Improving Detectors for X-Ray Spectroscopy

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Introduction

The following presentation is an extended version of presentations that were given at the 2018 European Conference on X-ray Spectroscopy and at the 2018 Denver X-ray Conference. Text has been added to the plots shown at the conference. The ideas will be more formally developed in a paper to be submitted to "X-Ray Spectrometry".

Readers are welcome to use the plots and analysis shown in the presentation, as long as they include an explicit reference to

> *R.H. Redus, A.C. Huber, R. Dubay, "Improving detectors for X-ray spectroscopy", presented at 2018 European Conf. on X-ray Spectr., Ljubljana, Slovenia, 2018.*

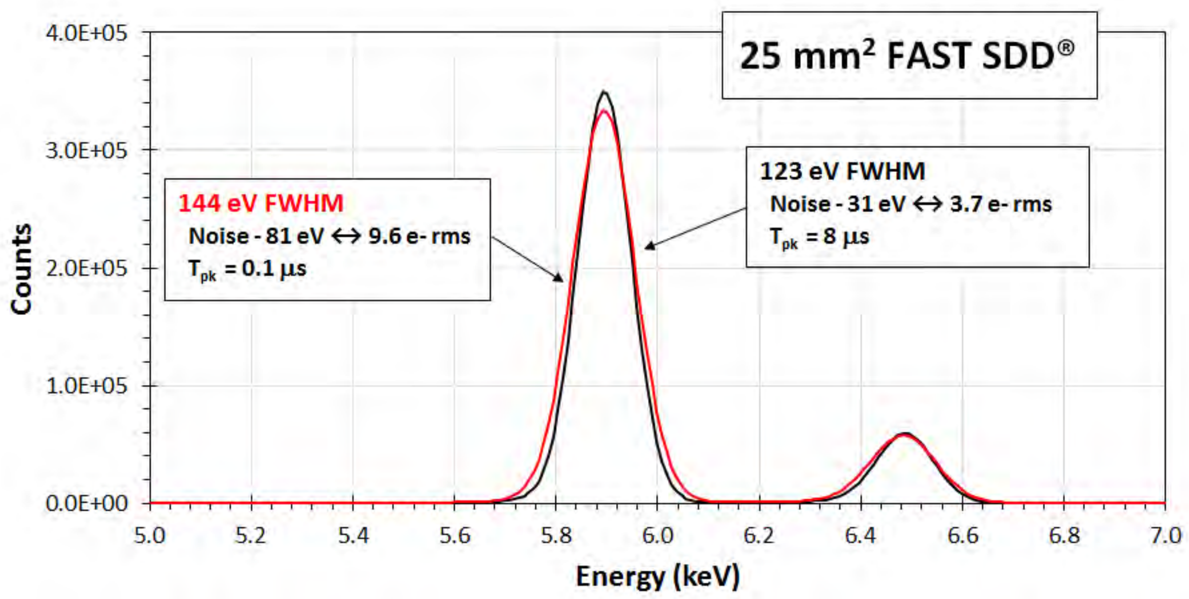
Introduction

- **What makes a detector "improved“ or even “good”?**
  - *Many people focus resolution at ^{55}Fe as a “figure of merit”.*
- **But end users care about the spectroscopic measurement:**
  - *Better precision ↔ shorter measurement time*
  - *Better accuracy*
  - *Lower detection limits*
  - *Practical: Small size, low power, rugged, low costs, …*
- **Which detector characteristics primarily drive these?**
  - *Does ^{55}Fe FWHM matter for end user performance? If not, what matters?*
  - *We must define what it means to improve detectors and spectrometers before we can discuss recent improvements.*
  - This work is an extension of *Figure of Merit for Spectrometers for EDXRF,* Redus & Huber, X-ray Spectrometry, Vol 41, issue 6, pp 401-409 (2012)

Introduction

^{55}Fe Full Width at Half Maximum (FWHM)

- *Plot below: ^{55}Fe spectra with same FAST SDD® at two T_{pk}*
  - **Black**: 123 eV FWHM, at T_{pk}= 8 µs. Noise is 3.7 e- rms or 31 eV FWHM
  - **Red**: 144 eV FWHM, at T_{pk}= 0.1 µs. Noise is 9.6 e- rms or 81 eV FWHM
- *Resolution and noise are different – but the spectra are very similar.*
  - How much does this impact analysis, e.g. precision, accuracy, LOD?
  - How important is higher count rate (R_{out}) of T_{pk}= 0.1 µs?



Measurement Equations

- **Concentration C_i of element i**

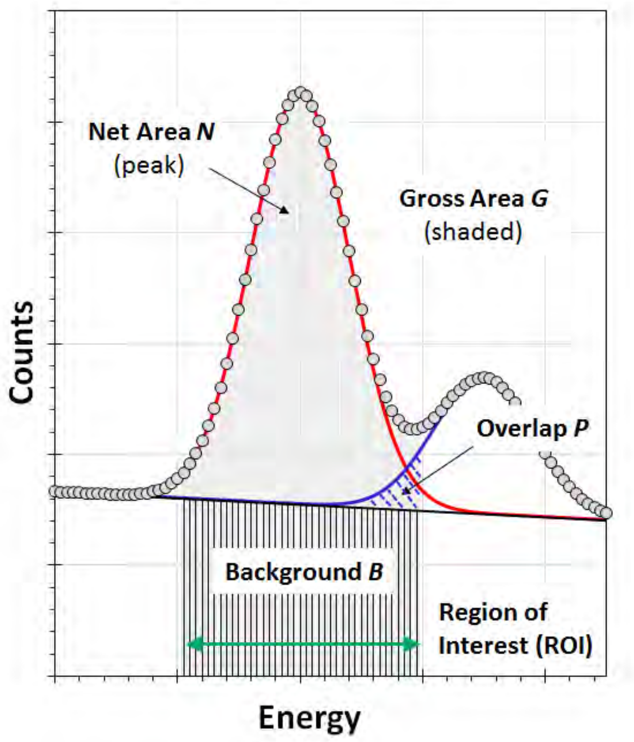
$$C_i = N_i K_i M$$

  - *K_i is calibration factor, M matrix correction*
  - *N_i is photopeak area (a.k.a. net area)*

- **Net Area N_i**

$$N = G - \left(B_{est} + P_{est}\right)$$

  - *G is gross area, directly measured*
  - *B_{est} is estimated background*
  - *P_{est} is estimated overlap*



- **Measurement uncertainty**

  Precision: *Measures reproducibility of a result (under unchanging conditions)*

  Accuracy: *Measures how close the (average) result is to the true value.*

  Detection Limit: *Measures smallest amount that can be detected (95% confidence)*

Measurement Uncertainty

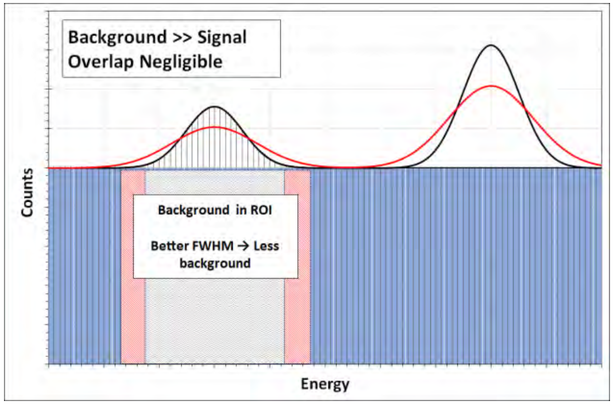
Sources of uncertainty

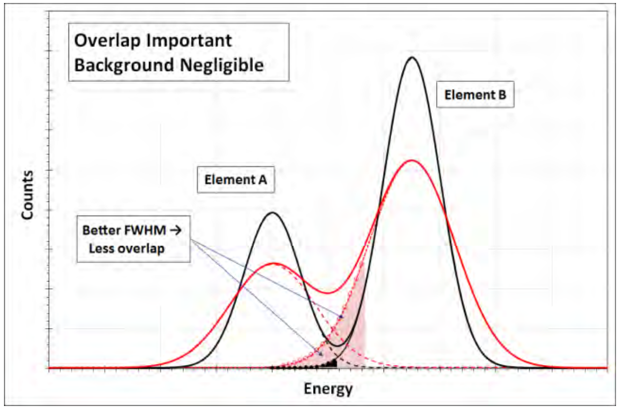
- *This presentation focuses on detector and spectrometer*
- *Many other factors important: X-ray source, geometry, software, calibration procedures, sample prep, etc. Not considered here.*

Precision

$$\frac{\sigma_N^2}{N^2} = \frac{\sigma_G^2 + \sigma_{est}^2}{N^2} = \left(\frac{N + B + P + \sigma_{est}^2}{N^2} \right)$$

- *Ideal limit: due to counting statistics*
- *Better FWHM reduces ROI width, thus reducing background counts B and overlapped counts P, thus improving σ_N.*
- *But higher count rates increase N, B, and P, also improving σ_N.*
- *Key question: Which improves it more or more easily?*





Measurement Uncertainty

- **Accuracy**

$$\frac{\sigma_C^2}{C^2} = \frac{\sigma_K^2}{K^2} + \frac{\sigma_M^2}{M^2} + \left(\frac{N + B + P + \sigma_{est}^2}{N^2} \right)$$

  - *Due to*
    - Changes in the response over time (e.g. calibration drift, change in K_i),
    - Errors in initial calibration (total uncertainty of K_i),
    - Errors in the models used to estimate background *B*, overlapping peaks *P*, matrix corrections *M*, etc.

- **Detection Limit**
  - *Due to*
    - Precision of estimates of background *B* and overlap *P*

$$N_{DL} \geq 4.6\sqrt{(B + P)} + 2.7$$

    - Accuracy of algorithms used to estimate *B* and *P*. Overlap usually dominates
    - Interference: When the analyte is present in the instrument

Key points

Precision

- *^{55}Fe FWHM alone is not the key parameter*
- *High count rates improve statistical precision far more than FWHM*
  - In modern detectors, FWHM ranges from 150 to 125 eV → FWHM improvements have a small impact on statistical precision
  - In modern spectrometers, count rates range from 5 to 500 kcps → Increasing count rates has a large impact on statistical precision
  - One can get more improvement through high count rate than good FWHM
  - True for both background limited case and overlapping peaks
- *If source is intense enough, short T_{pk} and high rate is best*

  → Amptek has focused on noise at short T_{pk} (less so long T_{pk})
  - BUT accuracy degrades if centroid, FWHM change at high rate

  → Amptek focuses on stability @ high rate: 1 Mcps FAST SDD®, 100 kcps SiPIN
- *If source is weak, increasing area or efficiency is best*

  → Amptek focuses on larger areas, thinner windows, high Z

Key points

- **Accuracy**
  - *Detector and spectrometer are not main factors limiting accuracy*
  - *Changes in gain, noise, or detector response degrade accuracy*
  - *Difference between model and actual response, e.g. non-Gaussian photopeak shapes, degrade accuracy*

- **Detection Limit**
  - *Statistical limit of separating background & overlap → High rate*
  - *Accuracy of separating overlapped peaks*
    - Accuracy degrades if FWHM or photopeak shape change at high rate
    - Accuracy degrades from non-Gaussian photopeak response

    → Amptek focuses on peak to background, peak to tail
  - *Minimizing detector interferences*

    → Amptek focuses on cleaner spectrum

Precision & Background

What do we expect?

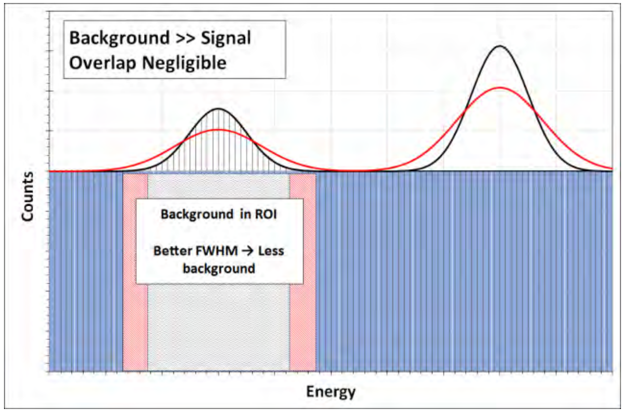
- Assume *P* negligible, *B* >> *N*, and that *B* scales with ROI width

$$\frac{\sigma_N^2}{N^2} \cong \frac{\sigma_G^2}{N^2} = \left(\frac{N+B}{N^2}\right) = \left(1+\frac{B}{N}\right)$$

  - Equal improvement by increasing *N* or decreasing *B*
  - But *B* only changes by ~25%; can change *N*, through count rate, x10
  - Therefore better to maximize count rate
- *Lower energies*
  - Lower energies

$$B \sim \sqrt{ENC^2 + F \bullet E}$$

  - *B* changes some with ^{55}Fe FWHM

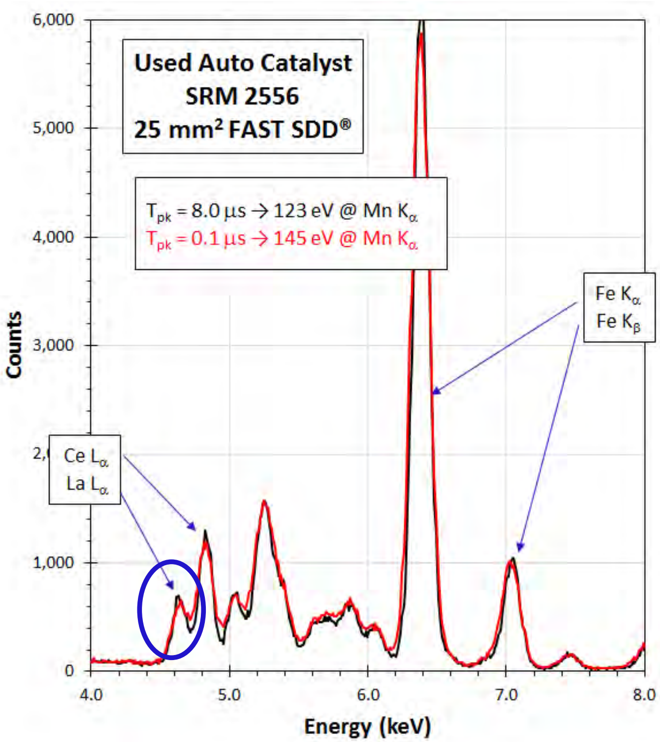


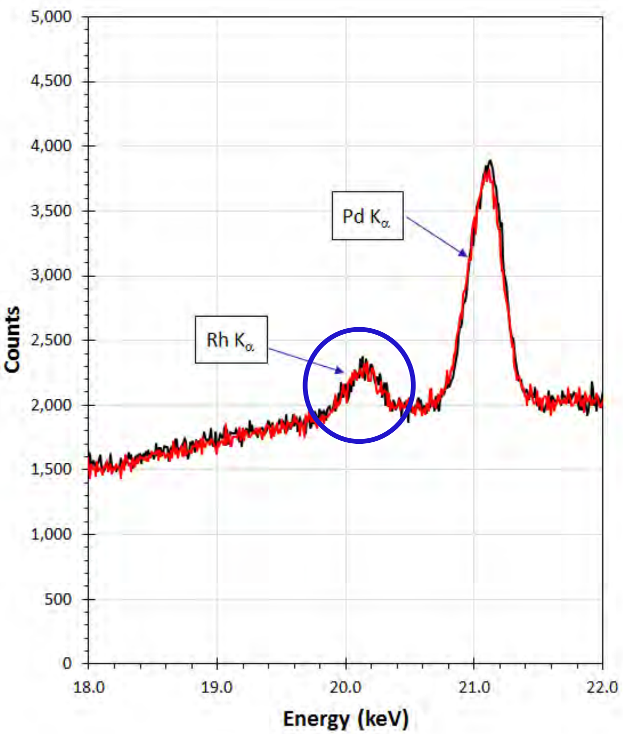
- *Higher energies*
  - At higher energies, line spacing dominates
  - Even if ^{55}Fe improves, ROI width is unchanged

Precision & Background

Practical example: Used auto catalyst (SRM2556):

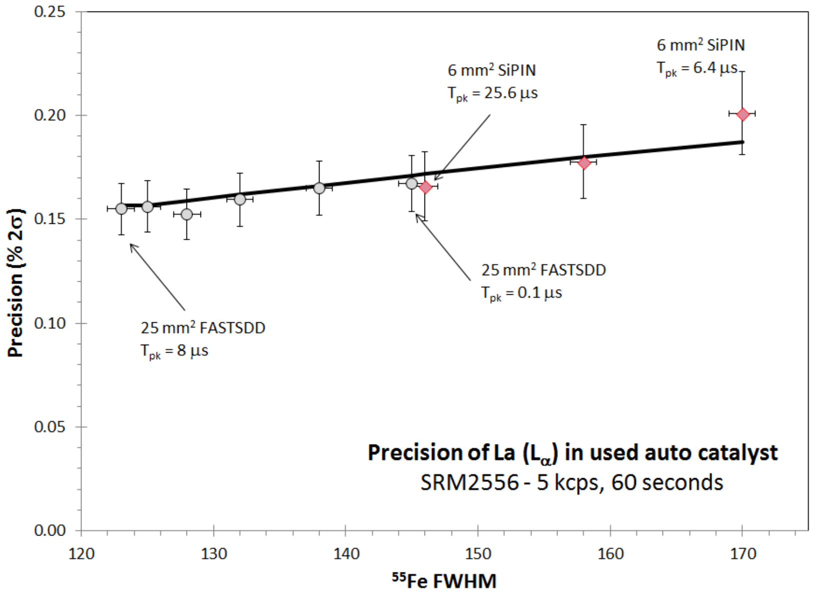
- Examined trade-offs using a specific sample. Varied T_{pk} to vary FWHM. Measured at constant count rate, constant dead time, etc.
  - La L_α (0.7%) : Background > 2x signal. ROI depends on T_{pk}
  - Rh K_α (50 ppm) : Background > 5x signal. But ROI width depends on Fano and peak splitting, does not change with FWHM.

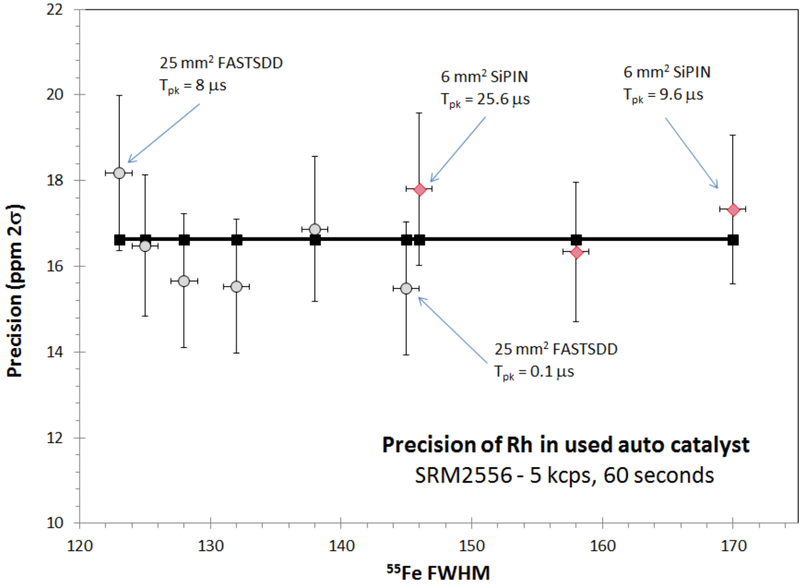




Precision & Background

- **How important is FWHM with background > peak?**
  - *Varied T_{pk} (FWHM) at constant count rate*

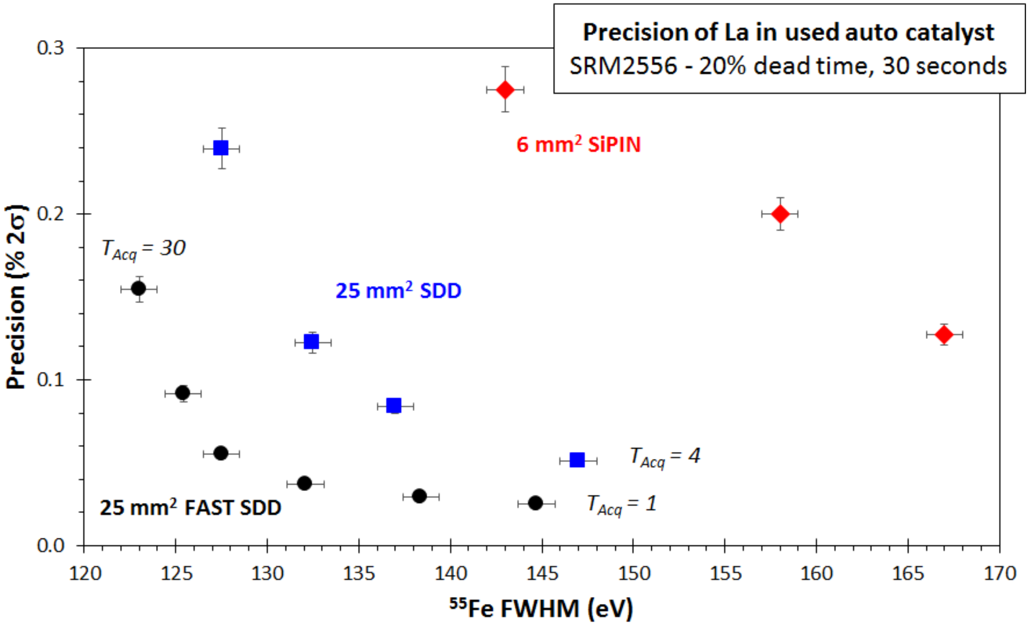




- *Improving FWHM alone helps precision but it’s a small effect*
- *This is because fractional change in FWHM is pretty small*

Precision & Background: Strong source

- **FWHM vs R_{in} (strong source case)**
  - *Varied T_{pk} and beam current for constant dead time*
    - FAST SDD® gives 6x better precision where FWHM is 144 eV
    - FAST SDD® gives same precision in 1/30th the time where FWHM is 144 eV
    - FAST SDD® gives same precision in 1/4th time of SDD, 1/20th of SiPIN



  - *Count rate is far more important than FWHM for precision*
    - **For a given detector, best precision is at short T_{pk} and high R_{in}**
    - **For selecting between SiPIN, SDD, FAST SDD®, count rate is primary**

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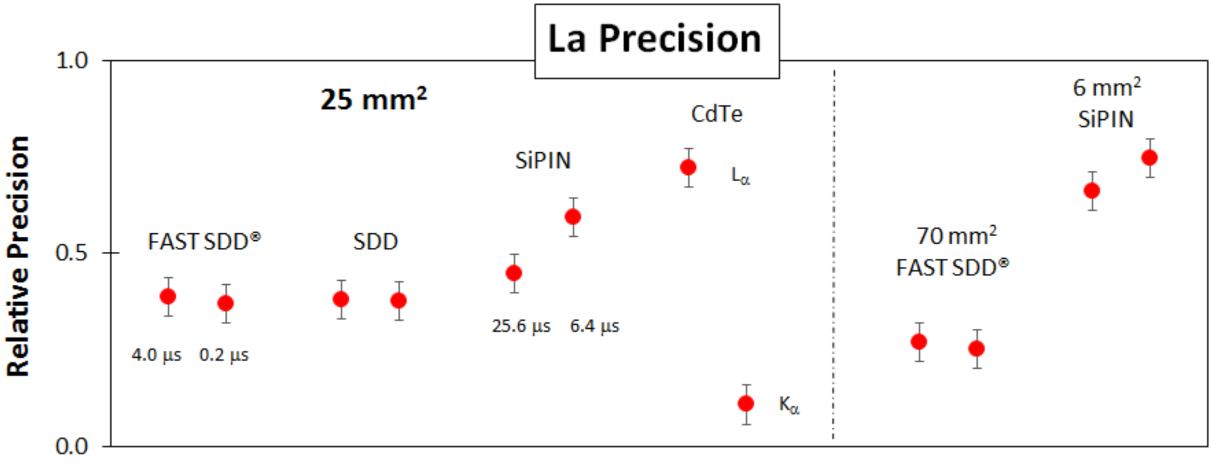
Precision & Background : Weak source

- **FWHM vs R_{in} (weak source)**
  - *Constant, low flux (4 kcps in 25 mm^2) at lower energies*
    - 25mm^2 FAST SDD®, SDD, and SiPIN yield almost the same precision

      25 mm^2 SiPIN at 6.4 μs is worse → FWHM begins to impact
    - 70mm^2 is √3x better while 6 mm^2 is 2x worse → *√Area*

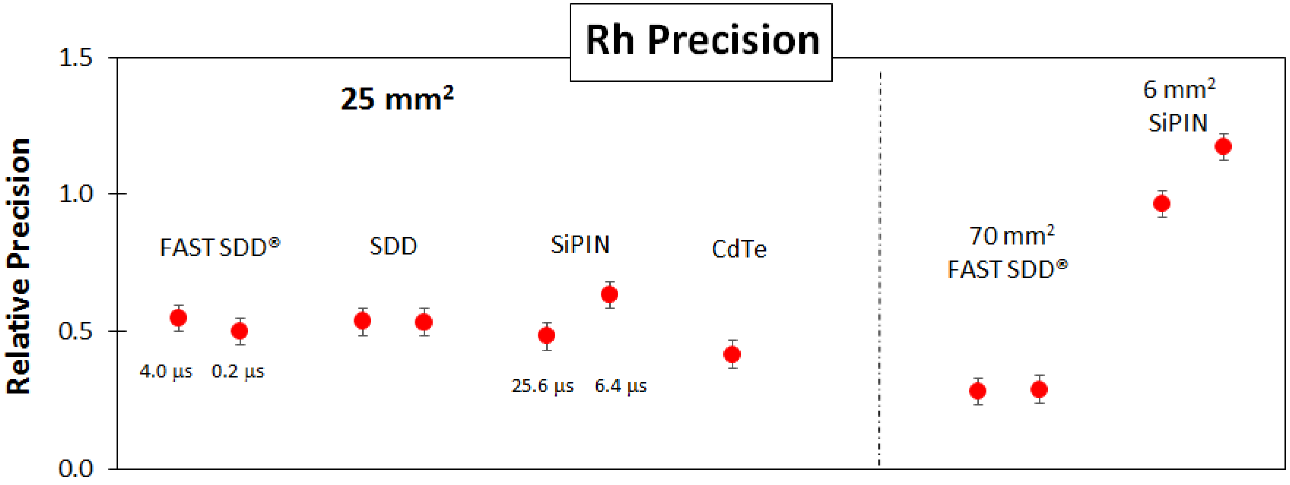
      CdTe K_α excellent due to better efficiency at high energies



  - <u>*Count rate is far more important than FWHM per se!*</u>
    - **With a weak source it is large area, not short T_{pk}, that matters**
    - **70 mm^2 FAST SDD® → Measure 3x as many samples as 25mm^2**

Precision & Background : Weak source

- **FWHM vs R_{in} (weak source)**
  - *Constant, low flux (4 kcps in 25 mm^2) at Rh K_α peak*
    - ROI width (and *B*) driven by $K_{\alpha 1} - K_{\alpha 2}$ spacing. No change with FWHM
    - All 25mm^2 FAST SDD®, SDD, and SiPIN are almost the same
    - 70mm^2 is √3x better while 6 mm^2 is 2x worse → √*Area*



  - <u>*Count rate is far more important than FWHM per se!*</u>
    - **At higher energies, detector's ^{55}Fe FWHM matters less**

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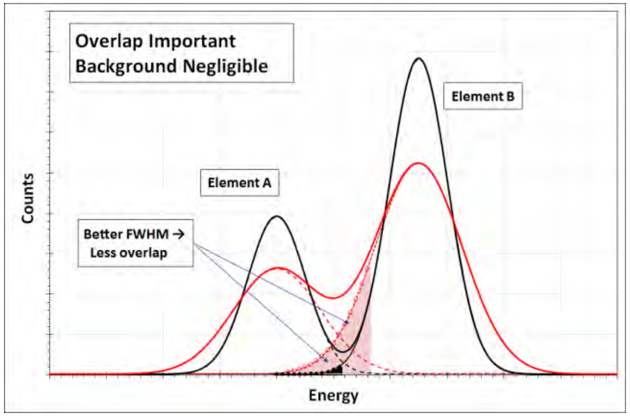
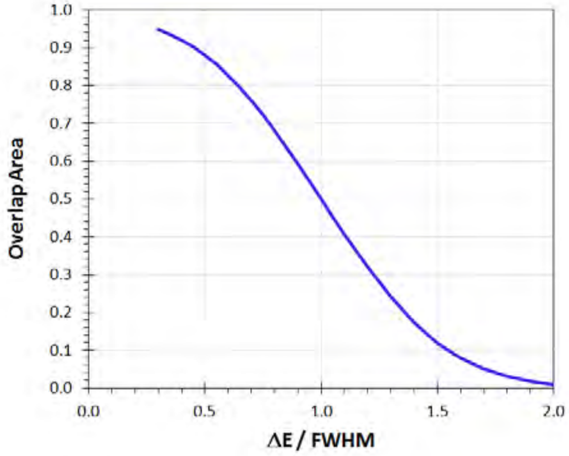
Precision & Overlap

What do we expect?

- *How much does the overlap change as FWHM improves?*
    - Assume Gaussian peak. Integrate tail of Gaussian overlapping adjacent ROI. Assume ROI is +/- FWHM.



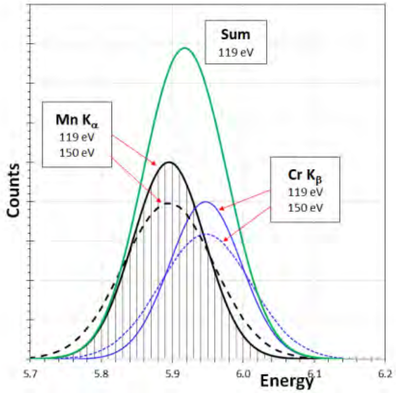
$$\int_{E_A-FWHM}^{E_A+FWHM} F_{Gauss}\left(E_B, FWHM_2\right) dE$$

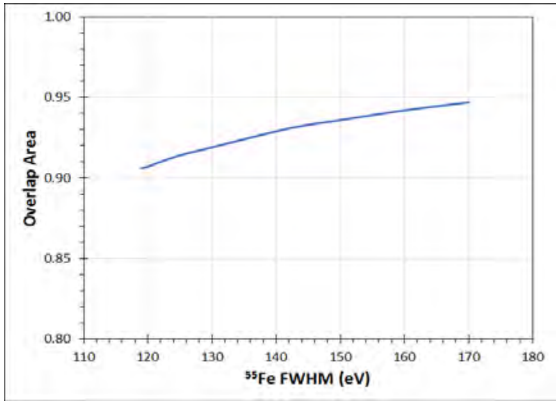


- If ΔE > 2x FWHM, overlap < 1%
    - For peaks separated this much, overlap is small so improving FWHM has little impact on precision.
- If ΔE ~ FWHM, changing FWHM by 20% changes overlap by 50%
    - Will impact precision by $\sqrt{1.5}$.
- Increasing count rate improves precision by $\sqrt{R_{out}}$

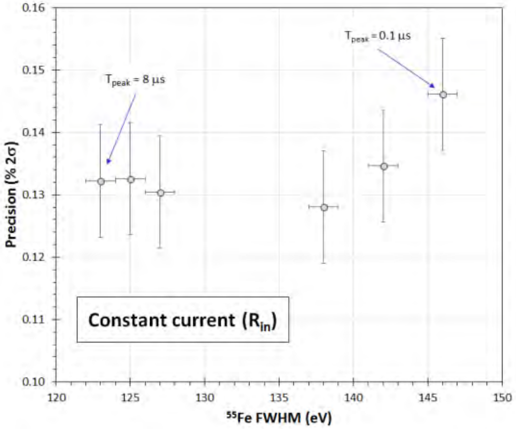
Precision & Overlap

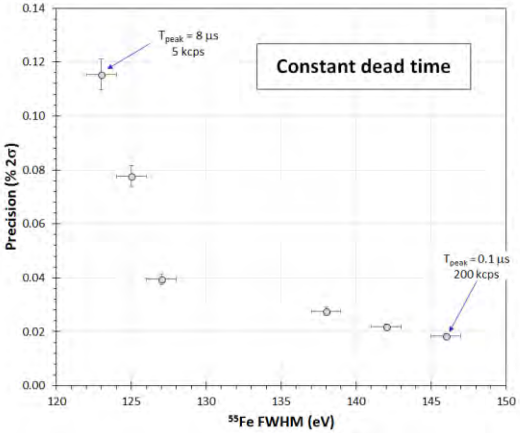
- **Practical example: Overlapping Mn/Cr K peaks in steel**
  - *Mn K_α overlaps Cr K_β → ΔE = 52 eV → Always significant overlap*
  - *Overlap of Gaussian does not change much with FWHM*





  - *FWHM at constant count rate (left) vs constant dead time (right)*

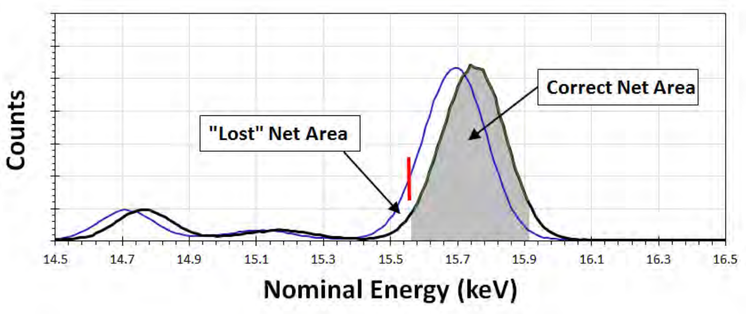


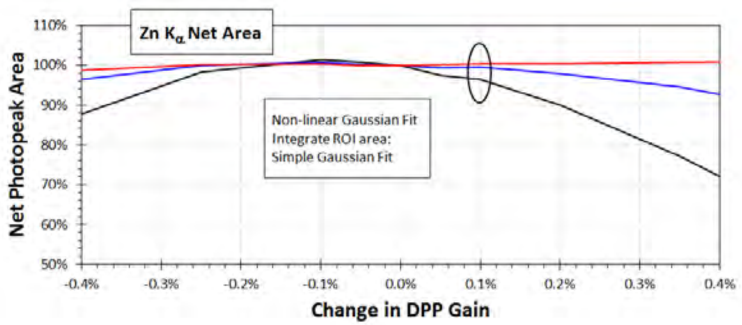


  - ***Count rate more important than FWHM for precision with overlap also***

Accuracy: Spectrum stability

Accuracy suffers if spectrum changes





- *Change centroid → Systematic error in N → Error in C_i*
  - Magnitude depends on algorithm: Gaussian fit (black) vs ROI sum (blue)
  - 0.05% change in gain (500 ppm) → 0.5% to 2% error in concentration
  - Can "adjust" centroid and FWHM on each spectrum (red) but correction is not perfect (some error), degrades precision, and adds complexity
  - In all cases, changes in centroid degrade accuracy

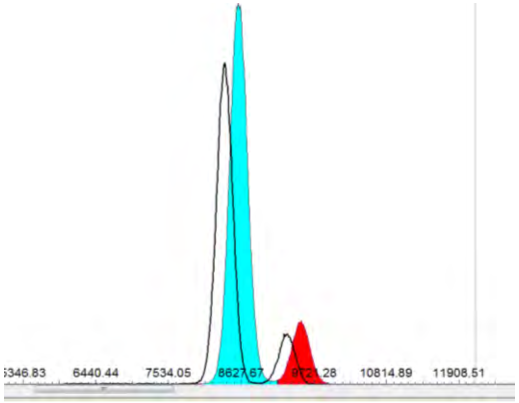
- *in FWHM or peak shape → Systematic error in overlap*
  - Magnitude of error also depends on algorithm
  - If FWHM increases, more counts "bleed" from one photopeak to next

- ***Accurate measurement ↔ Entire system must be stable***

Accuracy: Spectrum stability

What causes spectrum to shift?

Sample of poor BLR

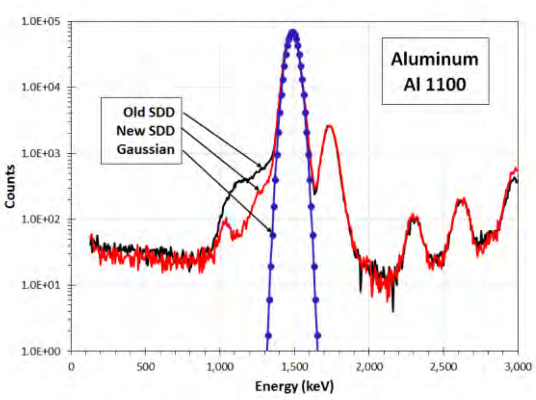


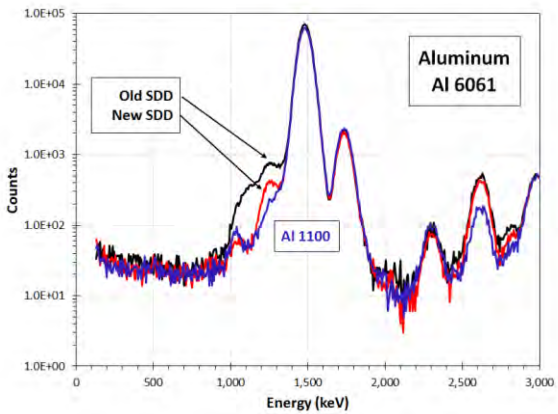
- *Count rate stability*
  - Baseline (offset) shifts with rate (AC coupling)
    - Baseline restoration keeps baseline stable
  - FWHM often degrades with rate
    - Many causes and mechanisms
  - Dead time correction is only approximate
- *Temperature stability*
  - Detector temperature impacts gain stability strongly
    - Energy required to create e-h pair changes by ~150 ppm/°C
    - Stabilizing detector temperature is crucial
  - Other electronics have small but non-zero temperature drifts
    - Careful design needed for stability
    - Software methods generally also used to mitigate drifts
- ***Accurate measurement ↔ Entire system must be stable***

Accuracy: Models are approximate

Non-Gaussian Photopeak

- *Photopeaks are never purely Gaussian*
  - Physics plus detector effects
- *How important is the tail from charge collection?*
  - Plot on left shows pure Al. Blue is ideal Gaussian. New SDD (red) has much less “tail”
  - Plot on right shows 1% Mg in Al. New SDD (red) has much less background in Mg ROI from the Al (a.k.a. “bleed).
  - Table shows analysis result. New SDD has better precision (fewer counts from overlap) and lower detection limit (accuracy of model)





Mg in Al alloys

		Old SDD	New SDD
Al 1100	0.0% ± 0.05%	0.5% ± 0.21%	0.1% ± 0.11%
Al 6061	1.0% ± 0.05%	2.1% ± 0.26%	1.0% ± 0.15%
Al 5086	3.7% ± 0.05%	4.4% ± 0.38%	3.5% ± 0.23%

- ***Non-Gaussian tail important for accuracy, especially near LOD***

Detection Limit: Precision and Accuracy

Precision and detection limits

- *Signal from analyte must be 3x the uncertainty. Statistical precision sets a limit for minimum N, based on B and P*

$$N_{DL} \geq 4.6\sqrt{(B+P)}+2.7$$

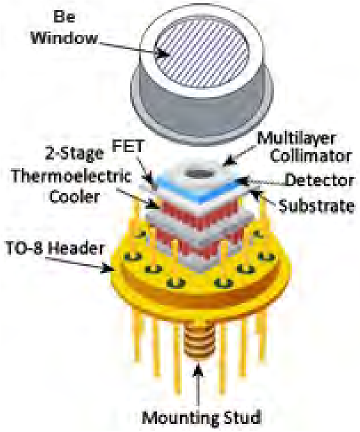
- *In practice, overlapping peaks usually more important than background*
- *As discussed, for best statistical limit, maximizing count rates is best*

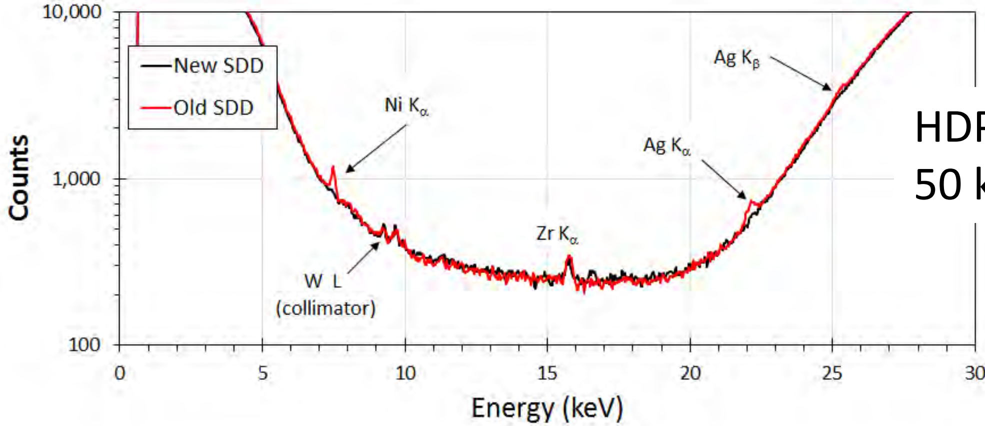
Accuracy and detection limits

- *Accuracy of models used to remove overlap usually drive detection limit*
- *Counts from one element "bleed" into adjacent → Misidentified counts*
  - Non-Gaussian photopeak tails
  - Changes in centroids and FWHM
  - Other artifacts (from electronics, detector, or physics) which are improperly modeled or change from calibration conditions
- *Methods to improve accuracy already discussed*

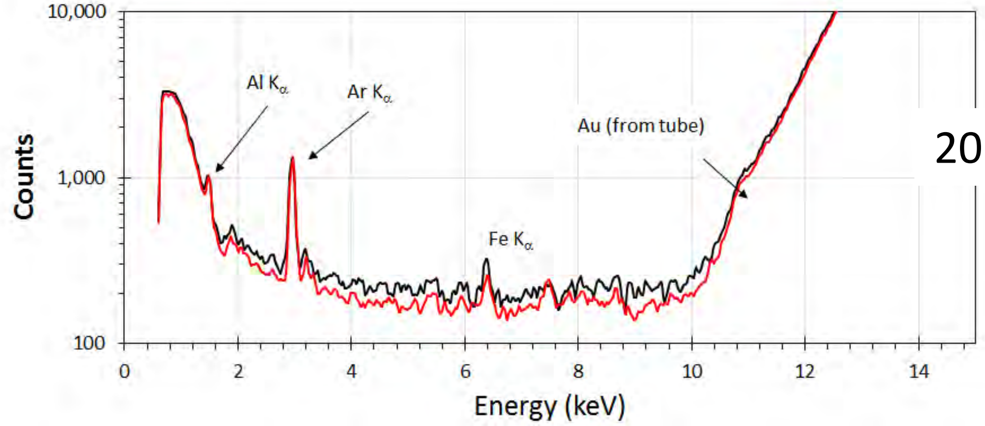
Detection Limit: Interference

- **Interfering lines from the instrument**
  - *Real detector surrounded by many materials → characteristic X-rays*
  - *Careful selection, layout, shielding to minimize*
  - *Amptek improved 25 mm^2 FAST SDD®, eMLC*

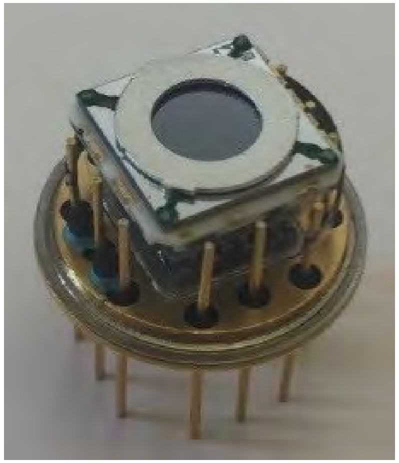




HDPE target
50 kV



20 kV



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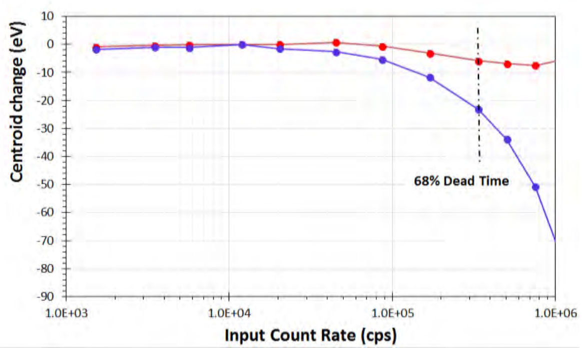
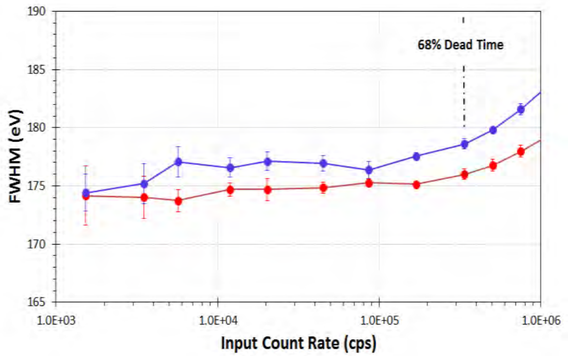
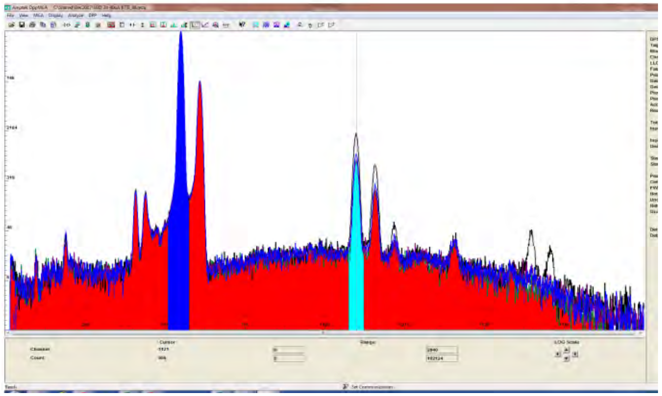
Stability at High Count Rates

- **Amptek has improved electronics for high rates**
  - *Baseline stability improved in new firmware*



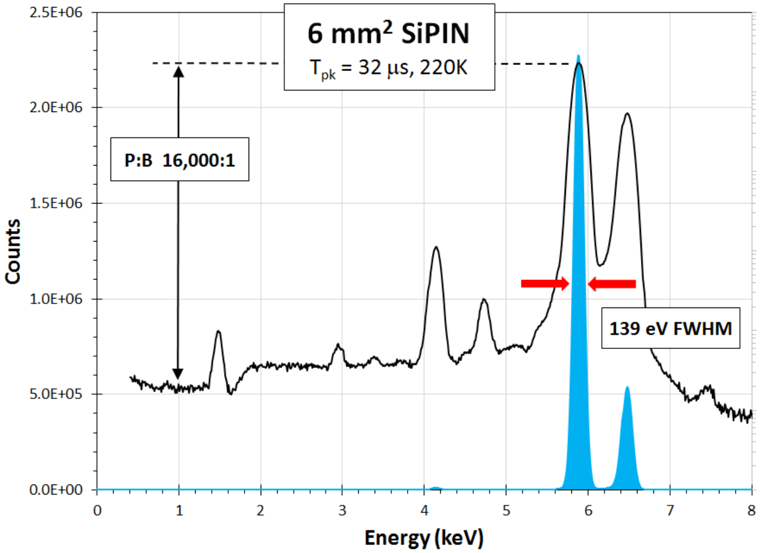


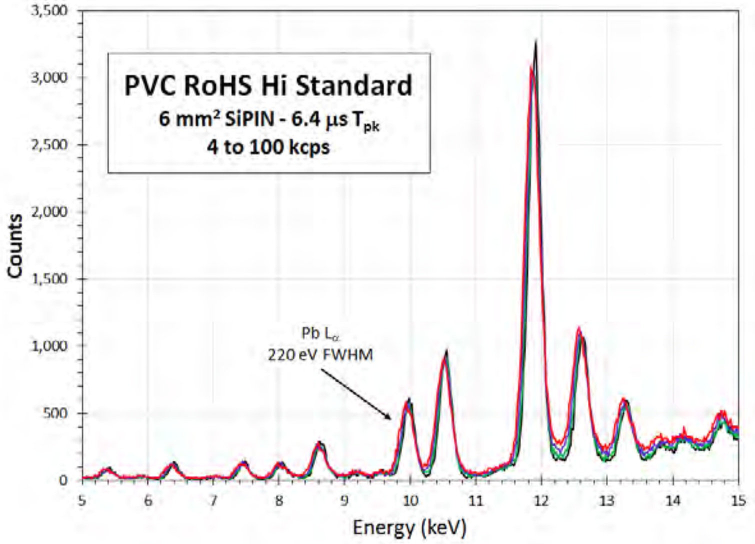
  - *Pile-up rejection improved in new firmware*



  - *Faster reset recovery, better temperature coefficients*

SiPIN: 6 and 25 mm^2





- **^{55}Fe spectrum as "figure of merit"**
  - *SiPIN FWHM is < 139 eV, P:B is typically 16,000*
  - *Significant improvements – but at T_{pk} of 32 μs where R_{out} is low*
- **PVC RoHS standard at 4 to 100 kcps**
  - *More meaningful indicator of "improvement"*
  - *At T_{pk} = 6.4 μs, 165 eV FWHM, R_{out} = 30 kcps, stable spectra*

SiPIN: 6 and 25 mm^2

Typical – 6 mm^2

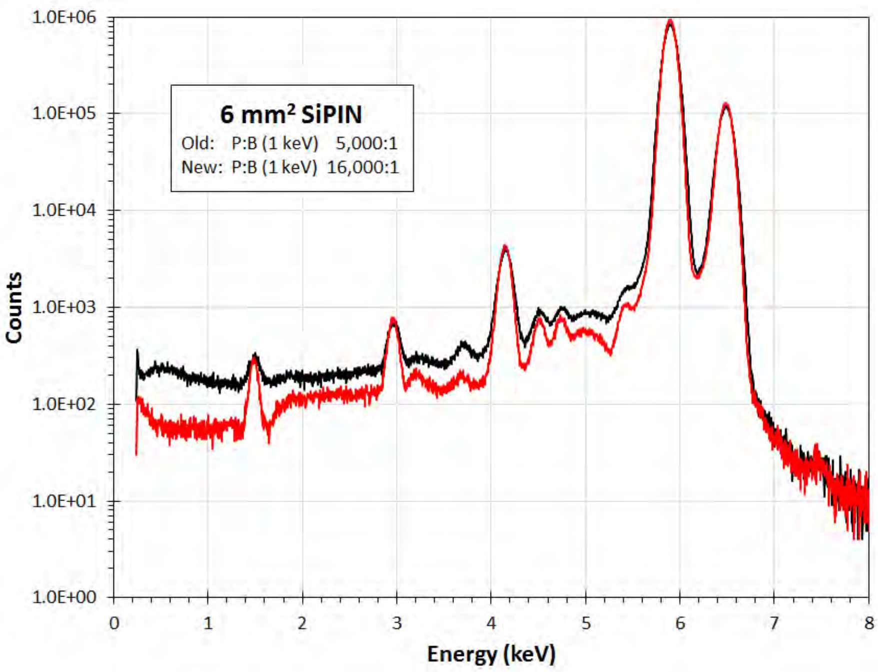
145 eV – 19 μs – R_{out}=10 kcps
160 eV – 19 μs – R_{out}=10 kcps @ 0°C

165 eV – 6.4 μs – R_{out}=30 kcps

Typical – 25 mm^2

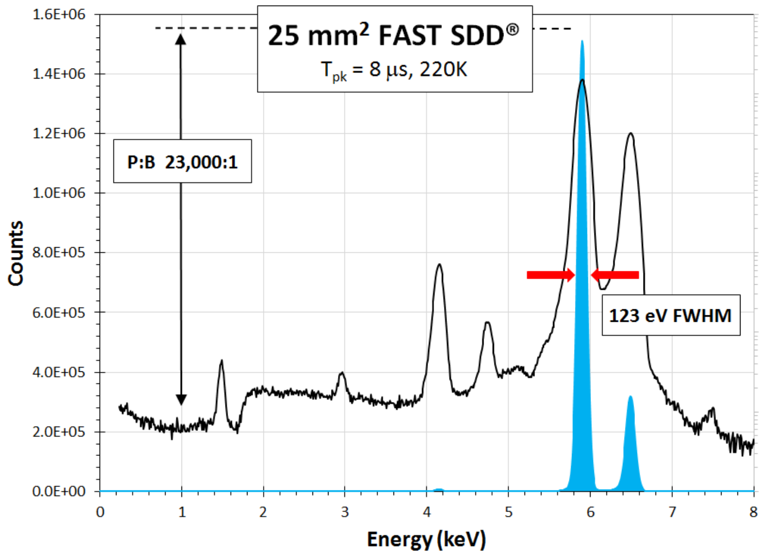
220 eV – 19 μs – R_{out}=10 kcps
260 eV – 19 μs – R_{out}=10 kcps @ 0°C

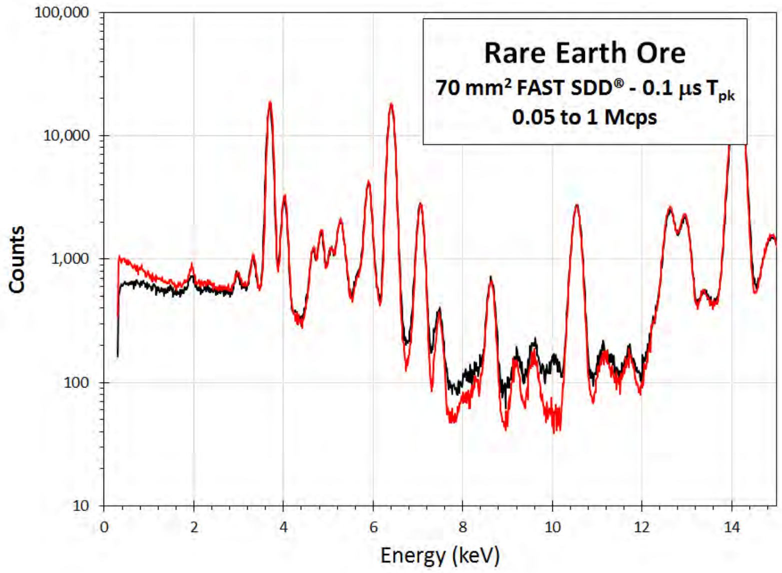
300 eV – 6.4 μs – R_{out}=30 kcps



- **Operation at 0°C is important**
  - *Excellent temperature stability over wide range of ambient conditions*
  - *Minimum power on TEC (40 mW at 20°C ambient)*
- **Performance of 25 mm^2 SiPIN is important**
  - *Excellent at higher energies, where line broadening dominates, up to 50 kcps*
- **Improved photopeak response is important**
  - *Reduced tail improves accuracy and detection limit of light elements*

FAST SDD®: 25 and 70 mm^2





- ^{55}Fe spectrum as "figure of merit"
  - *FAST SDD® FWHM can be 122 or 123 eV FWHM (both 25 and 70 mm^2)*
  - *Typical is 124 eV, P:B 23,000. Near Fano limit of 119 eV*
- Rare earth ore at 50 kcps to 1 Mcps
  - *More meaningful indicator of "improvement"*
  - *At T_{pk} = 1.0 µs, 126 eV FWHM, R_{out} = 170 kcps, stable spectra*
  - *At T_{pk} = 0.1 µs, 148 eV FWHM, R_{out} = 900 kcps, stable spectra*

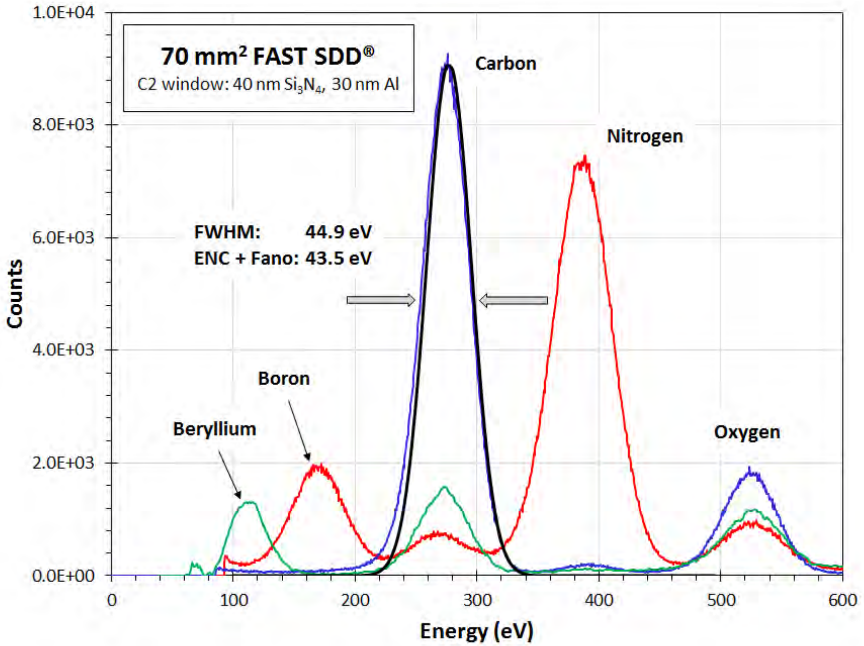
FAST SDD®: 25 and 70 mm^2

Typical – 25 mm^2

126 eV – 1.0 μs – R_{out}=170 kcps
130 eV – 1.0 μs – R_{out}=170 kcps @ 0°C

134 eV – 0.2 μs – R_{out}=600 kcps
148 eV – 0.1 μs – R_{out}=900 kcps

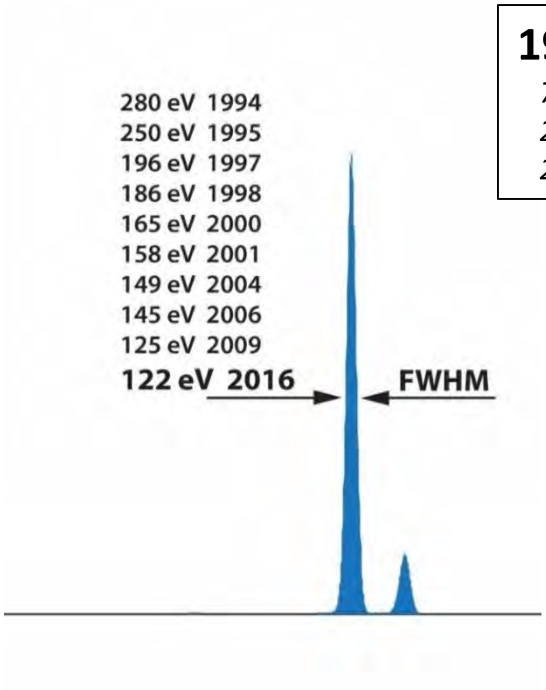
25 mm^2 70 mm^2 160 mm^2



- **Large areas: 25, 70, even 160 mm^2**
  - *With FAST SDD®, performance (nearly) independent of area*
- **Improved photopeak response is important**
  - *Even at C K_α deviation from Gaussian very small*
- **Operation at 0°C is important**
  - *Excellent temperature stability and low cooling power*

Conclusions

- **^{55}Fe FWHM alone is not the key parameter**
- **Precision**
  - *High count rates improves statistical precision far more than FWHM*
    - One can get more improvement through high count rate than good FWHM
    - True for both background limited case and overlapping peaks
  - *If source is intense enough, short T_{pk} and high rate is best*
  - *If source is weak, increasing area or efficiency is best*
- **Accuracy**
  - *Degraded if spectrum changes after calibration*
  - *Degraded if real response deviates from models*
- **Detection Limit**
  - *Needs statistical precision → maximize count rates*
  - *Needs accurate overlap model*
  - *Needs minimum detector interferences*
- **Amptek delivers range of products, optimized for these needs**

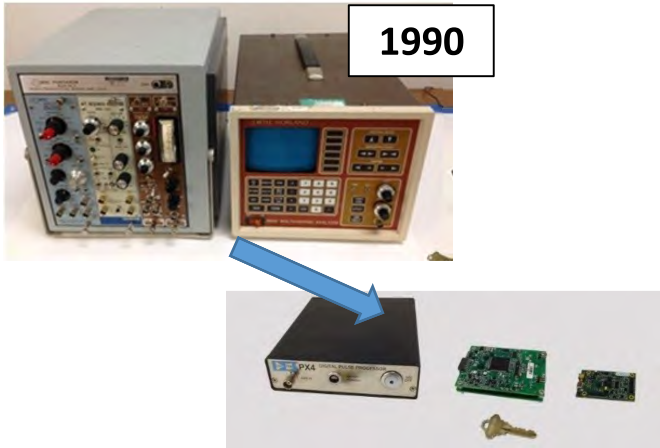


1994
7 mm^2
280 eV
2,000 cps

1998
7 mm^2
186 eV
20,000 cps

2008 SDD
25 mm^2
125 eV
100,000 cps

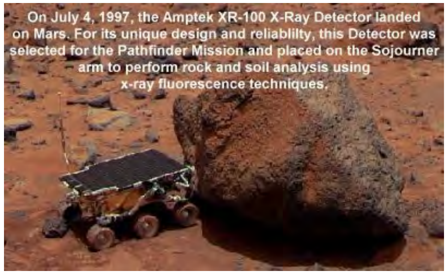
2016 FAST
70 mm^2
123 eV
2,000,000 cps



1990

2004 2008 2016

Since 1977: Amptek celebrates 40+ years of innovation!


On July 4, 1997, the Amptek XR-100 X-Ray Detector landed on Mars. For its unique design and reliablilty, this Detector was selected for the Pathfinder Mission and placed on the Sojourner arm to perform rock and soil analysis using x-ray fluorescence techniques.