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AN AUTOMATED MULTIDETECTOR SYSTEM FOR INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF GEOLOGICAL AND ENVIRONMENTAL MATERIALS

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ABSTRACT

An automated multidetector system for instrumental neutron activation analysis (INAA) of geological and environmental materials was constructed. The system was evaluated using NBS SRM's 1632a Coal and 1633a Coal Fly Ash. Data are presented to show the precision, accuracy, and stability of the system over a 3-month period. As a result of the evaluation, elemental concentrations for Dy, La, Eu, Tb, Yb, Lu, and Ta, which have not been reported in the literature, were determined.

INTRODUCTION

Several investigators have reported trace element concentrations in NBS SRM's 1632a Coal and 1633a Coal Fly Ash.[1-5] Because of the continuing need for standards that are reliable, independent data from other laboratories are of value to the scientific community.

The automated system was designed to process sediment samples from the National Uranium Resource Evaluation (NURE) program using the facilities at the Los Alamos National Laboratory Omega West Reactor (OWR).[6] Because of the nature of the NURE program, a large inventory of samples was the result. The system had to be capable of processing more than 60,000 samples annually.

System Description

There are two identical automated systems, each of which have a neutron detector and four Ge(Li) detectors. Standard ADS's, amplifiers and preamplifiers are used with the system and are

temperature controlled to ensure long term stability. Figure 1 illustrates schematically one of the automated systems. Samples are placed in ethylene-butylene co-polymer irradiation vials 1.2 cm in diameter and 6.0 cm long and are weighed on a top-loading electronic balance which is interfaced to a PDP-11/34 computer.[7] The samples are loaded into clips which can hold 50 horizontally stacked samples. These clips are uniquely numbered and encoded with a wired socket so that the code can be read into the computer when a matching plug of the loader (see Figure 1) is attached to the clip. Each automatic loader was designed to hold four clips, corresponding to a maximum throughput of 400 samples per day for the two systems.

All data acquisition and sample movements are controlled by a PDP-11/34 computer utilizing standard CAMAC interface electronics. The gamma-ray spectra are automatically dumped to 9-tract magnetic tape for subsequent data reduction on a PDP-11/60 computer.

System Operation

It is necessary to run 400 samples daily during the 8 hours of irradiation time available. There are two reactor ports available allowing 126 seconds for each sample to be irradiated and moved to and from the reactor. To optimize the sensitivity for a maximum number of elements, the short and long irradiation times were adjusted accordingly. The following activation scheme was developed

- Flux — 6×10^{12} n/cm^{2}sec
- Irradiation Time — 20 sec (short-lived activities); 20 + 96 sec (long-lived activities)
- Decay Time — 1274 sec (short-lived activities); 14 days (long-lived activities)

Initially, detector energy calibration, resolution, and ADC linearity were measured with a NBS 4216 mixed gamma-ray source containing ^{109}Cd, ^{57}Co, ^{139}Ce, ^{203}Hg, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{88}Y and ^{60}Co. The resolution and characteristic peak shape as a function of energy were determined for each detector, and the resolution was found to be less than 2 keV FWHM at the 1332 keV line of ^{60}Co for all eight Ge(Li) detectors.

Each sample is counted three times: first for delayed-neutron assay in a high efficiency neutron detector and subsequently for short-lived and long-lived activities.[7] The samples are first irradiated for 20 sec followed by a 10 sec delay, then a 20 sec neutron count to determine uranium, and after a 1274 sec decay period, they are counted for 496 sec in a fixed geometry for the short-lived gamma-ray activities. The electronic dead-time for a normal sediment sample is generally under 15%. Following the "shorts" count, the

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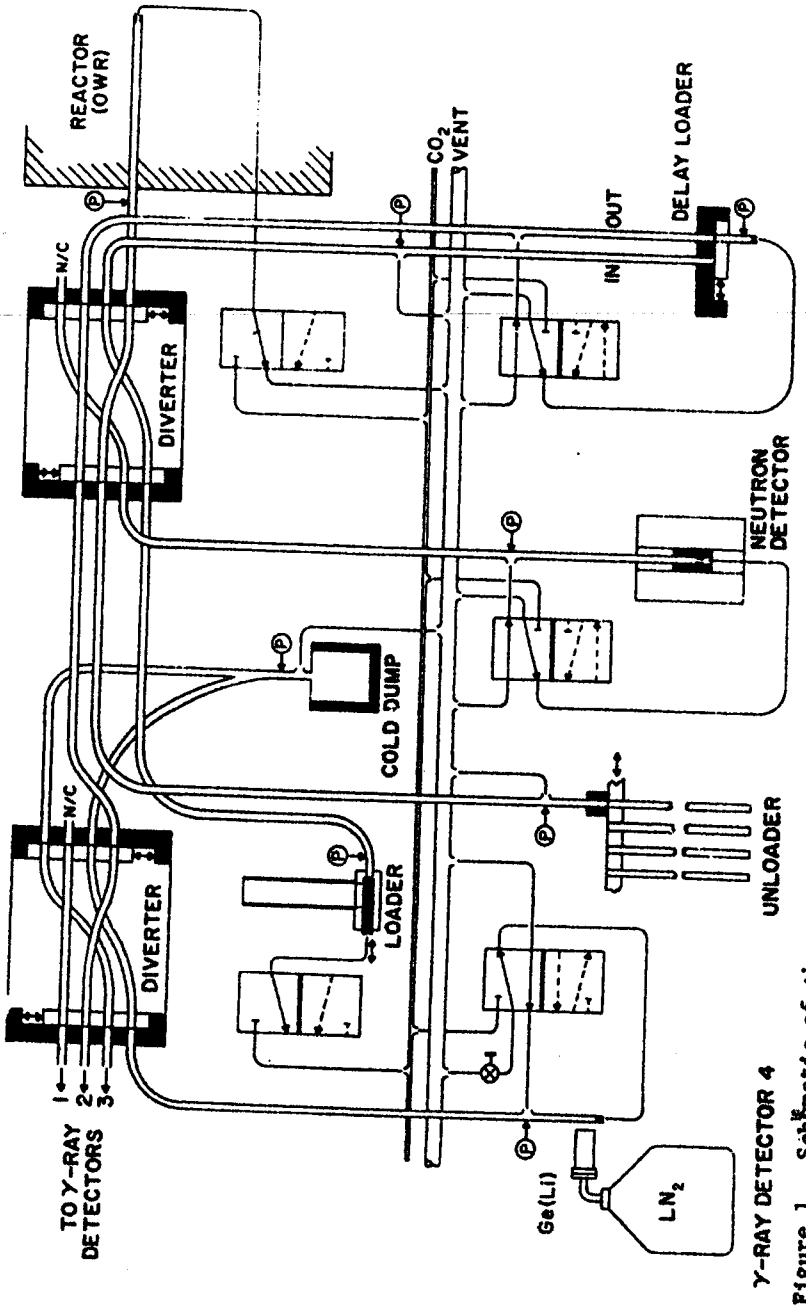

Figure 1. Schematic of the automated neutron activation system. P = Photocell, N/C = No Connection.

samples are returned to the reactor for an additional 96 sec irradiation to build up long-lived activities. The samples are then automatically unloaded and stored in pipes located underground for a 14-day decay period before being counted the third time. With each sample irradiation, a flux monitor reading is taken from a fission ion-chamber adjacent to the irradiation site and used for flux normalization.

EXPERIMENTAL

Pure element standards with a quoted metallic purity of 99.99% were used to prepare the trace element standards. The matrix used for the preparation of the pure element standards was silicon dioxide with a quoted metallic purity of 99.9% with a particle size less than 325 mesh. A Spex Industries 8000 Mixer/Mill was used for all mixing procedures. Polystyrene vials with methacrylate mortars were used for mixing the pure element standards.

A selected quantity of the stock pure element standard was pipetted onto 25 grams of silicon dioxide and evaporated to dryness under an infrared heat lamp. The standard was then mixed for 1 hour using the Spex Industries Mixer/Mill and triplicate splits taken to test for homogeneity. The standard deviation for the triplicate analysis was generally less than 2% for each standard prepared. Standards used for the "majors" were USGS standard rocks and NBS SRM's. Specifically the standards used were USGS QLO-1, STM-1, RGM-1, SCo-1, and NBS SRM's 1632a Coal and 1633a Coal Fly Ash.

The pure element and reference materials were irradiated following the activation scheme mentioned earlier in the text. The gamma-ray spectra are analyzed using an overlayed version of the computer code RAYGUN.[8,9] RAYGUN makes use of a library containing data on radionuclides of interest: half-life, cross-section, isotopic abundance, principal gamma-rays, and gamma-ray branching ratios. RAYGUN provides both qualitative and quantitative analysis of high resolution gamma-ray spectra. The code first determines a smooth background under a peak or peak-groupings then calculates whether the peak is too wide to be a singlet. If so, it attempts to split the peak according to the particular detector's characteristic peak shape at that energy. RAYGUN then calculates under each peak, or simply sums the area minus background for singlets or unsplittable groupings. Correction for known interferences is accomplished by extrapolating the intensity of the interfering line(s) from the intensities of the major lines of the interfering activity. The decay rate for each isotope is calculated from a weighted average of the various decay rates deduced from each of the gamma rays of the isotope. Elemental concentrations are then calculated from known cross sections, isotopic abundances, atomic weights, decay constants, neutron flux, and sample weight. There are 32 elements assayed from the automated analysis: 13 from the "shorts" analysis and 19 from the

"longs" analysis. They include Na, Mg, Al, Cl, K, Ca, Ti, V, Mn, Sr, Dy and U (DNA) for the "shorts" and Sc, Cr, Fe, Co, Zn, Rb, Sb, Cs, La, Ce, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Au and Th for the "longs". If one were to alter the counting scheme, additional radionuclides could be assayed at the expense of losing the high throughput achieved from the activation scheme described earlier. Other elements possible are Ga, As, W, Cd, Br, Au and Se.

RESULTS AND DISCUSSION

To evaluate the stability, accuracy and precision of the automated multidetector system, NBS SRM's 1632a Coal and 1633a Coal Fly Ash standards were used as the system evaluation materials. In-house and USGS rock standards were used to maintain a quality assurance program throughout the 3-month period this study was made. Long term stability was monitored using Na as a "shorts" reference element and Co as the "longs" reference element. These elements were chosen because there are no interfering peaks in their spectral analysis.

The results from the automated analysis of the NBS SRM's 1632a Coal and 1633a Coal Fly Ash are presented in Tables 1 and 2, respectively. The agreement of our elemental concentration with those of NBS and other values found in the literature is very good. From 50 data points accumulated over a period of 3 months, we find a standard deviation of 2.8% for the Na concentration and a 3.8% standard deviation for the Co concentration in 1633a Coal Fly Ash. It is important to recognize that these data points were collected from eight Ge(Li) gamma-ray detectors over the three month period.

In addition, we obtained values for several elements not previously assayed in NBS SRM 1633a Coal Fly Ash, including Dy, La, Eu, Tb, Yb, Lu, and Ta. We conclude that our systems have excellent long-term stability which is necessary for the production of high quality data.

Table 1. Multielement concentrations in NBS SRM 1632a Coal[a]. February 8 and 26, 1980 Activations

Element	Data Points	Average[b] ppm	Std Dev %	NBS[b] ppm	Literature[b] ppm
Na	24	884.	3.6		760[c], 850 ± 46[e]
Mg	3	1400	16		600-1300[c], 1300 ± 30[d]
Al(%)	24	3.07	4.1	(3.07)	2.97 ± 0.04[c], 2.9 ± 0.3[d], 3.01 ± 0.13[e]
Cl	24	897.	2.6		758 ± 50[c], 800 ± 70[d], 784 ± 17[e]
K(%)	18	0.43	15		0.41 ± 0.01[c], 0.42 ± 0.02[d], 0.42 ± 0.02[e]
Ca(%)	3	0.27	6.5		0.24 ± 0.02[c], 0.24 ± 0.02[d], 0.24 ± 0.02[e]
Ti	24	1720	9.8	(1750)	1650 ± 130[c], 1630 ± 70[d], 1620 ± 130[e]
V	24	46.9	5.4	44 ± 3	44[c], 44 ± 3[d]
Mn	24	33.7	3.6	28 ± 2	31 ± 2[c], 32 ± 3[d], 29 ± 5[e]
Ba	8	150	17		130[c], 122 ± 11[d]
Dy	22	2.56	10		2.2[c], 2.2 ± 0.3[d]
U[f]	24	1.28	5.9	1.28 ± 0.02	1.2 ± 0.1[c], 1.21 ± 0.1[d]
Sc	24	6.56	3.5	(6.3)	6.5[c], 6.8 ± 0.6[d]
Cr	24	36	17	34.3 ± 1.5	35[c], 34 ± 2[d]
Fe(%)	24	1.12	8.2	1.11 ± 0.02	1.13 ± 0.03[c], 1.16 ± 0.03[d], 1.11 ± 0.06[e]
Co	21	6.6	17	(6.8)	7.0[c], 6.5 ± 0.2[d]
Cs	3	2.4	35	(2.4)	2.0[c], 2.0 ± 0.3[d]
La	14	15	17		16[c], 18 ± 2[d]
Ce	24	31.1	11	(30)	29[c], 32 ± 4[d]
Sm	24	2.5	14		2.3 ± 0.3[c], 2.8 ± 0.3[d], 2.10 ± 0.07[d]
Eu	19	0.51	16	(0.54)	0.55[c], 0.55 ± 0.03[d]
Lu	8	0.18	37		0.2[c], 0.18 ± 0.03[d]
Hf	11	1.8	18	(1.6)	1.6[c], 1.55 ± 0.08[d]
Th	24	4.8	12	4.5 ± 0.1	4.5[c], 4.8 ± 0.2[d]

[a]Data from two automated systems which represents eight Ge-(Li) gamma-ray detectors. [b]Values are in ppm unless otherwise specified. The values in parenthesis are not certified by the NBS. [c]Ref. 5. [d]Ref. 4. [e]Ref. 5. [f]Ref. 7.

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ABSTRACT

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INTRODUCTION

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