Spectroscopic Studies of Aluminum Ion Binding by Soil Derived Humic Material: Fluorescence Enhancement

David K. Ryan

Department of Chemistry
University of Massachusetts Lowell

http://faculty.uml.edu/David_Ryan


1000ml
KIMAX
900ml
800
700
500
400
300
200
100

NOM^{y-}

NOM^{y-}

M^{x+}

M^{x+} M^{x+}

NOM^{y-}

M^{x+}

NOM^{y-}

M^{x+} = metal ion, toxic or non, of charge x+ (e.g., Cu^{2+}, Al^{3+}, etc.)

NOM^{y-} = natural organic matter of varying negative charge y-

$$M^{x+} + NOM^{y-} \leftrightarrow M\text{-}NOM^{(x-y)-}$$

$$K = \frac{[M\text{-}NOM^{(x-y)-}]}{[M^{x+}][NOM^{y-}]}$$

K = equilibrium constant describing complexation reaction

$M\text{-}NOM^{(y-x)-}$ = metal complex of natural organic matter

$$M^{x+} + NOM^{y-} \longleftrightarrow M\text{-}NOM^{(y-x)-}$$

↑ measure

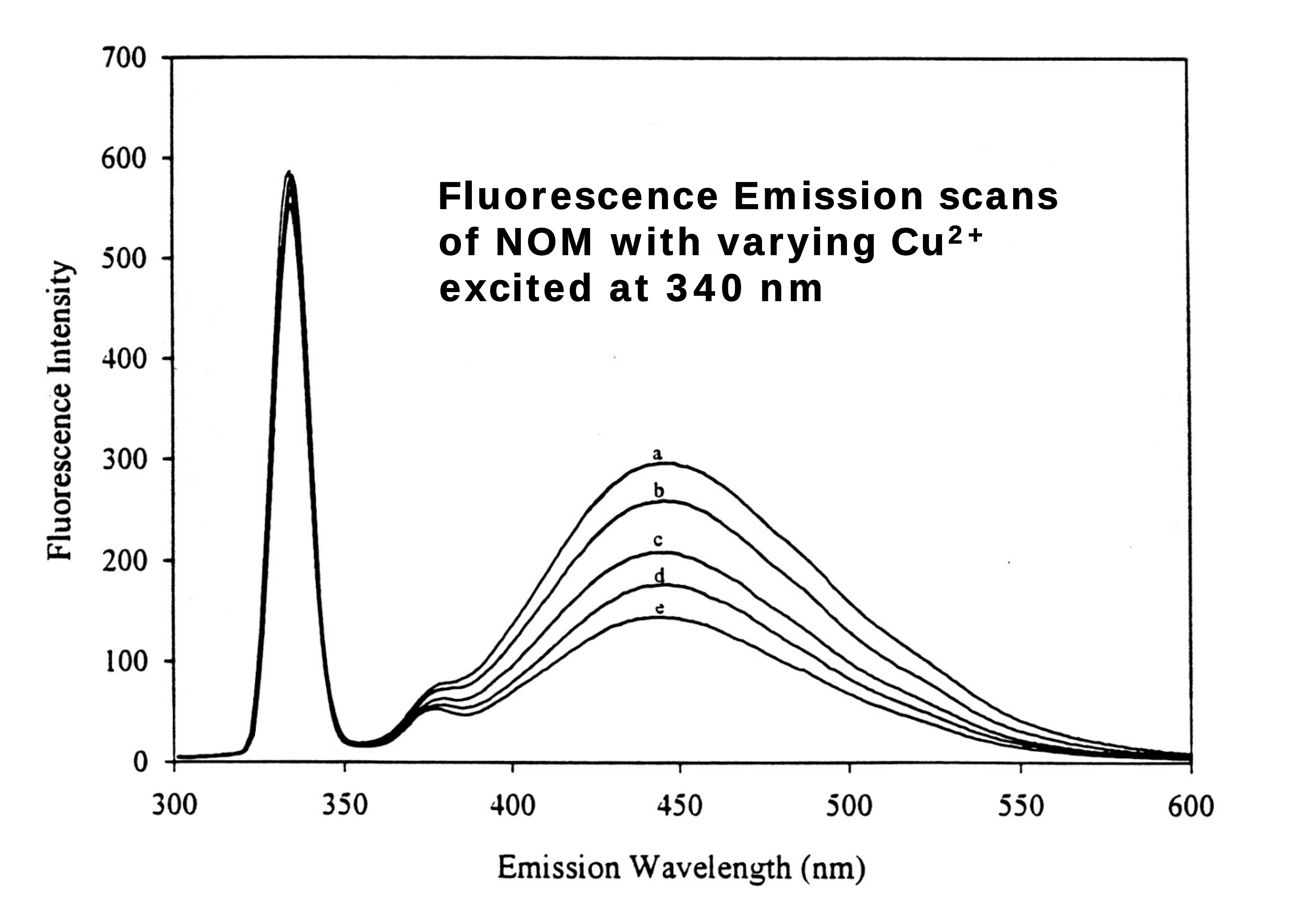
↑ or maybe measure

↑ or measure

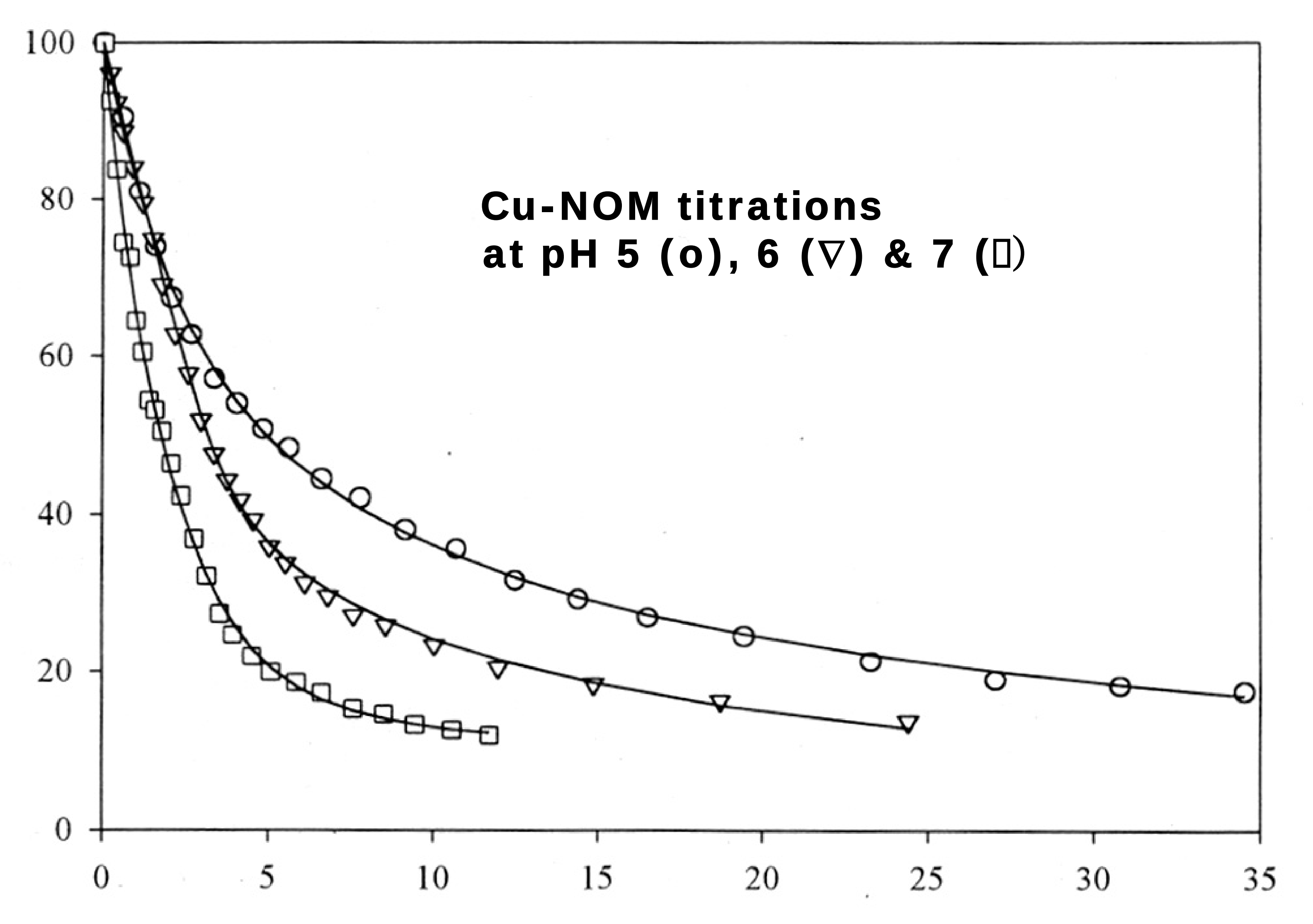
Metal Speciation = determination of the forms of metal in equilibrium with NOM

Measurement must not disturb equilibrium

Fluorescence Quenching

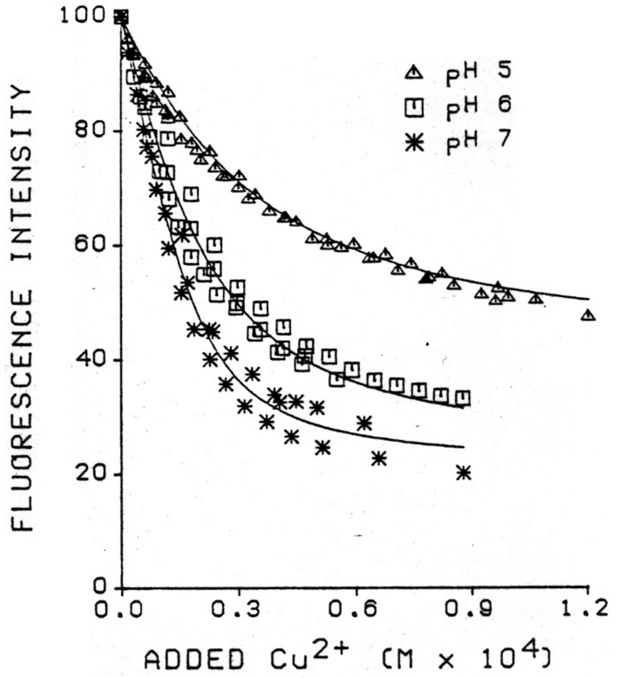


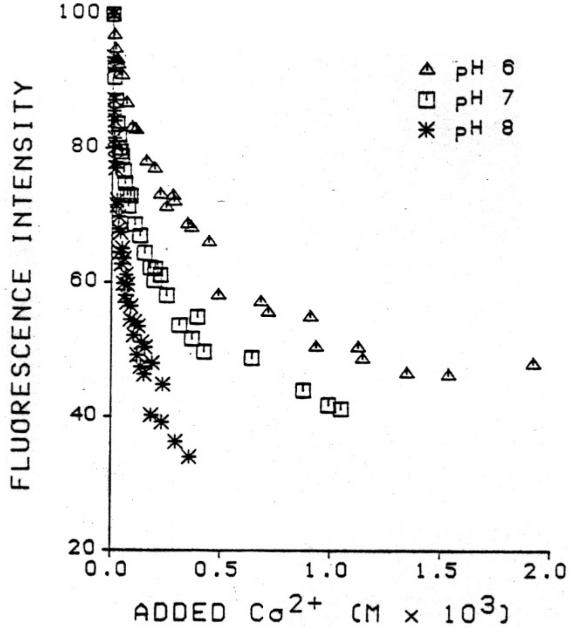
Fluorescence Quenching Curves



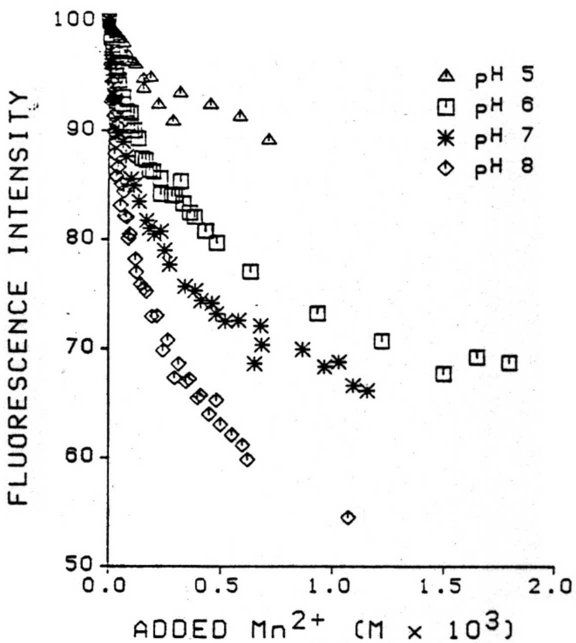
Relative Fluorescence Intensity

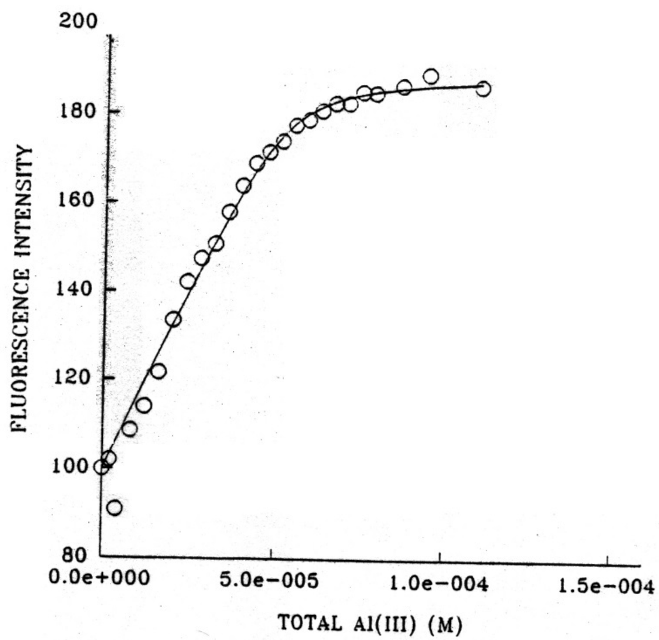
Added Copper Concentration (M x10[5])





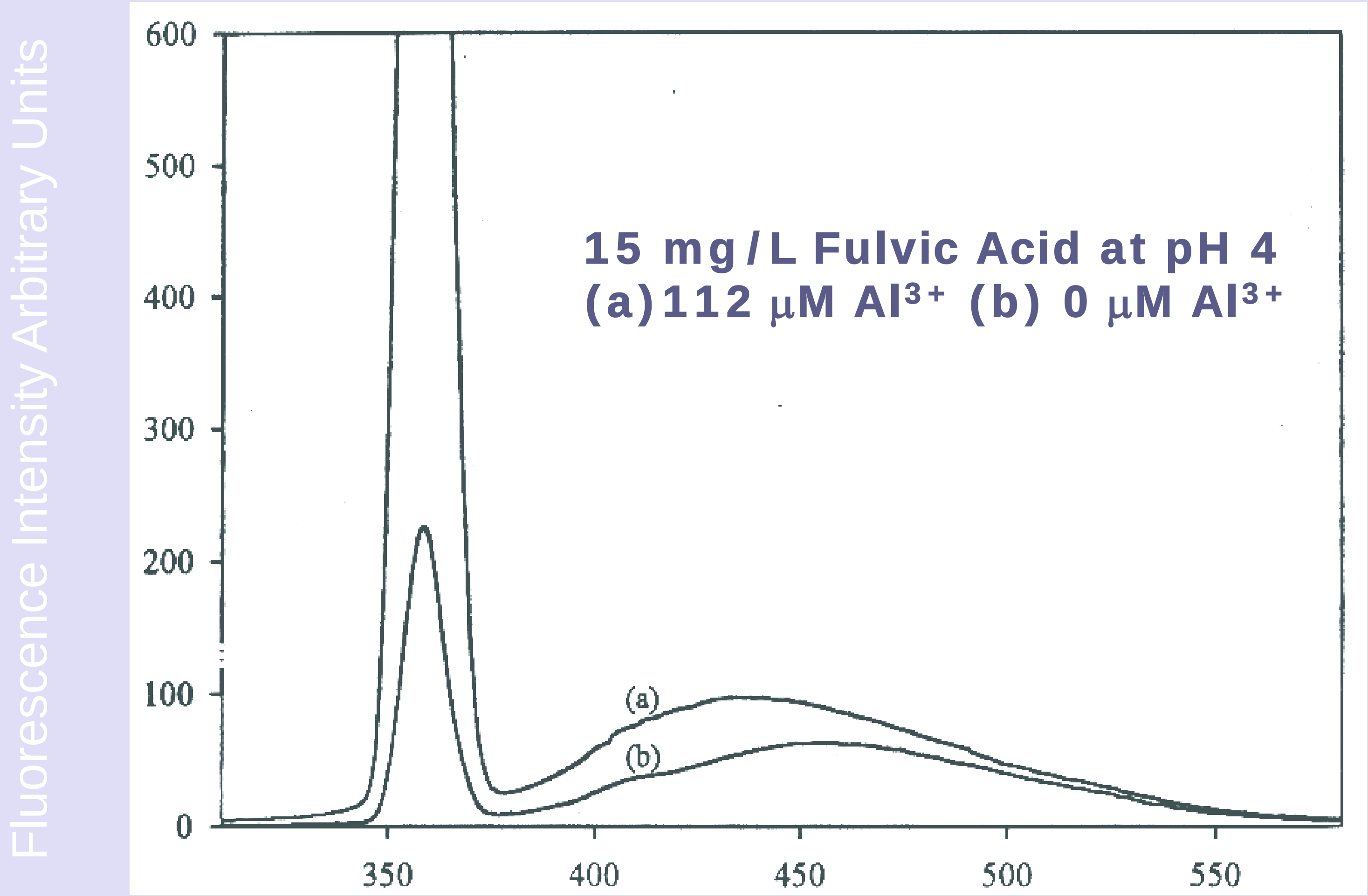
Fluorescence binding curves for Cu, Co, Mn & Al at pH values of 4-8





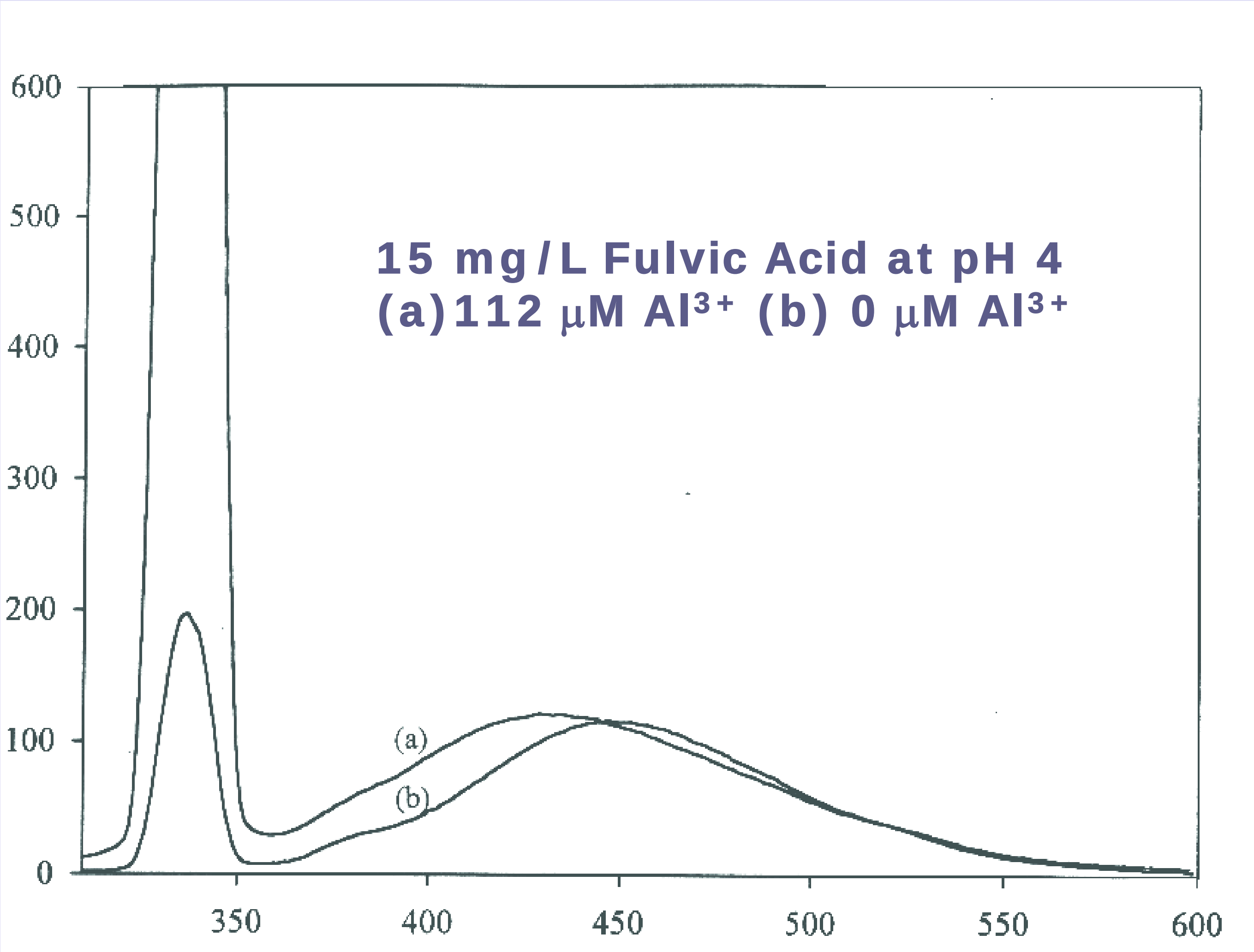
Fluorescence
- very sensitive
- does not disturb equilibrium
- few metals

Fluorescence Enhancement

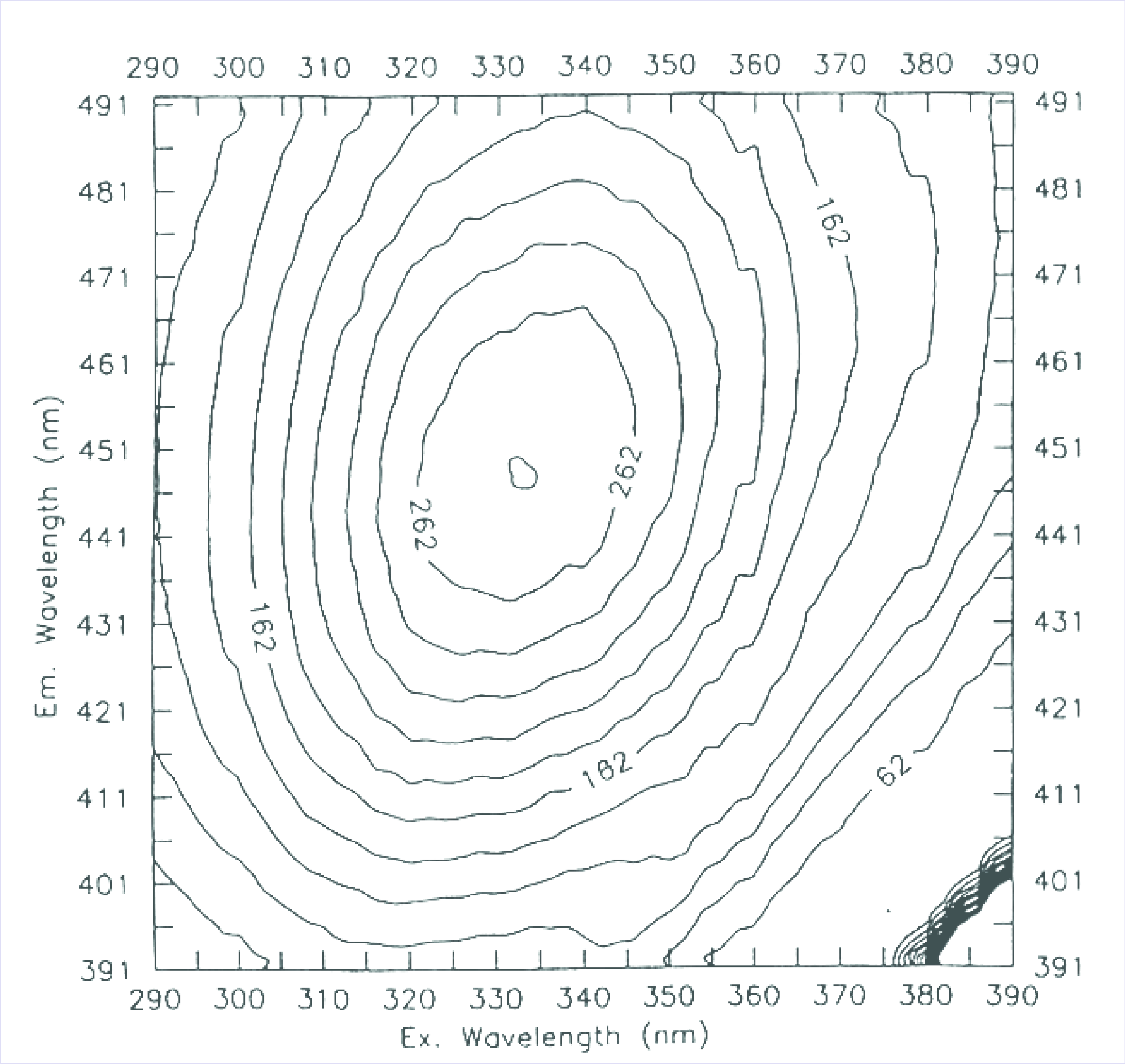


Emission Wavelength in nm with 360 nm Excitation

Fluorescence Enhancement

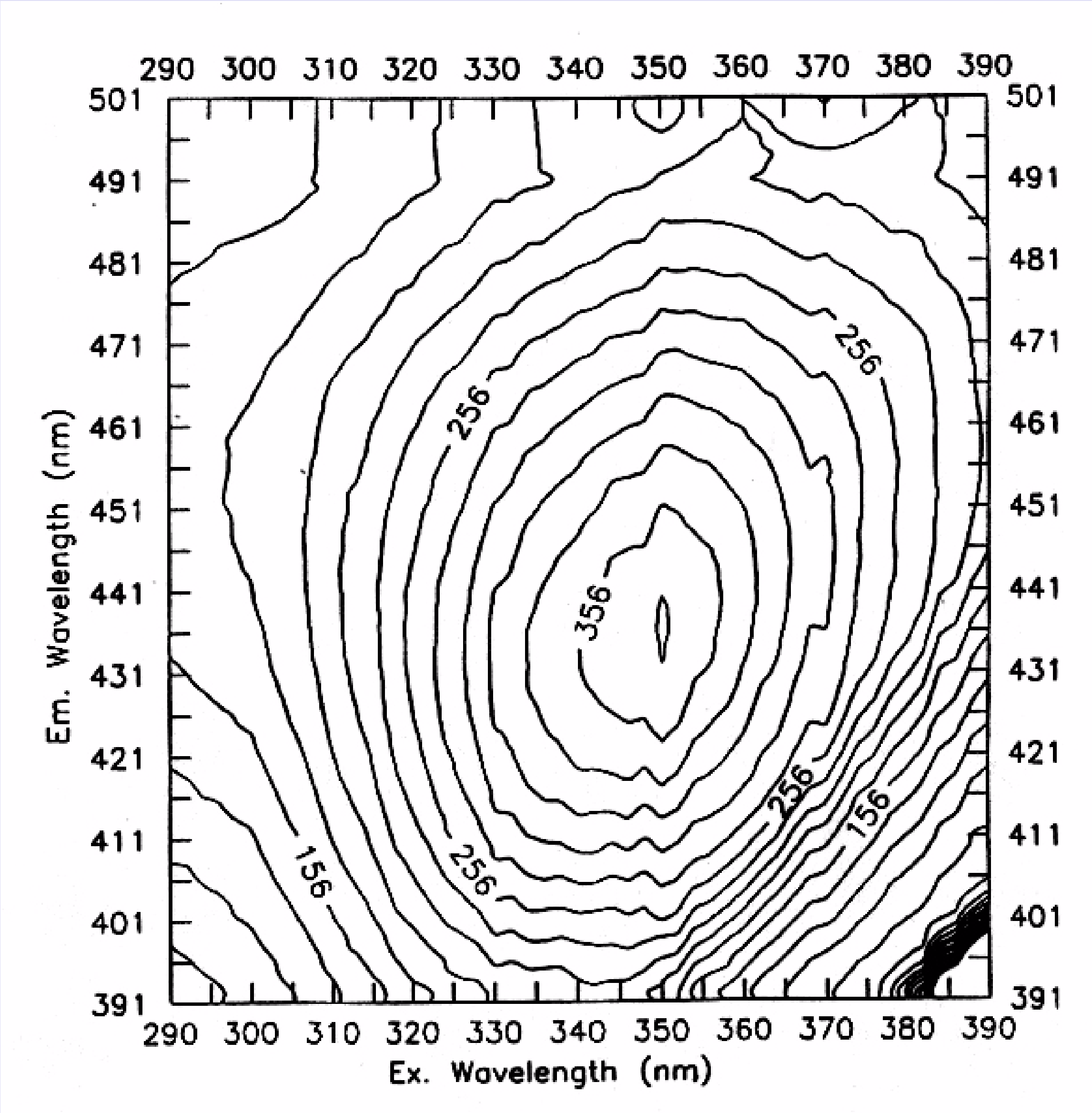


Excitation Emission Matrix



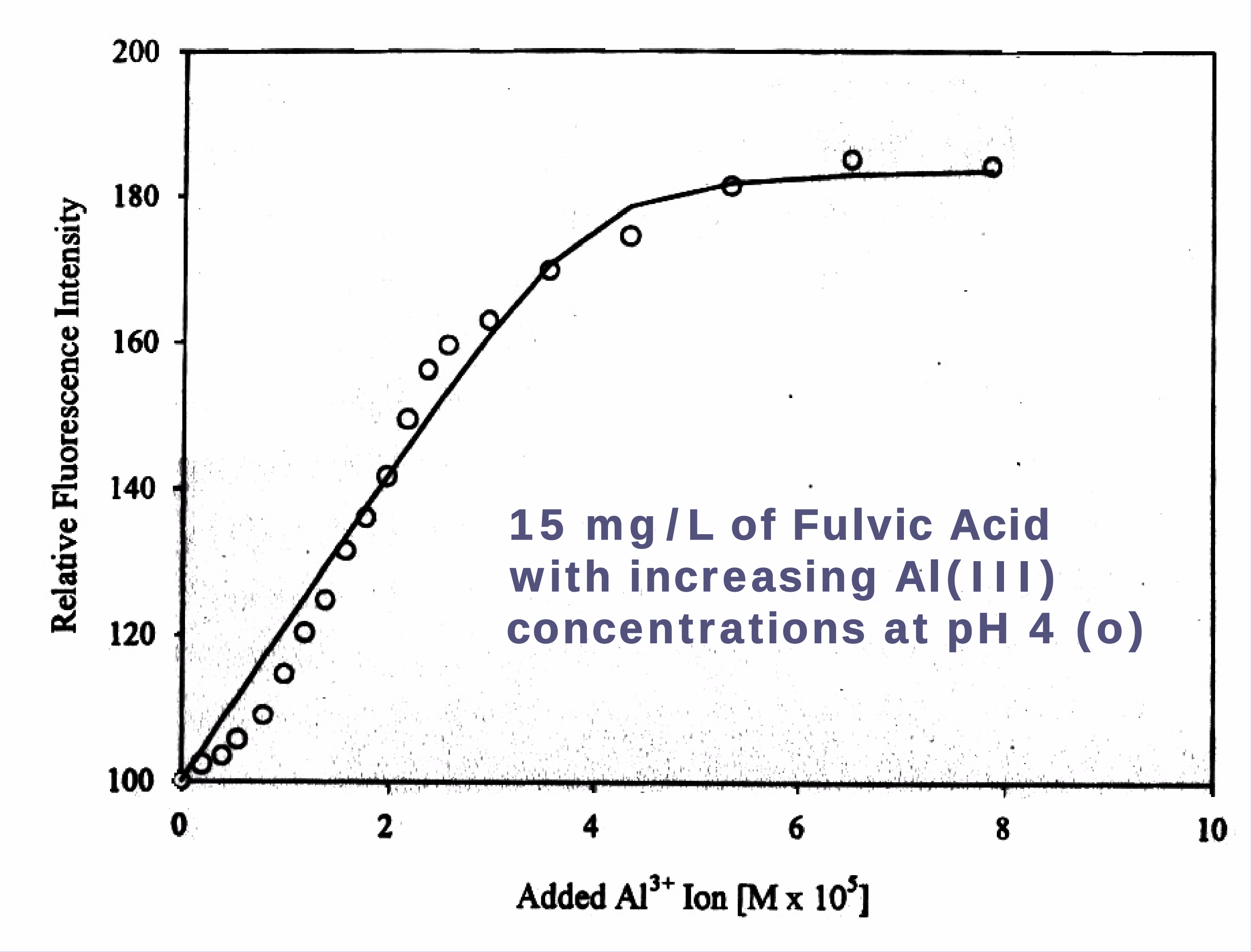
15 mg/L Fulvic Acid at pH 4 with no Al(III)

Excitation Emission Matrix

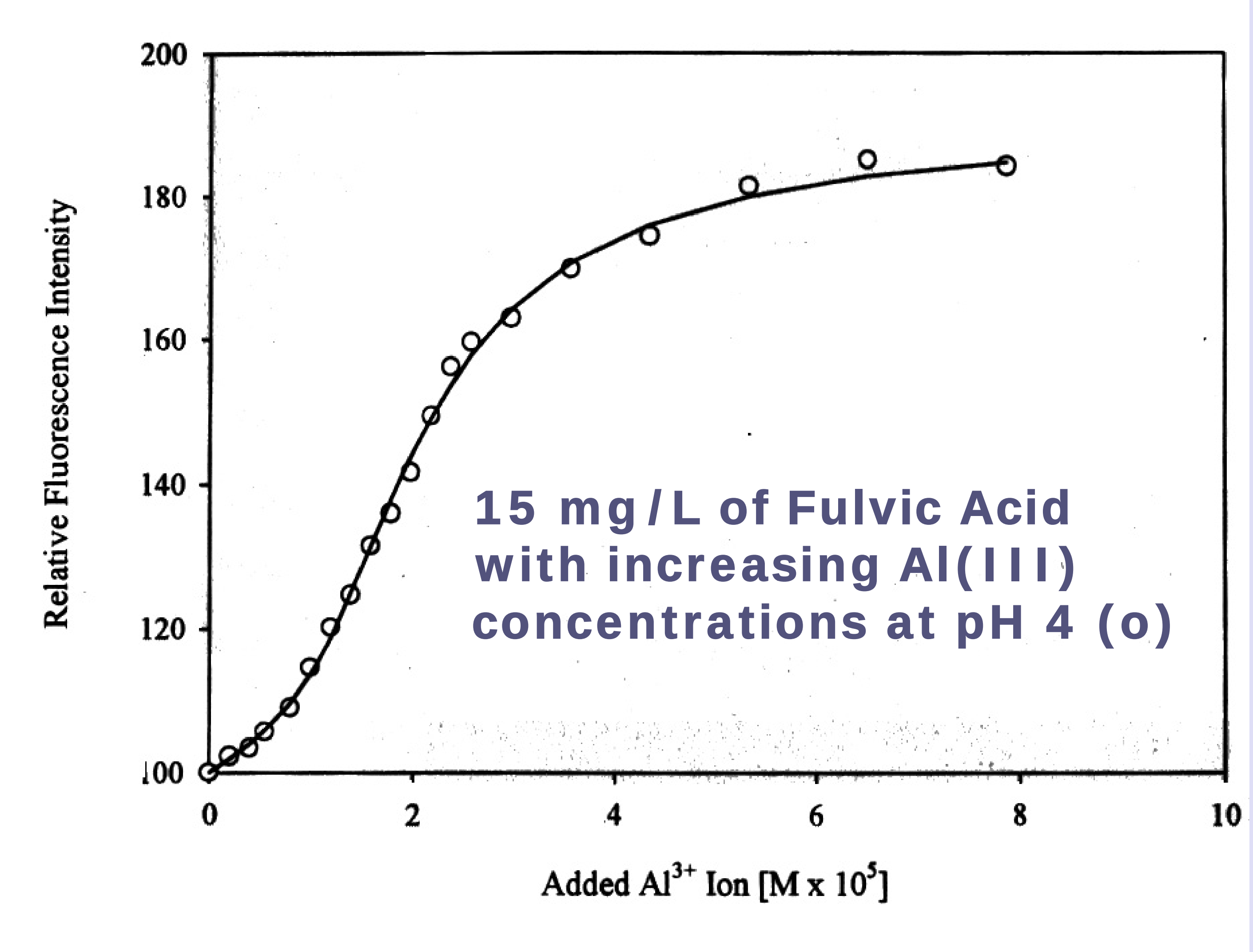


15 mg/L Fulvic Acid at pH 4 with Al(III)

Fluorescence Enhancement Curve with One-Site Model



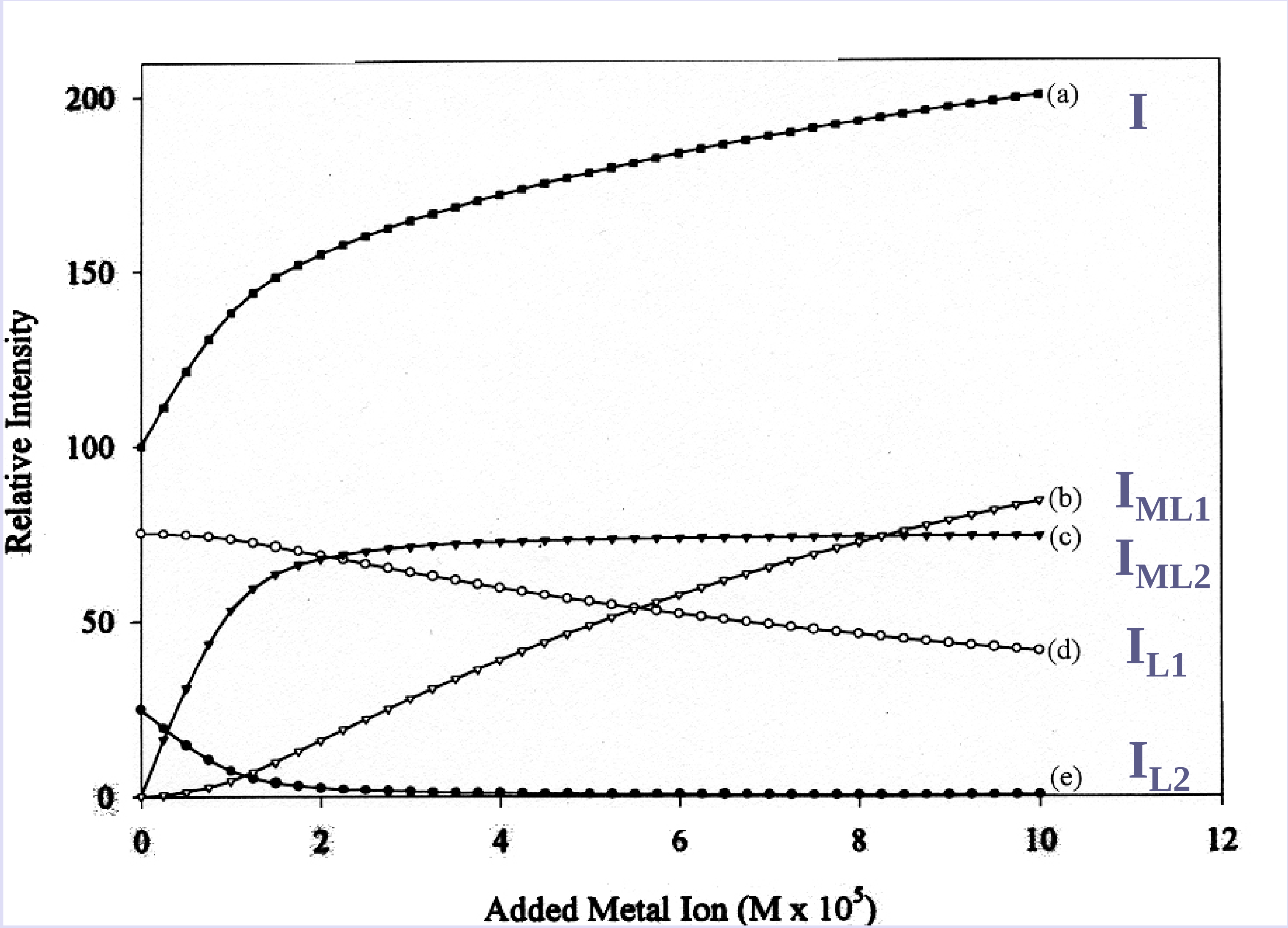
Fluorescence Enhancement Curve with Two-Site Model



Individual Fluorescence Intensities Making Up the Overall "I"

$$I = I_{L1} + I_{ML1} + I_{L2} + I_{ML2}$$

Hypothetical Fluorescence Intensity Curves Showing Component Intensities



Binding Data for Al^{3+} & FA
(15 mg/L)

pH	4.00
log K_1	6.56 ± 0.30
log K_2	5.16 ± 0.12
C_{L1}	13.1 ± 1.5 μM
C_{L2}	6.0 ± 0.9 μM
f_1	0.07 ± 0.02
I_{RES}	186.2 ± 9.7

Conclusions

- Al-NOM speciation can be measured by fluorescence enhancement & ^{27}Al NMR
  - Fluorescence sensitive – natural waters
  - NMR not sensitive – soil solutions
- Both techniques are sensitive to the complexed Al species
- Data modeled for predictive purposes
- Al^{3+} binds strongly as expected
- Multiple Al species present

Dissolved Organic World