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IN-PLANT MEASUREMENTS OF GAMMA-RAY TRANSMISSIONS FOR PRECISE K-EDGE AND PASSIVE ASSAY OF PLUTONIUM CONCENTRATION AND ISOTOPIC ABUNDANCE IN PRODUCT SOLUTIONS AT THE TOKAI REPROCESSING PLANT

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ABSTRACT

A field test has been carried out for more than 2 years for determination of plutonium concentration by K-edge absorption densitometry and for determination of plutonium isotopic abundance by transmission-corrected passive gamma-ray spectrometry.[1] This system was designed and built at Los Alamos National Laboratory and installed at the Tokai reprocessing plant of the Power Reactor and Nuclear Fuel Development Corporation as a part of the Tokai Advanced Safeguards Technology Exercise (TASTEX).[2]

For K-edge measurement of plutonium concentration, the transmissions at two discrete gamma-ray energies are measured using the 121.1- and 122.1-keV gamma rays from ^{75}Se and ^{57}Co. Intensities of the plutonium passive gamma rays in the energy regions between 38 and 51 keV and between 129 and 153 keV are used for determination of the isotopic abundances.

More than 200 product solution samples have been measured in a timely fashion during these 2 years. The relative precisions and accuracies of the plutonium concentration measurement are shown to be within 0.6% (1σ) in these applications, and those for plutonium isotopic abundances are within 3% for ^{238}Pu, 0.4% for ^{239}Pu, 1.2% for ^{240}Pu, 1.3% for ^{241}Pu, and 7% for ^{242}Pu. The time required is 10 min for the concentration assay, 10 min for the isotopics assay, and about 15 min for handling procedures in the laboratory.

PURPOSE

The purpose of the field test described in this paper was to determine plutonium concentration and isotopic abundances in the product solution by off-line, rapid, nondestructive techniques and to demonstrate the applicability of these techniques, incorporated into instruments owned and operated by the facility, to international safeguards inspections at irradiated fuels reprocessing plants. The tests were carried out by the Power Reactor and Nuclear Fuel Development Corporation (PNC) at the Tokai Works reprocessing plant in collaboration with the International Atomic Energy Agency (IAEA) and the Los Alamos National Laboratory.

TECHNOLOGY, EQUIPMENT, AND PROCEDURES

The absorption-edge technique in the present system involves the measurement of gamma rays from an external source that are transmitted through the sample to be detected and analyzed by a high-resolution gamma-ray spectrometer. The transmission sources for the K-edge instrument are the radioisotopes ^{75}Se and ^{57}Co. The 121.1- and 122.1-keV gamma rays emitted by these sources, respectively, closely bracket the K-absorption edge of plutonium at 121.8 keV. The logarithm of the ratio of the measured transmissions at these two gamma-ray energies is directly proportional to the concentration of plutonium.

The measured transmissions of other gamma rays emitted by the two sources can be used to correct for self-attenuation effects in the passive gamma-ray assay. This approach is used to evaluate the plutonium isotopics from data obtained during a separate passive count. All measured isotopic fractions are determined relative to that of ^{239}Pu. The ^{242}Pu isotopic fraction (relative to that of ^{239}Pu) is evaluated from an isotopic correlation based on the ^{240}Pu ratio to ^{239}Pu. The correlated relative results are used to determine the absolute isotopic fractions.

The K-edge instrument is designed to position the ^{75}Se and ^{57}Co sources, mounted on a wheel, in the transmission path in order to perform the two transmission measurements. A third positioning of the wheel shields both sources from the detector for the passive count.

Measurement control procedures assure the long-term validity of the parameters used to determine the absolute results for plutonium concentration and isotopic fractions. A plutonium foil assayed routinely by the K-edge technique accomplishes this purpose in the former case. Since the isotopics determination is sensitive only to relative gamma-ray detection efficiencies, the relative efficiency is verified using

the measured gamma-ray intensities obtained during the measurement of ^{75}Se in the absence of a sample. The unattenuated intensities (intensities without sample) of the ^{75}Se and ^{57}Co gamma rays are measured daily.

INSTALLATION, CALIBRATION, AND TESTING

Calibration measurements were performed at Los Alamos and at the PNC Tokai Works reprocessing plant using prepared nitrate solution samples of plutonium. The solution samples were characterized by destructive chemical analysis. Since the isotopics calibration at the PNC Tokai Works was based on the mass spectrometric measurements of a single sample, this calibration has been modified slightly, based upon the more extensive comparison results (mass spectometry vs passive assay) obtained with process solutions. The calibration at the Tokai Works was performed in October 1979 with 12 reference samples of varying plutonium concentration and identical isotopic composition.

Measurements with the calibrated instrument were performed on 121 product solution samples (including aged samples from the storage tanks) from November 1979 to March 1981. Count times of 2000 s were used for the (^{75}Se plus ^{57}Co) transmission measurement as well as for the passive count. These samples were also analyzed destructively for plutonium concentration and isotopics and compared with the K-edge and passive assay results.

Evaluation of the results for the product solutions and the storage tank solutions has been accomplished jointly by Los Alamos National Laboratory and PNC Tokai Works and is described in detail in the final report on TASTEX Task G.[2] These results were obtained prior to April 1981.

Count times of 600 s have been used since April 1981 for each measurement of plutonium concentration and isotopic content. These reduced count periods were adopted for the convenience of actual safeguards application of the instrument in the reprocessing plant. Eighty product solution samples were measured and compared with the conventional methods during the three campaigns from April 1981 to March 1982.

TEST RESULTS AND EVALUATION

Concentration

Destructive Analysis. The destructive analytical procedure for determination of plutonium concentration is a ceric back-titration to a potentiometric end point. The solution is sampled (for 10 to 25 mg of plutonium) and diluted with 2 mℓ of 5N nitric acid. After the valence is adjusted to Pu(VI) by mixing for 5 to 10 min with a strong oxidizing agent (AgO), nitrates and excessive AgO are decomposed from the mixture by addition of 6N sulfuric acid (5 mℓ) followed by 0.5 g of powdered sulfamic acid. A known volume (5 mℓ) of Fe(II) standard solution is introduced in excess by calibrated pipette to reduce the plutonium to Pu(IV). The Fe(III) is back-titrated to Fe(II) with a standard Ce(IV) solution to the potentiometric end point.

Following standardization of the Fe(II) solution (~0.05N) and Ce(IV) solution (~0.025N) with standard potassium dichromate, plutonium control and unknown samples are assayed. The control sample, prepared by purification of the plutonium product solution and standardized by primary plutonium metal standard, is used for confirmation of uncertainties related to reagents or titration apparatus. Assays of six aliquots taken from each unknown sample are performed, and the average is used to compare with the nondestructive measurement result.

Measurement Control (Plutonium Foil) Results. Figure 1 is a summary of the measurement control results obtained from the K-edge assay of the plutonium foil. The effective concentration (in grams/liter) is plotted vs date for the period of time from April 1981 to March 1982. Each data point is the average of 10 repeated 40-min measurements performed overnight. The reproducibility of the foil result over time is the measurement control requirement. The average of the 150 points in Fig. 1 is 236.6 g/ℓ and the standard deviation is 0.7 g/ℓ (0.30% relative). These values are similar to the results obtained from 123 foil measurements performed between January 1980 and March 1981. (The average was 236.7 g/ℓ and the standard deviation was 0.6 g/ℓ.) The foil results are expected to decrease slightly with time because of the decay of ^{241}Pu to ^{241}Am. However, the effects are small enough in the 2-yr period that the foil remains useful during this period to validate the reproducibility of the plutonium concentration measurement capability for solutions of a given thickness.

Nondestructive Measurements. The K-edge assay results for plutonium product solution are evaluated relative to those of destructive analysis performed on these samples. The measurements of 80 product solution samples have been performed since April 1981. The results are summarized in Fig. 2, which shows the percentage deviation of the K-edge assay from the reference value (relative result) plotted vs sample number. Live count times for the ^{75}Se and ^{57}Co measurements were 300 s each. The plotted data points are obtained from the average of the duplicate K-edge assay results for each sample. The average result and the standard deviation in all the relative data are shown as solid and dashed lines, respectively. Different symbols are used to distinguish the freshly separated and aged samples.

Since the sample cell has a taper large enough to cause a 0.25% change in the calibration parameter for a 1-mm change in vertical position, repositioning of the sample cell was performed in order to examine the contribution to the measurement uncertainties. The repositioning of the

cell between the duplicate assays gave an average reproducibility of 0.25% for the 80 samples. The K-edge precision computed from the counting statistics of the K-edge assay is 0.25%, in agreement with the observed results. This indicates that the contribution to the random error due to routine sample positioning is negligible.

The average and the standard deviation of the relative results for 46 freshly separated and 34 aged solution samples are given in Table I. The possibility of systematic effects in the assay result due to ^{241}Am buildup[2] is considered for the aged samples. However, a separate evaluation gives a 0.06% lower value for aged samples relative to the fresh. This difference is not significant, and therefore the results for aged and fresh samples combined are used for the final interpretation. The deviation between the K-edge and destructive results is −0.36%, and the standard deviation in the relative results is 0.54% for all samples. These values are in good agreement with those given in the final report on TASTEX Task G.[2] (The average deviation was −0.3% and the standard deviation was 0.6%.) Since a negative average deviation has persisted since January 1980, a recalibration of the K-edge assay using a plutonium standard solution is recommended.

Plutonium Isotopics

Destructive Analysis. Thermal ionization mass spectrometry is used to determine the mass fractions of the plutonium isotopes in the freshly separated solution samples. Anion exchange methods for separation of uranium and americium from the plutonium are used routinely in the preparation of the freshly separated samples for mass spectrometry. The americium content of these samples is too low to be of concern. However, since uranium (primarily as ^{238}U) is present at approximately a fourth part in 10^3 (U:Pu) in the plutonium product there is the possibility of contamination with ^{238}U of the mass spectrometric source unless anion exchange methods are carefully performed. The results of the mass spectrometry technique are used for comparison with the passive assay results for each plutonium isotope.

Nondestructive Measurements. Plutonium isotopics measurements have been performed for 28 freshly separated solution samples during the 1-yr period from April 1981 to March 1982. Count times for the passive measurement were 600 s. The average of duplicate assay results for each sample is compared with the mass spectrometry result. The isotopics results, evaluated separately for BWR- and PWR-type fuels, are summarized in Table II. The average deviation corresponds to the average percentage difference between the passive and the mass spectrometry measurements (average relative result). The accuracy of the passive assay is the average deviation, since the expected uncertainty (precision and accuracy) in the mass spectrometry result for ^{239}Pu, ^{240}Pu, ^{241}Pu, or ^{242}Pu is significantly less than the uncertainty in the corresponding passive assay result. The standard deviation in the relative results incorporates all random uncertainties, including the statistics of the 600-s counts. The standard deviation is consistently larger than the average deviation for each isotope and therefore represents the overall uncertainty (precision plus accuracy) of the 600-s passive assay.

Assays of 34 BWR and 30 PWR samples were performed during the TASTEX program from October 1979 to March 1981. (The average isotopic fractions were determined for 10 repeated 2000-s passive assays of each sample.)[2] The isotopics assay parameters were re-evaluated, based on these data, mainly to correct for the large deviation of +23% in the average of the BWR results for ^{242}Pu. This deviation was due to the fact that the original isotopic correlation parameters, derived from a limited data set, were not appropriate for BWR material. "Original" in Table II shows the results of 18 BWR samples that were evaluated using the original parameter set. "Modified" in Table II indicates the results of 20 BWR and 8 PWR samples that were evaluated using the modified parameter set. The modified set includes different correlation parameters for assay of BWR and PWR samples. Table II gives the average deviation and the relative standard deviation in the relative results for each isotope.

The conclusions of the isotopics evaluation are:

(1) The use of a separate set of parameters for the ^{242}Pu isotopic correlation for BWR- and PWR-type samples greatly

TABLE 1

PLUTONIUM CONCENTRATION RESULTS

Type	No. of Samples	Average K-Edge Reproducibility (%)	Deviation Between K-Edge and Destructive Assay: Average (%)	Deviation Between K-Edge and Destructive Assay: Standard Deviation (%,1σ)
Freshly separated plutonium	46	0.28	−0.33	0.56
Aged plutonium	34	0.20	−0.39	0.53
Freshly separated and aged	80	0.25	−0.36	0.54

TABLE II

PLUTONIUM ISOTOPICS RESULTS

Sample Type	Plutonium Isotope	No. of Samples	Average Deviation (%)	Relative Standard Deviation (%,1σ)
(Original)				
	238		-3.70	4.60
	239		-1.27	1.56
BWR	240	18	0.72	2.45
	241		-0.74	1.77
	242		31.86	21.66
(Modified)				
	238		-0.31	2.33
	239		0.09	0.40
BWR	240	20	-0.54	1.19
	241		0.81	1.08
	242		1.43	7.53
	238		-0.53	3.39
	239		0.39	0.53
PWR	240	8	-0.78	1.27
	241		0.84	1.90
	242		-3.63	4.52
	238		-0.37	2.61
BWR	239		0.18	0.45
+	240	28	-0.61	1.20
PWR	241		0.82	1.32
	242		-0.02	7.11

improves the accuracy of the passive assay of individual isotopes, especially for BWR-type samples.

(2) The overall relative uncertainty (1σ) in the isotopic fractions determined by passive assay of this set of samples is 0.4, 1.2, 1.3, and 7% for ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu, respectively, for 600-s passive counts.

(3) The average deviation (accuracy) for each isotope is substantially less than the overall uncertainty given in (2).

(4) The average deviation of the passive assay from mass spectrometry for ^{238}Pu is negative and less than 0.5%. This is rather good agreement between the passive and the mass spectrometry results, considering the low ^{238}Pu isotopic abundance (<1%) and the possibility of mass-238 contamination in the mass spectrometry assay. The relative standard deviation in the relative results for the ^{238}Pu assay is 3%, 1σ.

SAFEGUARDS APPLICATIONS

K-edge and passive assays of plutonium concentration and isotopic abundance of product solution samples have been carried out under TASTEX followed by the Japan Support Programme for Agency's Safeguards (JASPAS). The stability of the K-edge calibration was proven in the field test, which has exceeded a duration of 2 years. An inspection manual was prepared in collaboration with IAEA experts. As authentication procedures for this instrument, the following have been developed:

(1) Use of tantalum and plutonium foils as "working" standards.

(2) Visual inspection of electronics settings, parameters, and gamma-ray spectra on the multichannel analyzer display.

(3) Use of a separate software floppy diskette by IAEA inspectors.

The recent installation and use of a second dual floppy disk unit has made it possible to simultaneously store raw spectral data on each of two floppy diskettes (one for the facility and one for the IAEA) to maintain efficiency in routine operations during inspections. Furthermore, new improved sample cells have been designed and fabricated. The new cells are less susceptible to the vertical positioning problem because of a reduced taper compared with the old cell.

The calibration of the instrument was performed in October 1979, using nitrate solution samples of plutonium. Since these samples were characterized by destructive analysis performed by PNC, a recalibration of the instrument is planned in which the plutonium reference solutions will be analyzed by three different laboratories.

The feasibility of incorporation of this in-plant instrument into routine safeguards inspection procedures has been greatly enhanced by these collaborative field testing efforts supported by JASPAS and the International Safeguards Program Office. These efforts are still in progress.

REFERENCES

1. TASTEX, Tokai Advanced Safeguards Technology Exercise, International Atomic Energy Agency report TR-213 (Vienna, 1982).

2. F. A. Russo, S. T. Yeue, J. K. Sprinkle, Jr., S. S. Johnson, Y. Asakura, I. Kondo, J. Masui, and K. Shoji, "In-Plant Measurements of Gamma-Ray Transmissions for Precise K-Edge and Passive Assay of Plutonium Concentration and Isotopic Fractions in Product Solutions (Final Report on TASTEX Task G)," Los Alamos National Laboratory report LA-9440-MS, Power Reactor and Nuclear Fuel Development Corporation report PNCT-841-82-10, to be issued.

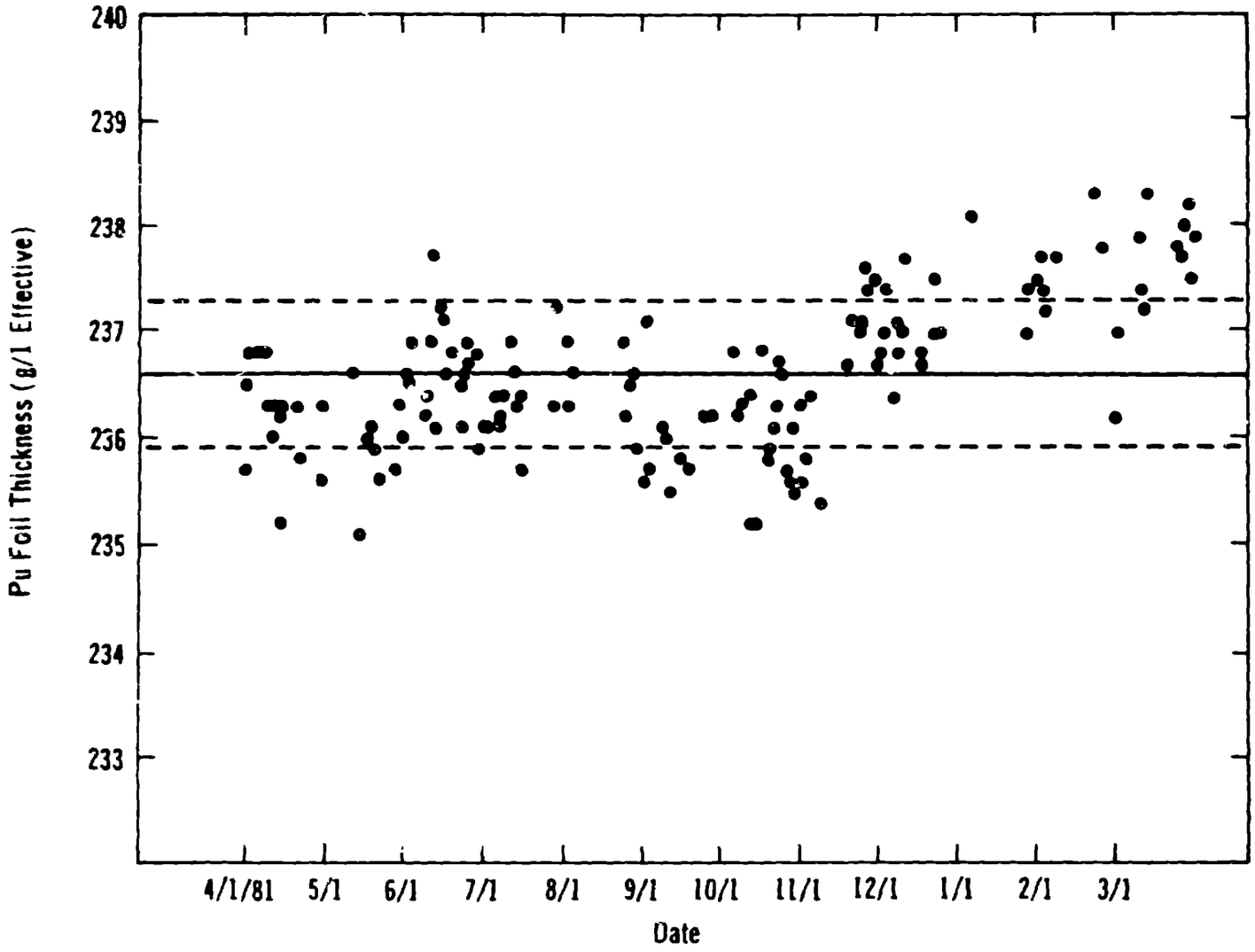

Fig. 1.
K-edge assay results (equivalent thickness in grams/liter) for the plutonium foil plotted vs date. The solid line is the average result of 236.6 g/ℓ. The dashed lines indicate the standard deviation of 0.7 g/ℓ (0.30% relative).

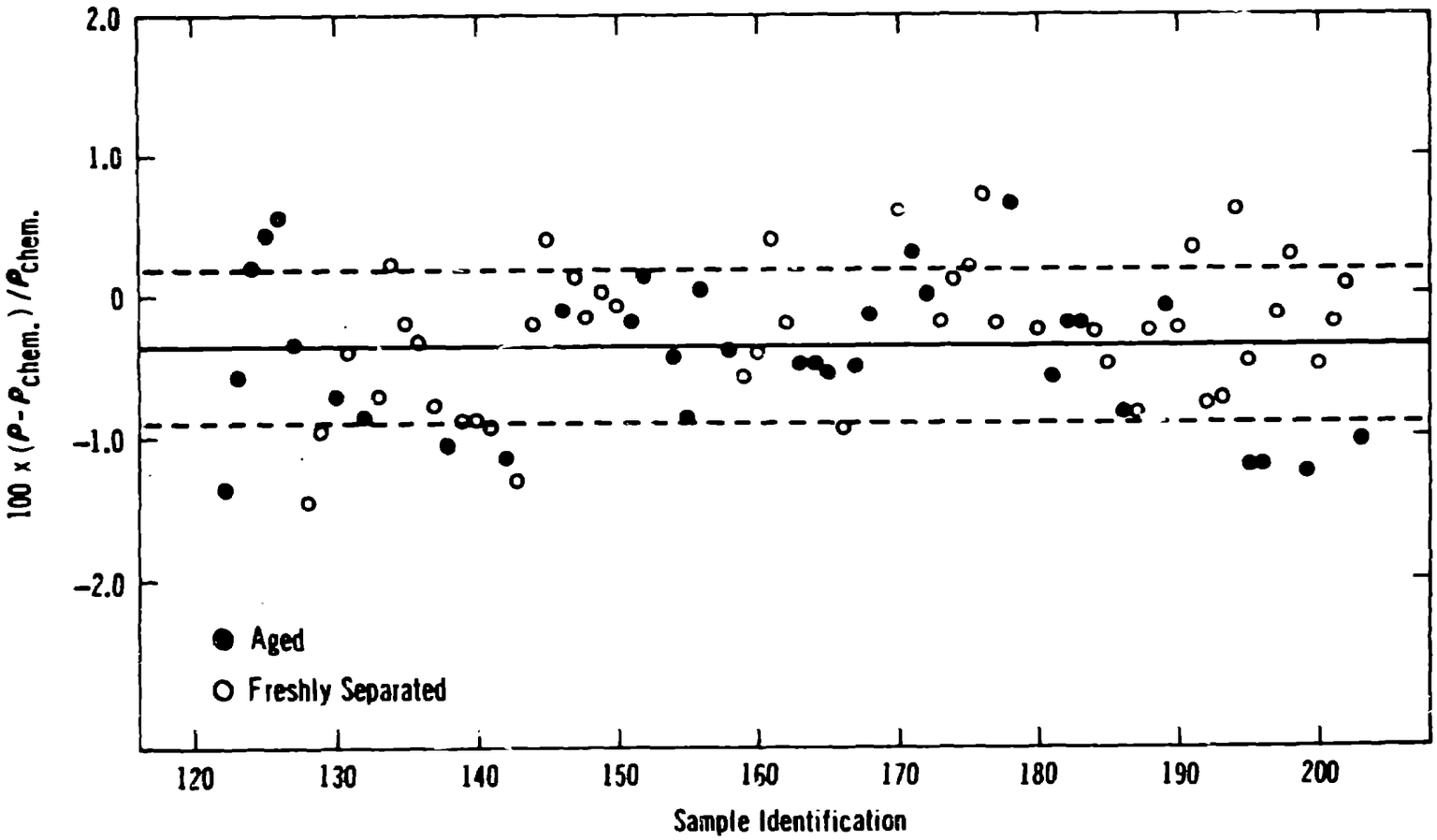

Fig. 2.
Per cent difference between K-edge and destructive assay (relative result) for plutonium concentration plotted vs sample identification number. The solid line is the average relative result of -0.36%. The dashed lines indicate the standard deviation of 0.54%.