UV Photolysis of DBPs in Chlorinated Recreational Water

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Presentation Outline

- Use of UV Radiation in Water Treatment
- Photochemistry Basics
- Swimming Pool Chlorination (DBPs)
- Experimental Methods
- Results
- Implications
- Future Work
- Acknowledgements

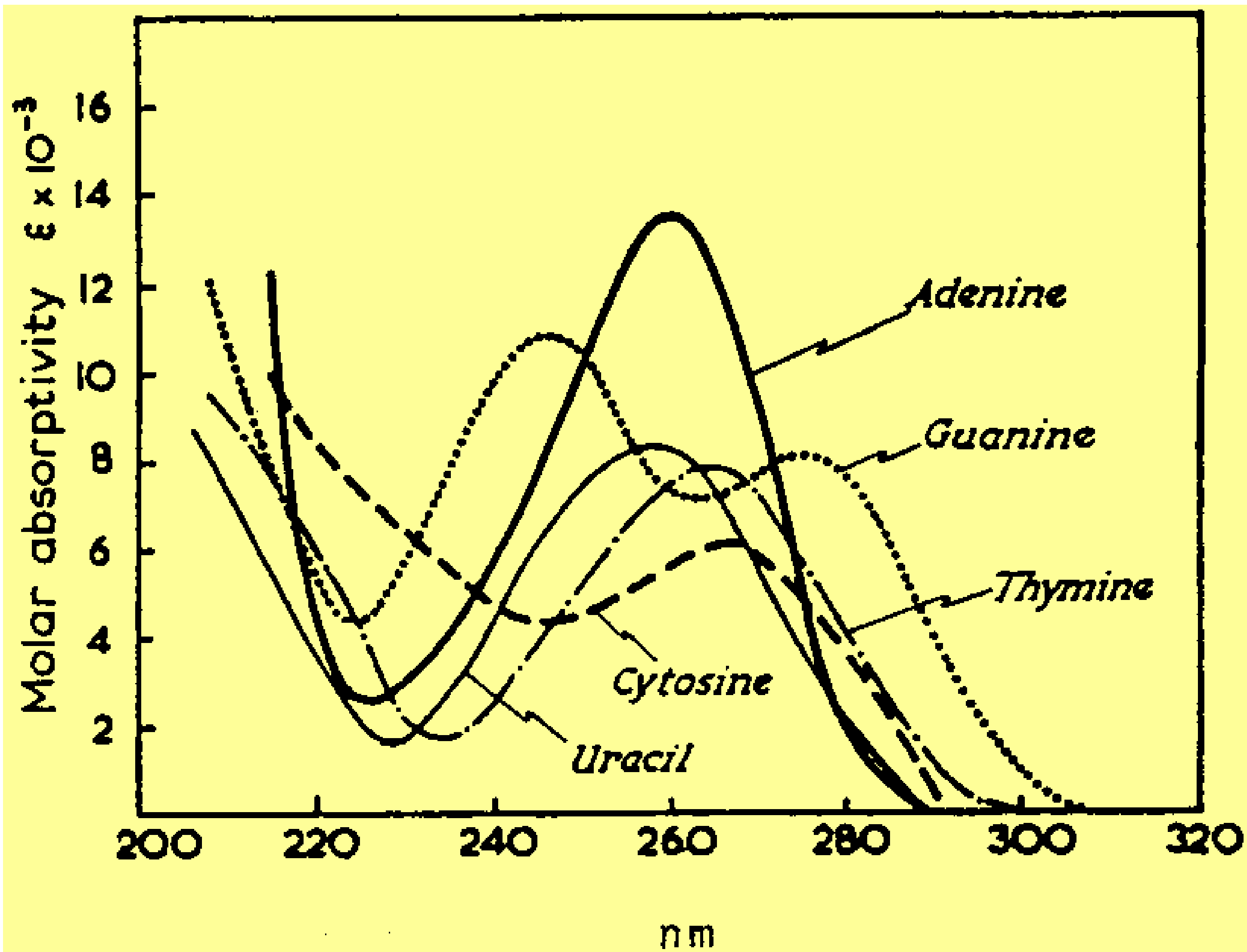
Uses of UV Radiation in Water Treatment

- Disinfection
  - Broad-Spectrum Antimicrobial Agent
    - Bacteria (spores, vegetative cells)
    - Viruses
    - Protozoa (*Cryptosporidium parvum*, *Giardia lamblia*)
  - Fast Reactions $\rightarrow$ Small Footprint
  - Low Cost
  - Minimal DBP Formation
  - Doses up to 200-300 mJ/cm^2
  - Wavelength Dependence (UV Source Dependence)
- Photolysis
  - Only Effective Against Absorbing Compounds
  - Dose Range Often Higher Than With Disinfection
  - Application Less Common Than Disinfection
  - Wavelength Dependence (UV Source Dependence)

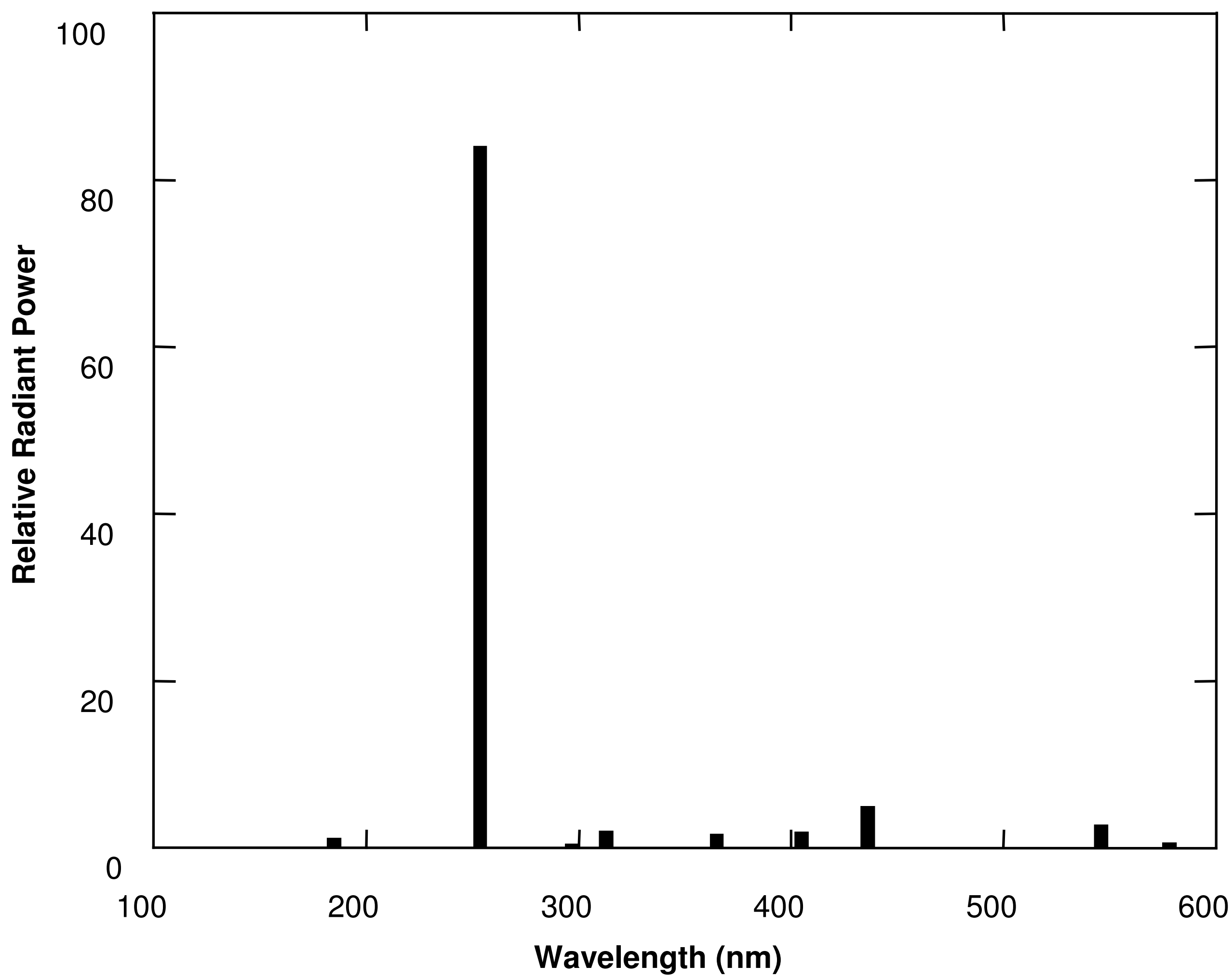
Photochemistry Basics

- Photochemical Reactions Require:
  - Absorption of Radiation by Target Molecule
  - Sufficient Photon Energy to Break or Form a Chemical Bond
- Photon Energy Depends on Wavelength
- Bond Energy Often Similar to Photon Energy Within Ultraviolet (UV) Spectrum

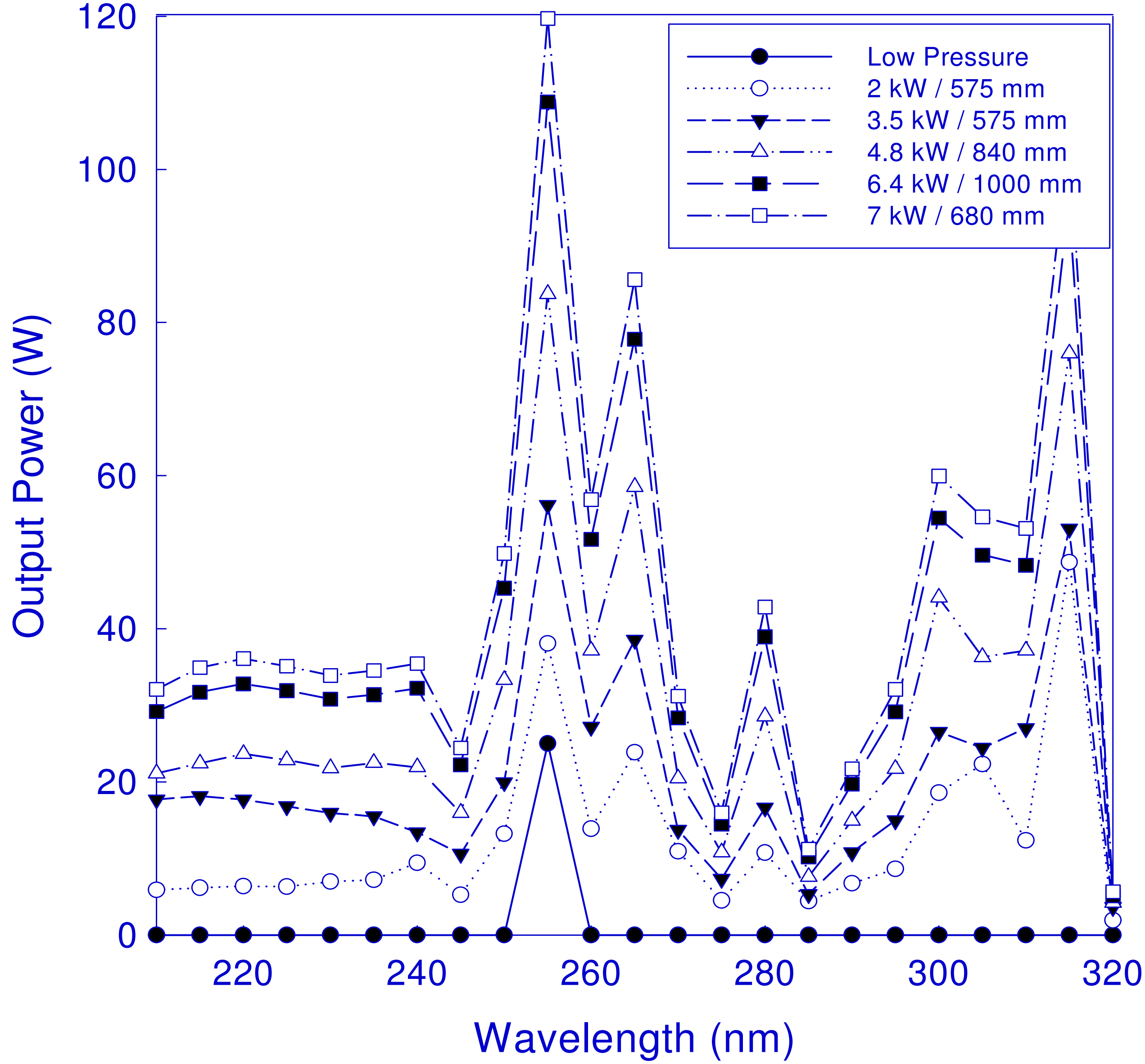
Absorption Spectra of Relevant Biological Molecules (Jagger, 1967)



Emission Spectrum
Low-Pressure Hg Lamp

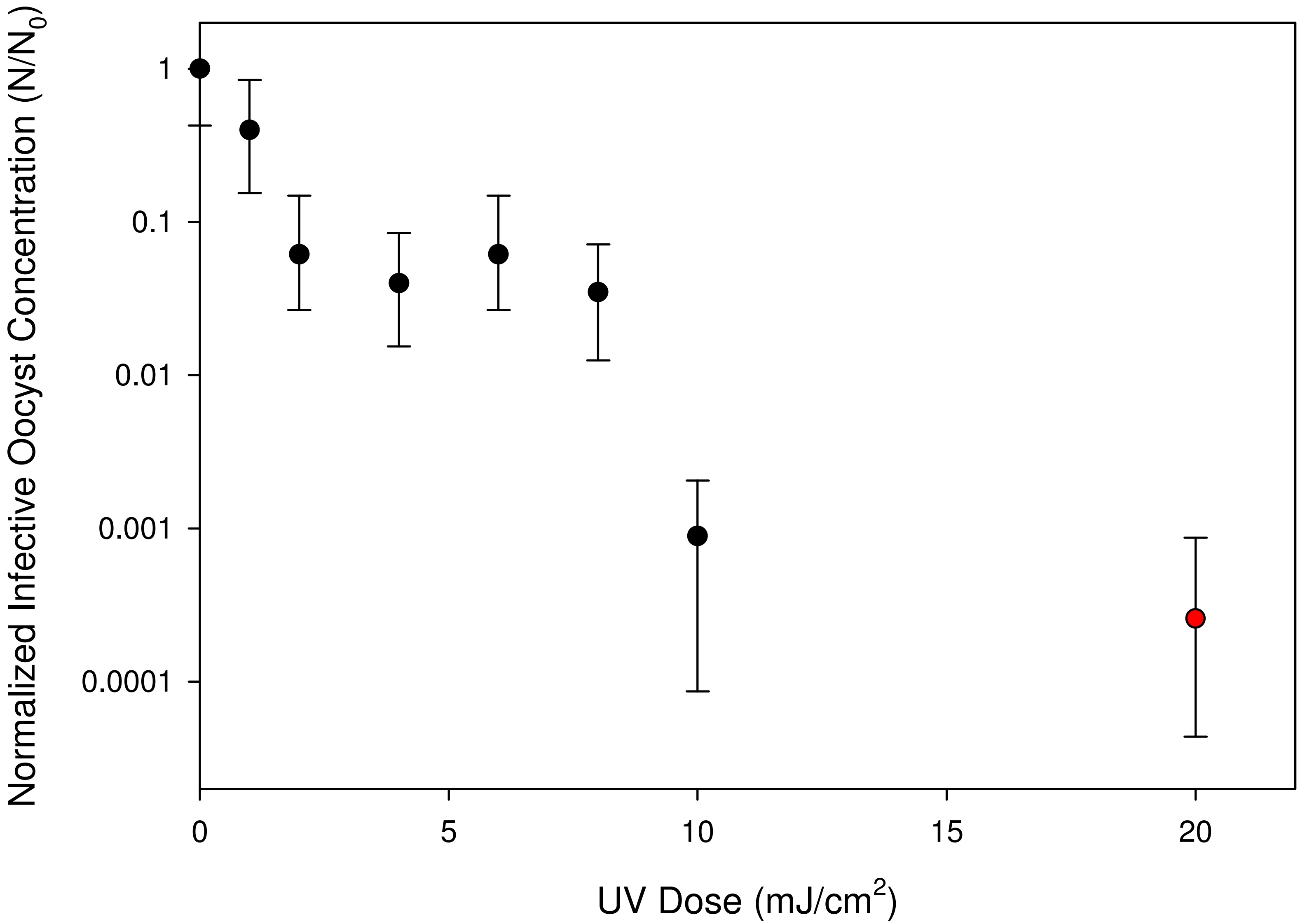


Emission Spectra: Medium Pressure Lamps



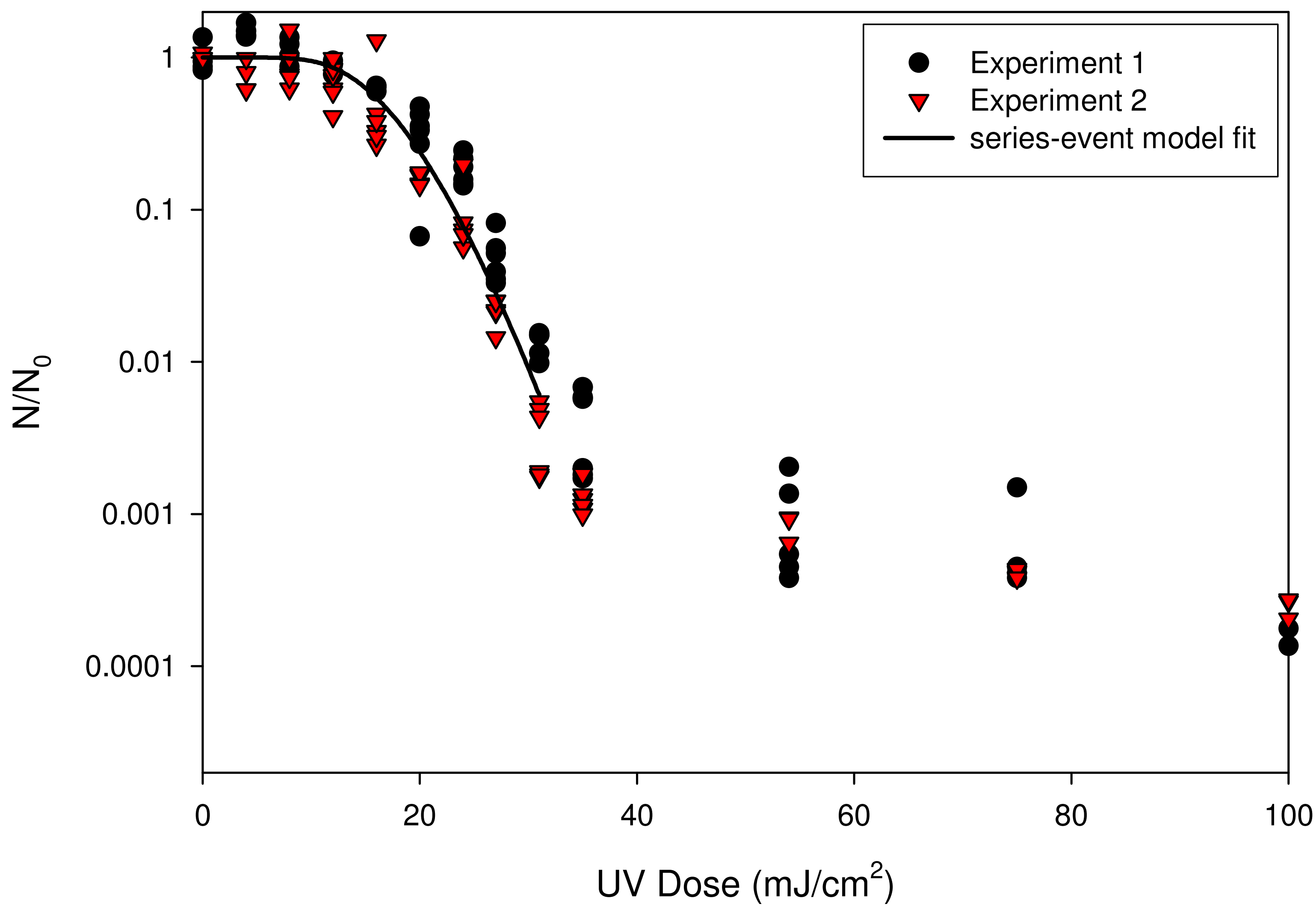
C. parvum UV_{254} Dose-Response Behavior

Landis, H.E.; Thompson, J.E.; Robinson, J.P.; Blatchley III, E.R. (2000) "Inactivation Responses of *Cryptosporidium parvum* to UV Radiation and Gamma Radiation," *Proceedings, Water Quality Technology Conference*, AWWA, Salt Lake City, UT; 7 November 2000.



B. anthracis (Sterne) Spore UV_{254} Dose-Response Behavior

Blatchley III, E.R.; Meeusen, A.; Aronson, A.I.; Brewster, L. (2005) "Inactivation of *Bacillus* Spores by Physical Disinfectants," *Journal of Environmental Engineering (ASCE)*, 131, 9, 1245-1252.



Chlorination of Recreational Waters (Swimming Pools)

- Microbial Inactivation
  - Effective control of (most)
    - Bacteria
    - Viruses
  - Poor control of protozoa
    - *C. parvum*
    - *G. lamblia*
- Recommended Concentration: 1-3 mg/L as Cl_2
- Disinfection By-Products (DBPs)

Organic Precursors in Swimming Pools

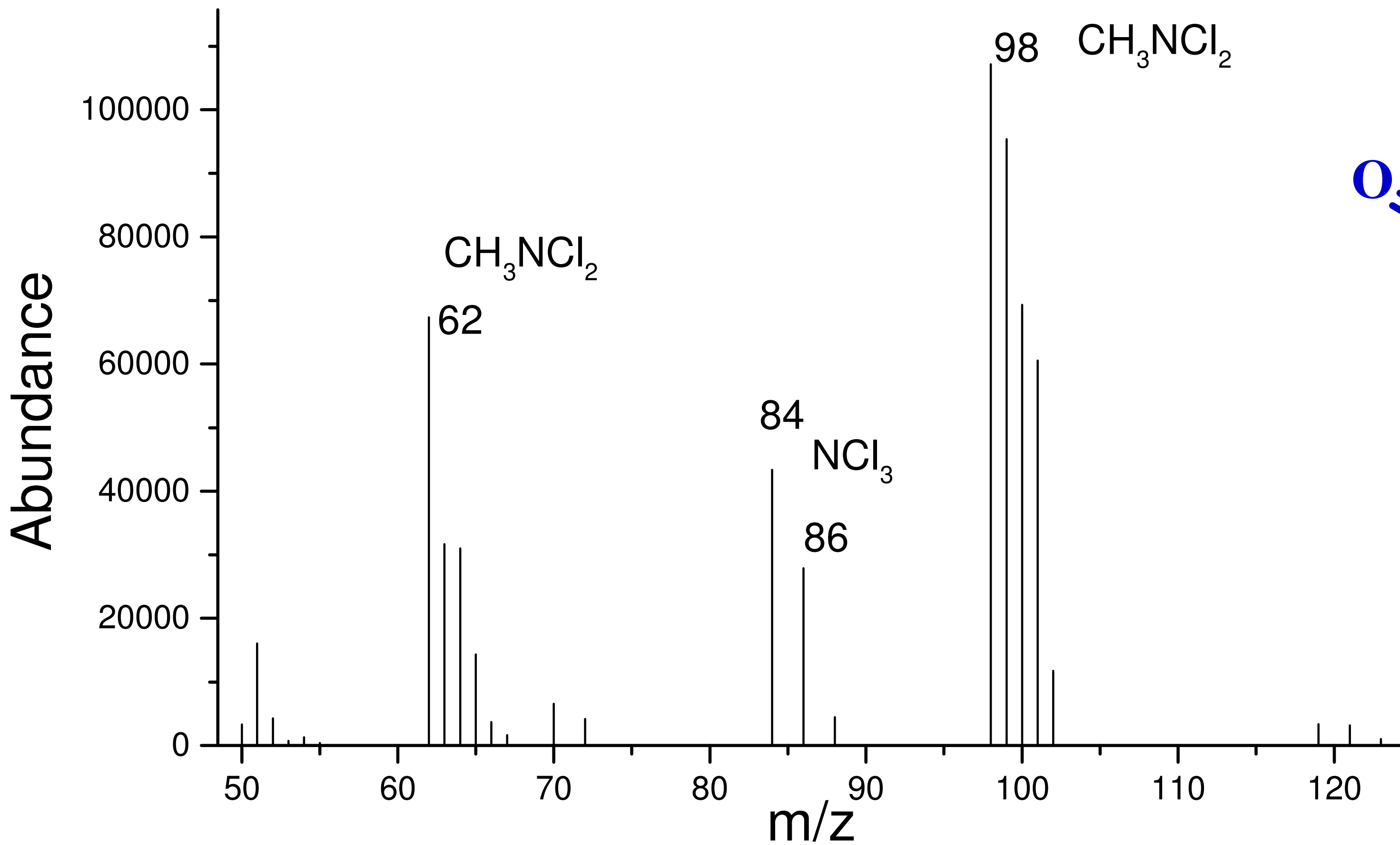
- Creatinine: Breakdown product of creatine phosphate in muscle tissue; present in sweat, urine
- Urea: Metabolic conversion of NH_3 in liver; present in sweat, urine
- Amino acids: Present in sweat, urine
- Personal care products
  - Deodorants
  - Make-up
  - Etc.

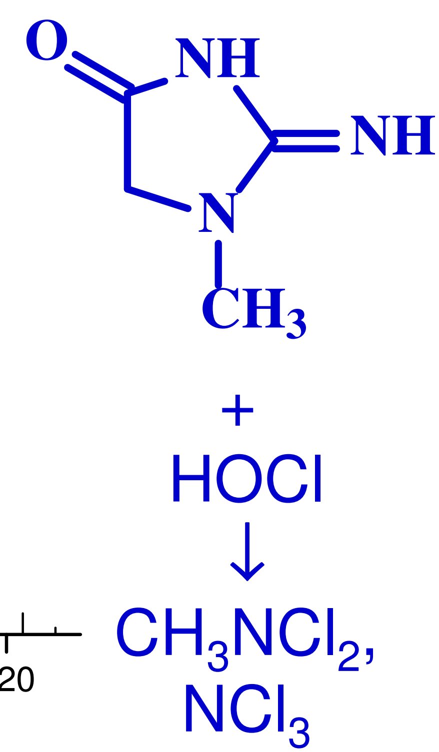
DBP Formation Experiments

Li, J. and Blatchley III, E.R. (2007) "Volatile Disinfection Byproduct Formation Resulting from Chlorination of Organic-Nitrogen Precursors in Swimming Pools," *Environmental Science & Technology*, 10.1021/es070871+

- Pure Compounds
  - Creatinine
  - Urea
  - L-histidine
  - L-arginine
- Body Fluid Analog
- Pool Water Samples

Chlorination of Creatinine
[P] = 1.8 x 10^{-4} M, Cl:P = 5; pH = 7.5





Volatile DBP Measurement in Samples of Recreational Water

Sample	NCl_3 (mg/L as Cl_2)	$CHCl_3$ (mg/L)	$CNCHCl_2$ (mg/L)	Free Chlorine (mg/L as Cl_2)	Inorganic Chloramine (mg/L as Cl_2)
A	0.08	0.07	0.01	1.5	1.34
B	0.07	0.13	0.03	1.95	0.25
C	0.09	0.14	0.01	0.68	1.36
D	0.16	0.08	0.02	6.52	1.76
E	0.1	0.13	0.01	5.92	1.28
F	0.07	0.08	0.01	1.72	0.76

A, C, E, F: Indoor lap Swimming Pool;
B: Outdoor General Use Swimming Pool; D: Outdoor Recreation Park
Pool A: 10 ppb dichloromethylamine; CNCl never found

Health Effects of Recreational Water Halogenated DBPs

Compound	Structure	Toxicology
Trichloramine	NCl_3	Eye, nose, throat irritant, may promote asthma
Dichloroaceto-nitrile	$N{\equiv}CHCCl_2$	Possible mutagen, respiratory irritant
Dichloromethyl-amine	CH_3NCl_2	Malodor, ?
Cyanogen chloride	$N{\equiv}CCl$	Suspected neurotoxicant, respiratory toxicant, skin and sense organ toxicant

- Volatile DBPs not limited to NCl_3, $CHCl_3$
- N-Containing DBPs may display greater toxicity than other DBPs

Effects of Swimming Pool DBPs on Human Health

- Increased Incidence of Respiratory Problems (Asthma)
- Incidence of Asthma Relatively High Among Swimmers, Lifeguards
- Effects Related to Chlorine Concentration
- Generally Attributed to NCl_3
- Swimming Often Prescribed as Therapy for Asthmatics
- Translation to Other Water Treatment Settings

http://www.usaswimming.org/RSS/2006%20U.S.%20Open%20-%20Swimming/Album5.htm

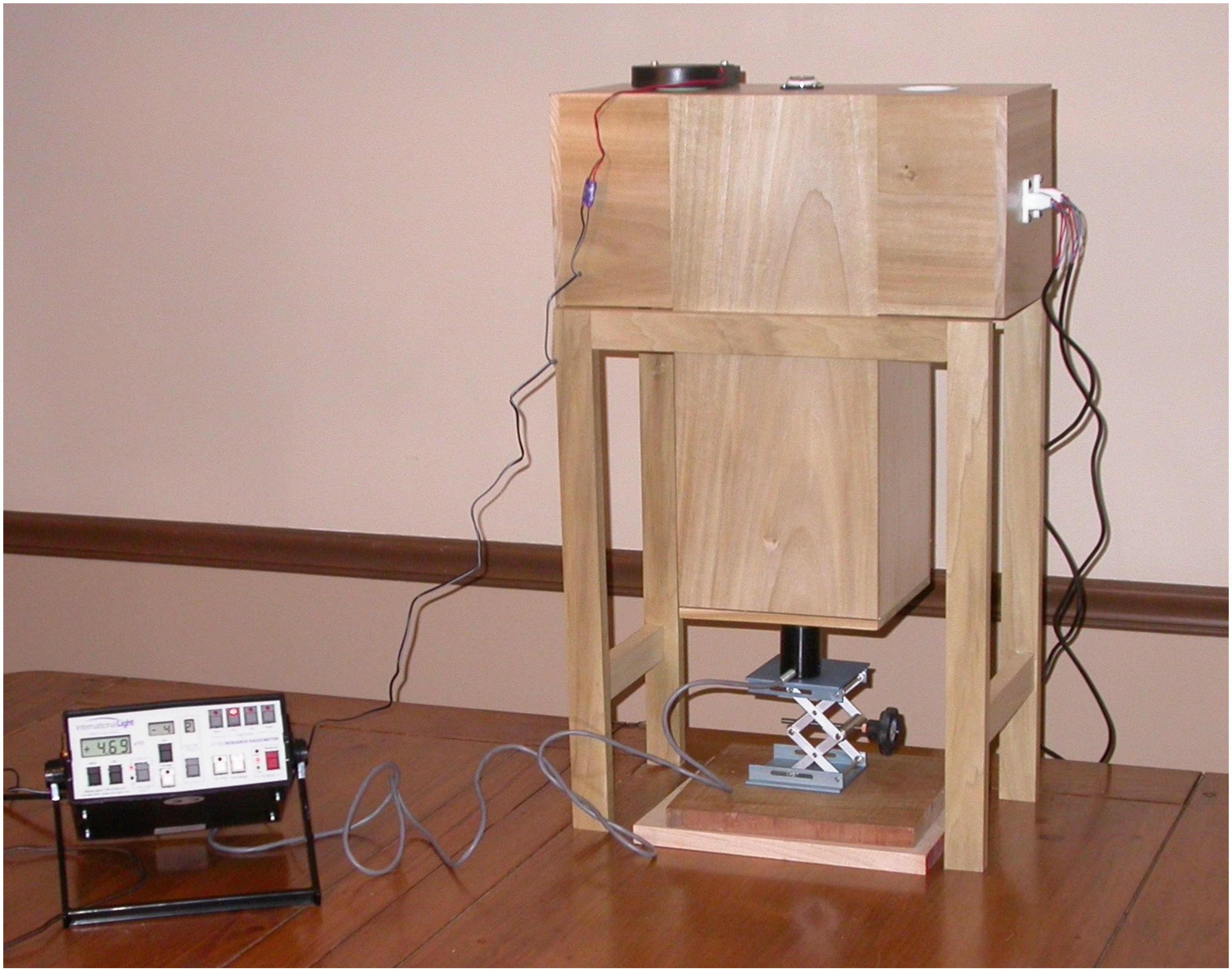
UV Use in Swimming Pools and Recreational Water

- Alternative Disinfectant
  - *Cryptosporidum parvum*
  - NY Water Park Outbreak
    - 3000 cases
    - UV now required in NY water parks
- Chloramine Control
  - Inorganic chloramines photodegrade
  - Free chlorine photodecays slowly
  - Selective removal of inorganic chloramines
- Effects on Chlorinated Organic-N Compounds?

DBP Photochemistry

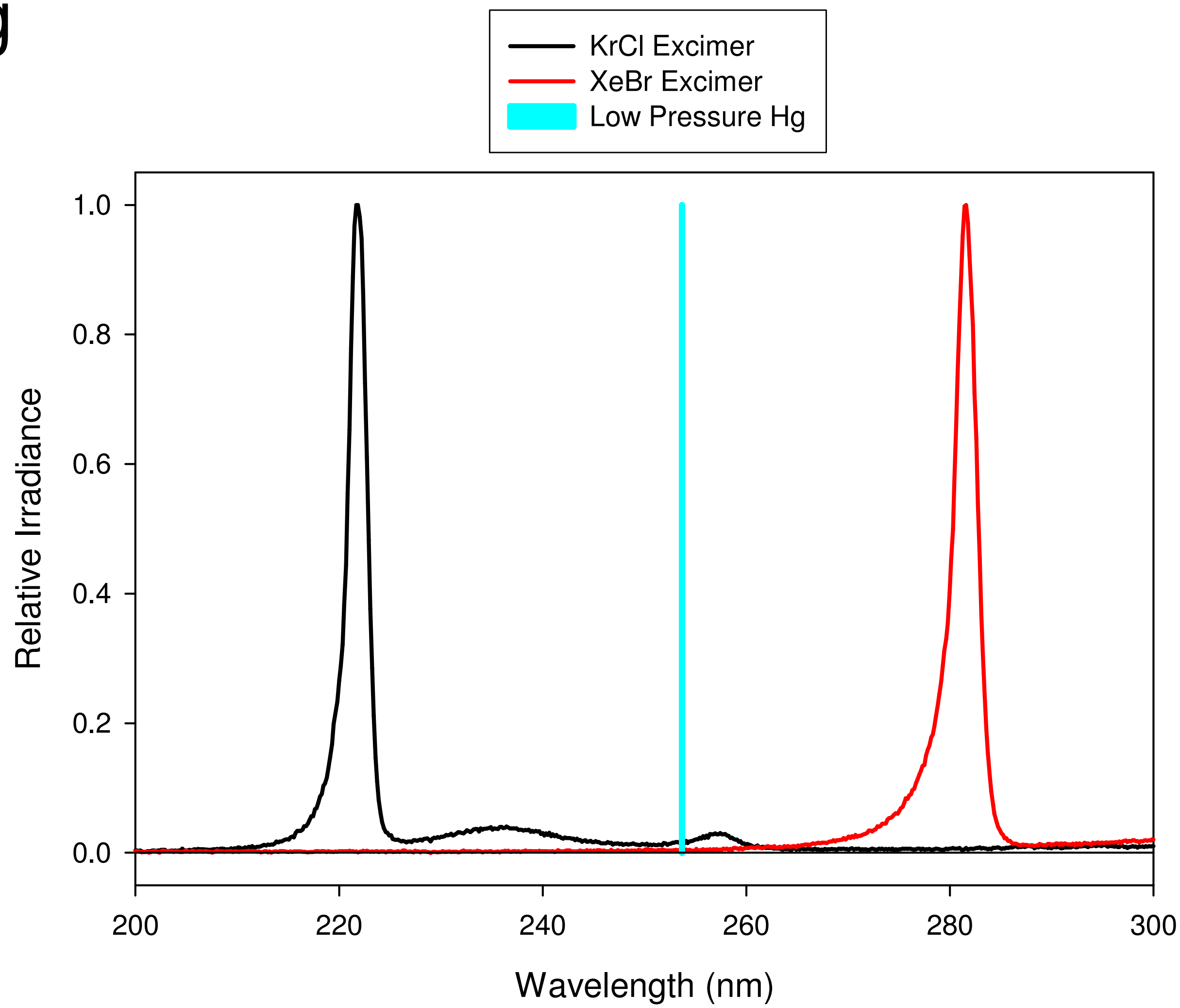
- Spectrophotometry
- Wavelength-dependent photodegradation
- Collimated beams
  - KrCl excimer lamp ($\lambda \approx 222$ nm)
  - LP Hg lamp ($\lambda \approx 254$ nm)
  - XeBr excimer lamp ($\lambda \approx 282$ nm)
- Monitor reaction progress with MIMS

Collimated Beam (UV Source)



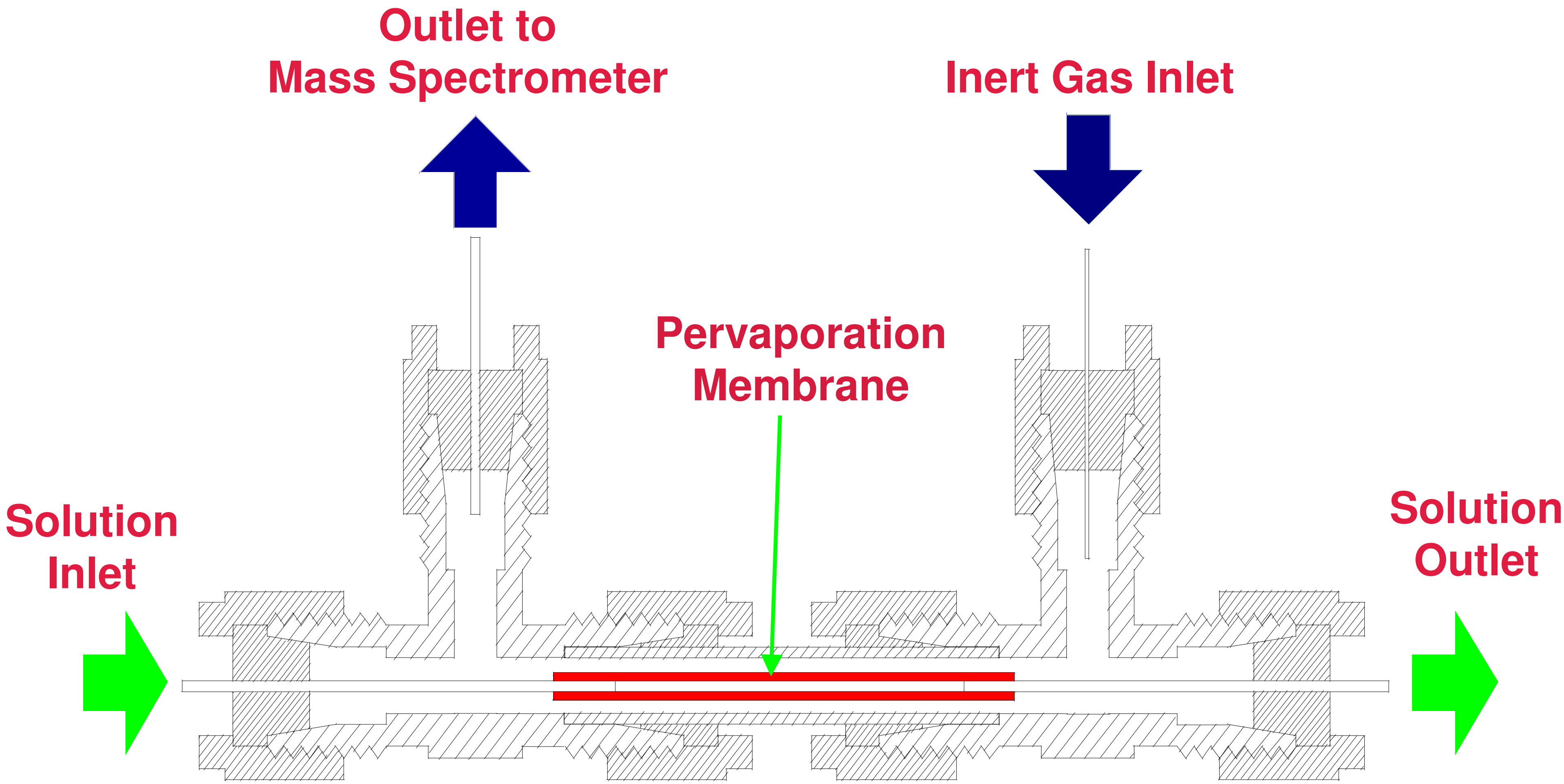
Collimated Beam Types Used in This Research

- Low-Pressure Hg
- Excimer Lamp
  - XeBr (282 nm)
  - KrCl (222 nm)



Membrane Introduction Mass Spectrometry (MIMS): Membrane Cell

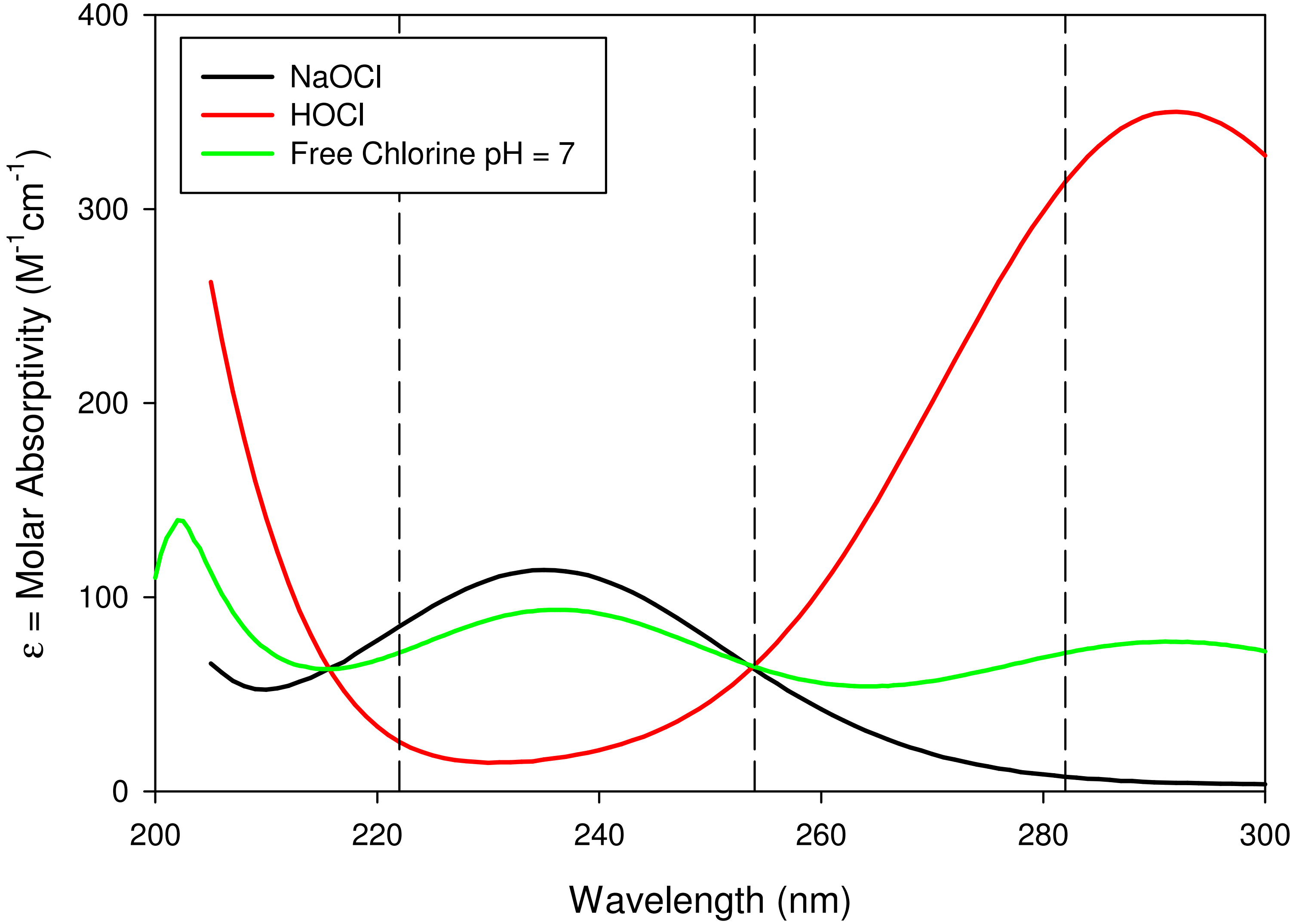
Shang, C., and Blatchley III, E.R. (1999) "Differentiation and Quantification of Free Chlorine and Inorganic Chloramines in Aqueous Solution by MIMS," *ES&T*, 33, 13, 2218-2223.



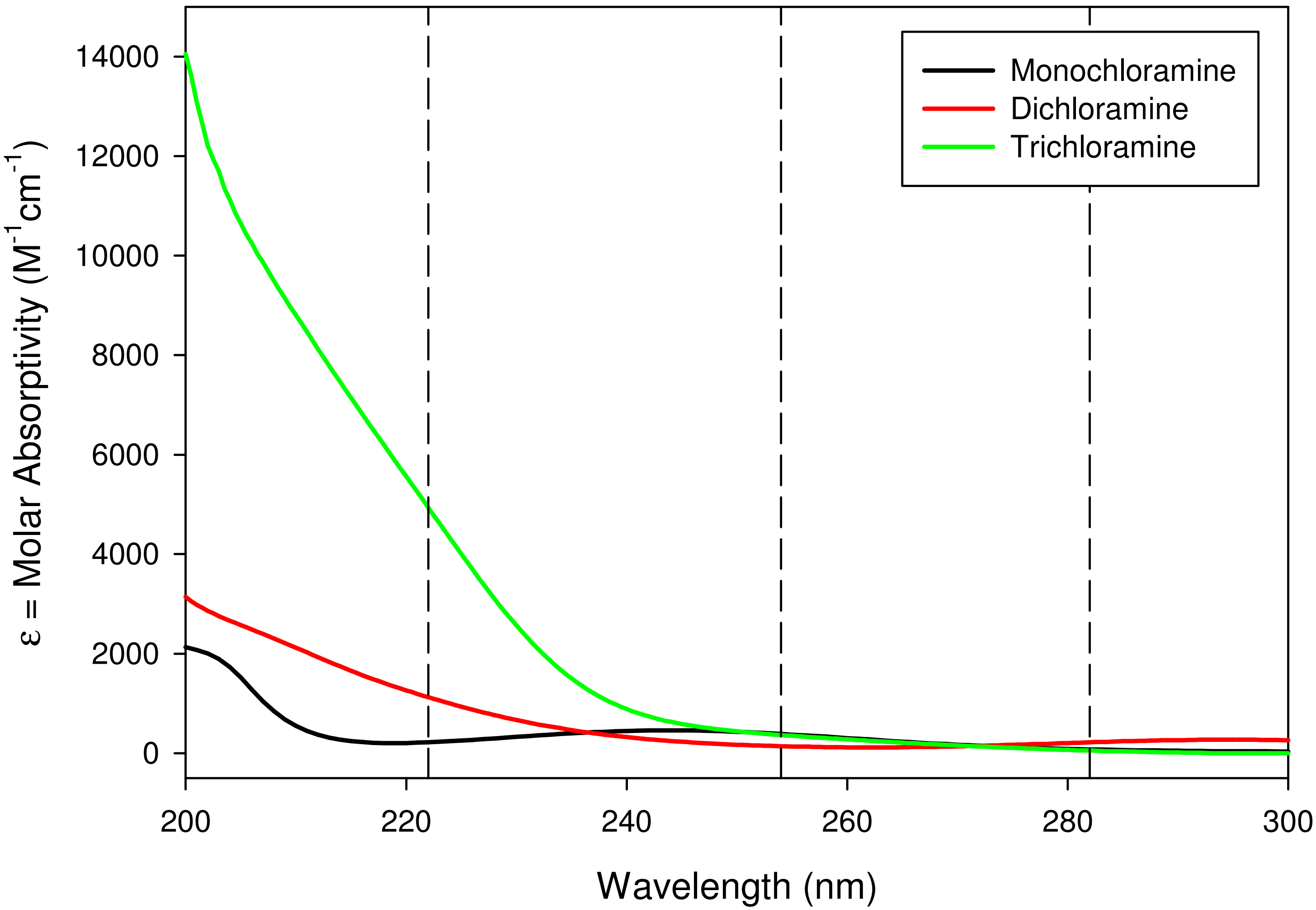
Other Analytical Methods

- Ion Chromatography
- UV-Visible Spectrophotometry
- Wet Chemistry
  - DPD/FAS Titration
  - DPD Colorimetric
  - Alkalinity Titration
- pH Probe

UV Absorbance Spectra: Free Chlorine ($HOCl + OCl^-$)



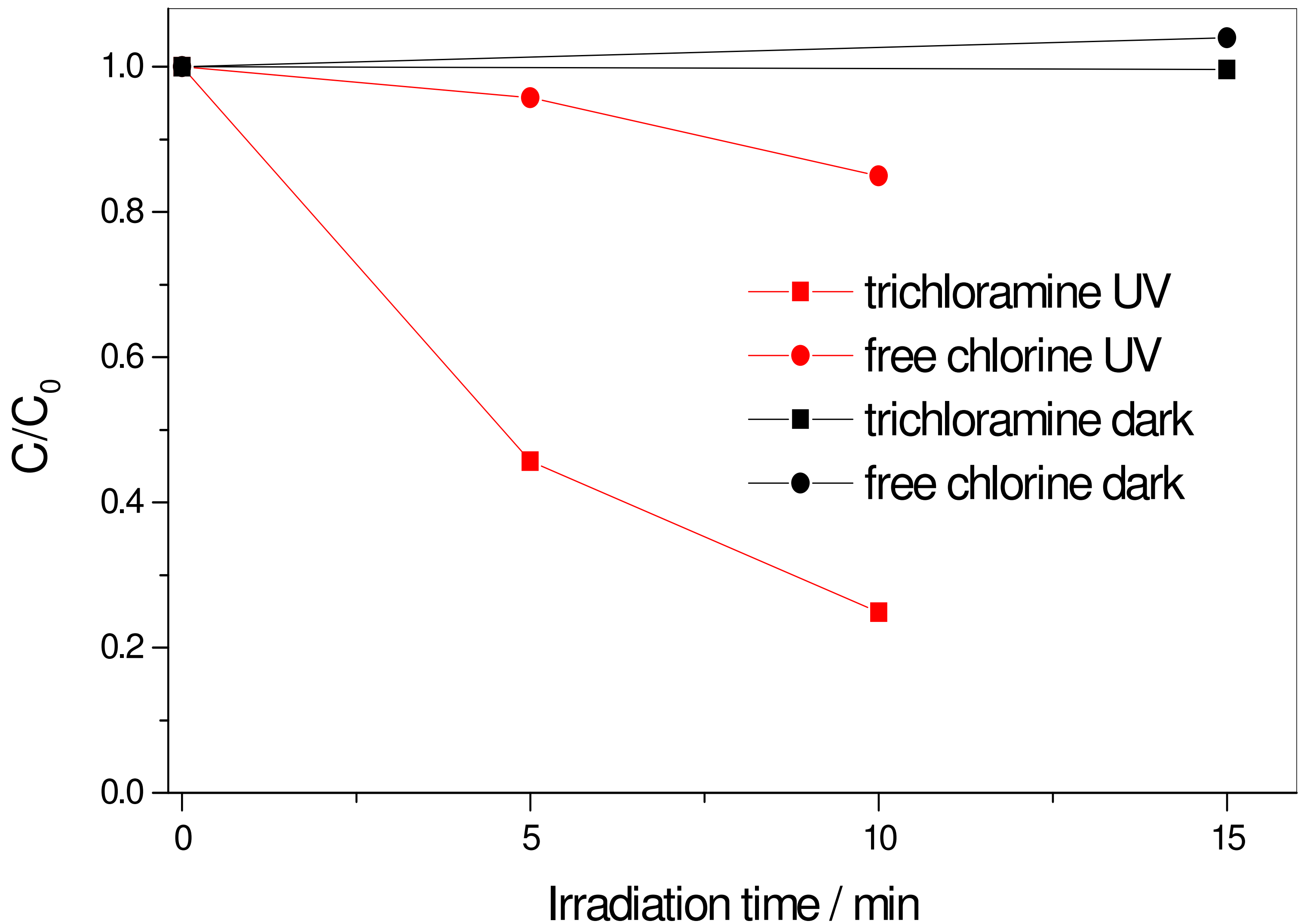
UV Absorbance Spectra: Inorganic Combined Chlorine (NH_2Cl, $NHCl_2$, NCl_3)



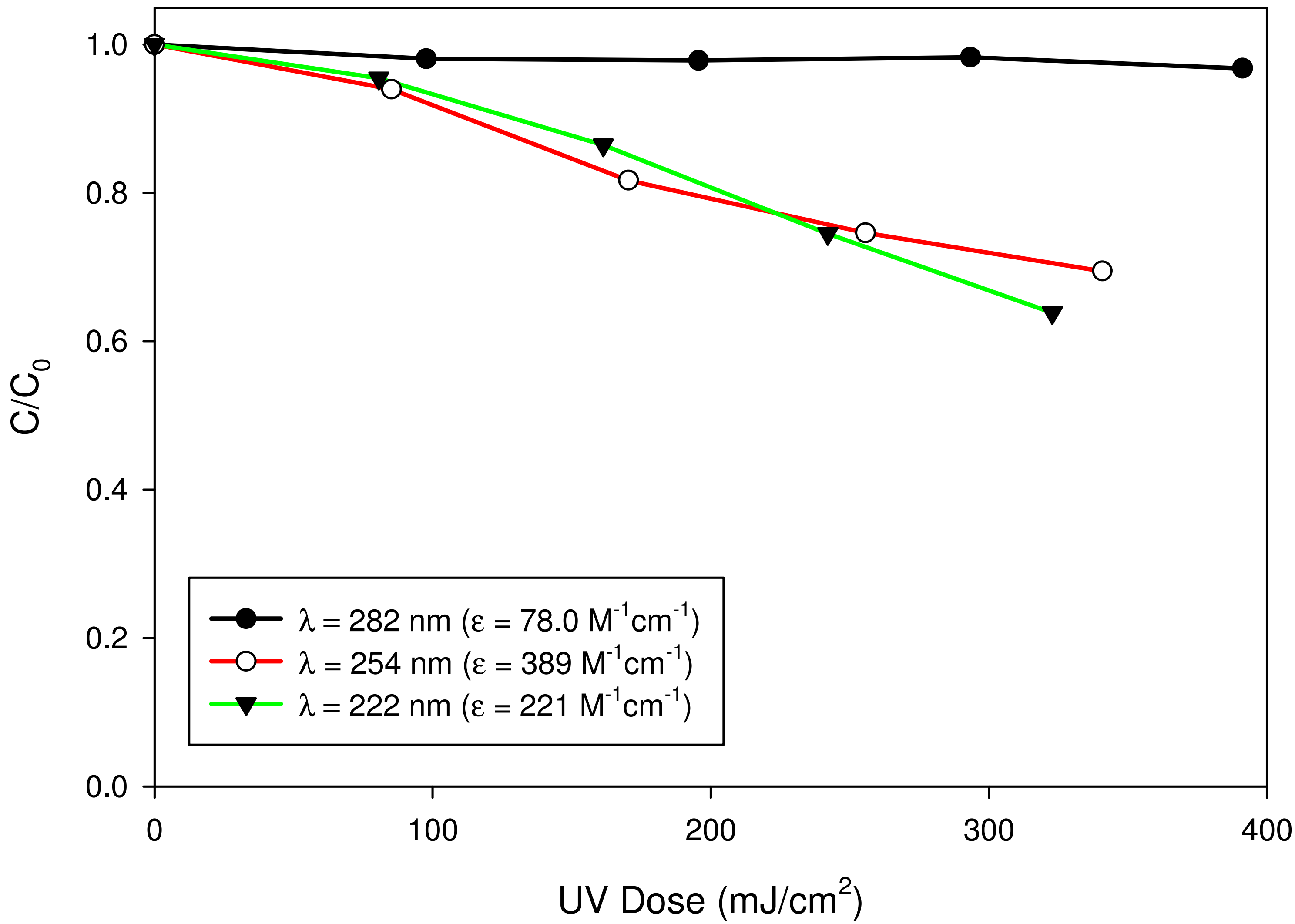
UV Absorbance: Free Chlorine and Inorganic Chloramines

- Free Chlorine:
  - HOCl, OCl^-
  - Poor Absorbers of Germicidal UV
  - Minimal Potential to Photodegrade
- Inorganic Combined Chlorine
  - NH_2Cl, $NHCl_2$, NCl_3
  - Moderate to Strong Absorbers of UV (λ)
  - May Photodegrade

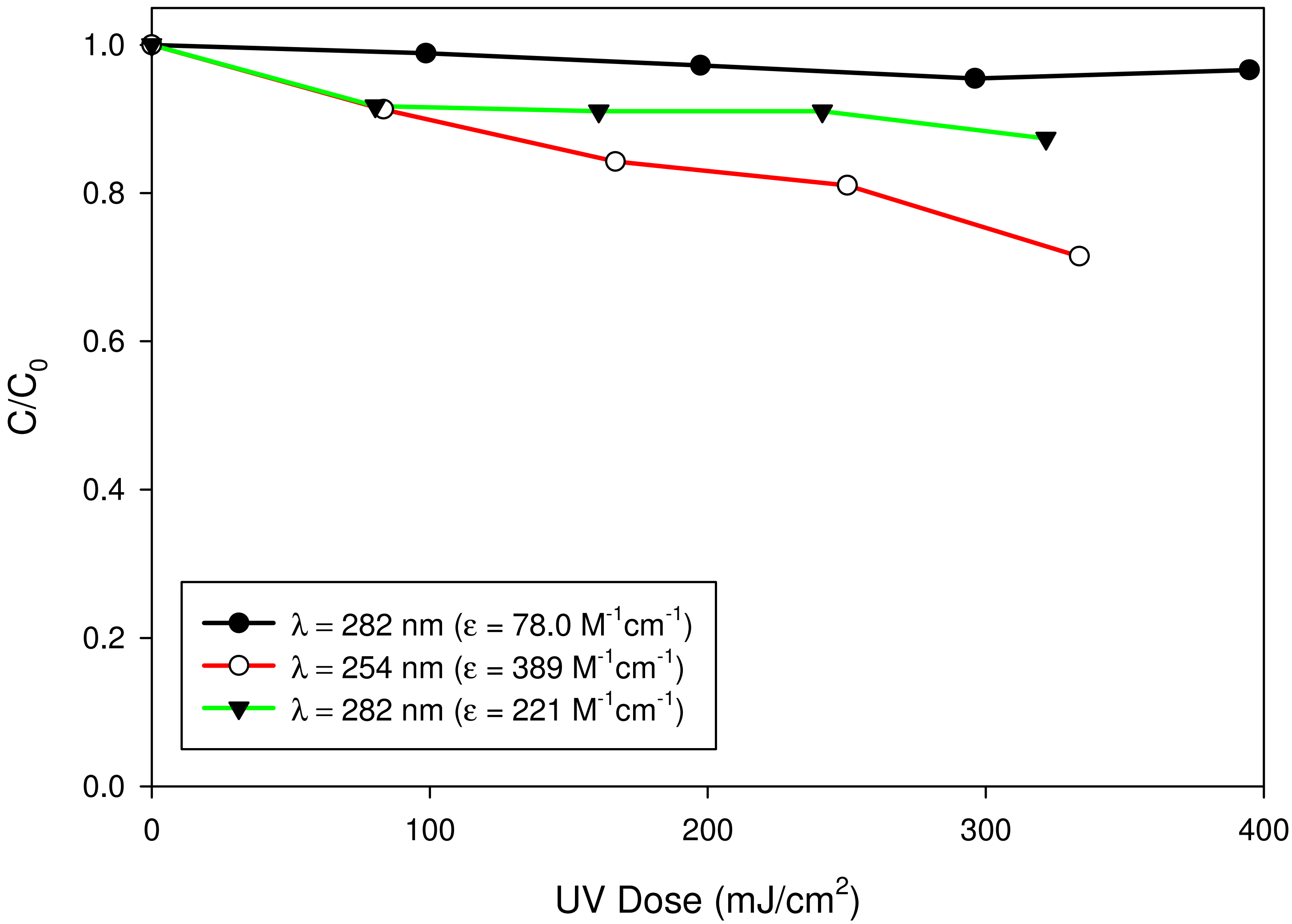
UV_{254} Irradiation: Free Chlorine + NCl_3
$I_0 = 560\ \mu W/cm^2$



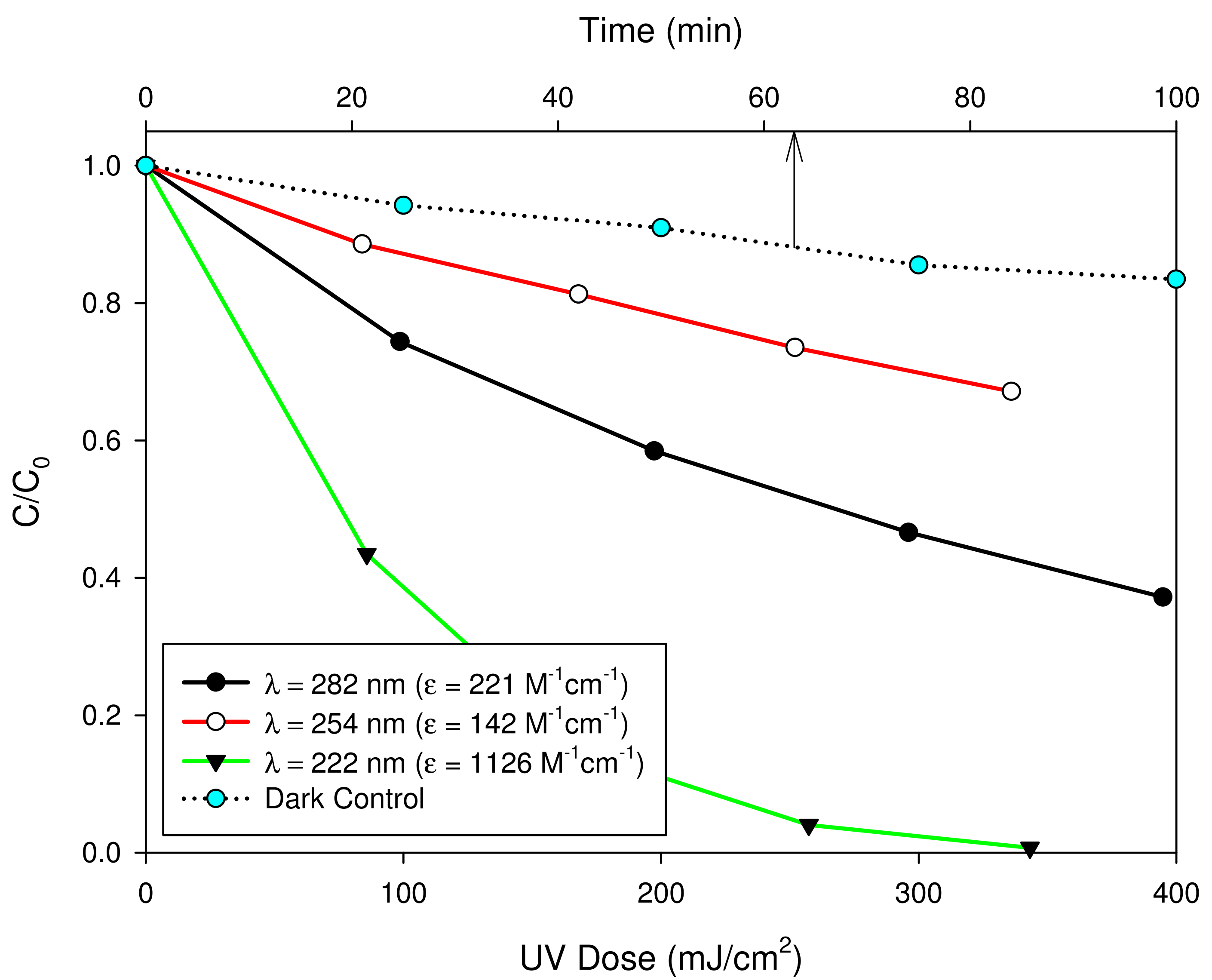
NH_2Cl Photodecay; pH = 7.5
Alkalinity = 120 mg/L as $CaCO_3$



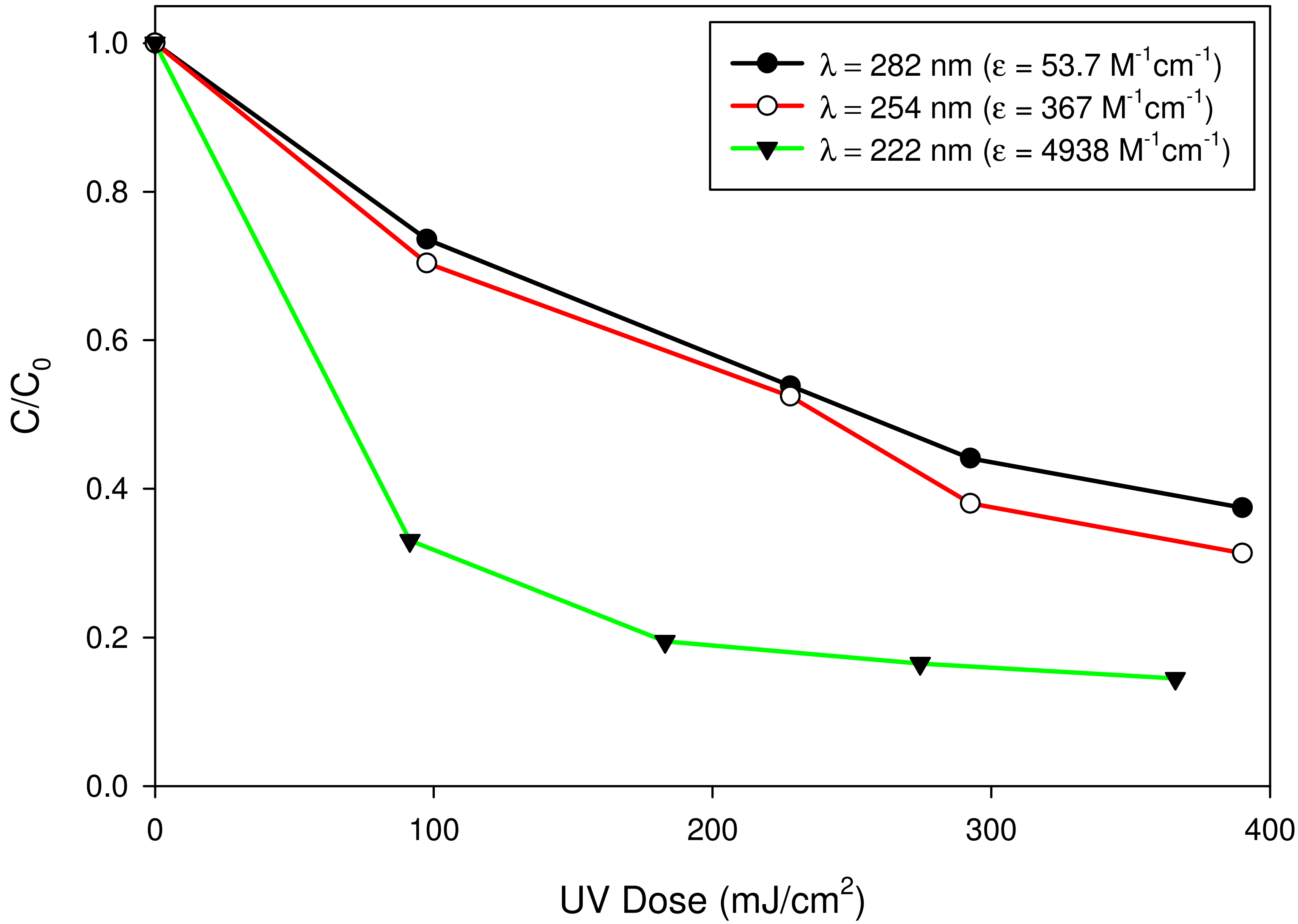
NH_2Cl Photodecay; pH = 6.5
Alkalinity = 120 mg/L as $CaCO_3$



$NHCl_2$ Photodecay; pH = 7.5
Alkalinity = 120 mg/L as $CaCO_3$



NCl_3 Photodecay; pH = 7.5
Alkalinity = 120 mg/L as $CaCO_3$



Photodegradation of Inorganic Chloramines

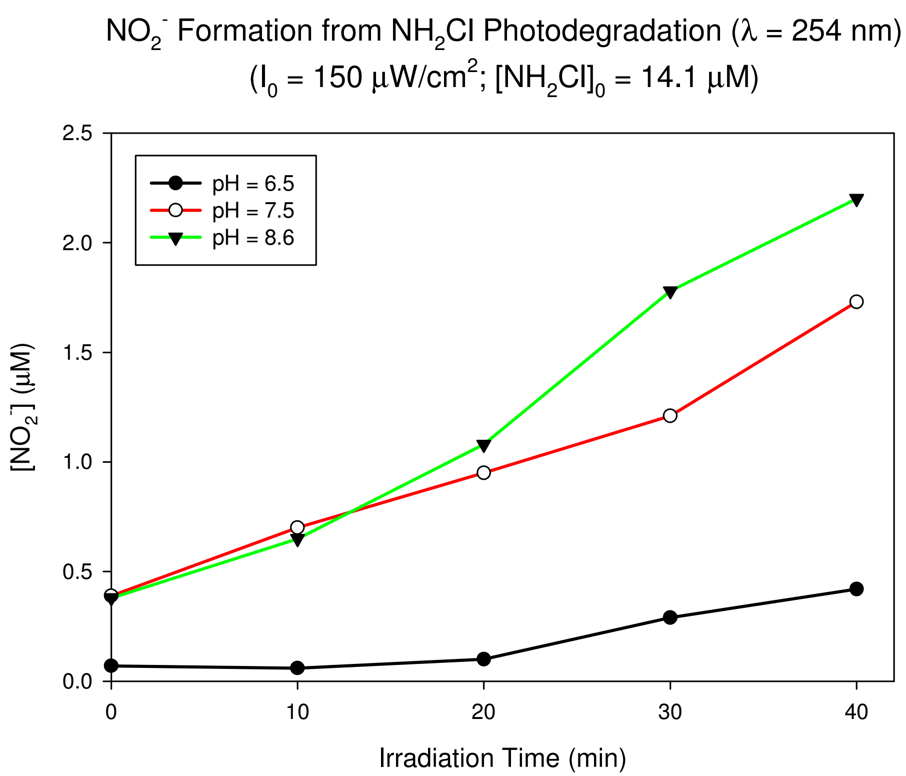
$$NH_2Cl \xrightarrow{h\nu} \bullet NH_2 + Cl\bullet \rightarrow ???$$

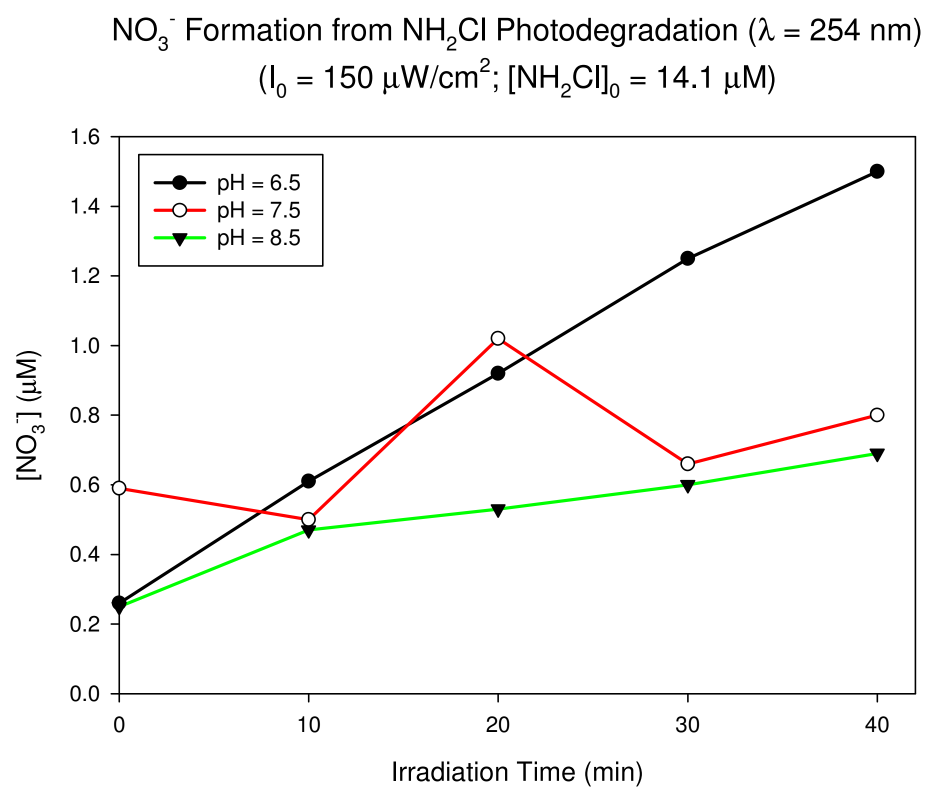
$$NHCl_2 \xrightarrow{h\nu} \bullet NHCl + Cl\bullet \rightarrow ???$$

$$NCl_3 \xrightarrow{h\nu} \bullet NCl_2 + Cl\bullet \rightarrow ???$$

Byproducts of UV_{254} Irradiation:

$$NH_2Cl \xrightarrow{h\nu} NO_2^- + NO_3^- + ?$$

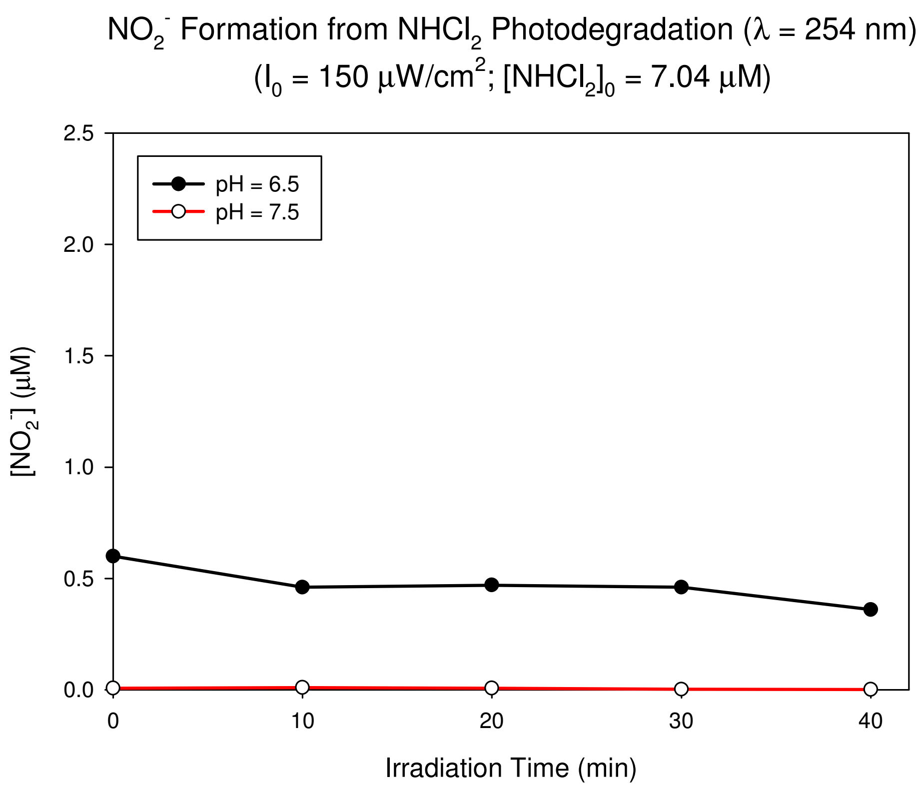


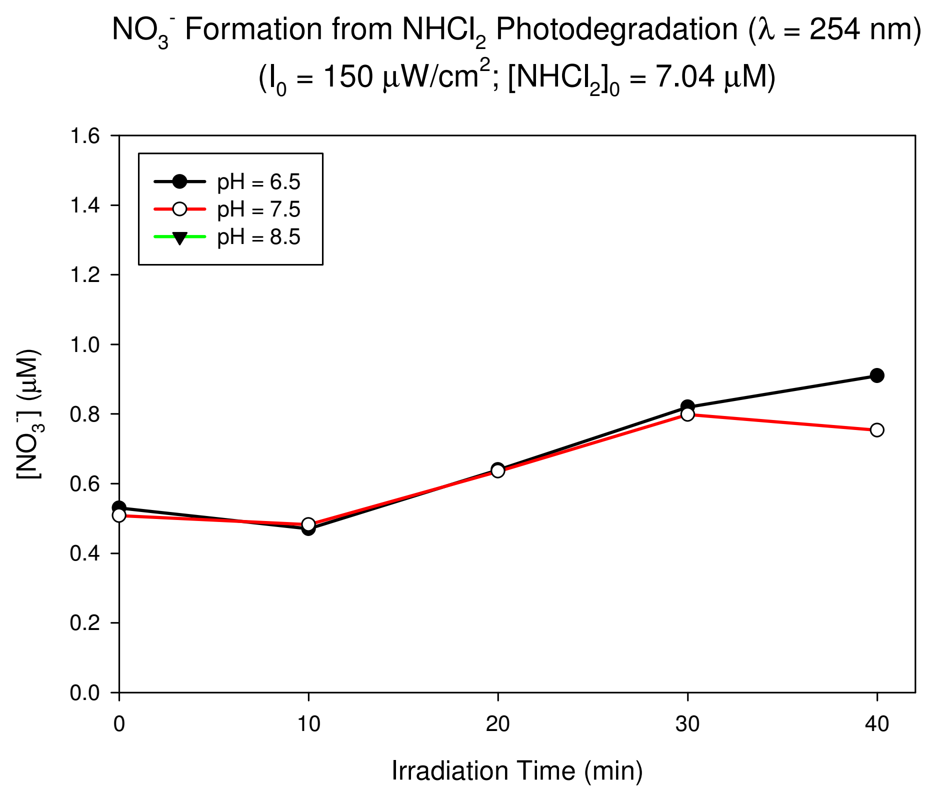


NO_2^- and NO_3^- formed account for 13-20% of Original Reduced-N Concentration

Byproducts of UV_{254} Irradiation:

$$NHCl_2 \xrightarrow{h\nu} NO_2^- + NO_3^- + ?$$

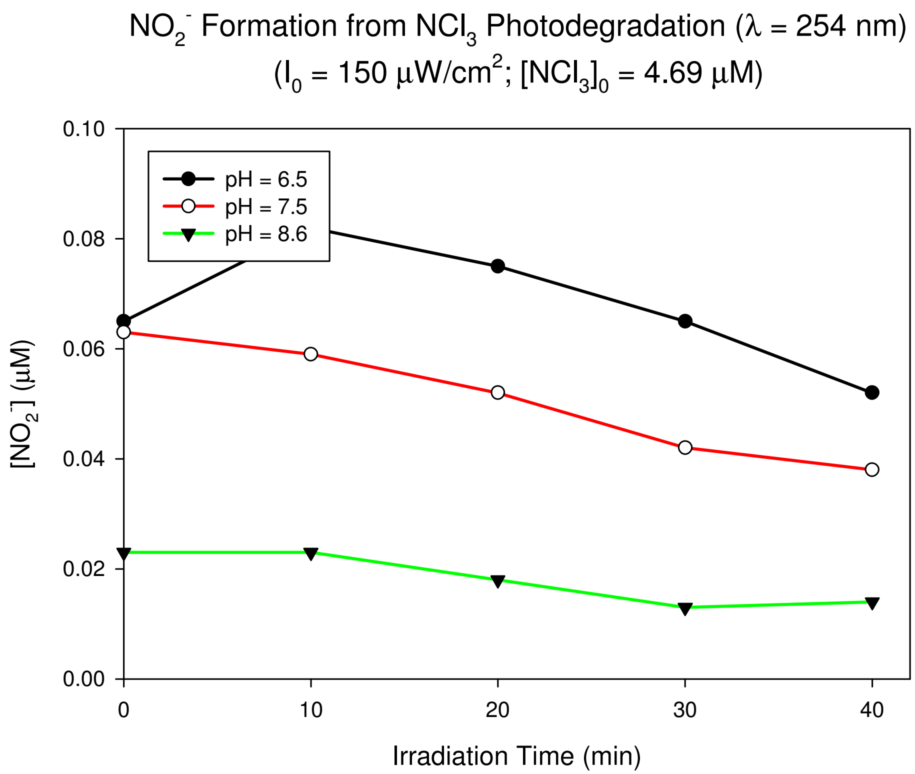


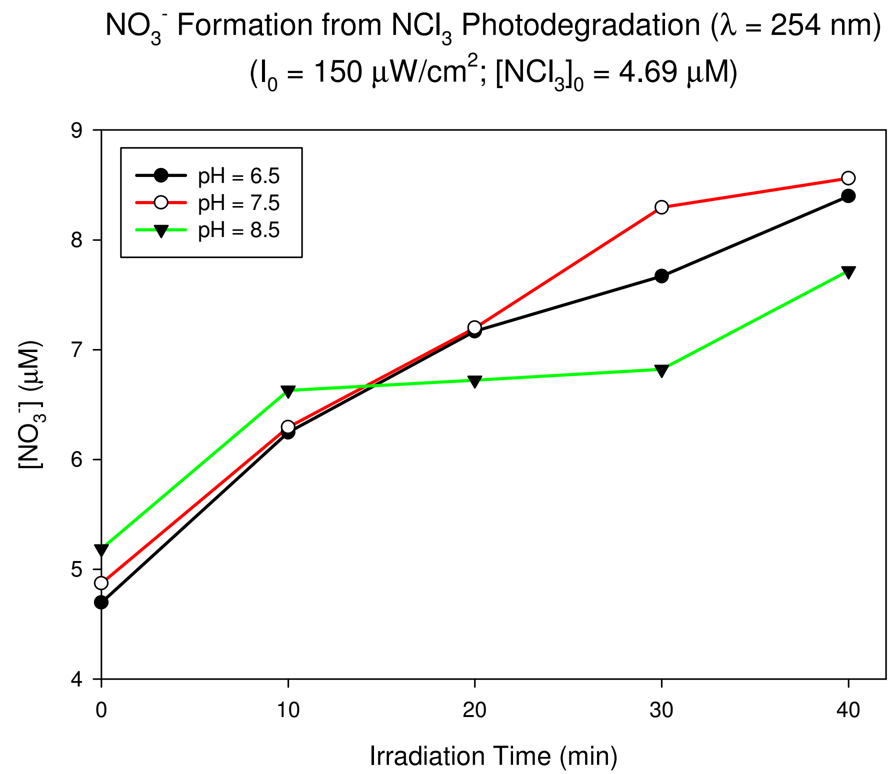


NO_2^- and NO_3^- formed account for 10-20% of Original Reduced-N Concentration

Byproducts of UV_{254} Irradiation:

$$NCl_3 \xrightarrow{h\nu} NO_2^- + NO_3^- + ?$$



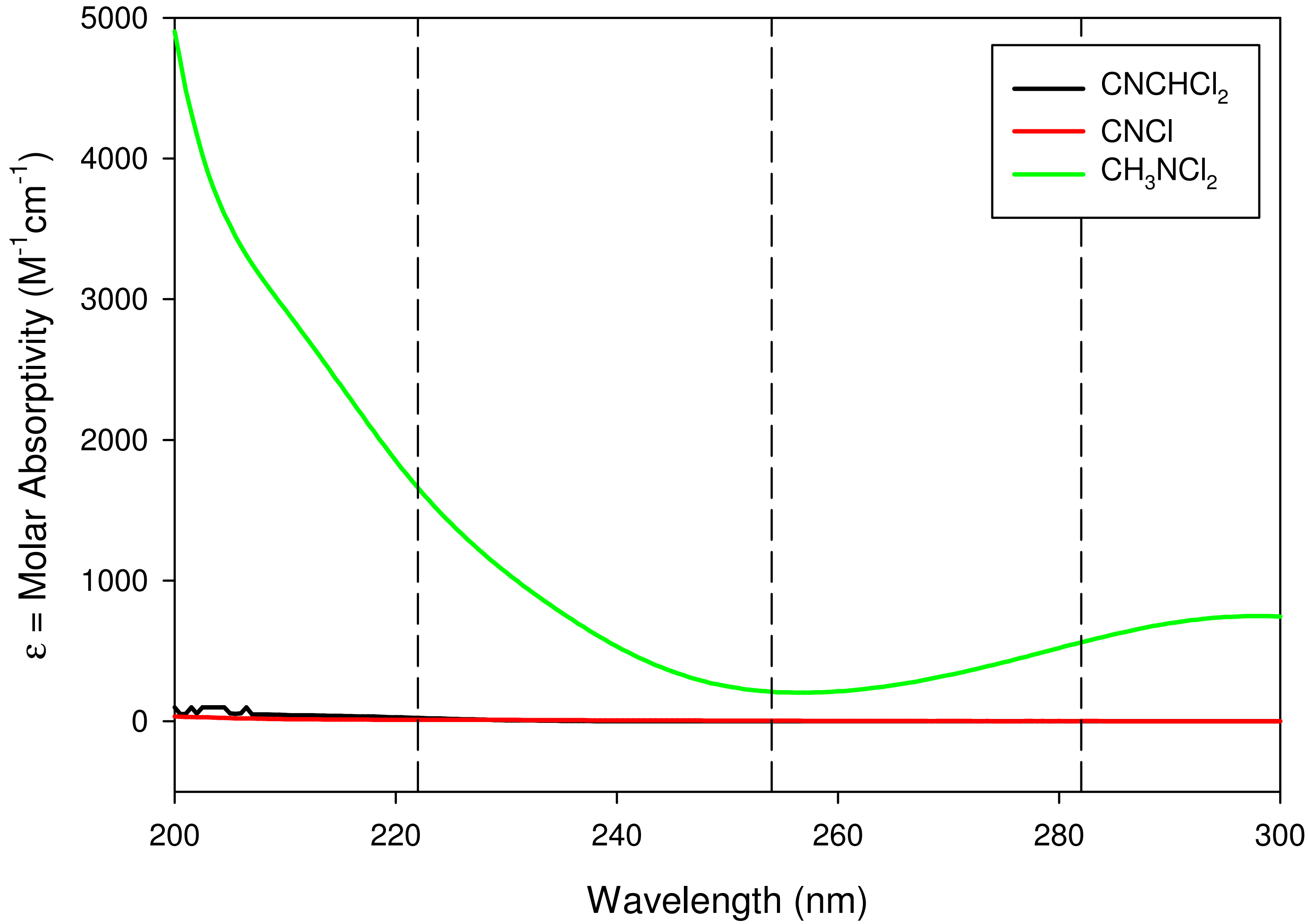


NO_2^- and NO_3^- formed account for 80% of Original Reduced-N Concentration

UV Photolysis of Residual Chlorine

- Free Chlorine Degrades Slowly
- Inorganic Chloramines Degrade at Germicidal UV Doses
- Products of Inorganic Chloramine Photolysis Include NO_2^- and NO_3^-
- Amounts of NO_2^- and NO_3^- Formed Depend on pH, Free Chlorine
- NCl_3 is Most Susceptible to Photodegradation, and Most Likely to be Present in Swimming Pools

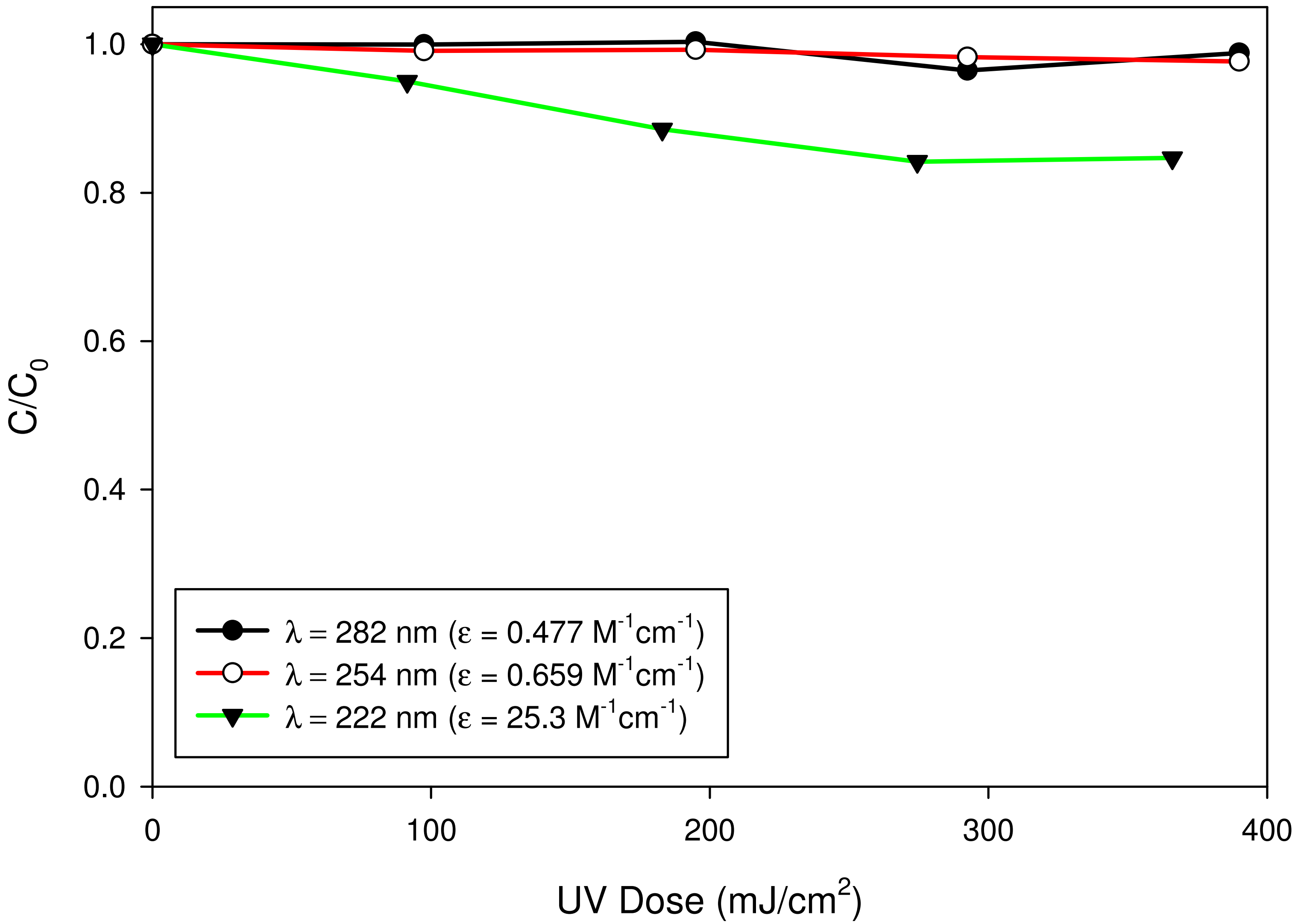
Volatile DBP Absorbance Spectra



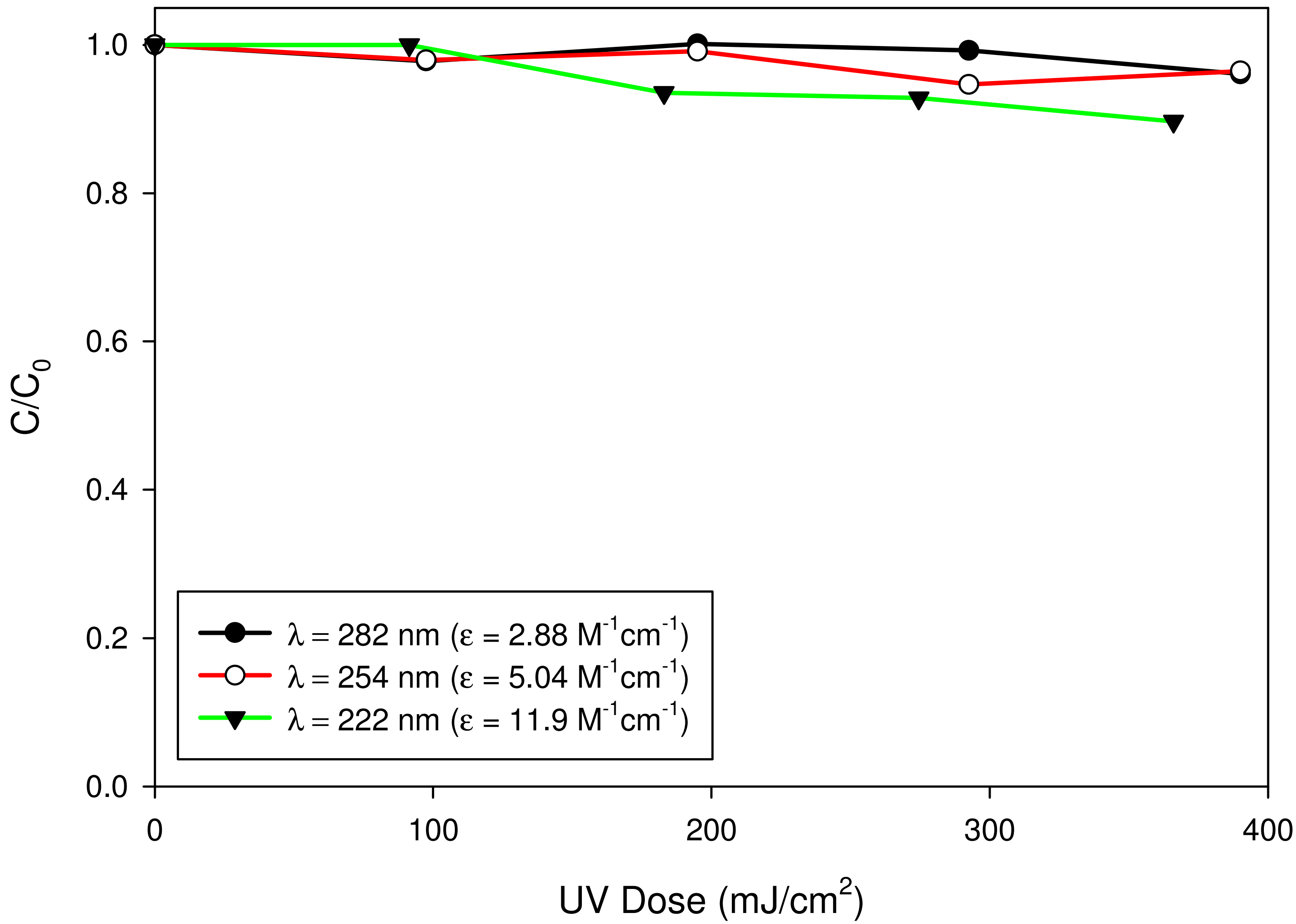
UV Absorbance: Chlorinated Organic-N Compounds

- $CNCHCl_2$, CNCl
  - Poor Absorbers of Germicidal UV
  - Minimal Potential to Photodegrade
- CH_3NCl_2
  - Moderate to Strong Absorber of UV (λ)
  - May Photodegrade

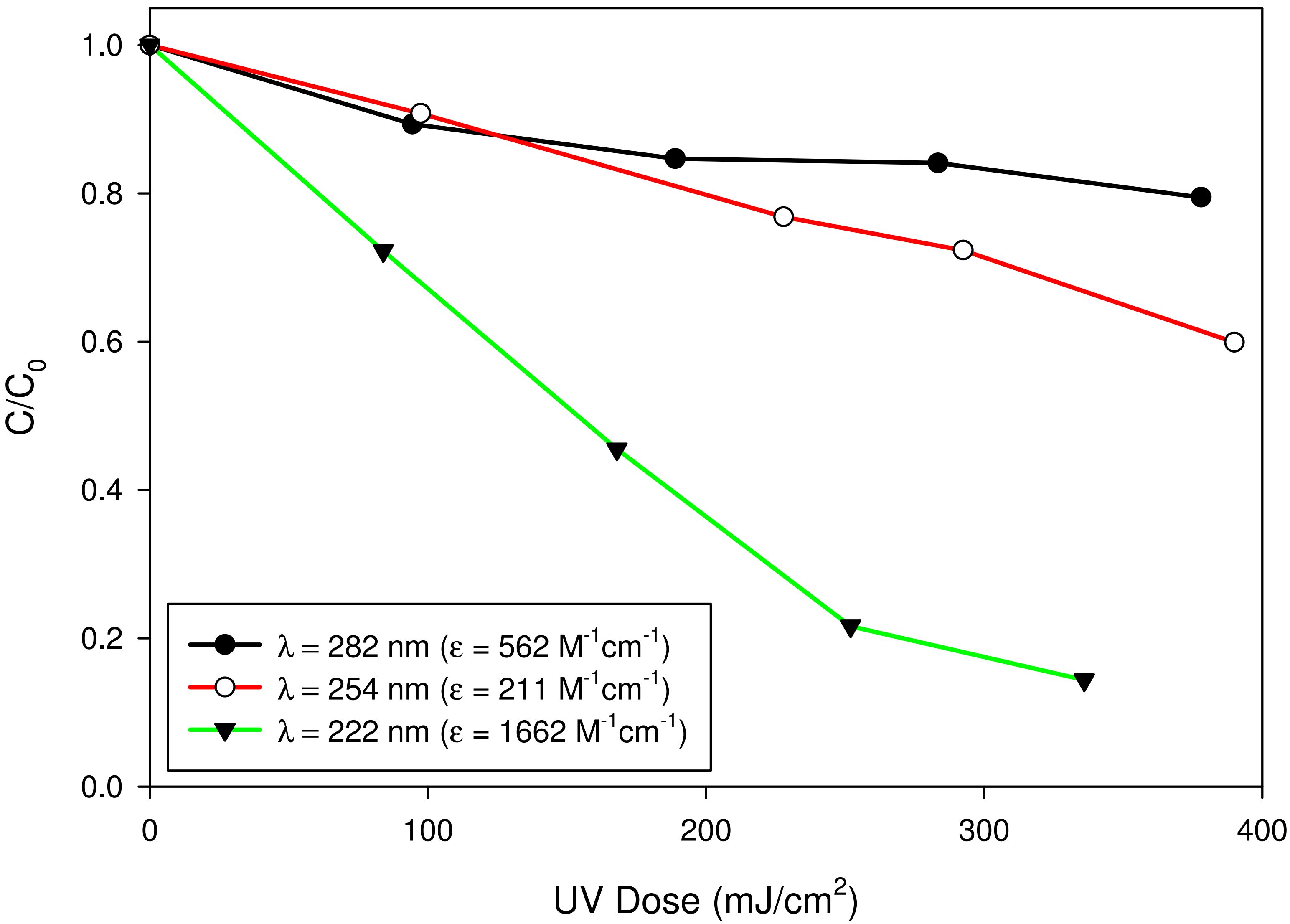
$CNCHCl_2$ Photodecay; pH = 7.5
Alkalinity = 120 mg/L as $CaCO_3$



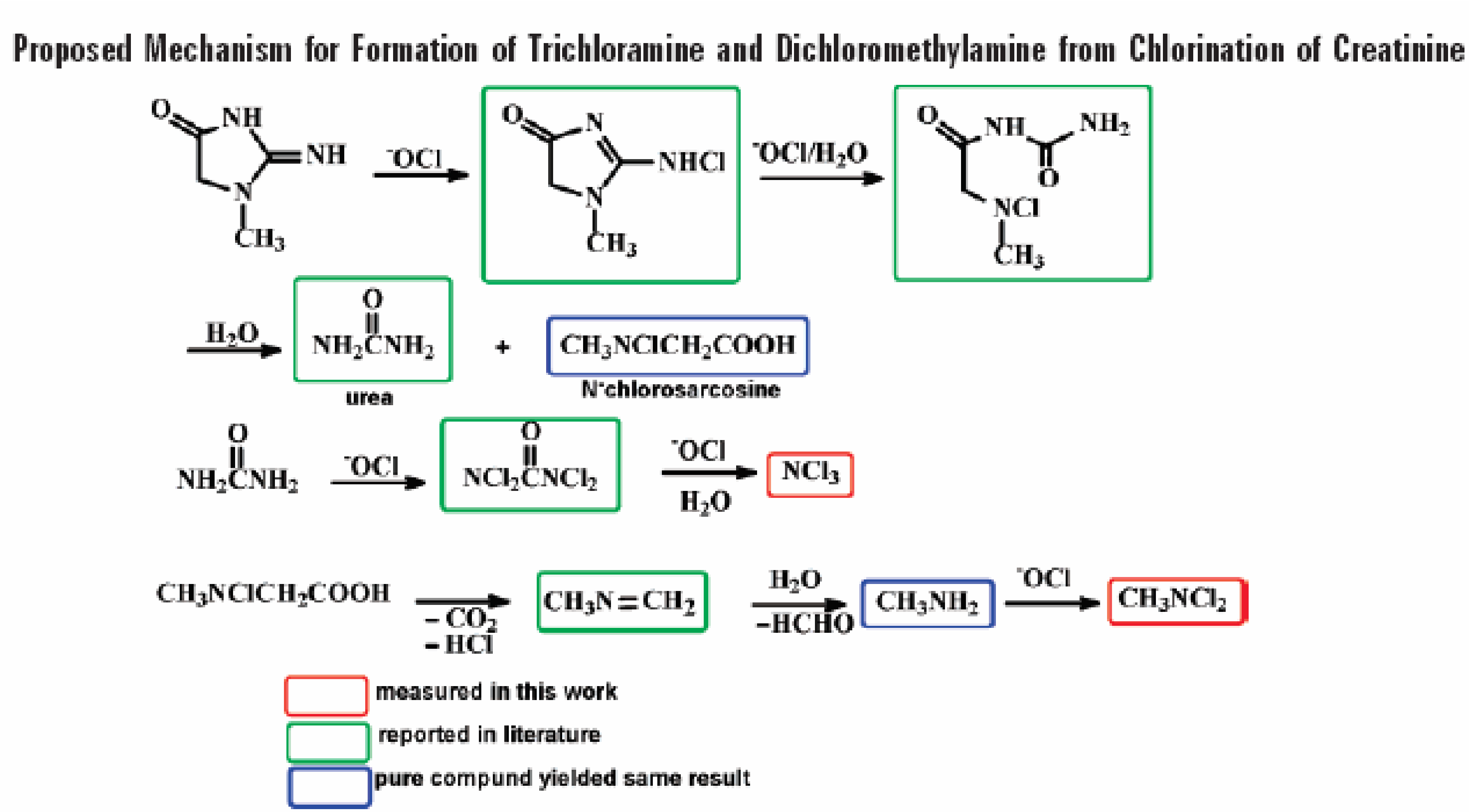
CNCl Photodecay; pH = 7.5
Alkalinity = 120 mg/L as $CaCO_3$



CH_3NCl_2 Photodecay; pH = 7.5
Alkalinity = 120 mg/L as $CaCO_3$

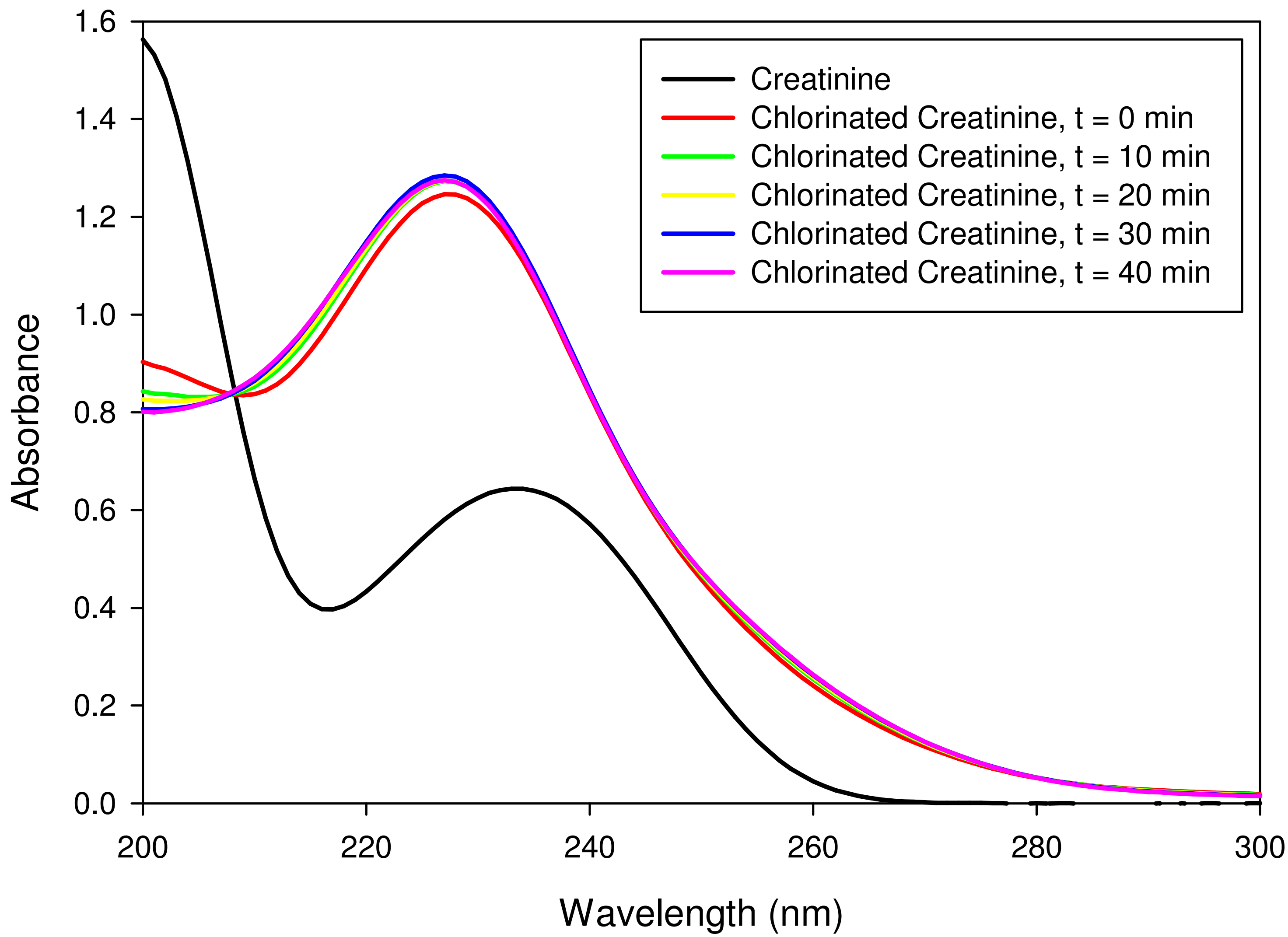


Photodecay of Chlorinated DBPs

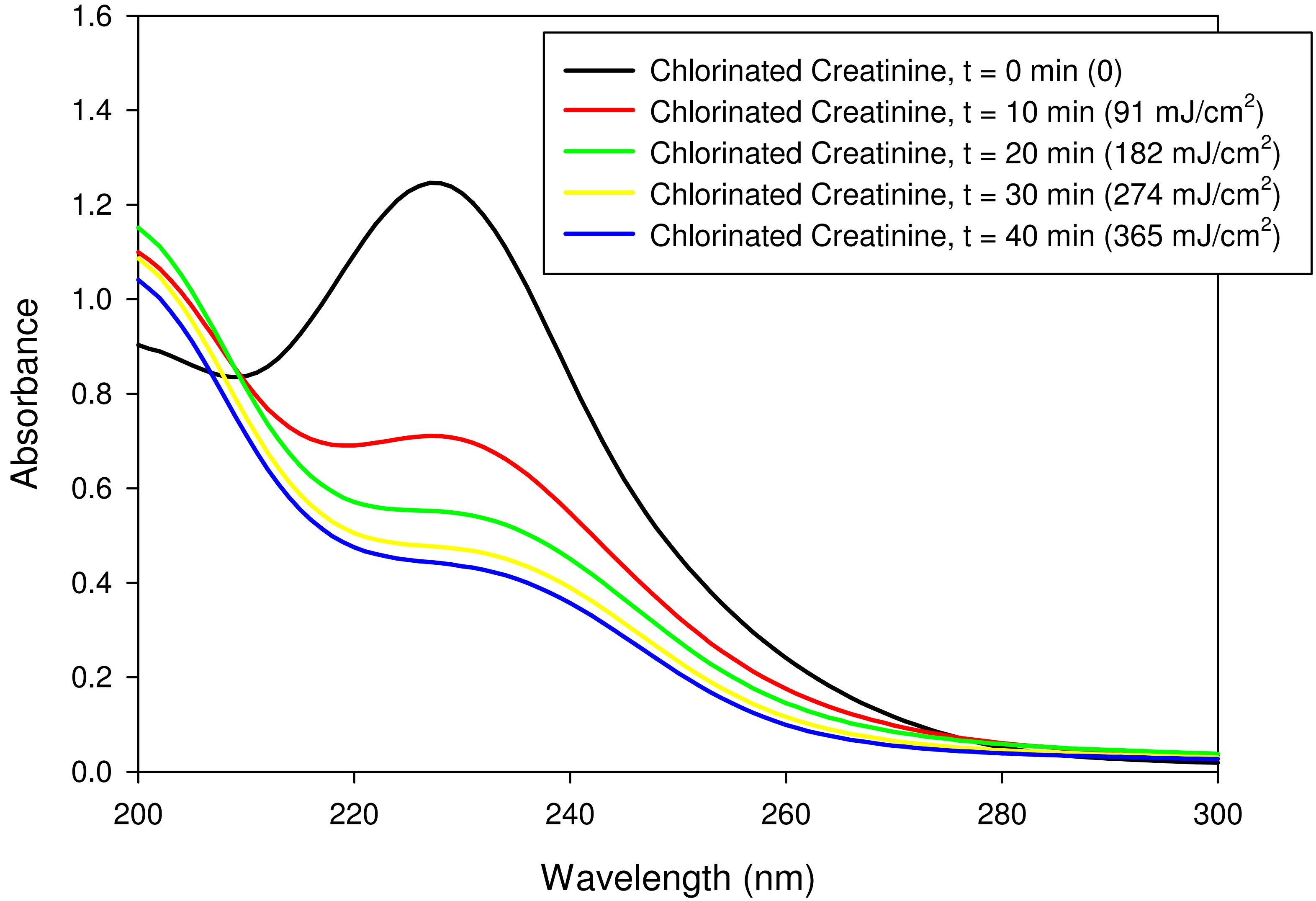


Li, J. and Blatchley III, E.R. (2007) "Volatile Disinfection Byproduct Formation Resultin from Chlorination of Organic-Nitrogen Precursors in Swimming Pools," *Environmental Science & Technology*, 10.1021/es070871+

Stability of Chlorinated Creatinine
1:1 Cl:P Ratio; pH = 7.5

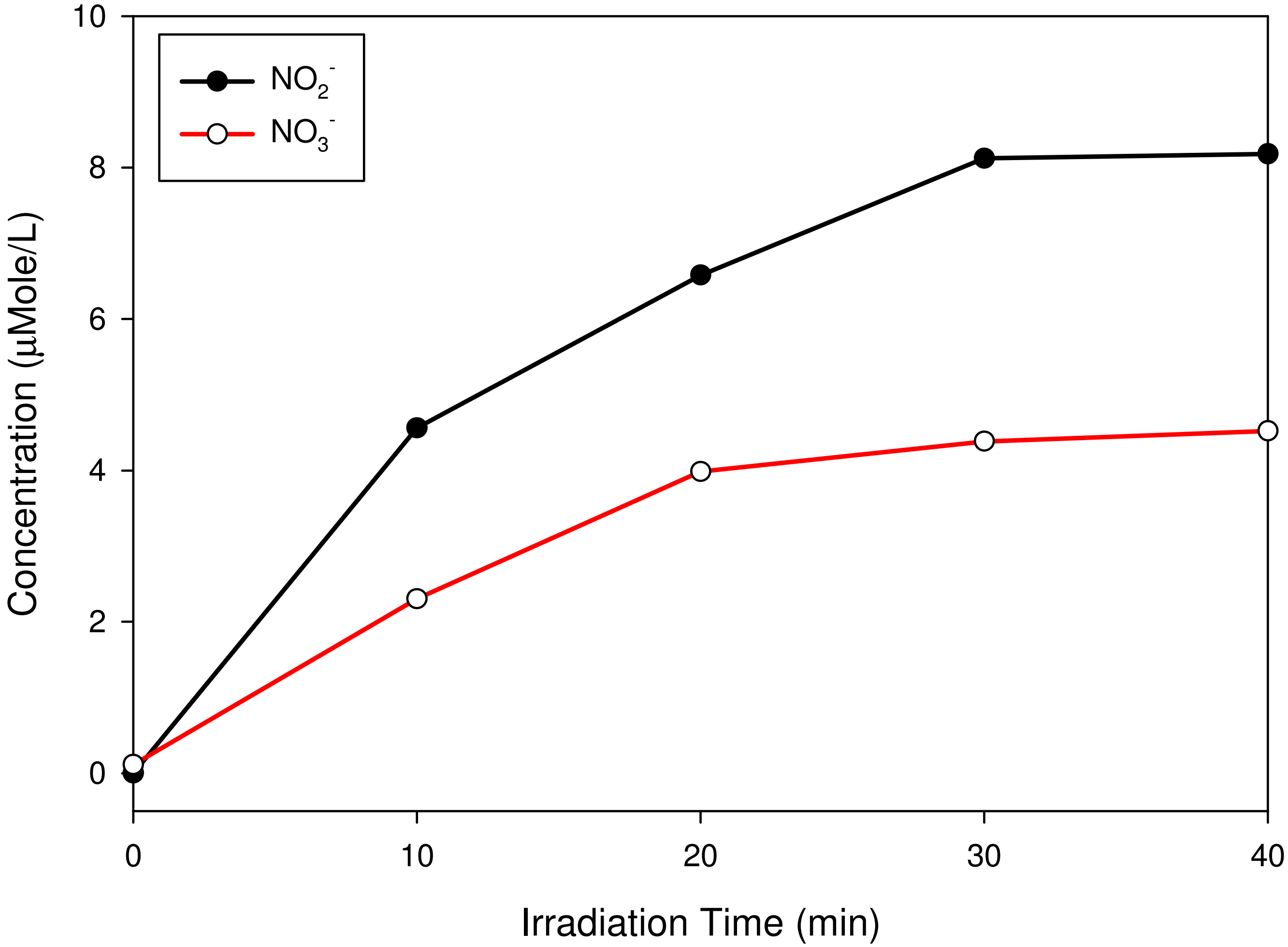


UV_{254} Photodecay of Chlorinated Creatinine
1:1 Cl:P Ratio; pH = 7.5



Nitrite and Nitrate Formation from UV_{254} Irradiation of Chlorinated Creatinine

Initial Creatinine Concentration = 100 µmole/L; I_0 = 150 µW/cm^2



NO_2^- and NO_3^- formed account for 5% of Original Reduced-N Concentration

Next Steps

- Effects of Solution Chemistry on Photochemical Kinetics
  - pH
  - Alkalinity
- Photochemical By-Products
- Combined Effects of Solution Chemistry and Photochemistry
- Other DBPs
  - Polar fraction
  - Low volatility
- Field Measurements of DBPs in Water, Air
- System Optimization

Long-Term Research Objectives: Engineering Systems Approach

- Improve Understanding of Swimming Pool Chemistry and Treatment Processes
- Define Rates of Gas:Liquid Transfer
- Simulate System Behavior
  - Reactions
  - Treatment Processes
  - Gas:Liquid Exchange
  - Mixing in Water and Air
- Optimize System Performance

Conceptual Model

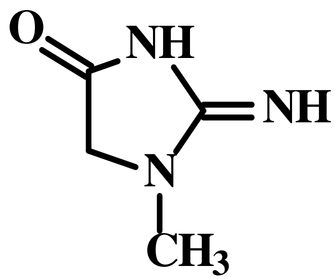
Future Research Direction on DBP Chemistry and Facility Operations

- Informal Meeting
- Thursday, October 4, 2007 7:30 AM
- Same Room as DBP Session

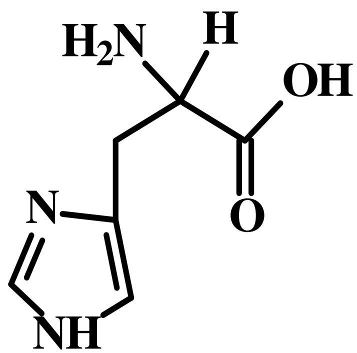
Acknowledgements

- DuPont Experimental Station
- National Swimming Pool Foundation

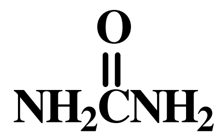
Organic-N Precursors



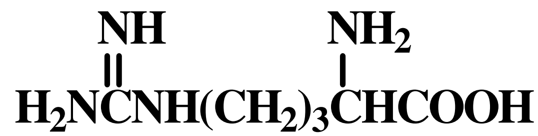
Creatinine



Histidine



Urea



Arginine

Volatile DBPs

NCl_3

Trichloramine

CH_3NCl_2

Dichloromethylamine

$CHCl_3$

Chloroform

$Cl_2N{-}C{\equiv}N$

Dichloroacetonitrile

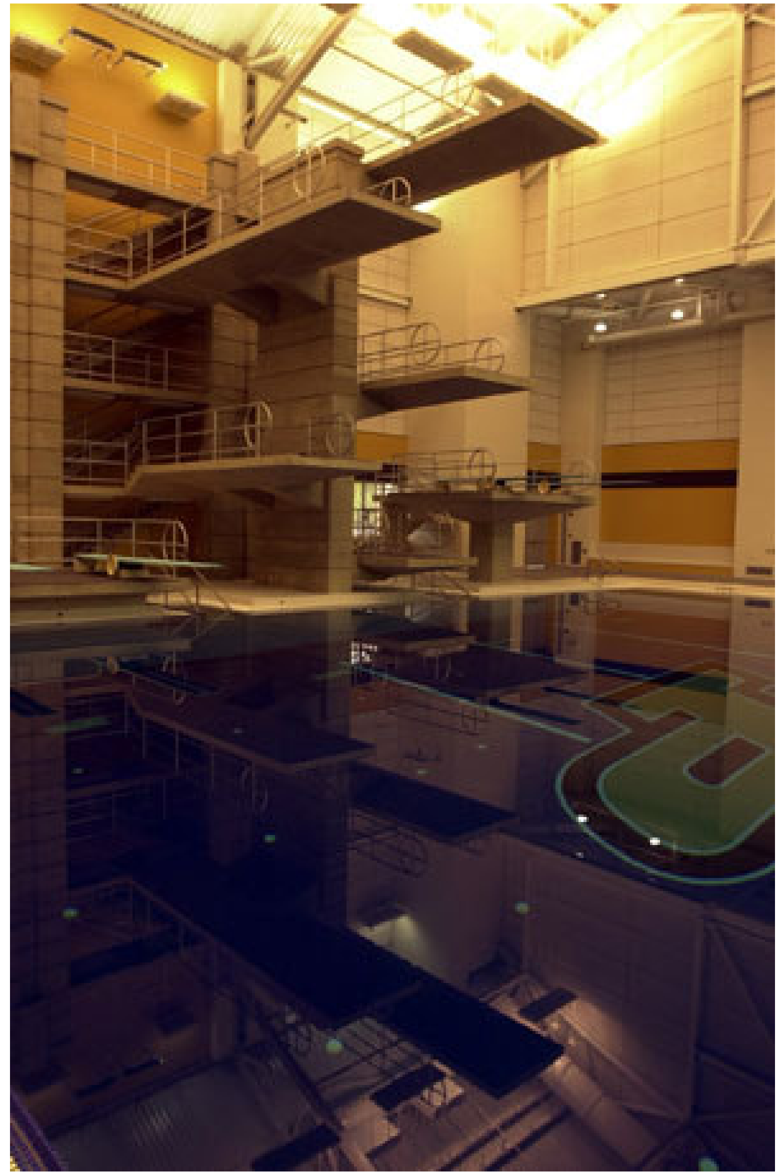
$Cl{-}C{\equiv}N$

Cyanogen Chloride

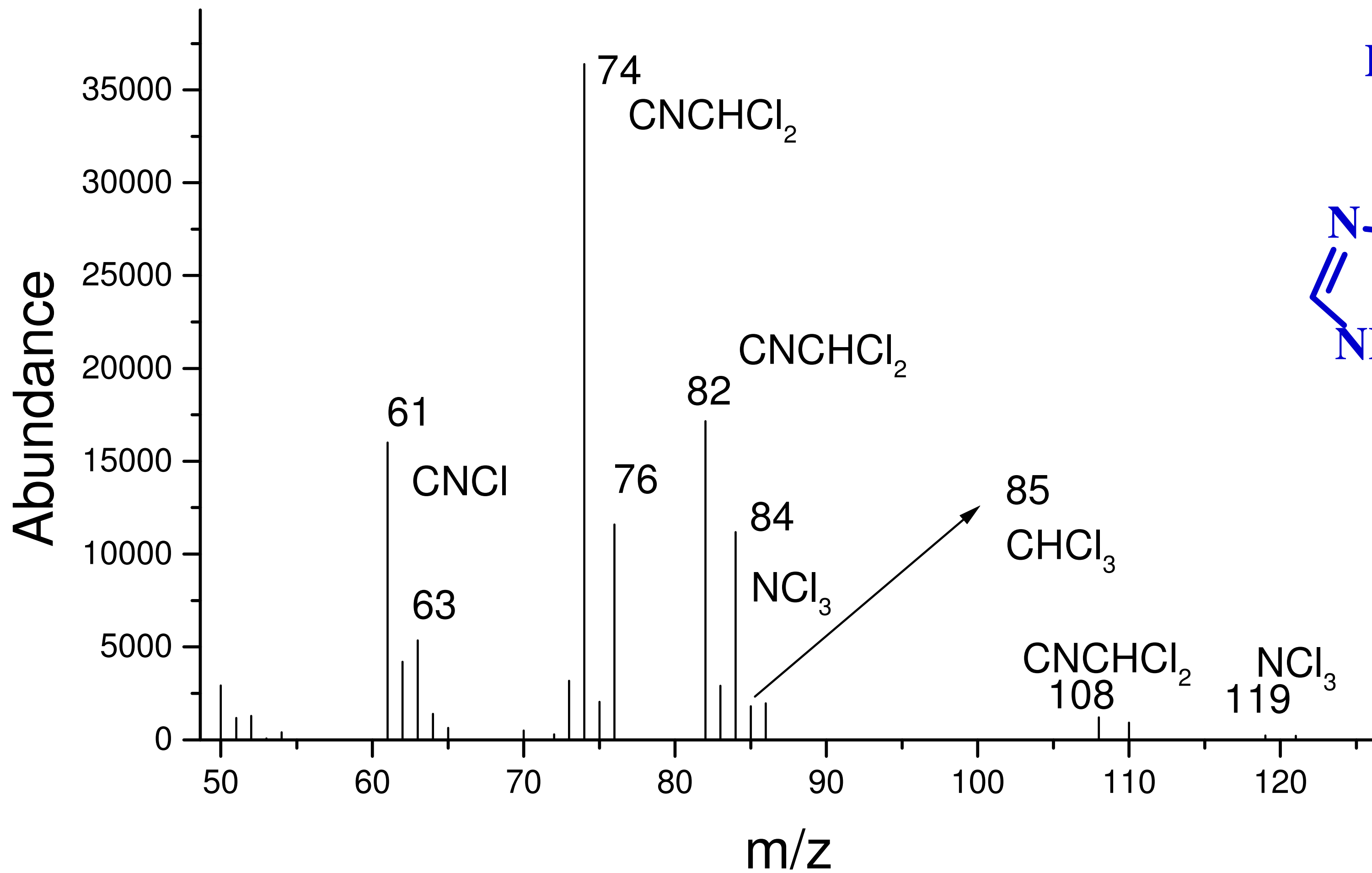
Molar Absorptivity Values ($M^{-1}cm^{-1}$) for volatile DBPs and free chlorine at different wavelengths

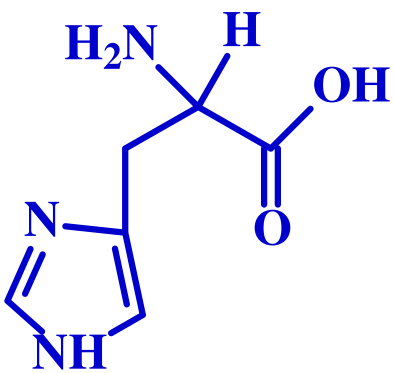
Species	λ=222 nm	λ=254 nm	λ=282 nm
$CNCHCl_2$	25	< 1	< 1
CNCl	-	< 1	< 1
CH_3NCl_2	1662	211	562
NCl_3	4938	367	54
NaOCl(HOCl) pH=7	71	64	71
$NHCl_2$	1126	142	221
NH_2Cl	221	388	78

Pool A: Competition Pool



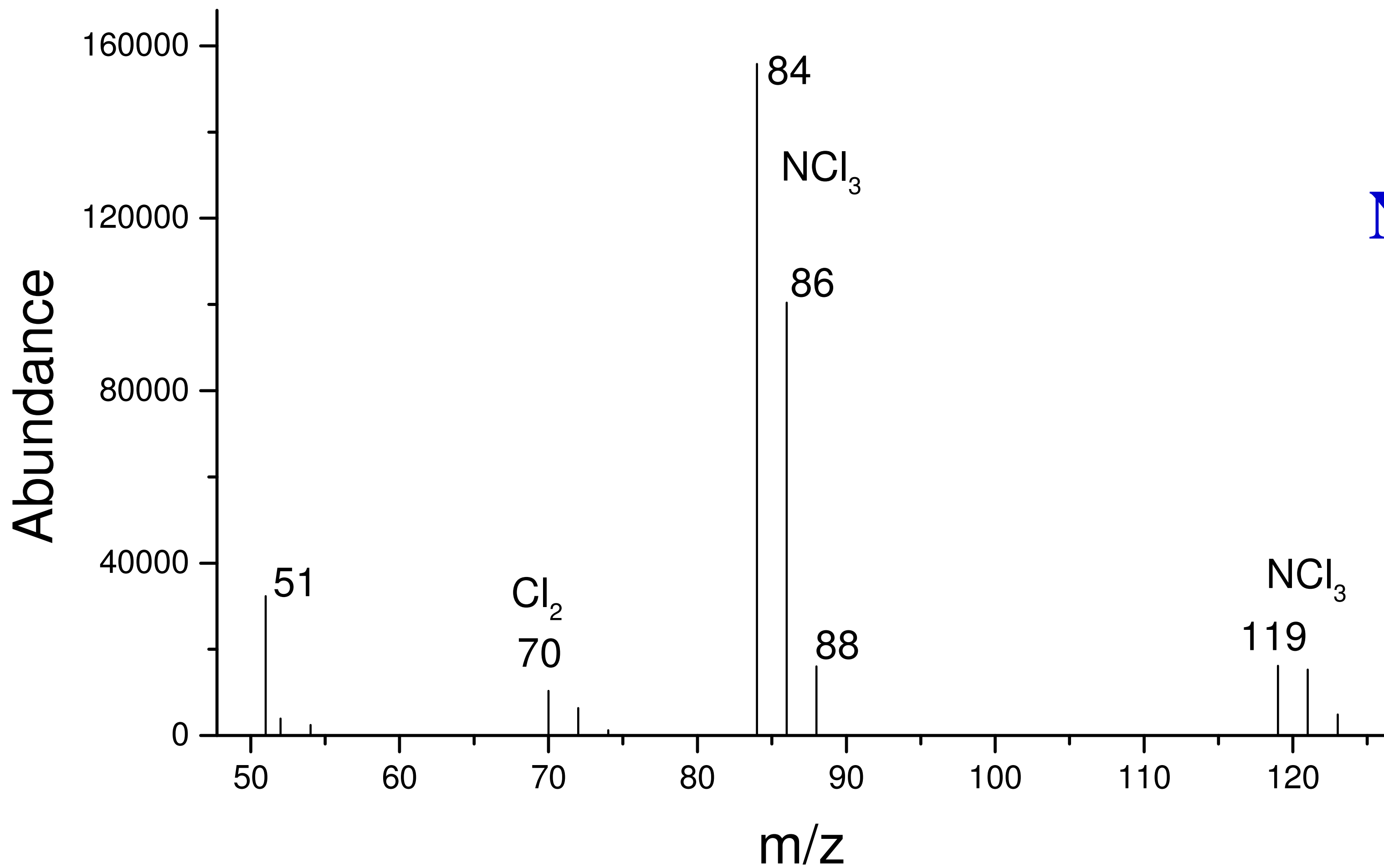
Chlorination of L-Histidine
[P] = 1.8 x 10^{-4} M, Cl:P = 5; pH = 7.5

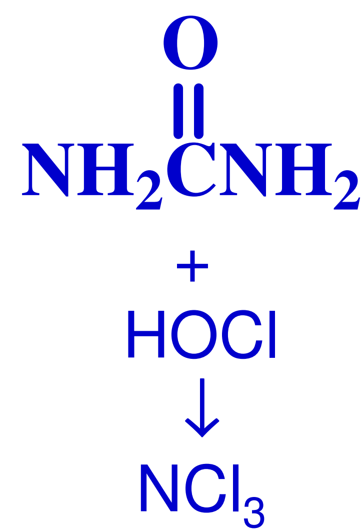




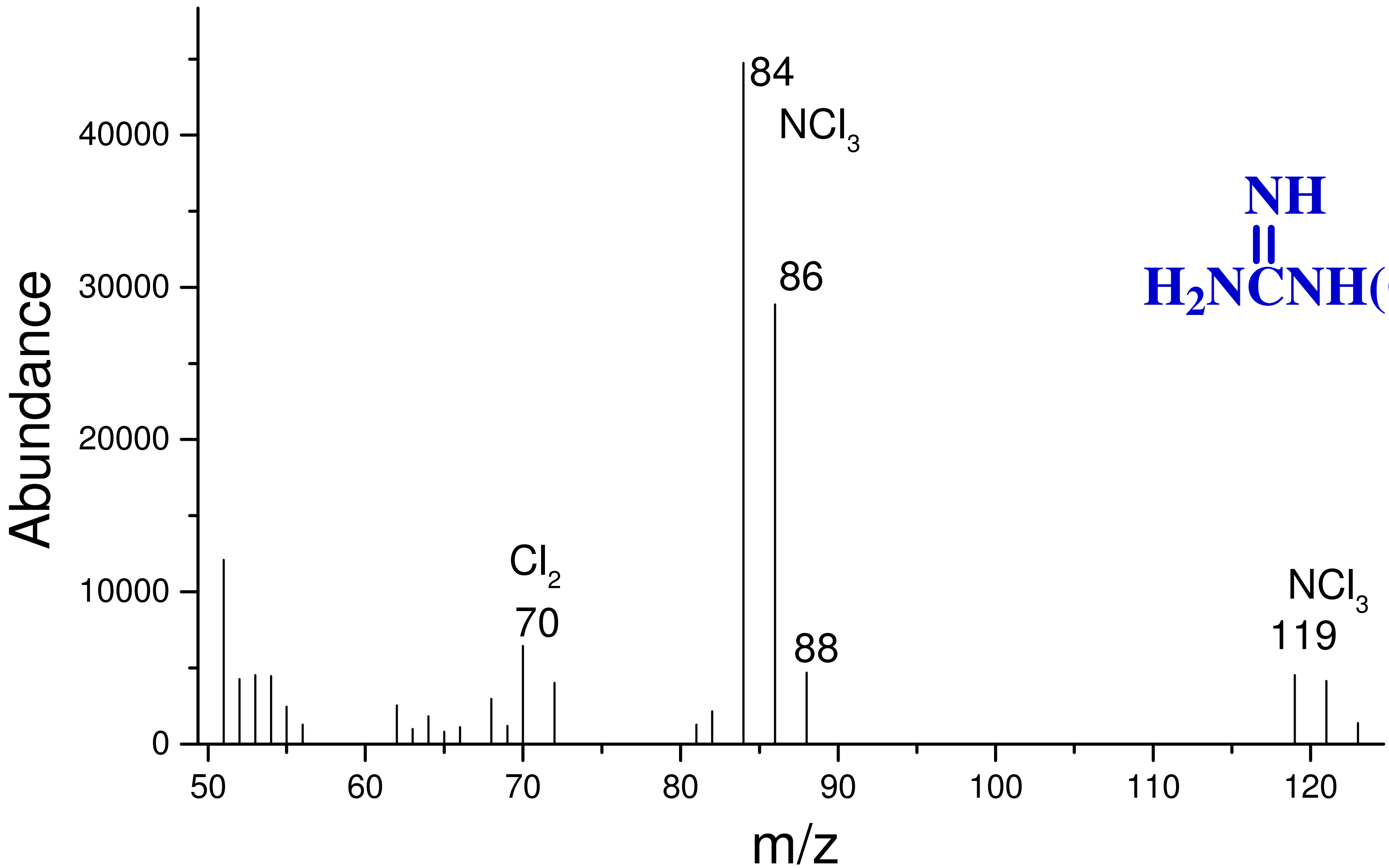
+
HOCl
↓
$CNCHCl_2$,
NCl_3,
CNCl,
$CHCl_3$

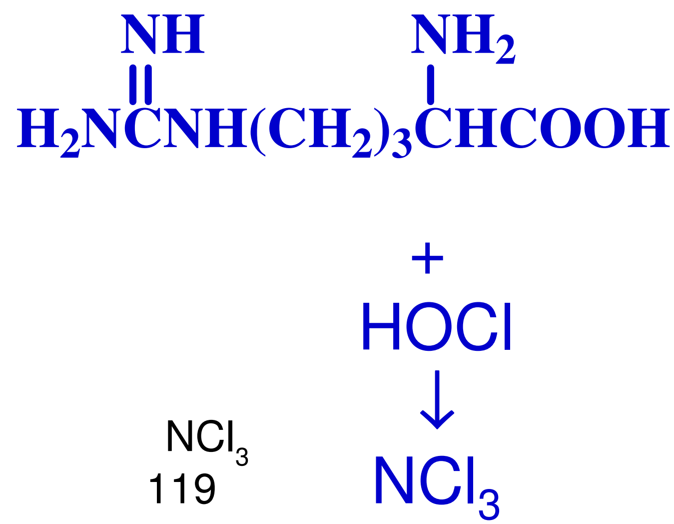
Chlorination of Urea
[P] = 1.8 x 10^{-4} M, Cl:P = 5; pH = 7.5



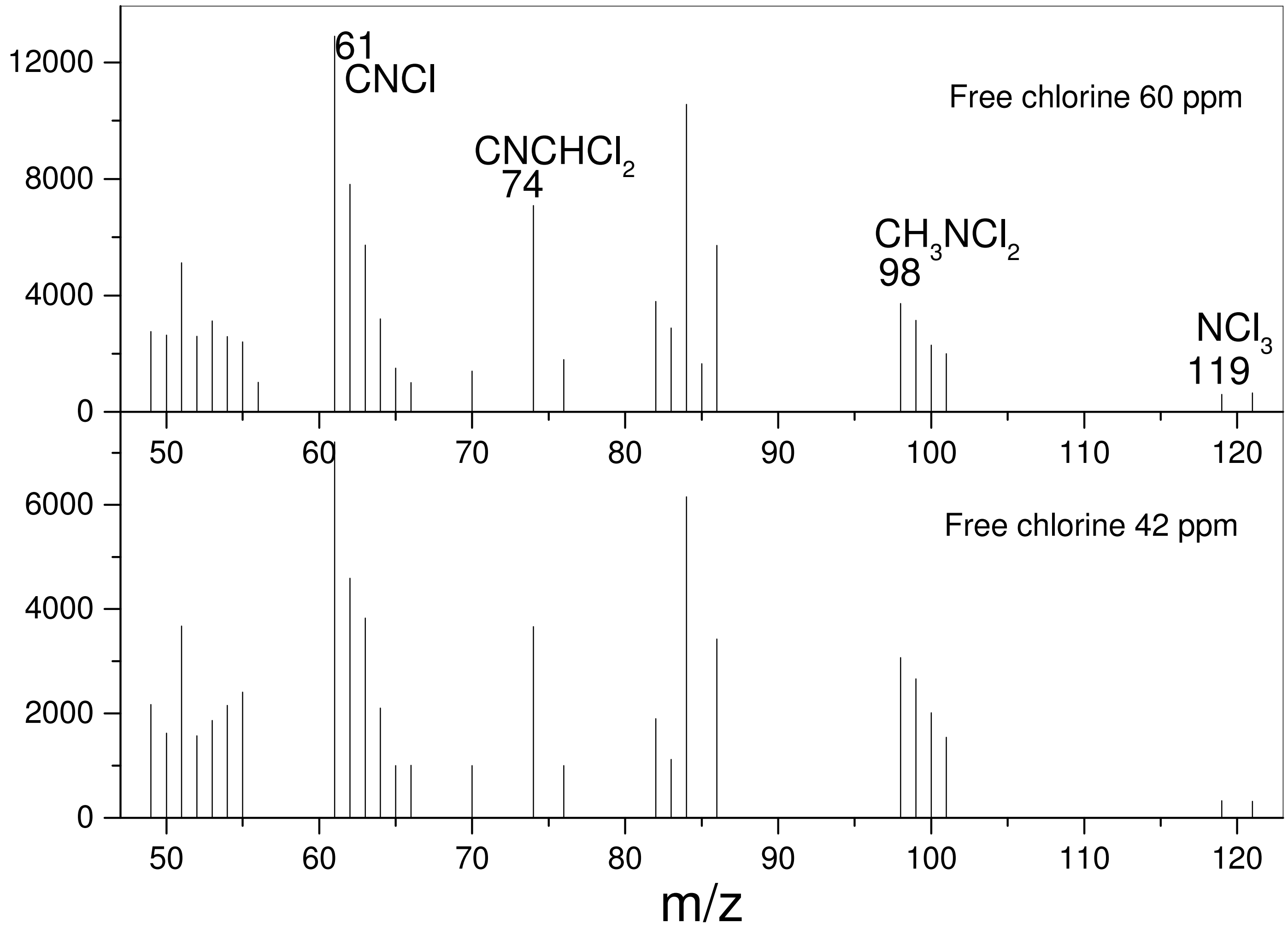


Chlorination of L-Arginine
[P] = 1.8 x 10^{-4} M, Cl:P = 8; pH = 7.5





Mass spectra of volatile byproducts from chlorination of BFA



L-Histidine: 12.1 ppm

L-Arginine: 5 ppm

Creatinine: 18 ppm

Urea: 148 ppm