

RADIOACTIVE METHODS OF ANALYSIS

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The application of radioactive materials to the study of the problems in biology, physics, chemistry, and industry is growing rapidly. This is mainly because of the utility of radioisotopes as analytical tools.

Radioactive methods of analysis are particularly useful for the detection and determination of trace quantities of materials and for the measurement of larger quantities in complicated systems or samples.

PROPERTIES OF RADIOISOTOPES

Radioisotopes are unstable atoms which decay by the emission of radiation, alpha, beta, or gamma rays.

Radioisotopes have two properties which make them important analytical tools: (1) They behave chemically the same as the isotopes of the elements, and (2) Their radiation indicates their position and quantity.

$$N = N_0 e^{-\lambda t}$$

The rate of disintegration and the energy of the radiation emitted are characteristic functions of a given radioisotope. The rate of decay is exponential, where N = the number of atoms at time t , N_0 = the number of atoms at time t_0 , and λ = the characteristic decay constant.

The rate of disintegration is conveniently described in terms of a half-life, that is, when

$$N = \frac{N_0}{2}$$
$$t_{1/2} = \frac{0.693}{\lambda}$$

The energy of the radiation emitted by a radioisotope may be expressed in terms of the absorption of the energy by matter. The absorption of gamma rays and, in some cases, of beta particles may be represented by the formula,

$$I = I_0 e^{-\mu d}$$

where I = the intensity at thickness d , I_0 = the original intensity, μ = the absorption coefficient, and d = the thickness of absorber.

$$\text{When, } I = \frac{I_0}{2}$$
$$d_{1/2} = \frac{0.693}{\mu}$$

The energy of the radiation may be defined in terms of the half-thickness, $d_{1/2}$, usually expressed in mg/cm².

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ISOTOPIC TRACING

Radioisotopes are used most frequently as isotopic tracers. A small, known quantity of a radioactive-labeled form of the compound to be traced is mixed with the experimental sample at the beginning of the work. The labeled form of the compound will behave the same as the nonactive compound during treatment of the sample. The measurement of the radiation from any fraction of the sample is proportional to the quantity of the compound present.

Examples of the conditions under which radioisotopes are useful as isotopic tracers are:

(1) The quantity of the material to be traced is very limited. For example, it is possible to detect as little as 10^{-12} grams of several of the radioisotopes. Some of the most interesting examples of ultramicrochemical work with tracers are found in the description of the isolation and identification of new elements, such as technetium, promethium, curium, and californium. None of these elements have been found in nature since they are radioactive and have half-lives which are short compared to the age of the earth.

In the production and identification of element 98, californium, Street, Thompson, and Seaborg (1950) worked with only a few thousand atoms of the new element. In addition, the investigation was complicated by the fact that californium-244 has a half-life of about 45 minutes. Prior to the experimental work, it was necessary to predict some of the nuclear and chemical properties of californium so that satisfactory chemical separation procedures and detection instruments could be used. The chemical properties were predicted by comparison of the lanthanide rare earth series of elements to the actinide series in which californium would fall. On this basis, element 98 should be an "eka-dysprosium." It should have a stable plus-three oxidation state and behave like a rare earth. Ion-exchange procedures which are effective for the separation of the lanthanide rare earths should be useful for the isolation of element 98.

It was believed that californium-244 would have a half-life of one-half to several hours and would decay by the emission of alpha particles with an energy of 7.0 to 7.3 Mev. The chemical separation procedure was designed so that a half-life as short as 20 minutes could be detected. The californium was produced by bombarding curium-242 with 35-Mev helium ions in the 60-inch cyclotron of the Crocker Radiation Laboratory. The target was dissolved in an acid and the metal ions were adsorbed on a cation-exchange resin. The separation of the cations from the resin was carried out by selective elution with a citrate solution. By comparison with the elution of the lanthanide series, for which the order of the removal from the resin is dysprosium, terbium, gadolinium, and europium, it had been predicted that californium would be eluted first and then berkelium, curium, and americium. The predictions were found to be valid. An alpha activity with an energy of 7.1 Mev and a half-life of 45 minutes was found. Although the new activity was contaminated by some curium-242, it was possible to distinguish between the two activities since the alpha particles from curium have a lower energy, about 6 Mev. Tracer experiments were conducted with the new element to study some of its chemistry. Oxidation experiments showed that californium could not be oxidized to the four or six valent states.

Radioactive microchemical methods are important in industrial research. Insecticides which have been synthesized with radioactive sulfur-35 have been used to measure the quantity of the insecticide which was taken up by insects and the plant material (Anonymous, 1950).

Another example is the determination of the separation efficiency of chemical processes. In the case in which it is required that a product of high purity be produced, radioactive forms of the impurities may be used to measure the contamination of the product.

(2) The material to be traced is associated with other materials which are difficult to separate from one another. For example, the metals hafnium and

zirconium are extremely difficult to separate. Through the use of either radioactive hafnium-181 or zirconium-95, the analysis may be made without a tedious separation.

(3) A material is to be located with reference to the position of other materials in a sample. The investigation of the segregation of trace elements in an alloy is an example of this application. Autoradiographic techniques in which the position of the radioactivity is found by the exposure of a photographic emulsion are frequently used.

(4) The sample must be analyzed nondestructively or in place. Radioactive dyes (Griffin, Goland, and Chamberlain, 1950) such as diiodofluorescein have been employed for the diagnosis of intracranial lesions. The dye is labeled with the gamma-emitting radioisotope iodine-131. Detection of the location of the dye in the diseased tissue in the brain is accomplished through the use of a directional gamma ray detector.

(5) A determination must be made rapidly before some further change occurs. Radioisotopes might be used to control a process in which several operations are being done automatically. For example, in the treatment of a fabric, traces of the soap used in the washing operation may interfere with the dyeing operation. A radioisotope-labeled soap could be used to insure that the soap had been removed prior to the dyeing of the fabric.

(6) The diffusion or reaction of a material with itself must be measured. It is possible to determine the self-diffusion coefficients of the metals. The kinetics of isotopic exchange reactions may be studied. For example, the rate of exchange between different oxidation states of the same metal may be measured.

ANALYSIS BY ISOTOPIC DILUTION

One of the most useful methods of analysis with radioactive materials is isotopic dilution. The method is based upon a comparison of the specific activity of a radioactive-labeled material before and after dilution with a nonactive form of the same material. Isotopic dilution is of particular advantage for the determination of a compound which is difficult to separate quantitatively from a sample.

The method may be illustrated by an example: (1) Assume a sample which contains an unknown A grams of X , (2) Mix B grams of X having a specific activity of S_B counts per minute per gram into the sample, (3) Separate a portion of X in pure form, and (4) Determine the specific activity of S_{AB} of this portion of X . Then the various quantities may be related through the equation,

$$BS_B = (A + B) S_{AB},$$

and A calculated by,

$$A = B \left(\frac{S_B}{S_{AB}} - 1 \right).$$

The technique may also be used to analyze an unknown radioactive sample. In this case, the sample is diluted with a portion of a nonactive form of the compound.

The specific activity before S_A , and after, S_{AB} , dilution are measured. The equations involved are,

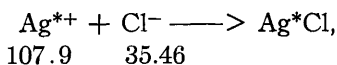
$$AS_A = (A + B)S_{AB},$$

$$A = B \frac{S_{AB}}{S_A - S_{AB}}.$$

RADIOMETRIC ANALYSIS

The process of analyzing a nonactive component by combination with a radioactive isotope is known as radiometric analysis

For example, radioactive silver might be used to determine a small quantity of chlorine in a sample. The radioactive silver, Ag^* , would combine with the chloride ions,



to form active silver chloride. The silver chloride could be separated from the solution by centrifugation or by collection on a precipitate of ferric hydroxide.

The weight of silver used could be calculated from the specific activity, S_{Ag} , of the silver added and the activity, A_{AgCl} , of the silver chloride:

$$\text{Weight of Ag} = \frac{A_{\text{AgCl}}}{S_{\text{Ag}}}$$

The weight of the chlorine could be found from the stoichiometry of silver chloride:

$$\text{Weight of Cl} = \frac{35.46}{107.9} \times \frac{A_{\text{AgCl}}}{S_{\text{Ag}}}$$

ANALYSIS WITH NEUTRONS

Several methods of analysis have been developed utilizing the absorption and scattering of neutrons by matter. Since neutrons are neutral particles, they can approach and enter a nucleus. High neutron energies are not required because a neutron does not have to overcome repulsive electrical forces. The cross section of a nucleus is the effective area presented to a neutron. The total cross section is made up of two components, an absorption and a scattering cross section. In the case of absorption, a nucleus takes on a neutron, and another form of radiation, such as an alpha particle or a photon of gamma rays is emitted. Scattering consists of a nucleus receiving a neutron and emitting a neutron.

Although neutrons are particles, they behave with wave-type properties. The wavelength, λ , of a moving neutron is defined as,

$$\lambda = \frac{h}{mv}$$

where h is Plank's constant and m and v are the mass and velocity of the neutron.

The best source of neutrons is a nuclear pile which produces 10^{10} to 10^{12} neutrons per square centimeter per second. A cyclotron which uses deuterons and a beryllium target may produce 10^8 to 10^9 n/cm²/sec.

Portable neutron sources which consist of an alpha- or gamma-emitting radioisotope and beryllium or boron are available. The neutrons are produced by the action of the radiation on the beryllium or boron. Portable sources may produce about 10^3 to 10^5 n/cm²/sec. Their use is limited because of their lower yield of neutrons.

Neutron Activation

Samples of some materials may be analyzed by neutron activation (Taylor and Havens, 1950). The sample is placed in a flux of slow neutrons. Some of

the atoms of the sample absorb neutrons and become radioactive isotopes. A determination of the half-life and energy of the radiation identifies the radioisotope present. The quantity of the original material present may be calculated.

The rate of production of the radioactive atoms is given by the difference between their rate of formation and their rate of decay:

$$\frac{dN^*}{dt} = N\sigma f + \lambda N^*, \quad (1)$$

where N^* = number of active atoms, N = number of original inactive atoms, σ = atomic activation cross section, f = flux of neutrons, λ = decay constant for N^* , and t = time.

Integration and substitution of the activity, $A = N^*\lambda$, gives

$$A = N\sigma f (1 - e^{-0.693t/t_{1/2}}) \quad (2)$$

where $t_{1/2}$ = half-life of N^* . When t is much greater than $t_{1/2}$, the saturation activity in the sample is approached and the formula simplifies to

$$A = N\sigma f. \quad (3)$$

If the measurement of the activity is made at a time t_1 after neutron irradiation is ended, the activity is related to the original activity in the following manner:

$$A_{t_1} = Ae^{-\lambda t_1}, \quad (4)$$

where A_{t_1} = the activity at time t_1 , and A = the activity at the end of neutron irradiation.

By substituting the expression for A in equation (3) into equation (4), we obtain

$$A_{t_1} = f\sigma Ne^{-0.693t_1/t_{1/2}}. \quad (5)$$

Since $N = 6.02 \times 10^{23} \times \frac{g}{M}$, the following formula for the weight, g , of the

material in the sample is obtained:

$$g = \frac{A_{t_1}M}{6.02 \times 10^{23} f\sigma e^{-0.693t_1/t_{1/2}}}. \quad (6)$$

Now, if t is not much greater than $t_{1/2}$, the formula needs to be corrected, since the activity of the sample was not at saturation:

$$g = \frac{A_{t_1}M}{6.02 \times 10^{23} f\sigma (1 - e^{-0.693t_1/t_{1/2}}) e^{-0.693t_1/t_{1/2}}}. \quad (7)$$

For accurate work, the absolute activity of the sample must be determined by comparison with a standard. The counting efficiency of most nuclear detectors is only about 5 to 35 percent. It is very difficult to determine absolute disintegration rates. Examination of formula (7) shows that those elements with large cross sections and short half-lives are the easiest to detect. Table 1 gives the atomic activation cross section, the radioisotope produced, and the half-life of the radioisotope for several elements. The minimum detectable quantity of the

TABLE 1
List of Cross Sections (Taylor and Havens, 1950)

Element	Cross Section, Barns	Radioisotopes	Half-Life*
Ir	285	Ir ¹⁹²	70 d
Ag	48	Ag ¹¹⁰	24 s
Cl	40	Cl ³⁶	2 x 10 ⁶ y
Co	22	Co ⁶⁰	5.3 y
Mn	11	Mn ⁵⁶	2.6 h
I	6.25	I ¹²⁸	25 m
Ni	2.9	Ni ⁵⁹	16 y
Cu	1.99	Cu ⁶⁴	12.8 h
Cr	0.49	Cr ⁵¹	26.5 d
Fe	0.15	Fe ⁵⁵	4 y
Mg	0.0054	Mg ²⁷	10.2 m

* s = seconds, m = minutes, h = hours, d = days, y = years.

elements may be calculated with the equation developed above. The formula is simplified if it is assumed (1) That the time of irradiation is long compared to the half-life of the radioisotope, and (2) That the activity measurement is made immediately after irradiation.

$$g \times 10^{-12} = \mu\mu g = \frac{kA_t 10^{12}}{6.02 \times 10^{23} f\sigma \times 10^{-24}}$$

where k = counting efficiency = 25 percent, A_t = 100 counts per second, $f = 10^{12}$ u/cm²/sec., and σ = cross section in barns.

The equation reduces to

$$\mu\mu g = \frac{41.5 \times M}{\sigma}$$

The calculation of the minimum detectable quantities of a few elements according to the previous assumptions is shown in table 2.

TABLE 2

Element	$\mu\mu g$	σ	M
Ir	1.5	285	193.1
Mn	208	11	54.93
Cu	1,320	1.99	63.57
Mg	187,000	0.0054	24.32

Samples in which two components are activated by neutron irradiation may be analyzed. The analysis becomes quite difficult if more than two active components are present. In a two-component system, the elements present may be detected

by the characteristic half-life and energy of the radiation of the radioisotopes formed. In order to distinguish between the two elements, it is necessary that the half-lives and energies of the radioisotopes be quite different. The half-lives of the two radioisotopes may be determined by plotting the time versus the log of the activity of the sample, Figure 1. The shorter half-life, *a*, is found by drawing a tangent to the curve at the time, t_0 . The longer half-life, *b*, is measured from the tail of the curve after all of the isotope, *a*, has essentially decayed. In this case, the half-lives of *a* and *b* were found to be 0.55 and 5.0 days, respectively.

The activity of the two components at t_0 may be found. In the case of *b*, this may be found by extrapolation of the tail back to t_0 . The activity of *a* is then equal to the difference between the total activity and that of *b* at t_0 . These activities may be used to calculate the quantity of *a* and *b* in the sample. The energy of the radiation from the two radioisotopes may be measured in a manner

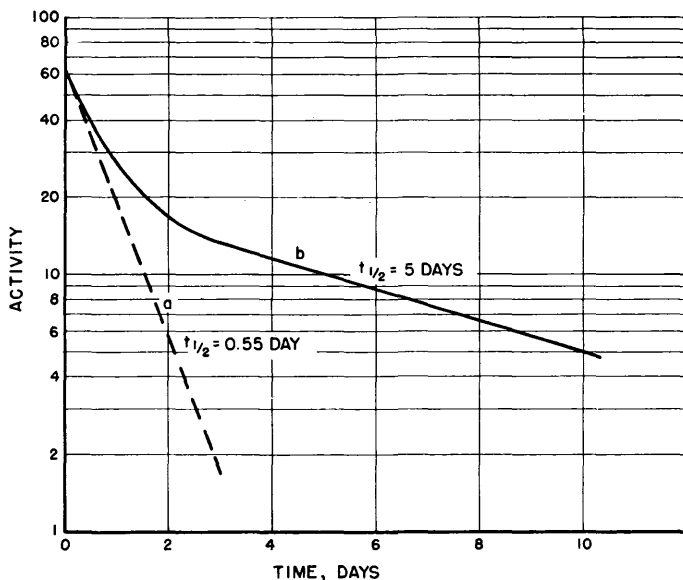


FIGURE 1. Determination of half-lives in a two-component system.

similar to that of the half-lives. An absorption curve is plotted by measuring the activity of the sample through different thicknesses of an absorber such as aluminum or lead (fig. 2). The half-thicknesses are determined in the same manner as the half-lives. The energies are found from curves or data on the half-thickness of various energies of the beta or gamma radiation being measured.

Neutron Absorption-Heterogeneous Beam

It is possible to determine small quantities of some elements which have large neutron absorption cross sections by the measurement of the transmission (Muelhause and Thomas, 1950) of a beam of neutrons, having energies up to 50,000 electron volts. The intensity of the beam is measured with and without the sample interposed.

The transmission data are related to the cross sections of the two components as shown in equation (1):

$$n_1 \sigma_1 + n_2 \sigma_2 = \ln \frac{I_0}{I}, \quad (1)$$

where n_1 and n_2 = the numbers of atoms of elements 1 and 2, respectively, σ_1 and σ_2 = the cross sections of elements 1 and 2, respectively, I_0 = the intensity of the neutron beam without the sample, and I = the intensity of the neutron beam with the sample.

The mass of the sample may be expressed by:

$$m = \frac{(n_1 A_1 + n_2 A_2)}{N},$$

where m = the mass of the sample per cm^2 , A_1 and A_2 = the atomic weights, and N = Avogadro's number.

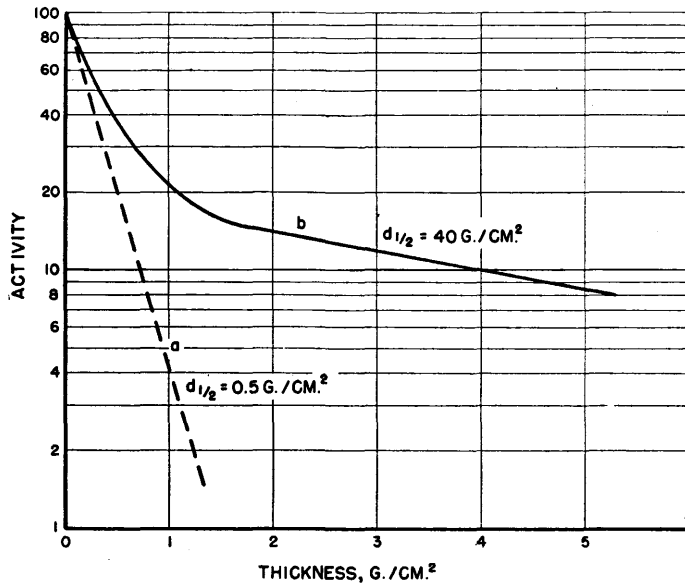


FIGURE 2. Determination of energy in a two-component system.

Combining equations (1) and (2),

$$n_1 = \frac{I_0 \left(\frac{mN \sigma_2}{A_2} - \sigma_1 \right)}{\sigma_1 \left(\frac{mN \sigma_2}{A_2} - \sigma_1 \right) - \sigma_2 I_0}. \quad (3)$$

An example of the use of the method is the determination of lithium in magnesium. A measurement of 5 percent lithium could be made to ± 0.2 percent.

Neutron Absorption—Two Neutron Energies

In the neutron energy range of about 0.1 to 1 electron volt, cross sections vary inversely with the square root of the energy (Taylor and Havens, 1950). The composition of a two-component system may be estimated if the two elements have different cross sections at two energies.

Through the use of a neutron spectrometer, the transmission of two neutron beams of different energies through the sample may be determined. Two equa-

tions of the type indicated for the absorption of a heterogeneous neutron beam are obtained:

$$n_1 \sigma_1^1 + n_2 \sigma_2^1 = \ln \frac{I_0}{I}$$

$$n_1 \sigma_1^2 + n_2 \sigma_2^2 = \ln \frac{I_0}{I}$$

where σ^1 and σ^2 = the cross sections at the two neutron energies. These two equations may be solved simultaneously to find n_1 and n_2 , the number of atoms of elements 1 and 2, respectively.

In order to make an analysis of this type, the cross sections of the two elements at the two energies must be known. Examples of application of the method are the estimation of manganese in iron and aluminum and tantalum in columbium.

Neutron Resonance Absorption and Scattering

Many of the elements exhibit a marked increase in their cross sections at definite neutron energies in the range of 1 to 5000 electron volts. This is known as neutron resonance absorption and scattering (Taylor and Havens, 1949). Resonance is usually associated with those elements with atomic masses over 100. Using a neutron spectrometer, it is possible to plot the transmission of a sample at various neutron energies. The observation of a resonance absorption may be used for the identification and determination of the quantity of a particular nuclear species in a sample. A few examples of analyses which may be made by resonance absorption are tantalum in columbium, hafnium in zirconium, and cobalt in steel.

Neutron Diffraction

Diffraction effects may be observed with thermal neutrons. These effects take place in accordance with the Bragg relation,

$$n\lambda = 2d \sin \theta.$$

Laue patterns may be obtained by passing a beam of thermal neutrons through a crystal. The neutrons may be used in a manner similar to X-rays. The major advantage of neutrons is that they may be used to locate the position in a crystal of the light elements, such as hydrogen, which have very low scattering power for X-rays. The diffraction pattern of neutrons must be detected by an indirect method since neutrons do not strongly affect a photographic emulsion. A thin sheet of a material having a high cross section, such as indium, is placed in front of the photographic emulsion. The radiation produced in the indium causes exposure of the film.

LIMITATIONS OF RADIOACTIVE METHODS

Radioactive methods of analysis are subject to limitations which require consideration. Foremost of these is the effect of radiation on the tissues of the human body. Specialized equipment and techniques are usually required to work safely with radiochemicals. The methods of detection of radioactivity present another limitation to quantitative measurements. Most of the common nuclear detectors do not have an efficiency greater than 35 percent. In addition, absorption of radiation may take place within the sample being measured, or secondary radiation may be produced. Care must always be exercised to correct a series of determinations on different samples which are to be compared to some standard set of conditions. Another complication of the use of radioisotopes is

that it may be difficult to introduce the radioactive material in the proper form. Although it is possible to purchase some radioisotope-labeled compounds, it is frequently necessary to synthesize the compound from some other form. In some cases, the synthesis may be difficult or impossible. In some cases, it is desirable to measure the quantity of more than one component of a system. The determination of even two radioisotopes in the same experiment becomes quite complicated.

While it is usually assumed that isotopes of the same element behave chemically the same, those of the lighter elements do not. For example, one may find a discrepancy of nearly 15 percent in the use of tritium as a tracer for hydrogen. In extremely dilute solutions, a material may have different properties than in more concentrated solutions. For example, the radioactive ions in a very dilute solution may be absorbed on dust particles and behave as colloidal particles.

In spite of these limitations, radioisotopes are powerful tools for the analyst. Radioactive methods should be considered along with other available methods of solving a particular problem. The procedure which appears to have the greatest advantage should be selected.

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