Calculations of exposure times for cyanotype and kallitype sensitisers using focused 405nm laser pulse

Input light source details

$M := \frac{mol}{L}$

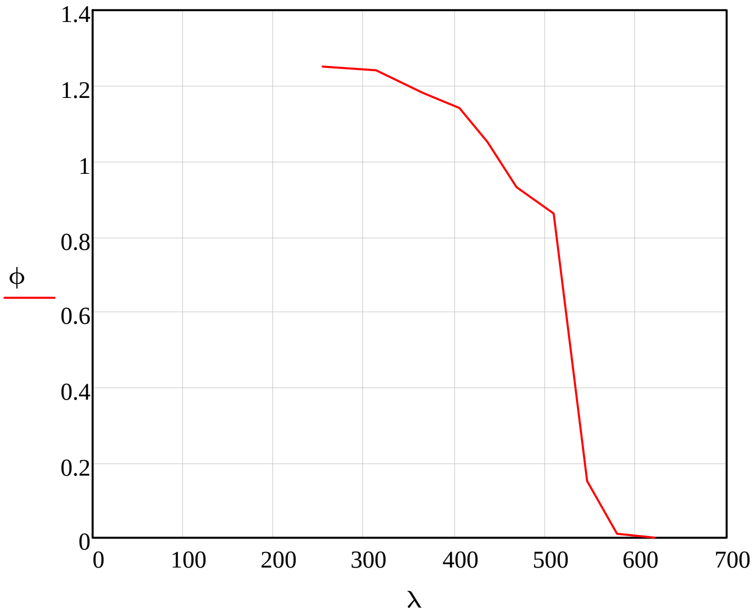
Laser wavelength $\lambda_{spot} := 405nm$

Max continous power $P := 450mW$

Area of spot $A_{exp} := 111.724\ \mu m^2$

Quantum Yield aqueous ferrioxalate / Fe(C2O4)3

Wavelength $\lambda := \begin{pmatrix} 254 \\ 313 \\ 365 \\ 405 \\ 436 \\ 468 \\ 509 \\ 546 \\ 579 \\ 620 \end{pmatrix} nm$ Quantum Yield $\phi := \begin{pmatrix} 1.25 \\ 1.24 \\ 1.18 \\ 1.14 \\ 1.05 \\ 0.93 \\ 0.86 \\ 0.15 \\ 0.01 \\ 0.00 \end{pmatrix}$



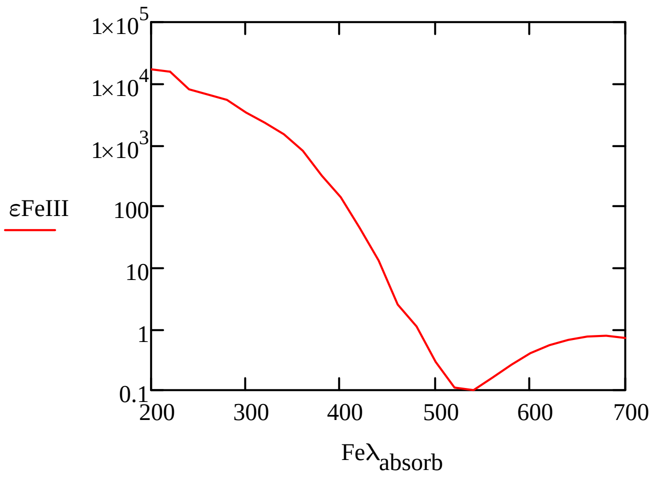
Ref. Ch.12. Quantitative Aspects of Siderotype Photochemistry, Fig 12.2 - Mike Ware

molar attenuation coefficient of Ammonium Iron(III) Oxalate; (NH4)3[Fe(C2O4)3].3H2O

Wavelength (nm) $Fe\lambda_{absorb} :=$ (vector below) nm

molar attenuation coefficient $\varepsilon FeIII :=$ (vector below) $L \cdot \frac{1}{mol} \cdot \frac{1}{cm}$

$Fe\lambda_{absorb}$ (nm)	$\varepsilon FeIII$ ($L \cdot \frac{1}{mol} \cdot \frac{1}{cm}$)
200	17000.00
220	15500.00
240	8000.00
260	6600.00
280	5400.00
300	3360.00
320	2280.00
340	1480.00
360	800.00
380	314.00
400	140.00
420	44.00
440	13.00
460	2.49
480	1.09
500	0.29
520	0.11
540	0.10
560	0.16
580	0.26
600	0.40
620	0.54
640	0.66
660	0.75
680	0.77
700	0.71



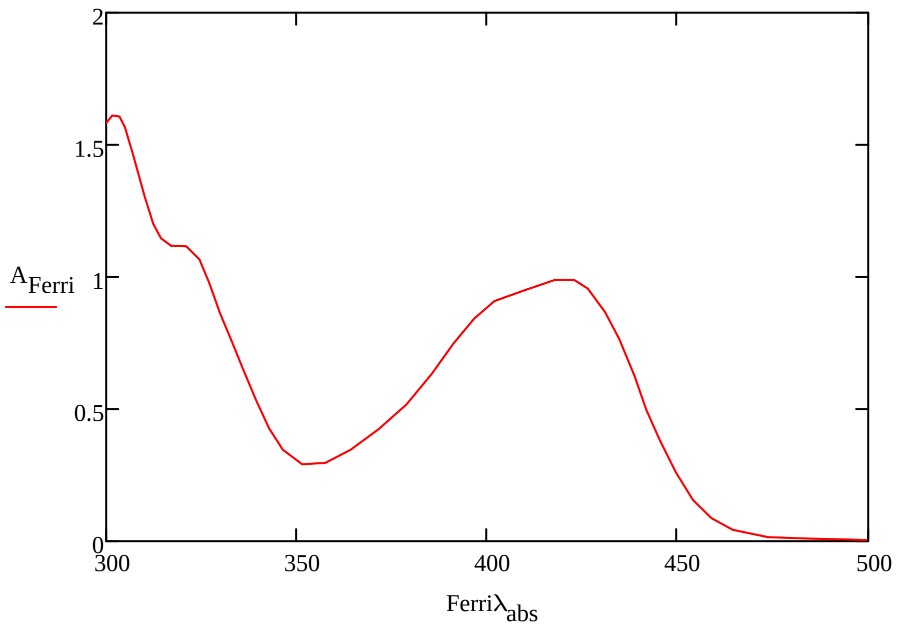
Ref. Ch.12. Quantitative Aspects of Siderotype Photochemistry, Fig 12.3 - Mike Ware

Absorption coefficients of ferricyanide; [Fe(CN)6]3-

Wavelength (nm) $Ferri\lambda_{abs} :=$ (vector below) nm

Absorption curve $A_{Ferri} :=$ (vector below)

$Ferri\lambda_{abs}$ (nm)	A_{Ferri}
300	1.58088
301.655	1.61029
303.516	1.60662
304.964	1.56618
307.032	1.46691
310.134	1.30515
312.41	1.19853
314.426	1.14522
317.063	1.11765
321.096	1.11489
324.509	1.06526
326.991	0.979779
329.938	0.861213
333.04	0.753676
336.143	0.643382
339.555	0.527574
342.813	0.425551
346.381	0.345588
351.499	0.290441
357.549	0.295956
364.219	0.345588
371.51	0.422794
378.8	0.516544
385.471	0.632353
391.21	0.748162
396.639	0.841912
401.913	0.908088
409.979	0.949449
417.735	0.988051
422.854	0.988051



Ref. App note - 5991-0388EN_AppNote _Cary60_PotassiumFer ricyanide

Published molar attenuation coefficient at 420 nm

$$\varepsilon_{420} := 1040\cdot\frac{1}{mol}\cdot\frac{1}{cm}$$

Extrapolate absorpbtion at 420nm

$$A_{420} := interp\left(cspline\left(Ferri\lambda_{abs}, A_{Ferri}\right), Ferri\lambda_{abs}, A_{Ferri}, 420\right) = 0.993$$

calculate concentration

$$c_{420} := \frac{A_{420}}{\varepsilon_{420}\cdot 1cm} = 9.55\times 10^{-4}\,mol$$

calculate attenuation based on single point molar attenuation coefficient

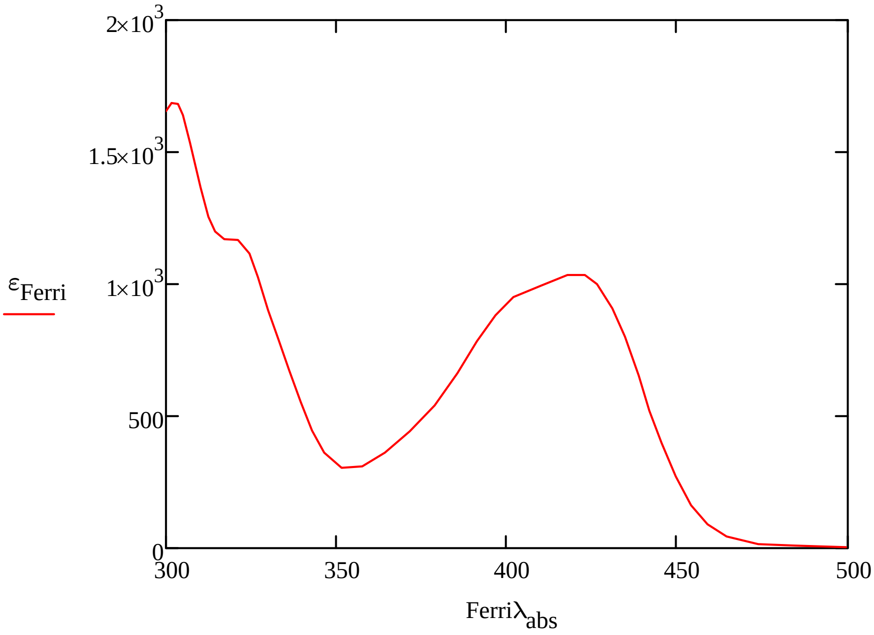
$$\varepsilon_{Ferri} := \frac{A_{Ferri}}{c_{420}\cdot 1cm} =$$

	0
0	$1.655\cdot 10^3$
1	$1.686\cdot 10^3$
2	$1.682\cdot 10^3$
3	$1.64\cdot 10^3$
4	$1.536\cdot 10^3$
5	$1.367\cdot 10^3$
6	$1.255\cdot 10^3$
7	$1.199\cdot 10^3$
8	$1.17\cdot 10^3$
9	$1.167\cdot 10^3$
10	$1.115\cdot 10^3$
11	$1.026\cdot 10^3$
12	901.804
13	789.198
14	673.706
15	...

$$\cdot\frac{1}{mol}\cdot\frac{1}{cm}$$

remove units to allow interpolation formula

$$\varepsilon_{Ferri} := \varepsilon_{Ferri}\cdot mol\cdot cm$$



Cyanotype calculations

'New' method cyanotype uses;
Ammonium Iron(III) Oxalate - (NH4)3[Fe(C2O4)3].3H2O
Ammonium Ferricyanide - (NH4)3Fe(CN)6

reacts with light to give ferric ferrocyanide [Fe(CN)6]4 or iron(III) hexacyanoferrate(II)

30g oxalate + 10g potasium ferricyanide, 15g potassim oxalate disposed of, so assume keeping 20g of oxalate

Molar mass oxalate	$\text{Fe(C2O4)3\_3H2O} := 428.06\,\frac{gm}{mol}$
Density oxalate	$\rho_{\text{Fe(C2O4)3\_3H2O}} := 1.78\,\frac{gm}{cm^3}$
mass oxalate	$\text{Fe(C2O4)3\_3H2O}_{mass} := 20gm$
solution volume	$\text{Fe(C2O4)3\_3H2O}_{vol} := 100mL$
Molar mass ferricyanide	$\text{(NH4)3Fe(CN)6} := 266.06\,\frac{gm}{mol}$
Density of potassium, rather than the ammonium, as data unavailable	$\rho_{\text{(NH4)3Fe(CN)6}} := 1.89\,\frac{gm}{cm^3}$
mass ferricyanide	$\text{(NH4)3Fe(CN)6}_{mass} := 10gm$
solution volume	$\text{(NH4)3Fe(CN)6}_{vol} := 100mL$
Total volume combined	$V_{total} := \text{Fe(C2O4)3\_3H2O}_{vol} + \text{(NH4)3Fe(CN)6}_{vol} = 0.2\,L$ equal parts A & B
Concentration of oxalate	$M_{\text{(NH4)3Fe(CN)6}} := \frac{\text{(NH4)3Fe(CN)6}_{mass}}{\text{(NH4)3Fe(CN)6}\cdot V_{total}} = 0.188\cdot M$
Concentration of ferricyanide	$M_{\text{Fe(C2O4)3\_3H2O}} := \frac{\text{Fe(C2O4)3\_3H2O}_{mass}}{\text{Fe(C2O4)3\_3H2O}\cdot V_{total}} = 0.234\cdot M$

Light absorbtion - Cyanotype

molar attenuation coefficient of photo sensitive Fe compound

$\varepsilon Fe := interp\left(cspline\left(Fe\lambda_{absorb}, \varepsilon FeIII\right), Fe\lambda_{absorb}, \varepsilon FeIII, \frac{\lambda_{spot}}{nm}\right)$

$\varepsilon Fe = 112.999 \cdot L\ mol^{-1} \cdot cm^{-1}$

Concentration of photoactive component

$C_{Fe} := M_{Fe(C2O4)3\_3H2O} = 0.234 \cdot M$

molar attenuation coefficient of inert filter substance, silver, potasium etc.

$\varepsilon m := interp\left(cspline\left(Ferri\lambda_{abs}, \varepsilon_{Ferri}\right), Ferri\lambda_{abs}, \varepsilon_{Ferri}, \frac{\lambda_{spot}}{nm}\right)$

$\varepsilon m = 972.602\ L \cdot mol^{-1} \cdot cm^{-1}$

Concentration of inert substance, calculated from stoicheiometry ratio 1:1

$C_m := C_{Fe} = 0.234 \cdot M$

Layer thickness for typical paper

$d := 0.024 \frac{L}{m^2} = 24 \cdot \mu m$

Beer-Lambert law: Optical Density

$D := \left(\varepsilon Fe \cdot C_{Fe} + \varepsilon m \cdot C_m\right) \cdot d = 0.609$

The fraction of incident light absorbed by the photoactive component only

$f := \frac{\left(1 - 10^{-D}\right) \cdot \varepsilon Fe \cdot C_{Fe} \cdot d}{D} = 7.846 \cdot \%$

molar coating weight

$W_{paper} := C_{Fe} \cdot d = 5.607 \times 10^{-3} \frac{mol}{m^2}$

Exposure times - Cyanotype

wavelength $\lambda_{spot} = 405 \cdot nm$

Pulse power $P = 450 \cdot mW$

Area of spot $A_{exp} = 111.724 \cdot \mu m^2$

Irradiance $I := \frac{P}{A_{exp}} = 4.028 \cdot \frac{mW}{\mu m^2}$

Quantum yield for frequency $\phi_{spot} := linterp\left(\lambda, \phi, \frac{\lambda_{spot}}{nm}\right) = 1.14$

Avagadros number $Av := 6.055 \cdot 10^{23} \cdot mol^{-1}$

Plancks constant $h := 6.626 \cdot 10^{-34} \cdot J \cdot s$

Speed of light $c = 2.998 \times 10^{8} \cdot m \cdot s^{-1}$

Number of moles of photo product $m_{product} := W_{paper} \cdot A_{exp} = 6.264 \times 10^{-13} mol$

exposure time $t := \frac{Av \cdot h \cdot c \cdot m_{product}}{I \cdot \phi_{spot} \cdot f \cdot \lambda_{spot} \cdot A_{exp}} = 4.622 \cdot \mu s$

Kalitype Calculations

Kallitype method uses;

silver nitrate - $AgNO3$
ferric oxalate / iron (III) oxalate hexahydrate - $Fe2(C2O4)3\text{-}6H2O$

to produce silver precipitate, that is then substituted for more noble platinum, paladium, gold or selenium

Molar mass oxalate $\quad Fe(C2O4)3\_6H2O := 483.84\,\frac{gm}{mol}$

Density oxalate $\quad \rho_{Fe(C2O4)3\_6H2O} := 1.78\,\frac{gm}{cm^3}$

mass oxalate $\quad Fe(C2O4)3\_6H2O_{mass} := 20gm$ $\quad$ 20% solution

solution volume $\quad Fe(C2O4)3\_6H2O_{vol} := 100mL$

Molar mass silver nitrate $\quad AgNO3 := 169.87\,\frac{gm}{mol}$

Density silver nitrate $\quad \rho_{AgNO3} := 4.35\,\frac{gm}{cm^3}$

mass silver $\quad AgNO3_{mass} := 10gm$ $\quad$ 10% solution

solution volume $\quad AgNO3_{vol} := 100mL$

Total volume combined $\quad V_{total} := Fe(C2O4)3\_6H2O_{vol} + AgNO3_{vol} = 0.2\,L$ $\quad$ equal parts A & B

Concentration of oxalate

$$M_{Fe(C2O4)3\_6H2O} := \frac{Fe(C2O4)3\_6H2O_{mass}}{Fe(C2O4)3\_6H2O \cdot V_{total}} = 0.207 \cdot M$$

Concentration of silver nitrate

$$M_{AgNO3} := \frac{AgNO3_{mass}}{AgNO3 \cdot V_{total}} = 0.294 \cdot M$$

Light absorbtion - Kalitype

molar attenuation coefficient of photo sensitive Fe compound

$$\varepsilon Fe := \mathrm{interp}\left(\mathrm{cspline}\left(Fe\lambda_{absorb}, \varepsilon FeIII\right), Fe\lambda_{absorb}, \varepsilon FeIII, \frac{\lambda_{spot}}{nm}\right)$$

$$\varepsilon Fe = 112.999\, L \cdot mol^{-1} \cdot cm^{-1}$$

Concentration of photoactive component

$$C_{Fe} := M_{Fe(C2O4)3\_6H2O} = 0.207 \cdot M$$

molar attenuation coefficient of inert filter substance, silver, potasium etc.

$$\varepsilon m := 0$$

$$\varepsilon m = 0 \cdot mol^{-1} \cdot cm^{-1}$$

Concentration of inert substance, calculated from stoicheiometry ratio to the trisoxalatoferrate(III)

$$C_m := C_{Fe} = 0.207 \cdot M$$

Layer thickness for typical paper

$$d = 24 \cdot \mu m$$

Beer-Lambert law: Optical Density

$$D := \left(\varepsilon Fe \cdot C_{Fe} + \varepsilon m \cdot C_m\right) \cdot d = 0.056$$

The fraction of incident light absorbed by the photoactive component only is a proportion given by

$$f := \frac{\left(1 - 10^{-D}\right) \cdot \varepsilon Fe \cdot C_{Fe} \cdot d}{D} = 12.108 \cdot \%$$

molar coating weight

$$W_{paper} := C_{Fe} \cdot d = 4.96 \times 10^{-3} \frac{mol}{m^2}$$

Exposure times - Kalitype

wavelength

$$\lambda_{spot} = 405 \cdot nm$$

Pulse power

$$P = 450 \cdot mW$$

Area of spot

$$A_{exp} = 111.724 \cdot \mu m^2$$

Irradiance

$$I = 4.028 \cdot \frac{mW}{\mu m^2}$$

Quantum yield for frequency

$$\phi_{spot} = 1.14$$

Avagadros number

$$Av = 6.055 \times 10^{23} \cdot mol^{-1}$$

Plancks constant

$$h = 0 \cdot J \cdot s$$

Speed of light

$$c = 2.998 \times 10^{8} \cdot m \cdot s^{-1}$$

Number of moles of photo product

$$m_{product} := W_{paper} \cdot A_{exp} = 5.542 \times 10^{-13}\, mol$$

exposure time

$$t := \frac{Av \cdot h \cdot c \cdot m_{product}}{I \cdot \phi_{spot} \cdot f \cdot \lambda_{spot} \cdot A_{exp}} = 2.65 \cdot \mu s$$