Measurement of Low-Level Radioactivity

Measurement of

Low-Level

Radioactivity

Preface

Scope of ICRU Activities

The International Commission on Radiation Units and Measurements (ICRU), since its inception in 1925, has had as its principal objective the development of internationally acceptable recommendations regarding:

(1) Quantities and units of radiation and radioactivity,

(2) Procedures suitable for the measurement and application of these quantities in clinical radiology and radiobiology,

(3) Physical data needed in the application of these procedures, the use of which tends to assure uniformity in reporting.

The Commission also considers and makes similar types of recommendations for the radiation protection field. In this connection, its work is carried out in close cooperation with the International Commission on Radiological Protection (ICRP).

Policy

The ICRU endeavors to collect and evaluate the latest data and information pertinent to the problems of radiation measurement and dosimetry and to recommend the most acceptable values and techniques for current use.

The Commission's recommendations are kept under continual review in order to keep abreast of the rapidly expanding uses of radiation.

The ICRU feels it is the responsibility of national organizations to introduce their own detailed technical procedures for the development and maintenance of standards. However, it urges that all countries adhere as closely as possible to the internationally recommended basic concepts of radiation quantities and units.

The Commission feels its responsibility lies in developing a system of quantities and units having the widest possible range of applicability. Situations may arise from time to time when an expedient solution of a current problem may seem advisable. Generally speaking, however, the Commission feels that action based on expediency is inadvisable from a long-term viewpoint; it endeavors to base its decisions on the long-range advantages to be expected.

The ICRU invites and welcomes constructive comments and suggestions regarding its recommendations and reports. These may be transmitted to the Chairman.

Current Program

The Commission has divided its field of interest into eleven technical areas and has assigned one or more members of the Commission to serve as sponsor for each area. A body of consultants has been constituted for each technical area to advise the Commission on the need for ICRU recommendations relating to the technical area and on the means for meeting an identified need. Each area is reviewed periodically by its sponsors and consultants. Recommendations of such groups for new reports are then reviewed by the Commission and a priority assigned. The Technical areas are:

Radiation Therapy
Radiation Diagnosis
Nuclear Medicine
Radiobiology
Radioactivity
Radiation Physics—X Rays, Gamma Rays and Electrons
Radiation Physics—Neutrons and Heavy Particles
Radiation Protection
Values of Factors—W, S, etc.
Theoretical Aspects
Quantities and Units

The actual preparation of ICRU reports is carried out by ICRU report committees working in each of these technical areas. The currently active report committees in the various technical areas are as follows:

Radiation Therapy	Methods of Arriving at the Absorbed Dose at any Point in the Patient (In Vivo Dosimetry)
	Methods of Compensating for Body Shape and Inhomogeneity and of Beam Modification for Special Purposes (Beam Modification)
	Dose Specification for Reporting
Radiation Diagnosis	Modulation Transfer Function, Its Definition and Measurement
Nuclear Medicine	Scanning of Internally Deposited Radionuclides
	Methods of Assessment of Dose in Tracer Investigations
Radiation Physics— Neutrons and Heavy Particles	High Energy and Space Radiation Dosimetry

iii

In 1962, the Commission decided to abandon its past practice of holding a meeting together with all its sub-units every three years. Instead, it was decided that the Commission would receive reports from the sub-groups at the time of their completion rather than at fixed deadlines. Meetings of the Commission and of the subgroups are held as needed.

ICRU Reports

In 1962 the ICRU, in recognition of the fact that its triennial reports were becoming too extensive and in some cases too specialized to justify single-volume pub-lication, initiated the publication of a series of reports, each dealing with a limited range of topics. This series was initiated with the publication of six reports.

ICRU Report 10a, *Radiation Quantities and Units*
ICRU Report 10b, *Physical Aspects of Irradiation*
ICRU Report 10c, *Radioactivity*
ICRU Report 10d, *Clinical Dosimetry*
ICRU Report 10e, *Radiobiological Dosimetry*
ICRU Report 10f, *Methods of Evaluating Radiological Equip-ment and Materials*

These reports were published, as had been many of the previous reports of the Commission, by the United States Government Printing Office as Handbooks of the National Bureau of Standards.

In 1967 the Commission determined that in the future the recommendations formulated by the ICRU would be published by the Commission itself. This report is published by the ICRU pursuant to this policy. With the exception of ICRU Report 10a, the other reports of the "10" series have continuing validity and, since none of the reports now in preparation is designed specifically to supersede them, they will remain available until the material is essentially obsolete. All future reports of the Commission, however, will be published under the ICRU's own auspices. Information about the avail-ability of ICRU Reports is given on page 60.

ICRU's Relationships With Other Organizations

The ICRU has developed relationships with other or-ganizations interested in the problems of radiation quantities, units, and measurements. In addition to its close relationship with the International Commission on Radiological Protection and its financial relation-ships with the International Society of Radiology, the World Health Organization, and the International Atomic Energy Agency, the ICRU has also developed relationships of varying intensity with several other organizations. Since 1955, the ICRU has had an official relationship with the World Health Organization (WHO) whereby the ICRU is looked to for primary guidance in matters of radiation units and measure-ments, and in turn, the WHO assists in the worldwide dissemination of the Commission's recommendations. In 1960 the ICRU entered into consultative status with the International Atomic Energy Agency. The Com-mission has a formal relationship with the United Na-tions Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), whereby ICRU observers are invited to attend UNSCEAR meetings. The Commis-sion and the International Organization for Standardi-zation (ISO) informally exchange notifications of meet-ings and the ICRU is formally designated for liaison with two of the ISO Technical Committees. The ICRU also corresponds and exchanges final reports with the following organizations:

Bureau International des Poids et Mesures
Council for International Organizations of Medical Sciences
Food and Agriculture Organization
International Council of Scientific Unions
International Electrotechnical Commission
International Labor Office
International Union of Pure and Applied Physics
United Nations Educational, Scientific and Cultural Organi-zation

The Commission has found its relationship with all of these organizations fruitful and of substantial bene-fit to the ICRU program. Relations with these other international bodies do not affect the basic affiliation of the ICRU with the International Society of Radi-ology.

Operating Funds

In the early days of its existence, the ICRU operated essentially on a voluntary basis, with the travel and operating costs being borne by the parent organizations of the participants. (Only token assistance was origi-nally available from the International Society of Radiology.) Recognizing the impracticability of con-tinuing this mode of operation on an indefinite basis, operating funds were sought from various sources.

Prior to 1959, the principal financial assistance to the ICRU had been provided by the Rockefeller Foun-dation which supplied some $11,000 to make possible various meetings. In 1959 the International Society of Radiology increased its contribution to the Com-mission, providing $3,000 for the period 1959-1962. For the period 1962-1965 the Society contributed $5,000. For each of the periods 1965-1969 and 1969-1973 the Society's contribution was $7,500. In 1960 the Rockefeller Foundation supplied an additional sum of some $4,000 making possible a meeting of the Quan-tities and Units Committee in 1960. The Council for International Organizations of Medical Sciences con-tributed $500 in 1960.

In 1960 and 1961 the World Health Organization made available the sum of $3,000 each year. This was increased to $4,000 per year in 1962, $6,000 in 1969, and $8,000 in 1970.

In connection with the Commission's Joint Studies with the ICRP, the United Nations allocated the sum of $10,000 for the joint use of the two Commissions.

The most substantial contribution to the work of the ICRU has come from the Ford Foundation. In December 1960, the Foundation made available to the Commission the sum of $37,000 per year for a period of five years. This grant was to provide for such items as travel expenses to meetings, secretarial services and other operating expenses. In 1965 the Foundation agreed to a time extension of this grant making available for the period 1966-1970 the unused portion of the original grant. To a large extent, it is because of this grant that the Commission has been able to move forward actively with its program.

In 1963 the International Atomic Energy Agency allocated the sum of $6,000 per year for use by the ICRU. This was increased to $9,000 per year in 1967.

In 1970 and again in 1971 the Statens laegevidenskabelige Forskningsråd of Denmark contributed $1,000 in support of the Commission's work.

The Radiological Society of North America contributed $5,000 in support of the Commission's work in 1971. The Commission received a grant of $1,900 from the John och Augusta Persson stiftelse of Sweden in 1971. As a result of the efforts of Prof. Flemming Norgaard, Honorary Secretary-Treasurer Emeritus of the International Society of Radiology (ISR), the Commission, in 1971, received over $500 in contributions from individual members of the ISR. In 1971 also, the Japan Association of Radiation Apparatus approved a grant to the ICRU of $1,200 per year for a period of three years.

In 1971 the BAT Cigaretten-Fabriken GMBH contributed $4,425 towards support of the Commission's activities. Also in 1971 the U.S. Bureau of Radiological Health of the Food and Drug Administration approved a grant of $25,000 per year for two years.

From 1934 through 1964 valuable indirect contributions were made by the U. S. National Bureau of Standards where the Secretariat resided. The Bureau provided substantial secretarial services, publication services and travel costs in the amount of several thousands of dollars.

The Commission wishes to express its deep appreciation to all of the organizations and individuals that have contributed so importantly to its work.

Composition of the ICRU

It is of interest to note that the membership of the Commission and its subgroups totals 91 persons drawn from 14 countries. This gives some indication of the extent to which the ICRU has achieved international breadth of membership within its basic selection requirement of high technical competence of individual participants.

The current membership of the Commission is as follows:

H. O. WYCKOFF, *Chairman*
A. ALLISY, *Vice Chairman*

K. LIDÉN, *Secretary*
F. P. COWAN
F. GAUWERKY
J. R. GREENING
A. M. KELLERER
R. H. MORGAN
H. H. ROSSI
W. K. SINCLAIR
F. W. SPIERS
A. TSUYA
A. WAMBERSIE

Composition of ICRU Subgroups Responsible for the Drafting of this Report

Initial work on this report was carried out by the Task Group on Measurement of Low-Level Radioactivity. Serving on the Task Group were:

R. A. DUDLEY, *Chairman*
L. A. CURRIE
C. R. HILL
J. RUNDO

R. P. PARKER served as a consultant to the Task Group.

The Task Group worked under the aegis of the Planning Board on Radioactivity—Fundamental Physical Parameters and Measurement Techniques. Serving on the Planning Board were:

F. W. SPIERS, *Chairman*
H. HOUTERMANS
W. B. MANN
J. K. MIETTINEN

K. LIDÉN and F. W. SPIERS served as Commission Sponsors for the Planning Board.

The Commission wishes to express its appreciation to the individuals involved in the preparation of this report for the time and effort they devoted to this task.

HAROLD O. WYCKOFF
Chairman, ICRU

Washington, D.C.
December 15, 1971

Contents

Measurement of Low-Level Radioactivity

1. Introduction

1.1 Scope of Report

The measurement of low-level radioactivity involves assay procedures of high sensitivity in a wide variety of circumstances. This report includes descriptions and discussions of many methods of measurement and assessments of their capabilities. In general, it has not been possible to give simple, explicit recommendations for all circumstances, but throughout the report guidelines have been given to assist the reader in choosing those procedures best suited to particular problems. A previous report by the ICRU (1963) has already treated a part of this field, including activity standardization, low-level radioactive contamination of materials, and general measurement techniques for samples and living subjects.

While a numerical definition of "low-level radioactivity" cannot usefully be given for an unspecified context, it may be said in general that this report is concerned with procedures that are particularly relevant when achievement of the desired precision of counting is difficult in the counting time available. Problems of this character may arise when the total available activity is low, or when concentration of the radionuclide is low, or when counts of extraneous origin are excessive. Generally, the concentrations of activity will lie in the range below 10^{-9} Ci/g, but this statement is not intended to be rigid or exclusive. That this subject merits special attention is attested to by the divergent results found in the IAEA's interlaboratory comparison on low-activity samples (Merten and Wortley, 1967).

Many of the principles and techniques that underlie the reliable measurement of low-level radioactivity are equally important in measurements of higher-level radioactivity. For example, the instrumentation is similar, there is the same need for meaningful selection of the sample, and in both cases reproducibility in source preparation is essential. The present report deals only briefly with these generally relevant principles and techniques. Instead, it focuses attention on problems of special importance in the assay of low-activity samples, especially those encountered in the field of environmental monitoring and in some aspects of medical and biological work. Consideration of the measurement of radioactivity in the living subject, however, is not included in the present report.

The report is divided into an introductory chapter and five major substantive chapters. Each of the latter is largely self contained, but the reader is advised before consulting a particular section in detail to take note of the relevant general principles in the introduction.

References to the literature have been selected primarily on the basis of their didactic merit. No attempt has been made to include a comprehensive bibliography, nor to give weight to priority of discovery. Coverage of the literature after mid-1968 is sporadic.

1.2 Extraneous Counts

A prominent complication in low-level counting is usually the occurrence of extraneous counts, which may be defined as counts having any origin other than the radioactive atoms of interest. Two origins of extraneous counts may be distinguished: (1) various agents producing background counts, and (2) interfering radioactivity in the sources.

By background counts are usually understood those counts that can in principle be observed, and thereby allowed for, by measuring a "dummy source" that is identical to the unknown source in all respects except for complete absence of radioactivity. These counts are attributable to environmental radioactivity, radioactivity in the detector itself, cosmic rays, electronic "noise" pulses, etc. The accuracy with which corrections for background can be determined depends greatly upon its stability. At best, fluctuations attributable only to counting statistics will occur; in practice, additional variability may also be present. Background is discussed in detail in Chapters 3, 4, and 5.

Interfering radioactivity may have various forms and effects. First, it may be found in the unknown or in the standard source. In the unknown it may be a contaminant originally present in the sample, or a

contaminant added during sample processing. A precaution commonly taken against errors caused by such contamination is to carry through an analysis on a "blank sample" (see Section 2.1) exactly as on the unknown sample of interest, and to subtract the apparent activity of the blank sample from that measured on the unknown sample. Alternatively, two or more radionuclides in the unknown source may in turn be of interest, and each may interfere with the measurement of the other. In the standard source the same problems with interfering radioactivity may be present, although their severity is usually less.

A second aspect of the interfering radioactivity is its radionuclidic composition. If the interfering nuclide in the unknown source is the same as the radioactive atoms of interest, it cannot be distinguished from these atoms by either chemical or physical techniques. If it is a different isotope of the same element, it cannot be distinguished by ordinary chemical procedures although it may be distinguishable by physical techniques. If it is a different element, it can always be distinguished by chemical separation, and it may be distinguishable also by physical methods.

Most common among the physical procedures for distinguishing between different radionuclides is selection according to half life, which is possible with any type of radiation and detector, or selection according to type and energy of radiation. In this latter case, effectiveness depends greatly on the type of radiation and the properties of the detector. Gamma rays from different radionuclides can often be distinguished by spectrometry with scintillation or semiconductor detectors. Similarly, α particles can often be distinguished according to their energy by gas-ionization, scintillation, or semiconductor detectors. Internal-conversion electrons have discrete energies that, in special circumstances, permit effective spectrometric analysis. Beta particles, on the other hand, have continuous energy spectra that allow only limited discrimination among different radionuclides. For certain decay schemes, coincidence techniques may provide additional selectivity.

Even when half-life selection, spectrometry, or additional instrumental techniques are used, it often happens that interference among radionuclides is only reduced, not eliminated. In these circumstances, an interfering radionuclide in a source contributes a number of counts that must be independently estimated and then subtracted, just like background counts, in order to obtain the net counts attributable to the radioactive atoms of interest. The accuracy with which corrections can be made for extraneous counts caused by interfering radioactivity depends on many conditions, especially the degree of separation possible by the chosen chemical or physical techniques and the

reproducibility of this separation. Even under the best conditions, statistical fluctuations of counts from the interfering component will introduce errors in a manner similar to the statistical errors contributed by background.

Reduction of interference by chemical and/or physical separation procedures is discussed in Chapter 2, and by instrumental techniques in Chapters 3, 4, and 5.

1.3 Considerations of Counting Statistics

The interest of this report in counting statistics is restricted to the comparative statistical merits of alternative measurement methods. Even in this very limited area, many questions can be raised that have no general answers. For example, if a measurement is required to yield several independent results, such as a spectrometric analysis of the activity of each of five γ-ray emitting radionuclides in a single sample, the concept of "a best measurement" is ambiguous and the choice among the analytical methods will be correspondingly ambiguous. Beyond this, digital computers are being increasingly used to reduce complicated data (e.g., γ-ray, spectra recorded on multichannel analyzers from mixtures of radionuclides) by sophisticated mathematical techniques such as weighted least-squares fitting procedures (Section 3.7.2). These techniques often have a high statistical efficiency, meaning that they extract nearly the maximum amount of information from the large amount of available data. They are therefore to be recommended in the analysis of results from specific measurements, especially if the results are complicated. However, they are not designed to give general comparisons between methods. Furthermore, they are not needed for the simple results yielded by many commonly used analytical methods.

Several simple concepts have long been used for comparing the statistical merits of alternative measurement procedures of the more elementary sort (Loevinger and Berman, 1951; NCRP, 1961; ICRU, 1963). As they may give useful insight into many problems in the assay of low-level activity, they are briefly described here. Underlying them all is the assumption that all counting rates are stable, i.e., that the only fluctuations occurring are those of counting statistics. In practice, other sources of instability may also be present, as is made evident if the results of replicate measurements show greater scatter than that attributable to counting statistics alone.

One of the most commonly used of these simple concepts is the *minimum combined time*, T, that must be spent counting the source in question and the background in order to attain a specified precision in the

net source counting rate. A second useful concept is the *background-equivalent activity* of a radionuclide, i.e., that activity which produces a reading of the instrument in question equal to its background reading. This concept, while easily comprehended, is not alone sufficient to identify the method which gives the highest counting precision. A third concept that has been used is the *minimum detectable activity*, i.e., that activity of a radionuclide which, in a given counting time, increases the reading of the instrument by an amount equal to three times the standard deviation of the background recorded in that time. Like the "background-equivalent activity," this concept does not uniquely identify the statistically most precise alternative among several measurement procedures for the source in question. Furthermore, its name is somewhat arbitrary, since the issue of the limit of detection is inherently a complicated one. This issue has been treated in the present context by Currie (1968).

In this report a *figure of merit* defined as $1/T$ is suggested for the comparison of different measurement methods. It is useful to examine this figure of merit in three representative measurement situations. In the first, the unknown source and its matched dummy source are assumed to be free of interfering radioactivity. The following terms are defined:

S = counting rate due to radioactive atoms of interest in unknown source

B = counting rate on dummy source

T_{s+B} = counting time on unknown source

T_B = counting time on dummy source

$\epsilon = \sigma_S/S$ = fractional standard deviation in S caused by statistical fluctuations of counting

It can be shown that the quantity $T_{s+B} + T_B$ takes on a minimum value for any specified counting precision when

$$\frac{T_{s+B}}{T_B} = \sqrt{\frac{S+B}{B}} \qquad (1.1)$$

Then the minimum combined time T is equal to $T_{s+B} + T_B$ and the figure of merit $1/T$ is given by

$$1/T = \epsilon^2 \times \frac{S^2}{(\sqrt{S+B} + \sqrt{B})^2} \qquad (1.2)$$

(see ICRU, 1963, p. 26)

Among the available alternative measurement systems, the most favored statistically is that which gives the maximum figure of merit for the source in question. Equation 1.2 reduces to simpler forms in special cases:

if $S \gg B$, $1/T \approx \epsilon^2 S$

if $S \ll B$, $1/T \approx \epsilon^2 S^2/(4B)$.

Therefore, in the two cases one simply seeks to maximize S or S^2/B, respectively, to achieve the maximum figure of merit.

As the second measurement situation, consider an unknown source for which a matched source has been prepared from an appropriate blank sample, with a counting rate I from interfering radioactivity included in the measurements on both sources. Then it can be shown that the analysis proceeds exactly as in the first situation if B is replaced throughout by $B + I$. Hence the measurement times should be distributed according to the relationship

$$\frac{T_{s+(B+I)}}{T_{(B+I)}} = \sqrt{\frac{S+(B+I)}{(B+I)}} \qquad (1.3)$$

and

$$\frac{1}{T} = \epsilon^2 \frac{S^2}{[\sqrt{S+(B+I)} + \sqrt{(B+I)}]^2} \qquad (1.4)$$

The third measurement situation is commonly met in spectrometry. For clarity, a specific example may be described: the assay of ^{85}Sr in a source also containing ^{47}Ca as interference, using a NaI(Tl) crystal and two single-channel pulse-height analyzers. Three measurements may be performed. (1) A pure ^{47}Ca source, having sufficiently high activity that statistical errors of counting are negligible, is measured. Counts are recorded in the two energy bands 0.48–0.54 MeV (where the ^{85}Sr peak in the unknown source will be located) and 1.25–1.35 MeV (where the main ^{47}Ca peak is located). The ratio r of the counting rate in the first band to that in the second band is calculated. In this and in many other cases where the energy bands are favorably selected, r ≪ 1. (2) A background measurement is made on a dummy source, yielding counting rates B in the energy band 0.48–0.54 MeV and B_1 in the energy band 1.25–1.35 MeV. (3) The unknown source is measured, yielding a counting rate $S + B + I$ in the energy band 0.48–0.54 MeV, and $(I/r) + B_1$ in the energy band 1.25–1.35 MeV. In conformity with previous notation, S is the ^{85}Sr counting rate sought and I is the counting rate in the same energy band from ^{47}Ca interference. It can be shown that the combined measurement time for step 2 (i.e., $T_{s+(B+I)}$) and for step 3 (i.e., T_B) takes on its minimum value T for a specified counting precision if

$$\frac{T_{s+(B+I)}}{T_B} = \sqrt{\frac{S+(B+I)+r^2(B_1+I_1)}{B+r^2B_1}} \qquad (1.5)$$

Finally, under this condition

$$1/T = \epsilon^2 \frac{S^2}{[\sqrt{S+(1+r)I+(B+r^2B_1)} + \sqrt{(B+r^2B_1)}]^2} \qquad (1.6)$$

If, as is often the case, $r \ll 1$, these expressions reduce to:

$$\frac{T_{S+(B+I)}}{T_B} \approx \sqrt{\frac{S+(B+I)}{B}} \qquad (1.5a)$$

and

$$1/T \approx \epsilon^2 \frac{S^2}{[\sqrt{S+(B+I)}+\sqrt{B}]^2} \qquad (1.6a)$$

Furthermore, if $I \ll B$ (negligible interfering radioactivity), equation 1.6a becomes equation 1.2. If $B \ll I$, equation 1.6a becomes

$$1/T \approx \epsilon^2 \frac{S^2}{S+I},$$

and $1/T$ approaches $\epsilon^2 S$ or $\epsilon^2 S^2/I$ depending on whether $S \gg I$ or $S \ll I$.

From these three examples, a simple statistical generalization can be drawn concerning many problems of the kind considered in this report. If the extraneous counting rate $X \equiv B + I$, then the figure of merit $1/T$ is nearly maximized by counting conditions that maximize S if $S \gg X$, or that maximize S^2/X if $S \ll X$.

It should be pointed out that the figure of merit is not dimensionless, and therefore numerical values are meaningless unless units are given. Quite often, however, no units are stated and the expression S^2/B is given a numerical value after setting S equal to (counts/disintegration) $\times$ 100, and expressing B in c/min. This practice should be discouraged.

1.4 Analytical Procedures

In a specific assay problem analytical procedures are, in principle, so chosen as to maximize S or S^2/X, as the case may be, while avoiding non-statistical errors leading to irreproducibilities in S and X. Consideration must be given to: (1) the possible benefits of alternative methods of treating the sample and preparing the source, (2) the type of radiation to be detected, and (3) methods for optimizing counting conditions. These issues are intertwined, so that the most effective assay procedure can be selected only after examining all of them.

Sample treatment refers to processes whereby the radionuclide of interest is segregated, in whole or in part, from the matrix of the sample and from other radionuclides also found in the sample. Source preparation, which cannot be uniquely distinguished from sample treatment, refers more particularly to conversion of the radionuclide of interest to a chemical and physical form appropriate to the particular detector used for its measurement. Sample treatment has two main purposes. First, the sample counting rate S may be increased through reduction of self-absorption of the radiation in the sample. Second, interfering radioactivity may be removed, with a resultant increase in S^2/I by possibly many orders of magnitude. In Chapter 2 the treatment of low-activity samples is discussed in detail, with illustrations and references to compendia of specific procedures. In Chapters 3, 4, and 5 certain problems of source preparation are examined for particular detectors and radionuclides.

For many radionuclides a choice is available between γ rays and β particles as the radiation to be detected. For a few radionuclides, or a few equilibrated decay chains, other options among α, β, and γ rays may exist. The mass of sample from which the radiation can reach the detector is closely linked with the range of the radiation in matter. The ranges of α, β, and γ rays, respectively, typically increase in steps of greater than one order of magnitude from (in matter of density 1 g/cm³) less than 0.1 mm to a few mm to many cm. On the other hand, for this reason, as well as for others, the backgrounds of the corresponding detectors also typically increase in steps of about an order of magnitude. If a sample mass of many grams is available and concentration of the contained radionuclide of interest is impossible or for some reason undesirable, assay of the sample by means of the emitted γ rays (if any) may allow the lowest concentrations of radioactivity to be measured. Thus the greater S which is provided by γ rays may more than outweigh the greater B of the detector in establishing favorable statistical conditions (e.g., high S^2/B). If, on the other hand, the sample mass is initially small, or if the radionuclide can be concentrated into a small source for measurement, S may depend little on the ability of the radiation to penetrate matter; the lower B associated with β-particle or (even more distinctively) α-particle detectors may then permit lower levels of activity to be determined.

Another consideration, if more than one type of radiation is available, is the degree of selectivity each offers against interfering radioactivity. As already mentioned, γ rays and α particles offer considerable spectrometric selectivity, while β particles offer little. Problems characteristically associated with the 3 types of radiation in low-level counting are discussed in Chapters 3, 4, and 5.

Many varied radiation detectors, and methods for using them, have been developed. For low-activity measurements the emphasis, according to purpose, has been on: (1) increasing S by locating the source near or in the detector, by developing large detectors,

and by selecting detectors whose probability of responding to an individual photon or particle is high, (2) reducing B by introducing heavy shielding and anticoincidence techniques, by using radioactively-clean materials, and by developing small detectors, and (3) reducing I by improving spectrometric or coincidence techniques. These developments have taken place with due attention to the needs for reliability and stability, because they are essential in the measurement of any source regardless of its level of activity. These issues are examined in detail in Chapters 3, 4, and 5.

The foregoing interrelated considerations may be illustrated by a practical example. Suppose a particular radionuclide decays with the emission of one β particle and one γ-ray photon. The β particles could be measured with a low-level proportional counter having a background of 1 c/min, an efficiency (counts per emitted β particle) of 0.30, and a sample capacity of 0.1 g. Alternatively, the γ rays could be measured with a 7.6 cm diameter, by 7.6 cm thick NaI(Tl) detector having a background (in the full-energy peak region only) of 20 c/min, an efficiency (full-energy peak region) of 0.10, and a sample capacity of 5 g. The relative counting times required to give any specified counting precision for a low-activity sample would be inversely proportional to S^2/B, with S proportional to efficiency multiplied by activity in the sample. In the absence of source concentration and interference from other radionuclides, and if enough sample is available to load either detector to capacity, the relative counting time would be:

$$\frac{T_\gamma}{T_\beta} = (S^2/B)_\beta/(S^2/B)_\gamma$$

$$= \frac{[(0.30)(0.10)]^2}{1} \Big/ \frac{[(0.10)(5.0)]^2}{20}$$

$$= 7.2 \times 10^{-2}.$$

Alternatively, if the available mass of sample is so small (e.g., 0.1 g) that the entire sample could be accommodated in either detector, the relative counting time would be:

$$\frac{T_\gamma}{T_\beta} = (S^2/B)_\beta/(S^2/B)_\gamma$$

$$= \frac{[(0.30)(0.10)]^2}{1} \Big/ \frac{[(0.10)(0.10)]^2}{20} = 180.$$

Thus if a large mass of sample is available, the γ-ray detector achieves the desired statistical precision in a much shorter measurement time, while if only a small mass of sample is available, the β-particle detector is more favorable.

However, treatment of the sample so as to concentrate the radionuclide would alter the above conclusions. In the limit of complete extraction of the radionuclide to give a source of negligible mass, the total activity of the total available sample could be measured with either detector, and the β-particle detector would always be preferred statistically. Likewise, the presence of interfering radionuclides would alter the picture according to whether they emitted β particles or γ rays, and if the latter, whether the different γ rays could be resolved by such instrumental procedures as spectrometry or coincidence counting. A separate decision would then be necessary as to whether sample treatment or instrumental procedures were more favorable for eliminating the interference.

1.5 Standardized and Reference Sources of Low-Level Radioactivity

Nearly all measurements of radioactivity, whether low-level or high-level, are based upon a comparison between the unknown source and a reference source. Very often the activity of the reference source need not be known in absolute units. Instead, it serves merely to normalize the result for the unknown source, for example, to permit the activity in 1 ml of plasma to be expressed as a percentage of the orally administered activity. In this circumstance the reference source is locally prepared during the course of the experiment, usually as an aliquot of the radioactive solution introduced into the system. Sometimes the reference is used in more than one experiment, and in more than one laboratory, as a means of providing a normalization common to a wider range of measurements. Here again the absolute activity of the reference need not be known, but special problems such as homogeneity of the bulk material prior to taking aliquots may be more important. Finally, in some situations, notably those in which the absorbed dose rates are required, the absolute activity of the unknown sample is indeed necessary and therefore the absolute activity of the reference source must be known, i.e., a standardized source must be used.

Standardized sources and reference sources have been discussed previously by the ICRU (1963, 1968). Attention was given to both high-activity and low-activity sources, the latter being subject to particular hazards from contamination and sometimes from losses during manipulation. In recent years extensive further developments in preparation of standardized sources and in interlaboratory comparisons have occurred. Those developments particularly relevant to low-level sources are discussed in Chapter 6.

2. Sample Treatment

2.1 Introduction

2.1.1 General Principles

The sample whose radioactivity is to be measured must initially be selected in such a manner that it accurately represents the material of interest. In this selection certain difficulties are involved, notably, assuring the homogeneity of the total material before withdrawing the sample, but these are often distinctive to the specific problem and are not discussed further. The next step is sample treatment, which in this report refers to procedures whereby the radionuclide of interest is segregated, in whole or in part, from the matrix of the sample and from other radionuclides also found in the sample. Normally it is desired that the total amount of the radionuclide of interest in the sample be transferred into the source finally measured. If losses occur, or if aliquots are taken, an accurate knowledge of their magnitude is required if the activity of the sample is to be accurately calculated from the radiation measurement finally performed.

Sample treatment procedures include, in order of increasing specificity: (1) bulk segregation by physical methods (e.g., evaporation, filtration), chemical methods (e.g., ashing), and biological processes, (2) chemical purification by separation of groups of elements or single elements, and (3) isotope enrichment or selection. More than one of these treatments may be applied to the same sample, achieving individually or collectively an increase in concentration of the radionuclide of interest with respect to the matrix and interfering radionuclides by many orders of magnitude. These procedures are discussed below. Since treatment itself poses a risk of contamination, it may be good practice to apply the simplest treatment that is effective, and to rely on instrumental methods for final selectivity.

Most issues that are germane to the treatment of samples containing comparatively high-level activity are also relevant to those containing low-level activity. These issues, particularly in so far as they concern chemistry, are reviewed in textbooks by Friedlander et al. (1964), Haissinsky (1964), and others. Several issues are of special interest in the measurement of low-level radioactivity, and have been reviewed, for example, by Anderson and Hayes (1956), Arnold (1961), Sugihara (1962), and Reynolds (1962). Harley (1967) has given, in addition to an excellent introduction to low-level radiochemistry, a collection of specific procedures for measurement of low-activity samples.

Douglas (1967) has edited a set of procedures developed especially for environmental samples. Additional references appropriate to particular details are noted in the remainder of this chapter.

2.1.2 Special Problems in the Treatment of Low-Activity Samples

Carriers and Tracers. Carriers and tracers serve the same functions in the treatment of low-activity samples as in the treatment of higher-activity samples, but their use may be more critical in the former circumstances. The unique role of the carrier, to prevent losses of the radionuclide of interest during sample treatment, may be of special importance for low-activity samples since such losses, even if of known magnitude, may cause an intolerable reduction in sensitivity. Tracers may be introduced early in the sequence of sample-treatment steps, as with higher-activity samples, to reveal the magnitude of losses of the radionuclide of interest during treatment. The stable carrier itself may sometimes serve as a suitable tracer, in which case the radioassay need not be complicated by the addition of foreign radioactivity. Alternatively, a radioactive tracer may be used, but it must often be selected with greater care for low-activity than for high-activity samples. Thus, the permissible amount of radioactive tracer is likely to be restricted to a narrow range; too much may interfere with the measurement of the radionuclide of interest, while too little may preclude statistically reliable assay of the tracer itself. It is therefore especially important that the radiation of the tracer be clearly distinguishable from that of the traced radionuclide. For example, ^{85}Sr is a particularly suitable tracer for ^{90}Sr (Harley, 1967): this isotope, unlike stable strontium, will not confound the analysis by occurring naturally in the sample itself, and by virtue of the respective decay schemes of ^{85}Sr and ^{90}Sr, and the assay techniques therefore appropriate to each, neither isotope can interfere with the measurement of the other.

Radiochemical Purity. At the lowest levels of activity, identification techniques such as decay and absorption measurements become relatively ineffective because of poor counting statistics. Chemical and mass identification, however, remain valid and, therefore, "re-cycling" has become a common method for qualitative identification (Arnold, 1961; Sugihara, 1962). In this method, the sample is "re-cycled" through different chemical procedures, each of which is specific to the element of

interest. Constant specific activity of the product is taken as an indication of radiochemical purity.

Blank Samples and Sources. Contamination during sample processing must be both minimized and accurately evaluated if a low-level assay is to be reliable. Evaluation is normally achieved with the aid of "blanks", i.e., a "blank sample" is carried through the same treatment as is the presumably active sample of interest, yielding a "blank source" whose apparent activity is judged to be contamination and is subtracted from that measured on the source of interest.

In principle, a blank sample should exhibit no radioactivity of both the type and origin at issue in the sample of interest, but should contain all other radioactivity found in that sample. For example, if the ^{90}Sr content of a soil sample is to be measured, an ideal blank sample would be constituted by soil of the same sort containing no ^{90}Sr but, nevertheless, all the other natural and fallout radionuclides in the same concentration as in the sample of interest. It is clear that the suitability of an alleged blank sample may often be in question, and the appropriateness of this blank sample is at least as critical an issue as the reliability of the standardized sample containing known activity.

The activity carried into the blank source exactly allows, in principle, for all contamination derived from interfering radionuclides in the sample, in the reagents, and in any other substance (e.g., air, container walls) with which the source of interest comes in contact during treatment and source preparation. Confidence in the measurement is increased if the blank source has low activity. Nevertheless, the blank source is to be distinguished from the "dummy source", referred to in Chapter 1, which in principle should never contain radioactivity.

A discussion of the problem of blanks is given by Sugihara (1962), and a separate examination of sample and reagent contamination appears below. Standardized blank samples are discussed in Chapter 6.

2.2 Methods of Sample Treatment

2.2.1 Bulk Concentration (Matrix Elimination)

Separation of the major part of the sample matrix may often be accomplished by a relatively simple bulk concentration process. Such a process, which usually serves as the first step for more complex chemical processing, is very desirable, for it may lead to a very large degree of concentration and should introduce little contamination. Several one-step procedures are

available, and they may be conveniently discussed in terms of physical and chemical methods.

Physical Methods. Among the physical concentration techniques, evaporation (including freeze drying) and volatilization are probably the most common. For example, Cherry (1964) and Eisenbud et al. (1964) discussed the evaporation of water samples prior to counting. Arnold (1961) outlined the procedure for concentrating rare-gas nuclides from meteorites by means of vacuum fusion. In the case of the water samples, one is interested in the residue, whereas the evolved gas is the important phase for the meteorites.

Filtration, particularly in the case of air samples, is also widely used. Details concerning the use and post-collection treatment of air filters appear in several of the references given at the end of Section 2.1.1.

Perhaps the most extreme example of physical concentration is the investigation of Davis (1955) seeking to detect antineutrinos by the reaction $^{37}Cl\,(\bar{\nu}, e^-)^{37}Ar$. In this experiment, 3900 l of carbon tetrachloride were exposed for 36 days to an antineutrino fluence rate of 4.4×10^{15} m^{-2} s^{-1}. By sweeping the carbon tetrachloride with 4000 l of purified helium, he removed 90% of the ^{37}Ar produced and achieved a concentration factor in excess of 4×10^9. The ^{37}Ar activity finally assayed was 0.55 pCi.

Chemical Methods. The most common form of chemical (bulk) concentration is combustion. Following combustion, metallic radionuclides may be sought in the ash (Cherry, 1964), whereas ^{14}C, ^3H, and ^{35}S may be recovered from gaseous products (Gupta, 1966; Kainz and Wachberger, 1966). Oxidation of organic matter may be "wet" or "dry" depending upon whether the oxidant is in the liquid phase (inorganic oxidizing acids) or in the gaseous phase (molecular oxygen). Due to the high temperatures involved (especially in the latter case), it is necessary to guard against undesired physical separation (volatilization) of inorganic species.

Low-temperature ashing, brought about by means of RF-excited and dissociated oxygen, is an attractive alternative to the conventional wet and dry ashing procedures (Gleit, 1963). As the ashing temperature remains between 100°C and 200°C, loss of volatile substances is greatly reduced, and container or reagent contamination is relatively unlikely. Low temperature ashing is rather slow, however, unless the sample presents a large surface area.

Ion exchange "filtering" serves as a somewhat selective form of bulk concentration for fission products in water (Brenan et al., 1966) or milk (Kahn et al., 1963). The resin may be further processed, if necessary, or it may be examined immediately by means of γ-ray spectrometry. Another common means of chemical

bulk concentration is coprecipitation or adsorption. Manganese dioxide has served to remove fission products from aqueous solutions (Pushkarev, 1965) and from large quantities of sea water (Shipman, 1966). Yamagata and Iwashima (1963) claim that the manganese dioxide method applied to 100 l of sea water allows the detection of about 2 pCi/l of various activation and fission products. Coprecipitation and ion exchange have been applied as concentration steps for uranium in urine (Currie et al., 1964), and rare-earth fission products may be concentrated from sea water by means of coprecipitation with ferric hydroxide (Sugihara et al., 1959).

Biological Processes. In certain analyses, concentration by natural biological processes has been exploited. Kahn et al. (1963) adopted a relatively simple chemical procedure for ^{131}I and ^{90}Sr in milk because of the "prior elimination of many interfering radionuclides by metabolic processes in the cow". In their search for cosmic-ray produced ^{32}Si, Lal et al. (1960) estimated that the concentration in sea water would be only about 12×10^{-18} Ci/l, and that, in order to detect such a level of ^{32}Si, they would have to process 3.8×10^4 l. Instead, they allowed sponges to concentrate the ^{32}Si for them, and the radionuclide was finally determined from 200 g of SiO_2 derived from the opaline structure of sponges. The observed specific activity in silicon was about 9 pCi/kg.

2.2.2 Chemical Purification

Group Separations. Isolation of groups of elements occupies an intermediate position between bulk concentration and elemental separation. That is, it is somewhat specific, reasonably simple and rapid, and it may bring about sufficient decontamination for instrumental means to complete the resolution of the constituent radionuclides. The same methods that are applicable to elemental separation (see below) are appropriate for group separations, namely, ion exchange, solvent extraction, precipitation, etc. The difference lies in the fact that simpler combinations of such methods, designed according to the decay characteristics of the expected nuclide, may be employed.

A semi-automatic method for separating a number of activation and fission products into five groups was devised by Mathers and Hoelke (1963). The sample (in an HCl medium) was placed on a cation exchange column which was then selectively eluted with HCl + $H_2C_2O_4$, HNO_3, and HCNS. The following groups of elements resulted: I (Sb, Ru, Zr, Nb), II (Cs), III (Co), IV (Sr), V (V, Y, rare earths). By combining γ-ray spectrometry with such a group separation, the

authors were able to determine quantitatively the principal radionuclides present in "aged" fission products. The powerful combination of ion-exchange group separations and γ-ray spectrometry has also been investigated by Wester et al. (1964). These authors devised an extensive scheme, including anion and cation exchangers, which was suitable for separating 23 elements into acceptable groups. The procedure was applied to biological specimens having low levels of activity.

Quantitative sequential separations without addition of carrier were developed by Ross (1964) in order to determine trace elements in high-purity materials by means of activation analysis. Group separation, which was again combined with γ-ray spectrometry, was essential in order to eliminate interferences by elements which differed greatly in abundance or cross section. The sequential procedure, which included acid solution, distillation, precipitation, and extraction, separated 49 elements into 6 groups with good yields and sufficient decontamination that quantitative γ-ray spectrometry could be applied.

Elemental Separation. Completely specific chemical separation may be necessary at the lowest levels of radioactivity or if there are concomitant high-level interfering activities. The separation procedures differ from standard radiochemical procedures only with respect to the necessity for good recovery and decontamination, and for obtaining low activity in the blank source. Separation techniques include volatilization; precipitation and coprecipitation; solvent extraction; gas, paper, and ion-exchange chromatography; and selective electrodeposition or reduction. Somewhat unusual techniques include the use of cation exchange foils (Bjornholm and Lederer, 1962), which permit the "chemical" preparation of thin sources having negligible self-absorption, and scintillating ion-exchange resin (Heimbuch et al., 1965), which is selective and serves as a counting medium that is insensitive to many of the problems of quenching. One unique selective chemical separation method which has been used by many workers is the purification of ^{3}H by means of its diffusion through palladium.

An extensive collection of radiochemistry monographs, covering most of the elements, has been prepared under the auspices of the U.S. National Academy of Sciences (NAS, 1960 ff). Although the procedures are not designed specifically for low-level application, many will be found suitable for such a purpose. Several collections of procedures are available, however, which are designed especially for low-level work. These should be consulted if a radiochemical separation scheme is desired for the isolation of a specific radionuclide (Olson, 1964; Everett et al., 1964; WHO/FAO, 1959; Guthrie and Grummitt, 1963; Harley, 1967).

2.2.3 Isotope Enrichment

Sample treatment involving isotopic separation according to mass number (A) is complementary to chemical separation according to atomic number (Z). In most cases isotopic separation follows chemical separation when an increase in specific activity is needed. The increasing availability of electromagnetic isotope separators, however, may lead to the combination of simple or group chemical separations and mass separation (Andersson and Rudstam, 1964). Mass separations of this type are characterized by poor recovery, wide applicability (most elements), excellent decontamination, and mass-number specificity. As illustrated by a situation involving ^{150}Nd (Cowan et al., 1956), mass separation is essential at the lowest levels of specific activity in order to achieve the maximum signal from ^{150}Nd and in order to have a proper blank source (Nd depleted in ^{150}Nd). A useful summary of isotope effects and isotope separation has been given by Haïssinsky (1964).

The principal applications of isotope enrichment to low-level problems, however, have involved physical or chemical processes in which the "isotope effects" are greatest for the lightest elements. Such applications have been concerned almost exclusively with ^{3}H and ^{14}C, which occur at very low concentrations in nature, and which are of sufficiently low atomic mass to exhibit significant isotope effects. The penalty paid for the ability to separate isotopes of carbon and hydrogen is the possibility of isotopic fractionation even in the "chemical" concentration of these elements. As a result, either one must be certain that all chemical steps are quantitative, or a monitor for possible fractionation must be employed. Most commonly, the ^{2}H content of a ^{1}H-^{3}H mixture, or the ^{13}C content of a ^{12}C-^{14}C mixture, serves as the monitor (Flint and Deevey, 1961).

Enrichment of low-activity tritium samples has been accomplished by a variety of methods, including *distillation* (Smith and Rawson, 1962; Zel'venskii et al., 1965), *electrolysis* (Kaufman and Libby, 1954; Cameron and Payne, 1965; Allen et al., 1966; Takahashi et al., 1965), *thermal diffusion* (von Buttlar and Wiik, 1965), and *gas chromatography* (Smith and Carter, 1962; Crespi and Perschke, 1964; Perschke et al., 1969). Electrolysis remains the most widely used technique, but its accuracy may suffer unless care is taken to prevent evaporation losses or to monitor the degree of enrichment by means of the ^{2}H content. Recent developments in gas chromatography, however, appear quite promising, as Perschke (1966) succeeded in processing 10 l of hydrogen (equivalent of 8 g of water) with a recovery of 98 % of the ^{3}H in a final volume of 0.9 l. The entire process, including reduction of the original water sample, took only 3 hours.

2.2.4 Radionuclide Specification

Identification or confirmation of a given radionuclide (specific Z and A) is normally achieved by instrumental methods which examine the decay characteristics (radiation emitted, energy, half-life). Such identification is necessary in the absence of chemical or mass separation, and desirable in combination with concentration techniques. As pointed out by Sugihara (1962), however, precise identification at very low levels may not be possible because of limited statistical accuracy of counting. He suggests chemical re-cycling as an alternative means of confirmation.

Instrumental means of identification are discussed in subsequent chapters, but one very specific "chemical" approach may be presented here. In the fortunate situation where a radionuclide decays to a radioactive daughter, one may utilize such a genetic relationship to identify the pair unambiguously by first separating the parent and then the daughter. The specificity is very great: only a parent-daughter pair corresponding to the two sequential element separations can give rise to radioactivity in the final product. Furthermore, the final sample can always be prepared carrier-free (or with a minimum of added carrier) and then a detector can be employed having a small size (therefore low background) and high efficiency. No efficiency decrease caused by lower-efficiency, higher-resolution methods of counting need be tolerated, because radionuclide identification will already have been achieved. The most common application of such genetic relationships is the determination of environmental ^{90}Sr (Harley, 1967). The procedure, to be described later in more detail, takes advantage of the possibility of secular equilibrium between ^{90}Sr and ^{90}Y; the ^{90}Y may be extracted carrier-free from a previously separated strontium salt. In an analogous situation, the ^{60}Co daughter of ^{60}Fe (Goel and Honda, 1965) made possible the determination of 0.4 pCi/kg of ^{60}Fe in 2.18 kg of Fe from the Odessa meteorite.

2.3 Sample and Reagent Contamination

2.3.1 General

"Radiochemical" and "radioisotopic" contamination were first extensively treated by DeVoe (1961). Pertinent data from DeVoe's report, together with supplementary material, were given in a previous report of the ICRU (1963). The present brief review, therefore, is limited to information that did not appear in either of the above sources, and that is related specifically to contamination that occurs in the original sample or that arises during source preparation. Contamination

as related to instrumental background is discussed in Chapter 3. The radionuclides ^{3}H and ^{14}C are treated separately.

2.3.2 Nuclides Other than Carbon-14 and Tritium

The general problem of low-level radioactive contamination has been under systematic investigation at the U.S. National Bureau of Standards and elsewhere. Fission products and decay products of the natural radioactive series remain primary sources of radioactive contamination. For example, the ^{85}Kr concentration had increased to about 144 pCi/mmol of krypton (Enhalt et al., 1963) by mid-1962. Atmospheric contamination levels of ^{85}Kr and ^{133}Xe produced by "bomb fission", and ^{14}C and ^{37}Ar produced by "bomb neutrons", have been estimated by the above authors. The ^{85}Kr contamination may set limitations on some measurements as illustrated in a low-level project in which ^{81}Kr was sought as a product of (n, γ) cosmic-ray reactions with atmospheric krypton (Aegerter et al., 1966). The low abundance of ^{80}Kr in the atmosphere, together with the low fluence of the cosmic-ray produced neutrons and the ^{85}Kr contamination level, eliminates any possibility of detecting ^{81}Kr in the present atmosphere. The investigation is therefore dependent upon reserves of krypton that had been removed from the atmosphere prior to the advent of nuclear explosions.

The problem of contamination by nuclides in the natural uranium and thorium series is particularly serious in the non-destructive investigation of the decay of very long-lived radionuclides. Watt and Glover (1962) referred to such a limitation in their investigation of the possible decay of ^{113}Cd, and Sonntag (1965) emphasized the role of such contamination in the wide variety of half-lives reported for ^{50}V. Atmospheric ^{222}Rn contamination is well known as a limitation in the estimation of ^{226}Ra body burdens by means of exhaled ^{222}Rn in the breath. By having the subjects breathe ^{222}Rn-free air for 3 minutes, Davies and Malatova (1965) were able to achieve a ten-fold reduction in such contamination, but Stehney and Lucas (1956) noted that even after the subject had breathed ^{222}Rn-free air for 5 hours, the ^{222}Rn still being exhaled as a result of his previous contamination with atmospheric ^{222}Rn was equal to that exhaled from an internal ^{226}Ra deposit of activity 100 pCi.

Contamination of the preceding type (^{222}Rn in breath) might be distinguished from "radioisotopic" by the term "isonuclidic". That is, the contamination is due to the very radionuclide being sought, and therefore it cannot, in principle, be removed. Isonuclidic contamination is of great importance in measurements of low levels of ^{14}C and ^{3}H. It was also regarded by Davis (1955) as responsible for all of the ^{37}Ar (0.55 pCi) observed in his neutrino experiment (the ^{37}Ar being produced by cosmic rays rather than by neutrinos). Honda et al. (1961) attempted to correct for isonuclidic contamination in their study of excess cosmogenic ^{40}K in meteorites, where "natural" ^{40}K amounted to 86% of the total. The problem of carrier contamination is well known in low-level ^{90}Sr analyses. If yttrium carrier is to be used successfully in procedures that call for the determination of ^{90}Sr by means of its radioactive daughter, ^{90}Y, such carrier must be purified. A suitable purification method has been given by Harley (1967).

One of the more dramatic types of contamination is cosmic-ray induced radioactivity in chemical reagents. Rama and Honda (1961) investigated the production by neutrons or muons of: ^{32}P in HCl, CCl_4, H_2SO_4 and SO_2; ^{39}Cl in argon; and ^{198}Au and ^{199}Au in mercury. Positive results were obtained in all cases, and the cosmic-ray origin was confirmed by exposing reagents to various cosmic-ray intensities by means of irradiations at mountain altitudes, at sea level, in a swimming pool, and in a cave. Saturation activities at sea level are listed in Table 2.1. Thus, the cosmic-ray induced reagent radioactivity "is not entirely negligible" at sea level, and it certainly should be reckoned with if very large quantities of such reagents are to be used in a given procedure. Also, the problem becomes considerably more serious at higher altitudes or in reactor or accelerator environments, since most of the above radionuclides were produced by neutron absorption.

2.3.3 Carbon-14 and Tritium

With the exception of ^{222}Rn, which may come from the atmosphere during sample treatment (Watt and Ramsden, 1964), or from the sample being processed (Long, 1965), the contamination most commonly found in the assay of ^{14}C or ^{3}H is isonuclidic. Long solved the ^{222}Rn problem by passing the sample (CO_2) over activated charcoal at $-40°C$. A common method for decreasing the ^{222}Rn contamination is to store the sample for two weeks before counting. The concentration of

TABLE 2.1—*Concentrations (pCi/kg) of cosmic-ray produced radionuclides in reagents at sea level* (Rama and Honda, 1961)

Target	^{198}Au + ^{199}Au	^{39}Cl	^{35}S	^{32}P	^{33}P	^{7}Be
Hg	0.054					
Ar		-0.09	0.034	0.015	0.018	
S					0.23	
Cl				0.04	0.11	
O						0.022