CHAPTER 15

Production of Radionuclides

Contents

This chapter discusses production of radionuclides for beneficial use in science, medicine and technology. The nuclear fundamentals for the production processes have been given in Chapters 11 to 14. The formation of radionuclides is discussed in several Chapters: e.g. cosmogenic reactions leading to the formation of short-lived radionuclides in nature (Ch. 5 and 10); thermonuclear reactions leading to the formation of long-lived radioactivity in the universe (Ch. 17); the synthesis of trans-uranium elements (Ch. 16 and 19-21). The production and isolation of separated fission products is treated separately (Ch. 19-21). This chapter discusses aspects of fundamental importance to the production of radionuclides by a variety of methods. Initially the principles are reviewed and, subsequently, the most advanced techniques for investigating short-lived radionuclides are described.

15.1. General considerations

Radioactive nuclides may be prepared by a wide variety of particle accelerators and nuclear reactors; however, only cyclotrons or reactors of at least moderate particle flux are able to produce sources of sufficiently high specific radioactivities to be of practical interest. These two methods of production supplement each other since, in general, they do not produce the same isotopes of an element.

In cyclotrons charged particles such as protons, deuterons, and α-particles bombard the target nuclei, and after emission of one or more particles to remove the excess excitation energy, a radioactive product nuclide may result. In the capture of positively charged particles and the subsequent emission of neutrons the product radionuclides are *neutron deficient* compared to the stable isotopes of the element; see Fig. 3.1 and 4.7. Another important point in cyclotron bombardments is that normally the product is not isotopic with the target. As a result, after chemical separations a product of high specific activity is obtained since it is not diluted by the target material. An example of an important cyclotron-produced radionuclide is ^{22}Na ($t_{1/2}$ 2.6 y) formed by the reaction:

$$^{24}_{12}\mathrm{Mg} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{22}_{11}\mathrm{Na}$$

This contrasts with the production of radionuclides by neutron irradiation, e.g. in a nuclear reactor, where the neutron absorption and subsequent de-excitation by emission of γ-rays produces *neutron rich* isotopes, frequently radioactive, which are isotopic with the target. A typical reaction is

$$^{23}\mathrm{Na}\,(n,\gamma)\,^{24}\mathrm{Na}$$

yielding another important isotope, ^{24}Na ($t_{1/2}$ 15.0 h), which is diluted by the ^{23}Na target atoms. Even if the same radioactive nuclide can be made in a nuclear reactor, cyclotron production may be favored if high specific activity is necessary for a particular use.

A second mode of production in reactors is by the fission process itself as the majority of fission products are radioactive and cover a wide range of atomic numbers of varying abundances. These radioactivities may be isolated with high specific activity in contrast to the neutron capture products. However, in fission products the isolation of any particular radioactive element can require a fairly lengthy separation from the large number of other radioactivities present; we discuss this further in Chapter 21.

Radioactive nuclides may also be obtained as daughters of parent activities which have been previously made either by cyclotron or reactor irradiation. Several examples of such radioactive isotope generators are discussed in §4.16.

Which mode or production is utilized depends on several factors. The length of time for production, separation and purification processes, the time from production to shipping, and the shipping time determine the half-life with which it is practical to work. The type of experiment and equipment available for handling and measurement determines the preferable decay type and intensity. All these factors must be considered in determining which nuclide is to be used. For example, if in an experiment requiring sodium tracer these aspects indicate the necessity of a time of at least several weeks, the use of reactor-produced ^{24}Na is excluded and cyclotron-produced ^{22}Na is required. If the experiment requires the use of very high specific activities, either cyclotron or fission product activities may be necessary. Reactor activities are usually much cheaper and easier to obtain on a routine basis because many targets can be irradiated simultaneously in the reactor whereas in a cyclotron only one target at a time can be bombarded.

Although these considerations are important in the choice of a radionuclide to use for a particular purpose, the possibilities of production may be limited either by the availability of facilities (reactors, different accelerator beams) or simply by the reaction cross-sections. Figure 4.7 (right side) shows the reaction paths needed to transform a given target nuclide into a product nuclide. If the target nuclide is denoted by ${}^{A}_{Z}\mathrm{X}$, a (n,γ) reaction yields the same product as a (d,p) reaction, i.e. ${}^{A+1}_{Z}\mathrm{X}$. The choice of reaction depends on the particular nuclides available, projectile energy, and the cross-sections (available in charts or tables of nuclear data). As pointed out in Chapter 14, the same projectile may yield several different products; e.g. Figure 14.2 shows six different α-induced reactions.

An induced nuclear reaction may be followed by rapid radioactive decay, leading to the desired radionuclide. Thus a (n,2n) reaction on ${}^{A}_{Z}\mathrm{X}$ may yield ${}^{A-1}_{Z}\mathrm{X}$, which rapidly decays to ${}^{A-1}_{Z+1}\mathrm{X}$ through β^--emission. For example, the formation reaction

$$^{238}\mathrm{U}\,(\mathrm{n},2\mathrm{n})\,^{237}\mathrm{U}$$

followed by

$$^{237}\mathrm{U} \xrightarrow[6.75\ \mathrm{d}]{\beta^-} {}^{237}\mathrm{Np}$$

These reactions are used to produce ^{237}Np for investigation of neptunium chemical behavior.

15.2. Irradiation yields

The production of a radioactive nuclide by irradiation in a reactor or an accelerator can be written as:

$$\mathrm{X}_{\mathrm{target}} + \mathrm{X}_{\mathrm{proj.}} \xrightarrow{k} \mathrm{X}_1 \xrightarrow{\lambda_1} \mathrm{X}_2 \xrightarrow{\lambda_2} \mathrm{X}_3 \tag{15.1}$$

We are mainly concerned with the product X_1 (produced at rate k), which is assumed to be radioactive, decaying in a single step or via a chain of decays to a final stable nuclide. The number of radioactive product atoms N_1 of X_1 present at any time t is the difference between the total number of product atoms formed and the number of radioactive decays that have occurred in time dt. This leads to the differential equation

$$\mathrm{d}N_1 = k\,\mathrm{d}t - \lambda_1 N_1\,\mathrm{d}t \tag{15.2}$$

Integration between the limits of $N_1 = 0$ (this assumes that no radioactive product nuclide X_1 exist at the beginning of the irradiation) and N_1 corresponding to an irradiation time t_{irr}:

$$N_1 = (k/\lambda_1)(1 - e^{-\lambda_1 t_{irr}}) \qquad (15.3)$$

N_1 increases exponentially with time towards a maximum value, which is reached when $t_{irr}\lambda_1 \gg 1$ (i.e. $t_{irr} \gg t_{½}$):

$$N_1(\text{max}) = k/\lambda_1 = k t_{½} / 0.693 \qquad (15.4)$$

However, for $t_{irr} \ll t_{½}$, by expanding the exponential into a Maclaurin series, $e^{-\lambda_1 t_{irr}} \approx 1 - \lambda_1 t_{irr}$ which in (15.3) gives

$$N_1 = k t_{irr} \quad (\text{for } t_{irr} \ll t_{½}) \qquad (15.5)$$

If we measure the irradiation time in number of half-lives, $a = t_{irr}/t_{½}$, we obtain

$$N_1 = N_{1,\text{max}}(1 - 2^{-a}) \qquad (15.6)$$

This equation shows that irradiation for one half-life ($a = 1$) produces 50% of the maximum amount, two half-lives give 75%, etc.

After the end of the irradiation time, the radioactive product nuclides continue to decay according to their half-lives. We indicate this decay time after the end of irradiation (termed the cooling time) as t_{cool}. The number of product nuclides, which is a function of the irradiation time t_{irr} and cooling time t_{cool}, is given by

$$N_1 = (k/\lambda_1)(1 - e^{-0.693\, t_{irr}/t_{½}})\, e^{-0.693\, t_{cool}/t_{½}} \qquad (15.7)$$

The effect of the cooling time is shown in Figure 15.1 for two sample nuclides.

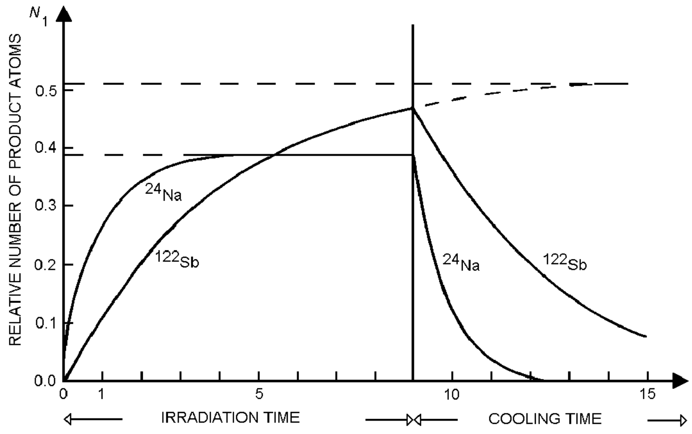


FIG. 15.1. Change in number of ^{24}Na ($t_{½}$ 15.0 h) and ^{122}Sb ($t_{½}$ 2.7 d) atoms during and after irradiation.

The production rate k is the number of transformations, N, leading to a number, N_1, of product atoms, divided by the irradiation time, t_{irr}. For a target in a neutron flux

$$k = \phi \, \sigma \, N_t \tag{15.8a}$$

where ϕ is the neutron flux (neutrons of appropriate energy per cm^2 per s), σ the reaction cross section (at the given neutron energy, in cm^2) and N_t the number of target atoms with cross section σ; cf. eqn. (14.4). In the case a fission product is produced, $\phi \, \sigma \, N_t$ is the fission rate, which has to be multiplied by the particular fission yield, y_{i}, for nuclide i.

If a target is bombarded by a beam of particles of charge z at a current of I A, the production rate k is

$$k = 6.24 \times 10^{18} \, I \, \sigma \, N_{\mathrm{v}} \, x \, z^{-1} \tag{15.8b}$$

where $N_{\mathrm{v}} \, x$ is the number of target atoms per unit area; cf. eqn. 14.5).

For (15.8) to be valid,

(i) the number of nuclear reactions must remain small compared to the total number of target atoms to justify the assumption of constant N_t or N_{v},

(ii) the projectile energy must be maintained constant in order that the reaction cross-section remains constant, and

(iii) the flux is not decreased in passing through the target. Depending on the conditions of the irradiation only one or two of these requirements may be valid. Corrections must then be introduced for the non-valid component(s).

Usually the radioactive decay rate A_1 is measured, rather than the number of atoms N_1. Recalling $A = \Delta N/\Delta t = \lambda \mathrm{N}$, (15.3) and (15.8a) yield

$$A_1 = k \, (1 - \mathrm{e}^{-0.693 \, t_{\mathrm{irr}}/t_{½}}) \, \mathrm{e}^{-0.693 \, t_{\mathrm{cool}}/t_{½}} \tag{15.9}$$

This equation represents the basic relationship for the production of radionuclides; in a reactor k is calculated according to (15.8a); for accelerator irradiation (15.8b) is used.

Let us take the production of radioactive sodium by reactor irradiation and cyclotron bombardment as examples of the application of these equations. $\mathrm{Na_2CO_3}$ (M = 106) is irradiated in a reactor to produce $^{24}\mathrm{Na}$, which has a half-life of 14.66 h and emits β^- and γ-rays. The reaction cross-section of $^{23}\mathrm{Na}$ (100% in natural sodium) is 0.53 b for thermal neutrons. For a 5 g sample, 60 h irradiation time, and a thermal flux of 10^{12} n cm^{-2} s^{-1}, the activity at the end of the irradiation time will be:

$$A = 10^{12} \times 0.53 \times 10^{-24} \times 2 \times 5 \times 6.02 \times 10^{23} \, (1\text{-}\mathrm{e}^{-0.693 \, \times \, 60/15})/106 = 2.8 \times 10^{10} \ \mathrm{Bq}$$

$^{24}\mathrm{Na}$ may be produced through accelerator irradiation of magnesium by the reaction $^{26}\mathrm{Mg}$ (d,α) $^{24}\mathrm{Na}$. With 22 MeV D^+ ions the reaction cross-section is about 25 mb. For a 0.1 mm thick magnesium foil (M = 24.3, ρ = 1.74 g cm^{-3}) with an area larger than the projectile beam, and a 2 h irradiation at 100 pA, the activity of $^{24}\mathrm{Na}$ produced (natural magnesium contains 11.0% $^{26}\mathrm{Mg}$) at end of irradiation is:

$$A = 6.24 \times 10^{18} \times 100 \times 10^{-6} \times 25 \times 10^{-27} \, (0.11 \times (1.74/24.3) \, 6.02 \times 10^{23} \times 0.01)$$

$$\times\ (1 - e^{-0.693\ \times\ 2/15}) = 6.53 \times 10^{7}\ \mathrm{Bq}$$

15.3. Second-order reactions

For large cross-sections, short half-lives, and long bombardments, second-order capture products may be formed. If the first-order product is radioactive, then its concentration at any time is dependent on (i) the decay constant, (ii) the cross-section for production of the second-order product, as well as (iii) the cross-section for its own production. These possibilities lead to a scheme such as Figure 15.2. For simplicity, we may assume that the induced nuclear transformations only involve single-neutron capture, and that only β^- decay occurs. However, it should be obvious that the scheme in Figure 15.2, with suitable additions, is applicable to all kinds of nuclear formation and decay reactions.

For the (n,γ) β^- case the upper horizontal row of Figure 15.2 represents the successive formation of higher isotopes of the target element (the constant Z-chain) and the vertical rows the isobaric decay chains of each of these isotopes (the constant A-chains). The first of these two rows is indicated by heavy arrows. Chains which involve both induced transformations and radioactive decay play a central role in theories about the formation of the elements in the universe, in the thermonuclear reactions in the stars (Ch. 17), and in the synthesis of transuranium elements (Ch. 16).

For each nuclide in Figure 15.2 we can write a differential expression for the change in concentration with time as a function of the irradiation and the radioactive decay:

$$\text{For } X_{11}:\ \mathrm{d}N_{11}/\mathrm{d}t = -(\phi\sigma_{11} + \lambda_{11})N_{11} = \Lambda_{11}\,\mathrm{N}_{11} \tag{15.10a}$$

$$X_{21}:\ \mathrm{d}N_{21}/\mathrm{d}t = \lambda_{11}N_{11} - (\phi\sigma_{21} + \lambda_{21})N_{21} = \Lambda^{*}_{11}N_{11} - \Lambda_{21}N_{21} \tag{15.10b}$$

$$X_{31}:\ \mathrm{d}N_{31}/\mathrm{d}t = \lambda_{21}N_{21} - (\phi\sigma_{31} + \lambda_{31})N_{31} = \Lambda^{*}_{21}N_{21} - \Lambda_{31}N_{31} \tag{15.10c}$$

$$\dots \qquad \dots$$

$$X_{12}:\ \mathrm{d}N_{12}/\mathrm{d}t = \phi\sigma_{11}N_{11} - (\phi\sigma_{12} + \lambda_{12})N_{12} = \Lambda^{*}_{11}N_{11} - \Lambda_{12}N_{12} \tag{15.10d}$$

$$X_{13}:\ \mathrm{d}N_{13}/\mathrm{d}t = \phi\sigma_{12}N_{12} - (\phi\sigma_{13} + \lambda_{13})N_{13} = \Lambda^{*}_{12}N_{12} - \Lambda_{13}N_{13} \tag{15.10e}$$

$$\dots \qquad \dots$$

$$X_{22}:\ \mathrm{d}N_{22}/\mathrm{d}t = \lambda_{12}N_{12} + \phi\sigma_{21}N_{21} - (\phi\sigma_{22} + \lambda_{22})N_{22} \tag{15.10f}$$

Let us now consider three different cases:

Case (i): *Successive radioactive decay*. This occurs after formation of the first radioactive (parent) member X_{11}. Thus we only consider the left vertical chain, and assume σ_{11}, σ_{21}, etc. $= 0$. In this $A + 1$ chain the second index is constant, and we omit it for case (i). This case is valid for all natural decay chains and for fission product decay chains. Each member of the decay chain can be described by the differential equation

$$\mathrm{d}N_i/\mathrm{d}t = \lambda_{i-1}N_{i-1} - \lambda_i N_i \quad (i > 1) \tag{15.11}$$

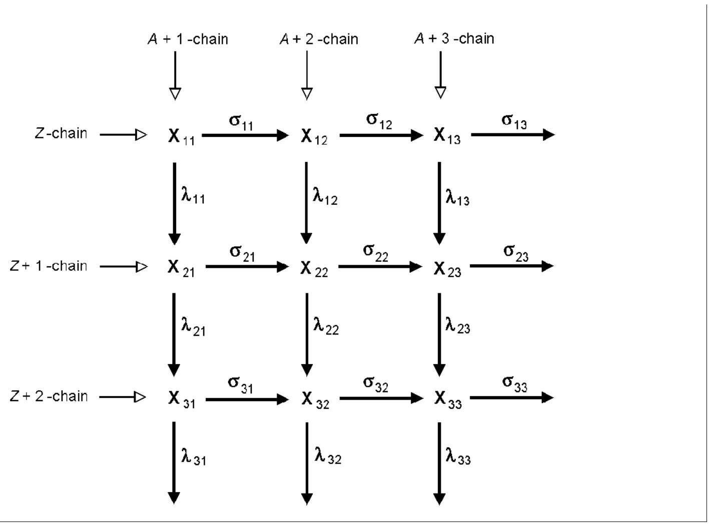


FIG. 15.2. Formation of higher nuclides through multiple neutron capture and their associated decay chains.

We have already solved this relation in §15.2 for the formation of X_1 (the radioactive mother), and in §4.15 we showed how the amount of X_2 (the radioactive daughter) varies with time.

The general solution to the case with many successive decays is usually referred to as the *Bateman equations* (H. Bateman 1910):

$$N_n(t) = \lambda_1 \lambda_2 \ldots \lambda_{n-1} N_1^0 \sum_1^n C_i \, e^{-\lambda_i t} \tag{15.12a}$$

$N_n(t)$ is the number of atoms for the nth species after time t, N_1^0 is the number of atoms of X_1 at $t = 0$, t is the *decay time,* and

$$C_i = \prod_{j=1}^{j=n} (\lambda_j - \lambda_i)^{-1} \quad \text{for } j \neq i \tag{15.12b}$$

For $i = 1$, eqn. (4.41a) for simple radioactive decay is obtained. It is assumed that $N_1^0 = 0$ for $(i > 1)$. If that is not the case, additional chains, starting with each $N_i > 0$, require a new series of Bateman equations which are added together. For $i = 3$ and $N_2^0 = N_3^0 = 0$ at $t = 0$ one obtains

$$N_3(t) = \lambda_1 \lambda_2 N_1^0 (C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t} + C_3 e^{-\lambda_3 t}) \tag{15.13}$$

where

$$C_1 = (\lambda_2 - \lambda_1)^{-1} (\lambda_3 - \lambda_1)^{-1}$$
$$C_2 = (\lambda_1 - \lambda_2)^{-1} (\lambda_3 - \lambda_2)^{-1}$$
$$C_3 = (\lambda_1 - \lambda_3)^{-1} (\lambda_2 - \lambda_3)^{-1}$$

Case (ii): *Successive neutron capture*. This is the upper horizontal row in Figure 15.2 (the constant *Z*-chain). Because the first index is constant in this chain, we omit it for case (ii). We assume λ_{11}, λ_{12}, etc. $= 0$. This is a valid approximation often used for the formation of transuranium elements in a nuclear reactor, which are long-lived in relation to the time of irradiation and observation. For each member of the formation chain we may write

$$\mathrm{d}N_i/\mathrm{d}t = \phi\sigma_{i-1}N_{i-1} - \phi\sigma_i N_i \tag{15.14}$$

By replacing λ_i with $\phi\sigma_i$ this equation becomes identical with (15.11). Thus the solution of case (ii) is obtained by using the Bateman eqn. (15.12). It should be noted that in case (ii) t is the *irradiation time* (t_{irr}).

Case (iii): *Combined induced transformation and radioactive decay*. These combined effects can be taken into account by using the Bateman equations with some modifications, as developed by Rubinson.

We introduce the abbreviations

$$\Lambda = \phi\sigma + \lambda \tag{15.15}$$

and

$$\Lambda^* = \phi\sigma^* + \lambda^* \tag{15.16}$$

Λ_i is referred to as the disappearance constant of nuclide i, while Λ_i^* is the partial formation constant, and σ^* and λ^* the partial reaction cross-sections and decay constants for nuclide $i + 1$; σ, σ^*, λ and λ^* may be equal to zero in some cases. The exact meaning of Λ and Λ^* is explained below with examples. Introducing these abbreviations for the formation of the $\mathrm{X}_{i\,1}$ species of the constant ($A + 1$)-chain, and dropping the second index, which is $= 1$ in the left vertical row in Figure 15.2, we obtain the equation:

$$\mathrm{d}N_i/\mathrm{d}t = \lambda_{i-1}N_{i-1} - \Lambda_i N_i = \Lambda^*_{i-1}N_{i-1} - \Lambda_i N_i \tag{15.17}$$

Similarly, we find for the formation of the $\mathrm{X}_{1\,i}$ species (the constant *Z*-chain)

$$\mathrm{d}N_i/\mathrm{d}t = \phi\sigma_{i-1}N_{i-1} - \Lambda_i N_i = \Lambda^*_{i-1}N_{i-1} - \Lambda_i N_i \tag{15.18}$$

where the first index ($=1$) has been dropped for simplicity. These two equations turn out to be identical, provided the partial formation constant Λ^* (15.16) for each nuclide (i.e. each index set) is used with the correct σ^* and λ^*; in (15.17) $\sigma^* = 0$, and in (15.18) $\lambda^* = 0$. With this reservation in mind the Bateman equations become

$$N_n(t) = \Lambda_1\Lambda_2^* \ldots \Lambda_{n-1}^* N_1^0 \sum_1^n C_i\,\mathrm{e}^{-\Lambda_i t} \tag{15.19a}$$

where

$$C_i \;=\; \prod_{j\,=\,1}^{j\,=\,n} (\Lambda_j - \Lambda_i)^{-1} \quad (j \neq i) \tag{15.19b}$$

The time t is the irradiation time t_{irr}.

The application of this expression and the use of Λ^* are best illustrated with a practical example.

If 1.0 mg of Tb_2O_3 (M = 366) is bombarded for 30 days at a flux of thermal neutrons of 10^{14} cm^{-2} s^{-1}, the following processes occur:

$$\begin{tikzcd}
{}^{159}\mathrm{Tb} \arrow[r, dashed, "(n,\gamma)", "\sigma_{169}\ {}^{25.5\text{ b}}"'] & {}^{160}\mathrm{Tb} \arrow[r, dashed, "(n,\gamma)", "\sigma_{160}\ {}^{525\text{ b}}"'] \arrow[d, "\lambda_{160}"', "t_{1/2}\,72.1\text{ d}"] & {}^{161}\mathrm{Tb} \arrow[d, "\lambda_{161}"', "t_{1/2}\ 6.90\text{ d}"] \\
& {}^{160}\mathrm{Dy}\text{ (stable)} & {}^{161}\mathrm{Dy}\text{ (stable)}
\end{tikzcd}$$

The appropriate (15.19) equation for the formation of ^{161}Tb (cf. also (15.13)) is:

$$\begin{aligned}
N_{161} = \Lambda_{159}\Lambda^*_{160}N^0_{159}[&e^{-\Lambda_{159}t}/\{(\Lambda_{160} - \Lambda_{159})(\Lambda_{161} - \Lambda_{159})\} \\
&+ e^{-\Lambda_{160}t}/\{(\Lambda_{159} - \Lambda_{160})(\Lambda_{161} - \Lambda_{160})\} \\
&+ e^{-\Lambda_{161}t}/\{(\Lambda_{159} - \Lambda_{161})(\Lambda_{160} - \Lambda_{161})\}]
\end{aligned} \tag{15.20}$$

By considering the different reaction paths, we obtain

$(\Lambda_1 =)$: $\Lambda_{159} = \phi\sigma_{159} = 10^{14} \times 25.5 \times 10^{-24} = 2.55 \times 10^{-9}\ s^{-1}$

$(\Lambda_2 =)$: $\Lambda_{160} = \phi\sigma_{160} + \lambda_{160} = 10^{14} \times 25 \times 10^{-24} + 0.693/(72.1 \times 24 \times 3600) =$

$1.64 \times 10^{-7}\, s^{-1}$

$(\Lambda_3 =)$: $\Lambda_{161} = \lambda_{161} = 0.693/(6.9 \times 24 \times 3600) = 1.162 \times 10^{-6}\, s^{-1}$

$(\Lambda^*_3 =)$: $\Lambda^*_{160} = \phi\sigma_{160} = 10^{14} \times 525 \times 10^{-24} = 5.25 \times 10^{8}\, s^{-1}$

$(N^0_1 =)$: $N^0_{159} = (2/366) \times 6.02 \times 10^{23} \times 10^{3} = 3.28 \times 10^{18}$ atoms

$(t =)$: $t = t_{\mathrm{irr}} = 30 \times 24 \times 3600 = 2.59 \times 10^{6}$ s

Note that Λ^*_{159} is the rate of formation of ^{160}Tb, and Λ^*_{160} the rate of formation of ^{161}Tb, while Λ_{159}, Λ_{160} and Λ_{161} are the rates of disappearance of ^{159}Tb, ^{160}Tb and ^{161}Tb. Introducing the experimental values yields $N_{161} = 5.68 \times 10^{14}$ atoms. The radioactive decay is $A_{161} = \lambda_{161} N_{161} = 1.162 \times 10^{-6} \times 5.68 \times 10^{14} = 6.60 \times 10^{8}$ Bq or 4×10^{10} dpm.

15.4. Target considerations

The success of an irradiation experiment depends to a large extent on the target considerations. In many nuclear experiments as much time has to be devoted to the target preparation as to the rest of the experiment. If the purpose is to produce a radionuclide for a simple tracer experiment, the consideration in this section may be sufficient. If, however, the requirements are a product of extreme purity, very high specific activity, or very short half-life, special techniques must be used, which are discussed in §§15.5-15.7.

15.4.1. *Physical properties*

In thin targets the flux and energy of the projectile do not change during passage through the target. When the projectile energy is considerably changed (in a thick target) it is more complicated to calculate the yield as the variation of energy with distance in the target and the variation of cross section with energy must be taken into account.

The exact specification of when a target is thin depends on the experiment; in most cases thin means a target with a surface weight of not more than a few mg/cm^2 or a thickness of a few µm or less. The *surface weight* (or *linear density*) is $x\rho$, where x is the target thickness and ρ its density. Thin targets are usually used in accelerator irradiations and are made of a solid material, either metal or compound. In order to have sufficient mechanical strength the target is usually supported on a *backing material* such as aluminum. The backing material may be part of a solid target holder which has provisions for cooling to dissipate the heat developed in the bombardment. Thin targets are fixed on the backing material through electrolytic precipitation, vacuum deposition, mass spectrometric collection (for isotopically pure targets), or a number of other techniques.

In reactor irradiations it is more common to use thicker targets in order to obtain higher yields. In traversing the target the effective flux (i.e. $\phi\sigma$) does not decrease as rapidly for neutrons as for charged particles and, therefore, thicker targets can still be considered "thin" in neutron irradiations. However, if the product σN is large, the neutron flux may decrease appreciably at the center of the target, although for thermal neutrons there is little energy change in such a situation.

The target material can be a solid, liquid, or gas. For reactor irradiations it is common to place the target material in a container of polypropylene or of some metal of relatively low neutron capture cross-section. Pyrex and soda glass are not good materials because of the reactions ^{10}B(n,α)^{7}Li (which has a large σ_{capt}) and ^{23}Na(n,γ)^{24}Na (which yields a long-lived γ-product). In silica some γ-active ^{31}Si ($t^{1/2}$ 2.62 h) is produced (σ_{capt} = 0.11 b for thermal n). When metal sample holders, usually aluminum and magnesium are used, some γ-activity is produced; however, the cross-sections for the formation of the products ^{28}Al and ^{27}Mg are small, and these nuclides decay rapidly ($t_{1/2}$ = 2.24 and 9.46 min, respectively). The primary requirement for the container is that it should be leak-tight and dissipate heat energy at a rate sufficient to avoid melting.

Sometimes of greater importance than whether the target is thin or thick is the extent of *burn-out* of the target by the irradiation. If the number of target atoms at the beginning of the irradiation is N^0_{target} and at time t_{irr} is N_{target}, then the burn-out can be estimated with the relation

$$N_{\text{target}} = N^0_{\text{target}}(1 - \sigma_{\text{tot}}\,\phi\,t_{\text{irr}}) \qquad (15.21)$$

where σ_{tot} includes all processes whereby the target atoms are reduced. Burn-out can be neglected when $\sigma_{\text{tot}}\,\phi\,t_{\text{irr}} \ll 1$.

In the example of the irradiation of the 0.3 mm thick gold foil in §14.1, from (14.2) we can calculate that the flux reduction is 17%; for a 0.01 mm thick foil it would be 0.62%, but for a 1 mm foil, 44%. The target thickness does not enter into the burn-out, eqn. (15.21). For a 10 min irradiation of 10^{13} n cm^{-2} s^{-1}, the burn-out is negligible. However, a one-month irradiation at the same flux yields 0.26% burn-out, while a month at a flux of 10^{15} gives about 20% burn-out.

15.4.2. *Chemical properties*

There are two ways to produce a pure radionuclide not contaminated with any other radioactivity. An extremely pure target can be used with a reaction path which is unique. Alternatively, the radioactive products can be purified after the end of the bombardment. For example, a 10 g sample of zinc irradiated for one week with 10^{13} n cm^{-2} s^{-1} yields a sample of ^{65}Zn ($t_{1/2}$ 244 d) with 7.1 × 10^9 Bq. If, however, the zinc target is contaminated with 0.1% of copper, in addition to the zinc activity, 3.0 × 10^9 Bq of ^{64}Cu ($t_{1/2}$ 12.7 h) is formed. In another example element $_{102}$No was believed to be discovered initially in a bombardment of a target of curium by carbon ions. The observed activity, however, was later found to be due to products formed due to the small amount of lead impurity in the target. Similarly, in neutron activation of samarium it must be very free of europium contamination because of the larger europium reaction cross-sections. Handbooks of activation analysis often contain information on the formation of interfering activities from impurities.

Even a chemically pure target may yield products of several elements, particularly in cyclotron irradiation, where many reaction paths are often possible. In the bombardment of magnesium with deuterons, the following reactions occur:

$$^{24}\text{Mg}(79\%)(\text{d},\alpha)^{22}\text{Na}(t_{1/2}\ 2.6\ \text{y})$$

$$^{25}\text{Mg}(10\%)(\text{d},\text{n})^{26}\text{Al}(t_{1/2}\ 7.2 \times 10^5\ \text{y})$$

$$^{26}\text{Mg}(11\%)(\text{d},\alpha)^{24}\text{Na}(t_{1/2}\ 14.66\ \text{h})$$

A short time after the irradiation ^{24}Na is the predominant activity; after longer cooling times the ^{22}Na is always contaminated by ^{26}Al. In such a case chemical purification after the irradiation is required to yield a pure product.

A suitable target material may be unavailable, or very expensive because of a low natural abundance. ^{45}Ca, which is the most useful calcium radioisotope ($t_{1/2}$ 164 d), is produced through n,γ capture in ^{44}Ca; unfortunately, ^{44}Ca only occurs to 2.1% in nature. While irradiation of natural calcium may yield a specific activity of ~ 0.3 TBq g^{-1}, isotope enrichment before irradiation to essentially pure ^{44}Ca yields ≤ 20 TBq g^{-1}.

When the target is a chemical compound its radiation stability becomes important. In general organic compounds are not stable towards either neutron or charged particle bombardment. However, with neutrons a very particular and useful kind of reaction, known as the Szilard-Chalmers reaction (see §15.6.3), may take place. Simple inorganic compounds like NaCl are stable, and for some inorganic compounds like Na_2CO_3 the radiation decomposition (to Na_2O and CO_2) are of little importance.

15.5. Product specifications

Most countries have one or more suppliers of *radiochemicals*. To locate suppliers, the simplest way is often to contact the nearest nuclear center, as it may be a producer of radionuclides, the national radiation safety organization, or the annual Byers' Guide of common nuclear journals. Product catalogs list the type of radioactive sources and compounds available, purity of the products, maximum and specific activities, radiation decay characteristics, accuracy of standards, labeling position, etc.

The radionuclides come in the form of calibration/reference sources, and as inorganic compounds and labeled organic compounds. They are packed in various ways, most commonly in a glass ampoule packed in a small aluminum can. To reduce the surface radiation dose rate (cf. Ch. 18) for high intensity radiation sources (usually > 10 MBq) the can is put in a lead block which is packed in a wooden crate for shipment. Opening of the aluminum can and glass ampoule may require remote control and should be done only by experienced, licensed personnel.

15.5.1. *Radiochemical processing*

It may be a long process between the removal of the irradiated target from the irradiation facility and the pure radiochemical substance or compound to be used in some experiment. The separation procedures needed to make a pure radiation source are chemically the same and (usually) independent of the "size" (i.e. its total radioactivity), but the experiments become more cumbersome — and often slower — when the radiation source is so large as to require considerable shielding.

Most chemical techniques can be applied in the processing: precipitation, ion exchange, solvent extraction, electrodeposition, electrophoresis, distillation, etc. The basic purposes are to eliminate radioactive contaminants and to avoid diluting the radionuclide by isotopic stable atoms. If the radionuclide or radiochemical is to be used in medical and biological work, the sample may have to be sterile. Some publications about radiochemical separation procedures are given in the literature list, §15.9.

15.5.2. *Specific activity*

The specific activity or concentration of a radionuclide, i.e. radioactivity per gram, mole, or volume, is a very important factor in radionuclide work, e.g. in chemical work with substances of low solubility, in microbiology, etc.

Radionuclides of high specific activity are produced either through accelerator irradiation or through secondary reactions in the target (§15.6) in a reactor. Maximum specific activity is obtained when the radioactive nuclide is the only isotope of the element. This is not possible to achieve in regular reactor irradiation through (n,γ) capture processes. For example, reactor-produced ^{24}Na may be obtained in specific activities of $\leq 2 \times 10^{11}$ Bq g^{-1}, while the specific activity of accelerator-produced ^{24}Na may exceed 10^{13} Bq g^{-1}; however, the total activities available are usually the inverse.

A *carrier-free* radioactive sample is usually one in which the radionuclide is not diluted with isotopic atoms. In reactor production of ^{24}Na from target ^{23}Na, each ^{24}Na is diluted with a large number of ^{23}Na atoms. ^{24}Na cannot be made carrier-free in a reactor. If a carrier-free radionuclide has been produced, e.g. through accelerator irradiation, which then must be purified, its concentration is so low that it may not follow the normal chemical rules. A macroscopic amount of *carrier*, either isotopic or not, may have to be added to carry the radionuclide through the proper chemical purification steps. We discuss this further in §9.2.

15.5.3. *Labeling*

A radioactively *labeled* (or "*tagged*") compound is one in which one of the atoms is radioactive. Preparation of labeled compounds may involve lengthy chemical synthesis starting with the radioactive nuclides in elementary form or in a simple compound.

Most syntheses of ^{14}C-labeled organic or biochemical compounds follow conventional methods with appropriate modifications to contain the radioactivity. $^{14}CO_2$ gas liberated by action of an acid on labeled $Ba^{14}CO_3$ is used commonly as a starting point in the syntheses. Three examples can illustrate how compounds can be labeled at different sites of the molecule:

1. Acetic acid-2-^{14}C:

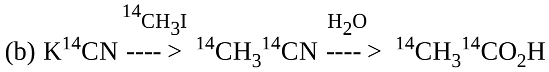
$$Ba^{14}CO_3 \xrightarrow{HCl} {}^{14}CO_2 \xrightarrow[\text{catalyst}]{H_2} {}^{14}CH_3OH \xrightarrow{PI_3} {}^{14}CH_3I \xrightarrow{KCN} {}^{14}CH_3CN \xrightarrow{H_2O} {}^{14}CH_3CO_2H$$

2. Acetic acid-1-^{14}C:

$$Ba^{14}CO_3 \xrightarrow{HCl} {}^{14}CO_2 \xrightarrow{CH_3MgBr} CH_3{}^{14}CO_2H$$

3. Acetic acid-1,2-^{14}C:

$$\text{(a) } Ba^{14}CO_3 \xrightarrow[\text{heat}]{Mg} Ba^{14}C_2 \xrightarrow[\text{catalyst}]{H_2O} {}^{14}C_2H_2 \xrightarrow{H_2O} {}^{14}CH_3{}^{14}CHO \xrightarrow{[O]} {}^{14}CH_3{}^{14}CO_2H$$



(b) $K^{14}CN \xrightarrow{{}^{14}CH_3I} {}^{14}CH_3{}^{14}CN \xrightarrow{H_2O} {}^{14}CH_3{}^{14}CO_2H$

In these examples labeling is said to be *specific* in that only one position in the compound contains radioactive nuclides. Alternatively, labeling may be *general* when all positions are labeled, which often is the case for tritium-labeled compounds (cf. §15.6.2).

Complicated organic compounds, e.g. penicillin, can be labelled through *biosynthesis*. For example, if penicillin is grown in a substrate containing a simple ${}^{35}S$ compound, ${}^{35}S$ is incorporated into the penicillin mold. Since other ${}^{35}S$-containing products may be formed also, the ${}^{35}S$ penicillin must be purified, e.g. through solvent extraction or paper chromato-graphy (§9.2.6).

Thousands of labeled organic compounds are commercially available and some organizations offer labeling service on request.

15.5.4. *Radiochemical purity*

An important consideration in the use of radionuclides is their radiochemical purity since, should several radionuclides of different elements be present in a tracer sample used in an experiment, the result could be ambiguous and misleading. In a radio-chemically pure sample, all radioactivity comes from a single radioactive element. If the radioactivity comes from a single isotope, the sample may be said to be radio-isotopically pure.

The radioisotopic purity of a sample may be ascertained by measuring the half-life. This method obviously can be used only with radionuclides that show sufficient decay during the time of observation for a reliable half-life to be calculated. For radioactivity of longer half-lives the radioisotopic purity can be checked by measurement of the type and energy of the emitted radiations (Ch. 8) or by processing the tracers through one or more chemical steps characteristic of the element of which the radioactivity is presumably an isotope. For example, in the use of ${}^{90}Sr$ (half-life 28.5 y), the radioactivity can be processed through a number of typical reactions characteristic of strontium. If the radioactivity follows the expected chemistry, then the experimenter can be rather certain that it is strontium. This chemical check does not preclude the possibility that there might be several isotopic nuclides in the sample. However, the presence of several isotopes need not be a handicap in tracer studies concerned with the characteristic properties of a particular element.

When a compound labeled with a radioactive nuclide is used to study molecular behavior, it is necessary to ascertain the *radiochemical purity of the compound* and not just the purity of the radioactive isotope. This means it is necessary to be certain that the radioactivity comes only from a specific element and only from a specific compound incorporating that element. This can be determined through selective chemical operations in which it is frequently desirable that the compound should not be destroyed. Examples of such methods involve preparative gas chromatography, thin-layer chromatography, paper chromatography, dialysis, ion exchange, and solvent extraction. Checking that an element or compound is radiochemically pure is important not only for sources of samples prepared in the laboratory but for commercial samples as well. For example, ${}^{14}C$-tagged organic compounds obtained commercially may have been prepared at varying times prior to purchase. Frequently, the decomposition in the sample due to the radiolysis that accompanies the radioactive decay results in the presence of products that interfere with the course of the experiment for which the labeled compound is to be used.

In some cases the radioactive product after a period of storage will have grown a sufficient amount of radioactive daughter that it is no longer sufficiently pure radiochemically. In these cases, the daughter activity must be separated prior to use. For example, the ^{90}Y normally present in a ^{90}Sr sample must be eliminated if the tracer solution is to be used to study strontium chemistry.

15.6. Recoil separations

15.6.1. *Target recoil products*

When a projectile of high energy reacts with a target atom, the reaction products are emitted in the direction of the projectile, measured in laboratory coordinates. We use the term *recoil* to describe this. The products, whose kinetic energy can be calculated by the conservation laws of Ch. 12, are slowed and eventually stopped through collision with other atoms. Consequently, if the target is relatively thin, there is a certain probability that the recoil range of the product exceeds the thickness of the target and the target atoms can therefore escape the target. In such cases the recoiling products be caught on special foils behind the target (*catcher foils*). These catcher foils can be stationary or they can be a moving band or metal or plastic, or even a gas, which sweeps past the target material.

The recoil technique was used in the discovery of the first transuranium element, neptunium, by E. McMillan and P. H. Abelson in 1939. A uranium salt, $(NH_4)_2U_2O_7$, was fixed on a paper and surrounded by more layers of thin paper to form a "sandwich" which was irradiated by thermal neutrons. At the time of fission the fission products ejected with high kinetic energy and were caught in the layers of paper. From the number of layers of paper penetrated by individual fission products, their energy and mass could be calculated. A strong β^- activity was found in the first layers of paper, showing that it had relatively little recoil energy. From chemical experiments it was concluded that this activity was not a fission product but was due to ^{239}U which decayed into ^{239}Np:

$$^{238}\mathrm{U}(\mathrm{n},\gamma)^{239}\mathrm{U} \xrightarrow{\beta^-} {}^{239}\mathrm{Np}$$

In this particular case, the thermal neutron did not carry any kinetic energy, but the emission of the γ-ray caused the ^{239}U to recoil from the uranium sample prior to decay (with very little recoil) to ^{239}Np. This type of reaction is common in neutron irradiation processes, and is referred to as n,γ-recoil.

Recoil techniques have been used extensively in the synthesis of higher transuranium elements. As an example, consider the formation of element 103, lawrencium (Fig. 15.3). The $_{103}$Lr nuclides, which were formed in the reaction in the target between ^{252}Cf and projectiles of ^{11}B, recoiled out of the thin target into the helium gas where they were stopped by atomic collisions with the He-atoms. These recoil species became electrically charged cations as they lost electrons in the collision with the gas atoms. They could, therefore, be attracted to a moving, negatively charged, metal coated plastic band, which

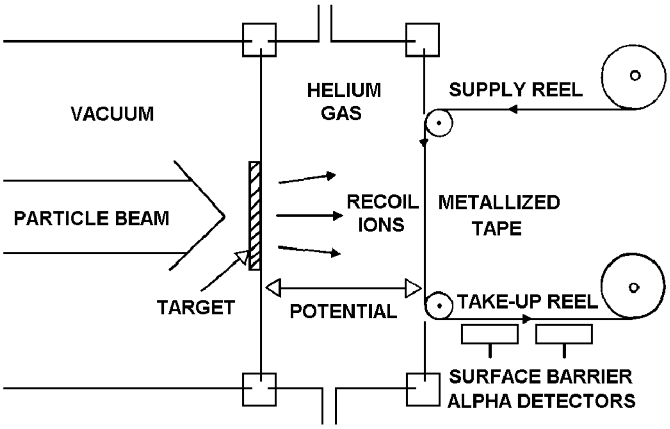


FIG. 15.3. Principle of target cage system for recoil collection of the products formed.

carried the Lr atom on its surface to a number of α-particle detectors where the α-decay of the lawrencium was measured. From the velocity of movement of the plastic band and the measurement of the radioactivity by energy sensitive nuclear detectors, the half-lives and α-energies of the product nuclei could be determined. Comparison of these data with predictions from theory allowed assignment of the mass number of the nuclide.

Target recoil products may have a detrimental effect also. In reactor irradiation of biological samples to determine their trace metal concentration it was found that n,γ products formed in the material of the sample container recoiled out of the container wall into the sample, contaminating it. Such contamination can be eliminated by using a container which forms a minimal amount of such products.

15.6.2. *Hot atom reactions*

The momentum imparted to a nucleus in a nuclear reaction with a charged particle or a fast neutron almost invariably is sufficient to result in the rupture of chemical bonds holding the atom in the molecule. The same is true for the recoil energy imparted to a nucleus by the emission of an α-particle as well as in β-decay, γ-decay, etc.; the recoil energies in radioactive decay are discussed in §§4.3-4.5.

These recoiling atoms are known as *hot atoms* since their kinetic energy is much in excess of thermal equilibrium values. A hot atom may move as much as several hundred atomic diameters after the rupture of the bond before being stopped even though this takes only about 10^{-10} s. Initially the hot atom is highly ionized (e.g. for $Z = 50$ ionic charges up to +20 have been observed). As the hot atom is slowed down to thermal energies, it collides with a number of other particles in its path producing radicals, ions, and excited molecules and atoms. At thermal energies it may become a neutral atom (particularly if the matrix material is metallic), an ion, possibly in a different oxidation state (a common situation in inorganic material), or it may react to form a compound with molecules in its path (the prevalent situation in matrices of covalent material).

Chemical effects of nuclear transformations (*hot atom chemistry*) have been extensively studied in connection with induced nuclear transformations, both in the gas phase, in solution and in the solid state. In the latter cases the dissipation of the kinetic energy and neutralization of the charge within a small volume produces a high concentration of radicals, ions, and excited molecules in the region where the recoiling atom is slowed to energies where it can form stable bonds. Usually the product molecule is labeled neither very specifically nor completely randomly. The topic of hot atom behavior is also treated in Ch. 7.

Hot atom reactions can be used for synthesis of labeled compounds. So far this technique has been used primarily for ^3H and ^{14}C labeling. For example, an organic gaseous compound is mixed with ^3He and the sample is irradiated with neutrons. The reaction $^3He(n,p)^3H^{\rightarrow}$ produces tritium as hot atoms (indicated by the small arrow) with kinetic energies of approximately 0.2 MeV. These hot atoms react with the organic molecules to produce labeled compounds. An example is the formation of labeled butanol

$$C_4H_9OH + {}^3H^{\rightarrow} \rightarrow C_4H_9O^3H + {}^1H^{\rightarrow}$$

The reaction is referred to as a *hot atom displacement* reaction. In an alternate method the solid organic compound may be mixed with Li_2CO_3, and this solid mixture irradiated with neutrons to cause the reaction: $^6Li(n,\alpha)^3H^{\rightarrow}$. Again the hot tritium atom combines with the organic species to cause labeling. In a third and simpler method, the organic compound is simply mixed with tritiated gas. The β-radiation from tritium decay causes excitation and decomposition which leads to capture by the organic radicals of some of the remaining tritium. These reactions are not selective because reactions with decomposition products also occur. Therefore the tritium labeled product must be purified. Gas phase labeling usually results in incorporation of tritium in several sites of the molecule, e.g. toluene has about 9% of the total label in the CH_3 group, 54% in the *ortho* sites of the ring, 24% in the *meta* sites, and the remaining 13% at the *para* site.

^{14}C-labeling can be achieved in a similar manner by using the $^{14}N(n,p)^{14}C^{\rightarrow}$ reaction. The recoiling ^{14}C energy is about 0.6 MeV. A suitable labeling mixture is NH_4NO_3 + the organic compound: cf. ref. Wolf (1960).

15.6.3. *The Szilard-Chalmers process*

In 1934 L. Szilard and T. A. Chalmers discovered that bond breaking could occur for atoms following nuclear reaction or radioactive decay even though the recoil energy in the initial process is not sufficient to overcome the bonding energy. In the case of thermal neutron capture the processes involved in the emission of the γ-ray, which removes the nuclear excitation energy, impart recoil energy to the atom to break most chemical bonds (n,γ-recoil). If, after rupture of the bonds, the product atoms exist in a chemical state different and separable from that of the target atoms, the former may be isolated from the large mass of inactive target. This provides a means of obtaining high specific activities in reactions where target and product are isotopic.

This process is known as the *Szilard-Chalmers reaction* and was discovered when, following the irradiation of ethyl iodide with thermal neutrons, it was found that radioactive iodide could be extracted from the ethyl iodide with water. Moreover, when iodide carrier and silver ions were added to this aqueous phase, the radioactive iodide precipitated as silver iodide. The obvious interpretation of these results is that the neutron irradiation of the ethyl iodide, which caused the formation of ${}^{128}\text{I}$, ruptured the bonding of this atom to the ethyl group. The bond energy of iodine to carbon in C_2H_5I is about 2 eV. Since this exceeds the recoil energies of neutron capture, the bond breakage must have resulted from the γ-emission which followed neutron capture and not the capture process itself. The reaction can be written:

$$C_2H_5{}^{127}\text{I} + \text{n} \rightarrow [C_2H_5{}^{128}\text{I}]^* \rightarrow C_2H_5 + {}^{128}\text{I}^{\rightarrow} + \gamma$$

The ${}^{128}\text{I}^{\rightarrow}$ loses its kinetic energy and is stabilized as an iodine atom or iodide ion; it can also be recaptured by the C_2H_5 radical (*retention* of activity in C_2H_5I). In addition to the necessity that the recoiling species have sufficient energy to rupture the bond, it is also necessary for a successful enrichment of specific activity by the Szilard-Chalmers process that there is no rapid exchange at thermal energies between the active and inactive iodine atoms in ethyl iodide:

$$C_2\,H_5{}^{127}\text{I} + {}^{128}\text{I} \overset{\text{slow}}{\rightleftarrows} C_2H_5{}^{128}\text{I} + {}^{127}\text{I}$$

After the rupture of the bond, the hot atoms may also replace iodine or even hydrogen atoms from ethyl iodide molecules, similar to the thermal exchange:

$${}^{128}\text{I}^{\rightarrow} + C_2H_5{}^{127}\text{I} \rightarrow C_2H_5{}^{128}\text{I} + {}^{127}\text{I}$$

Again, the result is retention of the activity within the organic molecule. Retention is decreased by diluting the ethyl iodide with alcohol which reduces the probability of collision and exchange with C_2H_5I molecules as the hot atoms of ${}^{128}\text{I}^{\rightarrow}$ are being slowed.

Isomeric transitions which proceed by emission of γ-rays may not provide sufficient recoil energy to break covalent bonds. However, in these cases or very low energy isomeric transitions, the extent of internal conversion is large. This results in vacancies in the inner electron orbitals (§4.5). When electrons in outer orbitals move to fill the vacancies, the difference in electron binding energies is sufficient to cause some ionization, resulting in relatively high charge states for the atom, leading to bond rupture. An example of such a process is seen in the reaction whereby an alkyl bromide is irradiated with thermal neutrons. During neutron irradiation the reactions are

$$\text{RBr} + \text{n} \left\langle \begin{array}{l} \xrightarrow{\sigma\ 2.9\ \text{b}} \text{R} + {}^{80\text{m}}\text{Br (4.4 h)} \\ \qquad\qquad\qquad\quad \downarrow \text{IT} \\ \xrightarrow[\sigma\ 8.5\ \text{b}]{} \text{R} + {}^{80}\text{Br (18 min)} \end{array} \right.$$

Extraction by water of this bromide produces an aqueous sample containing both ^{80}Br and ^{80m}Br. Some ^{80}Br and ^{80m}Br are retained as alkyl bromide in the organic phase. If, after a period of an hour, a new extraction is carried out on the organic phase, only the ^{80}Br is found in the aqueous sample. This ^{80}Br results from the following reaction

$$R^{80m}Br \xrightarrow{IT} R + {}^{80}Br + \gamma$$

In addition to the organic halides a number of inorganic systems undergo similar reactions. From neutron irradiation of acid or neutral solutions of permanganate most of the ^{56}Mn activity is removable as MnO_2. From solid or dissolved chlorates, bromate, iodate, perchlorates, and periodates, active halide samples may be isolated in relatively high yields. Systems with Te, Se, As, Cu, and several Group VIII elements have been shown to be applicable to the Szilard-Chalmers process. The great advantage in all these cases is that a relatively small amount of activity may be isolated from a large mass of isotopic inactive target. Because of retention there is also some labeling of the target molecules.

15.7. Fast radiochemical separations

Short-lived radioactive nuclides are of interest (i) to nuclear science to establish the outer boundary for nuclide formation, which yields information on nuclear structure, (ii) to chemistry to extend the limits of the periodic system, i.e. the actinides and transactinides (or *superheavy elements*); these studies are also of interest to cosmology since these heaviest elements are believed to be formed in supernovae, and (iii) to medicine where they offer a unique tool to identify and treat some diseases (§9.5). Short-lived radionuclides are also used in chemical and industrial research, one of their advantages being that they rapidly disappear, eliminating radioactive waste problems. We arbitrarily define short-lived as meaning half-lives < 10 minutes. Because many of the lightest elements of greatest interest in organic chemistry and biology lack long-lived radionuclides, the production of their short-lived isotopes are of particular interest; see Figure 4.7. At the other end of the periodic system there are no stable isotopes at all, and for the transuranium elements the half-lives of the most stable isotopes become shorter and shorter for each higher element, e.g. the longest-lived isotope of $Z = 105$ has $t_{1/2}$ ~ 34 s. Thus, research on the production of short-lived radionuclides has been particularly intense for the lightest and heaviest elements. It is obvious that studies and uses of these short-lived nuclides requires special techniques, which often are rather costly. A brief description of some of the techniques used follows.

The sequence of procedures necessary for the production and study of very short-lived nuclei are:

1) target preparation and irradiation,
2) primary (preliminary) target purification (at irradiation site),
3) transport of product (e.g. through pneumatic tubes in which the transport velocity may be up to 100 m s^{-1}) from irradiation site to nuclear chemistry laboratory,
4) isolation of desired product and eventual labeling, and

5) final use in physico-chemical experiments or in applied areas; e.g. hospitals or industry.

A primary requirement for work with short-lived nuclides is that the site or production and the site of use be close together. In 5 – 30 seconds it is possible to use rapid manual separation procedures consisting of (a) target dissolution, followed by (b) chemical isolation of the radionuclide through solvent-extraction-stripping or high pressure/temperature ion exchange, and/or (c) precipitation or electroplating before (d) measurement. In this scheme eventual chemical studies can be included, usually between steps (b) and (c). For very short-lived nuclides, all steps must be automated.

There are a number of non-chemical techniques involving time-of-flight and magnetic mass analysis of target recoil products, energy sensitive detectors, etc., with which half-lives down to 10^{-12} s can be measured. However, of more interest to us are the fast chemical systems. Let us review a few representative types.

15.7.1. *Production of ^{11}C labeled compounds*

In §9.5.3 (c) we described the use of the PET medical imaging technique, which requires the use of positron emitters. Many interesting positron emitters are very short-lived (see Table 9.5) requiring rapid synthesis of the labeled compound. One of the more frequently used positron emitters is ^{11}C ($t_{1/2}$ 20.3 m) because it can be introduced into almost any organic compound. Glucose derivatives are of special interest because glucose is the main energy source of the brain; as a consequence, the areas in which glucose accumulates indicate places of highest physiological activity. Also, glucose derivatives are relatively easy to synthesize. To illustrate the technique, consider the synthesis of 2-deoxy-D-[1-^{11}C] glucose (^{11}C-2DG) which is used to study tumor metabolism in the brain (steps 1 and 2 in §9.5.3 (c)):

By irradiating a target consisting of a mixture of 95% N_2 + 5% H_2 in a cylinder, 400 mm long and 60 mm in diameter, at 10 bar pressure by 20 MeV protons, $^{11}CH_4$ and $^{13}N_2$ are produced. After an irradiation of 30-60 minutes, the gas is mixed with ammonia and allowed to react at elevated temperature on a platinum catalyst to produce $H^{11}CN$ (~ 80% conversion at 850°C). The yield is about 5 GBq per µA of proton current. The subsequent synthesis is a series of elaborate steps in which $Na^{11}CN$ is digested with preformed reactive glucose derivatives in presence of Ni/Al-alloy in formic acid. The reaction mixture is purified through several ion exchange columns and finally collected on an anion exchanger. The total synthesis, from end of irradiation, takes about 1 hour with an over-all yield of ~ 80% relative to the $H^{11}CN$ yield.

Many procedures for rapid ^{11}C-labelling are described in the literature. In some cases labeled compounds can be ordered from radiopharmaceutical companies, but for the ^{11}C-compounds the $t_{1/2}$ mandates production and synthesis at the place of use.

15.7.2. *Auto-batch procedures*

Figure 15.4 shows an auto-batch procedure for isolation and separation of rare earths obtained from spontaneous fission of ^{252}Cf. The rare earths plus other fission products are

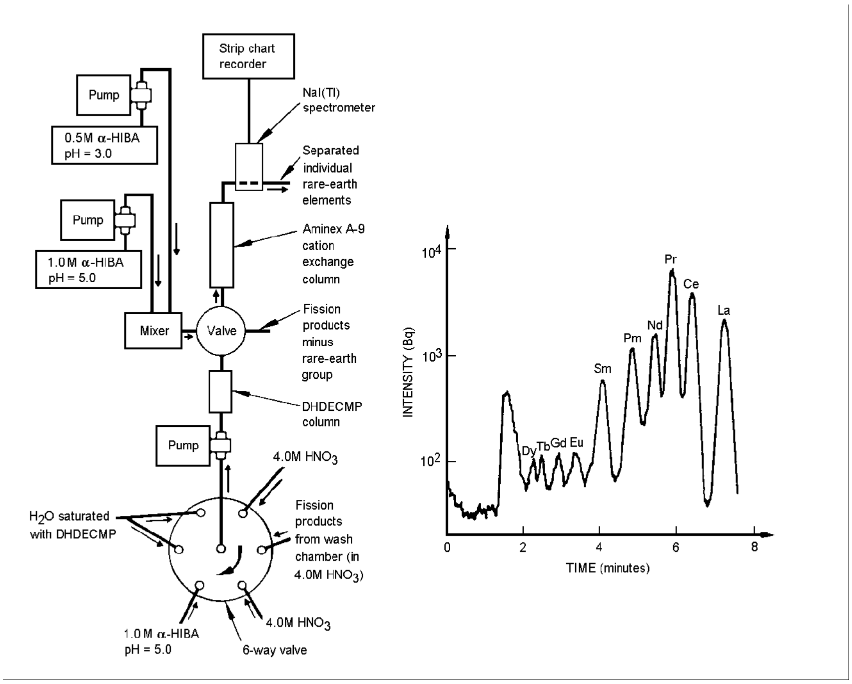


FIG. 15.4. Schematic of auto-batch lanthanide chemistry system and elution curve obtained. (From Baker et al.)

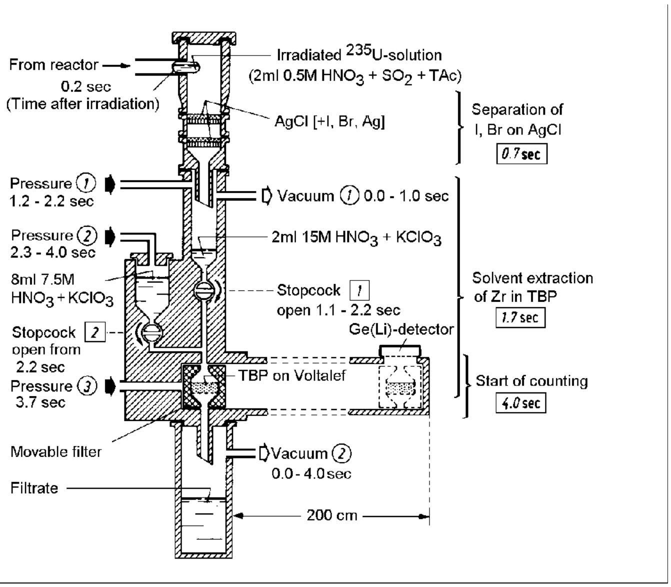


FIG. 15.5. Auto-batch system for identification of short-lived zirconium isotopes. (From Trautmann et al.)

washed from the target chamber by nitric acid and extracted by high-pressure liquid chromatography onto a column containing dihexyl diethyl carbamoyl-methylphosphonate (DHDECMP). After removal from this column, the rare earths are sorbed on a cation exchange column, from which they are eluted sequentially by hot (95°C) α-hydroxy isobutyric acid (HIBA). Figure 15.4 shows a typical elution curve. The total separation procedure takes about 10 minutes.

Figure 15.5 shows a much more rapid procedure to recover zirconium isotopes formed by fission. (a) A solution of ^{235}U sealed in a plastic capsule and irradiated with thermal neutrons is projected pneumatically into the apparatus where the capsule is crushed. (b) The solution is filtered through two layers of preformed, inactive silver chloride, which, by heterogeneous exchange, rapidly removes I and Br. (c) The next step involves solvent extraction with an organic phase containing the reagent tri-butyl phosphate (TBP) adsorbed on the surface of small plastic grains. The filtrate from (b) is mixed with strong $HNO_3 + KBrO_3$ and drawn through the stationary organic phase (marked "movable filter" in the Figure), to remove zirconium. (d) After washing the organic phase with nitric acid, the filter layer containing the zirconium is transferred pneumatically to the detector (to the right in the Figure). (e) Counting is started 4 s after the end of irradiation. The Figure shows the time sequences for the operations in numbers. Stopcocks are operated pneumatically and valves magnetically by signals from electronic timers. The chemical yield of zirconium amounts to about 25%. This experiment led to the identification of ^{99}Zr with a half-life of 1.8 s. The ARCA (Automatic Rapid Chemistry Apparatus) in Darmstadt is a modification of the system in Figure 15.5; because the separations are done by ion exchange resins, it is considerably slower, requiring nuclides with $t_{½} > 20$ s.

In these systems proper modification of conventional techniques provided very fast separations. Precipitation (using a preformed precipitate and heterogeneous exchange), solvent extraction (by reversed phase chromatography), and ion exchange (with heating and pressure) have been used in the identification and study of short-lived transuranides (elements 102 and higher).

15.7.3. *On-line procedures: gas phase separation*

Recoil techniques (§15.6) have been used extensively with *gas-jet transportation systems* for studying short lived radionuclides. As an example, consider the formation of element 103, lawrencium. The $_{103}$Lr nuclides, which were formed in the reaction in the target between ^{252}Cf and projectiles of ^{11}B, recoiled from the thin target into the helium gas where they were stopped by atomic collisions with He-atoms. These recoil species became electrically charged cations as the result of loss of atomic electrons in the collision with the gas atoms. They could, therefore, be attracted to a moving, negatively charged, metal coated plastic band, which carried the Lr atoms on its surface to α-particle detectors where the α-decay of the lawrencium was measured; see Fig. 15.3. Instead of collecting the particles on a moving band, they could also be swept by a gas or aerosol stream into an apparatus for chemical processing.

Separation may be achieved by having a target containing a reactive compound or having the recoiling species continue in the gas phase by using either a reactive gas or using gas-solid separation. Figure 15.6 illustrates the separation of bromine from other fission

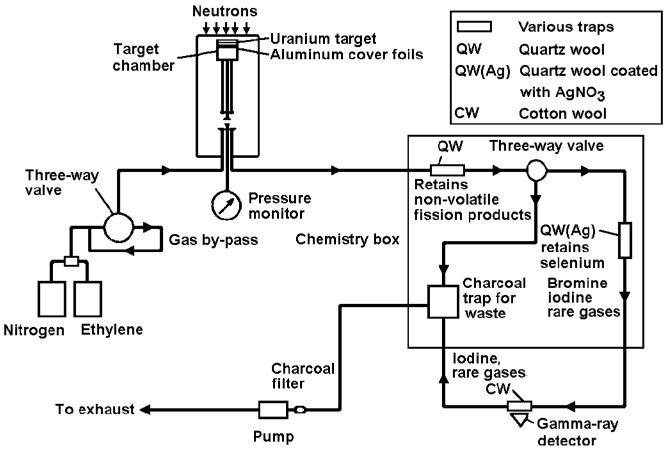


FIG. 15.6. On-line gas-phase separation system for isolation of bromine products. (From Rengan et al.)

products by using gas-solid reactions on quartz and cotton wool. Figure 15.7 illustrates another technique: a chemically reactive thermo-chromatographic column is placed after the target cage. The target N_2-gas contains a KCl-aerosol to which the fission product nuclides

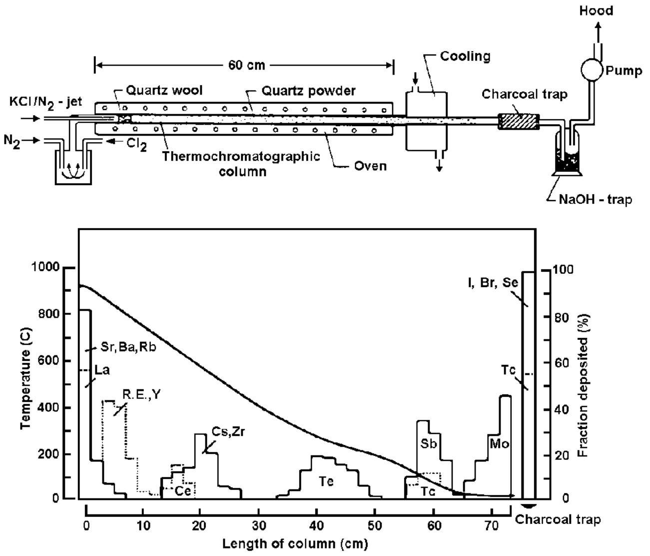


FIG. 15.7. On-line thermo-chromatographic system. (From Hickmann et al.)

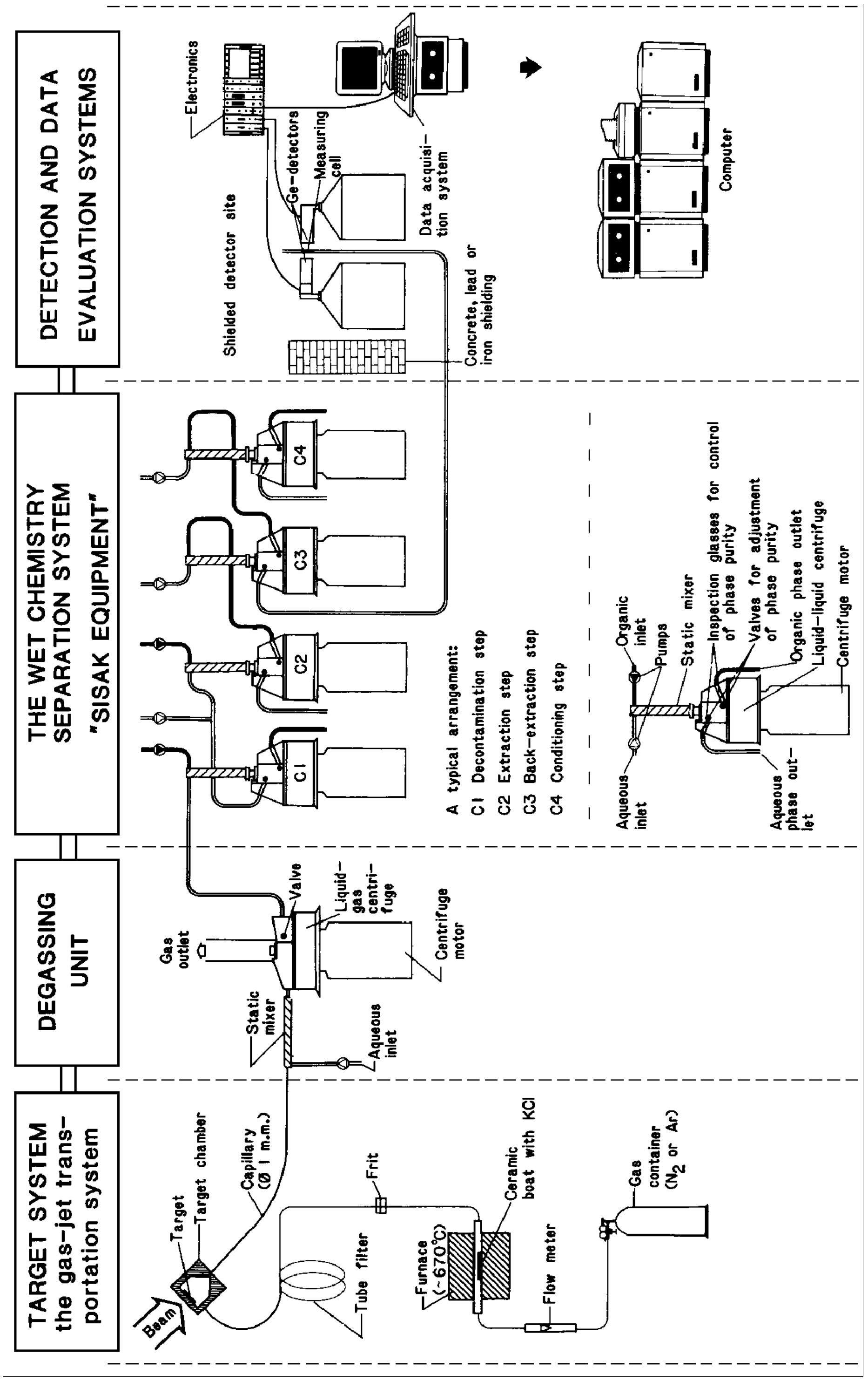


FIG. 15.8. The SISAK fast solvent extraction system. (Courtesy Skarnemark)

attach. The gas-aerosol stream passes through a tube or column containing a partly selective adsorbent (e.g. quartz powder, KCl, $BaCl_2$, K_2CrO_7). The temperature gradient along the tube leads to deposition at different positions of elements (or compounds) of different vapor pressure. Rather selective deposition can be achieved, although the technique is not totally element specific. Nuclides with half-lives down to 0.1 s have been determined in identification of spallation products, fission products, and transuranium elements. An example is the OLGA system (On-line Gas Chemistry Apparatus) in Darmstadt which was used to identify ^{263}Ha (atomic number 105); see Ch. 16.

15.7.4. *On-line procedures: solvent extraction*

The SISAK (Short-lived Isotopes Studied by the AKUFVE) technique is illustrated in Figure 15.8. A target containing an element (e.g. uranium) on a thin foil is bombarded with projectiles, while a gas stream containing "catcher" particles (e.g. C_2H_4 or KCl) behind the target continually removes the products recoiling into the gas stream. The gas jet is thoroughly mixed with an aqueous solution in the static mixer and then degassed. The aqueous solution containing the radioactive products is passed through a series of fast and selective solvent extraction loops, where continuous flow mixers and centrifugal separators are used (the AKUFVE-technique, §9.4.3). The solution from the final separation passes through a "hold-up" cell, which may contain also some absorbent to capture the element of interest. The cell is viewed by a detector system. The procedure can provide high selectivity for a particular element and takes about 3 s from target to final detector. Because it is an on-line technique, SISAK has mainly been used mainly to obtain detailed decay schemes of very short lived nuclides ($t_{1/2}$ ~ 1 to 10 s).

15.7.5. *Mass separator procedures*

In the ISOLDE (Isotope Separation On Line DEvelopment) collaboration at CERN, the target material is fixed in a solid but porous chemical matrix and irradiated by protons or heavy ions. The products react with the target matrix, and those with the "right" chemistry diffuse from the target (which may be heated to increase the diffusion rate) and are swept by a gas stream into the ionization chamber of a mass spectrometer where the products are separated. Figure 15.9 shows the schematic for such a system: At 1, a 600 MeV proton beam is focused on the target 2. The beam of spallation products is accelerated to 60 keV, focused by magnet 3 and separated by electrostatic deflectors at 4 to yield a number of beams which are analyzed by various techniques (nuclear spectroscopy, laser spectroscopy, atomic beam magnetic resonance, range measurements, etc).

15.8. Exercises

15.1. ^{24}Na is produced through the reaction ^{26}Mg(d,α)^{24}Na. A 0.2 mm thick magnesium foil is irradiated for 1 h by a current of 130 μA of 22 MeV D^+ ions in a cyclotron. The foil has a much larger area than the cross-section of the beam. What is the specific activity of ^{24}Na if the magnesium foil (3 cm^2) contains 0.003% Na and σ for the reaction is assumed to be 25 mb?

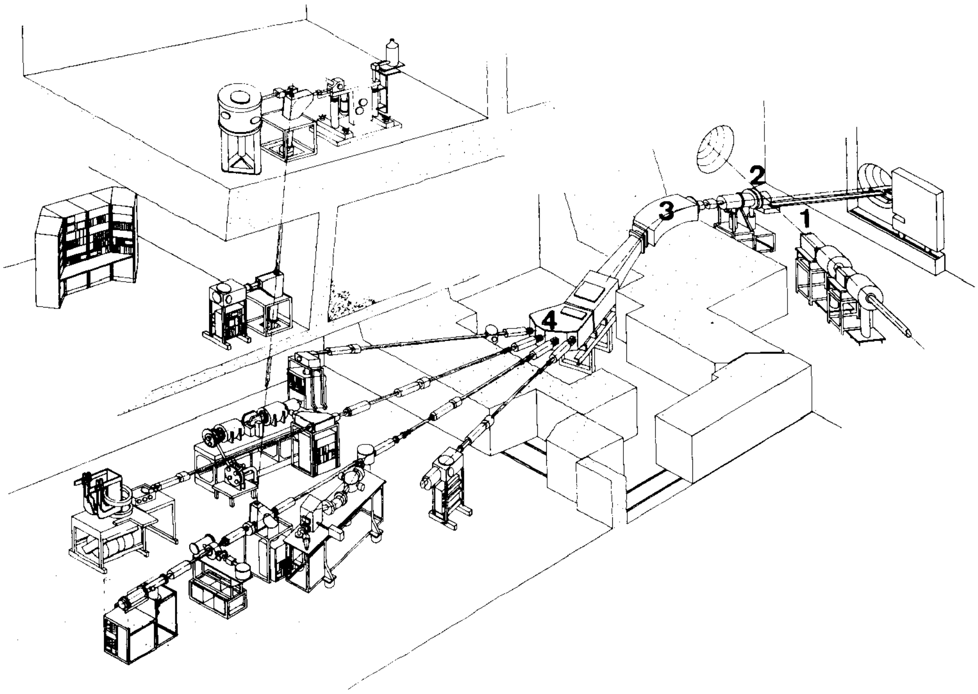


FIG. 15.9. The ISOLDE separator system at CERN. (Courtesy Rudstam)

15.2. Oxygen can be determined through the reaction $^{16}O(n,p)^{16}N \rightarrow (\beta,\gamma\ 7\ s)$; σ_{np} at 14 MeV n is 49 mb. 3.982 g of a fatty acid were irradiated for 20 s in 4×10^{12} n m^{-2} s^{-1}. After the irradiation the sample was rapidly transferred with a rabbit system to a scintillation detector which had an efficiency of 1.1% for the ^{16}N γ-rays (~6 MeV). Exactly 8 s after the end of the irradiation, the sample was counted for 1 min, yielding 13 418 counts above background. What was the oxygen fraction of the sample?

15.3. ^{199}Au can be formed through two successive n,γ-reactions on ^{197}Au (100% in nature). If 1 g ^{197}Au is irradiated with 10^{18} n m^{-2} s^{-1} during 30 h, what will the disintegration rate of ^{199}Au be at the end of the irradiation? The chain of events to be considered is:

^{197}Au ($\sigma_{n,\gamma}$ 98.8 b) ---> ^{198}Au ($t_{1/2}$ 2.694 d, $\sigma_{n,\gamma}$ 25 100 b) ---> ^{199}Au ($t_{1/2}$ 3.139 d, $\sigma_{n,\gamma}$ 30 b) --->
Neglect self shielding.

15.4. ^{246}Cm has a half-life of 4 730 y. It can be obtained through neutron capture in ^{245}Cm, which has a half-life of 8 500 y; the reaction cross-section is 345 b. Both isotopes are also fissioned by thermal neutrons, σ_{245} 2 020 b and σ_{246} 0.17 b. ^{246}Cm also has a n,γ cross-section of 1.3 b. Because one does not want to loose too much ^{245}Cm, the irradiation is timed to give a maximum yield of ^{246}Cm. If the neutron flux is 2×10^{18} n m^{-2} s^{-1}, (a) when does the ^{246}Cm concentration reach its maximum? (b) What is the ratio between the amount of ^{246}Cm produced and amount of ^{245}Cm consumed at that time?

15.5. A sample containing 50 g ethyl iodide was irradiated with neutrons from a RaBe source of 1×10^{9} n m^{-2} s^{-1} for 2 h. If there is a 20% retention and separation occurs 5 min after end of irradiation, what will be the activity of the AgI sample 10 min after separation? The detector has an 8% efficiency for the emitted γ-radiation. Assume the reaction cross-section for $^{127}I(n,\gamma)^{128}I \rightarrow (\beta^{-}, 25.0\ min)$ to be 6.2 b.

15.6. ^{59}Fe of high specific activity can be produced through thermal neutron irradiation of a solution of 1 ml 0.1 M potassium hexacyanoferrate. The recoiling (free) iron atoms, which are produced with a 40% yield, are quantitatively extracted into an organic solvent. How long must the irradiation be in a reactor at 3×10^{19} n m^{-2} s^{-1} to obtain 37 MBq ^{59}Fe? The reaction cross-section for $^{58}Fe(n,\gamma)^{59}Fe \rightarrow (\beta,\gamma\ 45.1\ d)$ is 1.15 b and the isotopic abundance of ^{58}Fe is 0.3% in natural iron.

15.9. Literature

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