CANMET

REPORT 78-22

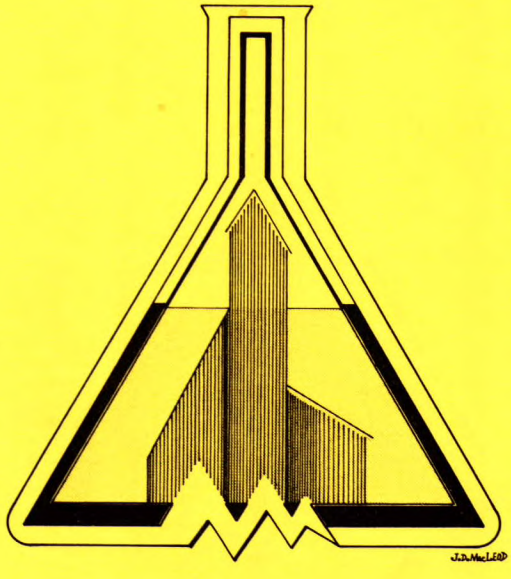
Canada Centre for Mineral and Energy Technology

Centre canadien de la technologie des minéraux et de l'énergie

RADIOCHEMICAL PROCEDURES FOR DETERMINATION OF SELECTED MEMBERS OF THE URANIUM AND THORIUM SERIES

JANUARY 1979

ENERGY RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES



Energy, Mines and Resources Canada
Énergie, Mines et Ressources Canada

E R R A T A

Page 17. Last sentence in first paragraph should read:
"Gamma tracers are recommended for use in alpha or beta determinations, beta traces in alpha determinations or even alpha tracers in alpha determinations which are performed by alpha spectroscopy."

Page 34. Caption for Fig. 1 should read:
"Emanation Bubble-Cell Configuration for Radon De-emanation."

Page 50. Step 3 in Determination should read:
"Add 14 ml of 4% oxalic acid and 2 ml of saturated ammonium chloride. Heat to dissolve and adjust pH to 4.00 with NH_4OH."

TO BE INSERTED IN CANMET REPORT 78-22 Cat. No. M38-13/78-22

RADIOCHEMICAL PROCEDURES FOR DETERMINATION OF SELECTED MEMBERS OF THE URANIUM AND THORIUM SERIES

Compiled and edited by: Gene L. Smithson*

Final preparation by: J.L. Dalton** and G.L. Mason***

CANMET REPORT NO. 78-22

* Senior Research Chemist, Chemistry Division, Saskatchewan Research Council, Saskatoon, Saskatchewan S7N 0X1

** Supervisor, X-ray Fluorescence and Radiochemistry Group, Spectrochemistry Section, Chemical Laboratory, Mineral Sciences Laboratories, CANMET, Ottawa, Ontario K1A 0G1

*** Head, Spectrochemistry Section, Chemical Laboratory, Mineral Sciences Laboratories, CANMET

FOREWORD

The growing concern of environmental regulating agencies, in connection with radioactive pollution arising from the mining and milling of uranium ores, has resulted in directives to the uranium mining industry in Canada to provide analytical data on selected radionuclides from the uranium and thorium decay series. However, the problem arises as to how such data can be provided, since (a) few, if any, of the Canadian mining companies now have the capability to carry out all the required analyses and (b) many of the current radiochemical methods are unsuitable for use at a mine site. The transport of sample from a mine to a private analytical laboratory involves time delay and the inevitable risk of spillage during transit. On-site radiochemical analyses would not only eliminate these problems but, at the same time, considerably accelerate changes in process control systems, with accompanying benefits.

The urgent need to encourage mine-site radiochemical analytical capabilities was recognised in ongoing work in connection with CANMET Minerals Research Program, Mineral Resource Determination Activity, Project No. 336203 (Control of Effluents from Tailings Basins). Arising from this, through the overtures of Dr. D. Moffett, (then with CANMET Mining Research Laboratory, Elliot Lake, Ontario), two contracts were awarded to Dr. G. Smithson (Saskatchewan Research Council), one to prepare a manual of methods for radiochemical analysis, and the other to develop a radiochemical method for the accurate routine determination of Pb-210, through the beta-counting of its daughter Bi-210; these methods to be applicable to mine-site location, their precision and accuracy to be established by the Contractor. Agreement on these contracts (D.S.S. No's OSQ77-00174 and OSQ77-00099) was completed in December, 1977, between Dr. Smithson and J.L. Dalton, acting as Scientific Authority for CANMET.

Dr. Smithson's manuscripts were received in April, 1978 and the editing completed jointly by J.L. Dalton and G.L. Mason (both of Mineral Sciences Laboratories, CANMET). This compilation of methods fills a long-standing void in the uranium industry and as such should be in considerable demand.

R.L. Cunningham,
Chief,
Mineral Sciences Laboratories

AVANT-PROPOS

Suite à l'interêt que portent les agences de réglementation à la protection du milieu contre la pollution par la radioactivité causée par l'exploitation et la transformation des minerais d'uranium, des directives ont été adoptées par l'industrie d'exploitation de l'uranium au Canada qui fournira les données analytiques sur des radionuclides précis provenant des produits de désintégration de l'uranium et du thorium. Il s'agit maintenant de surmonter les problèmes de prélèvement de telles données puisque a) peu de compagnies d'exploitation minière canadiennes ont la capacité d'effectuer en ce moment les analyses qui s'imposent et b) plusieurs méthodes de radiochimie actuelles ne peuvent pas être employées à l'emplacement même de la mine. Le transport d'un échantillon d'une mine vers un laboratoire d'analyse privé occasionne des retards et un risque de perte. Les analyses radiochimiques effectuées sur place peuvent non seulement éviter ces problèmes mais aussi accélérer les modifications apportées aux systèmes de contrôle des procédés et ses avantages.

Lors de travaux de recherche effectués dans le cadre du Programme de recherche sur les minéraux du CANMET, Activité de détermination des ressources minérales, Projet n^{o} 336203 (la limitation des effluents dans les bassins de stériles) le besoin s'est fait sentir d'encourager les capacités d'analyses radiochimiques effectuées sur place. A cette fin, deux contrats ont été accordés au Dr G. Smithson (Saskatchewan Research Council) à la recommandation du Dr D. Moffett (anciennement avec le Laboratoire de recherche minière de CANMET à Elliot Lake en Ontario). Un des contrats vise à préparer un manuel des méthodes d'analyse radiochimique et l'autre à mettre au point une méthode radiochimique précise de détermination du Pb-210 par un comptage-béta des produits de filiation du Bi-210. Ces méthodes seront employées à l'emplacement même des mines. L'entrepreneur décidera de la précision et de l'exactitude nécessaire. L'entente entre Dr Smithson et J.L. Dalton, responsable scientifique pour CANMET, sur les contrats (D.S.S. n^{o} OSQ77-00174 et OSQ77-00099) a pris fin en décembre 1977.

Les manuscrits du Dr Smithson ont été reçus en avril 1978. J.L. Dalton et G.L. Mason (tous deux des Laboratoires sur les sciences minérales, CANMET) ont revisé le rapport. Cette compilation de méthodes a été longtemps attendue car elle remplie un besoin de l'industrie d'uranium et par ce fait devrait être en demande.

R.L. Cunningham
Chef,
Laboratoires sur les sciences minérales

PREFACE

The radiochemical procedures contained in this manual are adaptations of those developed and published by many radiochemists. In many cases the identity of the originator is not clear and usually many modifications in the original procedure have been made by subsequent workers. Nearly all of the basic radiochemical techniques and separations in use today were developed during the Manhattan Project and can be found in U.S.A.E.C. reports published from 1945 to 1953. This manual contains methods for the determination of Pb-210, Po-210, Ra-226, Ra-228, Th-228, Th-230 and Th-232.

Most of this early work is described in the Nuclear Science Series: Monographs on Radiochemistry and Radiochemical Techniques, which are available from the National Technical Information Service, Springfield, Virginia. The series contains individual monographs on uranium, thorium, radium, lead, polonium, and many other elements. These booklets contain a wealth of information and should be available in all radiochemical laboratories.

A book that is mandatory for use with this manual is the HASL Procedures Manual edited by John H. Harley, Health and Safety Laboratory, U.S. Energy Research and Development Administration, 376 Hudson Street, New York, N.Y. 10014. Many references in this manual refer to information contained in the HASL Manual. In addition, some diagrams and preparation methods contained herein have been taken directly from the U.S. Manual. The HASL Procedures Manual is an extensive collection of radiochemical procedures, analytical procedures and very detailed discussions of radiochemical principles and techniques. The cost of the HASL Procedures Manual is less than $30.00 and its contents are updated periodically.

Another laboratory that has made extensive contributions to radiochemical methodology is the U.S. ERDA Health Laboratory at Idaho Falls, Idaho. This laboratory was previously under the direction of C.W. Sill and a large number of procedures have been published in Analytical Chemistry from 1959 to the present under his and his co-workers' authorship. Many of the procedures in this manual are derived from their publications.

G.L. Smithson,
March, 1978

PREFACE

Les procédés radiochimiques dont on traite dans le présent manuel ont été adaptés d'après ceux qui ont été mis au point et publiés par plusieurs radiochimistes. Très souvent, l'identité de l'inventeur n'est pas connue et de toute façon la procédure originale a subi plusieurs modifications de la part des chercheurs subséquents. Presque toutes les techniques et séparations radiochimiques de base employées aujourd'hui ont été mises au point durant le "Manhattan Project". On peut les retrouver dans les rapports du U.S.A.E.C. publiés de 1945 à 1953. Le manuel présente les méthodes de détermination du Pb-210, Po-210, Ra-226, Ra-228, Th-228, Th-230 et Th-232.

La majorité des travaux initiaux sont décrits dans les "Nuclear Science Series: Monographs on Radiochemistry and Radiochemical Techniques" disponibles au "National Technical Information Service", Springfield, Virginia. Les séries mentionnées contiennent des monographies sur l'uranium, le thorium, le radium, le plomb, le polonium et plusieurs autres éléments. Ces livrets contiennent une multitude de renseignements et devraient être disponibles dans tous les laboratoires de radiochimie.

Il est indispensable de joindre au présent manuel, le manuel des procédures "HASL Procedure Manual" rédigé par John H. Harley du Health and Safety Laboratory (Laboratoire de la santé et de la sécurité) du U.S. Energy Research and Development Administration (Bureau de recherche et du développement de l'énergie des E.U.) 376 rue Hudson, New York, N.Y. 10014. Plusieurs références données dans le présent manuel se rapportent directement au Manuel HASL. De plus, certains diagrammes et méthodes de préparation mentionnés ont été puisés directement du Manuel des E.U. Le Manuel des procédures HASL consiste d'une collection des procédures radiochimiques et analytiques ainsi que des explications détaillées des principes et des techniques de radiochimie. Le coût de ce manuel des procédures HASL est de moins de $30.00 et le contenu est remis à jour périodiquement.

Un autre laboratoire ayant contribué à la méthodologie radiochimique est le "U.S. ERDA Health Laboratory" de Idaho Falls, Idaho. Ce laboratoire était jadis dirigé par C.W. Sill. Lui et ses confrères sont les auteurs d'un grand nombre de procédures publiées dans le "Analytical Chemistry" à partir de 1959 jusqu'à nos jours. Plusieurs procédures parues dans le présent manuel ont pris leur origine dans ces publications.

G.L. Smithson,
Mars 1978

CONTENTS

CONTENTS (cont'd.)

RADIOCHEMICAL FUNDAMENTALS

RADIOACTIVE DECAY

All radiochemical procedures are based on the measurement of alpha (α), beta (β), or gamma (γ) disintegrations. These arise from an instability in the nucleus of an atom and are therefore referred to as nuclear radiations. The instability of the nucleus is caused by an imbalance in its preferred neutron-to-proton ratio. As one progresses down the Periodic Table to elements of higher atomic number, the deviation of the actual neutron/proton ratio from the preferred ratio becomes greater and greater. Eventually, for most elements with atomic number greater than 82 (lead), this deviation is so great that all of their naturally occurring isotopes are radioactive. By undergoing nuclear decay (loss of mass and energy) these elements are transformed through a series of other radioactive elements, of decreasing mass or neutron/proton ratio, to a stable nuclear configuration. A decrease in atomic weight and atomic number is produced by the ejection from the nucleus of an alpha particle (two neutrons plus two protons-mass of 4 atomic units). Beta emission results from the decay of a neutron into a proton (retained in the nucleus) and an electron (ejected from the nucleus as the beta particle). The emission of an alpha particle causes the atomic number to decrease by 2 (2 protons) and the atomic weight to decrease by 4 (2 protons + 2 neutrons). The emission of an electron (beta particle) causes an increase in atomic number of 1 (because of the new proton created in the nucleus) and no appreciable change in atomic weight. In this manner both the atomic weight and neutron/proton ratio decrease until the result is a stable element. For example, the ultimate decay product of uranium-238 is stable lead-206 and for thorium-232 it is lead-208. The role of gamma rays in this process is to remove energy from nuclei that are left with excess energy after undergoing alpha or beta decay. A nucleus left in a metastable state after particle emission will emit electromagnetic radiation (gamma rays) as it decays to a stable state. The process can be considered to be simultaneous with the alpha or beta emission (usually within 10^{-12} seconds).

From this foregoing discussion it can be seen that the radioactive decay of one chemical element results in the formation of a different chemical element. It is on the basis of this differing chemical composition that separations of the naturally occurring radionuclides can be made. Once they are separated, the characteristic nuclear radiation of each isotope may be measured and used to determine the quantity of that isotope present. This is the fundamental basis of that field of analytical chemistry known as radiochemistry.

There are four natural radioactive decay series for the elements with atomic number greater than 82. Of these, only three are observed to occur in nature and are referred to as the uranium, thorium and actinium series. The fourth, the americium or neptunium series, does not occur naturally because none of its members have half-lives long enough to have allowed them to survive the initial formation of terrestrial matter. Schematic representations for all four decay series are shown in Figures 1 to 4. These representations have been simplified by excluding all decay branches which are less than 2% of the activity of the parent radionuclide.

RADIOACTIVE DECAY CALCULATIONS

Radioactive decay is a first order reaction process. That is, the rate of decay of any radioactive isotope is proportional to the concentration or amount of that isotope raised to the first power.

$$\text{rate} = \text{constant} \times (\text{concentration})^1$$

$$\text{or} \qquad \frac{dN}{dt} = -\lambda N$$

where N is the number of atoms present
t is the elapsed time
λ is the decay constant

This first-order rate equation may be integrated to give

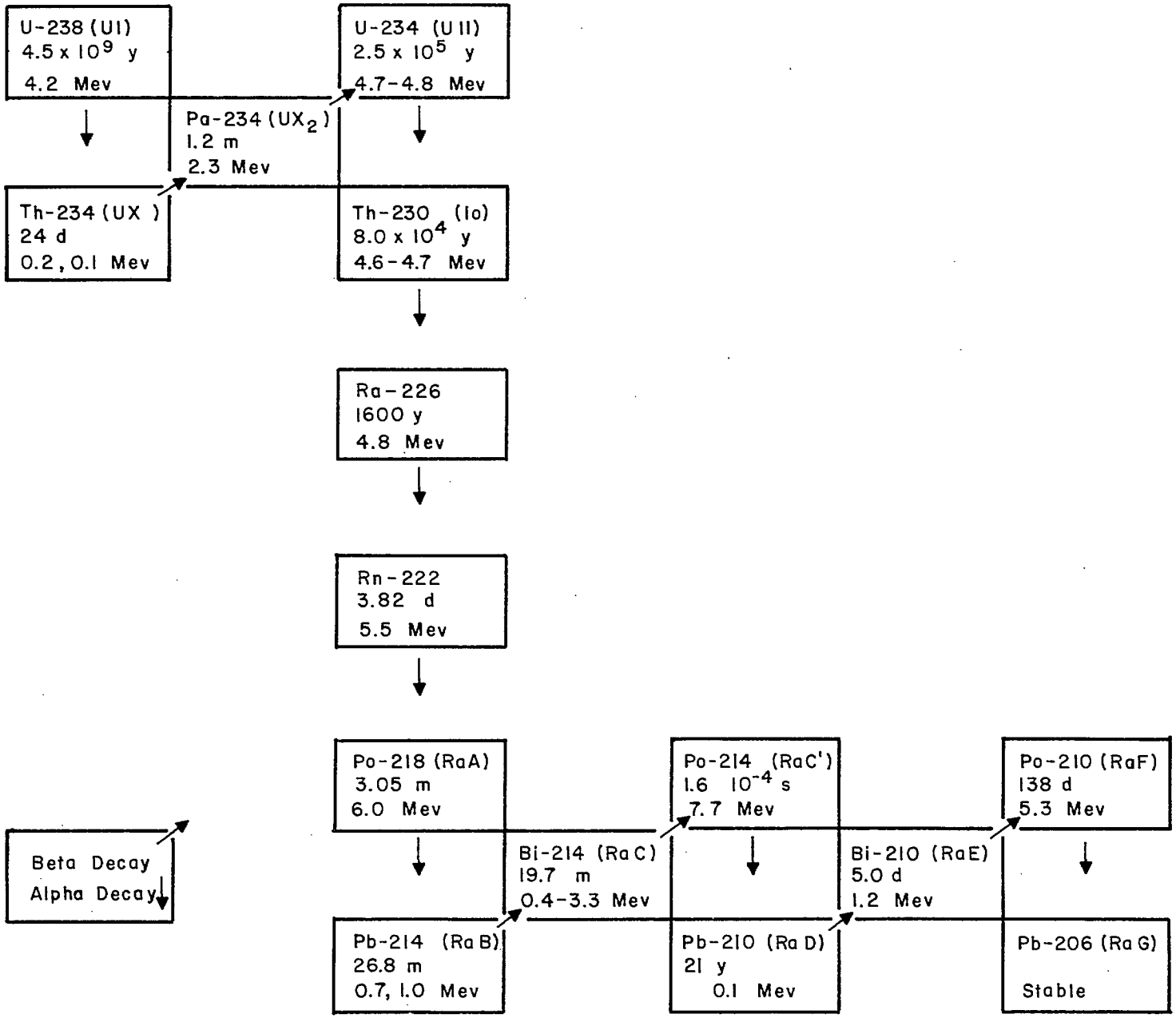


Fig. 1 Principal Decay Scheme of the Uranium Series.

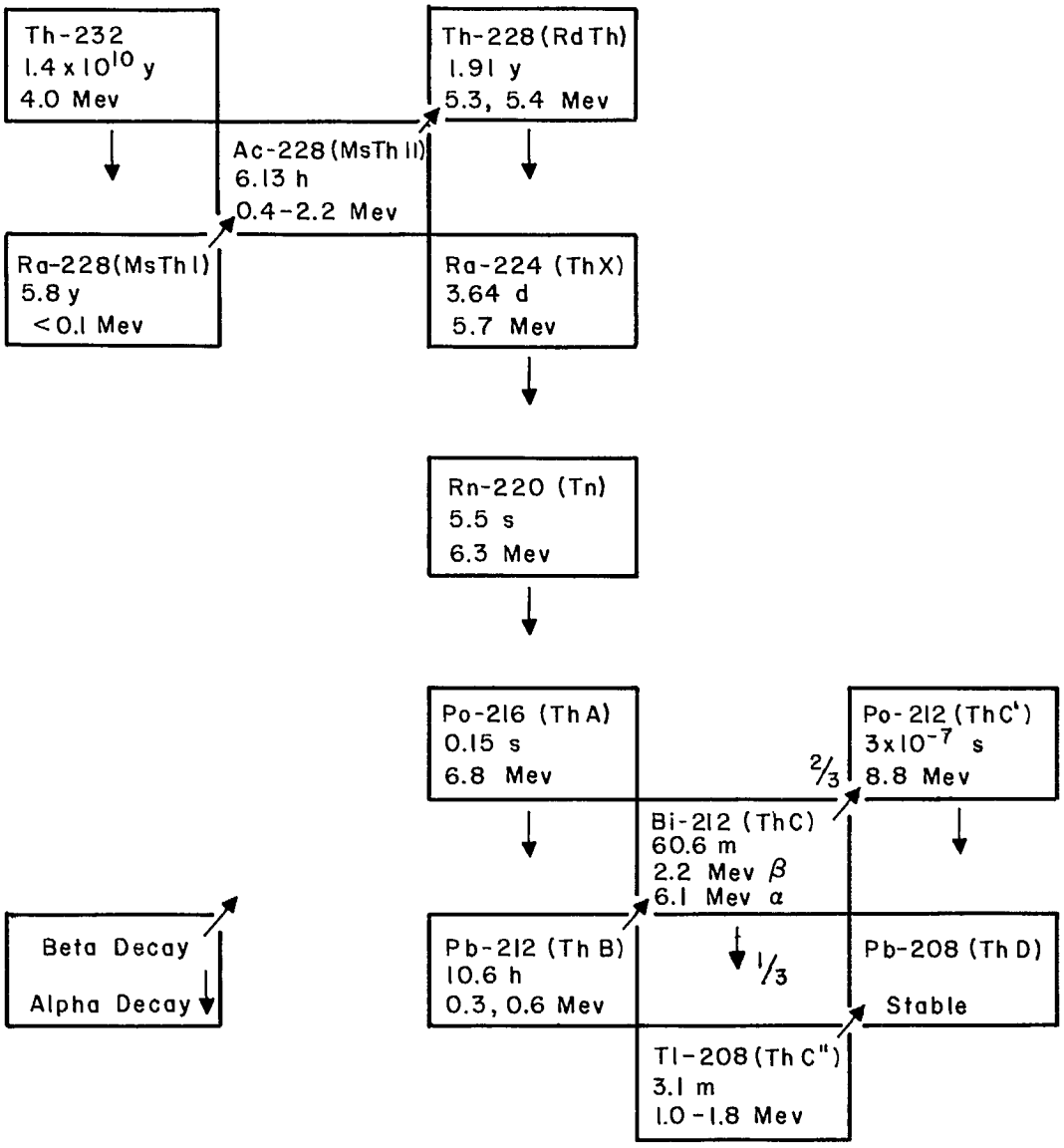


Fig. 2 Principal Decay Scheme of the Thorium Series.

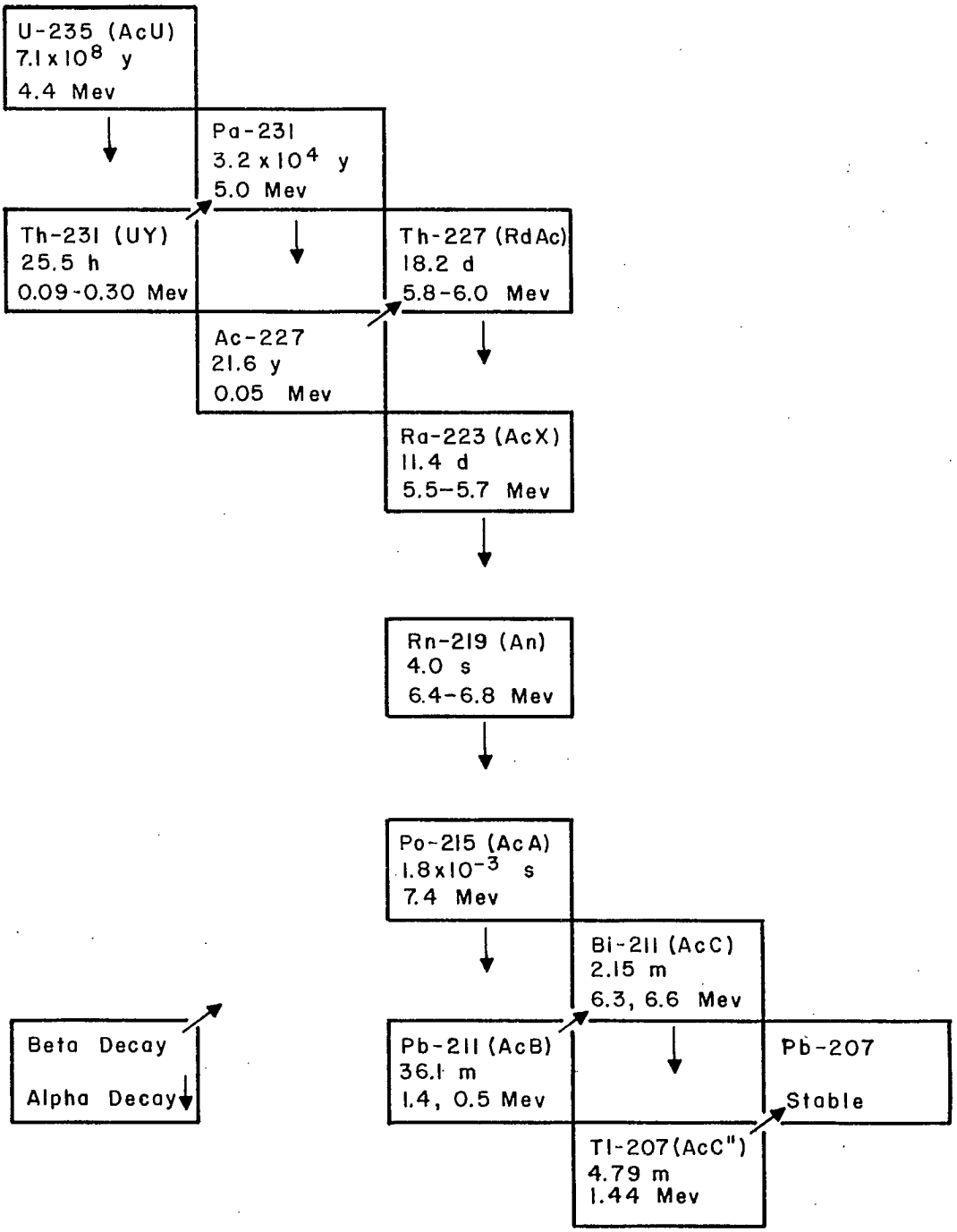


Fig. 3 Principal Decay Scheme of the Actinium Series.

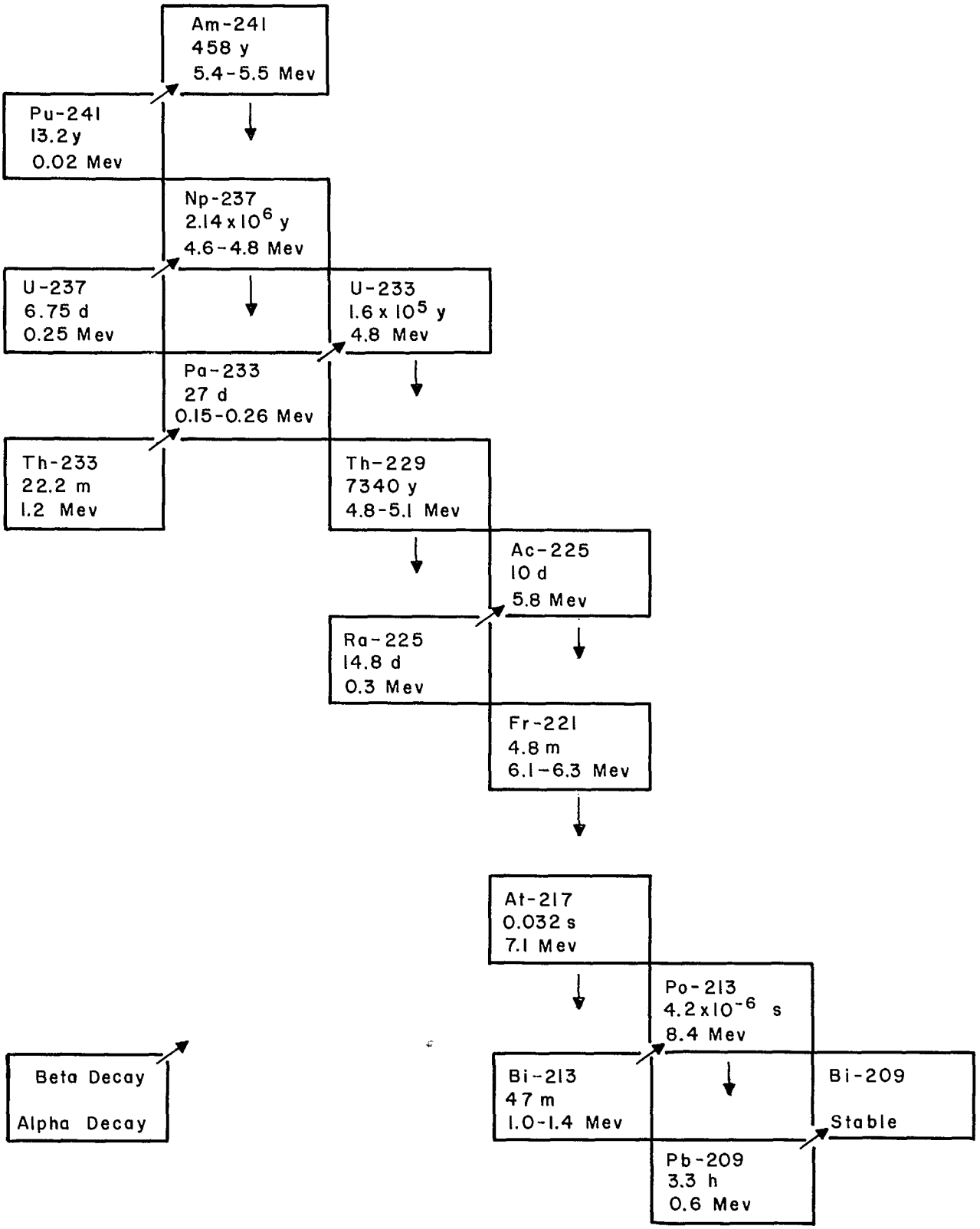


Fig. 4 Principal Decay Scheme of the Americium Series.

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

where N is the number of atoms present at time t

N_0 is the number of atoms present initially.

The equation can be used to calculate the fraction of a particular isotope that has decayed in a given time period. The time required for one-half of the initial atoms to decay is commonly referred to as the half-life ($t_{\frac{1}{2}}$) and has the following relationship to the decay constant.

$$\frac{N}{N_0} = 0.5 = e^{-\lambda t}$$

$$\ln 0.5 = -\lambda t_{\frac{1}{2}}$$

or $$t_{\frac{1}{2}} = \frac{0.6932}{\lambda}$$

The decay constant and half-life are funadamental characteristics of each radionuclide. In all radioactive decay calculations the units of time for λ and t must be consistent.

If one considers the process of radioactive decay in one of the natural series it is evident that all of the intermediate daughters in the chain are being formed and are decaying simultaneously. The rate at which each is formed is dependent on the amount of the immediate precursor that is present. The rate of decay is proportional to the amount of the radionuclide itself that has accumulated. The net rate of increase is given by

$$\frac{dN_d}{dt} = \lambda_p N_p - \lambda_d N_d$$

where the subscript p refers to parent and d refers to daughter.

For the special case where there is no daughter present initially the foregoing equation can be integrated to give

$$N_d = \frac{\lambda_p N_p}{\lambda_d - \lambda_p} (e^{-\lambda_p t} - e^{-\lambda_d t})$$

The equation for the second daughter in a series becomes more complex because it is dependent on the decay of the parent, the decay of the first daughter and its own decay. The resulting integrated rate equation for the amount of the second daughter present at time t (no first or second daughter present initially) is

$$N_3 = \lambda_1 \lambda_2 (N_1)_0 \left[\frac{e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} + \frac{e^{-\lambda_2 t}}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2)} + \frac{e^{-\lambda_3 t}}{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)} \right]$$

where the subscript ^{1} refers to the parent, ^{2} refers to the first daughter and ^{3} refers to the second daughter.

This equation can be extended to the third, fourth, fifth daughters and on. The general equation for any radionuclide in such a series is known as the Bateman equation and is written as:

$$N_i = \lambda_1 \lambda_2 \cdots\cdots \lambda_{i-1} (N_1)_0 \sum_{j=1}^{i} \frac{e^{-\lambda_j t}}{\prod_{k \neq j} (\lambda_k - \lambda_j)}$$

This equation can be programmed on a computer or one of the more sophisticated programmable calculators and is very useful in calculating ingrowth and decay relationships within the natural series.

When sufficient time has elapsed, all the members of a radioactive decay series reach a state of equilibrium with one another. That is, the rate of formation and the rate of decay of all the members becomes equal. This condition is referred to as secular equilibrium. Although the activity (rate of decay) of each isotope is equal to that of the parent at the head of the series, the quantity of each isotope is proportional to the reciprocal of its specific activity. The specific activity may be calculated as follows:

$$A(\text{curies/g}) = \frac{\lambda N}{3.7 \times 10^{10} M} = \frac{a}{t_{\frac{1}{2}} M}$$

where A = specific activity in curies per gram

N = Avogadro's number (6.025×10^{23} atoms/g-atom)

M = atomic weight of the radionuclide

λ = decay constant (sec^{-1})

3.7×10^{10} = disintegrations per second in one curie

a = 1.13×10^{13} curies.sec.g-mole when time is in seconds

a = 1.88×10^{11} curies.min.g-mole when time is in minutes

a = 3.14×10^{9} curies.hour.g-mole when time is in hours

a = 1.31×10^{8} curies.day.g-mole when time is in days

a = 3.58×10^{5} curies.year.g-mole when time is in years

$t_{\frac{1}{2}}$ = half-life of radionuclide in same time units as a.

The curie was formerly defined as the disintegration rate of the radon in equilibrium with one gram of radium. It is now defined as 3.7×10^{10} disintegrations per second (dps). In terms of this new definition, 1 g of radium-226 is equivalent to 0.988 curies. Another abbreviation commonly used in radiochemistry is counts per second (cps) or counts per minute (cpm). The distinction between dps and cps is that disintegrations usually refer to the total activity of a given mass of radionuclide, whereas counts refer to the actual number of disintegrations detected by a particular counter measurement. The counts per second will always be less than the disintegrations per second for a given mass of isotope. This is because it is virtually impossible to measure every individual disintegration. Self-absorption within the radioisotope itself, counter geometry and counter efficiency all lead to a decrease in measured counts as compared to the total number of disintegrations. The count rates measured for environmental levels of most natural radionuclides are usually well below 100 cpm. This would correspond to something in the order of 4.5×10^{-11} curies. Such numbers are cumbersome to use routinely in calculations, so normal practice is to use the metric prefix pico (10^{-12}), nano (10^{-9}), micro (10^{-6}) or milli (10^{-3}) to express these lesser amounts. The foregoing example (4.5×10^{-11} curies) would be more conveniently expressed as 45 pico-curies (pCi).

PROPERTIES OF RADIOACTIVE EMISSIONS

Alpha particles, as we have already seen, are composed of two protons and two neutrons and carry a positive charge of 2. They are equivalent to the nucleus of a helium atom and are the most massive of the radioactive emissions. The velocity of alpha particles ranges from approximately 1 to 2 $\times 10^{9}$ cm/sec. This velocity results in energies ranging from 2 million electron volts (MeV) to about 8 MeV.

The higher energies are normally associated with nuclides of shorter half-life. All alpha particles emitted by a given radionuclide have either a single energy or have at most a few discrete energy values closely grouped.

Alpha particles interact with matter by producing ionization. They release electrons from the atoms with which they collide leaving a trail of ion pairs in their wake. As the alpha particle loses energy the distance between collisions becomes less and less, resulting in the heaviest density of ionization near the end of its path. Typical ionization density curves for the absorption of alphas of different energies in air are shown in Figure 5. Extrapolation of the vertical part of the curve to zero ionization gives the mean path length for that particular energy. The variation of mean range with energy for alpha particles in air is shown in Figure 6. The range of alpha particles in solids and liquids is very short. They are completely absorbed in the outer layers of skin or by a single sheet of paper. Because of this short range, alpha particles do not constitute an external health hazzard to humans. However, if alpha emitters are ingested or inhaled they are very toxic because of the large amount of ionization and cell disruption produced in the surrounding tissue.

Beta particles are negative electrons travelling at close to the speed of light (3×10^{10} cm/sec) or about 10 to 20 times faster than alphas. In spite of their higher velocity, beta particles usually have energies lower than that of alpha particles because of their much smaller mass (0.000544 atomic mass units). The maximum beta energy in the natural radioactive series is about

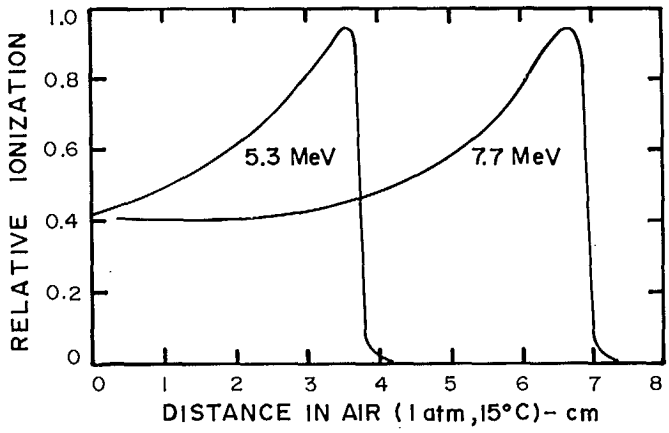


Fig. 5 Ionization vs Path Length Curves for Alpha Particles in Air.

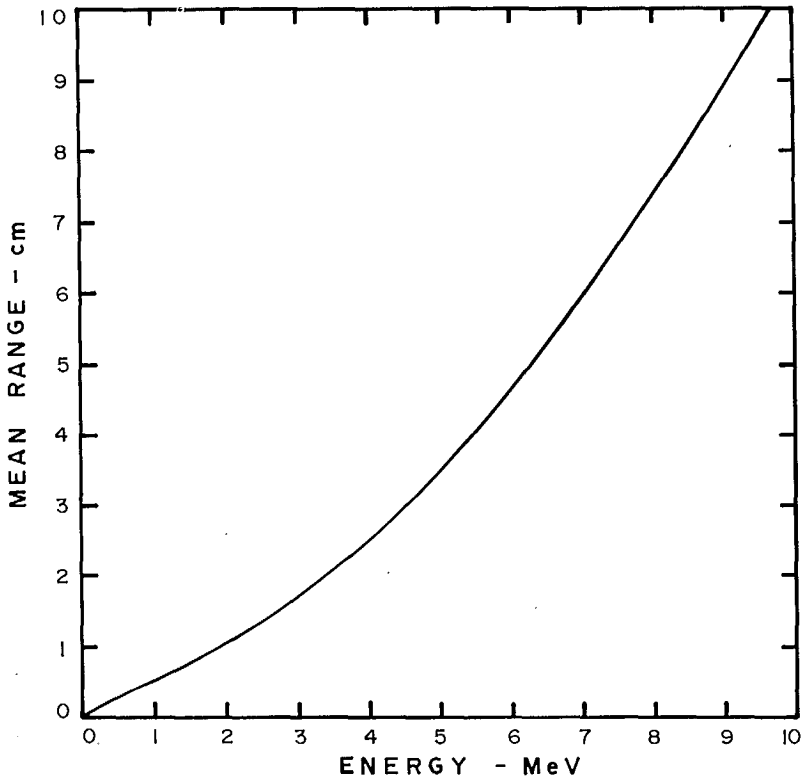


Fig. 6 Range vs Energy Curve for Alpha Particles in Air (STP).

3.3 MeV (Bi-214). The distribution of beta energies emitted by a single radionuclide is much different than for alpha or gamma emission. Instead of discrete energies, the betas have a continuous distribution of energies between zero and their characteristic maximum. A typical energy distribution is shown in Figure 7. This distribution of energy is explained by postulating that a second particle, the neutrino, is emitted along with the electron and the sum of the energies carried by the electron and the neutrino is equal to the maximum observed beta energy.

The absorption of beta particles in matter should be similar to that of alpha particles but in fact differs considerably because of several factors. The first of these has been mentioned above, that is, a continuous spectrum of beta energies occurs rather than discrete values. A second factor is that, because of their very low mass, beta particles are easily scattered (by as much as 180° in some cases) and this scattering contributes to the apparent absorption. There is no mathematical expression which is capable of combining all these factors (ionization, energy spectrum and scatter) into a single relationship. Consequently, beta absorption curves are normally determined experimentally by measuring the decrease in count rate as successively thicker layers of aluminum are placed between the source and the detector. A typical plot of $\ln A/A_0$ (where A is the activity with the absorber in place and A_0 is the activity with no absorber) vs the thickness of aluminum (mg/cm^2) is shown in Figure 8. If the plot is made on 3-cycle semilog paper, the point where the absorption curve intercepts the aluminum thickness axis is a close approximation of the range for that particular radionuclide. Measurements of this type can be used to qualitatively identify an isolated isotope.

The range of 1 MeV betas is 1.4 mm of aluminum, 4 mm of water and about 3 metres in air (Figure 9). Consequently, highly-active beta sources can cause severe radiation burns to the skin and underlying tissue. The levels of beta activity normally encountered in low-level radiochemical operations will pose no serious health hazard. However, ingestion must be avoided because many of the heavy-element beta emitters become fixed in bone and this can result in long term health problems.

Gamma rays are photons of electromagnetic radiation, given off when a nucleus undergoes transition from a state of higher energy to one of lower energy. The relationship between energy and wavelength is given by

$$E = \frac{hc}{\lambda}$$

where E = energy
h = Planck's constant, 6.62×10^{-27} erg/sec
c = velocity of light, 3×10^{10} cm/sec
λ = wavelength, cm.

For the common gamma emitters the energy varies between 0 and 2.5 MeV. The wavelength corresponding to an energy of 2.5 MeV is 0.05 Å and for 0.05 MeV gammas it would be 0.25 Å. Gamma rays are very short wavelength x-rays and can penetrate great thicknesses of matter before being absorbed. Because of their electromagnetic nature, gamma rays undergo exponential absorption. That is, a certain fraction of the incident gammas will be absorbed afer passing through a definite thickness of a given material. For example, 1 cm of lead will absorb approximately 50% of 1.2 MeV gamma rays, 2 cm will absorb 75%, 3 cm will absorb 87.5% and so on.

Due to their high penetrability, gamma rays can produce radiation damage deep within the human body. Of the three types of radiation from radionuclides, gamma radiation is the most serious external hazard. When working with high levels of gamma-emitting tracers, appropriate shielding must be used.

It is good practice to monitor incoming samples, standard solutions and tracers with a radiation survey meter to ensure that they may be safely handled in routine operations. Film badges

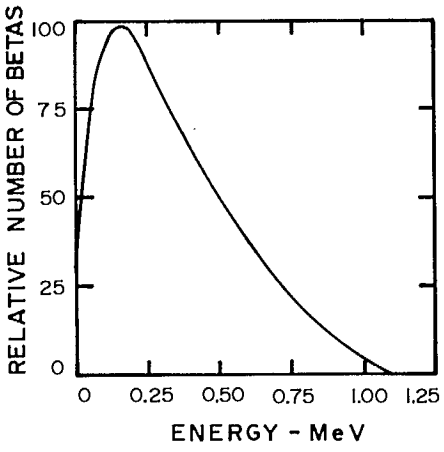


Fig. 7 Typical Energy Distribution of Beta Particles From a Single Radionuclide.

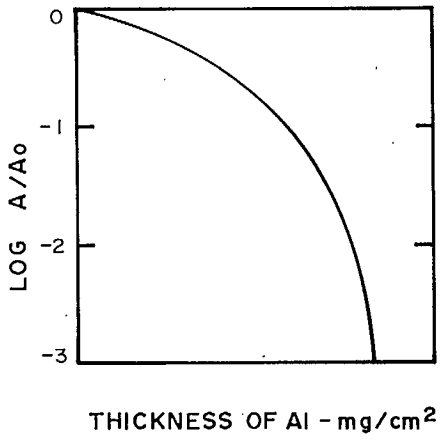


Fig. 8 Absorption of Beta Particles by Varying Thickness of Aluminum.

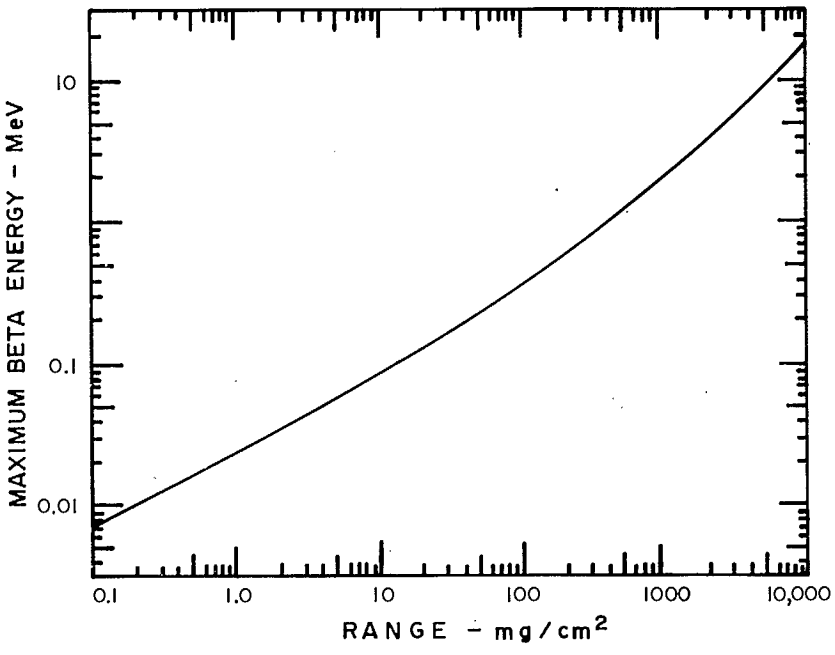


Fig. 9 Beta Particle Energy vs Range in Aluminum.

will provide an extra measure of security against prolonged exposure to moderate levels of beta and gamma emissions.

RADIATION DETECTION

One of the first reported measurements of radioactivity was the discovery by Becquerel in 1896 that the invisible emanations from uranium minerals would darken a photographic plate. This was followed by a period of extensive research into all aspects of radioactivity and radiochemistry. During this time, several devices were introduced which could produce quantitative measurements of nuclear radiation directly and these gradually replaced photographic measurements. Two of the new devices were the gold-leaf electroscope and the Lauritsen electroscope which responded to the ionization produced by the passage of nuclear radiation. Following these, the ion chamber was developed and this eventually evolved into the proportional and Geiger-Müller counters. There are three main categories of radiation detectors in common use today. These are the gas-filled detectors, the scintillation detectors and the solid-state detectors.

GAS-FILLED DETECTORS — The two most commonly used gas-filled detectors are the proportional counter and the Geiger-Müller counter. Both are basically ion chamber detectors. An enclosed, gas-filled chamber with a pair of internal electrodes is connected to a voltage source. As the voltage is increased to several tens of volts the ions produced in the gas by alpha particles can be collected at the electrodes and measured by a sensitive electrometer. Increasing the voltage further brings the device into the region of saturation collection (hundreds of volts) where all the ionization pulses produced by alpha particles are detected. The magnitude of the output pulses remains fairly constant over a wide range of applied voltage. In this region an ion chamber can be used as a specific detector for alpha particles. Beta particles do not produce sufficient ionization to be detected. As the voltage is increased further gas amplification occurs. The applied voltage (1000 to 2000 V depending on detector design) is now sufficient to accelerate the initially-formed electrons to energies high enough to cause ionization of the fill gas. The result is that each primary electron causes an avalanche of secondary electrons which results in a much larger pulse of current when these are collected at the anode. The amplification factor is about 10^5 greater than in the saturation region, and even the ionization produced by beta particles can be detected. In this region the size of the output pulse is proportional to the degree of primary ionization produced by the alpha or beta particle which in turn is proportional to the energy of the particle. Consequently, devices operated in this voltage region are known as proportional counters. Most commercial gas-flow counters operate in this mode to allow for discrimination between alpha and beta particles. The amplification factor increases exponentially with applied voltage. If a certain pulse size has been selected as the cut-off point between alpha and beta disintegrations it will be necessary to maintain very close regulation of the applied voltage to prevent alpha and beta pulses from being shifted above or below the cut-off point.

As the voltage applied to the ion chamber is increased even further the detector is brought into the Geiger region. Now, the acceleration of electrons by the applied voltage is so strong that even the secondary electrons produce further ionization in the vicinity of the anode. The result is a continuous discharge along the entire anode for each primary ionization event. The collected charge is independent of the degree of initial ionization so that every ionizing event produces the same size of output pulse. The main advantage of the Geiger region is that the output pulse height is several volts in magnitude. This means that virtually no amplification is required to detect the output of this type of counter.

A characteristic common to both the proportional and Geiger regions is the existence of a plateau in the counting rate as the applied voltage is varied between certain limits. The proportional plateau is determined by measuring the count rate of a source at increasing increments of

high voltage and plotting a curve of count rate vs. applied voltage. Initially, the count rate will rise rapidly with increasing high voltage and then, in the plateau region, will level off for several hundred volts. As the high voltage is increased further there will be another region of rapidly increasing count rate followed by a second plateau (Geiger plateau). The proportional plateau has a slope* of 1-2% per hundred volts whereas the Geiger plateau will have a slope of 5-7% per hundred volts. For either plateau, normal practice is to operate at a voltage which is at least 100 V above the low-voltage end of the plateau. A counter's plateau should be checked periodically to make sure it has not shifted sufficiently to require a new high-voltage setting.

Ion-chamber detectors of both common types (proportional and Geiger) may be operated as sealed units or as continuous gas-flow devices. The sealed units provide portability but suffer from a finite lifetime and a gradually changing sensitivity. The gas-flow types are not portable but normally provide a more reproducible sensitivity. Of the two types, the proportional detector is most commonly used because it provides for energy discrimination and has a much smaller dead time than Geiger detectors. The dead time is the period immediately following detection of an ionizing event in which the detector is incapable of responding to additional ionizing events. For Geiger counters this interval is from 100 to 300 μsec whereas most proportional counting systems will have overall dead times of less than 1 μsec. The net result is that proportional detectors remain linear up to count rates of several tens of thousand counts per second whereas many Geiger detectors will exhibit non-linearity at several thousand counts per minute.

SCINTILLATION DETECTORS — The first scintillator used to detect radioactivity was a screen coated with zinc sulphide crystals. Sir William Crookes observed flashes of light on such a screen when it was exposed to the radiations from radium and observed under a low-power microscope. The individual flashes of light (scintillations) are the result of the impact of single alpha particles and are known to last for about 25 μsec each. Current practice is to detect these individual scintillations by coupling the scintillator to a photomultiplier and measuring the output pulses with a suitable counting system. One type of scintillator consists of a plastic sheet coated with a thin layer of silver-activated zinc sulphide. By placing the zinc sulphide surface in direct contact with the sample a counting efficiency of at least 50% is achieved. The zinc sulphide scintillator is sensitive only to alpha particles and produces a very low background. A similar system is available for beta counting of prepared solid samples, in which the zinc sulphide scintillator is replaced with a plastic disc into which an organic beta phosphor has been incorporated. There are many other organic scintillators available for beta counting. They are available in liquid, gel and solid form but the most commonly used are the liquid "cocktails" for internal counting of low-energy beta emitters. By mixing the beta emitter with the scintillator solution much higher efficiencies are obtained than is possible by other counting techniques. Another very common scintillation detector is the thallium-activated sodium iodide crystal used for gamma ray detection. The high effective molecular weight of the detector crystal results in very high efficiencies for gamma counting. These detectors have been used for gamma spectroscopy but the resolution is sufficient to resolve only relatively simple spectra.

SOLID-STATE DETECTORS — These are semiconductor diodes made from either silicon or germanium crystals. One surface of the crystal is treated to form a rectifying junction (diode) and a bias voltage is applied across the detector. When radiation produces ionization in the bulk of the crystal the bias voltage sweeps these charges to their oppositely-charged electrode surfaces producing a pulse of current. The size of this pulse is very accurately proportional to the energy of the absorbed radiation. The accuracy of

*Count rate vs applied voltage

the pulse size is due to the fact that only 3.5 eV (silicon) or 2.9 eV (germanium) are required to produce an ion pair. This means that a 3.5 MeV alpha particle would produce 10^6 electron pairs in silicon. From Poisson statistics the 1σ standard deviation for 10^6 events is $\pm 10^3$ events which corresponds to a deviation of ±3.5 eV for the 3.5 MeV particle. In other words the original 3.5 MeV alpha peak will only be broadened to a width of 7 eV (2 x 3.5) at the half-maximum height of the peak (FWHM). The potential resolution is even greater in germanium.

The superior resolution of these detectors allows them to be used for high-resolution spectroscopy measurements. The so-called surface barrier detectors made from silicon are used for alpha spectroscopy and also detect beta particles. The background count rates in the alpha energy region are very low (< 0.02 cpm per 1 MeV energy width) but the high background in the beta region (∿ 10 cpm) makes them unsuitable for low-level beta counting. The surface layer of normal surface barrier detectors is extremely sensitive to mechanical damage and for this reason the ruggedized versions are preferred for routine counting applications. All semiconductor detectors have a limited lifetime as they are physically damaged by each particle they absorb. A figure of 10^{10} total counts has been suggested as an expected lifetime for certain of these detectors.

Because of the much higher atomic weight of germanium, lithium-drifted germanium detectors are used for gamma spectroscopy. They have a much higher thermal electron noise than silicon detectors and are normally operated at liquid-nitrogen temperatures to minimize this noise. In addition, because of the lithium drifting which is used to reduce the leakage current (noise), these detectors must be maintained at liquid-nitrogen temperatures even when not being used. If allowed to warm to room temperature the lithium will drift from the crystal and the detector will be seriously damaged. Apart from the initial cost of these detectors, they are expensive to operate and maintain.

A new generation of germanium detectors has been introduced in the past few years. These are the so-called "intrinsic germanium" detectors. They are made from ultra-pure germanium and do not require lithium drifting for successful operation. Consequently they can be allowed to stand by at room temperatures with no resulting damage. They are, however, operated at liquid-nitrogen temperatures to achieve the maximum resolution required from gamma spectoscopy. The "intrinsic" detector has a major advantage over the lithium-drifted detector in that it does not contain the dead areas produced by the lithium drifting. This means that the counting efficiency of the "intrinsic" detector for low-energy gammas is greatly superior to the Ge(Li) crystals. Some investigative work has been performed on the use of these "intrinsic germanium" detectors for low-level measurement of uranium, thorium and their decay products in soil and tailings samples. The advantage over conventional radiochemical analyses is that no sample preparation is required other than pressing the sample into a disc before counting. However, even with the most sensitive of these new detectors the detection limit for the natural radionuclides is well above the levels found in most environmental samples. Perhaps new developments will bring about the ultimate detector so that chemical separations will no longer be required.

DETECTOR SELECTION

ALPHA COUNTING — The simplest and least expensive system for low-background gross alpha counting is the ZnS phosphor-scintillation counter. All that is required is a 1 to 2 inch photomultiplier in a light-tight enclosure, a preamplifier and a scaler. No heavy shielding or anticoincidence detectors are necessary. The background on such a system should be in the neighbourhood of 0.01 counts per minute.

Gas-flow proportional counters are relatively expensive because of the necessity for heavy lead shielding and an anticoincidence system. They are available in manual or auto-sample changing versions and will have a background of about 0.1 counts per minute for the 1-

inch detector version. They are only suitable for gross alpha counting.

For alpha spectroscopy the recommended system consists of a ruggedized surface barrier detector (300-450 mm^2), preamp, bias supply, linear amplifier, vacuum chamber and a multichannel analyzer. There are several multichannel analyzers on the market for $6000 or less which are adequate for routine alpha spectra measurements. Such systems can of course be used for gross alpha counting with a background of less than 0.1 cpm.

BETA COUNTING — The systems most commonly used for low-background beta measurements are the shielded, anticoincidence, gas-flow counters operated in the proportional or Geiger mode. A proportional system has the advantage that it can also be used for alpha counting. Another possibility for low-background beta counting is to use beta phosphor discs with a bare-photomultiplier system, as detailed in the HASL Procedures Manual, page G-10.

Surface barrier detectors are not suitable for low-background beta counting because they have a high beta background. The 450-mm^2 detector has a beta background of about 12 cpm.

GAMMA COUNTING — For gross counting of tracer yield, a NaI(Tl) detector provides the highest sensitivity. Coupled to a preamp and scaler, a fairly inexpensive system can be assembled. For gamma spectroscopy the detector of choice is the newer "intrinsic germanium" diode. These are more expensive than Ge(Li) detectors but have greater low-energy gamma sensitivity and do not require liquid-nitrogen cooling when not in use.

COUNTING ELECTRONICS

SCALERS — The most commonly used instruments are the NIM module scalers, counters and counter-timers. A scaler is a counter with a built-in timer. A counter-timer may be used for either function but not both at the same time. There are some dual counter-timers which can be operated as a scaler (counter and timer) or as two independent counters. Some recent models have a timer channel and two or three independent counters. The reliability of these units is very good and the cost is such that spare units can be kept on hand for direct replacement if a fault should develop. There are several manufacturers of NIM instrumentation and due to the reliability of modern transistor and integrated circuit designs they can all be assumed to be equivalent.

MULTICHANNEL ANALYZERS — Multichannel analyzers are used for alpha and gamma spectroscopy. For alpha spectroscopy as few as 128-256 channels will suffice although most of the modern inexpensive analyzers have from 512 to 2048 channels. These are more than adequate for routine alpha spectrum measurements.

For gamma spectroscopy, 2048 or 4096 channels are preferred because of the high resolution required in some complex spectra. Most sophisticated gamma spectroscopy is now analyzed by computer techniques. The interfacing of the analyzer to a computer must be kept in mind when deciding on a system. Some recent multichannel analyzers have a microprocessor built into them which is capable of performing much of the spectrum analysis.

COUNTING FUNDAMENTALS

GENERAL — Some of the factors which influence the counting of alpha-emitting radionuclides are self-absorption, air absorption, backscatter and absorption by the detector window. Self-absorption can be minimized by using the smallest amount of carrier that can be reliably recovered. The ultimate reduction is to perform carrierless separations or use electrodeposition as the final sample preparation step. If it is not possible to use either of these techniques then whichever carrier is used should be as finely divided and uniformly distributed as possible. When using an in situ precipitation of barium (radium) sulphate on glass planchettes errors of up to 50% were encountered in the counting rate of standards prepared by different analysts. These huge errors are caused by variations in the way a drop of sulphuric acid is added to the barium chloride solution on the planchette, and in the distribu-

tion of the resulting barium sulphate precipitate by smearing the surface with a glass rod. Consequently, a change was made to the precipitation of barium (radium) sulphate in a constant volume of solution followed by filtration through a membrane filter. This method is much more consistent for any one analyst and does not change appreciably from one analyst to another. However, the conditions of concentration and temperature during the precipitation must be closely controlled or variations in the crystal size of the precipitate will lead to large counting errors. Air absorption can be reduced by placing the prepared sample surface as close to the detector as possible. Inverting cup planchettes and depositing the sample on the back of the planchette is one way of minimizing the sample to detector distance. When performing alpha-spectroscopy it is necessary to place the sample and detector in an evacuated chamber to minimize the degradation of resolution caused by air absorption. Window absorption is reduced by using the thinnest window available for the detector. For alpha measurements, the 80-100 $\mu g/cm^2$ windows give excellent transmission but are very fragile. Since backscatter improves counting rates it is not desirable to reduce it but only to make it uniform from sample to sample. This can be accomplished by always using the same type of planchette for a particular procedure. Backscatter is entirely dependent on the effective atomic number of the planchette material.

These foregoing factors effect beta counting in a similar manner and can be dealt with by corresponding techniques. Air absorption and window absorption are not too critical for the more energetic betas but will have measurable effects on low-energy betas.

Absorption and scattering are not serious problems in gamma measurements so long as a consistent sample-detector orientation is maintained along with uniform sample density. In some cases it is preferable to press the sample into a uniform disc or cylinder to obtain a consistent sample form. Many samples are simply poured into a special sample holder (Marinelli beaker) which is self-positioning with respect to the detector.

The sample-detector geometry is critical in all radiocative counting techniques. The sample and calibration standards should be in identical forms and held in identical positions with respect to the detector. For example, a calibration performed with point-source standards is not applicable to samples that are spread over a larger area. The sample-holding device should be rigid and well machined to ensure reproducible positioning.

For alpha and beta counting, the detector is best calibrated by carrying standards through the procedure and counting these in the same form and manner as samples. Not only will this compensate for all the variables mentioned above but it will correct for recovery through the chemical separations of the procedure. Suitable standard solutions are available from Amersham in Oakville, Ontario, or from NBS in the United States.

It may be necessary in some cases to make corrections for non-linearity of detector response caused by dead-time losses. Non-linearity may occur at fairly low count rates with beta Geiger detectors (2000 to 20,000 cpm) but should not be a problem with proportional, surface barrier, scintillation or solid-state detectors below 100,000 cpm. If non-linearity at a high count rate is suspected, take a smaller aliquot and repeat the analysis. There are split disc standards available from suppliers which can be used to measure the dead time of a detector. The two halves of the disc are counted separately and then are combined for a total count rate. If the total is less than the sum of the two halves there is non-linearity and the dead time may be calculated.

$$\tau = \frac{r_1 + r_2 - r_T - r_B}{2r_1 r_2}$$

where τ = the dead time or resolving time
r_1 = count rate of one half of disc, cps
r_2 = count rate of other half of disc, cps
r_T = count rate with both halves together, cps
r_B = background count rate, cps.

COUNTING STATISTICS — The accuracy of determined counting rates can be calculated statistically if one assumes a Poisson distribution of counting data. The standard deviation is given by

$$s = \sqrt{N}$$

where s = the standard deviation of the total count.

N = the number of counts accumulated.

The standard deviation of the count rate, s_R, is

$$s_R = \frac{\sqrt{N}}{t}$$

where t = length of time to accumulate N counts, min or sec.

Thus if one were to count a sample with a count rate of 100 cpm for 10 min, the standard deviation of the count rate would be $\frac{\sqrt{100 \times 10}}{10} = \pm 3.16$ and the count rate would be expressed as 100 ± 3 cpm. Note the necessity of rounding off and retaining the same number of significant figures in both the count rate and its uncertainty. As the sample count rate approaches the background count rate the uncertainties in both counts must be combined. The standard deviation for the net count rate is

$$s_{NR} = \frac{\sqrt{N_G + N_B}}{t}$$

where s_{NR} = the standard deviation of the net count rate

N_G = total number of counts for the sample

N_B = total number of counts for the background

t = counting time (assumes equal times for sample and background)

For a 100 min count on a sample with a gross count rate of 0.20 cpm and for a background of 0.10 cpm the calculation is

$$s_{NR} = \frac{\sqrt{20 + 10}}{100} = 0.055$$

and the net count rate would be expressed as 0.10 ± 0.06 cpm.

DETECTION LIMIT — A simplified method of calculating detection limits based on the background count rate and the counting time is given on page D-08-05 of the HASL Procedures Manual. For a 95% confidence level of detecting activity due to the presence of the radionuclide the calculation is

$$LLD = (4.66) \frac{\sqrt{N}}{t}$$

where LLD = the lower limit of detection in cpm.

N = the total number of counts in time t.

t = counting time, minutes (assuming equal count times for sample and background).

As an example, for a 100 min count and a background of 0.10 cpm the LLD would be

$$LLD = 4.66 \ \frac{\sqrt{10}}{100} = 0.15 \text{ cpm.}$$

RADIOCHEMICAL OPERATIONS

Radiochemistry is that branch of analytical chemistry which isolates elements by chemical separations and then determines the quantity of particular radioisotopes of that element by measuring their characteristic nuclear radiation. In the majority of cases the amounts to be determined range from 10^{-6} to 10^{-12} g. In a few instances, quantities as small as 10^{-17} g are routinely measured. Performing chemical separations on such small amounts poses many problems. Most of the naturally-occurring heavy metal radionuclides, when in solution, are adsorbed on the walls of sample containers, on glassware and on traces of precipitate present. These losses from solution can be very serious sources of error. The normal method of preventing severe losses is to add macro amounts of a stable isotope of the element or, if no such isotope exists, another element which is chemically similar. For example, there are no stable radium isotopes but barium is sufficiently similar chemically that it can be used to carry

along the small radium population. This carrier technique is used in nearly all complex radiochemical procedures. The recovery of the trace radionuclide is assumed to be proportional to that of the carrier which can usually be quantitatively measured because of the amount present. In some cases an element is added which is chemically identical or similar to a contaminant that must be separated from the analyte and its carrier. This is known as a hold-back carrier and is normally used to prevent coprecipitation or co-carrying with the analyte carrier. Another method of determining recovery is to add a radioactive tracer which is chemically identical or similar to the isotope of interest. For example, barium-133 can be used to "trace" the recovery of radium. Barium-133 is a gamma emitter and if reasonably high levels are added to the sample at the beginning of the procedure, a quick determination of the amount present in the final prepared sample will provide a measure of the recovery of radium. The radioactivity of the tracer should be easily distinguished from that of the analyte. Gamma tracers are recommended for use in alpha or beta determinations, beta traces in alpha determinations or even alpha tracers, in alpha determinations which are performed by alpha spectroscopy.

The operations which are performed in radiochemical separations are identical to those used in normal analytical routines such as weighing, pipetting, solvent extraction and so on. Many procedures involve centrifugations to separate precipitates from solutions. The bulk of the solution may be decanted and the last traces removed with a disposable pipette fitted with a rubber bulb. Large amounts of solution are conveniently decanted from beakers by aspirating them through a glass-tipped rubber tube connected to a filter flask which in turn is connected to a vacuum source. Small (10 x 2 mm) Teflon-coated stir-bars are convenient for stirring the contents of centrifuge tubes. Several centrifuge tubes with stir-bars can be placed in a beaker on a magnetic stirrer and stirred simultaneously. When performing solvent extractions, it is preferable to use Teflon separatory funnels as they do not adsorb or retain trace quantities of contaminating elements. Adsorption of measurable traces of lead, radium, thorium, polonium and other heavy metals occurs frequently on glassware. If possible, high-level (> 10 pCi) and low-level glassware should be isolated from each other. This is very important when dealing simultaneously with environmental samples and mill process streams. The use of special glassware cleaners such as Decon 75 is very beneficial in removing adsorbed contamination. In cases of severe contamination it is probably cheaper to discard the glassware or use it for normal analytical work rather than try to clean it.

With care, common sense and patience, radiochemical separations and measurements can be performed as reliably as any moderately complex, conventional analytical procedure.

THE DETERMINATION OF LEAD-210*

PRINCIPLE

The direct determination of lead-210 is very difficult due to the extremely low energy of its beta emission (0.06 MeV maximum energy). Consequently, it is necessary to determine lead-210 indirectly through its high-energy beta-emitting daughter, bismuth-210 (1.2 MeV maximum energy). In this procedure, the bismuth-210 resulting from a definite ingrowth period or known to be in secular equilibrium with lead-210 is isolated by solvent extraction and then precipitated as bismuth oxychloride for beta counting. From the determined bismuth-210 concentration and the degree of equilibrium existing between parent and daughter it is possible to calculate the lead-210 concentration.

APPLICATION

This method can be used to determine lead-210 concentrations in water, biological, soil, ore and rock samples. The solvent extraction with diethylammonium diethyldithiocarbamate (DDTC) in chloroform is performed in 2M hydrochloric acid. This high acid concentration prevents the hydrolysis and precipitation of all metals normally encountered such as thorium, iron, aluminum and others as well as bismuth. The two major interferences in the extraction are iron and copper. The interference of ferric iron can be eliminated by reducing it to ferrous with an excess of ascorbic acid. Copper, if present at interfering levels, can be removed by extracting the sample, prepared in 8M HCl, with 1% DDTC in chloroform. By diluting to 2M HCl the bismuth can next be extracted with 0.1% DDTC in chloroform. The precipitation of BiOCl as the final form for radioactive counting serves as an additional purification step in removing trace levels of radioactive contaminants.

The single solvent extraction followed by back extraction into aqueous solution and the precipitation of BiOCl can be performed rapidly on a routine basis. This makes it possible to process a larger number of samples in a given time than can be accomplished with other Pb-210 methods.

The 5-day half-life of Bi-210 means that samples must be captive for at least 30 days, to allow for ingrowth, if greater than 98.5% equilibrium between Pb-210 and Bi-210 is to be assumed. For samples that must be analyzed within a few days of sampling it is necessary to extract and discard the existing Bi-210 so that a definite time period for Bi-210 ingrowth can be established. There is always a great deal of uncertainty in the degree of Pb-210/Bi-210 equilibrium existing in natural aqueous samples because of the ease with which bismuth compounds precipitate at pH's greater than 2. Once the samples are acidified and stored for more than 30 days this uncertainty is eliminated.

APPARATUS

1. Low-background beta-counting system.
   (a) Shielded, anticoincidence, flow proportional counter
   or (b) Bare-photomultiplier scintillation counting system used with beta phosphor discs (HASL Procedures Manual, Specification G-10-01).
2. HASL ring-and-disc assemblies. Specification G-13-01 in HASL Procedures Manual.
3. Cellulose acetate, membrane filters 25 mm diameter (0.45-micron pore size).
4. Aluminum foil (approx. 7 mg/cm^2).
5. Centrifuge with a head for 40 to 50-ml centrifuge tubes.
6. Combination stirrer-hot plate.
7. Separatory funnels with Teflon stopcocks (250 ml, 500 ml and 1 litre sizes).
8. Teflon-coated magnetic stir-bars. 10 x 3 mm size, for use in centrifuge tubes.

*Radiochemical Determination of Lead-210 in Environmental Samples and Samples resulting from Uranium Mining-Milling Operations. Smithson, G., Fahri, M. and Petrow, M. Method developed under a contract with E.M.R. See Appendix B.

9. Atomic Absorption Spectrophotometer and Bi Lamp.
10. Lead-210 Standard Solution — Available from Amersham, Oakville, Ontario.

REAGENTS

1. DDTC Extractant (0.1% and 1.0%) — dissolve 0.50 g of diethylammonium diethyldithiocarbamate (for 0.1%) and 5.00 g (for 1%) in 500 ml of chloroform. Make up fresh as required.
2. Mixed Lead-Bismuth carrier solution — dissolve 2.321 g of $Bi(NO_3)_3 \cdot 5H_2O$ and 1.598 g of $Pb(NO_3)_2$ in 10% HNO_3 and dilute to 1 litre. One millilitre of this solution contains 1 mg each of lead and bismuth.
3. Bismuth carrier solution — dissolve 11.605 g of $Bi(NO_3)_3 \cdot 5H_2O$ in 10% HNO_3 and dilute to one litre. One ml of this solution contains 5 mg of Bi.

SAMPLE PREPARATION

WATER SAMPLES — For acidified samples that are clear or have been filtered, take 1010 ml for analysis and add 190 ml of concentrated HCl plus 1 ml of mixed carrier solution. Proceed to the DETERMINATION.

If the sample contains organic constituents or suspended matter, treat 1010 ml with 1 ml of mixed carrier solution, 10 ml of HNO_3 and 3 ml of $HClO_4$. Evaporate and heat to strong fumes of perchloric acid. Repeat the HNO_3-$HClO_4$ treatment if necessary to destroy all organic matter. Dilute to 165 ml with deionized water and add 35 ml of concentrated HCl. Proceed to the DETERMINATION.

BIOLOGICAL SAMPLES — Ash the samples by either a combination of wet ashing with HNO_3 followed by dry ashing, or by dry ashing alone.* The final ashing temperature should be kept below 500-550°C. To 1 g of the prepared ash add 1 ml of the mixed carrier solution and 10 ml of HNO_3. Evaporate until about one-half of the HNO_3 has been removed, then add 40 ml of water plus 10 ml of HCl and heat until a clear solution is obtained. Add an additional 75 ml of HCl and dilute to 500 ml with deionized water. In some cases the ash may dissolve directly in HCl alone. If so, make the final solution 2N in HCl. Proceed to DETERMINATION.

ORE, ROCK AND SOIL SAMPLES — Weigh a 1 g sample into a 200-ml beaker and add 1 ml of mixed carrier solution followed by 10 ml of HNO_3 and 10 ml of $HClO_4$. Heat on a hot plate until fumes of $HClO_4$ are evolved and all organic matter has been oxidized. If necessary, add more HNO_3 and $HClO_4$ and redigest. Evaporate the solution until about 1 ml of $HClO_4$ remains. Cool, add 50 ml of 10% HCl and boil for 5 minutes to dissolve bismuth phosphate and metallic sulphates. Transfer the contents of the beaker to a centrifuge tube, centrifuge and return the solution to the beaker. Transfer the solid residue to a Teflon beaker and treat with 2 ml of H_2SO_4 and 10 ml of HF. Evaporate slowly to SO_3 fumes, cool slightly and add 20 ml of 10% HCl. If any barium sulphate precipitate forms at this stage it may be separated by centrifuging and discarded. The presence of HCl in the solution will prevent traces of lead or bismuth from being carried by the barium sulphate precipitate. Combine this solution with the main digest solution, add 26 ml of HCl and dilute to 200 ml. Add sufficient ascorbic acid to the hot solution to reduce all ferric iron present and leave an excess of about 0.5 g. If it is known that the sample contains more than 0.5 mg of copper, or if the subsequent extraction with DDTC turns a very dark brown to black, it will be necessary to pre-extract the copper. This is done by making the final sample digest solution 8M in HCl and repeatedly extracting with 20-ml portions of 1% DDTC in chloroform until a light-coloured extract is obtained. Now dilute the solution to 2M in HCl and proceed to the DETERMINATION.

DETERMINATION

1. For water and mill solutions that have been captive for less than 30 days it will be nec-

*Gibson, W.M., "The radiochemistry of lead, Nuclear Science Series"; National Academy of Sciences and National Research Council. NAS-NS-3040 (1961) available from NTIS.

essary to extract and discard the bismuth and then allow a definite time for ingrowth of bismuth-210 (half-life 5 days). Following the ingrowth period, the newly-formed bismuth-210 is extracted and analyzed as usual. The bismuth extractions are performed according to the following steps.

2. Transfer the prepared sample solution (2M HCl) to an appropriately-sized separatory funnel. Add a suitable volume of 0.1% DDTC extractant (10 ml for 200-ml samples and 20 ml for 500- to 1000-ml samples) and shake vigorously for 1 minute. Note the time as the beginning of the Bi-210 decay.
3. Drain the organic extract into a suitably-sized beaker (50-ml beaker for 10-ml extracts or 100-ml beaker for 20-ml extracts).
4. Repeat the extractions until a colourless organic phase is obtained. Normally, the first two extractions will be yellow and the third colourless. If small amounts of copper, selenium, antimony, arsenic or molybdenum are present it may be necessary to perform a further 2 to 3 extractions before obtaining a final colourless extract.
5. Combine all extracts and evaporate to dryness.
6. Dissolve the residue in 5 ml of HNO_3 and heat gently until all organic residue is destroyed.
7. Dilute to 25 ml and transfer 1.0 ml to a 10-ml volumetric flask. Dilute to the mark and determine bismuth by atomic absorption spectrometry. From this determination, calculate the recovery of bismuth through the extraction procedure.
8. Transfer the remaining 24 ml of the sample solution to a 40-ml centrifuge tube and add an additional 5 mg of bismuth carrier (1 ml of the bismuth carrier solution). This addition is to provide an amount of bismuth which is convenient to handle in the following precipitation separation.
9. Adjust the solution to pH 8 using NH_4OH. A combination pH-reference electrode allows this to be done directly in the centrifuge tube. At this pH, bismuth oxychloride, bismuth hydroxide and other metallic hydroxides will precipitate. Heat the centrifuge tube in a beaker of hot water on a stirrer-hot plate and stir for 5-10 min with a small magnet in the centrifuge tube.
10. Remove the centrifuge tube, cool in cold water and centrifuge. Discard the supernate.
11. Dissolve the precipitate with 5 drops of HCl and then dilute to 40 ml with deionized water. Heat the sample with stirring as in Step 9. This time only bismuth oxychloride will precipitate.
12. The BiOCl precipitate may be prepared in two ways for counting. The first is to filter it through a 0.45μ membrane filter in a HASL ring-and-disc filter assembly, air dry briefly, then cover with Al foil and push the ring in place. The second is to transfer the BiOCl precipitate to a ringed, stainless steel planchette. Centrifuge the precipitate first and discard the supernate. Wash with a few mls of water, centrifuge and decant. Then wash with a few mls of ethanol and centrifuge. Discard the washes. Re-slurry in about 1 ml of ethanol and transfer to the planchette. Dry under a heat lamp and cover with aluminum foil.
13. Allow 12 to 18 hours for the decay of bismuth-211, bismuth-212 and bismuth-214. The samples are then counted in a low-background, flow proportional beta counter. Alternatively, the sample can be contacted with a beta phosphor disc and counted in a bare-photomultiplier scintillation counter.
14. Analyze a series of standards (0.1 to 1000 pCi Pb-210) and blanks starting with the solvent extraction. A calibration curve plotted from these values will contain an averaged correction for the recovery of bismuth in the BiOCl precipitation.

CALCULATIONS

Correct all observed count rates for the ingrowth of bismuth-210, the decay of bismuth-210 and the recovery of bismuth in the solvent extraction. As previously mentioned it is assumed that the recovery of bismuth in the BiOCl precipitation

will be sufficiently reproducible that it can be incorporated in the calibration curve. The corrected count rate is calculated as follows:

$$R_c = \frac{R_n}{E.e^{-\lambda t_2}(1 - e^{-\lambda t_1})}$$

where R_c = the corrected net count rate
R_n = the observed net count rate (observed gross count rate minus the blank's count rate)
E = the fractional recovery of bismuth in the solvent extraction as determined by A.A. spectrometry
λ = the decay constant for bismuth-210 (0.1386 $days^{-1}$)
t_1 = the length of the ingrowth period for bismuth-210 (days)
t_2 = the time elapsed between the completion of the solvent extraction and the counting of the prepared planchette (days)

If the BiOCl precipitate is deposited on a planchette for counting a separate correction for the recovery of BiOCl can be made. The weight of BiOCl on the planchette is determined by weighing the planchette before and after the deposition. An additional correction factor, which goes in the denominator of the previous equation, is calculated as follows:

$$F = \frac{W}{E + 5}$$

where F = the additional correction factor for the recovery of bismuth in the BiOCl precipitation
W = the weight of bismuth contained in the BiOCl precipitate (mg)
E = the fractional recovery of bismuth in the solvent extraction. This equals the weight of bismuth because the amount present for the extraction was one milligram
5 = the weight of bismuth added prior to the BiOCl precipitation (mg).

If this extra correction is to be used it must also be applied to the standard samples before plotting the calibration curve.

The calibration curve is prepared by making a log-log plot of R_c (cpm) for the standards vs the amount of lead-210 (pCi) in the standard. The corrected net count rate for the samples is used to read off the amount of lead-210 present in the sample aliquot.

PRECISION AND DETECTION LIMIT

The relative standard deviation for this method is approximately ± 4% of the amount present for levels above 10 pCi of lead-210. The detection limit for a 100-minute count and a reagent blank of 0.3 cpm is approximately 0.5 pCi of lead-210.

THE DETERMINATION OF POLONIUM-210

PRINCIPLE

Polonium is preferentially separated from prepared HCl solutions by spontaneous deposition on silver metal. The prepared silver disc is alpha counted and compared to similarly prepared standards to determine the amount of polonium-210 present.

APPLICATION

The method is extremely specific for polonium-210. In some cases, traces of other radionuclides such as lead and bismuth can be adsorbed or deposited on the silver. Of these, only bismuth has an alpha-emitting isotope with a half-life long enough to be a potential interference. However, even this isotope, bismuth-212, with a half-life of 60.5 minutes, will have decayed completely if the prepared silver discs are stored 24 hours before being alpha counted. The half-life of polonium-210 (138.4 days) is long enough that the discs can be stored for a few weeks without a serious loss in the sensitivity of the method.

Iron is the only major interference in the spontaneous deposition of polonium on silver. This problem can be eliminated by adding an excess of ascorbic acid which reduces all iron to the non-interfering ferrous state. Selenium and tellurium may form coloured deposits on the silver but the levels normally encountered do not interfere with the deposition of polonium.

The main problem encountered in analyzing for polonium is the preparation of solutions from solid samples. Soil, ore and rock samples should not be dissolved or fused in platinum vessels as there is a high probability that significant amounts of polonium may plate out on the platinum. For this reason such samples should be digested in Teflon or glass. Biological samples cannot be dry ashed because of the extremely low volatility of polonium and some of its compounds. It is necessary to use wet ashing techniques to bring these samples into solution. Another problem that is encountered when handling solutions containing polonium is the formation of radiocolloids (which adsorb on traces of suspended matter) and the physical adsorption of polonium on metals, glass and plastics, even in acid solutions. Losses of polonium during sample preparation can be determined by adding polonium-208 as a tracer at the beginning of the procedure. Polonium-208 is an alpha emitter (5.11 MeV) and can be determined simultaneously with polonium-210 (5.305 MeV) if a surface barrier detector-multichannel analyzer is employed for counting. If gross alpha counting techniques are used, an estimation of polonium losses can be made by digesting and analyzing sample aliquots spiked with polonium-210.

APPARATUS

1. Alpha counting system
   (a) Surface barrier detector-multichannel analyzer system.
   (b) Bare-photomultiplier, scintillation counting system employed with ZnS-Mylar discs (HASL Procedures Manual, Specification G-11-01).
   (c) Low-background flow-proportional counting system.
2. Silver discs — 0.015 in. thick by 1 in. diameter or any other convenient size. Available from Johnson, Mathey and Mallory, 110 Industry St., Toronto, Ontario, M6M 4M1, or Engelhard Industries, 512 King St. East, Toronto, Ontario, M5A 1M2. These discs can be re-used several times by cleaning with powdered Bon Ami household cleanser after each use.
3. Spontaneous deposition cell.
   (a) Plastic nursing bottle. Modified as in Figure 1, or
   (b) Silver-disc holder for use in beakers. Figure 2.
4. Stirring motor with glass stirrer for cell 3(a).
5. Hot water bath to operate at 90°C for cell 3(a).
6. Magnetic stirring, hot plate for use with cell 3(b).
7. Teflon-coated stir-bars (1 inch x 3/8 inch).

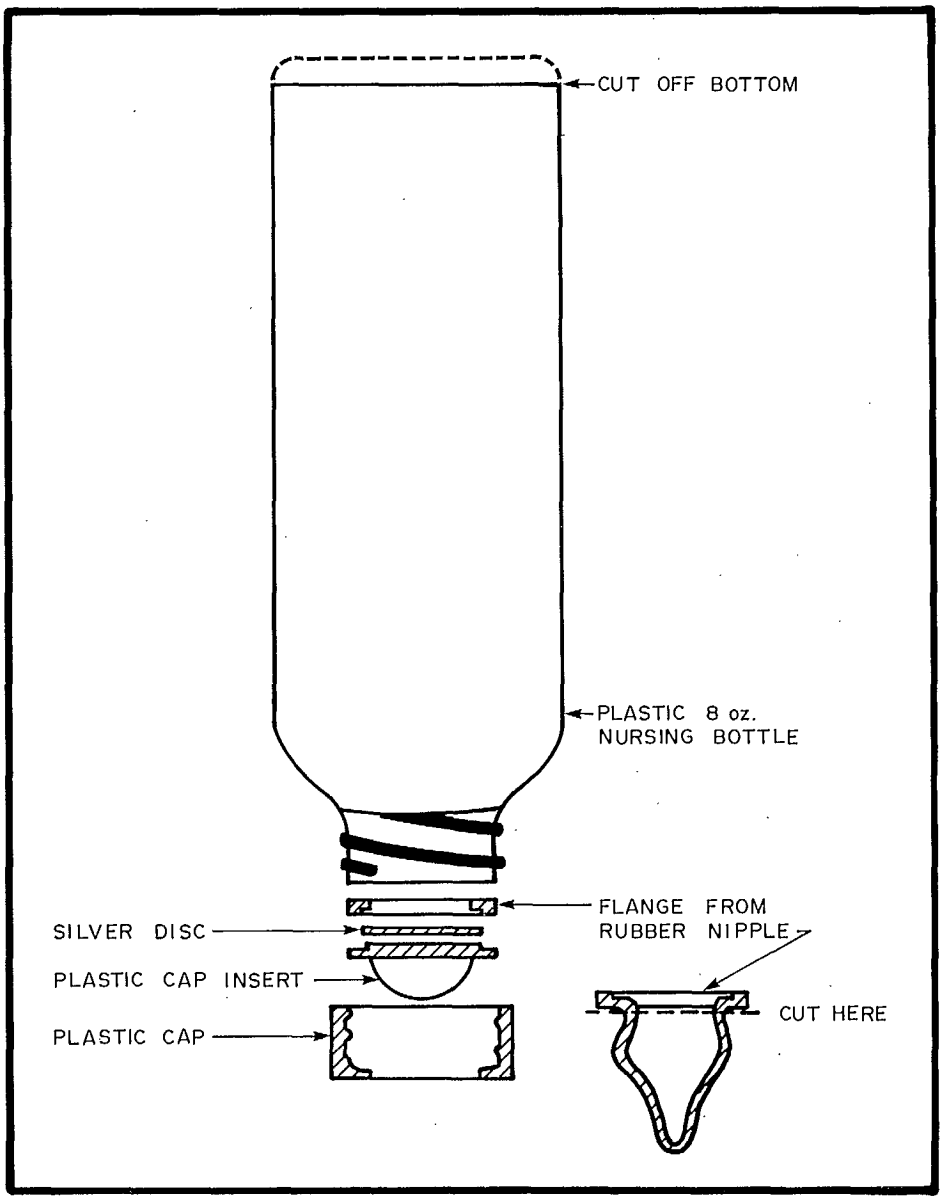


Fig. 1 Nursing Bottle Plating Assembly. (From — Radioassay Procedures for Environmental Samples, National Center for Radiological Health, Rockville, Maryland. January 1967. Available from NTIS.)

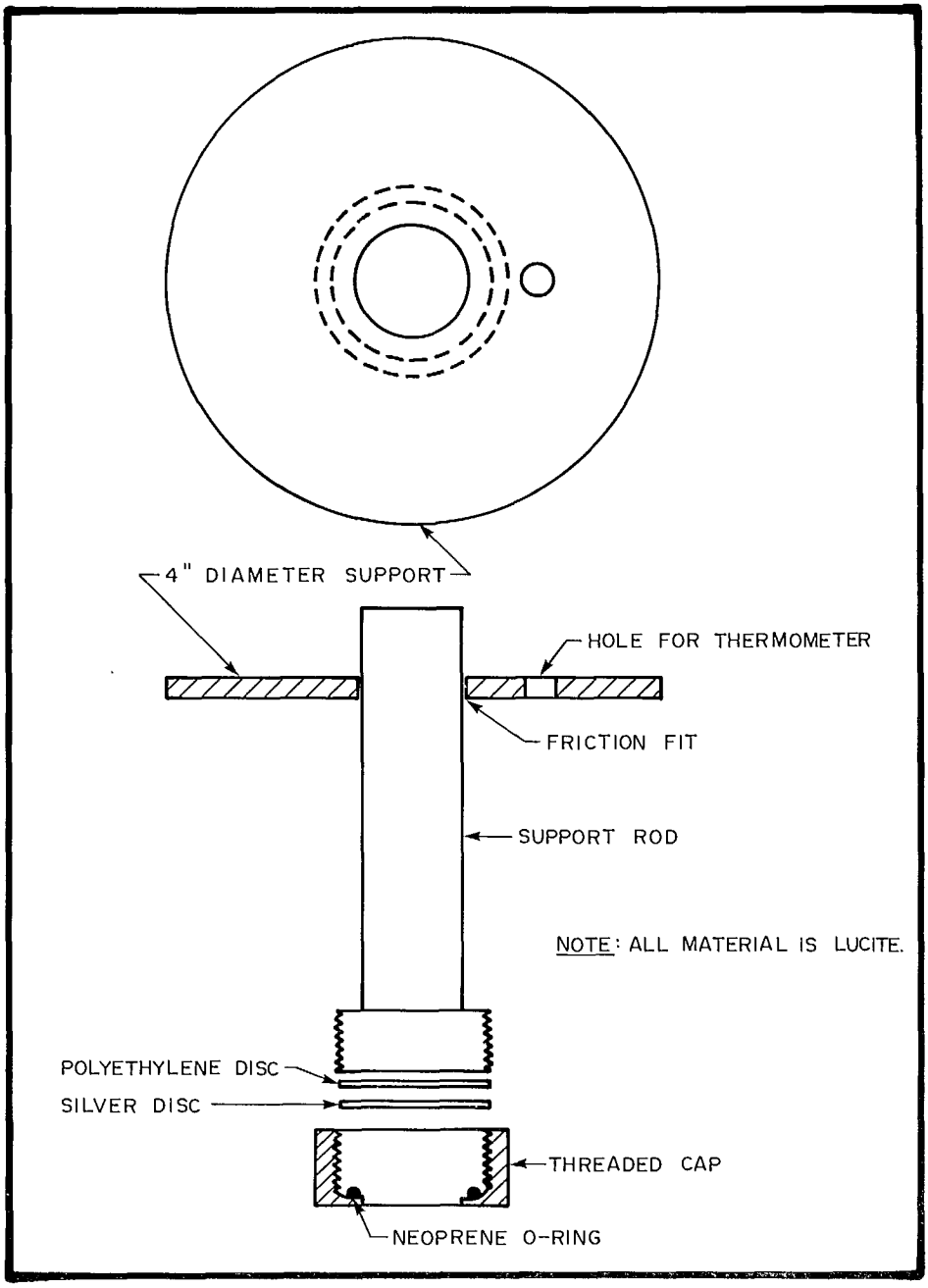


Fig. 2 Plating Holder for Silver Disc.

REAGENTS

1. L-Ascorbic Acid, powder.
2. Lead carrier solution (10 mg Pb/ml) — dissolve 15.98 g of $Pb(NO_3)_2$ in 1% HNO_3 and dilute to 1 litre.
3. Thioacetamide solution — 100 g of thioacetamide per litre of water.
4. Standardized Po-208 tracer solution — dilute stock solution to give approximately 10 dpm per ml. Store in a polyethylene bottle. Polonium-208 is available from Amersham, Oakville, Ontario.
5. Standardized Po-210 solution — a standard Pb-210 solution in which Po-210 is in secular equilibrium. May be purchased from Amersham.

SAMPLE PREPARATION

WATER SAMPLES AND SOLUTIONS — Transfer one litre of sample to a 1-litre beaker, add 5 ml of perchloric acid and evaporate to fumes of perchloric acid to destroy all organic matter and remove the HNO_3 added for sample preservation. Continue the evaporation until 1-2 ml of perchloric acid remains. Cool, add 4.3 ml of concentrated HCl and dilute to 100 ml with deionized water. Add 200 mg of ascorbic acid and proceed to DETERMINATION.

SOIL AND ROCK SAMPLES — Weigh a 1-g sample into a Teflon or Pyrex beaker. Add 1 ml each of lead carrier solution and Po-208 tracer solution. Add 10 ml of HNO_3 and 10 ml of 48% HF. Heat moderately so that the solution does not boil and repeat the additions of HNO_3 and HF until no further dissolution takes place. Add 10 ml of HNO_3 and reduce the volume to about 5 ml. If any residue remains, transfer the solution to a centrifuge tube, centrifuge and discard the insol. Dilute to about 35 ml and adjust the pH to 3.5 to 4 with NH_4OH. Add 5 ml of thioacetamide solution and digest for 1 hour in a steam or hot water bath. Cool, centrifuge and discard the supernate. Dissolve the precipitate in 2 ml of HCl and dilute to about 35 ml. Repeat the adjustment of the pH and the precipitation with thioacetamide as before. After the 1-hour digestion, cool, centrifuge and discard the supernate. Dissolve the precipitate in 4.3 ml of HCl and dilute to 100 ml. Filter through a Whatman #41 paper, wash with 0.5N HCl and add 200 mg of ascorbic acid. Proceed to DETERMINATION.

BIOLOGICAL SAMPLES — Due to the extreme volatility of polonium, biological samples must be prepared by wet ashing. The digestion of vegetation samples with nitric acid is not too difficult but the nitric-perchloric digestion required for flesh and bone samples is both time-consuming and dangerous. The main danger results from the quantity of organic material that must be digested at one time. Thousands of nitric-perchloric digestions have been performed in this laboratory on a wide variety of samples without mishap. In all cases, however, the digestion was carried out on no more than 1 to 2 g of organic material. Much larger quantities of flesh and bone must be digested for radiochemical analyses and there is a natural tendency to rush the initial nitric acid digestion process. If perchloric is added before most of the organics have been destroyed by nitric acid, the subsequent reaction on heating can be explosive. Unless one has extensive experience in performing small-scale nitric-perchloric digestions these large-scale digestions should not even be attempted. In the event that this digestion must be performed, complete familiarity with the monograph on the use of perchloric acid by G.F. Smith* is essential. The only sample preparation technique that will be detailed here is the somewhat less-hazardous nitric acid digestion of vegetation.

Dry the vegetation sample at 105°C until constant weight is reached. Weigh 100 g of the dried sample into a 600 to 1000-ml beaker. Add 1 ml of lead carrier solution and, if desired, 1 ml of the polonium-208 tracer solution. Add 100 to 200 ml of nitric acid and stir with a Teflon stirbar on a magnetic stirrer-hot plate at low heat for 1 hour or more. Evaporate to a final volume of about 25 ml. Split the solution between two

*G.F. Smith, "The wet ashing of organic matter employing hot concentrated perchloric acid"; Anal. Chim. Acta; 8:397; 1953.

50-ml centrifuge tubes and evaporate on a steam bath to about 5 ml in each tube. Dilute each to about 35 ml and adjust the pH to 3.5-4.0 with NH_4OH. Add 3 ml of thioacetamide solution to each tube and digest for 1 hour on a steam bath. Cool the samples and centrifuge one of them, discarding the supernate. Transfer the second sample slurry to the tube containing the precipitate from the first. Again centrifuge and discard the supernate. Dissolve the combined precipitates with 2 ml of HCl. Dilute to 35 ml, adjust the pH to 3.5-4.0 and repeat the precipitation with 2 ml of thioacetamide solution. Digest for 1 hour on the steam bath, cool, centrifuge and discard the supernate. Dissolve the lead sulphide in 4 ml of HCl and dilute to 100 ml. Filter the solution through Whatman #41 filter paper, wash with 0.5N HCl and add 200 mg of ascorbic acid. Proceed to the DETERMINATION.

DETERMINATION

1. Transfer the prepared sample solution to an assembled plating cell as in Figure 1 or alternatively, transfer to a 150 or 200-ml beaker if the apparatus of Figure 2 is to be used.
2. If the Figure 1 apparatus is used, clamp it in a 90°C water bath and stir the sample with a motor-driven glass or Teflon stirrer. Reduce the speed so that there is no splashing in the cell. If the apparatus of Figure 2 is used, place a Teflon-coated stir-bar in the beaker, set the disc holder in place and then stir and heat at 90°C on a combined stirrer-hot plate.
3. Continue the self deposition of polonium for at least 2 hours.
4. At the end of the plating period transfer the liquid from the Figure 1 cell to a beaker and save for lead-210 analysis if desired. If the Figure 2 apparatus is used, remove the assembly from the beaker and save the solution if required.
5. Dismantle the cell or assembly, rinse the disc with water and then with ethanol. Store the disc for a minimum of 24 hours if either of the gross counting techniques are to be used. If alpha spectrometry is to be performed, the disc may be counted immediately.
6. Analyze a series of polonium-210 standards (0.1 to 1000 pCi) and several blanks by performing only the self deposition in the presence of ascorbic acid in 0.5N HCl. Plate for exactly the same length of time as the samples. The recovery of polonium through the sample preparation stage can be determined from the Po-208 result obtained from the Po-210 calibration curve.

CALCULATIONS

Prepare a calibration curve by plotting the corrected count rates for the Po-210 standards vs the amount of polonium present (pCi) on log-log paper. The corrected count rate is calculated as follows:

$$R_c = \frac{R_n}{e^{-\lambda t}}$$

where R_c - is the corrected count rate

R_n - is the observed net count rate (the observed gross count rate minus the "blank" count rate).

λ - is the decay constant for Po-210 ($0.005008\ day^{-1}$).

t - the time elapsed between the self deposition and the counting of the sample (days).

Samples that have not been traced with Po-208 are read directly from the calibration curve after correcting for decay of Po-210. For samples that are traced with Po-208 an additional correction for recovery through the sample preparation stage can be made. The sample result read from the calibration curve is divided by the ratio of added polonium-208 to polonium-208 recovered. The amount of polonium-208 recovered is determined from the polonium-210 calibration curve. In all cases the correction for plating efficiency is included in the calibration curve.

PRECISION AND DETECTIDN LIMIT

The relative standard deviation of this method is approximately ±5% of the amount present for Po-210 levels above 10 pCi. The detection limit by alpha spectrometry with a blank level of 0.05 cpm and for a 100-minute count is about 0.05 pCi. Gross alpha-counting methods will have a detection limit of about 0.1 to 0.2 pCi due to their higher background count rates.

DETERMINATION OF RADIUM BY BARIUM SULPHATE PRECIPITATION AND GROSS ALPHA COUNTING

PRINCIPLE

Radium is removed from prepared sample solutions by coprecipitation with lead sulphate. The lead sulphate is then dissolved in alkaline EDTA (or DTPA), barium carrier added and barium sulphate preferentially precipitated by lowering the pH to 4.5. Radium coprecipitates with the barium sulphate which is redissolved and reprecipitated to remove traces of other radionuclides (lead, bismuth, thorium). This purified barium (radium) sulphate is filtered on a membrane filter, contacted with a zinc sulphide-Mylar disc and the alpha disintegrations counted on a bare-photomultiplier scintillation counter. The ingrowth of the radium daughters increases the sensitivity of the method and the degree of this ingrowth must be taken into account when calculating results. The method is not specific for radium-226. Other alpha-emitting radium isotopes (radium-224 from the thorium series and radium-223 from the actinium series) must be corrected for by differential decay analysis. Refer to Method Ra-02 for further discussion of the interference of these two isotopes in Ra-226 determinations.

APPLICATION

Although this method is not specific for radium-226 it has certain advantages over the emanation method. These are the greater number of samples that can be processed in a given time and the lower cost and quantity of apparatus required. For ores that contain low levels of thorium this method is one of the most convenient for rapid, routine monitoring. The radium-223 associated with the normal 140:1 ratio of uranium-238 to uranium-235 will contribute a positive 4.4% error when a 6-day ingrowth period is employed. For ingrowth periods less than 6 days the positive error due to radium-223 is much greater. The error reaches a maximum of 17.4% at 1 to 5 hours ingrowth and then drops to 11.8% at 1 day, 8.7% at 2 days, 6.9% at 3 days, 5.7% at 4 days and 5.0% at 5 days. For environmental levels below 1 pCi this error is not significant but when accurate values of radium-226 at high levels are required it must be taken into account.

Waste streams that have been treated by the precipitation of barium sulphate may have levels of radium-223 many times higher than that of radium-226. In these cases it is best to determine radium-226 by the emanation method.

APPARATUS

1. Bare-photomultiplier scintillation counting system.
2. HASL ring-and-disc filter assemblies. Specification G-13-01 in HASL Procedures Manual.
3. Zinc sulphide-Mylar discs. Specification G-11-01 in HASL Procedures Manual.
4. Mylar film. Specification G-03-01 in HASL Procedures Manual.
5. Centrifuge with head for 40-ml or 50-ml centrifuge tubes.
6. Combination hot plate – magnetic stirrer.
7. Teflon-coated stir-bars. 10 x 3 mm, for use in centrifuge tubes. One-inch stir-bars for use in beakers.

REAGENTS

1. 1N Lead nitrate – dissolve 3.30 g of $Pb(NO_3)_2$ in deionized water and dilute to 100 ml.
2. 0.25M EDTA – dissolve 40 g NaOH in approximately 300 ml of water in a 1-litre beaker. While still hot add 73 g of ethylene diaminetetraacetic acid and mix until dissolved. Cool and dilute to 1 litre. Adjust the pH to 10 using NaOH or perchloric acid. Filter if necessary and store in a polyethylene bottle. For 0.17 M DTPA use 32 g of NaOH and 67 g of diethylenetriaminepentaacetic acid and prepare as for EDTA solution.
3. 0.0343 M $BaCl_2$ – dissolve 7.143 g of $BaCl_2$ (or 8.38 g of $BaCl_2.2H_2O$) in water and dilute to 1 litre. One ml of this solution is equivalent to 8.0 mg of $BaSO_4$.
4. 20% Na_2SO_4 – dissolve 20 g of reagent grade

sodium sulphate in 1 litre of deionized water.

5. 6M acetic acid — dilute 345 ml of glacial acetic acid to 1 litre.
6. Radium-226 Stock Standard — One microcurie of Ra-226 plus the associated $BaCl_2$ carrier are diluted to 100 ml with 5% HNO_3. Store in a Teflon FEP or polypropylene container. Radium-226 is available from Amersham, Oakville, Ontario.

SAMPLE PREPARATION

WATER SAMPLES — For total Ra-226 the sample is normally acidified to 1% HNO_3 in the field. Samples for dissolved Ra-226 are filtered through a 3-micron membrane filter* and then acidified to 1% HNO_3. If the level of Ra-226 is below 100 pCi/l, use one litre of sample. Take 500 ml of sample for levels between 100 and 1000 pCi/l and proportionately less for higher concentrations. Treat the sample with 5 ml of perchloric acid and evaporate to $HClO_4$ fumes to destroy all organic matter. Dilute back to a suitable volume (300 to 400 ml) and go to Step 1 of the procedure. Water samples that do not contain organic or suspended matter do not require the perchloric acid digestion. Start at Step 1 of the determination with such samples.

BIOLOGICAL SAMPLES — All biological samples are ashed and an aliquot of the ash is dissolved in acid to provide the solution for analysis. Samples of flesh and vegetation are dried and charred at low temperatures on a hot plate before they are ashed in a muffle furnace. Suitable containers for the entire ashing operation are porcelain evaporating dishes or stainless steel trays. The final temperature for ashing flesh and vegetation should be kept below 550°C. Samples of bone may be ashed at temperatures up to 800°C. Normally, it is necessary to remove the samples from the furnace at intervals and grind and mix the residue to ensure complete oxidation. In most cases a very white ash can be obtained with continued heating, grinding and mixing. For a very detailed discussion of ashing techniques see Procedure E-Sr-01 in the HASL Procedures Manual. When ashing is complete, a 1-g sample is dissolved in 1:1 HNO_3, diluted to a suitable volume (300-400 ml) and analyzed starting with Step 1 of the determination. It is good practice to add carriers as early in the procedure as possible so as to minimize losses of the radionuclide analyte which may occur through adsorption and coprecipitation. Therefore, it is recommended that the lead carrier be added during the 1:1 HNO_3 dissolution rather than at Step 2.

SOIL, ORE and ROCK SAMPLES — Most soil and rock samples can be dissolved by first performing a fusion with potassium pyrosulphate or sodium carbonate and then dissolving the melt in hydrochloric or nitric acid. For the pyrosulphate fusion, weigh a dried, 1-g sample into a platinum crucible, ash all organic matter by heating over a burner or by heating overnight at 550°C in a muffle furnace. Add 3 ml of H_2SO_4, 10-20 ml of HF and heat on a hot plate to drive off the silicon tetrafluoride and excess HF. Repeat with the addition of HF if necessary to remove all silica. Heat to strong fumes of SO_3 and cool. Add 5 g of potassium pyrosulphate and begin heating over a gas burner. Continue heating and swirling until a clear melt is obtained. Cool and dissolve in 100 ml of 10% HCl. Dilute to 200 ml and proceed with the DETERMINATION. Some samples may be brought into solution more readily with a sodium carbonate fusion. We have found no difference in the determined radium concentrations for samples prepared by either type of fusion. Samples containing phosphates or sulphides may cause severe attack on platinum when fused by either method. For such samples an acid digestion with HCl-HNO_3 followed by fuming with $HClO_4$ is to be preferred. The residue remaining from the acid digestion may then be safely fused in platinum, dissolved and added to the acid digest.

Another fusion procedure which is very effective on larger soil and ore samples is the

*or, as specified in the appropriate regulation.

KF-pyrosulphate fusion of Sill*. This method requires large platinum dishes and a blast burner and must be performed in a fume hood. It can be used to advantage when several radionuclides are to be determined on the same sample.

DETERMINATION

1. To 1 litre of the prepared sample solution add 20 ml of 1:1 H_2SO_4 and 40 g of K_2SO_4. Use proportionately less acid and K_2SO_4 for volumes less than 1 litre. Heat the solution to near boiling.
2. Add (dropwise) 2 ml of 1N $Pb(NO_3)_2$ to the hot sample solution while stirring with a magnetic stirrer.
3. Maintain the temperature just below the boiling point and continue stirring for 30 minutes.
4. Remove from the stirrer-hot plate, remove the stir-bar and allow the precipitate to settle for one hour or overnight if possible.
5. Siphon off most of the clear supernate. Wash the precipitate into a 50-ml centrifuge tube using the residual supernate as wash solution. Centrifuge and discard the supernate.
6. Dissolve the lead sulphate precipitate in 15 ml of 0.25M EDTA (or 0.17M DTPA). Place the centrifuge tube in a beaker of water heated on a stirrer-hot plate and stir with a 10 x 3 mm stir-bar.
7. If any undissolved residue remains at this stage it may be centrifuged and discarded.
8. Add 1 ml of 0.0343M $BaCl_2$ to the lead sulphate solution and mix.
9. Add 1 ml of 20% sodium sulphate and 11 ml of deionized water. Mix thoroughly.
10. While swirling the solution in the centrifuge tube, add 2 ml of 6M acetic acid. Place the centrifuge tube in a beaker of hot water on a stirrer-hot plate and stir for 5 minutes.
11. Cool the sample in a cold water bath for 5 minutes and then centrifuge. Discard the supernate.
12. Redissolve the barium sulphate in 7.5 ml of 0.25M EDTA (or 0.17M DTPA) with heat and stirring.
13. Add 1 ml of 20% sodium sulphate and 10 ml of deionized water. Mix thoroughly.
14. With constant swirling add 1 ml of 6M acetic acid. Reprecipitate the barium sulphate with heat and stirring. Record the time of this second precipitation as the beginning of the ingrowth of the radium daughters.
15. After digesting the precipitate for 5 minutes, filter through a HASL ring-and-disc filter assembly using a 0.45-micron cellulose acetate membrane filter.
16. Continue drawing air through the precipitate for several minutes to remove excess water. Separate the disc and filter chimney and place a zinc sulphide-Mylar disc on top of the precipitate (zinc sulphide coating in contact with the barium sulphate precipitate). Cover with Mylar film and press the ring into position.
17. After allowing a suitable time for daughter ingrowth the sample is counted on a bare-photomultiplier, scintillation counter. A 6-day ingrowth period will give 75% of the maximum attainable sensitivity.
18. If a scintillation-type counter is not available it will be necessary to perform the gross alpha count with a gas-flow proportional counter or a surface barrier detector. For these systems, the barium sulphate is filtered in an ordinary membrane filter assembly and the membrane filter plus precipitate must then be mounted on a planchette or a holder which can be accommodated by the counter.
19. Prepare a calibration curve by carrying a series of radium concentrations (0.1 to 1000 pCi/l) and a reagent blank through the entire procedure. One or two standards and a blank should be processed with each set of samples as a check on the recovery of Ra-226 and the level of contamination on glassware and in reagents.

*Sill, C.W., Puphal, K.W. and Hindman, F.D. Anal. Chem; 46:1725-1737; 1974.

CALCULATIONS

Prepare a calibration curve by plotting the net counting rate of the standards vs their total Ra-226 content in pCi (log-log plot). These count rates must be corrected to a standard ingrowth period. Either zero ingrowth or a six-day ingrowth (75% of equilibrium) period is convenient. All sample count rates are converted to this standard ingrowth period before they are read from the graph. The conversion is as follows:

$$Rc = Rn \cdot \frac{4 - 3e^{-\lambda t_o}}{4 - 3e^{-\lambda t}}$$

where Rc = net count rate corrected to standard ingrowth period.

Rn = measured net count rate (gross count rate minus background count rate)

λ = decay constant for Rn-222 (0.1810 day^{-1})

t_o = standard ingrowth time, days.

t = time elapsed between second barium sulphate precipitation and the mid-point of the count period, days.

The factor of 3 in the numerator and denominator of the equation is for the three alpha emitting daughters of Ra-226, namely, Rn-222, Po-218 and Po-214.

For samples in which all of the U-238 and U-235 decay products are in secular equilibrium, a factor can be calculated to correct the determined radium-226 value for the presence of radium-223. Table 1 contains calculated values of the factor by which the experimental radium-226 levels must be divided to correct for various ingrowth periods. This ingrowth is the actual time period between preparation and counting and should not be confused with the standardized ingrowth period.

TABLE 1

Correction factors for the contribution of radium-223 to gross alpha, radium count rates at various ingrowth periods. The initial radium-223 activity is assumed to be 4.67% of the radium-226 activity (when U-235 is 0.71% of U-238 and all daughters are in secular equilibrium). The corrected radium-226 value is the observed value divided by the factor.

INGROWTH PERIOD hours	Correction Factor	INGROWTH PERIOD days	Correction Factor	INGROWTH PERIOD days	Correction Factor
1	1.168	2	1.087	9	1.032
2	1.174	3	1.069	10	1.029
3	1.173	4	1.057	11	1.027
5	1.167	5	1.050	12	1.024
10	1.150	6	1.044	13	1.023
24	1.118	7	1.038	14	1.021
		8	1.035	15	1.020

PRECISION AND DETECTION LIMIT

The relative standard deviation for this method is approximately ±10% of the amount present for levels above 5 pCi. Below 5 pCi this RSD increases gradually to ±100% at 0.1 pCi, which is the detection limit for a 100-minute count with a background of 0.05 cpm.

DETERMINATION OF RADIUM-226 BY THE EMANATION METHOD

PRINCIPLE

A prepared solution of radium-226 is first stripped of radon-222 which is then allowed to grow back into the solution for a definite time period. The ingrown radon-222 is then stripped from the solution and transferred to a sealed, ZnS-coated, scintillation cell. The scintillations produced in the ZnS by the alpha emissions of radon and its daughters are counted by means of a bare-photomultiplier scintillation counter. The method is very specific for radium-226.

APPLICATION

This is the preferred method for determining radium-226 in the presence of high levels of radium-223 and radium-224. It is much less sensitive to these interferences than the gross alpha counting method. For example, a 100:1 ratio of radium-223 to radium-226 would result in an error of approximately 2300% if the sample was counted, by the gross alpha method, after a 6-day ingrowth period and all the activity was assumed to be radium-226. The emanation method, with a 6-day ingrowth period, would result in an error of less than 8%. The presence of high levels of radium-224 would result in similar errors for the two methods. Consequently, in mill discharges that have abnormally high radium-223 to radium-226 ratios or any sample containing high levels of thorium-232, the quickest and most accurate method for determining radium-226 is this emanation method.

The one disadvantage of the emanation method is the large capital expenditure required to equip a laboratory with sufficient scintillation cells and bubblers to perform a large number of determinations on a routine basis. This can be overcome to some extent by in-house fabrication of scintillation cells and radon bubblers. Another disadvantage is that the emanation method is more time-consuming than the gross alpha-counting method.

APPARATUS

1. Bare-photomultiplier scintillation counting system.
2. Radon scintillation cells. Lucas cells or similar type. May be purchased from the following suppliers:
   (a) EDA Instruments Inc., 1 Thorncliffe Park Drive, Toronto, Ontario M4H 1G9.
   (b) Rocky Mountain Scientific Glass Blowing Co., 2520 Galena St., Aurora, Colorado, 80010.
   (c) Johnston Laboratories, Inc., 3 Industry Lane, Cockeysville, Maryland, U.S.A. 21030.

   Alternatively, scintillation cells may be fabricated according to the design of A.C. George (Scintillation Flasks for the Determination of Low-Level Concentrations of Radon. Proceedings of the 9th Midyear Health Physics Symposium, Denver, Colo., Feb. 1976). See also, Specification G-25 in HASL Procedures Manual.
3. Radon bubblers may be purchased from 2(b) above or fabricated by a glass blower according to Specification G-07 in the HASL Procedures Manual (Figure 1).
4. Nitrogen or helium gas — aged at least 30 days to ensure complete decay of radon-222.
5. Gas-pressure regulator (with needle valve outlet) to fit compressed-gas cylinder.
6. Centrifuge with head for 40-or 50-ml centrifuge tubes.
7. Combination hot plate-magnetic stirrer.
8. Teflon-coated magnetic stir-bars. 10 x 3 mm, for use in centrifuge tubes. One inch for use in beakers.

REAGENTS

1. 1N lead nitrate — dissolve 3.30 g of Pb (NO_3) in deionized water and dilute to 100 ml.
2. 0.25M EDTA — dissolve 40 g of NaOH in about 300 ml of water in a 1 litre beaker. While still hot add 73 g of ethylenediaminetetra-

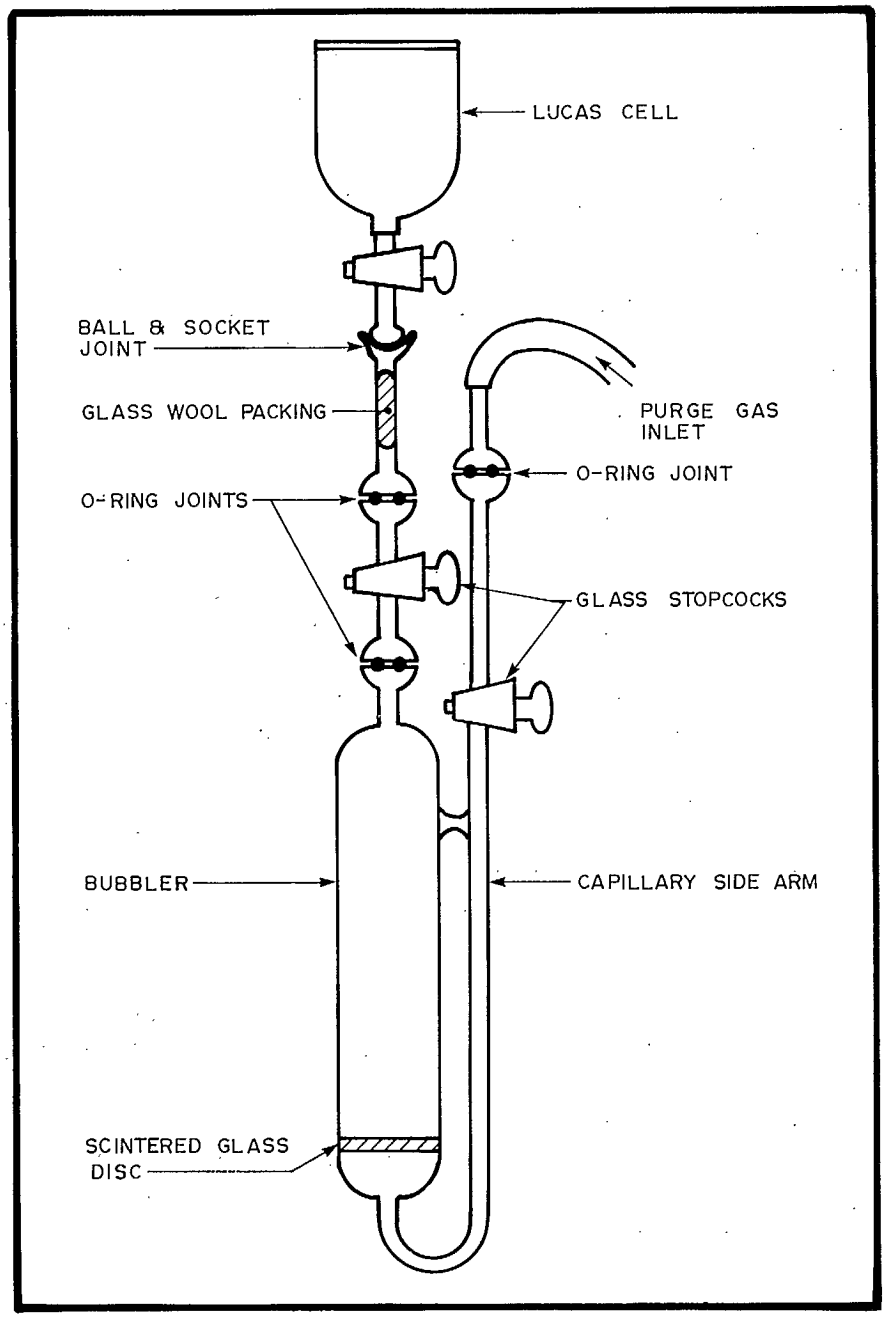


Fig. 1 Emanation Cell-Bubble Configuration for De-emanation.

acetic acid and mix until dissolved. Cool and dilute to one litre. Adjust the pH to 10 using NaOH or perchloric acid. Filter if necessary and store in polyethlene bottle. For 0.17M DTPA use 32 g of NaOH and 67 g of diethylenetriaminepentaacetic acid and prepare as for EDTA solution.

3. 0.0343M $BaCl_2$ — dissolve 7.143 g of $BaCl_2$ (or 8.38 g of $BaCl_2 . 2H_2O$) in water and dilute to 1 litre. One ml of this solution is equivalent to 8.0 mg of $BaSO_4$.
4. 20% Na_2SO_4 — dissolve 20 g of reagent grade Na_2SO_4 in water and dilute to 1 litre.
5. 6M acetic acid — dilute 345 ml of glacial acetic acid to 1 litre.
6. Radium-226 stock standard — one microcurie of Ra-226 plus the associated $BaCl_2$ carrier are diluted to 100 ml with 5% HNO_3. Store in Teflon FEP or polypropylene container. Radium-226 is available from Amersham, Oakville, Ontario.

GENERAL COMMENTS

The range of alpha particles is approximately 3.7 times greater in helium than in nitrogen. In helium, at pressures below atmospheric, all the alpha particles emitted by radon and its daughter have ranges exceeding the internal dimensions of the Lucas-type scintillation cells. Consequently, the counting efficiency remains constant over the normal range of final cell pressures (up to atmospheric pressure). With nitrogen the range of radon-222 and polonium-218 alpha particles fall below the maximum internal cell dimension at pressures exceeding 500 and 600 mm Hg respectively. Therefore, there is a decrease in counting efficiency for nitrogen of 0.35% at 400 mm, 0.9% at 500 mm, 2% at 600 mm and 4% at 700 mm. Due to the pressure drop across the glass frit in the bubbler, the final pressure reached in the cell is normally about 80% of the inlet pressure. For an atmospheric pressure of 720 mm Hg plus 2 psig from the regulator the final cell pressure will be approximately 600 mm Hg. At this pressure helium will give a counting efficiency about 3% higher than for nitrogen.

Great care must be exercised when air is introduced into evacuated scintillation cells. The flow of air should be kept as low as possible to prevent mechanical loosening of the ZnS coating and the introduction of stopcock grease into the cell. Use a pipe cleaner to remove the excess stopcock grease from the inside of the inlet tube.

Radon bubblers may be cleaned by the following procedures. If the level of radium-226 in the bubbler is less than 10 pCi it may be cleaned with 1% HCl. Attach the outlet of the bubbler to a suction flask with a short piece of Tygon tubing. Invert the bubbler and place the open end of the inlet side-arm in a beaker containing about 100 ml of 1% HCl. Open the inlet stopcock, turn on the vacuum and draw the contents of the beaker through the bubbler. Continue by rinsing with 20-30 ml of distilled water. Return the bubbler to its upright position and draw out residual solution through the side-arm. Bubblers that have contained more than 10 pci radium-226 should be soaked for 30 to 60 minutes in a hot (90°C) solution of 1% EDTA — 1% sodium carbonate. Drain most of the solution from the bubbler and rinse with 1% HCl, followed by distilled water as described above.

SAMPLE PREPARATION

Samples of water, biological materials, soil, rock, ore and sediment may be prepared by the same methods listed in the precipitation, gross alpha-counting method for radium-226 (Ra-01).

DETERMINATION

1. To one litre of the prepared sample solution add 200 ml of 1:1 H_2SO_4 and 40 g of K_2SO_4. Use proportionately less acid and K_2SO_4 for smaller volumes. Heat the solution to near boiling. (Refer to para 25, page 37, re blank.)
2. Add (dropwise) 2 ml of 1N $Pb(NO_3)_2$ to the hot sample solution while stirring with a magnetic stirrer.
3. Maintain the temperature just below the boiling point and continue stirring for 30 minutes.

4. Remove from the stirrer-hot plate, remove the stir-bar and allow the precipitate to settle for one hour or overnight if possible.
5. Siphon off most of the clear supernate. Wash the precipitate into a 50-ml centrifuge tube using the residual supernate as wash solution. Centrifuge and discard the supernate.
6. Dissolve the lead sulphate precipitate in 15 ml of 0.25M EDTA (or 0.17M DTPA). Place the centrifuge tube in a beaker of water heated on a stirring-hot plate and stir with a 10 x 3 mm Teflon stir-bar.
7. If any undissolved residue remains at this stage, it may be centrifuged and discarded.
8. Add 1 ml of 0.0343M $BaCl_2$ to the lead sulphate solution and mix.
9. Add 1 ml of 20% Na_2SO_4 and 11 ml of deionized water. Mix thoroughly.
10. While swirling the solution in the centrifuge tube, add 2 ml of 6M acetic acid. Place the centrifuge tube in a beaker of hot water on a stirring-hot plate and stir for 5 minutes.
11. Cool the sample in a cold water bath for 5 minutes and then centrifuge. Discard the supernate.
12. Redissolve the barium sulphate in 7.5 ml of 0.25M EDTA (or 0.17 M DTPA) with heat and stirring.
13. Transfer the EDTA solution to a clean radon bubbler using up to 7.5 ml of 0.025M EDTA solution to complete the transfer.
14. Connect the outlet of a compressed-gas regulator (nitrogen or helium) to the inlet of the bubbler and bubble gas through the solution for about 3-4 minutes. Maintain a froth about 2-5 cm high at the surface of the solution. The primary purpose of this gas purge is to replace the air in the bubbler with the purge gas as the previous chemical treatment removes essentially all radon-222 from the sample.
15. Close the side-arm stopcock, then the outlet stopcock and record the time as the beginning of the radon-222 ingrowth.
16. Allow 5 to 7 days for ingrowth of radon-222.
17. At the end of the ingrowth period, connect the inlet of the bubbler to the purge-gas regulator and bring the pressure to 1-2 psig.
18. Connect an evacuated scintillation cell to the outlet of the bubbler. See Figure 1. Open the stopcock on the scintillation cell and slowly open the outlet stopcock of the bubbler until bubbles begin rising from the sintered glass disc. When the initial frothing has subsided, close the stopcock on the scintillation cell.
19. Open the inlet stopcock of the bubbler just sufficiently to start the flow of gas through the sintered glass disc. Now, slowly open the stopcock on the scintillation cell and adjust it so that the froth at the surface of the solution is 2 to 4 cm high. The frothing will gradually decrease as the de-emanation proceeds. About 5 to 10 minutes will be required to complete the transfer.
20. When only a few columns of gas bubbles are rising through the solution, close the scintillation cell and side-arm stopcocks. Remove the scintillation cell.
21. If desired, the outlet stopcock may now be closed and a second ingrowth period started. This provides a check on the de-emanation recovery.
22. Record the time as the completion of radon-222 ingrowth and the beginning of radon decay and daughter ingrowth.
23. Although most procedures call for a 4-hour holding period before counting is started (to allow for equilibrium of the radon daughters) it is possible to start counting as soon as one hour after de-emanation so long as a correction is made for the partial ingrowth of polonium-218 and polonium-214. This correction is subject to a slightly higher error than that following a 4-hour holding period but in some cases it may be necessary to obtain a result as quickly as possible.
24. Place the scintillation cell in a bare-photomultiplier scintillation counter and count for a period of time sufficient to produce the desired statistical accuracy. Record the times for the beginning and end of the count period along with the count rate.

25. Prepare a calibration curve by carrying a series of radium concentrations (0.1 to 1000 pCi/l) and a few reagent blanks through the entire procedure.

CALCULATIONS

Prepare a calibration curve by plotting the corrected count rates of each standard vs the quantity of radium-226 in the standard. For samples which have undergone a minimum 4-hour period after de-emanation, the corrected rate may be calculated as follows:

$$R_c = \frac{R_n\left(\frac{\lambda t_3}{1 - e^{-\lambda t_3}}\right)}{e^{-\lambda t_2}(1 - e^{-\lambda t_1})}$$

where R_c = the corrected count rate

R_n = the observed net count rate (observed gross count rate minus "reagent blank" count rate)

λ = decay constant for radon-222 (0.1810 day^{-1} or 0.007541 $hour^{-1}$)

t_1 = ingrowth period for radon-222

t_2 = time between de-emanation and start of count (minimum of 4 hours)

t_3 = length of counting period

The correction factors in the foregoing equation can be read directly from Table 1 which is taken from Rushing et al*.

For post de-emanation periods of less than 4 hours it is necessary to make a correction for the partial ingrowth of polonium-218 and polonium-214. These corrections, calculated by means of the Bateman equation, are listed in Table 2. The time used to determine the correction factor is the total time from the completion of the de-emanation to the mid-point of the counting period. The corrected count rate is

$$R_c = \frac{R_{n.F}}{(1 - e^{-\lambda t_1})}$$

where all variables are as previously defined and F is the correction factor read from Table 2 for a time equal to the holding time plus one-half of the count time.

Calibration curves prepared from either of the foregoing corrected count rates also correct for mean cell counting efficiencies and mean recovery of radium in the chemical separation. Consequently, the quantity (pCi) of radium-226 in a given sample aliquot is the value from the calibration curve corresponding to the corrected count rate (R_c) of the sample.

PRECISION AND DETECTION LIMITS

The relative standard deviation for this method for sample aliquots containing more than 10 pCi of radium-226 is approximately ±3% of the amount present. The detection limit with a reagent blank of 0.2 cpm and a 100-minute count is approximately 0.1 pCi of radium-226.

*Rushing, D.R., Garcia, W.J. and Clark, D.A. Proceedings of Symposium on Radiological Health and Safety in Mining and Milling of Nuclear Materials, Aug 26-30, 1963, Volume 2, IAEA, Vienna, Austria.

TABLE 1

Ingrowth and Decay Factors for Radon-222 Counting

A. Decay of Radon (in Minutes, Hours, and Days)
B. Growth of Radon from Radium (in Days)
C. Multiplicative Factor for Correction of Radon Activity for Decay during Counting (in Hours)

(Based on 3.825 days as half-life of radon)

Time	A. $e^{-\lambda t}$			B. $1-e^{-\lambda t}$	C. $\frac{\lambda t}{1-e^{-\lambda t}}$
	Minutes	Hours	Days	Days	Hours
0	1.000,0	1.000,0	1.000,0	0.000,0	1.000,0
1	0.999,9	0.992,5	0.834,3	0.165,7	1.003,7
2	0.999,8	0.985,0	0.696,0	0.304,0	1.007,5
3	0.999,6	0.977,6	0.580,7	0.419,4	1.011,4
4	0.999,5	0.970,3	0.484,4	0.515,6	1.015,2
5	0.999,4	0.963,0	0.404,1	0.595,9	1.019,0
6	0.999,3	0.955,7	0.337,2	0.662,8	1.022,8
7	0.999,1	0.948,5	0.281,3	0.718,7	1.026,7
8	0.999,0	0.941,4	0.234,7	0.765,3	1.030,5
9	0.998,9	0.934,3	0.195,8	0.804,2	1.034,4
10	0.998,7	0.927,3	0.163,3	0.836,7	1.038,2
11	0.998,6	0.920,3	0.136,3	0.863,7	1.042,1
12	0.998,5	0.913,4	0.113,7	0.886,3	1.046,0
13	0.998,4	0.906,5	0.094,8	0.905,2	1.050,0
14	0.998,2	0.899,7	0.079,1	0.920,9	1.053,8
15	0.998,1	0.892,9	0.066,0	0.934,0	1.057,7
16	0.998,0	0.886,2	0.055,1	0.944.9	1.061,6
17	0.997,9	0.879,6	0.045,9	0.954,1	1.065,5
18	0.997,7	0.872,9	0.038,3	0.961,7	1.069,5
19	0.997,6	0.866,4	0.032,0	0.968,0	1.073,4
20	0.997,5	0.859,9	0.026,7	0.973,3	1.077,4
21	0.997,4	0.853,4	0.022,3	0.977,8	1.081,4
22	0.997,2	0.847,0	0.018,6	0.981,4	1.085,4
23	0.997,1	0.840,6	0.015,5	0.984,5	1.089,3
24	0.997,0	0.834,3	0.012,9	0.987,1	1.093,3
25	0.996,9	0.828,0	0.010,8	0.989,2	1.097,3

TABLE 1 - con't.

Time	A. $e^{-\lambda t}$			B. $1-e^{-\lambda t}$	C. $\frac{\lambda t}{1-e^{-\lambda t}}$
	Minutes	Hours	Days	Days	Hours
26	0.996,7	0.821,8	0.009,0	0.991,0	1.101,4
27	0.996,6	0.815,6	0.007,5	0.992,5	1.105,4
28	0.996,5	0.809,5	0.006,3	0.993,7	1.109,4
29	0.996,4	0.803,4	0.005,2	0.994,8	1.113,5
30	0.996,2	0.797,3	0.004,4	0.995,6	1.117,5
31	0.996,1	0.791,3	0.003,6	0.996,4	1.121,6
32	0.996,0	0.785,4	0.003,0	0.997,0	1.125,7
33	0.995,9	0.779,5	0.002,5	0.997,5	1.129,7
34	0.995,7	0.773,6	0.002,1	0.997,9	1.133,8
35	0.995,6	0.767,8	0.001,8	0.998,2	1.137,9
36	0.995,5	0.762,0	0.001,5	0.998,5	1.142,1
37	0.995,4	0.756,3	0.001,2	0.998,8	1.146,2
38	0.995,2	0.750,6	0.001,0	0.999,0	1.150,3
39	0.995,1	0.744,9	0.000,9	0.999,2	1.154,4
40	0.995,0	0.739,3	0.000,7	0.999,3	1.158,6
41	0.994,9	0.733,8	0.000,6	0.999,4	1.162,8
42	0.994,7	0.728,3	0.000,5	0.999,5	1.166,9
43	0.994,6	0.722,8	0.000,4	0.999,6	1.171,1
44	0.994,5	0.717,3	0.000,3	0.999,7	1.175,3
45	0.994,4	0.712,0	0.000,3	0.999,7	1.179,5
46	0.994,2	0.706,6	0.000,2	0.999,8	1.183,7
47	0.994,1	0.701,3	0.000,2	0.999,8	1.187,9
48	0.994,0	0.696,0	0.000,2	0.999,8	1.192,1
49	0.993,9	0.690,8	0.000,1	0.999,9	1.196,4
50	0.993,7	0.685,6	0.000,1	0.999,9	1.200,6
51	0.993,6	0.680,4	0.000,1	0.999,9	1.204,9
52	0.993,5	0.675,3	0.000,1	0.999,9	1.209,1
53	0.993,4	0.670,2	0.000,1	0.999,9	1.213,4
54	0.993,2	0.665,2	0.000,1	0.999,9	1.217,7
55	0.993,1	0.660,2	0.000,1	1.000,0	1.222,0
56	0.993,0	0.655,2	0.000,0	1.000,0	1.226,3
57	0.992,9	0.650,3	0.000,0	1.000,0	1.230,6
58	0.992,7	0.645,4	0.000,0	1.000,0	1.234,9
59	0.992,6	0.640,5	0.000,0	1.000,0	1.239,2
60	0.992,5	0.635,7	0.000,0	1.000,0	1.243,5

Table 2

Correction factor, F, for Radon-222 daughter ingrowth periods of less than 4 hours

Time (min)	F.	Time (min)	F.	Time (min)	F.
5	0.615	85	0.387	165	0.349
10	0.535	90	0.382	170	0.349
15	0.506	95	0.378	175	0.348
20	0.491	100	0.375	180	0.347
25	0.480	105	0.371	185	0.347
30	0.470	110	0.368	190	0.346
35	0.460	115	0.365	195	0.346
40	0.451	120	0.363	200	0.346
45	0.442	125	0.361	205	0.345
50	0.433	130	0.359	210	0.345
55	0.425	135	0.357	215	0.345
60	0.417	140	0.355	220	0.345
65	0.410	145	0.354	225	0.344
70	0.404	150	0.352	230	0.344
75	0.397	155	0.351	235	0.344
80	0.392	160	0.350	240	0.344

THE DETERMINATION OF RADIUM-228

PRINCIPLE

The direct determination of radium-228 is very difficult due to the low energy of its beta emission (maximum of 0.05 meV). Normal practice is to separate the actinium-228 produced during a definite ingrowth period and measure its easily-detected beta emission (maximum of 2.1 to 2.2 MeV). Radium-228 and all other radium isotopes are initially separated from the bulk of the sample solution and most elements by coprecipitation with lead sulphate. This precipitate is dissolved in a solution of DTPA. Next, barium chloride and sodium sulphate are added and then barium sulphate is preferentially precipitated by lowering the pH with acetic acid. The precipitated barium sulphate carries the radium isotopes and separates them from other radionuclides such as actinium, lead, bismuth and thorium. The barium (radium) sulphates are stored for 24 to 36 hours to allow for the ingrowth of actinium-228 (half-life of 6.13 hours). The sulphates are redissolved in DTPA solution and reprecipitated by the addition of sodium sulphate and acetic acid. The supernate containing the actinium-228 is separated from the precipitate and extracted with bis (2-ethylhexyl) phosphoric acid in petroleum ether to isolate the actinium from the DTPA solution. The actinium is next stripped from the organic phase with 1M nitric acid and coprecipitated with lanthanum oxalate. This precipitate is mounted for beta counting by filtering on a membrane filter in a HASL ring-and-disc, filter assembly or by deposition on a stainless steel planchette. The sample is covered with aluminum foil to screen out alpha particles and counted on a low-background, beta-counting system. Alternatively the precipitate may be contacted with a beta phosphor disc and counted on a bare-photomultiplier scintillation counter.

APPLICATION

This method is specific for radium-228. Recovery through the whole process is about 97% ± 2%, according to Percival and Martin*. Performance of this procedure must be scheduled so that the counting of the prepared samples may proceed immediately. This is necessary because of the short half-life of actinium-228.

An ingrowth period of 24 hours produces 93.4% of the equilibrium level of actinium-228 and 36 hours gives 98.3%.

The method may be applied to water, biological, soil, ore and rock samples.

APPARATUS

1. Low-background beta-counting system.
   (a) Lead-shielded anticoincidence flow proportional counter.
   or (b) Bare-photomultiplier scintillation counting system using beta phosphor discs (HASL Procedures Manual, Specification G-10-01).
2. HASL ring-and-disc filter assemblies. Specification G-13-01 in HASL Procedures Manual.
3. Aluminum foil ($\sim$7.2 mg/cm^2) — most household aluminum foils are suitable.
4. Centrifuge with head for 40- or 50-ml centrifuge tubes.
5. Combination hot plate-magnetic stirer.
6. Teflon-coated stir-bars. 10 x 3 mm, for use in centrifuge tubes. One-inch stir bars for use in beakers.
7. Separatory funnels — 125 ml with Teflon stopcock.

REAGENTS

1. Bis (2-ethylhexyl) phosphoric acid (15% HDEHP and 5% HDEHP) — Dilute 150 ml of HDEHP to 1 litre with petroleum ether (60°-80°C boiling point range) and wash twice, for 1 minute periods, with 200-ml portions of a 1 to 1 mixture of 2M diammonium citrate and concentrated ammonium hydroxide. Complete the purification by washing with two 200-ml portions of 4M

*Percival, D.R. and Martin, D.B. Anal. Chem; 46: 1742; 1974.

nitric acid. To prepare 5% HDEHP, add 300 ml of the washed 15% HDEHP to 600 ml of petroleum ether and wash twice with 4M HNO_3.

2. 0.17M DTPA (sodium diethylenetriaminepentaacetate) — Dissolve 67 g of diethylenetriaminepentaacetic acid and 32 g of sodium hydroxide pellets in approximately 300 ml of water. Filter the solution if necessary. Dilute to 1 litre and adjust the pH to 10 with NaOH or $HClO_4$. Store in a polyethylene bottle.
3. Actinium wash solution — Dissolve 100 g of monochloroacetic acid (handle with care), 10 g of DTPA (acid form) and 33 g of NaOH in water and dilute to 1 litre. Adjust the pH to 3.0 with NaOH or $HClO_4$.
4. Lead sulphate wash solution — dissolve 25 g of potassium sulphate in 1% H_2SO_4 and dilute to 1 litre.
5. Lanthanum carrier solution — dissolve 0.234 g of La_2O_3 in 1 ml of concentrated nitric acid and dilute to 200 ml.
6. 0.2M Ammonium oxalate — dissolve 14.2 g of ammonium oxalate in water and dilute to 500 ml.
7. 1N Lead nitrate — dissolve 33.1 g of lead nitrate in water and dilute to 200 ml.
8. 2M Monochloroacetic acid — dissolve 189.0 g of monochloroacetic acid ($CH_2ClCOOH$) in water and dilute to 1 litre.
9. 0.0172M $BaCl_2$ — dissolve 3.57 g $BaCl_2$ in water and dilute to 1 litre.
10. 20% Sodium sulphate — dissolve 20 g of Na_2SO_4 in water and dilute to 1 litre.
11. 6M Acetic acid — dilute 345 ml of glacial acetic acid to 1 litre.
12. Saturated sodium acetate solution.
13. Radium-228 Standard — aged thorium nitrate is available from Amersham, Oakville, Ontario. In this material the radium-228 is in secular equilibrium with the thorium-232.

SAMPLE PREPARATION

The methods recommended for preparing water, biological, soil, ore and rock samples for the determination of radium-228 are the same as those listed for radium-226 (Ra-01-04).

DETERMINATION

1. To the prepared sample solution add 20 ml of 1:1 H_2SO_4 and 40 g of K_2SO_4. Use proportionately less acid and K_2SO_4 for volumes less than 1 litre. Heat the solution to near boiling.
2. Add (dropwise) 2 ml of 1N $Pb(NO_3)_2$ to the hot sample solution while stirring with a magnetic stirrer.
3. Maintain the temperature just below the boiling point and continue stirring for 30 minutes.
4. Take the sample from the stirrer-hotplate and remove the magnet. Allow the precipitate to settle for one hour or overnight if possible.
5. Siphon off most of the clear supernate. Wash the precipitate into a 50-ml centrifuge tube using the residual supernate as wash solution. Centrifuge and discard the supernate.
6. Dissolve the lead sulphate precipitate in 15 ml of 0.17M DTPA. Place the centrifuge tube in a beaker of water heated on a stirrer-hot plate and stir with a 10 x 3 mm Teflon stirbar.
7. If any undissolved residue remains at this stage it may be centrifuged and discarded.
8. Add 2 ml of 0.0172M $BaCl_2$ to the lead sulphate solution and mix.
9. Add 1 ml of 20% Na_2SO_4 and 10 ml of deionized water. Mix thoroughly.
10. While swirling the solution in the centrifuge tube, add 2 ml of 6M acetic acid. Place the centrifuge tube in a beaker of hot water on a stirrer-hot plate and stir for 5 minutes while the barium sulphate precipitates.
11. Cool the samples in a cold water bath for 5 minutes. Add an additional 4 drops of 0.0172M $BaCl_2$ at 5-second intervals to ensure complete recovery of radium in the barium sulphate precipitate. Cool an additional 10 minutes.
12. Centrifuge and discard the supernate.
13. Dissolve the barium sulphate in 8 ml of 0.17M DTPA with heating and stirring. Add 1 ml of 20% Na_2SO_4 and 10 ml of deionized water.
14. Reprecipitate the barium sulphate by addition of 1 ml of 6M acetic acid. Centrifuge and

discard the supernate. Record this time as the start of the actinium ingrowth. Add 1 ml of water and allow 24 to 36 hours for ingrowth.

15. At the end of the ingrowth period add 15 ml of 0.17M DTPA and dissolve the barium sulphate precipitate with heating and stirring.
16. Add 1 ml of 20% Na_2SO_4 and 11 ml of water. While swirling the sample add 2 ml of 6M acetic acid to reprecipitate the barium sulphate. Record this time as the completion of the ingrowth period and the beginning of the actinium-228 decay.
17. Add an additional 4 drops of 0.0172M $BaCl_2$ to the solution to scavenge any residual dissolved radium.
18. Centrifuge and decant the supernate into a second 40-ml centrifuge tube using 3 ml of lead sulphate wash solution to complete the transfer. Save the precipitate for the determination of radium-226 if required.
19. Heat the decantate, and while stirring, add 2 ml of 0.0172M $BaCl_2$. Continue stirring for about 5 minutes while the barium sulphate precipitates. Cool in a cold water bath for 5 minutes.
20. Centrifuge and decant the supernate into a 125-ml separatory funnel containing 5 ml of 2M monochloroacetic acid. Use 3 ml of water to complete the transfer. Combine the barium sulphate precipitate with that from Step 18 if radium-226 is to be determined.
21. Wash some 15% HDEHP for about 1 minute with an equal volume of water and then with a one-half volume of actinium wash solution. Add 10 ml of this washed extractant to the separatory funnel containing the sample.
22. Shake vigorously for 2 minutes and then let the phases separate. Drain the aqueous phase into a clean separatory funnel and extract with a second 10-ml portion of the washed extractant. Discard the aqueous phase and combine the two organic phases in the first separatory funnel. Wash twice with 10-ml portions of the actinium wash solution. Discard the washes.
23. Strip the actinium-228 from the organic phase by extracting with 10 ml of 1M HNO_3 for 1 minute. Allow the phases to separate and drain the acid layer into a 40-ml centrifuge tube.
24. Repeat Step 23 and combine the two acid extracts. Add 6 ml of saturated sodium acetate solution and 5 ml of 0.2M ammonium oxalate to the acid extract.
25. Heat the sample while stirring and add 5 ml of lanthanum carrier solution. Continue heating and stirring for 5 minutes while the lanthanum oxalate precipitates carrying with it the actinium-228.
26. Cool the sample for 10 minutes in a cold water bath.
27. Filter the lanthanum oxalate on a 0.45-micron, membrane filter in a HASL ring-and-disc filter assembly. Air dry for a few minutes then remove the disc and filter, cover them with aluminum foil and push the ring into place. Count immediately in a low-background flow proportional counter. If a bare-photomultiplier scintillation counter is being used, place a beta phosphor disc in contact with the aluminum foil, cover with Mylar and then push the ring in place. Count as soon as possible.
28. Prepare a calibration curve from a series of standards made from a standard solution of aged thorium nitrate. The activity of radium-228 in secular equilibrium with thorium-232 is 0.109 pCi per microgram of thorium-232. Carry several reagent blanks through the entire procedure and average them.

CALCULATIONS

Prepare a calibration curve by plotting the corrected, net count rate of the standards vs their radium-228 content (pCi) on log-log paper. The corrected, net count rate is calculated as follows:

$$Rc = \frac{Rn\ e^{-\lambda t_2}}{(1-e^{-\lambda t_1})}$$

where Rc - is the corrected, net count rate.
Rn - is the observed, net count rate (gross sample count rate minus count rate of blank).
λ - is the decay constant for actinium-228 (0.1131 hour^{-1}).
t_1 - the length of time for ingrowth of actinium-228
t_2 - is the length of time from the separation of actinium-228 and radium-228 to the mid-point of the counting interval.

The corrected net count rate for samples can be read directly on the calibration curve to give the amount of radium-228 present in the sample aliquot. The calibration curve corrects for the recoveries of radium-228 and actinium-228.

PRECISION AND DETECTION LIMIT

The relative standard deviation for this method is approximately ±3% of the amount of radium-228 present. The detection limit for a 100-minute count on a low-background flow proportional beta-counting system with a blank count rate of 0.8 cpm is about 1 pCi radium-228.

THE COLORIMETRIC DETERMINATION OF TOTAL THORIUM

PRINCIPLE

Two of the most sensitive methods for the detection of thorium-232 are chemical methods, the fluorimetric determination with morin[1] and the colorimetric determination with arsenazo III[2]. Due to the low specific activity of thorium-232 (0.109 pCi/µg) these photometric methods are capable of detecting lower levels of this radionuclide than can be detected by alpha-counting methods. Of the foregoing methods, the colorimetric determination with arsenazo III has been selected. Because arsenazo III is not specific for thorium but reacts with many quadrivalent ions, it is necessary to chemically isolate thorium before applying the colorimetric development. Thorium is isolated from prepared sample solutions by coprecipitation first with lanthanum hydroxide then with lanthanum fluoride followed by extraction with thenoyltrifluoroacetone (TTA) in a suitable solvent. The organic extract is stripped with a nitric acid solution to produce an aqueous solution of thorium. The colour development is performed by reacting a strong HCl solution (approx 6M) of the isolated thorium with an aqueous solution of arsenazo III. The colorimetric measurement is then performed at a wavelength of 665 nm.

APPLICATION

This method may be applied to all types of water, biological, ore and soil samples following their transformation to appropriate aqueous solutions. The lanthanum fluoride coprecipitation and TTA extraction of thorium provides adequate isolation for most samples. There are some cases where extra chemical separations will be required. One of these is the analysis of bone ash. Due to high levels of calcium and phosphate in this material, a very heavy precipitate of calcium phosphate will form when the precipitation of lanthanum (thorium) hydroxide is attempted. Consequently it is necessary to make a separation of lanthanum and calcium oxalates from the phosphate. After calcining the oxalate and redissolving the oxides, lanthanum may be separated from the calcium by precipitating lanthanum (thorium) hydroxide at a pH of 9. The hydroxides are dissolved and lanthanum (thorium) fluoride may now be precipitated without the interference of calcium. Other samples which are high in aluminum or calcium plus phosphate will normally require the extra oxalate separation.

Although the fluorometric morin method is about 5 times more sensitive than the arsenazo III method, it has certain requirements which make it not as suitable for routine application. Because it is a fluorometric method it is very susceptible to interference from trace impurities in reagents and is quite sensitive to temperature fluctuations in the sample solution during the measurement of fluorescence. In addition, it requires a fluorimeter with a tungsten light source. Not all filter-type fluorimeters have provision for tungsten lamp excitation. The arsenazo III method can be performed with commonly available spectrophotometers and will provide sensitivity adequate for most purposes.

The detection limit for the arsenazo III spectrophotometric method is approximately 0.05 µg of thorium. For thorium-232 this corresponds to 0.0055 pCi. This is a much smaller activity than can be detected by alpha spectrometry. For thorium-228 and thorium-230 the most sensitive method is alpha spectrometry because of the much higher specific activity of these isotopes.

APPARATUS

1. Spectrophotometer capable of accommodating 4- or 5-cm light-path cells.
2. Spectrophotometer cells; 4- or 5-cm path length.

---

[1] Sill, C.W., and Willis, C.P. Anal. Chem; 36: 622; 1964.

[2] Bazzano, E., and Gersini, G. Anal. Chim. Acta; 38: 460; 1967.

3. Separatory funnels; 125-ml, with Teflon stopcock.
4. Magnetic stirrer.
5. Teflon-coated magnetic stir-bars; 10 x 3 mm and 1 x 3/8 inch.
6. Plastic centrifuge tubes, 50-ml.
7. Platinum crucibles, 30-ml.
8. Vycor crucibles, 45-ml.

REAGENTS

1. 0.25M TTA (Thenoyltrifluoroacetone) — dissolve 27.8 g of TTA in benzene and dilute to 500 ml.
2. Arsenazo III solution — dissolve 0.4 g of arsenazo III in water and dilute to 1 litre. Store in the dark.
3. Lanthanum carrier solution — dissolve 11.728 g of La_2O_3 in 15 ml of concentrated HNO_3 and dilute to one litre. This solution contains 10 mg La per ml.
4. Fluoride wash solution — dilute 60 ml of HNO_3 and 30 ml of HF to one litre with deionized water. Store in a plastic bottle.
5. Oxalic acid solution — dissolve 100 g of oxalic acid in water and dilute to 1 litre.
6. Oxalic acid wash solution — dilute 100 ml of the oxalic acid solution to 1 litre.
7. 5% $NaHSO_4$ — dissolve 5 g of $NaHSO_4.H_2O$ in water and dilute to 100 ml. Filter before using.
8. 2M HNO_3 — dilute 130 ml HNO_3 to 1 litre with deionized water.
9. 2M $Al(NO_3)_3$ solution — dissolve 750 g of $Al(NO_3)_3.9H_2O$ in water and dilute to 1 litre.
10. Saturated ammonium acetate — add an excess of solid ammonium acetate to deionized water.
11. pH 1.5 wash solution — add 20 ml of saturated ammonium acetate to 1 litre of deionized water and adjust the pH to 1.5 with HNO_3 and NH_4OH.

SAMPLE PREPARATION

WATER SAMPLES — Samples should be acidified to 1% HNO_3 in the field when they are collected. For dissolved thorium only, the sample is filtered through a 3.0-μ membrane filter before acidification. To 1010 ml of sample add 5 ml of perchloric acid, 2 ml of lanthanum carrier and evaporate to perchloric fumes to destroy all organic matter. Repeat with the addition of 10 ml of nitric acid if necessary. Add 5 ml HNO_3 and transfer to a 100-ml centrifuge tube. Dilute to about 75 ml and proceed to the DETERMINATION.

BIOLOGICAL SAMPLES — All samples may be dry ashed. See procedure Ra-01 for ashing conditions. For flesh and vegetation ash dissolve 1 g of ash plus 2 ml of lanthanum carrier in 1:1 HNO_3 and dilute to about 100 ml. Proceed to DETERMINATION. If large amounts of silica are present in the ash it should be treated with HNO_3 and $HClO_4$ and then heated to fumes of $HClO_4$ in order to dehydrate the silicates. Redissolve in 5 ml HNO_3, dilute to 30 ml and centrifuge, discarding the silica precipitate. Return the supernate to the centrifuge tube and proceed to the DETERMINATION.

For bone samples it is necessary to perform the oxalate separation. Dissolve 1 g of bone ash plus 2 ml of lanthanum carrier solution in 1:1 HNO_3 and bring the final volume to about 100 ml with water. Adjust the pH to 4 with 20% NaOH and heat to near boiling. While stirring add 4 ml of oxalic acid solution. Digest the precipitate for an additional 5-10 min then cool and centrifuge. Discard the supernate. Wash the precipitate with 30 ml of oxalic acid wash solution, centrifuge and discard the supernate. Dissolve the precipitate in 5 ml HNO_3 and add 0.5 g $KClO_3$. Heat very cautiously to decompose the oxalate and continue until gas evolution ceases. Dilute to approximately 75 ml in a 100-ml centrifuge tube and proceed to the DETERMINATION.

SOIL, ORE AND ROCK SAMPLES — Weigh a dried, 1-g sample into a platinum crucible, add 2 ml of lanthanum carrier and ash all organic matter by heating over a burner or by heating overnight at 550°C in a muffle furnace. To the cooled, ashed sample add 3 ml H_2SO_4 plus 10-20 ml HF. Heat on a hot plate in a fume hood to drive off the silicon tetrafluoride and the excess HF. If necessary, repeat with the addition of HF to remove all silica. Heat to strong SO_3 fumes and cool. Add 3 to 5 g of potassium pyrosulphate (depending on the amount of residue) and begin heating over a gas burner. Continue heating and

swirling until a clear melt is obtained. Cool and dissolve in 100 ml of 10% HCl (use a 200-250 ml beaker). Proceed to DETERMINATION.

DETERMINATION

1. To the 75 ml of sample solution in the centrifuge tube or 100 ml of soil or ore digest in a beaker, add NaOH to pH 9. Digest the precipitate for 30 minutes in a hot water bath, cool and centrifuge. Discard the supernatant liquid.
2. Redissolve the hydroxide precipitate in 5 ml HCl. Heat if necessary. Dilute to 75 ml (100 ml for soil or ore samples) and repeat the precipitation with NaOH (pH 9). Digest, cool and centrifuge. Discard the supernate.
3. Redissolve the hydroxides in 4 ml HNO_3. If the precipitate is hard to dissolve, the addition of 5-10 drops of 30% hydrogen peroxide may facilitate the process.
4. Transfer the dissolved lanthanum hydroxide solution to a transparent plastic centrifuge tube with washing and dilute to 30 ml.
5. Add 5 ml of 48% HF and stir at room temperature for 1 hour. Centrifuge and discard the supernate.
6. Wash the lanthanum fluoride precipitate with 10 ml of the fluoride wash solution. Centrifuge and discard the wash solution.
7. Add 5 ml of 2M $Al(NO_3)_3$ and 2 ml HNO_3 to dissolve the lanthanum fluoride precipitate. Add 1 ml of saturated ammonium acetate and dilute to 30 ml. Adjust the pH to 1.5 using NH_4OH.
8. Transfer the solution to a 125-ml separatory funnel with washes of pH 1.5 wash solution.
9. Add 20 ml of 0.25M TTA-benzene extractant and shake for 5 minutes. Allow the phases to separate and transfer the aqueous phase to a clean 125-ml separatory funnel.
10. Add a second 20-ml volume of extractant to the aqueous phase and shake for 5 min. Allow the phases to separate and discard the aqueous phase. Transfer the second organic extract to the separatory funnel containing the first extract.
11. Wash the combined organic extracts with 25 ml of the pH 1.5 wash solution. Allow the phases to separate and discard the wash solution.
12. Add 20 ml of 2M HNO_3 to the washed organic extracts and shake for 5 minutes. After the phases have separated, drain the nitric acid solution into a 50-ml beaker.
13. Repeat the 2M HNO_3 strip with an additional 20 ml and combine with the first strip.
14. Add 2 ml of $HClO_4$ and 2 ml of 5% $NaHSO_4$ to the combined strip solutions and evaporate to fumes of $HClO_4$. Continue heating on hot plate with a surface temperature of 200°C to incipient dryness. Do not bake the residue or insoluble thorium salts may be formed.
15. Dissolve the residue in a few mls of 1:1 HCl and transfer to a 10-ml volumetric flask containing 1 ml of Arsenazo III solution. Wash the beaker with small amounts of 1:1 HCl and continue adding these to the volumetric flask until the 10-ml volume is reached.
16. Measure the absorbance of this solution at 665 nm using 4-cm cells. Use 1 ml of Arsenazo III solution diluted to 10 ml with 1:1 HCl as the reference blank.
17. Carry a set of thorium standards (0.1 to 5 µg Th) through the entire procedure for calibration purposes.

CALCULATIONS

Prepare a calibration curve by plotting absorbance (665 nm) vs amount of Th (µg). This calibration curve will correct for recovery throughout the entire procedure. The amount of thorium contained in the original sample aliquot can be read directly from the calibration curve.

PRECISION AND DETECTION LIMIT

The relative standard deviation for thorium standards carried through the procedure is approximately ±3% of the amount present above 0.5 µg Th. The detection limit when using 4-cm cells is 0.05 µg Th. For a 500-ml water sample this corresponds to a detection limit of 0.1 µg/litre.

THE DETERMINATION OF THORIUM ISOTOPES BY ALPHA SPECTROSCOPY

PRINCIPLE

When it is desirable to determine thorium-230 or all the thorium isotopes individually in a sample it is necessary to electroplate the isolated thorium on stainless steel and count with an alpha spectrometer. The same thorium isolation procedure that is used in the colorimetric method can be used to prepare the sample for electrodeposition. The alpha spectrometer will normally consist of a surface barrier detector with its associated pre-amp, amplifier and bias voltage source; a vacuum chamber; and a multichannel analyzer.

APPLICATION

The types of samples that may be analyzed by this method are the same as those listed in the APPLICATION section of the total thorium procedure. The principles of the thorium isolation methods are also discussed in that section.

One limitation in the electrodeposition of thorium is that the total amount of thorium that may be efficiently deposited on a 2.5 cm^2 area of stainless steel is about 100 µg. Consequently, the size of the initial sample or the size of the aliquot of the isolated thorium taken for analysis should be selected with this limit in mind.

The isolation and electrodeposition of thorium can lead to variable recoveries. For this reason it is advisable to use thorium-234 as a tracer through the entire procedure. The recovery of thorium-234 is determined by beta-counting the final electroplated disc. A correction should be made for high levels of thorium-234 contained in samples that are high in uranium-238 whose immediate daughter is thorium-234. A procedure for preparing thorium-234 tracer from uranium compounds is given in Appendix A.

APPARATUS

1. Surface barrier detector — the preferred detector is a 300-450 mm^2 ruggedized surface barrier detector with a 500-µ depletion depth.
2. Preamplifier, bias voltage supply and linear amplifier to be used in conjunction with the surface barrier detector.
3. Multichannel Analyzer — any modern, solid-state MCA with 512 to 2048 channels will be suitable.
4. Beta-counting system — any available beta-counting system can be used, as the background will not be critical when measuring recoveries of the high level of thorium-234 added (1800 dpm).
5. Electrodeposition cell — a suitable cell is described in Specification G-18 of the HASL Procedures Manual.
6. D.C. Power Supply — a 24V D.C. power supply capable of delivering a current of 1 amp. Radio Shack Model 22-8230 is suitable.
7. Polished Stainless Steel Discs — for the HASL cell (Specification G-18) an 11/16 inch diameter disc is required. These may be purchased from:
   (a) Ketchum Manufacturing Co., 396 Berkley Ave., Ottawa, Ontario K2A 2G6. (1-inch discs only).
   (b) Metallic Valve Company Ltd., Bridge Street, Birkenhead, England.
   (c) Salt Lake Stamp Company, P.O. Box 2399, Salt Lake City, Utah 84110.
8. Platinum Anodes — Specification G-17-01 in HASL Procedures Manual. May be purchased by special order from:
   (a) Johnson, Matthey & Mallory Ltd., 111 Industry Street, Toronto, Ontario M6M 4M1.
   (b) Engelhard Industries of Canada Ltd., 512 King St. East, Toronto, Ontario M5A 1M2.
9. 1-oz polyethylene bottles with a 20-mm threaded screw cap.
10. Separatory funnels; 125-ml, with Teflon stopcock.
11. Magnetic stirrer.
12. Teflon-coated magnetic stir-bars; 10 x 3 mm and 1 x 3/8 inch.
13. Plastic centrifuge tubes, 50-ml.
14. Platinum crucibles, 30-ml.

15. Vycor crucibles, 45-ml.

REAGENTS

1. All reagents listed for the total thorium procedure, except the Arsenazo III solution, are required for the chemical isolation of thorium.
2. 15% Na_2SO_4 — dissolve 150 g of anhydrous Na_2SO_4 in water and dilute to one litre. Filter before using.
3. Thorium-234 tracer solution — see Appendix A.

SAMPLE PREPARATION

The sample preparation techniques are the same as in the total thorium procedure with the exception that 2 ml of the thorium-234 tracer solution is added at the beginning of the preparation of each sample.

DETERMINATION

1. After adding the thorium-234 tracer and preparing samples as in the total thorium method, continue to the end of Step 14 in the total thorium DETERMINATION.
2. Dissolve the residue in 2 ml of 6M HBR and 2 drops of 1M DTPA made in 1:1 NH_4OH. Evaporate until only 2 or 3 drops remain.
3. Add 14 ml of 4% oxalic acid and 2 ml of saturated ammonium chloride. Heat to dissolve and adjust pH to 4.00 with HN_4OH.
4. Assemble the electrodeposition cell with a stainless steel disc that has been cleaned in alcohol to remove traces of paper backing adhesive, then rinse with 1:1 HNO_3 and deionized water.
5. Transfer the solution to the electrodeposition cell with hot rinses of oxalic acid. Rinse the beaker with deionized water and add these rinses to the cell until a total volume of 15 ml is reached. Add 3 drops of 1:5 hydrofluoric acid.
6. Place the anode in position (spaced about 1 cm from the cathode) and connect the electrodes to the power supply. Electroplate for 3 hours at 1 amp. Make up evaporation losses during the electrodeposition with deionized water.
7. At the end of the deposition add 2 ml of NH_4OH, switch off the current after 2 minutes. Disconnect the cell and wash the stainless steel disc with 0.1M NH_4OH by directing the rinse onto the unplated portion.
8. Dry the disc on a hot plate for 5 minutes at 150-200°C to remove any traces of Po-210.
9. Beta-count the disc to determine the recovered activity of thorium-234. The overall recovery efficiency is determined by dividing this count by that obtained from 2 ml of the thorium-234 carrier deposited directly on a stainless steel disc and evaporated to dryness.
10. Determine the alpha spectrum of the sample by counting for a suitable period of time in a vacuum-chamber alpha spectrometer.
11. Carry standards of uranium (thorium-230) and thorium (thorium-232 and thorium-228) through the entire procedure in order to produce individual calibration curves.

CALCULATIONS

Prepare calibration curves for each thorium isotope by plotting corrected net count rate vs the amount of thorium isotope present. The corrected net count rate is calculated as follows:

$$R_c = \frac{R_n}{E}$$

where R_c = the corrected net count rate
R_n = the observed net count rate (observed gross count rate for an isotope minus the background count rate taken over the same analyzer channels)
E = the recovery factor for thorium-234. Observed beta count rate for the sample disc divided by the observed count rate for 2 ml of thorium-234 tracer solution evaporated to dryness on a stainless steel disc.

The amount of each thorium isotope in a sample is determined by reading the pCi corresponding to the corrected count rate for that isotope from the appropriate calibration curve.

PRECISION AND DETECTION LIMIT

The relative standard deviation for this method, after the thorium-234 correction has been made for recovery, is approximately ±5% for levels in excess of 10 pCi. The detection limit for Th-232 and Th-230 with a 100-minute count is approximately 0.1 pCi and for Th-228 approximately 0.2 pCi.

APPENDIX A

PREPARATION OF THORIUM-234 TRACER SOLUTION

Column Preparation

Prepare three anion-exchange columns (Specification G-05 in HASL Procedures Manual) with 25 ml of Dowex 1-X4 (100-200 mesh, chloride form) resin (Specification G-04 in HASL Procedures Manual). Convert the resin to the proper form by washing with 10 column volumes (250 ml) of 7N HCl.

Initial Separation

1. Weigh 5 g of U_3O_8 into a 250-ml beaker and dissolve in HCl.
2. Make the solution up to about 100 ml of 7N HCl.
3. Transfer the solution to the ion-exchange column, police and wash the beaker with 7N HCl. Transfer the washings to the column.
4. Wash the column with 250 ml of 7N HCl.
5. Discard the effluent and washings containing thorium-234 and thorium-230.
6. Strip the uranium from the column with 250 ml of 1N HCl into a 400-ml beaker. Evaporate the solution to dryness.
7. Allow the thorium-234 ($t_{\frac{1}{2}}$ = 24.1 d) to build up for 24 hours. (Note — allowing a 24- hour build-up period produces about 9 x 10^4 dpm of Th-234 and only 0.1 dpm of Th-230.)

Final Tracer Preparation

1. Dissolve the previously-separated uranium salt in 100 ml of 7N HCl.
2. Transfer the solution to a 7N HCl anion-exchange column, police and wash the beaker with 7N HCl. Transfer the washings to the column.
3. Allow the solution to drain into a 250-ml beaker.
4. Transfer the effluent to a second ion-exchange column. Collect the effluent containing the thorium-234 in a 400-ml beaker.
5. Wash the second column with 50 ml of 7N HCl. Combine with the effluent in the 400-ml beaker.
6. Strip the uranium from the two columns with 250 ml of 1N HCl. Combine the solutions, evaporate to dryness and retain the salt for future additional tracer production. Discard the resin.
7. Evaporate the thorium-234 solution to near dryness, wet ash with HNO_3 and make up to 50 ml of 1N HNO_3. Store the thorium-234 tracer solution in a polyethylene bottle.
8. Weigh an aliquot of thorium-234 tracer solution onto a platinum disc, dry, flame and beta-count.

NOTE: For sequential uranium-thorium analyses, the thorium-234 tracer solution must be checked fluorimetrically for possible uranium contamination.

APPENDIX B

RADIOCHEMICAL DETERMINATION OF LEAD-210 IN ENVIRONMENTAL SAMPLES AND SAMPLES RESULTING FROM URANIUM MINING-MILLING OPERATIONS

Dr. Gene Smithson, Muzaffer Fahri and
Mervin Petrow, Saskatchewan Research Council,
Saskatoon, Saskatchewan

FOREWORD

The following analytical procedure was developed because of the need for a rapid and easily performed method to determine lead-210 in water, biological, ore and soil samples. The procedure and the required equipment have been kept as simple as possible so that the method may be performed in modestly equipped laboratories. The main equipment requirements are a low-background, beta-counting system and an atomic absorption spectrophotometer. It is even possible to carry out the procedure without an atomic absorption spectrophotometer if one is willing to accept the lower accuracy that results from not measuring the recovery of bismuth in the solvent extraction step. This loss in accuracy will be less than 5% for water samples containing low levels of iron (<1 mg/l) and copper (<0.05 mg/l). Sample preparation methods for all sample types are given along with the detailed analytical procedure.

INTRODUCTION

The radiochemical determination of lead-210 is normally accomplished by measuring the beta emission (maximum energy of 1.17 MeV) of its bismuth-210 daughter or the alpha emission (5.31 MeV) of its polonium-210 granddaughter. This indirect measurement is necessary because of the very weak beta particles (0.018 MeV) emitted by lead-210. Such weak betas are very difficult to measure with commonly available beta-counting systems. Since it is the daughter or granddaughter radionuclide that is isolated and quantitatively measured it is necessary to know the degree of equilibrium that exists between it and the parent lead-210. Normally, lead-210 is isolated and then the daughters are allowed to grow in for a definite time period before they are separated and measured. For bismuth-210 (half-life of 5.01 days) an ingrowth period of 10 days produces approximately 75% of the equilibrium value, whereas for polonium-210 (half-life of 138 days) a 30-day ingrowth produces only 14% of equilibrium and over three months are required for 50% ingrowth. Although the radiochemical determination of polonium-210 is rapid, sensitive and specific, the long ingrowth period required to achieve high sensitivity for lead-210 makes this an impractical method for monitoring rapidly fluctuating uranium mining and milling operations. Even the 5 to 10-day delay required to achieve reasonable sensitivity through bismuth-210 ingrowth will be impractical for some monitoring applications. In these cases the samples may be analyzed for bismuth-210 immediately and the stripped aqueous solution saved to allow ingrowth of bismuth-210. If the lead-210 value determined by the ingrown bismuth-210 does not agree with the "immediate" value, the degree of dis-equilibrium can be calculated. If it is found that the degree of dis-equilibrium for a particular process stream does not change appreciably with time, the mean value can be used to correct the "immediate" lead-210 value in subsequent determinations. When samples must be analyzed for lead-210 as quickly as possible they should be prepared and stripped of bismuth-210 immediately. After a definite ingrowth period (5 to 10 days) the ingrown bismuth-210 is determined and the lead-210 is calculated. When possible, storage of samples for at least one month will insure that any bismuth-210 not associated with lead-210 will have decayed to about 1% or less of its original value and ingrown bismuth-210 will be in near equilibrium.

The most popular methods for isolating and separating lead-210 and bismuth-210 are solvent extraction (2,3,4,5,6,7), precipitation separation (1,3.4,8a) and ion exchange (4,9,10). The method previously used in our laboratory was one of precipitation separation which was very time consuming and required the use of extremely corrosive, fuming nitric acid (1). In searching for a more suitable method our attention was directed to solvent extraction procedures mainly because of the inherent slowness of column ion exchange and a lack of alternate precipitation separation methods.

There is an excellent solvent extraction method for the determination of lead-210 published by Sill and Willis (2,3). It is free of interferences and is capable of high precision. Its only drawback is that it requires two separate solvent extractions to isolate and separate lead and bismuth. The first extraction is with diethylammonium diethyldithiocarbamate (DDTC) in chloroform. This isolates lead and bismuth from the majority of cations. The extracted lead and bismuth are then returned to aqueous solution by evaporation and acid treatment. The pH of this aqueous solution is adjusted to 9.5, citrate and cyanide are added to complex iron, copper and other metals and then the lead and bismuth are extracted into chloroform containing dithizone. Lead is stripped by washing with a pH 2.7 buffer solution. Bismuth in the organic phase is recovered by evaporation and dissolution into an acid solution. Finally, the bismuth is coprecipitated with barium sulphate, filtered onto a planchette and counted. From this brief description of the method it can be seen that it is fairly complex and time consuming.

A literature review and preliminary investigations indicated that a single solvent ex-

traction procedure using sodium diethyldithiocarbamate (NaDDC) or DDTC was feasible (2,3,12,13, 14). A single extraction procedure with dithizone was not practical (2,4,15). The main problem was the formation of precipitates (for certain ore samples) which could not be kept in solution by the recommended complexing agents at the pH necessary for extraction (pH 9-10). In addition, an extra extraction was required to strip the lead from the organic dithizone phase in order to separate lead and bismuth. Another reagent which is capable of separating lead and bismuth in a single extraction is di(2-ethylhexyl) phosphoric acid (16). It is also known to extract lanthanides, actinium and thorium which would cause problems with certain samples and was not investigated further. The HASL Radiochemical Procedures Manual contains a method for determining lead-210 which is recommended for water and biological samples (8a). In this procedure the sample is decomposed with nitric acid and taken to dryness. The dried residue is redissolved in 3M hydrobromic acid and extracted with Aliquat-336 in toluene. Decomposition of some ores in nitric acid and redissolution in hydrobromic acid would be extremely difficult. Because of the limitations and problems anticipated with the three foregoing methods it was decided to place major emphasis on developing a single extraction method using sodium diethyldithiocarbamate or diethylammonium diethyldithiocarbamate.

EXPERIMENTAL

The work of Yamane et al (12) shows that bismuth can be separated from lead by extracting an aqueous HCl solution of the two metals with a solution of zinc dibenzyldithiocarbamate (ZnDBDTC) in carbon tetrachloride. According to their results, only bismuth is extracted if the solution is 3M HCl. They have determined the effect of HCl concentration on the extraction efficiency of ZnDBDTC for lead, bismuth and several other metals. Their results are plotted in Figure 1. Our results for the extraction efficiency of NaDDC and DDTC as extraction agents for lead and bismuth are also plotted in Figure 1. This data was obtained by extracting 200 ml of the appropriate HCl solution containing 1 mg each of lead and bismuth and 1 g of ascorbic acid with two ten-ml portions plus a five-ml wash of a 0.1% chloroform solution of either reagent. These results show a shift in the extraction curves for either lead or bismuth to higher HCl concentrations in the order DDTC < NaDDC < ZnDBDTC. The relative spacing, in terms of HCl concentration, between the lead and bismuth extraction curves remains fairly constant for the three reagents. The optimum HCl concentrations for maximum separation of lead and bismuth and maximum recovery of bismuth would be 2M for DDTC, 2.8M for NaDDC and 3.5M for ZnDBDTC. For all subsequent work DDTC was selected as the extractive reagent. The reasons for this choice were that DDTC is readily soluble in chloroform, this solution is relatively stable and the optimum acid concentration is lowest for this reagent. However, any one of the three reagents will give equivalent results.

There are several references to the instability of dithiocarbamates in solutions of high acid concentration (2, 12). For this reason it is best to dissolve the dithiocarbamate in the organic extractive phase rather than adding it directly to the concentrated acid solution. In order to determine the effect of inter-phase contact time on the stability of the dithiocarbamate as well as the efficiency for extracting bismuth, extractions were performed for varying time intervals. The extractive conditions were the same as those described in the preceding paragraph with the hydrochloric acid concentrations maintained at 2M. The results of this study are shown in Figure 2. The concentration of bismuth in the organic extract was determined by direct-aspiration atomic absorption spectrometry within one hour of completing the extractions. The extracts were stored for 24 hours and the bismuth concentrations were redetermined. No change in bismuth concentration was observed except for the 5-minute extraction which underwent a significant decrease. An explanation for this may be that increasing amounts of HCl are absorbed in the organic phase with increased contact time, until eventually sufficient

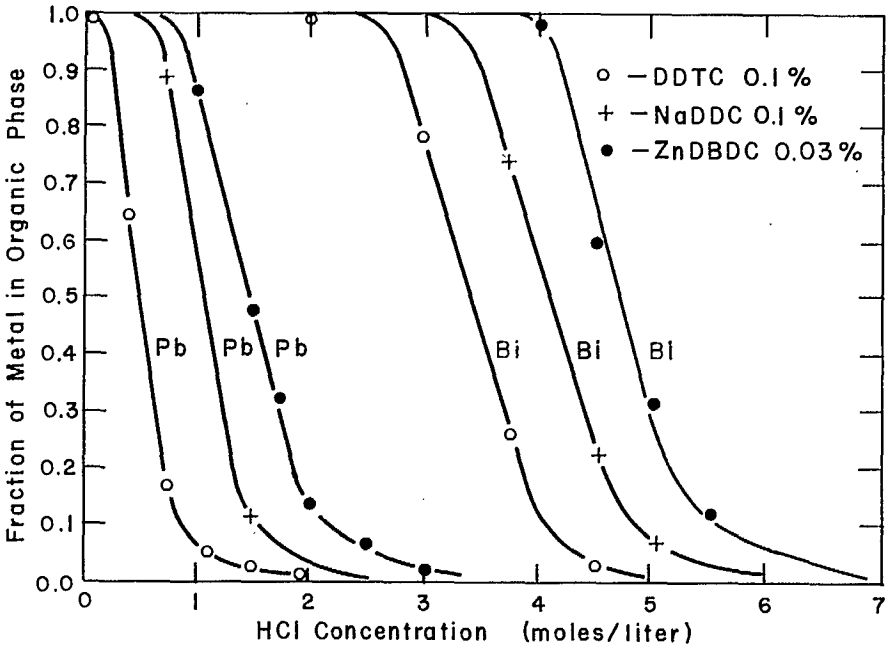


Fig. 1 Fractional Extraction of Lead and Bismuth vs HCl concentration for diethylammonium diethyldithiocarbamate (DDTC), sodium dibenzyldithiocarbamate (NaDDC) and zinc dibenzyldithiocarbamate (ZnDBDTC).

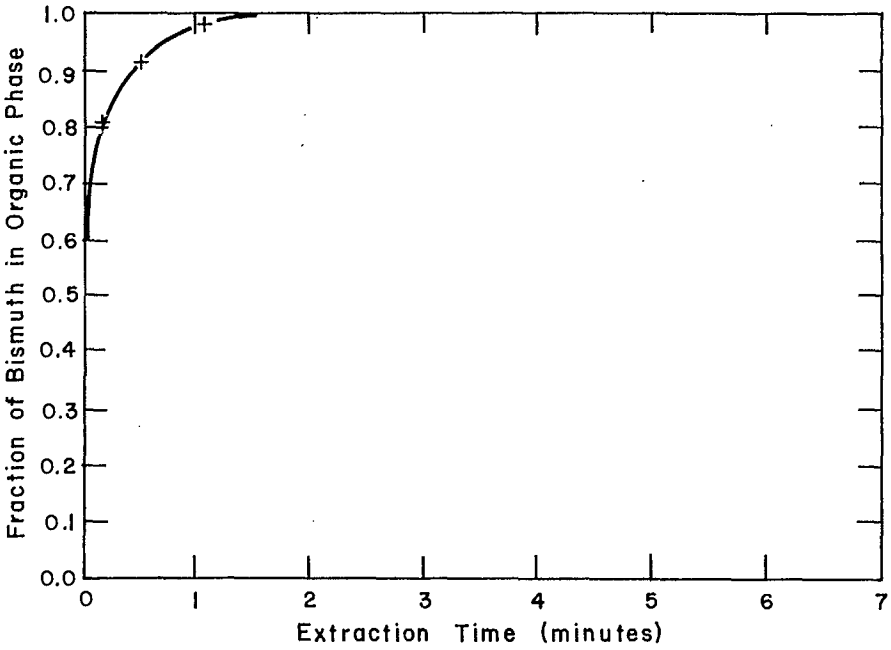


Fig. 2 Fractional Extraction of Bismuth vs Extraction Time.

HCl is absorbed to cause subsequent decomposition of the bismuth-diethyldithiocarbamate complex. Shorter contact times (1 to 2 min) presumably do not transfer sufficient acid to the organic phase to destroy the complex. The optimum extraction period is about 60 seconds. This gives maximum recovery of bismuth and a highly stable organic extract.

The efficiency of a single extraction was determined by extracting a 2M HCl solution containing 1 mg each of bismuth and lead with one 10-ml portion of 0.1% DDTC in chloroform. The recovery varied from 78 to 80 per cent. Two 10-ml extractions followed by a 5-ml wash resulted in 98 to 99 per cent recovery of the bismuth. Nearly identical results were obtained for NaDDC at 2.5M HCl. Less than 1% of the lead is extracted under any of these conditions.

There is a tendency for chloroform to remain suspended in the aqueous phase for prolonged periods. It is necessary to allow a 5 to 10-min standing period following the second extraction before adding the organic wash in order to efficiently recover a maximum of the organic extractant.

The extraction curve for lead with DDTC in Figure 1 does not agree with the results obtained by Sill and Willis (2). In their procedure they were able to extract lead completely at approximately 0.9M HCl. Our results show that only about 10% of the lead should be extracted under their conditions. This discrepancy was resolved when the effect of DDTC concentration on the extraction of lead and bismuth was examined. The extraction curves for both metals with three different levels of DDTC are shown in Figure 3. From this it can be seen that lead can be extracted from nearly 2M HCl with a 1% solution of DDTC (as used by Sill and Willis). However, when 0.1% DDTC is used, as in our procedure, none of the lead is extracted with the bismuth. The same separation can be achieved using 1% DDTC if the HCl concentration is increased to about 4 molar. In most cases it will be desirable to work at as low a hydrochloric acid concentration as possible, therefore the use of 0.1% DDTC at 2M HCl was selected in our procedure.

One problem that may occur when extracting with 0.1% DDTC is the interference of metal ions that form stronger complexes with DDTC than does bismuth. Because of the low concentration of DDTC it is possible for high concentrations of metals such as copper to completely complex with all of the DDTC so that none remains to form the extractable bismuth complex. In such cases it would be necessary to repeatedly extract the aqueous phase until all the copper had been removed and continue until bismuth is completely extracted. A 200-ml volume of 2M HCl containing 1 mg each of copper and bismuth was repeatedly extracted with 10-ml portions of 0.1% DDTC until no colour was observed in the organic phase. The first two extracts were a very dark brown, the third was a medium brownish orange, the fourth was yellow, the fifth was slightly yellow and the sixth was clear. The bismuth was extracted almost completely in the third and fourth extracts. There was less than 0.5% of the bismuth in the fifth extract and none in the first, second or sixth. The first two extracts contained nearly all of the copper. If the amount of copper exceeds 2 mg, the number of extractions required to recover the copper and bismuth becomes excessive.

In order to cope with high levels of copper an additional extraction technique was developed. The extraction curves for copper with two levels of DDTC were determined for HCl concentrations up to 12M and are shown in Figure 4. From this it can be seen that it is possible to separate copper from bismuth by preferentially extracting the copper at a hydrochloric acid concentration of 7 to 8M using 1% DDTC. The higher concentration of DDTC is preferred because it reduces the number of extractions required to extract high concentrations of copper. In addition, 8M HCl should be used in order to limit the extraction of bismuth when repeated extractions for copper are required. This method was tested by extracting 200 ml of 8M HCl solution containing 1 mg Bi, 5 mg Fe, 10 mg Cu and 1 g ascorbic acid with 1% DDTC in chloroform (20-ml portions). The first three DDTC-chloroform extracts were nearly black,

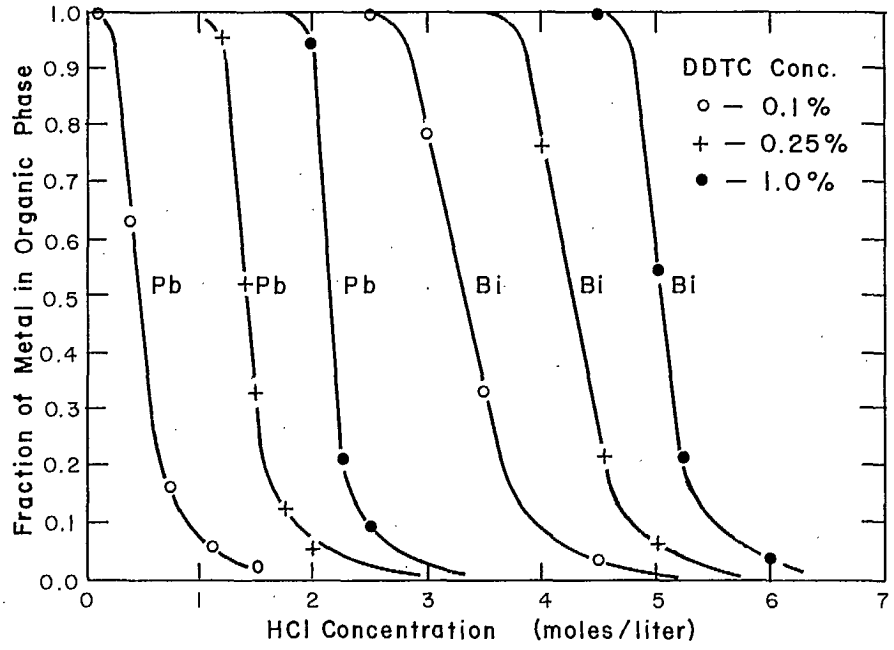


Fig. 3 Fractional Extraction of Lead and Bismuth vs HCl concentration at three concentrations of DDTC.

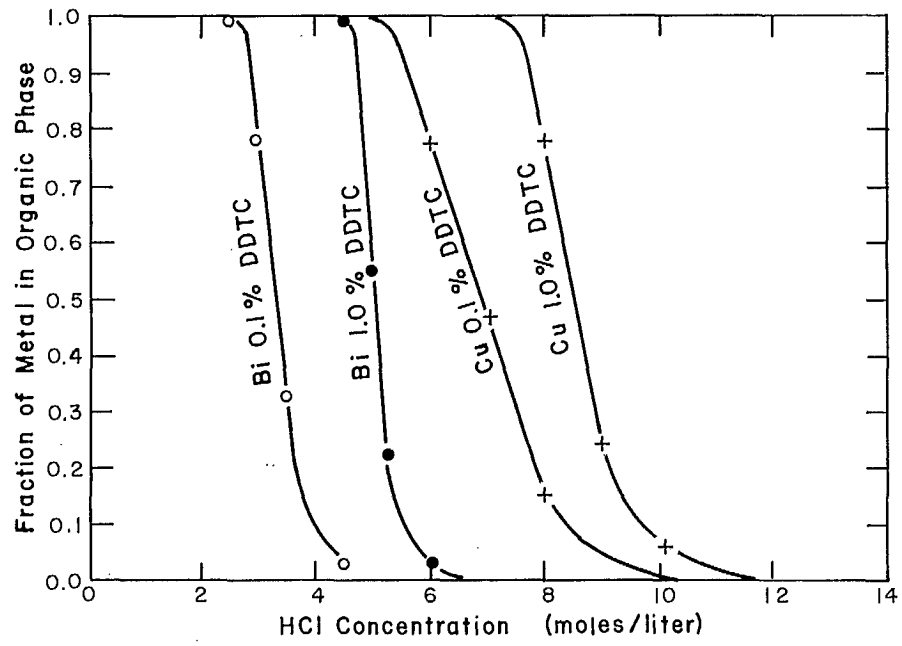


Fig. 4 Fractional Extraction of Bismuth and Copper vs HCl concentration at two concentrations of DDTC.

the fourth was brown and faded to a light pink after standing 5 min and the fifth was a medium green which quickly faded to a light pink. This fifth extract was found to contain less than 1% of the original copper. Next, the aqueous solution was diluted to 800 ml with water to lower the HCl concentration to 2M. The dilute aqueous phase was extracted with three 20-ml portions of 0.1% DDTC in chloroform. The first extract was a dark yellow colour, the second was light yellow and the third was colourless. When combined, the first two extracts accounted for over 98% of the bismuth and the third contained less than 1%. The pure yellow colours obtained for the first two extracts indicated that there was no appreciable copper interference. From this it may be concluded that high concentrations of copper (>2 mg) can be successfully eliminated as an interference by pre-extracting the copper from 8M HCl with 1% DDTC. The bismuth is subsequently recovered by diluting to 2M HCl and extracting with 0.1% DDTC.

Another major interference in the DDTC extraction of bismuth is iron. However, this interference is easily eliminated by reducing all ferric iron to ferrous with an excess of ascorbic acid (2). Under these conditions the amount of iron found in most ore and rock samples does not cause problems. Other potential interferences are silver, mercury, antimony, thallium, molybdenum (VI), selenium, tellurium, palladium and platinum (17). Normally, the concentrations of these elements will be below the level at which they interfere. In those cases where interfering levels are present, the DDTC extractions should be continued until a colourless extract is obtained. The final step in the procedure (preparing the bismuth in a form suitable for beta-counting) has been selected to eliminate extracted amounts of these interfering elements.

Two methods which have been used to precipitate or carry bismuth, are the precipitation of BiOCl (4,8a,9) and coprecipitation with $BaSO_4$ (3). We have selected the BiOCl precipitation method because it gives a further separation from traces of extracted lead and from other elements which may extract with DDTC. The precipitation procedure is simple and gives 98-99% recovery of the bismuth. The chloroform extract is evaporated to dryness and the residue is redissolved in nitric acid. This solution is diluted to approximately 30 ml and NH_4OH is added to precipitate $Bi(OH)_3$. After centrifuging, the solution is discarded and the precipitate is redissolved in 5 drops of concentrated HCl. Dilution of the dissolved precipitate to 40 ml results in a pH of 1.1 to 1.5 and BiOCl precipitates. This suspension may be filtered directly and counted or deposited on a stainless steel planchette for counting.

One interference that is carried through the entire procedure is polonium-210. Since this radionuclide is an alpha emitter it is possible to eliminate any counting interference by counting through a 7 mg/cm^2 aluminum foil. Regular weight, household aluminum foil is suitable for this purpose.

Results

The developed method has been applied to the analysis of a standard pitchblende sample which is known to be in secular equilibrium and for which the uranium concentration is known accurately. Lead-210 levels of 6.05×10^3 and 6.16×10^3 were obtained which agree almost exactly with the accepted value of $6.06 \pm 0.04 \times 10^3$ dpm/g.

In addition, a large number of uranium rock and ore samples were analyzed. In all cases the determined lead-210 values were within ±5% of the values calculated for secular equilibrium with the known uranium concentrations.

Samples containing thorium or those that were spiked with thorium showed no apparent interference.

ANALYTICAL PROCEDURE

Sample Preparation

A. Water Samples

If the samples are clear or have been filtered and acidified, one litre may be taken for extraction. Add 185 ml of 12N HCl, 1 mg each of lead and bismuth carriers and proceed to the DDTC

extraction. Water samples collected in the field are normally preserved with 10 ml HNO_3 per litre of sample. Consequently, the amount of HCl added is 185 ml per litre rather than the 200 ml which would be added to unacidified samples.

For water samples that contain suspended material or organic compounds, treat one litre with 1 mg each of lead and bismuth carriers, 10 ml HNO_3 and 3 ml $HClO_4$. Evaporate and heat to fumes of $HClO_4$. Repeat the HNO_3-$HClO_4$ treatment if necessary to destroy all organics. Dilute to 165 ml with deionized water and 33 ml of concentrated HCl. Proceed to the DDTC-chloroform extraction.

B. Biological Samples

Ash the samples by either a combination of wet ashing with HNO_3 followed by thermal ashing or by thermal ashing alone (4). The final ashing temperature should be kept below 500°C. Add 1 mg each of bismuth and lead carriers to 1 g of ash and dissolve in 10 ml of concentrated HNO_3. Evaporate until about one-half of the HNO_3 has been removed, then add 40 ml of water plus 10 ml of HCl and heat until a clear solution is obtained. Add an additional 65 ml of HCl and dilute to 500 ml with deionized water. Some ash samples may be dissolved directly in HCl. Proceed to the DDTC-chloroform extraction.

C. Ore, Rock and Soil Samples

Work by Sill and Willis (2,3) has shown that severe losses of lead can occur when samples are fused with potassium fluoride or potassium pyrosulphate in platinum crucibles. For this reason they recommend an acid dissolution procedure performed in a Teflon FEP beaker (3). We have found the following procedure suitable for many types of solid siliceous samples. Transfer a 1-g sample to a 200-ml Erlenmeyer flask and add 1 mg each of lead and bismuth carriers followed by 10 ml HNO_3 and 10 ml $HClO_4$. Heat on a hot plate until fumes of $HClO_4$ are evolved and all organic matter has been oxidized. If necessary add more HNO_3 and $HClO_4$ and redigest. Evaporate the solution until about 1 ml of $HClO_4$ remains. Cool, add 50 ml of 10% HCl and boil for about 5 minutes to dissolve bismuth phosphate and metallic sulphates. Transfer the contents of the Erlenmeyer flask to a centrifuge tube, centrifuge and transfer the solution back to the rinsed Erlenmeyer. Transfer the solid residue to a FEP Teflon beaker and treat with 2 ml H_2SO_4 and 10 ml HF. Evaporate to SO_3 fumes, cool slightly and add 20 ml of 10% HCl. If any barium sulphate precipitate forms at this stage it may be separated by centrifuging. The presence of the HCl will prevent lead or bismuth from being carried by the barium sulphate precipitate. Combine this solution with the main digest solution, add 26 ml of HCl and dilute to 200 ml. Add sufficient ascorbic acid to the hot solution to reduce all ferric iron present and leave an excess of about 0.5 g. Cool the solution and proceed with the DDTC-chloroform extraction. If the sample contains more than 0.5 mg of copper it will be necessary to pre-extract the copper with 1% DDTC after making the solution 8M in HCl. Repeat the extractions until a colourless or light pink organic extract is obtained. Discard all organic extracts. Dilute the aqueous phase four-fold (2M HCl) and proceed to the bismuth extraction.

Reagents

Bismuth carrier. Prepare a solution of bismuth nitrate in 10% HNO_3 to contain 1 mg Bi per ml.

Lead carrier. Prepare a solution of lead nitrate in 10% HNO_3 to contain 1 mg Pb per ml.

DDTC – chloroform extractant. Dissolve 1.0 g of diethylammonium diethyldithiocarbamate in chloroform and dilute to 1 litre.

All acids are reagent grade.

Procedure

Transfer the prepared sample solution (2M HCl) to an appropriately-sized separatory funnel. Add a suitable volume of DDTC-chloroform extractant (10 ml for 200-ml sample and 20 ml for 500 or 1000-ml samples). Shake vigorously for 1 minute and draw off the extract into a 50-ml or 100-ml

beaker depending on the extract volume used. Note the time of this first extraction as the beginning of the bismuth-210 decay. Repeat the extraction until a colourless organic phase is obtained. Normally, the first two extractions will be yellow and the third colourless. If small amounts of copper, selenium, antimony, arsenic or molybdenum are present it may be necessary to perform an extra 2 to 3 extractions before obtaining a final colourless extract. Combine all extracts and evaporate to dryness. Dissolve the residue in 5 ml of concentrated nitric acid and heat gently until the organic residue is destroyed. Dilute to 25 ml. Pipette one ml of this solution into a 10-ml volumetric flask, dilute to the mark and then determine bismuth by atomic absorption spectrometry. This result can be used to calculate the recovery of bismuth through the extraction procedure. Transfer the remaining 24 ml of the first dilution to a 40-ml centrifuge tube and add an additional 5 mg of bismuth carrier. This is done to provide an amount of bismuth which is convenient to handle in the following precipitation separation.

Adjust the solution to pH 8. A combination electrode is convenient to measure the pH in the centrifuge tube. Place the centrifuge tube in a beaker of hot water heated by a combined hot plate-magnetic stirrer and stir the contents of the centrifuge tube with a small stir bar (3 x 10 mm). Heat for 5-10 min then remove the centrifuge tube, cool and centrifuge, discarding the supernate. Dissolve the precipitate with 5 drops of concentrated HCl and dilute to 40 ml with deionized water. Heat in a beaker of hot water with stirring as before. The bismuth oxychloride precipitate may be mounted in two different ways for beta-counting. The first method is to filter the hot suspension through a 0.45-micron membrane filter in a HASL ring-and disc-filter assembly (8b). Remove the filter chimney, cover the filter and disc with household aluminum foil ($\sim$7 mg/cm^2) and press the ring into place. Trim excess foil and the assembly is ready for counting after allowing 12-18 hours for decay of bismuth-214, bismuth-212 and bismuth-211. Using this filtering method the recovery of bismuth by the BiOCl precipitation is reproducible and a recovery correction is not necessary. The calibration curve prepared from standard solutions will correct for the small amount of bismuth not precipitated (1 to 2%). The second method involves mounting the BiOCl precipitate on a stainless steel planchette. Centrifuge the hot BiOCl suspension and discard the supernate. Wash the precipitate with 5 ml water, centrifuge and discard the water. Wash with 5 ml of ethyl alcohol, centrifuge and discard the alcohol. Slurry the precipitate with 2 ml of ethyl alcohol and transfer to an inverted, ringed planchette. Dry under a heat lamp, cool and weigh. Use this weight to calculate the recovery of bismuth. Allow sufficient time for decay of bismuth-212 (minimum 10 hours), cover with aluminum foil and count in a low-background beta counter.

Calibration and Calculations

It is possible to calculate the amount of bismuth-210 in a sample from the counter efficiency, the fractional recovery of the extraction and the fractional recovery of the BiOCl precipitation. However, rather than use a single value for the counter efficiency, it is preferable to prepare a calibration curve of net counts per minute vs pCi Pb-210 from a series of Pb-210 concentrations varying from 0.5 pCi/ℓ to 1000 pCi/ℓ. Such a calibration provides valuable information on the precision of the method and the reproducibility as performed by different analysts. Once an acceptable calibration curve has been produced by each analyst it is only necessary to repeat a few standards with each batch of samples. The two types of calculation that follow are for the BiOCl filtration method and the BiOCl planchette deposition method.

BiOCl Filtration

No correction is made for the fractional recovery of the BiOCl precipitate as it is assumed that the variation between samples can be neglected and the recovery observed for standards will represent the mean recovery. This mean recovery is included in the calibration curve. It is,

therefore, necessary to correct only for the fractional recovery of the DDTC extraction.

$$\text{Pb-210} = \frac{C_F}{E \cdot D} \text{ pCi}$$

where C_F = pCi of Pb-210 corresponding to the net count rate of the sample, R_N. Read from the filtration calibration curve.

E = Fractional recovery of Bi in the DDTC extraction.

D = Decay factor for Bi-210 ($e^{-\lambda t}$ - where t is the time elapsed between the extraction and the mid-point of the count)

R_N = Observed count rate less background count rate.

BiOCl Deposition

The following formula is based on the addition of 1 mg of Bi carrier prior to the DDTC extraction and the addition of 5 mg of Bi prior to the BiOCl precipitation.

$$\text{Pb-210} = \frac{C_D}{E \cdot D \cdot \left(\frac{W}{E+5}\right)} \text{ pCi}$$

where C_D = pCi of Pb-210 corresponding to the net count rate of the sample, R_N. Read from the planchette deposition calibration curve in which corrections are made for both the extraction and BiOCl precipitation fractional recoveries.

E = Fractional recovery of Bi in the DDTC extraction.

D = Decay factor for Bi-210 ($e^{-\lambda t}$ - where t is the elapsed time between the extraction and the mid-point of the count).

R_N = Observed count rate less background count rate.

W = Weight of Bi in the final BiOCl precipitate.

5 = the weight of bismuth added prior to the BiOCl precipation (mg).

Precision and Detection Limit

From repeated analysis of standard samples the relative standard deviation for this method is approximately 4% of the amount present. The detection limit using a low-background counter, with a background of about 0.3 cpm and counting for 100 minutes is approximately 0.5 pCi.

REFERENCES

1. Harley, J.H. et al. U.S. Atomic Energy Commission Report NYO-4700, revised Aug., 1962.

2. Sill, C.W. and Willis, C.P. Anal. Chem; 37: 1661; 1965.

3. Sill, C.W. and Willis, C.P. ibid; 49:302; 1975.

4. Gibson, W.M. "The radiochemistry of lead, Nuclear Science Series"; U.S. National Academy of Sciences and National Research Council; NAS-NS3040; 1961.

5. Petrow, H.G. and Cover, A. Anal. Chem; 37: 1659; 1965.

6. Aronson, A.L. and Hammond, P.B. Nucleonics; 22:90; 1964.

7. Talvitie, N.A. and Garcia, W.J. Anal. Chem; 37:851; 1965.

8a. Harley, J.H. "HASL Procedures Manual; Procedure E-Pb-01"; U.S. Atomic Energy Commission, 376 Hudson St., New York, N.Y. 10014.

8b. Ibid; Procedure G-13-01.

9. National Centre for Radiological Health, Rockville, Maryland, U.S.A., "Radioassay procedures for environmental samples"; PB-189-357:7-34; January, 1967.

10. Bhattacharyya, D.K. Separation Science; 9: 257; 1975.

11. Maynes, A.D. and McBryde, W.A. Anal. Chem; 29:1259; 1957.

12. Yamane, T., Mukoyama, T. and Sasamoto, T. Anal. Chim. Acta; 69:347; 1974.

13. Cheng, K.L., Bray, R.H. and Melsted, S.W. Anal. Chem; 27:24; 1955.

14. Rooney, R.C. Analyst; 83:83; 1958.

15. Powell, R.A. and Kinser, C.A. Anal. Chem; 30: 1139; 1958.

16. Neirinckx, R.D. Anal. Chim. Acta; 54:357; 1971.

17. Bode, H. and Neumann, F. Z. Anal. Chem; 172: 1; 1960.

CANMET REPORTS

Recent CANMET reports presently available or soon to be released through Printing and Publishing, Supply and Services, Canada (addresses on inside front cover), or from CANMET Publications Office, 555 Booth Street, Ottawa, Ontario K1A 0G1:

Les récents rapports de CANMET, qui sont présentement disponibles ou qui ce seront bientôt peuvent être obtenus de la direction de l'Imprimerie et de l'Edition, Approvisionnements et Services, Canada (adresses au verso de la page couverture), ou du Bureau de Vente et distribution de CANMET, 555 rue Booth, Ottawa, Ontario, K1A 0G1:

78-2 Revision of recommended values for reference ores MP-1 and KC-1; G.H. Faye and W.S. Bowman;
Cat. No. M38-13/78-2, ISBN 0-660-01712-1; Price: $1.00 Canada, $1.20 other countries.

78-3 Certified and provisional reference materials available from the Canada Centre for Mineral and Energy Technology, 1978; G. Faye;
Cat. No. M38-13/78-3, ISBN 0-660-01804-7; Price: $1.25 Canada, $1.50 other countries.

78-5 Certification of reference iron ore SCH-1 for sodium and potassium; R. Sutarno, D.J. Charette, W.S. Bowman and G.H. Faye;
Cat. No. M38-13/78-5, ISBN 0-660-01808-X; Price: $1.00 Canada, $1.20 other countries.

78-6 Catalogue of CANMET publications — Catalogue des publications de CANMET 1976/77; C. Mamen, Editor;
Cat. No. M38-13/78-6, ISBN 0-660-01849-7; Price: $4.00 Canada, $4.80 other countries.

78-8 Preparation of a ceramic electrolyte in the system $MgO-K_2O-TiO_2$; H.H. Quon and T.A. Wheat;
Cat. No. M38-13/78-8, ISBN 0-660-10006-1; Price: $3.00 Canada, $3.60 other countries.

78-9 Design guidelines for multi-seam mining at Elliot Lake; D.G.F. Hedley;
Cat. No. M38-13/78-9, ISBN 0-660-10047-9; Price: $1.25 Canada, $1.50 other countries.

78-10 Block flow slope stability; D.F. Coates and Y.S. Yu;
Cat. No. M38-13/78-10, ISBN 0-660-10019-3; Price: $1.00 Canada, $1.20 other countries.

78-11 Equipment and procedures to determine ground stresses in a single drill hole; G. Herget, P. Miles and W. Zawadsky;
Cat. No. M38-13/78-11, ISBN 0-660-10007-X; Price: $1.25 Canada, $1.50 other countries.

78-14 The mineral sources of silver and their distribution in the Caribou massive sulphide deposit, Bathurst area, New Brunswick; J.L. Jambor and J.H.G. Laflamme;
Cat. No. M38-13/78-14, ISBN 0-660-10105-X; Price: $1.00 Canada, $1.20 other countries.

78-15 Performance of high alumina cement concrete stored in water and dry heat at 25, 35 and 50°C; D.H.H. Quon and V.M. Malhotra;
Cat. No. M38-13/78-15, ISBN 0-660-10037-1; Price: $2.50 Canada, $3.00 other countries.

76-40F Evaluation des charbons marchands canadiens: Nouvelle-Ecosse et Nouveau Brunswick - 1975; T.E. Tibbetts et W.J. Montgomery;
Cat. No. M38-13/76-40F, ISBN 0-660-01821-7; Price: $3.00 Canada, $3.60 other countries.

76-22F Manuel sur la pente des mines a ciel ouvert - Chapitre 1 - Sommaire; R. Sage;
Cat. No. M38-14/1-1978F, ISBN 0-660-90030-0; Price: $2.50 Canada, $3.00 other countries.

77-55F Ressources canadiennes en rebuts mineraux rapport n° 2 - Les rebuts mineraux au Quebec; R.K. Collings;
Cat. No. M38-13/77-55F, ISBN 0-660-90019-X; Price: $1.75 Canada, $2.10 other countries.