

A Maximum Information Utilization Approach in X-ray Fluorescence Analysis

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Abstract

X-ray fluorescence data bases have significant contradictions, and inconsistencies. We have identified that the main source of the contradictions, after the human factors, is rooted in the signal processing approaches. We have developed signal processors to overcome many of the problems by maximizing the information available to the analyst. These non-paralyzable, fully digital signal processors have yielded improved resolution, line shape, tailing and pile up recognition. The signal processors account for and register all events, sorting them into two spectra, one spectrum for the desirable or accepted events, and one spectrum for the rejected events. The information contained in the rejected spectrum is mandatory to have control over the measurement and to make a proper accounting and allocation of the events. It has established the basis for the application of the fundamental parameter method approach.

A fundamental parameter program was also developed. The primary x-ray line shape (Lorentzian) is convoluted with a system line shape (Gaussian) and corrected for the sample material absorption, x-ray absorbers and detector efficiency. The peaks also can have, a lower and upper energy side tailing, including the physical interaction based long range functions. It also employs a peak and continuum pile up and can handle layered samples of up to five layers. The application of a fundamental parameter method demands the proper equipment characterization. We have also developed an inverse fundamental parameter method software package for equipment characterisation. The program calculates the excitation function at the sample position and the detector efficiency, supplying an internally consistent system.

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Introduction.

X-ray spectroscopy with energy dispersive detectors, (Si(Li) HPGe, PIN diodes, silicon drift detectors, SDD) is frequently used in elemental analysis. If applied with tedious calibration methods, and a deep level of understanding it can be very successful approach to elemental analysis. However, all too often the methods as applied result in frequent failures. In our view the general status of this field is that there are significant scattering in the experimental data needed in the analysis of x-ray spectra, much of which has been determined using energy dispersive x-ray spectroscopy with many of the results contradicting basic conservation laws of parity and angular momentum, and simple arithmetic [1,2]. We do not intend to detail here the significant problems, as this has been done previously [1,2], however it is important to stress that there are problems at even the basic level. We will mention a few simple examples from a field where the same techniques are used. A simple example is the experimental ionisation cross sections for particle impacts, which have large scatter, in a range of a factor of three while each individual measurement accuracy is claimed to be better than twenty per cent [3]. The large scatters of the data are handled by the analytical community by taking a statistical average, and accepting this value. We do not share this view. In our understanding of statistics and logic we argue that only one value can be good at most. Even if one measurement is good, averaging all measurements will yield an average, dominated by the bad measurements. The statistical prediction can only be that the next measurements will probably be a bad measurement.

One idea to improve EDS measurements was to characterise the detector response function. Indeed for some detector systems the line shape is so disturbed that it is mandatory. It is a general approach to measure the response function of the detector and characterise it as a main Gaussian peak and low energy tailing. Although it is customary to assume that the so-called detector tailing is exclusively a property of the Si crystal and various layers were invented to describe them, like the so called incomplete charge collection layer, dead layers etc. This approach has clearly failed as they claim that the detector tailing is much larger for the $K\beta$ radiation than for a same energy $K\alpha$ radiation [4]. This contradicts elementary logic, as a given energy x-ray alone does not have the information whether it is $K\alpha$ or $K\beta$ radiation. In an extensive study [5] we have identified what signatures the detector tailing must have if it is originating from the escape of components of the energy transfer channels. With pre-amplifier approaches applied up to now, a majority of the signal processors are not capable to reach such a level and the detector tailing is dominated by imperfections in the system.

We have identified that the main source (after the human factors) of the unexplainable results is rooted in the signal processing electronics. This identification can be easily justified and we give here some trivial examples. The best analog signal processor we have used before developing our own processor, gave an output rate that reached a maximum of seventy per cent of the indicated input rate. We always wondered where the other 30% could be. Recognizing the difficulties, several companies so called digital x-ray processors (DXP) are marketed as having the key advantage that the user can tailor the embedded processing algorithm to do exactly what is required for a particular application. It is shipped only with a demonstration software package. Using such DXPs the onus to develop the proper algorithm and prove its adequacy is on the analyst.

Although we have used very excellent systems, [6,7] we had some reservations. In our work we dared to use such systems up to the level of measuring relative intensities within a spectrum, or

set of spectra. We had reservations about attempting to make absolute measurements. After using almost all the available systems, we decided that it was necessary to develop a different signal processor. We developed a line of fully digital signal processors [8] that have yielded improved resolution, line shape, tailing and pile up recognition. The signal processors are time variant, non-paralyzable signal processors. The signal processors account for and register all events, sorting them into two spectra, one spectrum for the desirable or accepted events, and one spectrum for the rejected events. Although the information on the rejected events is always necessary, we recently realized it has additional benefits in high input rate analytical measurements (10^5 - 10^6 cps). Having all the information available, we were surprised to learn how different our conclusions were and the increase in our level of understanding that was made possible. In detector characterization, detector efficiency and spectrum evaluation methodology, the extra information explains many of the previous contradictions.

As has been known from the beginning of the application of EDS (Energy Dispersive Spectroscopy) [9,10], the observed spectra depend on the spectral distribution of the original spectra. Therefore for a proper measurement the sample spectrum has to be measured and then a standard from a large standard library with a closely similar spectrum should be measured at the same input rate, and under same noise conditions, to allow for establishing the spectral dependent correction factors. This task is alleviated in our case by the availability of the rejected spectrum and the recording of all events. The recording of all events allows for quality assurance and maximizes the information available to the analyst. It also creates the technical basis necessary for the application of the fundamental parameter analysis method. This increased level of information allows us to see the x-ray spectra differently and provide explanations for the contradictions.

The observed tailing features can also originate in the pre-amplifier and/or signal processing electronics. It remains to be seen what scientific explanations can be given to justify ignoring the contributions of the pre-amplifier and signal processor as is the usual case in most analyses. In fact it is desirable to have a signal processor that modifies the spectrum to have better resolution, better line shape, less pile up, therefore not keeping in the spectrum all the pile ups, noise and degraded events. This spectrum “massaging” is necessary for improved sensitivity, and a series of calibration procedures are necessary to calculate the number of rejected events. With our processor this is alleviated as all the rejected events are collected in a second spectrum.

Such an approach makes absolute measurement much simpler where otherwise it is a difficult issue. Relative measurements with energy dispersive spectroscopy has frequently been used to determine x-ray intensity ratios. These ratios have an unusually large scatter. Some authors use the ratios to draw conclusions on the chemical state. We were cautious in that context, and used only the energy shift to correlate with the chemical state [11].

We do not question that in some cases correlation between the intensity change and the chemical state can be found, however many difficulties may arise.

Here we present a small subset of our experience with such analyses and show how maximizing the signal processor information available to the analyst often results in improved understanding.

The structure of an x-ray spectrum measured with an energy dispersive system.

The basic structure of the expected spectrum is presented in [5], for the case of the type of pre-amplifiers frequently used nowadays. Here we present a brief summary of the spectral structure. Some of the x-ray interactions happen near the detector surface with K or L x-rays of the detector crystal material produced in the interaction escaping the system resulting in the characteristic “escape” peaks. Some of the Auger and photo-electrons that lose their energy in the crystal via small quanta of plasmons, phonons and electron-hole pairs, exit the crystal resulting in a broad energy signature with a cutoff energy.

A typical response function measured with a Si(Li) detector is given in Figure 1. However it must be stressed again and again, this is the spectrum of accepted events. We do not know anything about the number and nature of the rejected events. Therefore, caution is warranted in attempting any absolute measurements. A similar quality spectrum can nowadays be achieved with Si (PIN) and Si SDD detectors as well. In figure 2 we present two spectra, measured with a Ge detector, using a synchrotron beam excitation, and a spectrum of an ^{55}Fe source measured immediately after the synchrotron beam measurements. The ^{55}Fe source measurement was carried out at 100 counts per second of the Mn $K\alpha$ and $K\beta$ intensities. In addition to the expected pedestal structure the line shape is a perfect Gaussian for the synchrotron measurement at this energy. Therefore it seems to be a justifiable conclusion that the existing dead layers do not cause the presence of a frequently seen exponential tail at the low energy side. As we see, the ^{55}Fe spectrum does have significant low energy tailing. The possible explanation is beyond the context of this paper and will be presented in technical papers. Our detailed analysis indicates it would be premature to assign it to radiative Auger transition or some other real x-ray events. This is a very small tailing component, while many authors report much larger tailing features.

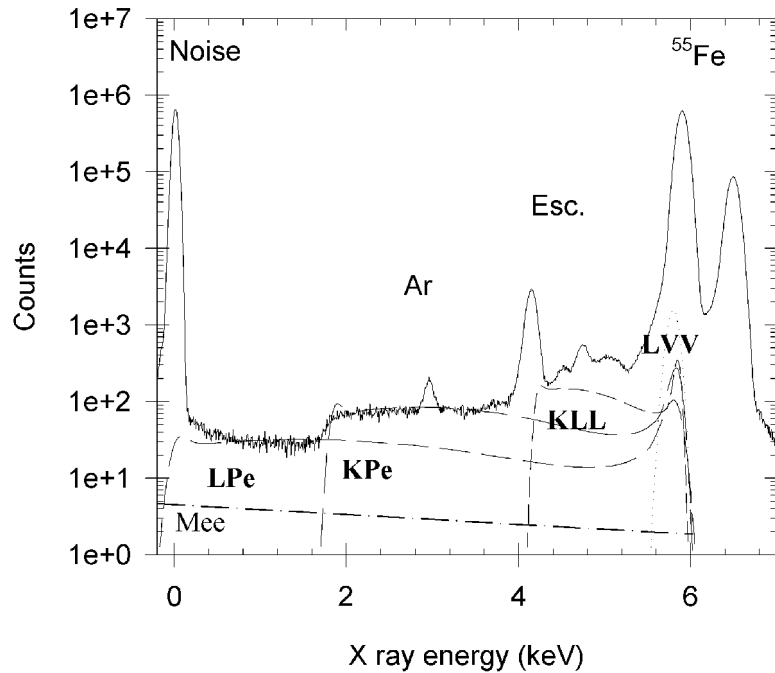


Figure 1. An ^{55}Fe source x-ray spectrum measured with a Si(Li) detector. The pedestal structure of the response function is expected from escaping energetic electrons close to the detector front contact. The escaping energetic electrons deposit energy in the Si(Li) detector, and the expected distribution is derived from measured electron spectra [5]. It is drawn under the measured x-ray spectrum, but only for the 5.9 keV $K\alpha$ x-ray component. Notation: LPe, L shells photoelectrons escaping the detector; KPe, silicon K photoelectrons escaping the detector; KLL, silicon KLL Auger electrons escaping the detector; LVV, L shell valence-valence Auger electrons escaping the detector; Mee, multiple electron escape or other processes.

We have given some examples for the components of the x-ray spectrum identified as originating in the detector in figure 1. Tailing features can also originate in the pre-amplifier and signal processing electronics.

Whether visible in the spectrum or not, noise is always present in addition to the x-rays. The signal processing can be triggered by the noise, thus making a noise peak and a noise and an x-ray event pile up presence in the spectrum. The noise and a mono-energetic x-ray event pile up shows up in the spectrum as events that stretch from a negative energy to above the mono-energetic peak energy. The event plus event pile ups stretch from the mono-energetic peak to the energy of two times the mono-energetic peak energy. Many authors consider only the double energy peak as pile up. This is frequently called the sum peak. However, the sum peak represents only a small portion of the pileup events. It is the signal processor's job to eliminate as much of these pile ups and noise events as is possible in order to create the best possible spectrum.

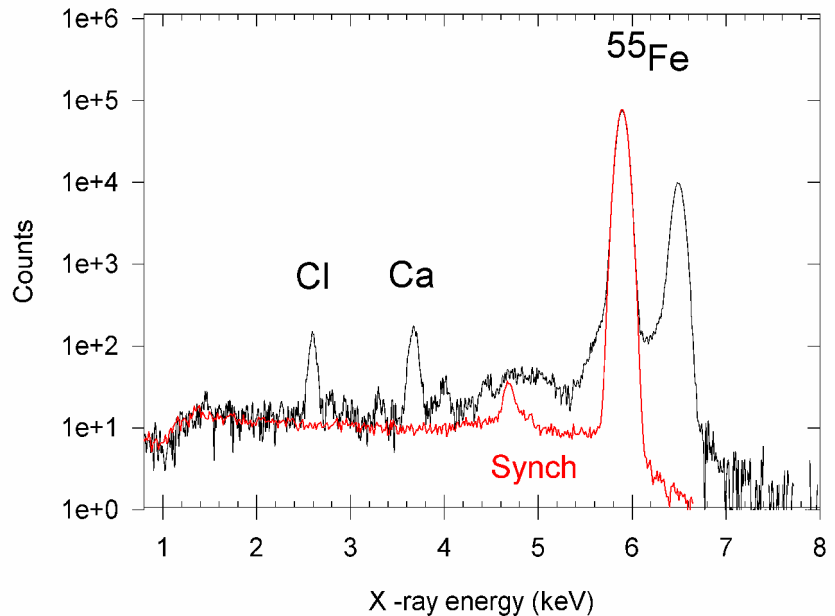


Figure 2. Response function of a HPGe detector for a monoenergetic x-ray radiation (red line) from a Synchrotron monochromatized beam, and an ^{55}Fe source (black line) measured at the same position. Because at the time of measurement there was no available signal processor presenting the rejected spectrum, full information was not available. It is not possible to determine whether the extra line shape features at the low energy side originate from real x-rays from the source or are rooted in the signal processing. Later measurements indicate that it is partly pile up in origin, as opposed to the frequently claimed dead layer and incomplete charge collection layer of the detector crystal.

In figure 3 we present an expected spectrum of a noise and a mono-energetic peak, without discrimination against the noise and pile up. This discrimination could be achieved in various ways, even a pile up discriminator could discriminate against some part of the noise and noise discrimination against the pile up. How the signal processor creates the x-ray spectrum and how the noise filters act, on what basis and how the discriminations are established, generally is not available, as companies treat it as proprietary information. It is always up to the analyst to figure out how to handle the detection system. As noise and electronic disturbances are highly variable in time, amplitude and rate, it is always a risk to assume that it is the same for both a sample and calibration standard that are measured at different times. One method to minimise this effect has been to run standards and samples in consecutive pairs and hope that the measuring system has not changed significantly in that short time. The signal processor's job is to improve the spectrum, by eliminating the pile up and noisy events. However, it must be known how many and what types of events have been eliminated. Some

information may be derived from the input rate indicator, which is mandatory for all processors. However, the input rate indicator alone as a single number cannot give the necessary information. One issue is that it is useful only if the input rate is constant. If it is varying, it cannot be used reliably for a correction. Beyond this it does not provide information about the exact nature of the rejected event, ie. whether the rejected event was a noise event, a degraded event, a noise plus event pile up, or a pile up of two noises etc. The noise is identified as pulses, and their rate can be and in general is much higher than the real event rate. It is advantageous in some cases not to process them in order to reduce the dead time. One way to achieve this is to use a signal recognition level setting high enough that the noise will not trigger the signal processing. It can be identified from the spectrum, as the spectrum does not start at zero energy.

Another way, in a non digital signal processing approach, is to raise the lower level discrimination on the ADC unit. Since the rate of the noise peak is not in the spectrum, the derivation of the true pile up rate is not possible, as no information on the noise peak rate is available. Also, the event and noise pile up, and the noisy signal and the good signal may not be processed in the same way, or with the same signal recognition probability. Furthermore the pile up is not only the sum peak, but also the continuous pile up plateau as well, therefore to determine the pile up rate exclusively from the sum peak is not possible. To our surprise we have found that for increasing input rates the pre-amplifier rise time is increasing in several systems. This makes a simple correction impossible. As a conclusion, conventional systems do not give the full information, not even the necessary information needed for accurate spectroscopy especially at increasing input rates.

If the amplitude of the noise is above the signal recognition level, the noise will be processed. This will be seen as an event, although in reality we have measured some parameters of the noise, e.g., amplitude mean or some combinations of other moments, depending on the nature of the signal processor. The dead time of the signal processor should also account for such cases. The pile up rejection also has to eliminate the noise pile up, and a decision has to be made whether it was an event or noise pile up. If it was recognized as a noise pile up, then it should be counted only as a single event, instead of a double event. With our signal processors this burden is eased as the rejected

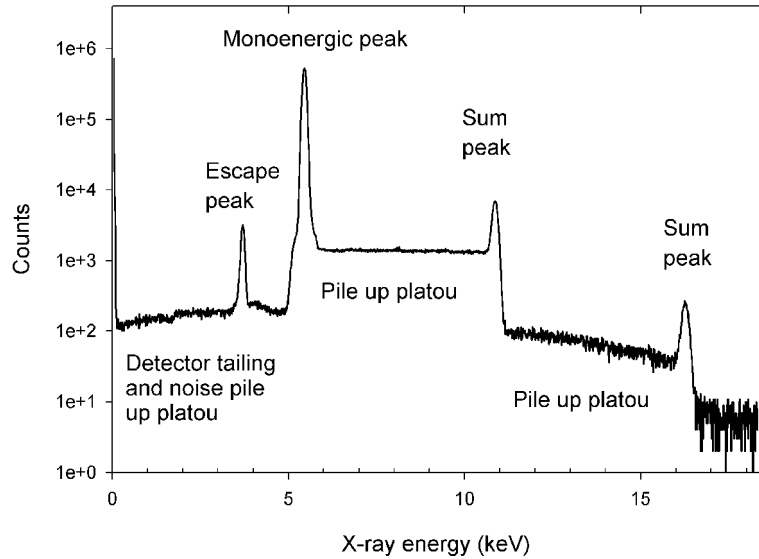


Figure 3. The expected spectrum of a Silicon material based detector Si(Li), Si PIN diode, or Silicon Drift Detector, when all events are processed without noise and pile up discrimination. The first part could be very much higher if the measurement is made in a noisy environment, or the analyst is not careful to eliminate ground loops and follow other standard processes in noise reduction.

spectrum directly gives the information.

The noise-triggered plateau can be very high for some systems, while moderate for other systems. The low plateau alone is not a sufficient test for the goodness of the system, as it is possible to reduce the low energy tailing with stringent criteria, that will reject not only the plateau events but the low energy noisy x-ray events. It is obviously necessary to know what fractions of the low energy x-rays are rejected.

We have developed a fully digital signal processor, which differs in concept from all other processors. It's main significance is that all the events are presented, and stored. The signal processor in general can create sixteen spectra from the pre-amplifier signal. This allows complete accountings of all the events. For the analyst with less demand for the full details of the x-ray spectra it offers two spectra, one for the accepted and one for the rejected events. This approach allows quality assurance at the signal processor level. Quality assurance approaches have to be kept at every phase including sample preparation, equipment constancy, spectra evaluation. However the significant improvement we offer is quality assurance at the signal processing level.

Quality assurance capable signal processing approach

We have developed a series of digital signal processors. They have achieved excellent resolution [12], line shape, high throughput rate and background reduction [13]. These are very significant in their own right, but beyond these it processes and keeps all events in the way that the necessary information is available on a user-friendly way for the analyst. The signal processor front end electronics digitizes the pre-amplifier signal at the earliest possible time and all the signal processing is then made with digital signal processing techniques, using a digital signal processor chip.

The most frequently used models are the CSX2 with two discriminators, rise time and pile up. It is intended for short shaping time applications and as a consequence has a high throughput rate capability. What throughput rate means we will elaborate in a later section. The CSX3 has three discriminators, rise time pulse shape and noise. To have statistical meaning it is necessary to use longer shaping times, ranging from 1-150 microseconds, depending on the application. The CSX4 has four discriminators: rise time, pulse shape, noise and pile up. As we have mentioned previously, a specific discriminator can identify many unwanted disturbances of the pre-amplifier signal for an event. A noise on the signal trail of an event can be found by the noise discriminator and by the pulse shape discriminator, as it can have a different pulse shape. But the pile up discriminator can also eliminate it as a pile up. Similarly an electronic disturbance could cause a change in the pre-amplifier signal that will not meet the criteria of any of the discriminators. The greatest reduction in observable pile up in the accepted spectrum can be achieved by the CSX4 model. The processors have proven to be able to process very low energy x-rays, even 250 eV x-rays. They have various pulse shaping options, including cusp shaping, which could give the best resolution. All parameters are set via the user interface program, and no parameter is set via any hardware potentiometer or switch. It counts the input rate, the preamplifier reset rate, it allows proper handling of the so-called bucket effect, and has a user friendly easy setup. All the measurements can be made in setup mode where in addition to the two spectra of accepted and rejected events, the spectra rejected by each individual discriminator are presented to the analyst. For the CSX4 model it yields six spectra. These spectra are generated

on line. The events are inspected, and sorted into accepted or rejected spectra. If it is rejected then the spectrum of the rejecting discriminator is also incremented.

A typical spectrum of a Si(Li) detector is presented in figure 4, measured with the CSX4 signal processor in setup mode. A Cr $K\alpha_1$ x-ray is selected by an x-ray monochromator, from a Cr anode x-ray tube. Because the detector is aging and can change its performance, the electronic noise and disturbances are different at the analyst site than in the factory, therefore the optimum setup is not necessarily valid in the analyst's laboratory. If it is noisier, then more events will be rejected than the optimum,

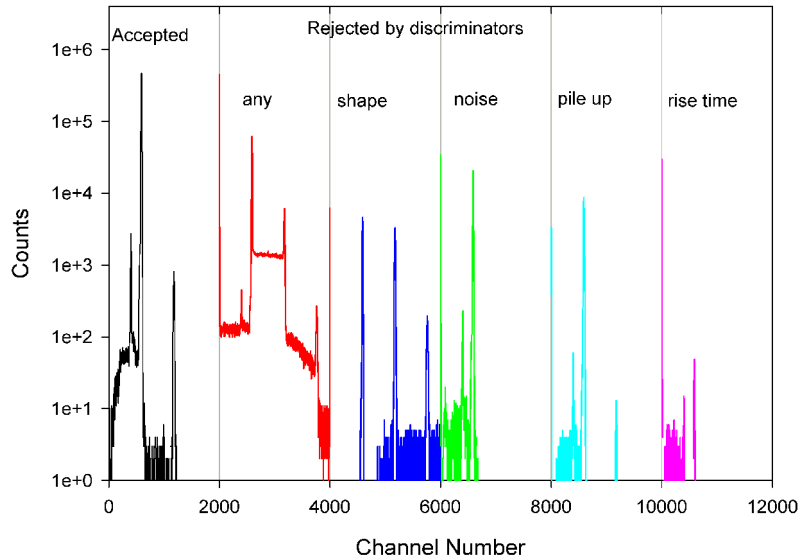


Figure 4. A Cr $K\alpha_1$ spectrum measured with a Si(Li) detector and CSX4 quality assurance capable fully digital signal processor in setup mode, from a Cr anode x-ray monochromator. In setup mode beside the accepted and rejected spectra, the spectra rejected by each discriminator are presented. The rejected spectra by each individual discriminator allow fine tuning their values, and a user friendly fast optimisation of the signal processor for the specific application.

and the electronic efficiency should be established by the analyst. If the rejection criteria are set to be very weak, then the line shape, pile up and resolution will not be optimum. In the additional four spectra the analyst immediately sees the effect of each discriminator on the measurement, and can choose an optimum value for the discriminator, via the user interface program. To explain the details we present the first two spectra, the accepted and rejected spectra in figure 5.

The accepted spectrum has the Cr $K\alpha_1$ spectrum in first and in second orders, the escape peak at the lower energy part of the peak, and the so called low energy tailing. It is worth noting in such a case the sum peak is overlapping with the second order reflection peak. This would make the even the standard incomplete pile up correction impossible without the availability of the second (rejected) spectrum. The rejected spectrum is generally never seen by the analyst, therefore it needs some explanation. The first part of the spectrum from zero to 5.41 keV is the noise and event pile up. From 5.41 keV to 10.82 keV are the event and event pile up, which had to be counted twice for the input rate, as they correspond to two rejected events. From 10.82 keV to 16.2 keV we have the triple event pile up. This area has to be counted thrice for the number of input events, and this procedure should continue for higher pile ups. The last channel is the overflow channel, where all events with energy larger than the selected energy range are placed. The x-ray energy range of the spectrum is selected by the gain settings.

Some analysts might not be familiar with the fact that the pile up is not only the sum peak, therefore we elaborate the explanation further. For time variant signal processors the signal

recognizer will start the signal shaping procedure, and a second signal could arrive at a later time but within the signal shaping time interval. Therefore the second signal will be measured for a shorter time interval and will contribute with a partial energy. If both signals are real events, then the generated pile up event will be an upper energy plateau. If a signal originating from an E1 energy photon arrives first and within the time period dedicated to an event processing a second signal, originating from a photon of E2 energy arrives, and there is not any pile up recognition, the pile up will stretch from E1 to E1+E2 energy [9]. This is what we see in the 5.41 keV to 10.82 keV energy range in

our case as rejected by the pile up discriminator. It must be emphasized, that for the sum peak the two events come very close in time, usually within the rise time of the pre-amplifier. Completely different methods are used to identify and eliminate the pile up for those situations when the two events arrive within the pre-amplifier rise time, or when the second event arrives at a later time. Therefore it is not possible to determine the overall pile up rate from the sum peak alone without more knowledge or very specific assumptions, and it is not surprising that this has never been told to the analyst. We can talk about it as we can offer a solution, via the rejected spectrum.

The first event can also be a false trigger by a noise. If the noise signal (E1) has arrived first and initiates the signal processing, and the photon event signal (E2) arrives within the signal processing

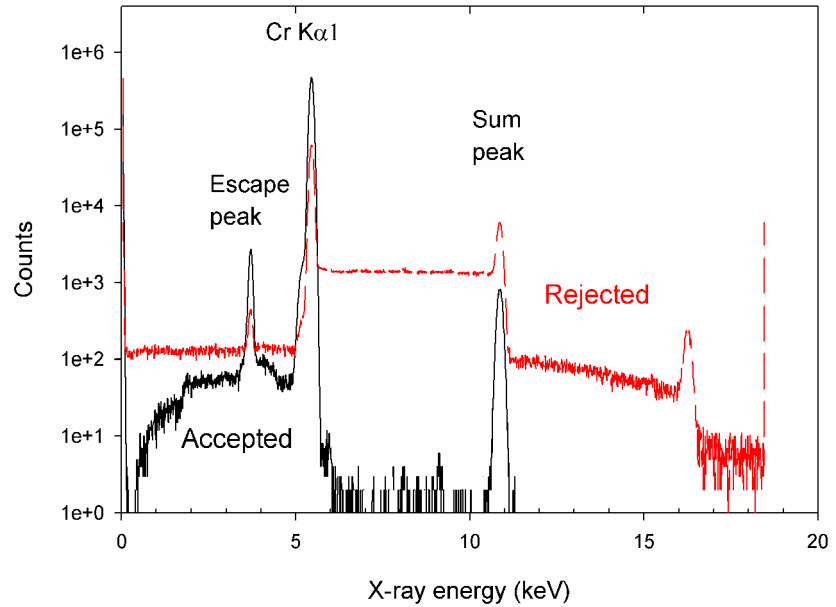


Figure 5. The accepted (black line) and rejected (red line) spectra for monochromatised Cr K α 1 x-rays measured with a Si(Li) detector and CSX4 signal processor. The first two spectra of figure 4 is drawn onto the same scale. All features are justifiable in both the spectra and should be present.

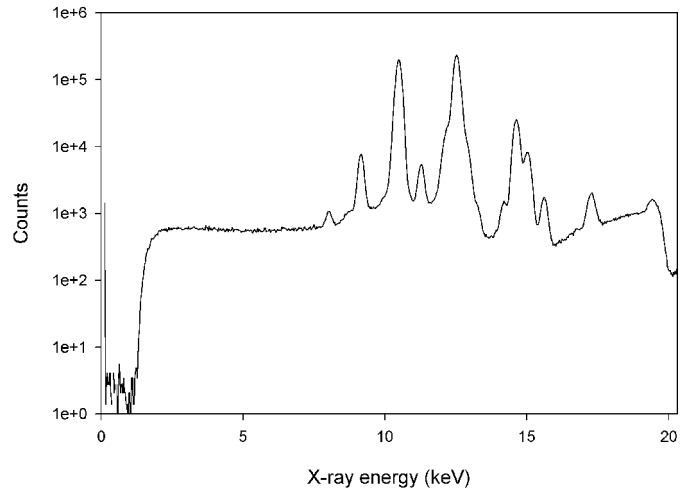


Figure 6. An x-ray spectrum of a thick lead (Pb) sample measured with an industrial XRF equipment with a Silicon Drift Detector (SDD) and CSX2 signal processor. The X-ray tube has a Mo pre-filter and the scattered primary excitation spectra is seen above the Pb spectrum. The measurement was made at 260 000 counts per second input rate of the SDD detector.

period, then E1 is at zero energy, and the pile up will be seen as a low energy plateau up to E2. However, the noise signal is not necessarily similar to the photon signal, and its recognition by the inspection circuitry may not be the same as for two real events piling up. Therefore, in general the pileup plateau from the noise peak to the photon peak will be different in size than the plateau from the photon peak to its sum peak. It is generally assumed that the noise probability distribution is such that it yields a zero mean value, for a long measuring time. The peaking time interval, however samples only for a short duration of time and the mean of the noise during this interval can have a negative or a positive value. In addition, the shape of the plateau varies with the shaping methods. For triangle shaping it is expected to be a flat plateau. For semi-Gaussian shaping the end of the pile up plateau will be raised and for cusp shaping, which could give the best resolution, it is a decaying curve, starting at the peak.

The impact of pile up on the overall shape of the spectrum strongly depends on the signal processing electronics, and in many cases the detailed knowledge of the signal processor is necessary to evaluate the spectrum. With our processors this is not necessary, as the rejected events' spectrum is always available.

Time distribution

Many of the corrections used in XRF analysis (dead time, pile up etc.) depend on the assumption of random occurrence of the x-rays in time. If the x-rays arrive in "bursts" system analysis can be difficult. If this is in question then one of the spectra our processors can present is the time or arrival distribution of consecutive events. In figure 6 we present a lead (Pb) spectrum of a thick lead sample, measured on an industrial XRF equipment with 260,000 cps input rate, with an SDD detector. The sample was excited by an x-ray tube with W anode and Mo pre-filter. At such a rate the rejected spectrum allows the proper calculation of the input rate and to derive quantitative data. In figure 7 we present the time distribution of the events. We see that for this x-ray tube, the distribution has two components, with different decay constants. Whether it is the property of this specific x-ray tube or it is a general concept in x-ray tube operation, is beyond the scope of this paper. From the analyst's point of view it is sufficient that it is verified that the time distribution is sufficiently random.

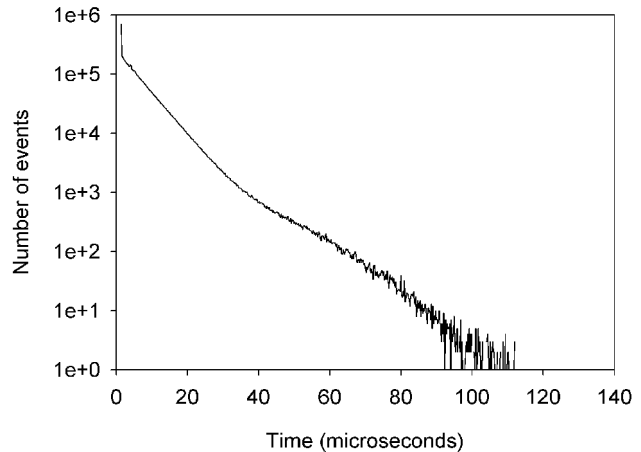


Figure 7. The time distribution histogram spectrum of the lead sample measurement, presented in figure 6. The CSX signal processor family generate sixteen spectra, which allow full information approach to the measurements. One of these spectra is the arrival time interval value between consecutive x-ray events. This allows one to check whether the x-ray source has a different time structure than the random distribution.

Some myths and fallacies

We have not been specific in this paper on many frequently mentioned properties of signal processing including detector resolution and the Fano factor, input rates and throughput rates, detector efficiency and line shapes, and pileups.

The first issue is the detector resolution, as it is used in many analytic softwares. We have already mentioned many contradictions in ref [1,2]. Here we repeat the first myth. In this paper we will not elaborate whether Fano factor could exist at all for Si and Ge based detectors, merely call the attention to the fact that there are two significant different definitions for it as discussed in [1].

There is a problem with the input rate indicator for many systems. Does this number include noise events, does it properly separate pile up into two or more events in the case of photon + photon events and only single events in the case of noise + photon pile up? In general in many systems the input rate indicator is only an inaccurate approximation of the photon input rate. In our system the input rate indicator can be corrected by observations of the exact nature of the rejected spectrum.

We are puzzled by what the throughput rate means. If we look at the data sheets of many detectors, we can see that at 20 microseconds peaking time, or in some cases shaping time, they have one million counts per second throughput rate. The output rate is highest for equidistant signals in time. If the peaking time is 20 microseconds the maximum output rate could be around 50,000. This is far short of the claimed one million. The explanation is that some in the industry use the throughput rate as that input rate that still produces some output signal or their system remains unparalyzed. The usefulness of such a convention is not clear to us. Our signal processor is a time variant non paralyzable processor. A more useful measure is the output rate vs the input rate but even this is made complicated by the discriminator settings and the amount of pile up in the accepted spectrum.

For instance with our present hardware and a total processing time of about 1 microsecond we have achieved output rates as high as 600 kcps. However, the input rates to achieve these results were several million cps and much of the output rate was contained in the sum peaks. At these high input rates the pre-amplifier rise time became much longer and the pile up peaks grew disproportionately larger than at lower input rates with smaller rise times. At these rates the pile up correction is so large that an accurate pile up representation must be employed, which can only be accomplished by analyzing the rejected spectrum.

With our signal processor it is up to the interest of the analyst to decide what part of the spectrum is sorted into the desirable, accepted, best quality first spectrum, or the rejected, undesirable, not perfect second spectrum. If very good quality is in demand, the shaping time should be optimized for the detector and noise environment. It will determine the highest optimum input rate. Although, with many detectors, higher input rates can be managed without deteriorating the quality of the main peaks a larger fraction will be rejected and sorted into the second spectrum as well as a larger fraction of the accepted spectrum events will be shifted to the sum peak regions. Both of these features imply larger corrections in the analytical results, that are readily available from the rejected spectrum in our system.

Detector efficiency and detector line shape is exclusively identified in the literature as a property of the detector. As we have described previously, in our experience we have found that although the detector is a very significant element in the detection chain, it is only one element. It also depends on the pre-amplifier, the signal processor, and the final element, the human factor, who is responsible for choosing the proper noise environment, ground loop elimination, and signal

processor settings as well as the proper identification of the spectral features. All these elements are important in determining the detector efficiency and line shape. In our approach more information is available, and quality control is possible, making the human element less critical.

Pile up: It is customary in the literature to consider only the sum peak as pile-up. We have elaborated above that the sum peak is only a small subset of the total pile-up. The pile up in general is not a peak, but has a continuous part that may also include pile up with noise. Both of these features are often seen, depending on the quality of the pile up recognition in the system, but go unrecognized or not remarked upon in spectra. The sum peak is not sufficient for the determination of the pile up rate. The pile up recognition could also depend on the noise environment, especially for lower energy x-rays. These features are readily seen in the rejected spectrum.

The signal processor's impact on the $K\beta/K\alpha$ ratio and Compton scattered peaks

Very few reports are available, where different signal processors are used for the same measurements and comparative data are presented. We have made such a comparison in our developments and reported in [1,13]. Many signal processors have control parameters. Any study would need to involve the optimization of these parameters, and establishing how strongly the signal processor performance is affected by the settings. We have reported that the settings effect very significantly the response function for the analog processor [5], that was of very high quality and considered to be the industry standard. We have demonstrated [13] that using the same detector using different signal processors, the signal processors generated spectra with very different tailing features. In a recent paper we have reported that the tailing components have significant contribution from unrecognized pile ups. [1].

Recently a paper was published where the intensities of two X-ray lines were measured with two different detectors [14]. This gives a possibility of a direct comparison. There are two X-ray lines in a 1 keV neighborhood around 5 keV and 6 keV. The 5 keV X-ray line has the same intensity, but the 6 keV line is smaller in one of the detectors. Since both detector crystals are sufficiently thick to guarantee 100% efficiency, more than a factor of two deviation between the two peaks demands an explanation. Furthermore in other spectra the difference in the bromine line intensity makes the case even more confusing. These issues further point out the necessity for proper quality control measures.

We consider very significant the report of Harada and Sakurai [15], therefore we discuss it in detail, as it presents common issues. They use the same detector but two different electronics to process the Gd K x-ray spectrum. They have observed that for one set of electronics the $K\beta_2/(K\beta_1 + K\beta_2)$ ratio increases as a function of the count rate. In their spectrum, the $K\alpha_1$ peak has an associated upper energy tail or peak. In our understanding it is a pile up peak. It could either be part of the plateau pile up that we have shown previously but that has not been entirely eliminated on the upper side of the peak or pile up with an unreported noise peak. In this case the pile up recognition was poor, and the pile up was significant even at this very low count rate suggesting pile up with a large noise peak. Therefore a similar shadow peak is expected for the $K\beta_1$. In this case it will be underneath the $K\beta_2$ peak. In their evaluation the peak model did not allow for such a possibility, therefore they counted this $K\beta_1$ peak pile up into the $K\beta_2$ peak. The outcome of this is a changing intensity ratio, as a function of input rate. Since they have made a careful study, they have recognized it. However, if they had not recognized it and had used the technique to measure different chemical

compounds, the input rate could have been very different for the compounds, resulting in a changing ratio of the $K\beta$ components, with a result that would imitate some chemical state dependence. Their other processor did not show such dependence, although this alone would not give the necessary security.

If the setting of the pile up discrimination and noise discrimination is available to the analyst, then varying it may allow one to identify whether it was an event and event or event and noise pile up. The dependence of the $K\beta_2/(K\beta_1+K\beta_2)$ ratio resembles a linear function, that implies that it is an event and noise pile up. It needs a very fine tuning of the noise and pile up recognition, as if it set too stringent it will eliminate the peaks as well and skew the relative intensities. intensity ratio, as a function of input rate. Since they have made a careful study, they have recognized

Measuring with our processor, such a situation can easily be monitored at all times. In figure 8 and 9 we present two measurements, where two spectra of Cu $K\alpha_1$ is collected from the x-ray monochromator, using a Cu anode. For the measurement shown in figure 8 the pile up discriminator was not set sufficiently high and we have some upper energy pile up. However, in our case the rejected spectrum is also available and we immediately see in the rejected spectrum, that there is a strong dip, which indicates that at this energy the pile up was not rejected. If we use a much stronger pile up recognition setting, we will eliminate some of the peak area as well, which is presented in figure 9. In this case the, pile up rejection was too strong, but we can know by exactly how much. If it is in the same ratio in all the measurements, we can warrant that the results are valid. We can have correct relative intensities and have to use a correction factor for the absolute intensities. The proper option would be to simply optimize the discriminators using values between the two presented cases.

The spectra also suggest that the signal processor pile up and noise recognition capability and discrimination value settings can also impact on the measurement of $K\alpha$ and $K\beta$ ratio. The two cases presented in figure 8 and 9 indicate that the pile up in the near vicinity of the upper energy side of the peak can be very different, depending on the noise condition. The background underneath the $K\beta$ peak could be very different, depending on the noise, the pile up recognition capability and the settings, and cause a $K\beta/K\alpha$ ratio change if the spectrum evaluation procedure is not sufficiently

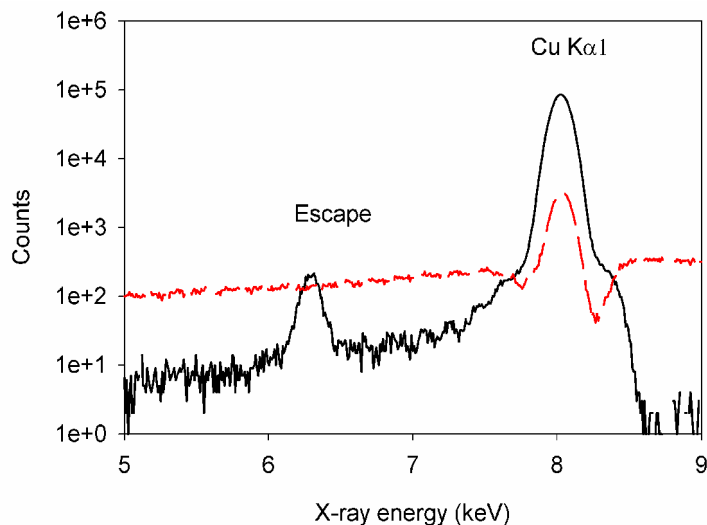


Figure 8. A Cu $K\alpha_1$ spectrum measured with a Si(Li) detector and CSX4 quality assurance capable fully digital signal processor in quality assurance mode, from a Cu anode x-ray monochromator. The dip in the rejected event spectrum (red line) at the same position where an excess structure is visible in the accepted spectrum (black line) immediately indicates that the higher energy shoulder peak on the upper energy side is unrejected pile up, and the setup parameters were not optimum for this measurement. The lower energy side also has a signal processing origin. A proper setting presented in figure 9 allows a comparison.

sophisticated. It also clearly indicates that someone could conclude not considering the upper energy pile up tail that the $K\beta$ and $K\alpha$ have different tailing. In reality the pile up part of the $K\alpha$ is counted into the $K\beta$ lower energy tailing. With the availability of the rejected spectrum, the adequacy of the signal processor settings can always be verified.

Further noticeable is the Compton peak shape between the two processors in the report of Harada and Sakurai [15]. The Compton peak is used in many applications to identify and quantify the bulk component of the sample in trace element analysis. Since the Compton peak does not have a well characterized sharp peak shape and as it also strongly depends on the scattering geometry, it is important that it is not contaminated by pile up. If someone assumes that pile up is only a sum peak then they would not consider such a possibility.

We have made comparative measurements with another third party signal processor, which is a DXP (digital X-ray processor) and the comparative spectra are presented in figure 10. We were looking for traces of lead in a copper sample. For this measurement the DXP was optimized by an expert using this DXP. As we see in the figure, the CSX2 processor gives a spectrum, as expected, and the trace lead (Pb) is very visible and quantifiable. The DXP spectra however, has a broad peak, resembling a Compton peak, overlapping the Pb L x-ray region of the spectrum. In reality the pile up was not removed properly. The continuous pileup between the Cu and Cu sum peaks was removed at both ends but not in the middle. This is very common with other processors including analog processors, and frequently seen as so called ghost peaks.

Closing this chapter we repeat that the maximum information approach is not only necessary for quality control but it also makes measurements easier, simpler, the evaluation procedure faster and more reliable.

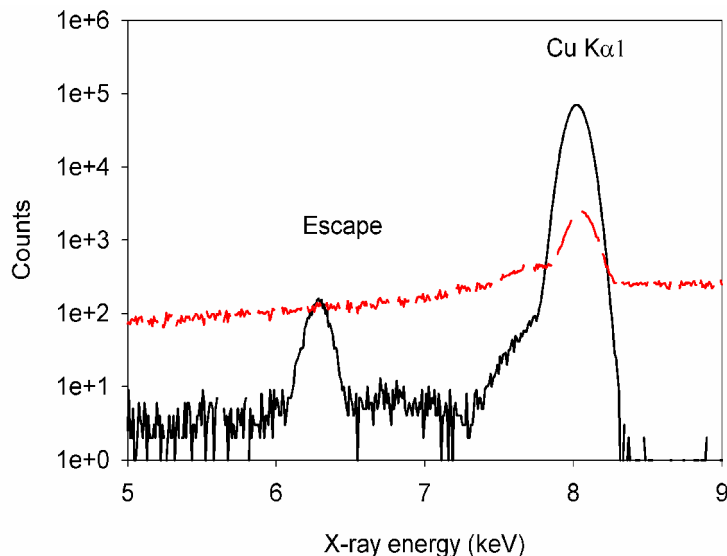


Figure 9. The measurement presented in figure 8 is repeated at an optimum discriminator setting. The pile up peak has been eliminated, and the spectrum also has much lower energy tailing. The excessive low energy tailing visible at Cu $K\alpha 1$ line has been frequently observed by many authors, and various models have explained its origin with the assumption of various detector processes. Using the CSX Detector Analyser it was possible to identify its origin for this Si(Li) detector as a problem of the pre-amplifier. With another Si(Li) detector from the same manufacturer we could measure a spectrum with no exponential tail component. Although this detector was not optimum either, as the application of the CSX detector analyser identified that the second detector has a crystal surface structure problem. An exponential tail free spectrum is presented in figure 2.

Demand on the Industrial Analyst

As we have indicated above there are large discrepancies in academic based measurements using energy dispersive detectors. Thus a more robust system is required for industrial applications of energy dispersive XRF as the method can readily slip out of the realm of straight forward measurements. This is especially true for measurements that must be accomplished with reasonable resolution in a short period of time (seconds or minutes) for trace elements of low concentration and that thus require relatively high counting rates, eg. several tens of thousands or higher cps values.

One of the methods of XRF is using the so called working curve method for calibration and determination of the elemental concentrations. However, when high energy x-rays, eg. Cd K x-rays, or high energy scattered primary filter radiation are involved in the

analysis of low Z materials such as plastics, soils or biological materials the working curve method takes on the additional dimension of sample thickness (areal density) as the assumption of an infinitely thick target generally no longer applies. For example, to satisfy the infinitely thick criteria for Cd K x-rays in polyethylene (PE) the sample must be several centimetres thick and that is rarely the case.

One way around this is to scale the results to the scattered radiation observed in the spectrum and a more recent trend is to use the scattered radiation with the fundamental parameter method approach. This can be applied to the scattered Bremsstrahlung continuum or as is more usually done to the characteristic lines of the anode or primary filter. Information from the Compton and Rayleigh scattered radiation can be used to help determine the thickness (areal density) and average Z of the target material. The intensities of both are proportional to the number of atoms of the sample in the beams path while the ratio of the Compton to Rayleigh scattering can give information on the average Z of the target. However, if the calculated thickness and density are incorrect, then the thick target correction will be skewed and will generate improper concentrations.

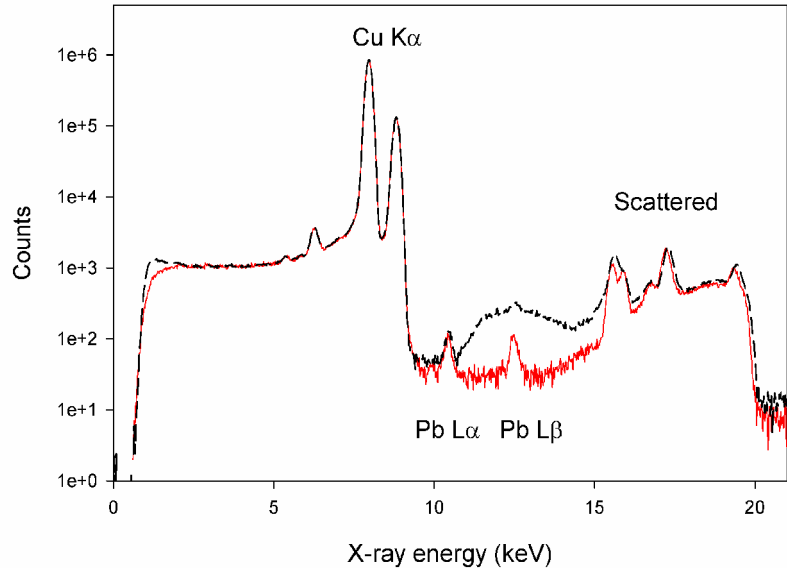


Figure 10. Two x-ray spectra measured in parallel with two processors, splitting the pre-amplifier signal and feeding it to the two signal processors. The spectrum presented with the red line was measured with the CSX2 processor. The spectrum with black line was measured with a third party DXP optimized by experts. A thick Cu slab was tested for Pb contamination. The DXP (black line) spectrum has an excessive feature between the Cu K β line and the sum and scattered peaks. It has some resemblance to scattered x-rays, and we present it to demonstrate that the frequently observed ghost peaks and scattered structures could have signal processing origin. If maximum information, or quality assurance signal processing approach is applied, the rejected spectrum would have a correlated structure in the opposite direction. It allows quick and reliable spectrum processing, as the two spectra can be screened and correlated automatically.

Problems with this approach can arise in several ways. One is if there are traces of the primary filter material in the sample that will contribute a component that will directly overlay the Rayleigh scattered peaks making it impossible to distinguish between the scattered and fluorescence response. A second problem is that generally the Compton response appears in the spectrum as a broadened Gaussian peak with a large long range low energy tail with the exact features depending on the setup and geometry of the measuring system. The presence of either a Bremstrahlung or pile up continuum or low concentrations of sample elements with x-rays that overlap this region can make a proper determination of the Compton area difficult.

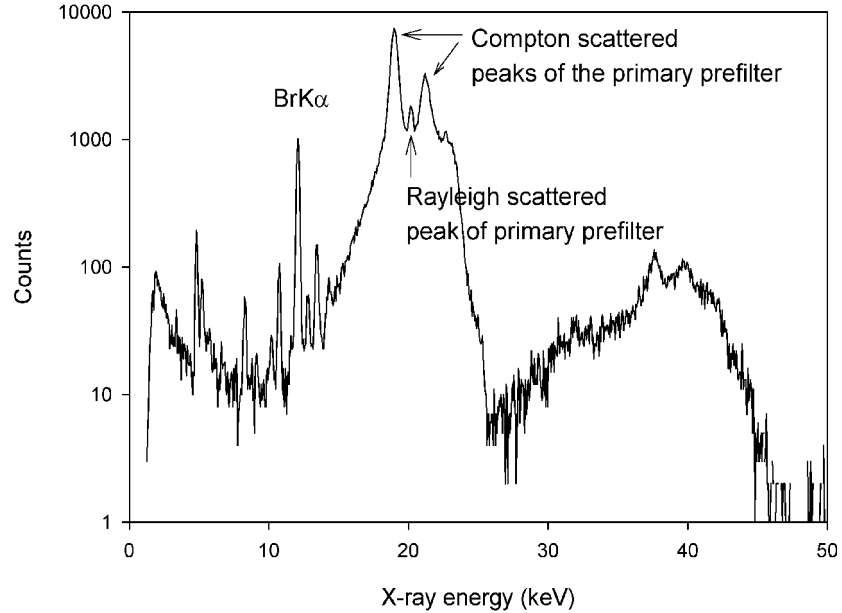


Figure 11. An XRF spectrum of a thick polyethylene sample measured on an industrial XRF system for a 30 seconds measuring time. It has a good resolution and a small visible pile up in the 36-45 keV range.

One issue that the analyst needs to control is that of pile up. The first problem the analyst faces in analysing different samples with different base and trace elements, with different thicknesses, and with different low Z components, where the x-ray yield from the sample may be dominated by the Compton scattering of the primary radiation, is to select the x-ray tube voltage and current to be optimum for the unknown sample. In principle this could only be done iteratively, or by using a very conservative approach where the current is kept low to guarantee a low count loss condition. This would be optimum for the measurement accuracy, but would demand a long measuring time, as opposed to a higher current with its higher count rate and shorter measurement time. If tube currents are set for thin samples and a thicker sample is then analyzed, the count rate can grow significantly and the pile up exponentially. If the processor does not properly remove the pile up while still properly accounting for it then measurements will not be accurate.

A typical spectrum of a PE sample measured with a CSX2 signal processor and an SDD detector on an industrial XRF analyser is presented in figure 11. This XRF analyser is a different product than the one mentioned in the previous chapters. In this case the X-ray tube current was optimized on a moderately thin target and at a later time a thicker PE sample was measured and this is what is shown in figure 11. If we look at the spectrum it has a good resolution, and a very small sum peak on top of the scattered Bremsstrahlung spectrum. The small pile up peaks do not tell the entire pile up story. In figure 12 we show the same spectrum overlaid with the rejected spectrum which is essentially pile up. If the processor does not correctly remove this pile up, for example see figure 10, it may appear as a larger Bremstrahlung or Compton continuum depending on exactly where it occurs in the spectrum.

Processors capable of counting at high input rates do not have significant dead time, therefore a small change in the measurement dead time might not indicate a potential problem. Suspicion might only be aroused if there were significant changes in the input and output rate indicators. However, because the input rate indicator also counts the potential noise events, it could also be assumed that the noise has increased as the noise environment, particularly in industrial settings, can be quite variable. Therefore there is no clear evidence of a potential problem. The rejected spectrum, however indicates immediately that there is a potential problem, increasing security for the industrial analyst, and increasing the reliability of the analysis.

With a quality assurance capable processor the rejected spectrum is available, and together with the accepted spectrum, the analyst can see immediately that there is a huge pile up continuum, which rightfully is rejected by the CSX2 signal processor. This can be used as a correction factor for count loss, and could also immediately indicate that a measurement with a lower count rate is warranted. The advantage here beyond the capability of proper accounting of count loss due to pile up is that there is less of a burden placed on the industrial analyst to warrant that the measurement was made within the limit of the capability of the XRF method as well as within the optimal setup range.

The XRF program

We have produced a commercially available X-ray fluorescence (XRF) elemental analysis program to take advantage of the extra information that is made available by the Cambridge Scientific line of digital signal processors with the accepted and rejected spectrum. It is a fundamental parameter based code that uses a calibration or correction factor to allow for errors in the system description or the theoretical data base. Presently it comes in two forms - an interactive form and a "black box" file based calculation engine that is used by OEM's who wish to supply their own interface.

The methods applied are those that have been successfully used in several PIXE codes, including the GUPIX code [16,17] to perform quantitative analysis of PIXE spectra for decades.

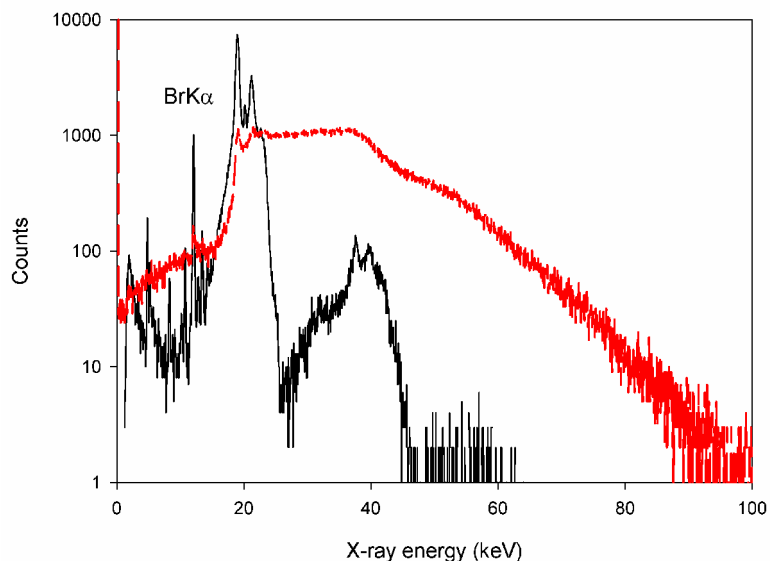


Figure 12. The same spectrum as in figure 11, but the rejected spectrum is also presented (red line). It readily presents that the count rate was very high, resulting in a large number of pile ups, indicating that smaller beam current would be optimal. It is remarkable that the accepted spectrum line shape remained unchanged and the same superior quality at this very high input rate.

Some of the X-ray data bases used are the same with the particle induced ionization cross-sections of GUPIX replaced with photon induced ionization cross sections. Details of the theoretical data base used and the operation of the code will be provided in a later article, however, a brief description will be given below.

The Engine Code:

The calculation engine code uses input files that contain the X-ray data base information, the spectrum and system description information to estimate element peak areas that in turn are used to estimate element concentrations with the information output to various files for use by the analyst.

In general energy dispersive XRF elemental analysis spectra are comprised of many x-ray peaks superposed on a background of scattered radiation. The signature of each element in the spectrum is one or more series of peaks corresponding to the K, L and or M X-ray lines and their associated escape peaks. The peak shapes are modelled as Voigtians which result from the convolution of the natural Lorentzian X-ray line shape with the Gaussian instrumental line shape. In addition, parameterized low and high energy tailing can be associated with each peak. Since every element produces a multi line signature in the spectrum and each peak if analyzed separately would require several fit parameters to describe it; the X-ray data base is used along with the system description to reduce each series (K,L,M) of lines to a single parameter that is used along with two parameters that convert peak energy to channel position as well as two more parameters that are used to estimate the Gaussian width vs. energy.

In moderate to high count rate measurements unrecognized event pile ups will produce a pile up signature in the spectrum. In a well-tuned system this may appear as a series of sum peaks that can be modelled as single element with relative line intensities proportional to the component intensities. If a large background continuum is present, it is often preferable to model the pile up as a convolution of the spectrum with itself superposed back onto the spectrum. The effect of this operation is to produce a series of sum peaks as well as a series of smaller continuum components offset by the energy of each peak. If pile up with noise is present in the spectrum, the users' options are currently limited to modelling the noise pile up as high and low energy tailing or hoping that the noise pile up is broad enough to be removed by the background treatment.

The spectral background will generally depend on the excitation source used. In the case of excitation by a mono-energetic beam the background will consist of the scattered radiation that will show up in the spectrum as a coherent (Rayleigh) and incoherent (Compton) scatter peaks. The Rayleigh peaks will be simple peaks indicative of the detector response function at the given energy while the Compton complex is usually a much broader lower energy peak with amplitude, shape and position relative to the Rayleigh peak dependent on the peak energy, setup geometry and the physical composition of the target.

If the excitation source is a radioactive isotope then the excitation spectrum will be comprised of a series of lines generated by the source each of which can produce a scattered Rayleigh and Compton presence in the spectrum. If the source is a more broadly based source such as the Bremsstrahlung continuum from an X-ray tube, the scattered source signature in the spectrum will also be broadly based. If anode or primary filter lines are also present in the spectrum, they will have the characteristic Rayleigh and Compton shapes.

As at least some components of the background are generally slowly varying or much broader than the peaks a digital filter is applied to the spectrum [18,19] and it is the digitally filtered spectrum

that is fit with a digitally filtered model spectrum using a modified form of the nonlinear least squares algorithm of Marquardt [20].

Once the code has determined the peak areas for each element these peak areas are converted to elemental concentration using knowledge of the excitation source, system setup and geometry, the sample composition and areal density, and intervening X-ray absorbers as well as the detector via the following formula:

$$C(Z) = PA(Z) / [H(Z) * Y(Z,E) * Nph(E) * SA * Abs(Z) * Deff(Z)], \quad (1)$$

where $C(Z)$ is the concentration of element Z ; $PA(Z)$ the elemental peak area adjusted for loss due to tailing, pile up and dead time; $Y(Z,E)$ is the theoretical yield of element Z per excitation photon of energy E for the given sample matrix and thickness and specified geometry expressed as X-rays per steradian per exciting photons of energy E per ppm of concentration; $Nph(E)$ is the number of excitation photons of energy E that struck the sample; SA is the solid angle the detector makes with respect to sample in steradians; $Abs(Z)$ is the transmission through any X-ray absorbers between the sample and the detector; $Deff(Z)$ is the detector efficiency of X-rays of element Z (both physical and electronic); and $H(Z)$ is the calibration or correction value that is used to correct the above relation for inaccuracies in the data base or any of the components listed above. For very well characterized systems $H(Z)$ will be approximately one and independent of Z but in general H will be Z (and even type K,L,M) dependent. The above equation can be extended to multi-line or polychromatic X-ray sources by summing the $Y(Z,E) * Nph(E)$ terms over the list of E values.

There are many details buried in this general description but suffice it to say that accurate analysis depends on an accurate description of each component in the above formula. This is especially true in high count rate measurements where the peak area corrections for pile up and dead time can become large and information obtained from the rejected spectrum is critical.

System calibration program

When an X-ray tube is used as the excitation source in XRF analysis, it is critical to know the number of and the energy distribution of the photons striking the sample. This can become especially complicated when primary filters are used to modify the excitation source. In addition, knowledge about the detector crystal thickness and the $H(Z)$ correction factors are also essential for elemental analyses.

In order to facilitate the analysis process we have developed a code that in effect inverts the above formula for determining the elemental concentrations to find the best estimate of the excitation function ($Nph(E)$), detector crystal thickness (part of $Deff(Z)$) and $H(Z)$ values using known concentration values, sample and setup information.

The primary tube excitation function is assumed to be a Bremstrahlung spectrum modified by primary filters that also add their own characteristic lines to the excitation spectrum.

The procedure is to collect spectra from one or more standards and use the XRF code to determine peak areas of elements of known concentration. Then the system calibration program will fit the excitation parameters and detector crystal thickness to get the best match between theoretical yields and peak areas with the discrepancy at any given value becoming the $H(Z)$ value. The code produces the excitation and H value files that will be used by the XRF code in sample analyses.

Conclusions

Reliable analyses of energy dispersive X-ray spectra is greatly enhanced by the information made available by the rejected spectrum provided by the Cambridge Scientific line of digital signal processors.

The rejected spectrum used in conjunction with the normal accepted spectrum provides a quality assurance factor in the analysis that is simply not available without its use. One can immediately see if pile up has been uniformly rejected, whether or not the measurement was extremely noisy, if noise pile up is an issue or if there is an energy dependence to the rejected spectral events. In addition it helps provide a more reliable input rate as well as pile up corrections and dead time calculations. This is useful in all classes of measurements but is critically important for high or variable count rate measurements or high noise environments where spectral corrections become large. A fundamental parameter energy dispersive XRF code package has been developed to take advantage of this additional information. Combined with the equipment characterization package, the equipment characterization and electronics optimization can be verified at any measurement, in an efficient way.

Adding this quality control at the signal processor level should go a long way to rationalizing future measurements and provides an additional opportunity to clear up some of the inconsistencies in past measurements.

It is hoped that in the future maximizing the information available to the analyst will ensure higher quality measurements. Quality assurance approaches have to be kept at every phase including sample preparation, equipment constancy and spectrum evaluation. However the significant improvement we offer is quality assurance at the signal processing level.

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