CHAPTER 14

RADIOCHEMICAL AND NUCLEAR METHODS

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Radiochemical analysis[1-4] is concerned with the determination of the radioactivity associated with the elements in a sample. Such measurements may subsequently be used to compute masses or concentrations, but the activity measurement is the primary one. The radiochemist must be familiar with the chemistry of many elements, including the rarer ones, and must know something of the physics of radioactive decay and radiation detection. Radiochemistry became of great importance over 20 years ago with the beginning of the Manhattan Project,[5] and this importance has increased with the establishment of the U.S. Atomic Energy Commission (AEC) programs, the widespread use of radioisotopes, the worldwide construction of reactors, and the development of radioactivation analysis.

14–1 TECHNIQUES AND APPARATUS

14–1.1 Separation Methods

Radiochemical separation methods[6-11] include precipitation, solvent extraction, distillation, ion exchange, and chromatography. Published methods, such as those described in sec. 14–4 and in various chapters of this book, furnish many examples. Since radioelements are often present in very low chemical concentrations, effects such as sorption on surfaces, anomalies in solvent extraction, etc., must be guarded against. These effects may be eliminated by the addition of an acid, a complexing agent, or a carrier to a radioelement solution. A carrier is a material chemically similar to, or identical with, a given radionuclide. An isotopic carrier is the ordinary stable element with which the radioactive species is isotopic.

In separations employing an isotopic carrier, the interchange of the carrier and the radioelement is an essential first step (Refs. 1, 4, 5, and 12). This interchange is achieved by acidification, by the formation of a complex, or by oxidation and/or reduction. Once the interchange has been achieved, losses of carrier and radionuclide are proportional; therefore the radioactivity ultimately measured can be simply corrected for yield or recovery. Later steps in a typical analysis include separation from other activities and inactive species,

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Table 14.1—INSTRUMENTS USED FOR VARIOUS TYPES OF RADIOACTIVITY

Instrument*	Radiation			
	Alpha	Beta ($\beta^- + \beta^+$)	Gamma	X-ray†
Windowless proportional counter	X	X		
Thin-window proportional counter	X	X		
Solid scintillation detector	X	X		
NaI(Tl) [15]			X	
Thin NaI(Tl) wafer				X
Liquid scintillation counter [16]	X	X (especially for low-energy beta)		
Semiconductor detector [17]	X	X		
End-window or glass-wall Geiger counter		X	X	X
Ionization chamber		X		
With high-pressure gas			X	

*Text references apply except for ones specifically noted in this table.

†For example, from electron-capture decay.

measurement of recovery (by gravimetric, colorimetric, or other method), and activity determination.

14–1.2 Measurement

Instruments used for measuring various types of radioactivity are summarized in Table 14.1 (Refs. 1, 2, 4, 13, and 14). For testing reproducibility of instrument performance, a reference standard is used. This standard is a long-lived source of the type of radiation measured by a given instrument. Thus Pu^{239} or Am^{241} is a suitable alpha standard; Pa^{234} (UX_2) in equilibrium with U^{238} (natural uranium) is satisfactory for beta; and Cs^{137} or Ra^{226} can be used for gamma detectors. For absolute measurements, standards are used to calibrate measuring devices. Such standards are usually prepared by 4π counting, coincidence counting, and defined-geometry techniques.[12, 18, 19] Standards are supplied in the United States by the National Bureau of Standards and private companies. Calibrations must be made under the conditions encountered in the use of the instruments, with respect to the size and positioning of the source, solids content (especially for alpha and beta counting), etc.

14–1.3 Instrumental Analysis

The half life and the type and energy of radiation of a nuclide can be used to identify it and to make quantitative analyses of mixtures (Refs. 1, 2, 4, 14, and 15). In a mixture of nuclides, an analysis can be made by resolving decay data by graphical or analytical means, provided the half lives are short and sufficiently different. Mixtures of beta emitters can be resolved in a similar way by taking absorption data in aluminum.

The most important instrumental methods involve the use of spectrometers. Mixtures of alpha-emitting nuclides are frequently analyzed by spectra obtained from gridded ionization chambers[14] or diode detectors.[17] Beta spectro are obtained by scintillation spectrometry with organic solid or liquid phosphors. Much use is made of gamma spectrometry in which cylindrical sodium iodide detectors are employed. The principles and applications of the method have been discussed extensively elsewhere (Refs. 1, 2, 4, 14, 15, 20, and 21). It is sufficient to note that data are available for converting observed counting rates under photopeaks to absolute photon-emission rates (hence to disintegration rates), that techniques (at present largely graphical) are available for resolving spectra of mixtures to obtain quantitative activities of individual components, and that many instruments (both simple and complicated) are commercially available. Table 14.2 lists a number of nuclides commonly measured by gamma spectrometry, along with their principal energies and intensities of gamma radiation.[21]

14–1.4 Statistics

All measurements are subject to random error since the measurement of radioactive decay is itself a statistical process. At low activity (few counts) large errors occur, and at high activity dead-time losses become important. Such errors have been discussed in Refs. 1, 2, 14, 22, and 23. It should be noted that any radiochemical method has an inherent error, independent of the random error in measurement, which may range from a fraction of one percent to several percent. Properly, the method error should be combined with the counting error (root-mean-square combination) to estimate the error in a particular analysis.

14–1.5 Sources of Nuclear Data

Properties of radionuclides, such as half lives, radiation energies, and intensities, etc., can be found in various tabulations (Refs. 15, 21, and 24 to 27). In preparing one of these tabulations, Ref. 21, an attempt was made to select the best values of half lives and absolute gamma intensities. In gamma spectrometry it is essential that the absolute gamma intensities be known.

14–2 ACTIVATION ANALYSIS

In radioactivation analysis the elemental content of radioisotopes induced by nuclear-particle bombardment is measured (Refs. 1 to 4, 9, 10, and 28 to 31). Several different types of bombarding particles have

Table 14.2—IMPORTANT GAMMA-RAY EMITTERS

Nuclide*	Half life	Decay mode	Major gammas	
			Energy	Intensity †
Ar^{41}	110 min	β^-	1.30	0.99
$Ag^{110m,\ 110}$	253 days	β^-	0.66	0.9
			‡0.90	1.0
Am^{241}	460 years	α	0.060	0.40
Au^{198}	2.69 days	β^-	0.41	0.95
Ba^{140}	12.8 days	β^-	0.54	0.25
Br^{82}	36 hr	β^-	0.77	0.83
Ca^{47}	4.5 days	β^-	1.30	0.71
Ce^{141}	33 days	β^-	0.145	0.43
Ce^{144}	285 days	β^-	0.134	0.11
Co^{60}	5.27 years	β^-	1.17	1.00
			1.33	1.00
Cs^{134}	2.05 years	β^-	0.60	0.97
Cs^{137}–Ba^{137m}	30 years	β^-	0.66	0.85
Fe^{59}	45 days	β^-	1.10	0.56
			1.29	0.44
Hg^{203}	46 days	β^-	0.28	0.83
I^{131}	8.08 days	β^-	0.36	0.81
K^{42}	12.5 hr	β^-	1.52	0.18
Kr^{85}	10.6 years	β^-	0.52	0.0040
La^{140}	40 hr	β^-	1.60	0.95
Mn^{54}	314 days	§ϵ	0.84	1.00
Mn^{56}	2.58 hr	β^-	0.84	0.99
Na^{22}	2.6 years	$\beta^+\epsilon$	¶0.51	1.80
			1.27	1.00
Na^{24}	15.0 hr	β^-	1.37	1.00
			2.75	1.00
Nb^{95}	35 days	β^-	0.76	0.99
Ru^{103}	40 days	β^-	0.50	0.90
Ru^{106}–Rh^{106}	1.0 years	β^-	0.51	0.21
			0.62	0.11
Sb^{124}	60.4 days	β^-	0.60	0.98
			1.69	0.46
Sb^{125}	2.8 years	β^-	‡0.44	0.4
Sc^{46}	84 days	β^-	0.89	1.00
			1.12	1.00
Sn^{113}-In^{113m}	112 days	ϵ	0.39	0.68
Sr^{85}	64 days	ϵ	0.51	0.99
U^{235}	7.1×10^8 years	α	0.185	0.55
Xe^{133}	5.3 days	β^-	0.081	0.35
Zn^{65}	245 days	$\epsilon(\beta^+)$	1.11	0.50
			¶0.51	0.03
Zr^{95}	65 days	β^-	0.72	0.55
			0.76	0.43

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*In alphabetical order of symbols.

† Photons emitted per disintegration.

‡ Mixture of gammas not resolved by scintillation spectrometry.

¶ Annihilation radiation.

§ ϵ=electron capture.

been employed, but the most useful is the neutron, which is copiously available in nuclear reactors. Charged-particle reactions are not discussed in this section. The radionuclides produced possess characteristic half lives[5] and types and energies of decay. These characteristics make possible identification of radionuclides and lead to identification of the elements present in a sample. Activation thus constitutes a qualitative tool of some versatility.

14–2.1 Quantitative Determinations

Measurements of the quantity of a given element may be done on the basis of the equation

$$W=\frac{AM}{0.60\sigma\phi[1-\exp(-\lambda t)]}$$

where W = weight of target element, g
A = activity of product radionuclide, sec^{-1}
M = atomic weight of target element
σ = atomic activation cross section, barns
ϕ = neutron flux, neutrons/cm^2/sec
λ = decay constant of radionuclide, sec^{-1}
t = time of bombardment, sec

The cross section is the probability of the reaction, which is dependent on the target nuclide and the energy of the neutrons. Tabulations of cross sections for neutron reactions are available.[32] Values are usually given in barns; a barn is 10^{-24} cm^2. Values are normally given for particular nuclides. A useful quantity is the atomic-activation cross section for capture of neutrons, which is the product of the cross section of a given nuclide for the production of a radioactive product multiplied by its natural isotopic abundance. For example, the cross section of Fe^{58} for the production of Fe^{59} is 1 barn; its abundance is 0.3 per cent. The atomic-activation cross section of iron for the production of Fe^{59} is thus 0.003 barn.

The above discussion is the basis for the absolute method of activation analysis, in which a sample is bombarded for a definite time at a known flux, the disintegration rate of the element of interest is measured, and the weight of that element is calculated from the values for the cross section and the half life. This method is often not satisfactory because it is not easy to measure the neutron flux accurately and because cross sections are not known precisely for many elements. A simpler and more accurate approach is the comparative method, in which a standard containing a known amount of the element of interest is bombarded along with the unknown sample. The activity of the desired element is measured in the standard and the unknown; a simple activity ratio gives a resultant value in terms of the weight of the element in the unknown.

In simple cases much of the induced activity in a sample may be due to the element or elements of interest. A nondestructive method such as gamma spectrometry can be used for analysis. In general, however, a chemical separation of the desired element is necessary. In most analyses a carrier is used.

The procedure consists of the following steps: (1) preparation of the sample [grinding, cutting, or other steps (preseparation occasionally is necessary)]; (2) bombardment of the sample and the standard; (3) separation of the activity of the desired element from other activities (if necessary); and (4) measurement of the activity of the element in the sample and the standard.

14–2.2 Advantages and Limitations

The advantages and limitations of activation analysis have been discussed at length.[29, 33, 34] Among the advantages the most important is its spectacular sensitivity for many elements.[29, 35] From the equation given earlier, the weight of a given element required to produce a preassigned activity is readily calculated. If this activity is the smallest quantity that can be readily measured, the weight of the target element becomes the limit of measurement. Note that high flux, a large cross section, and a short half life lead to a low limit, or great sensitivity. Winchester[36] has prepared a table of the limits in nanograms (10^{-9} g) for 73 elements, assuming that the activity of the product radionuclide is 10 dis/sec, the neutron flux is 10^{13} neutrons/cm^2/sec, and the times are 1 and 150 hr. For many elements the limits by activation are lower than by any other method.[35] They range upward from the order of 10^{-12} g for rhodium, indium, europium, and dysprosium. Typical values in nanograms (ng) are: sodium, 0.08, aluminum, 0.2, chlorine, 0.4, vanadium, 0.02, copper, 0.03, and silver, 0.003. On the other hand, the sensitivity for some elements is very poor because of a low cross section or a long half life.

The activation method is quite fast and simple in many instances. It is usually free of interference because the activity of the desired element is unlikely to be introduced after bombardment, and tests for the presence of foreign activities can be made by instrumental techniques. Thus no special precautions are necessary to avoid introducing small amounts of the desired constituent, once bombardment has been completed; and methods of assuring that the desired activity is being measured are easily applied. Limitations, in some cases, include intense radioactivity of certain samples, self-shielding and moderation by the sample matrix material, and nuclear reactions in other elements yielding the desired radionuclide. Matrix effects include an enhancement of several per cent in the specific induced activity of a given element by the moderation of neutrons by low atomic number element atoms, particularly hydrogen in aqueous samples.[37] More serious errors can result from self-shielding if the matrix of the sample or the standard has a high absorption cross section for neutrons of either thermal or resonance energies;[37] such an error can be as large as 50 per cent or more.

14–2.3 Facilities and Applications

In choosing a source of neutrons for activation analysis, one must consider a number of factors.[31] These include the magnitude of the flux, its stability and spatial gradient, and the spectrum (energy distribution). Further, one must think of the temperature developed in the target, the accessibility of the bombardment position, the ease of handling the materials, and the economics of the operation. The most prolific source of slow neutrons is a reactor, and most activation analysis has involved the use of such a device.[29] Accelerators, particularly of the Cockroft-Walton and Van de Graaff type, are also used as neutron sources (Refs. 29, 33, 38, and 39). So-called "isotope sources" are also used; these consist of an alpha or gamma emitter in contact with beryllium or boron. Examples are antimony-beryllium[40] and americium-beryllium[41] preparations. The accelerator and isotope sources furnish fast neutrons, which are useful for the determination of oxygen,[42] nitrogen, and other light elements. Transportation and laboratory facilities range from very simple[40] to rather complex ones,[29, 43] depending upon the levels of radioactivity. Applications have been numerous.[29] In addition to those uses listed in Sec. 14–5.1(*c*), activation has been used for determining rare earths,[44] for analysis of marine organisms,[45] and for many other purposes.[9, 10]

14–3 NEUTRON ABSORPTION

Neutron absorptiometry[1, 41, 46] depends upon the fact that each nuclide has a characteristic cross section for the capture of neutrons. Nuclides of large cross section can therefore be determined in samples of low cross section. The treatment of Strain[41] is followed in the following paragraphs (see Figs. 14.1, 14.2, and 14.3).

The apparatus in Fig. 14.1 is used for analysis by neutron transmission through foils or cuvettes. From basic principles[1] the equation for such transmission is

$$CR = CR_0 \exp(-N_a\sigma)$$

where CR = count rate with sample present

CR_0 = blank count rate

n_a = atoms per square centimeter of absorber element or elements

σ = total cross section of absorber element or elements, cm ^{2}

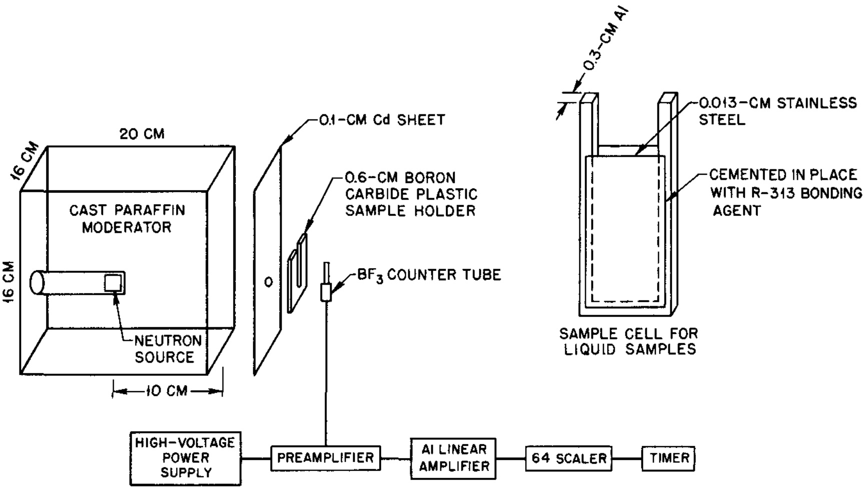

Fig. 14.1—Neutron transmission apparatus.

Rearranging and substituting,

$$\frac{CR_0}{CR} = \exp\,(-n_a\sigma) \cong 1 + Km\sigma'$$

where m = millimoles of absorber per square centimeter
K = empirical constant
σ' = experimentally determined cross section, barns

The type of calibration curve obtained is shown in Fig. 14.2.

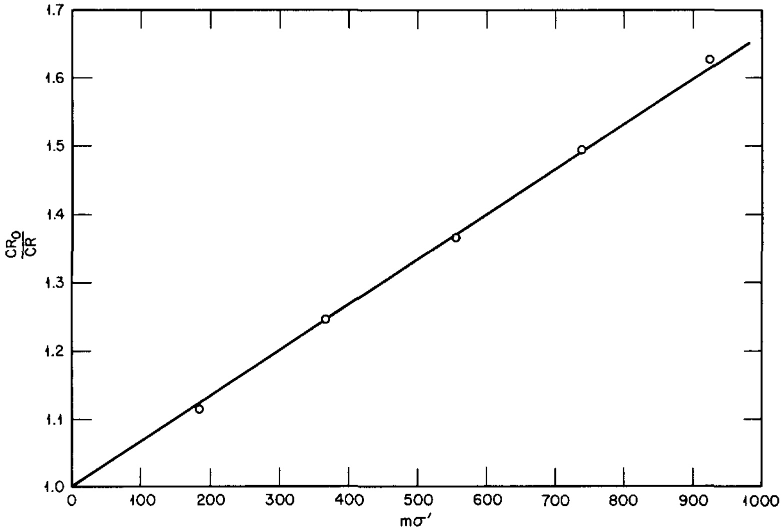

Fig. 14.2—Neutron transmission calibration curve.

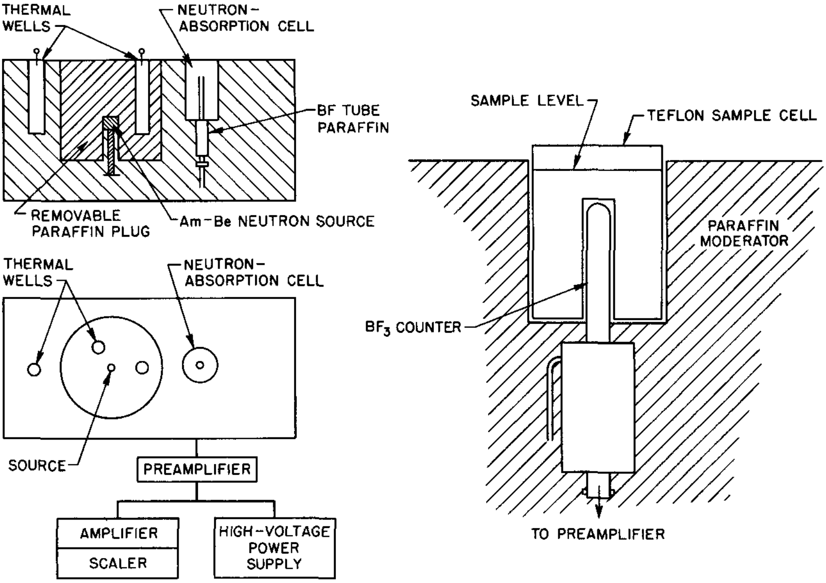

Fig. 14.3—Neutron absorption apparatus.

If the sample surrounds the detector, as shown in Fig. 14.3, an equation of similar form [41] applies:

$$\frac{CR_0}{CR} = 1 + KX\sigma_a$$

where X = molar concentration of absorbing element
σ_a = absorption cross section, barns

The method is of considerable value in determining such elements as cadmium, boron, indium, and certain nuclides of interest [see Sec. 14–5.3(b)].

14–4 ASSAY BY RADIOACTIVITY MEASUREMENTS

14–4.1 Uranium

The naturally occurring isotopes of uranium are alpha active and are parents of radionuclides having alpha, beta, and gamma activities.[1, 47] Each of the types of activity is used, under various conditions, for the measurement of uranium. A review of the radiochemistry of uranium is given in Ref. 48.

(a) *Alpha Measurements.* The specific alpha activity of natural uranium is 1.50 dis/min/μg, and alpha measurements are used on this basis for assays, e.g., in water and urine.[49] The methods require the separation of uranium by a suitable technique[48] and the preparation of an alpha plate, often by electrodeposition of uranium on platinum or nickel disks.

Care must be taken to employ the proper specific activity in calculations, especially for enriched U^{235} preparations, since most of the alpha activity of these preparations is due to U^{234}. The ratio of U^{234} to U^{235} is somewhat variable. It is necessary to know, or to determine, the specific activity before valid uranium assays can be made. (An activity of approximately 150 dis/min/μg has been observed in some enriched-uranium samples.)

(b) *Beta Measurements.* Several of the daughters of the uranium isotopes are beta emitters, and a limited application of beta-counting

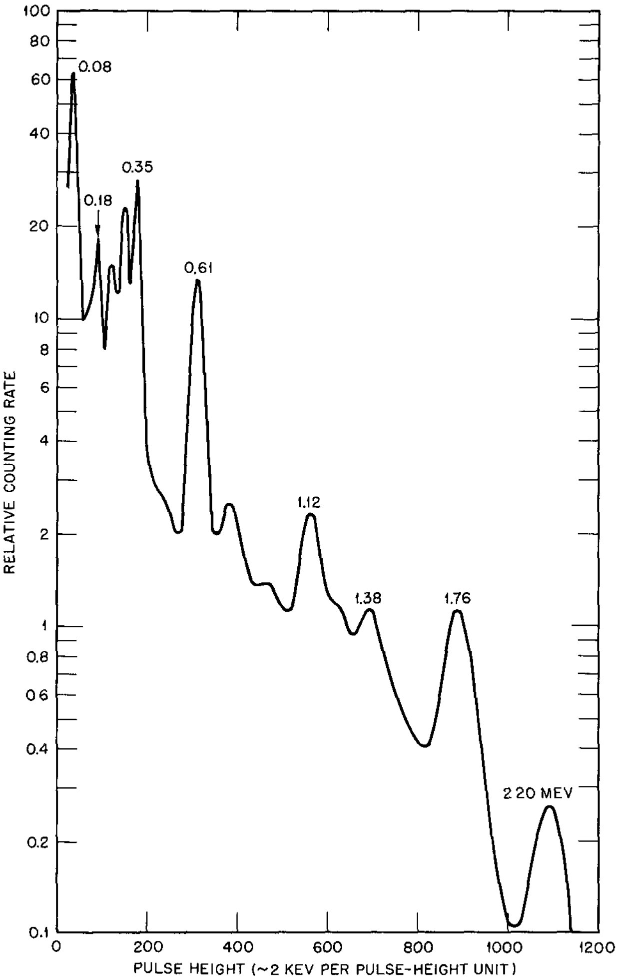

Fig. 14.4—Gamma spectrum of uranium ore.

techniques has been made.[50] Interference from K^{40} and thorium-series beta activities must be guarded against.

(c) *Gamma Measurements.* Most radiometric assays for uranium are made through gamma activity. These are exemplified by prospectors with their Geiger counters and by analysts with scintillation spectrometers.[51] This method is limited to ores in which radioactive equilibrium exists. Most workers measure the 1.76- or 0.61-Mev gamma (both from Bi^{214}). The 0.61-Mev gamma, however, is subject to interference from the 0.58-Mev gamma in the thorium series (see Sec. 14–4.2). The gamma spectrum of uranium ore, measured with a 3- by 3-in. NaI(Tl) crystal, is shown in Fig. 14.4. The chief sources of error in this method lie in radon escape during grinding or other treatment and in geochemical separation of the early members of the series from the later (radium family) members.

The procedure is quite straightforward. It consists in the measurement of the counting rates at 1.76 and 0.18 Mev, with the sample weight used dependent on uranium content. (*Note:* If the sample has been treated in such a way that radon is driven out, it must be sealed after it is weighed and retained 2 weeks or more to permit the regrowth of radon and its daughters.) The peak counting rates of a standard of similar concentration are determined under the same conditions of weight and geometry. (Such standards are available from the AEC's New Brunswick Laboratory.) The ratio of counting rates at the two peaks should be the same in the sample and the standard; if not, another method must be used. The limit of measurement is about 0.1 to 1 ppm.

14–4.2 Thorium

Radiometric measurements of thorium are essentially limited to gamma spectrometry of ores, except in the special cases of Th^{228} (radiothorium) and Th^{230} (ionium). The specific alpha activity of natural thorium (Th^{232} and Th^{228}) recently separated from a uranium-free ore is approximately 0.48 dis/min/μg. The Th^{228} decays with a 1.9-year half life.[47] Alpha measurements are of little use because of low sensitivity and dependence on past history. Similarly, beta-activity measurements are dependent on previous history.[47]

(a) *Gamma Spectrometry.* Most workers measure thorium in ores and rocks through the 2.62-Mev gamma radiation [52] of its daughter, Tl^{208}. The spectrum of a thorium ore sample is shown in Fig. 14.5. No difficulty is likely to arise because of nonequilibrium in natural material, since equilibrium of the whole series requires approximately 67 years.[47] The half life of the gas thoron is 52 seconds, resulting in quick regrowth if loss should occur.

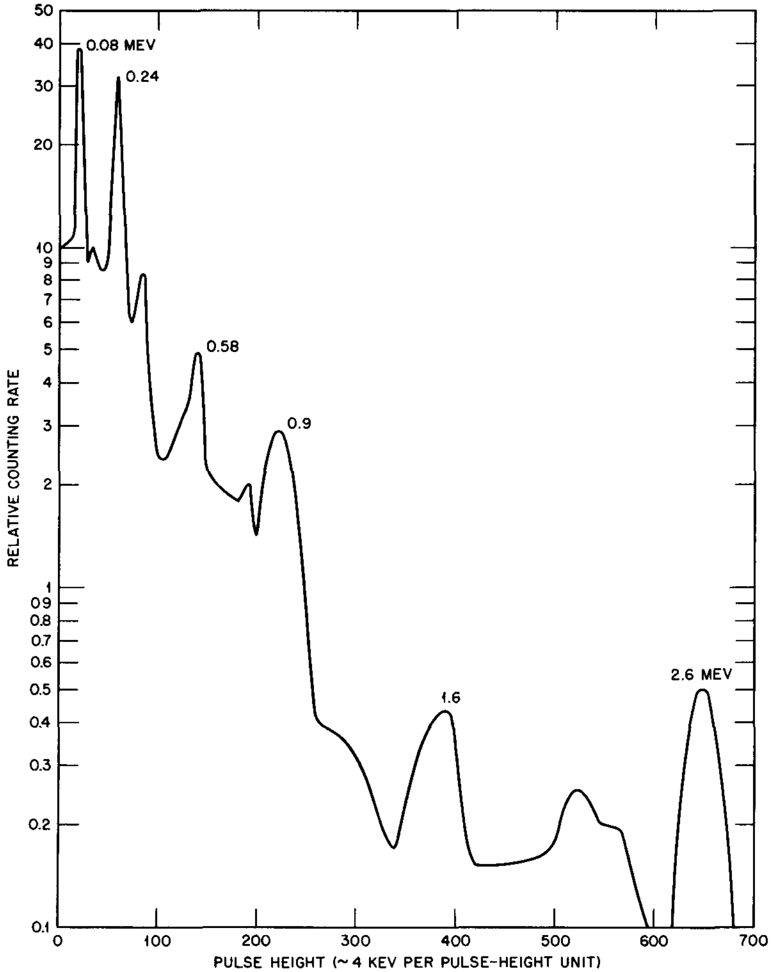

Fig. 14.5—Gamma spectrum of thorium ore.

The procedure is similar to that used for uranium [see Sec. 14–4.1(c)], but it requires measurement of only the 2.62-Mev peak in the sample and the standard. (Thorium standards may be obtained from the AEC's New Brunswick Laboratory.) The practical limit of measurement is approximately 1 ppm.

(b) *Ionium.* For the chemical separation of ionium (Th^{230}), the procedure of Moore[53] is rapid and highly selective. It consists in carrying of thorium from an oxidized solution by lanthanum fluoride, dissolution in aluminum nitrate solution, and extraction into thenoyltrifluoroacetone (TTA)-xylene at pH 1.4 to 1.5. An aliquot of the extract is evaporated on an alpha plate for measurement. Other radiochemical methods[54] are useful in various applications.

14–4.3 Radium

A general review of radium radiochemistry is given in Ref. 55.

(a) *Gamma Methods.* If Ra^{226} is the principal gamma emitter in a sample it can be determined by direct gamma measurement with an ionization chamber or scintillation detector. Such a technique, for amounts above approximately 10^{-8} g, has been reported in detail,[56] with descriptions of the ionization chamber and the sample vials and with corrections for self-absorption and other gamma activities. If it is necessary to distinguish radium-family gammas from others, a scintillation spectrometer can be used. As in uranium measurement [see Sec. 14–4.1(c)], the 0.61- and 1.76-Mev radiations of Bi^{214} are measured. Standard solutions containing 10^{-9} g or more of radium are available from the U. S. National Bureau of Standards.

(b) *Emanation (Radon) Method.* Many workers measure radium by driving out its gaseous daughter radon (Em^{222}) and counting its alphas and those of its short-lived daughters in an ionization chamber,[57] proportional counter, or scintillation counter.[58] In a typical method [57] radon is swept out of the sample solution by nitrogen, the flask is sealed, and radon is allowed to regrow for a definite time. Then radon is swept into an ionization chamber, allowed to stand for 4 hr (to establish equilibrium between radon and its short-lived daughters), and the alpha counting rate determined. It is necessary to calibrate with standards. Good precision (approximately 1.5 per cent) was demonstrated in the determination of 10^{-11} to 10^{-7} g.

(c) *Carrier Methods.* A number of radiochemists employ methods involving the carrying of radium on a suitable precipitate, followed by alpha counting. Typical of such methods are those of Goldin [59] and Petrow.[60, 61] In Goldin's method citric acid is added to the sample, the resulting solution is made alkaline with ammonia, and 2 milliequivalents of lead and 0.1 milliequivalent of barium (as nitrates) are added to it. A sulfate precipitate is formed by the addition of sulfuric acid, and it is washed twice with concentrated nitric acid. The precipitate is then dissolved in alkaline EDTA (disodium salt of ethylenediaminetetraacetic acid). Barium sulfate is reprecipitated by the addition of acetic acid. The barium sulfate is transferred to a tared alpha plate, dried, weighed to determine yield, and counted. Calibration with a standard radium solution is necessary.

The procedure of Petrow involves the carrying of radium on 500 mg of lead sulfate. The lead sulfate is dissolved in ammonium acetate and precipitated by the addition of ammonium carbonate. The carbonate is dissolved in dilute nitric acid, and the nitrate is precipitated by the addition of fuming nitric acid. After centrifugation, excess acid is evaporated, and the precipitate is dissolved in water.

Lead is partially removed by the addition of concentrated hydrochloric acid; the remainder is extracted into a quaternary amine–benzene solution. The raffinate containing the radium is evaporated, ignited, and taken up in nitric acid. A portion is evaporated on an alpha plate for counting. No yield correction is possible, and calibration with a standard radium solution is required.

14–4.4 Protactinium

A review of the radiochemistry of protactinium is given in Ref. 62, and a rapid and selective radiochemical method has been described by Moore.[63] This method involves the extraction of protactinium from a 6*M* hydrochloric acid–4 per cent oxalic acid solution into diisobutylcarbinol. Both Pa^{231} and Pa^{233} can be measured by gamma spectrometry since they have characteristic radiations at approximately 0.1 and 0.3 Mev.

14.5 ISOTOPIC ANALYSIS

14–5.1 Uranium

(a) *Gamma Spectrometry.* The application of this technique has been in the determination of U^{235} in enriched or depleted material by measurement of its 0.18-Mev gamma. Among reports of the use of this method,[64–66] that of Eldridge[64] is typical. Uranium is separated from other active materials, ignited to U_3O_8, and weighed. The intensity of the 0.18-Mev gamma is measured by a suitable spectrometer. This intensity is directly proportional to the weight of U^{235} in the sample measured. Standards of known U^{235} abundance must be used for calibration.

(b) *Alpha Spectrometry.* The principal alpha energies of the commonly encountered uranium isotopes are listed in Table 14.3 Routine alpha spectrometry permits the measurement of U^{232} in U^{233} preparations, U^{234} in U^{235} preparations, etc. Either a gridded ionization chamber or a diode detector may be used. Sensitivity in some cases is quite good; e.g., U^{232} can be measured easily in samples in which its

Table 14.3—URANIUM ALPHA ENERGIES

Isotope	Energy, Mev
U^{232}	5.32
U^{233}	4.82
U^{234}	4.77
U^{235}	4.40
U^{236}	4.50
U^{238}	4.20

activity is 0.1 per cent of that of U^{233}; this corresponds to an isotopic abundance of 0.5 ppm.

(c) *Neutron Activation.* Uranium isotopes, particularly U^{235}, have been determined by activation analysis involving the production of a particular fission product[67] (usually Ba^{140}) or a fission-product mixture that is subsequently gamma-counted;[68, 69] by a count of the delayed neutrons from fission products;[70] and by a count of U^{239} or Np^{239} for the U^{238} nuclide.[67] The same methods obviously apply to the determination of uranium in various materials[71] if it is assumed that the normal isotopic abundances exist. All these methods are quite sensitive. For example, the delayed-neutron technique can be used for the determination of about 1 ng of U^{235}; it has a precision of about 3 per cent.[70]

14–5.2 Thorium

The alpha-emitting isotopes of thorium can be determined by alpha spectrometry. [Also see Sec. 14–4.2(b).] Th^{232} is determined by neutron activation;[72] by this means readily measurable Pa^{233} is produced. The determination of Th^{232} is, of course, tantamount to the measurement of natural thorium.

14–5.3 Lithium

(a) *Neutron Activation.* Leddicotte[73] has reviewed the determination of Li^6 and Li^7 by three methods: (1) tritium evolution, i.e., $Li^6(n,\alpha)H^3$, followed by measurement of H^3 in an ionization chamber; (2) Li^8 production; and (3) triton activation, in which H^3 is used to produce, for example, F^{18} from O^{16}. All methods were found to be reasonably successful.

(b) *Neutron Absorption.* The cross section of Li^6 for thermal neutrons is 945 barns, whereas that of Li^7 is only 0.04 barns.[32] Obviously, measurement of the cross section, or simple neutron absorption, of lithium samples by methods[41] described in Sec. 14–3 make possible the isotopic analysis.

REFERENCES

1. G. Friedlander and J. W. Kennedy, *Nuclear and Radiochemistry*, John Wiley & Sons, Inc., New York, 1955.
2. R. T. Overman and H. M. Clark, *Radioisotope Techniques*, McGraw-Hill Book Company, Inc., New York, 1960.
3. A. C. Wahl and N. A. Bonner (Eds.), *Radioactivity Applied to Chemistry*, John Wiley & Sons, Inc., New York, 1951.
4. S. A. Reynolds, *Record Chem. Progr.*, **16**: 99 (1955).
5. C. J. Rodden (Ed.), *Analytical Chemistry of the Manhattan Project*, National Nuclear Energy Series, Division VIII, Vol. 1, especially pages 662 to 692, McGraw-Hill Book Company, Inc., New York, 1950.

6. H. L. Finston and J. Miskel, in *Annual Review of Nuclear Science*, Vol. 5, pp. 269–296, Annual Reviews, Inc., Palo Alto, Calif., 1955.
7. Source Material for Radiochemistry, *Natl. Acad. Sci.-Natl. Res. Council Publ.*, No. **825** (1960).
8. National Academy of Science–National Research Council monographs on radiochemical methods, Reports NAS–NS–3001 *et seq.*
9. W. W. Meinke, *Anal. Chem.*, **28**: 736 (1956) ; **30**: 686 (1958) ; and **32**: 104R (1960).
10. G. W. Leddicotte, *Anal. Chem.*, **34**: 143R (1962).
11. C. D. Coryell and N. Sugarman, *Radiochemical Studies: The Fission Products*, National Nuclear Energy Series, Division IV, Vol. 9, McGraw-Hill Book Company, Inc., New York, 1951.
12. S. A Reynolds, *Health Phys.*, **8**: 391 (1962).
13. A. H. Snell (Ed.), *Nuclear Instruments and Their Uses*, John Wiley & Sons, Inc., New York, 1962.
14. W. J. Price, *Nuclear Radiation Detection*, McGraw-Hill Book Company, Inc., New York, 1958.
15. C. E. Crouthamel (Ed.), *Applied Gamma-Ray Spectrometry*, Pergamon Press, Inc., New York, 1960.
16. C. G. Bell and F. N. Hayes (Eds.), *Liquid Scintillation Counting*, Pergamon Press, Inc., New York, 1958.
17. J. W. T. Dabbs and F. J. Walter (Eds.), Semiconductor Nuclear Particle Detectors, *Natl. Acad. Sci.-Natl. Res. Council Publ.*, No. **871** (1961).
18. *Metrology of Radionuclides*, International Atomic Energy Agency, Vienna, 1960.
19. Measurements and Standards of Radioactivity, *Natl. Acad. Sci.-Natl. Res. Council Publ.*, No. **573** (1958).
20. R. L. Heath, USAEC Report IDO–16408, Phillips Petroleum Company, July 1, 1957.
21. S. A. Reynolds, in *Handbook of Analytical Chemistry*, L. Meites (Ed.), McGraw-Hill Book Company, Inc., New York, 1963.
22. A. C. Kuyper, *J. Chem. Ed.*, **36**: 128 (1959).
23. A. H. Jaffey, *Nucleonics*, **18**(11) : 180 (1960).
24. *Nuclear Data Sheets*, National Academy of Sciences-National Research Council. (Current)
25. D. Strominger, J. M. Hollander, and G. T. Seaborg, *Revs. Mod. Phys.*, **30**: 585 (1958).
26. W. H. Sullivan, *Trilinear Chart of Nuclides*, Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 1957. (Frequent revisions)
27. J. R. Stehn, *Nucleonics*, **18**(11) : 186 (1960).
28. G. E. Boyd, *Anal. Chem.*, **21**: 335 (1949).
29. G. W. Leddicotte, *Pure and Appl. Chem.*, **1**: 61 (1960).
30. R. C. Koch, *Activation Analysis Handbook*, Academic Press Inc., New York, 1960.
31. W. S. Lyon (Ed.), *Guide to Activation Analysis*, to be published as a USAEC report.
32. D. J. Hughes and R. B. Schwartz, *Neutron Cross Sections*, USAEC Report BNL–325(2d ed.) with supplements, Superintendent of Documents, U.S. Government Printing Office, Washington, D.C.
33. G. W. Leddicotte, Radioactivation Analysis—Specific for Trace Element Determinations, in *Am. Soc. Testing Materials, Spec. Tech. Publ.*, No. **308** (1961).

34. D. H. F. Atkins and A. A. Smales, in *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 1, H. J. Emeleus and A. G. Sharp (Eds.), pp. 315–345, Academic Press Inc., New York, 1959.
35. W. W. Meinke, *Science*, **121**: 177 (1955) and *Anal. Chem.*, **31**: 792 (1959).
36. J. W. Winchester, in *Progress in Inorganic Chemistry*, Vol. II, F. A. Cotton (Ed.), pp. 1–32, Interscience Publishers, Inc., New York, 1960.
37. S. A. Reynolds and W. T. Mullins, *Intern. J. Appl. Radiation Isotopes*, **14**: 421 (1963).
38. W. W. Meinke and R. W. Shideler, *Nucleonics*, **20**(3) : 60 (1962) ; and Report MMPP–191–1, University of Michigan, December 1961.
39. J. E. Strain, in USAEC Report ORNL–3397, pp. 92–93, Oak Ridge National Laboratory, Feb. 8, 1963, and unpublished data.
40. A. K. De and W. W. Meinke, *Anal. Chem.*, **30**: 1474 (1958).
41. J. E. Strain and G. W. Leddicotte, USAEC Report ORNL–3335, Oak Ridge National Laboratory, Sept. 6, 1962.
42. E. L. Steele and W. W. Meinke, *Anal. Chem.*, **34**: 185 (1962).
43. W. W. Meinke, *Nucleonics*, **17**(9) : 86 (1959).
44. W. W. Meinke and R. E. Anderson, *Anal. Chem.*, **26**: 907 (1954).
45. R. Fukai and W. W. Meinke, *Limnol. Oceanogr.*, **4**: 398 (1959) and **7**: 186 (1962).
46. T. I. Taylor and W. W. Havens, Jr., *Nucleonics*, **5**(6) : 4 (1949) ; **6**(2) : 66 (1950) ; and **6**(4) : 54 (1950).
47. S. A. Reynolds, in *Progress in Nuclear Energy, Series III, Process Chemistry*, Vol. 2, edited by F. R. Bruce, J. M. Fletcher, and H. H. Hyman, pp. 562–572, Pergamon Press, Inc., New York, 1958.
48. J. E. Gindler, Report NAS–NS–3050, National Academy of Sciences-National Research Council, 1961.
49. G. W. Royster, *Health Phys.*, **2**: 291 (1960).
50. E. Franklin and R. K. Barnes, British Report AERE–EL/R–1175, 1953.
51. J. S. Mero, *Geophysics*, **25**: 1054 (1960).
52. S. A. Reynolds, *Talanta*, **10**: 611 (1963).
53. F. L. Moore, *Anal. Chem.*, **30**: 1020 (1958).
54. E. K. Hyde, Report NAS–NS–3004, *National Academy of Sciences-National Research Council*, January 1960.
55. M. L. Salutsky, *The Radiochemistry of Radium*, Report NAS–NS——, National Academy of Sciences-National Research Council. (In preparation)
56. J. E. Hudgens, R. C. Meyer, C. Zyskowski, and L. C. Nelson, USAEC Report NBL–128, March 1957.
57. J. E. Hudgens, R. O. Benzing, J. P. Cali, R. C. Meyer, and L. C. Nelson, *Nucleonics*, **9**(2) : 14 (1951).
58. M. A. Van Dilla and D. H. Taysum, *Nucleonics*, **13**(2) : 68 (1955).
59. A. S. Goldin, *Anal. Chem.*, **33**: 406 (1961).
60. H. G. Petrow, O. A. Nietzel, and M. A. De Sesa, *Anal. Chem.*, **32**: 926 (1960).
61. H. G. Petrow and R. Lindstrom, *Anal. Chem.*, **33**: 313 (1961).
62. H. W. Kirby, Report NAS–NS–3016, National Academy of Sciences-National Research Council, December 1959.
63. F. L. Moore and S. A. Reynolds, *Anal. Chem.*, **29**: 1596 (1957).
64. S. A. Reynolds and J. S. Eldridge, in USAEC Report TID–7531[Pt. 2 (Del.)], pp. 47–52, 1957.
65. G. H. Morrison and J. F. Cosgrove, *Anal. Chem.*, **29**: 1770 (1957).

66. L. C. Nelson and C. J. Rodden, in *Selected Measurement Methods for Uranium and Plutonium in the Nuclear Fuel Cycle*, pp. 176–182, Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 1963.
67. G. W. Leddicotte and W. A. Brooksbank, in USAEC Report TID–7531(Pt. 1), pp. 71–77, 1957.
68. L. Nelson and D. Aaron, in USAEC Report TID–7531(Pt. 1), pp. 78–96, 1957.
69. H. Bussell, C. L. Zyskowski, and L. C. Nelson, Jr., in USAEC Report TID–7655, pp. 61–89, Oct. 22, 1963.
70. F. F. Dyer, J. F. Emery, and G. W. Leddicotte, USAEC Report ORNL–3342, Oak Ridge National Laboratory, Oct. 16, 1962.
71. H. A. Mahlman and G. W. Leddicotte, *Anal. Chem.*, **27**: 823 (1955).
72. G. W. Leddicotte and H. A. Mahlman, in *Proceedings of the First United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955*, Vol. 8, pp. 250–253, United Nations, New York, 1956.
73. G. W. Leddicotte, J. E. Strain, and L. C. Bate, Determination of Lithium Isotopic Ratios by Neutron Radioactivation Analysis, American Chemical Society Meeting, Atlantic City, N.J., Sept. 13–18, 1959. (Proceedings not published)