LA-UR--83-3383

DE84 003843

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

TITLE MATERIALS LOSS-DETECTION SENSITIVITIES USING PROCESS-GRADE MEASUREMENTS AT AGNS BNFP

AUTHOR(S) H. A. Dayem, E. A. Hakkila, A. L. Baker, and D. D. Cobb

SUBMITTED TO ANS/INMM Conference on Safeguards Technology: The Process-Safeguards Interface, November 28-December 2, 1983, Hilton Head Island, South Carolina

DISCLAIMER

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

MATERIALS LOSS-DETECTION SENSITIVITIES USING PROCESS-GRADE MEASUREMENTS AT AGNS BNFP

H. A. DAYEM, E. A. HAKKILA, A. L. BAKER, and D. D. COBB
Los Alamos National Laboratory
Los Alamos, New Mexico, 87545
(505) 667-6394

ABSTRACT

Process quality measurement data from cold runs at AGNS BNFP are used to demonstrate near-real-time accounting by closing hourly materials balances and to evaluate contactor inventory estimation techniques. Loss-detection sensitivities for 1 day of between 4 and 18 kg uranium, at 50% detection probability and 2.5% false-alarm probability, are calculated for selected accounting areas. Pulsed-column inventory estimators are used to calculate an inventory that is generally within 10% of column dump measurements. Loss-detection sensitivity could be improved by incorporating on-line waste stream measurements, improving laboratory measurements for process streams, and refining the pulsed-column inventory estimates.

I. INTRODUCTION

In 1980 and 1981 Los Alamos participated in seven minirun experiments conducted at the Allied-General Nuclear Services (AGNS) Barnwell Nuclear Fuels Reprocessing Plant (BNFP). Our objectives for these miniruns were to demonstrate near-real-time accounting (NRTA) concepts and principles, to evaluate advanced data analysis techniques and materials loss detection, and to develop estimation techniques for contactor inventories. We reported on the development of NRTA concepts and gave examples of NRTA results for the first five miniruns.[1-4] In this paper, we give estimates of NRTA materials loss-detection sensitivities for different portions of the process and compare column inventories calculated using a linear pulsed-column model with column dumps.

II. MINIRUN HISTORY AND DESCRIPTION

In 1977 AGNS, under the sponsorship of DOE, began the development and testing of a Computerized Nuclear Material Control and Accounting System (CNMCAS).[4] Initial work on CNMCAS involved the entire chemical separations line and focused on computerization of measurement, measurement control, and accounting procedures for "conventional" accounting. ("Conventional" accounting is the measurement of inputs and outputs for a materials balance area, coupled with periodic cleanout and physical inventory to close the materials balance.)

As on-line measurement and computer capabilities improved, AGNS began to experiment using routine measurements of process variables to estimate the quantity of material in process. These experiments were initially conducted for the entire process, but by 1980 reduced funding required AGNS to find a less costly mode of testing. Because of the widespread and continuing interest in computerized nuclear materials control and near-real-time accounting methods, the minirun concept was devised.

The minirun cycle (Fig. 1) consists of four pulsed-column contactors (2A, 2B, 3A, and 3B); concentrator (3P); and seven product, feed, and blending tanks. Support systems include aqueous waste tanks, a waste evaporator and acid fractionator, a solvent surge and recycle tank, an off-gas system, and associated process and chemical distribution systems. This represents a good cross section of routinely used plant equipment for development of improved materials control and accounting methods. A modified Purex solvent-extraction flowsheet is used with unirradiated natural uranium in place of plutonium for the tests.

The normal starting inventory for each run was 400-500 kg of uranium. After attaining equilibrium, a "process inventory" (pulsed columns, lines, product evaporator) of about 70-75 kg was observed, with the remaining material distributed among product tanks. Waste losses from the system varied from run to run, averaging approximately 100 kg for each run.

III. PROCESS MEASUREMENTS

The process control instruments in the plutonium purification cycles at AGNS are de-

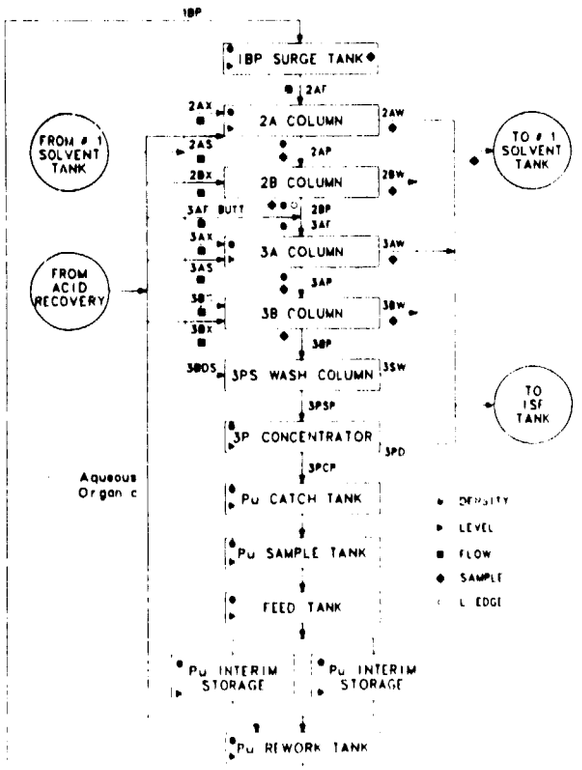

Fig. 1. Minirun flowsheet.

signed to measure (1) volumes and densities in all static tanks and (2) flow rates of major feed streams (aqueous feed to the plutonium purification cycles, aqueous and organic streams to columns). All process measurement signals are received in the control room; analog signals are digitized and transmitted to the materials accounting computer. Process samples are taken in the plutonium analytical glovebox at key sampling points (column product streams, feed points). These samples are analyzed in the analytical chemistry laboratory and analytical results are fed into the Laboratory Data System.

The available process and laboratory measurements for the first six miniruns are shown in Fig. 1 as solid circles, triangles, or squares. For minirun 7 additional measurements were added in the 2BP stream (aqueous product from the 2B column) and to the combined organic waste stream from the "B" and wash columns (2BW, 3BW, 3SW), the combined aqueous waste streams from the "A" columns, and the overheads from the concentrator (2AW, 3AW, 3PD). The measurement in the 2BP stream was obtained using an L-absorption-edge densitometer designed and constructed at Los Alamos. Measurements in waste streams were performed using a K-x-ray fluorescence spectrometer designed at Livermore and adapted at AGNS to the AGNS process lines. X-ray fluorescence analyzers also were installed in the 1BP and 3BP product streams.

A. Volume and Density Measurements

Process volume and density measurements were obtained using commercial Taylor* dip-tube manometers that had been installed during BNFP construction. Tests by AGNS indicated a drift in output as a function of time. Therefore, AGNS personnel designed an automatic calibration technique (AUTOCAL) for all volume and density probes.[5] The AUTOCAL system uses a Ruska** densimeter to correct for nonlinearity and drift in signals from process differential-pressure transmitters. Thus, transmitters with a stated manufacturer's accuracy of 5-10% are corrected to an accuracy of 0.2%.[6] Temperatures of flowing streams are measured using in-line thermocouples, and all densities are corrected for temperature.

B. Analytical Laboratory Uranium Analyses

Process control samples at BNFP are analyzed for uranium using a modified Davies-Gray procedure. In the standard Davies-Gray method, uranium first is reduced to the tetravalent state using Fe(II) in phosphoric acid. Then, the tetravalent uranium is oxidized quantitatively to the hexavalent state with dichromate, and the end point is detected potentiometrically. The method is capable of precision and accuracy of 0.1%. In the modified method, the end point is detected colorimetrically. The modified method is rapid, requiring 10 min per sample, but accuracy is of the order of 5%.

C. L-Edge Densitometry

For minirun 7, an L-edge densitometer was installed in the 2BP stream by Los Alamos.[7] A flow-through sample cell with a 1-cm path length was installed on line to permit

*Taylor Models 1502 to 1508, Taylor Instrument Co., Rochester, NY.

**Ruska model DDR6000, Ruska Instrument Corp., Houston, Texas.

continuous analysis of the flowing sample stream. The instrument was calibrated for optimum assay results between 50-60 g/L. During minirun 7, the instrument obtained a uranium concentration measurement every ~5.5 min with a precision of 0.7%. At concentrations of 35 g/L, a positive calibration bias of 0.15% is anticipated.

D. K-X-Ray Fluorescence Analysis

An x-ray analysis system based upon energy-dispersive K-x-ray analysis was developed for uranium analysis of process and waste streams. During minirun 7, x-ray fluorescence detectors were installed in the 1BP and 2BP streams and in the organic and aqueous waste or recycle streams from the plutonium purification cycles.

The precision of the x-ray fluorescence method was reported to be 2% in the 20-150 g/L concentration range.[8] Matrix effects caused by introduction of other heavy metals or by variations in acid concentration are not included in the data evaluation methods. The minimum detectable concentration is 0.1 g/L; hence, aqueous waste and organic recycle streams anticipated under normal operating conditions could not be measured. For concentrations in the range of 0.2 to 0.4 g/L, as normally encountered in the 3BW stream, the precision is reported to be 38%.

E. Uranium Concentration from Solution Density and Acidity Measurements

The density measurement is used in reprocessing plants for measuring in-process inventory, primarily for process control, and can be used to determine in-process inventory for NRTA. The method is sensitive to nitric acid concentration and temperature. A predictive equation for uranium concentrations in the range 0.05 to 0.6 M (12-143 g/L) was proposed by Brodda.[9] Errors in determining uranium concentration are in the range 0.8-3.9%. Measurements of LWR dissolver solutions with a relative standard deviation of 0.8-1.2% were reported.[10] For measurement of uranyl-nitrate product solution, a relative standard deviation of better than 0.2% was reported.

The development work at AGNS for predictive equations[11] was aimed at determining uranium concentration in both aqueous and 30% TBP in dodecane solutions. Three separate predictors were developed:

- o high-level aqueous U-CALC for 160-400 g uranium/L,
- o low-level aqueous U-CALC for 10-80 mg uranium/g, and
- o organic U-CALC, 10-80 mg uranium/g and 30% TBP.

IV. MINIRUN NEAR-REAL-TIME MATERIALS ACCOUNTING

Measurement data from the AGNS process control instrumentation, including estimates of random and correlated measurement uncertainties, were received hourly in a data file (ARANGE). In addition, sample data from the analytical laboratory were added to the ARANGE file as they became available from the Laboratory Data System. Samples for chemical analysis were taken normally once per shift (see Fig. 1 for sample points). Table 1 lists the ARANGE file data entries for the seventh minirun. Measurement points used for NRTA are given along with their respective random and correlated errors. The instruments were not recalibrated during the miniruns; thus, all measurements made with the same instrument are correlated for all accounting periods.

TABLE 1: CONTENTS OF ARRANGE DATA SETS: AGNS MINIRUN NO. 7

Measurement Point		σ^2 Random	σ^2 Correlated
Data Set No.		-	-
Time		-	-
Date		-	-
Initial Inventory		0	0
Pu Storage 01 (305)	V	$(0.6/V)^2$	$(0.26/V)^2$
Pu St. 01 (Taylor)	C	6.1×10^{-4}	2.4×10^{-5}
Pu St. 02 (306)	V	$(0.6/V)^2$	$(0.26/V)^2$
Pu St. 02 (Taylor)	C	6.8×10^{-5}	1.1×10^{-3}
Pu Rework Tank	V	$(5.3/V)^2$	$(4.8/V)^2$
Pu Rework (Taylor)	C	7.4×10^{-3}	1.8×10^{-4}
1BP Tank	V	$(5.3/V)^2$	$(7.1/V)^2$
1BP Tank (Taylor)	C	4.1×10^{-3}	1.0×10^{-2}
2AP (FR205)	F	4.0×10^{-4}	4.0×10^{-4}
2AX (FR543)	F	5.6×10^{-5}	5.6×10^{-5}
1BP Tank Sample	C	3.6×10^{-3}	2.2×10^{-4}
2AB (FR-638)	F	4.0×10^{-4}	4.0×10^{-4}
2AP Sample	C	4.0×10^{-4}	9.0×10^{-4}
2A Column (kg U)	W	$(4.0/kg\ U)^2$	$(4.0/kg\ U)^2$
2AP (Taylor)	C	6.4×10^{-4}	1.6×10^{-2}
2BX (FR-639)	F	4.0×10^{-4}	4.0×10^{-4}
2BP Densimeter	C	4.0×10^{-4}	2.5×10^{-3}
2BP Sample	C	3.6×10^{-3}	1.0×10^{-4}
2BP L edge densitometer	C	1.0×10^{-4}	2.5×10^{-5}
2B Column (kg U)	W	$(2.0/kg\ U)^2$	$(2.0/kg\ U)^2$
3AP Butt (FR-633)	F	4.0×10^{-4}	4.0×10^{-4}
3AX (FR 542)	F	4.0×10^{-4}	4.0×10^{-4}
1BP Taylor & Conduc.	C	4.1×10^{-3}	2.0×10^{-2}
3AR (FR 618)	F	4.0×10^{-4}	4.0×10^{-4}
3AP Sample	C	4.0×10^{-4}	9.0×10^{-4}
3AP (Taylor)	C	3.4×10^{-4}	8.4×10^{-3}

Table 1 (cont)

Measurement Point		σ^2 Random	σ^2 Correlated
3P Column (kg U)	W	$(9.0/\text{kg U})^2$	$(9.0/\text{kg U})^2$
3BP Densimeter	C	4.0×10^{-4}	2.5×10^{-3}
Pu Prod. Tank (Sample)	C	3.2×10^{-4}	7.5×10^{-5}
3BX (FR-619)	F	4.0×10^{-4}	4.0×10^{-4}
3BP XRF	C	9.0×10^{-4}	2.2×10^{-4}
3BP Sample	C	3.6×10^{-3}	1.0×10^{-4}
1BP XRF	C	9.0×10^{-4}	2.2×10^{-4}
3B Column (kg U)	W	$(3.0/\text{kg U})^2$	$(3.0/\text{kg U})^2$
1SP XRF	C	0.25	133
3PC Column (kg U)	W	$(0.17/\text{kg U})^2$	$(0.17/\text{kg U})^2$
#1 Solv. Feed Tank	V	4.0×10^{-6}	2.5×10^{-5}
#1 Solv Feed Sample	C	4.0×10^{-2}	4.0×10^{-2}
3P Concentrator	V	6.4×10^{-5}	3.6×10^{-5}
3P Concent.(Taylor)	C	6.8×10^{-5}	1.1×10^{-3}
Pu Catch Tank	V	$(0.35/\text{V})^2$	$(0.17/\text{V})^2$
Pu Catch (Taylor)	C	6.1×10^{-4}	2.4×10^{-5}
Pu Prod. Tank	V	$(1.03/\text{V})^2$	$(0.18/\text{V})^2$
Pu Prod. (Taylor)	C	6.1×10^{-4}	2.4×10^{-5}
Pu Storage #3 (304)	V	$(0.37/\text{V})^2$	$(0.24/\text{V})^2$
Pu Storage #3 (Taylor)	C	6.1×10^{-4}	2.4×10^{-5}
2AW Sample	C	-	-
2BW Sample	C	-	-
3AW Sample	C	-	-
3BW Sample	C	-	-
POR XRF	C	0.25	0.025

Three computer programs (RADAR, FUNNEL, and DECANAL) were implemented at ACNS for analyzing minirun measurement data. RADAR is a utility code that reads the measurement data from ARANGE and performs minimal formatting and data checking before writing the input measurement data file for the FUNNEL program. FUNNEL is the executive program that calculates materials balances; it was written specifically for the AGNS minirun process. The program allows the user to select and analyze data spanning particular time periods and to choose any of several unit process accounting areas (UPAAs) that include different process areas. The major UPAAs are

(1) full process UPAA - includes the entire closed loop of the plutonium purification process (Fig. 1), as operated for the miniruns;

(2) column UPAA - isolates the columns in a single accounting area bounded by the 1BP tank and the 3P concentrator;

(3) 1BP surge tank UPAA - isolates the 1BP surge tank with the plutonium rework tank and the 2AF stream;

(4) PPP UPAA - includes the columns and the 3P concentrator with boundaries at the 1BP surge tank and the Pu catch tank (alternatively, PPP and sample UPAA--the catch tank can be included in the UPAA, and the sample tank can be used for the output transfer measurement); and

(5) tank UPAA - isolates any single tank in the process as a separate UPAA.

For a specified UPAA and time period, the FUNNEL program combines the raw measured values to calculate net transfers, and in-process inventories and their statistical uncertainties, and transmits them to the decision analysis (DECANAL) package for further analysis.[12]

V. PULSED-COLUMN INVENTORY ESTIMATES

UPAAs that included pulsed columns required estimates of the inventory based on measurements of the feed, product, and waste stream concentrations and flows. The estimator[13] has a form given by

$$H = H_f(C_f \cdot F_f) + H_p(C_p \cdot F_p) + H_w(C_w \cdot F_w) \quad ,$$

where H is the total column inventory; the subscripts f, p, and w, respectively, indicate the feed, product, and waste streams; H_f, H_p, and H_w are constants related to the inventory at some nominal operating conditions and are determined experimentally and through engineering models for each pulsed column; C_f, C_p, and C_w are combinations of measured and nominal concentrations; and F_f, F_p, and F_w are combinations of measured and nominal flow rates. We used this estimator in two forms, with the concentration and flow dependence and with concentration dependence only.

At the end of miniruns 1, 5, 6, and 7, the pulsed columns were valved off, the phases separated by pulsing, the columns drained into holding tanks, holding tank volumes measured, and samples taken for chemical analysis. Column inventories from these dumps and from the two forms of the estimator are given in Table 2. These preliminary comparisons show that the estimator is always lower than the column dump measurements. The estimator that has both concentration and flow rate dependence agrees with measured values from the column dumps within the error of the estimator. Comparisons for individual columns range from 27% higher to 30%

TABLE 2: PULSED-COLUMN INVENTORY COMPARISON

	Inventory (kg U)		
		Estimator	
Minirun	Column Dump	Flow Rate and Concentration	Concentration
1	80.2	74.1 (-7.6%)	-
5	48.1	45.2 (-6.0%)	40.4 (-16.0%)
6	42.0	41.6 (-1.0%)	37.0 (-11.9%)
7	58.7	61.5 (+4.8%)	41.3 (-29.6%)

lower than the column dumps. Analysis of these results is underway to determine the factors contributing to these differences and to refine the estimator and the column dump experiments.

VI. LOSS-DETECTION SENSITIVITIES

Estimates for materials loss-detection sensitivities and material inventory and through-put for selected accounting areas in the mini-runs are given in Table 3. These estimates are for 1-day accounting periods and are based on a fixed-length test having a 50% detection probability and a 2.5% false-alarm probability. They are based on measurement error estimates at the end of the minirun series (Table 1). These detection sensitivity estimates are not applicable to all the miniruns because the measurement error estimates were refined with each minirun.

TABLE 3: ESTIMATED MATERIALS LOSS-DETECTION SENSITIVITY

Accounting Area	Inventory (kg U)	Through-put (kg U/day)	Detection Sensitivity (kg U)
Small static tank	60	0	4
Large dynamic tank	90-20	144	11
Columns	40-45	144	12
PPP & sample	95-100	144	18

The loss-detection sensitivity is ~4 kg uranium for small static tanks such as the interim storage tanks (Fig. 1). This tank normally has an inventory of ~60 kg uranium. The sensitivity is dominated by the concentration measurement error and the amount of material measured and can be improved by using a concentration measurement having a precision of 1% or better. A volume balance has a detection sensitivity of ~1.2 L. Because the tank is static, the detection sensitivity is not a function of time or correlated measurement errors.

Materials balances for large dynamic tanks, such as the 1BP tank, are based on volume balances because of relatively large biases between the rework and 1BP tank concentration measurements and the lack of an independent concentration measurement on the 7AF stream. The 1BP tank solution volume is normally in the range of 300-1500 L with a concentration of ~60 g uranium/L. The daily throughput for the 1BP tank is ~144 kg uranium/L. The volume balance has a loss-detection sensitivity of ~100 L. A balance based on the volume and a single concentration measurement in the 1BP tank for all streams has a sensitivity of ~15 kg uranium, and can be improved by providing more frequent (i.e., continuous NDA or density) measurements of concentrations.

The loss-detection sensitivities for the column UPAA (40-45 kg uranium inventory and 144 kg uranium throughput/day) and the PPP and sample UPAA (95-100 kg uranium inventory and 144 kg uranium throughput/day) are ~12 kg uranium and ~18 kg uranium, respectively. These sensitivities are dominated by the transfer measurement errors. The PPP and sample UPAA has a larger detection sensitivity principally because of the way the output transfers are calculated and because of the larger in-process inventory. Output transfers from the PPP and sample UPAA are a combination of volume and process-quality concentration measurements in the sample and feed tanks (Fig. 1). For safeguards, accountability quality concentration measurements should improve detection sensitivity.

VII. DISCUSSION

NRTA demonstrations during the AGNS miniruns show that materials balances can be drawn in near-real time using process-grade measurements. We cannot emphasize this point enough--useful information can be extracted from process monitoring data. Although the materials loss-detection sensitivities achieved for 1-day periods generally are not comparable to international goals, they illustrate the efficacy of the NRTA concepts.

Process-grade measurements can usually provide estimates of in-process inventories. Efforts to improve these estimates should concentrate on concentration measurements and on estimation of solvent-extraction contactor inventories.

Measurements of significant feed and product streams can often be made on a batch basis. However, measurements of flow rates and concentrations are needed on process streams, including waste streams, that cross accounting area boundaries.

The reprocessing facility is an integrated whole, and the materials accounting system must address the entire facility. Therefore, we plan

to participate in future experimental tests to continue the development and demonstration of NRTA and to explore methods for international verification of materials balances in reprocessing facilities.

ACKNOWLEDGMENTS

This work was supported by the US Department of Energy, Office of Safeguards and Security. The work could not have been performed without the cooperation of the AGNS staff. We particularly acknowledge the assistance of J. M. Crawford, M. H. Ehinger, and J. H. Ellis.

REFERENCES

1. COBB, D. D., DAYEM, H. A., BAKER, A. L., "Demonstration of near-real-time accounting at the AGNS Barnwell Plant," Safeguards and Nuclear Materials Management (Proc. 3rd Annual Symposium Karlsruhe, Federal Republic of Germany, 1981) ESARDA 13, 323-328.

2. COBB, D. D., DAYEM, H. A., BAKER, A. L., ELLIS, J. H., EHINGER, M. H., CRAWFORD, J. M., "Demonstration of Near-Real-Time Accounting: the AGNS 1980 Miniruns," Nucl. Mater. Manage. X(), 34-43 (1981).

3. COBB, D. D., HAKKILA, E. A., DAYEM, H. A., SHIPLEY, J. P., BAKER, A. L.," Development and Demonstration of Near-Real-Time Accounting Systems for Reprocessing Plants," Nucl. Mater. Manage. X (1981) 411-421.

4. CRAWFORD, J. M., EHINGER, M. H., JOSEPH, C., MADEEN, M. L., "Development of a Computerized Nuclear Materials Control and Accounting System for a Fuel Reprocessing Plant," Nucl. Mater. Manage. VIII (Proceedings Issue) (1979) 405-415.

5. CRAWFORD, J. M., "Automated Calibrations and Dynamic Corrections for Differential Pressure Transmitters," Nucl. Mater. Manage. IX (1980) 138-147.

6. ELLIS, J. H., "Development and Testing of a Near-Real-Time Accounting System for the Barnwell Reprocessing Facility," Nucl. Mater. Manage. X (1981) 402-410.

7. RUSSO, P. A., MARKS, T., JR., STEVENS, M. M., BAKER, A. L., COBB, D. D., "Automated L-Edge Measurements of SNM Concentration On-Line for Near-Real-Time Accounting," Los Alamos National Laboratory report LA-9480-MS (September 1982).

8. CAMP, D. C., RUHTER, W. D., "Nondestructive, Energy-Dispersive, X-ray Fluorescence Analysis of Product Steam Concentration from Reprocessed Nuclear Fuels," Measurement Technology for Safeguards and Materials Control, National Bureau of Standards Special Publication 582, 584-601 (June 1980).

9. BRODDA, B. G., "Establishing the Calibration Functions for In-Line Determinations of Uranium and Thorium in Various Process Flows of the Experimental Jupiter Reprocessing Plant," Julich Nuclear Research Institute report JUL-968-CT (June 1973).

10. BERG, R., "Verification of Reprocessing Plant Input and Output Analyses," Nuclear Safeguards Technology 1978 (Proceedings IAEA Symposium Vienna, 1978) Vol. II, 661-668, IAEA, Vienna (1979).

11. POSTLES, R. L., CRAWFORD, J. M., "Development and Applications of Algorithms to Predict Uranium Concentrations from Solution Density and Acidity Measurements," Allied-General Nuclear Services report AGNS-35900-2.3-138 (August 1981).

12. MARKIN, J. T., BAKER, A. L., SHIPLEY, J. P., "DECANAL User's Manual," Los Alamos National Laboratory Report LA-9043-M (April 1982).

13. COBB, D. D., BURKHART, L. F., BEYERLEIN, A. L., "In-process Inventory Estimation for Pulsed Columns and Mixer-Settlers," Safeguards and Nuclear Materials Management (Proc. 2nd Annual Symposium Edinburgh, Scotland, 1980) ESARDA 11, 145-151.