COINCIDENCE X-RAY FLUORESCENCE (CXRF) SPECTROMETRY FOR IN VIVO QUANTITATIVE MEASUREMENT OF BONE LEAD

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ABSTRACT

In previous work, the main interfering background for the in vivo lead in bone measurement was found to be from back-scattered Compton and Rayleigh source photons, which is, therefore, also the main problem for the improvement of sensitivity. Based on the physics of atomic transition, certain fractions of the characteristic K-series X-rays and L-series X-rays are in true coincidence. With an advanced CAMAC data acquisition system, experimental results are presented and preliminary quantitative methods for analyzing coincidence spectra are treated. A prototype coincidence spectrometer was proposed in previous work and is studied by benchmarked Monte Carlo simulation in this work. Additional information is provided by this method (CXRF) and measurement sensitivity is improved.

INTRODUCTION

X-ray fluorescence spectrometry has been recognized as an indispensable and powerful elemental analysis technique for many years [1-3]. XRF measurement techniques have focused primarily on detecting individual X-rays. According to previous work [4-7], the main problem for sensitivity improvement of in vivo lead in bone measurement is the background from back-scattered source photons. With the objective of improving measurement sensitivity, the authors are applying and investigating the use of Coincidence X-Ray Fluorescence (CXRF) spectrometry in the measurement of lead in bone.

Coincidence spectrometry has been applied previously to various fields, such as radioisotope standardization [8, 9] and gamma-gamma or particle-gamma coincidence measurements [10, 11], to improve measurement sensitivity and to better understand the physical processes involved. The fundamental idea of coincidence spectrometry is to detect multiple events that are correlated in time of emission, which has the effect of minimizing the background. Suppose two detectors are available for a radiation detection experiment. For events that are not emitted at the same time, the singles counting rate in the two detectors is $N_1$ and $N_2$, respectively. For coincidence measurement, a very short time window, $\tau$ (often of nanosecond magnitude), is applied for the measurement. If two events, one from each detector, are detected within that time window, a coincidence event is scored. This is illustrated in Figure 1, where only events of case A will be scored. Of all the coincidence events scored, there will be some events caused by chance or
random coincidence. Mathematically, the chance coincidence events can be estimated from the following equation [12],

\[ N_{\text{chance}} = \tau N_1 N_2 \]

which shows that with the time window of $10^{-9}$ seconds or less, the chance coincidence rate can be reduced greatly. Therefore, the signal to noise ratio can be increased.

![Figure 1. Schematics of correlated and uncorrelated pulses in time](image)

When an incoming photon falls onto a specimen, one of three basic interactions may occur: Rayleigh (coherent) scattering, Compton (incoherent) scattering, or photoelectric absorption. For scattering interactions, the photon changes direction according to a certain distribution and loses energy in the Compton scattering case. After a photoelectric absorption interaction (Figure 2a), the target atom is excited by absorbing the photon energy with an inner-shell electron. This electron will be ejected out of the shell when the incident photon energy is greater than its binding energy, and this leaves a hole in the shell. This hole will then be occupied by another electron from an outer shell accompanied by the emission of a non-radiative Auger electron (Figure 2b) or an X-ray photon (Figure 2c), or sometimes both (satellite lines). It is noted that the hole “transitions” to a new shell with lower binding energy than the original shell after the first step of relaxation. With the probability equal to the fluorescence yield of the shell where the core hole exists, one more X-ray may be emitted from the atom in the second step of relaxation. The transition time for this process is of the order of $10^{-15}$ seconds [13]. This is the fundamental physical basis of the proposed CXRF spectrometry in this work.

![Figure 2. Schematics of characteristic X-ray coincidence emission](image)
CXRF EXPERIMENTAL RESULTS

Two experiments were made for CXRF measurement. For both experiments, one rectangular piece of pure lead of 2mm thickness was used as the sample. Cadmium-109 was used as the activation source, which was collimated in the direction of sample. One of the experiments used two X-ray NaI(Tl) detectors (25mm radius × 1mm thickness), Figure 3a, and the other one substituted one detector by a low energy Ge detector (LEGe) (25mm radius × 15mm thickness), Figure 3b.

![Figure 3. Schematics for experimental geometry](image)

By using a CAMAC system for data acquisition, the singles and coincidence spectra for both detectors were obtained and recorded at the same time. Subsequently, a 2-D histogram for the coincidence measurement was sorted on line with the Sparrow software Kmax 7.

The singles and coincidence spectra for the two NaI(Tl) detectors and for one NaI(Tl) and one LEGe detector is shown in Figures 4a and 4b, respectively.

![Figure 4. Experimental singles and coincidence spectra comparison](image)

It is clear that the scattered source photons (both Cd-109 88 keV Gamma rays and Ag X-rays, 22.2 keV and 24.9 keV) are minimized in the coincidence spectra. The Pb K and L X-ray intensities are enhanced relative to the continuum.

To obtain information from the energy coincidence relationship, 2-D histograms were sorted for
both measurements (Figure 5a and Figure 5b). The X axis and Y axis in Figure 5 represent
the energy information of each detector, respectively. The intensity of each point in the figure
represents the measured intensity of the coincidence event with energy deposition in the two
detectors as the corresponding values on the X and Y axes. Various interesting ways are possible
to obtain information from the 2-D histogram. The region projection method is currently under
investigation. The basic idea of region projection is to first identify regions according to pertinent
specific rules over the 2-D scatter plot. A 1-D histogram (spectrum) can be formed by projecting
the region to one of the axes along each channel. Several rules of region identifications are of
primary interest:
1. Complete regions (CR). This is the same as the total coincidence spectrum from one of the
detectors.
2. Parallel regions (PR) relative to one of the axes, projected to that axis (Region 1 and Region 2
in Figure 5a). This forms the spectrum by one detector in coincidence with the energy deposition
of some specific range of values in the other detector.
3. Diagonal regions (DR) (Region 3 in Figure 5b). This forms the spectrum for which only
coincidence events with energy summation equal to a specified range are taken into account.

MONTE CARLO SIMULATION

To further investigate the CXRF, a Monte Carlo simulation code named CEARXRC has been
developed based on the previous CEARXRF code by adding Monte Carlo simulation capability
for coincidence X-rays.

The geometry in Figure 3b was simulated to benchmark the Monte Carlo simulation code. The
experimental spectrum was formed by selecting a diagonal region according to the lead K
absorption edge (as in region 3 of Figure 5). The current Monte Carlo simulation code is not
capable of simulating the cross talk effect. So the experimental spectrum was further processed
by filtering out the cross talk peaks (Iodine X-rays). This diagonal summing coincidence
spectrum is compared to the Monte Carlo simulated spectrum in Figure 6 and shows good
agreement.

To apply the coincidence measurement to the lead in bone measurement, the overall low coincidence rate needs to be dealt with due to the trace level amount of lead in human bones. The prototype X-ray coincidence spectrometer, shown in Figure 7, was proposed previously [14]. It combines the advantage of a high resolution Ge detector and a large area (6-inch diameter) NaI(Tl) detector of high total efficiency. The Monte Carlo simulation for this prototype spectrometer shows promising results by improving the coincidence efficiency by an order of magnitude over that for the benchmark experiment with a 2-inch diameter NaI detector. A comparison of the Monte Carlo simulation results for the two cases is shown in Figure 8.

**QUANTITATIVE RESULTS**

With the current experimental facilities, both singles spectra and coincidence spectra are obtained simultaneously as well as generation of the 2-D histogram with energy coincidence pair information. A very large amount of additional information is available compared to either the traditional singles measurement or the traditional coincidence measurement. Heuristically, better results are guaranteed, since the additional coincidence measurement data obtained must improve the singles measurement.

Two preliminary cases have been treated for quantitative lead determination with least-squares analysis.
The first case analyzed the pure lead sample measurement results. For this case, the experimental spectrum in Figure 6 was taken as the lead library spectrum and the difference between it and the total coincidence spectrum was treated as the background spectrum. With these two spectra as libraries, the total coincidence spectrum was fitted as the unknown. The fitted reduced Chi-square value is 1.36 and the lead amount obtained is $0.96 \pm 1.5\%$.

The second study treated the simulated coincidence spectrum by the proposed X-ray coincidence spectrometer. In the simulated spectrum, the diagonal summing data (Figure 8) was treated as the total spectrum. Lead was considered to be the only element that can contribute in that region except chance coincidence background. The fitted reduced Chi-square value is 0.98 and the lead amount is $162\text{ppm} \pm 0.10\%$. Compared to the analytical results by singles spectrum and libraries of $164 \pm 0.94\%$ [15], the sensitivity is improved as much as a factor of 10.

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