IMPROVING TRACE ELEMENT DETECTION IN EDXRF BY REDUCING PILEUP ARTIFACTS

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ABSTRACT

Pileup artifacts appear in energy-dispersive X-ray spectra at high count rates when X-rays arrive at the detector with time separations less than the resolving time of the pulse processor. These artifacts often appear as extra peaks in the spectrum and can mask (or be mistaken for) weak peaks of trace elements. In X-ray fluorescence (XRF) the background is very small compared to charged-particle excitation techniques. This makes it ideal for trace element quantification but also makes it particularly susceptible to pileup artifacts.

Recent improvements in high-speed digital discrimination have improved rejection of near-simultaneous events leading to pile-up at very high count rates. This new capability also improves the predictability of pileup rejection, which is essential for accurate modeling and reliable removal of the inevitable events that get past the pileup inspection. We have successfully reduced pileup artifacts by a combination of hardware changes and software correction. We will report the results for a variety of spectra to demonstrate their effectiveness.

To evaluate the effect of pileup artifacts on trace element determination, we will show spectra and quantitative analysis for trace amounts of Zr in a Ni alloy and for trace levels of Cu in glasses, with and without the new pileup rejection methods.

INTRODUCTION

The phenomenon of pileup appears when the random arrival times of X-rays cause two X-ray absorption events to appear together in time, thus distorting the energy measured by energy dispersive detectors. The time overlap need only be within the resolving time of the pulse processor to produce distortion. Typically the distortion takes the form of an event being attributed to an energy higher than either of the two actual photon energies and producing a single count in the spectrum at the higher energy rather than two counts at the correct energies. When the overlap is nearly complete, the resultant energy is near the sum of the two photon energies. This produces the well-known sum peaks in the measured spectrum. Note that pileup events can occur anywhere between the energy of the larger-energy photon and the sum of the two energies. However, the details of the pulse processor and the extent of hardware pileup rejection will dramatically affect the actual measured pileup spectrum. With modern digital pulse processing and its efficient pileup rejection, the main pileup artifacts appear near the sum energies.
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The sum peaks that appear in the measured spectrum as a result of pileup events can distort, mask, or be confused for trace element peaks. Software pileup correction algorithms have been developed that can quantitatively reduce the pileup artifacts in a spectrum given the measurement conditions [1]. In this work, we have undertaken a study to measure the ability of such correction algorithms to reduce the distortion of trace element peaks due to pileup from major element peaks. Such distortion can affect the quantitative analysis of trace element content. We attempt to correct the trace element peaks and then perform the analysis on the corrected spectra. A comparison of the measured trace element concentration with and without pileup correction gives a quantitative measure of the effectiveness of the correction algorithm in these particular situations. The two novel aspects of this work are the careful matching between the hardware pileup rejection and the pileup probability used in the software correction, and the use of quantitative analysis of trace elements to evaluate the effectiveness of the pileup rejection and correction methods.

Measurements were made on two nickel alloys that contain about 0.1% Zr. The Zr Kα peak is coincident with the Ni Kα + Ni Kβ sum peak, as shown in Figure 1. The blowup of the Zr region in Figure 2 clearly shows the distortion of the Zr peak at 40% dead time compared to a spectrum taken at 5% dead time.

![XRF Spectrum of Ni Alloy MBH 11224](image)

Figure 1. X-ray fluorescence spectrum of a Ni alloy containing 0.15 wt. % Zr. The red curve was taken with a count rate of 17,000 counts per second resulting in a dead time of 40%. For the blue spectrum, the X-ray tube current was reduced to make the dead time 5%.

PILEUP CORRECTION

Correction of the pileup effects was performed using the algorithm described by Bristow and Harrison[2]. This description gives the most detailed analysis of the pileup spectrum.
as it relates to pulse shape and X-ray statistics. It is a comprehensive analysis of pileup effects and contains a relatively complete list of references. Statham [3] gives a treatment of the role of pileup inspection thresholds in the presence of noise that is especially useful.

The result of applying the pileup correction to the spectrum in Figure 2 is shown in Figure 3.

![XRF Spectrum of 0.15% Zr in Ni Alloy MBH 11224](image)

**Figure 2.** Expanded region near the Zr peak of the spectrum from Figure 1.
Figure 3. The data from Figure 2 with software pileup correction (described in the text) applied to the 40% dead time spectrum.

Note that the algorithm does not do a perfect job of correcting the peak at 15 keV just to the left of the Zr peak. The spectrum taken at 5% dead time shows that there is a peak present at this energy, possibly due to an unreported amount of Y (the certificate of analysis is silent regarding Y). With only the 40% dead time spectrum, it would not be possible to make a definitive determination whether either of the two elements were present in the specimen. With the software pileup correction, the presence of the Zr peak can unambiguously be verified.

MEASUREMENTS

All samples were well-characterized reference materials intended for use as standards and having certified compositions available. The specimens were measured on an EDAX Eagle III XRF instrument with a Rh anode X-ray tube and a Si(Li) detector. This instrument had a 40 μm poly-capillary optic in the primary beam. A digital pulse processor was used with a pulse shaping time of 12.8 microseconds and hardware pulse pileup rejection. The Ni alloys were measured as cylindrical pellets with a machined face. The X-ray tube was operated at 42 kV and an Al filter of 250 μm thickness was employed. The glass samples were chips mounted in epoxy resin and surface polished. For these measurements, the X-ray tube was operated at 25 kV and no filter was used. The standard Vision software supplied with the Eagle (version 4.962 dated Jan. 28, 2008) was used for quantification. The pileup correction was performed in separate program using the algorithm described in reference [2]. The amount of Zr in the Ni alloys was quantified using the standardless fundamental parameters method. For the glasses, the fundamental parameters with standards method was used to quantify the amount of Cu in the glass specimens. The spectrum of glass BIR-1 collected at 5% dead time used as a standard. The Al content was entered as a known composition because the Al peak was weak and had significant variations due to statistical fluctuations. This avoided changes in the Cu concentration due to matrix correction with variations in Al content. Typical live times for the Ni alloy spectra were 1200 seconds for the 40% dead time data. These data were taken with a count rate of 17,000 counts per second.

RESULTS

The amount of Zr in this alloy and Ni alloy MBH 199, containing 0.05% Zr, was quantified using the Zr Kα peak in the measured spectra. The values obtained were compared to the certified Zr content and plotted as a function of dead time. The graph is given in Figure 4. As expected from the distortion visible in Figure 2, the amount of Zr increases with dead time. Thus the relative error increases from near zero at 5% dead time to near 100% at 60% dead time (the upper curves in the figure). The software pileup correction algorithm was applied to the spectra and the identical quantification performed again. The results are displayed in the lower curves in Figure 4. The improvement is dramatic. For dead times of 40% and below, the relative error in Zr quantification is
reduced to near zero. This is consistent with the plot of the corrected spectrum in Figure 3. This implies that the software correction algorithm is quantitatively correct for this range of dead times. At higher dead times, the improvement is equally dramatic but the results are not as good as those below 40% dead time. For dead times of 40% and below, the corrected spectra give results as good as the uncorrected spectrum taken at 5% dead time.

Figure 4. Measured results for Zr content in two Ni alloys compared to certified values for spectra at different dead times with and without software pileup correction. Note the dramatic improvement realized by the correction, especially at dead times of 40% and below.

Similar measurements were made for glass samples with trace amounts of Cu at 125 parts per million. Again, the quantitative results were compared to the certified values and the relative error plotted against dead time. The results of this study are shown in Figure 5. In this case, the Cu peak is completely overwhelmed by the pileup artifact from the Si + Fe K\(\alpha\) photons (the Si K\(\alpha\) and K\(\beta\) are not resolved and both contribute to the sum peak). The relative error after software correction is again near zero for dead times of 30% and below. This confirms that the software pileup correction is able to make quantitative correction of the pileup artifacts in this range.

CONCLUSIONS

Pileup can have significant quantitative effects on trace element peaks. However, pileup inspection in modern digital pulse processors reduces these pileup effects to negligible levels for low dead times. Software pileup correction can then be used to operate at higher dead times and still correct the spectrum to get more valuable information. At dead times up to 30% or 40%, the use of software correction can provide results comparable to those obtained at 5% dead time without software correction. Software
Pileup correction can also be used to validate peaks for trace elements by providing quantitative information about the amplitude of pileup peaks and clearly identifying them in the spectrum. Pile-up rejection and correction are becoming more important to quantitative accuracy as silicon drift detectors are being used at count rates beyond what was possible with Si(Li) detectors. SDDs can be operated at shorter shaping times and still retain good energy resolution. At the shorter shaping times, hardware pileup rejection becomes more difficult, making the software correction methods evaluated here especially important.

![Figure 5. Measured results for trace Cu concentration in two glasses compared to certified values for spectra at different dead times with and without software pileup correction. The software pileup correction reduces the relative error to near zero for dead times below 30%.

REFERENCES