Radiochemical Methods

Roentgen announced the discovery of X-rays in 1895. This led to extensive use and study of these phenomena, which had already been studied since 1859 without the realization of its true nature. By 1897, a number of injuries caused by X-rays had already been reported from laboratories all over the world.[1] In the same year Bequerel discovered radioactivity and soon after, in 1900, the first skin burn caused by radioactivity concentrated from uranium ore, was produced. The Curies learned to produce radium, which found use in luminous paints in instruments and clocks during and after World War I. The health effects of radium were unknown to the public and workers involved in painting licked the brushes to point them. This digestion of radium, and the use of radium for medical purposes, led to many deaths from bone cancer and aplastic anemia. As late as 1944 – 1951 a radium compound was used as a cure for tuberculosis in Germany. It has been estimated that more than 100 persons died from the effects of radium. Another cause of a number of deaths from cancer caused by radioactivity is radon and its daughters. In Eastern Europe many mines for heavy metals also contain uranium. Radon and its daughters that are incorporated into uranium caused a fatal lung disease, which was later identified as cancer. Information about this did not reach miners in the USA. Therefore the intense uranium mining that took place in the USA, starting after World War II, also caused numerous fatalities from lung cancer.

These cases have been studied thoroughly leading to an understanding of the effects of radiation and how to avoid it. Thus, early experiences with the use of nuclear reactors and in building atomic bombs during World War II could be managed with a good safety record.

The health effects of the atomic bombs in Hiroshima and Nagasaki have also been thoroughly investigated, yielding a great deal of information. As a consequence the health effects of ionizing radiation are well known. Based on this knowledge, international safety regulations have been set on allowed doses, allowed radionuclide concentrations in water, food and air and so on. It can safely be said that the regulations are such that human beings are much better protected against radioactivity than against chemical toxicity.

After World War II the cold war resulted in the nuclear weapons race. Both the USA and the Soviet Union con- ducted nuclear weapons tests above ground. The fallout of fission and activation products from these tests spread over the northern hemisphere. This started research in all countries, in which the environmental pollution and transport of these radionuclides were studied. Much work was done in the development of analytical methods for the determination of radionuclides. The nuclear indus- try, nuclear power plants and reprocessing plants during their normal operation caused some additional release of radionuclides. Major releases were caused by accidents in the Soviet Union, USA and UK. New threats have appeared with the disintegration of the Soviet Union. Lack of funds has increased the risks of accidental releases from nuclear submarines, reprocessing plants and nuclear power plants. All these are good reasons for continuous monitoring of radionuclides in the environment. New reasons for measurement of low activities and long-lived radionu- clides have developed in connection with research on the disposal of spent fuel and reprocessing waste. As a consequence, new methods of making these measurements are continuously being developed. In addition to the classical radiometric methods, new mass spectrometric methods are published.

Properties of Radionuclides

1.1 Nuclides and Radioactive Decay

An element is identified by the number of positively charged protons in its nucleus and the consequent number of negatively charged electrons. In addition to protons, the nucleus contains neutrons, which do not carry any charge. Neutrons and protons have an atomic weight of unity. The mass of electrons is negligible compared with the mass of protons or neutrons. All elements consist of isotopes. Each isotope of an element is identified by the number of neutrons. Thus all isotopes of a specific element contain the same number of protons, which is determined by the atomic number, Z. The mass (M) of the isotope is the sum of the number of protons and neutrons in the nucleus. A specific combination of protons and neutrons is called a nuclide. A nuclide is identified by its Z and M values. The chemical symbol gives the Z and the mass is given as a superscript on the left side of the chemical symbol. ^{238}U is uranium with mass 238; it is called uranium-238. ^{3}H

is called hydrogen-3, or tritium. Most elements, but not all of them, have several stable isotopes, in a ratio that is constant. Thus nuclides with the same Z are called isotopes, nuclides with the same mass are called isobars and nuclides with the same number of neutrons are called isotones.

In addition to the stable isotopes, all elements have radioactive isotopes with variable half-lives. A radionuclide is unstable, which means that the nucleus decays releasing energy and particles. This is seen as emission of radiation of various kinds. Part of the energy is released in the form of electromagnetic radiation, like γ- rays, and partly as kinetic energy of emitted particles. This energetic ionizing radiation is what makes radionuclides hazardous for living organisms. The rate of decay is characteristic for each radionuclide. If there are N atoms the rate is dN/dt, which is proportional to N according to Equation (1)

$$\frac{dN}{dt} = -\lambda N \qquad (1)$$

Instead of the disintegration constant λ, the half-life T is commonly used. The relation is, Equation (2)

$$\lambda T = \ln 2 = 0.692 \qquad (2)$$

The half-lives of the different radionuclides vary between fractions of seconds to billions of years. The energy released is expressed in units of electron volts, eV. This is the energy required to transport an electron through a potential difference of 1 V. Because nuclear binding energies are of the order of 8 MeV per nucleon, nuclear reactions always release significant amounts of energy. Therefore the kinetic energies of the emitted particles usually vary from a few kiloelectron volts to several megaelectron volts.

The amount of an element is usually expressed as a weight unit like kilogram or gram, or a concentration unit like grams per kilogram, grams per liter or such. Lately the more scientific unit, the mole, is used, in order to relate the quantity to the number of atoms or molecules. The amount of stable nuclide is usually expressed as isotopic percentage that is the ratio of the total number of atoms of the element. The amounts of very long-lived radionuclides are also expressed in this way, for instance ^{238}U and ^{235}U. Of course the amount of both stable nuclides and

radionuclides may be expressed in absolute mass units or as the number of nuclides. Particularly when the amount of a long-lived radionuclide has been determined by mass spectrometry, it is not uncommon to give the results in mass concentration units.

The mass of a radionuclide with a short half-life is very small compared with its activity. The activity also has the benefit of being proportional to its toxicity, which is the usual reason for determining the concentration. The methods most commonly used for the determination of the radionuclide are radiometric, which give the activities directly. For these reasons the amounts of radionuclides are usually expressed in units of radioactivity. The activity of a radionuclide is expressed as disintegrations per unit of time. The basic unit is the Bequerel, Bq. This is the number of disintegrations per second. Greater and smaller units are kBq, MBq, GBq and mBq.

An older unit of activity, seen in older texts and still in use in the USA, is the curie (Ci). One Ci is 3.7 10^{10} Bq. Because the unit is quite large it is common to use smaller units like mCi, µCi, nCi and pCi especially in expressing environmental activities.

1.2 Decay Modes

Radionuclides decay in different ways. Isomeric transitions (IT), that is transitions between different energy levels of the same nuclide, result in emission of energy only, normally in the form of a γ -ray, $^{60m}Co \longrightarrow {}^{60}Co + \gamma$. This usually occurs in connection with emission of particles, but separate IT with measurable half-lives are also known. When the transition energy is greater than 1.022 MeV, pair production may occur. This means that an electron positron (positively charged electron) pair is emitted instead of the γ -ray. There is also a third mode of IT: internal conversion in which an electron from the electron cloud carries the de-excitation energy and a conversion electron is emitted.

β-Decay is the most common form of decay of a radionuclide. Most radionuclides formed by fission or by neutron activation reactions are neutron rich, and they decay mainly by emitting a negatively charged *β*-particle, that is a *β*-particle or radiation. In most cases, but not always, the daughter nuclide is left in an isomeric state which decays either immediately or with a measurable half-life

by emitting one or several *g*-rays.

Proton-rich nuclides, usually produced by γ -ray or charged particle reactions, disintegrate by positron- (β^+) emission or by electron capture. In electron capture the charge of the nucleus is adjusted by capturing a negative electron instead of emitting a positive β-particle. In this case the only measurable radiation is the X-ray which is emitted when the captured electron is replaced by another from a higher energy level.

Heavy nuclides, $Z > 82$ with a few exceptions, may decay by emission of an α-particle, which is a ^{4}He nucleus. The α-particles usually carry much energy. The most heavy elements, $Z > 90$, may undergo spontaneous fission in which the nucleus is divided into two fractions of comparable, but not equal, size. Two to three neutrons are also emitted, and often also γ -radiation.

Medical Use of Radionuclides

As has been indicated above radionuclides were used for their believed health effects early in the period following the discovery of radionuclides. One of the most important applications is the use of radiation for cancer treatment. In the beginning large ^{60}Co sources were used to treat cancer. These pose a potential environmental hazard because the ^{60}Co sources have to be disposed of in some way. ^{60}Co sources have largely been replaced by linear accelerators. The radiation doses have to be measured and controlled with high accuracy.

Different short-lived radionuclides, inserted into humans in a number of ways, are used for both treatment and diagnostics. The radionuclides are usually used as labeled compounds. The substrate on to or into which they are adhered are chosen so that they transport the radionuclides into specific organs of the human body. They can then be determined by measuring the gamma radiation which they emit. Gamma cameras enable the measurement of the radionuclide distribution in two or three dimensions. These measurements reveal tumors and other kinds of deficiencies in the human body. The radioisotopes used in medical applications are usually so short-lived that they do not pose any environmental hazards. Radionuclides are also used as labels in radioim- munoassay, which is used for the determination of biologically active compounds.

Industrial Use of Radionuclides

The production of nuclear weapons and the use of nuclear energy have been the largest industrial-scale activities involving radionuclides. The first nuclear weapons were based on enriched uranium, but soon plutonium was used instead. The plutonium is produced by irradiating uranium in research reactors. The plutonium has to be chemically separated from the uranium and large amounts of radionuclides are produced by fission of uranium during the irradiation. The use of nuclear energy involves radioactivity during uranium mining and reprocessing of the fuel. These activities cause large amounts of radioactive waste, which have to be stored in a safe way. This has not always been successful, as will be indicated below. Uranium and plutonium and their isotopes have to be measured during the different stages of the processes. Other industrial uses involve radioactive sources in a number of gauges. Radiography using ^{60}Co and ^{137}Cs sources is in use. In industrial plants such parameters as thickness and density are commonly measured in the process using gauges based on radioactive sources. These usually do require calibration measurements and after dismantling they need to be disposed of in a safe way.

Use of Radionuclides In Research

Radionuclides are produced in research reactors and accelerators for use in medicine, as tracers and in analytical chemistry. The medical uses have already been mentioned. Radioactive tracers are used as labels in biochemical and chemical research in order to study chemical reactions. Radioactive tracers are also used to study industrial processes, transport of water and air and wear of engines, to mention some applications.

Nuclear reactions and activation analysis are used for materials research and trace element analysis of environmental, geological, archaeological, biological and industrial materials.

Origin of Radionuclides In The Environment

Radionuclides occur naturally in the environment.(1) They can be found in the atmosphere, in all natural waters, in rocks, and so on. Usually the amounts are small, but sometimes quite large activities can be found. All living systems contain radionuclides. Most of them are of natural origin, but after World War II an

increasing amount of radioactivity has been distributed in the environment by human activity.

Uranium and thorium are elements which exist in amounts in the microgram per gram range in ð rocks, particularly granitic rocks. Both are radioactive con- sisting mainly of the isotopes ^{235}U with a half-life of 7.13×10^8 years, ^{238}U with a half-life of 4.468×10^9 years and ^{232}Th with a half-life of 1.405×10^{10} years, sufficiently long half-lives to enable the isotopes to have survived the billions of years in which the earth has existed. These long-lived radionuclides support a long line of daughter nuclides with variable half-lives, the uranium – actinium, uranium– radium and thorium series. These series have the gas radon, Rn, as an intermediate isotope. As an inert gas, radon emanates and is thus spread into houses and the atmosphere in areas of high uranium content in the bedrock. For instance in Finland, 75% of the radiation dose to the population from natural sources is caused by ^{222}Rn and its daughters. Because of the volatility of radon, its daughters ^{210}Pb and ^{210}Po may be found in the atmosphere. A part of the ^{210}Po is directly volatilized when coal is burned in power plants. Some coals contain significant amounts of uranium and its daughters. These three natural series all end of instable nuclides of lead. Thus ^{206}Pb, ^{207}Pb and ^{208}Pb are at least partly of radiogenic origin, and therefore the lead isotope ratios are not constant, which is opposite to the case for most other isotope ratios. As uranium and thorium are natural constituents of rocks, they can also be found in all materials containing stone, such as the concrete walls in houses. Another original radionuclide in the bedrock is ^{40}K, with a half-life of 1.26×10^9 years. ^{40}K is mixed with all the potassium of the earth in a constant ratio. Therefore all rocks, building materials, waters and living systems also have their share of ^{40}K.

New radionuclides are constantly produced in small amounts by cosmic ray-induced nuclear reactions in the atmosphere. More than ten different nuclides are produced. The most significant ones in respect of quantity are ^{3}H, ^{10}Be, ^{14}C, ^{26}Al, ^{26}Cl and ^{39}Ar. Radionuclides have significant uses in medicine, industrial processes, industrial measurement systems and science. Thus radionuclides are produced artificially by different kinds of accelerators and nuclear reactors. How- ever, most of these radionuclides has short half-lives and the contamination of the environment from these sources is insignificant. Artificial nuclides that have been incorporated into the environment mainly originate from nuclear weapons tests and the nuclear energy fuel cycle. In nuclear weapons tests and nuclear power production the main process is

fission of ^{235}U (reactors) or ^{239}Pu (bombs). In both instances radionuclides are produced via two kinds of nuclear reaction. The main process is the fission itself, but significant amounts of radionuclides are also produced by activation via neutrons which are released in the fission process. During fission, all radionuclides in the mass range 80 – 110 and 125 – 155 are produced. The most significant ones in regard to safety are ^{131}I with a half- life of 8 days, ^{90}Sr with a half-life of 28.5 years and ^{137}Cs with a half-life of 30.2 years. The neutron activation reaction produces some rather short-lived nuclides like ^{54}Mn (312 days) and ^{60}Co (5.3 years), but the most significant with respect to safety are the long-lived actinides, such as ^{239}Pu (24 110 years). The nuclear weapons tests per- formed in the atmosphere during the 1960s severely contaminated the globe with these radionuclides. In 1986 the Chernobyl accident contaminated large areas of Europe with significant amounts of radioactivity. Start- ing from World War II, local contamination has occurred in several locations dealing with nuclear weapons production and reprocessing of nuclear fuel especially in the USA, UK and Russia. Although local, the radionuclide contamination from Windscale (Sellafield), UK, can be seen in the ocean up to the North Pole. Compared to these releases, releases from nuclear power plants are insignificant. Research connected with the final disposal of spent nuclear fuel has increased interest in the behavior of other long-lived nuclides produced in nuclear fuel. In addition to ^{239}Pu, nuclides like ^{99}Tc, ^{129}I and ^{237}Np have been increasingly studied. In Europe the disintegration of the Soviet Union has introduced new needs for radionuclide measurements through threats from the disintegration of nuclear submarines in the Barents Sea and the poor maintenance of nuclear power plants.

Measurement of Radionuclides

Originally radionuclides were always measured by radio- metric methods, that is by measuring the radiation emitted at the decay.[3] This is convenient for several reasons. In most cases it is the simplest way of doing the measure- ment. The sensitivity is excellent, the instrumentation usually of low cost, and instrumental detection is often possible. Short-lived radionuclides have a high activity, whereas the mass of the nuclide is usually very low. The signal per unit weight material obtained is very high for short- lived nuclides. This can be illustrated by the fol- lowing examples. One Bq corresponds to 0.3 pg of ^{137}Cs (half-life 30 years), 27 pg of ^{226}Ra (half-life 1599 years) and 152 ng of ^{129}I (half-life 1.57 X 10^7 years). Therefore nonradiometric methods have not been

considered for the determination of important radionuclides like ^{90}Sr, ^{137}Cs, ^{241}Am and the different Cm isotopes. Radiometric methods also give the measure of the property sought directly that is the radiological toxicity. Therefore radio- metric methods are dealt with first and more thoroughly. A number of compilations and conference proceedings describe methods to determine radionuclides.