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SIMULATION OF X-RAY FLUORESCENCE SPECTRA*

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ABSTRACT

A method for simulating x-ray fluorescence (XRF) spectra in hybrid densitometry is presented. This technique allows simulation of XRF spectra for solutions with arbitrary concentrations of special nuclear material and minor actinides excited by an x-ray generator. Spectra for mixed uranium and plutonium solutions with U/Pu ratios ranging from 100 to 1 have been generated. This range of ratios applies to most solutions found in plutonium reprocessing plants. XRF simulation can provide important data for estimating instrument precision, evaluating analysis techniques, and training system operators. Applications of XRF simulation in the development of the Los Alamos Hybrid K-Edge/XRF Densitometer system are described.

INTRODUCTION

The Hybrid K-Edge Densitometer (KED)/X-Ray Fluorescence (XRF) technique was first implemented at plutonium reprocessing plants in the late 1980s.¹ Most hybrid systems are used to measure the concentrations of uranium and plutonium in the dissolver solutions of reprocessing plants. The potential for use of hybrid systems in analytical laboratories has also been explored.²

Current hybrid analysis techniques were designed primarily for the assay of dissolver solutions. In light-water reactor reprocessing plants, a typical dissolver solution has a uranium concentration of 200 to 250 g/l, with a U/Pu ratio of 100, a Pu/Np ratio of 30, and a Pu/Am ratio of 30. In analytical laboratory samples, the concentration of the major element (either U or Pu) could range from 10 to 450 g/l, and could contain several grams per liter of other actinides. Samples encountered in analytical labs, therefore, may be drastically different from dissolver solutions. This wide sample variance presents a challenge for current hybrid analysis techniques.

Improved algorithms for KED and XRF analysis would boost the precision and flexibility of the hybrid technique. These improvements would make hybrid systems more versatile for analytical laboratories. New analysis techniques are being explored, and validation of these methods is essential. One way to validate new XRF methods is through the analysis of real and simulated XRF spectra. This report gives a brief description of hybrid analysis and presents a method for producing simulated XRF spectra.

HYBRID ANALYSIS

The hybrid system implements two solution assay techniques: KED and XRF. A schematic illustration of the Los Alamos Hybrid Densitometer is shown in Fig. 1. The basic elements of the hybrid system are an x-ray generator, sample vial, and separate high-resolution detectors for the KED and XRF systems. The glass sample vial is 2 to 4 cm in length and holds a liquid solution. The solution may be blank (3.0 molar nitric acid) or contain any number of dissolved actinides.

The x-ray generator irradiates the sample with a filtered x-ray beam. The KED detector is positioned behind the sample and measures the transmitted portion of the beam. The XRF detector is positioned behind a long, narrow collimator that points toward the front of the sample. The angle between the incident beam and XRF collimator is 30 degrees. The XRF detector measures fluoresced x-rays that are emitted from the front portion of the solution.

In hybrid analysis, KED is used to determine the concentration of the major element, usually uranium or plutonium. XRF is used to determine various ratios of concentrations, such as U/Th, U/Pu, Pu/Am, and Pu/Np. Measured ratios are used to determine the ratio of each minor element to the major element. It is then a simple

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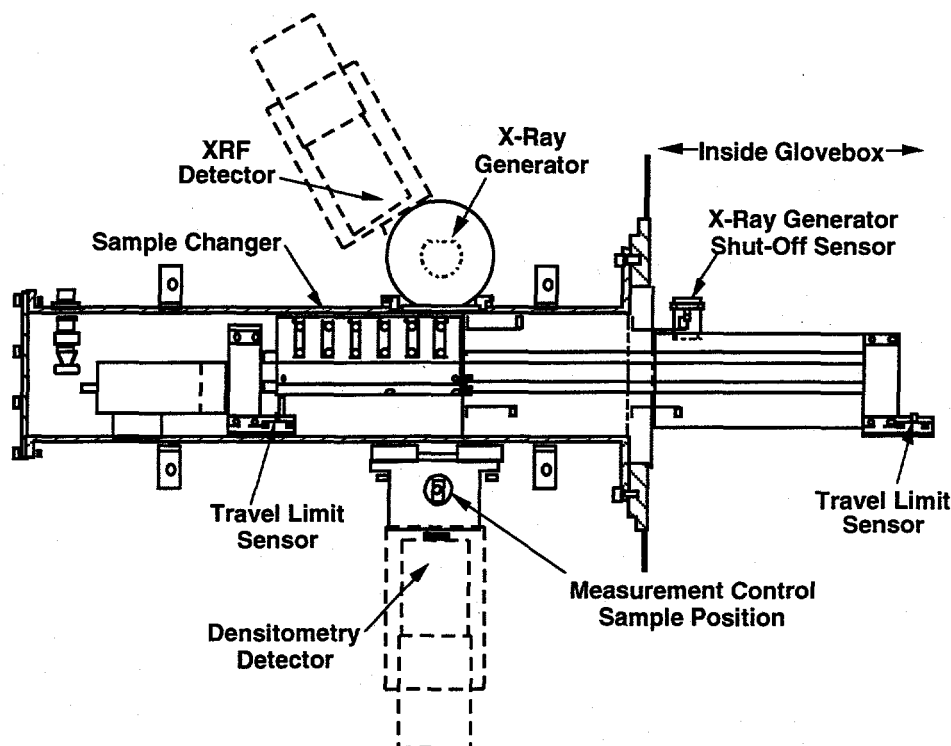


Figure 1. Schematic of Hybrid Densitometer system (top view), showing positions of x-ray generator, sample tray, KED detector, and XRF detector.

matter to calculate the concentrations of the minor elements. Hybrid analysis takes advantage of the strengths of the KED and XRF techniques. The remainder of this paper will focus on the XRF system of the hybrid densitometer.

In the XRF analysis code, a response function fitting technique is used to determine x-ray peak areas.³ The fitting routine takes into account the line broadening of the x-rays because of their intrinsic natural width. The quality of peak fitting is especially important in cases where actinide concentrations vary over a wide range of values.

Though several x-ray peaks are produced by each element, the current XRF analysis code reports the areas of only two or three peaks per element. These are the ($K_{\alpha 1}$, $K_{\alpha 2}$, and $K_{\alpha 3}$) peaks of thorium, uranium, and plutonium, and the ($K_{\alpha 1}$ and $K_{\alpha 2}$) peaks of neptunium and americium. Usually, the $K_{\alpha 1}$ peak areas are used to determine the concentration ratio of two actinides. For example, the ratio of uranium and plutonium concentrations can be determined from the measured areas of the U $K_{\alpha 1}$ and Pu $K_{\alpha 1}$ peaks as follows:

$$\frac{\rho_U}{\rho_{Pu}} = \frac{AM(U)}{AM(Pu)} \cdot \frac{A_m(U, K_{\alpha 1})}{A_m(Pu, K_{\alpha 1})} \cdot \frac{RE(Pu, K_{\alpha 1})}{RE(U, K_{\alpha 1})} \cdot \frac{1}{R_{U/Pu}}, \quad (1)$$

where

- ρ_i = concentration of element i ,
- $AM(i)$ = atomic weight of element i ,
- $A_m(i, j)$ = analyzed peak area for peak j of element i ,
- $RE(i, j)$ = relative detection efficiency at centroid of peak ij , and
- $R_{U/Pu}$ = factor describing the ratio of excitation probabilities for emission of U $K_{\alpha 1}$ and Pu $K_{\alpha 1}$ X-rays in the primary beam.

In normal hybrid analysis, the XRF analysis code is used to (1) determine x-ray peak areas in real or simulated spectra, and (2) calculate the concentration ratios of various actinides. In the applications of the XRF analysis code related to XRF simulation, only the peak fitting capability will be utilized.

SIMULATION METHOD

Our goal is to simulate hybrid XRF spectra for solutions containing arbitrary concentrations of actinides. Our current XRF simulation program, named SIMXRF, recognizes five actinides: Th, U, Np, Pu, and Am. The concentration, ρ , of each actinide in the solution is measured in grams per liter. The concentrations of the

actinides represent components of a "solution vector," $\bar{\rho}$, defined as follows:

$$\bar{\rho} \equiv \begin{pmatrix} \rho_{Th} \\ \rho_U \\ \rho_{Np} \\ \rho_{Pu} \\ \rho_{Am} \end{pmatrix}, \quad (2)$$

where ρ_{Th} , ρ_U , ρ_{Np} , ρ_{Pu} , and ρ_{Am} are actinide concentrations. Though hybrid solutions also contain 3.0 molar nitric acid, $\bar{\rho}$ completely characterizes the contents of a solution for the purposes of XRF simulation. In fact, $\bar{\rho}$ can symbolize an arbitrary hybrid sample or solution. This provides a convenient shorthand notation in the text and equations that follow.

To simulate an XRF spectrum, we must determine the number of counts needed in each channel of the spectrum. The present version of the XRF simulation code has 2 048 channels of data in each spectrum. Suppose that each vector \bar{S} represents the data in a 2 048-channel spectrum ($S_0, S_1, \dots, S_{2047}$). Let \bar{S}_{Sim} represent the spectrum we want to simulate. In XRF simulation, we create a simulated spectrum by superimposing individual x-ray peaks and background profiles upon an incoherent spectrum. For each actinide present in the simulated solution, 10 x-ray peaks are generated: $K_{\alpha 3}$, $K_{\alpha 2}$, $K_{\alpha 1}$, $K_{\beta 3}$, $K_{\beta 1}$, $K_{\beta 5}$, $K_{\beta 2/1}$, $K_{\beta 2/2}$, $K_{\beta 4}$, and $K_{\beta 2/3-4}$. The fundamental equation for XRF spectrum simulation is as follows:

$$\bar{S}_{Sim} = \bar{S}_{Incoh} + \sum_{i=1}^{N_{el}} \sum_{j=1}^{N_{pk}} [\bar{S}_{Peak}(i, j) + \bar{S}_{Bgnd}(i, j)], \quad (3)$$

where

- \bar{S}_{Sim} = the simulated spectrum,
- \bar{S}_{Incoh} = the incoherent spectrum,
- i = index of actinide element,
- j = index of x-ray peak,
- N_{el} = number of actinide elements,
- N_{pk} = number of simulated x-ray peaks per element,
- \bar{S}_{Peak} = simulated x-ray peak profile for peak ij , and
- \bar{S}_{Bgnd} = simulated step-like background profile for peak ij .

The incoherent spectrum \bar{S}_{Incoh} represents the spectrum we would simulate if the sample vial contained only 3.0 molar nitric acid, with no actinides. The incoherent spectrum is a smoothed version of the reference

spectrum, scaled for consistency with the simulated live time and current. The reference spectrum is acquired in the laboratory using a blank (3.0 molar nitric acid) sample and a very long live time (10 000 s or longer). The reference spectrum is smoothed using a seven-channel running mean, and multiplied by ratios of the simulated and reference spectrum currents and live times. The incoherent spectrum is calculated as follows:

$$\bar{S}_{Incoh} = \bar{S}'_{Ref} \cdot \left(\frac{I_{Sim} t_{Sim}}{I_{Ref} t_{Ref}} \right), \quad (4)$$

where

- \bar{S}_{Incoh} = the incoherent spectrum,
- \bar{S}'_{Ref} = the smoothed reference spectrum,
- I_{Sim} = simulated x-ray tube current (mA),
- t_{Sim} = simulated live time (s),
- I_{Ref} = x-ray tube current during acquisition of reference spectrum (mA), and
- t_{Ref} = live time of reference spectrum (s).

Examples of a reference spectrum and incoherent spectrum are shown in Fig. 2.

The spectral profile of each simulated x-ray peak \bar{S}_{Peak} is generated using a peak shaping algorithm developed by Ray Gunnink.⁴ The method described by Gunnink generates an x-ray peak with a specified height. This algorithm was modified to generate a peak that has a specified area. The shape, height, and position of a simulated x-ray peak \bar{S}_{Peak} depend upon several parameters: (1) the energy of the peak, (2) the desired area of the peak, (3) the natural line width of the peak, (4) the detector's full width at half maximum at the given energy, and (5) the amplitude and slope of the peak's short-term tailing function. The XRF simulation code predicts what the area of each x-ray peak should be and generates peaks with those areas. A simulated x-ray peak profile is shown in Fig. 3.

The simulated area of a peak depends upon several factors: (1) the concentrations of actinides in the solution, (2) the average atomic mass of the element that contributes the peak, (3) the relative efficiency of the detector at the energy of the peak, (4) the simulated live time, (5) the simulated x-ray generator current, (6) the relative yield of the peak, (7) the attenuation-corrected excitation integral for that peak, and (8) the SIMXRF calibration factor for that peak. The dependence of simulated area upon these factors is as follows:

$$A_{Sim}(i, j, \bar{\rho}, I, t, K_{Sim}) = \left(\frac{\rho(i) \cdot RE(i, j) \cdot W(i, j, \bar{\rho}) \cdot Y(i, j) \cdot I \cdot t}{AM(i)} \right) \cdot K_{Sim}(i, j), \quad (5)$$

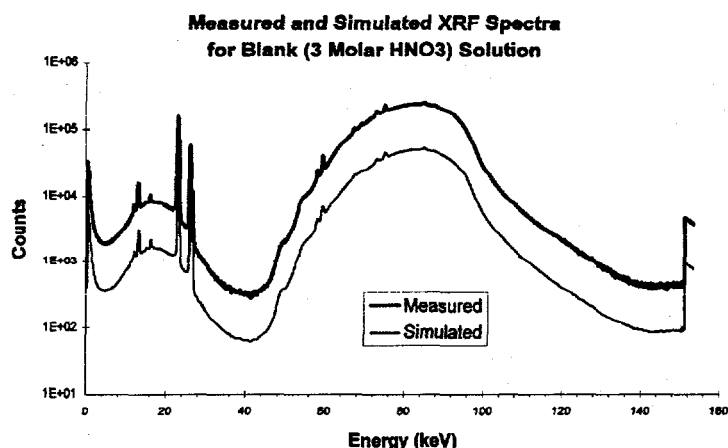


Figure 2. Comparison of reference and incoherent XRF spectra. Broad line represents a measured reference spectrum, with a live time of 10 000 s and x-ray generator current of 5 mA. Thin line shows calculated incoherent spectrum corresponding to 1 000-s live time and 10-mA current.

where

- A_{sim} = simulated area of peak;
- I = index of actinide element;
- j = index of x-ray peak;
- $\rho(i)$ = concentration of element i (g/l);
- $RE(i, j)$ = relative efficiency of detector at energy E_{ij} ;
- $W(i, j, \bar{\rho})$ = attenuation-corrected excitation integral for peak ij , in solution $\bar{\rho}$;
- $Y(i, j)$ = relative x-ray yield for peak j of element i , normalized so that $Y(i, K_{\alpha 1}) = 100$;
- I = x-ray tube current (mA);
- t = live time of spectrum (s);
- $AM(i)$ = average atomic mass of element i (g/mol); and
- $K_{sim}(i, j)$ = SIMXRF calibration factor for peak ij .

Our goal in XRF spectrum simulation is to mimic the detector's response to incoming x-rays. The spectral

profile \bar{S}_{Peak} mimics the detector's full energy response to x-rays from a particular peak. However, not all the x-rays which enter the germanium crystal are detected as full-energy events. Some of the incident x-rays are detected at less than full energy, because scattered photons and/or electrons escape the crystal. Such an event may cause counts to be observed in channels below that of the incoming x-ray. These background counts are an important part of the detector's response to incoming x-rays, and must be included in XRF simulation as \bar{S}_{Bkgnd} .

The background profile, \bar{S}_{Bkgnd} , for a given peak mimics the detector's response to background events triggered by x-rays from that peak. If x-rays were monoenergetic, \bar{S}_{Bkgnd} could be approximated as a simple step function, with all background counts below the x-ray energy. However, x-rays are emitted in a Lorentzian energy distribution, similar in form to \bar{S}_{Peak} in Fig. 3, but with a narrower peak shape. Because the incoming x-rays are distributed in this fashion, the background profile of a single x-ray peak resembles a

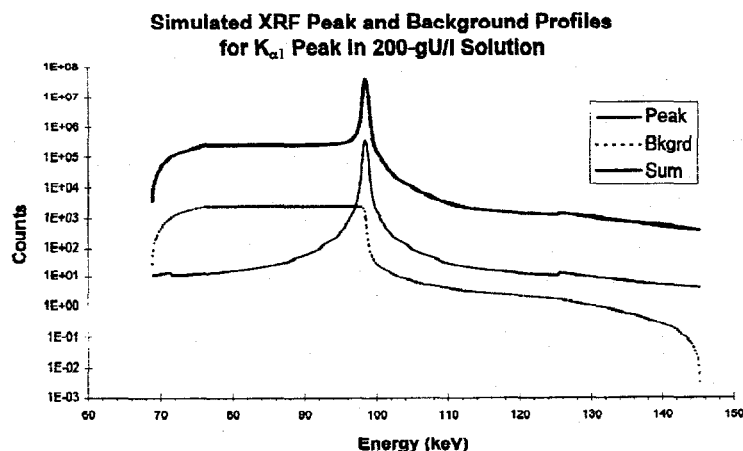


Figure 3. Simulated x-ray peak in 200-gU/l solution. Thin line represents simulated profile \bar{S}_{Peak} of the $K_{\alpha 1}$ peak. Dashed line represents simulated step-like background profile \bar{S}_{Bkgnd} resulting from $K_{\alpha 1}$ peak. Broad line shows sum of \bar{S}_{Peak} and \bar{S}_{Bkgnd} , multiplied by 100 for illustrative purposes.

smoothed out step function. Several techniques for calculating \bar{S}_{Bkgd} are described in Debertin and Helmer.⁵ In our XRF simulation code, the Gunnink background-shaping method is used. The background profile for a simulated peak is shown in Fig. 3.

Recall that the various \bar{S}_{Peak} and \bar{S}_{Bkgd} profiles are superimposed upon the incoherent spectrum. Figure 4 shows the cumulative peak (and background) profiles that result from the addition of all 10 individual \bar{S}_{Peak} (and \bar{S}_{Bkgd}) profiles in the simulation of a uranium solution. The sum of the cumulative peak and background profiles is shown in Fig. 4. This sum is added to the incoherent spectrum to create the simulated spectrum. Finally, random statistical fluctuations are applied to the counts in each channel of the simulated spectrum.

A simulated spectrum is shown, along with a real spectrum, in Fig. 5. Both spectra correspond to a 200-gU/l solution, with a live time of 1000 s and x-ray generator current of 10 mA. Figure 6 is a detail of Fig. 5, showing an expanded view of the uranium x-ray peaks.

CALIBRATION METHOD

To achieve a degree of realism in simulated spectra, it is beneficial to calibrate the simulation code. Calibration is done by adjusting the SIMXRF calibration factors K_{sim} so that the simulated peak areas are consistent with measured peak areas for at least one calibration sample. The K_{sim} value for any peak is the ratio of the analyzed area in a measured spectrum to the analyzed area in a simulated spectrum.

The predicted, or uncalibrated, area of a peak is obtained by evaluating Eq. 5 without the K_{sim} term. This expression for predicted area provides a functional form that agrees with trends observed in measured peak

areas. Other terms that would affect peak area, such as collimator length and diameter, have been left out of the expression. As a result, the area of an actual peak is found to be proportional to the area we predict. The K_{sim} term in our expression for simulated area represents this proportionality constant. To calibrate our simulation code we must measure K_{sim} for as many peaks as possible, and estimate K_{sim} for the remaining peaks.

A technique for single-spectrum calibration is as follows. Suppose a uranium solution is used for calibration. With the simulation code uncalibrated ($K_{sim} = 1$), a simulated spectrum \bar{S}_{sim} must be generated with the same $\bar{\rho}$, current, and live time as the calibration spectrum \bar{S}_{cal} . Both the measured and simulated spectra must be analyzed. Recall that for uranium solutions, the XRF analysis code reports only the areas of the $K_{\alpha 1}$, $K_{\alpha 2}$, and $K_{\alpha 3}$ peaks. As a result, K_{sim} can be measured for only these peaks. A weighted least-squares fit is performed on the three data points to determine the empirical slope and intercept in K_{sim} versus peak energy space. To estimate K_{sim} for each of the 47 remaining peaks, the fitted function is evaluated at the energy of each peak. If desired, these K_{sim} values can be used to generate a new \bar{S}_{sim} , and the above process repeated. For simulated and measured areas to agree within one percent, up to five iterations are needed.

The collection of measured and estimated K_{sim} values constitutes a complete SIMXRF calibration, also referred to as a calibration function. K_{sim} data for a uranium solution are shown in Fig. 7. The calibration spectrum was obtained using a 200-gU/l solution, with an x-ray generator current of 10 mA, and a detector live time of 1000 s. This calibration was used to generate the simulated spectrum shown in Figs 5 and 6.

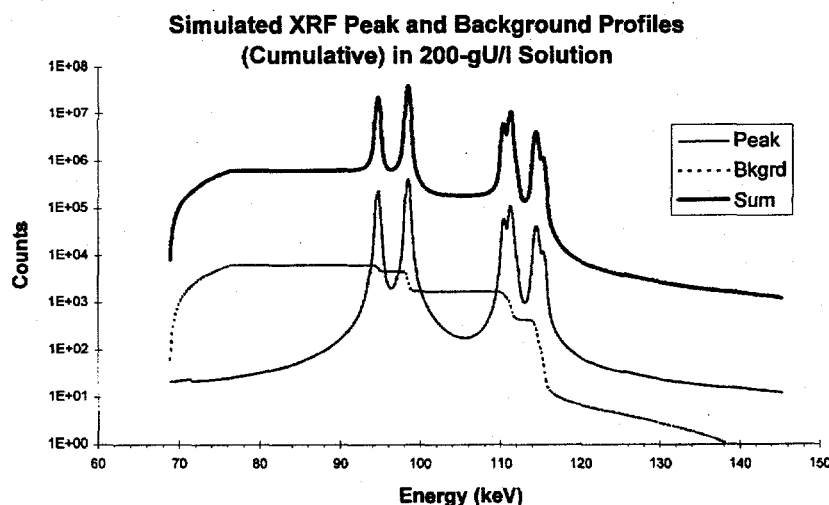


Figure 4. Cumulative profiles in 200-gU/l solution. Thin line represents sum of \bar{S}_{Peak} profiles for all 10 simulated x-ray peaks of uranium. Dashed line shows sum of \bar{S}_{Bkgd} profiles for the same 10 peaks. Broad line shows sum of cumulative profiles, multiplied by 100 for illustrative purposes.

Measured and Simulated XRF Spectra
for 200-gU/l Solution

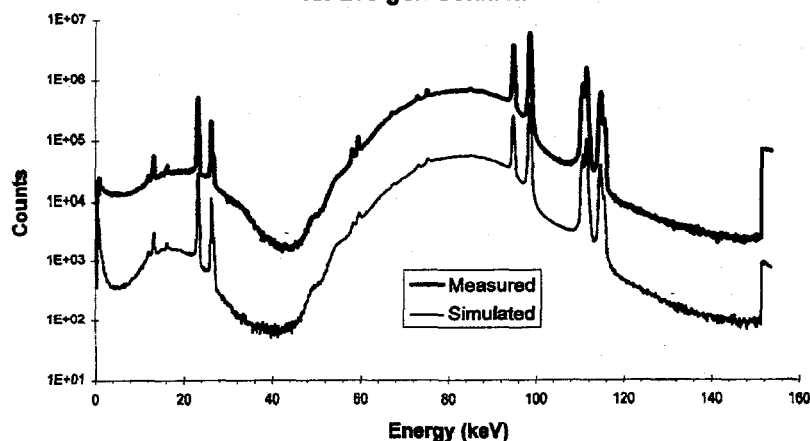
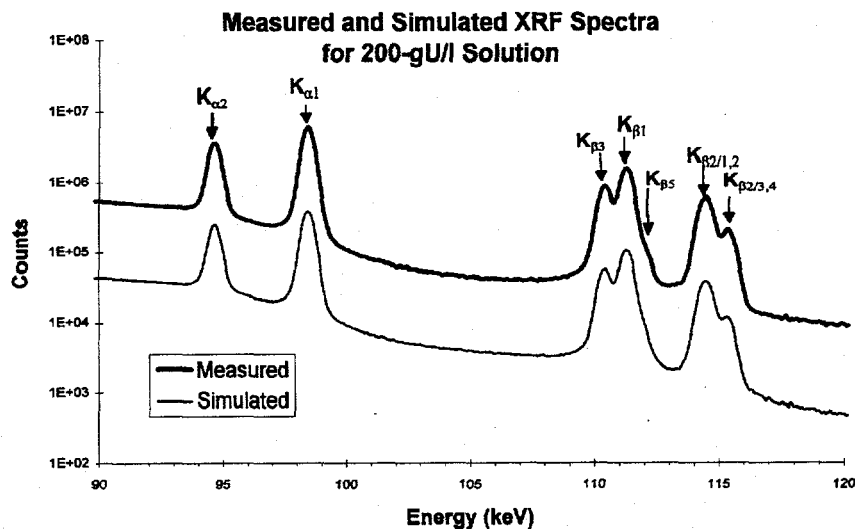


Figure 5. Measured and simulated XRF spectra, wide view. Broad line shows measured spectrum for a 200-gU/l solution, with a 1000-s live time and 10-mA current. Thin line shows simulated spectrum using same U concentration, x-ray generator current, and live time. Measured spectrum is multiplied by a factor of 15 for purposes of comparison.

Figure 6. Measured and simulated XRF spectra, close-up view. Broad line shows measured spectrum for a 200-gU/l solution, with a 1000-s live time and 10-mA current. Thin line shows simulated spectrum using same U concentration, x-ray generator current, and live time. Measured spectrum is multiplied by a factor of 15 for purposes of comparison.



SIMXRF Calibration Function, Obtained Using
Measured Spectrum from 200-gU/l Solution

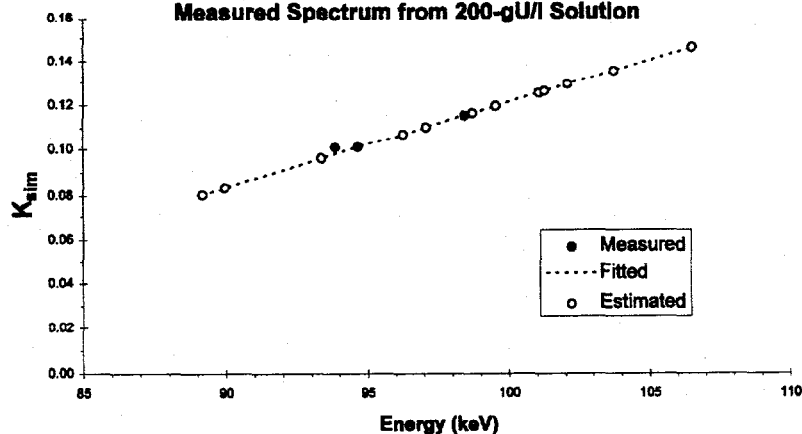


Fig. 7. SIMXRF calibration function using 200-gU/l solution. Solid dots represent measured K_{sim} values for uranium $K_{\alpha 3}$, $K_{\alpha 2}$, and $K_{\alpha 1}$ peaks. Dashed line represents linear trend of measured values. Outlined dots show estimated K_{sim} for K_{α} peaks of Th, Np, Pu, and Am. Estimated K_{sim} values for K_{β} peaks are not shown.

In practice, it is desirable to determine the SIMXRF calibration by using data from more than one calibration spectrum. If there are N calibration spectra, up to N measured K_{sim} values may exist for any given peak. An algorithm to average these K_{sim} values is required. Possible weighting factors in the determination of average $K_{sim}(i,j)$ include (1) the analyzed area of peak ij in the calibration spectrum, (2) the uncertainty in the concentration of element i in the calibration solution, and (3) the concentration of element i in the calibration solution. Techniques for multiple-spectrum calibration are currently being explored.

APPLICATIONS

Thorough testing of analysis software for the hybrid system requires a large number of test spectra. These spectra should represent a variety of samples with a broad range of actinide concentrations and different combinations of actinides. Ideally, we would have a calibration standard prepared for every sample we wanted to use in the trials. Once the standards were prepared, each sample would be assayed in the hybrid system; all our test spectra would be obtained by direct measurement.

If we wanted to use, say, 100 different solutions in our validation, the above process for obtaining test spectra would be very costly in terms of time and money. With XRF simulation, we might calibrate our code using five calibration standards. Once the code is calibrated, simulated test spectra for hundreds of samples could be generated in a single day. The use of SIMXRF would allow a substantial cost savings in sample preparation and a richer diversity of test cases to be examined by the analysis code.

In addition to peak areas, the XRF analysis code also reports the uncertainties in the measured areas of x-ray peaks. These uncertainties contribute to the uncertainty in the calculated ratio of two actinides (see Eq. 1). The relative abundance of minor actinides may bias the analyzed U and Pu K_{α} peak areas and their uncertainties. It is necessary to understand the bias effects of minor actinides and to know how the precision of the hybrid instrument is affected. Simulated spectra can be used to test the bias effects of minor actinides, allowing the precision of the hybrid system to be estimated for various types of solutions.

Because simulated spectra are created and displayed in a rapid fashion, the SIMXRF code provides a unique, interactive tool for use in training hybrid system

operators. By simulating various spectra, users may learn to identify x-ray peaks, observe peak height variations by changing actinide concentrations, and gain insight into the underlying physics.

CONCLUSION

This report summarizes our approach to generating simulated x-ray fluorescence spectra. The simulation program provides XRF spectra which closely resemble actual spectra obtained in the laboratory. This resemblance is verified by the XRF analysis code, which reports similar areas for x-ray peaks in measured spectra and their simulated counterparts. XRF spectrum simulation will be a valuable tool in the development of tomorrow's hybrid analysis techniques, thereby helping to enhance the precision and versatility of the Hybrid Densitometer.

ACKNOWLEDGMENTS

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