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ANALYSIS METHODS AND PERFORMANCE OF AN AUTOMATED SYSTEM FOR MEASURING BOTH CONCENTRATION AND ENRICHMENT OF URANIUM IN SOLUTIONS

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ANALYSIS METHODS AND PERFORMANCE OF AN AUTOMATED SYSTEM FOR MEASURING BOTH CONCENTRATION AND ENRICHMENT OF URANIUM IN SOLUTIONS*

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ABSTRACT

For the 1992 INNM meeting, we reported on the general characteristics of an automated system—then under development—for measuring both the concentration and enrichment of uranium in solutions.¹ That paper emphasized the automated control capability, the measurement sequences, and safety features of the system. In this paper, we report in detail on the measurement methods, the analysis algorithms, and the performance of the delivered system. The uranium concentration is measured by a transmission-corrected x-ray fluorescence method. Cobalt-57 is the fluorescing source and a combined ¹⁵³Gd and ⁵⁷Co source is used for the transmission measurements. Corrections are made for both the absorption of the exciting ⁵⁷Co gamma rays and the excited uranium x-rays. The ²³⁵U concentration is measured by a transmission-corrected method, which employs the 185.7-keV gamma ray of ²³⁵U and a transmission source of ⁷⁵Se to make corrections for the self-absorption of the ²³⁵U gamma rays in the solution samples. Both measurements employ high-resolution gamma-ray spectrometry and use the same 50-ml sample contained in a custom-molded, flat-bottomed, polypropylene bottle. Both measurements are intended for uranium solutions with concentrations ≥ 0.1 g U/l, although at higher enrichments the passive measurement will be even more sensitive.

INTRODUCTION

The customer for whom this solution enrichment system (SES) was developed desired to measure both total uranium concentration and the enrichment [defined here as (concentration ²³⁵U/concentration U) • 100] over a wide range in both quantities. Measurement capability was required for concentrations ≥ 0.1 g U/l and for enrichments $\geq 0.3\%$. We note that 400 g U/l is about the maximum concentration at which uranium can be kept in solution and that solutions with uranium enrichment up to ~97% are expected. For optimum accuracy it appeared that the best procedure was to measure the ²³⁵U and total uranium concentrations separately and compute their ratio to get the enrichment. We had previously developed methods for ²³⁵U concentration measurements,^{2,3} which could be adapted to the the present system with little

change. Because of the necessity of measuring total concentration down to 0.1 g U/l, x-ray fluorescence became the choice of necessity for that measurement. K-edge densitometry can make excellent total element concentration measurements at high concentrations but cannot reach 0.1 g U/l.

The problems that cause error in chemical procedures for measuring concentration are generally different from those that cause error in nondestructive assay (NDA) procedures such as those reported herein. In most gamma-ray NDA procedures, the size, shape, and location of the sample relative to the germanium gamma-ray detector are crucial. They must be constant and reproducible. These requirements dictated the use of a custom-molded bottle of fairly stiff plastic to achieve the necessary tolerances in shape and position.

The ²³⁵U concentration is found by a passive gamma-ray method, which will be referred to herein as the PGR method or the PGR measurement. The total uranium concentration is found by an x-ray fluorescence method and will similarly be identified by the acronym XRF. It will be useful to briefly review the general measurement philosophy used, which is the same for both the PGR and XRF measurements.

In both PGR and XRF measurements, a sample large enough to provide adequate signal at the lower concentrations and enrichments will suffer significant data loss from self-attenuation at higher concentrations. Furthermore, the higher count rates generated at higher concentrations will also cause significant data losses from the combined effects of the rate-related processes of pulse pileup and deadtime. We, therefore, compute a total corrected count rate for the appropriate full-energy peak (be it from a gamma ray or x-ray):

$$TCR = RR \cdot CF(RL) \cdot CF(AT)$$

or

$$CR = FEIR \cdot CF(AT) , \quad (1)$$

where TCR = total corrected rate,
 RR = raw rate of data acquisition,

*This work is supported by the US Department of Energy, Office of Safeguards and Security.

$CF(RL)$ = correction factor for rate-related electronic losses,
 $CF(AT)$ = correction factor for self-attenuation in sample, and
 $FEIR$ = full-energy interaction rate = $RR \cdot CF(RL)$.

TT = true time of spectral acquisition, and
 $A(Ref)$ = full-energy peak area of the selected reference source gamma ray.

If the correction factors are properly defined and computed, TCR is the data-acquisition rate that would have been observed if there were no electronic losses and if there were no self-attenuation of gamma rays or x-rays in the sample. Thus computed, TCR is proportional to the concentration of ^{235}U in the PGR measurement and to the total uranium concentration in the XRF measurement. We can thus write

$$TCR = K \cdot C, \quad (2)$$

where C is the concentration of the quantity being measured and K is a calibration constant. The calibration constant K is found by using appropriate standard samples and includes the effects of detector efficiency, gamma ray emission rates (in PGR), cross sections for x-ray fluorescence (in XRF), and geometrical effects. It should be emphasized that $CF(AT)$ fully accounts for variations in uranium concentration and matrix composition. There is therefore no need for standards with matrix composition similar to all expected unknowns. Both calibration effort and expense for standards are greatly reduced.

Because the finding of $CF(RL)$ is essentially the same for the PGR and XRF methods, besides being generic to many gamma-ray-based NDA methods, we discuss its determination now. We use a reference source method in which an appropriate source is fastened directly to the end cap of the detectors so that they see a constant (subject only to decay of the source) flux of gamma rays from the source. In this method, we must assume that all full-energy peaks in the gamma-ray spectrum suffer the same fraction of loss from the combined effects of deadtime and pileup. Especially over a limited energy range, this assumption is very good, both in theory and practice. The full energy interaction rate (FEIR), which is the rate at which a gamma ray undergoes full-energy actions—those which can fall into the full-energy peak—is the key here. It can easily be shown that

$$CF(RL) = \frac{[FEIR(Ref) \cdot TT]}{A(Ref)}, \quad (3)$$

where $FEIR(Ref)$ = FEIR of the selected reference source gamma ray,

We do not need to calculate the $CF(RL)$ explicitly; however, the FEIR of the selected gamma ray or x-ray is what we really want [see Eq. (1)] and it is given by

$$FEIR(\gamma) = \left[\frac{A(\gamma)}{A(Ref)} \right] \cdot FEIR(Ref), \quad (4)$$

where $A(\gamma)$ and $FEIR(\gamma)$ are the peak area and FEIR of any selected gamma ray or x-ray from the assay sample. It is usually possible to obtain quite accurate values for $FEIR(Ref)$, but it is, in fact, not necessary. In systems calibrated with the help of standards, it does not matter if the assumed value of $FEIR(Ref)$ is wrong because it cancels from the calibration equations. Only if we want to accurately know the magnitude of $CF(RL)$ is the value of $FEIR(Ref)$ important. This matter and details of the method are discussed in Chap. 5 of Ref 2. We close this discussion of $CF(RL)$ by observing that experiments show that the reference source method can correct for deadtime and pileup losses with accuracies near 0.1% over a wide count-rate range.

THE PGR MEASUREMENT

Figure 1 shows the geometry of the PGR measurement, including the location and approximate activities of the various sources involved. As indicated, the reference source is $\sim 3\mu\text{Ci}$ of ^{241}Am . Though ^{241}Am has many gamma rays, the 59.5-keV one is by far the most intense and is used as the reference gamma ray. The 433.6-yr half-life of ^{241}Am eliminates the need to change the source during the life of the detector, the ~ 60 -keV gamma ray is useful as an ever-present peak with which to stabilize the low-energy end of the spectrum, and the Compton and pileup distributions from it do not in any way interfere with the 185.7-keV peak upon which the ^{235}U assay is based. It is an ideal reference source for ^{235}U measurements—as long as the uranium samples do not have any significant plutonium or ^{241}Am contamination. If there is such contamination, another reference source must be chosen, perhaps ^{109}Cd , which is used in the XRF measurement.

The high-purity, 52-mm-diam and 35-mm-long germanium detector used in the PGR measurement has an efficiency in the usual definition of $\sim 18\%$. The reference source is on top of a thin filter of 0.020-in. copper whose

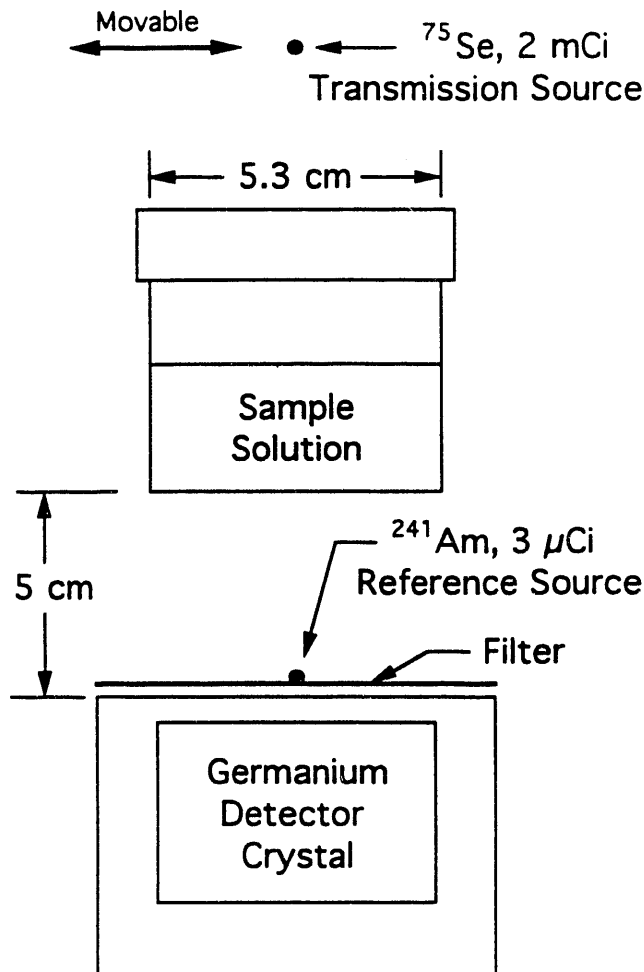


Fig. 1. Schematic of the PGR measurement geometry, including important dimensions and source information.

purpose is to reduce the intensity of L x-rays and low-energy gamma rays from the reference source. An additional 0.016 in. of cadmium is on top of the reference source to provide additional filtering for low-energy photons from the assay sample and transmission source. The ~5-cm sample-to-end-cap distance is a reasonable compromise between the necessity for reasonable count rate and the desirability of reducing $1/R^2$ effects caused by small differences in sample positioning.

Now let us discuss the measurement of $CF(AT)$. If the linear attenuation coefficient μ^L of the sample solution is known, along with the assay geometry (dimensions of sample and position relative to detector), the $CF(AT)$ can be calculated. Neither determining μ^L nor computing $CF(AT)$ are particularly simple. Generally, values for μ^L are found by measuring the transmission T (the fraction of gamma rays passing through the sample without being scattered or absorbed), which is related to μ^L by

$$T = \exp(-\mu^L d), \quad (5)$$

where d is the path length of the gamma rays through the sample. The μ^L are, of course, functions of atomic number, energy, and density. It is impractical to use a ^{235}U transmission source so that μ^L at 185.7 keV is measured directly. We must therefore measure the transmissions at one or more other energies and interpolate or extrapolate to the transmission at 185.7 keV to compute μ^L at 185.7 keV. Finding a suitable source is not always easy. Ytterbium-169 has strong gamma rays at 177.2 and 198.0 keV, just above and below the 185.7-keV energy of the ^{235}U gamma ray, making it easy to do an accurate interpolation. Unfortunately, the 32.0-day half-life of ^{169}Yb makes its use difficult and/or expensive, especially in recent years when prices have increased sharply and availability has decreased equally sharply. For these reasons, it was eliminated from consideration for PGR use. Holmium-166m, with a half-life of 1200 years, has a well-placed gamma ray at 184.4 keV, but the nuclide is very expensive, as well as having numerous high-energy gamma rays that make proper shielding more difficult. It was therefore also eliminated from consideration. We finally settled on the use of ^{75}Se , which has an acceptable half-life of 120 days, along with reasonable price and availability. The two most intense gamma rays are at 136.0 and 264.7 keV, both farther removed from 185.7 keV than one would like. Various schemes were tried to do the required interpolation. The most obvious ones—linear fit to $\log T$ vs $\log E$, and linear or quadratic fits to $\log(-\log T)$ vs $\log E$ —were not adequate. Finally, a variation of the scheme sometimes used to find the spatial density of the components of a two-component mixture by measuring the transmissions through it at two energies proved successful. Because the scheme may prove generally useful when transmission interpolation within a wide energy range is required, we will give the essential relations.

Assume a two-component mixture and that the mass-attenuation coefficients for both components are known for the two transmission energies and for the energy for which we want the interpolated transmission. Also assume the components are uranium and matrix (everything else in the solutions). We can then write

$$T_l = \exp[-(\mu_{l,u} \rho_u + \mu_{l,m} \rho_m)d] \quad (6)$$

$$T_h = \exp[-(\mu_{h,u} \rho_u + \mu_{h,m} \rho_m)d], \quad (7)$$

where subscripts u and m indicate uranium and matrix, respectively,

where subscripts ℓ and h indicate low and high energy, respectively, and

where T = transmission,
 μ = mass attenuation coefficients
 ρ = spatial densities of the components, and
 d = thickness of sample.

If we take the natural logarithm of both sides of the equations, we get simple linear equations in two unknowns with the solutions.

$$\rho_u = \frac{1}{d} \left[\frac{(\mu_{\ell,m} \ln T_h - \mu_{h,m} \ln T_\ell)}{(\mu_{\ell,u} \mu_{h,m} - \mu_{\ell,m} \mu_{h,m})} \right] \quad (8)$$

and

$$\rho_m = \frac{1}{d} \left[\frac{(\mu_{h,u} \ln T_n - \mu_{\ell,u} \ln T_\ell)}{(\mu_{\ell,u} \mu_{h,m} - \mu_{\ell,m} \mu_{h,m})} \right]. \quad (9)$$

With ρ_u and ρ_m known, they are used with the known μ values to compute the transmission at 185.7 keV. The question immediately arises about possible error arising from using incorrect μ values, particularly for the matrix, the composition of which we do not know in detail. It can easily be shown that if the attenuation coefficients of the elements in the matrix differ from one another at all energies by only constant multiplicative factors, no error in the interpolated T will occur. An examination of tables or plots of mass-attenuation coefficients show that this is essentially true for $136 \text{ keV} < E < 265 \text{ keV}$ for all elements up to about $Z = 15$, in particular, including H, C, N, O, and F, which are the most common matrix elements in solutions. The same considerations apply to the high- Z component, where in the required energy range all the elements from at least $Z = 80$ upwards have attenuation coefficients differing by nearly equal multiplicative factors. It therefore does not matter whether we use the μ values for one high- Z element or another in the permitted range, nor which low- Z element or low- Z compound in the permitted range. To preserve an appearance of reality, we use the attenuation coefficients for uranium and water. One could extend the expressions to three transmissions and three components using, for example, the 136.0-, 264.7-, and 400.6-keV gamma rays of ^{75}Se with water, iron, and uranium as low- Z , mid- Z , and high- Z components. However, trials show that there is not enough difference in the μ values, nor high enough precision in the data to give any distinct advantage in the current application. Significant quantities of middle- Z elements, those

outside the two "allowed" ranges, could cause modest error but it is regarded as highly unlikely to occur, and for the sake of better accuracy in all the expected situations we use this method.

After we have found the correct μ^ℓ at 185.7 keV, we must calculate the $CF(AT)$. In "near field" geometries such as the PGR device, there are no simple analytic functions that are sufficiently accurate. We have adopted a relatively simple model consisting of a cylindrically shaped sample axially centered above a disk-shaped detector of uniform efficiency over its whole area. The integral expressions for this model can be easily written, and though they cannot be integrated in terms of elementary functions, they can be easily evaluated by numeric integration. The sample-to-detector distance—not very well defined, at best, because of the variable depth of interaction of the gamma rays in the detector—is used as an adjustable parameter by which compensation is made for imperfections in the model. Values good to 0.1%, or better, while $CF(AT)$ changes by a full factor of 2 are obtained by this scheme. To avoid lengthy numeric integrations during PGR operations, we calculate $CF(AT)$ for a set of transmissions covering the expected range and fit the values to a fourth-order polynomial in $\log E$. The coefficients of the polynomial are stored and allow quick and accurate computation of $CF(AT)$ for all transmissions. In the PGR system as currently constituted, $1.2 < CF(AT) < 2.4$ for uranium concentrations ranging from 0 to 400 g U/ ℓ . The transmission increases from about 0.15 to 0.70 as the total uranium concentration decreases from 400 to 0.0 g U/ ℓ .

In the PGR measurement, all the required spectral peaks are clean and well resolved. We therefore use simple region-of-interest (ROI) methods to obtain all the net full-energy peak areas and estimates of the standard deviations thereof. The background continuum subtraction is usually by a simple smoothed step algorithm. Propagation of errors through all the analysis is straightforward and results in accurate estimates of the statistical precision of the calculated ^{235}U concentrations, as shown by comparing the propagated estimates with the sample standard deviation from replicate assays. Our conventions and expressions for obtaining net areas and estimates of standard deviations thereof by ROI methods are given in detail in Chap. 5 of Ref. 2.

Let us now discuss PGR measurement performance. Figure 2 presents $\text{TCR}/(\text{g U}/\ell)$ for a set of standards made from ~97%-enriched uranium. The horizontal axis is logarithmic merely to spread out the low concentration points for convenient viewing. If everything has been done correctly, all the $\text{TCR}/(\text{g U}/\ell)$ values will be equal

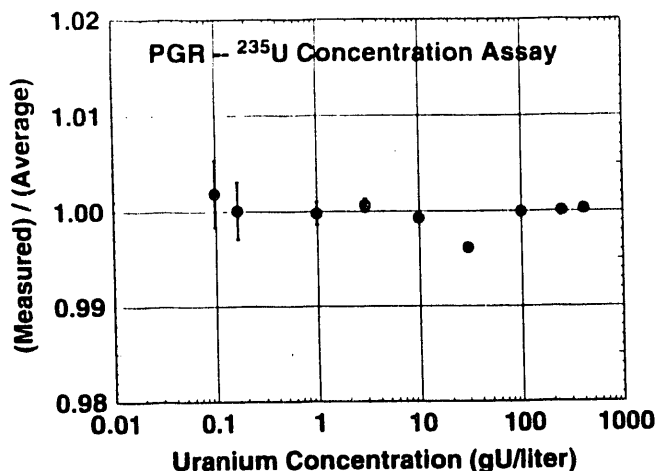


Fig. 2. For the PGR system, fractional deviations of $TCR/(g^{235}U/l)$ values from average for the set of 97%-enriched solution standards.

save for their statistical variation. With the exception of the ~ 30 g U/l standard, all the values are within $\sim 0.1\%$ of an average value. We believe the reported value of that standard to be in error. This errant point emphasizes an important property of this type of NDA instrument: that such instruments are good at detecting inconsistencies within a set of standards. Another important point is that such instruments require self-consistent, accurate sets of standards to be calibrated to give accurate results. In principle, one could use measured detector efficiencies, calculated solid angles, and tabulated values of half-life and emission probabilities to make assays without the use of uranium-bearing standards. However, the result of using several parameters, which are only known to a few percent, might well result in a device accurate to only a few percent, while with appropriate standards for calibration, accuracies within a few tenths of a percent are possible, as indicated in Fig. 1. Reference 4 explains the advantages we see in presenting calibration data in this way.

In the PGR system we could, for higher concentrations, measure the transmission peaks and the ^{235}U peak simultaneously. However, at low concentrations the Compton continuum from the higher energy ^{75}Se gamma rays may bias the measured area of the 185.7-keV gamma ray and will surely degrade to some extent the precision of the area. Because of this, we chose to make the PGR a two-measurement instrument. After the transmissions are measured, the ^{75}Se transmission source is "turned off" with a tungsten shutter and the uranium spectrum is obtained with minimum interference and maximum sensitivity. For a given total count time, the precision of the

TCR is clearly a function of how the measurement time is divided between the transmission and sample-only spectra. It is easy to measure the precision per unit time for any sample or standard and with that information we can compute the optimum division of time for best precision. Indeed we may then estimate the precision for any division of count time. Figure 3 shows the precision with optimal time division for several total times as a function of total uranium concentration for the 97%-enriched standards. The curves turn up slightly at concentrations greater than 100 g U/l because of the poorer statistical precision of the low fractional transmissions and the decreasing fraction of escape of 185.7-keV gamma rays from the sample. Figure 4 shows the precision for a total of 2000 live-time seconds as a function of the transmission time fraction for standards with concentrations down to 0.1 g U/l. As expected, the curves are broad and shallow over a significant range of transmission fraction. For the 97%-enriched standards, it appears that a transmission fraction between 0.2 to 0.3 would suffice for the whole range of concentrations with little loss of precision. For samples of lower enrichment, the minimum points will shift even further toward small transmission fractions and one might reduce the transmission fraction to 0.1 for low-enriched samples. However, if one wants a single choice for all concentrations and enrichments, it appears that 0.2 is as good as any.

THE XRF MEASUREMENT

Figure 5 shows the geometry of the PGR measurement, including important dimensions and the location and approximate activities of all the sources used. As

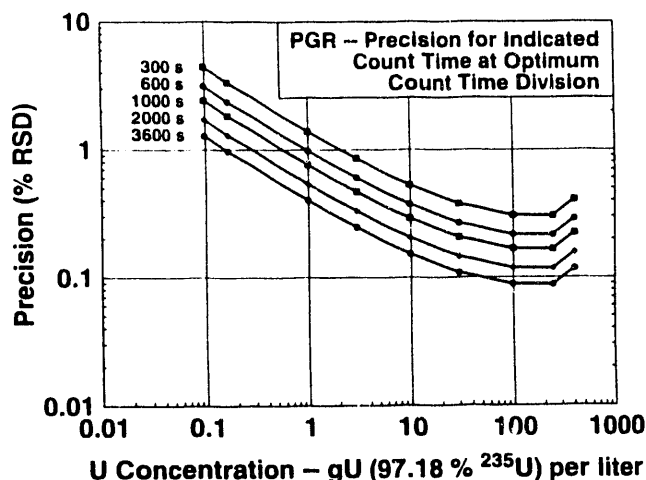


Fig. 3. PGR measurement precision (%RSD) for the set of 97% enriched solution standards as a function of concentration for several total count times. The total count time is optimally divided between the transmission and passive spectra.

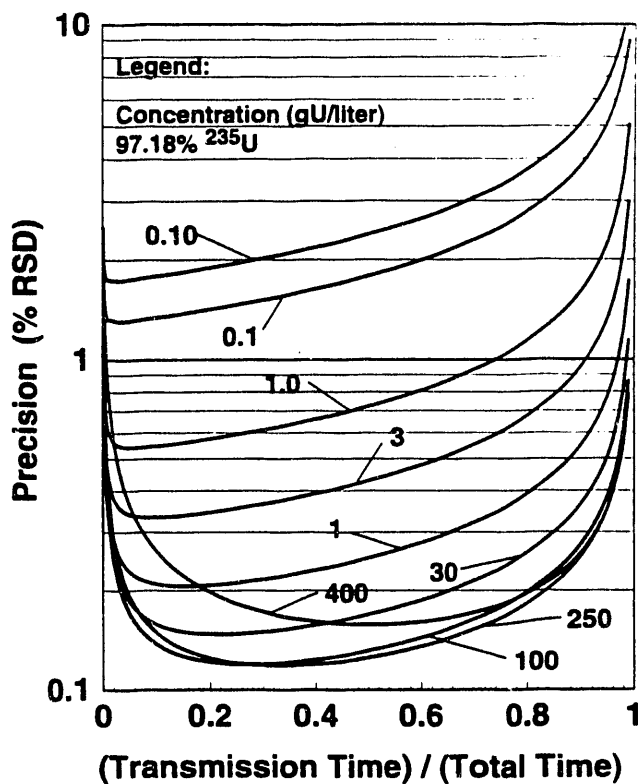


Fig. 4. PGR measurement precision (%RSD) for the set of 97%-enriched solution standards as a function of the time fraction of the transmission spectrum. Total time was 2000 live-time seconds in all cases.

indicated, the reference source is $\sim 200 \mu\text{Ci}$ of ^{109}Cd , which has a half-life of 452 days. The single major gamma ray of 88.0 keV is used as reference. Both price and availability are reasonable. Cadmium-109 is used instead of ^{241}Am because two americium gamma rays, though weak, interfere directly with other gamma rays and x-rays required in the analysis, and because tungsten has an x-ray at 59.5 keV—sure to be excited if we use tungsten collimator—which interferes with the 59.5-keV ^{241}Am gamma ray.

The 122.1 and 136.5-keV gamma rays of ^{57}Co (half-life of 272 days) are almost ideal to fluoresce the K x-rays of uranium whose K-absorption edge is at 115.6 keV. The XRF system uses a single ^{57}Co source in a 0.31-in.-diam, 0.20-in.-long, stainless steel capsule. When fresh, the source is 25 to 30 mCi and can be used for about a year before replacement.

The detector is a high-purity planar germanium unit having a front circular area of 5 cm^2 and thickness of 1.3 cm. Because the collimator constrains the effective

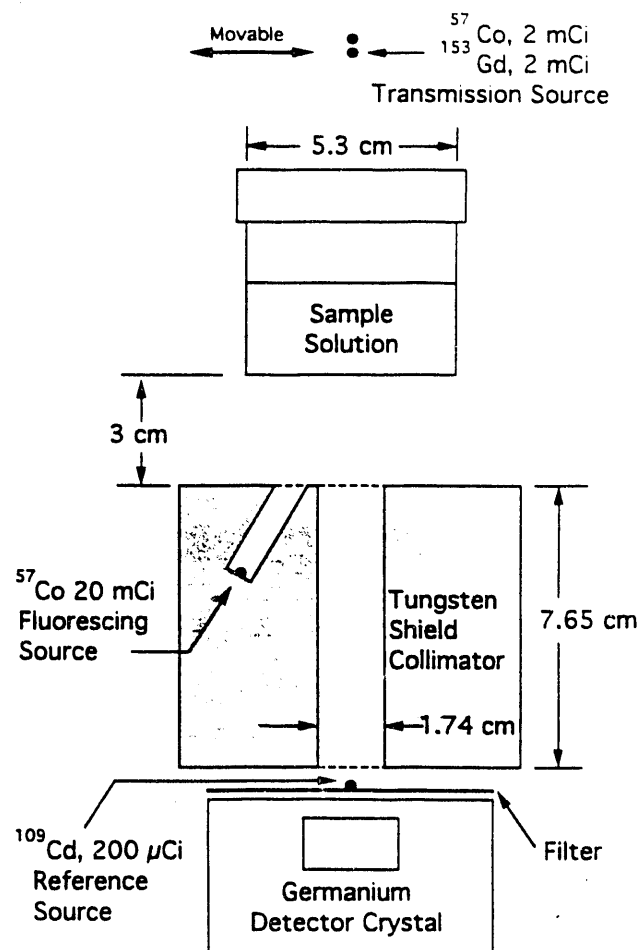


Fig. 5. Schematic of the XRF measurement geometry, including important dimensions and source information.

area of the detector, and because the maximum energy of concern is 136 keV, we do not need a large detector and indeed benefit from the better resolution of a smaller size.

The analysis for total uranium concentration is based on the 98.44-keV uranium $K_{\alpha 1}$ x-ray. Because of lesser intensities and poorer placement relative to the Compton-scattered continuum, it is not worth attempting to use the $K_{\alpha 2}$ or any of the K_{β} x-rays.

Finding $CF(AT)$ is much more difficult in the XRF system than in the PGR system because we must correct for the attenuation of the ^{57}Co fluorescing gamma rays as well as the attenuation of the fluoresced x-rays. The μ^L at 98.44, 122.1, and 136.5-keV are therefore required along with the dimensions of the assay geometry. To find the required μ^L , we must obtain the transmissions at the energies specified. To do this, we use a combined source of

^{153}Gd (242-days half-life) and ^{57}Co (272-days half-life). Gadolinium-153 with gamma rays at 97.4 and 103.2 keV (emission probabilities of 56% and 42%, respectively) is ideal for interpolating to the required 98.44 keV, although procurement is sometimes difficult. Ruhter and Camp,⁵ who developed a somewhat similar XRF system for analysis of uranium and plutonium solutions, first suggested the use of ^{153}Gd . We use a linear fit to $\log(-\log T)$ vs $\log E$ for the interpolation. This seemingly curious choice assumes that μ^L is a power law function of energy, which is nearly true for higher uranium concentrations where highest accuracy is required. The ^{57}Co part of the transmission source, of course, gives transmissions at exactly the energies required.

Again, $CF(AT)$ is found by numeric integration based on the known values, a simple model of the assay geometry and some simplified physics. Simplifications include assuming a point detector, "perfect" collimators, and ignoring fluorescence by scattered photons. In this case, the intensity of the 136.5-keV gamma ray relative to the 122.1-keV gamma ray provides the adjustable parameter by which we compensate for imperfections in the approximate model. Because of the essentially squared correction, the $CF(AT)$ for the XRF measurement are much greater than for the PGR system for the same uranium concentration. For

$$0.1 \text{ g U/l} < \rho_u < 400 \text{ g U/l},$$

the corresponding correction factor range is $\sim 1.4 < CF(AT) < \sim 5.4$. Experience indicates that the computed $CF(AT)$ is good to within 0.5% or better over the range required.

In the XRF measurement spectra, several overlapping doublet and triplet peaks occur involving both gamma rays and x-rays. As a result, we cannot use the simple ROI methods for extracting the required peak areas that were used with the PGR measurement. Instead, a response function method is used in which the peak centroids, peak half-widths, and low-energy tail parameters are specified and the peak amplitudes are computed by a least-squares routine. The necessary centroid and peak shape information is extracted from the measurement spectra. An additional complication is that the x-ray peaks have an intrinsic Lorentzian shape that must be convoluted with the Gaussian instrumental broadening. The required convolution is accomplished by numeric methods during each analysis. A final difficulty in obtaining the area of the $K_{\alpha 1}$ x-ray peak is that at lower concentrations the peak rides on a large concave background continuum arising mostly from doubly scattered photons and Compton interactions of higher energy gamma rays (the ^{57}Co always contains a

little ^{56}Co and ^{58}Co). It is this essentially irreducible continuum that imposes a practical lower concentration limit of about 0.1 g U/l for the XRF measurement. Great care must be exercised in subtracting this continuum from beneath the x-ray peak, especially at lower concentrations, to avoid measurement biases. At higher concentrations, we use an exponential background, and for concentrations below ~ 3 g U/l, we use a quadratic fit to 20 channels of the continuum on each side of the K x-ray peak.

As in the PGR system, a transmission spectrum is required (the fluorescing source being shut off). The second required spectrum is the fluoresced spectrum (the transmission source being shut off). And part of the time, a passive spectrum is required with both fluorescing and transmission sources shut off. This requirement arises because at higher concentrations and enrichments, the uranium solutions fluoresce themselves sufficiently to require correction for the effect.

Let us now discuss the XRF measurement performance. Figure 6 presents $TCR/(g \text{ U/l})$ for the set of 97%-enriched standards just as was done in Fig. 2 for the PGR system. Again, if everything has been done correctly, all the $TCR/(g \text{ U/l})$ values will be equal save for their statistical variation. They do fall within $\pm 1\%$, which cleanly meets the customers' specifications, though it appears that there is a "bowing" of the curve that might well be reduced by improving the $CF(AT)$ calculation. We note that as in Fig. 2, the 30 g U/l point lies beneath the apparent curve defined by the other points, strengthening the suspicion that its reported value is somewhat in error.

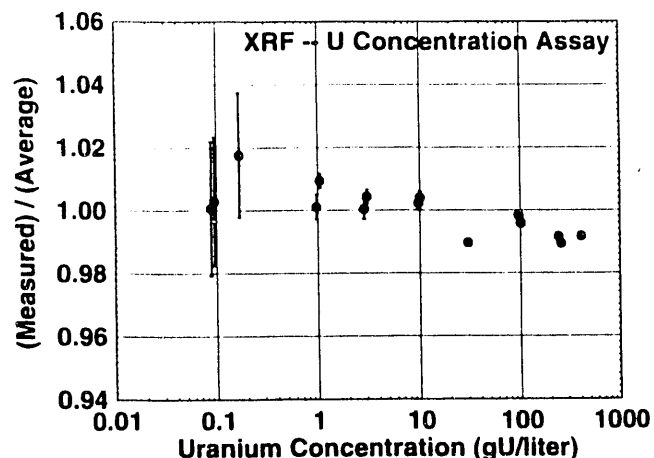


Fig. 6. For the XRF system, $TCR/(g \text{ U/l})$ values for the set of 97%-enriched solution standards.

Figure 7 gives the precision for concentration measurements of 2000-s live time, optimally divided. We have ignored the influence of the passive spectrum, if required, which is small. The passive spectrum time is in addition to the basic 2000 s of live time, which is divided between the transmission and fluorescence spectra. Estimating the precision is harder for the XRF measurement than for the PGR measurement. The scatter of points in Fig. 7 is mainly caused by using sample standard deviations from sets of only ~15 replicate assays.

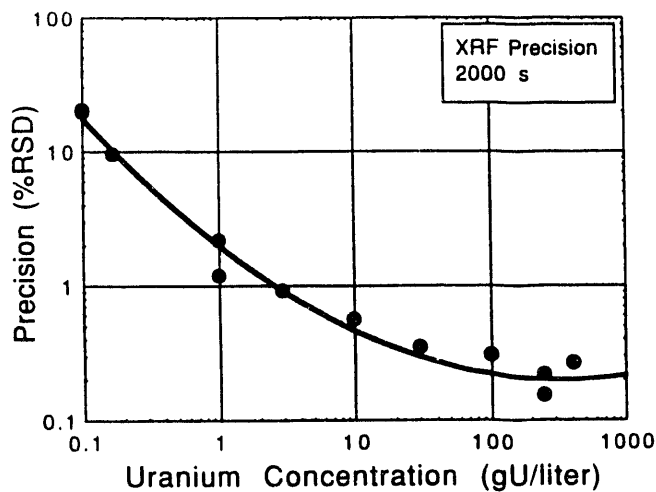


Fig. 7. XRF measurement precision (%RSD) for the set of 97%-enriched solution standards as a function of concentration for 2000 live-time seconds, optimally divided between the transmission and fluorescence spectra. The passive count, when required, influences the precision but little if it is for a time comparable to the fluorescence count.

REFERENCES

1. E. C. Horley, K. Gainer, W. J. Hansen, T. A. Kelley, et al., "Automated Assay of Uranium Solution Concentration and Enrichment," *Nucl. Mater. Manage.* XXI (Proc. Issue), 476-480 (1992).
2. D. Reilly, N. Ensslin, H. A. Smith, Jr., S. Kreiner, Eds., *Passive Nondestructive Assay of Nuclear Materials*, NUREG/CR-5550 (US Nuclear Regulatory Commission, Washington, D.C., 1991).
3. J. L. Parker, T. E. Sampson, L. R. Cowder, E. A. Kern, et al., "The Development of a State-of-the-Art Assay System for Uranium-235 in Solutions," Los Alamos National Laboratory report LA-10793-MS (December 1986).
4. T. E. Sampson and A. Goldman, "Analysis of NDA Instrument Calibration Data," Los Alamos National Laboratory report LA-11316-MS (August 1988).
5. W. D. Ruhter and D. C. Camp, "Transmission-Corrected X-Ray Fluorescence Analysis of Uranium and Plutonium Solutions using a Dual Transmission Source," in *Proceedings of the Third International Conference on Facility Operations-Safeguards Interface* (American Nuclear Society, Inc., La Grange Park, Illinois, 1988), ANS Order No. 700132, 300-305.

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