Acquisition Condition Selection

Choosing optimal acquisition conditions for XRF analysis is a complex and critical part of the art. Selecting the proper acquisition conditions can mean the difference between measuring an element at PPM levels, or not seeing it at all. There are two fundamental principles that must be met to achieve optimal analysis conditions.

A) There must be a significant source peak above absorption edge energy of the element of interest. This may be either the K or L edge depending on which one is within the measurable range of the instrument with the preference usually going to K line measurements. The closer the source energy is to the absorption edge, the higher the intensity and sensitivity (counts/sec/PPM) will be for the element of interest. The ideal energy would be precisely at the absorption edge energy, but that is usually not possible.
B) The other fundamental principle is that the background x-rays within the element of interest region should be reduced as much as practical.

The difficulty is that these two principles work in opposition to each other, as the best sensitivity is often achieve when the background is highest, and the background is lowest when the sensitivity is worst. Add to this that the best theoretical detection limits are achieved when the sensitivity is highest, while the net count rate extraction, matrix corrections, and long-term analytical stability are best when the background is lowest. Optimal analytical performance is achieved by finding the best compromise between these two principles, given the instrument hardware.

Elements of Interest

The first step to figuring out how to set up an analysis is to determine the elements of interest. This seems obvious, and sometimes it is, but other times it is not. If a sample has never been analyzed for every conceivable element, the odds are high that it contains something that the people producing it are not aware of. Some samples come into a laboratory as complete unknowns. If a sample is not well characterized it is a good idea to perform a qualitative examination of the material using three or more acquisition conditions designed to cover high, medium, and low energy ranges. Qualitative acquisition conditions will be covered below.

Source Selection - Isotopes

Isotopes are the simplest source to configure. The most common isotopes are in the table below. Select a source that emits x-rays that are closest to and immediately above the absorption edge energy for the element of interest. To avoid problems with high background the element of interest peak should be at least 2-3 times the FWHM detector resolution away from the source peak.

Isotope	Fe-55	Cm-244	Cd-109	Am-241	Co-57
Energy (keV)	5.9	14.3, 18.3	22, 88	59.5	122
Elements (K-lines)	Al – V	Ti-Br	Fe-Mo	Ru-Er	Ba - U
Elements (L-lines)	Br-I	I- Pb	Yb-Pu	None	none

Sources Selection – X-ray tubes

X-ray tube selection is often done by the manufacturer without much input from the customer, but there are some selection rules that are useful. X-ray tubes emit a broad bremstrahlung spectrum that spans from 0 to X KeV where X is the kV potential across the x-ray tube. The peak intensity in the Bremstrahlung spectrum is at roughly ½ the maximum energy. The x-ray tube also emits line energies that are characteristic of the target element, so target selection is usually based on selecting a target that will provide optimal excitation for the most important elements of interest. Or, alternatively the selection is based on having a line energy that doesn't increase the background in the region of any important element. Since the amount of x-ray flux is proportional to the atomic number of the target element, targets such as W are also selected on the basis of having the highest total flux. Targets can be any of several high melting point metals. Common target choices include, Sc, Ti, Cr, Fe, Co, Ni, Co, Y, Zr, Mo, Rh, Pd, Ag, W, and Pt.

Multiple target tubes have been used in XRF instrument, and they allow the operator to select the target on a per element basis, using the rule that the target with a line energy immediately above the absorption edge is the one selected, providing it is at least 2-3 times the FWHM detector resolution away from element line. If there is no target available with an emission line above the element of interest select the highest atomic number target available, to maximize the total x-ray flux from the tube.

Source Selection - X-ray Tube Filters

Filters can be placed in the x-ray path between the x-ray tube and the sample in order to modify the shape of the source spectrum. Filters can be made of any element that can be formed into a stable solid or film. They are usually metal or plastic, although plastic filters deteriorate when bombarded by x-rays.

The key to the function of filters is the filter elements absorption edge energy. The filter readily absorbs source x-rays immediately above the absorption edge while those below the absorption edge are transmitted. Very high energy x-rays are also transmitted. This produces a low background valley immediately above the filter's absorption edge that is great for analyzing elements in the energy range beginning 2 FWHM detector resolution widths above the absorption edge.

Filters also fluoresce their own characteristic line energies, which combine with the Bremstrahlung that is transmitted by the filter to for a peak that looks a little like a right triangle. This secondary filter fluorescence peak can be used as a source peak for elements that are about 3 atomic numbers or more less than the filter element.

Multilayer filters are also used. The filter nearest the x-ray tube has an absorption edge above the element of interest and a second filter place on the sample side has an absorption edge below the filter. This makes the source peak less triangular and more monochromatic looking while reducing the background. This is the optimal filter method for exciting one element.

Another type of filter is a neutral absorbing filter such as aluminum or plastic. These filters are intended to filter lower energy source x-rays in order to reduce the background in the region of the element of interest. A thin neutral density filter may be useful for measuring elements like S, or P with an Rh, Pd, or Ag target x-ray tube, while thicker Al filters can eliminate these target peaks entirely creating a source that is good for analyzing x-rays between 2 and 10 keV.

Source Selection - Secondary Targets

The theory behind a secondary target is that the characteristic line energies of the target material are used to excite the sample. The source points at the target rather than the sample and then the target is oriented so that fluorescence from it shines on the sample. Secondary targets produce a highly monochromatic peak with very low background. In some instruments the target may be oriented orthogonally with respect to the sample. Since the bremstrahlung is polarized when scattered off a surface, the orthogonal arrangement minimizes scatter at the detector. In either case there is very little energy x-ray intensity above the characteristic line energy of the target element.

Selecting the optimal target is simply a matter of choosing the lowest energy target that is above the element of interest absorption edge energy provided it is not so close that they Compton scatter doesn't overlap the region of interest. In most high-resolution instruments the element of interest energy should be less than or equal to the element two atomic numbers below the target element.

Barkla Scatterer

There is another secondary target called a Barkla scatterer that scatters the entire continuum rather than relying on producing characteristic line energies. These are almost always used with polarizing optics, since they would otherwise produce very high background intensities. Different scatterers are more efficient at different energies, generally increasing with atomic number. Materials like carbon or boron carbide are used to excite elements below 5 kV while alumina is used for higher energies.

Source Selection – Overview

Depending on the x-ray tube, x-ray tube filters, and secondary target options in a particular analyzer there may be several options for a given element. So now the question becomes, what is the best choice. Because filters and secondary targets perform differently in deferent energy regimes it is useful to split things up into ranges.

Low Energy (<3 keV)

In this range filters and targets do not perform well, so direct excitation using L-lines from Mo, Rh, Pd and Ag targets will usually give the best performance. A thin neutral density filter can be used to reduce the background somewhat, but it will make the sensitivity worse. In special cases such as measuring Al in concentrated Si, a secondary target helps (Si in this example), because one can be selected that does not excite the major element in the sample.

Medium Energy (3-23 keV)

In this regime secondary targets are almost always superior. Metals from Sc to Sn fluoresce well producing monochromatic source peaks with low background. The combination that comes close to rivaling a target in this regime is when the x-ray tube target itself used with a x-ray tube filter of the same element to clean up the background, (EX. Rh tube and filter, or Ti tube and filter).

The next best choices are among x-ray tube filters, and are largely dependant on filter thickness. Thick filters (3 or more half thicknesses*) from Ti – Zn make excellent secondary fluoresors that can rival secondary target performance for lower energy elements using less than a tenth the power. Thin filters (1 to 3 half thicknesses*) that most analyzers come equipped with are optimal when their absorption edge is below the element of interest energy. (* A half thickness is allows 50% transmission of the filters characteristic K or L x-rays)

The last choices are to use thin filters that have florescence lines above the element of interest, or neutral density filters.

High Energy (>23 kV)

Because secondary target excitation requires x-ray tube high voltages around twice the target’s absorption edge energy for optimal excitation, most commercial analyzers limited to 50-70 kV do not readily excite secondary targets above Sb. It does not help that elements immediately above Sb in energy are not common stable metals. Consequently, in this energy range, direct excitation with filters is once again optimal. The filter is chosen based on having an absorption edge below the element of interest energy. A thick W or Cu filter is often used to produce a broad high energy source spectrum for analyzing multiple heavy elements.

Detector Filters

Some hybrid EDXRF/NDXRF instruments will have detector filters particularly if they have a low resolution proportional counter detector, since filters may be necessary to separate the spectra of adjacent elements. There are two types of filter methods.

A. Hull Method - A hull filter is a single filter. It has an absorption edge immediately above the element of interest, and is used to filter x-rays from higher energy elements and the source.
B. Ross Method – The Ross filter method requires that two filters be used for an element. The first like the Hull filter is the transmitting filter. The second is an absorbing filter. The intensity is the difference in counts in the elements region of interest. The filters must be physically or electronically balance so that a zero concentration sample has zero net counts. In combination they act as a band pass filter.
C. Neutral Density or Absorbing Filters – When analyzing a higher energy element it is possible to reduce the intensity of a lower Z element by using a neutral density or absorbing filter. One example is iron in sand. Even though the source peak is far from Si, there is still a significant peak. We can use an Al detector filter to

eliminate the Si peak allowing us to increase the current and iron sensitivity by a factor of two or more.

Detector filters are usually half thickness* filters, although they can be somewhat thicker, particularly when used as an absorber. When properly applied a Hull filter can improved the signal to noise ratio by a factor of 4 or more, provided there is enough available current overhead to maintain optimal count rates. For a fixed output source like a radioisotope there is no benefit to using filters when there is not a spectral overlap problem.

The problem with filters is that some of the absorbed x-rays are converted to filter fluoresce that goes into the detector increasing the background. The fluorescence yield is lower at lower atomic numbers, so filters work best in the 0-4 keV range. Above 4 kV filter fluorescence leads to worse performance, when spectral overlap is not a problem. Since filters are usually application specific, refer to the manufacturers instructions when preparing the acquisition conditions.

Detector filters are usually not used with small area detectors such as Si(Li)'s or PIN diodes, because there usually is not enough current overhead available to take advantage of the signal to noise improvements.

High Voltage

Once the type of acquisition is set determining the optimal x-ray tube high voltage is the next step. Because of the broad energy distribution created by the x-ray generation process of an x-ray tube, the optimal high voltage is usually 1.5 to 2 times the absorption edge energy of the highest energy element in the acquisition setup. This element may be an element of interest but is more commonly the x-ray tube target, secondary target or filter material. It may also be the K absorption edge Kab, or the L absorption edge Lab depending on which lines are being excited. If optimal deadtime or count rates cannot be achieved at the 1.5x value due to current limitations of the tube or high voltage power supply, then the high voltage should be increased until they are.

A. X-ray tube target excitation - If a characteristic target line is used to excite some elements, then select a high voltage 1.5 to 2 times the its absorption edge. For example if Rh K-lines are used as the excitation source its Kab energy is 23.2 keV, and high voltage in the 35 – 45 keV range is recommended.
B. Bremstrahlung excitation – If the broad continuum is the source then the high voltage should be 1.5 to 2 times the highest energy element of interest excited in that analysis condition. For example if we are measuring the Cd K-alpha line with its 26.7 keV absorption edge, then 40-55 kV potential is recommended.
C. Secondary target excitation – With secondary targets the excitation energy should 1.5 to 2 times the secondary target elements absorption edge energy. Take Ge for example with an 11.1 keV K absorption edge, it requires 17-22 keV. Because secondary target excitation is inefficient and XRF systems current limited, operating high voltages are normally much higher. An operating voltage of 35 kV

is not unusual for a Ge target, and 20 kV is often required for a low Z target like Si.

D. Secondary filter fluorescence excitation - If the filter is above the element of interest in energy, the high voltage should be 1.5 to 2 times the absorption edge energy of the filter material. For a Ti filter with 4.5 keV Kab energy 7.5 to 9 kV is usually optimal. This method requires far less current than secondary target excitation, so the calculated voltage is usually sufficient.

E. Bremstrahlung excitation with filter – In this case the filters absorption edge is below the energy of the element of interest, and the high voltage setting is based on the highest energy element of interest as in case B above.

F. Barkla scatterer excitation - A Barkla scatterer is also treated like cases A and E, however higher voltage is usually needed to get reasonable count rates since these devices are inefficient.

Current

There is one simple rule for setting the current, measure the count rates or deadtime at the lowest current setting, usually 1 or 10 uA. The x-ray flux from the tube increases in direct proportion to the current so it is simple to extrapolate the needed current. The detector response is not quite linear, so estimate the current needed to reach the instrument manufacturers specified optimal counts, and adjust the current upward. Repeat this process until the optimal count rate range is achieved. The reason to do it this way is that detectors do not respond well to excessive count rates, and if the maximum count rate has been unknowingly exceeded the instrument will fail to make a proper measurement. Depending on the instrument design it may be difficult to tell that the maximum usable count rate has been exceeded.

If the maximum current allowed is reached and the count rate or dead time is still less than optimal, then the voltage must be increased in steps. The x-ray flux from the tube increases with nearly the square of the voltage, so increasing the voltage in smaller 2-5 kV increments is usually adequate. Some systems have a fixed current limit that will not require further adjustment, while others are power limited, so the current has to be reduced as the voltage is increased.

In general, higher current is required when operating at low voltages, less than 10 keV. Higher currents are also needed with secondary targets and polarizers. In some cases an instrument may have too high a count rate at the minimum current. In that case the high voltage must be reduced or a different filter or collimator selected.

Collimators

Collimators are another option in XRF analyzers. In EDXRF analyzers they usually have a single hole in the middle and can vary in size from 25um to several millimeters. Collimators are usually selected when small spot sizes are needed either because the sample is small or a specific point of interest on a sample is small. As mentioned above collimators are also used to reduce the x-ray intensity in some cases.

For small spot size analysis microcapillary and other types of x-ray focusing optics are available. The can overcome the problem with small collimators that often reduce the flux below the point where useful analytical work can be done. The µXRF section covers these devices in more detail.

Atmosphere

Air readily absorbs low energy x-rays, particularly for elements below argon in the periodic table. Since argon makes up 1% of the composition of air and has an absorption edge below K and Ca, air also absorbs x-rays from those elements. It is common when analyzing low Z elements to change the atmosphere by purging the chamber with helium or evacuating it entirely.

Evacuating the analysis chamber is preferred when analyzing all the low Z elements, since a vacuum does not absorb x-rays. Unfortunately, liquid samples cannot exist in a vacuum and powdered samples, if they are not covered in micro-porous they can be sucked into a vacuum system. Either one will make quite a mess if put under vacuum. Helium is used in cases where vacuum is not a good idea, or when the instrument chamber is not vacuum tight.

Hydrogen is not recommended, since it is an explosion hazard, particularly with high voltage components nearby. High purity nitrogen can help with K and Ca analysis and cost less than but keep in mind that many types of nitrogen generators actually concentrate the argon with the nitrogen. Nitrogen is not much more transparent than air to the other low Z x-rays, so it is not useful as a general-purpose purge gas, it can however also be used to flush the chamber when highly corrosive samples are being analyzed.

Purging is also not recommended when analyzing higher energy elements. Because the light element x-ray intensities are higher when the chamber is purged, there are fewer available counts for the heavy elements. When air is in the chamber more current is required to achieve optimal count rates, and the net affect is improved sensitivity for the heavier elements. The air functions as a neutral density detector filter that reduces light element intensities.

Count Time

The standard criteria for selecting count times are convenience and precision. Most operators will use measurement times from ten seconds to ten minutes. Shorter count times 10-30 seconds are used more for qualitative scanning and sorting. In the laboratory a good rule of thumb is to count for as long as it takes to prepare the sample. Why should anyone spend several minutes preparing the sample, and then rush the analysis? The concentration range of the elements of interest is also important. Major elements in percent concentrations can be analyzed in a minute or less, while minor elements at PPM concentration may need to be analyzed for 3 to 10 minutes or longer.

The other and ultimately more important criterion is precision. Unfortunately measurement precision cannot be determined until after a calibration is complete, because only then is the calibration slope known. Most operators will use longer count times than necessary at first, in order to avoid having to repeat the calibration later. Alternatively a quick two point calibration should be attempted so that the ultimate precision can be estimated, and the optimum count time selected. Refer to the calculation section.

Shaping Time or Throughput

Most mid range and high end EDXRF systems allow the operator to select from two or more shaping times. The trade off involved with shaping times is that the detector resolution is better with longer shaping times, but the throughput or count rate is limited. Longer shaping times are therefore used for qualitative and semi quantitative work, or in cases where resolution is important because of spectral overlaps.

Because higher count rates can be achieved with shorter shaping times it is often possible to get significantly better precision and lower detection limits by selecting the shortest shaping time. However, the background intensity increases as the sensitivity improves, so the net performance gain is sometimes negligible. Ultimately the difference in performance must be determined experimentally for a given application. Sometimes it is not possible to take full advantage of high throughput due to power limitations of the high voltage supply.

Many chemists prefer to use the highest resolution for their routine work and only consider using shorter shaping times when pressed to improve precision or decrease the counting time. Other analysts prefer to operate at the highest throughput looking to achieve the best possible precision, and only consider low throughput if there is a problem with spectral overlaps. The choice depends mostly on the amount of qualitative and semi-quantitative work a person does. Both approaches are OK.

Energy Range

Energy Range selection is another feature of many mid and high end EDXRF analyzers. The purpose behind this feature is to have narrower, fewer eV per channel, blocks of data within a spectrum. This is most important at low energies where the resolution is highest. In general it is necessary to have 10 or more channels across a peak in order to model the Gaussian shape of the curve in a mathematical precise way. Precise modeling of the peaks is required for many intensity extraction and peak deconvolution routines.

For example, if an instrument has a multi-channel analyzer (MCA) with 1024 channels it will have 10 eV/channel over a 0-10 keV scale and only 40 eV/channel over a 0-40 keV scale. If we then consider a typical Si(Li) detector it has approximately 100 eV FWHM resolution at Al. That means the full width of the peak is 200 eV, so over a 0-10 keV scale there will be 20 channels across the peak. If on the other hand the 0-40 keV range is chosen, there will only be 5 channels across the Al peak. The intensity extraction and peak deconvolution routines will do a much better job if the 0-10 keV energy range is used for analyzing Al. Fortunately with most Si(Li) detectors the full width of elements with peaks above 10 keV is 400 keV or more, so there are at least 10 channels across those peaks when analyzed with 1024 channel MCA over a 0-40 keV scale.

Detectors come in a wide variety of types and resolutions, and most manufacturers select an MCA that gives them a reasonable number of channels over the width of a peak. For example, a 256 or 512 channel MCA may be adequate when used with a gas filled proportional counter with 600-1000 eV resolution. Other manufacturers will use 4096, 8196 or more channels and not have to worry about having enough channels over a peak over any energy range with any resolution detector.

Qualitative Acquisition Conditions

It is impossible to come up with a single acquisition condition that excites every element well with low background in every region of interest. To overcome this problem a qualitative analytical procedure will consist of three or more different sets of acquisition conditions. It should come as no surprise that the three basic acquisition conditions will cover the same low, medium, and high energy ranges discussed previously.

A. **Low Range (<3 keV)** The best approach at low energy is to use the direct tube target fluorescence, from a Mo, Rh, Pd or Ag tube target. If the instrument does not support direct excitation, use a secondary target or scatterer in that energy range. The chamber should be purged with helium or evacuated. The voltage should be in the 4-7 kV range and the current at a few hundred microamps. By using 7 kV it is possible to excite K and Ca as well. The lowest energy range should be selected.

B. **Medium Range (3-23 keV)** The best approach in this range is to use a secondary target chosen from something between Mo and Sn in the periodic table. With a direct excitation only instrument, it is usually preferred to use the K-line fluorescence of the tube target along with a filter made of the same element, like an Rh filter over an Rh target tube. Usually between 35 and 45 kV is used. The current will be a few hundred microamps with secondary target excitation and a few tens of microamps with tube target excitation. An energy range that covers 0-25 keV should be selected

C. **High Range (>23 keV)** At the high end it is once again best to use direct excitation, but this time it is necessary to select a filter that absorbs the tube target peak. A thick W or Cu filter is ideal when using tube targets like Mo, Rh, Pd, and Ag. A combination like a Mo filter over an Rh tube works well too. The voltage is set to maximum, while the current will be in the tens of microamps. Purging is not recommended. An energy range that covers at 0-40 keV should be selected, or within 20 keV of the high voltage setting if it is greater than 60 kV. With a secondary target only machine use the highest energy target or a scatterer that works well at high energy, set the voltage to maximum, and adjust the current as needed .

In each of these acquisition conditions the longest shaping time should be selected to give the best resolution. Detector filters are generally not used in qualitative methods, and collimators should be based on sample size. If someone adds additional procedures, it is usually done by adding acquisition conditions to the medium energy range, by selecting from unused targets or filters.