

MULTI-SPECTRAL XRF COUNTING: SQUEEZE TWICE AS MUCH INFORMATION FROM YOUR DETECTOR

W.K. Warburton,¹ P. Grudberg,¹ J. Harris,¹ G. Roach² and B. Cross³

¹XIA LLC, Newark, CA USA; ²CSIRO Minerals, Sydney, NSW Australia

³Crossroads Scientific, El Granada, CA USA.

ABSTRACT

Counting small peaks on large backgrounds in XRF applications is a process limited by the statistics of estimating both the counts and the background in the peak region. Improving energy resolution ΔE helps by increasing peak/background ratio and providing a more accurate estimate of the background but also reduces counting statistics due to increased pileup losses. Time variant filtering techniques have not been useful because their detector response functions vary with counting rate, precluding the accurate use of standards. Here we present a new time variant approach that takes a small set of shaping filters, applies the longest one to each detector output pulse, and places the result into a spectrum specific to that filter. By not commingling the filters' results, we produce multiple spectra whose detector response functions do not depend upon input count rate and can thus be used with standards-based analyses. Both theoretical and experimental measurements show that this approach allows the filters' information to be fully preserved, so that an optimized multi-spectral spectrometer can achieve the same signal to noise ratio in approximately half the counting time required by an optimized single filter spectrometer.

INTRODUCTION

A common requirement in XRF measurements is to determine the spectral line intensity I_L of a weak peak sitting on a large background. Figure 1 indicates the situation schematically. The

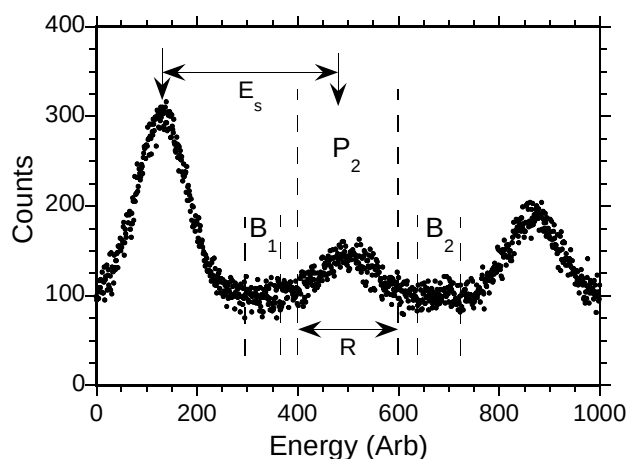


Figure 1: Weak spectral line bounded by neighboring lines.

desired value I_L is the sum of the counts in a region of interest (ROI) P_2 that includes the peak minus an estimate B of the background obtained from regions B_1 and B_2 , whose extent is typically limited by neighboring peaks that are separated from the peak of interest by values E_s . In difficult cases, where E_s is less than R , deconvolution methods will be required. R 's value scales with the spectrometer's energy resolution ΔE . For example, for R to include 95% of the peak area, its value would be $1.76 \Delta E$.

In general the statistical accuracy of I_L can be improved both by collecting more counts, making both the ROI area and background estimates more accurate, and by reducing ΔE ,

which both reduces the number of background counts in ROI P_2 and increases the regions B_1 and B_2 over which B can be measured. Thus, while counting time to a required signal to noise ratio (SNR) can be reduced by increasing output counting rate (OCR) and reducing ΔE , these two variables cannot be adjusted independently for a given detector because increasing the OCR requires decreasing the spectrometer's peaking time τ_p , which increases ΔE . OCR is related to the input count rate ICR by the dead time formula $OCR = ICR \exp(-\tau_d ICR)$ ⁽¹⁾, where $\tau_d = 2(\tau_p + \tau_g)$ in a digital spectrometer, τ_g being a trapezoidal filter's flat top time. Figure 2 shows data from an 80 mm² HPGe detector, where counts were collected for 10 sec at the point of maximum

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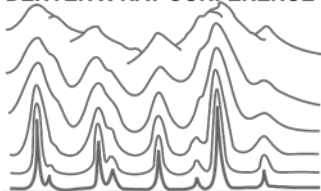
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OCR for four τ_p values. This particular 60% Fe, 39% Ni and 1% Co sample and was developed to mimic a cobalt stainless steel alloy.

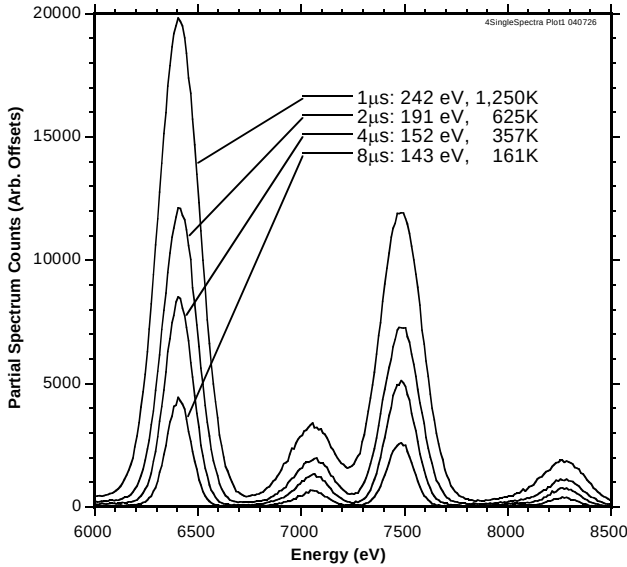


Figure 2: Maximum ICR spectra at 4 peaking times, 10 sec.

QUALITY FACTOR Q_f

The question Figure 2 raises is: “Which spectrum detects the Co best?” We can answer this question by calculating a Quality Factor Q_f , which is $1/t_m$, the time required to collect enough counts to detect a peak of interest to a desired SNR. The system with the largest Q_f is then the best. Using the terms shown in Figure 1, defining K as the desired SNR for the peak area minus the background, s as the line intensity as a fraction of counts in the full spectrum and b as the background as the fraction of counts in the full spectrum per eV, we derive that:

$$Q_f = \frac{s^2 OCR}{b K^2 R} \left(1 + \frac{R}{2(E_s - R)} \right)^{-1}, \quad (1)$$

where b is found by measuring over the background regions B_1 and B_2 whose widths are $(E_s - R)$. The maximum of Eqn. 1 versus τ_p is then found by using the maximum value $OCR_{max} = 1/(e \tau_d) = 1/2e(\tau_p + \tau_g)$, from the throughput equation. The resolution, $R = 1.76 \Delta E$ can be written as $R = (R_0 + R_1/\tau_p + R_2\tau_p)^{0.5}$, where R_0 , R_1 , and R_2 are constants of the detector. The detector producing the data in Figure 2, for example, had values $R_0 = 39,558$, $R_1 = 122,121$, and $R_2 = 184.4$. Since the factor $s^2/(b K^2)$ is a constant, we will compute only the τ_p dependent part of Q_f , namely $Q_{fp} = Q_f b K^2/s^2$. Table 1 shows results for E_s equal to 350 eV, 450 eV, 550 eV, and 650 eV to demonstrate the sensitivity of the results on the widths of regions B_1 and B_2 . As the optimum (bold) results in the four columns show, there is no unique “best” peaking time for all situations. Rather, τ_p should be selected depending upon the spectral environment of the peak of interest.

Table 1: Quality factors for five time invariant filters versus E_s .

τ_p (μs)	OCR_{max} (kcps)	R (eV)	Q_{fp} for E_s as shown			
			350 eV	450 eV	550eV	650 eV
0.75	175	476	NA	NA	87	156
1.0	141	425	NA	35	123	171
2.0	80	336	18	96	133	155
4.0	43	281	50	83	100	110
8.0	22	234	39	54	62	67

TIME VARIANT PULSE PROCESSING

The above results are for time invariant filtering. Over the years, various time variant schemes have sought to increase the information extracted from the detector’s signal stream to improve ΔE at a given OCR by making better use of the available data.⁽²⁾ Figure 3 demonstrates this approach with some output signal captured from the detector of Figure 2 and Table 1. The pulses in this signal are Poisson distributed, with their intervals indicated in microseconds. Whereas, in time invariant processing, each pulse is analyzed using only 1 peaking time’s data on each side (or rejected as piled up if one of the intervals is too small), in time variant filtering data from full intervals are used to establish the signal levels before and after each pulse. Thus the first pulse may be processed using 5.7 μs of leading data and 1.0 μs of trailing data; the

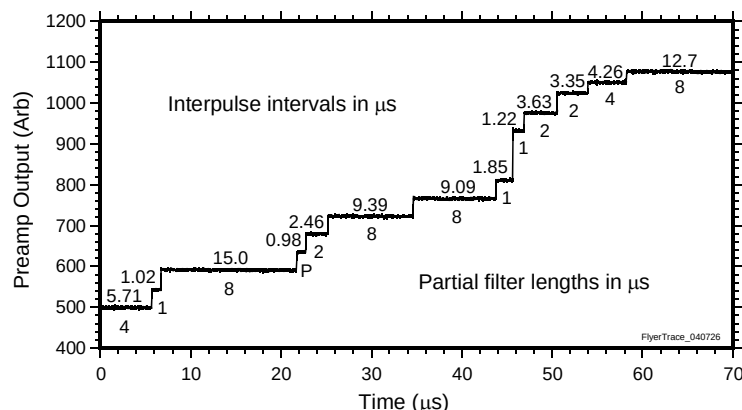


Figure 3: Preamplifier signal with indicated inter-pulse intervals.

the distribution of inter-pulse intervals varies with ICR and because the relationship between τ_p and ΔE is non-linear, as per the equation for R used above. Thus “standard” spectra taken at one ICR cannot reliably be used to fit data taken at a different ICR. As a result, time invariant methods have remained the mainstay of modern pulse processing in accurate XRF applications.

THE MULTI-SPECTRAL (M-S) APPROACH ⁽³⁾

In the M-S approach we retain most of the advantages of time variant filtering while avoiding the variation of ΔE with ICR that is its major disadvantage. Our approach is the following. First, we create a small set of M time invariant filters. Second, we process each pulse using the filter that produces the best energy resolution without pileup. Third, we place the result into a spectrum unique to the selected filter. This is the critical step: we do not co-mingle results from filters with different energy resolutions – each spectrum is produced by a single time invariant filter.

In one convenient implementation, we use 16 filters F_{ij} , each the difference of two running sums A_i and A_j separated by a constant gap time τ_g and denoted by $[i,j]$. The length of sum A_m is 2^m times the length of the shortest sum A_1 , which is set by the worst resolution ΔE that can be tolerated in the $[1,1]$ filter. If we set A_1 to $1\mu s$, for example, we can process the first pulse in Figure 3 using a $[4,1]$ -filter) and the second pulse using a $[1,8]$ -filter, while the third pulse is piled up because one of its intervals is less than $1\mu s$. All results from $[4,1]$ -filtering are placed into a $[4,1]$ -spectrum, all $[1,8]$ results into a $[1,8]$ spectrum, and so forth. Because ΔE of an $[I,J]$ -filter and a $[J,I]$ filter are the same, they can share a spectrum, thereby producing 10 unique spectra: $[1,1]$, $[1,2]$, $[1,4]$, $[1,8]$, $[2,2]$, $[2,4]$, $[2,8]$, $[4,4]$, $[4,8]$, and $[8,8]$. Since each spectrum's data come from a time invariant filter, its energy resolution will not vary with count rate. The number of counts in each spectra will obviously vary with ICR, with more counts going into the $[1,1]$ -spectrum at high rates and more into the $[8,8]$ -spectrum at low rates, but the shapes of the individual spectra will not vary. Thus a set of standard spectra taken at one ICR can be used to analyze unknowns measured at other ICRs. By separating these filter sums by a flat-top width we can also preserve the benefits of trapezoidal filtering in the M-S approach.

Figure 4 shows a M-S set of the above 10 spectra from the same spectrometer used to produce Figure 2. Because the base $[1,1]$ -filter corresponds to a $1\mu s$ trapezoidal filter, the total number of counts in all the spectra after 10 seconds of data collection is the same as in Figure 2's $1\mu s$ spectrum, 1,250 kcts. While, in Figure 2, they are all in one spectrum with a FWHM of 242 eV, in Figure 4 they are distributed into 10 spectra with FWHM values ranging from 242 to 143 eV. In fact, only 4% of the counts are now in the 242 eV $[1,1]$ spectrum! 12% are in the 218 eV $[1,2]$ spectrum, 12% in the 205 eV $[1,4]$ spectrum, and so on. Surprisingly, the largest number of

second pulse uses $1.0\mu s$ and $15.0\mu s$ of data; and so forth. In different flavors of time variant processing the data may be equally or unequally weighted (e.g. with cusp filtering), depending upon their separation from the pulse.

While these methods optimally extract available information, they have not been popular for spectroscopic analysis because their resolution functions vary with ICR. This is both because

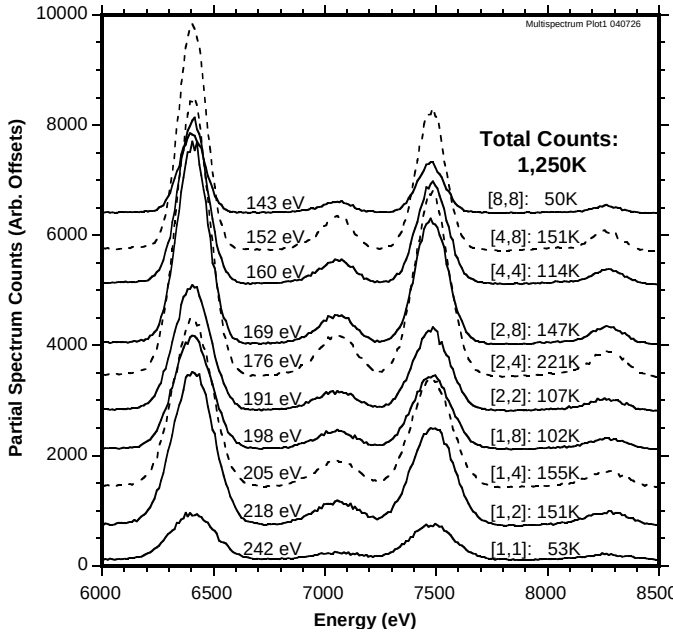


Figure 4: Data at 240 kcps ICR sorted into 10 multi-spectra.

10 case's improvement using 16 filters, allowing simplified designs (for example with analog filters) for special purposes or applications where reduced data processing is important.

M-S QUALITY FACTORS

Extending the single spectrum approach to Q_f in Eqn. 1 shows that Q_f in the M-S case is just the sum of the Q_f 's of the individual $[i,j]$ spectra and the peaking time dependent term Q_{fp} becomes:

$$Q_{fp} = \sum_{i,j} \frac{OCR_{i,j}}{R_{i,j}} \left(1 + \frac{R_{i,j}}{2(E_s - R_{i,j})} \right)^{-1} \quad (2)$$

Eqn. 2 shows explicitly that the additional spectra at higher energy resolutions help in two ways: by decreasing both the resolution $R_{k,l}$ and the ratio $R_{k,l}/(E_s - R_{k,l})$, in the denominator. The first contribution reflects the reduced background component in the ROI integral, the second reflects the increased accuracy with which the background between the peak and its neighbor may be determined. Then, given a value of E_s , a M-S spectrometer is optimized as follows. First, by extension from the single filter case, an expression is found for the spectrometer's energy resolution as a function of the lengths of the sums in its various filters:

$$R(\tau_i, \tau_j) = [R_0 + R_1 / 2\tau_i + R_1 / 2\tau_j + R_2\tau_i / 2 + R_2\tau_j / 2]^{0.5}. \quad (3)$$

Second, using Poisson statistics, we develop an expression for the filter's output counting rate, realizing that it will process pulses only up to inter-pulse separations that cannot be handled by the next longest set of running sums. Thus we find:

$$OCR(\tau_i, \tau_j) = ICR e^{-2\tau_j ICR} \left(e^{-\tau_i ICR} - e^{-\tau_{i+1} ICR} \right) \left(e^{-\tau_j ICR} - e^{-\tau_{j+1} ICR} \right). \quad (4)$$

For a particular value of E_s we can then find an optimum filter in three iterative steps. First, for a pair of values of τ_1 and ICR, we compute Q_p as a sum of Q_{fp} over all 16 filters. Second, we vary ICR to find the maximum Q_p for that τ_1 value. Third, we adjust τ_1 to find the global maximum of Q_p over both τ_1 and ICR. Table 2 shows the results of optimizing a 16-filter (i.e. four partial filters) M-S spectrometer to the same four E_s cases shown in Table 1. Three important features are immediately obvious. First, Q_f values are improved by factors of nearly 2. Second, the M-S

counts, 18%, is in the 176 eV [2,4] spectrum. The 143 eV [8,8] and 242 eV [1,1] spectra actually have the same number of counts. The average ΔE of the set is 184 eV, a substantial improvement over 242 eV. To match this with a single, peaking time filter would require a τ_p of about 2.25 μs , which would then take over twice as long to collect the same number of counts. We therefore expect the Q_f of the M-S approach to be about twice that of the best single spectrum system. In general, employing M starting filters, will then generate $M' = (M+1)M/2$ unique spectra. Modeling shows that values of M between 4 and 6 are adequate to achieve most of the benefits of the M-S method (M' between 10 and 21). Even using just symmetric four filters (i.e. [1,1], [2,2], [3,3] and [4,4]) produces 75% of the $M' =$

first peaking time is significantly shorter than the single filter optimum because the method has longer peaking times available to achieve better energy resolution when possible. Third, the method achieves substantially higher throughputs than a single filter, because its shorter peaking times can capture pulses that would be piled up in the single filter. These latter two factors explain much of the M-S Q_f improvement, the remainder coming from the use of separate spectra, so that low resolution data do not "pollute" high resolution spectra, losing information.

Table 2: Quality factors using multi-spectral filters, showing gains over single filters.

E_s (eV)	Min τ_p (μ s)	OCR _{max} (kcps)	Q_{fp}	Q_{fp} Gain (Multi/Single)
350	1.75	74.4	89	1.78
450	0.90	131	178	1.85
550	0.55	187	257	1.93
650	0.40	229	322	1.88

A FIRST EXPERIMENTAL TEST

Theory and model calculations are all very well, but any new approach needs to be carefully tested experimentally before it is adopted. Here we begin by reporting some initial results with a realistic test case based on a $Fe_{60}Co_1Ni_{39}$ alloy, which is somewhat difficult because the strong $Fe-K_\beta$ and $Ni-K_\alpha$ lines partially overlap the weak $Co-K_\alpha$ and $Co-K_\beta$ lines, respectively. We then captured (one at a time) the 10 M-S spectra shown in Fig. 4 and analyzed them using commercial XRF software developed by one of us (BC). In this early work, each M-S spectrum was analyzed independently, the results for each element were summed, and their error counts added in quadrature. Table 3 compares the results of this analysis to those for the 4 single τ_p curves shown in Fig. 2. We stress that all spectra were taken for the same 10 second counting time. It may readily be seen that, while there is only modest improvement in the estimates of the majority Fe and Ni peaks, the accuracy for the Co measurement has improved from the best single τ_p error of 2.58% to 1.89%, a factor of 0.732, which compares well to the 0.707 expected from a pure factor of 2 improvement in counting efficiency. Since actual improvements in Q_f are more typically 1.85, however, (per Table 2), and errors scale as $1/\sqrt{Q_f}$, we therefore compare $1/\sqrt{1.85} = 0.735$ to the experimental value 0.732. It thus appears that the method works precisely as expected. This result therefore supports the view that we can expect the Multi-Spectral method to reduce counting times by factors of nearly two to achieve comparable SNR.

Table 3: Measured concentrations of Fe, Co and Ni in a $Fe_{60}Co_1Ni_{39}$ alloy.

τ_p (μ s)	Fe Total (cts)	Fe Error (cts)	Fe Error (%)	Co Total (cts)	Co Error (cts)	Co Error (%)	Ni Total (cts)	Ni Error (cts)	Ni Error (%)
8	65607	512	0.78%	1691	82	4.86%	41331	406	0.98%
4	149607	772	0.52%	3614	120	3.32%	91986	605	0.66%
2	259134	1078	0.42%	4321	111	2.58%	159664	840	0.53%
1	520992	1508	0.29%	5553	156	2.81%	316482	1186	0.37%
M-S	531919	1459	0.27%	11163	211	1.89%	351932	1187	0.34%

EXTRACTING EMISSION LINE INTENSITIES

In general, the M-S spectra should not be fit independently but simultaneously, since there is physically only a single set of L sample emission line intensities α_i that will be collected in all spectra simultaneously. Thus, if, in spectrum m, the unit area detector resolution function R_{mij} describes the intensity in channel j due to a unit strength emission line located in channel i, and there are OC_m total counts, then the expected counts S_{mj} in channel j will be given by:

$$S_{mj} = OC_m \sum_{i=1}^L \alpha_i R_{mij} , \quad (5)$$

Here the important points are that the same set of coefficients $\{\alpha_i, i=1,L\}$ describes the line intensities in all M spectra and that, because the filters are time invariant, the resolution functions R_{mij} are count rate invariant. To find the α values by least squares fitting, for example, we would define an error function F^M and set its partial derivatives with respect to the α 's to zero:

$$F^M = \sum_{m=1}^{10} \sum_{y_{mj}>0} \left(\frac{y_{mj} - S_{mj}}{\sigma_{mj}} \right)^2 = \sum_{m=1}^{10} \sum_{y_{mj}>0} \left(y_{mj} - OC_m \sum_{i=1}^L \alpha_i R_{mij} \right)^2 \sigma_{mj}^{-2} , \quad (6)$$

giving

$$\frac{\partial F^M}{\partial \alpha_k} = 0 = \sum_{m=1}^{10} \sum_{y_{mj}>0} \left(y_{mj} - OC_m \sum_{i=1}^L \alpha_i R_{mij} \right) \frac{OC_m R_{mkj}}{\sigma_{mj}^2} , \quad (7)$$

where the weighting terms σ_{mj} are Poisson error estimates of the counts y_{mj} . Rearranging, we get L equations in the L unknown α_i values

$$\sum_{i=1}^L \alpha_i \left(\sum_{m=1}^{10} OC_m^2 \sum_{y_{mj}>0} (R_{mkj} R_{mij} \sigma_{mj}^{-2}) \right) = \sum_{m=1}^{10} OC_m \sum_{y_{mj}>0} (R_{mkj} y_{mj} \sigma_{mj}^{-2}) \quad (8)$$

and, assuming there are enough counts per channel to allow approximating σ_{mj}^2 by y_{mj} , find:

$$\sum_{i=1}^L \alpha_i \left(\sum_{m=1}^{10} OC_m^2 \sum_{y_{mj}>0} (R_{mkj} R_{mij} y_{mj}^{-1}) \right) = \sum_{m=1}^{10} OC_m \sum_{y_{mj}>0} R_{mkj} \quad (9)$$

This exercise shows that the major change in adapting an existing algorithm for processing a single spectrum (no sums over m) to processing M-S spectra is that sums over the single spectrum are summed again over the M-S spectra in setting up the linear equations to solve for the α_i values representing the unknown emission line strengths. Adapting to M-S spectral processing should therefore be a relatively straightforward operation in most cases.

CONCLUSIONS

We have introduced a time variant, Multi-Spectral signal processing method for use in XRF spectrometers. In M-S filtering, a small set of time invariant filters sort results into a set of output spectra whose resolution functions do not vary with input counting rate, each signal pulse being processed by the optimum member of the set. We have shown that the method works in a simple system and also shown that, when detecting small peaks on large backgrounds, it essentially halves the counting time required to achieve a specified signal to noise ratio. Further, adapting existing data processing algorithms to the new method should be readily achievable.

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