RADIONUCLIDES IN CHEMICAL RESEARCH

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Contents

Summary

In this chapter, several methods of chemical analysis, material research and industrial process controlling are collected. The common feature of these methods is that all of them apply radionuclides. The radiation these nuclides produce is the primary source of information. The cardinal information the radiation carries can be the chemical concentration of an element, the image of a human brain or the exact location of a leak on a pipeline but every method discussed below measures the intensity and/or the energy of some nuclear radiation.

1. Introduction

Since the discovery of radioactivity, nuclear radiations became important tools in chemistry and material research. The use of radiations and radioactive nuclides is based on their special properties and may be categorized accordingly.

Radioisotopes certainly differ from stable isotopes in their ability to emit radiation while being chemically identical with the stable isotope(s). This allows using them as chemically inert probes, i.e. labeling of a molecule or a substance is possible without interfering with its chemical properties. This leads to the development of various tracer techniques.

If a sample to be studied is radioactive, its radioactivity allows us to identify the nuclides emitting the radiation (alpha- and gamma-spectroscopy). Gamma-spectroscopy is particularly important in Activation Analysis where radioisotopes are generated in the material under investigation by neutron irradiation (or by other means). Neutron absorption results mostly in radioactive nuclides and with this method the majority of the stable isotopes of the elements in the Periodic Table can be made radioactive and by

measuring the resultant radiation qualitative and quantitative chemical (i.e., elemental) analysis of the sample can be carried out with high efficiency.

Sometimes the emitted radiation of a radionuclide can be used as a tool in chemical analysis. For example, beta emitting sources are frequently used in X-ray Fluorescence Analysis (XRF) for the electronic excitation of target atoms. Since the characteristic X-rays emitted by the target are not isotope specific they can be assigned to elements. (Isotope effects cannot be measured at the resolution of regular scintillation or even semiconductor based spectroscopic methods.)

Although this chapter is dedicated only to the use of radioisotopes, one should not forget that nuclide specific properties can be used in chemical research even if a particular nuclide is not radioactive.

The trivial difference between isotope atoms of an element is the mass of these atoms due to the different number of neutrons in their nuclei. This fact can be utilized in Mass Spectrometry (MS) the use of which, however, goes far beyond isotopes. Sometimes the very existence of isotopes makes chemical analysis of molecular composition by MS even more complicated. Of course, the nuclear mass of radioisotopes can be significantly different from that of their stable counterparts (except for nuclear isomers that are pure gamma emitters), and if the decay constants are extremely low, their quantitative determination can be more effective by MS than by measuring their radiation. Typical examples are natural radioactive elements like ^{235}U, ^{238}U, ^{232}Th as well as some transuranium elements. Another, rather exotic application of MS is when the stable isotope composition is checked. This method, making use of biological isotope effects, can reveal if a particular molecule (e.g., a natural stimulator drug) was produced artificially or in a natural process in the human body.

Finally, it should be mentioned that if the masses of two nuclei differ because of the different numbers of neutrons they contain, there are several other nuclear properties that also have to differ. Since the neutron has its own non-zero magnetic moment, the different isotope atoms of the same element will possess their characteristic nuclear moment. These nuclei can therefore be brought into resonance with an external AC electromagnetic field, and making use of the dependence of the resonance frequency on the chemical environment, this nuclear property can be very effectively used for structural research of molecular systems. Therefore it should be emphasized that Nuclear Magnetic Resonance (NMR) is also a nuclear method even if in some applications (medical) the abbreviation NMR had been reduced to MR due to some preconception about anything called “nuclear”. NMR Spectroscopy has been developed from Hydrogen- (or proton-) NMR by now to a multi-elemental technique (see also: *NMR Spectroscopy*).

Returning to radioisotopes, in this chapter, we will discuss some aspects of Neutron Activation Analysis, Radiotracer techniques, gamma-spectroscopy and X-ray Fluorescence Analysis.

2. Neutron Activation Analysis

There is a detailed treatise on this topic elsewhere in the EOLSS (see also: *Radioactivation Analysis and Isotopic Tracers*). Therefore here we would only like to recall the very basics and add some information on a relatively new branch of the method (Prompt Gamma Activation Analysis) that has made it more powerful.

Neutron Activation Analysis (NAA) is based on making stable nuclides in the sample radioactive, and measuring the gamma emission (if any) of the beta decaying radionuclides. Gamma rays with their energy characteristic of a particular nuclide make qualitative analysis possible while the intensity measurement contains the information on the concentration of that particular element in the sample. Due to the high penetration depth of neutrons and gamma rays, the method hardly depends on the matrix. The γ-intensity–concentration relationship can be standardized. Several well established standardization methods have been developed to gain concentrations from gamma ray intensities.

Assuming that nuclide 1 (X_1) is activated with a rate constant λ_1 to nuclide 2 (X_2) which then decays with a decay constant λ_2:

$$X_1 \xrightarrow{\lambda_1} X_2 \xrightarrow{\lambda_2}, \tag{1}$$

the following set of differential equations has to be solved:

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = \lambda_1 N_1 - \lambda_2 N_2, \tag{2}$$

where N_1 and N_2 refer to the amounts of the respective nuclides. This is the general case for a simple consecutive decay and the solution for the activity of X_2 is well known:

$$A_2 = N_2\lambda_2 = \frac{N_{1,0}\lambda_1\lambda_2}{\lambda_2 - \lambda_1}\left(\mathrm{e}^{-\lambda_1 t_i} - \mathrm{e}^{-\lambda_2 t_i}\right) \tag{3}$$

For the case of neutron activation, λ_1 can be expressed as the product of the neutron flux (Φ) and the neutron absorption cross section (σ): $\lambda_1 = \Phi\sigma t_i$ is the irradiation time. Since under the usual experimental conditions of NAA the consumption of the irradiated nuclide is negligible, practically N_1=const.=$N_{1,0}$, the following approximation can safely be applied:

$$\begin{aligned} &\lambda_1 << \lambda_2 \\ &\mathrm{e}^{-\lambda_1 t_i} \cong 1 \end{aligned} \tag{4}$$

so that

$$A_2 = N_{1,0}\sigma\Phi\left(1 - \mathrm{e}^{-\lambda_2 t_i}\right), \tag{5}$$

where $N_{1,0}$ is the concentration of the nuclide to be measured.

This formula must be completed with two further terms in regular NAA taking into account the cooling time as well as the time length of the measurement if the latter is not negligible as compared to the half-life of X_2.

Although NAA is very powerful in multiple elemental analysis, the necessity of allowing cooling time to avoid strong overlap of simultaneously decaying radionuclides naturally requires that the half-lives of the activated products should not be too low. On the other hand, light elements will certainly decay at a very high rate because neutron absorption causes a huge change in the neutron to proton ratio of the nucleus resulting in instability. Thus light elements cannot be measured by regular NAA. For long-lived radionuclides, the long measuring time (and also irradiation time!) can be problematic.

These drawbacks can be partially avoided by detecting the prompt gamma photons emitted by the newly formed excited nucleus right after the neutron absorption process, instead of measuring the radioactivity of the resultant activated product (i.e. gamma quanta after the beta decay). This branch of activation analysis is called Prompt Gamma neutron Activation Analysis (PGAA). The absorption of a thermal neutron can produce nuclear states with energies of up to about 11 MeV, which usually decay through a cascade of gamma rays. This makes the gamma spectrum very complex, therefore there is a demand for high resolution detectors and fast electronics which are readily available today.

Note that in PGAA the formulas used in regular NAA which take into account time evolution of the activity of the daughter nuclide X_2 can safely be discarded (even the simple formula (5)) because the intensity of the prompt gamma radiation is simply proportional to the concentration of the nuclide X_1 (as well as to the neutron flux and the neutron absorption cross section). Sometimes special beam interruption technique is used to measure daughter nuclides with very short half-lives. In this case, which is some kind of an intermediate situation between regular NAA and PGAA, the NAA formalism must be used.

In addition to light elements which do not produce radioactive isotopes of long enough half-life by (n,γ) reaction, PGAA complements NAA with a number of heavier elements with high cross sections whose normal decay products may be difficult to measure in the presence of high activities induced in certain matrices. The light elements investigated most are H, B, C, N, Si, P, S, and Cl, and the heavier elements are Cd, Sm, and Gd.
The source of neutrons for PGAA is almost exclusively a beam of neutrons extracted from a nuclear reactor into an external irradiation position. This offers an opportunity to increase sensitivity by cooling the neutrons (with liquid nitrogen or even liquid helium) to increase the neutron absorption cross sections. Detection limit for certain elements may be reduced by two orders of magnitude with this method.

Table 1 lists detection limits for various elements achieved by cold neutron PGAA in

the Budapest Neutron Center.

Element	DL (μg)	Element	DL (μg)	Element	DL (μg)	Element	DL (μg)
H	0.3	Ti	1	Mo	5	Gd	0.002
Li	20	V	1	Ru	6	Tb	30
Be	160	Cr	4	Rh	0.5	Dy	0.1
B	0.001	Mn	0.4	Pd	3	Ho	1.2
C	460	Fe	9	Ag	1.4	Er	0.3
N	60	Co	0.9	Cd	0.006	Tm	2
O	10 000	Ni	4	In	0.3	Yb	2
F	200	Cu	7	Sn	90	Lu	1.3
Ne	80	Zn	20	Sb	5	Hf	0.35
Na	5	Ga	4	Te	5	Ta	7
Mg	75	Ge	6	I	9	W	20
Al	12	As	4	Xe	2	Re	5
Si	24	Se	4	Cs	6	Os	9
P	100	Br	10	Ba	50	Ir	2
S	10	Kr	0.4	La	20	Pt	3.2
Cl	0.5	Rb	100	Ce	60	Au	0.2
Ar	8	Sr	8	Pr	13	Hg	0.08
K	4	Y	12	Nd	0.5	Tl	56
Ca	11	Zr	70	Sm	0.003	Pb	150
Sc	0.8	Nb	50	Eu	0.01	Bi	1200
						Th	140
						U	130

Table 1. Maximum detection limits (DL) of elements with PGAA method for 100 000 s measuring time in cold neutron beam. (Source: Budapest Neutron Center)

3. Radiotracers

The story of labeling a substance with a radioisotope began in 1913 when Hevesy and Paneth measured the extremely low solubility of lead salts by using naturally occurring ^{210}Pb as a radioactive tracer. Since then various artificially produced radionuclides became available, and this technique has been widely employed in chemical analysis. It is also an essential technique in other fields such as biochemistry, biology, health sciences, geology and environmental studies.

3.1. The Tracer Principle

As mentioned in the Introduction of this chapter, the fundamental principle of the radioactive tracers is that the chemical behavior of radioactive isotopes is identical with that of their stable isotopes in any chemical process. The very minor isotope effects may safely be ignored especially at high atomic numbers. Isotope effects (see: *Isotope Effects, Isotope Separation and Isotope Fractionation*) deserve some attention only in the case of tritium labeling if the labeled molecule is light. In this case, diffusion rates, equilibrium constants, especially the strength of H-bonds may be affected.

The effect of radiation emitted by the radioactive tracers on a chemical or biological system under study is also usually negligible. The amount of a radioactive tracer necessary for an experiment is usually so small that detectable radiolysis never occurs in the system. This statement refers to the time of measurement which is normally a few minutes or maximum a few hours. If a long-term storage precedes the use of a radiolabeled organic compound, possible radiolytic effects should be considered. A quite different case is the human application where biological consequences occur well before any detectable radiolytic effect.

The high sensitivity of radioactive tracer technique to measure chemical concentration is due to fact that decay events can be counted one by one at the molecular level while one mole of substance contains 6×10^{23} potentially labeled entities. Thus in a carrier-free tracer application, elements can be easily detected in pictogram amounts or less within a reasonable time of measurement using conventional detectors. This feature presents the dominant advantage or radio-labeling in radioimmunoassay. The higher the decay constant, the lower is the detection limit for a labeled molecule, thus tracers of toxic elements such as As, Tl and Hg or poisonous carrier compounds such as HCN can be used with no hazardous effects. Thanks to the sensitive detecting techniques, the activity needed for a particular measurement is sometimes so low that the amount of radioactive material is far below the exempt level (see: *Nuclear Waste Management and the Nuclear Fuel Cycle*), so it can be legally considered as a non-radioactive substance. (No isotope laboratory is required for performing such measurements.)

Radioactive tracing needs a radiation that penetrates large masses of materials without considerable scattering or absorption. On the other hand, according to the tracer principle, the source of the radiation should be a radionuclide. These requirements are fulfilled precisely with high energy gamma radiation and gamma decaying radionuclides. Therefore, most tracers are high energy gamma emitters but positron emitters and, in special cases, pure beta emitters are used, as well. Due to the features of gamma radiation (see: *Interactions of gamma Radiation* in *Radiochemistry and Nuclear Chemistry*), tracing of the labeling radionuclide is free of any matrix effect (physical and chemical condition of the sample) and does not depend on temperature, pressure, presence and concentration of chemicals and so on, either.

Although several non-radioactive labeling techniques have been developed, there are applications that can only be performed with the use of an isotopic tracer. Among them are the studies on self-diffusion and isotopic exchange reaction. Examples of such studies will be given below.

The radiotracer method depends on the existence of appropriate tracers. Therefore it cannot be used with some light elements such as He, Li, B, and Ne. Only short-lived radioisotopes are available for N (^{13}N, $t_{1/2}$=9.965 min) and O (^{15}O, $t_{1/2}$=2.037 min), which also limits the use of the method in these cases.

Radio-labeling does not necessarily mean replacing an atom of a particular element with its radioactive isotope atom (internal labeling). It is also possible that a chemically different radioactive atom replaces the original atom in the molecule (e.g., H is often replaced by ^{18}F). This is called external labeling, and the chemical effect of the external atom should be carefully considered. Especially in biochemical applications, when large molecules are labeled, a smaller group with easy labeling option (e.g., iodine-labeled aromatic ring) may be attached to the large molecule without affecting the key biological function. This is called conjugation labeling. Sometimes the interference with the biological function helps accumulation of the carrier compound in the target tissue (e.g., as fluorine stops metabolic degradation of ^{18}F-deoxy-glucose in a cell).

It should be mentioned that radio-tracing is also possible in a principally different way: a non-radioactive tracer is used which is made radioactive later by neutron irradiation. This is sometimes safer, especially if a large amount of material is to be labeled for an industrial application. One has to make sure, of course, that the radiation damage causes no problems.

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Biographical Sketches

Zoltán Homonnay was born in Eger, Hungary, in 1960. He is a professor at Eötvös Loránd University, Budapest, where he teaches nuclear chemistry, radiation safety and nuclear environmental protection. His main research interest is Mössbauer Spectroscopy applied in various fields of chemistry and materials science. Ha has received his first degree (Candidate of Science awarded by the Hungarian Academy of Sciences, an analogue of PhD) in the field of Al-Fe alloys, and then turned toward high-temperature superconductors on which he published his most important papers and received his Doctor of Academy title (DSc). He had substantial contribution to a chapter about Mössbauer Spectroscopy in the Handbook of Nuclear Chemistry [Kluwer Academic Publishers Dordrecht-Boston-London (2003)]. He is heading subdivisions in the Hungarian Chemical Society (Radioanalytical Chemistry) and in the Hungarian Academy of Sciences (Nuclear Methods in Structural Chemistry).

Károly Süvegh was born in Oroszlány, Hungary, in 1962. He received his MSc in chemistry from Eötvös Loránd University (ELTE), Budapest, in 1986. He received his CSc (PhD) in nuclear chemistry from the Hungarian Academy of Sciences in 1995. He has been working for ELTE ever since graduating there. Presently he is Associate Professor in the Laboratory of Nuclear Chemistry, Institute of Chemistry, ELTE. In the meantime he was Visiting Scientist at Lehigh University, Bethlehem, USA (1987). His research field has been chemical applications of positron annihilation spectroscopy. He teaches nuclear chemistry, particle physics and physics lab to chemistry majors. He co-edited with Prof. Vértes and Dr. Nagy a book listed in the Bibliography. He also co-authored several chapters in different books.