Characterization of CdTe Detectors for Quantitative X-ray Spectroscopy

R. Redus, *Member, IEEE*, J. Pantazis, T. Pantazis, A. Huber, B. Cross

***Abstract*— Silicon diodes have traditionally been the detectors of choice for quantitative X-ray spectroscopy but they have limited sensitivity at energies above 30 keV. Recent environmental regulations, such as Europe's RoHS/WEEE Initiative, require non-destructive measurement of heavy metals such as lead and mercury, with K X-ray emissions well above 30 keV. CdTe has much higher stopping power, making it an attractive alternative in these applications. With a Schottky diode structure and Peltier cooling, electronic noise is around 500 eV for a 5 mm x 5 mm x 0.75 mm device, providing adequate energy resolution for distinguishing peaks of interest. However, the response function of a CdTe detector has some important differences from that of Si detectors and these differences must be understood and quantified to achieve accurate results. This paper will discuss several important effects in the response of CdTe, including hole tailing due to poor charge transport, escape peaks, spectral background, linearity, and stability. This paper will show the impact of these effects on X-ray spectra and will present correction techniques.**

I. Introduction

Historically, cryogenic Si(Li) detectors were the primary sensors used in quantitative X-ray fluorescence. In recent years, Si-PIN diodes with Peltier cooling have come into common use [1], delivering a resolution of 150 eV FWHM at 5.9 keV. These were initially used in portable applications but increasingly in laboratory settings . However, the sensitivity of Si detectors falls at energies above 15 keV. Recent environmental regulations, such as Europe's RoHS/WEEE Initiative [2], require non-destructive measurements of heavy metals such as Pb, Cd, and Hg. Applications such as mining or alloy analysis require measurement of metals such as Sb or Au. The L lines of these elements are below 20 keV but are closely spaced, leading to interferences. The K lines are more widely spaced, permitting much clearer identification of these metals, but Si detectors have very low sensitivity for these X-rays. Because CdTe has much higher stopping power, CdTe detectors are a viable alternative. Both the total probability of interaction and the photofraction are far higher for CdTe than for Si for energies above 20 keV, dramatically improving the signal-to-background ratio for the K lines of higher Z elements. Using a Schottky diode structure and Peltier cooling, electronic noise is adequate for distinguishing peaks above 30 keV.

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R. Redus, J. Pantazis, A. Huber, and T. Pantazis are with Amptek, Inc., 14 DeAngelo Dr., Bedford MA 01730 USA (781-275-2242; e-mail: rhredus@amptek.com).

B. Cross is with CrossRoads Scientific, 414 Av. Portola, P.O. Box 1823 El Granada, CA 94018-1823 (650-726-6769)

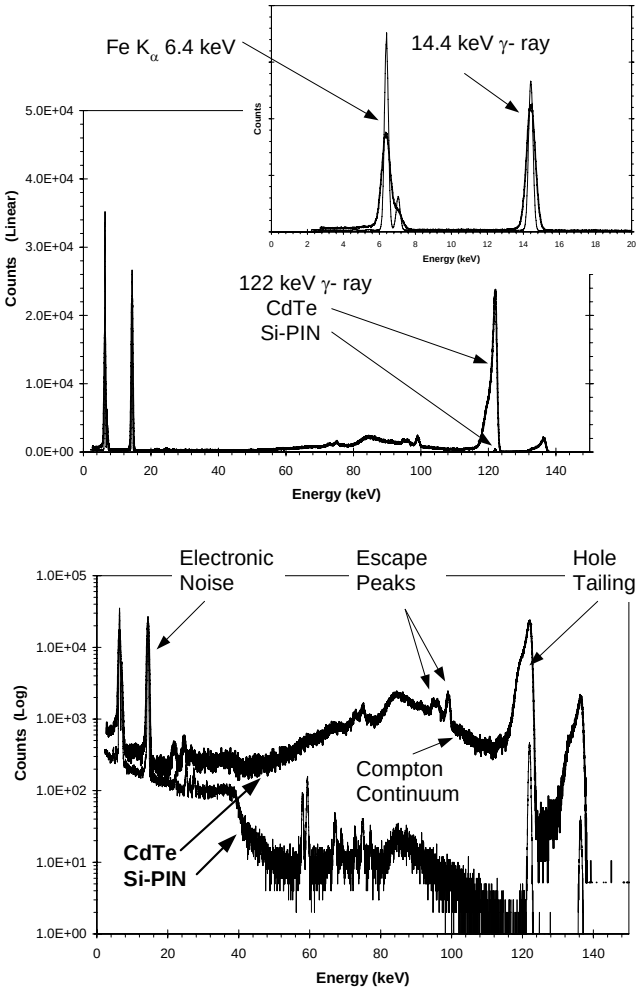

Fig. 1. ^{57}Co spectrum measured by Si-PIN (thin line) and CdTe (thick line) detectors, both of 25 mm^2 active area. The plot on the top is on a linear scale, with the inset showing the low energy range. The plot on the bottom is on a log scale and illustrates the major spectral features discussed in this paper.

Figure 1 shows two ^{57}Co gamma-ray spectra, using a Si-PIN and a CdTe detector, in the same geometry and normalized for the same acquisition time. Both are 25 mm^2 active area, with 500 (750) μm thickness for the Si-PIN (CdTe). The linear plot shows that at 6.4 keV they have the same photopeak area so equal sensitivity. At 14.4 keV, the CdTe detector has 25% greater photopeak area. At 122 keV, the CdTe detector has 140 times the photopeak area of the Si-PIN. A 0.75 mm CdTe detector has >90% photoelectric

efficiency up to 65 keV.

The response function of a CdTe detector has some important differences from that of Si detectors and these differences must be understood and quantified to achieve accurate quantitative X-ray analysis results. Applying the spectral processing algorithms used with Si will lead to errors, so changes must be made to the algorithms. The log scale plot of Figure 1 shows the most important of these spectral characteristics. This paper will present data on the unique spectral characteristics of CdTe for X-ray spectroscopy, analysis and models of them, and techniques to correct for them. These effects include electronic noise, hole tailing due to poor charge transport, escape peaks, and the continuum in the spectrum due to scattering. This paper will also characterize other key CdTe properties, including noise, linearity, and stability.

II. Experimental Apparatus

CdTe is a wide bandgap compound semiconductor, which has been used for X-ray and γ -ray measurements for over 30 years. Its material properties are well known [3]. Its bandgap of 1.44 eV reduces leakage current and makes near room temperature operation feasible. Its constituents have atomic numbers of 48 and 52, and it has a density of 6.2 g/cm^3, so it has much better stopping power than Si. For these reasons, it has been used for room temperature X-ray and γ-ray measurements.

All of the data reported in this paper were taken using XR-100T-CdTe systems from Amptek, Inc. These systems have been described in more detail elsewhere [4] but the key parameters will be repeated here. The detector elements were 5 mm x 5 mm x 0.75 mm CdTe with a Schottky diode structure (an M-π-n structure), procured from Acrorad, Ltd. with contacts and packaged by Amptek. The detectors are packed inside a TO-8 hybrid, mounted on a two-stage Peltier cooler which can achieve an 80°C temperature differential. Also on the cooler are the input FET, the feedback capacitor, and the low frequency feedback circuitry, which for the results reported here was a transistor feedback circuit to minimize electronic noise [5]. A 100 μm Be window is in front of the detector. The preamp signals were processed by Amptek's digital processors, including the PX4, the DP4, and the X123, using trapezoidal shaping and no risetime discrimination. Unless otherwise stated, peaking times were 1.6 to 3.2 μs and the flat top was 0.4 to 0.6 μs. The digital processors include a multichannel analyzer and all necessary power supplies, including close-loop temperature regulation and the bias voltage for the detector. Unless stated otherwise, data were taken at 230K and at 500V bias. Data were acquired by the ADMCA.EXE software provided with Amptek's digital processors. Spectrum analysis was carried out using the XRF-FP software, developed jointly by Amptek and by CrossRoads Scientific. Special analysis algorithms have been developed for CdTe, which are incorporated in the commercially available package.

III. Spectroscopic Features

A. Gaussian Broadening

At low to intermediate energies, the resolution of a CdTe detector is dominated by electronic noise and by Fano broadening. At short shaping times, the noise is nearly identical for Si-PIN and CdTe detectors with the same area. However, the leakage current of the CdTe is higher, as is the 1/f noise. A typical 25 mm^2 x 750 μm CdTe detector at 500V bias has 500 to 600 eV FWHM of electronic noise at a peaking time of 4.8 to 6.4 μs. The Fano factor is generally taken as 0.1, contributing about 500 eV at 60 keV [6].

B. Hole Tailing

One of the most obvious features in the CdTe response above 50 keV is hole tailing. The 122 keV photopeak in Figure 1 is clearly not Gaussian but has a shoulder extending towards lower energies. In the linear plot this looks like a smooth tail but in the logarithmic plot it is clear that the tail goes down to a specific value and terminates. Hole tailing arises from the short lifetime of the holes due to the density of trapping sites in the crystal. The defect density and thus hole lifetime are intrinsic properties of the CdTe and, although much research has gone into improved crystal fabrication, the defect density remains high enough to be important [3].

When an interaction occurs near the cathode, the signal is mostly due to the electron current, collected in 10 ns with negligible charge loss. When an interaction occurs near the anode, the holes must travel the full detector thickness. With a transit time of 0.1 μs and a lifetime of 1 μs, 5% of the charge is

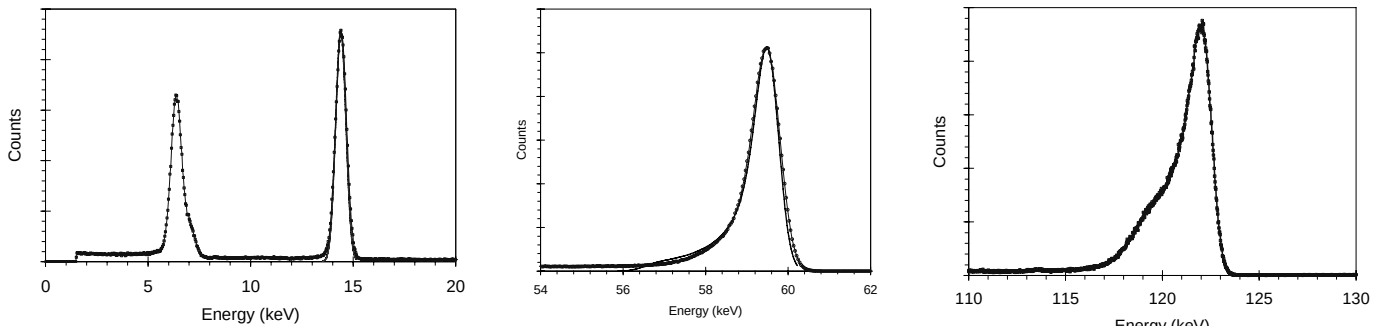

Fig 2. Plots showing the measured and modeled photopeak shape as a function of energy. At 14.4 keV (left), the photopeak is Gaussian. At 59.5 keV (middle), the photopeak exhibits a smooth asymmetric tail to lower amplitudes. At 122 keV (right), additional counts in the tail lead to a step at the anode charge collection efficiency.

lost. This transit time implies that trapezoidal pulse shaping, with a flat top of at least 0.4 μs, will minimize the tail.

For quantitative analysis of the photopeak area, it is important that the tail terminates near 95% of full charge collection for a typical detector rather than extending to zero energy. Previous compound semiconductors such as CZT exhibited tailing to a few percent [7], while models for charge loss in the dead layers of Si detectors extend exponentially to zero [8]. In CdTe, hole tailing arises in the bulk and terminates at a specific value, independent of energy, due to charge loss from interactions near the anode.

Amptek, Inc. has developed a quantitative model of the photopeak shape in CdTe detectors which includes (1) charge trapping, modeled by the Hecht equation and thus assuming a uniform electric field, (2) exponential attenuation due to photoelectric interactions, and (3) Gaussian broadening due to electronic noise and the Fano factor [7], [9]. Figure 2 shows a measured and a model photopeak shape as a function of energy. At 14.4 keV interactions all occur near the cathode so there is no variation in charge collection efficiency. At 59.5 keV, enough photons interact near the anode to cause a visible asymmetry in the peak, but the counts fall off smoothly, with no visible step. At 122 keV, the attenuation length is much longer than the detector so interactions occur uniformly throughout. Many photons occur near the anode, leading to a more significant tail and to a clearly visible step termination to the tail at the charge collection efficiency of the anode.

Amptek's photopeak shape model is useful for design and for estimating system performance but cannot be expressed in a closed form so is not easily used for spectroscopic analysis. We are actively exploring models and algorithms, which are both simple enough for practical analytical software yet handle the range of photopeak shapes with sufficient accuracy. At the lowest energies a straight Gaussian is adequate. For energies up to 60 or 70 keV a simple tail function [8] is suitable, with an energy-dependent weighting of the tail. For higher energies, this tail function must be multiplied by a step function to account for the anode collection efficiency. An accurate model of the photopeak shape is necessary to separate closely spaced peaks and to accurately determine net area.

A. Linearity

It is common for spectroscopic software to use the centroid of the photopeak to determine the energy of a peak. In CdTe, the centroid is shifted by the asymmetry due to hole tailing. This centroid shift increases with energy, leading to an apparent nonlinearity. The correct technique is to use the peak channel rather than the centroid. We measured the peak channel versus energy with isotopes to obtain ten energies spanning 14.4 to 136 keV, for several detectors. The response is linear, with a correlation coefficient typically >0.99999.

B. Escape peaks

Escape peaks have a much more pronounced effect in CdTe than in Si detectors. The physical process is the same: Secondary x-rays produced in the detector by the interaction with Cd or Te escape the detector and thus reduce the measured energy. But three intrinsic properties of Cd and Te make them more prominent. First, in Si only 5% of the atoms decay with emission of an X-ray, while in Cd and Te the yield is near 85% [10], so far more X-rays are produced. Second, in Si only the K_α peak is usually visible. In CdTe, both the Cd and the Te produce both K_α and K_β peaks, so each primary photopeak produces four escape peaks. Third, in Si the characteristic X-rays have low energy, 1.74 keV, so only exit the detector for interactions near the surface. In CdTe, the characteristic energies are 23.2 and 26.1 keV for the Cd K_α and K_β, and 27.5 and 31.0 keV for the Te peaks. These have longer range so are important at higher energies.

Figure 3 shows the spectrum measured from a ^{241}Am source, with an Al filter used to remove the γ-ray and X-ray lines below the 59.5 keV γ-ray line. The four distinct escape peaks are clearly visible and include a significant fraction of the photopeak events. Spectrum analysis software must correct to obtain an accurate photopeak area, to prevent these escape peaks from obscuring real X-rays at this energy, and to avoid misidentifying these as real peaks in the incident energy spectrum.

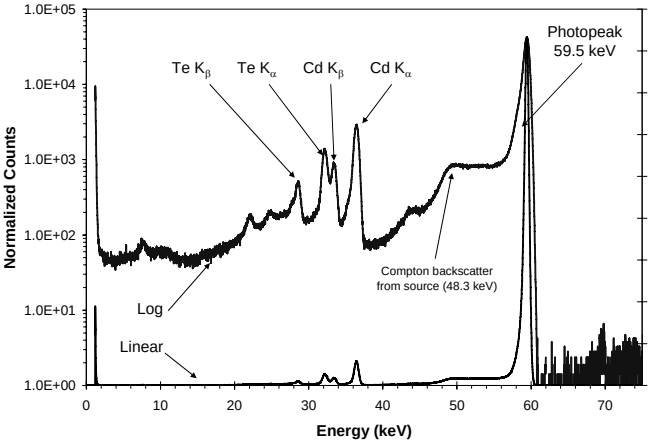

Fig 3. Spectrum measured using a filtered ^{241}Am source, showing the four escape peaks produced from the 59.5 keV primary peak. Also visible is the asymmetry due to hole tailing and a "shelf" due to photons Compton scattering out of the isotopic source and into the detector.

Our correction technique is based on work carried out by Paul Bennet of RMD, Inc. [11] First, the EGS4 Monte Carlo simulation software [12] was used to determine the fraction of events escaping the CdTe volume as a function of energy. Monoenergetic simulations were carried out for incident energies from 24 to 140 keV. In each simulation, 10^6 photons were incident on a 5 x 5 x 0.75 mm^3 slab of CdTe, at normal incidence and random locations. The total energy deposited in

the CdTe was determined for each photon and from this the ratio of counts in each escape peak to the photopeak determined. These ratios were fit to a polynomial form to obtain the escape peak yield versus energy. The maximum correction is 15% for the Cd K_α and 3% for the Cd K_β, for photons incident just above the 26.7 keV Cd K edge. At energies above 100 keV the yield asymptotically approaches 5% for Cd K_α, 1.5% for Cd K_β and Te K_α, and 0.4% for the Te K_β. We measured the escape fraction using isotopic sources, obtaining spectra such as that in Figure 3, and found good agreement with the EGS4 simulation results.

The correction software begins with the highest energy channel, treating it as a 1 channel photopeak. The four channels for the corresponding escape peaks are calculated. The ratio of escape to photopeak counts is calculated from the polynomials for each escape peak. These counts are subtracted from the escape channels and added to the photopeak channel. The process is repeated with the next lower energy channel, using the processed spectrum, and continuing down to the Cd escape edge, channel by channel.

Figure 4 illustrates the correction for the spectrum from an 80 kVp tungsten anode tube. An aluminum filter should stop all X-rays below 15 keV, except for the Al peak at 1.5 keV. Two artifacts are clearly visible in the raw spectrum: there are many counts seen below the filter cut-off and the continuous brehmstrahlung spectrum shows steps at 26.7 and 31.8 keV. These are the Cd and Te K edges. A fraction of X-rays incident with energy just above the edge deposit less energy, because secondary X-rays escape, causing the discontinuity in the continuum with these events appearing in low energy channels. The dashed trace shows the escape events moved up in energy, while the corrected spectrum shows the end product of the correction algorithm.

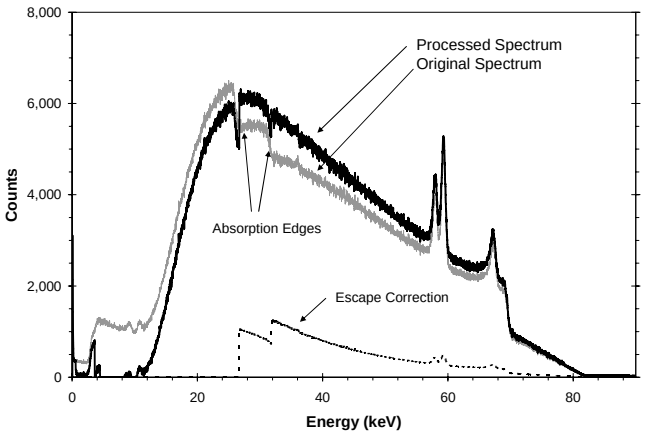

Fig 4. Plot showing the results of the escape peak correction algorithm, applied to a spectrum measured from an 80 kVp tungsten anode X-ray tube. The raw spectrum is shown, with the clear absorption edges and with counts below the expected cut-off due to the filter. Also shown is the escape correction, and then the final processed spectrum.

It has proven necessary to adjust some parameters to obtain a good fit. In particular, the Cd K edge value has been adjusted from the nominal 26.7 to 26.1 keV. The reason for this adjustment is not currently known and is an active research question. This correction algorithm has some implicit simplifying assumptions, which limit its accuracy and could be addressed in future work. First, the measured peaks exhibit Gaussian broadening, while the actual escape is a line process, and the correction algorithm assumes a line process. Second, the Cd and Te characteristic X-rays only escape for interactions near the contacts of the detector. The hole tailing in the photopeak spectrum implies that the correction should only be applied to events near the bounds of the photopeak shape. The combined effect of hole tailing and escape peaks will lead to spectral characteristics more complex than either alone. The current algorithm neglects these subtleties, carrying out the first order correction for escape events to significantly reduce spectral distortions.

C. Compton Continuum

All spectrum analysis software must separate the photopeaks from a continuum upon which the peak is superimposed. This continuum arises from many physical processes, including Compton scattering. In the energy range where Si detectors are most often used, the cross-section for Compton scattering from collimators, samples, and other materials is low. At the energies where CdTe is useful, the cross-section for Compton scattering is much higher and therefore spectral analysis algorithms are much more sensitive to continuum removal. This does not arise from the CdTe per se but from the higher energy range where CdTe is useful. The XRF-FP continuum removal algorithms can be applied to CdTe but the parameters must be changed to increase the background curvature. Continuum removal is applied to the spectrum prior to escape peak removal.

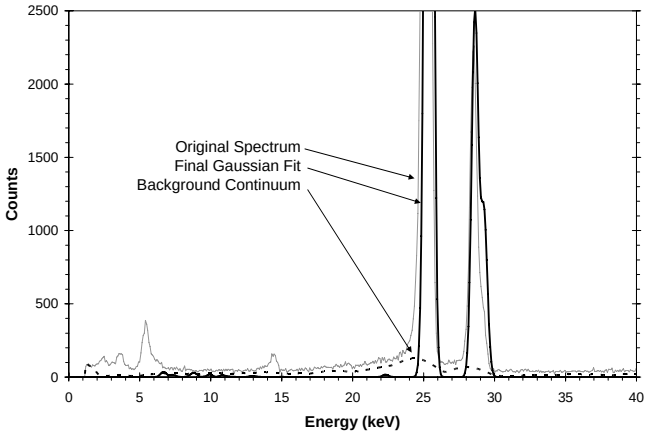

Fig 5. Plot showing Sn characteristic X-rays measured by CdTe. The plot shows the raw spectra, the background continuum which has been removed, and then the Gaussian fits to the resulting spectrum.

Figure 5 shows a Sn characteristic X-ray spectrum, with a ^{57}Co excitation source, measured by CdTe. This plot shows the raw spectrum (thin line), with escape peaks and continuum, the continuum model, and then the result of correction, the remaining K_α and K_β Sn peaks. The asymmetry in these peaks due to hole tailing is clearly visible, so a Gaussian fit is only approximate.

D. Other Issues

Stability of the detector output is critical to quantitative analysis. With the operating conditions of the XR-100T-CdTe, the response is stable over several days. It is known that CdTe detectors with Schottky contacts exhibit polarization. [13] Over time at a sustained bias voltage, one observes a progressive degradation of energy resolution and a shifting of the photopeak to lower energies. This results from the accumulation of negative charge on a deep acceptor level and causes the electric field strength in the bulk of the CdTe to decrease with time, degrading charge collection.

Fortunately, the rate of polarization is reduced at low temperatures and at high bias voltages, which are the operation conditions of the Peltier cooled XR-100T-CdTe. At room temperature (25˚C) and at low bias voltage (200 V on a 0.75 mm detector), the peak shift was measured and found to be >2% per hour. At the XR-100T-CdTe operating conditions, 220 K and 750 V bias, a ^{57}Co spectrum was acquired every 2 minutes for 5 days. As shown in Figure 6, the peak shift was measured to be 1±2 ppm per day, statistically indistinguishable from zero. The photopeak counts decreased with time at the ^{57}Co known decay, with a half life of 271.6 days. Polarization is observed in CdTe, and is quite important at room temperature and low bias voltages, but under the operating conditions of the XR-100T-CdTe, it is not important over many days.

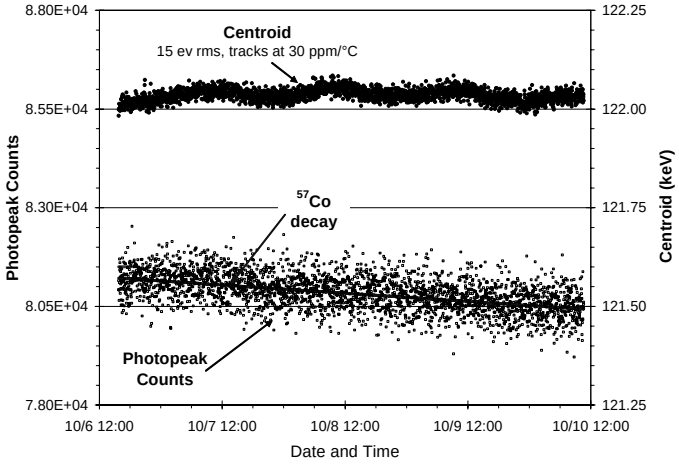

Fig 6. Plot showing stability of the devices at a temperature of 220 K and a bias of 1 kV/mm.

Reproducibility of the detector spectra is also critical to practical instrumentation. The wide bandgap compound semiconductors which were available ten years ago exhibited considerable variability from one device to the next. The resistivity, leakage current, and carrier lifetimes covered a wide range, causing electronic noise, optimum bias voltage, and magnitude of hole tailing to vary considerably from one detector to the next. Each system required tweaking of operating parameters and the analysis software would include detector specific parameters. In a recent production lot of 25 CdTe detectors, one was observed to have a spectrum noticeably different from the others. Of the 24 similar units, the resolution at 59.5 keV was measured to be 853 ± 67 eV FWHM, yielding good reproducibility for overall resolution. There is no broadly accepted simple measure of hole tailing, but one can parameterize this by looking at the ratio of counts at a specific channel to photopeak counts. For this lot, we found the ratio at 58.0 keV to the photopeak. Figure 2 (center) shows that these counts are largely due to the hole tailing and will vary sensitively with tailing. In this lot of 24, the ratio was found to be 5.5±1.2%, indicating that there is little variation in the counts at this portion of the tail.

IV. Application

As an example of the use of CdTe, a quantitative analysis was performed on a Pb-Sn solder material, shown in Figure 7. Using a ^{57}Co source, spectra were acquired from pure Pb and pure Sn samples to calibrate the analysis parameters. A spectrum was then acquired from a sample of 63% Sn and 37% Pb. The algorithms discussed here were applied to address spectral artifacts, then the results were processed by the XRF-FP software, which identified both elements and computed a Sn fraction of 63% to 68%, in good agreement with the actual sample.

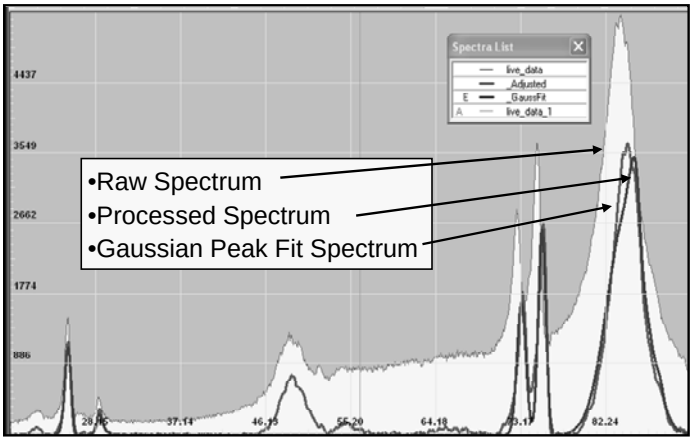

Fig 7. Plot showing the analysis of a Sn-Pb solder, showing the raw spectrum, the processed spectrum after correction for escape peaks and the continuum, and then Gaussian fits to the primary photopeaks.

V. Conclusion

CdTe detectors clearly have much higher sensitivity than Si devices at energies above 20 keV, corresponding to K lines for elements heavier than Ru. Although the Si detectors can measure these lower energies with very high resolution, heavy metals in samples produce many L lines, which can interfere and make quantitative analysis difficult and inaccurate. The CdTe detectors can measure the K lines with high sensitivity, but to obtain quantitative results, the algorithms used to analyze CdTe spectra must be modified from those usually used with Si detectors. This paper has presented data and analysis of the most important distinctions between Si and CdTe, methods to address spectral artifacts and distortions, and the result of the corrections. With appropriate use of these correction algorithms, CdTe is capable of quantitative

X-ray analysis. The maturity of the CdTe detectors combined with proper analysis tools makes CdTe a useful detector for XRF.

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