

## 1 Activation analysis - the general principle

### 1.1 Introduction and history of photon activation analysis

Activation analysis has now been established as a versatile and useful method of elemental determination for more than forty years. Activation analysis is the only elemental analytical method which is based upon reaction in the nucleus of the atom. By activating radiation - particles or photons - target element nuclei are transferred to an excited state which can decay by quasi-prompt particle or gamma emission into product nuclei which in most cases are radioactive.

Both the prompt radiation and the radiation emitted by the radioactive product nuclide can be measured with appropriate radiation detectors. From the energy and the count rate of the detected particles, qualitative and quantitative data of the target material composition can be derived. Thus it is clear that by activation analysis methods only elements - not chemical species - can be determined directly. With help of suitable radiation spectrometers (high resolution detectors), simultaneous multielement determinations can be performed without chemical separation of the components. As will be shown later on, extremely high sensitivities can be achieved in many cases, and there are yet other advantages of activation analysis which will be explained in the relevant chapters.

However, activation analysis methods compete with other modern analytical techniques. Compared with these other methods activation analysis has the disadvantage of relatively large requirements concerning both instrumental equipment and personnel qualification. These consist in the availability of a radiation source which provides sufficiently high flux densities of activating particles at a suitable energy range (particle accelerator or nuclear reactor) and appropriate instrumentation for nuclear radiation measurement as mentioned above. Moreover, the handling of radioactive matter unavoidably requires special laboratory installations and equipment and also special working procedures to meet the legal radiation protection requirements. Finally, the laboratory personnel have to be specially trained and experienced in the handling of radioactive material, which generally means a longer training period than commonly necessary in conventional analytical laboratories. Additionally, there is a special problem in photon activation analysis; very often chemical analysts have only limited access to suitable radiation sources. This phenomenon becomes obvious

and explainable along with a closer view of the historical development of photon activation analysis. This problem will be discussed in more detail later. These drawbacks are some of the reasons why activation analysis is not yet as broadly applied in analytical science as other techniques, although it offers a good list of convincing advantages to the analyst. Even supplied with sufficient equipment and well-trained laboratory personnel people do not necessarily become active in activation analysis, because the special advantages of the method are not yet commonly known and frequently they tend to keep solving their analytical problems along conventional lines, even though they could be solved more efficiently with the help of activation analysis.

In the following short summary of the historical development emphasis will be placed upon photon activation analysis. Excellent historical reviews on the history of activation analysis in general can be found in the basic literature on neutron activation analysis; see e.g. Ref.<sup>973</sup>.

The first photonuclear activation for analysis purpose was performed with help of radionuclides as an activating radiation source. These applications are reported first in the beginning of the 1950's<sup>1,2</sup>, although apparently the first beryllium determinations by photodisintegration were performed in the late 1930's<sup>3</sup>, which would make the beginning of photon activation analysis contemporary with the fundamental works on neutron activation analysis by v. Hevesy and Levy<sup>4</sup> and charged particle activation analysis by Seaborg and Livingood<sup>5</sup>. However, there is no contemporary information available about this pioneering work in the Soviet Union.

Although the analytical sensitivity is relatively poor and the applicability is restricted to the analysis of deuterium, beryllium, several fissile nuclides, and a few nuclei which have low-lying isomeric states, radionuclides as exciting radiation sources are still in use nowadays as will be subsequently explained. Later on, small static accelerators have also been used for determinations of the mentioned elements. After the advent of high energy cyclic electron accelerators (betatron, microtron, linac) the high energy bremsstrahlung produced by these machines has been used for photon activation analysis. As a result, the list of determinable elements increased dramatically and now, with a few exceptions, has covered the entire Periodic Table. The analytical potential of these radiation sources was first recognised at the beginning of the 1950's. Basile et al.<sup>6</sup> proposed to analyse some of the light elements (C, N, O) using photonuclear reactions induced by bremsstrahlung from a betatron.

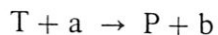
In the case of the analysis of these elements, in general, a chemical separation from the sample matrix must be performed after bremsstrahlung exposure. A great deal of fundamental work was devoted to this problem during the 1960's. These publications are discussed in more detail in chapter 6.1.

Along with the maturity of improved gamma spectroscopy equipment the extension of the method to heavier elements was straightforward. It is not easy to find out who did the pioneer work on instrumental photon activation analysis of elements with  $Z$  greater than 10; as will be shown in chapter 6.2, there were several analytical groups in the early 1960's who did - more or less independently - the first instrumental photon activation analysis work on these elements.

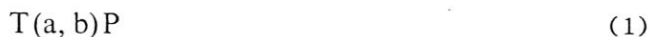
Currently, in finalising this short historical review, photon activation analysis has been established as a complementary method to other instrumental analytical techniques with a good list of special features which can not be offered by other methods, and, of course, with some unavoidable drawbacks. More detailed information on the historical development are given at the beginning of each of the following chapters.

## 1.2 Types of nuclear reactions used for activation analysis

Generally expressed, as mentioned above, radiation of a suitable energy can transform target nuclei into product nuclides. This process is accompanied by prompt emission of particles or photons. It can be expressed such:



or, more concisely,



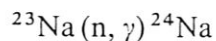
where T is the nucleus to be activated (target), a the incident radiation particle, b the promptly emitted particle and P the activation product nuclide. The type of the nuclear reaction depends upon the target nucleus and the nature and energy of the incident radiation. Both a and b can be nucleons or photons. In the most cases the activation product P is a radionuclide decaying by  $\beta^-$  or  $\beta^+$  emission or by electron capture. Often the product nuclides emit gamma- and X-rays which are characteristic for each nuclide. Thus it is of advantage to use photon spectroscopy for product nuclide identification and radioactivity measurement. Moreover, because of the low absorption of photon (gamma and X) radiation, one generally does not have to take into account significant matrix absorption during counting of radioactivity.

In the following, the different types of analytically usable nuclear reactions are delineated.

### 1.2.1 Neutron activation

Among the various nuclear activation methods, the analysis by activation with neutrons was developed first (Hevesy and Levy<sup>4</sup>) and still nowadays is the most frequently applied. In general, thermal neutrons (ca. 0.025 eV = 2200 ms<sup>-1</sup>) from nuclear reactors have been utilised for activation. Thermal neutron flux densities of some 10<sup>13</sup> to some 10<sup>15</sup> cm<sup>-2</sup>s<sup>-1</sup> are common in modern nuclear research reactors.

Using these neutrons as activating particles, a neutron capture reaction is the most probable one, e.g.:



Neutron activation as performed with reactor neutrons is particularly useful for trace element analysis because of the high intrinsic sensitivity of this method for the determination of many elements; detection limits of some  $10^{-9}$  grams and even lower are not unusual. However, differences in the sensitivities among the elements are large; they cover many orders of magnitude. In some special cases this might turn to advantage, e.g., if the matrix of the sample to be analysed consists of elements with small thermal neutron activation cross sections while the trace elements to be determined have very large ones. However, in many cases analyses are severely hampered by excessive matrix activities after thermal neutron activation, so that a chemical separation step must be included into the analytical procedure.

Neutrons from radionuclide sources, e.g.  $^{241}\text{Am}/\text{Be}$  or  $^{252}\text{Cf}$  have also been used frequently for activation. The particular advantage of isotope neutron sources is the absolute source intensity stability of the nuclide. Furthermore, they do not require excessive space and they are relatively inexpensive; both the financial effort and the space required for a ready-to-use irradiation facility is largely governed by its radiation shielding. The neutron flux density of an isotopic source is lower than available in thermal neutron irradiation positions of nuclear reactors by many orders of magnitude. Therefore, the application is restricted.

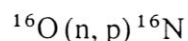
Isotope sources are frequently used for on-stream analyses within industrial production processes, if rapid determinations of major or minor components are required; trace element analyses are possible only in a few exceptionally advantageous cases.

A similar field of application is found for d,T-neutron generators. By nuclear reaction of deuterons with tritons monoenergetic neutrons of about 14 MeV are produced. In a neutron generator deuterons are produced, accelerated by high voltage of typically 150 kV and then absorbed by a metal target which contains up to some  $10^{12}$  Bq of tritium. The 14 MeV-neutrons thus produced induce different reactions in an irradiated target element; the most probable reactions are of the  $(n, 2n)$ ,  $(n, p)$ , or  $(n, \alpha)$  type. The activation cross sections of these

reactions are smaller by one to three orders of magnitude than those of  $(n,\gamma)$  reactions induced by thermal neutrons. Moreover, the flux densities achievable with conventional neutron generators are comparatively low, typically some  $10^8 \text{ cm}^{-2}\text{s}^{-1}$ . Therefore, as in the case of isotope sources, trace component analyses are possible in only very few cases<sup>7</sup>.

More recently, high flux 14 MeV irradiation tubes have been developed which provide neutron flux densities up to  $10^{11} \text{ cm}^{-2}\text{s}^{-1}$ , and thus the area of application of fast neutron activation analysis can be extended to more trace determinations<sup>8,9,10</sup>.

A typical application of 14 MeV neutron activation analysis is the oxygen determination via the reaction



In this exceptional case detection limits of some tens of micrograms per gram are possible (Neider et al.<sup>11</sup>).

### 1.2.2 Activation with charged particles

Charged particles produced by ion accelerators, e.g. cyclotrons or van de Graaff accelerators, can be used for activation. The major difference is due to the small range of charged particles in matter compared to uncharged particles like neutrons or photons. Therefore, in using charged particles for activation, one must be aware of a strongly inhomogeneous spatial activity distribution in the irradiated sample. This can be an advantage if a surface analysis is required. One can easily predetermine the thickness of the activated layer by selecting a proper particle energy. Thus, a surface layer with well-known thickness is exposed to the incident radiation rather than the bulk of the sample. Shortly after the discovery of the phenomenon of induced radioactivity a variety of machines were developed to accelerate particles capable of inducing radioactivity in matter. Among them, only van de Graaff accelerators and small cyclotrons have found widespread use in charged particle activation analysis. Currently, compact cyclotrons are available which supply light ion beams with energies of some tens of MeV at beam currents up to a hundred microamperes. Particles with much higher energies are not useful for activation analysis since high energies lead to possible interference by unwanted reactions in the

sample (see Ch.2). Moreover, equipped with light element converter targets, cyclotrons can also produce neutrons at energies convenient for activation analysis; typical achievable flux densities are several  $10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ .

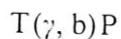
Finally, alpha-emitting radionuclides, e.g.  $^{242}\text{Cm}$ , should be mentioned, which in very special cases can be used as an activating alpha radiation source (Turkevich et al.<sup>12</sup>, Wakita<sup>13</sup>).

The particles which are commonly used for activation are: protons, deuterons, tritons,  $^3\text{He}$ , and alpha particles<sup>14-31</sup>. Heavy ions have also been proposed<sup>32-42</sup>. One can also exploit the prompt radiation in charged particle activation analysis. Also the measurement of the X-ray fluorescence excited by charged particles should be mentioned, although this is not based on a nuclear activation process. A special advantage of charged particle activation analysis is the possibility of simultaneous measurement of the particle-induced X-ray emission and the promptly emitted gamma radiation utilising an appropriate detector system. Other particular advantages compared with other nuclear methods are:

- The large variety of particles available for activation
- the quasi-free choice within a large range to favour desired nuclear reactions
- the high intrinsic sensitivity, especially for light element analysis; detection limits in the subnanogram level are not uncommon.

### 1.2.3 Photon activation

According to eq.1 in paragraph 1.2, a photonuclear reaction is described by:



where b may stand for a large variety of particles, depending primarily upon the incident photon energy. Usually b is equal to gamma or n, but  $(\gamma, 2n)$ ,  $(\gamma, 3n)$ ,  $(\gamma, p)$ ,  $(\gamma, np)$  and other reactions can be induced as well during photon irradiation. The first applications of activation analysis with photons comprised, as already mentioned, the determination of the light elements (deuterium, beryllium, carbon, nitrogen, oxygen and fluorine). The nuclear properties

of these elements favour the exploitation of photonuclear reactions for their determination, as their nuclear properties are unfavorable for thermal neutron activation analysis. Isotope sources were used for the first photon activation experiments. Consequently, the analytical application was then restricted to two groups of elements:

- a) Those with neutron binding energies less than the gamma energies emitted by practically usable (due to their half-lives and available activities) radionuclide sources like  $^{24}\text{Na}$ ,  $^{60}\text{Co}$ ,  $^{124}\text{Sb}$  etc.

The two only stable nuclides which can be analysed under these conditions are  $^2\text{H}$  and  $^9\text{Be}^{1,2,3}$ . In this book only those applications are discussed in detail which include the use of delayed activity counting. Therefore, the photodisintegration analysis of deuterium, beryllium and fissile elements using prompt radiation counting is only mentioned marginally if relevant.

- b) Nuclides which have isomeric states with sufficiently long half-lives can be excited by  $(\gamma, \gamma')$ -reactions induced by gamma-rays from the mentioned radionuclides, e.g.  $^{77}\text{Se}$ ,  $^{107}\text{Ag}$ ,  $^{115}\text{In}$ .

With the advent of high energy accelerators, photon activation analysis was first extended to the determination of carbon, nitrogen, oxygen, and, somewhat later, fluorine. The reaction products of these elements decay by  $\beta^+$ -emission exclusively, hence only unspecific annihilation radiation is available for activity measurement. Consequently, in almost all cases a radiochemical separation of the activity to be counted from the sample matrix after bremsstrahlung exposure is required. Usually large scintillation crystal detectors have been used for activity measurement. The four mentioned elements are among those with the lowest intrinsic sensitivity for photon activation analysis; their photonuclear reactions have comparatively unfavorable nuclear data. Nevertheless, they have been determined frequently with help of photon activation, since this method is relatively free from problems of apparatus blanks and surface contaminations, whilst conventional chemical analysis methods frequently suffer from these interferences. Therefore, in spite of the comparatively small cross sections the detection limits of these elements in photon activation analysis are extremely low; nanogram amounts are easily determinable in some cases (see Ch.6.1).

In considering the determination of the heavier elements, there is a number of elements heavier than neon which can be analysed more advantageously by photon



activation than e.g. by neutron activation. These will be discussed in detail in Ch.6.2.

While the photon activation products of the light elements - as mentioned above - give rise to annihilation radiation only, the photonuclear reaction products of the heavier elements - as in neutron activation - usually emit characteristic gamma and X-rays. When determining these elements, one generally strives for an analytical procedure without chemical separation. Especially in the case of full-scale analysis of a multi-component sample one has to be concerned with complex gamma- or X-ray spectra after activation. Thus it is necessary in the most cases to perform activity measurement with the aid of high-resolution semiconductor photon spectrometers.

Data processing by computer systems including microprocessor-equipped multi-channel pulse-height analysers with many thousands of channels available has become more and more sophisticated; quasi-full automatic analysing devices are not unusual nowadays (see Ch.4).

Generally, the differences of sensitivities among the elements are by far not as large as in neutron activation analysis; typically the detection limits - assuming a purely instrumental analysis - lie between 0.01 and 1 microgram. The practical sensitivity is often limited by high matrix radiation background.

Photon activation analysis, as well as other activation analysis methods, generally is quantified by comparison of the activities in the sample with those in a reference material of known elemental composition which was irradiated simultaneously. This is necessary particularly in photon activation analysis since some of the machine parameters of the accelerator and also some of the nuclear data of the reactions are, respectively, either unknown or not precisely determinable. Moreover, some machine parameters of the photon source cannot be considered constant throughout the exposure period. By the use of reference materials which are simultaneously irradiated with the sample under identical conditions these parameters are implicitly accounted for. Frequently certified multielement reference materials are used whose matrix compositions are similar to those of the samples to be analysed. There are many problems associated with reference materials and their proper use; these are discussed in Ch.6.

Finally, the various fields of application are discussed. With the general availability of high resolution spectrometers instrumental multielement photon activation analysis has been involved in routine analysis work with a broad

application spectrum. In this book the following applications are reported and discussed:

- Geo- and cosmochemistry
- Oceanography
- Environmental science
- Industrial raw- and end product analysis
- High purity material analysis
- Organic material analysis (biological and medical material)
- Forensic analysis
- Analysis of objects of art and archaeology
- Certification analysis of candidate reference materials

Among these applications, instrumental analyses are discussed in detail; in this book, radiochemistry in photon activation analysis is restricted to the determination of the light elements and a few selected examples of analysis of heavier elements.

For more general information about photon activation analysis the reader might refer to Ref's. 16-25,30,31,43-86,683. It is also recommendable to study the contributions about photon activation analysis in the proceedings of several analytical - radioanalytical in particular - conferences; see Ref's. 62-68,70,74,87-94.

### 1.3 Calculation of the induced activity

The quantitative analysis utilising any kind of nuclear activation is almost invariably based upon comparison of the radioactivity induced in the analytical sample and the reference material, as noted in the preceding paragraph. Therefore, the actual activity induced in the element to be analysed does not have to be determined explicitly for analytical evaluation. However, for a variety of reasons, it is of advantage to have knowledge about the activity of an element after activation, e.g. for comparison of sensitivities, calculation of integral matrix activities to be expected etc.. Therefore, in the data section of this book (Ch.5) relative activity yields are presented. These values are derived from the following mathematical considerations.

During exposure to any kind of activating radiation both stable and radioactive nuclei are formed. In the following, only radioactive products are taken into consideration, since stable product nuclei generally are of no analytical relevance. The variation of the number of product nuclei as a function of time may be expressed thus:

$$\frac{dN}{dt} = \dot{N}^+ - \lambda \cdot N(t) \quad (1.1)$$

$N(t)$  = number of radioactive nuclei at the time  $t$

$\dot{N}^+$  = production rate of the product nuclei

$\lambda$  = decay constant of the reaction product

In this linear differential equation the balance of production and decay is described. The solution of this equation under the initial condition

$$N(t = 0) = 0$$

yields:

$$N(t) = \frac{\dot{N}^+}{\lambda} \cdot (1 - e^{-\lambda \cdot t}) \quad (1.2)$$

At the end of the irradiation period  $T_i$  the total number of product nuclei is:

$$N(T_i) = \frac{\dot{N}^+}{\lambda} \cdot (1 - e^{-\lambda \cdot T_i}) \quad (1.3)$$

$T_i$  = irradiation period

After the irradiation the production rate becomes zero and eq. 1.1 is then modified thus:

$$\frac{dN}{dt} = -\lambda N(t) \quad (1.4)$$

The solution of eq. 1.4 under the initial condition given by eq. 1.3 is:

$$N = N(T_i) \cdot e^{-\lambda \cdot (t - T_i)} \quad (1.5)$$

The number of product nuclei after the decay period  $T_D$  measured from the end of the irradiation is:

$$N(T_D) = N(T_i) \cdot e^{-\lambda T_D} \quad (1.6)$$

From eq. 1.6 the activity of the product follows:

$$A = \left| \frac{dN}{dt} \right| = \lambda \cdot N(T_D) \quad (1.7)$$

and, including the expression for the formation of the product during activation (eq. 1.3):

$$A(T_i, T_D) = \dot{N}^+ \cdot (1 - e^{-\lambda \cdot T_i}) \cdot e^{-\lambda \cdot T_D} \quad (1.8)$$

### Calculation of the production rate ( $N^+$ )

The number of product nuclei per time unit in a target sample can be expressed as:

$$d\dot{N}^+ = n_T \cdot V_T \cdot \sigma(E) \cdot \varphi_E(E) dE \quad (1.9)$$

$n_T$  = number of target nuclei of the isotope under consideration per target volume

$V_T$  = homogeneously irradiated target volume

$\sigma(E)$  = cross section of the activation reaction as a function of the incident particle energy (see Fig.1.1)

$\varphi_E(E)dE$  = flux density of the incident particles between the energies  $E$  and  $E + dE$  (see Fig.1.1)

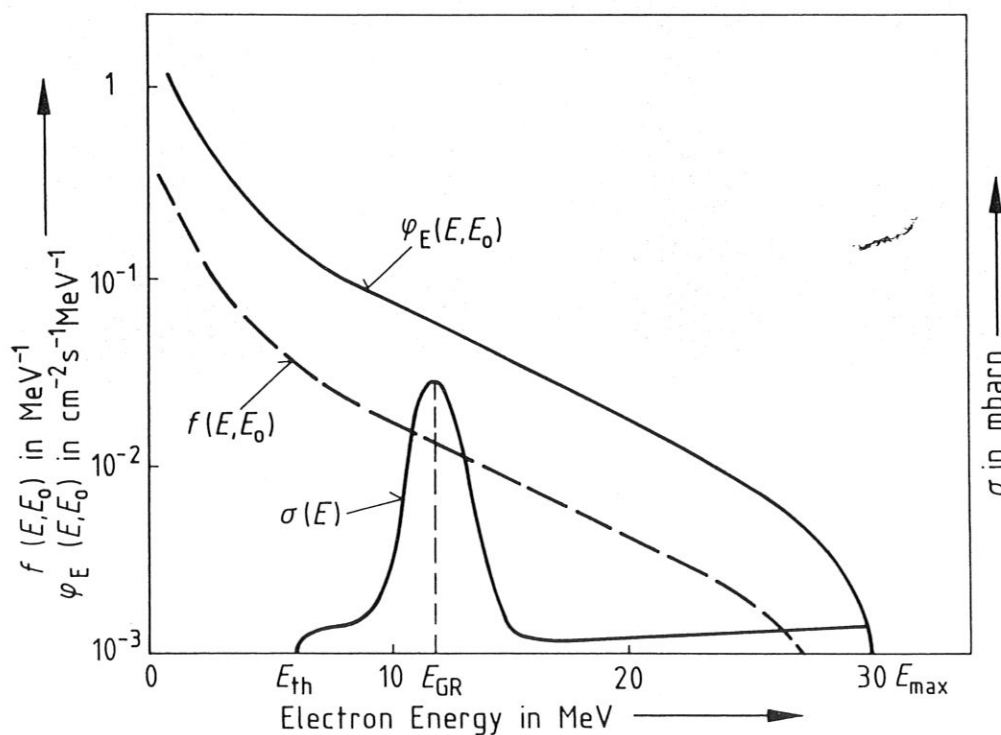


Fig.1.1: Bremsstrahlung spectrum and photonuclear cross section

$\varphi_E(E, E_0)$  = differential bremsstrahlung flux density;  $f(E, E_0)$  = normalised bremsstrahlung spectrum;  $\sigma(E)$  = photonuclear reaction cross section;  $E_0$  = electron energy;  $E_{th}$  = threshold energy;  $E_{max}$  = maximum bremsstrahlung energy (=  $E_0$ )

Using more convenient physical quantities,  $V_T \cdot n_T$  may be replaced by:

$$V_T \cdot n_T = \frac{\rho \cdot L \cdot h \cdot V}{A_r} = \frac{m \cdot L \cdot h}{A_r} \quad (1.10)$$

$\rho$  = density of the element under consideration in the sample

$m$  = mass of the element

$L$  = Avogadro's number ( $=6.023 \cdot 10^{23} \text{ mol}^{-1}$ )

$h$  = abundance of the target isotope

$A_r$  = relative atomic mass of the target isotope

Integrating eq. 1.9 one yields the following expression for the production rate of the active nuclei in the target:

$$\dot{N}^+ = \frac{m \cdot L \cdot h}{A_r} \cdot \int_{E_{th}}^{E_{max}} \sigma(E) \cdot \varphi_E(E) dE \quad (1.11)$$

Insertion of eq. 1.11 into eq. 1.8 yields the general activation equation:

$$A(T_i, T_D) = \frac{m \cdot L \cdot h}{A_r} \cdot \int_{E_{th}}^{E_{max}} \sigma(E) \cdot \varphi_E(E) dE \cdot (1 - e^{-\lambda \cdot T_i}) \cdot e^{-\lambda \cdot T_D} \quad (1.12)$$

The integral in eq. 1.12 may be evaluated by introducing the normalised spectrum of the activating radiation and the effective cross section of the nuclear reaction:

$$\varphi_E = f(E) \cdot \varphi \quad (1.13)$$

$\varphi_E$  = energy differential flux density

$\varphi$  = integral flux density

$f(E)$  = normalised spectrum of the incident radiation

The integration of this expression yields the normalisation condition:

$$\int_{E=0}^{E_{\max}} \varphi_E dE = \varphi = \varphi \cdot \int_{E=0}^{E_{\max}} f(E) dE \quad (1.14)$$

which means that the expression

$$\int_{E=0}^{E_{\max}} f(E) dE$$

equals unity. Consequently, the effective cross section may be defined as (see Fig. 1.1):

$$\sigma_{\text{eff}} = \int_{E_{\text{th}}}^{E_{\max}} f(E) \cdot \sigma(E) dE \quad (1.15)$$

$\sigma_{\text{eff}}$  = integral effective cross section of the regarded nuclear reaction

Using these definitions the integral in eq. 1.12 may be expressed as:

$$\int_{E_{\text{th}}}^{E_{\max}} \sigma(E) \cdot \varphi_E(E) dE = \sigma_{\text{eff}} \cdot \varphi \quad (1.16)$$

which yields the following expression for the activity of the sample:

$$A(T_i, T_D) = \frac{m \cdot L \cdot h}{A_r} \cdot \varphi \cdot \sigma_{\text{eff}} \cdot (1 - e^{-\lambda \cdot T_i}) \cdot e^{-\lambda \cdot T_D} \quad (1.17)$$

This expression can be conveniently used for activity yield calculations, based upon experimentally obtained results. This is demonstrated in Ch.5.