Chapter 1

Spectrochemical Information

CHEM 640: Spectrochemical Analysis
Instructor: Dr. Abdul Muttaleb Jaber
Textbook: *Spectrochemical Analysis*, J. D. Ingle, Jr., and S. R. Crouch, Prentice Hall, 1988.

- **Spectrochemical analysis is one of the major tools of analytical chemistry.**

- **"Spectrochemical" is a compound word that comes from *spectrum* and *chemical.***
- **A spectrum is a display of the intensity of radiation emitted, absorbed, or scattered by a sample versus a quantity related to photon energy, such as wavelength or frequency.**
- **The term *spectrochemical* implies that a spectrum or some aspect of a spectrum is used to determine chemical species and to investigate the interaction of chemical species with electromagnetic radiation.**
- **Spectrochemical methods can involve a direct optical measurement of the photons emitted or transmitted or an indirect measurement of a quantity related to the result of photon absorption.**
- **As examples of the latter, the number ions or a quantity related to the kinetic energy produced by absorption can be monitored and plotted as a function of wavelength to obtain a spectrum**

Radiation/Matter Interactions

- ***Spectroscopy*** **is the science that deals with the interactions of electromagnetic radiation with matter.**
- **Several types of interactions are possible. Many of these involve transitions between specific energy states of chemical species and are observed by monitoring the absorption or emission of EMR.**
- **In these types of interactions it is useful to consider electromagnetic radiation as being composed of discrete packets of energy which we call photons.**
- **Electromagnetic radiation also has a wave character, and we can relate the energy of a photon to its wavelength and frequency by**

$$E = h\nu = \frac{hc}{\lambda}$$

where *E is* the energy in joules (J), ν is the frequency (Hz or s^{-1}), *h is* Planck's constant (6.63×10^{-34} J s), c is the speed of light (3.00×10^{8} m s^{-1} in a vacuum), and λ is the wavelength (m).

- ***Spectrometry***

  is a more restrictive term than spectroscopy and denotes the quantitative measurement of the intensity of EMR at one or more wavelengths with a photoelectric detector.

- **Types of radiation/matter interactions:**

  reflection, refraction, diffraction; some types of scattering that does not involve transitions between energy states, but rather cause changes in the optical properties of the radiation (e.g., direction and polarization).

  - **These interactions are often related to the bulk properties of the sample rather than to specific chemical species.**
  - **Several analytical techniques are based on these bulk interactions.**

- **Spectrochemical analysis**, in general, deals with electromagnetic radiation of an enormous range of frequencies, from the radio frequencies (<20 kHz) to gamma rays (>10^{19} Hz).
- **Optical spectrochemical analysis**, covers a more restrictive range, the near ultraviolet (UV), the visible, and the infrared (IR) regions,
  - In these ranges instrumental requirements are similar, and the materials used for dispersing, focusing, and directing the radiation are conventional optical materials (glass, quartz, or alkali halide crystals).
- Optical spectrochemical techniques are
  - atomic spectroscopic techniques and
  - molecular spectroscopic techniques.
- Atomic spectroscopy deals with free atomic species that are usually in the vapor state,
- Molecular spectroscopy deals with molecular species in the vapor state, or in solution, or in the solid state.

- **The wavelength of radiation in this region is usually expressed in nanometers (1 nm = 10^{-9} m), angstroms (1A ° = 10^{-10} m), or micrometers (1 μm = 10^{-6} m).**
- **One electron volt of photon energy corresponds to radiation with a wavelength of 1240 nm.**
- **Because the wavelength is inversely proportional to energy, the wave number is often used, particularly in the IR region.**
- **The wavenumber, ν, is the number of cycles per unit length (usually cm) and thus the reciprocal of the wavelength, $\bar{\nu} = 1/\lambda$.**
- **The wavenumber is usually expressed in cm^{-1}. It is directly proportional to the photon energy,**

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{E}{hc}$$

The energy or wavelength of the photon determines the type of transition or interaction that occurs, as shown in the Table

Regions of electromagnetic spectrum

Designation	Wavelength range, λ	Frequency range, ν (Hz)	Wavenumber or energy range	Transition
γ-Ray	<0.05 Å	$>6 \times 10^{19}$	$>2.5 \times 10^{5}$ eV	Nuclear
X-Ray	0.05–100 Å	3.0×10^{16}–6.0×10^{19}	124–2.5×10^{5} eV	*K*- and *L*- shell electron
Far (vacuum) UV	10–180 nm	1.7×10^{15}–3.0×10^{16}	7–124 eV	Middle shell electrons
Near UV	180–350 nm	8.6×10^{14}–1.7×10^{15}	3.6–7 eV	Valence electrons
Visible	350–770 nm	3.9×10^{14}–8.6×10^{14}	1.6–3.6 eV	Valence electrons
Near IR	770–2500 nm	1.2×10^{14}–3.9×10^{14}	12,900–4000 cm^{-1}	Molecular vibrations
Middle or fundamental IR	2.5–50 μm	6.0×10^{12}–1.2×10^{14}	4000–200 cm^{-1}	Molecular vibrations
Far IR	50–1000 μm	3.0×10^{11}–6.0×10^{12}	200–10 cm^{-1}	Molecular rotations
Microwave	1–300 mm	1.0×10^{9}–3.0×10^{11}		Molecular rotations
Radio waves	>300 mm	$<1 \times 10^{9}$		Electron and nuclear spin

Nature Of Spectrochemicalanalysis

- **Types of analysis**
- **Samples**
- **Spectrochemical phenolmena**
- **Analysis of real samples**

Types of analysis

- **Spectrochemical methods are used for the identification of chemical species *(qualitative analyses)* and for the determination of the amount of a particular species *(quantitative analyses).***
- **Qualitative analysis can be considered as merely a low resolution type of quantitative analysis,**
  - **often involving a simple binary, yes or no**
- **The constituents determined in a spectrochemical analysis can cover a broad concentration range.**
- **In some cases spectrochemical methods are used to determine major constituents. These are considered here to be species present in the relative weight range 1 to 100%.**
- **Minor constituents are species present in the range 0.01 to 1%,**
- **Trace constituents are those present in amounts lower than 0.01% (100 $\mu g\ g^{-1}$).**

Types of analysis according to size of sample

- **A macro analysis is one carried out on a sample weighing more than 0.1 g.**
- **A semimicro analysis (sometimes called a *meso analysis)* utilizes a sample size in the range 0.01 to 0.1 g**
- **A micro analysis employs a sample size in the range 10^{-4} to 10^{-2} g.**
- **Ultramicro may be used when the sample size is lower than 10^{-4} g**
- **The term ultra-trace analysis is considered to be the determination of a trace constituent in an ultramicro sample.**

Samples

- **The nomenclature for dealing with the samples used in spectrochemical analyses is often confusing and contradictory.**
- **Here, initial sample will mean a portion or subset of the bulk material or population about which analytical information is desired.**
  - **For example, a liter of water (the initial sample) is obtained from a lake (the bulk material) in order to determine the mercury content,**
- **The analytical sample indicates that portion of the initial sample which is presented to the instrument for spectrochemical analyses.**
- **In all cases of sample pretreatment the analytical sample must be representative of the concentration of the sought-for species in the bulk material.**
- **Errors made in sampling or sample preparation are carried through the entire process and lead directly to errors in the final result**

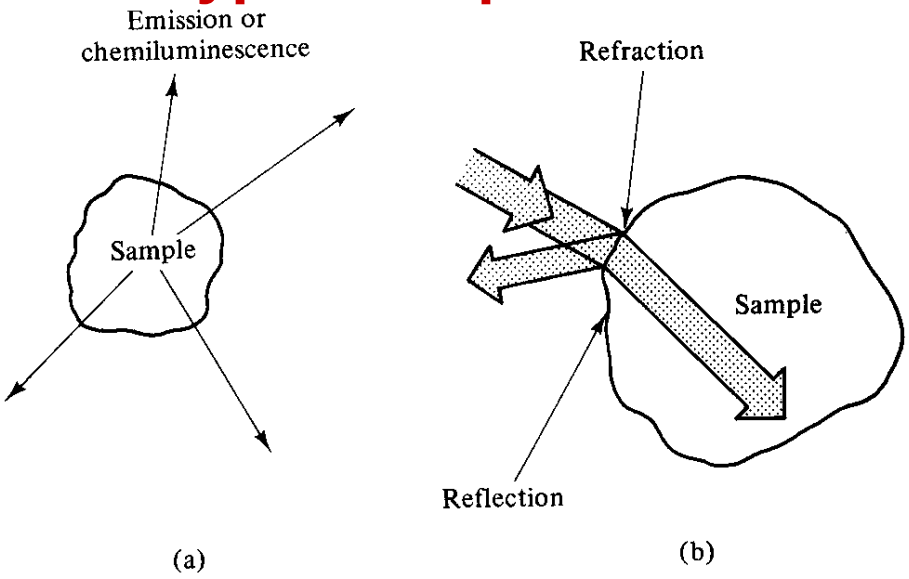
- **Analyte is The species to be determined in the analytical sample.**
- **The term matrix refers to the collection of all the constituents in the sample.**
- **The analytical matrix refers specifically to the matrix of the analytical sample which may differ from that of the initial sample due to the substances added or removed in the various sample treatment stages.**
- **The matrix as defined here includes the analyte as well as all the other constituents, which are called concomitants.**
- **In trace analyses the analyte is present in such small amounts that it is convenient to speak of the analyte and the matrix separately.**
- **Thus for trace analysis we sometimes think of the matrix as being composed of the concomitants.**
- **In major constituent determinations, the analyte is a major part of the matrix.**
  - **For example, in determining iron in steel, the analyte (iron) is present in such large amounts that it determines the bulk properties of the sample.**
  - **Here the matrix is no longer composed of just concomitants.**

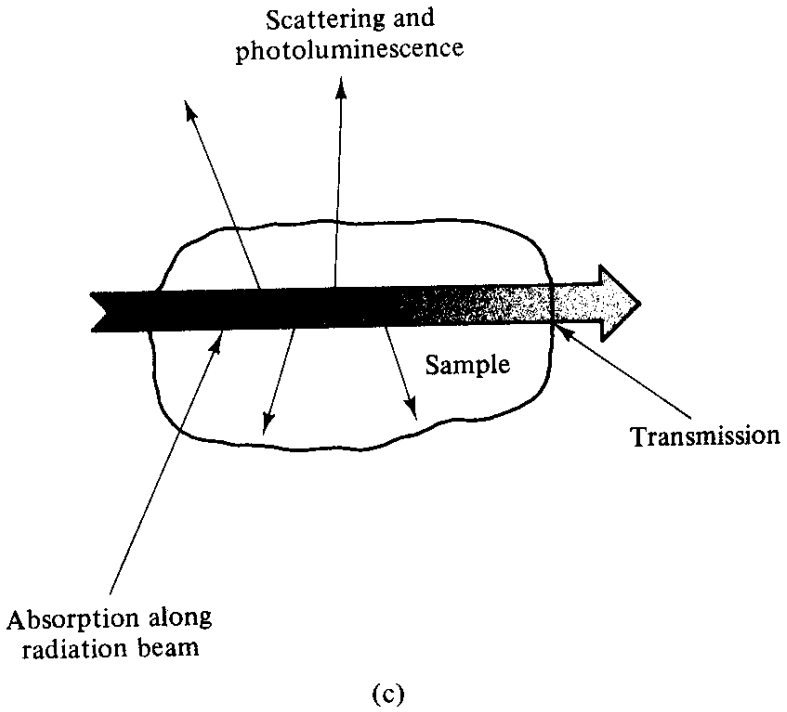
- **Chemical speciation is concerned with determining the concentration of specific chemical forms of the analyte (e.g., the amount of metal in a particular oxidation state or the amount of a drug bound to protein, Fe^{2+} and Fe^{3+}).**
- **The nature of the sample matrix and the effect of the matrix on a determination depend upon the chemical interactions among matrix components and between matrix components and the analyte.**
- **Thus the chemical form(s) of the analyte and of the matrix components is critical.**

Spectrochemical Phenomena

- To obtain spectroscopic information about chemical samples, the species to be determined is usually stimulated in some way by the application of energy in the form of heat, electrical energy, radiation, particles, or a chemical reaction.
- Several spectroscopic phenomena depend on transitions between energy states of particular chemical species.
- Prior to the application of external energy, the analyte is often in its lowest energy or ground state.
- The applied energy then causes the analyte species to be momentarily in a higher energy or excited state.
- Spectrochemical information is provided by measuring the EMR emitted by the species as it returns to the ground state from an excited level or by measuring the amount of EMR absorbed in the excitation process.
- Other spectroscopic techniques depend on the changes in the optical properties of EMR that occur when it interacts with the sample or analyte or on photon-induced changes in chemical form (e.g., ionization or photochemical reactions).

Some types of optical interactions





(a) In the absence of an external radiation source the analyte can be excited by collisional processes or chemical reactions and the resulting emission or chemiluminescence measured.

(b) and (c), a radiation beam from an external source is directed into the sample.

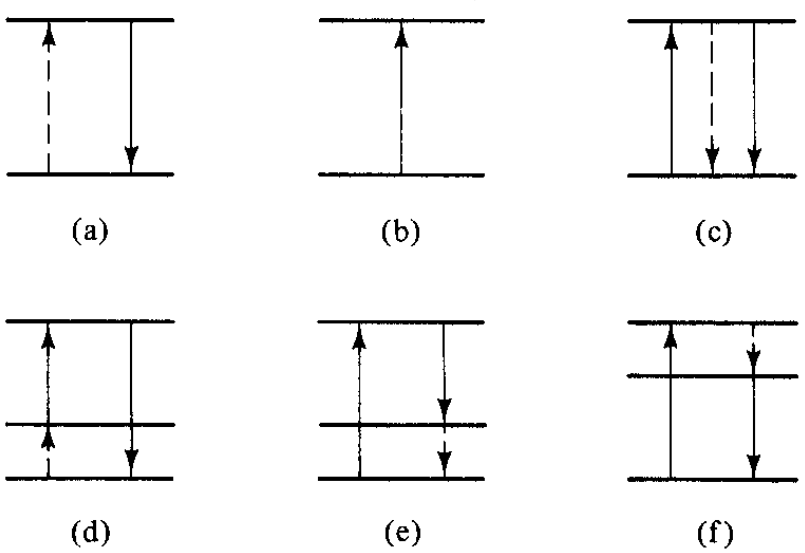
(b) interactions such as reflection and refraction cause a change in direction of the beam at the sample interface.

(c) radiation can be scattered or absorbed by the analyte and the decreased intensity of the transmitted beam can be measured.

- The term **emission** is the process of a photon being emitted.
- **Emission spectroscopy** usually refers to spectral information that results from **nonradiational activation** processes.
- The emission that results from species excited by chemical reactions is usually termed **chemiluminescence**.
- What spectrochemical phenomena could happen when the **sample is exposed to an external source of EMR:**
  - **Reflection and scattering** are optical phenomena resulting in a change in direction of the incident photon.
  - Reflection and elastic light scattering do not involve a change in the frequency of the incident photon
  - however, there are spectroscopic techniques such as Raman spectroscopy that involve inelastic scattering in which the change in the energy of the scattered photon is related to molecular energy levels

- **Absorption of the incident photons by the analyte promotes the analyte to an excited state; this results in a reduction in the intensity of the electromagnetic radiation transmitted by the sample.**
- **In absorption process, the species excited by absorption of photons can lose the excess energy by radiational or nonradiational processes; the latter leads to an increase in the kinetic energy of the sample.**
- **Radiational deactivation processes result in emission of photons. The emission of photons from excited states produced by radiational activation (absorption) is called photoluminescence.**
- **Flu*orescence* and *phosphorescence* are particular types of photoluminescence.**
- **In photoluminescence, the frequency of the emitted photon may be the same as the frequency of the incident photon, or it may be different,**
- **The term luminescence refers to emission from cool bodies or to emission from hot bodies that is not due to thermal excitation.**
- **Thus in this text chemiluminescence of molecules in solution is considered together with molecular fluorescence and phosphorescence as being molecular luminescence.**

Common types of optical transitions



(a) the basis of **emission or chemiluminescence** in which theanalyte is excited by a thermal, a chemical or some other nonradiative process

(b) the analyte is excited by absorption of a photon and the resulting **reduction in intensity of the photon signal** is measured

(c) the emission of a **photon** following **radiative excitation**, termed **photoluminescence,** is measured. The dashed line and arrow indicate that the excited state can also lose its energy by a **nonradiative pathway**.

(d & e) excitation or deactivation can involve a combination of radiative and nonradiative transitions in which the wavelength of the emitted photon can be less (Stokes transition) or greater(anti-Stokes transition) than that of the excitation photon.

(f) the species undergoes a **nonradiative** deactivation to a lower excited level before photon emission occurs.

Analysis of real samples

- **The analyte is present as part of a sample matrix.**
- **Concomitant species in the matrix can undergo the same spectrochemical process (absorption, luminescence, scattering, etc.) as the analyte, or they can affect the ability of analyte species to undergo the desired process.**
- **Concomitants can also affect the ability to observe or measure the optical interaction of the analyte.**
- **All these effects due to the concomitants can give rise to interference effects which are often termed matrix effects.**
- **Sources of concomitant species:**
  - **reagents and solvents used to treat the sample prior to the analysis,**
  - **or from contamination during the sample acquisition, storage, and preparation steps.**
- **Concomitants can also interfere by other means such as chemical reaction with the analyte species.**

- **How does Selectivity in emission, absorption, and luminescence methods arise?**
  - **because the spectral signals from the analyte occur at certain frequencies (wavelengths).**
- **Thus the optical information concerning the analyte can often be distinguished from information from concomitants by using instrumentation that allows monitoring of specific wavelengths and/or excitation of the sample by photons of specific wavelengths.**
- **Selectivity can be enhanced by using another optical property, such as polarization, in conjunction with intensity and wavelength informa-tion or by employing selective chemical reactions involving the analyte.**
- ***We will follow the accepted convention that samples are analyzed, but that concentrations or species are determined*.** **Thus we can properly speak of the analysis of paint for lead or the determination of lead in paint, but it is incorrect to speak of the analysis of lead in paint.**

Blank

- **The ideal blank contains all the sample constituents except the analyte.**
- **In practice the blank is treated as identically to the sample as possible.**
- **The instrumental response from the blank is then subtracted from that of the sample in order to compensate for the effects of concomitants**
- **An ideal blank can eliminate some types of interference effects due to concomitants but cannot compensate for concomitant species that affect the production and measurement of the analyte response.**
- **It is difficult to prepare an ideal blank because the concomitants and their concentrations are not usually known. A more desirable approach is to arrange measurement conditions to minimize the response due to concomitants.**

Containers (Sample cells)

- **Actual analyses is complicated because the sample is almost always confined during measurement by a container, except for a few insitu measurements.**
- **In molecular spectroscopy, the container is typically a glass, quartz, or salt cell.**
- **Optical interactions with the container walls can give rise to additional interference effects.**
- **In atomic spectroscopy the container is typically a flame, a plasma, or a heated chamber.**
  - **The hot gases produced can emit or absorb radiation which can also be a potential source of interference.**
- **In some cases the sample matrix can alter the interference effects of the container.**

Expressions Of Analytical Information

- **Several different types of information are required in order to develop, apply, and optimize an analytical technique.**
- **How to express spectrochemical information in a convenient manner so that analyte concentration data can readily be extracted? or the dependence of the results on chemical, physical, or instrumental variables can easily be summarized?**
- **The following will be discussed:**
  - **Calibration data**
  - **Atomic and molecular spectra**
  - **Optimization of the response function**

Calibration Data

- **The desired concentration of the analyte is almost never obtained directly as the result of an absolute measurement of an optical signal,**
- **However, conc. is obtained indirectly through calibration, subtraction of blanks, comparison with standards, and other procedures.**
- **The total spectrochemical signal is: defined as the unmodified readout signal obtained from measurement of a sample or standard.**
- **The blank or reference signal is defined as the readout signal obtained from measurement of the blank. It includes the background signal due to optical signals from the sample container and the concomitants in the blank.**
- **The analytical signal is extracted from the total spectrochemical signal. Ideally, it is directly related to the analyte concentration.**

- **In some automated instruments the readout signal may be the analytical signal if the instrument carries out the appropriate modifications internally.**

- **A plot of the analytical signal versus analyte concentration, with all the other variables in the calibration function held constant, is called the calibration curve, the analytical curve, or the working curve.**

Atomic and Molecular Spectra

- **A spectrum is a plot of the analytical signal versus wavelength, frequency, or wavenumber with all other variables held constant.**
- **The peaks (lines or bands) are characterized by their shape, height (intensity), width, and position (wavelength).**
- **Usually, the width is expressed as the half-width ($\Delta\lambda$), which is the width in wavelength units at half the net peak height.**
- **The half-width is also called the, full width at half maximum (FWHM).**
- **A spectrum is an essential summary of spectral information of any spectrometric technique because it indicates the wavelength to use for quantitative analysis in order to obtain the maximum analytical signal.**
- **The analyte spectrum along with spectra of concomitants allows the wavelength of analysis to be chosen both to maximize the analytical signal and to discriminate against background signals.**

- **Spectrum of the analyte is the basis of qualitative and quantitative analysis**
- **For qualitative analysis spectra with numerous resolvable peaks are needed**
- **The spectra of atoms in the UV, visible, and near-IR regions arise from purely electronic transitions of outer-shell (valence) electrons.**
- **Because the quantized energy levels are relatively far apart, atomic spectra are narrow line spectra.**
- **A transition to or from the ground electronic level is a *resonance transition*, and the resulting spectral line is a resonance line.**
- **Atomic spectra are often quite simple because many of the possible transitions are forbidden transitions.**
- **Atomic spectral lines have a finite width (typically, much less than 1 A^{o}) even though the transitions are between two distinct energy levels because of line broadening due to lifetime effects, the Doppler effect, and collisions.**
-

Molecular Spectra

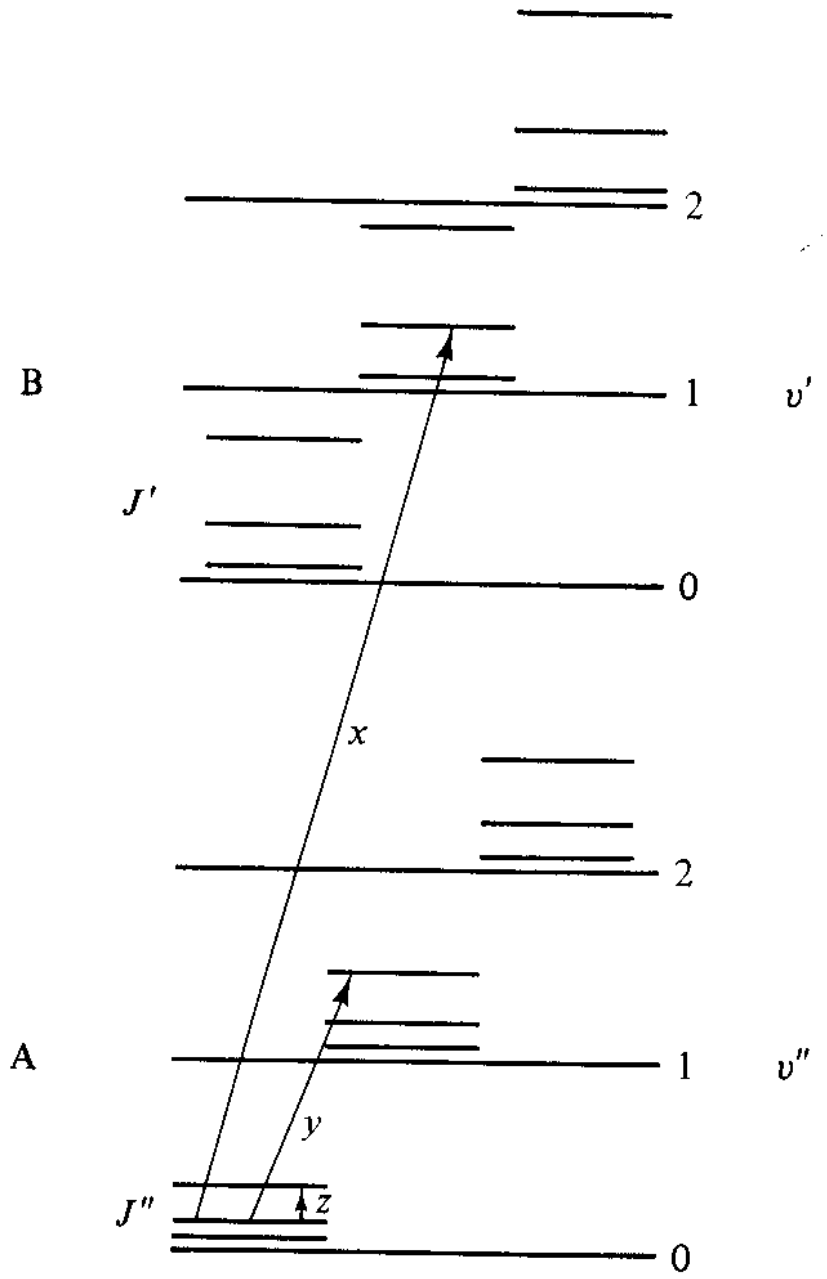
- Because molecules have quantized vibrational and rotational levels in addition to electronic levels, their spectra are necessarily more complicated than the spectra of isolated atoms.
- There are three distinct types of spectra we can observe for molecules.

1. **Band spectra**: **Molecular electronic spectra** observed in the UV, visible, and near-IR regions of the spectrum and are due to transitions between a vibrational and rotational level in one electronic state to a vibrational and rotational level in another electronic state.
   - In the gas phase, we can observe the vibrational and rotational structure.
   - In the condensed phases, much of the structure of molecular spectra is blurred because of frequent molecular collisions and level perturbations due to near-neighbor interactions
   - Molecular electronic spectra of liquids and solutions often consist of one or more broad, featureless bands (typically, 10 to 100 nm wide), where each band is an envelope of the multitude of possible transitions between vibrational-rotational levels in two electronic states.

2. **Vibration-rotational spectra involve transitions from the rotational levels of one vibrational level to the rotational levels of another vibrational level of the same electronic state and are observed most often in the IR region of the spectrum.**

- **The rotational structure of infrared spectra is usually lost in condensed phases.**

3. **Rotational spectra involve transitions from one rotational level to another rotational level of the same vibrational level of the same electronic state.**
   - **Purely rotational spectra are normally observed in the microwave region of the spectrum. Raman spectroscopy also gives information**



- **The vibrational levels are given by V" and v', while the rotational levels are given by J" and J'.**
- **The three arrows show the three types of transitions pos-sible: electronic (x), vibration-rotation (y), and pure rotation (z)**

Optimization of the response function

- **The dependence of calibration function on all possible variables cannot realistically be determined.**
- **Variables of interest depend upon the technique and particular application and can include:**
  - **instrumental variables, such as excitation light source intensity, volume element of total sample in the instrument that is actually probed, and slit width,**
  - **physical and chemical variables such as temperature, pH, ionic strength, reagent concentrations, and concentrations of concomitant species.**
- **Results of studies of the influence of experimental variables are used to choose optimum operating conditions**

Evaluation Criteria in spectrochemical Techniques

Practical considerations

Factors to be considered to choose a spectrophotometric technique:

1. cost, sample size required, simplicity, portability, and robustness.

2. Speed of analysis: time for preparation and matrix modification if necessary and calibration

Automation and multiple species capability

Automation, the performance of tasks without operator assistance can free the operator of tedious tasks and increase precision due to more reproducible performance of steps formerly requiring operator skill.

- **Tasks that could be automated include:**
  - **The selection of preprogrammed instrumental variable values for a given analyte, measurement of spectral signals, construction of calibration curves, and presentation of analytical and statistical information.**
  - **Further steps which may be automated include sample preparation, cleanup, and introduction.**
  - **Automation is particularly needed for situations involving unattended analysis of samples at night or at remote locations.**

- **Multiple-species analysis is more convenient with automated instrumentation.**
  - **Multiple-species analysis can be carried out by some instruments which measure each analyte in a sequential manner or by others which measure all analytes simultaneously.**
  - **Simultaneous analysis is faster than sequential analysis and requires less sample for the situation where *n* spectral signals are measured from one analytical sample.**

Interferences and Selectivity

- **The accuracy of all spectrometric techniques can be degraded by interferences.**
- **An interferent is a substance present in the analytical sample which affects the magnitude of spectral signal measured for the analyte.**
- **Thus the choice of a spectrochemical technique depends on the expected interferences and their concentrations in the sample to be analyzed. Once a technique is chosen, the preparation of the sample for analysis may still have to be carried out in a manner that reduces interference effects to an acceptable level.**
- **Many analytical techniques are quite selective, but few are truly specific, a term which implies complete freedom from interferences**

Figures of merit

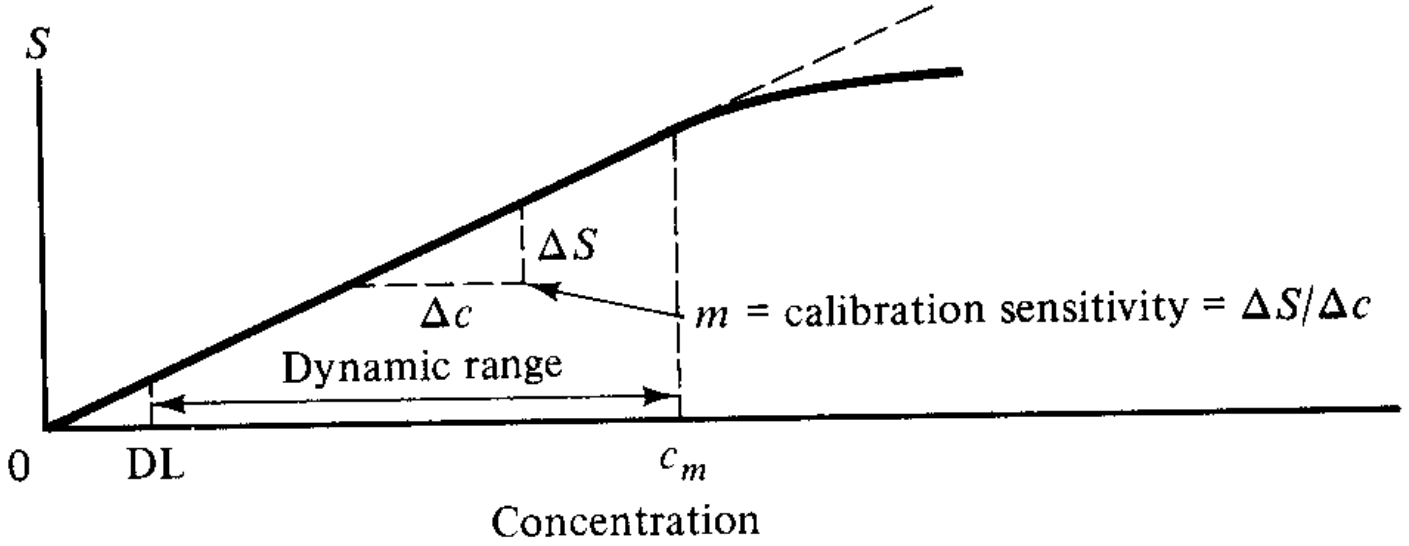
- **The characteristics of a spectrochemical technique for a given analyte are indicated by several figures of merit, such as accuracy, precision, sensitivity, detection limit, and dynamic range.**
- **The accuracy indicates how close the measured analyte concentration is to the true analyte concentration in the sample and is normally expressed as the relative percent error (i.e., a 1% error indicates that the measured concentration is within 1% of the true analyte concentration).**
  - **The accuracy depends on the analyte concentration, the precision, and interference effects.**

- **The precision, usually expressed as a percent RSD, indicates the reproducibility of repetitive measurements of equivalent analyte solutions.**
- **Averaging of repetitive measurements can be used to improve precision, and thus the accuracy, if random errors are limiting rather than systematic errors due to interferents or other factors.**
- **Sensitivity may have several meanings. It usually indicates the response of the instrument to changes in analyte concentration and is expressed as the slope of the calibration curve or the change in analytical signal per unit change in analyte concentration.**

- **The detection limit (DL) is typically defined as the analyte concentration yielding an analytical signal equal to two or three times the standard deviation of a blank measurement (33 to 50% RSD).**
- **DL is indicative of the lowest analyte concentration that can be reported as being detected with a specified degree of certainty.**
- **Spectrometric technique cannot be used without preconcentration steps if the analyte concentration in the analytical sample is below the DL.**
- **The analyte concentration should normally be higher than 10 times the detection limit to obtain reasonable precision (5% RSD or less).**
- **Detectability is a term that denotes the ability to provide low detection limits**

- **Dynamic range can be specified as the concentration range or analytical signal range over which the analytical curve is linear or the calibration slope is constant.**
- **It is usually defined at the lower end by the detection limit and at the upper end by an analyte concentration where the analytical signal deviates a specific relative amount (e.g., 5%) from the extrapolated linear portion of the curve or where the slope deviates a specific relative amount from the slope in the linear portion**
- **A linear calibration curve is usually preferred because it is easier to detect an abnormality and because it is easier to work with mathematically (i.e., fewer points are needed to establish the calibration curve and a linear, straight line, least-squares curve-fitting model can be employed).**
- **A large dynamic range is preferred because a wide range of analyte concentrations can be used without sample dilution.**
- **In some samples, a large dynamic range is not required.**

- **A nonlinear calibration curve can be used as long as enough standards are measured to establish the calibration function.**
- **Many computerized instruments incorporate least-squares software for fitting data.**



- **The calibration sensitivity *(m)* is the slope of the calibration curve at a particular concentration or the derivative of the calibration function at a particular concentration**
- **The detection limit (DL) indicates the lowest analyte concentration that can be measured with a specified degree of certainty and is often defined by DL = $2s_{bk}/m$ or DL = $3s_{bk}/m$, where s_{bk} is the standard deviation of the blank measurement.**
- **The dynamic range is defined by DL and c_m, where c_m is the maximum concentration that can be measured before the calibration curve deviates a specific amount from the extrapolated linear portion**