Soil Spectroscopy: Principle and Applications



Prof. Eyal Ben Dor Department of Geography and Human Environment

Brno Czech Republic, June 25-26



INVESTMENTS IN EDUCATION DEVELOPMENT

Soil Spectroscopy

Lesson 2









Expert Working-Groups / Hyperspectral Applicatio

Description	Meetings	Documents	Mailing
<u>Description:</u> Hyperspectra	I Applications for	or Soil	
HYRESSA (the HYRESS	Contract Numbe A website.	r 026194), a Sp	ecific Sup
<u>Coordinator o</u> Ben dor Eyal	f the Hyperspect	ral Applications f	or Soil working o

If you are interested in this working group, please enter your login/password or subscribe.

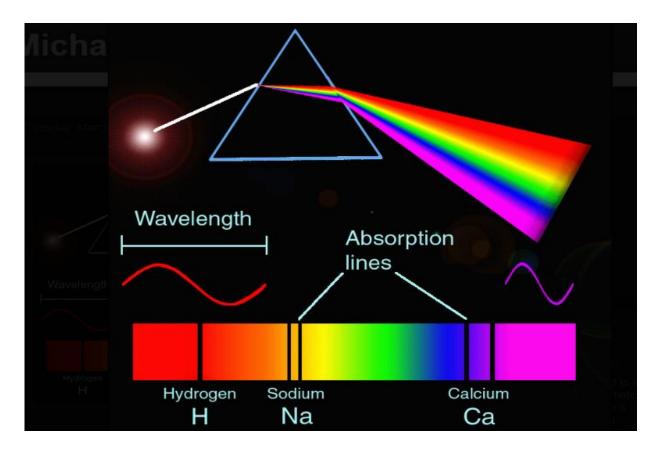
A ~		
Working groups designation	Coordinator	
Active remote sensing	Jacques Pelon	
Cloud Microphysics	Manfred Wendisch	
Gas phase chemistry	Jim Mcguaid	
Hyperspectral Applications for Soil	Eyal Ben dor	
Hyperspectral Applications for Vegetation	Michael Schaepman	
Hyperspectral Applications for Water	Steve Groom	
Imaging remote sensing	Jose-antonio Gomez-sanchez	
In-Situ Aerosols	Paola Formenti	
Polar Research	Tom Lachlan-cope	
Radiation	Thomas Ruhtz	
Stratospheric Measurements	Fred Stroh	
Thermodynamics	Martin Zoger	
Turbulence	Marco Esposito	

253 members



Spectroscopy

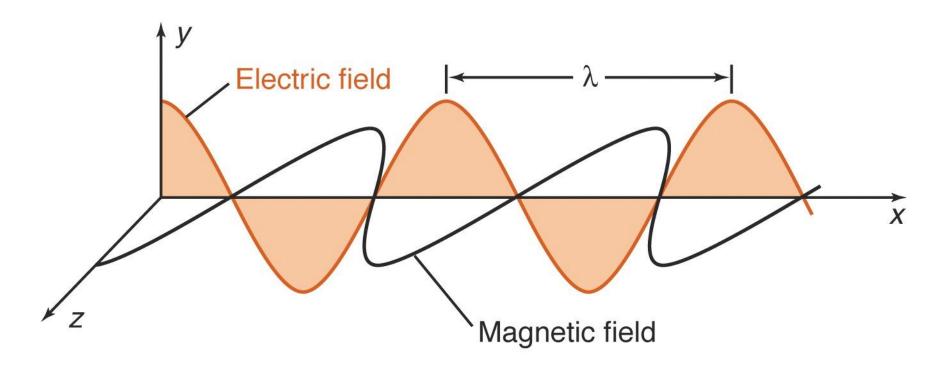
The science of tracking after the EM interaction with matter





Properties of Electromagnetic Radiation

"Plane-polarized electromagnetic radiation of wavelength λ , propagating along the x axis. The electric field of the plane-polarized light is confined to a single plane. Ordinary, unpolarized light has electric field components in all planes."







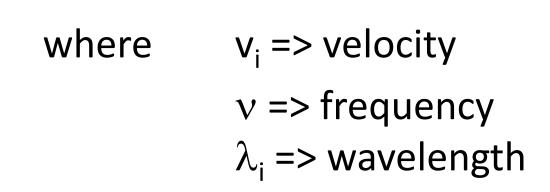
Properties of Light

Electromagnetic Radiation

- energy radiated in the form of a WAVE caused by an electric field interacting with a magnetic field
- result of the acceleration of a charged particle
- does not require a material medium and can travel through a vacuum



Properties of Electromagnetic Radiation





 $v_i = v \lambda_i$

7

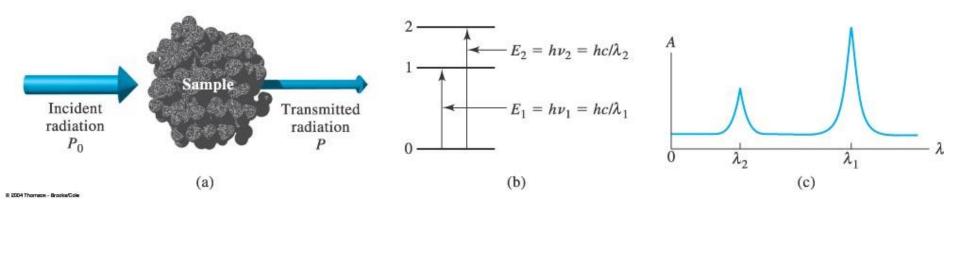
Properties of Electromagnetic Radiation

in vacuum, velocity is independent of frequency, maximum value

$$c = v\lambda = 2.998 \times 10^8 \text{ m/s}$$



Spectrum: A plot of the interaction of EM with matter



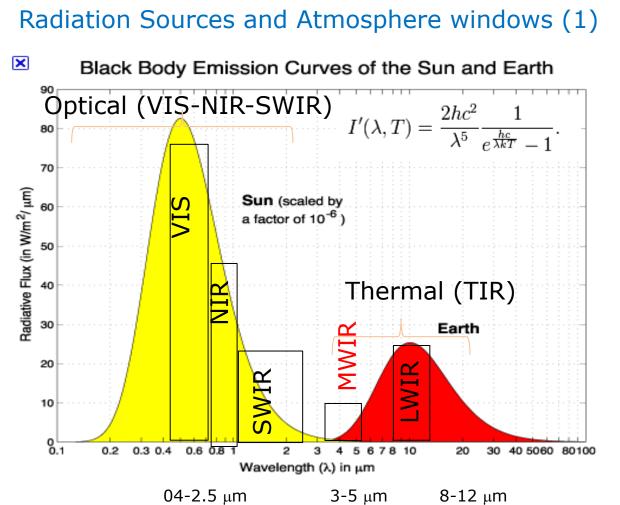
Interaction

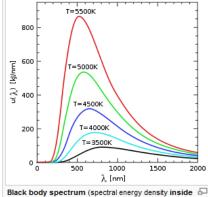
Theory

Spectrum



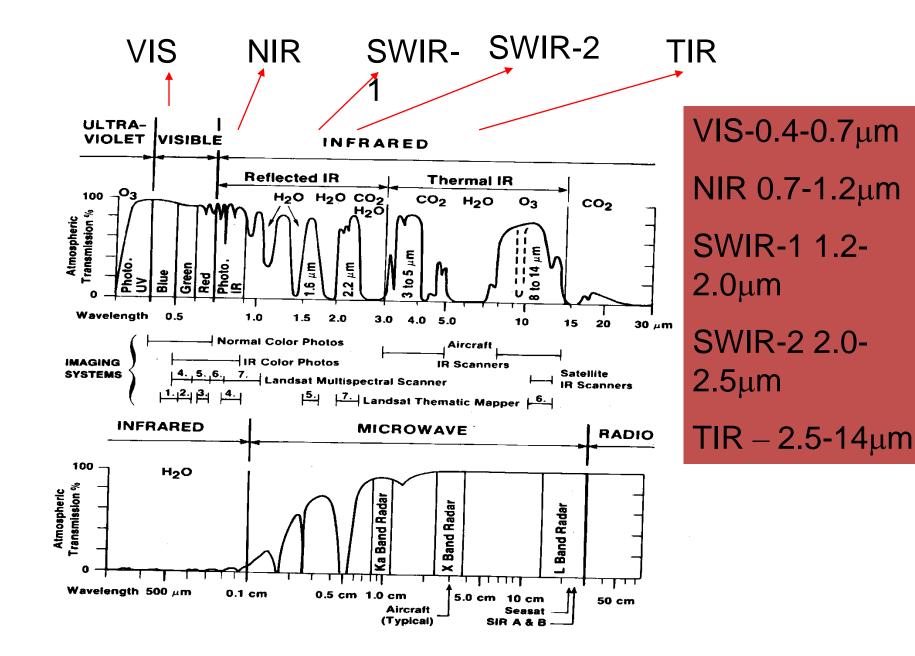
Black Body and Plank Theory





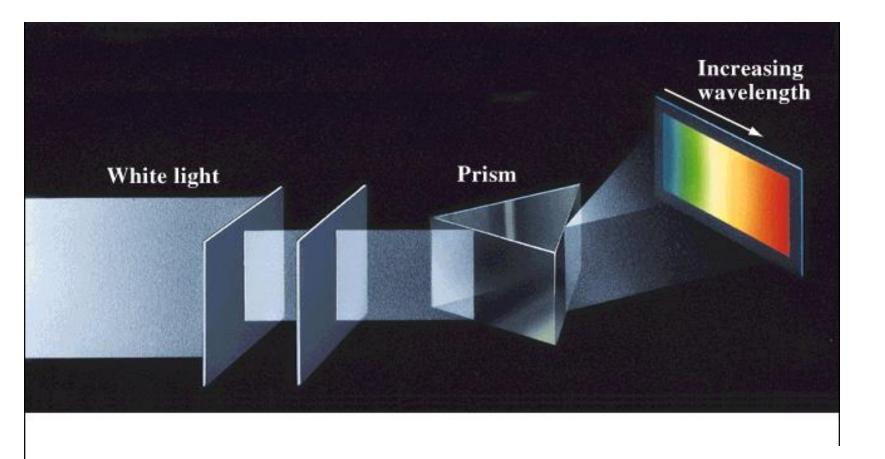
Black body spectrum (spectral energy density inside a blackbody cavity). Indicated units are correctly kJ/m⁴, or nJ/cm³/µm. Scale by c/4 π to achieve $I'(\lambda, I)$.







White Light consist of many wavelengths









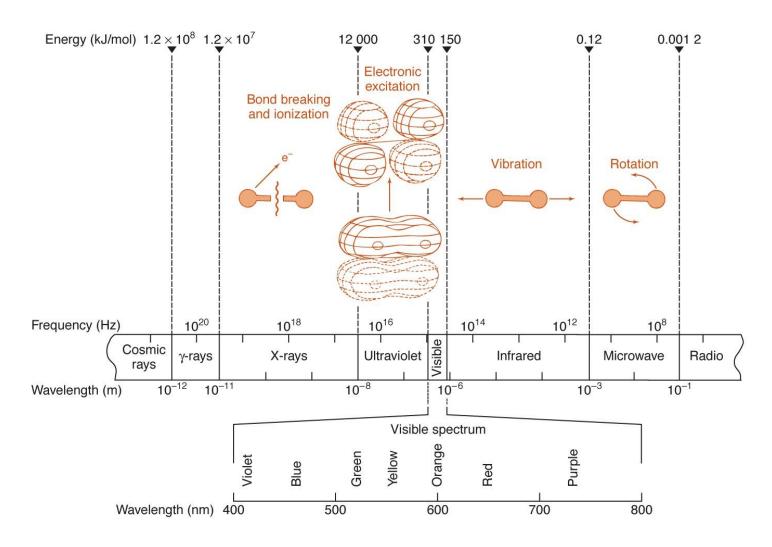
Colors of Visible Light

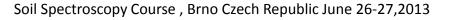
Wavelength	Absorbed	Observed
380-420	violet	green-yellow
420-440	violet-blue	yellow
440-470	blue	orange
470-500	blue-green	red
500-520	green	purple
520-550	yellow-green	violet
550-580	yellow	violet-blue
580-620	orange	blue
620-680	red	blue-green
680-780	purple	green





Energy and Processes at the Electromagnetic Spectrum





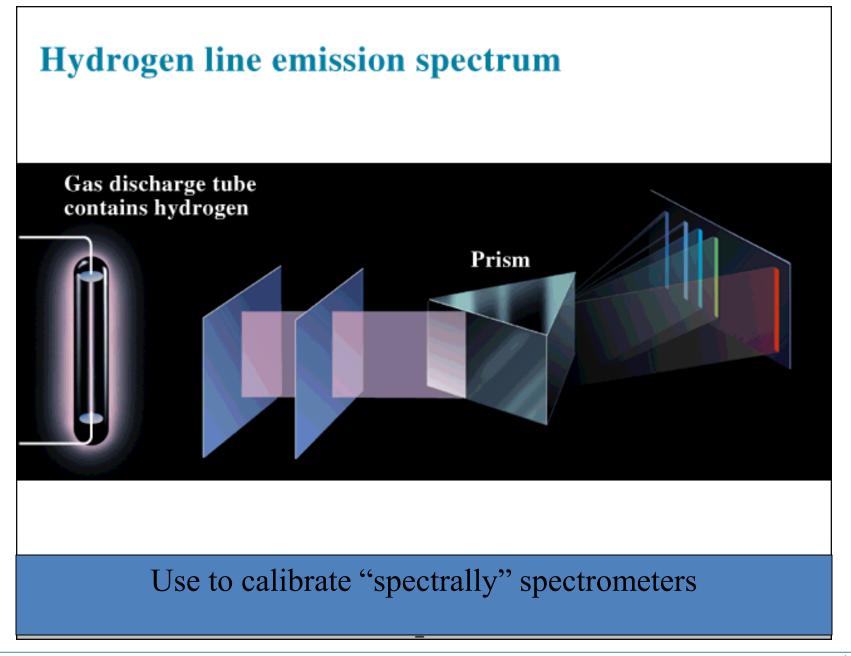




Line Spectrum

A spectrum produced by a luminous gas or vapor and appearing as distinct lines characteristic of the various elements constituting the gas.









Ground State

The state of least possible energy in a physical system, as of elementary particles. Also called *ground level*.

Excited State

Being at an energy level higher than the ground state.



Emission Spectrum

 The spectrum of emitted energy from a specific emitting substance subjected to a specific kind of excitation.

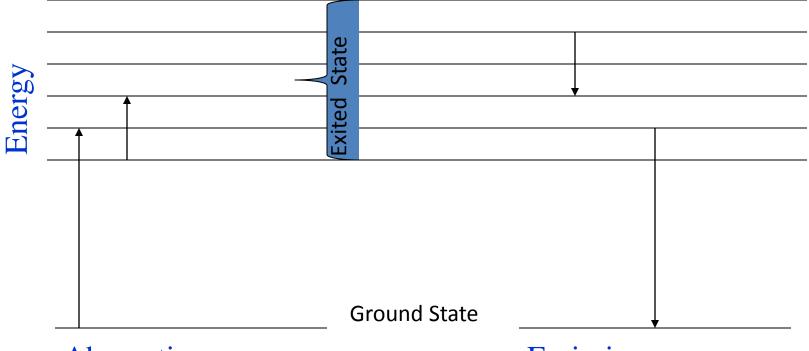


Absorption Spectrum

- Light shinning on a sample causes electrons to be excited from the ground state to an excited state or vibration levels to be changed
- wavelengths of that energy are removed from transmitted/reflectcted spectra

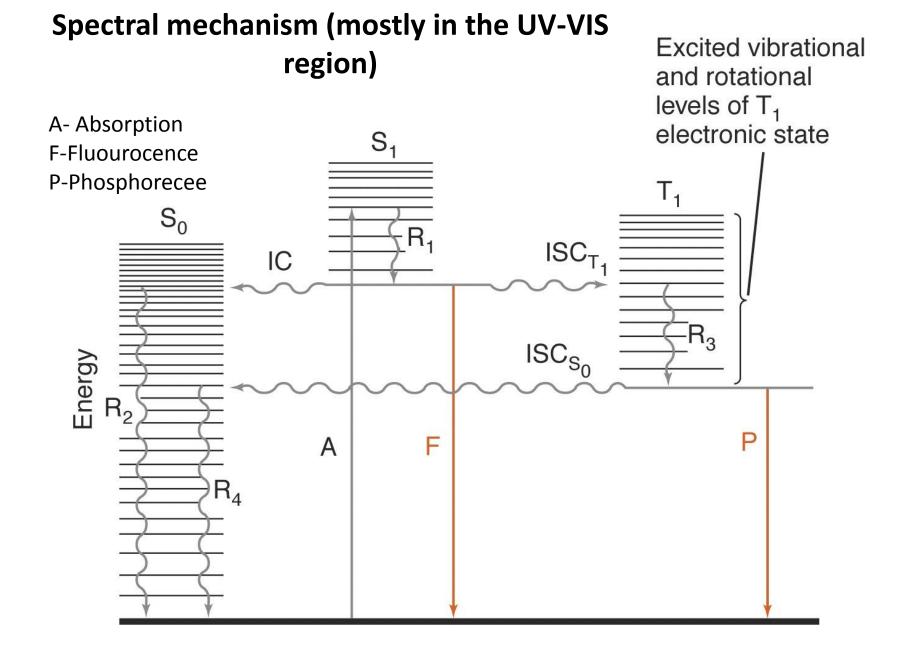


Absorption and Emission of Light

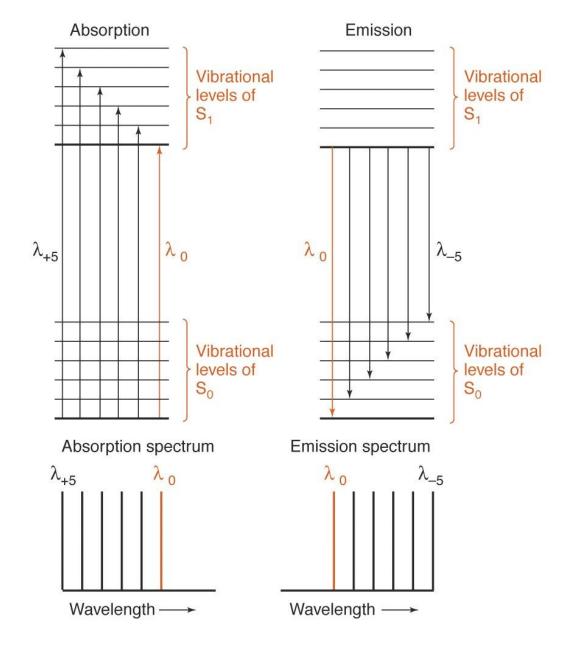


Absorption

Emission



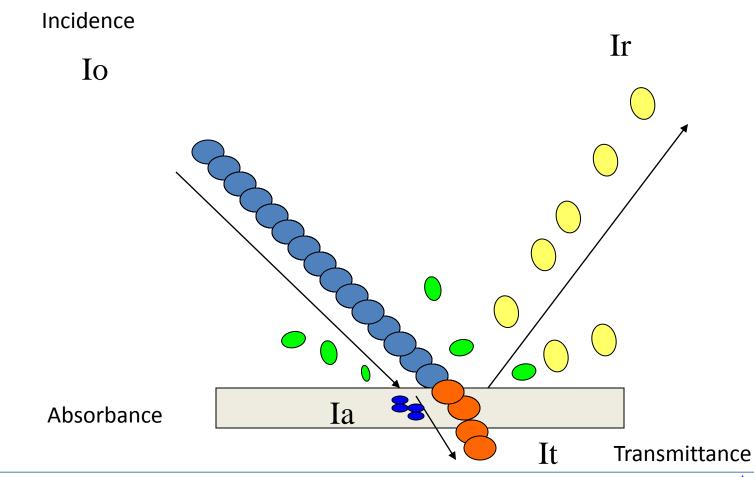






A Photon: a pack of energy with no mass traveling in the speed of light (and lower)

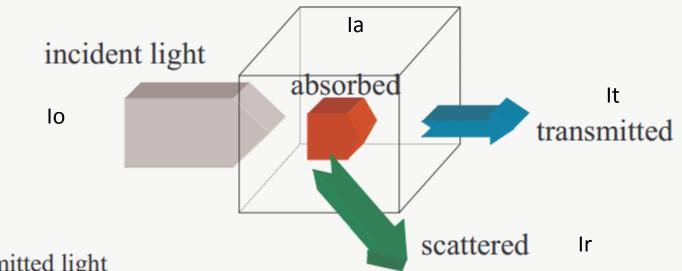
reflectance







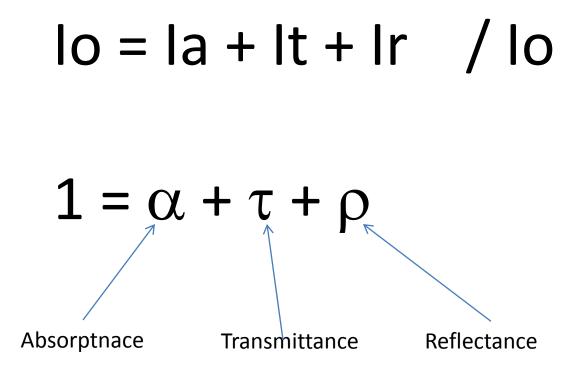
- Consider a beam of light on a material
 - It can be scattered, absorbed, or transmitted



- Transmitted light
 - Light emerges propagating in the same direction as the incident light
- Absorbed light
 - Energy from light is absorbed in the volume of the material
- Scattered light
 - Light emerges in a different direction from the incident light











Absorption Methods, Transmittance (Reflectance =0)

$$T = I/I_{o}$$
where T => transmittance
$$I => power of transmitted$$
radiation
$$I_{o} => power of incident$$
radiation
$$%T = (I/I_{o})*100$$
where %T => percent transmittance



Absorption Methods, Transmittance

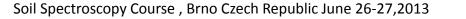
$$A = -\log_{10}T = -\log_{10}(I/I_{o})$$

where A => absorbance



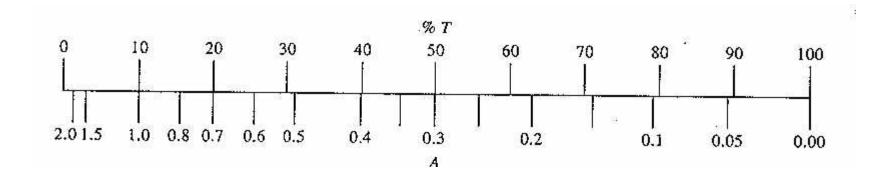
Relation Between Transmittance and Absorbance (Ref = 0)

_ / _o	%Т	A
1	100	0
0.1	10	1
0.01	1	2





Relationship of Transmittance and Absorpbance



transmittance (reflectance) scale is linear

absorbance scale is exponential thus, read transmittance, then calculate absorbance



Absorption Methods, Reflectance (Transmittance =0)

$$R = I/I_{o}$$
where R => reflectance
$$I => power of reflectance
radiation
$$I_{o} => power of incident
radiation
% R = (I/I_{o})*100
where %R => percent reflectance$$$$



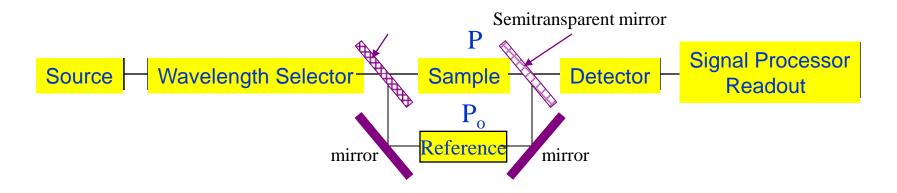
Absorption Methods, Reflectance

$$A = -\log_{10}R = -\log_{10}(I/I_{o})$$

where A => absorbance

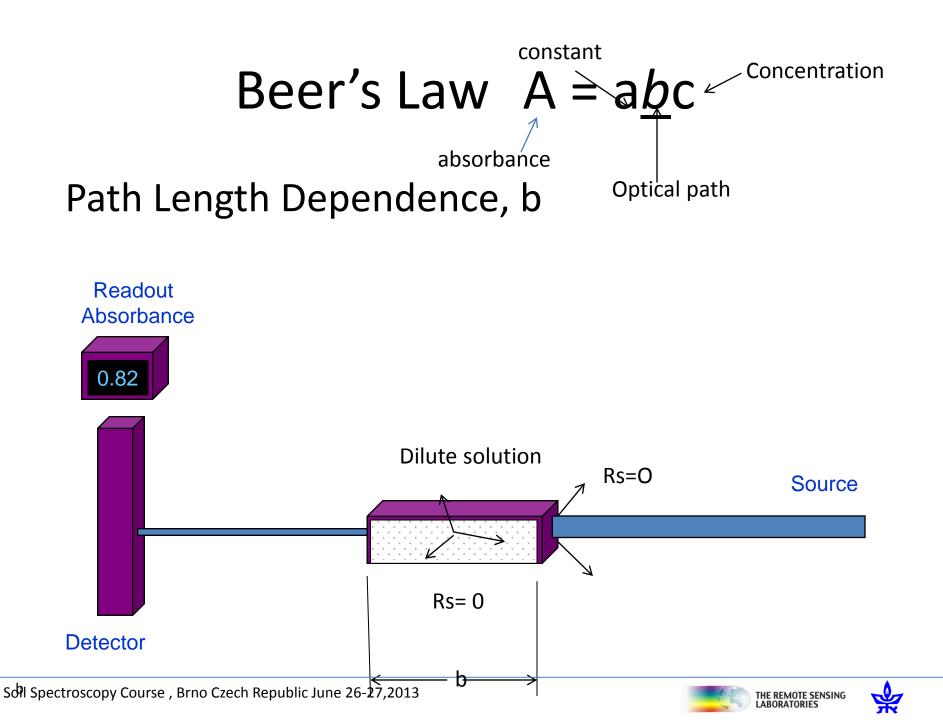


Components of Optical Instruments to do the analysis



Transmittance Spectrometer Reflectance Spectrometer Emission Flame Photometer Flame Atomic Absorption Spectrometer Fluorescence and/or Scattering Spectrometer





Absorption Methods, Beer's Law

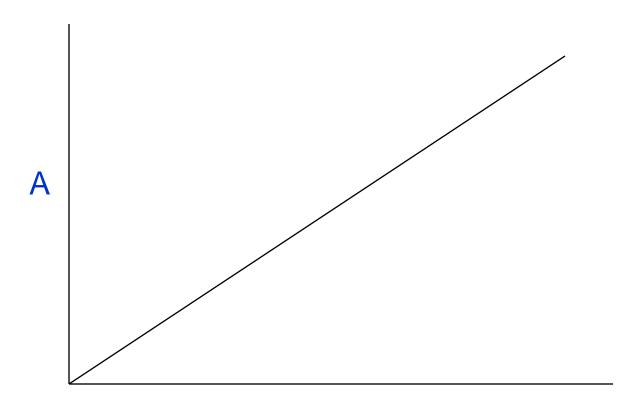
 $A = abc = \varepsilon bc$

- where a => absorptivity
 - b => path length
 - c => concentration
 - $\epsilon \Rightarrow$ molar absorptivity



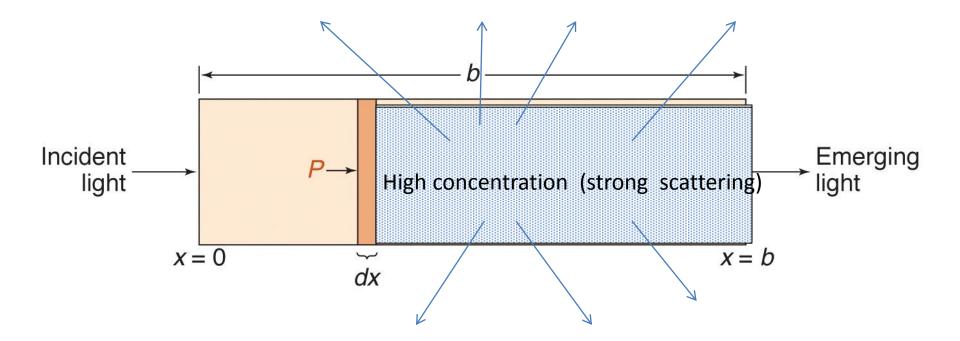
Beer's Law

$A = abc = \varepsilon bc$





Attenuation of Light



Beers law does not work for High concentration as the scattering effect is significant

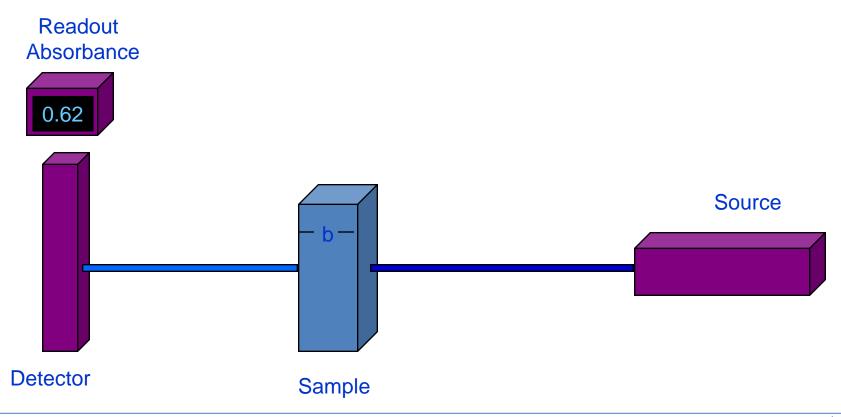






Beer's Law $A = a\underline{b}c$

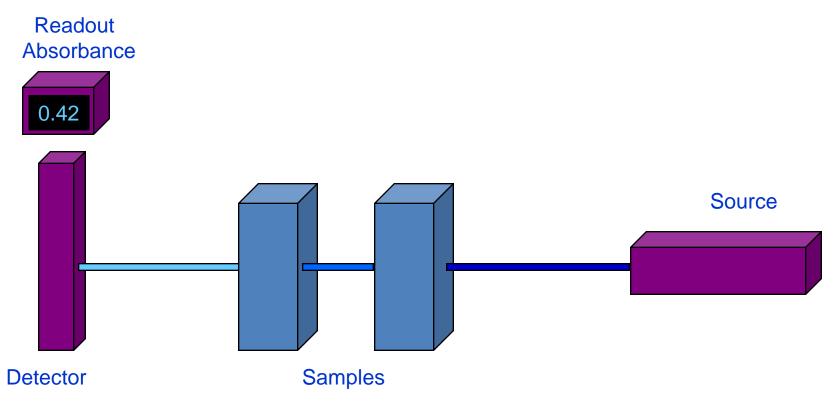
Path Length Dependence, b





Beer's Law $A = a\underline{b}c$

Path Length Dependence, b

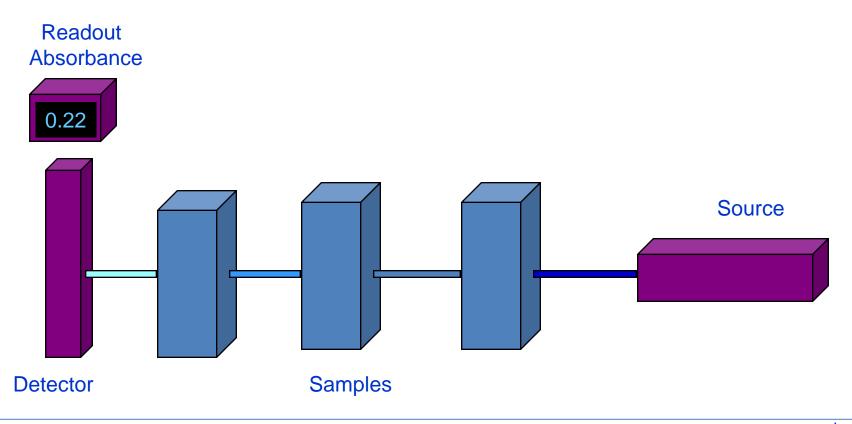




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Beer's Law $A = a\underline{b}c$

Path Length Dependence, b





39

Beer's Law A = ab<u>c</u>

Concentration Dependence, c

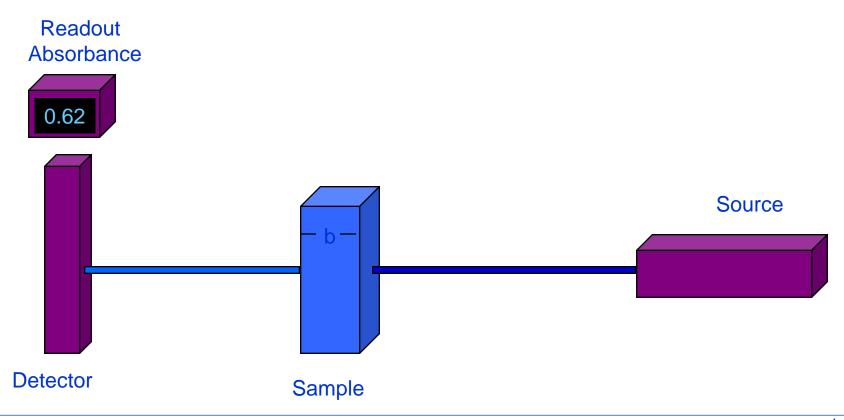






Beer's Law A = abc

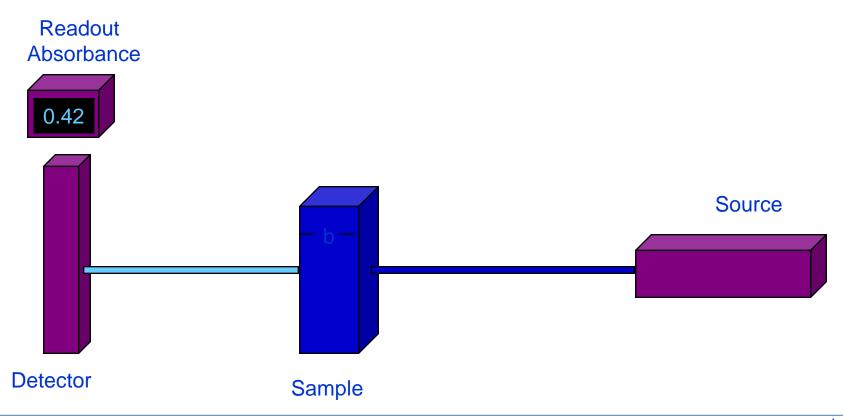
Concentration Dependence, c





Beer's Law A = abc

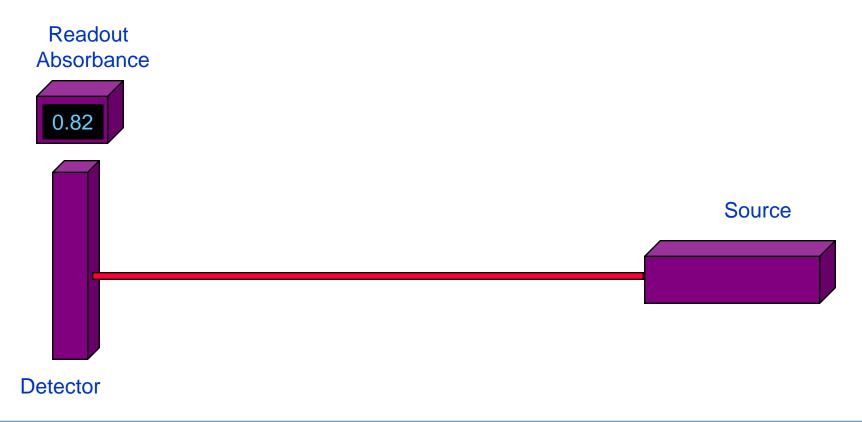
Concentration Dependence, c





Beer's Law $A = \underline{a}bc$

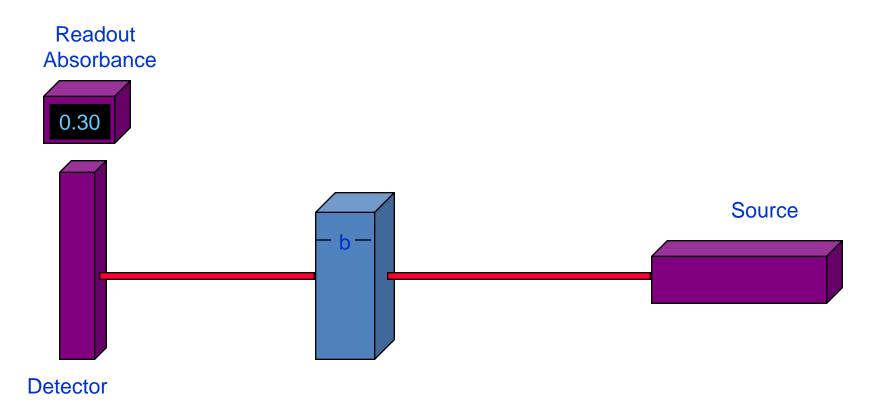
Wavelength Dependence, a





Beer's Law $A = \underline{a}bc$

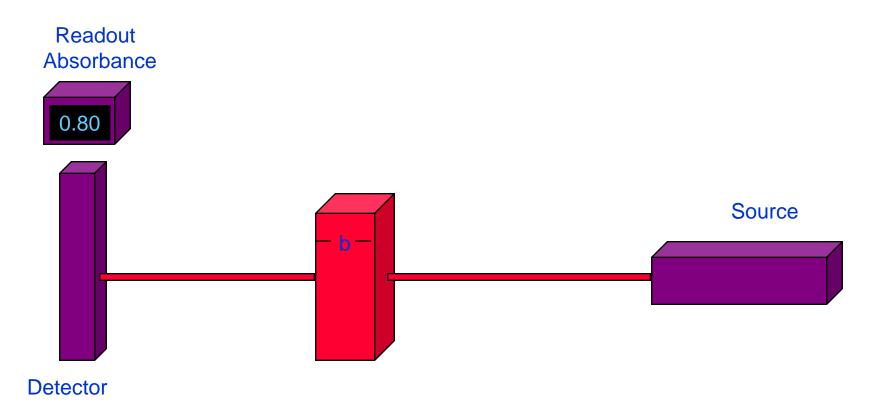
Wavelength Dependence, a





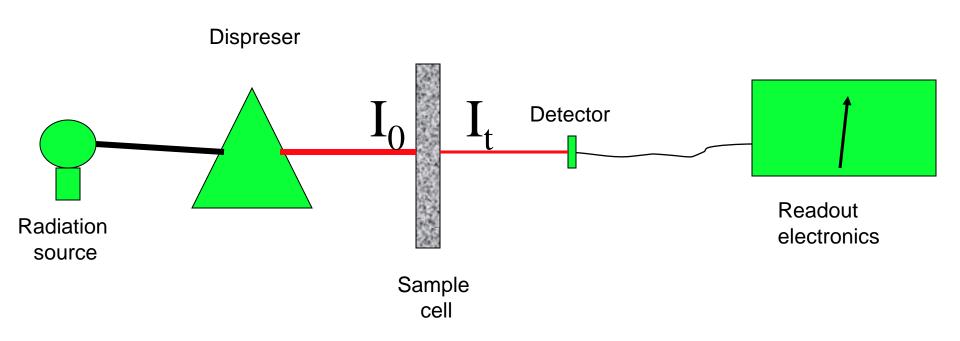
Beer's Law $A = \underline{a}bc$

Wavelength Dependence, a

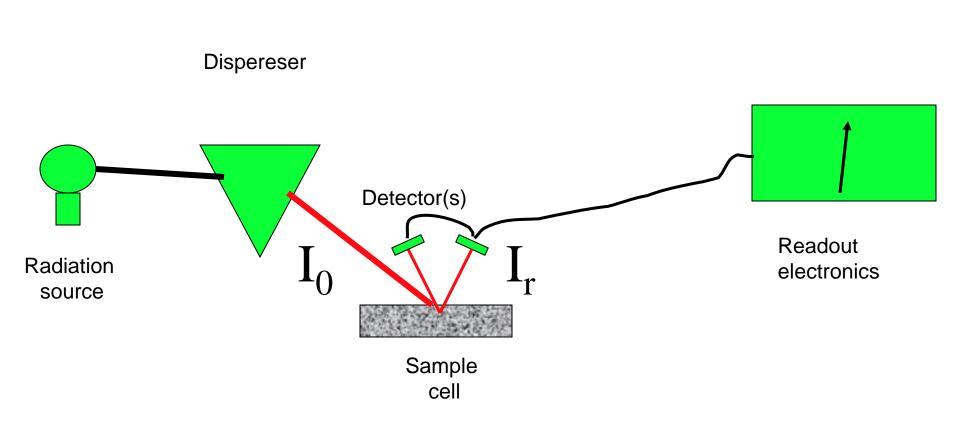




Transmission



Reflection



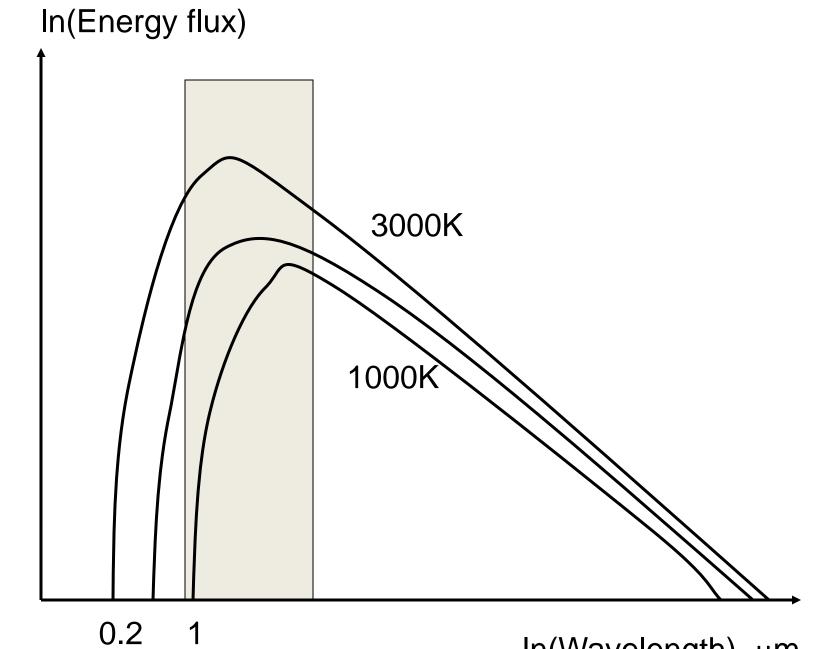
- Spectroscopy?
- Instrumentation
- Modes of measurement

What can be changed?

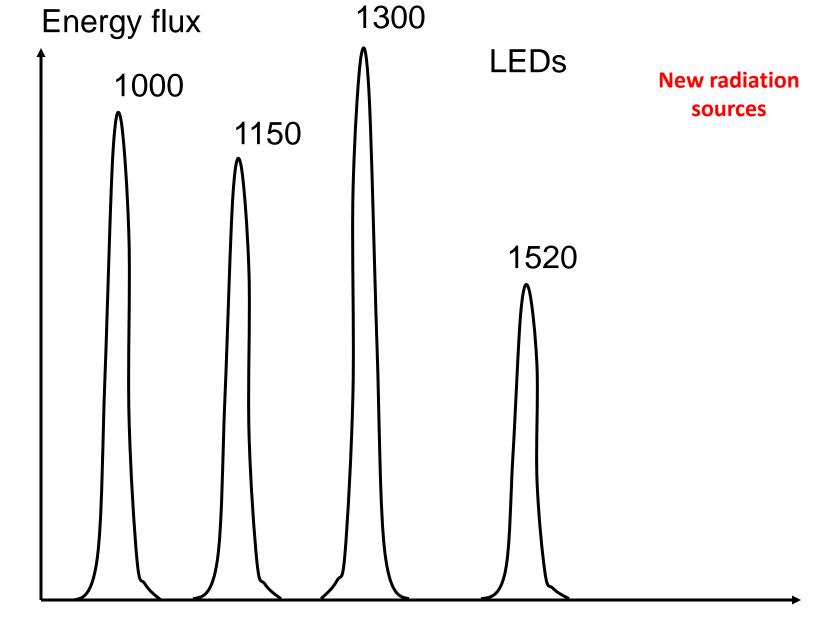
- Radiation source
- Dsipreser
- Sample cell
- Detector

Radiation source

- Tungsten-halogen lamp (Car type)
- Coated tungsten SiC
- Laser(s)
- LEDs
- LED arrays



In(Wavelength), µm



Wavelength, Dm

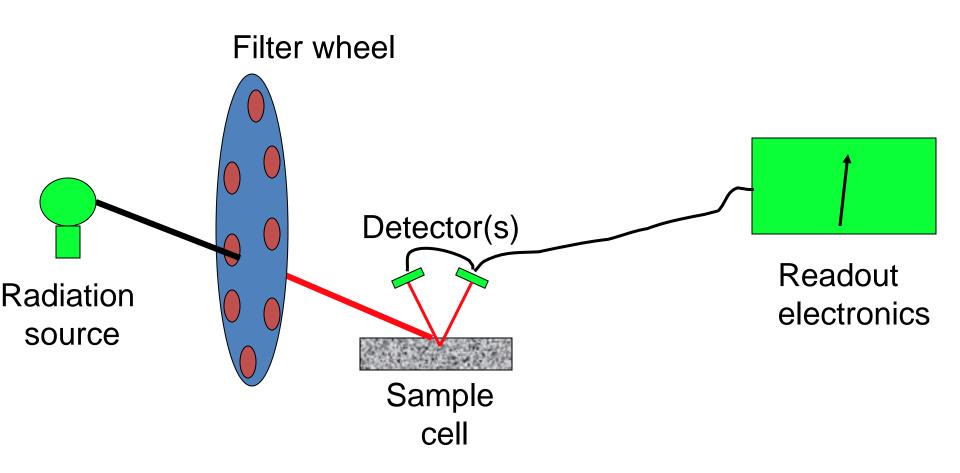
What can be changed?

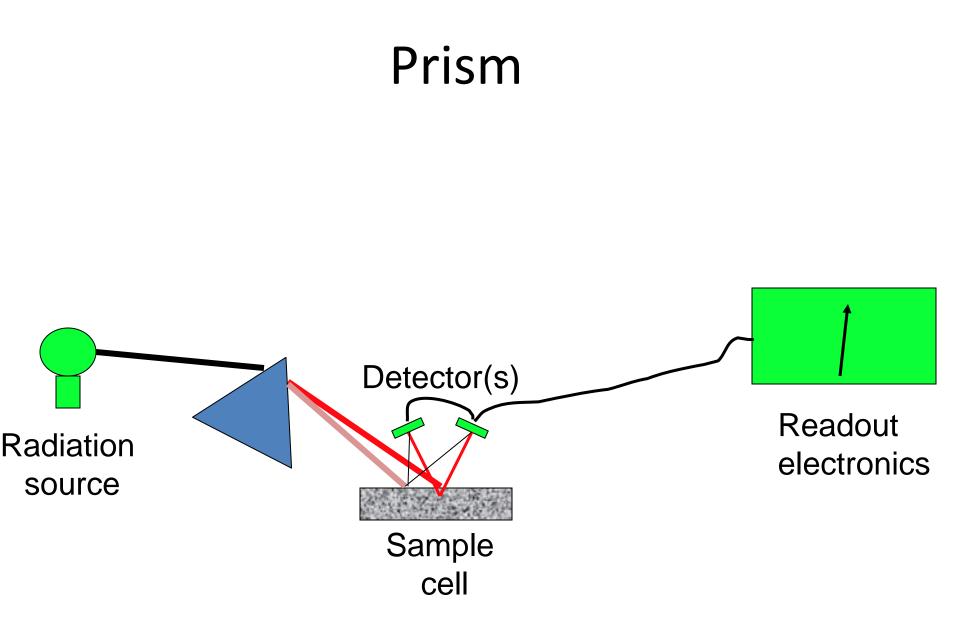
- Radiation source
- Dispreser
- Sample cell
- Detector

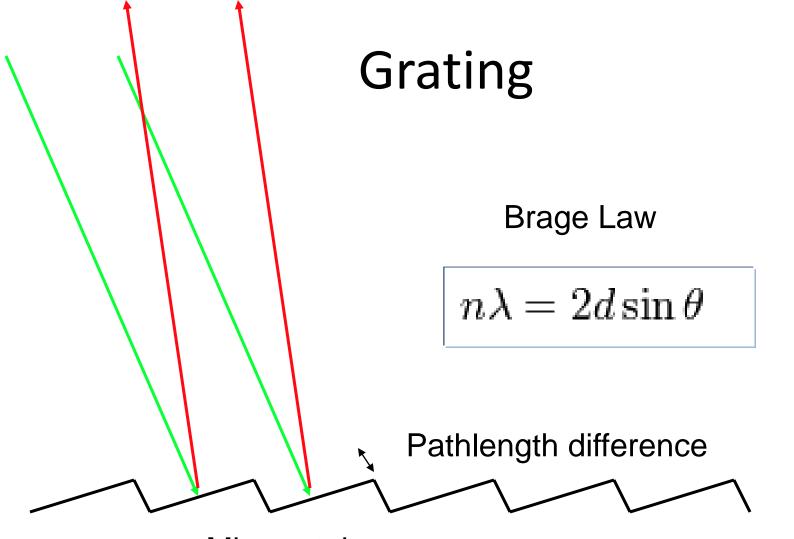
Dispreser

- "Glass filter"
- Interference filters
- Prism
- Grating
- Interferometer
- Electrooptical

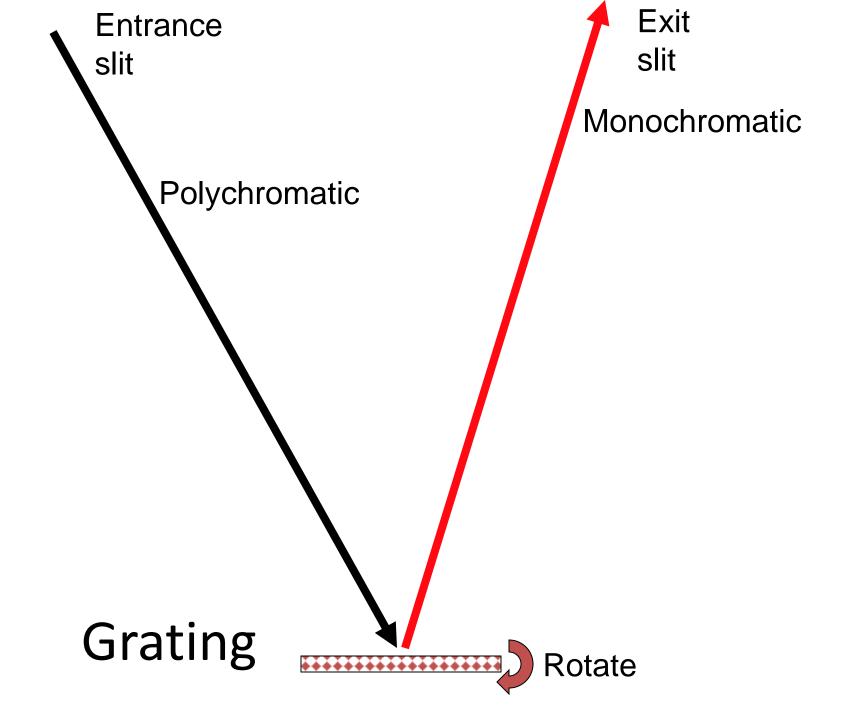
Filter wheel



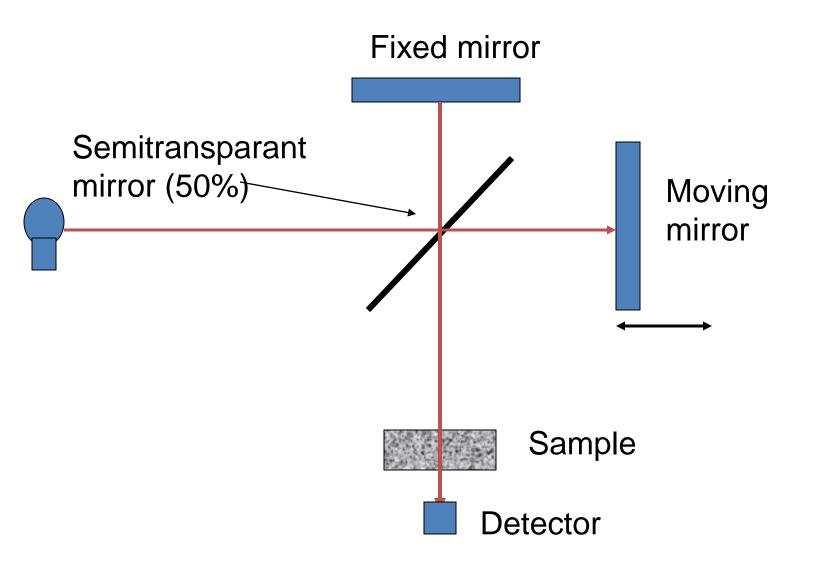




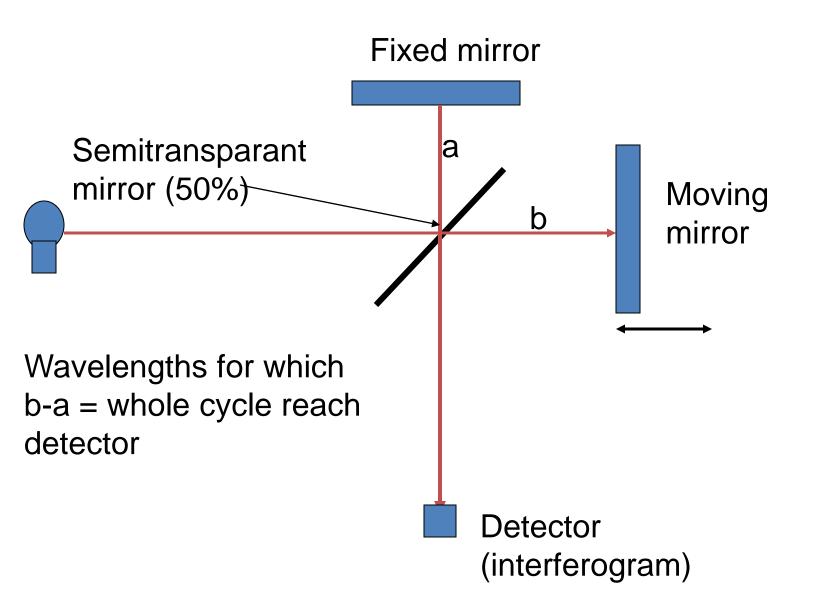
Mirror staircase



Interferometer

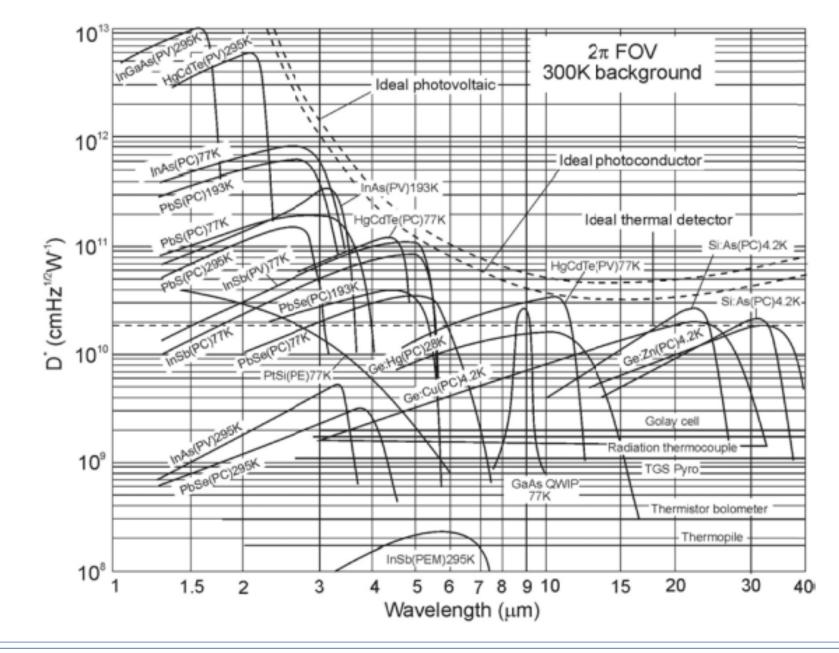


Interferometer

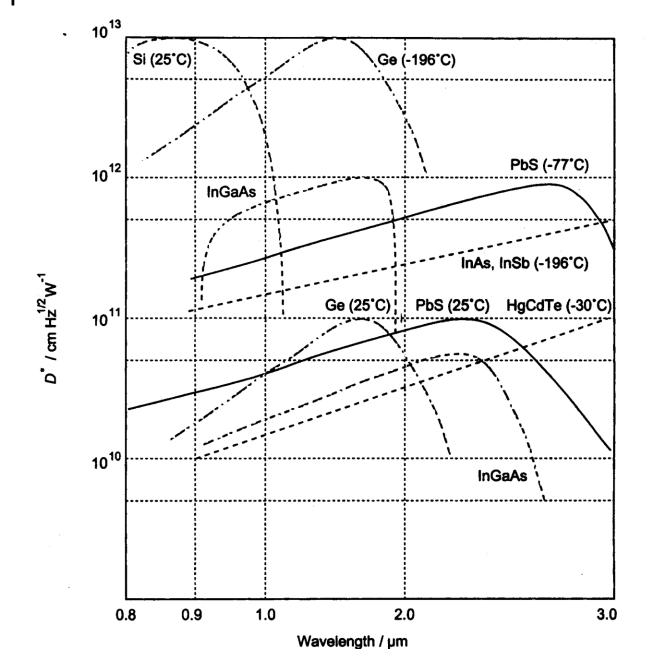


What can be changed?

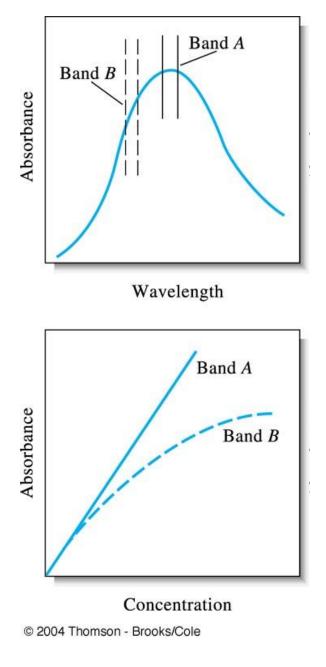
- Radiation source
- Monochromator
- Sample cell
- Detector







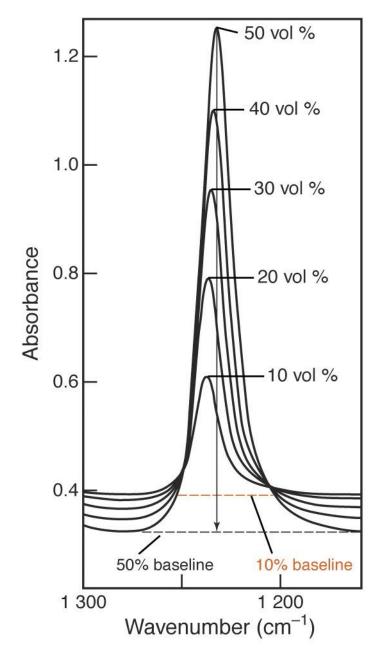
Quantitative Approach at Absorbance region

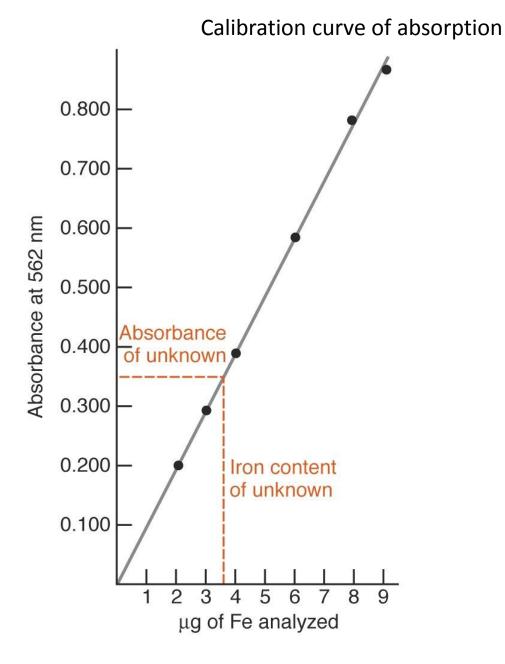


Position to account for the EM-Matter Interaction

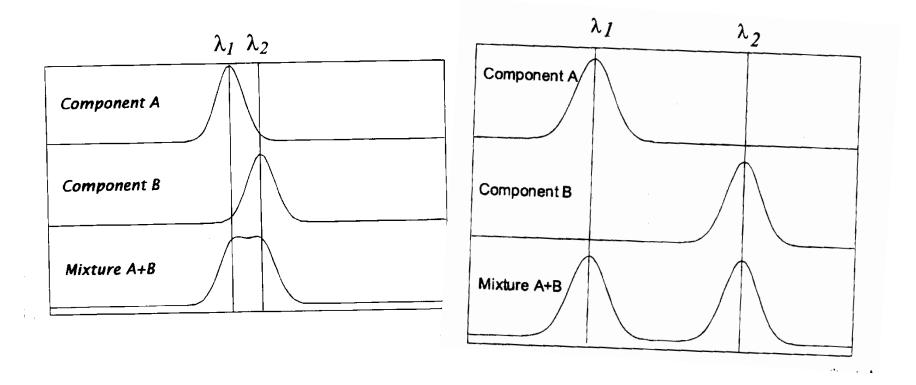








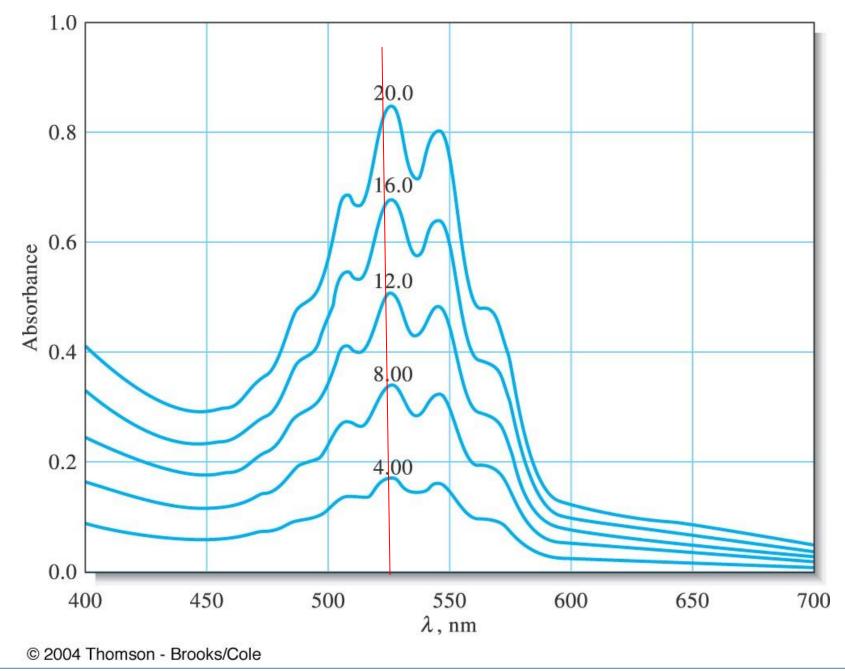




Peaks Orientation: Super - position or absorption features of two different component: A LINEAR MIXTUR



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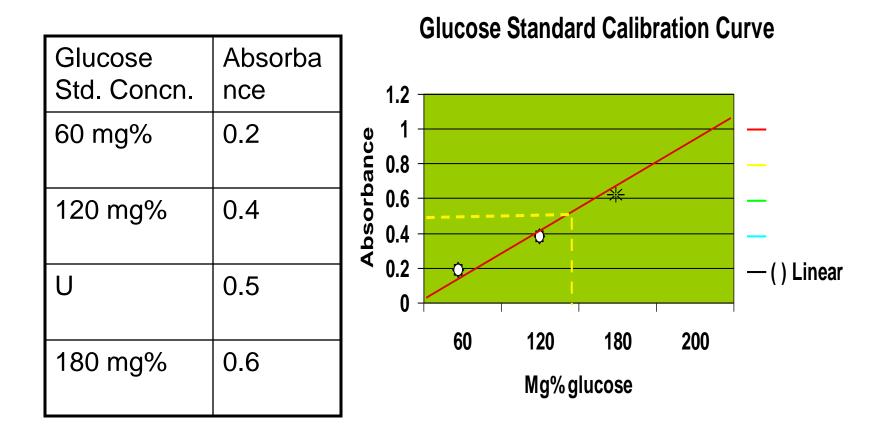


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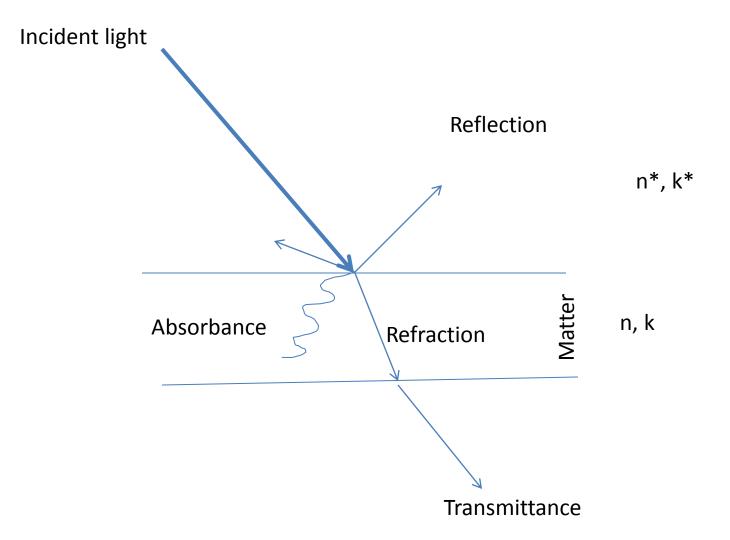
Calibration Curve at 525nm





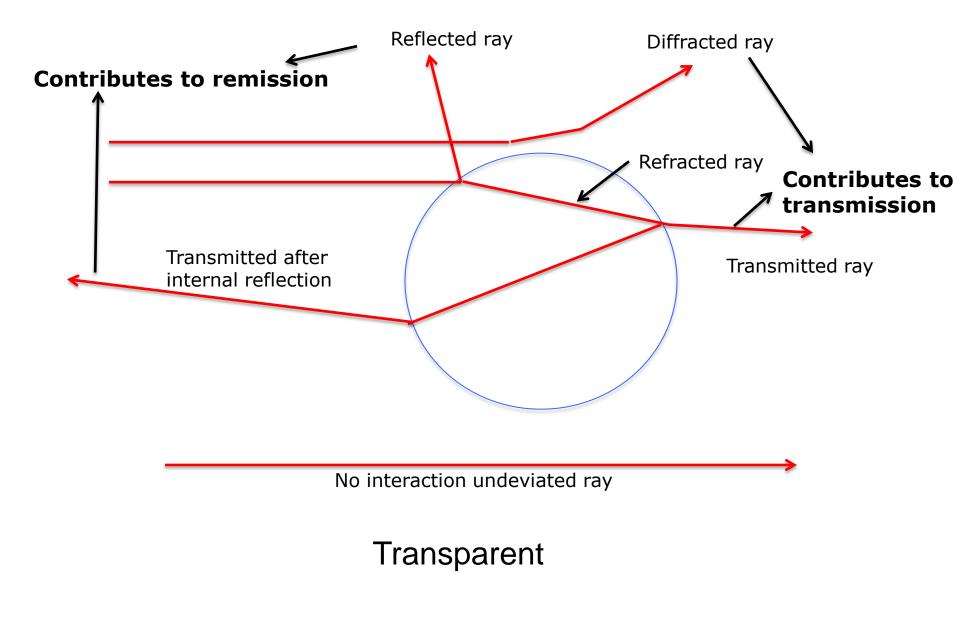


Refraction Theory

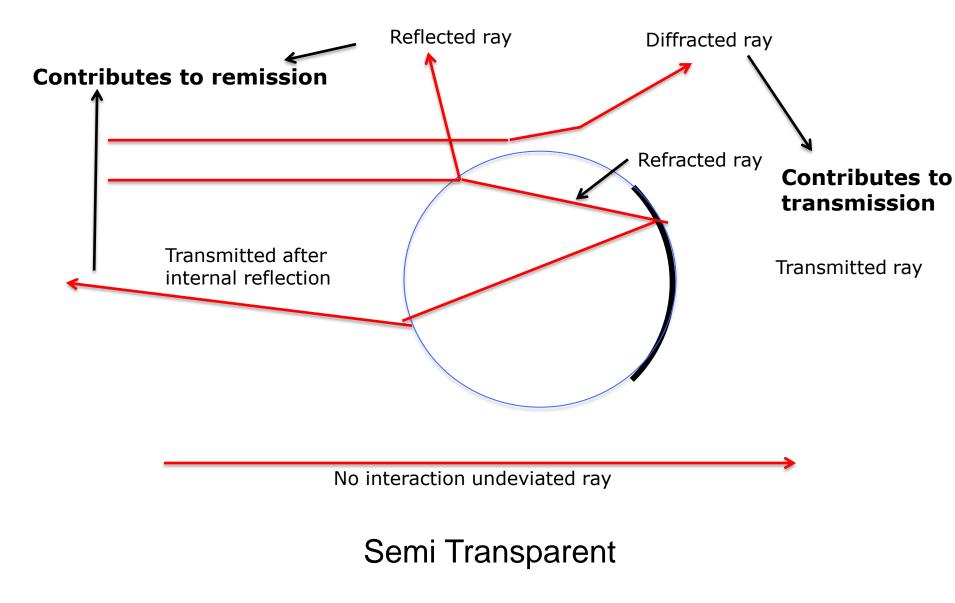




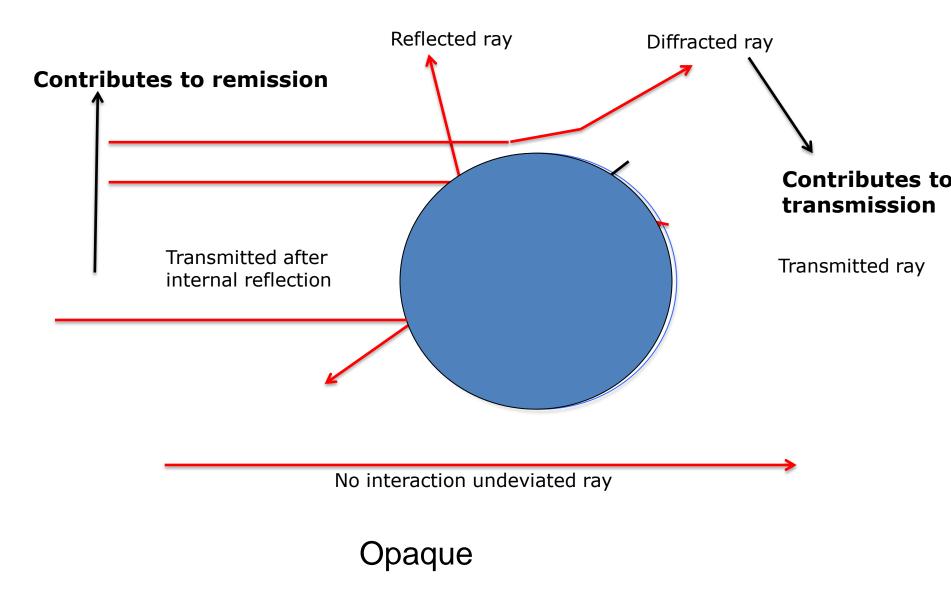
Particle interaction with radiation

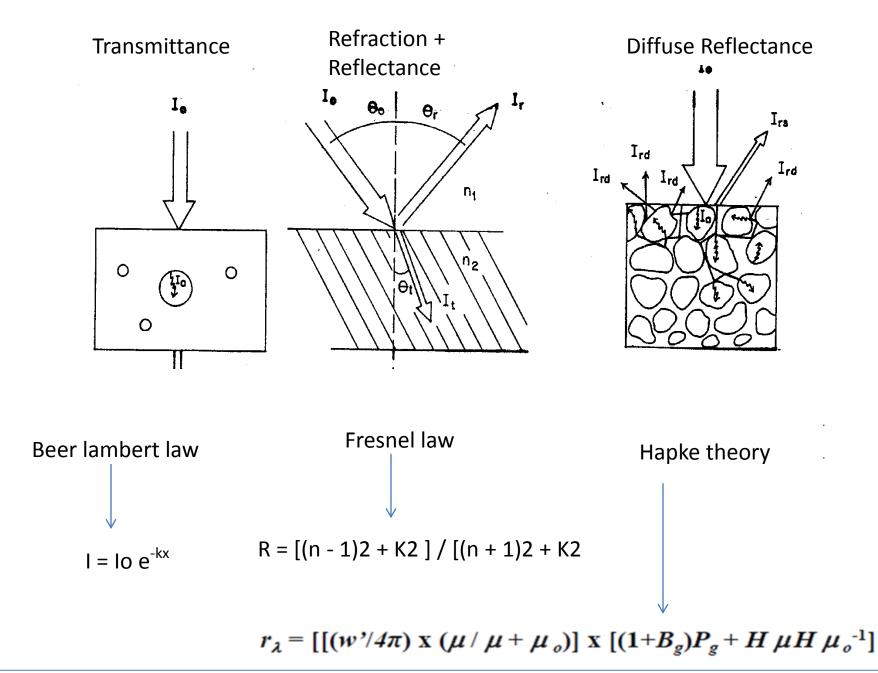


Particle interaction with radiation



Particle interaction with radiation







complex index of refraction (m)

n is the real part of the index, $j = (-1)^{1/2}$ and K is the imaginary part of the index of refraction (extinction coefficient)

$$k = 4 \pi K / \lambda$$

$$\lambda K / 4 \pi = K$$

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Fresnel Equation

The reflection of light, R, normally incident onto a plane surface is described by the Fresnel equation:

$$R = [(n - 1)^{2} + K^{2}] / [(n + 1)^{2} + K^{2}]$$



If the real part of the refraction index ${\bf n}$ is constant then the imagery part ${\bf k}$ is changing.

In Beer law: concentration is low, the optical path is constant, and the incident light hit at 900 (no scattering nor reflection) $\rightarrow \mathbf{n}$ is minimal and constant while k is correlated to the material interact with the radiation.

When photons enter an absorbing Beer medium, then :

$$I = Io e^{-kb}$$

where \mathbf{I} is the observed intensity, \mathbf{IO} is the original light intensity, \mathbf{k} is an absorption coefficient and \mathbf{b} is the distance traveled through the medium.

The absorption (extinction) coefficient is related to the complex index of refraction by the equation:

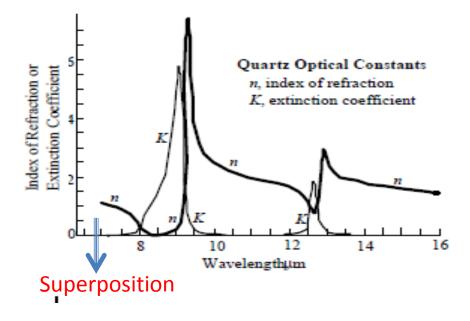
k = 4
$$\pi$$
 K/ λ

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Example index of refraction, \mathbf{n} , and extinction coefficient, \mathbf{K} are shown in quartz.



Index of refraction and extinction coefficient of quartz for the wavelength interval 6-16 mm



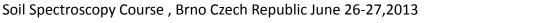


Hapke's Theory

Clark (1999) suggests that it is possible to model the reflectance from an exposed rock consisting of several minerals or a single mineral based on Hapke's (1993) equation:

$r_{\lambda} = [[(w'/4\pi) \times (\mu / \mu + \mu_o)] \times [(1+B_g)P_g + H \mu H \mu_o^{-1}]]$

Where r_{λ} is the reflectance at wavelength λ , w' is the average single scattering albedo from the rock or mineral of interest, μ is the cosine of the angle of emitted light, u_o is the cosine of the angle of incident light onto the rock or mineral of interest, g is the phase angle, B_g is a back-scattering function, P_g is the average single particle phase function, and H is a function for isotropic scatterers.







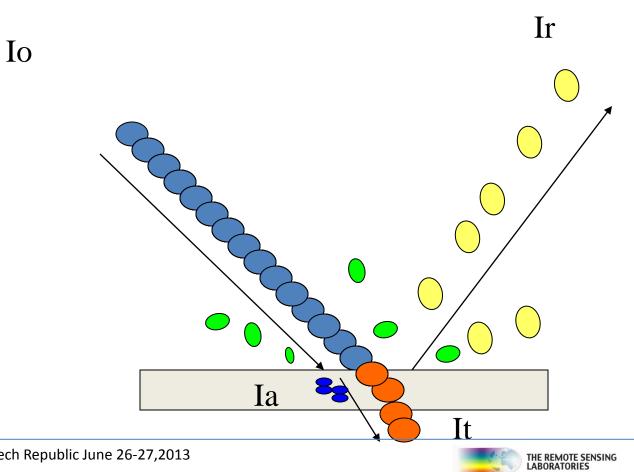
Hapke Theory: References to read

- Hapke B.W. 1981a Bidirectional reflectance spectroscopy I. Theory. Journal of Geophysical Research 86:3039-3054.
- Hapke B.W., 1981b Bidirectional reflectance spectroscopy: 2 Experiments and observation. *Journal of Geophysical Research* 86:3055-3060.
- Hapke B.W, 1984 Bidirectional reflectance spectroscopy: Correction for macroscopic roughens. *Icarus* 59:41-59.
- Hapke B.W. 1986, Bidirectional reflectance spectroscopy 4: The extinction coefficient and the opposition effect. *Icarus* 67:264-280
- Hapke B.W. 1993 *Theory of Reflectance and Emittance Spectroscopy*, Cambridge University Press, New-York.



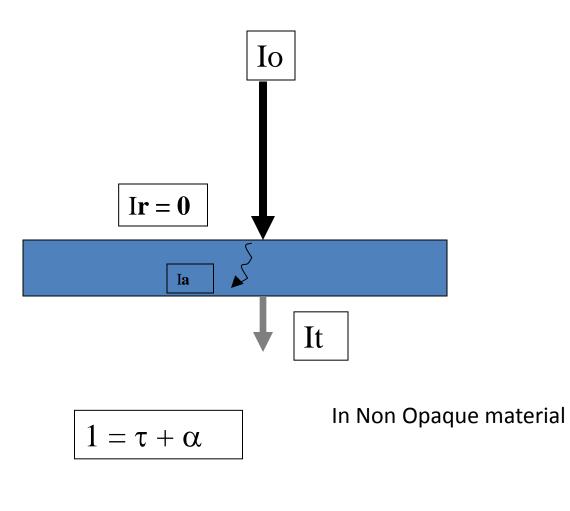
The "particle" theory of light (photons)





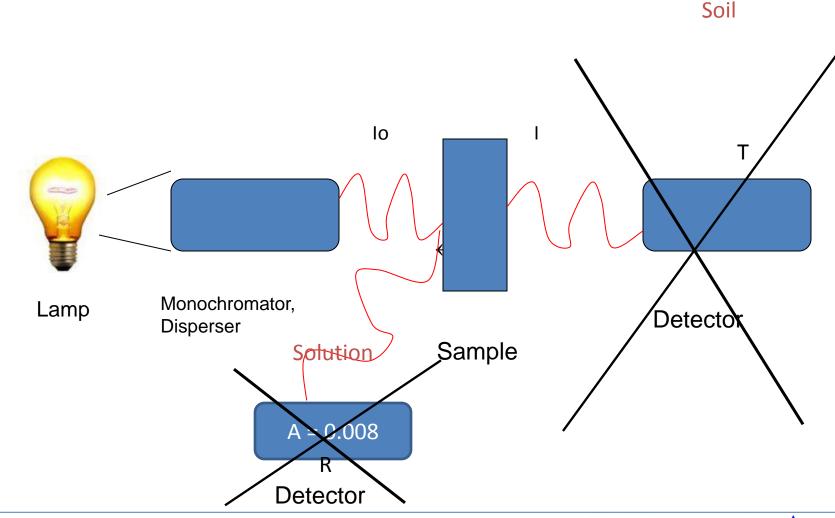
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A Leaf Model



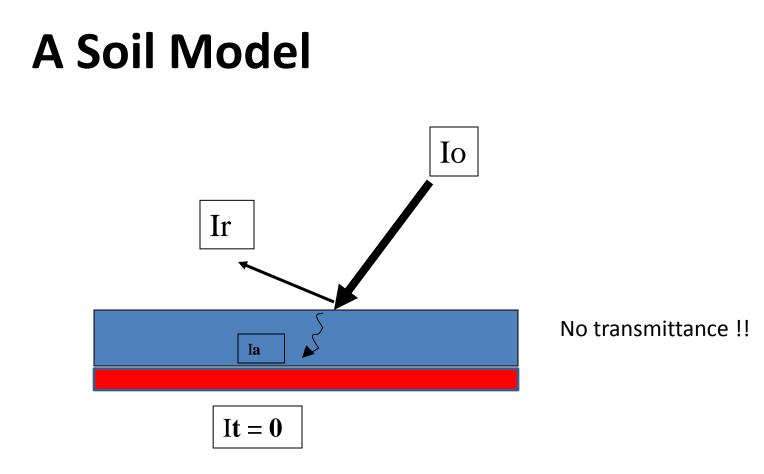


Spectroscopy of Vegetation, Solution and Soil



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In Opaque material (such as soil)

$$1 = \rho + \alpha$$

$$\log 1/\rho = \alpha$$

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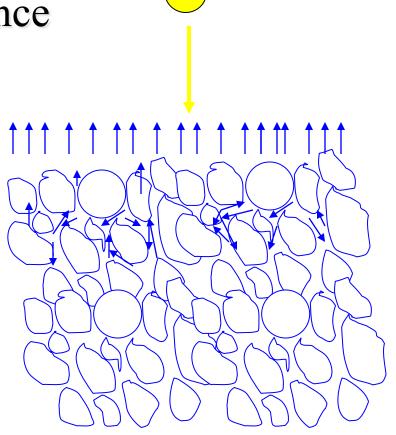




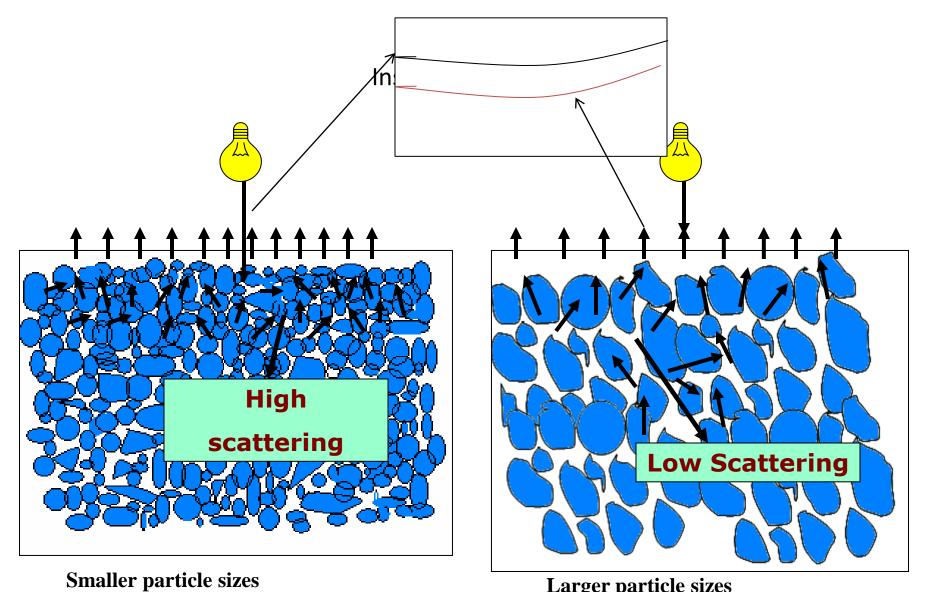
Scattering and Diffuse Reflectance

• Light propagates by scattering.

• As light propagates, both scattering and absorption occur, and the intensity of the radiation is reduced.



The radiation that comes back to the entry surface is called diffuse reflectance.



Larger particle sizes

Less remission, more transmission

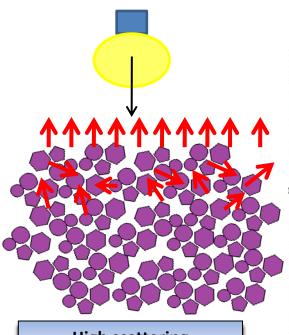
*Multiple path lengths are possible

More remission, less transmission





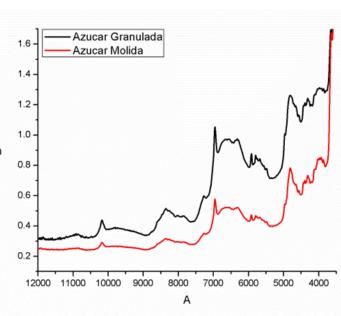
Particle Size and Scattering



High scattering

Smaller particle sizes

More remission, less transmission



Absorbing power (absence of scattering)

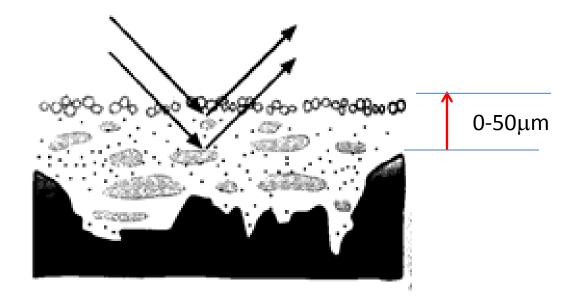
Absorption coefficient (includes effects of voids, surface reflection, distance traveled)

Low Scattering

Larger particle sizes Less remission, more transmission

The real part is dominant the imagery part is constant

Soil and Radiation

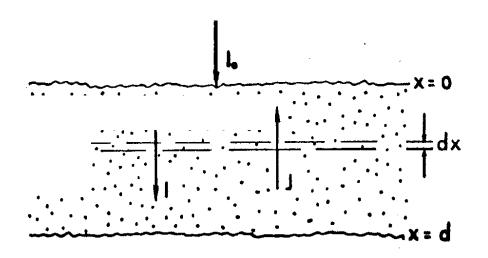








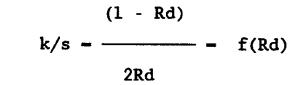
Kubelka Munk Theory

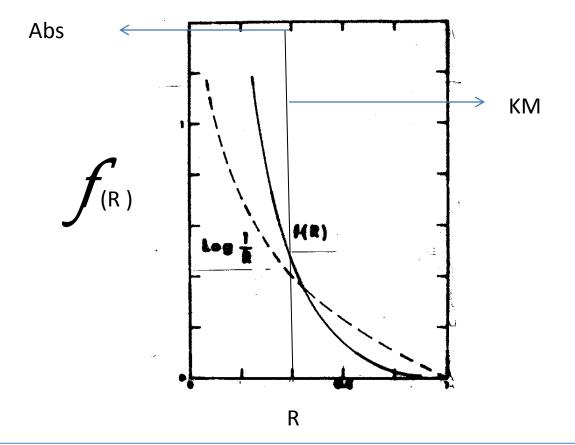


$$\frac{(1-R_{\infty})^2}{2R_{\infty}}=\frac{k}{s},$$

where R_{∞} is the diffuse reflectance, k is the absorption coefficient, and s is the scattering coefficient.











Spectrophotometers

- Light source (Lamp)
- Optical filters or prism(light dispression)
- Tube or cuvette (sample holder)
- Detector (photones counter)



A Chromophore

• A substance in the material that affect the incidence light

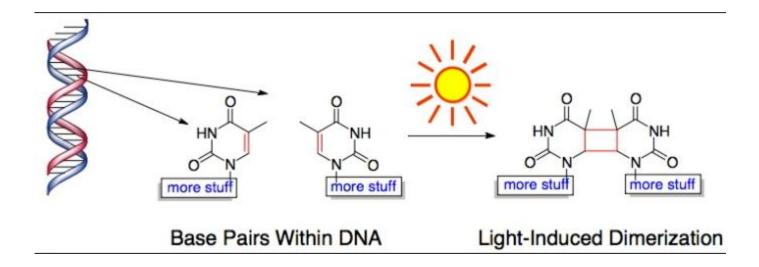
Melanin



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Physical and chemical chromosphere

Physical: No absorption occur (real part of the refraction index)

Chemical: Absorption occurs (imaging part of the refraction index)

For quantity analysis of soils it is important to keep the physical property constant



Spectral Reflectance of Soils

- Spectral Reflectance of Soils controlled by:
 - Soil moisture (physical and chemical n, k)
 - Particle size (physical, n)
 - Organic matter (chemical and physical k,n)
 - Mechanical Composition (physical and chemical, k,n)
 - Mineral contents, including Iron oxide and carbonates (chemical and physical k,n)
 - Surface roughness (physical n)

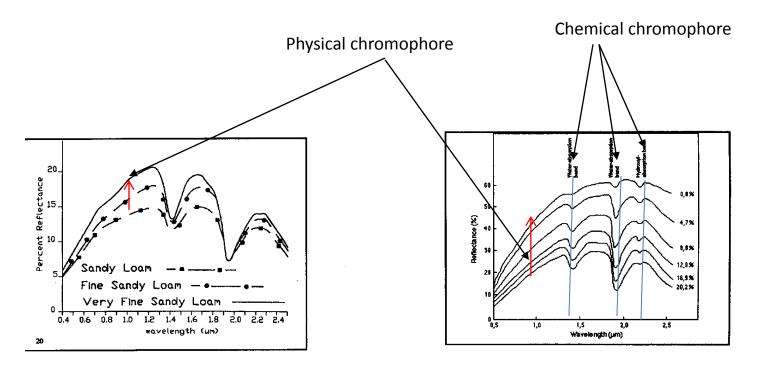




Soil Grain Size (mainly n)

- Different size particles play different roles in soil:
 - Sand (0.05 to 2.0 mm): large air spaces, rapid drainage of water
 - Silt (0.002 to 0.05 mm): enhance movement and retention of soil capillary water
 - Clay (< 0.002 mm): enhance movement and retention of soil capillary water; carry electrical charges which hold ions of dissolved minerals (e.g. potassium and calcium)





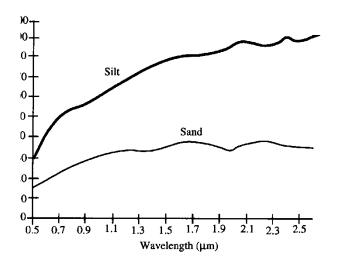
Grain size effect (n)

Moisture effects (k)

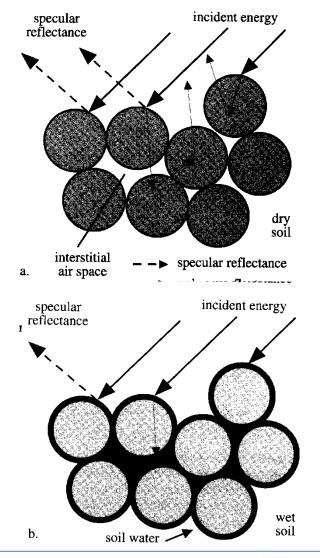


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Another look on Grain Size and Soil Moisture

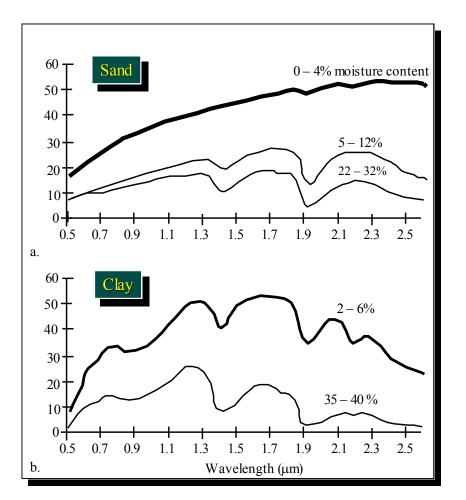


'e 13-5 In situ spectroradiometer reflectance curves for dry silt and sand soils. Reflectance generally increases with increasing wavelength throughout the visible, near- and middle-infrared portions of the spectrum.





Soil Moisture and Texture



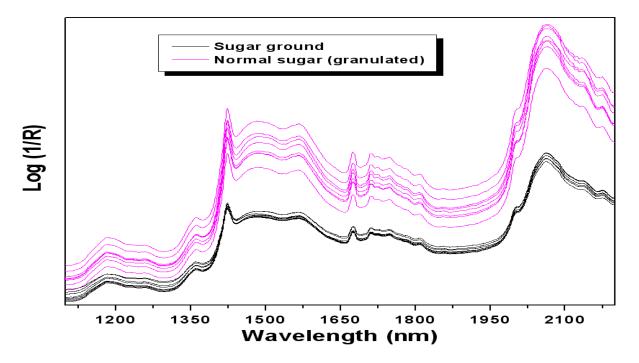
- -Clays hold more water more 'tightly' than sand.
- -Thus, clay spectra display more prominent water absorption bands than sand spectra.
- -AVIRIS can be useful for quantifying these absorption features.



Problems in Spectral Measurements of Reflectance

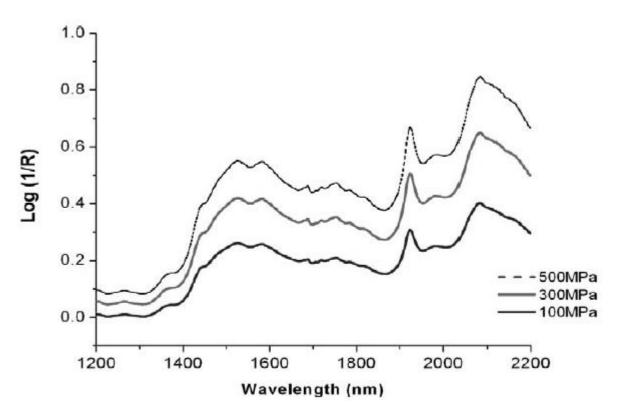
Changes in spectra due to physical properties of a material

Particle size effect



Jackeline I. Jerez, Sept. 2009

Changes in spectra due to physical properties of a material



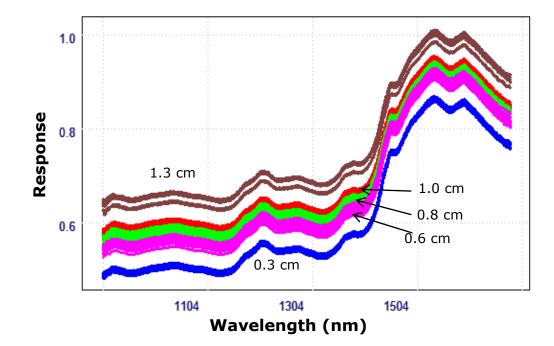
Tablet Packing density

NIR spectra of pure lactose tablet at different packing density

Ropero, J. et al. 2011. Near-Infrared Chemical Imaging Slope as a New Method to Study Tablet Compaction and Tablet Relaxatio. Appl. Spect. 65, 4.

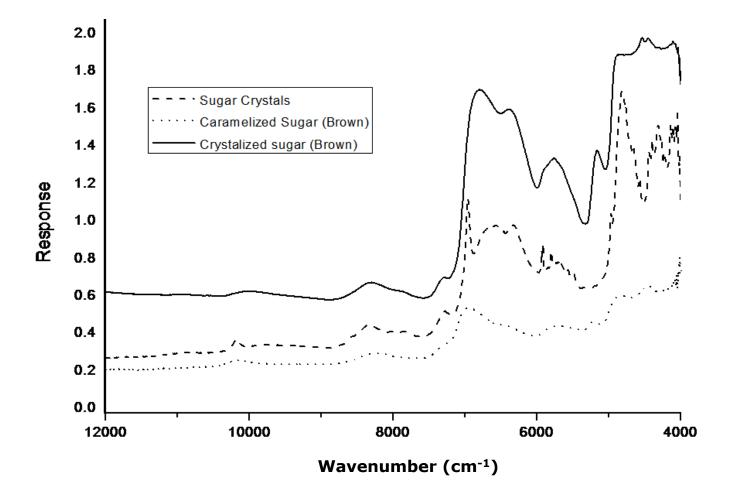
Changes in spectra due to variation in the measurement geometry

Probe-sample distance



NIR spectra of pure lactose analyzed at different distances

Changes in sugar spectra due variation in temperature



Effects of Organic Matter on Soils Spectrum

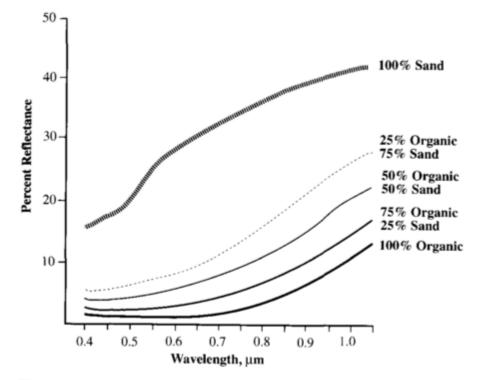


Figure 13-8 The greater the amount of organic content in a soil, the greater the absorption of incident energy and the lower the spectral reflectance.

Organic matter is a strong absorber of EMR, so more organic matter leads to darker soils (lower reflectance curves). Also the curve shape is changing



Effect of Iron Oxides on soil spectrum

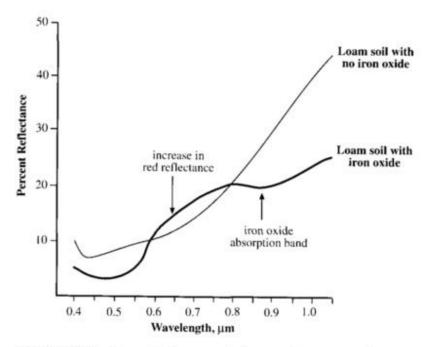
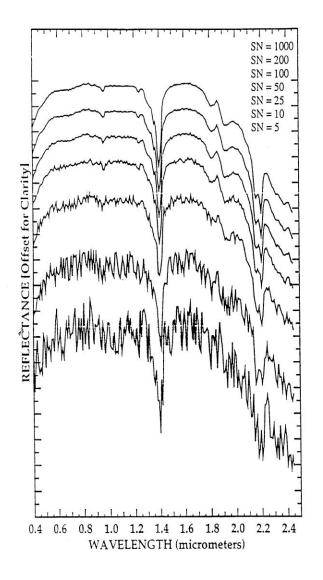


Figure 13-9 Iron oxide in a sandy loam soil causes an increase in reflectance in the red portion of the spectrum (0.6 -0.7μ m) and a decrease in reflectance in the nearinfrared region (0.85 - 0.90 μ m). Effect of Fe-oxide: Increase in the 600 – 700 nm reflectance, decrease in 400 – 600 nm reflectance, decrease in near-IR (absorption feature at ~875 nm)



Effect of the SNR on the soil spectrum







For applying quantities analysis of a chromophore we need to maintain the other chromophore constant

For example:

to track after chemical chromophors we need to keep the following factors constant (using measurement condition and post processing techniques):

Experimental

- Maintain particle size (2mm>)
- Maintain soil moisture (usually room temperature)
- 3) Maintain same material
- 4) Standard measurement protocol
- 5) Use the same spectrometer (SNR)

Mathematical

- 1) Base line correction
- 2) Derivation

Question: What are needed to track after soil aggregation capability?





- Spectroscopy?
- Instrumentation
- Modes of measurement



Modes of measurement

For soil which is a complex material an effort to reduce all physical effects (real part of the electromagnetic radiation interaction with material)

This can be done by using same protocol, same spectrometer, same geometry, same operator.....

Not always possible to maintain thus- standardization is needed Feinstein method for soil measurements:

For that purpose we need a protocol

Soil Measurement Protocol **RSL-TAU** AND G.I.S. LABORATORIES

Soil Spectral Measurements

Problem: A wide range of factors can affect soil reflectance spectra when using different spectrometers or even when repeating a specific sample's measurements in the same spectrometer. These factors result in subtle or strong alterations in wavelength location, peak absorption shape or albedo intensity. In addition to the instrumentation itself, internal electronic noise can affect the measurements and mechanical noise factors (e.g. homogeneity and purity of the white reference panel, or subtle movement when holding the fiber optic) can strongly affect the consistency of the resulting measurements. In soil samples, where very weak spectral features are monitored for chemometric purposes, these noise factors can alter the robust use of a selected spectral model for a wide range of spectrometers and users.

To test this issue and quantify it accordingly for soil environments, 12 soil samples were selected and three different materials were considered as internal standards. This population was measured in one laboratory with three identical spectrometers (Analytical Spectral Devices, Inc.) using a strict measurement protocol. The samples and spectrometers were then sent back to their laboratories of origin where the soils samples were measured using the respective labs' protocols and conditions, Pimstein A., Ben Dor E. and G. Notesco 2010 (*).

An exercise will be followed



A soil library (SSL)

Unlike rocks' library Soil Library MUST contains :

- 1) Chemical attributes (as done by wet chemistry standard methods)
- 2) Reflectance spectra acquired under a routine protocol and spectrometer

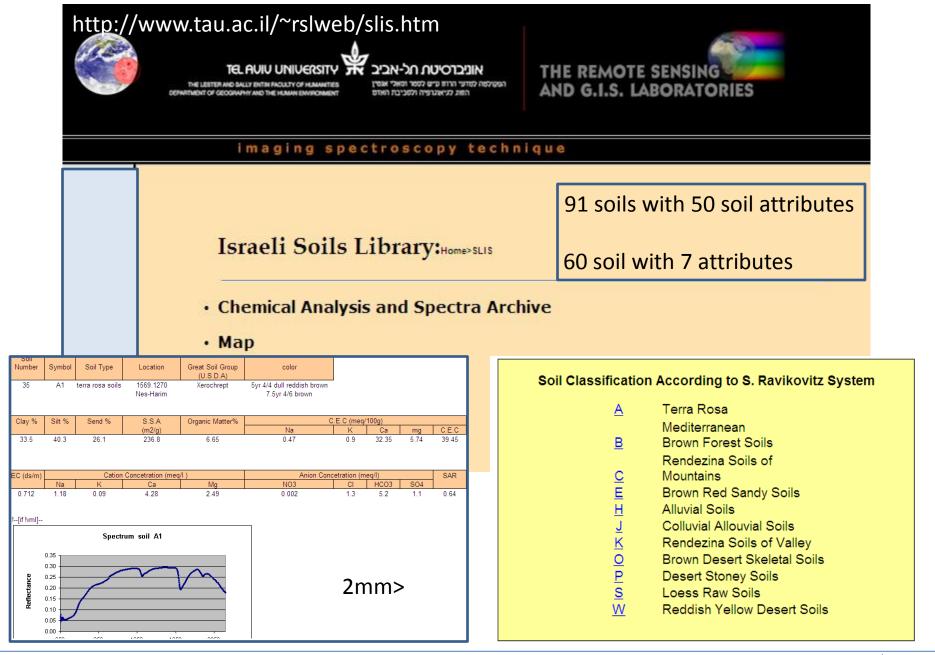




Several Soil Spectral Library are existed world wide

- Each were measured with a different protocol and spectrometers
- Still problematic to use as is for robust utilization

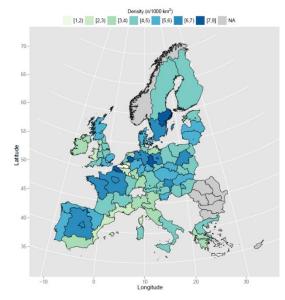




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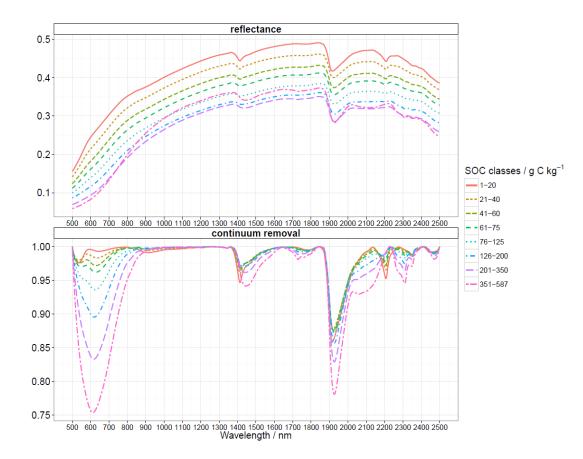


The LUCAS spectral library



Current status:

- 23 European countries
- ~20,000 high quality spectral readings
- Metadata: Clay, silt, sand, OC, pH, CEC, CaCO₃, Geographical coordinates, land use, etc



Creation of four subsets: Cropland,

Grassland, Woodland, and Organic soils

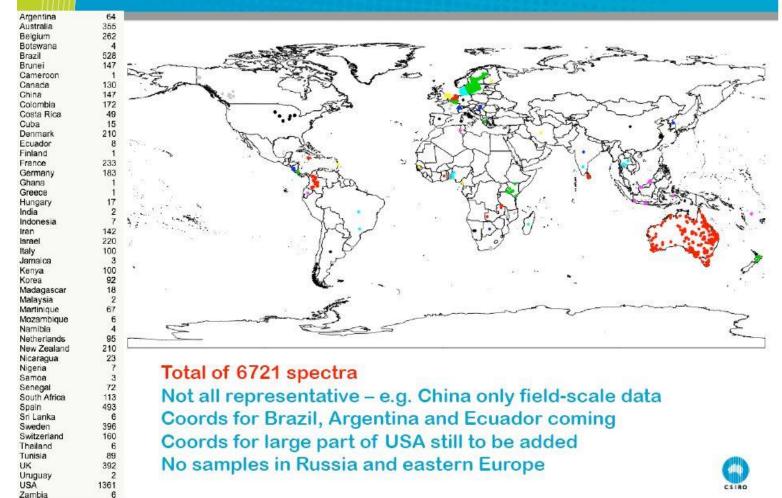
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Soil Spectral Library

Current global distribution of spectra



http://groups.google.com/group/soil-spectroscopy/files

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Recommended reading

- J. Coates, "Vibrational Spectroscopy: Instrumentation for Infrared and Raman Spectroscopy", Applied Spectroscopy Reviews, 1998, 33(4), 267 425.
- A.S. Bonanno, J. M. Olinger, and P.R. Griffiths, in Near Infra-Red Spectroscopy, Bridging the Gap Between Data Analysis and NIR Applications, Ellis Horwood, 1992.
- C.E. Miller, "Chemical Principles of Near Infrared Technology", Chapter 2 in Near Infrared Technology: In the Agricultural and Food Industry, P. Williams and K. Norris (Editors), Amer. Assn. of Cereal Chemists; 2nd Ed. (November 15, 2001).
- H.W. Siesler, "Basic Principles of Near Infrared Spectroscopy", In Handbook of Near Infrared Analysis Ed. D.A. Burns and E.W. Ciurczak, 3rd ed., CRC Press, Boca Raton, FLA.
- M. Blanco, J. Coello, A. Eustaquio, H Iturriaga, and S. Maspoch, Development and Validation of a Method for the Analysis of a Pharmaceutical Preparation by Near-Infrared Diffuse Reflectance Spectroscopy, Journal of Pharmaceutical Sciences, 1999, 88(5), 551 556.
- Dahm DJ, Dahm KD. 2001. The Physics of Near-Infrared Scattering. In Williams P, Norris K, editors. Near Infrared Technology in the Agricultural and Food Industries, 2nd ed., Saint Paul: American Association of Cereal Chemists, p 19-37.