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ANALYSIS OF STANDARD REFERENCE MATERIALS
BY ABSOLUTE INAA*

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Three standard reference materials were analyzed by a method of absolute IMAA. Two different light water pool-type reactors were used to produce equivalent analytical results even though the epithermal to thermal flux ratio in the reactor was higher than that in the other by a factor of two.

Introduction

Neutron activation analysis (using reactor neutrons to induce fission) can be done in a comparative mode by concurrent irradiation of known weights of elemental standards and of samples to be analyzed. Or, the same analysis can be done in an absolute mode by measuring the neutron flux and using thermal and fast neutron cross section values to calculate the amounts of radionuclides that would be produced per microgram of each element present. In both modes, the amount of element in the sample analyzed is determined from the ratio of the disintegration rate for each radionuclide product in the sample to that expected per microgram of element irradiated. In the Environmental Sciences Division of Lawrence Livermore

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National Laboratory, the second method was used for analysis of samples irradiated in the 3 MW Livermore Pool Type Reactor (LPTR). This reactor was moderated and cooled by light water in a tank-type pool. It was fueled by fully enriched ^{235}U fuel elements of the materials-test-reactor type. The epithermal to thermal neutron flux ratio in the LPTR varied with location in the reactor and in the irradiation positions used for activation analysis was observed to range between .02 and .05. In March 1980 the LPTR was shut down and subsequent INAA irradiations were done at the University of California, Berkeley, using the 1 MW TRIGA Mark III reactor operated by the Department of Nuclear Engineering. This reactor is also light water cooled and moderated. However, in the irradiation position used (the "central thimble" position) the epithermal to thermal neutron flux ratio was found to lie in the range .085 to .105 which is significantly higher than that in the LPTR.

As a quality control measure in the analysis program we had periodically included in the sample sets irradiated in the LPTR standard reference materials - NBS SRM 1633 Flyash and IAEA Soil 5. When the irradiations were transferred to the TRIGA reaction we made additional irradiations of these materials to determine whether our analytical procedure would still be workable at the higher epithermal flux ratio. The analysis results for these two materials collected over a three-year interval and at a variety of epithermal/thermal flux ratios are reported below. In recent months, using the TRIGA facility we have made a number of irradiations of ten milligram quantities of SRM 361, an iron alloy for which a number of elements of interest accurately know. Results for this material are also included.

Procedure

Experimental

Two hundred milligram aliquots of the dried soil and flyash materials were pelletized by mixing the powder with an equal weight of microcrystalline cellulose and compressing into a disc of .75 cm diameter and .15 cm thickness. Irradiations were carried out in sealed aluminum capsules for sufficient time to provide a total of 10^{17} neutron per cm^2 . Each capsule irradiated contained two or more dual flux monitors, each of which was a 50 μm aliquot of an acid solution evaporated onto a 5/8" diameter filter disc to give 5 micrograms each of uranium and scandium. Samples and flux monitors were counted on lithium-drifted germanium detectors for 8000 seconds after 3 days cooling and for 20,000 seconds after 15 days cooling. The spectral data were collected in 4096 channel analyzers, stored on magnetic tape and transferred to a Control Data Corporation 7600 computer for analysis.

Calculations

All spectral data were analyzed by computer code GPMMAI developed at LLNL by Gammink and Niday.¹ The code operates in two steps, first the spectral data are fitted to a spectrum in which individual photopeaks and a smoothed baseline are determined. Photopeak energies and absolute disintegration rates in each photopeaks are calculated based on linearity, counting efficiency, and peak shape parameter data furnished by the experimenter in the form of sets of coefficients for polynomial functions and a peak shape function. The values of the coefficients are determined from prior analysis

of gamma ray calibration standards, such as NBS SRM 4215-F, Mixed Radionuclide Gamma-Ray Emission-Rate Point Source Standard, on which our current calibrations are based. Under the irradiation, cooling, and counting conditions described, a typical flyash spectrum will contain some 90 resolved photopeaks at 3 days and perhaps 150 at 15 days. The second step in the analysis of these spectra is to determine the least-squares solution to a matrix of equations developed by associating each of the photopeaks found with all possible contributing product nuclides. This requires that the absolute branching intensity for each gamma-ray for each nuclide be provided. This data is supplied to GAMANAL as a binary library. The one used by us contains all (n, γ) products of greater than 2 minute half-life and greater than 90 Kev in energy. It also contains gammas for Fission products of greater than .1% yield in thermal fission of ^{235}U and (n,p) products such as ^{58}Co and ^{54}Mn which are commonly produced in reactor fluxes.

For each nuclide all gamma-rays of greater than one percent relative intensity are included. Where a nuclide has only a few gamma-rays, all are included in the library. The library we use carries 185 radionuclides and 1611 gamma-rays. The final output of the GAMANAL code is a table of radionuclides, for each of which is given the absolute disintegration rate at the time the sample was counted. A typical flyash spectral analysis will list some 25 nuclides at 3 days and 35 at 15 days.

The disintegration rates of the nuclides at count time are used as input to a second computer code NADAC² which combines irradiation data, thermal and epithermal flux values and thermal and epithermal cross-section data to determine elemental abundances in the irradiated samples. The relationship

between element amount and disintegration rate used is:

$$w = \frac{A_{\text{OBSVD}}}{kF(\lambda t) [\phi_0 \sigma_0 + \phi_1 RI]}$$

where w = element amount in micrograms
 A_{OBSVD} = absolute disintegration rate of radionuclide produced
 $F(\lambda, t)$ = radioactive decay term for nuclide measured
 ϕ_0 = thermal neutron flux (units of 10^{13} neutron/cm² sec)
 ϕ_1 = epithermal neutron flux (units of 10^{13} neutron/cm² sec)
 σ_0 = thermal neutron cross-section (bans)
 RI = resonance integral cross-section (bans)
 k = constant which relates cross-sections to production.

The function $F(\lambda, t)$ depends on whether nuclide counted is that which was formed or is a daughter. For the first case, in which a radiation time, τ , a cooling time, y , and counting time, c , occurred and radioactive decay constant of the nuclide counted is λ ,

$$F(\lambda, t) = (1 - e^{-\lambda\tau})e^{-\lambda y}(1 - e^{-\lambda c})/e^{-\lambda c}$$

$$k = 3.614 \times 10^6 \text{ G/M}$$

where G = isotopic abundance of target nuclide in percent
 M = atomic mass of element in grams

All the nuclear parameters required by NADAC are stored in a library. A listing of the values used has been reported.²

Results

The values found for the elemental compositions of the reference standards are given below. In this treatment, we have used the epithermal/thermal flux ratio determined from the uranium/scandium dual flux monitors ratios for each irradiation. This nuclide pair is particularly useful for resolving the two fluxes. For the reaction $^{235}\text{U}(n, \gamma)^{236}\text{U}$, $\frac{RI}{\sigma_0} = 102.94$ while for $^{45}\text{Sc}(n, \gamma)^{46}\text{Sc}$ the same ratio is only 0.44. The thermal neutron flux was calculated for each sample by using the scandium in the sample as

internal flux monitor. SRM 1633 scandium was taken to be 26.7 $\mu\text{g/gm}$ while for IAEA Soil 5 the scandium was taken to be 15.3 $\mu\text{g/gm}$. We could have used the externally determined thermal flux (from U/Sc) but the internal flux is more accurate and provides a better picture of how the analysis results may vary with changing epithermal/thermal rates.

Although we have data on more than 30 elements space does not permit us to cover them all. We have instead chosen to include only those 10 elements for which data for the Iron alloy, SRM 361, are available. This set includes a wide range of epithermal/thermal cross-section ratios and will serve to illustrate the effectiveness of the methods used. These results are given on an element by element basis in Tables 1 through 10.

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Table 1

Comparison of Elemental Concentration of Chromium (ppm)
 $^{50}\text{Cr}(n,\gamma)^{51}\text{Cr}$

Nuclear Parameters: $G = 4.31\%$ $E_\gamma = 320.1 \text{ Kev}$ $P_\gamma = .098$ $\sigma_0 = 15.5 \text{ b}$ $RI/\sigma_0 = .57$								
Reference Material	This Work		Other					
	LPTR	IRIGA		Ref		Ref		Ref
IAEA Soil 5	33.2 ± 1.0	30.8 ± 1.0	38 ± 2	4	30 ± 3	5	--	
NBS Flyash (SRM1633)	132 ± 2	128 ± 2	129 ± 3	6	127 ± 6	7	131 ± 2	8
ASI 4340 Steel (SRM361)	--	$.00695 \pm .00006$	--		--		.00694	8

Table 2

Comparison of Elemental Concentration of Iron (%)

 $^{58}\text{Fe}(\text{n},\gamma)^{59}\text{Fe}$

Nuclear parameters: $G = .33\%$ $E_\gamma = 1099.32 \text{ Kev}$ $P_\gamma = .562$ $\sigma_0 = 1.14 \text{ b}$ $RI/\sigma_0 = 1.06$								
Reference Material	This Work		Other					
	LPTR	TRICA		Ref		Ref		Ref
IAEA Soil 5	$4.68 \pm .04$	$4.72 \pm .04$	4.85 ± 1.0	4	$4.45 \pm .19$	5	--	
NBS Flyash (SRM1633)	$6.25 \pm .04$	$6.10 \pm .06$	$6.20 \pm .05$	6	$6.2 \pm .3$	7	6.18	8
ASI 4340 Steel (SRM361)	--	95.6	--		--		95.6	8

Table 3

Comparison of Elemental Concentration of Cobalt (ppm)

 $^{59}\text{Co}(n,\gamma)^{60}\text{Co}$

Nuclear Parameters: $G = 100\%$ $E_\gamma = 1173.23 \text{ Kev}$ $P_\gamma = 1.000$ $\sigma_0 = 37.5 \text{ b}$ $R1/\sigma_0 = 2.00$								
Reference Material	This Work		Other					
	LPTR	TRIGA		Ref		Ref		Ref
IAEA Soil 5	$14.7 \pm .1$	$14.7 \pm .2$	$14.2 \pm .3$	4	$14.8 \pm .8$	5	--	
NBS Flyash [SRM1633]	$40.2 \pm .4$	$39.3 \pm .3$	$40.3 \pm .4$	6	41.5 ± 1.2	7	(38)	8
ASI 4340 Steel [SRM361]	--	$(.0305 \pm .0003)\%$	--		--		.032%	8

Table 4

Comparison of Elemental Concentration of Arsenic (ppm)

 $^{75}\text{As}(n, \gamma)^{76}\text{As}$

Nuclear Parameters: $G = 100\%$ $E_\gamma = 559.07 \text{ Kev}$ $P_\gamma = .446$ $\sigma_0 = 4.0 \text{ b}$ $RI/\sigma_0 = 15.75$								
Reference Material	This Work		Other					
	LPTR	TRIGA		Ref		Ref		Ref
IAEA Soil 5	$88.6 \pm .9$	$86.4 \pm .9$	--		93.9 ± 7.5	5		
NBS Flyash [SRM1633]	$50.3 \pm .5$	$50.1 \pm .5$	$61.5(T)$ $58.0(E)^*$	6	58 ± 4	7	61 ± 6	8
ASI 4340 Steel [SRM361]	--	$(.0172 \pm .0002)\%$					.017%	8

* (T) = Thermal (E) = Epithermal

Table 5

Comparison of Elemental Concentration of Selenium (ppm)

Nuclear Parameters: $G = .87\%$ $E = 136.00 \text{ Kev}$ $P = .586$ $\sigma_s = 46 \text{ b}$ $R1/\sigma_s = 9.00$							
Reference Material	This Work		Other				
	LPR	TRIGA	Ref		Ref		Ref
IAEA Soil 5	--	$1.2 \pm .8$	--	(1,4)	5	--	
NBS Flyash (SRM1633)	$9.2 \pm .8$	$9.4 \pm .4$	$10.8 \pm .8$	6	10.2 ± 1.4	7	$9.4 \pm .5$ 8
AS1 4340 Steel (SRM361)	--	$(.0039 \pm .0002)\%$	--	--	--	(.004%)	8

Table 6

Comparison of Elemental Concentration of Molybdenum (ppm)
 $^{99}\text{Mo}(n, \gamma)^{99}\text{Mo}$

Nuclear Parameters: $\sigma = 23.78\%$ $E = 739.46 \text{ KeV}$ $\lambda = .1058$ $\sigma_a = .136 \text{ b}$ $R1/\sigma_a = 49.2$							
Reference Material	This Work ^a		Other				
	LTP	TRI-A	Ref		Ref		Ref
IAEA Soil 5	$1.9 \pm .5$	$2.3 \pm .4$	--	(1.7)	5		
NBS Flyash [SRM1633]	16.5 ± 1.4	$21.9 \pm .9$	22.3 ± 1.6	6	--	--	
AST 4340 Steel [SRM361]	--	$(.187 \pm .002)\%$	--	--	--	.19%	8

^a ^{99}Mo values were corrected for ^{235}U fission produced ^{99}Mo .

Table 7

Comparison of Elemental Concentration of Antimony (ppm)
 $^{121}\text{Sb}(n, \gamma)^{121}\text{Sb}$; $^{123}\text{Sb}(n, \gamma)^{123}\text{Sb}$

Nuclear Parameters:		57.25% G= 42.75%	564.08 KeV E= 602.79 KeV	1210 1920	5.90 b 3.78 b	R1/σ ₀ = $\frac{28.3}{26.2}$		
Reference Material	This Work				Other			
	LEIR	TRIGA		Ref		Ref		Ref
IAEA Soil 5	14.08 ±	15.30 ± .07	14.8 ± .8	4	14.3 ± .2	5	--	
NBS Flyash [SRM1633]	6.13 ± .06	6.41 ± .06	6.0 ± .2	6	6.9 ± .6	7		
ASI 4340 Steel [SRM361]	--	(0.00426±.0005)%		--	--		.0042%	8

Table 8

Comparison of Elemental Concentration of Lanthanum (ppm)
 $^{139}\text{La}(n, \gamma)^{140}\text{La}$

Nuclear Parameters: $\phi = 10.91\%$ $E = 1596.20 \text{ KeV}$ $P = .9552$ $\sigma = 9.18 \text{ b}$ $R1/\sigma_c = 1.372$							
Reference	This Work		Other				
Material	LPIR	FWGA	Ref		Ref	Ref	
IAEA Soil 5	$29.6 \pm .5$	$28.4 \pm .5$	27.3 ± 1.0	4	28.1 ± 1.5	5	
NBS Flyash [SRM1633]	$75.3 \pm .6$	$74.3 \pm .5$	$84.0(T)$ $81.2(E)^*$	6	82 ± 2	7	
ASI 4340 Steel [SRM361]	--	$(.00098 \pm .00001)\%$	--		--	.001%	8

* (T) = Thermal Neutron, (E) = Epithermal neutron analysis

Table 9

Comparison of Elemental Concentration of Tantalum (ppm)
 $^{181}\text{Ta}(n,\gamma)^{182}\text{Ta}$

Nuclear Parameters: $G = 100\%$ $E_\gamma = 1121.28 \text{ Kev}$ $P_\gamma = .352$ $\sigma_s = 19.1 \text{ b}$ $R1/\sigma_s = 32.72$								
Reference Material	This Work		Other					
	LPTR	TRIGA	Ref		Ref		Ref	
IAEA Soil 5	$.65 \pm .03$	$.73 \pm .02$	$.81 \pm .02$	4	$.76 \pm .06$	5		
NBS Flyash (SRM1633)	$1.65 \pm .04$	$1.71 \pm .05$	$2.00 \pm .06$	6	$1.8 \pm .3$	7		
ASL 4340 Steel (SRM361)		$(.0200 \pm .0001)\%$					.020	8

Table 10

Comparison of Elemental Concentration of Tungsten (ppm)

 $^{186}\text{W}(n, \gamma)^{187}\text{W}$

Nuclear Parameters: $G = 28.41\%$ $E = 685.70 \text{ KeV}$ $P = .320$ $\sigma = 36.6 \text{ b}$ $R1/\sigma = 11.64$								
Reference Material	This Work		Other					
	LPT	TRIGA	Ref			Ref		Ref
IAEA Soil 5	$5.3 \pm .4$	$5.4 \pm .4$	--		(5.1)	5	--	
NBS Flyash (SRM1633)	$5.5 \pm .3$	$5.1 \pm .2$	3.9(T) 4.2(E)*	6	4.6 ± 1.6	7		
ISI 4340 Steel (SRM361)	--	$(.0173 \pm .0001)\%$	--		--		.017%	8

* (T) = Thermal Neutron, (E) = Epithermal neutron analysis