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**AMETEK**<sup>®</sup>  
MATERIALS ANALYSIS DIVISION

## Using Amptek X-ray Detectors to Measure Low Energy X-rays

Amptek's X-ray detectors can measure characteristic X-rays down to the Li  $K_{\alpha}$  line (52 eV) - a very low energy! But there are many challenges, which grow harder as the energy goes down.

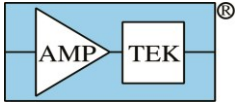
### Challenges to low energy X-ray spectroscopy

- 1) The X-rays have short attenuation lengths in the sample.** At the aluminum  $K_{\alpha}$  line, the attenuation length in silica, for example, is only 4  $\mu\text{m}$ . Since the primary beam will penetrate more deeply than this, the analyte's characteristic X-rays undergo self-absorption in the sample and so the signal is weak. Addressing this challenge requires properly selecting the excitation conditions, so that the range of the primary beam is not too deep.
- 2) The X-rays are absorbed in air between the sample and detector.** At the aluminum  $K_{\alpha}$  line, the attenuation length in air is 5 mm. At a 1 cm sample-target distance, 84% of the signal is lost in air. A 0.5 mm change in distance leads to a 10% change in intensity, limiting accuracy; daily fluctuations in atmospheric pressure cause measurable changes in absorption. To address this challenge, the lowest energy X-rays must be measured in vacuum. A helium purge can be used at moderate energies. For low energy measurements in air, a very tight geometry is necessary.
- 3) The X-rays are absorbed in the detector window.** Amptek's detectors are in vacuum, so they can cool properly; a window is needed to maintain vacuum, but the window will attenuate the incident signal. Addressing this challenge requires selecting the correct window option: the C2 window offers the least attenuation so is necessary for the lowest energies. The C1 and Be windows are appropriate for higher energies.
- 4) There tends to be significant spectral background from the scattering of the primary beam.** In EDS, electrons produce both bremsstrahlung and scattered electrons while X-rays undergo scattering from the sample and also backscatter from the detector. Addressing this challenge requires (a) careful attention to the excitation conditions and (b) obtaining good energy resolution (since the background in a region of interest is proportional to the FWHM of the peak).
- 5) There are many characteristic lines from heavier elements which can overlap the lines of interest.** At energies near the K lines of low-Z elements, one will find the L lines of moderate Z elements and the M or higher order lines of higher-Z elements. One also finds the escape peaks of higher energy elements. Addressing this challenge requires (a) obtaining good energy resolution (since overlap is proportional to FWHM), (b) a clean setup to minimize extraneous peaks, and (c) good software to deconvolve the inevitable overlaps.

### X-Ray Fluorescence or Energy Dispersive Spectroscopy

The first decision to make is: Will the primary beam excite the sample with X-rays or electrons?

In **X-Ray Fluorescence (XRF)**, X-rays are used to excite the atoms in the sample. Advantages of XRF include the fact that it can be used in air and that the sources and setups are relatively simple. XRF can be used quite well to measure higher energy characteristic X-rays, in addition to the lower energy ones (but not simultaneously: the X-ray tube energy required to produce higher energy X-ray lines will yield a weak signal and high background for low energies; two or more spectra are needed). A disadvantage of XRF is that the primary X-rays penetrate too deeply to see the lightest elements. XRF in vacuum can be used down to the C  $K_{\alpha}$  line (with great care), and XRF in air can be used down to the Mg  $K_{\alpha}$  line (with great care), but XRF best above these energies.



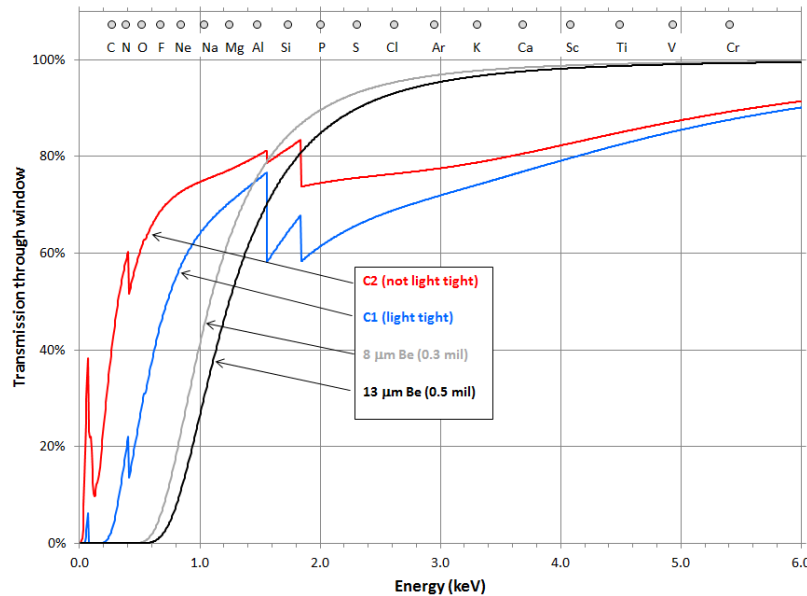
In **Energy Dispersive Spectroscopy (EDS)**, electrons are used to excite the atoms in the sample. The advantage of EDS is that one can measure the lowest energies: the electrons have a short range in the sample, so efficiently produce characteristic X-rays very near the surface. A second advantage is that the spot size can be kept to a few microns, for very high spatial resolution elemental analysis. But EDS can only be carried out in vacuum and requires a much more elaborate and expensive experimental setup (it is usually carried out in an SEM).

### Choosing the detector

For low energies, Amptek recommends using either the 25mm<sup>2</sup> SDD or the 25mm<sup>2</sup> FastSDD. These detectors have the best performance and that's needed for low energies. They both have lower electronic noise than Amptek's SiPIN detector, 125 eV FWHM at the 5.895 keV Mn K<sub>α</sub> line, and low noise is important for low energies, for improving the signal to background ratio and minimizing overlapping peaks. They also have a large active area (useful if the signal is weak) and can run at high count rates. The SiPIN detectors can be used for lower energy XRF but the performance will be marginal.

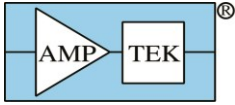
### Choosing the detector window

The plot below shows the transmission of Amptek's various windows versus energy. It should be clear that the C2 window is required for the lowest energies. The C2 window is only available with Amptek's FastSDD detector.



A separate application note discussed the C windows in some detail but a few key points will be mentioned here:

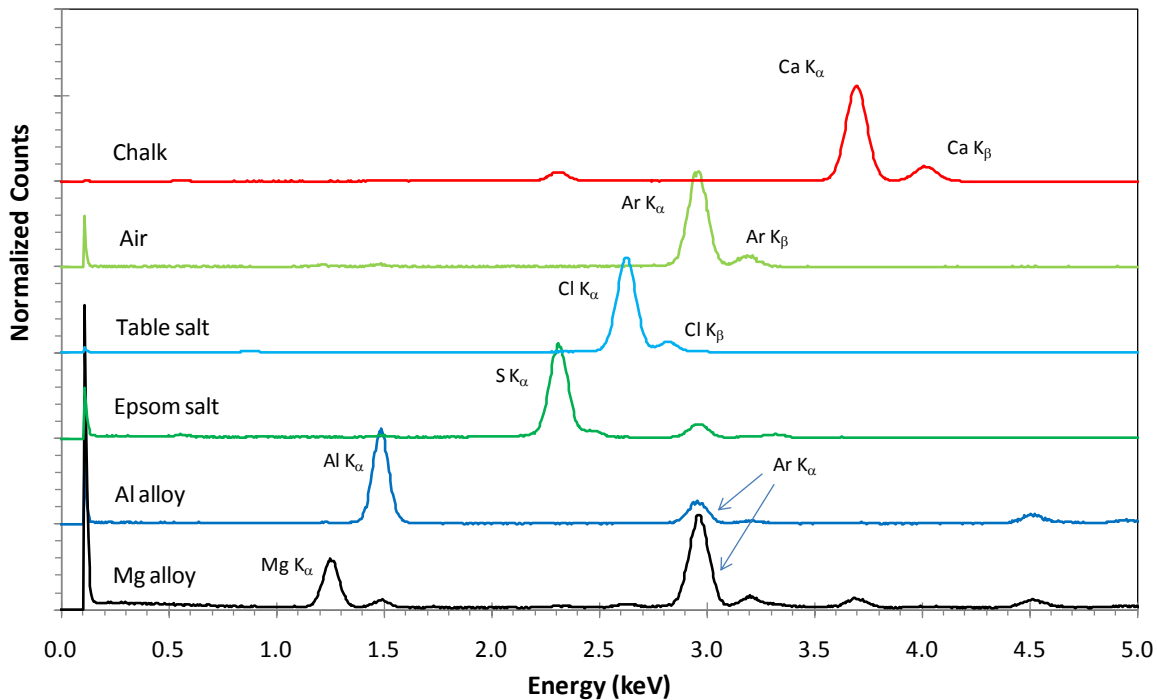
- The C windows are made out of thin Si<sub>3</sub>N<sub>4</sub> (40 nm for C2), which is mounted on a thicker silicon grid (80% open area) and then covered with aluminum. The Be windows are made from aluminum and coated with a thin layer of Parylene for protection. Note that the C windows will produce N, Si, and Al characteristic X-rays.
- The C2 window is not light-tight; if it is used where light is present, there will be a photocurrent through the SDD which prevents detection of X-rays. The C1 and Be windows are light tight.



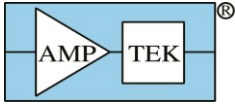
- All of the windows are fairly fragile. None can be touched with any object, including anything used to clean the detectors. None will break spontaneously and all can withstand many cycles of vacuum to air and back. But the C2 windows are more susceptible to breakage by small bits of debris (often blown about when a system is pumped or vented) and to shocks with rapid pumping and venting.
- The standard C windows are not He tight while the Be windows are He tight.
- For the very lowest energies, Amptek's detectors can be supplied with no window but these are exceptionally delicate: the thermoelectrically cooled SDD becomes a cold trap, so any contamination in the system will condense on the SDD and immediately destroy it. Windowless detectors are offered with no warranty and most users find them to fail often. Only in UHV systems, which are permanently maintained at ultrahigh vacuum, have we found windowless detectors to be reliable.

**Sample Spectra: EDS**

**Sample Spectra: Low Energy XRF**

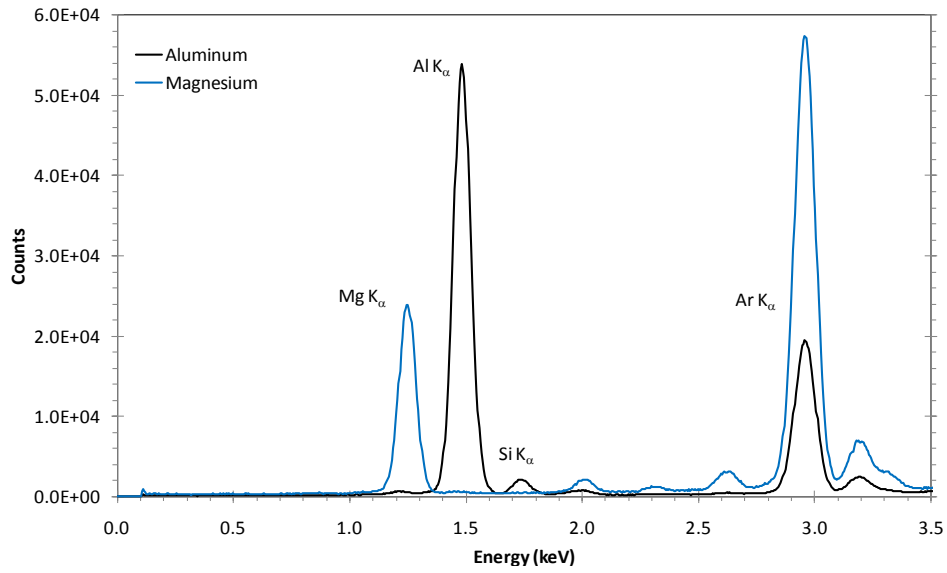


Plot showing spectra measured by Amptek's 25 mm<sup>2</sup> SDD, using a 12 μm Be window, in light element XRF.

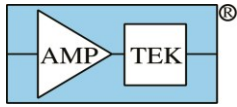


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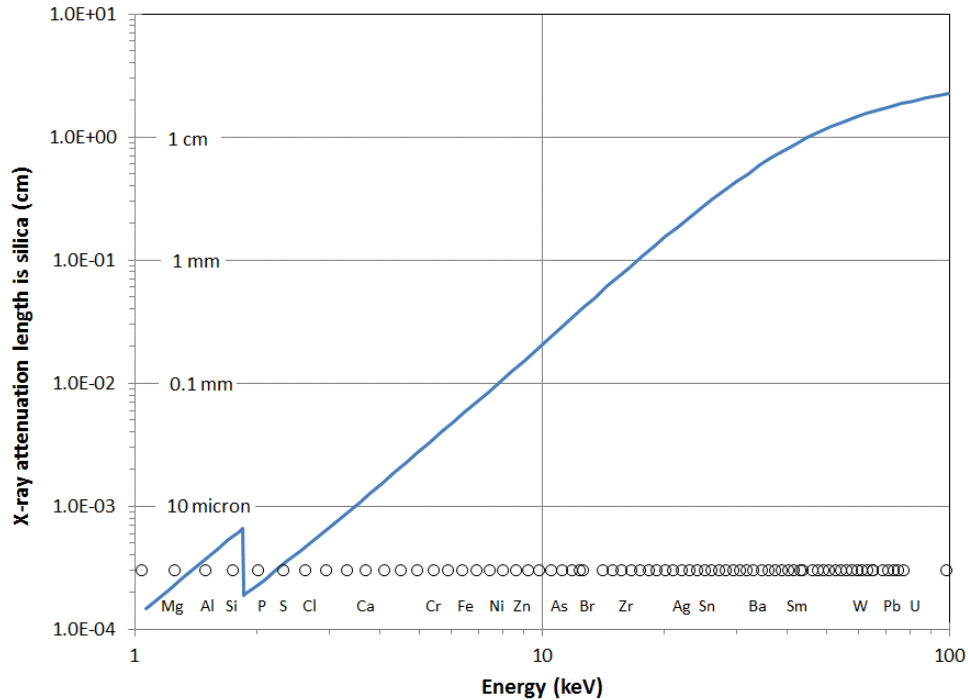


Plot showing spectra measured from Mg and Al samples with an SDD in air, with a Be window. The clear separation between the Mg and Al K<sub>α</sub> peaks at this low energy is clear. The Ar K<sub>α</sub> line arises from argon in air. Note how much lower the Mg Ka line is, relative to the Ar Ka line, than the Al line. The combination of self-absorption in the sample and absorption in air reduced the sensitivity about five fold in going from 1.48 to 1.25 keV.



### Excitation conditions for low energy XRF

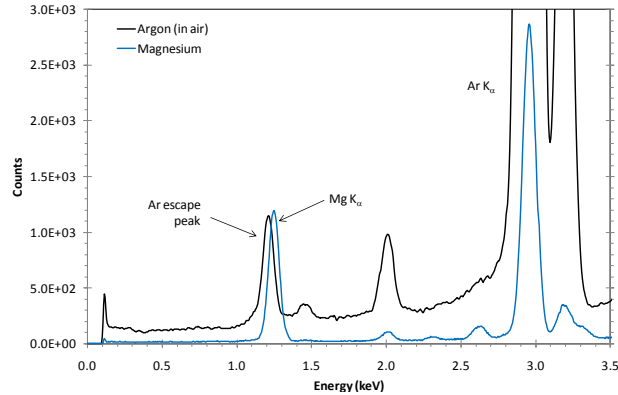
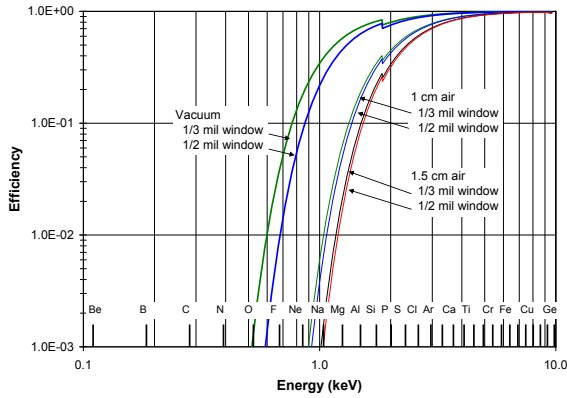
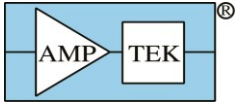
Using the correct excitation conditions is vital to obtain good results at low energies, particularly with XRF. There are two issues: attenuation depth and fluorescence yield. The chart below shows the attenuation length versus energy in silica, a major component in rock and soil. If one excites the sample with 10 keV X-rays, where the attenuation depth is 300  $\mu\text{m}$ , then the elements in the silica are producing X-rays throughout this depth. The attenuation length for the Al  $K_{\alpha}$  X-rays is only 4  $\mu\text{m}$ ; if the aluminum is uniform through the sample, 99% of the Al X-rays will be absorbed by the sample matrix before reaching the surface. What's more, the probability of a photoelectric interaction falls with energies well above the K line. Even a high concentration of aluminum is going to give a weak signal!



The usual rule of thumb is that, for XRF, the excitation energy should be 1.5 to 2 times the K edge of the analyte. To measure Al, this would mean an excitation energy of 3 to 4 keV. If one uses a 30 or 40 keV excitation source, then the signal from the elements producing low energy characteristic X-rays will be extremely weak.

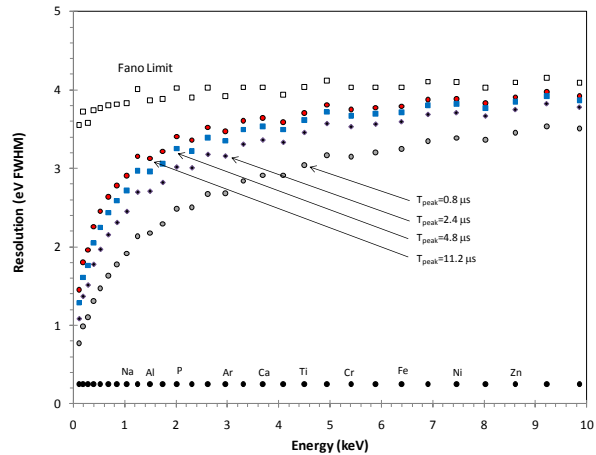
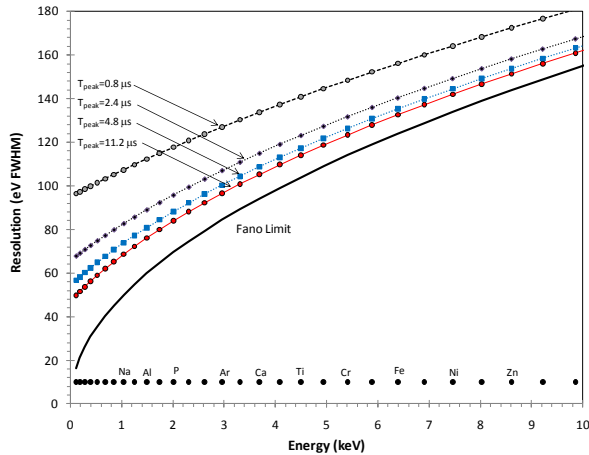
### Air Path

The plot below on the left below **Error! Reference source not found.** shows the effect of air path. For Al, the sensitivity falls from 16% for 1 cm of air to 9% for 1.5 cm of air. This makes it very difficult to obtain quantitative results: if the geometry of the sample under test and of the calibration reference changes by a fraction of a millimeter, significant errors result. This is why low energy XRF is usually carried out under a He purge or in vacuum. The plot on the right below illustrates another issue: air contains Ar, and its characteristic X-rays and their escape peaks produce spectral interference. This plot compares a Mg spectrum, measured in air, with the result of exciting only an air column. Argon is an important component of air, yielding the strong peak at 3.0 keV, present in essentially all measurements. Note the proximity of the Ar escape peak (1.21 keV) is to the Mg  $K_{\alpha}$  peak (1.25 keV).



### Resolution

The plots below show the energy resolution of the 25 mm<sup>2</sup> SDD for the light elements, at several different peaking timings. The energy resolution arises from Fano broadening and electronic noise, which add in quadrature. Fano broadening is the dominant term for elements above Na, for  $T_{peak}=11.2 \mu\text{sec}$ . For heavier elements, the noise is less important, so the resolution does not depend as much on the signal processing settings. To run at high count rates, one should use a short peaking time. This will degrade the resolution most for the light elements. The plot on the right shows, on the vertical axis, the ratio of the energy resolution (eV FWHM) and the spacing between the K $\alpha$  lines of adjacent elements. This is an indicator of the ability of the system to resolve the lines of closely spaced peaks.



Plots showing the resolution of the SDD as a function of energy and peaking time. The plot on the left shows the raw resolution values. The plot on the right shows the ratio of the energy resolution (eV FWHM) to the spacing between nearest K $\alpha$  lines. This is a measure of the resolvability of the peaks.