UV-Vis Absorption Spectra

ELECTRONIC EXCITED STATES

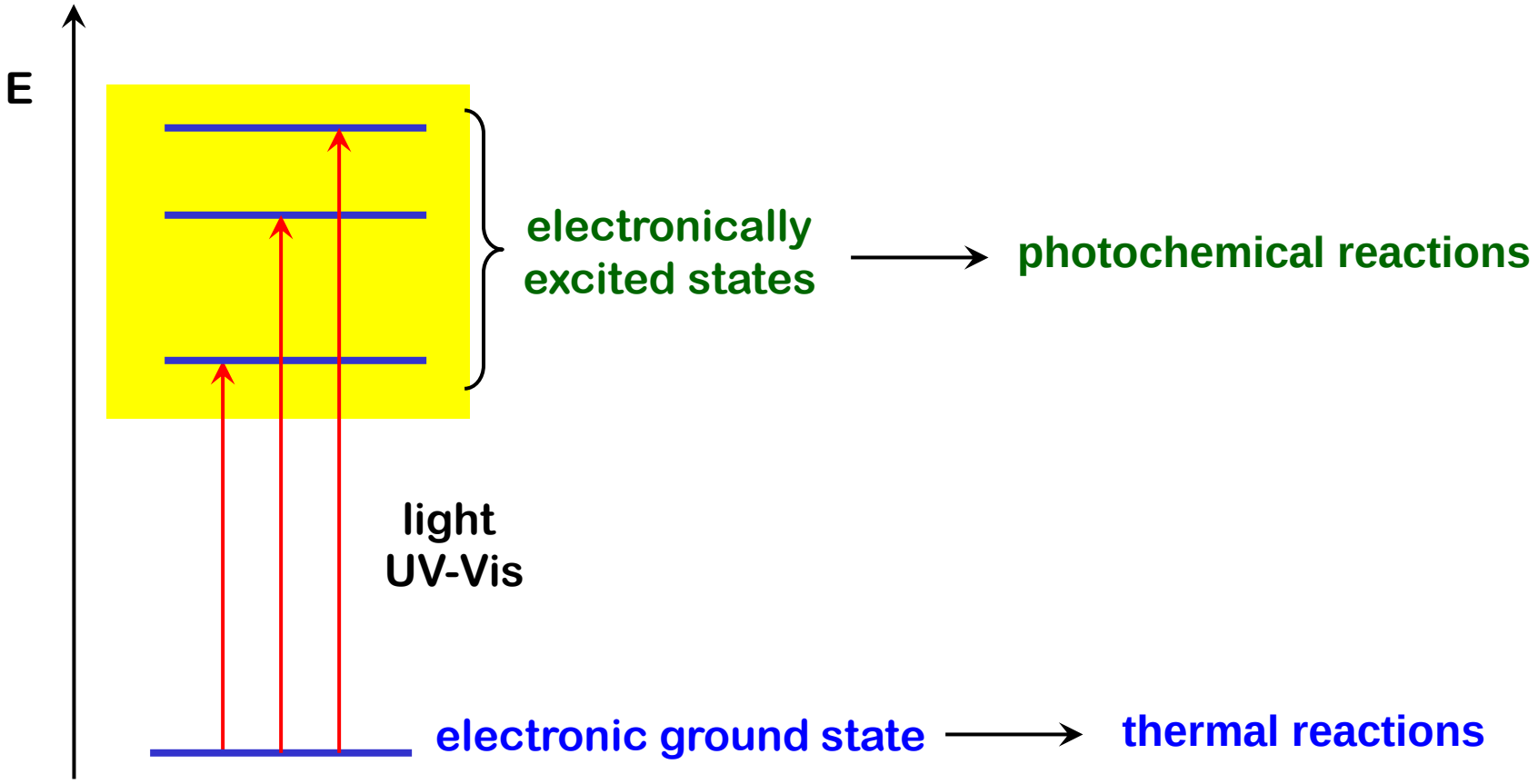
photon of
suitable energy

$A + h\nu \longrightarrow A^*$

ground state

electronically excited state

The excited state is a **NEW CHEMICAL SPECIES** with its own chemical and physical properties



Radiative transitions

Absorption

$$\Psi_i + h\nu \rightarrow \Psi_f$$

necessary but not sufficient condition:

$$h\nu = E_f - E_i = \Delta E$$

$$P_{abs} \propto (TM)^2$$

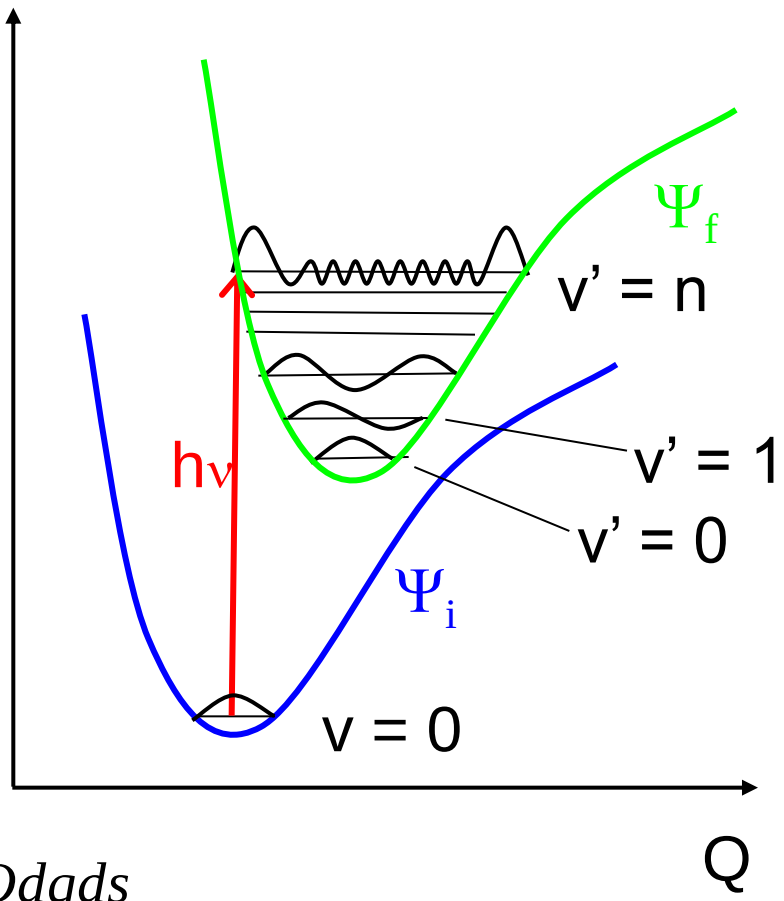
transition moment

absorption probability

$$TM = \int \Psi_i \, \mu \Psi_f \, d\tau$$ ***μ = electric dipole moment***

$$\Psi(Q,q,s) = \Lambda(Q)\Theta(q)S(s)$$

$$TM = \int \Psi_i \, \mu \Psi_f \, d\tau = \int (\Lambda_i \Theta_i S_i) \mu (\Lambda_f \Theta_f S_f) dQ dq ds$$



Franck-Condon factor

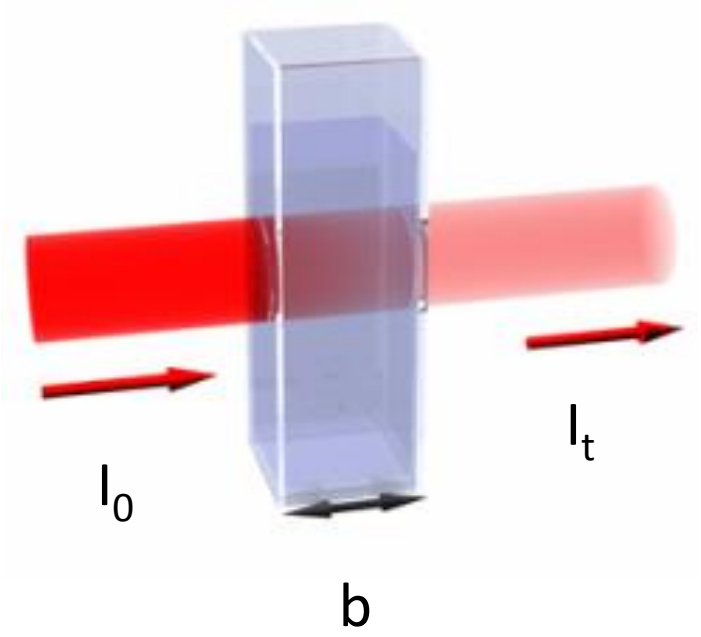
$$TM = \int \Lambda_i \Lambda_f dQ \int \Theta_i \mu \Theta_f dq \int S_i S_f ds$$

$\int \Lambda_i \Lambda_f dQ$ is large only for v=0 and v' = n

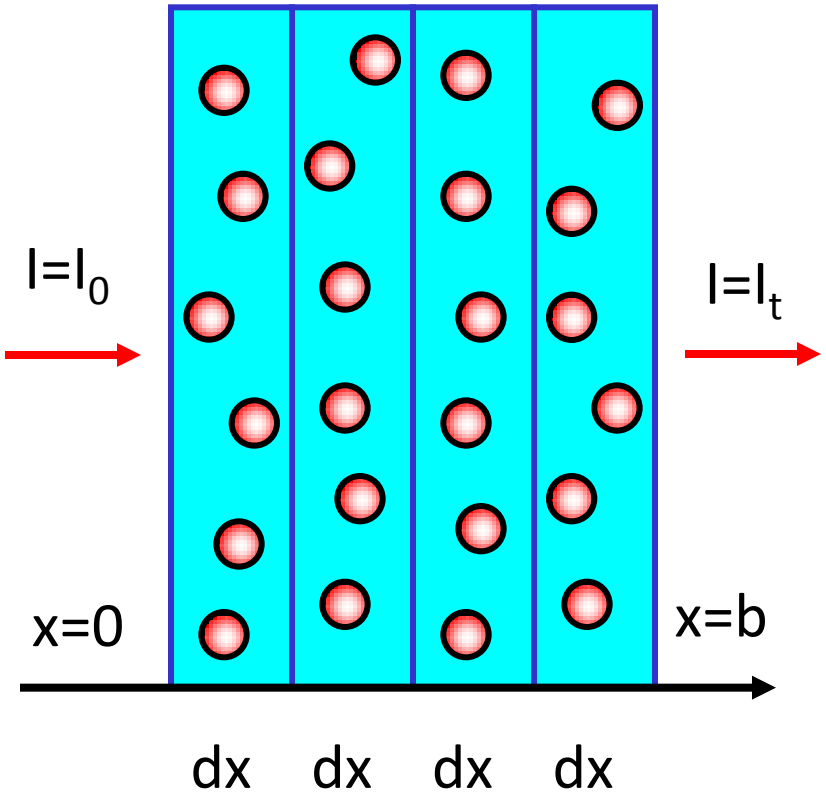
Legge di Lambert-Beer

Light intensity decrease inside the sample from I_0 to I_t

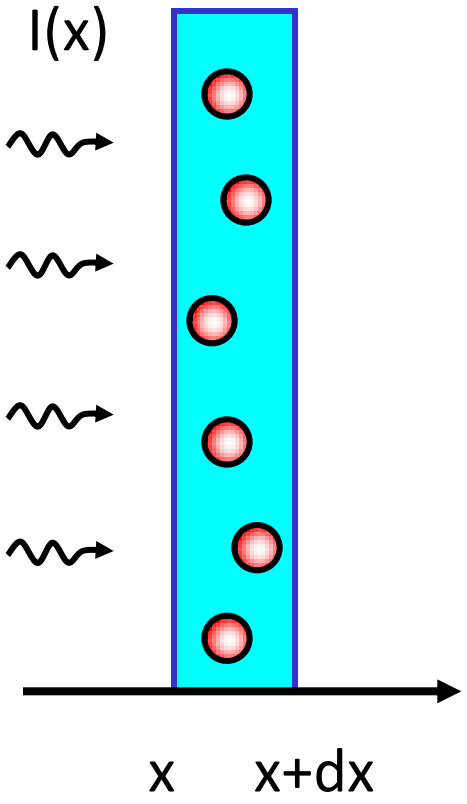
Molar concentration= c



I(x)=????



Lambert-Beer low



Molecule-photon “collision”

The number of adsorbed photons (**-dI**) is proportional to the number of incident photons (**I**) and to the number of molecule for surface unit (**c dx**)

Considering a very thin layer of solution dx
I(x) can be considered do be constant

Lambert-Beer low

Introducing the molar absorption coefficient ε

$$dI \propto -I \cdot c \cdot dx$$

$$\frac{1}{I} dI \propto -c \cdot dx \qquad \int_{I_o}^{I_t} \frac{1}{I} dI \propto -\int_{0}^{b} c \cdot dx$$

$$A = \log \frac{I_0}{I_t} = \varepsilon \cdot c \cdot b$$

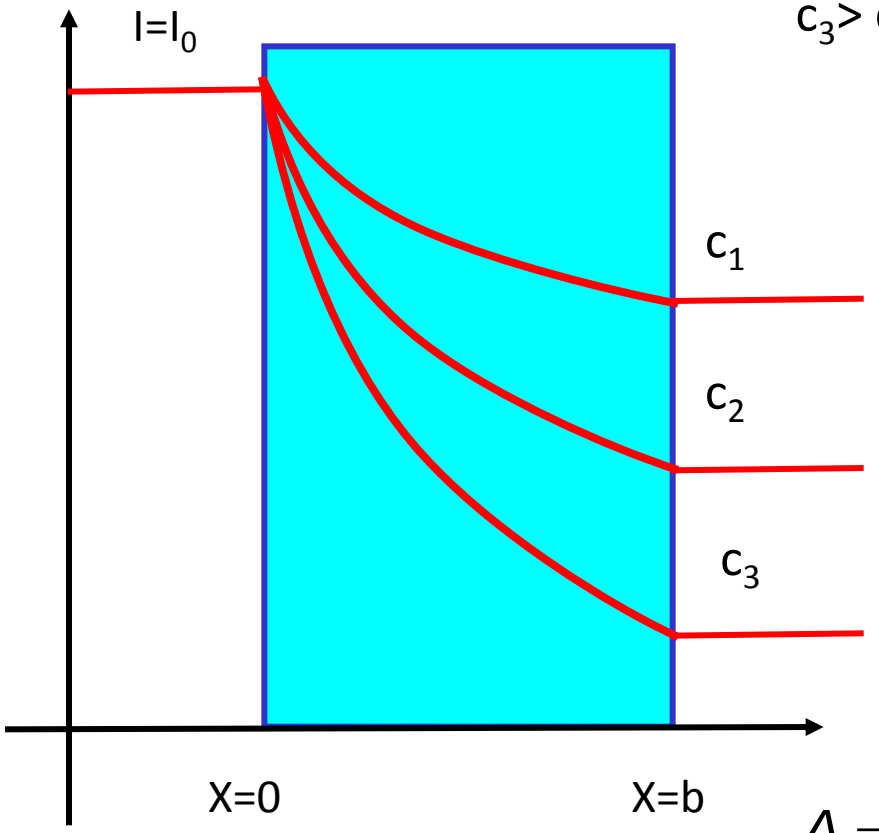
log is decimal logarithm!

$$I_t = I_0 \cdot 10^{-A} = I_0 \cdot 10^{-\varepsilon \cdot c \cdot b}$$

$$I(x) = I_0 \cdot 10^{-\varepsilon \cdot c \cdot x}$$

Lambert-Beer low

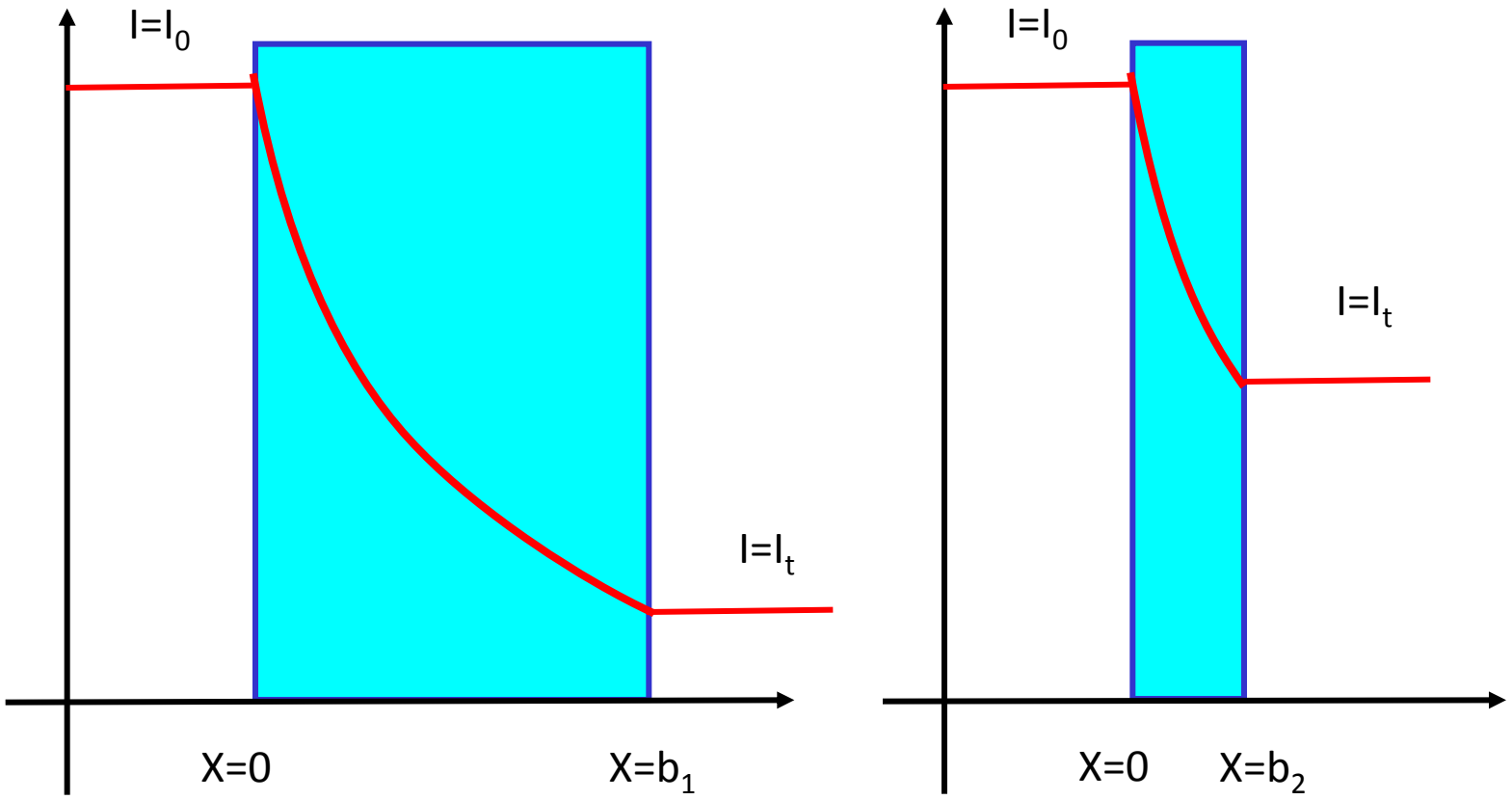
Effect of concentration



$$A = \log \frac{I_0}{I_t} = \varepsilon \cdot c \cdot b$$

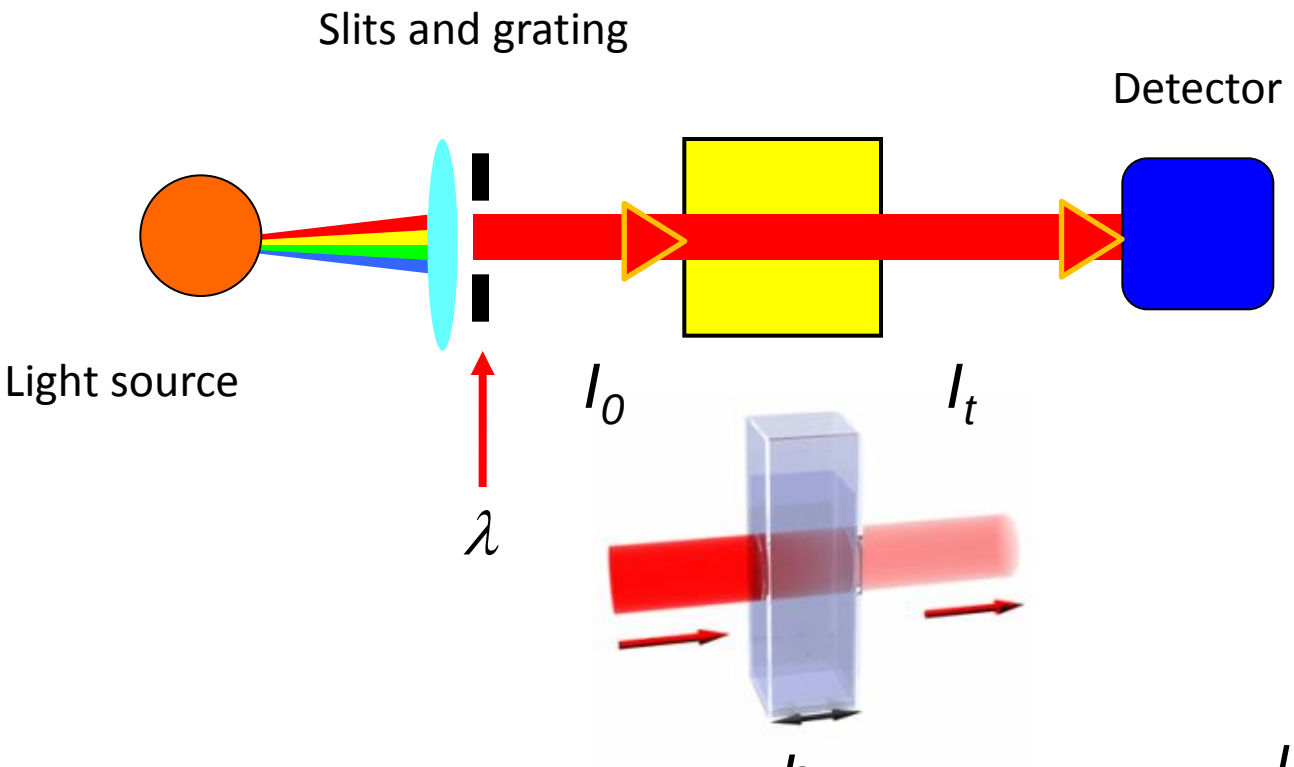
Lambert-Beer low

Effect of the optical path



SPECTROPHOTOMETER: SINGLE BEAM

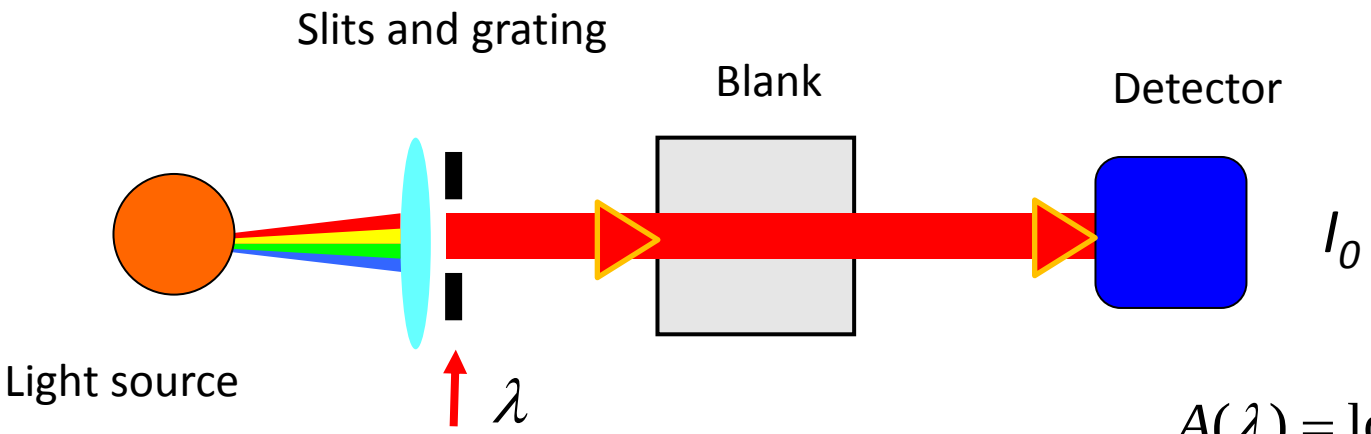
(UV-VIS ABSORPTION SPECTRA)



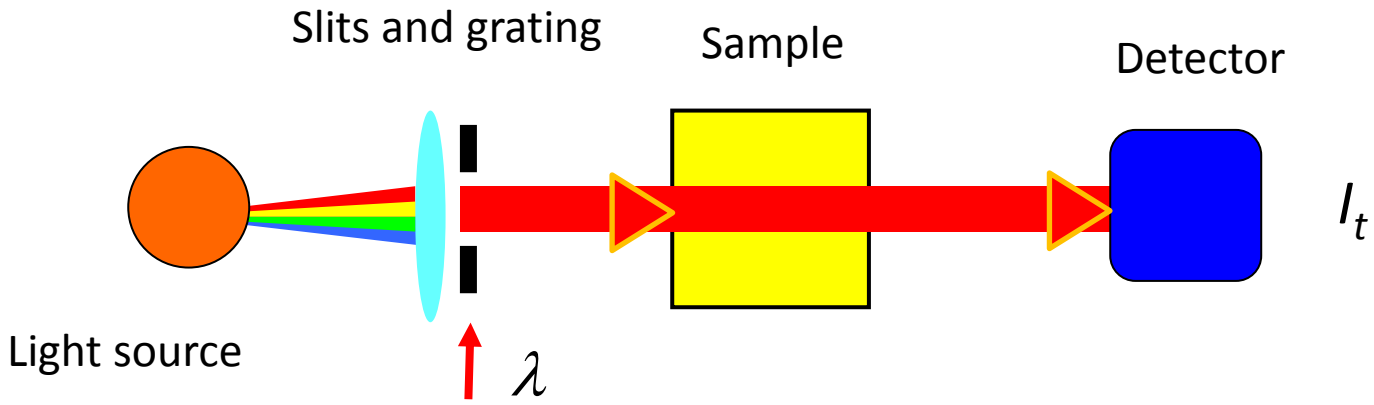
$$A(\lambda) = \log \frac{I_0(\lambda)}{I_t(\lambda)}$$

SPECTROPHOTOMETER: SINGLE BEAM

I_0 and I_t are measured at different times

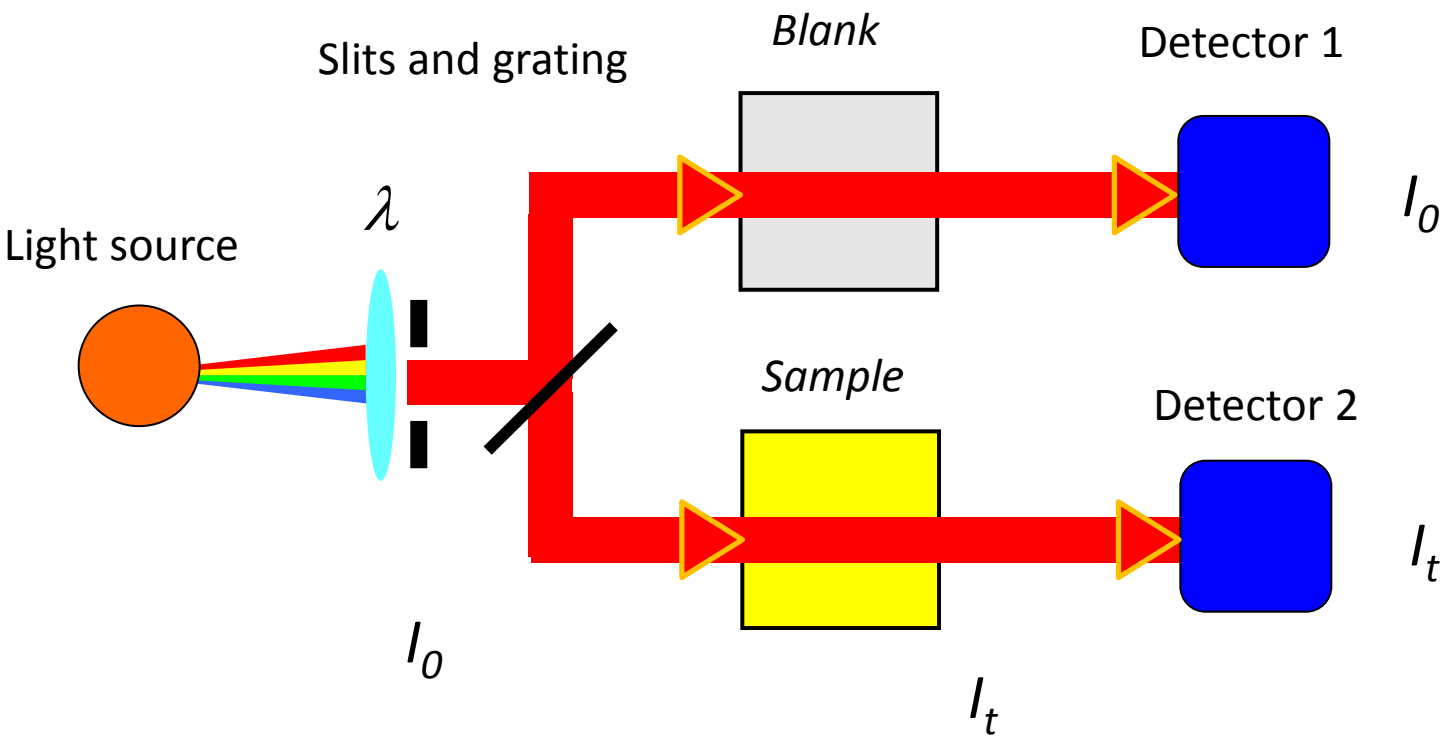


$$A(\lambda) = \log \frac{I_0(\lambda)}{I_t(\lambda)}$$



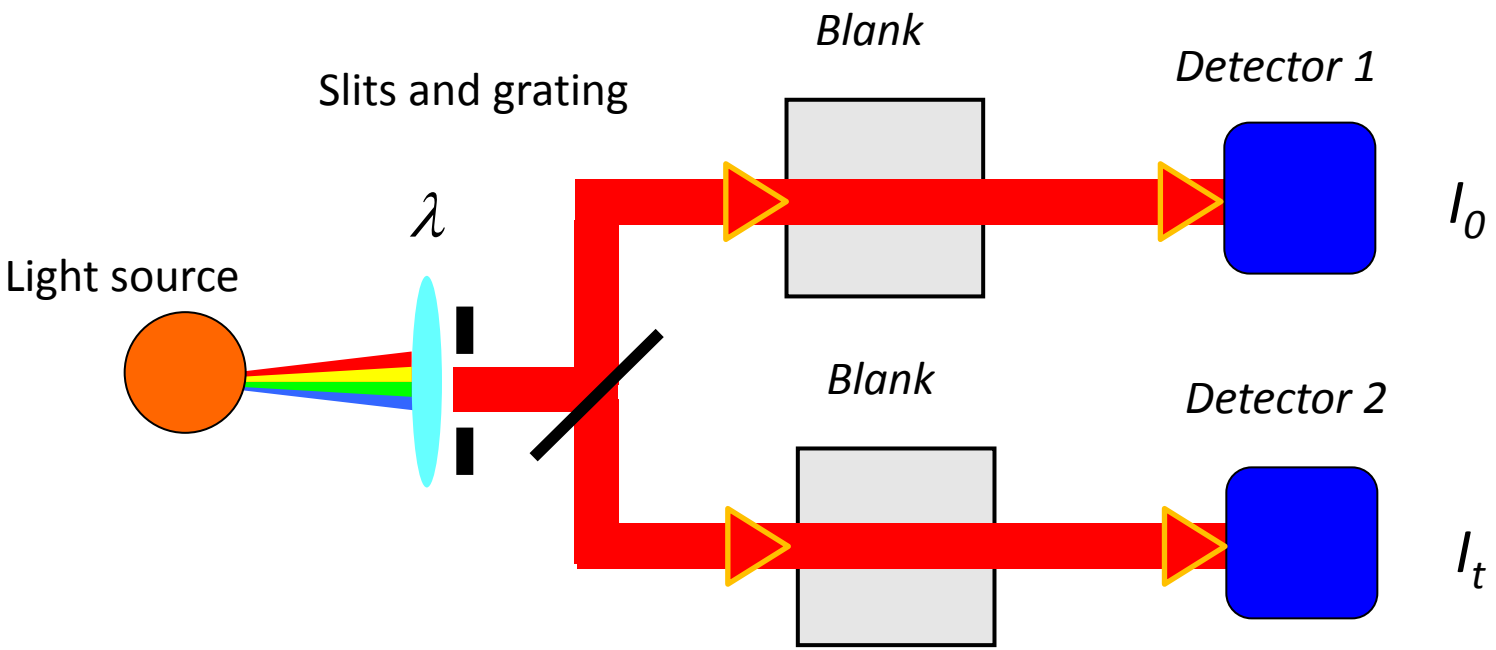
SPECTROPHOTOMETER: DOUBLE BEAM

I_0 and I_t are measured simultaneously



$$A(\lambda) = \log \frac{I_0(\lambda)}{I_t(\lambda)}$$

BASELINE (ZERO)



-The absorption spectrum is measured blank against blank or air against air
-The spectrum obtained is automatically subtracted from the new spectra

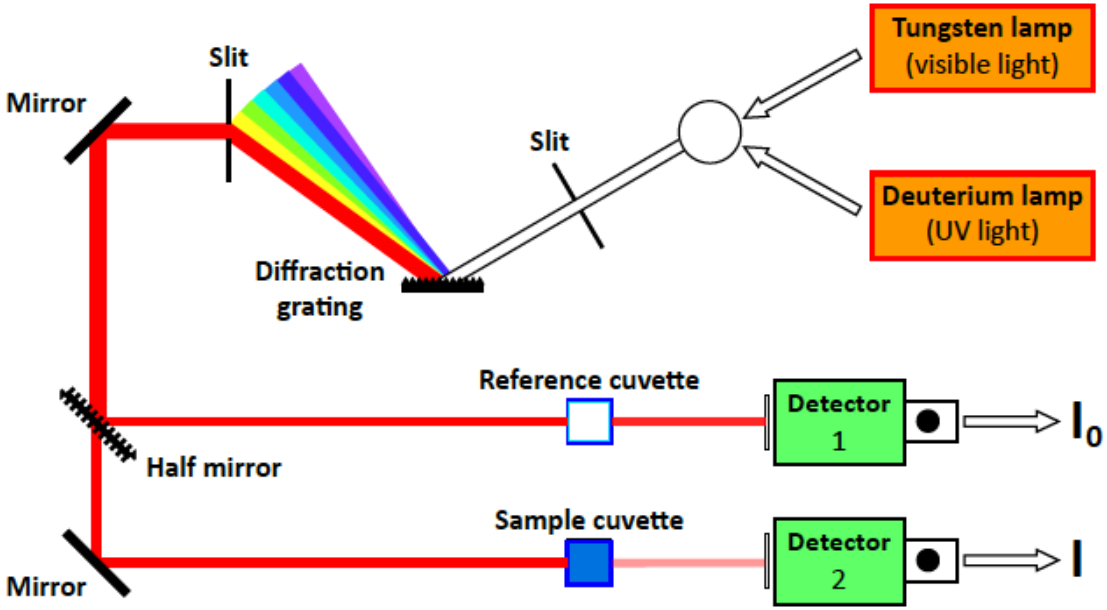
What A values can be measured?

Maximum value: *the instrument measures the current of each detector (1 and 2). This current is greater than zero even if the sample completely absorbs the incident light (dark current)*

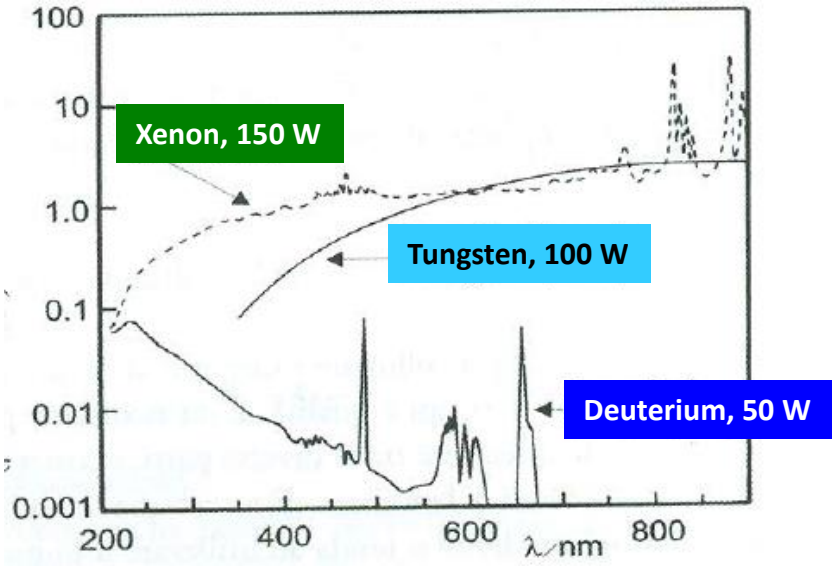
$$A(\lambda) = \log \frac{I_0(\lambda)}{I_t(\lambda)} \qquad A(\lambda) = \log \frac{i_1 + i_{1,buio}}{i_2 + i_{2,buio}} \qquad A(\lambda) = \log \frac{i_1 + i_{1,buio}}{i_{2,buio}}$$

Minimum value: *the stability of the zero line is not absolute and the variation represents the minimum limit for measurement (typically 0.001, in very well controlled conditions).*

LIGHT SOURCES

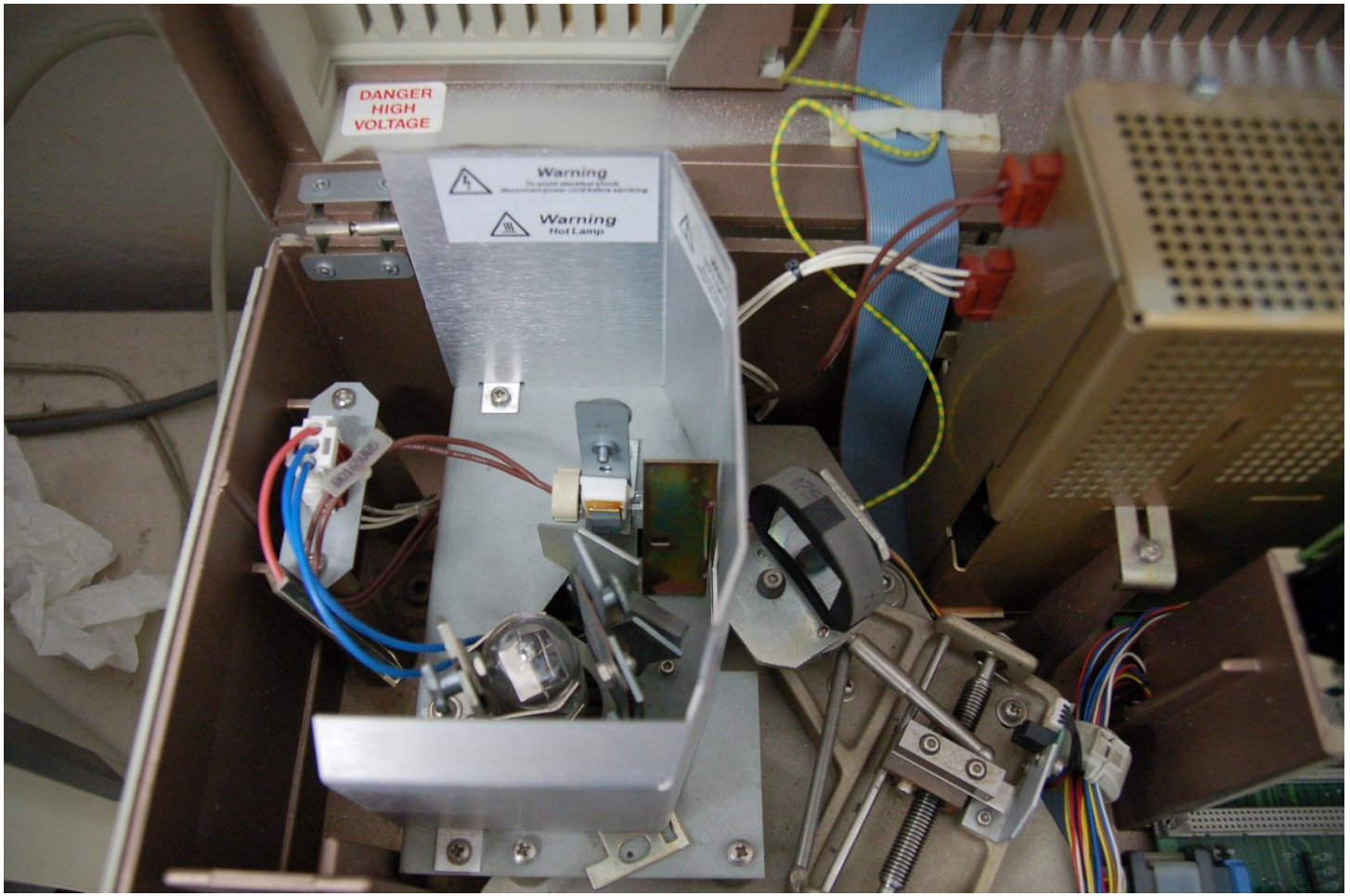


LIGHT SOURCES

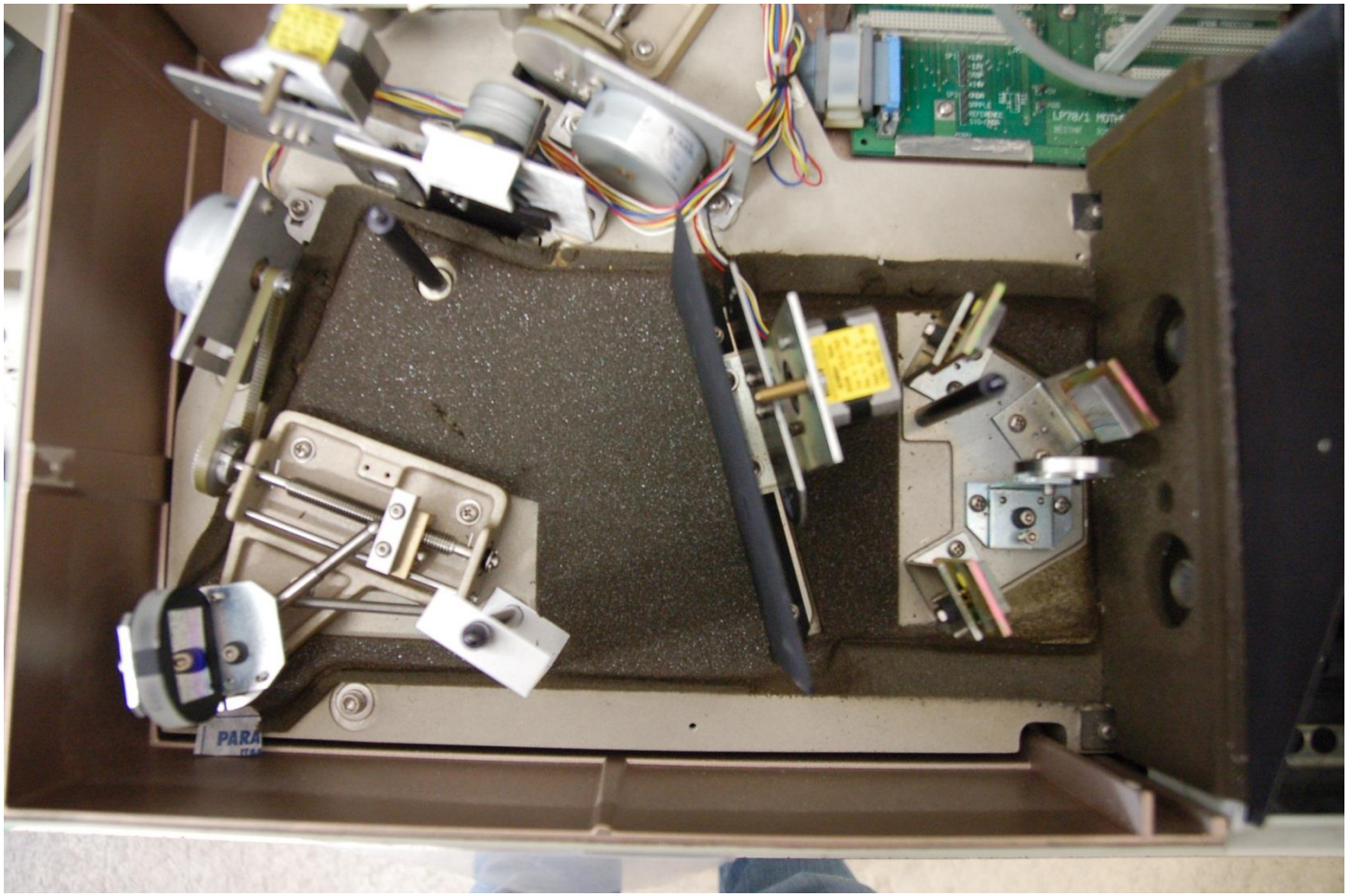


PERKIN ELMER Spectrophotometer

Lamps



Grating and beam splitter



Sample holder and detector

Parameters to set

Spectral range: λ_{max}, λ_{min} in nm

Choise is based on the properties of the chromophore and the solvent

Scan speed: in nm /min

Increasing the speed worsens the resolution of the spectrum
Increase the noise
In the same spectral range decreases the acquisition time

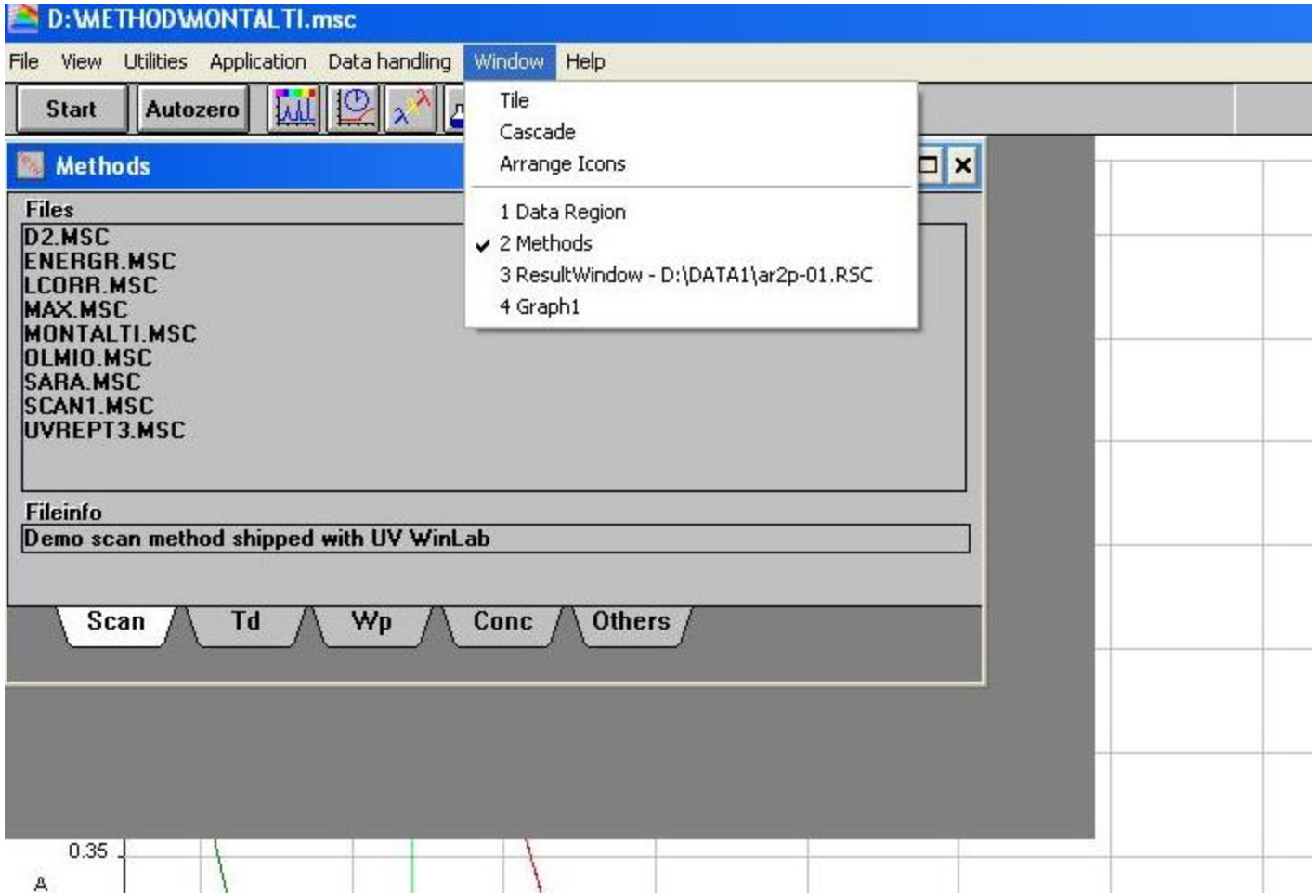
Interval between successive points: in nm

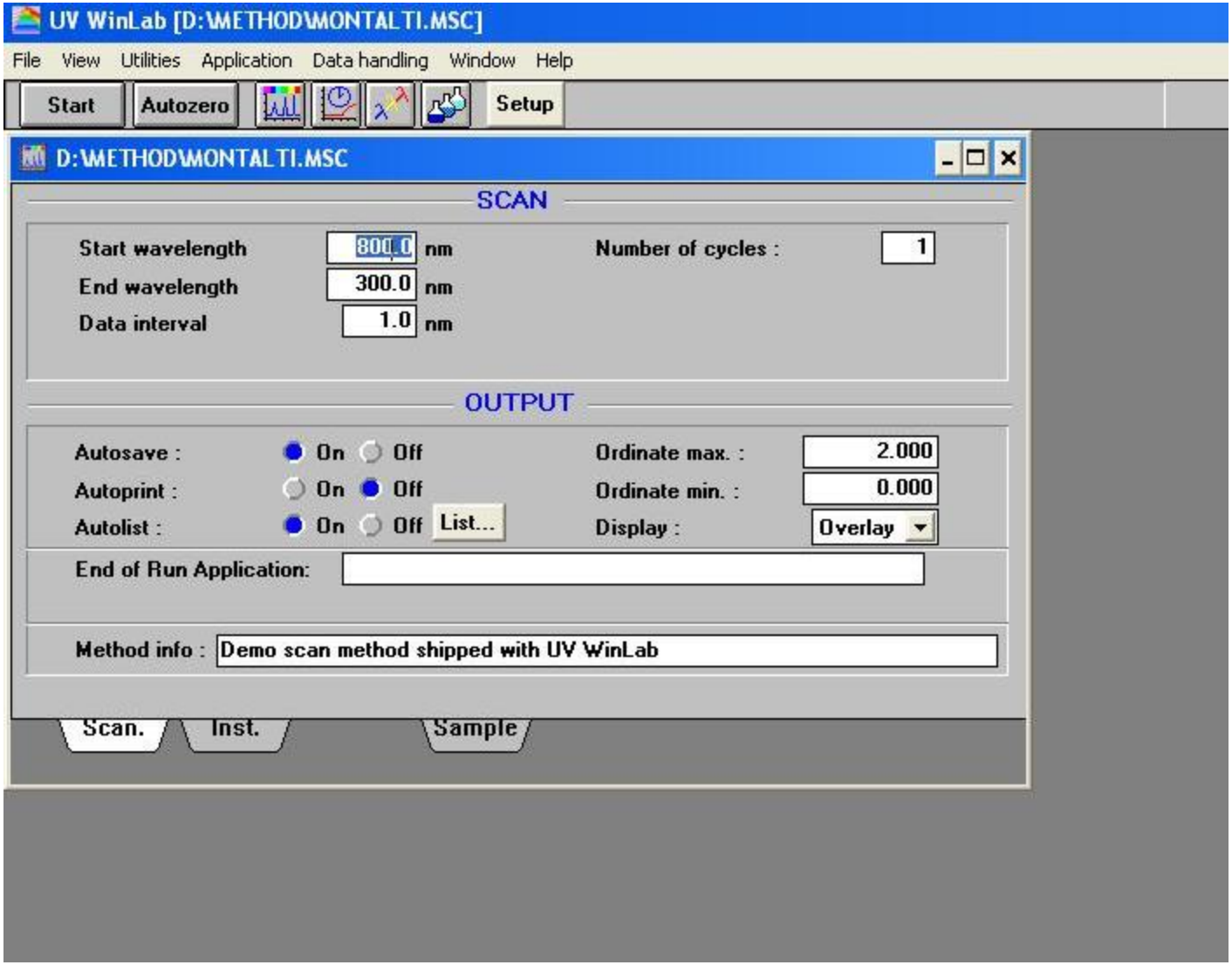
Increasing the range decreases the resolution

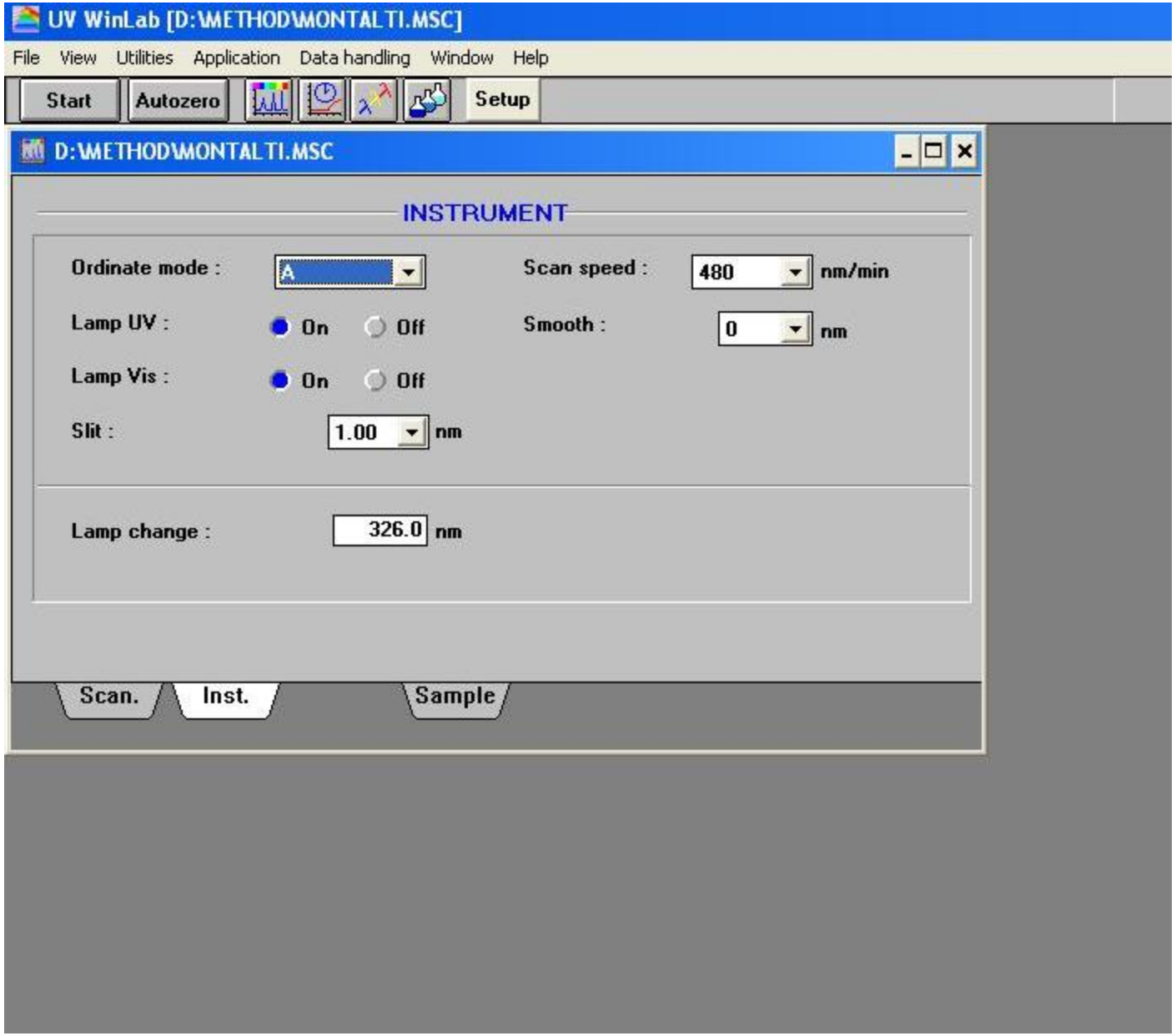
Slit: in nm

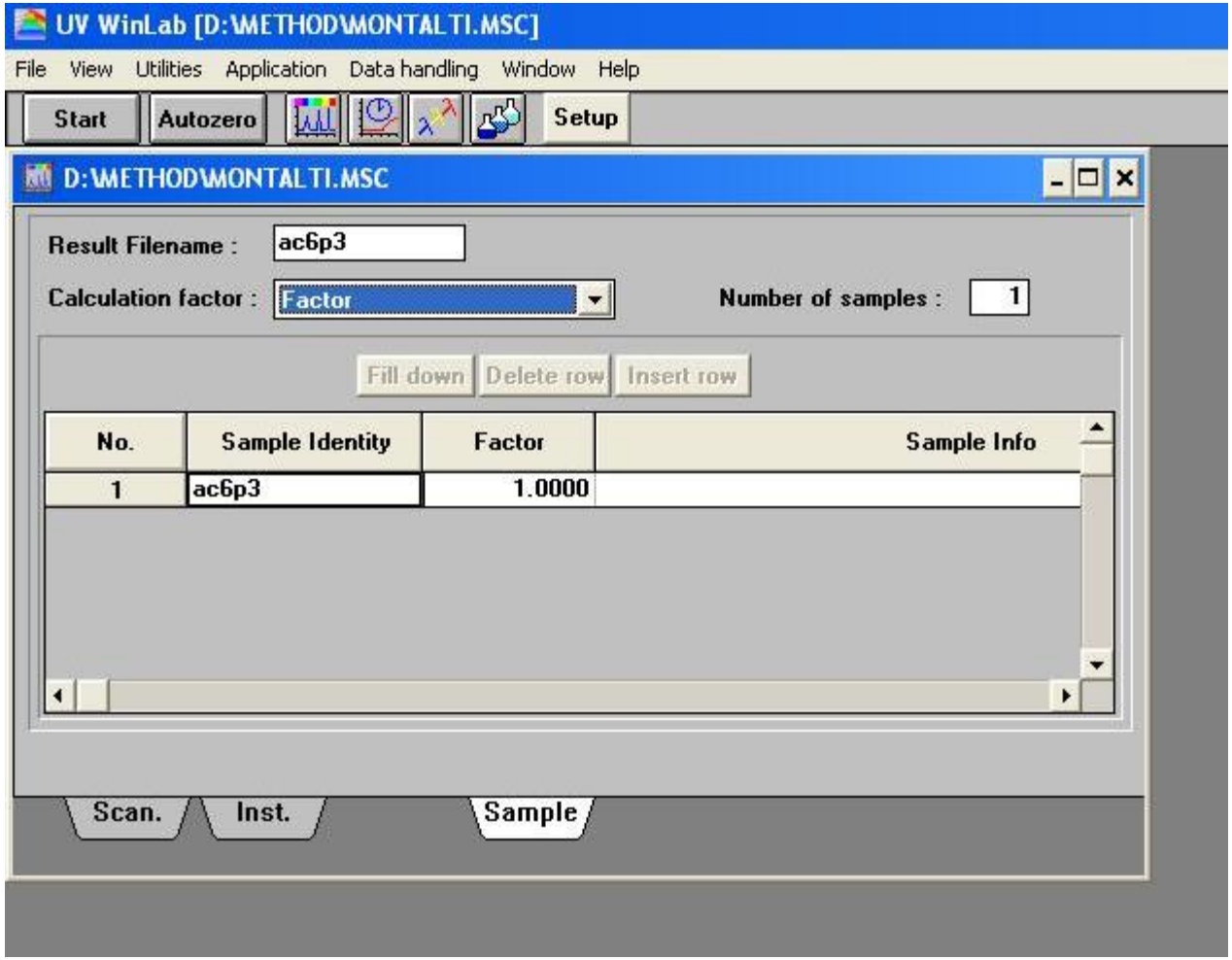
It is expressed as a passband
Increasing the slit decreases the resolution

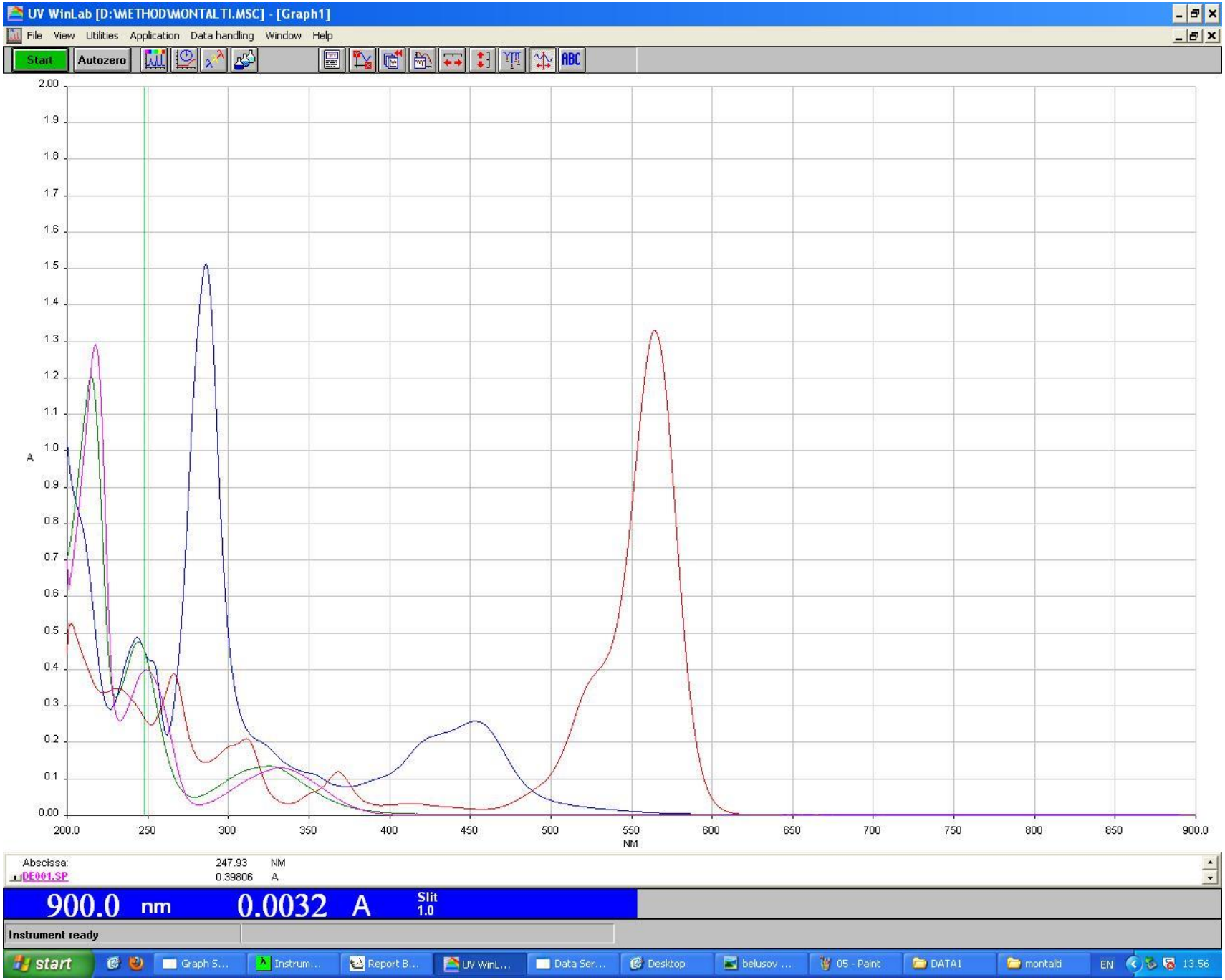
SOFTWARE: UVWINLAB




UV WinLab [D:\METHOD\MONTALTI.MSC]
File View Utilities Application Data handling Window Help
Start
Autozero
Setup
D:\METHOD\MONTALTI.MSC
SCAN
Start wavelength
800.0
nm
End wavelength
300.0
nm
Data interval
1.0
nm
Number of cycles :
1
OUTPUT
Autosave :
On
Off
Autoprint :
On
Off
Autolist :
On
Off
List...
Ordinate max. :
2.000
Ordinate min. :
0.000
Display :
Overlay
End of Run Application:
Method info :
Demo scan method shipped with UV WinLab
Scan.
Inst.
Sample


UV WinLab [D:\METHOD\MONTALTI.MSC]
File View Utilities Application Data handling Window Help
Start
Autozero
Setup
D:\METHOD\MONTALTI.MSC
INSTRUMENT
Ordinate mode :
A
Scan speed :
480
nm/min
Lamp UV :
On
Off
Smooth :
0
nm
Lamp Vis :
On
Off
Slit :
1.00
nm
Lamp change :
326.0
nm
Scan.
Inst.
Sample


UV WinLab [D:\METHOD\MONTALTI.MSC]
File View Utilities Application Data handling Window Help
Start
Autozero
Setup
D:\METHOD\MONTALTI.MSC
Result Filename :
ac6p3
Calculation factor :
Factor
Number of samples :
1
Fill down
Delete row
Insert row
No.
Sample Identity
Factor
Sample Info
1
ac6p3
1.0000
Scan.
Inst.
Sample


UV WinLab [D:\METHOD\MONTALTI.MSC] - [Graph1]
File View Utilities Application Data handling Window Help
Start
Autozero
ABC
2.00
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
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0.4
0.3
0.2
0.1
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A
200.0
250
300
350
400
450
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750
800
850
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NM
Abscissa: 247.93 NM
DE001.SP 0.39806 A
900.0 nm 0.0032 A Slit 1.0
Instrument ready
start
Graph S...
Instrum...
Report B...
UV WinL...
Data Ser...
Desktop
belusov ...
05 - Paint
DATA1
montalti
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13.56