Summary Spectroscopy

Ch-1 - Nuclear Physics

Bohr's Atomic Model: The idea, that electrons move in elliptical orbits. Since each orbit has a particular energy associated with it, electron motion in the permitted orbits are fixed in values; i.e. quantized.

Quantum Number: According to quantum mechanics, the distribution of electrons labels the state of the electron and specifies the value of a property in an atom.

- *n* - **Principal** QN. (shell number): The average distance of the electron from the nucleus in a particular orbital; can have integral values of 1, 2, 3, and so forth (higher values ≈ greater average distance) e.g.: 1 = 1st period, 7 = 7th period;
- *l* - **Angular Momentum** QN.: (subshell of one shell): Its value reflects the orbital shape; it correlates with n; ($l = n$-1); which reveals 0 for the **s**-, 1 for **p**-, 2 for **d**-, 3 for **f**-, 4 for **g**-, 5 for the **h**-orbital.
- m_l - **Magnetic** QN.: It describes the orientation of the orbital in space and depends upon the value of l; ($m_l = 2 \cdot l+1$), e.g.: $m_l = 1$ a sphere; $m_l = 3$ gives -1/0/+1 (x,y,z-orientation); $m_l = 5$ gives -2/-1/0/1/2 etc.
- m_s - **Electron Spin** QN.: According to the electromagnetic theory, spinning electrons posses a magnetic orientation; ($m_s = n$) m_s can either be $-^1/_2$ (↓)or $+^1/_2$(↑); with m_s =3 giving 3 magnetic spins: $-^1/_2$ / $+^1/_2$ / $-^1/_2$.

Pauli Exclusion Principle: No two electrons in an atom can have the same four quantum numbers; i.e. in a particular orbital, electrons can not possess the same energy.

Electrons per Shell: The principles outlined by both the atomic Bohr model and the rules of the quantum number, only a certain amount of electrons can occupy each orbital:

$e_N = 2 \cdot n^2$

e_N, number of e/shell [-]
n, principal shell number [-]

Electromagnetic radiation (EMR) Is the most recognizable as visible light and as radiant heat; less obvious spectra include γ-ray, X-ray, UV, microwave, and radio-frequency radiation.

$p = h/\lambda = m \cdot v$

$\lambda = \frac{h}{m \cdot v}$ [m]

h, plank's constant = $6.626 \cdot E^{-34}$[J·s]
p, impulse [kg·m/g]
m, mass [kg]
v, velocity [m/s]

EMR requires no supporting medium for its transmission and thus passes readily through vacuum. EMR is viewed as a stream of discrete particles or wave packets of energy called photons with the energy of a photon being proportional to the frequency of the radiation, this dual views of radiation as particles and as waves are complementary. This duality is also found in the behavior of streams of electrons and other elementary particles such as protons, resulting in the interaction of matter with EMR and vice versa. It is completely rationalized by wave mechanics.

$E = h \cdot \nu = \frac{h \cdot c}{\lambda} = h \cdot c \cdot \bar{\nu}$ [J]

$1J = 2.39 \cdot E^{-1}cal = 6.24 \cdot E^{18}eV = 5.03 \cdot E^{22}cm^{-1}$
ν, frequency [Hz] = [1/s]
c, speed of light = $3.0 \cdot E^8$ [m/s]
$\bar{\nu}$, wavenumber [1/m]

Photon: Is a particle of electromagnetic radiation having zero mass and the energy $E = \nu \cdot h$

Wave Properties: EMR is conveniently represented as electric and magnetic fields that undergo in-phase, sinusoidal oscillations at right angles to each other and to the direction of propagation. Plane-polarized electromagnetic radiation implies that all oscillations of either the electric or the magnetic fields lie within a single plane.

- The electric component is responsible for transmission, reflection, refraction, and absorption.
- The magnetic component is responsible for the absorption of radio waves in nuclear magnetic resonance.

A - **Amplitude**: The vector quantity of a wave that provides a measure of the electrical or magnetic field strength at a maximum in the wave.

ν - **Frequency**: the number of oscillations that occur per second and is equal to 1/T in [Hz].

T - **Period**: Time required for 2 successive wave crests or throughs to pass a fixed point, in [1/s].

c - **Speed**: The speed of propagation of a radiating wave in time and space. In a vacuum, the velocity is $2.99792 \cdot E^8$[m/s], in air is slightly lower (≈ 0.03% less).

$c = \lambda/T$ [m/s]

λ, wavelength [m]
T, period [1/s]

λ - **Wavelength**: Distance between corresponding points of 2 successive periodic waves in the direction of propagation, for which the oscillation has the same phase (for example, successive maxima or minima) in [m].

$\bar{\nu}$ - **Wavenumber**: It is the reciprocal of the wavelength (λ) in [cm], is another way to describe electro-magnetic radiation. The wavenumber is used in infrared (IR) and Raman spectroscopy, it is directly proportional to the energy of the radiation:

$\bar{\nu} = k \cdot \nu$ [cm^{-1}]

k, medium dependant proport. constant
ν, frequency [Hz] = [1/s]

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Radiation and Interaction with Matter: Electromagnetic radiation (EMR) is emitted when an atom makes a transition from an excited state to a state of lower energy. while EMR is absorbed when an atom makes a transition from a lower state to a higher state. According to quantum mechanics, the uptake and release of EMR occurs in discrete units (so-called "quanta"); though, most detectors though are not able to discriminate (resolve) these discontinuous transitions. Matter reveals both particle and wave properties (particle-wave dualism); in combination with the law of momentum conservation, which depicts a momentum transfer (but no loss of momentum), the almost mass-less electrons easily interact with photonic energy. Interaction of EMR with matter generates also elastic scattering (without transfer of energy) or inelastic scattering (involves energy transfer). In addition, EMR experiences reflection (return of light rays from a surface), diffraction (deviation of light from rectilinear propagation), and polarization (alignment of the electric vectors to a certain orientation).

- **Elastic scattering** (Rayleigh scattering): The energy of the incoming photon is too small to excite outer shell electrons of an atom to a higher state. The incoming and outgoing or scattered photons have the same energy, the scattering is said to be elastic.
- **Inelastic scattering** (Raman scattering): Occurs when the incident photon has enough energy to cause the atom to make a transition to an excited state. The energy of the scattered photon ($E = h \cdot f'$) is less than the incident photon ($h \cdot f$) by ΔE, the difference between the energy of the ground state and the energy of the excited state.
- **Resonance absorption**: The energy of the incident photon is just equal to the first excited state of the atom (i.e. outer-shell electrons). Upon irradiation of outer nuclear electrons with a continuos spectrum, the transmitted spectrum shows dark lines corresponding to absorption of light at discrete wavelengths (photonic energy is used to do work; i.e. lifting outer shell electrons into higher orbits). Since atoms and molecules at room temperature are in either their ground states or low-lying excited states (UV-Vis; IR, NMR, AAS), absorption spectra are usually simpler than emission spectra. After having lifted the stimulated electron into the higher orbit it will eventually decay back to the ground state with the emission of a photon whose energy is equivalent to that of the incident photon. Relaxation into the ground state can also occur by emitting the absorbed energy as heat
  Electronic Transition: Involves the transfer of an electron from one electronic orbital to another. An atom lacks $E_V + E_R$; $E = E_e + E_V + E_R$ [J·s]
  E_e, electron associated energy
  E_V, interatomic vibrational energy
  E_R, molecular rotational energy
- **Fluorescence**: The energy of the incident photon is great enough to excite the atom to one of its higher excited state. The atom then loses its energy by spontaneous emission (emission frequency is lower than that of absorbed frequency) as it makes one or more transmission to lower energy states. However, some excited states have much longer lifetimes (second or minutes), in that their metastable state emit light long after the original excitation.
- **Photoelectric effect**: Absorption of a photon ionizes the atom by causing the emission of an electron (photovoltaic cell) without the emission of a concomitant photon.
- **Compton scattering**: The energy of the incident photon is much greater than the ionizing energy. A photon is emitted along with the ionization of the atom, liberating electrons.
- **Stimulated emission**: Stimulation of an atom or molecule to an excited state E_2 with the energy of the incident photon equal to $E_2 - E_1$ (with E_1 the energy of a lower or ground state). The oscillating electromagnetic field associated with the incident photon stimulates the excited atom, which then emits a photon in the same direction and in phase as the incident photon (e.g. laser light).

With spectroscopic methods, particles (atoms, ions, molecules, as well as atomic- and molecular compounds) can be characterized as they absorb or emit electromagnetic radiation (EMR).

Spectroscopy plays a vital role in the development of modern atomic theory. In addition, spectrochemical methods provide tools for the elucidation of the structure of molecular species as well as the quantitative and qualitative determination of both inorganic and organic compounds.

Radiant Power and Intensity: The power of radiation (P) is the energy of the beam reaching a given area per second whereas the intensity (I) is the power per unit solid angle. These quantities are related to the square of the amplitude. (I and P are used synonymously).

Ch-2 - Molecular Chemistry

Covalent Bond: A bond in which two electrons are shared by two atoms. In a coordinate covalent bond the pair of electrons is supplied by one of the two bonded atoms; e.g. H-Cl, by sharing each others electrons, both obtain noble gas configuration.

n - **a nonbonding electron** (orbital) is a valence-shell atomic orbital that has not been used to form a bond to another atom; e.g. the lone pair on the oxygen or the nitrogen are termed as electrons of a nonbonding orbital **:**O**::**, **:**NH_3; non-bonding orbitals are easily ionizable - this effect is commonly used in Mass Spectroscopy.

- **Coordinative** (Dative) B.: The lone pair of one compound is occupied by a cation; e.g.: $NH_3 + H^+ \rightarrow NH_4^+$

π - **Pi** B.: A covalent bond formed by sideways overlapping orbitals; its electron density is concentrated above and below the plane of the nuclei of the bonding atoms. Electrons involved in double and triple bonds of organic molecules are not as strongly held as σ-bonds and are therefore more easily excited by radiation; thus, species with unsaturated bonds generally exhibit useful absorption peaks - e.g. unsaturated functional groups as in chromophores.

σ - **Sigma** B.: A covalent bond formed by orbitals overlapping end-to-end; it has its electron density concentrated between the nuclei of the bonding atoms. The shared electrons in such a single bond (as C-C or C-H) are so firmly held that their excitation requires energies corresponding to wavelengths in the vacuum UV-region (<180nm). Single bond spectra have not been widely exploited for analytical purposes, because of the experimental difficulties of working in this region.

Molecular Orbit: In a covalently bonded molecule (π-bonding), the atomic electron orbits spreads over all the atoms. The formation of a bonding molecular orbital is caused by the orientation of the electron spin within the orbital; e.g.: H-H atom: $1s\sigma^*$ = antibonding (repelling, opposite spin); $1s\sigma$ = bonding (attraction, same spin);

i) every molecular orbital can accept two electrons;

i) bonding molecular orbitals are energetically far more stable than antibonding MO's;

e.g.: $E1s\sigma < E1s\sigma^*$; or $E2s\sigma < E2s\sigma^* < E2p_x\sigma < E2p_y\pi$; $E2p_z\pi < E2p_y\pi^*$; $E2p_y\pi^* < E2p_x\sigma^*$

Dipole: A molecule with a separate regions or net negative and net positive charge, so that one end acts as a positive pole and the other as a negative pole. The dipole moment is a precondition for IR-spectroscopy ($\mu \neq 0$; $\alpha = 0$), whereas polarizability is for Raman spectroscopy ($\mu = 0$; $\alpha \neq 0$):

μ - **Dipole Moment** (DM): The electrostatic force required to align a dipolar molecule parallel to the electrostatic field; the force required increases as the separation of the molecular charges decreases; The product of charge and the distance between the charges in a molecule: q, charge [C]

$\mu = q \cdot d$ $[C \cdot m] = [D]$; $1Debey = 3.336 \cdot 10^{-30}$ $[C \cdot m]$ d, distance [m]

The overall DM is obtained by adding the individual vector-amounts of the involved atoms.

α - **Polarizibility**: The inter-atomic distances change by simultaneously shortening followed by simultaneous stretching of bonding atoms due to the delocalization of the electrons upon interaction with the oscillating electromagnetic field)

Molecular Oscillations: The stimulating incident radiation excites atoms in a molecule. Prior to ionization, the entire molecule can oscillate according to its distinct resonance frequencies determined by the atomic species involved in each bonding. This oscillation changes both the dipole moment (essential for IR-spectroscopy) and the polarizability (essential for Raman-spectroscopy) of such bonds (usually a triplet structure) which as a vector interacts with the electrical vector of the electromagnetic radiation.

- **Stretching Vibration** (also valence vibration): It involves a continuos change in the interatomic distance along the axis of the bond between the atoms (usually one centrally located atom and two bonding sideward atoms.
  Asymmetrical SV.: Inter-atomic distances change alternatively by shortening of one bonded atom while the other one stretches - causes a periodic change in dipole moment.
  Symmetrical SV.: Inter-atomic distances change by simultaneously shortening followed by simultaneous stretching of bonding atoms - causes a periodic change in polarazibility.
- **Bending Vibration** (deformative vibration): Are characterized by a change in the angle between two bonds and are of four types: scissoring, rocking, twisting, wagging - causes a periodic change in dipole moment.

Electronic Transition: Involves the transfer of an electron from one electronic orbital to another. An atom lacks $E_V + E_R$; $E = E_e + E_V + E_R$ $[J \cdot s]$

E_e, electron associated energy
E_V, inter-atomic vibrational energy
E_R, molecular rotational energy

Ch-3 - Basics of Spectroscopy

Spectroscopy: A general term to describe analytical methods based on absorbance, chemi-luminescence, emission, or fluorescence; i.e. an optical method mainly based on the interaction between electromagnetic radiation and matter. The process of resolving electromagnetic radiation (e.g. light, ultraviolet, infrared, microwave, etc.) into its component wavelengths to produce spectra, plotting the function of radiant intensity versus wavelength or frequency.
Electromagnetic spectra used in Spectroscopy: It encompasses a wide range of wavelength (1fm - 10m) and frequencies and energies, in which the visible region extends only from about 400nm to 700nm; the most common spectroscopic methods based on electromagnetic radiation are:

Type of spectroscopy	Wavelength Range λ [m]	Wavenumber Range $\bar{\nu}$ [1/cm]	Type of Quantum Transition
Gamma-ray emission	$0.05\text{-}15\cdot E^{-9}$	-	Nuclear
X-Ray absorption, emission, fluorescence, and diffraction	$0.001\text{-}10\cdot E^{-9}$	-	Inner electron (e^- of the K-, L-, or M-shell)
Vacuum ultraviolet absorption	$10\text{-}180\cdot E^{-9}$	$1\cdot E^{6}$ to $5\cdot E^{4}$	Bonding electrons (e^- of the outer shells)
Ultraviolet visible absorption, emission, and fluorescence	$180\text{-}780\cdot E^{-9}$	$5\cdot E^{4}$ to $1.3\cdot E^{4}$	Bonding electrons (e^- of the outer shells)
Infrared absorption and Raman scattering	$0.78\text{-}300\cdot E^{-6}$	$1.3\cdot E^{4}$ to $3.3\cdot E^{1}$	Rotation/vibration of molecules
Microwave absorption	$0.75\text{-}3.75\cdot E^{-3}$	1.3-27	Rotation of molecules
Electron spin resonance	$30\cdot E^{-3}$	0.33	Spin of electrons in a magnetic field
Nuclear magnetic resonance	0.6-10	$1.7\cdot E^{-2}$ to $1\cdot E^{3}$	Spin of nuclei in a magnetic field

Optical Spectroscopy: Optical methods are spectroscopic methods, that utilize ultraviolet (UV), visible, and infrared (IR) radiation for visually identifying the elements in a sample that have been excited. In optical spectrometry, the instrumentation used is quite simple; it basically consists of the following units:

- **Radiation source**: A device that is used to excite orbiting outer shelled electrons of the sample; it can be either a line source (several very narrow bands) or a continuos source (wavelengths within a given spectral region).
- **Sample holder**: The unit housing the sample which absolutely must not interact with the radiation spectrum.
- **Monochromator**: A wavelength selector that permits the isolation of a restricted wavelength region; i.e. a prism (dispersion) or a grating (diffraction) to produce a narrow band of radiation; the wavelengths used can be selectively chosen by gradually tilting the monochromator to obtain absorption spectra.
  Grating: A hard optically flat, polished surface with 1000-3000 parallel and closely spaced grooves per mm. Constrictive interference is obtained according to: $d\cdot\sin\alpha = m\cdot\lambda$ — d, groove distance [m]; α, angle of m^{th} interference [°]; m, interference order (±1, ±2, ±3.... [-]; λ, wavelength [m]
  To avoid distortion effects, higher orders are simply filtered out.
  Holographic grating: A state of the art grating obtained of the recorded interference pattern resulting from two wave fronts. The use of holographic gratings (up to 8000 lines/mm further improves resolution ($\lambda/\Delta\lambda$).
  Refraction Prism: The bending of an oblique ray of light when it passes from one transparent medium of one density to another with a different density, caused by a difference in the speed of light in those media (e.g. violet travels about 1% slower in ordinary glass than does red light (the higher the frequency, the more absorption in a glass prism).
  R. **Index**: The refractive power of a medium compared with that of air, designated 1; $n_{diamond} = 2.4$; $n_{water} = 1.3$:
  $n = c_{vacuum}/v_{\text{of light in medium}}$ — c, speed of light $3\cdot E^{8}$ [m/s]
  $n_1\cdot\sin\theta_1 = n_2\cdot\sin\theta_2$ [-] — θ, angle ($\perp$ to surface) [degree]
- **Detector**: A device that converts radiant energy to a measurable signal (usually electrical) and feeds it to a signal processor and readout unit.
  Photodiode D.: A photoelectric cell consisting of a wire anode and a photosensitive cathode encapsulated in an evacuated glass or quartz envelope and maintained at a potential of about 90V; a current is produced when the cathode is illuminated. State of the art photodiodes are made of semi-conducting materials.
  Photodiode-Array D.: A set of parallel arranged photosensitive diodes. As each photodiode is spatially separated , it enables instant detection of an entire spectrum. The spatial distance of each photodiode (typically 15µm) along with the dispersive power of the grating determine overall resolution of the instrument. A photodiode-array is an essential part in multi-channel instruments.

Phototube D.: It consists of a semi-cylindrical cathode and a wire anode sealed inside an evacuated transparent envelope. The concave surface of the cathode supports a layer of photo-emissive material, such as an alkaline metal or metel-oxide, that tends to emit electrons upon beam irradiance. When a voltage is applied the emitted photoelectrons flow to the wire anode, producing a current that is readily amplified and displayed or recorded.
Photomultiplier tube D. (PMT): A very sensitive light detector in which amplification is accomplished by a series of dynodes, which produce a cascade of electrons for each photon received by the tube. Its cathode surface is similar in composition to that of a phototube, with electrons being emitted upon exposure to radiation. The emitted electrons (e^-) are accelerated toward a dynode maintained at a potential of +90V. Upon striking the 1st dynode surface, each accelerated photo- e^- produces several additional e^-, all of which are then accelerated to dynode 2, kept at +180V; e.g. a cascade of 8 units is capable to amplify an incoming photon by a factor of $1 \cdot E^7$.

Parameters relevant in Spectroscopy:

Lambert Beer's Law (LB-law) Characterizes absorption properties of liquids or gases containing moderate quantities of a solute. If the solute does not represent the solvent itself, this law as a semi-quantitative measurement, can be used to determine the solute's concentration:

$I_{(x)} = I_0 \cdot e^{-k \cdot c \cdot d}$

I_0, initial photon intensity [W/m^2]
k, absorption coefficient [m^2]
d, depth of penetration [m]
c, concentration [$part./m^3$]

Absorption can only be accurately determined between 0.1 and 0.5 absorption units (1.5 - 2 magnitudes). These limitations result from inhomogenic distribution of the analyte within the atomic cloud (T-dependant), and slight deviations in the monochromatic properties of the detected radiation (absorption peaks are 3-times wider than radiation peaks). Therefore, a dilution series is required to operate within the linear portion of the law.

- A - **Absorbency**: The logarithm of the ratio between the initial power of a beam radiation and its power after it has traversed an absorbing medium; usually given as absorbance units [au].
  $A = \log I_0/I = -\log_{10} T$ [au] I, Intensity of electromagnetic radiation [W/m^2]
- T - **Transmittance**: The fraction of incident electromagnetic radiation that is transmitted through a sample:
  $T = \frac{I}{I_0} \cdot 100$ [%] I, Intensity of electro-magnetic radiation [W/m^2]

Spectrum: The "salad" of wavelengths that is used to determine qualitative properties;
Continuous S.: It does not have a line character; generally produced by heating solids to a higher temperatures.
Band S.: It is made up of many closely spaced lines that are difficult to resolve.
Line S.: The line widths in a typical atomic spectrum are about 1pm and unique for each element.

- **Absorption** S.: A continuous spectrum, like that of white light, interrupted by dark lines or bands that result from the absorption of certain frequencies of light by a substance through which the radiant energy passes; a plot of absorbance as a function of wavelength (e.g. Frauenhofer lines).
- **Emission** S.: The distribution of wavelengths in the light from a luminous source; every element has its particular distinguishable pattern of electron energy level (responsible for chemical properties) and therefore emits its own characteristic collection of spectral lines that are observed when species in excited states relax by giving off their excess energy as electromagnetic radiation ($E = \nu \cdot h$); common applications are seen in street lights and neon lights: $Hg + energy \rightarrow Hg^* \rightarrow Hg + bluish\text{-}green\ light$
  $Na + energy \rightarrow Na^* \rightarrow Na + yellow\ light$
  $Ne + energy \rightarrow Ne^* \rightarrow Ne + orange\text{-}red\ light$
- **Sample and Screening Procedures**: Spectroscopic methods often require several preparative steps before a sample can be scanned. Most spectroscopic methods even rely on comparative analysis rather than on absolute determination of the analyte concentration. In such cases, analytes have to be compared with a dilution series derived from a reference sample (i.e. standard):
  i) calibration standard which include additives that simulate the matrix of the analyte;
  i) determination of screening technique according to standardized operation procedure (SOP);
  i) sample conversion from solid to liquid (for AAS, AES, MFS, RS, IR, UV-VIS, etc. only);
  i) calibration of spectrometric setup;
  i) actual measurement of sample;
  i) evaluation of obtained spectra: sensitivity, detection limits (DL), alternatively, determination limits (= 6·DL); interference check, cross selectivity check (i.e. matrix selectivity); determination of dilution factor (e.g. 100·DL); determination of blank values, offsets, etc.;
  i) interpretation of results upon precision, correctness, detection limits, sensitivity (the steeper the calibration curve, the more sensitive the system); retreavability rate method in use;

Ch-4 - Molecular Spectroscopic Methods:

UV/VIS Absorption Spectroscopy: A technique that detects radiation associated with π-bonded electron transitions ($\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$) in molecules within the electromagnetic spectrum between 180-780nm. Photon absorption arises from the transition of a "bonding" electron (excitation) from the ground state to one of the many vibrational and rotational energy states which results in a shift of the absorption lines (ionization threshold is hardly ever reached). UV-VIS features moderate to high sensitivity for entire molecules, good accuracy, ease and convenience.

Instrumentation: Some are designed for the visible region alone. Others have ranges that extend from 180 to 200nm in the UV (requires sample holders made of quartz-glass) through the VIS region to 800nm. A few cover the UV/VIS region and stretch into the NIR to 3000nm. Simple **photometers** use absorption filter or an interference filter to trim down the spectral band. Although, these instruments are low cost, simple, portable, easy to maintain, and are used to obtain quick references, they have a are lower versatility, and are unsuitable to generate whole spectra. UV photometers are important detectors in high-performance liquid chromatography (HPLC). More sophisticated UV-VIS spectrometer - be it a single- or double-beam (uses a reference beam for comparison) instruments - consists of the following units (refer also to chapter 3):

- **Radiation Source**: A Tungsten/halogen- or even better a Deuterium-lamp serves to provide a continuos light spectrum in the UV-region (due to red-shifts, absorption spectra are visible in the VIS-region).
- **Monochromator**: In UV-VIS mostly diffraction gratings (holographic) are used.
- **Detectors**: To measure extinction in UV-VIS, the photodiode; is commonly used.

Qualitative applications: UV-VIS is quite poor in species identification (IR spectroscopy provides better results); comparing the spectral plot with library data though, a good approximate of the substances screened can be given. Similar molecules however do not differ distinctively, making further analysis necessary. There is also only moderate absorption in the spectral wavelengths of 200-800nm (aliphates, certain alcohols, ethers, acids, and esters). Aldehyds and ketons yield a narrow but unspecific peak at around 280nm.

- **Absorption by inorganic compounds**: Ions and complexes of inorganic elements in the first two transition series appear colored as they absorb broad bands of visible radiation at least in one of their oxidation states. Absorption spectra of ions of the lanthanide and actinide transition series tend to be narrow and relatively unaffected by the species involved in bonding with the outer electrons (e^- responsible for absorption are shielded by e^- that occupy orbitals with larger principal quantum numbers "*n*").
- **Absorption by organic compounds**: Saturated organic compounds containing heteroatoms (such as O, N, S, Cl, Br), contain nonbonding electrons that can be excited by radiation in the 170-250nm range. Electrons involved in double and triple bonds of organic molecules are easily excited by radiation. π-π^* transitions (207-215nm), n-π^* transitions (275-295nm), σ-σ^* transitions (too stable for UV-VIS, which explains why aliphates, ethers, acids and esters are UV-VIS insensitive). The resulting electronic absorption bands are made up of numerous closely packed but discrete lines. UV- VIS absorbing groups are known as **chromophores**.

  Chromophore: Unsaturated organic functional groups that absorb in the ultraviolet or visible region. Such chromophores can be isolated or conjugated groups. The presence of π-bonds in chromophores lead to the bathyochrome effect (red-shift) The more chromophoric groups are present within a molecule, the stronger the red-shift (e.g. in polyene). Aromatic ring systems have autochromatic groups with very pronounced delocalized π-orbits and are thus UV-VIS sensitive. and hypochrome (blue-shift) effects. As UV-VIS is very selective to chromophores, it is a powerful tool to distinguish among isomers; e.g. ortho-, meta-, para-benzene. In **ketons** (functional group is -C=O) and **aldehyds** (functional group is -C=O-H) only the -C-atom is involved in π-bonding, while the lone e^-pair of the O-atom is responsible for the hypochrome effect - both π-bonds and blue-shift result in weak absorption bands at around 280nm.

Quantitative applications: In order to achieve linearity (between energy and concentration - see Lambert-Beer, chapter 3), highly monochromatic radiation should be used (grating with narrow slits). Furthermore, no concentration dependant reactions should be scanned (energy shifts), and the influence of the solute should be neglectable. In order to achieve reliable results, a reference standard (in form of a dilution series) is required.

Sample Preparation: Suitable solvents that are not affected by UV/VIS-radiation; i.e. w/o absorbance like polar solvents, perfluoridic alkanes, pentone, hexane, cyclohexane and chloroform (all for wavelengths around 240nm). Above 280nm, benzene, toulene, or tetra-hydro-furane should be used.

Spectrometric Determination of pH: The pH of an unknown buffer is determined by addition of an acid/base indicator and spectro-photometric measurement of the absorbance of the resulting solution. Because overlap exists between the spectra for the acid and base forms of the indicator, it is necessary to evaluate individual molar absorptivities for each with two wavelengths.

Molecular fluorescence spectroscopy (MFS): Excitation of compounds with radiation in the UV/VIS-spectrum relax by loosing their energy via spontaneous emission predominantly in the visible band. This effect is only evident with π-bonding electrons (e.g. aromatic and heterocyclic molecules) and does not occur in σ-bonds. The absorbed energy is higher than the emitted energy ($E_{in} = h \cdot \nu_{in} > E_{out} = h \cdot \nu_{out}$) in that the wavelengths of the emitted radiation becomes longer (red-shifts). Similarly, the red-shift becomes more evident as more functional groups are attached to the central molecule. Delayed photonic emission in MFS can be of the following:

- **Fluorescence**: Is an analytically important emission process (over $1 \cdot E^{-5}$ s or less) in which atoms or molecules are excited by the absorption of a beam of electromagnetic radiation. The excited species then relaxes to the ground state, giving up their excess energy as photons; i.e. anti-parallel spin $S_{R*} \rightarrow S_{R0} + h \cdot \nu$ [ns]
  Fluorescence bands: consist of a host of closely spaced lines.
  Resonance fluorescence: has an identical wavelength to the radiation that caused fluorescence.
  Stokes Shift fluorescence: is longer in wavelength than the radiation that caused fluorescence.
- **Phosphorescence**: It may go on for several minutes or even hours, in which atoms or molecules are excited by the absorption of a beam of electromagnetic radiation. The excited species then relax to the ground state, giving up their excess energy as photons; i.e. parallel spin $S_{T*} \rightarrow S_{R0} + h \cdot \nu$ [s, min, h]. As phosphorescence is less energetic than fluorescence, it displays far greater red-shifts that fluorescence.

Instrumentation: Mercury- or xenon lamp for UV and laser light for VIS, two monochromators (one for the radiation source and the other at 90° to the incident beam for the detection of the emission intensities), and a PMT detector (photo-multiplier tube - see also chapter 3). Fluorescence is generally a fairly strong signal; as it spreads homogeneously in any direction it is possible to detect in perpendicular orientation to the incident radiation. Such an arrangement makes sure that only the fluorescence and not the excitation radiation is registered. Most MFS-devices record both fluorescence and phosphorescence emission spectra. By cooling the sample holder down to 77K, it is possible to extend the lifetime of such emission spectra. MFS is often used as a detection device in HPLC.
Qualitative Analysis: A spectrum with one or more unstructured peaks does not reveal simple identification of the samples involved; it rather requires a library database for identification. Identification of molecular structure is not practicable. Aliphatic groups that predominantly are σ-bonded are not MFS-sensitive.
Quantitative Analysis: Mathematically expressed as:
$F_x = \phi \cdot I_0 \cdot (1 - 10^{\varepsilon \cdot c \cdot d})$ [W/m²]
due to the several unknown variables, absolute quantitative determination is not easy; it is thus more practicable to rely on relative means to obtain quantitative results; i.e. by using a standard and the analyte:
$c_X = c_{St} \cdot (F_X / F_{St})$

ϕ, photonic flow	[photons/mol]
I_0, initial photon intensity	[W/m²]
ε, coefficient of extinction	[L/(mol·m)]
c, concentration	[mol/L]
l, thickness of sample	[m]
c_{St}, concentration of standard	[mol/L]
F_X, fluorescence of analyte	[phot./mol]
F_{St}, fluorescence of standard	[phot./mol]

As only the emitted fluorescence spectrum is processed, MFS is a highly sensitivity and selectivity method. Therefore, it can be used for trace-analysis with detection limits in the $1 \cdot E^{-9}$-range.

Molecular absorption spectroscopy: Molecules undergo three types of quantized transitions when excited by UV, visible and IR radiation (vibration and rotation). It is widely used for the identification and determination of a myriad of inorganic, organic, and biochemical species. Molecular UV/VIS absorption spectroscopy is employed primarily for quantitative analysis and is probably more widely used in chemical and clinical laboratories. Infrared absorption spectroscopy is one of the most powerful tools for determining the structure of both inorganic and organic compounds of environmental pollutants.

Infrared Absorption Spectroscopy (IR): Any molecule possessing a dipole moment (DM) is IR-sensitive. Vibrational and rotational absorption of IR-frequencies of nuclei result in an IR-spectrum, which shows closely spaced absorption peaks resulting from transitions among the various vibrational and rotational quantum levels of functional groups in the sample molecule. IR is not useful in determining quantitative measurements but provide a powerful tool for qualitative analysis since most molecular species absorb IR radiation (except for a few homo-nuclear molecules such as O_2, N_2, Cl_2, etc. do not have a DM). IR utilizes radiation spectra in the far (FIR), middle (MIR), and near (NIR) bands; thus, it provides good data of the functional groups present within a compound.
Oscillations relevant for IR: In a 3-atomic molecule (e.g. H_2O), the stimulating incident light causes the terminal appending atomic nuclei to oscillate around the centrally located atom. But only certain oscillation change the dipole

moment of a given molecule (refer also to chapter 2). In IR- spectroscopy, the bending and asymmetrical stretch vibration are relevant whereas the symmetrical stretch vibration is not (dipole moment $\mu = 0$):

- **Asymmetrical Stretching Vibration** (i.e. valence vibration): A change in the interatomic distance along the axis of the bond between atoms, in that one interatomic bond shortens while the other one stretches.
- **Bending Vibration** (deformative vibration): Are characterized by a change in the angle between two bonds and are of four types: scissoring, rocking, twisting, wagging.

$$\nu_{osc} = \frac{1}{2\cdot\pi} 100 \cdot \sqrt{\frac{K}{m_{GM}}} \quad [1/s]$$

$$m_{GM} = (m_1 \cdot m_2) / (m_1 + m_2) \quad [g]$$

π, circle constant 3.14 [-]
K, spring constant [N/m] = [g/s^2]
m_{GM}, geom. mass equivalent [g]
$m_{1,2}$, atomic masses of atoms [g]

IR is one of the most powerful tools in the identification of pure organic and inorganic compounds. Except for chiral molecules in the crystalline state, each molecular species has a unique infrared absorption spectrum. It is less satisfactory for quantitative analysis because of its narrow peaks that usually lead to deviations from Lambert-Beer's Law. As it is less precise, it provides at least a degree of selectivity in quantitative measurements.

Instrumentation: A 2-beam IR spectrometers uses is a Si-carbid- or Tungsten lamp, that irradiates equally strong IR-beams through a sample compartment and a parallel aligned reference compartment. A photometer detects the differences in incoming radiation and feeds it via a monochromator to the detecting device (usually a thermo-element). A readout unit finally displays the wavenumber versus transmittance onto a screen or plotter. Fourier-Transform IR-spectrometers a somewhat different as they are based on the Michelson interferometer (explained further below).

- **Sample holder**: IR usually involve liquid or gaseous samples, but samples embedded in KBr-chips allow analysis ("shining through") of solid analytes. The sample holder typically is made of NaCl, KCl (both fairly unstable) or other materials that do not posses dipole character, which would otherwise interfere with the probe. Microsamples are spread on a thin film, while attenuated total reflection analysis (ATR) involves radiation at a low incident angle, and registration of the reflected spectrum. Gaseous samples can also be screened with IR.
- **Types of IR spectrometers**: Out of three types of instruments are found in modern labs - the Dispersive spectrometers, (or spectro-photometers for quantitative analysis), the Filter photometers (designed for quantitative analysis of simple compounds - works without grating or prism to disperse radiation), and the Fourier-Transition (FTIR) spectrometers - the latter one is the most commonly used device for quantitative analysis. FTIR do not contain gratings or prism to disperse radiation. All wavelengths are detected and measured simultaneously. In order to separate wavelengths, it is necessary to modulate the transmitted signal in such a way (i.e. movable mirror) so it can be decoded by Fourier transformation (is a mathematical operation that will resolve any periodic wave form into a series of simple sine waves). FTIR yields a time-resolved interferrogram (time domain), that after transformation yields a frequency-resolved spectrogram (frequency domain). FTIR offers not only the advantage of unusually high sensitivity, resolution, and speed of data acquisition (<1s), but equally important the good signal-to-noise ratio (SNR); with every acquisition run peak intensity can be improved while noise acquisition rises only with the square root of the total number of acquisitions (which cannot be done with dispersive or filter IR-spectrometers).

Qualitative analysis: Measuring thermal energy change rather than radiation, IR-spectroscopy does not easily reveal the nature of a molecular substance. Furthermore, relatively simple compounds often contain an array of sharp peaks and minima that are useful for the identification of functional groups (at wavenumbers >1500cm^{-1}) and a fingerprinting region (<1500cm^{-1}). Identification of the functional groups in a molecule is seldom sufficient to positively identify a compound. It is more suitable to match the entire spectrum with an electronic library database; e.g. $\bar{\nu} \approx 1500\text{cm}^{-1}$ stretching and bending vibrations; $\bar{\nu} \approx 2500\text{cm}^{-1}$ stretching vibration (C≡C, C≡N, etc.); $\bar{\nu} \approx 3000\text{cm}^{-1}$ for stretching vibrations (O-H, C-H, etc). As ortho-, meta-, para-isomers differ significantly in the 1500cm^{-1} range, IR is a very powerful tool to distinguish them; e.g. o-,m-, p-xylene.

Quantitative analysis: Due to interaction of rotational and stretch vibrations, peak-broadening occurs regularly in IR (in this aspect UV-VIS is more suitable). The complex spectrum, with broadened absorption bands and often inclining baselines require some approximations which can be applied by the following equation (see also Lambert-Beer's law - chapter 3):

$$E_\lambda = \log \frac{I_0}{I} \quad [-]$$

I_0, initial intensity [%]
I, detected intensity [%]

Raman Spectroscopy (RA): Vibrational and rotational absorption of both atomic nuclei and orbiting electrons result in a Raman spectrum. It is the result of inelastic scattering of photons of the analyte aimed at. Raman is most useful in the analysis of non-polar (hydrophobic) and scarcely hydrophilic substances (C≡C, C=C, N=V, C-C, O-O, S-S, CO_2, etc.) that are polarizable ($\alpha \neq 0$; bonding e^--cloud can be deformed) but do not posses a dipole moment; e.g. the vibration in N_2 is not IR- but Raman-active, because only the polarizability of the molecule is changed during the N-N vibration the delocalized electrons interact with the oscillating electromagnetic field.
The scattered radiation is termed *Stokes* and *anti-Stokes* (emission peaks due to inelastic scattering differ in wavelength of the excitation frequency), and *Rayleigh* (elastic scattering, equal to excitation frequency - the signal intensity of the latter, $1 \cdot E^{-4}$ is significantly more intense than either of the former, approx. $1 \cdot E^{-8}$). The Stoke (=Raman) peaks with identical patterns, are found in either side of the Rayleigh peak. Shifts toward higher energies (higher frequencies) are termed *anti-Stokes* while those with longer wavelengths are termed *Stokes*; quite generally, anti-Stokes lines are appreciably less intense than the corresponding Stokes lines. For this reason, only the Stokes part of a spectrum is generally used. The energetic differences between Rayleigh and Stokes lines reveals the frequency of the vibration of the molecular species. Any fluorescence effects occurring during excitation with a laser makes Raman unsuitable, as the fluorescence flood the relatively weak antistoke / stoke signals.
Oscillations relevant for Raman: In a 3-atomic molecule, the stimulating incident light causes the terminal appending atomic nuclei to oscillate around the centrally located atom. But only certain oscillation change the polarizibility of the molecule, i.e. the **Symmetrical Stretching Vibration**. The inter-atomic distances change simultaneously in that shortening of all inter-atomic bonds is followed by synchronous stretching.
Instrumentation: As Raman spectra are incredibly weak signals, they are best obtained by irradiating a sample with a powerful laser source of visible or infrared monochromatic radiation. During irradiation, the spectrum of the scattered radiation is measured at some angle (usually perpendicularly) with a suitable spectro-photometer (increased sensitivity can be obtained by cooling the detecting device with liquid N_2 to 77K). At the end of the signal processing path, a readout device displays the emitted Stoke-peaks versus wavenumber.
Qualitative analysis: Measuring structural vibrations of nuclei and electrons alike, makes Raman spectroscopy a powerful complementary tool to IR-spectroscopy; i.e. IR-spectroscopy detects vibrational motion involving a dipole moment, whereas Raman spectroscopy registers polarizibility of molecues.
Fluorescence may interfere seriously with the observation of Stokes shifts but not with that of anti-Stokes shifts. With fluorescing samples, anti-Stokes signals may therefore be more useful, despite their lower intensities.
Quantitative analysis: Similarly as in IR-spectroscopy, peak intensities can be utilized to measure the species intensity by comparing it to a series of standardized reference solutions.

Nuclear Magnetic Resonance (NMR): Rotation of nuclei about an axis implies an angular momentum {$p = h/(2 \cdot \pi)$} of the nucleus and a magnetic momentum (μ) of the circulating electrons. Nuclei with $m_s = 0$ have no nuclear momentum and can't be observed by NMR ($\sum(p+n)$ = even mass numbers of atoms or isotopes do not posses any μ; thus are not NMR sensitive; e.g. ^{12}C, ^{16}O, and ^{32}S). Isotopes with $m_s \geq ½$ are NMR active (e.g. ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P, etc.).

Mathematical notion of the magnetic momentum

$$\mu = \gamma \cdot m_s \cdot \frac{h}{2 \cdot \pi} \quad [J \cdot s]$$

γ, gyromagnetic moment		[-]
m_s, spin quantum number		[-]
h, Planck's con.	$6.626 \cdot E^{-34}$	[J·s]
π, circle constant	3.14	[-]

These tumbling nuclei with $m_s \geq ½$ possess "p" while their spinning electrons possessing "μ", generate a tiny magnetic field on their own. These randomly oriented nuclei will align themselves as soon as a static external magnetic field (B_0) is applied. Quantum mechanics dictates a distinct angle of tilting (54.4°); thus, the oscillation, results in a double cone with an angular speed of:

$$\omega = 2 \cdot \pi \cdot f = \gamma \cdot B_0$$

A certain population of nuclei (N^+, m = +½) will align themselves with the magnetic vector B_0 while the remaining nuclei (N^-, m = -½) against B_0. At room temperature, with more nuclei in the lower energetic state (N^-), a resultant macroscopic magnetization (M_0) in the direction of the externally applied field will result ($N^- > N^+$ or $N^+/N^- \approx 7 \cdot E^{-6}$). The slight population excess in the lower level absorbs energy from the irradiating field. Accordingly, the energy between these two energy levels is proportional to B_0:

$$\Delta E = E_{-1/2} - E_{+1/2} = (-\mu_{-1/2} \cdot B_0) - (-\mu_{+1/2} \cdot B_0) = \mu \cdot B_0$$

μ, magnetic moment	[J·s]
B_0, magnetic flux density	$[V \cdot s/m^2] = [T]$

Transition between the two energy levels can occur when an additionally irradiated frequency (ν), usually in the form of RF-signal (Radio Frequency) meets the energetic difference of the two energy states:

$$\Delta E = h \cdot \nu_{RF}$$

ν_{RF}, radio frequency [Hz]

Transition from the lower (N^-) to the upper energy level (N^+) correspond to an absorption of energy, and those in the reverse direction to an emission of energy. Each transition is associated with a reversal of the spin orientation.

Chemical Shift: It is the frequency shift as a result of the shielding molecular environment; i.e. the nuclei under investigation are shielded by neighboring molecules, which weakens the externally applied magnetic field B_0.

$B_{eff} = B_0 \cdot (1-\sigma)$ σ, shielding constant [-]

The total range of chemical shifts in ^1H and ^{13}C NMR spectroscopy is approx. 10ppm and 220ppm respectively. Since $B_0 \propto \nu_{res}$, it is a lot more practicable to measure the frequency difference ($\Delta\nu$) between the resonance signals of the sample and that of a reference compound (in ^1H- and ^{13}C-NMR spectroscopy, tri-methyl-silane - TMS is used). For this purpose the dimensionless quantity δ (rho) is defined:

$$\delta = \frac{\Delta\nu \cdot 1 \cdot E^6}{\nu_{observed}} \quad [ppm]$$

$\Delta\nu$, frequency difference [Hz]

$\nu_{observed}$, observing freq. [Hz]

In reference to TSM, a compact molecule as 1-nitro-propane (CH_3-CH_2-CH_2-NO_2) generates three resonance bands in ^1H-NMR. Usually the apical methyl-group (CH_3, with e^--pulling properties) will experience a less intense shift than the centered methylene group (CH_2), while the outermost CH_2-group (with e^--pushing properties) will experience the largest shift.

Spin-Spin coupling: The coupling mechanism - which can stretch as far out as 3 atomic layers - and according to Pascal's triangle, generates a characteristic multiplet pattern; e.g. ethyl-bromide (CH_3-CH_2-Br) in ^1H-NMR, the methyl group (CH_3) with 3H-atoms causes a quadruplet interference pattern (1:3:3:1) onto the neighboring methylene-group (CH_2), while the latter with only 2 H-atoms itself will interact with the former and splits it up into a triplet pattern (1:2:1). In isolated nuclei of ^1H NMR there is just one peak (-X$\mathbf{H_x}$ n=0 → 1), in a 2-spin system there is a doublet (-X$\mathbf{H_x}$ coupled to -H; n=1 → 1:1), in a 3-spin system there is a triplet (-X$\mathbf{H_x}$ coupled to -XH_2; n=2 → 1:2:1), in a 4-spin system there is a quadruplet (-$\mathbf{H_2}$ coupled to XH_3; n=3 → 1:3:3:1), and so forth.

Number of patterns $M = 2 \cdot n \cdot m_s + 1$ n, neighboring equivalent nuclei [-]

Resonance criteria: Is the energy ($\Delta E = h \cdot \nu_{RF}$) required to turn the magnetic spin m_s from $-^1/_2$ to $+^1/_2$.

- At a preset externally applied field (B_0), every isotope shows a distinct resonance frequency, that can be traced with a tunable frequency generator; (or vice versa: fixed frequency and an adjustable magnetic field).
- Instruments and spectra are determined by the frequencies; i.e. 90MHz instrument or 90MHz spectrum.
- ν_{res} of different nuclei at a given magnetic field flux of 1T are spaced several MHz from each other.
- High-resolution instruments even yield the doublet or triplet structure of a distinctive isotope. Impossibility to provide a constant and stable magnetic field and interaction with surrounding molecules (mainly dipole moment and covalent bonding) causes band broadening.

Instrumentation: A magnet aligns the nuclei along or against a magnetic field (poles of magnet in z-axis); a RF-sweeping signal (tunable ν_{RF}) lifts the spinning electrons into an excited state; as the wavelength of the RF-signal becomes longer ($<\nu_{RF}$) or even switched off, the excited nuclei (N^+) spontaneously fall back to the ground state by emitting a characteristic frequency (emission in x-axis), and a receiver detects changes in the magnetic flux (physically, the RF-loop is popped over the sample tube and oriented in the x-axis). Using pulsed RF-signals though provide an interferogram rather than a continuos spectrum. Applying the mathematical operation of the Fourier transformation converts this time domain into the frequency domain (intensity vs. frequency shift).

To improve resolution, it is necessary to cool the sample to 77K (via liquid $^{14}N_2$); as this temperature forces all nuclei into the relaxed N^--state, it requires a higher induction energy ($>\nu_{RF}$) to raise nuclei into the N^+-state.

To avoid interference of the solute with the solvent, the solvent must be NMR-ineffective; in ^1H NMR: deuterium (^2H). In ^{13}C NMR spin-spin coupling can be suppressed. Because the ^{13}C-isotope is less readily available (γ of ^{13}C = $1/6000^{th}$ of ^1H), thus, more RF-energy is required; e.g. pulsed RF avoids carbonization of the substance; subsequent Fourier transformation reveals the ^{13}C pattern.

Qualitative analysis: Structural determination of molecules as well as differentiation among isomers is possible. The spin-spin coupling, e.g. a triplet vs. quartet (3:2) in ^1H NMR spectroscopy reveals the number of protons involved (as stated by the Pascal triangle). In two-dimensional (2D) NMR both axes are frequency axes, while the intensities are encoded in the third dimension. In this way either ^1H-^1H or ^1H-^{13}C correlated spectrograms are obtained (H,H-COSY or H,C-COSY); in this way for every hydrocarbon-molecule (HC) a specific 2-dimensional map is obtained.

Quantitative analysis: The amplitudes of singulets or multiplets are direct quantitative indicators, and integration of these patterns reveal the number of protons or carbon-isotopes involved (^1H-NMR). In H,H-COSY or H,C-COSY, the third dimension encodes the intensities of each multiplet pattern. For statistical evaluation of the integrative data refer to XRFS p.20.

Mass Spectroscopy (MS): MS is based on the generation of gaseous ions, isotopes (charged species) from analyte molecules under evacuated conditions, and their subsequent separation in electro-magnetic/-static field. Separation is achieved according to their mass-to-charge ratio (m/z); this ratio is proportional to the extent of deflection of the externally applied field. MS in combination with GC, LC, and HPLC is a powerful tool in species identification.
Instrumentation: Roughly about four building blocks are required to successfully setup an MS. The Sample introduction system (1) comprise controlled leaks for the introduction of analyte vapor from a reservoir (low volatility liquids, and solids originating from several chromatographic sources). In general, samples are introduced into a high vacuum region, where the ion source, the mass analyzer, and the ion detector are housed. Ionization (2) of the analyte can be performed in a number of ways and usually is brought about by electron ionization, chemical ionization, desorption ionization, or other means. After generation, these ions are separated in a mass analyzer (3), most commonly used are magnetic sector, quadrupol mass filter, quadrupol ion trap, time of-flight, and ion-cyclotron resonance instruments. Detection (4) of ions in most cases is performed with an electron multiplier.

- **Ionization** techniques: It is done by bombarding the analyte with electrons, ions, molecules, or photons. In this way usually positive ions (cations) are generated (the smaller, lighter particles capture the electron as their inter-nuclear distance is smaller than the bombarded molecule); several ionization methods can be employed:
  Electron Ionization (EI): The analyte vapor is subjected to a bombardment of energetic electrons from a direct electrically-heated tungsten or rhenium filament. The maximum energy that can be transferred during ionization is the difference between the electron energy (typically 70eV = 6.8MJ/mol) and the ionization energy of the analyte (usually 6-10eV). While most electrons are elastically scattered (rotational and vibrational effects), others, upon interaction, cause electronic excitation of the analyte molecules, while a few cause the complete removal of an electron from the analyte molecule. As a result, a singly-charged, radical cation, and two electrons are produced: $M + e^- \rightarrow M^+\bullet + 2e^-$
  Desorption Chemical Ionization (CI): It is basically an indirect ionization of the target molecule via an inter-mediate reactant agent. The agent is exposed to a 50-200µm wire to which direct or rapid electrical heating can be applied; such reactants are noble gases (e.g. Ar), or organic gases (e.g. CH_4). As this reaction takes place in a pressurized chamber, the ionized reactant come into contact with the target gas (M) to perform the net charge transfer. CI is also termed as "soft" ionization, as it avoids unnecessary fragmentation of the molecular analyte species: $2CH_4 \rightarrow$ e-bombardment $\rightarrow 2[CH_4]^+\bullet + 2e^- \rightarrow [CH_5]^+ + [CH_3]\bullet$
  $[CH_5]^+ + M \rightarrow CH_4 + [M]^+$
  Field Desorption (FD): A sample solution is deposited on a 10µm tungsten wire (anode). The anode is placed at a high electric potential (10kV), which results in a high local electrical field strength at the tip of the wire (typically $1{\cdot}E^8$ V/m). The field enables electron tunneling from the sample to the anode, where they take up an electron ($M + e^- \rightarrow M^-$; $M^- + M \rightarrow M^- + M^+\bullet$) and ultimately followed by desorption of a radical cation. This ion may be detected directly or react with other analyte ions in ion-molecule reactions, resulting in a current of protonated molecules which is subsequently detected. FD is suited for the ionization of biomolecules.
  Fast Atom Bombardment (FAT): The analyte is dissolved in an appropriate non-volatile matrix solvent (e.g. glycerol). The solution is deposited as a homogenous thin film on a metal target (direct insertion probe). The target is transferred to the high vacuum of the ion source and bombarded with 8keV particles of Ar or Xe atoms (the noble gas molecules are first ionized, accelerated and neutralized before hitting the target molecules - similar to Billiard). Upon impact, M^+ are liberated, while the negative charges remain attached to the solvent.
  $Ar° + 8keV \rightarrow Ar^+ + e^-$; $Ar^+ + Ar° \rightarrow fastAr° + Ar^+$; $fastAr° + M \rightarrow M^+ + Ar° + e^-$;
- **Quadrupol MS**: Generated ions are electrostatically extracted from the ionization chamber and introduced into a quadrupol mass filter (cheaper than magnetic separation). It consists of 4 stainless steel hyperbolic or circular rods that are accurately positioned parallel in a radial array. Opposite rods are charged by either a positive or a negative direct current (DC), at which an alternating current (AC) is superimposed. The AC ($\omega = 2{\cdot}\pi{\cdot}\Delta f$ in the RF region) successfully reinforces and overwhelms the DC field. Ions fed into the system start to oscillate in a plane perpendicular to the rod length as they transverse through the quadrupol filter. According to the ions m/z ratio, a certain frequency results in a stable trajectory; therefore, these ions are transmitted towards the detector. In ions with unstable trajectories, the resonance frequency equals the mass to charge ratio, their oscillating amplitude becomes infinite which causes them to crush against the rods before even leaving the filer.
- **Electron multiplier**: Detection of ions by means of an electron multiplier is based on the emission of secondary electrons, resulting from the collision of energetic particles at a suitable surface. The secondary electrons can be multiplied by consecutively striking subsequent surfaces. The electron multiplier may be either of the discrete or of the continuos dynode type (similar to PMT - chapter 3). The typical gain of an electron multiplier is $1{\cdot}E^6$.

Qualitative analysis: MS is not only the most sensitive spectrometric technique for molecular analysis but "the" tool in the determination of molecular mass, molecular formula, or elemental composition, and in structure elucidation (structural elucidation of unknown compounds such as natural substances, metabolites, xenobiotics, and synthetic compounds). Determination of molecular mass is achieved by analyzing the isotope cluster at the highest m/z end in the spectrum which usually corresponds to the molecular ion mass. The assignment can be checked with the nearest fragment ions (every molecule produces a specific MS-spectrum). Confirmation some-times involves requires soft ionization methods to suppress fragmentation of the parental molecule. Furthermore, ions with even number of electrons do have greater stability than uneven, i.e. radical-ions (**even electron rule**).

- **Fragmentation series**: Fragmentation occurs as charged molecules are quite unstable. Structure elucidation of the molecular ion is a complex network of competing and consecutive reactions, the yield of which are determined by the stability of both the precursor and the product ions. The stability and thus the intensity of the molecular ion peak decreases in the series (n- and π-bonding electrons are easily protonized):
  Aromates > conjugated alkenes > cyclic compounds > organic sulfides > short n-alkanes > mercaptans.
  Ketones > amines > esters > ethers > carboxylic acids, aldehydes, and amides.
  Primary Fragmentation: Molecular ions resulting from the fragmentation of the parental molecule; if the energetic content is still high enough, these ions can further break into a group of secondary progeny (secondary fragmentation) and so forth /the neutral fragment is not detectable - only charged fragments are detectable).
  Fragmentation Rule: Fragmentation of the molecular ion may involve either the loss of a radical, thus resulting in an evenly charged fragment ion ($odd^+ \rightarrow even^+ + radical^\bullet$) or the loss of a neutral, thus resulting in an odd-electron fragment ion ($odd^+ \rightarrow odd^+ + neutral$); the former is far more stable than the latter.
  Stephenson's Rule: It states that in a simple bond cleavage, the fragment with the lowest ionization energy will preferentially take the positive charge;
- **Isotope Identification**: Bio-molecules often involve bromide and chloride components; in both cases a wide selection of isotopes of the respective elements form characteristic clusters. If the chloride is present as a functional group its variability follows the pattern of the Pascal triangle.

Quantitative analysis: MS enables characterization and is thus applied in developing reference methods, and in the quantification of macromolecules (drugs).

Some characteristic fragment ions in electron ionization mass spectra:

m/z	Ion	Functional group	m/z	Ion	Functional group
15	CH_3^+	Methyl, alkane	50,51	$C_4H_2^+$ or $C_4H_3^+$	Aryl
29	$C_2H_5^+$ or HCO^+	Alkane, aldehyde	77	$C_6H_5^+$	Phenyl
30	$CH_2{=}NH_2^+$	Amine	83	$C_6H_{11}^+$	Cyclohexyl
31	$CH_2{=}OH^+$	Ether or alcohol	91	$C_7H_7^+$	Benzy (tropylium ion)
43	$C_3H_7^+$ or CH_3CO^+	Alkane, ketone	105	$C_6H_5C_2H_4^+$ or	Sustituted benzene,
45	CO_2H^+ or CHS^+	Carboxylic acid, thiophene		$CH_3C_6H_4CH_2^+$ or $C_6H_5CO^+$	Disubstituated benzene, benzoyl

Some characteristic *neutral* loss (not detectable as they are uncharged) in electron ionization mass spectra:

Mass loss	Composition	Functional group	Mass loss	Composition	Functional group
15	CH_3	Methyl	31	CH_3O	Methoxy
16	CH_4 or NH_2 or O	Methyl, amide, oxide	32	CH_3OH	Methyl ester
17	OH	Acid, tertiary oxide	33	$H_2O + CH_3$ or HS	Alcohol, mercaptan
18	H_2O	Alcohol, aldehyde	35	Cl	Chloro compounds
19	F	Fluoride	36	HCl	Chloro compounds
20	HF	Fluoride	42	CH_2CO	Acetate
26	C_2H_2	Aromatic	43	C_3H_7	Propyl
27	HCN	Nitrile, heteroaromatic	44	CO_2	Anhydride
28	CO or C_2H_2 or N_2	Phenol, ether, azo	46	NO_2	Aromatic nitro
29	C_6H_5	Alkyl	50	CF_2	Fluoride
30	CH_2O or NO	Methoxy, aromatic nitro			

- **Isotope Dilution Analysis**: In order to determine the unknown isotope concentration within the sample, the ratio between a radioactive isotope and inactive species of the same element must be known (e.g. 99% ^{12}C vs. 1% ^{13}C). By adding a known quantity of a mixture with reversed isotopic distribution enables quantification of the unknown analyte according to:

$$Q = Q_T \cdot \frac{T-X}{X-P} \cdot \frac{\sum P_{ik} \cdot m_i}{\sum T_{ik} \cdot m_i} \quad [\%]$$

The activity resulting from the addition of the activated isotopes before and after the mixing event in both the sample and the reference are used to determine the isotopic ratio within the analyte.

T, isotope ratio of tracers (99% ^{13}C vs. 1% ^{12}C)
X, isotope ratio of selected isotopes in mixture (1% ^{13}C vs. 99% ^{12}C)
P, isotope ratio of samples
m, atomic mass
i,k, indices of the isotopes under question

Ch-5 - Atomic Spectroscopic Methods:

Atomic Absorption Spectroscopy (AAS): A method used for the qualitative and quantitative determination of elements of the periodic table. Detection of limits in AAS lie typically in the ppm to ppb range. Spectroscopic determination is only done in a gaseous medium in which individual atoms are well separated from one another and are energetically present in their ground state.

Instrumentation: AAS is based on the effect when a beam of polychromatic UV or VIS radiation passes through a medium containing gaseous atoms, only a few frequencies are attenuated by absorption, and the spectrum consists of a number of very narrow (≈ 0.005 nm) absorption lines. Absorption spectra for the alkali metal are much simpler than those of elements with additional outer electrons (higher grouped elements of the periodic table). Atomic spectra of the transition metals are particularly complex, with some elements exhibiting thousands of lines.

- **Atomizer**: The first step in all atomic spectroscopic procedures is atomization: a process in which the sample is volatilized and decomposed in such a way as to produce an atomic gas; i.e. an aerosol spray. The efficiency and reproducibility of the atomization step determines the method's sensitivity, precession, and accuracy. The following atomizers are currently in use:

  Flame AAS: A pneumatic nebulizer (generates a fine aerosol spray) converts the sample solution into an aerosol (suspension of finely divided liquid or solid particles in a gas) that is then fed into a burner. Aspiration, powered by a high pressure stream of combustible oxidant, sucks up the sample solution along with the fuel through a fine capillary tube. A series of baffles remove all but the finest droplets. The majority is drained off to the waste container (this explains why only about 20% of the sample solution is actually utilized and forwarded to the nebulizer; this also implies that flame AAS can not be used to determine absolute concentrations, but rather require standardized references with identical or similar matrices in order to obtain real concentrations). Limit of detection is the ppm-range.

  According to the fuel used, combustion temperatures can vary between 1700-3100°C. Generally, the higher the temperature, the higher the total atom population of the flame and thus the sensitivity (except alkali metals). At temperatures exceeding 3000K, nearly half of the species are ionized. As the emission and absorption spectra of ground level and excited (ionized) species differ considerably, control of the flame temperature is very important, in order to avoid ionization (atomic species should remain in the ground state).

  Electrothermal AAS (Graphite-tube or carbon tube atomizer): Electrothermal atomizers provide enhanced sensitivity (better than in flame-AAS) and enable absolute determination as the entire sample is atomized and detected in a short period. Limit of detection of electrothermal-AAS in the ppb-range.

  A few mL of "isoformed" liquid or a few mg of finely grounded solid sample are first evaporated at a low temperature (80-100°C) and then ashed (mineralized) at a somewhat higher temperature (350-1600°C) in an electrically heated graphite tube or cup. After ashing, the current is rapidly increased to several hundred Amps (peak-power dissipation ≤ 5kW), which causes the temperature to soar to almost 3000°C; atomization of the sample occurs in a fraction of a few ms to seconds. The absorption of the atomized analyte is then monitored in the region immediately above the heated surface. Atomization occurs in a cylindrical 5cm long graphite tube, which is open at both ends and has a central hole for introduction of sample by means of a micropipet. The interchangeable graphite tube fits snugly into a pair of cylindrical graphite electrical contacts located at the two ends of the tube. The contacts are held in a water-cooled metal housing. Two inert gas streams are provided - the external stream prevents the entrance of ambient air (otherwise would incinerate the graphite tube), the internal stream flows into the two ends of the tube and out at the central sample port.

  Cold-Vapor AAS: A method used for the absolute determination of volatile metallic compounds like Se, Sb, As, and especially Hg. A sample containing the for example Hg is decomposed in a hot mixture of nitric acid and sulfuric acid, which converts the mercury to mercury(II) salts. These are then further reduced to the metal with a mixture of hydroxyl-amine sulfate and tin(II) sulfate (isoformation). Air pumped through the solution, carries the mercury-containing vapor through the drying tube (reduces adsorptive effects) and into the atomizer (electrothermally heated quartz-oven). Detection of mercury is then achieved as described above. To increase the sensitivity of that method, a gold-membrane can be introduced into the feeding pipe of the atomizer. As Hg comes into contact with the Au, it forms an amalgamate. This reaction can be reversed upon a sudden exposure to high temperatures, which forces the mercury to be liberated and injected at once into the atomizer.

  Samples containing Se, Sb, and As are treated with a mixture of tinhydrite ($SnCO_2$) and sodium-boronhydrite ($NaBH_4$) - both strong reducing agents, which convert these metals into a stable hydrate (corresponds to the process of iso-formation).

- **Radiation Source**: To maximize absorption of the atomized analyte sample it is necessary to use a source that emits in the identical lines as the analyte is capable to absorb. Such resonance criteria are best met when the cathode material of the source is made of the same material as the analyte whose absorption is sought. The atoms of the radiation source are dislodged to form an atomic cloud (this process, called sputtering ejects atoms or ions from a surface by a beam of charged particles). As the atoms producing emission lines are at signifi-cantly lower temperature than the analyte atoms in the flame, the emission lines from the radiation source are broadened less than the absorption peaks in the flame. Several radiation sources are currently in use:
  Hollow-Cathode Lamp (HCL): A metal vapor lamp consisting of a tungsten anode and a cylindrical cathode (same as analyte metal) are sealed in a glass tube containing an inert gas (e.g. Ar). A potential of 300V across the electrodes generates a current that ionizes an inert gas (e.g. Ar). These accelerated ions strike the cathode to dislodge some of the analyte metal and thereby produce a sputtered atomic cloud with some of them in an excited state; as they relax, they emit their characteristic wavelengths (e.g. Na emits a yellowish-orange light).
  Electrodeless Discharge Lamp (EDL): Is a sealed quartz tube containing an inert gas (e.g. Ar) and a small quantity of the analyte metal. The lamp without electrodes, is energized by an intense high-frequency field (EMR), causing the ionized Ar-atoms to collide with the analyte atoms of the metal whose spectrum is sought.
  Continuum Radiation Source: A Deuterium vapor (^2H) lamp that emits a continuos spectrum (160-375nm i.e. UV-VIS-range). In combination with both the HCL or EDL, it is used to detect and quantify continuos spectral noise (won't work with structured background noise! - see below, spectral interference).
- **Monochromator**: The widths of atomic absorption peaks are much smaller than the effective bandwidths of most monochromators; to filter out any absorptive effects that would otherwise interfere with the final reading, monochromators are tuned to the bandwidth that corresponds to the absorption frequency of the solvent element. Both Doppler (shift in detected wavelengths) and Pressure Broadening (slight temperature dependant energy differences between ground and excited states) can be limited by monochromators.
- **Detector**: A photomultiplier is usually used to detect and amplify the reference and sample peak of a particular wavelength. A subsequent computing device calculates the absorbed quantity, which is finally forwarded to the read-out system. Absorbance is directly proportional to the concentration of the element in the atomizer. In low concentrations, it behaves according to the law of Lambert Beer (see page 5 for both PMT and LB-law).

Additives used in AAS: Additives are mixed into the sample to minimize disturbing effects during atomization;
Ionization Suppressor: A readily ionized species that represses ionization of an analyte by providing a high concentration of electrons in the flame.
Isoformation: The addition of certain additives convert the analyte compounds from ionic or various oxidative stages into a hydrate (with a single oxidation number).
Matrixmodifier: Additives that are used to facilitate the dissociation of complex molecules to obtain single species (i.e. reduce analyte atoms into their ground state).
Protective Agent: Reagents that form stable volatile complexes with an analyte and thus prevent interference by anions that form nonvolatile compounds with the analyte.
Radiation Buffer: A substance that is added in large excess to both samples and standards to swamp out the effect of matrix species and thus minimize interference.
Releasing Agent: Cations that react selectively with anions and thus keep anions from interfering in the determination of a cationic analyte.

Interferences experienced in AAS: Two types of interference are encountered in atomic absorption methods;

- **Spectral Interference**: Occur when particulate matter from the atomization process scatters the incident radiation (of an acidic matrix, e.g. H_2SO_4, soot, spectral noise, etc.) or when absorption by an interfering species is so close or even overlap with the absorption peaks of the analyte wavelength.
  Means to reduce Spectral Noise:
  i) **Background Noise Compensation**: A truly continuous spectrum in the UV-region is produced by the electrical excitation of deuterium or hydrogen at low pressure. Chopping alternatively between the radiation source (e.g. HCL) of a particular wavelength and a continuos radiation source (such as a ^2H-lamp) enables quantification of background noise; i.e. yields the effective peak intensity of the absorption frequency.
  i) **Zeeman Effect**: Under the influence of a perpendicularly oriented intense magnetic field, the absorption peak can be split up into three sub-peaks; i.e. resonance peak (π) and two laterally shifted spectral peaks ($\pm\sigma$). Subsequent insertion of a polarizer suppresses the resonance peak, while the lateral spectral peaks are enhanced. The amount of peak enhancement equals the background noise at that particular excitation frequency.
  i) **High Current Operation mode** (with HCL only): Intensifying the current of the HCL causes the resonance peak to attain an M-shaped profile. While peak broadening takes place, the center frequency at which

resonance was first observed, experiences a depression. The extent of the depression is directly related to the amount of background noise present at the resonance-frequency. Even though operation of the HCL in high current mode suppresses background radiation due to self-absorbance, it reduces the lifespan of the lamp significantly.

- **Non-spectral Interference**: Originate from chemo-physical effects and are only observed in flame AAS.
  Chemical I.: Results from various chemical processes that occur during atomization and alter the absorption characteristics of the analyte. Chemical effects observed range from poorly dissociated analyte compounds via formation of radical molecules, to ionization in overheated samples. Such interference can often be resolved by using a continuum radiation source (solvent).
  Physical I.: Results from physical properties of the analyte and matrix of the sample solution. Such physical effects are dependant upon inhomogeneous aerosol formation, altered viscosity, and variabilities in surface tension of the sample solution.

Qualitative Analysis: Species identification occurs as absorption of the incident radiation results in a significant absorbance resonance peak at the detector; signal to noise ratio (SNR) should at least be greater than 3.

Quantitative Analysis: As most of the sample solution is lost during nebulization, concentrations of the analyte in the solvent can only be achieved by comparative means; i.e. referring to a standard.

Absorption is determined as follows:

$A = -\log(I_x/I_0) = k \cdot c \cdot d$

k, extinction coefficient	$[m^2]$
c, concentration	$[mol/m^3]$
d, depth of penetration	[m]

- **Calibration Curve**: In order to use absorbance for analytical purposes, it is necessary to prepare a calibration curve by measuring the absorbances of a series of standard solutions with known concentrations of the analyte complex. The curve is then used to determine the concentration of the unknown solution(s) by finding the absorbance(s) of the known(s) on the absorbance axis of the plot and reading the corresponding concentrations on the concentration axis.
  The steepness of the calibration curve is an indicator of the sensitivity of the method; the steeper the graph (the larger S), the more sensitive the method;

  $S = dA/dc$

A, absorbence	[-]
c, concentration	[mol/L]

- **Standard Addition Method**: It involves adding one or more increments of a standard solution to a sample aliquots of the same size. Each dilution is then diluted to a fixed volume before measuring its absorbance. When the amount of sample is limited, standard additions can be carried out by successive introductions of increments of the standard to a single measured aliquot of the unknown. Measurements are made on the original and after each addition. Placing a regression line through the absorptive data points and interpolating it till crossing the abscissa, yields the initial analyte concentration of the sample.

Preparative steps in AAS: To determine inorganic compounds, the sample analyte must be treated in order to rupture strong bonds between elements. Thus, a suspension of the sample in acid is heated by a flame or a hot plate until the dissolution is judged to be complete by the disappearance of a solid phase. The temperature of the decomposition is the boiling point of the acid reagent. Decomposition should:
i) completely destroy the organic matrix (i.e. to isolate atomic analytes).
i) should not alter the amount of analyte contained;
i) should bring the analyte completely into solution;

- **Wet Ashing Treatment**: It involves strong oxidizing acids, like: concentrated hydrochloric acid is an excellent solvent for inorganic samples but finds limited application for decomposing organic materials; hot nitric acid is a strong oxidant that dissolves all common metals with the exception of Al and Cr. Many materials are decomposed and dissolved by hot concentrated sulfuric acid. Hot concentrated perchloric acid, a potent oxidizing agent, attacks a number of iron alloys and stainless steels (care must be taken because of its potential explosive nature!). *Aqua regia*, a mixture containing 3 volumes of concentrated HCl and 1 of HNO_3, is a well known oxidizing agent for organic matrices. Hydrofluoric acid is mainly used to decompose silicate rocks and minerals in the determination of species other than silica. Wet ashing treatment can be done in open-vessel decomposition, in exhaustive extractions (Soxhlet), or in closed-vessel decomposition.
- **Microwave Decomposition**: Microwave digestion can be carried out in either closed or open vessels, but the former are much preferred because of the higher pressures and thus higher temperatures that are realized. Closed-vessel microwave decomposition is essential in the decomposition of volatile samples like mercury etc.

Atomic Emission Spectroscopy (AES): A method used for the qualitative (and quantitative) determination of elements of the periodic table. Detection of limits in AES methods lie typically in the ppb-range. Spectroscopic determination is usually done in a gaseous medium in which individual atoms are well separated from one another and are energetically present in their excited state. AES can be used to scan both solid and liquid samples.
AES is based on the production and the detection of line spectra emitted during the radiative relaxation process of excited electrons. These electrons belong to the outer shell of the atoms and are called optical electrons. As stated by the Pauli exclusion principle, each line spectrum is specific for an element. The heat promotes the single outer electron of the atoms from their ground state 3s orbital to 3p, 4p, or 5p excited orbital. After a microsecond or less, the excited atoms relax to the ground state giving up their energy as photons of visible or UV radiation.
Instrumentation: An atomic emission spectrometer consists of a radiation source, a sample introduction or presentation system, an optical dispersive system, a detector, and electronics for data acquisition, processing and editing.

- **Atomizer**: The sample can be an aerosol, thermally generated vapor, or a fine powder. An aerosol (similar as in AAS), uses a pneumatic nebulizer, driven by a peristaltic pump, converts the sample solution into an aerosol that is then fed into the radiation source. To obtain a constant flow and homogenous aerosol, a series of baffles remove all but the finest droplets. As a result, the majority of the sample is collected in the bottom of the mixing chamber, where it is drained off to the waste container (this explains why only about 20% of the sample solution is actually utilized and forwarded to the nebulizer; this also implies that flame AES cannot be used to determine absolute concentrations, but rather require standardized references with identical or similar matrices in order to obtain real values). Quite often, the combination of acids and bases that result in the formation of salt depositions clog the system. Solid samples are directly atomized by utilizing a laser-gun, an arc, spark, etc.
- **Radiation Source**: Excitation of atomic species is achieved by using a powerful energy source that is capable to ionize atomized species by intra-atomic collision; currently 2 major types of radiation sources are used in AES:
  i) Sources mostly suited for the analysis of liquids; flames, plasma-, grimmer-, and graphite-furnace;
  i) Sources mostly suited for the analysis of solids; arc, spark, and to a larger extent the laser source;
  The emitted spectrum consists of atomic lines, lines of ionic species, spectrally resolved and convoluted bands of molecules, radicals, and continuum radiation.
  The background radiation is emitted by the sample when each component is present except the analyte. Background emission consists of the lines emitted by the other elements (concomitants, matrix species) and the continuum arising from nonquantized radiation.
  Arc: A stable electrical discharge of a high current and low burring voltage between two (graphite) electrodes.
  Spark: An intermittent, oscillating electrical discharge of high voltage and relatively low current between two electrodes. One electrode consists of the sample to be analyzed whereas the others are usually made of tungsten.
  Grimmer: The emission of light is obtained by electrical discharges b/w two electrodes in a low pressure discharge (<100kPa). The sample to be analyzed usually forms the cathode (glow discharge lamp - GDL).
  Laser: A pulsed UV-laser is used to create a transient plasma at the surface of the solid target.
  Flame: A flame is obtained by the chemical reaction between a fuel gas and an oxidant gas.
  Plasma: A gas containing a relatively high concentration of ionic species like cations and electrons.
  Inductively coupled Plasma (ICP): The most common technique to maintain the plasma involves the use of a radio-frequency induction coil (RF: 5-100MHz / 2kW) which transduces the RF-energy into the SiO_2-torch to the "inert" Ar-gas flow. Ionization of the flowing Ar is initiated by a spark from a Tesla coil. The resulting Ar-ions and their associated electrons then interact with the fluctuating magnetic field from the induction coil. This interaction causes the ions and electrons within the coil to flow in closed annular paths. Ohmic heating is the consequence of their resistance (Ar-ions and electrons) which absorb sufficient power from the RF to main-tain a temperature at which further ionization sustains the plasma indefinitely (ionization due to e^--impact).
  $Ar + e^- \rightarrow Ar^+ + 2e^-$ ..... $Ar + e^- \rightarrow Ar^m + 2e^-$ Ar^m, meta-stable & long-living Ar-species
  $M + e^- \rightarrow M^+ + 2e^-$ ..... $M + Ar^+ \rightarrow M^+ + Ar$..... $M + Ar^m \rightarrow M^+ + Ar$
  The typical plasma has a very intense, brilliant white, nontransparent core topped by a flamelike tail. The core, which extends a few mm above the tube produces a spectral continuum upon which the atomic spectrum for Ar is superimposed. The continuum apparently results when the Ar and other ions recombine with electrons.
  In the region 10-30mm above the core, the continuum fades and the plasma is optically transparent. Spectral observations are generally made 15 to 20mm above the induction coil. Here the background radiation is remarkably free of Ar-lines and is well suited to spectral measurements (suitable to detect emission spectra of analytes).
  By the time the sample atoms reach the observation point in the plasma where temperatures as great as $10 \cdot E^3$ K are encountered, they have had a residence time of about 2ms at temperatures ranging from $6 \cdot E^3$ - $8 \cdot E^3$ K. These

times and temperatures are 2-3 times as great than those attainable in the hottest combustion flames. As a consequence, atomization is more complete and almost no chemical interferences are encountered. Several other advantages are associated with ICP. First, atomization occurs in a chemically inert environment, which enhances the lifetime of the analyte. In addition, the temperature cross section of the plasma is relatively uniform. Therefore, calibration curves tend to remain linear over several orders of a magnitude of concentration.

- **Monochromator**: The grating in AES are similar to those used in AAS; special variations that employ a combination of a holographic grating and a perpendicular oriented prisma enable the investigation of higher refraction orders - this is of essential importance if interferences of lower orders hinder the quantitative determination of the species involved - e.g. Echelle grating;
- **Detector**: Photomultiplier tubes are currently the most widely used types of transducers for detecting UV-VIS radiation. In some cases even SIT-vidicon systems are used; this detectors convert the incoming photons to electrons (Cs-layer) which are then electronically amplified (see also page 5 - PMT).

Interferences encountered in AES: Three types of interference are encountered in atomic emission methods;

- **Ion-Molecule Reaction**: A major complication regarding ICP is encountered when Ar-ions combine with other species of the analyte to form a new molecule; as their atomic masses seem to be identical with other atoms of the periodic table, it may be wrongly identified; i.e. $^{35}Cl + {}^{40}Ar \rightarrow {}^{75}ArCl$, is easily confused with ^{75}As. In such cases only a double-focusing MS is able to differentiate between these similar species by determining the mass to charge ratio up to the 5^{th} digit after the comma.
- **Spectral Interference**: The sheer infinite number of spectral lines obtained from iron can easily obscure other analyte spectral lines; separation of both can only be achieved with high resolution instruments.
- **Viscosity** (in liquid samples): Changes in viscosity of the analyte solution interferes w/ nebulization efficiency.

Qualitative Analysis: Species identification occurs as excited atoms and ions relax to their ground state by emitting a very species-specific pattern of lines.

- Species Analysis: The combination of a chromatographic unit, e.g. HPLC with an IPC and ultimately to an MS, makes it possible to differentiate between organic, inorganic or even between same species of different oxidation numbers (e.g. Cr^{IV} and Cr^{VI}). To make sure that the MS can be operated at vacuum conditions (extends the average free pathway of ions), the ICP has to generate a fine particle flow of ionic species that does not flood the suction capacities of the MS. Therefore, the cone at the exit of the ICP is a precisely manufactured and mounted tool in order to guarantee a substantial flow of species from the ICP to the MS-unit. a major difficulty in this approach are the observed memory effects of sequential scans and the meticulously acurately manufactured skimmer nozzle (at the ICP-MS interface) the separate neutral aerosols from charged ions. For details (see MS page 11).

Quantitative Analysis: AES and especially ICP yield significant better quantitative analytical data than other emission sources. The excellence of these results stems from the high stability, low noise, low background, and freedom from interference of the sources. In general, detection limits with the ICP enables the quantification of species in the ppb-range. As nebulization in the flame atomizer does allow absolute measurements, a calibration curve is required. In contrast to AAS, calibration curves in AES tend to remain linear over several orders of a magnitude of concentration.

Preparative steps in AES: The analyte solution / solid probe cannot be directly fed into the plasma; a series of steps are required to eliminate matrix effects: Initial conditioning (50°C); drying (120°C); ashing, deoxigenation, and mineralization, (800°C); vaporization (e.g. 2400°C); base line stabilization (800°C); Cleaning (e.g. 2600°C).

Nuclear Activation Analysis (NAA): Activation analysis is a method for the determination of elements and isotopes. Although, minor and major elemental components can be detected, its full potential is realized only when it is applied to trace and ultratrace elemental analysis. Amongst other techniques, thermal NAA is by far the most important and widely used method. This technology is used for certified and accredited standards; as NAA works with nuclei rather than orbiting electrons, this technology relies on the generation of radionuclei and can only be executed in highly secured and specially adapted laboratories.

Principle: A stable element (analyte) is exposed to a flux of neutrons in order to add an extra mass unit (conversion of elements); i.e. generating radionucleides. The resulting decay activity (highly radioactive radiation) is quantitatively analyzed and can be of three different kinds (the unit of radiation is Becquerel [Bq], = 1 disintegration/s):

- α-decay (targeted element emits an α- (He) -particle),
- β-decay (emission of a fast electron e^-, leaving behind a cation; is the primary radiation used in NAA!)
- γ-decay (emission of energetic photons; i.e. electromagnetic radiation $E = h \cdot \nu$).

Nomenclature in NAA is simplified to a 2-letter code: n,α; n,β; n,γ; here, in each case the neutron "n" is the activating agent while the greek suffix represents the decay process observed in the analyte.

- **Radiation source**: The most powerful method to generate a dense flux of "thermal" neutrons (also said to be "slow" as they can be moderated with a graphite rods) are obtained by a nuclear fission reactor; ϕ =density [n/cm^3] · speed [cm/s] = $1 \cdot E^{11}$ - $1 \cdot E^{14}$ [n·cm^{-2}·s^{-1}].
  A more practical source to obtain neutrons simply employ the use of radioactive beryllium:
  ^{9}Be(α,n): $^9Be + {}^4He \rightarrow {}^{13}X$, an unstable particle that emits a neutron w/ 5.7MeV to become ^{12}C.
  ^{9}Be(γ,n): $^9Be + h \cdot \nu \rightarrow 2\,{}^4He + 1\,{}^1H + n$
  Be yields only a net neutron flux of $\phi = 1 \cdot E^3$ - $1 \cdot E^5$ [n·cm^{-2}·s^{-1}]; the use of a highly unstably radionucleide-source like Californium (^{252}Cf); it yields a net neutron flux $\phi = 2 \cdot E^9$ [n·cm^{-2}·s^{-1}].
  The amount of activated radionucleides is directly proportional to the neutron flux, the number of radioactive nuclei available, and the aperture's cross section (the higher the flux of "n", the more atoms can be made radioactive). As the decay reaction takes place even during n-bombardment, the decay-constant (or half-life) has to be taken into account:

  $$\frac{dN^*}{dt} = \phi \cdot N \cdot \sigma - (\lambda \cdot N^*) \quad [-]$$

N*, number of activated particles	[-]
ϕ, neutron flux	[cm^{-2}·s^{-1}]
σ, cross section of aperture	[cm^2]
t, time of exposure	[s]
λ, decay constant	[1/s]

  Extending exposure times substantially does not necessarily increase the yield in activation. The following equation can be expressed:

  $A_\infty = \phi \cdot N \cdot \sigma$ — A_∞, saturated activation after t= ∞ [1/s]

  It is important to note that σ changes inversely to the speed of "slow" neutrons (energy <100eV), while it remains constant once "fast" neutrons exceed energies of 3MeV (1[eV] = $1.6 \cdot E^{-19}$[J]).
- **Detector**: β-detectors most commonly used in NAA register the counts vs. the energetic spectrum.
  Geiger counter: Low in sensitivity and but sufficient for simple analysis (for details refer to X-Ray spectr.).
  Scintillation counter: Good for quantitative detection; poor in resolution (for details refer to X-Ray spectr.).
  Semiconductors: Suitable for qualitative analysis as its energetic resolution is far better than the above (-"-).

Qualitative Analysis: Analysis of single elements are quite simple and straight forward. Limit of detection can reach levels as low as [ng]. As shown in the following example of the semiconductor industry, a selection of several elements present within a sample can make identification quite difficult as both elements are just 1 mass unit apart. Secondary reaction in the verification of 0.0001% P in doted high grade Si-wafers modifies the 99.9999% Si to P according to the following reaction: ^{31}P(n, γ): $^{31}P + n \rightarrow {}^{32}P$
^{30}Si (n,γ): $^{30}Si + n \rightarrow {}^{31}Si \rightarrow {}^{31}Si + e^- \rightarrow {}^{31}$P(n, γ): $^{31}P + n \rightarrow {}^{32}P$ (secondary reaction due to measurement)
Disadvantages: As not all elements of the periodic table can be activated in this way or yield a suitable decay signal; NAA is limited to a selected elements only.
Advantages: By increasing the flux of "n", it is possible to detect even very tiny (ultratrace) concentrations of analyte elements in a probe.

Quantitative Analysis: As NAA involves several parameters that are not that easy to quantify, it is more suitable to use it in relative measurements; i.e. a reference standard is used to compare the activity between the standard and the probe. Practically, both the standard and the sample with identical geometry and matrix composition are exposed to the radiation source and analyzed simultaneously.

$$\frac{G_X}{G_S} = \frac{Z_X}{Z_S}$$

$G_{X,S}$, amount of analyte / standard
$Z_{X,S}$, count rate of sample / standard

X-Ray-(Fluorescence) Spectroscopy (XRFS): This method allows direct and non-destructive elemental analysis of solid and liquid matter with minimal sample treatment. The sample is irradiated with X-rays that interact with the innermost electrons of the atom (K- and L-shells). X-rays are photons (electromagnetic radiation) with energies situated between UV-radiation and γ-rays. As the binding energy of inner electrons in the atom is of the same order of magnitude as the energy of the incident X-ray photons, the radiation can interact with these electrons. In principle, all elements from B to U can be determined. The binding energy of the innermost electrons within a sample atom is highest and sharply decreases as one moves away from the nucleus. An X-ray photon with an energy of 20keV can eject a K- or an L-shell electron (8.981keV to eject and 11.02keV to accelerate the photoelectron); however, an X-ray of 5keV can only eject an L-shell electron.

Binding energy of Cu-subshell	K: 8.981 k[eV]	L_1: 1.102 k[eV]	L_2: 0.953 k[eV]	L_1: 0.933 k[eV]

Principle: In photoelectric absorption, a photon is completely absorbed by the atom and an (inner shell) electron is ejected. Part of the photon energy is used to overcome the binding energy of the electron and the rest is transferred to the electron as kinetic energy. After the interaction, the atom (ion) is left in a highly excited state. The vacancy created by the photoelectric absorption will be filled by an electron from a higher shell. As the atom returns to a more stable electron configuration, a characteristic X-ray photon will be emitted (this fluorescence effect is characteristic for each element). When X-ray pass through matter, some photons will be lost by photoelectric absorption (resulting in "bremsstrahlung" while others will be scattered away; consequently, the number of photons will be reduced but their energy is unchanged. The mass attenuation coefficient μ [cm^2/g] is therefore related to the cross section for photoelectric absorption. Elastic and inelastic scattering, depends on the type of atoms constituting the matter, and on the energy of the interacting photons; i.e. low-energy (soft) X-rays are more strongly absorbed by matter than high-energy (hard) X-rays. High z-material (e.g. Pb) attenuate X-rays more strongly (due to the shielding effect of the orbiting outer electron cloud) than low-z materials like C.

Instrumentation: XRFS instruments are built around an X-ray tube, a sample holder, and a spectrometer. The spectrometer measures the wavelength (or energy) and the intensity of the (fluorescence) radiation emitted by the sample. Depending on how the characteristic X-rays are measured, one can distinguish between wavelength-dispersive and energy-dispersive XRFS.

Wavelength-dispersive (WD-XRFS): WD X-ray spectrometers are based on the principle of Bragg diffraction:

$n \cdot \lambda = 2 \cdot d \cdot \sin\theta$

The X-ray is elastically scattered by the atoms of the crystal which acts as a monochromator. According to the crystal used, the radiation splitting effect changes respectively. Therefore, WD-XRFS instruments are characterized by high resolution. As it uses high energetic X-Ray sources, it is used to analyze heavier metals. WD-XRFS relies on Geiger or scintillation counters for detection.

n, order of diffraction	integer, 1, 2, 3, ...	[-]
d, lattice distance		[m]
λ, wavelength		[m]
θ, incoming /outgoing angle of radiation		[°]

Energy-dispersive (ED-XRFS): In this approach, the "dispersion" (selection of the particle energy) and the counting of the number of X-rays (of that particular energy) are done in one step. ED-XRFS are built around a liquid N_2-cooled semiconductor crystal (see next page). As no crystal is used to generate monochromatic radiation, ED-XFRS detects “polychromatic” radiation; i.e. an array of semiconductors is used to simultaneously register several wavelengths along with their intensities. As practical as this may seem, this fairly quick detection technique is less sensitive than the WD-XRFS. ED-XRFS is suitable to screen lighter metals as it utilizes low energetic X-ray sources.

- **Radiation source**: The X-ray tube is made of a tungsten filament (cathode) and anode both mounted in a highly evacuated glass tube. The anode is made from a very pure metal such as Mo, Ag, W, or other than the analyte elements to screen. The filament is heated by the current from a low voltage power supply. This causes thermo-ionic emission of electrons from the wire. Applying a negative high voltage (e.g. -30kV) to the filament, the electrons will be accelerate to bombard the grounded anode. The generated X-ray from inner shell interaction of the anode atoms escape from the tube via a Be-window. The interaction of the electrons with the atoms of the anode causes the production of continuous and characteristic X-rays; i.e. in just one collision, the electron can lose anything between zero and all of its energy, resulting in a continuous spectrum; the super-imposed characteristic X-rays (bremsstrahlung) are the result of direct interaction with the orbiting electrons of the anode material. As the X-ray tube is very low in efficiency, most applications employ a water-cooled radiation source. Every X-ray tube emits a distinct spectrum that is characteristic to the anode material used; therefore, an anode made of molybdenum can't be used to detect Mo; likewise a tungsten tube is unsuitable to scan for W; etc. The harder the anode (heavy z-elements), the “harder” the fluorescence X-rays emitted.
- **Collimator**: A monochromatic device, usually a crystal, used to direct the emitted X-rays towards a particular target area; it limits beam broadening by blocking radiation that deviates from a given exit angle.

- **Detector**: Less energetic fluorescence radiation is best registered by semiconductors, while data evaluation is done by displaying counts versus energetic contents.
  Geiger counter: This flow proportional counter consists of a cell filled with Ar-gas. A thungsten wire at the center of the cell is held at a potential of 1kV. Low energy X-ray entering the cell via a very tiny window interact with the Ar-atoms (photoelectric absorption) resulting in the creation of an Ar^+ ion and an energetic photoelectron. This electron looses its energy by ionizing other Ar atoms, releasing more electrons. These e^- will be accelerated towards the wire and on their way will collide with other Ar atoms causing further ionization and release of e^-. The total number of e^- produced in this way becomes very large but remains proportional to the energy of the X-ray. Finally, the e^- will arrive at the wire causing momentary charging of a capacitor. A preamplifier connected to it converts the charge pulses into a voltage proportional to the incident radiation.
  Scintillation counter: High energy X-rays are best detected with a scintillation counter. A Tl-activated NaI crystal is used as the main detection device. The absorption of an X-ray results in the emission of light photons with a wavelength of 410nm. The photons fall onto the photocathode of a photomultiplier where multiples of electrons are produced (see p. 5 - PMT). The scintillation counter thus also produces one pulse for each X-ray that enters the detector and the height of the pulse is again proportional to the energy of the X-ray.
  Semiconductors: Either a Li doped Si crystal or a hyperpure Ge-crystal is used. The energy difference between the valence and the conduction band is around 4eV. At room temperature, a number of electrons are in the conduction band so that the crystal is a (semi) conductor. By cooling the crystal to the temperature of liquid N_2 (77K = -196°C) almost all e^- will remain in the valence band and no current can flow when a voltage is applied over the crystal. A negative voltage of ca -500V is applied to the front contact (p-layer) of the crystal, while the other end (n-layer) is attached to the detection circuit. The incoming X-ray photon interacts with the crystal. This results in the formation of the so-called "e^- -hole" pairs. Electrons are promoted from the valence to the conduction band, leaving positive "holes" in the valence band. Thus the crystal becomes temporarily conducting. Because of the applied bias voltage, the e^- are swept to the rear contact, and the holes to the front contact, and for a very short moment of time a current will flow through the crystal. This current is proportional to the energy of the high energy X-ray that entered the detector.

Qualitative Analysis: The re-emitted energy (i.e. wavelength) of these fluorescence X-rays are distinct for each element. WD-XRFS provides far better results than ED-XRFS; as WD-XRFS operate sequentially, a 2θ scan needs to be made (i.e. detection of the diffracted beam at twice the angle of the incident radiation). The identification of trace elements can be complicated by the presence of higher order reflections from major matrix elements. With ED-XRFS, the entire X-ray spectrum is acquired simultaneously. The identification of peaks is, however, hampered by the lower resolution of this approach.
Mosele's law depicts the mathematical relation of the emitted (analyte specific) wavelength upon bombardment with X-rays (for short $\lambda \propto 1/Z$);

$$\lambda = k_1/(Z-k_2)$$

$k_{1,2}$ variables related to the orbital distance [-]
Z, mass number [-]

Criteria for qualitative analysis include the material the X-ray tube is made of (a Mo-tube is unsuitable to detect Mo in the sample), at least the most dominant metal line sought must be visible, lines of higher orders must be visible, tube's acceleration voltage must be constant, and matrix composition of sample must be known.
With WD-XRFS, the qualitative analysis yields an "intensity vs. wavelength-spectrum" (with shorter wavelengths close to the origin and the longer ones further afield), while the ED-XRFS yields an "intensity vs. energy-spectrum" (with the lower energies, i.e. lighter z-elements close to the origin and the heavier z-elements of the periodic table further away).
Quantitative Analysis: The number of characteristic X-rays of a certain element (proportional to its concentration), provides the basis for quantitative analysis. Trace element analysis (ppm-range) and the determination of minor and major element concentrations (%-range) can be performed on the same sample. Quantitative analysis is based on the relation between the intensity of the characteristic line of an element and the concentration of that element in the sample. Quantitative analysis is further complicated by the fact that one needs to use the net intensities; i.e. continuum corrected and interference free intensity of the characteristic lines. The combination of matrix absorption and enhancement effects results in calibration curves that are non-linear; furthermore, secondary excitation due to the primarily radiated matrix may result in radiation-interaction within the sample itself, or weaken the incident radiation all together; in addition the outer electron cloud of each analyte atom absorbs fluorescence radiation emitted from inner electron shells.

Poisson Statistics: As with any impulse detecting data gathering application (NMR, FTIR, XRFS, etc.) results are based on the Poisson rather than the Gaussian distribution; rearranging the equation (shown below) to aim at a standard deviation of 1% requires a minimal number (N) of > 10000 scans measurements are required:

	Poisson Statistics	Gaussian statistics
Standard deviation:	$\sigma_{Poission} = \pm \frac{100}{\sqrt{N}}$	$\sigma_{Gaussian} = \pm 100 \cdot \sqrt{\frac{\sum(xn - \bar{x})}{n - 1}}$

Net-intensity of the analyte's sample peak is obtained by subtracting the background-intensity from the sample-peak intensity:

$$\sigma_{Poission} = \pm \frac{100}{\sqrt{N}} \cdot \frac{\sqrt{(1 + a \cdot z^2)}}{1 - a \cdot z}$$

$a = lines_{Backgrd} / lines_{Matrix}$

$z = measuring\ time_{Backgrd} / measuring\ times_{Matrix}$

Special Variations of the X-Ray Spectroscopy:

- **Total Reflection Fluorescence Spectroscopy** (TXRF): The angle between the quartz-support (that holds the analyte sample, i.e. residue of an evaporated drop of water) and the narrowly collimated X-ray beam is ≈ 0.1° so that the X-rays totally reflect from the support rather than penetrate it, causing fluorescence and scattering. The X-rays only interact with the very thin sample (just as if the sample is suspended in the air without support). As a result, the continuum, which is mainly due to scattering is virtually absent in a TXRF spectrum. Absolute detection limits in the **pg**-range are obtained in this way!
- **X-Ray Diffractometry**: Incident X-rays are redirected according to the lattice properties of the sample crystal under investigation; according to Bragg's equation: $n \cdot \lambda = 2 \cdot d \cdot \sin\delta$

n, order of diffraction	[-]
λ, wavelength	[nm]
d, lattice distance	[nm]
δ, angle of incident/exiting radiation	[-]

  In order to register the diffracted X-rays, the detector has to be placed in the reflection angle, or if the sample turns to rotate with doubled angular speed (Goniometer). In the latter case, a 360° scan can be obtained which reveals characteristic diffraction peaks that can be assigned to a particular crystal.
- **Proton Induced X-Ray Emission Spectroscopy** (PIXE): This spectrometer uses protons (positively charged building blocks of matter; e.g. α-particles in the form of H^+, He^{2+}) rather than photons ($E = h \cdot \nu$) as the radiation source. The beam of protons routed to the sample will generate an X-ray emission spectrum that is characteristic to the analyte's composition. The X-ray emission spectrum is usually registered with both a wavelength- and a energy-dispersive detector. As PIXE is not an absolute measurement device but based on relativity of sample and standard, a reference sample has to be used in order to obtain accurate results. A major disadvantage of PIXE is often encountered as the generation of X-rays by the analyte results in secondary excitation and re-emissions (fluorescence) within the analyte material. By modifying the angle of the incident beam from a slanting angle to a perpendicular orientation, enables sputtering off atomic layers of the sample material. By increasing the proton-flux, sputtering represents an elegant way to remove atomic layers from the sample in order to analyze strata underneath (i.e. used to analyze inclusions). Limit of detection can be as low as 0.5µg/g.
- **Scanning Electron Microscopy** (SEM) and **Electron Probe X-ray Microanalysis** (EPXMA): As both procedures are integrated into the same instrument, SEM is utilized for imaging, while EPXMA for elemental analysis. An electron beam produced by emission from a tungsten or LaB_6 filament is accelerated to an energy between 1 and 50keV. Carrying a beam current in the range of 10pA-1µA, it is focused to a diameter between 1 and 100nm with electrostatic lenses and directed to the surface of the (Au-sputtered) sample. Thus, providing a maximal resolution of about 10nm.

  The resulting emissions due to the bombardment of the sample result in distinct emissions patterns:

  i) The emerging secondary electrons have a low kinetic energy of about <50eV and therefore accelerated by a potential of several 100V for detection with a scintillator crystal.

  i) AUGER-e^- with a moderate kinetic energy of <2keV are used to analyze surface reactions of catalysts (i.e. catalytic converters).

  i) The back-scattered (secondary) electrons whose energy is close to the primary e^- energy (1-40keV) are detected without acceleration using either a scintillator or a semiconductor device to generate 3-dimensional images (SEM). Using electrons rather than light, resolution is enormous (λ/2; i.e. 0.5nm = 0.25nm!), while magnification with a staggering $100 \cdot E^3$ fold is likewise spectacular.

  i) Cathode-luminescence radiation ($1 \cdot E^{-2}$eV)

  i) The characteristic X-Ray spectrum (1-40keV) is used for the measurement of energy and intensity. Both energy- and wavelength-dispersive spectrometers are used in elemental identification.

i) The focusing primary electron beam can also be used as a microprobe to analyze surface structure or surface layers (up to 1mm thick); semiconductors and non-metals can't be scanned as the buildup of a space-charge cloud shields the sample from the primary target beam.

In point analysis, where the e^- beam targets a single spot on the sample, the attached EDXRF-spectrometer detects and analyzes the secondary scattered X-ray radiation from the target area. Two-dimensional images are created by line and area scans with the aid of a beam scanning (wobble) generator.

Application of X-Ray Spectroscopy:

- Element distribution and allocation within a given sample
- Dust, asbestos, and fiber analysis (Chrysotil contains Mg and Si; identification by tuning to their K-α-lines)
- Verification of cleansing efficiency; e.g. microfilters used in diesel engines of container ships
- Material science, analysis and testing
- Multi-element analysis
- Al-, Fe-, and steel-processing industry as in smelters
- Concrete production (scanning of additives)
- Generation of alloys
- Animal feed and fertilizer industry (scanning of heavy metals)
- Biological and cytological applications in natural sciences