A Compact L-Edge Densitometer for Uranium Concentration Assay

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by

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ABSTRACT

A new L-edge densitometer has been designed around a compact, commercial x-ray generator weighing less than 5 kg. The dc generator x-ray spectrum was tailored to produce a continuum of x-ray energies from 14 to 20 keV. The x rays were transmitted through uranium reference solutions, and the measured transmissions near the uranium L_{III} -absorption edge were used to compute the uranium concentration assay result. The range of uranium concentrations in the reference solutions included 5 to 50 g/l. In this concentration range, the assay uncertainty for short count times and the flatness of the specific assay response were better than 0.5%. Thus, the precision and accuracy of this compact densitometer are equal to those demonstrated previously for the L-edge technique. The compact dimensions and optimized transmission geometry increase the practicality, versatility, and range of the L-edge applications.

I. INTRODUCTION

A. L-Edge Performance in Field Tests

L_{III} -absorption-edge densitometry^{1,2} is a nondestructive assay technique that gives individual concentrations of single or multiple elemental components in solution. The method has been demonstrated for assay of uranium and plutonium concentrations in a variety of field test³⁻⁶ situations. Good precision and accuracy in short count times (better than 0.5% in 20 min or less) are achieved for concentrations of special nuclear materials (SNM) in the range of 3 to 300 g/l. This performance, along with the insensitivity of the L-edge assay response to sample radioactivity and to most matrix components,

has given the technique a potential role as a safeguards assay tool in reprocessing or scrap recovery facilities.

Field testing of an L-edge instrument for demonstration of assay precision took place during a 2-yr (1978-1980) evaluation at the Savannah River Laboratory (SRL).³ The L-edge solution cell was plumbed directly into a bypass line on the coprocessing demonstration facility glove box at SRL. Concentrations of uranium and plutonium in solutions of single or mixed SNM components in the range of 1 to 100 g/l were assayed by the instrument. A second, extensive field evaluation of the precision and accuracy of the L-edge instrument took place at the USDOE New Brunswick Laboratory (NBL) in 1980-1981.⁴ The solution categories and concentrations included the range addressed by the SRL testing. The evaluation was controlled to assure that the solution reference concentrations used for comparison with the L-edge results were both accurate and precise (exceeding the accuracy and precision of the L-edge assay by an order of magnitude), as well as representative of the actual solutions analyzed by the L-edge instrument. The NBL evaluation included a demonstration of the insensitivity of the L-edge assay to solution matrix variations. A third field test demonstrated application of the L-edge method to on-line nuclear materials accounting in near-real time. This took place in 1981 at the Allied General Nuclear Services (AGNS) reprocessing facility in Barnwell, South Carolina.⁵ The L-edge solution cell was plumbed in series with a bypass on the aqueous product stream from the second extraction in the plutonium cycle. The bypass was routinely used for withdrawal and external analysis of solutions. The L-edge assays of the flowing solutions, precise to 0.7%, were available every 5 min for automatic shipping to the materials control and accounting system (MACS) computer, which correlated these and other near-real-time assay results to draw timely materials balances. The L-edge instrument operated continuously for the 7-day cold-run demonstration, measuring uranium concentrations from 0 g/l (startup) to 60 g/l. Comparisons between the L-edge results and external sample assays, as well as comparisons with other on-line assay results, were consistent within the known uncertainties.

In-house testing of the L-edge method has taken place at Los Alamos since 1977. The sensitivity of the assay to the presence of fission products in the assay solutions was examined using the instrument that was field tested at SRL and NBL.⁶ The results showed that the L-edge method can be applied to

reprocessing plant solutions beyond the first separation cycle with no observable bias in the assay results.

B. L-Edge Assay Principles

The L_{III} -edge assay of a specific element concentration requires the measurement of the transmissions of gamma rays at two fixed energies through the solution. The two energies must bracket as closely as possible the L_{III} -absorption edge of the elemental species being analyzed. This energy (the L_{III} -electron binding energy) is 17.17 keV for uranium and 18.06 keV for plutonium. The resolution of HPGe or Si(Li) detectors permits the simultaneous assay of uranium and plutonium by the L-edge method. The transmitted gamma rays originate from an external source. To reduce background that originates from the sample, the sample-to-detector geometry is collimated and then the source strength established so that the detector count rate is dominated by gamma rays that originate from the external source.

The transmission of gamma rays through a sample is the ratio of intensities, I/I_0 , of the incident and transmitted radiation. For a fixed gamma-ray energy i and a two-component solution consisting of matrix m and uranium u , the transmission can be given as a product of two exponentials:

$$T_i = e^{-\mu_{iu}\rho_u x} e^{-\mu_{im}\rho_m x}, \quad (1)$$

where μ_{iu} and μ_{im} are the gamma-ray mass attenuation coefficients at energy i for the uranium and matrix, respectively, ρ_u and ρ_m are the concentrations (densities) of uranium and matrix, respectively, and x is the solution thickness. If the ρ values are in units of g/cm^3 and x is in units of cm , then the units of μ are cm^2/g .

Figure 1 is a plot of gamma-ray mass attenuation coefficients vs gamma-ray energy for various materials. The sharp discontinuities in the energy dependence of the μ values at the electron binding energies are illustrated for uranium and plutonium. Of all the absorption edges, the (lowest energy) L_{III}

Fig. 1. A log-log plot of the mass attenuation coefficient (μ) vs gamma-ray energy for uranium, plutonium, and the matrix materials--water, hydrogen, nitrogen, and oxygen.

edge has the largest change, $\Delta\mu$, in the mass absorption coefficient for a given element.

The absorption-edge assay method can be illustrated by defining two energies L and H (low and high, respectively) that bracket a specific absorption edge of one and only one element, uranium. Using the form of Eq. (i), a transmission ratio can be defined as

$$R = \frac{T_L}{T_H} = e^{-\Delta\mu_u \rho_u x} e^{-\Delta\mu_m \rho_m x}, \quad (2)$$

where

$$\Delta\mu_u = \mu_{Lu} - \mu_{Hu}$$

and

$$\Delta\mu_m = \mu_{Lm} - \mu_{Hm} \quad .$$

Taking the logarithm of both sides of Eq. (2) gives

$$-\ln R = \Delta\mu_u \rho_u x + \Delta\mu_m \rho_m x \quad . \quad (3)$$

Because $\Delta\mu_u \gg \Delta\mu_m$, the matrix term in Eq. (3) can be ignored to give

$$\rho = \frac{-\ln R}{\Delta\mu x} \quad , \quad (4)$$

where

$$\rho = \rho_u \text{ and}$$

$$\Delta\mu = \Delta\mu_u \quad .$$

The quantity R can be easily determined using high-resolution gamma-ray spectroscopy to measure transmission at the two energies L and H . For a sample

cell of fixed path length x , the quantity $\Delta\mu x$ is constant. This constant can be determined empirically by absorption-edge measurements of reference solutions with well-defined uranium concentrations.

The relative uncertainty in the value of ρ determined by Eq. (4) is

$$\frac{\delta\rho}{\rho} = \frac{\delta R}{R\Delta\mu\rho x} \quad . \quad (5)$$

Because of the appearance of $\Delta\mu$ in the denominator of this expression for relative uncertainty, the L_{III} -absorption-edge assay is sensitive over a larger concentration range than the K-absorption-edge assay.

C. Practical Limitations to L-Edge Applications

The equipment required for the L-edge instruments that have been tested previously is illustrated in Fig. 2, which is a photograph of the AGNS L-edge densitometer. The rack at the left in Fig. 2 holds the required equipment for the measurement station. The remaining equipment (signal processing, data processing, and data storage units in the tall cabinet at the left and the hard-copy unit at the right) can be located remotely from the area where the solutions reside.

The major limitations of the L-edge method are the size of the measurement station equipment and the requirement for thin or low-Z windows on the sample cell for reasonable transmission of x rays in the 17- to 18-keV region. Space is extremely limited in typical plant environments, and hardening of equipment against the effects of corrosive atmospheres in solutions-handling areas is more difficult with bulky equipment. Most important is the difficulty of satisfying the containment requirements for plutonium solutions with bulky measurement station equipment and thin or low-Z sample cell windows.

The measurement station equipment shown in Fig. 2 for the AGNS L-edge densitometer is identical to that designed for the SRL/NBL instrument. It includes a 50-keV x-ray generator, which is responsible for the bulk of this equipment, a sample cell, and a Si(Li) gamma-ray detector. The flow-through sample cell is fabricated of stainless steel and fitted with two 0.8-mm-thick

Fig. 2. AGNS L-edge densitometer equipment. The measurement station equipment, consisting of the x-ray generator, sample cell inside plastic containment box, and detector (obscured by the containment box), is at the center. The rack at the left holds (bottom to top) the minicomputer, multichannel analyzer, NIM electronics, oscilloscope, and dual disk drives. The hard-copy terminal is at the right.

Kel-F transmission windows. The x-ray generator produces a gamma-ray continuum that is used as the transmission source.

Most fielded K-edge instruments use radioisotopic transmission sources that are compact, even with shielding. The absence of natural radioisotopic sources with gamma rays that bracket the L-absorption edges is the reason that the x-ray generator has been used exclusively for the L-edge instruments. The range of intensities available with the x-ray generator and the ability to adjust the energy to assay different elements are advantages of the x-ray generator as a laboratory tool that analyzes a wide range of concentrations of a variety of elements. However, the constraints of a plant laboratory or process environment cannot tolerate the bulky equipment.

D. Scope of Compact L-Edge Evaluation

The L-edge measurements described in this report were performed using a new, compact x-ray generator. Elimination of the bulk of the previous instruments permitted optimization of measurement geometries by reduction of source-to-sample and sample-to-detector distances.

The evaluation of this compact L-edge densitometer included examination of the stability of the new x-ray generator, evaluation of the L-edge precision, investigation of possible systematic effects in the L-edge assay results, and optimization of the counting statistics. The evaluation includes an assessment of possible applications for the L-edge method.

II. EXPERIMENTAL METHODS

Figure 3 consists of scale drawings of the experimental setup showing the x-ray generator, sample cell, collimation assembly, and detector. Figure 4 is a photograph of the equipment. The compact x-ray generator dimensions are 10 by 14 by 15 cm. The weight is approximately 3 kg. The generator connects with a single cable to the external control unit, which is shown in Fig. 4(a). The generator is available either as a convection- or water-cooled unit; in this case, circulated water from a commercial external cooling unit (34 by 48 by 11 cm) flowed to and from the generator through Tygon hoses. The x-ray tube uses a solid tungsten target with a 0.25-mm beam spot. The voltage and current ranges of the generator are 0-25 kV and 0-2 mA, respectively.

Fig. 3. Drawing to scale of cross-sectional views of the experimental setup. (a) is a horizontal cross section drawn through (and parallel to) the collimated x-ray beam and (b) is the analogous vertical cross section showing the x-ray generator, sample cell slot, collimation, and detector. The cross-hatched material is brass. The horizontal arrows show the path of the x-ray beam.

(a)

(b)

Fig. 4. Experimental setup. View (a) shows beam-collimating hardware between the x-ray generator and the detector, as well as the control box for the x-ray generator; view (b) is a close-up of the beam collimation hardware with one of the 0.16-cm-diam collimators and a sample cell in the foreground.

The x-ray generator spectrum was tailored to produce a continuum of x rays of energies 14 to 20 keV. A sharp upper energy cutoff was achieved by placement of 0.15-mm-thick molybdenum foil (K-edge at 20.0 keV) between the x-ray generator exit window and the sample cell. The molybdenum foil also served the purpose of reducing the x-ray intensity to achieve the required intensity at the minimum current setting. The x-ray generator was operated at 20.0 kV and the current was adjusted to achieve a count rate of $15\,000\text{ s}^{-1}$ in the germanium detector for each solution sample that was assayed.

The exit window of the x-ray generator was 0.82 cm from the 1.2-cm-wide sample cell, which was 0.32 cm from a 2.5-cm-long, 0.16-cm-diam collimator. The collimation restricted the scattering angle of the incident beam by the sample to 1.4° . The geometry of this setup is improved over that of previous instruments for which scattering angles were restricted to 1.7° and x-ray source-to-sample distances were 10 cm. The collimator was directly in front of a planar intrinsic germanium detector.

The detector resolution was 187 eV FWHM at 5.9 keV. An amplifier shaping time of 3 μs was used during data acquisition, and pulse pileup rejection was

employed. An analog-to-digital converter converted 10 V to 1024 channels. A ^{109}Cd source was attached to the detector with fixed geometry. The 22.1-keV photopeak in channel 797 was used for single-point digital stabilization of gain. The spectra were stored in a computer-based multichannel analyzer where the display was updated in real time during data acquisition.

The sample cells used were polystyrene spectroscopic cells with inner dimensions of 1.0 cm by 1.0 cm by 4 cm high. The uranium concentrations of reference solutions that were analyzed were 1.021, 2.541, 5.058, 9.999, 19.941, 29.924, 40.021, 51.13, and 73.97 g/l. They were made with 4 molar nitric acid and depleted uranium and were analyzed by the NBL-modified Davies-Gray procedure⁷ to obtain the reference concentrations.

A spectrum of the room background (no sample cell in place and x-ray beam off) and the reference spectrum (sample cell filled with water and x-ray beam on) were collected at the beginning of each day. The reference spectrum was used to obtain the incident (or unattenuated) intensities, the I_0 values, below and above the L_{III} -absorption edge. Each reference spectrum was acquired for 2000 s, and the room background spectrum was collected for 1000 s. Also, a 0.05-mm-thick yttrium foil (whose K-absorption edge at 17.039 keV lies very close to the uranium L_{III} -absorption edge) was analyzed each day using the same procedure used for solution analysis. The measurement control acceptability criterion for the assay of the yttrium foil was that the assay be within 0.8% (2σ) of the nominal value.

The solution spectra were usually collected in sets of six cycles (autocycles) of 1000 s each without repositioning the sample between cycles. At the lower concentrations, where the assay sensitivity is not as good, and for the 74-g/l solution, which did not yield a count rate of $15\,000\text{ s}^{-1}$, cycles were extended to 2000 or 4000 s at times, and the autocycles included as many as 14 cycles.

III. RESULTS

Figure 5 shows typical raw spectral data and the reduced data obtained by the analyses used in this experiment. The reference spectrum, Fig. 5(a), includes the continuum of x rays produced by the generator as well as the 22.1-keV photopeak that was used for gain stabilization. Figure 5(b) shows the

Fig. 5. An example of the data obtained from a uranium solution assay. Shown are (a) the reference spectrum, which includes the x-ray generator spectrum and the 22.1-keV photopeak from the ^{109}Cd source, (b) the x-ray spectrum attenuated by a 40-g/l uranium solution, (c) the transmission spectrum (the solution spectrum divided by the reference spectrum), and (d) the difference spectrum, which is the derivative of the log of the transmission spectrum.

x-ray spectrum transmitted through a 40-g/l uranium solution. The L_{III} -absorption edge can be seen at 17.168 keV (approximately channel 614). Figure 5(c) is the transmission spectrum (that is, the solution spectrum divided, channel by channel, by the reference spectrum). The difference spectrum, Fig. 5(d), was obtained by taking the natural logarithm of the transmission spectrum and then the channel-by-channel difference (derivative) in the vicinity of the absorption edge. Only data in channels corresponding to the regions of interest that were analyzed are plotted in Figs. 5(c) and 5(d).

Two methods of data analysis were used to obtain the L-edge assay result. The difference method uses the difference spectrum illustrated by Fig. 5(d).

The peak corresponds to the L_{III} -absorption edge of uranium, and the net area under the peak is mathematically equivalent to $\ln R$. The linear fit method uses the transmission spectrum illustrated by Fig. 5(c). An extrapolation to the absorption edge of a linear fit to the data in regions of interest on each side of the edge gives the two transmission values used to compute the ratio R . The linear fit method has the advantage that it minimizes the statistical contribution to the random uncertainty. Analysis of the reference solutions used the measured values of R and the reference values of ρ to deduce the calibration constant $\Delta\mu x$ from Eq. (4).

The effect that repositioning the sample cell had on assay results was tested by running 10 individual assays on a 50-g/l uranium solution, repositioning the cell between assays. Also, between assays the x-ray generator was turned off and turned on again. The relative standard deviation in the 10 runs (analyzed by the difference method) was 0.28%, which compares well with the predicted standard deviation of 0.26% based on counting statistics.

Figure 6 is a plot of the results of the yttrium foil assays (obtained by the difference analysis) over a 3-wk period. The error bars are the predicted

Fig. 6. The results of the yttrium foil assay are plotted vs date. The error bars are the standard deviations predicted by counting statistics (0.43%), and the horizontal line is the average result, 29.7. The relative standard deviation in the data used to compute the average is 0.56%.

standard deviations based on counting statistics (0.43%). The average value of 29.7 (g/l, effective) is shown as a horizontal line. The relative standard deviation in the data used to compute the average is 0.56%, 1σ .

Figure 7 is a plot of the calibration constant ($\Delta\mu x$) obtained from the difference analysis vs uranium concentration. Each point represents a single 1000-, 2000-, or 4000-s assay cycle, and those appearing in a vertical line were taken during the same autocycle. All data points in this plot were normalized to the same reference spectrum. Figure 8 is the same plot as Fig. 7, except that the linear fit analysis was used to get the $\Delta\mu x$ values.

Fig. 7. A plot of $\Delta\mu x$ calculated from the difference analysis vs uranium concentration. (Actually, each grouping of points corresponds to a single uranium concentration.) All analyses were performed with the same reference spectrum. Each point represents a single 1000-, 2000-, or 4000-s assay, and those points that lie in a vertical line were collected during one autocycle. (The horizontal line was computed from the 5- to 50-g/l data shown in Fig. 9.)

Fig. 8. The same plot as Fig. 7, except that the linear fit data analysis was used to obtain these results. (The horizontal line was computed from the 5- to 50-g/l solution data shown in Fig. 10.)

Figure 9 is a plot of $\Delta\mu_x$ vs uranium concentration for the difference analysis. Each error bar is the standard deviation of five different analysis results obtained by using five different reference spectra for normalization. The horizontal line is the weighted mean $\Delta\mu_x$ ($58.7 \text{ cm}^3/\text{g}$) computed over the concentration range of 5 to 50 g/l, inclusive. This average is also shown as a horizontal line in Fig. 7. The relative standard deviation in the mean is 0.11%.

Figure 10 is the same plot as Fig. 9, except that the linear fit analysis was used to get the $\Delta\mu_x$ values. The mean value of $\Delta\mu_x$ in the concentration range from 5- to 50-g/l is shown as a horizontal line in Fig. 10 and also in Fig. 8, and is $58.9 \text{ cm}^2/\text{g}$. The relative standard deviation in the mean is 0.10%.

Fig. 9. A plot of $\Delta\mu_X$ calculated from the difference analysis vs uranium concentration. (Actually, each grouping of points corresponds to a single uranium concentration.) Each point represents a different autocycle assay average. The error bars give the standard deviation in five assays, each assay using a different reference spectrum but the same uranium spectra. The horizontal line is the weighted average of $\Delta\mu_X$ computed over the 5- to 50-g/l concentration range. This same solid line has been plotted in Fig. 7.

Fig. 10. The same plot as Fig. 9, except that the linear fit data analysis was used to obtain these results. (The horizontal line is also plotted in Fig. 8.)

Results of the difference analysis are shown in Table I. All results shown used the same reference spectrum for normalization. Column 1 lists the uranium reference concentrations of the solutions that were analyzed. The count time is the duration of the data acquisition of each cycle in the autocycle; N is the number of cycles in the autocycle; $\overline{\ln R}$ and $\overline{\Delta\mu x}$ are the average values calculated from the N cycles; $1\sigma_{\text{stat}}$ is the relative standard deviation for a single cycle predicted from counting statistics [Eq. (5)], and $1\sigma_{\text{calc}}$ is the actual relative sample standard deviation within the autocycle. The N individual results used to obtain the values of $\overline{\Delta\mu x}$ in Table I are the points plotted in vertical lines in Fig. 7. Table II lists the same data analyzed

TABLE I
DIFFERENCE ANALYSIS

Uranium Reference Concentration (g/l)	Count Time (s)	N	$\overline{\ln R}$	$\overline{\Delta\mu x}$ (l/g)	$1\sigma_{\text{stat}}$ (%)	$1\sigma_{\text{data}}$ (%)
73.97	2000	6	4.305	0.05820	0.22	0.30
73.97	2000	6	4.309	0.05825	0.22	0.24
51.13	1000	6	2.987	0.05842	0.26	0.50
51.13	1000	6	3.004	0.05875	0.26	0.15
51.13	1000	6	3.011	0.05888	0.26	0.34
40.021	1000	6	2.348	0.05867	0.30	0.42
40.021	1000	6	2.355	0.05885	0.30	0.45
40.021	1000	6	2.341	0.05847	0.30	0.54
29.924	1000	6	1.752	0.05855	0.39	0.51
29.924	1000	6	1.765	0.05897	0.39	0.34
29.924	1000	6	1.743	0.05824	0.39	0.24
19.941	1000	6	1.164	0.05839	0.57	0.78
19.941	2000	6	1.165	0.05844	0.46	0.35
9.999	1000	6	0.5851	0.05852	1.14	1.18
9.999	4000	10	0.5820	0.05820	0.81	1.07
5.058	1000	6	0.2989	0.05909	2.22	3.54
5.058	4000	12	0.2953	0.05839	1.60	1.23
2.541	1000	5	0.1544	0.06078	4.35	3.98
2.541	1000	6	0.1582	0.06227	4.24	4.85
2.541	4000	13	0.1514	0.05957	3.17	2.51
1.021	1000	6	0.0658	0.06447	10.23	9.81
1.021	1000	10	0.0694	0.06796	8.71	10.27
1.021	4000	14	0.0596	0.05834	8.06	4.31

TABLE II
STRAIGHT-LINE ANALYSIS

Uranium Reference Concentration (g/l)	Count Time (s)	N	$\overline{\ln R}$	$\overline{\Delta\mu x}$ (l/g)	$1\sigma_{\text{stat}}$ (%)	$1\sigma_{\text{data}}$ (%)
73.97	2000	6	4.319	0.05839	0.09	0.18
73.97	2000	6	4.324	0.05846	0.09	0.19
51.13	1000	6	2.987	0.05842	0.10	0.16
51.13	1000	6	3.003	0.05874	0.10	0.12
51.13	1000	6	3.000	0.05867	0.10	0.18
40.021	1000	6	2.364	0.05907	0.12	0.16
40.021	1000	6	2.355	0.05885	0.12	0.24
40.021	1000	6	2.355	0.05885	0.12	0.14
29.924	1000	3	2.354	0.05881	0.15	0.08
29.924	1000	6	1.764	0.05896	0.15	0.17
29.924	1000	6	1.753	0.05859	0.15	0.14
19.941	1000	6	1.169	0.05861	0.21	0.32
19.941	2000	6	1.174	0.05888	0.17	0.18
9.999	1000	6	0.5872	0.05873	0.42	0.37
9.999	4000	10	0.5894	0.05895	0.32	0.54
5.058	1000	6	0.2966	0.05864	0.83	1.02
5.058	4000	12	0.2995	0.05921	0.62	0.48
2.541	1000	5	0.1497	0.05893	2.92	1.56
2.541	1000	6	0.1514	0.05957	2.92	2.52
2.541	4000	13	0.1519	0.05978	2.10	1.06
1.021	1000	6	0.0550	0.05384	4.41	2.29
1.021	1000	10	0.0567	0.05548	4.41	5.87
1.021	4000	14	0.0623	0.06103	3.18	1.84

with the linear fit analysis. The N individual results used to obtain the values of $\overline{\Delta\mu x}$ in Table II are the points plotted in vertical lines in Fig. 8.

IV. DISCUSSION

A. Performance of the Compact L-Edge Instrument

The data in Table I and the results plotted in Fig. 9 indicate that the performance of this compact densitometer is equal to that demonstrated in the evaluation of the previous instrument.⁴ Both evaluations show that the calibration response is flat in the concentration range from 5 to approximately

60 g/l and that the precision of a 1000-s (20-min) assay is 0.5% or better in the range 20 to 90 g/l. Positive and negative deviations from the flat calibration response that occur at concentrations below 5 g/l and above 60 g/l (respectively) appear in the results of both evaluations. Because the sample cell dimensions and the data reduction and analysis methods were the same for both evaluations, the matching results indicate that the compact x-ray generator is a practical substitute for larger models used previously in L-edge applications, with no obvious sacrifices in performance.

B. Comparison of Analysis Methods

The previous L-edge publications³⁻⁶ gave results that were analyzed by the difference method only. The present analysis by the straight-line method predicts an improvement by a factor of 2.5 in assay precision over that obtained by the difference method. This is illustrated by comparing the results in the column labeled $1\sigma_{\text{stat}}$ in Table II to the analogous results in Table I. The observed standard deviations in the results of replicate runs ($1\sigma_{\text{data}}$ in Tables I and II) show that the actual random uncertainty for the straight-line method has improved by the factor predicted by counting statistics.

The appearance of systematic effects in the average results of replicate runs for the straight-line analysis (Fig. 10) indicates that the overall uncertainty (random plus systematic errors) may not be improved over that for the results of the difference analysis. However, by using the straight-line method, a significant decrease in counting time (to 200 s per assay) will yield the same precision achieved by a 1000-s assay analyzed by the difference method.

The systematic effects observed in the straight-line assay results might arise from the linear extrapolation to the absorption edge. The advantage of this extrapolation is that the matrix term in Eq. (3) is zero (because $\Delta\mu$ is zero). However, it is possible that small variations in spectral shape parameters or small changes in detector resolution⁸ are enhanced in the assay result by the extrapolation used in the straight-line method. For certain applications in which matrix variations from sample to sample can be ignored, it is possible to include a constant matrix term in the analysis and to omit extrapolation to the absorption edge and still achieve the same precision demonstrated by the straight-line method. The difference method is inherently less precise than the straight-line method because fewer data points are used in the difference analysis.

Because the systematic effects in the straight-line method of analysis are not well understood, and because all present and previous data have been analyzed by the difference method, the subsequent discussions draw only on results of the difference analysis. However, the improved precision achieved by using the straight-line method is large enough to justify a continued investigation of this or an equivalent approach to the L-edge analysis.

C. Concentration Range for Precise and Timely Assay

The ability to optimize the geometry for sample irradiation with the compact x-ray generator has resulted in a much more intense transmitted x-ray beam (despite 2.5 times less current provided by the x-ray generator) for the compact densitometer. For this evaluation, measurements of 1-cm-thick solution samples with uranium concentrations up to 74 g/l were performed. The x-ray generator beam intensity was too high to use the 0.5-cm-diam collimator used in the previous L-edge evaluations,³⁻⁵ and consequently the sample collimator diameter was reduced to 0.16 cm. Additional attenuation (with 0.15-mm-thick molybdenum foil) was required in order to obtain the $15\,000\text{ s}^{-1}$ count rate for the reference spectra (x rays transmitted through a water-filled sample cell) at the minimum current setting of the x-ray generator. At the maximum current setting with the sample cell filled with the least transparent solution (74 g U/l), the count rate was 8000 s^{-1} .

The results show that the criteria for timely (≤ 20 -min assay periods) and precise ($\leq 0.5\%$) assays are achieved with the experimental setup used in this evaluation in the uranium concentration range from 20 to 90 g/l, the relative precision becomes worse as $1/\rho$ (to first order), where ρ is the uranium concentration in grams per liter, as shown by Eq. (5). However, an increased sample thickness can compensate for this effect, as Eq. (5) also shows. Figure 11(a) is a plot of the concentration lower limit for 0.5% precision vs cell thickness. (A 1000-s assay of a 5-g/l solution in a 4-cm-thick cell, for example, will be precise to 0.5%.) Below these limiting concentrations, the assay precision depends only on $1/\rho$, to first order. This concentration dependence of the precision at low concentrations is shown for different cell thicknesses in Fig. 11(b).

The attenuation of the x-ray beam by the solvent and the sample cell walls is a limiting factor in the maximum permissible solution thickness and in the composition and thickness of the sample cell walls. Table III consists of

Fig. 11. (a) Plot of the lower limit of (uranium) concentration for 0.5% (1σ) L-edge assays in 1000-s count periods with 1-cm transmission path lengths. (b) Plot of per cent precision (1σ) vs uranium concentration [at low concentrations where the $1/\rho$ -dependence dominates in Eq. (5)] for 1000-s L-edge assays and different transmission path lengths.

TABLE III
ATTENUATION DATA FOR 17.5-keV GAMMA RAYS

Substance (Empirical Formula)	Density(d,g/cm ³)	$\mu \cdot d(\text{cm}^{-1})$	$\mu(\text{cm}^2/\text{g})$
Water (H ₂ O)	1.00	1.10	1.10
Polyethylene (C ₂ H ₄)	0.96	0.51	0.53
Polystyrene (C ₂ H ₂)	1.05	0.57	0.54
Polyvinyl chloride (PVC) (C ₂ H ₃ Cl)	1.38	6.7	4.84
Teflon (C ₂ F ₄)	2.2	4.4	1.99
Kel-F (CCl ₂ F ₂)	2.2	18.0	8.2
Pyrex (SiO ₂)	2.2	8.0	3.6
Glass (SiO ₂)	2.5	10.2	3.9
Aluminum (Al)	2.7	14.8	5.5
Iron (Fe)	7.9	319	40.4
Molybdenum (Mo)	9.0	174	19.3

gamma-ray attenuation data for relevant absorbing materials for a gamma-ray energy of 17.5 keV (midway between the uranium and plutonium L_{III}-absorption edges). The product of the mass attenuation coefficient μ and the density d appear in the exponent of the expression for gamma-ray transmission:

$$T = e^{-\mu dx} ,$$

where x is the thickness of the absorber. The transmission of 17.5-keV gamma rays through a given thickness of chlorine-substituted plastic (such as Kel-F) is equivalent to the transmission through a much thicker nonsubstituted plastic

(polystyrene that is 32 times thicker than Kel-F, for example). This is the result of both the larger μ values for the higher-Z elements (such as chlorine) and the larger densities of the substituted hydrocarbon plastics. Furthermore, each centimeter of water in the transmission path reduces the transmission by a factor of 3.

Table IV is a ratio of the transmission T through the sample cell and water solvent (for different cell-material and solution-thickness combinations) to the transmission T_{Mo} through the 1-cm water-filled polystyrene cell (the cell used in this evaluation) plus the 0.15-cm-thick molybdenum foil. The molybdenum alone reduces the transmission at 17.5 keV by a factor of 14.1, as indicated by the value of the ratio entered for the 1.0-cm polystyrene cell. The ratio gives the intensity factor for the transmitted x-ray beam (at 17.5 keV, which is the approximate centroid of the x-ray generator spectrum) with the molybdenum foil removed and with the cell material and/or transmission path length varied from those used in this evaluation. Replacement of the 0.16-cm-diam collimator with the 0.5-cm-diam collimator used in previous evaluations

TABLE IV
INTENSITY FACTOR, $T \div T_{Mo}$, AT 17.5 keV

	Cell Material (Single Wall Thickness)			
	Polystyrene (0.06 cm)	Kel-F (0.08 cm)	Glass (0.10 cm)	PVC (0.40 cm)
0.5 cm ^a	244. ($\rho \leq 400$ g/l)	17. ($\rho \leq 290$ g/l)	43. ($\rho \leq 330$ g/l)	1. ($\rho \leq 180$ g/l)
0.5 cm	24.4 ($\rho \leq 310$ g/l)	1.7 ($\rho \leq 200$ g/l)	4.3 ($\rho \leq 240$ g/l)	0.1 ($\rho \leq 90$ g/l)
1.0 cm	14.1 ($\rho \leq 140$ g/l)	1.0 ($\rho \leq 90$ g/l)	2.5 ($\rho \leq 110$ g/l)	0.1 ($\rho \leq 40$ g/l)
2.0 cm	4.7 ($\rho \leq 60$ g/l)	0.3 ($\rho \leq 30$ g/l)	0.8 ($\rho \leq 40$ g/l)	0.0
3.0 cm	1.6 ($\rho \leq 30$ g/l)	0.1 ($\rho \leq 10$ g/l)	0.3 ($\rho \leq 20$ g/l)	0.0
4.0 cm	0.5 ($\rho \leq 20$ g/l)	0.0	0.1 ($\rho \leq 10$ g/l)	0.0

^aCollimator diameter = 0.5 cm.

increases the detector count rate by a factor of 10, as indicated by the first and second rows of values for the intensity factor. The polystyrene and Kel-F cell wall thicknesses given in Table IV match those of the polystyrene cells used in this evaluation and those of the Kel-F cells used in the previous L-edge evaluations.³⁻⁵ The glass cell dimensions match those of standard glass or quartz cells (manufactured for visible or ultraviolet spectroscopy) that might also be used for L-edge measurements. The heavy-walled PVC "cells" might actually correspond to thick PVC tubing bearing solutions from process vessels.

The upper limit on solution concentration for a high-precision assay with a given measurement configuration is the computed maximum uranium or plutonium concentration for which a 0.5% assay can be achieved in ≤ 20 min. These limits are the parenthetical entries in Table IV. In this evaluation, the detector count rate at 74 g/l was 8000 s^{-1} with the maximum x-ray generator current setting. The precision of a 20-min assay, computed from Eq. (5), was 0.3%. At 85 g/l, the detector count rate would be reduced to $\sim 5000 \text{ s}^{-1}$ and the 20-min assay precision would be $\sim 0.5\%$, primarily because of the very low count rate above the absorption edge at the higher concentration. Therefore, to achieve 0.5% precision in 20 min with the experimental setup used in this evaluation, the uranium concentration must be in the range from 20 to 85 g/l. However, by removal of the molybdenum foil (increasing the beam intensity by a factor of 14), the upper limit to the uranium concentration range increases to 140 g/l, as indicated in Table IV. Furthermore, by reducing the polystyrene sample cell thickness to 0.5 cm and replacing the 0.16-cm-diam collimators with 0.5-cm-diam collimators, the upper limit rises to 400 g/l. Therefore, it is practical to define the useful high-precision (0.5% results in 20 min) range as 5 g/l to 400 g/l.

To achieve high precision, a measurement station is required in which collimators can be interchanged, molybdenum absorbers can be inserted and removed, sample cell thicknesses can be varied, and polystyrene cells can be used to contain solutions. For uranium or plutonium solutions, these requirements constrain solution handling operations to a well-controlled environment such as that provided by a dedicated glove box. However, this type of performance (wide range with high precision over the entire range) is usually required of a laboratory instrument that measures a large number of discrete samples removed from numerous process locations.

A production instrument dedicated to a specific stream might address a limited concentration range and could be fabricated with a fixed configuration (solution thickness, molybdenum absorber thickness, and collimator dimension) designed for optimum precision in that range. In such applications, a flow-through cell might be desired. Using the examples of the thick-wall PVC tubing in Table IV, the useful range for high precision with the 0.5-cm-thick solution is 40 to 180 g/l with the larger collimator and 40 to 90 g/l with the smaller collimator.

D. Fission Product Sensitivity Limits

A previous evaluation of the L-edge sensitivity to fission products⁶ showed that the assay method can tolerate solution fission product levels up to 4 Ci/g Pu (or U) in the assay solutions with the original L-edge instrument design using a 0.25-cm-diam collimator. Because of improved geometry in the new compact instrument, the equivalent sample cell (1-cm solution thickness, Kel-F windows) can be used with more restrictive collimation to assay the same concentration range with high precision and with a higher tolerance to fission products. This qualifies the L-edge method as a practical approach to the assay of uranium or plutonium in solution streams beyond the first fission product extraction in reprocessing and perhaps farther upstream for uranium assay.

E. Summary and Conclusions

The evaluation of the compact L-edge densitometer has shown that the performance of this instrument equals that of L-edge instruments demonstrated previously in terms of the stability of the electronics and the precision and accuracy of the assays performed in short count times. As a wide-range analytical tool, 0.5% precision can be achieved in 20 min or less for assays of uranium or plutonium concentration up to 400 g/l. A specific instrument of this type might use polystyrene cells with two alternative cell thicknesses, 2.0 cm (with a 0.5-cm collimator diameter) and 0.5 cm (with a 0.16-cm collimator diameter), to measure the lower and upper portions (respectively) of the concentration range. The assay precision, Eq. (4), is plotted vs concentration for the alternative cells in Fig. 12. The minimum precision of 0.2% is defined by the short count time (20 min) and optimum count rate ($15\,000\text{ s}^{-1}$) requirements. The 2.0-cm-thick cell gives the required 0.5% precision in the concentration range from 10 g/l to 60 g/l, and the 0.5-cm-thick cell satisfies the

Fig. 12. Plot of per cent precision (1σ) vs uranium concentration calculated for 20-min L-edge assays using two different (polystyrene) cell thicknesses. The dashed line ($1\sigma = 0.5\%$) defines the high-precision concentration range for each cell thickness.

precision requirement in the range from 40 g/l to 400 g/l. These range results are in agreement with previous calculations⁹ of the useful concentration range for L-edge assays. By using new state-of-the-art high-count-rate technologies¹⁰ for high-resolution gamma-ray detectors, or by using the straight-line data analysis methods, the short-count-time criterion of 20 min can be reduced by a factor of 4 or more for high-precision performance in the same concentration range.

Because of the improved geometry that is possible with the compact x-ray generator, a good portion of the full high-precision range, namely 40 to 180 g/l, can be measured with thick-walled PVC surrounding the sample without violating the high-precision and short-count-time constraints. A higher tolerance to fission products is also the result of improved geometry, which allows more restrictive collimation of the sample.

The compact instrument is more suitable than previous L-edge densitometers for in-plant operation because it occupies less space, because it is easier to harden against plant environments, and because more substantial solution containment can be tolerated. The use of newer, room-temperature solid-state

detectors with intermediate resolution, which are frequently very small in size (HgI_2 , for example), can now be considered for some L-edge applications because of the optimized transmission geometry in the compact instrument. Room-temperature detectors would simplify instrument hardening, further reduce demands on space, and minimize plant procedures for routine instrument maintenance. The sacrifice in energy resolution that accompanies the use of room-temperature detectors might have an insignificant effect on accuracy if the assay is dedicated to a process (or process stream) with one component (uranium or plutonium) in solution.

Because all of the electronics and software needs for densitometry can be satisfied by compact programmable multichannel analyzers,¹¹ it is practical to consider the design for a portable L-edge instrument that uses a portable germanium or a room-temperature detector. The portable x-ray generator, as opposed to secondary (radioisotopic) sources for the L-edge measurements,¹² has the advantages of transportability, higher and tunable intensity, and longer lifetime, making it more suitable for portable applications and for wide-range and low-maintenance operation.

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