

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)

Instrumental neutron activation analysis (INAA) is used to determine the concentration of trace and major elements in a variety of matrices. A sample is subjected to a neutron flux and radioactive nuclides are produced. As these radioactive nuclides decay they emit gamma rays whose energies are characteristic for each nuclide. Comparison of the intensity of these gamma rays with those emitted by a standard permit a quantitative measure of the concentrations of the various nuclides.



Figure 1. Core of research reactor.

FUNDAMENTAL PRINCIPLES

The n-gamma reaction is the fundamental reaction for neutron activation analysis. For example, consider the following reaction



^{58}Fe is a stable isotope of iron while ^{59}Fe is a radioactive isotope. The gamma rays emitted during the decay of the ^{59}Fe nucleus have energies of 142.4, 1099.2, and 1291.6 KeV, and these gamma ray energies are characteristic for this nuclide. The probability of a neutron interacting with a nucleus is a function of the neutron energy. This probability is referred to as the capture cross-section, and each nuclide has its own neutron energy – capture cross-section relationship. For many nuclides, the capture cross-section is greatest for low energy neutrons (referred to as thermal neutrons). Some nuclides have greater capture cross-sections for higher energy neutrons

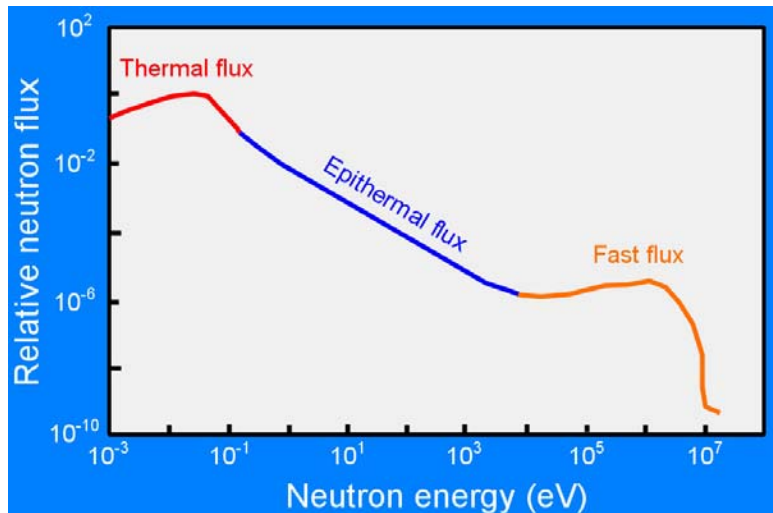


Figure 2. Relative neutron flux as a function of neutron energy for a typical research reactor.

(epithermal neutrons). For routine neutron activation analysis we are generally looking at nuclides that are activated by thermal neutrons.

The activity for a particular radionuclide, at any time t during an irradiation, can be calculated from the following equation

$$A_t = \sigma_{\text{act}} \phi N (1 - e^{-\lambda t})$$

where A_t = the activity in number of decays per unit time, σ_{act} = the activation cross-section, ϕ = the neutron flux (usually given in number of neutrons $\text{cm}^{-2} \text{s}^{-1}$), N = the number of parent atoms, λ = the decay constant (number of decays per unit time), and t = the irradiation time. From this equation we can see that the total activity for a particular nuclide is a function of the activation cross-section, the neutron flux, the number of parent atoms, and the irradiation time. Note that for any particular radioactive nuclide radioactive decay is occurring during irradiation, hence the total activity is determined by the rate of production minus the rate of decay. If the irradiation time is much longer than the half-life of the nuclide, saturation is achieved. What this means is that the rate of production and decay is now in equilibrium and further irradiation will not lead to an increase in activity. The optimum irradiation time depends on the type of sample and the elements of interest. Because the neutron flux is not constant, the total flux (called fluence) received by each sample must be determined using an internal or external fluence monitor.

It is sometimes useful to convert from half-life to decay constant. This can be done using the following equation

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

where $t_{1/2}$ is the half-life and λ is the decay constant.

After the sample has been activated, the resulting gamma ray energies and intensities are determined using a solid-state detector (usually Ge). Gamma rays passing through the detector generate free-electrons. The number of electrons (current) is related to the energy of the gamma ray. Because there can be thousands to hundreds of thousands of gamma ray interactions per second with the detector, an important criteria in system design is the response time of the detector to gamma ray interactions (as measured by the dead time). Each radioactive nuclide is also decaying during the counting interval and corrections must be made for this decay. The standard form of the radioactivity decay correction is

$$A = A_0 e^{-\lambda t}$$

where A is the activity at any time t , A_0 is the initial activity, λ is the decay constant and t is time.

When subjected to a thermal neutron flux ^{235}U atoms in a sample will undergo fission producing a variety of fission products, some of which are nuclides of interest. Hence, a correction that must be made, when U is present, is for the amount of a nuclide produced by the fission process.

Given the differences in half-lives for various nuclides, there are optimum times to count an activated sample. In general nuclides with relatively short half-lives, on the order of hours to days, are determined within the first week of irradiation. Nuclides with half-lives on the order of weeks to months are determined 4 to 8 weeks after irradiation. Hence, activated samples are counted several times after irradiation.

INSTRUMENTATION

A gamma-ray spectroscopy system consists of a detector (and high voltage power supply for the detector), pre-amplifier, spectroscopy amplifier, analog-to-digital converter, multi-channel analyzer, and an output device. A sample is presented to the detector (Ge in the case of gamma-ray analysis). In order to minimize thermal noise the detector is kept at cryogenic temperatures (liquid nitrogen, temperature = 77K). The initial signal is very small and the pre-amplifier, attached directly to the detector, amplifies this signal. The signal is shaped by the spectroscopy amplifier and then converted from an analog to a digital signal by the analog-to-digital converter. The results are stored in digital form (multi-channel analyzer). In modern gamma-ray spectroscopy systems the high-voltage power supply, spectroscopy amplifier, analog-to-digital converter, and multi-channel analyzer are combined into a single module. A computer is used to visually show the resulting spectrum and to

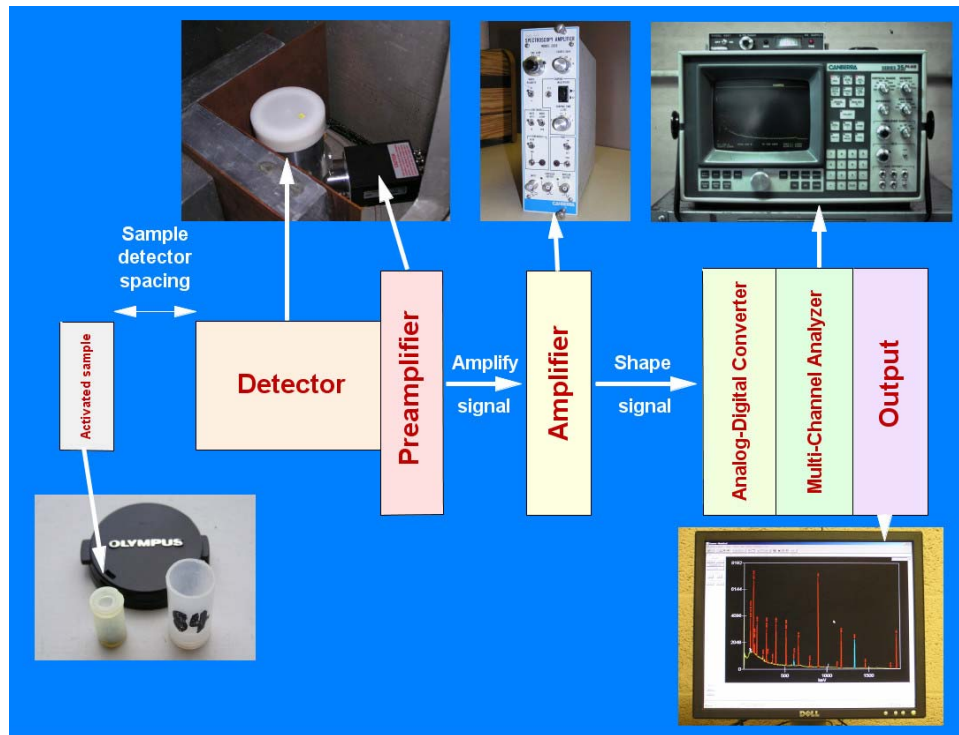


Figure 3. Flow chart for a gamma-ray spectroscopy system.

do calculations on the spectrum. Various algorithms are used to determine the shape and energy of each gamma-ray peak present in a spectrum and to determine the area encompassed by the peak (i.e., the gamma-ray intensity). Subsequent decay, interference (if required), fluence, and fission product corrections, and comparison with a standard, lead to a quantitative analysis.



Figure 4. Gamma-ray spectroscopy system (automated sample changer). The detector is kept at liquid nitrogen temperatures (dewar under cave). The small box on top of the cabinet combines all the functions of the HV power supply, spectroscopy amplifier, and analog-to-digital converter. The resultant spectrum is shown on the computer screen.

APPLICATIONS

While liquid samples (if certain precautions are taken) can be analyzed by INAA, solids are the matrix of choice for this technique. Virtually any material can be analyzed and limitations are largely due to the chemistry of the matrix. For example, it would be difficult to obtain low detection limits for a sample of pure iron because given the half-life (44.6 days) of ^{59}Fe , the sample will have a high background for an extended period of time and shorter half-life isotopes will be gone from the sample before this background is reduced. Examples of the types of materials that can be analyzed by INAA are

- Rocks, minerals, and soils
- Atmospheric aerosols
- Archaeological artifacts
- Tree rings
- Dust in ice cores
- Hair, nails, skin, etc.
- Plant and animal matter
- Coal

1																	2
H																	He
3	4											5	6	7	8	9	10
Li	Be											B	C	N	O	F	Ne
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	¹ La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	89	104	105													
Fr	Ra	² Ac	Rf	Db													
¹ Lanthanide		58	59	60	61	62	63	64	65	66	67	68	69	70	71		
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
² Actinide series		90	91	92	93	94	95	96	97	98	99	100	101	102	103		
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		
		No n-gamma radioactive isotopes															
		Radioactive isotopes can be produced. Limitation is short half-life or flux energy															
		Elements routinely determined by INAA															

Figure 5. Periodic table showing elements that can be analyzed by neutron activation analysis.

STRENGTHS

The strengths of INAA are

- Can analyze a large number of elements simultaneously
- Very low detection limits for many elements
- Small sample sizes (1 – 200 mg)
- No chemical preparation
- Non-destructive. The material is available for other analytical techniques

Additionally, compared to many analytical techniques, the instrumentation cost is relatively low. In 2007 it would cost about \$50,000 to set-up and INAA laboratory.

LIMITATIONS

There are very few limitations. The major limitation is the number of elements that can be analyzed by this technique. Several elements of geological interest, such as Nb, Y and some transition metals, are better determined by other analytical methods. For example, more precise Rb, Sr, Y, Nb, and Zr concentrations can be obtained by x-ray fluorescence (XRF). In fact, INAA and XRF are complimentary techniques and rock and mineral chemistries are often determined using both INAA

and XRF. Also, because there is no chemical pre-separation, the sensitivity of the method is dependent upon the sample matrix. For example, detection limits for all elements are lower in tree ring samples than in rock samples.

SAMPLE COLLECTION AND PREPARATION

Because of the low detection limits for many elements, sample collection and preparation is critical. Great care must be taken not to introduce contaminants. Virtually any solid material can be analyzed by this method, but there are geometric constraints – the sample must fit into the irradiation vial and should present a consistent geometry. Before selecting material for analysis consideration should be given to the geometrical factors.



Figure 6. Sample vial (smaller vial) and counting vial.

DATA COLLECTION, RESULTS, AND PRESENTATION

In modern laboratories the final results are presented as concentrations, in weight percent, ppm, or some other convenient unit. All the data reduction is handled by computer codes.

LITERATURE

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Gordon, G. E., Randel, K., Goles, G. G., Corliss, J. B., Benson, M. H., and Oxley, S., 1968, Instrumental activation analysis of standard rocks with high resolution gamma-ray detectors. *Geochimica et Cosmochimica Acta* 32, 369-396.

Lieser, Karl H., 2001, *Nuclear and Radiochemistry*, 2nd Ed.: John Wiley & Sons, Inc.

Muecke, G.K., ed., 1980, *Neutron Activation Analysis in the Geosciences: Mineralogical Association of Canada Short Course Handbook* 5.

RELATED LINKS

www.canberra.com - technical descriptions of the various components of a gamma ray spectroscopy system.

http://web.missouri.edu/~glascockm/naa_over.htm - overview of neutron activation analysis.

http://en.wikipedia.org/wiki/Neutron_activation_analysis - description of INAA, includes links to other sites.