RADIOCHEMICAL TECHNIQUES

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Summary

In this chapter some techniques utilizable for radiochemical separation and reproducible sample mounting in connection with activity measurements, low-level counting, short-lived radionuclides, micro-amounts of radioactive substances, nuclides of high specific activity have been reviewed. Bearing in mind that some of the prospective readers may not be familiar with radioactive sources and with the significance of their proper applications, an attempt was made to discuss the crucial aspects of these issues. Some useful counting methods for determining absolute decay rates have also been outlined. Special attention is paid to highlight the significance of the contamination phenomena. The last section which is the main part of this chapter gives an overview of the practical decontamination techniques, dealing with the selection criteria and classification of decontamination techniques utilized in nuclear power plants. Finally, some illustrative examples on surface chemical effects of AP-CITROX decontamination technology are presented and discussed.

1. Introduction

The success of a radiochemical experiment is especially dependent upon the source or target considerations. In many nuclear experiments as much time has to be devoted to the target preparation as to the rest of the experiment.

In order to produce applicable sources, different separation and source mounting techniques have to be applied. In many respects the chemical separations of radioactive materials are very similar to the common analytical procedures; however, there are a few fundamental differences. One of these is the time factor which is often introduced by the short half-lives of the species involved. In the case of very high activity levels the chemical effects of the radiations, such as radiolysis of water and other solvents, and heat effects may affect the above procedures, too.

To achieve adequate counting efficiency it is obvious that the counting arrangement must be chosen carefully. The radiations emitted by the substance and the available measuring equipment are among the determining factors. Special attention has to be paid to sources of low-energy radiations, if samples of very low activity need to be measured and when absolute disintegration rates have to be determined.

In radioactive workplaces if the radioactive material is not in a sealed source container, it might be spread onto other objects. This type of contamination should be eliminated immediately by using an appropriate decontamination method. In a nuclear reactor almost all fission products and actinides formed are contained in fuel elements. In practice there are however independent processes through which radionuclides leave the reactor vessel, causing radioactive contamination. For this reason, decontamination technologies have been elaborated in order to reduce the radiation field prior to in-situ inspection, maintenance or even dismantling during the normal operation as well as the decommissioning of nuclear power plants. The technology for decontamination of nuclear reactors and equipment is a fairly recent development, since the need for decontamination procedures did not extensively arise until the first nuclear reactor was constructed. Since corrosion and contamination processes just as the two countermeasures (decontamination and corrosion-prevention) in the primary cooling circuit of nuclear reactors are essentially interrelated, establishing proper links between corrosion and contamination phenomena should lead to a good approach in handling the problem.

An inspection of relevant literature data reveals that the significance of electrochemical aspects has not been taken into account in the evaluation of standardized investigation methods of contamination processes and decontamination procedures for a long time. Recently, industrial practice has proven that a number of contamination-decontamination issues cannot be satisfactorily interpreted, if the adequate explanation of important electrochemical effects is disregarded.

The very aim of this chapter therefore is to highlight some techniques utilizable for radiochemical separation and reproducible sample mounting in connection with activity measurements, low-level counting, short-lived radionuclides, micro-amounts of radioactive substances, nuclides of high specific activity. Some useful counting methods for determining absolute decay rates will also be presented and discussed. Special attention is paid to review the contamination-decontamination processes. Finally, the last section which is the main part of this chapter provides an overview on the practical decontamination techniques.

2. Characterization of the Radioactive Targets and Sources

In nuclear experiments *physical properties* of radioactive sources have to be kept in mind for successful applications. In thin targets the flux and energy of the projectile do not change during passage through the target. When the projectile energy is considerably changed (in a thick target) it is more complicated to calculate the yield as the variation of energy with distance in the target and the variation of cross section with energy must be taken into account. When a target is thin the exact specification depends on the experiment, in most cases thin means a target with a surface density of not more than a few mg cm^{-2} or a thickness of a few µm or less. The *surface density* is $x\rho$, where x is the target thickness and ρ is the (mass) density. Thin targets – made of a solid material, either metal or compound – are usually used in accelerator irradiations. In order to have sufficient mechanical strength the target is usually supported on a *backing material* such as aluminum. Thin targets are fixed on the backing material through electrolytic precipitation, vacuum deposition, mass spectrometric collection, or a number of other techniques. In reactor irradiations it is more common to use thicker targets in order to obtain higher yields. The target material can be a solid, liquid, or gas. For reactor irradiations it is common to place the target material in a container of polypropylene or of some metal of relatively low neutron capture cross-section. The primary requirement for the container is that it should be leak-tight and dissipate heat at a rate sufficient to avoid melting. The extent of *burn-out* of the target by the irradiation is sometimes of greater importance than its thickness.

In addition to physical characteristics *chemical properties* are also very important. There are two ways to produce a *pure radionuclide* not contaminated with any other radionuclide. An extremely pure target can be used with a reaction path which is unique. Alternatively, the radioactive products can be purified after the end of the bombardment. Handbooks of activation analysis often contain information on the formation of interfering activities from impurities. Even a chemically pure target may yield products of several elements, particularly in cyclotron irradiation, where many reaction paths are often possible. When the target is a chemical compound its radiation stability becomes important. In general organic compounds are not stable towards either neutron or charged particle bombardment. To express the activity of a sample we can use the term *activity concentration*, quotient of the activity of a material and the volume of this material. The *specific activity* of the material (activity per mass) and the concentration of a radionuclide (moles per volume) are very important quantities in radiochemical work. Radionuclides of high specific activity are produced either through accelerator irradiation or through secondary reactions in the target in a reactor. Maximum specific activity is obtained when the radioactive nuclide is the only isotope of the element. A *carrier-free* radioactive sample is usually the one in which the radionuclide is not diluted with non-radioactive isotopic atoms. If a carrier-free radionuclide has been produced, e.g. through accelerator irradiation, which then must be purified, its concentration is so low that it may not follow the normal chemical rules. A macroscopic amount of inactive component, either isotopic or not, may have to be added to carry the radionuclide through the proper chemical purification steps. The non-radioactive component is called a *carrier*, as it carries the radioactive one and ensures normal chemical behavior. For that purpose, the carrier must be in the same chemical state as the radionuclide considered. In the case of the radioisotopes of stable elements (e.g. ^{60}Co and ^{32}P) small amounts (traces) of the stable isotopes (e.g. ^{59}Co and ^{31}P) are always present, due to their ubiquity. The amount of the stable isotopes is, in general, higher than that of the short-lived radioisotopes, and the omnipresent traces act as isotopic carriers for the short-lived radionuclides, provided that they are in the same chemical state. In the case of the isotopes of radioelements, such as ^{226}Ra or ^{210}Po, however, stable nuclides are absent and the amount of the radionuclides is identical with that of the elements, provided that the presence of longer-lived radioisotopes can be excluded. Traces or compounds, respectively, of other elements with similar properties may serve as non-isotopic carriers for radioisotopes of stable elements as well as for isotopes of radioelements. Many applications of radiotracers involve combining the tracer atoms with a much larger amount of non-radioactive isotopic atoms prior to use. In this case isotopic exchange can occur. If it is not known a priori that such exchange takes place between two compounds with a common element this must be determined by preliminary experiments that the tracer and the carrier would act similarly in a chemical system. This consideration must be borne in mind if the radioactive tracer and the inert carrier are in different oxidation states when mixed.

A radioactively *labeled* (or tagged) compound is the one in which one of the atoms is radioactive. Preparation of labeled compounds may involve lengthy chemical synthesis starting with the radioactive nuclides in elementary form or in a simple compound. Compounds can be labeled at different sites of the molecule. Labeling is said to be *specific* if the radionuclide can only be found at one specific site in the compound; alternatively, labeling may be *general* when all possible sites are labeled. Thousands of labeled organic compounds are commercially available and some companies offer labeling service on request.

An important factor in the use of radionuclides is their *radiochemical purity* since, should several radionuclides of different elements be present in a tracer sample used in an experiment, the result could be ambiguous and misleading. In a radiochemically pure sample, the total radioactivity is originating from a single radioactive element. If the radioactivity is related to a single isotope, the sample may be said to be *radioisotopically pure*. The radioisotopic purity of a sample may be ascertained by measuring the half-life. This method obviously can be used only with radionuclides that show sufficient decay during the time of observation for a reliable half-life to be calculated. With longer half-lives, the radioisotopic purity can be checked by measuring the type and energy of the emitted radiations or by processing the tracers through one or more chemical steps characteristic of the element whose isotope is believed to cause the radioactivity. When a compound labeled with a radioactive nuclide is used to study molecular behavior, it is necessary to ascertain the *radiochemical purity of the compound* not just the purity of the radioactive isotope. In other words, it has to be made sure that the radioactivity comes only from a specific element and only from a specific compound incorporating that element. This can be determined through selective chemical operations in which it is frequently desirable that the compound should not be destroyed. If the radioactive product is stored for a relatively long time, its radioactive daughter may accumulate to a degree when the product is no longer sufficiently pure radiochemically. In such cases the daughter activity must be separated prior to use.

3. Separation Techniques of Radioactive Elements

Chemical separations carried out on radioactive materials are in many respects very similar to ordinary analytical procedures. However, there are a few fundamental differences. One of these is the time factor which is often introduced by the short half-lives of the species involved. An otherwise very simple procedure such as the separation of two common cations may become quite difficult when it is to be performed in a few minutes, and the final precipitates are to be dried and mounted within that time, too. Where the usual procedures involve long digestions, slow filtrations, or other slow steps, completely different separation procedures must be worked out for use with short-lived nuclides. Ingenious chemical isolation procedures taking as little as a few seconds, have been developed. High yields in radiochemical separations are not always of great importance, provided that the yields can be evaluated. High chemical purity may or may not be required for radioactive preparations, depending on intended use. For identification and study of radioactive species and for many chemical tracer applications it is not important; for most biological work it is. On the other hand, it is usually required and often has to be extremely good. Specific effects of the radiations may be of importance when radioactive substances are separated. In case of very high activity levels the chemical effects of the radiations, such as decomposition of water and other solvents, and heat effects, may affect the procedures. However, this is generally not as important as the fact that even at much lower activity levels the person carrying out the separation receives dangerous doses of radiation unless protected by shielding or distance. For this reason it is often necessary to carry out separations behind lead shields and to perform operations with the use of tongues and other tools; for very high activity levels more elaborate remote-control methods are needed. It is obvious that separation is more difficult to perform under such conditions and the standard procedures have to be modified considerably to adapt them for remote-control operation.

Fractional crystallization was one of the first methods used in radiochemistry by Marie and Pierre Curie to separate $^{226}\mathrm{RaCl}_2$ from BaCl_2. In most radiochemical separations, as in conventional analytical schemes, *precipitation* reactions play a dominant role. Precipitation is only applicable if the solubility of the product is exceeded, i.e. if the concentration of the radionuclide to be separated is high enough. If the concentration is too low, co-precipitation may be applied by adding a suitable carrier. Application of isotopic carriers is very effective, but it leads to a decrease in specific activity. Therefore, non-isotopic carriers with suitable chemical properties are preferred. Hydroxides such as iron(III)hydroxide or other sparingly soluble hydroxides give high co-precipitation yields, because of their high sorption capacity. If co-precipitation of radionuclides present in low concentrations is to be avoided, hold-back carriers are added. For filtration, Hahn suction filters are convenient. Co-precipitation reactions are often found useful, especially if the subsequent separation of the radionuclide from the non-isotopic carrier can be accomplished by some technique other than precipitation. A radionuclide that can exist in two oxidation states can be effectively purified by precipitation in one oxidation state followed by scavenging precipitations for impurities while the element of interest is in another oxidation state. Adsorption on the walls of glass vessels and on filter paper, which is sometimes bothersome, has been put to successful use in special cases.

Ion-exchange procedures have also found broad application in radiochemistry. An exceedingly useful separation technique has been developed for use both with and without carriers. This technique involves the adsorption of a mixture of ions on an ion-exchange resin followed by selective elution from the resin. Both cation- and anion-exchange resins have been used very successfully. Most of the cation resins are synthetic polymers containing free sulfonic acid groups. The anion exchangers usually contain quaternary amine groups with replaceable hydroxide ions. The distribution of any given ionic species between a solution and the resin depends on the composition of the solution, and for practically any pair of ions conditions can be found under which they will show some difference in distribution. In practice, a solution containing the ions to be separated is run through a column of the finely divided resin, and conditions (solution composition, column dimensions, and flow rate) are chosen such that the ions to be adsorbed will appear in a narrow band near the top of the column. In the simplest kind of separation, some ionic species will run through the column while others are adsorbed. More commonly a number of ionic species may be adsorbed together on the column and separated subsequently by the use of eluting solutions differing in composition from the original input solution. Frequently, complexing agents which form complexes of different stability with the various ions are used as eluents. There exists then a competition between the resin and the complexing agent for each ion, and if the conditions are close to equilibrium each ion will be exchanged between resin and complex form many times as it moves down the column. The number of times an ion is adsorbed and desorbed on the resin in such a column is analogous to the number of theoretical plates in a distillation column. The rates with which different ionic species move down the column under identical conditions are different, because the stabilities of both the resin compounds and the complexes vary from ion to ion; separations are particularly efficient if both factors work in the same direction, that is, if the complex stability increases as the metal-resin bond strength decreases. As the various adsorption bands move down the column their spatial separations increase, until finally the ion from the lowest band appears in the effluent. The various ions can then be collected separately in successive fractions of the effluent. The most striking application of cation-exchange columns is the separation of rare earths from each other using e.g. the complexing agent α-hydroxi-i-butyric acid, both on a tracer scale and in gram or hundred-gram lots. For rather rapid target chemistry, anion exchange is often more useful than cation exchange, because larger flow rates can usually be used with anion columns. A large number of elements form anionic complexes under some conditions, and available data make it appear likely that a general scheme of analysis based entirely on ion-exchange-column separations could be worked out for these elements.

Distillation and *volatilization* methods often give very clean separations provided that proper precautions are taken to avoid contamination of the distillate by spray or mechanical entrapment. Most volatilization methods can be done without specific carriers, but some non-isotopic carrier gas may be required. Precautions are sometimes necessary to avoid loss of volatile radioactive substances while dissolving irradiated targets or during the irradiation itself.

Solvent extraction is widely used for separation of radionuclides, because this technique is simple, fast and applicable at low concentrations. Under certain conditions compounds of some elements can be quite selectively extracted from an aqueous solution into an organic solvent, and often the partition coefficients are approximately independent of concentration down to tracer concentrations. In other cases, particularly if dimerization occurs in the organic phase, carrier-free substances are not extracted. Solvent extractions often lend themselves particularly well to rapid and specific separations. In most cases the extraction can be followed by “back-extraction“ into an aqueous phase of altered composition. Several organic substances have been found to form chelate complexes with a large number of metal ions. These complexes are preferentially soluble in nonpolar solvents such as benzene, and, since the dissociation constants of the different metal chelates show different pH dependence, specific separation procedures can sometimes be devised using several extraction steps at different pH values. Occasionally it may be possible to leach an active product out of a solid target material. This has been done successfully in the case of neutron- and deuteron-bombarded magnesium oxide targets; radioactive sodium is separated rather efficiently from the bulk of such a target by leaching with hot water.

Electrolysis or *electrochemical deposition* may be used either to plate out the active material of interest or to plate out other substances leaving the active material in solution. For example, it is possible to separate radioactive copper from a dissolved zinc target by an electroplating process. Carrier-free radioactive zinc may be obtained from a deuteron-bombarded copper target by solution of the target and electrolysis to remove all the copper. Chemical displacement may sometimes be used for the separation of carrier-free substances from bulk impurities. The separation of polonium from lead by deposition on silver is a classical example.

Chromatographic separation techniques are based on adsorption, ion exchange or partition between a stationary and a mobile phase. Gas chromatography (GC) is applied for separation of volatile compounds. Thermo-chromatography (isothermal or in a temperature gradient) is frequently used for the study of the properties of small amounts of radionuclides. For the investigation of radionuclides of extremely short half-life the thermo-chromatographic column, usually a quartz tube, may be operated on-line with the production of the radionuclide by an accelerator, aerosols may be added as carriers and chemical reactions may be initiated by injection of reactive gases into the column. For separation of radionuclides in solution, high-performance liquid chromatography (HPLC), paper chromatography or ion-exchange chromatography may be applied. Reversed-phase partition chromatography (RPC) offers the possibility of using organic extractants as the stationary phase in a multi stage separation.

Recoil separations are correlated with hot atoms. When a projectile of high energy reacts with a target atom, the reaction products are emitted in the direction of the projectile, measured in laboratory coordinates. We use the term *recoil* to describe this. The products are slowed and eventually stopped through collision with other atoms.

Consequently, if the target is relatively thin, there is a certain probability that the recoil range of the product exceeds the thickness of the target and the target atoms can therefore escape the target. In such cases the recoiling products are caught on special foils behind the target. Recoil techniques have been used extensively in the synthesis of higher transuranium elements. As an example, consider the formation of element 103, lawrencium. The Lr atoms, which were formed in the reaction in the target between ^{252}Cf and projectiles of ^{11}B, recoiled out of the thin target into helium gas where they were stopped by atomic collisions with the He-atoms. These recoil species became electrically charged cations as they lost electrons in the collision with the gas atoms. They could, therefore, be attracted to a moving, negatively charged, metal coated plastic band, which carried the Lr atom on its surface to a number of α-particle detectors where the α-decay of the lawrencium was measured. From the velocity of movement of the plastic band and the measurement of the radioactivity by energy sensitive nuclear detectors, the half-lives and α-energies of the product nuclei could be determined. Comparison of these data with predictions from theory allowed assignment of the mass number of the nuclide.

The momentum imparted to a nucleus in a nuclear reaction with a charged particle or a fast neutron almost invariably is sufficient to result in the rupture of chemical bonds holding the atom in the molecule. The same is true for the recoil energy imparted to a nucleus by the emission of an α-particle and it can also occur after β-decay, γ-decay, etc. These recoiling atoms are known as *hot atoms* since their kinetic energy is much in excess of thermal equilibrium values. A hot atom may move as far as several hundred atomic diameters after the rupture of the bond before being stopped even though this takes only about 10^{-10} s. Initially the hot atom is highly ionized. As the hot atom is slowed down to thermal energies, it collides with a number of other particles in its path producing radicals, ions, and excited molecules and atoms. At thermal energies it may become a neutral atom, an ion, possibly in a different oxidation state or it may react to form a compound with molecules in its path. Hot atom reactions can be used for synthesis of labeled compounds. So far this technique has been used primarily for ^{3}H and ^{14}C labeling. For example, an organic gaseous compound is mixed with ^{3}He and the sample is irradiated with neutrons. The reaction $^{3}He(n,p)^{3}H^{\rightarrow}$ produces tritium as hot atoms (indicated by the arrow) with kinetic energies of approximately 0.2 MeV. These hot atoms react with the organic molecules to produce labeled compounds. In a more simple method, the organic compound is simply mixed with tritiated gas. The β-radiation from tritium decay causes excitation and decomposition which leads to capture by the organic radicals of some of the remaining tritium. These reactions are not selective because reactions with decomposition products also occur, therefore the tritium labeled product must be purified.

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

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Biographical Sketches

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