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Nondestructive, Energy-Dispersive, X-Ray Fluorescence Analysis* of Product Stream Concentrations from Reprocessed Nuclear Fuels

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ABSTRACT

Energy-dispersive x-ray fluorescence analysis (XRFA) can be used to measure nondestructively pure and mixed U/Pu concentrations in process streams and hold tank solutions. The 122-keV gamma ray from ^{57}Co excites the actinide K x rays which are detected by a HPGe detector. A computer- and disk-based analyzer system provides capability for making on-stream analyses, and the noninvasive measurement is easily adapted directly to appropriate sized pipes used in a chemical reprocessing plant. Measurement times depend on concentration and purpose but vary from 100s to 500s for process control of strong to weak solutions. Accountability measurements require better accuracy thus more time; and for solutions containing plutonium, require a measurement of the solution radioactivity made with an automatic shutter that eclipses the two exciting sources. Plutonium isotopic abundances can also be obtained. Concentrations in single or dual element solutions from less than 1 g/l to over 200 g/l are determined to an accuracy of 0.2% after calibration of the system. For mixed solutions the unknown ratio of U to Pu is linearly related to the net U/Pu K x-ray intensities. Concentration values for ratios different than the calibration ratio require only small corrections to the values derived from a calibration polynomial. Minor fission product contamination does not prevent concentration determinations by XRFA. The computer-based system also allows real-time dynamic concentration measurements to be made.

KEY WORDS: X-ray fluorescence analysis, nondestructive measurements; uranium, plutonium concentration and isotopics determinations; reprocessing plant process control, accountability, inventory control, dynamic concentration measurements, on-line real-time measurements; computer-based system.

INTRODUCTION

Product Accountability and Process Control

In the event that spent nuclear fuel is reprocessed to reclaim uranium or plutonium, several nondestructive analytical techniques can be used to obtain process control and product accountability information. Generally, reprocessing begins with dissolution of the spent fuel followed by separation of the fission products; and finally purification of the desired actinide elements, uranium and plutonium. These two elements may appear in separate streams or may occur together as a coprocessed stream. The single and/or dual element streams will usually be concentrated and sent to a hold tank for accountability. Throughout the separation there is a need to control the process, that is, to monitor and regulate the actinide concentrations in order to satisy chemical engineering or criticality safety considerations.

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Input concentrations into the various process, hold, and final accountability tanks will encompass a wide range of concentrations. Values from less than 1 g/l to perhaps more than 200 g/l can be expected. Furthermore, a wide range in the uranium to plutonium ratio may occur in coprocessed streams. These various process streams and tank concentrations can be monitored on-line, rapidly, nondestructively, and quantitatively using the analytical technique or energy dispersive x-ray fluorescence analysis (XRFA). The technique also provides sufficient accuracy for Safeguards accountability purposes over the entire range of single or dual element stream concentrations expected at a reprocessing facility.

Eventually, the coprocessed product may be precipitated and converted to a powder blend of uranium and plutonium oxide. This mixed oxide (MOX) product may be packaged in standard amounts, e.g. canisters containing 2000 g of MOX. Since spent fuel received from different reactors will not have the same burnup, the elemental and isotopic compositions of various MOX batches will differ. Thus, for accountability, inventory control, and subsequently fuel fabrication purposes, there is a need to know the percentage of plutonium enrichment. Furthermore, the isotopic composition of the product is required for fissionability information. These two measurements, enrichment and isotopics can be made by the nondestructive technique of gamma-ray spectrometry. Descriptions of these measurement procedures[1] and techniques[2] can be found elsewhere. This paper is limited to a discussion of how energy dispersive XRFA can be used to quantitatively measure actinide solution concentrations that are encountered throughout reprocessing facilities.

Overview of XRFA

The analytical technique of XRFA depends upon the ability to excite atoms within a sample, and to measure accurately the characterisitic x rays emitted from the excited atoms. The atoms may be excited in many different ways. These include the use of ordinary x-ray tubes, with or without filtered anodes; irradiation by α, β, γ, or x rays from radioisotopes; bombardment by charged particles from accelerators; bombardment by electrons, as in electron microprobes; irradiation by secondary x rays from a selected target element, or by polarized x or γ rays such as from synchrotron radiation; self-excitation, if the sample contains radioactivity; and by observing x rays that follow certain nuclear decay modes.

Phenomenologically, XRFA can be understood as follows. Assume that a flux of exciting radiation composed of photons of energy, E_p, is incident on a sample. A small part of the incident radiation flux may not interact with the sample at all; another part may scatter, either with or without some energy loss; and part of the flux may be completely absorbed by the sample. A simplified representation of one interaction is illustrated in Fig. 1. If the incident quantum is totally absorbed, and if E_p(keV) is greater than the binding energy of one of the atom's electrons, then one of the shell electrons will be ejected. This creates a vacancy in one of the atomic shells, which leaves the atom in an excited state.

If the vacancy created is in the K-shell, then it may be filled by a transition of an electron from an outer shell into the inner shell vacancy. This results in either the emission of one of the atom's characteristic x rays or an Auger electron (which rarely escapes the sample). If an x ray is emitted and escapes the sample, it is available for spectroscopic analysis. Since all of the characteristic x rays associated with an element are well-known, it is possible to identify most of the elemental constituents of a sample through x-ray fluorescence analysis. A more detailed discussion of the technique can be found elsewhere.[3]

The next section describes the experimental equipment, including the computer-based analytical support instrumentation, and the procedures used in obtaining and reducing the data. The section entitled "Experimental Results" will present results obtained on single and dual element nitrate solutions for a range of concentrations. This section also discusses the effects that any fission product activity in the process streams will have on the determination of actinide concentrations.

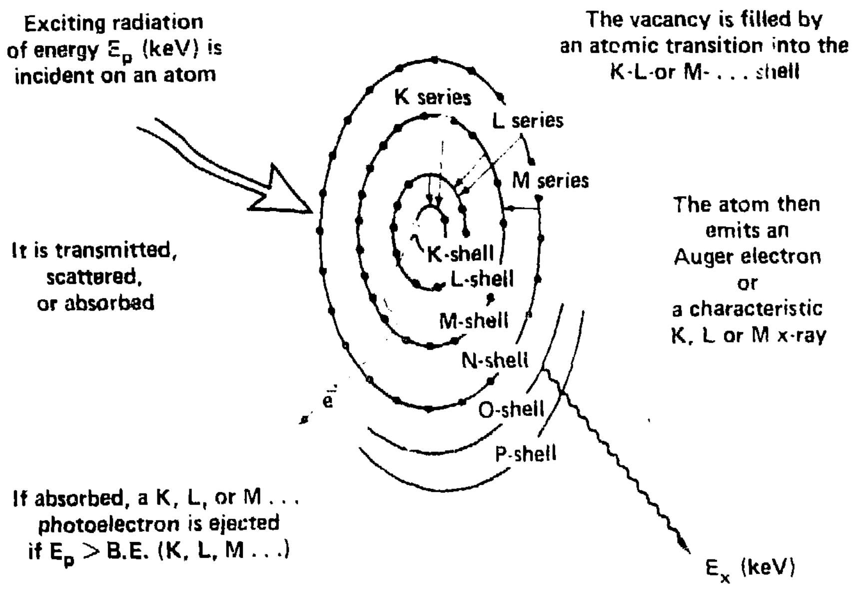

Fig. 1. A representation of energy-dispersive x-ray fluorescence analysis (XRFA). The number of electrons within a shell and the number of shells depend on the particular atom.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

Excitation Source Requirements

Gamma rays can be used to excite x rays from atoms within a sample. The binding energies of K electrons in uranium and plutonium are 115.59 and 121.72 keV, respectively. Since the primary gamma ray emitted by ^{57}Co has an energy of 122.05 keV, it is an optimum exciting radiation for these two actinide elements. The exciting radiation is usually collimated in some fashion that depends on the geometry of the sample. This reduces the radiation fluorescence of, or the scatter from, nonsample materials. In the application of interest here the sample was a solution contained within a cylindrical geometry, usually a stainless steel cell. The collimated 122-keV gamma rays interact with atoms in the solution, creating x rays characteristic of those elements dissolved in the solution. A portion of the emitted x rays strike the detector, and from the energies and intensities detected the elemental concentrations in the solution can be determined.

Lithium-drifted silicon, Si(Li), is an excellent radiation detector for x rays with less than 30 keV of energy, but it becomes very inefficient for radiation detection above 60 keV. Since the K x-ray energies of uranium and plutonium extend from 94 to 122 keV, a lithium drifted or high-purity germanium detector, Ge(Li) or HPGe, is used. For this work a 10-mm deep, 200-mm^2 HPGe detector was used. It had an energy resolution of 515 ev FWHM for the 122.05-keV gamma-ray peak of ^{57}Co. Since ^{57}Co also emits 570- and 692-keV gamma rays with branching intensities of about 0.16%, as well as other weaker gamma rays above 300 keV, their intensities must be strongly attenuated by introducing shielding between the source and the detector.

Clearly, the x-ray intensity recorded by the detector increases as the sample to detector distance decreases. However, as the distance is decreased, less shielding is possible between the intense ^{57}Co sources and the detector. The higher energy gamma rays, which pass through Hevimet shielding (a tungsten alloy) and interact with the HPGe detector, create a Compton continuum that appears as a constant, energy independent background beneath the U and Pu x rays. This background contribution increases with decreasing amounts of shielding, degrading the x-ray signal-to-noise ratio. Additional high Z shielding is required around the detector housing (above the cryostat) to reduce background radiation detected from the local environment and source-air sampling. X rays from lead and Hevimet can also be excited by the source gamma rays; hence, absorbers of cadmium and copper are used as liners on the top and bottom surfaces to eliminate these x rays. A central 12.5-mm collimation hole lined with cadmium allows part of the x rays released within the sample to strike the detector.

The source-detector collimation assembly is shown in Fig. 2. It is 7.[illegible] cm in diameter and 5.0 cm thick. Two ^{57}Co sources are collimated to create two beams. The radioactivity was electroplated onto a 1.6-mm-diameter spot on nickel foil and encased in a welded stainless steel capsule* 4.8 mm in diameter and [illegible] mm thick. The 0.37-mm thick stainless steel plate indicated in Fig. 2 is part of the bottom of a glove box, which was used when handling all of the solutions. The source-detector collimation assembly and liquid-nitrogen (LN) dewar are separate from, and located below, the glove box. It was used when handling solutions containing plutonium so that contamination would be confined in the event of a spill.

Computer-Based Analysis System

X rays emitted from the solution samples were detected by the HPGe detector, and their corresponding pulses were preamplified and routed to a Canberra 1413 amplifier and 1468A pile-up rejector. Valid output pulses were processed by a Nuclear Data ND600 pulse height analyzer (PHA). The PHA, with its own LSI-11 microprocessor, was coupled to an LSI-11 microcomputer that had a 32K 16-bit-word memory. A dual floppy disk was coupled to the LSI-11 and each disk has a 216K-byte (108K-word) capacity. Also, a dual hard disk system with a 10M-byte capacity was coupled to the LSI-11. Other system peripherals included a Hazeltine video teletypewriter terminal, an LA-180 high-speed line printer, and a Tektronix digital data plotter.

The computer and disc-based PHA capability adds a considerable amount of versatility to the experimental system. In fact, in an actual reprocessing installation a computer-based data analysis system would be essential, and probably linked to the plant's centralized computer center. This particular system allowed successive spectra to be stored on disk and permitted spectral analysis to be carried out simultaneously with data acquisition. Whatever automatic analysis sequence is desired, appropriate software can be written and stored on floppy or hard disk.

EXPERIMENTAL RESULTS

Spectra and Concentration Ranges

Pure Uranium Solutions. The present work focussed on pure uranium solution concentrations in the range from 0.6 g U/l to 180 g U/l. Earlier work[4] investigated solutions from less than 1 to almost 400 g U/l. The top spectrum shown in Fig. 3 is the result of an x-ray fluorescence analysis of 3M uranium nitrate solution at 176 g U/l concentration contained in a 25.4-mm diameter stainless steel cell with 1.7-mm wall thickness. Total analysis time was 200 live time seconds at 26% analyzer dead time using two 8.5 mCi ^{57}Co sources. The energy region extends from 0 to about 225 keV (55 eV/channel). The broad, intense peak centered at about channel 1570 is a result of the primary exciting radiation (122.05-keV gamma rays) incoherently or Compton scattering through a mean angle of 140°. The cadmium $K\alpha$ and $K\beta$ x rays appear below channel 500 and result from fluorescence of the inner wall

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*Available from Isotopes Products Laboratories, Burbank, CA. Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Department of Energy to the exclusion of others that may be suitable.

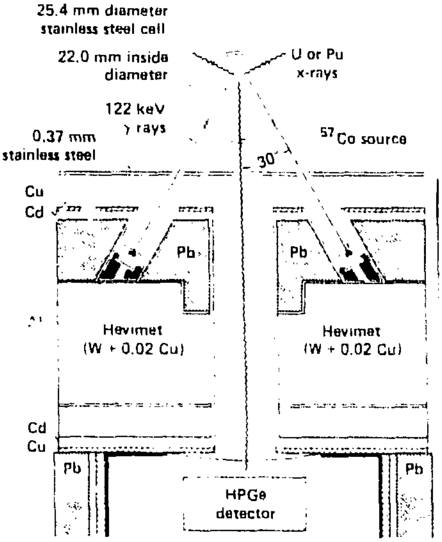


Fig. 2. A cross section of the cylindrical source-exciter and detector-collimator assembly. The stainless steel plate is part of the bottom of a glove box assembly.

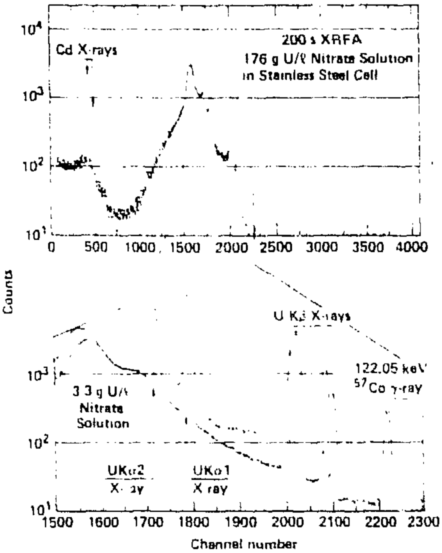


Fig. 3. The top spectrum is a 200 second, 4096-channel, XRFA of uranium nitrate solution at 176 g U/l. The solution in a 25.4-mm diameter stainless steel cell with 1.7-mm thick walls. The lower two spectra show the 80- to 125-keV region expanded. The more intense peaks represent 176 g U/l; the less intense ones 3.3 g U/l. The broad incoherently scattered peak at 85 keV is more intense for the weaker solution.

liner body of the detector collimation shielding. Gain and zero stabilizers were used for all data obtained. The Kα Cd x ray was used for zero stabilization, while usually, the uranium Kα1 x-ray (or Kα1 plutonium) was used for gain stabilization. The 122.05 and 136.47-keV gamma-ray peaks result from coherent scattering of the ^{57}Co source emissions. A nearly flat plateau of 10 counts or less exists above channel 2200. This plateau results from the Compton distribution of higher energy gamma rays (340-, 352-, 570- and 690-keV, et al.) which penetrate the Heavimet shielding and Compton scatter out of or into the HPGe detector.

The lower section of Fig. 3 shows an expanded view of the 80- to 130-keV region of two spectra, one representing 176 g U/l, the other 3.27 g U/l. The data are shown as if equivalent counting times (200s) were used for the two concentrations. Note that as the solution concentration increases, the x-ray peak intensity increases as expected, but the intensity of the incoherent scattering peak decreases. The intensity of the coherently scattered 122.05-keV peak also increases with concentration; however, most of the coherent scattering observed here occurs off of the stainless steel cell. The singlet Kα2 and Kα1 uranium x ray peaks appear at about channel 1720 and 1790, respectively; while the

K_β x ray multiplets: $(K_{\beta 1} + K_{\beta 3} + K_{\beta 5})$ and $(K_{\beta 2} + K_{\beta 4} + K_{O})$ appear near channels 2000 and 2100, respectively. Only the intensities of the K_α x rays are determined and usually only the $K_{\alpha 1}$ peak is used in establishing a calibration relationship (discussed below). The $K_{\alpha 1}$ x-ray peak contains 2.0×10^5 counts for the 176 g U/l solution; while for the 3.27 g U/l solution the $K_{\alpha 1}$ peak contains 7600 counts. This latter figure corresponds to an accuracy of 1.15% from statistics alone for a 200-second counting analysis (4-minutes clock time) through stainless steel pipe.

Pure Plutonium Solutions. The concentration range examined for pure plutonium solutions extended from 3.3 g Pu/l to 60.4 g Pu/l. The top spectrum shown in Fig. 4 is the result of an x-ray fluorescence analysis of 3M plutonium nitrate solution with 60.4 g Pu/l contained in the 25.4-mm stainless steel cell with 1.7-mm wall thickness. Total analysis time was 200 live time seconds at nearly 45% deadtime. The energy region is the same as that for Fig. 3, i.e. 0-225 keV. Note however, that the natural radioactivity arising from the plutonium isotopes and their decay products adds numerous gamma rays throughout the spectrum. The broad, intense, Compton scattered peak from the 122.05 keV exciting radiation is still prominent, but no longer dominates the spectrum. The very strong peak just above channel 1000 is the 59.53-keV gamma ray from the decay of ^{241}Am, a daughter activity of ^{241}Pu. This peak would not be nearly so intense in freshly reprocessed solutions.

The top spectrum in the lower section of Fig. 4 shows an expanded view of the 50- to 130 keV region of the 60.4 g Pu/l solution spectrum. The other spectrum is a 200s count of the solution radioactivity. It was obtained using an automatic shutter that can totally eclipse the two ^{57}Co exciting sources. The first two peaks in the radioactivity spectrum (at channels 1720 and 1760) are the $K_{\alpha 2}$ x rays of uranium and neptunium (U$K_{\alpha 1}$ at 1790 and Np$K_{\alpha 1}$ at 1835), which are results of the α-decays of ^{238}Pu and ^{240}Pu to ^{234}U and ^{236}U, and ^{241}Am to ^{237}Np, respectively. The complex multiplet located between channels 1865 and 1900, is a composite of the ^{241}Am 102.97-keV, ^{239}Pu 103.02-keV, ^{241}Pu 103.68-keV, and ^{240}Pu 104.24-keV gamma rays. The presence of the ^{239}Pu 98.78 keV and the ^{241}Am 98.95 keV gamma rays on the upper energy side of the uranium $K_{\alpha 1}$ x ray at channel 1790 is also clearly evident. The weak satellite located at about channel 1910 is from the $K_{\alpha 2}$ x-ray of plutonium and the 99.86-keV gamma ray from ^{238}Pu. The plutonium x ray is a result of the gamma-ray activity within the solution self-fluorescing the resident plutonium.

All of this additional x- and gamma-ray activity adds considerable complexity to the spectrum. Clearly, the complexity added will depend both on the plutonium isotopics and the age of the solution since reprocessing. Because it is impossible to know this contribution a priori, the experimental procedure, that leads to the most accurate quantitative results, is to subtract the solution radioactivity data from the XRFA data to obtain the net, externally excited, plutonium x-ray intensities. This requires two counting periods, one for solution fluorescence, a second for solution radioactivity. The length of each measurement period will be governed by the desired purpose of the measurement and the solution concentration. That is, process control concentration values need not be determined as accurately as those to be used for accountability or inventory purposes. As a general rule, if equal counting times are used for the XRFA and solution radioactivity measurements, sufficiently accurate concentration values can be obtained.

Fig. 5 shows the $K_{\alpha 2}$ and $K_{\alpha 1}$ x rays of uranium and plutonium obtained in two separate XRFA spectra, one taken of pure 60.5 g U/l; the other a result of the net (total XRFA minus solution radioactivity) XRFA spectrum from 60.4 g Pu/l. Only the 90- to 107-keV region of the spectra are shown. Both are 200s counts; however, the plutonium solution was excited 34 days after the uranium solution and has not been corrected for decay of the ^{57}Co sources. Including corrections for both the concentration difference and the half-life, the fluoresced intensity for plutonium is 2.2% greater than that for uranium. This arises primarily from the fact that the K edge of plutonium (121.72 keV) is nearer the exciting radiation (122.05 keV) than is the uranium K-absorption edge (115.59 keV). The careful observer will note near channel 1850 that the plutonium spectrum in Fig. 5, which is the difference between the two spectra shown in Fig. 4, shows more counts, yet more statistical fluctuation, than the uranium spectrum.

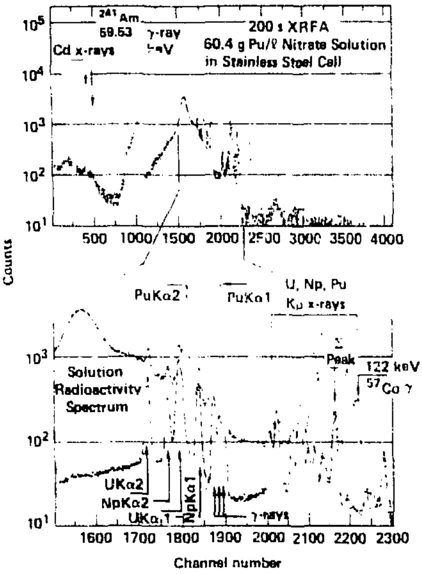


Fig. 4. The top spectrum shows an XRFA of plutonium nitrate with 60.4 g Pu/l in the stainless steel cell. The lower two spectra show an expansion of the 80- to 125-keV region for the XRFA spectrum and its natural radioactivity (two exciting sources eclipsed). The difference between the two yields the net XRFA spectrum (see Fig. 5).

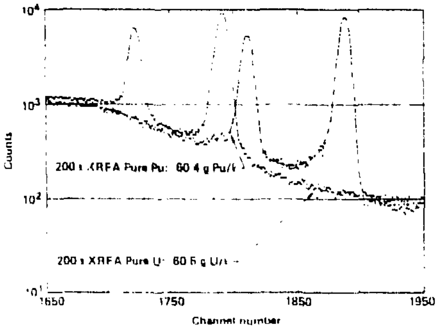


Fig. 5. Two individual spectra are superimposed for the 90- to 107-keV region. The two left most peaks are Kα2 and Kα1 of uranium, respectively; the two right most peaks are these same x rays for plutonium. The solution concentrations are nearly equal; however, no correction for exciter half-life has been applied to either spectrum. The plutonium spectrum is the difference spectrum (XRFA − activity) of the two spectra shown in the lower part of Fig. 4.

Spectrum Analysis. The number of counts in an x-ray line must be determined to calibrate the XRFA technique, or deduce an unknown solution concentration once the system is calibrated. For pure uranium solutions the total or gross number of counts within a fixed channel window surrounding the Kα1 x ray can be used to calibrate[4] the system. For pure plutonium or mixed uranium-plutonium solutions this method will not yield quantitatively accurate concentrations. Instead, the net counts above the background continuum must be determined.

The peaks of interest in XRFA spectra are x rays which have a more complicated shape[5] than gamma rays. Gamma-ray peak shapes arising from germanium detectors consist of a gaussian distribution, plus short and long-term tailing components on the lower energy side of a peak. The gaussian term arises because of the statistical sharing of energy deposited between electron-hole production and phonon production (vibration or heating of the germanium crystal structure). The full width at half the maximum peak height (FWHM) of this gaussian depends on the detector capacity, peak energy, and pulse amplifying electronics. The short-term tail is a result of the intrinsic charge collection capability of a detector, which depends primarily on the germanium material quality and detector configuration (planar, coax, 5-sided). For a given detector the energy dependence of the gaussian FWHM and short term tail components is defined by measuring strong singlet gamma rays throughout the spectral region of interest. The long term tail is sample dependent, e.g. massive samples give rise to more small angle, forward scattered gamma rays than do point sources.

An x-ray peak shape includes all of the effects arising for gamma rays plus an intrinsic Lorentzian line shape, which extends symmetrically to both lower and higher energies about the peak centroid. For the U and Pu Kα x rays, the Lorentzian widths vary from 106 to 114 eV. The distribution observed in a spectrum, then, is a convolution of the Lorentzian, gaussian, and short-and long-term tailing components. Figure 6 shows the form all of these components take for the $K\alpha_2$ and $K\alpha_1$ x rays of uranium.

The gamma- and x-ray fitting algorithms were combined into a code called GRPANL (group analysis).[6] To determine the energies and/or intensities of one or more peaks within a spectral region, the user must specify (1) the number of peaks in that region; (2) whether they are gamma or x rays; (3) if x rays, their Lorentzian widths; (4) their approximate peak positions; (5) their intensities, or specify if they are to be determined; (6) the background slope over the region, if any; and (7) the approximate (or exact) values for the peak shape parameters (gaussian FWHM, short-and long-term tailing amplitudes and slopes). Generally, the latter are known from strong singlet gamma rays that were recorded and analyzed earlier. The energy calibration for the region is specified by entering the conversion gain (eV/channel) and the intercept energy, or by entering the energies of two strong peaks in that region. Thus, GRPANL is a code used to determine the intensities of peaks with known positions, and is not a general purpose code designed to resolve multiplets of unknown complexity.

For an analysis of the pure uranium solutions the same channel region (from 1696 to 1812) was used for all of the concentrations measured. Similarly, for pure plutonium solutions, the region from 1780 to 1910 was used, and for mixed solutions, the region 1696 to 1916 was used. A somewhat wider window was used when carrying out an isotopic analysis of the natural radioactivty spectrum.

Calibration. Sets of solution standards have been prepared using ACS grade natural uranium (for pure uranium) and plutonium metal (for the pure plutonium solutions). Sufficient HNO_3 acid was used to adjust the acid concentration to 3.0M. At least two runs and generally three were made for each concentration. All data were obtained using the same 25.4-mm stainless steel cell, which was thoroughly rinsed and dried between solution changes. A fiducial line was inscribed lengthwise on the outside of the cell. Two lucite "feet" captured and positively positioned the cell on the stainless steel floor of the glove box. These "feet" and the fiducial line on the cell allowed the cell to be accurately repositioned above the source-exciter, and detector-collimation housing.

Figure 7 shows the net counting rate (left ordinate scale) for the uranium or plutonium $K\alpha_1$ x ray as a function of solution concentration (top scale). The plutonium count rate is 2.2% greater than uranium for a given concentration when corrected for half-life (the two curves are not resolved in Fig. 7). As the concentration increases, there is less than a linear increase in the count rate. This decrease in the count rate slope is a combination of increasing self-absorption of the $K\alpha_1$ x ray within the solution and an effective decrease in the solution volume (penetration of the exciting radiation) as the concentration is increased. Clearly, the net count rate observed will depend on the ^{57}Co source strength ($T_{1/2}$ = 270 d), the experimental geometry, the cell or pipe wall thickness, and the HPGe detector efficiency. Furthermore, at 150 g U/l the rate of change of count rate with concentration becomes less sensitive, i.e. a 1% change in count rate corresponds to almost a 3% change in concentration for the 25.4-mm cell. The observed count rate is also sensitive to changes in geometry, and to changes in the system dead time which varies with concentration. Air bubbles in a flowing stream would also affect the observed count rate. Thus, it is not desirable to use the count rate vs concentration curve to define a calibration relationship. Rather, it is better to define one that is independent of the source half-life and system dead time; that is insensitive to minor changes in geometry and stream flow conditions; and, that is more sensitive to concentration changes with increasing concentration.

It was noted in the two spectra shown in the lower portion of Figure 3 that as the x-ray intensity increases, the 140° incoherently scattered 122-keV radiation peak intensity near 86 keV decreases. A ratio of the net $K\alpha_1$ x-ray intensity to a portion of the spectrum that includes the incoherent peak is more sensitive to concentration than the count rate. The concentration in g/l can be related to this ratio through the relationship:

$$C = K\left(\frac{NK\alpha_1}{GI}\right) \qquad (1)$$

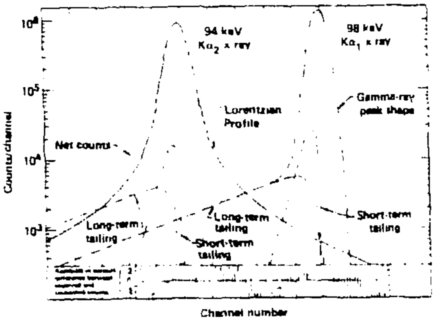


Fig. 6. The Kα2 and Kα1 x-ray peak distributions of uranium observed with a germanium detector. The x ray peaks are fit with a convolution of four mathematical functions, short and long term exponential tailing, a Lorentzian profile, and gaussian distributions.

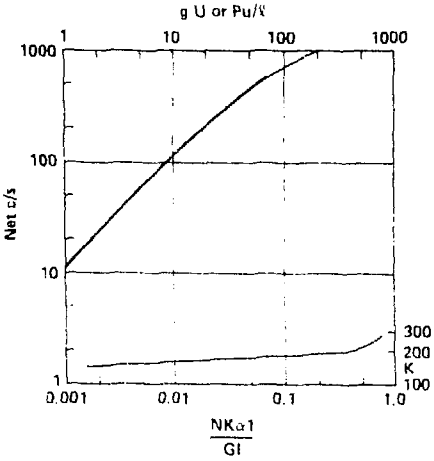


Fig. 7. A log-log plot of count rate (left) vs solution concentration (top) for single element solutions. The curve for plutonium is 2% greater than that for uranium, which is not resolved from uranium (thin line) on this plot. The lower curve shows the behavior of K (right) vs the experimental ratio (bottom). The K curves for uranium and plutonium are similar but not identical.

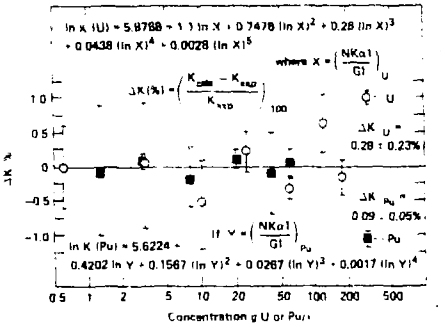


Fig. 8. A semilog plot for the residual in ΔK vs concentration for U (open circles) and Pu (filled squares). The polynomials representing K for both elements are shown as well as the average absolute value differences between the polynomial expression and the experimental data. Error bars indicate relative precision at each concentration.

where NKα1 is the net number of counts in either the uranium or plutonium Kα1 x-ray peak, GI is the gross number of counts in the incoherent peak channel 1500-1640, and K is a nonlinear calibration parameter having units of g/l. This ratio is independent of source exciter half-life, changes in dead time, and small changes in geometry.

The lower portion of Figure 7 shows the behavior of K (right ordinate scale) vs this ratio (lower scale) for the stainless steel cell containing a uranium nitrate solution. A similarly shaped relationship exists for the plutonium K calibration parameter. The increase in K at higher concentrations is effectively a result of increasing self-absorption of the U or Pu Kα1 x rays and decreasing fluoresced volume as the solution concentration increases. A least squares fit to ln(K), expressed as a polynomial function of the natural logarithm of the parenthetical ratio, results in the equations shown as insets in Fig. 8 at the top for uranium, and at the bottom for plutonium. Also shown is the percentage deviation between the calculated and experimental K as a function of solution concentration in the cell. The mean absolute value difference is 0.28% with a root mean square deviation of 0.23% for uranium and 0.047+0.05% for plutonium. The error bar shown at each individual concentration calibration value represents the reproducability or precision obtained for 3 runs. The counting statistics obtained for the Kα1 x ray for any single run varied between 0.2% and 0.5%.

Mixed Uranium-Plutonium Solutions. The probable range of solution concentrations of interest for mixed U-Pu solutions extends from several grams per litre to perhaps several hundred grams per litre. The uranium to plutonium ratio may have almost any value but for this study was confined from 2.3 to 1 to 7.0 to 1. Table I lists the range of solution concentrations measured for three different uranium to plutonium ratios, and indicates in parentheses the estimated concentration error made in solution preparation. Both stock solutions were 3M nitrate solutions. The estimated errors vary from 0.1% for the most concentrated solution to just over 1% for the weakest solution.

TABLE I. RANGE OF MIXED SOLUTION CONCENTRATIONS MEASURED

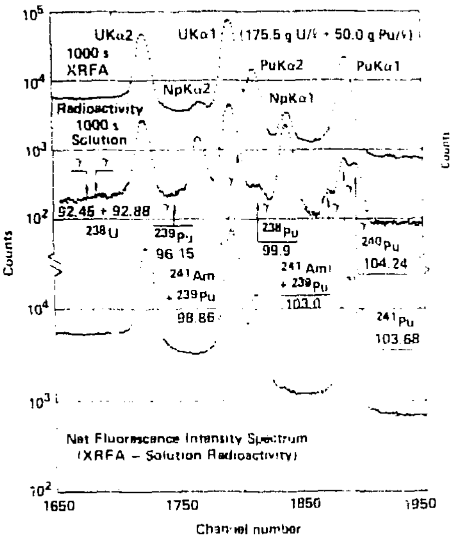
2.33:1		3.5:1		7.0:1	
U (g/l)	Pu	U (g/l)	Pu	U (g/l)	Pu
		3.51(4)	1.00(1)		
10.49(6)	4.50(1)	10.53(5)	3.00(2)	10.08(3)	1.46(1)
35.00(12)	15.01(5)	35.10(6)	10.01(4)	41.94(13)	5.95(4)
70.00(26)	30.02(9)	70.20(23)	20.02(6)	69.81(24)	10.07(7)
		105.3(3)	30.02(8)		
		140.4(4)	40.03(10)		
		175.5(2)	50.04(3)		

a) The maximum estimated error made in the solution preparation is shown in parentheses.

Three 90- to 107-keV spectra are shown in Figure 9. The top spectrum represents a 1000s XRFA of a nitrate solution containing 175.5 g U/l and 50 g Pu/l. The middle spectrum represents a 1000s spectrum of the solution radioactivity obtained by eclipsing the two excitation sources. This complicated spectrum contains a total of 16 gamma and x rays within a 10 keV region and suggests why an accurate quantitative analysis of the top spectrum is very difficult. The lower spectrum is the difference between the top two spectra, that is, the net fluoresced intensities of the uranium and plutonium Kα x-rays. Note that the neptunium x rays seen in the upper spectrum are completely absent in the lower spectrum. Their presence in the upper spectrum is solely a result of the solution radioactivity being counted simultaneously with the fluoresced activity. It is necessary to use GRPANL on the lower spectrum to correctly resolve UKα1 from PuKα2 seen near channel 1800. For all mixed solutions the same region (channel 1696 to 1916) was analyzed.

The top two spectra shown in Figure 9 were accumulated for counting times that might be used for an accountability measurement. The total clock time required for both measurements was about 45 minutes, and the resulting accuracy in the peak area determinations for the difference spectrum is under 0.3% for UKα1 and about 0.4% for PuKα1. Thus, results accurate to better than 0.5% can be obtained for high concentration solutions in less than one hour, and without the necessity of doing any off-line analyses. In the event process control information were needed for such a concentrated mixture, an entire measurement would require no more than ten minutes, i.e. a 100s live time fluorescence count and a 100s radioactivity measurement, plus analysis time. The overall accuracy of the concentrations determined would then be of the order of 1%.

The top spectrum shown in Figure 10 represents a 500s fluorescence of a mixture containing 35.1 g U/l plus 10 g Pu/l. Once a solution's total actinide concentration falls below 50 to 60 g/l, the spectral region containing the U-Pu x rays of interest cannot be accurately analyzed by GRPANL unless a distribution for scattered radiation from pure nitric acid is subtracted from the fluoresced data. The intensity distribution of the incoherently scattered exciting radiation in the vicinity of the uranium and plutonium x rays decreases by more than a factor of ten within 12 keV, and does so with a steep, compound exponential



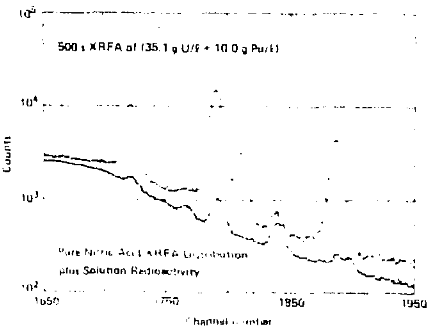


Fig. [illegible] [illegible] region spectra [illegible] mixed U-Pu nitrate [illegible].1 g U/l plus [illegible] g Pu/l. Analysis of the top spectrum would yield concentration values sufficiently accurate to control the process chemistry. The lower spectrum is a sum of the solution's natural radioactivity plus a [illegible]s spectrum of pure nitric acid (dashed line continuum).

Fig. 9. Three 90- to 107-keV region spectra of mixed U-Pu nitrate with 175.5 g U/l plus 50.0 g Pu/l. The top spectrum would provide sufficient accuracy for an accountability measurement. The middle spectrum shows the solutions natural radioactivity. The top spectrum minus the central spectrum results in the lower spectrum, the net XRFA of the mixture.

slope (see also Figure 3, the 3.2 g U/l spectrum). The shape resulting from the scattered exciting radiation for pure nitric acid is represented by the continuum level (dashed lines) in the lower spectra.

The peaks that appear in the lower spectrum of Figure 10 are a result of adding the 500s solution radioactivity spectrum to a pure nitric acid distribution. GRPANL was used to determine the net uranium and plutonium x-ray intensities on a spectrum (not shown) which is the difference between the upper and lower spectra shown. The statistical accuracy in the channel to channel data in the difference spectrum (not shown) will not be the same as that of the original data, particularly in non-peak regions, e.g. above channel 1900. Thus, in order to obtain a realistic chi squared value from the GRPANL fit, a constant is added to the entire region. The constant added has a standard deviation equal to the mean value of the standard deviations for the average number of counts in the pre- and post-background regions (i.e. 1686-1695 and 1917-1926).

The 500s live-time XRF spectrum shown in Figure 10 represents the amount of time that might be used for a process control measurement of solutions having median value uranium-plutonium concentrations. If the typical 20% analyzer dead time is included, the XRFA measurement would require 10 minutes (clock time), and would yield concentration values accurate to about 2%, even without making a quantitative correction for the solution radioactivity. That is, in order to control the chemical process it may be sufficient to determine the solution concentration to only a few percent. This assumes that the plutonium isotopics do not vary widely from day to day (or batch to batch). However, for accountability or inventory control measurements where better accuracy is required, the solution radioactivity must be measured and the more exact quantitative procedures described above used. Accountability measurements cannot be done as quickly as those for process control; and generally, will also require replicate analyses.

Calibration of Mixed Solutions. Just as was done for the pure uranium or plutonium solutions, it is possible to determine a calibration parameter, K, for the mixed solutions. However, because the U/Pu ratio can vary, K will be valid only for a single value of the uranium to plutonium ratio. Seven of the 13 solutions measured (see Table I) had a concentration ratio of 3.5 to 1, thus K was evaluated for this ratio. The smooth curve shown in the top portion of Figure 11 shows the behavior of K versus the ratio of the net counts contained in both the uranium and plutonium Kα1 x rays to the area of the gross incoherent peak (channels 1500-1640). Note that the numerator of the abcissa now contains the total actinide Kα1 x-ray intensity. The resulting polynomial for ln(K) is shown as an inset in the top most graph of Figure 11. The fit of this expression to the experimental data is shown in the lower graph of Figure 11. The mean for the absolute values of the differences is 0.18±0.27%. The error bars shown for each point represent the reproducibility obtained for 3 runs; while for any single run of any mixture, better than 0.6% counting statistics were obtained in NPuKα1, and better than 0.3% for NUKα1.

The uranium to plutonium ratio is not always 3.5. Nevertheless, the total actinide concentration may be obtained from the calibration parameter polynomial after a small correction is applied. The necessity for this correction depends on the U/Pu ratio. Clearly, for solutions containing unknown concentrations of U and Pu, their ratio is also unknown. However, because their fluorescence efficiencies, their Kα1 x-ray energies, and their absorption coefficients are very nearly equal, their actual concentration ratio is nearly equal to the ratio of their experimental count rates. The top graph in Figure 12 shows that the observed U/Pu count rate ratio increases linearly with the ratio of concentration of U/Pu. This linear relationship holds true over the range from U/Pu = 2.3 to U/Pu = 7, the concentration ratios range examined in this study. That is,

$$(U/Pu)_{\text{conc.}} = 1.046 \left(\frac{NUK\alpha 1}{NPuK\alpha 1} \right) \qquad (2)$$

The approximate total actinide concentration can be determined from the calibration polynomial shown at the top of Figure 11. Then, a small correction is applied. That correction in percent is given by ΔP, and its behavior vs concentration ratio is shown in the lower graph of Figure 12. This correction is positive for all U/Pu ratios greater than 3.5 (i.e., K yields too small of a total actinide concentration) or negative for all ratios of U/Pu less than 3.5. Thus, the total actinide concentration is given by

$$C(U + Pu) = K \left[\frac{NUK\alpha 1(U+Pu)}{GI} \right] \left(1 + \frac{\Delta P}{100} \right) \qquad (3)$$

where

$$\Delta P(\%) = -1.98 + 0.59 \left(\frac{NUK\alpha 1}{NPuK\alpha 1} \right) \qquad (4)$$

The individual plutonium and uranium concentrations are given by

$$C(Pu) = \frac{C(U+Pu)}{\left[1+1.046\left(\frac{NUK\alpha 1}{NPuK\alpha 1}\right) \right]} = \frac{C(U+Pu)}{(1+R)} \qquad (5)$$

and

$$C(U) = \frac{R}{(1+R)} \left[C(U+Pu) \right] \qquad (6)$$

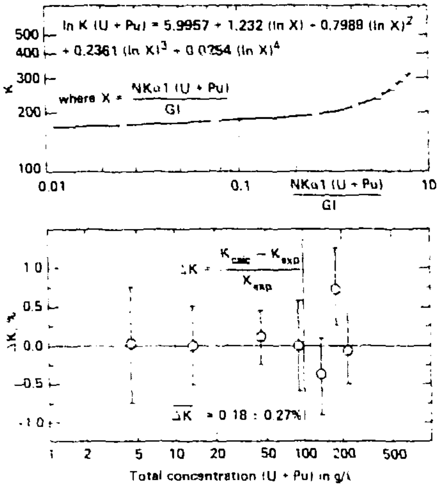


Fig. 11. The upper graph shows the K calibration parameter vs experimental ratio for mixed solutions having U/Pu = 3.5/1. Note that the polynomial expression is based on the sum of the net x ray peak intensities of uranium and plutonium. The individual error bars indicate reproducibility resulting from three individual runs.

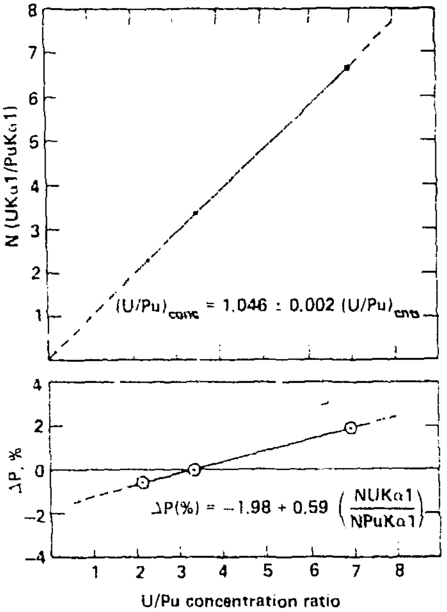


Fig. 12. The upper graph shows a linear relationship between observed U/Pu net counts and actual U/Pu concentration. The lower plot shows the correction factor ΔP that must be applied to the concentration value vs the U/Pu concentration ratio.

It is clear that the linear relationships shown in Fig. 12 will not necessarily hold for very large ratios (greater than 20/1) or very small ratios (less than 1). To insure validity of the XRFA method, it must be calibrated over the entire range of concentrations and elemental ratios that are expected to occur.

Dynamic Concentration Measurements. One of the advantages offered by the nondestructive XRFA technique is its ability to yield concentration values for flowing streams. Appropriate precautions must be taken to insure that the stream will not be subject to foam or sporadic air bubbles at the measurement location. In the earlier work[4] detailed experiments were carried out to demonstrate the techniques ability to make dynamic concentration measurements. Here, only a summary of those results will be presented.

The top section of Figure 13 shows a set of 24 measurements. The first and last six measurements were made with the solution static, while the central 12 measurements were made with the solution flowing at 80 l/h. The static and flow results overlap well within the precision of their standard errors. The flow system consisted of a reservoir and tygon tubing connected to a 25 mm diameter pyrex cell and a peristaltic pump. The pump forced the solution to circulate through the tubing and cell and return to the reservoir by a cylical squeezing action. Once a known volume of a specific concentration is introduced into a dry cell and tubing system, additional small volumes of pure acid or of a more concentrated solution will change the initial concentration accordingly.

The lower section of Figure 13 illustrates a dynamic concentration measurement. Initially, 100.0 ml of the 100.0 g U/l standard solution was introduced into the flow system with the cell and tubing dry. Appropriate volumes of 3M HNO_3 were calculated and measured out, then introduced at regular intervals into the flow system. This caused a concentration reduction of exactly 1.0 g U/l for each of five times. Then, appropriate volumes of more concentrated uranium nitrate solutions were introduced to increase the solution concentration 2.0 g U/l for each of three steps. This brought the concentration to about 101 g U/l, whereupon a final calculated volumetric addition of 3M HNO_3 returned the solution to its original 100.0 g U/l concentration.

The pause time of 100s was selected on the basis of earlier dynamic concentration runs. It was somewhat longer than the time required for the solution volume to reach equilibrium after introduction of an additional volume. Each 100s analysis had approximately the same statistical accuracy of ±0.53%, however, the mean values and precisions indicated at each successive concentration are determined from just the measurements made within that interval. Note that the mean of the first and last five dynamic concentrations measurements is 100.35±0.63 g U/l, in excellent agreement with the mean value of 100.13±0.40 g U/l from the first 24 static/flow cycle measurements.

Fission Products in Product Streams. It is possible that additional levels of radioactivity might be associated with the reprocessed actinide products. These activities might be purposely added (e.g. ^{60}Co or ^{238}Pu), or they could be fission products, which were not completely separated during the earlier stages of chemical purification. It is beyond the scope of this report to discuss the relative advantages or disadvantages of adding such spikes. Suffice it to say that if significant levels of activity are found in the process stream and product forms - solutions or oxides, then many of the nondestructive analytical techniques, which have required years of development time and at significant costs, may not be useable. For the purposes of this study, a simple experiment was conducted in order to evaluate the behavior of the XRFA technique to additional levels of activity in the process or product streams.

In order to simulate fission product activity in the stainless steel cell, 4.8 mCi of ^{137}Cs activity was chemically prepared in nitric acid solution, and loaded into the same cell as that used to count the pure and mixed actinide solutions. For the counting geometry used throughout these experiments, this activity represented very nearly the limiting count rate that the non-optimized commercial electronics could process. The system dead time approached 70%. The lower spectrum in Fig. 14 shows a 500s XRFA of the 90- to 107-keV region of a 10.5 g U/l plus 4.5 g Pu/l mixed solution. The top spectrum represents a 500s count of this solution plus 4.8 mCi of ^{137}Cs activity. Thus, assuming that there were no fission product gamma rays within the 90- to 107-keV region, the major effect of fission product activities on XRFA in process or product streams is to raise the background continuum level in the region of the x-ray peaks of interest, but the x rays can still be analyzed accurately. The top spectrum, then, corresponds to a solution containing 10.5 g U/l, 4.5 g Pu/l, and 27.7 mCi/gPu of fission product gamma-ray activity. Since the system's counting electronics were very near their maximum count rate limit, any further increase in the stream's uranium or plutonium concentration would lock-up or shut-off the electronics. Therefore, if higher plutonium solution concentrations were expected, then the decontamination factors in the earlier stages of separation would have to be improved. That is, a solution containing about 150 g U/l and 45 g Pu/l could be counted if it contained less than 2.8 mCi of fission product activity per gram of plutonium.

Relative Isotopic Abundances. The absolute abundance of each of the plutonium isotopes, except ^{242}Pu, can be determined from measurements of the solution radioactivity and concentration. A radioactivity measurement is made when an automatic, horseshoe shaped shutter is activated to eclipse the two exciting sources. The ultimate purpose of, and thus the accuracy required from, the isotopic abundance measurement will govern the measurement time. For example, a 1000s XRFA and solution radioactivity measurement of a 175 g U/l plus 50 g Pu/l solution was sufficiently long enough to accurately determine its concentration for accountability or inventory control purposes (see discussion above).

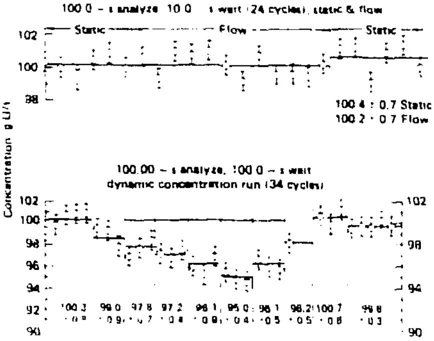


Fig. 13. Two plots of solution concentration vs time. Analysis and pause times vary. The first and last six measurements were made with the solution static, the center 12 with it flowing. The lower set is a dynamic concentration run (see text). The error bars indicate 1σ statistical counting accuracy only.

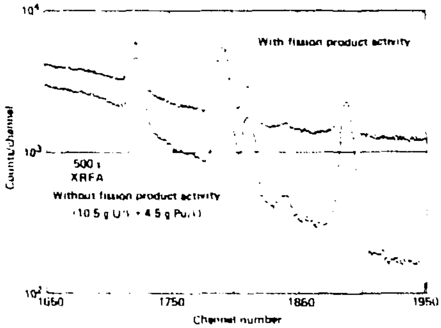


Fig. 14. Two 90- to 107-keV spectra with (upper spectrum) and without (lower spectrum) fission product activity within the solution. The mixed U-Pu solution has a concentration of 10.5 g U/l plus 4.5 g Pu/l. Nearly 30 m was required to record the upper spectrum because of excessive dead time caused by the fission product radioactivity (28 mCi/g Pu).

However, if the isotopic abundances of the same solution were also desired to an equivalent accuracy (sub 0.5%), then the 1000s radioactivity measurement time is insufficient. This arises not because of a lack of solution radioactivity, but because the HPGe detector is almost an order of magnitude further away from the sample than it need be, a result of the shielding required for the XRFA measurement. If an additional detector were located immediately adjacent to the pipe, the activity count rate would be considerably greater. Thus, an optimum system for an on-line accountability measurement of the final product might consist of two detectors, one devoted to XRFA, the other optimized to determine the relative isotopic abundances from the solution radioactivity. The computer-based analyzer system could be programmed to control both detector systems, their measurements times, and all data reduction required for both analyses.

SUMMARY

The experimental results discussed above have demonstrated that energy dispersive x-ray fluorescence analysis (EDXRFA) can determine the concentration of uranium, plutonium, or mixed uranium-plutonium solutions in flowing or static streams. The EDXRFA technique is nondestructive and can be adapted directly to pipelines in facilities that have process or product streams containing these actinide elements. The technique can also be used to make off-line measurements. By using an automatic shutter to eclipse the exciting radiation, the natural radioactivity of the solution mixture can be measured. Thus, the relative plutonium isotopic abundances can be determined for plutonium solutions; while for uranium solutions, the degree of enrichment in ^{235}U can be deduced after calibration of the system.

The time required for the measurement depends on the purpose of the measurement and the concentration of the solution. Generally, measurements made to control or monitor the process chemistry need not be made as accurately as those for accountability and inventory control. Typical analysis times for process control information are from 100 to 500 seconds for solution concentrations from several hundred to a few grams per liter, respectively. Longer measurement times are required for inventory control purposes where accuracies better than 1% are desired. The XRFA method is capable of yielding such accuracy if it is carefully calibrated and reproducible counting geometry is maintained.

For concentrated solutions containing mixed uranium and plutonium, the contributions to the uranium x-ray intensities from plutonium decay and to the plutonium x-ray intensities from its gamma-ray activities must be removed. This is accomplished by subtracting (via the computer) the solution radioactivity spectrum from the XRFA spectrum. Then, the unknown uranium to plutonium concentration ratio is determined from the net intensities of their x rays, and the individual concentrations are calculated from simple expressions. Thus, accountability measurements may require from one to two hours, the longer times being required for the weaker concentrations. But, since on-line results can be obtained automatically, and without any personnel-sample interaction, the method should still be cost-effective.

Finally, actinide solution concentrations can be measured, even if a small amount of fission product radioactivity exists in the product solution. The limiting factor is the maximum count rate that the electronics can handle. The actinide x-ray intensities stimulated by the 122-keV exciting radiation from Co are sufficiently intense to be seen above low levels of fission product background continuum; and the x-rays can be analyzed without a sacrifice in measurement accuracy, even for relatively low solution concentrations. In conclusion then, this technique should prove to be of great interest to enrichment facilities and to spent nuclear fuel reprocessing facilities in which single or dual element actinide solutions must be measured or monitored for concentration and isotopic content.

REFERENCES

1. W. D. Ruhter and D. C. Camp, "Nondestructive Assay of Mixed Uranium Plutonium Oxides by Gamma-Ray Spectrometry," UCRL-52625 (1979).

2. R. Gunnink, J.B. Niday, A. L. Prindle, W. D. Ruhter and D. C. Camp, "Determination of Plutonium Isotopics by Gamma-Ray Spectrometry," UCRL - Publication in preparation (1980).

3. D. C. Camp, "An Introduction to Energy Dispersive X-Ray Fluorescence Analysis," UCRL-52489 (1978).

4. D. C. Camp, W. D. Ruhter, and S. Benjamin, "Nondestructive, Energy Dispersive X-Ray Fluorescence Analysis of Product Stream Concentrations from Reprocessed LWR Fuels," UCRL-52616 (1979).

5. R. Gunnink, "An Algorithm for Fitting Lorentzian-Broadened, K-Series X-Ray Peaks of the Heavy Elements," UCRL-78707 (1976).

6. R. Gunnink and W. D. Ruhter, "A Generalized Computer Code for Resolving Overlapping Gamma-Ray and X-Ray Peaks - GRPANL," UCRL Report in Preparation (1980).