LA-UR- 08-5480

*Approved for public release; distribution is unlimited.*

*Title:* RADIOACTIVE SAMPLE EFFECTS ON EDXRF SPECTRA

*Author(s):* Christopher G. Worley

*Intended for:* Advances in X-ray Analysis
Proceedings of the 2008 Denver X-ray Conference

Los Alamos
NATIONAL LABORATORY
EST.1943

# RADIOACTIVE SAMPLE EFFECTS ON EDXRF SPECTRA

**Christopher G. Worley**

*Los Alamos National Laboratory, MS G740, Los Alamos, NM 87545*

## ABSTRACT

Energy dispersive X-ray fluorescence (EDXRF) is a rapid, straightforward method to determine sample elemental composition. A spectrum can be collected in a few minutes or less, and elemental content can be determined easily if there is adequate energy resolution. Radioactive alpha emitters, however, emit X-rays during the alpha decay process that complicate spectral interpretation. This is particularly noticeable when using a portable instrument where the detector is located in close proximity to the instrument analysis window held against the sample.

A portable EDXRF instrument was used to collect spectra from specimens containing plutonium-239 (a moderate alpha emitter) and americium-241 (a heavy alpha emitter). These specimens were then analyzed with a wavelength dispersive XRF (WDXRF) instrument to demonstrate the differences to which sample radiation-induced X-ray emission affects the detectors on these two types of XRF instruments.

## INTRODUCTION

Pulse pile-up, escape peaks, and sample diffraction effects can complicate EDXRF spectra, but these artifacts are recognizable by an experienced analyst. Radioactive alpha emitters, however, emit X-rays due to internal processes that result from alpha decay, which further complicates spectral interpretation. (Gamma rays emitted by radioactive samples are indistinguishable to the detector from X-rays of the same energy, but gamma energies are normally too high to be of concern in EDXRF.) This alpha decay effect can be seen in plutonium-239 spectra which exhibit a prominent uranium L X-ray emission peak series. When a plutonium-239 atom alpha decays, there is some probability that the uranium-235 daughter nucleus will be left in an excited state that can then transfer its excess energy to an electron through internal conversion.[1] If the electron is then ejected upon absorption of this energy, an X-ray photon or Auger electron will be emitted. Hence, the uranium L X-ray series is present due to sample radioactive decay rather than source-induced X-ray fluorescence. Therefore, quantifying the uranium based on observed peak intensities can lead to erroneous results.

Portable instruments are particularly susceptible to this effect due to the small distance between the specimen and the detector. In the present study, Pu-239 metal was analyzed with a portable EDXRF instrument consisting of a detector closely coupled to the analysis window to maximize analyte signal. The same specimen was also examined by WDXRF, where the detector was located much further from the specimen with a diffraction crystal in between the specimen and detector to demonstrate the effect that instrumental geometry and detectors have on detecting alpha event X-rays.

In another experiment, dissolution and ion exchange solid phase extraction were used to separate americium-241 from an old Pu-239 metal sample, and the eluate solution was analyzed with the portable EDXRF instrument. Am-241 is a strong alpha emitter. Thus, this study was used to compare the differences observed in EDXRF spectra collected from moderate alpha emitters such as Pu-239 versus heavy emitters like Am-241.

## EXPERIMENTAL

*Instrumentation.* The portable EDXRF instrument was a Keymaster Technologies Tracer III-V containing a silver X-ray anode. The maximum operating voltage was 40 kV, and the maximum power was ~0.5W. A Ti/Al filter was used in front of the source to reduce background counts. The WDXRF instrument used was a PANalytical PW2404 with a 4000 W rhodium anode. The data were collected while flushing the analysis chamber with helium. A LiF(220) crystal was used for wavelength separation. A 150 μm collimator was used in front of a scintillation detector, and a 200 μm aluminum tube filter was employed. A 30 mm source collimator mask was used.

*Plutonium metal.* An ~0.5 g chunk of Pu-239 metal containing ~30 ppm uranium was sealed inside a 40 mm plastic XRF specimen cup with 7.5 μm Kapton. A 4 μm Prolene secondary film was placed over the primary film for analysis. The specimen was analyzed qualitatively with the handheld EDXRF at high and low power settings (40 kV, 10 μA and 5 kV, 0.1 μA respectively) for 30 sec each. The specimen was also qualitatively scanned for 60 sec over the Pu Lα and U Lα energy range with the WDXRF instrument at high power (60 kV, 66 mA) and low power (20 kV, 10 mA) settings.

*Americium eluate.* Approximately 0.5 g of an ~21 year old Pu-239 metal sample containing ~1820 ppm Am-241 was dissolved in 6 M HCl. The americium was separated from the plutonium using ion exchange solid phase extraction (Bio-Rad AG MP-1 200 to 400-mesh resin used). An ~5 mL aliquot of the americium eluate (~88 ppm Am) was transferred to a 40 mm plastic specimen cup and sealed with 7.5 μm Kapton. A 4 μm Prolene secondary film was placed over the primary film for analysis. Qualitative spectra were collected from the solution for 30 sec each with the handheld EDXRF instrument operated at 40 kV, 2.6 μA and then at 5 kV, 0.1 μA.

## RESULTS AND DISCUSSION

*Plutonium metal.* The detector is located in close proximity to the specimen in portable EDXRF instruments in order to collect ample signal while using a very low powered, battery operated X-ray source. This also results in the presence of substantial specimen radiation-induced X-ray peaks. Spectra collected from plutonium metal at low and high power are compared in figure 1. The low power setting was used to simulate collecting a spectrum with the source off. (The instrument will not collect data with the source actually turned off). Hence, only sample radiation-induced X-ray emission was detected in this spectrum.

Because Pu-239 alpha particle ejection and the subsequent internal conversion process results in the emission of uranium X-rays, a uranium L peak series was present in the plutonium spectrum.

The sample only contained ~30 ppm uranium, but a marked uranium L peak series was present even in the spectrum collected with the source at 5 kV. This voltage was not nearly high enough to induce uranium L fluorescence. Hence, the uranium peaks were clearly due to the Pu-239 alpha decay and internal conversion process.

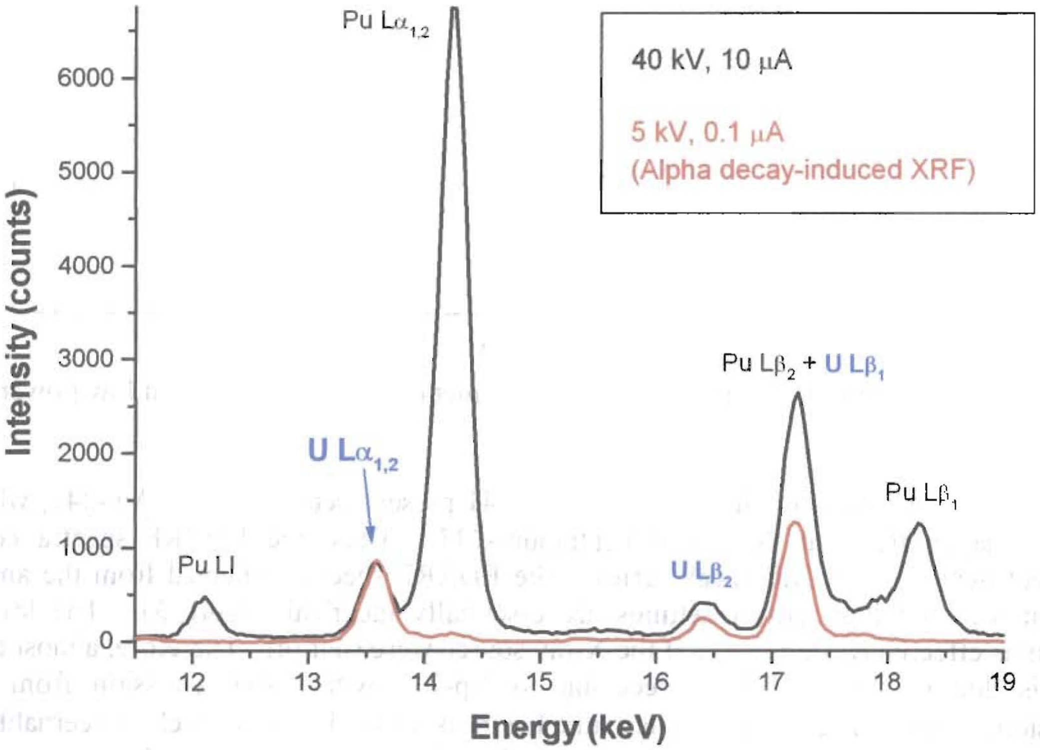

Figure 1. EDXRF spectra from plutonium metal acquired at high and low power.

When the same specimen was analyzed by WDXRF (figure 2), no uranium L peaks were observed. A high powered X-ray source is necessary to collect adequate analyte signal due to attenuation by the large distance and diffraction crystal between the specimen and detector. Thus, the relatively weaker alpha decay-induced fluorescence signal is severely attenuated in this geometry and not detected. To simplify spectral analysis, WDXRF is therefore preferable to EDXRF for analyzing alpha emitters.

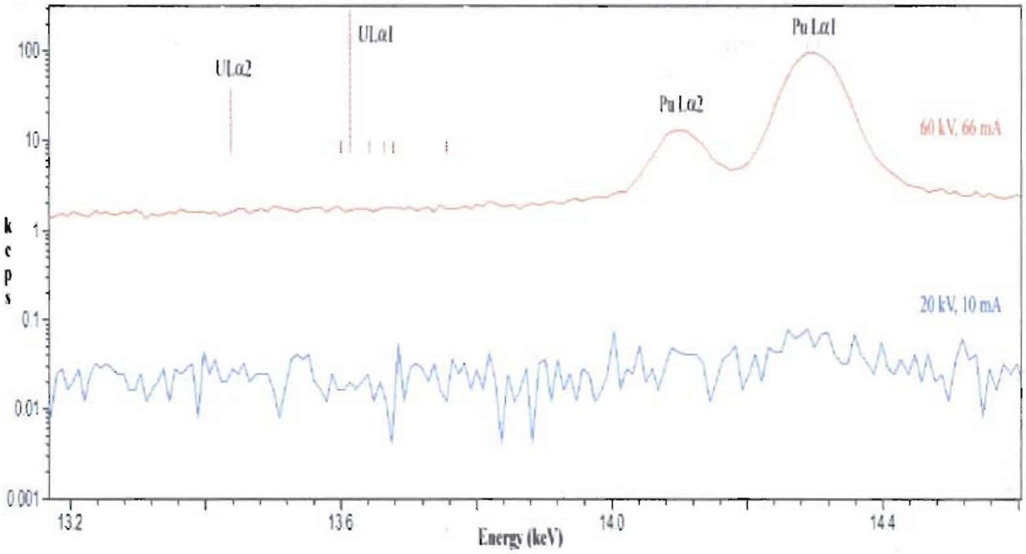

Figure 2. WDXRF spectra from plutonium metal acquired at high and low power.

*Americium eluate.* As plutonium ages, any Pu-241 present beta decays to Am-241, which is a strong alpha emitter that decays to neptunium-237. Thus, the EDXRF spectra contain a prominent neptunium L XRF peak series. The EDXRF spectra collected from the americium eluate at low and high power settings are essentially identical (figure 3). The low power spectrum is effectively the same as if the X-ray source were shut off. Therefore, almost all of the signal is due to Am-241 alpha decaying to Np-237 with X-ray emission from internal conversion. The source-excited americium Lα peak (14.6 keV) is barely discernable above background. The analyzed solution contained ~88 ppm americium and a meager 4 ppm neptunium. However, the signal-to-background of the neptunium L peak series would lead one unfamiliar with analyzing radioactive samples to conclude that neptunium was a major component of this sample. Given that the source-excited americium peak is just above background, and a marked neptunium L series is present, the alpha decay and internal conversion XRF process must be very efficient compared with source-excited fluorescence. Thus, these results demonstrate that one must be very cautious in interpreting sample content or performing elemental quantification of alpha emitters using EDXRF.

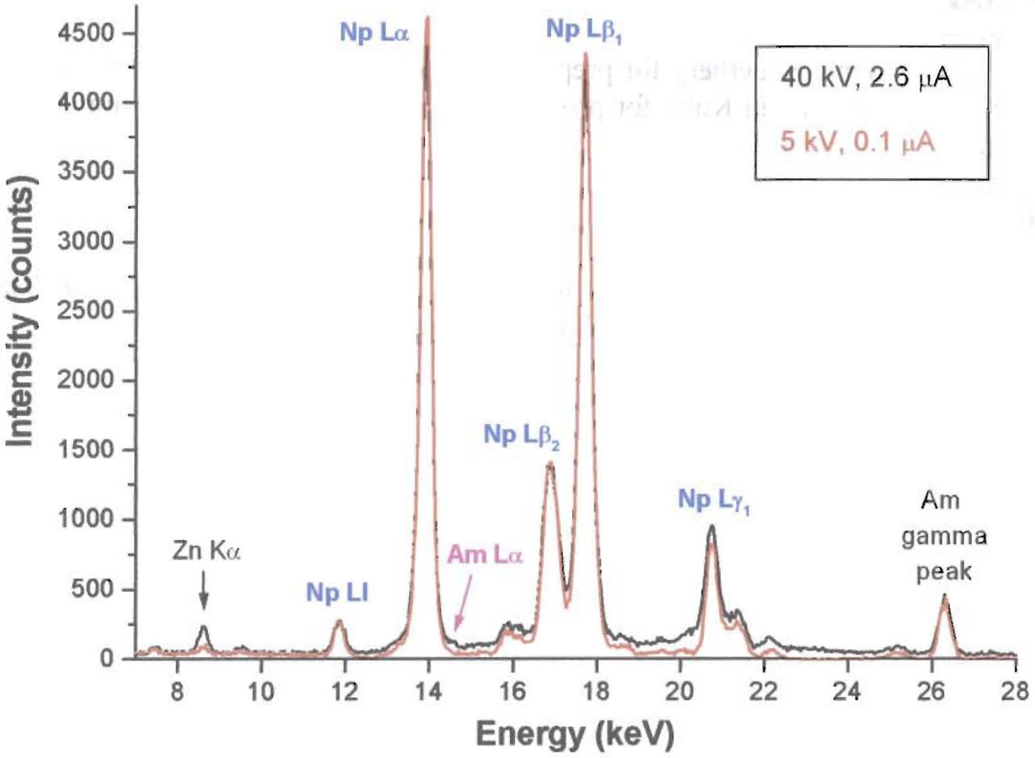

Figure 3. EDXRF spectra from americium eluate solution acquired at high and low power.

## CONCLUSION

Interpretation of EDXRF spectra is typically straightforward; however, spectra from alpha emitters are complicated by X-ray peaks from the radionuclide daughter element (atomic number Z-2). The stronger the alpha emitter, the more pronounced these peaks will be. Hence, the analyst must be careful when interpreting EDXRF spectra collected from radionuclides; peak intensities do not necessarily correlate with elemental concentration.

As demonstrated here, portable EDXRF instruments are particularly affected by this phenomenon due to the close coupling of the specimen and the detector. EDXRF spectra collected from plutonium and americium specimens exhibited prominent X-ray peaks due to alpha decay daughter products. Analysis of an americium solution demonstrated that even when the americium content was relatively low, enormous neptunium daughter X-ray peaks were present. This sample radiation effect is much less pronounced when using WDXRF; spectra from a plutonium specimen did not contain any uranium L peaks as were detected with EDXRF. This is because the radionuclide-induced X-ray signal is severely attenuated by the large distance and crystal between the specimen and the detector. Hence, WDXRF is more suitable for analyzing alpha emitters when quantification or trace analysis is needed in the energy range where the alpha decay daughter X-ray emission peaks are located.

## ACKNOWLEDGMENTS

I would like to thank Connie Soderberg for preparing the americium eluate solution. I am also grateful to Lav Tandon and Kevin Kuhn for providing the age of the plutonium sample used to prepare the americium specimen.

## REFERENCES

[1] D. Reilly, N. Ensslin, and H. Smith, Jr. *Passive Nondestructive Assay of Nuclear Materials*, U.S. Government Printing Office: Washington, D.C., 1991.