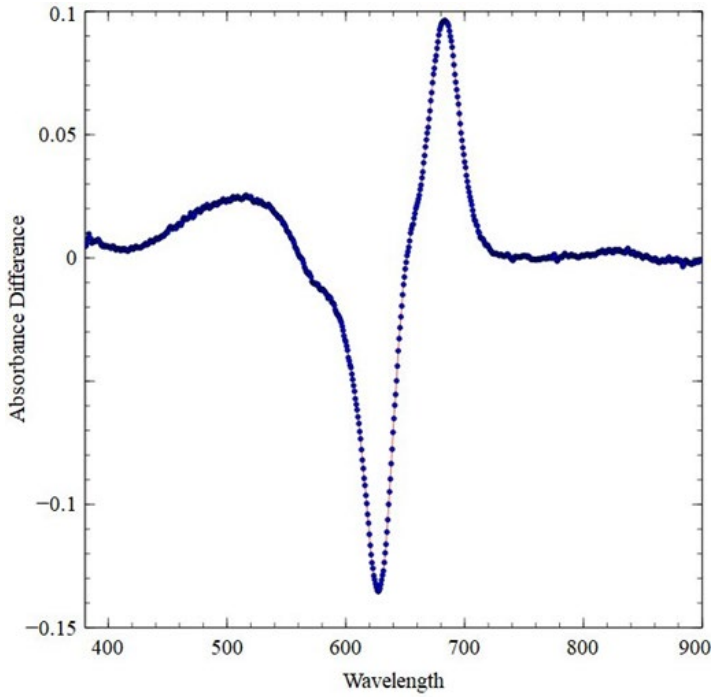
- Absorbance values are lower with FeTSPc treated resin
- FeTSPc treated resin may be more effective at DBA removal
- Absorbance measurements only differ by 0.05 between the two resins



Resin Efficiency Comparison

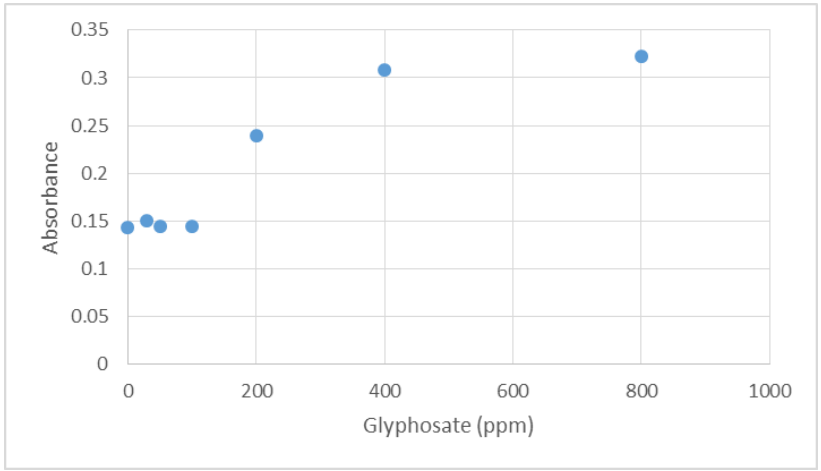
GLYPHOSATE DETECTION

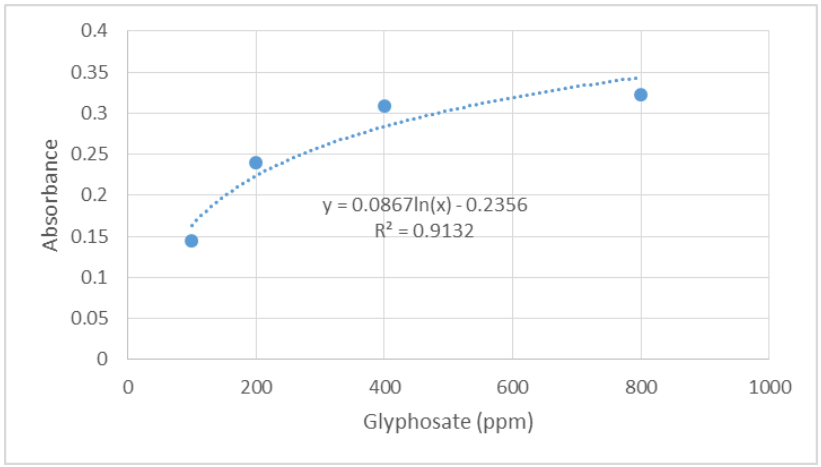
- Initial tests began by following the same process as with DBA
- Difference between 200 ppm glyphosate and 0 ppm glyphosate
- Similar response but peak difference is at 683.5 nm



Spectrum difference between 0 and 200 ppm glyphosate

ANALYTICAL METHOD





FeTSPc / Glyphosate Calibrations Curves

- Measurements take at 30° C after 40 minutes at 683.5 nm
- Response is less consistent
- Estimated detection limit is 228 ppm (99% CI)
- Adjustments needed if even a viable quantification method
- $R^2 = 0.9132$

Glyphosate (ppm)	Absorbance @ 683.5 nm
0	0.143
30	0.151
50	0.144
100	0.145
200	0.240
400	0.309
800	0.322

CONCLUSIONS

Pros

- FeTSPc can be used as an easy screening test for DBA and glyphosate in water
- The method is inexpensive
- Can be used quantitatively in certain concentration ranges
- FeTSPc can be attached to anion exchange resin and may provide increased DBA removal

Cons

- Detection limit vs MCL (sensitivity)
- Poor specificity / selectivity
- Time & temperature requirements
- Limited quantitative range
- Additional steps to make FeTSPc resin

FUTURE WORK

- Further investigation of Glyphosate and FeTSPc reaction conditions including oxidative remediation (Jenna Stewart)

- Investigation of other MPc's with DBA and glyphosate

REFERENCES

1. Pesticides industry sales usage 2016, EPA.
   - Phillips McDougall, AgriService (2008-2012)
   - Agricultural Market Research Proprietary Data (2005-2012).
   - Non-Agricultural Market Research Proprietary Data (2005-2012)
   - USDA/NASS Quick Stats (http://www.nass.usda.gov/Quick_Stats/)

2. Sutarlie, L.; Yang, K.-L., Colorimetric responses of transparent polymers doped with metal phthalocyanine for detecting vaporous amines. *Sensors and Actuators B: Chemical* ***2008, 134 (2), 1000-1004.***

ACKNOWLEDGEMENTS

- Dr. Dane Scott – Research Advisor
- Dr. Cassandra Eagle – Committee Member
- Dr. Gregory Bishop – Committee Member
- Dr. Hua Mei – Graduate Coordinator
- Philip Brown – Research partner first semester
- Wendy Bittner – Wife
- Jordon Clem – Step Son
- Matt Hathaway – HSAAP Research Manager

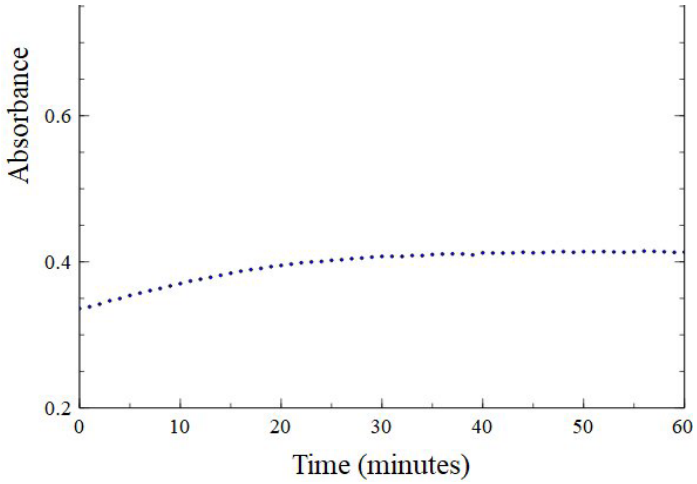
QUESTIONS

BACKUP SLIDES

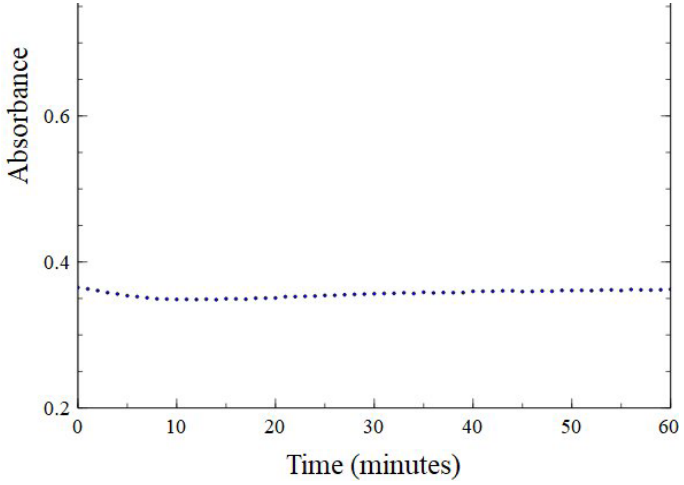
FeTSPc/Buffer OVER TIME

No observable interaction in absorbance with phosphate buffer

Sample #	FeTSPc Stock (mL)	Phosphate Buffer (mL)	2,000 ppm DBA (mL)	DI Water (mL)	DBA Concentration in Sample (ppm)
1	2.50	-	-	2.50	0
2	2.50	0.50	-	2.00	0
3	2.50	0.50	2.00	-	800

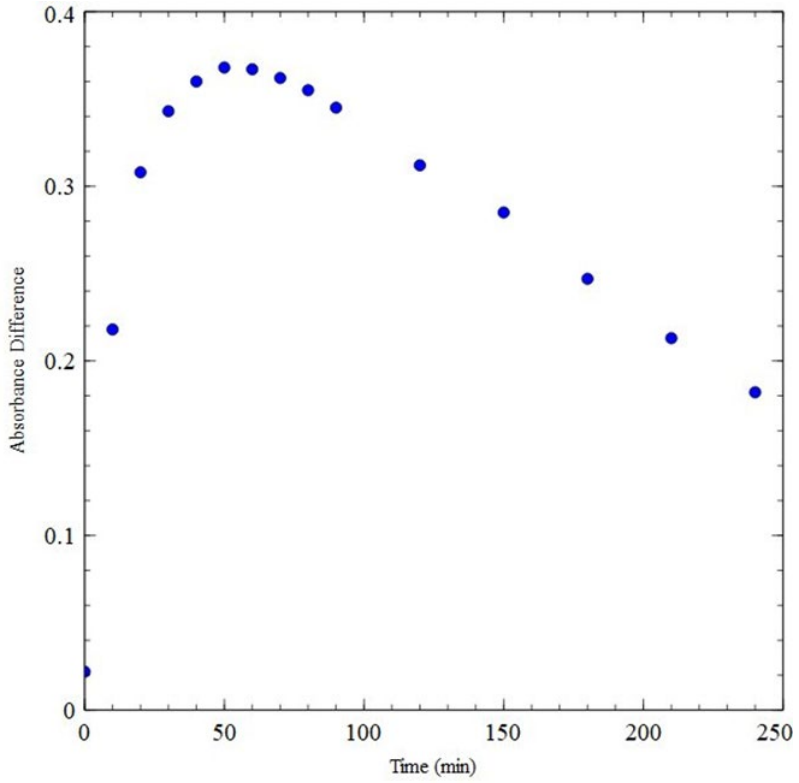


FeTSPc over 60 min (sample 1)



FeTSPc and Buffer over 60 min (sample 2)

FURTHER INVESTIGATION



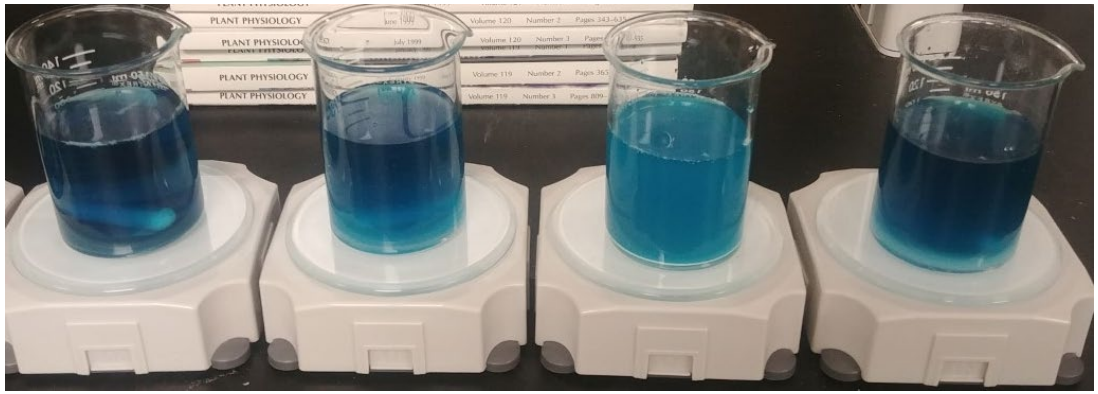
FeTSPc Interaction with DBA over 4 hours at 30 °C

- Similar behavior as seen at 40° C
- Decline begins after 60 min
- Time and temperature are critical for consistent analysis

ABSORPTION MEDIA

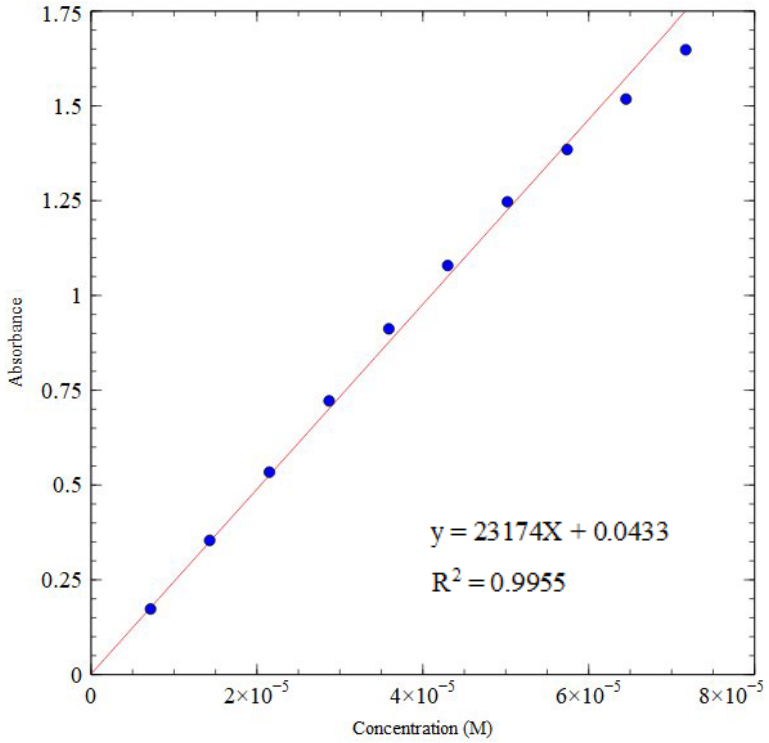
- Absorbance media added incrementally to 100 mL of FeTSPc solution
- Stirred 5 minutes → let settle for 5 minutes → Measured Absorbance

Time (min)	ANION RESIN (1)			SILICA GEL (2)			ALUMINA (3)			OSU-6 (4)		
	grams added	grams total	Abs	grams added	grams total	Abs	grams added	grams total	Abs	grams added	grams total	Abs
0	Initial absorbance with no media present = 1.630											
5	0.126	0.126	1.559	0.111	0.111	1.656	0.106	0.106	1.704	0.107	0.107	1.654
10	0.507	0.633	1.232	0.503	0.614	1.663	0.531	0.637	1.812	0.513	0.62	1.659
15	0.531	1.164	0.816	1.034	1.648	1.677	1.036	1.673	1.935	1.005	1.625	1.674
20	0.501	1.665	0.536	1.012	2.66	1.688	1.008	2.681	1.568	1.004	2.629	1.665
25	0.505	2.17	0.323	-	-	-	-	-	-	-	-	-
30	0.515	2.685	0.183	-	-	-	-	-	-	-	-	-



(from left to right) anion resin, silica gel, alumina, OSU-6

MOLAR ABSORPTIVITY



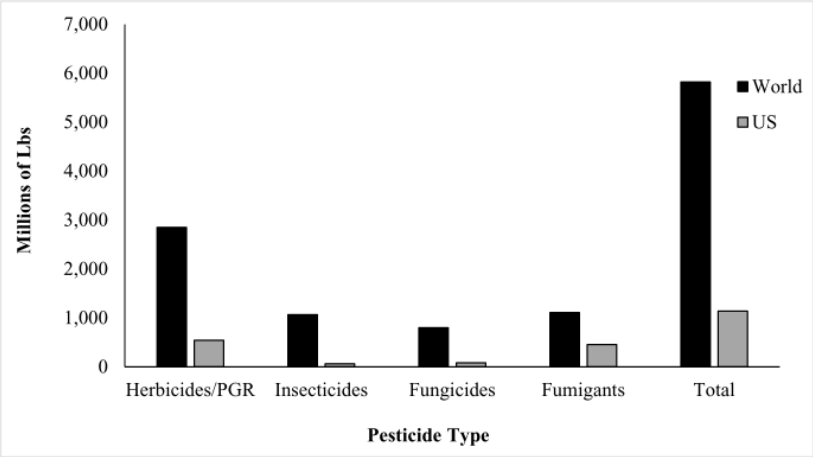
FeTSPc Molar Absorptivity Plot

FeTSPc Molar Absorptivity Data

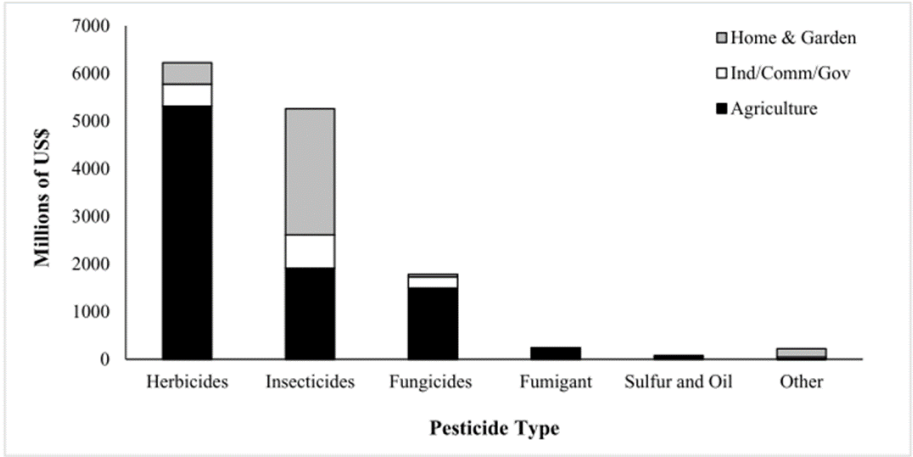
Sample number	% stock	Concentration (M)	Peak Absorbance
0	100	7.17E-05	1.648
1	90	6.45E-05	1.518
2	80	5.74E-05	1.385
3	70	5.02E-05	1.247
4	60	4.30E-05	1.079
5	50	3.59E-05	0.912
6	40	2.87E-05	0.722
7	30	2.15E-05	0.534
8	20	1.43E-05	0.354
9	10	7.17E-06	0.173

$A = 23{,}174\ (L\ mol^{-1}\ cm^{-1}) \times (1\ cm)\ C\ (mol\ L^{-1}) + 0.0433$

PESTICIDE USAGE



World and U.S. Pesticide Amounts of Active Ingredient at Producer Level by Pesticide Type, 2012 Estimates from a 2016 EPA release[1]



User Expenditures on Pesticides in the United States by Pesticide Type and Market Sector, 2012 Estimates from a 2016 EPA release[1]