CHEM*3440

Chemical Instrumentation

Topic 15

Radiochemical Methods

Nuclear Stability

Atomic nuclei consist of protons and neutrons held together by the strong nuclear force, in balance with the electromagnetic and weak forces. Most nuclei are unstable and decay by various emission pathways.

A narrow proportion of neutrons:protons leads to a stable nucleus. All others (most) are unstable.

The degree of stability is measured by the nuclear lifetime. Observed variation in lifetimes throughout the periodic table spans more than 25 orders of magnitude (from μs to 10^{18} years).

All elements have at least 1 unstable (radioactive) nucleus. Technetium (Tc) is the lightest element to have no known stable nuclei.

Radioactive Decay Products

Possible products ejected from a decaying nucleus:

Product	Symbol	Charge	Mass
Alpha Particle	α	+2	4
Beta Particle			
electron	β^-	-1	1/1840
positron	β^+	+1	1/1840
Gamma Ray	γ	0	0
X-Ray	X	0	0
Neutron	n	0	1
Neutrino	ν	0	0

Decay Processes

Alpha Decay	α
Beta Decay: Electron Emission or Positron Emission	β^- or β^+
Electron Capture	EC
Isomeric Transition: Gamma Ray Emission	γ
Internal Conversion: X-Ray Emission	X
Neutron Emission	n
Spontaneous Fission	SF

Alpha Decay 1

Nucleus ejects an alpha particle (^{4}He nucleus).
More common process found amongst the heavier nuclei (6th row elements and above)
Ejected alpha particle carries most kinetic energy (some recoil left in daughter nucleus). Energy is difference in binding energy of two nuclei and is unique to a specific parent nucleus decay process.

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}\ (E_{kinetic} = 4.196\,\mathrm{MeV})$$

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}\ (E_{kinetic} = 4.149\,\mathrm{MeV}) + \gamma\,(E = h\nu = 47\,\mathrm{keV})$$

2 alpha decay pathways for the U-238 nucleus

Alpha Decay 2

Alpha particles are charged and massive; they interact very strongly with matter. Ultimately, they capture two electrons to become a He atom.

This strong interaction makes them easy to detect.

They ionize material they pass through in the process of losing their energy.

Strong interaction also gives them low penetrating power; stopped by a few inches of air.

Not usually a problem to human health outside the body, but is a problem when it lodges in the lung. (This is why radon is a health hazard.)

Beta Decay 1

Nucleus ejects a positron or an electron. Kinetic energy varies continuously from 0 up to a maximum. Can only happen if a third particle participates: a neutrino.

$$^{14}_{6}\mathrm{C} \rightarrow ^{14}_{7}\mathrm{N} + \beta^{-} + \overline{\nu}$$

$$^{65}_{30}\mathrm{Zn} \rightarrow ^{65}_{29}\mathrm{Cu} + \beta^{+} + \nu$$

The first reaction has a neutron become a proton with the ejection of an electron.

The second reaction has a proton become a neutron with the ejection of a positron.

Difference in nuclear binding energies are carried away by the kinetic energy of the leptons (electrons and neutrinos and their anti-particles).

Beta Decay 2

Smaller masses involved mean that the emitted particles interact more weakly with matter than do α particles. Neutrinos can pass through the entire earth without interaction.

Beta particles can penetrate much deeper than α particles though they can still be detected.

Positrons end their existence by a matter-antimatter reaction when they combine with an electron, annihilate each other, producing two 0.511 MeV gamma ray photons departing at 180° to each other. (Key event in Positron Emission Tomography, PET scans).

Electron Capture

What is motion of s-electron? What is s-electron's radial probability distribution?

When an electron is inside the nucleus, it can combine with a proton to produce a neutron.

$$^{48}_{24}\mathrm{Cr} + ^{0}_{1}\mathrm{e} \rightarrow ^{48}_{23}\mathrm{V} + \mathrm{X-rays}$$

When the orbital electron suddenly disappears, it leaves a hole in the electronic structure of the atom. As other electrons fall into this hole to return the atom to is neutral state, they give off X-rays.

The X-ray emission is not a nuclear process, but the creation of the hole that gives rise to the X-rays is.

The X-ray energy can uniquely identify the product atom.

Gamma Ray Emission 1

Often, an alpha or beta emission process leaves a nucleus in a metastable, excited condition. Note: it is the nucleus, not the atomic electrons, that is excited.

The nucleus relaxes to its ground state, and the excess energy is shed as a gamma ray photon.

$$^{60}_{27}\mathrm{Co} \rightarrow {}^{60}_{28}\mathrm{Ni}^{*} + \beta^{-} + \overline{\nu}$$

$$^{60}_{28}\mathrm{Ni}^{*} \rightarrow {}^{60}_{28}\mathrm{Ni} + \gamma$$

γ-rays and X-rays are both just electromagnetic radiation. γ-rays are of a much higher energy and arise from nuclear transitions, while X-rays arise from electronic transitions.

Gamma Ray Emission 2

γ-rays are highly penetrating and hence interact more weakly with matter. They can be detected and the interaction arises *via* three possible mechanisms.

Photoelectron emission. Low energy γ-rays can be absorbed by atomic electrons, ejecting them with kinetic energy left over after escaping the atom's binding energy.

Compton effect. Moderately energetic γ-rays. Electron partially absorbs γ-ray energy. A lower energy γ-ray also exits in a new direction.

Pair production. High energy γ-rays. Photon in nuclear field disappears, producing an electron-positron pair (requiring 1.02 MeV); excess energy is kinetic energy in separating pair partners.

Internal Conversion

An excited nucleus can decay in by an alternate pathway, whereby it ejects a core electron. Excess energy is carried away kinetically.

This process leaves a hole in the atomic shell, which when filled by another electron, gives rise to X-ray emission.

Rates of Radioactive Decay

Nuclear decay processes follow first-order kinetics.

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = kN$$

This differential equation can be integrated to give

$$\ln \frac{N}{N_0} = -kt \qquad N = N_0 \exp(-kt)$$

k is the characteristic decay constant for the process. It has units of time^{-1}. It specifies the logarithmic fraction of material that has not yet decayed per unit time.

Radioactive Half-Life

Another way of specifying a processes reaction rate is to report the half-life, the time it takes for the remaining material to become 1/2 of the starting amount.

$$\ln \frac{\left(N_0/2\right)}{N_0} = -\, k t_{1/2} = \ln\left(\frac{1}{2}\right)$$

$$t_{1/2} = -\frac{\ln\left(\frac{1}{2}\right)}{k} = \frac{\ln 2}{k} \approx \frac{0.69315}{k}$$

Half-lives have units of time. They range from fractions of a second to billions of years and more. (Hypothesized that the proton has a half-life of 10^{31} years.)

Activity

Activity is defined as the disintegration rate.

$$A = -\frac{\mathrm{d}N}{\mathrm{d}t} = kN$$

Reported in units of "becquerel" (Bq) which is 1 decay per second. Older unit is the curie (Ci) which was defined in terms of the activity observed for 1 gram of radium-226.

$$1\ \mathrm{Ci} = 3.70 \times 10^{10}\ \mathrm{Bq}$$

Activities encountered in the lab usually range from nanocuries (nCi) to millicuries (mCi) - or from Bq up to megabecquerels (MBq).

Measure Counting Rates

One seldom measures absolute activities; the counting geometry can only collect a fraction of the emitted radioactive decay particles. If the same geometry and detector are used, one is able to make accurate relative activity measurements.

$$R = cA = ckN$$

The "c" is the detection coefficient, essentially the fraction of the total that is collected and counted. Since the same c is applied to the detection of the activity at all times in the process, the decay constant is unchanged. We can still write

$$R = R_0 \exp(-kt)$$

Count rate measurements can still accurately determine the kinetic constants of the decay process.

Counting Statistics

Data is always obtained by measuring counts. These are discrete events. Also, you cannot have a "negative number of counts". Zero is as low as it goes. Because of this, the data is distributed according to Poisson statistics, rather than Gaussian statistics.

Distribution is no longer symmetric, but is skewed towards the higher count rate side of the average count rate. At high count rates, the difference is small but at low count rates, it can make a real difference.

Main consequence: the standard deviation of the distribution depends only upon the counts measured and the length of time it was counted.

$$\sigma_M = \sqrt{M}$$

$$\frac{\sigma_M}{M} = \frac{\sqrt{M}}{M} = \frac{1}{\sqrt{M}}$$

M is the number of counts.
St. Dev. Increases with number of counts, but Rel. St. Dev. decreases.

Error in Count Rate

The count rate R is just the total counts, M, divided by the counting time t.

$$R = \frac{M}{t}$$

The error in the count rate is given by

$$\sigma_R^2 = \left(\frac{\partial R}{\partial M}\right)^2 \sigma_M^2 + \left(\frac{\partial R}{\partial t}\right)^2 \sigma_t^2 \qquad \approx 0$$

$$\sigma_R^2 \approx \left(\frac{\partial R}{\partial M}\right)^2 \sigma_M^2$$

$$\frac{dR}{dM} = \frac{d}{dM}\left(\frac{M}{t}\right) = \frac{1}{t}$$

$$\therefore \sigma_R^2 = \frac{\sigma_M^2}{t^2} = \frac{M}{t^2}$$

$$\sigma_R = \frac{\sqrt{M}}{t} = \frac{\sqrt{Rt}}{t} = \sqrt{\frac{R}{t}}$$

$$\frac{\sigma_R}{R} = \frac{\sqrt{R/t}}{R} = \sqrt{\frac{1}{Rt}}$$

Background Corrections

One invariably must measure the background count rate (passing cosmic rays, radon in the air, uranium in the building's construction materials, etc.).

$$R_c = R_M - R_b$$

The error in this final measurement is that found from the relative error of the two measurements.

$$\sigma_{R_c} = \sqrt{\sigma_{R_M}^2 + \sigma_{R_b}^2} = \sqrt{\frac{R_M}{t_M} + \frac{R_b}{t_b}}$$

We measure a signal and its background for known time periods. We then can calculate a corrected signal and its standard deviation. By comparing this measurement with that for a known standard, we can make quantitative determinations of the contents of the sample.

Detectors

The same devices that were used for X-ray detection are employed here including

- gas-filled transducers (ionization, proportional, and Geiger)
- scintillation counters
- semiconductor transducers

The energy of these particles is much higher than that for x-rays and as such generally produce copious quantities of conductors. Different schemes are used to isolate one type of radiation from another.

Alpha Detectors

The challenge here is the minimal penetration depth of these He-4 nuclei because they interact so strongly.

- samples are made as thin films (to avoid self-absorption).
- placed inside a window-less proportional counter (to avoid absorption by window materials).
- placed directly on a solid-state detector, often in vacuum (to avoid absorption by gases.
- dissolved in a solution of the scintillating compound. The solution is observed by a PMT.

Beta Detectors

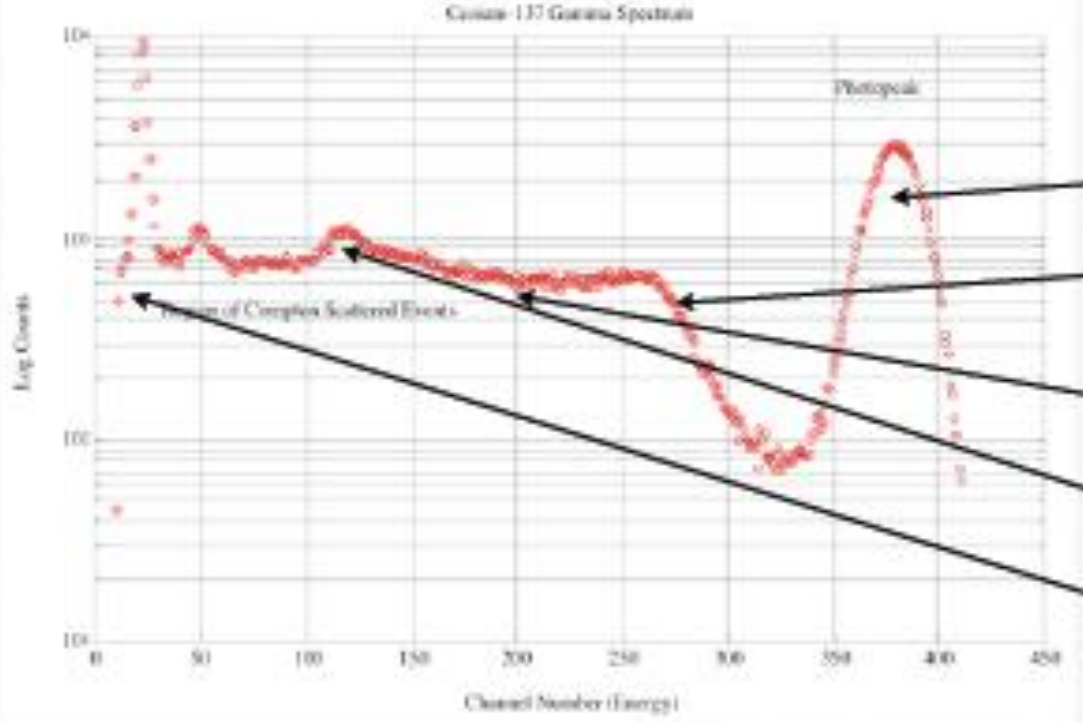
More penetrating than alpha particles but still strongly absorbed.

- high energy beta emitters (> 0.2 MeV) can be monitored through a thin-windowed Geiger or proportional counter.
- low energy beta emitters (^{14}C, ^{35}S, ^{3}H, …) are generally monitored in liquid scintillators.
- liquid scintillation generally accomplished with coincidence counting. Two PMTs observe same sample from opposite directions. An event is counted only when both detectors observe a flash at the same time. This minimizes influence of noise in both systems.
- pulse analysis not useful with beta emitters because emission range is continuous up to the maximum.

Gamma Detectors

Very penetrating. Discriminate against alpha and beta rays by covering a proportional counter window with an Al or mylar covering. This allows in only γ-rays.

Use pulse height analysis to record spectrum against bin or channel number.



Spectrum for ^{137}Cs.

Photopeak

Compton Edge

Compton Plateau

Backscattered γ-rays

X-rays

Two Analytical Experiments

There are two important analytical experiments to consider:

- scintillation counting
- neutron activation analysis (NAA)

They standout as important analytical tools because the first is a mainstay in biochemical studies for following biomolecular chemical transformations. The second is perhaps the most sensitive technique available for atomic analysis.

Scintillation Counting 1

Chemical reactants can be radiolabeled - synthesized with a radioactive isotope in place of a stable elemental component. This reagent can be used to introduce this radiolabel into a target compound and its evolution overtime as it responds to a changing chemical environment can be monitored to study the kinetics of the chemical process.
Common isotopes employed are:

^{3}H	12.3 years	0.0186 MeV β^-
^{14}C	5730 years	0.156 MeV β^-
^{32}P	143 days	1.71 MeV β^-
^{35}S	88 days	0.167 MeV β^-
^{45}Ca	165 days	0.252 MeV β^-
^{125}I	60 days	0.149 MeV E.C.

X-rays lead to scintillator excitation

Scintillation Counting 2

Aliquot of sample is taken and mixed with the liquid scintillation cocktail (consists of a solvent, pH buffer system, fluorescent solute molecule).
Decay event ejects high energy electron, transferring its energy to solvent molecules.

These excited solvent molecules relax by emitting UV photons.
These photons are absorbed by the fluorescing solute and reemitted in the visible spectrum where the PMT can observe them.
About 10 visible photons/keV of decay energy are produced. PMT intensity correlates to initial energy of beta particle.

Beckman LS 6500 Scintillation Counter
- over 650 samples loaded at once
- 0.06 keV energy resolution in spectrum

Scintillation Counting 3

- Be careful of handling materials: ^{3}H is low energy emitter but ^{32}P is very high energy emitter and is much more penetrating. Must be shielded with at least 2 cm of plexiglass.
- Watch out for lifetime of emitter with respect to duration of experiment. (^{14}C vs. ^{32}P) If experiment is over in 10 minutes, no problem. But if it takes 1 month, ^{32}P must be corrected but not ^{14}C.
- Short lifetimes give good signal (high intensity) but long lifetimes give stable signal.
- Understand quenching in the system: photon quenching (β^{-} energy incompletely transferred to solvent), chemical quenching (solvent energy incompletely transferred to fluorescent compound, optical quenching (solvent is coloured or turbid, absorbing or scattering the fluorescence). Must calibrate for this.
- Measure two emitters simultaneously; from standard energy dispersion curves and intensity measurement at two energies, can solve for two concentrations.

Neutron Activation Analysis

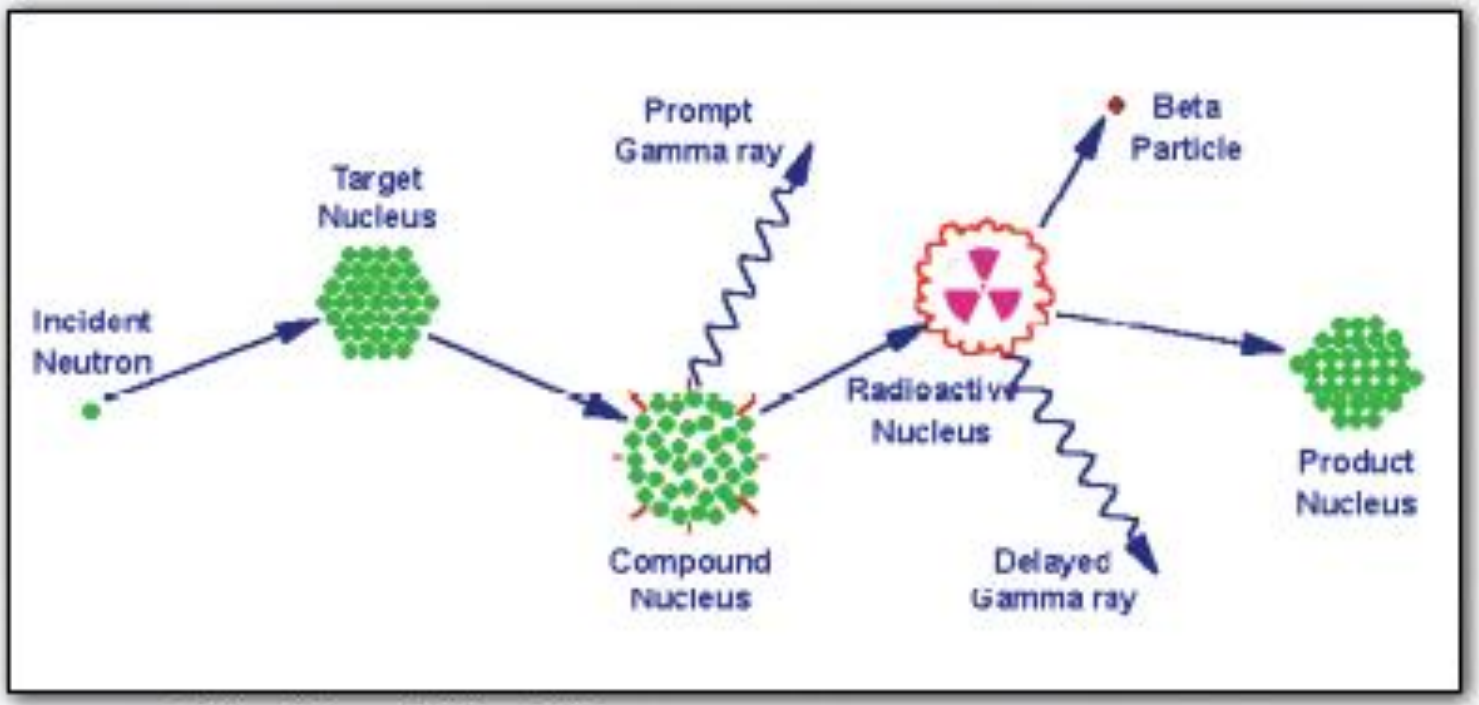
This technique induces radioactivity in samples by irradiation with neutrons. Much of the periodic table can be analyzed by creating a signature radioactive signal in this manner.

Experiment requires:

- a source of neutrons, moderated to a desired kinetic energy for maximal reactivity
- sample irradiation
- a cooling off period to eliminate intense radioactivity immediately following activation
- counting and processing to determine concentration

NAA 2

Incident neutron creates an excited compound nucleus. Prompt γ-rays, delayed γ-rays, or β-particles can all be used for detection of the event.



$$^{23}\mathrm{Na} + {}^{1}\mathrm{n} \rightarrow {}^{24}\mathrm{Na} + {}^{0}\gamma$$

$$^{24}\mathrm{Na} \rightarrow {}^{24}\mathrm{Mg} + {}^{0}\beta^{-} + {}^{0}\gamma\,(1.37\,\mathrm{MeV}) + {}^{0}\gamma\,(2.75\,\mathrm{MeV})$$

Neutron Sources

There are three main sources of neutrons employed in NAA:

- reactors
- radionuclides
- accelerators

Neutrons are categorized into three energy regimes:

- thermal
- epithermal
- fast

Nuclear Reactors

Neutron reactor at National Institutes of Standards and Technology (Gaithersburg, Md.).

Reactors produce tremendous flux of neutrons. Typically 10^{11} to 10^{14} n cm^{-2} s^{-1}. They are widely used for NAA and provide the lowest detection limits.

Radionuclide Sources

- Convenient and inexpensive compared to a reactor ($750 million)
- Flux is much lower than reactor 10^5 to 10^{10} n cm^{-2} s^{-1}
- Detection limits not as good as with reactor
- Usually from the fission of transuranium elements

  ^{238}Cf is a common source
- Also from mixtures of heavy with light elements

Mix an alpha emitter (Pu, Am, Cu, etc.) with a light element such as Be. Alpha particles react with light elements to produce neutrons *via* a fusion process.

$$^{9}_{4}\mathrm{Be} + ^{4}_{2}\mathrm{He} \rightarrow ^{12}_{6}\mathrm{C} + ^{1}_{0}\mathrm{n} + 5.7\,\mathrm{MeV}$$

Particle Accelerators

An ion source produces deuterons which are accelerated to 150 keV and slammed into tritium which has been adsorbed on a Ti or Zr target.
A fusion reaction liberates very high energy neutrons (~14 MeV).

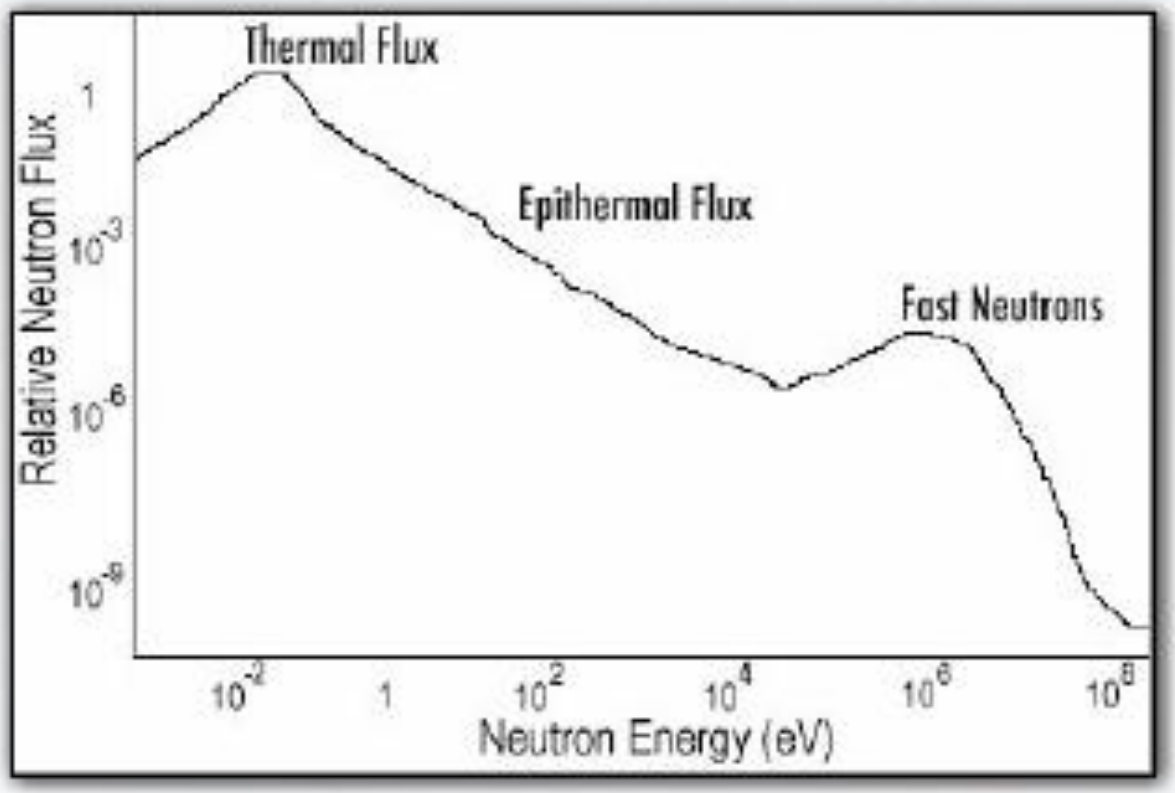
$$^{2}_{1}\mathrm{H} + ^{3}_{1}\mathrm{H} \rightarrow ^{4}_{2}\mathrm{He} + ^{1}_{0}\mathrm{n}\,(14\,\mathrm{MeV})$$

Modern accelerators under development are spallation sources. These are big. Particle beam energy of 2 GeV. Smash into a heavy target (Hg) and strips off neutrons at very high energies.

Spallation source at Oak Ridge Tenn., fist neutron beam April 2006.

Energy Distribution

The kinetic energy with which the neutrons leave the source varies widely. Reactivity with heavy elements is best achieved with slow moving neutrons.



Neutrons are slowed by a moderator (sometimes just paraffin wax) which equilibrates them to room temperature (~0.25 eV). Partially equilibrated neutrons form the epithermal flux. Fast neutrons are useful in reactions with light elements.

NAA 3

Nuclear activation analysis proceeds by irradiating a sample and standards with the same neutron flux.

Occasionally the prompt γ-ray can be used to detect the presence of the analyte atom. More often, however, the sample is allowed to cool following irradiation to shed itself of the intense radiation that could interfere. Subsequently, the delayed radioactive processes are monitored.

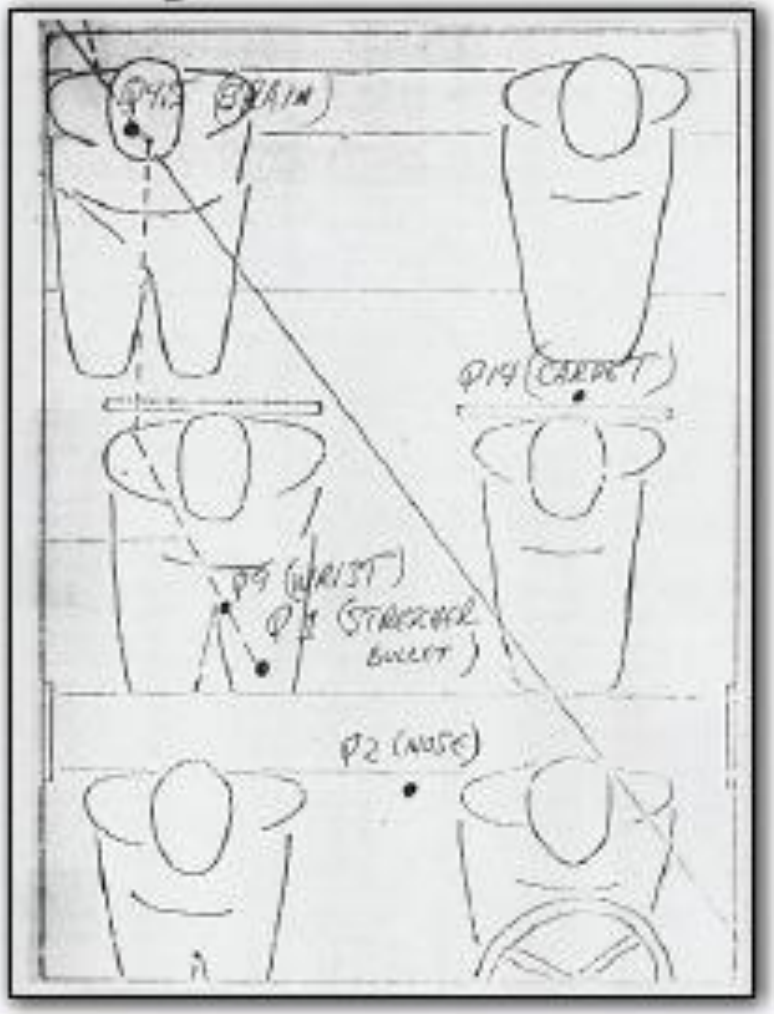
Gamma energies are determined in a multichannel analyzer.

Amount of γ-ray is related to amount of material present.

Sample is irradiated for a time equal to 4 or 5 times the half-life of the product nuclei. Sample transmutation is saturated. Analyte weight is directly proportional to count rate (when compared against the standard).

$$W_{unknown} = \frac{R_{unknown}}{R_{standard}} W_{standard}$$

Very Famous Mystery Solved



Drawing from the proceedings of a governmental commission regarding an important event in American history.

NAA was used to conclusively resolve the debate (though some film makers continue to revel in the possibilities of it being more).

What is this?

Sensitivity

Sensitivity (pg/g)	*Elements*
1	**Dy, Eu**
1 - 10	**In, Lu, Mn**
10 - 100	**Au, Ho, Ir, Re, Sm, W**
100 - 1000	**Ag, Ar, As, Br, Cl, Co, Cs, Cu, Er, Ga, Hf, I, La, Sb, Sc, Se, Ta, Tb, Th, Tm, U, V, Yb**
1000 - 10,000	**Al, Ba, Cd, Ce, Cr, Hg, Kr, Gd, Ge, Mo, Na, Nd, Ni, Os, Pd, Rb, Rh, Ru, Sr, Te, Zn, Zr**
10,000 - 10^5	**Bi, Ca, K, Mg, P, Pt, Si, Sn, Ti, Tl, Xe, Y**
10^5 - 10^6	**F, Fe, Nb, Ne**
10^6 - 10^7	**Pb, S**