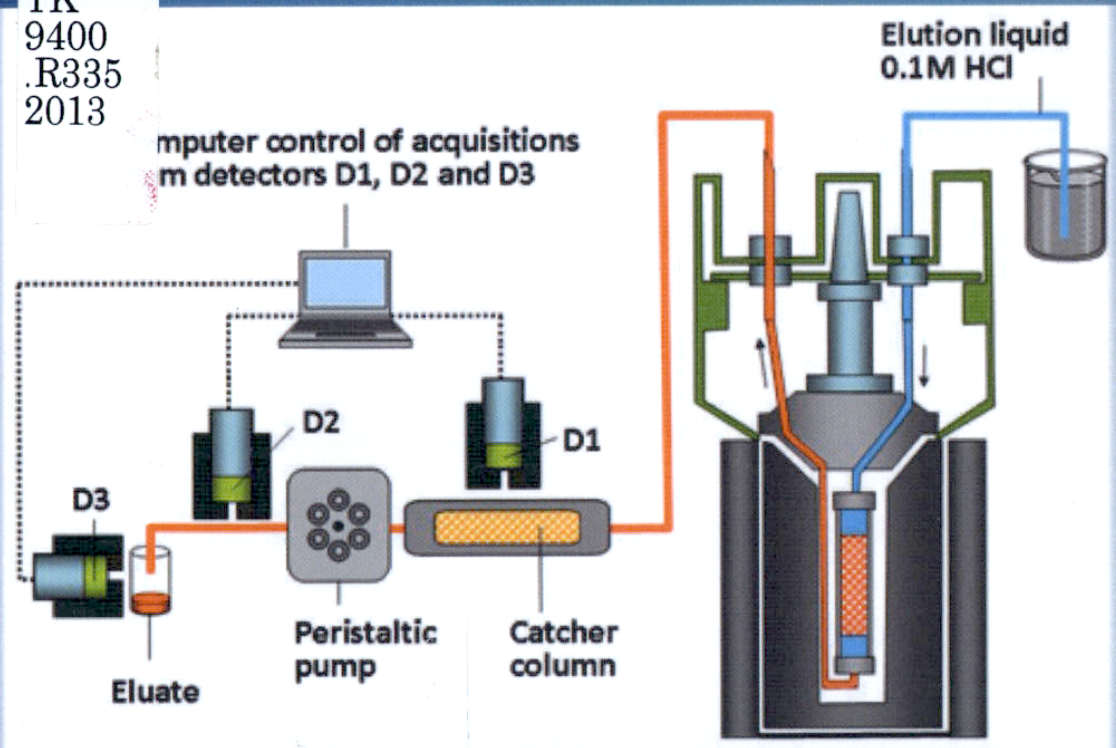


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Radiotracer Generators for Industrial Applications

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IAEA RADIATION TECHNOLOGY SERIES No. 5

RADIOTRACER GENERATORS FOR INDUSTRIAL APPLICATIONS

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2013

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FOREWORD

Radiotracers have been widely used throughout industry to optimize processes, solve problems, improve product quality, save energy and reduce pollution. Their technical, economic and environmental benefits have been recognized by both the industrial and the environmental sectors. The most important radiotracer techniques have been transferred to many developing Member States through IAEA Technical Cooperation projects.

However, in spite of their manifest benefits, radiotracer techniques continue to be underutilized, not only by developing countries but also by more industrialized nations. There are a number of factors that restrict the usage of the radioisotope techniques, but chief among them is the timely availability of suitable radiotracers. Ensuring timely availability of suitable radionuclides is a main hurdle to the use of radiotracer techniques in industry. For developing countries that do not possess radioisotope production facilities, the long time required for import of radionuclides not only completely rules out the use of short half-life nuclides, but also makes it impossible for the radioisotope applications teams to respond to problems of an urgent nature. Many possible radiotracer investigations are not being carried out in developing countries because of this problem.

Even in industrialized countries, radionuclide supply is often a problem, as many of the former suppliers of industrial radionuclides have switched their production facilities to serve the more lucrative radiopharmaceuticals market. Obtaining continuity of supply of radionuclides with which to carry out extended studies in difficult-to-access locations, such as offshore oil platforms, is also a significant challenge.

Making use of tracers from radionuclide generators can alleviate the difficulties associated with radioisotope supply. Two commercially available medical radionuclide generators, $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ and $^{113}\text{Sn}/^{113\text{m}}\text{In}$, have been used for this purpose, but their use has been restricted because their half-lives are relatively short and only a limited number of radiotracers derived from them have been proven under industrial conditions.

Recognizing the potential usefulness of several radionuclide generators, including $^{68}\text{Ge}/^{68\text{Ga}}$ and $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$ and of radiotracers derived from them, the Agency organized a Coordinated Research Project (CRP) on the Evaluation and Validation of Radionuclide Generator-based Radiotracers for Industrial Applications. The objectives of the CRP, which was implemented over the period 2007–2011, was to coordinate the development of industrial radionuclide generators and to validate generator based radiotracers for use in harsh industrial conditions. It was anticipated that an important outcome would be the production of radionuclide generators designed specifically for industrial purposes. Their

cost would be considerably lower than those of medical generators since the high costs of the facilities required to produce generators suitable for in vivo use can be avoided.

The IAEA facilitates the transfer of technology, and an important part of this process is the provision of relevant literature that may be used for reference purposes or as an aid to teaching. This monograph contains guidelines for the selection and preparation of radiotracers derived from radionuclide generators, as well as reports from participants of the CRP. The book has been prepared with contributions from all CRP participants. The IAEA wishes to express thanks to all the contributors and especially to T. Bjørnstad and T.S. Charlton for their contributions to this publication. The IAEA officers responsible for this publication were Joon-Ha Jin and P. Brisset of the Division of Physical and Chemical Sciences.

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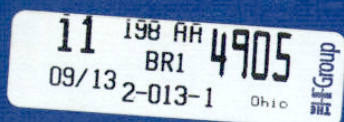
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Radionuclide generators represent a cost effective strategy to ensure a continuous and reliable supply of short lived radionuclides for radiotracer investigations. Making use of radiotracers from radionuclide generators can alleviate the difficulties associated with radioisotope supply. Another advantage is the ease with which the daughter product can be separated on demand and converted into a radiotracer by some tailor-made labelling procedure at the site. This publication contains guidelines for the selection and preparation of radiotracers derived from radionuclide generators. It describes the results of research undertaken in the characterization of $^{68}\text{Ge}/^{68}\text{Ga}$, $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$, $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ and $^{113}\text{Sn}/^{113\text{m}}\text{In}$ radiotracer generators and their validation in industrial process investigations. Radiotracers have been widely used throughout industry to optimize processes, solve problems, improve product quality, save energy and reduce pollution. Recent trends in the industrialization process of developing countries suggest that radiotracer techniques will continue to play an important role in industry for many years to come.

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radiotracers based on short lived radionuclides and help Member States to realize more fully the economic benefits to be derived from radiotracer technology.

2. THEORETICAL ASPECTS

2.1. MOTHER/DAUGHTER NUCLEAR RELATIONSHIPS AND THE BATEMAN EQUATION

A nuclear mother/daughter relationship consists of a radionuclide (mother) that, upon radioactive decay, produces another, but shorter lived, daughter radionuclide (i.e. $T_{1/2}(\text{mother}) > T_{1/2}(\text{daughter})$). The nuclear chart contains more than 110 mother/daughter nuclear relationships from the lightest, $^{28}\text{Mg}/^{28}\text{Al}$, to the heaviest below uranium with some practical use, $^{234}\text{Th}/^{234\text{m}}\text{Pa}$. Some of them may be useful for industrial purposes.

The decay process is illustrated in the schematic and simplified decay scheme in Fig. 1. The mother radionuclide is indexed by 1, the daughter radionuclide is indexed by 2 and the granddaughter indexed by 3.

In this decay scheme, $N(t)$ is the number of mother radionuclides at time $t = t$, $N(0)$ is the initial number of mother radionuclides at time $t = 0$, $D(t)$ is the

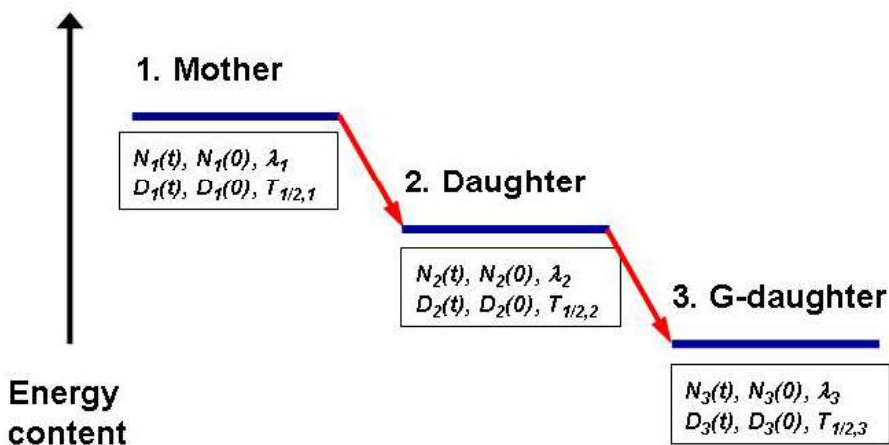


FIG. 1. Simplified decay scheme of a radionuclide generator illustrating the decay of the mother into the daughter and further into the granddaughter.

disintegration rate at time $t = t$, $D(0)$ is the disintegration rate at time $t = 0$, $T_{1/2}$ is the half-life of the nuclide and λ is the decay constant, $\lambda = \ln 2 / T_{1/2}$.

The mathematical relationship between the parameters is described by the Bateman equation. The Bateman equation is not a single equation; rather, it is a method of setting up differential equations describing the decay in the chain of interest.

For the first derivation, it is supposed that $N_2(0) = 0$ and $N_3(0) = 0$ and that the granddaughter product is stable, which is the case for most useful radionuclide generators. The stability of the granddaughter is characterized by the fact that $\lambda_3 = 0$.

Then, one can set up the following differential equation for the decrease of the number of parent nuclides as a function of time:

$$\frac{dN_1(t)}{dt} = -\lambda_1 N_1(t) \quad (1)$$

The solution of Eq. (1) leads to the well-known decay equation of a single radioactive nuclide, i.e.:

$$N_1(t) = N_1(0)e^{-\lambda_1 t} \quad (2)$$

Since the disintegration rate is defined by:

$$D_1(t) = \lambda_1 N_1(t) \quad (3)$$

it follows from Eqs (2) and (3) that:

$$D_1(t) = D_1(0)e^{-\lambda_1 t} \quad (4)$$

Similarly, one may set up a differential equation for the number of daughter nuclides at any time t . Supposing that the only source of the daughter nuclide is from decay of the mother nuclide, i.e. $N_2(0) = 0$, then:

$$\frac{dN_2(t)}{dt} = \lambda_1 N_1(t) - \lambda_2 N_2(t) \quad (5)$$

Equation (5) describes the rate of change of the daughter nuclides that is equal to the supply by the decay of the mother and diminished by the rate of loss through its own decay. The solution of this equation results in the following expression:

$$N_2(t) = N_1(0) \frac{\lambda_1}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (6)$$

In analogy with Eq. (4):

$$D_2(t) = D_1(0) \frac{\lambda_2}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (7)$$

For the sake of completeness, the corresponding equations for the granddaughter will also be provided. Equation (7) describes the rate of change of the number of atoms of the granddaughter fed only by the decay of the daughter. Since the granddaughter is stable, the number of atoms is continuously accumulating:

$$\frac{dN_3(t)}{dt} = \lambda_2 N_2(t) \quad (8)$$

The number of stable granddaughter nuclides at any time t will then be the initial number of mother nuclides minus the remaining number of mother nuclides at time t minus the existing number of daughter nuclides at time t , expressed by:

$$N_3(t) = N_1(0) - N_1(t) - N_2(t) \quad (9)$$

Introducing Eqs (2) and (6) gives:

$$N_3(t) = N_1(0) - N_1(0)e^{-\lambda_1 t} - N_1(0) \frac{\lambda_1}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (10)$$

Rearranging Eq. (10) gives:

$$N_3(t) = N_1(0) \left[1 - \frac{1}{\lambda_2 - \lambda_1} (\lambda_2 e^{-\lambda_1 t} - \lambda_1 e^{-\lambda_2 t}) \right] \quad (11)$$

For more information on these subjects, see Refs [1–3].

2.2. RADIOACTIVE EQUILIBRIUM

Equilibrium is a condition established in a mother/daughter mixture when both mother and daughter are radioactive and when the daughter's half-life is shorter than that of the mother. If the daughter's half-life exceeds that of the parent, equilibrium will never be reached. There are two types of equilibrium: secular and transient.

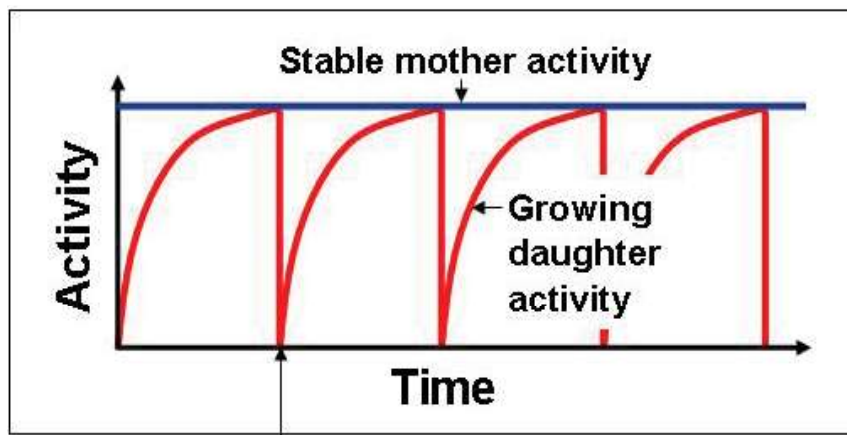
2.2.1. Secular equilibrium

Strict definitions of secular and transient equilibria hardly exist. However, it may be regarded that if $T_{1/2,1} \gg T_{1/2,2}$, a condition of secular equilibrium exists. This means that the activity of the mother radionuclide does not decrease measurably during a reasonable period of time, i.e. subsequent elutions of the daughter with equal spacing in time will yield the same daughter activity (provided the elution efficiency stays constant). This situation for the general case is illustrated in Fig. 2.

A practical example is illustrated in Fig. 3, which shows the activities (disintegration rates) in becquerels for the mother and the daughter nuclides and their activity ratios for the generator system $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$, which is an example of secular equilibrium. Here, $T_{1/2}(^{137}\text{Cs}) = 30 \text{ a}$ and $T_{1/2}(^{137\text{m}}\text{Ba}) = 2.55 \text{ min}$, giving a half-life ratio of $T_{1/2}(^{137}\text{Cs})/T_{1/2}(^{137\text{m}}\text{Ba}) = 6.18 \times 10^6$.

In the equilibrium mixture, the daughter appears to decay with the half-life of the parent. When the daughter is isolated from the mixture, it has its own expected half-life. Perhaps the simplest explanation for their appearing to be equal is that the daughter cannot decay until it is formed, and so the rate of formation of the daughter equals the rate of decay of the parent, which is very slow.

Thus, in secular equilibrium, mixture activity of the mother stays approximately constant while the daughter activity grows to a constant value. Correspondingly, their ratio (mother/daughter) decreases in the beginning and



**Instantaneous
elution
of daughter**

FIG. 2. Illustration of growth of daughter activity with subsequent 'instantaneous' elutions at equal time intervals in a generator system under secular equilibrium.

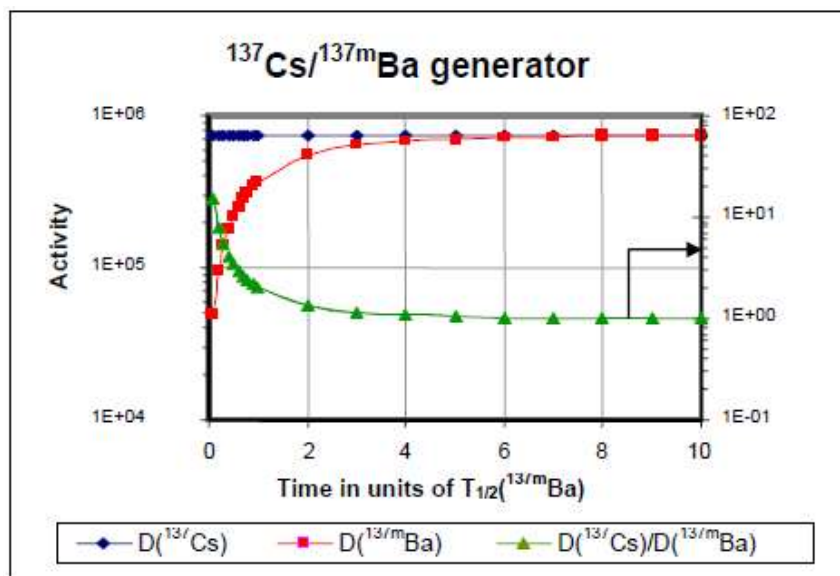


FIG. 3. Activity of mother (^{137}Cs) and daughter ($^{137\text{m}}\text{Ba}$) and ratio of their activities (right axis) for a $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$ generator where the initial number of ^{137}Cs radionuclei has been set to $N_1 = 10^{15}$.

approximates a constant value after a time $t > 10T_{1/2,2}$. Often, one says that for secular equilibrium, Eq. (6) may be simplified to:

$$N_2 \approx \frac{\lambda_1}{\lambda_2 - \lambda_1} \cdot N_1^0 \cdot e^{-\lambda_1 t} \quad (12)$$

since $T_{1/2,1} \gg T_{1/2,2} \Rightarrow \lambda_1 \ll \lambda_2 \Rightarrow \exp(-\lambda_1 t) \gg \exp(-\lambda_2 t)$ so that the last exponential can be neglected. This leads again to:

$$\frac{N_1}{N_2} \approx \frac{\lambda_2 - \lambda_1}{\lambda_1} \quad (13)$$

and

$$\frac{D_1(t)}{D_2(t)} \approx \frac{\lambda_2 - \lambda_1}{\lambda_2} \quad (14)$$

This expression is only strictly valid for $t > 10T_{1/2,2}$. For $t \gg 10T_{1/2,2}$ and $T_{1/2,1} \gg T_{1/2,2}$, λ_1 in Eq. (14) can be omitted, and the ratio of the disintegration rates is ~ 1 .

2.2.2. Transient equilibrium

If $T_{1/2,1} \geq T_{1/2,2}$, i.e. the half-life of the mother is not several orders of magnitude larger than the half-life of the daughter and, in addition, the mother decays considerably during the period of application, then transient equilibrium is established. This situation is illustrated generally in Fig. 4.

In order to exemplify transient equilibrium, the mother/daughter relationship $^{72}\text{Se}/^{72}\text{As}$ is chosen.

Figure 5 illustrates the activities in becquerel for the mother (D_1) and the daughter (D_2) nuclides and their activity ratios. Here, $T_{1/2}(^{72}\text{Se}) = 8.5 \text{ d}$ and $T_{1/2}(^{72}\text{As}) = 26.0 \text{ h}$, giving a half-life ratio of $T_{1/2}(^{72}\text{Se})/T_{1/2}(^{72}\text{As}) = 7.85$.

There is a rule of thumb regarding how long it takes to reach equilibrium:

- Transient equilibrium is reached in $\sim 4T_{1/2,2}$;
- Secular equilibrium is reached in $\sim 6T_{1/2,2}$.

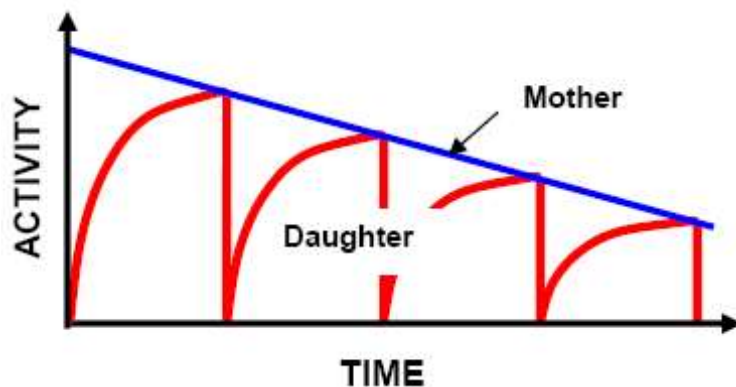


FIG. 4. Illustration of growth of daughter activity with subsequent 'instantaneous' elutions at equal time intervals in a generator system under transient equilibrium.

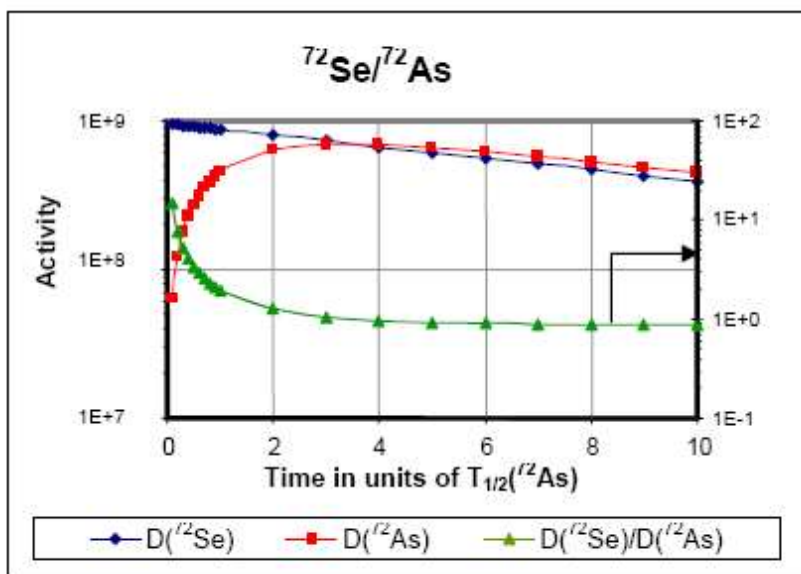


FIG. 5. Activity of mother (^{72}Se) and daughter (^{72}As) and the ratio of their activities for a $^{72}\text{Se}/^{72}\text{As}$ generator where the initial number of ^{72}Se radionuclei has been set to $N_1 = 10^{15}$.

The activity of the daughter radionuclide obtained per elution cycle (batch) is the main parameter for the application of a generator system. The activity of the daughter radionuclide generated at a given time can be calculated using the above

equations. However, the useful amount of activity for a radiotracer experiment also depends on the elution efficiency of the generator as well as the chemical yield in the labelling process, as will be illustrated later.

It should also be mentioned here that in real applications, interest is focused mainly on the gamma decay rate of a certain gamma energy than on the total disintegration rate of the daughter radionuclide. The gamma intensity (or gamma yield) can be found in decay schemes for the individual radionuclides, for instance, in the 'Table of Isotopes' [4] for the different gamma energies.

Such intensities for single gamma lines of special interest following beta decay range between 50 and 100%. For β^+ decay, the intensity can reach 200% for the 511 keV annihilation radiation, here defined by the β^+ branching ratio. It is now possible to define a gamma activity, A_γ , for a special gamma line. The shape of the gamma activity line is identical to the shape of the daughter activity in Figs 2 and 4, and is derived by multiplying these activities by the proper gamma intensity.

2.3. RADIONUCLIDE GENERATOR PRINCIPLE

A radionuclide generator is a self-contained system housing a mother/daughter mixture in equilibrium and designed to produce a daughter radionuclide formed by the decay of a mother radionuclide free from contamination of the mother [5–7]. The mother/daughter nuclear relationships offer the possibility to make radionuclide generators to separate the short lived daughter at suitable time intervals. For practical reasons, most radionuclide generator systems that can be used for industrial radiotracer applications involve secular equilibrium, where the parent radionuclide has a half-life significantly longer than that of the daughter. This scenario permits long shelf life of the generator.

There must be a method of removing the daughter and leaving the mother behind to regenerate more daughter activity. The daughter radionuclide is a different chemical element to the mother, and will therefore exhibit chemical and physical properties different from those of the mother. With this difference in characteristics between mother and daughter radionuclides, the latter can usually be separated by chemical or physical means. It is said that the daughter is *eluted* from the generator (a radionuclide generator is also commonly called a 'cow' and the elution process 'milking of the cow'). Once the activity of the daughter is recovered, there is a growth of the daughter activity on the generator until it again reaches equilibrium with the mother. This separation and growth can be continued as long as there are useful amounts of the parent radionuclide available, and the breakthrough of the mother stays within acceptable limits.

Thus, the useful shelf life of a radionuclide generator depends mainly on the half-life of the mother and on the radiation resistance of the generator constituents. Separation may be performed before equilibrium is reached, and the amount of daughter activity recovered will depend on the time elapsed since the last separation. In most cases, the generator can be eluted after 1–2 half-lives of the daughter; 50–75% of the equilibrium activity has then been generated.

2.3.1. Properties of an ideal IRNG

An ideal IRNG should possess the following properties [8, 9]:

- The chemical and/or physical properties of the daughter must be different from those of the mother to permit efficient separation of daughter from mother.
- The separation of the daughter radionuclide should be easy and efficient using appropriate chemical or physical techniques.
- The daughter radionuclide separation should involve no violent chemical reactions.
- Human intervention in generator operation should be minimal to minimize radiation dose.
- The daughter radionuclide to be used as a tag on tracers for radiotracer investigations should be short lived and gamma emitting.
- In any case, a gamma emitter with a high gamma branching ratio is desirable.
- The elution yield and purity of the daughter radionuclide should be within the acceptable range.
- The physical half-life of the parent should be long enough for extending the shelf life of the generator.
- The generator constituents (i.e. eventual column packing material, liquids involved, tubings and fittings) should be radiation resistant.
- The daughter chemistry should be amenable to the preparation of a wide variety of compounds for radiotracer applications (such as water tracing, oil tracing, particle tracing, etc.).
- Shielding, handling and transportation of the generator, even across national borders, should be straightforward.
- The granddaughter should be stable (or very long lived) to limit concern about site contamination, environmental persistence and waste disposal issues.

2.3.2. Additional specific criteria for an IRNG

Although many parent/daughter pairs have been evaluated as radionuclide generator systems in a clinical context, only a few generators are suitable for routine industrial and research use. While selecting parent/daughter pairs, the following criteria need to be satisfied [8, 9]:

- *Half-life of the mother radionuclide:* It is important to select a generator with an appropriately long half-life of the mother radionuclide. A generator that remains useful for a period of several months to a year or more may be appropriate for industrial applications. In some cases, it should be possible to install the generator ‘permanently’, for instance, to monitor the operations of a multiphase separator over time.
- *Half-life of the daughter radionuclide:* The daughter radionuclide should have a half-life that is compatible with the duration of the radiotracer study. Half-lives in the range of several minutes to several hours or more are useful for most fluid and particle industrial tracing operations. For cases involving tracing of gas transport, transit times of the order of seconds may be expected, and radiotracers with half-lives of the order of minutes are most useful. However, the present document has no special focus on gas monitoring.
- *Type and energy of radiation of daughter radionuclide:* Gamma ray emitting radionuclides are preferred for most industrial applications because of the ability of gamma radiation to penetrate the wall of a vessel or pipeline. For some investigations, a simple gamma ray spectrum (containing one single photo peak) is desirable (for instance, in simple residence time distribution (RTD) experiments, flow rate monitoring, etc.). In other types of investigation, two or more gamma rays with a certain energy difference are desirable (when depth information, for instance, from a chemical reaction vessel, is required).
- *Availability and cost of mother radionuclide:* An ideal situation would be if the selected radionuclide generators (see later) were commercially available. However, in most cases, they are not at the present time, and will probably not be (in industrially suitable versions) for the foreseeable future since the global market probably is too small. The minimum requirement is then that the mother radionuclides should be readily producible in reactors or cyclotrons at reasonable costs.

In line with the criteria cited in paragraphs 2.3.1 and 2.3.2, some nuclear genetic relationships have been found to be suitable for production of IRTGs. Some potential generators are listed and specified in Table 1.

TABLE 1. POTENTIAL RADIONUCLIDE GENERATORS FOR INDUSTRIAL RADIOTRACER APPLICATIONS

Radionuclide generator	Mother nuclides			Daughter nuclides			Applications ^a	
	Production	Half-life	Decay mode	Main E_{γ} (keV)	Half-life	Decay mode		
⁴⁴ Ti/ ⁴⁴ Sc	⁴⁵ Sc(p,2n) ⁴⁴ Ti	60 a	EC	67 (94.4%), 78 (96.0%)	3.93 h	β^+	511 (188.7%), 1157 (99.9%)	①–⑨
⁶⁸ Ge/ ⁶⁸ Ga	⁶⁹ Ga(p,2n) ⁶⁸ Ge	270 d	EC	No γ	1.135 h	β^+	511 (178.3%), 1077 (3.2%)	①–⑦, ⑨
⁸² Sr/ ⁸² Rb	Mo(p,spall.) ⁸⁵ Rb(p4n) ⁸² Sr	25.6 d	EC	No γ	1.273 min	β^+	511 (190.9%), 776 (15.1%)	①–⑦, ⑨
⁹⁹ Mo/ ^{99m} Tc	Fission product	60 h	β^-	740	6.00 h	γ	141 (89.4%)	①–⑤, ⑨
¹¹³ Sn/ ^{113m} In	¹¹² Sn(n, γ) ¹¹³ Sn	115 d	EC	No γ	1.65 h	γ	392 (64.1%)	①–⑤, ⑨
¹³⁷ Cs/ ^{137m} Ba	Fission product	30.0 a	β^-	No γ	2.55 min	γ	661 (90.1%)	①–⑤, ⑨
¹⁴⁴ Ce/ ¹⁴⁴ Pr	Fission product	285 d	β^-	133	17.3 min	γ	696 (1.34%)	①–⑤, ⑨
¹⁷² Hf/ ¹⁷² Lu	¹⁷³ Ta(p,2n) ¹⁷² Hf	1.87 a	EC	24, 125	6.7 d	γ	1093 (63.0%)	①–⑤, ⑨

Note: Intensities taken from Nuclear Data Evaluation Research, Japan Atomic Energy Agency Group, <http://www.ndc.jaea.go.jp/NuC/index.html>, modified on 2011/05/09.

^a ① Flow rate measurement, ② residence time distribution measurement, ③ leak detection and location, ④ mixing study, ⑤ mass balance, ⑥ positron emission tomography, ⑦ single particle tracing, ⑧ sediment transport study, ⑨ nuclear science education.

After further evaluation of the existing and potential generators and the anticipated demands for industrial investigations, it was decided to put most emphasis on the following three radionuclide generators: $^{68}\text{Ge}/^{68}\text{Ga}$, $^{113}\text{Sn}/^{113\text{m}}\text{In}$ and $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$. In addition, some attention has been paid to $^{44}\text{Ti}/^{44}\text{Sc}$, $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$, $^{144}\text{Ce}/^{144}\text{Pr}$ and $^{172}\text{Hf}/^{172}\text{Lu}$.

In recent decades, the majority of developments of radionuclide generators has been mainly driven by the need for new short lived radiopharmaceuticals, both for diagnostics and therapy in nuclear medicine. The methods and techniques developed are, of course, tailor-made for the physical, microbiological and chemical system of the human body. Thus, the technology developed on generator design, chemical form of the eluted radionuclides and the tracer molecules derived from these radionuclides cannot necessarily be applied for other purposes.

In the paragraphs below, a survey of different radionuclide generator types are given.

2.4. RADIONUCLIDE GENERATOR TYPES

A radionuclide generator makes available a daughter radionuclide produced from the decay of a parent radionuclide. The goal is to acquire the daughter radionuclide from the parent with a sufficiently large decontamination factor $\text{DF} = N_{\text{M}}/N_{\text{D}}$, where N_{M} and N_{D} are the number of atoms of the mother and the daughter, respectively, in the purified daughter radionuclide fraction. In general, the DF should be in the range 10^{-5} to 10^{-7} . There are technical and environmental arguments for these numbers: with regard to the quality of most industrial investigations, a DF of $\approx 10^{-5}$ can be readily accepted.

Environmental considerations may require lower limits of mother breakthrough. The required decontamination factor may depend on the nature of the mother radionuclide. If the mother is not very long lived and decays exclusively by electron capture, a decontamination factor in the lower end may be acceptable.

In principle, a radionuclide generator system designed for use in industrial radiotracer applications should be simple, give reproducible mother/daughter separation results and provide a high yield of the daughter radionuclide.

There are various radionuclide generator principles. Some of them are listed below:

- Mother fixed on solid support in column (ion exchanger/reversed phase), elution of daughter by simple aqueous solution (salinity, pH).

- Mother on solid support in column, elution by aqueous phase with complexing agent (plus salinity and pH), to ease removal of daughter radionuclide, possibly extractable into organic solution.
- Mother on solid support in column, elution by organic solution, possibly with complexing agent to convert daughter directly into a complex extractable into organic solution.
- Mother on solid support in column, elution by cold, hot or wet air (gas) to produce the daughter as a gas tracer.
- Mother on solid support in column, elution by hot air (gas) to volatilize the daughter, which may be converted by chemistry to aqueous, organic or solid tracer.
- Mother dissolved in liquid (organic), separation of daughter by liquid-liquid extraction, whereupon the daughter may be converted to various types of tracers.
- Mother as a gas and the daughter, which may have a much lower vapour pressure, precipitating on container walls. Mother and daughter are then separated by cryopumping followed by conversion of daughter to various tracer types.
- Mother dissolved in aqueous solution. Separation of the daughter is achieved by selective precipitation with carrier.
- Mother dissolved in aqueous solution. Separation of the daughter is carried out by electrodeposition.
- Mother dissolved in aqueous solution. Separation of the daughter performed by electrolysis.
- The supported liquid membrane (SLM) generator where the mother is dissolved in an aqueous solution and separation of mother and daughter takes place over a passive extracting membrane between the mother radionuclide reservoir and an extraction liquid reservoir.
- Generator involving a gaseous component in the decay chain where separation is achieved by electrostatic attraction on a cathode in the gas phase.
- Generators not based on a mother/daughter relationship, but on use of a small isotropic neutron source for production of short lived radionuclides by neutron irradiation, separation of reaction products by chemical or physical methods.

Some of these principles are briefly described below.

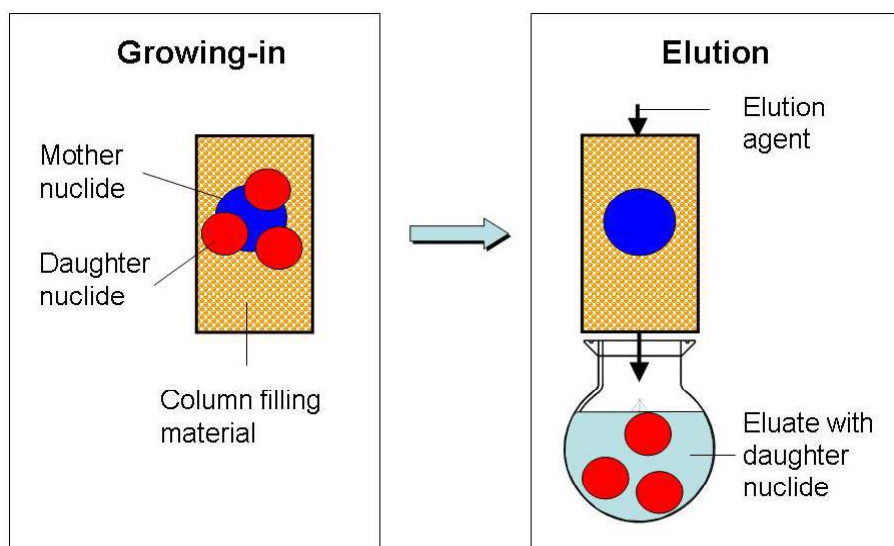


FIG. 6. Principle of a column based radionuclide generator.

2.4.1. Generators based on mother fixed on to solid support in columns

The most common radionuclide generators are based on sorption of the mother radionuclide on a column support material with subsequent and selective elution of the daughter radionuclide from the column with some elution agent (Fig. 6) while the mother remains on the column support. This category includes those mentioned above. Both organic and inorganic supports are used. The most common organic supports are cation and anion exchanger materials based on styrene-divinylbenzene co-polymer with ionogenic groups such as $-\text{SO}_3\text{H}$ and $-\text{N}(\text{CH}_3)_3\text{Cl}$, respectively.

Here, the H^+ and Cl^- are exchangeable with other cations and anions, respectively. Inorganic materials are most often stable (or even refractory) metal oxides like Al_2O_3 , TiO_2 , MnO_2 , ZnO , SnO , SnO_2 , etc., but other types of material are used as well.

For high activity generators, which are intended for a long shelf life (say >100 d), it is important that radiation damage on the support material by radiolysis is kept at a minimum. In these cases, inorganic material is preferred whenever possible.

When performing parent/daughter separation, there are many aspects that must be considered: separation scheme, column type, column dimension, chemical nature of the mobile phase, species of interest, sample throughput and

reagent usage for elution of daughter radionuclide [9]. This technique offers the following advantages:

- *Selectivity*: Separation selectivity is ensured by the selection of a suitable separation scheme.
- *Sensitivity*: High sensitivities down to the picomol range could be achieved, which is extremely important in using carrier free mother radionuclide.
- *Speed of separation*: The time necessary to perform the separation becomes an increasingly important aspect because of the short half-life of the daughter radionuclide.
- *Operational simplicity*: A major advantage of this technique in contrast to other techniques is its technical simplicity that not only reduces the radiation exposure to the operating personal, but also precludes the site contamination in an operational set-up.
- *Stability of the separator columns*: The stability of separator columns very much depends on the chemical nature of the packing material being used and the radiation characteristics of the mother and daughter radionuclides (alpha and high energy beta decay is more detrimental than EC decay). The shelf life also depends on the storage conditions (if possible, long time storage of the generator should be carried out with the column in a dried-out form in order to reduce degradation due to radiolysis of the liquid with formation of very reactive radicals).
- *Frequent elution repeatability*: The system can be operated repeatedly during the shelf life of the generator, and the operations can readily be made automatic if required.
- *Product reproducibility*: Product reproducibility can be excellent, provided that measures are taken to ensure standardization in the elution procedure and high radiation stability of the column material.
- *Elution performance*: This system provides unmatched performance in terms of yield and ensures high chemical and radiochemical purity of the daughter radionuclide.

Normally, elution liquids contain no carrier of the daughter radionuclide. Thus, the daughter radionuclide product will be of high specific activity and is referred to as 'carrier free'. In some cases, the elution and the following chemistry may be eased by addition of a certain amount of stable elemental carrier. Generators of this type are small in size and simple to build, and the daughter radionuclide is available by a simple elution process. A schematic diagram of a column chromatography generator system appropriate for industrial radiotracer applications is shown in Fig. 7.

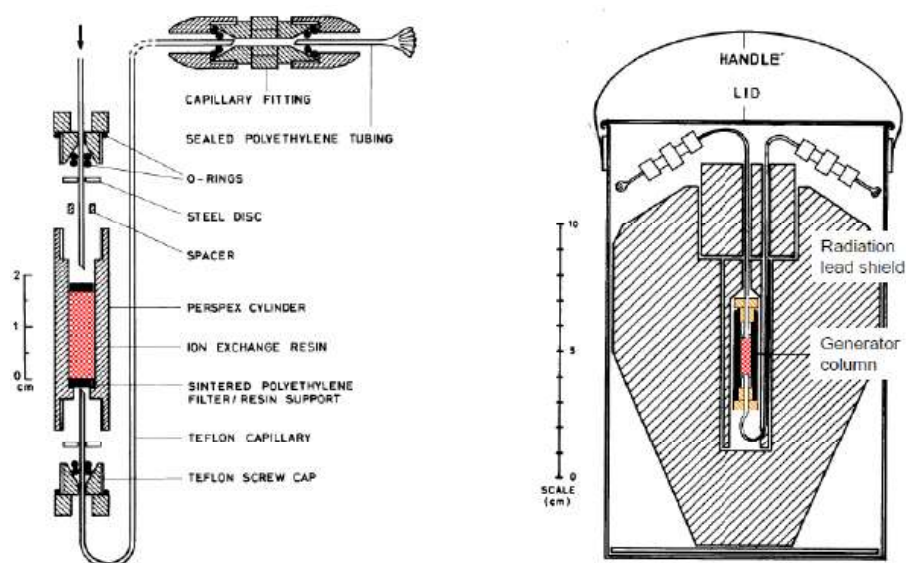


FIG 7. Schematic diagram of a column based radionuclide generator with a small column system to the left and the column placed in a lead shield to the right [10].

Other column based methods, where the column itself constitutes the generator or where the column separation plays a major role in separating mother and daughter, may, in principle, also include extraction chromatography, partition chromatography, adsorption chromatography and gel permeation chromatography in various forms.

Novel extraction chromatographic resins exhibiting enhanced parent metal ion retention capacity, excellent selectivity, improved radiation and chemical stability offer promise in the development of radionuclide generators [11]. Although extraction chromatography has been shown to provide a means of performing a number of separations of potential use in radionuclide generator systems, the application of the technique to generator development has thus far been limited.

For partition and adsorption chromatography, many of the same arguments may be applied.

Low capacity, limited radiation stability, long term instability of the column under harsh industrial conditions and bleeding organic impurities under repeated elution are among the factors that inhibit its wide scale applicability for the preparation of IRNGs.

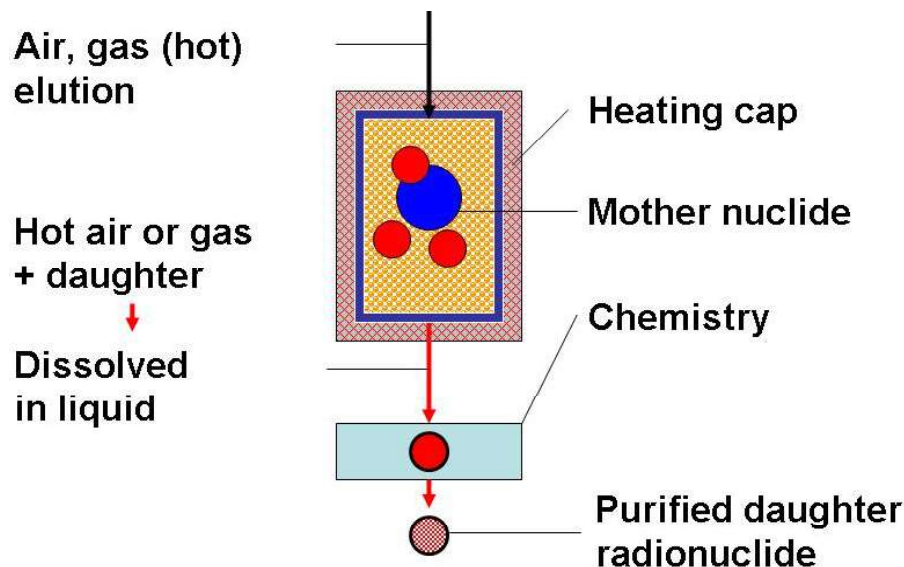


FIG 8. Principle of a column based radionuclide generator with a high temperature heating cap [8].

Gel permeation chromatography has already, to some extent, been developed for generator production of radionuclides [12, 13], but is not considered further in the present publication.

2.4.2. Column based generator with a heating cap

A variation of the generator type described above is the case where the daughter product is not a gas, but may still be evaporated from the column at elevated temperatures (up to $>1000^{\circ}\text{C}$). The requirement is that the daughter element has a considerably higher vapour pressure than the mother element in the form in which it is bound to the column material. This kind of separation principle has been developed for laboratory studies but, to our knowledge, has not yet been implemented in radionuclide generators. One example may be the generator $^{128}\text{Ba}/^{128}\text{Cs}$ where the mother nuclide is fixed in a ceramic column packing material as BaO , and Cs is removed by evaporation at $T > 1000^{\circ}\text{C}$. The principle is sketched in Fig. 8.

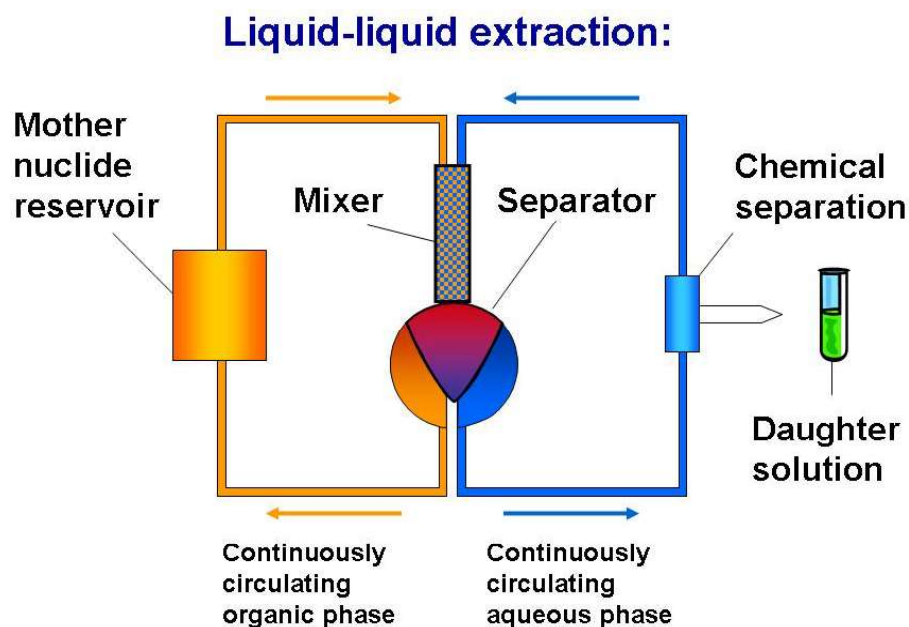


FIG 9. Illustration of a solvent extraction generator with continuously flowing organic and aqueous phases [10].

2.4.3. Radionuclide generators based on separation by solvent extraction

Solvent extraction is a technique in which an organic solvent, with or without an extractant, is used to separate the daughter radionuclide from its mother [14].

The method is based on the relative solubility of the mother and the daughter radioelements in two immiscible liquids, usually water and an organic solvent. After agitation for a sufficient length of time, the layers are allowed to separate. If the aqueous phase originally contains the mother, the organic liquid, now containing the daughter radionuclide, is removed, and the aqueous layer containing the mother radionuclide is kept for subsequent daughter recovery.

It is also possible for the mother radionuclide to be dissolved in the organic phase. In this case, the daughter would be stripped into the aqueous phase for further processing. The principle of the process is illustrated in Fig. 9 for a generator that is based on continuously flowing liquids and on-line phase separation (either by mixer settlers or by continuously operating centrifuges).

In order to optimize separation, complexing agents may be added to the aqueous phase and extraction agents to the organic phase, and, most often, pH, ion strength and temperature are important parameters to consider. The separation

of mother and daughter is governed by their respective distribution ratios in the selected organic–aqueous system. The distribution ratio D for a chemical species is defined as:

$$D_M = \frac{(C_M)_{\text{org}}}{(C_M)_{\text{aq}}} \quad \text{and} \quad D_D = \frac{(C_D)_{\text{org}}}{(C_D)_{\text{aq}}} \quad (15)$$

where C_M and C_D are, respectively, the concentrations of the mother and the daughter radionuclides (expressed by their activities corrected for decay and gamma branching ratios), in the organic (org) and aqueous (aq) phases.

In the case where the mother radionuclide is dissolved in the aqueous phase, a good separation is achieved in one separation step if, for instance, $D_D > 100$ and $D_M < 0.01$. If the mother nuclide reservoir consists of the organic phase, a good separation is obtained in one separation step if $D_M > 100$ and $D_D < 0.01$.

An example of the first situation is the separation of ^{144}Pr from ^{144}Ce (the $^{144}\text{Ce}/^{144}\text{Pr}$ generator) where ^{144}Ce is dissolved in the aqueous phase. This can be achieved by extraction of $^{144}\text{Ce}^{4+}$ with, for instance, diethylhexyl orthophosphoric acid (HDEHP) dissolved in an organic (kerosene) solvent from an aqueous and weak acidic (HNO_3) solution. The $^{144}\text{Pr}^{3+}$ will remain in the aqueous phase.

A variation of the extraction method is illustrated in Fig. 10. In this example, the mother radionuclide is dissolved in an aqueous solution that is slightly acidified in order to avoid hydroxide formation of metal cations. After growing-in of the daughter to an acceptable level, the aqueous solution is percolated through a column where the column support has been impregnated with an organic phase containing an appropriate extracting agent for the daughter. In this process, the daughter nuclides will be sorbed in a narrow band near the top of the column, together with traces of the mother nuclide. The exit solution from the column containing the mother is pumped back to the mother nuclide reservoir.

In order to purify the daughter fraction, there are two alternative routes to follow:

- (i) An elution liquid is applied that effectively removes (strips) any remaining mother activity from the column, leaving pure daughter activity in a somewhat broadened distribution on the column. The daughter is then removed from the column and dissolved into an aqueous phase by stripping with (often) more acidic solution.

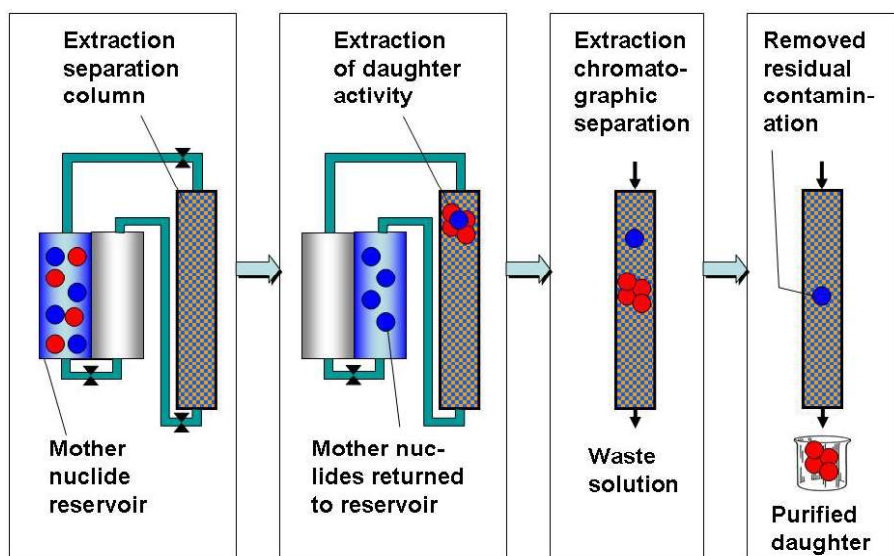


FIG. 10. Illustration of a generator where the mother nuclide is in an aqueous phase and the mother/daughter separation is achieved by percolating the aqueous fluid through an extraction chromatography column [8].

- (ii) A specially engineered elution liquid is applied for the chromatographic separation of the daughter and its mother contaminant as the fluid moves through the column at moderate speed. Under these conditions, the mother and daughter have different affinities to the column material. Owing to this difference, the mother and daughter will move with different speeds down the column, and exit at the end in different chromatographic bands. This procedure is illustrated in Fig. 10.

Novel extraction chromatographic resins exhibiting enhanced parent metal ion retention capacity, excellent selectivity, improved radiation and chemical stability offer promise in the development of radionuclide generators [15].

Another version of the solvent extraction method is represented by Ref. [16]. Here, a small static extractor is constructed for extraction of $^{99m}\text{TcO}_4^-$ with methyl-ethyl-ketone (MEK) from an aqueous solution of $^{99}\text{MoO}_4^{2-}$ with an efficiency of >80% after three extraction cycles.

An example of a generator where the daughter is extracted into the organic phase while the mother remains in the aqueous phase is the $^{99}\text{Mo}/^{99m}\text{Tc}$ generator based on extraction by MEK. An alkaline solution of $^{99}\text{MoO}_4^{2-}$ is extracted with highly purified MEK. The daughter nuclide in the form of $^{99m}\text{TcO}_4^-$ is extracted

into the MEK solution, while the molybdate remains in the basic aqueous solution. The MEK phase will then be isolated, washed and finally evaporated to dryness. The ^{99m}Tc compound is redissolved in an isotonic saline solution for preparation of radiopharmaceuticals by off-line labelling procedures. This procedure makes use of low specific activity ^{99}Mo and produces ^{99m}Tc at high purity and high radioactivity concentration [12, 17–19].

Advantages of the solvent extraction process are as follows:

- Offers selective separation due to the use of a specific extracting reagent mixture designed for the purpose.
- A high separation (or decontamination) factor is achievable.
- Quick separation process.
- High capacity: low specific activity mother can be used, for instance, by addition of carrier, both for the mother and the daughter to ease the separation process.
- Low running costs: the costs of the chemicals involved are low.
- Regeneration and recharging are possible.
- The process is scalable (volumes and activity) to a certain degree as per the need (see below).

Disadvantages of the solvent extraction process are as follows:

- There may be a limit to the activity concentration due to radiolytic reactions in the solvent chemicals that may, over time, degrade the solvent itself and change the chemical state of both mother and daughter nuclides and thus interfere with the separation process.
- Operation of this system requires highly skilled and trained personnel.
- Considerable volumes of organic extractants may be required to achieve satisfactory performance, dependent on the design of the generator.
- Thus, the operation of the solvent extraction generator may be complicated and cumbersome.
- There is also a potential for cross-contamination of the aqueous stream with the organic solution mainly due to formation of (relatively stable) micro-emulsions.
- The handling of considerable volumes of organic reagents may pose possible fire or explosion hazards. This can be counteracted by selecting solvents with low vapour pressure.

The technical difficulties make this procedure less desirable than the standard chromatographic generator system, and this system is not widely used.

Generators based on the solvent extraction technique are generally not the first choice for the preparation of an IRNG.

2.4.4. Generators based on separation by distillation or sublimation

In this method, the mother/daughter equilibrium mixture is chemically treated to form a compound in which the daughter radionuclide will have lower boiling points, whereas the parent is non-volatile.

There are two versions:

- (i) The distillation method, which operates with the mother solution in a liquid solvent under moderate temperatures ($<150^{\circ}\text{C}$);
- (ii) The sublimation method, which operates under reduced pressure (vacuum), either with solid mother nuclide matrices or melts at elevated temperatures ($>150^{\circ}\text{C}$).

For both versions, on heating the mixture, the vapour will be richer in the daughter radionuclide that is distilled out of the mother solution. The process is illustrated in Fig. 11.

In order to facilitate the separation, a chemical compound may be mixed into the mother solution for version (i) and led over the solid matrix or melt in the form of a gas for version (ii). These components react with the daughter radionuclide and make it more volatile. The evaporate then condenses as a purified compound on a cooled surface, for instance, a cold finger, leaving the non-volatile parent radionuclide behind. Once heating ceases (and the vacuum is removed for version (ii)), the purified compound may be collected from the cooling zone, either by removing the cold finger or, as illustrated in Fig. 11, by directing a dissolving liquid into the apparatus and collecting the solution containing the daughter nuclide in a separate vessel. The distillation or sublimation processes are relatively fast, permitting the use of a low specific activity mother, and generating a daughter radionuclide of high purity. However, the success of these methods depends upon the possibility of forming a volatile daughter product compound with sufficient vapour pressure difference with respect to the mother nuclide. The necessary equipment is relatively bulky, partly fragile and requires careful operation. Automated versions suitable for operation under harsh industrial conditions have yet to be developed.

An example of this methodology is one version of the $^{99\text{m}}\text{Tc}$ generator that uses the difference in volatilities of the oxides of molybdenum and technetium to achieve a separation. Reactor produced ^{99}Mo is placed in a tube furnace and oxygen is passed over the heated, finely powdered metal. Technetium forms the

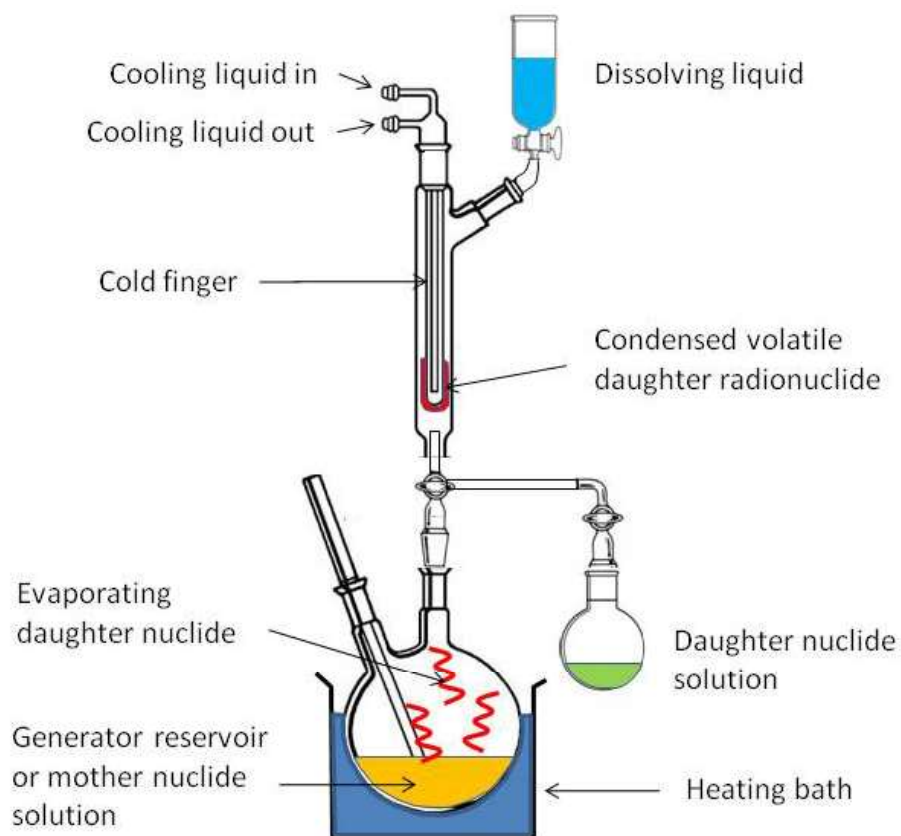


FIG. 11. Radionuclide generator based on sublimation (or distillation) of the volatile daughter radionuclide or a compound of the radionuclide from a mother radionuclide matrix.

oxide species Tc_2O_7 , which becomes volatile at temperatures of 550°C , while molybdenum oxides have a much higher sublimation temperature of above 1000°C . The sublimated $^{99\text{m}}\text{Tc}_2\text{O}_7$ can be trapped by cooling followed by dissolution in an aqueous solution [20, 21]. Figure 12 sketches the principle of such a generator, adapted from Ref. [21].

2.4.5. Generators based on cryogenic distillation

Cryogenic separation of a gaseous daughter radionuclide from the mother radionuclide represents an effective strategy to providing an efficient separation with a high purity of the daughter product. It represents the selective removal either of the daughter radionuclide in the gaseous form from the non-volatile

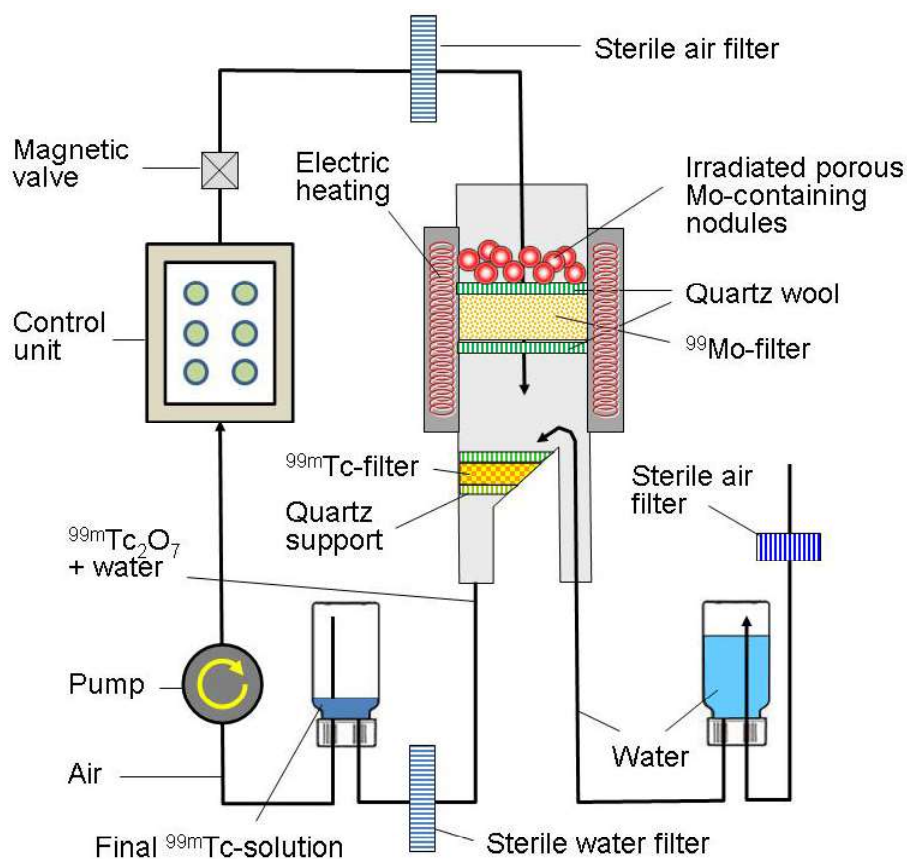


FIG. 12. Concept of the sublimation generator SICCATEC, where ^{99m}Tc is separated as $^{99m}\text{Tc}_2\text{O}_7$ from the irradiated porous $\text{MoO}_3\text{-V}_2\text{O}_5\text{-SiC}$ target material in a flow of air, caught in the alumina based Tc filter and subsequently redissolved in distilled water or a slightly saline solution [21].

mother or the removal of the gaseous mother radionuclide from the non-volatile daughter by connecting a closed chamber of the mother/daughter mixture to a cold chamber where either the volatile daughter or the volatile mother is solidified, leaving the other component in the original mixture chamber.

An effective cryogenic separation depends on a low vapour pressure for one of the components and a high vapour pressure for the other component at room (or moderately elevated) temperature. Figure 13 illustrates the principle of a cryogenic distillation.

An example of this type of generator is the $^{122}\text{Xe}/^{122}\text{I}$ mother/daughter relationship where the volatile mother ^{122}Xe is cryopumped away from the original mixture, leaving the less volatile ^{122}I behind. Cryogenic pumping is a low

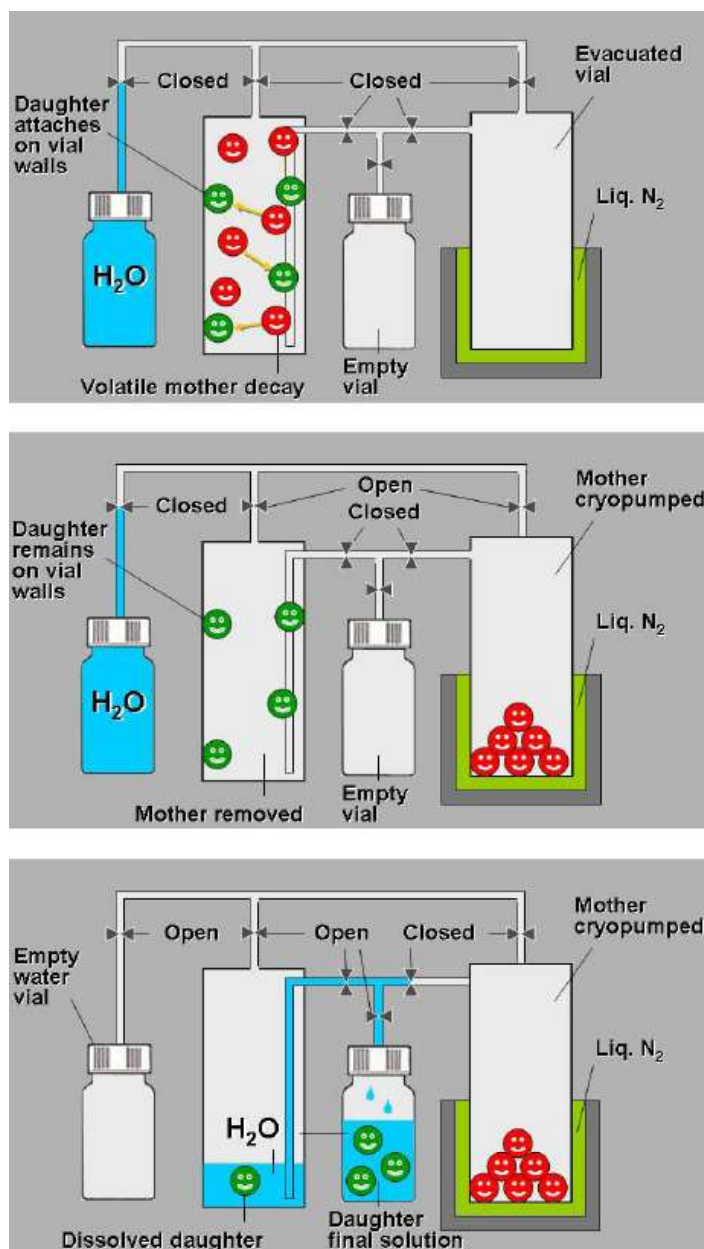


FIG. 13. Schematic illustration of various steps in operation of a cryogenic distillation generator, from top to bottom.

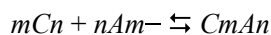
temperature physical approach to separation, in which the mother or daughter radionuclide is isolated directly by phase change.

The main advantage of cryogenic separation is that both a large quantity and a high purity of the daughter radionuclide are achievable. The yield of this separation is generally >90%.

A major disadvantage of cryogenic separation is the amount of energy required to provide the refrigeration necessary for the process, particularly for dilute gas streams. The cooling may be performed with liquid N₂, but at remote locations, electrically cooling equipment may be required. Cryogenic separation requires the use of significant amounts of process equipment at considerable capital cost. It is technically difficult to make a lightweight portable version.

2.4.6. Generators based on chemical precipitation

The relative solubility of the mother and daughter metal ion in a chemical environment can be exploited for the selective separation of the daughter radionuclide from the mother. When solubility of the mother and the daughter metal salts are very different, they can be separated by precipitation. The component that exhibits the lowest solubility will be precipitated first. One converts the component into an insoluble form or by changing the ionic composition of the solution or by adjusting pH and temperature, for instance. Under certain defined conditions, the solubility of every salt is governed by the solubility product K_{sp} . For a chemical reaction of the form:



the stoichiometric solubility product of the compound $CmAn$ is expressed by:

$$K_{sp} = [C]^m \cdot [A]^n \quad (16)$$

If the actual ionic concentrations are so large that their product according to Eq. (16) exceeds K_{sp} for the particular compound, one has reached the required conditions for precipitation. In a stringent treatment of this subject area, one should, in fact, use the thermodynamic solubility product instead, where the concentrations C and A are exchanged with the expressions $a_C \cdot \gamma_C$ and $a_A \cdot \gamma_A$, respectively, where a is the ionic activity and γ is the activity coefficient. Hence, the condition for precipitation is defined by Eq. (17), where SR is the saturation index:

$$SR = \frac{[C]^m \cdot [A]^n}{K_{sp}} \geq 1 \quad (17)$$

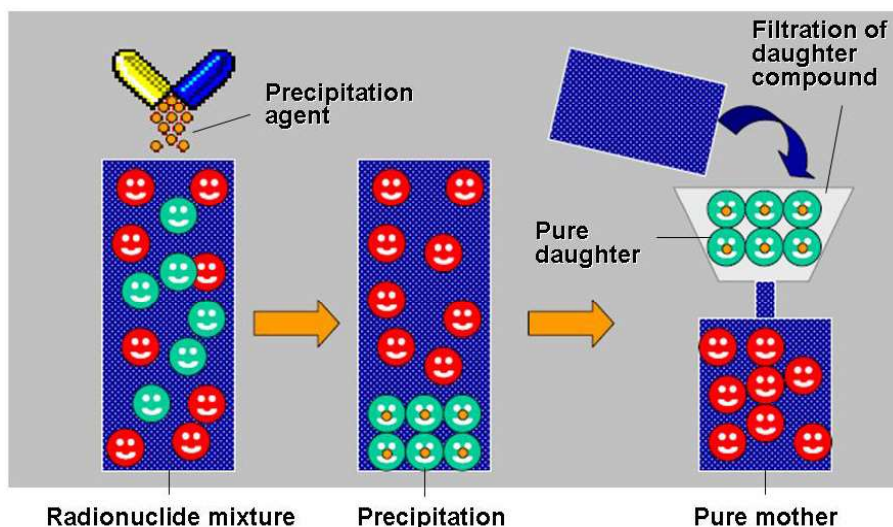


FIG. 14. Schematic illustration of a chemical precipitation system with precipitation of the daughter nuclide.

The practical implementation of the process involves adding a specific precipitating reagent containing the counter ion of the ionic compound of interest to the mother/daughter equilibrium mixture to precipitate either the mother or the daughter ions or ionic compounds.

In order to achieve a high chemical yield and an acceptable decontamination factor for the purified daughter product, carrier substances may be added for both the mother and daughter nuclides. Most often, a large excess of the added precipitation agent is used. This reduces the need for a high carrier concentration. Thus, a higher specific activity can be achieved.

Such precipitation methods can be systematically developed by sequencing of pH, adjusting the added portions of precipitating agents, and selecting the optimum temperature time period for quantitative precipitation. A schematic illustration of a chemical precipitation system is depicted in Fig. 14.

Advantages of the precipitation process are as follows:

- Convenient, simple process that provides the only practical method of separation in some cases;
- Can be highly selective and virtually quantitative (depending on a low K_{sp} value);
- High degree of decontamination is possible (depending on the relative values of $K_{sp, \text{daughter}}$ and $K_{sp, \text{mother}}$);

- Provides a large range of scale, both with respect to amounts treated and to the number of chemical elements for which the method is applicable;
- Not energy or resource intensive compared with other techniques (e.g. solvent extraction).

Disadvantages of the precipitation process are as follows:

- This system is applicable to those cases where there is a significant difference in solubility product of the actual compound of the mother and daughter radionuclide.
- It is sensitive to many chemical parameters such as concentration of the reactants, order of mixing, reaction temperature, etc., and any deviation from the standard operating procedure may result in failure.
- The multistep separation process to digest, filter or wash the precipitate may be time consuming and labour intensive.
- The precipitation often has to be complemented by some other separation method to purify the daughter product.
- It is hardly possible to achieve a carrier free (non-carrier added) product, so the specific activity (in the case of an isotopic carrier) or the activity concentration (in the case of a non-isotopic carrier) will not be very high.

One example of a generator where precipitation plays a main part is given in Ref. [22], where ^{90}Y is separated from its mother ^{90}Sr by precipitation of the ^{90}Sr followed by subsequent purification of the ^{90}Y by column chromatography.

2.4.7. Generators based on electrochemical separation

The principle of the electrochemical separation of a daughter radionuclide (or its compound) from its mother radionuclide (or its compound) is based on a difference in their electrochemical potential. The practical implementation of the separation process comprises the steps of dissolving the mother/daughter equilibrium mixture in an electrolyte followed by selective deposition of the daughter radionuclide on an electrode in accordance with their electrochemical potential.

This deposition can be achieved either by a spontaneous process or by applying an external voltage. Both variations are treated briefly below.

Spontaneous deposition, also called autodeposition (and sometimes incorrectly even electroplating or electrodeposition), is based on a difference in electronegativity between the mother and the daughter. For preferential deposition of the daughter, it has to exhibit a higher reduction potential than the mother.

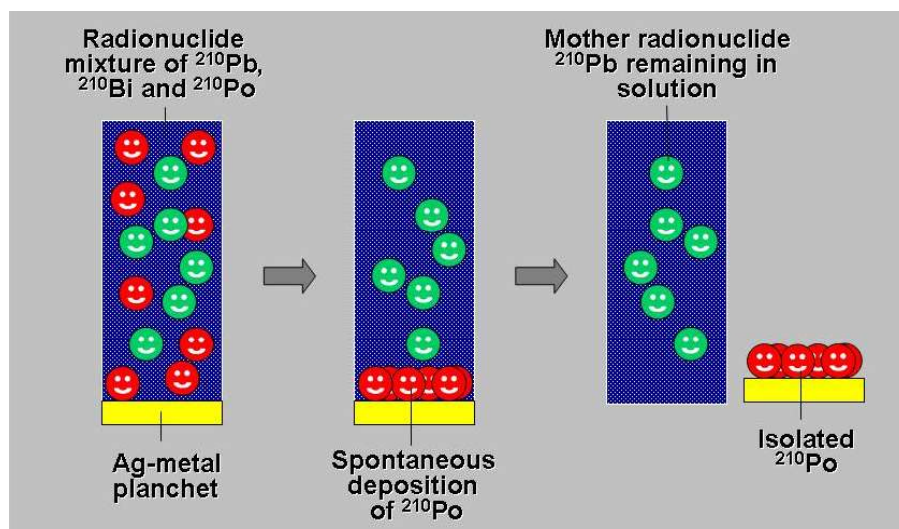


FIG. 15. Schematic illustration of a spontaneous deposition (autodeposition) process illustrated by the separation of ^{210}Po ($T_{1/2} = 138.4$ d) from its grandmother ^{210}Pb ($T_{1/2} = 22.3$ a).

Spontaneous deposition can take place on metallic surfaces with a lower reduction potential. The process is often demonstrated in primary courses in chemistry by dipping a rod of metallic zinc into an electrolyte of copper ions (Cu^{2+}). Metallic copper is spontaneously deposited (reduced to Cu^0) on the zinc rod, while the zinc rod is correspondingly dissolved (oxidized to Zn^{2+}). For the $^{210}\text{Pb}/^{210}\text{Bi}/^{210}\text{Po}$ nuclear genetic relationship, the ^{210}Po may be separated by autodeposition of a metallic nickel surface [23]. It is reported to be a very robust method. This creates potential for development of a $^{210}\text{Pb}/^{210}\text{Po}$ radionuclide generator for special purpose use. In this case, deposition on to a silver surface would be required since the nickel surface may also partly deposit the progeny ^{210}Bi and ^{210}Pb [24]. A schematic outline of the method is given in Fig. 15. The spontaneous deposition method has not yet been extensively exploited for more general mother/daughter separation in radionuclide generator technology.

The electrolysis method, also called electroplating (or electrodeposition), comprises an electrolyte containing the mother/daughter radionuclide mixture, two electrodes of an inert material like platinum and an external power source with variable high voltage connected to the electrodes, forming a cathode and an anode. The negative potential applied to the cathode causes the daughter radionuclide (as a positively charged ion) to be reduced and deposited on to the surface of the cathode. Reversing the potential causes the deposited daughter

radionuclide to return back to the aqueous phase, thus allowing its recovery [11, 19, 25, 26].

Advantages of electrochemical separation are:

- Electrolysis requires few steps and product yield is high.
- Capacity is not limited by the amount of adsorbent or extractant.
- Simple to operate.
- Requires low cost equipment.
- Relatively fast process.
- Permits carrier free and clean separation from the parent.

Disadvantages of electrochemical separation are:

- Not a universal method; still in developmental stage with respect to radionuclide generators.
- Applicable to those systems where there is a significant E^0 difference of parent and daughter.
- A generator version suitable for field application has yet to be developed.
- Production of gaseous components during electrolysis must be taken care of to reduce any explosion danger (H_2 production).

A typical example of this method is the $^{90}\text{Sr}/^{90}\text{Y}$ generator developed at Bhabha Atomic Research Centre (BARC), India [25]. The experimental set-up is depicted in Fig. 16. In this generator, the separation of ^{90}Y from ^{90}Sr is achieved due to the difference between the electrochemical potentials of Y^{3+} and Sr^{2+} . On applying a suitable electric potential, ^{90}Y is selectively deposited at the cathode from a mixture of ^{90}Sr and ^{90}Y . The generator involves two electrolysis steps of purification. The first electrolysis is performed for 90 min in $^{90}\text{Sr}(\text{NO}_3)_2$ feed solution at pH 2–3 at a potential of -2.5 V with a 100–200 mA current using platinum electrodes. The second electrolysis is performed for 45 min in 3M HNO_3 at a potential of -2.5 V with 100 mA current. In this step, the cathode from the first electrolysis containing ^{90}Y is used as the anode, whereby the yttrium again redissolves and is deposited on a fresh circular platinum cathode. The ^{90}Y deposited on the circular cathode after the second electrolysis is dissolved in acetate buffer for further production of useful tracer compounds.

2.4.8. Generators based on SLM separation

This separation technique is basically a continuously operated extraction stripping process. It includes the operation of an extracting liquid membrane

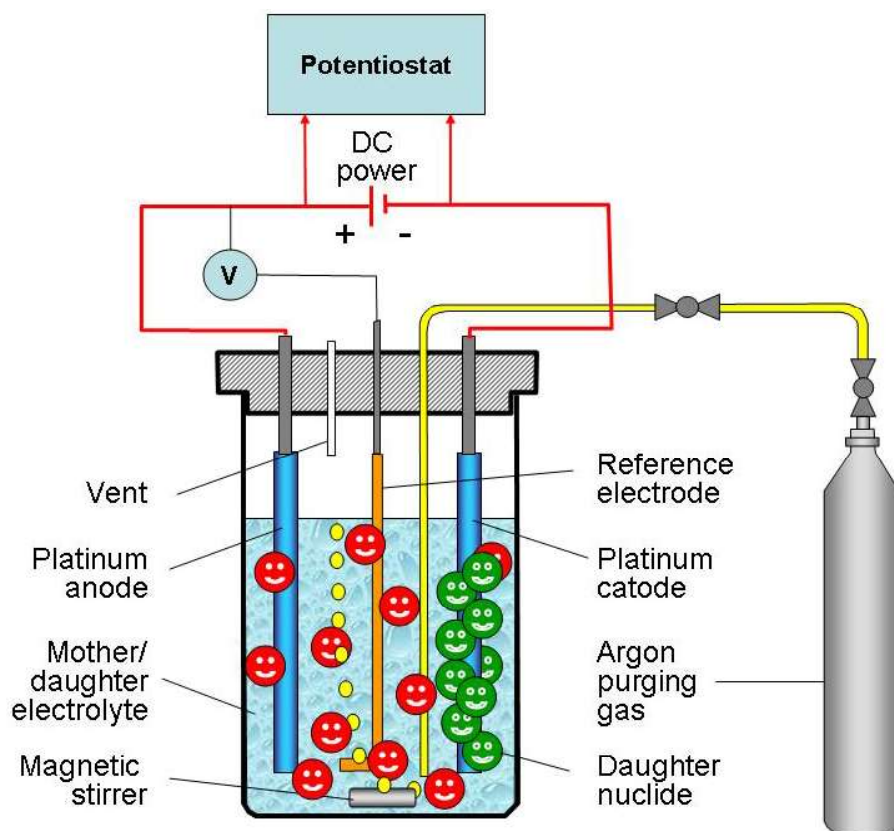


FIG 16. Schematic diagram of electrolytic separation of ^{90}Y from a $^{90}\text{Sr}/^{90}\text{Y}$ electrolyte mixture, adapted from Ref. [22].

where the solute (daughter radionuclide) partitions between three liquid phases: the feed, the membrane and the receiving phases. This may be described as the ‘supported liquid membrane’ (SLM) technique.

The organic liquid (possibly including an extractant) is immobilized within the pores of a porous membrane. The porous membrane itself serves only as a framework or supporting layer for the organic liquid film. Such a membrane can be easily prepared by impregnating a hydrophobic porous membrane with a suitable organic solvent possibly modified with an extractant. The membrane can be defined essentially as a barrier, which separates two aqueous phases and restricts the transport of the mother radionuclide in a selective manner. The transport through the membrane is affected by the concentration gradient across it. The feed aqueous solution initially contains the mother/daughter equilibrium mixture.

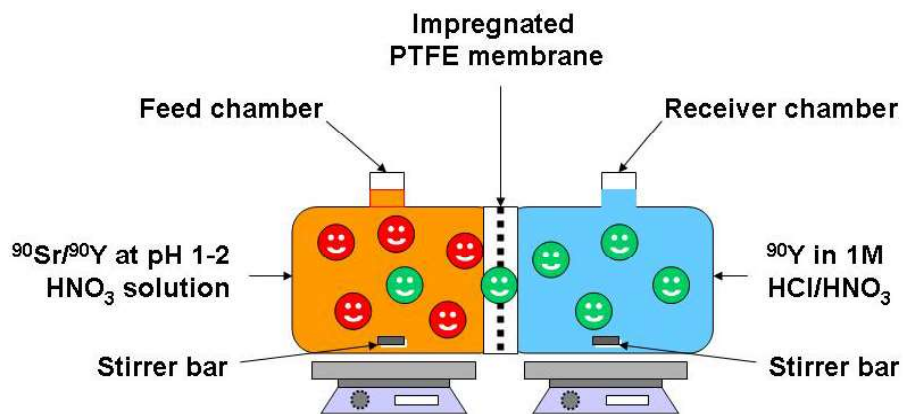


FIG. 17. Two chamber SLM $^{90}\text{Sr}/^{90}\text{Y}$ generator; adapted from Ref. [22].

Separation of the daughter from the mother by transport of the daughter through the membrane requires that the distribution ratio D_D (Eq. (15)) for the daughter to the organic phase in the membrane is high and the distribution ratio D_M for the mother correspondingly low. Then, the separation factor will be high. The aqueous solution present on the opposite side of the membrane, which is initially free from the daughter radionuclide, is referred to as the strip solution. For an efficient stripping (or back extraction) of the daughter from the organic phase in the membrane, the strip solution has to be designed so as to make the D_D value as low as possible on the stripping side of the membrane.

The performance of the process is strongly affected by the properties of the organic solvent and the selectivity of the possible complexing agent or extraction agent used in the membrane, the carrier concentration for the daughter or holdback carrier for the mother, the fluid dynamic of the phases (viscosity) and the membrane characteristics such as pore size and pore size distribution. In contrast to ordinary solvent extraction, this overall process is governed by kinetics and concentration differences rather than equilibrium parameters [27–29]. The principle of the process is sketched in Fig. 17.

Advantages of the SLM separation technique are:

- It offers selective separation depending on the selectivity of specific extracting reagents.
- Simple operation, both extraction and stripping are feasible in one stage, and the process does not include manual interaction.
- It does not use any external force such as pressure or high tension, but is based on difference of the chemical potential as a driving factor of the process.
- Larger interfacial area permits high efficiency.

Disadvantages of the SLM separation technique are:

- It is not yet a mature technology but still under development. A version suitable for industrial application has yet to be developed.
- Transport processes of the daughter are slow (slow kinetics), so it cannot be used for very short lived daughter activity.
- The equipment is still somewhat mechanically unstable, especially due to short lifetime and instability of the membrane.
- The release of the organic phase from the pores of an SLM into the receiver chamber represents a problem as it leads to chemical impurity in the separated product.
- It is essential to recharge the membrane periodically.

A generator system using the above concept has been developed for the preparation of carrier free ^{90}Y from ^{90}Sr in BARC, India [27] by employing an SLM using 2-ethylhexyl-2-ethylhexyl phosphonic acid (KSM-17 equivalent to PC 88A) supported on a poly-tetrafluoro-ethylene (PTFE) membrane (Fig. 17). After adjusting to pH2 with NaOH, the $^{90}\text{Sr}/^{90}\text{Y}$ solution is used as a feed in a single stage membrane cell partitioned with a PTFE membrane impregnated with KSM-17 and having a feed and receiver compartment with 5.0 mL capacity each. The receiver compartment is filled with a 0.5M HNO_3 or 0.5M HCl stripping solution. Yttrium-90 alone is preferentially transported across the membrane, leaving behind ^{90}Sr in the feed compartment. This technique can yield ^{90}Y in millicurie levels in a pure and carrier free form. The feed can be reused repeatedly after allowing for ^{90}Y buildup.

Out of all the generator principles briefly described above, it was decided that the chromatographic type generator was to be the method of choice for further development in the CRP, which is the basis for this publication. The chromatographic type radionuclide generator has, at this stage, the best overall potential for being further developed into a suitable radiotracer generator for industrial application by coupling a selective chemical treatment for the daughter radionuclide of interest to a suitable radionuclide generator.

2.4.9. Special case: Generator based on electrostatic radionuclide separation

When one of the decay products in the decay chain from the mother radionuclide is gaseous, it may emanate from the mother radionuclide compound. The following decay will produce positively charged daughter products that may be collected on an electrode at negative charge. One example is generation of carrier free ^{212}Pb from decay of ^{228}Th through the following decay chain:

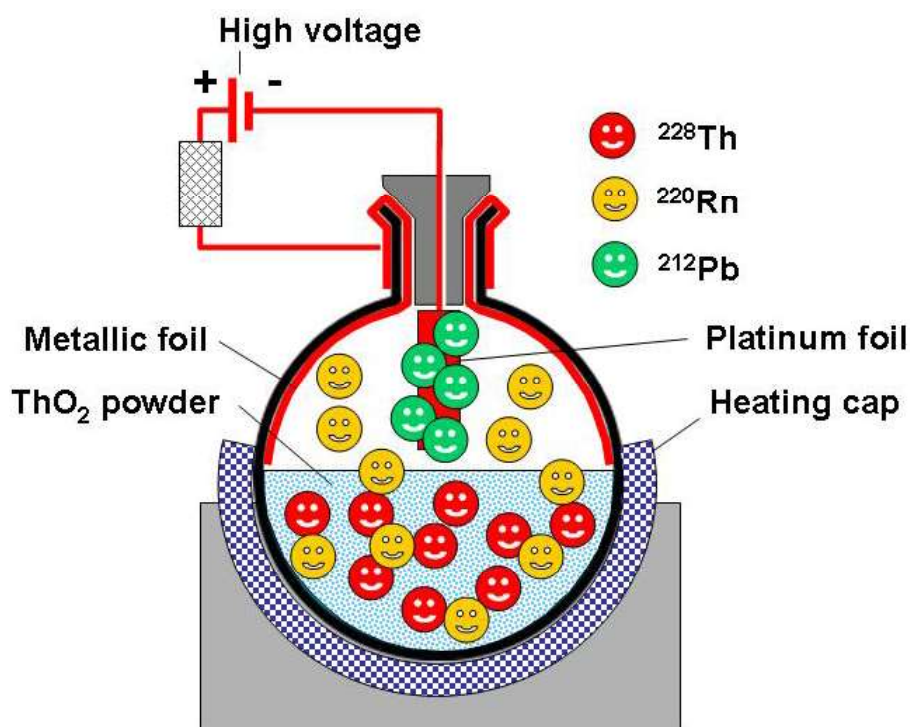
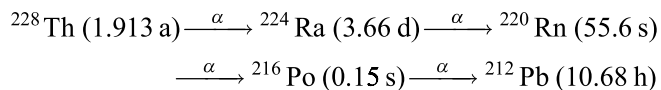


FIG. 18. Schematic diagram of the electrostatic $^{228}\text{Th} \rightarrow \dots \rightarrow ^{212}\text{Pb}$ generator.



Here, both the very short lived ^{216}Po , as well as ^{212}Pb itself, will be collected at the cathode during alpha decay of their progeny. This generator was first published by Rutherford in 1900 and is often referred to as 'Rutherford's thorium cow' [30].

Thorium-228 is readily found in compounds of the naturally occurring mother ^{232}Th . If the thorium compound is 'old', i.e. at least 60 years since its elemental isolation in order to allow for in-growth of its decay product ^{228}Ra (5.75 a), the ^{228}Th is in nuclear equilibrium with ^{232}Th . Therefore, the emanating compound normally loaded into the generator is ordinary ThO_2 . A sketch illustrating the principle of operation of the generator is given in Fig. 18.

The high tension is normally in the range 100–1000 V, the amount of ThO_2 is 10–100 g and the collection time 10–24 h. After the collection period, the

platinum foil is removed and the deposited ^{212}Pb rinsed off (dissolved) with dilute nitric acid. If there is a need for several experiments during 1 d (or one collection period), several generators may be connected in parallel (battery of generators) on the same high temperature source. In order to achieve a sufficiently high emanation rate from the ThO_2 powder, it has to be finely grained and preferentially heated to some 50–60°C. A ^{212}Pb activity of 0.5–5 μCi may be obtained per collection. The operation and typical generator yields are given in Ref. [31].

Out of all the generator principles briefly described above, it was decided that the chromatographic type generator was to be the method of choice for further development in the CRP, which is the basis for this publication. The chromatographic type radionuclide generator has, at this stage, the best overall potential for being further developed into a suitable radiotracer generator for industrial application by coupling a selective chemical treatment for the daughter radionuclide of interest to a suitable radionuclide generator.

2.5. RADIOTRACER GENERATORS BASED ON RADIONUCLIDE GENERATORS

Radionuclides from radionuclide generators are the first step on the way to producing radiotracers for use in industrial process studies [32]. Radionuclide generators make radionuclides readily available at locations remote from irradiation facilities (reactors or particle accelerators). In addition, the short half-life of the daughter radionuclide ensures that any radioactive waste remaining after an industrial investigation is minimal and that any contamination of plant, product streams or environment discharges is negligible.

Although it is sometimes possible to use the daughter radionuclide directly to trace process streams, more often, it is necessary to chemically modify it so as to ensure full compatibility with the stream to be traced.

2.5.1. Design of an IRNG

For industrial applications, the most common type of generator is the column type, described in Section 2.4.1. The designs of the components of a column based radionuclide generator will vary from one manufacture to another, but the objective is always to facilitate the separation and elution of the daughter radionuclide from the parent radionuclide. The components in a typical column based generator are given below.

Column: The column, usually glass, containing a bed of sorbent as a support to which the mother radionuclide will bind strongly and not be washed off during

the subsequent elution of the daughter radionuclide. Removal of the daughter radionuclide from the sorbent column is attributed to the lack of affinity of the daughter radionuclide for the sorbent, whereas the mother radionuclide is essentially completely bound to the sorbent and cannot be removed by the elution liquid, regardless of the volume of eluent passing through the column. Removal of the mother radionuclide requires an eluent of different chemical composition.

Tubing: Tubing is connected to the column to allow it to be washed with an eluent or rinsing solution. In a traditional generator design, the inlet tube will generally be accessible usually via a needle on to which a vial of the eluent can be attached as needed. Other generator designs provide an internal reservoir of eluent for this purpose. The outlet tube is also accessible and generally terminates as a needle to which an empty collecting vial can be attached. Most generators use an evacuated vial for collection so that eluent from the inlet side is drawn through the column and into the outlet vial. No pumps are needed. The driving force is the evacuated vial that creates a very significant differential pressure over the column since the eluent side of the generator is always at atmospheric pressure.

Filters: Filters serve to maintain the integrity of the sorbent bead within the column so as to prevent fluid channelling that would reduce the elution efficiency. The filters are usually glass frits with pore sizes suitable to remove any small particles of the sorbent from the eluted sample. The filters can also be made of porous plastic materials (for instance, polyethylene or Teflon).

Catcher column: Some generators come with a catcher column. This column contains a bed made of the same absorber material as the main column and is mounted at the outlet side of the main column. The purpose is to catch (bind chemically) any mother radionuclides that might have been eluted from the main column. The catcher column should be readily exchangeable without needing to dismantle the lead shield around the main column (see below).

Shielding: Heavy shielding is required for operator safety, as both the parent and the daughter radionuclides emit radiation. The glass column acts as a partial shield, but cannot stop the penetrating gamma radiation. Most generators will therefore have a lead shield around the column and outlet tubing. Additional shielding is used during the collection process and, of course, the eluted daughter radionuclide must be shielded once it is collected from the generator.

Handles: Generators are contained in a housing and have handles to allow manual or mechanical lifting and positioning. There is a cover to protect the inlet and outlet needles and appropriate labelling on the generator housing.

One typical generator design is shown in Fig. 7. Another design is given in Fig. 19.

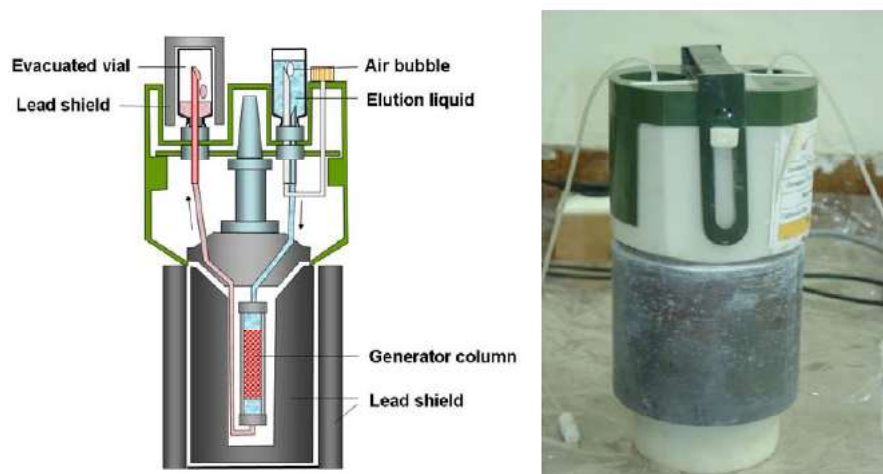


FIG. 19. Left: A column generator in its lead shield. Elution is performed by a vacuum vial, also in a lead shield. Right: A typical lead-shielded and closed radionuclide generator.

A set-up where the generator is eluted with a vacuum pump from an external elution liquid reservoir is illustrated in Fig. 20.

Principal features of the generator to be determined before use are the elution yield of the daughter as a function of the eluant flow rate and the degree of mother breakthrough. The activity requirements must be considered in order to optimize the elution flow rate in relation to the total injected volume, the duration of the examination and the residence time of the system to be studied.

Once the activity of the daughter is eluted, there is a growth of the daughter on the column until it again reaches a maximum and finally is in close equilibrium with the mother. This elution and regrowth can be continued as long as there are useful amounts of the mother radionuclide available. Elution may be performed before equilibrium is reached, and the amount of daughter activity eluted will depend on the time elapsed since the last elution.

Radionuclide generators intended for radiotracer applications must meet regulatory and quality control requirements. The production of the mother radionuclide in nuclear reactions by irradiation in a reactor or a particle accelerator, its separation from the target material, and the chemical and technical construction of the radionuclide generator are factors that must be considered carefully, so that the end result is a generator that is efficient and easy to operate. Processes for the production of radionuclide generator systems for radiotracer applications should follow good manufacturing practice standards.

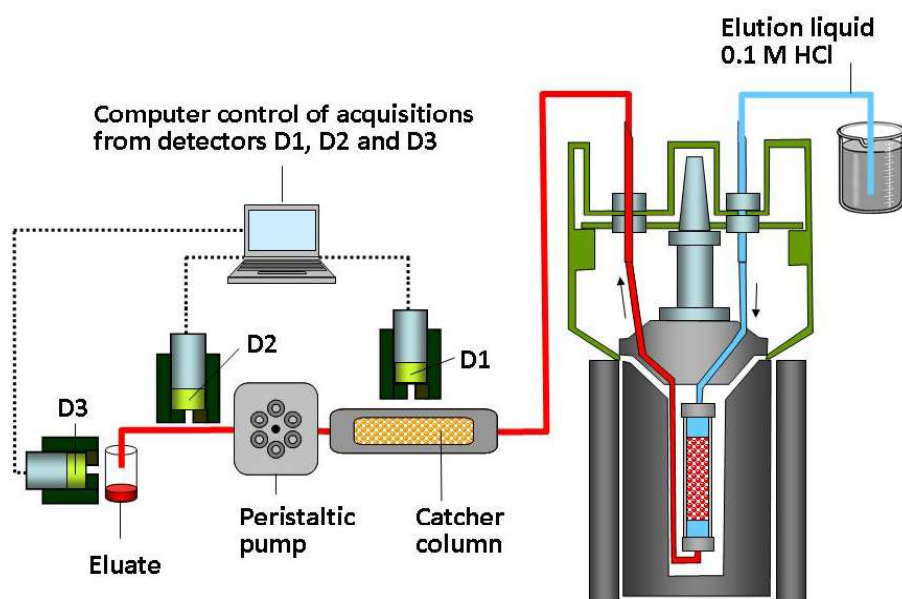


FIG. 20. A generator set-up that is eluted by means of a peristaltic vacuum pump and with a catcher column outside the main generator housing for easy detection of mother radionuclide breakthrough.

For some applications, it is possible to incorporate the generator into the tracer injection system. The system software initiates the elution of the generator at preset intervals and also controls the duration of the elution and the flow rate of the eluent. Such a system can be mounted permanently on a process stream for purposes of routine monitoring.

The choice of a specific daughter radionuclide for any given application depends on the following factors:

- Energy of photon emitted (in some cases, more than one photon energy);
- Half-life;
- Elution yield;
- Physical and chemical form, which leads into the next point;
- Possibility of converting the radionuclide into a useful radiotracer for various tracing scenarios.

2.5.2. Activity requirement

Estimating the required activity is an important step in any industrial experiment with radioactive sources. For radiotracers, the lower limit of the

activity is determined by the measurement sensitivity of the detector, desired accuracy, dilution between injection and detection points, and background radiation level. The upper limit is set by radiological safety considerations. The amount of the required activity depends on the following factors:

- Desired accuracy;
- Efficiency of measurement or calibration factor of the detection system;
- Expected level of dilution/dispersion;
- Half-life of the daughter radionuclide;
- Background radiation level and number of repeated measurements;
- Mode of injection and detection (delta function versus continuous or extended pulse width);
- Expected losses of activity (should not really happen).

2.5.3. Industrial tracing situations

Industrial conditions for radiotracer applications vary considerably from case to case. Basically, the following conditions may be encountered in a radiotracer experiment:

- High temperature (up to hundreds or thousands of degrees celsius);
- High pressure (up to hundreds of megapascals);
- Vast volume (up to millions of cubic metres);
- Multiple phases (solids, liquids (aqueous, organic, supercritical), gases);
- Complex processes;
- Quick transit time (down to milliseconds);
- Complex media;
- Unexpected tracer degradation (microbiological attack, sorption, thermal or chemical degradation);
- Adsorption potential;
- Harsh working environment.

The increasing application of generator produced radiotracers in industry has stimulated the extensive development of a multitude of new radiotracers and novel radiolabelling procedures. Radiolabelling with these short lived radionuclides represents a remarkable challenge. Special attention has to be paid to synthesis time and specific labelling techniques due to the short physical half-life of the respective radionuclides. Development of procedures for producing radiotracers for industrial application must take this into account.

2.5.3.1. Aqueous liquid tracing

The radionuclide eluted from a radionuclide generator can be of various chemical forms. In order for the eluted radionuclide to be used directly as a passive radiotracer, the chemical form of the radioactive daughter compound should possess the following properties.

The radioactive material should be soluble in the process stream under the prevailing conditions of pH, temperature and pressure. It should not degrade in any way and not behave differently from the traced material itself.

Ideally, the radionuclide eluted from the generator should be in a chemical form that is physically and chemically compatible with the material to be traced so that it can be injected into the process stream of interest without delay and without complicated chemical manipulation. However, in most cases, the generator eluate does not satisfy all these characteristics. In order to utilize the eluted radionuclides effectively for radiotracer investigation, further chemical manipulation is most often necessary.

Chemical conversion makes the production of a wide spectrum of appropriate radiotracers possible, and opens up the window for utilization of these compounds in different situations. The eluted radionuclide is generally treated with an appropriate ligand to form an inert complex having sufficient thermal stability. For water tracing, the best performing tracers are anionic. In simple one component water tracing, neutral and positively charged compounds may be used depending on the process to be traced. In multiphase flow, where one component is water and the other an oleic phase, a neutral component can only be used if it does not contain a lipophilic fraction, which makes it soluble in the oil phase as well as in the water. In addition, for very short lived radionuclides, the synthesis process must be rapid in order to avoid detrimental decay during the process.

In order to develop synthesis and/or labelling techniques that can be adopted for industrial tracing, it is a good starting point to look at the work conducted for labelling of radiotracers for nuclear medicine purposes. Of course, this is a much simpler system than encountered in most industrial situations, especially when considering the temperature, acidity and chemical compositions of the systems to be investigated.

Radiopharmaceutical scientists have designed, developed and tested many potentially useful and 'on the spot' labelling kit formulations using 'cold' kits. A cold kit contains the ligand to be complexed, an adequate quantity of reducing or oxidizing agent (if needed), a buffer to adjust the pH to suit the labelling conditions and other required chemical components or modifiers. Radiolabelling with kits is fairly easy, can be easily accomplished with high complexation yield and provides a novel route to make radiotracers. Kit formulations are not only

effective in carrying out the tasks, but also save time during field tracer investigations.

Here, two such examples are illustrated:

- (i) The eluted chemical form of ^{99m}Tc from the $^{99}\text{Mo}/^{99m}\text{Tc}$ radionuclide generator is pertechnetate, $^{99m}\text{TcO}_4^-$. This anion is a good water tracer provided the temperature is below about 90°C and the chemical conditions are not reducing. At reducing conditions, technetium is reduced from oxidation state +7 to +4 and forms $^{99m}\text{TcO}_2$. This is a non-charged molecule that will attach to any solid surface and not behave as a water tracer any more. Hence, ^{99m}Tc has to be stabilized preferably as an anion by complexation with suitable ligands. Such a ligand is EDTA, a readily obtained chelate. It has been shown to be effective in the process evaluation of wastewater treatment plants as it precludes absorption of the radiolabelled molecule on the vessel or pipe walls or on suspended solids during the course of tracing [33].
- (ii) A radiotracer experiments was carried out on a model of a rectangular settler with a volume of 3 m^3 . Several different aqueous phase tracers were injected consecutively. The tracers were (i) non-radioactive fluorescein (a strongly coloured dye that, in these experiments, is taken as a reference water tracer), (ii) the eluate from a $^{68}\text{Ge}/^{68}\text{Ga}$ generator eluted with 0.1N HCl solution and no further treatment and (iii) ^{68}Ga complexes with 1,4,7-triazacyclononane-1,4,7-triacetic acid (NOTA) and 1,4,7,10-tetrazacyclododecane-1,4,7,10-tetraacetic acid (DOTA).

The obtained RTD functions indicated that the directly eluted ^{68}Ga (in the form of solvated Ga^{3+}) did not work as a water tracer in the settler. However, the complex compounds of gallium were stable in the water phase and were not adsorbed on the vessel walls. These complexes can be recommended as tracers of the water phase in similar experiments and under similar experimental conditions [34].

The preparation procedure is as follows:

- Elute Ga^{3+} from the generator with about 5 mL of 0.1N HCl solution;
- Add about 1 mL of a 0.01M solution of the macrocyclic compounds DOTA or NOTA;
- Adjust pH to 3.5;
- Heat the mixture to $90\text{--}95^\circ\text{C}$ for 20–30 min.

The above procedure for $^{68}\text{Ga}^{3+}$ ion complexation with DOTA and NOTA can be recommended as a useful synthetic route for production of ^{68}Ga labelled passive water phase tracers of ^{68}Ga eluted on-site from the $^{68}\text{Ge}/^{68}\text{Ga}$ generator.

Table 2 summarizes some of the common applications of radiotracers.

TABLE 2. SOME EXAMPLES OF CHEMICAL MODIFICATIONS OF RADIONUCLIDES ELUTED FROM THREE SELECTED GENERATORS AND APPLICATIONS OF THESE ‘MODIFIED’ RADIOLABELLED COMPOUNDS

Labelled phase	Generator		
	$^{137}\text{Cs}/^{137\text{m}}\text{Ba}$	$^{99}\text{Mo}/^{99\text{m}}\text{Tc}$	$^{113}\text{Sn}/^{113\text{m}}\text{In}$
Surface water	$^{137\text{m}}\text{Ba-EDTA}^{\text{a}}$ $^{137\text{m}}\text{Ba-DTPA}^{\text{b}}$	$^{99\text{m}}\text{TcO}_4^-$ (as eluted)	$^{113\text{m}}\text{In-DTPA}$
Groundwater	Too short lived	Unstable?	$^{113\text{m}}\text{In-DTPA}$
Water WWTP ^c	$^{137\text{m}}\text{Ba-EDTA}$ $^{137\text{m}}\text{Ba-DTPA}$	$^{99\text{m}}\text{Tc-EDTA}$	$^{113\text{m}}\text{In-DTPA}$
Sludge WWTP	Too short lived	$^{99\text{m}}\text{TcO}_4^- + \text{SnCl}_2 \rightarrow ^{99\text{m}}\text{TcO}_2$, sorption on to particles	$^{113\text{m}}\text{In}^{3+}$ will sorb on to particles
Mud in surface water	Too short lived	$^{99\text{m}}\text{TcO}_4^- + \text{SnCl}_2$, reaction as above	$^{113\text{m}}\text{In}^{3+}$ will sorb on to particles
Organic phase tested <120°C	$^{137\text{m}}\text{Ba-DC18C6}^{\text{d}}$ – HDNNS ^e	$^{99\text{m}}\text{TcO}_4^- + \text{TBP}^{\text{f}}$, i.e. generator eluted directly with TBP	
Catalyst in organic phase tested <120°C			$^{113\text{m}}\text{In}^{3+}$ will sorb on to particles
HT ^g /HP ^h water (<350°C, 40 bar)		$^{99\text{m}}\text{TcO}_4^- + 8$ hydroxy quinoline $^{99\text{m}}\text{TcO}_4^- + \text{TcMAG3}^{\text{a}}$	

^a EDTA: ethylene diamine tetraacetic acid.

^b DTPA: diethylene triamine pentaacetic acid.

^c WWTP: wastewater treatment plant.

^d DC18C6: crown ether: dicyclo-hexano-18-crown-6.

^e HDNNS: dinonylnaphthalenesulphonic acid.

^f TBP: tributyl phosphate.

^g HT: high temperature.

^h HP: high pressure.

2.5.3.2. Organic phase tracing

By using optimal reaction conditions, the daughter radionuclide can be extracted from an aqueous phase into a non-miscible organic liquid. Several solvent extraction reaction mechanisms are possible, most involving extra complexing agents (for instance, chelate formers) and some also involving adduct formers. Some examples are given below.

(a) Technetium-99^m tracer in MEK

The ⁹⁹Mo/^{99m}Tc generator based on an MEK solvent extraction system (Section 2.4.3) can be used to obtain ^{99m}Tc in MEK. An alkaline solution of 18.5 GBq (500 mCi) sodium molybdate [⁹⁹Mo] solution (7.4–14.8 GBq (200–400 mCi) per g Mo) is transferred into the extraction system. After extraction, the MEK phase is sampled by extracting an aliquot that can be used directly for organic phase tracing.

(b) Gallium-68 tracer in isopropyl ether

The solvent extraction method was used to prepare a ⁶⁸Ga tracer suitable for use in a single organic phase. Gallium-68 is eluted in 4N HCl (20 mL) from a ⁶⁸Ge/⁶⁸Ga generator based on a TiO₂ column. This acid (and chloride) concentration is sufficient to ensure that the chemical form of gallium is ⁶⁸GaCl₃, which is non-charged. 10N HCl (20 mL) was added to the eluted 4N HCl solution in order to make it 6M, which is the optimum molarity to ensure maximum extraction of ⁶⁸Ga. Isopropyl ether (20 mL) was used to extract ⁶⁸Ga from the aqueous phase (two sequential extractions) without addition of extra extraction agents. Efficient liquid mixing was achieved by bubbling nitrogen through the combined fluids for 10 min.

(c) Gallium-68 tracer in MEK

The ⁶⁸Ga is eluted with 1M HCl. A few mL of the aqueous phase containing ⁶⁸Ga is equilibrated with an equal volume of MEK to extract ⁶⁸Ga.

(d) Gallium-68 labelled acetylacetonate, Ga(acac)₃

The ⁶⁸Ga³⁺ in the form of GaCl₃ is eluted from an ionic ⁶⁸Ge/⁶⁸Ga/SnO₂ generator with 1M HCl. The solution was evaporated by heating to dryness in a test tube. The residue was dissolved in an ethanol solution containing 0.002% acetylacetone. The solution was heated for 20 min in a 65°C water bath to

facilitate formation of ^{68}Ga labelled acetylacetonate. The complex is suitable for oil tracing in single phase flow, but it has not been tested sufficiently in multiphase processes.

(e) Barium- ^{137}m complex with DC18C6 and HDNNS

A radionuclide column generator consisting of ^{137}Cs absorbed on $\text{K}_2[\text{CoFe}(\text{CN})_6]$ coated silica gel is eluted with a mixture of 0.1M HCl and 0.145M NaCl. The eluate is vigorously stirred with a solution of DC18C6 and HDNNS (1:2) and 1-dodecanol in isooctane. The resulting complex shows a high distribution ratio, also at elevated temperatures (60°C). It has also been tested with formation waters from oil reservoirs and shows acceptably low back extraction [35]. This complex (patent pending) may be used for multiphase oil tracing under typical oil–water separator conditions in the petroleum industry.

2.5.3.3. *Solid tracing*

Radiotracing using radiolabelled solid particles is an important tool to obtain invaluable information about movement of solid particulate material in industrial fluid flow, deposition in mines, geological tracing, surface water and river transport and movements of shore sediments. A few methods are described briefly below.

The degree of labelling may be proportional to the volume of the non-porous part of the solid material or proportional to the surface (internal and/or external) of the particle.

(a) Electrostatic sorption/ion exchange techniques

The generator eluate can be directly used for labelling solid particles utilizing electrostatic sorption/ion exchange techniques. This kind of labelling is, in principle, proportional to the surface of the particle. A larger percentage of the daughter radionuclide can be adsorbed at low tracer concentrations because a larger surface area is available compared to the amount of tracer present. Dilution with carrier decreases the amount of tracer adsorbed because the carrier is competing for adsorption, and the relative amount of the radioactive label interacting with the adsorbate is much less. Such a technique depends on the following factors:

- *Chemical state of the radionuclide*: Adsorption increases with increasing charge on the ion.

- *Nature of the surface material:* Surfaces that have a negative charge or that contain hydroxyl groups can interact with cations through electrostatic attraction and hydrogen bonding, respectively. For tracing of geological matter (sands), the charge should typically be positive.
- *Surface area:* Porous particles have larger surface areas than typical crystalline particles and have, therefore, a higher capacity for sorption. In addition, internal surfaces are shielded against wear and erosion of the radiolabel. If the pore size distribution throughout the particle is homogeneous and constant, the labelling in this case can also be taken to be proportional to the *volume* of the particle.
- *pH:* Generally, adsorption decreases with a lower pH (higher hydrogen ion concentration) because the ions interact with negatively charged surfaces, and the hydronium ions compete with other cations for the available binding sites.

Examples include:

- *Labelling of organic ion exchange material:* The daughter radionuclide eluted from the generator can be equilibrated with a specific amount of ion exchange material after adjusting the pH of the external solution. In this way, cation exchangers (with negatively charged sorption sites) can be labelled with a suite of cationic radionuclides. Likewise, anion exchangers (with positively charged sorption sites) can be labelled with radionuclides of anionic form. Organic ion exchangers, for instance, based on polymerization of styrene with divinylbenzene as a cross linker, represent a flexible structure that may expand or contract, depending on the ion strength in the surrounding solution. As such, one can hardly define a difference between surface and volume labelling; in this case, it is both.
- *Labelling of geological and other inorganic material:* Natural inorganic sorbents such as various clays (kaolinite, illite, montmorillonite, vermiculite, etc.), perlite, glass wool, sands (silicate rich or carbonaceous), volcanic ash, etc. can also be used for preparing solid radiotracers. The procedure is similar to the previous one. The process is based on the adsorption of the radiolabel on to, or into (for porous material), the available surface of the solid particles.

While choosing a sorbent, the following points must be considered:

- Rate and capacity of absorption/adsorption;
- Retention capacity (i.e. is the absorption thermodynamically irreversible in the intended tracing process?);

- Physical shielding of the label (i.e. can it be removed by erosion or wear?);
- Ease of application.

(b) Internal labelling

When the starting point is a radionuclide generator, there is only one form of internal labelling (disregarding the above comment on organic ion exchangers): the radiolabelled solid particles are produced by chemical precipitation of the material that contains the radiolabel. It can be direct precipitation with a carrier concentration with stable isotopes of the same chemical element or it can be by co-precipitation with other chemical elements.

Further treatment of the precipitate involves crushing and, possibly, grinding before sieving into special particle size fractions. For precipitation with a carrier of the same element, one always ensures that all the particles are homogeneously labelled (i.e. activity in Bq/g is constant), regardless of the particle size. For the case of co-precipitation, two situations have to be considered:

- Precipitation is performed in a thoroughly stirred solution, in which case, one achieves a homogeneous precipitation, i.e. the precipitated material is homogeneously labelled throughout the precipitate volume and the particles fabricated from the precipitate are also all homogeneously labelled (and the activity concentration is constant for all particles).
- If vigorous stirring is not carried out, there is the risk that the precipitation will be non-homogeneous. The first formed core particles have a higher activity concentration than the precipitated layers that grow on the initial particles. Thus, there will be a concentration gradient from high activity in the core towards lower activity at the precipitate surface at the end of the precipitation process. The various particles produced subsequently will then not have a homogeneous volumetric label: those from the surface area will have lower activity and those from the core will have higher activity.

(c) Preparation of radiocolloids

It is also possible to generate radiocolloids by chemical reactions such as hydrolysis. A method of forming an aerosol is to produce a liquid spray with a gas jet. The process can be facilitated by separating the liquid into droplets with electrostatic repulsions by applying a charge to the liquid. Emulsions are usually prepared by vigorously shaking the two immiscible phases together, often with the addition of an emulsifying agent, e.g. a surfactant such as soap, in order to

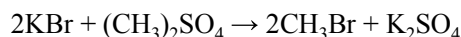
stabilize the product formed. Semi-solid colloids, known as gels, may possibly be formed from the cooling of lyophilic sols that contain large linear molecules and have a much greater viscosity than the solvent.

2.6. EXAMPLES OF RADIOTRACER GENERATORS NOT BASED ON A MOTHER/DAUGHTER NUCLEAR RELATIONSHIP

2.6.1. The methyl bromide generator

Methyl bromide ($\text{CH}_3^{82}\text{Br}$) is a radiolabelled gamma emitting gas used for gas tracing. Since it is oil soluble, it is also used as a tracer for organic liquids in single phase tracing, especially for localization of leaks in underground pipelines. When dealing with strongly radioactive organic liquids, autoradiolysis is always an issue. Ideally, such tracer molecules should be prepared just before use. Below is a description of how to generate $\text{CH}_3^{82}\text{Br}$ on-site from concentrated solutions of reactor produced $^{82}\text{Br}^-$.

Neutron irradiation of potassium bromide (KBr) is regularly carried out at reactors to produce $^{82}\text{Br}^-$ ($T_{1/2} = 36 \text{ h}$) for tracing of aqueous systems, and the availability of this radionuclide is relatively good. The transformation of solid radioactive potassium bromide to gaseous methyl bromide is carried out in a mobile chemical reactor, called a methyl bromide generator. It consists of a lead-shielded chamber containing the irradiated KBr. The KBr is dissolved in sulphuric acid and dimethylsulphate is added. Upon heating, the gaseous reaction product $\text{CH}_3^{82}\text{Br}$ is formed together with non-radioactive $\text{CH}_3^{79}\text{Br}$ and $\text{CH}_3^{81}\text{Br}$ according to the reaction:



The gaseous products are condensed in a second lead shielded and actively cooled chamber from where it can be injected in aliquots. The generator is pictured in Fig. 21.

One important feature in the development of such a system is to enable storage of the CH_3Br gas in a 'cryocanister' that prevents its release to the atmosphere. The canister has sufficient capability to store large quantities of $\text{CH}_3^{82}\text{Br}$ for the useful lifetime of the radiolabel (about 1 week).

Depending on the requirements in the various industrial tracing situations, generator activities up to 379 GBq (10 Ci) can be prepared and transported.

Different versions of mobile generators have been constructed with total weights ranging from 100 kg up to 400 kg to enable production of the required

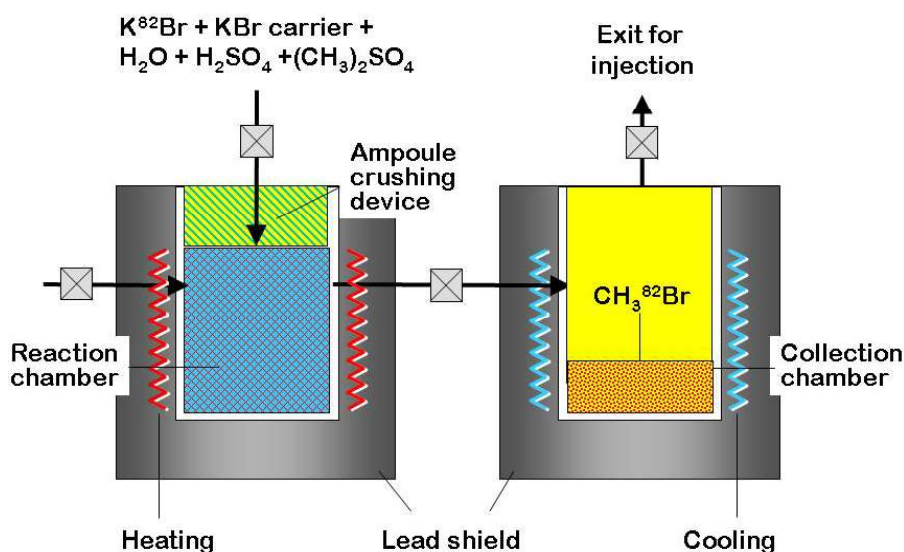


FIG. 21. Photograph and schematic diagram of the $CH_3^{82}Br$ radiotracer generator.

activity for various experiments. The fact that this particular generator design allows radioactive KBr to be transported separately in well shielded lead containers, allows for simpler logistics: it is simpler to transport a very small volume of radiolabelled solid salt than the corresponding activity as a radioactive gas.

The production process of $CH_3^{82}Br$ at the work site is as follows:

- Crush the quartz ampoule containing the solid salt $K^{82}Br$ using a special integrated crusher.

- Add sulphuric acid and methyl sulphate agents to the reactor for the dissolution of $K^{82}Br$.
- Clean the crusher and make it ready for the next operation.
- Close the valves connected to the reaction chamber to seal it off to prevent any accidental leakages.
- Heat the reactor to $70^{\circ}C$ for about 30 min. The chemical reaction starts.
- Close the top valve on the collection chamber and open carefully the valve between the chambers.
- The temperature of the cooling chamber is brought to $5^{\circ}C$ (liquefaction temperature of methyl bromide) by submerging the chamber in dry ice. The $CH_3^{82}Br$ gas is transported from the reaction chamber to the collection chamber by cryopumping and condensed there.
- Allow natural heating of the collection chamber by removing the dry ice. Once the storage tank reaches ambient temperature, release of $CH_3^{82}Br$ gas is possible.
- Connect special containers to the exit valve on the collection chamber and open the valve to transfer $CH_3^{82}Br$ to the containers.
- $CH_3^{82}Br$ can be dispensed from the container into special ampoules for injection in subsequent tracer experiments.
- Clean and prepare the containers to make the system ready for another synthesis operation.

2.6.2. Radionuclide generators from on-site activation with isotropic neutron sources

Table 3 shows a number of short lived radionuclides that can be produced by irradiation with isotopic neutron sources because of very high activation cross-sections of target nuclides.

The calculated reaction yields are based on the following assumptions:

- Irradiation time: $10T_{1/2}$.
- Thermal neutron flux: $10^9 \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$.
- Amount of target material: 1 g molecule ($\text{mol} = 6.023 \times 10^{23}$ target atoms).

Typical commercial neutron sources are ^{252}Cf (spontaneous fission with emission of neutrons) and $^{241}Am/Be$, in which neutrons are generated by the following α particle reaction:

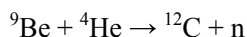


TABLE 3. NUCLEAR DATA AND CALCULATED REACTION YIELDS (IN NUMBER OF γ EVENTS EXPRESSED AS BECQUERELS OF THE MAIN γ RAY ENERGY) FOR SEVERAL SHORT LIVED RADIONUCLIDES THAT MAY BE PRODUCED BY SMALL ISOTOPIC NEUTRON SOURCES

Radionuclide	Half-life	Nuclear reaction	n th cross-section	γ energy (intensity)	Irradiation time	Reaction yield of γ
^{52}V	3.75 min	$^{51}\text{V}(n, \gamma)$	4.9 b	1434 keV (99.75%)	37.5 min	2.9 GBq
^{56}Mn	2.58 h	$^{55}\text{Mn}(n, \gamma)$	13.3 b	847 keV (100%)	25.8 h	8.0 GBq
$^{60\text{m}}\text{Co}$	10.5 min	$^{59}\text{Co}(n, \gamma)$	20.7 b	59 keV (100%)	105 min	12.4 GBq
$^{80\text{g}}\text{Br}$	17.6 min	$^{79}\text{Br}(n, \gamma)$	8.3 b	616 keV (50.7%)	176 min	2.5 GBq
^{104}Rh	42 s	$^{103}\text{Rh}(n, \gamma)$	134 b	556 keV (100%)	7 min	80.4 GBq
$^{108\text{g}}\text{Ag}$	2.41 min	$^{107}\text{Ag}(n, \gamma)$	36 b	663 keV (51.8%)	24.1 min	11.2 GBq
$^{110\text{g}}\text{Ag}$	24 s	$^{109}\text{Ag}(n, \gamma)$	87 b	658 keV (48.2%)	4 min	25.2 GBq
$^{116\text{m}}\text{In}$	54 min	$^{115}\text{In}(n, \gamma)$	73 b	1294 keV (95.7%)	540 min	41.9 GBq

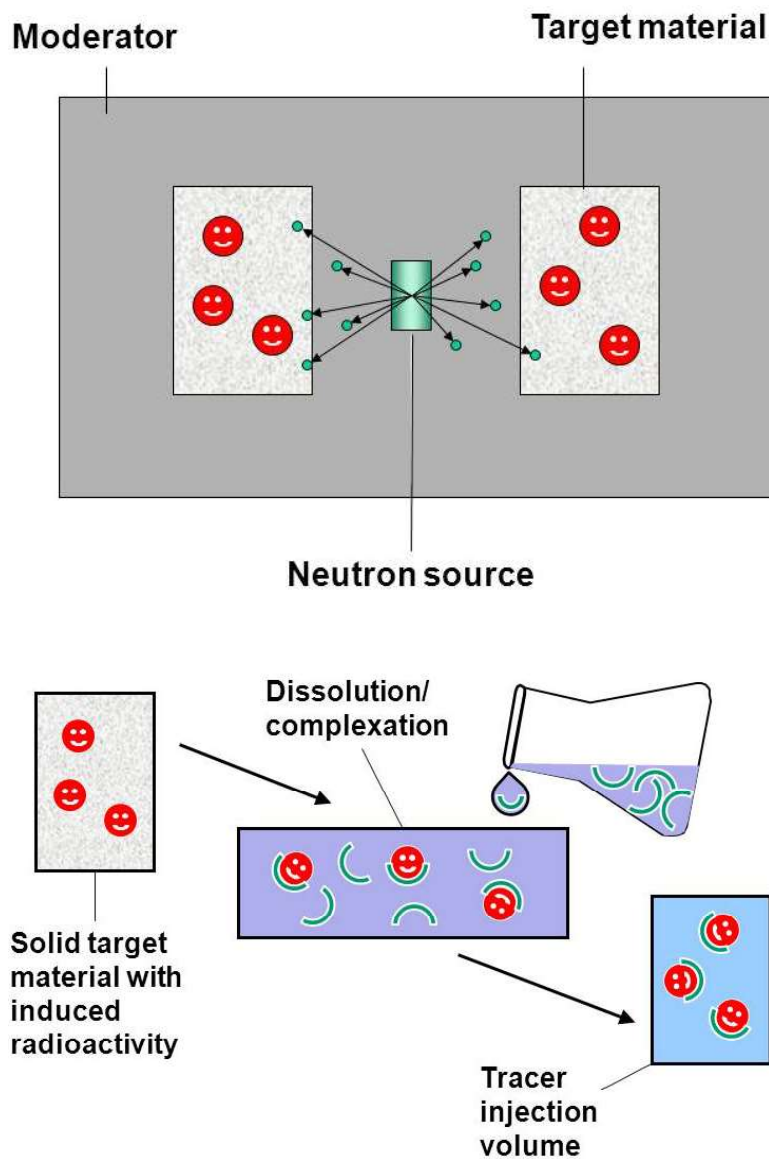


FIG. 22. Activation of solid target with thermal neutrons from a small isotopic neutron source (upper part) followed by dissolution of the target and complexation of the radionuclide of interest (lower part) to produce a suitable tracer compound.

The process is schematically illustrated in Fig. 22.

Decay of ^{252}Cf by alpha emission (96.91% probability) and spontaneous fission (3.09% probability) results in an overall half-life of 2.645 a and neutron

emission of $2.314 \times 10^6 \text{ s}^{-1} \cdot \mu\text{g}^{-1}$, with a specific activity of 19.832 GBq per μg (0.536 mCi/ μg). Thus, it is an intense neutron emitter that is routinely encapsulated in compact, cylindrical source capsules. A source the size of a person's little finger can emit up to 10^{11} neutrons/s. However, the use of such a source requires bulky and heavy shielding. For instance, a 3 mg source requires a cylindrical transport container of height 121 cm, diameter 112 cm and weight 1723 kg.

The ^{252}Cf sources of several different neutron outputs are, in principle, available commercially, but are expensive in the sizes needed to produce a slow neutron flux of $10^9 \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, which is used in the calculation of the reaction yields in Table 3. However, a lower flux may still be of interest. The yields given are then simply scaled down linearly with the neutron flux.

The half-life of ^{241}Am is 432 a, and neutron sources based on this radionuclide have therefore a much longer useful lifetime than the ^{252}Cf sources. However, the neutron output is lower. In general, for commercially available sources, the neutron output is $2.2 \times 10^6 \text{ n} \cdot \text{s}^{-1} \cdot \text{Ci}^{-1}$. Typical commercial source strengths are in the range 1 μCi (smoke detectors) to >20 Ci (irradiators, oil well logging tools, etc.). The strongest sources will produce fluxes in the range 10^5 – $10^6 \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, which is three to four orders of magnitude lower than the flux used for the calculations in Table 3. The results are yields of the order of megabecquerels, which may nevertheless still be useful for some tracing purposes.

Transportable neutron generators utilizing the T(d,n) or the D(d,n) reaction can also be used for radionuclide production, as described briefly in Section 2.6.3 below.

2.6.3. Radionuclide (radiotracer) generators based on on-line use of neutron generators

Tracers to follow a mass flow can be generated in situ if the flowing material contains an activable component. For illustration purposes, the most obvious and simple example is activation of water itself with fast (14 MeV) neutrons from a neutron generator based on the reaction $\text{T(d,n)}^4\text{He}$. This activation leads to the nuclear reaction:



Nitrogen-16 is radioactive with a half-life of 7.13 s and emits high energy γ rays of 6.1 and 7.1 MeV. This process is possible due to recent development of small sealed tube and transportable neutron generators.

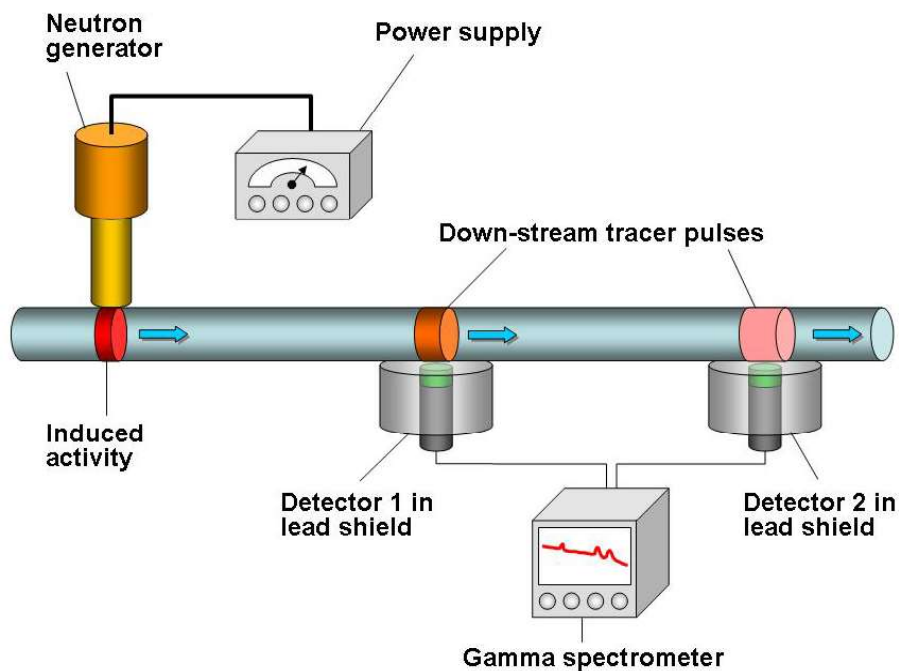


FIG. 23. Schematic diagram of a pulse of a tracer induced in a mass flow by a short (or pulse) irradiation with a neutron generator, and the subsequent downstream detection of gamma radiation.

The principle of activation, or ‘tracer injection’, with subsequent radiation measurement is illustrated in Fig. 23.

Although activation of ^{16}O has been used as an example here, there is a suite of other radionuclides that may be generated in situ by this method, but whether or not the above technique is feasible depends to a considerable degree on the nature and the elemental composition of the flow. If the flow does not have an appropriate concentration of activable elements that produce useful tracers, it is possible to inject easily activable material into it.

Examples of useful activation reactions are $^{12}\text{C}(\text{n},2\text{n})^{11}\text{C}$ ($T_{1/2} = 20.3$ min), $^{14}\text{N}(\text{n},2\text{n})^{13}\text{N}$ ($T_{1/2} = 9.97$ min), $^{19}\text{F}(\text{n},\text{p})^{19}\text{O}$ ($T_{1/2} = 26.9$ s), $^{20}\text{Ne}(\text{n},\text{p})^{20}\text{F}$ ($T_{1/2} = 11.0$ s), $^{24}\text{Mg}(\text{n},2\text{n})^{23}\text{Mg}$ ($T_{1/2} = 11.32$ s), $^{28}\text{Si}(\text{n},\text{p})^{28}\text{Al}$ ($T_{1/2} = 2.25$ min), $^{31}\text{P}(\text{n},2\text{n})^{30}\text{P}$ ($T_{1/2} = 2.50$ min), $^{37}\text{Cl}(\text{n},\alpha)^{34}\text{P}$ ($T_{1/2} = 12.4$ s), $^{55}\text{Mn}(\text{n},\text{p})^{55}\text{Cr}$ ($T_{1/2} = 3.50$ min), etc.