Part IX

Radionuclide Production and Activation Analysis

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SECTION I

Radionuclide Production

A. Reactor Production: Radionuclides produced by neutron irradiation or by neutron induced fission. Nuclei produced are neutron rich so decay by β^- emission.

1. can irradiate more than one sample simultaneously
2. can irradiate large samples
3. thermal neutron capture cross-sections are relatively high;

$$\sigma_n \propto \frac{1}{E_n} \qquad (1)$$

(thermal neutrons-relatively low energy neutrons with a thermal (Boltzmann) distribution of energies)

4. product nuclei are usually isotopic with target
5. fission products can be carrier free (not diluted by non-radioactive isotopes.

B. Production by Particle Accelerator: Radionuclides produced by bombardment of charged particles with emission of one or more light particles (neutrons,

protons, deuterons, etc.) Nuclei produced are neutron deficient and decay by E.C. or β^+ emission.

Characteristics:

1. only one sample irradiated at a time
2. only surface of solid sample is irradiated
3. charged particle reaction cross-sections are much lower than thermal neutron capture (σ_n, γ) cross section
4. product nuclei are usually not isotopic with target material

C. Choice of Mode of Radionuclide Production

1. Considerations involving time
   a. distance from production site and shipping time
   b. length of time of separation and purification
   c. length of time of experiment
2. Consideration of specific activity
   a. carrier free activity requires accelerator or fission produced activity

3. Consideration of cost

   a. economically, reactor produced activities are preferred

D. Quantitative Aspects of Radionuclide Production

Table of Notation

X - specific isotope of element X involved in the production of the desired radionuclide

Y - desired nuclide produced in the reaction Y may or may not be the same element as represented by X

N_X - number of atoms of X in a sample of $\underline{w}$ g. of the element of atomic weight $\underline{M}$; the total number of atoms of the element multiplied by the fractional isotopic abundance, f, of X.

$$N_X = 6.02 \times 10^{23} \cdot \frac{w}{M} \cdot f \qquad (2)$$

N_Y - number of atoms of Y

λ - decay constant of Y in sec^{-1}

σ - cross section for the production of Y from X in cm^2

Φ - particle flux from reactor or accelerator

T - irradiation time

t - time after end of irradiation

1. Rate of Production of Desired Nuclide

$$A_y = N_x \sigma \Phi (1-e^{-\lambda T}) \tag{3}$$

a. if $T >> t_{1/2}$

$$A_y = N_x \sigma \Phi \tag{3a}$$

b. If $T << t_{1/2}$

$$A_y = N_x \sigma \Phi \lambda t \tag{3b}$$

c. Units of N_x and ϕ

TABLE I

	Reactor	Accelerator
N_x	Total number of target atoms	Total number of target atoms/cm^2
Φ	neutrons/cm^2/sec	charged particles/sec

2. Rate of Decay of Product after Irradiation

$$A_y = N_x \sigma \Phi (1-e^{-\lambda T}) e^{-\lambda t} \tag{4}$$

3. Determination of Necessary Irradiation Time

$(1-e^{-\lambda T})$- saturation factor

When $T = t_{1/2}$ 50% saturation

$T = 2t_{1/2}$ 75% saturation

$T = 3t_{1/2}$ 87% saturation

Usually irradiate for 1 or 2 half lives

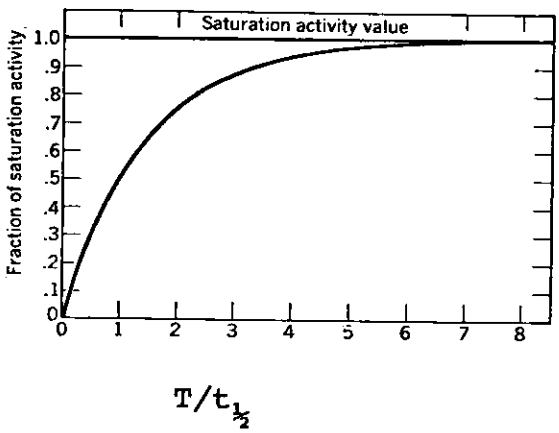


FIG. 1. The rate of approach to saturation in production of a radioactive species as a function of the irradiation time in half life units.

SECTION II

Activation Analysis (AA)

A method of elemental analysis using formation of radionuclides; neutron irradiation (neutron activation analysis, NAA) most common, but irradiation by various charged particles also used.

A. Basic Activation Equation

$$W = \frac{A \cdot M}{\sigma \Phi f (1-e^{-\lambda T}) \ (6.02 \times 10^{23})} \qquad (5)$$

W = weight of element irradiated

A = induced activity in dps at end of irradiation

M = atomic weight of that element

f = fractional isotopic abundance of the nuclide acting as target

B. Comparative Method

Difficult to know cross section, σ, and flux, Φ, accurately so use comparison with activity produced in standard sample.

$$\frac{\text{Weight of element in unknown}}{\text{Weight of element in standard}} = \frac{\text{Activity of element in unknown}}{\text{Activity of element in standard}} \qquad (6)$$

Measurements are relative in both the production and detection steps. Some standards available from NBS (Table 2).

TABLE 2

Composition values for NBS-SRM 614, 615; trace elements in a glass matrix, 1 ppm from certificate of analysis (revised Aug. 3, 1972).

Element	Value
Antimony	1.06
Boron	1.30±0.2
Cadmium	0.55
Cobalt	0.73±0.02
Copper	1.37±0.07
Europium	0.99±0.04
Gallium	1.3
Gold	0.5
Iron	13.3±1
Lanthanum	0.83 0.02
Lead	2.32±0.04
Nickel	0.95
Potassium	30 ± 1
Rubidium	0.855±0.005
Scandium	0.59±0.04
Silver	0.42±0.04
Strontium	45.8±0.1
Thallium	0.269±0.005
Thorium	0.748±0.006
Titanium	3.1±0.3
Uranium	0.823±0.002

C. Types of AA

1. Instrumental Activation Analysis (IAA)

The radionuclides produced in the activation are identified instrumentally by detecting their characteristic gamma spectra using Ge(Li) or NaI (Tl) spectrometry.

2. Radiochemical Activation Analysis (RAA)

The desired radionuclides are isolated using radiochemical techniques and counted.

3. Comparison of IAA and RAA

IAA is non-destructive, lends itself to the measurement of short-lived activities and to automated analysis.

RAA - original sample is altered; RAA may be necessary if interferring radionuclides prevent accurate measurement of the desired activities by IAA.

D. Typical Steps in AA

1. Design of experiment

   a. Choice of nuclear reaction based on

      1) reaction cross section

      2) particle flux, Φ, available at irradiation facility

      3) decay scheme of desired activity

      4) consideration of possible interfering reactions

   b. Determination of irradiation time

2. Sample preparation

   a. Sample and standard should be prepared in exactly the same manner, i.e. same chemical treatment.

   b. Weights of sample and standard should be the similar and known accurately.

3. Irradiation of both sample and standard

4. Chemical isolation of activities of interest, if necessary

5. Measurement of activities in sample and in standard by appropriate detection system

   a. short-lived nuclides: must count immediately after irradiation

   b. Longer lived nuclides: irradiate for long periods, allow short lived activities to decay before counting

   c. If γ ray counting, should follow decay of two γ rays in decay sequence of nuclide to verify radiochemical purity

E. Advantages and Disadvantages of AA

Advantages

1. Trace analysis - micro- to pico-gram (10^{-6} - 10^{-12}g) sensitivity level

2. Simultaneous determination of several elements possible

3. Can be nondestructive

4. Often accuracy of few percent at nanogram level

5. Freedom from reagent and laboratory contamination concerns

Disadvantages

1. Cost of irradiation

2. Expensive equipment required

3. Precaution required for working with higher than normal level of radioactivity

Periodic Table of the Elements
Activation analysis sentivities

Sensitivities are expressed as the micrograms of the naturally occurring element that must be present in the entire sample to be detected and determined by the Activation Analysis Service at General Atomic. By special arrangement, the sensitivities of many of the elements can be increased up to 100-fold. Sensitivities are for interference-free conditions.

1 H NA																	2 He NA
3 Li 0.0008 p	4 Be 15. p											5 B 1.1 p	6 C 0.1c	7 N 1.c	8 O 1.c	9 F 0.4	10 Ne 2.
11 Na 0.004	12 Mg 0.5											13 Al 0.004	14 Si 1. FS	15 P 0.2 b	16 S 4. bFS	17 Cl 0.05	18 Ar 0.002
19 K 0.2	20 Ca 4.	21 Sc 0.001	22 Ti 0.1	23 V 0.002	24 Cr 0.3	25 Mn 0.0001	26 Fe 2. FS	27 Co 0.01	28 Ni 0.7	29 Cu 0.002	30 Zn 0.1	31 Ga 0.002	32 Ge 0.1	33 As 0.005	34 Se 0.01	35 Br 0.003	36 Kr 0.01
37 Rb 0.02	38 Sr 0.005	39 Y 0.4	40 Zr 0.8	41 Nb 3.	42 Mo 0.1	43 Tc NA	44 Ru 0.04	45 Rh 0.005	46 Pd 0.03	47 Ag 0.004	48 Cd 0.005	49 In 0.00006	50 Sn 0.03	51 Sb 0.007	52 Te 0.03	53 I 0.002	54 Xe 0.1
55 Cs 0.001	56 Ba 0.02	57 La 0.005	72 Hf 0.0006	73 Ta 0.1	74 W 0.004	75 Re 0.0008	76 Os 1.	77 Ir 0.0003	78 Pt 0.1	79 Au 0.0005	80 Hg 0.08	81 Tl 1.b	82 Pb 0.5 p	83 Bi 1.b	84 Po NA	85 At NA	86 Rn NA
87 Fr NA	88 Ra NA	89 Ac NA															

L	58 Ce 0.2	59 Pr 0.03	60 Nd 0.03	61 Pm NA	62 Sm 0.001	63 Eu 0.0001	64 Gd 0.007	65 Tb 0.03	66 Dy 0.00003	67 Ho 0.003	68 Er 0.002	69 Tm 0.2	70 Yb 0.02	71 Lu 0.0003
A	90 Th 0.2	91 Pa NA	92 U 0.003	93 Np NA	94 Pu NA	95 Am NA	96 Cm NA	97 Bk NA	98 Cf NA	99 Es NA	100 Fm NA	101 Md NA	102 No NA	103(Lw) NA

Key
Atomic number → 33 As ← Symbol
0.005 ← Sensitivity in micrograms (interference free)

FS - Fast neutrons Fission spectrum; b - Beta count. p - Reactor pulse;
c - Bremsstrahlung radiation required. NA - Analysis not normally performed at GGA

FIG. 2. Table of activation analysis sensitivities as offered by the General Atomic Company, San Diego, Calif.

D. Applications of AA

1. Biological: trace elements in living systems, in vivo analysis, toxicology, metabolic and pathological studies.

2. Forensic science

3. Industrial: quality control, trace elements in metals, foods, semiconductors, etc.

4. Environmental: determination of trace elements in water, sediments, rocks, aersols, etc.

TABLE 3

Estimated Detection Limits of Instrumental Neutron Activation Analysis of Biological Material (μg/g Dry Tissue)

Element	*Typical Concentration In Marine Organisms	Detection Limit**
Na	500-1500	0.05
K	1000-30,000	20
Rb	0.5-8	1
Cs	0.02-0.4	0.0001
Fe	1-500	2
Zn	10-200	0.5
Br	10-200	0.05
As	<1-50	0.3
Cd	<0.1-10	1
Ag	<0.001-5	0.001
Co	0.001-0.5	0.001
Cr	<0.02-1	0.02
Hg	0.05-5	0.02
Se	0.5-50	0.05
Sb	0.0001-0.05	0.001
Sc	0.00001-0.002	0.00005

* Typical Ranges in various tissues, with the low ranges usually associated with muscle and high ranges with liver.

** 300 mg of freeze-dried tissue; integral thermal neutron exposure of 3×10^{17} n/cm^2; 20 min. and 1000 min. counts after decay periods of 3 to 5 days and 20 to 30 days, respectively; 20 to 40 cc Ge(Li) diode detection, except where specified.

TABLE 4

Estimated Minimum Detectable Concentrations of Pollutant Elements in Seawater by INAA and by NAA with Separations

Trace Element	Typical Reported Concentrations in Open Ocean (micrograms/liter)	Minimum Detectable Concentrations (in micrograms/liter)	
		INAA*	NAA with Separations**
Hg	0.02-0.2	0.05	0.001
Cd	0.06-0.7	16,000	0.001
Ag	0.002-0.05	1.0	0.003
As	2-3	Not Possible	0.0001
Cu	0.5-2	Not Possible	0.002
Cr	0.02-0.6	0.03	0.003
Zn	0.5-10	0.02	0.01
Sn	0.02	Not Possible	9
Se	0.08	0.2	0.02
Sb	0.2	0.02	0.00003

* 25 ml seawater; 24 hour irradiation at 10^{13} n/cm^2/sec; 40 days decay; 1000 minute count on 20 cc Ge(Li) diode detector; based on 3σ above Bkg-Compton contribution in peak areas.

** 500 ml seawater; elements chemically separated; 24 hour irradiation at 10^{13} n/cm^2 sec; 3 days decay; 500 minute count on a 20 cc Ge(Li) diode detector; based on twice Bkg contribution in peak areas.

TABLE 5

Estimated Detection Limits for the INAA of Trace Elements In Marine Sediments

Element	Typical Concentration Ranges in Marine Sediments (µg/gm)	INAA Sensitivity* (µg/gm)
Ag	0.01-0.5	0.1
Al	10,000-90,000	10
As	2.20	1
Ba	60-8100	100
Ce	40-70	5
Cd	205	10
Co	1-200	0.1
Cr	10-200	0.8
Cs	0.3-15	0.2
Cu	10-700	1
Dy	0.2	0.1
Eu	0.2-10	0.05
Fe	20,000-60,000	200
Hf	0.1-18	0.1
Hg	0.05-3	0.5
K	3000-30,000	5000
La	2-60	2
Lu	0.2	0.1
Mn	100-10,000	10
Na	2000-40,000	100
Pb	10-200	---
Rb	1-100	1**
Sb	0.5-15	0.1
Sc	0.2-30	0.02
Se	0.1-1	2
Em	0.5-30	0.3
Sn	0.5-15	500
Sr	200-2000	100**
Ta	0.03-3	0.01

TABLE 5 (con't.)

Tb	0.1-7	0.1
Th	0.3-10	0.08
V	10-500	10
Yb	1	0.3
Zn	5-4000	5**
Zr	100-400	70

* 100 to 800 mg of dried sediment; samples irradiated at optimum intervals ranging from 1 minute to 6 hours in a flux of 10^{11} to 10^{13} n/cm^2/sec and counted at optimum intervals after the irradiation for 1 minute to 200 minutes; Ge(Li) diode detectors, 20 cc to 60 cc volumes

** Determined by counting on a coincidence-anticoincidence shielded Ge(Li) gamma ray spectrometer.

F. Charged Particle Activation Analysis

1. Usually used for elements of Z<10; limited to surface analysis.

2. Reactions used: (p,n) (d,n) (^{3}He,d)
(p,pn) (d,2n) (^{3}He,α)
(p,α) (d,p)

TABLE 6

Detection Limits for $^{3}He^{\ddagger}$

Element	Limits (ppm)	Surface Concentration ($\mu g/cm^2$)
B	0.05	0.02
C	0.3	0.01
N	1.0	--
O	0.5	0.01
F	--	0.1

‡ 5 MeV ^{3}He, 0.5 μamp, 10 m irradiation

SECTION III

Problems

1. The disintegration rate of a nucleus produced in a reactor or an accelerator as a function of irradiation time is given by

$$A = \Phi\sigma N_x(1-e^{-\lambda T})$$

Discuss the variation of the saturation factor with T for the following cases

a) $T >> t_{1/2}$

b) $T << t_{1/2}$

[Hint: e^{-x} where x is a large number $\to 0$, and e^{-x} where x is a small number can be approximated by $(1 - x)$]

2. The saturation activity is defined as the maximum activity in dpm that can be obtained for 1g of a given element in a reactor of known flux. Assuming a neutron flux of 10^{12} neutrons/cm^2/sec calculate the saturation activities in dpm/μg for the following elements

Target isotope		Abundance %	$t_{1/2}$ of product	σ for (n,γ) in ba
a)	^{55}Mn	100	2.58h	13.3
b)	^{70}Zn	0.62	2.2 m	0.085
c)	^{127}I	100	25 m	5.6
d)	^{63}Cu	69.1	12.8 h	4.3

3. A target containing 10^{-4}g of ^{55}Mn was irradiated for four hours in a reactor with a neutron flux of 10^{13} neutron/cm^2/sec. If the target was counted two hours after the irradiation was completed what would be the activity in dpm?

4. A sample of ^{127}I was irradiated (I = 10^{12} neutrons/cm^2/sec) for twice the half life of the product nucleus ^{128}I and then counted immediately on a counter which was 25% efficient. The observed count rate was 1.4×10^8 cpm. How much ^{127}I was orginally present in the sample?

5. The activity of a 10^{-3}g sample of ^{70}Zn was found to be 10^5 dpm after irradiation for 4 minutes. Calculate the neutron flux of a reactor in neutron/cm^2/sec.

6. Two samples containing ^{63}Cu are irradiated in a reactor. One of the samples is known to have 10^{-5}g of ^{63}Cu. The sample of known ^{63}Cu concentration was observed to have an activity of 1.7×10^4 dpm. The activity of the other sample determined on the same counter was found to be 0.9×10^4 dpm. What is the weight in grams of ^{63}Cu in the unknown sample? If two different detectors had been used for the counting of the samples how would you have corrected your data?

7. For the production of the following nuclides, choose and explain the basis for choice between cyclotron irradiation, reactor irradiation or fission.

^{137}Cs	^{35}S
^{14}C	^{197}Hg
^{147}Pm	^{36}Cl
^{58}Co	^{58}Co

8. The cross section of the product nucleus can be sufficiently large that second order neutron capture products are formed during irradiation of moderate duration. If the first order product is radioactive, then its concentration at any time is dependent on the decay constant and the cross secion for the production of the second order product as well as the cross section for its own production. A destruction constant Λ_2 may be defined as

$$\Lambda_2 = (\lambda_2 + \Phi\sigma_2)$$

The number of atoms of the second-order product at a time T is given by

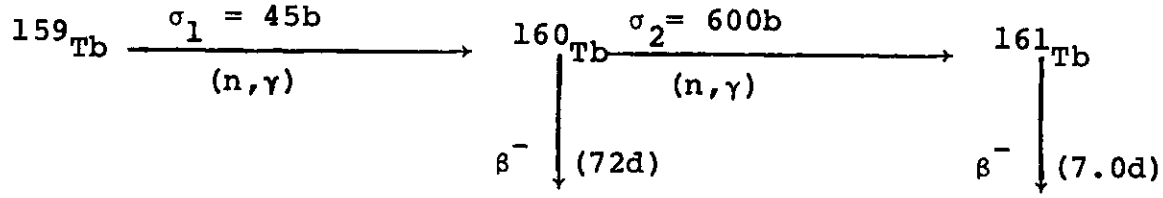
$$N_3 = \Lambda_1\Lambda_2^*N_1^0 \left[\frac{e^{-\Lambda_1 T}}{(\Lambda_2-\Lambda_1)(\Lambda_3-\Lambda_1)} + \frac{e^{-\Lambda_2 T}}{(\Lambda_1-\Lambda_2)(\Lambda_3-\Lambda_2)} + \frac{e^{-\Lambda_3 T}}{(\Lambda_1-\Lambda_3)(\Lambda_2-\Lambda_3)}\right.$$

where $\Lambda_1 = \Phi\sigma_1$

$\Lambda_3 = \lambda_3$

$\Lambda_2^* = \Phi\sigma_2$

If a milligram of Tb_2O_3 is bombarded for 30d at a flux of 10^{14} neutrons/cm^2/sec the following processes occur:



Calculate the activities of both ^{160}Tb and ^{161}Tb.

9. In the same manner calculate what percent of the total activity at end of the bombardment in a 1 gram sample of gold foil will be due to ^{199}Au following a 1.5d irradiation with a flux of 10^{14} neutrons/cm^2/sec.
[σ_{197}=96b, σ_{198}=3.5x10^4b, $t_{1/2}$(198)= 2.7d, $t_{1/2}$(199)=3.15d]?

10. In a flux of 10^{13} neutrons/cm^2/sec, how long an irradiation is necessary to reduce the amount of ^{186}W (σ= 37 barns, 28.4% abundant) present in tungsten foil by 10%?