Supplementary information for:

Water soluble sapphyrins: potential fluorescent sensors for phosphate anions.
Jonathan L. Sessler, Julian M. Davis, Vladimir Král, Thomas Kimbrough, Vincent Lynch.

The effective equilibrium constants for sapphyrins **1**-**6** with phosphate (cf. Table 1) were determined from fluorescence emission titration studies carried out in aqueous solutions containing 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl. The emission intensity at 690 nm was observed while using an excitation wavelength of 450 nm. Data fits were performed using the computer software package KaleidaGraph 3.52 assuming a 1:1 binding model. Specifically, equation 12.5 of ref. 26 was computer fit using F/Fo and $[P_i]$ as the dependent and independent variables, respectively:

$$F/Fo = (1+(k_{11}/k_s)K_{11}[L]/(1+K_{11}[L])$$

This equation in terms of the variables used in the computer program fit is:

y = (1+m1*m2*m0)/(1+m2*m0) where

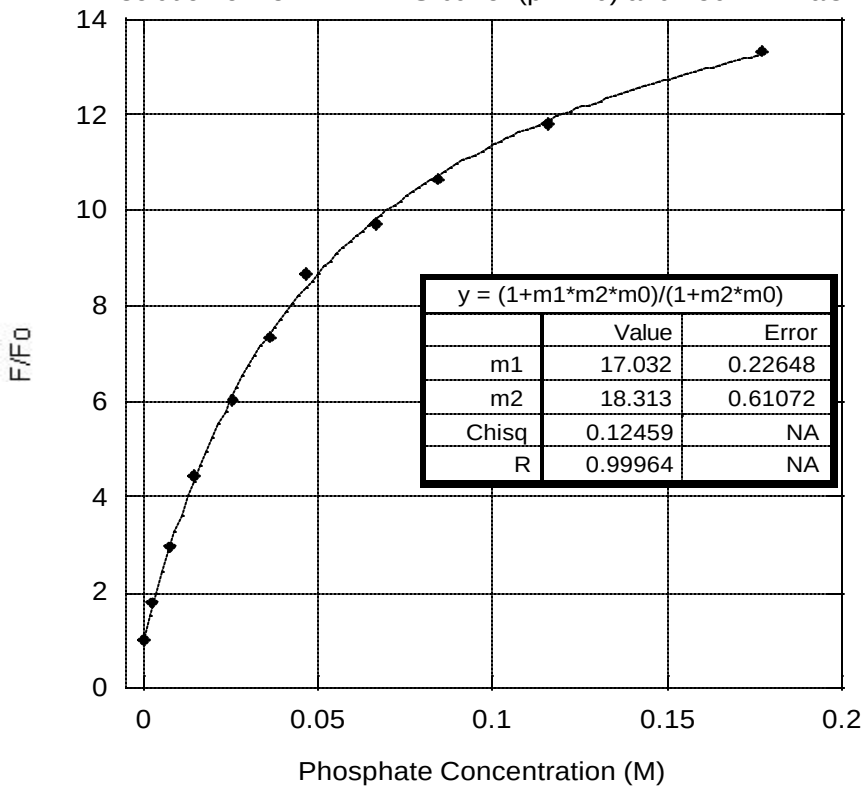
y = F/Fo = ratio of emission intensity over initial emission intensity

m0 = [L] = $[P_i]$ = phosphate concentration. Within the concentration regime used ($[P_i]$>>[Sap]), the simplifying assumption that $[P_i] \sim [P_i]_o$ holds.

m1 = k_{11}/k_s = ratio of the proportionality constants connecting the intensities and concentrations of the species (k_{11} for the sapphyrin-phosphate anion complex, k_s for the unbound, aggregated sapphyrin)

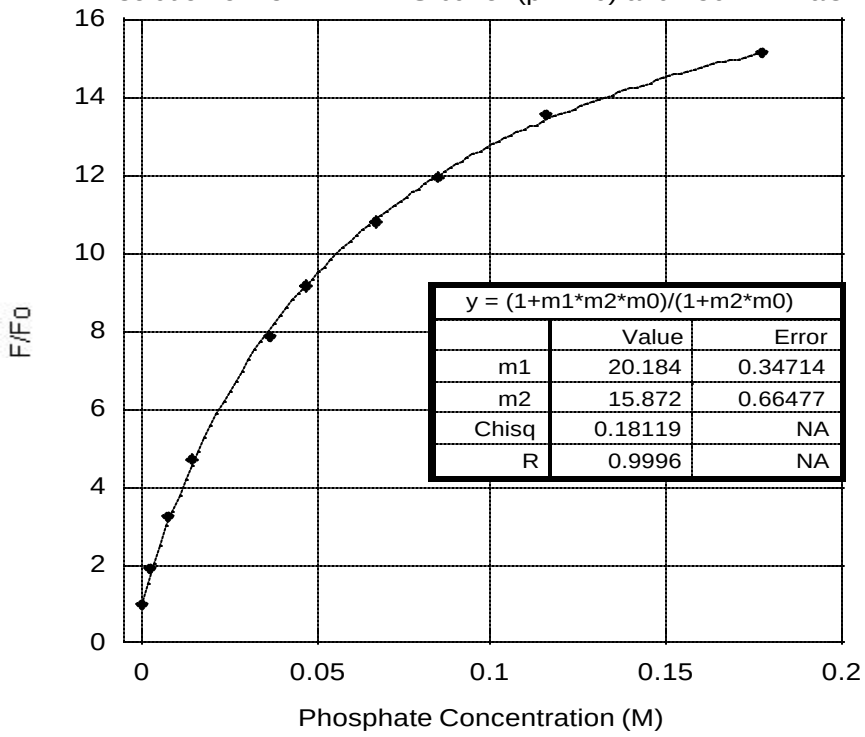
m2 = K_{11} = K = effective equilibrium constant

Sapphyrin **1** (2.7 μM) titrated with 0-200 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



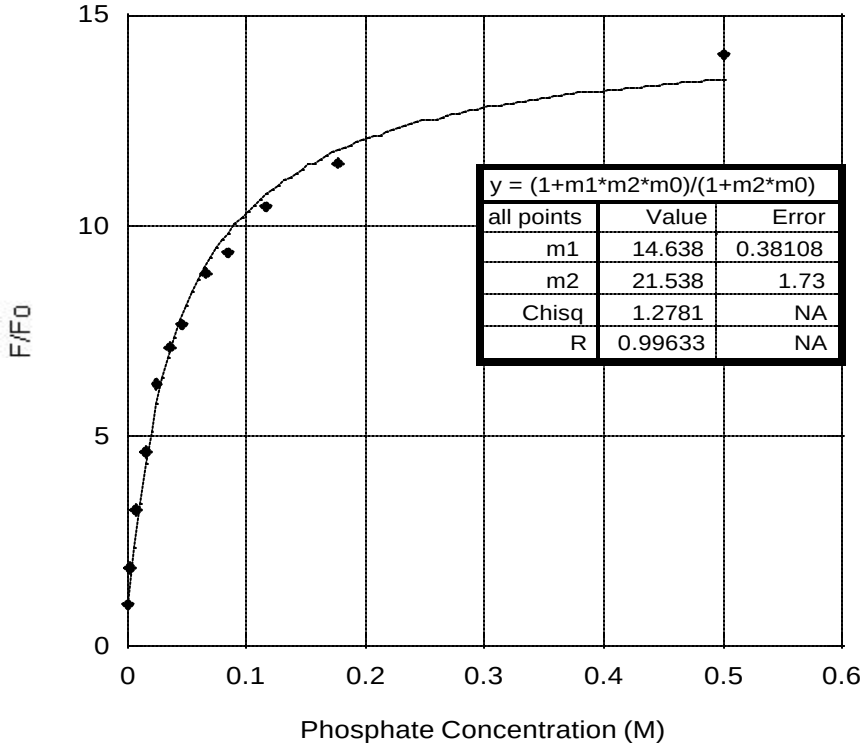
y = (1+m1*m2*m0)/(1+m2*m0)		
	Value	Error
m1	17.032	0.22648
m2	18.313	0.61072
Chisq	0.12459	NA
R	0.99964	NA

Sapphyrin **1** (2.7 μM) titrated with 0-200 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl

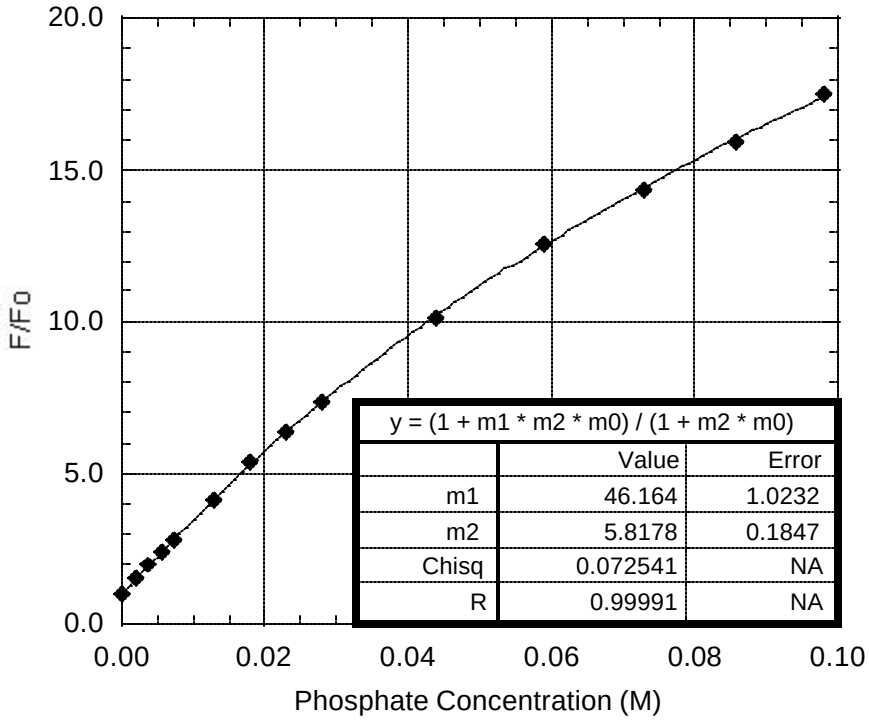


y = (1+m1*m2*m0)/(1+m2*m0)		
	Value	Error
m1	20.184	0.34714
m2	15.872	0.66477
Chisq	0.18119	NA
R	0.9996	NA

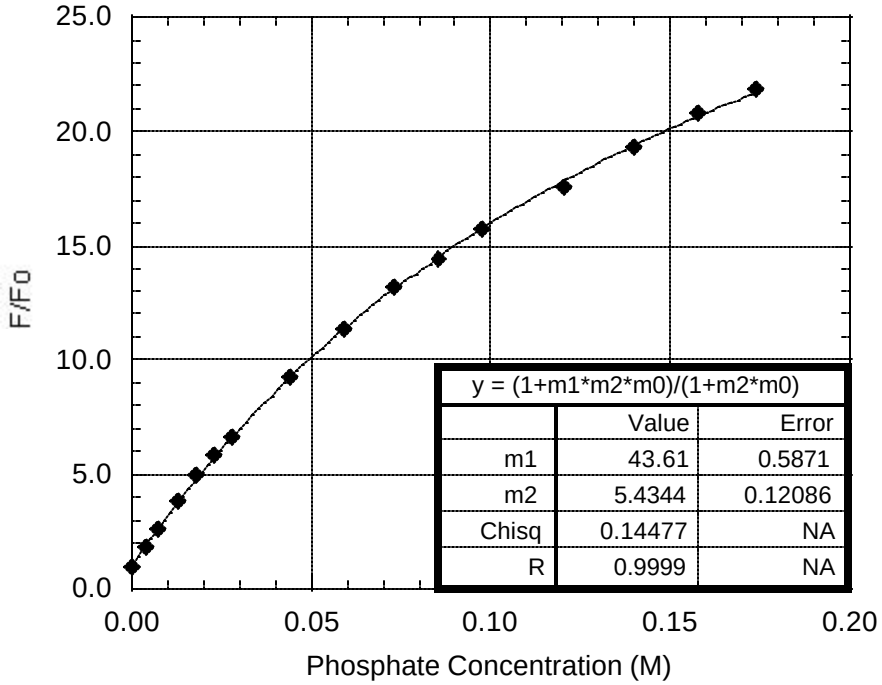
Sapphyrin **1** (2.7 μM) titrated with 0-500 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



Sapphyrin **2** (2 μM) titrated with 0-100 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl

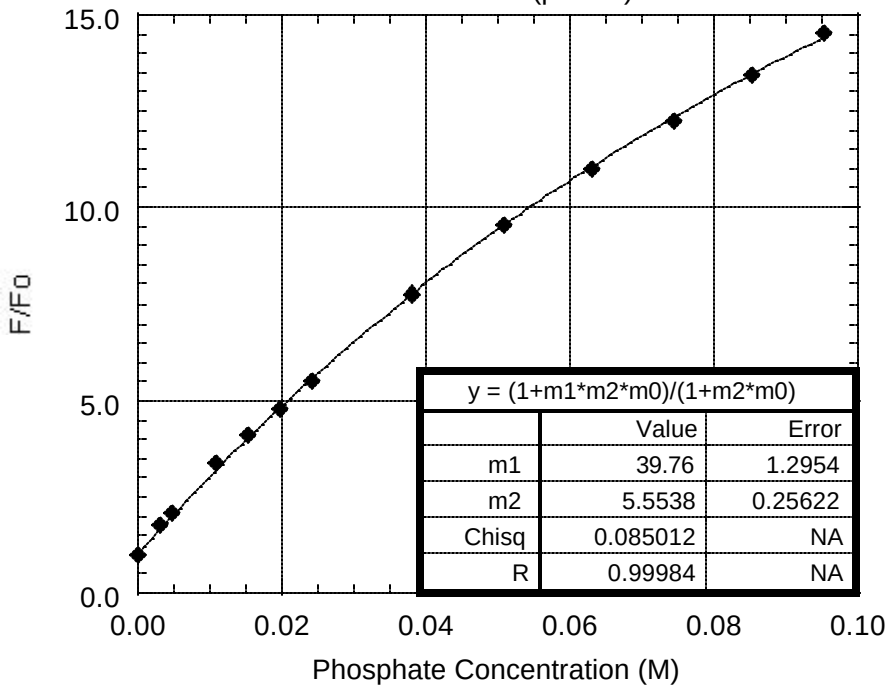


Sapphyrin **2** (3 μM) titrated with 0-200 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



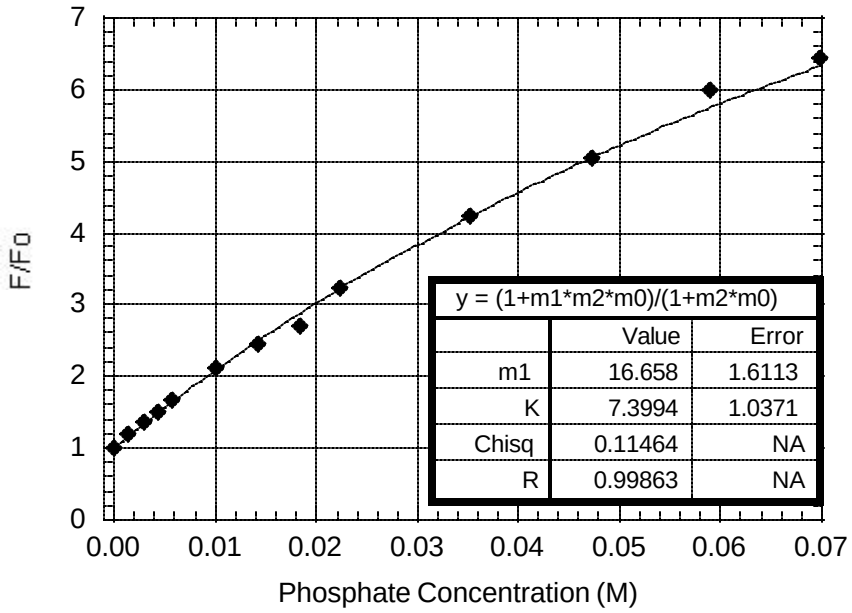
y = (1+m1*m2*m0)/(1+m2*m0)		
	Value	Error
m1	43.61	0.5871
m2	5.4344	0.12086
Chisq	0.14477	NA
R	0.9999	NA

Sapphyrin **2** (2 μM) titrated with 0-100 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



y = (1+m1*m2*m0)/(1+m2*m0)		
	Value	Error
m1	39.76	1.2954
m2	5.5538	0.25622
Chisq	0.085012	NA
R	0.99984	NA

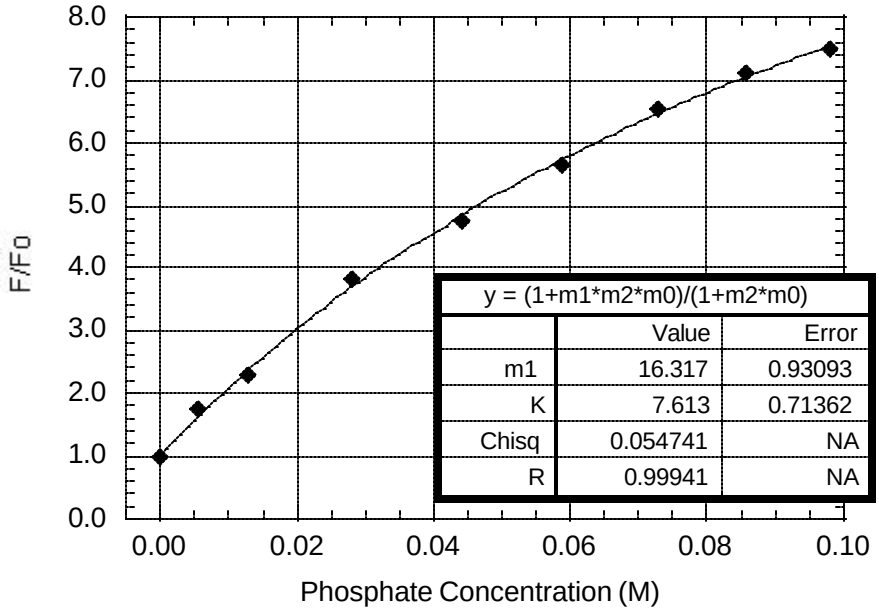
Sapphyrin **3** (2 μM) titrated with 0-70 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



y = (1+m1*m2*m0)/(1+m2*m0)

	Value	Error
m1	16.658	1.6113
K	7.3994	1.0371
Chisq	0.11464	NA
R	0.99863	NA

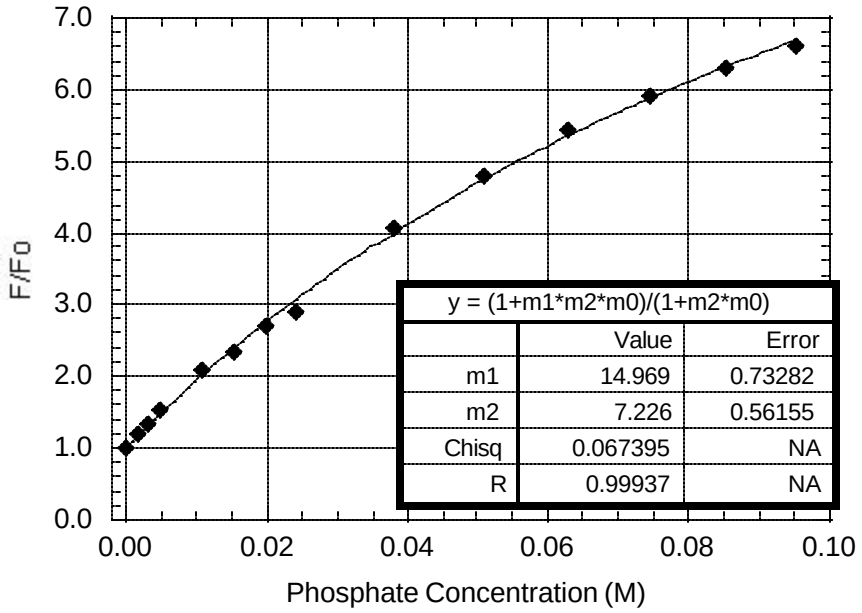
Sapphyrin **3** (2 μM) titrated with 0-100 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



y = (1+m1*m2*m0)/(1+m2*m0)

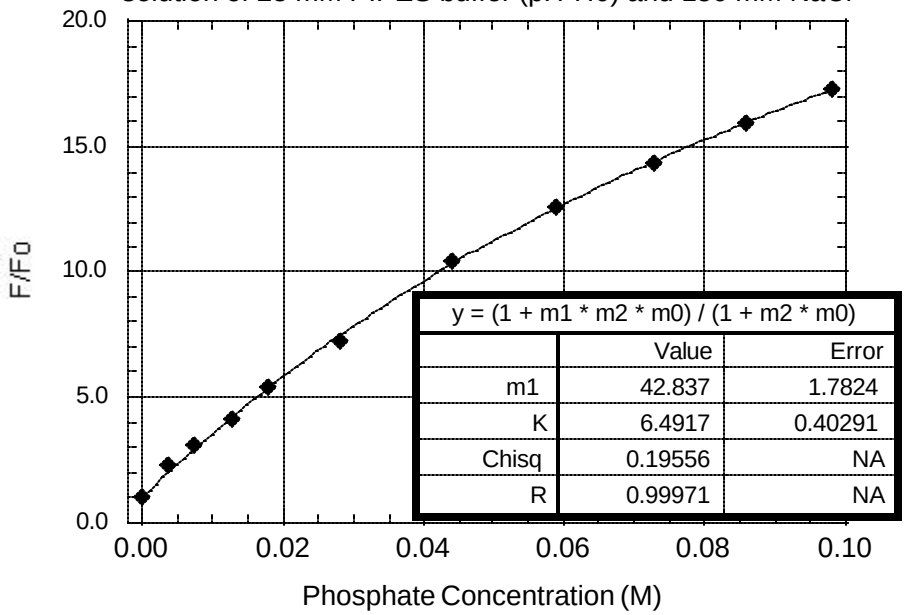
	Value	Error
m1	16.317	0.93093
K	7.613	0.71362
Chisq	0.054741	NA
R	0.99941	NA

Sapphyrin **3** (2 μM) titrated with 0-100 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



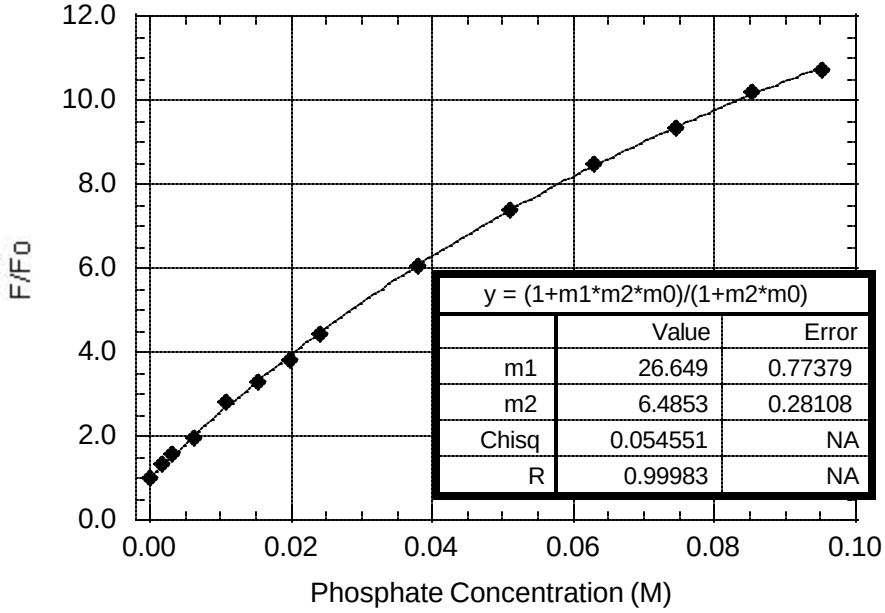
y = (1+m1*m2*m0)/(1+m2*m0)		
	Value	Error
m1	14.969	0.73282
m2	7.226	0.56155
Chisq	0.067395	NA
R	0.99937	NA

Sapphyrin **4** (2μM) titrated with 0-100 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



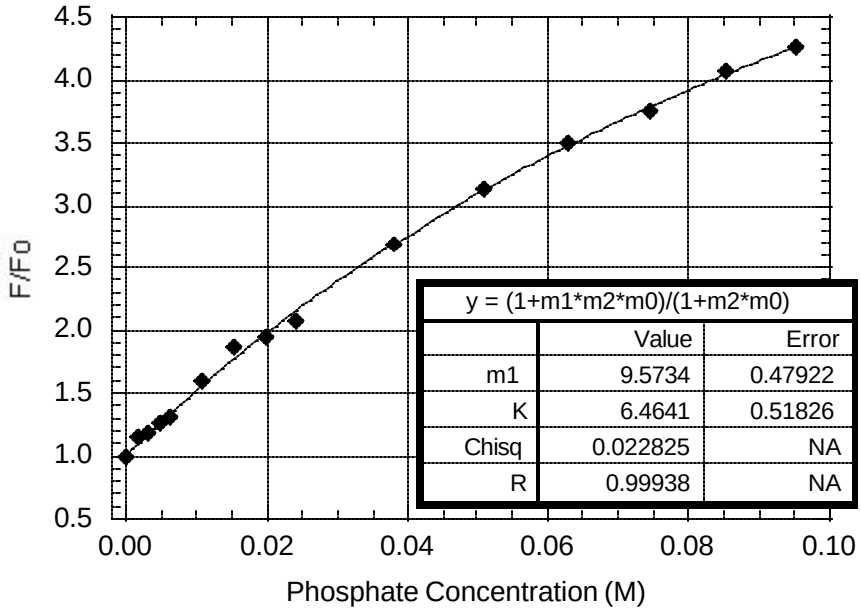
y = (1 + m1 * m2 * m0) / (1 + m2 * m0)		
	Value	Error
m1	42.837	1.7824
K	6.4917	0.40291
Chisq	0.19556	NA
R	0.99971	NA

Sapphyrin **4** (2 μM) titrated with 0-100 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



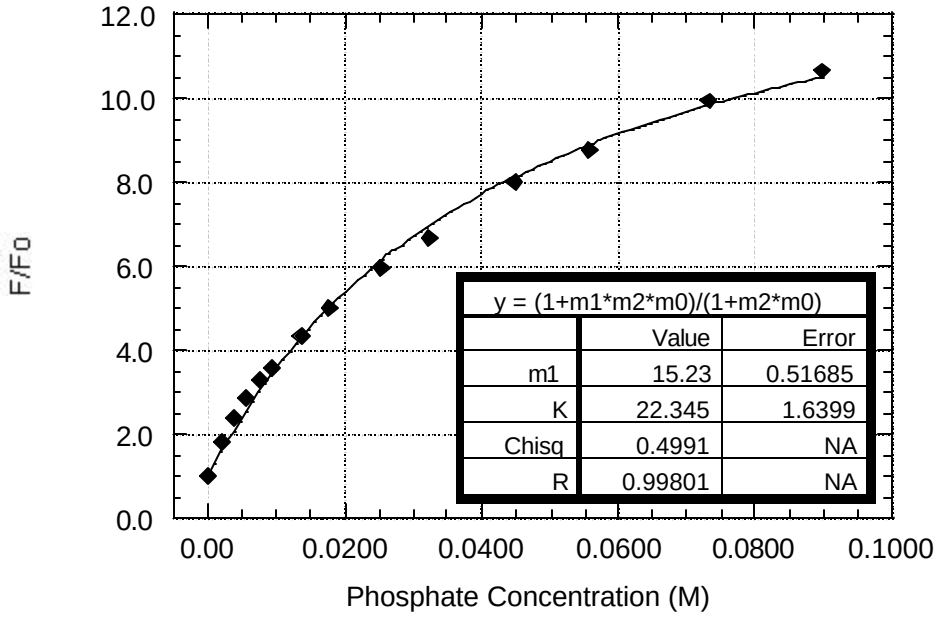
y = (1+m1*m2*m0)/(1+m2*m0)		
	Value	Error
m1	26.649	0.77379
m2	6.4853	0.28108
Chisq	0.054551	NA
R	0.99983	NA

Sapphyrin **4** titrated with 0-100 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl

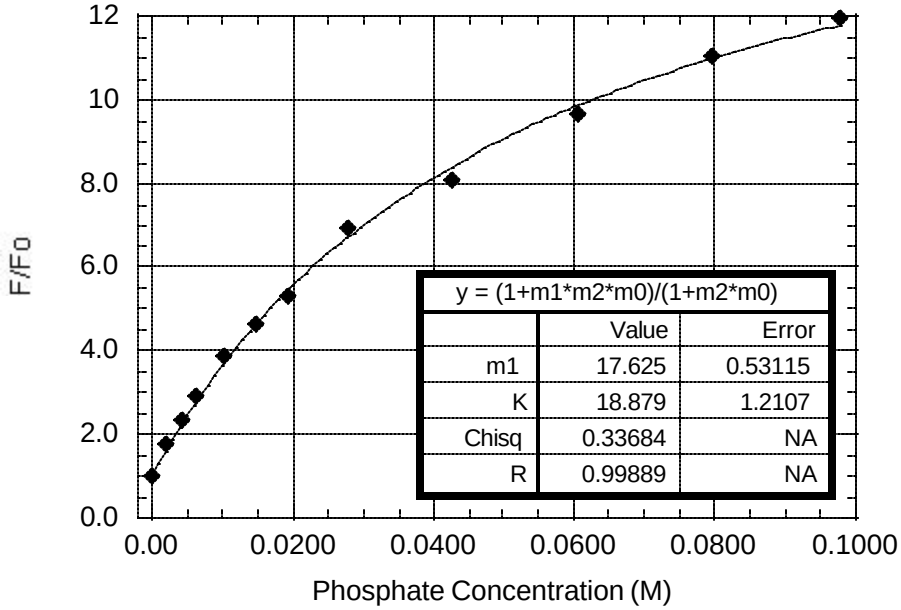


y = (1+m1*m2*m0)/(1+m2*m0)		
	Value	Error
m1	9.5734	0.47922
K	6.4641	0.51826
Chisq	0.022825	NA
R	0.99938	NA

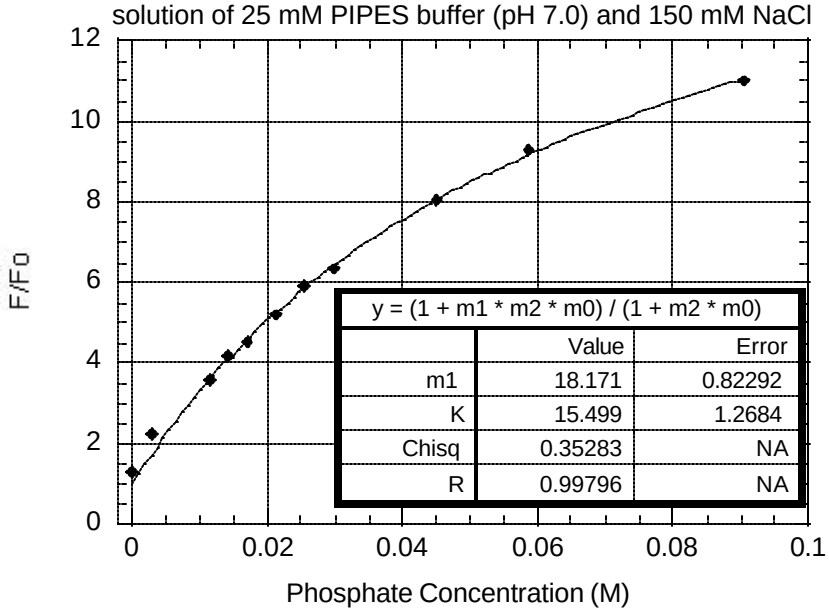
Sapphyrin **5** titrated with 0-100 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



Sapphyrin **5** titrated with 0-100 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



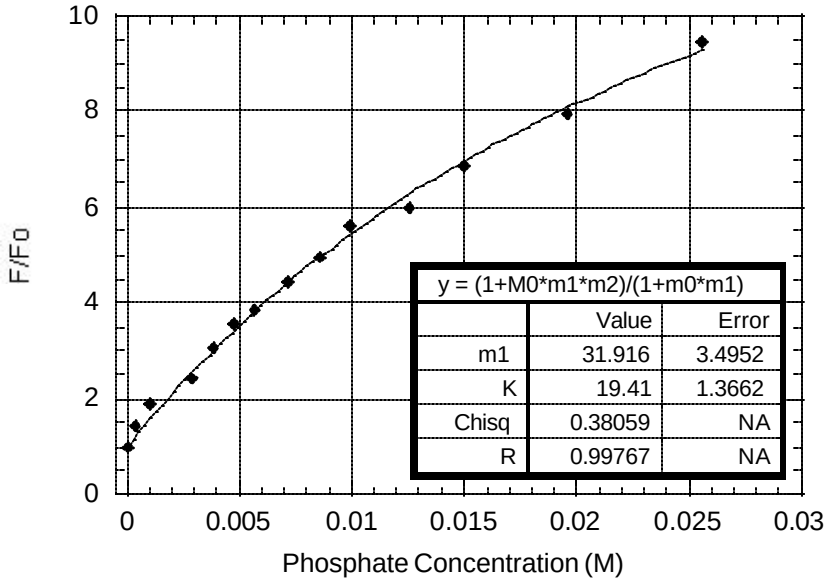
Sapphyrin **5** titrated with 0-100 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



y = (1 + m1 * m2 * m0) / (1 + m2 * m0)

	Value	Error
m1	18.171	0.82292
K	15.499	1.2684
Chisq	0.35283	NA
R	0.99796	NA

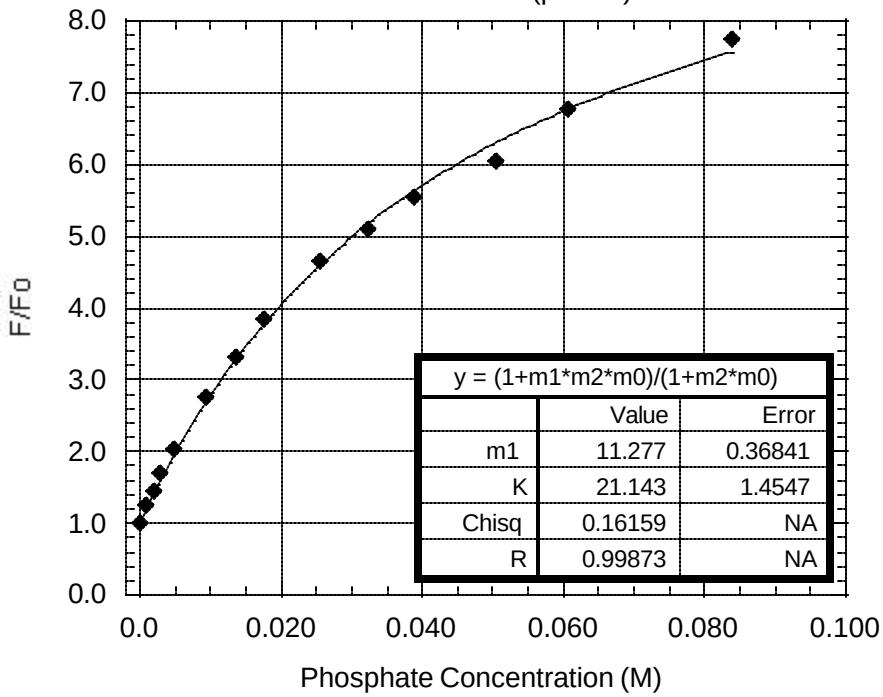
Sapphyrin **5** titrated with 0-25 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



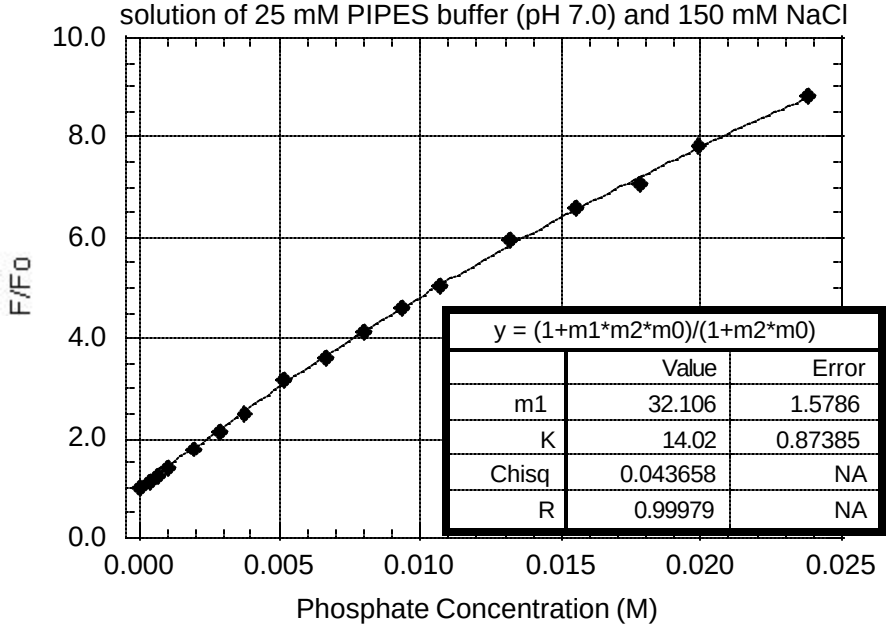
y = (1+M0*m1*m2)/(1+m0*m1)

	Value	Error
m1	31.916	3.4952
K	19.41	1.3662
Chisq	0.38059	NA
R	0.99767	NA

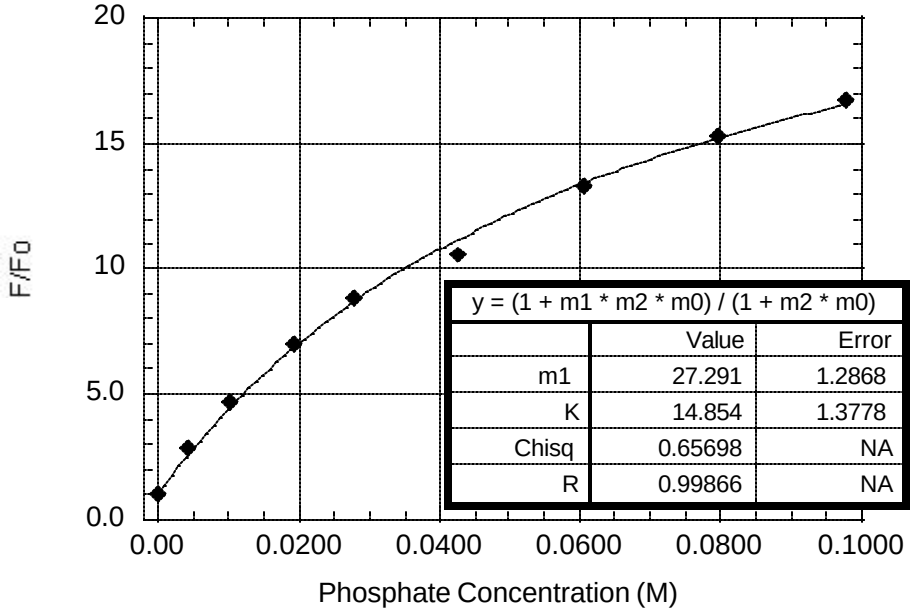
Sapphyrin **5** titrated with 0-100 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) without chloride



Sapphyrin **6** titrated with 0-25 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



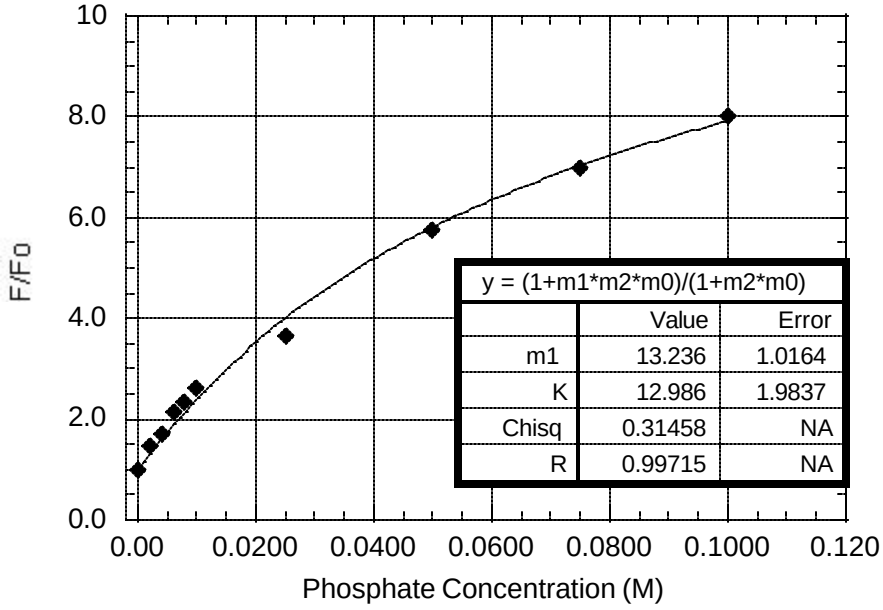
Sapphyrin **6** titrated with 0-100 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



y = (1 + m1 * m2 * m0) / (1 + m2 * m0)

	Value	Error
m1	27.291	1.2868
K	14.854	1.3778
Chisq	0.65698	NA
R	0.99866	NA

Sapphyrin **6** titrated with 0-100 mM phosphate in a solution of 25 mM PIPES buffer (pH 7.0) and 150 mM NaCl



y = (1+m1*m2*m0)/(1+m2*m0)

	Value	Error
m1	13.236	1.0164
K	12.986	1.9837
Chisq	0.31458	NA
R	0.99715	NA

The dimerization constants of sapphyrins **7**-**9** in methanol, reported in Table 2, were determined using the method of Pasternack.[29] Specifically, equation 8 of ref. 29 was computer fit with Kaleidagraph 3.52 using Ao-A and [Sap] as the dependent and independent variables, respectively:

$$Ao\text{-}A = (2\varepsilon_{monomer} - \varepsilon_{dimer})(4KCo+1-(1+8KCo)^{0.5})/8K$$

This equation in terms of the variables used in the computer program fit is:

y = m1*((4*m2*m0+1-(1+8*m2*m0)^0.5)/(8*m2) where

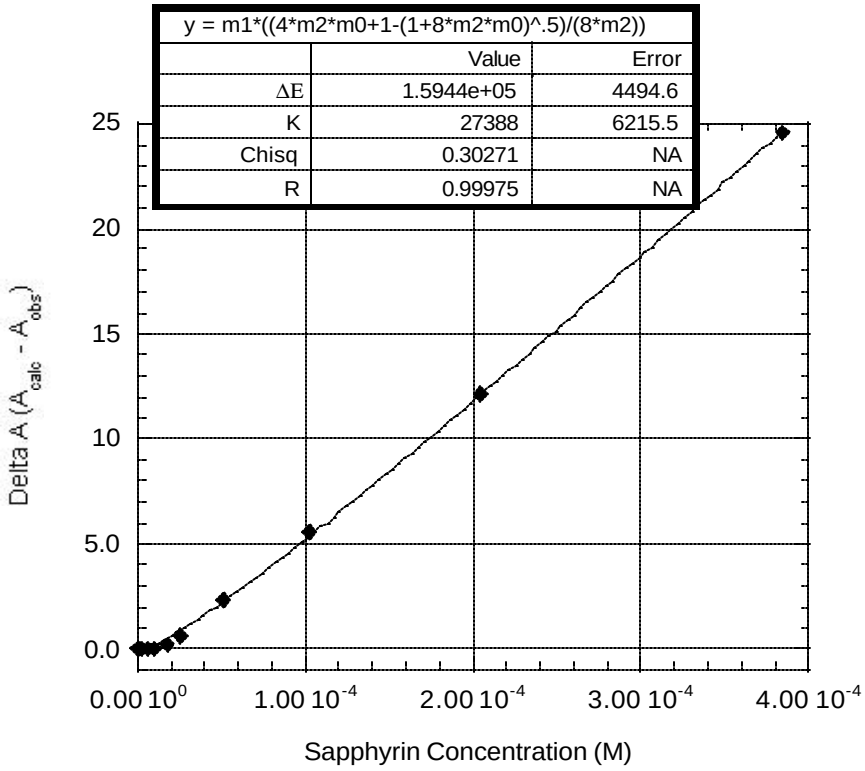
y = Ao-A = ΔA = A_{calc}-A_{obs} = difference between extrapolated absorbance (if all sapphyrin was monomeric) and the observed absorbance

m0 = Co = total sapphyrin concentration

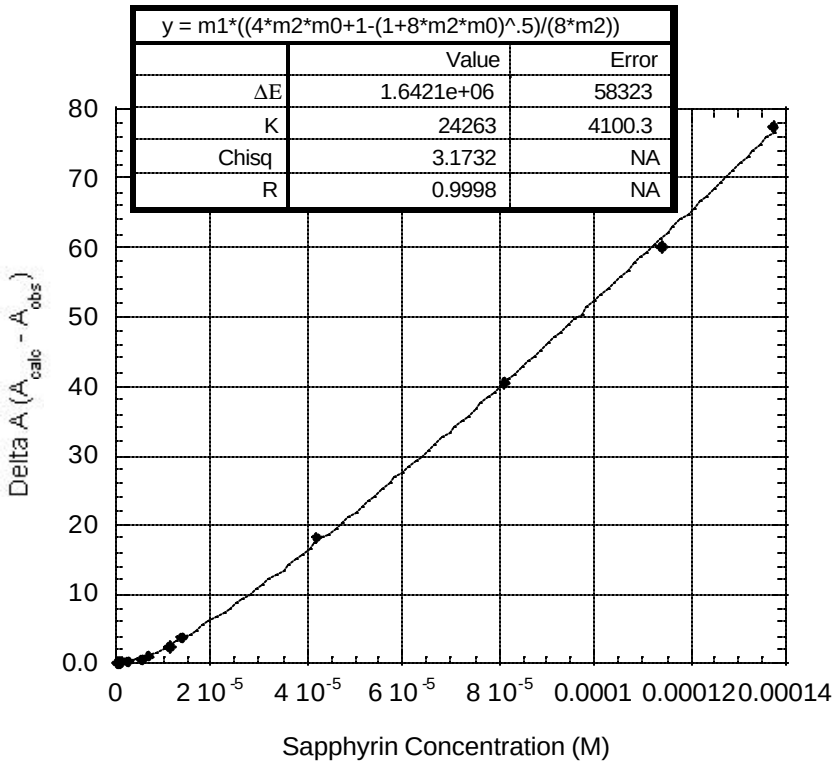
m1 = $(2\varepsilon_{monomer} - \varepsilon_{dimer})$ = $\Delta\varepsilon$ = difference between the molar absorptivity of two equivalents of the sapphyrin monomer and one equivalent of the sapphyrin dimer.

m2 = K = dimerization constant

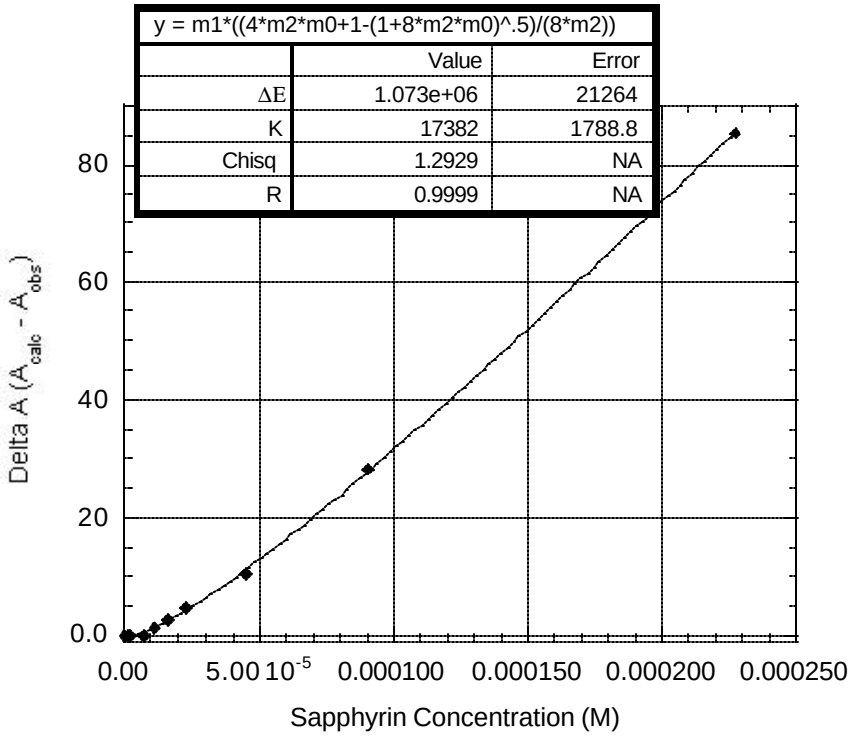
Sapphyrin **7** (2TFA salt) Dilution Study in Methanol



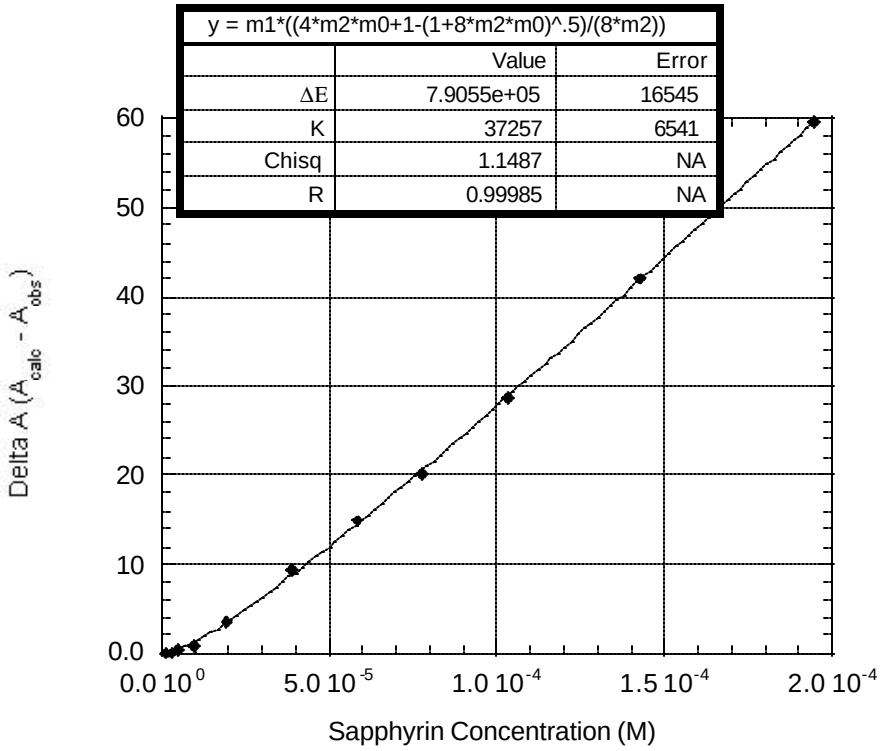
Sapphyrin **7** (2TFA salt) Dilution Study in Methanol



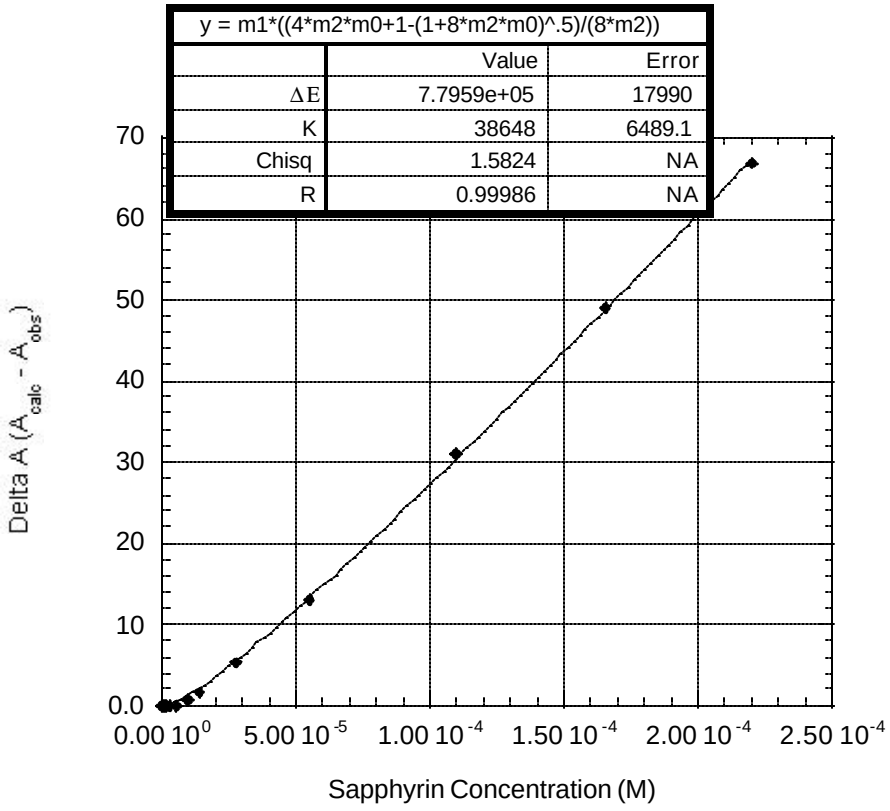
Sapphyrin **7** (2TFA salt) Dilution Study in Methanol



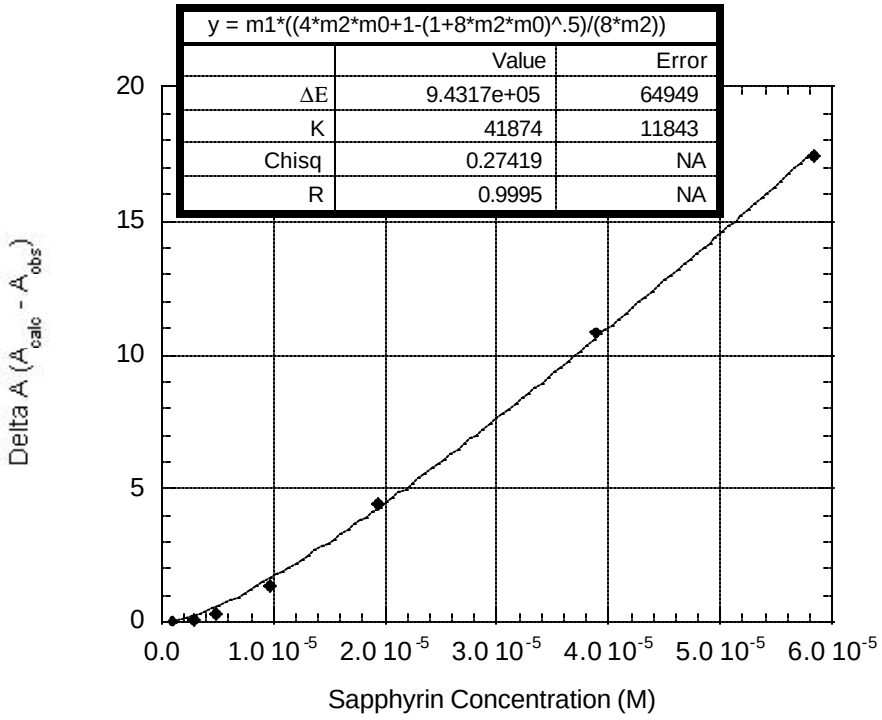
Sapphyrin **7** (2HCl salt) Dilution Study in Methanol



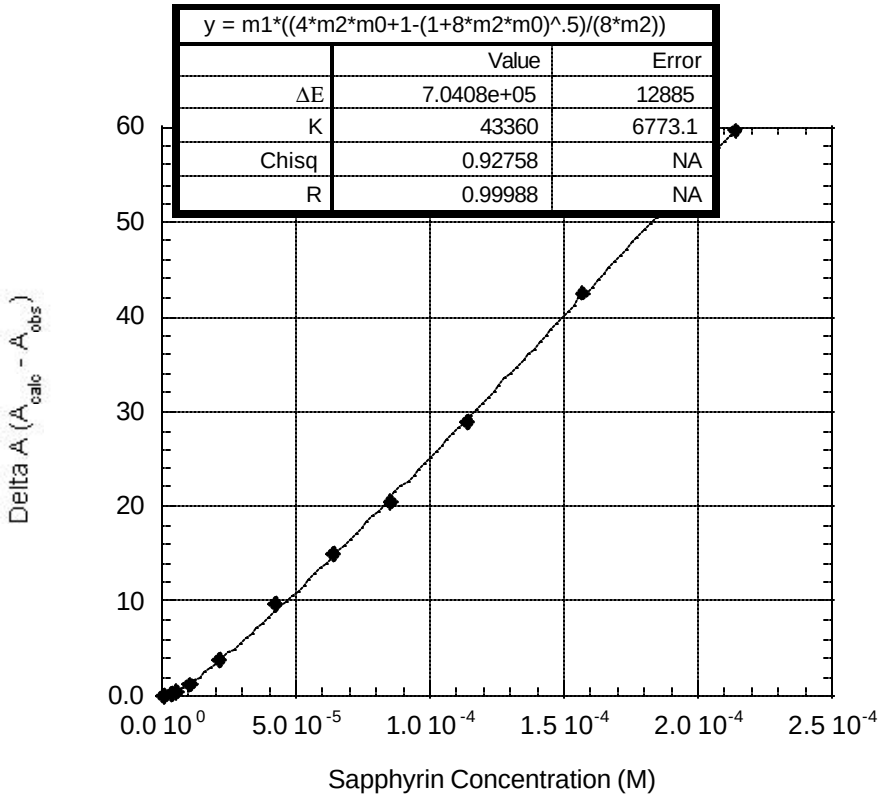
Sapphyrin **7** (2HCl salt) Dilution Study in Methanol



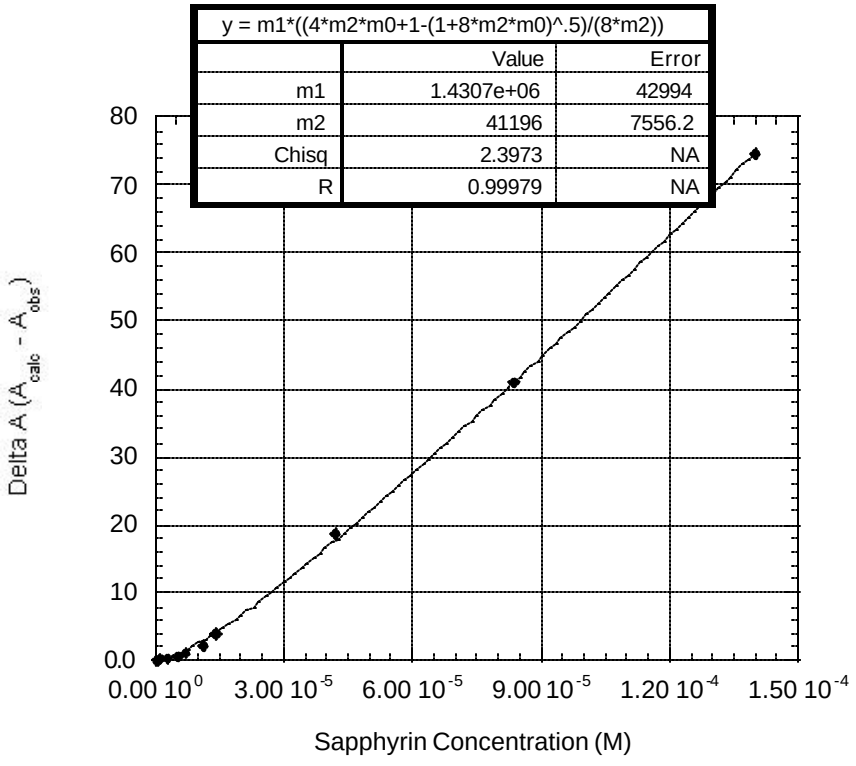
Sapphyrin **7** (2HCl salt) Dilution Study in Methanol



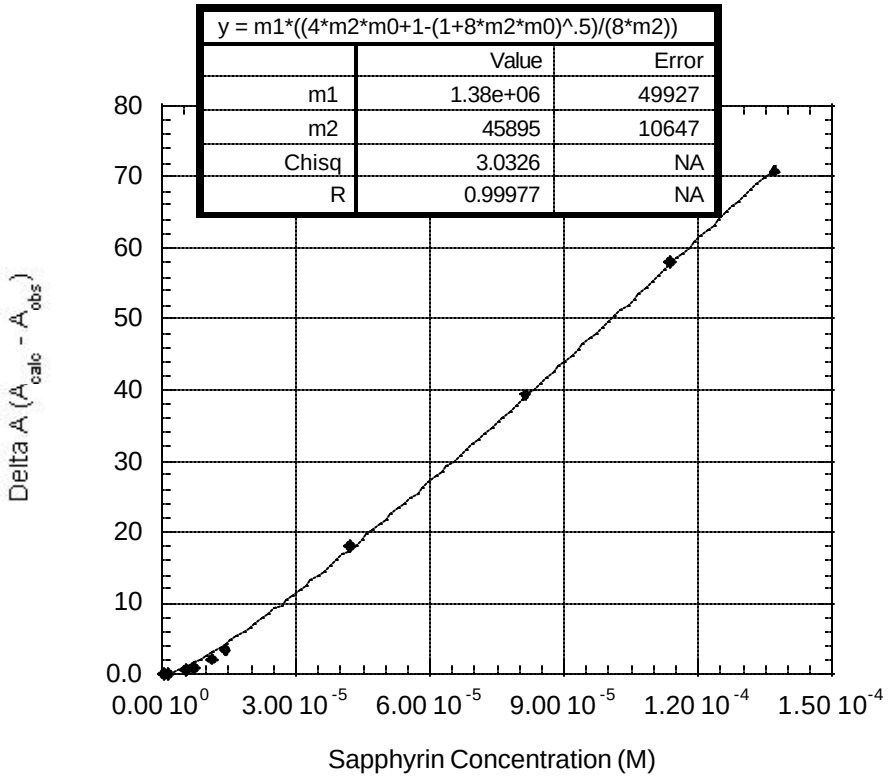
Sapphyrin **7** (2HCl salt) Dilution Study in Methanol



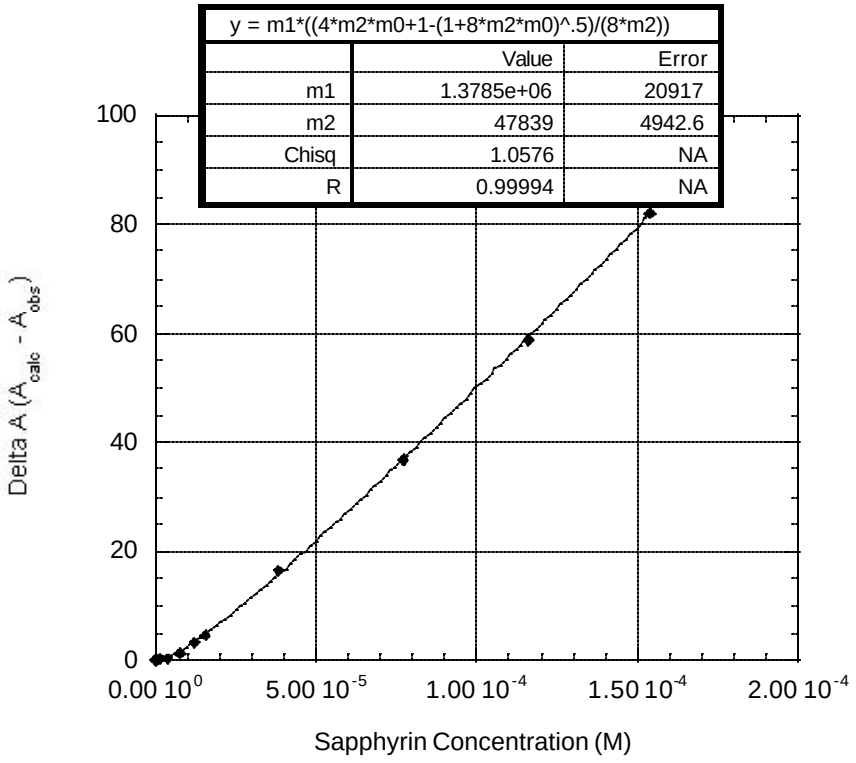
Sapphyrin **8** (2HCl salt) Dilution Study in Methanol



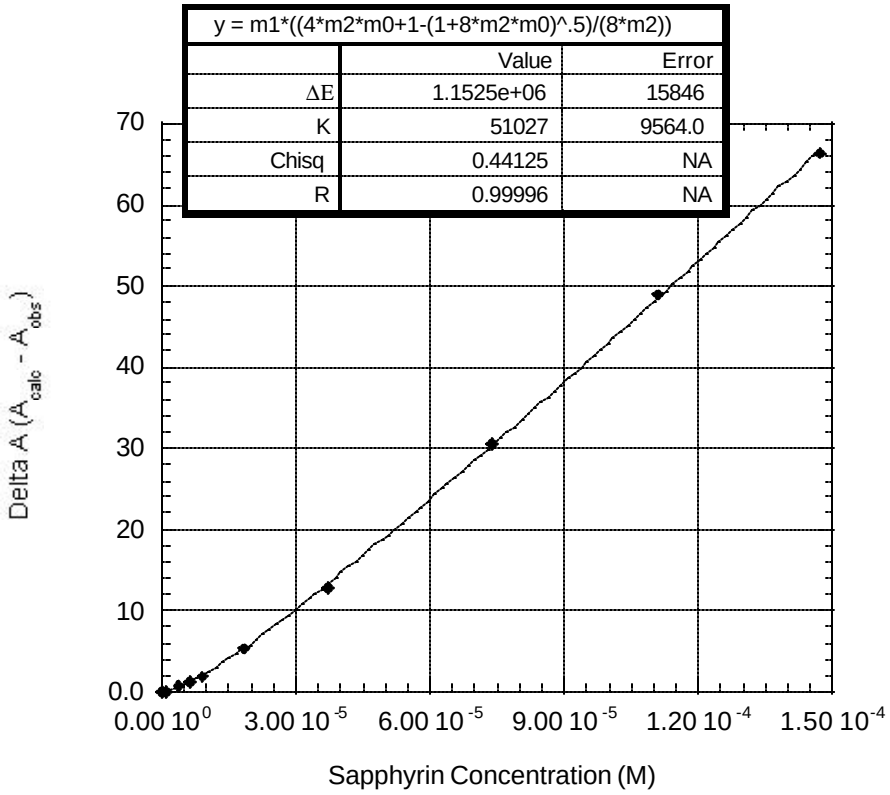
Sapphyrin **8** (2HCl salt) Dilution Study in Methanol



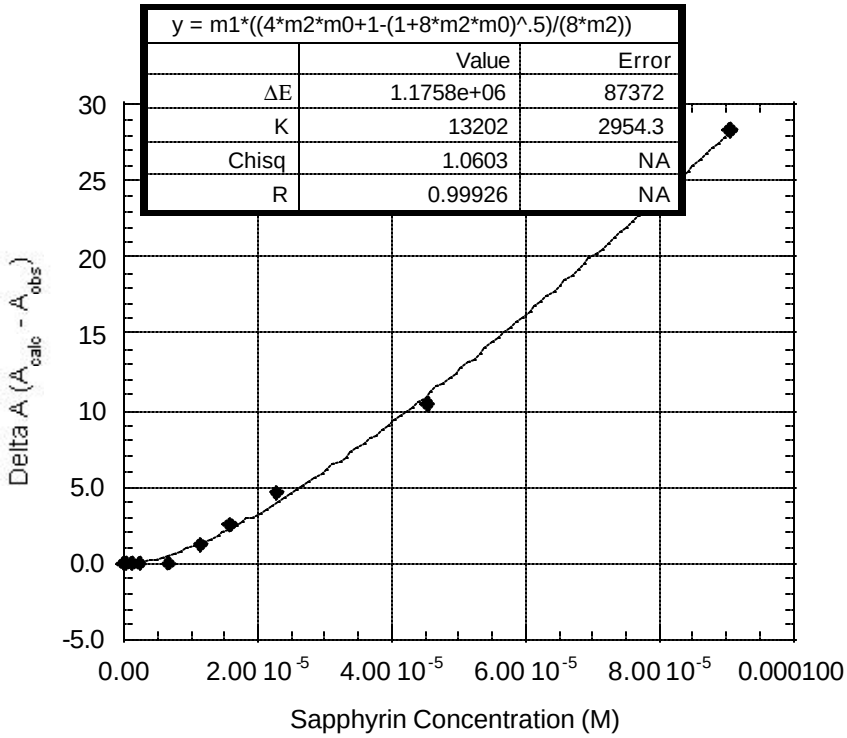
Sapphyrin **8** (2HCl salt) Dilution Study in Methanol



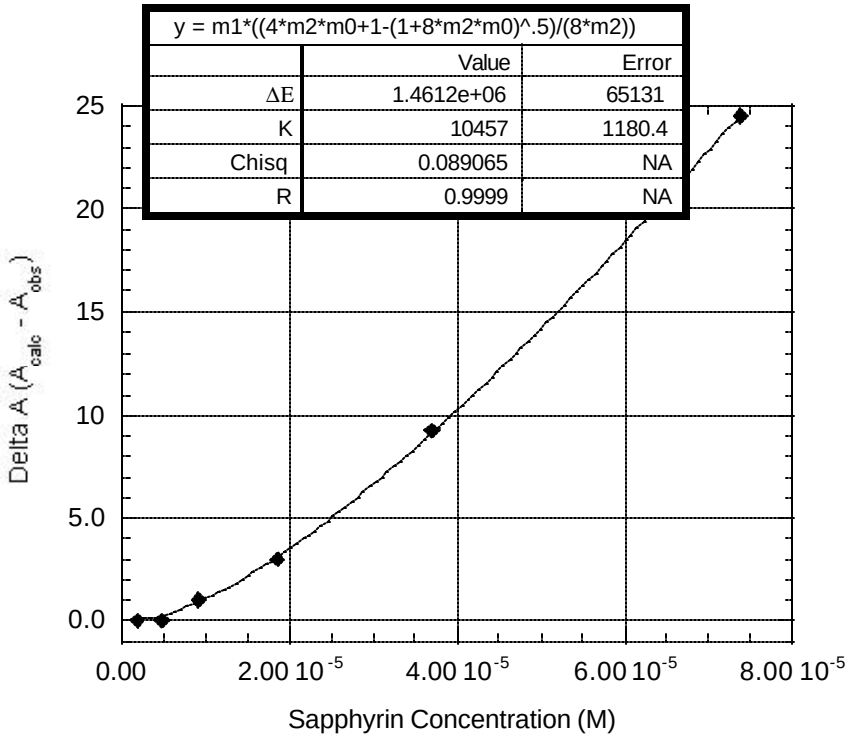
Sapphyrin **8** (2HCl salt) Dilution Study in Methanol



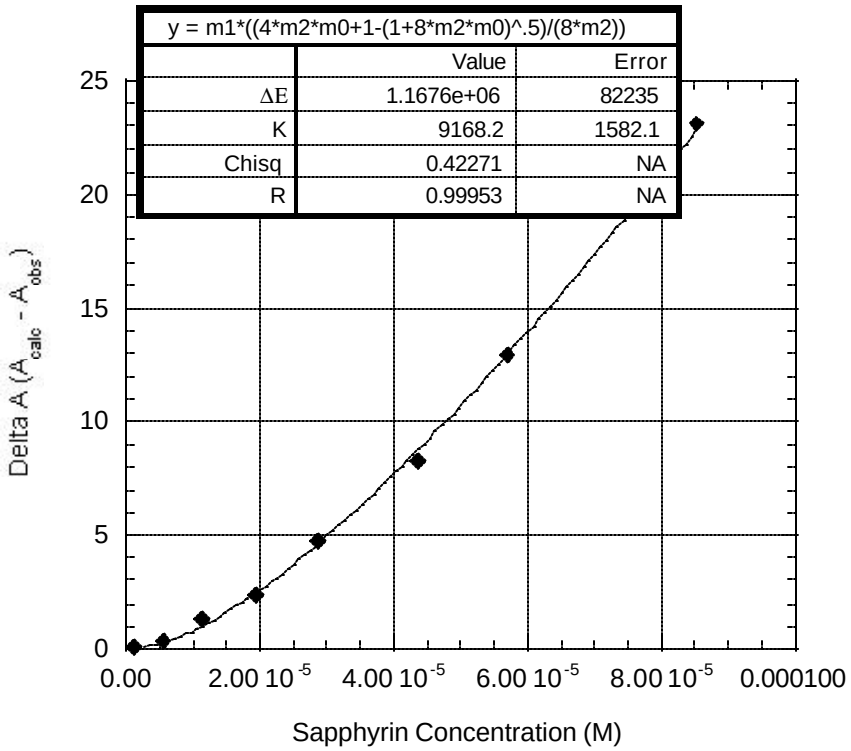
Sapphyrin **9** (2HCl salt) Dilution Study in Methanol



Sapphyrin **9** (2HCl salt) Dilution Study in Methanol



Sapphyrin **9** (2HCl salt) Dilution Study in Methanol



Sapphyrin **9** (2HCl salt) Dilution Study in Methanol