ANALYSIS OF TRACES AT ORNL'S NEW HIGH-FLUX
NEUTRON ACTIVATION LABORATORY*

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ABSTRACT

A new facility for neutron activation analysis (NAA) with a thermal flux of $5 \times 10^{14} \text{ cm}^{-2} \text{ sec}^{-1}$ has recently been installed at the ORNL High Flux Isotope Reactor. This unusually high flux together with a small computer and necessary software for γ -ray spectrometry with a Ge(Li) detector makes possible shorter irradiation, faster data analysis, and more economical analysis than is possible using more conventional facilities. We discuss features and tests of the new High-Flux NAA Laboratory, as well as results of comparator and absolute NAA of several types of environmental matrices for mercury, cadmium, bromine, arsenic, chlorine and sodium.

NEW ANALYTICAL TRENDS AND THE NEW LABORATORY

The present need in biomedical and environmental sciences is for determination of many trace elements in a variety of samples. Thus, one approach is to develop methods for multielement analysis at reasonable cost.** In such determinations, however, quality cannot be sacrificed for speed. Our aim is to develop techniques (preferably instrumental) for simultaneous analysis of numerous trace elements while concurrently reducing the price of quality serial analyses for specific elements by non-destructive methods. The new High-Flux NAA Laboratory can meet these demands. The very high thermal neutron flux permits determination of elements with extreme sensitivity, while also requiring shorter irradiations. Thus, a larger number of samples can be irradiated than would be possible at a lower flux.

Figure 1 shows the new facility in detail; particularly, the pneumatic transfer system. Hot-sample handling cell and counting room are provided along

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with a computer-analyzer for processing spectra. We may transfer samples, automatically, to any of three stations: a sample-loading station shielded in a hot cell (No. 12, Fig. 1), an in-vessel irradiation station (No. 4), and an in-pool holding station (No. 8) to allow for preliminary decay of samples having high short-lived radioactivity. The in-vessel (irradiation) station, located in the reactor's beryllium neutron reflector (No. 3), is exposed to a thermal neutron flux of $5 \times 10^{14} \text{ cm}^{-2} \text{ sec}^{-1}$ and to a resonance neutron flux of $1 \times 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$. We may preset irradiation time so that the sample is automatically returned to either the loading or the holding station in approximately 3 seconds.

Because the irradiation station is in beryllium, the neutron flux gradient across the width of the rabbit is only 5%, on the average, as illustrated by Table I. This makes possible accurate analyses without detailed attention to the placement of samples in the capsules. For greater accuracy the rabbits can rotate during irradiation, in which case the flux gradient would be only 2.5% from outside to center. We have not found any measurable gradient along the capsule axis (Table I). The beryllium moderator also causes enhancement of the thermal to resonance flux ratio (~50), so that resonance activation is minimized, and absolute activation analysis accurately performed. Interfering fast-neutron products are also reduced.

Air columns stop the rabbits at both the loading and the in-vessel stations; we can thus irradiate fragile capsules without breakage. Because the very high neutron and gamma fluxes (~6 watt/g) in this facility cause excessive radiation damage to polyethylene rabbits, their use is limited to irradiations of up to 30 minutes. We use capsules made of high-purity graphite and magnesium (both fragile) for longer irradiations and/or to prevent excessive heating of samples. Polyethylene and graphite activate very little, and only ^{27}Mg (9.5 min.) is significantly induced in the magnesium capsules.

The counting-computing complex uses a Ge(Li) detector with 12% relative efficiency (75 cm^3), and a Nuclear Data 50/50 system, consisting of a 4096-word (24 bit) analyzer and a 8192-word (18 bit) PDP-15 computer with two readers for magnetic tape and one for paper tape. Presently, the software used to process gamma spectra consists of 17 subroutines divided into 9 relocatable overlays. The most important routines are:

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CALIB: Sets energy and counting efficiency scales for Ge(Li) spectra. Determines thermal and resonance neutron flux, from activation of gold and manganese monitors, by solving system of two equations.

NETPK: Searches spectra for peaks; computes energies, count-rates (total area minus base-line), photon-emission rates and corresponding statistical errors.

MULT: Finds peak multiplets (up to 5 components) and computes individual peak parameters (as NETPK).

SMPDPS: Computes (a) comparator activation analysis results from NETPK rates; (b) disintegration rates, by using NETPK rates and radioisotope nuclear data from a master tape; (c) absolute activation analysis results from disintegration rates and flux data (from CALIB).

LIM: Computes analytical limits of detection (basis: 3.5 standard deviations over background).

RESULTS AND DISCUSSION

Comparator Activation Analysis

Due to the importance of mercury in environmental studies, we analyzed a number of samples -- some of them N.B.S. standards and round-robin specimens -- nondestructively for mercury at the High Flux NAA Laboratory. Table II compares these results with those obtained either by other techniques or by conventional NAA methods. In some of the latter, mercury was separated radiochemically by first leaching samples with a nitric-sulfuric acid mixture and then precipitating mercuric sulfide for counting.

Most of the data show satisfactory agreement with those obtained by other methods, even at the lower ranges of concentration. The results for the Allen Steam Plant coal, however, show a serious positive systematic error. We list them to point out a pitfall encountered in NAA for mercury by counting 65-hr ^{197}Hg with the Ge(Li) detector. Rare-earth radionuclides formed in these samples by irradiation emit x-rays of various energies -- the 105 KeV photon of ^{155}Sm is very intense. These x-rays excite the K absorption edge (80.7 KeV) in the gold lining on the face of the Ge(Li) detector. The resulting fluorescence interferes seriously with the counting of the ^{197}Hg radiations -- particularly that of 77 KeV -- since these are all gold x-rays. We solved this problem by using the standard addition technique on the other samples, as Table II shows.

Mercury loss under irradiation is a serious problem in NAA, and was of concern to us in our facility, since we have a relatively high rate of gamma heating. Table III shows the effects of increasingly longer irradiations on known amounts of solutions of mercury nitrate, dried into irradiation capsules. No loss is observed during irradiations of up to 12 minutes in the High Flux NAA Laboratory. Our bombardments of mercury samples never exceeded 6 minutes.

We have also made some preliminary determinations of cadmium in the Allen Steam Plant samples. Contrary to statements that NAA is insensitive for this element, our results show that the method is feasible -- even without chemistry-- down to 1 ppm at the High-Flux NAA Laboratory.

Ecologists are concerned about transport of arsenic from sprayed plants, by insects. Grasshoppers were exposed for several days to water contaminated with arsenical insecticides. We later analyzed these insects for arsenic by counting the 559 KeV photon from 26.4 hr ^{76}As . Table IV lists results, which generally correspond to the increasing amounts of poisoning. Most analyses were nondestructive; we counted after sufficient decay of interference ^{24}Na (15.0 hr). The determinations corresponding to 0.015 and 0.15 ppm arsenic water levels required chemical separations, however. Here we dissolved the dried (or ashed) grasshoppers in nitric acid, added sodium bromide, boiled off the interfering bromine (2 or 3 times), and precipitated arsenic sulfide with thioacetamide for counting. The errors (Table IV) are acceptable throughout the range of concentrations found (0.48 - 903 ppm).

Absolute Activation Analysis

We have just begun to study environmental multielement baselines of pristine regions, and contamination levels of more polluted areas. Table V gives results for four background elements in clean samples of Whatman No. 42 air filter paper. We obtained the necessary thermal and resonance flux data by simultaneous bombardment of aluminum-diluted manganese ($\sigma_0 = 13.3\text{b}$, $I_0 = 15.6\text{b}$) and gold ($\sigma_0 = 98.8\text{b}$, $I_0 = 1558\text{b}$) monitors, and by using the CALIB subroutine at the PDP-15 computer. The table also shows satisfactory results of an accuracy test of the absolute activation analysis subroutines (NETPK and

SMPDPS) for which known concentrations of manganese and gold in aluminum (monitors) were redetermined. Clearly, the preliminary detection limits listed (subroutine LIM) can be easily improved and the number of elements increased, by adequate combination of irradiation and decay times.

Having proved the usefulness of the new High-Flux NAA Laboratory for serial quality trace analysis by the comparator method, we are now developing the absolute technique for multielement analysis. Both efforts are directed toward solution of environmental type problems.

TABLE I
FLUX GRADIENT ACROSS HFIR CAPSULE BY
TANTALUM ACTIVATION

Tantalum Wire Position	EXPERIMENT #1		EXPERIMENT #2		EXPERIMENT #3		EXPERIMENT #4
	Specific Activity ^c	Deviation	Specific Activity ^c	Deviation	Specific Activity ^c	Deviation	Specific Activity ^c
	cps/g	%	cps/g	%	cps/g	%	cps/g
WIDTH: ^a							
1	2210	0	9278	0	11888	0	9110
2	2276	3.0	9481	2.2	12072	1.6	9276
3	2311	<u>4.6</u>	9641	3.9	12352	3.9	9481
4	2301	4.1	9712	<u>4.7</u>	12508	<u>5.2</u>	9642
5	2217	0.32	9536	2.8	12256	3.1	9353
6	2231	0.95	9402	1.3	11958	0.59	9254
LENGTH: ^b							
Top	3851	0	3499	0			
Bottom	3796	-1.4	3544	1.3			

^aAround (cylindrical) rabbit circumference, clockwise. ^bSix Ta wires were placed vertically parallel, around the inside circumference of rabbit. ^cFrom ¹⁸¹Ta 112d.; sum of 1221 and 1121 KeV peaks after Ge(Li) counting. Normalized to equal decay. error 0.3%.

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Specific Activity ^c	Deviation	Specific Activity ^c	Deviation	Specific Activity ^c	Deviation	Specific Activity ^c	Deviation
cps/g	%	cps/g	%	cps/g	%	cps/g	%
2210	0	9278	0	11888	0	9110	0
2276	3.0	9481	2.2	12072	1.6	9276	1.8
2311	<u>4.6</u>	9641	3.9	12352	3.9	9481	4.1
2301	4.1	9712	<u>4.7</u>	12508	<u>5.2</u>	9642	<u>5.8</u>
2217	0.32	9536	2.8	12256	3.1	9353	2.7
2231	0.95	9402	1.3	11958	0.59	9254	1.6
3851	0	3499	0				
3796	-1.4	3544	1.3				

cylindrical) rabbit circumference, clockwise. ^bSix Ta wires were placed vertically and around the inside circumference of rabbit. ^cFrom $^{181}\text{Ta}(n,\gamma)^{182}\text{Ta}$ of 1221 and 1121 KeV peaks after Ge(Li) counting. Normalized to equal decay. Counting %.

TABLE II
COMPARISON OF MERCURY DETERMINATIONS AT THE
HIGH-FLUX NAA LAB. WITH THOSE BY OTHER METHODS

Series	Sample	Mass Spectrometry	Atomic Absorption ^a	Neutron Activation Analysis		
				High-Flux NAA Lab. (Nondestructive)	Conventional, with NaI (TI) ^a	
					Chem. Sep.	Nondestructive
	No.	ppm	ppm	ppm	ppm	ppm
Round Robin	Sediment:					
	72C5643		113 - 110	100 - 101	135 - 115	143 - 128
	72C5644		42.9 - 43.9	38.6 - 38.7	47.0 - 46.6	49 - 43
	72C5645		.089 - .056	< 1 - < 1	.05 - .06	
N.B.S. Standards ^b	Orchard Leaves	.12 - .13	.12 - .13	.167	.158	
	Coal			.106	.105	
Allen Steam Plant	Coal: ^c					
	A		.064	.18	.060	
	B		.069	.19		
	C		.076	.32	.049	
	D		.060	.26		
Allen Steam Plant	Slag:					
	E(Solid)			.09		
	F(Water)		.001	n.d.		
	G(Solid)			.07		

^a Private communications from L. C. Bate (NAA) and C. Feldman (atomic absorption), O.R.N.L., Oak Ridge, Tenn., U.S.A.

^b N.B.S. Values: Orchard Leaves .155 ppm; Coal .13 ppm. ^c These results have large systematic error due to interfering x-ray fluorescence from detector (see text).

TABLE III
INFLUENCE OF HFIR IRRADIATION LENGTH
ON MERCURY LOSS (MAGNESIUM RABBIT)

Irradiation Length	Amount Hg used	Specific Activity ^a	Deviation (from avge. 4 min.)
min.	ug	cps/ug	%
1		251	-3.6
2		254	-2.5
3		252	-3.3
4		262	0.58
4 ^b	19.9	259	-0.58
4	6.74	265	1.7
6	7.32	259	-0.58
12	7.33	259	-0.58
18	7.20	221	-15.2
18	6.92	205	-21.3

^aFrom $^{202}\text{Hg} (n, \gamma) ^{203}\text{Hg}$, 45.8 d; normalized to 1 min. irradiation and to equal decay, after Ge(Li) counting of 279 KeV peak. Counting error 1%. ^bStart of second experiment series; average of this result with 4-min result of first series is basis for deviation % calculation.

TABLE IV
As DETERMINATION IN GRASSHOPPERS
SUBJECTED TO ARSENICAL DIETS

Arsenical Used	As Level In Water Feed	As Concentration In Grasshoppers		Counting Error ^a
		1st Set	2nd Set	
	ppm	ppm	ppm	%
As ₂ O ₃	0.015	0.48	0.48	6.3
	0.15	1.6	0.69	1.4
	1.50	6.2	5.1	5.9
	15.0	65.3	60.4	6.8
	150	97.6	158	8.7
As ₂ O ₅	0.15	2.3		
	15.0	33.8	65.3	13.3
	150	107	101	8.1
	1500	164	374	2.6
Cacodylic Acid	1.50			
	15.0	75.4	(21)	(45)
	150	97.9	285	4.5
	1500	78.7	472	2.4
	"	429		
	"	903		
	"	458		
	15000		437	2.3
Phytar	0.15	3.5		
	15.0	16.6	(5.2)	(40)
	150	330	150	5.9
	1500	769	660	1.4

^aOnly for 2nd. set of grasshopper samples.

TABLE V
PRELIMINARY ABSOLUTE NAA RESULTS

Element	Measured Product		Analysis of Whatman No. 42 Air Filter Paper		Test of Absolute Activation Analysis Method		Error	Corresponding Detection Limits ^c
	Nuclide	Half-Life (hr.)	Sample 1 (p.p.m.)	Sample 2 (p.p.m.)	Found (%)	Known (%)	(%)	(p.p.m.)
Na	²⁴ Na	15.0	16.8	16.8			0.7 - 0.6	0.09
Cl	³⁸ Cl	0.62	291	282			1.2 - 1.7	3.1
Mn	⁵⁶ Mn	2.58	0.27	0.26	0.0887	0.087	0.9 - 3.8 ^a -0.3 ^b	0.002
Br	⁸² Br	35.3	0.24	0.22			4.2 - 5.6	0.009
Au	¹⁹⁸ Au	64.8			0.109	0.109	0	

^aWhatman filter Analysis. ^bTest of absolute A.A. subroutine. ^cOnly for conditions of 10-min. irradiation and 3-4 hr. decay.