

# M5052

## CHARACTERIZATION OF MATERIALS AND NANOMATERIALS

*Graduate Program in Nanotechnology*

## UV-VIS SPECTROSCOPY

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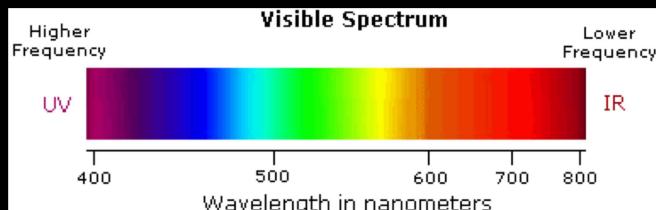


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### ULTRAVIOLET-VISIBLE SPECTROSCOPY

- UV-vis measures absorption of light with  $\lambda = 200\text{--}800\text{ nm}$
- Visible spectrum:  $\lambda=800\text{--}400\text{ nm}$
- Ultraviolet Spectrum :  $\lambda = 400\text{--}10\text{ nm}$ 
  - UVA: 315–400 nm
    - “Black lights” emit UVA
  - UVB: 280–315 nm
  - UVC: 100–280 nm
- EUV:  $\lambda = 10\text{--}121\text{ nm}$ , extreme UV, ionizing radiation
- Atmosphere absorbs UV with  $\lambda < 200\text{ nm}$ 
  - “Vacuum Ultraviolet” range



**Violet:** 400 - 440 nm  
**Blue:** 440 - 490 nm  
**Green:** 490 - 570 nm  
**Yellow:** 570 - 585 nm  
**Orange:** 585 - 620 nm  
**Red:** 620 - 780 nm

A strip of LED “black lights” glows violet since its emission overlaps the end of the visible spectrum

Photo taken from: Amazon Germany: <https://www.amazon.de/Schwarzlicht-Streifen-SMD3528-300LED-beleuchtung/dp/B01MFGAHJW/>

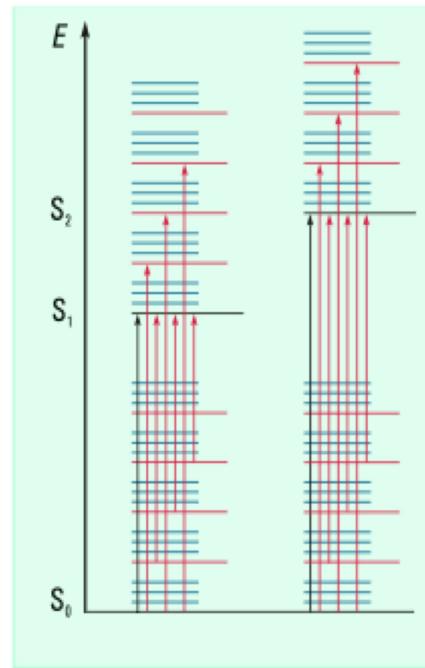


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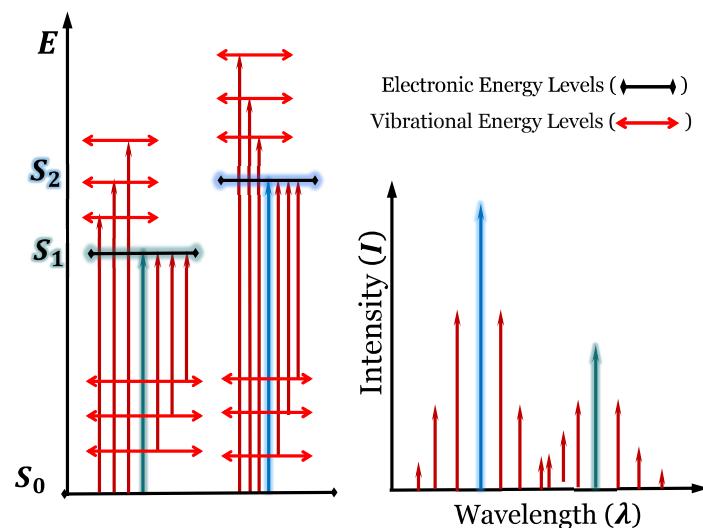
# ULTRAVIOLET-VISIBLE ABSORPTION

- In practical usage the range  $\lambda = 200\text{--}800\text{ nm}$  is used in UV-vis
- Absorption occurs if the photon energy is equal to the difference between two energy levels of an orbital
  - Quantized transitions
- Photons excite electrons to antibonding states
  - Electrons from both bonding and non-bonding orbitals
  - Energy of photons from 800 – 200 nm is equivalent to 35 – 143 kcal/mol (150–600 kJ/mol)
  - Less than the energy required to break most covalent bonds



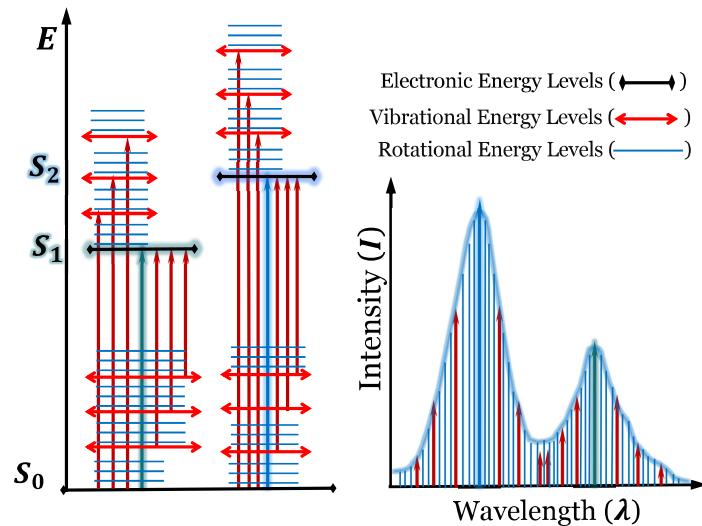
# UV-VIS BAND BROADENING

- Excitation to electronic levels define main peak positions
- Each electronic level has **vibrational levels** with different transition energies
  - Less energy required from transition of vibrational states of  $S_0$  to  $S_1$  (or  $S_2$ , etc.)
  - More energy required for transitions from  $S_0$  to vibrational levels of excited electronic states ( $S_n$ )



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- Each vibrational level has different **rotational levels**
  - Small energy difference for transitions to and from those rotational levels



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## UV-VIS BAND BROADENING

- Different bond **vibrations** and rotations are associated to the different electronic energy levels of molecules
- Electron transitions can occur between different **vibrational** and **rotational** energy levels around the transition energies of **electronic levels**
- UV or visible photons excite electrons from the ground level and its sublevels to excited electronic levels, and their sublevels

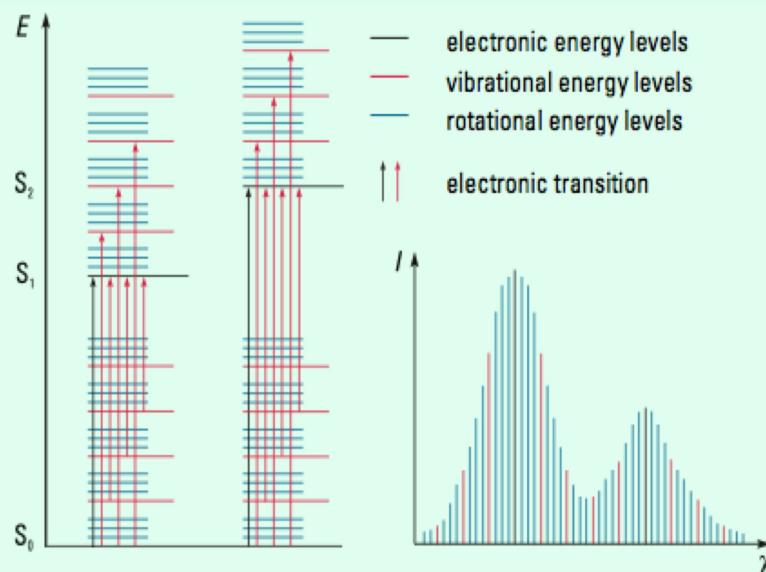


Image taken from: Tony Owen, "Fundamentals of modern UV-visible spectroscopy – A Primer" Agilent Technologies, Germany, 2000. Downloaded from: [https://www.agilent.com/cs/library/primers/public/59801397\\_020660.pdf](https://www.agilent.com/cs/library/primers/public/59801397_020660.pdf)

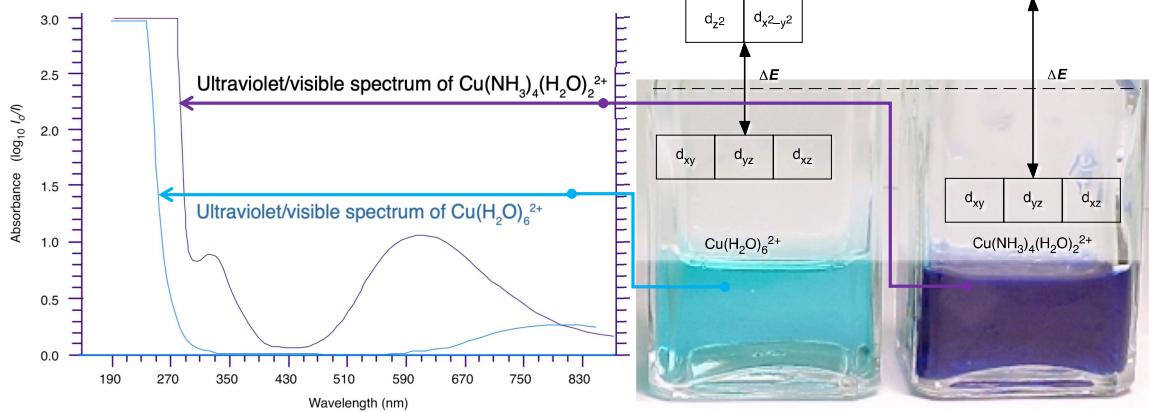


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# CHEMICAL ENVIRONMENT EFFECT ON ABSORPTION

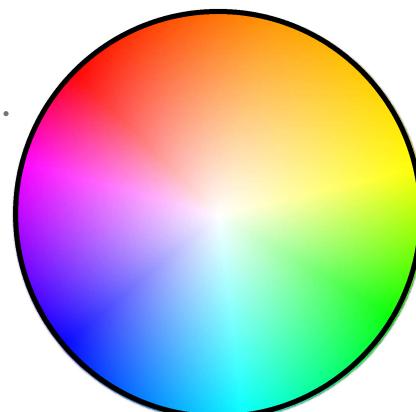
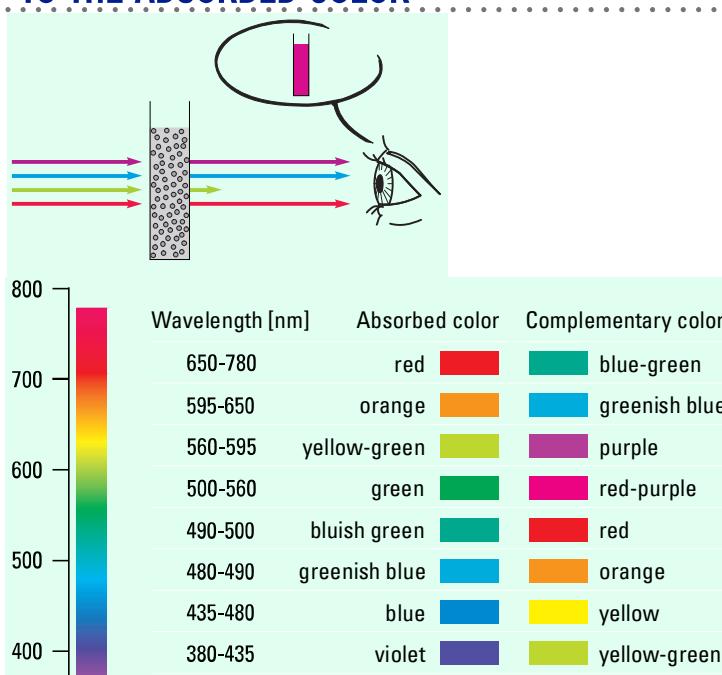
- Example: Copper (II) coordination complexes
- Uncomplexed Cu(II) cations do not absorb in the visible
  - They absorb shorter waves (higher energy) and are colorless
- For complexed ions 3d energy levels are split allowing absorption of lower energy photons
- Hydrated Cu(II) cations absorb in the visible (red) and solution looks blue
- Ammonia complex has a blue-violet color
  - Different separation between energy levels due to interaction of ammonia with d orbitals of Cu(II)
  - Position of the absorption peak changes



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## OBSERVED COLOR IS COMPLEMENTARY TO THE ABSORBED COLOR



COLOR WHEEL

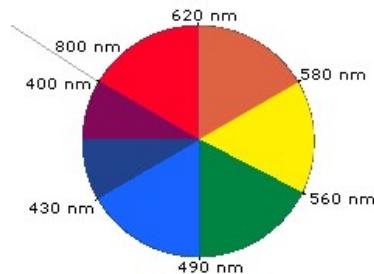


Table and image above from: Tony Owen, "Fundamentals of modern UV-visible spectroscopy – A Primer" Agilent Technologies, Germany, 2000. Downloaded from: [https://www.agilent.com/cs/library/primers/public/59801397\\_020660.pdf](https://www.agilent.com/cs/library/primers/public/59801397_020660.pdf)

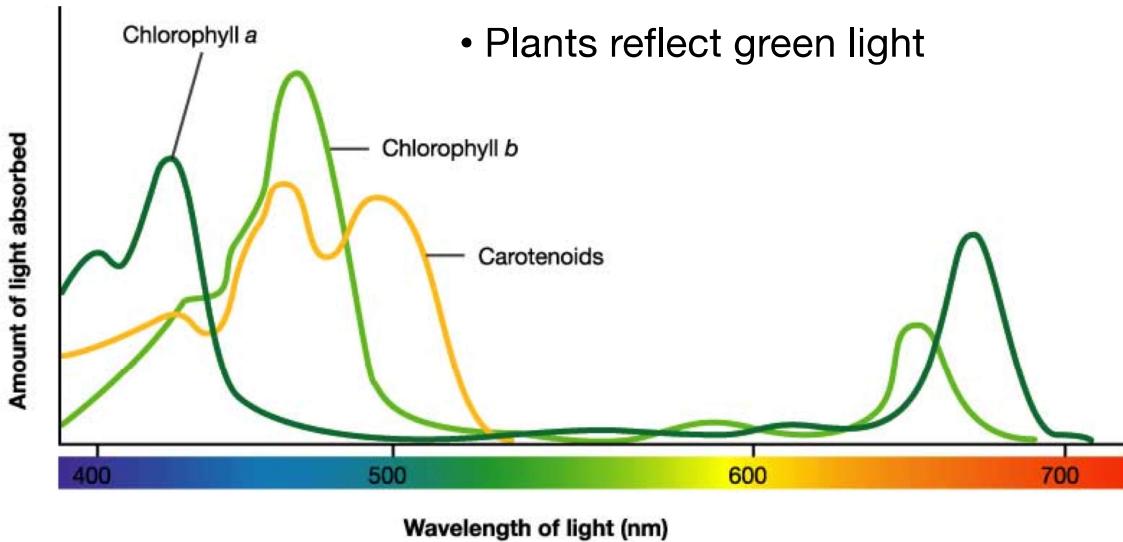


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# UV-VIS SPECTRUM OF CHLOROPHYLL

- Chlorophyll absorbs red and blue
- Plants reflect green light



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## SOLVENT EFFECT

- Maximum of the absorption peak may shift due to polarity of the solvent
  - Formation of hydrogen bonds also affects peak position

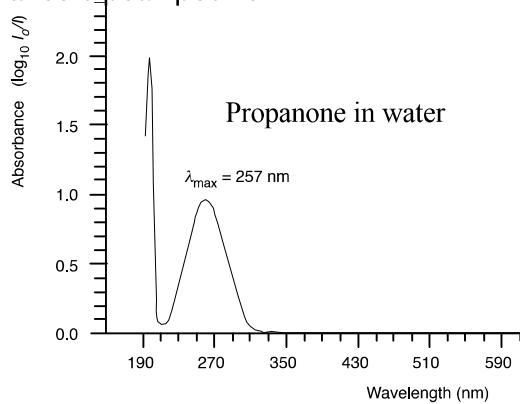
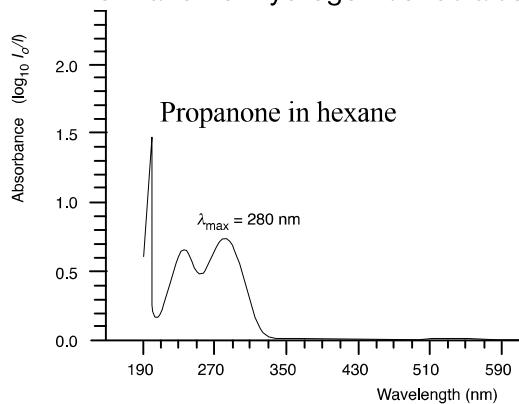


Table 3 The effect of the solvent on the absorption maximum of propanone

Solvent	$\lambda_{\max}/\text{nm}$	$\epsilon$ at $\lambda_{\max}$
Hexane	280	14.8
Trichloromethane	277	17.0
Ethanol	271	15.2
Water	257	17.4

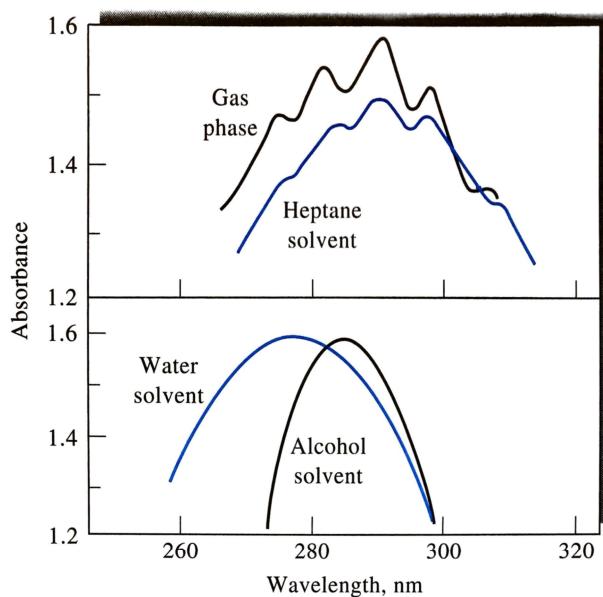


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# SOLVENT EFFECTS

- Shape and position of absorption bands can change for a molecule in different solvents



**FIGURE 14-6** Effect of solvent on the absorption spectrum of acetaldehyde.

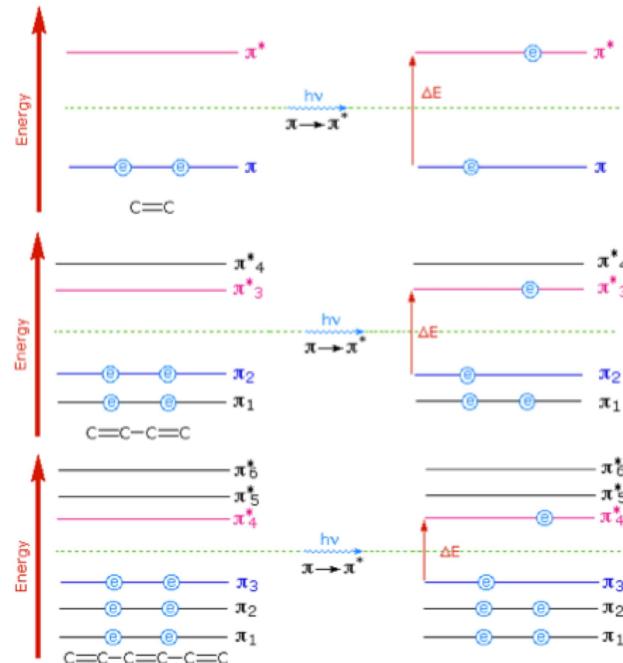
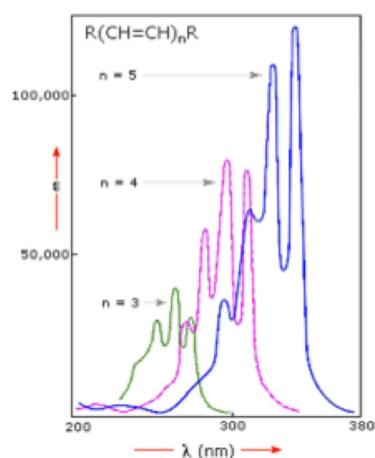


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## CONJUGATION EFFECT

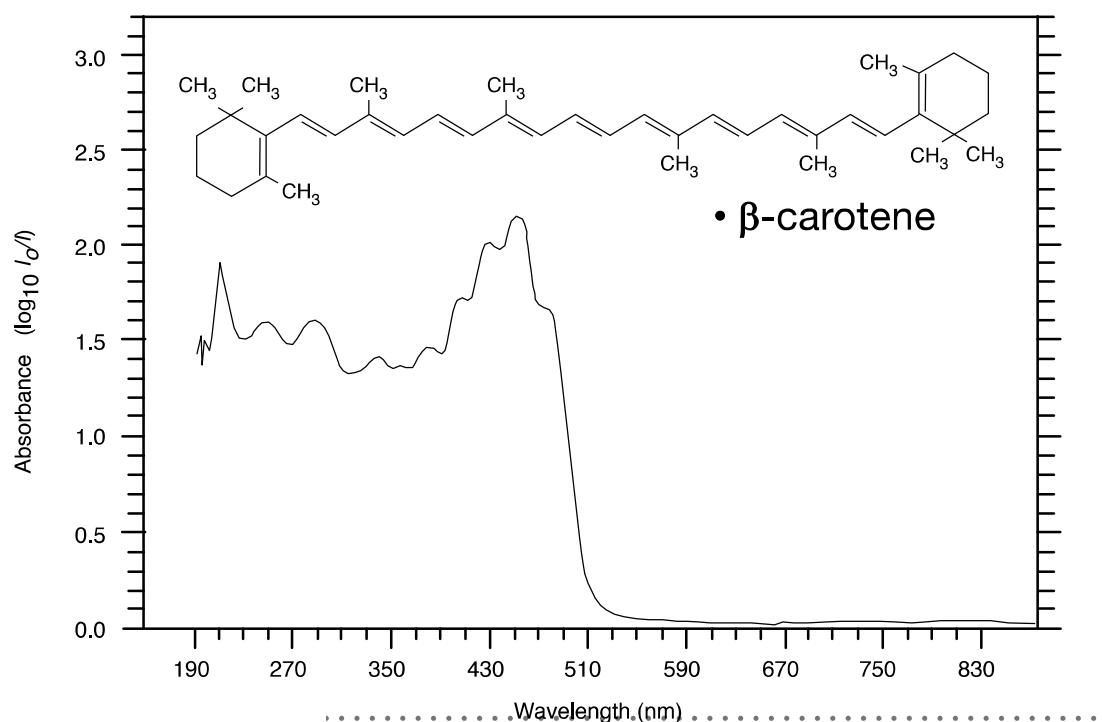
- Conjugation of  $\pi$  bonds has a large effect on UV-Vis spectra
- HOMO and LUMO become closer
- Lower energy, larger  $\lambda$



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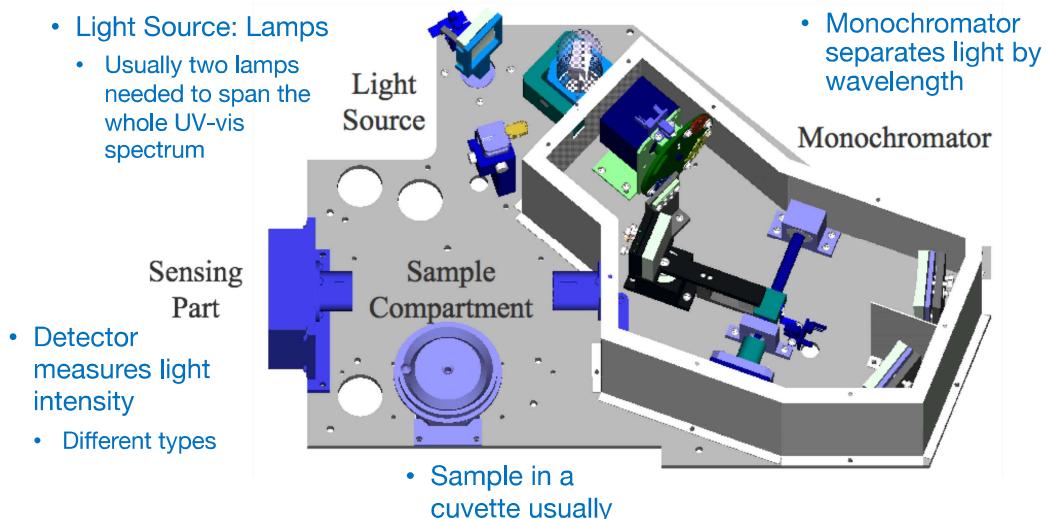
# CONJUGATION EFFECT



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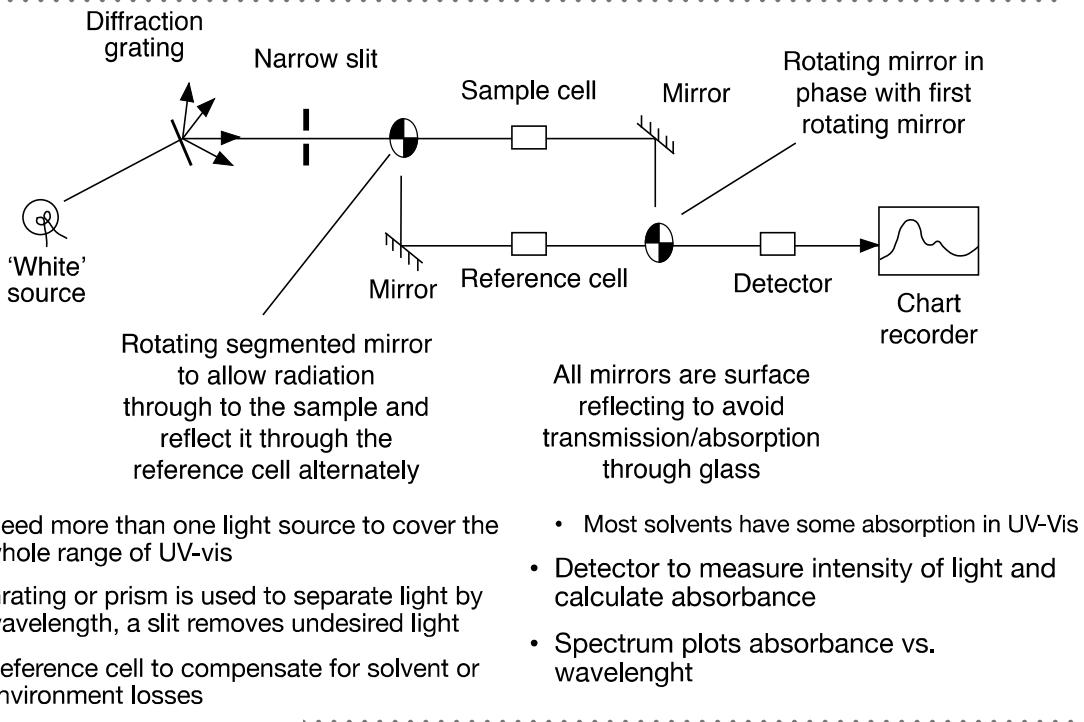
## SCHEMATIC DIAGRAMS OF UV-VIS SPECTROPHOTOMETERS



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# SCHEMATIC OF A UV-VIS SPECTROPHOTOMETER



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## TYPES OF UV-VIS PHOTOMETERS AND SPECTROPHOTOMETERS

- Conventional Single-beam Instruments
  - Light from source (collimated into a beam by slit) passes through a monochromator (dispersing device plus slit), then through the sample and then to a detector
- Single Beam Spectrophotometer:
  - The dispersion device is used to scan different wavelengths sequentially
  - Absorption is measured on a spectrum (range of wavelengths)
- Single Beam Photometer
  - Measures absorbance at a specific point of the spectrum (colorimetry)
  - Dispersion device and slit used to select a specific wavelength (a narrow band)

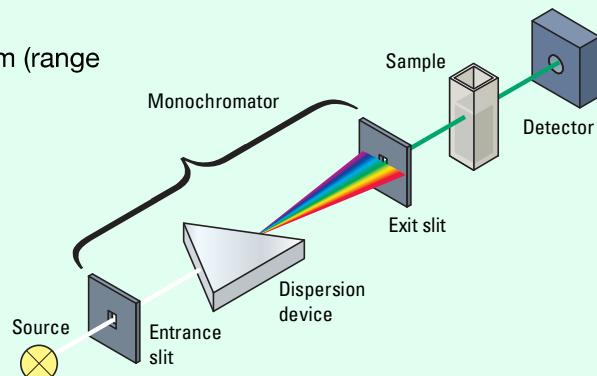


Diagram taken from: Anthony Owen, "Fundamentals of modern UV-visible spectroscopy – A Primer" Agilent Technologies, Germany, 2000. Downloaded from: [https://www.agilent.com/cs/library/primers/public/59801397\\_020660.pdf](https://www.agilent.com/cs/library/primers/public/59801397_020660.pdf)

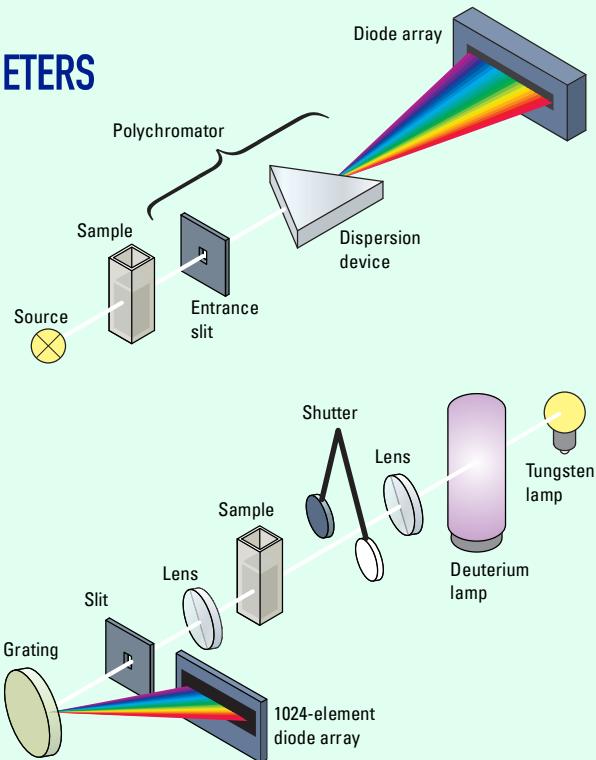


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## MULTI-CHANNEL SPECTROPHOTOMETERS

- A photodiode array is used as detector allowing to detect several spectral bands at the same time
- The dispersion device is placed after the sample
  - Since it is not selecting a single wavelength it is called a polychromator instead of monochromator
  - Polychromators allow simultaneous measurement of several wavelengths
- Multi-channel instruments can measure the full spectrum in very short times



Diagrams taken from: A. Owen, "Fundamentals of modern UV-visible spectroscopy – A Primer" Agilent Technologies, Germany, 2000. Downloaded from: [https://www.agilent.com/cs/library/primers/public/59801397\\_020660.pdf](https://www.agilent.com/cs/library/primers/public/59801397_020660.pdf)



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## DOUBLE BEAM SPECTROPHOTOMETER

- Measurement alternates between sample and reference
  - Better compensation of any variation in intensity of the light source
  - A “chopper” (rotating segmented mirror) directs the beam either to the sample or the reference

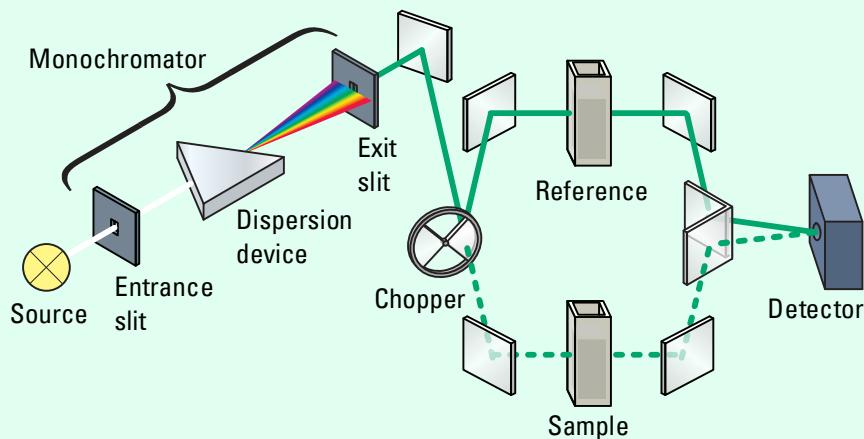


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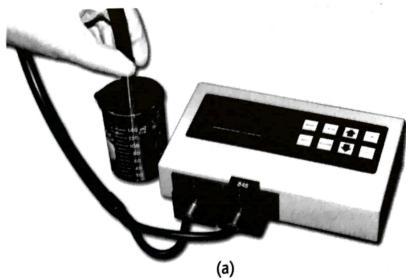


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# PROBE-TYPE SPECTROPHOTOMETER

- A probe can be inserted to measure an analyte in a solution instead of placing a sample in a cuvette
- In some cases this can be used to monitor a reaction continuously

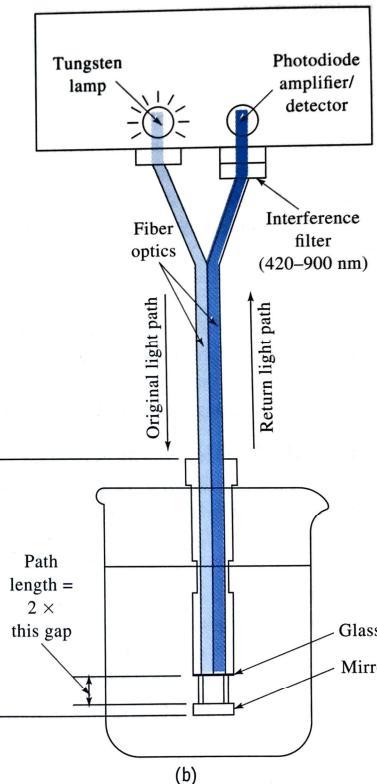


(a)

Figure from Skoog et al. Principles of Instrumental Analysis, 7<sup>th</sup> ed. Cengage Learning, 2017



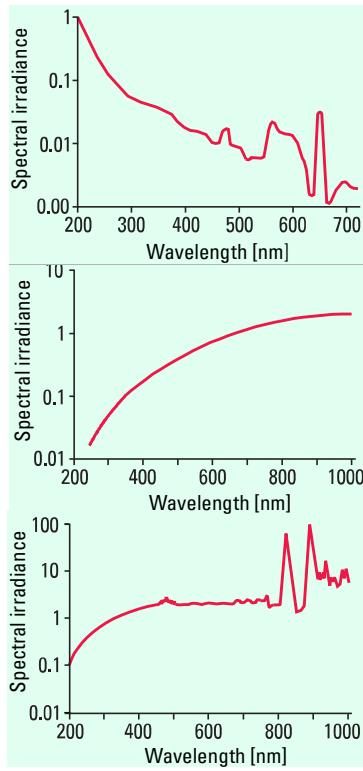
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**FIGURE 13-18** Photograph (a) and schematic diagram (b) of a probe-type photometer. (Courtesy of Metrohm USA, Riverview, FL.)



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## LAMPS FOR UV-VIS

- Deuterium Arc
  - 190–420 nm (UV)
- Tungsten Filament
  - Incandescence due to electric heating in an inert gas
  - 390–2500 nm (from near UV to near IR)
- Tungsten Halogen
  - Adds a small amount of halogen in the bulb
  - Extended range: down to 240 or 315 (depends on model)
- Xenon Arc
  - 190–800 nm (UV-VIS)
  - Extends to the IR range,
  - Characteristic emission lines of Xe emitted between 750 and 1000 nm



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## MONOCHROMATORS

- Select a narrow band of wavelengths for analysis
- Entrance slit defines area of source viewed
  - Can filter undesired signals such as ambient light
- Collimator produces a parallel beam of radiation
  - Lens or mirror directs all light in a single direction
- Dispersing element separates light by wavelength
- Focusing element (lens or focusing mirror) to condense the beam
- Exit slit to isolate the desired spectral band

Figures modified from Skoog et al. Principles of Instrumental Analysis, 7<sup>th</sup> ed. Cengage Learning, 2017

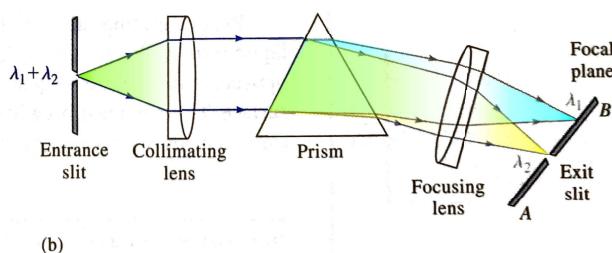
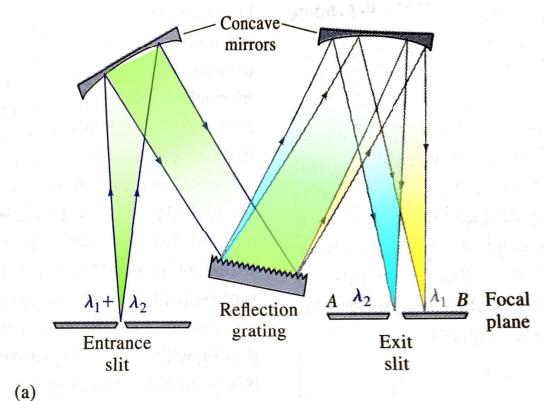


FIGURE 7-18 Two types of monochromators: (a) Czerny-Turner grating monochromator and (b) Bunsen prism monochromator. (In both instances  $\lambda_1 > \lambda_2$ .)



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# DISPERSING ELEMENTS

- Prism or reflection grating
- Light dispersed at different angles for different wavelengths

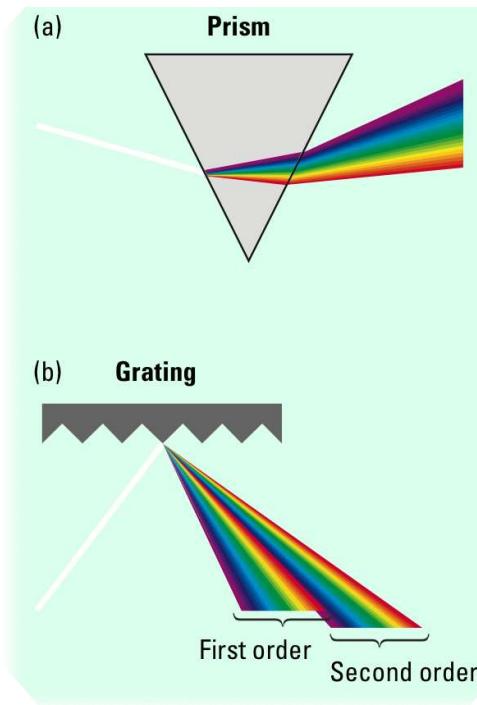


Figure above taken from: A. Owen, "Fundamentals of modern UV-visible spectroscopy – A Primer" ©Agilent Technologies.  
Photo of diffraction on a Compact Disc ©Fernando JRM, released under a creative commons license CC-BY-SA



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## WAVELENGTH BANDS

- Most dispersion elements only allow to select a band, not a pure monochromatic beam
- Output of wavelength selector (monochromator or filter) is defined by:
  - Nominal wavelength
  - The center of the peak of a band of wavelength
  - Peak shape is usually Gaussian
- Effective bandwidth
  - **FWHM** (full width at half the maximum intensity)
- Transmittance
  - Percent of the intensity relative to that of the source
- Effective bandwidth affects resolution

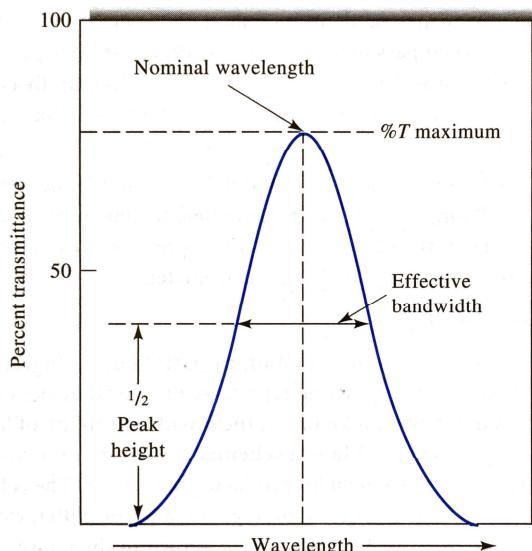


FIGURE 7-11 Output of a typical wavelength selector.

Figure from Skoog et al. Principles of Instrumental Analysis, 7<sup>th</sup> ed. Cengage Learning, 2017



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# FILTERS

- Used in photometers (colorimeters) to select a band from the spectrum
  - Also used to eliminate second order reflections from diffraction gratings
- Absorption Filters
  - Colored glass or dye film between glass plates
  - Absorb all wavelengths outside of a band

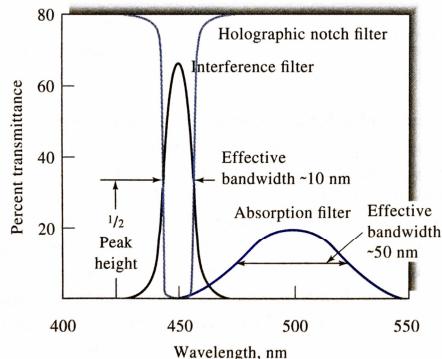


FIGURE 7-16 Effective bandwidths for three types of filters.



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- Cutoff filters

- Transmit wavelengths above or below a cut-off value

- Interference Filters

- Constructive interference selects a narrow band

- Holographic Notch Filters

- Reject a narrow band and transmit all others
- Not used much in UV-vis, widely used in Raman

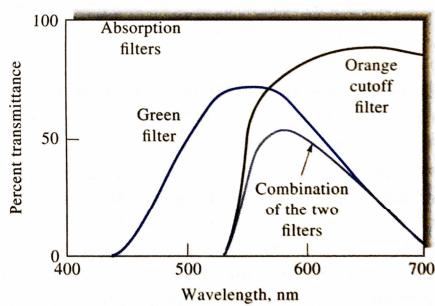


FIGURE 7-17 Comparison of various types of absorption filters for visible radiation.

Figures from Skoog et al. Principles of Instrumental Analysis, 7<sup>th</sup> ed.  
Cengage Learning, 2017

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# DETECTORS FOR PHOTOMETRY

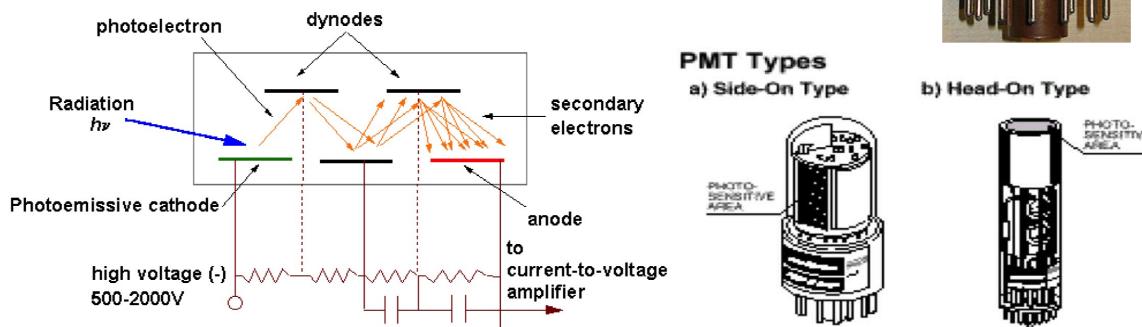


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# PMT DETECTORS

- Photomultiplier Tubes convert light intensity to a proportional electric signal
  - Photon collision in a photoemissive cathode emits a photo-electron
  - Signal is amplified by a series of electrodes charged to high voltage (dynodes)
  - Voltage is larger on each successive dynode multiplying the number of electrons emitted each time
- Generated photocurrent can be amplified further with electronic circuits

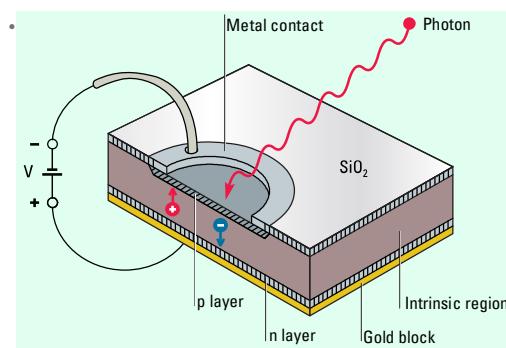


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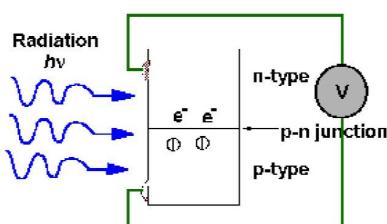
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# PHOTODIODE DETECTORS

- Absorption of a photon generates electron-hole pairs in a semiconducting diode
  - Electrons “jump” from the valence band to the conduction band
  - Junction between p-doped and n-doped material leads to separation of charges
  - This generates the electronic signal (photocurrent)
  - Silicon based photodiodes have a good response for detecting light from 170 to 1100 nm



Photodiode schematic taken from: A. Owen,  
“Fundamentals of modern UV-visible spectroscopy –  
A Primer” © Agilent Technologies



Unmounted photodiodes photo taken from: [https://www.thorlabs.com/newgroupage9.cfm?objectgroup\\_id=285](https://www.thorlabs.com/newgroupage9.cfm?objectgroup_id=285)

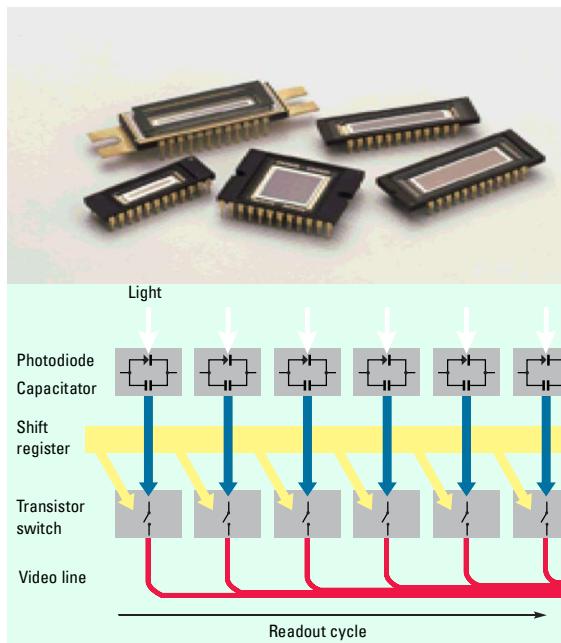


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# CHARGE-COUPLED DEVICE ARRAY DETECTORS

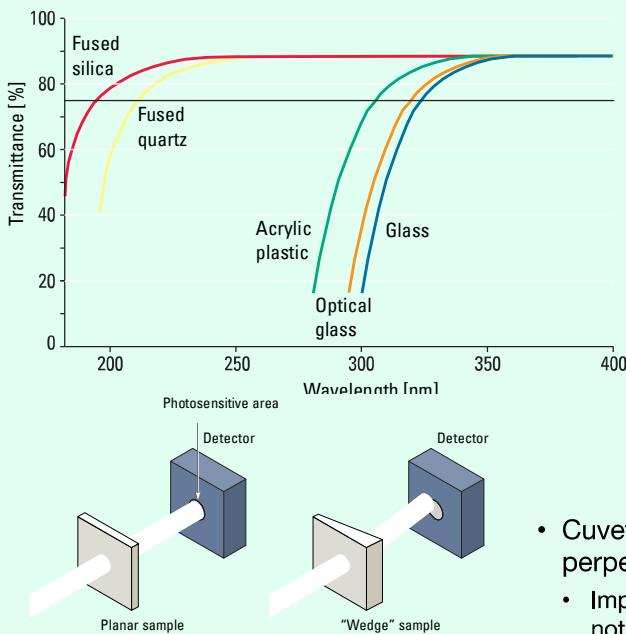
- A Charge-Coupled Device (**CCD**) is a device that transfers charge from the photoactive region (photodiode) via shift registers (capacitors) to a processing and/or recording circuit
  - Charge generated in each photodiode is proportional to number of photons
- CCD Arrays allow multiplexed measurements in spectroscopy
  - Each of the adjacent photodiodes in a linear array detects one narrow band of wavelengths
  - All wavelength bands detected at the same time
- Solid State Devices, usually very durable
- NOTE: CCD square arrays are used in many digital imaging applications, including astronomy and cameras



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## SAMPLE CELLS (CUVETTES)



- Standard width: 1 cm
- Different material options
  - ❖ Plastic (acrylic)
    - Absorbs below 300 nm
    - Inexpensive, but not durable
    - Low chemical resistance to some solvents
  - ❖ Glass
    - Absorbs below 320 nm
    - Very good chemical and mechanical resistance
  - ❖ Fused Silica or Fused Quartz
    - Absorption below ~190 nm
    - Very good chemical and mechanical resistance
- Cuvette walls must be very straight and perpendicular to the beam
  - Imperfections deviate light from the path and it does not reach the detector

Figures taken from: A. Owen, "Fundamentals of modern UV-visible spectroscopy – A Primer" Agilent Technologies, Germany, 2000. Downloaded from: [https://www.agilent.com/cs/library/primers/public/59801397\\_020660.pdf](https://www.agilent.com/cs/library/primers/public/59801397_020660.pdf)



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## EXAMPLES OF CUVETTES



• Micro cells, for  $\mu\text{L}$  volumes



• Flow through cells



Screw-cap cells, for anaerobic measurement, or long-term storage



Taken from: <https://www.sigmaaldrich.com/catalog/product/sigma/z600199>  $\wedge$  <https://www.fireflysci.com/screw-cap-spectrophotometer-cuvettes/>  $\wedge$  <https://www.sigmaaldrich.com/catalog/product/sigma/z626929>  $\wedge$  <https://shimadzu.com.au/cuvettes-spectrophotometry>

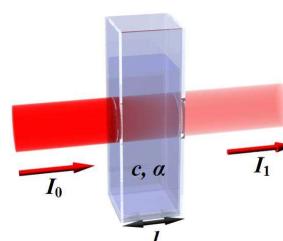


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## QUANTIFICATION IN SPECTROPHOTOMETRY BEER LAW

- Absorbance is proportional to concentration and path length  $A = \epsilon bc$
- $\epsilon$  : molar absorptivity (molar attenuation coefficient)  
Units:  $L/mol \cdot cm [=] mol^{-1} \cdot dm^{-3} \cdot cm^{-1}$
- $c$  : concentration of the absorbing chemical species ( $M$ ,  $mol/L [=] mol \cdot dm^{-3}$ )
- $b$  : path length, distance light travels through the sample ( $l, cm$ )
- $\lambda_{max}$  : wavelength of maximum absorption, the one used to measure absorbance
  - Linear relation of absorbance to  $\epsilon$  means that peak of maximum absorption gives better sensitivity for quantification
- Maximum absorbance in instruments is usually 4, due to exponential relation of absorbance to transmittance
  - $A = 4$  corresponds to 0.0001 transmittance
  - Dilution to absorbance below 3 is common for quantification



$$A = -\log_{10} T$$

$$A = \log_{10} \frac{P_o}{P}$$

Image taken from: [https://sk.wikipedia.org/wiki/Súbor:Lambert-Beerov\\_zákon.png](https://sk.wikipedia.org/wiki/Súbor:Lambert-Beerov_zákon.png)



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# INTERFERENCE CORRECTION

- If the spectrum of an interferent is known its absorption can be subtracted to find the real concentration of an analyte
- If absorption of interferent is Gaussian the absorbance at a reference wavelength can be estimated to be the same as the absorbance at the analytic wavelength
- This type of correction is called *isoabsorbance*

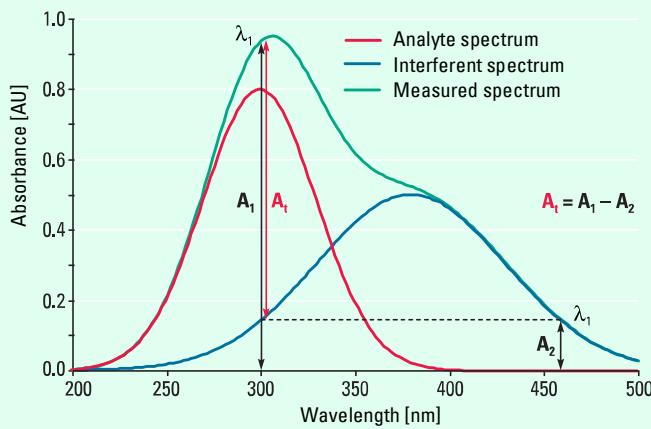


Figure taken from: A. Owen, "Fundamentals of modern UV-visible spectroscopy – A Primer" Agilent Technologies, Germany, 2000.



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## DERIVATIVE SPECTROPHOTOMETRY

- Taking the derivative of the spectrum can reveal additional details
  - First order derivative of absorbance with respect to wavelength ( $dA/d\lambda$ ) plotted as function of wavelength
  - Higher order derivatives can also be used
- *Feature Enhancement:* Derivative spectrum can allow distinguishing between two compounds with overlapping spectra
  - Derivative allows visualizing more clearly the positions of overlapping bands
- NOTE: differentiation degrades signal to noise ratio
  - High quality spectra with low noise are required for derivative spectrophotometry

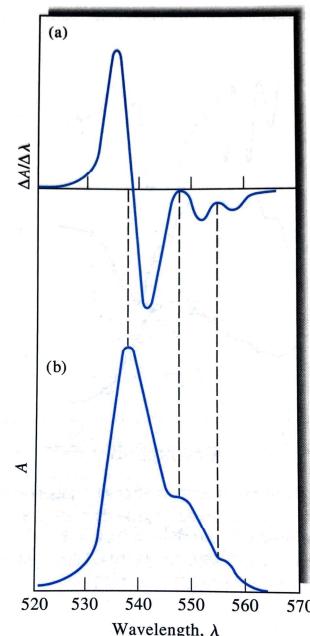


Figure from Skoog et al. Principles of Instrumental Analysis, 7<sup>th</sup> ed. Cengage Learning, 2017

**FIGURE 14-10** Comparison of a derivative spectrum (a) with a standard absorption spectrum (b).



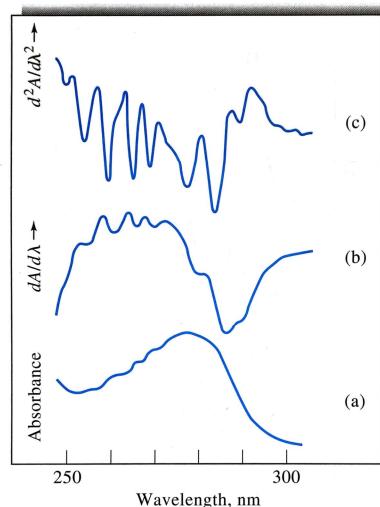
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# DERIVATIVE SPECTROPHOTOMETRY

- Derivative spectroscopy can reveal details lost due to scattering
  - Scattering of light leads to a broad band appearing in the UV-vis spectrum
- Example: proteins scatter light leading to a broad absorption band
  - Signals from absorption bands of aminoacids are lost
  - Sharp bands of aromatic aminoacids (tryptophan, tyrosine, phenylalanine) between 280 and 300 nm are revealed in the derivative spectra of bovine albumin

Figure from Skoog et al. Principles of Instrumental Analysis, 7<sup>th</sup> ed. Cengage Learning, 2017



**FIGURE 14-11** Absorption spectra of bovine albumin: (a) ordinary spectrum, (b) first-derivative spectrum, (c) second-derivative spectrum. (Reprinted with permission from J. E. Cahill and F. G. Padera, *Amer. Lab.*, **1980**, *12* (4), 109. Copyright 1980 by International Scientific Communications, Inc.)



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## SAMPLE PREPARATION FOR UV-VIS

- Most samples are analyzed in a dilute solution
  - Many solvent choices, depending on solubility of analytes
- Solvent Polarity may be important
  - Can cause peak shifts
- Calibration curves should be made with the same solvent used for the sample
- Different solvents have a different “cut-off wavelength”
  - Measurements below this lower wavelength are not trustworthy since the solvent itself absorbs too much light

**TABLE 14-3** Solvents for the UV and Visible Regions

Solvent	Lower Wavelength Limit, nm	Solvent	Lower Wavelength Limit, nm
Water	180	Diethyl ether	210
Ethanol	220	Acetone	330
Hexane	200	Dioxane	320
Cyclohexane	200	Cellosolve	320
Carbon tetrachloride	260		



Table from Skoog et al. Principles of Instrumental Analysis, 7<sup>th</sup> ed. Cengage Learning, 2017

Photo taken from: <http://lab-training.com/2016/09/14/select-right-cuvette-material-uv-vis-absorbance-studies/>



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# UV ABSORPTION BY SOLVENTS

**Table 4** Minimum wavelength at which different solvents are useful

Solvent	Minimum wavelength (nm)
Ethanonitrile	190
Water	191
Cyclohexane	195
Hexane	201
Methanol	203
Ethanol	204
Ethoxyethane	215
Dichloromethane	220
Trichloromethane	237
Tetrachloromethane	257

- Below the cut-off or minimum wavelength solvent absorbance is significant
- The cut-off is taken as the point where solvent absorbance is 1 (10% transmittance)
- Health and safety hazards may also need to be taken into account

## Properties of some common solvents

Solvent	Polarity *	Cut-off wavelength (nm)**	Hazard***
Distilled water	78.5	< 195	none
Hexane	1.9	199	F
Ethanol (absolute)	24.3	207	F
Methanol	32.6	210	F
Cyclohexane	2.0	211	F
Chloroform	4.8	246	F/T
Dimethylsulfoxide	none	270	H
Acetone	20.7	331	F

\* Dielectric constant at ambient temperature

\*\* Wavelength at which transmittance of 10-mm path length is < 25 %

\*\*\* F = flammable; T = toxic; H = health hazard

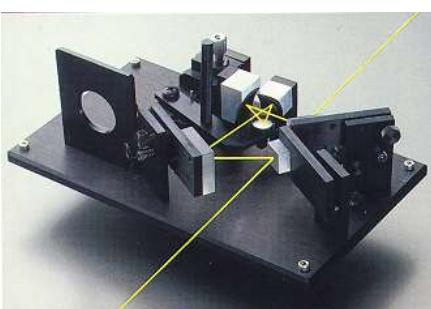


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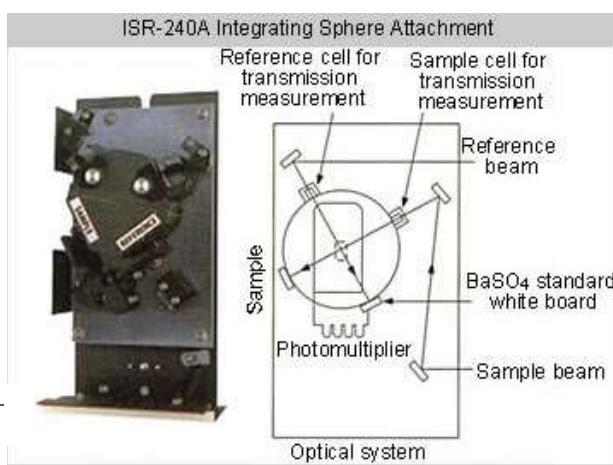
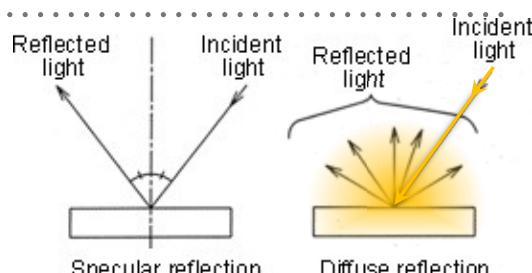
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# ANALYSIS OF SOLID SAMPLES BY UV-VIS

- Solid samples can be analyzed by diffuse reflectance
  - Wavelengths that are not absorbed get reflected in random directions
  - Sample can be diluted mixing with a powder that does not absorb UV-Vis
- Measurement of reflectance relative to a reference standard white board



Images taken from <https://www.ssi.shimadzu.com/products/uv-vis-spectrophotometers/diffuse-reflectance-measurement.html>



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# APPLICATIONS OF UV-VIS SPECTROSCOPY



## QUALITATIVE V. QUANTITATIVE ANALYSIS BY UV-VIS

- UV-Vis is rarely used for qualitative analysis
  - Band broadening makes it difficult to make definitive identifications
  - Separation of characteristic electronic transitions is not easy due to the many vibrational and rotational transitions
- UV-vis can be used to *verify* the identity of a substance by comparison to reference spectra
  - Compare the shape of the spectrum, and the wavelength of maximum absorption ( $\lambda_{max}$ )
  - Determine the molar absorptivity coefficient ( $\epsilon$ )
- Both numbers *together* ( $\lambda_{max}$  and  $\epsilon$ ) can be used to identify a substance
  - Values are characteristic of a substance
  - But both values may change with the solvent and other factors (pH, T), which limits usability for qualitative analysis
- UV-vis spectroscopy is used mostly as a quantitative technique
  - Easy to calculate concentrations knowing  $\lambda_{max}$  and  $\epsilon$



# GENERAL APPLICATIONS OF UV-VIS SPECTROPHOTOMETRY

- Applications on Quantitative Analysis
  - Solvents
  - Functional groups
  - Cleanliness/purity of Materials
- Photometric and Spectrophotometric titrations
  - Color change of indicator or absorbance of a reactant or product
- Verify identity of compounds
  - Organic Compounds
    - Aromatic compounds and
- compounds with conjugated double bonds
  - Polymers
  - Bio-macromolecules
  - Et cetera, Etc. &c...
- UV-vis absorption spectra of nanoparticles and other nanomaterials
  - Quantum Dots
  - Metal Nanoparticles
  - Core-shell nanoparticles
  - Fluorescent carbon dots

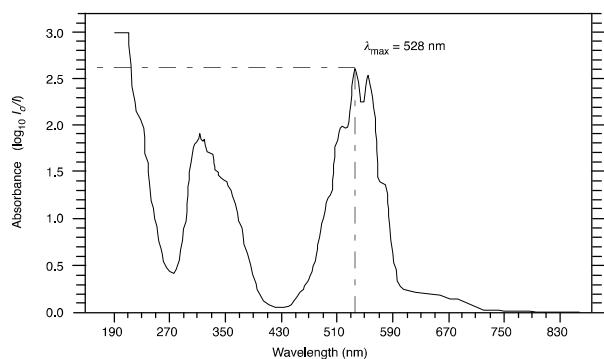


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## APPLICATIONS OF UV-VIS FOR ELEMENTAL ANALYSIS

- Inorganic Compounds
  - Lanthanides
  - Colored ions
  - Organometallic Coordination Complexes
- Analysis of solutions of transition metal ions
- Determination of metals in materials
  - Example: determine manganese in steel
  - Dissolve steel alloy
  - Oxidize Mn to manganate ion, Mn(VII)
  - Determine concentration by UV-Vis



The solution used to obtain this spectrum contained 1.227 mg of potassium manganate(VII) in 5.0 cm<sup>3</sup> of solution. From the spectrum  $\epsilon$  is found to be  $1.68 \times 10^3$



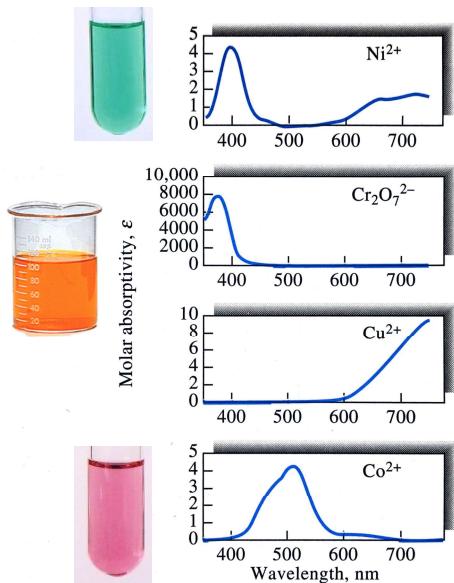
$\text{MnO}_4^-$  (manganate)



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## UV-VIS ABSORPTION OF SOME METAL IONS

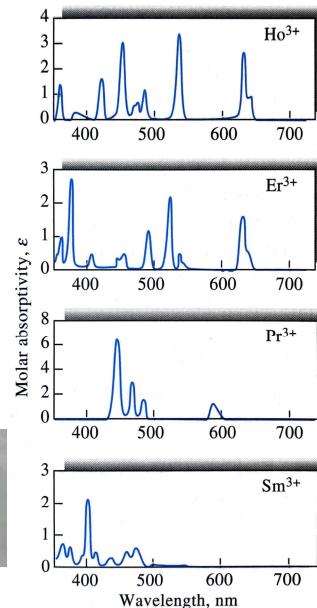


**FIGURE 14-3** Absorption spectra of aqueous solutions of transition metal ions.

Figures from Skoog et al. Principles of Instrumental Analysis, 7<sup>th</sup> ed. Cengage Learning, 2017 // Photos of solutions of Ni(II), Co(II), Er(III), and Sm(III) by "Cyberchemist" at Flickr: www.flickr.com/photos/37388341@N00/1507307061 / www.flickr.com/photos/37388341@N00/1508161024 / www.flickr.com/photos/37388341@N00/1490867161 / www.flickr.com/photos/37388341@N00/1490866103  
Dichromate solution from: http://www.chem.uiuc.edu/webfunchem/chromate/shift.htm



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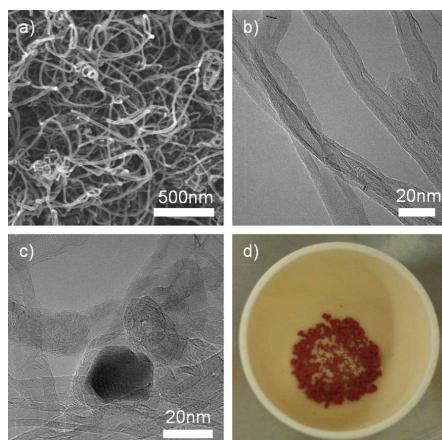


**FIGURE 14-4** Absorption spectra of aqueous solutions of rare earth ions.

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## EXAMPLE: IRON CONTENT IN CARBON NANOTUBES BY UV-VIS

- Iron is used as catalyst for the growth of CNT
  - Carbon encapsulated iron nanoparticles are a common impurity
- Oxidizing acid digestion was used to extract iron in solution from a sample of Carbon Nanotubes (CNT)
- Complex of iron with phenantroline used for quantification
  - Intense color (large molar absorptivity) of coordination complex allows determining much smaller amounts than with ion alone
- Elsy Agustina, et al. "Simple and Precise Quantification of Iron Catalyst Content in Carbon Nanotubes Using UV/Visible Spectroscopy" ChemistryOpen 2015, 4, 613 – 619



**Figure 1.** a) SEM and b) TEM images of CNTs. TEM images show their multi-layered structure and an average diameter of 15.5 nm, calculated from 90 nanotubes. c) TEM image of a metal particle encapsulated in multiple graphitic layers. d) Red-colored ash formed by oxidizing CNTs at 900 °C, 3.51% by weight, taken by a digital camera.



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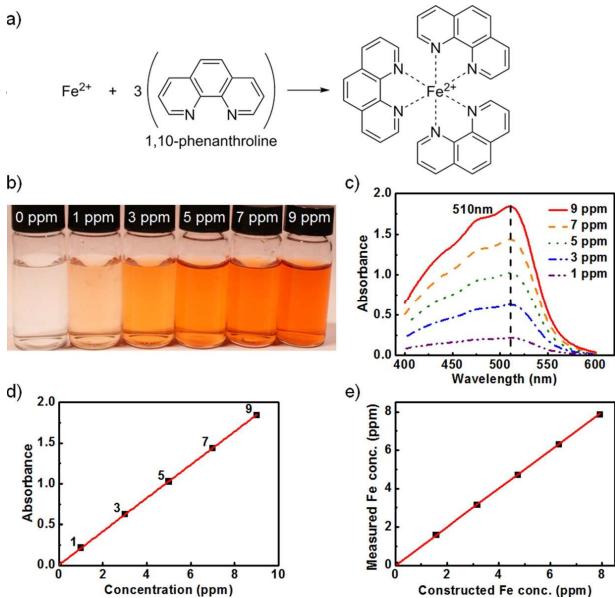
## EXAMPLE:

### IRON CONTENT OF CARBON NANOTUBES

- Calibration curve used to determine iron content of an unknown sample
- Elsye Agustina, et al. "Simple and Precise Quantification of Iron Catalyst Content in Carbon Nanotubes Using UV/Visible Spectroscopy" ChemistryOpen 2015, 4, 613 – 619



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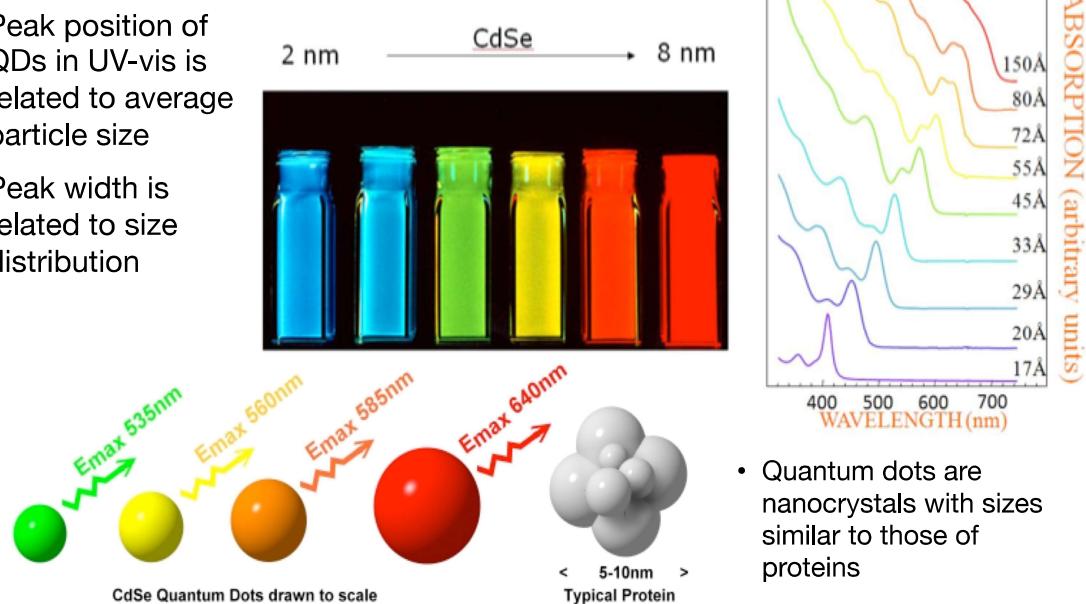
**Figure 2.** a) Scheme of Fe-phen complex formation; coordination of an  $\text{Fe}^{2+}$  ion with three phen molecules via lone-pair electrons on the N atoms of phen. b) Standard solutions of Fe-phen complex used for calibration, containing Fe concentrations from 0–9 ppm, taken by a digital camera. The red-orange color of the solutions becomes stronger as the Fe concentration increases. c) Absorption spectra of the standard solutions in the visible spectral range, measured by UV/Vis spectroscopy. The absorbance was measured at the maximum peak position of 510 nm for the absorption spectra shown in panel c. Linear relationship between optical absorbance and Fe concentration for the standard solutions. The absorbance was measured at the maximum peak position of 510 nm for the absorption spectra shown in panel c. Linear fitting:  $A = 0.20423C + 0.00716$ ,  $R^2 = 0.99994$ . The coefficient of determination to designate linearity is calculated using  $R^2 = \frac{\sum(y_i - \bar{y})^2}{\sum(y_i - \bar{y})^2}$ . Here,  $y_i$  is the observed absorbance value,  $\bar{y}$  is the mean absorbance, and  $\hat{y}_i$  is the fitted absorbance value. e) Fe concentrations measured from the constructed solution by mixing pure Fe and Al solutions. Linear fitting:  $y = 0.99114x + 0.00701$ ,  $R^2 = 0.99998$ .

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### UV-VIS SPECTROSCOPY FOR NANOMATERIALS:

#### QUANTUM DOTS

- Peak position of QDs in UV-vis is related to average particle size
- Peak width is related to size distribution

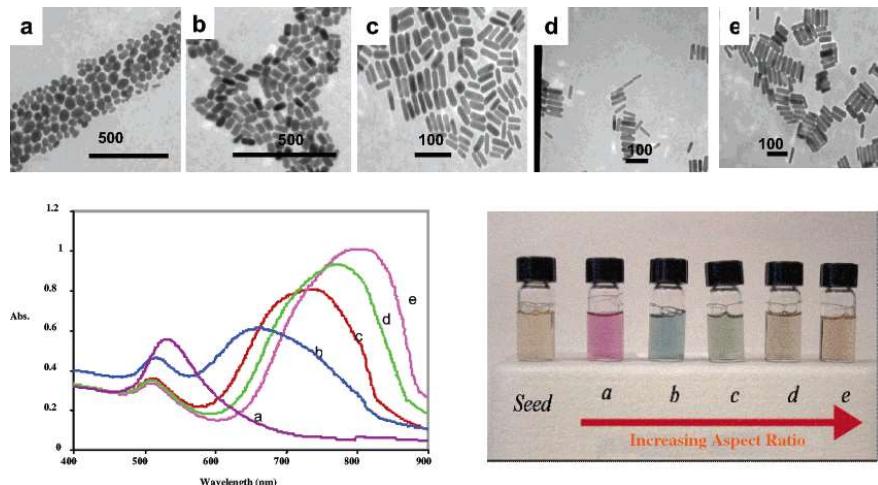


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# UV-VIS SPECTROSCOPY FOR NANOMATERIALS: ANISOTROPIC GOLD NANOPARTICLES

- The UV-vis absorption spectrum varies with changes in the aspect ratio of the nanoparticles



**Figure 1.** Transmission electron micrographs (top), optical spectra (left), and photographs of (right) aqueous solutions of gold nanorods of various aspect ratios. Seed sample: aspect ratio 1; sample a, aspect ratio  $1.35 \pm 0.32$ ; sample b, aspect ratio  $1.95 \pm 0.34$ ; sample c, aspect ratio  $3.06 \pm 0.28$ ; sample d, aspect ratio  $3.50 \pm 0.29$ ; sample e, aspect ratio  $4.42 \pm 0.23$ . Scale bars: 500 nm for a and b, 100 nm for c, d, e.

C.J. Murphy, T.K. Sau, A.M. Gole, C.J. Orendorff, J. Gao, L. Gou, S.E. Hunyadi, T. Li "Anisotropic Metal Nanoparticles: Synthesis, Assembly, and Optical Applications" J. Phys. Chem. B **109** (2005) 13857



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## GLOSSARY: SOME COMMON TERMS IN SPECTROSCOPY

- Spectrometer
  - Separates particles (photons, molecules, atoms) into a spectrum in a particular scale (mass, energy, momentum)
- Spectrophotometer
  - Measures intensity of light (absorption) in a part of the electromagnetic spectrum (range of wavelengths)
- Photometer (Colorimeters)
  - Measures absorption in a certain (limited) band of the spectrum
- Chromophore.
  - Covalently bonded unsaturated group responsible for an electronic absorption. ( $\text{C}=\text{C}$ ,  $\text{C}=\text{O}$ ,  $\text{NO}_2$ )
- Auxochrome.
  - Unsaturated group with non-bonding electrons that alters the wavelength or intensity of absorption of a chromophore to which it is bonded ( $\text{OH}$ ,  $\text{NH}_2$ ,  $\text{Cl}$ )
- Bathochromic Shift ("red shift")
  - Shift of absorption maximum to a longer wavelength due to group substitution or solvent effects
- Hypsochromic Shift ("blue shift")
  - Shift of absorption maximum to a shorter wavelength due to group substitution or solvent effects.
- Hyperchromic Effect
  - Increase in absorption intensity
- Hypochromic Effect
  - Decrease in absorption intensity



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## WEB RESOURCES:

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### VIDEO DEMONSTRATION OF UV-VIS

- Videos showing use of UV-vis for silver nanoparticle characterization
- Part 1: General use of the UV-vis spectrophotometer and how a sample is measured
  - <https://youtu.be/wK7ue8Uesbw>
- Part 2: Quantitative measurements
  - <https://youtu.be/TYqF-aLzi9o>
- Part 3: Data analysis for measuring concentration and for relating spectra to particle size
  - <https://youtu.be/yRNacc3L5b0>



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