Alüminyum Test Eğitim ve Araştırma Merkezi

Mart 2017

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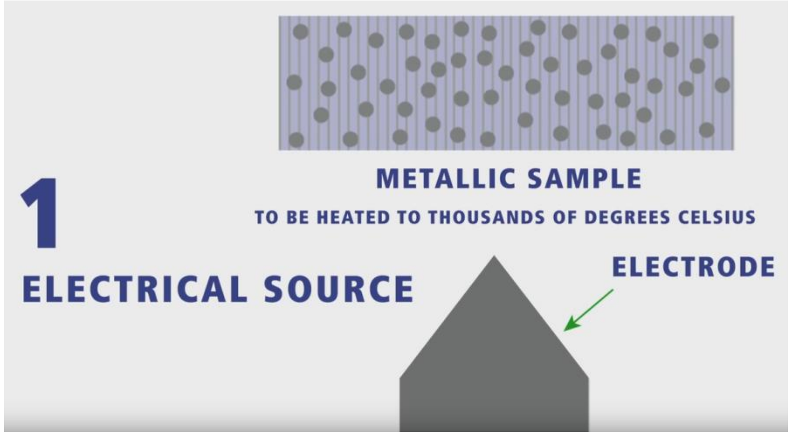
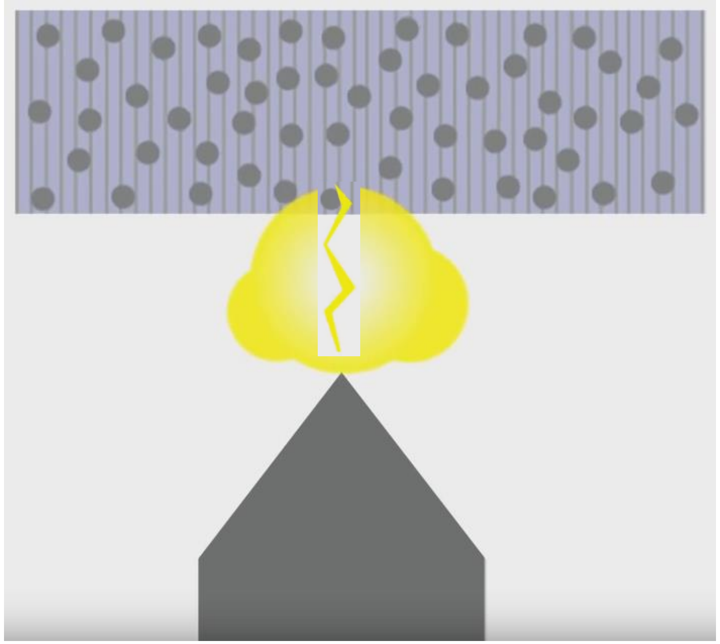
Comparison of Optical Emission Spectroscopy (OES) and Energy Dispersive Spectroscopy

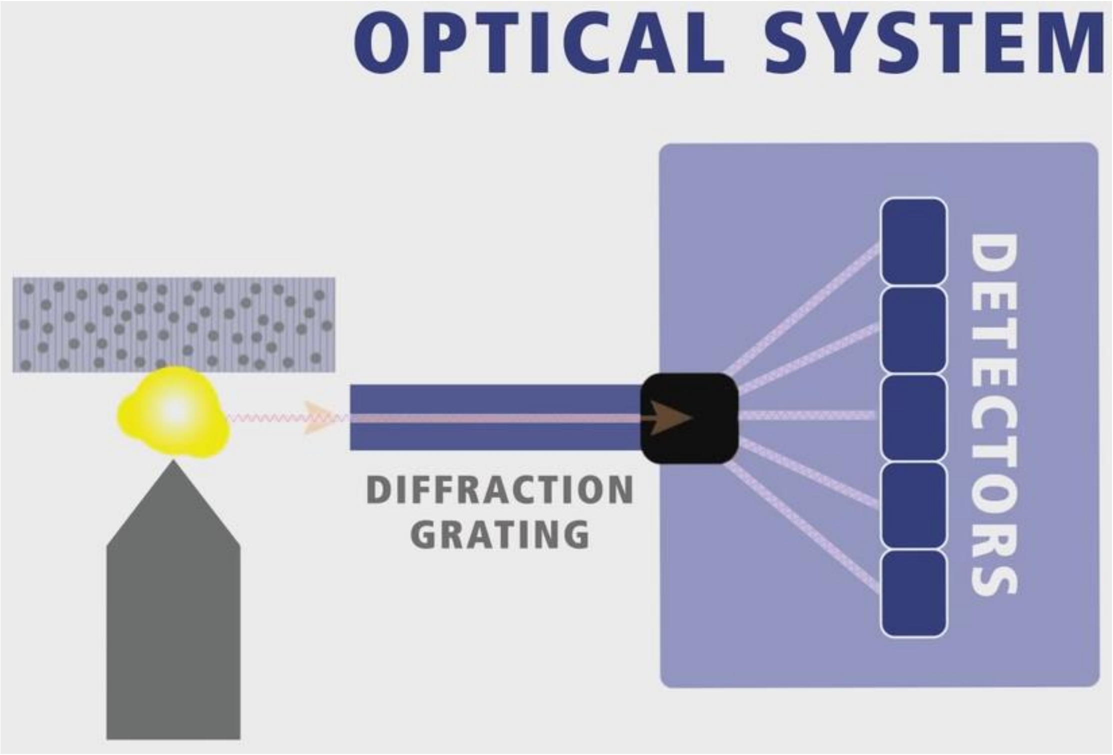
Excitation - Electrical Source





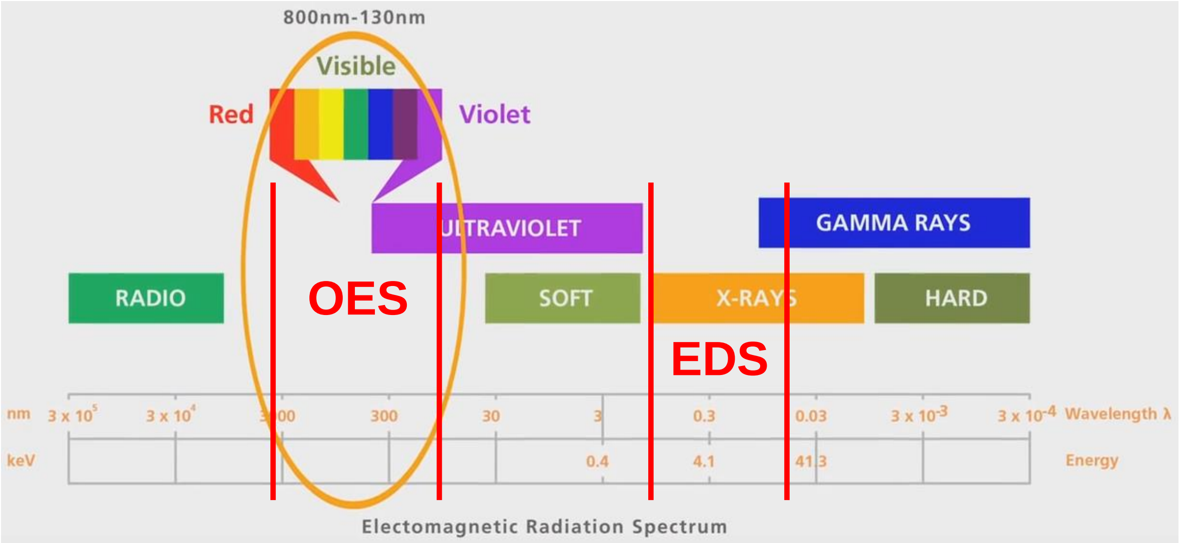
- Sample is heated by arc or spark depending on element and accuracy required
- Optical emission is generated by outer shell ionisation
- Optical emission 'lines' are characteristic of the elements present and proportional to the concentration

Optical System



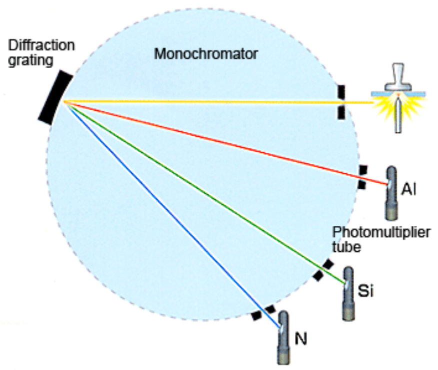
- Light emitted from the arc/spark enters the optical system;
- Entrance slit
- Projected onto an optical grating of 3,600 grooves/mm

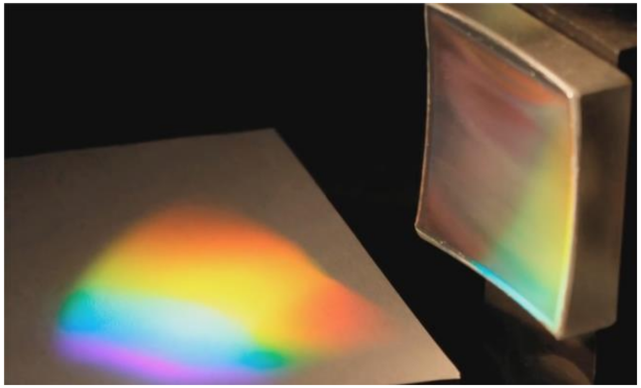
The spectrum – OES & EDS compared

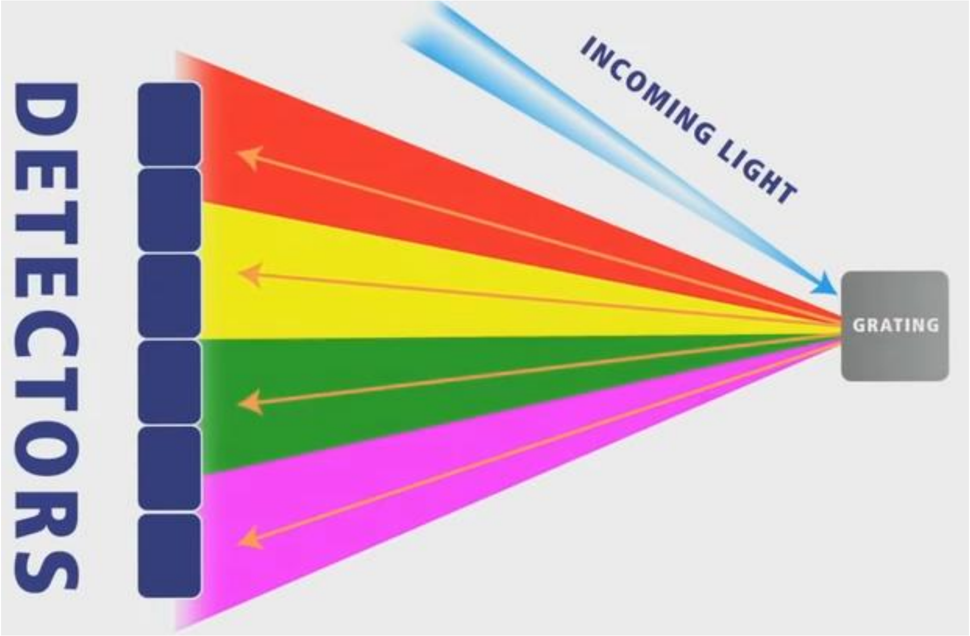


- OES Visible light plus part of UV
- 130nm – 800nm wavelength
- EDS typically between 0.2nm – 0.02nm wavelength;
- 1 - 30kV energy

Principle of operation

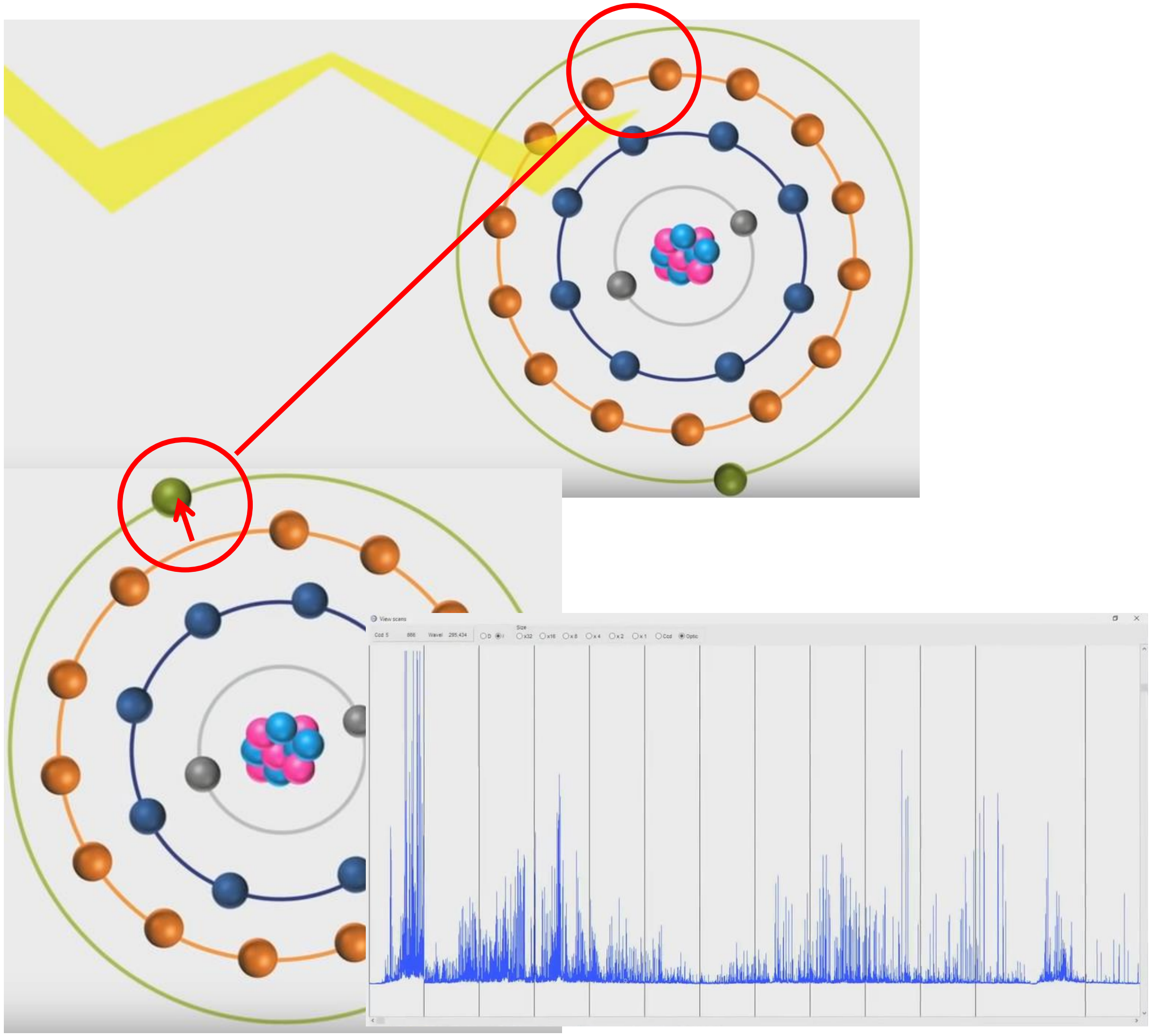






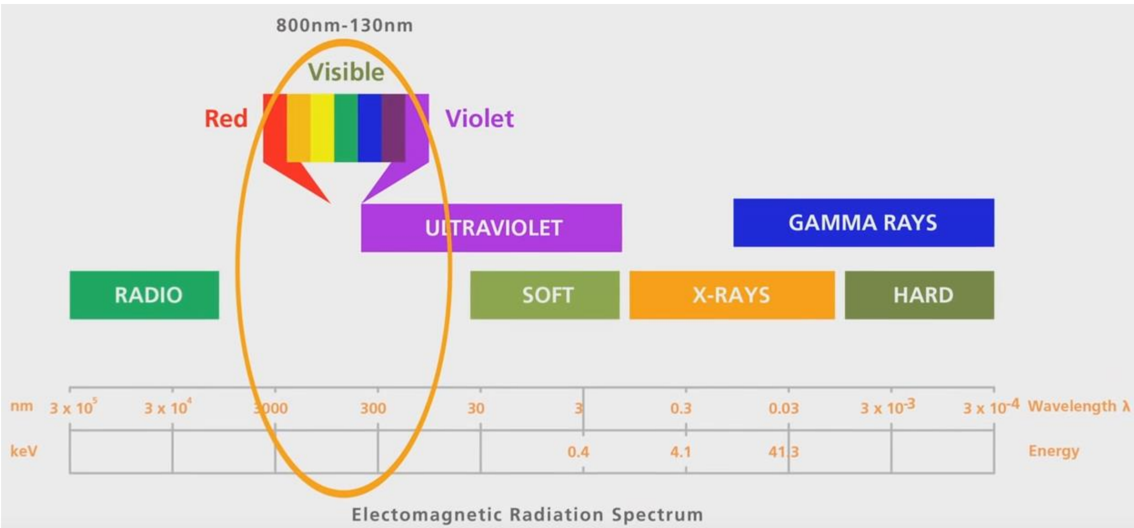
- The different wavelengths of light corresponding to individual element 'lines' fall on accurately positioned detectors
- The intensity recorded is proportional to the concentration of each element

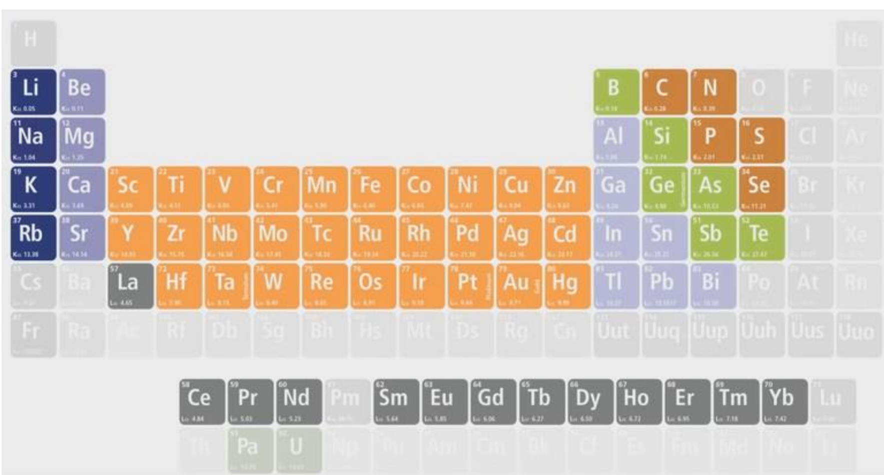
Characteristic Optical Emission



- Optical emission is generated by ***outer shell ionisation***
- Optical emission 'lines' are characteristic of the elements present and proportional to the concentration
- Many wavelengths of light are emitted for each element
  - Optimum must be selected for each element
- Thus many lines are present for the different transitions for each element/shell

Analytical Range





- Lithium to Uranium, wide concentration range
- High accuracy
- Low detection limit

Quantitative Analysis

Analysis

Start | New | Print | Del

Sample: 126788||344576A|||316L|45*5*3||No|235|||

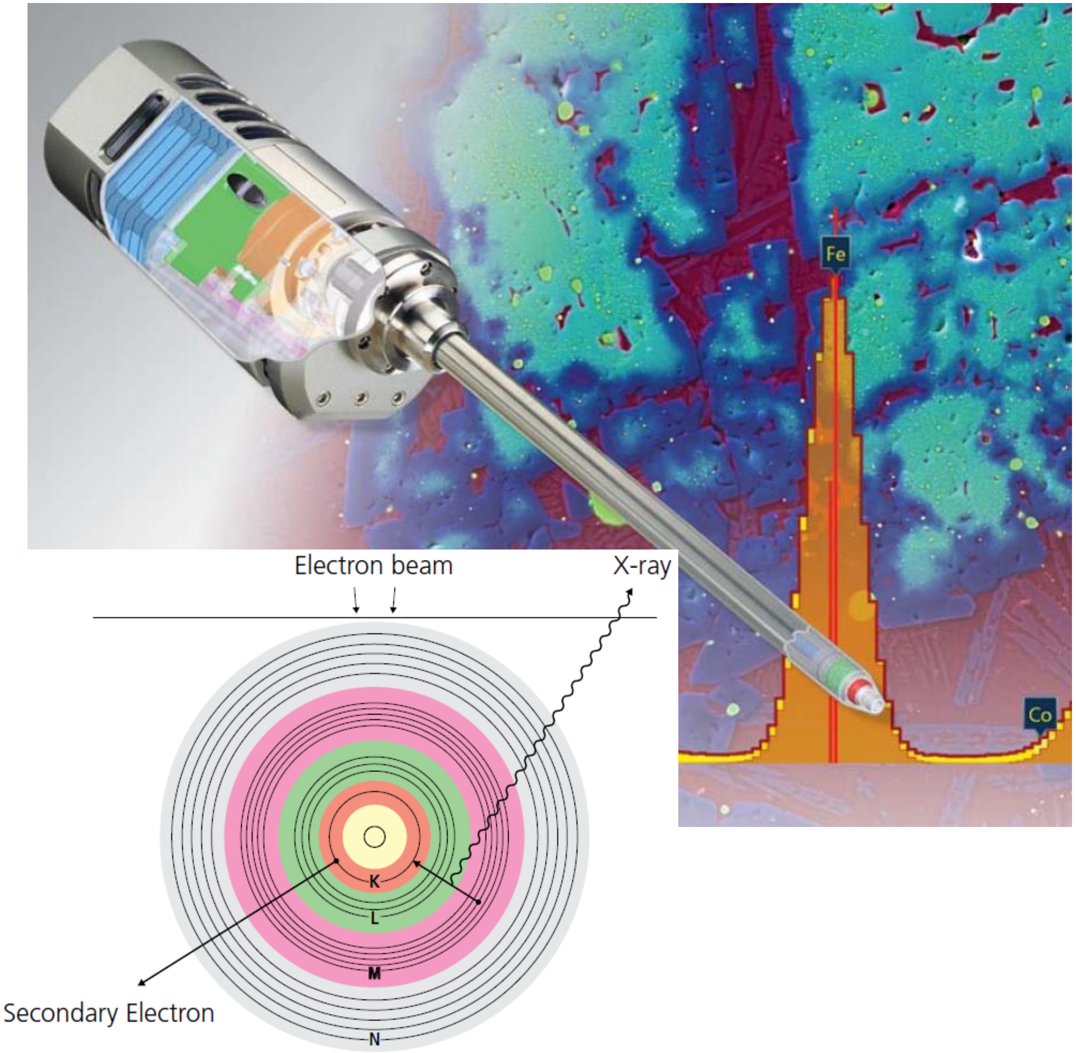
Average	RSD	Element	Burn 1	Burn 2	Burn 3
67.9	0.1%	Fe %	67.9	67.8	67.9
0.0255	1.3%	C %	0.0257	0.0251	0.0257
0.414	1.3%	Si %	0.419	0.413	0.409
1.47	0.3%	Mn %	1.47	1.48	1.47
0.0292	2.3%	P %	0.0299	0.0285	0.0292
0.0243	6.4%	S %	0.0249	0.0226	0.0256
16.9	0.5%	Cr %	16.8	16.9	16.9
2.26	0.6%	Mo %	2.28	2.26	2.25
10.3	0.4%	Ni %	10.3	10.3	10.2
< 0.0010	0.0%	Al %	< 0.0010	< 0.0010	< 0.0010
0.198	3.7%	Co %	0.204	0.190	0.199
0.342	2.2%	Cu %	0.350	0.340	0.335
0.0056	30.6%	Nb %	0.0076	0.0045	0.0047
0.0021	10.2%	Ti %	0.0022	0.0019	0.0023
0.0503	1.0%	V %	0.0507	0.0503	0.0498
0.0317	8.0%	W %	0.0312	0.0345	0.0295
< 0.0050	0.0%	Pb %	< 0.0050	< 0.0050	< 0.0050
0.0046	10.2%	Sn %	0.0051	0.0044	0.0042
0.0004	18.7%	B %	0.0005	0.0003	0.0004
0.0022	14.4%	Ca %	0.0023	0.0019	0.0025
0.0473	3.9%	N %	0.0485	0.0483	0.0452
0.0281	3.3%	Se %	0.0291	0.0273	0.0279
< 0.0020	0.0%	Sb %	< 0.0020	< 0.0020	< 0.0020
0.0419	5.8%	Ta %	0.0446	0.0399	0.0412

- Quantitative when calibrated on certified reference materials – standards
- ~30 seconds exposure
- Results tabulated

Advantages and Disadvantages

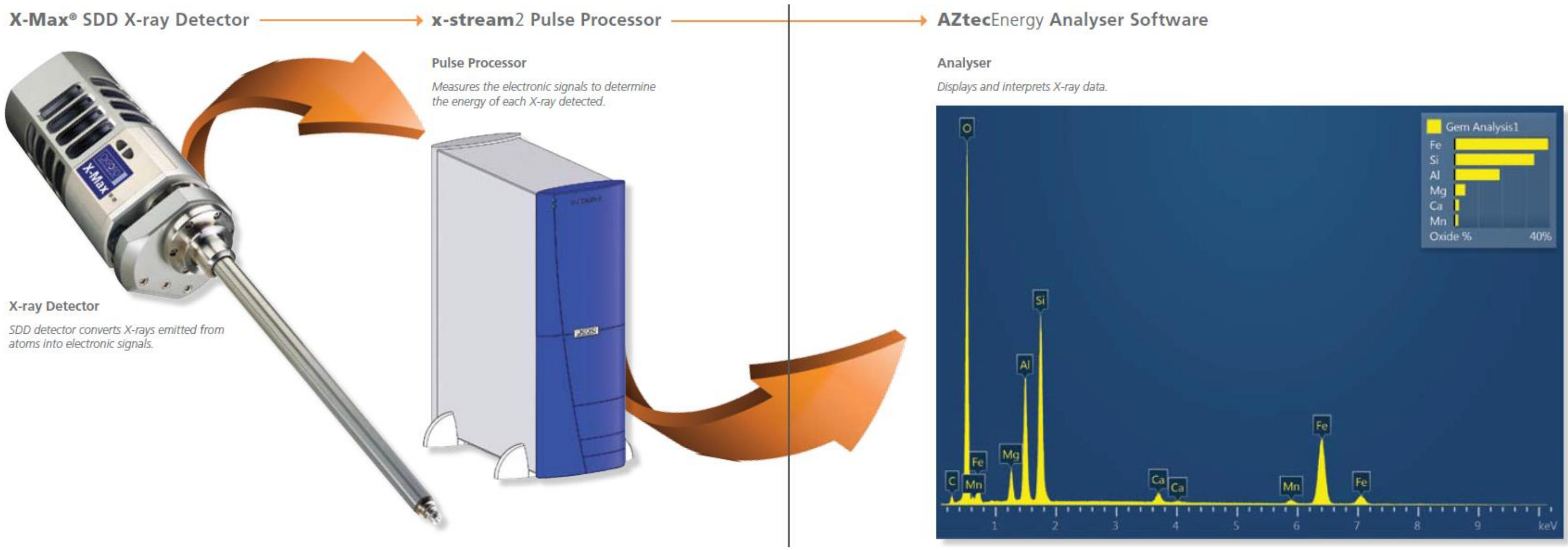
- Fast and relatively easy to use
- Wide range of elements and concentrations
- Good detection limit – good for trace element analysis
- Relatively low cost
- No image
- No correlation with macro/micro/nanostructure

Energy Dispersive Spectroscopy of X-Rays

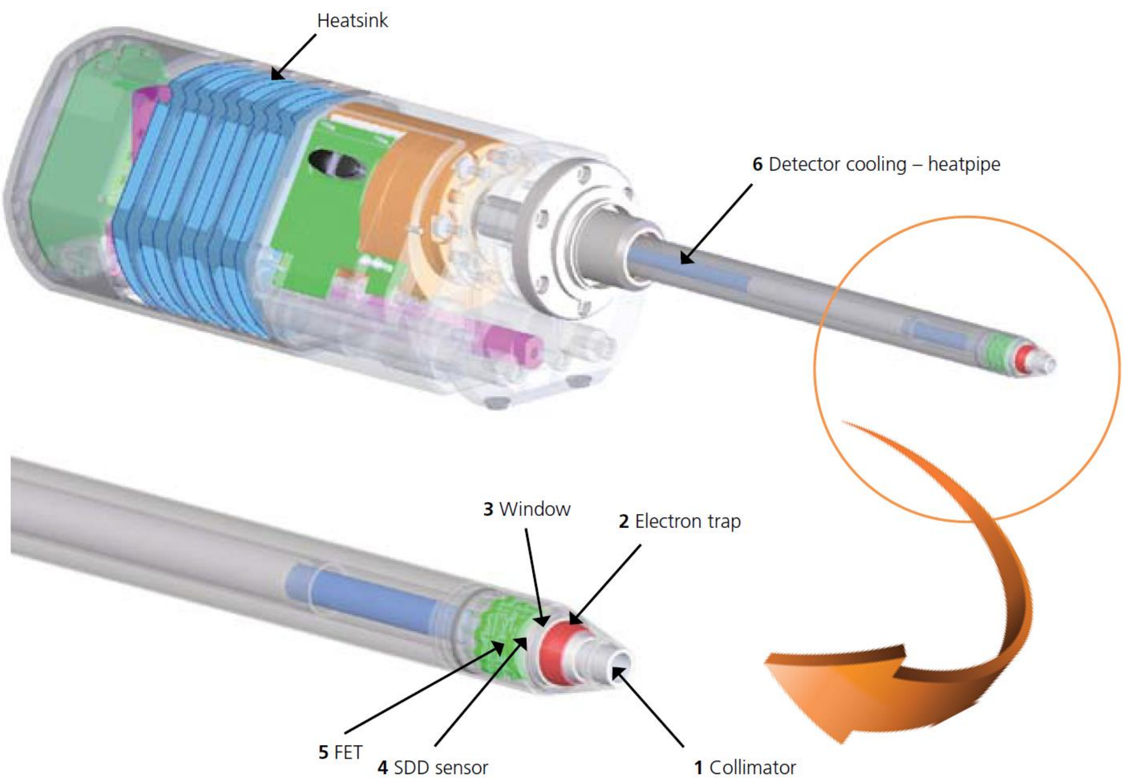


- EDS on the SEM – samples are struck by an energetic beam of electrons
- Characteristic x-rays generated by ***inner shell ionisations*** are resolved and quantified by energy (not wavelength) and intensity
- A variety of images/ elemental maps can be generated
- Quantitative analysis possible without resorting to running standards

Principle of Operation

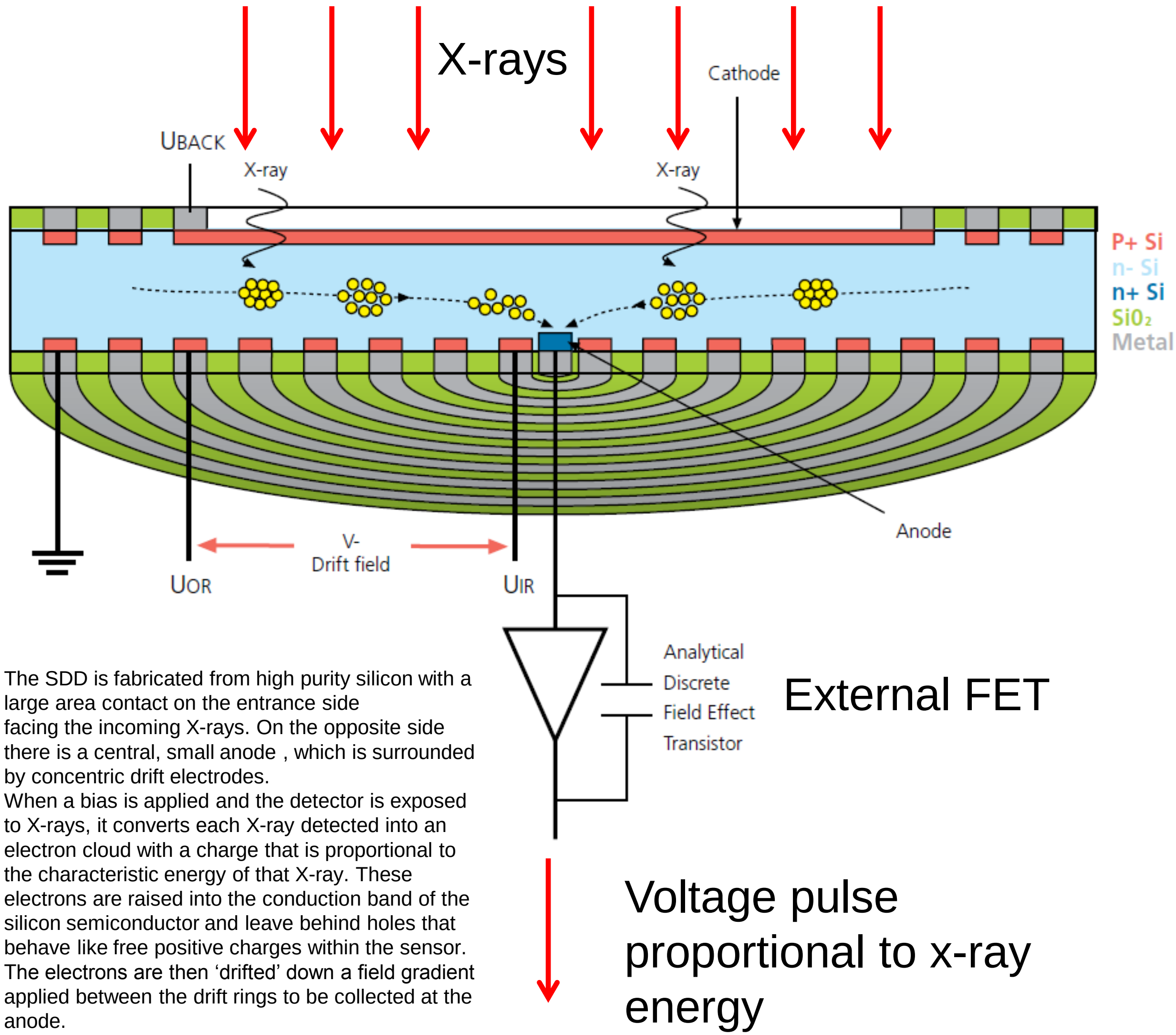


Detector Components



1. **The collimator** prevents stray X-rays entering the detector.
2. **Electron Trap** permanent magnet prevents stray electrons entering the detector
3. **Window** - Ultra thin polymer window allows detection of x-rays down to 100 eV.
4. **Silicon Drift Detector** (SDD) use a field gradient applied by concentric ring electrodes to collect the charge liberated by each X-ray detected, at the anode.
5. **Field Effect Transistor** (FET) First stage of amplification process - measures the charge of an incident X-ray and converts it to a voltage output.
6. **Detector Cooling** - SDD cooled to a few tens of degrees below zero by Peltier (thermoelectric) device. Heat is transferred to cooling fins.

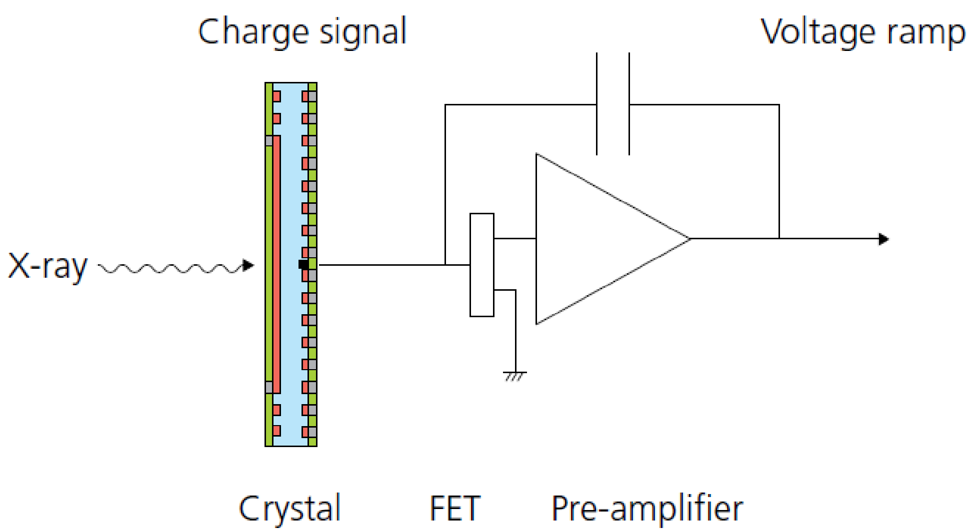
How the SDD works



The SDD is fabricated from high purity silicon with a large area contact on the entrance side facing the incoming X-rays. On the opposite side there is a central, small anode , which is surrounded by concentric drift electrodes.
When a bias is applied and the detector is exposed to X-rays, it converts each X-ray detected into an electron cloud with a charge that is proportional to the characteristic energy of that X-ray. These electrons are raised into the conduction band of the silicon semiconductor and leave behind holes that behave like free positive charges within the sensor. The electrons are then 'drifted' down a field gradient applied between the drift rings to be collected at the anode.

- The SDD converts the energy of each individual X-ray into a voltage proportional to the energy;
- Firstly the X-ray is converted into a charge by the ionization of atoms in the semiconductor
- Secondly this charge is converted to voltage by the FET preamplifier.
- Finally the voltage is input into the pulse processor for measurement.
- The output from the preamplifier is a voltage 'ramp' where each X-ray appears as a voltage step on the ramp.
- EDS detectors are designed to convert the X-ray energy into voltage signals as accurately as possible.
- Electronic noise must be minimised to allow detection of the lowest X-ray energies.

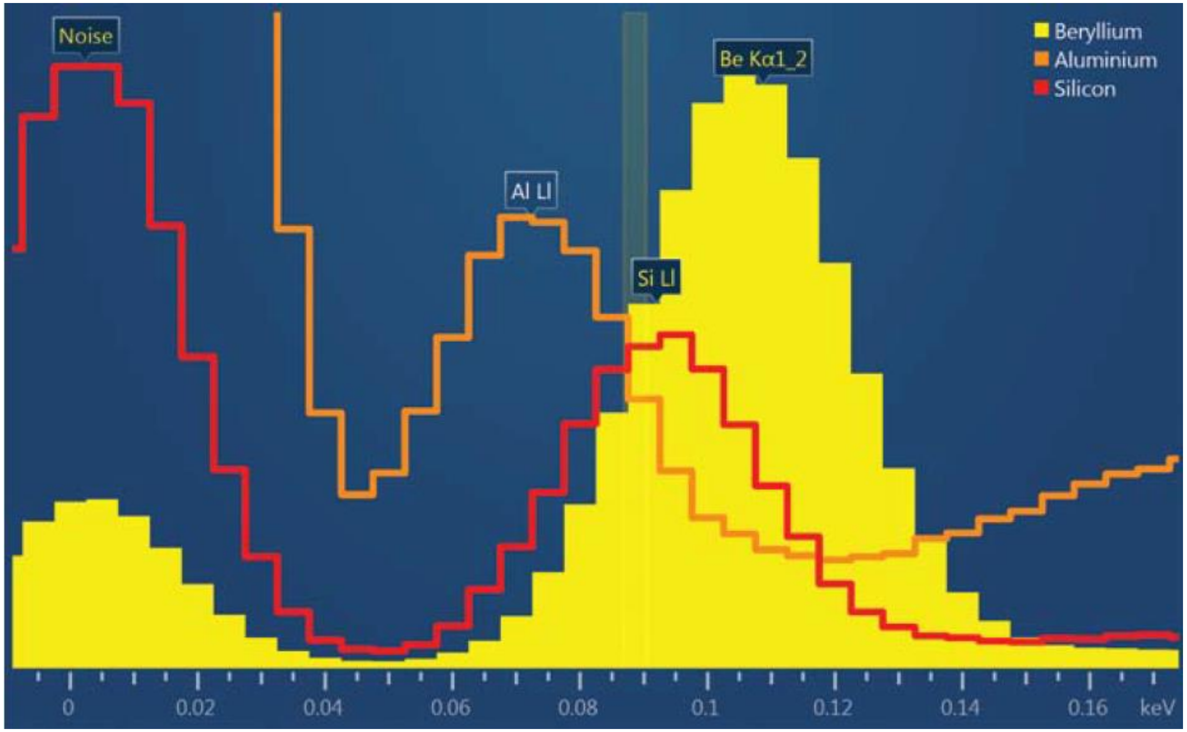
Role of the FET



The charge which accumulates at the anode is converted to a voltage by the FET preamplifier. During operation, charge is built up on the feedback capacitor.

- There are two sources charge;
  - current leakage from the sensor material
  - X-ray induced charge from the photons that are absorbed in the detector
- The output from the preamplifier caused by this charge build-up is a steadily increasing voltage 'ramp' due to leakage current, onto which is superimposed sharp steps due to the charge created by each X-ray event.
- The accumulating charge has to be periodically restored to prevent saturation of the preamplifier. Therefore at a pre-determined charge level the capacitor is discharged, a process called restoration, or 'reset'.
- **The output waveform exhibits fluctuations due to noise** that limit how precisely each step can be measured. If the measurement is imprecise, this spreads the histogram of measurements for photons of the same energy. Thus, **noise affects the width of X-ray peaks**, particularly at low energies.
- **Noise is influenced by the FET gain**, the input capacitance and the leakage current.
- Low noise is required to distinguish low energy X-rays such as beryllium Kα, silicon Ll and aluminium Ll from noise fluctuations

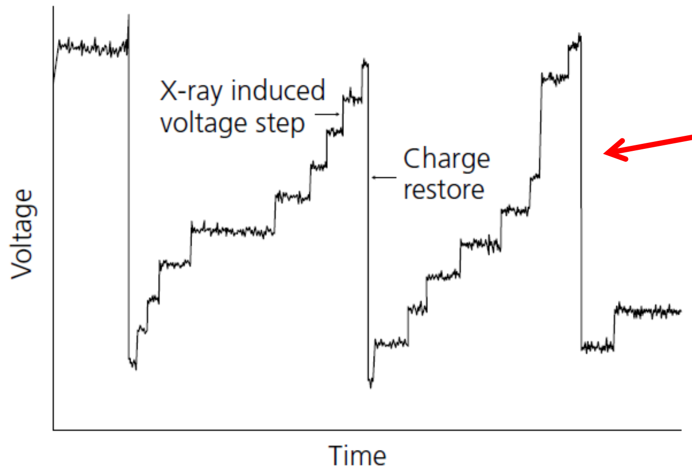
Requirement for Low Noise

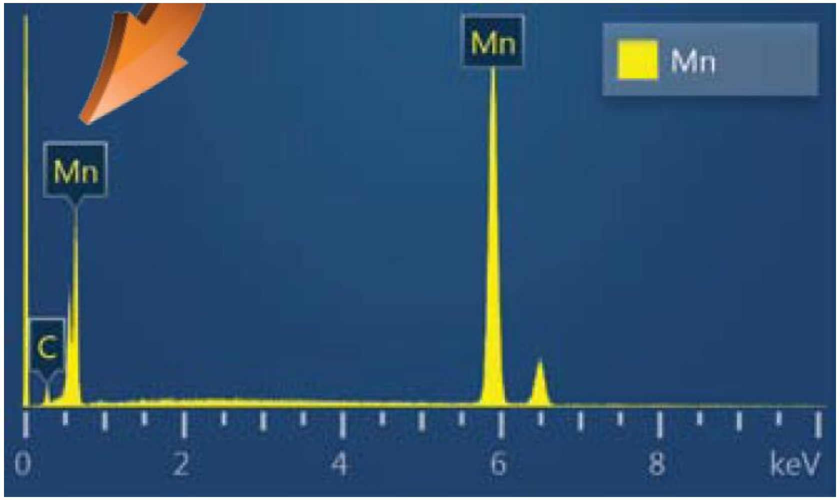


Spectra from Al, Si and Be showing separation of K and L peaks from baseline noise.

- **Noise is influenced by the FET gain**, the input capacitance and the leakage current.
- ***Low noise*** is required to ***distinguish low energy X-rays*** such as beryllium Kα, silicon Ll and aluminium Ll from noise fluctuations

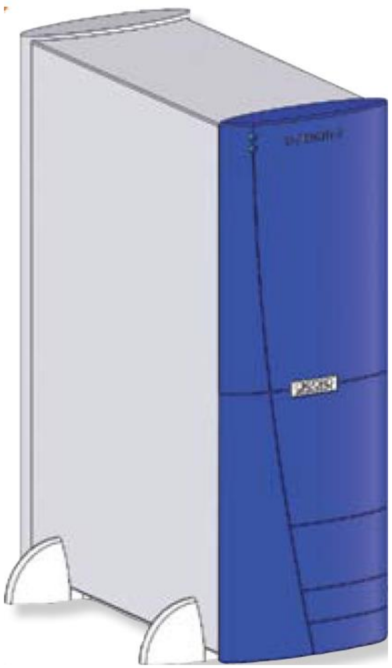
Pulse Processor





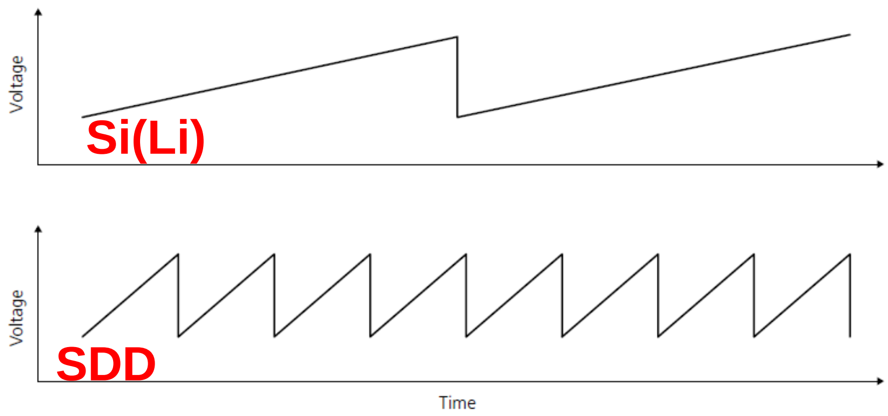
- The charge of an individual X-ray photon appears at the output of the preamplifier as a voltage step on a linearly increasing voltage ramp.
- The pulse processor measures the energy of the incoming X-ray, and gives it a ***digital count in the corresponding channel in the spectrum***
- It must ***optimise the removal of noise*** present and recognise quickly and accurately a wide range of energies of X-ray events from below 100 eV up to 40 keV.
- It also needs to differentiate between events arriving in the detector very close together in time to ***prevent pulse pile-up effects***

Digital Pulse Processing



- The ***signal from the preamplifier is digitised*** at the input of the pulse processor using digital pulse shaping and noise reduction
- The preamplifier output is sampled continuously by an analogue to digital converter (ADC). X-ray pulse heights are typically measured by subtracting the average of one set of values, measured before an X-ray event, from that for another set, measured after the event.
- The resultant value of the ***step measurement*** is then sent directly to the computer multi-channel analyser.
- The ***noise on the voltage ramp*** from the detector is effectively ***filtered out by averaging*** the signal.
- The time over which the waveform is averaged is referred to as the ***process time***

Hardware Performance – resolution & noise



Leakage current (gradient on the voltage ramp) is larger for SDDs but ***<u>since process time is shorter, leakage current is of lesser importance</u>*** *than with Si(Li) detectors*

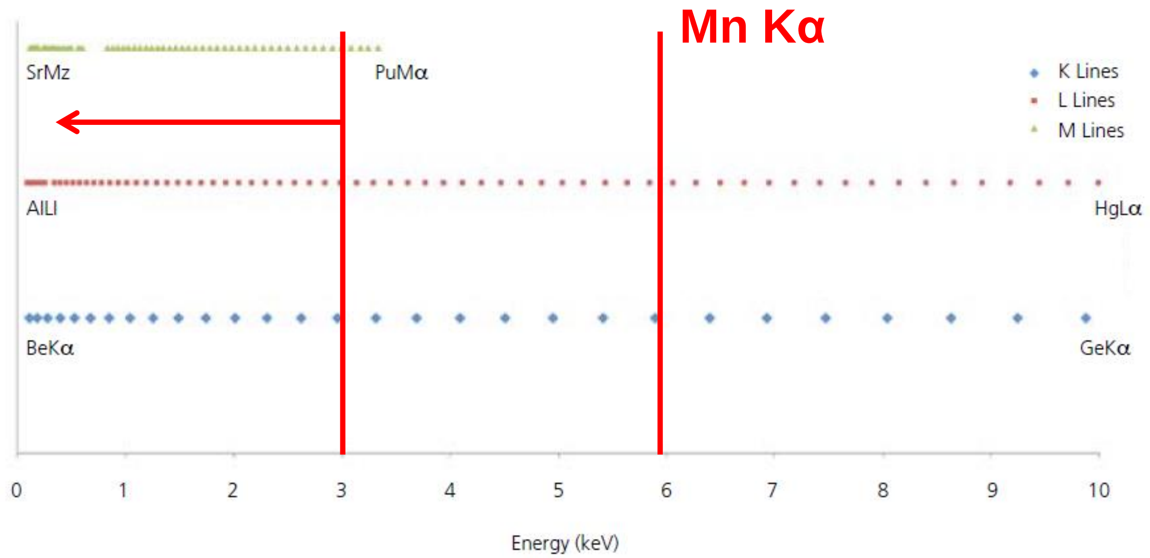
•**Leakage current** - results from the bias voltage applied to the sensor, gives rise to the slope on the voltage ramp (above). ***Leakage current affects resolution at long process times***. Leakage is proportional to the area and thickness of the sensor and increases with increased temperature. To achieve best resolution, Si(Li) detectors require long process times to reduce voltage noise extensive LN2 cooling to minimise leakage current noise.

•***SDD sensors achieve the same voltage noise at shorter process times*** and tolerate higher leakage current for the same resolution. SDDs work very well at the higher temperatures which can be ***maintained by Peltier cooling***.

- Resolution – a measure of detector quality providing a useful indication of performance.
- Resolution ***is quoted as the width of the peak at half its maximum height (FWHM).*** The lower the number the better the resolution a detector has and the better it will be at resolving peaks due to closely spaced X-ray lines.
- The resolution achieved by a detector is dependent on the sources of noise from the sensor and how they are processed by the counting chain. ***Unwanted noise has three main sources:***
- **Voltage noise** - FET gain and capacitance of components, notably the sensor anode***. SDDs*** have much ***smaller anodes*** than Si(Li) detectors, i.e. lower capacitance and ***much less voltage noise***.
- Voltage noise is reduced by averaging i.e. longer process times. With SDDs much shorter process times can be used to reduce this noise to an equivalent level of a SiLi detector.
- ***SDDs can maintain good resolution at much higher count rates*** than was previously possible with Si(Li)s
- Permits high speed mapping and fully quantitative analyses at short acquisition times
- **1/F Noise.** The 1/F contribution to resolution is due to the properties of the detector (e.g. contacts and dielectric materials – ***integrated or discrete FET***) and is largely independent of the process time

SDD has better noise characteristics than Si(Li) – <u>LN2 not required</u>

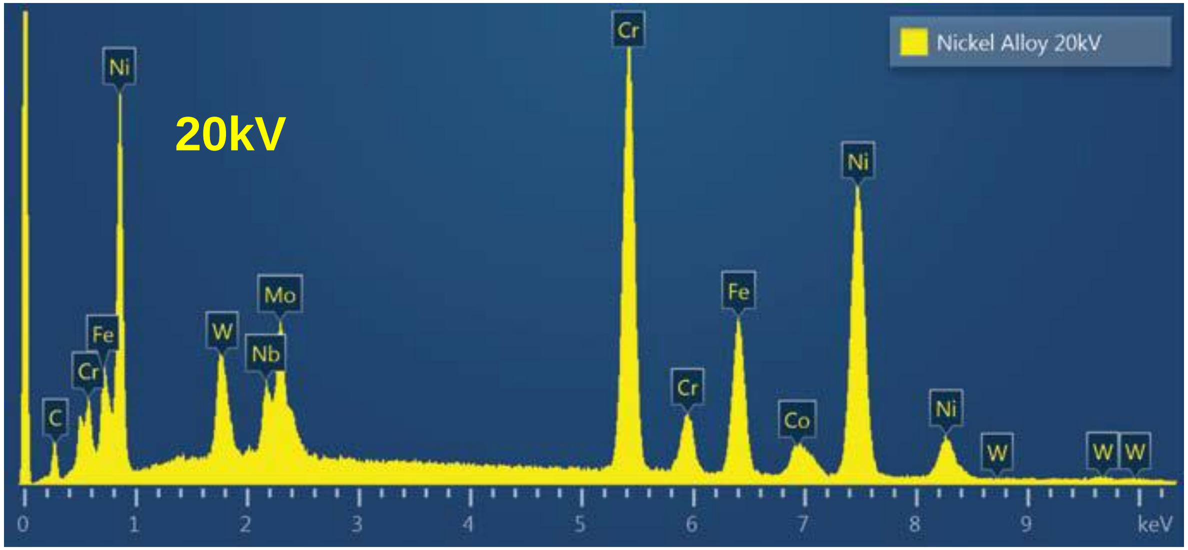
Importance of Low Energy resolution

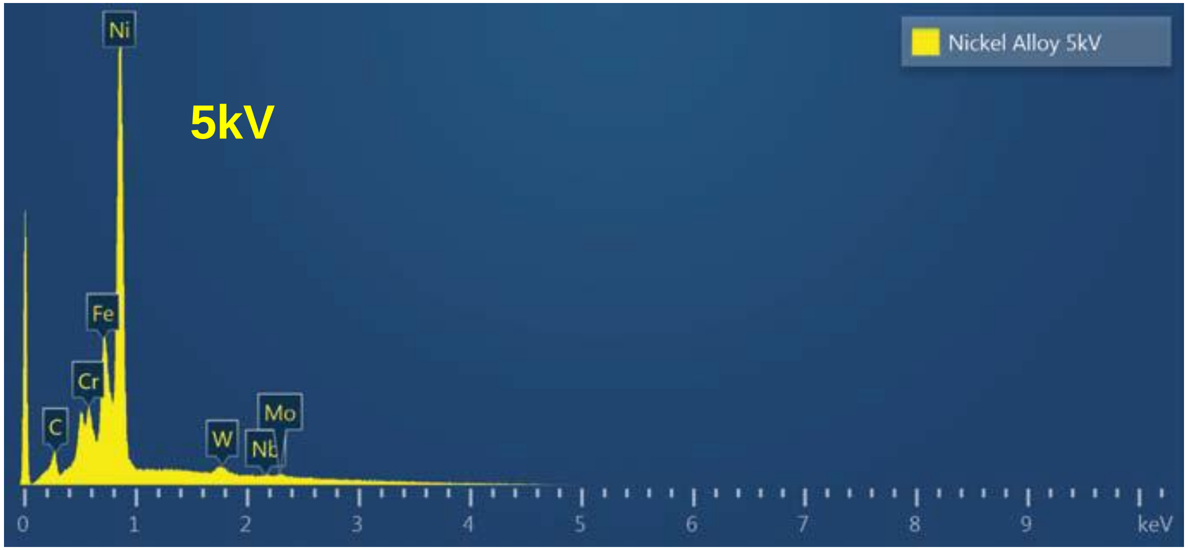


Showing the energy of the major lines for K, L and M series for all elements. Note that the resolution at Mn (5.9KeV), peaks are well separated. However, X-ray lines are closer together at lower energies, notably below 3kV where overlaps become significant. Thus ***resolution and deconvolution performance at low kV is critical***

- Resolution is measured using the X-rays of the manganese Kα line (MnKα). This is convenient during manufacture because a MnKα emitting 55Fe radioactive source can be used without the need for an EM.
- MnKα resolution can also be easily measured in the microscope by placing a piece of pure Mn under the beam.
- ***The identification and quantification of closely spaced X-ray peaks becomes easier and more accurate as the peak energy increases*** and the separation between them increases. ***X-ray lines are closer together at low energy***

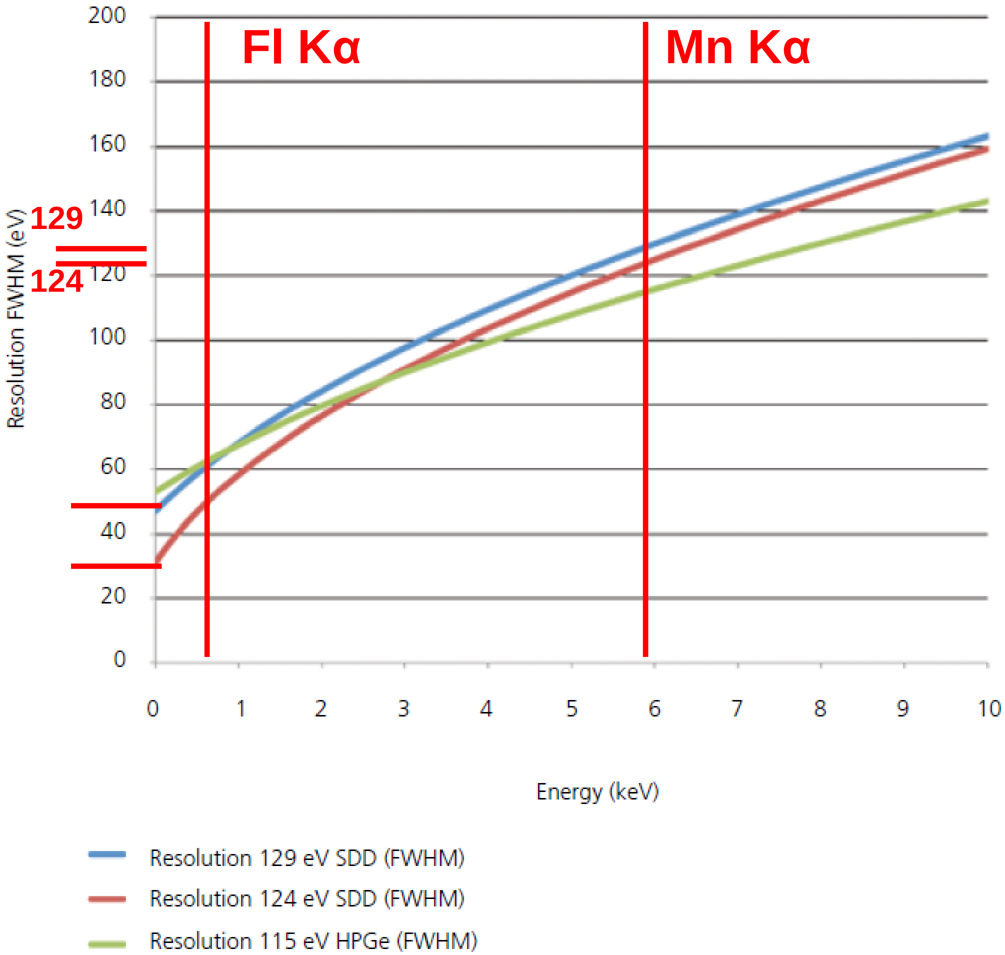
Spatial resolution and accelerating voltage





- Features <1 µm require lower kV to avoid a matrix contribution.
- At low kV only low energy lines are available for analysis.
- Spectra collected from a nickel alloy at 20 kV and 5 kV illustrate the importance of resolution at low energy.
- When working at 20 kV, the separation of widely spaced K lines of Cr, Fe and Ni, will not be affected much by a few eV variation in resolution.
- When working at 5 kV however, where identification relies on L lines which are very close in energy, a detector with better resolution will allow the L lines of Cr, Fe and Ni to be separated enough for confident identification

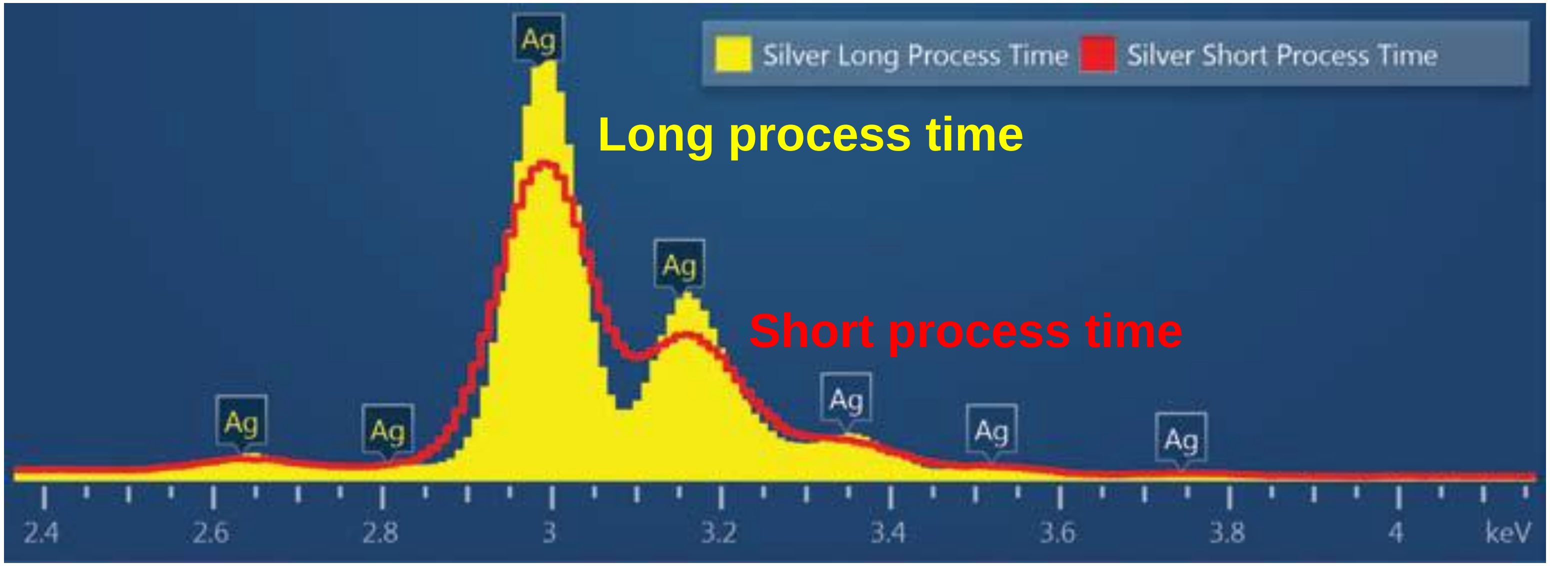
Low energy performance – Fluorine Kα FWHM



- The width of the peaks in a spectrum will vary depending on the energy of the X-ray line
- The curves demonstrate that as energy decreases, the resolution increases.
- The variation is different for SDD and other detector types. ***At low energy the electronic noise contribution (FWHMnoise) has a greater effect on resolution***.
- **Mn FWHM resolution is not a good measure to characterise noise and predict the resolution at low energy**.
- To characterise low energy performance, determine the resolution of fluorine Kα.
- SDD detectors can have significantly better lower energy resolution than other detectors even though SDD Mn resolution lower.

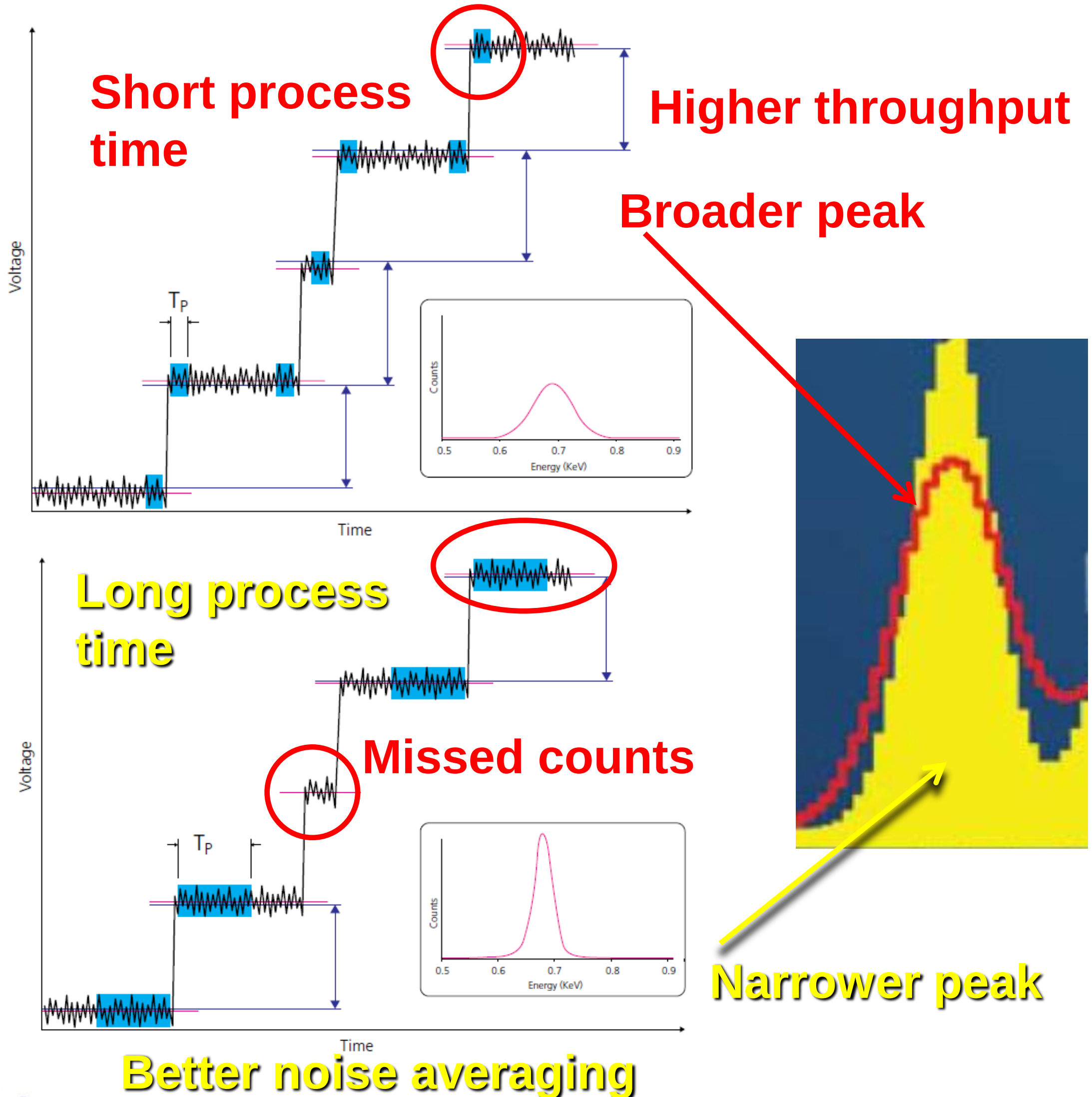
Variation with energy calculated to show resolution change with X-ray with different Mn resolution specifications. The curves are calculated from the equation FWHM2 = k.E + FWHMnoise2 where k is a constant for the detector material, and E is the energy.

How resolution changes with count rate and the effect of process time



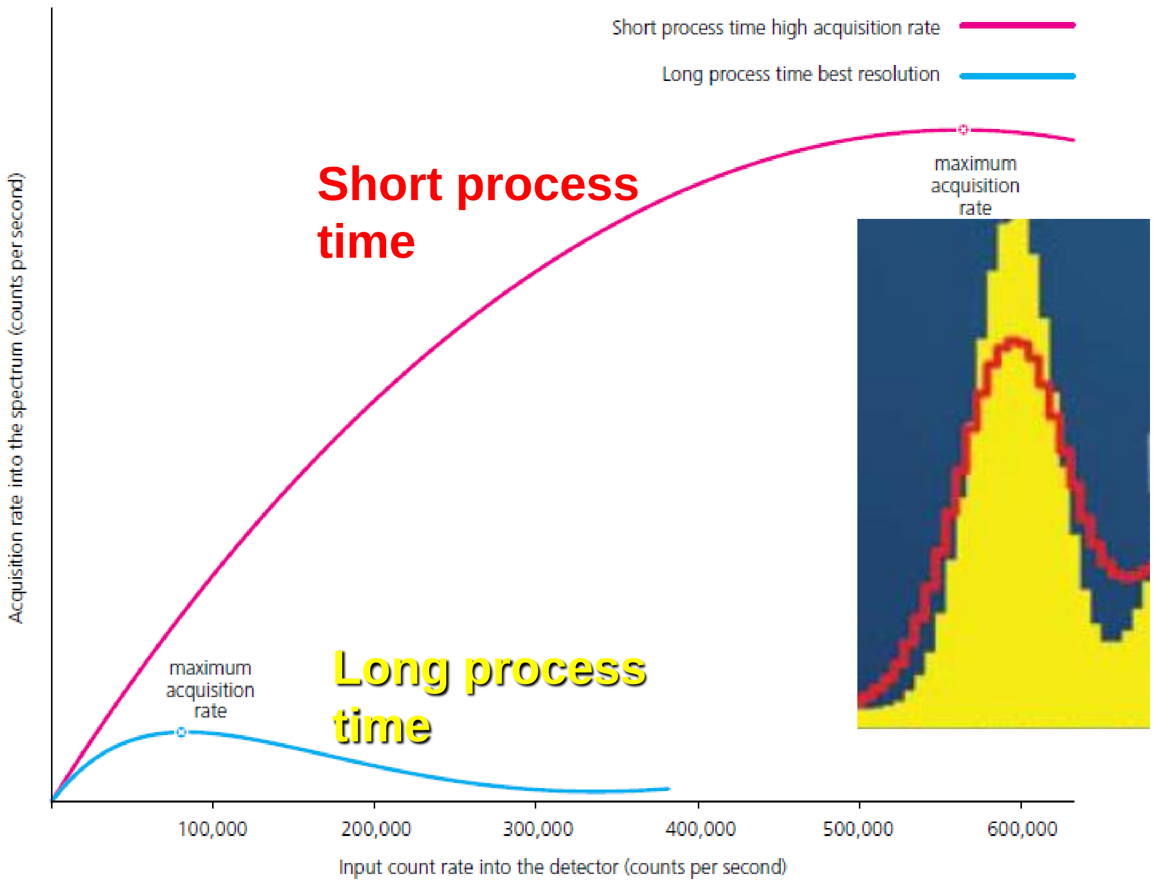
- The longer the process time, the lower the voltage noise and the better the resolution of the peak displayed in the spectrum
- Long process time reduces the speed at which data can be measured;
- The longer the process time, the more time is spent measuring each X-ray, and the fewer events that can be measured, i.e. Longer 'dead' time.
- The longest process time used by a processor gives the best resolution possible while the shortest process time gives the maximum throughput into the spectrum, but with lower resolution.

How resolution changes with count rate and the effect of process time



- Throughput depends on the rate of counts ***measured***, called the acquisition rate, rather than the input rate (into the detector).
- As the input rate increases so does the acquisition rate, **but an increasing number of events are rejected because they arrive in a shorter time period than the process time**
- ***If input rates increase excessively***, the proportion rejected will exceed the increase in measured events and the ***acquisition rate will start to decrease*** with further increases in input rate.

Process time and count rate



- ***For each process time there is a maximum acquisition rate*** which corresponds to the maximum speed possible for a chosen resolution.
- The maximum acquisition rate for each process time is ***characteristic of the detector pulse processor***.
- By determining, for each processor setting, the maximum acquisition rate and the resolution at this rate, the productivity and performance of a detector/processor measurement chain can be evaluated.
- The trade off of resolution vs process time is true of both SDD and Si(Li) detectors, however due ***to much lower voltage noise of SDD, process times are much shorter for equivalent resolution performance***.
- This means best resolutions can be achieved at 10s of thousands of counts per second (input rate) and maximum throughputs are measured in 100s of thousands of counts per second.

SDD design – integrated vs. discrete FET

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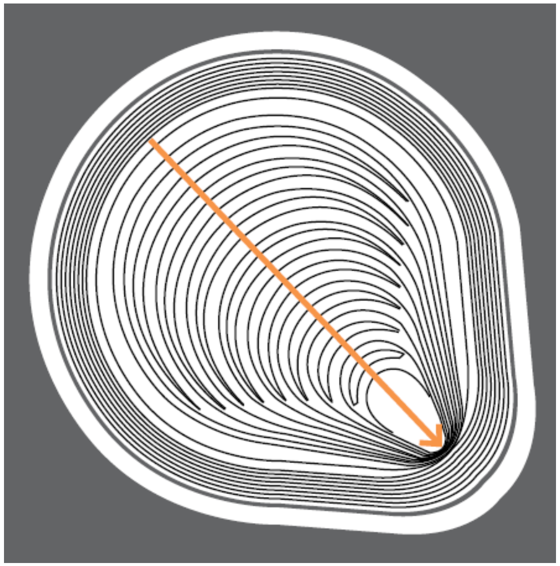
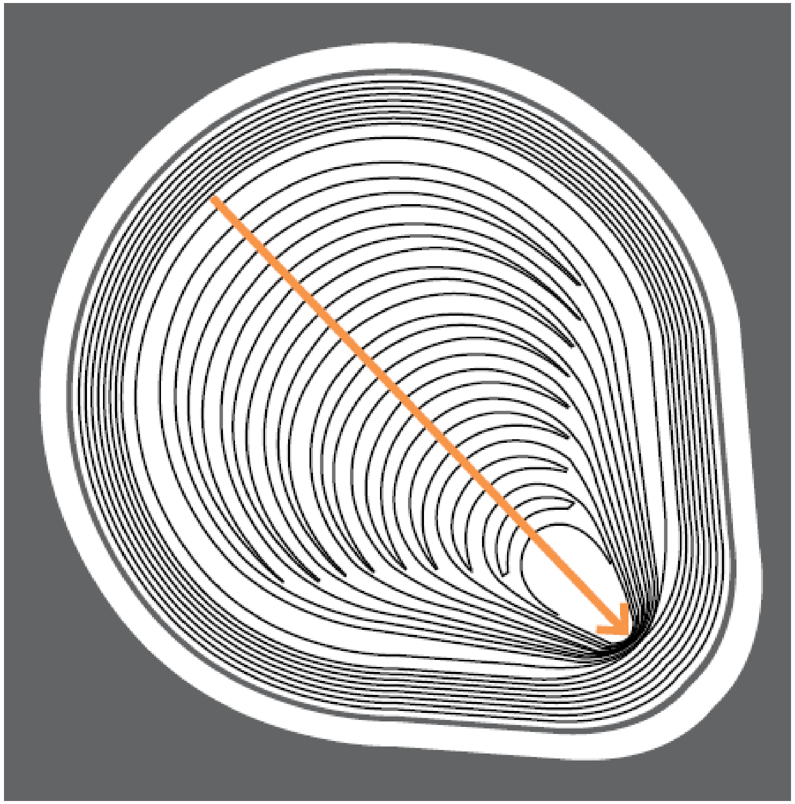


Most common SDD shapes: Tear-drop with integrated FET. The FET is at the periphery of the design meaning greater charge cloud travel distance than required for a radial design B) where an external FET is bonded to a central anode.

- Two basic types – integrated, side FET or radial, centre external discrete FET
- Incorporating the FET in the SDD minimises capacitance
- BUT ***high resistivity Si is used for SDD***
- ***FET requires low resistance Si*** - FET performance is compromised if incorporated in SDD
- ***External discrete FET constructed from low resistivity Si delivers best noise & gain*** characteristics
- Contact capacitance must be minimised

SDD with Integrated FET



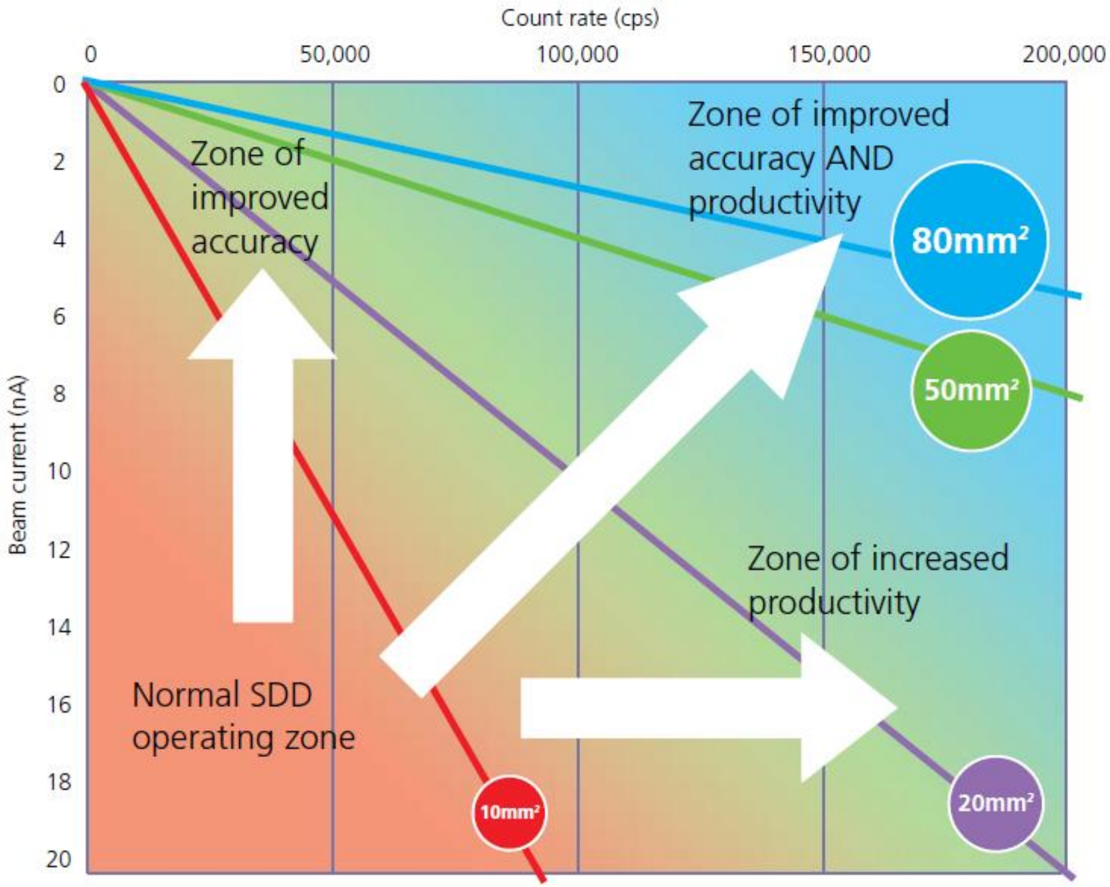
Tear-drop shape (to protect FET) with integrated FET, is subject to charge collection issues, and electrical characteristics causing ***resolution & peak shifts, plus size limitations***

- Integrated FET - avoids bond capacitance and minimises overall voltage noise.
- ***Lower voltage noise promotes good resolution at short process time***, maintained at high count rates.
- Central integrated FET is susceptible to irradiation by X-rays and electrostatic fields resulting in ***performance losses at low energies***
- ***Anode placed at edge for protection*** by the collimator
- However cloud collection distance ~3X that of radial design = longer max. signal rise time
- Consequently ***maximum size of detector severely limited*** to avoid charge collection deficits.
- Electrical characteristics and capacitance requirements to reset the integrated FET lead to ***changes in resolution or peak position*** with start up, time or count rate changes.

SDD with discrete external FET

- A discrete, external FET is bonded to the central anode. Some capacitance effects are associated with the bonding
- FET (& capacitor) constructed with ideal materials and device architecture to deliver best gain and noise characteristics
- Cloud collection distance 1/3rd that of teardrop SDD design, giving shortest possible signal collection distance and minimum signal rise time
- ***External FET can use a dedicated, external feedback capacitor*** of ideal characteristics. Using a feedback capacity is a well proven method of pulsed charge restoration. ***Sensor and measurement chain have high stability and linearity*** – important for accurate element ID and standardless quant. ***No changes in peak positions***
- Detector size can be scaled up without compromise

Advantages of central discrete FET SDD



Count rate vs beam current for different sensor sizes. At the same beam current a large area SDD sensor receives a much higher count rate than a 10 mm2 sensor

- Large area sensors with centre anode reduce rise time effects.
- External FET design allows a small central anode and avoids the problems due to having a FET integrated with this anode. Thus, ***very good low energy performance can be achieved even with large area sensors.***
- SDD can handle high count rates delivered by higher beam current
- However, it may be undesirable or possible to use higher beam current
- In such cases larger area detectors are the answer
- Sizes: 20, 50, 80, 100mm^2 are available

Large Area SDD

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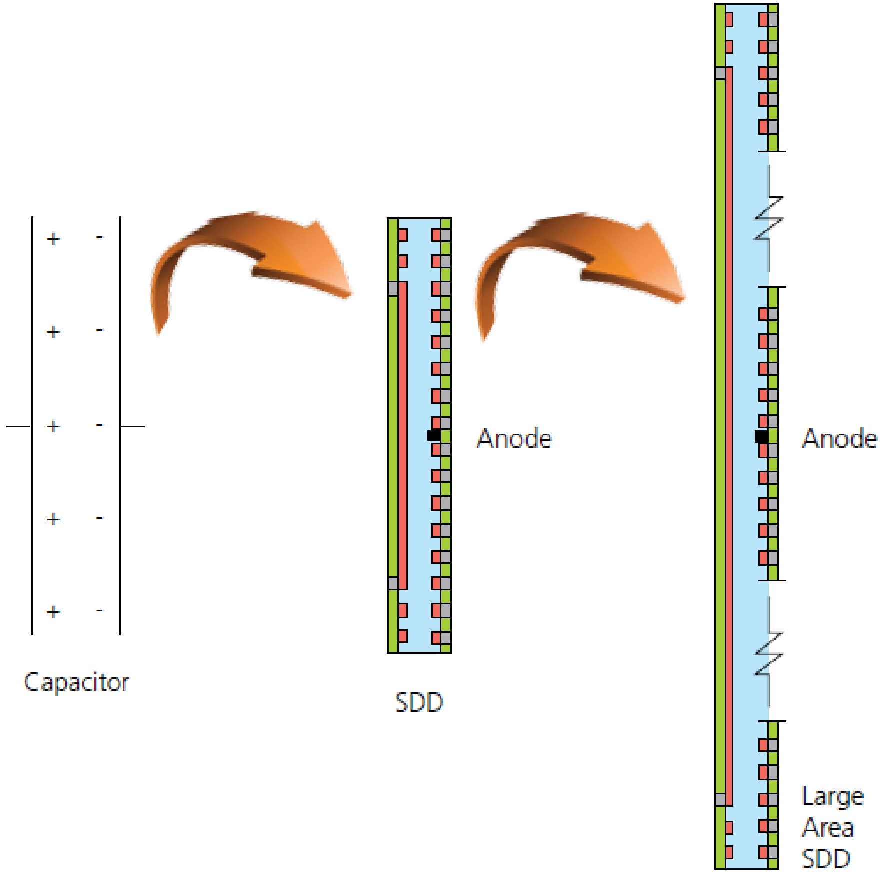
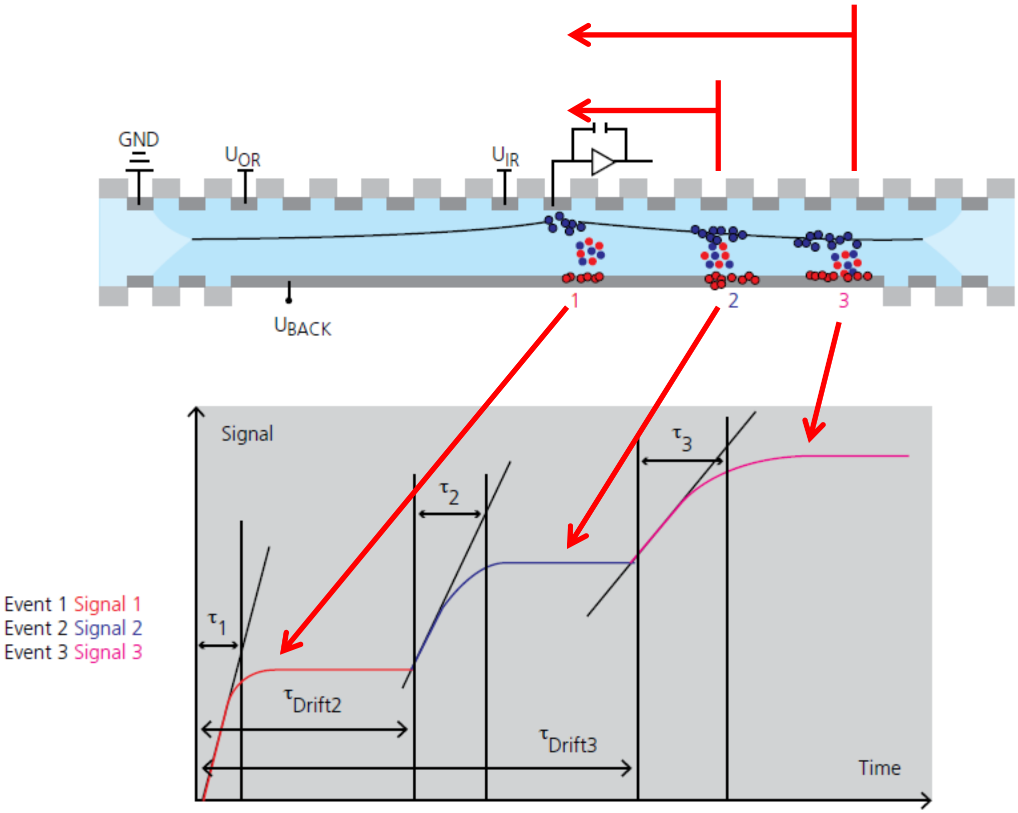


- The drift field focuses the electrons on a very small anode, thus drastically reducing readout capacitance.
- Thus the SDD anode capacitance is not affected by detector area and offers the potential for much larger sensors with good resolution.
- The ability to operate at very high count rates introduces analytical challenges...
- Ballistic deficit
- Pulse pile-up

The capacitance is proportional to the area of the electrodes. SDD: front surface = cathode, anode = small area on the back where the drift field is focussed. ***The area can be increased without changing the size of the anode****. Thus the same capacitance and resolution performance with count rate can be achieved, even for large area SDD*

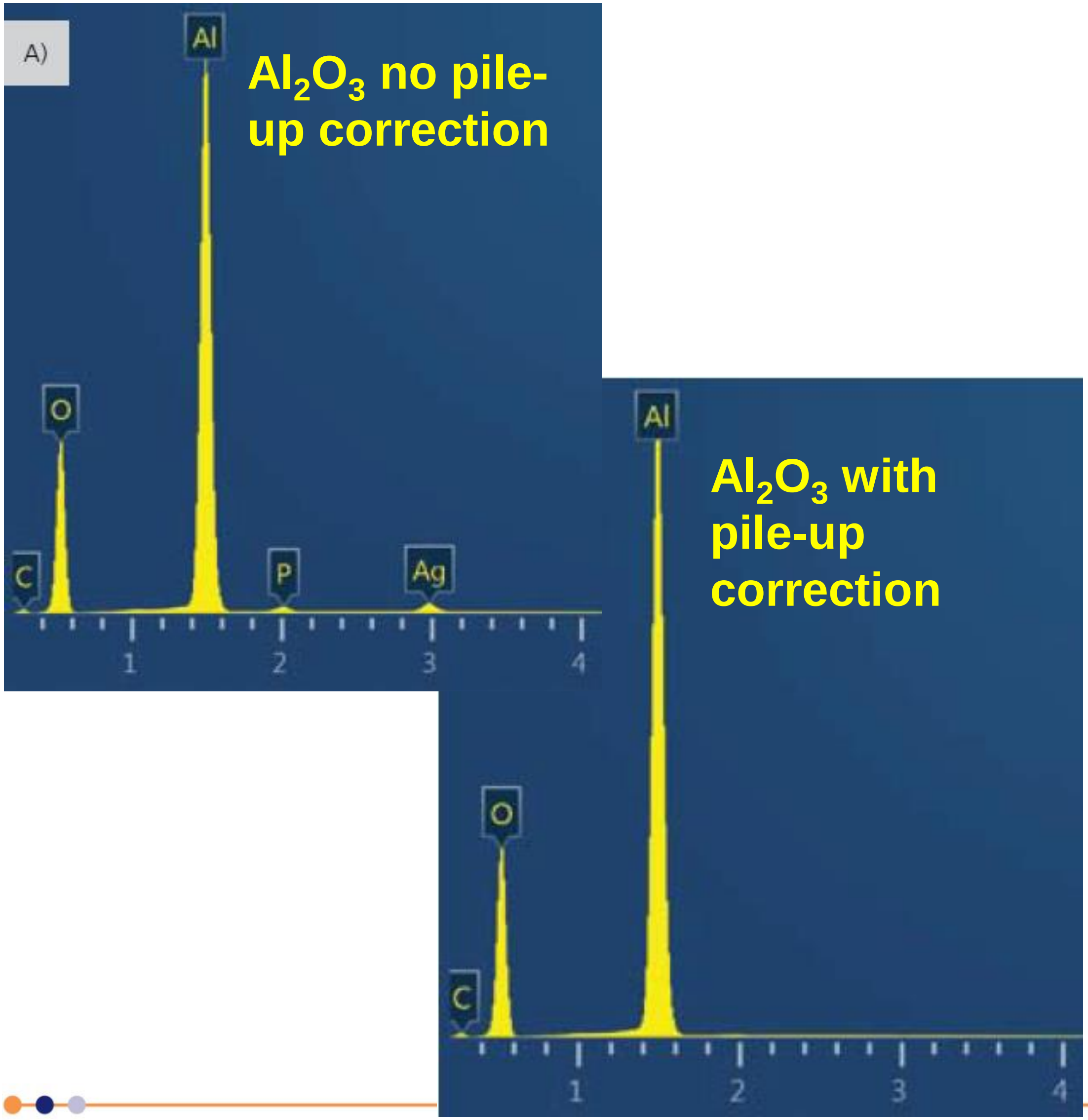
Working at high count rates – Ballistic deficit



X-Ray events far from the anode take longer to be counted – minimised by a central electrode

- Special pulse processing techniques are used to account for ballistic deficit and maintain analytical accuracy at high count rates

Working at high count rates – Pulse pile-up



- If two x-Ray events occur simultaneously, a pulse may be registered as the sum of the two x-Ray energies – a ‘sum peak’
- Such ‘pile-up’ of counts is manifest as sum peaks in the spectrum, which may be erroneously identified as other elements
- Pulse pile up correction identifies sum peaks and rather than just delete the peaks from the spectrum, restores the counts to the correct channels
- Pile-up can affect the background as well as peaks – it is vital for analytical accuracy that pile up is correctly modelled and compensated for
- Particularly important at high count rates

Teşekkürler..

Mart 2017