STATUS OF THE MONTE CARLO - LIBRARY LEAST-SQUARES (MCLLS) APPROACH FOR XRF ANALYSIS WITH APPLICATION TO ERROR ANALYSIS

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TOPICS

- Introduction
- Correction of Pulse Pile-Up Spectral Distortion
- The Monte Carlo – Library Least-Squares (MCLLS) Approach for XRF Analysis
- The CEARXRF Monte Carlo Code
- Implementation with a GUI
- Results with a Cd-109 Source
- Discussion, Conclusions, and Future Work

INTRODUCTION

EDXRF has always had the two problems of:

(1) measuring X-ray intensity and

(2) dealing with non-linear response.

The present MCLLS approach provides the means for a practical very accurate solution to both of these problems – thus providing a practical very accurate solution to the EDXRF inverse problem. LLS provides the first and MC the second.

INTRODUCTION, 2

- What are the differences between the **Fundamental Parameters** (FP) and the **Monte Carlo – Library Least-Squares** (MCLLS) Approaches?

1. FP, with assumptions, is usually analytical and can be used in real time or near real time analysis.
2. **Do these assumptions introduce significant error?**
3. MCLLS is capable of full simulation of the usual XRF conditions.
4. For useful accuracy, simulations have taken too much time for real time analysis – **in the past!** **The introduction and use of Differential Operators has changed this.**

CORRECTION OF PULSE PILE-UP SPECTRAL DISTORTION

- For a number of reasons one may encounter or have to use high counting rates and the resulting pulse pile-up spectral distortion in XRF analysis. (For example: *In Vivo* Pb in bone and portable units.)
- The new digital counting electronics only increase the counting rate levels somewhat that can be used without this distortion – and this is usually with resolution and unknown variance penalties.
- In most cases this distortion can be completely corrected for by mathematical means without these penalties.

CORRECTION OF PULSE PILE-UP SPECTRAL DISTORTION, 2

- **CEAR has been working for some time on an off-line approach and more recently on an on-line approach. These will be briefly described here. Our most recent references on these are:**
- **Off-Line Approach**: W. Guo, R.P. Gardner, and F. Li, A Monte Carlo code for simulation of pulse pile-up spectral distortion in pulse-height measurement, Denver X-Ray Conference, 2004.

  W. Guo, S. H. Lee, and R. P. Gardner, The Monte Carlo Approach MCPUT for Correcting Pile-Up Distorted Pulse-Height Spectra, Nuclear Instruments and Methods in Physics Research A, **531**, pp. 520-529, 2004.
- **On-Line Approach:** W. Guo, R.P. Gardner, and C.W. Mayo, A study of the real-time deconvolution of digitized waveforms with pulse pile up for digital radiation spectroscopy, Nuclear Instruments and Methods in Physics Research A, **544**, pp. 668-678, 2005.

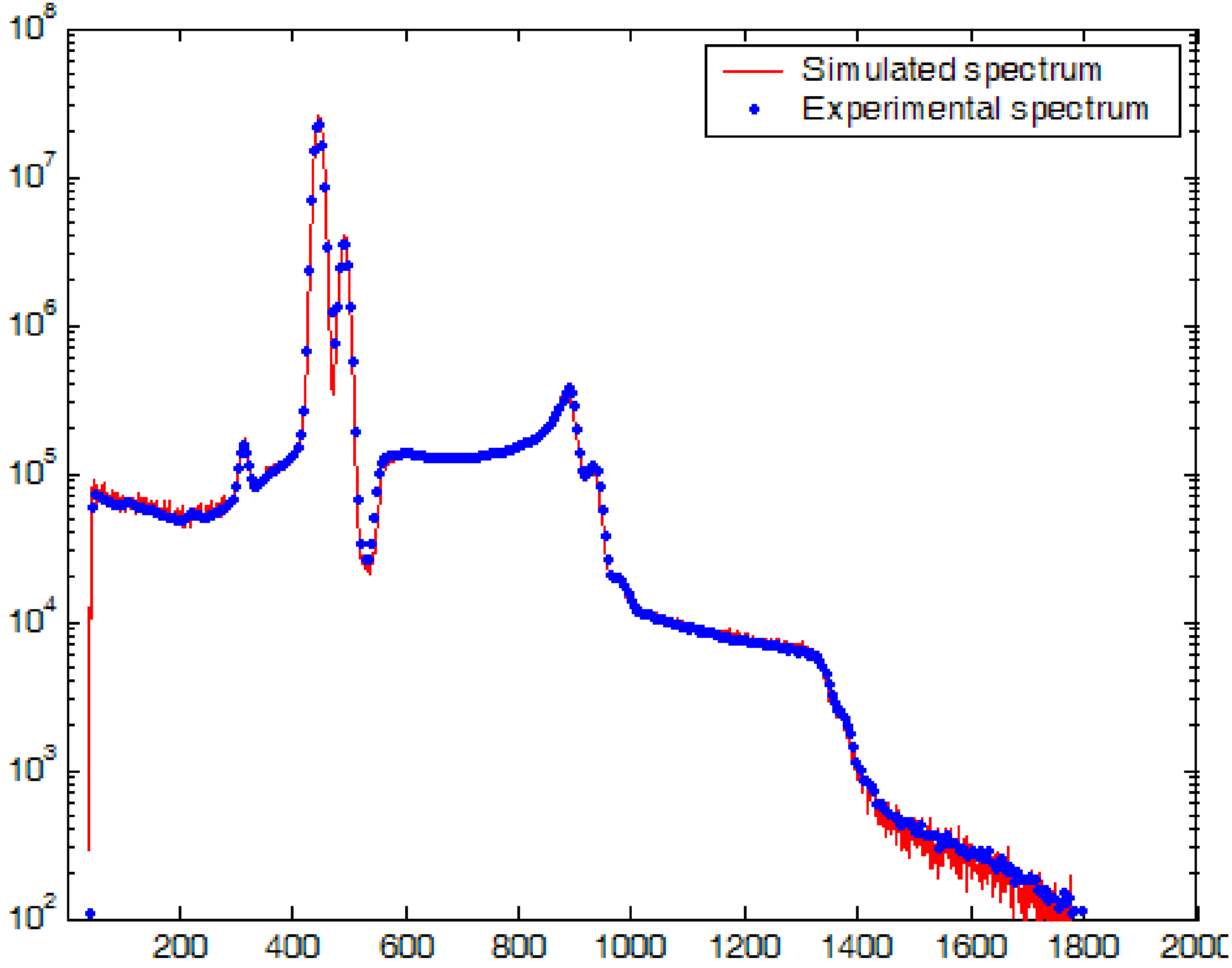
THE OFF-LINE APPROACH

- The off-line approach developed at CEAR consists of first developing an accurate Monte Carlo code (CEARPPU) to treat the forward calculation of the pile-up distorted spectrum from the known (or assumed) true spectrum. This is in the Public Domain - PSR-528 @ RSICC. ORNL (Available from Radiation Safety Information Computational Center (RSICC) at Oak Ridge National Laboratory, ORNL.)
- This code is fast enough (one case takes a minute or two) that it can be iterated to give the required true spectrum.

ADVANTAGES/DISADVANTAGES OF THIS APPROACH

- ADVANTAGES: (1) for a constant or known form of the counting rate with time, it is very accurate; (2) if the range of the true pulse-height energy is known, it can even treat random true coincidences and iterations converge rapidly; and (3) under these specified conditions, the true spectrum is generated with original resolution and Poisson variance. (Could add Differential Operators.)
- DISADVANTAGE: The necessary conditions may not exist.

CEARPPU – Simulation Results for an Fe-55 Source and a Si(Li) Detector



THE ON-LINE APPROACH

- When the conditions necessary for using the off-line approach are not present – an on-line, real-time approach may be more appropriate.
- CEAR has been working on the use of a digitizer and a PC to replace the use of Multi-channel Analyzers -preliminary studies have been promising.
- This approach consists of digitizing the signal at the preamplifier output without further pulse shaping. Then differentiation of this signal train and use of simple pulse models allows the generation of the true pulse-height spectrum.

NEW ON-LINE APPROACH RESULTS

Fig. 9 shows the simulated spectra at two different counting rates. It is obvious that the standard features in a gamma-ray spectrum are completely smeared at 4M cps. Fig. 10 shows the simulated spectra acquired when the DPD real-time deconvolution approach was applied. The peak resolution at 4M cps is still maintained very close to the one at the low counting rate of 1k cps. The overall spectral shape was maintained and the chi-square test for these two spectra reported a reduced chi-square value of 1.6.

NORMAL SPECTRAL RESULTS

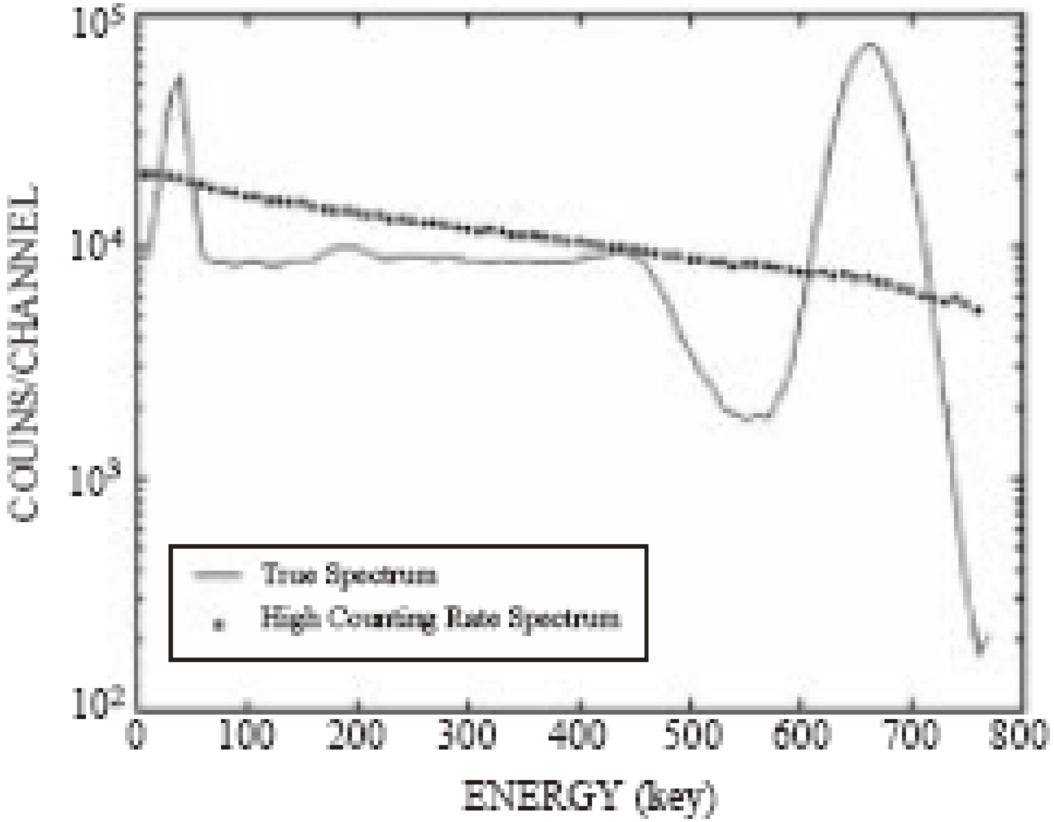


Fig. 9. NaI(Tl) spectra for variable counting rates without application of the pulse pile-up deconvolution approach.

RESULTS FOR THE ON-LINE APPROACH

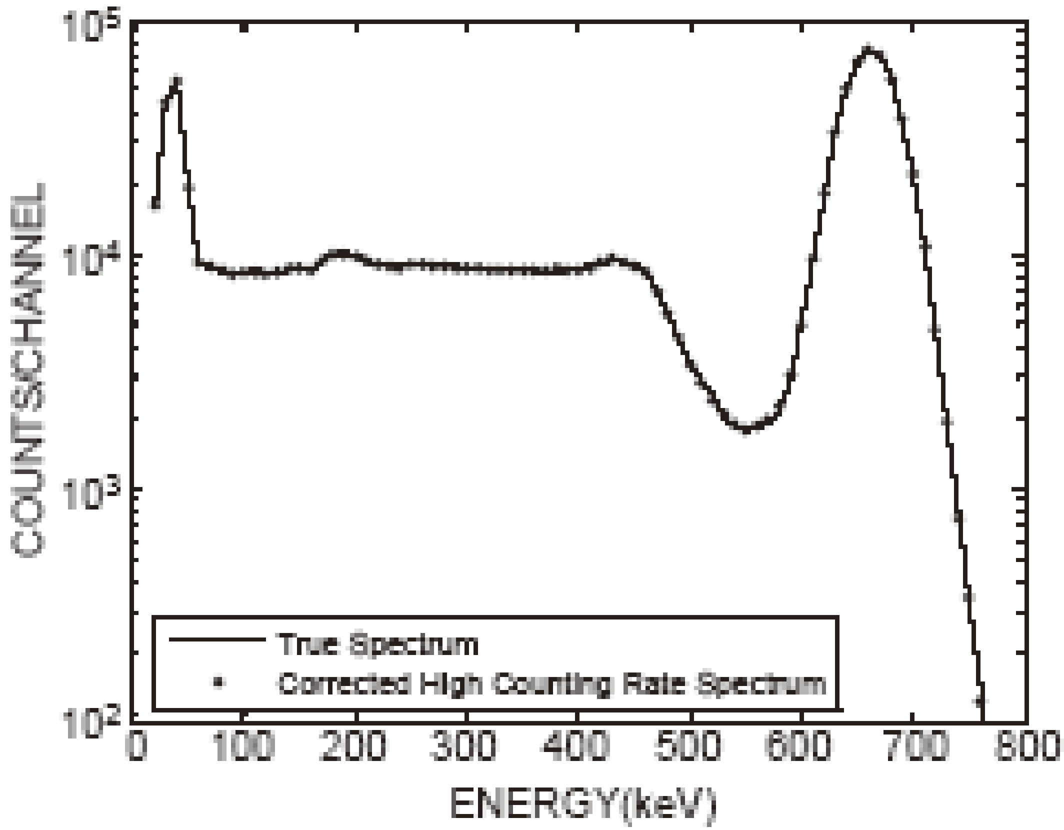


Fig. 10. NaI(Tl) spectra for variable counting rates with the pulse pile-up deconvolution approach applied.

THE MCLLS APPROACH FOR XRF ANALYSIS

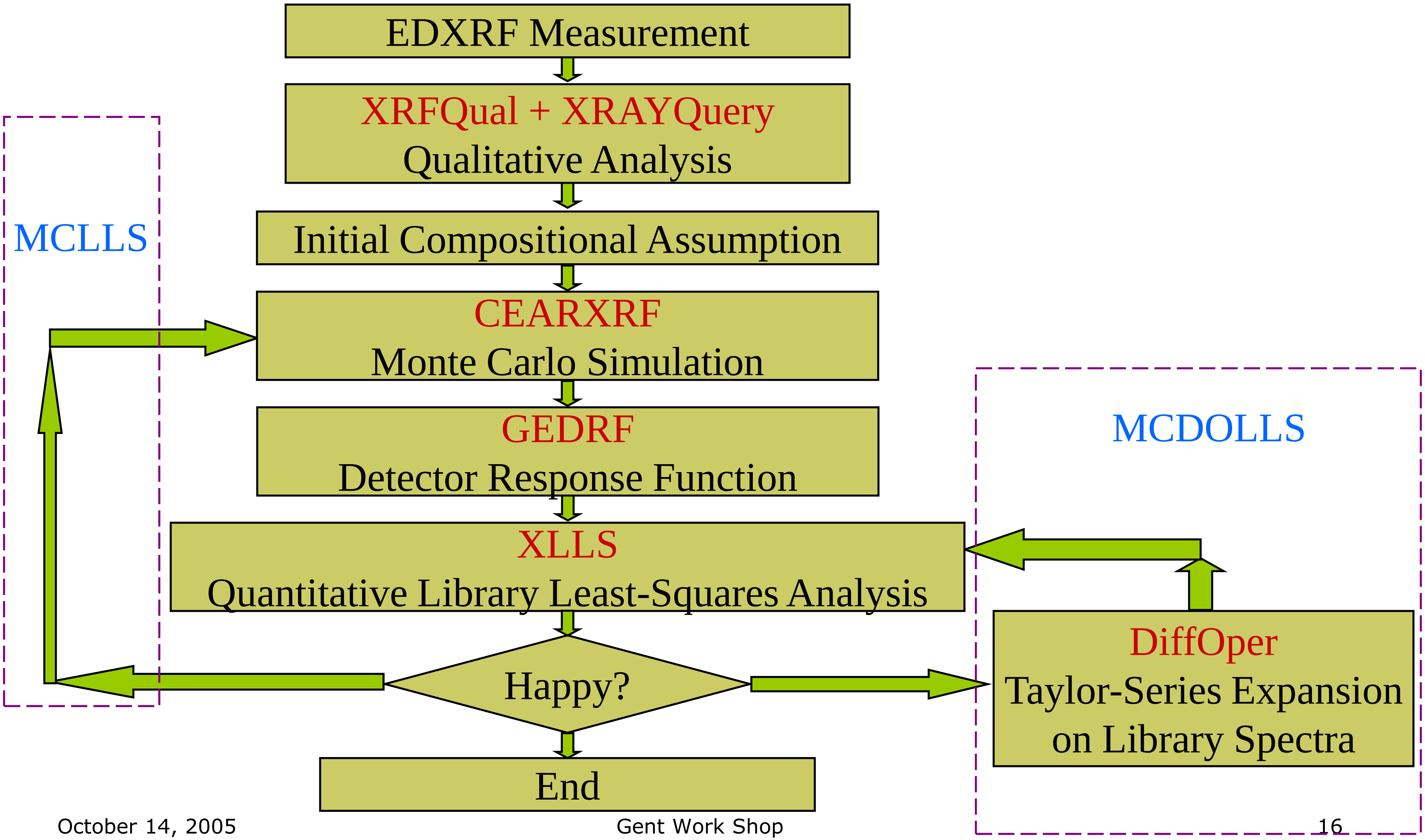
The MCLLS approach consists of:

1. Assuming a sample composition as close to the actual one as possible.
2. Using Monte Carlo simulation to simulate the individual responses to each element in the sample to provide elemental libraries.
3. With these elemental libraries and the experimental sample spectrum use the (linear) library least-squares (LLS) approach to calculate the sample composition.
4. If the calculated and assumed compositions do not match, assume a new sample composition equal to the calculated one and iterate from Step 2 until they converge.

ADDITION OF THE DIFFERENTIAL OPERATOR APPROACH

- The MCLLS approach just described suffered from the disadvantage that the Monte Carlo simulation takes a long calculation time (about three hours at present) so that iteration steps were not practical.
- A new approach called Differential Operators has been devised that allows a Taylor Series type extension to the Monte Carlo simulation. This extension allows iterations that are very fast -- allowing real-time iterations to be made.

MCLLS Analytical Procedure

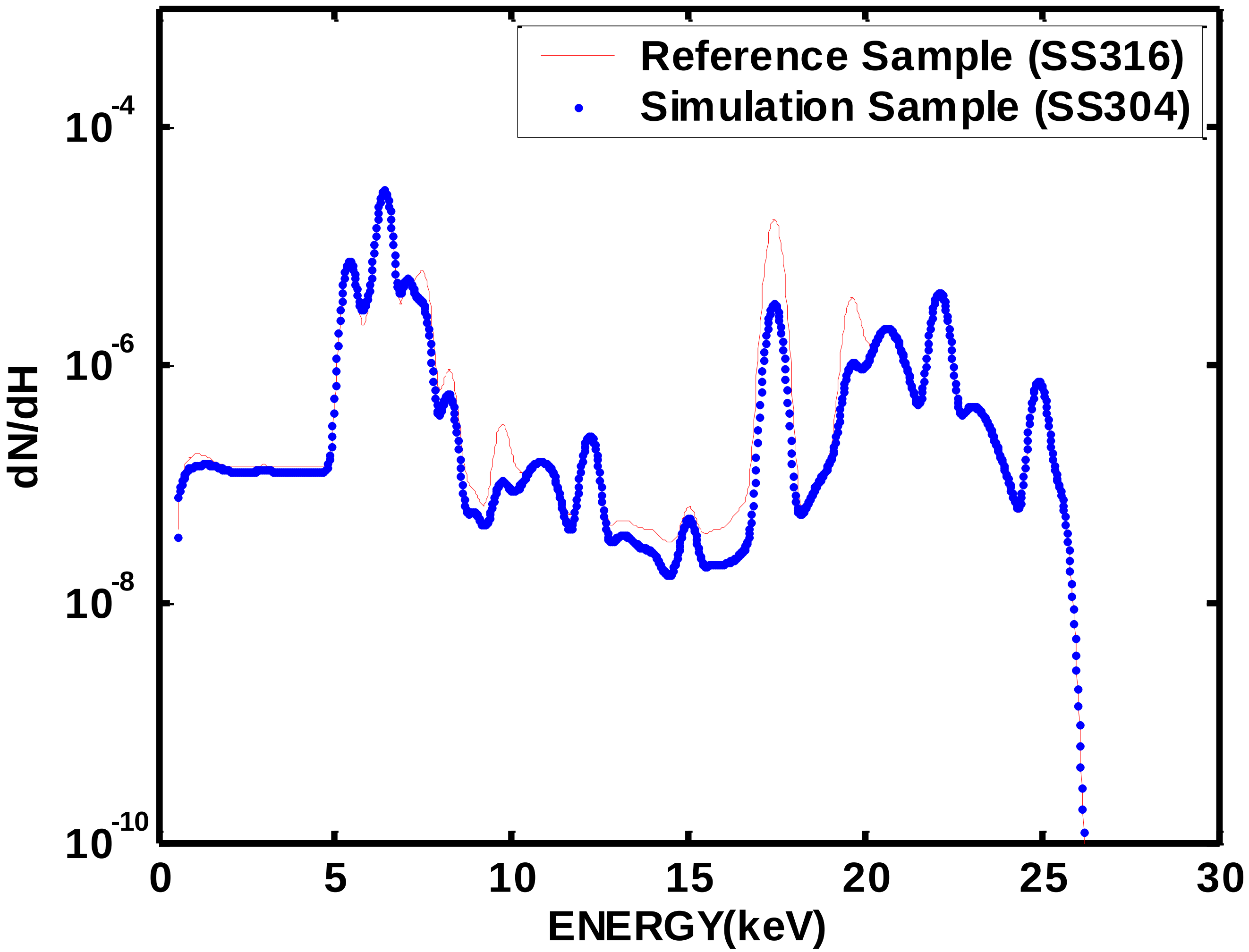


Differential Operators – Taylor Series Expansion

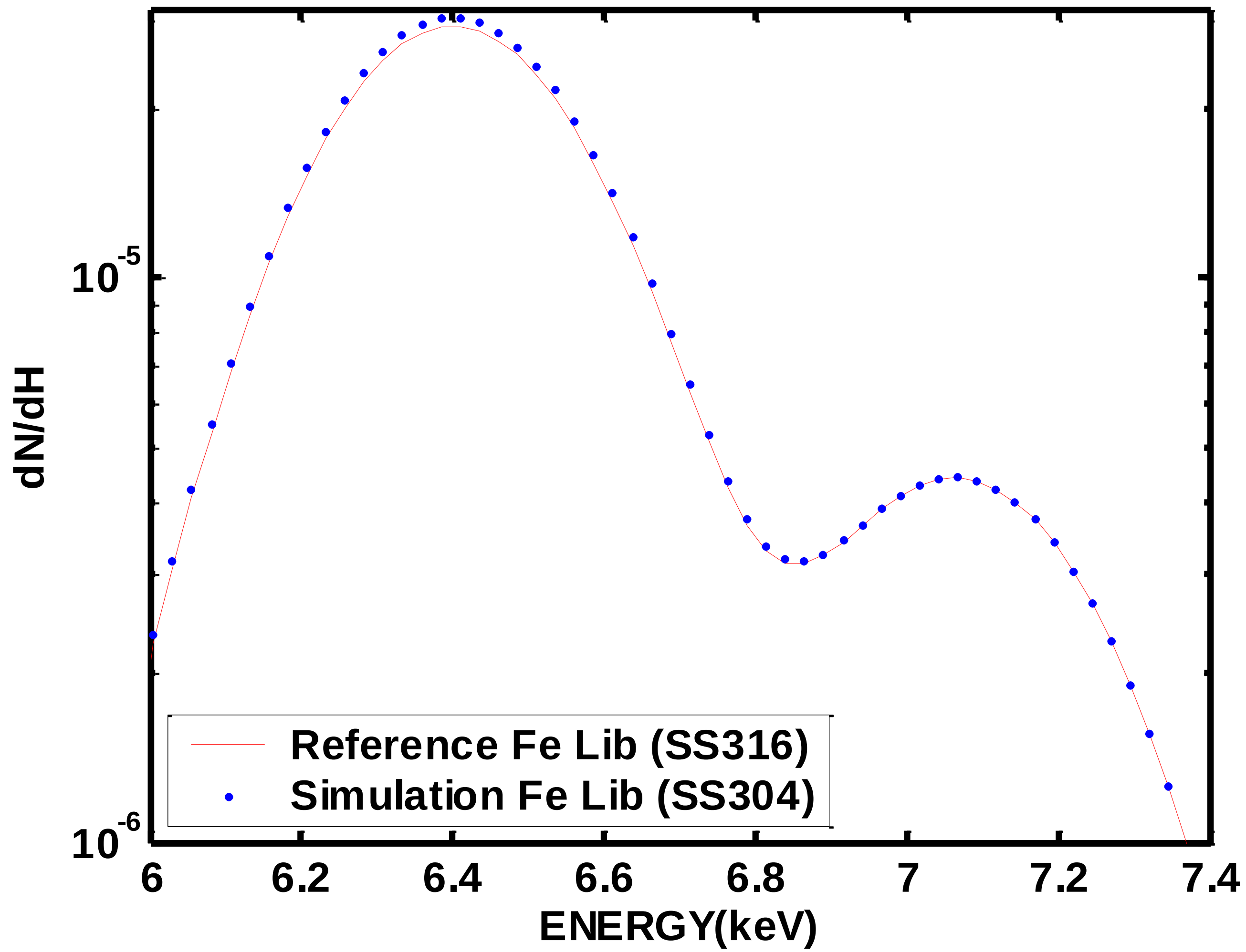
$$R(w_{1,x}, w_{2,x}, \ldots w_{n,x}) = R(w_{1,0}, w_{2,0}, \ldots w_{n,0}) +$$

$$\sum_{i=1}^{n} (\partial R / \partial w_{i,x})(w_{i,x} - w_{i,0}) + O(w_x - w_0)^2$$

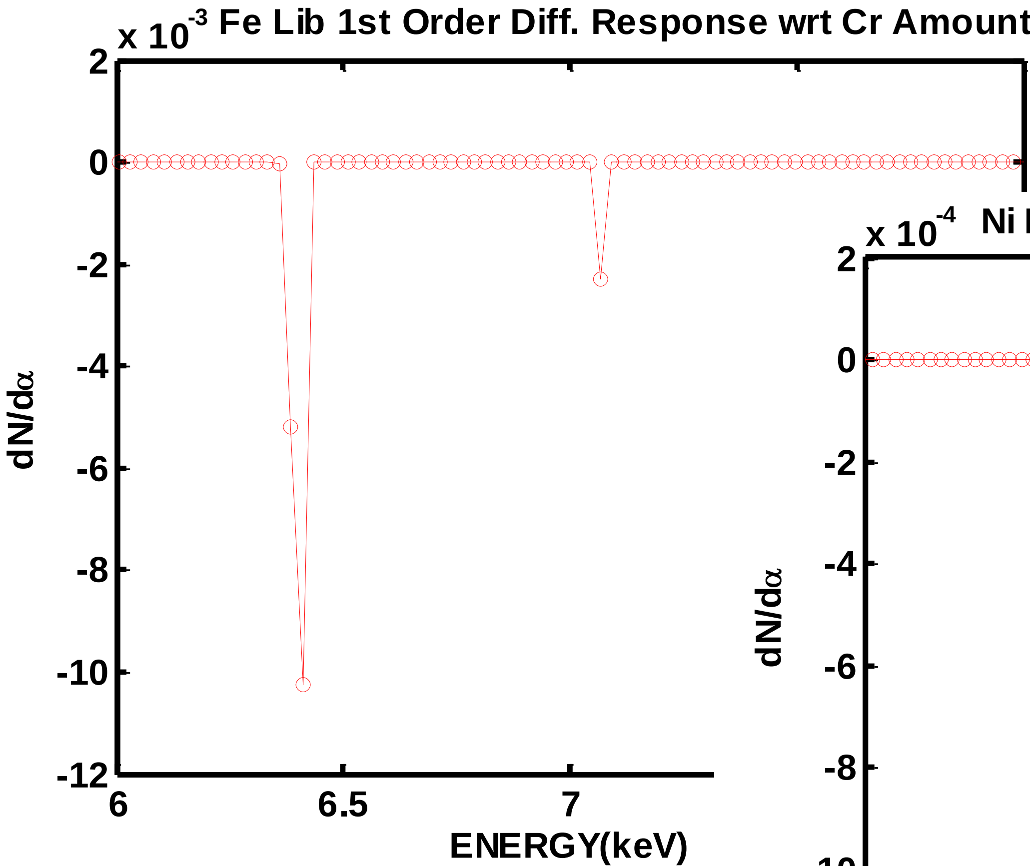
Differential Operators – Sample Spectra Comparison

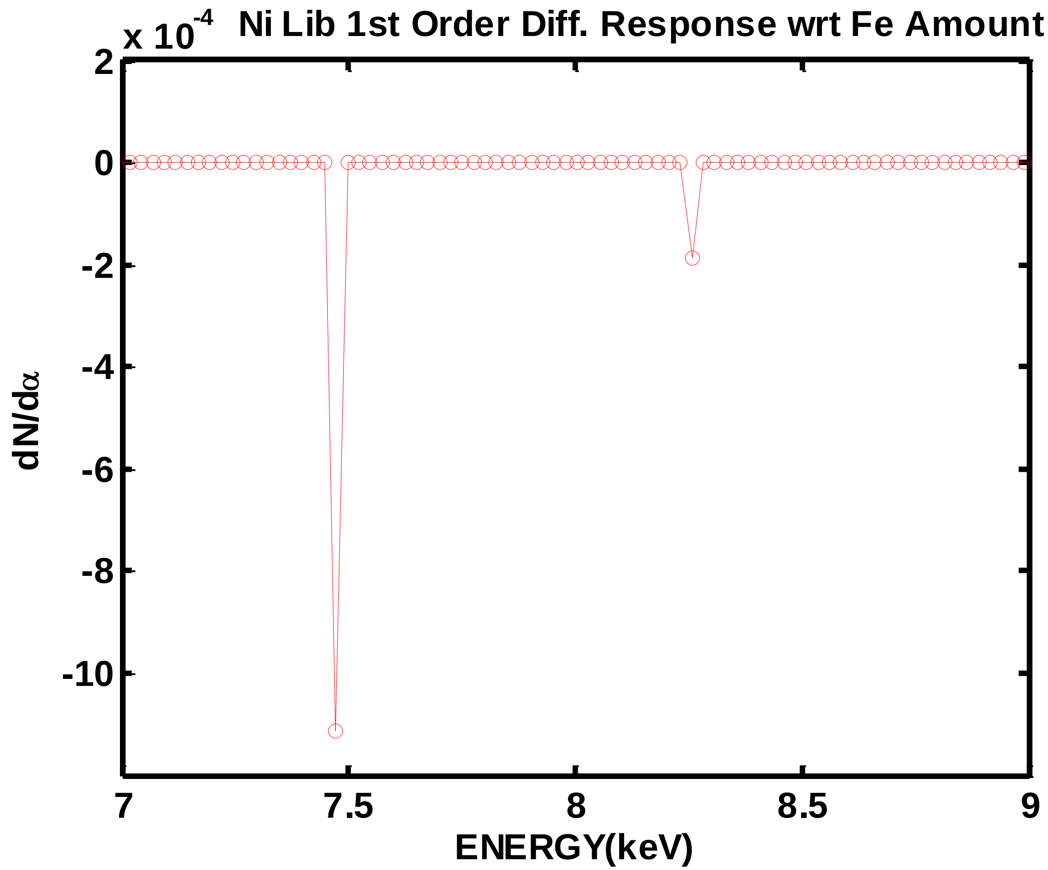


Differential Operators – Library Spectra Comparison

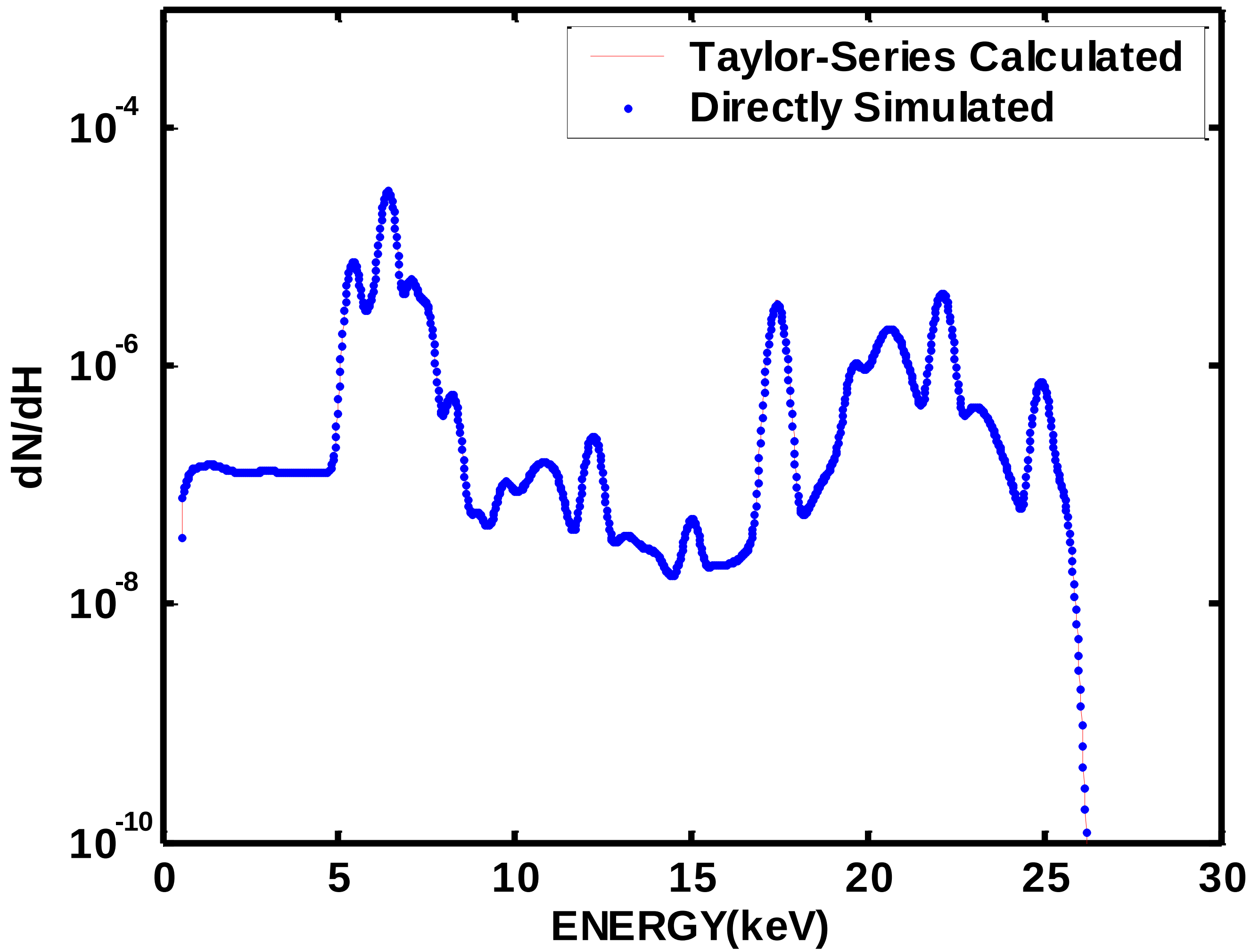


Differential Operators – Differential Responses

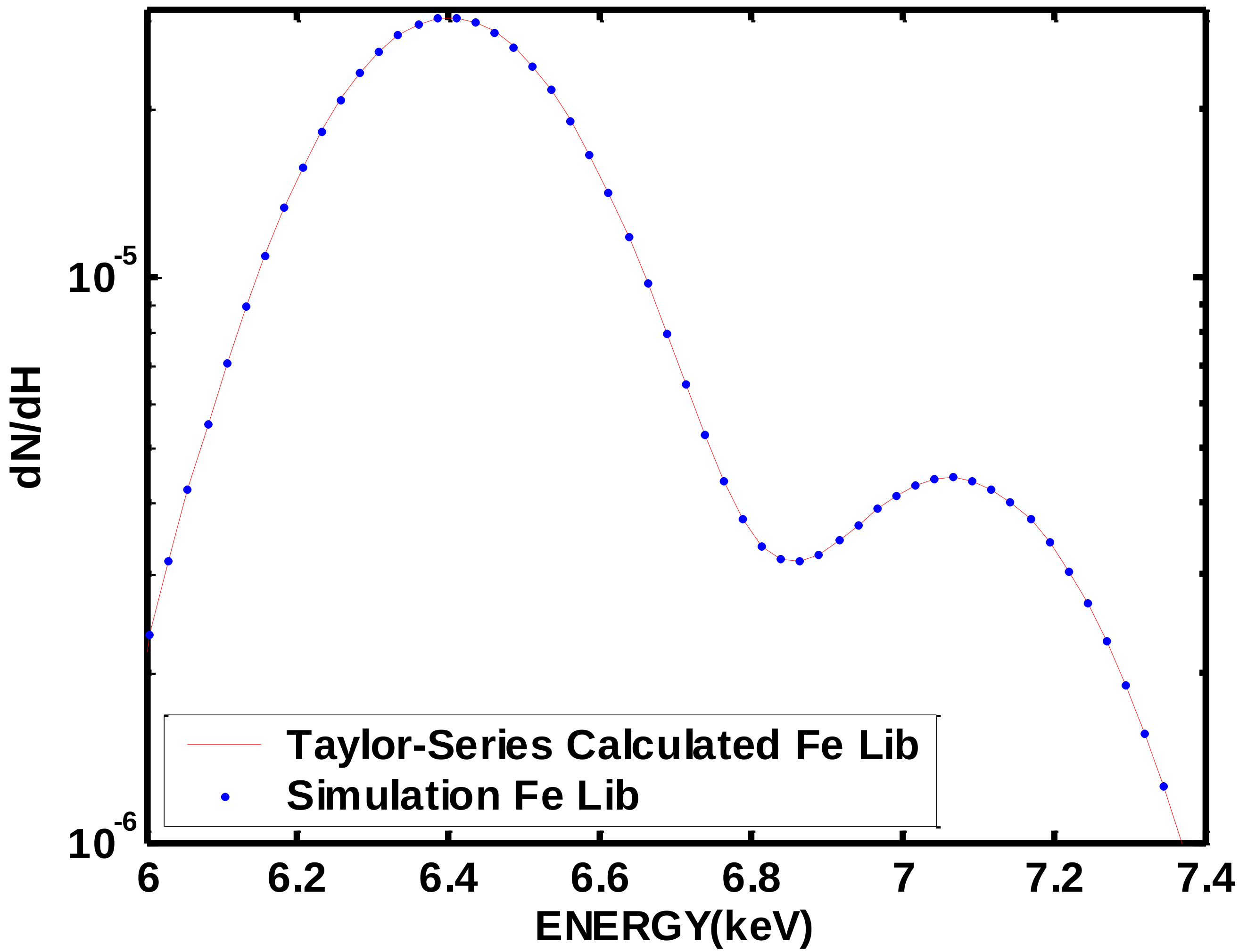




Differential Operators – Sample Spectra



Differential Operators – Library Spectra



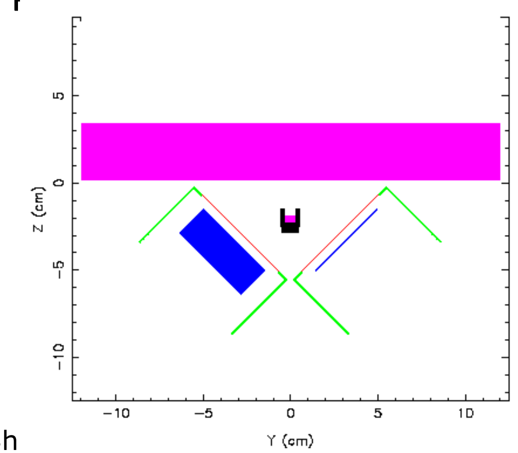
THE CEARXRF MONTE CARLO CODE

- Monte Carlo codes for simulating photon transport
  - All three interactions for low energy photon transport
    - Compton scattering
      - Klein-Nishina Differential CS + Incoherent scattering function + Doppler broadening
    - Rayleigh scattering
      - Thomson Differential CS + Atomic form factor
    - Photoelectric effect
      - Shell-wise cross section data for all K, L1, L2 and L3.
  - K and L X-ray coincidence model (CEARXRC)
  - Accepts both radioisotope or X-ray tube as activation source
  - Flexible sample definition for both shape and composition
  - Simulation of Polarization physics
  - Includes coincidence counting
- Developed and continuously updated by our center, CEAR @ NCSU
- Coded in Fortran 77 on Sun Solaris, ported to PC (both Cygwin and Windows)
- The Detector Response Function (DRF) is a major variance reduction approach.

CEARXRF – How to use it?

- Text input file (for Cd-109)
  - (dene(i),temp1(i),temp2(i),i=1,ndisc)
  - 21.988e-03 .275983 1.
  - 22.162e-03 .520282 1.
  - 24.907e-03 .049169 1.
  - 24.938e-03 .095633 1.
  - 25.452e-03 .024778 1.
  - 88.035e-03 .034155 1

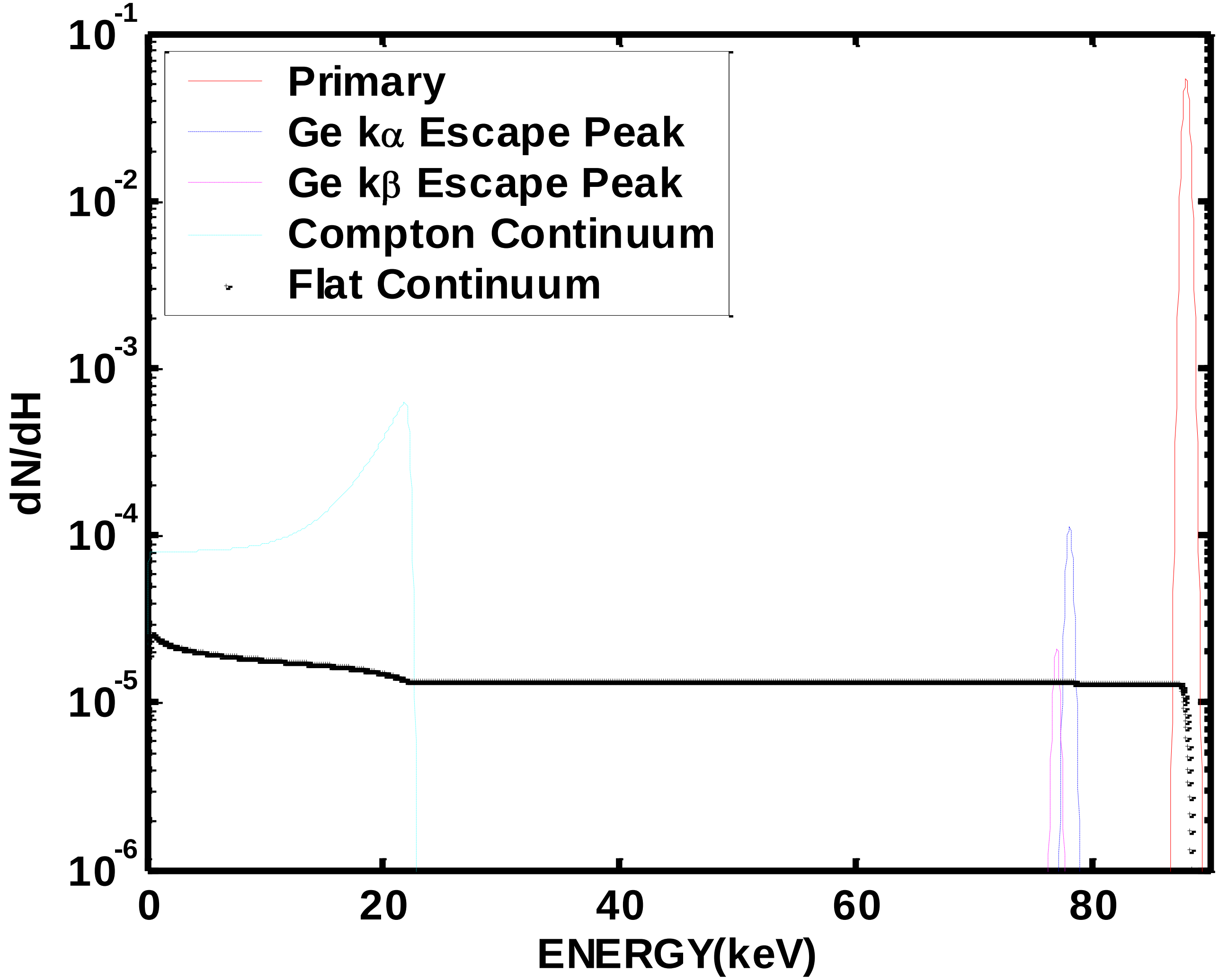
- Text geometry file



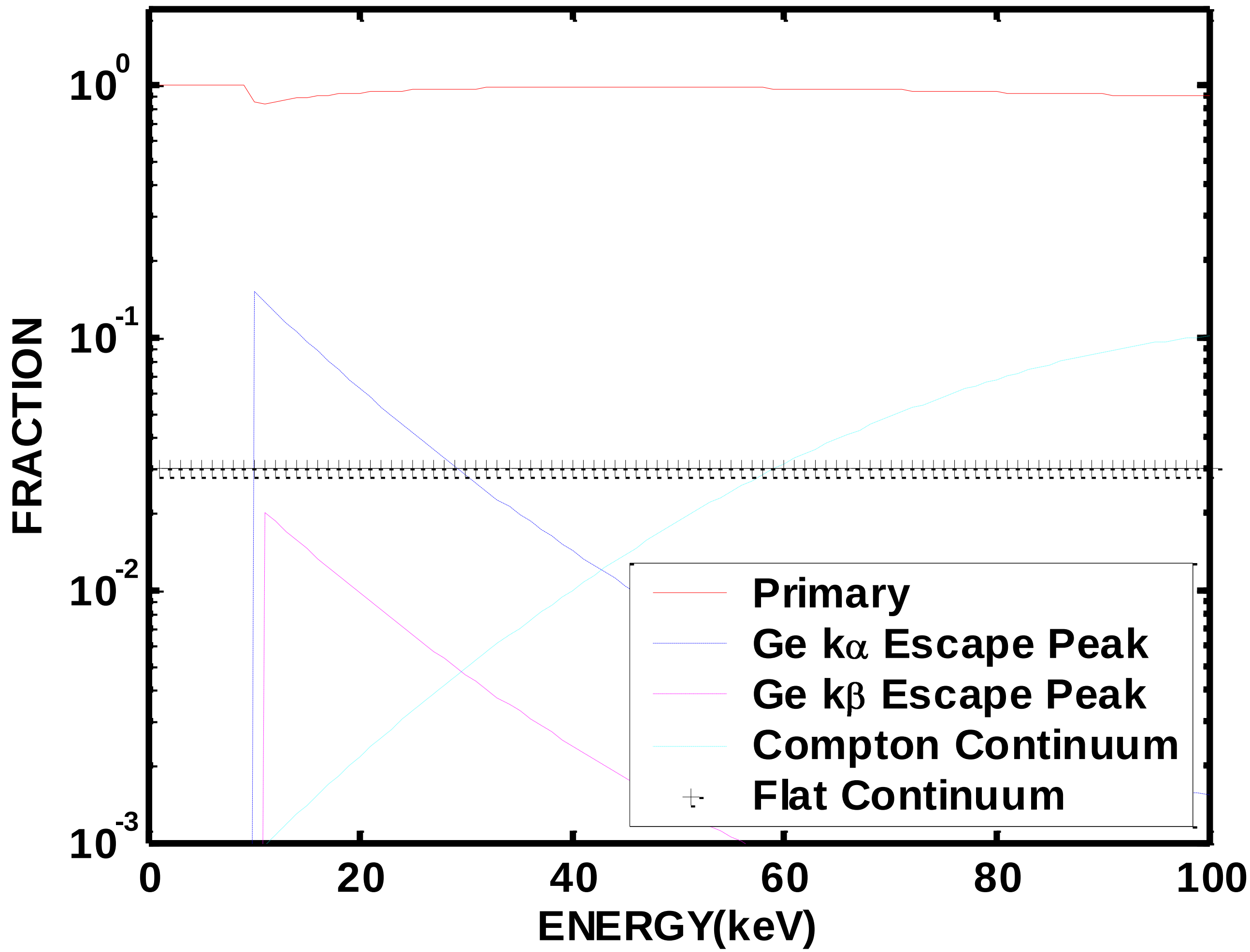
CEARXRF – What can it calculate?

- Sample EDXRF Spectral Response
- Elemental (Components) Spectral Response Libraries
- Sample Differential Spectral Responses for Composition Variation
- Elemental Library Differential Spectral Responses for Composition Variation (To Quantify the Inter-elemental Matrix Effect)

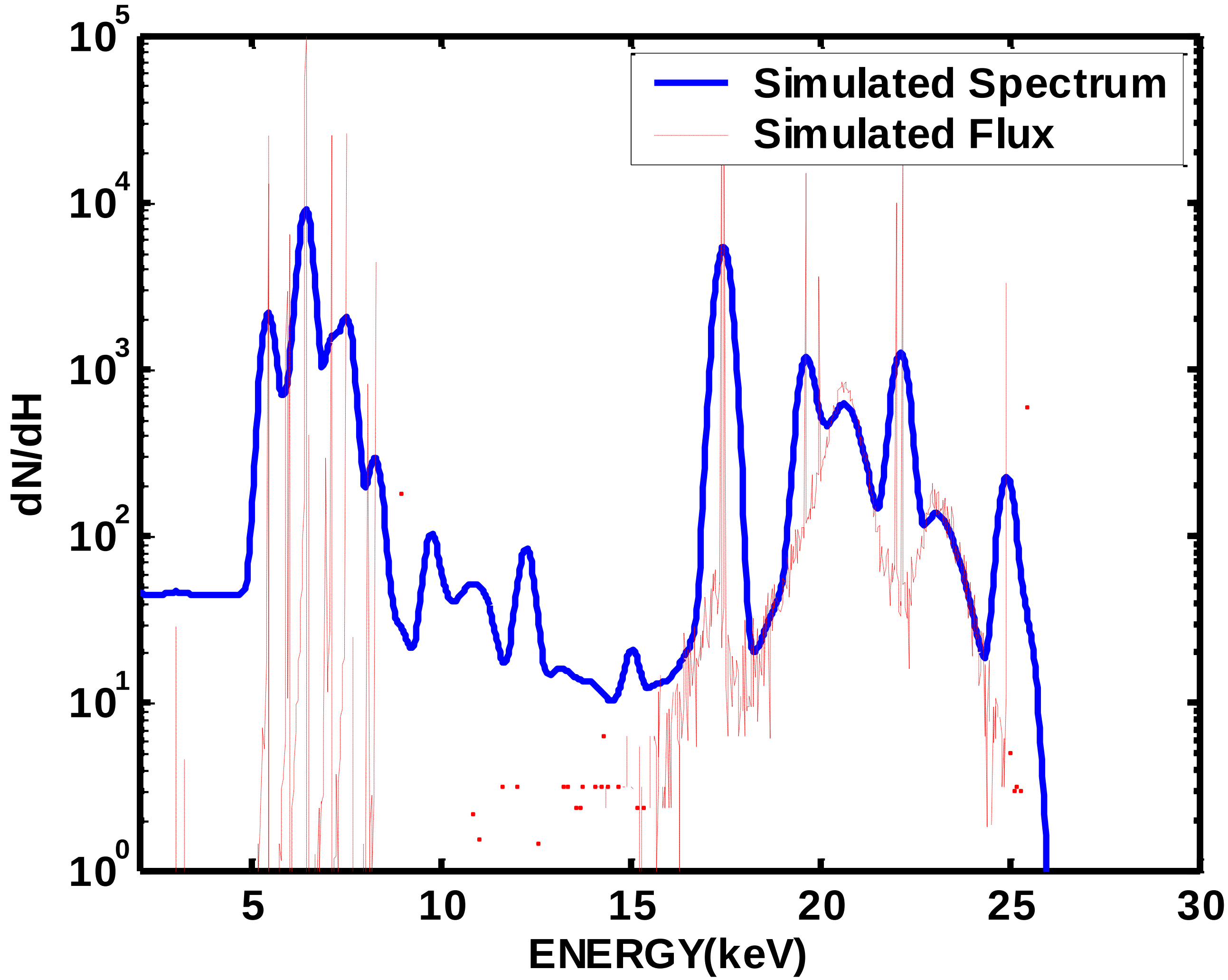
DETECTOR RESPONSE FUNCTION (DRF) COMPONENTS FOR Ge



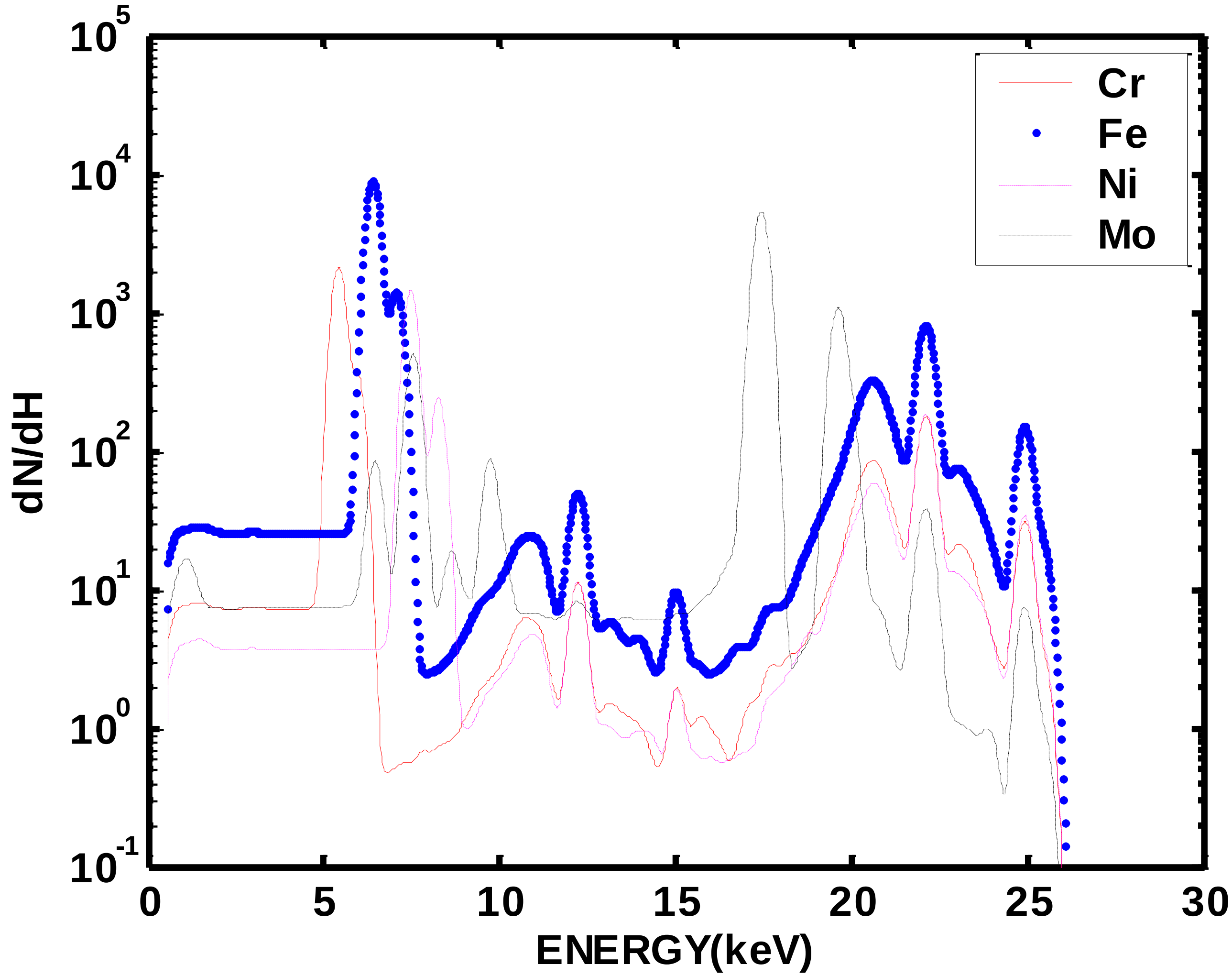
Ge DRF COMPONENT INTENSITIES



Simulated Flux & Spectrum



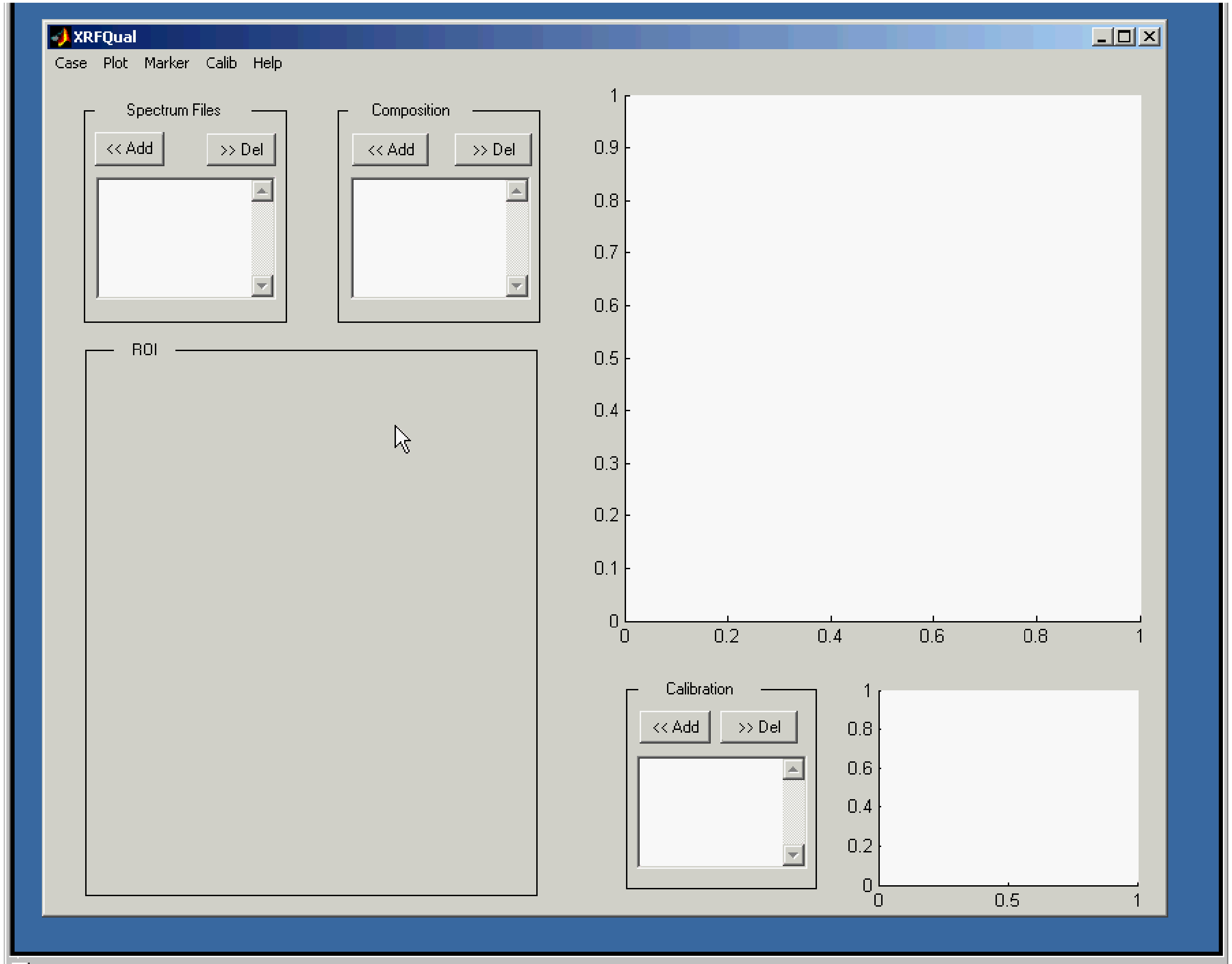
Monte Carlo Library Spectra



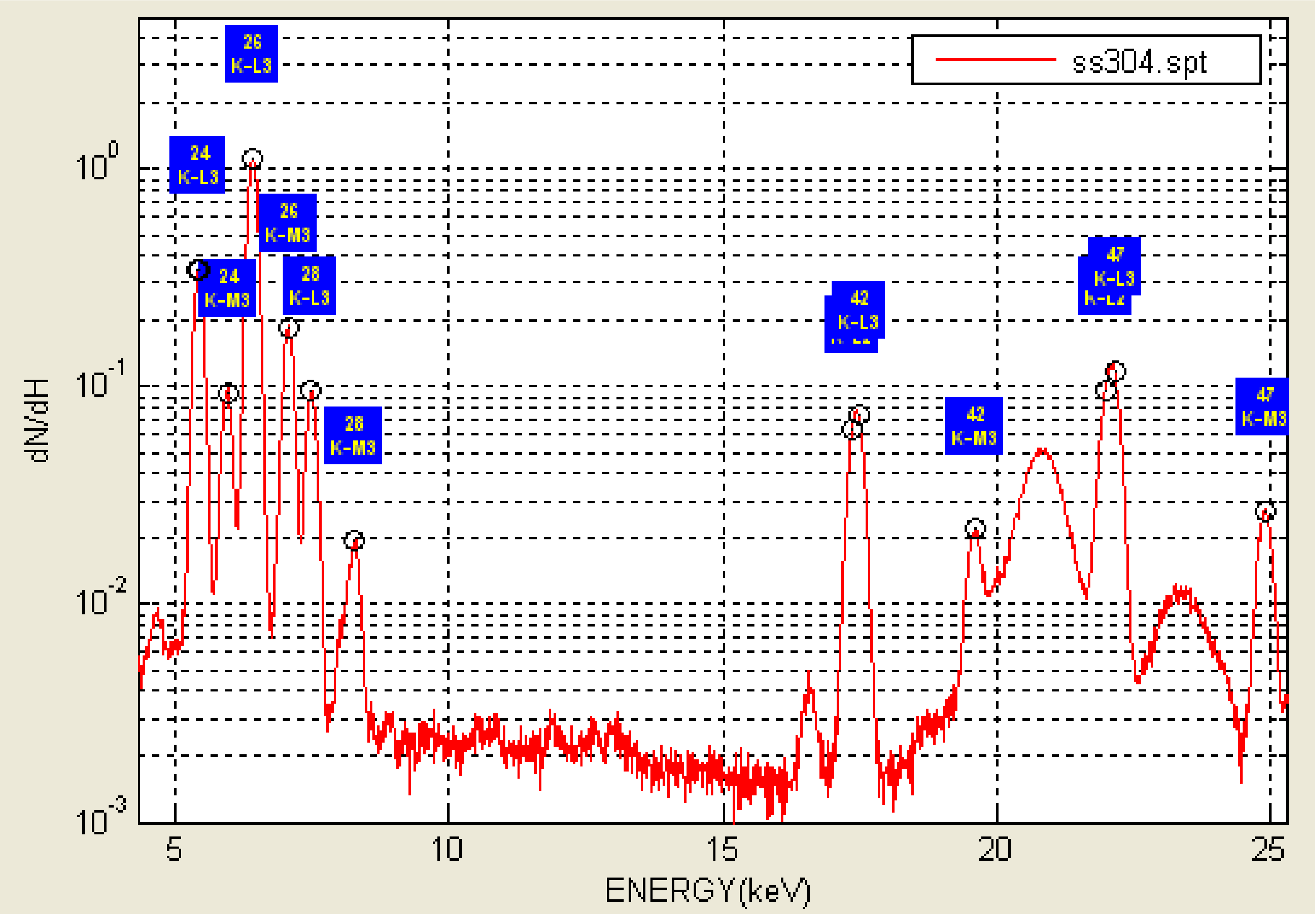
IMPLEMENTATION WITH A GUI

- XRFQual + XRayQuery
  - XRFQual: Qualitative analysis of XRF measured spectrum
    - Energy Calibration
    - Composition Identification
  - XRayQuery
    - Interactive tool for X-ray physics, such as characteristic x-ray line energy, yield, etc.
- XLLS
  - Quantitative LLS analysis to determine elemental composition

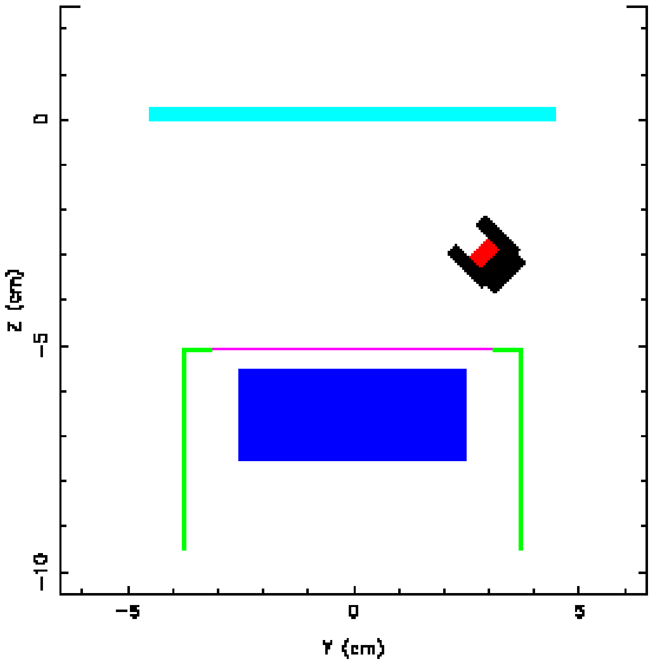
XRFQual + XRayQuery Demo



STAINLESS STEEL (SS304) QUALITATIVE ANALYSIS

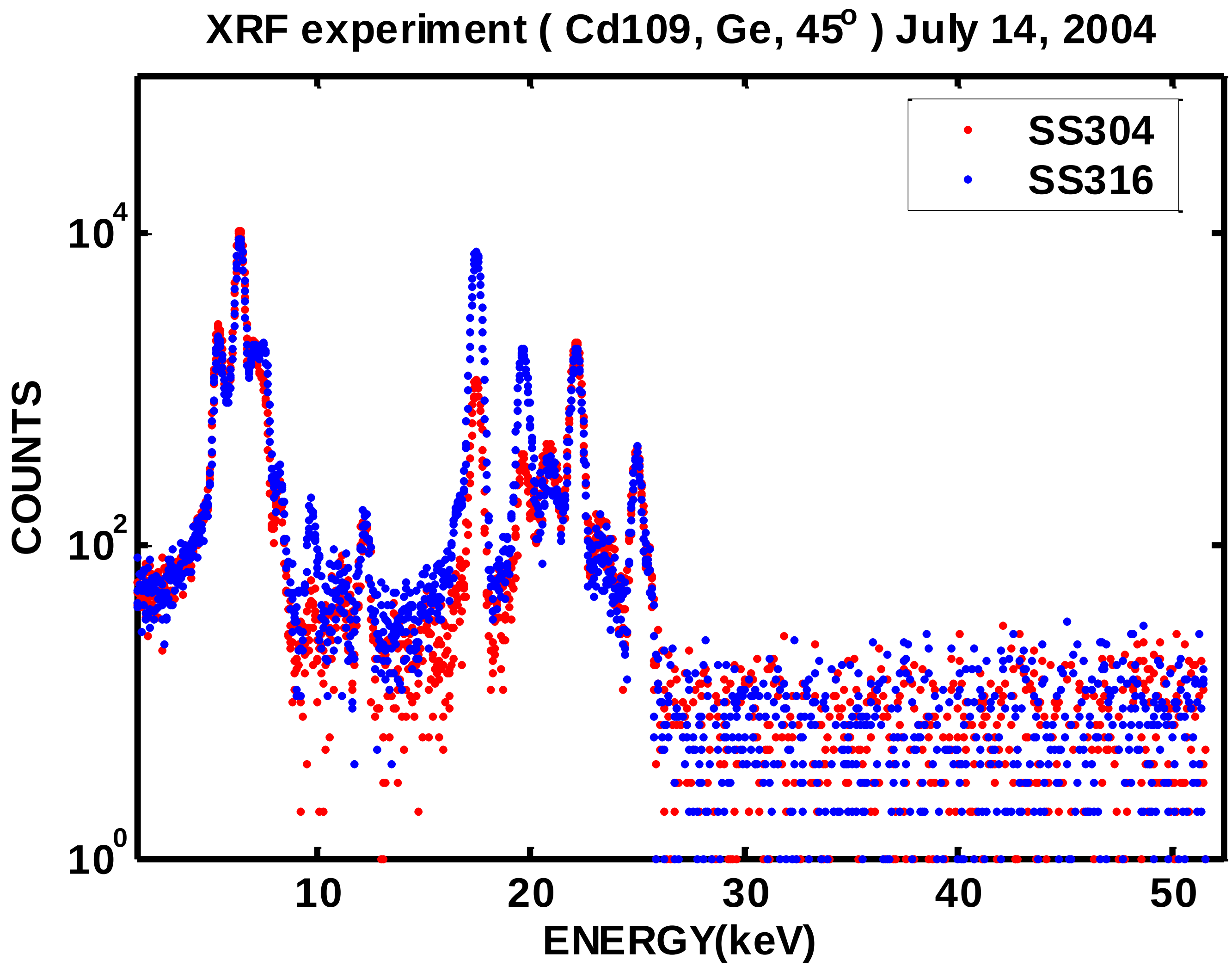


EDXRF Measurement of Stainless Steel

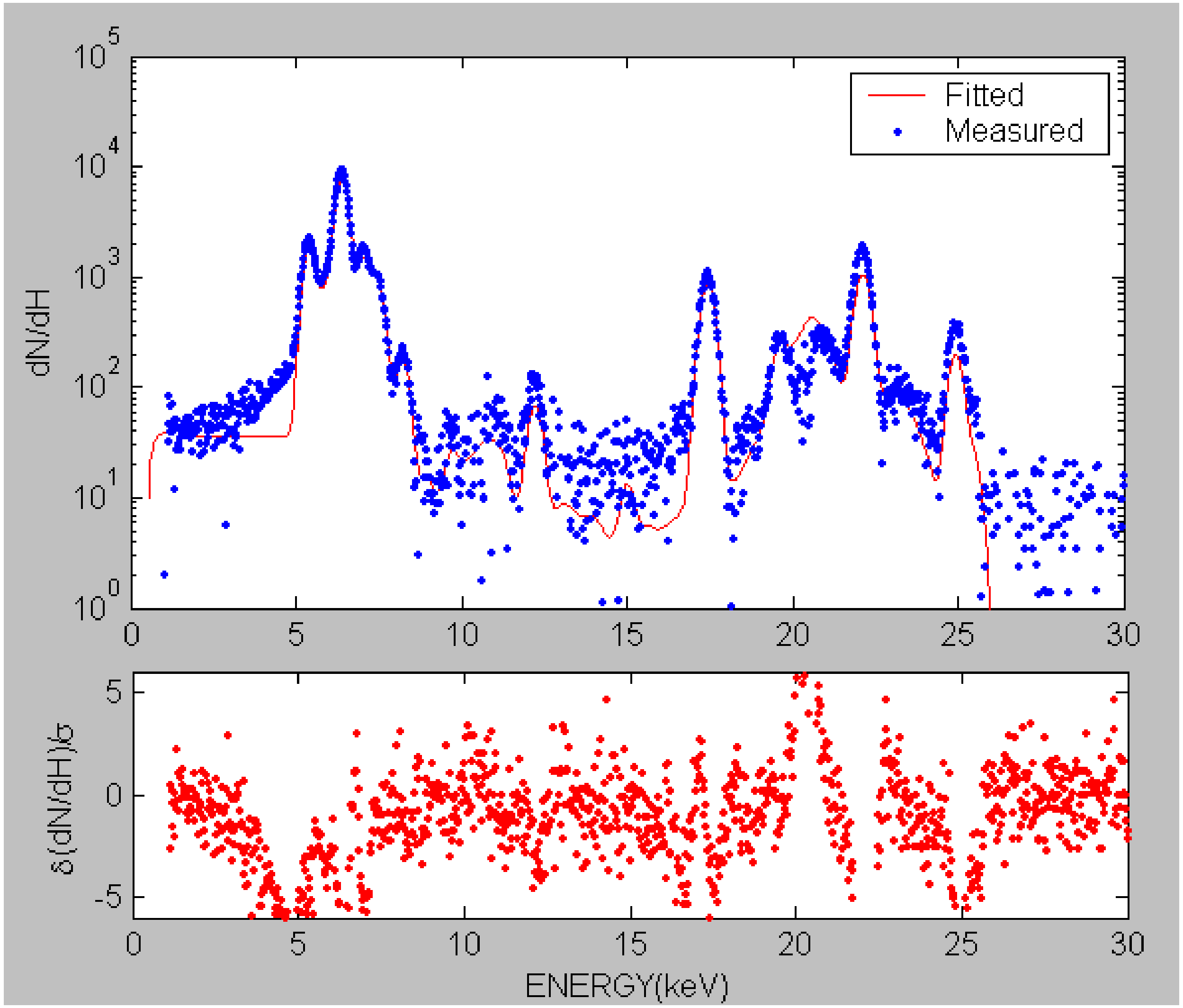


- 3mm slab
  - Infinitely thick, average path length 10^{-2} mm for source silver X rays)
- Stainless steel 304 & 316
  - Fe:60.0 - 70.0%
  - Cr: 18.0 – 20.0% (16.0 – 18.0%)
  - Ni: 8.0 – 10.5% (10.0 – 14.0%)
  - Mo: - (2.0 – 3.0%)

Experimental EDXRF Spectra



SS304 LLS Fitted Spectrum vs. Experimental Spectrum



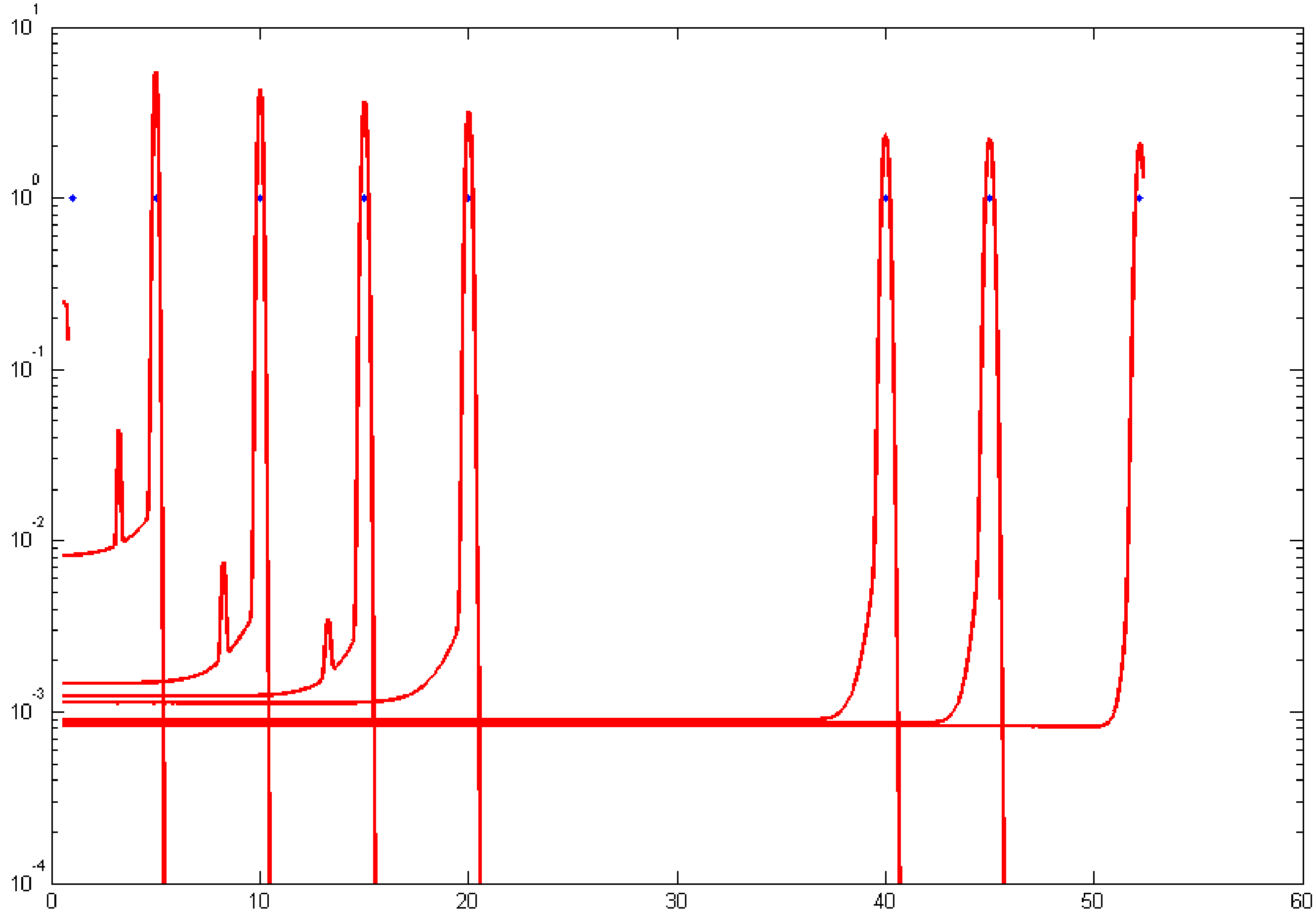
RESULTS WITH A Cd-109 SOURCE

- Stainless steel (304 and 316) samples with a Ge detector
- Stainless steel sample with a Si(Li) detector
- Aluminum alloy samples with a Si(Li) detector

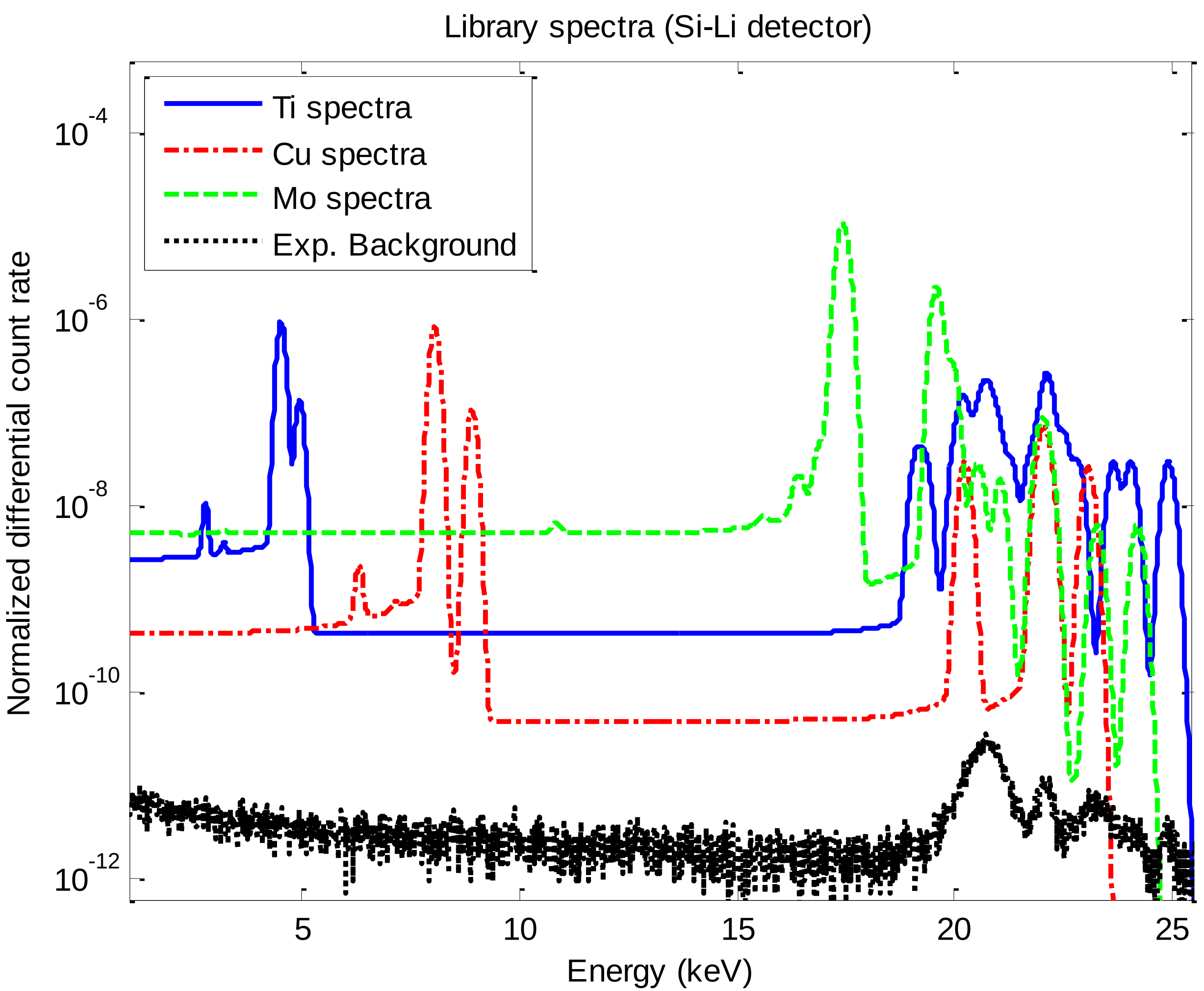
LLS Quantitative Results for Ge

	W.F.% (SS 304)	Nominal	W% (SS 316)	Nominal
Cr	18.4	18.0-20.0	16.4	16.0-18.0
Fe	68.2	60.0-70.0	64.5	60.0-70.0
Ni	8.1	8.0-12.0	11.4	10.0-14.0
Mo	0.4	-	2.8	2.0-3.0

Si(Li) DETECTOR RESPONSE FUNCTIONS



LIBRARY SPECTRA – Ti, Cu, Mo, & BACKGROUND NOISE



STAINLESS STEEL 304 (SS304) EXPERIMENTAL & FITTED DATA

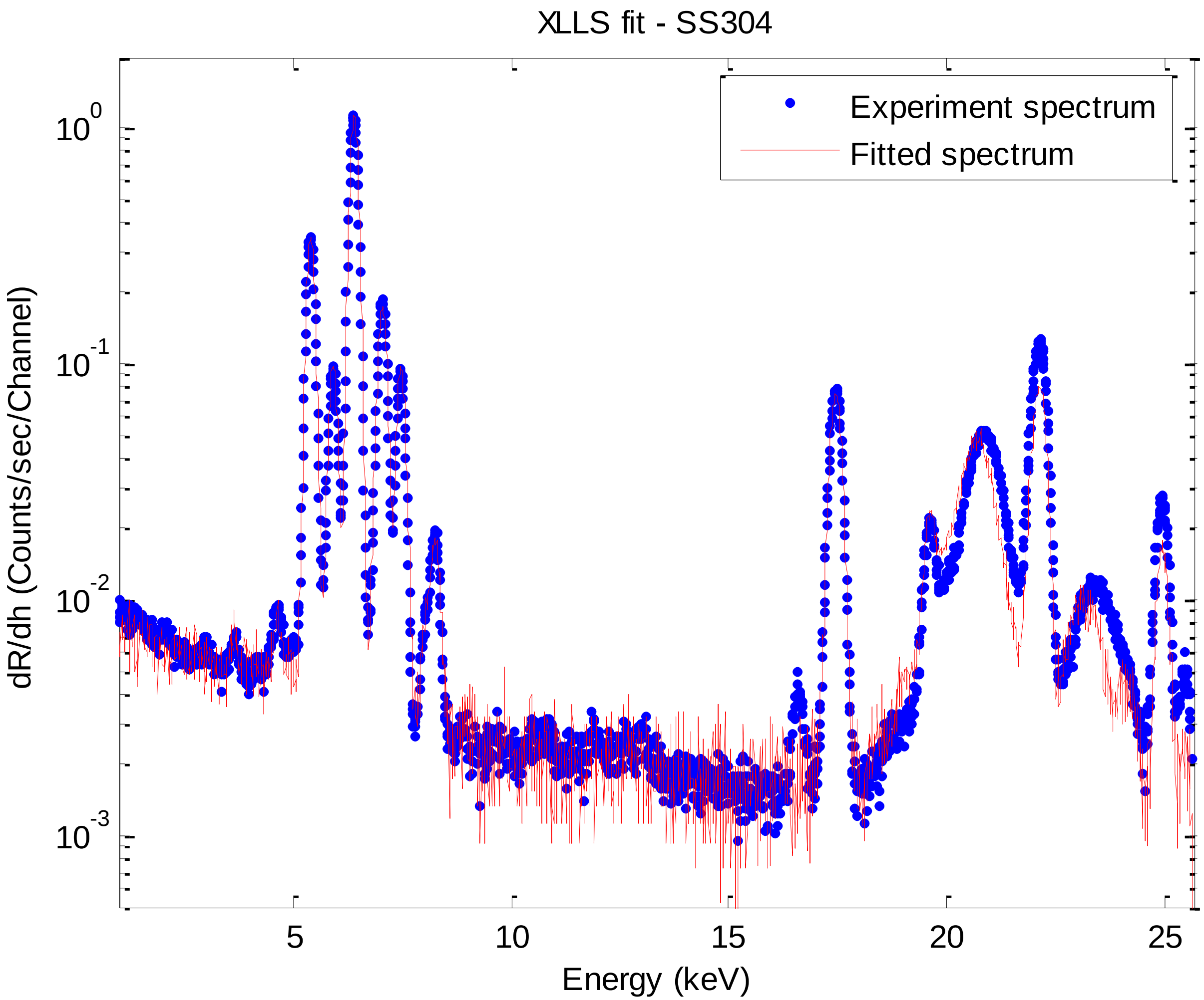
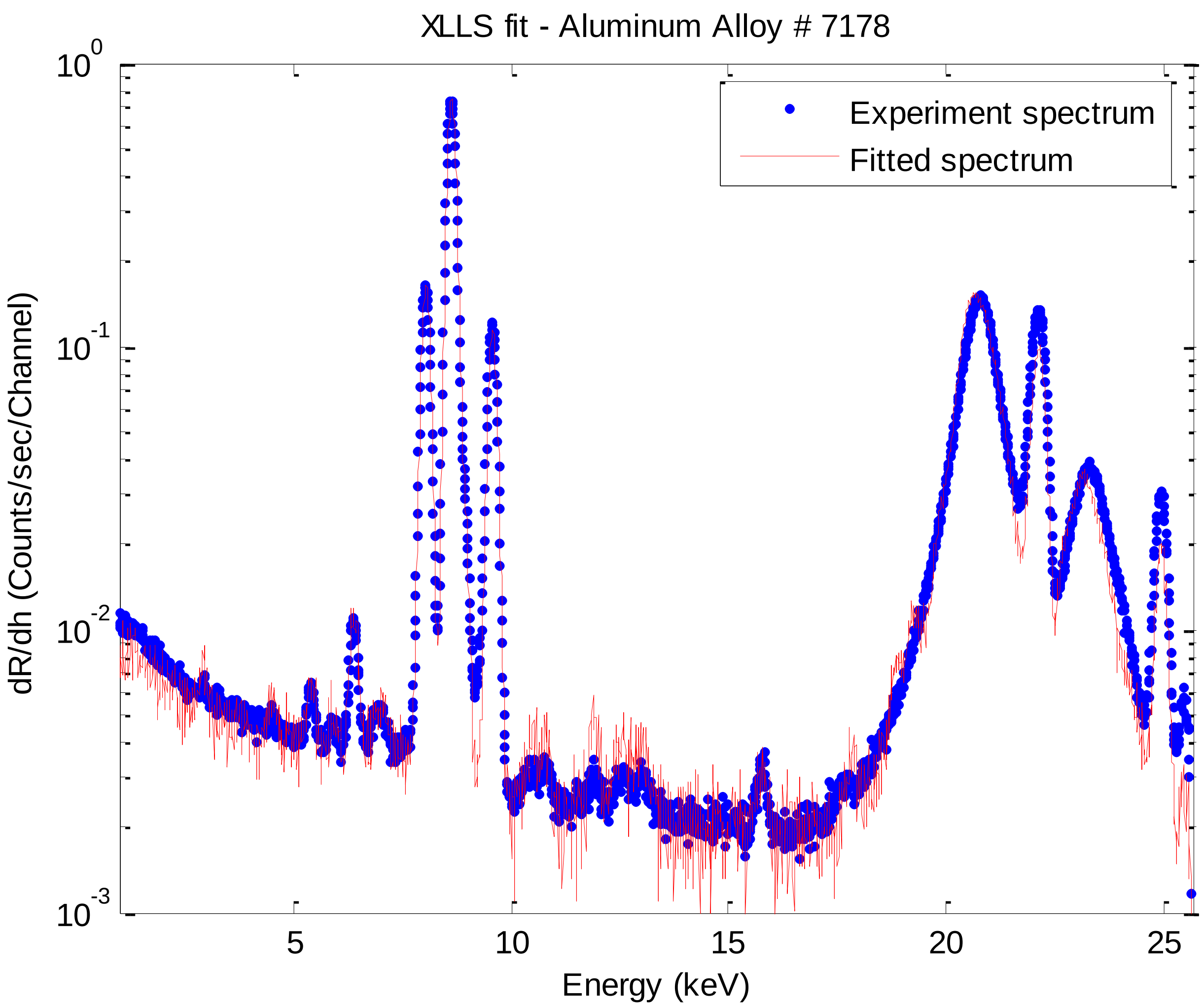


TABLE 1. SS304 FIT RESULTS

Element (SS304)	Initial Guess	Final fit results	Reference value(SS304)
Cr	0.2270	**0.1842**	*0.18-0.20*
Mn	0.0162	**0.0224**	-
Fe	0.5516	**0.6842**	*0.6-0.7*
Co	0.0012	**0.0136**	-
Ni	0.1790	**0.0891**	*0.08-0.105*
Cu	0.0045	**0.0033**	-
Mo	0.0205	**0.0032**	-

ALUMINUM ALLOY 7178 (AA7178) EXPERIMENTAL AND FIT SPECTRA



Fe-55 EXCITATION OF Al

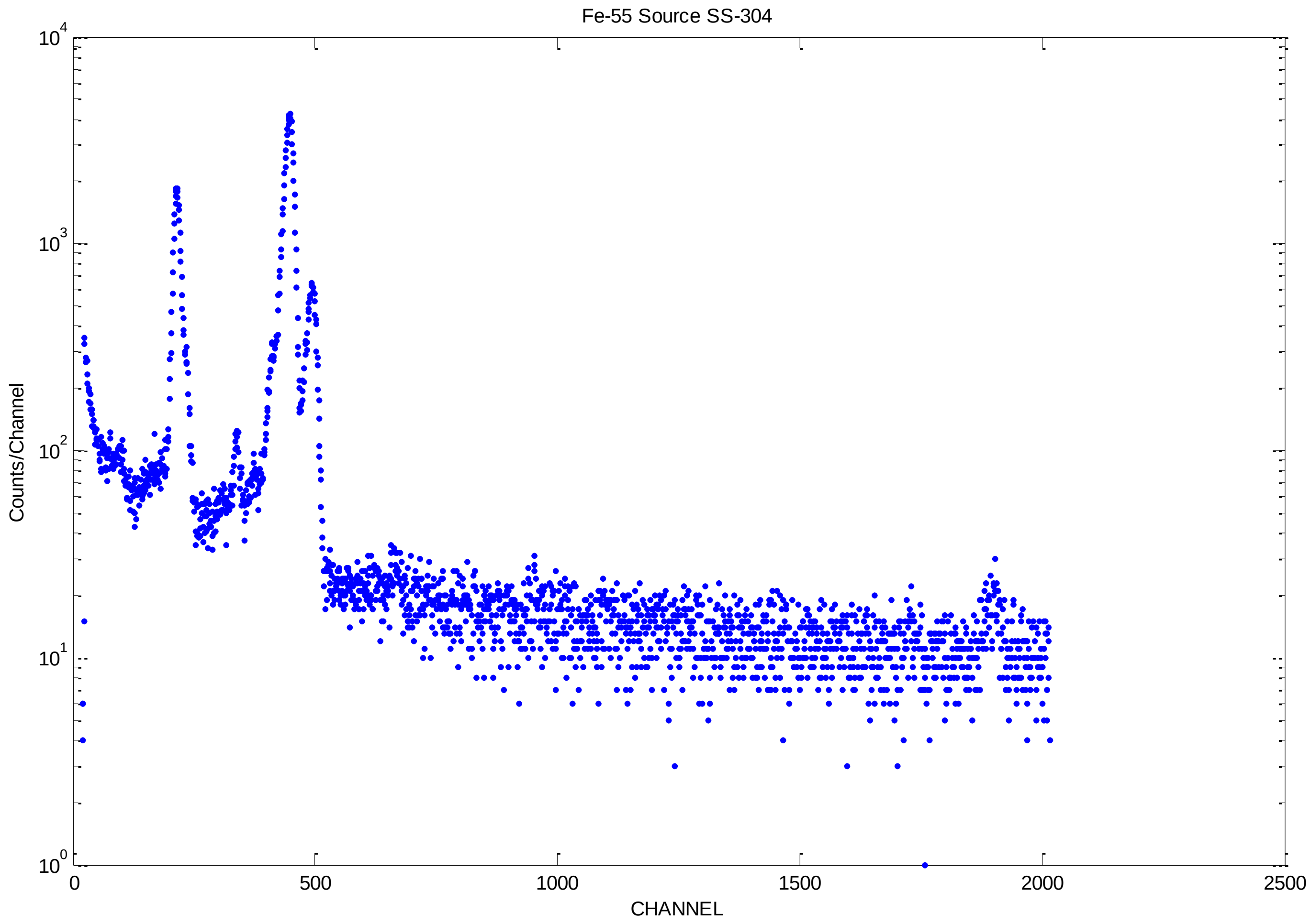


TABLE 2. AA7178 FIT RESULTS

Element (AA7178)	Initial Guess	Final fit results	Reference value(AA7178)
Mg	0.0200	0.0255*	*0.0255*
Al	0.8200	0.8830*	*0.8830*
Si	0.0200	**0.0004**	*0.0006*
Ti	0.0200	**0.0002**	*0.0003*
Cr	0.0200	**0.0016**	*0.0020*
Mn	0.0200	**0.0001**	*0.0002*
Fe	0.0200	**0.0010**	*0.0020*
Cu	0.0200	**0.0175**	*0.0199*
Zn	0.0200	**0.0704**	*0.0661*
Zr	0.0200	**0.0003**	*0.0004*

* Assumed to be the true value, not participating in the XLLS fit

ALUMINUM ALLOY 3004 (AA3004) EXPERIMENTAL & FIT SPECTRA

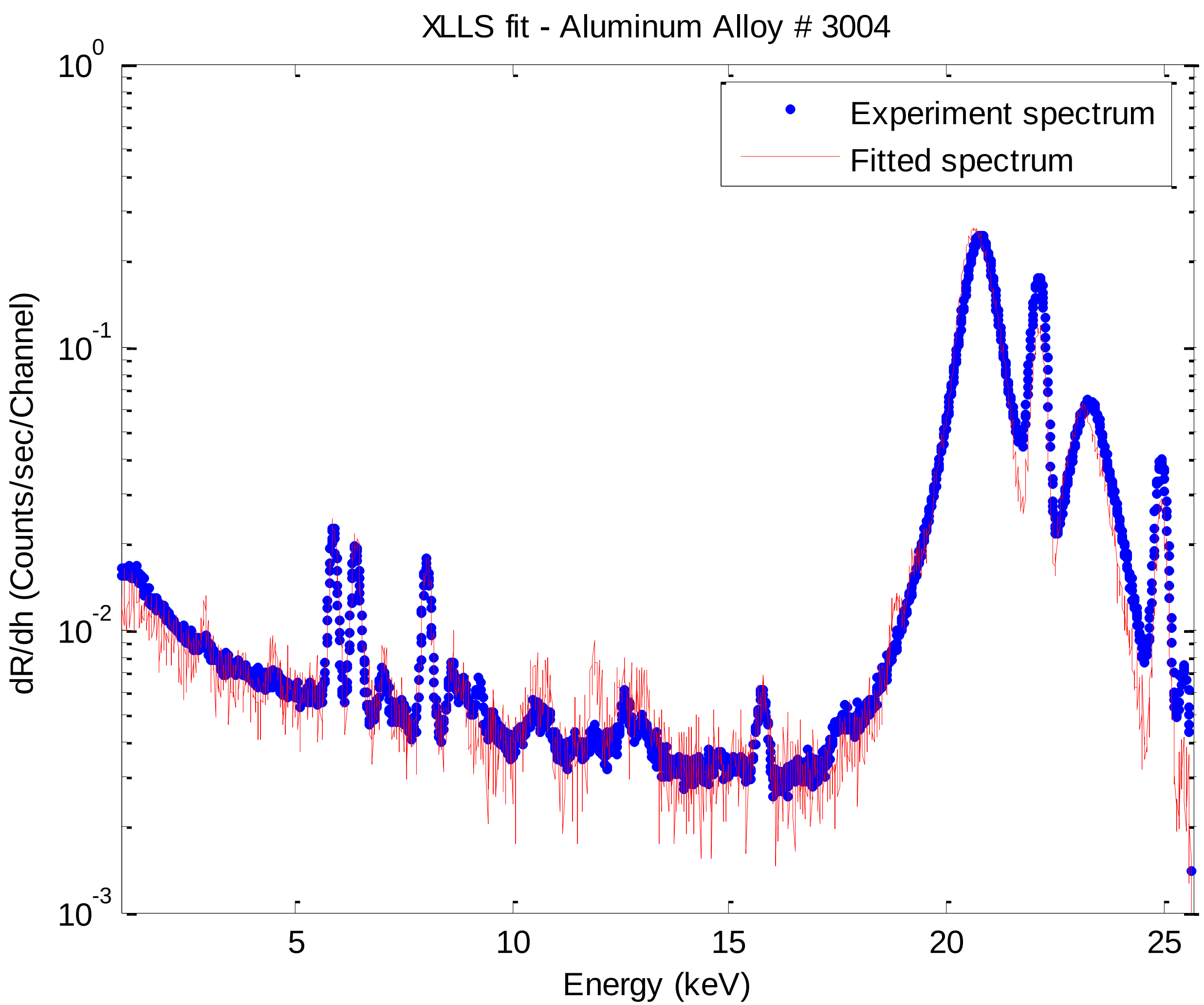


TABLE 3. AA3004 FIT RESULTS

Element (AA3004)	Initial Guess	Final fit results	Reference value(AA3004)
Mg	0.0200	0.0104*	*0.0104*
Al	0.8400	0.9712*	*0.9712*
Si	0.0200	**0.0029**	*0.0018*
Ti	0.0200	**0.0003**	*0.0004*
Cr	0.0200	**0.0001**	*0.0001*
Mn	0.0200	**0.0090**	*0.0108*
Fe	0.0200	**0.0040**	*0.0037*
Cu	0.0200	**0.0020**	*0.0013*
Zn	0.0200	**0.0001**	*0.0003*

* Suppose it is the real value, not participating in XLLS fit

DISCUSSION, CONCLUSIONS, AND FUTURE WORK

- Results so far indicate the approach is accurate.
- The CEARXRF code and a DRF for the detector provide all that is needed for the inverse problem.
- The GUI that has been developed and Differential Operators added to CEARXRF makes the approach practical.
- Now we need to develop the approach for all commercial analyzers – including those with X-Ray machines and Secondary fluorescers.

DISCUSSION, CONCLUSIONS, AND FUTURE WORK , 2

For Routine XRF Sample Analysis the Advantages of this Approach are:

1. Use of CEARPPU makes all the data available with known Poisson statistics.
2. Use of MCLLS corrects for all matrix effects including tertiary and beyond. It will be easy (?) to include other refinements (such as electron transport) as necessary.
3. Use of LLS avoids all problems with intensity measurement and gives statistical estimates of results automatically.
4. An error analysis of existing FP approaches will be made.

ACKNOWLEDGEMENT

The author acknowledges two grants by the National Institute of Environmental Health Services of the NIH for providing the opportunity for optimizing the XRF approaches for the *in vivo* measurement of lead in bone.