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NEUTRON ACTIVATION ANALYSIS FOR URANIUM AND ASSOCIATED ELEMENTS

by

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DISCLAIMER

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ABSTRACT

Neutron activation analysis is a reliable and efficient technique for determining uranium and associated elements in the thousands of sediment and water samples arising from a hydrogeochemical reconnaissance survey. The samples obtained by the Savannah River Laboratory as part of the National Uranium Resource Evaluation program are activated in the intense neutron flux from a Savannah River Plant production reactor. A pilot-scale facility was installed at the reactor site to provide analyses of samples through the initial phase of the program and to develop design data for a full-scale facility.

When a sample is exposed to a neutron source, many elements absorb neutrons and are transformed (activated) to radioactive isotopes, each of which has characteristic decay energies and half-life. The quantity of radioactivity induced in the element is proportional to the amount of element present in the sample, regardless of the element's chemical form. Sediments are analyzed by direct activation of 0.5-g samples. However, to analyze ground or surface water samples, mineral elements from 1-liter samples are concentrated on ion exchange resin and then ∿5-g samples of resin are activated. Uranium concentration is determined by counting neutrons emitted from specific short-lived products of fission induced in ^{235}U by the primary neutron flux. Repetitive short cycles of irradiation and counting permit detection and determination of <0.1 μg of uranium. Elements associated with uranium are determined by spectral analysis of the gamma ray activities induced by the cyclic and subsequent longer irradiations.

The pilot facility consists of four irradiation positions (plus 2 spare positions), a sample loader and unloader, and counting stations with neutron and gamma ray detectors, all interconnected with a pneumatic sample transport system. A computer controls both the transport system and the data acquisition devices. Gamma ray counting data are stored on magnetic tape for further processing by a large central computer. Facility hardware and software are described. The facility has processed approximately 5,000 samples.

Repetitive analyses of standards have shown an accuracy within ±10% for uranium values and within ±25% for associated elements. A quality assurance program has been developed to maintain these levels of reliability.

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INTRODUCTION

Background

The National Uranium Resource Evaluation (NURE) Hydrogeochemical Stream Sediment Reconnaissance (HSSR) survey presents a formidable analytical problem. Several hundred thousand samples are to be analyzed primarily for uranium at concentrations in the ppm range in sediments and down to tens of pptr in ground and surface water samples. In addition, many of these same samples require analyses for other elements associated with uranium, such as thorium, vanadium, hafnium or zirconium, etc. Each of four laboratories has surveyed its analytical capability to perform these analyses. The technique of Neutron Activation Analysis (NAA) is used by each of the four laboratories for uranium in sediment samples and at least two of the laboratories are using NAA for the elements associated with uranium.

Principle of Neutron Activation

NAA involves irradiating a sample in a flux of thermal neutrons. Nuclei of elements in the sample (target nuclei) have a characteristic probability (cross section) of absorbing a neutron and becoming radioactive. Each radioactive product then decays by radiating energy of a type (particle or ray) and intensity (in energy units) and with a half-life that are all characteristic of the decaying radionuclide. A measurement of the type and intensity of the radiated energy serves to identify the radionuclide. The rate at which decay energy is emitted is proportional to the number and half-life of radioactive nuclei present. The number of radioactive nuclei, when combined with neutron flux and cross section, allow determination of the number of target nuclei in the sample. For performing NAA, required equipment principally includes a neutron source of adequate flux (usually a nuclear reactor) for activating the sample and instrumentation for detecting and measuring ("counting") induced radioactivity. Because the neutron-irradiated samples become radioactive, a sample handling system is also required. This is usually a pneumatic transport system that moves encapsulated samples into the neutron flux and into the counting instruments. With high-throughput facilities, the transport systems are usually under the control of a computer. Because of differences in the construction and operating power levels of reactors, the neutron flux level and neutron energy distributions differ. These differences are reflected in the designs of the sample transport systems and in the specific analytical regimes used by the various laboratories. To achieve the best analytical results from each facility, system design and analytical regime should be tailored to the neutron-source facility and analytical experience.

NAA Experience at Savannah River Laboratory (SRL)

SRL neutron activation experience stems primarily from operation of the ^{252}Cf activation facility. In that facility we developed a recycle activation technique to take advantage of short-lived activation products, and to improve counting statistics by alternately irradiating and counting the sample for short time periods.[1] This recycling technique was coupled with delayed-neutron counting to achieve very high sensitivities for the assay of fissile material. Unfortunately, the neutron flux in the ^{252}Cf facility is too low for processing NURE samples at the required throughput and sensitivity. A pilot-scale activation facility[2] was therefore installed at one of the Savannah

River Plant production reactors to demonstrate the applicability of the technique to HSSR samples. Samples that were processed initially were obtained from orientation studies. Operation of the facility also provided design criteria for a larger facility capable of processing samples at the required throughput for the reconnaissance phase of the HSSR program.

DISCUSSION

Description of Samples and Analysis Regimes

Two types of orientation-study samples were collected for processing by the pilot activation facility: 1) 0.5 g of stream sediment sieved to finer than 100 mesh, and 2) 5 g of mixed cation and anion exchange resin on which dissolved minerals from 1-liter samples of ground or surface water were concentrated.[3] These samples are packaged in polyethylene capsules (Figure 1). Samples which do not fill the capsule are firmly packed at the bottom because the neutron flux is highest at this end of the capsule in the irradiation position.

General-purpose analysis regimes (summarized in Table 1) were devised for these sediment and resin samples to detect and determine uranium and as many other elements as practical. A test analysis determines whether or not a sample can proceed through the complete activation process without becoming excessively radioactive. The recycle regime is designed for analyzing elements with short-lived activation products, especially uranium via delayed-neutron counting and for analyzing other elements via simultaneous gamma ray spectrometry. A 15 to 30 minute irradiation followed by a series of gamma ray counts delayed by appropriate decay intervals is designed for the detection and determination of longer-lived activation products, especially those of thorium.

Sample Transport System

The pneumatic transport system installed to implement the analysis regimes is shown in Figure 2. There are six irradiation positions; four of which are connected to the transport system by a 4-way diverter unit. Another 4-way diverter unit allows selection of one of four possible transport paths. Encapsulated samples enter the transport system through an automated loader and exit through an automated unloader. Counting station D1 contains an array of BF_3 detectors for delayed-neutron counting and a lithium-drifted germanium (GeLi) detector for simultaneous gamma ray spectrometry. Counting station D2 has only a GeLi detector. During a typical activation run, one sample is being recycled between an irradiation position and detector station D1, three samples are receiving their 15 to 30 minute irradiation, and another sample is being counted. A separate delayed counting routine processes two samples at a time, one for each GeLi detector.

NAA Pilot Facility

An elevation view of the pilot facility is shown in Figure 3. The six irradiation positions are housed in an assembly which penetrates the reactor biological shield and rests next to the reactor tank wall. Radiation-generated heat is removed from this assembly by a closed-loop cooling water system. Each of the

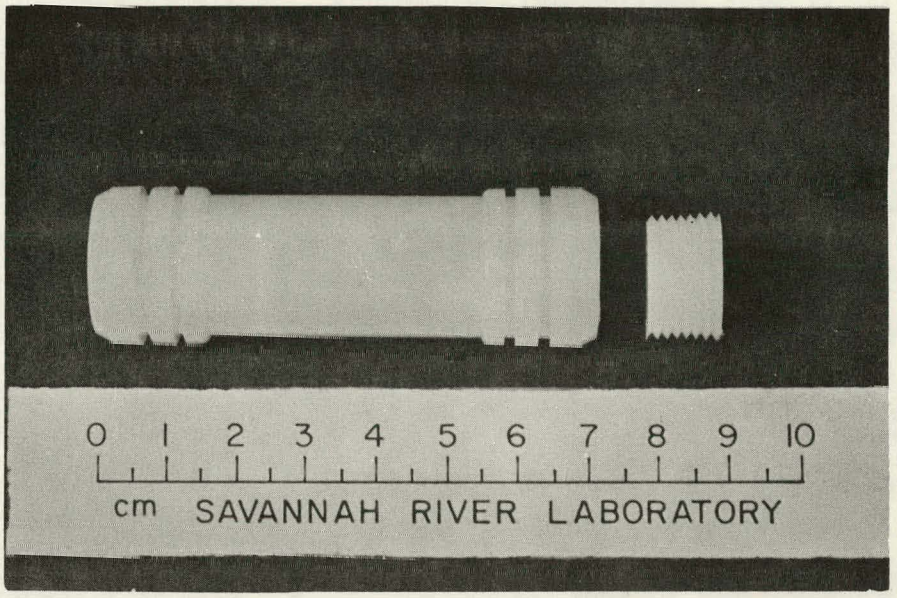

FIGURE 1. Sample Capsule

TABLE 1

ANALYSIS REGIMES FOR ORIENTATION SAMPLES[a,b]

Step	No. of Cycles	T_a	T_d	T_c	T_r
Test	1	2 s	1.3 s	2 s	1.1 s
Recycle	20(40)[c]	6 s	1.3 s	6 s	1.1 s
Long Irradiation		900 s(1800 s)	2.5 s	300 s(600 s)	
Delayed Count 1			8-16 hr	10 min	
Delayed Count 2			3-5 d	10 min	
Delayed Count 3			15-20 d	20-50 min	

a. 0.5 g of sediment or 5 g of ion exchange resin.

b. T_a, T_d, T_c, and T_r are durations of activation, decay, counting, and sample return, respectively.

c. Numbers in parentheses apply to resin samples.

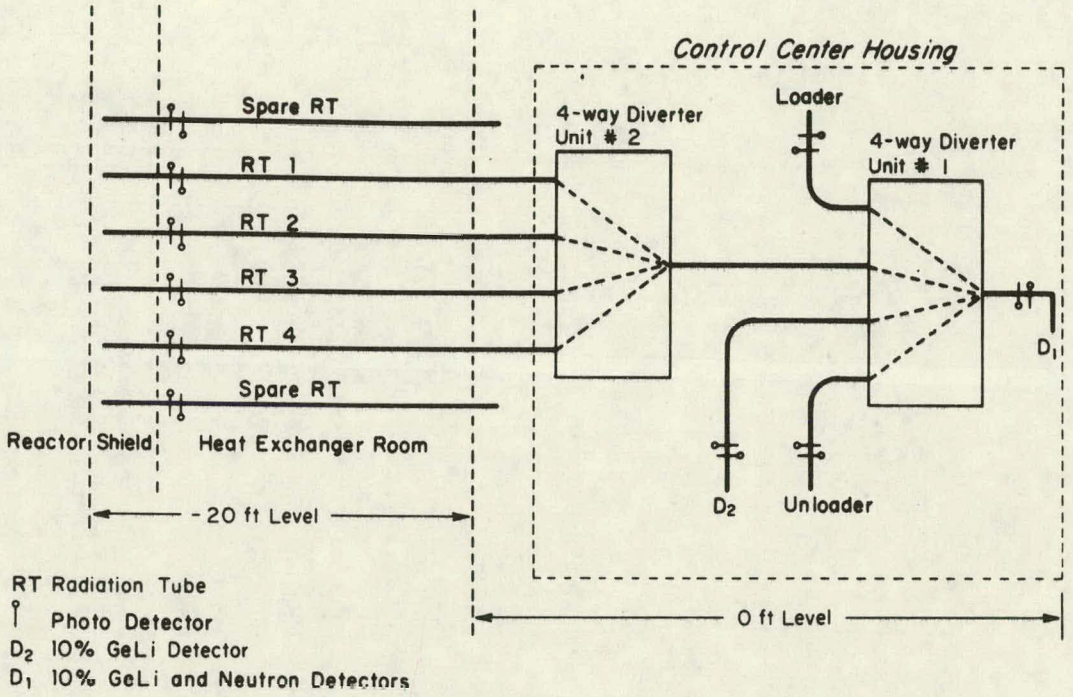

FIGURE 2. Pneumatic Sample Transport System

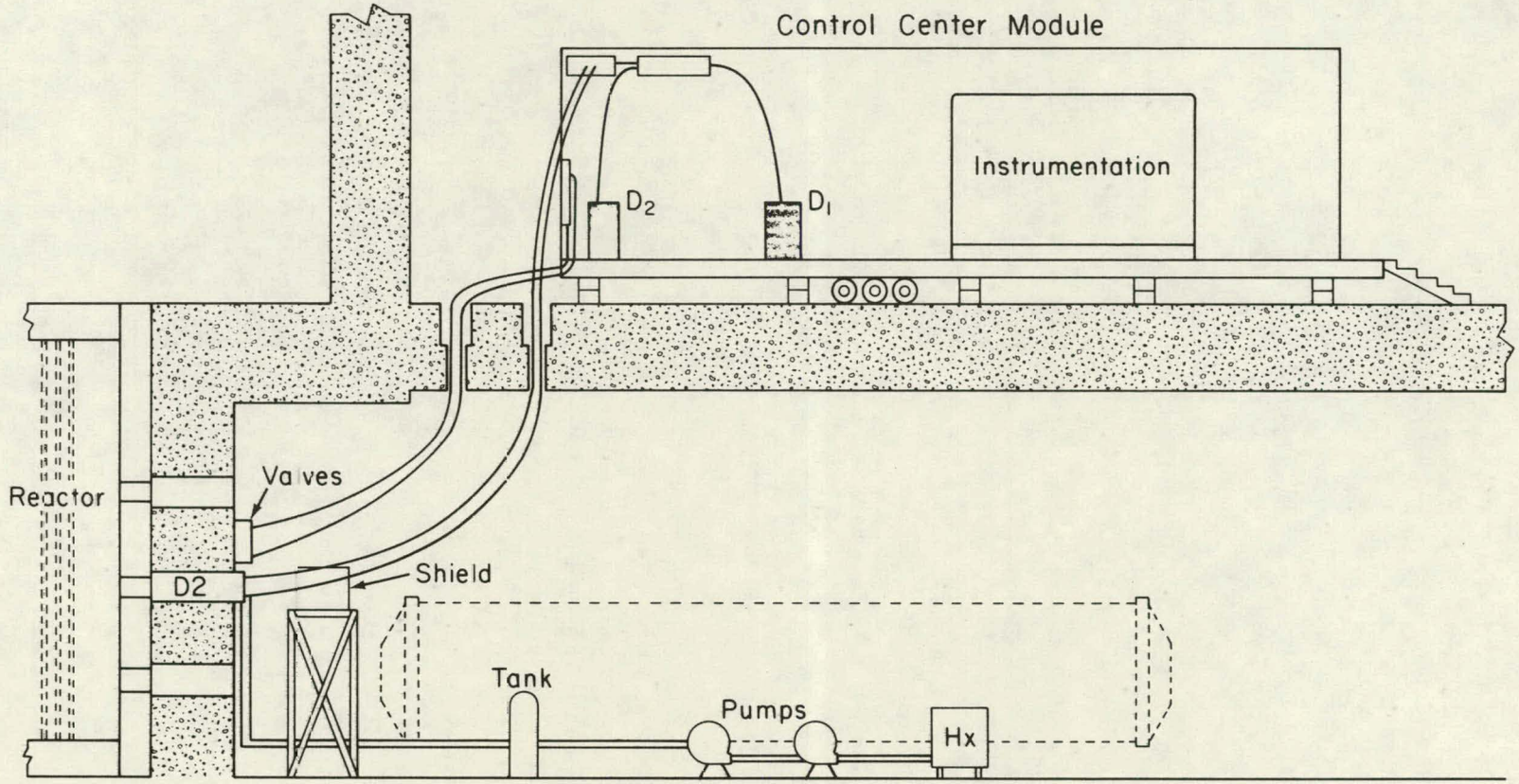

FIGURE 3. Pilot Neutron Activation Facility, Elevation View

irradiation positions is connected by polyethylene transport tubing to the control center module. This module houses the 4-way diverter units, detector stations, loader, unloader, and all control and data acquisition electronics.

Figure 4 shows one view of the control center module. From left to right the major components shown are: 1) a clean box for loading capsules into the sample storage barrel attached to the back wall, 2) air pressure control manifold, 3) detector station D2, and 4) the unloader with shielded sample storage barrel on the floor. Figure 5 shows detector station D1 (array of BF_3 detectors shielded by lead with a GeLi detector penetrating the shielding).

Another view of the control center module (Figure 6) shows the control and data acquisition electronics. Specific units include (from the right): 1) cooling water system monitor, 2) pulse height analyzer and associated electronics, 3) PDP-9 computer and associated peripherals, and 4) a microprocessor unit built at SRL to control the pneumatic transport system components.

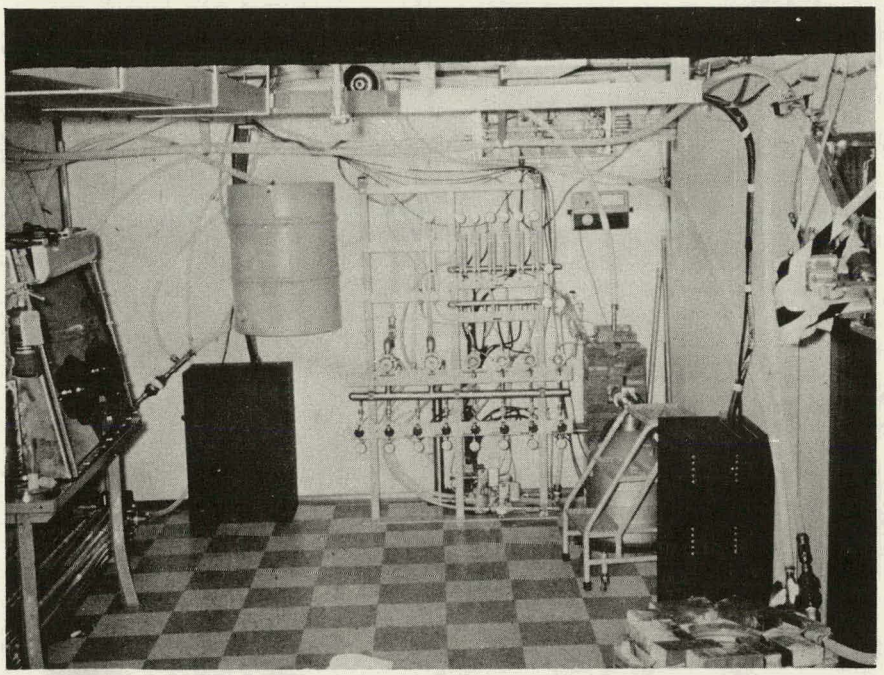

FIGURE 4. Portion of Sample Transport System in Control Center Module

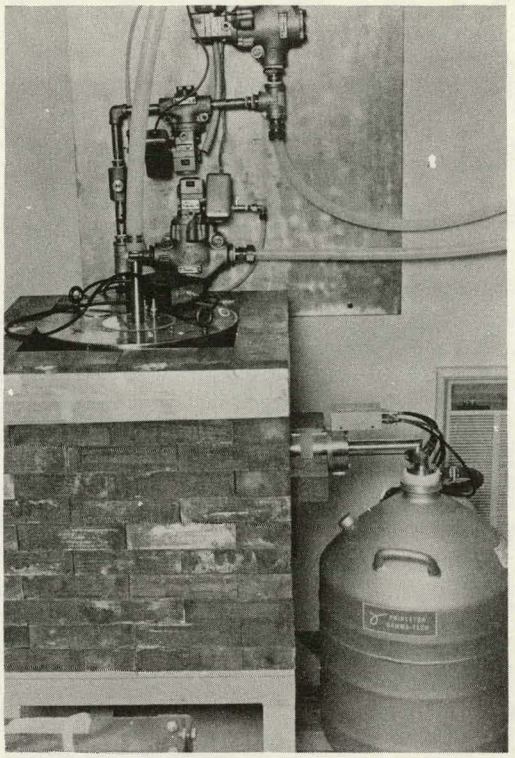

FIGURE 5. Delayed Neutron-Gamma Ray Detection Station D1

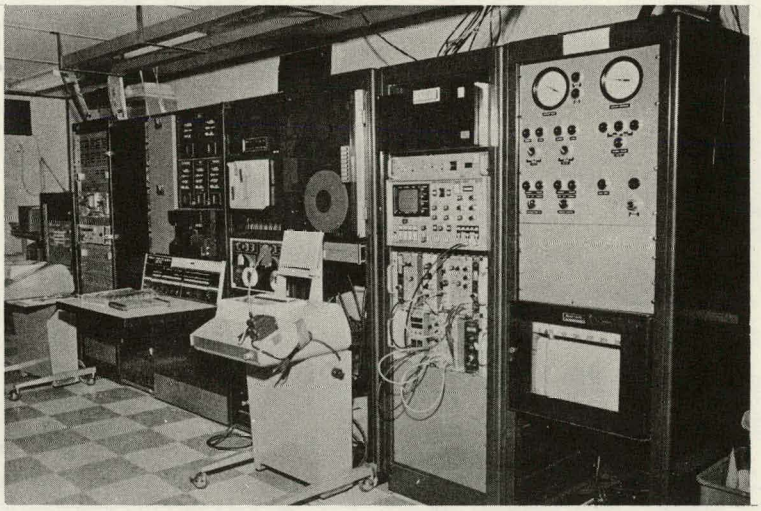

FIGURE 6. Control and Data Acquisition Electronics

Data Processing

Gamma ray counting data are recorded on magnetic tapes. The data are reduced on an IBM 360/195 computer as outlined in Figure 7. Irradiation and counting data are converted to a standardized format and stored on disc under the sample identifier by two programs, JCMPI and JCMPII. The gamma ray spectra are reduced using program RAGS.[4] When all spectra have been acquired and reduced for a sample, another program, RICHES, transforms these data into concentration units for the elements detected. The concentration values are then reformatted for inclusion directly into the NURE Data Management System (NDMS).

Analytical History and Results

Table 2 summarizes the production history of the pilot facility. The results from analyses of orientation study samples have indicated that the entire general purpose analysis regime is not required to provide the necessary information for elements associated with uranium. For reconnaissance samples, the analysis regime has been shortened (Table 3). The pilot facility capacity of 675 samples per week will not be adequate for the reconnaissance phase of the program. Accordingly, the activation facility is scheduled for upgrading (Figure 8). The necessary increase in sample throughput is achieved by utilizing six (instead of four) irradiation positions, two (rather than one) combined delayed neutron-GeLi detector stations, and at least four (and possibly eight) GeLi detectors dedicated to delayed gamma counting. A more sophisticated computer has been purchased to control the upgraded pneumatic systems and to acquire and reduce (at least partially) the necessary data.

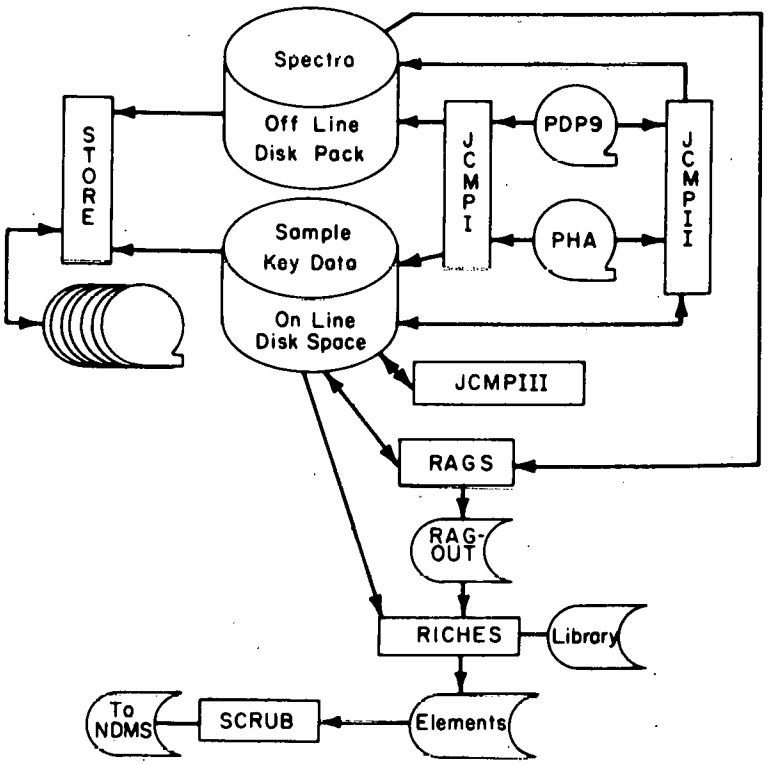

FIGURE 7. Neutron Activation Data System (NADS)

TABLE 2

PILOT FACILITY PRODUCTION HISTORY

June - July 1975	- Installation.
August - September 1975	- Program debugging.
October - December 1975	- ∿450 orientation samples. Uranium analysis only.
December 1975 - December 1976	- ∿3000 orientation samples. Multi-element analyses.
January 1977	- Reconnaissance samples, ∿500/week.

TABLE 3

ANALYSIS REGIMES FOR RECONNAISSANCE SAMPLES[a]

Step	No. of Cycles	T_a	T_d	T_c	T_r
Test	1	2 s	1.3 s	2 s	1.0 s
Recycle	20(40)	6 s	1.3 s	6 s	1.0 s
Long Irradiation	1	900 s (0 s)	1.3 s	300 s (600 s)	
Delayed Count			10-17 d	900 s	

(Values) are used for resin samples.

	Capacity
Activate 225 samples/day	3 days/week
Delayed count	675 samples during remaining 4 days/week.

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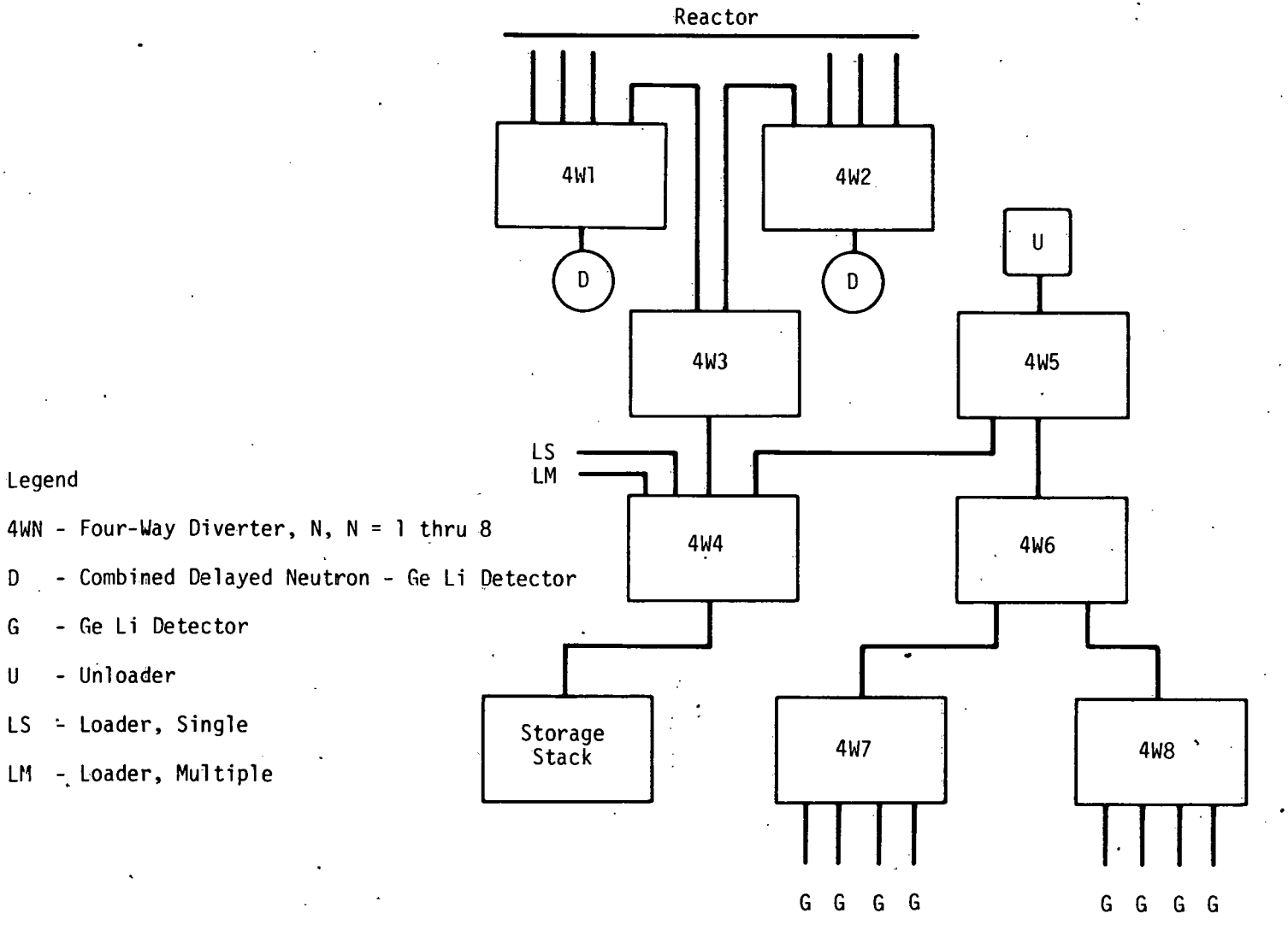
a. See footnotes to Table 1.

To demonstrate the quality of the analytical data obtained from the facility, data for the element of primary interest, uranium, are presented in Table 4. In general, the uranium analyses agree with certified values to within ±10%. For elements associated with uranium, the values from neutron activation agree with certified values to within ±25% wherever counting statistics warrant.



Legend

4WN - Four-Way Diverter, N, N = 1 thru 8

D - Combined Delayed Neutron - Ge Li Detector

G - Ge Li Detector

U - Unloader

LS - Loader, Single

LM - Loader, Multiple

FIGURE 8. Upgraded Pneumatic Sample Transport Facility

TABLE 4

ANALYSES OF URANIUM STANDARDS

Oak Ridge Sediment, ppm U

Sample No.:	R-1	S-1	T-1
Theoretical	5	10	95
SRL Average	5.3	11.2	97
Standard Deviation	0.4	0.6	3

USGS Rock Standards, ppm U

Sample No.:	AGV-1	G-2	BCR-1	GSP-1
Theoretical	2.0	2.0	1.8	2.56
SRL Average	2.1	2.3	1.8	2.61

Intersite Crosscheck, ppm U[a]

Sample No.:	SRL-1	LASL-2	LASL-3	OR-1	OR-2	LLL-1	LLL-2
SRL	1.45	5.1	3.5	1.48	2.4	6.5	8.2
LASL	1.7	4.9	3.5	2.0	2.6	6.7	7.3
LLL	1.2	5.2	2.6	1.2	2.1	7	8.3
ORGDP	-	5.0	-	-	2.5	-	6.8

Water Standards, ppb U

Sample No.:	A-1	B-1	C-1
Theoretical	0.82	7.77	100.2
SRL Average	0.82	7.6	94
Standard Deviation(± or)	0.04	-	-

a. Sites included, in order listed, Savannah River Laboratory, Los Alamos Scientific Laboratory, Lawrence Livermore Laboratory, and Oak Ridge Gaseous Diffusion Plant.

Quality Assurance

To assure a continuation of the quality of analytical results, a quality assurance plan (summarized in Table 5) has been implemented. If the results for successive standards agree within prescribed limits of established values, values for samples processed between those standards are assumed to be acceptable. If a standard does not meet specified criteria, data from associated samples are individually scrutinized before acceptance into the NURE data base. A series of standards and blanks are processed monthly to assure that all facility hardware and software are operating properly.

TABLE 5

QUALITY ASSURANCE PLAN FOR RECONNAISSANCE SAMPLES

Sediments	- 1 blank and 1 standard for each group of 23 samples.
Water	- 1 blank and 1 standard for each group of 123 samples.
Calibrations	- 25-50 calibration standards and blanks monthly.

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