

Instrumental Neutron Activation Analysis (INAA)

Overview:

Unlike most analytical techniques INAA requires no chemical processing of the samples, therefore it is described as Instrumental NAA rather than radiochemical NAA. This characteristic has several advantages:

- (1) Rapid, i.e., less labor required to prepare samples.
- (2) Precludes the possibility of contaminating the samples.

As shown in Fig. 1 (Periodic Table), in terrestrial sediments INAA typically obtains precise abundance data (i.e. duplicate analyses agree within 5%) for many elements, typically occurring as trace elements in the parts per million (by weight) range.

The concept of INAA is to produce radioactive isotopes by exposing the samples to a high flux of neutrons in a nuclear reactor. These isotopes typically decay by beta decay and in the process gamma rays (electromagnetic radiation) with discrete energies are emitted). These discrete energies are the fingerprint for an isotope. Note that this technique determines abundance of isotopes, but because isotopic abundances of most, at least high atomic number, elements are constant in natural materials, isotopic abundance is readily translated to elemental abundances.

Gamma rays arise from transitions between nuclear energy levels whereas X-rays arise from transitions between electron energy levels. An advantage of gamma rays is that many are much more energetic than X-rays; therefore gamma rays are less readily absorbed and matrix corrections (see lecture on electron microprobe) are not usually important.

Periodic Table of the Elements.

IA		IIA				1		2				IIIB		IVB		VB		VIB		VIIB		0	
3 Li	4 Be					H		He				5 B	6 C	7 N	8 O	9 F	10 Ne						
11 Na	12 Mg	III A	IV A	VA	VIA	VII A	VIII			IB	IIB	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar						
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr						
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe						
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn						
87 Fr	88 Ra	89 Ac																					
		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu								
		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr								

Figure 1. Abundance of the elements highlighted in color can be precisely determined by INAA of natural materials, such as soils, sediments and rocks. Since only 10 elements (Na, Mg, K, Ca, Ti, Mn, Fe, Al and O) are major elements in most rocks and soils, INAA is principally a technique used for analyses of trace elements.

Figure by MIT OCW.

Absorption of a neutron by a nucleus increases the N/P ratio ($N = \text{neutron}$, $P = \text{proton}$). Since stable isotopes are characterized by restricted N/P ratios, typically unity at low $N+P$ and increasing to >1 as $N+P$ increases (Fig. 2), the addition of neutrons creates radioactive isotopes which decay by beta minus decay.

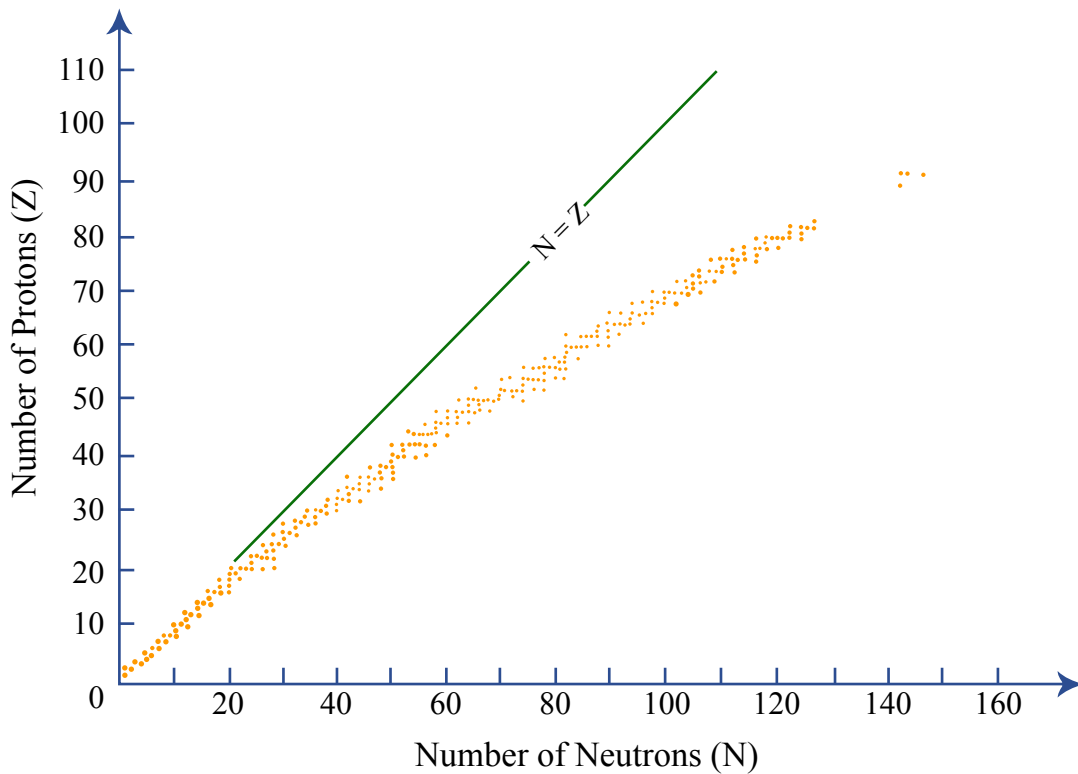


Figure 2. Z (number of protons = atomic number) vs. N (number of neutrons) in stable nuclides (orange dots). Note that for stable nuclides with Z and N < 20 , $Z = N$, but as Z and N increase the Z/N of stable nuclides decreases.

Figure by MIT OCW.

Radioactive and Stable Isotopes of Sodium (Na) and Magnesium (Mg)

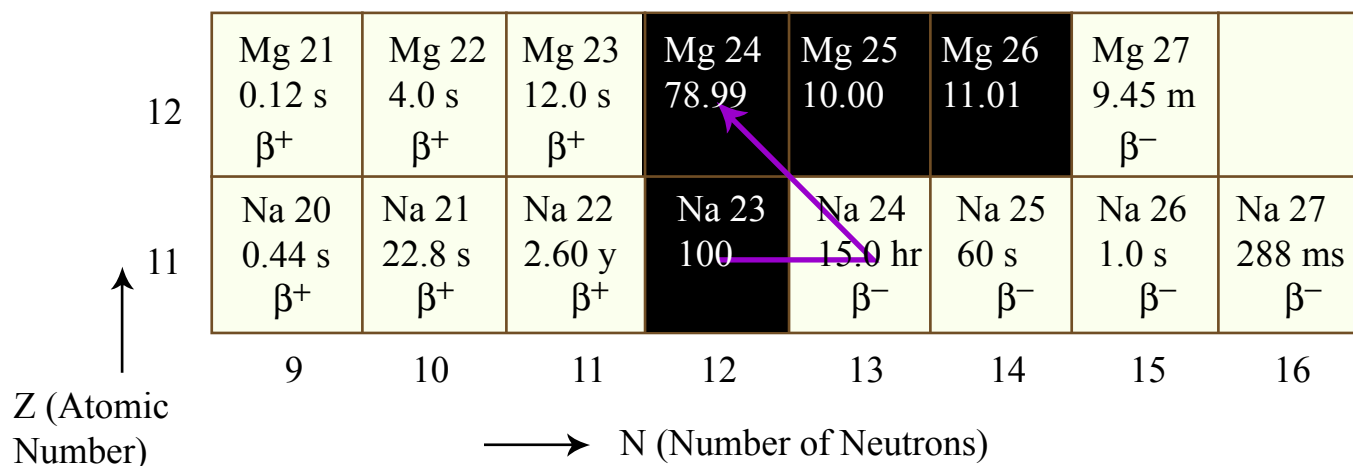


Figure 3.

Radioactive Isotopes: Open squares showing radioactive half-life in seconds (s), milliseconds (ms), hours (hr), years (y) and mode of beta decay.

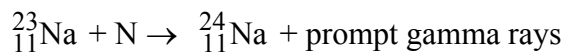
Stable Isotopes: Black squares indicate abundance (in percent) of stable isotopes for Na and Mg.

Trajectory (Purple arrow): Shows that in a neutron flux ${}_{11}^{23}\text{Na}$ becomes ${}_{11}^{24}\text{Na}$ which decays to ${}_{12}^{24}\text{Mg}$.

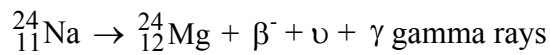
Figure 3 is a portion of the nuclide chart which is a plot of N (horizontal axis) vs. Z (vertical axis). Z is equal to number of protons in a nucleus and is known as atomic number. Hence each horizontal row in this figure shows isotopes for a given element. At the proper N/P

ratio the isotopes are stable but as N/P increases (or decreases) relative to the optimum ratio the isotopes are radioactive. Note that odd Z elements typically have only 1 stable isotope; for example Z=9 (Fluorine) and Z=11 (Sodium).

In order to understand the principles of INAA, look at Figure 3, find ${}_{11}^{23}\text{Na}$, the only stable isotope of NA. Now consider what happens when ${}_{11}^{23}\text{Na}$ is in a nuclear reactor? U fission leads to a source of neutrons (typical neutron flux $\sim 2 \times 10^{13}$ N/cm² sec). Although in theory multiple neutrons (N) can be absorbed, the probability of N absorption is very small, measured in units of 10^{-24} cm⁻², and most commonly only one N is absorbed. Therefore:



but ${}_{11}^{24}\text{Na}$ is radioactive via beta minus decay



$$t_{1/2} \text{ (half-life)} = 15 \text{ hrs}$$

Note that effectively a neutron has been converted into a proton with formation of a beta particle (β^{-}), a neutrino (ν) and gamma rays (γ). Gamma rays, like X-rays, are electromagnetic radiation (photons) with quantized, i.e., discrete energies which are characteristic of a nucleus. Hence, they are “detector of specific nuclei”.

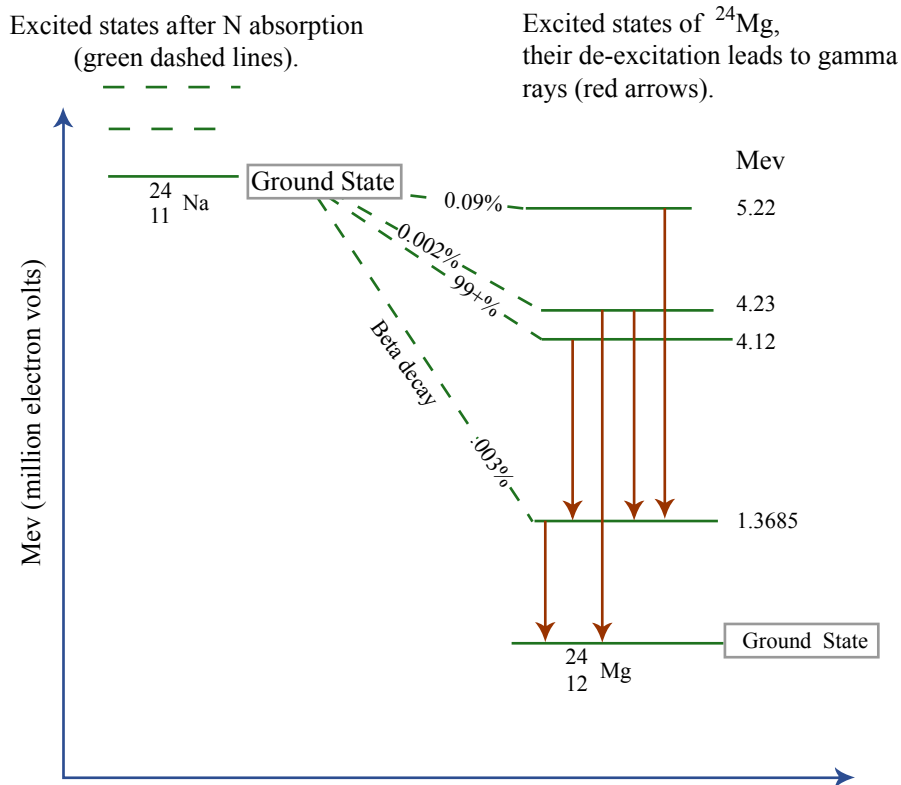


Figure 4. Nuclear energy level diagram for $^{24}_{12}\text{Mg}$ showing the excited states populated during beta decay of $^{24}_{11}\text{Na}$.

Notes:

- (1) During de-excitation of ^{24}Mg not all transitions are allowed. Moreover because Beta decay preferentially populates specific excited states, the relative intensity of different gamma rays varies; the highest intensity gamma rays arise from deexcitation of the 4.12 mev state.
- (2) We use gamma rays arising from de-excitation of ^{24}Mg energy levels to detect ^{23}Na .
- (3) Typically, the energy of gamma rays is much larger (mev) than that of X-rays (<100 kev); therefore matrix effects are usually not important for INAA.

Figure by MIT OCW.

Figure 4 shows a simplified energy level diagram for $^{24}_{12}\text{Mg}$ which is created by radioactive decay of ^{24}Na . You can see that gamma rays are created by transitions between

nuclear energy levels of $^{24}_{12}\text{Mg}$ and that the number of these gamma rays are proportional to the number of ^{23}Na nuclei in the sample. Note that all transitions between energy levels are not allowed so the intensity of specific gamma rays differs. In this case the most intense gamma rays arise from the transitions from 1.3685 meV (million electron volts) level to the ground state and from the 4.12 level to 1.37 level (i.e. a 2.75 meV gamma ray).

In detail, neutrons created in a nuclear reactor by fission of U have high energy (described as fast) and are less readily absorbed than lower energy neutrons (described as thermal); e.g., the neutron capture cross-section (i.e., probability of neutron absorption) for Cd is highest for thermal neutrons (Figure 5a). Hence within a nuclear reactor the high energy fission neutrons are reduced in energy before they impact our samples (Figure 5b). Therefore we are typically doing INAA with thermal neutrons.

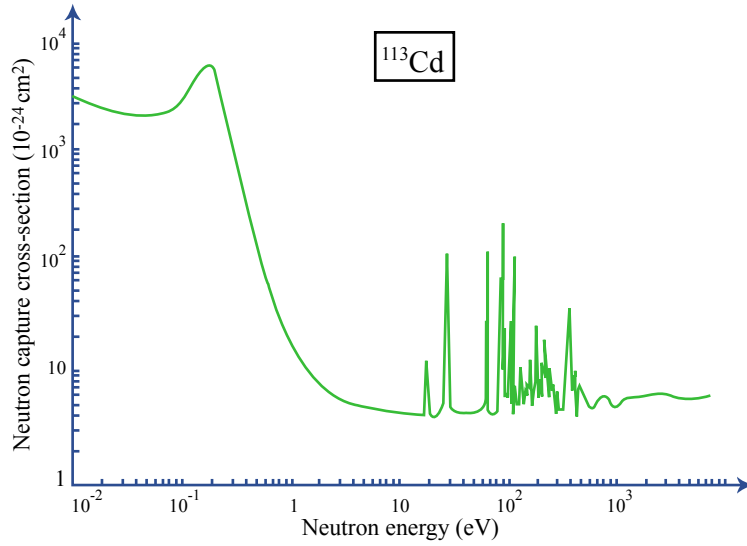


Figure 5a. Neutron cross-section, i.e. probability of neutron absorption, as function of neutron energy for ^{113}Cd .

Note that cross section is highest for low energy neutrons.

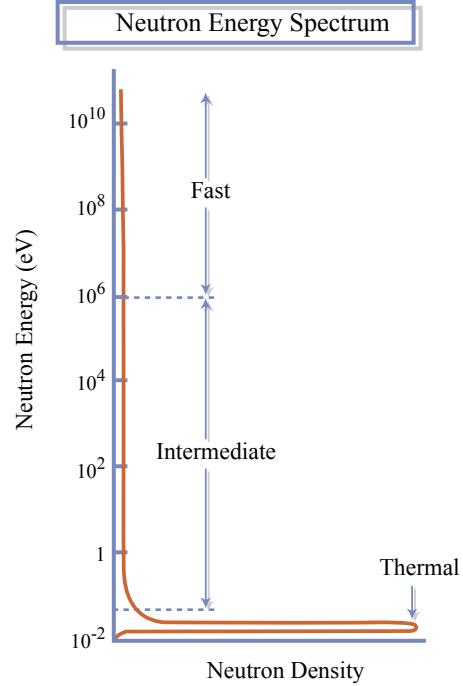


Figure 5b. Because cross section is higher for low energy neutrons, the fast (high energy) neutrons created during fission of U in a reactor are thermalized, i.e. lowered in energy, for INAA.

Figures by MIT OCW.

Radioactive Decay

If N is the number of radioactive nuclei the decrease in N with time is given by a first order rate

law $\frac{dN}{dt} = -\lambda N$ where λ is the decay constant. Integration of this equation yields:

$$\ln N = -\lambda t + C$$

assume at $t = 0$ that $N = N_0$, then $\ln N = -\lambda t + \ln N_0$

$$\ln (N/N_0) = -\lambda t$$

$$N = N_0 e^{-\lambda t}$$

This is the decay equation showing the exponential decrease in N with time.

The definition of half-life $t_{1/2}$ is given by

$$\frac{N}{N_0} = 0.5 = e^{-\lambda t_{1/2}}$$

$$\ln 0.5 = -\lambda t_{1/2}$$

or

$$t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

THE FUNDAMENTAL EQUATION FOR NAA

Consider an isotope A; in the nuclear reactor, it absorbs a neutron (N).

(1) $A + N \rightarrow A^* + \gamma$ (prompt gamma rays) where A^* designates radioactive. A^* atoms decay via beta minus decay which converts a N (neutron) to a P (proton) thereby creating a stable isotope of B, a negative electron, an antineutrino (ν) and gamma rays (γ 's).

(2) $A^* \rightarrow B + e^{-1} + \nu + \gamma$.

So in the nuclear reactor we form A^* and it decays. Hence, A^* with time is given by an equation for accumulation = production in reactor – disappearance by decay.

That is.

$$(3) \quad \frac{dA^*}{dt} = \phi\sigma A_0 - \lambda A^* \quad \text{where}$$

ϕ = neutron flux in neutrons/cm² sec

σ = cross section, i.e., probably of absorbing neutrons in cm²

λ = decay constant

A_0 = original number of A put into reactor

This equation can be integrated to obtain

$$(4) \quad A^* = \frac{\phi\sigma A_0}{\lambda} (1 - e^{-\lambda t_{\text{irrad}}})$$

$$A^* = \frac{\phi\sigma A_0}{\lambda} (1 - e^{-0.693 t_{\text{irrad}} / t_{1/2}})$$

The term within parentheses is called the Saturation Factor “S” because when

(a) $t_{\text{irrad}} \gg t_{1/2}$, $S = 1$

(b) $t_{\text{irrad}} \ll t_{1/2}$, $e^{-\lambda t} \sim 1 - \lambda t$, so

$$(5) \quad A^* = \phi A_0 \sigma t_{\text{irrad}}$$

Assessing Gamma Ray Intensity

Now we typically do not assess gamma ray intensity until several days after the irradiation and we “count”, i.e. assess gamma ray intensity, several samples sequentially. Hence we need to correct to a common time. This is done using

$$A^0 = A^* e^{\lambda t} \quad (\text{as derived before from } \frac{dA^*}{dt} = -\lambda A^*)$$

We measure A^* over a period of time, typically 2 to 5 hours so what we measure is $\frac{dA^*}{dt}$. Since

$$\frac{dA^*}{dt} = \lambda A^*$$

equation 4 becomes:

$$(6) \quad \frac{dA^*}{dt} = \phi \sigma A_0 (S) e^{(0.693t_{\text{decay}})/t_{1/2}}$$

(7) Note that:

$$(a) \quad A_0 = \left(\frac{\omega \text{ gm}}{\text{At. wt}} \right) (N_{AVO}) (\text{Isotopic Abundance}).$$

Also we need terms for efficiency of detector (ϵ) and gamma ray yield (Y).

(b) Our unknown to be determined is the amount by weight of the element being analyzed in the sample (i.e., ω gm).

In fact flux, cross-section and detector efficiency are not precisely known; therefore isotopic abundance, proportional to weight of element in grams, is determined by comparing the activity of the unknown with the activity of a standard whose concentration of the element of interest is well known (note activity is $\frac{dA^*}{dt}$ and not the “activity” commonly used in thermodynamics). Therefore, we use the equation

$$\frac{(dA^*/dt)_{\text{unknown}}}{(\text{wt. element})_{\text{unknown}}} = \frac{(dA^*/dt)_{\text{standard}}}{(\text{wt. element})_{\text{standard}}}$$

and solve for (wt element)_{unknown}; using such an equation, the terms ϕ , σ etc. cancel out. This approach is used for many other analytical techniques, e.g., atomic absorption and inductivity coupled mass spectrometer (to be discussed).

Because a standard is most reliable when it is similar in composition to the unknown (i.e., a study of clay-rich sediment should use a clay-rich standard, etc.), the preparation of standards of various types with known trace element concentrations is not a trivial task. Typically such standards are purchased from organizations that specialize in preparation of such materials. Two sources are:

- 1) United States Geological Survey for standard rocks, sediments, etc.; see “Geochemical Reference Materials and Certificates” at USGS Web site.
- 2) National Institute for Standards and Technology (NIST). They supply Standard Reference Materials (SRMs) ranging widely in composition, e.g., metals, ores, leaves, fly ash, silicate glasses and water with known abundances of various trace elements.

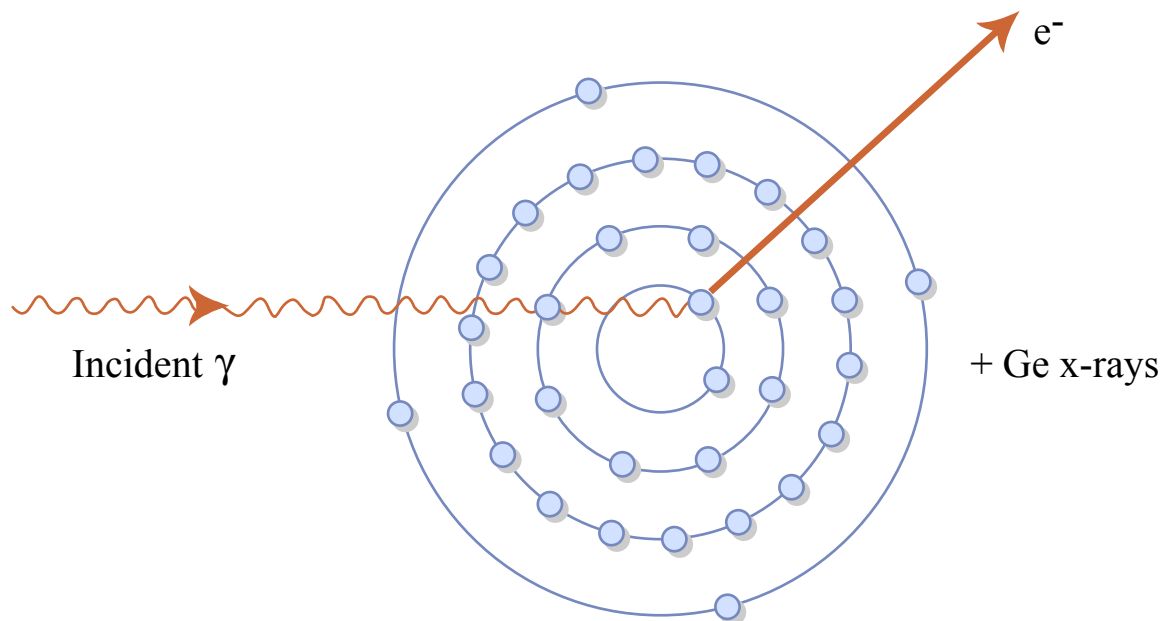
Obtaining the electronic signal that is a measure of isotopic abundance

We know that gamma rays with discrete energies are created by beta minus decay which occurs upon creating a radioactive isotope with a high N/P ratio. Now we consider how does an electronic signal arise when gamma rays interact with matter, i.e. a detector.

Gamma rays can interact with the detector material (typically Ge) in several different ways, as indicated in Figure 6 which shows the possible interactions of an incident gamma ray interacting with a single atom of Ge (32 electrons). Specifically, they are: □□□□

- a) Photoelectric effect
- b) Compton Scattering
- c) Pair production
- d) Bremsstrahlung

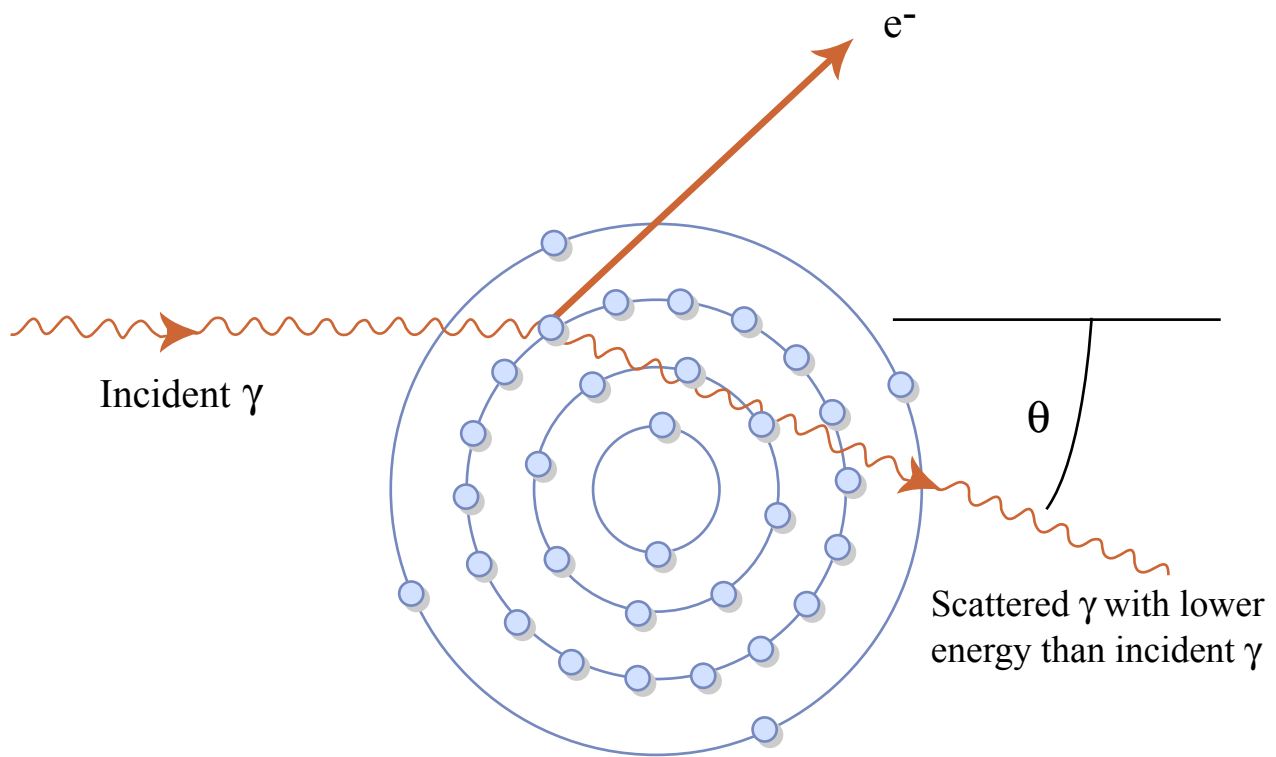
Our objective is for all of the gamma ray energy to be deposited in our detector; this is typically accomplished by the photoelectric effect or multiple Compton scattering events.



6a. Photoelectric Effect

6a. The photoelectric effect is the interaction between a gamma ray and an orbital electron with almost complete transfer of energy to the electron occurs. For detection of gamma rays the detector (i.e., the target material) is usually a Germanium (Ge) semi-conductor; therefore Ge X-rays are created subsequent to formation of the Ge photoelectron. A small proportion of the energy of the incident gamma ray is used to overcome the ionization potential of the electron: The remainder appears as kinetic energy in the electron. This interaction is most likely to occur with orbital shells close to the nucleus (especially the K-shell). The vacancy left by the ionized electron is filled by an electron falling from the next higher shell, simultaneously emitting the characteristic K x-rays of germanium. Thus, photoelectric interactions always yield characteristic x-rays of the detector material. Energies of the both ionized electron and x-ray are usually absorbed by further ionization of detector atoms. However, there is a possibility that the x-rays may escape from the detector without further interaction. The total energy then absorbed within the detector equals the full energy of the incident gamma photon less the energy of germanium x-ray (12 keV for a Ge K-line). This event is called an escape peak, and is observed as a subsidiary peak at an energy 12 keV below the principal gamma photon line.

Figure by MIT OCW.



6b. Compton Scattering

6b. Compton Scattering:

Compton scattering results from an inelastic collision between gamma-ray and (most probably) an outer orbital electron, in which only part of the gamma energy is transferred to the electron. The remainder is reirradiated as a lower energy gamma-ray emitted so that both total energy and momentum are preserved. Maximum transfer of energy results from a head-on interaction following which the secondary gamma-ray is emitted at 180° to the first. The secondary gamma photon can itself be absorbed by further Compton or photoelectric interactions. However, there is a probability that this gamma will itself escape from the detector. The detected event then corresponds to the full energy of the incident photon less that of the Compton escape gamma-ray. Compton scattering in the detector is the main cause of the high background continuum below the energies of principal gamma photopeaks recorded on germanium detectors.

Figure by MIT OCW.

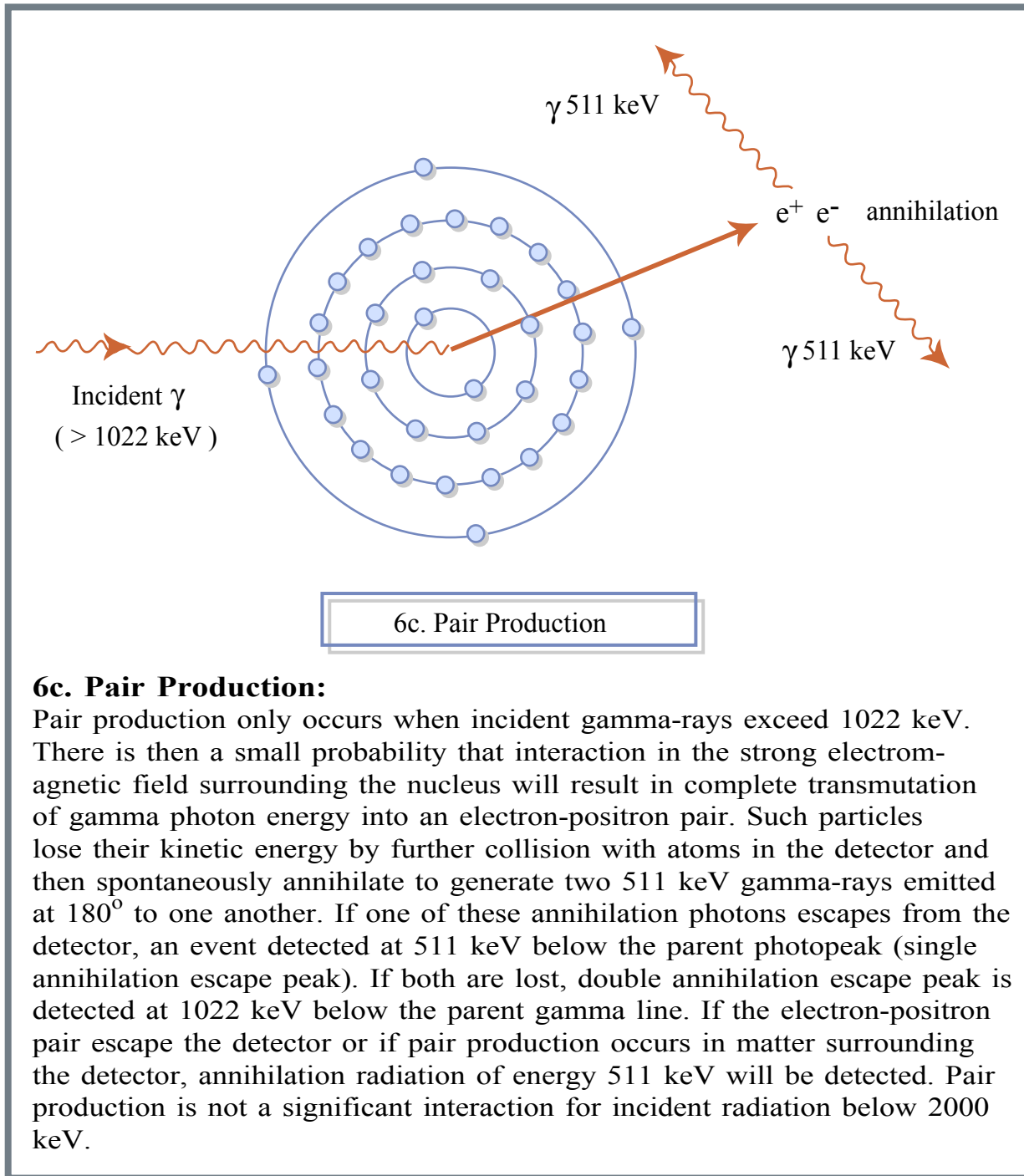


Figure by MIT OCW.

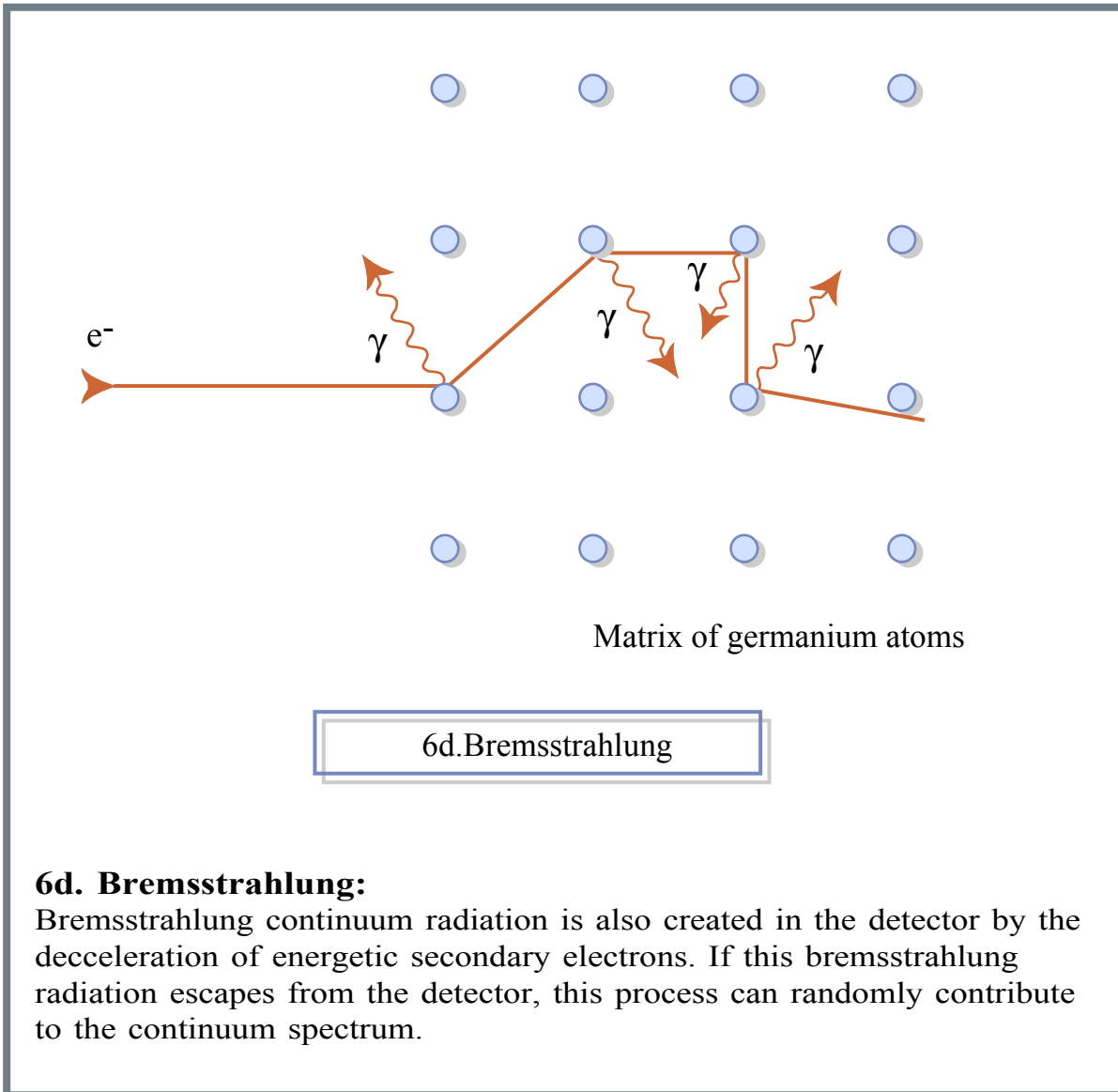


Figure by MIT OCW.

Gamma Ray Detector for Neutron Activation

We want a material that is normally a non-conductor (Si or Ge) but when a gamma ray enters the detector and generates photoelectrons we want to have an electrical current generated whose amplitude is proportional to the gamma-ray energy. This is accomplished by using a semi-conductor, a substance whose outermost electrons are in an energy level known as the “valence band”. These electrons are used in bond formation, and at 0°K they do not move about in the metallic lattice. Thus the material is a poor conductor. In a semi-conductor there is, however, an excited level for electrons that is only slightly higher in energy than the “valence band”. This excited level is known as the “conduction band”. As shown in the Figure 7 the proportion of electrons in these bands is very sensitive to temperature.

The detectors that we use are made of Ge because

- (a) Ge has a higher Z (32) than Si (14), so it is a better absorber of gamma-rays.
- (b) Ge can be made very pure; i.e., free of other metallic atoms which could contribute electrons to the conduction band.
- (c) The energy gap between VB and CB is small (0.73 eV).

The detector is kept at the temperature of liquid N₂, and when photoelectrons are generated within the detector by gamma-rays, this results in transfer of Ge electrons from VB to CB. A high voltage is applied to the detector to collect this electrical current which is directly proportional to the energy deposited in the detector. In practice to create an electron-hole pair (i.e., electron transfer for VB to CB) in Ge requires 2.95 eV (rather than 0.73 eV) so that a 1000 KeV gamma-ray may create 3.4×10^5 electrons in the conduction band.

Germanium Semi-Conductor Detector

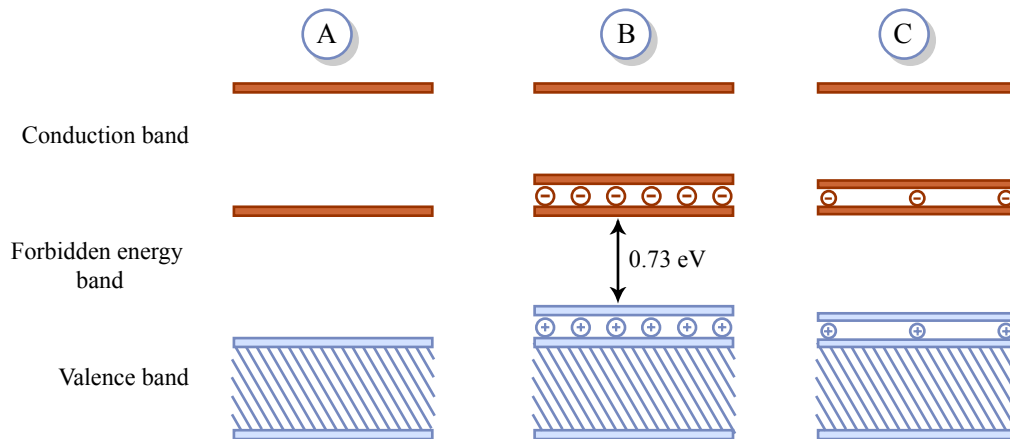


Figure 7. KEY:- Shading indicates valence band fully occupied by electrons. Arrows indicates transfer of electrons from valence to conduction band.

Schematic behavior of a semiconductor crystal:

- A: Perfect (intrinsic) semi-conductor at 0°K. The valence band is fully occupied by electrons, and the conduction band is empty, in this state the semiconductor cannot conduct.
- B: Semiconductor at room temperature. There is significant thermal excitation of electrons from valence (+symbol) to conduction band (- symbol); in this state the semiconductor will conduct.
- C: Semiconductor cooled to temperature of liquid N₂ (77°K). Relatively few electrons (-) are excited from valence band (+) to conduction band (-). Consequently, the Ge detector serves as a conductor, and an electrical current is generated, only when gamma rays emitted by the radioactive sample interact with the detector and create Ge photoelectrons which populate the conduction band. The number of electrons in the conduction band is proportional to the energy of the gamma ray.

Figure by MIT OCW.

The unknown samples and standard (irradiated together in the nuclear reactor) are sequentially placed in front of the detector (see radiation source in Figure 8). Note that activities from samples and standards must be corrected to a common time. Also it is imperative that a sample holder be used so that samples and standards are placed in the same location relative to the detector.

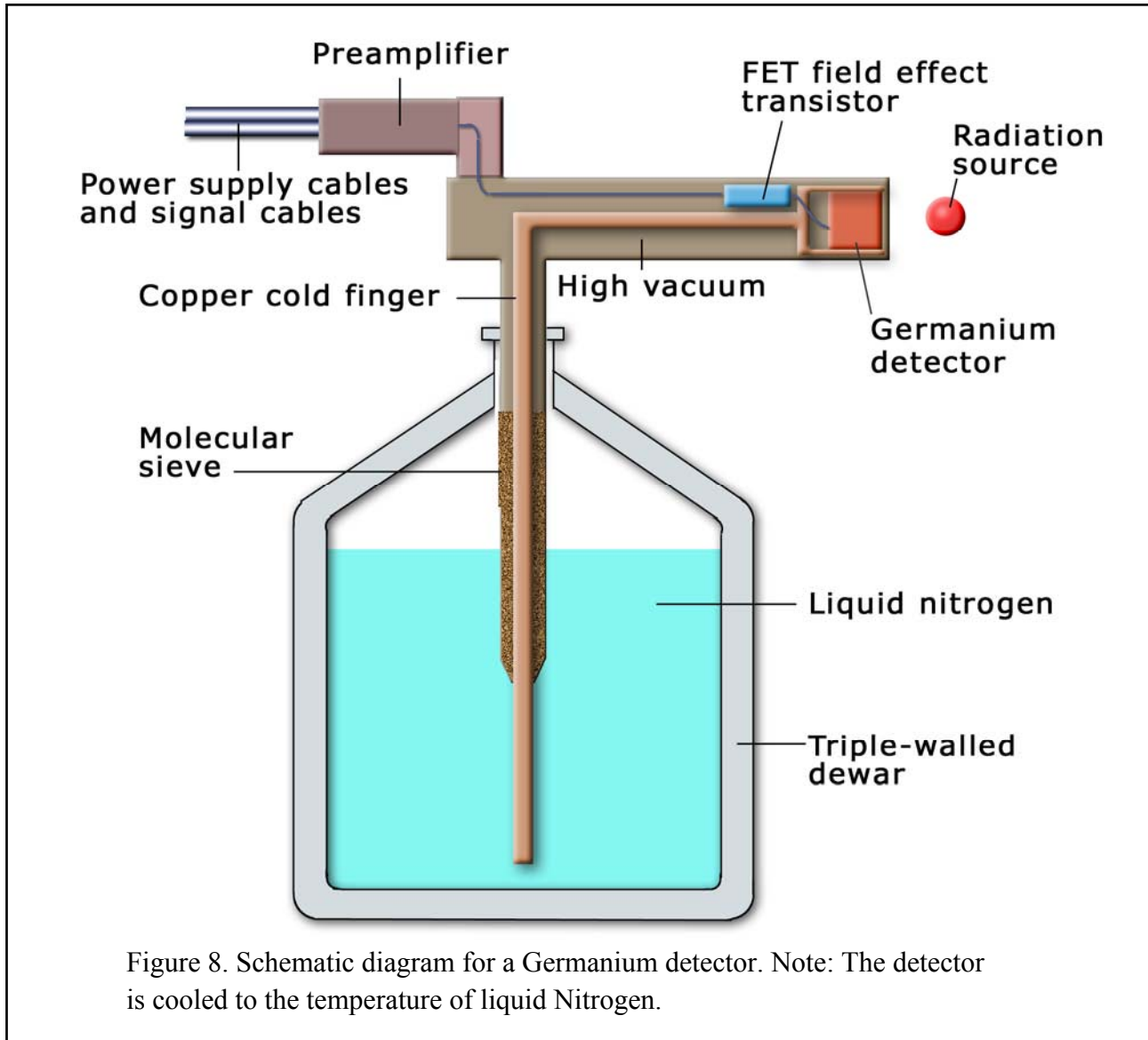
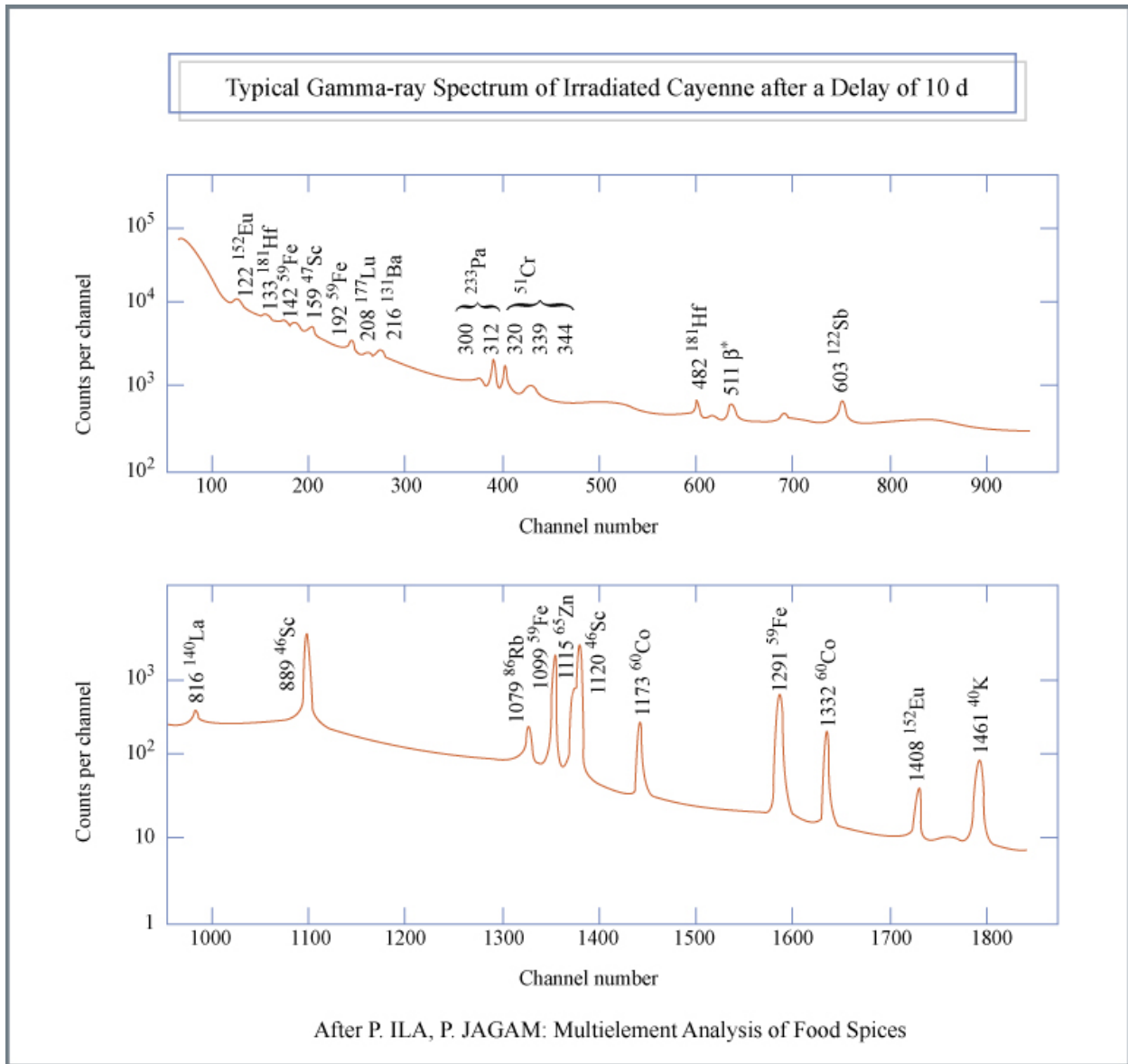


Figure by MIT OCW.

The output of the detector is a gamma-ray spectrum, i.e., a plot of gamma ray intensity versus energy which is typically divided into 4096 or 8192 channels (see Figure 9). Multiple gamma rays are detected, often two or more from the same isotope, e.g. 1173 and 1322 Kev

peaks of ^{60}Co . The area beneath these peaks is integrated, typically using computer code, for both samples and standard, and this area is proportional to isotope abundance.



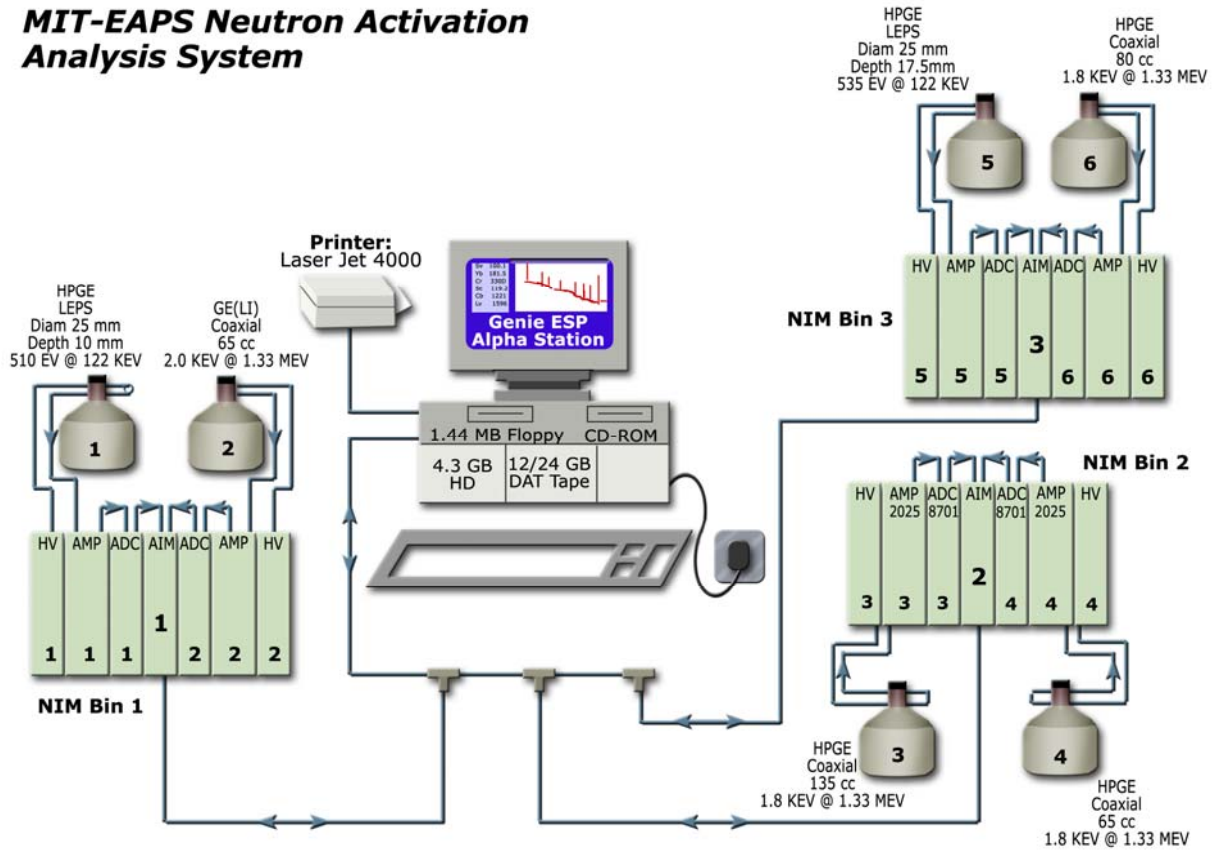
Important aspects of typical gamma-ray spectrums from natural materials (e.g. cayenne pepper in Fig. 9) are:

- (1) Many peaks are crowded together at low energy but there are isolated peaks at higher energy (>500 Kev). Hence energy resolution of detectors is an important characteristic; resolution is a measure of the ability to distinguish between peaks that are similar in energy. Generally large, more efficient Ge detectors have lower energy

resolution than small, less efficient detectors. Therefore an INAA facility typically has several Ge detectors varying in efficiency and resolution capabilities (Fig. 10).

- (2) A unique feature of gamma ray spectra is that detectors have well-defined energy resolution capabilities, but there is also the concept of time resolution; that is two isotopes may have gamma rays with very similar energies but quite different half-lives. Hence, by delaying the time of counting after irradiation for several days or even weeks, one can wait for the intensity of the gamma ray from the relatively short half-life isotope to dissipate. Consequently, INAA facilities typically determine activities at several times, perhaps 1, 7, 15 and 30 days after irradiation.

MIT-EAPS Neutron Activation Analysis System



Summary Comments on Instrumental Neutron Activation

Advantages

- 1) INAA is sensitive for a variety of trace elements that have proper nuclear characteristics, e.g., rare-earth elements, As, Hf, Ta, Co, Cr, Sc. For major oxides, in sediments and rocks the main use is for determining Na₂O abundance.
- 2) For rocks and sediments no sample dissolution or chemical procedures are required for INAA; hence there is no blank, i.e., contamination, problems and the process is not labor intensive.
- 3) Analyze for many elements simultaneously.
- 4) Precision is variable, 1-5% is typical. Precision and data quality can often be evaluated by using several different gamma rays for a given element. Also one has the capability of both time and energy resolution.
- 5) Accuracy is controlled by use of standard materials; i.e. we compare the intensity of signal from unknown to that of a sample with known concentrations.

Disadvantages

- 1) Need access to nuclear reactor and gamma ray detectors.
- 2) Must work with low level radioactivities.
- 3) Good for some specific elements, but probably not all that may be of interest.
- 4) Precision is unlikely to be better than 1%.

Sources of Error

- 1) Counting statistics – you cannot do better than $N \pm \sqrt{N}$ with errors propagated for peak and background areas in unknown and known (N is number of events recorded for a given gamma ray.)
- 2) Matrix effects are typically negligible if we use gamma rays with energy >80 keV.
- 3) Major error source (which can be controlled) is geometry; i.e. one must have a reproducible location of sample and standard with respect to detector.

12.119 INAA Assignment

March 21, 2008

1. The weights of empty vial, empty vial + sample powder were taken 6 times. Calculate the standard deviation. Using the formula for the propagation of errors, calculate the error in the weight of the sample powder.

Weights (in grams) of the empty vial, weighed separately for 6 times.

1.14470, 1.14475, 1.14472, 1.14476, 1.14478, 1.14475

Weights (in grams) of the vial + sample powder, weighed separately for 6 times.

1.35041, 1.35040, 1.35029, 1.35018, 1.35026, 1.35035

2. Arsenic is determined in river sediment samples.

The abundance of As in the standard is 145 ppm.

The gamma-ray energy of ^{76}As is 559 keV.

The gamma peak areas of the sample and standard are respectively, 32699, and 1533496 for the same counting times.

The delays from the end of irradiation for the sample and the standard counting are 5.953 d, and 4.252 d.

The weights of the sample and standard are 0.38476 g and 0.41669 g.

Calculate the abundance in the sample.

Estimate the propagation of errors. You may use the weighing error from problem 4 above.

3. A standard has been analyzed 10 times.

Nd is one of the Rare Earth Elements. Its measured abundance values (in ppm) are

24.0 \pm 0.7, 23.7 \pm 0.7, 24.0 \pm 0.5, 24.3 \pm 0.9, 23.7 \pm 1.0,
24.3 \pm 1.0, 24.0 \pm 0.7, 23.8 \pm 0.6, 24.0 \pm 0.7, 24.7 \pm 0.9.

The reference value of this standard is 24.7 ± 0.3 .

Calculate the precision and accuracy of this measurement.
Express the precision and accuracy in percentage.

4. Two elements Molybdenum and Antimony are of interest in a study. What are the radioisotopes that can be used for the thermal neutron activation analysis. Provide all the relevant information of the $X + N = Y + \text{gammas}$ reaction, identify the parent and daughter nuclei, the activation cross section, the half-life of the daughter product, and the predominant gamma-ray energy for identification.

5. A filter sample was brought to the reactor for analysis.
The gamma spectrum revealed significant gamma-ray peaks of energy

320 KeV, 1368 keV and 2754 keV.

Identify the content (elements) of the sample.

Suggested Text Book:

Table of Nuclides Appendix D, p 606 -650,

Gamma-ray sources Appendix E 651-660,

Nuclear and Radiochemistry by

G. Friedlander, J. Kennedy, E. S. Macias, J. M. Miller

QD601.F911 1981

P. Ila

MIT-EAPS