LA-UR -82-2649

LA-UR--82-2649

DE83 000666

Conf-821119--5

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

PORTIONS OF THIS DOCUMENT ARE AVAILABLE
FOR REPRODUCTION AT THE LOWEST Possible Available
Copy To Permit The Broadest Possible Avail-
ability.

TITLE: AUTOMATED ON-LINE L-EDGE MEASUREMENT OF SNM
CONCENTRATION FOR NEAR-REAL-TIME ACCOUNTING

MASTER

AUTHOR(S) P. A. Russo, T. Marks, Jr., M. M. Stephens,
S. T. Hsue, A. L. Baker, and D. D. Cobb

SUBMITTED TO International Symposium on Recent Advances
in Nuclear Materials
Vienna, Austria
November 8-12, 1982

DISCLAIMER
This document contains information which has been classified as "Confidential" by the U.S. Government. It is the property of the U.S. Government and is loaned to you. It and its contents are not to be distributed outside your organization. If you are not an authorized recipient, you should not have received this document. If you are an authorized recipient, you should not discuss the contents of this document with anyone outside your organization. If you have any questions, please contact your supervisor.

111
REPRODUCTION OF THIS DOCUMENT IS UNLIMITED

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

AUTOMATED ON-LINE L-EDGE MEASUREMENT OF SNM CONCENTRATION
FOR NEAR-REAL-TIME ACCOUNTING*

ABSTRACT

The L-edge densitometer developed at Los Alamos National Laboratory has been modified, tested, and demonstrated for on-line assay of special nuclear material concentration in flowing solution streams. The demonstration was part of a larger demonstration of near-real-time nuclear materials accounting during a continuous, week-long, cold operation of the Allied General Nuclear Services facility in Barnwell, South Carolina. The L-edge data were automatically analyzed and the results were transmitted to the materials accounting computer once every 5.5 min for the duration of the cold run. This report compares the results of the L-edge analyses with the delayed results obtained from destructive analysis of samples withdrawn from the same process line. Comparisons are also made with the results obtained in near real time from an automated process control instrument installed in series with the L-edge densitometer. The performance of the L-edge instrument was reliable throughout the continuous operation. The assay precision was consistent with that predicted by the counting statistics of the measurement. The results of the L-edge assays show good agreement with

*This work was supported by the US Department of Energy/Office of Safeguards and Security.

those of the destructive assays. A gradually varying discrepancy (of a few percent) between the L-edge and the process control results remains unexplained.

1. INTRODUCTION

The demonstration of techniques for computerized accounting and control of special nuclear material (SNM) at reprocessing facilities in near real time (NRT) ranks among the most highly visible and internationally significant efforts in safeguards at Los Alamos National Laboratory. Throughout 1980 and 1981, Los Alamos developed, tested, and evaluated techniques in this area, focusing on the Allied General Nuclear Services (AGNS) fuel reprocessing plant in Barnwell, South Carolina.

AGNS devised a series of week-long "cold runs" during which uranium solutions of natural enrichment are recycled (in a closed loop) through the plutonium purification process. During these runs, all data used by the facility for process monitoring and materials control are made available for nuclear materials accounting demonstrations. Details of these miniruns and early results of efforts for NRT accounting have been presented elsewhere.[1] The areas cited for improvement of materials accounting included the need for accurate, on-line NRT assay of SNM concentration. In response to this need, the L-edge densitometer developed at Los Alamos[2] was modified for operation on flowing solution streams and used in the AGNS minirun of August 1981.

II. CALIBRATION AND DEVELOPMENT EFFORTS AT LOS ALAMOS

A solution sample cell dimension of 1 cm was chosen to optimize the L-edge assay for SNM concentrations of 55 g/L. A 240-s (live) count time was used to make the assay period shorter than the shortest time elapsed between successive interrogation cycles of the materials accounting and control (MACS) computer, which automatically stores data from on-line process monitors at the AGNS facility. The precision (1 σ) of the L-edge assay obtained with count times of 240 s is plotted vs uranium concentration in Fig. 1. The curve is obtained from the standard deviation in repeated measurements of static solution samples and agrees with the precisions computed from the counting statistics of the measurement data. The minimum in this curve at the uranium concentration of 55 g/L is a result of the choice of sample cell thickness. This minimum shifts up or down (in concentration) with use of thinner or thicker sample cells, respectively.

The on-line demonstration at AGNS required shipment of a calibrated instrument. For the purpose of calibration, the flow-through sample cell was filled with a well-characterized reference solution of SNM and sealed. These efforts were carried out at Los Alamos using solutions of depleted uranium at concentrations of 30, 45, and 60 g/L. Reference concentrations were determined by destructive chemical analysis.

The calibration results (the ratios of the uranium concentration determined by the L-edge technique to the reference 1981.

shown as solid points were obtained using the results of chemical assay of solution withdrawn from the sample cell as the reference value. The + symbols refer to data obtained using concentrations determined by weighing the reference materials. Because of the possibility of contamination of the samples by residual cell contents, the concentrations obtained by weighing the reference materials are believed to be less representative of the cell contents than those obtained by destructive analysis of solutions withdrawn from the cell.

The observed systematic effect of an apparent concentration-dependent calibration factor has been documented previously.[2] Precise measurements of this effect were performed[3] during calibration of an instrument of nearly identical design at the New Brunswick Laboratory (NBL). The results of these highly controlled measurements are shown (for the uncalibrated NBL instrument) as the solid line labeled NBL in Fig. 2. A parallel line has been drawn to intersect the ordinate value of 1.0 at approximately 55 g/l. This line shows good agreement with the solid calibration points. The instrument was designed for optimum assay results between 50 and 60 g/l. Thus, the calibration constant was chosen to give zero bias at 55 g/l. Therefore, the L-edge assays were negatively biased at higher concentrations and positively biased at lower concentrations, as indicated by the solid line drawn through the data points in Fig. 2. The magnitude of the bias at 35 g/l was 0.15%.

An L-edge measurement of a 50 mg/cm^2 uranium foil was performed daily throughout the calibration and testing period.

The equivalent uranium concentration of a foil of this thickness is 50 g/l. The measurement control requirement imposed upon the instrument during and after calibration is the ability to reproduce, within the limits of counting statistics, the thickness of the well-characterized foil by routine, frequent L-edge assay. Count times of 1000 s were used, typically for acquisition of measurement control data with the foil. The statistical uncertainty in the corresponding L-edge results is 0.3%, 1σ . Previous measurements with the NBL instrument had demonstrated the reproducibility of daily foil measurements (consistent with the calculated 1σ statistical uncertainties) during 14 months of continuous operation of the instrument.[4]

The use of a transmission measurement such as that employed in the L-edge assay of SNM concentrations in flowing solution streams requires[5] the capability for automatic control of the x-ray generator (transmission source) current in order to maintain a constant count rate in the Si(Li) detector as the sample concentration (and hence the transmission) changes. The design and testing of the required electronics for this capability was one of two development efforts (the other being software) required to modify the existing instrument design for on-line operation.

III. INSTALLATION AND OPERATION

The L-edge instrument, shown in Figs. 3, 4, and 5, was shipped to AGNS during the week of August 3, 1981, and installed and tested during the week of August 10. The testing consisted

of repeated L-edge assays of the well-characterized uranium measurement control foil to demonstrate the consistency of the precision and the absolute result of the measurement with the result obtained at Los Alamos during calibration of the instrument. The instrument operated on-line, continuously and automatically, for the 1-wk duration of the minirun beginning August 18, 1981. The instrument transmitted uranium concentration results, statistically precise to approximately 0.7%, to the MACS computer once every 5.5 min throughout the run. These results were accessed automatically by the programs designed for demonstration of NRT accounting.

The L-edge flow-through cell was plumbed into the line that continuously samples the product of the 2B solvent extraction column (that is, the 2BP stream). This stream is shown conceptually within the plutonium purification cycle in the flow diagram in Fig. 6. In series with the L-edge cell in the 2BP sampling line was an instrument for determination of solution density. The densimeter, developed at AGNS, is used for process control purposes to evaluate uranium concentration from the measured density and an assumed acidity. The densimeter results for uranium concentration were accessed automatically, once every 15 min, by the MACS computer. Destructive analysis of solutions withdrawn from the 2BP sampling line was also performed, approximately once every 8 h. The destructive assay results were manually entered into the MACS data files by the operator. Because these results were typically delayed by

1 to 3 h relative to the sampling time, they were not useful for NRT accounting purposes.

IV. RESULTS OF ON-LINE OPERATION

Figure 7 is a plot of the 2BP uranium concentration (in g/l) determined by the L-edge instrument vs time (in days) during the minirun. The assay results of the 240-s (live) counts were available once every 5.5 min. For simplification, Fig. 7 shows only every fourth assay result.

Frequent sharp changes in concentration vs time are a result of operator adjustment of the process. The sharpest change, occurring soon after day 1, was associated with a column upset that occurred before steady state was achieved.

The steady-state concentration of approximately 35 g/l for the 2BP stream was significantly lower than the 60-g/l flow sheet value of the 2BP steady-state concentration for which this instrument was optimized. This discrepancy results in a positive and approximately constant bias of 0.15% in the L-edge results (for reasons discussed in Sec. 11). The expected precision for the 240-s assays (refer to Fig. 1) is approximately 0.7%, rather than the 0.5% precision that would be expected for 60 g/l.

A portion of the L-edge data has been used to estimate an upper limit in the actual random uncertainty in the 240-s L-edge assays during the minirun. The portion used was a 10-h interval (± 5 h around day 3) during which the process had achieved a reasonably steady state. The standard deviations in the results

were determined for each of the 28 groups of 4 successive runs (corresponding to a period of 22 min per group) in this 10-h interval. The average result for the 28 groups, and the uncertainty (1 σ) in this average, is $0.76\% \pm 0.07$. This result is in reasonable agreement with the expected result of 0.7% for the L-edge assay precision because it also includes a contribution caused by changes in the process stream concentration in a 22-min period.

Figure 8 is a plot of the 26P uranium concentration (in g/L) vs time (in days) during the minirun. Plotted are the L-edge assay results (circles) as well as the off-line destructive assay results (large squares) and the on-line densimeter results (triangles). For simplification, Fig. 8 shows only every third densimeter result and every twelfth L-edge assay result. These L-edge and densimeter results appear in time-correlated pairs in that the data points correspond to pairs of L-edge and density measurements obtained on-line within the 5.5-min (single L-edge assay cycle) period. All of the destructive assay results are plotted.

With two exceptions (occurring just before day 3 and just before day 4), relatively good agreement is observed between the results of destructive analysis and L-edge assay. The two discrepancies were cited by the facility to be due to incorrect recording of the destructive assay results. Because of the low frequency of the data and the relatively large scatter in the destructive assay results, it is not possible to verify the

predicted 0.15% bias in the 35-g/L L-edge results based upon this comparison.

The agreement between the densimeter results and the L-edge assay results is best around day 5, with the L-edge results tending to be lower than the densimeter results before day 5 and larger after day 5. The relative magnitude of the time-correlated pairs (the ratio of the densimeter assay to the time-correlated L-edge assay) is plotted in Fig. 9 vs time (in days). The scatter of less than 1% (1 σ) in the relative data is a result of the combined standard deviations of 0.7% for the L-edge assays and a slightly lower value for the densimeter results. The densimeter/L-edge ratio is approximately 1.015 for the period before day 2.5; the ratio then jumps to 1.03. The ratio decreases continuously and gradually from 1.03 to 0.98 for the duration of the minirun. No obvious cause can be cited for this larger and changing bias. Because of the large scatter in the destructive assay results for the 2BP samples, it is not possible to determine which of the on-line assays shows better agreement with the destructive analysis of the samples.

V. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn concerning the on-line operation of the L-edge instrument during the week-long AGNS minirun.

- The on-line L-edge instrument produced assays of 2BP uranium concentration that were precise to 0.7% once every 5.5 min for the week-long duration of the minirun. Thus

the on-line performance was consistent with expectations for precision and reliability.

- The comparison of the L-edge data with the results of the off-line destructive analysis was favorable. The existence of a 0.15% positive bias predicted in the L-edge assay results at the steadystate concentration of the 2BP line could not be verified in this comparison because of the large scatter in the destructive assay results.
- A gradually changing bias in the relative, time-correlated results of the two on-line measurements (L-edge and densimeter) in the 2BP line remains unexplained. An effect of this magnitude (roughly 5%) is not consistent with the long-term stability of the L-edge calibration, which was demonstrated to be within 0.25% over periods exceeding 1 yr.[4]

Improved precision and accuracy in the destructive assay capability applied to samples withdrawn from the process would establish the origins of the unresolved discrepancies between the two on-line measurements. Such improvements are probably not essential to the intended purpose of the off-line destructive analysis (namely, to monitor the calibrations of the process control instruments) and could represent substantial additional operations overhead. Therefore, shipment of sealed samples withdrawn from the process to off-site laboratories where such capabilities are exercised routinely is recommended for future demonstrations of this type.

The computer programs designed at Los Alamos for demonstration of NRT nuclear materials accounting used fewer than every tenth L-edge measurement result during the AGNS demonstrations. This was primarily due to limitations in the capabilities of the multipurpose MACS computer. Therefore, a practical and more efficient alternative for on-line operation of the L-edge instrument involves multiple-stream assay accomplished by a computer-controlled switching mechanism. Implementation of this option is recommended for future demonstrations.

REFERENCES

- [1] COBB, D. D., et al., "Demonstration of near-real-time accounting systems for reprocessing plants", Nucl. Mater. Manage. X, 411-421 (1981).
- [2] RUSSO, P. A., et al., "An x-ray L_{III} -edge densitometer for assay of mixed SNM solutions", (Proc. 1st Ann. Symp. on Safeguards and Nucl. Mater. Manage.", Brussels, 1979) pp. 235-240.
- [3] ZOOK, A. C., et al., "Application of a chemical calibration protocol to the evaluation of a nondestructive assay system", Nucl. Mater. Manage. X (1981) 276-280.

- [4] RUSSO, P. A., et al., "Nuclear safeguards applications of energy-dispersive absorption-edge densitometry", Nucl. Mater. Manage. IX, (1980) 730-772.
- [5] HENRY, C. N., et al., Comp., "Program status report: safeguards research and development, February-July 1981", Los Alamos National Laboratory report LA-9110-PR (1982) pp. 33-34.

FIGURE CAPTIONS

Fig. 1. Precision ($\%, 1\sigma$) of L-edge assay of static uranium solution samples, obtained with (live) count times of 240 s, plotted vs uranium concentration.

Fig. 2. Ratio of L-edge assay result for uranium concentration to the reference value plotted vs uranium concentration for three well-characterized solution samples. The reference values for the data indicated by the solid points were obtained by destructive analysis of solution samples withdrawn from the sample cell. The reference values for the data indicated by the + symbols were obtained by weighing the reference materials during preparation of the solutions. The solid line labeled NBL shows the concentration dependence measured at NBL. The solid line labeled AGNS is drawn parallel to the NBL line.

Fig. 3. L-edge equipment before on-line installation at AGNS. The environmentally controlled electronics rack (left) contains (bottom to top) the minicomputer, multichannel analyzer and display, signal-processing electronics, oscilloscope, and dual floppy disk drive. The center rack contains the x-ray generator power supply and controls and the measurement station (refer to Fig. 4). The hard-copy terminal is at the right.

Fig. 4. Vertical cross section of the L-edge densitometer measurement station at the x-ray beam center.

Fig. 5. Measurement station for the L-edge densitometer: (left to right) x-ray head, plastic box for secondary containment of solution in the cell, and Si(Li) detector. The inlet and outlet tubes for the flow-through solution cell are shown extending from the side of the secondary containment box. These tubes were plumbed into the 2BP sampling line for on-line measurement of the flowing process stream.

Fig. 6. Flow diagram of closed-loop operation of the plutonium purification cycle at AGNS. The on-line location of the L-edge densitometer is indicated, along with the on-line densitometer and the sampling point in the 2BP line.

Fig. 7. The 2BP uranium concentration (in g/l) determined by L-edge assay plotted vs time (in days) during the minirun. The result of every fourth 5.5-min L-edge assay is plotted.

Fig. 8. The 2BP uranium concentration (in g/l) plotted vs time (in days) during the minirun. Every twelfth L-edge result (circles), every third densitometer result (triangles), and all of the off-line destructive assay results (large squares) are plotted. The L-edge and densitometer results are time-correlated pairs. (Refer to text.)

Fig. 9. Ratio of the densimeter assay to the time-correlated L-edge assay of the 2BP uranium concentration plotted vs time (in days) during the minirun. The results plotted in Fig. 8 were used to compute the ratios.

Fig. 2. Ratio of L-edge assay result for uranium concentration to the reference value plotted vs uranium concentration for three well-characterized solution samples. The reference values for the data indicated by the solid points were obtained by destructive analysis of solution samples withdrawn from the sample cell. The reference values for the data indicated by the + symbols were obtained by weighing the reference materials during preparation of the solutions. The solid line labeled NBL shows the concentration dependence measured at NBL. The solid line labeled AGNS is drawn parallel to the NBL line.

Fig. 1. Precision ($\%, 1\sigma$) of L-edge assay of static uranium solution samples, obtained with (live) count times of 240 s, plotted vs uranium concentration.

Fig. 3. L-edge equipment before on-line installation at AGNS. The environmentally controlled electronics rack (left) contains (bottom to top) the minicomputer, multichannel analyzer and display, signal-processing electronics, oscilloscope, and dual floppy disk drive. The center rack contains the x-ray generator power supply and controls and the measurement station (refer to Fig. 4). The hard-copy terminal is at the right.

Fig. 4. Vertical cross section of the L-edge densitometer measurement station at the x-ray beam center.

Fig. 5. Measurement station for the L-edge densitometer: (left to right) x-ray head, plastic box for secondary containment of solution in the cell, and Si(Li) detector. The inlet and outlet tubes for the flow-through solution cell are shown extending from the side of the secondary containment box. These tubes were plumbed into the 2BP sampling line for on-line measurement of the flowing process stream.

Fig. 6. Flow diagram of closed-loop operation of the plutonium purification cycle at AGNS. The on-line location of the L-edge densitometer is indicated, along with the on-line densimeter and the sampling point in the 2BP line.

Fig. 7. The 2BP uranium concentration (in g/l) determined by L-edge assay plotted vs time (in days) during the minirun. The result of every fourth 5.5-min L-edge assay is plotted.

Fig. 8. The 2BP uranium concentration (in g/l) plotted vs time (in days) during the minirun. Every twelfth L-edge result (circles), every third densimeter result (triangles), and all of the off-line destructive assay results (large squares) are plotted. The L-edge and densimeter results are time-correlated pairs. (Refer to text.)