

## A röntgen fluoreszcencia spektroszkópia elméleti és mérés technikai alapjai Roncsolásmentes elemanalízis

[http://en.wikipedia.org/wiki/X-ray\\_fluorescence\\_spectroscopy](http://en.wikipedia.org/wiki/X-ray_fluorescence_spectroscopy)

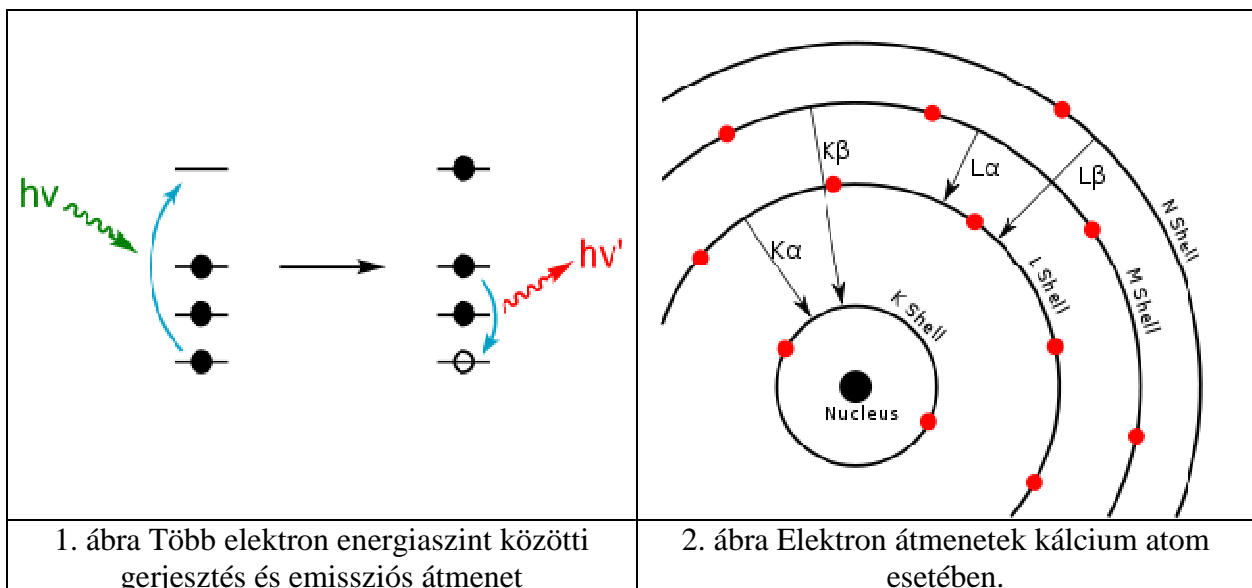
1. Röntgen fluoreszcencia spektroszkópia elméleti alapjai
2. Energia diszperzív spektrometria
3. Hullámhossz diszperzív spektrometria

### 1. Röntgen fluoreszcencia spektroszkópia elméleti alapjai

A röntgen fluoreszcencia (**X-ray fluorescence - XRF**) a minta karakterisztikus (fluoreszcencia) sugárzása az ált érte röntgen sugárzást követően. (gamma rays). Ez a spektroszkópia széles körben használatos az elemanalízis terén, különösen a fémek, az üvegek, kerámiák, talajok és az építőanyagok terén. Ilyen kutatási területeken alkalmazzák eredményesen, mint a geokémia, bűnüldözés, kormeghatározás. (archaeológia).

A hordozható RFA berendezések lehetőséget adnak lényegében bármely helyszínen mérésekre. Ez biológiai és környezeti méréseknél nagy segítséget jelent, de például vitatott Csontváry-festményről is derült már ki RFA méréssel, hogy másolat. Csontváry idejében még nem használtak olyan összetételű festéket, amelyet az analízis kimutatott. Ugyancsak egyedülálló vizsgálati módszer más égitestek kőzeteinek vizsgálatában. Ezt használták a Hold-utasok a helyszínen a kőzetek elemzése során, vagy ilyen készülékkel vannak felszerelve a Mars-járók.

A röntgen-fluoreszcencia módszer során valamely kis energiájú röntgen-, vagy gamma-sugárzás gerjeszti a minta atomjainak egy mélyebb elektronenergia szinten levő elektronját úgy, hogy az magasabb energiájú állapotba jut, mint az atom alapállapota esetében a legmagasabb energia szinten levő „legkülső” elektronja. Ehhez az szükséges, hogy a gerjesztő sugárzás energiája nagyobb legyen, mint ezen állapot átmenetéhez szükséges energia, de még ne legyen olyan nagy, hogy ionizálja az atomot.. A gerjesztést követően az atom ebből a magasabb energiájú állapotból egy (ahol az elektronok gyengébben kötöttek) abba az alacsonyabb energiájú állapotba megy át, amelyből az elektront a röntgen sugárzás gerjesztette, eközben pedig az atom ezen két nívója közti energia különbségnek megfelelő energiájú karakterisztikus röntgensugárzást bocsát ki. Ezt a folyamatot hívjuk röntgen-fluoreszcenciának. (1. ábra)



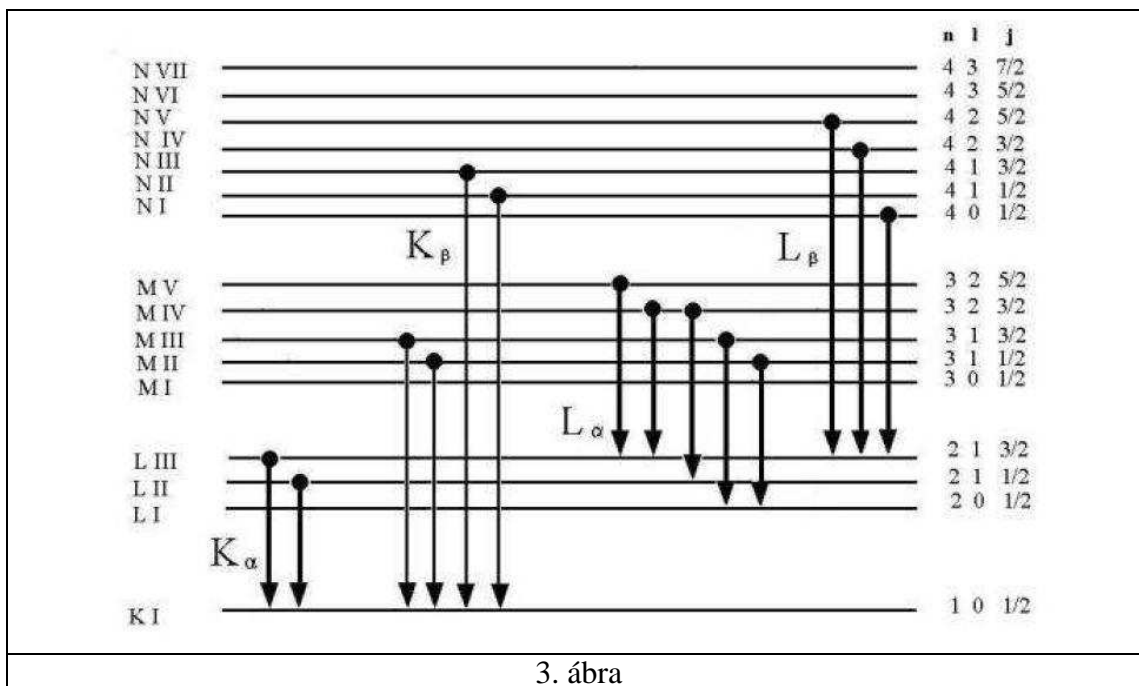
Az adott elemek elektron energia szint elrendezése jellemző rájuk, ezért ezen szintek közötti energia átmeneteknek megfelelő röntgen sugárzás szintén jellemző lehet rájuk. Ezért lehet ezt a jelenséget **minőségi analízis céljára** alkalmazni. (2. ábra)

A röntgen fotonok energiája, a megfigyelések szerint a rendszám négyzetével arányos. A kibocsátott karakterisztikus sugárzás intenzitásából, a hatásokok és az önnyelődés meghatározása után az adott elem koncentrációja meghatározható. Az intenzitás mérés alapján pedig **menyiségi analízist** lehet végezni.

Természetesen csak olyan anyagoknak kelthető a karakterisztikus röntgensugárzása, amelyeket alkotó atomoknak legalább két elektronhéja van (Li, Be, B,...), és amelyek között átmenet engedélyezett is. Egyéb okok (Auger effektus, alacsonyenergiás detektálási hatások) is nehezítik az alacsony rendszámú elemek meghatározását. A legerjesztődés (dezaktiváció) nagyon rövid, jellegzetesen  $10^{-15}$  másodperc nagyságrendű idő alatt megy végbe.

A karakterisztikus röntgen sugarak energiatartománya kb. 100 eV-100 keV, a gamma sugaraké kb. 1 keV-5 MeV. A főbb elektron átmeneteknek a betűjelzésére a következőket használjuk. Az elektron héjak jelei (belülről kifelé haladva: K, L, M, N,...) Az L→K szintek közötti átmenetet  $K_{\alpha}$ , az M→K szintek közötti átmenetet  $K_{\beta}$ , míg az M→L szintek közötti átmenetet  $L_{\alpha}$  jelzéssel írjuk le, stb.

Sokelektronos atomokban a főkvantumszámon kívül a belső héjak energiája kissé függ az l mellékvantumszámtól ( $l=0, \dots, n-1$ ) és a j belső kvantumszámtól is. A legfontosabb röntgenátmeneteket ennek megfelelően a 2. ábrán mutatjuk be.



### Dispersion

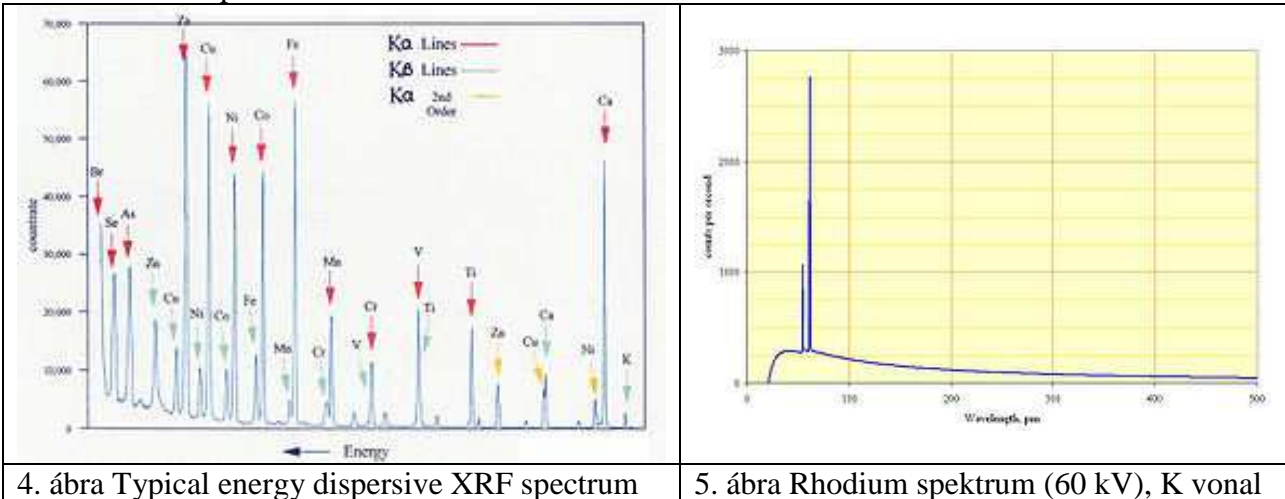
**In energy dispersive analysis**, the fluorescent x-rays emitted by the material sample are directed into a solid-state detector which produces a "continuous" distribution of pulses, the voltages of which are proportional to the incoming photon energies. This signal is processed by a multichannel analyser (MCA) which produces an accumulating digital spectrum that can be processed to obtain analytical data.

In **wavelength dispersive analysis**, the fluorescent x-rays emitted by the material sample are directed into a diffraction grating monochromator. The diffraction grating used is usually a single crystal. By varying the angle of incidence and take-off on the crystal, a single x-ray wavelength can be selected. The wavelength obtained is given by the [Bragg Equation](#):

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

where  $d$  is the spacing of atomic layers parallel to the crystal surface.

Két mért színeképet mutat a 4. ábra és az 5. ábra.



## 2. Energia diszperzív spektrometria

### Detection

In energy dispersive analysis, dispersion and detection are a single operation, as already mentioned above. [Proportional counters](#) or various types of solid state detectors ([PIN-diode](#), [Si\(Li\)](#), [Ge\(Li\)](#), [Silicon Drift Detector SDD](#)) are used. They all share the same detection principle: An incoming x-ray [photon](#) ionises a large number of detector atoms with the amount of charge produced being proportional to the energy of the incoming photon. The charge is then collected and the process repeats itself for the next photon. Detector speed is obviously critical, as all charge carriers measured have to come from the same photon to measure the photon energy correctly (peak length discrimination is used to eliminate events that seem to have been produced by two x-ray photons arriving almost simultaneously). The spectrum is then built up by dividing the energy spectrum into discreet bins and counting the number of pulses registered within each energy bin. [EDXRF](#) detector types vary in resolution, speed and the means of cooling (a low number of free charge carriers is critical in the solid state detectors): proportional counters with resolutions of several hundred eV cover the low end of the performance spectrum, followed by PIN-diode detectors, while the Si(Li), Ge(Li) and Silicon Drift Detectors (SDD) occupy the high end of the performance scale.

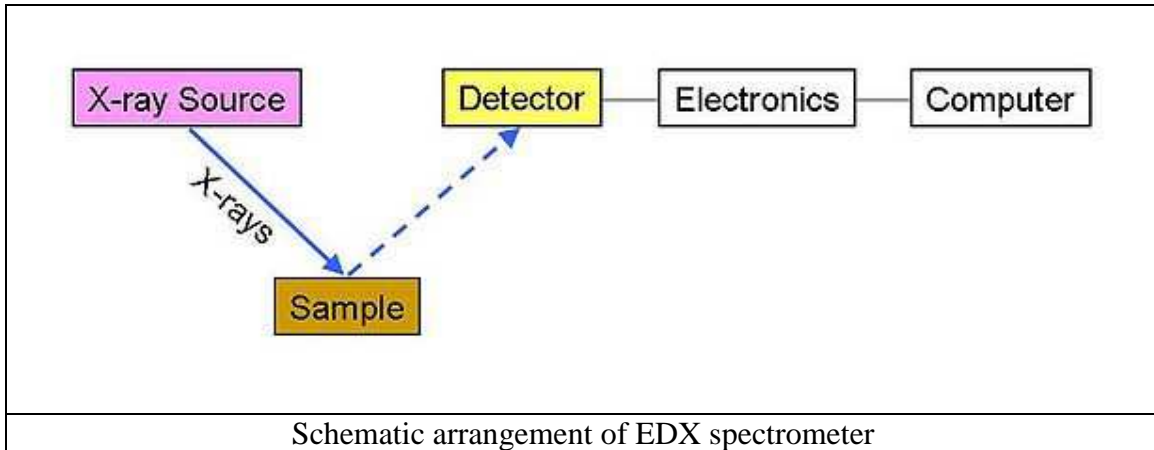
### X-ray intensity

The fluorescence process is inefficient, and the secondary radiation is much weaker than the primary beam. Furthermore, the secondary radiation from lighter elements is of relatively low energy (long wavelength) and has low penetrating power, and is severely attenuated if the beam passes through air for any distance. Because of this, for high-performance analysis, the path from tube to sample to detector is maintained under high vacuum (around 10 Pa residual pressure).

This means in practice that most of the working parts of the instrument have to be located in a large vacuum chamber. The problems of maintaining moving parts *in vacuo*, and of rapidly introducing and withdrawing the sample without losing vacuum, pose major challenges for the design of the instrument. For less demanding applications, or when the sample is damaged by a vacuum (e.g. a volatile sample), a helium-swept x-ray chamber can be substituted, with some loss of low-Z intensities.

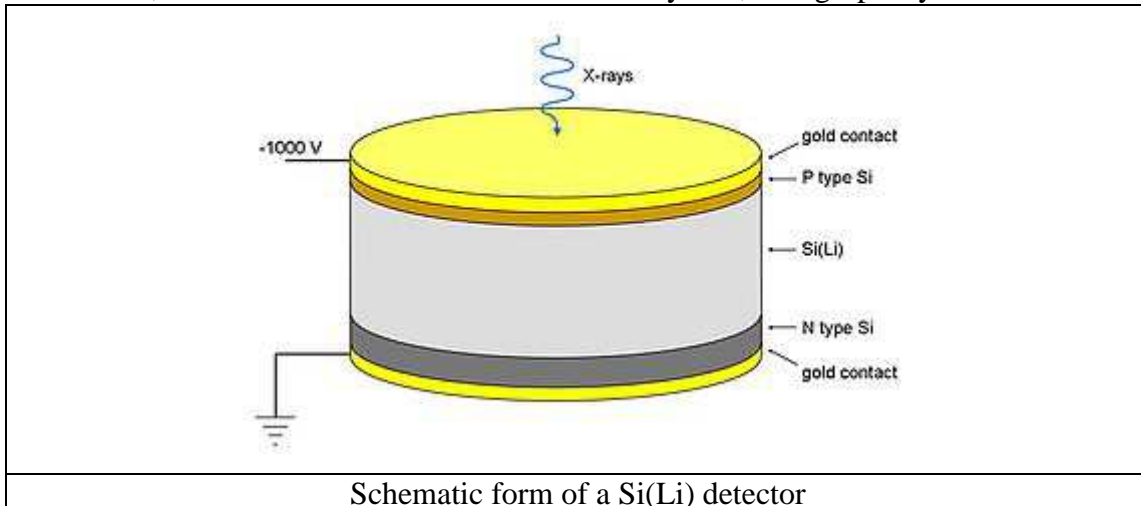
### XRF in chemical analysis

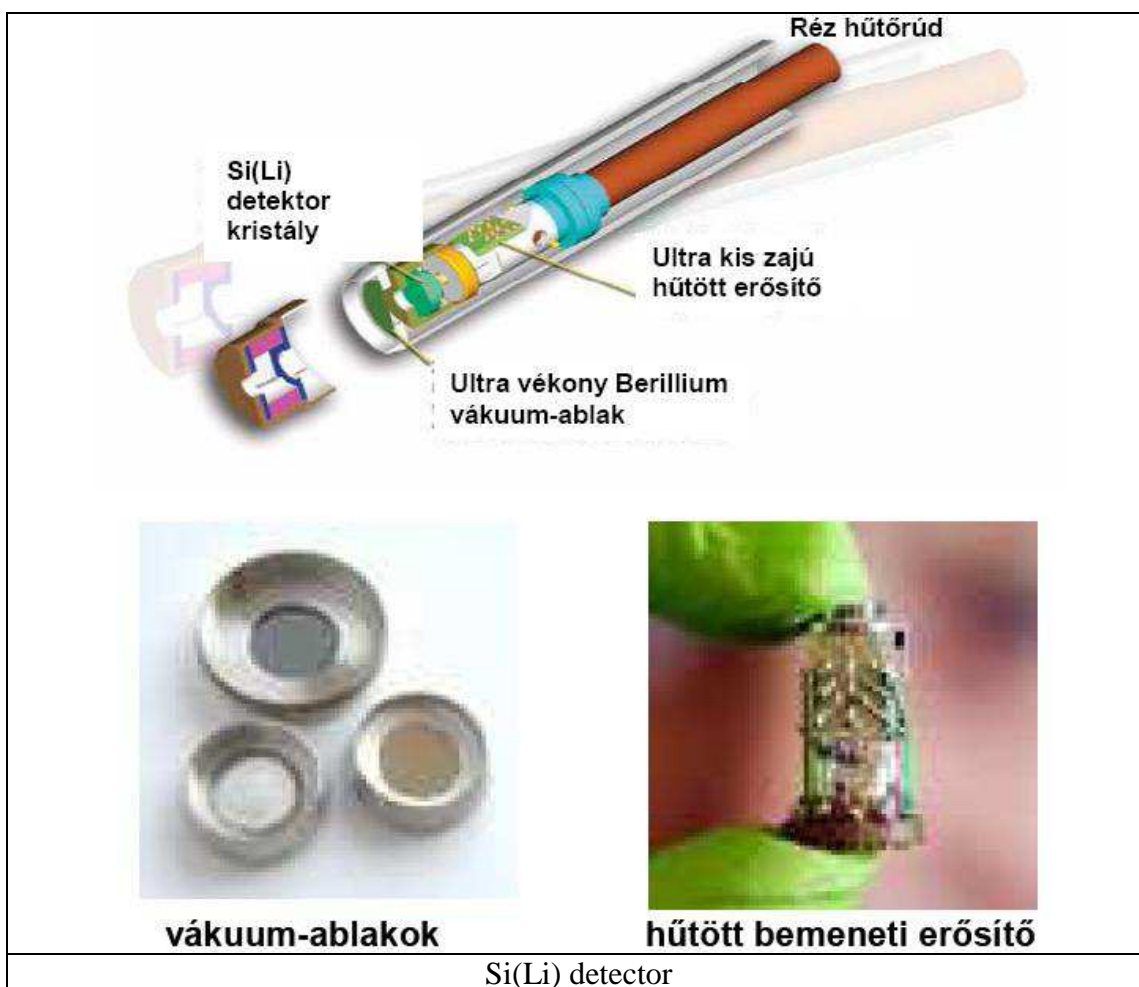
In principle, the lightest element that can be analysed is [beryllium](#) ( $Z = 4$ ), but due to instrumental limitations and low x-ray yields for the light elements, it is often difficult to quantify elements lighter than [sodium](#) ( $Z = 11$ ), unless background corrections and very comprehensive interelement corrections are made.



### Energy dispersive spectrometry

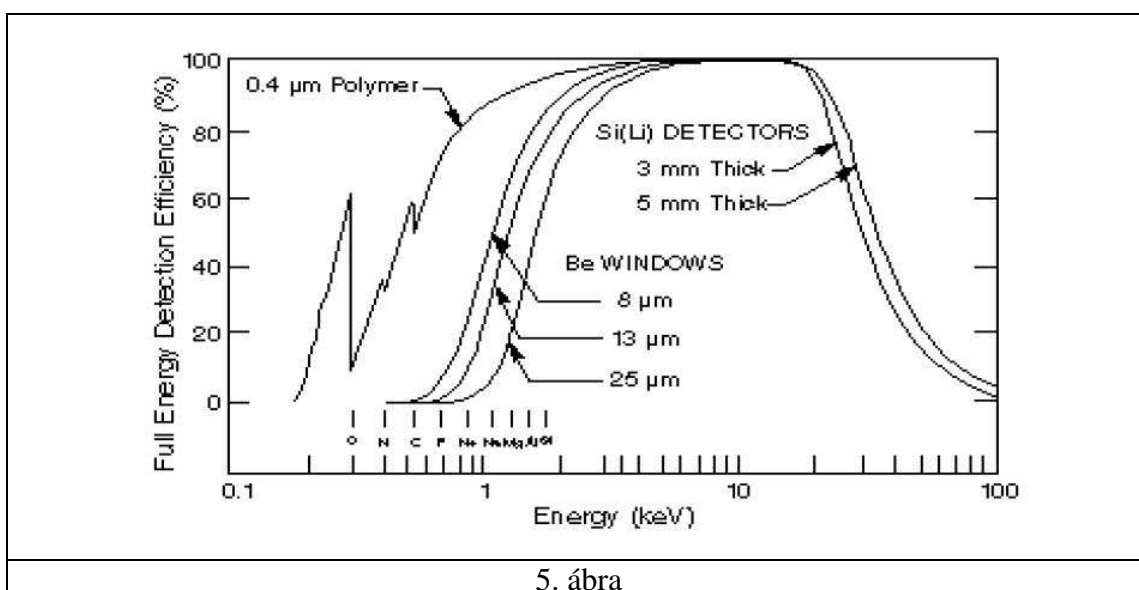
In energy dispersive spectrometers (EDX or EDS), the detector allows the determination of the energy of the photon when it is detected. Detectors historically have been based on silicon semiconductors, in the form of lithium-drifted silicon crystals, or high-purity silicon wafers.





### Si(Li) detectors

These consist essentially of a 3-5 mm thick silicon junction type p-i-n diode with a bias of -1000 V across it. The lithium-drifted centre part forms the non-conducting i-layer. When an x-ray photon passes through, it causes a swarm of electron-hole pairs to form, and this causes a voltage pulse. To obtain sufficiently low conductivity, the detector must be maintained at low temperature, and liquid-nitrogen must be used for the best resolution. With some loss of resolution, the much more convenient Peltier cooling can be employed.



5. ábra

## Wafer detectors

More recently, high-purity silicon wafers with low conductivity have become routinely available. Cooled by the Peltier effect, this provides a cheap and convenient detector, although the liquid nitrogen cooled Si(Li) detector still has the best resolution (i.e. ability to distinguish different photon energies).

## Amplifiers

The pulses generated by the detector are processed by pulse-shaping amplifiers. It takes time for the amplifier to shape the pulse for optimum resolution, and there is therefore a trade-off between resolution and count-rate: long processing time for good resolution results in "pulse pile-up" in which the pulses from successive photons overlap. Multi-photon events are, however, typically more drawn out in time (photons did not arrive exactly at the same time) than single photon events and pulse-length discrimination can thus be used to filter most of these out. Even so, a small number of pile-up peaks will remain and pile-up correction should be built into the software in applications that require trace analysis. To make the most efficient use of the detector, the tube current should be reduced to keep multi-photon events (before discrimination) at a reasonable level, e.g. 5-20%.

## Processing

Considerable computer power is dedicated to correcting for pulse-pile up and for extraction of data from poorly resolved spectra. These elaborate correction processes tend to be based on empirical relationships that may change with time, so that continuous vigilance is required in order to obtain chemical data of adequate precision.

## Usage

**EDX** spectrometers are superior to **WDX** spectrometers in that they are smaller, simpler in design and have fewer engineered parts. They can also use miniature X-ray tubes or gamma sources. This makes them cheaper and allows miniaturization and portability. This type of instrument is commonly used for portable quality control screening applications, such as testing toys for Lead (Pb) content, sorting scrap metals, and measuring the lead content of residential paint. On the other hand, the low resolution and problems with low count rate and long dead-time makes them inferior for high-precision analysis. They are, however, very effective for high-speed, multi-elemental analysis. Field Portable XRF analysers currently on the market weigh less than 2 kg, and have limits of detection on the order of 2 parts per million of Lead (Pb) in pure sand.

## 3. Hullámhossz diszperzív spektrometria

In wavelength dispersive spectrometers (WDX or WDS), the photons are separated by diffraction on a single crystal before being detected. Although wavelength dispersive spectrometers are occasionally used to scan a wide range of wavelengths, producing a spectrum plot as in EDS, they are usually set up to make measurements only at the wavelength of the emission lines of the elements of interest. This is achieved in two different ways:

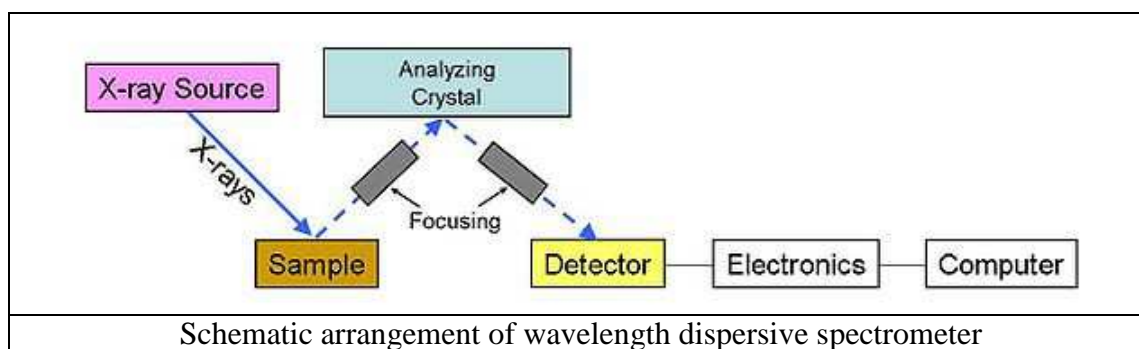
Monochromators

Analysis Lines

Crystals

Detectors





In wavelength dispersive analysis, the single-wavelength radiation produced by the monochromator is passed into a photomultiplier, a detector similar to a Geiger counter, which counts individual photons as they pass through. The counter is a chamber containing a gas that is ionised by x-ray photons. A central electrode is charged at (typically) +1700 V with respect to the conducting chamber walls, and each photon triggers a pulse-like cascade of current across this field. The signal is amplified and transformed into an accumulating digital count. These counts are then processed to obtain analytical data.

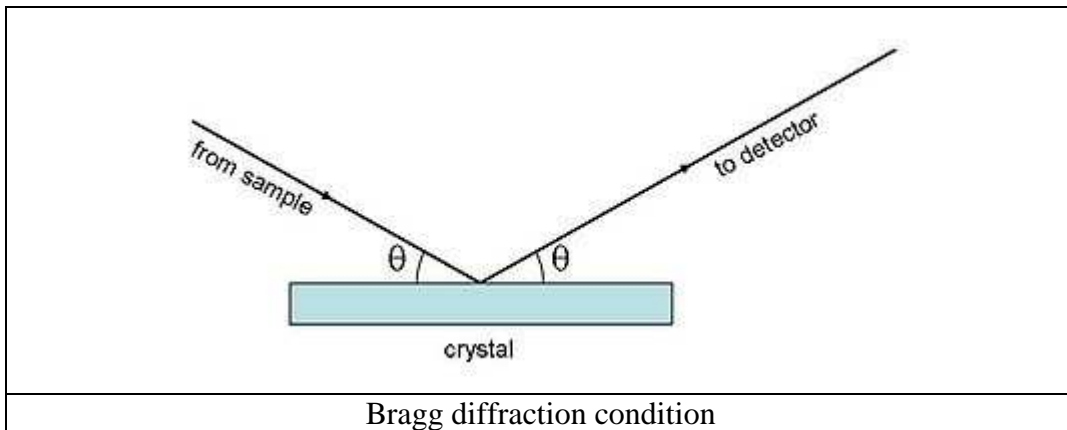
- **"Simultaneous" spectrometers** have a number of "channels" dedicated to analysis of a single element, each consisting of a fixed-geometry crystal monochromator, a detector, and processing electronics. This allows a number of elements to be measured simultaneously, and in the case of high-powered instruments, complete high-precision analyses can be obtained in under 30 s. Another advantage of this arrangement is that the fixed-geometry monochromators have no continuously moving parts, and so are very reliable. Reliability is important in production environments where instruments are expected to work without interruption for months at a time. Disadvantages of simultaneous spectrometers include relatively high cost for complex analyses, since each channel used is expensive. The number of elements that can be measured is limited to 15-20, because of space limitations on the number of monochromators that can be crowded around the fluorescing sample. The need to accommodate multiple monochromators means that a rather open arrangement around the sample is required, leading to relatively long tube-sample-crystal distances, which leads to lower detected intensities and more scattering. The instrument is inflexible, because if a new element is to be measured, a new measurement channel has to be bought and installed.
- **"Sequential" spectrometers** have a single variable-geometry monochromator (but usually with an arrangement for selecting from a choice of crystals), a single detector assembly (but usually with more than one detector arranged in tandem), and a single electronic pack. The instrument is programmed to move through a sequence of wavelengths, in each case selecting the appropriate X-ray tube power, the appropriate crystal, and the appropriate detector arrangement. The length of the measurement program is essentially unlimited, so this arrangement is very flexible. Because there is only one monochromator, the tube-sample-crystal distances can be kept very short, resulting in minimal loss of detected intensity. The obvious disadvantage is relatively long analysis time, particularly when many elements are being analysed, not only because the elements are measured in sequence, but also because a certain amount of time is taken in readjusting the monochromator geometry between measurements. Furthermore, the frenzied activity of the monochromator during an analysis program is a challenge for mechanical reliability. However, modern sequential instruments can achieve reliability almost as good as that of simultaneous instruments, even in continuous-usage applications.

## Sample presentation

In order to keep the geometry of the tube-sample-detector assembly constant, the sample is normally prepared as a flat disc, typically of diameter 20-50 mm. This is located at a standardized, small distance from the tube window. Because the X-ray intensity follows an inverse-square law, the tolerances for this placement and for the flatness of the surface must be very tight in order to maintain a repeatable X-ray flux. Ways of obtaining sample discs vary: metals may be machined to shape, minerals may be finely ground and pressed into a tablet, and glasses may be cast to the required shape. A further reason for obtaining a flat and representative sample surface is that the secondary X-rays from lighter elements often only emit from the top few micrometers of the sample. In order to further reduce the effect of surface irregularities, the sample is usually spun at 5-20 rpm. It is necessary to ensure that the sample is sufficiently thick to absorb the entire primary beam. For higher-Z materials, a few millimetres thickness is adequate, but for a light-element matrix such as coal, a thickness of 30-40 mm is needed.

## Monochromators

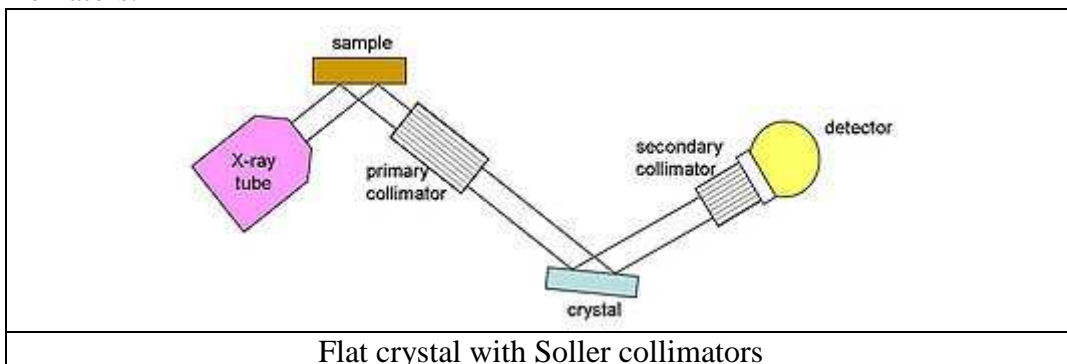
The common feature of monochromators is the maintenance of a symmetrical geometry between the sample, the crystal and the detector. In this geometry the Bragg diffraction condition is obtained.



The X-ray emission lines are very narrow (see figure 2), so the angles must be defined with considerable precision. This is achieved in two ways:

- **Flat crystal with Soller collimators**

The Soller collimator is a stack of parallel metal plates, spaced a few tenths of a millimetre apart. To improve angle resolution, one must lengthen the collimator, and/or reduce the plate spacing. This arrangement has the advantage of simplicity and relatively low cost, but the collimators reduce intensity and increase scattering, and reduce the area of sample and crystal that can be "seen". The simplicity of the geometry is especially useful for variable-geometry monochromators.





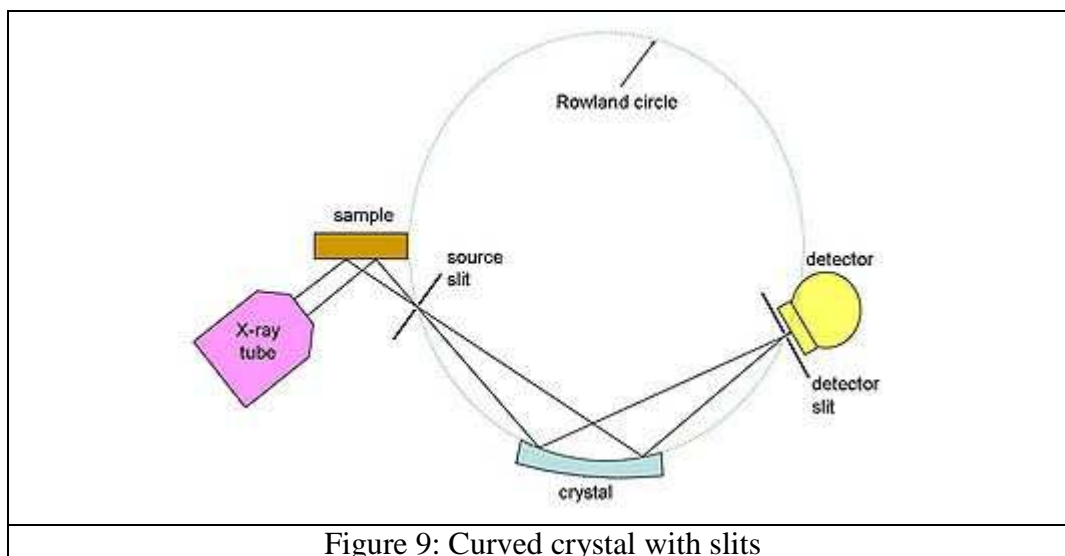


Figure 9: Curved crystal with slits

### Curved crystal with slits

The Rowland circle geometry ensures that the slits are both in focus, but in order for the Bragg condition to be met at all points, the crystal must first be bent to a radius of  $2R$  (where  $R$  is the radius of the Rowland circle), then ground to a radius of  $R$ . This arrangement allows higher intensities (typically 8-fold) with higher resolution (typically 4-fold) and lower background. But the mechanics of keeping Rowland circle geometry in a variable-angle monochromator is extremely difficult. In the case of fixed-angle monochromators (for use in simultaneous spectrometers), crystals bent to a logarithmic spiral shape give the best focusing performance. The manufacture of curved crystals to acceptable tolerances increases their price considerably.

### Analysis Lines

The spectral lines used for chemical analysis are selected on the basis of intensity, accessibility by the instrument, and lack of line overlaps. Typical lines used, and their wavelengths, are as follows:

element line	wavelength (nm)	element line	wavelength (nm)	element line	wavelength (nm)	element line	wavelength (nm)
Li	$K\alpha$ 22.8	Ni	$K\alpha_1$ 0.1658	I	$L\alpha_1$ 0.3149	Pt	$L\alpha_1$ 0.1313
Be	$K\alpha$ 11.4	Cu	$K\alpha_1$ 0.1541	Xe	$L\alpha_1$ 0.3016	Au	$L\alpha_1$ 0.1276
B	$K\alpha$ 6.76	Zn	$K\alpha_1$ 0.1435	Cs	$L\alpha_1$ 0.2892	Hg	$L\alpha_1$ 0.1241
C	$K\alpha$ 4.47	Ga	$K\alpha_1$ 0.1340	Ba	$L\alpha_1$ 0.2776	Tl	$L\alpha_1$ 0.1207
N	$K\alpha$ 3.16	Ge	$K\alpha_1$ 0.1254	La	$L\alpha_1$ 0.2666	$L\alpha_1$	0.1175
O	$K\alpha$ 2.362	As	$K\alpha_1$ 0.1176	Ce	$L\alpha_1$ 0.2562	Bi	$L\alpha_1$ 0.1144
F	$K\alpha_{1,2}$ 1.832	Se	$K\alpha_1$ 0.1105	Pr	$L\alpha_1$ 0.2463	Po	$L\alpha_1$ 0.1114
Ne	$K\alpha_{1,2}$ 1.461	Br	$K\alpha_1$ 0.1040	Nd	$L\alpha_1$ 0.2370	At	$L\alpha_1$ 0.1085
Na	$K\alpha_{1,2}$ 1.191	Kr	$K\alpha_1$ 0.09801	Pm	$L\alpha_1$ 0.2282	Rn	$L\alpha_1$ 0.1057
Mg	$K\alpha_{1,2}$ 0.989	Rb	$K\alpha_1$ 0.09256	Sm	$L\alpha_1$ 0.2200	Fr	$L\alpha_1$ 0.1031
Al	$K\alpha_{1,2}$ 0.834	Sr	$K\alpha_1$ 0.08753	Eu	$L\alpha_1$ 0.2121	Ra	$L\alpha_1$ 0.1005
Si	$K\alpha_{1,2}$ 0.7126	Y	$K\alpha_1$ 0.08288	Gd	$L\alpha_1$ 0.2047	Ac	$L\alpha_1$ 0.0980
P	$K\alpha_{1,2}$ 0.6158	Zr	$K\alpha_1$ 0.07859	Tb	$L\alpha_1$ 0.1977	Th	$L\alpha_1$ 0.0956

S	$K\alpha_{1,2}$ 0.5373	Nb	$K\alpha_1$ 0.07462	Dy	$L\alpha_1$ 0.1909	Pa	$L\alpha_1$ 0.0933
Cl	$K\alpha_{1,2}$ 0.4729	Mo	$K\alpha_1$ 0.07094	Ho	$L\alpha_1$ 0.1845	U	$L\alpha_1$ 0.0911
Ar	$K\alpha_{1,2}$ 0.4193	Tc	$K\alpha_1$ 0.06751	Er	$L\alpha_1$ 0.1784	Np	$L\alpha_1$ 0.0888
K	$K\alpha_{1,2}$ 0.3742	Ru	$K\alpha_1$ 0.06433	Tm	$L\alpha_1$ 0.1727	Pu	$L\alpha_1$ 0.0868
Ca	$K\alpha_{1,2}$ 0.3359	Rh	$K\alpha_1$ 0.06136	Yb	$L\alpha_1$ 0.1672	Am	$L\alpha_1$ 0.0847
Sc	$K\alpha_{1,2}$ 0.3032	Pd	$K\alpha_1$ 0.05859	Lu	$L\alpha_1$ 0.1620	Cm	$L\alpha_1$ 0.0828
Ti	$K\alpha_{1,2}$ 0.2749	Ag	$K\alpha_1$ 0.05599	Hf	$L\alpha_1$ 0.1570	Bk	$L\alpha_1$ 0.0809
V	$K\alpha_1$ 0.2504	Cd	$K\alpha_1$ 0.05357	Ta	$L\alpha_1$ 0.1522	Cf	$L\alpha_1$ 0.0791
Cr	$K\alpha_1$ 0.2290	In	$L\alpha_1$ 0.3772	W	$L\alpha_1$ 0.1476	Es	$L\alpha_1$ 0.0773
Mn	$K\alpha_1$ 0.2102	Sn	$L\alpha_1$ 0.3600	Re	$L\alpha_1$ 0.1433	Fm	$L\alpha_1$ 0.0756
Fe	$K\alpha_1$ 0.1936	Sb	$L\alpha_1$ 0.3439	Os	$L\alpha_1$ 0.1391	Md	$L\alpha_1$ 0.0740
Co	$K\alpha_1$ 0.1789	Te	$L\alpha_1$ 0.3289	Ir	$L\alpha_1$ 0.1351	No	$L\alpha_1$ 0.0724

## Crystals

The desirable characteristics of a diffraction crystal are:

- High diffraction intensity
- High dispersion
- Narrow diffracted peak width
- High peak-to-background
- Absence of interfering elements
- Low thermal coefficient of expansion
- Stability in air and on exposure to X-rays
- Ready availability
- Low cost

Crystals with simple structure tend to give the best diffraction performance. Crystals containing heavy atoms can diffract well, but also fluoresce themselves, causing interference. Crystals that are water-soluble, volatile or organic tend to give poor stability.

Commonly used crystal materials include LiF (lithium fluoride), ADP (ammonium dihydrogen phosphate), Ge (germanium), graphite, InSb (indium antimonide), PE (*tetrakis*-(hydroxymethyl)-methane: penta-erythritol), KAP (potassium hydrogen phthalate), RbAP (rubidium hydrogen phthalate) and TlAP (thallium(I) hydrogen phthalate). In addition, there is an increasing use of "layered synthetic microstructures", which are "sandwich" structured materials comprising successive thick layers of low atomic number matrix, and monoatomic layers of a heavy element. These can in principle be custom-manufactured to diffract any desired long wavelength, and are used extensively for elements in the range Li to Mg.

### Properties of commonly used crystals

ADP material	101 plane	0.5320 d (nm)	0.0859 $\lambda$ (nm)	0.0600 $\lambda$ (nm)	+ intensity	thermal expansion	++ durability
Ge	111	0.3266	0.085	0.0614	+++	+	+++
LiF	200	0.3354	0.088	0.338	+++++	+++	+++
InSb	111	0.3740	0.098	0.708	++++	+	+++
PE	062	0.4391	0.174	0.829	+++	+++++	+++

KAP	1010	1.325	0.346	2.490	++	++	++
RbAP	1010	1.305	0.341	2.453	++	++	++
Si	111	0.3135	0.082	0.589	++	+	+++
TIAP	1010	1.295	0.338	2.434	+++	++	++
6 nm LSM	-	6.00	1.566	11.276	+++	+	++

## Detectors

Detectors used for wavelength dispersive spectrometry need to have high pulse processing speeds in order to cope with the very high photon count rates that can be obtained. In addition, they need sufficient energy resolution to allow filtering-out of background noise and spurious photons from the primary beam or from crystal fluorescence. There are four common types of detector:

- gas flow proportional counters
- sealed gas detectors
- scintillation counters
- semiconductor detectors

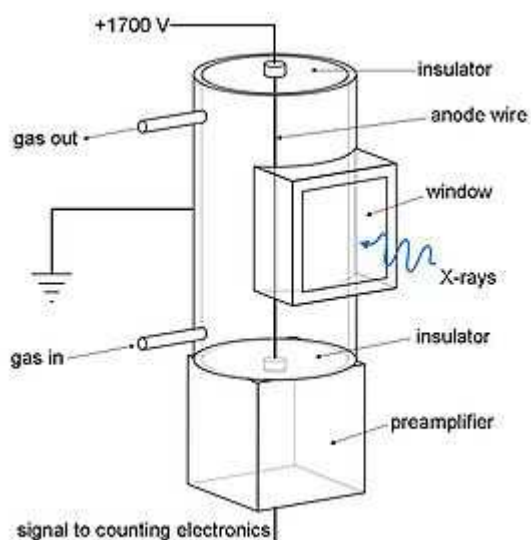


Figure 10: Arrangement of gas flow proportional counter

**Gas flow proportional counters** are used mainly for detection of longer wavelengths. Gas flows through it continuously. Where there are multiple detectors, the gas is passed through them in series, then led to waste. The gas is usually 90% argon, 10% methane ("P10"), although the argon may be replaced with neon or helium where very long wavelengths (over 5 nm) are to be detected. The argon is ionised by incoming X-ray photons, and the electric field multiplies this charge into a measurable pulse. The methane suppresses the formation of fluorescent photons caused by recombination of the argon ions with stray electrons. The anode wire is typically tungsten or nichrome of 20-60  $\mu\text{m}$  diameter. Since the pulse strength obtained is essentially proportional to the ratio of the detector chamber diameter to the wire diameter, a fine wire is needed, but it must also be strong enough to be maintained under tension so that it remains precisely straight and concentric with the detector. The window needs to be conductive, thin enough to transmit the X-rays effectively, but thick and strong enough to minimize diffusion of the detector gas into the high vacuum of the monochromator chamber. Materials often used are beryllium metal, aluminised PET film and aluminised polypropylene. Ultra-thin windows (down to 1  $\mu\text{m}$ ) for use with low-penetration long wavelengths are very expensive. The pulses are sorted electronically by "pulse height selection" in order to isolate those pulses deriving from the secondary X-ray photons being counted.

**Sealed gas detectors** are similar to the gas flow proportional counter, except that the gas does not flow through it. The gas is usually krypton or xenon at a few atmospheres pressure. They are applied usually to wavelengths in the 0.15-0.6 nm range. They are applicable in principle to longer wavelengths, but are limited by the problem of manufacturing a thin window capable of withstanding the high pressure difference.

**Scintillation counters** consist of a scintillating crystal (typically of sodium iodide doped with thallium) attached to a photomultiplier. The crystal produces a group of scintillations for each photon absorbed, the number being proportional to the photon energy. This translates into a pulse from the photomultiplier of voltage proportional to the photon energy. The crystal must be protected with a relatively thick aluminium/beryllium foil window, which limits the use of the detector to wavelengths below 0.25 nm. Scintillation counters are often connected in series with a gas flow proportional counter: the latter is provided with an outlet window opposite the inlet, to which the scintillation counter is attached. This arrangement is particularly used in sequential spectrometers.

**Semiconductor detectors** can be used in theory, and their applications are increasing as their technology improves, but historically their use for WDX has been restricted by their slow response (see EDX).

A glass "bead" specimen for XRF analysis being cast at around 1100°C in a Herzog automated fusion machine in a cement plant quality control laboratory. Figure 1: fusing, figure 2: preheating the mould, figure 3: pouring the melt, figure 4: cooling the "bead"



A Philips PW1606 X-ray fluorescence spectrometer with automated sample feed in a cement plant quality control laboratory