Neutron Activation Analysis (NAA)

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Abstract

A description of the general principles of Neutron Activation Analysis (NAA) is followed by a discussion of advantages, limitations, and applications. Landmine detection and radioisotope power generation were identified as the two promising future applications.

Keywords: Landmine detection, radioisotope power generation, multi-element analysis, prompt gamma radiation, delayed gamma radiation.

Introduction

Neutron Activation Analysis (NAA), discovered in 1936, is an important technique for quantitative multi-element analysis of major, minor, trace, and rare elements. The initial step in neutron activation analysis is irradiating a sample with neutrons in a nuclear reactor or sometimes in other neutron sources (Siddappa et al., 1996). The stable nucleus absorbs one neutron and becomes a radioactive nucleus. The concentration of the stable element of interest in the sample can be measured by detecting the decay of these nuclei (Nuclear Science Division and Contemporary Physics Education Project 2000).

The radioactive nuclei emit characteristic gamma rays. Detection of the specific gamma rays (of specific energy) indicates presence of a particular element. Suitable semiconductor radiation detectors may be used for quantitative measurement. The concentrations of various component elements in given samples are found by computer data reduction of gamma ray spectra. Sequential instrumental neutron activation analysis allows quantitative measurement of up to about 35 elements in small samples of 5 to 100 mg. The lower detection limit is in parts per million or parts per billion, depending on the element (Radiation Center 2003).

An example of a nuclear reactor used for irradiating samples is the Oregon State University TRIGA Reactor (OSTR), which is a water-cooled, swimming pool type of research reactor that uses uranium/zirconium hydride fuel elements in a circular grid array (Radiation Center 2003). The reactor core is surrounded by a ring of graphite that serves to reflect neutrons back into the core. The core is situated near the bottom of a 22 feet deep, water-filled tank, and the tank is surrounded by a concrete monolith that acts as a radiation shield and structural support. The reactor is licensed by the U.S. Nuclear Regulatory Commission to operate at maximum steady state power of 1.1 MW, and can also be pulsed up to a peak power of 3,000 MW.

General Principles

In typical NAA, stable nuclides (\(^{\text{A}}\text{Z}\), the target nucleus) sample undergo neutron capture reactions in a flux of (incident) neutrons (Missouri University homepage 2003). The radioactive nuclides (\(^{\text{A}+1}\text{Z}\), the compound nucleus) produced in this activation process usually decay by emission of a beta particle (\(\beta^-\)) and gamma ray(s) with a unique half-life. A high-resolution gamma-ray spectrometer is used to detect these ‘delayed’ gamma rays in the presence of the artificially induced radioactivity in the sample for both qualitative and quantitative analysis.

The sequence of events that occur during the most common type of nuclear reaction used
for activation analysis is shown in Fig. 1. The incident neutron hits the target nucleus, which captures the neutron and is converted into a compound nucleus. The latter immediately emits radiation called prompt gamma radiation and forms the radionuclide, which then kicks out a beta particle and emits the delayed gamma radiation (since it is emitted after some time delay), forming the product nucleus.

Natural sodium $^{23}$Na target may be taken as a specific example. On neutron capture it is converted to radioactive sodium $^{24}$Na. The usual procedure involves placing the samples to be analyzed plus a number of suitable standards into the neutron field produced by a research nuclear reactor. The samples are then analyzed using an appropriate gamma ray detector system. The $^{24}$Na decays to stable $^{24}$Mg with the release of gamma rays having energies of 1368.53 and 2754.09 kilo-electron volts (keV). On striking a suitable detector the gamma ray energies are converted to an electrical signal that is processed as a count in an energy spectrum. The accumulation of gamma counts at a particular energy generates a curve, the area of which is proportional to the radioactivity of the characteristic radionuclide. Comparing against standards allow the establishment of a relationship that can be used to determine the abundance of a particular element or elements. An example of a gamma-ray spectrum is shown in Fig. 2 (Nuclear Science Division and Contemporary Physics Education Project 2000).

The energies of the delayed gamma rays are used to identify component sample elements. The count of gamma rays of a specific energy indicates the amount of an element in the sample. For example, when a silver sample is irradiated, a fraction of the $^{109}$Ag atoms in the sample will capture a neutron and become $^{110}$Ag. The radioactive $^{110}$Ag atoms have a half-life of 24.6 seconds. Beta decay of $^{110}$Ag atoms to $^{110}$Cd occurs 4.5% of the time with emission of a 658 keV gamma ray. The amount of silver in the original sample can be determined by measuring the count of 658 keV gamma-rays emitted from the sample in a given time interval after irradiating the sample.

\[ ^{109}\text{Ag} + n \rightarrow ^{110}\text{Ag} \]
\[ ^{110}\text{Ag} \rightarrow \beta^- + ^{110}\text{Cd} + \gamma \ (658 \text{ keV}) \]

The measured count rate ($R$) of the gamma rays from the decay of a specific isotope ($^{110}$Ag) in the irradiated sample can be related to the amount ($n$) of the original, stable isotope ($^{109}$Ag) in the sample through the following equation (1) (Nuclear Science Division and Contemporary Physics Education Project 2000).

\[ R = \varepsilon I_\gamma A = \varepsilon I_\gamma n \phi \sigma (1-e^{-\lambda t_i}) e^{-\lambda t_d} \]

- $R$ = measured gamma-ray count rate (cps)
- $A$ = absolute activity of isotope $^{A+1}Z$ in sample
- $\varepsilon$ = absolute detector efficiency
- $I_\gamma$ = absolute gamma-ray abundance
- $n$ = number of atoms of isotope $^{A}Z$ in sample
- $\phi$ = neutron flux (neutrons·cm$^{-2}$·sec$^{-1}$)
- $\sigma$ = neutron capture cross section (cm$^2$) for isotope $^{A}Z$
- $\lambda$ = radioactive decay constant (s$^{-1}$) for isotope $^{A+1}Z$
- $t_i$ = irradiation time (s)
- $t_d$ = decay time (s)

If the neutron flux $\phi$, neutron captures cross section $\sigma$, absolute detector efficiency $\varepsilon$, and absolute gamma-ray abundance $I_\gamma$ are known, the number of atoms $n$ of isotope $^{A}Z$ in the sample can be calculated directly. In most cases, however, a standard is irradiated and counted under similar conditions as the sample, and the mass of the element in the sample ($W_{sam}$) is found by comparing the measured count rates ($R$) for the sample and standard through the following equation (2):

\[ W_{sam} = W_{std} \frac{R_{sam}}{R_{std}} \]

- $W_{sam}$ = mass of element in sample (g)
- $W_{std}$ = mass of element in standard (g)
- $R_{sam}$ = sample gamma-ray count rate (cps)
- $R_{std}$ = standard gamma-ray count rate (cps)

Advantages and Limitations

As the vast majority of samples are completely transparent to both the probe (the neutron) and the analytical signal (the gamma ray) NAA is free of matrix interference. Also, reagent or laboratory contamination is minimized because NAA does not require sample pretreatment such as digestion or dissolution.
Interferences can still occur when different component sample elements produce similar gamma rays. This problem can be circumvented by choosing alternate gamma rays or by counting only after the shorter-lived nuclide had decayed. Other interferences can occur if another type of nuclear reaction concurrently produces the radionuclide of interest in addition to the simple neutron capture process described here.

Sensitivities and accuracy depends on the concentration of the element and radionuclide parameters (i.e., parent isotope abundance, neutron cross-section, half-life, and gamma ray abundance). Element sensitivities vary from $10^{-3}$ to $10^{-10}$ grams per gram of sample. Accuracy is usually between two and ten percent of the reported value, depending on the element analyzed and its concentration in the sample.

The detection limit for a particular element depends upon the measured count rate ($R$) of the gamma ray being monitored and the background radiation. As seen from equation 1, the measured count rate ($R$) for a given isotope and consequently the S/N (signal to noise ratio), can be increased by any combination of the following:

1. Increasing the detector efficiency (moving the sample closer to the detector)
2. Increasing the irradiation time ($t_i$)
3. Decreasing the decay time ($t_d$).

In many cases the sensitivity of the measurement can be improved by increasing the measurement time ($t_m$), which enhances the overall signal or total number of counts ($R \cdot t_m$). Another common limitation of instrumental NAA is caused by the bulk matrix. When it produces a large background that masks the signal of interest, the S/N becomes very low and the detection limit is reduced extensively. Time delays or chemical separations may be used to minimize this effect.

### Applications

Advances in semiconductor detector systems coupled with improvements in nuclear reactors have widened the scope of the neutron activation analysis. A strong testament to the reliability and accuracy of NAA is its use in analyzing the lunar samples from the Apollo missions. Instrumental neutron activation analysis and radiochemical neutron activation analysis have made it possible for high sensitivity non-destructive determinations. Neutron activation analysis has been used successfully in research as diversified as nutrient uptake in plants, petro-genetic modeling of geologic phenomena, identification of impurities in new metals and alloys, environmental monitoring, and analysis of forensic evidence for criminal and civil cases. A prominent example is the use of NAA in JFK assassination investigation (Rahn 2001).

Small samples (as small as a few micrograms) of 30 to 35 major, minor, and trace elements may be routinely analyzed by instrumental neutron activation analysis. Radiochemical neutron activation analysis techniques, although destructive to the sample, enhance the number of determinable elements to about 50. Some scientific, engineering, and industrial applications of neutron activation analysis are listed in Table 1 (Radiation Center 2003).

A simple example of neutron activation analysis involves the measurement of iridium in soils (Nuclear Science Division and Contemporary Physics Education Project 2000). This is the measurement that led to the theory that the extinction of the dinosaurs, 65 million years ago, was caused by the impact of an asteroid or comet somewhere on Earth.

In 1979, a group of scientists that included Nobel Laureate physicist Luis Alvarez, his son geologist Walter Alvarez and nuclear chemists Isadore Perlman, Frank Asaro and Helen Michel reported that neutron activation analysis had shown unusual amounts of the element iridium in Italian Cretaceous-Tertiary boundary sediments (Nuclear Science Division and Contemporary Physics Education Project 2000).

Since iridium is a metal that has very low abundance on earth, they attributed the excess iridium to an impact of a 10-km diameter asteroid. Since then, anomalous amounts of iridium have been found at the Cretaceous-Tertiary boundary in over 100 sites worldwide and many experiments have confirmed its impact origin.
Many types of thickness gauges exploit the fact that gamma rays are attenuated when they pass through material. This process is used in common industrial applications such as:

1. The automobile industry – to test steel quality in the manufacture of cars and to obtain the proper thickness of tin and aluminum.
2. The aircraft industry – to check for flaws in jet engines.
3. Construction – to gauge the density of road surfaces and sub-surfaces.
4. Pipeline companies – to test the strength of welds.
5. Oil, gas, and mining companies – to map the contours of test wells and mine bores, and
6. Cable manufacturers – to check ski lift cables for cracks.

Home and business smoke detectors; thickness gauges that measure and control metal foil thickness during manufacturing processes; toxicity meters that measure levels of toxic lead in dried paint samples; and site detectors that help determine where oil wells should be drilled, all use the $^{241}$Am isotope.

The $^{252}$Cf (a neutron emitter) isotope is used for neutron activation analysis, to inspect airline luggage for hidden explosives, to gauge the moisture content of soil and other materials, in bore hole logging in geology, and in human cervix-cancer therapy.

There are extensive uses in agriculture. In plant research, radiation is used to develop new plant types to speed up the process of developing superior agricultural products. Insect control is another important application; pest populations are drastically reduced and, in some cases, eliminated by exposing male insects to sterilizing doses of radiation. Fertilizer consumption has been reduced through research with radioactive tracers. Radiation pellets are used in grain elevators to kill insects and rodents. Irradiation prolongs the shelf life of foods by destroying bacteria, viruses, and molds.

Application of radioisotopes can extend to the arts and humanities. Neutron activation analysis is extremely useful in identifying the chemical elements present in coins, pottery, and other artifacts from the past. A tiny unnoticeable fleck of paint from an art treasure or a microscopic grain of pottery suffices to reveal its chemical makeup. Thus the works of famous painters can be ‘fingerprinted’ so as to detect the work of forgers.

Studies of ceramic objects in archeological excavations are observed (Begg and Riley 1990; De Sena et al., 1995; De Sena and Friedman 1997; Descantes et al., 2001). Studies on Roman pottery include the use of neutron activation analysis in determining provenience of pottery (Esse and Hopke 1986); and a discussion of two types of provenience studies on ancient pottery to determine manufacturing groups and movement of populations (Wiseman and Hopke 1991). Estimation of precious metals such as gold and silver (Gordus and Shimada 1995) and coinage metals (Gordus 1995; Aung 1989) is popular.

Some rare studies include lipid study (Valtuena and Kehayias 2003); a mobile analysis system, using prompt gamma neutron activation analysis, for the nondestructive identification of chemical warfare agents and explosives in different kinds of ammunition (Heller et al., 2003); and trace elements in 52 Chinese medicines (Lin et al., 2003). It was reported that use of epithermal neutrons reduces the background counts in low energy of gamma rays, and consequently raises the S/N for the determination of trace elements like As, Cd, Cr, Hg and Zn.

Neutron scattering has proved to be a valuable tool for studying the molecular structure and motion of molecules of interest to manufacturing and life processes. Accelerators and reactors produce low-speed neutrons with wavelength appropriate to ‘see’ structures of the size of magnetic microstructures and DNA molecules. Neutrons can penetrate deeply into bulk materials and use their magnetic moment or strong interaction forces to preferentially scatter from magnetic domains or hydrogen atoms in long chain nucleosomes. Based on their reflectivity properties, neutrons are also used in materials surface and interface studies. Intense sources of neutrons include: the IPNS at Argonne National Laboratory in Illinois and LANSCE at Los Alamos National Laboratory in New Mexico.
Future Applications

Landmine detection and radioisotope power generation are identified as possible future applications of NAA (Nuclear Science Division and Contemporary Physics Education Project 2000).

Detection of Landmines

It is estimated that 100 million abandoned mines that can maim and kill unsuspecting civilians are dispersed all over the globe. Techniques such as nuclear quadruple resonance, similar to airport weapons detectors, have been considered for detecting and neutralizing these mines. Nitrogen, a common component in explosives, has an ellipsoid shaped nucleus. Different crystal lattice environments can distort the ellipsoid to different degrees and produce a unique set of very narrowly spaced energy levels that is characteristic of the crystalline solid itself. Thus an explosive compound can be identified by the subtle effect of its constituent nitrogen atoms. Also it will be possible to differentiate explosive canisters from scrap metals.

Radioisotope Power Generation

Remote or inaccessible equipment (being underground, inside bodies, inside tight small spaces) demands long-lived power sources. These may be obtained by choosing a radioactive element with a sufficiently long half-life. The element should have the following properties:

1. Producing easily shielded weakly penetrating radiation.
2. Containing a specific power of at least 0.2 kW/kg.
3. Having good corrosion resistance.
4. Is insoluble in water.
5. Is made of reasonably available material.

Among the transuranium elements, oxides of the alpha-emitting nuclides $^{238}$Pu ($t_{1/2} = 87.7$ years) and $^{244}$Cm ($t_{1/2} = 18.1$ years) are useful fuels. It is possible to convert the resultant heat flow into usable electricity by using thermoelectric devices that do not have moving parts.

Such lightweight and rugged small power sources are already been used in the SNAP (Space Nuclear Auxiliary Power) units used to power satellites and in remote sensing instrument packages. Cardiac pacemakers use $^{238}$Pu or lithium batteries. Since 1970s Over 3,500 units were implanted and most remain functioning.

Conclusion

The many diverse applications in varied fields show that NAA is extremely useful, even though it is a relatively simple analytical method. Irradiation of samples may be done at nuclear reactors that offer such services. Such centers are easily accessible nowadays. Even if these centers are inaccessible, other neutron sources that emit thermal neutrons may be used. Hence any laboratory that has a gamma counter can perform NAA experiments. Development of research programs based on NAA is accessible to any laboratory that is willing to invest a minimal amount of funds. Landmine detection and radioisotope power generation are especially interesting fields.

References


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<tr>
<th>Application</th>
<th>Examples</th>
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<tbody>
<tr>
<td>Agriculture</td>
<td>beet pulp, lipids, hay, oil, fish</td>
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<tr>
<td>Archeology/Anthropology</td>
<td>Ceramic utensils, obsidian, teeth, bones</td>
</tr>
<tr>
<td>Biology</td>
<td>chemicals, sugar, enzymes, solutions, ants</td>
</tr>
<tr>
<td>Botany</td>
<td>wheat spores</td>
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<tr>
<td>Chemistry</td>
<td>oxides, salts, pure crystals, and metals</td>
</tr>
<tr>
<td>Engineering &amp; Industry</td>
<td>pure metals, chemical compounds, oils, thin film deposits, plastic films, alloys, rocks</td>
</tr>
<tr>
<td>Fisheries</td>
<td>fish, shells</td>
</tr>
<tr>
<td>Forestry</td>
<td>wood, phloem, tree needles, soil</td>
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</tbody>
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Table 1. Some Applications of NAA
Geology | rocks, meteorites, moon samples, gems, minerals
---|---
Medicine | water, skin, hair, nails, alternative medicine components
Oceanography | fossils, sediments, basalts
Pharmacy | chemicals
Forensic | bullets, paint, glass, metals, gunshot residue swabs

(Radiation Center, Oregon State University, 2003)

Fig. 1. Sequence of events that occur during the most common type of nuclear reaction used for activation analysis
(Nuclear Science Division and Contemporary Physics Education Project 2000).

Fig. 2. An example of gamma-ray spectrum from the activation of a human nail
(Nuclear Science Division and Contemporary Physics Education Project 2000).