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Techniques of Water-Resources Investigations
of the United States Geological Survey

Chapter A5

METHODS FOR DETERMINATION OF RADIOACTIVE SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

By L. L. Thatcher and V. J. Janzer, U.S. Geological Survey,
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Book 5
LABORATORY ANALYSIS

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PREFACE

This series of manuals on techniques describes methods used by the Geological Survey for planning and executing water-resources investigations. The material is grouped under major subject headings called books and is further subdivided into sections and chapters. Book 5 is on laboratory analysis. Section A is on water. The unit of publication, the chapter, is limited to a narrow field of subject matter. "Methods for determination of radioactive substances in water and fluvial sediments" is the fifth chapter to be published under Section A of Book 5. The chapter number includes the letter of the section. The looseleaf format of this methods manual is designed to permit flexibility in revision and publication. Supplements, to be prepared as the need arises, will be issued to purchasers at no charge as they become available.

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METHODS FOR DETERMINATION OF RADIOACTIVE SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

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Abstract

Analytical methods for the determination of some of the more important components of fission or neutron activation product radioactivity and of natural radioactivity found in water are reported. The report for each analytical method includes conditions for application of the method, a summary of the method, interferences, required apparatus and reagents, analytical procedures, calculations, reporting of results, and estimation of precision. The fission product isotopes considered are cesium-137, strontium-90, and ruthenium-106. The natural radioelements and isotopes considered are uranium, lead-210, radium-226, radium-228, tritium, and carbon-14. A gross radioactivity survey method and a uranium isotope ratio method are given. When two analytical methods are in routine use for an individual isotope, both methods are reported with identification of the specific areas of application of each. Techniques for the collection and preservation of water samples to be analyzed for radioactivity are discussed.

Introduction

Purpose

This manual describes the analytical methods used by the U.S. Geological Survey for the collection and analysis of water samples for radioactive substances. The analytical methods are intended for the radiochemist who applies his expertise to the analysis of water. Adequate grounding in the principles and practice of radiochemistry is assumed. Therefore, such subjects as nuclear instrumentation, statistics, and radiation characteristics are not discussed. References are given to several excellent textbooks available on these subjects.

Generally, each analytical method is described in sufficient detail and is adequately referenced so that an experienced radiochemist could set up the analytical method with reasonable assurance of success. Two exceptions are: the determination of tritium by gas counting and the determination of carbon-14. Because of the complexity of the equipment and the extreme importance of certain critical details in both the instrumentation and operating procedure, any attempt to convey the fully detailed analytical procedure for direct duplication has a low probability for success. There is no substitute for actual operating experience in laboratories equipped for the gas-counting determination of tritium and the determination of carbon-14. For the above reasons, the descriptions of these two analytical procedures concentrate on the principles and major operating conditions involved.

In several analytical methods, reagents or equipment are cited by proprietary name. This is due to inadequate information on chemical composition on which to base a chemical name, or to special requirements known to be met by the cited reagent or equipment. In every case equivalent products that meet requirements may be substituted. No endorsement is intended.

Organization

Each determination includes a section on "Application," "Summary of the method," "Interferences," "Apparatus," "Reagents," "Procedure," "Calculations," "Report" (of results), and "Precision." The "Calculation" section under each determination differs slightly from the practice in chapter A1 in that reference is made to a general equation

when possible. Radioactivity calculations for different nuclides follow similar principles which can be summarized in a general equation. The general equation, with its modifications to fit particular requirements, is considered in a following section.

Nuclear data

Data on half-lives were taken from the "Chart of the Nuclides" (Holden and Walker, 1969). Data on decay schemes and energies of nuclear radiation were taken from "Table of Isotopes" (Lederer and others, 1968). The "Chart of the Nuclides" was reproduced in "Radiological Health Handbook" (U.S. Dept. of Health, Education, and Welfare, 1970), and data on the more important nuclides listed in Lederer, Hollander, and Perlman (1968) were also reproduced in the HEW publication.

Unit, symbols, and abbreviations

Terms that are generally used throughout the text are listed below. Terms that are used infrequently, usually in connection with one analytical method, are defined at the first usage in the text. Terms that are used in calculation of data are defined under the general equation in the "Calculations" sections.

Ci _____curie (3.7×10^{10} disintegrations per second)
μCi ____microcurie (3.7×10^{4} disintegrations per second)
pCi ___picocurie (3.7×10^{-2} disintegrations per second)
μCi/l __microcuries per liter
pCi/l __picocuries per liter

cpm ___counts per minute
dpm ___disintegrations per minute

keV ___thousand electron volts
MeV __million electron volts

d ______day
hr _____hour
min ___minute
sec ____second
yr ____year

e ______2.718....., base of the natural logarithms
ln _____logarithm of any number N, to the base e
log ____logarithm of any number N, to the base 10

ml ____milliliter
gal ____gallon (3.785 liters)

m _____meter
cm ____centimeter
mm ___millimeter
in. ____inch (2.54 cm)
ft _____foot (30.48 cm)

g _____gram
mg ____milligram

M _____molarity of a solution
N _____normality of a solution
meq ___milliequivalent
psi ____pounds per square inch

Sources of radioactivity in water

Radioactivity in water may be of natural or artificial origin. The principal natural processes that bring radioactivity into water are the weathering of rocks containing radioactive minerals and fallout of cosmic-ray-produced nuclides. The major sources of artificial radioactivity are the nuclear power industry, nuclear weapons testing, and the peaceful applications of nuclear materials and devices.

Natural radioactivity

The principal radionuclides introduced naturally into surface and ground waters are uranium, radium-226, radium-228, radon, potassium-40, tritium, and carbon-14. All but the last two derive from radioactive minerals. Radioactive elements including uranium, thorium, and actinium and radioactive daughters resulting from these decay series are important primarily for reasons of health and as potential energy sources. These three natural decay series are headed respectively by uranium-238 (half-life 4.51×10^{9} yr), thorium-232 (half-life 1.41×10^{10} yr), and uranium-235 (half-life 7.13×10^{8} yr). In areas of the world where radioactive minerals are particularly abundant as in the Joachimsthal region of Czechoslovakia, the Minas Gerais region of Brazil, and the Colorado Plateau of the United States, radioactivity in some waters may greatly exceed the average concentrations

present in most continental waters. Dissolved natural uranium is the major radioactive constituent in most of these waters.

Tritium and carbon-14 are produced by the interaction of cosmic-ray neutrons with nitrogen in the upper atmosphere. The tritium is eventually rained out as tritiated water, and the radiocarbon is incorporated into atmospheric carbon dioxide. The principal reservoir for both radionuclides is ultimately the ocean. Both radionuclides are also produced by thermonuclear weapons testing. In 1963, the year when radioactive fallout reached its maximum, the atmospheric concentration of thermonuclear tritium exceeded that of natural tritium by approximately 3 orders of magnitude. The additional carbon-14 of thermonuclear origin was much lower and approximately equalled the carbon-14 naturally in the atmosphere. Radioisotope concentrations in fallout have diminished rapidly since 1963 as a source of radioisotopes in water. Tritium is also a fission product, and by 1970 the nuclear power industry had probably become the largest source of tritium (Jacobs, 1968).

Artificial radioactivity

Nuclear waste disposal is the principal possible source for the leakage of artificial radionuclides (fission products and activation products) into water. Most of the waste is derived from the reprocessing of nuclear fuel. Reprocessing is required at intervals to remove neutron-absorbing fission products and to recover the uranium and plutonium. Until reprocessing, 99.9 percent of the fission and activation products produced remain locked inside the fuel element. The fuel element is dissolved in acid, and chemical separations of the highly radioactive wastes are carried out. The final waste consists of a low-level solution, which may be sent to seepage ponds, and a high-level solution or "hot" solution that must be stored for many years to allow radioactive decay. Strontium-90 (half-life 28.9 yr), cesium-137 (half-life 30.2 yr), iodine-129 (half-life 1.6×10^{7} yr) and plutonium-239 (half-life 24,390 yr) are major radioisotopes of concern. It is estimated that by 1980, several million gallons of high-level waste with radioactivity on the order of 10 billion curies will be in storage as a result of nuclear power production (Hogerton, 1963, p. 448).

A relatively smaller amount of radioactivity may leak to the environment as a result of daily operation of a nuclear powerplant because of neutron activation of salts in the coolant water, neutron activation of dissolved corrosion products, and possible release of fission products by a defective fuel element. Although every nuclear powerplant has built-in safeguards against release of radioactivity, the possibility of accidental leakage must always be considered.

In addition to tritium and carbon-14, aboveground nuclear weapons testing releases strontium-90, radiocesium isotopes, iodine-131, and other nuclides to the environment. The fraction of these radionuclides that fall out or rain out into water bodies or watersheds constitute a significant source of water contamination.

Peaceful applications of nuclear explosives, such as nuclear gas stimulation and nuclear mining, present a possible source of locally intense contamination of ground water. If venting occurs, the possibility of contamination of surface water by fallout also exists.

Nuclear research laboratories, hospitals, and the very limited number of industries that use radioactivity constitute a relatively minor source of possible radionuclide leakage, but may be of local significance.

Measureable radioactive material may derive from sources not normally considered radioactive. Examples are fly ash from the combustion of fossil fuel (coal may contain uranium and radium) and the ceramics industry (uranium salts are used in the preparation of some glazes).

Permissible concentrations of radioactivity in effluents to unrestricted areas

Current values are tabulated in Part 20, "Standards for Protection Against Radia-

tion," published and updated periodically by the U.S. Nuclear Regulatory Commission (1976). The Commission is the source of the permissible concentrations of radioactivity in effluent (PCRE) values reported for the nuclides in this manual. The significance of the values and the basis for their computation is described in National Bureau of Standards (NBS) Handbook 52 (1953) and NBS Handbook 69 (1959). The U.S. Public Health Service has published recommended maximum concentrations for radium-226, strontium-90, and gross beta activity in drinking water (Drinking Water Standards, 1962). Updated standards published in "Water Quality Criteria, 1972" (1973) are quoted in addition, when applicable.

Additional drinking-water regulations were published in the Federal Register, volume 41, No. 133, July 9, 1976, as a supplement to Title 40, Code of Federal Regulations (CFR), Part 141. The National Interim Primary Drinking Water Regulations (Part 141) have been published (1975), but were in the process of revision at the time this paper was written.

Radiological safety

The radiochemist or chemist who uses the methods in this manual should have an adequate training in radiological health and safety practice in the laboratory. Such training is a requirement for obtaining the U.S. Nuclear Regulatory Commission license to use radionuclides. Analysis of even environmental-level samples will generally require the use of various radioactive calibration planchets or standardized solutions, some of which are hazardous if not properly used. Discussions of various aspects of radiological safety are given in the following suggested references. An introduction to the subject is found in the chapter on the radiological laboratory in "Guide for Safety in the Chemical Laboratory" (M.C.A., 1954). A comprehensive exposition of radiological health physics is found in "Principles of Radiation Protection" (Morgan and Turner, 1971). The safety series of the International Atomic Energy Agency includes reports of particular value to laboratory users of radioactivity. "Safe Handling of Radioisotopes" (1962) and the "Health Physics Addendum" (1960) are cited. Precautions against contamination and procedures for decontamination are detailed in the National Bureau of Standards publication "Control and Removal of Radioactive Contamination in Laboratories" (1951). Procedures to be followed in event of an accident involving radioactivity are described in "Medical Aspects of Radiation accidents" (Saenger, 1963).

Geochemistry of radioactivity in water

Dissolved and particulate radioactivity in water is controlled by the same mechanisms that affect other trace and macro constituents in the geohydrologic environment. Radioactive disintegration of an atom by alpha and beta decay results in the formation of an atom of a new element, frequently in an excited state. Gamma emission results from such an atom in the excited state going to a lower energy state. The geochemical behavior of a daughter element may be grossly different from that of the radioactive parent, although its occurrence, distribution, and transport may be governed by the parent.

Carbon-14

Carbon-14 is the radioactive isotope of carbon with a half-life of 5,730 years. The older half-life value of 5,568 yr is generally used for the calculation of ages in order to maintain consistency with carbon-14 dates in the older literature. Ages based on the older half-life value are converted to the basis of the newer half-life by multiplying by 1.03. Carbon-14 decays by the emission of a beta particle with the low maximum energy of 156 keV.

Neutrons produced by primary cosmic radiation interact with stratospheric nitrogen to produce carbon-14 and hydrogen:

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}H.$$

The rate of production in the atmosphere is estimated at approximately 2.4 atoms per second per square centimeter of the Earth's surface (Libby, 1955). Carbon-14 is also a product of thermonuclear weapons testing. This source had approximately doubled the atmospheric concentration of carbon-14 and had increased the concentration in surface ocean water by about 20 percent by the late 1960's (Nydal, 1966). Possible contamination of ground waters by thermonuclear carbon-14 imposes a severe limitation to the application of carbon-14 dating.

Carbon-14 produced by cosmic radiation is oxidized to carbon dioxide and is transported to the lower atmosphere by mixing processes where it enters the biological cycle. Some radioactive carbonates enter the hydrological cycle and provide the basis for carbon-14 dating of older ground waters. The specific activity of cosmic-ray produced carbon-14 in the atmosphere, surface waters, and all living matter was determined by Libby (1955) to be 16 dpm per gram of carbon, but is now considered to be lower. Suess (1965) determined 14 dpm per gram of carbon.

The specific activity of carbon-14 in carbonaceous material cut off from contact with the atmosphere, such as the carbonate species in ground water, decreases at a rate controlled by the carbon-14 half-life. The carbon-14 to carbon-12 ratio is also affected by exchange of carbonates between the water and aquifer, biochemical effects, and possible reactions with silicates. Compensation for exchange effects has been attempted through the carbon-13 to carbon-12 ratio (Pearson, 1965).

Cesium-137 and cesium-134

Eleven cesium isotopes are fission products, but usually only cesium-137 is significant to water quality. Cesium-134 is produced in fission by the neutron activation of cesium-133, a fission product. The half-life of cesium-137 is 30 yr and that of cesium-134 is 2.7 yr. Cesium-137 has been deposited throughout the world, with much higher concentrations in the Northern Hemisphere than in the Southern Hemisphere as a result of nuclear weapons testing.

Either the beta or gamma radiation associated with the cesium isotopes may be used for their detection. Detection by beta radiation is more sensitive but less specific. The use of gamma radiation permits distinguishing between the isotopes by means of energy discrimination since the energy peak for cesium-137 (barium-137m) is at 662 keV, and the principal peaks for cesium-134 are at 605 keV and 796 keV. Preconcentration of the radiocesium is used before counting, in either case, to permit detection at low environmental levels. Four to 20 liters of sample have been used with the gamma-counting technique depending on sensitivity required. A few hundred milliliters are usually adequate for the beta-counting technique.

Lead-210

Lead-210 originates from the decay of radon-222. The isotope is a beta emitter with half-life of 22 years. Lead 210 formed underground is probably trapped on exchange sites of clay minerals or other reactive material and presumably has very limited migration. The lead-210 formed by decay of atmospheric radon enters the hydrologic cycle principally through precipitation. A smaller part is removed from the atmosphere as dry fallout. Most of the lead-210 falls on the oceans where it finds use as a tracer for the investigation of vertical mixing. Some lead-210 enters terrestrial surface waters and the permanent snow fields. The half-life is convenient for dating more recent snow deposits, and the natural level of lead-210 has not been upset by nuclear weapons testing as is the case with tritium. Estimation of the lead-210 input through precipitation, a requirement for dating of snow and ice, must be based on actual measurements of the lead isotope since calculation on the basis of equilibrium with prevailing radon concentrations is not accurate. This was shown by Patterson and Lockhart (1964) who made a latitudinal survey of lead-210 in ground-level air.

The lead-210 content of precipitation appears to vary greatly with individual storms, probably depending on the trajectory of the air mass. Rama and Goldberg (1961) reported 0.05 pCi/l for surface ocean water and 0.13 to 6.7 pCi/l for Colorado River water. Holtzmann (1964), using the more sensitive polonium-210 alpha-counting technique, found an average of 0.127 pCi/l of lead-210 in untreated Illinois surface waters and 0.051 pCi/l in well waters. As expected, the sorption of lead by soil reduces the concentration in ground water. Holtzmann found that lead-210 concentrations in potable waters of Illinois were generally much below radium-226 concentrations.

Radium

Radium is a radioactive member of the alkaline-earth family that is widely disseminated throughout the crust of the Earth. Four isotopes of radium are members of the three natural radioactive series. The isotopes with their natural series and decay data are listed below.

Isotope	Series	Half-life	Decay mode
Radium-223	Actinium	11.43 d	α
Radium-224	Thorium	3.64 d	α
Radium-226	Uranium	1,602 yr	α
Radium-228	Thorium	5.75 yr	β

The concentrations of the radium isotopes in geologic and hydrologic materials vary greatly in nature depending on the uranium and thorium concentrations in the source and the geochemical history of the material.

Chemically, radium is analogous to barium; the carbonates, sulfates, and chromates are insoluble, while the chlorides, nitrates, and hydroxides are soluble in water. The distribution of radium is governed more by the distribution of uranium and thorium, however, than by the geochemistry of radium.

Radium-226 and radium-228 are the most important isotopes of radium found in water because of their longer half-lives, health significance, and as geochemical indicators of uranium and thorium respectively. On the basis that the world abundance of thorium is approximately three times that of uranium and the specific activity of thorium-232 is approximately one-third that of uranium-238, the world activity inventories of radium-226 and radium-228 should be roughly equal. World activity inventory for radium-224 should also be equal to that of radium-228 since the two are in radioactive equilibrium. The local relative abundances of the 226 and 228 radium isotopes may vary greatly, however, as a function of the local uranium to thorium ratios. Also there may be extreme local variations in the ratio of radium-228 to radium-224 because the latter is produced from the former through an actinium and a thorium isotope. Because the geochemistry of actinium and thorium are significantly different from that of radium, there is great opportunity for local disequilibria.

Radium is found in waters from most geologic terranes because of the wide distribution of the parent elements in nature. Concentrations of radium-226 in freshwater usually are less than 1–2 pCi/l. Concentrations of radium-226 in the Cambrian and Ordovician limestones of North Central United States often exceed 3 pCi/l, and in certain aquifers of the Colorado Plateau, the concentration may be much higher (Scott and Barker, 1959). Water that leaches waste piles from uranium mining and milling operations may contain radium at much higher levels.

While most of the radium investigations have centered on the 226 isotope, work in the U.S. Geological Survey has shown the importance of radium-228. Johnson (1971) reported that concentration of radium-228 in several streams of the Front Range near Denver exceeded the concentration of radium-226. This agrees with the twice normal abundance ratio of thorium to uranium for the area. Krause (1959) reported relatively high concentrations of radium-228 in wells tapping deep ground-water aquifers in Iowa, Wisconsin, Illinois, and Missouri.

All radium isotopes are hazardous because of the bone-seeking properties of the element. Concentrations in the bone can lead to malignancies. The U.S. Public Health Service has recommended 3 pCi/l as the upper limit

for radium-226 in water for public consumption. The U.S. Nuclear Regulatory Commission (NRC) (1976) gave the following permissible concentrations of radioactivity in effluent (PCRE) values for radium (soluble) in waste solutions that may be released to water bodies accessible by the public:

Radium-223	700 pCi/l
Radium-224	2,000 pCi/l
Radium-226	30 pCi/l
Radium-228	30 pCi/l

The "Water Quality Criteria, 1972" (EPA, 1973) recommended a radium-226 intake limit of 0.5 pCi/d. Assuming a 2 l/d consumption rate, this is equivalent to a 0.25 pCi/l concentration limit.

Three analytical methods for radium isotopes are reported, each serving a different purpose. A determination of the gross alpha radioactivity of radium is the simplest procedure and is satisfactory where identification of individual alpha-emitting isotopes is not required. A second procedure is specific for radium-226 and a third for radium-228.

Ruthenium-106 and ruthenium-103

Ruthenium-106 and ruthenium-103 are the important ruthenium isotopes produced in nuclear fission. They may be present in precipitation and surface waters after atmospheric nuclear testing. The short half-life of ruthenium-103 (39.8 d) essentially rules out its presence in ground water. Ruthenium-106 (half-life 368 d) may be found in ground water in the immediate vicinity of underground nuclear tests. Both isotopes are beta emitters with maximum energy of 0.0392 MeV for ruthenium-106 and maximum energy of 0.70 MeV (3 percent) and 0.22 MeV (97 percent) for ruthenium-103. Ruthenium-106 is determined by counting the daughter, rhodium-106, with which it is in secular equilibrium. The more energetic beta particles of rhodium-106 (3.53, 3.1, 2.4, and 2.0 MeV,) are more easily detected.

The NRC–PCRE value for ruthenium-106 in effluents released to uncontrolled areas is 1×10^{-5} μCi/ml (10,000 pCi/l). Ruthenium concentrations determined by procedure R–1150–76 are reported as ruthenium-106, although ruthenium-103 may also be present in the sample. After 8 months decay (6 half-lives), the ruthenium-103 concentration is usually insignificant.

Strontium-90

Nuclear fission produces two important isotopes of strontium: strontium-90 (half-life 38.9 yr) and strontium-89 (half-life 50.8 d). Although the latter nuclide has initially greater activity, the longer half-life of strontium-90 makes it more significant to worldwide environmental pollution. Except for short periods following atmospheric nuclear testing, strontium-90 is the predominant radioisotope of this element on the Earth's surface. This nuclide is now widely distributed in man's environment from stratospheric and tropospheric fallout. Higher concentrations exist in the Northern Hemisphere. It is often detected in soils, foods, water, and biological materials. The "Water Quality Criteria, 1972" (EPA, 1973) recommended limit on strontium-90 intake in water used for public supply is 5 pCi/d. Assuming a 2 l/d consumption rate, this is equivalent to a 2.5 pCi/l concentration limit.

Tritium (hydrogen-3)

Tritium is the radioisotope of hydrogen with atomic weight of 3. It decays by pure beta emission with half-life of 12.33 yr. The beta particles have an average energy of 5.7 keV and maximum energy of 18.6 keV. Tritium is formed in the upper atmosphere by cosmic-ray spallation and by the interaction of fast neutrons with nitrogen:

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{3}_{1}H + ^{12}_{6}C.$$

The natural production rate of tritium is on the order of 30 atoms per square centimeter of the Earth's surface per minute. (Kaufman and Libby, 1954).

Tritium is also produced by thermonuclear weapons testing. The first tritium from this source was detected in 1952, and by 1954 the thermonuclear tritium was substantially greater than the natural tritium. (Begemann

and Libby, 1957). Thermonuclear tritium reached a peak in 1963 when the concentration in the Northern Hemisphere exceeded the natural level by approximately 3 orders of magnitude.

Tritium is principally of interest to the hydrologist as a water-dating tool and as a tracer, introduced either naturally or artificially, for investigating ground-water hydrodynamics in areas of relatively rapid flow. The tritium dating of ground water that entered as recharge before 1952 is based on radioactive decay of tritium and the "prebomb" concentration of approximately 8 tritium units (Tu), (1 Tu=1 T atom/10^{18} H atoms) determined by Kaufmann and Libby (1954).

The dating of ground water originating as recharge after 1954 is based on the correlation of tritium concentrations in the ground water with known fallout peaks. The applications of tritium in hydrology are reviewed by Thatcher (1969).

Tritium is also of interest in public health inasmuch as concentrations much exceeding the natural level may be released to the environment in the course of tritium tracer experiments, nuclear power production, weapons testing, nuclear waste disposal, and "Plowshare" activities. "Water Quality Criteria, 1972" (EPA, 1973) notes that a tentative limit of 3,000 pCi/l of tritium has been prepared for the revised edition of "Drinking Water Standards." The NRC (1975) PCRE value for tritium in effluents released to uncontrolled areas is 3 μCi/l. The liquid-scintillation counting technique provides all the sensitivity required for monitoring tritium concentrations at the levels significant to public health.

Although tritium is not a major fission product, there is a significant production of tritium in nuclear power reactors. The greater part of the tritium remains enclosed in the fuel element until the latter is dissolved for reprocessing. The production of tritium in reactors depends greatly on the reactor type, and estimates of total production are subject to many uncertainties. It seems clear, however, that the reactor contribution to the tritium inventory is substantial. Sources of tritium have been reviewed by Jacobs (1968).

Determination of tritium radioactivity is complicated by the very low energy of the beta radiation which necessitates mixing the tritium intimately with the counting medium. Gas phase counting is carried out by introducing the tritium as a gas (HT) into a proportional counter containing the proper pressure of hydrocarbon gas to assure operation in the proportional region. Liquid scintillation counting of tritium is carried out by mixing the tritiated water sample with an organic scintillator suspended or dissolved in an organic medium compatible with water. The efficiency of gas phase counting may be very high, 60–80 percent. The efficiency of liquid scintillation counting is on the order of 20–25 percent.

Since the decay rate for 1 Tu concentration in water is only 0.007 dpm/ml and the background count (gas counting) is on the order of 2 cpm, it is obvious that enrichment of the tritium in the water sample is required when low concentrations of tritium are to be determined. Enrichment is carried out by electrolysis using essentially the same process as is used for the preparation of heavy water. Passage of electric current through water results in the liberation of the light hydrogen isotope (protium) at a faster rate than the heavy isotopes (deuterium, tritium), thus enriching the latter in the residual water.

Uranium

Uranium is widely disseminated in the lithosphere, and most natural waters contain detectable concentrations of this element. The average concentration in the ocean is about 3 μg/l (Rona and others, 1956). The uranium content of ground and surface waters varies greatly, from less than 0.1 μg/l to several milligrams per liter (mg/l). In most natural waters the concentration is less than 10 μg/l. The limit on uranyl ion (UO_2^{+2}) in public supplies (Water Quality Criteria, 1972) is 5 mg/l.

Dissolved uranium in natural waters exists principally as uranyl ion (UO_2^{+2}) which may

be complexed with carbonate. While uranium in surface waters is almost entirely hexavalent, there may be an appreciable percentage of tetravalent uranium under reducing conditions found in some ground waters. The latter is predominantly complexed and is highly insoluble in basic solution.

Uranium in natural water is important in geochemical prospecting and as an indicator of pollution from mining operations. It is unlikely that uranium could reach concentrations significant to health, although a high concentration of uranium could be indicative of possible high levels of the much more hazardous radium isotopes.

There are the three natural uranium isotopes:

Isotope	Abundance (percent)	Half-life (yr)
U-238 (U series)	99.27	4.51×10^{9}
U-235 (Ac series)	.72	7.1×10^{8}
U-234 (U series)	.006	2.47×10^{5}

Uranium-234 is related to uranium-238, the parent of the uranium decay series, by the following decay sequence:

$$U^{238}\xrightarrow{\alpha}Th^{234}(24.1\ d)\xrightarrow{\beta}Pa^{234}(1.18\ min)\xrightarrow{\beta}U^{234}.$$

The total world radioactivities of the 234 and 238 isotopes must be equal since the two are in secular equilibrium. Local physical and chemical effects may result in local disequilibria which are of geochemical interest and have been given intensive study. Disequilibria may result from physical or chemical mechanisms. The principal physical mechanism is the energetic alpha recoil associated with the decay of uranium-238 to thorium-234. This may rupture chemical bonds and permit thorium to go into solution in ground water where it decays to uranium-234. Although thorium is considered to be sorbed by sediment, the presence of dissolved organic matter or other complexing agents may tend to stabilize it. Since both intermediates, thorium-234 and protoactinium-234, are chemically different from uranium, chemical differentiation may occur. Difference in oxidation state between the 234 and 238 isotopes can have an additional effect. These effects frequently lead to enrichment of uranium-234 in water (Chalov and others, 1964; Cherdyntsev and others, 1961; Thurber 1962). Depletion of the 234 isotope is less common. Isotopic dating of waters, correlation of disequilibria with rapid leaching (important in pollution studies), and the geochemistry of uranium transport are examples of the possible application of uranium isotope disequilibria studies.

While the usual objective of the analysis is determination of the uranium-234 to 238 activity ratio, it is also possible to determine the activity ratio of the 235 isotope to 238. The uranium-235 to 238 ratio is constant (1:137) in the absence of artificial depletion or enrichment. Therefore, an increase of the 235 isotope is reason to suspect the presence of material processed for nuclear fuel.

Collection and treatment of samples

The principal requirements to be met in sampling a water body for the determination of radioactive constituents are the same as for other constituents, that is, collection of samples in an orderly sequence that provide a representative analysis of the water body both areally and temporally. Considerations involved in setting up a sampling program that yields the required representative information are discussed in detail in an earlier chapter (Brown and others, 1970) in this series of Techniques of Water Resources Investigations of the U.S. Geological Survey. Reference is made to the earlier chapter for discussion of site selection, sampling frequency, equipment, sample identification, and other elements of an organized sample-collection program. Guidelines for the collection and field analysis of ground-water samples are given by Wood (1976). If analyses for the determinations described in this manual are to be made by a U.S. Geological Survey Water Resources Division central laboratory, the appropriate section chief should be contacted. Specific information can then be obtained for collecting the samples, obtaining the necessary sampling supplies, and so forth.

The overriding problem in sampling for radioactivity is preservation of the extremely dilute concentration of radionuclides (usually in the nanogram- and picogram-per-liter range) in their original conditions until the analysis can be performed. While preservation of the original condition of the sample is a general problem in water analysis, the extreme dilution of the radionuclides greatly intensifies the problem. Although extensive research has been given to the chemistry of extremely dilute solutions, the practical results in terms of preservation of the sample have not been completely effective. Indeed, conclusions from different investigations are often at variance, and indicate that the essential phenomena are not completely understood.

Early in the history of radiochemistry the term "radiocolloid" came into use as a result of apparently colloidal phenomena observed in radioisotope solutions (dialytic separation, nonionic migration behavior in the electric field, and so forth). Although radioactivity produces electrically charged centers (which could attract other ions to form aggregations), it is unlikely that the phenomena in very dilute solutions of radioisotopes are greatly different from phenomena in very dilute solutions of nonradioactive ions. Starik (1959) has exhaustively reviewed the earlier work and finds both colloidal and noncolloidal behavior depending on conditions.

Starik also investigated the effect of filtration and found that radioisotopes were retained in varying ratios by different filter media depending upon the pH and other chemical factors. Overall, both sorption loss and filtration loss are functions of the concentration, pH, oxidation state, electrolyte composition, and presence of traces of colloidal material in the solution such as colloidal silica as well as numerous other factors. Many observations of "radiocolloids" are apparently attributable to sorption of the radionuclide on traces of colloidal silica.

Tests suggest that the sorption loss in natural-water samples, as against sorption loss in very dilute distilled-water solutions, may be relatively small. Many of the tests reported in the literature are based on distilled-water solution, and thus are not entirely relevant.

Similar tests with uranium showed no significant loss under any condition. Hexavalent uranium is stable in natural water exposed to the atmosphere, particularly when bicarbonate is present. Earlier tests by Janzer (unpub. data) are in agreement with the above findings. Surface-water samples were collected in polyethylene bottles under three conditions: no treatment, filtered and acidified at time of collection, and filtered at time of collection but not acidified. The concentrations of radium, uranium, and gross alpha-beta activity determined repetitively in all three samples agreed closely and did not significantly change with time.

It is generally recommended that acid should be added to very dilute solutions of trace elements for the purpose of minimizing sorption loss of trace elements from the solution while it is in contact with a sample container. This is the practice recommended herein, but it should be noted that the experimental evidence is not at all conclusive. There appears to be significant evidence from both radioactive and nonradioactive work with trace elements that the individual chemistry of the elements must be considered, and optimum preservation techniques for each element, or for chemically related groups of elements, are required. Starik (1959) reported, for example, that polonium is sorbed most strongly (on glass) at pH 4.5, and while the sorption is much less below pH 4, it is reduced to the minimum above pH 8. He also reported minimum sorption of radiotantalum at pH 10 with maximum sorption at pH 3.5, and maximum sorption of niobium-95 at pH 2.

Ground-water samples are usually clear initially but may become turbid as hydrated iron and manganese oxides form on exposure to air. It is essential to prevent the formation of these precipitates because they can coprecipitate radioactive elements. Precipitation of hydrous oxides is prevented by acidifying the sample after filtration. Sufficient reagent grade hydrochloric or nitric acid should be

added to the filtered sample to obtain a pH of 1 or less.

A 4-liter sample is usually adequate for radiochemical analysis of gross alpha, gross beta, uranium, and radium. Additional sample may be required if other analyses or reruns are desired. Recommended sampling procedures for surface and ground waters are described as follows:

1. Collect and store the samples only in specially washed and labeled 4-liter polyethylene sampling bottles provided by the radiochemical laboratory. The bottles are cleaned by the following procedure: Wash with tap water; add 10 ml nitric acid, and refill with tap water; allow to stand overnight; empty, and finally rinse several times with small amounts of distilled water; and drain, and allow to dry before capping and storing.
2. Surface-water samples are collected to obtain a representative sample of well-mixed water at a single point, generally near the center of the stream or river if possible. Preferably only clay- or silt-sized particles should be present in the sample if samples are to be analyzed for suspended gross alpha and beta radioactivity. No filtration or acidification is usually required if dissolved and suspended gross alpha and beta radioactivity and dissolved radium or uranium are desired. (Other analyses may require special handling, and the appropriate Central Laboratory section chief should be contacted for specific details.) Leave an air space of several centimeters to allow for volume changes with temperature. Seal the cap with vinyl tape. Ground-water samples should be filtered through a 0.45-micrometer membrane filter at the time of collection. Add sufficient reagent-grade hydrochloric acid (preferred), or nitric acid, to lower the pH to approximately 1. Minimum value of concentrated acid that should be added to a 4-liter sample is 8 ml. Alkaline waters may require more acid. Test with pH paper. Seal the cap with vinyl tape.
3. At the time of collection, fill out appropriate sample data form as completely as possible and include with the sample in the manner prescribed by the analyzing laboratory. When compiling the results of the analysis, it is essential to have all the information possible pertaining to the conditions which existed at the time the sample was collected.
4. Box the samples in the cartons provided, and ship as soon as possible after collection. Be sure that return address is on the shipping label.
5. During winter months, it is essential to mark the cartons "Water Sample. Keep from freezing."

When sampling a ground-water system for tritium or carbon-14, it is particularly important to select the sampling wells with care so that a representative sample is obtained. The well should be properly sealed to minimize surface-water contamination, and it should preferably be in constant use. A highly productive well is preferred to a low-yield well. The well should be thoroughly pumped before the sample is taken. A perfectly dry bottle or barrel is used. During and after the collection of the sample, minimize contact with the atmosphere which may contain carbon-14 and tritium at concentrations ranging from several-fold to several orders of magnitude higher than the radionuclide in the water sample.

Calculations of radionuclide concentrations

The method used to calculate concentrations of radionuclides for most of the determinations in this manual may be expressed in the form of a general equation. Exceptions are the calculations for uranium, uranium isotope ratio, and carbon-14 age. The general method of calculation compares the activity of a sample against the activity of a standard, and corrects for decay of the radionuclide in the sample between time of collection

and time of analysis. If the recommended practice of minimizing time delay between sampling and analysis is followed, the correction for decay through this interval becomes negligible for many radionuclides.

A more significant correction is that necessitated by decay of the standard between the date of its certification by the National Bureau of Standards (or other supplier) and the date of its use to calibrate the analytical method. This time interval may amount to several years and is significant, relative to the half-lives of several radionuclides.

The following general equation applies when in-growth of daughter activity is not a factor, and when the half-life is long relative to the counting time. This is the usual situation.

$$C=\frac{1000\overline{c}}{KVEf(e^{-\lambda t})}, \qquad (1)$$

where

C = concentration of radionuclide. This is usually expressed in pCi/l.

$\overline{c}=\overline{c_s}-(\overline{b_1}+\overline{b_2})$. Average count rate of the sample in counts per minute (cpm) after correction for background and blank,

where

$\overline{c_s}$ = average gross sample count rate (cpm),

$\overline{b_1}$ = average blank count rate (cpm), and

$\overline{b_2}$ = average background count rate (cpm).

Usually $\overline{b_1}$ and $\overline{b_2}$ are experimentally determined as a combined quantity.

K = factor to convert disintegration rate in disintegrations per minute (dpm) to curies. The value of K for different concentration expressions (C) is:

C	K
mCi/l	2.22×10^9
μCi/l	2.22×10^6
pCi/l	2.22

V = volume of sample in milliliters,

E = counting efficiency for the nuclide under the counting conditions specified for the determination. E is usually determined by analyzing standards in the same analytical procedure as for samples (a modified procedure is used in two methods described in this report),

f = fractional recovery of the nuclide in the sample,

λ = decay constant of the nuclide determined by: $\frac{\ln 2}{T_{1/2}}$,

where

$T_{1/2}$ = half-life of the nuclide of interest in the appropriate time units, and

t = elapsed time between collection of the sample and count of radioactivity (in same time units as used for λ).

The counting efficiency factor E, is calculated by the following general equation:

$$E=\frac{\overline{c_n}}{d_n f_n(e^{-\lambda t_n})}, \qquad (2)$$

where

$\overline{c_n}$ = average count rate of standard in cpm after correction for background and blank,

d_n = disintegration rate of standard (dpm),

f_n = fractional chemical recovery of the nuclide in the standard, and

t_n = elapsed time between certification of the standard and the count, in some units as the respective λ.

In the determinations of gross alpha and beta activity, cesium-137 and 134, tritium (without electrolysis), radium-228, radium as radium-226, and radium-226, the chemical recovery factors f and f_n are not determined. The product Ef_n is determined by counting the standard and is substituted for Ef in equation 1. This procedure is valid when f and f_n are equal and reproducible (within experimental limits) and effectively cancel out. The usual situation is that f and f_n are very close to unity.

Equations 1 and 2 apply when the sample and standard are counted under the same

conditions on the same detector. This is the normal situation. In the determination of radium-226 the individual samples and standards are counted in individual alpha scintillation cells, each of which has its own counting efficiency (cell constant). Hence, in the determination of radium-226 an individual counting efficiency is determined for each cell.

In the determination of lead-210, radium-226, and radium-228, the radioactivity count is made on a relatively short-lived daughter of the nuclide determined. This necessitates the introduction of an "in-growth" or "build-up" factor, which is the fraction of the equilibrium concentration of daughter that had grown in at the time of separation from the parent nuclide. Since the daughter nuclides are relatively short lived with respect to the counting time, it is necessary to introduce a correction factor for decay during the counting interval. With radium-226 and radium-228 it is also necessary to introduce a factor that corrects for decay of the daughter during an aging period prior to counting.

Although a daughter nuclide is counted (in addition to the parent) in the determination of strontium-90, an in-growth factor is not used because the daughter is allowed to reach a constant level (99.5 percent of equilibrium) before counting.

The relationship of the three correction factors to the time intervals involved in the counting of a daughter nuclide is illustrated in figure 1. The figure shows growth and decay of the daughter with time and identifies the significant time intervals. The general equation for use with ingrown nuclides is:

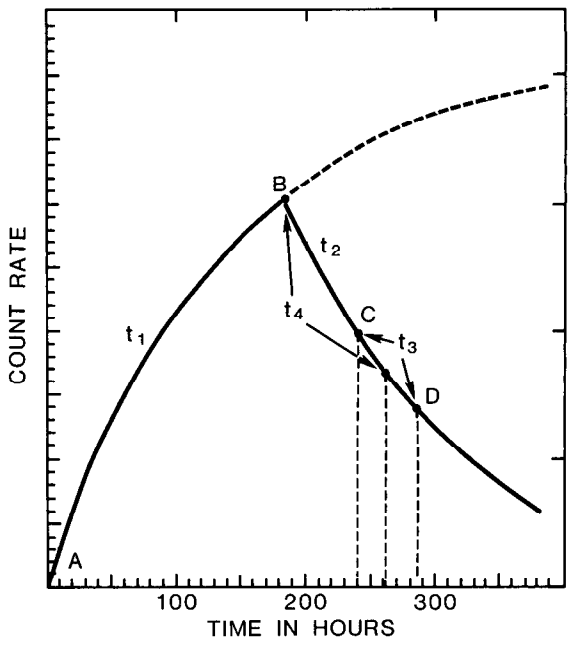
$$C=\frac{1000\bar{c}Z}{KVEf(e^{-\lambda t})XY}, \qquad (3)$$

where

C = concentration of radionuclide. This is usually expressed in pCi/l.

$\bar{c}$ = average count rate of sample in cpm after correction for background and blank,

$X=1-e^{-\lambda t_1}$ (in-growth of daughter),



A-B IN-GROWTH OF DAUGHTER NUCLIDE IN TIME t_1 (NUCLIDE ILLUSTRATED HAS HALF-LIFE OF 3.82d)
B SEPARATION OF DAUGHTER FROM PARENT
B-C DECAY OF DAUGHTER BEFORE COUNTING, TIME INTERVAL t_2
C BEGINNING OF COUNT
C-D DECAY OF DAUGHTER DURING COUNTING INTERVAL t_3
t_4 TIME INTERVAL BETWEEN SEPARATION OF DAUGHTER FROM PARENT AND MIDPOINT OF COUNTING INTERVAL

Figure 1.—In-growth and decay of a daughter nuclide, significant time intervals.

$Y=e^{-\lambda_1 t_2}$ (decay of daughter between separation from parent and beginning of count),

$Z=\frac{\lambda_1 t_3}{1-e^{-\lambda_1 t_3}}$ (decay of daughter during counting period),

where

λ = decay constant of parent nuclide,

t = elapsed time of parent between collection of the sample and separation of daughter,

λ_1 = decay constant of daughter nuclide,

t_1 = in-growth time of daughter, point A to B (fig. 1),
t_2 = delay before counting, point B to C. Separation of the daughter from the parent at time B, and
t_3 = time interval for counting of the daughter, point C to D.

K, V, f, and E are as defined for equation 1. The efficiency calculation for ingrown nuclides is:

$$E = \frac{\bar{c}_n}{d_n f_n (e^{-\lambda t_n}) XY}, \quad (4)$$

with symbols and units as defined in equations 2 and 3.

Because of the short counting time permitted by the higher concentration of the standard, the counting time is short relative to the half-life. Hence the correction factor for decay during counting is eliminated.

The general equations are modified in accordance with specific conditions prevailing in the determination of individual radionuclides. For example, f and f_n are eliminated when chemical separations are not used or when the chemical recovery factor is included in the determination of overall efficiency. Decay terms are eliminated when the half-life of the nuclide permits.

The terms used in equations 1 to 4 are not repeated under the calculation section of the individual determinations unless required for clarification.

Glossary

Confidence level. The stated probability, under the experimental conditions employed, that the value will be within the interval indicated by the precision around the mean.

Decay. The spontaneous radioactive transformation of one nuclide into a different nuclide or into a different energy state of the same nuclide. Every decay process has a definite half-life.

Dissolved. The sample is filtered through a 0.45 micrometer membrane filter and the filtrate analyzed.

Filterable solids. Those dissolved solids capable of passing through a 0.45 micrometer membrane filter and dried to constant weight at 180°C.

Half-life. The time required for the decay of a given quantity of a radioactive substance to one-half its original mass; thus it is a measure of the rate of such processes.

Minimum detection level. The least amount or concentration that can be detected and quantified by a test method.

Nonfilterable solids. Those solids which are retained by a 0.45 micrometer membrane filter and dried to constant weight at 103°–105°C.

Precision. The degree of agreement of repeated measurements of the same property expressed in terms of dispersion of test results about the mean result obtained by testing of a homogeneous sample(s) under specific conditions.

Sorption. A general term for the processes of absorption and adsorption.

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