12 Neutron activation analysis

12.1 Introduction

Neutron activation analysis was first proposed as an analytical technique by von Hevesy and Levi in 1936. However, its successful application to geology (Gordon et al., 1968; Hertogen and Gijbels, 1971) had to await the commercial development of high-resolution germanium detectors during the 1960s to allow satisfactory analysis of the complex gamma spectra obtained from irradiated silicate rock samples.

The technique is used predominantly for the analysis of specific trace elements down to detection limits in the ppm to ppb range, and is especially sensitive for the rare-earth elements (La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu), Sc, Co, Cr, Cs, Hf, Ta, Th, U and some others.

Samples are 'activated' by irradiation with neutrons, usually in a nuclear reactor. Specific isotopes become radioactive by neutron capture-type nuclear reactions. After removal from the reactor, samples are allowed to decay ('cool') to permit unwanted short-lived activity (for example, from $^{24}$Na) to diminish. Gamma-ray spectra from activated samples are then measured using solid-state germanium gamma-ray detectors, usually over the energy range 60 to 1600 keV. Specific isotopes may be identified by their gamma-rays of characteristic energy and quantitative determinations are made by comparing the areas of these photopeaks with those in the spectrum of a standard sample, irradiated and counted under identical conditions.

The two general procedures employed are classified as:

(i) instrumental neutron activation analysis (INAA) which involves the irradiation and analysis of rock powders that undergo no chemical treatment in the course of the analysis (this procedure may, therefore, be considered as a non-destructive technique) and (ii) radiochemical neutron activation analysis (RNAA), which involves taking up irradiated samples into solution so that a chemical separation procedure may be carried out to isolate specific trace elements from the more active matrix. This latter procedure lowers detection limits by perhaps one to two orders of magnitude and significantly extends the range of elements that may be successfully analysed. However, such procedures are more time-consuming and involve specialized laboratory facilities for manipulation of radioactive material.

Neutron activation analysis has the advantage of being very sensitive for specified elements and virtually free of matrix interference effects (except overlap interferences in complex gamma spectra). The disadvantage is that the technique requires specialized irradiation facilities and for this reason is largely confined to establishments adjacent to nuclear reactors.

In the determination of the REEs, neutron activation analysis cannot achieve the high precision nor low detection limits claimed for isotope dilution mass spectrometry (e.g. Hooker et al., 1975). Furthermore, recent developments in inductively coupled plasma emission spectrometry (e.g. Bolton et al., 1983; Walsh et al., 1981) indicate that sensitive REE determinations may be made by this technique provided sample preparation procedures include a chemical separation. Nevertheless, during the 1970s, INAA was the only technique available for the routine determination of REEs in rock samples and is still extensively used in this field. INAA is one of the few routine techniques available for the determination of other geochemically important trace elements including Ta and Hf (and Th), these elements being difficult to incorporate in schemes that involve solution chemistry.

In this chapter the theoretical and practical application of instrumental NAA is discussed in detail, this being the simplest and most widely used form of the technique. Other analytical derivations are then discussed more briefly.

Most counting systems are not purchased as integrated commercial packages but are sometimes put together as combinations of equipment from different manufacturers. A discussion is, therefore, included on individual instrumental components in the signal accumulation system with which a user must interact.

INAA is, by reputation, sometimes considered to be a technique of variable routine precision. It is felt that this is in part due to the "do-it-yourself" way in which systems are put together by users and to the fact that calibrations are often set up against a single reference material. Data are presented to demonstrate that, provided care is taken in optimizing and controlling instrument parameters, precisions equivalent to other instrumental procedures used for trace analysis can be achieved.

12.2 The growth and decay of radioactivity

12.2.1 Neutron sources—the nuclear reactor

The most commonly used source of neutrons for activation analysis is the nuclear reactor. Most research reactors depend on the fission of $^{235}$U. This isotope is naturally radioactive, with a half-life of $7.038 \times 10^8$ years, and will spontaneously decay by nuclear fission, in which the nucleus splits into isotopic fragments, releasing high-energy neutrons and energy. If moderated (i.e. slowed down) these neutrons can
12.2 NEUTRON ACTIVATION ANALYSIS

10° neutron activation analysis. Their energies are moderated by interaction with a material of low atomic number in which efficient loss of kinetic energy occurs. Water is particularly effective for this purpose. The resultant energy spectrum of neutrons (Figure 12.1) may be subclassified as follows:

(a) Thermal neutrons. Thermal neutrons have very low energies, in the range 0 to 0.5 eV, but with a most probable energy of 0.025 eV at 20°C (corresponding to a mean neutron velocity of 2200 m s^{-1}). This energy is equivalent to that predicted by a Maxwellian distribution function for neutrons that have attained thermal equilibrium with their surroundings. Thermal neutrons efficiently promote \((n,\gamma)\) reactions which are the basis of most neutron activation analysis measurements.

(b) Epithermal neutrons. Epithermal neutrons have energies in the range of 0.5 eV to 10 keV and may be used to selectively activate particular isotopes in neutron activation analysis (see section 12.15). The threshold of 0.5 eV is chosen because of an unusual property of cadmium. A thin foil of this material (0.5–1mm thick) strongly absorbs neutrons with energies below this threshold (Figure 12.2), predominantly by the nuclear reaction

\[
\text{\textsuperscript{113}Cd}(n,\gamma)\text{\textsuperscript{114}Cd}
\]

where the product isotope \textsuperscript{114}Cd is stable. Higher-energy neutrons are only weakly attenuated, as is apparent from the neutron capture cross-section diagram of \textsuperscript{113}Cd (Figure 12.2). For this reason, this region is also known as the epi-cadmium neutron spectrum. Resonance neutron capture occurs when an isotope shows high neutron capture cross-sections at discrete neutron energies in the epithermal region (Figure 12.2). An appreciable degree of activation may then result from capture of resonance neutrons, permitting selective analysis of such isotopes in comparison with those that are only strongly activated by a thermal neutron flux. This extension of conventional thermal neutron activation analysis is known as epithermal neutron activation analysis (ENAA). Elements that may be preferentially activated in this way include U, Ta, Sb, Mo, Au, and Ir.

12.2.2 Energy spectrum of neutrons

Neutrons emitted during the fission of \textsuperscript{235}U have energies in the range 0–25 MeV and are far too energetic to efficiently promote the activation of isotopes required for conventional neutron activation analysis. Their energies are moderated by interaction with a material of low atomic number in which efficient loss of kinetic energy occurs. Water is particularly effective for this purpose. The resultant energy spectrum of neutrons (Figure 12.1) may be subclassified as follows:

(a) Thermal neutrons. Thermal neutrons have very low energies, in the range 0 to 0.5 eV, but with a most probable energy of 0.025 eV at 20°C (corresponding to a mean neutron velocity of 2200 m s^{-1}). This energy is equivalent to that predicted by a Maxwellian distribution function for neutrons that have attained thermal equilibrium with their surroundings. Thermal neutrons efficiently promote \((n,\gamma)\) reactions which are the basis of most neutron activation analysis measurements.

(b) Epithermal neutrons. Epithermal neutrons have energies in the range of 0.5 eV to 10 keV and may be used to selectively activate particular isotopes in neutron activation analysis (see section 12.15). The threshold of 0.5 eV is chosen because of an unusual property of cadmium. A thin foil of this material (0.5–1mm thick) strongly absorbs neutrons with energies below this threshold (Figure 12.2), predominantly by the nuclear reaction

\[
\text{\textsuperscript{113}Cd}(n,\gamma)\text{\textsuperscript{114}Cd}
\]

where the product isotope \textsuperscript{114}Cd is stable. Higher-energy neutrons are only weakly attenuated, as is apparent from the neutron capture cross-section diagram of \textsuperscript{113}Cd (Figure 12.2). For this reason, this region is also known as the epi-cadmium neutron spectrum. Resonance neutron capture occurs when an isotope shows high neutron capture cross-sections at discrete neutron energies in the epithermal region (Figure 12.2). An appreciable degree of activation may then result from capture of resonance neutrons, permitting selective analysis of such isotopes in comparison with those that are only strongly activated by a thermal neutron flux. This extension of conventional thermal neutron activation analysis is known as epithermal neutron activation analysis (ENAA). Elements that may be preferentially activated in this way include U, Ta, Sb, Mo, Au, and Ir.