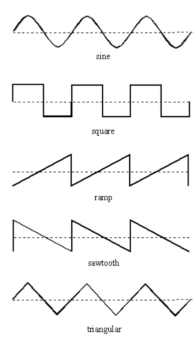
SPECTROSCOPY
Basic concepts
part 1

Umeå 2006-04-10 Bo Karlberg

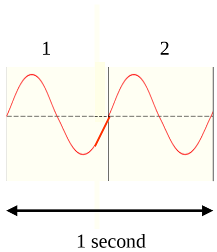
<u>Spectroscopy</u> is the science of spectra, i.e. it involves a measurement of a property that is a function of the frequency of the light

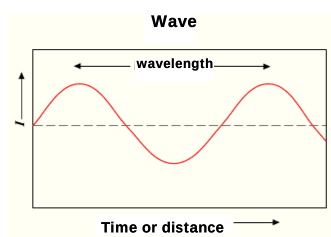
Light = electromagnetic radiation

Frequency = the number of a repeatedly occurring event per time unit

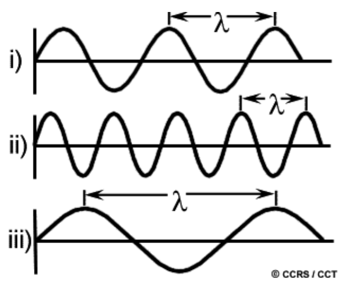


Example: Frequency = 2/s (2 Hz)





Definition of wavelength, λ



What about the wavelength of light?

The wavelength depends on the type of radiation we take into account

λ for visible light is in the range 380-780 nm

nm = nanometer, i.e. 10^{-9} m (one thousandth of a micrometer)

What about <u>the wavenumber</u> of light?

In spectroscopy we usually express *frequency* in the unit *wavenumber*, the dimension is **cm^{-1}** (reciprocal cm)

Conversion of nm to cm^{-1}
(and vice versa)

$$cm^{-1} = 10^7 / nm$$

$$nm = 10^7 / cm^{-1}$$

Exemple:

2500 nm – how many reciprocal cm?

$$cm^{-1} = 10^7 / 2500 =$$

$$10000000/2500 = 4000$$

Light is a wave motion but can also be regarded to be a stream of photons.
All these photons have an energy that is defined by the wavelength of the light.

An X-ray photon has a high energy whilst a radiowave photon has a low energy.

- An X-ray photon or a UV photon can degrade chemical compounds
- A photon in the visible range can change the electron structure of a chemical compound
- A photon in the IR range accomplish vibrations and rotations of molecules

Wiens law:

$\lambda_{max} T = b$

where T is the absolute temperature and b is a constant

Thus:

A hot body radiates photons with high energy while a cold body radiates photons with low energy

Exemple: sun – earth

The inner temperature of the sun is several billions degrees. This corresponds to lethal X-ray radiation. However, our experience is that the sun emits yellow light, i.e. light in the visible range.

Exemple: sun – earth

This is explained by the fact that the surface temperature is about 6000 K.

The atmosphere is transparent to visible light. The ozone layer absorbs parts of the UV light.

Exemple: sun – earth

The average temperature of the earth’s surface is about 20 C or 300 K.

The earth emits IR radiation to the universe

Exemple: sun – earth

Normally, the sum energy of incoming radiation = sum energy of outgoing radiation

Exemple: sun – earth

The greenhouse effect??

The earth emits IR-radiation that is absorbed by carbon dioxide and water in the atmosphere.

These species absorb the radiation for a short while and then they reemit the radiation to the atmosphere – but also to the earth!

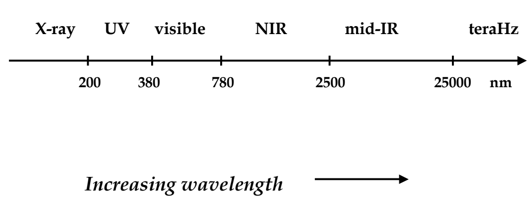
Exemple: sun – earth

An astronaut in outer space ”sees” the carbon dioxide-water layer of the earth – not the surface. This layer is significantly colder than the earth’s surface.

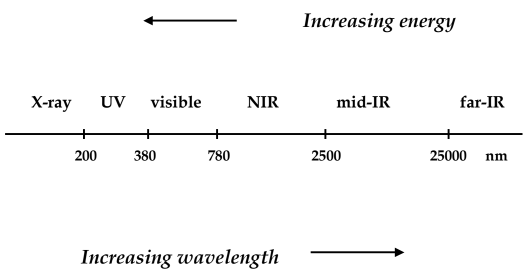
Exemple: sun – earth

If the earth surface had accounted for all the radiation that is emitted from our planet then the temperature here would have been 35 C lower than what it is today!

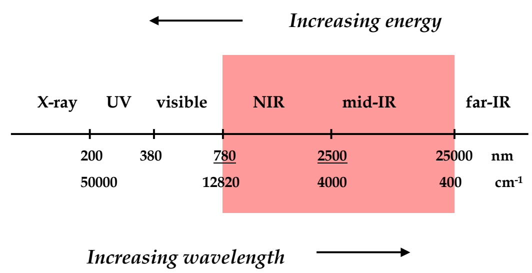
Light = electromagnetic radiation



Light = electromagnetic radiation



Our focus: NIR and mid-IR



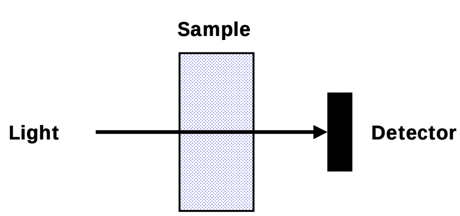
SPECTROSCOPY Basic concepts part 2

Let us examine the following concepts

- Transmittance
- Absorbance
- Reflection
- Scattering
- Polarisation

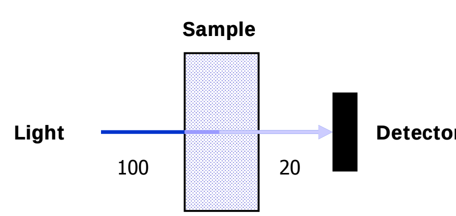
Transmittance

The sample absorbs a fraction of the light



Transmittance

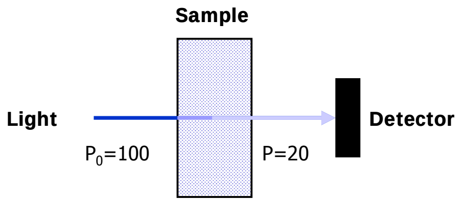
The sample absorbs a fraction of the light



100 photons enter, 20 leave

Transmittance,

Usually denoted **T**



P, P_0 = power (suitable unit)

The transmittance, **T**,

is defined as

$$\mathbf{T = P/P_0}$$

In our example

T = 20/100 = 0.2

i.e. 20%

Absorbance?

$$\mathbf{A = \log (P_0/P)}$$

In our example:

A = log (100/20) = log5 =

= 0.699

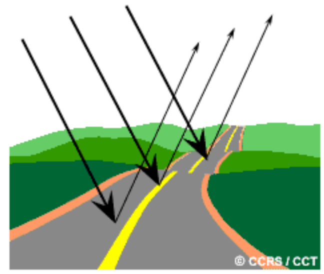
Note that

$$\mathbf{A = \log (P_0/P) = -\log T}$$

We can conclude that...

the light can be completely or partly absorbed by a sample. The light can also be reflected.

Reflection

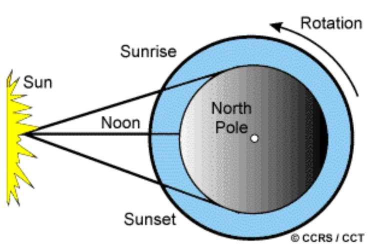


We get **specular** reflection when the surface is smooth, mirror reflection, i.e. all (almost all) light energy leaves the surface in a certain direction.
Diffuse reflection occurs when the surface is rough. Light is reflected in all directions.
Most surfaces yield a mixture of specular and diffuse reflection.
An important parameter is the ratio between the "roughness" and the wavelength of the light.
If the wavelength is much less than the surface variations or particle size then diffuse reflection dominates.

Exemple, fine grain sand is experienced to be smooth by microwaves but is experienced as rough by visible light.

Scattering

Rayleigh scattering occurs when the radiated objects are smaller than the wavelength. Objects = dust particles and down in size to molecules. Rayleigh scattering occurs more commonly at short wavelengths in comparison with long wavelengths. Rayleigh scattering is the dominating scattering mechanism in the upper part of the atmosphere. The blue color of the sky is a result of this phenomenon. When the radiation from the sun passes through the atmosphere, the short wavelengths (i.e. blue light) in the visible spectrum are "scattered" more than the longer wavelengths. At **sun rise and sun set** the light from the sun has to penetrate a longer distance in the atmosphere in comparison with the situation at daytime. The scattering of the short wavelengths the increases and we observe light with longer wavelengths.



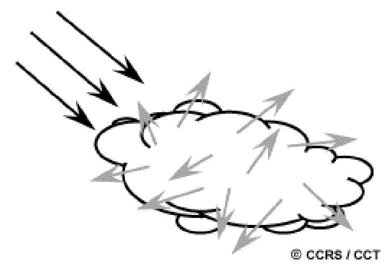
Scattering

Mie scattering occurs when the particles are of the same size as the wavelength of light. Dust, smoke and water vapor are common causes to Mie scattering. Compared with Rayleigh scattering Mie scattering occurs to a higher degree at long wavelengths. Mie scattering occurs in the low layers of the atmosphere where large particles are found and it dominates when the weather is cloudy.

Scattering

Nonselective scattering occurs when the particles are much larger than the wavelength of the light. Water drops and large dust particles give rise to this type of scattering. All wavelengths are "scattered" at the same degree – this explains the name *nonselective scattering*.
White clouds are white since the blue, green and red light will be scattered at the same degree. The eye observes blue + green + red light = white light.

Non-selective scattering



Polarisation

The electrical (and magnetical) field strength of an electromagnetic wave oscillates perpendicularly versus the travel direction of the wave. In three dimensions this means that if the wave propagates in the *x* direction then the electrical field strength can oscillate both in *y* and *z* directions or vary between these two directions in an organised or in an unorganised manner. The electromagnetic wave is said to have different modes of **polarisation**.

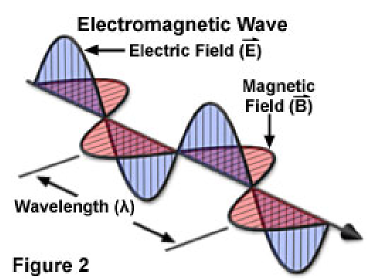


Figure 2

Polarisation

If we examine the light emitted by an ordinary tungsten lamp we will find that the electrical field strength can oscillate in all directions and randomly in the *yz*-plane. When there is no defined relationship between the time and the direction of the electrical field strength the light is said to be *unpolarised.* An unpolarised wave will oscillate in the *y* and *z* directions over time with the same probability. Consequently, we can assume that 50% of the intensity of an incoming unpolarised wave falls along the *y* axis – the other 50% falls along the *z* axis (or direction).