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and the "Oxide" Attribute**

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March 7, 2000

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**



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Origin of The 871-keV Gamma Ray and the "Oxide" Attribute

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3/7/00

Summary

This brief paper concludes our study of the origin of the 871-keV observed for many plutonium oxide samples. Analysis of a variety of experimental results confidently establish the following conclusions:

- The 871-keV gamma ray arises solely from the reaction $^{14}\text{N}(\alpha, p)^{17}\text{O}$.
- Even the experimentally inferred maximum possible contribution from the reaction $^{17}\text{O}(\alpha, \alpha')^{17}\text{O}^*$ would not be measurable in any oxide sample.
- The presence of air within or surrounding the oxide powder leads to a measurable 871-keV gamma-ray flux.
- A nitrogen impurity of roughly 200 ppm would lead to a measurable 871-keV gamma-ray flux. (Samples measured at PNNL did not contain this level of nitrogen impurity.)

The implications of these results for arms control are complex. Clearly, the presence of an 871-keV gamma-ray flux indicates that a sample is not metallic. Unfortunately, the converse assertion is far from true. That is, the lack of a measurable 871-keV gamma-ray flux does not indicate that the sample is metallic. Plutonium in the oxide form can easily be "disguised" via compaction, purification, or atmospheric control. We would suggest that a more appropriate name for this attribute would be "presence of nitrogen." This new name accurately conveys the strengths and weaknesses of this attribute as we now understand them.

These conclusions were established via a series of spectral measurements of plutonium and americium in a variety of physical states. Acidified solutions, solid oxide powder, and metallic forms were analyzed. The atmosphere surrounding the powder was controlled and varied between argon, air, and nitrogen. Chemical processing was employed on the oxide powder to remove all solid nitrogen impurity. The aqueous solutions were in both hydrochloric and nitric acids of varying molarity.

A comprehensive theoretical analysis of the experimental results is able to consistently explain the full suite of results. While the underlying nuclear reaction cross sections for production of the 871-keV gamma ray in nitrogen and oxygen are not known, the constraints placed upon the necessary cross sections are not unreasonable.

Introduction

This work concludes the investigation of the "oxide" attribute of current interest for the characterization of stored plutonium. Originally it was believed that the presence of oxide could be ascertained by measurement of the 871-keV line in a high-resolution gamma-ray spectrum (Hsu, 1982). However, recent work has suggested that the 871-keV gamma ray in plutonium oxide arises from the reaction $^{14}\text{N}(\alpha, p)^{17}\text{O}$ rather than the inelastic scattering reaction $^{17}\text{O}(\alpha, \alpha')^{17}\text{O}^*$ (Geelhood, 1999; Marlow, 1999; Peurrung, 1999). This conclusion, though initially surprising, was obtained during efforts to determine the relative importance of americium and plutonium alpha-particle decay for the production of the 871-keV gamma ray. Several questions were raised by previous experiments:

- What role, if any, does ^{17}O have in the generation of the 871-keV gamma ray?
- How does sufficient nitrogen come to be present in plutonium oxide?
- Under what conditions is the 871-keV gamma ray measurable in plutonium oxide?

This paper describes the answers to these questions. We can state confidently that ^{17}O has no significant role in the generation of the 871-keV line for any oxide samples. There are arguably three different ways that nitrogen comes to be present in plutonium oxide. First, nitrogen may be present as an impurity at roughly the 1000-ppm level or higher. Such nitrogen would lead to an 871-keV gamma-ray flux that is easily measurable under ordinary conditions. Second, immersion of a powder in air causes significant amounts of nitrogen to permeate the pore spaces between the individual oxide particles. Third, a measurable 871-keV gamma-ray flux could arise merely from the interaction of alpha particles (from plutonium decay) with air surrounding a small oxide sample. Thus, a measurable 871-keV gamma-ray flux should be observable only when the oxide either contains significant nitrogen as an impurity, or when air is present within or around an oxide powder. We believe that the 871-keV line will not be observed from oxide under any of the following conditions:

- The oxide is surrounded by a gas such as argon or helium that contains little nitrogen.
- The oxide is compacted and sealed with little extra space for air.
- The oxide is immersed in or dissolved in a liquid such as oil or water that does not contain nitrogen.

The 871-keV peak is not observed from a metal sample because the surface area potentially in contact with surrounding ^{14}N is much smaller than for an oxide sample. Measures taken to prevent oxidation of metal components (e.g. plating or inert gas atmosphere) also prevent the alpha interaction with ^{14}N .

Experiments

The work incorporates both the earlier experiments with ^{241}Am and ^{239}Pu dissolved in aqueous solutions of hydrochloric and nitric acids, and newer experiments with plutonium oxide powder. In all cases, a high-resolution gamma-ray spectrometer was used in conjunction with sufficient lead attenuator to reduce dead time to acceptable levels. Counting times ranged from minutes to hours, depending upon the length of time necessary to acquire a spectrum with adequate statistics for measuring and comparing the 871-keV flux. In at least one case a sophisticated low-background cave was used to

lower background and permit measurement of the 871-keV gamma-ray flux from a rather weak source (11 μCi of ^{239}Pu).

The goal of the most recent experiments was to fully characterize the nitrogen within a plutonium oxide sample and quantify its role in the generation of the 871-keV gamma ray. To this end, a sample of roughly 5.2 grams of dry plutonium (weapons-grade with 0.42% ^{241}Am grown in) oxide powder was subjected to a variety of physical and chemical manipulations. The atmosphere surrounding this powder was controlled and variously selected to be ordinary air, pure argon, and pure nitrogen. In order to remove any nitrogen impurities, the powder sample was then subjected to the following sequential steps:

- An oxalate wash followed by drying and calcining¹ at 1000°C to convert any remnant of oxalate or carbonate into oxide. This step also removed some fluoride impurities and should have removed any soluble nitrogen impurities.
- Vigorous Dissolution in sodium hydroxide and hydrogen peroxide ("sodium fusion") followed by acidification in hydrochloric acid.
- Precipitation with oxalate and calcining at 1000°C.

It should be noted that the physical character of the powder (density, granularity, etc.) was observed to change as a result of these manipulations.

Results

Although the region of the plutonium spectrum near 871-keV contains many peaks, the 871-keV line can be sufficiently strong that its presence can be determined with high statistical confidence in less than an hour using a typical HPGe spectrometer. Figure 1 shows six spectra taken during the course of this work. Five of the spectra are of the plutonium oxide powder sample under various conditions. The two "pre-wash" spectra are the oxide (as originally received) under nitrogen and argon atmospheres. The "washed" spectrum is under air. Finally, the two "purified" oxide spectra are the final purified powder under nitrogen and argon atmospheres. For comparison, a plutonium bulk-metal spectrum is shown. The metallic plutonium is material with a different mass, isotopic composition, age, and counting geometry. Nevertheless, it serves as a useful comparison spectrum. All spectra, except the Pu metal, have been normalized to the strong 769-keV peak from ^{239}Pu , which is not shown in Figure 1. Figure 2 shows essentially the same data as Figure 1, but with the strongest nearby peaks from ^{239}Pu and ^{241}Am shown to illustrate this normalization process. Note the recoil-broadened ^{72}Ge neutron peak that increases in energy starting at 834 keV. The feature is due to fast neutrons from the sample that undergo inelastic scatter on ^{72}Ge within the detector crystal itself.

There are a number of peaks in the general region other than the 871-keV peak, as seen in Figure 1. These peaks arise not only from plutonium and americium, but also from

¹ N.B. — "Calcine" is the chemical term for heating a refractory material to a high temperature to drive off volatile components or to convert a compound to a simpler chemical form. For the plutonium sample used in this study, the purpose was to convert any nitrate, oxalate, or carbonate to the oxide (Cleveland, 1967). The process here does not involve any reactions with calcium, but rather, the term "calcination" derives historically from the production of lime (calcium oxide) by roasting calcite (i.e. limestone, chalk, or marble as principal sources of calcium carbonate), which decomposes the carbonate radical and drives off the resulting carbon dioxide.

^{228}Th daughters, inelastic neutron scattering gamma rays (Zhou, 2000), and even other (α, n) reactions. A listing of the identified peaks is provided in Table 1.

Table 1. Additional Peaks and Associated Branching Fraction as Identified in the 870-keV Region of Figure 1.

Peak	Branching Fraction	Comments
851.72 keV	$2.03 \cdot 10^{-9}$	Pu-238
860.30 keV	—	Tl-208 (daughter of Th-228)
862.6 keV	$5.3 \cdot 10^{-7}$	Am-241
870.8 keV	—	$^{14}\text{N}(\alpha, p)^{17}\text{O}$ ← 871-keV Peak of interest
872.7 keV	$7 \cdot 10^{-7}$	Am-241
873.94 keV	$5.8 \cdot 10^{-7}$	Pu-240
881.0 keV	—	$^{206}\text{Pb}(n, n')^{206}\text{Pb}^*$
883.24 keV	$1.11 \cdot 10^{-6}$	Pu-238
890.9 keV	—	$^{19}\text{F}(\alpha, n)^{22}\text{Na}$

Note that both the 873-keV and 874-keV peaks from Am-241 and Pu-240 are close enough to the 871-keV peak that resolution of the two separately is difficult or impossible. This fact complicates statistical identification of the 871-keV peak when it is weak.

We conclude that the 871-keV flux arises from nitrogen impurities and from nitrogen gas surrounding the powder, as seen in Figures 1 and 2. Clearly the ratio of the 871-keV flux to the 769-keV flux would not change (as was observed) were oxygen the dominant source of 871-keV gamma-ray emission. Instead, we find that the amplitude of the 871-keV peak varies with atmosphere at each of the three stages in our purification process. The effect of our efforts to remove nitrogen impurities in the oxide powder is harder to determine conclusively. There appears to be a decrease in the 871-keV line intensity between the nitrogen-atmosphere spectra before and after the washing and calcining steps. However, the 871-keV line returns again to nearly its original intensity after the dissolution, acidification, and precipitation steps. We believe these seemingly paradoxical results are the result of the fact that the 871-keV line arises primarily from alpha-particle interactions with the nitrogen gas. The powder's density (void fraction) changes after each step as does the amount of powder that adheres to the sides of the container. We thus take this behavior as evidence that gas-phase interactions are of primary importance.

The clearest evidence for the prevalence of gas-phase interactions is shown in Figure 3. This figure shows only the spectra of the purified oxide powder with argon and nitrogen atmospheres. Note that the full spectra are virtually identical except for the 871-keV line. The remaining nitrogen impurity concentration for these spectra should be both greatly reduced relative to the original concentration and completely insignificant in the context of 871-keV gamma-ray generation. Based upon these results it is hard to imagine attributing the 871-keV flux to any source other than alpha-particle interactions with gas-phase nitrogen.

These results are not surprising upon careful consideration. Previous results found that 1.1 mCi of ^{239}Pu in an 8 molar solution of nitric acid emitted the 871-keV gamma ray at a rate of roughly 2.1 per second. The same amount of plutonium emits the 769-keV gamma ray at a rate of 4.6 per second as a result of plutonium decay. We know conclusively that the 871-keV flux from the nitric acid solution arises from nitrogen interactions for two reasons:

- 1) The flux scaled linearly with the molarity of the nitric acid solution for two different samples.
- 2) No measurable 871-keV flux was present when americium was dissolved in a hydrochloric acid solution, but is manifest when nitric acid is added.

It is reasonable to expect that the ratio of the 871-keV flux to the 769-keV flux should scale linearly with both the nitrogen concentration and the range of the alpha particle. The alpha-particle range for the aqueous solution is roughly 40 microns. The range in plutonium oxide depends, of course, on the powder density. Although the nominal density of plutonium oxide is roughly 11.5 g/cm^3 , the density for our powder was in the range of $3\text{-}4 \text{ g/cm}^3$. Consequently, the alpha-particle range in our purified oxide powder was also close to 40 microns. These calculations are based upon Figure 2-8 ("Range-energy curves calculated for alpha particles in different materials") of Knoll's text on radiation detection (Knoll, 1989). We hypothesize, therefore, that the ratio of the 871-keV flux to the 769-keV flux for both aqueous acid solutions and fine, low-density oxide powders should scale approximately with the nitrogen concentration. (We neglect differential attenuation for these small samples.) The nitrogen concentration in the 8M nitric acid solution is $4.8 \times 10^{21} / \text{cm}^3$. The presence of air within the powder results in a nitrogen concentration of roughly $3.5 \times 10^{19} / \text{cm}^3$. One would therefore expect the line ratio to be roughly 140 times lower in the oxide than in the acid solution. In fact, the ratio was observed to be roughly 18 times lower, leaving a discrepancy of a factor of roughly 7.6.

This additional factor of 7.6 is believed to arise from alpha-particle interactions in the gaseous nitrogen *external*, rather than internal, to the powder. There is only about 0.8 cm^3 of nitrogen gas within the powder, whereas there is roughly 10 cm^3 of gas in the space around the powder. Since the range of alpha particles in air is roughly 3.5 cm, the nitrogen reaction will be possible during roughly the first centimeter of a 5-MeV alpha particle's track through the air. While exact calculations are impossible given the unknown distribution of oxide on the sides of the container, it seems clear that such interactions easily account for the bulk of the 871-keV gamma-ray generation.

Two quantitative results of importance can be gathered from these experiments. First, we can state that the nitrogen impurity concentration necessary to lead to 871-keV peak generation of significance is roughly $3 \times 10^{19} / \text{cm}^3$, which corresponds to 200 ppm. Amounts significantly less than this would not be able to generate a measurable 871-keV flux. Second, we can estimate the maximum contribution to the 871-keV flux that oxygen could account for. Measurement of the hydrochloric acid solution of 86 μCi of americium placed an upper bound of 0.004 photons/second on the 871-keV emission rate. Assuming conservatively that plutonium alpha particles produce 871-keV gamma rays at the same rate as plutonium gamma rays, we can place an upper bound on the oxygen generation rate in our powder sample. Calculations indicate that the 871-keV flux from oxygen can be no more than 10% of the value observed for the pure oxide powder in a nitrogen atmosphere. Even at this maximum possible level, the flux would be hard to measure in a reasonable time, especially in light of the nearby ^{241}Am and

^{240}Pu peaks. (These peaks will be more pronounced for plutonium containing more ^{240}Pu than the 6% for this oxide sample.)

Conclusion

The experimental data resulting from high resolution spectra of plutonium oxide powder and aqueous solutions of plutonium and americium allow us to conclude that the 871-keV gamma ray observed for many oxide samples always arises from the reaction $^{14}\text{N}(\alpha, p)^{17}\text{O}$. We further conclude that this nitrogen is present in the gas within and around the powder sample. This is the only hypothesis that can quantitatively explain the full spectrum of experimental observations:

- The linear scaling of 871-keV flux with nitric acid molarity.
- The similar 871-keV gamma-ray production rates for americium and plutonium alpha particles.
- The lack of an observable 871-keV flux for americium in a nitrogen-free solution.
- The lack of an observable 871-keV flux for a variety of plutonium oxide samples. (Martin, 1965; Marlow, 1999)
- The lack of an observable 871-keV flux for purified plutonium oxide powder in a nitrogen-free atmosphere.
- The reasonable scaling of the 871-keV flux with nitrogen concentration and alpha-particle range for both aqueous and powder samples.

The "oxide" attribute should be re-evaluated in light of these results. While this attribute clearly retains some value, it has less than originally claimed. The implications of these results for arms control are complex. Clearly, the presence of an 871-keV gamma-ray flux indicates that a sample is not metallic. Unfortunately, the converse assertion is far from true. That is, the lack of a measurable 871-keV gamma-ray flux does not necessarily indicate that the sample is metallic. Plutonium in the oxide form can easily be "disguised" either via compaction, purification, or atmospheric control. We would suggest that a more appropriate name for this attribute would be "presence of nitrogen." This new name accurately conveys the strengths and weaknesses of this attribute, as we now understand them.

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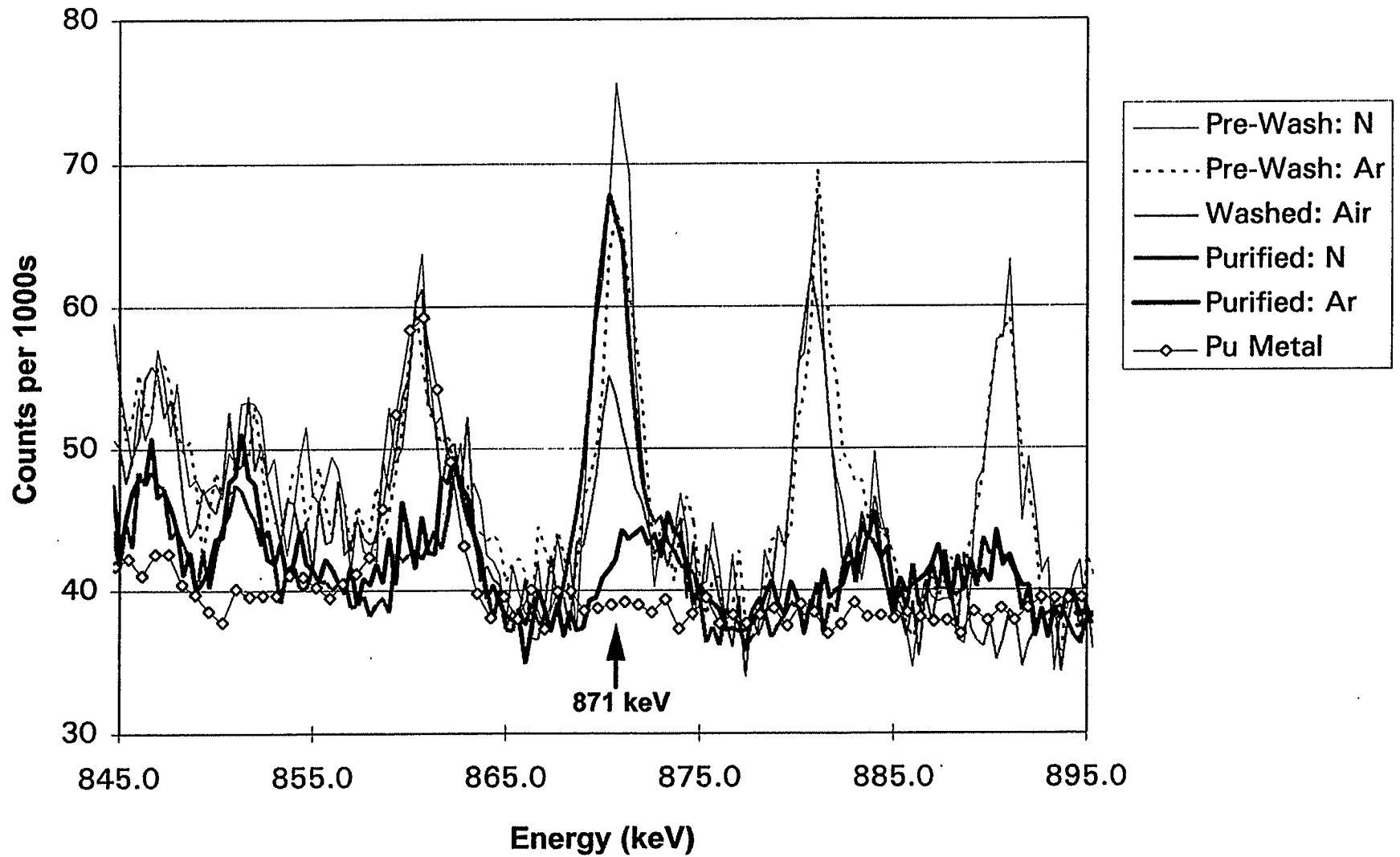


Figure 1. Comparison of Normalized Spectra for the Same Raw, Washed, and Purified Plutonium Oxide Sample. Please note that spectra for the purified sample are elevated by 10 counts/1000s for comparison.

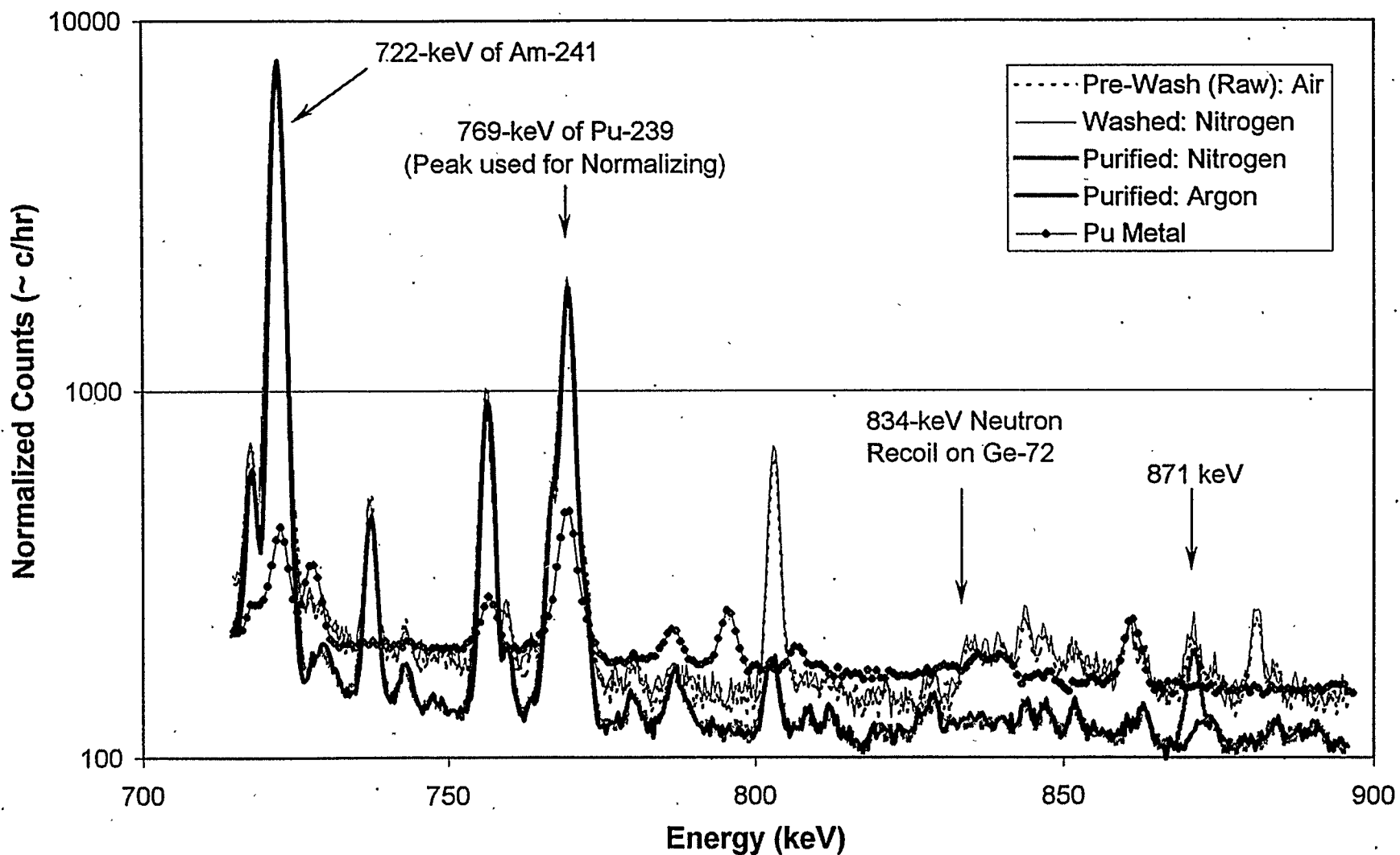


Figure 2. Comparison of Normalized Spectra for Raw, Washed, and Purified Plutonium Oxide Sample, Expanded to a Wider Energy Range. Note the arrow indicating the 769-keV ^{239}Pu peak used for normalization.

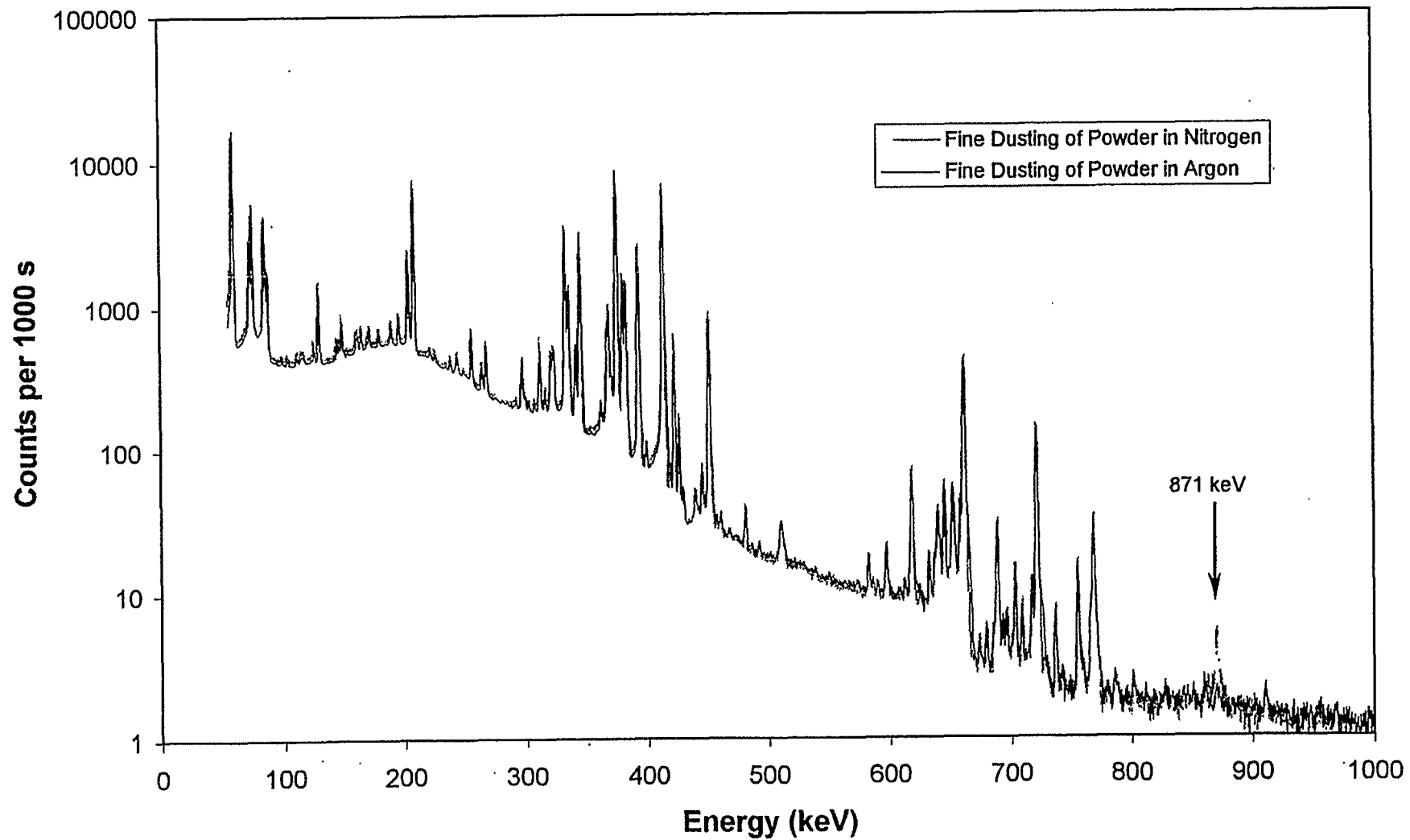


Figure 3 Normalized Spectra for Dusting of Purified Plutonium Oxide Powder under Argon and Nitrogen. Note the intensity of the 871-keV line as the only major difference between the spectra.

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