**PACIFIC NORTHWEST LABORATORY
ANNUAL REPORT FOR 1966
TO THE
USAEC DIVISION OF BIOLOGY
AND MEDICINE
VOLUME II: PHYSICAL SCIENCES
PART 2. RADIOLOGICAL SCIENCES**

DECEMBER 1967

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Part 2. Radiological Sciences

By
Staff Members of
Radiological Sciences Section
Environmental and Radiological Sciences

Edited by
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RADIOLOGICAL CHEMISTRY

COSMIC-RAY PRODUCED RADIONUCLIDES AS TRACERS
OF ATMOSPHERIC PRECIPITATION PROCESSES

N. A. Wogman, C. W. Thomas, J. A. Cooper,
R. J. Engelmann* and R. W. Perkins

During the past few years numerous cosmic-ray spallation products of atmospheric oxygen, nitrogen, and argon have been found in aerosols and rainwater.⁽¹⁾ Some of the long-lived radionuclides, with half-lives greater than one week, have been useful in defining tropospheric and stratospheric mixing rates. The shorter-lived isotopes with half-lives of minutes to hours have a potential in defining the precipitation scavenging mechanisms. When highly sensitive multidimensional gamma-ray spectrometers were used, the two short-lived cosmic-ray produced radionuclides ^{38}Cl (37.3 min) and ^{38}S (2.9 hr) were discovered in rainwater⁽²⁾ and techniques for the measurements of three other short-lived radionuclides $^{34\text{m}}\text{Cl}$ (32.4 min), ^{39}Cl (55 min), and ^{24}Na (15.0 hr) in precipitation were developed. For their measurement the chlorine isotopes are precipitated from rainwater samples of 2 to 100 liter volumes, while the ^{38}S and ^{24}Na are contained in the residue

from evaporation of the water samples. The five radionuclides are then measured by direct counting on a multidimensional gamma-ray spectrometer⁽³⁾ which has two 11 in. diam by 6 in. thick NaI(Tl) crystals serving as the principal detectors. The concentrations of these radionuclides observed in various rain samples are listed in Table I. The concentrations in rainwater of the various cosmic-ray produced radionuclides vary with precipitation rate. During periods of light rain with accompanying small drop sizes, the number of condensation nuclei per unit liquid volume is high, resulting in a high concentration of radionuclides.

The ratios of these five radionuclides provide information on the scavenging rate and removal efficiency of the atmospheric aerosols to which they are attached, while the absolute concentrations of these radionuclides provide information on the average altitude of the air mass from which precipitation formation occurred. The distribution of the isotope production

* Atmospheric Sciences Section

TABLE I. Cosmic-Ray Produced Radionuclides in Rainwater^(a)

Date	Precipitation Rate, cm/hr	Collection Time, min	Volume, liters	dis/min/liter				
				⁵⁹ Cl	⁵⁸ Cl	^{54m} Cl	⁵⁸ S	²⁴ Na
6-15-64	(b)	(b)	60					0.70 ± 0.2
6-17-64	(b)	(b)	6.64					2.22 ± 0.25
6-18-64	(b)	(b)	14.52					0.59 ± 0.09
7-29-64	(b)	50	5.10	200 ± 17	147 ± 15	(b)	15 ± 5	2.0 ± 0.2
8-01-64	(b)	50	5.50	15 ± 3	9 ± 5	(b)	(b)	(b)
8-12-64	(b)	5	2.20	62 ± 12	42 ± 15	(b)	(b)	2.3 ± 0.4
1-14-66	0.255	30	30.16	24.4 ± 1.1	20.4 ± 2.1	0.5 ± 0.1	1.22 ± 0.16	0.227 ± 0.017
1-28-66	0.0767	44	15.32	60.5 ± 1.6	45.3 ± 3.0	0.7 ± 0.2	2.07 ± 0.31	2.06 ± 0.08
2-01-66	0.316	25	97.87	37.2 ± 0.8	22.9 ± 1.5	0.5 ± 0.1	1.85 ± 0.14	0.608 ± 0.019
2-12-66	0.0515	40	25.50	108.7 ± 2.0	82.7 ± 3.4	1.1 ± 0.2	8.24 ± 1.5	6.14 ± 0.13
2-13-66	0.0638	37	29.20	95.5 ± 1.6	60.5 ± 2.5	1.4 ± 0.2	3.29 ± 0.67	1.77 ± 0.10
1-26-67	0.155	40	76.80	59.2 ± 1.3	43.9 ± 2.3	0.9 ± 0.3	1.11 ± 0.16	1.06 ± 0.03
1-26-67 ^(c)	0.0384	40	19.0	181.6 ± 3.2	113.9 ± 4.9	1.5 ± 0.4	(b)	1.07 ± 0.12

(a) ± values are the standard deviation for the measurement

(b) Not determined

(c) End of rain 1-26-67

rates within the atmosphere can be calculated from cosmic-ray energy and intensity data and from theoretical expressions for high energy spallation yields.⁽⁴⁾ In addition, the atmospheric concentrations or production rates are being experimentally obtained between sea level and the middle stratosphere by aircraft sampling. The principal feature of this distribution is a continual increase of production rate from sea level to about 12 km which varies somewhat with geomagnetic latitude. The wide variation observed in the ^{38}Cl (37.3 min)-to- ^{24}Na (900 min) ratio in the rain samples is indicative of the "in-cloud" time spent by the condensation nuclei; this is a major cloud physics parameter. The lowest ^{38}Cl -to- ^{24}Na ratios were observed during the beginning of a rain storm while the highest ratios were observed near the end. This suggests that the initial precipitation occurs from a slow formation of droplets in the cloud allowing much of the

initially-present ^{38}Cl to decay; whereas, the final precipitation results from relatively rapid droplet development.

This technique provides a unique method for studying fallout rates and mechanisms and permits the investigation of processes which cannot be studied by any other method.

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COSMIC-RAY AND ENVIRONMENTAL CONTRIBUTIONS TO THE BACKGROUND IN NaI(Tl) CRYSTAL GAMMA-RAY SPECTROMETRY*

N. A. Wogman and R. W. Perkins

Sources of the environmental and cosmic-ray produced background observed by NaI(Tl) crystal gamma-ray spectrometer systems have been studied. The systems used were of three general types: (1) single NaI(Tl) crystals, (2) anticoincidence-guarded NaI(Tl) crystals, and (3) anticoincidence-guarded dual crystal systems for multidimensional gamma-ray spectrometers. The background spectrum and its consistency for these various spectrometer systems was determined over the energy range 0 to 150 MeV. An analysis of the radionuclides present in the hardware of a spectrometer system was performed to determine the

* BNWL-SA-1109.

types, amounts, and location of the radionuclides and to develop counting methods which would minimize their effect. In the region of 0 to 10 MeV, the gamma-ray background is from both environmental and cosmic-ray sources; in the higher region up to 150 MeV, it is from cosmic ray reactions. The high energy region contains a broad peak with an energy which is dependent on the crystal thickness and originates from the cosmic-ray muons which penetrate the crystal. The low energy region contribution of muons and muonic X-rays from the shield components was also determined. Cosmic-ray produced neutrons interact with various components of the spectrometer system creating prompt gamma-ray photopeaks at 2.225 and 6.8 MeV. Methods of reducing the background in both the lower and higher energy regions by use of anticoincidence shielding and neutron shielding techniques were found which increase the sensitivity of NaI(Tl) spectrometers while reducing their backgrounds.

The natural radionuclides, ^{232}Th , ^{238}U , their decay products, and ^{40}K were found in NaI(Tl) spectrometer hardware including the MgO reflector material, the aluminum cladding, and the Pyrex windows used to couple the crystal to the phototubes. Alternate hardware materials were found which could be used to minimize the environmental background contribution.

ATMOSPHERIC BEHAVIOR OF AIRBORNE RADIONUCLIDES

C. W. Thomas and N. A. Wogman

The concentrations of ^7Be , ^{22}Na , ^{46}Sc , ^{54}Mn , ^{60}Co , ^{65}Zn , ^{88}Y , ^{95}Zr - ^{95}Nb , ^{103}Ru , ^{106}Ru , $^{110\text{m}}\text{Ag}$, ^{124}Sb , ^{125}Sb , ^{134}Cs , ^{140}Ba - ^{140}La , ^{144}Ce and ^{228}Th in air near ground level have been measured continuously at three latitudes in the world. Data suggest that the annual latitudinal spring increase of radionuclide concentration results from rapid stratospheric mixing and indicates a mean residence half-time of 11.7 ± 0.088 months for stratospheric debris. The amplitude, width and arrival time of the spring concentration maximum showed a latitude dependancy. The ^7Be concentration was of great interest but additional sampling at more latitudes will be needed to define its various relationships. Short half-life radionuclides which were injected into the troposphere by Chinese testing have suggested a tropospheric radionuclide residence half-time of 9 days and have indicated a circum-navigating time of 10 days for nuclear debris at 45°N latitude.

INTRODUCTION

Long term variations have been observed for nuclear debris inserted into the atmosphere during the large yield detonation of 1961-1962 as well as short term variations arising from the Chinese and French small-yield detonations. This report presents a

comprehensive analysis of the data and interprets the movement of the radionuclides in the lower tropospheric levels as well as contributing measurements of intermixing in various air masses.

Ground level behavior of radioactive fallout debris, including both radionuclides produced from fission

and from natural processes, have been studied by this laboratory for many years. An initial summary of this study⁽¹⁾ which included the concentrations of thirteen radionuclides at Richland, Washington, was published in the proceedings of the Second Conference on Radioactive Fallout from Nuclear Weapons Tests and included measurements covering the period January 1962 through September 1964. These studies have continued and expanded to include 18 radionuclides from additional sampling stations at Point Barrow, Alaska, and Rio de Janeiro, Brazil.

Even though the concentrations of nuclear debris in the troposphere are variable, they can be effectively used as a meteorological tracer. Many investigations^(2,3,4) have shown the tropospheric residence time of this material to be approximately 30 days while the stratospheric residence half time is about one year depending on the latitude and debris insertion altitude. With the cessation of weapons testing at the beginning of 1963, it was apparent that the fission product inventory of most of the long-lived radionuclides in the stratosphere could be assigned to the massive 1961-1962 nuclear test period. Therefore, after 1963, change in the ground level radionuclide concentrations reflect movement of radionuclides from the stratosphere to the ground.

The large drop in the atmospheric radionuclide concentration over the past four years has now produced levels where the minute amounts of radionuclides released to the atmosphere from

the plant operations at Hanford are evident in the air samples collected at Richland, Washington. Unfortunately some of the radionuclides released are the same as those being monitored in fallout and this has caused some problem in interpreting the nuclear weapons fallout contributions during the last year.

In the latter part of 1964, the Peoples' Republic of China detonated a low-yield device and, since that time, have continued to test periodically. Most of the radioactive debris from these tests was contained in the troposphere.⁽⁵⁾ The concentrations of short-lived radionuclides at Richland, Washington were measured after each detonation and afforded a method to study the movement of debris from the troposphere to ground level. During 1966, France conducted nuclear weapons tests in the southern hemisphere which contributed to the southern atmosphere and could be studied by the sampling station at Rio de Janeiro, Brazil.

SAMPLING AND MEASURING METHODS

Part of this study consisted of measuring radionuclide concentrations in ground level air masses. Samples were collected continuously by large 2.8 m³/min vacuum pumps on membrane filters of 5 μ pore size. These membrane filters had been shown to have 100% collection efficiencies for fallout radionuclides.⁽¹⁾ Filters were composited monthly or semimonthly and pressed into a standard counting geometry of 1.25 cm thick by 2.5 cm diam.

In February 1965, larger vacuum pumps (19.8 m³/min) were used, and the geometry for counting was changed to 1.25 cm thick by 5.0 cm diam. After each Chinese test, air samples were collected using the smaller vacuum pump on a daily frequency so that short term variations could be studied. From mid-1964 to mid-1966, fallout samples were collected using 80 ft² trays containing about one-half inch of water representing the total deposition of the radionuclides by either dry fallout or rainfall.

Multidimensional gamma-ray spectrometer systems^(6,7,8) were used to measure the radionuclide concentrations. They consisted of three gamma-ray detectors arranged in a manner so that the sample was counted between two NaI(Tl) detectors while a third detector served as the anticoincidence shield. These instruments measure both the single and coincidence gamma-rays emitted from the sample and store the events in a 4096 word computer memory at locations which uniquely define the energies of the gamma ray. In addition, the use of large volume Ge(Li) detectors has allowed the measurement of airborne radionuclides with gamma-ray energies only 3 keV apart.

RESULTS

The radionuclides shown in Figure 1 result from fission and neutron activation during atomic tests; from interactions of cosmic rays with nitrogen, oxygen, and argon in the atmosphere; and from naturally-occurring radioactive species. These radionuclides have been segregated into four separate

groups for comparison according to the manner in which their concentration varied. The first group (²²Na, ⁵⁴Mn, ⁸⁸Y, ¹⁰⁶Ru, ¹²⁵Sb, ¹³⁷Cs, and ¹⁴⁴Ce) typified radionuclides whose air concentration decreased over a long period of time and showed prominent seasonal variations. The second group of radionuclides (⁷Be, ⁴⁶Sc, ⁶⁵Zn, and ²²⁸Th) also showed seasonal variations, but the air concentration did not decrease with time. The third group (⁶⁰Co, ¹²⁴Sb, and ¹³⁴Cs) contained radionuclides whose concentrations varied erratically and whose production was apparently enhanced by other processes than those numerated above. Finally, the fourth group (⁹⁵Zr-⁹⁵Nb, ¹⁰³Ru, and ¹⁴⁰Ba-¹⁴⁰La) represented radionuclides whose present air concentration depended mainly on recent detonations. Where appropriate, the radionuclide air concentration was corrected for radioactive decay to December 1962, and the resultant curves represented the apparent residence half-times for these radionuclides. The mean residence half-times reflected conditions both in the stratosphere and in the troposphere as well as any intermixing effects between local air masses.

Richland, Washington (45° N Lat.)

The mixing of stratospheric and tropospheric air, resulting in the large annual concentration increase in the spring,⁽⁹⁾ was very pronounced in this study and all radionuclides in group 1 reflected this increase. ²²Na (2.60 years), a cosmic-ray spallation radionuclide, was produced in very

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FIGURE 1. Fallout Concentrations for Various Years

large quantities during the 1961-1962 test period;⁽¹⁰⁾ and the data indicated that nearly all the measured activity can be attributed to this source. The annual spring peak concentration of ^{22}Na , since its addition, has decreased from 49 to 3.7 dis/min/ 10^6ft^3 . These concentrations compare favorably with those reported by Rodel⁽¹¹⁾ (1965). When correcting the ^{22}Na concentration for radioactive decay, a mean residence half-time of 14 months was indicated.

^{54}Mn and ^{88}Y were produced in large amounts from neutron activation during the 1962 test series,⁽¹²⁾ and since that time they have shown a marked decrease in concentration. ^{54}Mn (312 days) reached its highest concentration level of 2×10^4 dis/min/ 10^6ft^3 in the spring of 1963 and, during the spring of 1966, was found at 1.5×10^3 dis/min/ 10^6ft^3 . It has been reported⁽¹²⁾ that ^{54}Mn was produced abundantly during the 1961 USSR tests along with ^{55}Fe and ^{124}Sb . The mean residence half-time as indicated for this isotope was 10 months. Although produced in large amounts at what appeared to be the same time as ^{54}Mn , ^{88}Y (107 days) exhibited fallout characteristics that were unique. As indicated in Figure 2, the concentration during the spring of 1963 and 1964 varied by only 30%; yet the radionuclide had gone through more than three half-lives. If the ^{88}Y was inserted at a relatively high altitude during the last days of December 1962, it is possible that small fractions would be associated with the tropospheric spring increase in 1963 and might account for this type of fallout

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FIGURE 2. ^{140}Ba Conc. in Ground Level Air from Chinese Detonations, Richland, Washington

pattern. If so, this would then indicate that ^{88}Y and ^{54}Mn were associated with different test shots. From 1964 to date, the ^{88}Y rate of decrease due to stratospheric transport cannot be measured due to the short half-life of the isotope.

The radionuclide ^{106}Ru (1 year), a fission product, showed a mean residence half-time of 13 months and, during 1966, appeared to reach levels where possible interference from Chinese debris could make a large contribution. Fission product ^{125}Sb (2.7 years) indicated the longest mean residence half-time (20.5 months) of any isotope measured. However, it appears that some contributions came from the Hanford plant during the spring of 1966. Corrections for this gave a curve similar to that of ^{88}Y and a mean residence half-time of 9 months, a number which appears more plausible considering the other data. Apparently this radionuclide is produced and released in small amounts to the environs at Richland, Washington, where the large volume air pumps and spectrometry systems can detect it. Measurements of ^{137}Cs (30 years), a fission product, indicated a mean residence half-time of 11 months while ^{144}Ce (285 days) showed a half-time of 13 months.

The average of these residence half times was 11.7 ± 0.88 months, slightly greater than the 10 months reported by Feely et al.⁽⁵⁾ (1966) and about equal to the half-time of 1 year suggested by Mahlman.⁽¹³⁾ A residence half-time of the magnitude shown by this study would indicate that 5.5 megatons of fission product debris (not corrected for decay) from nuclear weapons tests conducted in the atmosphere are still present in the stratosphere.⁽¹⁴⁾ Calculations also indicate about 0.35 megaton of ^{106}Ru from the 1961-1962 tests is available in the

stratosphere and that the concentration of radionuclides with half-lives similar to that of ^{106}Ru is sufficiently low as to show the effects of any additional Chinese tests.

Group 2 consisted of radionuclides who showed seasonal variations but whose concentrations did not decrease with time. ^7Be (53 days), a cosmic-ray produced radionuclide, was reported in the atmosphere by Arnold and Al-Salih in 1955.⁽¹⁵⁾ Although some ^7Be was reported as produced in weapons testing,⁽¹⁶⁾ due to its short life the amount measured during this study was nearly all from spallation reactions in the atmosphere. Its concentration varied from 2 to 8×10^3 dis/min/ 10^6ft^3 in excellent agreement with the concentrations of 1.5 and 6.1×10^3 dis/min/ 10^6ft^3 reported by Parker,⁽¹⁷⁾ and Lindblom,⁽¹⁸⁾ for the years 1960 and 1961. ^{46}Sc (84 days) is a Hanford plant-associated isotope. It appeared to have a seasonal variation but differed considerably from other radionuclides by peaking in the winter months. ^{65}Zn (243 days) appeared to have a seasonal variation similar to radionuclides associated with nuclear debris; however, the likelihood of this being the primary source has not been determined. $^{110\text{m}}\text{Ag}$ (260 days) was noted in the lower polar stratosphere in samples taken in 1963⁽⁵⁾ and is associated with nuclear debris. ^{228}Th is a natural radionuclide and its presence in air was from airborne dust particles. Since the air concentration of ^{46}Sc , ^{65}Zn , $^{110\text{m}}\text{Ag}$, and ^{228}Th measurements originated in 1965, the results indicate

only the magnitude of their concentration and no time-dependent conclusions can be drawn.

The group 3 radionuclides appeared to have a seasonal trend; however, the results were quite erratic throughout the sampling period. ^{60}Co (5.2 years), an activation product, appeared to have a seasonal variation as indicated in Figure 1; but interspersed throughout the data were unexpectedly high concentrations assumed to be from other than fallout. ^{124}Sb (60 days), also a neutron activation product, was formed in what must have been huge amounts in the tests of late 1962⁽¹²⁾ and showed a residence half-life curve similar to that of ^{88}Y . The concentration appears now to be enhanced by the plant contribution as is ^{134}Cs (2.1 years), whose seasonal variation is completely masked by this source.

Group 4 radionuclides represent a class whose concentrations are dependent on current detonations. ^{95}Zr - ^{95}Nb (65 days), ^{140}Ba - ^{140}La (12.8 days) and ^{103}Ru (40 days) represent this group. During 1963 and the spring of 1964, ^{95}Zr - ^{95}Nb showed seasonal trends but since the half-life was short compared to the residence half-time, these variations were not prominent. The concentration at present is dependent only on current detonations. ^{103}Ru and ^{140}Ba - ^{140}La were measured only intermittently during this period.

Point Barrow, Alaska (70° N Lat.)

The concentration of radionuclides in ground level air at Point Barrow, Alaska, has been measured on a monthly

basis since 1965 and generally showed concentrations between one-half and one-quarter the concentration at mid-latitude. With the exception of ^7Be , all long-lived radionuclides measured at this latitude indicated no production source other than fallout and showed distinct seasonal variations similar to group 1 radionuclides. The mean residence half-time appeared to be longer here in the high latitudes, similar to Brewer's⁽¹⁹⁾ report when he compared seasonal ozone variations with latitudes; however, this is only an estimate since these results are based on two seasonal cycles. ^7Be concentrations ranged from 0.6 to 5×10^3 dis/min/ 10^6ft^3 , values which are lower than the concentrations at either 45° N or 51° N (Parker).⁽¹⁷⁾

Rio de Janeiro, Brazil (30° S Lat.)

The sampling station at Rio de Janeiro, Brazil, was activated just after the two French tests on July 2 and 19, 1966 over Moruroa, a Pacific atoll, about 750 miles southeast of Tahiti.⁽²⁰⁾ Both detonations were plutonium fission devices with the first reported as "tactical size" and the second as "low yield." The first samples received from this sampling station covered the months of August and September and showed ^{54}Mn , ^{88}Y , ^{106}Ru , and ^{144}Ce concentrations which were equivalent to the norther hemisphere midlatitude samples, while ^{22}Na , ^{137}Cs , and ^{228}Th were about one-half this value, and ^{125}Sb and $^{110\text{m}}\text{Ag}$ were about one-tenth. Assuming that both hemispheres have similar spring increases at midlatitudes reaching a

maximum about May for northern hemisphere and about November for southern hemisphere, the months of August and September should represent a period which can be compared. Krey,⁽²¹⁾ reported that the gamma activity levels from long-lived radionuclides in 1965 were about equal in the two hemispheres. The Chinese detonations in July 1966 and the two French detonations in July 1966 injected short half-life material into the atmosphere increasing the gamma activity in the southern hemisphere to twenty-fold greater than in the northern hemisphere. Future testing could change this relationship, since rapid intertransport of nuclear debris from the northern hemisphere USSR tests into the southern hemisphere has been reported.⁽²²⁾ The concentrations of most long-lived radionuclides in both hemispheres now appear to be of 1961-1962 origin.

DISCUSSION

The manner in which the concentration of bomb-produced and cosmic-ray-produced radionuclides changed over this period of time at 45° N and 70° N latitude indicated the influence of certain atmospheric processes. The pronounced seasonal variations showing the influence of stratospheric air was prominent at both northern latitudes from a comparison of the concentration of bomb-produced radionuclides to the cosmic-ray radionuclide ⁷Be. The minimum to maximum seasonal variation, i.e., the amplitude, indicated by artificial radionuclides was about five-fold at both latitudes while the amplitude of ⁷Be, at 45° N was about

four-fold and at 70° N was about nine-fold. This would indicate that a larger fraction of the ⁷Be was of the stratospheric origin at high latitudes than at midlatitudes which is similar to findings of other investigators.^(17,23) Junge⁽²⁴⁾ states that the amplitude of the annual variation of ⁷Be should decrease at the lower latitudes due to an increasing tropospheric production. The width at half-maximum of the bomb-produced radionuclides and the variation of ⁷Be is about the same at both latitudes; whereas, the width of the ⁷Be peak appears to be much broader at 45° N than at 70° N. This indicates rapid stratospheric mixing during the seasonal variation and indicates the contribution from tropospheric ⁷Be at 45° N and lower latitudes. In addition, the artificially-produced and cosmic-ray-produced isotopes peak arrived 2 to 3 months earlier at 70° N than they did at 45° N latitude. This apparent latitude dependence on the surface arrival time has been reported by Brewer⁽¹⁹⁾ from studies of ozone concentrations at various latitudes. The relationship of ⁷Be peak amplitude, width, arrival time, and absolute concentrations, with latitude should contribute toward defining the movement of air masses.

²²Na, also a cosmic-ray spallation product, was produced during the 1961-1962 test period; and, because of its long half-life, this latter method of production still accounts for the major part of the radionuclide. If spallation value concentration levels of ²²Na are achieved, the ratio of ⁷Be (53 days) and ²²Na (2.6 years) in the air

will afford a method of defining long term air masses mixing. Calculations of Lal et al.⁽²⁵⁾ indicate that the ^{22}Na production rate in air from spallation at 50° N geomagnetic latitude should be 2.5×10^7 atoms/m²-yr. Concentrations twenty times this value were observed in 1963 after the massive tests and, since that time, have decreased by fallout and radioactive decay at a rate which indicates spallation concentration attainment in the spring of 1967. The present data indicate that natural spallation levels will not be obtained this early but could possibly be reached by 1968.

Chinese Fallout

The concentration of long-lived (greater than 1 year) radionuclides in the atmosphere is almost entirely the result of the large yield weapon tests conducted in 1962. Since that time, five low-yield atmospheric tests, three of which occurred in 1966, have been conducted by the Chinese. On October 16, 1964, a low-yield surface device was tested in the Lop Nor Basin Province of Sinkiang Province by the Chinese,⁽²⁶⁾ interrupting a moratorium on atmospheric testing which had begun in early 1963. Six months later, on May 14, 1965,⁽²⁶⁾ a second device of slightly higher yield was tested and was followed nearly one year later, on May 9, 1966,⁽²⁶⁾ by a high altitude test of similar yield. On October 27, 1966,⁽²⁶⁾ a fourth device of a reported 20 kiloton yield was tested and was followed two months later on December 27, 1966,⁽²⁶⁾ by a fifth test of a reported 100 kiloton or larger

device, the largest in the series thus far. These tests are responsible for the presence of most short-lived radionuclides in the atmosphere of the northern hemisphere. The magnitude of these devices indicates that radioactive debris was mainly contained in the troposphere. The tests have periodically increased the concentration of the medium-lived radionuclides such as ^{95}Zr - ^{95}Nb to 1964 concentration levels. The last test (December 1966) was of a magnitude and type (air detonation) that could measurably increase the concentration of some of the longer-lived radionuclides in the stratosphere.

The ^{140}Ba - ^{140}La concentrations associated with each of these tests is shown in Figure 2. Three of these tests (first, fourth, and fifth) were sampled over a long time period to delineate the circumnavigational period of the air mass associated with ground-level samples. In addition to ^{95}Zr - ^{95}Nb and ^{140}Ba - ^{140}La , other short-lived radionuclides were quite apparent in the samples taken at Richland, Washington. These include ^{132}Te - ^{132}I , (78 hours), ^{90}Mo (67 hours), and ^{239}Np , (56 hours), the last named indicating the use of uranium in the fission device. The global circumnavigational time, the time from detonation to the sampling site, and the peak concentration of ^{140}Ba - ^{140}La and ^{239}Np are presented in Table I for the five Chinese tests.

The average period of time for the radionuclide concentration to peak at Richland, was 8.4 days after detonation while the average time to circumnavigate the globe was 10 days. Since

TABLE I. Measurements of ^{140}Ba and ^{239}Np Concentrations and Circumnavigation Times Associated with Chinese Fission Devices

Test Date	Detonation to Richland, days	Circum- navigating Time, days	^{140}Ba dis/min/ 10^3ft^3	^{239}Np dis/min/ 10^3ft^3	$^{239}\text{Np}/^{140}\text{Ba}$	Fissile Material
10/16/64	8	11	35	97	2.75	^{235}U
05/14/65	8	--	3	4	1.33	^{235}U
05/09/66	11	--	25	55	2.23	^{235}U
10/27/66	9	9	57	98	1.73	^{235}U
12/27/66	6	10	169	540	3.20	^{235}U

the distance from Lap Nor to Richland is about 43% of the distance around the globe, a circumnavigational time for the radioactive cloud could be calculated. The calculated circumnavigational time of 19.5 days is much longer than the observed time of 10 days. Since air velocities usually increase with altitude, the circumnavigational data indicate that the initial arrival of the fallout cloud was associated with lower altitudes than were later ones. Forty days after explosion of the fission device, the radionuclide concentration in the troposphere was insignificant. The data indicate a mean residence half-time of 9 days in the troposphere which is one-half of Stewart's (1955)⁽²⁾ value obtained from radioactivity in a cloud produced by an early Nevada detonation. According to Machta (1960)⁽⁹⁾ such a half-time of 9 days would be expected if the radionuclides had been introduced near 11,000 ft. A low-yield detonation is thus indicated.

Fallout by Deposition

Starting in 1964, the gravitational deposition of nuclear debris was mea-

sured at Richland, Washington, to supplement data obtained from air pumps. The average annual rainfall in this arid region is only about 6.4 in.; and during 1964, 1965, and 1966 the rainfall was 5.4, 3.7, and 5.9 in., respectively, this means that the relative contribution from dry deposition is correspondingly great. The average monthly rainfall distribution becomes maximum during November, December, and January and then decreases to minimum during July, August, and September. Consequently, rainfall does not interfere with the annual spring deposition increase. The lack of rainfall makes dry deposition fallout more important than observed by investigators elsewhere.

During the 24-month period from mid-1964 to mid-1966, dry fallout was collected in plastic lined trays of 80 ft² area filled with about 1/2 in. of water. Samples were evaporated to near dryness and residual material measured as described earlier. The concentrations of ^7Be , ^{22}Na , ^{54}Mn , ^{60}Co , ^{88}Y , ^{95}Zr - ^{95}Nb , ^{106}Ru , ^{124}Sb , and ^{137}Cs obtained by this method are presented in Figure 3. The concentrations of these radionuclides, with the exception of ^{60}Co and possibly

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FIGURE 3. Fallout Expressed in $\text{dis}/\text{min}/\text{ft}^2$ for Various Years

^{124}Sb , changed in a manner similar to those measured by air sampling. The ^{60}Co concentration increased ten to one hundred-fold during the period of measurement indicating a relatively

large contribution from sources other than the stratospheric inventory.

Small (1960)⁽²⁷⁾ found that the ratio of radionuclide concentration

in the air at the ground to the concentration in the rain (both expressed in the same units) was quite constant and averaged 0.9×10^{-6} . The present data give a nearly constant ratio of radionuclide concentration in the air at the ground to the radionuclide concentration associated with deposition by dry fallout of 37×10^{-6} (see Table II). This compares favorably with a similar ratio of 24×10^{-6} calculated in the same way from ^{22}Na data reported by Rodel.⁽¹¹⁾

CONCLUSIONS

Stratospheric residence half-times, which were calculated from the decrease in bomb-produced radionuclide concentrations, suggested an average residence half-time of 11.7 ± 0.88 months. The seasonal variation in-

dicated rapid stratospheric mixing while the amplitude and width of the annual spring peak, as measured by ^7Be , indicated a prominent latitude dependency. This was not indicated in bomb-produced radionuclide measurements. Both artificial and cosmic-ray induced radionuclides indicated a latitude-dependent seasonal increase and defined a time of 2 to 3 months difference between 70°N and 45°N latitude. The residence half-time in the troposphere as indicated by ^{140}Ba - ^{140}La concentrations from the Chinese tests was about 9 days with a circumnavigational time of 9 to 11 days. The concentration of long-lived radionuclides in the tropospheric air in 1966 at 45°N latitude was slightly higher than at the 30°S latitude and between 2 and 4 times higher than at the 70°N latitude. The concentration of short-lived material at Richland,

TABLE II. Comparison of Radionuclide Air Concentration and Dry Deposition During 1965 Annual Spring Increase

Radionuclide	Deposition dis/min/ft ²	Air dis/min/ft ³	Air/Deposition
^7Be	400	8×10^{-5}	20×10^{-6}
^{22}Na	0.25	8×10^{-6}	32×10^{-6}
^{54}Mn	20	7×10^{-4}	35×10^{-6}
^{60}Co	0.4	2×10^{-5}	50×10^{-6}
^{88}Y	0.09	4×10^{-6}	44×10^{-6}
^{95}Zr - ^{95}Nb (a)	1100	5×10^{-3}	45×10^{-5}
^{106}Ru	90	4×10^{-3}	45×10^{-6}
^{124}Sb	10	1×10^{-5}	1×10^{-6}
^{137}Cs	70	2×10^{-5}	29×10^{-6}
		$\bar{x} =$	$37 \times 10^{-6} \text{ (b)}$

(a) ^{95}Zr - ^{95}Nb showed influence of Chinese Test of 4-9-66.

(b) ^{95}Zr - ^{95}Nb and ^{124}Sb were not used for this average.

Washington, was an order of magnitude higher than at Point Barrow, Alaska. A comparison of the northern and southern hemispheres was dependent upon the time and frequency of Chinese and French detonations; at mid-1966 the southern hemisphere concentration was many times higher than that in the northern hemisphere. Fallout measured by dry deposition indicated that the ratio of air concentration to dry deposition is constant averaging 37×10^{-6} compared to a ratio of the air and rain concentrations of 0.9×10^{-6} reported by Small (1960).⁽²⁷⁾

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KRYPTON-85 AS AN ATMOSPHERIC TRACER

J. D. Ludwick

A study of ^{85}Kr as an atmospheric tracer was completed. The gas can be released in a puff or in a continuous stream. Downwind samples of air containing the tracer were readily analyzed by beta-counting, and real-time measurements could be made routinely.

INTRODUCTION

Particulate tracer materials, although useful in predicting the behavior of other particulates, have some limitations as tracers for air diffusion measurements. They are, of course, affected by gravitational attraction; however, more seriously, tracer depletion occurs due to ground effects. Also, since it is difficult to disperse a particulate material in any precise size distributions, the diffusion models derived from particulate data are subject to reaction or adsorption as downwind travel takes place.

In a search for an atmospheric tracer with more suitable characteristics, it was determined that the chemically-inert radioactive gas, ^{85}Kr , best fitted the various needs.

EXPERIMENTAL

An experimental survey was undertaken to determine the most advantageous combination of radiation detector and rare gas radioisotope. Laboratory experiments were conducted to test the efficiency of various detectors in atmospheres containing radioactive rare gases.

Figure 1 illustrates the physical arrangement of these tests. The detector was held at the top of a 7 ft stand fitted with a sliding block through which the gas and the electrical

connections were led. The neck of a large meteorological balloon was fitted over the sliding block and a small amount of helium gas was introduced for partly inflating the balloon. Next a known amount of the tracer gas under test was introduced, and the balloon was filled with air to a size sufficiently large to simulate the atmospheric condition such that the distance from detector to wall was greater than the normal air range of the radiation to be measured. After filling, the mixture of gases was exhausted in steps, and measurements were made of the counting rate versus radius of the balloon. In this way, concentrations of the tracer were related to the effects on the detector.

Several xenon and krypton radioisotopes were tested for possible application to the tracer problem; and various detectors, organic crystals, plastic scintillators, thin NaI (Tl) crystals, and various end window Geiger Detectors were tried. Each inert gas radioisotope was calibrated for specific activity by measurement of a known volume of the gas in a liquid scintillation spectrometer described previously.⁽¹⁾ Results from these tests indicated the suitability of the ^{85}Kr isotope for measurement with a large-window beta detector since the beta energy of this isotope (0.69 MeV) was sufficient to penetrate the rugged window necessary to prevent detector

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FIGURE 1. Experimental Gas Atmosphere Chamber

damage under some of the expected field conditions. In practice, a 4 mg/cm^2 , Amperex Model 18546 Geiger Counter with 51 mm diameter end-window was used.

In the field, the detectors are housed in a 7 in. length of thick-wall lead pipe which acts both as a radiation and an environmental shield. Also housed inside the pipe is an electronic booster circuit to prevent loss of the signal in traversing the

cable distance from field location to recording equipment location. Each sampler is fitted with a removable front face cover to prevent window damage when not in use. The samplers were bolted to the existing stakes in the present meteorological arc for testing.

Two field tests have been conducted over the course of the Hanford Meteorological Grid. Two prototype field beta detectors were strategically

positioned downwind from the source along the 200 m arc. A cylinder containing 4 curies of ^{85}Kr was pressurized with a small amount of inert krypton and a much larger quantity of argon carrier gas. The mixture was released at a controlled rate for 110 sec and data from the samplers were taken by dual scalers and recorded every 15 sec. These preliminary data indicate the potential of this real-time analytical method for studying and defining atmospheric diffusion phenomena. Figure 2 illustrates the results from the most recent of these tests.

CONCLUSIONS

Krypton-85 appears to satisfy most of the criteria necessary to make it a nearly ideal tracer for wind diffusion experiments. Its ease in handling, decay characteristics, detectability, and half-life make it compatible with the unusual demands of unpredictable field experiment programming. It is reasonably priced (\$10.00/Ci) and can be obtained in suitable containers ready for instantaneous release in any necessary amount. Its chemical inertness allows it to follow the diffusion process precisely. After proper dilution of the tracer gas in a pressure cylinder, any source strength can be released at a controlled rate. With the proper selection of electronic measuring equipment, data from the field samplers can be relayed instantly and displayed, if desired, at a central counting station.

FIGURE 2. Real-Time Concentration Analysis of Downwind ^{85}Kr Gas

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IDENTIFICATION AND MEASUREMENT OF HYDROGEN CHLORIDE GAS
IN THE ATMOSPHERE BY SPECTROPHOTOMETRIC AND RADIOMETRIC ANALYSIS

J. D. Ludwick

INTRODUCTION

The radionuclides released from nuclear testing and nuclear plant operation include inert gases, reactive gases, and particulate materials. The reactive gases may deposit downwind on exposed surfaces. Depletion of downwind air concentrations by such a mechanism makes uncertain the worthiness of diffusion predictions, if the model were based on particulates or on a less reactive gas. For this reason, techniques were wanted for the release, collection, and determination of hydrogen chloride gas in the atmosphere. A very sensitive technique was needed to measure the long distance air concentrations and any fluctuations that might occur because of reactions between the gas and particulate phases. The nature of the mechanism of removal of this gas from the atmosphere could then be investigated.

Several analytical methods were available for the determination of chloride in excess of 5×10^{-6} g chloride per sample: these include coulometric, turbidimetric, controlled potential titration, and colorimetric techniques. A few methods are described in the literature utilizing spectrophotometric analysis in the range of 10^{-7} to 10^{-6} g per sample. None of these techniques appeared suitable for measurement of chloride ion in the anticipated range of 10^{-8} to 10^{-5} g per sample.

Several unrelated analytical techniques are based upon the interference of one material with the fluorescence or the photometric absorption spectra of another. Several fluorescent materials were studied, but the chloride ion failed to extinguish the emission satisfactorily.

Larger quantities ($>10^{-6}$ g) of chloride ion reduced the fluorescence of quinine sulfate, for example; but none of the methods provided the necessary sensitivity for our needs.

A study was made of the interference of chloride with certain light-absorbing materials. It was expected that interference could be obtained in a spectrophotometric procedure involving dithizone and its silver complex, silver dithizonate. A technique was developed utilizing this principle which detected as little as 1×10^{-8} g of chloride. The sensitivity of this method was excellent, but it required the dilution of the more concentrated chloride solutions and was, therefore, less than ideal for field use.

Efforts were then made to develop a simpler method by which almost any field-collected chloride sample could be analyzed. A reasonably sensitive radiometric technique was developed involving precipitation of the chloride with ^{110}Ag , thus tagging the chloride precipitate.⁽¹⁾ The method is sensitive to less than 2×10^{-7} g of chloride ion and is readily adaptable to routine operation.

THE RADIOMETRIC CHLORIDE METHOD

In developing the method, standardized chloride solutions were treated with suitable volumes of silver nitrate solution tagged with ^{110}Ag . The solution with the precipitated AgCl was then centrifuged and filtered through a 50 μ membrane filter. The precipitate was washed and counted. A series of measurements using this technique indicated rather poor precision for the very small precipitates, many of which were invisible to the eye. The time involved in filtering each sample was also prohibitive.

This procedure was modified to take an aliquot of the supernatant solution for gamma analysis, rather than attempting to recover the precipitate. A direct correlation was found between the amount of chloride in the sample and the ^{110}Ag activity in the solution. If a standard solution containing the proper specific activity of ^{110}Ag is used, there is no upper limit for chloride determination; and as little as 2×10^{-7} g can be rapidly measured.

HCl GAS FIELD SAMPLER

To sample hydrogen chloride gas from the atmosphere, a scrubber-column collector was designed and assembled. Two glass scrubber-columns were arranged in series with each sampler. Fifteen milliliters of 0.05N NaOH solution was introduced into each column of the sampler, all glassware and solutions having first been washed with Cl^- -free water. The inlet air to the sampler was filtered through a 5 μ membrane-type filter for collection of any particulate materials; chloride

could be determined in the collected material if desirable. Air flow control through the system was accomplished with a critical orifice calibrated to pass 0.1 ft^3/min . A gasoline-driven air pump was used to operate the sampler.

FIELD TESTS

Two field tests using HCl gas were conducted over the Meteorology Grid network. The HCl gas emission was controlled by a valve on a pressure cylinder. About 5 pounds of HCl was released over a period of 10 minutes in each test. Twelve samplers were arranged downwind on the two innermost arcs located 200 and 800 meters from the source.

A commercial portable HCl gas sampler was evaluated for analytical sensitivity. The instrument, a Billion-Air Analyzer, (Model No. 706P—Mine Safety Appliance Co., Pittsburgh, Pa.) was moved along the Meteorology arcs as emission of HCl took place. The instrument was sufficiently sensitive to detect and measure the HCl at the 800 meter distance. Real-time measurements made with the portable instrument agreed with analytical results of chloride content from the field collectors by the radiometric technique described. The peak field concentration of HCl gas at 800 meters corresponded to an air concentration of about 2×10^{-7} ppm.

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THE USE OF INERT TRACERS AND NEUTRON ACTIVATION
ANALYSIS IN ATMOSPHERIC PRECIPITATION STUDIES

W. A. Haller

The washout of aerosols or gases by snow or rain has been measured under field conditions^(1,2,3) where a known quantity of a tracer was released at a known height in the air, and the amount of washout on an arc subtending the plume was measured. The amount of tracer deposited on the arc was determined from that collected in equally-spaced plastic lined precipitation collectors. The amounts of tracer found per unit volume of water were generally in the parts-per-billion range or lower, thus requiring a sensitive analytical method. Neutron activation and multidimensional gamma-ray analysis provide the necessary sensitivity⁽⁴⁾ with a minimum of chemical operations.

Since collection of the particulates that serve as nucleation sites for the formation of rain and snow and of dust particles scavenged by the falling precipitation is unavoidable, an essential factor in the selection of a tracer was that its natural abundance in the rain or snow should be lower than the amount of tracer that would be scavenged during the experiment. A good estimate of this background from such sources during the experiment may be obtained by the simultaneous collection of a blank precipitation sample upwind from the test site and comparing with the collections associated with the release of the tracer. Where contamination occurs from relatively large amounts of dirt which

are picked up with the precipitation, the trace element background is drastically increased as seen, for instance, in Table I.

Iodine and bromine were released as gases in the molecular state by rapidly heating them in large evaporating dishes. Following collection in the field, the test samples were transferred from collection containers to Vycor beakers, about 2 ml of doubly-distilled concentrated ammonium hydroxide was added, and the mixture evaporated to a few milliliters. This was then transferred to a 30 ml Vycor crucible, evaporated to about 0.1 ml, and transferred to 6 mm ID vitreous silica ampoules using several washings of doubly-distilled water containing 0.01 ml of doubly-distilled NH_4OH . Following neutron irradiation, the ^{128}I was extracted with carbon tetrachloride and precipitated as AgI for measurement of the 0.445 MeV gamma ray by standard gamma-ray spectrometry. The iodine in the sample was calculated by comparing its ^{128}I content with that of a standard iodine solution irradiated together with the sample. The bromine measurements required the same preirradiation treatment as the iodine, but no chemical separation was required after the irradiation. The water samples were simply evaporated on a standard counting dish and the ^{82}Br determined by direct counting on a multidimensional gamma-ray spectrometer⁽⁵⁾ utilizing triple coincidence

of the 0.777, 0.82 and 1.044 MeV gamma rays. Results of a test-run appear in Table II and show washout-to-background ratios for bromine of approximately 4. An increase by a factor of ten in the amount of bromine released would be needed to obtain washout measurements of sufficient accuracy. The washout to background ratios for iodine ranged from approximately 6 to 50 which is in the proper range of precision for most of our washout measurements.

Silver, scandium, cesium and strontium were tested for use as particulate tracers. Particulates were produced in a standard propane-burning silver iodide generator (the "Sky Fire Generator") which is a type used routinely in cloud-seeding work.

Aqueous solutions of scandium nitrate, cesium nitrate, and strontium nitrate were used while the standard acetone mixture was used for the silver iodide. Following collection of the rain or snow from the field, the samples were placed in Vycor beakers which had been cleaned by leaching with hot concentrated nitric acid. One milliliter of doubly-distilled nitric acid was added to each sample and they were evaporated to approximately 0.1 ml. They were then quantitatively transferred with doubly-distilled HNO_3 to 6 mm ID vitreous silica ampoules. The samples were irradiated to an integrated neutron flux of about 10^{19} neutrons/cm², then stored for 15 days to allow the ^{24}Na and ^{82}Br to decay. The ampoules were opened, the samples

TABLE I. Trace Element Concentrations in Precipitation Samples

Particulate, mg per 100 ml precipitation	Trace Element, ng/100 ml				
	Sb	Ag	Zn	Co	Sc
>10	16	30	240,000	760	44
>10	8.4	7.9	140,000	1200	66
<0.1	1.6	0.2	500	1.8	0.2
<0.1	1.5	0.2	660	3.0	0.1

TABLE II. Washout of Gaseous Tracers

Tracer	Approx. Amount Released	Daughter Determined	Background, (a) ng/100 ml	Washout, ng/100 ml
Br	10 ml	^{82}Br	1.0	4.2
Br	10 ml	^{82}Br	0.7	3.8
Br	10 ml	^{82}Br	1.8	7.9
I	100 g	^{128}I	0.35	2.1
I	100 g	^{128}I	0.02	1.0
I	100 g	^{128}I	0.05	0.49

(a) Taken concurrently with sample

removed by washing with 8N nitric acid and dried on a standard counting dish. The radionuclide concentrations were measured by multidimensional anticoincidence shielded gamma-ray spectrometry.⁽⁵⁾ The amount of tracer in the sample was calculated by comparing the radionuclide content with that of the standard solution irradiated with the samples. Results of these determinations appear in Table III and indicate that washout-to-background ratios for cesium, scandium, and AgI range from 2 to 12. To reduce the effect of background variation, the amount of tracer released during the tests should be increased by a factor of 5. Strontium has such a high natural background that at least two orders of magnitude increase in its release would be required for its successful use as a tracer.

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TABLE III. Typical Washout of Particulate Tracers

Tracer	Amount Released, g	Daughter Determined	Gamma-Rays Measured	Background, (a) ng/100 ml	Washout, ng/100 ml
Cs	0.26	¹³⁴ Cs	0.603 0.797 ^(b)	4.2	9.7
Cs	0.25	¹³⁴ Cs	0.603 0.797 ^(b)	1.4	7.6
Cs	0.10	¹³⁴ Cs	0.603 0.797 ^(b)	4.4	9.6
Sc	0.10	⁴⁶ Sc	1.118 892 ^(b)	0.2	2.2
Sc	0.03	⁴⁶ Sc	1.118 892 ^(b)	0.2	0.3
Sc	0.24	⁴⁶ Sc	1.118 892 ^(b)	0.4	0.6
Sr	0.06	⁸⁵ Sr	0.515	1100	1500
Sr	0.38	⁸⁵ Sr	0.515	3600	2600
Sr	0.22	⁸⁵ Sr	0.515	800	2100
AgI	1.4	¹¹⁰ Ag	0.706 0.656 1.560 ^(c)	2.0	4.2
AgI	1.2	¹¹⁰ Ag	0.706 0.656 1.560 ^(c)	1.0	12.0
AgI	0.5	¹¹⁰ Ag	0.706 0.656 1.560 ^(c)	1.1	7.9

(a) Measured concurrently with sample.

(b) Coincidence measurement.

(c) Triple coincidence measurement.

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AIR SAMPLING EQUIPMENT AT REMOTE LOCATIONS

H. G. Rieck

In March 1964, the 100 cfm air blower located at the Arctic Research Laboratory, Point Barrow, Alaska,⁽¹⁾ was replaced with a 400 cfm unit.* The existing building was used; additional structural support was installed in the floor area and a new power line was required to handle the large drive motor. This unit was operated continuously with filter changes twice per month. Flow rates are 380 to 420 scfm.

Another 400 cfm blower was equipped with a 230 V, 10 hp, dc motor; and the unit was installed on the bridge deck of the R/V Yaquina** in April 1966 prior to a long ocean cruise (Oregon State University designated YACOC 66). The unit was welded to the deck and equipped with a suitable weather proof enclosure. Power for the motor was furnished from an electrical distribu-

tion panel in the engine room. Continuous operation of the air sampler was anticipated during the 100 day cruise between Newport, Oregon; Hawaiian Archipelago; Aleutian Islands; Gulf of Alaska; and back to Newport. The unit was operated for approximately 65 days; at the end of this time the ship was near Adak, Alaska and the unit was turned off because of noise arising from vibration. Filters were changed every four days between Newport and Hawaii and weekly thereafter. Flow rates are 320 to 360 scfm.

In June 1966, a 400 cfm blower was installed on a 2 ton truck with a 35 hp diesel generator to supply power for the motor-blower unit. A wire fence enclosure was built around the truck bed to prevent unauthorized access while the truck is unattended. This unit has been used to sample locations remote from available power. Filters are changed on a 2 week basis and the fuel capacity allows for 2 weeks of continuous operation. Flow rates are 320 to 360 scfm.

An air sampling station was established in Rio de Janeiro, Brazil, in

* Roots-Connersville Blower, RAI 610 Blower, 1160 RPM, Connersville, Indiana.

** Oceanographic Research Vessel, Oregon State University, Corvallis, Oregon.

August 1966. A 400 cfm unit was installed on the upper level of the Science Building at the Universidade Catolica. A 6 x 6 ft plywood enclosure was fabricated in a corner of an elevator room above the fifth floor of the Physics Wing of the building. The blower unit was supported on a cork-concrete slab inside the enclosure to minimize noise problems. Intake to the filter head was provided by a window above the unit. Filters are changed more frequently than twice per month because of dusty conditions in the area. Flow rates are 250 to 300 scfm.**

A new filter head design is now used in these installations. In this new unit, a 12 x 12 in. membrane fil-

ter* is attached to each of four sides of a 14 in. cubical housing. A screen supports each filter, and tape is used to seal the filter to the metal edges. The filter head can be removed from the intake to change the filters. Flow rates through the blower are determined from impact tube or orifice installations in the pump inlet.

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* Millipore Filter Co., SMWP305FO, Bedford, Connecticut.

** 50-cycle power results in lower sampling rate.

A PORTABLE BOOM-TYPE AIR SAMPLER

J. D. Ludwick

A completely portable air sampler mast was constructed with vertical sampling capabilities ranging from 0.25 to 12 meters. This mast was installed on a mobile, power-equipped vehicle that allowed air sampling while the vehicle was in motion. The emission plumes from a plant exhaust stack and from reactor effluent water basins were sampled.

INTRODUCTION

One of the most difficult problems associated with predicting atmospheric downwind exposure levels from various sources is that of defining the vertical distribution of the emitted material at a long distance.

Sampling of occasional releases from a plant is complicated by the fact that they are unplanned or, at best, scheduled for a specific date rather than being coordinated with convenient meteorology. Thus, the proper position for downwind sampling can be determined only after the release has started.

In addition to a capability in long distance sampling, there was also need for a mobile sampling arrangement of sufficient height to traverse the entirety of small emission plumes. These types of plumes occur, for example, at reactor cooling basins. Measurement made with such sampling equipment allow one to calculate the total material released to the atmosphere from the source.

A portable sampling arrangement was then needed with special characteristics to best take advantage of the particular sampling situation. Many of the problems associated with measurement of the vertical distribution of a tracer material lie in determining the concentration close to the ground level. Extreme variations may occur in such a location because the tracer is depleted due to contact and impact with the vegetation and ground.

To determine this effect, the sampling arrangement required close spacing of sample positions below 2 m. Practical considerations limited the upper size of the apparatus but a minimum height of 10 m was necessary to provide definitive results from both sampling situations.

EXPERIMENTAL

Construction of the sampling boom was based upon its use with power wagon vehicle housing an electrically-operated extension ladder. It was desired to use as large a diameter material as practicable for the main boom section to allow large collectors and, thus, to maximize the collection volume and provide greater sensitivity.

For this purpose, a 4 in. aluminum water irrigation pipe was used as the main boom material. Standard 4 in. irrigation saddles were attached at the desired sample locations with Neoprene gaskets surrounding predrilled holes in the boom. Each saddle was fitted with a one-hole rubber stopper as a fitting to the actual air sampler. A small iron chain about 12 in. above each saddle was attached to the outer end of the sampler housing to lend added support.

The main upper portion of the boom was directly attached to the extended ladder of the truck. After the boom was attached, the ladder could be lowered or raised as desired for long distance transport. With the ladder in the upright position, the lower end of the boom was coupled by means of a "T" connection into a high volume air pump located on the bed of the power wagon. The remaining arm of the "T" connection was coupled to a lower sampler section. Both the upper and lower sections and their respective samplers are illustrated in Figures 1 and 2. Another method of connecting the lower section involved physical support from the "T" so that the entire sampler in a fixed array became completely portable.

The samplers were constructed using a front aluminum housing and a rear plastic cartridge. A 4 in. diam membrane-type filter was held in the aluminum housing and the rear cartridge contained a similar section (0.001 in. thick) of silver-plated thin copper-turnings followed by a 2 in. thick activated-charcoal collector.

Neg 0662671-5

FIGURE 1. The Portable Boom-Type
Air Sampler (Upper Section)

Neg 0662671-4

FIGURE 2. The Portable Boom-Type Air Sampler (Upper Section)

A high-volume air pump rated at 100 cfm was used to operate the samplers. Power for the pump was obtained from a 30 kW gasoline-powered generator located on a trailer bed. The vertical locations of the air samplers were at 0.25, 0.50, 1.0, 2.0, 4.0, 6.0, 8.0 and 12 m heights. The air flow through each sampling head

was calibrated and found to be approximately 11 cfm. The flow rate was essentially constant at the various sampling positions.

¹³¹I Sampling

The sampling boom was utilized to sample radioiodine emitted from a

plant exhaust stack during a period of unusually high release level. Both visual observation of the plume (using the associated NO_2 fumes) and meteorological data were used to position the sampling boom. Samples were taken 4 to 8 miles from the source over periods of several hours. Occasional repositioning of the boom was necessary as meteorological changes occurred. Samples at the source were taken from a small gas loop at the base of the stack to identify the physical and chemical form of the ^{131}I activity at that point.

Reactor Basin Gas Sampling

The sampling boom was also utilized for traversing the visible exhaust cloud released at a reactor cooling basin. The boom, while operating, was driven through the emission cloud thus defining both the vertical and horizontal radioisotope distributions. The time in the plume was determined by stopwatch.

Sampling of the basins could be accomplished only where close access to their edges was convenient. The warm plume rises rapidly and the upper edge was generally beyond the uppermost sampler when within 50 meters of the basin and with winds of under 15 knots. Sufficient windspeed was, therefore, necessary before sampling so that the top of a plume would not be significantly higher than the uppermost sampler. Figure 3 illustrates the portable sampler traversing the final edge of a plume from a reactor basin.

DISCUSSION

Samples from the stack indicated that the iodine was almost entirely gaseous and not particulate. A large percentage (72%) was in the reactive form as determined by the amount found on the silver section. Results from the assay of three samples taken from the stack gas are summarized in Table I. It is interesting to note the high fraction (25%) of unreactive ^{131}I directly at the source. Table II illustrates the characteristics of the tracer downwind compared to those at the source; also given is the vertical distribution as measured by the boom samplers. Similar behavior had been observed⁽¹⁾ in previous controlled iodine releases, as downwind travel takes place. That is, the gaseous free iodine is quite reactive and readily attaches itself to airborne particulates; the active iodine also combines with atmospheric components to form unreactive gases. Additionally, the iodine may form particulate iodine crystals. The net result of these processes is a steady reduction in the content of reactive iodine with time. Reduction of the reactive species is increased by a decrease in the vertical stability of the air mass.

The vertical iodine distribution found in air samples is also of interest. At about 5 miles from the source, a marked decrease in relative concentration from 4 m to ground level was noted and this can be attributed to lower level depletion of the tracer;

Neg 0670484-8

*FIGURE 3. Sampling the Plume from
a Reactor Effluent Cooling Basin*

TABLE I. Characteristics of the ^{131}I at the Source

Sampler Section	Relative ^{131}I Activity			Percent Present
	A	B	C	
Filter (Particulate Material)	18	31	65	3.5
Silver Bed (Reactive Iodine)	213	492	1737	71.5
Charcoal Filter } (Unreactive Iodine)	35		446	25.0
Charcoal Bed }	42	190	149	

TABLE II. Vertical Distribution of ^{131}I 5 Miles Downwind from Source
(Average percent present: Particulate, 14.5; Reactive, 30.0; Unreactive, 55.5.)

Height, m	Relative ^{131}I Activity
0.25	150
0.5	180
1.0	190
2.0	230
4.0	400
6.0	120
8.0	200
10.0	110

however, the reduced activity above 4 m indicates the lack of vertical diffusion of the source plume. One would

conclude that considerable vertical diffusion must have taken place and significant radioiodine activity should be present to a considerable elevation. Further work in this regard is necessary, and all is in readiness for future long range sampling of any advantageous source.

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DESIGN CRITERIA FOR GAMMA-RAY SPECTROMETER SYSTEMS

N. A. Wogman and R. W. Perkins

Numerous criteria which must be considered in the design of a gamma-ray spectrometer system have been studied with the aim of defining sources of background, minimizing gamma-ray scatter, and maximizing the peak efficiency. During the course of the investigation, concentrations of terrestrial radionuclides-- ^{40}K , ^{232}Th , and ^{238}U --were determined in the hardware, reflective coatings, and light pipe material of a NaI(Tl) crystal assembly. The effect on the backgrounds of these radionuclides plus the prompt gamma rays from cosmic-ray secondary neutron capture processes-- $^{127}\text{I}(n,\gamma)^{128}\text{I}$ of a NaI(Tl) crystal or $^1\text{H}(n,\gamma)^2\text{H}$ of a plastic phosphor detector--was determined. Methods of external or anticoincidence shielding plus neutron shielding were found which reduced the background due to the cosmic ray and natural radionuclides. Anticoincidence shielding was also studied with the view of reducing the effect of Compton-scattered gamma rays and improving the gamma peak measurement. All of these factors may be used to design either single or multidimensional gamma-ray spectrometer systems incorporating NaI(Tl) crystals and/or plastic phosphor assemblies.

The design of ultra low background, low Compton, and high sensitivity gamma-ray spectrometers requires consideration of Compton minimization,

energy peak maximization, and background reduction. During the development of several multidimensional gamma-ray spectrometers,⁽¹⁻³⁾ data

were accumulated which can be used to design any spectrometer system.

BACKGROUND REDUCTION

A major requirement in the design of a low level gamma-ray spectrometer system is the minimization of background. Background events are due to natural or cosmic-ray induced radioactivity either in the detector, hardware, or shield components. The natural radionuclides-- ^{40}K , ^{232}Th , and ^{238}U --have been found (see Table I) in much of the hardware of a NaI(Tl) crystal assembly. A possible solu-

tion would be to clad the NaI(Tl) crystal in pure aluminum; however, this is not often practicable for large detectors. A substitute, practical cladding is thin (~ 15 mil) stainless steel with an entrance window of thin (~ 10 mil) pure aluminum. MgO is used as the reflector and quartz for the phototube window. Since large amounts of ^{40}K are found in the phototube glass,^(4,5) a light pipe is desirable although an alternate solution would be the recently developed ceramic phototubes* with very low ^{40}K

* RCA C70145A Type

TABLE I. Comparison of ^{232}Th , ^{238}U , and ^{40}K in Components of a NaI(Tl) Crystal Assembly

Crystal Assembly Material	dis/min/g		
	^{232}Th	^{238}U	^{40}K
MgO ^(a) reflector	0.088	0.14	<0.23
MgO ^(b) reflector	<0.05	<0.05	<0.2
Al ₂ O ₃ ^(a) reflector	0.11	<0.07	<0.3
Pyrex ^(a) window	0.45	0.27	3.8
Quartz ^(a) window	<0.018	<0.018	<0.07
Quartz ^(b) window	<0.018	<0.018	<0.07
CdF ₂ ^(a) Light Pipe	<0.003	<0.003	<0.01
Al ^(a)	0.12	<0.07	1.
Al (6061) ^(c)	0.42	0.04	<0.05
Al (1100) ^(c)	0.24	<0.017	<0.06
Al (1100) ^(d)	0.08	<0.026	<0.11
Al (3003) ^(c)	0.10	<0.026	0.56
Al ^(e)	<0.005	<0.005	<0.01
Stainless Steel (304) ^(f)	<0.006	0.007	0.06
Stainless Steel (304-L) ^(f)	<0.005	<0.005	<0.02

(a) Sample received from Harshaw Chemical Co. 8/66

(b) Sample received from Harshaw Chemical Co. 12/66

(c) Sample obtained from Aluminum Company of America 12/66

(d) Sample obtained from Aluminum Company of America 1/66

(e) Sample obtained from United Mineral and Chemical Co., New York, Ingot 99.9999% Al.

(f) Manufacturer unknown.

content. The data of Table I also apply to components of anticoincidence shields and external lead or iron shields. The construction of external shields from pre-World War II steel and lead help to lower the background created by the fallout radionuclides and those used to determine burnup in the present day smelters.

The backgrounds of NaI(Tl) and plastic phosphors are also affected by interaction of cosmic-ray produced neutrons with shield or principal crystal components. Neutrons produced in the lead or iron shields, in NaI, and in the phosphors can readily thermalize and react with the hydrogen of the plastic phosphors creating a 2.225 MeV gamma ray⁽⁶⁾ from the reaction $^1\text{H}(n,\gamma)^2\text{H}$. A similar reaction can occur from thermal and epithermal neutrons interacting with the ^{127}I of the NaI(Tl) crystal producing prompt gamma rays up to 6.8 MeV.⁽⁶⁾ Techniques were studied to eliminate the neutrons before interaction.

A borated paraffin shield, between the external neutron-producing shield and the principal crystal of phosphors, thermalizes and captures most of the externally produced neutrons. Large NaI(Tl) anticoincidence shields, if available,* could replace large phosphor anticoincidence systems and thus eliminate the thermalizing medium in this type of spectrometer. Counts due to the numerous prompt gamma rays of the $^{127}\text{I}(n,\gamma)^{128}\text{I}$ reaction resulting from epithermal neutron capture in large NaI systems are

largely cancelled by anticoincidence shielding.

Copper and cadmium shields are also effective in reducing the effect of neutrons. If a thermalizing medium is present, both these elements may be activated. The cadmium produces many prompt gamma rays with energies up to 9 MeV⁽⁷⁾ of which one is usually detected by an anticoincidence shield and the event cancelled. Copper, however, produces ^{64}Cu with a 12.9 hr half-life and creates a peak in the background at 0.51 MeV from positron annihilation which is generally not cancelled since there are only two gammas being emitted. This makes copper less desirable as a construction material in low background NaI(Tl) crystals. CdF_2 light pipes could be used in anticoincidence spectrometer systems because of the high efficiency of cancellation.

Since backgrounds are also lowered by the use of anticoincidence shields and appropriate electronics, their operating parameters must be included in the design criteria. Up to the present time, large NaI(Tl) crystals could be effectively shielded only by large plastic phosphor or liquid scintillator systems due to the unavailability of large NaI(Tl) ingots which have relatively high cost. Large plastic phosphors (36 in. diam by 36 in. high) have been operated at Hanford with various phototubes, surfaces, and reflector conditions. Table II gives some of the results from a small N.E. 102 phosphor to demonstrate the changing resolution and light output as phototube, surface, and reflector conditions are changed.

* Harshaw Chemical Company, 15 in. diam NaI(Tl) crystal

TABLE II. Comparison of ^{137}Cs Resolution and Light Output from an N.E. $^{102}\text{Phosphor}^{(a)}$ as a Function of Changing Reflector, Surface, and Phototube Parameters

<u>Phototube^(b)</u>	<u>Detector Surface</u>	<u>Reflector</u>	<u>FWHM ^{137}Cs</u>	<u>^{137}Cs Relative Gain</u>
Dumont 6364	Rough ^(c)	Japalac ^(d)	83%	40 $\pm$ 1
Dumont 6364	Polished	Aluminum	103%	38 $\pm$ 1
Dumont 6364	Polished	Teflon	103%	40 $\pm$ 1
RCA 8055	Polished	Teflon	86%	38 $\pm$ 1 ^(e)
RCA 8055	Polished	Aluminum	89%	38 $\pm$ 1
RCA 8055	Polished	Japalac	84%	46 $\pm$ 1
RCA 8055	Rough	Teflon	101%	37 $\pm$ 1
RCA 8055	Rough	Aluminum	95%	39 $\pm$ 1
RCA 8055	Rough	Japalac	74%	53 $\pm$ 1

(a) The phosphor was 9 in. wide by 6 in. thick by 19 in. long.

(b) Placed parallel with the 6 in. thick dimension.

(c) Roughened using "coarse" grade emery cloth.

(d) The Glidden Company.

(e) Gain adjusted to 38 with High Voltage (dropped 150 volts or tube gain by about a factor of 3).

The results indicate than an RCA 8055 (5 in. phototube) will operate at a lower voltage (consider a change of 100 V at the tube to be equivalent to a factor of two in gain) than the Dumont 6364 and has increased resolution. The reflector materials--Teflon, aluminum, and Japalac*--had about equal efficiency on a smooth polished surface; however, an adherent coating of Japalac reflector on a rough surface gave an increased gamma-ray resolution and light output at the phototube. Further studies of large phosphor anticoincidence systems have shown that each system must be evaluated as to surface and reflector for optimization of detector efficiency.

* The Glidden Company

COMPTON EFFECT MINIMIZATION

A second major consideration is Compton effect minimization. Anti-coincidence shields are required for this purpose. The use of large crystals which will totally absorb the energy of the gamma ray with a high efficiency is a major step. However, no matter how efficient the anticoincidence shield is, a few Compton events do occur. A 4π anticoincidence shield can effectively reduce the Compton interference if (1) it has high efficiency and (2) if no Compton events are lost before reaching the anticoincidence detector. The former design criterion can be met by using large, highly efficient, anticoincidence shields. The latter criterion can be best met by designing the

spectrometer system with minimal mass between the principal detector and the anticoincidence shield. Although a minimum amount of nonscintillating material (cladding, reflector, etc.) is desirable, a compromise must be made in the design of multidimensional gamma-ray spectrometers to minimize the Compton interference between two principal crystals. The minimal cladding will be used between the principal detector and the anticoincidence shield for reasons already discussed; however, the interference from backscattered gamma rays from Compton events occurring in one of the two principal crystals may be minimized by either an anticoincidence detector between the two crystals or by shielding the first principal detector from the second with a material such as lead.

Figure 1 includes the total absorption diagonal and the Compton lines which are typical in ^{60}Co spectra obtained on the multidimensional gamma-ray spectrometer system. The two photopeaks of ^{60}Co on the total absorption line arise from complete absorption of the 1.17 MeV gamma ray in one principal detector and the 1.33 MeV gamma ray in the second detector. The remainder of the total energy diagonal absorption line is also due to total absorption of the two ^{60}Co photons but in a manner which involves scatter of one or both photons between the principal detectors. Thus, a material which would intercept or cancel backscatter photons would lower the absolute count rate of the total absorption diagonal relative to its photopeaks.

Compton lines in the energy-energy plane are produced when one gamma-ray

is completely absorbed by one of the crystals while a second gamma ray loses only part of its energy to the second crystal (Figure 1). Increased intensity of Compton lines and total absorption effects from various radionuclides may produce an intolerable interference in the measurement of other radionuclides which have gamma-ray peaks located on these lines. It may then become necessary to minimize one of the effects even at the expense of the other. Table III lists the effect of various materials and backscatter detector conditions for the reduction of these lines. The data show that lead or a NaI(Tl) backscatter detector reduces the total absorption diagonal to 1/25 but that they increase the intensity of the Compton lines about factors of 1.7 and 1.2, respectively. (Pure tungsten would also be an appropriate material.) Figure 2 illustrates the effect of the various antibackscatter shields on the counting rate along the total energy diagonal for ^{60}Co . The backscatter peaks are reduced to about 1/15 by the 3/4 in. thick lead absorber. A similar reduction is obtained with the 2 1/4 in. NaI(Tl) crystal, but a relatively small reduction is obtained with the 2 1/2 in. thick plastic phosphor. The effect of these absorber systems in reducing the backscatter of single gamma events from ^{60}Co is illustrated in Figure 3. Here again the lead absorber is most efficient, providing reduction to 1/4 of the total absorption line.

The final choice of an antibackscatter detector must depend on the radionuclide mixtures which are to be measured. If a sample contains many

FIGURE 1. Mechanism of Production and Illustration of the Locations of the Compton Lines, Total Absorption Diagonal, and Equal Energy Diagonal for a ^{60}Co Spectrum

radionuclides with decay involving cascade gamma-ray emission and the best measurement in the energy-energy plane, a lead antibackscatter absorber may be the most satisfactory. However, if radionuclides which emit a single gamma ray per disintegration are of most interest, an antibackscatter detector would be more desirable. The lead backscatter absorber is excellent in preventing scatter between the princi-

pal detectors which is recorded in the energy-energy plane, but it does increase the Compton events on the axis. This effect is illustrated in Figure 4. For ^{60}Co , the lead backscatter absorber increases the single crystal Compton response on the axes about tenfold. Therefore, optimum configuration for any measurement must be determined by factors relative to the mixture to be counted.

TABLE III. Effects of Various Antibackscatter Shields on the ^{60}Co Response

Absorber Material	Total Absorption Diagonal(a)	Compton Lines(a)
Air, 3/4 in. thick	1.	1.
Air, 2 1/4 in. thick	0.39	1.8
Air, 2 1/2 in. thick	0.39	1.8
Pb, 3/4 in. thick	0.036	1.7
NaI(Tl), 2 1/4 in. thick by 10 in. diam	0.04	3.3
NaI(Tl), 2 1/4 in. thick by 10 in. diam anticoincidence	0.04	1.2
Plastic phosphor, 2 1/2 in. thick by 18 in. diam	0.20	3.5
Plastic phosphor, 2 1/2 in. thick by 18 in. diam, anticoincidence	0.20	1.2

(a) Total absorption photopeaks normalized to the 3/4 in. thick air response.

FIGURE 2. Comparison of ^{60}Co Backscatter Along the Total Absorption Diagonal at 2.50 MeV with Various Antibackscatter Conditions

FIGURE 3. Comparison of ^{60}Co Backscatter Along the Total Absorption Line at 1.33 MeV with Various Anti-backscatter Conditions

SPECTROMETER SYSTEM EFFICIENCY

A final consideration in the design of a system, which must be balanced by cost, is the size or efficiency of a NaI(Tl) spectrometer system. The efficiency of a 6 in. thick by 11 in. diam crystal system for point sources of radioactivity is compared with that of a 6 in. thick by 5 in. diam and a 4 in. thick by 6 in. diam Na(Tl) crystal system in Figure 5. The counting efficiency, E , is defined as the fraction of the gamma rays, emitted by a source, that is totally absorbed in one detector. The total coincidence counting efficiency, $2E_1E_2$, is defined as the probability of total absorption

of two gamma rays, one in each of the two detectors. The coincidence counting efficiency of an 11 in. diam by 6 in. thick NaI(Tl) dual crystal system is three to five-fold greater than that of a 5 in. diam by 6 in. thick NaI(Tl) system for energies above 1 MeV. An additional major advantage of the larger system, compared with a smaller system, is its high counting efficiency for large diameter samples. Both the single crystal and the coincidence counting efficiencies decrease very slowly for increasing source diameter. For example, the coincidence counting efficiency of ^{60}Co on the smaller system drops almost three times as fast in going from a point source to

FIGURE 4. Comparison of Axis Compton Events for ^{60}Co with Various Anti-backscatter Conditions

a 5 in. diam source. Thus, the total coincidence counting efficiency of a 5 in. diam ^{60}Co source would be approximately nine times greater on the large detector system than on the smaller detector systems. This allows the direct counting of many large, low activity, samples without ashing or other treatment to reduce their size. Such large samples must be used in studying the various biological, oceanic, geological, and meteorological processes which occur in nature.

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FIGURE 5. Total Counting Efficiencies and Total Coincidence Counting Efficiencies of Three NaI(Tl) Crystal Assemblies

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A LARGE DETECTOR ANTICOINCIDENCE SHIELDED
MULTIDIMENSIONAL GAMMA-RAY SPECTROMETER*

N. A. Wogman, D. E. Robertson, and
R. W. Perkins

A multidimensional gamma-ray spectrometer has been fabricated using two, 11 in. diam by 6 in. thick NaI(Tl) crystals which are shielded from their phototubes with 4 in. thick pure NaI light pipes. Each NaI(Tl) crystal is surrounded by a 36 in. diam by 18 in. thick plastic phosphor which is viewed by six, 5 in. phototubes and which functions as an anticoincidence shield. The spectrometer is coupled to a 4096 channel multiparameter analyzer and utilizes the gamma-ray decay characteristics of each radionuclide for its identification and measurement. This is accomplished by viewing the sample with the two NaI(Tl) detectors operating in coincidence and cancelling those events not totally absorbed in the principal detectors by the plastic phosphor anticoincidence annulus. Coincidence counts are stored in the energy-energy plane of the memory according to their photon energies, while single gamma rays which interact with either crystal are stored in normal manner on the X or Y axis.

The development of the present detector system has provided a highly efficient coincidence counting system. However, initial background measurements contained two prominent peaks. One at 2.22 MeV originates from cosmic ray produced neutrons which were attenuated and captured by the hydrogen in the phosphor annulus, ${}_1\text{H}^1(\text{on}^1, \gamma){}_1\text{H}^2$. A broad peak at 6.8 MeV was also neutron-induced. To estimate the fraction of the background resulting from neutron capture, a single crystal background comparison was made in (1) a 4 in. thick lead cave with 4 in. thick paraffin walls and (2) a 4 in. thick lead cave with 4 in. thick borated polyethylene walls. The background was reduced 1/10 at the two peak areas (2.2 and 6.8 MeV) by the use of the borated polyethylene walls. Background reductions in the energy-energy plane were accomplished by inserting a 0.75 in. thick lead collimator, with the sample in a hole at its center, between the two principal detectors. This procedure reduces the coincidence background about 1/7 for 1 MeV coincidence photons. The counting efficiency of this large detector system is approximately a factor of three higher for a ${}^{60}\text{Co}$ point source than a similar system using 6 in. thick by 6 in. diam NaI(Tl) crystals. In addition, no appreciable loss in counting efficiency occurred in the present system until the sample size exceeded a 6 in. diam. This allowed the direct measurement of large samples which are often required in studying the various biological, oceanic, geological, and meteorological processes which occur in nature. The combination of greater efficiency plus a large sample allows the direct measurement of radionuclides at concentrations several-fold lower.

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A LARGE WELL CRYSTAL WITH ANTICOINCIDENCE SHIELDING*

N. A. Wogman, D. E. Robertson, and R. W. Perkins

The measurement of radionuclides in environmental and biological materials generally requires very sensitive detection equipment. The normal procedure usually involves collecting as large a sample as practicable and counting this for a long period of time on a large sensitive detector. Recent advances in solid state detectors have made NaI(Tl) crystals obsolete for many applications; however, where high counting efficiency is essential, as in the case of many environmental and biological samples, large NaI(Tl) well crystals remain the detectors of choice. These large well crystals provide a nearly 4 π geometry and, thus, allow maximum counting efficiency for the radionuclides present in the sample. However, the natural background counting rates of these large detectors are very high, and this high background is a limiting factor in the detection and precise measurement of low level radionuclides.

A reduction of the high background has been accomplished by the development of an anticoincidence-shielded gamma-ray spectrometer which has been fabricated using a 9 3/8 in. diam by 8 13/16 in. thick NaI(Tl) crystal with a well of sufficient size to accommodate a 500 ml polyethylene bottle. The crystal is shielded from its phototubes by a 5 in. thick pure NaI light pipe and is enclosed in a 36 in. diam by 36 in. thick plastic phosphor which serves as an anticoincidence annulus. A 4 in. thick boron-paraffin shield serves to reduce the background contribution from cosmic-ray-produced neutrons. The background in the energy region of 0.1 to 4 MeV is reduced by five- to thirty-fold by the combined shielding techniques. The Compton response for a ^{65}Zn point source is reduced by two- to three-fold while that of ^{60}Co Compton response below the 1.17 MeV photopeak is reduced by six- to seven-fold. For our standard geometry 500 ml aqueous samples, the photopeak counting efficiency of ^{65}Zn in the large well crystal is forty times higher than with a 3 in. X 3 in. crystal, yet the background of a large well crystal is only two-fold higher.

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ANALYSIS OF METEORITES BY MULTIDIMENSIONAL
GAMMA-RAY SPECTROMETRY

N. A. Wogman

The analysis of meteorites can provide unique information on the cosmic ray or solar particle exposure of extra-terrestrial matter. Due to the scarcity of meteoritic material and the need to conserve samples, a non-destructive method of analysis is desirable for much of the work. The first suggestion that cosmic-ray-produced nuclei might be detected in meteorites, was made in 1947.⁽¹⁾ Since that time, many stable and radioactive spallation products have been detected in meteorites.

Gamma-ray spectrometry offers a unique nondestructive, noncontaminating method of determining qualitatively and quantitatively many of the radionuclides produced by cosmic ray bombardment of the meteorite and such measurements provide information on the spectrum intensity of solar and galactic cosmic radiation, its time variation, the preterrestrial meteorite size, the time of fall, and cosmic or "radiation" age. After standardization of the detector system for the sample geometry and the gamma rays of interest, a quantitative determination of the radionuclides can be performed. The nondestructive nature of the method is emphasized by the fact that the more energetic gamma rays can even be observed from the center of large (kg) meteorite specimens. Our development of a large NaI(Tl) crystal multidimensional gamma-ray spectrometer system⁽²⁾ offers the highest reported sensitivity, through a combination of very low background and high counting

efficiency, for the quantitative analysis of large environmental samples.

The detectors for this system are 11 in. diam by 6 in. thick NaI(Tl) crystals with 4 in. thick pure sodium iodide light pipes, and these detectors are enclosed in a 36 in. diam by 36 in. thick plastic phosphor anti-coincidence shield. This whole assembly is contained in a 4 in. thick lead shield, which is lined with 4 in. of 5% boron-impregnated paraffin to thermalize and capture cosmic-ray-produced neutrons. The coincidence counting efficiency for a point source of ⁶⁰Co in this new detector system is three-fold higher than for a similar system with 5 in. diam NaI(Tl) crystals. The efficiency of the new 11 in. diam detector system for a 5 in. diam ⁶⁰Co source is an order of magnitude higher than for the 5 in. diam detector system.

The combined high counting efficiency in this large detector system, plus its very low background obtained by a combination of mass shielding, neutron shielding, and anticoincidence shielding, provides the capability for the determination of many radionuclides at levels of 1 to 0.1 dis/min in the presence of orders of magnitude higher concentrations of other natural or artificial radionuclides. This counting system provides, by far, the most sensitive known method for the direct measurement of complex radionuclide mixtures at the levels encountered in most environmental materials.

The single and coincidence gamma-ray spectra of two olivine-hypersthene chondrites (Leedey and Bruderheim), a fine octahedrite (Maria Elena), and a pallasite (Salta) were determined with this system. Potassium-40 and ^{26}Al are the predominant radionuclides determined. Minor constituents included the gamma-ray emitters-- ^{22}Na , ^{44}Ti , ^{60}Co --and ^{232}Th and ^{238}U daughters; ^{54}Mn was not observed since its short half-life of 312 days precluded its presence--the shortest terrestrial age of these meteorites was 7 years for the Bruderheim sample. The meteorite, Maria Elena, was obtained from E. P. Henderson, Curator at the Smithsonian Institution, Washington, D.C.; it is a fine octahedrite and a "find" from Chile. The Salta meteorite also was obtained from the Smithsonian Institution; it is a pallasite found in Argentina. The two olivine-hypersthene chondrites, Leedey and Bruderheim, were obtained through the cooperation of Dr. C. Menninga, Livermore, California. Leedey was an "observed fall" in Dewey County, Oklahoma, on November 25, 1943; it has a U-Th-He age of 2.2 aeons and a cosmic-ray exposure age of 7×10^6 million years. The sample which was analyzed consisted of two pieces of meteorite each of which had a fusion crust; thus, the pieces were exposed to atmospheric ablation and possible terrestrial contamination. Bruderheim fell in Alberta, Canada, on March 4, 1960; the K-Ar age has been determined as 1.6 aeons and it has a cosmic-ray exposure age of 30 million years.

The problems which are encountered in the quantitative determination of

radioisotopes by the interpretation of gamma-ray spectra arise from unknown geometries and unknown self-absorption factors. However, in the present system the geometry problem is minimized by the design of the spectrometer while the self-absorption factor can be determined on meteorite mockups. For example, the geometrical coincidence counting efficiency for ^{60}Co varies less than 3% when changing from a 1 in. to a 3 in. diam source. Thus, a geometrical standardization of all the isotopes using sources which are meteoritic mockups produced no appreciable error. The self-absorption factors were determined using variable density sources. The samples were counted for 1000 to 8000 min in 1000-min cycles. Backgrounds were taken using pieces of dunite rock that had been chipped to a size and weight which approximated the meteorite under investigation.

The results are listed in Table I. The Bruderheim data agree with the few previously published values to within a standard deviation except for the ^{40}K values. The disagreement may be due to inhomogeneity of ^{40}K in the meteorite since the present value was obtained from a count of a 41 g sample; whereas, the earlier value was determined from a 2.15 kg sample, or it could be due to some contamination. Edwards and Urey⁽⁷⁾ in measurements of ^{40}K in 21 chondrites found an average ^{40}K content of 1490 dis/min/kg with upper and lower limits of 1870 and 1063 dis/min/kg, respectively. Of the eight radionuclides, only ^{40}K is cosmic; the ^{232}Th and ^{238}U are natural; the rest were produced by cosmic-ray

TABLE I. Radioactivity in Meteorites

		dis/min/kg (g)				Radiation
		Bruderheim 41 g	Leedey 34.6 g	Maria Elena 477 g	Salta 877 g	
^{22}Na	(a)	95 $\pm$ 19				β^+ , γ 1.28 MeV
	(b)	90 $\pm$ 10				
^{26}Al	(a)	57 $\pm$ 6	67 $\pm$ 3	1.4 $\pm$ 0.7	13 $\pm$ 1	β^+ , γ 1.83 MeV
	(b)	60 $\pm$ 6				
^{40}K	(a)	1340 $\pm$ 43	1216 $\pm$ 21			ϵ , γ 1.46 MeV
	(c)	1645 $\pm$ 74				
^{44}Ti	(a)	3 $\pm$ 1.1	5 $\pm$ 1		0.4 $\pm$ 0.2	β^+ , γ 1.16 MeV ^(d)
	(b)	2 $\pm$ 0.2				
^{60}Co	(a)	12 $\pm$ 4	39 $\pm$ 16			β^- , γ 1.17, 1.33 MeV
	(b)	9 $\pm$ 1				
^{232}Th	(a)	13 $\pm$ 6	2.3 $\pm$ 1.4	<1	<1	β^- , γ 0.58, 2.61 MeV ^(e)
	(b)					
^{238}U	(a)	25 $\pm$ 10	1.5 $\pm$ 1.7	<1	<1	β^- , γ 0.61, 1.12 MeV ^(f)
	(b)					
^{54}Mn	(b)	100 $\pm$ 13				

(a) *This paper.*(b) *Reference 3 and 5.*(c) *Reference 4.*(d) *The daughter ^{44}Sc .*(e) *The daughter ^{208}Tl .*(f) *The daughter ^{214}Bi .*(g) *On date of fall or September 1, 1966 if a "find".*

bombardment. The ^{22}Na is probably produced from the spallation of magnesium, and the ^{54}Mn from spallation of iron. Aluminum-26 results from spallation reactions on ^{28}Si , ^{26}Mg , and ^{27}Al . The ^{44}Ti arises from reactions on titanium and chromium while ^{60}Co is produced from titanium and cobalt.

The ^{232}Th values are only semiquantitative due to the large standard deviations associated with their measurement. The ^{232}Th from Bruderheim (13 dis/min/kg) yields a value of 5×10^{-8} g Th/g meteorite (Leedey yields a value of 1×10^{-8} g Th/g meteorite) which

compares favorably to values of 4.0 to 9.0×10^{-8} g Th/g meteorite in chondritic material.⁽⁸⁾ The ^{238}U values typically are about 1/3 or 1/4 of those concentrations; the ^{238}U value obtained in this study for Bruderheim is 3×10^{-8} g ^{238}U /g meteorite or about one-half of the thorium concentration.

The ^{26}Al values for the two chondrites are in good agreement with an average of 51 dis/min/kg found by Rowe⁽⁶⁾ in 14 chondrites. The value of 1.4 dis/min/kg ^{26}Al for the iron meteorite agrees very well with earlier

values⁽⁹⁾ which ranged from 0 to 2.70 dis/min/kg for 10 iron meteorites. These values were all obtained by γ - γ coincidence counting and are 2/3 to 1/3 of the values obtained by β -counting. Similarly, the measured concentrations of ^{44}Ti have been questioned for the past few years due to deviations of 1.2 to 2.4 when comparing γ - γ measurements to β -counting. These discrepancies have even occurred on identical samples.⁽⁹⁾

Since β -counting is not specific for a radionuclide, the possible contamination of samples or standard in β -counting analysis is a major problem. This may account for the differences between β -counting and the γ - γ results.

The terrestrial age of Salta could be calculated if the average values for ^{44}Ti in pallasite were known.

Additional gamma-ray emitting isotopes which could be found by this ultrasensitive detector method in large samples of extraterrestrial materials are the short-lived radionuclides ^{46}Sc , ^{56}Co , ^{58}Co , ^{48}V , ^{51}Cr , and ^{54}Mn . If it were possible to obtain the sample within a day after arrival on earth, the short-lived radionuclides-- ^{24}Na (15.0 hr), ^{42}K (12.4 hr), and ^{64}Cu (12.9 hr) and perhaps others-- could probably be measured.

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DEVELOPMENTS IN THE TECHNOLOGY FOR NEUTRON ACTIVATION ANALYSIS OF BIOLOGICAL MATERIAL

W. A. Haller

In the past several years, interest has increased in the study of trace element concentrations in plant and animal tissue. Many reports have been published showing relations between trace elements and yield of crops.⁽¹⁾ Also during the same period, studies have increased on the variation of trace element concentration between diseased (e.g. cancerous⁽²⁾) and healthy animal tissue. To aid in these studies, an analytical system using neutron activation and multi-dimensional gamma-ray spectrometry has been developed that is capable of determining 9 to 12 elements without the need of chemical separations.

PREPARATION OF SAMPLES

All preparation of samples was done in an Agnew-Higgins Model 43, clean air hood to eliminate contamination from dust in the air. Large, high moisture content samples, such as potatoes, were first sectioned with a Lucite knife, then a secondary section was taken with a Lucite borer (3/8 in. by 1 in. length) and placed in a previously-prepared polyethylene container. Small grain samples, such as peas and wheat, were added directly to the polyethylene containers.

Animal tissue samples were cut with either a stainless steel razor blade or a quartz knife. Experiments with a control sample of tissue showed that the quartz visibly chipped during sample cutting whereas the razor

blade showed little if any damage when viewed with a 400X microscope.

CONTAINERS FOR NEUTRON ACTIVATION

Polyethylene containers (Nalgene No. 25) which had been previously leached for 10 minutes with doubly distilled water, and 8N doubly distilled HNO_3 were used as primary activation analysis containers. Because several types of samples had high moisture content when they were added to the polyethylene containers, it was imperative to prove that the leachable trace element content of the polyethylene Nalgene was low in comparison to the trace element concentrations in the biological samples. Experiments with empty Nalgene containers that were handled in exactly the same manner as actual sample containers were neutron-activated and washed with H_2O and 8N HNO_3 . Analysis of the washings showed the low leachable trace element content reported in Table I.

PREPARATION OF SAMPLES BY FREEZE DRYING

Samples were encapsulated in polyethylene containers with a cut in the container cap to allow venting during the freeze-drying process. It was found that 2 days was sufficient to completely dehydrate all types of biological samples used. A sintered glass filter, packed with a Gelman

TABLE I. Trace Elements Removed from Irradiated Polyethylene Containers by 10 Minute Leaching with Cold 8N HNO₃ and H₂O

Element	Daughter Radionuclide Determined	Approximate Integrated Flux	Picograms Integral Container	Leached Ruptured Container
Na	²⁴ Na	5×10^{13}	200	(a)
Mn	⁵⁶ Mn	5×10^{13}	50	(a)
Cu	⁶⁴ Cu	5×10^{13}	30	(a)
Br	⁸² Br	5×10^{13}	30	(a)
Sb	¹²⁴ Sb	5×10^{17}	22	80
Co	⁶⁰ Co	5×10^{17}	10	56,000
Sc	⁴⁶ Sc	5×10^{17}	5	300
Fe	⁵⁹ Fe	5×10^{17}	<1,000	100,000
Zn	⁶⁵ Zn	5×10^{17}	<1,000	1,000,000
Cs	¹³⁷ Cs	5×10^{17}	<1,000	10,000

(a) Containers did not fail with low integrated fluxes.

10 mu filter, purified the incoming air of particulate matter when the vacuum on the freeze dryer was released.

SAMPLE ENCAPSULATION FOR IRRADIATION

After freeze-drying, the perforated caps were replaced with new caps that had been cleaned in the manner previously described. Samples were irradiated both with and without outer containers. It was found that sealing the polyethylene with plastic tape or heat sealing was sufficient to control contamination of the samples from the outside environment where a low integrated flux of about 5×10^{13} n/cm² was used. However, where integrated fluxes as high as 5×10^{17} n/cm² were used, this method was not applicable. Thermal heat and radiation caused a buildup of gas pressure from the degradation of the biological material and in several

instances small pressure holes developed in the containers. To experimentally evaluate the effect of container failure on trace element concentrations, empty polyethylene containers with a 1/16 in. cut in the side wall were activated in the same manner as a normal sample. Comparison of washings from these containers with washings from similar containers that were sealed from the irradiation facilities environment revealed gross contamination with several long-lived radionuclides (see Table I).

Because of the risk of rupture of the polyethylene, a two container system was used. Aluminum cans made of high purity aluminum were used as secondary containers. A polyethylene container was placed in the aluminum can, irradiated, and washed out in the usual manner of sample treatment. Low washout of long-lived radionuclides was obtained. Because the

aluminum cans, needed to encapsulate the polyethylene containers, were slightly larger than the irradiation facility could easily handle, they tended to jam during discharge. Approximately one out of ten cans experienced difficulty during discharge resulting in a larger than normal gamma dose rate to the irradiation facilities personnel. Studies of the feasibility of wrapping the polyethylene can in several thin layers of aluminum are in progress.

SAMPLE DECAPSULATION

After neutron irradiation the outer containers were removed. The outer surface of the polyethylene container was then heavily lacquered to insure that surface contamination would not be transferred during sample discharge. The cap of the container was then removed and the irradiated sample was transferred to a one-inch dish for counting.

ANALYSIS AND RESULTS

All gamma-ray measurements were made with an anticoincidence-shielded multidimensional gamma-ray spectrometer.^(3,4) Tables II and III show the concentrations of elements found in plant and animal tissue. Comparison of the trace element concentrations in Tables II and III with the contamination concentrations of Table I indicate that a large number of trace elements with wide ranges of concentrations may be measured in biological tissue with good precision by this technique.

TABLE II. Concentration Ranges of Trace Elements in Plant and Animal Tissues Measured Using an Integrated Flux of 5×10^{13} n/cm²

Element	Plant Tissue	Animal Tissue
	ppm Wet Weight	
Na	5-200	900-8000
K	800-4000	
Cu	0.8-8	
Mn	0.5-6	
Br	0.5-50	

TABLE III. Concentration Ranges of Trace Elements in Plant and Animal Tissue Measured Using an Integrated Flux of 5×10^{17} n/cm²

Element	Plant Tissue	Animal Tissue
	ppm Wet Weight	
Fe	1-20	10-200
Co	0.01-0.1	0.01-0.1
Zn	1-20	5-25
Sb	0.0001-0.01	0.001-0.02
Sc	0.0001-0.05	0.0001-0.008
Cs	0.0001-0.01	0.001-0.02

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DETERMINATION OF SELENIUM IN BIOLOGICAL MATTER BY NEUTRON
ACTIVATION AND Ge(Li) DIODE COINCIDENCE COUNTING

C. W. Thomas

The concentration of selenium in various materials is of considerable interest due to both its toxicity to animal life and its apparent need by vegetation. In 1933 it was discovered that selenium was required and concentrated by certain forms of vegetation which when consumed by animals could be fatal.⁽¹⁾ Concentrations between 0.5 and 5 ppm in common foods and liquids are now believed potentially dangerous.⁽²⁾ Although toxic in high concentration, selenium may be essential since it has been reported that certain body cells have seleno-organic compounds as part of their structure.⁽²⁾ The precise determination of the low concentrations of selenium in these various seleno-organic compounds and in foods and liquids has been difficult due to the chemical characteristics of selenium. Activation analysis combined with gamma-ray spectrometry has the potential sensitivity for the precise determination of selenium at concentrations of interest. The determination of selenium in tissue was studied using

neutron activation and Ge(Li) detectors in coincidence for direct instrumental analysis.

Until recently the best means of gamma-ray measurement of high sensitivity and selectivity has been through use of large NaI(Tl) detector systems, and especially the use of these detectors in various coincidence arrangements. This allowed nondestructive activation analysis with the determination of several trace elements at the same time. More recently, Ge(Li) diodes with their excellent resolution have become available. Because of the excellent intrinsic resolving power of the germanium diodes compared to the NaI(Tl) crystals and the good efficiency of the diodes at low gamma-ray energies, these detectors are far superior to NaI(Tl) crystals for some applications.

The source of interference in non-destructive activation analysis using gamma-ray spectrometry is the activation of both trace elements and major constituents in the sample. This interference results from the Compton

events of higher energy gamma rays or from bremsstrahlung radiation from high energy beta particles. In biological samples, ^{24}Na (15 hr) and ^{32}P (14.7 day) are the two common radionuclides which contribute the greatest interference. This interference can be reduced in the case of ^{75}Se determination by arranging the detectors in a coincidence mode. ^{75}Se is one of the activation products of selenium; and since it decays by emission of two low-energy gamma rays in cascade, two Ge(Li) diodes were used as detectors in a coincidence mode. These planar diodes each had depletion volumes of 2 cubic centimeters and were used in conjunction with a 4096 channel multiparameter analyzer in a 64 by 64 channel array. Tissues were activated in a Hanford reactor after which part of the sample was used as a blank and the other part was spiked with various concentrations of ^{75}Se equivalent to selenium concentrations between 0.01 and 10 ppm. These samples were then analyzed at various times after irradiation with Ge(Li) detectors used singly and in coincidence. The results showed

that selenium could not be determined during the first few days following irradiation due to the large interference from ^{24}Na . After 10 days decay, only ^{75}Se concentrations at about 10 ppm or larger could be determined using a single Ge(Li) diode because of the large bremsstrahlung continuum from ^{32}P beta particles. However, by using two Ge(Li) diodes in a coincidence mode, the interference from the bremsstrahlung radiation was reduced to a level where concentrations as low as 0.01 ppm of selenium could be determined. The ^{75}Se coincident gamma-ray peaks due to the 136 and 265 keV cascade and the 121 and 280 keV cascade were readily distinguishable thus showing the merits of this selective type of detector arrangement.

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PRODUCTION OF PROMETHIUM-143 AND -144 BY PROTON IRRADIATION

T. M. Beasley and H. E. Palmer

The increasing interest in the use of ^{147}Pm as a possible heat source of space vehicles has also stimulated interest in its metabolic behavior following inhalation and ingestion. Since ^{147}Pm decays primarily by the emission of a weak beta particle ($E_{\text{max}} = 0.23 \text{ MeV}$) it does not lend itself to detection by whole body counting techniques, and its determination in excreta requires radiochemical separation. For animal experimentation a gamma emitting isotope with a reasonably long half-life would greatly facilitate the data collection. Both ^{143}Pm and ^{144}Pm satisfy these requirements in that both isotopes decay by electron capture and subsequent gamma-ray emission and both isotopes have reasonably long half-lives (267 days and 349 days, respectively).⁽¹⁾

Approximately 100 mg of enriched $^{144}\text{Nd}_2\text{O}_3$ (94.4%) was irradiated in the proton beam of the 84 in. cyclotron at Oak Ridge National Laboratory on February 3, 1966. The energy of the incident protons was $20.5 \pm 0.5 \text{ MeV}$ and the integrated beam current was $80.7 \mu\text{A-hr}$. Under these conditions

of irradiation, approximately $74 \mu\text{Ci}$ of ^{143}Pm (p,2n) and $4 \mu\text{Ci}$ of ^{144}Pm (p,n) were produced. Figure 1 shows the spectrum obtained when an aliquot of the irradiated material was counted with a lithium-drifted germanium detector. All of the photopeaks observed can be attributed to ^{143}Pm and ^{144}Pm .

The radioactive promethium isotopes can be separated from the stable neodymium target by ion exchange techniques.⁽²⁾ The effluent from such a separation was analyzed by emission spectrographic techniques and showed a neodymium concentration of $<13 \text{ ppm}$ using a starting neodymium concentration of some 4000 ppm.

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FIGURE 1. Ge(Li) Detector Spectrum of Promethium-143-144 Produced by Proton Irradiation of Neodymium

TRACE ELEMENTS AND ^{137}Cs IN SEA WATER BY
GAMMA-RAY SPECTROMETRIC TECHNIQUES*

D. E. Robertson and R. W. Perkins

The trace elements cesium, uranium, antimony, cobalt, and scandium were determined simultaneously in sea water without performing a chemical separation; activation analysis and multidimensional gamma-ray spectrometry techniques were used. Sea water samples (0.5 to 1 ml) were irradiated to an integrated neutron flux of about 10^{19} neutrons/cm² and allowed to decay for about 5 weeks. The samples were then counted for 1000 minutes on a multidimensional gamma-ray spectrometer. This technique was used on surface samples taken at several locations in the Pacific Ocean between the Oregon coast and Hawaii and in a depth profile taken 500 miles off the California coast. The average concentrations in the surface samples of U, Sb, Cs, Co, and Sc were 5.4 ± 1.8 , 3.2 ± 0.7 , 0.31 ± 0.02 , 0.050 ± 0.020 , and 0.0014 ± 0.007 $\mu\text{g/liter}$, respectively. The average concentrations in the depth profile (down to 1200 meters) for Sb, Cs, Co and Sc were 2.0 ± 0.06 , 0.35 ± 0.05 , 0.028 ± 0.011 , and 0.0024 ± 0.0010 $\mu\text{g/liter}$, respectively. Within the limits of precision of the method, no variation in concentrations versus depth were noted. The nuclear weapons-produced ^{137}Cs was also determined in a depth profile by separation of the ^{137}Cs on a small potassium hexacyanocobalt(II) ferrate(II) column which was then counted directly. The concentration of ^{137}Cs remained fairly constant at about 1.5 dis/min/liter down to a depth of about 50 meters but dropped to less than 3% of this value at 270 meters. The variations in concentration of the trace elements, their physical forms, and the analytical problems involved in measurements at the sub-parts-per-billion range are discussed.

* BNWL-SA-674A.

TRACE ELEMENTS IN MARINE ORGANISMS

D. E. Robertson

Ashed samples of squid, lantern fish, rat-tail fish, saury, euphausiid, and sable eel were analyzed for their trace element content by neutron activation analysis followed by direct counting of the sample on a multidimensional gamma-ray spectrometer. Using these techniques, the elements silver, antimony, cobalt, scandium, and zinc were determined from a single count. The concentrations of these elements were much higher in the organisms relative to their concentrations in sea water. Enrichment factors as high as 1 to 2×10^4 for silver were observed in squid and lantern fish, while rat-tail fish concentrated scandium by a factor of 1.6×10^4 . The cobalt and zinc were concentrated to a somewhat lesser extent, while antimony was not significantly accumulated in the bodies of these organisms.

Most of the trace elements are present in the oceans in the sub-parts-per-million concentration range. The elements phosphorus, iron, zinc, copper, manganese, and cobalt, which are considered essential to plant and animal growth, range in concentration from 70 parts-per-billion for phosphorus, to less than 0.5 parts-per-billion for cobalt. These elements are accumulated in marine organisms during their normal metabolism. Previous investigations have shown that these enrichment factors cover a range from less than unity to values as large as 10^6 .⁽¹⁻⁵⁾ A knowledge of these enrichment processes is important in understanding the biochemistry of marine organisms and the role of trace elements in the marine food chain. Not only do these marine organisms concentrate stable elements, but they also concentrate the various trace radionuclides deposited in the oceans from nuclear weapons testing and nuclear waste disposal. Defining the steady state concentrations of trace elements in the ocean allows one to estimate the behavior of radionuclides of these elements which have been or may be deposited in the oceans.

Recent developments in our laboratory in multidimensional gamma-ray spectrometry in conjunction with neutron activation analysis have made possible the simultaneous determination of many elements in a complex mixture without performing tedious and difficult chemical separations.⁽⁶⁻⁸⁾ The speed and ease of this technique provides the opportunity of simultaneously determining many elements in a large number of samples. This pre-

sent work was conducted to determine the feasibility of measuring trace elements in marine organisms by neutron activation analysis and multidimensional gamma-ray spectrometry.

Samples of ashed marine organisms were furnished by Dr. William Pearcy of the Oregon State University Department of Oceanography. About 100 mg samples of the ash were sealed in Spectrosil* vitreous silica ampoules and irradiated in a Hanford production reactor to an integrated thermal neutron flux of about 6×10^{18} neutrons. After the irradiations, the samples were allowed to decay for several weeks to allow the ^{24}Na (15 hr) to decay to insignificance. The ash was then dissolved in HNO_3 , and an aliquot was evaporated on a standard counting dish and counted for 1000 min on a multidimensional gamma-ray spectrometer. The normal gamma-ray spectra were almost completely masked by the intense bremsstrahlung radiation produced by the high concentrations of ^{32}P in the samples. However, by sandwiching the sample between two thin Pb-Cd absorbers (0.7 mm Pb followed by 0.7 mm Cd) to attenuate the bremsstrahlung, the elements silver, antimony, cobalt, scandium, and zinc could be determined from a single count on a multidimensional gamma-ray spectrometer. The concentrations and the enrichment factors which were attained for these elements in the organisms are tabulated in Table I.

* Ultra-pure, synthetically produced by the Thermal American Fused Quartz Co., Montville, New Jersey.

TABLE I. Trace Element Concentrations and Their Enrichment Factors in Marine Organisms

Sample	Trace Element Concentrations in Ashed Samples, μg/g ash				
	Ag	Sb	Co	Sc	Zn
1. Squid	8.1	0.46	0.93	0.010	710
2. Lantern Fish	4.4	~0.83	0.22	0.009	210
3. Rat-Tail Fish	<1	2.5	0.56	0.16	270
4. Saury	<1	~1.6	0.38	0.006	410
5. Euphausiid	<1	1.9	0.63	0.016	430
6. Sabel Eel	<1	<0.2	0.14	0.045	180
7. Sea Water	4×10^{-5}	0.003	5×10^{-4}	1×10^{-6}	0.01

Sample	Enrichment Factors (a)				
	Ag	Sb	Co	Sc	Zn
1. Squid	20,000	15	2000	1,000	7000
2. Lantern Fish	10,000	~30	400	900	2000
3. Rat-Tail Fish	--	100	1000	16,000	2700
4. Saury	--	~60	800	600	4000
5. Euphausiid	--	60	1300	1,600	4300
6. Sabel Eel	--	<7	300	4,500	1800

(a) Assuming the ash to be 10% of the total wet weight of the marine organisms.

These concentration factors are similar to those reported for other organisms by previous investigators.⁽¹⁻³⁾ The high concentration factors for silver in squid and lantern fish suggest that this element may be essential in their body metabolism. Silver was first observed to be concentrated in squid by Folsom,⁽⁹⁾ who detected ^{110m}Ag in squid taken from the Pacific Ocean. Brooks and Rumsby⁽³⁾ found similar enrichment factors for silver in the kidney of scallops and the heart and visceral mass of oysters; and they cite the work of Rapoport and Luebering⁽¹⁰⁾ on an enzyme system that is activated by Hg^{++} and Ag^+ ions. Goldberg⁽⁵⁾ found high concentrations of silver (5-30 ppm) in the liver of albacore and yellowfin tuna. Thus, it

may be possible that silver is an essential element in the metabolism of certain marine organisms. The role of zinc as an enzyme activator and constituent of several important metalloprotein enzymes is well known and it is considered likely that zinc is of importance in some marine biochemical systems. Cobalt has been shown to be essential for the growth of marine organisms because it is associated with vitamin B^{12} which exists in sea water at concentrations of about 0.001 ppb. Thus, marine organisms become enriched with cobalt by concentrating vitamin B^{12} , as well as inorganic cobalt. The role of scandium in biological systems is unknown. However, the high concentration of scandium in rat-tail fish may be explained

by the fact that this fish is a bottom dweller and is in constant contact with sediments which are relatively high in scandium.⁽¹¹⁾ Antimony appears to have no biological significance, since it is not greatly concentrated by marine organisms.

The simplicity, sensitivity, and selectivity of this method is well adapted to the trace element analysis of marine organisms. By performing one or two simple group separations, many other elements, such as calcium, iron, cadmium, chromium, and copper, could probably be determined.

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TRACE ELEMENTS IN MARINE SEDIMENTS

D. E. Robertson

The trace element content of two samples from a marine sediment core taken in the Astoria Canyon about 40 miles east of the mouth of the Columbia River were measured by neutron activation and multidimensional gamma-ray spectrometry techniques. The elements iron, chromium, zinc, scandium, uranium, cobalt and antimony were determined with good precision from a single 1000 min count. The trace element concentrations of these sediments reflect the contribution made by the Columbia River runoff.

A thorough knowledge of the biogeochemical processes taking place in the oceans cannot be obtained without a clear understanding of the geochemistry of the marine sediments. The major source of marine sedimentary material and dissolved matter is furnished by way of rivers.⁽¹⁾ Another source of sedimentary material is derived from the atmosphere, where terrigenous volcanic and meteoric dust fall from the air into the sea. The organic detrital matter and the skeletal remains from marine organisms also make an important contribution to the sediments. In some locations, inorganic precipitation of dissolved ocean constituents has occurred. Calcium carbonate, gypsum or anhydrite, are often deposited along with various other salts. Other examples of chemical precipitation are the well-known phosphate and manganese nodules which grow on the sea floor. A knowledge of the trace element behavior in the marine environment during all of these sedimentation processes is basic to an understanding of the routes, rates, and reactions by which the sediments are formed. In addition, a knowledge of the steady state distributions of the trace elements aids in predicting the fate of the radionuclides deposited in the

oceans from nuclear weapons testing and nuclear waste disposal. This study was initiated to determine the applicability of measuring the trace element content of marine sediments by neutron activation analysis and multidimensional gamma-ray spectrometry.

Several samples of marine sediments were obtained from Dr. Laverne Kulm of the Oregon State University Department of Oceanography. These samples were obtained from a core section taken from the Astoria Canyon about 40 miles directly west from the mouth of the Columbia River (lat. 46° 05.2', long. 125° 00.1'), at depth of 1490 meters. The core material was homogeneous to a depth of 205 cm, at which point a carbonate layer was penetrated. Carbon-14 analysis showed this layer to have an age of 5600 yr B.P. (before present).⁽²⁾ Using these data and assuming a linear deposition rate, these sediments accumulated at the rate of 0.037 cm/year. This sedimentation rate is about three orders of magnitude higher than in the so-called deep sea sediments and reflects the contribution made by the Columbia River.

Sections of this core taken at 7 to 25 cm (average age of 430 yr B.P.), and at 80 to 100 cm (average age of 2400 yr B.P.), were used in the

trace element analysis. Samples of the sediment (about 50 mg), were sealed in "Spectrosil"* vitreous silica ampoules and irradiated in a Hanford reactor to an integrated thermal neutron flux of about 4×10^{18} neutrons/cm². After the samples had stood for several weeks to allow the high concentrations of ²⁴Na to decay to insignificance, they were dissolved in aqua regia. A small amount of acid-insoluble siliceous residue was dissolved by boiling in HF, and the HF was removed by fuming to near dryness with concentrated HNO₃. The clear solution was combined with the acid soluble fraction and aliquots were taken to dryness on standard counting dishes. The dishes were counted for 1000 min on a multidimensional gamma-ray spectrometer.⁽³⁾ The elements iron, chromium, zinc, scandium, uranium, cobalt, and antimony could be determined with good precision from a single count without performing a chemical separation. Although the normal gamma-ray spectra were composed almost entirely of the gamma rays from the high concentrations of ⁵⁹Fe and ⁵¹Cr, the radionuclides ⁶⁵Zn, ⁴⁶Sc, ¹⁴⁰Ba-La (from U fission), ⁶⁰Co, and ¹²⁴Sb could easily be measured by utilizing their coincidence gamma rays. The data obtained from these measurements are included in Table I.

The concentrations of the trace elements in these samples is undoubtedly greatly influenced by the Columbia River runoff. The concentrations

of chromium and cobalt are similar to those in near-shore sediments analyzed by other investigators.⁽⁴⁾ The uranium concentrations were a factor of 4 to 15 times higher than those found in the deep sea sediments but were generally in agreement with the higher concentrations found in near-shore sediments and in those sediments of a terrestrial origin.⁽⁵⁾

The concentrations of scandium, zinc, and antimony in the marine sediments are not well known, although manganese nodules have been shown to concentrate zinc and other elements from sea water.⁽⁶⁾ The scandium was greatly enriched in these sediments relative to its concentration in sea water.

TABLE I. Trace Element Concentrations and Enrichment Factors in a Marine Sediment Core

Element	Concentration, ppm	
	7-25 cm Section, (430 yr B.P.)	80-100 cm Section, (2400 yr B.P.)
Fe	49,000	73,000
Cr	323	441
Zn	18.2	17.7
Sc	14.2	18.9
U	12.8	15.8
Co	11.7	16.1
Sb	8.4	9.8

Element	Enrichment Factors, Ratio of Concentration in the Sediment to the Concentration in Sea Water
Fe	5×10^6
Cr	6×10^6
Zn	2×10^3
Sc	7×10^6
U	4×10^3
Co	2×10^5
Sb	3×10^3

* Ultra-pure, synthetically produced by the American Thermal Fused Quartz, Co., Montville, New Jersey.

Neutron activation analysis in conjunction with multidimensional gamma-ray spectrometry has been shown to be a very powerful analytical method for measuring the trace element content in marine sediments. The high sensitivity and selectivity permit precise determination of up to seven elements in a sediment sample. By performing a few simple group chemical separations to remove iron, chromium, and short-lived interferences, the number of elements which could be determined would be increased significantly.

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THE ROLE OF CONTAMINATION IN THE ULTRA-TRACE ELEMENT ANALYSIS OF SEA WATER

D. E. Robertson

Some of the potential sources of contamination in the ultra-trace element analyses of sea water were investigated. Samples of purified water, nitric acid, hydrochloric acid, chloroform, carbon tetrachloride, polyethylene, glassware, filters, hydrowires, and a variety of chelating reagents were analyzed for trace element impurities by neutron activation and multidimensional gamma-ray spectrometry techniques. The purified reagents, in general, contained very low concentrations of trace element impurities. Pyrex glass contained relatively high concentrations of iron, antimony, zinc, hafnium, scandium, and cobalt, while Vycor glass contained extremely high concentrations of antimony (1090 ppm) and arsenic (11.4 ppm). Polyethylene containers contained much lower concentrations of trace element impurities than glassware, but contained 10 ppm of iron. Most of the chelating reagents contained relatively high concentrations of iron and zinc and lesser amounts of antimony, cobalt, silver, and copper. The marine hydrowires contained relatively high concentrations of antimony, cobalt, and copper.

Sea water is a complex solution containing, either in a dissolved or particulate state, all of the elements of the earth's crust. Yet, only thirteen of these elements exist at concentrations greater than one part-per-million, while the majority of them are present in the sub-parts-per-billion range. The analytical problems involved in measurements at these low concentrations are considerable. Normally, chemical pre-separations are required for preconcentration or removal of interfering elements before an analysis can be performed.⁽¹⁾ These procedures greatly increase the risk of contaminating the sea water sample. Contamination may come from reagents, vessels, and other apparatus used for the separations and even from the airborne particulate material in the atmosphere of the laboratory. These sources are briefly discussed by other investigators.⁽²⁻⁴⁾ Serious contamination may also result from faulty sampling techniques. Metallic components associated with most sampling apparatus and the corrosion products accumulated on hydrowires could significantly contaminate a sea water sample during the sampling process.

The literature on the trace element content of sea water frequently shows extreme variations in the concentrations of many trace elements. Many of these large deviations are probably due to faulty analytical methods, or more precisely, to contamination of the sea water samples. In our initial trace element analyses of sea water by neutron activation analysis and multidimensional gamma-ray spectrometry,^(5,6) it was observed that serious contam-

ination of several elements does occur even where unusual care is exercised. These contaminants originated from impurities present in containers and filters and from airborne particulate material in the laboratory. This method was purely instrumental and required only a minimum of handling and no pre-treatment of the sea water samples. Thus, the magnitude of the contamination could be more directly identified. This present study was conducted to determine the potential sources of contamination in the ultra-trace element analyses of sea water.

Previous studies have shown that certain vitreous silica ampoules previously used as irradiation containers contained sufficiently high concentrations of antimony to significantly contaminate a sea water sample. A later investigation⁽⁷⁾ showed that irradiation ampoules made from the synthetically produced material, "Spectrosil,"* greatly minimized this contamination problem. These ampoules were cleaned by refluxing them overnight in doubly distilled nitric acid, rinsing them several times with doubly distilled water, and drying them by centrifugation. This type of ampoule was used in all of the trace element analyses discussed below.

Samples of some of the solvents and reagents commonly used in the trace analysis of sea water⁽¹⁾ were neutron-irradiated in "Spectrosil" ampoules or polyethylene vials, and the samples were counted directly on a multidimensional gamma-ray spectrometer.

* American Thermal Fused Quartz Co.,
Montville, New Jersey.

Also, samples of containers, filters, polyethylene hose, and marine hydro-wires were likewise analyzed for trace element impurities (See Table I). The distillation of the water, nitric acid, hydrochloric acid, chloroform, and carbon tetrachloride was performed in a Pyrex glass distillation apparatus and stored in polyethylene bottles (except for the chloroform and carbon tetrachloride which were stored in Pyrex bottles). The distilled water was obtained from commercially available "all-quartz" distillation assemblies. The glass, polyethylene, and hydrowire samples were all washed with doubly distilled nitric acid and doubly distilled water both before and after the neutron irradiation. The chelating reagents were commercially available products which were analyzed as supplied by the vendor. Most of the laboratory operations were performed in a positive pressure laminar flow hood containing an absolute filter (0.5μ) to minimize airborne contamination.

As Table I indicates, the distilled solvents are extremely low in trace element impurities. However, the concentrations of many of these elements are about the same order of magnitude as their concentrations in sea water. Therefore, if relatively large volumes of these solvents are used in preconcentration or preseparation procedures, they could contribute significant contamination to the sea water sample.

The doubly distilled nitric acid contained a relatively high concentration of silver. The distilled water contained higher concentrations of

antimony and scandium relative to the doubly and triply distilled water and may be a reflection of high impurity levels of these elements in the components of the still. The Millipore filters contained relatively high concentrations of chromium and zinc with lesser amounts of antimony, cobalt, scandium, cesium, and iron.

Pyrex glass contained high concentrations of iron, hafnium, and antimony, plus significant amounts of scandium, cobalt, and zinc. Therefore, care should be taken not to perform any pretreatment of the sea water sample in Pyrex glassware which would result in the leaching of these elements from the glass surface. Vycor glass, (a high silica glass with improved thermal stability), made by Corning Glass Co., has such high concentrations of antimony (1090 ppm) and arsenic (11.4 ppm) that the measurement of other elements was not possible by using direct counting techniques. Again, care must be taken not to use procedures which could lead to dissolution of this glass. The polyethylene samples generally contained low impurity concentrations except for relatively high concentrations of iron and lesser amounts of chromium and zinc. Polyethylene, therefore, appears to be a suitable container (from the trace element impurity standpoint) for use in ultra-trace element analysis.

Most of the chelating reagents contained significant concentrations of many metals--notably iron, zinc, copper, silver, antimony, and cobalt. No attempts were made to purify these reagents after receiving them from the

Sample	Zn	Fe	Sb	Co	Cr	Sc	Cs	Ag	Cu	Ia	Hf
Quartz Distilled Water (325 Bldg)	~1	~1	~0.06	~0.04	~2	0.0022	<0.01	<0.02	N.D.	N.D.	<0.005
Quartz Distilled Water (320 Bldg)	9.5	<0.2	~0.10	~0.20	<10	0.0025	0.12	<0.02	N.D.	N.D.	<0.005
Triply Distilled Water	~0.5	~1	~0.02	<0.02	12	~0.0002	<0.01	<0.02	N.D.	N.D.	<0.001
Doubly Distilled Water	~1	<0.2	<0.01	<0.02	~2	<0.0001	<0.01	<0.02	N.D.	N.D.	<0.001
Doubly Distilled HNO ₃ (a)	~2	~1	~0.04	~0.03	13	~0.008	<0.1	0.29	N.D.	N.D.	0.011
Doubly Distilled HCl(a)	~1	~1	~0.04	~0.08	6	~0.001	<0.01	<0.02	N.D.	N.D.	0.010
Doubly Distilled CCl ₄ (b)	1.2	9.8	0.33	~0.003	<50	~0.002	<0.1	<0.005	0.12	0.04	<0.005
Doubly Distilled CHCl ₃ (c)	2.1	1.6	0.05	~0.003	<100	~0.00003	<0.02	<0.005	0.29	<0.008	<0.005
Millipore Filter(d)	2370	330	39	13	17,600	0.79	1.54	<0.05	N.D.	N.D.	<0.5
Pyrex Glass(e)	730	278,000	2,900	81	U.D.	106	<100	<0.001	N.D.	N.D.	597
Vycor Glass(e)	U.D.	U.D.	1.09 x 10 ⁶	U.D.	U.D.	U.D.	U.D.	<0.5	U.D.	N.D.	U.D.
Polyethylene(f)	27.6	10,400	0.18	0.072	76	0.008	<0.05	<0.1	6.6	N.D.	<0.5
Polyethylene(g)	25.0	10,600	0.83	0.31	19	0.36	<0.05	<0.1	15	N.D.	<0.5
Dithizone(h)	1150	<7,000	0.8	1.2	<2,000	0.15	<10	<10	420	19	<0.10
Cupferron(i)	7,000	<600	0.3	0.68	<200	0.04	<1	~3	160	0.20	<1
Nitroso-R(j)	1,420	360,000	39.5	111	U.D.	0.65	<100	436	N.D.	N.D.	<100
Thionalide(k)	120	<300	3.7	5.1	U.D.	0.10	<1	4.6	100	N.D.	<1
2-benzimidazolethiol(l)	53,000	69,000	45	21	U.D.	0.29	<10	<2	0.4	N.D.	<100
1-pyrrolidine carbodithioic acid(m)	1,970	~5,000	1.9	1.3	U.D.	0.11	<1	11	4	N.D.	<10
Sodium diethyldithiocarbamate(n)	39.5	<600	42	0.56	U.D.	0.02	<1	<10	N.D.	N.D.	<1
Thenoyltrifluoroacetone(o)	329	11,300	6.2	4.9	192	0.09	<10	209	16	N.D.	<1
8-hydroxyquinoline(p)	U.D.	U.D.	1,210	U.D.	U.D.	0.14	U.D.	<10	290	N.D.	U.D.
Polyethylene hose(q)	55	7.4	9,000	140	254	11	<100	<300	N.D.	0.04	<100
Starboard hydrowire(r)	U.D.	-	95,200	66,100	U.D.	<50	N.D.	N.D.	40,300	N.D.	N.D.
Port hydrowire(r)	U.D.	-	54,300	57,000	U.D.	<50	N.D.	N.D.	19,700	N.D.	N.D.

N.D. = Not Determined

U.D. = Unable to determine because of interfering radionuclides

(a) Baker and Adamson, C. P. Reagent

(b) Baker Analyzed Reagent

(c) Mallinckrodt Analytical Reagent

(d) Millipore Filter Corporation

(e) Corning Glass Company

(f) Nalgene, No. 6250, 8 ml volume polyethylene container

(g) CRC Plastic Flip-Top Vials, 2/5 dram volume, The Chemical Rubber Company

(h) Baker Analyzed Reagent, Crystal

(i) Eastman Organic Chemicals

(j) Baker Technical Grade

(k) Baker Grade

(l) Baker Practical

(m) Baker Guide

(n) Baker Analyzed Reagent, Powder

(o) Baker Analyzed Reagent

(p) Fisher Scientific Certified Reagent

(q) Interstate Plastics Company

(r) From ship Oceanographer

TABLE I. Trace Element Impurities in Solvents, Reagents and Container Material

vendor. Although the trace element impurities in these reagents are present in relatively high concentrations, they may or may not contribute to contamination, depending upon the amount and procedure used in the analysis. Usually, very small amounts of these chelating reagents are used, but an experimenter should be aware of the impurity levels present. The high antimony concentration in the 8-hydroxyquinoline may be the result of contamination of this reagent since the sample was obtained from a previously opened bottle used in one of our laboratories.

Samples of oceanographic hydrowires from the ship Oceanographer contained antimony, cobalt, and copper impurities as determined by directly counting the neutron-irradiated steel wire. The high concentrations of ^{59}Fe prevented a more thorough analysis by direct counting techniques. A sample of 1 in. diam polyethylene irrigation hose, which will be used by our laboratory for large volume deep-sea sampling for trace radionuclide studies, showed relatively high concentrations of chromium, antimony, zinc, iron, cobalt, and scandium. If significant amounts of these trace elements are leached from the hose on passing sea water through it, the water would not be satisfactory for analysis for such elements.

The excellent sensitivity and selectivity of neutron activation analysis in conjunction with multidimensional gamma-ray spectrometry has allowed the simultaneous determination of many trace element impurities in a variety of solvents, reagents, and container materials normally encountered in the

ultra-trace element analysis of sea water. This study was conducted to define the analytical problems which are involved in the analysis of trace elements in sea water and to emphasize the relative ease by which a sample can become contaminated. It should be pointed out that the impurity levels observed in this study must reflect the differences in the manufacturer's method of preparation and purification of solvents, reagents, and other materials. Other reagents and materials may have a very different spectrum of impurities. It is, however, essential to know the order of magnitude of contaminants to minimize contamination if they must be used in sample collection or processing.

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RADIONUCLIDE CONSTITUTENTS IN SURFACE WATER OF THE PACIFIC
OCEAN BETWEEN THE OREGON COAST AND THE HAWAIIAN ARCHIPELAGO

H. G. Rieck

Concentrations of five radionuclides were measured in a series of surface water ocean samples collected during a cruise between Newport, Oregon and Hawaii.

In April and May 1966, a series of samples was collected during a cruise of the R/V Yaquina between Newport, Oregon and Honolulu, Hawaii. A supply of uncontaminated surface water was obtained while the ship was under way by using a planing device tethered to a boom over the side of the ship. The intake to a plastic sample line attached to the device was approximately 3 ft below the surface and 8 ft from the side of the ship. Sampling periods were continuous and generally of about 24 hr duration. A self-priming centrifugal pump* moved the sample water through a prefilter, membrane filters, and ion exchange beds. A 5 μ cartridge prefilter unit** was

used in all but one sampling run. Following the prefilter, four membrane filters*** with a pore size of 0.3 μ were used in 12 runs and two were used in 4 runs. The filters were operated in parallel flow and the effluent was passed through exchange beds. Three different chemical exchange beds were used in series flow: aluminum oxide,[†] chelating resin,^{††} and potassium hexacyanocobalt(II)ferrate(II).^{†††} The bed materials were contained in the filtration unit previously described⁽¹⁾ and were separated by 12 in.

* 1320 gal/min, SBN-3840B, Montgomery Ward Model

** Model 1M1 and 2278-B2 Cartridge, Cuno Engineering Co., Meridian, Connecticut.

*** Millipore No. PHWP 30500

† Alumina Woeln Neutral, Alupharm Chemicals

†† Chelex 100, 50-100 mesh, Bio Rad Laboratories

††† KCF-1, 25-50 mesh, Bio Rad Laboratories

ID plastic rings and filter paper supported on perforated stainless steel stock. The exchange beds were located in the top section of the filtration unit and flow was upward through them.

The retention of various radionuclides on the bed materials was determined by passing spiked ocean water, at the same bed velocity used in the ocean runs, through glass columns containing a bed thickness equivalent to the bed used in the ocean runs. The efficiencies of removal for the radionuclides removed by the bed materials are summarized in Table I. The soluble radionuclide fraction is estimated from these efficiencies; for example, in the case of ^{54}Mn , the soluble fraction is the amount found in the alumina bed plus 1/0.64 times the amount measured in the Chelex bed.

The radionuclides in each filter component and exchange bed were determined by multidimensional gamma-ray spectrometry.⁽¹⁾ Direct counts were made on each component of the filter system after it had been dried and compacted. Cuno filter cartridges were ashed prior to counting. The radionuclide concentrations found in each sample are given in Table II. In

TABLE I. Retention of Soluble Radionuclides from Spiked Ocean Water on Exchange Beds

Radionuclide	Percent Retained		
	Alumina	Chelex	KCF-1
^{144}Ce	91	--	--
^{106}Ru	78	--	--
^{54}Mn	--	64	--
^{60}Co	--	36	--
^{137}Cs	--	--	98

TABLE II. Radionuclide Concentrations and Percent as Particulates in Samples Collected Between Newport, Oregon and Honolulu, Hawaii

Sampling Run Number	^{54}Mn		^{60}Co		^{106}Ru		^{137}Cs Concentration (a)	^{144}Ce	
	Conc. (a)	% Part.	Conc. (a)	% Part.	Conc. (a)	% Part.		Conc. (a)	% Part.
1	6.8	26	2.1	37	170	7.8	--	640	<6.5
2	18	22	2.3	12	360	7.5	--	1300	9.5
3	9.7	20	1.5	20	230	12	--	760	11
4	7.1	24	0.53	32	240	6.2	--	780	<3.4
5	--	--	2.3	8	530	4.1	--	860	<8.1
6	16	16	1.1	18	380	6.5	1850	900	<5.3
7	--	--	0.78	19	280	5.6	--	980	<3.9
8	15	18	3.5	10	360	18	1870	1200	10
9	11	28	1.4	22	240	18	--	800	11
10	7.9	37	0.81	60	260	21	1680	860	13
11	8.0	25	1.6	34	170	19	--	730	10
12	9.1	25	1.5	32	150	15	1260	660	9.5
13	7.3	19	1.2	21	120	11	--	480	7.6
14	7.2	32	1.5	22	120	18	720	550	<5.7
15	--	--	1.1	36	100	23	580	470	14
16	--	--	0.92	28	84	22	540	410	23

(a) Concentration units = $\text{dis}/\text{min}/10^3$ liters.

that table "particulate" refers to the material retained on the prefilter and 0.3 μ membrane filters. The sampling locations are shown in Figure 1.

The concentrations of artificial radionuclides ^{54}Mn , ^{106}Ru , and ^{144}Ce increased during the early part of the cruise, then dropped off gradually after Sample No. 9 to low values near the Hawaiian Archipelago. Fallout from Chinese nuclear testing may be responsible for these fluctuations. Air samples taken concurrently⁽²⁾ during the cruise indicated an increase in airborne fallout during the early part of the cruise. The air concentrations are shown in Table III for samples taken at locations also shown on Figure 1. The concentrations of ^{60}Co fluctuate about a mean of 1.5 dis/min/ 10^3 liters. This concentration is comparable to values reported previously.⁽¹⁾

TABLE III. Radionuclide Concentrations in Air Over Ocean* Between Newport, Oregon and Hawaii

Sampling Run Number	Radionuclide Concentration, dis/min/ 10^6 ft ³ (STP)				
	^{54}Mn	^{60}Co	^{106}Ru	^{137}Cs	^{144}Ce
1	48	8.5	449	420	896
2	175	7.0	1299	1489	2704
3	133	5.0	818	657	169
4	161	6.3	898	745	1504

* Air samples collected by large volume sampler⁽²⁾ on board R/V Yaquina.

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FIGURE 1. Map of Cruise Showing Sampling Locations

NATURAL AND ARTIFICIAL RADIONUCLIDES IN FISH FLOUR

Y. M. Jones and T. M. Beasley

Fish flour samples received from the U.S. Bureau of Commercial Fisheries and Viobin Corporation, Monticello, Ill., were analyzed for measurable levels of various radionuclides. ^{210}Pb , ^{54}Mn , ^{60}Co , ^{137}Cs , ^{226}Ra , ^{228}Th , and ^{55}Fe were detected and their concentration levels established. ^{210}Pb and ^{226}Ra appear to be the only two radionuclides that occur in biologically significant quantities. The concentration levels in fish flour correspond to concentration factors over sea water of 4000 for ^{210}Pb and 230 for ^{226}Ra .

In continuing search for new food sources for an expanding world population, attention has been increasingly focused on the untapped resources of the sea. It was recently pointed out by the United Nations Food and Agricultural Organization that, although the oceans of the world are capable of sustaining a minimum annual harvest of 230 billion kilograms--an almost five-fold increase over present production rates, the world's 1970 deficit of animal protein will amount to about 6 billion kilograms.⁽¹⁾ To alleviate not only the growing shortage in the world food supply, but also to provide a relatively cheap source of animal protein, an intense research effort has been directed toward the development of a satisfactory fish protein concentrate for human consumption. The U.S. Bureau of Commercial Fisheries and Viobin Corp., of Monticello, Illinois⁽²⁾ are currently developing a flour made from whole fish. This fish flour at the present stages of development is approximately 80% protein and can serve as a protein supplement to the human diet in areas of chronic food shortages.

The fact that ocean organisms are capable of concentrating trace radionuclides by several orders of magni-

tude from ocean waters has been demonstrated by several authors. Oyster ^{65}Zn concentrations, which were about 10^5 times higher than environmental sea water, have been observed.⁽³⁾ More recent studies of ^{55}Fe in ocean salmon⁽⁴⁾ have shown concentrations of at least 10^6 above sea water levels. These same concentrations processes could cause fish flour produced from whole fish to contain significant levels of some natural and fallout radionuclides. To test this hypothesis, several different samples of fish flour were analyzed for detectable levels of various radionuclides. The radionuclides included ^{210}Pb , ^{226}Ra , ^{228}Th , ^{60}Co , ^{54}Mn , ^{137}Cs , and ^{55}Fe . The samples tested reflected various methods of processing as well as different species type and age. When a sufficient time interval had elapsed from the time of catch for equilibrium conditions to exist, ^{210}Pb concentrations were determined by alpha-energy analysis of ^{210}Po electroplated from wet-ashed samples. Levels of ^{210}Pb in fresh samples which had not reached an equilibrium condition, were determined by chemical separation of lead and low level beta counting.⁽⁵⁾ The procedure for the determination of ^{55}Fe has been outlined previously⁽⁶⁾ and involves

counting the soft 6 keV X-ray emitted from ^{55}Mn . Following ^{55}Fe decay the gamma emitting radionuclides or gamma emitting daughters of ^{226}Ra , ^{228}Th , ^{60}Co , ^{54}Mn and ^{137}Cs were determined by directly counting the dry-ashed samples on a multidimensional gamma-ray spectrometer.⁽⁷⁾ In this manner, a good estimate of ^{226}Ra was possible by determining its ^{214}Bi daughter. Similarly, ^{228}Th was determined by counting its ^{208}Tl daughter.

Salient information on specimen type and time of catch and processing when available are contained in Table I for the samples analyzed. The observed radionuclide concentrations are also included in this table along with the calculated percentage of the daily maximum permissible concentration (% MPC) of these radionuclides. Sample No. 5 was a fish protein concentrate produced by the Viobin Corporation of Monticello, Illinois. All other samples were obtained from the U.S. Bureau of Commercial Fisheries and were processed from fish caught in the Atlantic Ocean in the vicinity of Block Island.

The calculated percentage of the daily maximum allowable intake of the various radionuclides is based on allowable total body exposure levels for the nonoccupationally exposed population at large. In computing this value, we have assumed that the average daily intake of fish flour will be 30 g and that the daily MPC for fish is the same as that for water. This MPC is cited as being 1/30 of the MPC for nonoccupationally exposed individuals living in controlled areas (i.e., in the environs of a nuclear installation) which in turn is 1/10 of the limit allowed for occupational exposure.⁽⁸⁾

From the results of our initial study as listed in Table I, ^{210}Pb , ^{137}Cs , ^{54}Mn , and ^{55}Fe occur in fish flour at relatively comparable radioactive levels. However, due to its long effective half-life in the body, the average % MPC for ^{210}Pb is considerably higher. The MPC for ^{226}Ra was an order of magnitude lower than that for ^{210}Pb . Thus, while the average concentration of ^{226}Ra was found to be less than that for ^{210}Pb (0.062 dis/min/g versus 0.464 dis/min/g) its corresponding contribution to the allowable daily intake was comparable. From our cursory study, it appears, therefore, that ^{210}Pb and ^{226}Ra are the only radionuclides in fish flour which would conceivably contribute a significant fraction to the allowable daily intake of the general populace.

Using the data published in Skirrow,⁽⁹⁾ we were able to calculate a best estimate, according to available literature data, of the ^{210}Pb concentration in sea water as about 10^{-4} dis/min/g. Using this same source, the ^{226}Ra concentration was found to be 2.6×10^{-4} dis/min/g. The measured radioactive concentrations in fish flour would then correspond to concentration factors of approximately 4000 for ^{210}Pb and 230 for ^{226}Ra .

Although the ^{210}Pb and ^{226}Ra are derived from natural sources, their comparison to the MPC allowed for artificially-produced isotopes is meaningful since the activity levels in this foodstuff are at a level that would cause attention had it come from artificial sources. The implications from these measurements are therefore clear. As we turn to the ocean for more and more of our foodstuffs, the

TABLE I. Natural and Artificial Radionuclide Concentrations in Fish Flour

Sample Number	Fish Type or Process	Date of Catch	Radionuclide dis/min/g						
			²¹⁰ Pb	²²⁶ Ra	²²⁸ Th	⁶⁰ Co	⁵⁴ Mn	¹³⁷ Cs	⁵⁵ Fe
1	(b)	(July 1966) (d)	0.66						
2	(c)	(Apr. 1966) (d)	0.72						
3	Unspecified	May 1965	0.63						
4	Flounder	Feb. 1965	0.25						
5	Unspecified		0.38	0.056	0.21	0.005	0.62	0.11	10.6
6	Immature Red Hake	Aug. 1966	0.37	0.09	0.07	0.004	0.06	0.09	0.65
7	Red Hake	Jan. 1965	0.42	0.04	0.05	0.003	0.61	0.13	0.44
8	Yellowtail Flounder	Mar. 1965	0.29	0.06	0.03	--	1.14	0.24	0.26

Sample Number	Percent MPC ^(a)						
	²¹⁰ Pb	²²⁶ Ra	²²⁸ Th	⁶⁰ Co	⁵⁴ Mn	¹³⁷ Cs	⁵⁵ Fe
1	12.3						
2	13.2						
3	11.5						
4	4.5						
5	7.1	5.2	0.009	0.00009	0.00014	0.010	0.01
6	6.9	8.5	0.0003	0.00007	0.00001	0.0084	0.0006
7	7.8	3.7	0.0002	0.00006	0.00014	0.012	0.0004
8	5.4	5.5	0.0001	--	0.00026	0.022	0.00024

(a) Percent MPC Calculated for a 30 g per day Intake Using ICRP Recommendations of 1/30 MPC for Non-Occupationally Exposed Individuals.

(b) Freeze-Dried Whole Fish

(c) Same as Above but Unspecified Different Processing Method

(d) Date Processed

significance of these nuclides will become increasingly important.

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RADIONUCLIDE DISTRIBUTION IN THE OLYMPIC NATIONAL PARK ENVIRONMENT

N. A. Wogman, H. G. Rieck, and R. W. Perkins

An initial survey of the environmental radionuclide distribution in soils, stream sediments, flora, fauna, the atmosphere, and rainwater has been conducted in the Olympic National Park. This is a unique area with a rainfall of about 100 to 200 inches per year. This high rainfall rate brings a high washout of airborne radioactivity, which results in high radionuclide concentrations in the ecosystem. The concentrations of 23 radionuclides throughout this ecosystem have been studied. Most of these are determined by direct instrumental analysis, while a few require radiochemical separations. The radionuclide concentrations in Olympic National Park lichen are about three-fold higher than those in the Alaskan lichen; however, this does not result in as high a concentration in the elk from the Olympic National Park as has been observed in caribou from Alaska. The reason for this appears to be the fact that lichen are a minor part of the elk diet in this area while they are a major part of the diet for the Alaskan caribou. The deposition of 17 radionuclides in the various organs of elk and deer from the Olympic Peninsula have been measured and they define the concentration factors of these radionuclides in this ecosystem.

An initial survey of the environmental radionuclide distribution in the soils, glacial and nonglacial streams, fauna, flora, the atmosphere, and precipitation has been conducted on the Olympic Peninsula (Washington State). This is a unique area with an annual rainfall rate which varies from 40 to 200 inches in a distance of less than 50 miles. The concentrations of over 23 fallout radionuclides--including ^7Be , ^{22}Na , ^{40}K , ^{54}Mn , ^{55}Fe , ^{60}Co , ^{65}Zn , ^{95}Zr , ^{95}Nb , ^{103}Ru , ^{106}Ru , $^{110\text{m}}\text{Ag}$, ^{125}Sb , ^{134}Cs , ^{137}Cs , ^{150}Ba , ^{140}La , ^{144}Ce ,

^{207}Bi , ^{208}Tl , ^{210}Pb , ^{210}Po , and ^{214}Bi --are being studied to better understand their normal distributions and their subsequent redistribution in areas of high rainfall. Most of these radionuclides are being determined by direct counting on multidimensional gamma-ray spectrometers⁽¹⁾ while others, including ^{55}Fe , ^{210}Pb , and ^{210}Po , are being determined by X-ray spectrometry and radiochemical techniques. In all, more than 60 samples were collected for gamma or X-ray spectrum analysis. Although this initial study in itself

is very significant, it represents only the first samples to be taken throughout the year and an extensive interpretation of the data will not be attempted until samples collected during a full calendar year have been analyzed.

In Table I the concentrations of seventeen radionuclides in the plant life on the Olympic Peninsula are compared. The data show that while the ^{40}K remains relatively constant, the uptake of ^{137}Cs varies over two orders of magnitude. The short-lived isotopes which have resulted from nuclear weapons testing such as ^{140}Ba (12.8 days) and ^{95}Zr (65 days) reflect the recent air radionuclide concentrations while the long-lived radionuclide concentrations are the result of accumulation over several years. The mosses and lichens, as in Alaska,⁽²⁾ contain the highest concentrations of the radionuclides. The radionuclide ^{207}Bi was measured in only one sample because other interfering radionuclides prevented a direct instrumental analysis.

Table II compares the air, the rain, and the lichen radionuclides concentrations in the Olympic National Park to radionuclide concentrations in lichens from Alaska. The Olympic National Park samples were taken about 2 years later than the Alaskan samples, yet the ^{137}Cs concentrations were three times higher than the unusually high values found in Alaskan lichens. The Alaskan lichens are the first link in the food chain which leads to ^{137}Cs concentrations in Alaskan natives of one hundred fold higher than in residents of the other continental forty-

eight states. A typical Olympic Rain Forest lichen, *Lobaria Oregana*, had a ^{137}Cs concentration of 44,800 dis/min/g while the concentration in a moss, *Selagenella Serpens*, was 57,800 dis/min/kg. These plants, due to their slow growth rate and unique physical characteristics, contain the highest quantity of fallout. At the time these samples were taken, one kilogram of lichen had a ^{137}Cs content equal to that in about 10^9 ft^3 of air or 10^5 liters of rain water. The average ^{134}Cs -to- ^{137}Cs ratio in the lichens and mosses was 0.0010 which is equal to the values found in Alaskan caribou flesh in January 1965. All of the shorter-lived and a significant fraction of the long-lived radionuclides, particularly in the atmosphere, resulted from nuclear testing by the Chinese on Oct. 16, 1964; May 14, 1965; May 9, 1966; Oct. 27, 1966; and Dec. 27, 1966.

The deposition behavior of seventeen of these radionuclides was determined in samples of deer and elk obtained from the Olympic Peninsula. The radionuclide concentrations observed in the various organs of these animals are summarized in Table III, and are generally one-half to one-quarter of the values found during 1963 through 1965 in Alaskan caribou.^(2,3) This probably results from the dilution of the lichen ^{137}Cs by grasses, leaves, and other browse which serve as the diet for the Olympic elk. The Alaskan caribou feeds primarily on lichens during the winter months. The ^{22}Na concentrations are comparable to those found in lichens, and the ^{22}Na -to- ^{137}Cs ratio is several

Sample Type	Collection Date	Area	Concentration, dis/min/kg wet weight																	
			⁷ Be	²² Na	⁴⁰ K	⁵⁴ Mn	⁶⁰ Co	⁶⁵ Zn	⁹⁵ Zr- ⁹⁵ Nb	¹⁰³ Ru	¹⁰⁶ Ru	^{110m} Ag	¹²⁵ Sb	¹³⁴ Cs	¹³⁷ Cs	¹⁴⁰ Ba- ¹⁴⁰ La	¹⁴⁴ Ce	²²⁶ Ra	²³² Th	²⁰⁷ Bi
Lichen-Lobaria Oregana	9-14-66	(c)		7.9	5630	1060	133	49.2	1550		6950	5.8	4000	42	44800	14	11800	66	7.5	
Moss-Selagenella Serpens	9-14-66	(c)		14.3	6470	3530	321	103.0	1110		12800	8.0	15000	72	57800		28400	77	34	
Horsetail Fern - Equisetum Arvense	9-14-66	(c)	3860	2.1	5250		2		530	110	120	1.2			338	4	314	9.3	7.7	
Salmonberry - Rubus Spectabilis (Leaf)	9-14-66	(c)	9000	3.5	6940	725	6.9	14.2	3950	400	375	1.5	400		2070	36	1510	18	8.1	
Fern	9-14-66	(c)		4.8	8690	390	3.4	10.0	800	370	280			11	14900	16	6120	65	20	
Assorted Meadow Grasses	9-14-66	(c)	4830	5.0	5370	861	4.7	5.0	380		249	0.7			3100	6	712	11	1.9	
Assorted Evergreen Tips	9-14-66	(d)		0.67	4840	434	7.9	21.0	667	300	180		390		2610	0.5	813	12	3.5	
Moss-Sphagnum - Downed Log	9-14-66	(d)		7.4	2070	4280	254	34.0	1180		13000	11.0	10600	54	57500		30300	61	46	
Maple Leaf	9-14-66	(d)	6300	1.0	5300	240	7.0	8.1	2350	250	308				1650	22	1170	13	5	
Alder Leaf	9-15-66	(e)	2700	0.50	3600	167	2.2	2.5	415	100	94	0.2	94		672	6	355	9.6	4	
Fern ^(a)	9-15-66	(e)		2.2	8690	310	9.4	6.5	490		268	0.9	260		2520		1840	24	16	
Assorted Grasses ^(a)	9-15-66	(e)	1390	5.8	6320	257	4.3	5.5	263	110	184		203		967		500	36	25	
Moss-Selagenella Serpens ^(a)	9-15-66	(e)		7.5	5940	2880	237	20.0	778		12200		13600	60	49700		19700	375	423	
Assorted Evergreen Tips ^(b)	9-16-66	(f)		2.2	3580	1270	25	8.0	979		1420	1.7	1300	6.3	9930	2	6500	16	23	
Assorted Grasses ^(b)	9-16-66	(f)	2300	4.3	7320	508	5.8	5.1	371	130	180		190		2010	8	2070	14	19	
Moss-Sphagnum ^(a)	9-16-66	(f)		3.8	1800	2250	117	23.0	332		5694	4.2	5560	24	26600		13900	33	34	17
Fungus-Log	9-16-66	(f)		0.1	5160	26	1.3		27.5		69			2.2	4600		165		3	

(a) Sample obtained under heavy tree cover.

(b) No overhead.

(c) Sample taken at or within 100 yards of elk forage plot number three, Olympic National Park, Washington, upper Hoh River Campground.

(d) 0.87 mile inside Olympic National Park boundary on Hoh River.

(e) 2.9 miles east on the Queets River from the Olympic National Park boundary.

(f) 0.9 mile upstream from Queets River-Clearwater River junction.

TABLE I. Radionuclides in Flora From the Olympic National Park Ecosystem

TABLE II. Comparison of Radionuclide Concentrations in Air, Rainwater, and Lichen in the Olympic National Park and Alaska

Radionuclide	Half-life	10^6 ft^3 of air ^(a)	10^3 liters of rainwater ^(b)	ONP ^(c)	Alaska ^(d)	Alaska ^(e)
^7Be	53 d	1583	22400			
^{22}Na	2.60 yr			7.9	21	33
^{40}K	1.3×10^9 yr			5630	1070	560
^{54}Mn	312 d			1060	4180	5130
^{60}Co	5.24 yr	1.1	19.4	133	85	92
^{65}Zn	243 d			492		
^{95}Zr - ^{95}Nb	65 d	194	2140	1550	975	560
^{103}Ru	40 d	218	4127		3	
^{106}Ru	1 yr	34	560	6950	12400	14900
$^{110\text{m}}\text{Ag}$	260 d	4.2	3.3	5.8	12	7.6
^{125}Sb	2.7 yr		303	4000	3830	4990
^{134}Cs	2.1 yr			42	50	38
^{137}Cs	30 yr	34.0	567	44800	13700	18100
^{140}Ba	12.8 d	42.2	6430	7.1		
^{144}Ce	285 d	880	3360	11800	35300	35000
^{226}Ra	1620 yr		10	66	26	35
^{232}Th	1.39×10^{10} yr	6.6	4.0	7.5	15	15

(a) Sample obtained 1-5-67 to 1-19-67.

(b) Sample obtained 11-15-66.

(c) Sample obtained 9-14-66 in the Olympic National Park (ONP).

(d) Sample *Cladonia* spp-*Cetraria* spp obtained 10-15-64.

(e) Sample *Cetraria Cuculata* and *Cetrarin Islandica* obtained 1-19-65.

fold lower than the ratios observed in Alaskan animal tissue.^(2,3) The reason for their difference is not immediately clear. The concentrations of most of the radionuclides in the tissues of the elk and deer were lower than those of the mosses and lichens; however, the ^{54}Mn , ^{60}Co , and ^{65}Zn are concentrated in the bone about 10 to 30 fold more than in soft tissues and exceed the concentrations in much of the vegetation. The average ^{134}Cs -

to- ^{137}Cs ratio in the soft tissues is about 0.001 for both the elk and deer and is in agreement with the value of 0.001 found in the lichens and mosses.

In addition to the radionuclides which can be determined by instrumental analysis, some others require chemical separations. These have included ^{210}Pb and ^{210}Po , which are deposited from the atmosphere as a result of radon decay, and ^{55}Fe , the decay of which involves only the emission of a

Sample Type	Collection Date	Concentration, dis/min/kg wet weight																
		⁷ Be	²² Na	⁴⁰ K	⁵⁴ Mn	⁶⁰ Co	⁶⁵ Zn	⁹⁵ Zr- ⁹⁵ Nb	¹⁰³ Ru	¹⁰⁶ Ru	^{110m} Ag	¹²⁵ Sb	¹³⁴ Cs	¹³⁷ Cs	¹⁴⁰ Ba	¹⁴⁴ Ce	²²⁶ Ra	²³² Th
Elk (a)																		
Pancreas	11-15-66		28.8	4060	29.2	0.49							6.4	6120	36	173		3
Heart	11-15-66		21.1	4689		1.6							6.2	6730	8	168		2
Thyroid	11-15-66		24.3	3010	34.2	4.4	18	44					3	3480	52			
Liver	11-15-66		22	3660	8.4	6.8	9			14	2.5		6.9	7460	20	321		5
Kidney	11-15-66		37	4110		3.2							10.8	10700	42	173		16
Lung	11-15-66		32	3320		0.6							3	3950	26	283		3
Muscle																		
Shoulder	11-15-66		7.6	5500		0.3				13	0.03		6.1	8230	5	721		0.6
Fat																		
Internal Area	11-15-66		9.65	1920	19	0.5	32	30		7.9			2.72	2960	39	121		2
Fat																		
Muscle Area	11-15-66		9.44	930	38	1.3	10	210		30			1.10	2100	490	91	3.4	
Leg Bone	11-15-66		69.6	1240	129	108	286	150	241	12		644		1460	578		310	360
Hide	11-15-66	720	23.5	2247		0.76		181		27	0.3		2.32	2670	484	207		3.2
Stomach																		
Content	11-15-66	2000	43.3	3830	739	4.38		1950	1490	197	0.7		5.75	6298	5700	2129	56	22
Deer (b)																		
Shoulder																		
Muscle	11-10-66		13.3	5800		0.1							1.3	3750		174		0.4
Neck																		
Muscle	11-10-66		11.5	5770		0.3							1.5	3490		227		2.6
Shoulder																		
Bone	11-10-66		74.6	4150	140		312	265	598			735		2130			400	227
Hide	11-10-66		12.5	3450		0.34		197					1.5	2190	460	107		3.7
Stomach																		
Content (c)	11-10-66	1790	33.4	3100	213	1.5		69		35				1290		206	20	10

(a) Sample obtained 1.5 miles east of U.S. 101 on the Hoh River road in the Olympic Forest.

(b) Sample obtained near Aberdeen, Washington.

(c) The stomach content was mainly apples.

TABLE III. Radionuclides in Elk and Deer Samples from the Olympic Peninsula

weak X ray. In Table IV the concentrations of these three radionuclides on lichen and moss samples are compared. In addition the ^{55}Fe concentrations are included for a few materials from this area. The lichen from the Olympic National Park is about one-third as high in ^{55}Fe and ^{210}Pb - ^{210}Po as the moss. The ^{210}Pb and ^{210}Po concentrations in the Olympic National Park lichen and mosses are about one-third of those in Alaskan lichen. The iron shows a wide variation in concentration on the vegetation increasing by about 200-fold in going from meadow grass to moss samples. Tables V and VI show the radionuclide concentrations in river water and suspended sediments and in bottom sediments in the Olympic Na-

tional Park. In Table V the radionuclides held on a $0.3\ \mu$ membrane filter are compared with those passed through the filter for river samples from various locations.

While the concentrations in the particulate form represent good determinations, the concentrations in the solution must be considered tentative because of the small size of sample and other problems encountered in these initial measurements. These do indicate the approximate concentrations and problems associated with their measurement. This present sampling program was started during the end of the dry season at the Olympic National Park. Studies throughout a calendar year will be required to determine seasonal variations in radionuclide behavior. The

TABLE IV. ^{55}Fe , ^{210}Pb , and ^{210}Po Concentrations in Selected Olympic National Park Samples

Sample Type	Collection Date	Concentration dis/min/kg wet weight		
		^{55}Fe	^{210}Pb	^{210}Po
Lichen Lobaria Oregana(a)	9-14-66	24400	6620	2950
Moss-Selagenella Serpens(a)	9-14-66	66600	28600	14500
Assorted Meadow Grasses(a)	9-14-66	377		
Moss-Sphagnum(b)	9-14-66	45500		
Maple Leaf(b)	9-14-66	1220		
Evergreen Tips(b)	9-14-66	1110		
Elk Heart(c)	11-15-66	9990		
Elk Liver(c)	11-15-66	18900		

(a) Samples taken within 100 yards of elk forage plot number three, Hoh River Campground.

(b) Samples taken 0.87 mile inside the Olympic National Park boundary on the Hoh River.

(c) Samples obtained 1.5 miles east of U.S. 101 on the Hoh River road in the Olympic National Forest.

TABLE V. Radionuclides in Suspended River Water Sediments and in Solutions on the Olympic Peninsula September 14-16, 1966

Radionuclide	Concentration, dis/min/10 ⁵ liters									
	Particulate >0.3 μ					Soluble <0.3 μ				
	(a)	(b)	(c)	(d)	(e)	(a)	(b)	(c)	(d)	(e)
⁷ Be									94	
²² Na	0.01			0.15	0.34	4.5	0.04	9.0	6.0	8.0
⁴⁰ K	89	11	86	71		250		850	320	500
⁵⁴ Mn	3.4	0.46		0.8	5.0	20		50		25
⁶⁰ Co	1.15	0.27	1.24	0.6	6.6	8.0	1	20	2	3
⁶⁵ Zn	2	0.3			15	400		500	200	500
⁹⁵ Zr- ⁹⁵ Nb	5.8	0.57	6.6	5.7	11.5	40	4	120	40	100
¹⁰⁶ Ru	30.8	2.6	40.9	13.1	32.6	340	80	440	400	500
¹²⁵ Sb	27		17.8	30.9	88.4	30				
¹³⁴ Cs	0.1									
¹³⁷ Cs	51	3.2	37.8	8.1	7.9	10		10	10	13
¹⁴⁴ Ce	36.7	8.3	140		51					
²²⁶ Ra	5.0	1.9	7.4	5.6	1.6	8	24	48	48	120
²³² Th	6.5	1.9	5.3	5.4	3.6	9				

- (a) Sample taken from the Hoh River, 0.87 mile inside the Olympic National Park boundary, 9-14-66; 432 gallons.
- (b) Sample taken from a tributary creek to the Hoh River, 1.87 miles west of the Olympic National Park boundary, 9-14-66; 1028 gallons.
- (c) Samples taken from the Hoh River near the old Oil City-Hoh River Bridge. Slight precipitation the evening of 9-14-66 and during the sample time of 9-15-66; 164 gallons.
- (d) Sample taken from the Queets River, 5.9 miles east from the Olympic National Park boundary. Precipitation during the sample on 9-15-66; 216 gallons.
- (e) Sample taken from the Clearwater River, 0.9 mile upstream from the Queets-Clearwater River junction on 9-16-66. Heavy logging operations upstream created some pollution of the river; 93 gallons.

area does provide an excellent outdoor ecological laboratory and it is planned to make a detailed study including meteorological, biophysical, and biological factors affecting the initial deposition and recycling of radionuclides. Such a comprehensive study would make it possible to predict the behavior in other areas where nuclear excavation debris may be deposited.

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TABLE VI. Radionuclide Concentrations in River Bottom Sediments on the Olympic Peninsula September 14-16, 1966

Radionuclide	Concentration, dis/min/kg dry weight				
	(a)	(b)	(c)	(d)	(e)
^{40}K	19600	22900	16900	21800	19300
^{54}Mn	39	39	23	16	
^{60}Co	3	2.4	2.9	4.6	6.0
^{106}Ru	450	235	215	290	370
^{137}Cs	750	910	335	697	1380
^{140}Ba	180	190	210	230	220
^{226}Ra	1120	1380	1060	1340	1360
^{232}Th	1250	1460	1000	1770	1610

(a) Sample taken from the Hoh River, 0.87 mile inside the Olympic National Park boundary.

(b) Sample taken from a tributary creek to the Hoh River, 1.87 miles west of the Olympic National Park boundary.

(c) Sample taken from the Hoh River, near the old Oil City-Hoh River Bridge.

(d) Sample taken from the Queets River, 2.9 miles east from the Olympic National Park boundary.

(e) Sample taken from the Clearwater River, 0.9 mile upstream from the Queets-Clearwater River Junction.

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PHYSICAL AND CHEMICAL FORMS OF COLUMBIA RIVER
RADIONUCLIDES DURING AN EXTENDED REACTOR OUTAGE

C. W. Thomas

On July 7, 1966, operation of all Hanford reactors was suspended for a period of 48 days marking the first time for such an outage. During this period the amount of Columbia River water used as a coolant for the reactors was reduced to about 20% of the normal value and only small amounts of radionuclides entered the river from erosion of isotopes in the reactor piping and storage basins. Mass balance studies showed that the main source of radionuclides in river water was erosion and dissolution of the river bottom sediments. This source contributed 42 to 91% of the radionuclides in the river. Ion exchange studies of Columbia River water radionuclides during this period indicated that a larger than normal fraction of the radionuclides was associated with particulate material. Of the fraction in solution a larger percentage showed nonionic characteristics. During the period when the amount of suspended sediment was at a minimum in the river, a much smaller fraction of the radionuclides was associated with particulates.

On July 7, 1966, operation of all Hanford reactors was suspended for a period of 48 days marking the first time for such an outage. During this period the amount of Columbia River water used as a coolant for the reactors was reduced to about 20 percent of the normal value, and the radionuclides entering this water resulted entirely from erosion of isotopes in the reactor piping and storage basins.

The reactor outage presented a unique opportunity to study the physical and chemical forms of the Columbia River radionuclides; the main source of activity was the river bottom sediments. Mass balance studies showed that 42 to 91% of the radionuclide concentration in the river was due to erosion and dissolution from river bottom sediments. Shortly after shutdown a series of Columbia River and reactor effluent samples was taken below and above the reactors using a filtration-sorption assembly which removed particulates down to 0.3 μ in size by membrane filtration and then removed dissolved salts on a cation-

anion exchange assembly. Radionuclides passing through the filter were considered to be in solution, and those passing through the cation and anion exchange beds were considered to be uncharged or neutral. The material removal by ion exchange beds represents the ionic species of the radionuclide plus some of the less than 0.3 μ particles entrapped by the beds. The observed concentrations of the radionuclides ^{46}Sc , ^{51}Cr , ^{54}Mn , ^{60}Co , ^{65}Zn , and ^{124}Sb in the Columbia River samples taken below the reactors at a position just above McNary Dam are shown in Table I and are compared with 1965 measurements⁽¹⁾ when the reactors were in operation. The data show that ^{46}Sc is mainly in the particulate form with a much smaller fraction of the ionic species held by the anion bed than during the 1965 measurements. Also, a much larger percentage of the soluble fraction was unchanged (not ion exchangeable). ^{51}Cr was much more strongly associated with particulates during this study and more of the soluble species were unchanged. ^{54}Mn ,

TABLE I. Forms of Radionuclides in Columbia River at McNary Dam

Radionuclide	Sample Date	Percent Particulate	Percent in Solution		
			Cationic	Anionic	Neutral
^{46}Sc	1965	90	14	79	7
	7-15-66	96	27	21	52
	7-18-66	96	33	19	48
	7-20-66	97	20	29	51
	8-02-66	96	26	20	54
	8-11-66	97	42	35	23
^{51}Cr	1965	7	3	93	3
	7-15-66	65	0	100	0
	7-18-66	59	2	88	12
	7-12-66	57	1	80	20
	8-02-66	25	0	94	6
	8-11-66	0	1	100	0
^{54}Mn	1965	70	95	2	3
	7-15-66	52	81	2	17
	7-18-66	53	90	1	9
	7-20-66	60	72	1	27
	8-02-66	95	91	2	7
	8-11-66	96	82	3	15
^{60}Co	1965	63	91	4	5
	7-15-66	13	1	6	93
	7-18-66	62	81	2	17
	7-20-66	65	57	3	40
	8-02-66	79	45	15	40
	8-11-66	78	31	16	53
^{65}Zn	1965	77	98	1	1
	7-15-66	82	53	5	42
	7-18-66	87	61	2	37
	7-20-66	88	44	2	54
	8-02-66	88	25	4	71
	8-11-66	89	27	8	65
^{124}Sb	1965	2	0	22	78
	7-15-66	89	4	16	80
	7-18-66	53	2	5	93
	7-20-66	46	0	4	96
	8-02-66	25	0	15	85
	8-11-66	24	3	13	84

^{60}Co , and ^{65}Zn were predominantly particulate as was the case in the 1965 study. The soluble fraction for these three radionuclides was less in the cation fraction and more in the uncharged fraction than in 1965.

^{124}Sb was associated much more with particulates during this period than in 1965. In general the results indicated that a larger percentage of radionuclides was associated with

particulate material with a larger fraction of the soluble species in the uncharged form. This suggests that the erosion of bottom sediments was releasing particulates and uncharged soluble material into the river.

Studies, similar to those made on the Columbia River water, were made of the physical and chemical form for the radionuclides in the coolant streams from each of the reactors.

The results from these studies for the radionuclides ^{46}Sc , ^{51}Cr , ^{54}Mn , ^{58}Co , ^{60}Co , ^{65}Zn , ^{95}Zr - ^{95}Nb , ^{124}Sb , ^{137}Cs , and ^{140}Ba are presented in Table II.

With the exception of ^{46}Sc and ^{95}Zr - ^{95}Nb in the reactor effluent water of B, C, and KW reactors, the radionuclides during this period were mostly

TABLE II. Forms of Radionuclides in Reactor Effluent Water During Reactor Shutdown (Samples Collected 7-19-67)

Radionuclide	Form	Percent in Form From Reactor			
		B	C	D	KW
^{46}Sc	Particulate	91	78	82	61
	Cationic	42	39	28	34
	Anionic	14	39	45	11
	Neutral	44	22	27	55
^{51}Cr	Particulate	0	23	0	69
	Cationic	0	0	6	4
	Anionic	95	72	91	96
	Neutral	5	28	5	0
^{54}Mn	Particulate	0	0	94	0
	Cationic	100	43	10	100
	Anionic	0	12	2	0
	Neutral	0	45	88	0
^{58}Co	Particulate	3	10	74	0
	Cationic	99	51	56	94
	Anionic	0	9	16	0
	Neutral	1	40	28	6
^{60}Co	Particulate	6	4	86	5
	Cationic	98	45	51	87
	Anionic	1	11	19	5
	Neutral	1	44	50	8
^{65}Zn	Particulate	11	4	38	6
	Cationic	97	43	62	76
	Anionic	1	10	21	2
	Neutral	2	47	17	22
$^{95}\text{Zr-Nb}$	Particulate	--	100	95	92
	Cationic	--	--	0	0
	Anionic	--	--	20	60
	Neutral	--	--	80	40
^{124}Sb	Particulate	0	11	0	0
	Cationic	5	0	4	0
	Anionic	62	56	77	84
	Neutral	55	44	19	16
^{137}Cs	Particulate	0	0	0	0
	Cationic	100	71	78	100
	Anionic	0	0	0	0
	Neutral	0	29	22	0
^{140}Ba	Particulate	0	0	0	0
	Cationic	97	34	63	56
	Anionic	0	10	14	44
	Neutral	5	56	23	0

in a soluble form. The effluent from D reactor contained more radionuclides in the particulate fraction than the other reactors, but this may simply have been due to greater erosion of particulate from this reactor. The cationic, anionic, and neutral fractions were similar to those observed in earlier studies made in 1965.⁽¹⁾

The radionuclides in the Columbia River above the reactors are from fallout produced by weapons testing or from cosmic ray spallation processes with spectrum and concentrations different from those produced in the coolant water of the Hanford reactors. The more abundant radionuclides such

as ^{106}Ru , ^{22}Na , ^7Be , ^{40}K , and ^{95}Zr - ^{95}Nb in the Columbia River above the reactors appear as very minor constituents in the mixture present below the reactors, and the radionuclides of major importance such as ^{65}Zn , ^{60}Co , ^{51}Cr , and ^{46}Sc , produced by the reactors and present in water below the reactors, are either not present or are just barely detectable in the water above the reactors (see Table III).

A direct comparison of physical and chemical forms of these two types radionuclides is difficult. One major difference in radionuclide forms above and below the reactors was the degree

TABLE III. Forms of Radionuclides in the Columbia River Above Reactors (Vernita Ferry)

Radionuclide	Percent Particulate	Percent in Solution		
		Cationic	Anionic	Neutral
^7Be	55	9	13	78
^{22}Na	10	91	1	8
^{40}K	7	85	0	15
^{54}Mn	11	96	2	2
^{60}Co	14	14	3	85
^{65}Zn (a)	7	59	4	37
$^{95}\text{Zr-Nb}$	79	4	67	29
^{103}Ru	55	5	61	34
^{106}Ru	9	3	32	65
^{125}Sb	2	0	14	86
^{137}Cs	9	94	4	2
^{140}Ba	8	13	7	80
^{141}Ce (a)	95	22	25	55
^{226}Ra	10	82	4	14

(a) Values are only approximate since activity levels were only just above the detection limit.

of association with particulates. Most of the radionuclides in the water above the reactors were not in or on particulates. At McNary Dam downstream from the reactors and at the confluence with the more turbid Snake River, the water purity was much lower and the radionuclides were largely associated with particulates. ^{95}Zr - ^{95}Nb , ^{141}Ce and, to a lesser extent, ^7Be and ^{103}Ru were exceptions. Of the soluble fraction in the water above the reactors, ^{24}Na , ^{40}K , ^{54}Mn , ^{137}Cs , and ^{226}Ra were mostly cationic while ^{95}Zr - ^{95}Nb and

^{103}Ru were anionic; ^7Be , ^{60}Co , ^{106}Ru , ^{125}Sb , and ^{140}Ba were in the fraction that was uncharged.

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AIRBORNE RADIONUCLIDES NEAR EFFLUENT BASINS

C. W. Thomas

Many radionuclides become airborne during normal operation of nuclear reactors. These include both reactive and nonreactive gases as well as aerosols. In the Hanford reactors near Richland, Washington, Columbia River water is used on a once-through basis as a reactor coolant. This water is retained in cooling basins for a few hours prior to its release to the river. Under operating conditions, purified Columbia River water enters the reactor cooling lines at river water temperatures and during the process of cooling the reactors, the water temperature increases to near boiling. Upon entrance to the retention basins many of the dissolved gases escape. The radionuclides previously known to be present in the released gases were short half-life activation products of nitrogen, oxygen, noble gases, etc. Preliminary

air sampling studies near these effluent water basins have shown that not only the gaseous radionuclides but also relatively large amounts of solid radionuclides from the effluent water basins become airborne.

Although the air concentrations of these radionuclides are extremely small, they are of unique interest because of the mechanism by which they became airborne. Measurements of desert grass samples taken around the basins indicate the build-up of some of the long-lived radionuclides associated with basin fallout debris. Air samples of the basin off-gases were taken, using portable vacuum pumps equipped with membrane filters, at distances out to 1000 yards. Solid radionuclides including manganese, sodium, zinc, copper, chromium, arsenic, lanthanum, scandium, cobalt,

and also ^{139}Ba and ^{138}Cs were collected on these filters. The radioactive nitrogen, oxygen, iodine, chlorine, and other noble gases were not held up on the membrane filter material and were not studied in this initial work. The filters were pressed into standard counting geometries and the radionuclides were determined using an anticoincidence-shielded multidimensional gamma-ray spectrometer. The ratio of the concentrations of the solid radionuclides in the air to those in the basin water showed extensive fractionation. The ratios of these concentrations normalized to 1 for ^{24}Na are presented in the Table I. The reason for the high enrichment in air of several solid radionuclides relative to ^{24}Na and ^{56}Mn is not known. None of these radionuclides has a gaseous precursor except ^{140}La , and its formation from its grandparent ^{140}Xe in the atmosphere would have required the presence also of its parent ^{140}Ba in the sample. The relatively high concentrations of ^{46}Sc and ^{60}Co

TABLE I. Ratios of the Reactor Effluent Water Radionuclide Concentrations in Air to the Concentrations in Water Normalized to 1 for ^{24}Na

Radionuclide	Normalized Ratio Air/Water
^{24}Na	1.0
^{46}Sc	360
^{51}Cr	41
^{56}Mn	0.4
^{60}Co	600
^{64}Cu	40
^{65}Zn	16
^{76}As	5.0
^{140}La	160

which become airborne may explain the presence of these radionuclides on local air filters in amounts greater than expected from nuclear weapons fallout.

Additional studies are required not only to verify these enrichment factors but to determine chemical forms of the radionuclides, the rate of release, and the fates after entering the atmosphere.

FURTHER STUDIES OF THE CHEMICAL NATURE OF RADIONUCLIDES RETAINED BY COLUMBIA RIVER BOTTOM SEDIMENTS

J. L. Nelson and V. W. Thomas

In a previous report⁽¹⁾ we described a procedure attempting to separate the radionuclides held by Columbia River bottom sediments into fractions such as exchangeable, acid soluble, organic, and reducible forms. A series of equilibrium extractions started with

neutral normal ammonium acetate to remove the exchangeable ions, then a density gradient separation of organics with bromoethanol was applied. The sediment was then treated with H_2O_2 , to destroy remaining organic material in the presence of ammonium acetate

to prevent resorption of nuclides onto inorganic particles. This was followed by a reduction with sodium dithionite with citrate present to complex iron, etc., and finally, 0.1N HCl was used to extract acid-soluble forms.

In checking some parts of the procedure, it has been found that about 99% of the ^{60}Co , ^{65}Zn , ^{54}Mn , and ^{51}Cr are in solution in the bromoethanol "organic" fraction as determined by filtration through 0.1 μ Millipore filter, instead of in particulate form as it had been presumed to be. Thus the bromoethanol is dissolving the nuclides and acting as an extracting agent. For example, it has been observed that bromoethanol will dissolve or complex and remove nearly 100% of the ^{54}Mn in sediment. Other gradient density agents have recently been suggested⁽²⁾ which are supposed to be more inert to river sediments and these will be investigated.

Other tests indicated that it was not necessary to have ammonium acetate present with the hydrogen peroxide and indeed, more radionuclides were extracted in this stage without it. However, the citrate was found to be necessary for extraction with sodium dithionite. It appears that the citrate complexes with and removes some ions per se.

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EFFECTS OF SHUTDOWN OF THE HANFORD REACTORS ON RADIONUCLIDES IN BOTTOM SEDIMENTS OF THE COLUMBIA RIVER

J. L. Nelson

As reactor effluent radionuclides move down the Columbia River, a major portion of most of radionuclide species is removed from the water by attachment to sediment and biota and finds its way into bottom sediment of the river. It has been reported⁽¹⁾ that an inventory of about ten to forty thousand curies of radionuclides reside in the river bed from Pasco to

Vancouver, Washington. The distribution of these radionuclides with depth in the sediment in sedimenting areas is mostly a function of half life since reactor releases and deposition have been relatively constant.

The shutdown of all of the Hanford reactors during most of July and August 1966 provided the first opportunity to note the effects of a major change in

the pattern of steady additions to the river and thus to the sediment. Analytical data for water and suspended sediment samples from the Columbia River during the shutdown period indicated that, immediately following the shutdown, transport rates of radionuclides were higher at downstream points than could be accounted for from the reduced flow of reactor coolant plus fallout isotopes found to be in the river above the reactors.⁽²⁾ The obvious inference is that this excess activity was leached or bled from bottom sediments and biota.

Core samples were taken during the period of the shutdown to see if any leaching could be measured in a direct manner. These cores were all taken at the same site near a buoy about 1,000 yards upstream from McNary Dam. This site has been shown to be a major sediment deposition area probably

during all parts of the year.⁽³⁾ The cores were frozen, sliced into 0.5 to 1.0 in. slices, dried, and counted for gamma emitters. The data are plotted versus depth on semilogarithmic paper in Figures 1, 2, 3, 4, and 5.

The radionuclide concentrations in the top three, 1/2 in. sections of the core taken on August 22 show a definite decrease from those taken in July. The flattening of all of the curves for the top of the cores has been noted previously during this time of the year and is believed to be due to rapid deposition of sediments of relatively low activity during the spring period of high water and high suspended sediment.⁽³⁾ Deeper parts of the cores are not significantly different from each other.

The decrease in radionuclide content in the sediment surface samples during the reactor shutdown could be

FIGURE 1. ⁶⁵Zn Activity in McNary Cores

FIGURE 2. ^{46}Sc Activity in McNary Cores

due to any or all of three phenomena: (1) radioactive decay of previously deposited nuclides, (2) deposition on the sediment surface of relatively low-level silt, or (3) leaching of radionuclides from the sediment by the river water, probably by a slow hydrolysis.

The degree of decrease of activity in the top layers during the shutdown is somewhat a function of half life as would be expected, but is too large for decay to be the sole contributor to

the loss of activity. It can be calculated that approximately 80% of the decrease is accounted for by decay in the case of ^{51}Cr and ^{46}Sc , but only about 50% of the decrease for ^{65}Zn , and 25% of the decrease for ^{54}Mn and ^{60}Co . Previous studies⁽⁴⁾ have indicated that ^{51}Cr and ^{46}Sc are held more tightly to sediment than are the other three radionuclides, probably due to their trivalent form as compared to the divalent form of the other three nuclides. This evidence suggests that amounts of radionuclides

FIGURE 3. ^{51}Cr Activity in McNary Cores

are leached from the river bed sediments over a period of time in a way related to the ionic attraction with which they are held by the sediment.

It is hoped that this shutdown was of sufficient duration and had sufficient effect to provide a "dating layer" of decreased radioisotope content in the sediment for reference use in future years.

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FIGURE 4. ^{54}Mn Activity in McNary Cores

FIGURE 5. ^{60}Co Activity in McNary Cores

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EFFECTS OF SHUTDOWN OF THE HANFORD REACTORS
ON RADIONUCLIDE TRANSPORT IN THE COLUMBIA RIVER

J. L. Nelson and W. L. Haushild

As a part of a larger study of the behavior of radionuclides in the Columbia River, Battelle-Northwest and the U. S. Geological Survey have cooperatively obtained and analyzed samples of Columbia River water and sediment since 1963. Samples have been taken at Pasco and Vancouver, Washington, about every other day and composited for two weeks. During most of 1965 and 1966, similar samples were also obtained at Umatilla, Oregon. To follow the effects of shutdown of the reactor during July and August 1966 on the river environment, the sampling was increased considerably, especially just after the shutdown and the startup.

Radionuclides being transported in the Columbia River during a period of shutdown of all of the Hanford reactors could come from three sources: (1) fallout isotopes coming downstream from above the reactors, (2) cooling water still being passed through the reactors, and (3) releases from the sediment and biota of the river bed.

Radionuclide data on a sample of river water obtained at Vernita (above the reactors) during reactor shutdown are shown in Table I. These numbers are orders of magnitude less than those found for the river below the reactors.

The coolant flow through the reactors is decreased during shutdown periods to between 5 and 15% of operating levels. The concentrations of relatively long lived radionuclides in this reduced flow do not decrease appreciably because most of them are formed over a period of

TABLE I. Curies per Day of Five Radionuclides Found in the Columbia River Above the Hanford Reactors

Radionuclide	Transport Rate, Ci/day
⁵⁴ Mn	0.07
⁴⁶ Sc	0.08
⁵¹ Cr	3
⁶⁵ Zn	0.4
⁶⁰ Co	<0.01

time in the film on the tubes and fuel elements. Release to the effluent is by leaching and sloughing from this film and this continues to some extent after shutdown, even though there is little or no additional formation of activation products. Due to the sudden drop in coolant flow at shutdown, the total activity being released to the river dropped immediately to about 5% of operating levels for ⁵⁴Mn, ⁶⁰Co, and ⁶⁵Zn, to about 10% for ⁴⁶Sc and to about 1% for ⁵¹Cr. During the shutdown period, levels of ⁵⁴Mn, ⁶⁵Zn, and ⁵¹Cr being released continued to decline regularly while ⁶⁰Co and ⁴⁶Sc did not change perceptibly. At startup of the reactors, most of the nuclides returned to operating levels, or nearly so, within a few days.

In Figures 1 through 5 are given the transport rates in curies per day of five major gamma-emitting radionuclides found in the Columbia River at Pasco, Umatilla, and Vancouver. The transport rates given are for a combination of that found in solution and in suspended

FIGURE 1. Transport Rate of ^{65}Zn at Three Points in the Columbia River

FIGURE 2. Transport Rates of ^{46}Sc at Three Points in the Columbia River

FIGURE 3. Transport Rate of ^{51}Cr at Three Points in the Columbia River

FIGURE 4. Transport Rate of ^{54}Mn at Three Points in the Columbia River

FIGURE 5. Transport Rate of ^{60}Co at Three Points in the Columbia River

sediment. These values should be compared with similar data for a previous year⁽¹⁾ which are reproduced in Figure 6. These data show that during the high water period of May, June, and early July, scouring of radionuclide-containing sediments causes the transport rates to be high and more or less the same for downstream points at Pasco. However, the normal observation is that transport at Vancouver decreases for several isotopes to about 1/10 of that during July and August. Thus, in Figures 1 through 5, the decreases shown

at Umatilla and Vancouver for ^{65}Zn , ^{54}Mn , ^{60}Co , and ^{46}Sc following shutdown are only slightly steeper and greater than those that would be expected in a year with no shutdowns.

Transport rates at Pasco, in contrast, dropped steeply in the few days following shutdown and recovered rapidly after startup. However, the drop in transport rate in the river at Pasco was not nearly so rapid as would be expected from reactor effluent data, indicating some release from the river bed. As an example, Figure 7 shows the period of

FIGURE 6. Transport Rate of Radionuclides by the Columbia River at Pasco, Washington, Hood River, Oregon, and Vancouver, Washington for the period January 1964 through January 1965

FIGURE 7. Periods of Uptake and Release of ^{65}Zn by the Bed of the Columbia River Between the Hanford Reactors and Pasco, Washington

bleeding or leaching of ^{65}Zn from the river bed. These data were calculated by subtracting the ^{65}Zn in reactor effluent and that at Vernita from amounts measured in the river at Pasco. The scouring period shown in May and June is normal for that time of year as is the change to a situation of accumulation in the river bed in early July (depletion from river water). At shutdown, however, when activity being added to the river dropped rapidly, the situation changed to one of "bleeding" or leaching of ^{65}Zn from the river bed. This gradually decreased to zero during shutdown and then at startup, accelerated depletion was seen which then gradually returned to normal for that time of year. The same effects are shown in Figure 8 for the river reach from the reactors

to Vancouver (on a different scale). On this plot a dotted line shows about what would be expected for a year in which the reactors were not shut down. ^{54}Mn , ^{46}Sc , and ^{60}Co react in a manner similar to that of ^{65}Zn in the river, but ^{51}Cr is not depleted, scoured, or leached to nearly so large an extent due to its different chemical form⁽¹⁾. The data shown indicate that the Columbia River bed acts as a buffer to take up (and thus deplete in the water) radionuclides during most of the year and especially during low water and/or high rates of release of radionuclides to the river. Then in periods of high water and/or low additions to the river, the river bed gives up some of its load of isotopes to the water. This phenomenon could

FIGURE 8. Periods of Uptake and Release of ^{65}Zn by the Bed of the Columbia River Between the Hanford Reactors and Vancouver, Washington

have far reaching effects in the event of a major accidental release to the river. Data such as those presented here could be used to predict the appreciable decreases in amounts of such released materials that would be expected to reach downstream points.

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SEDIMENT MOVEMENT ON THE CONTINENTAL SHELF
NEAR WASHINGTON AND OREGON*

M. Grant Gross** and J. L. Nelson

The nuclides ^{65}Zn and ^{60}Co associated with river-borne particulate matter are incorporated in sediment on the continental shelf near the Columbia River. Changes in the relative concentrations of ^{65}Zn and ^{60}Co and in the ratio of the activity of ^{65}Zn and ^{60}Co suggest that radioactive sediment moves northward 12 to 30 kilometers per year along the shelf and 2.5 to 10 kilometers per year westward away from the coast.

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^{207}Bi IN THE ATMOSPHERE FROM NUCLEAR TESTS

C. W. Thomas

The presence of ^{207}Bi in the atmosphere as a result of nuclear weapons testing has been observed and its concentration measured. Bismuth-207 has been reported to be formed during nuclear testing from a probably ^{209}Bi (n,3n) ^{207}Bi reaction.^(1,2) It was first observed in certain marine life at Eniwetok Atoll in 1961.⁽²⁾ The concentration in air at Richland, Washington was determined from a sample which was taken with a large (19.8 m³/min) vacuum pump during the period September 26, 1966 through October 3, 1966. The radionuclide activity was determined by chemically separating the ^{207}Bi ⁽²⁾ and measuring it from its coincidence gamma ray spectrum on a multidimensional gamma-ray spectrometer.⁽³⁾ Results of this measurement showed a concentration of 4 dis/min/10⁶ ft³. This concentration can be compared to 400 dis/min/10⁶ ft³ for ^{106}Ru or 1 dis/min/10⁶ ft³ for $^{110\text{m}}\text{Ag}$. Analysis of an old air filter

sample taken in May 1963 indicated a ^{207}Bi activity in air of 20 dis/min/10⁶ ft³. Since mid-1963, concentrations of the long-lived fallout radionuclides have decreased by about an order of magnitude and the observed concentration in late 1966 is in accord with the expected value.

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AN EVALUATION OF MULTIDIMENSIONAL ANALYSIS FOR USE
IN WHOLE-BODY COUNTING

H. E. Palmer and N. A. Wogman

An evaluation of multidimensional gamma-ray spectrometry for whole body counting was reported previously.⁽¹⁾ This system used two, 9 3/8 in. x 4 in. NaI(Tl) crystals surrounded with plastic scintillator anticoincidence shielding; the latter reduces the background and cancels any event from single gamma rays which leave only part of their energy in the NaI(Tl) crystals and scatter into the anticoincidence shielding. The conclusion from this evaluation was that the sensitivity for measuring coincident gammas in humans was not improved by using multidimensional rather than single-crystal analysis.

Two larger crystals, 11 1/2 in. diam by 6 in. thick with 4 in. thick non-activated NaI light pipes became available for counting humans by multidimensional spectroscopy.⁽²⁾ These were surrounded with anticoincidence shielding and are described in another paper in this report.⁽³⁾ Two subjects with

low levels of ^{24}Na were counted on this system in a stationary position with the lower end of the sternum bone at the center of the crystals. The crystals were spaced 10.5 inches apart with the subject located between them. The total body burdens of ^{24}Na in the subjects were 1.1 and 0.25 nCi, respectively. The results of 30 min counts on the two subjects and a phantom composed of sugar sacks for a background measurement are presented in Table I.

Although there is essentially no background in the energy plane of the 2.75 and 1.38 MeV coincidence, there are very few counts from the subject when compared to the detection of single gamma rays in both crystals. Hence, the precision is better using the sum of the single-event gamma rays in both crystals even though the sensitivity of the two methods is similar.

Another study, using two sets of three, 4 in. x 9 3/8 in. NaI(Tl)

TABLE I. Comparison of Coincident Counting and Noncoincident Counting ^{24}Na in Humans

Counting Mode	Counts per 30 min ^(a)		Sugar Sack Phantom
	Subject #1	Subject #2	
Coincidence of 2.75 and 1.38 MeV gamma rays	35 ± 34%	6 ± 82%	0
Sum of counts in both crystals for 2.75 MeV gamma ray	2999 ± 4%	712 ± 10%	499

(a) The percent error was calculated for the 95% confidence level using the sugar sack background.

crystals, was conducted with the subject or phantom between the two sets which were operated in coincidence. These crystals were not surrounded with plastic scintillator anticoincidence shielding. The counting of ^{60}Co and ^{24}Na in the phantom and subject also showed a similar sensitivity but greater counting precision when single gamma ray events were used rather than the coincident gamma rays.

A third study was conducted with three Eskimos having body burdens of about 400 nCi of ^{137}Cs and much smaller quantities of ^{134}Cs and ^{22}Na . They were measured between the two, 11 1/2 in. x 6 in. NaI(Tl) crystals which were centered over the end of the lower sternum; coincident counts from the ^{134}Cs and ^{22}Na could not be positively identified. When the crystal faces were brought within 2 feet of each other and the hand of one of the Eskimos centered between them and counted, ^{22}Na was positively identified. The quantity of ^{22}Na was

not determined because a geometry factor was not available. This experiment did show that an isotope emitting coincident gamma rays and existing in humans in the presence of a large quantity of another isotope or mixture of isotopes can be measured by multi-dimensional gamma-ray spectroscopy when it cannot be measured by any other conventional method.

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INDUCED RADIOACTIVITY IN HUMANS RESULTING FROM EXPOSURE TO HIGH ENERGY BREMSSTRAHLUNG PHOTONS

H. E. Palmer, T. M. Jenkins, and R. C. McCall

A few instances have occurred when people were accidentally exposed to the high energy bremsstrahlung radiation associated with high energy electron accelerators. In the present work a study was made to determine the induced activity in a human from (γ, n) reactions with the elements in the

body. For this purpose an Alderson Remab phantom with the enclosed human skeleton was filled with a solution which contained all the main elements of the body in the normal proportion. The solution contained the appropriate quantities of water, sugar, urea, KCl, $\text{Na}_2\text{S}_2\text{O}_3$, $\text{Fe}(\text{SO}_4)_2$ and H_2SO_4 .

The phantom was exposed for two minutes near a collimator of the electron beam of the Stanford Mark III Accelerator. The average gamma-ray dose to the body was 400 Rads and the neutron dose was about 0.5 Rad and composed of approximately 40% thermal neutrons and 60% fast neutrons up to an energy of 20 MeV. The gamma-ray dose was estimated using LiF thermoluminescence dosimeters placed at several points inside and on the surface of the phantom. The neutron flux was determined with indium, aluminum, and plastic scintillators. The energy of the electrons hitting the collimator was about 750 MeV and bremsstrahlung produced was assumed to have a spectrum with maximum photon energy of about 750 MeV. After exposure the phantom was transferred to another building and counted at intervals in a

shadow shield whole body counter containing a 4 in. x 9 3/8 in. NaI(Tl) detector. The phantom was also counted with a 3 in. x 3 in. NaI(Tl) detector placed on the lap and against the abdomen with the phantom in a sitting position.

The main gamma-ray activity was the 0.51 MeV annihilation gamma from the decay of ^{11}C . The activity in the phantom was initially too high to count in full view of the 4 in. x 9 3/8 in. crystal so it was collimated to a 2 in. slit until 127 min (about 6 half-lives) after irradiation. To compensate for the decay, the bed speed of the shadow shield counter was adjusted to decrease exponentially with the same half-life as the 20.5 min ^{11}C . Figure 1 shows the spectra obtained from three, 5.3-min counts taken at intervals up to 26 hr after irradiation.

FIGURE 1. Shadow Shield Counts of Phantom at Various Times After Irradiation

The only other significant gamma-ray energy observed was that of ^{24}Na from neutron activation.

Figure 2 shows the decay rate of the 0.51 MeV peak as measured with the 3 in. x 3 in. NaI(Tl) detector placed on the lap of the phantom in a sitting position. The decay rate corresponds precisely to that of ^{11}C . The total body content of ^{11}C in the phantom, extrapolated back to the end of the exposure, was 860 μCi or 2.15 μCi per Rad of absorbed dose of high energy photons. The total body content of ^{24}Na was 0.18 μCi . At these levels of ^{11}C production, a high energy photon dose of only 10 mRads would produce enough activity that it could be measured easily in a whole body counter for up to an hour after exposure. Without any shielding, the 3 in. x 3 in. NaI(Tl) crystal can easily measure the ^{11}C activity from a 1 Rad exposure for a period of 1 hr after exposure. Therefore, the radiation dose to a man accidentally exposed to high energy bremsstrahlung spectrum of type examined

FIGURE 2. Decay of 0.51 MeV Activity in Phantom as Measured by a 3 x 3 in. NaI Detector on its Lap (Initial Bremsstrahlung Dose = 400 Rads)

in this experiment can be estimated with rather simple and commonly used instruments.

THE FEASIBILITY OF MEASURING INDUCED RADIOACTIVITY IN HUMANS AFTER A LOW LEVEL EXPOSURE TO NEUTRONS

H. E. Palmer

Several elements in the human body can be activated to produce measurable quantities of radionuclides by exposure to a low flux of fast neutrons with total radiation doses much lower than those currently acceptable in diagnostic X-ray or radiographic studies and lower than the permissible dose to employees

working in the atomic energy industry. Anderson et al.⁽¹⁾ have estimated total body sodium and chlorine in humans by this method and Maletskos et al. have made similar studies using animals.⁽²⁾ More recently we have developed a method for determining total body calcium.⁽³⁾ Other detectable isotopes

in the body, after neutron irradiation, are ^{28}Al from phosphorus, ^{13}N from nitrogen and oxygen, and ^{42}K and ^{128}I in the thyroid.

Of the isotopes listed above, some are produced by thermal neutron reactions and others by fast neutrons. By using appropriate neutron energies and exposure times the production of particular isotopes can be enhanced or suppressed. Figure 1 shows a gamma-

ray spectrum obtained from a water-filled Remab phantom after exposure to neutrons of significantly different energies. The exposure to 14 MeV neutrons, from the deuteron bombardment of tritium at the positive ion accelerator produced mostly ^{13}N and ^{27}Al activity from fast neutron reactions. When the phantom was exposed to a neutron spectrum of lower energy having an average energy of 4 MeV, the ratio

FIGURE 1. Gamma-Ray Spectra From a Remab Phantom Filled with Tissue Equivalent Solution After Irradiation with 0.1 Rad Dose of Neutrons [Count made with one, $4 \times 9 \frac{3}{8}$ in. NaI(Tl) Detector]

of thermal-to-fast neutron reaction products was increased. The cross section for the $^{31}\text{P}(\text{n}, \alpha)$ reaction is 120 mb for 14 MeV neutrons, but only 3 mb for 4 MeV neutrons.⁽³⁾ The two gamma-ray spectra are not exactly comparable because the exposure to 14 MeV neutrons was 10 min long, over 4 times the half life for ^{27}Al ; whereas, that for the lower energy neutron was only 1 min long. If the difference in exposure times and neutron dose is considered, the ^{27}Al activity is probably about 100 times higher from the 14 MeV neutron than from the 4 MeV average energy neutron flux. Further studies of phosphorus activation in the phantom show that with a radiation dose of only 20 mRads from 14 MeV neutrons, a count rate with a standard deviation of 1% is obtained on our most sensitive whole body counter.⁽⁴⁾

For the spectra presented in Figure 1, the phantom contained only water during the irradiation with both 14 and 6 MeV neutrons. The photopeak at 0.51 MeV was probably due to induced ^{13}N from a small amount of nitrogen in the skeleton and from a fast neutron reaction on water which also produces ^{13}N . Other studies show that a phantom, filled with tissue-equivalent solution containing the normal body content of nitrogen, would produce a 0.51 MeV peak 15 times greater than that shown in Figure 1 for the 14 MeV neutron irradiation. Since the threshold for the $(\text{n}, 2\text{n})$ reaction on ^{14}N is 10.6 MeV, the lower production of 0.51 MeV gammas after the 4 MeV average energy irradiation is expected.

Since most of the iodine in the body is located in the thyroid glands, it might be possible to measure stable iodine after irradiation of the neck area with low energy neutrons to produce ^{128}I . An experiment was conducted in which the phantom thyroid containing stable iodine was irradiated with a relatively large dose of 100 keV neutrons. The ^{128}I was detectable but the results of this single experiment are not sufficient to assess the feasibility for measuring stable iodine in the thyroid.

Due to the interference of ^{24}Na and naturally-occurring ^{40}K with the counting of ^{42}K , the use of the latter in determining potassium content will probably offer no advantage over counting the ^{40}K .

The usefulness of in vivo activation analysis has not been well demonstrated up to the present time. The measurement of total body calcium appears to be the most immediately important use. When this technique is refined to allow precise measurements of other components of the body following exposure to low levels of neutrons, this method should find many uses in medical research and in diagnostic practice.

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THE DETERMINATION OF TOTAL BODY CALCIUM IN HUMANS BY LOW LEVEL IRRADIATION WITH NEUTRONS

H. E. Palmer, W. B. Nelp*, R. Murano*, C. Rich*

Present methods for estimation of the calcium content of the body, 98% of which is within the skeleton, utilize indirect means such as measuring relative bone density in the appendicular skeleton by noting the radiographic appearance of the skeleton or by observing pathologic changes in the skeleton associated with loss of bone mass. Quantitative measurements of total skeletal mass have been performed only on cadavers and very few such measurements have been made. Because of the fundamental importance of metabolic and pathologic processes relating to the skeletal mass, an easily repeated method for precise and accurate quantification of skeletal mass in man would be most useful.

Important unanswered questions abound. These include: What is the normal skeletal mass in adult life and how does it change with aging? How is skeletal mass affected by prolonged periods of rest or weightlessness and does any given agent such as sodium

fluoride or calciatonin reduce any loss that may occur? To what extent is skeletal mass decreased when vertebral fractures occur in osteoporosis? Do agents such as fluoride, calcium, sex steroids, magnesium, or calciatonin enhance the deposition of skeletal calcium during treatment of osteoporosis? To what extent is bone mass lost in diseases where prolonged treatment with glucocorticoids is required (rheumatoid arthritis, nephrosis, rheumatic fever) and does treatment with any of the agents mentioned above control this loss? What is the relationship between skeletal mass and the intestinal absorption of calcium? How well do estimations of bone density by radiographic and photon absorption techniques reflect actual skeletal mass? Although much indirect information has been acquired relating to some of these questions, direct quantitative measurements of skeletal mass would greatly extend the understanding.

In this study we are attempting to measure total body calcium (skeletal mass) in man by quantitating, through total body counting, the ^{49}Ca radioactivity induced by uniform exposure

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of the body to high energy cyclotron-produced neutrons. The technique must be without hazard to the patient and must deliver amounts of radiation which are as low as or lower than those currently acceptable in a diagnostic radiographic study (such as a radiographic bone survey) and the measurements must be precise and accurate. If the human body can be exposed in a uniform fashion to a flux of high energy neutrons, a small fraction of the neutrons penetrating the body will interact (both thermalized and fast neutrons) to produce trace amounts of induced radioactivity. Most prominent interactions would be those with the bulk elements sodium and chlorine producing ^{24}Na and ^{38}Cl by $n\text{-}\gamma$ reaction. Another $n\text{-}\gamma$ interaction is that with ^{48}Ca within the skeleton to produce ^{49}Ca , a radioisotope with a half-life of 8.8 min. If the total radiation exposure from fast neutrons as well as the resulting induced radioactivity in the body is less than 0.1 Rad, less than 1.0 rem of total body exposure results. These levels are generally acceptable for diagnostic radiographic procedures. If, immediately following neutron irradiation, the subject is counted in a total body counter using sodium iodide detectors and gamma-ray spectrometry, identification and quantification of certain of the induced radionuclides is possible. Because ^{49}Ca has a primary gamma photon energy of 3.1 MeV, its radioactivity can be clearly distinguished from the photo-peaks of other induced radionuclides in the body.

Studies of in vivo neutron activation analysis using animals and calcium

in bone activation in bone phantoms have been done by Maletskos and others.^(1,2,3) This approach to the determination of body composition was recently described by Anderson and associates.⁽⁴⁾ In their experiments, two subjects were irradiated for one hour to a total body dose of 1 rem using a Cockcroft-Walton neutron generator. Total body counting was not carried out until 30 or more minutes after irradiation. Although the object of these studies was to estimate total body sodium, observations on chlorine were also made. They observed a photo-peak identical to that of induced ^{49}Ca and a preliminary estimation of calcium content was attempted. However, due to the long irradiation time and the long decay time prior to counting, no quantitative data were obtained. We have determined that a more uniform neutron exposure can be accomplished in as little as 10 seconds using the University of Washington cyclotron. By placing a total body counter in the immediate vicinity of the cyclotron, total body counting can begin 3 to 4 minutes after irradiation. This results in much higher levels of ^{49}Ca remaining at the time of counting, less interference from induced isotopes, and thus provides a feasible approach for calcium measurements.

Using a deuteron-bombarded beryllium target as a source of neutrons, the resulting high energy neutron flux was mapped out at various locations within the cyclotron room. In a region approximately 16 feet from the target and at an angle 90° from the incident beam, a uniform field of neutrons could be obtained over an area considerably

larger than that of the human body. Estimates of the neutron energies indicated they are from 14 MeV downward, with the peak flux between 6 to 8 MeV. With the use of gamma and neutron dosimeters, including a tissue-equivalent dosimeter, it was estimated that 70% of the absorbed dose delivered to this area is from neutrons and 30% is from gamma rays. With the cyclotron running at a current of 15 to 20 microamperes, a total dose (neutron plus gamma) of 0.1 Rad can be delivered in 10 to 15 seconds. To monitor the accumulated dose, a neutron-sensitive LiI detector has been calibrated in Rads, and its output is displayed at the cyclotron control panel. When the accumulated scaler reading from the monitor indicates a desired given dose, the cyclotron is instantly shut off.

Following these experiments a Remab skeletal phantom* was repeatedly irradiated under these conditions with tissue-equivalent neutron dosimeters⁽⁵⁾ placed throughout the body both internally and externally. The results indicated that exposure throughout the body was uniform within $\pm 5\%$ after irradiating in two settings with rotation of the phantom through 180° . To enhance the uniformity of irradiation, a moderator of paraffin 2 in. thick was placed in the front and on the side of the phantom.

Subsequent to these experiments, a total body counter was developed which uses a cylindrical array (six, 4-in. thick x 9-in. diam sodium iodide crystals) through which a fiber glass

trough-like bed carrying the skeletal phantom was moved on a track (See Figure 1). The speed of the bed decreases exponentially with a half-life the same as ^{49}Ca to compensate for the decay of the isotope in the body. The detectors were not shielded against background because only energies above 2 MeV where background was acceptably low were analyzed. Gamma-ray spectrum analysis of the skeletal phantom following irradiation indicated good separation of the ^{49}Ca photopeak with sufficient count rate information to provide good statistical precision for the calcium measurement.

Following these experiments, a human cadaver was irradiated under similar circumstances. This provided a matrix of elements containing the approximately normal amounts of sodium, chloride, and other bulk and trace elements which may be encountered in man. After a 0.1 Rad dose, the ^{49}Ca photopeak could be identified readily, and sufficient count rate information was available to provide precise measurements (See Figure 2). The count from the cadaver is compared to the count rate of a calcium standard which is irradiated at the same time as the cadaver. A 0.14 Rad dose to the cadaver gave a net count of about 9000 counts per 12.4 min for the 3.1 MeV gamma rays with a background of 4400 counts. This provides a count with a standard deviation of $\pm 1.3\%$. The lower curve in Figure 2 shows a count of the cadaver 95 min later when all of the ^{49}Ca and most of the ^{38}Cl had decayed.

The main interfering nuclides that are induced in the body along with ^{49}Ca are ^{38}Cl , ^{24}Na , and ^{37}S . The

* Made by Alderson Research Labs., Inc., Long Island City, New York.

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FIGURE 1. Whole Body Counter for Calcium Determination

^{24}Na and ^{38}Cl are visible in Figure 2, but ^{37}S has the same energy as ^{49}Ca (i.e., 3.1 MeV) and has a shorter half-life so its presence is not obvious. The ^{37}S is produced from the ^{37}Cl (n,p) reaction so it will be formed in a constant ratio to the amount of ^{38}Cl formed. The ^{38}Cl peak can then be used to correct for the interference of ^{38}Cl Compton and ^{37}S . In the future

it should be possible to reduce all of these interferences. The ^{24}Na interference can be reduced by using detectors of better resolution and the ^{38}Cl interference can be reduced by using an anticoincidence system between the coincidence events happening in any two of the six crystals since the 3.80 MeV peak is really the sum of the coincident 1.6 and 2.2 MeV gamma

FIGURE 2. Gamma-Ray Spectrum of Cadaver Irradiated to 0.14 Rad and Counted with Six Crystal Array

FIGURE 3. Gamma-Ray Spectrum of a Cadaver After a 0.7 Rad Dose of Neutrons

rays. Figure 3 is a count from a cadaver irradiated to 0.7 Rad and then counted with a single crystal with 8.5% resolution; this shows the expected interference reduction of $^{24}\text{Na} + ^{38}\text{Cl}$. The ^{37}S can be reduced by using a source of neutrons with an average energy lower than the threshold of the (n,p) reaction.

This approach to the quantification of skeletal mass in humans is feasible with the desired accuracy and safety. Studies are presently underway to determine the best irradiation position, comparator standards, and counting arrangement. The method will be calibrated by making measurements on several

cadavers followed by ashing and chemical analysis of the total calcium content.

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A SENSITIVE ROTATIONAL METHOD WHOLE BODY COUNTER

H. E. Palmer and J. C. Langford

Anderson and Olson⁽¹⁾ have described a technique in which the human subject is rotated during radioactivity measurement while in a position standing on a turntable and the detector is moved vertically along the body. The count rate of activity in the body using this method is almost independent of the distribution of the isotope in the body. This paper describes a method which employs a similar principle but uses a circular array of six, 4 x 9 3/8 in. NaI(Tl) detectors which move by the subject as he, in a reclining position, is oscillated back and forth through one-sixth of a revolution. This gives the effect of a uniform cylindrical detector over the entire length of the person.

Figure 1 shows a section of the counter which has been set up in a lead shielded room 5 ft wide, 10 ft long and 6 1/2 ft high. The crystals are mounted on a circular holder and the mounting is adjustable such that they

can be arranged in a circular array having a diameter of 16 to 22 in. The curved bed for the subject is 82 in. long and it is fabricated from fiberglass and epoxy resin; it is oscillated by a stepping motor. The speed of oscillation of 8 times per minute seems to be about optimum for subject comfort and counting considerations. For a 10 min count the crystals move longitudinally at a speed of about 9 in./min, while the bed oscillation rate of 8 times per minute allows about 1.1 in. of movement per oscillation. This is a small distance compared to the width of the crystals.

Except for a small end effect, which can be eliminated by slightly collimating the crystals, the count rate is completely independent of the distributions of a source. Without the effect of absorption by the body, a point source placed anywhere within the volume of the body gives essentially the same counting rate at each position.

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*FIGURE 1. Six Crystal Rotational
Whole Body Counter*

The effect of absorption by the body is being studied and has not yet been evaluated.

Figure 2 shows a gamma-ray spectrum of a subject who was counted for 20 min with a single, 4 x 9 3/8 in. crystal in the tilted chair geometry and also in the six-crystal array. Because two of the crystals in the array have poor resolution, the peaks obtained are broader than for the single crystal

count, but the area under the peaks is 4.5 times greater with the six-crystal array. The faces of the crystals were set on a 21 in. diameter but this could be reduced to smaller diameters to obtain a better counting efficiency.

This very unique whole body counter with its high sensitivity and its distribution-independent counting efficiency will be extremely valuable in

FIGURE 2. Comparison of the Gamma-Ray Spectrum From a Subject Counted with a Single $4 \times 9 \frac{3}{8}$ in. Crystal in the Tilted Chair Geometry and with a Circular Array of Six Crystals

health physics, medical, and environmental studies which involve radioactivity measurements in the human

body. When the calibration and evaluation of this counter is completed, its full potential can be realized.

EVALUATION OF RADIOCHEMICAL METHODS FOR BIOLOGICAL PURPOSES

C. W. Thomas and D. E. Robertson

A program to provide adequate testing and evaluation prior to publication of laboratory procedures suitable for radiological purposes was initiated in 1964 under the auspices of the Division of Biology and Medicine. Procedures covering radionuclides chosen by a committee functioning under the DBM were evaluated for media of water, air, urine, tissue, excreta, soil, and vegetation. Procedures found suitable were written in manual form to meet the requirements of the Division of

Licensing and Regulation. When suitable methods were not available, appropriate modifications to make them suitable were made. The completion of this study has resulted in the compilation of a standard procedure manual which was published for the Division of Biology and Medicine.

This study was completed in July 1966. During the course of the work, methods were tested and the procedures written in standard form for the radionuclides in the media listed in Table I.

TABLE I. *Radionuclides and Media Evaluated*

<u>Radionuclide</u>	<u>Air</u>	<u>Water</u>	<u>Tissue</u>	<u>Urine</u>	<u>Feces</u>	<u>Soil</u>	<u>Vegetation</u>
Am	x	x	x	x	x		
Au		x		x			
Ba		x		x			
Ce		x		x	x	x	
Cs		x		x			
Np	x	x	x	x	x		
P		x		x	x		
Pm		x		x			
Po		x		x			
Pu	x	x	x	x	x		
Ru		x		x		x	
Sr	x	x	x	x	x	x	x
U	x	x	x	x	x		
Xe	x		x				
γ -spectra	x	x	x	x			x

NONDESTRUCTIVE DETERMINATION OF MEAT COMPOSITION IN LIVE ANIMALS
AND IN BUTCHERED MEATS BY FAST NEUTRON ACTIVATION

H. E. Palmer and L. L. Nichols

Several investigators have studied the relationship between the lean meat to fat ratio and the ^{40}K content^(1,2,3) in live and butchered meats. These methods, which are based on ^{40}K counting have been only partially successful because of the limited statistical accuracy of the low counting-rates of the ^{40}K in the meat and because the correlation coefficient between lean meat and ^{40}K is not always constant.⁽³⁾

The nitrogen (or protein) content of meat can be measured with a greater sensitivity by fast neutron analysis than any other element in meat. After an exposure of 1 to 10 minutes to 14 MeV neutrons, the three main radio-nuclides formed in beef tissue are ^{16}N from oxygen, ^{28}Al from phosphorus, and ^{13}N from nitrogen. After allowing a few minutes for the ^{16}N (half-life, 7.1 sec) and ^{28}Al (2.3 min) to decay, essentially all the remaining activity is from ^{13}N which is a positron emitter with a 10 min half-life.

Figure 1 shows the decay of ^{13}N which was produced in 135 g samples of beef fat, and lard rendered from the fat. From these curves, it is seen that the ^{13}N activity induced in lean meat is 30 times that in pure fat (lard). Fat, water, carbohydrates, or any oxygen-containing compounds give a small amount of ^{13}N from a neutron reaction (possibly $n, n^3\text{H}$) on the oxygen.

Pure water gives about one-tenth as much activity as lean meat and, therefore, is only a minor interference.

Figure 2 shows the different counting rates of different arrangements of the same quantity of lean and fat meat. This indicates that the information as to the distribution and content of lean meat in a live animal might be obtained by irradiating a position on the animal with a portable neutron generator followed by the counting of that position with a NaI crystal. A suitable flux monitor could be irradiated and counted at the same position. The determination of lean meat would be much easier in butchered meats where the irradiation and the counting geometries could be better controlled.

These measurements could be made with absorbed doses of 0.1 Rad at the position of irradiation on a live animal and with much lower doses to butchered meat samples using more sensitive gamma-ray detection equipment.

This initial work demonstrates the feasibility of this method and plans have been made to study its practicability.

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FIGURE 1. Activity of Meat and Fat
after 10 min Exposure to 14 MeV Neutrons

FIGURE 2. The Difference in Counting Rate of Different Arrangements of the Same Quantity of Lean Meat and Fat After 10 min exposure to 14 MeV neutrons

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⁵⁵Fe IN WORLDWIDE POPULATIONS DURING 1966

H. E. Palmer and T. M. Beasley

Since the 1961-1962 nuclear tests, ⁵⁵Fe has increased from a minor fraction of fallout to the most abundant of all fallout isotopes and it is easily measurable in almost all living organisms. Although it produces only a small radiation dose, the study of its transfer and concentration in various organisms is of interest because iron is an essential element to most of these organisms. An extensive study was conducted on the levels of ⁵⁵Fe in man at many places on the earth. Studies of the levels in foods and in the ocean environment led to correlations of the observed levels in man with his consumption of ocean fish. The average levels of ⁵⁵Fe range from 5 nCi in people in South Africa to 1100 nCi in some of the Alaskan Eskimos. Average levels in women are significantly higher than in men. The highest levels in humans are associated with a high consumption of ocean fish.

The ⁵⁵Fe levels in many organisms of the biosphere have been reported.^(1,2) Those preliminary studies indicated that significant differences existed in body burdens of ⁵⁵Fe in various groups of people. We have recently collected blood samples from many locations throughout the world and the results of the analysis of these samples are presented in Table I. With the exception of the Japanese and Alaskan samples, all the samples were from blood banks and, except for the Alaskan results, the values are the average of 100 males and 25 female blood samples from each location. These samples were taken at the time of donation or are from outdated blood samples of known volume and known concentration of anticoagulant additive. The blood bank samples have one apparent disadvantage in that people with low hemoglobin are not allowed to give blood so this segment of the population (mostly women) is not included in any average value which may be calculated from the analysis of blood bank samples.

The people in South Africa and Australia seem to have the lowest ⁵⁵Fe

body burdens while the Japanese people and some Alaskan natives have the highest content. Individual values range up to 2300 nCi for Alaskan natives and up to 1800 nCi for some of the Japanese people. These results and the results of the analyses of several species of ocean fish and many types of food⁽¹⁾ indicate that those people who eat large quantities of ocean fish such as salmon, tuna, and mackerel have a much higher content of ⁵⁵Fe than those people with a low consumption of these foods. The ⁵⁵Fe content of a few samples of meat and fish sampled at a Japanese market are presented in Table II; and these results show a much higher ⁵⁵Fe content in the fish than in the other meats. These same differences have been measured in meat and ocean fish in the United States. Also, the Alaskan natives who eat mostly fish (salmon) have higher ⁵⁵Fe body burdens than those who eat both fish and caribou; and these, in turn, have higher body burdens than those who eat mostly caribou and very little fish. Next to seafood, meat and grains are the highest contributors of ⁵⁵Fe in the

TABLE I. ^{55}Fe Content in Humans Throughout the World^(a)

Sampling Location	Average ^{55}Fe Body Burden, nCi	
	Male	Female
Sydney, Australia	8	9.2
Johannesburg, South Africa	5.8	5.7
Winnipeg, Canada	22	21
Hamilton, Canada	23	22
Toulouse, France	17	22
Tokai-Mura, Japan ^(b)	634	919
Oslo, Norway	58	64
Amsterdam, The Netherlands	9.1	14.3
United States		
New York City, New York	22	26
Milwaukee, Wisconsin	13	20
Seattle, Washington	26	33
Kwethluk, Alaska (fish-eating natives) ^(b)	--	1100 (18) ^(c)
Southeastern Alaska, Yukon River mouth area (fish-eating natives) ^(b)	544 (6) ^(c)	700 (7)
Tanana, Alaska (fish-and caribou-eating natives) ^(b)	250 (6)	--
Anaktuvuk, Alaska (caribou-eating natives) ^(b)	80 (6)	--

(a) Blood specimens collected during first half of calendar year, 1966.

(b) Blood samples obtained from adult population and not blood banks.

(c) Numbers in parentheses indicate the number of samples analyzed.

TABLE II. ^{55}Fe Content in Japanese Fish and Meat

Sample	nCi/kg
Salmon	38
Mackerel	25
Horse Mackerel	6
Tuna	1.2
Oysters	0.12
Beef	0.20
Pork	1.5

diet.⁽¹⁾ Although the high ^{55}Fe body burdens of the Southwestern Alaskan natives result largely from the fish consumed in their diets, there is also a high incidence of iron deficiency anemia among these people. This leads to a higher uptake of available iron from the diet and probably contributes

in part to the unusual ^{55}Fe body burdens observed.⁽³⁾

The low ^{55}Fe body burdens in South Africa and Australia correlate well with the lower amount of radioactive fallout in the southern hemisphere. For instance, tuna fish in the southern oceans have a much lower ^{55}Fe content than those in the northern oceans. The Norwegian body burdens are significantly higher than those in most of the other countries and this probably reflects an above average amount of ocean fish in their diet.

SEX DIFFERENCES

The results in Table I also show that the levels of ^{55}Fe in females are generally higher than the levels in

males. This difference is probably caused by the menstrual blood loss in women which causes a higher turnover rate of iron in the body. With this higher turnover of iron, a greater percentage of the ingested ^{55}Fe will be absorbed and the level of ^{55}Fe in females will be closer to an equilibrium with the diet. Therefore, the level in the females will be higher than the level in the males. This is clearly shown in the Japanese and Alaskan native samples none of which were obtained from blood banks. The blood bank samples do not show these large differences because women with iron deficiency anemia and the resultant higher levels of ^{55}Fe are excluded from donating blood.

AGE DIFFERENCES

The ^{55}Fe level in people seems to vary with age. This is shown in Table III by measurements of blood taken from a family of fish-eating Eskimos. The concentration is higher in the very young members of the family which indicates a greater uptake from the diet at early ages. However, this trend is reversed after the age of about 25 and levels increase with the age of the people. Table IV shows the results obtained from a population of 156 male blood samples from Seattle, Washington, which were analyzed according to age and shows that the 50 to 60 year old males have significantly higher levels of ^{55}Fe than those 20 to 30 years old. The reason for this difference could be a higher uptake of iron by older people, but a more probable reason is that the diet of

TABLE III. ^{55}Fe Content in Blood from Several Members of an Eskimo Family

<u>Member</u>	<u>Age</u>	<u>nCi/liter of blood</u>
Father	34	46
Mother	30	50
Son	3	95
Son	6	59
Son	7	44

TABLE IV. Blood Content of ^{55}Fe in Seattle Males of Different Ages

<u>Age</u>	<u>No. of Samples</u>	<u>nCi/liter of blood</u>
16-20	23	19.2
20-30	45	16.9
30-40	39	19.3
40-50	32	22.2
50-60	17	26.7

older people may be different and that they eat more of the foods with high ^{55}Fe content than do the younger people.

^{55}Fe IN THE ARCTIC

The original source of ^{55}Fe in animals and humans is that deposited directly from fallout onto plants that are used for foods. Only a very small fraction of the ^{55}Fe content in plants is due to uptake through the root system because of the large dilution of the ^{55}Fe by the stable iron in the soil. In the temperate zones of the earth, the plants used as food for beef cattle and other animals are new growth and the amount of ^{55}Fe ingested by the animal depends on the recent rate of fallout. For instance, the deposition of ^{55}Fe in Westwood, New

Jersey, in 1965 was 45% of the 1964 levels; and our measurements show that the average ^{55}Fe concentration in cattle blood samples in Washington was 40% of that in 1964.

In the Arctic food chain--lichen-caribou-man, the long-growing lichens do not die each year and act as accumulators of fallout which deposits on their surfaces. Therefore, even though the fallout rate is decreasing, the amount on the lichens is increasing and will continue to increase until the amount derived from fallout is less than the amount lost from the lichens due to radioactive decay. The levels in caribou feeding on lichens should increase each year until they are in equilibrium with their intake or until the content of the radioisotope on the lichens begins to decrease. In contrast to the decreasing levels in cattle described above, increasing ^{55}Fe levels in the caribou are shown by average blood concentrations in caribou of 87 and 114 nCi per liter in early winter of 1964 and 1965, respectively. The Eskimos who eat these caribou had an average body burden of 61 and 81 nCi in January 1965 and November 1965, respectively.

The ^{55}Fe levels reported in lichen, reindeer, and man in the Swedish and Finnish Lapland^(4,5) are about two times those for the same components in the Alaskan Arctic. The reason for this is not clear since the ^{137}Cs levels in both the Laplanders and Alaskan Eskimos have been very similar for several years.

RADIATION DOSE

Because of its long radioactive half-life (2.7 yr) and its long biological half-life in animals and humans, ^{55}Fe will be present in the biosphere for several years. However, at present levels, the low energy of the X rays and Auger electrons of ^{55}Fe does not produce a high radiation dose in humans when compared with the dose from natural sources of radiation. The body burdens of about 1000 nCi in the Alaskans and Japanese are far below the maximum permissible body burdens of 100,000 nCi for members of the general population not exposed to ^{55}Fe in the course of their occupations.⁽⁶⁾ The radiation dose to the red blood cells of a person with a constant ^{55}Fe body burden of 1000 nCi would be about 30 mRad per year. This estimate is calculated using both the X ray and the Auger electron dose to the erythrocyte fraction of the blood as suggested by Wrenn.⁽⁷⁾ This dose is about 30% of the yearly dose to the body from natural sources such as cosmic rays and internally deposited ^{40}K and radium.

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¹³⁷Cs IN ALASKAN ESKIMOS

H. E. Palmer and W. C. Hanson

During the summer of 1966 a trip was made to Anaktuvuk, Alaska, to determine the levels of ¹³⁷Cs in the people of that village, to check the cross calibration of the 3 in. x 3 in. NaI(Tl) portable lap counter⁽¹⁾ with the shadow shield by counting the people on both counters, and to assist the Canadian Department of Health and Welfare to cross calibrate their portable lap counter with the shadow shield counter.

All of these purposes were accomplished. It was found that no change was necessary in the original lap counter calibration curve. The average

levels of ¹³⁷Cs in the residents of Anaktuvuk were 1127, 934, and 290 nCi for the adult males, adult females, and children, respectively. These levels are similar to those obtained during the last two summers for the same groups. The 1966 levels for the males may not be very meaningful since most of the adult males were out of the village fighting forest fires and were not counted.

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LEAD-210 IN BIOLOGICAL SPECIMENS FROM ALASKA

T. M. Beasley and W. C. Hanson*

As part of a continuing study to characterize the levels of ^{210}Pb in biological specimens from Alaska, measurements of the concentration in the soft tissue and bone of several animal species have been made. Determination of ^{210}Po , another naturally occurring isotope and one of the daughter products in the decay of ^{210}Pb , was not possible in the present series of samples due to the long period of time (2 to 5 years) between collection of the specimens and their analysis. The methods used in the

analysis of these particular specimens have been previously described.⁽¹⁾ All of the samples were collected from locations in Alaska which were above the Arctic Circle.

The radionuclides observed are presented in Table I. Several of the specimens have been reported in terms of ash or dry weight in addition to wet weight to facilitate their comparison with other similar samples analyzed from Arctic regions.⁽²⁾ The concentrations reported are those existing at the time of collection.

The value of ^{210}Pb in caribou bone is consistent with similar measurements

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TABLE I. ^{210}Pb Concentrations of Some Selected Biological Specimens from Alaska

Animal	Sample	nCi/kg wet wt.	nCi/kg ash wt.	nCi/kg dry wt.
Caribou	Muscle	0.021 ± 0.0006		
Caribou	Bone	10.99 ± 0.18	16.47 ± 0.27	
Caribou	Bone	6.26 ± 0.18	9.26 ± 0.27	
Caribou	Bone	14.43 ± 0.35	21.36 ± 0.52	
Wolf	Muscle	0.0063 ± 0.0014		
Wolf	Bone	0.280 ± 0.007		
Wolf	Muscle	0.0043 ± 0.0011		
Wolf	Bone	0.688 ± 0.015		
Wolverine	Muscle	0.0050 ± 0.0012		
Wolverine	Bone	0.327 ± 0.012		
Wolverine	Bone	0.275 ± 0.010		
Wolverine	Bone	0.479 ± 0.018		
Fox	Muscle	0.0077 ± 0.0011		
Fox	Bone	0.095 ± 0.009		
	Lichens	28.5 ± 0.26		29.3 ± 0.27
	Lichens	26.5 ± 0.22		27.2 ± 0.23
	Lichens	4.80 ± 0.06	153.6 ± 1.9	
	Lichens	4.34 ± 0.06	169.5 ± 2.3	
	Lichens	4.77 ± 0.06	183.2 ± 2.3	
	Sedge	0.124 ± 0.004		0.425 ± 0.014
	Sedge	0.182 ± 0.006		0.566 ± 0.019

made at this laboratory and elsewhere.⁽²⁾ The levels of the isotope in wolf, wolverine, and fox are generally an order of magnitude less than those observed in caribou for the same organs.

The apparent anomaly in the activities observed in the lichen specimens can be explained by considering their origin and type. The higher activity lichens (Cornicularia, Cetvaria Delisei) were harvested at Cape Thompson, Alaska, from snow barren ridges and presumably have been exposed to the atmosphere during most of the year. By contrast, the lichens of lower activity (Cladonia, Cetvaria) were taken at Anaktuvuk Pass, Alaska, and are generally covered with snow during the winter months. This

difference in activity levels for the two types of exposure is consistent with those observed for ^{137}Cs ⁽³⁾ although the difference in activity levels is not as great as that observed for ^{210}Pb - ^{210}Po .

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DETERMINATION OF ^{210}Pb - ^{210}Po EXCRETION RATES IN ALASKAN ESKIMOS

Y. M. Jones and H. E. Palmer

The ^{210}Po levels of caribou-eating Alaskan natives are considerably higher than those observed in individuals who do not include caribou in their diets. These high levels are directly attributable to passage of these radionuclides through the lichen-caribou-Eskimo food chain⁽¹⁾ found responsible for the high ^{137}Cs body burdens determined in these same Anaktuvuk Pass natives. Since ^{210}Pb and ^{210}Po are beta and alpha emitters, respectively, their detection in the body is not amenable to whole body counting which was used so effectively to measure ^{137}Cs body

burdens in these inhabitants. Therefore, unless autopsied or biopsied samples become available, methods for determining ^{210}Pb body burdens are limited to the indirect method of analysis of excreta. If a correlation between excreted ^{210}Po and systemically absorbed ^{210}Pb could be established, measurement of ^{210}Po excretion could be used as an index of ^{210}Pb body burdens. Since caribou feed on lichen only when other food is unavailable (i.e., in winter months only), the ^{210}Po content⁽²⁾ of the resultant labeled caribou meat should exhibit seasonal

fluctuations similar to those observed for ^{137}Cs .⁽³⁾ These winter fed caribou are slaughtered in the spring and are the source of meat in the Eskimo diet throughout the summer months. Since the autumn slaughtered caribou will be relatively low in ^{210}Po , the main source of ingested ^{210}Po will be the spring killed caribou pool in which the ^{210}Po is decaying with an effective half-life of about 30 days. Thus, the seasonal fluctuation in the ^{210}Po content of caribou should be reflected in a delayed but similar fluctuation in ^{210}Po excretion patterns of Alaskan natives. The ^{210}Po excretion rate should reach a maximum during the summer months and decrease rapidly thereafter.

The limited analyses of the urinary excreta of Anaktuvuk Pass natives collected in the spring and fall of this year, are consistent with expectations. During the approximately five months for which the ^{210}Pb and ^{210}Po excretion rates were determined, the average ^{210}Pb excretion rate remained essentially constant. Although ^{210}Po

excretion rates exhibited large individual variations, the fall excretion rates were significantly lower than the spring values. Unfortunately, no samples could be obtained during July and August when the maximum for the ^{210}Po excretion rate was expected to occur. From these data, however, it appears that most of the excreted ^{210}Po in these Eskimos comes from the decay of their ^{210}Pb body burdens and a smaller fraction comes from ^{210}Po ingestion.

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RADIATION CHEMISTRYCOMPARISON OF EFFECTS OF IONIZING RADIATION AND CHEMICAL
OXIDATION ON AROMATIC COMPOUNDS IN AQUEOUS SOLUTION

D. R. Kalkwarf and R. N. Diebel

Several long-lived organic radicals have now been discovered to be formed in irradiated aqueous solutions as a result of addition of a hydrated electron or by reaction with other reducing radicals.⁽¹⁻³⁾ Fewer examples of long-lived radicals resulting from oxidation of organic compounds have been observed in irradiated aqueous solution. To determine optimum conditions for detecting such radicals in the irradiated flow system,⁽⁴⁾ parallel experiments were conducted to measure the electron spin resonance (ESR) spectra of organic radicals formed in aqueous solution by ceric-ion oxidation in a Varian-4549 liquid-flow mixing-chamber.

Aromatic nitroso-compounds were selected first for this study. One of these compounds, p-nitrosodimethylaniline has been reported to react rapidly with hydroxyl radicals in irradiated aqueous solution,⁽⁵⁾ and other investigators have found that it forms a relatively stable free radical upon oxidation with ceric ion.⁽⁶⁾ Oxidation of this compound with ceric sulfate in 0.1N H₂SO₄ using the Varian mixing-chamber produced radicals with the ESR spectrum shown in Figure 1. This spectrum shows the large splitting of 34.5 gauss due to a nitrogen nucleus and a further splitting of 3.6 gauss, most probably due to a single proton. The previous investigators⁽⁶⁾ had reported this large nitrogen splitting

but had not been able to resolve any further splittings. On the basis of their results and comparisons with the spectra of similar compounds, they suggested that the structure of the radical was

The added splitting of 3.6 gauss found in the present work further confirms this structure since the two protons which are ortho to the nitroso group would be structurally nonequivalent and the cis-proton would be expected to produce a moderately large nuclear hyperfine splitting. Decay of the signal was measured after stopping the flow through the mixing chamber and the lifetime of the radical was estimated to be 0.4 min.

Other nitrosoaromatic compounds were oxidized in the same way with ceric sulfate and found to form radicals with a similar structure; p-nitrosodimethylaniline was converted into a radical whose ESR spectrum is shown in Figure 2. The nitrogen splitting was 34.2 gauss and the proton splitting was 4.4 gauss. The shape of the absorption peaks also indicates that further splitting is unresolved. This further splitting, due to the trans-proton in the position ortho to the nitroso group, showed up clearly in

FIGURE 1. ESR Spectrum of Radical Produced by Oxidizing $1 \times 10^{-3}M$ *p*-Nitrosodimethylaniline in Aqueous Solution with $1 \times 10^{-3}M$ Ceric Sulfate in $0.1N$ H_2SO_4 .

FIGURE 2. ESR Spectrum of Radical Produced by Oxidizing $1 \times 10^{-2}M$ *p*-Nitrosodiethylaniline in Aqueous Solution with $1 \times 10^{-2}M$ Ceric Sulfate in $1N$ H_2SO_4 .

the ESR spectrum of the radical derived from *p*-nitrosophenol shown in Figure 3. For this radical, the nitrogen splitting was 33.2 gauss; the *cis*-proton splitting, 4.0 gauss; and the *trans*-proton splitting, 1.6 gauss. Decay measurements on

both of these radicals indicated that they existed in aqueous solutions of $0.1N$ H_2SO_4 for about 0.3 min at room temperature.

No ESR spectra were detected after irradiating any of these compounds in

FIGURE 3. ESR Spectrum of Radical Produced by Oxidizing $1 \times 10^{-2}M$ p-Nitrosophenol in Aqueous Solution with $1 \times 10^{-2}M$ Ceric Sulfate in $1N$ H_2SO_4 .

aqueous solutions even though several environmental factors were varied. Dissolved oxygen was removed from the solution to minimize line broadening and further oxidation; the solutions were saturated with nitrous oxide to remove hydrated electrons that might react with the radicals; the solution temperature was lowered to $7^\circ C$; the pH was varied from 1 to 13; and the flow rate through the irradiator was decreased until the delay time between the irradiator and the ESR cavity was only 0.3 sec. Oxidation of these compounds with hydroxyl radical either produces a radical unlike that produced by ceric-ion oxidation or the dose-rate received in the irradiator, approximately 2400 Rads/min, is insufficient to produce a detectable concentration of radicals at the fast flow rates and radical decay rates.

A similar comparison was carried out between ceric-ion oxidation and electrolytic oxidation of other aromatic compounds. Ceric oxidation of p-amino-

benzoic acid in $1N$ H_2SO_4 produced radicals whose ESR spectrum is shown in Figure 4. This spectrum disappeared more rapidly after cessation of flow-mixing than did those for the nitroso radicals and no spectrum was detected in the irradiated flow system. Solutions of tryptophan gave the simple singlet ESR spectrum shown in Figure 5 following oxidation in $1N$ H_2SO_4 with ceric ion. The lifetime of the radical was found to be less than 0.1 sec and, again, no ESR spectrum was observed when this compound was irradiated in the flow system.

Numerous lines of evidence point to the formation of organic free radicals by oxidation in irradiated aqueous solutions. As can be seen from the results described above, their detection by electron spin resonance in the presently available irradiated flow system is difficult. Still, their identification would greatly aid the understanding of the development of radiobiological damage. Further efforts

FIGURE 4. ESR Spectrum of Radical Produced by Oxidizing $1 \times 10^{-2}M$ p-Aminobenzoic Acid in Aqueous Solution with $1 \times 10^{-2}M$ Ceric Sulfate in $1N$ H_2SO_4 .

FIGURE 5. ESR Spectrum of Radical Produced by Oxidizing $1 \times 10^{-2}M$ Tryptophan in Aqueous Solution with $1 \times 10^{-2}M$ Ceric Sulfate in $1N$ H_2SO_4 .

will be made to stabilize such free radicals in solution so that their structures can be revealed.

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LONG-LIVED ORGANIC RADICALS FORMED BY IRRADIATION OF
ARTIFICIAL FOOD COLORINGS IN AQUEOUS SOLUTION

D. R. Kalkwarf and R. N. Diebel

Organic compounds that can form relatively long-lived free radicals in gamma-irradiated aqueous solutions are of interest since their presence in irradiated living systems would slow down the rate of radical chain reactions which extend radiobiological damage. More time would thus be available for natural repair or postirradiation therapy. Several compounds have already been reported⁽¹⁾ to form long-lived radicals in irradiated aqueous solution at room temperature; and now several nontoxic triphenylmethane dyes, often used as artificial food colorings, can be added to the growing list of such compounds. These substances are of particular interest because they have also been shown to be effective chemical protective agents in aqueous biochemical systems.^(2,3)

Following irradiation, aqueous solutions of each of the dyes shown in Table I were examined by electron spin resonance (ESR) spectrometry using a Varian V-4500 instrument with 100 kHz modulation. Deaerated solutions were prepared and handled by techniques described previously,⁽¹⁾ and all solutions were passed through a Millipore HA filter before ESR observation. This latter precaution was taken to remove any solids precipitated during irradiation which would undoubtedly show a stable ESR signal.

Previous results indicated⁽¹⁾ that radicals generally are most stable at either a very high or a very low pH where electrostatic forces retard the

TABLE I. Variation of Structure in Triphenylmethane Dyes

Dye	R ₁	R ₂	R ₃
FD&C Blue No. 1	SO ₃ ⁻	H	H
FD&C Green No. 1	H	H	H
FD&C Green No. 2	H	H	SO ₃ ⁻
FD&C Green No. 3	H	SO ₃ ⁻	OH

combination rate of similarly charged species. Since these dyes decompose in strongly basic solution, dilute sulfuric acid was added to transform the dyes into their more positively charged forms. Previous experience with radiation-induced radicals also suggested that addition of a hydroxyl-radical scavenger such as ethanol would increase the yield of organic radicals formed in deaerated solutions by preventing their oxidation.

All of the dyes listed in Table I except FD&C Green No. 2 were found to form relatively stable radicals in irradiated aqueous solution. In each case, the ESR spectrum was a broad

singlet absorption band with a width of 9.6 gauss at half-maximum intensity. Application of high-resolution techniques failed to resolve any fine structure although shoulders on the spectra suggest a further splitting of about 1.5 gauss. This is illustrated by the spectrum for FD&C Blue No. 1 shown in Figure 1.

Since the ESR spectra themselves give little evidence for the chemical structure of the radicals, chemical effects on their yields were investigated to characterize these species. The ESR spectra of the radicals could be detected in the presence of either 0.5M ethanol or 0.5M methanol but not in the absence of both. This indicated that the radicals were reduction products; however, further experiments are required to distinguish the nature of the reducing species. Addition of molecular oxygen to the radical solu-

tions caused the spectra to disappear rapidly again suggesting that they were reduced forms of the parent dye molecules. In acid solution, such radicals would be expected to have the structure:

With the unpaired spin density concentrated on the central carbon atom, the ESR spectrum would be expected to be the simple singlet observed.

Quantitative evaluations of radical concentrations were made by comparing

FIGURE 1. Electron Spin Resonance Spectrum for $10^{-3}M$ FD&C Blue No. 1 in Aqueous Deaerated $1.0N$ H_2SO_4 - $0.5M$ CH_3OH After Absorbing 6.4×10^4 Rads.

the first moments of the first-derivative spectra for the dye-radicals with those for standard solutions of the stable free radical, Wursters Blue, by the method described previously.⁽⁴⁾ Radical concentrations in the range of 10^{-4} to 10^{-3} mole were readily obtained following absorption of 10^5 Rads. Following irradiation, the radicals disappeared from solution at rates which were second order in radical concentration out to at least 80% complete reaction. This is illustrated in Figure 2, and suggests that the radicals disappear by either disproportionation or dimerization. Table II shows the magnitude of these rate constants and the much slower decay of the radicals in 10N sulfuric acid.

Perhaps the most interesting feature in the chemistry of these dye-radicals is the correlation between the stabilities of the radicals and the abilities of their parent compounds to protect agarose jellies from radiation-induced liquefaction. As described previously,⁽³⁾ FD&C Blue No. 1 offers the greatest chemical protection to this system, followed in order by FD&C Green No. 3, Green No. 2, and Green No. 1; the latter two compounds offer the same

small amount of protection. As seen in Table II, this order is also followed by the rate constants for radical disappearance with radicals from FD&C Green No. 2 disappearing too rapidly to be detectable 15 min after irradiation. As pointed out elsewhere in this report,⁽⁵⁾ flavin mononucleotide, which forms stable radicals in deaerated aqueous solutions,⁽¹⁾ also

FIGURE 2. Second Order Plot of the Decay for FD&C Blue No. 1 Dye-Radicals in 1.0N H_2SO_4 -0.5 CH_3OH at 22 °C (M = moles/liter).

TABLE II. Rate Constants for the Disappearance of Dye Radicals in Aqueous Solutions at 22 °C

Dye	Solvent	k
FD&C Blue No. 1	aqueous 1N H_2SO_4 , 0.5M C_2H_5OH	$3.8 \text{ M}^{-1}\text{sec}^{-1}$
FD&C Blue No. 1	aqueous 1N H_2SO_4 , 0.5M CH_3OH	$3.4 \text{ M}^{-1}\text{sec}^{-1}$
FD&C Blue No. 1	aqueous 10N H_2SO_4 , 0.5M C_2H_5OH	$0.32 \text{ M}^{-1}\text{sec}^{-1}$
FD&C Green No. 3	aqueous 1N H_2SO_4 , 0.5M C_2H_5OH	$2.1 \text{ M}^{-1}\text{sec}^{-1}$
FD&C Green No. 1	aqueous 1N H_2SO_4 , 0.5M C_2H_5OH	$\sim 10.0 \text{ M}^{-1}\text{sec}^{-1}$

protects agarose jellies. It thus appears that compounds which do form relatively stable radicals during irradiation are of value for inhibiting damage and thus present a fresh approach toward the chemical protection of living systems.

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INVESTIGATION OF RADIATION-INDUCED RADICALS IN AQUEOUS SOLUTION OF NITROAROMATIC COMPOUNDS

R. N. Diebel and D. R. Kalkwarf

The surprisingly long lifetimes of free radicals derived from p-nitroaniline and p-nitrobenzoic acid in irradiated aqueous solutions^(1,2,3) suggested that organic compounds in irradiated living organisms might also form radicals which were relatively stable even in water-rich tissue. Such species could have a profound effect upon the development of radiobiological damage. To understand

factors which promote radical stability in aqueous systems, investigation of nitroaromatic radicals has continued^(4,5) and the most recent results are reported herein.

Aqueous solutions of nitrobenzene were irradiated in a flow system⁽⁶⁾ to determine the effect of substituents on radical stability in more detail. In deaerated solutions at pH 13, radicals were formed which produced

the electron spin resonance spectrum shown in Figure 1. This 54-line spectrum is consistent with that expected from the nitrobenzene radical-anion

with a triplet splitting of 14.1 gauss due to the nitrogen nucleus, a triplet splitting of 3.3₅ gauss due to two equivalent ortho-protons, a triplet splitting of 1.1₄ gauss due to two equivalent meta-protons, and a doublet splitting of 3.6₀ gauss due to one para-proton. These spectral features are essentially the same as reported for radicals produced by electro-reduction in aqueous solution⁽⁷⁾ and by the reducing action of dithionite ion.⁽⁸⁾

The nitrobenzene radical-anion was formed in irradiated aqueous solutions by the addition of a hydrated electron to the nitrobenzene molecule. Prior to irradiation, saturation of the solution prior to irradiation with nitrous oxide, an efficient scavenger of hydrated electrons,⁽⁹⁾ prevented the formation of any ESR spectrum. Since traces of oxygen in the solution also prevented formation of the ESR spectrum, commercial nitrous oxide of >99.7% purity was used as the solute. Although reaction of hydrated electrons with nitrous oxide increases the yield of hydroxyl radicals in irradiated solutions, no evidence for production of a hydroxy-substituted aromatic radical was found.

In irradiated aqueous solutions containing other organic solutes, the nitrobenzene radical-anion could be

FIGURE 1. ESR Spectrum of a $9 \times 10^{-3}M$ Solution of Nitrobenzene in Aqueous 0.1M Sodium Hydroxide, Following Gamma-Irradiation.

formed by other mechanisms. In the presence of sodium formate or methanol, the ESR spectral intensity increased by up to five fold and, while saturation of the solution with nitrous oxide reduced the intensity, the spectrum could not be eliminated. Formate and methanol react with hydroxyl radicals to produce the $\dot{\text{CO}}_2^{-(10)}$ and $\dot{\text{CH}}_2\text{O}^{-(11)}$ radicals respectively, and these organic radicals can apparently transfer an electron to nitrobenzene. Griffiths et al.⁽¹²⁾ observed a change in the ESR spectrum of the nitrobenzene radical-anion formed in reaction mixtures of $\text{Ti}^{4+}\text{-H}_2\text{O}_2$ if methanol was present. This was attributed to formation of a charge-transfer complex between $\dot{\text{CH}}_2\text{OH}$ and nitrobenzene. No such change was seen in the ESR spectra of irradiated aqueous solutions of nitrobenzene in the presence of methanol.

Decay of the nitrobenzene radical-anion concentration was found to be a first-order process with a 7 min half-life out to 80% complete reaction. This is considerably longer than the 10 sec half-life attributed to the decay of this radical by Asmus et al.⁽¹¹⁾ who observed the optical absorbance of a species in aqueous nitrobenzene solutions following absorption of 2- μ sec pulses of electrons. The several minute half-life of the nitrobenzene radical-anion is more comparable to that of the p-nitrobenzoic radical-anion than to the much shorter half-life of the p-nitroaniline radical anion.⁽⁵⁾ This suggests that the strong electron-donating effect of the amino group in the latter radical is effective in promoting its further

reaction. A decay process which could utilize this effect and which would also be first order in radical concentration is simply the release of the added electron by the nitroaromatic radical-anion to the aqueous environment where it would be consumed by other processes.

Efforts to remove molecular oxygen more completely from the irradiated solutions were continued by elimination of glass-joints and replacement of stopcocks with needle valves in the flow system. As a result, the p-nitrobenzoate radical-anion, formerly not detected below a pH of 10⁽⁵⁾, was observed at pH 6.8.

Other experiments with p-nitrobenzoate in alkaline solutions showed that prolonged irradiation produced additional detail in the ESR spectra of the solutions. As shown in Figure 2, several new lines were added to the usual 27-line spectrum of the p-nitrobenzoate radical-anion.⁽⁴⁾ These are most clearly seen between the triplet bands in the spectrum of the latter radical; however, they also overlap the triplet bands themselves. While the source of these lines has not been identified, their intensities were found to increase initially after irradiation and at the same rate as the initial decay of the p-nitrobenzoate radical-anion lines. After approximately 15 minutes, both groups of lines decayed in intensity at approximately the same rate. Further examination of this phenomenon should reveal more aspects of the reactions of radiation-induced radicals in aqueous systems.

FIGURE 2. Partial ESR Spectrum of a $1 \times 10^{-3}M$ Solution of *p*-Nitrobenzoate Ion in Aqueous 0.1M Sodium Hydroxide Following Absorption of 3×10^5 Rads of ^{60}Co -Gamma Radiation. The portion shown lies between the major peaks in two triplet bands of the *p*-nitrobenzoate radical-anion spectrum.

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EFFECT OF ADDED SOLUTES ON THE STABILITY OF ORGANIC RADICALS IN AQUEOUS SOLUTION

D. R. Kalkwarf

The observation reported earlier⁽¹⁾ that radiation-induced radicals derived from methylene blue could be stabilized in concentrated aqueous solutions of sodium sulfate at pH 7 instigated a further series of experiments exploring the effect of various aqueous environments on organic-radical stability. Such measurements are of particular importance in radiobiology since many solutes are available in a living organism to either react with or stabilize free radicals formed as a result of irradiation. Environments which stabilized particular radicals could slow down the development of radiobiological damage and thus increase the time available for natural repair and postirradiation therapy.

The yield and stability of the radical formed by irradiation of methylene blue in aqueous 2M Na₂SO₄ was investigated further. As pointed out earlier,⁽¹⁾ the ESR spectrum obtained for this species, while composed of at least 30 lines, is not sufficiently resolved to specify the chemical structure; however, the reaction of this radical with molecular oxygen and its

formation in the presence of hydroxyl-radical scavengers suggest that it is a reduction product of methylene blue. The initial yield of this radical in deaerated solutions was found to be $G = 1.0$ radical/100 eV in either H₂O, 2M Na₂SO₄, or 60% aqueous sucrose solution. However, the actual concentrations of radicals obtainable in the latter two solutions were substantially greater than in pure water due to the difference in decay rates. Figure 1 shows how the radical concentration varied with absorbed dose and that eventually it decreased due to either further reduction or oxidative degradation. These values were obtained by comparing first moments of the spectra for the dye radicals with those for standard solutions of the stable free radical, Wursters Blue, by the method described previously.⁽²⁾ Although unfiltered solutions were measured to obtain the values shown, measurements on the same samples after filtration through a Millipore HA filter differed by less than 30%. This small decrease was attributed to reaction of the radicals with the filter

FIGURE 1. Yield of Methylene Blue Radicals Formed by γ -Irradiation of $1.00 \times 10^{-3}M$ Methylene Blue in Various Aqueous Media

materials, and it was concluded that the values shown in Figure 1 represent radicals in true solution rather than on suspended solid particles.

The rate of disappearance of the methylene blue radical in the absence of molecular oxygen was extremely slow. In water, the self-reaction rate constant was found to be $0.3M^{-1}sec^{-1}$, while in $2M Na_2SO_4$, the intensities of the ESR spectra remained constant to within 10% for at least 60 hr. This contrasts sharply with the results of Parker⁽³⁾ who measured the value $1.5 \times 10^9 M^{-1}sec^{-1}$ for the self-reaction rate constant of the radical formed in photoreduced methylene blue.

On exposure to molecular oxygen, the concentration of methylene blue radicals decreases; however, here also, the effect of $2M Na_2SO_4$ is to slow the reaction. In air-saturated water, the rate constant for reaction between the radicals and molecular oxygen was found

to be $6.0M^{-1}sec^{-1}$; while in air-saturated $2M Na_2SO_4$, the corresponding rate is only $2.8M^{-1}sec^{-1}$. While these rate constants are far smaller than those expected for encounter-controlled reactions, they are inversely proportional to the viscosities of the media. The reactions are so slow in fact that no precautions need to be taken to exclude air from the solutions during irradiation in order to observe the radical spectrum for several minutes after irradiation.

As seen from Figure 1, 60% aqueous sucrose is also a stabilizing environment for the methylene blue radicals and, in the absence of air, the radicals are stable for days in this medium. The ESR spectrum of the radicals does not contain the hyperfine structure shown by radicals in $2M Na_2SO_4$, but consists merely of a broad singlet absorption. This is probably due to the 20 fold greater viscosity of the sucrose solution which tends to increase the anisotropic dipolar interaction between the unpaired electron and nuclear moments, flattening out the fine structure.

Aqueous solutions of 60% sucrose were also found to stabilize radicals formed from flavin mononucleotide. As reported earlier,⁽¹⁾ flavin mononucleotide forms a transient free radical in irradiated neutral solutions which decays completely within a few minutes. In aqueous 60% sucrose, a broad singlet ESR spectrum was observed after irradiation of either deoxygenated or air-saturated solutions; see Figure 2. The intensity of this spectrum remained constant for at least a day following irradiation.

FIGURE 2. ESR Spectrum of Radicals Produced by Irradiating an Air-Saturated Solution of Flavin Mononucleotide in Aqueous 60% Sucrose. Absorbed Dose Equalled 2.5×10^5 Rads; Irradiated solution was filtered before examination.

The aqueous environments provided organic radicals by $2M$ Na_2SO_4 and 60% sucrose would seem to be considerably different in electrostatic-force fields and hydrogen-bonded structure, yet both inhibited the self-reaction of at least two organic radicals. In irradiated biological systems, free radicals could be formed in many different environments and their abilities to promote radiobiological damage by initiating radical-chain reactions would be greatly influenced by the medium in which they were formed. Further analysis of these environmental factors thus appears to offer a new and useful technique for understanding the differences in radiation sensitivity of biological systems.

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FURTHER STUDIES ON THE CHEMICAL PROTECTION OF
AGAROSE JELLIES FROM RADIATION DAMAGE

D. R. Kalkwarf

As described earlier,⁽¹⁾ several nontoxic artificial food colorings have been found effective in protecting aqueous jellies of the polysaccharide--agarose--from radiation-induced liquefaction. Since the physical state of many regions in living tissue is that of an aqueous jelly, compounds which can protect such structures from radiation damage are of particular interest in the search for chemical methods to protect humans subjected to ionizing radiation and also for protecting the texture of radiation-processed food-stuffs. For this reason, additional experiments were performed to determine the role of the dyes in protecting the jellies and to observe the effect of other nontoxic additives.

First, the possibility of synergistic effect of the dyes was explored. In previous experiments,⁽¹⁾ FD&C No. 1, a triphenylmethane dye, and FD&C Blue No. 2, an indigo dye, were found to be the most efficient protective agents for agarose jellies from among the group of artificial food colorings tested. When present at a concentration of $8 \times 10^{-3} \text{ M}$ in 0.2% agarose jellies, these dyes increased the radiation dose required to liquify the jellies by factors of 14 and 15 respectively. To determine the effectiveness of a mixture of these dyes at the same molecular concentration, agarose jellies containing both FD&C Blue No. 1 and FD&C Blue No. 2, each at $4 \times 10^{-3} \text{ M}$, were prepared and the liquefaction dose was found to

be 17 times that required to liquefy the unprotected jelly.

More information was also needed to determine the mechanism by which these dyes protect the jelly structure. Since the dyes were incorporated into the jelly by dissolving them in molten agarose and letting the jelly form on cooling, a possible mechanism was the formation of a more radiation-resistant structure between the dyes and agarose during the solidification procedure. This was disproved, however, by incorporating the dyes into solid agarose jellies by diffusion and noting no change in their protective efficiency. This is also the mode of incorporation which would have to be used on biological organisms.

Nitrous oxide has proved to be a valuable diagnostic reagent for radiation-induced reactions in aqueous systems because it converts hydrated electrons rapidly to hydroxyl radicals according to the equation:

Saturation of 0.2% agarose jellies with nitrous oxide lowered the liquefaction dose to 0.6 times that required to liquefy the untreated jelly, supporting the hypothesis that the jellies are liquefied by chemical reactions with hydroxyl radicals.

During the irradiation, the degradation of the agarose chains was also followed to determine the magnitude of the process occurring. The unirradiated product was found to have

a viscosity-average molecular weight of 55,000 by measuring its intrinsic viscosity $[\eta]$ and using the equation,

$$\bar{M}_v = 2.7 \times 10^3 [\eta],$$

found to be applicable to aqueous solutions of agar.⁽²⁾ This equation was also assumed to describe irradiated agarose solutions, and viscosity measurements on unprotected agarose solutions which had received the liquefaction dose of 0.63 MRad⁽¹⁾ revealed that the viscosity-average molecular weight had been reduced to 3000. Since the above equation for molecular weight is linear in intrinsic viscosity, the viscosity-average molecular weight is equal to twice the number-average molecular weight;⁽³⁾ and the radiation yield of polymer chain breaks at the liquefaction point could be calculated to be $G = 1.9$ chain breaks/100 eV absorbed. This value is close to the radiation yield of hydroxyl radicals, $G_{OH} = 2.4$, and indicates that hydroxyl-radical attack on the agarose chains is a reasonable mechanism for liquefaction of the jellies.

To understand the role of chemical protective agents for the agarose jelly system, other nontoxic compounds were tested for their protective effect. Of these, flavin mononucleotide showed outstanding protection as illustrated in Figure 1, where the dose extension factor refers to the ratio of the liquefaction dose in the presence of the protective agent to that in its absence. While flavin mononucleotide is an efficient OH-scavenger, whose rate constant for reaction with hydroxyl radical is 0.37 times that of FD&C

Blue No. 1 as measured by the dye-competition technique,⁽⁴⁾ it also forms stable free radicals in deaerated aqueous solutions by addition of a hydrated electron.⁽⁵⁾ This capability may allow flavin mononucleotide to function as a particularly efficient mediator for neutralizing the damaging effects of both the hydrated electrons and the hydroxyl radicals formed by water radiolysis. By forming a stable, one-electron reduction product with the hydrated electron, it may be able to react subsequently with hydroxyl radical to give the original structure without further oxidative degradation. In this way, one flavin mononucleotide molecule could counterbalance several hydrated electron-hydroxyl radical pairs before hydroxyl radical attack eventually degraded the molecule to the state where it lost this capability. In any case, flavin mononucleotide is an outstanding protective agent for agarose jellies, extending the liquefaction dose by factors of up to 18 times that required to liquefy the unprotected jellies.

FIGURE 1. Extension to Liquefaction Dose of 0.20% Agarose Jellies Provided by Addition of Flavin Mononucleotide.

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PULSE RADIOLYSIS STUDIES IX. REACTIONS
OF THE OZONIDE ION IN AQUEOUS SOLUTION*

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and Leon M. Dorfman

The radiation chemistry of strongly basic aqueous solutions containing oxygen and nitrous oxide has been investigated by the pulse radiolysis method with particular attention to the decay kinetics of the ozonide ion. The apparent discrepancies in the literature concerning the kinetic order of the ozonide decay may be understood as an effect of pulse intensity and oxygen concentration.

Absolute rate constants have been determined for the following reactions at 25 °C:

as determined by competitive kinetics based on a rate constant of $2.5 \times 10^9 M^{-1} sec^{-1}$ for the reaction $O^- + O_2$.

The rate constant for the reaction $O_3^- + O_3^-$ is substantially lower than previously reported and shows an inverse functional dependence on the oxygen concentration. This rate constant, at pH 13.5, seems to be leveling off at a value of $2k = (0.9 \pm 0.2) \times 10^6 M^{-1} sec^{-1}$ at $[O_2] = 3.1 \times 10^{-3} M$, the highest oxygen concentration we attained. This value is based on our determination of $\epsilon_{O_3}^{4300} = 1900 \pm 120 M^{-1} cm^{-1}$ for the molar extinction coefficient of the ozonide ion at 4300 Å.

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** Based on work performed while on assigned leave at Ohio State University.

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APPLICATION OF AN ANALOG SIMULATOR PROGRAM
TO OZONIDE ION DECAY KINETICS

W. D. Felix

A proposed reaction mechanism is often accepted or rejected by comparison of the experimental concentration-time data with those predicted by the mechanism. In differential form the rate equations for the assumed mechanism may appear simple; however, their analytical solutions are usually difficult if possible at all.

Application of digital computer techniques to the analysis of systems of nonlinear differential equations has helped ease the solutions of complex chemical reaction-rate equations. Experimentally determined values for the concentrations of the reacting species can be combined with assumed values for the rate constants and an integrated theoretical rate curve can be determined. Dependent on the success of the attempted fit, values for the rate parameters can be changed and the calculations repeated until the theoretical curves are reconciled with the data or until the operator concludes that the mechanism is incompatible with the data. Many iterations may be required for a reasonable fit. If explicit concentrations for the proposed interacting species cannot be uniquely determined, the com-

plexity of the problem increases. For example, when spectrophotometric techniques are employed, several absorption peaks may overlap. The unraveling of absorbances of specific species then becomes interrelated with the solution of the rate-equations. For these complex systems, analog or analog simulation techniques become extremely valuable. Analog simulation techniques are usually digital computer programs which combine the programming flexibility of the analog computer with the reliability of the digital computer. One such program, MIMIC, developed at Wright Patterson AFB, uses a high order Runge-Kutta method of integration.⁽¹⁾ Programming parallels the written equations to be solved.

As an example of the use of an analog simulation technique as applied to the study of reaction kinetics, MIMIC was used for an analysis of formation and decay data of the species absorbing in the ultraviolet region concurrent with ozonide ion (O_3^-) decay. One mechanism which has been proposed for the decay of the ozonide ion would account for the inverse dependence on oxygen concentration.⁽²⁾

$$2k_1 = 1 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1} \text{ }^{(3,4)} \quad (1)$$

$$\text{very rapid} \quad (2)$$

$$k_3 = 1.7 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1} \text{ }^{(5)} \quad (3)$$

$$k_4 = 250 \text{ sec}^{-1(6)} \quad (4)$$

$$k_5 = 8.9 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1(3,4)} \quad (5)$$

The rate of decay of the ozonide dimer was assumed to be much more rapid than its rate of formation.

Thus, the differential equations to be solved were

$$\begin{aligned} \frac{d(O_3^-)}{dt} = & 2k_1(O_3^-)^2 + k_4(O_3^-) \\ & + k_5(O_3^-)(HOO^-) \\ & - k_2(O_6^{=})(O_2) \end{aligned} \quad (6)$$

$$\frac{-d(HOO^-)}{dt} = k_5(O_3^-)(HOO^-) \quad (7)$$

$$\begin{aligned} \frac{d(O_2^-)}{dt} = & -2k_3(O_2^-) \\ & + k_2(O_6^{=})(O_2) \end{aligned} \quad (8)$$

$$\frac{d(O_3)}{dt} = k_2(O_6^{=})(O_2) \quad (9)$$

$$\begin{aligned} \frac{d(O_6^{=})}{dt} = & -k_2(O_6^{=})(O_2) \\ & + k_1(O_3^-)^2 \end{aligned} \quad (10)$$

Making the steady state assumption for $O_6^{=}$,

$$k_2(O_6^{=})(O_2) = k_1(O_3^-)^2 \quad (11)$$

Equation (6) becomes

$$\begin{aligned} \frac{-d(O_3^-)}{dt} = & k_1(O_3^-)^2 + k_4(O_3^-) \\ & + k_5(O_3^-)(HOO^-) \end{aligned} \quad (12)$$

The spectrophotometric parameters for the ozonide absorption in the ultra-violet were treated as unknowns. Recently Thomas et al.⁽⁷⁾ presented an observed absorption spectrum in the ultraviolet ascribed to the hydroxyl radical. In neutral solution, the peak maximum was at 210 nm with a molar absorptivity of $885 \text{ M}^{-1} \text{ cm}^{-1}$. Thus it would not be unexpected to find that O_3^- absorbs in the same region. Adams et al. have, in fact, obtained experimental evidence for the ultraviolet absorption of ozonide.⁽⁴⁾ The unknown parameters were then the absorptivity, band width, and wavelength at maximum absorbance for O_3^- . Adjustment in these values was made during the course of the calculations toward the reproduction of the experimental results. The spectrophotometric parameters for O_3^- , O_2^- , and HOO^- were taken from their absorption spectra as reported in the literature^(5,6,7) and are given in Table I.

The absorption spectrum of each of the species was calculated using a student "t" distribution

TABLE I. Spectrophotometric Parameters of Ultraviolet Absorbing Species in Ozonide Decay, Proposed Mechanism

Species	λ_{max} , nm	Half width at half maximum	$\epsilon_{\lambda_{\text{max}}}$	Reference
O_3	260	11.8	3650	(8)
O_2^-	240	18.5	1060	(5)
HOO^-	216	18.6	460	(9)
O^-	210	--	885	(7)

$$y = y_0 \left\{ \frac{1}{1 + \frac{(x - x_0)^2}{\sigma}} \right\}^2$$

where x_0 is the wavelength at peak maximum having an absorption y_0 . The constant, σ , was determined by the half width at half maximum,

$$\sigma = \frac{x_a - x_0}{0.648}$$

where x_a is the wavelength at half maximum. This distribution has been found to give much better approximation to real absorption spectra than does either the Lorentzian or the Gaussian distribution.⁽¹⁰⁾

The MIMIC program analog flow chart is shown in Figure 1 for the Equations (7) through (10) and (12). The program determined the concentrations of HOO^- , O_2^- , and O_3 , and O_3^- at incremented times following the synthetic pulse. The initial concentrations of O_3^- from the synthetic pulse were given as $1 \times 10^{-4} \text{M}$ with $(\text{HOO}^-)_0$ and $(\text{O}_2^-)_0$ being 10% of that; the 10% value arose from a consideration of the relative rates of formation and G values of HOO^- and O_2^- . A $2k_1$ value of $1 \times 10^7 \text{M}^{-1} \text{sec}^{-1}$ was used corresponding to an oxygen concentration of $3 \times 10^{-4} \text{M}$.⁽²⁾

To begin the analysis, estimated values for the unknown parameters were chosen for O_3^- . These parameters were then modified until a reasonable fit to the available data was found. An example of the fit for one set of these parameters is shown in Figure 2.

Processing time on a UNIVAC 1107 computer was 1.25 min for the compilation of the machine language program, the computation of concentrations of the four species, and summing of the total absorption at 20 different wavelengths for four different sets of parameters. Calculations for each set of parameters were made from synthetic time 0 to 1.0 msec incremented by 100 μsec and from 0 to 7 msec incremented in 1 msec steps. Figure 3 shows the experimental absorption spectra of the ultraviolet-absorbing species formed during radiolysis of aerated, alkaline water. These results were obtained on the Ohio State University accelerator. A qualitative comparison shows that the longer wavelength peak occurs in nearly the same position as found in the synthetic curve.

The decay behavior of the species absorbing at 220 nm is not satisfactorily accounted for in the synthetic system. If the self-reaction rate of the O_2^- were too large, a rapid

FIGURE 1. Analog Flow Diagram for MIMIC Program. X_i , Y_i , Z_i are absorption factors at wavelengths λ ; S is the $1/2$ width at $1/2$ maximum.

FIGURE 2. Synthetic Curves of the Complex Ultraviolet Spectrum at Various Times After the Imaginary Electron Pulse. [Curves created by program MIMIC with assumed initial conditions: $(\text{HOO}^-)_0 = 1 \times 10^{-5} \text{M}$; $(\text{O}_2)_0 = 1 \times 10^{-5} \text{M}$; $(\text{O}_3)_0 = 1 \times 10^{-4} \text{M}$. Ozonide parameters: absorption peak at 215 nm; width at half maximum, 17.5 nm; absorptivity, $1500 \text{M}^{-1} \text{cm}^{-1}$.]

decay of the 240 region would be anticipated. However, Heidt, in a recent review of oxygenated water chemistry, reports that he was unable to detect an EPR signal from photolyzed, alkaline water and concluded that O_2^- could not be responsible for the long-lived ultraviolet peak.⁽¹¹⁾ Two alternative explanations must also be explored. Noise levels in the spectrophotometric

system were such that the experimental data at wavelengths shorter than 230 nm are less reliable than at the higher wavelengths. Improvements need to be made in ultraviolet signal detection. Secondly, it is possible that other absorbing species have been neglected.

The use of analog simulation techniques has thus allowed visualization

FIGURE 3. Absorption Spectra Observed in the Far Ultraviolet Following a 1.6 μ sec Pulse of Electrons. (The dose was approximately 2×10^{18} eV/g at 2-3 MeV. The solution was approximately $1.1 \times 10^{-2}M$ and $7 \times 10^{-4}M$ in N_2O and O_2 , respectively, at a pH 13.7.

of a rather complex mechanism with multiple overlap of absorbing species. Such visualization is of considerable value in determining which experimental steps should be taken to further elucidate the mechanism.

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ELECTRON PULSE RADIOLYSIS USING SWEEP BEAMS
FROM A 2 MeV VAN de GRAAFF ACCELERATOR

W. D. Felix

In the relatively short time since the development of pulse radiolysis techniques, a great deal of new information on the mechanisms of reactions of radiation chemistry has been generated. Observations have been made of organic and inorganic free radicals, molecular ions, the solvated electron in polar liquids, and triplet electronic states of aromatic molecules. Absorption spectra of the transient species have been recorded and rate constants calculated over a wide range of molecular species.

While this early phase of the development of the pulse-radiolysis methodology emphasized the generation of very short pulses and the detection of the extremely short-lived transients, the reactions of longer-lived secondary intermediates are equally important. It is these reactions of intermediate radicals and molecular species which produce biological damage, and an understanding of their mechanisms can illuminate the problem of radiation protection.

To investigate long-lived intermediates formed during irradiation, a 2 MeV Van de Graaff has been converted to pulsed operation. An earlier version of this system has been reported.⁽¹⁾ However, because of the failure of certain components under high voltage conditions, pulses were not reproducible. A modification of the Van de Graaff at the high voltage terminal was also attempted. Size restrictions, however, led to the use of components which

could not withstand the transient charges from internal sparking.

The system presently used employs a beam deflection assembly that utilizes a thyatron for the high voltage switching. In operation, electrons travel down the flight tube past a single plate charged to 8000 V. The electrons are thereby deflected into a graphite block located immediately outside the thin aluminum exit window. Momentary interruption of the potential on the plate allows the electrons to pass through a slit (3 mm x 8 mm) in the graphite block. Pulse widths of 0.1 to 10 msec are normally used. The trigger and plate charging circuits are shown in Figure 1.

Background dose was minimal when the machine operated with the beam in the deflected position. However, when integrated over a time period of seconds and when compared to a pulse length of milliseconds, the background dose contributed a major part of the total dose received by the sample. A significant dose was also received when the machine was first turned on at the beginning of an experiment. To reduce the background dose, a lead shutter arrangement was devised to operate synchronously with the beam sweep so that it would open for only a few milliseconds before and after the pulse.

Transient species were detected photometrically. Two low-resolution, high-aperture monochromators were used to monitor white light passed through

FIGURE 1. Beam Sweeping Circuit.
(Upper section located in control room,
lower section in accelerator room.
Trigger pulse to thyatron is 150 V,
5 μsec wide. The electron pulse width
is determined by the capacitance in
the lower circuit.)

the sample cell. Intensity levels of the light at selected wavelengths were monitored by 1P28 photomultiplier tubes. At the slow pulsing rate used, it was necessary to have a very stable light source. Arc lamps such as the superpressure mercury-xenon lamps which are most frequently used for pulse radiolysis work give a fluctuating light output during operation due to wandering of the arc. Because of their excellent stability, quartz halogen lamps have proved most effective as light sources.

Signals from the photomultiplier were fed into an impedance matching box, the circuit of which is shown in

Figure 2. With this circuit, the signals were driven from the photomultiplier tube through 100 ft of 93 Ω cable to an oscilloscope in the control room. By switching in different capacitances across the operational amplifier, the rise time of the cable driver could be selected to give the optimum signal-to-noise ratio while remaining compatible with the half time of the transient response.

An example of the results from a pulse radiolysis experiment with the present equipment is shown in Figure 3. The species was formed in pulse irradiated, alkaline, air saturated water (0.5N NaOH). The absorption recorded

FIGURE 2. Current to Voltage Transistor and Cable Driver. A circuit (for RG62U Cable). Bias circuit used to zero initial output to facilitate amplification of the change in absorbance as observed on the oscilloscope.

at 430 nm corresponds to the ozonide ion. The signal was ac coupled and represents an expansion from a 3.7 V dc signal at zero time. The maximum absorption corresponds to a concentration of 5.1×10^{-6} M ozonide or an absorbed dose of 1500 Rads [calculations assume that $G_0^- = 3.3$ at pH 13.7 and $\epsilon_{O_3^-}(430 \text{ nm}) = 1900$].⁽²⁾ The calculated rate constant for the first order decay is 360 sec^{-1} and is in

agreement with previous work done under conditions of higher radiation intensities and shorter pulse lengths.⁽³⁾

The system as presently developed represents a convenient technique for measuring the production and decay of long-lived transients formed following low intensity bursts of electrons. The effect of irradiation at the dose level near the biological LD_{50} for many species can thus be conveniently

FIGURE 3. Decay of Ozonide Ion at 430 nm in an Air-Saturated Solution, pH 13.5. Upper curve: Absorption curve showing formation of O_3^- during pulse and subsequent decay. Ac coupled, 0.05 V/cm, 2 msec/cm. Pre-pulse photomultiplier signal was 3.7 V. Lower curve: Beam pulse, 0.05 V/cm, 2 msec/cm.

explored. Successful operation at low intensity irradiation levels depends on optimization of the signal-to-noise ratio. Although the low noise

characteristics of the present system have been encouraging, further noise reduction may well be achieved optically by using multiple light paths, and electronically by adding filtering to the power supplies and by cooling the photomultiplier tubes. The contribution of Mr. E. M. Sheen of the Instrumentation Section, Battelle-Northwest, in designing the electronic circuitry described here is gratefully acknowledged.

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RADIOLOGICAL PHYSICSINSTRUMENTATION FOR TIME-RESOLVED SPECTROMETRY

L. L. Nichols and W. E. Wilson

Because of their widespread use in the detection of ionizing radiation, scintillating solids, liquids, and gases have been the subject of a continuing research effort. With commercially available fast electronic equipment, one can measure, by the delayed coincidence technique, excited-state lifetimes in the region of 10^{-10} seconds.⁽¹⁾

S. Heron, et al.⁽²⁾ first applied the delayed coincidence method to the measurement of atomic lifetimes; researchers have since provided variations and improvements.^(3,4) This report describes a system for atomic lifetime measurements with still further improvements. A novel feature of the system is the use of pulses of high energy (up to 2 MeV) protons for excitation rather than the more conventional electron gun.

A block diagram of the apparatus is shown in Figure 1. A beam of protons from a Van de Graaff accelerator is chopped into pulses of 1 to 3 nsec width by a crystal controlled oscillator. The protons pass through a 2.54×10^{-4} cm thick nickel foil into the target chamber where they ionize and excite the gas under investigation.

The gas target chamber is an aluminum cylinder 5 cm in diameter and 15 cm long. A viewing port at 90° to the cylinder has a fused quartz window for maximum transmission of ultraviolet. The proton pulse enters

the chamber on axis and has a cross-sectional area of approximately 14 mm^2 . The pressure is measured with calibrated gauges. The chamber is evacuated with a liquid nitrogen trapped fore pump for several hours before target gases are admitted to the chamber.

A 0.5 m Ebert scanning spectrometer analyzes the radiation emitted at 90° from the direction of the incident proton beam. Quartz lenses focus a short section of beam path on the entrance slit of the spectrometer. Rotation of the spectrometer grating allows any spectral line in the 250.0 to 800.0 nm range to be focused on the exit slit of the spectrometer where a suitable photomultiplier tube is positioned.

The major components of the delayed coincidence system consist of a commercial time-to-amplitude converter (TAC) and a multichannel analyzer that is programmed by a small on-line digital computer. Other necessary electronics include two discriminators, a zero crossing detector, and two wide band amplifiers. A count rate meter and chart recorder are used to record the emission spectra as a function of wavelength.

The start pulse for the time-to-amplitude converter is derived from the r.f. oscillator. The sine wave signal from the oscillator is sent through a delay line and a zero crossover detector⁽⁵⁾ to a pulse shaping trigger whose output is applied to the start

Neg 0670193-4

FIGURE 1. Block Diagram of Apparatus for Time Resolved Spectrometry Measurements

input of the TAC. The zero crossover detector prevents the start pulse from shifting in phase when the amplitude of the chopping oscillator is changed. The stop pulse for the TAC is obtained from the PM tube at the exit slit of the spectrometer. This signal is amplified by two cascaded wide band amplifiers and then sent to a discriminator trigger which provides the proper pulse shaping to trigger the

stop input of the TAC. By deriving the start pulse from the r.f. oscillator, the major portion of the time spectrum is stored in lower channel numbers, thus reducing average dead time.

The programmable multichannel analyzer accumulates and displays the output of the TAC. Software programs are used to subtract the background due to PM tube dark current and to calculate the lifetime. The total

time required to complete a lifetime measurement is as short as four minutes in the most favorable cases. The memory size of the on-line computer limits the data analysis to single exponentials. If two or more exponentials are involved in the spectral decay then the interval between beam pulses must be several times greater than the maximum lifetime of interest; this is necessary to prevent overlap of excitation. However, when the spectral decay is a single exponential, the time between pulses need be only long enough to achieve a statistically significant distribution for analysis.

Care must be taken to insure that the probability of detecting a photon per pulse is considerably less than unity. This is a necessary condition for assuming that the mean lifetime can be obtained from the observed distribution of time intervals. To demonstrate the time resolution of the system, helium at 760 Torr pressure was introduced into the target chamber. At this pressure, the (observed) lifetime is shortened by collisions to a time much less than the electronic resolution. In this manner, it was possible to obtain the prompt spectrum shown in Figure 2. The full width at half maximum of this semilog distribution is 3.26 nsec, and the slope at 1/5 maximum gives an e-folding time of 0.8 nsec which places the lower limit for lifetime measurements at about 1.0 nsec.

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FIGURE 2. Prompt Spectrum Obtained with Collision Quenched Helium Emission at $\lambda = 501.6$ nm

OPTICAL EMISSION FROM PROTON IRRADIATION OF GASES

L. L. Nichols and W. E. Wilson

In the radiation physics, there is considerable interest in the relaxation processes in short lived (10^{-5} to 10^{-9} sec) excited states in gases irradiated by ionizing radiation. Mean lifetimes in this time region can be measured by time resolved spectroscopy using delayed coincidence counting techniques. A description of the experimental apparatus and techniques is given in the preceding report. A brief collection of some preliminary results is presented here to illustrate the performance and capabilities of the experimental system.

Figure 1 shows a typical set of raw data as displayed by the programmable

multichannel analyzer. The mean lifetime (all lifetimes referred to in this report are the reciprocal of the decay constant) of the transition is calculated by measuring the slope of the single exponential decay. This calculation is done by a software program within the analyzer so that the only output consists of a single value of the lifetime. Table I lists the results of our measurements of helium lifetimes along with values reported by other workers; the agreement is taken as evidence that the system is operating reliably. The lifetime of the 3^1P level showed a pronounced pressure dependence which

FIGURE 1. A Typical Semilogarithmic Plot of the Data. This sample is emission from helium at $\lambda = 501.6 \text{ nm}$ and pressure of 4 Torr.

TABLE I. Lifetimes of Levels of Helium

Level	3^1P	4^1D	4^3S
Wavelength, nm	501.6	492.2	471.3
	τ , nsec		
Pendleton & Hughes ^(a)	72 ± 1	47 ± 5	68 ± 1
Holzberlein ^(b)		35 ± 4	59 ± 6
Kindlmann & Bennett ^(c)	71 ± 5	33 ± 6	65 ± 4
Present Work	73 ± 5	43 ± 5	65 ± 3
Theoretical ^(d)	73.2	37.8	63.8

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(b) T. M. Holzberlein. "Direct Measurement of Atomic Lifetimes: Helium," *Rev. Sci. Instr.*, vol. 35, p. 1041. 1964.

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has been investigated and reported previously.⁽¹⁾

Tank nitrogen, which had been dried and purified by passing it through liquid N_2 cooled traps, was put into the target cell and the lifetimes of N_2^+ (0,0) and N_2 (0,0) transitions were measured. The 391.4 nm transition of N_2^+ was measured to be 65.9 ± 1 nsec and the 337.1 nm transition of the second positive system of N_2 was found to be 46.3 ± 1 nsec. These values agree quite well with the lifetimes reported by Bennett and Dalby⁽²⁾ of 65.8 ± 3.5 and 44.5 ± 6 , respectively.

Table II shows lifetimes of several vibrational levels measured as a function of pressure. The error is ± 0.2 nsec based on probable errors using several determinations. Figure 2 shows some of the data in Table II plotted

versus pressure. Extrapolated values of the data at zero pressure correspond to lifetimes of 45.4 nsec for N_2 (0,0), which agrees well with the above value, and 31.2 nsec for N_2 (1,0).

The sensitivity of the system is quite low at gas pressures below 0.05 Torr. The efficiency of the optical collection-detection system and the maximum proton beam current available force this limitation. To get optimum use of accelerator time, lifetime measurements may be determined by extrapolating the data to zero pressure. For nitrogen at a pressure of 0.05 Torr or less, a typical data run required 2 to 3 hr depending on the intensity of the line. At pressures above a few Torr, a collision quenched measurement can be made in just a few minutes and with very good statistical accuracy.

TABLE II. Collision Quenched Lifetimes of States in N_2

Pressure, Torr	Vibrational Band Wavelength, nm	τ , nsec				
		0,0	0,1	0,2	1,0	1,4
		337.1	357.7	380.5	315.9	399.8
395		5.5	5.6	5.5	2.9	2.8
300		7.0	7.1	7.2	3.7	3.5
100		15.9	16.1	16.1	8.9	8.5
50		24.3	24.9	24.9	14.0	13.6

FIGURE 2. Pressure Dependence of the Lifetime in the Second Positive System of Nitrogen

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IONIZATION IN THIN TISSUE-LIKE GAS LAYERS BY MONOENERGETIC PROTONS*

W. A. Glass and D. N. Samsky

The ionization resulting from the passage of monoenergetic protons through thin layers of tissue-like gas has been measured. Samples equivalent to 0.3, 0.5, and 1.0 micron of unit density absorber were investigated for incident proton energies ranging from a few keV to about 2 MeV. Results are presented showing the mean rate of ionization as a function of incident proton energy. Maximum values for the mean rate of ionization were found to be 104, 103, and 101 keV/ μ m for samples of 0.3, 0.5, and 1.0 micron, respectively.

* This paper has been accepted for publication by Radiation Research Society.

ENERGY STRAGGLING IN THIN TISSUE-LIKE ABSORBERS

W. A. Glass and D. N. Samsky

As a beam of monoenergetic protons traverses a thin absorber, there is a variation in the energy lost by the individual protons. This variation, referred to as energy-loss straggling, results because the energy lost by individual protons is given up in a finite number of independent collisions with the atomic electrons of the absorber. The energy transferred in each collision as well as the number of collisions is subject to statistical variation and depends on the nature of the absorber and the energy of the incident proton. The energy-loss straggling of protons has been treated theoretically by a number of authors^(1,2,3,4) since 1944. The most complete analysis of the problem was presented by P. V. Vavilov in 1956.⁽³⁾ Since then, S. M. Seltzer and M. J. Berger⁽⁵⁾ of the National Bureau of Standards have tabulated energy-loss distributions according to the Vavilov theory for representative

values of generalized parameters and have presented experimental results which show good agreement of 37-MeV protons.

It is the purpose of this report to compare the results obtained for ionization losses of low energy protons in very thin layers of tissue-like gas ($\sim 10^{-5}$ g/cm²) with the Seltzer and Berger tabulations. The shape of the distribution depends on the ratio of the mean energy-loss to the maximum energy ($\epsilon_{\max}$) that can be given up in a single collision between the proton and an electron. This shape parameter is called κ .

$$\kappa = \frac{\xi}{\epsilon_{\max}}$$

where

$$\xi = \frac{2\sigma}{\beta^2} \frac{mc^2 x}{\beta^2}$$

and

$$\epsilon_{\max} = \frac{4E}{M/m}$$

In the above expressions, σ is the classical radius of an electron, m is the mass of an electron, c is the velocity of light, β is the ratio of the velocity of the proton to that of light, E represents the energy of the proton, and M is the mass of the proton. For TE gas, κ has a value of $1.66 \frac{x}{E^2}$ with x in units of micrometers of unit density material and E in MeV. The experimental distributions reported are for values of κ of 0.07 and 0.4 with absorber thicknesses between 0.1 and 1.0 μm of unit density material.

The distributions were measured by collecting the electrons from the ionization produced in a well-defined layer of gas through which a micro-beam of monoenergetic protons was passed. The collected electrons then entered a proportional counter. After amplification, the proportional counter signals were sorted and stored in a multichannel analyzer. A detailed

description of the proportional counter and the apparatus for producing the proton micro-beam can be found in other articles appearing in this annual report.

Figures 1 and 2 show the experimental data compared with the theoretical distributions. Since κ depends on both the absorber thickness and the proton energy, we have shown more than one experimental distribution for the same value of the shape parameter for the case of $\kappa = 0.4$. The probability curves are plotted as functions of the energy losses (ϵ) to the thin absorber. This quantity is related to the shape parameter through the following equation for nonrelativistic protons:

$$\epsilon - \bar{\epsilon} = \xi(\lambda + 0.423 + \ln \kappa)$$

where $\bar{\epsilon}$ is the mean energy loss and λ is the dimensionless independent variable used in the Berger and Seltzer tabulation.

FIGURE 1. Comparison of Experimental Data Taken at Two Different Times with Vavilov Theory for Shape Parameter of 0.07. Agreement of the two sets of data indicates typical reproducibility of experimental conditions.

FIGURE 2. Comparison of Experimental
 Data with Vavilov Theory for Four
 Different Absorber-Energy Combinations
 with Shape Parameter 0.4

It should be emphasized that this experiment was designed to measure only the ionization resulting in a thin layer due to the passage of a proton; whereas, the theory concerns the energy lost by the proton. These two quantities will differ because some δ -rays produced by the protons have a significant range in the gas; hence, the observed ionization is not necessarily a result of proton energy losses occurring in the specified layer. For example, for the 0.1 μm absorber and $\epsilon_{\text{max}} = 3.15$, the experimental points for high energy losses lie below the theoretical curve. This is believed to be due to the considerable range of the more energetic δ -rays which were able to carry energy out of the thin absorber. The increased probability of observing small losses can also be explained as a result of the relatively long (compared to the thickness of the absorber) range of the δ -rays.

The applicability of the Vavilov theory to low energy protons in tissue-like materials is significant when considering neutron dose to microscopic absorption sites. Neutron-absorbed dose in biological materials is delivered principally through recoil protons. It can be shown that, for neutron-absorbed doses of a few hundred

Rads and less, absorption sites of the order of a micrometer in diameter will seldom be crossed by more than one proton recoil. Hence, when considering dosimetry at the microscopic (cellular) level, it becomes important to understand the distribution of energy losses produced by single protons traversing very thin absorbers. The preliminary results reported here indicate that the Vavilov theory adequately describes these losses.

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CALORIMETER FOR MEASUREMENT OF RADIATION INDUCED
ENDOTHERMIC REACTIONS IN TISSUE-LIKE PLASTIC

D. M. Fleming and W. A. Glass

Calorimetry provides a means of directly measuring the energy absorbed from an ionizing radiation field. In principle, it is a technique capable of high accuracy and with a direct interpretation of absorbed dose. As such, calorimetry remains an important research tool. One important application of calorimetry stems from the fact that the absorber can be made, in most cases, of the material for which the absorbed dose is required. In the case of dose in soft tissue, a plastic having atomic composition similar to the tissue of interest is used. However, it has been recognized^(1,2,3) that, in such complex materials as plastic, all the absorbed energy does not appear as heat. Some of it is retained by the plastic as changes in chemical binding energies. Milvy, Genna, Barr, and Laughlin⁽¹⁾ have estimated that between 1 and 3 percent of the absorbed energy does not appear as thermal energy in plastic.

This paper describes a calorimeter which has been designed to measure the fraction of the energy absorbed from protons in Shonka plastic⁽⁴⁾ that appears as endothermic changes in the chemical structure. Two essentially identical calorimeters, one with an aluminum absorber and the other with a plastic absorber, will be simultaneously exposed to identical proton beams. Each calorimeter is capable of 0.5% accuracy with 2 mW input power (2 MeV protons with a beam current of 1 nA). The differences in response of the two

calorimeters are to be interpreted as radiation-induced endothermic reactions in the plastic, as no changes are expected in the aluminum.

The proton beam is to be obtained from our 2 MeV electrostatic accelerator. This machine is capable of energy control to about 0.1%; however, the beam current is very poorly regulated. A device has been built (see Sheen, Glass, and Ratcliffe, this annual report)⁽⁵⁾ to regulate the beam current at ± 0.001 nA and at the same time provide a uniform irradiation of the calorimeter.

A sectional view of the calorimeter is shown in Figure 1. The absorbers were formed by first machining a shallow 1.9 cm diam by 0.25 mm thick aluminum disk. A flat calibration coil of #40 manganin wire was then wound and attached to the bottom of the disk with epoxy cement. A 0.25 mm thick aluminum disk was then placed over the coil and secured with epoxy, completing the assembly. The resistance of each calibration coil is about 95 ohms. One lead of each of the calibration coils is attached electrically to the aluminum absorber and is used to measure the beam current. The temperature of the absorbers is measured by a Y.S.I. #44011 thermistor attached to the back of each one.

The absorbers are attached with epoxy to a 3 mm thick polystyrene disk which in turn is attached to the electron suppression shield (Figure 1). This shield completely encloses the

FIGURE 1. Cross Section of Calorimeter for Measurement of Radiation-Induced Endothermic Reactions in Tissue-Like Plastic

absorbers except for the two beam holes and is maintained at -300 V. A thin layer of plastic between the shield and the isothermal jacket provides electrical insulation and, at the same time, permits relatively good heat transfer.

The isothermal jacket is a 15 cm long, 6 cm ID aluminum tube which serves as a vacuum chamber. One end of the jacket is mated to the beam tube through a section of Lucite which provides thermal isolation. A 1 cm thick aluminum plate covers the other end of the jacket and serves as a mounting base for the electron suppression shield.

The aperture plate at the beam end of the calorimeter serves two purposes. First, it defines the beam so that all of the beam passing through the beam holes must fall on the absorbers. The second function of the plate is to serve as a mounting surface for the 6.4×10^{-5} cm thick nickel foils. These foils prevent radiative heat

transfer from the beam tube into the calorimeter. A 2 cm thick layer of Styrofoam completely encloses the calorimeter insulating it from changes in room temperature.

The temperature of the jacket is maintained by a proportional control feedback system. Two Y.S.I. #44011 thermistors are attached to the wall of the jacket and are connected electrically into a wheatstone bridge circuit. The signal out of the bridge is amplified with a Keithley Model 150 and is fed to a Minneapolis-Honeywell Electr-O-Volt proportional controller. The loop is completed by amplifying the signal out of the controller and feeding it to a heating coil wrapped around the jacket. Temperature control with this system is $\pm 10^{-4}$ °C.

Preliminary electrical calibration and sensitivity measurements have been completed for the calorimeter. Sensitivities for the two calorimeters are about 54.9 and 59.5 °C/W with time constants of about 1.3 and 1.4 min,

respectively. Stability of the temperature measuring system is about $\pm 5 \times 10^{-4}$ °C.

In a preliminary run the calorimeter was set up on the accelerator and operated successfully. At this time, data are not complete enough to provide conclusive results.

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A TWIN CALORIMETER FOR ABSORBED DOSE MEASUREMENTS

D. M. Fleming

An absorbed dose calorimeter has been designed and constructed. Preliminary measurements have been made in a ^{60}Co gamma-ray field. Two measurements gave a dose rate of 29 Rads/hr with an error estimated to be 10%.

Difficulties with equipment stabilities and changes incorporated to make the system tissue equivalent have reduced the sensitivity of the calorimeter. The difference in mass between the two absorbers, which is required when using a twin system in a radiation field, results in different time constants for the two absorbers. This causes a different time response for each of the absorbers to changes in their environment and partially negates one of the advantages of the differential system.

The construction of the calorimeter is shown in Figure 1. The absorbers are machined from tissue-equivalent plastic and have identical (3.3 cm diam x 1.1 cm long) outside dimensions. The hollow absorber was made by machining a plastic annulus and adding cover plates to the open sides. The wall thickness is 1 mm. The absorbers weigh 10.29 and 3.41 g. The surfaces of the absorbers were plated with aluminum to reduce the radiative heat transfer and also to provide an electrical contact with the plastic for attachment of heater leads. The first deposits of aluminum did not make electrical contact with the plastic. It was assumed that a layer of aluminum oxide was probably being deposited on the surface of the plastic.

FIGURE 1. Exploded View of Absorbed Dose Calorimeter

To prevent the formation of the oxide, a layer of gold was deposited under the aluminum and this prevented the plastic from outgassing. When this was done, good electrical contact was made with the plastic.

Nylon threads provide support for the absorbers and a thermopile is used for measuring the temperature difference between the two absorbers.

Immediately surrounding the absorbers is a 6 mm thick plastic shell which provides charged particle equilibrium. A 2.5 mm thick constant temperature copper jacket houses the plastic shell and doubles as a vacuum chamber. A 5 cm thick layer of Styrofoam completely surrounds the calorimeter. A second jacket of

0.76 mm thick copper is used to provide a constant temperature environment for the calorimeter. The electrical leads and vacuum line pass through this outer jacket and are attached to the jacket making a good thermal contact with it. This outer jacket is insulated from room temperature changes by 5 cm of Styrofoam.

The thermopile between the absorbers is made up of twelve junctions of iron and constantan. Wire sizes for the thermopile were optimized to provide minimum thermal conduction and maximum current output. A Keithley Model 148 nanovoltmeter is used as a null detector in the thermopile circuit. A strip chart recorder is used to monitor the nanovoltmeter output. Stability of this system is usually about $\pm 5 \times 10^{-6} \text{ }^{\circ}\text{C}$.

The resistivity of the tissue-equivalent plastic absorbers is utilized to provide uniformly distributed resistance heaters by passing current directly through the plastic. The temperature of the primary copper jacket is controlled by a proportional control feedback circuit shown in Figure 2. Temperature is sensed by 8 Y.S.I. #44011 thermistors arranged around the surface of the jacket. The

thermistors are connected in series-parallel so that the nominal resistance at room temperature is about 50 k Ω . A wheatstone bridge is used to monitor the resistance of the thermistors. Bridge output current is amplified by a Keithley Model 150 microvolt-ammeter which drives a Brown strip chart recorder. The recorder provides a signal for a Brown electrovolt three-mode proportional controller which provides an output current to heat the jacket. Temperature control of this jacket is usually $\pm 5 \times 10^{-5} \text{ }^{\circ}\text{C}$.

The temperature of the outer jacket is controlled with an on-off heater circuit. Jacket temperature is sensed by two Y.S.I. #44011 thermistors in one leg of a wheatstone bridge. The bridge output is fed to a Honeywell Model 2 HLA amplifier which in turn operates a strip chart recorder. A mercury switch on the recorder controls the current to a heater attached to the jacket. Temperature control with this system is usually $\pm 2 \times 10^{-3} \text{ }^{\circ}\text{C}$.

Operating procedure for the calorimeter is as follows: the calorimeter is first allowed to come to thermal equilibrium. The system is then exposed to radiation and enough electrical

FIGURE 2. Block Diagram of Proportional Control Circuit for Isothermal Jacket

power is added to the hollow absorber to match the temperature of the solid absorber. This condition is met when the nanovoltmeter indicates that the thermopile output is zero. The electrical power added to the hollow absorber is equal to the radiation power absorbed in the additional 6.88 g

of the solid absorber. This power per gram can be converted directly to absorbed dose rate in Rads per hour.

Preliminary measurements were made on a 3/4 curie ^{60}Co source. The measurements gave values of 29.3 and 28.9 Rads/hr at 17 cm. The estimated error is about 3 Rads/hr.

A PROGRAMMED DISTRIBUTION GENERATOR

D. N. Samsky

Rossi, Biavati, and Gross⁽¹⁾ introduced the quantity "local energy density", Z , to assist in relating the physical and biological effects of ionizing radiation at the microscopic level. The local energy density distribution, $P(Z)$, is the distribution of energy absorbed per unit mass by a spherical site a few microns or less in diameter. One or more single ionizing subevents, ΔZ , contribute to the total absorbed energy. Although the $P(Z)$ distribution is needed to assess the effects of the ionizing radiation, only the single subevent distribution, $P(\Delta Z)$, has been available. Roesch⁽²⁾ derived mathematical relations between the $P(\Delta Z)$ and $P(Z)$ distribution to avoid direct determination of $P(Z)$. This paper describes a method that will generate the $P(Z)$ distributions if the $P(\Delta Z)$ distribution is known.

Rossi⁽³⁾ has given a formula for calculating $P(Z)$ from $P(\Delta Z)$:

$$P(Z) = \sum_{n=0}^{\infty} e^{-m} m^n (n!)^{-1} P_n(Z) \quad (1)$$

where

$$P_n(Z) = \int_0^Z P(\Delta Z') P_{n-1}(Z - \Delta Z') d(\Delta Z') \quad (2)$$

and

$$P_0(Z) = \delta(Z), \quad (3)$$

the Dirac delta function. $P_n(Z)$ is the probability of a local energy density Z in n events; $e^{-m} m^n (n!)^{-1}$ is the Poisson probability of n random events when the average number is m . The integral in Equation (2), although simple in form, is difficult to solve in practice. Glass, Nichols, and Samsky⁽⁴⁾ determined the $P(Z)$ function for the case of a Dirac delta function. Using a small digital computer and associated hardware and software, it is possible to generate the $P(Z)$ distribution which is defined by Equations (1) through (3) for any initial $P(\Delta Z)$ distribution and any average number m .

The Programmed Distribution Generator consists of an interface and the PDP-8 analyzing system. A program controls the operation of the

generator and does the calculations necessary to generate the $P(Z)$ function.

The interface, shown in Figure 1, consists of two, 12-bit registers; a clock; an inhibit circuit; and break request and event complete signal generators. The registers are used as inputs to the PDP-8's data break facility. This facility transfers, in 1.5 μ sec, the value of one register to the memory location specified by the other register. A transfer is initiated each time the break request

signal is generated. The clock is used to increment the value register from an octal value of 6000 to a value of 6400. These values are related to the subevents, ΔZ , through the program. After each break request, the location register is incremented by one so that successive values are not stored in the same memory location. When the value register reaches 6400, it sends a signal to the PDP-8 indicating that no more subevents will contribute to this event. The event is analyzed

FIGURE 1. The Programmed Distribution Generator Interface Flow Diagram

(as if it came from an ADC), and the registers are reset. This process is repeated until the $P(Z)$ distribution is statistically significant. The inhibit circuit is used to stop the clock and to prevent additional break requests when the interface is in a break request, or when the value register had reached 6400 (i.e., when the event is complete). In this way, all values of the value register are equally probable for transfer to the PDP-8 if the external signal occurs randomly in time.

The operation of the generator can best be explained by the use of an arbitrary function $f(\Delta Z)$, Figure 2. The ordinate is the probability that a subevent with energy ΔZ will occur. Under program control the generator function $Z(t)$ in Figure 3 is calculated. This function, Z , is a measure of the energy deposited in a site at a generator time, t . Qualitatively, it can be seen from the figure that as the slope of $Z(t)$ increases, the probability of obtaining an event of energy Z decreases. Thus the values of t can be interpreted as a probability. The two functions are related by:

$$\frac{dZ(t)}{dt} = \frac{c}{f(\Delta Z)} \quad (4)$$

where c is a normalization constant.

Mathematically, it is possible to calculate the probability of obtaining an event with energy between Z and $Z + \delta Z$. The probability, $P(Z)$, of this event is the fraction of time the generator spends between the values of t_1 and t_2 , where $Z(t_1)$ is

FIGURE 2. An Arbitrary Function $f(\Delta Z)$.

FIGURE 3. The Generator Function $Z(t)$ Obtained From the Function $f(\Delta Z)$.

Z and $Z(t_2)$ is $Z + \delta Z$. If the total generator time for one event is T , then,

$$P(Z) = \frac{t_2 - t_1}{T} \quad (5)$$

By using the definition of the slope of the $Z(t)$ curve and Equations (4) and (5), the probability is given by,

$$P(Z) = C \cdot f(\Delta Z), \quad (6)$$

where C is another normalization constant. The probability of obtaining

an event with energy Z has the same functional dependence as the original function. If the number of subevents is restricted to one, then the value of ΔZ and Z are identical and a direct correspondence between $P(Z)$ and $f(\Delta Z)$ can be made. If, however, more than one subevent occurs, then the final distribution will be a sum of folded original distributions. This is the result sought in Equations (1) through (3).

The simplest function for $f(\Delta Z)$ that will test the operation of this generator is a delta function. Using this distribution the effects of the Poisson statistics can be seen very clearly. The differences seen in Table I, a comparison of the generator results to that of theory, can be attributed to counting statistics. The results show that the generator does fold the $P_n(Z)$ distributions compatibly with Poisson statistics.

The function,

$$f(\Delta Z) = A \exp\left(-\frac{\Delta Z}{b}\right) \quad (7)$$

TABLE I. Values of $P(Z)$ for $f(\Delta Z) = \delta(\Delta Z)$

n	$m = 1.16$	
	Generated	Calculated $e^{-m} m^n/n!$
0	0.313	0.313
1	0.363	0.364
2	0.210	0.211
3	0.081	0.081
4	0.025	0.024
5	0.006	0.006
6	0.001	0.001

was used to test the regeneration features of the generator. Figure 4, a comparison of the original function and the generated distribution, was used to determine that the decay constant b is 3.1. In Figure 5, m values of one and less are compared with the original distribution. As the average number of subionizing events increases, the "decay" constant also increases. Strictly speaking, it is not possible to assign a decay constant to any curve except $f(\Delta Z)$ since all the other curves are not pure exponentials. This is obvious even for the $m = 1.050$

FIGURE 4. An Unnormalized $f(\Delta Z)$ Function with an Exponential Dependence upon ΔZ . The Decay Constant, b , Is 3.1 and the Average Number of Subevents per Event, m , Is 0.009.

FIGURE 5. A Comparison of $P(Z)$ Function with $m = 0.153$, 0.437 , and 1.050 , and the Original Exponential Function

curve. The results in Figure 6 show not only a curvature but also a maximum at a point other than the origin. The peak shifts to higher Z values and approaches a value of mb . A comparison of the generated curve with $m = 25.31$ and a gaussian with a mean value of mb and variance of $2mb^2$ is made in Figure 7. These moments are the ideal values calculated by Roesch⁽⁵⁾ for an exponential input function. The curves have not been normalized so the results are only ratios of probabilities.

A physical interpretation of the exponential distribution might be the probability of the size of a signal detected in a proportional counter due to single electrons. About 25 ion pairs are formed when a charged particle loses 0.9 keV in a counter. This would be equivalent to the distribution shown in Figure 7.

Although there are no theoretical limitations to the accuracy of this method, certain practical approximations are made. The first is the use of the pulse height spectrum, or a

FIGURE 6. Three $P(Z)$ Functions with $m = 3.536$, 10.442 and 19.753 , Showing the Shift in the Peak Value Toward mb.

histogram, to represent the original function. Calculations are performed by a digital computer so that only a finite number of channels of information are available. As the input function is limited, so also is the generator function and the final distribution. Even though the generator function contains 256 channels, not all of them can be used if the choice of subevent is to remain a "random"

process. Thus an additional limit of about 30 subevents per event is imposed upon the system.

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ION CHAMBERS WITH INTEGRAL SWITCHES FOR PULSE READING

L. A. Braby

To extend the range of miniature ion chambers, more sensitive reading is needed. The pulse reading approach⁽¹⁾ could do this except that the voltage on the chamber seems to be accurate only to about 1 V. This inaccuracy is due to asymmetry of the contact parts of the chamber, which causes variations in the capacitance of the combined jig and chamber depending on orientation. It would be very difficult to improve this situa-

tion significantly on machined chambers. One way to avoid the difficulty is to build the switch into the chamber; then these capacitive changes are isolated from the ion chamber. A chamber of this type is illustrated in Figure 1. Since the switch used to separate the connector and sensitive part of the chamber will leak, the two parts are designed to discharge at the same rate when in a radiation field. Also, voltage disturbances

FIGURE 1. Type D Ion Chamber with Integral Switch

when making or breaking contact with the jig should be kept to a minimum. Best electrical connection between the chamber and jig is obtained with a socket type connector for the center electrode. However, because this type introduces large voltage change when the chamber is disconnected from the jig, the grounded shield type is necessary (see Figure 2). The contact between this

kind of jig and plastic chamber center electrode has a large resistance (order of 10 k Ω) which is quite sensitive to contact pressure. This resistance is greatly reduced by a spot of conducting paint on the end of the electrode.

Two chambers, designed specifically for determining neutron dose distributions in man-equivalent phantoms, have been built. Both are made of A 150

FIGURE 2. Schematic of Electrode Capacitances: (a) Chamber in simple jig, (b) Chamber removed, stray capacitance increases, (c) Jig with shield; chamber capacitance simulates that of b.

plastic⁽²⁾ and filled with air. Type "D" is 3.7 cm long and 1.1 cm in diameter with 0.16 cm thick walls. Its range, when charged to 80 V, is about 1.8 Rad. Type "E" is 2.4 cm long with 0.25 cm walls and is intended for a 20 Rad range.

Figure 3 is a typical calibration curve for a type D chamber. X-ray and gamma-ray measurements are compared to dose calculated from Victoreen R-Meter readings. In neutron fields, a 100 cm³ tissue equivalent ionization chamber is used for calibration. Chamber walls and collecting electrode are A 150 plastic with the walls 6.5 mm thick and the collecting electrode 3.5 mm in diameter. The chamber is filled with tissue equivalent (TE) gas (32.4% CO₂-3.2% N₂-64.4% CH₄) maintained with a flow of about 2 cm³/min. The vacuum tube electrometer used for readout is capable of 1×10^{-14} amp full scale, which corresponds to about 8 mRad/hr. However, currents generated by temperature changes in the cable that connects ion chamber and electrometer, often limit sensitivity to 100 mRad/hr. Several connection schemes of voltage source, cable, electrometer, and chamber were tried; and the most satisfactory proved to be with the chamber wall at high voltage, the guard ring at ground, and the collecting electrode 0.001 to 1 V off ground (determined by the electrometer scale).

Absorbed dose is calculated assuming that W for TE gas is 32.5 eV/ion pair and that the density of TE gas is 1.14 g/liter (STP).

FIGURE 3. Calibration of a Typical D Chamber

Ion collection as a function of voltage was checked in a 0.25 Rad/hr field of 4 MeV neutrons. Chamber current increased linearly 8% between 25 and 125 V.

When electrometer output is integrated by a voltage to frequency converter and when scaler and cable currents are biased out, dose rate measurements of 0.2 mRad/min are readily repeated to within 2%.

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NEUTRON DEPTH DOSE MEASUREMENTS

IN A MAN-EQUIVALENT PHANTOM

L. A. Braby and L. L. Nichols

Use of the $T(d,n)$ nuclear reaction for economical production of neutrons has become increasingly popular for activation analysis, neutron radiography, radiation damage studies, medical research, etc. This widespread use presents the need for experimental data to evaluate accidental personnel exposures and to aid in planning biomedical experiments.

Preliminary data on total absorbed dose and thermal flux as a function of position inside a man-equivalent phantom is presented here. Total dose was measured with calibrated tissue equivalent ion chambers. Thermal flux was measured by activation of MnO_2 capsules. In order to determine the effect of nearby moderating material on the dose distribution, experiments were performed in four different configurations:

(1) with no moderator, (2) with 15 cm of paraffin between source and subject, (3) with a 20 x 110 x 100 cm wall of paraffin immediately behind the subject, and (4) with paraffin in front and in back of the phantom.

The $T(d,n)$ reaction was used as the source of 14 MeV neutrons. A new tritium-loaded titanium target 2.5 mg/cm^2 thick was bombarded by 0.6 MV deuterons from a Van de Graaff accelerator. The tritium target was located over a pit in the center of an 8.5 x 8.8 m room. All sources of scattering or moderating material, other than those deliberately used, were 3 m or more from the target. A

precision long counter (PLC) was positioned at a lab angle of 135° and an effective 100 cm from the target. The counter was used as a flux monitor throughout the experiment.

Dose measurements were made in a phantom* filled with water. The phantom was positioned with the sternum at 0° with respect to the deuteron beam and 100 cm from the target to front surface of the phantom. A set of 20 identical ion chambers⁽¹⁾ was exposed inside the phantom for each run. Three of the chambers were positioned in the head, one in the neck, and the remaining 16 were divided into three groups and positioned on coordinate lines running through the torso.

Glass vials containing 28.5 g of MnO_2 powder were placed in similar positions to measure thermal flux, which was then correlated with the fast dose measurements through the PLC monitor.

The ion chambers were calibrated by comparison with a 100 cm^3 TE gas filled chamber.⁽²⁾ Accuracy of the ion chamber measurements is about $\pm 10\%$. Representative activation vials were calibrated in a sigma pile with a known thermal flux.

When paraffin was placed in front of the tritium target, scattered neutrons caused the PLC monitor

* Alderson Research Labs, Type REMAB, with full skeleton.

count rate to increase. The extent of this interference was determined by using the Be(d,n) reaction for which integrated beam current is a reliable monitor. The PLC responses with and without paraffin near the target, were compared. Data for paraffin in front and paraffin in back of the phantom were corrected for this interference. No change could be detected for paraffin only behind the phantom.

The results are presented in Figures 1 through 3. The dose and thermal fluence distributions are for an incident fast neutron fluence of $1.5 \times 10^8 \text{ cm}^{-2}$ at the front surface of the phantom. Figure 1 shows the neutron dose distribution "front-to-back" through the middle of the torso. It is clear that the maximum dose occurs inside the front surface of the body. Moderating material in front of the phantom moves this maximum forward and lowers the integrated dose for a given fluence. Also, placing a paraffin wall behind the phantom lowers the dose, possibly by absorbing neutrons reflected from a concrete wall two meters from the phantom (the thermal fluence is significantly reduced in this case, see Figure 3). The combination of paraffin in front and in back reduces the dose further.

Figure 2 presents the variation in the dose in the vertical and horizontal planes. Only the data for the first configuration are presented since the other cases are similar with only variations in magnitude which can be determined from the

FIGURE 1. Neutron Dose Distributions (front-to-back) in a Man-Equivalent Phantom in a 14 MeV Neutron Fluence of $1.5 \times 10^8 \text{ n/cm}^2$. Points plotted are the positions of the centers of ion chambers.

"front-to-back" data. Figure 3 gives the thermal neutron fluence as a function of position "front-to-back" through the middle of the torso.

Comparison of Figures 1 and 3 illustrates that dose and thermal fluence are not necessarily related; and, hence, one must be cautious about using activation methods for neutron dosimetry in moderating media.

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FIGURE 2. Neutron Dose Distribution on the Vertical and Horizontal Axes of the Torso.

FIGURE 3. Thermal Neutron Fluence-Depth Distribution Through the Torso.

QUALITY OF CYCLOTRON PRODUCED NEUTRONS*

J. N. Schultz and W. A. Glass

The results are reported of a study of the quality of the neutron radiation produced by the action of 40 MeV alpha particles and 20 MeV deuterons on a thick beryllium target. The results are presented as dose distributions in LET and in event size for microscopic absorption sites having diameters of 1, 3, and 5 microns. The dose average LET for the neutrons produced by alpha particles was found to be 61 keV/ μ and that for the deuterons was 41 keV/ μ .

* This paper has been accepted for publication in Health Physics.

A PRECISION LONG COUNTER FOR MEASURING
FAST NEUTRON FLUX DENSITY*

J. De Pangher and L. L. Nichols

A reproducible version of the Hanson-McKibben long counter was built and a comprehensive experimental investigation of its characteristics was made. The counter was fabricated from polyethylene and strengthened with aluminum instead of being paraffin strengthened with steel. It is called a precision long counter (PLC) because models built from a standard set of drawings have closely reproducible properties. Data are given to show how a PLC can be calibrated to within 1% for measuring neutron flux densities from radioactive sources. This calibration is obtained with a small calibrated PuBe neutron source inserted inside the PLC. The standard counter, H-1, is located at Pacific Northwest Laboratory in Richland, Washington, and the standard small source, M-1045, is located at Mound Laboratory in Miamisburg, Ohio. One counter, H-3, was selected as a "roving" counter, calibrated against H-1, and sent to the Mound Laboratory and to the Argonne National Laboratory to calibrate the two counters, ML-1 and ANL-1. The problem of using a PLC with accelerator neutrons is discussed and a solution offered.

* Published as BNWL-260, June 1966.

COMPARISON OF THE PRECISION LONG COUNTER AND TISSUE-
EQUIVALENT ION CHAMBER FOR ABSORBED DOSE MEASUREMENTS

L. A. Braby and L. L. Nichols

The precision long counter, though primarily a neutron flux measuring device, is frequently used to determine absorbed dose through the kerma table in NBS Handbook 75. Tissue equivalent (TE) ion chambers are also used for tissue dose measurements. A comparison of the results obtained by these two independent methods is presented here.

One of the Hanford precision long counters (PLC) was compared with the 100 cm³ TE plastic, TE gas-filled ion chamber described earlier.⁽¹⁾ The experiment was performed over the 6 1/2 x 6 x 3 meter pit at the Battelle-Northwest fast neutron facility. Ion chamber and PLC were placed at symmetric angles with respect to the accelerator beam so that they intercept neutrons of the desired energy from each charged particle reaction. Because there was a quantity of hydrogenous equipment (moderators, PLC's, etc.) located along one wall of this room, the scattered neutron background was not identical for the two detectors. Therefore, the positions of the PLC and ion chamber were interchanged and the results of the two geometries averaged to eliminate this effect. In the worst case, one measurement was 11% higher than the corresponding measurement at the alternate angle. The ion chamber was placed 40 cm from the target and the PLC was at an effective distance near 1 m. With the ion chamber and the PLC at $\pm 30^\circ$, respectively, the PLC was moved from

1.0 to 1.5 m, which about doubled the ion chamber to PLC distance, with no effect on the ion chamber reading. This indicates that neutrons scattered by the PLC were producing negligible dose at the ion chamber.

Results of the comparison are presented in Table I. The flux at 40 cm was obtained from the PLC data at 100 cm by using the inverse square law. The kerma for tissue equivalent plastic from Table A7, NBS Handbook 75, was used to calculate neutron dose. In most cases the measurements were repeated several times and were always reproducible to within $\pm 2\%$. The dose calculated from PLC measurements is consistently higher than the dose determined by the TE ion chamber. Part of this discrepancy can be explained by the "solid angle effect"⁽²⁾ which is caused by a nonuniform illumination of neutrons within the solid angle subtended by the PLC. Other possible errors are the kerma relations listed in NBS Handbook 75. A detailed investigation of other sources of error has not been undertaken at this time.

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TABLE I. Comparison of Ion Chamber and Long Counter Dose Measurements

Source Reaction	Ion Energy, MeV	Lab Angle	Neutron Energy, MeV	Neutron Fluence at 40 cm, n/cm ²	PLC Dose, mRad	Ion Dose, mRad	PLC/Ion
T(p,n)	1.5	75°	0.25	3.64×10^5	0.41	0.286	1.43
T(p,n)	2.0	30°	1.0	3.56×10^5	0.826	0.690	1.20
D(d,n)	1.5	45°	4.0	4.17×10^5	1.68	1.50	1.12
T(d,n)	1.5	60°	16.0	6.79×10^5	4.50	3.13	1.44

PARTICLE DOSIMETRY USING THE FISSION FRAGMENT DAMAGE PRINCIPLE*

W. V. Baumgartner**

Efforts to use the fission fragment damage principle in a personnel neutron dosimeter progressed to the fabrication and testing of prototypes. These have shown a marked improvement in dose response when compared to nuclear track emulsion (NTA) neutron dosimeters.

The new dosimeters use a neutron-fissionable foil placed next to a piece of plastic sheet; the latter to record the fission events caused by neutrons. After properly etching the surface of the detector material, the events appearing as tracks, can be counted under a microscope and the number of tracks can be related to the neutron dose.

Figure 1 illustrates the processes and procedures described above. Neutrons strike the fissile foil causing the ²³⁵U, for example, to

fission; fission fragments from the surface penetrate the plastic (Lexan) causing damage areas. The Lexan is developed by etching in hot 6N NaOH solution for about 45 minutes at 65 °C, then rinsed and dried. The Lexan is then inspected for the etched damage tracks under a microscope and these are counted at 200 or 400X; the latter when the number of tracks is large. A TV monitor may be attached to the microscope and is useful to reduce eyestrain.

The top half of Figure 2 is a plot of fission cross section for the nuclides ²³⁵U, ²³⁸U, and ²³⁷Np. The bottom half shows the results of irradiating the foils with neutrons. The foils were 1 cm² by 0.02 to 0.05 cm thick pieces of ²³⁵U (93%) and ²³⁸U (20-fold depleted) and 1 cm² by 0.25 cm thick foils of ²³⁷NpO₂ in polyester resin. The neutron energies used for calibration were obtained from a 2 MeV positive ion accelerator using various targets and supplemented by PuBe and PuF₄ sources. The observed ²³⁷NpO₂

* Not charged to the Division of Biology and Medicine Program

** Dosimetry Technology Section, Environmental Health and Engineering Department

G-102-1119

FIGURE 1. Fission Foil Neutron Dosimeter

response is less than that of the ^{235}U and ^{238}U responses since the surface of the foil in the Np case is about 75% polyester resin.

Using foils of 20-fold depleted uranium, $^{237}\text{NpO}_2$, bare ^{235}U (93%) and ^{235}U (93%) covered with 1 mm of cadmium on both sides, a prototype dosimeter was assembled as shown in Figure 3.

Theoretical and experimental studies indicate that fast neutron (energies above 0.7 MeV) doses of 150 mrem and thermal neutron and intermediate neutron doses of 1 mrem can be measured.

The overall size of the dosimeter is about 2.5 by 7.6 cm by about 0.6 cm thick. The foils were glued to aluminum about 1.2 mm thick. The double bag technique was used in

assembly to avoid spread of contamination. Several hundred measurements were made and no cross contamination of the foil surfaces was detected. As a precaution, the Lexan plastic on removal is placed in detergent and sequester solutions for cleaning before placing in the etch solution.

Prototype badges were used to measure neutrons in mixed radiation fields in several work areas. No employee has worn a prototype badge since there is a radiation level of about 15 mR/hr at the surface, primarily from the $^{237}\text{NpO}_2$ foil. Efforts are being directed at reducing the radiation level by using shielding materials and by design changes requiring less fissile materials. Using these methods, the dose rate should be reducible to less than 1 mR/hr at

FIGURE 2. Comparison of Cross Sections and Results of Fission Foil Exposures

the surface and the fission foil neutron dosimeter may then prove to be acceptable as a personnel neutron dosimeter also.

Table I is a summary of response of the fission foil neutron dosimeter to various calibrated sources. Measurements of sources shielded by 1/2 in. Lucite, simulating hood exposures, are included. The "Ratio of Tracks" in the table is felt to be useful in standardizing the response in the absence of spectrum data. For example, a very high ratio

for bare $^{235}\text{U}/\text{Cd}$ indicates that the spectrum is well thermalized. Unusual ratios are useful for adjusting the dose per neutron values in calculations to more precisely define the dose equivalent. Taking the value from the "Tracks/Neutron" columns and using equations developed to fit the calibration data, one obtains the values under the column "Dose Equivalent in (rem/n/cm²) x 10⁻⁸ Evaluated by Dosimeter." The dose equivalents in rem/n/cm² evaluated by the dosimeter are in good agreement with national standards.⁽¹⁾

TABLE I. Summary of Neutron Exposure

Source	Tracks/Neutron $\times 10^{-5}$ (a)				Ratio of Tracks		Dose Equivalent in (rem/n/cm ²) $\times 10^{-8}$ Evaluated by Dosimeter	Ratio of ϕ (Fluence) Evaluated by Dosimeter to Calibrated ϕ
	²³⁸ U (b)	NpO ₂ (c)	Cd+ ²³⁵ U (d)	²³⁵ U (d)	NpO ₂ / ²³⁸ U	²³⁵ U/Cd+ ²³⁵ U		
PuF ₄	0.248	0.476	1.60	5.71	1.9	3.6	3.3	1.06
PuF ₄ + 1.27 cm Lucite	0.191	0.378	4.54	17.6	2.0	3.9	2.6	0.93
PuBe	0.515	0.484	1.37	3.13	0.94	2.3	3.8	0.99
PuBe + 1.27 cm Lucite	0.473	0.412	1.58	3.62	0.87	2.3	3.2	0.84
3 MeV Neutrons from d(D,n)He ³	0.615	0.509	--	1.85	0.83	--	4.0	1.04
Thermal Neutrons from E Pile	0.175	--	6.9	237	--	35	0.11	1.06

(a) Most of the data are $\pm 15\%$ or better

(b) ²³⁸U is 20-Fold Depleted

(c) Neptunium-237 Oxide

(d) ²³⁵U is 93% Uranium-235

FIGURE 3. Prototype Neutron Dosimeter

The ratios of fluence data from the dosimeter to fluence data from calibrations results in the values in the last column of the table. The ratio of fluence for PuBe + 1.27 cm Lucite is probably low due to the statistical error resulting from the small dose received by the dosimeters.

Freedom from track fading and insignificant beta-gamma radiation sensitivity are major assets of this neutron dosimeter. This new dosimeter

principle used with a single $^{237}\text{NpO}_2$ foil will provide substantially improved neutron dosimetry in mixed radiation fields compared to the commonly used NTA emulsion dosimeters.

REFERENCE

1. *Protection Against Neutron Radiation up to 30 Million Electron Volts.* NBS Handbook 63, p. 15, Table II, p. 62, Figure 13. National Bureau of Standards, November 1957.

DEVELOPMENT OF A PORTABLE TISSUE EQUIVALENT
DOSIMETER FOR MIXED γ -NEUTRON RADIATION FIELDS*

G. W. R. Endres,** W. A. Glass and C. Malott**

The study conducted by Glass⁽¹⁾ investigating the energy deposited by ionizing radiation in microscopic absorption sites has led to a study to develop a suitable portable, tissue equivalent proportional counter for use in mixed radiation fields. In the previous investigation, a 10 cm diam spherical cavity surrounded by about 6 mm of tissue equivalent plastic was used. A spiral grid surrounding the anode was necessary to produce uniform gas multiplication regardless of the location of ionizing events within the cavity. This grid made the counter very sensitive to mechanical shock.

The present development is a scaled-down version (about 5 cm diam) of the 10 cm counter. It uses a single 0.001 in. diam wire as the anode without a spiral grid and is more stable and much less susceptible to mechanical shock. To simulate spherical absorption sites of the order of 1 μ diam, the counter is filled with the tissue equivalent gas mixture[†] and is operated at a pressure of a few Torr.

Exposures to monoenergetic neutrons of 1.0 and 0.48 MeV were conducted

to compare the measured dose distribution in event size, Y , of the 10 and 5-cm counters. The event size is defined as the energy deposited per event divided by the diameter of the counter. These comparisons are shown in Figures 1 and 2. Since the dose distribution measured by the 5 cm counter has generally the same shape as that measured by the 10 cm and the measured absorbed dose agrees reasonably well, it appears quite feasible to proceed with development of the 5 cm counter. The absorbed dose measured by the 5 cm counter agrees with the dose measured by the long counter within 20%.

Theoretical considerations show that the low LET secondaries from gamma interactions should generally produce much smaller pulses in the counter than secondaries from neutron interactions. Thus, it should be possible to separate these pulses and measure gamma dose and neutron dose separately.

Two exposures were taken with the 5 cm counter exposed to 1.0 MeV neutrons; one with a known amount of ⁶⁰Co gamma radiation present and one without, see Figure 3. The results of this comparison show that the pulses due to gamma-ray secondaries have no appreciable effect on the dose distribution due to the neutron secondaries. In this case, the exposure from the gamma source and the neutron source are about equal.

* Not Charged to the Division of
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** Dosimetry Technology Section,
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Engineering Department

† Methane 64.4 vol%-CO₂ 32.4 vol%-
N₂ 3.2 vol%

FIGURE 1. Dose Distribution in Y of Monoenergetic Neutrons for 5 cm and 10 cm Counters

The calculation of absorbed dose from pulse height information obtained in a proportional counter is the requirement of the electronic section of the instrument. If energy deposited is assumed to be a linear function of pulse height, dose rate may be approximated by the expression

$$D = K \int y f(y) dy \quad (1)$$

where y is pulse height, a random variable, and $f(y)$ is the frequency or probability of occurrence of a pulse height y . The constant K represents a normalization of the pulse height to absorbed energy scale and contains the mass of the absorption site. Equation (1) may be recognized as the first moment of the pulse height distribution function $f(y)$.

FIGURE 2. Dose Distribution in Y of Monoenergetic Neutrons for 5 cm and 10 cm

The experimental evaluation of D in Equation (1) is accomplished directly by causing pulses from the chamber to be averaged by a linear amplifier circuit driving a linear integrator. The electronics system is a two-channel instrument which uses this averaging method to find the first moment of pulse height distributions for information in each

of two channels. The channel thresholds are set so that pulses corresponding to neutron and gamma events are directed into their respective channels with a minimum number of errors. The lower limit, or threshold for the neutron counting channel is about one hundred times greater than the gamma channel threshold. To extract the neutron pulses from the amplified

FIGURE 3. Dose Distribution in Y for ^{60}Co Gamma Radiation and 1.0 MeV Monoenergetic Neutrons Using a 5 cm Counter

chamber output signal, it is necessary only to determine which pulses exceed a certain threshold and to gate these pulses into the neutron registering amplifier.

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DUAL ONE DIMENSIONAL DATA ANALYSIS AND DISPLAY PROGRAM*

D. N. Samsky

*This program was written for use with the combination of a PDP-8 and a modified ND-160F analog to digital converter. The one dimensional display and analysis program of the supplier** was used as a guide. Several other features were added. The most important additional features are faster data input through the data break and the facility to analyze two independent inputs simultaneously.*

*The PDP-8's memory is divided into four quadrants, the first of which (0-17778)*** contains the program. The other three quadrants (20008 - 37778, 40008 - 57778, and 60008 - 77778) are used as three 1024 channel memories for data storage. The program has been written in modular form to facilitate its alteration to meet specific future needs.*

* Published as BNWL-299, September 1966.

** The Digital Equipment Corporation, Maynard, Massachusetts.

*** Subscript 8 denotes octal numbers.

A MICRO-BEAM COLLIMATOR*D. N. Samsky, W. A. Glass
and H. V. Herndon

A collimator is described which restricts the beam from a 2 MeV proton accelerator to a few microns in radial extent. The collimator is a double-aperture device and provides a pressure differential of one atmosphere with no foil window. It is being used in the study of proton energy losses in thin tissue-like specimens.

* This paper has been submitted for publication in Review of Scientific Instruments.

WHOLE-BODY COUNTER DESIGN AND CALIBRATION*

F. L. Rising,** P. E. Bramson**
and H. V. Larson**

A shadow-shield whole-body counter and associated counting equipment was designed to be installed in a truck van. This counter has the additional advantage over an existing mobile counter of being more compact and having the van permanently attached to the truck bed. A unique sled-drive mechanism has been included that allows the sled-drive-rate to be varied according to the height of the subject as opposed to the fixed rate as used in the earlier design. The disadvantage of the fixed-rate drive is that only persons of a certain height, arbitrarily 70 inches, are counted in optimum geometry for the full examination period. The variable-rate drive allows the sled to be slowed if the subject is shorter than 6 feet and speeded up if he is taller so that part of the subject is under the detector and thus in optimum counting

geometry throughout the examination period. The result is increased sensitivity and accuracy for radioisotopes in people of other than "standard" stature.

The Division of Biology and Medicine conducted an intercomparison study of sixteen of the major U.S. Atomic Energy Commission whole-body counter laboratories. The purpose of the program was to compare the whole-body counting calibrations for cesium-137 and potassium-40. The final phase of our present work consisted of measuring two visiting human standards. One person contained a known elevated cesium-137 burden and a quantity of potassium normal for his physical characteristics while the other contained the commonly-encountered amount of cesium-137 and the normal quantity of potassium for his stature. The Hanford evaluations on both subjects were within 1% for cesium-137 and 13% for potassium-40 of the quantities estimated by the Los Alamos Scientific Laboratory which conducted the intercomparison study.

* Not charged to the Division of Biology and Medicine Program.

** Dosimetry Technology Section,
Environmental Health and Engineering Department

POTASSIUM DEPLETION MEASUREMENTS IN THE DYSTROPHIC*

H. V. Larson,** C. E. Newton, Jr.**
and P. E. Bramson**

The mobile whole-body counter was transported to the Children's Orthopedic Hospital in Seattle, Washington, where arrangements had been made to examine as many ambulatory dystrophic patients and their relatives as possible. The purpose of this preliminary study was to establish the body potassium levels and depletions of dystrophic and normal children with special emphasis on siblings, progeny, and parents of the dystrophic, and to determine from the data if further study is warranted in establishing whole-body counting techniques as a tool for early diagnosis of muscular dystrophy and related diseases in children.

A total of 27 muscular dystrophy patients and 156 relatives of patients, including 36 mothers, 20 fathers, 64 siblings, 20 progeny, and 16 other relatives were measured for whole body potassium. The ages of the dystrophic patients ranged from 4 to 53 years. Sixteen of the patients were 12 years or younger. Fourteen of these were ambulatory. Six of the patients have dystrophy known to be the Duchenne type. Some of the remaining 21 may have Duchenne dystrophy but, because of incompleteness of clinical records, cannot be classified with surety.

* Not charged to Division of Biology and Medicine Program

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DYSTROPHIC CHILDREN AND ADULTS

As shown in Figure 1 and 2, potassium concentrations were below the normal curve in most of the dystrophic patients examined. The normal curve was established from data that were obtained from the Hanford whole-body counters. The six patients with Duchenne muscular dystrophy show potassium concentrations below the average for normal males by about 35% within one year of onset of the disease.

PROGENY AND SIBLINGS

Progeny and siblings of the dystrophic who presently show no physical signs or symptoms of the disease were examined to determine if their potassium concentrations are markedly different from those of normal people of the same age group. Of the 84 siblings and progeny of the dystrophic examined in this study, 8 male siblings and progeny had potassium levels less than the average for normal male children by nearly two standard deviations. Because the disease is inherited by males, this group has a high probability of later becoming dystrophic. By closely following the potassium levels of these children, a relationship may be established between potassium levels and the time before and after the onset of the disease.

FIGURE 1. Average Potassium Concentrations for Normal Males, and Individual Potassium Concentrations for Dystrophic Males as a Function of Age

PARENTS OF THE DYSTROPHIC

The 36 mothers and 20 fathers all had potassium concentrations greater than the normal curve less two standard deviations. The data indicate that the detection of genetic "carriers" by measuring body potassium levels is not feasible.

SUMMARY

This study shows that muscular dystrophy patients have potassium levels that are lower than the average for normal children. This fact is in agreement with previously published data.⁽¹⁾ Data from six patients with Duchenne muscular

FIGURE 2. Average Potassium Concentrations for Normal Females, and Individual Potassium Concentrations for Dystrophic Females as a Function of Age

dystrophy indicate potassium concentrations below the average for normal children by about 35% the first year from onset. More data are needed on patients with Duchenne muscular dystrophy to establish this fact.

The detection of carriers of the disease by this method does not ap-

pear promising as no dystrophy-related trend in potassium concentration was observed in the parents of dystrophics. The male progeny and siblings of the dystrophic that were examined in this study should be re-examined on a schedule of twice each year for the next several years to see if a relationship can

be established between potassium levels and the time before and after the onset of the disease. Assuming that detectable potassium depletion occurs before the physical signs and symptoms, the data could be of assistance in the early diagnosis of muscular dystrophy. Also, on those patients that contract the disease, the time of appearance of the various physical signs and symptoms of the

disease could be definitely established as a function of the time from onset of the disease.

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THE ESTABLISHMENT AND UTILIZATION OF FILM DOSIMETER PERFORMANCE CRITERIA

C. M. Unruh,* H. V. Larson** and T. M. Beetle†

The competency of commercial and government-sponsored film dosimetry services is not presently evaluated by any nationally recognized authority. Advertising claims and apparent performance capabilities vary widely between film dosimeter services. The Film Dosimetry Calibration Laboratory Study is providing a detailed analysis of (1) schemes to implement the operation of such a laboratory, (2) film dosimeter performance criteria, (3) typical laboratory operating procedures, (4) equipment, facilities, staff, and cost required to establish such a laboratory, and (5) tests of

the practical workability of a film dosimetry calibration laboratory. Establishment of film dosimeter performance criteria includes consideration of the radiations, dose ranges, and radiation spectra for which personnel film dosimeters are used. The performance criteria statistics are being based on a carefully balanced assessment of practically attainable dosimeter performance and processor operating costs.

Current capabilities in both private and government processors were established by exposing film dosimeters from 36 processing laboratories in the United States, including 12 private, 15 Atomic Energy Commission, and 9 military processors. Selection of types, spectra, and dose equivalent ranges for the test radiation exposures was based on the most common sources of external radiations that are handled in both industry and

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medicine, on the maximum permissible dose equivalents established by the International Commission on Radiological Protection and on past experience. Photon energies of 17, 100 and 170 keV and isotopic sources of radium and ^{60}Co were used to provide a range of energies for the test radiation exposures. The exposures included X- and gamma-rays in the dose equivalent range from 0.05 to 600 rem, thermal and fast neutrons in the range from 0.05 to 0.80 rem, and beta rays in the range from 0.10 to 0.50 rem. Several mixtures of radiation that are commonly found in industrial work were also included in the study. Types of film packets, calibration sources, and geometries of calibration exposures currently

used by film dosimeter processors in the United States were summarized from a questionnaire that was completed by each participant.

A statistical model and program was developed to yield the most valid measurement of dosimeter performance within a minimum of test exposures. The statistical model determined the number of film dosimeters (4 to 12) needed at each radiation dose equivalent level to provide an adequate assessment of bias and variance at each test exposure for each test radiation type. These statistical variables were maintained at levels too low to contribute significantly to the bias and variance observed in the evaluation of each processor's performance.

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