Absorption spectroscopy

Metal ions

Assays

Matrix solutions

Fundamentals of the extinction coefficient
The absorption cross section, σ_A

The absorption cross section has units of area (cm^2).
It gives a probability for absorption. We have discussed the probability in terms of the transition dipole moment. M_{12} and shape in terms of the Franck-Condon factor, FC.

$$\sigma_A(\omega) \propto |M_{12}|^2 FC(\omega)$$

The absorption cross section is proportional to the well known extinction coefficient.

$$\epsilon(\omega) = \frac{\sigma_A(\omega) N_A}{1000}$$

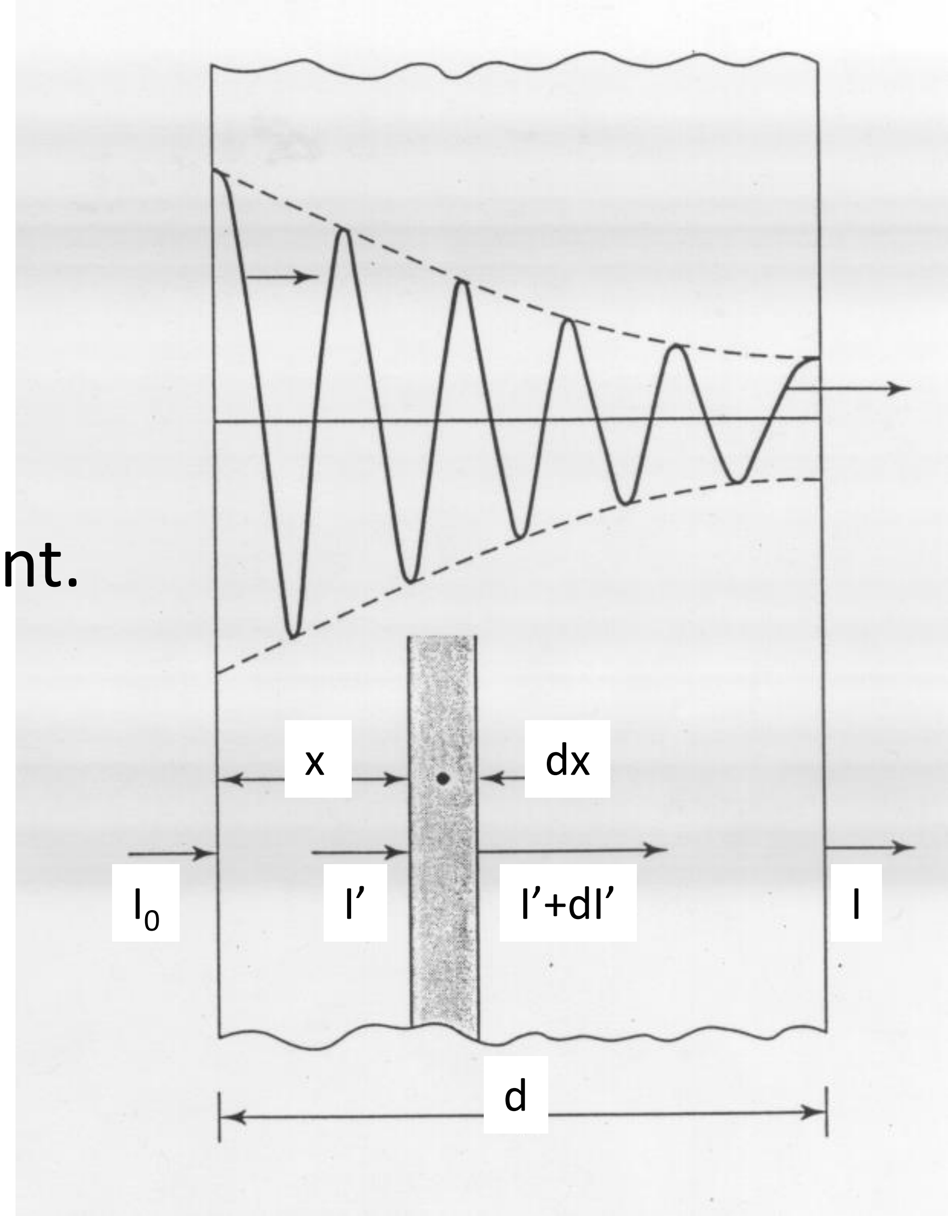
The extinction coefficient has units of $M^{-1}cm^{-1}$.

Beer-Lambert Law

$$I = I_0 10^{-A}$$

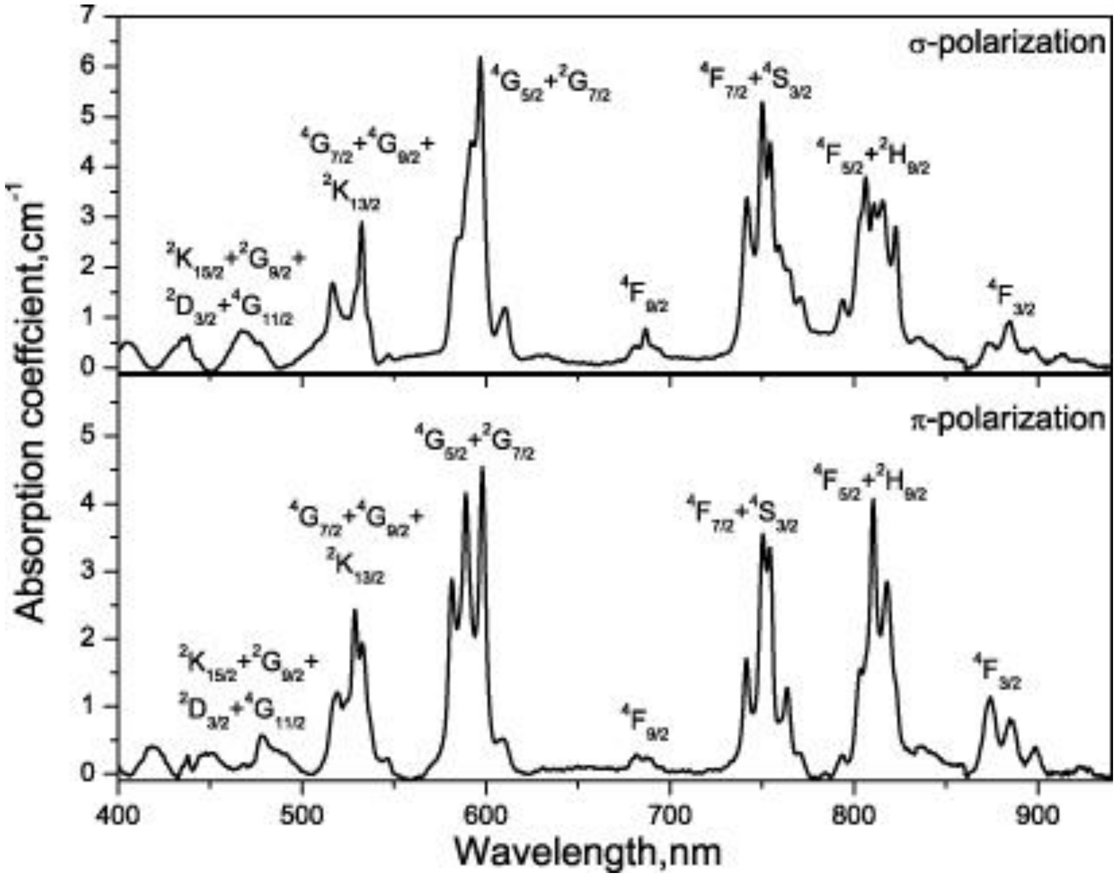
$$A = \epsilon(\lambda)cd$$

A is the absorbance.
$\varepsilon(\nu)$ is the extinction coefficient.
The unit of $\varepsilon(\nu)$ is $M^{-1}cm^{-1}$.
c is the concentration (M).
d is the pathlength (cm).
The exponential attenuation of the intensity is shown in the Figure.

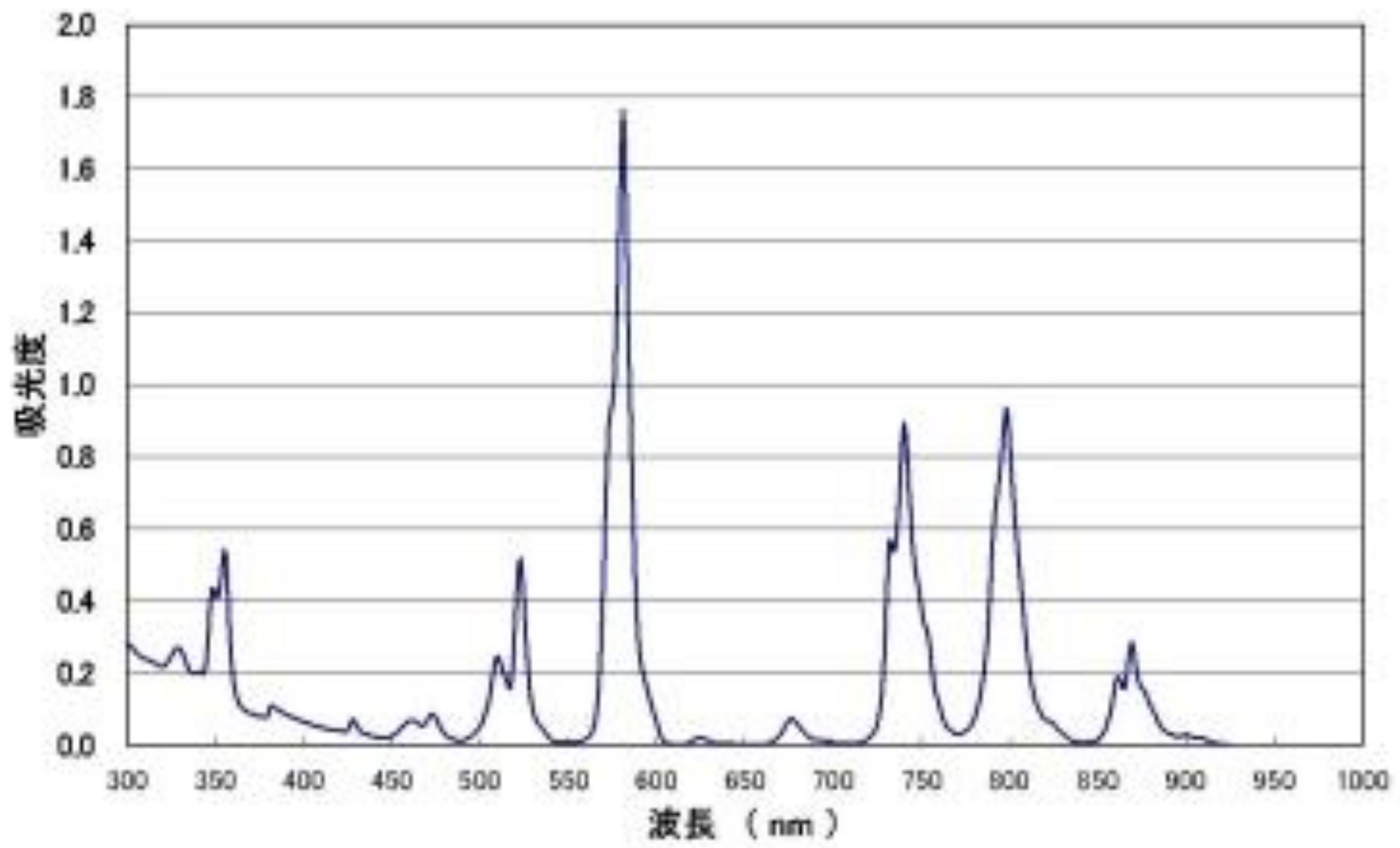


Neodymium spectroscopy: forbidden f-f transitions

The ground state electron configuration of Nd is $[Xe]4f^4 6s^2$. However, Nd(III) has a configuration $[Xe]4f^3$. Nd transitions observed in the absorption spectrum start from the $^4I_{9/2}$ ground state. Transitions to the following $^{2S+1}L_J$ levels can be observed: $^4F_{3/2}$, $^2H_{9/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^2H_{11/2}$, $^4G_{5/2}$, $^2G_{7/2}$, $^4G_{7/2}$, $^4K_{13/2}$, $^4G_{9/2}4$, $^2K_{15/2}$, $^4G_{11/2}$, $^2D_{3/2}$ and $^2G_{9/2}$. The spectrum shown is a high resolution spectrum of Nd-doped $LaTiO_3$.



Neodymium spectroscopy: expanded view



Copper sulfate spectroscopy: forbidden d-d transitions

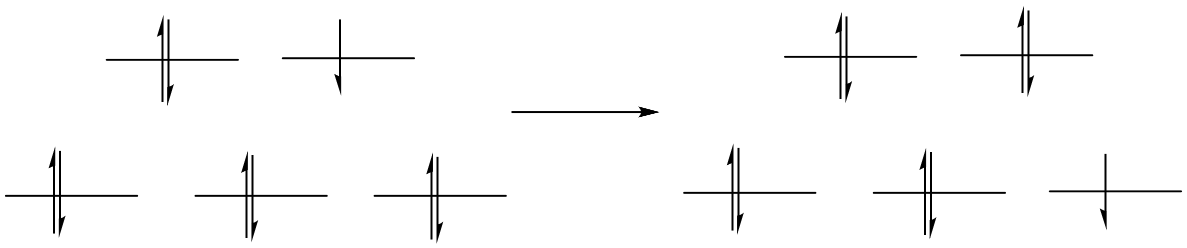
The ground state electron configuration of Cu is [Ar]$3d^{10}4s^1$. However, Cu(II) has a configuration [Ar]$3d^9$. In the hexahydrate there is an octahedral ligand field. It is an

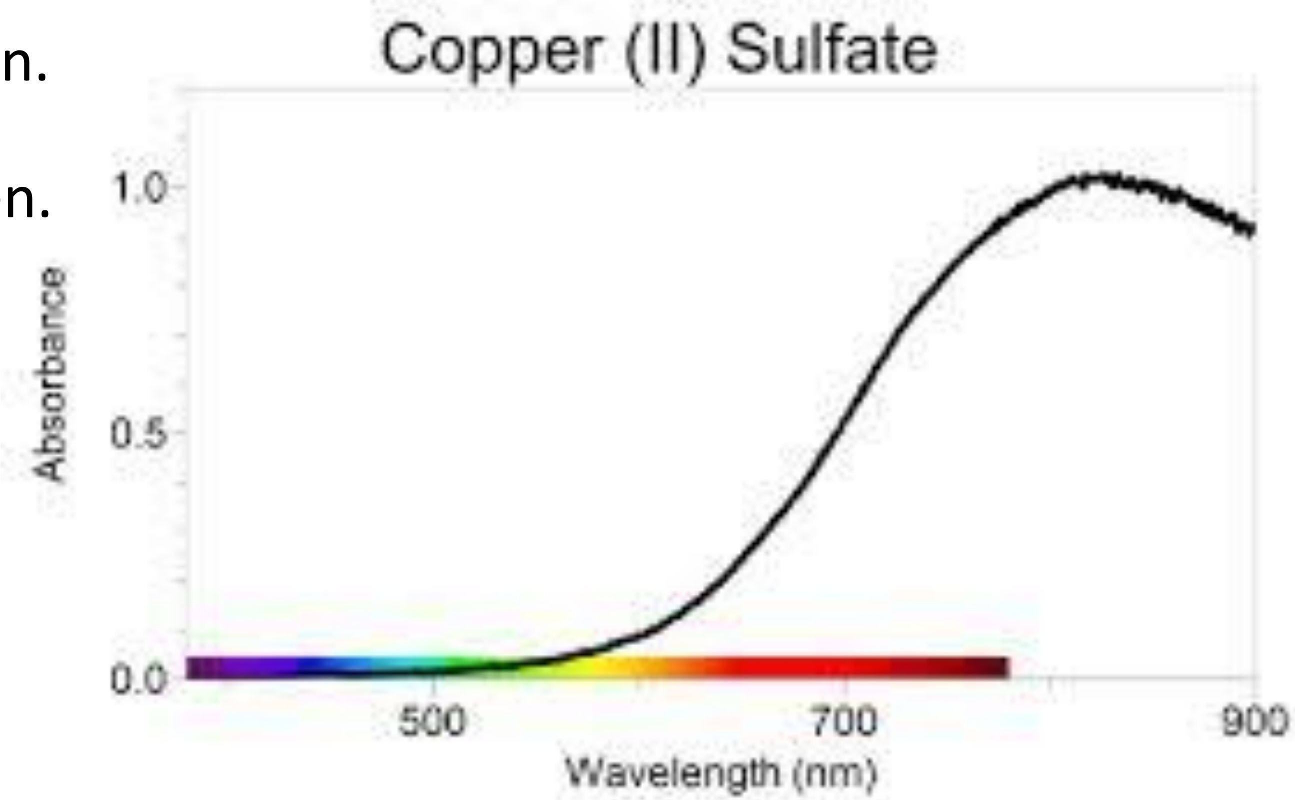
Unusual case because the water molecules all have the same Cu-O bond length.

There is no measurable Jahn-Teller distortion.

The electronic transition is LaPorte forbidden.

d-d transitions are broad.





Problem in linear analysis using analytical chemistry

A student determines absorbance of a solution known to contain 4 strongly absorbing dyes (labeled dye A, B, C and D) at four different wavelengths $\lambda = 495, 420, 470$ and 590 nm.
The extinction coefficients $\varepsilon_\lambda(\text{dye})$ for the 4 compounds at these 4 wavelengths are known (units lit/mol):

	A	B	C	D
ε_{395}	13500	2000	28000	7200
ε_{420}	180000	4500	14000	8000
ε_{470}	700	700	3000	32000
ε_{590}	8000	70000	400	1350

Problem in linear analysis using analytical chemistry

The absorbance values in a 1 cm pathlength are:

A_{395}	0.5
A_{420}	0.6
A_{470}	0.3
A_{590}	0.4

What are the four concentrations?

(*Hint*: Absorbance $A = \varepsilon_\lambda Lc$ is an additive quantity, so you can write out the problem as a set of linear equations. Then write this as a matrix formula and see if you can solve it by matrix algebra.

Method using matrix analysis

The equations have the form

$$A_1 = \varepsilon_{11}c_1 + \varepsilon_{12}c_2 + \varepsilon_{13}c_3 + \varepsilon_{14}c_4$$
$$A_2 = \varepsilon_{21}c_1 + \varepsilon_{22}c_2 + \varepsilon_{23}c_3 + \varepsilon_{24}c_4$$
$$A_3 = \varepsilon_{31}c_1 + \varepsilon_{32}c_2 + \varepsilon_{33}c_3 + \varepsilon_{34}c_4$$
$$A_4 = \varepsilon_{41}c_1 + \varepsilon_{42}c_2 + \varepsilon_{43}c_3 + \varepsilon_{44}c_4$$

We can write these compactly in matrix form as:

$$\boldsymbol{A} = \boldsymbol{\varepsilon c}$$

Where the knowns are the vector A of absorbances and the matrix of the extinction coefficients. We can solve for the concentrations using the matrix inverse:

$$\boldsymbol{\varepsilon}^{-1}\boldsymbol{A} = \boldsymbol{\varepsilon}^{-1}\boldsymbol{\varepsilon c}$$

Which tells us that

$$\boldsymbol{c} = \boldsymbol{\varepsilon}^{-1}\boldsymbol{A}$$

1350

A	B	C	D
13500	2000	28000	7200
180000	4500	14000	8000
700	700	3000	32000
8000	70000	400	1350

Sheet1

AVERAGE: 23334.375 COUNT: 16 SUM: 373350

{=MINVERSE(eps)}

A	B	C	D
13500	2000	28000	7200
180000	4500	14000	8000
700	700	3000	32000
8000	70000	400	1350

A	B	C	D
2.80055E-06	5.78133E-06	-8.03243E-07	-2.83609E-07
1.70701E-07	-6.47701E-07	-4.80915E-07	1.43273E-05
3.79525E-05	-2.77928E-06	-7.80958E-06	-8.27593E-07
3.50052E-06	1.4826E-07	3.20102E-05	-2.29619E-07

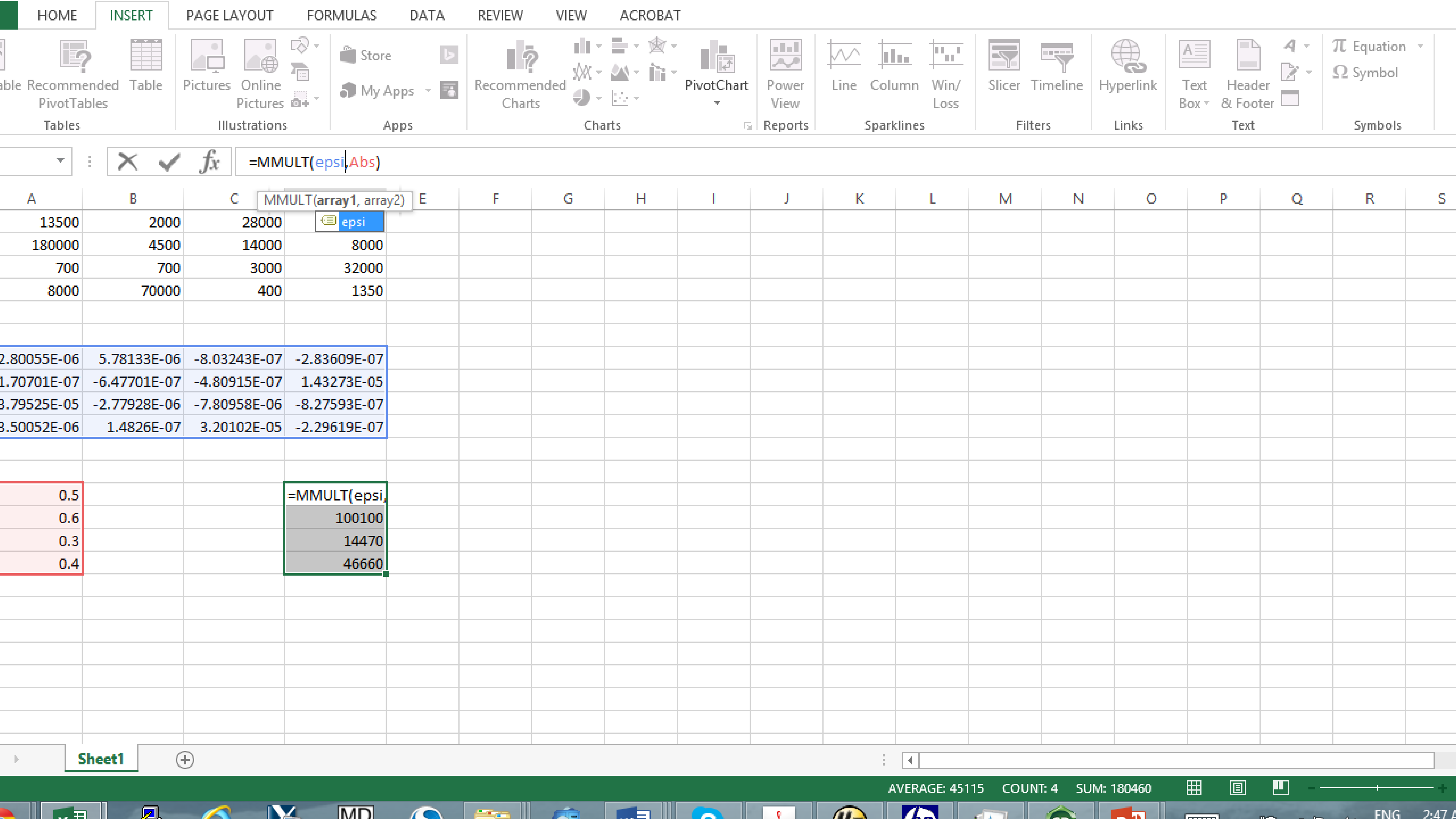
Sheet1

AVERAGE: 4.38923E-06 COUNT: 16 SUM: 7.02277E-05

A	B	C	D
13500	2000	28000	7200
180000	4500	14000	8000
700	700	3000	32000
8000	70000	400	1350
2.80055E-06	5.78133E-06	-8.03243E-07	-2.83609E-07
1.70701E-07	-6.47701E-07	-4.80915E-07	1.43273E-05
3.79525E-05	-2.77928E-06	-7.80958E-06	-8.27593E-07
3.50052E-06	1.4826E-07	3.20102E-05	-2.29619E-07
0.5			
0.6			
0.3			
0.4			

Sheet1

AVERAGE: 0.45 COUNT: 4 SUM: 1.8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Slicer
Timeline
Filters
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Header & Footer
Text
Equation
Symbol
Symbols
=MMULT(epsi,Abs)
MMULT(array1, array2)
A
B
C
E
F
G
H
I
J
K
L
M
N
O
P
Q
R
S
13500 2000 28000 epsi
180000 4500 14000 8000
700 700 3000 32000
8000 70000 400 1350
2.80055E-06 5.78133E-06 -8.03243E-07 -2.83609E-07
1.70701E-07 -6.47701E-07 -4.80915E-07 1.43273E-05
3.79525E-05 -2.77928E-06 -7.80958E-06 -8.27593E-07
3.50052E-06 1.4826E-07 3.20102E-05 -2.29619E-07
0.5 =MMULT(epsi,
0.6 100100
0.3 14470
0.4 46660
Sheet1
AVERAGE: 45115
COUNT: 4
SUM: 180460
ENG

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A	B	C	D
13500	2000	28000	7200
180000	4500	14000	8000
700	700	3000	32000
8000	70000	400	1350
2.80055E-06	5.78133E-06	-8.03243E-07	-2.83609E-07
1.70701E-07	-6.47701E-07	-4.80915E-07	1.43273E-05
3.79525E-05	-2.77928E-06	-7.80958E-06	-8.27593E-07
3.50052E-06	1.4826E-07	3.20102E-05	-2.29619E-07
0.5			1.7141E-06
0.6			5.28337E-06
0.3			1.46348E-05
0.4			7.84992E-06

Sheet1