Chapter 19 Radiochemical Techniques

Radiochemistry is defined as “the chemical study of radioactive elements, both natural and artificial, and their use in the study of chemical processes” (1). Operationally radiochemistry is defined by the activities of radiochemists, \textit{i.e.}, (a) nuclear analytical methods (b) the application of radionuclides in areas outside of chemistry, such as medicine (c) the physics and chemistry of the radioelements (d) the physics and chemistry of high activity level matter and (e) radiotracer studies. We have dealt with several of these topics in Chapters 4, 13, 15, and 16. In this chapter, we will discuss the basic principles behind radiochemical techniques and some details of their application.

Because of the small amounts of material involved, the presence of radioactivity which implies certain regulatory and safety concerns and the frequent need to deal with short-lived nuclei, these techniques are not the same as ordinary chemical techniques. Specialized techniques have evolved from the early part of the 20\textsuperscript{th} century when chemistry was a principal tool in identifying the basic nature of radioactive decay through the extensive use of chemistry in the Manhattan Project in World War II to the present, “high tech” character of many radiochemical manipulations. These techniques are quite important for they are often the key to a successful experiment even though they may get scant mention in descriptions of the experiment. Often the successful application of these techniques requires careful, painstaking attention to detail, frequent practice to develop the necessary manipulative skills and a thorough knowledge of the underlying scientific principles.
In addition to the discussions of these topics in textbooks such as this, there are excellent textbooks that focus primarily on radiochemistry [2-4].

19.1 Unique Aspects of Radiochemistry

Radiochemistry involves the application of the basic ideas of inorganic, organic, physical and analytical chemistry to the manipulation of radioactive material. However, the need to manipulate radioactive materials imposes some special constraints (and features) upon these endeavors. The first of these involves the number of atoms involved and the solution concentrations. The range of activity levels in radiochemical procedures ranges from pCi to MCi. For the sake of discussion, let us assume an activity level, D, typical of radiotracer experiments of 1 µCi (= 3.7 x 10^4 dis/s = 3.7 x 10^4 Bq), of a nucleus with mass number \( A \approx 100 \). If we assume a half-life for this radionuclide of 3 days, the number of nuclei present can be calculated from the equation

\[
N = \frac{D}{\lambda} = \frac{(1\muCi)(3.7 \times 10^4 \text{ dps/\muCi})(3 \text{ days})(24 \text{ hr/day})(3600 \text{ s/hr})}{\ln 2}
\]

where \( \lambda \) is the decay constant of the nuclide (= ln 2/t_{1/2}). Then

\[ N \approx 1.4 \times 10^{10} \text{ atoms} \]

\[ \text{Mass of sample} = 2.3 \times 10^{-12} \text{ g} \]

This quantity of material, if prepared as an aqueous solution of volume 1 L would have a concentration of 10^{-14} mol/L. This simple calculation demonstrates a number of the important features of radiochemistry, i.e., (a) the manipulation of samples involving infinitesimal quantities of material (b) the power of nuclear analytical techniques (since 1
µCi is a significant, easily detectable quantity of radioactivity) and (c) in an extension of the calculation, since the decay of a single atom might occur by α-particle emission (with 100% detection efficiency), the ability to do chemistry one atom at a time.

The small number of atoms involved in some radiochemical procedures can alter expected behavior. Although time dependent processes obeying first order kinetics are not changed by changes in concentration, the same is not true of second order kinetics. For example, at 10⁻² M, isotopic exchange between U (IV) and U (VI) has a lifetime of ~ 2 hours while at 10⁻¹⁰ M; the same lifetime is ~400 days. Another example is Np (V) which is unstable with respect to disproportionation and yet µCi/L solutions of NpO₂⁺ are stable. The extreme dilution in some solutions can mean equilibrium is not reached due to kinetic limitations. Fallout plutonium, present in the aqueous environment at concentrations of 10⁻¹⁸ – 10⁻¹⁷ M, has not reached equilibrium in over 40 years.

In addition to the limitations posed by kinetics or thermodynamics, there are certain practical problems associated with very low solution concentrations. An important problem is the adsorption of tracer levels of radioactivity on the surfaces of laboratory glassware. Glass has an ion exchange capacity of 10⁻¹⁰ mol/cm² along with a similar number of chemisorption sites. A 100 mL beaker can thus absorb ~10⁻⁸ mol which is significant if the concentration of the tracer is ≤ 10⁻⁶ M. One suppresses this absorption by having high [H⁺] (thus blocking adsorption sites), by treating glass surfaces with non-adsorbing silicone coatings or by the use of holdback carriers (see below).

Conventional analytical techniques generally operate at the ppm or higher levels. Some techniques such as laser photo acoustic spectroscopy are capable of measuring phenomena at the 10⁻⁸-10⁻⁶ mol/L level. The most sensitive conventional analytical techniques, time-
resolved laser-induced fluorescence and ICP-MS are capable of measuring concentrations at the part per trillion level, \(i.e.,\) 1 part in \(10^{12}\), but rarely does one see detection sensitivities at the single atom level as routinely found in some radioanalytical techniques. While techniques such as ICP-MS are replacing the use of neutron activation analysis in the routine measurement of ppb concentrations, there can be no doubt about the unique sensitivity associated with radioanalytical methods.

Along with the unique sensitivity and small quantities of material associated with radiochemistry, there is the need to comply with the regulations governing the safe use and handling of radioactive material. This task is a primary focus in the design and execution of radiochemical experiments and is often a significant factor in the cost of the experiment. Because so many of these rules are site specific, they are not treated in this chapter.

There are some chemical effects that accompany high specific activities that are unique to radiochemistry and are worth noting. Foremost among these are the chemical changes accompanying radioactive decay. The interaction of ionizing radiation from a radioactive source with air can result in the generation of ozone and the nitrous oxides, which can lead to corrosion problems. Sources containing Ra or Rn produced from the decay of heavier elements, such as U, will emanate Rn gas as the decay product of Ra. The decay products of gaseous Rn are particulates that deposit on nearby surfaces, such as the interior of the lungs, leading to contamination problems. In high activity aqueous solutions, one can make various species such as the solvated electron, \(e_{aq}^-\), hydroxyl radicals, \(\text{OH}^\bullet\), as well as the solvated proton, \(\text{H}_3\text{O}^\bullet\). The hydroxyl radical, \(\text{OH}^\bullet\), is a strong oxidizing agent with

\[
\text{OH}^\bullet + e^- \rightarrow \text{OH}^- \quad E_0 = 2.8 \, \text{V}.
\]
while the solvated electron, $e_{aq}^-$, is a strong reducing agent

$$e_{aq}^- + H^+ \rightarrow \frac{1}{2} H_2 \quad E_0 = 2.77 \text{ V}$$

Solutions involving high activity levels will change their redox properties as a function of time. For example, all the atoms in a 100 Bq/mL ($10^{-7}$ mol/L) solution of $^{239}$Pu will undergo a redox change in a period of one year. In general, it is hard to keep high specific activity solutions stable. Reagents, column materials, etc. can suffer radiation damage also. In radiotracer studies, the self-decomposition (radiolysis) of $^3$H or $^{14}$C-labeled compounds can lead to a variable concentrations and variable number of products.

Many of these effects of radioactive decay can be treated quantitatively using “G values.” Historically the G value was defined as the number of molecules or species decomposed or formed per 100 eV of absorbed energy. A newer (SI) definition of the G value is the number of moles of molecules or species formed or decomposed per Joule of energy absorbed. (Note that 1 mol/J = 9.76 x $10^6$ molecules/100 eV). G values depend on the radiation and the medium being irradiated and its physical state. Table 19-1 shows some typical G values for the irradiation of neutral liquid water

<table>
<thead>
<tr>
<th>Radiation</th>
<th>$G(-H_2O)$</th>
<th>$G(H_2)$</th>
<th>$G(H_2O_2)$</th>
<th>$G(e_{aq})$</th>
<th>$G(\cdot H\cdot)$</th>
<th>$G(\cdot OH)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$ and fast electrons</td>
<td>0.43</td>
<td>0.047</td>
<td>0.073</td>
<td>0.062</td>
<td>0.28</td>
<td>0.0027</td>
</tr>
<tr>
<td>12 MeV $\alpha$-particles</td>
<td>0.29</td>
<td>0.12</td>
<td>0.11</td>
<td>0.028</td>
<td>0.056</td>
<td>0.007</td>
</tr>
</tbody>
</table>
The actual final products of radiolysis are the result of a complex set of chemical reactions. Detailed quantitative estimates of product yields are therefore more complicated and beyond the scope of this book. The reader is referred to other textbooks that discuss how these estimates are made. [5]

Radioactive decay also causes chemical transmutations. The daughter nucleus in α or β-decay is a different chemical element than the mother nucleus, but it is in the same chemical environment as the mother nucleus. Change of oxidation state or bonding is a possibility.

In alpha decay, one expects all chemical bonds to the decaying atom to be broken as the recoil energy of the daughter nucleus exceeds chemical bond energies. Surprisingly, the oxidation state of the daughter nucleus is frequently that of the parent nucleus after all electronic and atomic re-arrangements have taken place. (An obvious exception is when the daughter cannot exhibit the parent’s oxidation state such as the α-decay of U(VI) as UO$_2$$^{2+}$ where the daughter does not exhibit the +6 oxidation state.)

In β$^-$ decay, especially for low energy β$^-$ emitters like $^{14}$C or $^3$H, the effects on chemical bonding are modest. So if we have

\[ ^{14}\text{CH}_4 \rightarrow ^{14}\text{NH}_4^+ \]

the β$^-$ decay can be considered an oxidizing process. In fact, β$^-$ decay (of $^{83}$SeO$_4^{2-}$ and $^{242}$AmO$_2^{2+}$) was used successfully to prepare new higher oxidation states (of $^{83}$BrO$_4^-$ and $^{242}$CmO$_2^{2+}$) of some elements. In electron capture or internal conversion decay, there are massive rearrangements of the atomic electrons, which makes these considerations more complicated.
Some tracers (usually cations) in solution behave as colloids rather than true solutions. Such species are termed radiocolloids and are aggregates of \(10^3 \text{ – } 10^7\) atoms, with a size of the aggregate in the range \(0.1 \text{ – } 500\) nm. They are quite often formed during hydrolysis, especially of the actinides in high oxidation states. One can differentiate between real radiocolloids and pseudo-colloids, in which a radionuclide is sorbed on an existing colloid, such as humic acid or Fe(OH)$_3$. Formation of real colloids can be prevented by using solutions of low pH or by addition of complexing agents. The chemical behavior of these radiocolloids is difficult to predict, as the systems are not at equilibrium.

There are certain unique features to the chemical separations used in radiochemistry compared to those in ordinary analytical chemistry that are worth noting. First of all, high yields are not necessarily needed, provided the yields of the separations can be measured. Emphasis is placed on radioactive purity, expressed as decontamination factors rather than chemical purity. Chemical purity is usually expressed as the ratio of the number of moles (molecules) of interest in the sample after separation to the number of \(all\) the moles (molecules) in the sample. Radioactive purity is usually expressed as the ratio of the activity of interest to that of all the activities in the sample. The decontamination factor is defined as the ratio of the radioactive purity after the separation to that prior to the separation. Decontamination factors of \(10^5 \text{ – } 10^7\) are routinely achieved with higher values possible. In the event that the radionuclide(s) of interest are short-lived, then the time required for the separation is of paramount importance, as it does no good to have a very pure sample in which most of the desired activity has decayed during the separation.

As indicated above, frequently the amount of material involved in a radiochemical procedure is quite small. To obviate some of the difficulties associated with this, a
weighable amount (~mg) of inactive material, the *carrier*, is added to the procedure at an early stage. It is essential that this carrier and the radionuclide (tracer) be in the same chemical form. This is achieved usually by subjecting the carrier + tracer system to one or more redox cycles prior to initiating any chemical separations to insure that the carrier and tracers are in the same oxidation state.

Carriers frequently are stable isotopes of the radionuclide of interest, but they need not be. Non-isotopic carriers are used in a variety of situations. *Scavengers* are non-isotopic carriers used in precipitations that carry/incorporate other radionuclides into their precipitates indiscriminately. For example, the precipitation of Fe (OH)₃ frequently carries, quantitatively, many other cations that are absorbed on the surface of the gelatinous precipitate. Such scavengers are frequently used in chemical separations by precipitation in which a radionuclide is put in a soluble oxidation state, a scavenging precipitation is used to remove radioactive impurities and then the nuclide is oxidized/reduced to an oxidation state where it can be precipitated. In such scavenging precipitations, *holdback carriers* are introduced to dilute the radionuclide atoms by inactive atoms and thus prevent them from being scavenged.

It is certainly possible, although usually more difficult, to do *carrier-free* radiochemistry in which one works with the radionuclides in their low, tracer-level concentrations. Such carrier-free radiochemistry is used when the presence of the additional mass of carrier atoms would lead to problems of sample thickness (alpha-emitters), biological side effects (radiopharmaceuticals) or where high specific activities are needed (synthesis of labeled compounds). (Formally, *specific activity* is the activity per mass unit, such as mCi/mg or µCi/µmol, etc.)
19.2 Availability of Radioactive Material

To do radiochemistry, one needs radioactive materials. As indicated in Chapter 3, radionuclides may be classified as primordial (remnants of nucleosynthesis), cosmogenic (being continuously generated by the action of cosmic rays with the upper atmosphere) or anthropogenic (made by man). Most of the radionuclides used in radiochemistry are of the latter type, *i.e.*, made artificially in response to perceived needs. In Table 4-1, we summarized the commonly used radionuclides and their method of preparation. As indicated in this table, a large number of these nuclides can be made by neutron irradiation in a nuclear reactor using \((n,\gamma)\) reactions. Such nuclei are, of course, not carrier-free, are largely \(\beta^-\) emitters and have low specific activities. Charged particle induced reactions, using cyclotrons, are used to synthesize neutron-deficient nuclei, that decay by EC or \(\beta^+\) emission. The short-lived nuclei used in PET or other procedures in nuclear medicine fall into this category.

The transuranium nuclei are a special class of radionuclides, being made by both reactor irradiation and production in charged particle accelerators. In Table 19-2, we summarize the properties and available amounts for research in the United States by qualified individuals.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>(t_{1/2})</th>
<th>Decay Mode</th>
<th>Amounts Available</th>
<th>Specific Activity (dpm/µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{237})Np</td>
<td>(2.14 \times 10^6) years</td>
<td>(\alpha, \text{SF}(10^{-10}%))</td>
<td>kg</td>
<td>1565.</td>
</tr>
<tr>
<td>Element</td>
<td>Half-Life</td>
<td>Activity</td>
<td>Decay Mode</td>
<td>SF (%)</td>
</tr>
<tr>
<td>---------</td>
<td>-----------</td>
<td>----------</td>
<td>------------</td>
<td>--------</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>433 years</td>
<td>$\alpha$, SF(10$^{-10}$%)</td>
<td>kg</td>
<td>10-100 g</td>
</tr>
<tr>
<td>$^{243}$Am</td>
<td>7.38 x 10$^5$ years</td>
<td>$\alpha$, SF(10$^{-8}$%)</td>
<td>100 g</td>
<td>4.4 x 10$^5$</td>
</tr>
<tr>
<td>$^{243}$Cm</td>
<td>28.5 days</td>
<td>$\alpha$, SF(10$^{-9}$%)</td>
<td>10-100 mg</td>
<td>7.4 x 10$^9$</td>
</tr>
<tr>
<td>$^{244}$Cm</td>
<td>18.1 years</td>
<td>$\alpha$, SF(10$^{-4}$%)</td>
<td>10-100 g</td>
<td>1.80 x 10$^8$</td>
</tr>
<tr>
<td>$^{248}$Cm</td>
<td>3.40 x 10$^5$ years</td>
<td>$\alpha$, SF(8.3%)</td>
<td>10-100 mg</td>
<td>9.4 x 10$^3$</td>
</tr>
<tr>
<td>$^{249}$Bk</td>
<td>320 days</td>
<td>$\beta$, $\alpha$(10$^{-3}$%), SF(10$^{-8}$%)</td>
<td>10-50 mg</td>
<td>4.4 x 10$^5$</td>
</tr>
<tr>
<td>$^{249}$Cf</td>
<td>350.6 years</td>
<td>$\alpha$, SF(10$^{-7}$%)</td>
<td>1-10 mg</td>
<td>9.1 x 10$^5$</td>
</tr>
<tr>
<td>$^{250}$Cf</td>
<td>13.1 years</td>
<td>$\alpha$, SF(0.08%)</td>
<td>10 mg</td>
<td>1.2 x 10$^9$</td>
</tr>
<tr>
<td>$^{252}$Cf</td>
<td>2.6 years</td>
<td>$\alpha$, SF(3.1%)</td>
<td>10-1000 mg</td>
<td>5.6 x 10$^8$</td>
</tr>
<tr>
<td>$^{254}$Cf</td>
<td>60.5 days</td>
<td>SF, $\alpha$(0.3%)</td>
<td>$\mu$g</td>
<td>1.1 x 10$^{10}$</td>
</tr>
<tr>
<td>$^{253}$Es</td>
<td>20.4 days</td>
<td>$\alpha$, SF(10$^{-5}$%)</td>
<td>1-10 mg</td>
<td>5.6 x 10$^{10}$</td>
</tr>
<tr>
<td>$^{254}$Es</td>
<td>276 days</td>
<td>$\alpha$, SF(0.2%)</td>
<td>1-5 µg</td>
<td>1.1 x 10$^{10}$</td>
</tr>
<tr>
<td>$^{257}$Fm</td>
<td>100.5 days</td>
<td>$\alpha$, SF(0.2%)</td>
<td>1 µg</td>
<td>1.1 x 10$^{10}$</td>
</tr>
</tbody>
</table>

One should also note that while large quantities of $^{239}$Pu are available, it is classified as a Special Nuclear Material because of its use in weaponry and very strict regulations govern the possession and use of this nuclide (along with $^{233}$U and $^{235}$U).

### 19.3 Targetry

As indicated above, a combination of reactor and cyclotron irradiations is used to prepare most radionuclides. While many of these radionuclides are available commercially, some are not. In addition, nuclear structure, nuclear reactions and heavy element research require accelerator or reactor irradiations to produce short-lived nuclei or to study the dynamics of nuclear collisions, etc. One of the frequent chores of radiochemists is the preparation of accelerator targets, and samples for reactor irradiation. It is this chore that we address in this section.

The first question to be addressed in preparing accelerator targets or samples for irradiation is the question of impurities and/or other chemical constituents of the sample. For neutron irradiation, one generally prefers metals or non-activable inorganic salts. The salts usually include nitrates, sulfates, etc., but not halides (especially chlorides due to the
activation of chlorine) nor sodium nor potassium salts. In general, one avoids materials that undergo radiolysis although it is possible, with suitable precautions, to irradiate materials, such as gasoline, oil, and other flammable materials in reactors. Liquid samples can be irradiated in reactors easily, but one must generally pay attention to pressure buildup in the irradiation container due to radiolytic decomposition of water. Unless purged with nitrogen, water will contain dissolved argon, which will activate to form $^{41}\text{Ar}$, and the radioactive atoms will be released upon opening the irradiation container. For irradiations of a few hours in moderate flux ($\sim 10^{12} \text{n/cm}^2\text{sec}$) reactors, the samples to be irradiated may be heat sealed in polyethylene vials, usually using double encapsulation. For long irradiations or higher fluxes ($\sim 10^{15} \text{n/cm}^2\text{sec}$) encapsulation in quartz is needed. One never uses Pyrex or other boron-containing glasses due to their high cross sections for neutron absorption. When irradiating larger samples, one must pay attention to self-shielding in the samples. For example, the flux reduction in a 0.5 mm Au foil is about 27% due to self-absorption. However, in irradiations of most liquid samples or geological samples, these self-absorption corrections can be neglected.

Preparation of the targets for charged particle irradiations requires more effort due to the large rate of energy loss of charged particles in matter. In general, material to be irradiated must be in vacuum, thus making the irradiation of liquids and gases more difficult. Solids must be in the form of thin foils or deposits on thin backing material. Typical backing materials are carbon, aluminum, beryllium, and titanium. The typical measure of thickness of accelerator targets is in units of areal density (mass/unit area, \textit{i.e.}, mg/cm$^2$). The thickness expressed in units of areal density (mg/cm$^2$) is the linear thickness (cm) multiplied by the density (mg/cm$^3$). One can weigh very thin samples and
determine their area and thus their areal density. Typical thicknesses of accelerator targets are \( \sim 0.1 - 5 \text{ mg/cm}^2 \), but depend, of course, on the rate of energy loss of the irradiating ion in passing through the target material. Target backings are frequently 10 - 100 \( \mu \text{g/cm}^2 \). Such thicknesses qualify as being “thin”, \textit{i.e.}, easily breakable and require special preparation techniques.

Because of the high rate of energy loss of charged particles in matter, one must pay attention to cooling the targets or in some way, dissipating the energy deposited in the target material as the beam nuclei pass through it. For example, consider the irradiation of a 0.5 \( \text{ mg/cm}^2 \)\(^{208}\text{Pb} \) target by 450 MeV \(^{86}\text{Kr} \) ions. Each Kr ion passing through the target deposits \( \sim 8.1 \text{ MeV} \) in the target. If the Kr beam intensity is 1 particle-\( \mu \text{a} \) (6.24 x \( 10^{12} \) ions/sec), then the rate of energy deposit in the target is \( \sim 5 \times 10^{13} \text{ MeV/s} = 8.1 \text{ J/s} \). If the foil has an area of 2 cm\(^2\), it would have a mass of 1 g. The specific heat of Pb is 0.130 J/g/°C. Thus, in the absence of any cooling, the temperature of the target would rise \( 8.1^\circ/\text{sec} \) and the foil would soon melt. Since the foil will generally be in vacuum, without further intervention, it would only cool radiatively, which will not suffice. Heat transfer from such a foil can occur by clamping it to the front of a cooled block (remembering now that the entire beam energy will be dumped into the cooling block). Alternately a jet of a light gas such as helium can be used to cool the backside of the foil or the particle beam can be spread over a larger area foil thus reducing the temperature increase.

Over the years, a number of specialized techniques have been developed for the preparation of accelerator targets. These techniques are also used in the preparation of thin sources for counting, such as those used in alpha or beta spectroscopy. The first and simplest technique for depositing a target material on a backing foil is by \textit{evaporation} of a
solution of the desired material on the foil. Generally this is a poor choice as the solute tends to deposit at the edges of the dried droplet, leading to variations of up to a factor of 100 in thickness over the area of the deposit. Uniformity can be improved by using a spreading agent such as insulin to coat the surface of the backing material prior to evaporation.

A method that was widely used in the past is **electrospraying**. A solution of the nuclide to be deposited is prepared in a volatile, non-conducting liquid like acetone, alcohol, etc. A capillary is drawn out to a fine point such that no liquid can escape under normal conditions and filled with the solution. A fine wire is threaded though the capillary to within a few mm of the tip. A high voltage (3 – 10 KV) is applied between the wire in the tube and the backing material on which the deposit is to be made. One gets a spray of charged drops that are collected on the backing material, placed ~ 1 cm from the capillary. The volatile solvent evaporates leaving a uniform film. The deposit can be calcined.

Another widely used technique for preparing thin deposits on a backing material is **electrodeposition**. Two types of electrodeposition are commonly used: (a) the direct deposit of a metal on a cathodic surface by reduction or (b) precipitation of a cationic species in an insoluble form on an electrode. This latter technique is widely used to deposit actinides and lanthanides. A 10 – 100 µL aqueous solution of the actinide or lanthanide is mixed with ~15 mL of isopropyl alcohol and placed in a plating cell (Figure 19-1). The inorganic material forms a positively charged complex in which the inorganic molecule is surrounded by a cluster of solvent molecules. A high voltage (~ 600 V) is applied between a rotating anode and the cathodic backing material. The positively charged complex is attracted to the cathode of the cell. The lanthanides/actinides precipitate as hydrous
oxides near the cathode which is a region of high pH. The alcohol is withdrawn from the cell and the deposit is dried and calcined. This technique is called molecular plating because the film is not that of the metal but some molecular form of it. Deposit thicknesses are restricted to < 0.5 mg/cm² but the deposition is rapid and quantitative and allows the use of active metals such as Al as backing foils. [6]

Figure 19-1 Schematic diagram of molecular plating cell. From Wang, Willis, and Loveland.

Vacuum deposition is a well-established technique for making very uniform deposits of non-refractory materials on a backing material. In Figure 19-2, we show a typical simple evaporation apparatus.
Figure 19-2 Simple schematic diagram of a vacuum deposition apparatus. From Wang, Willis and Loveland.

The material to be evaporated is placed in a sample holder. Frequently these sample holders are indented strips of W, Ta, or Mo, or wire baskets of the same metals, or carbon crucibles. These sample holders can be heated resistively by passing a large current through them, thus melting and then volatilizing the material. Alternatively the sample holder can be bombarded by low energy electrons to heat the sample. The entire process takes place in vacuum. Under reduced pressure, most materials melt readily and then evaporate. The substrate on which the vapors from the heated sample condense is placed some distance from the source of evaporating material. The area of the deposit may be defined by collimators. The deposits produced by vacuum evaporation are very uniform, but the process is not efficient, with < 1% of the sample material being deposited in typical
applications. Self-supporting deposits can be prepared if the substrate on which the vapors condense is coated with a release agent prior to evaporation.

The thicknesses of these thin targets can be measured using a variety of techniques. The simplest and most reliable method is weighing. One weighs a known area of target material and computes its areal density. Such a technique will give the average deposit thickness but no information about its uniformity or composition. The uniformity of targets or thin foils can be measured with $\alpha$-particle thickness gauges. In such devices, a collimated beam of low energy $\alpha$-particles passes through the foil whose thickness is to be measured. Changes in count rate are noted as the beam scans over the area of the target or foil. To get absolute thicknesses from such devices, calibration with foils of known thickness is needed. This technique works best when the energy of the $\alpha$-particle is so low as to barely pass through the foil. In this case, small changes in thickness are magnified in the observed count rate. X-ray fluorescence or neutron activation analysis can be used to determine the elemental composition of the target or source material. Approximate values of the target thicknesses can also be obtained by noting the energy loss of monoenergetic ions as they pass through a foil. The thicknesses are calculated from the observed $\text{d}E/\text{d}x$ and empirical stopping power relationships.

19.4 Measuring Beam Intensity and Fluxes

Measurement of charged particle beam intensities is largely done using physical methods, although some older radiochemical methods are used occasionally. The most common techniques to measure the intensity of a charged particle beam is through the use of a Faraday cup. The beam is stopped in an electrically isolated section of beam pipe referred to as a Faraday cup (Figure 19-3).
The collected charge is measured with an electrometer that functions as a current integrator. The beam intensity is just the current divided by the charge on each ion. Care must be taken regarding the loss of secondary electrons. (The beam will liberate secondary electrons in the material in which it stops). If these electrons escape, their positive ion partners will add to the positive charges of the stopped ions, thus causing an overestimate of the beam current. The Faraday cup is thus made as a long cylinder to inhibit electron escape geometrically, and a magnetic field is applied to the cup along with a suppressing voltage to further prevent electron loss.

When the energy of the charged particle beam is too large to easily stop the beam in a Faraday cup, the beam intensity is frequently monitored by a secondary ionization chamber. These ion chambers have thin entrance and exit windows and measure the differential energy loss when the beam traverses them. They must be calibrated to give
absolute beam intensities. If the charged particle beam intensity is very low (< 10^6 particles/sec), then individual particles can be counted in a plastic scintillator detector mounted on a photomultiplier tube.

When performing irradiations with neutrons or high energy protons, it is common to measure the beam intensity using a monitor reaction. A thin foil of a pure element is placed in the irradiating flux near the target and irradiated simultaneously with the target. Then both the reaction products from the target foil and the monitor foil are collected and counted. The flux is calculated using a known cross section for the monitor reaction.

Assuming that the monitor and target foils are exposed to the same irradiating flux, we have, for the activity of the monitor and target foils, A_{mon} and A_{tgt}, respectively, at the end of the irradiation

\[ A_{tgt} = N_r \sigma_r \phi (1 - e^{-\lambda_r t}) \]
\[ A_{mon} = N_m \sigma_m \phi (1 - e^{-\lambda_m t}) \]

where \( N_i, \sigma_i, \lambda_i \) are the number of target atoms, cross section and product decay constant for the \( i \)th reaction. The cross section for the reaction of interest, \( \sigma_r \), is

\[ \sigma_r = \frac{A_{tgt}}{N_r \phi (1 - e^{-\lambda_r t})} \]

Substituting for \( \phi \) in terms of the monitor reaction, we get

\[ \sigma_r = \frac{A_{tgt}}{A_{mon}} \cdot \frac{N_r}{N_{mon}} \cdot \left( \frac{1 - e^{-\lambda_r t}}{1 - e^{-\lambda_m t}} \right) \cdot \sigma_{mon} \]

If the irradiation is long enough to produce saturation activities in both the target and monitor foils, we have

\[ \sigma_r = \frac{A_{tgt}}{A_{mon}} \cdot \frac{N_r}{N_{mon}} \cdot \sigma_{mon} \]
For high energy protons, typical monitor reactions are $^{27}\text{Al} \rightarrow ^{24}\text{Na}$, $^{27}\text{Al} \rightarrow ^{22}\text{Na}$, $^{12}\text{C} \rightarrow ^{7}\text{Be}$, $^{27}\text{Al} \rightarrow ^{18}\text{F}$, $^{197}\text{Au} \rightarrow ^{149}\text{Tb}$, and $^{12}\text{C}(\text{p,pn})^{11}\text{C}$ where the arrows indicate a complex set of reaction paths leading from the initial nucleus to the product nucleus. Care must be taken in the case of reactions producing $^{24}\text{Na}$ or $^{11}\text{C}$ to correct for secondary neutron-induced reactions that produce these nuclides. In high energy reactions, the loss of recoils from the monitor or target foils can be corrected for by irradiating a stack of three identical foils and only counting the center foil. The forward-going recoils from the first foil enter the second foil and compensate for its forward recoil loss. The backward recoils from the third foil enter the second foil and compensate for its backward recoil loss.

The measurement of neutron fluxes by foil activation is more complicated because the neutrons are not monoenergetic and the monitor cross sections are energy dependent. The simplest case is monitoring slow neutron fluxes. Radiative capture $(n,\gamma)$ reactions have their largest cross sections at thermal energies and are thus used in slow neutron monitors. Typical slow neutron activation detectors are Mn, Co, Cu, Ag, In, Dy and Au. Each of these elements has one or more odd $A$ isotopes with a large thermal $(n,\gamma)$ cross section, $\sim 1\text{-2000 b}$. The $(n,\gamma)$ reaction products have half-lives ranging from minutes to hours. The activation cross sections generally vary as $1/v$ although some nuclides have resonances in the capture cross sections for neutrons with energies between 1 and 1000 eV. A correction for such resonance capture can be made by irradiating the monitor foils with and without a Cd cover. The $(n,\gamma)$ cross section for Cd below 0.4 eV is very large and is small for energies above this and thus very few low energy neutrons penetrate the Cd cover. Irradiation of a foil without a Cd cover will cause reactions induced by both thermal and resonance neutrons, while the Cd-covered foil will just respond to resonance neutrons.
One can also use so-called “threshold monitor detectors” where the activating reaction has an energy threshold, such as the \((n,\alpha)\), \((n,p)\), \((n,2n)\) reactions. By exposing a set of threshold detectors (involving different reactions with different thresholds) to a neutron flux, one can determine the relative amounts of different energy groups in the neutron spectrum. Further information about the use of activation detectors to measure neutron fluxes can be found in the textbooks by Knoll [7] and Tsoulfanidis [8].

**19.5 Recoils, Evaporation Residues (EVRs) and Heavy Residues**

In a nuclear reaction, the momentum transfer to the struck nucleus is not negligible. If an \(A=100\) nucleus fuses completely with a 100 MeV \(\alpha\)-particle projectile, the kinetic energy of the completely fused system is \(\sim 4\) MeV. A similar fusion of an \(A=100\) nucleus with a 100 MeV \(^{16}\text{O}\) projectile will give the completely fused system an energy of 13.8 MeV. These energies are extremely large compared to chemical bond energies. Depending upon the position in the target foil where the nuclear reaction takes place, some or all of these recoiling nuclei may escape from the target foil. These recoil nuclei, which are usually radioactive, can be collected or studied using physical or radiochemical techniques. In reactor irradiations, these recoils produce “contamination” on the surface of irradiation containers.

When these heavy recoil nuclei are the result of a complete fusion of the projectile and target nuclei, they are usually called *evaporation residues* because they result from a de-excitation of the primary complete fusion product by particle evaporation (emission). In intermediate energy and relativistic nuclear collisions, the momentum transfer to the target nucleus is much less and the energy of the recoiling nucleus is \(\sim 5-100\) keV/nucleon. Such recoils are usually called *heavy residues*. 
* It should be noted that in this discussion we are tacitly assuming “normal” reaction kinematics with the lighter nucleus being the projectile (that is in motion) and the heavier collision partner being at rest in the laboratory system. In reactions studied using “inverse kinematics” with a heavier projectile striking a lighter target nucleus, the momentum of the recoiling heavy nucleus is approximately the same as that of the projectile nucleus. In inverse kinematics reactions, the energies of the EVRs or heavy residues are large and their spatial and energy distribution is compressed accordingly. Collection of these recoils is relatively easy but high resolution is needed because of the spatial and energy compression.

There are a variety of ways to collect the recoiling heavy products of a nuclear reaction. One radiochemical technique is the so-called “thick target-thick catcher method.” Here a target foil whose thickness exceeds the average range of the recoils is surrounded by catcher foils of C or Al or some other material whose thickness exceeds the range of the recoiling product nucleus which will not lead to production of the nuclide of interest. The average range of the recoiling product, \(<R>\), (which can be related to its total kinetic energy) is given as

\[
< R > = \frac{N_c W}{N_c + N_w}
\]

where \(N_c\) is the number of recoils which escape from the target, \(N_w\) is the number that remains in the target and \(W\) is the thickness of the target. The fraction of product nuclei that recoil into the forward catcher foil, \(F\), and the fraction that recoil into the backward catcher foil, \(B\), can be used to deduce something about the relative velocity imparted to the recoiling nucleus by the initial projectile-target interaction, \(v\), and the isotropic velocity kick, \(V\), given to it by successive momentum kicks by sequential particle emission.

Formally we define the quantity \(\eta\) where \(\eta=v/V\). \(\eta\) can be related to \(F\) and \(B\)

\[
\eta = \frac{(F/B)^{1/2} - 1}{(F/B)^{1/2} + 1}
\]
So the thick target-thick catcher method can lead to crude information about the kinematics of the nuclear reaction under study [9]. This technique can be used to advantage in the study of intermediate energy and relativistic nuclear collisions where the energy of the heavy residues is low (~10-100 keV/nucleon). In this case, most of the residues stop in the target foil and cannot be studied any other way.*

For the study of recoils in low energy and some intermediate energy reactions, one can use a thin target (< 0.5 mg/cm²). The energy loss of the recoils in emerging from these targets is negligible or calculable and tolerable. With thin target irradiations, one can stop the recoiling nuclei in a catcher foil, which can be counted, perhaps after intervening chemical separations to isolate the products of interest. The “catcher foil” can take the form of a tape or rotating wheel that can rapidly transport the activity to a remote, low background location for counting. Alternatively, the “catcher foil” can take the form of a stack of thin foils that stop the products. These foils, upon disassembly and counting, can be used to construct a differential range distribution for products of interest. Catcher foils or stacks of foils can be mounted at various angles with respect to the incident beam and can be used to measure product angular or energy distributions. These catcher foil techniques are now only used to study reactions with very low cross sections where their use provides a high detection sensitivity.

The “catcher foil” can take the form of a jet of rapidly moving gas, a helium jet. The atoms produced in a nuclear reaction recoil out of a thin target and are stopped in ~1 atm of helium gas in the target chamber. The gas contains an aerosol, typically an alkali halide, to which charged reaction product recoils attach themselves via van der Waals forces. The helium gas (and the aerosol particles) escapes through a small orifice to a vacuum
chamber, with the gas achieving sonic velocity. The gas and aerosol can be transported for substantial distances in thin capillary tubes. The aerosol particles (and the attached atoms) are collected by allowing the gas stream to strike a collector surface. The resulting deposit can be counted directly or dissolved for further chemical processing. The aerosol loaded gas stream (jet) can also be used to transport the atoms through a thin capillary a distance of several meters in a few seconds. If the carrier gas is extremely pure helium gas, then the residues will remain ionized and can be collected using electrostatic devices. A number of systems have been developed and used to collect reaction products as ions without involving aerosols in the carrier gas.

The principal limitation of the isolation devices discussed previously (tapes, jets, etcetera) is that the reaction product must be stopped and mechanically transported to radiation detectors before product identification can occur. This restricts their use to studies of nuclei whose \( t_{1/2} > 1 \) ms. For detection and identification of species whose \( t_{1/2} < 1 \) ms, one employs instruments based upon direct magnetic and/or electrostatic deflection of target recoils. The most spectacularly successful of these devices is the velocity filter SHIP (Figure 15-7). Evaporation residues produced in compound nucleus reactions emerge from the target and pass through a thin carbon foil which has the effect of equilibrating the ionic charge distribution of the residues. The ions then pass through two filter stages consisting of electric deflectors, dipole magnets, and a quadruple triplet for focusing. The solid angle of acceptance of the separator is 2.7 msr with a separation time for the reaction products of \(~ 2 \) \( \mu \)s with a total efficiency of collecting evaporation residues of \(~ 20\% \) for \( A_{\text{proj}} > 40 \). Since complete fusion evaporation residues have very different velocities and angular distributions than target-like transfer and deep-inelastic products (a
factor of ~ 2 difference in velocity between transfer products and evaporation residues) and beam nuclei, the separator with its ± 5% velocity acceptance range and narrow angular acceptance very effectively separates the evaporation residues from the other reaction products and the beam. Following separation, the residues pass through a large area time of flight detector and are stopped in an array of position-sensitive detectors. From their time of flight and the energy deposited as they stop in the position sensitive detectors, a rough estimate of their mass may be obtained (dA/A ~0.01). The final genetic identification of the residues is made by recording the time correlations between the original position signals from the detectors and subsequent decay signals from the same location (due to alpha or spontaneous fission decay) and/or signals from γ or x-ray detectors placed next to the position-sensitive detector. This device for studying heavy element evaporation residues was used in the discovery of elements 107-112 (Chapter 15).

An alternate method of recoil collection and separation from other reaction products is the gas-filled separator. Unlike the vacuum separators SHIP at GSI or the Fragment Mass Analyzer at ANL that can only accept a limited range of charge-to mass ratios, a gas-filled separator is a magnetic separator that is filled with a low pressure (~ 1 torr) gas (usually H or He). Evaporation residues emerging from the target undergo charge charging collisions in the gas and quickly equilibrate to a common average charge state. The change in recoil charge states with gas pressure in a gas-filled magnet is shown in Figure 19-4. At a pressure ~ 1 torr, all recoils have a common average charge state. This charge state will differ from the charge of the projectile nuclei or other reaction products. This charge equilibration allows a
Figure 19-4 Changes in focal plane distributions in a gas-filled magnet for the reaction involving 350 MeV $^{58}$Ni ions. From M. Paul, Nucl. Instru. Meth. A277, 418 (1989).

very efficient collection of the recoils but with a loss of the detailed mass selection obtained in vacuum separators like SHIP that use both electric and magnetic fields for separation. The appropriate magnetic rigidity to collect a given product nuclide with a gas-filled separator can be roughly described by the simple formula

$$B\rho = \frac{mv}{q_{ave}} = \frac{mv}{[(v/v_0)eZ^{1/3}]} = 0.0227 A^{1/3} Tm$$
where \( m \), \( Z \), and \( v \) are the mass, atomic number and velocity of the recoiling ion, respectively and \( v_0 \) is the Bohr velocity, \( 2.18 \times 10^6 \) m/s. (In reality, \( q_{\text{ave}} \) is a sensitive function of the atomic structure of the recoiling ion and the gas [10]). The magnetic rigidity is proportional to the recoil velocity so that recoils of the same charge and velocity are focused. The primary beam is separated from the recoils right after the target by a dipole bending magnet followed by two quadrupole magnets that focus the beam onto the focal plane. For the study of heavy element production reactions, collection efficiencies of 25 – 50% can be achieved.

**19.6 Radiochemical Separation Techniques**

In the study of nuclear reactions, nuclear structure, and the heaviest elements, one frequently needs to *chemically* separate the nuclide(s) of interest from other radioactive species that are present. This is done by performing radiochemical separations that involve the conventional separation techniques of analytical chemistry adapted to the special needs of radiochemistry. For example, radiochemical purity is generally more important than chemical purity. When dealing with short-lived nuclides, speed may be more important than yield or purity. The high cost of radioactive waste disposal may require unusual waste minimization steps. As noted earlier, radiochemical separations need not be quantitative. One only needs to know the yield. Because of the availability of modern high resolution counting equipment, such as Ge \( \gamma \)-ray spectrometers, modern radiochemical separations frequently are designed only to reduce the level of radioactive impurities in the sample rather than producing a pure sample. (The counting instrumentation is used to “isolate” the nuclide(s) of interest from other nuclides). Thus,
modern procedures sometimes are similar to qualitative analysis schemes, breaking products into chemically similar groups and using instrumentation to further separate the group members. A recent review summarizes some newer developments of relevance to radiochemistry (11).

**19.6.1 Precipitation**

The oldest, most well established chemical separation technique is *precipitation*. Because the amount of the radionuclide present may be very small, *carriers* are frequently used. The carrier is added in macroscopic quantities and insures the radioactive species will be part of a kinetic and thermodynamic equilibrium system. Recovery of the carrier also serves as a measure of the yield of the separation. It is important that there is an isotopic exchange between the carrier and the radionuclide. There is the related phenomenon of *co-precipitation* wherein the radionuclide is incorporated into or adsorbed on the surface of a precipitate that does not involve an isotope of the radionuclide or isomorphously replaces one of the elements in the precipitate. Examples of this behavior are the sorption of radionuclides by Fe(OH)$_3$ or the co-precipitation of the actinides with LaF$_3$. Separation by precipitation is largely restricted to laboratory procedures and apart from the bismuth phosphate process used in WWII to purify Pu, has little commercial application.

As a practical matter, precipitation is usually carried out in hot, dilute aqueous solutions to allow the slow formation of large crystals. The pH of the solution is chosen to minimize colloid formation. After precipitation, the precipitate is washed carefully to remove impurities, dissolved and re-precipitated to cause further purification. The precipitate is collected by filtration (Figure 19-5).
The filter paper is supported by a glass frit clamped between two glass tubes. The precipitate is washed finally with acetone or alcohol to dry it. The precipitate is chosen to have a known stoichiometry to allow calculation of the yield of the separation and should not absorb water or CO₂ so that an accurate weight can be obtained. (The filter paper used in the filtration must be treated with all the reagents beforehand, dried and weighed so that any material loss in filtration is minimized.)

19.6.2 Solvent Extraction
Separation by liquid-liquid extraction (solvent extraction) has played an important role in radiochemical separations. Ether extraction of uranium was used in early weapons development, and the use of tri-butyl phosphate (TBP) as an extractant for U and Pu was recognized in 1946, resulting in the commercial PUREX process for reprocessing spent reactor fuel (see Chapter 16). In recent years, there has been a good deal of development
of solvent extraction processes for the removal of the transuranic elements, $^{90}$Sr, and $^{137}$Cs from acidic high level waste. Laboratory demonstrations of the TRUEX process that uses the neutral extractant CMPO (octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide) to separate the transuranium elements from acidic high-level waste have been successful. More recently crown ethers have been used as specific extractants for Sr and Cs.

In solvent extraction, the species to be separated is transferred between two immiscible or partially miscible phases, such as water and a nonpolar organic phase. To achieve sufficient solubility in the organic phase, the species must be in the form of a neutral, non-hydrated species. The transfer between phases is achieved by selectively complexing the species of interest causing its solubility in water to decrease with a concomitant increase in its solubility in the organic phase.

A hydrated metal ion ($M^{2+}$) will always prefer the aqueous phase to the organic phase. To get the metal ion to extract, some or all of the inner hydration sphere must be removed. The resulting complex must be electrically neutral and organophilic, that is, have an organic "surface" that interacts with the organic solvent. This can be done by:

a. forming a neutral complex $MA_2$ by coordination with organic anions $A^-$

b. replacing water in the inner coordination sphere by large organic molecules $B$ such that one forms $MB_N^{Z+}$ which is extracted into the organic phase as an ion-association complex $(MB_N)_x^{Z+}I_x^{Z-}$

c. forming metal complexes of form $ML_N^{Z-N}$ with ligands $L$ such that they combine with large organic cations $RB^+$ to form ion pair complexes $(RB^+_N)^{N-Z} (ML_N)_x^{Z-N}$
The extracting agents are thus divided into three classes, polydentate organic anions A, neutral organic molecules B or large organic cations RB⁺.

Polydentate organic anions, which form chelates (ring structures of 4-7 atoms) are important extracting agents. Among these are the β-diketonates, such as acetylacetonate, the pyrazolones, benzoylacetonate, and thenoyltrifluoroacetone (TTA), with the extraction increasing strongly through this sequence. Representing the organic chelating agent as HA, the overall reaction involved in the chelate extraction of a metal ion, Mⁿ⁺, is

\[ M^{n+}(aq) + nHA(o) \leftrightarrow MA_n(o) + nH^+(aq) \]

When an aqueous solution containing extractable metal ions is brought into contact with an organic phase containing chelating agent, the chelating agent dissolves in the water phase, ionizes, complexes the metal ion, and the metal chelate dissolves in the organic phase. The low solubility of the metal complexes and their slow rates of formation limit the industrial use of this type of anionic extraction.

However, a number of organophosphorus compounds are efficient extractants as they and their complexes are very soluble in organic solvents. The most important of these are monobasic diethylhexylphosphoric acid (HDEHP) and dibutylphosphoric acid (HDBP). The actinide MO₂²⁺ ions are very effectively extracted by these reagents as are the actinide (IV) ions.

Among the neutral extractants, alcohols, ethers, and ketones have been used extensively. The most famous example of these is the extraction of uranyl nitrate into diethyl ether, the process used in the Manhattan Project to purify the uranium used in the first reactors. In one of the early large scale processes (the Redox process) to recover
uranium and plutonium from irradiated fuel, methyl isobutyl ketone was used to extract the actinides as nitrates.

The most widely used neutral extractants, however, are the organophosphorus compounds, of which the ester, tributylphosphate (TBP), is the most important. TBP forms complexes with the actinide elements thorium, uranium, neptunium, and plutonium by bonding to the central metal atom via the phosphoryl oxygen in the structure

$$\text{(C}_4\text{H}_9\text{O})_3\text{P}^+\text{—O}^-$$

The overall reactions are

$$MO_2^{2+}(aq) + 2NO_3^-(aq) + 2\text{TBP}(o) \leftrightarrow MO_2(NO_3)_{2 \cdot 2TBP}(o)$$

or

$$M^{2+}(aq) + 4NO_3^-(aq) + 2\text{TBP}(o) \leftrightarrow M(NO_3)_4(TBP)_2(o)$$

These equilibria can be shifted to the right, increasing the degree of extraction by increasing the concentration of uncombined TBP in the organic phase or by increasing the concentration of \([NO_3^-(aq)]\). The latter increase is achieved by adding a salting agent such as HNO_3 or Al(NO_3)_3. These extraction equilibria are the basis of the PUREX process, used almost exclusively in all modern reprocessing of spent nuclear fuel.

A third group of extractants (the cationic extractants) are the amines, especially the tertiary or quarternary amines. These strong bases form complexes with actinide metal cations. The efficiency of the extraction is improved when the alkyl groups have long carbon chains, such as trioctylamine or triisooctylamine. The extraction is conventionally thought of as a "liquid anion exchange" in that the reaction for metal extraction can be written as an anion exchange, that is,
\[ xRB^+L^- (o) + ML_n^{3+} \leftrightarrow (RB^+)_{x} ML_n^{3+} (o) + xL^- \]

where \( ML_n^{3+} \) is the metal anion complex being extracted and \( RB^+ \) is the ammonium salt of the amine. Hexavalent and tetravalent actinides are efficiently extracted using this technique while trivalent actinides are not well extracted under ordinary conditions.

As a practical matter, the distribution ratio \( D \) is defined as

\[ D = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} \]

where \([M]_i\) is the metal ion concentration in the \( i \)th phase. The relevant equilibria, for example, to describe the extraction in systems of lipophilic acidic chelating agents are

\[ \text{HL}_{\text{org}} \rightleftharpoons \text{HL}_{\text{aq}} \]

\[ \text{HL}_{\text{aq}} \rightleftharpoons H^+ + L_{\text{aq}}^- \]

\[ M_{\text{aq}}^{3+} + 3\text{HL}_{\text{org}} \rightleftharpoons (ML_3)_{\text{org}} + 3H^+_{\text{aq}} \]

where \( K_e \) is the equilibrium constant for the last reaction. The distribution coefficient \( D \) is given as

\[ D = \frac{[ML_3]_{\text{org}}}{[M^{3+}]_{\text{aq}}} = \frac{K_e [HL]_{\text{org}}^3}{[H^+]_{\text{aq}}^3} \]

If one introduces a water soluble complexing agent into the system, the \([M^{3+}]_{\text{aq}}\) becomes \([M^{3+}] + [MX^{2+}] + [MX_2^{+}] + ... \) and the measured distribution ratio will include these species as well. The separation factor between two ions, \( S \), is given by the ratio of their distribution coefficients

\[ S = \frac{D_A}{D_B} \]
Thus, the most effective separations will involve cases where the target ion interacts strongly with the extractant but is less strongly complexed by the aqueous ligand X. The percent extraction is given by

\[
\%_{\text{extraction}} = \frac{100D}{D + \left(\frac{V_{\text{aq}}}{V_{\text{org}}}\right)}
\]

where \(V_i\) is the volume of the \(i^{th}\) phase.

19.6.3 Ion Exchange

Ion exchange is one of the most popular radiochemical separation techniques due to its high selectivity and the ability to perform separations rapidly. In ion exchange, a solution containing the ions to be separated is brought into contact with a synthetic organic resin containing specific functional groups that selectively bind the ions in question. In a later step the ions of interest can be removed from the resin by elution with another suitable solution that differs from the initial solution. Typically the solution containing the ions is run through a column packed with resin beads. The resins are typically cross-linked polystyrenes with attached functional groups. Most cation exchangers (such as Dowex 50) contain free sulfonic acid groups, \(\text{SO}_3\text{H}\), where the cation displaces the hydrogen ion. Anion exchangers (such as Dowex 1) contain quaternary amine groups, such as \(\text{CH}_2\text{N(CH}_3\text{)_3Cl}\) where the anion replaces the chloride ion. The resin particles have diameters of 0.08 – 0.16 mm and exchange capacities of 3-5 meq per gram of dry resin.

It is common to absorb a group of ions on the column material and then selectively elute them. Complexing agents, which form complexes of varying solubility with the absorbed ions, are used as eluants. A competition between the complexing agent and the resin for each ion occurs and each ion will be exchanged between the resin and the
complexing agent several times as it moves down the column. This is akin to a distillation process. The rates at which the different ions move down the column vary, causing a spatial separation between “bands” of different ions. The ions can be collected separately in successive eluant fractions (see Figure 19-6).

![Figure 19-6. Elution of tripositive lanthanide and actinide ions on Dowex-50.](image)

The most widely cited application of ion exchange techniques is the separation of the rare earths or actinides from one another. This is done with cation exchange using a complexing agent of $\alpha$-hydroxyisobutyric acid ("$\alpha$-but"). The order of elution of the ions from a cation exchange column is generally in order of the radii of the hydrated ions with the largest hydrated ions leaving first; thus lawrencium elutes first and americium last among the tri-positive actinide ions (see Figure 19-6). In the case of the data of Figure 19-6, the separation between adjacent cations and the order of elution is derived from the
comparative stability of the aqueous actinide or lanthanide complexes with α-
hydroxyisobutyrate. As shown in Figure 19-6, there is a strikingly analogous behavior in
the elution of the actinides and lanthanides that allowed chemists to prove the identity of
new elements in the discovery of elements 97-102 (Bk-No). For cation exchange, the
strength of absorption goes as $M^{4+} > M^{3+} > MO_2^{2+} > M^{2+} > MO_2^+$.

The anion exchange behavior of various elements has been extensively studied. For
example, consider the system of Dowex 1 resin and an HCl eluant. Typical distribution
ratios for various elements as a function of [Cl$^-$] are shown in Figure 19-7. Note that groups
i,2, and 3 are not absorbed on the column. One usually sees a rise in the distribution
coefficient D until a maximum is reached and then D decreases gradually with further
increases in [Cl$^-$]. The maximum occurs when the number of ligands bonding to the metal
atom equals the initial charge on the ion. The decrease in D with further increases in eluant
concentration is due to free anions from the eluant competing with the metal complexes for
ion-exchange resin sites. Figure 19-7 or similar data can be used to plan separations. For
example, to separate Ni(II) and Co (II), one needs simply to pass a 12 M HCl solution of the
elements through a Dowex 1 column. The Co (II) sticks to the column while the Ni (II) is
not absorbed. A mixture of Mn (II), Co (II), Cu (II), Fe (III), and Zn (II) can be separated by
being placed on a Dowex 1 column using 12 M HCl, followed by elutions with 6M HCl (Mn),
4 M HCl (Co), 2.5 M HCl (Cu), 0.5 M HCl (Fe) and 0.005 M HCl (Zn).
Figure 19-7. Elution of elements from anion exchange resin. (12).

In addition to the organic ion exchange resins, some inorganic ion exchanges, such as the zeolites, have been used. Inorganic ion exchangers are used in situations where heat and radiation might preclude the use of organic resins although the establishment of equilibria may be slow.

Newer developments have emphasized the preparation of more selective resins. Among these are the chelating resins (such as Chelex-100) that contain functional groups that chelate metal ions. Typical functional groups include iminodiacetic acids, 8-hydroxyquinoline or macrocyclic units such as the crown ethers, calixarenes or cryptands. The bifunctional chelating ion exchange material, Diphonix® resin—a substituted diphosphonic acid resin, shows promise in treating radioactive waste. Important newer resins include those with immobilized phosphorus ligands. [11]
19.6.4 Exchange Chromatography

Extraction chromatography is an analytical separation technique that is closely related to solvent extraction. Extraction chromatography is a form of solvent extraction where one of the liquid phases is made stationary by adsorption on a solid support. The other liquid phase is mobile. Either the aqueous or the organic phase can be made stationary. Extraction chromatography has the selectivity of solvent extraction and the multistage character of a chromatographic process. It is generally used for laboratory scale experiments although some attempts have been made to use it in larger scale operations. The common applications involve the adsorption of an organic extractant onto a variety of inorganic substrates such as silica or alumina or organic substrates such as cellulose or styrene-divinyl benzene copolymers. When the stationary phase is organic, the technique is referred to as reversed-phase high-performance liquid chromatography. The stationary phase is used in a column just as in ion-exchange chromatography. High pressure pumps are usually used to force the liquid phase through these columns, just as in conventional high-performance liquid chromatography.

The same extracting agents as used in solvent extraction can be used in extraction chromatography. Early applications of extraction chromatography have employed various traditional extractants such as the acidic organophosphorus compounds (di- (2-ethylhexyl) phosphoric acid, HDEHP) or TBP as extractants for the actinide elements. Recent advances have led to a variety of new solvent exchange extractants such as the crown ethers, cryptands or bifunctional organophosphorus compounds. A particularly successful application is the selective sorption of actinides on TRU resins, involving solutions of carbamolymethyl-phosphoryl (CMPO) compounds in TBP sorbed on Amberlite XAD-7.
This resin has found a number of applications in the isolation and subsequent determination of the actinides in complex matrices.

19.6.5 Rapid Radiochemical Separations

Many of the separation techniques we have described take hours to perform. Many interesting nuclei, such as the heavier actinides, the transactinides, or the light nuclei used in PET studies have much shorter half-lives. Thus, we will briefly review the principles of rapid radiochemical separations (procedures that take seconds to minutes) and refer the reader to (13-16) for details.

In most chemical separation procedures, the goal is to selectively transfer the species of interest from one phase to another, leaving behind any unwanted species. The phase-to-phase transfer is rapid, but the procedures to place the species in the proper form for transfer to occur are slow. The goal of rapid radiochemical separations is to speed up existing chemical procedures or to use new, very fast chemical transformations.

Two procedures are commonly used for rapid radiochemical separations, the batch approach and the continuous approach. In the batch approach, the desired activities are produced in a short irradiation, separated and counted with the procedure being repeated many times to reduce the statistical uncertainty in the data. In the continuous approach, the production of the active species is carried out continuously and the species is isolated and counted as produced.

One of the most widely used techniques for rapid chemical separation is that of gas chromatography, which has been developed for use with the transuranium elements by Zvara and co-workers (17). In gas chromatography, volatile elements or compounds are separated from one another by their differences in distribution between a mobile gas phase
and a stationary solid phase. Thermochromatography involves passing a gas through a column whose temperature decreases continuously with distance from the entrance. Thus the less volatile species condense on the column walls first with the more volatile species depositing last. Measurement of the migration times, the deposition temperature, the temperature gradient in the column, etc can allow one to deduce the molar enthalpy of absorption of the compound on the column material. This physical quantity can be compared to quantum chemical calculations of this quantity to gain insight into the bonding properties of the element in question. This technique was used to show the chemical properties (18-20) of the transactinides Rf-Hs and their behavior relative to their chemical congeners.

Another rapid chemical separation technique is separation by volatilization. There are a variety of volatile compounds that can be released from an irradiated material upon dissolution that can, with proper conditions, serve to rapidly chemically separate the elements involved. Examples of such volatile species include I₂, At, GeCl₄, AsCl₃, SeCl₄, OsO₄, RuO₄, Re₂O₇, Tc₂O₇, etc. Separation by volatilization has largely been used for the elements forming volatile hydrides, As, Se, Sn, Sb and Te.

**19.7.1 Low level measurement techniques**

**19.7.2 Introduction**

One of the areas in which the skills of radiochemists are used is the area of low-level chemistry and low level counting. Areas as diverse as the detection of solar neutrinos or the study of environmental radioactivity involve low level techniques. For example, despite concentration of the radiotracers of interest during sampling procedures in environmental studies, quite often one is left with a sample containing a small quantity <
10 ppm of radioactivity that must be assayed. Such essays are referred to as low level techniques. Let us begin our discussion of low level techniques by considering any chemical manipulations of the sample that must be made prior to counting it.

Understandably the fact of having activity levels < 10 dpm, puts severe restrictions on the nature of low level chemistry. Among the requirements for low level chemistry are a small constant blank, high chemical yields for all procedures, high radiochemical purity for all reagents employed, and the ability to place the sample in suitable chemical form for counting.

19.7.3 Blanks

The blank in low-level chemistry is defined as the contribution of the added reagents and other sample constituents to the activity being measured. The blank is determined by performing the chemical procedures without the radioactive sample being analyzed. Care must be taken to ensure that the blank is properly measured and includes all possible contributions to the activity that would be encountered in a real system. For example, in the determination of fission product $^{144}$Ce in seawater, the blank must be determined for each new bottle of reagents used due to the high variability of the $^{144}$Ce content in chemical reagents.

Clearly one of the most effective ways of dealing with a blank correction is to reduce it to its lowest level. Among the factors contributing to the blank correction that can be reduced with care is radiochemical contamination of analytical reagents used in chemical procedures. DeVoe and Sugihara have written extensive review articles [21,22] on this subject and their work should be consulted for detailed information. Typical contamination of most reagents is in the range of $\sim$ 10 to 100 ppm/g reagent, although
individual reagents may contain activity levels of > 10,000 ppm /gram. Some especially troublesome reagents are rare earths (Ce salts in particular), chlorine or sulfur-containing reagents which may contain $^{32}$P contamination, cesium salts (which may contain $^{40}$K or $^{87}$Rb) and potassium salts and other obvious offenders. Precipitating agents, such as tetraphenylborates and chloroplatinates are also particularly pernicious with regards to contamination problems.

Airborne contamination is another possible contribution to the black correction. Here one is chiefly concerned with sample contamination with the daughters of $^{222}$Rn, which have half lives in the 30 to 40 minute range. Steps that can be taken to avoid this problem include eschewing the use of suction filtration in chemical procedures, prefiltering of room air and use of radon traps.

Further lowering of the blank correction occurs when non-isotopic carriers in chemical procedures are used to replace inert carriers of the element of interest when it is difficult to obtain the inert carrier in a contamination free condition. Obviously only clean glassware should be used, reagents should not be reused, and the laboratory should be kept in an immaculate condition. Separations that have high chemical yields and high radiochemical purity reduce the blanks.

**19.7.3 Low level counting--general principles**

Once the low level radioactive sample has been collected and any chemical procedures performed prior to counting, it is ready for counting. Because of the extremely small disintegration rates encountered, special techniques, called low level counting, must be used to assay the sample. We shall survey some of the highlights of this area which is
been the subject of many articles and monographs. [7]

What are the most important characteristics the detector must possess for low-level counting? The first general characteristic is one of stability. Low level counting frequently requires counting periods of long duration; hence counter stability is quite important. If the sample count rate $S$ (source + background) is only slightly larger than the background rate $B$, one’s detector should be picked to maximize the ratio $S^2/B$-- that is, low background and high efficiency. If the sample count rate is large with respect to background, one need only maximize $S$-- that is, one chooses a high efficiency detector.

19.7.4--Low level counting-- details

For low level $\alpha$-particle counting, the choice is generally between the gas filled ionization chamber and a semiconductor detector system. The former can have a counting efficiency of approximately 50% and a background of approximately three to four cpm; the latter has a background rate of approximately 0.5 cph and a detection efficiency that approaches 50%. The semiconductor detector is usually the detector of choice although large sample sizes may be better assayed with gas filled ionization chambers. Background radiation is primarily due to $\alpha$-particle emitting impurities in the counter, counter support material and so on, plus the occurrence of cosmic ray induced $(n,\alpha)$ reactions. Because of its Ra content, Al is not used in constructing $\alpha$-spectrometers.

Low-level “soft” radiation counting has its own techniques. The term “soft radiation counting” refers to detecting EC and low energy $\beta$- emitters where the self-absorption of the radiation in the sample is important. To solve this problem, one typically tries to incorporate the radionuclide to be counted into the detector itself. One typical
method of assay is liquid scintillation counting, which is used to assay samples whose activity is greater than 10 pCi. Typical liquid scintillation counter backgrounds can be high as high as approximately 100 counts per minute whereas special counters have been built with a background rates of approximately 10 CPM or less. Liquid scintillation counting is a speedy, simple method of low level counting. Another technique that has been used to count low-level soft radiation samples involves the use of gas filled proportional counter. The sample to be counted is converted to gaseous form and added to the counter gas at a concentration of approximately 0.05 mole percent or less. This method of low-level counting, although tedious and time-consuming, allows one to assay samples whose activity is less than 0.5 picocuries. Typical counter backgrounds are ~1 to 2 cpm with 100% counting efficiency for energies as low as ~10 eV.

The counting of tritium in water is a special problem about which much has been written. Current methods for assay of tritium in water have a range of 0.1 to 5000 TU where a tritium unit (TU) has the value of 7.2 dpm/L. The most desirable feature of a tritium measuring system is that it be capable measuring a large number of samples is rapidly, simply and cheaply as possible with an uncertainty of ~ ±10% or better. It is generally more important to assay 100 samples with an uncertainty of ±10% than to assay 10 samples with an uncertainty of ±3%.

The basic feature of low-level β- counting that distinguishes it from ordinary β- counting is the use of an anticoincidence shield around the main β- counters. An anticoincidence shield is a single detector, or array of detectors that surrounds the primary detector. The output of the anticoincidence detector is fed to an anticoincidence circuit along with the output of the primary detector. When nuclear radiation passes through
both detectors simultaneously, as in the case of a highly penetrating cosmic ray striking both detectors, no output results from the anti-coincidence circuit. When the anticoincidence circuit receives a signal only from the primary detector, an output signal results. The net effect is that the anticoincidence shield detector “guards” or shields against exterior radiation background radiation entering the primary detector. Typical ring assemblies reduce the background rate in the primary counter by a factor of \(~50\). A well-designed guard ring will allow several different types of central counter to be inserted into it. Low background \(\beta\)-counters constructed of especially pure materials with anticoincidence shields have exhibited background rates of \(\sim 1\) cph with efficiencies of approximately 50%.

Low level counting of \(\gamma\)-ray emitters using solid scintillation counters is an extensively used technique. For detailed discussions of this technique, the reader is referred to the excellent review articles. The most important aspect of low-level solid scintillation counting is to decrease the counter background. Typical contributions to a solid scintillation counter’s background rate from various sources are shown in Table 19-3.

Table 19-3 Components of a NI(Tl) Scintillation Counter Background


| Outside Shield | 29.200 cpm |
Inside Shield

<table>
<thead>
<tr>
<th>Source</th>
<th>Activity (cpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cosmic Ray Mesons</td>
<td>116.4</td>
</tr>
<tr>
<td>Cosmic Ray Neutrons</td>
<td>19.4</td>
</tr>
<tr>
<td>$^{222}$Rn Daughters</td>
<td>25.9</td>
</tr>
<tr>
<td>$^{40}$K</td>
<td>8.6</td>
</tr>
<tr>
<td>Remaining Background</td>
<td>33.1</td>
</tr>
<tr>
<td>Total</td>
<td>203.4</td>
</tr>
</tbody>
</table>

Here four factors are seen as the major contributors to the detector background rate. They are (a) the cosmic ray shield (b) the atmosphere surrounding the detector (c) the detector itself and (d) the cosmic rays. For the cosmic ray shield about the detector, it is advisable to use old or virgin lead. *i.e.*, lead that was purified over 100 years ago, thus allowing any $^{210}$Pb present to decay. One should expect ~1 cpm/g shield material. Iron can also be used in constructing the detector shield, but care must be taken to ensure that the iron or steel is pre 1945 in origin. (Iron processed in the post-1945 period has $^{60}$Co contamination due to the use of $^{60}$Co in the blast furnace operation.) Mercury is a very good, easily purified shield material but is quite expensive. “Graded” shields consisting of an outer thick layer of Pb lined with Cd which in turn is coated with Cu are used to reduce the production of x-rays in the Pb shield material. The main portion of the atmospheric contribution to the detector background is due to radon and its daughters. Particularly troublesome in this regard is the fact that atmospheric radon concentrations can fluctuate by a factor of 40 during the course of a day. Once again the problem is best handled by filtering the room air, rapid air turnover and the use of inert atmospheres ($N_2$ from
evaporation of liquid nitrogen) inside counting assemblies. A NaI detector will contain some $^{40}$K impurity, which will contribute to the background. The detector housing is also a potential contributor to the background. Copper appears to be the best material for detector housing with aluminum being the least preferred, for it can be expected to contain $\sim 10^{-13}$ Ci Ra/g Al. In reducing the cosmic ray component of the background one tries to stop the “soft” cosmic rays (electrons, X and $\gamma$-rays) in the detector shield while using an anti coincidence system to stop the “hard’ component of the cosmic radiation (mesons, etc.)

At first one might think that germanium detectors with their low detection efficiencies would have little use in low level counting. However such is not the case because of the complexity of a radionuclide mixture found in environmental samples, the virtual impossibility of drawing significant conclusions from NaI detector spectra due to poor energy resolution. Clearly there are many cases in which the very good energy resolution of the germanium detector is a necessity. Furthermore, recent developments in detector fabrication techniques allow the production of germanium detectors with detector efficiencies equal to that of standard (3” x 3”) NaI detectors.

A number of special techniques have evolved to increase the detection sensitivity in $\gamma$-ray counting. One of the most important is the suppression of the Compton scattering events in the $\gamma$-ray spectrum by the use of anticoincidence annulus around the central $\gamma$-ray detector. The idea behind a Compton suppression spectrometer is that most events in which the incident photon undergoes one or more Compton scattering events in the central detector will result in partial energy deposition in the detector with a low energy photon escaping the detector. Suppression is accomplished by setting up an anticoincidence between the central detector signal and any signal coming from the
annulus. A photon that is Compton scattered from the central detector will probably give rise to a signal from the annulus. Thus, such events will not be accepted. Other events, such as photoelectric events in the central detector will not produce signals from the annulus and will be counted. This reduction in number of Compton scattering events in the $\gamma$-ray spectrum leads to a more easily interpreted spectrum since the peak to Compton ratios are much higher. Typically the use of such annuli reduces the number of Compton events tenfold. More sophisticated designs have been used to further improve the rejection of Compton scattering events.

19.7.5 Limits of Detection

Suppose you have performed a low level experiment and you wish to state your results in a statistically meaningful manner. You wish to answer such questions as “Is there a result/signal/event? What is the chance it will be detected with my apparatus? How big is it?” Currie [23] has provided answers to these questions by defining three different limits of detection:

- The critical level $L_C$, the signal level above which an observed instrument response may be reliably recognized as “detected”.
- The detection limit $L_D$, the true net signal that may be expected $a$ $priori$ to lead to detection
- The determination limit $L_Q$, the signal level above which a quantitative measurement can be performed with a stated relative uncertainty.

Operationally, the recipes for calculating these limits are as follows
<table>
<thead>
<tr>
<th></th>
<th>$L_C$</th>
<th>$L_D$</th>
<th>$L_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paired observations</td>
<td>2.33 $\sigma_B$</td>
<td>4.65 $\sigma_B$</td>
<td>14.1 $\sigma_B$</td>
</tr>
<tr>
<td>&quot;Well-known&quot; blank</td>
<td>1.64 $\sigma_B$</td>
<td>3.29 $\sigma_B$</td>
<td>10 $\sigma_B$</td>
</tr>
</tbody>
</table>

For example, if the background under a photopeak of interest in a $\gamma$-ay spectrum was 100 cpm, then $\sigma_B = \sqrt{100} = 10$ cpm. According to the recipes given above, one would need to detect a photopeak area of 23 cpm to say that a nuclide was present and would need to detect at least 141 cpm to measure the amount of nuclide present. One would need a count rate of 47 cpm to insure, before making the measurement, that the nuclide in question could be detected.

The relationship of these limits to other measures used to describe low level counting is shown in Figure 19-8.

Figure 19-8. Various measures of detection limits for low level counting.
References


General References

Problems

1. A beam of 1 particle-μampere of $^{48}\text{Ca}^{10+}$ ions is incident on an Al foil that is 5 mg/cm$^2$ thick. (a) Estimate the energy deposit/sec in the foil. (b) If the foil has an area of 4 cm$^2$ and it is mounted in a vacuum with no cooling, how long will it take until the foil reaches the melting point of Al (660° C)? Assume the specific heat of Al is independent of temperature and is 0.25 cal/°/g.

2. Au foils are to be used as flux monitors in a nuclear reactor. What is the maximum thickness that can be used if the self-shielding corrections are to be less than 10%?

3. The reaction $^{27}\text{Al}(p,3pn)^{24}\text{Na}$ is to be used to measure the proton flux in an irradiation with 300 GeV protons. The cross section for this reaction is known to be 10.1 mb. The flux monitor is 5.0 mg/cm$^2$. One measures a $^{24}\text{Na}$ counting rate (background corrected) of 10,000 cpm (in a 2% efficient detector) 24 hours after a 0.5 hour irradiation. What was the average proton flux during the irradiation?

4. Imagine you have for your use a nuclear reactor with a flux of $10^{13}$ n/cm$^2$/s in its irradiation facility and a cyclotron with a beam of 10.5 MeV protons, 21 MeV deuterons and 42 MeV α-particles. What would be the best way to prepare: (a) $^{140}\text{Ba}$ (b) carrier-free $^{99}\text{Tc}^{m}$ (c) carrier-free $^{144}\text{Ce}$ (d) $^{237}\text{Np}$ (e) $^{254}\text{Es}$ (f) carrier free $^{18}\text{F}$ for incorporation into glucose. Outline the target and reaction to be used, how the target would be prepared and any chemical separations to be done following irradiation.
5. What value of $B\rho$ would you use in a gas-filled separator if you wanted to separate $^{254}\text{No}$ produced in the reaction of 215 MeV $^{48}\text{Ca}$ with $^{208}\text{Pb}$. You may assume $q_{\text{ave}}$ for $^{254}\text{No}$ is 1 torr He gas is 17+.

6. As a radiochemist, you have been asked to prepare the following accelerator targets for your research group. They are: (a) $^{226}\text{Ra}$ (b) $^{208}\text{Pb}$ (c) $^{238}\text{U}$ (d) $^{244}\text{Pu}$ (e) $^{90}\text{Zr}$ (f) $^{124}\text{Sn}$. Assume all targets are to be 0.5 mg/cm$^2$. For each target, outline the best method of target preparation, the backing foil used, if any and the reasons for your choice. Describe any anticipated problems in each procedure.