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ASSAY OF LOW-LEVEL PLUTONIUM EFFLUENTS*

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ABSTRACT

In the plutonium recovery section at the Los Alamos National Laboratory, an effluent solution is generated that contains low plutonium concentration and relatively high americium concentration. Nondestructive assay of this solution is demonstrated by measuring the passive L x rays following alpha decay. Preliminary results indicate that an average deviation of 30% between L x-ray and alpha counting can be achieved for plutonium concentrations above 10 mg/L and Am/Pu ratios of up to 3; for plutonium concentrations less than 10 mg/L, the average deviation is 40%. The sensitivity of the L x-ray assay is ~1 mg Pu/L.

INTRODUCTION

In the plutonium facility at the Los Alamos National Laboratory, two processes are employed to recover or purify scrap plutonium: the lean residue process and the dissolver solution ion exchange process. The typical effluent solution generated from these processes contains low plutonium concentration (<100 mg/L) and relatively high americium concentration (Am/Pu < 20). Because this waste solution is generated in quantity, it is important from the process control point of view, as well as for safeguards, to have timely assays of the plutonium content. Chemical analysis is too time-consuming; it requires extracting the plutonium from the americium and measuring the plutonium content by alpha spectrometry.

To measure this type of solution by means of nondestructive assay, we need to utilize signals that are more abundant than the passive gamma-ray activities emitted from plutonium. Table I lists the specific alpha, gamma-ray, and L x-ray activities of the plutonium isotopes and ^{241}Am. The gamma rays—for example, the 413.7-keV line of ^{239}Pu—are useful for determining plutonium concentrations above 100 mg/L. Although alpha emission has higher specific activity compared to gamma-ray emission, in these solutions the alpha activity from americium dominates, accounting for 80% or more of the alpha signal. One possible solution is the use of L x rays following the alpha decay. Because the L x rays from the decay of plutonium and americium are different in energy, in principle they can be separated.

Figure 1 depicts an L x-ray spectrum from a plutonium-americium mixed solution with an Am/Pu ratio of ~2000 ppm. The spectrum from an americium foil is also shown in Fig. 1. The plutonium and americium emit uranium and neptunium x rays, respectively, following the alpha decay. The uranium 17.22-keV L-β_1 x ray, as well as the 20.17-keV L-γ_1 x ray, can be used to monitor the plutonium concentration. A Si(Li) detector having a resolution of 207 eV at 5.9 keV was used. (Note that x rays generated from fluorescence do not have much effect because they are plutonium or americium L x rays and are energy-separated from the uranium and neptunium x rays used in the measurement.)

In developing the passive L x-ray technique into a quantitative assay of the low-level plutonium solutions, two technical problems were encountered: (a) sample self-attenuation and (b) americium subtraction.

At low energies (here, 17 to 20 keV) and plutonium concentrations <1 g/L, the sample self-attenuation is dominated by the matrix concentration. By choosing a relatively thin sample (0.5 cm), the effect due to matrix variation is minimized. At 18 keV, the correction factor (CF) as a result of sample self-attenuation varies from CF = 1.245 to CF = 1.282, a change of <3% when the nitric acid normality varies from 2 to 7 N, respectively. Because the required accuracy for this effluent solution is ~20%, the self-attenuation variation is negligible.

The americium subtraction is more complicated. At 17.22 and 20.17 keV, the major peaks are the uranium Lβ_1 and Lγ_1 x rays, but there are also contributions from the neptunium L x rays following the americium decay. When the Am/Pu ratio is >1 the neptunium L x rays can contribute a significant portion of the 17.22- and 20.17-keV peak areas. The neptunium contribution

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TABLE I

SPECIFIC ACTIVITIES OF RADIOISOTOPES

Isotope	Alpha Specific Activity (α/s-g)	Major γ-ray Activities γ Energy (keV)	Major γ-ray Activities Activity (γ/s-g)	L X-Ray Activity[a] (x/s-g)
^{238}Pu	6.33×10^{11}	43.5	2.5×10^{8}	7.21×10^{10}
		152.8	6.4×10^{6}	
^{239}Pu	2.30×10^{9}	52.6	6.2×10^{5}	1.06×10^{8}
		129.3	1.4×10^{5}	
		375.0	3.6×10^{4}	
		413.7	3.5×10^{4}	
^{240}Pu	8.34×10^{9}	45.2	3.8×10^{6}	8.42×10^{8}
		160.4	3.5×10^{4}	
^{241}Pu	9.15×10^{7}	148.6	7.3×10^{6}	---
^{242}Pu	1.45×10^{8}	---	---	1.23×10^{7}
^{241}Am	1.27×10^{11}	26.3	3.1×10^{9}	4.6×10^{10}
		59.5	4.5×10^{10}	
		208.0	1.0×10^{6}	

[a]Tabulated is the total L x-ray intensity. The L x-ray yield per alpha decay is obtained from Ref. 2.

to the 17.22-keV peak is determined by the neptunium $L\alpha_1$ peak at 17.75 keV; the contribution to the 20.17-keV peak is determined by the neptunium $L\gamma_1$ peak at 20.78 keV. The relative efficiency of the detector (including the relative sample self-attenuation) is determined by the neptunium $L\alpha_1$-, $L\beta_1$-, and $L\gamma_1$-line intensities. The system deadtime and pileup correction are determined by the 5.9-keV line emitted by a ^{55}Fe source viewed by the detector.

To investigate the plutonium assay by means of the L x rays, we prepared a set of standard solutions containing 10 to 200 mg/L of plutonium with Am/Pu ratios ranging from 600 ppm to 0.15. The solutions, with their plutonium and americium concentrations known to 1%, were doubly contained in sample vials. Figure 2 shows the sample vials, the sample holder above the Si(Li) detector, and the shielding housing. The results of runs made with this set of solutions are shown in Fig. 3. The results indicate that the plutonium concentrations can be determined to 2% for this set of well-characterized solutions.

Effluent solutions were drawn from actual processes in the plutonium recovery section, and measurements were made with the L x-ray detector. Duplicate samples were sent for chemical analysis, which was performed approximately 1 day later; two types of chemical analysis were requested. The first type includes plutonium extraction,[1] evaporation of plutonium solution on to a disk, and alpha counting. The americium concentration of the original solution is determined by integral counting of the signal above 30 keV. The claimed precision of the plutonium concentration determination is ~10%. The second type of chemical analysis requested is isotopic dilution mass spectrometry (IDMS), which has better precision compared to alpha counting but requires longer analysis time. Because we have not yet received the results from the IDMS analysis, the L x-ray results are compared with the alpha counting; the comparison therefore should be considered preliminary.

The L x-ray assay precision is dominated by the americium subtraction (therefore the Am/Pu ratio), and to a lesser degree, by the plutonium concentration. Figure 4 shows the percent deviation as a function of the plutonium concentration and also as a function of the Am/Pu ratio. For plutonium concentrations <10 mg/L, the average deviation is 42%; for plutonium concentrations >10 mg/L, the average deviation is 30%. In each case the deviation is greater than that obtained for the standard solutions. The possible reasons

for the larger deviations are: (1) isotopic variations between samples, (2) higher Am/Pu ratio than in the standard solutions, and (3) post-precipitation of plutonium from the solutions. These causes are being investigated. An advantage of the L x-ray system is that by monitoring the 26.3- and 59.5-keV gamma-ray peaks, the americium concentration in the solution (from 0.01 to 10 mg/L) can be determined accurately to a few percent. In conclusion, the L x-ray system can provide a timely "go/no-go" measurement for deciding whether to recover the plutonium or send the solution to acid evaporation. As shown in Fig. 5, both the L x-ray and alpha counting arrived at the same conclusion for the 13 samples compared. The sensitivity of the L x-ray system is ~1 mg Pu/L.

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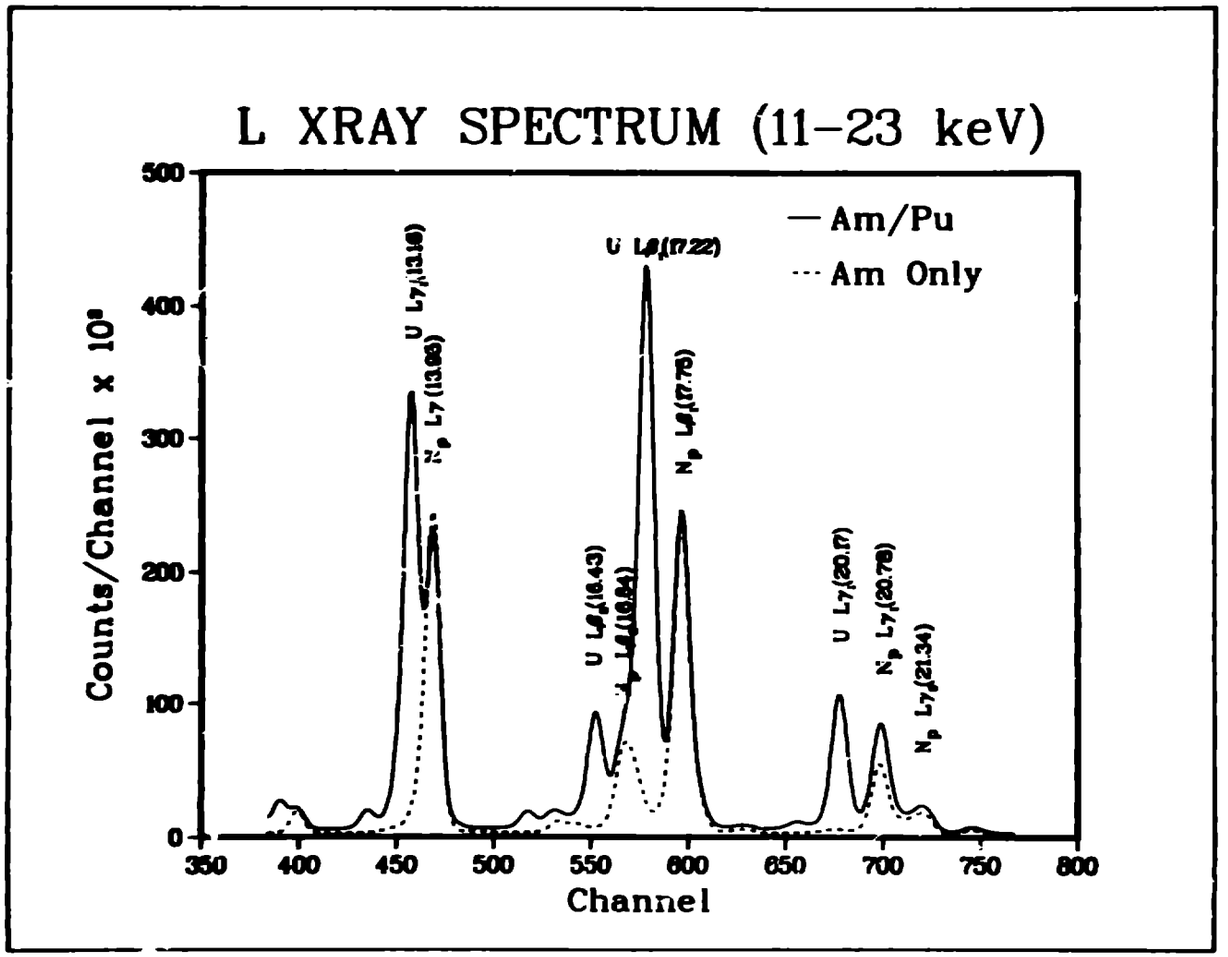

Fig. 1. L x-ray spectrum from plutonium and americium between 11 and 23 keV.

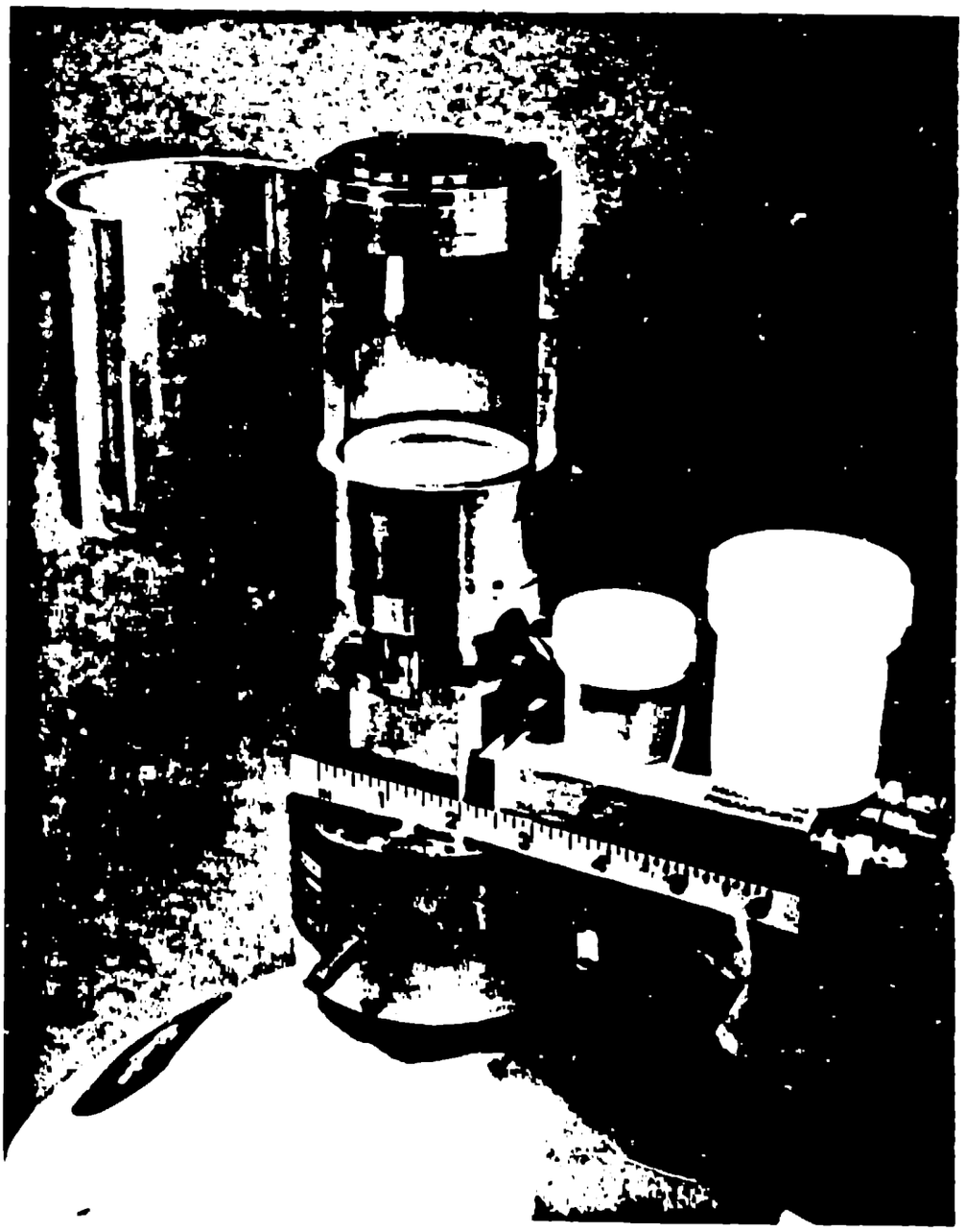

Fig. 2. Inner and outer sample vials and the sample holder on top of the Si(Li) detector.

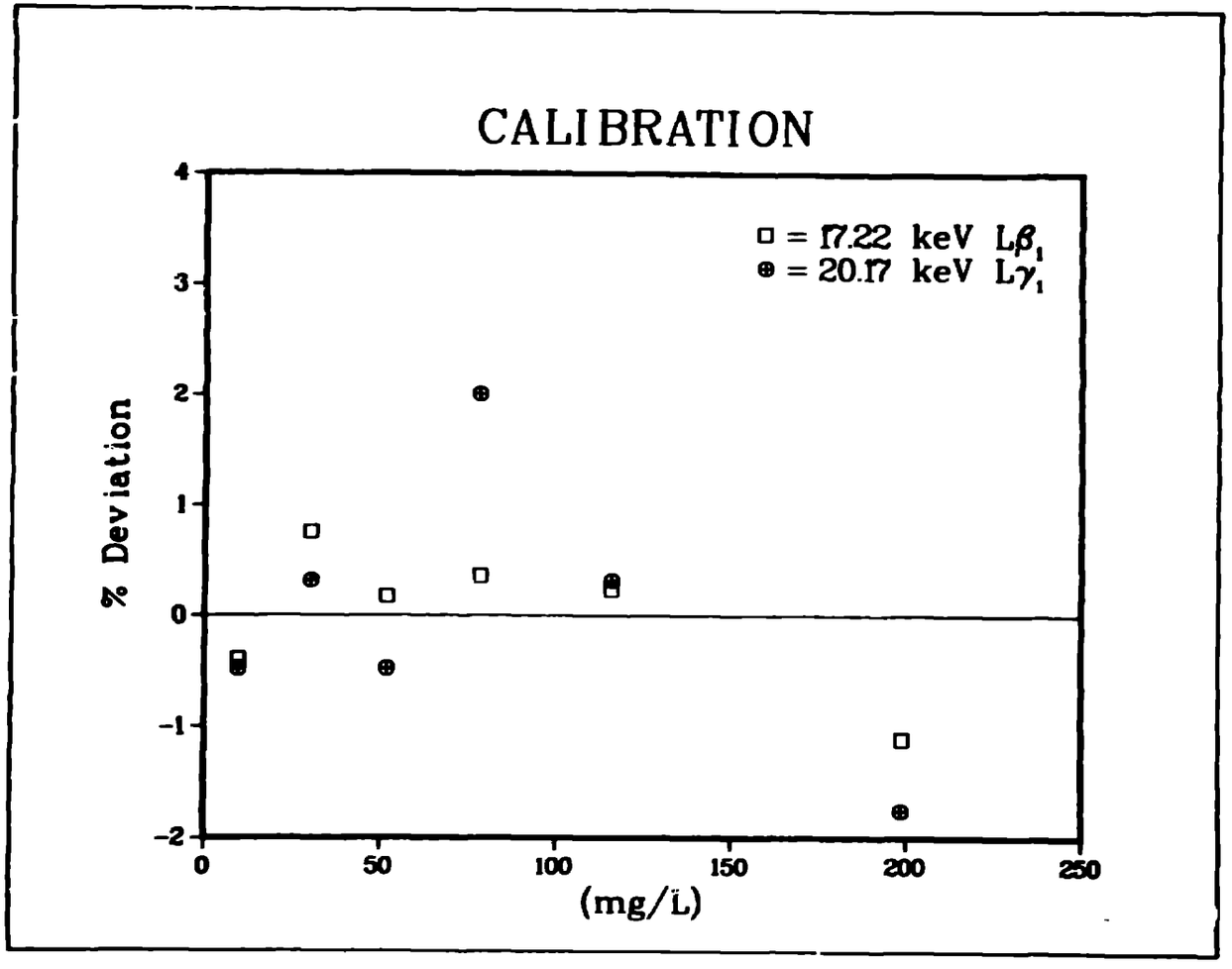

Fig. 3. Percent deviation between L x-ray counting and chemical analysis for a set of standard solutions.

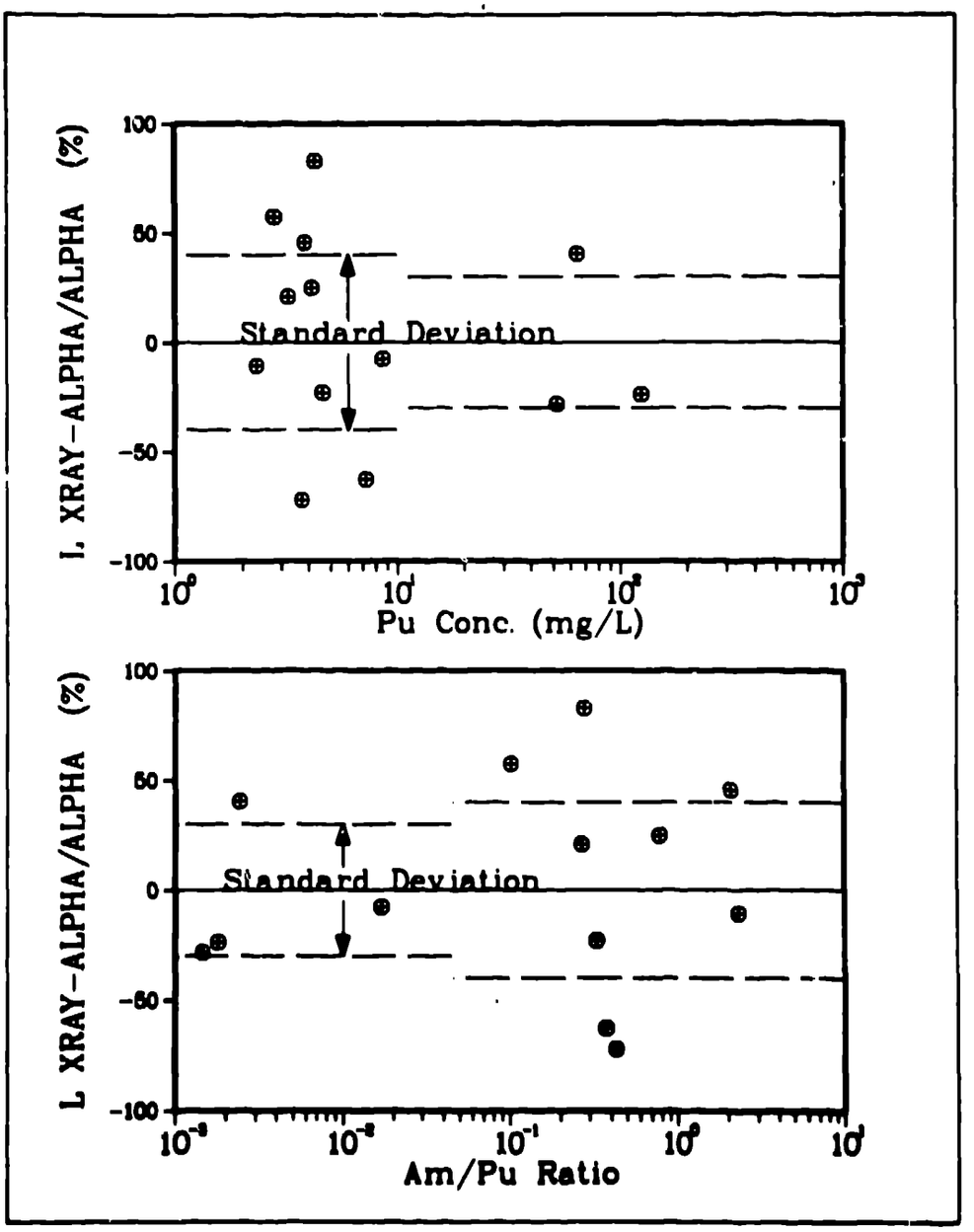

Fig. 4. Comparison between L x-ray and alpha counting (1) as a function of plutonium concentration and (2) as a function of Am/Pu ratios.

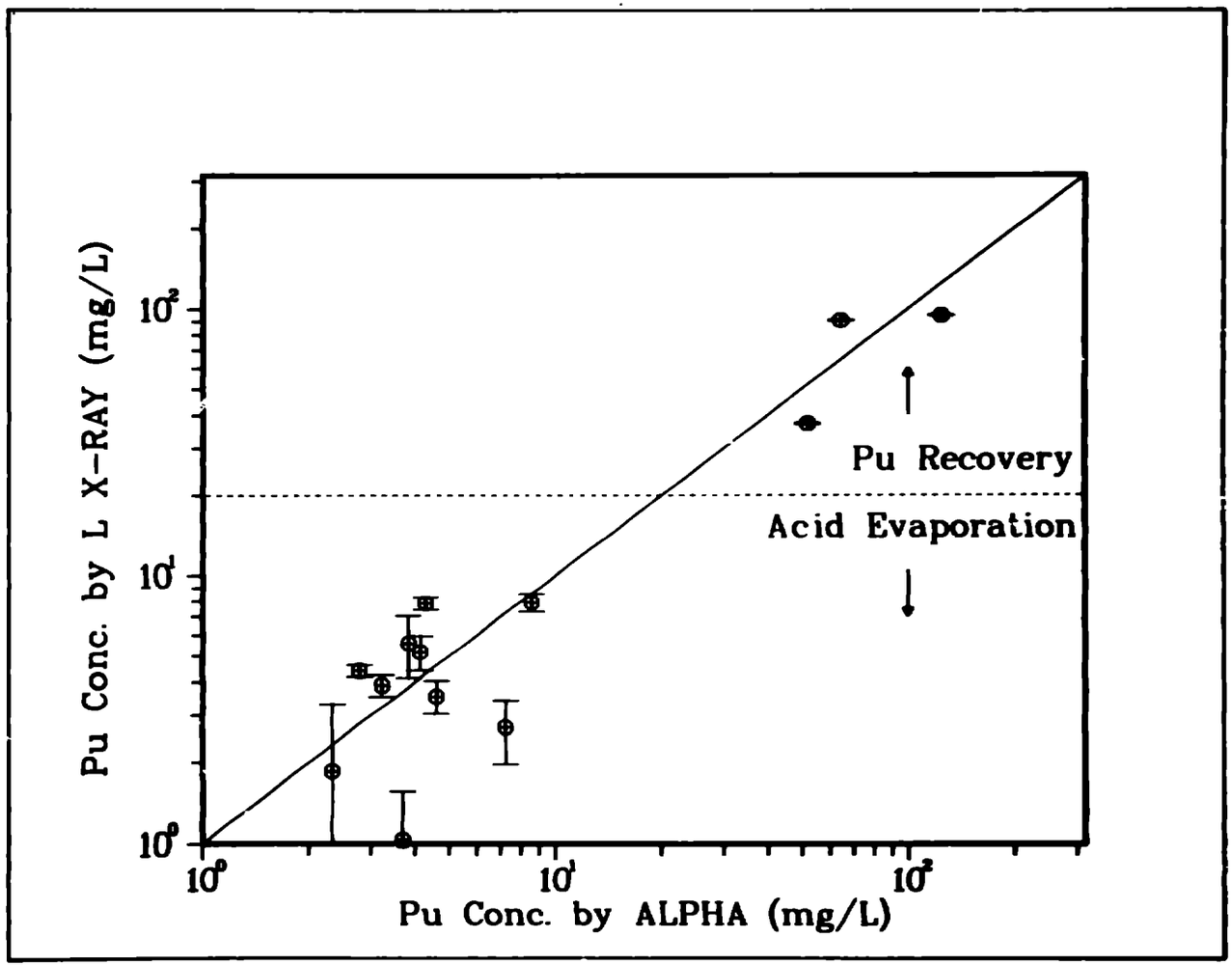

Fig. 5. Plutonium concentration by L x-ray counting vs plutonium concentration by alpha counting. The diagonal line designates perfect agreement between the two methods.