Determination of Beta Activity in Water

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1696-A

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By F. B. BARKER *and* B. P. ROBINSON

RADIOCHEMICAL ANALYSIS OF WATER

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ABSTRACT

Many elements have one or more naturally radioactive isotopes, and several hundred other radionuclides have been produced artifically. Radioactive substances may be present in natural water as a result of geochemical processes or the release of radioactive waste and other nuclear debris to the environment. The Geological Survey has developed methods for measuring certain of these radioactive substances in water.

Radioactive substances often are present in water samples in microgram quantities or less. Therefore, precautions must be taken to prevent loss of material and to assure that the sample truly represents its source at the time of collection. Addition of acids, complexing agents, or stable isotopes often aids in preventing loss of radioactivity on container walls, on sediment, or on other solid materials in contact with the sample.

The disintegration of radioactive atoms is a random process subject to established methods of statistical analysis. Because many water samples contain small amounts of radioactivity, low-level counting techniques must be used. The usual assumption that counting data follow a Gaussian distribution is invalid under these conditions, and statistical analyses must be based on the Poisson distribution.

The gross beta activity in water samples is determined from the residue left after evaporation of the sample to dryness. Evaporation is accomplished first in a teflon dish, then the residue is transferred with distilled water to a counting planchet and again is reduced to dryness. The radioactivity on the planchet is measured with an anticoincidence-shielded, low-background, beta counter and is compared with measurements of a strontium-90–yttrium-90 standard prepared and measured in the same manner. Control charts are used to assure consistent operation of the counting instrument.

INTRODUCTION

The Geological Survey has adopted analytical methods for certain radioactive species in water. These methods will be described in detail, with complete laboratory instructions, in the present and in succeeding chapters of this Water-Supply Paper. These methods, or modifications of them, are useful in studies of the purity of domestic and industrial water supplies, water pollution, radioactive-waste disposal, and hydrogeochemistry.

Messrs. H. P. Cantelow, of the Lawrence Radiation Laboratory, and W. L. Albrecht, of the Tennessee Valley Authority, reviewed the manuscript of this report.

SOURCES OF RADIOACTIVITY IN WATER

Many radionuclides (atomic species that undergo radioactive decay) occur in nature. All isotopes of elements of atomic number 83 and higher are radioactive, and several of the elements of lower atomic weight have one or more natural radioisotopes. Most of the radionuclides are members of the three naturally radioactive series: the uranium series, the actinouranium series, and the thorium series. In these series, the parent atoms change successively from element to element by the emission of alpha, beta, and gamma radiation. The major features of these series are illustrated schematically in figures 1, 2, and 3. The other naturally occurring radionuclides, together with

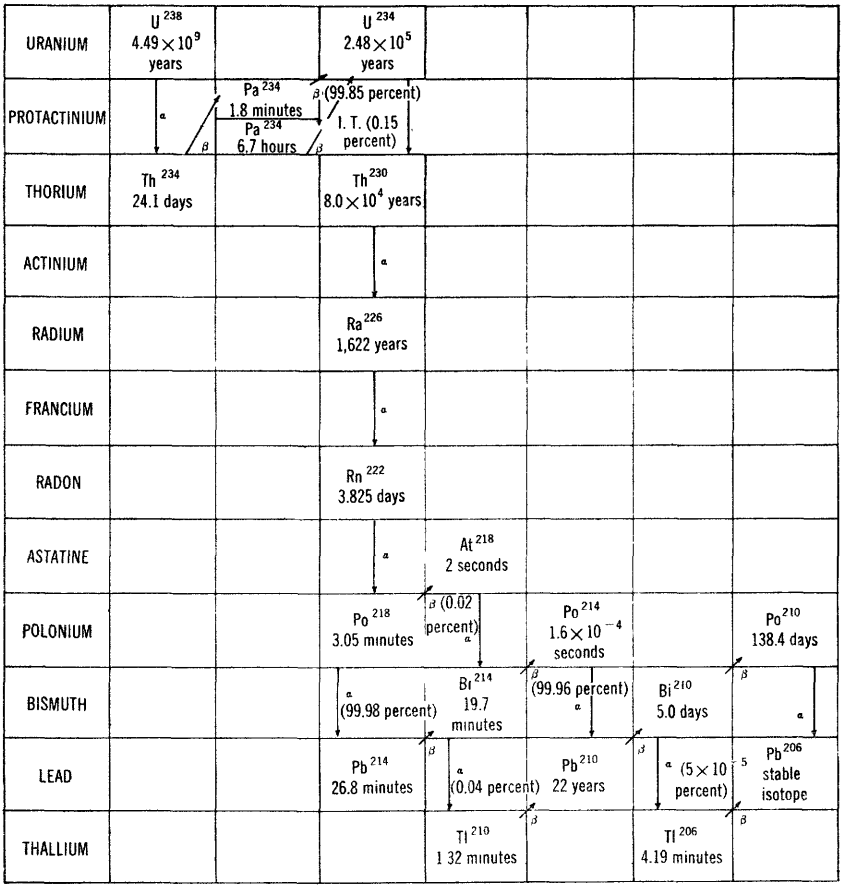

FIGURE 1.—The uranium series.

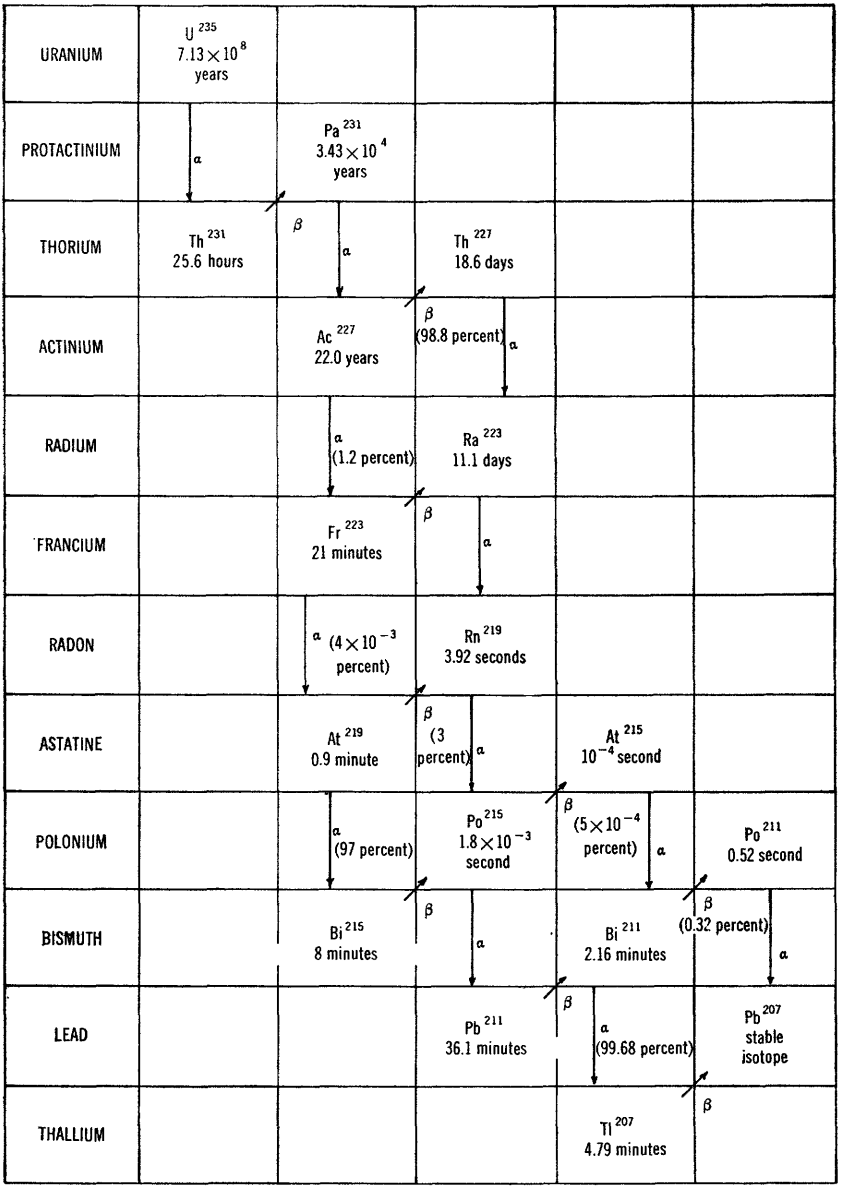

FIGURE 2.—The actinium series.

their half-lives and mode of decay, are listed in table 1. Some additional radionuclides are produced from the interaction of cosmic rays with stable atoms and from the spontaneous fission of uranium atoms; however, only two of these nuclides are of much importance: hydrogen-3 (tritium) and carbon-14.

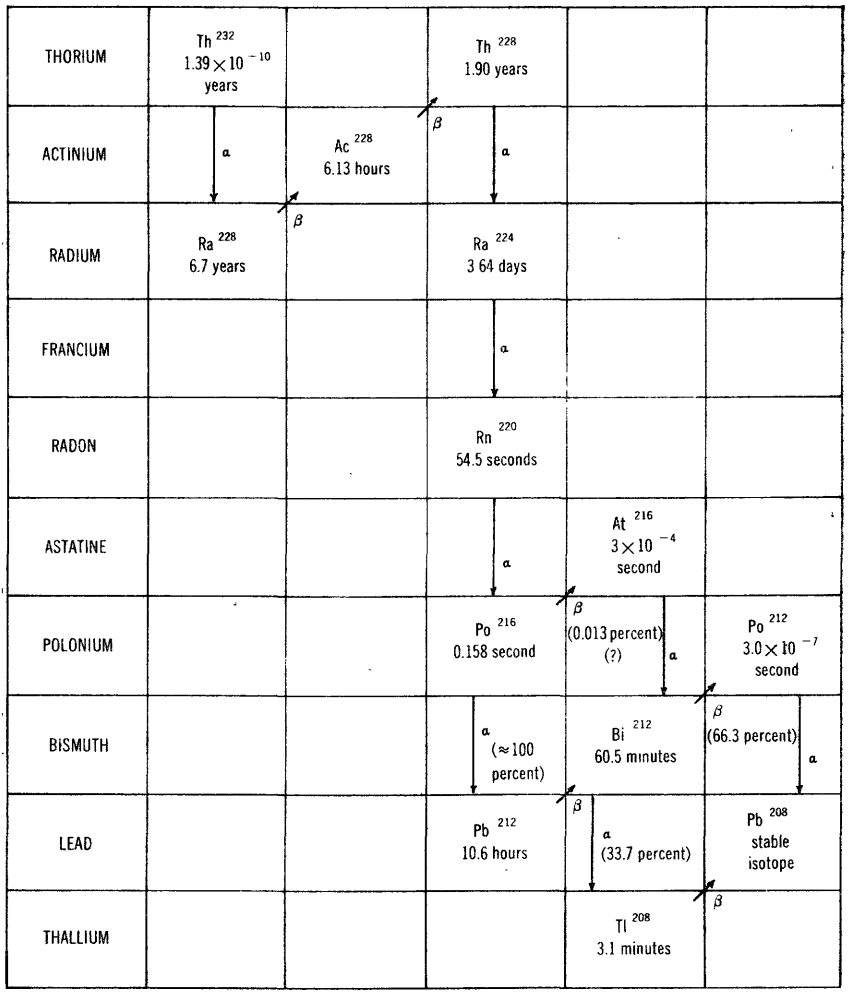

FIGURE 3.—The thorium series.

TABLE 1.—*Naturally occurring radionuclides, other than members of the natural radioactive series*

[From Friedlander and Kennedy, 1955]

Radionuclide	Relative isotopic abundance (percent)	Mode of decay [1]	Half-life (years)
Potassium–40	0. 012	β, K	1.2×10^{9}
Rubidium–87	27. 8	β	6.2×10^{10}
Indium–115	95. 8	β	6×10^{14}
Lanthanum–138	. 089	K, β	$\approx2\times10^{11}$
Neodymium–144	23. 9	α	$\approx5\times10^{15}$
Samarium–147	15. 1	α	1.3×10^{11}
Lutecium–176	2. 60	β	4.6×10^{10}
Rhenium–187	62. 9	β	$\approx5\times10^{10}$
Platinum–190	. 012	α	$\approx10^{12}$

[1] The mode of decay is indicated by the type of particle emitted (α, β). If decay also occurs by electron capture, this is indicated by K; the predominant mode is indicated first.

Within recent years, several hundred artificial radionuclides have been produced. The most important of these are the fission products—those nuclides produced in the course of the fission of uranium–235, plutonium–239, or uranium–233 atoms. Other radionuclides have been produced by various nuclear-bombardment reactions. A complete list of nuclides, with their half-lives and modes of decay, is given by Friedlander and Kennedy (1955, p. 413).

All natural water contains some radioactivity, if only that due to the ubiquitous element potassium. Before the development of atomic energy and nuclear devices, the radioactivity in water came primarily from radionuclide-bearing rocks and minerals with which the water came in contact, with lesser contributions from the cosmic-ray-produced radionuclides picked-up mainly by meteoric water. Since the advent of the atomic age, however, measurable amounts of other radioactive substances have found their way into the Nation's water resources as a result of fallout from nuclear explosions and discharge of radioactive waste from nuclear reactors, uranium mills, research laboratories, and other producers and users of radioactive materials.

COLLECTING AND PRESERVING THE SAMPLE

The results of an analytical determination can be no better than the sample used. Therefore, care must be taken when the sample is collected to assure that the sample truly represents the source. Also, any changes that might occur within the sample between the time of collection and the time of analysis must be kept to a minimum.

The methods used to collect samples will depend on several factors that vary with the type of investigation underway; however, certain criteria are of rather general application. The preferred methods of sampling surface-water supplies are (1) integration through the cross section of a stream, or (2) depth integration at points on a suitable network laid out on a lake or reservoir. A stream normally should not be sampled immediately below its confluence with another stream or below a waste outfall where mixing may not be adequate. Thorough mixing may require several miles, especially in broad, shallow, and sluggish streams. Wells, developed springs, and similar ground-water sources should be pumped before sampling to assure removal of stagnant water from the casing, pipes, and that part of the aquifer immediately adjacent to the well. Springs and seeps should be sampled as near the orifice as possible. These precautions should provide a sample that closely represents water typical of that in the undisturbed portion of the aquifer. Criteria for sampling waste streams and other process solutions usually are dictated by the plant operations.

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A more comprehensive discussion of the problems encountered in collecting water samples is given by Rainwater and Thatcher (1960, p. 3–27). The equipment and techniques described generally are applicable to the collection of samples for radiochemical analysis as well as those for chemical analysis. Many practical suggestions relating to sample collection also are included. This reference should be studied by anyone concerned with collecting water samples, particularly samples from natural sources.

Radioactive substances are often present in water samples in microgram quantities or less; therefore, significant amounts may easily be lost from solution by sorption on sediment and container walls, by carrying on precipitates formed after the sample is collected, and by biological uptake. In some samples, the concentrations of radioactive substances in solution may increase because additional material is leached from sediment present in the sample.

The tendency for calcium carbonate to precipitate may be reduced by stoppering the container tightly to prevent loss of carbon dioxide and by adding acid to lower the pH. Acidification also helps to prevent precipitation of iron, aluminum, and similar cations as the hydroxides and reduces the tendency of many ions to be sorbed on solid materials. Too low a pH, however, may cause excessive leaching of the sediment. Acetic acid produces a pH that provides a reasonable compromise between the two effects, although stronger acids are used sometimes. Complexing agents may be used to keep certain substances in solution; for example, sodium bicarbonate will inhibit precipitation of dissolved uranium and has less effect on most natural water-borne sediments than does acetic acid. Addition of a stable isotope of an element, either with or without other treatment, usually aids in keeping its radioactive isotopes in solution. Growth of algae, fungi, and other organisms can be inhibited by the addition of a small amount of chloroform, phenol, or other suitable growth inhibitor. Addition of a growth inhibitor is necessary when acetic acid or other organic acid is used as a preservative or when the sample contains considerable organic material. Filtering the sample immediately after collection reduces the number of complicating factors involved in preserving the sample.

The particular preservative, or combination of preservatives, to be used depends on the nature of the sample and on the specific radionuclides of interest. The Geological Survey uses acetic acid and chloroform for most samples, although other preservatives are used in special cases. The subject of sample preservation also is discussed by Rainwater and Thatcher (1960, p. 27–30).

The handling of samples before analysis is another factor of considerable importance that will affect the analytical results. For

example, keeping the delay between collection and analysis to a minimum reduces the magnitude of changes occurring within the sample and, when short lived activities are of interest, also reduces the losses due to radioactive decay.

Whenever concentrations are averaged over a period of time by compositing, as is often done in stream studies, the volumes used should be weighted according to some plan consistent with the major uses for the analytical data. The two general methods of compositing water samples are the time-weighted method and the water-discharge-weighted method. Compositing techniques, including selection of compositing periods and methods, are discussed by Rainwater and Thatcher (1960, p. 32–39).

Many samples contain both dissolved and suspended material. The distinction between the two phases should be defined, and when necessary, the samples should be treated to separate the phases. Geological Survey laboratories have used either filtration—through molecular-membrane filters, fritted-glass filters, or filter candles of specified porosity—or centrifugation under reproducible conditions as standard separations of the phases. Sometimes it is desirable to consider all radioactivity, both dissolved and suspended, carried by the water. Any separation of phases in such samples is avoided, and the samples are shaken vigorously before portions are withdrawn for analysis. The method to be used depends on the nature of the sample and the information desired.

The entire matter of collecting, preserving, and defining a water sample is complex, and no absolutely fixed rule can be stated. The general principles described above and those discussed in standard reference works should be followed (see, for example, Rainwater and Thatcher, 1960; American Society for Testing Materials, 1959, p. 85–101, 209–217, 531–535; and American Public Health Association, 1955, p. 3–7, 28, 221–222, 283). Nevertheless, the sample collector must use judgement based on the conditions existing at the sampling site at the time of collection, the type of data needed, the intended uses of the data, and other related factors.

MEASUREMENT OF RADIOACTIVITY

Detection and measurement of most radioactive substances is carried out by determining the number of particles or amount of radiation emitted by the sample. This quantity is directly proportional to the number of atoms, and, therefore, to the weight of the radioactive substance. A few substances of long half-life and low specific activity, notably natural uranium and potassium, usually are determined by chemical methods such as fluorometry and flame photometry; however, these are exceptional examples. Some general considera-

tions concerning the measurement of radioactivity are discussed in the following paragraphs, thus obviating the need for repetitious discussion of the subject along with the description of each method.

TECHNIQUES AND INSTRUMENTS

Many techniques and instruments are available for detecting and measuring radioactivity. Several of them make use of the electrical conductivity of gas ionized by the radiation. These instruments may be classified according to whether saturation collection is employed (ionization chambers) or whether the multiplicative collection region is used (proportional and Geiger-Müller counters). The magnitude of the electric current or the number of electric pulses produced in the chamber are proportional to the radioactivity of the sample. The currents or pulses are amplified if necessary and their magnitudes or number are denoted by some type of indicating or recording device. Examples of these devices include electroscopes, electrometers, electronic scalers, and counting-rate meters. The first two are used with ionization chambers, and the last two are used mainly with proportional and Geiger-Müller counters.

Several methods that do not depend on ion collection have been used for the detection of radioactivity (Friedlander and Kennedy, 1955, p. 236–240). The general blackening or fogging of photographic negatives is a historical method. Nuclear emulsions, designed especially to react to various ionizing radiations, are available. The Wilson cloud chamber, in which the particle track through a gas is made visible by condensation of water droplets on the ions produced, and the more recently introduced bubble chamber, in which the string of bubbles produced along the track of an ionizing particle in a superheated liquid is illuminated and photographed, are well known instruments for the detection of radioactivity. Another method for the measurement of radioactivity is based on calorimetry; the heating effect of radiations stopped in a calorimeter can be measured and the activity determined. Most widely used is the scintillation counter, whose operation depends upon discrete flashes of light produced when nuclear radiations strike a suitable crystal or other scintillator. The flashes can be detected by a photomultiplier tube, and the resulting output pulses recorded by an electronic scaler, counting-rate meter, or similar device.

The interested reader is referred to any general text on radiochemistry or nuclear physics for additional information on instruments for measuring radioactivity. Detailed information on ion-collection techniques may be found in "Electron and nuclear counters" (Korff, 1946) and in "Ionization chambers" (Rossi and Straub, 1949).

Radioactive substances found in natural water usually are meas-

ured by ion-collection techniques and scintillation counting. The Geological Survey generally measures alpha activity by means of scintillation counting with zinc sulfide phosphors or by counting with an internal-proportional counter, beta activity by means of proportional or Geiger counting, and gamma activity by means of scintillation counting with thallium-activated sodium iodide phosphors.

STATISTICAL CONSIDERATIONS

Disintegration of radioactive atoms is a random phenomenon subject to established methods of statistical analysis. For any given sample of radioactive material, the counting rate will be a function of the disintegration rate and, because of the random nature of the disintegration process, will fluctuate from one time interval to the next. It is impossible to predict from the counting measurements themselves which time interval yields the most accurate result—that is, the counting rate most nearly representing the true number of radioactive atoms present. The best that can be done is to compute the arithmetic mean (the average value) and consider this to represent the "true" counting rate. If the activity of the sample were determined again by taking the mean based on a different set of time intervals, the result most likely would be different. Therefore, some knowledge about the statistical dependability of the data as well as the average itself is desirable.

Radioactive disintegration obeys the binomial distribution law, and, for counting times that are short compared to the half-life of the material, the standard deviation of a count is equal to the square root of the average number of counts to be expected during the time of counting (see, for example, Friedlander and Kennedy, 1955; Overman and Clark, 1960; and Cook and Duncan, 1952); that is,

$$\sigma_m = \sqrt{M}$$

where

σ_m=standard deviation of the observation
M=average number of counts expected during the observation.

If a reasonably large number (m) of counts has been obtained, it may be substituted for the expected average, M, for an approximate evaluation of the standard deviation, σ_m. Thus, the standard deviation for a counting rate is

$$\sigma_R = \frac{\sigma_m}{t} = \frac{\sqrt{m}}{t} = \sqrt{R/t}$$

where

$R=m/t$=counting rate
t=time interval during which m was observed.

A Poisson distribution is obtained if, in addition to the restriction on the time of observation, the restriction is imposed that a large number of active atoms are observed (even though only a few undergo decay) and if use is made of the following mathematical approximations:

$$e^{\lambda t} \approx 1+\lambda t$$

$$x! \approx x^x e^{-x}\sqrt{2\pi x} \qquad \text{(Stirling's approximation)}$$

$$\lim_{N_0 \to \infty} \left(1-\frac{m}{N_0}\right)^{N_0} \approx e^{-m}, \qquad (\text{as } N_0 \gg 1)$$

With the above restrictions and approximations, and with the substitution

$$M=CN_0\lambda t$$

where

C=counting efficiency
N_0=number of atoms present
λ=decay constant

The Poisson distribution takes the form

$$P[m]=\frac{M^m e^{-M}}{m!}$$

where $P[m]$ is the probability of observing a count of exactly m when the expected average count is M.

The variance (square of the standard deviation) of the sum of two or more Poisson distributions is the sum of the individual variances, thus the standard deviation of the new distribution is

$$\sigma_s=\sqrt{\sigma_1^2+\sigma_2^2+\ldots}$$

where

σ_s=standard deviation of the sum

σ_i=standard deviation of the individual members of the sum.

The variance of the difference of two Poisson distributions is given by the sum of the individual variances; thus the standard deviation is

$$\sigma_d=\sqrt{\sigma_1^2+\sigma_2^2}$$

Under conditions such that the restrictions concerning the Poisson distribution are met, the counting rate of the sample and the standard deviation of this rate are given by

$$n=R-B$$

$$\sigma_n=\sqrt{\sigma_R^2+\sigma_B^2}$$

where

n=observed net counting rate

B=observed background counting rate

R=gross counting rate

If a reasonably large number of counts has been obtained for both background and sample-plus-background ($m>100$ in both cases) and if the net counting rate is several times greater than its standard deviation, the observed net counting rate may be used for the "true" average counting rate. Thus,

$$n\approx R-B$$

$$\sigma_n\approx\sqrt{R/t_R+R/t_B}$$

If a sample contains very little radioactivity, so that the number of counts arising from the sample is small compared to that arising from background, the random fluctuations in the background may exceed the counts due to the sample. This situation sometimes results in an observed sample-plus-background counting rate that is less than the observed background counting rate alone. When the approximation that the expected average may be replaced by the observed rate is used, the amount of radioactivity in the sample apparently is negative; this is, of course, physically meaningless. Some other means is needed for estimating the expected average, or composition of the universe, from the data of the observations.

One treatment of this problem, based on the assumption that all sample strengths are equally probable, has been given by R. W. Dodson (cited in Friedlander and Kennedy, 1955, p. 264). Dodson showed that counting observations may be fitted by a Poisson distribution with an average, M, equal to $m+1$ rather than to the measured value m. Therefore, the most probable value of M is $m+1$, and the standard deviation is $\sigma=\sqrt{m+1}$. Thus, for an observed count $m=0$, it is assumed that $M=1+1$; for $m=1$, $M=2+1.4$; and so on. For large values of the observed count ($m>>1$), $M=m+1\approx m$, and the earlier assumption is valid.

On the basis of Dodson's treatment, it is possible to derive a relation between the observed counting data for both sample and background and the net counting rate of the sample. Let

$$R=\frac{m+1}{t_R} \text{ and } B=\frac{b+1}{t_B};$$

the net counting rate is then

$$N=R-B=\frac{m+1}{t_R}-\frac{b+1}{t_B}=\frac{m}{t_R}-\frac{b}{t_B}+\left\{\frac{1}{t_R}-\frac{1}{t_B}\right\}$$

and the variance of the net counting rate is

$$\sigma_N^2=\frac{m+1}{t_R^2}+\frac{b+1}{t_B^2}=\frac{m}{t_R^2}+\frac{b}{t_B^2}+\left\{\frac{1}{t_R^2}+\frac{1}{t_B^2}\right\}$$

Thus, data calculated in the usual manner can be corrected by use of terms involving only the time intervals of observation. If the counting intervals are the same for both sample and background, the correction term for the net counting rate is zero, but that for the variance is finite.

D. J. Behrens (1951) has examined the problem of low-level counting when the background counting rate, B, is known with great precision and the amounts of radioactivity in the samples have equal probabilities. The most probable "true" number of gross counts from the sample was shown to be

$$M=\frac{(m+1)![1-P(m+2, Bt)]}{m![1-P(m+1, Bt)]}$$

where $P(j, a)$ is the sum from the j^{th} term to infinity of the terms of the Poisson distribution mean, a;

$$P(j, a)=\sum_{x=j}^{\infty}(a^x e^{-a}/x!).$$

Therefore, the most probable value of the "true" net counting rate, $\overline{N}$, is given by

$$\overline{N}=\frac{M}{t}-B=\frac{(m+1)}{t}\frac{Q(m+1, Bt)}{Q(m, Bt)}-B$$

where $Q(k, a)$ is the sum from zero to k^{th} term of the Poisson distribution with mean, a;

$$Q(k, a)=\sum_{x=0}^{k}(a^x e^{-a}/x!)$$

When m becomes larger than Bt, the value of $\overline{N}$ calculated from Behren's equation approaches the equivalent $\overline{N}$ (where B is precisely known) calculated by Dodson's method. Behren's $\overline{N}$ deviates from Dodson's value when m is smaller than Bt, approaching $1/t$ as a limit. The curves in figures 4 and 5 show the relation of Nt to m and Bt for both approaches discussed above.

The assumption that all quantities of radioactivity are equally probable results in the highest estimates of the "true" means of any physically-reasonable assumption of the distribution of sample activities (Behrens, 1951). Therefore, this approach is especially useful in evaluating the degree to which a water meets the criteria of radiological health because any deviations from the assumed distribution will tend to be on the safe side. Methods based on different assumptions concerning the distributions of activity in the samples might be more useful for other studies and should be chosen to fit the situation at hand.

CALIBRATION OF INSTRUMENTS

The instruments used in measuring radioactivity generally do not give absolute values and, therefore, must be calibrated against suitable standards. Certified standards of some radionuclides can be obtained from the National Bureau of Standards; others can be obtained from various commercial sources.

The choice of a standard for calibrating an instrument depends on the radiochemical analysis that is to be performed. If the method is one for determining a specific radionuclide, the instrument should be calibrated with that radionuclide. Whenever this is not practicable, a standard with similar critical characteristics should be chosen. Instruments to be used for a wide range of known or unknown radionuclides usually are best calibrated with an "average" standard that bears some resemblance to the entire group.

Radionuclides and equilibrium mixtures of radionuclides that have had common usage as "average" standards in the calibration of beta-counting instruments include (1) thallium-204, (2) equilibrium mixture of strontium-90 and yttrium-90, and (3) equilibrium mixture of cesium-137 and barium-137. Wehler and co-workers (1954) recommended thallium-204 as a standard for measuring beta activity in water. However, it now appears that the half-life is not known accurately, so that corrections for radioactive decay are uncertain. Conversion electrons are associated with the decay of barium-137, which necessitates a correction when the cesium-barium mixture is used as a standard.

Natural uranium, separated from its radioactive daughters, is a convenient standard for calibrating instruments for measuring alpha

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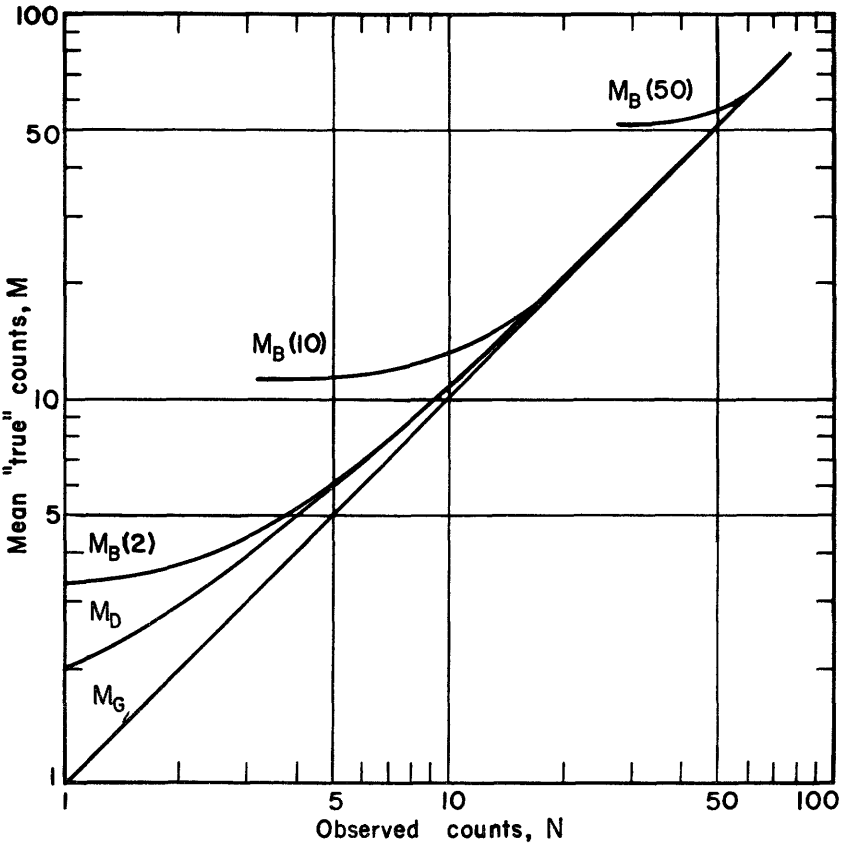

FIGURE 4.—Best estimate of "true" counts, all sample strengths equally probable. M_G, Gaussian distribution ($M=N$); M_D, Dodson's treatment ($M=N+1$); $M_B(b)$, Behren's treatment for background count b.

activity in water. The long half-lives of the uranium isotopes and their immediate alpha-emitting daughters obviates the need to correct for growth and decay of activity over a period of many years. Radium-226 is a suitable standard in many situations. However, partial loss of the radon-222 daughter can cause errors unless precautions are taken to minimize such loss or unless the magnitude of the loss is known and appropriate corrections are applied.

Several general methods are available for calibrating instruments with these standards; however, two of these methods are most commonly used. In one method, the instrument is calibrated with standards in a manner so that only those factors relating to the instrument—such as window thickness, air absorption, and geometry—are included in the correction factor. Those factors relating to the preparation and mounting of the sample—such as self-absorption, chemical yield, and back-scattering—require that one or more other correc-

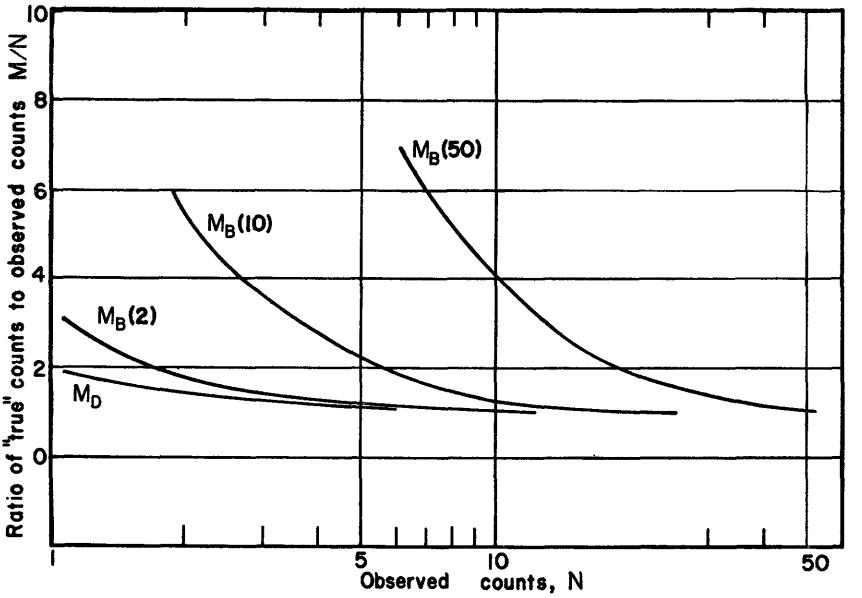

FIGURE 5.—Ratio of mean "true" counts to observed counts according to Dodson and Behren. M_D, Dodson's treatment ($M=N+1$); $M_B(b)$, Behren's treatment background count b.

tions be applied to the results. In the other common method, calibration is performed in a manner such that the standards are carried through the entire procedure. This method gives an efficiency correction for the entire procedure, with perhaps the exception of chemical yield, without the necessity of a series of individual corrections. The Geological Survey generally uses the latter method in calibrating instruments for the radiochemical analyses of water samples.

When calibrating the counting instruments by the second of the preceding methods, care must be taken to assure that the standards are prepared in a manner comparable to the preparation of the sample. This necessitates (a) the use of carriers having essentially the same self-absorption and self-scattering properties as the samples, (b) mounting the standards on planchets having the same geometry and back-scattering as those for the sample mounts, and (c) placing the standards in the instruments so that the the geometry and absorption are the same as for the samples. Also, the distribution of the activity on the planchet must be as nearly like that of the samples as possible. Usually, it is most convenient to prepare the standards and samples in an identical manner, using the same reagents, equipment, and techniques.

The exact calibration procedures to be used will depend largely on the nature of the investigation and on the potential uses of the data. The preceding discussion serves only as a guide in selecting calibration procedures; additional information may be found in any standard text on nuclear chemistry. (See, for example, Cook and Duncan, 1952; Friedlander and Kennedy, 1955; and Overman and Clark, 1960.) The procedures used by the Geological Survey will be discussed in more detail in the sections describing the individual methods.

CONTROL OF INSTRUMENT OPERATION

Uniform day-to-day operation of counting instruments is required whenever data collected over a period of time must be intercompared. Although major changes in the operating characteristics of instruments often are obvious, slowly occurring changes of small magnitude may be overlooked unless routine checks are made for purposes of control. An effective method of assuring uniform daily operation of an instrument is the use of control charts on background and on control-standard counting rates. The background control chart also permits establishment of a more precise average background counting rate than normally is available, especially for low-background instruments; this, in turn, improves the precision of the measurement of samples activities.

Effective control of counting instruments can be achieved only if they are operated at an optimum point considering both stability and sensitivity. This requires that one or more controls—such as high voltage, gain, and pulse-height discriminator—be adjusted to the most suitable positions. The technique used depends on the nature of the instrument. Two standard procedures, suitable for most systems used for gross-activity measurements, will be described. Special procedures—such as those used with pulse-height analyzers—will be discussed in the chapters concerned with methods requiring these procedures.

Control charts serve as a day-to-day check on the uniformity of operation of the instrument. The instrument can be presumed to be operating properly and uniformly if no changes, beyond statistical limits, occur on the charts. A sudden change on the standard control chart may indicate instrument malfunction, a change in the detector assembly, or incorrect settings of the controls; a slow but steady change may indicate deterioration of the detector, aging of tubes or other components, or voltage drifts. Changes in the background control chart may indicate instrument malfunction, contamination, or the presence of external radiation fields. The background control chart also yields the most precise value of the average background counting rate.

The control of instrument operation requires use of a radioactive control standard, both for determining the optimum criteria for instrument operation and for maintaining the standard control chart. This control standard can be any available radionuclide having a high percentage of emission of the radiation for which the counter is to be used, a half-life sufficiently long to minimize decay corrections, and particle energies sufficient to penetrate the window and any other absorbers present. The true disintegration rate need not be known, but the counting rate should be several thousand counts per minute. The radioactive material should be fixed permanently to the planchet and distributed uniformly over an area preferably smaller (<25 percent, if possible) than the window of the counter. If possible, the standard should be covered with thin aluminum or plastic to protect against damage and, for beta standards, to exclude any alpha particles originating from the standard. Any change in the activity of the control standard, other than by radioactive decay, necessitates establishment of a new standard control chart. The standard must be mounted so that it can be positioned in the counter reproducibly, preferably centered under the window.

Any of several commercially-available mounted standards are suitable and, in the uncalibrated form, are inexpensive.

OPTIMUM OPERATION OF G–M COUNTERS

Put the instrument into operation according to the manufacturer's instructions. If the instrument has gain or discriminator controls, adjust them so that only pulses above 0.2 to 0.25 v (volts) will be counted. With the high voltage set at the minimum, place the control standard in position and turn the "count" switch to the count position. Increase the voltage slowly until the first counts are observed and record this "threshold voltage." Turn the count switch to the "off position," raise the voltage 20 to 25 v (or some other convenient unit) above threshold, and determine the counting rate. Advance the voltage in similar convenient increments and determine the counting rate at each voltage. As the voltage is increased, the counting rate should rise initially, reach an approximately constant value, the "plateau," then increase rapidly at the "breakdown voltage." To prevent damage to the detector, the instrument should not be operated at or above the breakdown voltage after it has been identified. If the plateau extends 150 v above the threshold, additional measurements are not needed, and the voltage should not be increased to breakdown.

Plot the counting rate of the control standard against the indicated voltage. The plateau should have a minimum length of 100 v and a maximum slope of 3 percent per 100 v (as much as 6 percent slope per 100 v can be tolerated if a well-stabilized high-voltage power

supply is used). An operating voltage approximately 75 v above the "knee" of the curve or at the midpoint of the plateau, whichever is lower, should be used.

The plateau and operating voltage of the instrument should be checked regularly (once each month is convenient and generally satisfactory) and after any repair or major adjustment of the instrument. Shortening of the plateau length or an increase in slope indicates a deteriorating detector. When the plateau becomes less than 100 v long or has a slope of more than 3 to 6 percent, depending on the power supply, the counter tube should be replaced.

OPTIMUM OPERATION OF SCINTILLATION AND PROPORTIONAL COUNTERS

Put the instrument into operation according to the manufacturer's instructions. Set the gain control and pulse-height discriminator approximately to the center of the range and the high-voltage control to the minimum. Place a suitable radioactive control standard in position and turn the count switch to the count position. Slowly increase the voltage until a counting rate of about 300 cpm (counts per minute) is obtained. Determine the counting rate of the standard at five or more settings of the gain control or pulse-height discriminator. (Generally, only one of these controls must be varied, though the other may need resetting so that the first will cover the proper range.) Also determine the background counting rate at each of the settings, using a blank planchet or sample holder of the type to be used when counting samples. Advance the voltage by a convenient small increment (20 to 25 v) and again count the control standard and background at several settings of the gain control or pulse-height discriminator. Continue until a voltage is reached where the ratios of standard-to-background counts are less than those for some previous voltage setting.

Plot the ratio of the net counting rate of the standard to the background counting rate against the gain or pulse height, using the voltage that gives the highest values of this ratio. The curve should first increase as the gain decreases (or pulse height increases), then reach an approximately constant value. The gain or pulse-height setting corresponding to a point near the knee of the curve, but definitely on the plateau, should be used as the operating point. The validity of this point should be checked by measuring the net counting rate to background counting rate for nuclides with radiation energies near the upper and lower limits of the radiation energies of the sample. (It is convenient if the control standard also can be used as the high-energy check.) If the operating point is not common to all plateaus, a new setting should be chosen such that the operating point is included in all.

The ratio of the net counting rate of the standard to the background counting rate should be checked daily. However, the plateaus need to be redetermined only if standard or background counting rates change appreciably or after any repair or major adjustment of the instrument.

BACKGROUND CONTROL CHART

Put the instrument in operation using the previously selected operating conditions. Make 10 determinations of the background counting rate, using a clean sample mount in the counting position and equal periods of time for each count. If possible, the counting period should allow at least 300 counts to be collected, but larger counts would be desirable. When using instruments with extremely low background (a few counts per hour), the above suggestion is not practicable, and approximately 8- to 16-hour periods should be used.

Calculate the average background counting rate, B, from these data, then calculate the standard deviation of B by each of the two equations

$$\sigma_B = \sqrt{\frac{B}{t}}$$

$$\sigma_B = \sqrt{\frac{1}{10} \sum (b_i - Bt)^2}$$

where

t = counting time

b_i = observed total counts during each counting period.

If the two standard deviations do not agree reasonably well, as determined by application of the F-test (see any standard text on statistics), instrument malfunction or some source of variable background should be suspected.

If there is agreement between the two standard deviations, a form similar to that shown in figure 6 should be prepared. Each day the background should be measured for a convenient time (about 100 minutes is desirable for low-level counters, but 30 minutes or less may be used if the background is relatively high), and the proper entries made on the form.

If the previous average background counting rate is included within the 95 percent confidence limit of that just determined, the measurement is accepted, and the new average background counting rate and standard deviation

$$\sigma_B = \sqrt{\frac{B}{t_c}}, \text{ where } t_c = \text{cumulative time}$$

BACKGROUND CONTROL CHART DATA

Counter No._____ Period_____

Count Started		Total Counts		Time (min)		Daily count rate (cpm)	95% C.L. (cpm)	Mean Bkg. rate (cpm)	Std. dev. of bkg.
Date	Time	Daily	Cumulative	Daily	Cumulat.				

Date series started_____ Series_____ Page_____

FIGURE 6.—Form for background control chart data.

are calculated from the cumulative counts and times. If the previous average background counting rate is not included within the 95 percent confidence limit, another background measurement should be made. Possible malfunction of the instrument or contamination may be indicated if the second measurement also excludes the average background counting rate. On the average, about 1 in 20 background measurements should be expected to fall outside the 95 percent

confidence limits. If this average is grossly exceeded, a variable background or instrument malfunctions should be suspected.

It is convenient to prepare a linear graph of counts per minute against time in days on which are plotted the average background counting rate, the daily background counting rate, and fiducial limits for the 95 percent confidence level. Such a graph is valuable for evaluating the long-term stability of the background counting rate, and often it can indicate the gradual buildup of contamination.

The reliability of the average background counting rate increases with each successive daily measurement, as indicated by the decrease in its standard deviation. The most recent value of the rate should be used in all calculations. The standard deviation continues to decrease, but after it has reached a value of about 0.5 percent of the average background counting rate, it should be considered constant. This is because some variations not considered in the calculation of the standard deviation may become significant at approximately this level.

STANDARD CONTROL CHART

After establishing the background control chart, place the control standard in counting position and take ten 10-minute measurements. Calculate the average net counting rate and the standard deviation for a 10-minute count by the equation:

$$\overline{S}=\frac{\Sigma S_i}{100}-B$$

$$\sigma_{S,}(t=10)=\sqrt{\frac{\overline{S}}{10}}$$

where

$\overline{S}$=average counting rate of standard
S_i=gross count of standard for each 10-minute period
$\sigma_{S,}(t=10)$=standard deviation of the counting rate when the standard is counted for 10 minutes
B=average background counting rate.

Prepare a linear graph of counts per minute against time in days. Plot at day one the average net counting rate and the points representing ± 2 and $\pm 2.5\sigma$ (standard deviations) from the average. Extend lines to the right from these points. Each daily measurement of the control standard, or average of three successive measurements, that falls within the 2σ limits indicates normal operation of the instrument. If two successive measurements fall outside the 2σ limits, or one measurement falls outside the 2.5σ limits, the operating criteria should be checked. If, when the instrument is operating under optimum

conditions, the standard counting rate still falls outside the acceptable limits, malfunctioning should be suspected.

The data of the standard control chart must be corrected for radioactive decay at a frequency dictated by the half-life of the radionuclide used for the standard. Generally, this should be done whenever the decay amounts to one-tenth of the standard deviation used on the chart.

The counting rate of the control standard must be checked daily, but the operating criteria for the instrument need be checked and a new control chart established only when the standard falls outside the prescribed limits.

DETERMINATION OF GROSS BETA ACTIVITY IN WATER

Many beta-emitting radionuclides exist in nature. Several members of the three natural radioactive series are beta emitters, and other beta emitters are scattered through the periodic table. Some of these radionuclides are short lived and are found only in close association with a longer lived radioactive parent; others, of intermediate life, can exist independently, but their activity decreases exponentially with time; still others are so long lived that no decay can be detected over long periods of time. The more common natural beta-emitting radionuclides are listed in table 2. Other radionuclides exist in extremely small amounts as the result of cosmic-ray bombardment, spontaneous fission of heavy elements, or minor branching of decay chains.

Several hundred beta-emitting radionuclides have been produced artificially. The most important of these are the fission products, most of which are beta emitters. Many other beta emitters, including the positron emitters, are produced by nuclear-bombardment reactions. Like the natural beta emitters, the artificial ones have half-lives ranging from a fraction of a second to thousands of years; none, however, have half-lives in the order of millions of years or more as do some of the natural beta emitters.

The beta activity now found in most ground-water sources can be attributed almost exclusively to the naturally occurring radionuclides, mainly potassium-40, and the radioactive daughters of uranium and thorium. Much of the beta activity in surface water can be attributed to natural radionuclides; in some sources, however, artificial nuclides, mainly fission products, contribute a significant fraction of the radioactivity. The amounts of artificial radionuclides found in water depend on many factors, such as the location of the sampling site with respect to a nuclear facility or detonation, wind and rainfall pattern, lapse of time between a nuclear detonation and collection of the sample, and related factors.

TABLE 2.—*Beta-emitting radionuclides commonly found in nature*

Radionuclide	Radioactive series	Half-life [1]	Parent [2]
Actinium-227	Actinouranium	22 yr	
Actinium-228	Thorium	6.1 hr	Ra^{228} (6.7 yr)
Bismuth-210	Uranium	5.0 days	Pb^{210} (22 yr)
Bismuth-212	Thorium	1.0 hr	Ra^{224} (3.6 days)
Bismuth-214	Uranium	20 months	Rn^{222} (3.8 days)
Carbon-14 [3]		5,600 yr	
Hydrogen-3 (tritium) [3]		12 yr	
Indium-115		6×10^{14} yr	
Lanthanum-138		$\approx2\times10^{11}$ yr	
Lead-210	Uranium	22 yr	
Lead-211	Actinouranium	36 min	Ra^{223} (11 days)
Lead-212	Thorium	11 hr	Ra^{224} (3.6 days)
Lead-214	Uranium	27 min	Rn^{222} (3.8 days)
Lutecium-176		4.6×10^{10} yr	
Potassium-40		1.2×10^{9} yr	
Protactinium-234	Uranium	1.2 min	Th^{234} (24 days)
Radium-228	Thorium	6.7 yr	
Rhenium-187		$\approx5\times10^{10}$ yr	
Rubidium-87		6.2×10^{10} yr	
Thallium-207	Actinouranium	4.8 min	Ra^{223} (11 days)
Thallium-208	Thorium	3.1 min	Ra^{224} (3.6 days)
Thorium-231	Actinouranium	26 hr	U^{235} (7×10^{8} yr)
Thorium-234	Uranium	24 days	U^{238}(4.5×10^{9} yr)

[1] Half-life values were taken from Friedlander and Kennedy (1955, p. 10–15). More precise values were rounded to two significant figures.
[2] Parents are listed only for those radionuclides whose concentration in water samples is apt to be controlled by the concentration of a parent. The most likely controlling radionuclide, with the half-life, is listed.
[3] Produced mainly by cosmic radiation.

PRINCIPLE OF DETERMINATION

The quantitative determination of beta activity depends on measuring the number of beta particles (electrons) emitted by the sample in a given interval of time. This may be accomplished by several of the methods discussed in the section "Measurement of radioactivity." The Geological Survey generally measures beta activity in water by counting ionization pulses in the Geiger region.

The instrument used for most low-level samples is an anticoincidence-shielded, flowing-gas, Geiger-Müller counter. This instrument consists essentially of two thin-window (¼-mil mylar aluminized on both sides) counters, 2 inches in diameter. These counters are separated by a 1 inch shield of mercury contained in an epoxy-resin bottle; this shield reduces unwanted "cross-talk" between the two counters. The counters themselves are hemispherical chambers of epoxy resin, coated internally with stainless steel. Centrally located loops of fine wire serve as the anodes, and the stainless steel coatings in electrical contact with the aluminized mylar windows serve as the cathodes.

A slide of epoxy resin, designed to hold various types of counting planchets, is located beneath each counter. The slides rest on adjustable stages, thus insuring that optimum geometry can be obtained for various types of planchets by adjusting the stage height. Two samples can be measured simultaneously in this instrument, one with each of the two counters.

The instrument has a background of approximately 1 cpm at sea level and 2 cpm at Denver, Colo., through a combination of anti-

coincidence circuitry, massive steel shielding, and plastic construction of the detectors. An umbrella of 11 parallel-connected Geiger-Müller tubes forms the detector package for the anticoincidence circuitry that reduces the component of background due to cosmic radiation. The massive shield, consisting of 8 inches of steel surrounding the central chambers and anticoincidence umbrella, serves to reduce the component of background due to terrestrial gamma radiation, soft cosmic rays, and other similar radiation.

When the activity of the sample is sufficiently large (>50 cpm), a low-background counter is not needed and the more conventional end-window Geiger-Müller counter is used. This counter, having a mica window of 1.2–1.4 mg per cm^2 (milligrams per square centimeter), is contained in a steel shield 2 inches thick. The background counting rate is approximately 20 cpm at sea level and 40 cpm at Denver, Colo.

The procedure used in determining the gross beta activity of a water sample is relatively simple as to mechanical manipulation. A volume of the sample, chosen according to the dissolved-solids content, is evaporated to dryness in a platinum or Teflon evaporating dish, and the residue is transferred quantitatively to a planchet by policing with distilled water. A silica residue sometimes remains in the evaporating dish after the bulk of the residue has been transferred to the planchet. This residue can be transferred by policing with distilled water after adding a few milliliters of concentrated hydrofluoric acid and evaporating to dryness. The sample then is weighed and is stored in a dessicator until it is counted.

APPARATUS

Aluminum or stainless steel planchets: Approximately 1⅞ inches in diameter and 1/16 inch deep with a ⅛ inch wide lip.

Forceps for handling planchets.

Counter: Low-background, flowing-gas, beta counter equipped with thin-window counting chamber, anticoincidence Geiger tube umbrella, and suitable shielding, or end-window (<2 mg per cm^2) Geiger-Müller counter mounted in suitable shield, equivalent to at least 2 inches of iron, together with electronic circuitry as needed for the counter chosen.

Dessicators for storing samples.

Platinum or Teflon evaporating dishes: 125-ml capacity.

Ultrasonic instrument for cleaning evaporating dishes.

REAGENTS

Hydrofluoric acid: Concentrated, reagent grade.

Calcium sulfate dihydrate: Reagent grade.

Magnesium chloride: Crystals, reagent grade.

Magnesium sulfate: Crystals, reagent grade.
Potassium chloride: Reagent grade.
Potassium nitrate: Crystals, reagent grade.
Sodium carbonate: Anhydrous, reagent grade.
Sodium sulfate: Anhydrous, reagent grade.
Strontium–90—yttrium–90: NBS Standard No. 4919, Approximately 10^4 dps per ml (disintegrations per second per milliliter).
Standard "diluting solution": Dissolve 30 mg $SrCl_2.6H_2O$ and 24 mg $YCl_3.H_2O$ in 1 liter of 1*N* HCl.

PROCEDURE

1. Determine the sample volume needed by measuring the specific conductance of the sample in micromhos per centimeter and multiplying by 0.6. The resulting value represents the approximate dissolved-solids content of the sample in milligrams per liter. Choose a volume of sample that will give about 100–120 mg of residue on evaporation; this yields a deposit on the planchet of about 10–12 mg per cm^2.

2. Filter the sample, if turbid, and withdraw an appropriate volume by pipetting or syphoning into volumetric flasks. Do not disturb any sediment present on the bottom of the bottle containing clear unfiltered samples.

3. Evaporate the sample to dryness on a steam bath using a 125-ml platinum or Teflon evaporating dish. Rinse the empty volumetric flask, if used, with distilled water and add rinse water to the evaporating dish before evaporation is completed.

4. Transfer the residue from the evaporating dish to a weighed aluminum planchet by policing the dish several times with 1 or 2 ml of distilled water. Evaporate each portion nearly to dryness under an infrared lamp or by other suitable heat source before transferring the next portion.

5. If, after policing the evaporating dish several times, silica still adheres to the sides, add 5 ml of hydrofluoric acid and rotate the dish until all of the inner surface has been exposed to the acid. Evaporate to dryness and transfer the residue to the planchet by policing with distilled water as before. Place the entire residue in a good position for counting by distributing it evenly over the bottom surface of the planchet and away from the sides by use of a small glass rod during evaporation. Residues from water high in potassium chloride or sodium carbonate exhibit a tendency to creep up the side of the planchet and to deposit on the rim, and, therefore, it may be difficult to distribute them evenly over the planchet.

6. Allow the planchet containing the dry residue to cool in a dessicator, then weigh and calculate the amount of solids to the nearest milligram. Store the planchet in a dessicator until it is to be counted.

7. Determine the background counting rate of the instrument as described in the section "Control of instrument operation" and, if necessary, standardize the instrument as described in the following section.

8. Place the planchet containing the sample in position and count for at least 200 minutes.

CALCULATION OF RESULTS

Report all results in picocuries per liter (pc per l; 1 pc=10^{-12} curies=2.22 dpm [disintegrations per minute]) to two significant figures, and report the 95 percent confidence limits for the measurement. The calculations are made as follows:

1. Determine the standard deviation of the net counting rate from the equation:

$$\sigma_N=\sqrt{\sigma_B^2+\frac{R}{t_R}}$$

where

σ_N=standard deviation of net counting rate
σ_B=standard deviation of background counting rate
R=gross counting rate in cpm
t=number of minutes sample was counted.

2. If the net counting rate exceeds the background counting rate by more than two standard deviations, that is,

$$R-2B>2\sigma_N$$

calculate the beta activity from the equation:

$$\text{Beta activity in pc per l}=\frac{1{,}000(R-B)}{EV}$$

where

B=background counting rate in cpm
V=sample volume in ml
E=efficiency of instrument in cpm per pc.

Also calculate the 95 percent confidence limits for the measurement from the equation:

$$\text{95 percent confidence limits}=\pm\frac{2{,}000\sqrt{(R-B)^2\sigma_E^2+\sigma_N^2}}{EV}$$

where

σ_E=standard deviation of the counting efficiency estimated from the calibration data.

3. If the net counting rate does not exceed the background counting rate by more than two standard deviations, that is,

$$R-2B \leq 2\sigma_N$$

report the result as less than the minimum detection limit (MDL). The MDL is calculated from the equation

$$\text{MDL}=\frac{2{,}000\sigma_N}{EV}$$

NOTE: If the standard deviation of the background is small and relatively constant, and if all samples are counted for the same length of time, a graph showing the values of σ_N for various values of R is a convenient aid to the calculations.

CALIBRATION OF BETA COUNTERS

Although several beta standards are available (see p. A13), the Geological Survey generally uses a standard solution of strontium-90 and yttrium-90 obtained from the National Bureau of Standards, Washington, D.C., for calibrating instruments used for measuring beta activity in water. This standard consists of about 3 ml of solution having a specific activity of approximately 10,000 dps per ml of the equilibrium mixture of strontium-90 and yttrium-90. The most desirable activity for calibrating the instrument is about 300 cpm; therefore, the standard should be diluted for use in the procedure. A stock solution that is convenient for use in preparing standards for both this and the radiostrontium procedures is obtained by diluting the NBS standard 1 to 250. The original acid concentration (1*N* HCl) should be maintained and small amounts of stable strontium and yttrium carriers (approximately 10 mg of each per liter) should be added to stock solutions and to any others that are not to be used immediately.

When determining gross beta activity in water, the entire residue from the water sample is counted and, therefore, the chemical composition varies considerably. However, it is neither practical nor necessary to make standards that duplicate all possible combinations when calibrating instruments for such a determination. Although the self-absorption and the self-scattering of beta particles vary somewhat with the atomic number of the sample material, the majority of the atoms in the residue fall within a relatively small range of atomic numbers; thus, the sum of the self-absorption and self-scattering factors does not vary greatly from one water sample to another. The error introduced by using a calibration curve based on the "average composition" of the residues is much smaller than other errors encountered and may be neglected for most work.

The dissolved mineral matter in most natural water consists almost entirely of only seven ions—calcium, magnesium, sodium, potassium, bicarbonate, chloride, and sulfate; thus, the selection of salts to represent the dissolved solids in natural water is a relatively simple matter. Potassium salts can be used, but a correction must be made for their natural radioactivity. Chlorides have a tendency to creep, and this makes them somewhat troublesome to use. The other major ions found in natural water also creep, but to a lesser degree than chlorides; this presents no particular problem in using them to represent the natural solids because the latter also exhibit the tendency to creep. Several combinations of the above ions should be chosen so that the calibration includes the effects of common error-causing factors, such as the activity at the bottom or top of the residue. The calibration then will reflect some of the effects of these variables on the precision of the determination.

PREPARATION OF THE STANDARD

Open the ampoule containing the standard by carefully breaking off the neck after making a scratch with a file at the position of the break. The portion of the neck above the scratch is easily broken off by tapping it gently with a small piece of wood.

After the neck of the ampoule has been removed, pipet 2 ml of the solution into a 500 ml volumetric flask and make up to volume using a "diluting solution" containing the acid and the stable strontium and yttrium carriers. The specific activity of this stock solution is about 40 dps per ml. (The remaining strontium-90–yttrium-90 solution may be washed out of the ampoule into a small bottle using about 50 to 100 ml of diluting solution. This solution, whose concentration is unknown, may be useful for experiments where only relative activity, not absolute activity, is important.)

NOTE: When diluting the standard, rubber surgeon's gloves and an apron or smock should be worn, and all pipetting should be done with pipet aids such as suction bulbs. All solutions containing strontium-90 should be marked as such and labeled RADIOACTIVE. Solutions should be stored in a secure place where there is no likelihood of spillage.

Prepare a working solution, which will have a specific activity of approximately 500 dpm per ml, by diluting 10 ml of the stock solution to 50 ml. Calculate the specific activity of the working solution after correcting the standard for radioactive decay as described in the following section.

CORRECTION OF STANDARD FOR RADIOACTIVE DECAY

The half-life of strontium-90 is approximately 25 years, so that radioactive decay amounts to almost 3 percent in one year. There-

fore, the activity must be corrected for decay if more than a month has elapsed since standardization or the last correction. The specific activity of the standard solution is stated on the certificate as of a specified time, and correction of the activity to any other time is accomplished by the equation:

$$A=A_0e^{-\lambda t}=A_0 \exp\left\{\frac{-0.693t}{t_{\frac{1}{2}}}\right\}=A_0e^{-0.00227t}$$

where

A=activity at time t

A_0=initial activity

$\lambda=0.693/t_{\frac{1}{2}}$=decay constant

t=time elapsed since calibration date on certificate in years

$t_{\frac{1}{2}}$=half-life of Sr^{90}, approximately 25 years.

PROCEDURE FOR CALIBRATION

1. Clean and weigh 22 aluminum planchets.

2. Make up 250 ml of four salt solutions as follows: (a) 1 percent sodium carbonate, (b) 0.3 percent sodium sulfate, (c) 0.15 percent potassium chloride–0.15 percent magnesium sulfate–0.20 percent sodium carbonate, and (d) 0.2 percent magnesium chloride–0.3 percent potassium nitrate–0.2 percent calcium sulfate.

3. Select five volumes of each solution so that residues will fall in the range 10 to 160 mg, without overlap but concentrating in the region 80 to 120 mg. The following table indicates a suitable choice of approximate weights.

Solution 1:	10, 50, 85, 105, and 130 mg
Solution 2:	20, 60, 90, 110, and 140 mg
Solution 3:	30, 70, 95, 115, and 150 mg
Solution 4:	40, 80, 100, 120, and 160 mg

Transfer these volumes to platinum or Teflon evaporating dishes and add to each dish 2 ml of the strontium-90–yttrium-90 working solution so that the activity is about 1,000 dpm.

4. Evaporate these solutions to dryness and transfer the residues to preweighed planchets as described in the procedure for routine determination of beta activity.

5. Prepare two nearly weightless residues by evaporating the selected volume of strontium-90–yttrium-90 solution directly in the planchets.

6. Weigh the planchets with the residues and calculate the weight of solids on each planchet.

7. Measure the activity on the planchets by counting. The minimum total count of each planchet should be 10,000 so that the standard deviation of the counting will be no more than 1 percent.

After one-fourth of the allotted counting time has elapsed, rotate the planchet 90° and continue the counting. Repeat until all four quadrants have been counted.

8. Determine the counting rate of both the control standard and background by the methods described in "Control of instrument operation."

9. Calculate the counting efficiency of the instrument, in cpm per pc, by dividing the measured net count rate (counting rate of the standard minus background counting rate) of each planchet by the activity, in pc, of the standard plus any potassium (1 pc=2.22 dpm) in the planchet. The activity of the potassium-40 in the residue is taken as 0.79 pc per mg of natural potassium. This value is calculated from the average of values cited by Rankama (1954, p. 304) for the specific beta activity of potassium.

10. Plot the counting efficiencies against the weights of solids. From this plot, estimate and draw the best-fit calibration curve, and estimate the standard deviation of the calibration. This calibration curve is valid only so long as the standard control chart ("Control of instrument operation") does not change. If the control chart changes or if the detector assembly is modified in any way, this calibration should be checked or, if necessary, repeated completely.

ERRORS AND PRECISION

Determination of the beta activity in a water sample is subject to all of the counting errors arising from the statistical nature of radioactive decay (see the section "Statistical considerations"). However, additional errors are peculiar to this method. Although the counters used are about 100 percent efficient for those beta particles penetrating the window, only a fraction of the beta particles emitted by the sample penetrate the window. The size of this fraction depends largely on the geometry of the counting setup; it also depends partly on absorption in the window of the counter, in the air between the sample and the counter, in the sample itself, and partly on scattering from the sample and the sample mount. These factors vary with the energy of the beta praticles; thus, each radionuclide is counted with a different efficiency. Counting data can be transformed exactly into units of radioactivity only when the radionuclides present are known, and even then only with difficulty if the mixture is complex. It is, therefore, common practice to choose one reference radionuclide and to report all gross beta activity in terms of this reference when it is prepared and counted in the same manner as the samples. Thus, any difference in energy spectrum between the sample and the standard will result in a difference between the "true" and the reported activity levels.

This is not serious, however, if the meaning of the reported value (that is, the reference to a particular standard) is understood.

Both the samples and the standards must be prepared in a similar manner. If a sample is allowed to creep up the side of the planchet, the geometry will be changed and the result will be in error. If stratification of the residue occurs, the radioactivity may concentrate either in a lower level where the effects of self-absorption would be increased, or in an upper level where the effects would be decreased. Also, the geometry would be changed in a manner such that the errors would be additive. These errors can be minimized by careful preparation of the planchets; especially by mixing the residue thoroughly and centering it in the planchet during the final evaporation.

The position of the counting planchet with respect to the window of the counter is important; any variation has a marked effect upon the geometry. Both samples and standards must be placed in exactly the same positions for counting. If a counter is replaced, if the sample holders are adjusted, or if any other change is made in the positions of either the counter or sample holders, the instrument must be restandardized.

With reasonable care, the planchets can be reproduced with a standard deviation of about 10 percent. Irregularities in the distribution of activity throughout the residue and unevenness in the deposit of material on the planchet are major contributors to the variations. At the low levels usually encountered in the work of the Geological Survey, this factor generally is smaller than statistical errors when using Geiger-Müller counters, but it must sometimes be considered when using low-background counters.

Contamination of the hydrofluoric acid could cause erroneous results when it is used in the determination; therefore, as a precautionary measure, each new bottle of the reagent should be tested before use.

The accuracy of this determination is limited in part by the sensitivity of the counters for gamma radiation. This sensitivity varies with the energy of the gamma radiation, construction of the counter, and the physical nature of the counting assembly, but it is usually less than 5 percent. The beta-activity results will be too high by a percentage equal to the product of the gamma sensitivity and the gamma-to-beta ratio of the sample. The loss of volatile substances during the evaporation or large deviations from uniform distribution of the radioactivity within the residue also will decrease the accuracy of the determination.

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