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MASTER

AUTHOR(S): M. M. Minor
S. R. Garcia
M. M. Denton

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

AN AUTOMATED ACTIVATION ANALYSIS SYSTEM

M. M. Minor, S. P. Garcia, and M. M. Denton

Los Alamos National Laboratory
Los Alamos, NM 87545. USA

ABSTRACT

An automated delayed neutron counting and instrumental neutron activation analysis system has been developed at Los Alamos National Laboratory's Omega West Reactor (OWR) to analyze samples for uranium and 31 additional elements with a maximum throughput of 400 samples per day.

INTRODUCTION

An automated neutron activation analysis system has been developed to analyze large numbers of geological and environmental samples. Approximately 180,000 stream sediment samples have been analyzed for uranium concentrations using delayed neutron counting (JNC) and for 31 additional elements using instrumental neutron activation analysis (INAA) at maximum system throughput. At lower throughput, additional elements can be detected and excellent sensitivity for most elements is obtained.

The system utilizes two independent pneumatic transfer systems each having a sensitive neutron detector and four lithium-drifted germanium (Ge(Li)) gamma-ray detectors under the control of a single data acquisition computer. Samples are irradiated in the graphite thermal column of the OWR in a flux of $\sim 6 \times 10^{12}$ n/cm²/sec and are counted immediately for delay-neutron emission to obtain the uranium assay. The samples are then routed to a delay device where the samples are allowed to decay for a preset time (typically 10 min.) before they are counted for short-lived gamma activities. The samples are then given a second irradiation and stored for later counting of the longer-lived

activities at night when the reactor is shut down. System parameters are summarized in greater detail elsewhere.¹

Gamma-ray spectra along with timing and flux data and DNC data are collected and dumped to magnetic tape for subsequent data reduction by a second on-line minicomputer. Automatic analysis of data is performed by a code which identifies gamma-ray peaks and calculates elemental concentrations.

SYSTEM DESCRIPTION

I. Hardware

A. Pneumatic Sample Handling Facilities

Samples to be entered into the automated system are loaded into 4 cm³ irradiation vials (rabbits) 1.2-cm dia. by 6.0-cm long. The pneumatic system is designed to automatically load a sample and rapidly move the sample into the thermal column of the OWR and from there to the neutron detector, and later to a shielded location in front of a Ge(Li) gamma-ray detector for subsequent radioactive decay counting.

The individual samples are weighed and loaded into loader clips. The automatic loader for each system can hold four clips and can sequentially load a maximum of 200 samples into the pneumatic system on command from the control computer. The samples are irradiated in a thermal neutron flux in a special irradiation port placed in the graphite thermal column of the OWR. A fission ion chamber is inserted in the graphite stringer adjacent to the end position to monitor the relative neutron flux at the irradiation position.

A delay loader was designed for use in the system to allow the irradiated samples to decay for set periods after irradiation before they are gamma-ray

counted. A number of samples are allowed to stack up on the input side of the delay loader and then are removed one at a time from the bottom of the stack, at the sample rate at which samples are being added to the top of the stack.

In order to route samples between the loader and reactor and the various counting stations in the system, two four-way pneumatic diverters are used in the system. After samples have been irradiated a second time, the samples are blown to a storage unloader where the samples can be stored for any length of time in the same order in which they were irradiated. The unloader is mounted at the top of cased hole which extends underground for shielding.

B. Control and Data Acquisition

The control and data acquisition system is normally controlled by a PDP-11/34 minicomputer. A second computer, a PDP-11/60, is used for on-line data analysis. All hardware in the system are interfaced to the control and data acquisition computer through CAMAC. Photo detectors are installed in the pneumatic system to detect the passage of samples at eleven locations to detect any malfunctions.

The neutron detector used in the system is described in detail elsewhere.² Delayed neutrons are counted in a CAMAC scaler which can be cleared and read by the computer. Each multielement analysis system utilizes four Ge(Li) gamma-ray detectors employing standard electronics and conventional nuclear ADCs set for 4096 channel conversion gain. Spectra are stored in 4096 word CAMAC memory modules. The memory modules can be cleared, read out, and enabled or disabled to accept digital conversions on command from the computer. Since the samples counted vary greatly in gamma-ray source strength, real times and live times are accumulated with each gamma-ray count.

II. Software

A. Control and Data Acquisition

Two basic programs exist to acquire 1) Multielement data from short half-life isotopes, and 2) Multielement data from long half-life isotopes. The multielement analysis program for short half-life activities, SHORTS, in addition to the delayed neutron counting cycle, includes a decay period, a gamma-ray count period, and an additional second irradiation for each sample. Each sample cycle takes a minimum of 32 minutes to complete, thus there can be as many as 15 samples in each system at any given time. The program automatically backs up accumulated gamma-ray spectra to magnetic tape and stores all pertinent data including irradiation times and fluxes required by the long half-life analysis program.

The multielement analysis program for intermediate and long half-life activities, LONGS, includes only a gamma-ray counting cycle for each sample. The LONGS program loads and counts samples which have normally decayed for 4 or more days after being processed by the SHORTS program. The LONGS program is usually run at night or on weekends while the reactor is shut down.

B. Gamma-Ray Data Reduction

The computer program for gamma-ray data reduction, RAYGUN, is a variant of GAMANAL³ tailored to the PDP-11. Data to be analyzed are shipped to the Data Analysis Computer as a 4096 channel spectrum in which the data of the first 30 channels have been replaced by a header block of constants required for data reduction.

The RAYGUN analysis code requires approximately 24K words of PDP-11 memory in which to run. A single spectrum can be fit, gamma-ray peaks identified, and elemental concentrations calculated in approximately 17 seconds.

SYSTEM PERFORMANCE

The analytical detection of uranium using DNC has been employed for many years.⁴ The standard DNC measurements in the system are calibrated for fixed irradiation (20 sec), decay (11 sec), and count (30 sec) times using samples of known natural uranium concentrations. The counting scheme is less than optimal but results in a high specific sensitivity for geological samples (e.g., a four-gram sample with 2 ppm uranium will yield 5000 net neutron counts with a statistical accuracy of 1.4%).

The INAA techniques employed are novel only in respect to the high degree of automation and analysis volume. Sample irradiation times are selected on the basis of desired precision and sample size. Short and long sample irradiations of 20 and 96 seconds induce sufficient activity for sample masses greater than 1 gram and provide good counting statistics for the majority of elements of interest. For higher precision, irradiation times of 20- and 220-seconds are typically used.

The samples are counted directly in their irradiation vials. The vials are sufficiently free of trace elements that analyses are made with no blank subtraction. Counting room background subtractions are not required for short-lived activities since contributions to the nuclides of interest are negligible. Minor contributions to ⁴⁶Sc, ⁵⁹Fe, ⁶⁰Co, and ⁶⁵Zn are present when counting long-lived activities. Provision for discrete background subtraction is incorporated in the analysis code.

At minimum throughput the automated system yields elemental assays for 15 elements from the "shorts" analysis (See Table 1.); 14 elements from the "intermediate" analysis (See Table 2.); and 18 elements from the "longs" analysis (See Table 3.) in typical geological samples. Tables 1-3 give detection limits in geological samples for specified irradiation, decay, and count times. The tables were compiled from data on a large number of geological samples and standards. Uncertainties in the measured trace-element concentra-

tions are usually less than 10% at concentration values one order of magnitude above the lower detection limits.

DISCUSSION

The automated activation analysis system has thus far been used mostly for high volume analysis of samples. The new software currently employed on the system allows much more flexibility in the choice of irradiation, decay, and count times. These changes allow a much greater variety of sample size and matrix to be analyzed with greater sensitivity and precision with the advantages and reproducibility⁵ of a fully automated INAA system.

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Table 1. Elemental Lower Limits of Detection^{1,2}

Shorts Analysis			
Isotope	Half-life	Principal γ -ray Analytic Lines (keV)	Detection Limit (ppm)
Na ²⁴	15.0h	1368.6, 2753.85	1000
Mg ²⁷	9.46m	843.76, 1014.24	2700
Al ²⁸	134.40s	1779.00	3200
Cl ³⁸	37.00m	1642.68	120
K ⁴²	12.40h	1524.66	4500
Ca ⁴⁹	8.70m	3084.15	1500
Ti ⁵¹	5.80m	320.08	750
V ⁵²	3.77m	1434.05	8.0
Mn ⁵⁶	2.58h	846.75, 1810.66	60
Cu ⁶⁶	5.10m	1039.00	350
Sr ⁸⁷	2.83h	388.52	400
I ¹²⁸	24.98m	442.87, 526.38	40
Ba ¹³⁹	83.20m	165.85	200
Dy ¹⁶⁵	2.35h	94.68, 361.66	0.9
U ²³⁵		(DNC) ³	.05

¹Lower limit values were calculated on the basis of a nominal 4 gram sample.

²Based on a 20 sec irradiation; 1275 sec delay; 480 sec gamma ray count.

³Based on a 20 sec irradiation; 10 sec delay; 30 sec neutron count. (DNC)=Delayed Neutron Counting

Table 2. Elemental Lower Limits of Detection^{1,2}

Intermediate Analysis			
Isotope	Half-life	Principal γ -ray Analytic Lines (keV)	Detection Limit (ppm)
Na ²⁴	15.00h	1368.6, 2753.85	300
K ⁴²	12.40h	1524.66	4500
Ga ⁷²	14.10h	834.07, 630.	45
As ⁷⁶	26.50h	657.04, 559.09	3.0
Br ⁸²	35.39h	776.5, 619.09	4.0
Sb ¹²²	2.70d	564.09	1.0
Ba ¹³¹	11.70d	496.2, 373.	800
La ¹⁴⁰	40.28h	1596.2, 487.01	7.0
Sm ¹⁵³	47.00h	103.18	4.0
Yb ¹⁷⁵	4.21d	396.32	1.0
Lu ¹⁷⁷	6.70d	208.40	0.2
W ¹⁸⁷	23.8h	685.72	5.0
Au ¹⁹⁸	2.70d	411.79	0.04
U ²³⁹	2.35d	106.13, 277.9	10

¹Lower limit values were calculated on the basis of a nominal 4 gram sample.

²Based on a 240 sec irradiation; 5 day delay; 1800 sec gamma ray count.

Table 3. Elemental Lower Limits of Detection^{1,2}

Longs Analysis			
Isotope	Half-life	Principal γ -ray Analytic Lines (keV)	Detection Limit (ppm)
Sc ⁴⁶	83.80d	889.26	0.04
Cr ⁵¹	27.72d	320.08	2.5
Fe ⁵⁹	45.10d	1099.22, 1291.56	300
Co ⁶⁰	5.20y	1173.21, 1332.46	0.20
Zn ⁶⁵	242.94	1115.52	15
Se ⁷⁵	120.02	279.5, 264.5	5
Rb ⁸⁶	18.66d	1076.77	20
Sb ¹²⁴	60.20d	602.7, 1691.00	0.50
Cs ¹³⁴	2.05y	604.73, 795.84	0.60
Ba ¹³¹	11.70d	496.2, 373.0	300
Ce ¹⁴¹	32.50d	145.44	4.0
Eu ¹⁵²	13.4y	1408.02, 778.87	0.09
Tb ¹⁶⁰	71.99d	879.36	0.15
Yb ¹⁶⁹	30.69d	197.99, 307.68	0.50
Lu ¹⁷⁷	6.70d	208.40	0.06
Hf ¹⁸¹	42.00d	482.18	0.35
Ta ¹⁸²	115.00d	1221.38, 1189.02	0.45
Th ²³³	27.40d	311.9	0.35

¹Lower limit values were calculated on the basis of a nominal 4 gram sample.

²Based on a 240 sec irradiation; 21 day delay; 2 hour gamma ray count.