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PACIFIC NORTHWEST LABORATORY
ANNUAL REPORT FOR 1968
TO THE USAEC DIVISION
OF BIOLOGY AND MEDICINE
VOLUME II: PHYSICAL SCIENCES
PART 2. RADIOLOGICAL SCIENCES

June 1969

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Biology and Medicine

PACIFIC NORTHWEST LABORATORY
ANNUAL REPORT FOR 1968
to the
USAEC Division of Biology and Medicine
VOLUME II: PHYSICAL SCIENCES
Part 2. Radiological Sciences

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RADIOLOGICAL CHEMISTRY

THE DETERMINATION OF TRACE LEVELS OF U, ^{230}Th , ^{210}Pb , and ^{210}Po
IN SOFT TISSUES

P. O. Jackson and B. O. Stuart*

A method for the determination of trace concentrations of U, ^{230}Th , ^{210}Pb , and ^{210}Po in soft tissues of animals exposed to airborne uranium ore dust has been developed. The techniques have been applied to such tissue samples as lung, liver, spleen, kidney, and lymph node, as well as bioassay material such as urine.

The evaluation of radiation exposure to uranium miners from the inhalation of airborne uranium ore dust requires information on the concentration of uranium and its daughters in the various body organs. Previous workers⁽¹⁾ have used laboratory exposure and subsequent organ analyses of small animals such as rats to investigate the deposition and translocation processes. To minimize early toxic symptoms, long-term large animal experiments use uranium ore exposure levels such that the concentration of uranium ore decay chain members in organs other than lungs are near the detection limit of the most sensitive available techniques. In this study, several existing techniques^(2,3,4,5) were adapted for the determination of

trace concentrations of U, ^{230}Th , ^{210}Pb , and ^{210}Po in soft tissues, such as beagle dog lungs, livers, spleens, kidneys, lymph nodes, and bioassay materials.

The sample is decomposed to a slurry in warm 2M HNO_3 . Uranium-233, thorium-234, and polonium-208 tracers are added, and the sample is wet ashed with HNO_3 , 30% H_2O_2 , and HClO_4 . HF is used to volatilize any siliceous material. The salts are dissolved in dilute nitric acid, filtered, and the filters are alpha and beta counted to determine that dissolution is complete before proceeding. The complete procedure, as shown in Figure 1, allows

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FIGURE 1. The Flow Chart Details the Overall Separation Scheme

the analysis of biological samples for the trace levels of U, ^{230}Th , ^{210}Pb , and ^{210}Po .

Thorium-230 d/m is calculated by applying the usual detector efficiency, volumetric, and decay corrections. The radiochemical recovery is determined from a ^{234}Pa beta count taken through a 54 mg/cm² aluminum absorber eliminating ^{234}Th betas. Significant ^{228}Th (plus its decay products) may be present since the ^{233}U tracer contains ^{232}U . The tracers should be purified immediately before analysis, and the thorium should be separated within one or two weeks to minimize ingrowth. Thorium-228 ingrowth is calculated from the time interval between ^{233}U purification and the thorium separation using the ^{232}U content measured by alpha energy analysis. Thorium-228 decay products (^{224}Ra , ^{220}Rn , ^{216}Po , ^{212}Bi , and ^{212}Po) are estimated by assuming their ingrowth from the time they are volatilized from the mounted thorium fraction.

The total uranium mass in the sample is determined fluorimetrically. Results must be corrected for the mass of added ^{233}U tracer present and the radiochemical yield of the separation. The alpha and the fluorimetric results contain contributions from both natural uranium and ^{233}U . Those contributions are determined by successive approximations to the following equations before the radiochemical recovery is determined and applied:

$$[\text{Net } ^{233}\text{U d/m}] = [\text{Gross alpha d/m}] - [1.55 (\mu\text{g U})] \quad (1)$$

$$[\text{Net } \mu\text{g U}] = [\text{Gross } \mu\text{g U}] - [4.75 \times 10^{-5} (\text{d/m } ^{233}\text{U})] \quad (2)$$

The net d/m ^{233}U measures the radiochemical yield. The d/m of ^{234}U (parent of ^{230}Th) is computed from the net uranium mass.

The measured fraction of the alpha spectrum from 4 to 6 MeV, which is due to ^{210}Po , is multiplied by the gross alpha d/m of the source, giving net ^{210}Po d/m. Radiochemical recovery is measured similarly from the product of the fraction of ^{208}Po alphas and the gross alpha d/m. The usual differential equation solution⁽⁶⁾ and decay corrections are applied for ingrowth from ^{210}Pb present at sacrifice.

The ^{210}Pb is determined from measurements taken on ^{210}Po separated after a period of ingrowth following lead separation. The calculation technique is identical with the above except for appropriate changes in the buildup and decay parameters. Lead-212 gammas at 0.24 MeV are used to measure the radiochemical recovery during the lead separation. Polonium-208 is used for the Po separation yield. Recovery during ashing is not determined, but losses should not exceed those measured with ^{208}Po or ^{234}Th .

The ashing procedure was designed to minimize losses of ^{210}Po by volatilization and losses of all the measured radionuclides by coprecipitation with

insoluble residues. Recent studies⁽⁷⁾ have demonstrated that losses of organically-bound polonium may occur at temperatures as low as 100 °C during dry ashing. High recoveries of ^{208}Po tracer do not preclude losses of unexchanged organically-bound ^{210}Po during wet ashing. However, the slow initial decomposition used in the method allows a maximum opportunity for solubilizing polonium, allowing early exchange with the tracer. In addition, formation of insoluble residues, especially from liver samples, was reduced by fuming with perchloric acid. A fine precipitate tended to form on dilution with 4M HNO_3 when samples were ashed with $\text{HNO}_3 + \text{H}_2\text{O}_2$ alone. An alpha and beta analysis of

the filterable residues indicated negligible losses of the added tracers.

Table 1 presents radiochemical recoveries measured for separations performed on several typical samples. The average recoveries for ^{208}Po , ^{233}U , and ^{234}Th were satisfactory approximations for computation purposes. Those tracers could be omitted once the average is established for laboratory operations.

Contamination levels encountered in reagent blanks are presented in Table 2. These blanks demonstrate that the tracers added were often the major source of contamination. The ^{228}Th and ^{233}U from ^{233}U tracer have been discussed previously. The ^{210}Pb contamination apparently came from

TABLE 1. Radiochemical Recoveries Measured for Samples of Ashed Beagle Organs

		Radiochemical Recovery, %			
Sample		^{233}U	^{234}Th	^{208}Po (a)	^{212}Pb (b)
Reagent Blank	1	89	87	---	---
	2	83	65	---	---
Liver	1	76	88	105	67
	2	82	78	107	71
Lung	1	80	85	110	90
	2	84	88	99	83
Kidney	1	93	85	97	97
	2	92	84	102	90
Lymph Node	1	92	82	93	87
	2	90	85	88	94
Spleen	1	93	83	99	89
	2	94	84	92	90
Average		87	83	99	86

a. ^{208}Po recovery measurements were $\pm 10\%$ because of propagation of counting statistic variations in the calculation technique and the nonuniformity of tracer material directly mounted for comparator sources.

b. ^{212}Pb recoveries are the product of recoveries measured for the extraction and ion exchange column steps.

TABLE 2. Reagent Blank Activity Levels

Determination	d/m from Tracers	Source	d/m from Reagents ^(a)
Fluorimetric U (as ^{234}U)	0.06	~ 2000 d/m ^{233}U ^(b)	0.03
^{230}Th	1.2 - 3.6	~ 2000 d/m ^{233}U (^{228}Th)	0.5
^{210}Pb	1.6 ^(c)	$\sim 30,000$ d/m ^{212}Pb	---
^{210}Po	0.08 ^(d)	~ 140 d/m ^{208}Po	<0.4

- a. Fluorimetric U and ^{230}Th results are residual reagent blanks after correction for tracer source contribution; ^{210}Po result was based on runs with no tracer added.
- b. Contribution from ^{233}U was based on its mass, interpreted as natural uranium in calculating the d/m of ^{234}U .
- c. ^{210}Pb added with ^{212}Pb tracer was determined from the ingrowth of ^{210}Po in an aliquot of that tracer. ^{212}Pb d/m is immediately following separation.
- d. No decay correction included.

traces of ^{230}Th in the ^{232}Th used for milking, since its level varied with the time between milkings. Extracting and discarding lead 24 hr prior to the milking for tracer use would have reduced the level of ^{210}Pb to <0.1 d/m. The ^{210}Po added with ^{208}Po was only 0.06% of the 5.1 MeV ^{208}Po alphas. Polonium-209 is also present in the tracer to an extent of approximately 1%; however, its 4.87 MeV alphas do not interfere in the procedure.

In this group of samples, the interference would have been reduced had less tracer been used. However, the choice of tracer levels was based on a higher expected level of sample activity.

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THE MULTIELEMENT ANALYSIS OF HUMAN LUNG TISSUE

L. A. Rancitelli, R. W. Perkins, and A. D. Renzetti, Jr.*

Human lung tissue obtained from individuals with experience in copper ore processing, uranium mining, uranium processing, and heavy metals processing have been analyzed by instrumental neutron activation analysis. The concentrations of 19 elements are reported in the lungs of these individuals and are compared with the concentrations measured in a normal individual. The uranium miner was found to have 2 ppm U and the uranium processor 27 ppm U, compared to 0.001 ppm U in the normal individual. The lung from the subject with a heavy element exposure had a normal uranium concentration but contained 8 times the normal Th.

The incidence of lung cancer among uranium miners has been attributed to many factors. The miners are subjected to an atmosphere containing the Rn daughters, organic pollutants originating from diesel fuel, and uranium ore dust. This is complicated further by the cigarette smoking of each individual. The radiological effects of the inhalation of Rn daughters, uranium, and the biological effects of cigarette smoking have received a great deal of attention, while the possible synergistic effects of dust in the mine atmosphere have been neglected. In an attempt to obtain a better understanding of the inorganic materials deposited and retained in

the lungs, a program was initiated to permit the measurement of about 19 trace constituents in autopsy and biopsy samples. A multielement technique of instrumental neutron activation analysis was developed^(1,2) and applied⁽³⁾ to autopsy samples which had been taken for pathological examination.

Samples of the upper and lower lobe of both lungs, together with medical histories of each subject, are being obtained from the University of Utah Medical Center and from sources in Richland, Washington. The samples are

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freeze dried, irradiated in a Hanford production reactor to an integrated neutron exposure of 10^{18} n/cm², and analyzed on a Ge(Li) spectrometer and multidimensional gamma-ray spectrometers after appropriate decay intervals. This permits the direct measurement of Na, K, Rb, Cs, Cl, Br, Zn, Al, Fe, Au, Co, Cr, Se, Sc, Sb, Hg, Ag, Th, and U in a single sample of lung tissue.

If we are to understand the effects of inorganic pollutants in the lung, we must first establish a normal base line for each element of interest. This is being accomplished by analyzing specimens taken from individuals with no known history of pulmonary disease or mining experience. The analysis of selected samples from a normal subject are presented in Table 1. The concentrations of the three elements Ag, Th, and U were below our detection limits in these

samples; however, even the upper limit presented in Table 1 for each element is low enough to provide a valuable base line for comparison with the concentrations in subjects with mining experience. The alkali metals show some variation throughout the lung, K, Rb, and Cs vary by a factor of 2, while Na varies 40%. Since the amount of blood associated with the tissue sample will almost certainly affect the observed concentrations of the alkali metals and Fe, some caution should be exercised in attaching any significance to these variations. The Br, Zn, Co, and Se content of the lung is relatively constant, while large variations in the Cr, Sc, Sb, and Hg content are observed.

Samples of lung tissue from individuals with various types of dust exposures are also being analyzed. Table 2 contains the results of the analysis of lung tissue samples from

TABLE 1. Trace Element Content of Normal Human Lung Tissue

Sample	$\mu\text{g/g Dry Tissue (a)}$												
	Na	K	Rb	Cs	Br	Zn	Fe	Co	Cr	Se	Sc	Sb	Hg
Left Lung													
Upper Lobe	9,400	11,100	17.4	0.135	45	57	560	0.165	0.31	1.1	0.002	0.06	0.36
Lower Lobe	13,700	14,600	21.5	0.155	67	64	420	0.245	0.58	1.7	0.002	0.07	0.63
Right Lung													
Upper Lobe	9,500	9,500	18.2	0.135	49	62	1,020	0.250	0.92	1.4	0.014	0.50	0.48
Middle Lobe	13,700	7,700	11.8	0.088	62	57	580	0.165	0.34	1.3	0.004	0.23	0.40
Lower Lobe	11,900	8,500	9.3	0.069	55	39	640	0.170	0.46	1.3	0.009	0.27	0.37

Upper Limits in all Samples:

Ag <0.02
Th <0.1
U <0.001

a. Errors 10%

TABLE 2. Trace Element Content of Human Lung Tissue

Element	$\mu\text{g/g}$ Dry Tissue (a)				
	Normal (b)	Heavy Element Exposure (c)	Copper Ore Exposure (d)	Uranium Mine Exposure (d)	Uranium Processing Exposure (e)
Na	11,600	8,900	9,000	---	6,900
K	10,300	6,600	6,300	---	10,400
Rb	15.6	13.8	10.4	---	12.0
Cs	0.116	0.054	0.041	---	0.094
Al	---	---	190	---	---
Br	56	35	15	8	94
Cl	---	---	11,000	---	---
Zn	56	38	55	88	50
Fe	640	860	430	1,480	1,200
Co	0.200	0.130	0.092	0.076	0.079
Cr	0.52	1.4	1.1	1.4	0.77
Se	1.4	1.2	1.1	0.46	---
Sc	0.006	0.040	0.021	0.056	0.051
Sb	0.230	0.230	0.070	0.048	0.088
Ag	<0.02	0.02	0.019	0.021	---
Hg	0.45	0.45	<0.1	1.2	---
Au	---	0.023	0.04	4.5	0.014
Th	<0.1	0.83	---	---	---
U	<0.001	≤ 0.005	<0.01	2.1	27.0

a. Errors 10%

b. Average of Right and Left, Upper and Middle Lobes

c. From Great Britain

d. From Colorado

e. From Richland, Washington (3 pack/day smoker)

individuals with heavy metal exposure, and copper ore processing, uranium mining, and uranium processing experience. The average concentrations found in the normal individual (Table 1) are also included in Table 2 for comparison. The individual with heavy element exposure had high concentrations of Th (0.8 ppm)

and Cr (1.4 ppm) while maintaining "normal" concentrations of the other elements. The individual with copper ore exposure was also "normal" with respect to all the elements measured. The uranium miner had high concentrations of U (2.1 ppm) and Au (4.5 ppm) in his lung compared to the normal subject and the individuals with

heavy metal and copper ore exposures. The lung tissue from the individual with uranium processing exposure had a U concentration (27 ppm) 13 times higher than the uranium miner and 27,000 times higher than the normal individual. The Br content (94 ppm) of this subject was 2 to 10 times higher than the other individuals.

These comparisons are made with a limited amount of data. Many of the subtle variations noted in this work may be a result of natural variations in biological systems. However, variations of several orders of magnitude between individuals, such as those observed for Au, Th, U, and Sc, probably have an environmental rather than a biological origin. The analysis of additional samples from normal subjects and individuals with known chronic exposures to dust is continuing in an effort to establish the deposition and retention effects in man of the inorganic constituents in the atmosphere and their possible relation to pulmonary diseases.

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THE DETERMINATION OF THE RATIO OF ^{241}Am
TO $^{239\&240}\text{Pu}$ IN SOFT TISSUES

P. O. Jackson and J. F. Park*

An electrodeposition procedure for the simultaneous deposition of plutonium and americium allowing precise determination of the ratio $^{241}\text{Am}/^{239\&240}\text{Pu}$ in ashed tissue samples by means of alpha energy analysis is evaluated.

Evaluation of the radiation exposure from the inhalation of airborne plutonium and americium compounds requires a technique for estimating the lung burden. In addition, knowledge of the pathways of both plutonium and americium in the body following exposure is necessary to establish the MPC of a particular mixture. If americium and plutonium could be shown to behave identically in the body, it would greatly simplify the solution of both problems. The 60 keV gamma photon of ^{241}Am within the lung can be more easily measured by external detectors than can the low-energy L X-rays from plutonium decay. Thus, if the relative behavior of Pu and Am was established, body burden determination based on the externally measured counting rate of ^{241}Am could be evaluated. Many tissue samples originally obtained for studies of plutonium transport following inhalation of particulate plutonium compounds by beagle dogs were analyzed for plutonium and americium. Since the plutonium used contained quantities of ^{241}Am that were dependent on the history of reactor exposure and subse-

quent chemical separation, a precise determination of the plutonium to americium ratio in a sufficient number of samples would establish the behavioral relationships in question.

An analysis technique was needed which minimized the risk of preferential loss of either radionuclide. An electrodeposition procedure, which simultaneously deposits both actinides on a platinum disc suitable for alpha energy analysis, has the advantage of a single-step process with minimal manipulation. Such a plating procedure,⁽¹⁾ adapted for use with ashed tissue samples, was employed. The method is summarized as follows:

1. Ash sample with HNO_3 , 30% H_2O_2 , HClO_4 . Store in 4M HNO_3 .
2. Convert a suitable aliquot to chlorides with HCl . Evaporate.
3. Add ~0.1 g hydroxylamine hydrochloride and dissolve salts in 4 ml saturated NH_4Cl solution. Transfer to electroplating cell.
4. Add 10 μl 2.7M HF , 5 μg U, and three drops methyl violet.
5. Electroplate at 2A onto a platinum disc.
6. Add 5 μg U again after 5 min and 15 min.
7. After 45 min, add 3 ml concentrated NH_4OH and remove current.

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8. Rinse electrolyte to beaker with water, acidify with concentrated HNO_3 , evaporate, and mount for alpha assay.
9. Dismantle cell and rinse disc with water and ethanol. Dry and flame disc.
10. Use silicon surface barrier detector for alpha energy analysis with multichannel analyzer.
11. Measure the ratio

$$\frac{5.15 \text{ MeV alphas } \left(\begin{smallmatrix} 239\&240_{\text{Pu}} \\ 241_{\text{Am}} \end{smallmatrix} \right)}{5.48 \text{ MeV alphas } \left(\begin{smallmatrix} 238_{\text{Pu}} \\ 239\&240_{\text{Pu}} \end{smallmatrix} \right)}$$

The ratio

$$\frac{5.48 \text{ MeV alphas } \left(\begin{smallmatrix} 238_{\text{Pu}} \\ 239\&240_{\text{Pu}} \end{smallmatrix} \right)}{5.15 \text{ MeV alphas } \left(\begin{smallmatrix} 239\&240_{\text{Pu}} \\ 241_{\text{Am}} \end{smallmatrix} \right)}$$

is determined with the same procedure after extracting Pu into 0.45M TTA in xylene from 1M HNO_3 and back extracting into 8M HNO_3 .

Lung sections, bronchial lymph nodes, and livers from beagles exposed to PuO_2 and PuF_4 dusts were wet ashed with HNO_3 , 30% H_2O_2 , and HClO_4 . Bone samples were partially dry ashed and then wet ashed with HNO_3 and 30% H_2O_2 . After dilution in 4M HNO_3 , selected samples were filtered through 0.45 μ membrane filters and the filters alpha counted to assure complete solution. The total alpha content of the samples was between 200 and 250,000 d/m. Interference from the sample matrix was minimized where possible by using 0.1 to 4% aliquots for electrodeposition.

A 270 keV energy band was summed for each alpha peak in alpha energy analysis calculations. Peak resolution was approximately 60 keV (F.W.H.M) for thin sources. Counting periods were sufficient to achieve a minimum of 50,000 counts in each peak.

Correction for alpha tailing was made by assuming that the 5.48 MeV peak overlapped the 5.15 MeV peak in proportion to a similar peak overlap between the 5.15 MeV and the region at 4.82 MeV.

By using successive approximations, the following expressions converge to yield the net 5.15 MeV peak count corrected for tailing from 5.48 MeV:

1. Net 5.15 MeV = Gross 5.15 MeV
- (Net 4.82 MeV) $\left(\frac{\text{Gross 5.48 MeV}}{\text{Net 5.15 MeV}} \right)$
2. Net 4.82 MeV = Gross 4.82 MeV
- (Gross 4.49 MeV) $\left(\frac{\text{Gross 5.48 MeV}}{\text{Net 5.15 MeV}} \right)$
3. No tailing corrections are required for the 5.48 MeV peak.

The ratio of americium to plutonium is calculated as follows:

$$\left[\frac{\text{Net 5.48 MeV count}}{\text{Net 5.15 MeV count}} \right]_a$$

$$- \left[\frac{\text{Net 5.48 MeV count}}{\text{Net 5.15 MeV count}} \right]_b = \left[\frac{241_{\text{Am}} 238_{\text{Pu}}}{239\&240_{\text{Pu}}} \right]$$

$$- \left[\frac{238_{\text{Pu}}}{239\&240_{\text{Pu}}} \right] = \left[\frac{241_{\text{Am}}}{239\&240_{\text{Pu}}} \right]$$

where "a" is the total sample and "b" is the separated Pu fraction.

Careful techniques were necessary to achieve consistent quantitative recoveries. Excessive salts from the sample matrices had an inhibiting effect on the radionuclide deposition. Previous investigators^(2,3) have shown that iron and aluminum inhibit plating from ammonium chloride or ammonium nitrate electrolytes. Fluoride had been shown to mask the effect of iron expected to be present in tissue samples.⁽¹⁾ In the present analyses, a

reduced plating efficiency was always accompanied by a white or gray deposit on the cathode. Bone samples always had a heavy white deposit and serious plating loss. Liver samples formed a visible deposit but quantitative recoveries were achieved when 0.1 to 1% of the organ was used. Quantitative thin deposits were normally attained for the lung and lymph node aliquots. Recovery losses were corrected on a second deposition, indicating operational error rather than matrix inhibition. The effects of a low recovery on the measured ratio of the 5.15 MeV peak to the 5.48 MeV peak are shown in Table 1.

Recoveries below 90% were accompanied by a lower ratio, indicating a preferential loss of plutonium. Recoveries were determined both from comparison of the gross alpha content of the electrodeposited source with the alpha content of aliquots dried on counting dishes and from the alpha content of the electrolyte after electrodeposition. Because of count-

ing variations in the dried sources from self-absorption and scatter, the recovery precision measurements were approximately $\pm 5\%$. All recoveries measured as 95% or greater were considered quantitative.

The reproducibility of $^{241}\text{Am}/^{239\&240}\text{Pu}$ ratios in replicate electro-deposition with recoveries exceeding 95% is shown in Table 2.

Table 2 shows an average and maximum precision of $\pm 1.4\%$ and $\pm 3.6\%$, respectively. Based on these results, a difference of 7% between two independent ratio determinations would be significant.

In Table 3, the typical results for several tissue samples from a single dog exposed to PuO_2 are presented. The variations between samples and exposure material were not significant, with the possible exception of bronchial lymph node Number 3.

This method has been satisfactory for the high specific activity soft tissue samples resulting from laboratory exposures of Pu and Am compounds.

TABLE 1. The Effects of Electrodeposition Yield in the Measured Ratio of $^{239\&240}\text{Pu}$ to $^{241}\text{Am}\&^{238}\text{Pu}$

Sample	Recovery, %	Ratio $\left(\frac{\text{Net 5.15 MeV count}}{\text{Net 5.48 MeV count}}\right)$
1	71	1.53
	97	1.61
2	87	1.63
	98	1.62
3	65	1.05
	97	1.64
4	86	1.38
	99	1.64
5	90	1.38
	100	1.66

TABLE 2. Precision of Replicate Analyses

Sample	Recovery, %	$^{241}\text{Am}/^{239\&240}\text{Pu}$	Range	σ (a)	$\sigma/\bar{x}$
1	99	0.515	0.0018	0.0016	0.0031
	98	0.517			
2	95	0.547	0.022	0.020	0.036
	95	0.525			
3	96	0.526	0.0011	0.00098	0.0019
	97	0.525			
4	100	0.531	0.0187	0.0110	0.020
	100	0.546			
	100	0.550			
5	97	0.569	0.0065	0.0058	0.010
	96	0.576			

Average Coefficient of Variation ($\sigma/\bar{x}$) = 0.014a. σ based on range estimateTABLE 3. $^{241}\text{Am}/^{239\&240}\text{Pu}$ Ratios in Organs from a Beagle Exposed to Airborne PuO_2

Sample	d/m $^{241}\text{Am}/\text{d/m } ^{239\&240}\text{Pu}$
Lung 1	0.52
Lung 2	0.54
Lung 3	0.54
Lung 4	0.52
Lung 5	0.53
Bronchial Lymph Node 1	0.53
Bronchial Lymph Node 2	0.54
Bronchial Lymph Node 3	0.59
Bronchial Lymph Node 4	0.52
Exposure Material	0.54

For bone samples or low specific activity tissues, a method of removing matrix interference constituents such as calcium is under investigation.

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RADIONUCLIDE DISTRIBUTION IN THE ALASKAN ARCTIC ECOSYSTEM

C. E. Jenkins and W. C. Hanson*

Eighteen gamma-emitting natural and artificial radionuclides were measured in the Arctic biosphere. The comparison of the accumulation of radionuclides in plant and animal tissues shows distinct variations and differences in the behavior of these individual radioelements. Generally, retention of these radionuclides was found to be location and species dependent in lichen and sex and age dependent in caribou.

The Arctic ecosystems have received attention because of their unique capability for transmitting significant quantities of fallout radionuclides to human populations. Most attention has centered on ^{90}Sr and ^{137}Cs because of radiological health considerations and ease of measurement. Numerous other fallout radionuclides are present in measurable quantities and are important because of concentration variability in the ecosystem. They provide a unique opportunity to study trace element uptake, pathways, and behavior within a terrestrial food web.

Many studies have been made of Arctic ecosystems which show that the moss-lichen community acts as the single most important radionuclide fallout reservoir.⁽¹⁾ This basic component in the Alaskan food web determines future radionuclide levels in the second and third trophic levels (lichen-caribou-wolf or man). As part of a program to identify the pathways, retention, and concentration factors of three trophic levels; lichen, caribou, and wolf samples were obtained from Anaktuvuk Pass,

Alaska (68°10'N Lat.). The procedure for handling the samples has previously been described.⁽²⁾ Each sample was analyzed on multidimensional gamma-ray spectrometers⁽³⁾ and large Ge(Li) diode systems,⁽⁴⁾ providing concentration measurements of 18 gamma-emitting radionuclides. These artificial fallout radionuclides were measured in air and biological samples, and the average concentrations are presented in Table 1. These results permit comparisons between trophic levels and various types of tissue in the animals. The uptake, retention, and location of various radionuclides permit a rough prediction of the biological hazard involved for a given organism within a given location and the variation in radionuclide concentration in each trophic level.

Maximum ^{22}Na concentrations occurred in the bone tissue of caribou and wolf. The caribou and wolf soft-tissue radionuclide concentrations were uniform, although the wolf tissue concentration was twofold greater than that observed in the caribou. Caribou and wolf muscle ^{22}Na concentrations were factors of 10 and 20, respectively, above levels observed in lichen.⁽⁵⁾ The ^{22}Na uptake and retention were the highest observed

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TABLE 1. Average Radionuclide Concentrations for Air,^(a)
Lichen, Caribou and Wolf - Anaktuvuk Pass, Alaska 1967

Radionuclide	(d/m/kg wet wt)								
	Air ^(a) dpm/10 ⁶ SCF	Lichen (3) ^(b)	Caribou Muscle (3)	Caribou Liver (3)	Caribou Bone (3)	Caribou Kidney (3)	Wolf Muscle (2)	Wolf Liver (1)	Wolf Bone (2)
²² Na	0.506	9.35	110	70.9	555	120	218	202	430
⁴⁰ K	---	638	6,160	3,830	2,310	3,180	7,580	5,340	3,900
⁵⁴ Mn	7.7	465	43.3 (1)	7.85	321	ND	ND	ND	ND
⁶⁰ Co	0.46	75.4	16.5	18.5	8.0	18.8	ND	ND	ND
⁶⁵ Zn	2.24	ND ^(c)	ND	ND	ND	ND	ND	ND	ND
⁸⁸ Y	1.10	0.738	0.0357 (1)	ND	1.25 (1)	ND	ND	ND	ND
⁹⁵ Zr-Nb	539	247	ND	ND	450	ND	ND	ND	ND
¹⁰⁶ Ru	87	1,640	57.5 (2)	70.3	225	93	ND	ND	ND
^{110m} Ag	0.13	1.74	0.87	13.8	6.1 (2)	1.46	ND	ND	ND
¹²⁵ Sb	30.0	1,500	ND	ND	1,540	ND	ND	ND	ND
¹³⁴ Cs	0.07	28.9	10.9 (2)	8.6	6.25 (1)	ND	11.8	8.9	ND
¹³⁷ Cs	92	17,000	20,000	12,100	4,300	19,000	38,000	29,600	11,100
¹⁴⁴ Ce	117	8,540	900	268	ND	ND	ND	ND	ND
¹⁵⁵ Eu	---	1,900	ND	44.9	ND	ND	ND	ND	ND
²⁰⁷ Bi	0.046	24.7	ND	ND	ND	ND	ND	ND	ND
²⁰⁸ Tl	0.44	6.8	2.4	6.4	130	3.2	ND	ND	ND
²¹⁰ Pb	---	2,360	ND	571	4,090	ND	ND	ND	ND
²¹⁴ Bi	0.31	15.8	ND	ND	213	ND	ND	ND	ND
²²⁶ Ra	---	ND	ND	ND	1,130 (2)	ND	ND	ND	ND

a. C. W. Thomas Data (Ref. No. 9)

b. Number of samples in parentheses

c. Nondetectable.

for any radionuclide except for ²²⁶Ra and may reflect a lack of natural Na (biological half-life 11 d) in the Arctic terrestrial ecosystem. Cesium-137 concentrations in caribou muscle and kidney tissue and lichen were approximately equal. Wolf muscle contained approximately twofold higher ¹³⁷Cs levels than in the caribou muscle.⁽⁶⁾ Caribou bone had 1/3 and 1/5 and wolf bone had 1/3 and 1/4 as much ¹³⁷Cs/kg wet weight as liver and muscle tissue, respectively.

The ratio between ¹³⁴Cs and ¹³⁷Cs in various samples indicates a rapid turnover rate in the soft tissues compared to bone tissue.⁽⁶⁾ Europium-155 was detected for the first time in the terrestrial biota (lichen and caribou liver), although it has been observed in fallout air samples.⁽⁷⁾ Manganese-54 concentrations in caribou ranged from <1 to 10% and from 50 to 96% in muscle and bone tissue, respectively, compared to lichen. Caribou liver concentrations were three- to four-fold that

of muscle tissue while concentrations in wolf were nondetectable.

Cobalt-60 concentrations in caribou muscle ranged from 1 to 50% of that measured in lichen, while its concentrations in caribou liver, kidney, and bone tissue were 20 to 30%, 25%, and 4 to 30% of lichen concentrations, respectively. Wolf tissue concentrations were below 0.01% that in the lichen.

Ruthenium-106 uptake through the gastrointestinal tract wall has been reported to be very low;⁽⁸⁾ however, the observations indicate sufficient amounts enter the blood stream to provide substantial concentrations in the bone, liver, kidney, and muscle tissue. The ^{106}Ru concentrations observed in this study were highest in the bone tissue. Concentrations in kidney and liver tissue were similar and were higher than observed for muscle tissue. The concentrations of ^{106}Ru in wolf were nondetectable.

Caribou liver tissue has the highest $^{110\text{m}}\text{Ag}$ concentrations observed in a terrestrial ecosystem.⁽⁵⁾ The average concentration factor for caribou liver is nearly a factor of 10 above that in lichen; however, on an individual basis, values range from 4 to 30 times the levels observed in lichen.

On an activity per kg wet-weight basis, ^{54}Mn , ^{60}Co , ^{88}Y , $^{95}\text{Zr-Nb}$, ^{106}Ru , ^{125}Sb , ^{144}Ce , ^{155}Eu , ^{207}Bi , ^{210}Pb , and ^{214}Bi appear to be discriminated on each successive trophic food level. Uptake and retention of

various radionuclides by lichen appear to be species dependent. Although the location of the lichen must be important with respect to total fallout deposition, the highest concentrations were generally observed in the species with the greatest structural diversity. Caribou retention of radionuclides appears to be sex and age related. In general, tissues from a seven-year-old female had substantially higher concentrations of ^{24}Na , ^{54}Mn , ^{60}Co , and $^{110\text{m}}\text{Ag}$ than either of the other two caribou sampled. Concentration differences may be related to the total integration time involved for each caribou and the total lichen consumed.

The two male wolves (two and four years old) had similar concentrations of radionuclides except for ^{22}Na , which was approximately 1-1/2-fold higher in the older male bone tissue. The substantially higher ^{22}Na concentrations in older animals of the same species indicate the biological half-life in the terrestrial Arctic ecosystem may be considerably longer than the 11 days reported for man. The comparison of the accumulation of radionuclides in plant and animal tissues shows that distinct differences exist in the behavior of these individual radioelements. By application of existing sensitive gamma-ray spectrometry techniques,^(3,4) the absolute and relative behavior of these complex radionuclide groups are being defined.

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RADIONUCLIDE DISTRIBUTION IN PACIFIC SALMON*

C. E. Jenkins

Seventeen gamma-emitting radionuclides were measured in four different species of Pacific salmon. The concentrations of the radionuclides ^{54}Mn and ^{60}Co in salmon caught in northwestern Alaska were the highest and decreased in those caught in southern Alaska to the Oregon-Washington coast (approximately 1.5 to 3 and 4.5 to 12, respectively) while the concentration of ^{137}Cs decreased less (approximately 25 percent). The distribution pattern of other radionuclides was influenced by the Columbia River, Chinese nuclear testing, and other parameters. Concentrations of natural ^{226}Ra in Alaskan salmon tissue were sufficiently high to permit native fish-eating populations to exceed their maximum permissible concentrations (percent MPC calculated for a 600 g/day intake using ICRP recommendations of 1/30 MPC for non-occupationally exposed individuals). Other radionuclides measured were ^{22}Na , ^{40}K , ^{46}Sc , ^{51}Cr , ^{57}Co , ^{59}Fe , ^{65}Zn , ^{88}Y , ^{110}Ag , ^{140}Ba , ^{152}Eu , ^{203}Hg , and ^{208}Tl .

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RADIONUCLIDE COLLECTION EFFICIENCIESFROM OCEAN WATER WITH ALUMINA

W. B. Silker and H. G. Rieck

The efficiency with which alumina removes radionuclides from seawater was determined in the laboratory and with in-situ measurements at sea. Good agreement between these two methods was obtained for most radionuclides. Disagreement in values for ^{51}Cr and ^{54}Mn are ascribed to existence of different chemical or physical forms in the two systems.

Radionuclides from detonated nuclear devices, cosmic rays, and natural sources in the ocean have provided the means to substantially increase our knowledge of ocean processes. Until recently the use of radionuclides has been limited by their extremely low concentrations in seawater. This problem has been solved by the use of a filtration-sorption system,⁽¹⁾ which consists of eight 305 mm diameter filters in parallel and a sorption bed of aluminum oxide (0.63 cm $\times$ 305 cm diam) through which the water is forced. A critical evaluation of the retention efficiencies attained with the sampling unit for the various natural and artificial radionuclides in ocean waters was needed to fully utilize the system for accurate measurements in the marine environment. Initial evaluation of radioisotope retention⁽¹⁾ was based on laboratory studies where artificial seawater containing added radioisotopes was passed through a small bed. It was decided to employ fresh seawater in a re-evaluation of the collection efficiencies of radioisotopes indigenous to the Columbia River as well as the additional fallout species. The relative retentions

were evaluated, both in the laboratory and in the Pacific Ocean, where the radionuclides present in the seawater served as tracers for the process. The ocean experiment thus eliminated any inconsistencies resulting from differences in either the chemical or physical state between the prepared solution and the natural states of the various radionuclides.

Laboratory investigations were conducted with a small system that provided prefilters and a 1 cm² $\times$ 0.63 cm deep bed of aluminum oxide* adsorbent. A sample of seawater containing one or more radionuclides of interest was passed through this system at a flow rate of 50 ml/min, which is equivalent to the operational shipboard flow rate of 37.85 liters/min for the large ocean sampling system. Collection efficiencies, determined by gamma counting, were evaluated both by comparison of the spike concentrations in the influent and effluent streams, and by assay of the amounts retained by the bed with respect to the total

* Alumina, Woelhm Neutral Activity, Alupharm Chemical Co., New Orleans, Louisiana

throughput. Agreement was obtained by both of these methods. The retention efficiencies for the various radionuclides measured by this method are included in Table 1. Sorption of the radionuclides was constant at flow rates below 50 ml/min/cm², but decreased by 10% at 100 ml/min/cm² and 27% at 150 ml/min/cm². The retention efficiencies were maintained after passage of the equivalent of approximately 6000 liters through the ocean system, which is in excess of the 4000 liters normally required to adequately measure the concentration of ocean radionuclides.

TABLE 1. Percent Uptake of Soluble^(a) Radionuclides from Seawater by Alumina

Radionuclide	Laboratory Flow = 50 ml/min/cm ²	Ocean Test
⁷ Be	73	66 ± 14
⁴⁶ Sc	43	68 ± 35
⁵¹ Cr	25	0.5 ± 0.5
⁵⁴ Mn	1.5	44 ± 44
⁶⁰ Co	14	10 ± 6
⁶⁵ Zn	45	44 ± 45
⁹⁵ Zr-Nb	47	59 ± 13
¹⁰⁶ Ru	18	17 ± 2
¹²⁴ Sb	2.5	3 ± 2
¹⁴⁴ Ce	58	62 ± 29
²¹⁴ Bi (²²⁶ Ra)	2.5	4 ± 6
²³⁴ Th	56	40 ± 7

(a) Those materials that pass on 0.3 μ membrane filter are assumed to be soluble.

Utilizing the facilities aboard the R/V Yaquina, a research vessel operated by Oregon State University, the collection efficiencies of the radionuclides existent in the ocean were determined in-situ. A large reaction vessel on the ship allowed the separation of trace elements and radionuclides from about 600 liters of ocean water by precipitation-scavenging reactions, while a concurrent water sample was passing through the ocean sampling system. This experiment was repeated at four stations along the Oregon and Washington coasts, which were within the influence of the Columbia River plume, yet contained 32% salinity. The Columbia River proximity provided adequate concentrations of radioactive tracers for the experiment.

After collection of water in the reaction vessel, FeSO₄ was added to a concentration of 288 ppm. Addition of a stoichiometric quantity (100 ppm) of KMnO₄ thus resulted in formation of hydrous ferric and manganese oxides. Scavenging efficiencies for this precipitation reaction have been previously reported.^(2,3) The resulting suspension was agitated for 10-20 minutes and allowed to settle for 12-24 hours, after which the supernatant liquid was siphoned. The precipitate was removed and eventually isolated by filtration, dried and transferred into a suitable counting container. The filters and alumina, which were removed from the ocean sampler, were also dried and transferred into counting containers. All of these samples were analyzed with a multidimensional gamma-ray

spectrometer,⁽¹⁾ and the amounts of the various radioactive species determined from the resultant spectra. Bed efficiencies calculated according to the following equation are also included in Table 1:

$$\text{Efficiency} = \frac{d/m(\text{Al}_2\text{O}_3)}{d/m(\text{ppt}) - d/m(\text{filter})} \times 100$$

The quantities of radioisotopes used in the laboratory tests were such that the error due to counting statistics was less than 3%. Large errors attached to the values from the ocean test are due in part to the counting statistics from the low concentrations of radionuclides involved, and in part to the fact that they result from the division of a small number by the difference of two relatively large numbers. Good agreement was obtained between the two tests for all isotopes with the exception of ⁵⁴Mn and ⁵¹Cr. It is felt that these discrepancies resulted from differences in the chemical or physical form of the isotopes in the two systems, which emphasizes the

need for in situ evaluation under the conditions from which field samples are expected to be obtained. These comparisons also show that for cases where the natural state of the radionuclides can be duplicated, laboratory evaluation of retention efficiencies are satisfactory.

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$^{51}\text{Cr(VI)}$ SEPARATION FROM SEAWATER AND FRESH WATER
ON A REDUCTION SORPTION BED

R. W. Perkins

A procedure has been developed for the separation of ^{51}Cr from seawater and fresh water that simply involves passing the water through a 0.7 cm thick bed of SnCl_2 impregnated Al_2O_3 . At linear flow rates of 75 cm per minute, the retention is greater than 99%. The ^{51}Cr content is determined by direct counting of the sorption bed in a large NaI(Tl) well crystal. By use of this technique in conjunction with the standard 600 cm^2 ocean sampling bed, ^{51}Cr concentrations of 0.02 dpm/liter can be measured by sampling 4000 liters of seawater.

The radionuclide ^{51}Cr has a half-life of 27.8 days and is the prominent radionuclide resulting from reactor operations. Chromium is a constituent of stainless steel and other reactor structural components and dichromate salts are used as additives in reactor cooling water. At the Hanford reactors, $\text{Na}_2\text{Cr}_2\text{O}_7$ is added continuously as a corrosion inhibitor to the reactor process water; and the subsequent discharge of this water to the Columbia River following its exposure to the reactor neutron flux results in a continuous input of $^{51}\text{Cr(VI)}$ to the river. Although ^{51}Cr is by far the most abundant of the long-lived radionuclides being added to the Columbia River, it is a conservative radioisotope and is not taken up to a great extent by either the river sediments or the biota.⁽¹⁾ Recent studies have shown that greater than 95% of the ^{51}Cr is in the hexavalent form on entering the Columbia River and that it remains mainly in this form both on transit by the river to the ocean and its subsequent mixing in the ocean.

Because of its conservative properties and its continuous input to the Pacific Ocean, $^{51}\text{Cr(VI)}$ has been recognized as a potentially excellent tracer of the rates and mechanisms involved in the mixing of the Columbia River with the Pacific Ocean. However, to exploit its full potential, methods for its measurement at concentrations of 0.1 dpm/liter or even less must be available. Initial studies under the direction of Osterberg⁽²⁾ employed a basic precipitation technique for concentrating ^{51}Cr from 500 to 600 liter samples of ocean water. This technique was subsequently improved by Cutshall⁽³⁾ by addition of a reducing agent which insured a higher and more consistent recovery of ^{51}Cr . Although this technique proved successful at sea and was satisfactorily employed in conjunction with a shipboard analyzer for measurements at sea, it did require a few hours per sample for processing; and its application for detailed sampling was therefore limited.

To permit the detailed definition of the initial vertical and horizontal mixing of the fresh water and

seawater in the river estuary and its subsequent mixing to distances of several hundred kilometers at sea, a far more rapid and simple method would be required. To meet this objective, the direct collection of ^{51}Cr on sorption beds through which seawater or fresh water could be pumped was investigated.

In previous studies it had been shown that chromatographic grade aluminum oxide (Alumina, Woelm Neutral, Alupharm Chemicals, New Orleans, Louisiana) was very efficient in removing several radionuclides from seawater.⁽⁴⁾ Subsequent laboratory studies indicated that $^{51}\text{Cr}^{+3}$ could be quantitatively removed from either seawater or fresh water by passing the water at linear flow rates of 75 cm/min through 1 cm thick aluminum oxide beds. However, under these conditions, only 5 to 10% of the $^{51}\text{Cr(VI)}$ was retained. Experiments were therefore initiated to determine if the Al_2O_3 beds could be impregnated with a reducing agent which would reduce the $^{51}\text{Cr(VI)}$ and thus allow its retention.

Separate aliquots of the Al_2O_3 were impregnated with 1M solutions of ferrous ammonium sulfate, arsenic trichloride, and stannous chloride, dried at 125 °C in a nitrogen atmosphere, and tested for $^{51}\text{Cr(VI)}$ retention from fresh water and seawater at the above-mentioned flow rates. Retention efficiencies for fresh water of greater than 99, 85, and 84% were obtained for the SnCl_2 , $\text{Fe}(\text{NH}_4)_2\text{SO}_4$, and AsCl_3 impregnated beds, respectively. Retention efficiencies from seawater were also greater than 99% for the SnCl_2 impregnated beds and

substantially lower for the $\text{Fe}(\text{NH}_4)_2\text{SO}_4$ and AsCl_3 beds. Additional tests of the retention capacity indicated a greater than 99% retention of $^{51}\text{Cr(VI)}$ on a 1 cm² by 0.7 cm thick bed from 10 liters of seawater. A 600 cm² bed of the size normally employed in our seawater sampling programs should, therefore, be quantitative for total flow volumes of at least 6000 liters. Where a 4000 liter sample of seawater is pumped through a bed of such size and the bed counted directly in a large 9 in. well crystal,⁽⁵⁾ ^{51}Cr concentrations as low as 0.02 can be measured. The standard method adopted for preparation of the impregnated Al_2O_3 is as follows: 1 kg of Al_2O_3 is added to 2 liters of hot (90 to 100 °C) 1M SnCl_2 , and the mixture is stirred briefly and allowed to stand for 10 min. The solution is then removed by filtering through a large Buchner funnel, and the SnCl_2 impregnated Al_2O_3 is dried in a nitrogen atmosphere at 125 °C. The impregnated Al_2O_3 is stored under N_2 prior to use.

This procedure has been successfully demonstrated on fresh water and has been employed in a pilot study of the ^{51}Cr distribution in the Pacific Ocean.⁽⁶⁾

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RADIUM AND RADIOBARIUM MEASUREMENT IN SEAWATER AND FRESH WATER BY SORPTION AND DIRECT MULTIDIMENSIONAL GAMMA-RAY SPECTROMETRY

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A procedure is described which permits the removal of Ra and Ba radioisotopes from seawater and fresh water on sorption beds and the subsequent direct counting of these beds on a multidimensional gamma-ray spectrometer. By use of 0.5 to 1 cm thick BaSO₄ impregnated Al₂O₃ sorption beds, the Ba and Ra radioisotopes can be removed at linear flow rates of up to 1 m/min. Suitable techniques for impregnating the Al₂O₃ beds with BaSO₄ have been developed, and their efficiencies for Ba and Ra radioisotope retention have been determined. The feasibility for the rapid Ra isotope separation from several thousand liter volumes of seawater and the subsequent direct counting of the sorption beds for ²²³Ra, ²²⁴Ra, ²²⁶Ra, and ²²⁸Ra measurements was demonstrated from sampling performed on the November, 1968, cruise of the USC&GSS Surveyor between San Francisco, California, and Seattle, Washington.

The ocean geochemistries of ²²⁶Ra and Ba are interrelated, and their distributions appear to be controlled by major biological, chemical, and mixing processes. For example, both the ²²⁶Ra and Ba concentrations show a substantial increase with depth. However, while the barium depth profile appears to be mainly controlled by its uptake and subsequent

movement with biological detrital material, the Ra depth profile is also controlled by its radiogenic formation and subsequent release from bottom sediments.

The chemistry of Ba in seawater and sediments has been the subject of several studies. From these investigations, it is evident that Ba is substantially enriched in ocean

bottom sediments below areas of high productivity,^(1,2) that the Ba concentration does increase with depth,⁽³⁾ and although Ba is carried to deeper regions of the ocean and to the ocean floor by organic detritus, it is not accumulated by the skeletal material of ocean organisms. Chow and Goldberg⁽³⁾ have suggested that during bacterial oxidation of the organic detrital phase, high concentrations of sulfate ion are formed within the biomass, thereby causing precipitation of BaSO_4 to occur. The barite crystals incorporated in and sinking with the decomposing detrital material may either redissolve in deeper water or reach the ocean floor.

The similar chemical properties of ^{226}Ra would require that it participate in these processes; however, its main source in ocean water is radiogenic formation in ocean bottom sediments. The immediate parent of ^{226}Ra is ^{230}Th (80,000 yr half-life). Thorium-234 is almost completely precipitated from seawater and its reported concentrations appear to be at least 100 times lower than that of its ^{226}Ra daughter.^(4,5) Thus, while the ocean floor is essentially the only source of ^{226}Ra , the barium supplied by the ocean floor may not be a significant fraction of the ocean water barium.

Three other Ra isotopes are also present in seawater. These are ^{228}Ra , the 6.7 yr daughter of ^{232}Th ; ^{224}Ra (3.64 d), a third generation daughter of ^{228}Ra and the daughter of ^{228}Th ; and ^{223}Ra , the 11.1 d daughter of ^{237}Th (18 d) and a member of the ^{235}U chain.

It is apparent that measurements of the relative concentrations of the radium isotopes could provide unique and extremely useful information on oceanographic processes which occur on time scales comparable to the half-lives of these isotopes. Although there are no primordial or radiogenic Ba radioisotopes in seawater, the artificial radioisotopes ^{133}Ba and ^{140}Ba are added to the ocean continuously and intermittently by nuclear operations. The Columbia River, which is used to cool nuclear reactors, contributes both of these radionuclides to the ocean and they are also added periodically by nuclear weapons testing. The possibility of employing the natural isotope pair ^{228}Ra - ^{226}Ra in defining ocean circulation and mixing processes was recognized by Kaufman,⁽⁶⁾ who is presently making measurements of these isotopes for that purpose.

In work by Perkins, Robertson, and Rieck,⁽⁷⁾ it was found that several of the natural and artificial radionuclides in seawater could be collected by pumping seawater through an Al_2O_3 bed; however, Ra was only poorly retained. This procedure, which employed sorption beds of 0.6 cm thick by 28 cm in diameter allowed radionuclide separations in situ from several thousand liters of seawater and the subsequent measurement of the radionuclides by direct counting on a multidimensional gamma-ray spectrometer. Because of the great potential of Ra and Ba radioisotope measurements in clarifying numerous oceanographic processes, it was very desirable to develop a sorption bed for their direct removal from seawater.

The method developed involves the sorption of Ra and Ba on BaSO_4 impregnated Al_2O_3 . Yields of greater than 95% are obtained for bed thicknesses of 1 cm with linear flow rates of 1 m/min. Sorption bed preparation is performed in the following manner: One hundred grams of Al_2O_3 are placed in 200 ml of 1M Na_2SO_4 at the boiling temperature and allowed to remain for 5 min. It is then filtered, dried at 125 °C, and placed in 200 ml of boiling 1M $\text{Ba}(\text{NO}_3)_2$ for 5 min. Following filtration, the Al_2O_3 is again placed in boiling 1M Na_2SO_4 for 5 min, filtered, and dried at 125 °C. This BaSO_4 impregnated Al_2O_3 is then ready for use as a sorption bed.

The sorption efficiencies for ^{133}Ba and ^{226}Ra from seawater on BaSO_4 impregnated Al_2O_3 beds have been studied as a function of salinity. The sorption efficiencies are greater than 95% for both ^{133}Ba and ^{226}Ra saline-fresh water mixtures, ranging from 35 to 5‰ for fresh water (Columbia River water). For these measurements, a total of 2 liters/cm² of sorption bed was passed at a linear flow rate of 1 m/min. In subsequent measurements where a total of 10 liters/cm² was passed at the same flow rate, a similar high retention was obtained.

Measurements of the retention of ^{133}Ba and ^{226}Ra on normal (nonimpregnated) Al_2O_3 gave low and erratic retention. Although the separation technique is entirely satisfactory for removal of the Ba and Ra radioisotopes from seawater, the controlling mechanisms are not entirely clear. The sorption efficiencies for

^{133}Ba and ^{226}Ra from distilled water to which pure NaCl was added in amounts ranging up to that of normal seawater were all less than 50%, and for the pure distilled water the sorption yield was less than 10%. While it is evident that the natural constituents of seawater and river water substantially improve the Ra and Ba retention, the reasons are not obvious. The elucidation of this behavior will require further experimentation.

A major objective of this study was to develop a method for collecting the Ra and Ba radioisotopes from seawater on a material which could be directly counted for their measurement. The feasibility of measuring all four of the radium isotopes-- ^{223}Ra , ^{224}Ra , ^{226}Ra , and ^{228}Ra --on a BaSO_4 impregnated Al_2O_3 bed was demonstrated on samples collected during a recent cruise of the USC&GSS Surveyor. During a cruise between San Francisco, California, and Seattle, Washington, in November, 1968, four 1000 to 4000 liter samples of seawater were pumped through fiber glass prefilters followed by 28 cm-diameter by 0.6 cm-thick BaSO_4 impregnated Al_2O_3 sorption beds. The subsequent counting of these beds on a multidimensional gamma-ray spectrometer showed the characteristic photon spectra of the four Ra isotopes from which their concentrations could be calculated. The energy regions used in the measurement of these Ra isotopes, together with those which would be employed for the measurement of ^{133}Ba and ^{140}Ba if they were present, are listed in Table 1 and

TABLE 1. Energy Regions for the Measurement of Radium and Barium Radioisotopes by Multidimensional Gamma-Ray Spectrometry

Isotope	Half-Life	Gamma-Ray Energy Regions, MeV
^{226}Ra (^{214}Bi)	1620 yr	0.6094 and 1.120 (in coincidence)
^{228}Ra (^{228}Ac)	6.7 yr	0.912 + 0.970 (0.1586)
^{223}Ra	11.1 d	(0.1586 + 0.1541 + 0.1442) + 0.2696
^{224}Ra (^{208}Tl)	3.64 d	0.5831 and 2.615 (in coincidence)
^{133}Ba	7.2 yr	0.356
^{140}Ba (^{140}La)	12.8 d	0.4867 and 1.596 (in coincidence) 0.815 and 1.596 (in coincidence)

Figure 1, respectively. The reasonably high counting efficiency, together with the very low background of the multidimensional gamma-ray spectrometer, permits ^{226}Ra measurements from samples containing only a few disintegrations per minute.

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FIGURE 1. Energy Regions Used in the Direct Measurement of Radium and Barium Radioisotopes by Multidimensional Gamma Ray Spectrometry

Since ^{226}Ra is determined from the concentration of ^{214}Bi , which is a daughter of the noble gas ^{222}Rn (3.8 d half-life), it is essential that the sorption bed material be allowed to stand in a sealed container for a few half-lives of ^{222}Rn prior to counting.

The simplicity of the technique for Ra and Ba radioisotope measurements in the ocean will permit its rapid exploitation in oceanographic studies.

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SURFACE CONCENTRATIONS OF RADIONUCLIDES IN THE NORTH PACIFIC OCEAN

W. B. Silker

Samples were taken from the surface and at a depth of 25 m in the North Pacific Ocean off the coasts of Central and North America. Beryllium-7 concentrations in surface water were 600 to 700 d/m/10³ liters in equatorial waters and 50 to 100 d/m/10³ liters between 13° and 40°N Lat. Fission-product radionuclides exhibited two regions of high concentrations, one between 12°30' and 15°N and the other between 25° and 30°N. The ratio of radionuclide concentrations at surface and at 25 m depths indicated relatively slow mixing rates in this water column.

Transfer of radionuclides from the atmosphere to the earth's surface provides tracers for the investigation of various physical and biological processes. Fallout of the various radionuclides is a function of their air concentration, which is latitude dependent. Beryllium-7 is continually produced in the atmosphere by nuclear spallation of cosmic radiation with oxygen and nitrogen. The combined effects of radiation intensity, tropopause height, and transfer of stratospheric air into the troposphere result in ground-level air concentrations of this radionuclide that are lowest in equatorial regions and increase to maximum values at about 45° geomagnetic latitude.⁽¹⁾ Ground-level air concentrations of fission products exhibit a similar latitudinal distribution with the

highest concentrations occurring at the mid-latitudes due to exchange between stratospheric and tropospheric air through the tropopause gap.⁽²⁾ The amplitude of the peak fission product concentration is much greater than that for cosmic-ray-produced radionuclides since the latter are produced at all latitudes, while the fission products are transported from the point of injection to lower latitudes by diffusion processes.

Most of the available data on deposition of airborne radionuclides have been obtained from land-based sampling stations. Very few comparable measurements have been obtained for deposition in the world's oceans, with the exceptions of ⁹⁰Sr and ¹³⁷Cs. Samples were taken during

June, 1968, which provided the latitudinal distribution of radionuclides in the North Pacific waters. Samples were taken aboard the USC&GS ship Rainier, which followed a trackline off the western coast of Central and North America. They were obtained from surface and 25 m depths at 12 stations from the Panama Canal to northern California and were collected through polyethylene irrigation pipes with intakes 30 and 25 m below the surface. The 30 cm intake was positioned from a floating platform, while the 25 m intake was held in position with weights. Water was drawn with a self-priming centrifugal pump and forced at a rate of 37.9 liters/min through our ocean sampling system.⁽³⁾ After passage of approximately 4000 liters of water through the sampler, the unit was disassembled and the filters and alumina prepared for subsequent analysis in the laboratory. After being dried, the filters were compressed into a 1.25×5 cm-diameter PVC ring and the alumina transferred to a 2.54×15.2 cm-diameter plastic petri dish for analysis by one of two large crystal multidimensional gamma-ray spectrometers,^(3,4) using typical count times of 300 and 1000 min. The spectra obtained were then analyzed for radionuclides that had been previously detected in ocean water. These include the cosmic-ray-produced radionuclide ^7Be ; fission products $^{95}\text{Zr-Nb}$, ^{103}Ru , ^{106}Ru , ^{125}Sb , and ^{144}Ce ; neutron activation products ^{46}Sc , ^{51}Cr , ^{54}Mn , ^{60}Co , ^{65}Zn , and ^{124}Sb from both fallout and reactor effluents; and ^{208}Tl , ^{214}Bi , and

^{234}Th , all members of natural radioactive series. The spectrum was resolved by the computer solution of a series of simultaneous equations accommodating the contributions from each isotope to the energy interval of the others. The program was also written to compute the error resulting from counting statistics. Results from the surface and from the 25 m samples are given in Tables 1 and 2, respectively. The values listed for ^{234}Th are still in question since this isotope has two sources. The first is the collection of ^{234}Th from the seawater (calculations assumed this to be the only source); whereas, the second originates from collection of an undetermined fraction of uranium from the water, which supports ^{234}Th in the sample. Since the samples were counted several weeks after collection, correction for decay of ^{234}Th will yield erroneously high results if any uranium is contained by the sample.

The major fractions of all the radionuclides were present as soluble species. The radionuclides associating significantly with the filtered fraction were ^{208}Tl , which is collected on the beds as ^{228}Th , and ^{234}Th (25-50%), and $^{95}\text{Zr-Nb}$ and ^{106}Ru (5-10%). The predominance of ^7Be and the fission products in the soluble state implies either high solubility of the radionuclides in seawater or the rapid removal by sedimentation of the atmospheric aerosols to which they are attached.

Surface water concentrations of ^7Be dropped from 600 to 700 d/m/ 10^3

TABLE 1. Radionuclide Concentrations in Surface Water

N.	Lat.	W.	Long.	Date		d/m/10 ³ liters										
						⁷ Be	⁶⁰ Co	⁹⁵ Zr-Nb	¹⁰³ Ru	¹⁰⁶ Ru	¹²⁵ Sb	¹⁴⁴ Ce	²⁰⁸ Tl (²²⁸ Th)	²¹⁴ Bi (²²⁶ Ru)	²³⁴ Th	
8	01	83	42	6/7/68	S ^(a) I ^(b)	578 ± 15 ^(c) ND ^(d)	1.8 ± 0.7 0.5 ± 0.2	93.3 ± 1.6 4.2 ± 1.4	8.9 ± 6.8 ND	47.7 ± 8.1 6.8 ± 2.6	942 ± 109 28.7 ± 5.4	ND ND	0.6 ± 2.0 0.9 ± 1.4	202 ± 43 ND	5,700 ± 390 1,000 ± 400	
10	15	87	53	6/8/68	S I	741 ± 7 ND	1.7 ± 0.5 0.5 ± 0.1	81.8 ± 0.9 3.7 ± 0.6	ND ND	55.5 ± 5.2 3.9 ± 1.2	ND ND	338 ± 71 ND	ND 0.9 ± 0.7	44 ± 23 1.7 ± 0.5	3,270 ± 140 1,160 ± 120	
12	09	91	46	6/9/68	S I	633 ± 12 ND	1.4 ± 0.7 0.7 ± 0.1	143 ± 1.5 6.2 ± 0.6	ND ND	88.4 ± 8.5 4.0 ± 1.0	252 ± 79 21.9 ± 2.2	405 ± 110 ND	ND ND	85 ± 37 ND	6,240 ± 520 230 ± 120	
14	49	96	53	6/10/68	S I	416 ± 5 ND	0.2 ± 0.2 0.3 ± 0.2	113 ± 7 ND	25.4 ± 2.2 ND	91.5 ± 4.0 ND	137 ± 41 ND	317 ± 55 89 ± 44	1.0 ± 0.7 0.8 ± 0.5	74 ± 16 4 ± 1	5,760 ± 100 1,080 ± 90	
16	39	100	28	6/11/68	S I	110 ± 27 ND	0.7 ± 1.1 0.5 ± 0.3	56.3 ± 2.9 3.5 ± 1.5	ND ND	83.8 ± 13.5 5.9 ± 3.0	190 ± 125 21 ± 6	161 ± 168 ND	8.0 ± 3.9 ND	287 ± 63 ND	16,500 ± 1,340 ND	
19	09	105	38	6/12/68	S I	55.7 ± 4.8 ND	0.5 ± 0.3 0.3 ± 0.1	32.8 ± 0.6 0.8 ± 0.5	ND ND	46.0 ± 3.7 4.5 ± 1.1	75 ± 44 ND	171 ± 56 ND	2.2 ± 0.9 0.3 ± 0.6	95 ± 18 ND	4,300 ± 109 830 ± 120	
21	42	109	17	6/13/68	S I	46.1 ± 7.9 ND	1.6 ± 0.6 0.2 ± 0.1	30.3 ± 1.0 1.5 ± 0.5	ND ND	74.9 ± 6.5 1.9 ± 0.5	68 ± 57 ND	189 ± 76 ND	1.1 ± 1.7 0.7 ± 0.4	84 ± 28 ND	5,710 ± 230 1,010 ± 140	
25	03	113	36	6/14/68	S I	23.0 ± 14.7 ND	1.1 ± 0.9 0.6 ± 0.3	55.1 ± 1.7 ND	ND ND	140 ± 12 11.2 ± 3.4	464 ± 137 ND	126 ± 160 ND	2.6 ± 2.7 ND	411 ± 58 ND	4,630 ± 320 1,820 ± 340	
29	10	116	47	6/15/68	S I	61.5 ± 7.5 ND	0.9 ± 0.4 0.1 ± 0.1	39.3 ± 0.9 ND	ND ND	166 ± 6 3.3 ± 1.1	171 ± 57 ND	294 ± 79 ND	2.7 ± 1.1 1.0 ± 0.7	165 ± 24 0	8,020 ± 210 ND	
34	40	121	13	6/19/68	S I	140 ± 7.0 ND	1.4 ± 0.4 2.5 ± 0.1	19.0 ± 0.7 1.2 ± 0.4	8.9 ± 2.9 ND	64.8 ± 4.7 1.8 ± 0.6	200 ± 55 2.7 ± 1.3	93 ± 66 ND	2.0 ± 1.1 ND	106 ± 21 0.9 ± 0.3	3,780 ± 170 260 ± 120	
38	45	124	07	6/20/68	S I	50.9 ± 8.0 ND	1.9 ± 0.6 0.4 ± 0.1	37.2 ± 1.0 1.6 ± 0.8	ND ND	84.9 ± 7.1 3.5 ± 1.4	73 ± 62 ND	174 ± 84 ND	ND 0.9 ± 0.8	185 ± 33 1.1 ± 0.5	5,440 ± 210 1,020 ± 250	
42	49	124	55	6/21/68	S I	142 ± 43 ND	1. ± 1.6 1.1 ± 0.3	181.3 ± 3.0 ND	ND ND	170 ± 19 8.9 ± 3.2	180 ± 170 36 ± 7	406 ± 229 0	ND 2.4 ± 1.7	435 ± 90 ND	7,430 ± 610 4,040 ± 540	

a. That material passing a 0.3 μ filter is assumed to be soluble

b. That material retained by a 0.3 μ filter

c. Counting standard deviation

d. Concentrations that were less than two counting standard deviations.

TABLE 2. Radionuclide Concentrations at 25 Meters Depth

d/m/10 ³ liters													
N. Lat. ° ' "	W. Long. ° ' "	Date	⁷ Be	⁶⁰ Co	⁹⁵ Zr-Nb	¹⁰³ Ru	¹⁰⁶ Ru	¹²⁵ Sb	¹⁴⁴ Ce	²⁰⁸ Tl (²²⁸ Th)	²¹⁴ Bi (²²⁶ Ru)	²³⁴ Th	
8 01	83 42	6/7/68	S(a) I(b)	211 ± 6(c) ND(d)	1.0 ± 0.3 0.1 ± 0.1	38.0 ± 0.7 2.1 ± 0.6	ND ND	16.8 ± 3.2 ND	209 ± 44 12.3 ± 2.8	148 ± 56 ND	0.6 ± 0.8 0.5 ± 0.5	86 ± 18 ND	4,950 ± 170 220 ± 170
10 15	87 53	6/8/68	S I	414 ± 10 ND	1.7 ± 0.6 0.3 ± 0.1	31.0 ± 1.2 ND	ND ND	13.2 ± 5.9 2.6 ± 1.2	ND ND	ND ND	ND 1.2 ± 0.8	146 ± 32 ND	3,940 ± 360 1,030 ± 160
12 09	91 46	6/9/68	S I	ND ND	2.0 ± 0.7 0.5 ± 0.1	10.2 ± 1.1 2.6 ± 0.5	5.2 ± 4.1 ND	ND ND	194 ± 64 ND	ND ND	ND ND	121 ± 33 ND	5,420 ± 280 600 ± 130
14 49	96 53	6/10/68	S I	229 ± 5 ND	ND 0.1 ± 0.1	52.3 ± 0.6 4.2 ± 0.5	4.7 ± 2.1 ND	47.2 ± 3.6 1.6 ± 0.8	202 ± 43 ND	187 ± 54 ND	2.1 ± 0.8 0.3 ± 0.5	81 ± 17 ND	5,470 ± 110 310 ± 90
16 39	100 28	6/11/68	S I	83 ± 9 0	0.9 ± 0.4 ND	33.2 ± 1.0 1.5 ± 0.6	ND ND	44.4 ± 4.8 1.9 ± 0.8	90 ± 42 11 ± 3	104 ± 59 ND	1.6 ± 1.2 0	128 ± 22 0	9,150 ± 430 450 ± 140
19 09	105 38	6/12/68	S I	42.2 ± 7.7 ND	0.3 ± 0.3 0.5 ± 0.1	32.1 ± 1.0 0.8 ± 0.6	ND ND	30.6 ± 5.0 3.6 ± 1.1	130 ± 55 ND	92 ± 68 ND	1.8 ± 1.1 1.1 ± 0.7	146 ± 38 ND	4,450 ± 240 850 ± 110
21 42	109 17	6/13/68	S I	17.4 ± 5.3 ND	0.2 ± 0.3 0.2 ± 0.1	19.1 ± 0.6 1.1 ± 0.3	4.2 ± 2.4 ND	44.4 ± 3.6 1.0 ± 0.4	169 ± 42 ND	170 ± 54 ND	2.0 ± 0.8 0.4 ± 0.3	61 ± 16 ND	3,160 ± 150 1,190 ± 100
25 03	113 36	6/14/68	S I	20.6 ± 7.7 ND	0.8 ± 0.5 0.3 ± 0.1	24.2 ± 1.0 ND	ND ND	86.2 ± 6.8 4.7 ± 1.5	105 ± 58 ND	300 ± 87 ND	ND ND	230 ± 33 ND	4,820 ± 210 1,640 ± 170
29 10	116 47	6/15/68	S I	40.6 ± 4.9 ND	0.7 ± 0.3 0.1 ± 0.1	24.9 ± 0.6 0.7 ± 0.5	ND ND	97.1 ± 4.7 1.5 ± 0.6	67 ± 35 ND	214 ± 51 ND	2.8 ± 1.1 0.6 ± 0.4	68 ± 18 ND	6,390 ± 200 0
34 40	121 13	6/19/68	S I	ND ND	1.4 ± 0.4 0.4 ± 0.1	10.5 ± 0.7 ND	8.1 ± 2.9 ND	37.5 ± 4.3 0.6 ± 0.5	198 ± 53 ND	172 ± 68 ND	3.2 ± 1.1 ND	113 ± 21 ND	4,040 ± 170 760 ± 110
38 45	124 07	6/20/68	S I	6.8 ± 8.2 ND	2.0 ± 0.6 0.5 ± 0.1	25.4 ± 1.0 2.9 ± 0.9	ND ND	49.4 ± 6.7 1.1 ± 1.1	74 ± 63 ND	250 ± 88 ND	0.5 ± 1.8 1.9 ± 0.8	152 ± 33 ND	4,260 ± 220 ND
42 49	124 55	6/21/68	S I	28.6 ± 12 ND	1.4 ± 0.7 ND	83.5 ± 1.8 ND	ND ND	107.6 ± 8.2 ND	462 ± 130 ND	168 ± 113 ND	ND ND	287 ± 35 ND	3,300 ± 300 3,350 ± 230

a. That material passing a 0.3 μ filter is assumed to be solubleb. That material retained by a 0.3 μ filter

c. Counting standard deviation

d. Concentrations that were less than two counting standard deviations.

liters in equatorial waters to a relatively constant value of 50 to 100 d/m/10³ liters between 18° and 40°N Lat. This pattern is opposite that predicted by cosmic-ray production rate data. Since the measured values must reflect the integrated input at the various latitudes superimposed on the transport of surface water by currents, knowledge of the amounts of this isotope present might provide an index of the amounts of precipitation occurring at sea. In addition, the three fission products ⁹⁵Zr-Nb, ¹⁰⁶Ru, and ¹⁴⁴Ce all exhibited two regions of high concentration: one between 12°30' and 15°N and the other between 25° and 30°N latitude. The relative concentrations of these radionuclides in the lower latitude region compare favorably with those of ⁷Be, which is to be expected if the same process is acting to remove all these materials from the atmosphere. The high fission product concentrations between 25 and 30°N, however, were not accompanied by a corresponding increase in ⁷Be. One mechanism by which this anomaly could occur would be incursion of older water, in the sense that sufficient time had elapsed from its last exposure to the atmosphere to allow the decay of the shorter-lived ⁷Be from the water mass. This could originate from upwelling of water that had previously been exposed to the surface in a region of high radionuclide deposition. Increased ²¹⁴Pb concentrations might be used to corroborate upwelling of deeper waters. These data are, however, too limited to offer more than speculation.

The data given in Table 2 for radionuclide concentrations at a depth of 25 m were obtained for calculation of vertical transport rates between the surface and this depth. The relative concentrations of the fallout radionuclides and ⁷Be preclude diffusion or advective processes as the prime mechanisms for transport to this depth. For example, the surface to depth ratios for ⁷Be ($t_{1/2} = 53$ d) and ⁹⁵Zr-Nb ($t_{1/2} = 65$ d) in the southernmost sample were 2.7 and 2.5, respectively, which are in reasonable agreement. The respective ratios for the longer-lived ¹⁰⁶Ru ($t_{1/2} = 1.0$ yr) and ¹⁴⁴Ce ($t_{1/2} = 285$ d), however, were 2.8 and 4.5. Assuming a constant input rate for the various radionuclides, ratios of the longer-lived species should be significantly less than those of the more rapidly-decaying species if vertical diffusion transport predominated. The high ratios of the long-lived radionuclides require a high deposition of the radioactive species prior to the time of sampling. It is apparent from these data that the mixing rate for water in the top 25 m water column is not a rapid process.

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RADIONUCLIDE CONCENTRATIONS IN THE ATLANTIC OCEAN NEAR BARBADOS

W. B. Silker and H. G. Rieck

A preliminary study was conducted to determine the concentrations of several natural and artificial radionuclides in the Atlantic Ocean east of Barbados, W. I. Surface concentrations were constant throughout the sampling period, except for the introduction of fresh fission products from French nuclear testing. Vertical transport of radionuclides was inhibited by a strong thermocline. Greater than 95% of the ^7Be and $^{95}\text{Zr-Nb}$ was contained in the top 100 m and greater than 90% of the ^{106}Ru and ^{144}Ce resided above 200 m depths.

In preparation for the Barbados Oceanographic and Meteorological Experiment (BOMEX), scheduled for the spring and summer of 1969, water samples were obtained from both surface and depth in the North Equatorial Atlantic Ocean east of the island of Barbados, W. I., near 13°7'N latitude, 58°30'W longitude.

The purpose of this sampling was to establish the concentrations and gradients of ^7Be and other fallout and terrestrial radionuclides in the ocean area selected for the BOMEX project. Knowledge of the oceanic inventory of these radionuclides, together with their concentrations in the air mass above the water surface, should provide the necessary param-

eters for the calculation of the rates of exchange across the air-sea interface. In addition, determination of the concentration gradients with depth provide information on the vertical transport rates in the surface layer of the ocean.

An oceanographic research vessel, the Discoverer, operated by the Environmental Sciences and Services Administration, was used as the sampling platform. Subsurface samples were obtained through a polyethylene irrigation pipe that was lowered through the sampling well, a 5 × 8 ft shaft extending through the hull of the vessel, while surface samples were taken through a line which was floating from the stern of the ship.

Water was pumped directly through the ocean sampling system described in a previous section of this report.⁽¹⁾ Sampling from depths greater than 15 m was hindered by the ship's maneuvers, which consisted of a track two and one-half miles upwind of a reference buoy, and then a drift with wind and current to a point 2 1/2 miles downwind of the buoy. Owing to its large cross sectional area, the vessel would sail with the wind, in many instances 2 to 3 knots faster than the prevailing current. This resulted in drastic trailing of the sampling line. In one instance, with one hundred and seventy meters of line overboard, the depth recorder indicated that the sample was obtained from a depth of only forty meters. In Table 1, both the average sampling depth and the maximum variation from this average are given. This has a direct bearing on the reported radionuclide concentrations, since water from shallower depths contains higher concentrations of radionuclides than the deeper water, and therefore will contaminate the sample.

Water was passed through the sampling system at the desired operational flow rate of 37.9 liters/min,⁽¹⁾ which was easily maintained owing to the near absence of suspended material in the marine environment during the sampling period. About 4000 liters of water were sampled at each station, after which the collector was disassembled and the filters and alumina prepared for radiochemical analysis at the Richland laboratory. The samples were dried, transferred to a suitable

counting container and counted for 1000 min on a multidimensional gamma-ray spectrometer.⁽²⁾ Radionuclide concentrations determined from the resulting spectra are presented in Table 1. The values for the ²³⁴Th are subject to future revision due to a possible undefined source.⁽¹⁾

Beryllium-7 appeared to remain at a fairly uniform concentration during the five days that surface samples were taken. The same is true for the fission products except for ⁹⁵Zr-Nb and ¹⁰³Ru. They increased markedly in the last two days, reflecting deposition of bomb debris from French nuclear testing that had penetrated the northern hemisphere. This constancy is important as it must reflect a relatively uniform deposition over large areas of the ocean. This is particularly important with respect to BOMEX, since we will attempt to establish the inventory of ⁷Be in a water column by profile measurements. Concentrations which exist at depth result from vertical transport of material that had been deposited at great distance from the point of measurement. Surface salinities decreased during the five day period of surface sampling from 33.72‰ to 31.65‰, ostensibly due to incursion of fresh water derived from the Amazon River. Regardless of the origin of this low salinity water, it contained a steady state concentration of the various radionuclides. Its presence might, however, complicate vertical transport due to density gradients present.

The vertical distribution of radionuclides reflects the presence of a

TABLE 1. Radionuclide Concentrations in the BOMEX Area

Location	Date	⁷ Be	⁶⁰ Co	⁹⁵ Zr-Nb	¹⁰³ Ru	¹⁰⁶ Ru	¹²⁵ Sb	¹⁴⁴ Ce	²⁰⁸ Tl	²¹⁴ Bi	²³⁴ Th
Surface	8/12/68 S(a) I(b)	549 ± 9(c)		143 ± 1 16.7 ± 0.4	12.3 ± 4.1 1.6 ± 0.6	138 ± 8 1.6 ± 0.5	54.8 ± 59 4.3 ± 1.8	465 ± 89 6 ± 21	10.2 ± 1.9 0.5 ± 0.4	66.2 ± 4 0.2 ± 0.2	7,180 ± 230 130 ± 80
Surface	8/13/68 S I	468 ± 6	0.1 ± 0.3	105 ± 1 12.2 ± 0.30	0.9 ± 0.4 0.9 ± 0.4	106 ± 5 2.6 ± 0.4	100 ± 38 0.2 ± 1.2	367 ± 61 16 ± 14	11.6 ± 1.3 0.3 ± 0.2	94.4 ± 19.2 0.1 ± 0.2	5,430 ± 150
Surface	8/14/68 S I	509 ± 6	0.6 ± 0.4	142 ± 1 15.4 ± 0.3	11.1 ± 3.0 1.6 ± 0.4	92.2 ± 5.2 2.1 ± 0.4	202 ± 42 1.4 ± 1.3	284 ± 61 14 ± 16	11.3 ± 1.4 0.8 ± 0.3	130 ± 21 0.4 ± 0.2	6,540 ± 160 200 ± 60
Surface	8/15/68 S I	508 ± 5	0.3 ± 0.3	200 ± 1 24.3 ± 0.5	72.2 ± 2.2 5.0 ± 0.6	91.1 ± 4.1 2.1 ± 1.7	114 ± 31 2.1 ± 1.7	366 ± 50	7.5 ± 1.0 0.5 ± 0.3	85.3 ± 15.3	5,190 ± 110
Surface	8/16/68 S I	478 ± 5	0.2 ± 0.2	189 ± 1 14.8 ± 0.6	69.4 ± 2.3 1.8 ± 0.8	81.3 ± 3.9 4.3 ± 2.6	98.6 ± 30.4 4.3 ± 2.6	410 ± 51	8.9 ± 1.0 0.9 ± 0.5	84.7 ± 14.9	5,110 ± 120
15 Meters	8/13/68 S I	530 ± 6	0.2 ± 0.4	128 ± 1 14.6	12.6 ± 2.9 1.7	109 ± 6	80.7 ± 46 4.2	449 ± 70	8.1 ± 1.4 0.9	61.7 ± 21.3	6,850 ± 150
35 ± 3 Meters	8/14/68 S I	230 ± 7	1.1 ± 0.5	68.9 ± 0.9 2.9 ± 0.6	45.3 ± 5.5 1.1 ± 0.8	167 ± 50	310 ± 73 88 ± 37	13.4 ± 1.7	13.4 ± 1.7	82.9 ± 24.5	6,850 ± 200
30 ± 4 Meters	8/7/68 S I	284 ± 14	4.9 ± 1.0	99.8 ± 1.9 1.0 ± 1.3	79.2 ± 10.8	44.8 ± 105 7.2 ± 6.3	90 ± 123 106 ± 67	9.1 ± 3.2 1.4 ± 1.2	9.1 ± 3.2 1.4 ± 1.2	66.3 ± 48.2	9,470 ± 400
40 Meters	8/15/68 S I	171 ± 6		53.3 ± 0.7 4.2 ± 0.5	35.8 ± 4.5 1.2 ± 0.7	62.1 ± 41.2 2.5 ± 2.4	208 ± 58 12.9 ± 21	10.8 ± 1.4 0.8 ± 0.5	10.8 ± 1.4 0.8 ± 0.5	91.0 ± 20.9 0.3 ± 0.3	6,150 ± 150
40 ± 5 Meters	8/8/68 S I	224 ± 10	0.2 ± 0.6 0.1 ± 0.1	75.6 ± 1.3 4.5 ± 0.8	54.4 ± 7.7 0.3 ± 1.1	29.9 ± 72 9.5 ± 34	257 ± 99 1.7 ± 0.8	10.5 ± 2.3 0.1 ± 1.5	10.5 ± 2.3 0.1 ± 1.5	28.5 ± 8.6	10,020 ± 290
70 ± 1 Meters	8/8/68 S I	23.8 ± 6	0.1 ± 0.1	15.3 ± 0.6 1.5 ± 0.5	10.1 ± 0.3 0.3 ± 0.8		91.6 ± 55.4 40.1 ± 30	10.1 ± 1.1 0.3 ± 0.5	10.1 ± 1.1 0.3 ± 0.5	107 ± 18 0.4 ± 0.3	7,280 ± 170 50 ± 100
100 ± 1 Meters	8/8/68 S I	15.6 ± 7		7.0 ± 0.9 0.5 ± 0.6	34.4 ± 5.8	115 ± 52 0.6 ± 3	75.2 ± 66 39.1 ± 37	16.5 ± 1.9 1.7 ± 0.7	16.5 ± 1.9 1.7 ± 0.7	121 ± 27 1.7 ± 0.5	9,870 ± 2.0 250 ± 140
140 ± 5 Meters	8/9/68 S I	<10	0.3 ± 0.7	<5	20.7 ± 7.6	<50	68 ± 87 62 ± 49	12.8 ± 2.5 2.3 ± 0.9	12.8 ± 2.5 2.3 ± 0.9	107 ± 36 1.4 ± 0.7	8,980 ± 300
210 ± 40 M	8/8/68 S I	<10	0.9 ± 0.5	<5	10.8 ± 5.3	135 ± 53	51.1 ± 65 22.3 ± 35.6	9.8 ± 1.8 1.8 ± 0.7	9.8 ± 1.8 1.8 ± 0.7	71.7 ± 25.8 2.3 ± 0.6	9,830 ± 280

a. S, that fraction that passes on 0.3 μ filter

b. I, that fraction that is retained on the filter

c. The plus or minus values are the standard deviation due to counting statistics.

strong thermocline, whose top varied between 35 and 50 m during the sampling period. Penetration of the shorter lived radionuclides was only minimal across this barrier, with greater than 95% of the ^7Be and $^{95}\text{Zr-Nb}$ contained in the top 100 m of water. The longer lived fission products penetrated to at least 200 m; however, greater than 90% of the inventory of these isotopes were contained within this depth.

Results from analysis of these samples demonstrated that the oceans' inventory of ^7Be and fission products can be determined with relative ease. It is apparent that the distance between sampling depths will have to be decreased, especially near the top of the thermocline. The difficulties arising from the drift rate of the ship have been recognized and an anchoring arrangement will be provided during BOMEX to maintain a

fixed ship position. These data, together with measurements of the concentration of airborne radionuclides, indicate the potential of using these materials as tracers for measurement of the exchange rate across the air-sea interface.

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⁵¹Cr FROM THE COLUMBIA RIVER IN OCEAN WATER
OFF THE WEST COAST DURING NOVEMBER, 1968

R. W. Perkins

The ⁵¹Cr concentration in the Pacific Ocean has been characterized on a line extending from California waters to the Strait of Juan de Fuca and at distances of about 25 to 60 km offshore. Maximum concentrations on this sampling line were observed at about 170 km north of the mouth of the Columbia River. The sample collection employed a new sorption technique which required no chemical separations but allowed identification of Columbia River water at dilutions of up to 300,000-fold. The applicability of the sorption method for sampling while underway at sea and the important potential of these measurements together with salinity measurements were demonstrated.

The use of Columbia River water as a coolant for the Hanford reactors and the subsequent discharge of this neutron activated water to the river provides a unique labeling of the river. These radionuclides have permitted studies of their transport and their uptake both in the river and in the Pacific Ocean.^(1,2) As the Columbia River enters the ocean, ⁵¹Cr is by far the most abundant radionuclide with an average input to the ocean of about 1 Ci/day.⁽¹⁾ The actual concentration of ⁵¹Cr in river water reaching the ocean varies from about 1,000 to 10,000 d/m/liter with the seasonal changes in river volume. The ⁵¹Cr is mainly in the hexavalent state and does not appear to react rapidly with the sediments and biota of either the river or the ocean. These conservative properties of ⁵¹Cr permit its use in studying mixing rates and mechanisms of the Columbia River water at sea. In studies by Osterberg et al.⁽³⁾ of Oregon State University using large-volume chemical separations of ⁵¹Cr at sea, the

midsummer surface distribution of the Columbia River plume was characterized. This study clearly demonstrated the very unique potential of the Columbia River-supplied ⁵¹Cr in defining both the initial mixing of Columbia River water with the ocean and the subsequent transport and mixing processes of the ocean.

This present work describes the application of a new sorption technique for ⁵¹Cr⁽⁴⁾ which requires no radiochemical separations in tracing the winter distribution of the Columbia River plume at sea.

These measurements were performed on a cruise of the ESSA R/V Surveyor between San Francisco and Seattle from November 13, 1968, to November 16, 1968. Sampling was performed by pumping seawater at 10 gpm or less through an ocean sampler which contained four 30 cm-diameter fiberglass filters in parallel, followed by a 28 cm-diameter by 0.7 cm-thick sorption bed. The general description of this type of ocean water sampler has been published earlier.⁽⁵⁾

The sorption bed consisted of SnCl_2 impregnated Al_2O_3 ⁽⁴⁾ and provided quantitative retention of the dissolved ^{51}Cr . The filter-sorption bed combinations were changed periodically; and following their return to the laboratory, the ^{51}Cr was measured by direct counting in a 9 in. diameter well crystal.

These measurements showed that less than 1% of the ^{51}Cr was retained by the fiber glass filters. Figure 1 presents the observed ^{51}Cr concentrations on the 11 sampling legs. The ^{51}Cr concentrations on the first four legs were below the detection limits, which ranged from 10 to 20 d/m/1000 liters for the water volumes which were sampled. The first positive value of 45 d/m/1000 liters was observed on sampling leg 5 at a location about 60 km southwest of the Columbia River mouth. The concentration reached a maximum of 14,030 d/m/1000 liters at a location about 175 km north of the Columbia River mouth and then decreased on approaching and entering the Strait of Juan de Fuca. This point of maximum concentrations at 175 km from the river mouth verifies the rapid northern movement of the Columbia River plume along the Washington coast.

The objectives of this study were to demonstrate the feasibility of the sampling technique, determine its sensitivity for tracing the Columbia River at sea, and develop some information on the winter distribution of the Columbia River plume in the Pacific Ocean. The sensitivity of the technique can perhaps best be described in terms of the maximum di-

lution at which the Columbia River plume is detectable. The measurements of Perkins et al.⁽¹⁾ during 1964 indicated an average Columbia River ^{51}Cr concentration of about 3000 d/m/liter; and while the concentration is somewhat lower now because of modified reactor operations at Hanford, this value is adequate for calculating the approximate river dilutions that would be detectable at sea. Since a concentration of about 0.01 d/m/liter is measurable in ocean water and since river water enters the ocean at a concentration of about 3000 d/m/liter, it is possible to detect the Columbia River plume at dilutions of 300,000-fold. This sensitivity is far greater than could be obtained by salinity measurements since local rainfall, together with other fresh water sources from continental runoff, can affect the Pacific Ocean salinity by 1% or more. It is interesting to note that the very high ^{51}Cr concentrations observed on Sampling Leg 9 of 14 d/m/liter would require only a 300-fold dilution of the Columbia River water. Unfortunately, salinity measurements were not made on these waters; however, they could be very helpful and should certainly be included in all future studies. The use of ^{51}Cr measurements, together with salinity measurements, would provide a unique and powerful tool for defining the horizontal and vertical movement of the plume, the time scale of movement, and would help in the identification of the origin of low salinity water masses of the Pacific

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FIGURE 1. ^{51}Cr Concentrations on 11 Sampling Legs off the West Coast During November 13-16, 1968 (d/m/1000 liters)

Ocean within possible reach of the Columbia River plume.

Since the input of ^{51}Cr to the Pacific Ocean cannot be expected to continue indefinitely, every effort should be made to implement sampling programs on the West Coast oceanographic cruises which will help define the ocean mixing processes which are best characterized from ^{51}Cr measurements.

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RADIONUCLIDE CONCENTRATIONS IN NORTHEAST PACIFIC OCEAN SEDIMENTS
IN THE VICINITY OF THE COLUMBIA RIVER ESTUARY

D. E. Robertson and W. O. Forster*

The radionuclides ^{40}K , ^{46}Sc , ^{51}Cr , ^{54}Mn , ^{60}Co , ^{65}Zn , ^{124}Sb , $^{140}\text{Ba-La}$, ^{226}Ra , and ^{228}Th were measured in 15 Columbia River estuarine and adjacent Pacific Ocean sediments. Potassium-40, ^{46}Sc , ^{60}Co , ^{65}Zn , ^{226}Ra , and ^{228}Th were present in all samples, while ^{51}Cr , ^{124}Sb , and $^{140}\text{Ba-La}$ were present in only one atypical sample collected about five miles straight out from the mouth of the river. Concentration gradients of the radionuclides ^{46}Sc , ^{60}Co , and ^{65}Zn and the activity ratios of $^{46}\text{Sc}/^{65}\text{Zn}$ and $^{65}\text{Zn}/^{60}\text{Co}$ indicated that sedimentary material had moved mainly northward at a velocity of 0.1 to 0.5 cm/sec. The naturally occurring radionuclide ^{228}Th appeared to be a potentially valuable tracer of the distribution and movement of the suspended load of the Columbia River as it enters the ocean.

Over the past twenty-five years, the Columbia River has discharged a wide variety of artificial and natural radionuclides into the Pacific Ocean. Several of the artificial radionuclides, notably ^{46}Sc , ^{51}Cr , ^{60}Co , ^{65}Zn , and ^{124}Sb , are neutron activation products and originate mainly from the Hanford reactors. Fallout radionuclides such as the fission products $^{95}\text{Zr-Nb}$, $^{103-106}\text{Ru}$, and $^{141-144}\text{Ce}$, and the naturally occurring radionuclides are washed from the continent into the Columbia River system and eventually enter the ocean. The majority of these radionuclides enter the ocean mainly in particulate forms and become associated with sedimentary material.^(1,2) Several of these radionuclides, particularly ^{51}Cr , ^{60}Co , and ^{65}Zn , have been used by previous investigators as natural tracers in attempting to describe the distribution and offshore movement of the Columbia River sediments.^(3,4,5)

This study was conducted as part of a program designed to characterize the distribution and behavior of radionuclide and trace element concentrations in Columbia River estuarine and adjacent Pacific Ocean waters, organisms, and sediments.

In April 1968, during a cruise of the R/V Yaquina, sediment samples were collected at 15 stations (see Figure 1) in the Columbia River estuary and on the Oregon and Washington continental shelves using a Shippek grab sampler. Duplicate samples were usually taken at each station and stored in plastic bags. Upon returning to the laboratory, the sediments were dried, pulverized, and homogenized by mixing. Thirty-five grams of the dried sediments were pressed into 1/2 in.-thick by 2 in.-diameter polyvinylchloride discs and counted for 1000 min on a high sensitivity multidimensional gamma-ray spectrometer.⁽⁶⁾ Using this direct counting method, the radionuclides ^{40}K , ^{46}Sc , ^{51}Cr , ^{54}Mn , ^{60}Co , ^{65}Zn , ^{124}Sb , $^{140}\text{Ba-La}$, ^{226}Ra , and ^{228}Th could be detected.

The most striking feature of the radionuclide concentrations presented

* This study was conducted as a cooperative effort with the Oregon State University Department of Oceanography, Corvallis, Oregon.

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FIGURE 1. Sediment Sampling Locations for Radionuclide Analyses

in Table 1 is the lack of agreement between duplicate and triplicate samples. Station 4 is the best example of the heterogeneous nature of the estuarine and continental shelf sediments. At this station three sediment grabs were made no more than 100 m apart from each other. Sample 4A was taken in a pocket of organic ooze-type sediment; Sample 4B was composed mainly of a homogeneous gray-brown sand containing a small amount of organic material; and Sample 4C was composed entirely of a homogeneous gray-brown sand. The diverse origin of these three sediments is spectacularly reflected in their radionuclide content. Sample 4A contained extremely high concentrations of all radionuclides (except ^{228}Th) relative to Samples 4B and 4C and the other surrounding sediments. Even when replicate sediment samples exhibited similar physical appearances, their radionuclide concentrations showed extreme variation

(see Samples 3A-3B, 6A-6B, 12A-12C, 15A-15B, and 22A-22B). Part of this variation may be due to inconsistencies associated with the sampling, but it is obvious that the distribution of radionuclides in these sediments, even when sampled in close proximity to each other, is quite heterogeneous. Thus, to adequately characterize the movement of sediments offshore from the Columbia River estuary using these artificial radionuclides as tracers, it is evident that a much larger number of samples must be taken to sufficiently cover the areas of interest.

However, several general conclusions can be drawn from the data. The ^{46}Sc , ^{60}Co , and ^{65}Zn distributions indicate that the main movement of the sedimentary material was to the north of the river mouth. The highest radionuclide concentrations were found in an area about 5 miles straight out from the mouth of the river. These findings are supported by the results of Gross and Nelson⁽³⁾ and Osterberg et al.⁽⁴⁾ By plotting the $^{65}\text{Zn}/^{60}\text{Co}$ and $^{46}\text{Sc}/^{65}\text{Zn}$ activity ratios as a function of distance from the mouth of the river, a rough approximation of the rate at which this sedimentary material moves northward can be made. The $^{65}\text{Zn}/^{60}\text{Co}$ ratios give a velocity of about 0.1 to 0.3 cm/sec, while the $^{46}\text{Sc}/^{65}\text{Zn}$ ratios indicate a velocity of 0.3 to 0.5 cm/sec. Gross and Nelson,⁽³⁾ using $^{65}\text{Zn}/^{60}\text{Co}$ ratios, calculated northward velocities of 0.05 to 0.1 cm/sec. During the winter and early spring months, surface waters flow northward at speeds between

TABLE 1. Radionuclide Concentrations in Columbia River
Estuarine and Oregon-Washington Continental Shelf Samples

Station and Date		Location		Radionuclide Concentrations (d/m/kg Dry Sediment)													
				W. Long.	N. Lat.	⁴⁰ K (×10 ⁴)	⁴⁶ Sc (×10 ²)	⁵¹ Cr (×10 ⁴)	⁵⁴ Mn (×10 ²)	⁶⁰ Co (×10 ²)	⁶⁵ Zn (×10 ³)	¹²⁴ Sb (×10 ²)	¹⁴⁰ Ba-La (×10 ³)	²²⁸ Th (×10 ³)	²²⁶ Ra (×10 ³)	⁴⁶ Sc/ ⁶⁵ Zn	⁶⁵ Zn/ ⁶⁰ Co
2	4/28/68	124 11	46 10.1	2.9	9.4	<5	<2	2.8	3.7	<1	<2	1.6	1.5	0.25	8		
3A	4/21/68	124 11.5	46 12.8	2.7	55	<5	<2	8.0	15	<1	<2	2.8	1.7	0.38	18		
B	Average			2.6	38	<5	<2	5.1	8	<1	<2	2.1	1.3	0.46	16		
				2.7	42	---	---	6.6	11	---	---	2.5	1.5	0.42	17		
4A(a)	4/21/68	124 09.9	46 14.3	4.2	1,802	89.8	119	61	234	2.1	7.1	1.9	5.4	0.77	38		
B				2.8	54	5.8	10	7.3	15	<1	<2	1.6	1.1	0.39	20		
C				5.3	29	<5	13	5.0	10	<1	<2	2.4	1.6	0.30	19		
Average				4.0	42	---	11	6.2	12	---	---	2.0	1.4	0.35	20		
5A	4/21/68	Buoy 12		2.8	3.5	<5	<2	1.8	1.8	<1	<2	1.1	0.88	0.20	10		
B				2.5	2.6	<5	<2	1.7	1.7	<1	<2	1.0	0.80	0.16	10		
Average				2.7	3.1	---	---	1.8	1.7	---	---	1.1	0.84	0.18	10		
6A	4/21/68	Buoy 26		2.4	8.6	<5	6	4.8	4.0	<1	<2	0.96	0.72	0.22	8		
B				2.5	27	<5	8	16	12	<1	<2	1.2	1.5	0.23	8		
Average				2.5	18	---	7	10	8	---	---	1.1	1.1	0.23	8		
7A	4/21/68	Buoy 40		2.4	18	<5	6	3.7	8.7	<1	<2	0.99	0.86	0.20	23		
B				2.4	23	<5	6	4.0	9.1	<1	<2	1.2	1.1	0.26	23		
Average				2.4	21	---	6	3.9	8.9	---	---	1.1	0.96	0.23	23		
8A	4/21/68	123 41.3	46 15.0	2.3	3.3	<5	<2	0.55	7.1	<1	<2	1.1	0.92	0.05	128		
B				2.1	2.3	<5	<2	0.75	6.3	<1	<2	0.97	0.90	0.04	84		
Average				2.2	2.8	---	---	0.65	6.7	---	---	1.0	0.91	0.05	106		
10A	4/23/68	124 11.0	46 16.2	3.4	60	<5	8	13	26	<1	<2	2.1	1.6	0.23	19		
B				2.8	62	<5	7	7	13	<1	<2	2.2	1.5	0.47	17		
Average				3.1	61	---	7	11	19	---	---	2.2	1.5	0.35	18		
11A	4/23/68	124 0.04	46 16	2.7	4.2	<5	<2	1.7	2.0	<1	<2	2.2	0.96	0.21	12		
B				2.4	3.4	<5	<2	1.9	2.0	<1	<2	2.7	0.64	0.17	10		
Average				2.6	3.8	---	---	1.8	2.0	---	---	2.4	0.80	0.19	11		
12A	4/23/68	123 55.5	46 14.4	2.3	70	<5	12	9.2	11	<1	<2	0.91	1.0	0.63	12		
B				2.6	26	<5	10	6.2	6.4	<1	<2	1.75	1.1	0.40	10		
C				2.9	29	<5	7	1.9	5.6	<1	<2	2.81	1.2	0.63	24		
Average				2.6	42	---	8	5.8	7.4	---	---	1.7	1.1	0.55	15		
15A	4/24/68	124 13.2	46 16.6	2.9	23	<5	<2	4.4	8.2	<1	<2	1.9	1.2	0.28	19		
B				3.0	138	<5	9	8.2	19	<1	<2	2.1	1.8	0.74	23		
Average				3.0	81	---	---	6.3	13	---	---	2.0	1.5	0.51	21		
18	4/24/68	124 23.8	46 15.3	3.6	1.3	<5	<2	3.8	2.2	<1	<2	1.8	1.1	0.06	6		
20	4/25/68	124 40	46 50	3.1	1.1	<5	<2	1.0	0.91	<1	<2	2.3	1.3	0.12	9		
22A	4/25/68	124 19.8	46 29.7	3.2	2.8	<5	<2	6.6	4.2	<1	<2	2.0	1.2	0.07	6		
B				3.4	15	<5	<2	5.4	5.0	<1	<2	2.1	1.3	0.31	9		
Average				3.3	9	---	---	6.0	4.6	---	---	2.0	1.3	0.19	8		
23	4/25/68	124 27	46 30	2.4	1.8	<5	<2	3.0	1.8	<1	<2	1.5	0.74	0.10	6		

a. Organic ome-type sediment--excluded from average of Sample 4.

10 to 20 cm/sec.⁽³⁾ Thus, the sedimentary material is moving at a rate nearly two orders of magnitude slower than the surface water currents.

The distribution of ^{228}Th in these sediments indicates that this naturally occurring radionuclide may be an excellent tracer of the movement of sedimentary material from the estuary to positions along the Oregon-Washington continental shelf. It is well known that thorium isotopes are rapidly precipitated from the oceans by chemical processes.⁽⁷⁾ Thus, as thorium enters the ocean from the Columbia River, it engages in precipitation reactions and a fraction of the particulate thorium deposits with other sedimentary material. The ^{226}Ra (a daughter of ^{230}Th) distribution exhibits a similar pattern but not to the extent shown by ^{228}Th , since radium isotopes have been shown to be more soluble than thorium in seawater.⁽⁷⁾ It appears that a thorough mapping of the ^{228}Th distribution of this area would contribute to a better understanding of the movement of sedimentary material from the Columbia River estuary as it enters the ocean.

Chromium-51, which is the major radionuclide in estuarine waters, could be detected in only two sediment samples (4A and 4B).

Chromium-51 enters the ocean primarily in a soluble form^(1,2) and apparently does not engage in processes that lead to precipitation as it enters the ocean.

Antimony-124, which is a very conservative element in the marine environment and enters the ocean

mainly in a soluble form,^(1,2) and the fission product $^{140}\text{Ba-La}$ were detected in only one sample (4A).

The naturally occurring ^{40}K appeared to be rather uniformly distributed throughout the sediment samples.

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RADIONUCLIDE CONCENTRATIONS IN COLUMBIA RIVER ESTUARINE ORGANISMS

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The radionuclide content of a wide variety of Columbia River estuarine organisms was measured. These radionuclides, mainly neutron activation products originating from the Hanford reactors, included ^{40}K , ^{46}Sc , ^{51}Cr , ^{54}Mn , ^{60}Co , ^{65}Zn , $^{95}\text{Zr-Nb}$, ^{124}Sb , ^{137}Cs , ^{226}Ra , and ^{228}Th . Zinc-65 was the most abundant radionuclide in all organisms. Chromium-51, which is by far the most abundant radionuclide in the water, was detected in only one sample of copepods. Essentially all trophic levels of organisms were analyzed, thus providing a better understanding of the behavior and fate of radionuclides in the estuarine and adjacent Pacific Ocean food chain.

The increasing use of nuclear energy in a wide variety of applications has introduced low-level radioactive wastes into the marine environment. Although present levels of radioactivity in the oceans are extremely small and in most cases difficult to detect, it is of utmost importance to determine the pathways and behavior and to predict the ultimate fate of radionuclides in the marine environment.

The distribution of radioactivity in the oceanic ecosystem is greatly influenced by a wide variety of marine organisms which concentrate and transfer radionuclides throughout the marine food web. Throughout most of the oceans, the radionuclide levels are so extremely low that detailed studies of the uptake, retention, transfer, and excretion of radionuclides by marine organisms is not possible. However, the Oregon-Washington continental shelf and the estuarine waters of the Columbia

River provide a unique area for studying the biological fate of artificial radionuclides. Small but detectable amounts of radioactivity are transported to the Pacific Ocean from the Hanford reactors through the Columbia River system.⁽¹⁾ These radionuclides are mainly neutron activation products formed from trace elements in Columbia River water during its utilization as a reactor coolant. Although the concentrations of most of these radionuclides are rapidly diminished by radioactive decay and depletion processes in the river, a few of the longer-lived radionuclides eventually reach the ocean. The most abundant radionuclides reaching Astoria, Oregon, include ^{51}Cr and ^{65}Zn , plus smaller amounts of ^{46}Sc , ^{60}Co , and ^{124}Sb (Table 1). These radionuclides, particularly ^{51}Cr and ^{65}Zn , have previously been used by several investigators as natural tracers in characterizing a wide variety of biological processes in the estuary and on the continental shelves of Oregon and Washington.^(2,3,4)

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TABLE 1. Concentrations and Physical and Chemical Forms of Columbia River Radionuclides at Harrington Point and Astoria, Oregon

Radionuclide	Total d/m/liter	% Particulate	% Cationic	% Anionic	% Neutral
Station 35: Harrington Point - Fresh Water					
⁵¹ Cr	928	15	1	79	5
⁶⁵ Zn	49	93	6	0.2	1
⁴⁶ Sc	33	79	3	11	7
¹²⁴ Sb	10	2	0	96	2
⁶⁰ Co	0.74	100	0	0	0
Station 9: Astoria Dock - 5.57% Salinity ^(a)					
⁵¹ Cr	252	39	-	--	-
⁶⁵ Zn	29	80	-	--	-
⁴⁶ Sc	27	92	-	--	-
¹²⁴ Sb	2.9	3	-	--	-
⁶⁰ Co	0.46	100	-	--	-

(a) The salt content of this sample may have affected the quantitative sorption of the trace radionuclides on the ion exchange resins, so the present cationic, anionic, and neutral species are not included.

This study** was conducted as part of a comprehensive program designed to describe the distributions and behavior of the radionuclide and trace element constituents in the organisms, water, and sediments of the Columbia River estuary and adjacent Pacific Ocean.

In April, 1968, five otter trawls (bottom samples) and three mid-water trawls were made in the Columbia River estuary and adjacent Pacific

Ocean aboard the R/V Yaquina at the sampling locations shown in Figure 1. After each trawl, the organisms were separated into individual species and immediately frozen in plastic bags. Upon returning to the laboratory, the samples were thawed, weighed, and carefully ashed at 400 °C. The ash was then transferred to 1/2 in.-thick by 2 in.-diameter polyvinylchloride rings, which were counted for 1000 min on a multidimensional gamma-ray spectrometer.⁽⁵⁾ The extremely low background and Compton response of this detector system permitted very sensitive measurements of the low concentrations of radionuclides present in the samples.

** This study was conducted as a cooperative effort between Battelle-Northwest and Oregon State University.

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FIGURE 1. Sampling Locations for the Collection of Columbia River Estuarine and Adjacent Pacific Ocean Marine Organisms

The great abundance of biota collected in the estuary and on the adjacent continental shelf has presented the opportunity to study the intake and retention of radionuclides throughout the major levels of the marine food web and to study interspecies differences. The radionuclide concentrations in the organisms, expressed as d/m/kg wet weight, are presented in Table 2.

The most abundant radionuclide in the organisms was ^{65}Zn ; sand shrimp, goby, dungeness crab, and basket starfish generally contained the highest levels. Further inside the estuary, peamouth chub, smelt, flounder, sculpin, and copepods showed a high affinity for ^{65}Zn . A sample of detritus composed of decayed wood, leaves, and other organic matter was collected in a midwater trawl off Astoria, Oregon, and contained large amounts

of ^{65}Zn and other radionuclides. The high concentrations of radionuclides on the detritus were probably accumulated during its transit down the river to the estuary. The ^{65}Zn enters the ocean primarily in the particulate form (Table 1) and would be expected to be highly concentrated in first trophic-level and filter-feeding organisms. However, this did not seem to be the case. The high affinity for zinc by all trophic levels makes ^{65}Zn an unreliable indicator of feeding relationships.

The next most abundant and ubiquitous radionuclide in the organisms was ^{46}Sc . The highest levels were found in detritus, copepods, amphipods, and fish larvae. Peamouth chub, dungeness crab, tom cod, goby, sand sole, shiner perch, and sand shrimp also contained relatively high concentrations of ^{46}Sc . Scandium-46

TABLE 2. Radionuclide Concentrations in Columbia River
Estuarine and Pacific Ocean Marine Organisms

Station	Date and Time Location	Depth, m	Organism	Wet Wt., g	Ratio: Ashed Wt. Wet Wt.	d/m/kg Wet Weight											
						40 K	46 Sc	51 Cr	54 Mn	60 Co	65 Zn	124 Sb	137 Cs	228 Th	226 Ra	95 Zr-Nb	
4	4-21-68 at 1024' 124°09.9', 46°14.3'	26	Dungeness Crab	309	8.83	3180	263		210	95.8	11,250						
			Dungeness Crab	310	8.87	4620	386		145	109	14,850						
			Tom Cod	1032	29.5	5770	156		430	10.3	8,200						
			Goby	60	21.4	7090	654		730	137	17,180						
			Sand Shrimp	35	17.5	4720	107		28	18,590							
			Sea Bass	742	21.2	3680	16		34	5.8	3,576		73				
			Sand Sole	858	24.5	5430	214		87	16	7,360						
5	4-21-68 at 1214' 400 yd from #12 buoy	15	Shiner Perch	324	24.6	5760	18		56	24	3,080						
			Sand Shrimp	27	15.0	5000	85		78	36,200							
			Sand Sole	873	24.9	5200	6.4		87	11	8,960						
			Shiner Perch	483	24.2	5530	149		160	37	22,480						
19	4-24-68 at 1632' 124°21.0', 46°14.2'	120	Smelt	481	66.8	4270	66			13	21,370						
			Large Rex Sole	984	31.7	4270	16		30	10	2,130						
			Small Rex Sole	766	28.4	4270	31		15	15	4,130						
			Sand Sole	715	31.1	5480			14		1,172						
			Lemon Sole	796	33.2	4780	1.8			3.8	1,840						
			Dover Sole	1290	36.9	4570	18		120	7.6	2,580						
			Rosy Rock Fish	640	18.3	4540	1		30	1	2,290						
			Shrimp	119	22.5	4640	121		14	9.4	5,468		58				
			Sea Anemone	129	37.9	3160	93		14	4	5,880						
			Starry Skate	135	27.6	3720	11		183	260	15,000					340	
			Dungeness Crab	299	8.6	4160	124		25	11	2,410						
			Sea Pens	146	4.2	977	15		15	11	2,410						
			Basket Starfish	169	4.8	3890	142		13	10,700							
33A	4-26-68 at 1314' #39 buoy to #40 buoy	13	Staghorn Sculpin	35	32.8	5700	56		124	31	15,100			7.6	38		
			Starry Flounder	35	24.4	4670	223		304	74	28,900						
			Long Fin Smelt	941	55.4	4380	112		35	25,400		8.4					
35	4-26-68 at 1520' #3 buoy	13	Smelt	448	34.5	6280			2								
			Smelt	481	66.8	4250	55		206	14	19,880						
			Peamouth Chub	966	27.5	5520	604		221	111	24,000						
1st Mid-Water Trawl	46°10' 123°46'		Copepods, plus other small zooplankton Detritus; decayed wood, leaves, etc.	140	175.0	1999	23,950		110	14,500						1260	
2nd Mid-Water Trawl	46°6' 124°55'		Sand Shrimp	11.0	22.0	4920	39		120	31,230							
			Amphipods and Fish Larvae	755	60.4	2750	681		158	48	17,030				23		
3rd Mid-Water Trawl	44°38' 132°29'		Euphausiids	390	34.8	5300	326		150	14	8,540						
			Pleurobranchia	1948	60.9	3		0.4	219								
NH 45	44°35' 124°45'		Aurelia	1938	55.4	385	0.7			317							
			Valella Valella	1219	34.8	3260	8		47	13	4,210						
NH 45	44°35' 124°45'		Pelagic Barnacles	31.5	5.3	2220	181				4,760					580	

enters the ocean primarily in the particulate form (Table 1) and its behavior in the food chain is indicative of the uptake and transfer of particulate material from lower trophic-level organisms to higher trophic-level animals.

Cobalt-60 was present in all of the organisms. It was most highly concentrated in detritus, dungeness crab, goby, peamouth chub, copepods, and sand shrimp. Cobalt-60 also enters the ocean mainly in the particulate form (Table 1), but its behavior does not obviously follow the pattern exhibited by particulate ^{46}Sc . Cobalt is an essential element for most marine organisms; and higher trophic-level animals, such as dungeness crab, appear to concentrate more ^{60}Co than is available to them through the food web.

Manganese-54 was mainly present in detritus, starry flounder, peamouth chub, smelt, sand sole, dungeness crab, amphipods and fish larvae and euphausiids.

Chromium-51 was concentrated in only detritus and copepods, where it was present in relatively high concentrations. Although ^{51}Cr is the most abundant radionuclide in the estuary, it is effectively discriminated against by estuarine organisms. It enters the ocean mainly in a soluble anionic form, probably as $\text{CrO}_4^{=}$.⁽⁶⁾

Antimony-124 was detected only on detritus and in long-fin smelt. Antimony is a relatively conservative element in the marine environment and enters the ocean primarily in a soluble anionic form (see

Table I). It is not readily assimilated by marine organisms and is not transferred through the food web.

Cesium-137 was detected only in the two higher trophic-level fish, sea bass and rosy rock fish (a species of sea bass). This was consistent with the findings of Pendleton and Hanson,⁽⁷⁾ who reported that ^{137}Cs is particularly concentrated at higher trophic levels. Cesium is a relatively conservative element in the oceans and exists almost entirely as the soluble Cs^+ ion.⁽⁸⁾ The fact that ^{137}Cs was not passed through the food chain to the sea bass indicates that these higher trophic level fish concentrate cesium directly from seawater. Rancitelli et al.⁽⁹⁾ have shown that silver salmon preferentially assimilate cesium in muscle tissue relative to rubidium, and it may be possible that cesium plays an important biochemical role in these fish.

Zirconium-niobium-95 was present only in copepods and sand shrimp. This radionuclide was also discriminated against by higher trophic-level organisms and was not transferred through the food web.

The naturally occurring radionuclides ^{228}Th and ^{226}Ra were observed in detritus and in the bottom fish sculpin and dover sole. These fish ingest mud and sand into their bodies as they feed, and these sediments are the source of the ^{228}Th and ^{226}Ra . A sample of amphipods and fish larvae also contained ^{226}Ra .

The uptake and transfer of artificial radionuclides by marine organisms in the Columbia River estuary appears

to be a rather complex process. Certain radionuclides, such as ^{51}Cr , $^{95}\text{Zr-Nb}$, and ^{124}Sb , which are concentrated by lower trophic-level organisms were never detected in higher trophic-level animals. The radionuclides ^{60}Co and ^{65}Zn were ubiquitous in all organisms, and it appears that the higher trophic-level organisms are capable of concentrating large amounts of cobalt and zinc from the water in addition to that which is available to them in the food chain.

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PARTICULATE Pb, ^{210}Pb , AND ^{210}Po IN THE ATLANTIC OCEAN

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Particulates Pb, ^{210}Pb , and ^{210}Po were measured in Atlantic Ocean surface samples collected from various locations between the Bahama Islands and Sierra Leone, Africa. Particulate ^{210}Pb and ^{210}Po were in equilibrium. The particulate Pb concentration decreased ninefold from 25°38'N Lat. 72°20'W Long. to 24°48'N Lat. 59°20'W Long., then decreased only 20% to 5°48'N Lat. 16°35'W Long.

Various studies^(1,2) have been made of particulate Pb and ^{210}Pb in the ocean, with depth profiles at several locations. The locations were chosen to allow minimum interference from local sources, adequate ocean depth to avoid boundary effects and to give optimum sampling conditions. These studies, however, have not investigated the changing concentrations of the pollutant Pb and ^{210}Pb versus distance from the source. Such a study in the marine environment would show the extent of terrestrial pollution to the oceans and the possible use of elements, such as lead, as tracers of marine processes. This paper presents data obtained from filtered surface ocean water samples from the Atlantic Ocean between 0-30°N Lat. and 74°-15°W Long. (Table 1).

Particulate material from the filter collection procedure⁽³⁾ was wet ashed with concentrated HNO_3 and HClO_4 . After diluting in 0.6N HCl, ^{210}Po was spontaneously deposited on Ag discs by the method of S. C. Black⁽⁴⁾ and analyzed by its alpha emission. A ^{208}Po spike was added to allow radiochemical yield measurement. Stable Pb⁽⁵⁾ and ^{210}Pb were determined by atomic absorption and beta counting of the ^{210}Bi daughter, respectively.

In Table 1 the particulate ^{210}Po and ^{210}Pb concentrations in seawater are shown. The average concentrations of ^{210}Po and ^{210}Pb are 0.0124 ± 0.0037 d/m/liter and 0.0156 ± 0.0047 d/m/liter, respectively. There are no apparent trends with distance from the United States coastline. The

TABLE 1. Surface Atlantic Seawater Concentrations

Location		^{210}Po , d/m/liter	^{210}Pb , d/m/liter	Pb, $\mu\text{g/liter}$	Distance from U.S.A., miles
N. Lat.	W. Long.				
25°30'	74°	0.0067 ± 0.0007	0.0089 ± 0.002	0.45 ± 0.04	480
25°38'	72°20'	0.015 ± 0.001	0.016 ± 0.002	2.23 ± 0.02	600
25°10'	65°55'	0.014 ± 0.001	0.015 ± 0.002	0.72 ± 0.05	1,080
24°28'	62°18'	0.018 ± 0.002	0.011 ± 0.002	0.31 ± 0.03	1,320
24°48'	59°20'	0.017 ± 0.001	0.012 ± 0.002	0.254 ± 0.03	1,440
8°50'	38°28'	0.022 ± 0.002	0.0075 ± 0.002	0.24 ± 0.03	3,000
5°48'	16°35'	0.017 ± 0.002	0.017 ± 0.002	0.21 ± 0.03	4,570

particulate Pb concentration in seawater is a function of the distance from the United States as measured from the eastern coast of Florida.

Except for the first sample (25°30'N Lat. 74°W Long.), there is a rapid decrease in the particulate Pb concentration out to 1,440 miles. Thereafter, the concentration slowly decreases by 20% to near the African coast. It seems that the source of particulate Pb in the ocean is primarily from terrestrial sites, presumably by air pollution since the physical barriers of the Bahama Islands and the Gulf Stream would prevent most eastward flow of mainland rivers from the Florida coast.

The suggested mechanisms for the observed data are that out to 1,440 miles gravitational fallout⁽⁶⁾ has removed most of the particulate Pb particles large enough to be affected by these processes. After 1,440 miles, the slowly decreasing concentrations of particulate Pb result from washout. The low concentration of particulate Pb in the samples at 440 miles from the United States (taken at 25°30'N Lat. 74°W Long.) is probably due to the prevailing wind and oceanic circulation in the area. The Gulf Stream^(7,8) brings in water from the south and east, where the possibility of industrial pollution is greatly reduced.

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MULTIELEMENT ANALYSIS OF SEAWATER, MARINE ORGANISMS, AND SEDIMENTSBY NEUTRON ACTIVATION WITHOUT CHEMICAL SEPARATIONS*

D. E. Robertson, L. A. Rancitelli, and R. W. Perkins

Neutron activation and direct counting techniques were employed to measure the concentrations of numerous trace elements in seawater, marine organisms, and pelagic sediments. Neutron activated samples were counted directly on either a multidimensional gamma-ray spectrometer or a large volume, high resolution Ge(Li) diode spectrometer after optimized decay periods. Using these direct counting techniques, the concentrations of the trace elements Sr, Cs, U, Co, Sb, Zn, Fe, and Sc were measured in seawater samples; and their distribution over a wide geographical area of the Pacific and Atlantic Oceans was determined. The concentrations of Zn, Co, Ag, Cs, Sb, and Sc were measured in a large number of surface, mid-water, and benthic marine organisms from various trophic levels. The additional elements Na, K, Rb, Br, Fe, Se, and Hg were also measured in silver salmon and Alaskan king salmon tissue samples. The elements Mn, Fe, Cu, Zn, Co, La, Sc, and Sb were measured in pelagic sediments and in manganese nodules by directly counting neutron activated samples on a multidimensional gamma-ray spectrometer. By using a Ge(Li) diode detector and properly-selected irradiation and decay periods, it is also possible to measure the additional elements Al, V, Dy, Ba, Cr, Ce, Sm, Yb, Lu, Hf, and Th in sediment samples by direct counting. These direct counting methods greatly simplify the multielement analysis of samples from the marine environment by eliminating the uncertainties associated with many complex chemical preconcentration and separation procedures. Also, the inherent risk of contamination of the samples during such procedures is eliminated. The behavior of several artificial radioelements entering the marine environment as fallout, relative to their stable element counterparts, has been determined and points out the importance of chemical or physical form on the behavior of an element in the ocean. Methods for extracting trace radionuclides from large volumes of seawater to depths as great as 1600 m are described.

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TRACE ELEMENT CONCENTRATIONS IN ATLANTIC OCEAN WATERS
BETWEEN FLORIDA AND IVORY COAST, AFRICA

D. E. Robertson and J. M. Prospero*

Neutron activation and direct gamma-spectrometric techniques were employed in the measurement of the trace elements Sr, Cs, U, Sb, Co, Sc, Zn, and Fe in Atlantic Ocean seawater samples collected between Florida and Ivory Coast, Africa. Slight variations in the concentrations of the conservative elements Sr, Cs, U, and Sb were observed. Although the concentrations of these elements were, in general, closely related to the salinity of the seawater, small but significant localized variations in the Sr/salinity, Cs/salinity, U/salinity, and Sb/salinity ratios were observed. The concentrations of Co, Zn, and Fe were highly variable and apparently dependent upon the biological activity in the water. Scandium is rapidly depleted from the oceans and is present in extremely low concentrations.

A knowledge of the elemental composition of the oceans is basic to understanding the biogeochemical and physical processes occurring in the marine environment. Although the importance of many trace elements in these processes is well established, their concentrations, geographical and vertical distributions, and behavior are not well known. Concentrations reported for many elements have often been based on a single analysis, usually in seawater collected from harbors and coastal areas, which were atypical of well-mixed oceanic waters. Recently, with the advent of new sensitive analytical techniques, significant progress has been made in delineating the chemical composition of the marine environment.⁽¹⁾ A continuing effort is

being conducted at our laboratory to characterize the worldwide distribution and variations of trace elements in seawater, marine organisms, and sediments by neutron activation analysis.⁽²⁾ In addition to providing an understanding of the inventory of trace elements in the marine environment, these analyses are being combined with measurements of the natural and artificial radionuclides in the oceans and in marine organisms and sediments to provide a much better understanding of the complex processes occurring in the oceans.

As part of this program, seawater samples were collected during a 1967 cruise of the R/V Pillsbury on a leg between Florida and Ivory Coast, Africa (see Figure 1 for sampling locations). Surface sampling consisted of collecting seawater in a plastic container thrown from the bow of the ship as it cruised slowly forward. By use of this method, seawater samples free from contaminants leached or discharged from the vessel were obtained. Deep seawater samples

* This study was conducted as a cooperative effort with the University of Miami, Department of Oceanography, Miami, Florida. The sampling was conducted by J. M. Prospero of the University of Miami.

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FIGURE 1. Sampling Locations for Trace Element Analysis of Sea Water Collected Between Florida and Ivory Coast, Africa, 1967

were collected in plastic Niskin bottles. The seawater was stored in cleaned 500 ml polyethylene bottles containing 3 ml of high-purity hydrochloric acid to retard adsorption of trace elements onto the container surfaces.⁽³⁾ The samples were not filtered in an effort to minimize contamination. The seawater was prepared for neutron activation by slowly evaporating to dryness 20 ml of seawater in small, cleaned polyethylene vials under a heat lamp. All sample preparation was conducted in a laminar flow clean hood (Agnew-Higgins) to minimize contamination originating from airborne dust and particulate material. The vials were then sealed and neutron activated, together with

Co, Cs and U standards. The comparative method was used to calculate these trace element concentrations in seawater. The flux method, using cobalt as the monitor, was used to calculate the concentrations of Sb, Sc, Zn, and Fe. The accuracy of the flux method was improved by measuring reactor cross sections of Sb, Sc, Zn, and Fe relative to cobalt. The strontium analyses were conducted by evaporating 1 ml of seawater in small polyethylene vials and neutron activating these together with strontium standards. After the irradiation, the samples were stored for four to five weeks to allow the interfering short-lived activation products ^{24}Na ,

^{42}K , and ^{82}Br to decay to insignificant concentrations. The samples were counted directly on a multidimensional gamma-ray spectrometer⁽⁴⁾ and a 20 cm^3 Ge(Li) diode detector⁽⁵⁾ for 1000 min. In this manner, the trace elements Cs, U, Sb, Co, Sc, Zn, and Fe could be directly measured without performing any chemical manipulation. Strontium was measured by directly counting the sea salts for 20 min on a multidimensional gamma-ray spectrometer. The precision of the measurements, as determined from replicate analysis of a single seawater sample, ranged from about 1 to 2% for Sr to about 12% for Sc.

The trace element concentrations measured in the seawater samples are presented in Table 1. A strontium depth profile taken in the Gulf of Guinea is presented in Table 2.

The average surface concentration of strontium between Miami, Florida, and Ivory Coast, Africa, was 8.0 mg/liter and ranged from 7.8 to 8.1 mg/liter. A depth profile taken in the Gulf of Guinea, in which an interesting salinity maximum occurred at a depth of 50 m, showed an erratic decrease in strontium concentration with depth. There appeared to be no systematic relationship to the salinity maximum at 50 m. The Sr/salinity ratio in this profile varied from 2.5×10^{-4} to 2.0×10^{-4} , indicating that small but significant local variations in the Sr/salinity ratio do exist in the oceans. The variation observed in this profile represents the widest range in the Sr/salinity ratio reported by our laboratory over large areas of the world's oceans.⁽²⁾

The average surface concentration of Cs between Florida and Ivory Coast was 0.26 $\mu\text{g/liter}$ and ranged from 0.20 to 0.32 $\mu\text{g/liter}$. Although the majority of the measurements was near the average value of 0.26 $\mu\text{g/liter}$, significantly lower concentrations of 0.20 and 0.21 $\mu\text{g/liter}$ were observed in Samples 7 and 8. A significantly higher concentration of 0.32 $\mu\text{g/liter}$ was observed in Sample 16. Although cesium tends to be proportional to the salinity of the seawater, this relationship does not appear to be finely defined, and significant variation in the Cs/salinity ratio was observed.

Antimony was present in surface waters at an average concentration of 0.16 $\mu\text{g/liter}$ and ranged from 0.13 to 0.20 $\mu\text{g/liter}$. Antimony is a conservative element in the ocean, and its concentration is not greatly influenced by the biogeochemical processes occurring in the ocean. Therefore, the distribution of Sb throughout the oceans is rather uniform, with only large variations occurring in ocean waters greatly influenced by river drainage from the continents.^(2,8)

The average surface concentration of uranium between Florida and Ivory Coast was 3.0 $\mu\text{g/liter}$, with a range of 2.6 to 3.9 $\mu\text{g/liter}$. An area of significantly higher uranium concentrations occurred in Samples 15 to 17, with the highest value of 3.9 $\mu\text{g/liter}$ being present in Sample 16. Except for this area, most of the other measurements were close to the average concentration of 3.0 $\mu\text{g/liter}$. Uranium is reported to exist in seawater as

TABLE 1. Trace Element Concentrations in Atlantic Ocean Waters
Between Florida and Ivory Coast, Africa - 1967

Sample	Date	Location		Salinity, ‰	Concentration, µg/liter							
					Sr	Fe	Zn	U	Cs	Sb	Co	Sc
1	7-18-67	26°06'N	79°00'W	36.109	8100	--	3.5	3.2	0.26	0.13	0.014	0.0011
2	7-24-67	25°38'N	73°05'W	36.719		37	0.79	3.1	0.25	0.15	0.013	0.0007
3	7-25-67	25°17'N	69°20'W	36.675		25	2.8	--	0.27	0.17	0.022	0.0013
4	7-26-67	25°10'N	65°55'W	36.714		4.7	2.1	--	0.27	0.14	0.015	0.0010
5	7-28-67	24°25'N	58°50'W	36.500	8100	25	1.4	2.9	0.25	0.14	0.011	0.0006
6	7-30-67	21°30'N	60°37'W	35.941		23	6.5	3.0	0.23	0.13	0.022	0.0007
7	8-09-67	16°38'N	63°28'W	34.120		11	0.69	2.7	0.21	0.13	0.004	0.0005
8	8-10-67	14°49'N	60°40'W	33.887		3.4	0.40	2.7	0.20	0.13	0.008	0.0006
9	8-11-67	13°26'N	57°16'W	33.474		21	1.1	2.6	0.26	0.15	0.026	0.0009
10	8-11-67	13°00'N	56°40'W	35.047	8100	--	3.3	3.2	0.29	0.15	0.060	0.0009
11	8-12-67	12°06'N	55°00'W	35.265		39	4.2	3.0	0.27	0.16	0.043	0.0008
12	8-12-67	11°24'N	53°22'W	32.969		6.9	0.65	3.2	0.27	0.16	0.065	0.0007
13	8-13-67	10°29'N	51°16'W	32.205		13	0.52	3.1	0.28	0.19	0.080	0.0009
14	8-13-67	10°00'N	50°00'W	32.425		2.6	0.91	3.0	0.23	0.17	0.019	0.0011
15	8-14-67	09°25'N	47°25'W	35.588	8000	3.7	0.53	3.3	0.28	0.16	0.027	0.0003
16	8-14-67	09°30'N	45°57'W	35.975		--	0.62	3.9	0.32	0.20	0.019	0.0006
17	8-15-67	09°20'N	43°25'W	35.756		9.3	0.47	3.4	0.28	0.17	0.019	0.0006
18	8-15-67	09°15'N	41°48'W	34.474		19	5.4	3.1	0.27	0.16	0.036	0.0007
19	8-16-67	08°54'N	38°57'W	35.163		17	0.56	-	0.26	0.15	0.010	0.0005
20	8-16-67	08°45'N	37°34'W	35.153	8000	13	3.1	-	0.23	0.12	0.014	0.0005
21	8-17-67	08°12'N	34°28'W	35.390		11	0.68	-	0.24	0.13	0.019	0.0004
22	8-17-67	08°03'N	33°16'W	35.354		22	1.0	-	0.25	0.12	0.038	0.0008
23	8-18-67	07°45'N	30°46'W	35.438		9.4	0.57	-	0.26	0.15	0.013	0.0005
24	8-18-67	07°35'N	29°25'W	34.476		37	1.4	-	0.26	0.14	0.012	0.0010
25	8-19-67	07°15'N	26°40'W	35.131		7.4	0.64	-	0.26	0.15	0.009	0.0008
26	8-19-67	07°10'N	24°45'W	35.194		48	4.0	-	0.28	0.19	0.058	0.0021
27	8-20-67	06°48'N	22°11'W	35.161		--	0.61	-	0.28	0.15	0.013	0.0006
28	8-20-67	06°42'N	21°08'W	35.276		--	1.1	-	0.27	0.17	0.024	0.0006
29	8-21-67	06°04'N	18°30'W	35.327		18	3.0	2.7	0.23	0.16	0.029	0.0009
30	8-21-67	05°56'N	16°56'W	35.222	7900	14	0.81	3.0	0.24	0.17	0.014	0.0004
31	8-22-67	05°26'N	14°20'W	35.146		28	0.51	2.8	0.23	0.17	0.020	0.0007
32	8-22-67	05°07'N	12°42'W	35.296		37	2.7	2.9	0.26	0.17	0.030	0.0008
33	8-23-67	04°40'N	09°52'W	34.525		30	2.1	2.6	0.24	0.16	0.011	0.0005
34	8-23-67	04°22'N	08°25'W	36.127	7800	--	--	2.6	0.23	0.16	0.017	0.0011
35	8-24-67	05°00'N	05°35'W	35.436		27	--	2.6	0.22	0.17	0.027	0.0116
Average Concentration					8000 ±100	19	1.8	3.0 ±0.3	0.26 ±0.02	0.16 ±0.02	0.025	0.0011 ±0.0004
48		00°14'S 03°59'W										
(Depth Profile)		Depth, m										
		34	35.338	--	--	3.2	0.23	0.17	0.050	0.0008		
		36	35.571	--	--	2.7	0.22	0.16	0.050	0.0014		
		39	35.624	--	--	2.7	0.24	0.13	0.032	0.0002		
		42	35.698	--	--	2.8	0.23	0.17	0.011	0.0003		
		45	35.693	--	--	2.8	0.25	0.20	0.060	0.0006		
		192	35.280	--	--	3.2	0.26	0.16	0.011	0.0005		
		300	35.005	--	--	2.8	0.25	0.16	0.019	0.0006		

TABLE 2. Strontium Depth Profile Concentrations in the Gulf of Guinea - 01°19'N 04°00'W Station 49

Depth, m	Sr, mg/liter	Salinity	Sr/Salinity, × 10 ⁻⁴
1	8.7	35.314	2.5
33	8.2	35.316	2.3
39	8.4	35.356	2.4
42	8.6	35.533	2.4
45	8.3	35.572	2.3
50	7.9	35.640	2.2
60	7.3	35.533	2.1
156	7.1	35.377	2.0
200	7.5	35.307	2.1
300	7.5	34.956	2.1

the stable carbonate complex,⁽⁶⁾ $[\text{UO}_2(\text{CO}_3)_3]^{-4}$, and is conservative in its behavior in the marine environment. Our data indicate that the uranium concentration is rather uniformly distributed throughout the oceans at a concentration averaging near 3.3 µg/liter.⁽²⁾ However, significant localized variations from this average have been observed in our investigations.

The average surface concentration of cobalt in these waters was 0.025 µg/liter and ranged from 0.004 to 0.080 µg/liter. Cobalt is a biologically active element in the marine environment and is extensively assimilated by marine organisms. Thus, patches of seawater containing high abundances of marine organisms are frequently characterized by unusually high cobalt concentrations. Since our seawater samples were not filtered, plankton and other microscopic organisms enriched with cobalt contribute to the total cobalt concentration in the sample. Direct

evidence of this behavior is illustrated in Sample 18, which was collected in an area reported to contain large quantities of small organisms in the water. In this sample, a relatively high concentration of cobalt was present compared to surrounding waters. Also, high concentrations of Fe and Zn (which are also biologically active elements) were observed in this sample. The other high cobalt concentrations observed in Samples 10, 11, 12, 22, and 25 are also believed to be areas of high biological activity. Thus, the cobalt distribution throughout the oceans is quite variable and undoubtedly influenced by the amount of biological activity in the water.

Zinc was present in surface waters at an average concentration of 1.8 µg/liter and ranged from 0.40 to 6.50 µg/liter. The distribution of zinc in oceanic waters is, like cobalt, greatly influenced by the biological activity in the water, as evidenced in Sample 18. However, it appears that not all organisms have high mutual affinities for both Zn and Co, since Samples 1, 6, and 20 have relatively high Zn concentrations but no correspondingly high Co content. In most instances, however, high Zn concentrations are accompanied by high Co values. The zinc concentrations measured in this area of the Atlantic Ocean averaged three to five times lower than North Pacific Ocean waters.⁽²⁾

The average iron concentration in these waters was 27 µg/liter and ranged from 2.6 to 48 µg/liter. These values represent total iron,

which includes soluble and particulate fractions. Since the maximum concentration of dissolved, cationic, uncomplexed ferric iron that can exist at equilibrium at the pH of seawater is about 5×10^{-7} $\mu\text{g/liter}$, iron is mainly present as colloidal ferric hydroxide and ferric phosphate, or as soluble complexes formed between ferric iron and other species present in seawater.⁽⁷⁾

It is well known that particles of ferric hydroxide and phosphate are assimilated by marine organisms, which accounts for the highly variable distribution of iron throughout the oceans.

Scandium was present in surface waters between Florida and Ivory Coast at an average concentration of 0.001 $\mu\text{g/liter}$ and ranged from 0.0003 to 0.0120 $\mu\text{g/liter}$. Scandium is rapidly depleted from the oceans as it enters from river drainage of the continents.⁽⁸⁾ The high scandium content in Sample 35 was undoubtedly due to river drainage from Ivory Coast rivers, since a water color change from dark blue to green was reported to have taken place between Samples 34 and 35. It is interesting to note that no large corresponding increase in concentration was observed for the other trace elements in Sample 35 and suggests that perhaps these Ivory Coast rivers have extremely high Sc concentrations.

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THE DISTRIBUTION OF SIXTEEN TRACE ELEMENTS IN PELAGIC SEDIMENT CORES
FROM THE SOUTH PACIFIC OCEAN

D. E. Robertson

Neutron activation and direct gamma-spectrometric techniques were employed in the measurement of the trace elements Fe, Na, Sr, Mn, Cu, Cr, La, Ce, Sc, Th, Co, Hf, Sb, Yb, and Eu in pelagic sediment cores collected in the Tasman Sea area of the South Pacific Ocean. The majority of the sediments were of a calcareous composition, and their trace element content differed markedly from the deep-sea red clays predominantly found in the North Pacific Ocean. Several cores were spectacularly stratified with sediments of diverse origin, and the trace element composition of these layers provides a better understanding of the behavior of the oceans' trace elements during the various processes which lead to sedimentation and mineral formation on the ocean floor.

The deep-sea sediments are formed by a variety of processes. Rivers, marine organisms, land abrasions, and chemical precipitation all introduce sedimentary material to the oceans. Terrigenous, meteoric, and volcanic dust are other sources of sedimentary material. During various periods in the geologic past, one source of sedimentary material would dominate in certain areas of the oceans, resulting in sedimentary strata of widely-different chemical composition. A knowledge of the trace element distribution in each type of sediment can lead to an understanding of the behavior of the oceans' trace elements during the various processes that lead to sedimentation and mineral formation on the ocean floor. This information can then be extended to describe the behavior and fate of artificial radio-nuclides which enter the oceans from fallout, nuclear waste disposal, nuclear vessels, and effluents from nuclear reactors.

In October, 1967, the Pacific Oceanographic Research Laboratory (ESSA, Seattle) collected numerous deep-sea sediments from the Tasman Sea area of the South Pacific Ocean (Figure 1) during the global cruise of the USC&GSS Oceanographer. The cores were collected in plastic-lined coring tubes. Several grams of sediment from various strata in eleven cores were supplied to our Laboratory for the determination of trace constituents by neutron activation analysis. About 50 mg subsamples were dried, weighed encapsulated in polyethylene vials, and irradiated in a Hanford production reactor to an integrated thermal neutron exposure of about 3×10^{16} n/cm². The samples were stored for about two weeks and then were re-irradiated for a short time to an integrated thermal neutron exposure of about 3×10^{14} n/cm². Immediately after the short irradiation, the major activation products were ²⁴Na (15 hr) and ⁵⁶Mn (2.6 hr);

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FIGURE 1. Deep Sea Sediment Sampling Locations in the Tasman Sea

the concentrations of their parent elements, Mn and Na, were determined by counting a few hours after the irradiation on a 3 in. thick by 5 in. diameter NaI(Tl) crystal. Twenty-four hours later the samples were recounted on a multidimensional gamma-ray spectrometer⁽¹⁾ to determine Cu and La from their relatively short-lived activation products ^{64}Cu (12.8 hr) and ^{140}La (40 hr). After all of the short-lived activation products had decayed to insignificant concentrations, the samples were recounted on a multidimensional gamma-ray spectrometer and on a 20 cm³ Ge(Li) solid state detector⁽²⁾ to determine the concentrations of those elements which form relatively long-lived neutron activation products. By using these direct counting techniques, it was possible to measure the following elements by

purely instrumental methods: Fe, Na, Sr, Mn, Cu, Cr, La, Ce, Sc, Th, Co, Hf, Sb, Yb, and Eu. Activation standards of Co, Cu, La, Mn, and Fe were included with the samples during the irradiation, and the comparator method was used to determine these elements. The flux method was used to determine the concentrations of the remaining elements, using Co as the flux monitor. The accuracy of the flux method was improved by irradiating standards of all of the elements of interest and determining their reactor cross sections relative to cobalt. Most elements were measured with an estimated precision of about 2 to 10%. The concentrations of Fe, Na, Sr, and Mn as percent dry weight and Cu, Cr, La, Ce, Sc, Th, Co, Hf, Sb, Yb, and Eu as ppm dry weight are presented in Table 1.

In general, most of the sediment samples were of a calcareous composition and were characterized by higher Sr and lower Mn and Co concentrations relative to the deep-sea red clays predominantly found in the North Pacific Ocean.⁽³⁾ Most of the remaining elements had concentrations which averaged near those found in the deep-sea red clays.

There existed a strong correlation between the color of the sediment and its trace element content. Dark-colored sediments were generally characterized by relatively high concentrations of Fe and Na and low concentrations of Sr and Mn; whereas, light-colored sediments showed the opposite content.

TABLE 1. The Distribution of Major and Trace Element Concentrations
in Pelagic Sediment Cores Collected in the Tasman Sea Area of the
South Pacific Ocean

Sample No.	Depth, cm	Water Depth, m	Location	Dry Weight, %				Dry Weight, ppm										
				Fe	Na	Sr	Mn	Cu	Cr	La	Ce	Sc	Th	Co	Hf	Sb	Yb	Eu
156	1	3768	31°33.87'S 150°33.32'E	3.1	2.2	0.13	0.11	142	50	33	26	10	7.8	10	4	1	0.83	0.66
160	1	4565	31°37.2'S 154°14.0'E	3.6	2.4	0.084	0.047	156	53	34	29	10	8.8	2.2	5	0.73	0.95	0.68
167	1	4654	31°30.5'S 155°01.0'E	4.5	4.1	0.069	0.056	262	71	64	38	14	13	13	5	0.89	0.85	0.95
	49			3.8	2.4	0.14	0.15	150	69	39	31	13	28	13	6	0.71	0.89	0.76
	53			2.9	2.5	0.16	0.050	100	45	34	22	8.6	5.7	7.7	3	0.48	0.85	0.53
	63			2.3	2.4	0.35	0.067	57	36	38	22	8.2	23	7.6	3	0.59	0.92	0.58
	76			3.4	2.7	0.087	0.050	183	67	43	33	12	12	11	4	0.63	1.1	0.77
	195			6.0	2.2	0.096	0.086	99	42	42	45	11	10	12	3	0.69	0.58	0.69
	277			3.4	2.2	0.12	0.057	135	53	47	36	12	11	12	7	1.1	1.0	0.91
	500			2.6	1.5	0.18	0.065	162	48	51	23	9.2	6.4	8.1	3	0.88	0.81	0.61
	510			0.88	0.92	0.36	0.22	30	12	22	8	2.0	1.3	4.5	0.67	0.15	0.75	0.32
	517			4.3	3.1	0.060	0.042	150	72	79	38	15	16	15	7	1.4	1.1	0.98
	539			6.8	3.3	0.058	0.032	174	73	82	54	14	16	16	7	1.2	2.0	0.94
	611			2.9	2.1	0.18	0.084	196	53	55	30	9.5	6.7	7.5	3	0.44	0.91	0.84
	617			4.5	2.9	0.095	0.020	380	56	64	31	11	8.7	12	4	1.1	1.2	0.72
173	1	4838	31°29.18'S 155°44.82'E	2.9	1.4	0.21	0.045	50	43	28	24	10	27	8.8	3	0.42	0.64	0.61
176	1	4689	31°28.9'S 156°12.52'E	2.6	2.6	0.17	0.072	223	43	50	26	8.8	10	9.6	4	0.79	0.94	0.59
	10			4.1	1.7	0.083	0.069	77	56	47	32	11	13	11	6	0.77	1.2	0.81
	43			4.3	1.5	0.092	0.078	93	57	36	34	12	10	14	5	0.71	1.5	0.76
	77			2.6	1.4	0.16	0.064	62	41	27	24	8.5	10	8.6	6	0.88	1.3	0.70
	86			2.3	0.98	0.24	0.13	57	18	12	16	4.5	4.1	9.0	0.46	0.42	0.82	0.45
	89			4.0	0.94	0.15	0.12	112	22	25	18	5.0	4.9	15	2	0.82	0.90	0.43
	166			1.8	0.89	0.20	0.15	30	24	19	15	5.4	4.1	5.0	2	0.31	1.1	0.45
	179			3.7	1.7	0.097	0.044	151	62	41	37	12	14	10	8	0.79	1.2	1.0
	210			4.1	1.2	0.10	0.058	133	52	21	29	9.2	10	10	5	0.71	0.99	0.66
177	66	4283	31°30.5'S 156°54.3'E	4.7	1.9	0.12	0.058	56	62	32	38	9.3	11	9.4	4	0.49	0.87	0.94
184	208	3609	33°09.44'S 159°27.03'E	3.8	1.3	0.17	0.019	121	19	19	18	4.2	3.5	6.7	0.28	0.46	0.73	0.39
204	18	1834	33°31.08'S 164°03.03'E	0.59	0.93	0.24	0.054	69	7.5	11	5.2	2.0	1.9	4.1	7	0.25	0.35	0.24
208	24	3045	33°30.3'S 165°02.3'E	0.80	1.1	0.22	0.13	77	5.1	15	7.6	2.7	1.7	5.7	0.47	0.52	0.44	0.33
216	25	3044	33°28.0'S 166°00.7'E	0.85	0.89	0.23	0.14	174	17	5.7	6.7	2.6	2.7	8.0	0.46	2.4	0.34	0.34
	74			0.67	0.73	0.23	0.034	23	12	6.8	6.6	2.3	3.0	3.5	0.28	0.29	0.39	0.26
	78			0.68	0.76	0.22	0.035	155	10	8.3	5.8	2.1	3.2	13	1	0.75	0.48	0.24
223	49	2858	33°32.0'S 166°31.9'E	0.88	0.94	0.059	0.82	144	16	8.1	5.2	2.4	4.7	42	0.92	1.4	0.66	0.32
	124			0.96	0.92	0.19	0.031	136	15	15	6.4	3.1	2.1	47	0.94	0.21	0.52	0.35
	137			0.84	0.78	0.24	0.035	32	14	14	8.4	3.3	2.3	41	0.83	0.46	0.72	0.40
	158			0.84	0.85	0.24	0.035	53	12	14	9.1	2.7	3.0	3.3	0.68	0.12	0.30	0.35

A significant change in trace element composition occurred in Samples 204, 208, 216, and 223, which were collected further from the Australian continent and in somewhat shallower waters. In these samples, the Fe content was very low, which is characteristic of biologically-derived material such as globigerina oozes. The Cr, Sc, Th, Hf, and rare earth concentrations were also much lower, while some of the highest Co concentrations were found in these samples. Obviously, these sediments had accumulated by a different mechanism than the sediments in Cores 156 to 184.

The most interesting samples were those taken at various depths in Cores 167 and 176, which were spectacularly stratified with many sediment layers of diverse origin. The most unusual section of the core was at 510 cm, where a light-colored calcareous layer exhibited a very high Sr content and a relatively high Mn concentration while the remaining elements displayed very low concentrations in this layer. This sediment was deposited thousands of years ago, probably by biochemical precipitation and in the process, relatively large quantities of Sr and Mn were coprecipitated at a rate about five times higher than the present rate in this area of the ocean. This rate is evidenced by comparing the composition of present sedimentary material (1 cm) with that deposited at a depth of 510 cm.

The deposit at 510 cm contained relatively low concentrations of cobalt. Since most marine organisms

extensively concentrate cobalt in their bodies,⁽⁴⁾ either the organisms contributing to this sediment layer had no affinity for cobalt or the cobalt was leached from their skeletons as they sank to the ocean floor.

Throughout Cores 167 and 176, the rare earth concentrations seldom varied by more than a factor of two, indicating that the mechanisms leading to sedimentation for the rare earth elements were probably independent of biochemical precipitation processes. Wildeman and Haskin report that the rare earth elements present in pelagic sediments are primarily from a terrigenous source.⁽⁵⁾

The concentration and distribution of Hf and Sb in marine sediments are relatively unknown, and the values reported in this study constitute the first comprehensive measurements of these elements in marine sediments.

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IRON-55 IN BERING AND NORTH AMERICAN PACIFIC SALMON

C. E. Jenkins and J. C. Langford

Iron-55 concentrations in Pacific salmon are generally decreasing by a yearly factor of 2 to 4 in a given location and ninefold from Kotzebue, Alaska, to Sacramento, California. The concentrations of Fe in salmon are nearly species-independent and may offer a method for the determination of an integrated ^{55}Fe concentration in seawater from a given locale.

Fallout radionuclides deposited in the ocean show concentration variations with location and depth. These variations are functions of the atmospheric fallout rate and of the horizontal and vertical mixing rates of the ocean. Iron-55, a (n, γ) or (n,2n) product of ^{54}Fe or ^{56}Fe , respectively, is presently one of the highly abundant fallout radionuclides.⁽¹⁾ The deposition rate of this radionuclide following the United States and Russian nuclear tests in 1961 and 1962 produced initial ground concentrations comparable to ^{90}Sr and ^{137}Cs .⁽²⁾ However, since the ^{55}Fe half-life is 2.4 yr, compared to 28.8 yr and 30 yr for ^{90}Sr and ^{137}Cs , respectively, its concentration is decreasing more rapidly.

Iron-55 decays by electron capture to ^{55}Mn and emits a 5.9 keV X-ray which can be used to determine its concentration in biota and man. Although its radiation dose to man is low, ^{55}Fe must be determined since it is an essential element in fallout and has high uptake in the food chains that lead to man.^(1,3,4,5) Tuna, salmon, and many other marine organisms are extremely efficient in concentrating ^{55}Fe at levels considerably above those measured in terrestrial organisms.^(1,3,6,7)

Iron-55 concentrations in all five of the North American salmon species were observed at the sites shown in Figure 1. In general, samples were obtained from mature salmon as they began their spawning run; however, some

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FIGURE 1. Pacific Salmon Sampling Sites

immature fish were also sampled for comparative purposes. The specimens listed in Table 1 were prepared^(1,8) and subsequently analyzed by an argon-methane proportional counter after electroplating the iron by the method of Maletskos and Irvine.^(1,9) In general, the highest levels of ^{55}Fe are observed in salmon of far-north origin.⁽⁶⁾ Iron-55 and stable iron concentrations appear to be independent of the salmon species, although longer-lived salmon may have higher ^{55}Fe concentrations because of past abundances.

Fine structure in the distribution of ^{55}Fe was observed in two separate Chum salmon runs sampled at Kotzebue, Alaska. The July Chum salmon run is greater than

threefold higher in ^{55}Fe than the August run. Although the ^{55}Fe varied by over threefold between runs, the variation was less than 30% within a run, which indicates that the salmon were originally feeding in two separate locations or areas differing in ^{55}Fe concentration. The August Kotzebue Chum salmon have ^{55}Fe concentrations and specific activities similar to the Bristol Bay salmon, which may indicate the same feeding ground.

In 1968, the average concentration decreased by 8.1 ± 0.6 and 2.9 from Kotzebue, Alaska, to the western United States coast and Bristol Bay, Alaska, respectively. These factors agree with the values observed in 1967⁽⁶⁾ of 9 and 2.2 ± 0.2 from the Yukon River to the Columbia River and Seward, Alaska, respectively. The two- to threefold decline in average activity from 1967 to 1968 is approximately equal to previous years, as shown in Table 2. The average concentration of ^{55}Fe in Chinook and Coho salmon sampled in Washington, Oregon, and California shows only a slight decreasing trend from Washington to California.

In view of the oceanic migratory habits of the salmon,^(11,12,13) the variations in ^{55}Fe concentrations between species or "runs" suggest that Washington, Oregon, and California coastal salmon populations have, in some instances, a common feeding ground with Bristol Bay and southern Alaskan salmon.⁽⁸⁾

In an effort to determine if other marine organisms reflect the high ^{55}Fe levels observed in salmon from

TABLE 1. ^{55}Fe Concentrations and Specific Activity in Pacific Salmon - 1968

Sample Date	Sample	Sex	Location	^{55}Fe , d/m/kg (wet wt)	Stable Fe, mg/kg (wet wt)	Specific Activity
7/10	Chum Muscle	M	Kotzebue, Alaska	15,000 $\pm$ 236 ^(a)	11.5	1,300
7/10	Chum Muscle	M	Kotzebue, Alaska	20,500 $\pm$ 134	13.7	1,500
7/10	Chum Muscle	M	Kotzebue, Alaska	16,800 $\pm$ 239	11.3	1,490
7/10	Chum Muscle	M	Kotzebue, Alaska	12,300 $\pm$ 209	9.0	1,370
7/10	Chum Muscle	F	Kotzebue, Alaska	15,400 $\pm$ 246	10.0	1,540
7/10	Chum Muscle	F	Kotzebue, Alaska	10,900 $\pm$ 198	9.0	1,210
7/10	Chum Muscle	F	Kotzebue, Alaska	17,400 $\pm$ 288	13.2	1,320
8/15	Chum Muscle	F	Kotzebue, Alaska	5,110 $\pm$ 138	9.31	549
8/15	Chum Muscle	F	Kotzebue, Alaska	4,680 $\pm$ 133	7.1	659
8/15	Chum Muscle	M	Kotzebue, Alaska	4,470 $\pm$ 74	7.83	571
8/7	Chinook Muscle	F	King Salmon, Alaska	5,600 $\pm$ 126	8.4	666
8/30	Pink Muscle	F	King Salmon, Alaska	4,920 $\pm$ 173	10.3	478
7/21	Sockeye Muscle	M	King Salmon, Alaska	4,360 $\pm$ 41	7.7	566
7/21	Sockeye Muscle	M	King Salmon, Alaska	5,360 $\pm$ 168	10.1	531
7/21	Sockeye Muscle	M	King Salmon, Alaska	4,640 $\pm$ 233	13.0	357
7/21	Sockeye Muscle	F	King Salmon, Alaska	7,200 $\pm$ 112	10.3	699
8/29	Chinook ^(b) Muscle	M	La Push, Washington	532 $\pm$ 35	6.24	85.3
8/29	Coho Muscle	F	La Push, Washington	4,390 $\pm$ 89	11.5	382
8/29	Coho ^(b) Muscle	M	La Push, Washington	1,060 $\pm$ 48	8.3	128
8/14	Coho Muscle	M	Columbia River, Oregon	3,440 $\pm$ 78	10.3	334
8/14	Coho Muscle	M	Columbia River, Oregon	1,030 $\pm$ 47	6.75	152
8/14	Chinook Muscle	M	Columbia River, Oregon	2,100 $\pm$ 60	7.7	273
8/14	Chinook Muscle	F	Columbia River, Oregon	649 $\pm$ 42	7.66	84.7
9/30	Chinook Muscle	M	Trinity River, Calif.	1,280 $\pm$ 49	11.9	108
9/30	Chinook Muscle	F	Trinity River, Calif.	2,380 $\pm$ 60	14.1	169
9/30	Chinook Muscle	F	Trinity River, Calif.	1,650 $\pm$ 46	13.2	125

a. $\pm$ values = 1 σ .

b. Lap salmon are immature salmon.

TABLE 2. Levels of ^{55}Fe in Salmon Caught at Various Locations from 1965 to 1967

Sampling Location	Average ^(a) nCi ^{55}Fe /kg of wet muscle			
	1965	1966	1967	1968
Northeast Alaskan Coast	(2) 50	(44) 19	(10) 5.0	(7) 7.0 ^(b) (3) 2.2
Southern Alaskan Coast	(4) 33	(14) 25	(17) 5.6	(6) 2.4
Washington State Coast	(2) 9.0	(6) 0.91	(10) 1.5	(10) 0.8

a. Numbers in parentheses are the number of salmon included in the average

b. Two separate Chum salmon runs.

northern Alaska, Shee fish and seal samples were obtained at Kotzebue. The preliminary results, which are presented in Table 3, indicate that little ^{55}Fe is concentrated by these organisms in the Kotzebue region.

In Figure 2 a comparison is presented between the relative concentration of ^{55}Fe in rain, air, and

TABLE 3. ^{55}Fe and Specific Activity in Marine Animals at Kotzebue, Alaska - 1968

Sample	^{55}Fe Conc. d/m/kg wet wt	Stable Fe Conc. mg/kg wet wt	Specific Activity
Shee Fish Muscle	145 $\pm$ 51 (a)	8.5	17
Shee Fish Muscle	61 $\pm$ 57	7.7	8
Shee Fish Muscle	27 $\pm$ 44	8.6	3.1
Seal Muscle	67 $\pm$ 46	103	0.65

a. $\pm$ values = 1 σ

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FIGURE 2. A Comparison of the Relative Decrease of ^{55}Fe in Fallout, Salmon (Curves are not corrected for decay)

salmon from the period 1965 to 1968 at various locations. The data indicate that the rate of change of ^{55}Fe concentration in salmon is greater than the fallout measured in air and precipitation. The rapid yearly decrease^(3,6) of ^{55}Fe in the biosphere limits the effect of nuclear debris fallout. This results from a combination of the stratospheric residence half-life of 13 months,⁽¹⁴⁾ the sedimentation

rate in the ocean, and the 2.4 yr half-life of ^{55}Fe . Pacific Coast Salmon have the same decreasing ^{55}Fe trends as salmon from the Bering and Chukchi Seas. Since the ^{55}Fe concentration presently observed in salmon must reflect stratospheric fallout rates and tropospheric wash-out to the ocean, the ^{55}Fe can be used to integrate the fallout input to the local environment over the lifetime of the organism.

Both fallout and stable Fe appear nearly species-independent and may thus be independent of the trophic-feeding level. Fallout ^{55}Fe appears to be concentrated preferentially to stable Fe in salmon, indicating part of the stable Fe in the ocean may be biologically unavailable to organisms. The concentration of Fe appears to be directly related to the location of the major feeding ground of the salmon and the local organisms.

Investigation of the physical and chemical form of stable Fe and fallout ^{55}Fe in the oceans leads to an understanding of the uptake of ^{55}Fe by the biosphere. In Table 4 the particulate and Al_2O_3 -retained fractions of ^{55}Fe and stable Fe obtained in seawater samples are presented. Al_2O_3 could not be detected at 20 or 1639 m, which suggests little Fe exists in a finely-dispersed or soluble state at these depths. Slow vertical mixing rates in the ocean preclude a large concentration of this moderately short half-life radionuclide (2.4 yr) at a depth of 1639 m.

TABLE 4. 1967 Iron-55 Concentrations in Ocean Water
- Particulate and Al_2O_3 Fractions

Depth, m	Volume, liters	Particulate ^(a) ^{55}Fe , d/m/1000 liters	Particulate ^(a) Stable Fe, $\mu g/liter$	Specific ^(a) Activity ($\times 10^3$)	Al_2O_3 ^{55}Fe d/m/1000 liters	Al_2O_3 Stable Fe, $\mu g/liter$	Specific Activity ($\times 10^3$)
20	2615	33	12	2.73	<14	2.24	<5.36
328	7608	30	3.2	16	1101	0.294	344
656	3785	--(b)	11.6	--	15	0.66	22.7
984	4031	50	8.5	55	2.0	0.76	25.9
1639	3861	31	8.5	3.7	<8	0.75	<10.2

a. Data previously reported in Ref. 10

b. Sample lost.

A comparison of the particulate and finely-dispersed ^{55}Fe concentrations indicates that particulate ^{55}Fe is relatively constant with depth. The sample obtained from a 326-m depth appears to be unusual in two aspects: (1) Twice as much seawater was sampled by the filtering system⁽¹⁵⁾ because of the low concentration of particulate material and (2) the total stable particulate Fe and Al_2O_3 -retained material was twofold below that at any other depth. Slight maxima have been reported for other trace elements at 500 to 1500 m,⁽¹⁶⁾ and nutrients such as nitrates and phosphates have often exhibited maxima at these depths. One common explanation for the maxima has been that the increasing depth causes degeneration of particulate matter so that the descent rate decreases.⁽¹⁷⁾ The lack of particulate Fe and organic and inorganic matter at 326 m suggests that downward transport of

particulate Fe and organic matter by organisms in that region is small.

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IRON-55 CONCENTRATIONS IN COLUMBIA RIVER ESTUARINE AND PACIFIC OCEAN
MARINE ORGANISMS

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The uptake and transfer of ^{55}Fe and stable Fe by surface marine and Columbia River estuary organisms appear to be a function of distance from the river mouth. Stable Fe decreases with distance in all but the bottom-feeding organisms. Pacific Coast salmon have ^{55}Fe concentrations and specific activities 10- to 100-fold higher than Columbia River estuarine and marine organisms.

Nuclear weapons testing and the increasing use of nuclear reactors and associated chemical processing plants have introduced low-level radioactive materials into fresh water and marine environments. Although present levels of radioactivity are low in the marine environment, many radionuclides may be detected by use of ultrasensitive chemical and instrumental techniques.^(1,2) Measurement of the concentrations of these radionuclides is an important step in determining their behavior with respect to their stable element counterpart and their potential hazard in the biosphere.

With the great abundance of biota available in the Columbia River estuary and adjacent continental shelf, the intake, retention, and movement of radionuclides through the marine trophic levels and variation in individual species may be studied. Iron-55, one of the highly-abundant radionuclides, is produced in nuclear weapons testing and nuclear reactors by (n,γ) or $(n,2n)$ reactions on ^{54}Fe and ^{56}Fe , respectively. Since ^{55}Fe

is a biologically active element, it has a high uptake rate in the food chains leading to man and constitutes a potential hazard to man because it concentrates in the red blood cells. The highest ^{55}Fe levels have been measured^(3,4,5,6,7) in the marine food web. Most oceanic ^{55}Fe was originally deposited in the stratosphere during the 1961 and 1962 United States and Russian nuclear weapons testing series and has returned to the earth through tropospheric scavenging processes.⁽⁸⁾ Its oceanic distribution is a function of horizontal and vertical (sedimentation) mixing rates and biological activity. Preliminary ^{55}Fe measurements in the Columbia River estuary and the Oregon-Washington continental shelf were made to characterize the fallout distribution and behavior. Previous studies⁽⁹⁾ have shown that ^{55}Fe is produced in small amounts in the Hanford reactors when compared to the total stable iron; therefore, ^{55}Fe contribution to the total iron in Columbia River freshwater organisms is small.

In April, 1968, three mid-water and five otter trawls were made in

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the Columbia River estuary and adjacent Pacific Ocean from the R/V Yaquina at the locations shown in Figure 1. The organisms were separated into individual species and immediately frozen in plastic bags. The organisms were ashed at 450 °C in the laboratory, and a small aliquot of homogenized ash was taken for stable Fe and ^{55}Fe using a previously-described procedure.⁽⁴⁾ The ^{55}Fe and stable Fe concentrations and specific activities are presented in Table 1.

Long-finned smelt from the Columbia River (Station 33A) contained the greatest concentrations of both ^{55}Fe and stable Fe and the lowest specific activity. Further downriver (Station 5) other similar surface-feeding fish had lower Fe intakes and higher specific activities. Shiner perch taken from

Stations 5 and 4 have similar specific activities; however, the Shiner perch from inside the river mouth (Station 5) have approximately three times more total Fe. The Fe decrease in surface fish is not reflected in the Station 4 bottom-feeding organisms. Iron-55 concentrations in Station 35 and 4 organisms indicate that ^{55}Fe levels may decrease with depth. Iron-55 and stable Fe concentrations in Station 19 organisms suggest that the supply of stable Fe may be lower. Those organisms feeding on or near the bottom of the ocean appear to have higher Fe concentrations.

Valella Valella, an oceanic surface-floating organism, had the highest specific activity of any organism observed. This preferential ^{55}Fe uptake suggests that

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FIGURE 1. Sampling Locations for the Collection of Columbia River Estuarine and Adjacent Pacific Ocean Marine Organisms

TABLE 1. Iron-55 Concentrations in Marine Organisms
in Columbia River Estuary - April 1968

Station	Depth, m	Sample	^{55}Fe ($\pm 1\sigma$) d/m/kg wet wt	Total Fe ^(a) mg/kg wet wt	Fe Specific Activity, d/m/mg
33A	13	Long-Finned Smelt	1760 $\pm$ 550	1640.0	1.1
5	15	Smelt	693 $\pm$ 54	32.9	21
5	15	Shiner Perch	690 $\pm$ 108	53.7	13
35	13	Peamouth Chub	919 $\pm$ 48	64.0	14
4	26	Tom Cod	221 $\pm$ 58	47.8	4.6
4	26	Sand Sole	260 $\pm$ 51	76.2	3.4
4	26	Dungeness Crab	372 $\pm$ 135	123.0	3.0
4	26	Dungeness Crab	421 $\pm$ 246	66.9	6.3
4	26	Shiner Perch	218 $\pm$ 46	17.2	13
19	120	Sand Sole	194 $\pm$ 67	4.1	47
19	120	Lemon Sole	180 $\pm$ 46	9.2	20
19	120	Rex Sole	325 $\pm$ 40	93.6	3.5
19	120	Dungeness Crab	954 $\pm$ 155	250.0	3.80
44°35' 124°45'	Surface	Valella Valella	635 $\pm$ 35	2.44	260
44°38' 132°29'	20 m	Euphausiids	335 $\pm$ 70	23.0	15

a. Total error at the 1 σ level is less than $\pm 5\%$.

stable Fe concentrations near the surface of the ocean are biologically less available and that surface-feeding organisms may be expected to have the highest ^{55}Fe levels. Iron concentration in Euphausiids obtained further away from the river mouth indicate that more stable Fe is available to them than the surface-floating Valella Valella.

Many of these organisms comprise part of the food chain of Pacific salmon. Salmon and tuna^(3,4,5,6,10) have been shown to have ^{55}Fe concentrations 300-, 3-, and 1 1/2-fold those measured in cattle,^(5,6) caribou,⁽⁵⁾ and Swedish reindeer,⁽¹¹⁾ respectively. The organisms comprising this study are factors of 10 to 100 below ^{55}Fe concentrations and

specific activities observed in Pacific Coast salmon,^(6,10) except for the Valella Valella. The high specific activity observed in Valella Valella is approximately that of salmon.

The uptake and transfer of ^{55}Fe and stable Fe by estuarine and marine organisms need further investigation to adequately define the influence of the Columbia River. These preliminary data suggest that the highest ^{55}Fe levels are in oceanic surface organisms feeding away from sources of stable Fe, such as the Columbia River. Fallout ^{55}Fe appears to increase rapidly in surface-feeding organisms with distance from the river mouth and to be a complex function of the marine food web and depth.

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IRON-55 LEVELS IN HUMANS LIVING IN RICHLAND, WASHINGTON - 1968

C. E. Jenkins and J. C. Langford

Iron-55 concentrations in Richland, Washington, residents are presently decreasing 3 to 4 nCi per year and are 1.4 times the levels observed in 1968 cattle. Maximum ^{55}Fe concentrations occurred four years later than the atmospheric fallout peak concentrations.

Iron-55, which is produced by an (n, γ) or (n,2n) reaction on ^{54}Fe or ^{56}Fe , respectively, is presently one of the highly abundant fallout radio-nuclides. It decays to ^{55}Mn by electron capture and emission of a 5.9 keV X-ray. Although its radiation dose to man is low, ^{55}Fe must be determined since it is a predominant element in fallout, has high uptake in the food chains leading to man, and concentrates in the red blood cells.

High ^{55}Fe body burdens have been observed in population groups consuming large quantities of ocean fish compared to the average worldwide concentration in man.^(1,2,3) The average ^{55}Fe concentrations in Richland, Washington, residents are factors of 5 to 100 lower than observed for the Alaska natives because the natives consume substantial quantities of ^{55}Fe from salmon and caribou. Initially, females have higher body burdens than males because women have higher iron uptake and turnover rates than men.^(1,2) Iron-55 body burdens in people living in Richland, Washington, have been measured from 1964 to 1968 in fresh blood obtained from donors at Red Cross Blood Banks. Except for 1964 and 1965, approximately 1 ml of

blood was obtained from each donor, with a minimum 25 donors used for each composite sample.

In Table 1 the body burdens⁽⁴⁾ of Richland, Washington, residents based on 5 liters of blood per person are presented. These calculations assume that 60% of the total body iron is in the blood. The data indicate that the yearly ^{55}Fe body burden increases (1964-1966) and decreases (1966-1968) by 3 to 4 nCi per year. The October, 1968, specific activities reflect the faster iron turnover in women and indicate women are closer to environmental equilibrium than men.⁽⁵⁾

The human 1968 ^{55}Fe concentrations and specific activities based on 1 kg of raw blood average 1.4 times the levels measured in 1968 Richland cattle. The ^{55}Fe rate of decrease in humans and cattle is shown in Figures 1 and 2. This decrease, which is less rapid for humans than for cattle, reflects the longer ^{55}Fe exposure integration period involved for adult humans than for short-lived animals. The ^{55}Fe levels in humans reached a maximum in late 1966, which is four years after its insertion into the worldwide atmosphere. This rather substantial lag time is representative of the

TABLE 1. Total Body ^{55}Fe (a) in Adults in Richland, Washington

Sampling Date	Male		Female	
	Number of Samples	Average Body Burden, nCi	Number of Samples	Average Body Burden, nCi
November, 1964	4	9	--	--
October, 1965	4	13	--	--
January, 1966	100	21	25	16
March, 1966	--	--	25	18
December, 1966	100	24	25	22
July, 1967	84	17	--	--
October, 1968	60	14	27	14.5

October, 1968:

Blood (kg wet weight)	^{55}Fe , nCi/kg	Total Fe, $\mu\text{g/kg}$	Specific Activity, nCi/ μg Fe
Male	1.67	460	0.00363
Female	1.73	580	0.00298

a. Total body burdens calculated using 5 liters of blood per person and 60% of total Fe in blood.

Neg 0690598-1

FIGURE 1. Body Burden of ^{55}Fe and ^{137}Cs in Richland, Washington, Residents

Neg 0690598-2

FIGURE 2. Body Burden of ^{55}Fe in Cattle and of ^{55}Fe and ^{137}Cs in Humans from Richland, Washington

biological half-life of Fe (2.2 yr), which is much longer than one of the other predominant fallout radio-nuclides ^{137}Cs (60-100 d).⁽⁶⁾ Studies of ^{137}Cs in Richland residents reflected this shorter biological half-life since its maximum occurred about 18 months after the major nuclear testing period in 1961-1962. Iron-55 concentrations reached their maximum in cattle before the first measurements in Richland were made in 1964, indicating a short lag time between maximum fallout and concentrations in cattle.

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LEVELS OF IRON-55 IN HUMANS, ANIMALS, AND FOOD - 1964-1968*

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Iron-55 levels in the foods of humans have been decreasing since 1964 with the exception of caribou obtained from Arctic areas, which showed peak levels in 1965. The levels of ⁵⁵Fe in humans at Richland, Washington, increased until about January, 1967, and then began to decrease. This peak level in humans occurred about four years after the 1962 nuclear test series. This lag time of four years is much longer than that for ¹³⁷Cs in humans, where peak levels occurred 1-1/2 years after the nuclear tests stopped.

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ANALYTICAL PROCEDURES USED FOR MEASURING COSMIC-RAY-INDUCED RADIONUCLIDES
 ^7Be , ^{24}Na , $^{34\text{m}}\text{Cl}$, ^{38}Cl , and ^{39}Cl IN RAIN AND AIR

C. W. Thomas, J. A. Young, R. W. Perkins, and N. A. Wogman

Procedures were developed for the determination of ^7Be , ^{24}Na , ^{38}Cl , and ^{39}Cl in air, and $^{34\text{m}}\text{Cl}$, ^{38}Cl , and ^{39}Cl in rain.

In studying atmospheric precipitation and scavenging processes using cosmic-ray-induced radionuclides, analytical procedures were developed which are selective for the separation of Be, Na, and Cl from rain and air. Such methods were needed to separate these elements from daughter products of Rn and Th and from fission products.

The following procedures, coupled with multidimensional gamma-ray spectrometry, allow the cosmic-ray-produced radionuclides ^7Be (53 d), ^{24}Na (15 hr), $^{34\text{m}}\text{Cl}$ (32 min), ^{38}Cl (37.3 min), and ^{39}Cl (55 min) to be determined in the presence of greater than 10^8 d/m of Rn and Th daughters and/or fission products. The method for determining ^{24}Na , ^{38}Cl , and ^{39}Cl concentrations in air (Procedure A) is used in samples collected from 20,000 to greater than 60,000 ft. The method for determining $^{34\text{m}}\text{Cl}$, ^{38}Cl , and ^{39}Cl in rain (Procedure B) is used for samples ranging from 2 to 55 liters. A selective procedure for ^{24}Na determination in air (Procedure C) was developed for samples collected from ground level to 5000 ft. A method for determining ^7Be in air (Procedure D) is used when large concentrations of fission products are present.

Procedure A: Determination of ^{24}Na , ^{38}Cl , and ^{39}Cl in Air

1. Prepare solution containing 20 ml 8N HNO_3 , 500 ml ethanol, 1 ml 12N HCl , and 10 mg each Ru, Cs, Zr, Ce, and Na carriers.
2. Prepare solution containing 500 ml 4N HNO_3 , 1 ml 12N HCl , and 10 mg each of Ru, Cs, Zr, Ce, and Na carriers. Heat to 70-80 °C.
3. Rapidly remove IPC filter paper from air collector and tear into $\sim 4 \text{ cm}^2$ pieces and place in 1000 ml beaker.
4. Add half of solution from Step 1 and mix for ~ 2 min using air-driven stirrer. Transfer contents to Buchner filter funnel and apply vacuum. Save filtrate.
5. Transfer filter paper pulp to 1000 ml beaker and repeat Step 4. Wash pulp with a solution containing 100 ml ethanol and 10 ml 4N HNO_3 . Apply vacuum to remove wash solution from pulp. Save filtrate and wash and combine with filtrate of Step 4. Add 20 ml 1M AgNO_3 . Stir vigorously with glass-stirring rod, scratching side of beaker. Let stand. Filter through 11 cm diameter glass-fiber filter

- (Gelman, Type A). Save filter. Put filtrate in 4 liter beaker and save.
6. Transfer pulp from Buchner to 1000 ml beaker and add half of solution from Step 2. Mix for about 2 min using air-driven stirrer. Transfer to Buchner and apply vacuum. Save filtrate.
 7. Repeat Step 6. Wash pulp with 100 ml water. Combine filtrates and wash from Steps 6 and 7. Save pulp.
 8. To filtrate, add 20 ml of 1M AgNO_3 . Stir vigorously with glass rod, scratching sides of beaker. Filter, using 11 cm diameter glass fiber filter (Gelman, Type A) and vacuum. Combine filtrate with filtrate of Step 5 and start evaporating to dryness. Save filter.
 9. Dissolve separately AgCl precipitate from filters of Steps 5 and 8 by passing 200 ml of 1:1 NH_4OH . Wash filters with 50 ml H_2O . Combine into a single sample NH_4OH solutions and washes. Save filters.
 10. To ammoniacal solution carefully add 400 ml of 8N HNO_3 , 20 mg each of Pb and Bi carriers, and 20 ml of 1M AgNO_3 . Stir with glass rod, scratching sides of beaker. Filter through 11 cm diameter glass-fiber filter (Gelman, Type A). Wash with 100 ml water. Discard filtrate and wash unless Rn and Th daughters measurements are wanted.
 11. Fold filter paper containing AgCl and place in $1/2 \times 2$ in. diameter PVC ring for measurement of cosmic-ray-produced ^{38}Cl and ^{39}Cl .
 12. If fission products are to be measured, dry and combine filter pulp from Step 7 and filters from Steps 5 and 8 and press in a $1/2 \times 2$ in. diameter PVC ring.
 13. After filtrate from Step 8 has reached dryness and NH_4NO_3 fumes are no longer visible, remove residual salts by first scraping with a spatula and then cleaning beaker by rubbing with about 10 cm³ of dry DOWEX 50, H^+ form, 200 mesh resin. Place residual salts and resin in $1/2 \times 2$ in. diameter PVC ring for measurement of cosmic-ray-produced ^{24}Na .
- Procedure B: Determination of $^{34\text{m}}\text{Cl}$, ^{38}Cl , and ^{39}Cl in Rain
1. Collect 55 liters of rain on a 1000 ft² plastic tarp over a time period not exceeding 30 min. Transfer rapidly to a plastic carboy. Add 200 ml of concentrated HNO_3 , 5 ml of 12N HCl , 20 mg each of Pb and Bi carriers. Add 100 ml of 1M AgNO_3 and stir vigorously for 2 min using electric stirrer.
 2. Rapidly filter sample by applying pressure to the carboy. Use compressed N_2 to force sample from carboy through plastic filtering assembly that utilizes two 12 in. diameter, 300 mμ pore size membrane filters.
 3. Place filters in beaker and dissolve AgCl with 200 ml of

- 1:1 NH_4OH . Filter, save ammoniacal filtrate.
4. To filtrate add cautiously 200 ml of 1:1 HNO_3 , 20 ml of 1N AgNO_3 , and 20 mg each of Pb and Bi carriers. Stir with glass rod, scratching sides of beaker.
 5. Filter, wash with 100 ml of H_2O . Fold filter and place in $1/2 \times 2$ in. diameter PVC ring for measurement of ^{34}mCl , ^{38}Cl , and ^{39}Cl .

Procedure C; Determination of ^{24}Na in Air

1. Tear IPC filter into $\sim 4 \text{ cm}^2$ pieces and place in 1000 ml beaker.
2. Add 250 ml of ethanol containing 10 ml of 8N HNO_3 , 10 mg each of Pb, Na, Ru, and Fe carriers. Mix thoroughly, filter using Buchner funnel and vacuum. Save filtrate and filter pulp.
3. Transfer pulp to 1 liter beaker and repeat Step 2.
4. To pulp add 250 ml of hot 4N HNO_3 containing 10 mg each of Pb, Na, Ru, and Fe carriers. Mix thoroughly, filter using Buchner funnel and vacuum. Save filtrate and pulp.
5. Repeat Step 4. Wash pulp with 100 ml of H_2O . Save wash, dry pulp thoroughly and place in $1/2 \times 2$ in. diameter PVC ring.
6. Combine filtrates and wash from Steps, 2, 3, 4, and 5 in a 4 liter beaker. Add 150 ml of concen-

- trated NH_4OH and 2 ml of 1N $\text{Na}_2\text{Cr}_2\text{O}_7$, mix thoroughly, and filter through 11 cm diameter glass fiber filter (Gelman, Type A). Discard filter.
7. To filtrate add 20 mg of Pb carrier, stir thoroughly and filter using glass fiber filter (Gelman, Type A). Discard filter.
 8. Evaporate filtrate to dryness and remove residual salts by first scraping with knife blade spatula, then cleaning beaker walls by rubbing with 10 cm^3 of dry ion exchange resin (Dowex 50, H^+ form, 200 mesh). Transfer salts and resin into a $1/2 \times 2$ in. diameter PVC ring for measurement of ^{24}Na .

Procedure D: Determination of ^7Be in Air

1. Tear filter material into $\sim 1 \text{ in}^2$ pieces and place in 1000 ml beaker.
2. Add 100 ml hot 3N NaOH to filter material and 50 mg Be carrier. Stir vigorously for 10 min and filter through a glass fiber filter (Gelman, Type A). Save filtrate and pulp.
3. Repeat Step 2 twice. Discard pulp.
4. Combine filtrates from Steps 2 and 3.
5. Add 20 mg each of Cs and Fe. Stir, filter through glass fiber filter (Gelman, Type A).
6. Repeat Step 5 twice.

7. Saturate filtrate with NH_4Cl and filter through glass fiber filter (Gelman, Type A). Wash with 100 ml of H_2O . Fold filter and place in $1/2 \times 2$ in. diameter ring for ^7Be measurement.

A PROCEDURE FOR THE CONTINUOUS SEPARATION AND SUBSEQUENT DIRECT COUNTING
OF SHORT-LIVED COSMIC-RAY-PRODUCED RADIONUCLIDES IN RAINWATER

R. W. Perkins

A separation procedure has been developed for the continuous separation of the four short-lived cosmic-ray-produced radionuclides ^{24}Na , ^{38}S , ^{38}Cl , and ^{39}Cl from rainwater. The ^{24}Na is retained on a 1 cm thick cation-exchange resin bed, while the ^{38}S , ^{38}Cl , and ^{39}Cl are retained on a 1 cm thick anion-exchange bed. These radionuclides can be measured by direct counting of the resin beds on a multidimensional gamma-ray spectrometer. By use of large-volume samplers which contain 28 cm diameter ion exchange beds, these radionuclides can be quantitatively removed from 1000 liters of rainwater ($5 \times 10^{-4}M$ in NaCl) at flow rates of 60 liters per minute. The alternate operation of two of these units will allow the desired continuous measurement of radionuclides collected on a 5000 ft² rain collector at our precipitation scavenging study site at Quillayute, Washington.

The mechanisms involved in atmospheric precipitation processes are of basic importance to our understanding of and the eventual control of weather processes. Although precipitation serves as the principal mechanism for atmospheric purification and is, of course, the source of our terrestrial fresh water supply, the rates and mechanisms involved in precipitation formation, along with in-cloud and below-cloud scavenging, are not well known. It has been recognized that unique trace materials, either present in or intentionally added to the atmosphere could be of great value in characterizing precipitation and scavenging processes. While measurements of

nuclear-bomb-produced radionuclides and inert constituents in precipitation have provided a measure of the total scavenging, little is known about the time scales and mechanisms of the in-cloud and below-cloud processes.

It has been suggested by Perkins et al.⁽¹⁾ and by Bhandari et al.⁽²⁾ that the short-lived cosmic-ray-produced radionuclides in the atmosphere could serve as excellent tracers of both in-cloud and below-cloud scavenging processes. The short-lived cosmic-ray-produced radionuclides ^{24}Na (15 hr), ^{38}S (2.9 hr), ^{38}Cl (37.3 min), and ^{39}Cl (55 min) are particularly attractive both because

of their half-lives and because of their unique decay schemes which permit their very sensitive and absolute measurement by multidimensional gamma-ray spectrometry. Measurements of the absolute and relative amounts of these radionuclides in rainwater by Wogman et al.,⁽³⁾ Bhandari et al.,⁽²⁾ and Young et al.⁽⁴⁾ have provided valuable information on the time scale and mechanisms of raindrop formation.

The major difficulty in the use of cosmic-ray-produced radionuclides in studying precipitation mechanisms is their very low concentration in precipitation and the relatively high concentration of radon daughters. Procedures described by Perkins et al.⁽⁵⁾ permitted the direct counting by multidimensional gamma-ray spectrometry of ^{24}Na and ^{38}S in the residue of evaporated rainwater and of the Cl radioisotopes in a AgCl precipitate. However, the combination of large sample volumes (up to 100 liters) and low concentrations (1 to 10 d/m/liter for ^{24}Na and ^{38}S) has prevented the desired measurements in consecutively collected rain samples. The present work describes the technology that has been developed for the radionuclide measurements in consecutively collected rainwater samples at rainwater flow rates of up to 60 liters/min. These volumes can be expected from a 5,000 ft² plastic tarp collecting area which will be located on a World War II hangar at our rain collection site at Quillayute, Washington.

A stipulation of the procedure was that it should permit the quantitative retention of ^{24}Na , the Cl radioisotopes, and ^{38}S (assuming a SO_3^- or SO_4^{2-} state) from as much as 1000 liters of rainwater on a matrix which would allow direct counting of the radionuclides by multidimensional gamma-ray spectrometry. Our observations indicate NaCl concentrations in rainwater from this area are less than 3 mg/liter ($5 \times 10^{-5}\text{M}$); therefore, the quantitative retention of the NaCl from 1000 liters of rainwater would require a retention capacity of greater than 3 g (0.05M). A procedure that has proven satisfactory for radionuclide collection involves the use of ion exchange resins.

Laboratory studies have shown that greater than 99% of the ^{24}Na from a 10^{-4}M solution of NaCl is retained on a 1 cm thick bed of Dowex 50 $\times$ 8 (H^+ form, 100-200 mesh). This retention was obtained for a linear flow rate of 1 m/min and a total throughput of 2 liters/cm². With Dowex 1 $\times$ 8 (Cl^- form, 100-200 mesh) anion beds of this thickness and the above-stated flow conditions and concentrations, Cl and Na radioisotopes are also retained with greater than 98% efficiency.

Studies with rainwater have indicated that ^{24}Na can be measured by direct counting of the cation exchange bed on a multidimensional gamma-ray spectrometer. However, this bed does retain large amounts of the gamma-emitting radon daughters ^{214}Pb and ^{214}Bi from the rainwater; and depending on their concentration,

decay times of up to a few hours may be required to prevent high dead time losses on the analyzer.

In a field study, the anion exchange bed is located downstream from the cation exchange bed, and initial measurements indicate that interference from other radionuclides will not be sufficient to prevent the quantitative measurement of ^{38}S , ^{38}Cl , and ^{39}Cl by multidimensional gamma-ray spectrometry.

For holding the thin ion exchange beds, the Battelle Large-Volume Ocean Sampler⁽⁵⁾ is used. This unit permits parallel filtration through any desired number of 12 in. diameter filters, and the filtered water then passes to the sorption bed section and through 1 cm thick cation and anion exchange beds. Figure 1 shows a drawing and a schematic flow dia-

gram of the sampler with the filtration and ion exchange sections indicated. With the 28 cm diameter beds and linear flow rates of 1/min, flow volumes up to 60 liters/min can be processed. Where total sample volumes of approximately 1000 liters are passed through the system in periods of 15 min to 1 hr, the four cosmic-ray-produced radionuclides ^{24}Na , ^{38}S , ^{38}Cl , and ^{39}Cl can be measured with good counting statistics from counting periods of less than 1 hr.

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Neg 0690644-1

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SHORT-LIVED COSMIC-RAY-PRODUCED RADIONUCLIDES AS TRACERS OF ATMOSPHERIC PROCESSES

J. A. Young, N. A. Wogman, C. W. Thomas, and R. W. Perkins

Radionuclides are produced continuously in the atmosphere by cosmic rays. Their production rates vary considerably with altitude and latitude but remain relatively constant with time. Following formation, these radionuclides quickly become attached to atmospheric aerosols and can thus serve as tracers of the subsequent behavior of these aerosols. The natural atmospheric aerosols are vital to rain and snow formation since water droplets or ice particles are formed by the condensation of water vapor on aerosol particles. Aerosol particles are also picked up by a water droplet or ice particle after nucleation while it is still in the cloud or falling below the cloud. Not much is known about the relative efficiencies of nucleation and post-nucleation scavenging of the aerosol particles. The problem is difficult to study in the laboratory or by the introduction of artificial aerosols such as silver iodide into the atmosphere, since scavenging mechanisms are very sensitive to the properties, including electrical charge, of the aerosol particle. It is difficult, if not impossible, to duplicate the natural atmospheric aerosol distribution in the laboratory. It has been recognized that radionuclides with half-lives of minutes to hours would be useful in studying atmospheric precipitation scavenging mechanisms since their half-lives are of the same order of magnitude as the time scale on which precipitation processes occur. Of particular interest are the short-lived cosmic-ray-produced radionuclides ^{24}Na (15 hr), ^{34}Cl (32 min), ^{38}S (2.9 hr), ^{38}Cl (37 min), and ^{39}Cl (55 min).

In 1966 and 1967, several rain and snow samples were collected at our laboratory near Richland, Washington. In January of 1968, our portable laboratory was moved to Quillayute Air Base near Forks, Washington, on the western side of the Olympic Peninsula, where the average yearly rainfall is about 120 in. During a 5 day period, 37 rain samples, 1 snow sample, and 1 mixed snow and hail sample were collected on plastic sheets with surface areas of approximately 1000 ft².

The observed ³⁸Cl and ³⁹Cl disintegration rates in the rain and snow samples varied inversely with the precipitation rate with the concentrations of ³⁹Cl and ³⁸Cl decreasing by more than an order of magnitude when the rainfall rate increased from 0.015 to about 0.15 in./hr. When a cloud forms, water vapor condenses on aerosol particles present in the atmosphere. Regardless of the size of a cloud droplet, at least one aerosol particle is required for its formation. A major portion of the radionuclides present in the initial raindrop is due to this aerosol particle. Although increases in the drop size due to coalescence would tend to keep the radionuclide concentration constant, increases in size due to the condensation of moisture on drops already present would tend to decrease the radionuclide concentrations. Therefore, one would expect to find a maximum in radionuclide concentrations in small drops. Raindrops tend to be larger in heavier rains. There-

fore, the decrease in the ³⁸Cl and ³⁹Cl concentrations with an increase in rainfall rate could be caused by an increase in the drop size.

Two rain water samples were collected consecutively during each of five rain showers at Forks, Washington, and one rain shower at Richland, Washington. In five of the six showers, the ³⁹Cl concentration was considerably higher in the second sample than in the first. In one shower, the ³⁹Cl concentration was nearly 10 times as high in the second sample as in the first. The ³⁸Cl concentration, however, was higher in the second sample in only three of the six showers. In every shower, the ³⁹Cl/³⁸Cl ratio was higher in the second sample than in the first. Since ³⁹Cl has a longer half-life than ³⁸Cl, the ³⁹Cl/³⁸Cl ratio will continuously increase between the time the ³⁸Cl and ³⁹Cl are incorporated in the raindrop and the time the raindrop is collected. Therefore, the high ³⁹Cl/³⁸Cl ratio of the second sample in each shower may imply that the drops in the second sample spent a longer time in the cloud before falling as rain. Since the atmospheric ³⁸Cl and ³⁹Cl concentrations are about equal, the time between nucleation and rain collection was calculated by using a value of one for the ³⁹Cl/³⁸Cl ratio at nucleation. In each of the six showers, the calculated time between nucleation and collection was appreciably longer for the second sample. In one shower the time was

two hours longer for the second sample than the first. By using the times between nucleation and collection, the ^{38}Cl and ^{39}Cl concentrations in the rain water at the time of collection were decay-corrected back to the time of nucleation. When this was done, it was found that in all of the six showers the decay-corrected ^{38}Cl and ^{39}Cl concentrations were considerably higher in the second sample than in the first.

At Forks, Washington, several samples were collected consecutively during each of two rainstorms of about 2 hr duration. In the first storm, the ^{38}Cl and ^{39}Cl concentrations fluctuated somewhat but showed an overall increase as the storm passed through. In the second storm, the ^{38}Cl and ^{39}Cl concentrations at first showed relatively little change, reaching a small maximum late in the rain, then decreased considerably at the end of the rainfall. In each storm, the $^{39}\text{Cl}/^{38}\text{Cl}$ ratio reached a maximum at around the middle of

the storm and then decreased toward the trailing edge of the storm, which indicated that the time between nucleation and rain collection was at a maximum near the middle of the storm. If the ^{38}Cl and ^{39}Cl concentrations are decay-corrected back to the calculated time of nucleation, the ^{38}Cl and ^{39}Cl concentrations reach a maximum late in each storm and then decrease rapidly at the trailing edge of the storm.

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CONCENTRATIONS OF AIRBORNE RADIONUCLIDES DURING 1968
AT POINT BARROW, ALASKA; RICHLAND, WASHINGTON; AND RIO DE JANEIRO, BRAZIL
C. W. Thomas

The atmospheric concentrations of some 20 radionuclides were measured at ground level at Point Barrow, Alaska; Richland, Washington; and Rio de Janeiro, Brazil, during 1968 in a continuing study initiated in 1962. Nearly all radionuclide concentrations showed significant increases over the previous year, which reflect the high yield thermonuclear tests conducted by the Chinese in the northern hemisphere and the French in the southern hemisphere. In 1968, the shape of the annual spring concentration maximum measured at Point Barrow, Alaska, was notably different, showing a second peak in July. Rapid excursion of fresh nuclear debris from the southern hemisphere was measured in the northern hemisphere at Richland, Washington, and Point Barrow, Alaska.

The concentrations of some 20 radionuclides were measured continuously in air at ground level during 1968 at Point Barrow, Alaska (71°N Lat.), Richland, Washington (46°N Lat.), and Rio de Janeiro, Brazil (23°S Lat.) by filtering large volumes of air through membrane filters followed by gamma-ray spectrometric analysis. The radionuclides were products of both nuclear weapons testing and from natural processes. The nuclear-weapons-produced radionuclides included fission products and neutron activation products, while the natural radionuclides included decay products of radon and thoron, the natural activities in dust, and the cosmic-ray-produced radionuclides resulting from spallation reactions in the atmosphere. The measurement of this wide spectrum of radionuclides since 1962 has helped define the rates of the long-term stratospheric and short-term tropospheric processes in the northern hemisphere.⁽¹⁾

Since higher-yield nuclear testing resumed in both the northern and southern hemisphere has significantly increased the radionuclide concentration in the respective stratospheres, the continuation of these measurements should provide further understanding of the complex global atmospheric processes. The radionuclide concentrations as measured at the three sampling stations through 1968 reflect these tests and are shown in Figures 1 through 4.

The atmospheric concentrations of long-lived radionuclides in the northern hemisphere have been steadily decreasing since 1963 with a resident half-time of about one year.⁽¹⁾ This reduction has occurred even though low-yield testing has continued since the moratorium of 1963. This downward trend, however, was reversed during 1968, and nearly all radionuclides attained concentration levels equal to or greater than the 1967 values (Figures 1-4). The increases were attributed mainly to the high yield thermonuclear testing

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FIGURE 1. Radionuclide Concentration in Air at Ground Level. Top Curves (o) are Measured at Point Barrow, Alaska (71° N Lat); Middle Curves (●) at Richland, Washington, (40° N Lat); Bottom Curves (x) at Rio de Janeiro, Brazil (23° S Lat).

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FIGURE 2. Radionuclide Concentration in Air at Ground Level. Top Curves (o) are Measured at Point Barrow, Alaska (71° N Lat); Middle Curves (●) at Richland, Washington, (40° N Lat); Bottom Curves (x) at Rio de Janeiro, Brazil (23° S Lat).

Neg 0690490-3

FIGURE 3. Radionuclide Concentration in Air at Ground Level. Top Curves (o) are Measured at Point Barrow, Alaska (71° N Lat); Middle Curves (●) at Richland, Washington, (40° N Lat); Bottom Curves (x) at Rio de Janeiro, Brazil (23° S Lat).

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FIGURE 4. Radionuclide Concentration in Air at Ground Level. Top Curves (o) are Measured at Point Barrow, Alaska (71° N Lat); Middle Curves (●) at Richland, Washington, (40° N Lat); Bottom Curves (x) at Rio de Janeiro, Brazil (23° S Lat).

in mid-1967 by the Peoples Republic of China.⁽²⁾ The shape of the annual spring concentration maximum during 1968 measured at 71°N was notably different than previous years. A sharp second peak for nearly all radionuclides was apparent during late July, a period when concentrations at this latitude are approaching a minimum.

The presence of short-lived radionuclides ^{103}Ru , ^{131}I , ^{140}Ba , ^{141}Ce , and ^{147}Nd in the atmosphere at 46°N during the last part of August, 1968,⁽³⁾ was attributed to a rapid movement of French debris from the southern hemisphere and was measured at several locations and altitudes. The concentration ratios of these radionuclides indicate a detonation time during July, 1968, which coincides with the beginning of the southern hemispheric testing.⁽³⁾ The presence of these short-lived radionuclides was also noted in air sampled on the coast of Washington during the latter part of August and at 71°N latitude during October, 1968. The initial measurement of this debris was made on air samples taken during the early part of August at approximately 9,000 feet over the Caribbean Sea.⁽³⁾

The concentrations of cosmic-ray-produced ^7Be and ^{22}Na attained maximum values during 1968 that were approximately equal to last year. This would strongly suggest that both these radionuclides have attained concentrations that are controlled mainly by cosmic-ray spallation reactions and can be used with greater accuracy to measure long-term processes.

This assumes, of course, that the contribution of ^{22}Na from the recent Chinese tests has not been overwhelming. These data indicate that even though some ^{22}Na was produced during the Chinese tests, this atmospheric contribution should not seriously affect the use of this radionuclide in future studies.

In addition, the data indicate that the long-lived fission products have a different annual deposition rate than the natural cosmic-ray-produced ^7Be . From these measurements, an apparent stratospheric half-residence time of 11.8 months at 46°N latitude was calculated. The annual peak in the ground level air concentrations arrives three to four months earlier at 71°N than at 46°N. The cosmic-ray-produced ^7Be attains a maximum before the bomb-produced radionuclides at 71°N and later than the bomb-produced isotopes at 46°N. The radionuclide concentrations in ground level air are about twice as high at 46°N as at 71°N. The rate of increase toward the annual peak concentrations for all radionuclides at both 46°N and 71°N can be approximated by an exponential in which the concentration doubles approximately every sixty days. Likewise, the rate of decrease can be approximated by an exponential with a half-time of about forty days for all radionuclides at both latitudes with the exception of ^7Be at 46°N. Beryllium-7 shows an exponential decrease with a half-time of about 60 days.

The concentrations of fission and activation products in the southern hemisphere increased markedly during the last part of 1968. This sharp increase was due mainly to the thermonuclear testing in August and September by the Republic of France.⁽⁴⁾ Yields of the French tests were of a magnitude that much of the debris should have entered the stratosphere,⁽⁵⁾ thus following the general circulation patterns for the southern hemisphere. The measurement of a wide spectrum of radionuclides in the southern hemisphere will allow studies of atmospheric intermixing of the northern and southern hemispheric air masses.

It is apparent from the data (Figures 1-4) that the frequency of testing in the southern hemisphere and the resulting large tropospheric deposition has obscured the normal atmospheric processes. The debris from these tests has sporadically increased the air concentrations to levels approaching or surpassing the northern hemispheric concentrations. Just prior to the test of July 6, 1968, the most prominent radionuclide was ⁷Be, which was 100 times greater than ⁹⁵Zr-Nb, ¹⁰³Ru, and ¹³⁷Cs.

Some of the short-lived radionuclides produced in the July and August tests were detected at 23°S (Table 1). These data indicate that the radionuclide concentrations for both fission and activation products are the highest ever measured in the southern hemisphere. Apparently, some isotopes, such as ²³⁷U, are associated with a particular nuclear

event, while others are produced in all tests.

TABLE 1. Concentration in Air of Short-Lived Radionuclides

Month	Period	Lat.	d/m/10 ⁶ ft ³			
			¹³¹ I	¹⁴⁰ Ba	¹⁴⁷ Nd	²³⁷ U
January, 1968	Entire	71°N	---	340	---	---
		46°N	---	1921	---	---
		23°S	---	---	---	---
February, 1968	Entire	71°N	---	295	---	---
		46°N	---	---	---	---
		23°S	---	---	---	---
March, 1968	Entire	71°N	---	---	---	---
		46°N	---	---	---	---
		23°S	---	---	---	---
July, 1968	Entire	71°N	---	---	---	---
	Entire	46°N	---	---	---	---
	1-15	23°S	---	<10	---	---
	15-31	23°S	2712	7920	5160	1326
August, 1968	1-15	71°N	---	---	---	---
	15-31	71°N	---	---	---	---
	1-15	46°N	---	---	---	---
	15-31	46°N	148	188	15	---
	3-10	23°S	758	2355	1626	334
	12-19	23°S	1585	6188	2988	638
	19-26	23°S	743	2716	826	<35
	26-2	23°S	3566	15,722	4349	<138

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RADIONUCLIDE CONCENTRATIONS BETWEEN 5,000 AND 63,000 FEET
IN 1967 AND 1968

J. A. Young, N. A. Wogman, and C. W. Thomas

Radionuclides are produced continuously in the atmosphere by cosmic rays. Their production rates vary considerably with latitude and altitude but remain relatively constant with time. Measurements were made of the atmospheric concentrations of the cosmic-ray-produced radionuclides ^7Be (53 d), ^{24}Na (15 hr), ^{38}Cl (37.3 min), and ^{39}Cl (55 min); the radon daughters ^{208}Tl and ^{214}Bi ; and the nuclear-bomb-produced radionuclides. The ^{24}Na disintegration rate at 46°N increased approximately exponentially from 10^{-2} dpm/ 10^4 SCF at ground level to 25 dpm/ 10^4 SCF at 63,000 ft. The ^{38}Cl and ^{39}Cl disintegration rates at a given altitude were 7 to 10 times the ^{24}Na disintegration rate. At 60,000 ft the ^{24}Na disintegration rate increased from 6.5 dpm/ 10^4 SCF at the equator to 24 dpm/ 10^4 SCF at 60°N . The 53 day ^7Be half-life is long enough so that its atmospheric concentrations are considerably affected by air motions and deposition at the earth's surface. At 46°N the tropospheric ^7Be concentrations reached a maximum around June. In December of 1967 the ^7Be concentrations at 30,000 and 40,000 ft at 46°N increased sharply, presumably due to the transfer of radionuclides down to the low stratosphere in the winter. The French began a nuclear test series in the Pacific at 23°S on July 6, 1968. Tropospheric air samples collected from 35°N to 49°N on and after August 26, 1968, contained ^{140}Ba (12.8 d) from these tests. Maximum concentrations occurred at 40,000 ft. Barium-140 was not present in detectable quantities in the stratosphere at 60,000 ft from 35°N to 49°N . Presumably, the French debris was transported northward primarily in the upper troposphere where wind speeds are high.

Radionuclides are produced continuously in the atmosphere by cosmic rays. Their production rates vary considerably with altitude and latitude but remain relatively constant with time. Following formation, these radionuclides quickly become attached to atmospheric aerosols and can thus serve as tracers of the subsequent behavior of these aerosols. It has been recognized that cosmic-ray-produced radionuclides with half-lives of minutes to hours would be useful in studying atmospheric precipitation scavenging mechanisms

since their half-lives are of the same order of magnitude as the time scale on which precipitation processes occur.^(1,2)

The use of short-lived cosmic-ray radionuclides for studying air motions and precipitation scavenging has been limited by a lack of knowledge of their production rates as a function of altitude. Therefore, in March, 1967, we began measuring the atmospheric concentrations of the cosmic-ray-produced radionuclide ^{24}Na (15 hr) in air filter samples collected by

aircraft from 5,000 to 63,000 feet from 35°N to 47°N. Beginning June 9, 1968, we began measuring ^{24}Na in air filter samples collected at 60,000 ft from 30°S to 35°N. Beginning on January 29, 1968, we started using a newly-developed portable laboratory to measure the concentrations of the cosmic-ray produced radionuclides ^{38}Cl (37.3 min) and ^{39}Cl (55 min) and the radon daughter ^{214}Bi in air filter samples collected from 20,000 to 63,000 ft from 35°N to 47°N.

The concentrations of the cosmic-ray-produced radionuclide ^7Be (53 d), the radon daughter ^{208}Tl , and the nuclear-bomb-produced radionuclides were also measured in the air filter samples. The half-life of ^7Be is long enough so that its atmospheric concentrations are considerably affected by air motions and wet and dry deposition at the earth's surface. However, ^7Be is not produced in significant quantities by nuclear tests, so its concentration at a given latitude and altitude on a given date should be fairly constant from year to year. Therefore, when the ^7Be concentrations and production rates become well known, ^7Be should be a useful tracer in detailed studies of atmospheric transport and washout. At the present time, several investigators are measuring atmospheric concentrations of ^7Be . (3-19)

AIR SAMPLE COLLECTION

Ground level samples have been collected at Richland, Washington, since 1962. Beginning in March of 1967, high altitude air samples were obtained at approximately monthly intervals on IPC filter papers from aircraft flying from Albuquerque, New Mexico, to Spokane, Washington. These aircraft collected samples over Albuquerque in flight and on a north-south racetrack pattern from 46°N to 47°N, collecting thirty minute air samples at 5,000 to 10,000 ft altitude intervals from altitudes greater than 60,000 feet to 10,000 ft. Each sample was collected at a constant altitude.

Beginning on June 9, 1968, we began obtaining air filter samples once every three months from aircraft flying redeployment flights following Project Airstream. Samples were collected at 60,000 ft from 30°S to 35°N and at 50,000 and 60,000 ft from 65°N to 35°N. Each sample was collected over a 5° latitude interval.

ANALYSIS OF SAMPLES

Immediately after the filters were obtained from the aircraft, they were counted for the short-lived radionuclides ^{24}Na and ^{208}Tl . Beginning with the flights

of January 29, 1968, some of the filters were analyzed at the Spokane airfield using a newly-developed portable counting and chemical laboratory for the short-lived cosmic-ray-produced radionuclides ^{38}Cl (37.3 min) and ^{39}Cl (55 min) and the radon daughter ^{214}Bi (19.7 min). The concentrations of the cosmic-ray radionuclide ^7Be , the bomb- and cosmic-ray-produced radionuclide ^{24}Na , and the bomb-produced radionuclides ^{54}Mn , ^{60}Co , ^{65}Zn , $^{95}\text{Zr-Nb}$, ^{103}Ru , ^{106}Ru , ^{125}Sb , ^{137}Cs , ^{140}Ba , and ^{144}Ce were also determined with these or subsequent analyses.

RESULTS

Cosmic-Ray-Produced Radionuclides

^{24}Na

The measured disintegration rates of ^{24}Na at 46°N and 35°N are plotted as a function of altitude in Figures 1 and 2, respectively. The only ground level disintegration rate available was measured in early 1967 at the Hoh River Campground on the Olympic Peninsula in Washington State. There appeared to be no systematic variation in concentration with time. The concentration increased exponentially with increasing altitude by a factor of about 2000 between ground level and 62,000 ft at 46°N . Above 20,000 ft the concentration of ^{24}Na was somewhat lower at 35°N than at 46°N .

The scatter of the measured ^{24}Na concentrations (Figures 1 and 2) is

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FIGURE 1. ^{24}Na Disintegration Rate as a Function of Altitude at 46°N , 117°W in 1967 and 1968

Neg 0690330-8

FIGURE 2. ^{24}Na Disintegration Rate as a Function of Altitude at 35°N , 107°W in 1967 and 1968

greater than one would expect from the statistical counting errors. The variation in the disintegration rates could be due to vertical or meridional air motion, precipitation scavenging, or to short-term variations in the cosmic-ray flux.

The measured ^{24}Na disintegration rates at 60,000 ft are plotted as a function of latitude in Figure 3. The ^{24}Na disintegration rate increased by a factor of about 3.5 from 0° to 60°N . The rate of increase from 40°N to 60°N may have been lower than that from 0° to 40°N . The ^{24}Na concentrations in the samples collected south of the equator could not be measured accurately because of the relatively long delay time between sample collection and analysis and because of

Neg 0690330-2

FIGURE 3. ^{24}Na Disintegration Rate as a Function of Latitude at 60,000 ft

the presence of large amounts of debris from the nuclear tests conducted by the French in the South Pacific beginning in July, 1968.⁽²⁰⁾

The measured ^{24}Na disintegration rates at 50,000 ft are plotted as a function of latitude in Figure 4. The disintegration rate did not appear to change significantly with latitude from about 40°N to 63°N ; however, the disintegration rate may have decreased from 40°N to 35°N .

^{38}Cl and ^{39}Cl

The measured disintegration rates of ^{38}Cl and ^{39}Cl are plotted as a function of altitude in Figures 5 and 6, respectively. The disintegration rates increase roughly exponentially with altitude. There appeared to be no measurable difference between the ^{38}Cl and ^{39}Cl disintegration rates. They are seven to ten times the ^{24}Na disintegration rates. The scatter of the experimental points in

Neg 0690330-1

FIGURE 4. ^{24}Na Disintegration Rate as a Function of Latitude at 50,000 ft

Neg 0690330-9

FIGURE 5. ^{38}Cl Disintegration Rate as a Function of Altitude from 35°N to 47°N in 1968

Neg 0690330-5

FIGURE 6. ^{39}Cl Disintegration Rate as a Function of Altitude from 35°N to 49°N in 1968

Figures 5 and 6 is greater than would be expected from the statistical counting errors. The scatter could be due to short-term variations in the cosmic-ray flux. It also could conceivably be due to incomplete attachment of the ^{38}Cl and ^{39}Cl atoms to the atmospheric aerosols because of the short half-lives of these radionuclides. Vertical and meridional motions and precipitation scavenging are not likely to be the causes of the scatter because of the short half-lives of ^{38}Cl and ^{39}Cl and the fact that all the air filters were collected in cloud-free air. In the future, an attempt will be made to correlate the fluctuations in concentration with fluctuations in reported cosmic-ray fluxes.

^{38}S

It has been suggested that the ^{38}Cl measured in air and rain samples might actually be due to cosmic-ray-produced ^{38}S , which decays to ^{38}Cl with a 2.9 hr half-life. Therefore, large-volume air samples were collected at 40,000 and 42,500 ft on September 23-24, 1968. These samples were then immediately counted for consecutive 30-min periods to determine the half-life for the decay of the ^{38}Cl . If no ^{38}S was present, the ^{38}Cl would decay with a 37.3 min half-life. If ^{38}S was present in large amounts, the ^{38}Cl would decay with the 2.9 hr parent half-life. The ^{38}Cl disintegration rate in the 42,500 foot sample collected on September 24, 1968, decreased with a

half-life of approximately 37 min until the error limits of the determination became larger than the measured concentrations (Figure 7). It appears that if there was any ^{38}S in the samples, its initial disintegration rate was less than 10% that of ^{38}Cl . The sample collected at 40,000 ft on September 23, 1968, showed the same features.

Neg 0690330-6

FIGURE 7. ^{38}Cl Disintegration Rate as a Function of Time in an Air Sample Collected at 42,500 ft on 9-24-68 at 49°N , 118°W

^7Be

Beryllium-7 disintegration rates in 1967 and 1968 at 46°N 117°W are plotted as a function of time for several altitudes in Figure 8. The 53 day half-life of ^7Be is long enough so that its concentration is

significantly affected by air motions and rainout. At 46°N , the ^7Be concentration varies during the year, at least in the troposphere, with a concentration maximum occurring near June.⁽³⁾ In the stratosphere at 50,000 and 60,000 ft, the ^7Be concentration appeared to reach a small maximum in the summer, although the variation in the measured concentrations at these altitudes may not be statistically significant. Many of the measured concentrations are not very reliable because of the presence of large amounts of interfering radionuclides such as ^{95}Zr -Nb, ^{103}Ru , and ^{140}Ba from recent Chinese and French nuclear debris.^(20,21)

In addition to the expected summer maximum, there also appears to be another maximum occurring around December, 1968, at 40,000, 30,000, and possibly 20,000 ft.

Neg 0690330-14

FIGURE 8. ^7Be Disintegration Rate as a Function of Time at Several Altitudes at 46°N , 117°W

The measured ^7Be concentrations for 40,000, 50,000, and 60,000 ft on December 18, 1967, were about the same, with the 30,000 ft concentration being only slightly lower. However, these air samples contained considerable debris from a recent Chinese nuclear test,⁽²¹⁾ so the measured ^7Be concentrations are not very reliable. Since it is also possible that the high concentrations at 30,000 and 40,000 ft were the result of some local short-term process, continued ^7Be measuring will be necessary to see if this feature is repeated in the coming years.

It is generally believed that the spring and summer maximum in radionuclide concentrations at ground level is caused by the transport of radionuclides from the higher stratosphere down to the low stratosphere in the winter, followed by the diffusion of these radionuclides through the tropopause gap and eventually to ground level. The high ^7Be concentrations at 30,000 and 40,000 ft on December 18, 1967, could be the result of this transport of radionuclides from the upper stratosphere down into the low stratosphere. The subsequent decrease in radionuclide concentration at 30,000 ft in February could be caused by the rising of the tropopause and the northward migration of the tropopause gap in the spring.

Radon Daughters

Thallium-208 and bismuth-214 concentrations are plotted as a function of altitude in Figures 9 and 10, respectively. Thallium-208 concentra-

Neg 0690330-4

FIGURE 9. ^{208}Tl Disintegration Rate as a Function of Altitude

Neg 0690330-3

FIGURE 10. ^{214}Bi Disintegration Rates

tions were generally between 100 and 400 d/m/ 10^4 SCF at 5,000 ft, between 1 and 20 d/m/ 10^4 SCF from 10,000 to 40,000 ft, and too low to be detected in the stratosphere at 50,000 and 60,000 ft. There was no systematic change in concentration with altitude

between 10,000 and 40,000 ft. The concentrations at 35°N 107°W were generally somewhat higher than they were nearer the coast at 48°N 117°W. Bismuth-214 concentrations tended to decrease with altitude from approximately 10^4 to 10^5 d/m/ 10^4 SCF at 20,000 or 25,000 ft to about 10^3 d/m/ 10^4 SCF at 40,000 ft. Concentrations at 50,000 and 60,000 ft were too low to detect.

Bomb-Produced Radionuclides

The disintegration rates of the longer-lived bomb-produced radionuclides varied with altitude and time in much the same manner as did ^7Be . The concentrations of the shorter-lived radionuclides were seriously affected by recent Chinese and French nuclear debris.

The French began a nuclear test series at 23°S in the South Pacific on July 6, 1968.⁽²⁰⁾ On August 26, 27, and 28, 1968, air filter samples were collected from 5,000 to 40,000 ft from 35°N to 48°N. The disintegration rates of several radionuclides at 48°N are plotted as a function of altitude in Figure 11. Considerable ^{140}Ba from the French tests is present in the samples at 46°N, even though the tests began only 1-1/2 months earlier at 23°S. The ^{140}Ba concentration increased considerably more rapidly with increasing altitude from 5,000 to 30,000 ft than did the concentrations of the other radionuclides. The ^{140}Ba concentration was highest at 40,000 ft; at 30,000

Neg 0690330-13

FIGURE 11. Radionuclide Disintegration Rates at 48°N, 118°W on 8-27-68

and 40,000 ft the ^{140}Ba concentration was higher at 48°N than at 35°N; at 20,000 ft, however, the ^{140}Ba concentration was higher at 35°N than at 48°N.

On September 23, 24, and 25, 1968, another series of air filters was collected from 5,000 to 42,500 ft from 35°N to 48°N. The radionuclide concentrations at 48°N are plotted as a function of altitude in Figure 12. A sample taken at 60,000 ft from 50°N to 45°N on October 9, 1968, is also included in the figure. Both ^{140}Ba and ^{103}Ru from the French tests are present in the samples from 5,000 to 42,500 ft. The ^{140}Ba concentration increased considerably more from

Neg 0690330-12

FIGURE 12. Radionuclide Concentrations at 48°N, 118°W on 9-24-68. The 60,000 ft Sample Was Taken 10-9-68 from 50°N to 45°N

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FIGURE 13. Radionuclide Disintegration Rates at 35°N, 107°W on 10-28-68

5,000 to 15,000 ft than did the concentrations of the other radionuclides. There was no measurable ^{140}Ba or ^{103}Ru in the stratosphere at 60,000 ft.

Another set of samples was collected from 10,000 to 60,000 ft from 35°N to 47°N on October 28, 1968. As in previous flights, the ^{140}Ba and ^{103}Ru concentrations (Figure 13) reached a maximum at 40,000 ft and then decreased rapidly at higher altitudes. Ruthenium-103 was not detectable at 50,000 ft while ^{140}Ba , detectable at 50,000 ft, was not at 60,000 ft.

CONCLUSIONS

Evidently, the debris from the French test series beginning July 6, 1968, found from 35°N to 48°N in the troposphere beginning August 26, 1968, was transported northward primarily in the upper troposphere where wind speeds are high. This would explain why the ^{140}Ba and ^{103}Ru concentrations were maximum at 40,000 ft and why ^{140}Ba and ^{103}Ru concentrations were still negligible in the stratosphere north of 20°N at 60,000 ft on October 9, 1968, three months after the tests

started. The ^{140}Ba and ^{103}Ru in the lower troposphere from 35°N to 47°N could have diffused downward from the upper troposphere. The tropopause height decreases with increasing latitude; therefore, if the maximum ^{140}Ba and ^{103}Ru concentrations in the northern hemisphere occurred just below the tropopause, the altitude of maximum concentration would decrease with increasing altitude, explaining why concentrations were higher at 46°N than at 35°N at 30,000 and 40,000 ft in late August, 1968.

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THE RADIONUCLIDE CONCENTRATIONS IN AIR AT GROUND LEVEL
AT BARBADOS, BRITISH WEST INDIES

C. W. Thomas, J. A. Young, R. W. Perkins and N. A. Wogman

Preliminary measurements of radionuclides in air were conducted at Barbados, British West Indies, in support of the oceanographic-meteorological experiment BOMEX. The intrusion of fresh fission debris from the southern hemispheric French nuclear tests was detected on August 22, 1968. The ground level concentrations of ⁷Be were similar to those measured at Richland, Washington, at 46°N.

Preliminary measurements were made of the radionuclide concentrations in air at ground level at Barbados, British West Indies, during the period August 21, 1968, through September 12, 1968. These measurements will serve as partial background information for the massive Barbados Oceanographic Meteorological Experiment (BOMEX) to be undertaken in the spring and summer of 1969.⁽¹⁾

Samples were obtained by filtering air through 5 μ pore size membrane filters at flow rates of about 100 ft³/min.⁽²⁾ Filters were changed on a weekly basis, and the radionuclide measurements were made using multidimensional gamma-ray analysis with large 11 in. diameter $\times$ 6 in. thick NaI(Tl) detectors⁽³⁾ and large-volume coaxial Ge(Li) diodes with typical resolutions of 2.9 keV.⁽⁴⁾

Prior to and during these atmospheric radionuclide measurements, the French initiated their 1968 nuclear test series in the southern hemisphere,⁽⁵⁾ which eventually resulted in the deposition of fresh nuclear debris in the northern hemisphere.⁽⁶⁾ This debris, long-lived radionuclide debris from earlier northern hemispheric nuclear testing, and cosmic-ray-produced ^7Be , were readily measured in the air. The results presented in Table 1 indicate that the initial sample, collected from August 21, 1968 to August 22, 1968, contained predominantly old fission products and ^7Be . This sample did contain a small amount of fresh fission products, which demonstrates the rapid intrusion of southern hemispheric French debris into the northern hemisphere. The concentration ratio of ^{95}Zr and ^{95}Nb in this sample indicates a detonation time

many months prior to sampling. Subsequent air samples contained relatively large amounts of fresh fission products. The concentration of ^{95}Zr and ^{95}Nb during these latter periods indicates a detonation time a few weeks earlier.

Even though relatively large amounts of fresh fission products were in the air, ^7Be was readily measured by using a $\text{Ge}(\text{Li})$ diode. The concentration of this cosmic-ray-produced radionuclide is of great interest because of its important role as an atmospheric tracer in the BOMEX air-sea interaction study. These data indicate that the concentration of ^7Be at Barbados, British West Indies, is about equal to that at 46°N ⁽⁷⁾ and that it can be accurately determined by instrumental methods in the presence of fresh fission product fallout.

TABLE 1. *British West Indies Air Filters*

Radionuclide	d/m/10 ⁶ ft ³			
	8-21/8-22	8-22/8-29	8-29/9-5	9-5/9-12
^{147}Nd	<315	461	365	753
^{144}Ce	3520	2980	3440	2842
^{141}Ce	532	2695	3030	4065
^{131}I	<100	145	160	220
^7Be	11,346	8386	8430	5800
^{103}Ru	192	1032	1200	1482
^{106}Ru	1100	763	919	650
^{137}Cs	252	193	221	174
^{95}Zr	272	1185	1450	1842
$^{95}\text{Nb}(\text{a})$	569	1264	1580	1952
^{54}Mn	<24	24	<10	14
$^{140}\text{La}(\text{b})$	225	1133	1250	1723

a. Corrected back to sampling time using half-life of parent ^{95}Zr
b. Corrected back to sampling time using half-life of parent ^{140}Ba

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THE TRANSFER OF AIRBORNE RADIONUCLIDES ACROSS THE SEA SURFACE AT 13°N, 58°W

J. A. Young

Air filter samples were collected twice a day at 7, 25, and 76 ft above mean sea surface aboard the USC&GSS Discoverer stationed east of Barbados, British West Indies, at 13°N during August, 1968. Beryllium-7 (53 d), ⁹⁵Zr-Nb (65 d), ¹⁰³Ru (40 d), ¹⁰⁶Ru (1.0 yr), ¹³⁷Cs (30 yr), and ¹⁴⁰Ba (12.8 d) concentrations were determined in these samples. The radionuclide concentrations increased significantly from the 7- to the 25-foot sample, but averaged the same in the 25- and 76-foot samples. The concentration increase was greater for samples collected during the day than for those collected during the night. Rain samples and seawater samples down to 210 m were also collected aboard the Discoverer.

Beryllium-7 is produced at a relatively constant rate in the atmosphere by spallation reactions of cosmic rays on atmospheric oxygen and nitrogen; therefore, atmospheric and oceanic concentrations of ⁷Be should remain relatively constant. As a result, the measured concentrations of ⁷Be in air and water samples

can be used to calculate values for the vertical eddy diffusion coefficient K_z in the atmosphere and the ocean.

Air filter samples were collected twice a day at three elevations on the research vessel the USC&GSS Discoverer operated by ESSA and stationed east of Barbados, British West

Indies, at 13°N, 58°W. One of the samplers was located 7 ft above the mean sea surface on a platform directly behind the stern of the vessel. A second sampler was placed at deck level toward the bow at an elevation of 25 ft. The third sampler was secured to a mast at an elevation of 76 ft. One set of three samples was collected from about 8 p.m. to 8 a.m. each night and another set from 8 a.m. to 8 p.m. each day.

Unfortunately, air passing a ship is deflected upward to a considerable extent, especially if the ship is perpendicular to the wind. During about 65% of the sampling time, the Discoverer was drifting nearly perpendicular to the wind. The rest of the time it was steaming directly into the wind. Therefore, it is difficult to estimate the average altitude of the origin of the air passing through each of the three samplers. When the Discoverer was drifting perpendicular to the wind, the air sampled by the stern (7 ft) and mast (76 ft) samplers was not seriously deflected upward. However, it is difficult to estimate the path of the air passing through the stern sampler when the ship was steaming into the wind. The air could have passed either over or around the vessel. The air sampled by the deck sampler would have been deflected upward to a greater extent when the ship was perpendicular to the wind than when the ship was steaming into the wind.

The radionuclides which were measured were ^7Be (53 d), $^{95}\text{Zr-Nb}$ (65 d), ^{103}Ru (40 d), ^{106}Ru (1.0 yr), ^{137}Cs (30 yr), and ^{140}Ba (12.8 d).

Beryllium-7 is produced by spallation reactions of cosmic rays on atmospheric nitrogen and oxygen while the other radionuclides are fission products. The short-lived radionuclides ^{140}Ba and ^{103}Ru originated from a French nuclear test series beginning on July 6, 1968, at 23°S in the Pacific Ocean.⁽¹⁾ Barium-140 did not appear in measurable quantities in the air filter samples until August 14, 1968, while ^{106}Ru concentrations did not become measurable until August 17, 1968. Zirconium-niobium-95 concentrations also increased significantly after August 17, 1968, because of the debris from the French tests. The ^{106}Ru and ^{137}Cs concentrations did not significantly change.

The air concentrations of ^7Be , $^{95}\text{Zr-Nb}$, ^{106}Ru , ^{137}Cs , and ^{140}Ba usually increased with increasing altitude from the 7- to the 25-foot sample; however, the concentrations averaged about the same for the 25- and 76-foot samples. The concentration increase between the 7- and the 25-foot sample fluctuated considerably between successive sets of samples, the increase varying from 0 to almost 80% for ^7Be . The concentration increases for the five radionuclides were generally similar, but not identical, for a given set of samples. The average concentration increase between the 7- and 25-ft samples was significantly greater for the daytime samples than the nighttime samples. For example, the ^7Be concentration averaged 40% higher in

the 25-ft samples than in the 7-ft samples for 4 sets of samples collected during the day, but it averaged only 10% higher in the 25-ft samples than in the 7-ft samples for four nighttime sets of samples. The larger concentration gradient during the day was due to the lower concentrations in the 7-ft samples during the day. There was no significant difference in the 25- or 76-ft level concentrations between the night and day.

ATMOSPHERIC VERTICAL EDDY DIFFUSION COEFFICIENTS

The radionuclides ^7Be , $^{95}\text{Zr-Nb}$, ^{106}Ru , ^{137}Cs , and ^{140}Ba were extracted from seawater at depths of 0, 15, 30, 35, 40, 70, 100, 140, and 210 m aboard the Discoverer during the period from August 8, 1968, through August 16, 1968.⁽²⁾ In addition, the concentrations of these radionuclides have been determined in selected rainwater samples.

If one assumes that the horizontal radionuclide concentration variations in the sea are small, thus providing negligible horizontal radionuclide transport, then:

$$\frac{dn}{dt} = f_o + w - \lambda n \quad (1)$$

where n = the radionuclide content in a vertical profile of the sea, expressed in atoms cm^{-2} of the sea surface
 f_o = flux of radionuclides across the sea surface due to turbulent transport
 (atoms $\text{cm}^{-2} \text{ sec}^{-1}$)
 w = wet deposition by rainfall
 (atoms $\text{cm}^{-2} \text{ sec}^{-1}$)

λ = decay constant (sec^{-1})
 t = time (sec)

If the concentration of a given radionuclide equals zero at the bottom of the measured profile, then n can be calculated from the profile. The w can be measured from the measured radionuclide concentrations in rainwater and the distribution of rainfall in the area. λ , of course, is known for any of the measured radionuclides. If it is assumed that the radionuclide concentrations in the sea are at a steady state, so that $\frac{dn}{dt} = 0$, then Equation (1) can be solved for f_o . However, this assumption certainly is not true for the bomb-produced radionuclides. Their atmospheric concentrations are always changing in a manner determined by the recent history of nuclear testing. Moreover, the concentrations of the longer-lived bomb-produced radionuclides should be increasing in the sea, and their concentrations do not equal zero at the bottom of the measured profile.⁽²⁾ Beryllium-7, which has a 53 day half-life, is produced by cosmic rays at a relatively constant rate. This process provides a constant average atmospheric concentration and maintains a steady state oceanic concentration. Its measured concentration was essentially zero at the bottom of the profile.⁽²⁾ Therefore, if the seasonal variations in the ^7Be atmospheric concentrations are small at 13°N and if the amount of ^7Be in the sea is not changed too drastically by rainfall rate variations, then $\frac{dn}{dt} \approx 0$ for ^7Be , which provides a solution for f_o for ^7Be . During the water sampling period, there were no measurable

variations in the radionuclide concentrations in the sea, which supports the assumption that $\frac{dn}{dt} \approx 0$.

An air sampler placed on Barbados, British West Indies, is collecting air samples on a weekly basis to define the atmospheric radionuclide concentrations for BOMEX. During the BOMEX experimental period in the spring and summer of 1969, several seawater profiles will be collected and analyzed for all possible radionuclides. From these profiles, the average value of $\frac{dn}{dt}$ for the period between the collection of samples in 1968 and the collection of samples in 1969 can be calculated. It is hoped that variations in the oceanic concentrations will be detected during the 1969 sampling period so that $\frac{dn}{dt}$ may be evaluated for shorter periods of time.

The vertical flux, f , due to turbulent transport is given by

$$f = -K_z \left(\frac{\partial C}{\partial z} \right) \quad (2)$$

where K_z = vertical eddy diffusion coefficient ($\text{cm}^2 \text{sec}^{-1}$)

C = radionuclide concentration (atoms/standard cm^3 of air)

If horizontal transport is neglected and the radionuclide concentration is assumed to be constant, then $\frac{\partial f}{\partial z} = 0$ between sea level and the levels of the concentration measurements. Equation (2) can then be rewritten as:

$$f = f_0 = -K_z \left(\frac{C_2 - C_1}{\Delta z} \right) \quad (3)$$

where C_2 and C_1 are the concentrations at two different altitudes and K_z is the average diffusion coefficient between these two altitudes. K_z can then be calculated from the measured ^7Be concentrations at 7 and 25 ft and the value of f_0 for ^7Be calculated previously. The fluxes across the sea surface of the other measured radionuclides can then be calculated using these values of K_z in Equation (3).

VERTICAL EDDY DIFFUSION COEFFICIENTS IN THE SEA

If it is assumed that horizontal transport in the sea is negligible, the vertical flux f_z at some depth is given by:

$$f_z = \frac{dn_z}{dt} + \lambda n_z \quad (4)$$

where n_z = radionuclide content in the sea below depth z (atoms cm^{-2})

f_z = flux at depth z (atoms $\text{cm}^{-2} \text{sec}^{-1}$)

λ = decay constant (sec^{-1})

If the radionuclide concentration is constant below depth z , then $\frac{dn_z}{dt} = 0$ and f_z at any depth can be calculated from the measured radionuclide concentrations in the sea. Moreover,

$$f_z = -K_z \left(\frac{\partial C_z}{\partial z} \right) \quad (5)$$

where C_z = concentration at depth z (atoms cm^{-3}). Therefore, K_z can be calculated from the measured concentration.

The pre-BOMEX data have shown that measurable vertical concentration gradients of radionuclides exist in the first few meters above and below the sea surface and that in the ocean at 13°N and 58°W detectable amounts of ^7Be are confined to a rather shallow layer near the ocean surface. These conditions make it possible to use the above equations to calculate values for the vertical eddy diffusion coefficient in the atmosphere and ocean near the sea surface. During the BOMEX sampling period in 1969, we plan to obtain more accurate

and extensive measurements of the concentration gradients so that more accurate values of K_z may be calculated.

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FRACTIONATION OF RADIONUCLIDES DURING NUCLEAR TESTING

W. B. Silker and C. W. Thomas

Fractionation of fission products is examined with respect to the member of the isobar present at the time of particulate formation.

Nearly all radioactive species produced during a nuclear detonation will combine with particulate material formed as a result of the detonation. Knowledge of the size of particle with which the various radionuclides are combined is required for estimation of atmospheric transport and deposition characteristics of fallout debris. The amounts of specific radionuclides associated with the different particulates will govern the ultimate exposure to human population, both by direct assimilation and through the food chain.

The relative amounts of several fission products associated with various sized particles are shown in Figure 1. The concentrations of

FIGURE 1. Particle Size Distribution of Airborne Radionuclides (Concentration Normalized to 1 for Particles $\geq 12 \mu$)

^{137}Cs , ^{89}Sr , and ^{140}Ba increase as the particle size decreases, while the quantities of ^{103}Ru , ^{131}I , ^{133}I , and others present decreased with particle size. This fractionation of fission products can be explained by an examination of the chemical and physical forms of the specific isotopes of each isobar existent at the time of particle formation.

In Figure 2 the mass of the most probable charge of the fission fragments for ^{239}Pu fission is presented with their respective half-lives. It is normally assumed that 50% of the isobar is formed at the mass of the most probable charges and roughly 25% formed at the mass unit one charge above and below this member. Since the most probable mass

Neg 0682712

FIGURE 2. ^{239}Pu Decay Chains with Most Probable Zp for Fission Fragment Formation Shaded. Half-lives of the Fission Product Shown in the Upper Position of each Square Are in Seconds

of the isobars 89, 90, 91, 137, 140, and 141 is born as either a noble gas or an alkali metal isotope with a significant half-life, its association with particles is delayed either until the chain has decayed to its alkaline earth member or until the particles have cooled to a temperature below the boiling point of the alkali metals. These conditions dictate predominant association of these mass chains with the small particulates resulting from delayed condensation of material vaporized by the nuclear device. The isobars 103, 131, 133, and 141 originate with elements that are more refractory and are thus available for condensation with the larger particles formed by exposure of environmental material introduced into the fireball.

In Figure 3 fission product fractionation is also demonstrated by the direct correlation between the air concentrations of several fission products and the half-life of their respective gaseous or volatile precursors. These data suggest that during the interval between detona-

tion and sampling the larger particles have been selectively removed by deposition. These values thus provide a base line for estimating relative depositions by gravitational or scavenging processes at more distant locations.

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FIGURE 3. Relationship Between Airborne Radionuclide Concentration and Half-Life of Gaseous Precursor

POSSIBLE INTRUSION OF FRENCH NUCLEAR TEST DEBRIS
INTO THE NORTHERN HEMISPHERE

C. W. Thomas, J. A. Young, R. W. Perkins, and N. A. Wogman

Fresh fission product debris was measured in the northern hemisphere at several locations and altitudes shortly after the French initiated their 1968 nuclear test series. Concentration ratios of the radionuclides indicated a detonation date that coincided with these tests. If this debris was indeed due to French southern hemispheric testing, a mean latitudinal northern transport rate of 1° - 2° Lat. per day was evident. The French culminated the test series by detonating two high-yield hydrogen devices, placing much of the debris into stratospheric levels centered around 5° and 10° S Lat.

The French nuclear tests were conducted in the southern hemisphere on the South Pacific islands of Fangataufa and Mururoa, which are located in French Polynesia near 22° S Lat. 139° W Long., during the period July 6, 1968, to September 8, 1968. Included in these reported tests were nuclear detonations on July 7, 1968, July 15, 1968, and August 3, 1968, and thermonuclear detonations on August 24, 1968, and September 8, 1968.⁽¹⁾ All detonations were made from balloons several thousand feet above the atoll. The first three tests were announced by the French to be in the intermediate yield range. This range would place most of the debris in the high troposphere.⁽²⁾ The last two detonations were in the 2 megaton yield range and would insert most of the debris into the stratosphere.⁽²⁾ During this testing period, several investigations were under way to measure the fallout, cosmic-ray-produced, and terrestrial concentrations at several locations and altitudes in

the northern and southern hemispheres. In Table 1, the dates, locations, and altitudes in which fresh debris was first measured are presented, together with the air concentration of ^{140}Ba (12.8 d).

The initial measurement of this fallout debris was made on samples collected in the southern hemisphere at Rio de Janeiro, Brazil, during the latter part of July, 1968.⁽³⁾ Shortly after, on August 5, 1968, aircraft intercepted small amounts of fresh debris in the northern hemisphere over the Caribbean Sea at 9,000 ft at a position of 20° N Lat. 70° W Long. A 100 SCF air sampling pump was installed on the island of Barbados, British West Indies, 13° N Lat. 59° W Long., to make background measurements in support of the upcoming BOMEX study.⁽⁴⁾ The initial sample collected between August 21 and 22, 1968, contained large amounts of fresh debris. The concentration ratios of short-lived material coincided with the French tests. Between August 19-30, 1968, fresh debris was measured at Richland,

TABLE 1. Time Periods for Sampling Debris
of French Tests - 7-6-68/9-8-68

Station	Date, 1968	Position, Lat. Long.	Altitude, ft	^{140}Ba Conc., d/m/10 ⁶ ft ³
Test Site	7-6/9-8	22°S 139°W	---	---
Rio de Janeiro, Brazil	7-15/7-30	23°S 44°W	Surface	7.9×10^3
Rio de Janeiro, Brazil	8-3/8-10	23°S 44°W	Surface	3.2×10^3
Caribbean	8-5	22°N 72°W	9,000	1.9×10^3
Caribbean	8-5	20°N 68°W	9,100	8.7×10^2
Caribbean	8-8	21°N 69°W	8,000	1.6×10^3
Caribbean	8-8	23°N 72°W	8,000	9.6×10^3
Caribbean	8-12	15°N 62°W	10,000	1.2×10^3
Caribbean	8-12	19°N 68°W	10,000	6.9×10^2
Rio de Janeiro, Brazil	8-12/8-19	22°S 44°W	Surface	8.4×10^3
Rio de Janeiro, Brazil	8-19/8-26	22°S 44°W	Surface	2.7×10^3
Barbados, West Indies	8-21/8-22	13°N 59°W	Surface	2.8×10^2
Barbados, West Indies	8-22/8-29	13°N 59°W	Surface	1.1×10^3
Richland, Washington	8-19/8-30	46°N 119°W	Surface	1.9×10^2
Spokane, Washington	8-27	47°N 118°W	40,000	9.3×10^3
Rio de Janeiro, Brazil	8-26/9-2	23°S 44°W	Surface	1.6×10^4
Makah, Washington	9-5/9-11	47°N 125°W	Surface	6.0×10^1
Point Barrow, Alaska	10-16/11-1	71°N 156°W	Surface	5.8×10^0
Airstream	10-4	0°- 5°S	60,000	8.1×10^7
Airstream	10-4	5°-10°S	60,000	1.5×10^8
Airstream	10-4	10°-15°S	60,000	7.7×10^7

Washington, 46°N Lat. 119°W Long., in air at ground level.⁽³⁾ Also, during this period (August 27 and 28, 1968) a tropospheric air sampling profile was made which contained large concentrations of fresh fission products.⁽⁵⁾ The peak concentration occurred at 40,000 ft, the highest sample taken in the profile. During the period October 16, 1968, through November 1, 1968, small amounts of ^{140}Ba were measured in

surface air at Point Barrow, Alaska,⁽³⁾ 71°N Lat. 156°W Long., and presumably were of French test origin.

High altitude air samples from project Airstream⁽⁶⁾ were received on a redeployment assignment. These missions were flown at 50,000 and 60,000 ft from 60°N to 30°S Lat., generally following the western part of Canada and the United States,

crossing over to the eastern side of Central America, and then continuing south on the western side of South America. The Airstream samples contained large quantities of fresh fission products with peak concentrations approximately 10^8 d/m/ 10^6 SCF occurring between 5° to 10° S Lat., as shown in Tables 2 and 3 and Figure 1. In the northern hemisphere at 60,000 ft, cosmic-ray-produced ^7Be and fission-produced ^{144}Ce were the radionuclides that showed the highest concentrations, while in the southern hemisphere ^{237}U had the highest concentration, followed closely by ^{141}Ce , ^{103}Ru , ^{140}Ba , and ^{95}Zr in that order. The ratio of ^{95}Zr to ^{95}Nb in the northern hemisphere was much less than the ratio in the southern hemisphere, showing the effect of old debris in the northern hemisphere. The concentrations of long half-life radionuclides, such as ^{144}Ce , ^{137}Cs , and ^{106}Ru , in the southern hemispheric stratosphere were increased significantly and should be reflected in concentrations at ground level during their annual spring maximum next year. South of 20° S Lat. and north of 5° S Lat. the concentrations decreased rapidly. North of 35° N Lat. ^{140}Ba was not in detectable quantities at 60,000 ft but was readily measurable at lower levels over Spokane, Washington, and

Albuquerque, New Mexico, on September 23-25, 1968, and October 28, 1968 and in ground level air at Richland, Washington.

While the processes of atmospheric transport of nuclear debris are complex, especially those dealing with the transfer between hemispheres, these data indicate that a rapid intrusion of French nuclear debris originating in the southern hemisphere was detected at several locations in the northern hemisphere, as also shown in Figure 1. It would appear that the transport was at high levels in the troposphere, possibly between 40,000 and 50,000 ft. The rate and distance of movement is illustrated by the measurements made at 71° N Lat. about three months after testing.

Based on the detection of debris on August 5, 1968, the earliest the debris was measured, the most probable test to associate with this debris is July 6, 1968, or July 15, 1968. Assuming an average detonation date of July 11, 1968, a mean northern transport rate of about $1^\circ - 2^\circ$ Lat. per day is evident. This rapid latitudinal movement is similar to that reported by other investigators⁽⁷⁾ and is unique in that it covered at least half of the world and, in all probability, circumnavigated the earth several times.

TABLE 2. Radionuclide Concentration at 60,000 ft
in Project Airstream

Lat	Date	d/m/10 ⁶ ft ³														
		¹⁴⁷ Nd	¹⁴⁴ Ce	¹⁴¹ Ce	¹³¹ I	⁷ Be	¹⁰³ Ru	¹⁴⁰ Ba	¹⁰⁶ Ru	¹³⁷ Cs	⁹⁵ Zr	⁹⁵ Nb	¹⁴⁰ La	²³⁷ U	¹³² Te	¹³⁶ Cs
60°-55°N	10-9-68	----	5.0+5	----	----	4.8+5	----	----	1.9+5	7.0+4	3.8+4	6.4+4	----	----	----	----
	11-5-68	----	5.0+5	3.3+3	----	7.0+5	2.6+3	----	2.2+5	6.0+4	1.3+4	4.4+4	----	----	----	----
55°-50°N	10-9-68	----	5.1+5	----	----	6.5+5	----	----	3.7+5	6.6+4	2.9+4	6.5+4	----	----	----	----
	11-5-68	----	6.2+5	5.1+5	----	6.6+5	6.2+3	----	2.2+5	6.7+4	2.4+4	5.6+4	----	----	----	----
50°-45°N	10-9-68	----	7.2+5	----	----	9.3+5	1.8+3	----	2.6+5	8.0+4	3.8+4	7.8+4	----	----	----	----
	11-5-68	----	5.9+5	4.8+3	----	6.1+5	1.7+3	----	2.0+5	6.5+4	2.5+4	5.2+4	----	----	----	----
45°-40°N	10-9-68	----	7.9+5	1.5+4	----	6.3+5	----	----	3.7+5	7.1+4	4.6+4	8.4+4	----	----	----	----
	11-5-68	----	6.0+5	8.3+2	----	6.5+5	3.0+3	----	2.0+3	6.6+4	2.3+4	5.3+4	----	----	----	----
40°-36°N	10-9-68	----	6.1+5	----	----	6.7+5	----	----	3.2+5	7.9+4	----	1.1+5	----	----	----	----
40°-35°N	11-5-68	----	7.2+5	7.5+2	----	9.1+5	2.6+3	----	2.7+5	7.8+4	2.6+4	5.7+4	----	----	----	----
34°-30°N	10-9-68	----	8.7+5	4.0+4	----	8.6+5	3.6+4	----	2.7+5	8.2+4	6.7+4	1.2+5	----	----	----	----
30°-25°N	10-9-68	----	6.1+3	1.4+4	----	6.3+5	1.3+4	----	2.0+5	7.1+4	3.7+4	7.5+4	----	----	----	----
23°-19°N	10-5-68	----	6.8+5	3.8+3	----	7.2+5	2.2+4	----	2.5+5	8.7+4	4.0+4	1.1+5	----	----	----	----
20°-15°N	10-9-68	----	4.8+5	1.8+4	----	4.9+5	1.1+4	----	2.1+5	7.4+4	3.4+4	8.9+4	----	----	----	----
19°-14°N	10-5-68	----	3.4+5	2.2+4	----	2.5+5	1.1+4	----	9.5+4	5.2+4	2.9+4	7.5+4	----	----	----	----
14°-12°N	10-5-68	----	1.0+5	1.6+4	----	----	2.8+3	----	----	1.0+4	----	2.9+4	----	----	----	----
8°-5°N	10-4-68	7.1+4	4.4+5	6.7+5	1.3+5	6.1+4	2.9+5	2.1+5	----	3.4+4	3.0+5	3.4+5	3.0+5	6.9+4	----	----
8°-5°N	10-8-68	5.2+4	5.5+5	4.4+5	1.2+4	4.3+5	1.9+5	4.2+4	----	3.1+4	3.0+5	3.5+5	2.0+5	6.5+4	----	----
5°-0°N	10-4-68	1.3+6	2.5+6	1.0+7	2.0+6	----	5.6+6	4.1+6	----	7.5+4	5.9+6	5.1+6	6.0+6	2.1+6	1.4+5	----
5°-0°N	10-8-68	7.4+4	7.0+5	1.0+6	3.3+4	2.9+5	4.4+5	4.7+5	7.2+3	4.6+4	4.8+5	6.3+5	3.4+5	1.6+3	----	----
0°-5°S	10-4-68	6.6+7	3.6+7	1.8+8	3.3+7	----	1.2+8	8.1+7	1.4+7	6.0+5	7.0+7	----	----	1.3+8	7.3+6	1.5+6
0°-5°S	10-8-68	1.1+7	8.5+6	4.0+7	1.1+7	----	3.3+7	1.8+7	3.9+6	2.6+5	2.1+7	1.6+7	3.1+7	2.1+7	----	----
5°-10°S	10-4-68	8.6+7	3.3+7	2.3+8	1.1+8	----	2.0+8	1.5+8	2.0+7	8.8+5	1.1+8	----	----	2.4+8	1.7+7	4.2+6
5°-10°S	10-8-68	2.6+7	1.4+7	1.0+8	4.7+6	----	7.0+7	1.6+7	5.9+6	7.5+5	3.0+7	2.2+7	3.5+7	4.1+7	1.0+6	7.0+5
10°-15°S	10-4-68	5.9+7	3.1+7	5.5+7	5.5+7	----	1.0+8	7.7+7	9.2+6	5.7+5	5.4+7	----	----	1.3+8	8.7+6	2.1+6
10°-15°S	10-8-68	1.1+6	1.8+6	5.3+6	7.6+5	----	3.0+6	1.52+6	2.9+5	6.2+4	2.4+6	2.5+6	----	1.6+6	----	----
15°-20°S	10-4-68	3.6+7	1.7+7	1.0+8	4.8+7	----	8.7+7	6.1+7	8.3+6	2.2+5	4.7+7	3.4+7	1.1+8	9.8+7	6.9+6	----
*15°-20°S	10-8-68	2.1+6	2.4+6	9.4+6	2.0+6	----	7.4+6	4.8+6	8.6+5	1.3+5	5.5+6	4.7+6	6.4+6	4.6+6	----	----
20°-25°S	10-4-68	9.1+5	4.2+6	1.2+7	9.9+5	----	5.3+6	2.5+6	7.0+5	1.3+5	6.1+6	7.0+6	4.9+6	1.5+6	----	----
**20°-25°S	10-8-68	5.9+6	5.2+6	2.2+7	4.7+6	----	1.5+7	8.2+6	9.9+5	1.4+5	8.7+6	7.1+6	1.3+7	9.9+6	----	----
25°-30°S	10-4-68	----	1.2+6	3.2+6	1.7+5	3.6+5	1.7+6	3.2+5	2.7+5	2.0+4	2.4+6	3.2+6	8.9+5	----	----	----
***25°-30°S	10-8-68	4.2+6	5.0+6	2.0+7	4.5+6	----	1.5+7	7.7+6	1.5+6	2.4+5	1.1+7	1.1+7	1.2+7	7.8+6	----	----

* Measurements Made at 58,000 Ft.

** Measurements Made at 57,000 Ft.

*** Measurements Made at 56,000 Ft.

TABLE 3. Radionuclide Concentration at 50,000 ft
in Project Airstream

Lat	Date	d/m/10 ⁶ ft ³														
		¹⁴⁷ Nd	¹⁴⁴ Ce	¹⁴¹ Ce	¹³¹ I	⁷ Be	¹⁰³ Ru	¹⁴⁰ Ba	¹⁰⁶ Ru	¹³⁷ Cs	⁹⁵ Zr	⁹⁵ Nb	¹⁴⁰ La	²³⁷ U	¹³² Te	¹³⁶ Cs
65°-60°N	6-9-68	----	1.1+6	2.8+4	----	4.8+5	----	----	5.1+5	1.1+5	2.5+5	4.3+5	----	----	----	----
60°-55°N	6-9-68	----	1.1+6	2.6+4	----	1.1+6	2.7+4	----	5.8+5	1.1+5	2.1+5	5.3+5	----	----	----	----
60°-55°N	10-16-68	----	4.9+5	5.7+4	3.5+4	5.0+5	3.5+4	2.7+4	1.3+5	3.8+4	3.6+4	8.5+4	----	----	----	----
55°-50°N	6-9-68	----	1.1+6	1.0+5	----	5.4+5	----	----	3.3+5	7.3+4	1.5+5	3.2+5	----	----	----	----
55°-50°N	10-16-68	----	1.6+5	2.9+4	1.0+4	3.7+5	2.2+4	----	5.3+4	2.0+4	4.5+4	5.5+4	----	----	----	----
50°-45°N	6-9-68	----	1.3+6	9.6+4	----	6.7+5	1.9+4	----	3.7+5	9.1+4	1.9+5	3.1+5	----	----	----	----
50°-45°N	10-16-68	----	9.5+4	4.0+4	5.9+5	2.5+5	2.1+4	----	4.1+4	1.3+4	4.7+4	6.4+4	----	----	----	----
45°-40°N	6-9-68	----	1.5+6	8.4+4	----	5.9+5	6.5+4	----	6.8+5	8.8+4	1.7+5	4.6+5	----	----	----	----
45°-40°N	10-16-68	----	1.2+5	4.8+4	9.6+3	2.3+5	1.8+4	----	5.0+4	9.6+3	4.1+4	5.5+4	----	----	----	----
40°-35°N	6-9-68	----	9.9+5	1.4+4	----	1.0+6	4.1+4	----	3.2+5	6.0+4	1.5+5	3.5+5	----	----	----	----
40°-35°N	10-16-68	----	1.5+5	4.2+4	----	4.7+5	4.5+4	----	7.9+4	2.4+4	4.5+4	7.0+4	----	----	----	----

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FIGURE 1. Locations and Dates Where Fresh Debris Was
First Measured

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AN ANTICOINCIDENCE-SHIELDED Ge(Li) GAMMA-RAY SPECTROMETER*

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N. A. Wogman, W. A. Haller,** and A. L. Jackson

Although Ge(Li) gamma-ray spectrometers have provided greatly-enhanced selectivity in gamma spectrometry, there still remain numerous cases where photopeaks from the less abundant radionuclides are obscured by the Compton distribution from the photopeaks of the major radionuclides. Increased sensitivity is also very much to be desired, especially for environmental applications where amounts of radionuclides may be in very low abundance. An anticoincidence-shielded Ge(Li) gamma-ray spectrometer was developed which has high efficiency, resolution and Compton reduction and low natural radioactive content. As shown in Figure 1, it consists of a 20 cm³ coaxial diode centered inside an anticoincidence shield of a 26 in. diameter by 24 in. thick plastic phosphor. The anticoincidence shield reduces the ¹³⁷Cs Compton edge by a factor of 7.5 to provide a peak to Compton edge ratio of 245:1 without reducing the photopeak efficiency by more than 3%. This system provides a two- to four-fold lower natural radionuclide background than similar sized diodes. With this system, 1 pCi source of ¹³⁷Cs can easily be measured. An additional degree of selectivity is obtained by recording both the coincidence and anticoincidence spectra. In some cases this system gave improvements as much as a factor of 7 in the precision of measurements of radionuclides in mixtures.

* Detailed reports of this spectrometer are given in the following papers:

1. J. A. Cooper, N. A. Wogman, and R. W. Perkins. "An Anticoincidence-Shielded Ge(Li) Gamma-Ray Spectrometer for High Sensitivity Counting," IEEE Transactions on Nuclear Science, vol. 15, No. 3, pp. 407-412. 1968.
2. J. A. Cooper, L. A. Rancitelli, R. W. Perkins, W. A. Haller, and A. L. Jackson. An Anticoincidence-Shielded Ge(Li) Gamma-Ray Spectrometer and Its Application to Neutron Activation Analysis, BNWL-SA-2009, Pacific Northwest Laboratory, Richland, Washington, 1968.

** Educational Leave, Washington State University

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FIGURE 1. Anticoincidence Spectrometer System

THE EFFICIENCY CALIBRATION OF A LARGE-VOLUME
Ge(Li) GAMMA-RAY SPECTROMETER

J. A. Cooper and A. L. Jackson

The relative and absolute efficiency functions for a large-volume Ge(Li) gamma-ray spectrometer are reported for a point source at various distances from the detector.

In the past few years, large-volume Ge(Li) diodes have become routine tools to the analytical radiochemist. However, since much of their work is done by comparative techniques, very few studies have been conducted where the relative and absolute efficiencies were accurately and precisely characterized. Since there are many problems where compara-

tive techniques cannot be used and some where the ultimate in accuracy must be obtained, a study was initiated to precisely define a method for the determination of the Ge(Li) efficiency function.

The Ge(Li) spectrometer on which most of the work has been accomplished consists of a five-sided coaxial diode with an efficiency of 4.2% relative

to a 3 in. diameter by 3 in. thick NaI crystal as measured 25 cm from each detector with a ^{60}Co point source. It is housed in a "dipstick" type cryostat and is operated in conjunction with a low-noise preamplifier, amplifier, and a 4096 channel pulse height analyzer. The complete spectrometer provided a resolution (FWHM) of 3.0 keV at 1.332 MeV. A plastic sample holder was rigidly attached to the diode cryostat to accurately position sources along the diode axis to positions 8 in. from the face of the vacuum cap.

The relative efficiencies were determined by the Astrom⁽¹⁾ method, which utilizes gamma-ray sources which have two or more transitions with well-known relative intensities. The relative full-energy peak efficiencies were determined from the relative peak areas which were defined as the peak area above 5% of the peak height after subtracting a linear background. The relative efficiency curve was constructed by log-log plotting these sets of points and adjusting the efficiency axis to form a smooth curve. The absolute efficiency curves were then determined by measuring a few standards with known disintegration rates and adjusting the relative curves accordingly.

The relative and absolute efficiency functions for a point source were determined at three positions, 1/8, 4, and 7 in., from the face of the vacuum cap. Efficiency functions were also determined for 2 and 3 in. spheres located on the vacuum cap. In Figure 1, the relative efficiency function is shown for a point source

located 4 in. from the vacuum cap. The shape of the curve is precisely defined in the energy range from 30 to 3 MeV, with 42 gamma-ray energies from 12 radionuclides. All of the curves have linear plots on log-log paper above 200 keV and have slopes of -1.24. The shape of the curve changed very little with source position, and there was only a 3% difference in the slope for Shelf 1 and Shelf 7.

Figure 2 shows the absolute efficiency for a point source located 7 in. from the vacuum cap. The absolute standards used to adjust the relative efficiency curves were obtained from the International Atomic Energy Agency and are reported to have an overall uncertainty of less than 1.5%. However, the ^{203}Hg and ^{57}Co points are about 10% too high. Similar results were also obtained with two additional ^{203}Hg and ^{57}Co IAEA standards. Many of the previously-published efficiency curves based on these standards were distorted to pass through these points. However, because the shape of our relative efficiency curve for this diode is so well defined, the curve definitely cannot pass through the ^{203}Hg and ^{57}Co points. A more probable solution is either an error in the decay scheme as published for these radionuclides or the IAEA sources have a systematic error in their preparation.

The absolute efficiency for a 100 keV point source located on the vacuum cap is about 10%. One consequence of this high efficiency is that the coincidence-summing events

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FIGURE 1. Relative Efficiency Function

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FIGURE 2. Absolute Efficiency Function

can no longer be considered as insignificant. In this study, some low-energy photopeaks were reduced by as much as 10% by coincidence-summing. Thus, special care must be taken to obtain quantitative numbers for radionuclides with low-energy coincident transitions.

These curves should also be of particular value in the calibration of secondary standards for other instruments. With the use of the calibration curves for Shelf 7,

which have a minimal geometric contribution to the error, it should be possible to calibrate sources up to 2 cm in diameter with an absolute accuracy of about 3%.

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EVALUATION OF Ge(Li) COMPTON SUPPRESSION SPECTROMETERS FOR RADIOCHEMICAL ANALYSIS

J. A. Cooper

Three types of Ge(Li) Compton suppression spectrometers are discussed and evaluated relative to their application to the problems facing the analytical radiochemist.

Although Ge(Li) gamma-ray spectrometers have greatly enhanced the selectivity and sensitivity for the determination of many radionuclides in a variety of samples, numerous cases still remain where the photopeaks from the less abundant radionuclides are obscured by either the Compton distribution from the photopeaks of the major sample radionuclides or the natural background. In the past few years, a large number of sophisticated Ge(Li) Compton suppression spectrometers⁽¹⁻¹⁵⁾ have been developed to reduce this interference. These can be divided into three basic categories: (1) the

all-germanium system, (2) the anti-coincidence-shielded system with the source inside, or (3) outside the shield. The all-germanium Compton suppression spectrometers, or diodes, utilize two Ge(Li) gamma-ray detectors operated in a sum-coincidence mode. The Compton suppression spectrometers, which utilize scintillators for anticoincidence shielding, either reject diode pulses resulting from gamma rays that have deposited a fraction of their energy in both the diode and the scintillator or direct them to one-half of the analyzer memory, while those that deposit all their energy in the diode

are directed to the other half of the memory. These spectrometers are subgrouped according to whether the source is placed inside or outside the shield.

These systems have been evaluated as to their basic design and performance parameters, such as peak to Compton ratios, Compton reduction factors, resolution, and efficiency. They have not been evaluated as to the specific needs of the analytical radiochemist, who wants to know which system is most generally applicable to such problems as the measurement of natural and fallout radionuclides in caribou liver, in milk, on air filters, or those radionuclides in neutron activated lung tissue, rock samples, or fission products from bomb debris and reactor effluents.

The most complete general evaluation of the basic parameters and their interpretation was published by Galloway⁽¹⁶⁾ in 1967. He compared (Figure 1) the error (σ, σ') in the peak height (N, N') above the

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FIGURE 1. A Peak on a Smooth Background Before and After Background Suppression (see Reference 16)

background (N_B, N'_B) for an arbitrary peak on a smooth background before and after background suppression. He used these basic parameters without any assumptions to derive the general equation for the ratio (A/A') of the fractional error in the number of peak counts before background suppression (A) to the fractional error or accuracy after background suppression (A'):

$$A/A' = \{[er(R + 2)]/(rR + 2)\}^{1/2}$$

where e is the reduction in peak efficiency accompanying the background reduction (N'/N), R is the initial peak to background ratio (N/N_B), and r is the factor by which the peak to background ratio (R) has been improved (R'/R). Values of A/A' greater than 1 correspond to increased sensitivity and accuracy or reduced fractional error as a result of the background suppression.

In Figure 2, A/A' ⁽¹⁶⁾ is plotted versus the initial peak to background ratio R for various values of r and e . The broken line represents an A/A' value of 1, which is the dividing line between the improved and reduced sensitivity regions. There will be an improvement in the sensitivity after background reduction for those parameter values above this broken line. This figure shows that for large initial peak to background ratios (R), the ratio of A/A' approaches 1 for e values of 1; thus, the improvement in sensitivity is rather insignificant for large initial peak to background ratios. On the other hand, the most dramatic

improvements in sensitivity are obtained when R is small.

The importance of maintaining a high peak efficiency while reducing the background is also illustrated in Figure 2. For example, if $e = 0.1$, i.e. if the peak efficiency is reduced by a factor of 10 (as is often the case with the diode), the background must be reduced by more than a factor of 100 before any improvement in sensitivity can be

achieved ($r = 10$, $e = 0.1$). On the other hand, if the peak efficiency is not reduced at all, i.e. $e = 1$, then any reduction in the background will improve the sensitivity; however, the magnitude of the improvement will depend not only on the amount of background reduction, but also on the initial peak to background ratio. Thus, when evaluating Compton reduction techniques, one of the more important factors

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FIGURE 2. A Plot of the Ratio of the Fractional Error Before to the Fractional Error After Background Suppression Versus the Initial Peak to Background Ratio (See Reference 16)

to consider is the reduction in peak efficiency accompanying the Compton reduction.

The reduction factors ($\frac{1}{e}$) for the diode⁽¹⁷⁾ and the anticoincidence-shielded spectrometer with the source inside have been calculated for those radionuclides of interest to the analytical radiochemist. (The reduction factors were determined by estimating the difference between the normal and Compton suppressed count rates for the most intense peak in the normal spectrum.)

In Figure 3, the number of radionuclides with a specific reduction factor are plotted versus the reduction factor ($\frac{1}{e}$). One survey included

85 radionuclides from neutron activation with half-lives greater than 2-1/2 min and the other included 40 of the most commonly found radionuclides in neutron activated material with half-lives greater than 60 min. A reduction factor of one means that the photopeak is not reduced by Compton reduction and that the isotope will definitely have improved sensitivities. Those radionuclides with reduction factors greater than 10 cannot have improved sensitivities with either an anticoincidence-shielded system or the diode since neither can provide background reductions greater than 100 in the region where they might

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FIGURE 3. Photopeak Efficiency Reduction Factors for Neutron Activated Radionuclides

obtain a peak reduction of 10. The radionuclides with reduction factors between 1 and 10 may or may not have improved sensitivities depending on how much the background is reduced and the original peak to background ratio.

The results of this survey of 85 radionuclides show that 2/3 of these radionuclides will definitely have improved sensitivities with the anticoincidence-shielded system with the source inside the shield. On the other hand, the diode cannot improve the sensitivity for over half of these radionuclides, and the remaining ones are in the uncertain category. This same trend is also

evident for the more selective survey presented in Figure 3.

The detection of radioactivity in low-level environmental samples requires not only a reduced Compton continuum but also a maximum absolute peak efficiency and a minimum interference from the natural background radiation. The only system which fulfills all these requirements for most radionuclides in environmental samples is the anticoincidence-shielded Ge(Li) spectrometer with the source on the inside. In Figure 4 a frequency distribution is presented for the 30 most commonly measured radionuclides in environmental samples.

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FIGURE 4. Photopeak Efficiency Reduction Factors for Environmental Radionuclides

Again almost 2/3 of these radionuclides, when measured on the anti-coincidence system, have essentially no reduction in the full energy peak efficiency. Thus, any reduction in the Compton continuum and natural background will improve the sensitivity for these radionuclides. (If the coincidence spectrum is also stored, there will be no loss in sensitivity for the other 1/3.) However, it becomes questionable whether the sensitivity can be improved for radionuclides with reduction factors greater than two in low-level samples. Under these circumstances, it appears that the diode has no practical value for low-level samples since it has a minimum reduction factor of 4 and reduces the peak intensity by more than a factor of 10 for over 40% of these radionuclides.

The major disadvantage with the diode is the large reduction in the full-energy peak intensity which accompanies the Compton reduction. In addition, the absolute efficiency and resolution of the diodes have not been equal to the normal spectrometers which might be placed inside a Compton suppression shield. It definitely is of no value for low-level counting, and its application to high-level samples is questionable. It may be of practical value for the measurement of a few radionuclides in a few specific samples but generally is of little use to the analytical radiochemist.

Those systems where the source must be highly collimated and placed outside the shield, suffer from the

severe limitation that the absolute detection efficiency is reduced by a factor of at least 100 and has a maximum Compton reduction of about 10. Although these systems are not of value for the measurement of radionuclides in low level environmental samples, they are the best detection systems for the ultrahigh intensity samples such as irradiated fuel elements and studies of decay schemes. They should also have superior sensitivity for high activity samples which cannot be subdivided and some radionuclides in moderate-level samples.

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THE APPLICATION OF SOLID STATE DETECTORS TO ENVIRONMENTAL
AND BIOLOGICAL PROBLEMS*

J. A. Cooper, N. A. Wogman,
H. E. Palmer,** and R. W. Perkins

Investigations involving the behavior of a complex mixture of radionuclides in environmental and biological systems require highly sensitive and selective measurement techniques. Artificial radionuclide mixtures present in the environment are usually extremely complex and are often present at concentrations comparable to or lower than those of the natural radionuclides. The applicability of the new high-resolution solid state detectors has been evaluated in the analysis of several complex radionuclide mixtures, including both natural and neutron activated radionuclides in environmental and biological samples. These investigations have shown that, in many cases, the increased selectivity of the solid state counting system, when combined with proper sample preparation, allows much more precise analysis for many of the constituents than is possible with rather elaborate NaI(Tl) detector systems. The investigations studied the use of the solid state detector system in radionuclide mixtures from reactor effluents, atmospheric fallout, oceanography, and botanical, biological, and geological samples. The high resolution of these detectors, plus their low background, permitted the direct instrumental measurement of 15 to 20 radionuclides in these samples which would otherwise require slow and tedious chemical separations.

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** Radiological Physics

TRACE ELEMENT ANALYSIS OF BIOLOGICAL SAMPLES BY NEUTRON
ACTIVATION AND DIRECT INSTRUMENTAL ANALYSIS*

L. A. Rancitelli, J. A. Cooper, and R. W. Perkins

Trace elements are known to be well distributed throughout the biosphere; however, the function of only a few are well known. This is due both to the lack of information on the actual trace elemental concentrations in the various organs and body fluids of a given species and on the uptake and excretion rate of trace elements. Although numerous studies have been conducted in which the concentration of either a special element or group of elements was measured, neither a complete spectrum of trace element concentrations nor their relative distribution throughout the organism has been provided. The characterization of the behavior of a trace element relative to an essential trace element in the system can be an important step towards defining its metabolic function. A major problem in the accurate measurement of the trace element composition of tissue is that of contamination during sampling and subsequent analysis. This problem has been minimized with a procedure which involves the direct instrumental analysis of neutron irradiated freeze-dried tissue. A combination of germanium diode spectrometry and multidimensional gamma-gamma coincidence spectrometry facilitates the measurement of at least 14 elemental concentrations at levels as low as a few ppb. Replicate sample analysis has demonstrated a high degree of precision, negligible contamination and trace element loss. The trace element analysis of a variety of tissue samples is described, and the implications of these observations are discussed.

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THE INSTRUMENTAL ANALYSIS OF BLOOD BY NEUTRON ACTIVATION
AND Ge(Li) ANALYSIS*

W. A. Haller,** L. A. Rancitelli, and R. H. Filby**

The measurement of trace elements in blood in the ppm to ppb range requires careful and specialized techniques both in sample acquisition and subsequent analysis. An analytical technique based on neutron activation for elemental concentrations in blood has been developed which requires a minimum of preirradiation handling. Following activation, a direct measurement of the activated nuclides on a high resolution Ge(Li) spectrometer is made. This instrumental method, which requires no chemical or ashing manipulations, eliminates many of the inherent errors associated with chemical determinations. The samples are simply freeze-dried, neutron activated, and analyzed by the Ge(Li) gamma-ray spectrometer. The resulting spectra are reduced by standard techniques and compared to a system of standards, which were irradiated with the samples, to obtain elemental concentrations. By use of this method, 12 elemental concentrations are measured, including Rb, Cs, Fe, Zn, Co, Sb, Se, Hg, P, Na, K, and Br. The concentrations varied from the low ppb (Co, Sb, and Cs) to the ppt (Na, K, and P) range. Comparison of duplicate samples indicated an excellent reproducibility of concentrations.

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A HIGH PURITY CELLULOSE AS A POSSIBLE BIOLOGICAL
REFERENCE MATERIAL*

L. A. Rancitelli, T. M. Tanner,
and W. A. Haller**

Increased interest in trace element analysis of biological materials has pointed out the need for suitable comparative biological standard reference materials. Such materials should be ultrapure to insure precision in very low-level trace element analysis and have the same structural characteristics as biological materials. They could also serve as reference blanks in assessing the level of inherent background contamination associated with an analytical procedure and would be suitable matrices for the addition of known amounts of stable elements to produce "test samples." A material which fulfills the above criteria is a commercially available high purity cellulose filter. Trace element analysis by neutron activation was performed on random samples from two rolls of IPC filter material to demonstrate the homogeneity and purity of the material. Gamma-ray spectrometric analysis of the neutron activated samples were performed with two detector systems, a high resolution five-sided coaxial Ge(Li) detector with an active volume of 20 cm³ and an anticoincidence shielded gamma-gamma coincidence multidimensional analyzer using NaI(Tl) crystals. The average concentrations of fifteen elements (Na, Fe, Mn, K, Cl, Al, Zn, Br, Cr, Co, Cs, Sb, Sc, Ag, and U) found in the filter material are reported and compared to an established biological reference material. This comparison illustrates that not only trace elements but the most abundant constituents Na, K, and Cl, which are typically high in biological tissue, are extremely low in cellulose material.

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NEUTRON ACTIVATION ANALYSIS OF A STANDARD PLANT MATERIAL

L. A. Rancitelli

A standard biological reference material prepared from kale was analyzed by a technique of direct instrumental neutron activation analysis. The concentrations of 13 elements were measured in each of eight samples with excellent precision. The concentrations of potassium, sodium, iron, rubidium, zinc, bromine, chromium, cobalt, and antimony agreed very well with previously-reported values. The cesium content was somewhat higher than previously-published values, while large discrepancies occurred between the silver, scandium, and mercury concentrations reported in this paper and results reported elsewhere.

The interest in the elemental composition of biological materials, particularly the trace constituents, has shown a marked increase in the past few years. A variety of analytical techniques has been developed or modified to permit the elemental characterization of materials such as blood, the various animal tissues, and plant tissue. However, before a technique can be employed with confidence, its accuracy and precision must be ascertained by measuring the composition of materials whose elemental concentration is well known. Bowen,⁽¹⁾ recognizing the need for biological standards both for the calibration of analytical techniques and for providing interlaboratory comparisons, prepared a dry kale powder and dispersed samples to a number of laboratories for elemental characterization. The results of these analyses^(1,2) showed significant discrepancies in the concentrations of several elements measured by different techniques. In several instances, the concentration of an element had been measured by only one technique in one laboratory. Because of the discrepancy in results, as well as the lack of sufficient data, a multielement analysis of kale was made by a method of direct instrumental neutron activation analysis.⁽³⁾

Briefly, the method consisted of irradiating 100 mg samples of freeze-dried material in a Hanford production reactor to an integrated neutron exposure of 10^{18} n/cm². A gamma-ray analysis of the activated samples, after appropriate decay intervals, was made with both a Ge(Li) detector

system⁽⁴⁾ and an anticoincidence shielded multidimensional analyzer⁽⁵⁾ to measure the neutron-induced activities ²⁴Na, ⁴²K, ⁴⁶Sc, ⁵¹Cr, ⁵⁹Fe, ⁶⁰Co, ⁶⁵Zn, ⁸²Br, ⁸⁶Rb, ^{110m}Ag, ¹²⁴Sb, ¹³⁴Cs, and ²⁰³Hg. A comparison of these activities with those induced in known amounts of each element irradiated with the samples permitted the measurement of 13 elemental concentrations in a sample of kale.

Eight samples of kale were analyzed by neutron activation analysis. The results are presented in Table 1, together with the mean concentration and standard deviation. Also included in Table 1 are the concentrations reported by Bowen.⁽¹⁾ The agreement between the results of this work and those reported previously is generally good in the case of sodium, potassium, chromium, iron, rubidium, zinc, bromine, chlorine, cobalt, and antimony. The cobalt concentration in Sample 7 and the antimony concentration of Sample 2 were excluded from the mean for these elements based on Chauvenet's Criterion.⁽⁶⁾ A small difference occurred between the cesium concentrations measured in this work and those previously reported. The results of this work are significantly different than the concentrations of mercury, scandium, and silver previously reported.⁽¹⁾

A wide range of values has been reported for mercury. This may be due to a loss of the element during the pre-analysis sample preparation. Thus, the mercury concentrations measured in this work may be higher due to the fact that the samples were

TABLE 1. Results of the Elemental Analysis of a Standard Plant Material as Measured by Instrumental Neutron Activation Analysis

	Parts Per Million Dry Basis												
Sample No.	K	Na	Fe	Rb	Zn	Br	Cr	Hg	Cs	Co	Sb	Sc	Ag
1	26,200	2,240	115	55.0	32.5	25.5	0.32	0.21	0.079	0.064	0.062	0.0130	<0.01
2	25,500	2,270	119	52.4	29.0	23.6	0.25	0.21	0.070	0.061	0.145 ^(a)	0.0124	<0.01
3	26,300	2,210	108	52.6	30.4	24.5	0.33	0.19	0.077	0.058	0.047	0.0119	<0.01
4	25,500	2,140	110	51.7	30.3	25.4	0.32	0.23	0.080	0.062	0.060	0.0126	<0.01
5	24,300	2,140	103	50.3	29.0	22.2	0.27	0.21	0.080	0.063	0.047	0.0123	<0.01
6	25,600	2,210	129	48.3	29.8	26.8	0.23	0.24	0.078	0.064	0.049	0.0144	<0.01
7	25,600	2,210	122	48.2	29.7	27.5	0.30	0.25	0.078	0.077 ^(a)	0.048	0.0145	<0.01
8	23,500	2,100	112	46.2	28.6	26.5	0.24	0.26	0.075	0.060	0.046	0.0130	<0.01
Mean	25,300	2,190	115	50.6	29.9	25.2	0.28	0.22	0.077	0.062	0.051	0.0130	<0.01
±σ	±950	±58	±8.3	±2.9	±2.6	±1.8	±0.04	±0.02	±0.003	±0.002	±0.007	±0.0008	
Literature	24,630	2,594	119.5	52.8	31.9	24.3	0.331	0.012 to	0.0688	0.056	0.065	0.00835	≤0.50
Values ^(a)	±1,218	±617	±19.5	±6.2	±4.8	±1.6	±0.155	0.150	±0.0071	±0.008	±0.012	±0.00074	

a. Value excluded from mean.

freeze dried at room temperature rather than oven dried at elevated temperatures. Two samples that were not dried before analysis had a mercury content identical to the freeze dried samples after a correction was applied for the water content.

The silver concentration measured in this work was below our limit of detection of 10 ppb, whereas previously-reported results^(1,2) indicate a silver content of about 0.5 ppm. Preliminary results of an independent analysis of a second sample of kale confirm the silver analysis of this report.⁽⁷⁾ The only explanation seems to be a large inhomogeneity in the kale or errors in the earlier analyses. We are unable at this time to rule out either possibility concerning previous work.

The scandium content of kale re-

ported in this work is about 50% higher than previous measurements. Again, there is no readily-apparent reason for the discrepancy. Each scandium concentration in Table 1 represents the average of three determinations by direct comparison with a scandium standard, two measurements of the 889 keV photopeak with a Ge(Li) detector, and one coincidence measurement of the 889 keV and 1121 keV photopeaks with a multidimensional spectrometer.⁽⁵⁾ The correction for the production of ⁴⁶Sc from titanium was negligible. The reactor flux calculated from the ⁴⁶Sc activity of the scandium standard was identical to the flux calculated from the ⁶⁰Co, ⁶⁵Zn, ¹²⁴Sb, and ¹³⁴Cs activities of other standards. The only explanation remaining seems to be an inhomogeneity in the scandium content or a contaminated sample.

Initial indications from the ^{75}Se activities induced in the kale are that the selenium content is below 0.2 ppm. The samples will be permitted to decay for several months to reduce the background in the sample from ^{32}P (14 d), ^{51}Cr (27.8 d), ^{59}Fe (45 d), and ^{86}Rb (18 d) before measuring the selenium concentration.

A similar project has been initiated to perform a multielement analysis of a biological reference material prepared by the National Bureau of Standards. The material, an orchard leaf, is being analyzed for all the elements we measured in kale plus arsenic, lanthanum, and thorium. These measurements are being made both on an absolute basis and relative to the kale standard.

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TRACE ELEMENT CONCENTRATIONS IN THE ATMOSPHERE

L. A. Rancitelli

The concentrations of cesium, cobalt, iron, and scandium have been measured in the atmosphere using a technique of instrumental neutron activation analysis. High purity cellulose air filters were used to sample air at altitudes from 10,000 to 50,000 ft. The scandium content decreased by two orders of magnitude from 10,000 to 50,000 ft, while the iron concentration showed an eightfold decrease over the same altitude increment. The relative atmospheric concentrations of iron, cobalt, scandium, and cesium at 50,000 ft are compared with terrestrial meteoritic abundances. Preliminary indications are that the major portion of material collected is of terrestrial origin.

A program to establish both the origin of aerosols in the atmosphere and their variation with altitude was initiated using a sensitive method of trace element analysis.⁽¹⁾ The technique, which involves the instrumental neutron activation analysis of IPC filters exposed at high altitudes by U.S. Air Force aircraft, provides reliable trace element concentrations at 10,000 ft. However, above this altitude, even with meticulous care to avoid contamination, it is not possible to collect enough material on a filter with the exposure times used at 10,000 ft. This is due to the extremely diffuse nature and rapid decrease with altitude of particles in the atmosphere.

The problem of exceeding the background of the IPC filter has recently been reduced with several modifications in the sampling procedure. Instead of attempting to expose a filter at each of ten altitudes, one filter is exposed at a single altitude to provide a tenfold increase in the volume of air sampled. The air intake of the aircraft sampling system is cleaned

prior to takeoff⁽¹⁾ and then coated with a solution consisting of 20% kromisol and 80% ethanol in an attempt to reduce the level of contamination originating in the sampling system. The fifth filter of 13 filters is exposed at altitude. The remaining filters are used to provide a background correction to the exposed filter.

Three sampling missions were flown during 1968 between Spokane, Washington, and Albuquerque, New Mexico, at altitudes ranging from 29,000 to 50,000 ft. The concentrations of scandium, iron, zinc, cobalt, and cesium were measured in the exposed filters and converted to air concentrations at each altitude. The Fe and Sc concentrations, together with similar information at 10,000 ft,⁽¹⁾ are presented graphically in Figures 1 and 2. These concentrations, which were measured over a period of one year, are plotted versus altitude on a semilog scale. The scandium concentration decreases about two orders of magnitude between 10,000 and 50,000 ft, while the iron concentration decreases by a factor of about 80 over

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FIGURE 1. Iron Concentration in the Atmosphere Versus Altitude

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FIGURE 2. Scandium Concentration in the Atmosphere Versus Altitude

the same increment of altitude. Similar profiles for zinc, cobalt, and cesium are presently being analyzed.

In addition to establishing the atmospheric origin of the aerosol, its trace element composition must be defined. Particulate matter in the atmosphere has two major mechanisms of depletion, settling and rainout, while the major sources of accumulation are material swept up from the earth's surface and the influx of extraterrestrial matter. This latter source has been estimated to be as large as 10^7 tons per year.⁽²⁾ Thus, by measuring the relative concentrations of several elements in the atmosphere and comparing them with terrestrial and extraterrestrial abundances, it should be possible to estimate the contributions of each source to the observed aerosol composition.

The relative abundances of iron, scandium, cobalt, and cesium measured in an air sample collected at 50,000 ft are compared with relative abundances in the earth's crustal average,⁽³⁾ chondritic meteorites,⁽⁴⁾ and the aircraft's sampling system⁽¹⁾ in Table 1. The abundance of iron relative to scandium at 50,000 ft is about equal to the ratio in chondritic and a factor of two higher than the earth's crustal average and the aircraft sampling system. The concentrations of iron relative to cobalt, iron relative to cesium, and scandium relative to cesium in the atmosphere agree

TABLE 1. *Relative Trace Element Concentrations in the Atmosphere at 50,000 ft*

Relative Element Abundances	Atmosphere, 50,000 ft	Earth Crustal Average ⁽³⁾	Chondritic Meteorites ⁽⁴⁾	Sampling System ⁽¹⁾
Fe/Sc	$(2.3 \pm 0.4) \times 10^4$	1×10^4	2.6×10^4	1.2×10^4
Fe/Co	$(1.5 \pm 0.4) \times 10^3$	2.2×10^3	3×10^2	6×10^2
Sc/Cs	1.8 ± 0.4	5	1×10^2	8
Fe/Cs	$(4 \pm 1) \times 10^4$	5×10^4	2.6×10^6	9.6×10^4

with the earth's crust concentration and differ from meteoritic abundances by factors of 5, 60, and 50, respectively. Although the data are not conclusive, it appears that the major source of material at 50,000 ft is the earth's surface. This will be examined in more detail in future sampling missions between 10,000 and 60,000 ft.

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MULTIELEMENT ANALYSIS OF COLUMBIA RIVER WATER BY NEUTRON ACTIVATION AND CHEMICAL SEPARATION TECHNIQUES

L. A. Rancitelli and T. M. Tanner

An analytical method capable of determining nineteen elements in river water by use of neutron activation, group-chemical separations, and gamma-ray analysis is described. The elemental concentrations of Na, K, Rb, Cs, Sc, Cr, Mn, Fe, Co, Cu, Ag, Au, Zn, Hg, As, Sb, Se, Br and U were measured and the observed variations compared with previous work. Several trace element variations in the Columbia River appear to be related to seasonal changes.

Concern has been expressed over the introduction into water supplies of stable or radioactive trace materials which may prove to have toxic effects on man.⁽¹⁾ Industrial, municipal and farming wastes are major sources of stable elements in the Columbia River. Neutron activation

of impurities in the cooling water of the Hanford reactors, followed by discharge to the Columbia River, results in introduction of trace radio-nuclides.⁽²⁾ The uptake and retention of radioactive and stable elements in organisms within the Columbia River also become important

when one considers the food chain to man. Studies in this area require knowledge of the trace element distributions and their variation with time in the river. Thus, the trace element characterization of the Columbia River is essential to an understanding of the transport of the artificial radionuclides through the biosphere.

This investigation describes a method which has been used to determine the concentrations of nineteen elements in single samples of Columbia River water. River water samples were taken directly from the river into 1 oz. Nalgene polyethylene capsules. The collection capsules had been thoroughly cleaned prior to use by leaching in nitric acid and then rinsing with doubly-distilled water. The method used to collect the samples was to face an empty capsule upstream under water, remove the cap, and let the capsule fill to about 25 ml. The capsule was sealed, rinsed with doubly-distilled water to remove surface contamination, and frozen in dry ice.

Standard solutions⁽³⁾ containing the elements of interest were prepared in the same geometry as the sample. Standards and samples were each sealed in #500 Nalgene capsules cut to fit a specially-designed irradiation facility of a Hanford graphite-moderated production reactor. The frozen samples were irradiated in a well-thermalized neutron flux to an integrated exposure of 2×10^{16} n/cm². Samples remained frozen during the irradiation and were transported from the

reactor to the laboratory in dry ice. The standards, also frozen, were irradiated in the same position in the reactor. The frozen samples were removed from their containers and rinsed with distilled water to remove any external contamination. The etched sample was melted, weighed, and 0.1 µg each of the carriers Cr, Co, Cu, Ag, Fe, Hg, Zn, Au, Mn, Sb, Se, Sc, and La was added to the solution, which was filtered through a 0.45 µ Millipore filter to remove suspended particulate matter. A 100 µl portion of the filtered solution was pipetted onto a 1 in. SS dish for determination of Na in the sample. The filter was thoroughly washed and 0.1 mg of K, Cs, Rb, and Sr carriers was added to the filtrate. The solution was then transferred to a hot water jacketed mixed-bed precipitation column for the separation procedure. The precipitation column was prepared by adding one layer each of OH⁻, S⁼, and CO₃⁼-substituted DOWEX 1-X2 resin to a standard 1 cm ID jacketed distillation column to a total resin depth of about 15 cm. The activated water sample passed through the column at a flow rate of 0.5 ml/min, and the resin washed with three 5 ml portions of water. Fifteen elements, including Mn, Co, Fe, Cr, Cu, Zn, Ag, Au, Hg, Sc, Sb, Br, As, Se, and U, were removed from the sample by precipitation or exchange reactions with the mixed resin. The resin was quantitatively transferred from the column into a 1/2 × 2 in. PVC ring and thoroughly mixed with Plaster of Paris to produce a uniform source in

a standard counting geometry. The column effluent, which contained the alkali and alkaline earth metals, was collected in a beaker. An excess of 4% sodium tetraphenylboron was added to the effluent, and the resulting K, Rb, and Cs tetraphenylboron precipitate⁽⁴⁾ was allowed to digest in an ice bath for 30 min. The precipitate, which contained Cs, K, Rb, and several alkaline earths, was filtered and rinsed. The filter and precipitate were placed in the center of a 1/2 x 2 in. PVC ring which was then filled with Plaster of Paris to obtain a standard counting geometry. The irradiated standard solutions were prepared in the same geometry as the samples by thoroughly mixing 50 μ l of each with Plaster of Paris in PVC rings or, as in the case of Na, by pipetting onto a stainless steel dish.

A series of trace experiments involving known amounts of radioactive tracers demonstrated that the precipitation column quantitatively removed Sc, Cr, Mn, Fe, Co, Cu, Zn, Se, As, Br, Ag, Sb, Au, Hg, and U. Similar experiments involving ²⁴Na, ⁴²K, ^{87m}Sr, and ¹³⁴Cs established that the effluent from the column contained more than 99% of the Na, K, Sr, and Cs. A flow diagram of the analytical procedure is presented in Figure 1. All sources were analyzed on two gamma-ray detection systems--a five-sided coaxial Ge(Li) detector with an active volume of 20 cm³⁽⁵⁾ and an anticoincidence-shielded, gamma-gamma coincidence multi-dimensional analyzer.⁽⁶⁾ The specific activities of ²⁴Na, ⁴²K, ⁴⁶Sc,

⁵¹Cr, ⁵⁶Mn, ⁵⁹Fe, ⁶⁰Co, ⁶⁴Cu, ⁶⁵Zn, ⁷⁵Se, ⁷⁶As, ⁸²Br, ⁸⁶Rb, ^{110m}Ag, ¹²⁴Sb, ¹³⁴Cs, ¹⁹⁸Au, ²⁰³Hg, and ²³⁹Np (from U) were measured and compared with the activities of the standards to obtain the concentration of each element. When comparator standards were not available, calculations involving reactor flux were applied to determine trace element content; however, this method was avoided when possible since it could lead to unnecessary errors.

The trace element concentrations determined in four Columbia River water samples taken over a period of several months are presented in Table 1, together with an estimated experimental error based on counting statistics, self-shielding, side reactions, source inhomogeneity, and contamination for each element.⁽³⁾

Examination of the data shows seasonal variations in the trace element content of the river similar to those observed by Silker.⁽²⁾ The Mn, Cu, Zn, and As concentrations were relatively high during April, a period of increased Columbia River flow, while Na tended to increase in concentration as the flow decreased. Scandium was consistently low except for the August sample. Cobalt exhibited a maximum in September which was not quite in agreement with earlier observations showing a maximum cobalt concentration in June at the peak of the Columbia River flow. The K and Cs concentrations generally followed the pattern of Na concentration, while Sb and Br were observed to follow the pattern of

Neg 0690488-1

FIGURE 1. Multielement Analysis of Trace Constituents in Natural Water by Neutron Activation, Two-Group Chemical Separations and Gamma-Ray Analysis

Mn, Cu, Zn, and As. Of the other elements measured--Rb, Cr, Fe, Ag, Au, Hg, Se, and U--sufficient data which might permit a study of seasonal variations have not been collected.

Since the Columbia River is a dynamic and complex system, a single sample cannot be considered representative of the system. Certainly, though, as shown by Silker,⁽²⁾ sufficient sampling and analyses can

TABLE 1. Trace Element Concentrations in Columbia River Water Samples Collected Above the Hanford Reactors

Date Collected, 1968	Element Concentration, ppb									
	Na	K	Rb	Cs	Sc	Cr	Mn	Fe	Co	Cu
April 3	--	--	--	0.04	0.03	--	13.1	--	0.07	4.20
Aug. 1	880	325	--	0.34	1.70	--	5.20	--	0.04	≤0.01
Sept. 12	1700	400	--	0.84	0.004	--	5.5	355	0.10	0.26
Nov. 14	2220	1190	≤3.5	0.35	0.002	<0.4	2.8	13.0	0.02	≤0.13
Estimated Experimental Error, %	5	5	25	25	20	25	5	10 - 20	10 - 20	5 - 25

Date Collected, 1968	Element Concentration, ppb								
	Ag	Au	Zn	Hg	As	Sb	Se	Br	U
April 3	--	--	120	--	2.9	3.30	--	7.3	0.4
Aug. 1	--	0.01	5.70	--	1.0	0.30	--	2.2	--
Sept. 12	--	--	47.0	0.6	1.7	0.50	4.9	4.3	--
Nov. 14	<0.5	<0.03	7.50	≤0.1	2.5	0.24	0.25	5.6	≤0.7
Estimated Experimental Error, %	20	20	10	20	10	10 - 20	10 - 20	5	10 - 20

identify significant trends which can be correlated with environmental effects. Thus, these data should be interpreted only qualitatively since they are representative of the samples taken and not of the whole system. The main purpose of this work is to demonstrate the capability of the method to perform a multielement analysis at very low concentration levels. With proper care and planning, the list of elements determined by the method could be expanded to include Ca, Sr, Ba, and Cl.

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THE ELEMENTAL CONTENT AND RETENTION OF A RAINBOW TROUT

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The various soft tissues, internal organs, blood, and food of a fish raised under controlled conditions have been analyzed by a multielement technique of neutron activation analysis. The concentrations of Na, K, Rb, Cs, Br, Zn, Se, Co, Fe, Cr, Sc, Sb, Ag, and Hg are reported in the midline muscle, dorsal muscle, brain, spinal cord, liver, heart, spleen, kidney, blood, and food of a rainbow trout. Silver concentrates primarily in the liver (0.4 ppm), Cr and Sb in the kidney (12 ppm and 0.007 ppm, respectively), and Sb in the liver (0.006 ppm). The food contains 200 to 1000 times more Sc than any tissue of the fish. Several organs accumulated more than 1 ppm Hg even though less than 0.1 ppm Hg was found in the food. The Rb/K and Cs/K ratios varied throughout the fish and showed large departures from the ratios in the food. The Rb/Na+K and Cs/Na+K ratios based on chemical equivalents of each element were relatively constant throughout the fish and compared quite well with the ratios in the food.

The Columbia River ecosystem has been extensively studied from a radiological viewpoint. The natural and artificial radionuclides present in the river have been characterized and their transport properties defined.⁽¹⁾ The various radionuclides present in organisms associated with the river have been measured with low-level detection systems.⁽²⁾ However, if a complete model of the transport of radioactivity through the biosphere is to be developed, some consideration must be given to the dilution of radioisotopes by the stable elements present in the system and the possible preferential uptake of specific chemical species. Although some of the stable trace constituents present in the river have been characterized,⁽³⁾ information is lacking on the elemental concentrations present in the biota. Thus, in an effort

to understand the transport of radionuclides through the biosphere, a program has been initiated which will provide information on the uptake, retention, and excretion rates of trace elements by organisms.

A rainbow trout which was raised under controlled conditions was sacrificed, and samples of its soft tissues and blood were immediately collected. A multielement analysis was performed with a technique of instrumental neutron activation analysis⁽⁴⁾ which permitted the simultaneous measurement of 14 elemental concentrations in each sample. The heart was purged with distilled water to remove any blood prior to analysis.

The results of the analysis of the soft tissue and food of the trout are presented in Table 1, together with an estimated experimental error for each element. Samples of the red, or midline, muscle and the white muscle which were taken from each

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TABLE 1. Trace Element Content of Trout Muscle, Organs, Blood and Food: Micrograms Element/gram Dry Material

TISSUE	Na	K	Rb	Cs	Br	Zn	Se	Co	Fe	Cr	Sc	Sb	Ag	Hg
WHITE MUSCLE (R.S.)	620	20,000	16.6	0.11	10	11	0.64	0.011	8.5	0.041	0.00004	0.0002	0.0013	0.38
WHITE MUSCLE (L.S.)	570	17,800	16.7	0.11	11	12	0.70	0.011	10	0.19	0.00003	0.0006	0.0015	0.40
RED MUSCLE (R.S.)	820	7,600	8.0	0.052	18	24	0.49	0.045	77	0.070	<0.00001	<0.0001	<0.001	0.24
RED MUSCLE (L.S.)	770	6,300	6.2	0.051	16	26	0.37	0.034	50	0.12	0.00030	0.0004	0.001	0.24
BRAIN AND PIT.	5000	11,800	7.4	0.061	36	34	0.79	0.070	82	0.45	0.0007	0.0004	<0.001	0.54
SPINAL CORD	2800	10,300	9.1	0.054	27	28	0.49	0.014	12	0.580	0.0004	0.00050	<0.001	≤0.1
LIVER	2500	17,300	17.6	0.036	60	80	8.8	0.18	450	2.10	0.00040	0.0063	0.41	0.76
HEART	4200	19,500	24.4	0.22	50	110	1.1	0.18	220	0.42	<0.0002	<0.0001	<0.001	0.56
SPLEEN	1400	18,500	21.2	0.074	47	60	2.1	0.11	1500	1.8	<0.0002	0.0007	<0.001	1.2
KIDNEY-HEAD	3800	17,600	17.8	0.060	69	95	4.2	1.4	490	11	<0.0002	0.0069	0.0072	2.0
KIDNEY-TAIL	3900	14,400	17.5	0.068	62	82	5.2	2.5	380	12	<0.0002	0.0068	0.0034	1.7
BLOOD	4200	<1,000	12.5	0.022	74	70	1.7	0.22	2300	0.54	<0.0002	<0.0001	<0.001	1.3
DRY FOOD	3900	5,900	11.7	0.050	30	66	0.69	3.2	570	1.2	0.098	0.110	0.095	≤0.1
OREGON WET PELLETS	3400	6,900	9.4	0.055	78	100	1.6	0.42	360	0.79	0.027	0.052	0.096	≤0.1
ESTIMATED ERROR	5%	5%	5%	5%	5%	5%	10%	5%	5-10%	5-25%	10-50%	5-25%	10-20%	5-15%

side of the fish are listed in Table 1 as L.S. (left side) and R.S. (right side). The two samples of the kidney analyzed are listed as head and tail. The fish was raised on two types of foods which were also analyzed (see Table 1). With the exception of the Fe content of the red muscle tissue, the elemental concentrations in each type of muscle tissue were found to be relatively constant from the left to the right side of the fish. Similar variations in Fe have also been observed in the red muscle tissue of salmon.⁽⁵⁾ The K, Cs, Rb, and Sc concentrations were higher in the white muscle tissues than in the red, while the inverse relationship was observed for Na, Fe, Zn, Co, and Br. This is consistent with the observed concentrations in salmon. The brain had the highest and the white muscle the lowest Na content, while the white muscle had the highest and the blood the lowest K content. The

spleen, liver, and heart had higher concentrations of Fe, Zn, Hg, Co, Se, and Cr than the muscle tissue. Although several organs were found to contain 1 ppm Cr, the kidney (12 ppm) accounted for the majority of Cr in the fish. There was no correlation between the Fe content of an organ and the concentrations of Co, Zn, or Cr.

All tissue samples were found to contain less than 0.1 ppb Sc, while the food contained 27 to 98 ppb Sc. This suggests that either the Sc in the food is not in a chemical form which can be assimilated by the organism or that the element is required in very minute amounts. In either case, ⁴⁶Sc ingested from the environment offers no radiological hazard beyond the amount accumulated in the gastrointestinal tract of the organism.

The only appreciable quantities of Sb were found in the liver (6.3 ppb) and the kidney (6.8 ppb)

even though the food contained 50 to 100 ppb Sb. Silver was found to accumulate in the liver (0.4 ppm) and to a lesser degree in the kidney (0.005 ppm), while all other tissues contained less than 1 ppb. The presence of about 0.1 ppm Sb and Ag in the food indicates a sufficient quantity of each element was available to the organism to maintain a higher inventory.

The muscle tissues, spinal cord, and heart had low Hg concentrations, while the spleen, kidney, and blood were all found to contain more than 1 ppm Hg. This, coupled with the low Hg content of both food sources, demonstrates the well-known cumulative nature of Hg in a biological system.

A comparison of the elemental ratios in Pacific salmon with those in seawater has shown that the fish preferentially concentrate Cs relative to Rb and K.⁽⁵⁾ This appeared valid in the case of marine organisms since the fish and their food sources ultimately derived their trace element content from the seawater. This is not the case for this trout, however, since the food source is not contemporary with its environment. Hence, the elemental intake of the fish can be derived from the Columbia River water or the food sources. Since the values of Cs and Rb are not well known in the Columbia River, it is only possible to compare the alkali metal ratios in the fish with those in its food. This has been done in Table 2, where the concentrations of Cs and Rb relative to K have been tabulated for

TABLE 2. Relative Concentration of Cesium, Potassium, and Rubidium in Trout Tissue

Tissue	g/g K	
	Rb/K ($\times 10^4$)	Cs/K ($\times 10^6$)
White Muscle ^(a)	8.8 $\pm$ 0.5	5.8 $\pm$ 0.3
Red Muscle ^(a)	10.1 $\pm$ 0.4	7.4 $\pm$ 1.4
Brain	6.4 $\pm$ 0.5	5.2 $\pm$ 0.4
Spinal Cord	8.8 $\pm$ 2.0	5.2 $\pm$ 1.2
Liver	10.2 $\pm$ 1.1	2.1 $\pm$ 0.2
Heart	12.5 $\pm$ 1.3	11.3 $\pm$ 1.0
Spleen	11.6 $\pm$ 1.2	4.0 $\pm$ 0.6
Kidney ^(a)	11.1 $\pm$ 1.1	4.1 $\pm$ 0.6
Blood	>125	>20
Dry Food	19.8 $\pm$ 1.8	8.5 $\pm$ 0.9
Oregon Wet Pellet	13.6 $\pm$ 1.4	8.0 $\pm$ 1.0

a. Average of two measurements.

each tissue and the two types of food. The Rb/K ratio of all tissue samples, with the exception of the brain and blood, was relatively constant. The blood has a very high Rb/K ratio ($>125 \times 10^{-4}$) because it contains very little K while maintaining normal amounts of Rb and Cs. This suggests that Rb and Cs are neither completely correlated with K nor independent of Na.

Both food sources have higher Rb/K ratios than all tissue samples except the blood. The Cs/K ratio of the various trout tissue, with the exception of the blood and heart, is lower than the value in the food. If the food is the major source of alkali metals, the trout does not concentrate Cs relative to K. Although it is obvious from the data in Table 1 that Cs and K are not correlated with Na, we cannot discount the possibility that Cs and Rb are a function of the total Na and K

content. This possibility was investigated by normalizing the Rb and Cs concentrations in chemical equivalents to the sum of the Na and K in chemical equivalents (Table 3). When this is done, the Rb/Na+K ratio in the various tissues, with the exception of the blood, is nearly constant and equal to the value in the food. The Cs/K+Na ratio of all tissue samples except the liver and heart compare quite well with the ratio in the food. The contribution of the river water to these ratios cannot be excluded. This information is being compiled with a systematic multielement analysis of river water.⁽⁶⁾

The multielement analysis of fish raised under controlled conditions is providing valuable information on the uptake, retention, and excretion of several elements of radiological importance. The distribution of 14

elements is being measured in the various parts of the fish, as well as its food and surrounding water. Using this method, it is possible to study the behavior of an element throughout the environment and to perform accurate mass balance calculations based on the inventory of each component of the system.

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TABLE 3. Concentration of Rubidium and Cesium Relative to Sodium and Potassium (Equivalent per Equivalent) in Trout

Tissue	Rb/Na+K ($\times 10^4$)	Cs/Na+K ($\times 10^6$)
White Muscle ^(a)	3.8 $\pm$ 0.3	1.6 $\pm$ 0.1
Red Muscle ^(a)	3.9 $\pm$ 0.2	1.8 $\pm$ 0.2
Brain	1.7 $\pm$ 0.2	0.9 $\pm$ 0.1
Spinal Cord	2.8 $\pm$ 0.6	1.1 $\pm$ 0.3
Liver	3.7 $\pm$ 0.3	0.5 $\pm$ 0.1
Heart	2.1 $\pm$ 0.2	2.4 $\pm$ 0.4
Spleen	4.6 $\pm$ 0.5	1.0 $\pm$ 0.2
Kidney ^(a)	3.6 $\pm$ 0.2	0.85 $\pm$ 0.10
Blood	7.0 - 8.0	0.8 - 0.9
Dry Food	4.3 $\pm$ 0.3	1.2 $\pm$ 0.2
Oregon Wet Pellets	3.4 $\pm$ 0.3	1.3 $\pm$ 0.2

a. Average of two measurements.

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THE MULTIELEMENT ANALYSIS OF PACIFIC SALMON TISSUE

L. A. Rancitelli

Samples of each species of Pacific salmon have been collected, their dorsal muscle and liver tissue analyzed by instrumental neutron activation analysis, and the concentrations of the 14 elements Na, K, Rb, Cs, Br, Zn, Fe, Cr, Co, Se, Hg, Ag, Sb, and Sc measured. Sockeye salmon liver had the highest Se (48 ppm) and Ag (6.4 ppm) content of the five species, while the Silver salmon liver had the highest Co (0.21 ppm) content. The analysis of seven Chum salmon, four male and three female, revealed several variations which can be correlated with sex. The male liver contained an average Se content of 21.3 ± 3.3 ppm and Ag content of 5.8 ± 0.5 ppm, while the female liver contained 10.5 ± 2.5 ppm Se and 3.8 ± 1.0 ppm Ag. The total Se inventory of the female Chum salmon is equal to that of the male if the Se concentration of the roe is taken into consideration. The Cs concentration relative to K is reported for all salmon and compared with the values in seawater. All salmon are shown to preferentially concentrate Cs to varying degrees. The Silver salmon had a Cs/K ratio in the muscle tissue of 12.9×10^{-6} compared with a ratio in seawater of 0.8×10^{-6} . The Rb/K ratio was found to be lower in the muscle than in the liver for all species, but the deviation from the value in seawater was small.

Sensitive analyses of salmon muscle tissue⁽¹⁾ have revealed variations in the trace element concentrations which had previously been observed for the major elements Na and K.^(2,3,4) Not only did different types of muscle tissue in close physical proximity exhibit large elemental variations, but some organisms appeared to concentrate Cs relative to the chemically-similar elements K and Rb.⁽¹⁾ Since the salmon repre-

sents a major food source for a segment of the population and because Cs is biologically important due to the presence of the long-lived radionuclide ¹³⁷Cs in the biosphere,⁽⁵⁾ a program was initiated to study the variation of 14 major and trace elements of possible biological and radiological importance in five species of Pacific salmon.⁽⁶⁾ The investigation is establishing the

Mature male and female salmon are being systematically obtained by C. E. Jenkins of our laboratory at various sampling locations along the Pacific Coast between Southern California and Alaska. Each specimen is frozen at the sampling location, shipped to Richland, Washington, and analyzed by a multielement technique utilizing instrumental neutron activation analysis.⁽⁷⁾

dimensional spectrometer, ⁽⁹⁾ the neutron-induced activities ²⁴Na, ⁴²K, ⁴⁶Sc, ⁵¹Cr, ⁵⁹Fe, ⁶⁰Co, ⁶⁵Zn, ⁷⁵Se, ⁸²Br, ⁸⁶Rb, ^{110m}Ag, ¹²⁴Sb, ¹³⁴Sc, and ²⁰³Hg were measured. A comparison of these activities with those induced in known amounts of each element irradiated with the sample permitted a direct measurement of 14 elemental concentrations in a tissue sample. In Table 1 the major and trace element concentrations in µg/g dry tissue of five species of Pacific salmon are presented with their associated errors. ⁽⁷⁾

Since interspecies variations were detected in the initial study, an investigation was completed of the intraspecies variations in elemental concentrations of Chum salmon (Table 2). The Chum salmon concentrations of Na, K, Rb, and Cs (with the exception of sample Number 3), as well as Br, Zn, and Co, vary by

[illegible]

TABLE 2. Trace Element Concentrations of Chum Salmon

Sample	Micrograms Per Gram Dry Tissue													
	Na	K	Rb	Cs	Br	Zn	Fe	Cr	Co	Se	Hg	Ag	Sb	Sc
1. Muscle ^(b)	2200	16,200	3.9	0.067	28	14.3	10.6	<0.02	0.0090	1.4	0.21	<0.001	0.0008	0.00005
Liver	6300	13,800	5.8	0.059	82	120	1300	0.16	0.110	24.7	0.41	6.3	<0.001	<0.001
2. Muscle ^(b)	1500	17,000	3.4	0.066	21	13.6	11.9	<0.02	0.0081	1.6	<0.20	0.002	0.0006	0.00004
Liver	6600	14,900	5.8	0.058	95	117	690	0.09	0.097	22.9	0.49	5.5	<0.001	<0.0006
3. Muscle ^(b)	1500	15,400	3.3	0.062	20	13.4	16.9	0.62	0.0085	1.3	<0.20	<0.001	0.0006	0.00009
Liver	5500	14,200	4.0	0.036	78	95	690	0.24	0.075	21.2	0.36	5.3	<0.001	<0.001
4. Muscle ^(b)	1700	18,600	4.5	0.066	13	14.6	12.5	0.05	0.0048	1.5	0.20	<0.001	0.0007	0.00005
Liver	6600	15,500	5.5	0.056	51	110	620	<0.02	0.096	15.5	0.87	6.1	<0.001	<0.001
5. Muscle ^(a)	1500	18,400	4.0	0.079	10	13.1	11.2	0.04	0.0057	1.5	0.21	<0.001	0.0005	0.00004
Liver	5400	18,000	8.0	0.080	45	87	530	<0.02	0.066	7.2	<0.41	2.6	<0.001	<0.001
6. Muscle ^(a)	1400	17,400	4.1	0.071	13	12.3	16.4	<0.02	0.0080	1.4	0.29	<0.001	0.0010	0.00003
Liver	5300	16,000	7.7	0.077	48	92	770	0.58	0.085	10.9	0.41	4.8	<0.0005	<0.001
7. Muscle ^(a)	1300	15,200	4.1	0.070	18	8.9	11.3	0.15	0.0078	1.2	<0.2	<0.001	<0.0005	0.0002
Liver	4400	14,600	5.9	0.072	58	87	370	0.04	0.086	13.2	0.36	3.4	<0.001	<0.001

a. Female

b. Male

about twofold between individuals. Although the Fe and Se exhibit similar variations in muscle tissue, the concentrations vary by about a factor of three in the liver. A closer examination of the Se content of the liver reveals variation between the male and female of the species.

The average Se content in the liver of the four male Chum salmon is 21.3 ± 3.3 ppm (standard deviation), while the three female Chum salmon contain an average of 10.5 ± 2.5 ppm. This average, coupled with the observation of about 4 ppm of Se in Chum salmon roe,⁽¹⁰⁾ suggests that the difference between sexes might be connected to the reproductive cycle. A similar elemental variation between sexes was observed in the Ag content of the Chum salmon liver, which averaged 5.8 ± 0.5 ppm for the male and 3.8 ± 1.0 ppm for the female. The range in concentrations observed in Chum salmon is summarized in Table 3.

If one assumes that the elemental variations observed for individual Chum salmon are typical of those one might expect in the other species of Pacific salmon, the following interspecies variations appear. The K content of muscle and liver tissue is about equal for four species of salmon; however, the liver of the Silver salmon has a 30% higher K content than the muscle tissue. The Cs concentrations of Chum liver and muscle are about equal, while the other four species have higher Cs concentrations in the muscle tissue. The muscle tissue of the Pink salmon contains about twice as much Fe as the other species. It is difficult to ascribe any significance to the Fe variability in the livers since similar variations are noted in the Chum salmon. The Silver salmon contains three to four times as much Co in its liver⁽¹¹⁾ as the other species, yet its muscle tissue has essentially the same Co concentration. The Se

*TABLE 3. Concentration Range
Observed in Seven Chum Salmon*

Element	$\mu\text{g/g Dry Tissue}$	
	Dorsal Muscle	Liver
Na	1,300 - 2,200	4,400 - 6,600
K	15,200 - 18,600	13,800 - 18,000
Rb	3.3 - 4.5	4.0 - 8.0
Cs	0.062 - 0.79	0.036 - 0.080
Br	10 - 28	45 - 95
Zn	8.9 - 14.6	87 - 120
Fe	10.6 - 16.9	370 - 1300
Cr	<0.02 - 0.62	<0.02 - 0.58
Co	0.005 - 0.009	0.066 - 0.110
Se	1.2 - 1.6	7.2 - 24.7
Hg	<0.20 - 0.29	0.36 - 0.87
Ag	<0.001 - 0.002	2.6 - 6.3
Sb	<0.0005 - 0.0010	<0.001
Sc	0.0003 - 0.0020	<0.001

content of the Sockeye liver is four to ten times higher, and its Ag content is two to ten times higher than levels observed in the other species.

The concentrations of Cs, Rb, and K in the muscle and liver of the seven Chum salmon listed in Table 2 have been converted to a relative basis and presented in Table 4, to-

*TABLE 4. Relative Concentrations of
Cesium, Potassium, and Rubidium in
Chum Salmon Tissue*

Sample	Rb/K ($\times 10^4$)	Cs/K ($\times 10^6$)
1. Muscle	2.4 $\pm$ 0.3	4.1 $\pm$ 0.4
Liver	4.2 $\pm$ 0.5	4.3 $\pm$ 0.4
2. Muscle	2.0 $\pm$ 0.4	3.9 $\pm$ 0.4
Liver	3.4 $\pm$ 0.4	3.9 $\pm$ 0.4
3. Muscle	2.1 $\pm$ 0.5	4.0 $\pm$ 0.4
Liver	2.8 $\pm$ 0.4	2.5 $\pm$ 1.0
4. Muscle	2.4 $\pm$ 0.3	3.5 $\pm$ 0.4
Liver	3.5 $\pm$ 0.8	3.6 $\pm$ 0.4
5. Muscle	2.2 $\pm$ 0.4	4.2 $\pm$ 0.4
Liver	4.4 $\pm$ 0.7	4.4 $\pm$ 0.4
6. Muscle	2.4 $\pm$ 0.4	4.1 $\pm$ 0.4
Liver	4.8 $\pm$ 0.8	4.8 $\pm$ 0.4
7. Muscle	2.7 $\pm$ 0.3	4.6 $\pm$ 0.4
Liver	4.0 $\pm$ 0.6	4.9 $\pm$ 0.4
Mean $\pm$ σ		
Muscle	2.3 $\pm$ 0.2	4.1 $\pm$ 0.3
Liver	3.9 $\pm$ 0.7	4.1 $\pm$ 0.8
Seawater ^(12,13)	3.3	0.8

gether with their associated experimental errors. The average and standard deviation of the seven fish are also presented in Table 4, as well as typical relative concentrations in seawater.^(12,13) A comparison of the seawater and tissue elemental concentrations confirms our earlier observation for Silver salmon,⁽¹⁾ that the organism has the ability to preferentially concentrate Cs relative to Rb and K. The Rb/K ratio in the muscle tissue (Table 4) is consistently lower than the value in the liver, while the Cs/K ratio in the liver and muscle tissue is essentially the same. This suggests a small relative differentiation of Rb within the organism even though the relative concentration with respect to seawater is unchanged.

The relative concentrations and experimental errors of Cs, Rb, and K in all five species of Pacific salmon are summarized in Table 5 for comparison with the values in seawater. If it is assumed that the variation in relative concentrations observed for Chum salmon (Table 4) is typical of other species, one can observe that the Cs content relative to K has a characteristic value for each species. Although all species of salmon preferentially concentrate Cs, the Cs/K ratio in the liver and in the muscle of the Chum salmon is about equal, while the ratio in the King salmon muscle is twice as high as the liver and the ratio in the Silver and Sockeye salmon is about three times higher in the muscle tissue. The Silver salmon muscle exhibited the highest Cs/K ratio

(12.9×10^{-6}) of the five species, as well as the largest variation in the ratio between muscle and liver. The ratios measured in this investigation compare favorably with our earlier published values.⁽¹⁾ The smallest increase in the Cs/K ratio relative to seawater occurred in the liver of the Pink salmon (factor of 2) while the largest increase (factor of 16) occurred in the Silver salmon muscle tissue. The Rb/K ratio of each of the other four species of Pacific salmon had approximately the same variation as the ratio in seawater as was observed in Chum salmon. The ratio was lower than the value in seawater in the muscle tissue and higher in the liver. The only large departure in the Rb/K ratio from the value in seawater occurred in the Pink salmon liver.

The multielement analysis of Pacific salmon tissue is continuing in an effort to establish the normal elemental concentrations for each species. Variations in trace element concentrations which can be attributed to sex can be used in conjunction with radionuclide measurements in each sample⁽⁵⁾ to study the specific activity of several natural and artificial radionuclides throughout the biosphere. The multielement analysis of the various soft tissues and organs of the Chum salmon has been initiated in an attempt to identify the organs that might be expected to preferentially concentrate the radiologically important radionuclides.

TABLE 5. Rubidium and Cesium Concentrations in Pacific Salmon Relative to Potassium

Species	Rb/K ($\times 10^4$)	Cs/K ($\times 10^6$)
Chum Salmon		
Muscle	2.3 $\pm$ 0.2	4.1 $\pm$ 0.3
Liver	3.9 $\pm$ 0.7	4.1 $\pm$ 0.8
King Salmon		
Muscle	2.5 $\pm$ 0.2	7.7 $\pm$ 0.5
Liver	3.6 $\pm$ 0.3	3.9 $\pm$ 0.3
Silver Salmon		
Muscle	2.9 $\pm$ 0.2	12.9 $\pm$ 0.8
Liver	3.6 $\pm$ 0.4	4.5 $\pm$ 0.4
Red Salmon		
Muscle	2.0 $\pm$ 0.3	4.3 $\pm$ 0.4
Liver	3.1 $\pm$ 0.5	1.6 $\pm$ 0.2
Pink Salmon		
Muscle	2.4 $\pm$ 0.3	6.6 $\pm$ 0.5
Liver	5.1 $\pm$ 1.1	5.4 $\pm$ 0.5
Seawater ^(12,13)	3.3	0.8

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THE TRACE ELEMENT CONTENT OF AQUATIC ORGANISMS
FROM PANAMA AND COLOMBIA

L. A. Rancitelli, W. L. Templeton,*
and J. M. Dean**

The concentrations of fourteen elements in the muscle tissue of aquatic organisms from Central and South America were determined by a method of instrumental neutron activation analysis. In addition to the major constituents Na and K, the concentrations of Rb, Cs, Br, Zn, Se, Co, Fe, Cr, Sc, Sb, Ag, and Hg are reported. The organisms studied exhibited large variations in their trace element content while the Na and K concentrations were relatively constant. Several samples of a particular species collected from different rivers were quite similar in their trace element composition.

Battelle-Northwest is one of the principal investigators who are obtaining field data to evaluate the possible biological exposures associated with the construction of a sea level canal by controlled nuclear detonations. This effort would utilize the Plowshare Program technology which is being developed by the Atomic Energy Commission. In support of this work, a comprehensive program involving the trace elemental analysis of aquatic organisms from the two proposed canal routes has been initiated. The purpose of this study is to obtain trace element data of the major aquatic food sources common to the inhabitants of the regions under consideration. This information on trace element behavior in the environment will help provide a basis for estimating the biological effects of injecting various radioisotopes into these regions.

Two sampling expeditions to the regions of interest were conducted by Battelle-Northwest under the direction of W. L. Templeton. The first was in February, 1967, during the dry season and the second in September, 1967, during the wet season. Typical samples of water, sediment, and aquatic organisms were taken from the major river systems in the regions of the proposed routes in Colombia and Panama. Biological samples obtained during these collection intervals were, for the most part, limited to those species which comprise a major portion of the natives' diet. The samples were either caught by Battelle staff members or purchased from natives and frozen as soon as possible. The biological specimens were shipped frozen to Richland, Washington.

Due to the large number of elements desired, sensitivity required in the analysis, and the limited sample size, a method of neutron activation analysis was employed. The general method employed for the analysis of biological material has

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been described in detail.⁽¹⁾ Briefly, in the case of fish muscle, the method involves the following. Representative samples of red and white muscle tissue weighing several grams were dissected in a manner shown to introduce negligible contamination. The tissue was placed in specially-cleaned polyethylene containers, freeze dried, and irradiated with a thermal neutron exposure of about 10^{17} n/cm² together with aqueous solutions containing known amounts of the elements of interest. After a decay interval of several days, the sample was removed from the irradiation capsule, crushed, mixed with a hot 2% agar solution, and poured into a 1/2 x 2 in. ring to achieve a standard counting geometry. The sample and standards were then counted for ten minutes with a 20 cm³ coaxial Ge(Li) detector to determine the induced activities of ²⁴Na, ⁴²K, and ⁸²Br. A decay interval of about 20 days was then allowed to ensure the complete removal of ⁸²Br. At this time the sample was again counted with a 20 cm³ Ge(Li) diode for 1000 min to determine the activities of ⁵¹Cr, ⁵⁹Fe, ⁶⁰Co, ⁶⁵Zn, ⁷⁵Se, ⁸⁶Rb, ¹³⁴Cs, and ²⁰³Hg. Finally, the sample was counted for 1000 min with an anticoincidence shielded gamma-gamma coincidence multichannel analyzer to determine the activity of ⁴⁶Sc, ⁶⁰Co, ⁶⁵Zn, ^{110m}Ag, ¹²⁴Sb, and ¹³⁴Cs. The activity of each isotope, after applying a suitable decay correction to the sample, was compared with the specific activity of a standard irradiated together with the sample to determine the quantity of

each element present. The three elements cobalt, cesium, and zinc were determined by both the gamma-gamma coincidence method of analysis and with the solid state detector. The excellent agreement (10%) of results obtained by the two instrumental methods confirmed the reliability of the two methods of gamma-ray analysis.

Due to the large number of samples involved and the nature of this survey, it was not feasible to analyze duplicate samples. However, the precision (5-10%) of this method has been demonstrated in the analysis of replicate samples of a standard biological reference material.⁽²⁾ An estimate of the error associated with the determination of each element is presented in Table 1, along with the results. These estimates are based upon counting statistics, self-shielding errors, contamination, volatile loss during processing, and side reactions leading to the same isotope. In all but one case, this latter effect is negligible. In addition to neutron capture by ⁴⁵Sc, a fast neutron reaction on ⁴⁶Ti will produce ⁴⁶Sc; hence, the scandium content reported should be considered an upper limit to the actual value.

The results of all samples analyzed to date are presented in Table 1. The common or local name of the organism is given, together with the name of the river system from which it was taken. All values are reported as micrograms of the element per gram of freeze dried tissue. In several cases, no value is reported either because of detector

TABLE 1. Trace Elemental Composition of Aquatic Organisms from Central and South America

Specimen	River System	µg/g dry tissue													
		Na	K	Rb	Cs	Br	Zn	Se	Co	Fe	Cr	Sc(10 ⁻³)	Sb	Ag	Hg
Aguja	Rio Chico	ND	ND	17	0.029	4.4	27	2.0	0.053	ND	0.03	2.0	0.0002	<0.001	ND
Aguja	Rio Pirre	3000	20,000	23	0.039	19	31	3.7	0.019	28	<0.01	0.26	0.0002	<0.001	1.0 ± 0.1
Boco Chico	Rio Saludo	ND	ND	15	0.015	5.2	25	0.47	0.350	18	0.19	1.0	0.0006	~0.002	ND
Comanata	Rio Chucunaque	ND	ND	15	0.038	ND	18	0.62	0.098	49	0.04	23	0.002	0.004	0.8 ± 0.2
Congo	Rio Pirre	ND	ND	4.3	0.020	7.6	31	1.1	0.023	7.5	0.06	0.51	<0.0001	0.002	ND
Congo	Rio Uruseca	4200	15,000	13	0.028	36	25	1.9	0.260	23	<0.01	0.13	0.0007	<0.001	0.2 ± 0.1
Donsellia	Rio Atrato	ND	ND	18	0.052	8.3	38	0.75	0.038	11	0.01	2.6	0.0006	<0.001	6.1 ± 0.1
Guacoco	Rio Morti-Hydro	3000	17,000	3.4	0.018	12	37	1.1	0.590	24	9.0	0.21	0.0007	0.002	0.3 ± 0.1
Machana	Rio Pirre	2200	15,000	14	0.032	28	65	2.1	0.019	15	0.18	<0.01	0.0008	<0.001	0.2 ± 0.1
Machana	Rio Tuira	3600	20,000	15	0.042	30	39	2.6	0.030	19	<0.01	0.02	0.001	<0.001	0.58 ± 0.08
Mojarro	Rio Membrillo	2000	18,000	19	0.100	4.0	19	1.6	0.013	4.3	0.33	0.03	<0.0001	<0.001	3.8 ± 0.1
Mojarro	Rio Mogue	ND ^(a)	ND	34	0.120	7.0	15	1.6	0.025	ND	0.02	0.8	0.0008	<0.001	ND
Mojarro	Rio Uruseca	2500	19,000	17	0.034	8.4	27	5.2	0.012	4.5	<0.01	0.01	0.0004	<0.001	1.0 ± 0.1
Parbo	Rio Pirre	3200	20,000	24	0.044	23	45	1.9	0.028	52	<0.01	0.16	0.001	<0.001	0.4 ± 0.1
Parbo	Rio Tuira	2900	13,000	27	0.098	27	80	1.2	0.350	27	<0.01	0.29	0.005	<0.001	0.16 ± 0.08
Pez Perro	Rio Pirre	ND	ND	19	0.066	3.7	18	1.1	0.005	ND	0.03	1.6	0.0006	<0.001	ND
Sabaleta	Rio Chucunaque Uala	2300	22,000	32	0.091	8.5	24	1.8	0.002	24	0.34	0.01	0.0006	<0.001	0.4 ± 0.1
Sabaleta	Rio Membrillo	2700	21,000	45	0.170	5.8	33	1.4	0.005	14	<0.01	0.03	0.0006	<0.001	0.59 ± 0.0
Sabaleta	Rio Uruseca	ND	ND	5.0	0.009	7.8	22	4.0	0.120	ND	0.02	2.0	0.0008	ND	ND
Camarons	Rio Chico	ND	ND	6.7	0.018	7.6	120	3.6	0.410	600	0.4	230	0.0009	0.050	ND
Grand Camaron	Rio Pirre	ND	ND	11	0.015	15	56	2.4	0.057	10	0.05	5.1	0.003	0.055	ND
Cayman	Rio Uruseca	ND	ND	14	0.032	9.1	31	1.1	0.004	14	0.32	1.4	0.005	<0.001	ND
Snails	Rio Morti Village	ND	ND	6.2	0.007	16	59	0.87	0.051	100	1.5	4.1	0.001	0.003	ND
Turtle	Rio Pirre	ND	ND	10	0.012	5.2	250	1.7	0.018	100	0.18	5.8	0.004	<0.001	ND
Estimated Error		5%	5%	10%	10%	5%	5%	10%	10%	10%	20%	50%	25%	20%	See Above

a. ND - Did not determine

problems or the loss of a standard during irradiation. The last five samples reported in Table 1 represent aquatic organisms other than fish, and it was not possible to obtain a sample of muscle tissue which was completely free of extraneous material. This was particularly true of Camarons, Camaron Grande, and the snail which had portions of tissue in intimate contact with its gastrointestinal tract. This is reflected in the high scandium content of these samples, a condition which arises from contamination with soil. The range in the trace element contents of the 19 fish reported in Table 1 is summarized in Table 2. The major trace elements Na and K have a rather

narrow range of values, while other essential trace elements, such as Rb, Cs, Br, Se, and Zn vary by an order of magnitude. This is not surprising since an analysis of various

TABLE 2. Range of Trace Element Concentrations in Aquatic Organisms

Element	Range of Elemental Content, ppm	Variation Factor	Number of Analyses
Na	2000 - 4200	2.1	11
K	13,000 - 22,000	1.7	11
Rb	3.4 - 45	13	19
Cs	0.015 - 0.170	11	19
Br	3.7 - 36	10	18
Zn	15 - 65	4.3	19
Se	0.62 - 5.2	8	19
Co	0.002 - 0.590	300	19
Fe	4.3 - 52	12	15
Cr	<0.01 - 9.0	>900	19
Sc	<0.00001 - 0.023	>2300	19
Sb	<0.0001 - 0.005	>50	19
Ag	<0.001 - 0.004	>4	19
Hg	<0.20 - 6.1	>30	13

types of muscle tissue of a silver salmon showed rather substantial variations.⁽³⁾ An interesting result of this work is the high mercury content of several samples. Donsellia, from Colombia, South America, contained as much as 6 ppm Hg. Samples of a given species collected from different locations were quite similar in their trace element content even though large variations occurred between different types of organisms.

This study has been extended with the analysis of biological and river water samples collected in February, 1968. The results of this work, together with information concerning the trace element content of the river water and the major, minor, and trace element concentrations measured by other analytical techniques, have been compiled in a comprehensive report.⁽⁴⁾

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RADIATION CHEMISTRYRATE CONSTANTS OF ORGANIC COMPOUNDS WITH HYDROXYL RADICALS

D. R. Kalkwarf

Since the course of damage in irradiated biochemical systems is determined largely by the relative speeds of the induced chemical processes, understanding and control of this damage requires quantitative information of the rate constants for the reactions involved. Hydroxyl radicals appear to be particularly important reactants in such systems; and rate constants for their reactions with an extensive group of simple and complex biochemicals have been measured utilizing competitive kinetic studies with the dye, eriochlorine.⁽¹⁾ Table 1 lists rate constants for additional reactions investigated in the past year by this method.

TABLE 1. Bimolecular Rate Constants for Reactions of Biochemicals with Hydroxyl Radicals

Compound	Rate Constant ($\times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$)
Salicylate	9.6
Homocysteine	8.1
Mandelate	7.2
Histamine diphosphate	6.2
Mannitol	2.7
Mannose	2.5
Isoleucine	1.9
Sarcosine	1.8
Nicotinate	1.8
Mannose-6-phosphate	1.4
Nicotinamide	1.1
Malonate	0.10

Many organic dyes react rapidly with hydroxyl radicals, and those which are suitable as food additives are of particular interest because they can be used to scavenge hydroxyl radicals in irradiated human tissue. Since these dyes are highly colored themselves, the usual competition with eriochlorine was not sufficiently precise to measure their reaction rate constants with hydroxyl radicals. Therefore, another technique was devised. Each dye was allowed to compete with ethanol and sodium benzoate separately during irradiation of aerated aqueous solutions. Destruction of dye was measured photometrically, and dye absorbance was found to decrease exponentially with absorbed dose in each case. Assuming that all the reactions involved competition for hydroxyl radicals, relative rate constants for the competing reactions could be evaluated by the method described previously.⁽¹⁾ The rate constant for reaction of sodium benzoate with hydroxyl radicals is precisely 2.8 times that for ethanol with hydroxyl radicals.⁽¹⁾ Therefore, only data in which the ratio of relative rate constants having this value were taken to evaluate absolute reaction rate constants with hydroxyl radicals. These values are listed in Table 2.

TABLE 2. Bimolecular Rate Constants for Reactions of Triphenylmethane Dyes with Hydroxyl Radicals

Compound	Rate Constant ($\times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$)
FD&C Green No. 1	1.4
FD&C Green No. 2	1.3
FD&C Violet No. 1	1.2
FD&C Green No. 3	1.1
Patent Blue	0.95
Patent Blue A	0.95
Alkali Fast Green	0.29

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LONG-LIVED ORGANIC RADICALS FORMED BY IRRADIATION OF FD AND C BLUE NO. 2 IN AQUEOUS SOLUTION

D. R. Kalkwarf and R. N. Diebel

As reported earlier,⁽¹⁾ the indigo dye, FD&C Blue No. 2, forms long-lived free radicals in irradiated aqueous solutions and also offers significant protection to biochemical gels subject to radiation-induced liquefaction. Since this substance has been cleared for human consumption as a food coloring, it could prove to be a useful radiation protective agent for many types of living tissue. To anticipate systems where radiation damage could be controlled most effectively by this agent, further information was sought concerning the chemical structure and properties of its free radical.

Examination of the ESR spectra obtained from helium-sparged aqueous solutions of FD&C Blue No. 2 after irradiation showed that free radicals were present throughout the pH

range 7.6 to 13. Radical concentration increased with pH and with addition of ethanol prior to irradiation. Still higher radical yields were obtained by reducing FD&C Blue No. 2 with sodium dithionite, allowing better resolution of hyperfine structure. A spectrum of such a solution is shown in Figure 1. Only the center 19 groups of quintets could be distinguished in the spectra shown by irradiated solutions of the dye due to the lower concentration of radicals; however, since the line spacings and relative intensities were identical with the spectrum of the dithionite-reduced species, it was concluded that identical radicals were formed by the two processes. This was confirmed by comparing the optical absorption spectra of the solutions.

FIGURE 1. ESR Spectrum of $1.00 \times 10^{-3} M$ FD&C Blue No. 2 After Partial Reduction with Sodium Dithionite

The ESR spectrum of the radical together with the chemical conditions required for its formation showed that it was the product of electron addition to the dye. In irradiated solutions, production was largely due to reactions with hydrated electrons formed by water radiolysis; and addition of nitrous oxide to remove these transient species also prevented formation of dye radicals. Reactions with organic reducing radicals such as $\text{CH}_3\dot{\text{C}}\text{HOH}$, derived from hydroxyl-radical attack on ethanol, also produced the same dye radicals by electron transfer. Extensive irradiation of the solutions in the absence of molecular oxygen eventually reduced the radical concentration to zero. Dye-radicals with the same ESR spectra could be generated in these solutions by careful dissolution of oxygen gas, although too much exposure to oxygen elimi-

nated the ESR signal. These results are consistent with the reaction mechanism shown in Figure 2.

In the absence of oxygen, the radicals formed from FD&C Blue No. 2 were stable for days even at pH 7 and room temperature. In the presence of air, the normally rapid reaction of the radical with molecular oxygen could be inhibited by lowering the oxygen solubility with sodium sulfate or raising the solution viscosity with agarose. Both of these effects would also be expected to stabilize the radicals in living tissue. Firm aqueous jellies of agarose containing the dye were also irradiated to determine whether the gel structure might not also inhibit radical disproportionation. At agarose concentrations up to 1%, no inhibition was detected; however, more concentrated gel structures may prove more effective.

FIGURE 2. Proposed Reactions of FD&C Blue No. 2 in Irradiated Aqueous Solutions

Due to its ability to form a long-lived radical, FD&C Blue No. 2 can at least slow down the chain of reactions leading to radiobiological damage so that natural repair mechanisms can be more effective. Further studies will be directed toward determining whether this dye can be utilized to completely terminate

radical chain-reactions before any permanent damage occurs.

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REDUCING RADICALS FORMED DURING GAMMA RADIOLYSIS
OF SELECTED BIOCHEMICALS

R. N. Diebel

Previous work examined the use of nitrobenzene radical ions as indicators for production of reducing species⁽¹⁾ in methanol, ethanol, serine, valine and alanine. Results have now been obtained for histidine, proline, hydroxyproline, mannitol, glucose, thymine, and citric acid. The results are summarized in Table 1.

The enhancement of the ESR signal amplitude in the basic solution of $10^{-3}M$ nitrobenzene is due to the scavenging of OH radical by the added solute. Production of an ESR signal in the presence of nitrous oxide (N_2O), an added solute, is the evidence for production of a reducing species (radical?).

The positive results for methanol, ethanol and serine might seem to indicate that a primary hydroxyl group can produce a reducing species, but since glucose and citric acid do not give reducing species, the presence

of a hydroxyl group is obviously not a sufficient requirement. In addition, the nonhydroxylated amino acids, alanine and proline, produce some reducing species. It is not yet possible to say whether any specific chemical group is sufficient or necessary for achieving a reducing species when attacked by radiolytically produced hydroxyl radicals.

The enhancement of the ESR signals appears to be a combination of hydroxyl radical scavenging and production of reducing species. This can be seen by comparing the rate constants for reactions with hydroxyl radical^(2,3) with Table 1. The only exception is thymine, which has a large rate constant for reaction with OH but did not enhance the ESR signal. This result can probably be explained by the large difference in pH, i.e., 12 here versus 7 for the rate constant data.

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TABLE 1. Effect of Selected Solutes on Production of ESR Signals from Irradiated Aqueous Nitrobenzene Solution

<u>Solute</u>	<u>pH</u>	<u>ESR Enhancement</u>	<u>ESR in Presence of N_2O</u>
Methanol or ethanol	11	+++	+++
Serine	11	+++	+++
Valine	11	++	0
Histidine	11	+++	0
Proline	11	++	+
Hydroxylproline	11	++	++
Thymine	12	+ (?)	0
Citric Acid	11	0	0
Mannitol	11	+++	+
Glucose	10.9	++	0

The SCR conducts only during the discharge of C7 into the ignitor and is triggered into conduction by a positive gate pulse from the pulse transformer, T-2.

To initiate a discharge cycle, a positive pulse from either the input connector or the manual switch appears on the base of Q1, a normally "ON" transistor.

Transistor Q2 conducts when Q1 is OFF, and emitter follower Q3 provides current gain to give the necessary trigger current to the pulse transformer. Diode D8 protects the SCR gate from pulse transformer reverse polarity transients and diodes D1 and D2 provide a positive-going logical "OR" function.

The flash lamp is placed parallel to the sample cell. For optical analysis in the visible range, the light source is a 300 W quartz-iodine lamp, for the ultraviolet, a 150 W, miniature, pressure, sealed beam, xenon short arc lamp (Varian 150 × 8P) is used. The

analysis light passes through the cell into a 1 m, Czerny-Turner monochromator. Optical absorbance is measured with photomultiplier tubes (R212 or R213) mounted on a polychromator housing attached to the exit window of the monochromator. In this way, more than one wavelength may be monitored at a time using a dual beam oscilloscope or multiple entry digital memory oscilloscope. Photomultipliers are directly coupled to the oscilloscope, the signal from the analysis light beam being nulled prior to the flash. Subsequently, absorption caused by the formation of a transient during the flash is represented as a small (1 to 10%) change on a large dc signal level.

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FLASH PHOTOLYSIS OF AQUEOUS SOLUTION OF HYDROGEN
PEROXIDE AND PHENYLALANINE

W. D. Felix

The radiation chemistry of amino acids is an active area of study because of the obvious direct implications to living systems. Heretofore the major fast reaction studies have dealt with the reactions of hydrated electrons with the amino acids; much less data is available on the reactions of hydroxyl radicals with amino acids. Even less data are extant for such reactions in oxygenated solution.

The flash photolysis technique is a convenient method for the study of transient radical reactions peculiar to radiation chemistry. Hydroxyl radicals are generated when hydrogen peroxide solutions are flashed. This report is concerned with the radicals formed during photolysis of hydrogen peroxide in oxygenated aqueous solution, their reactions with hydrogen peroxide and each other, and the reactions of the intermediate radical derivatives of phenylalanine.

EXPERIMENTAL

The apparatus used for flash photolysis was the same as that described in a separate contribution to this annual report.⁽¹⁾ Hydrogen peroxide and phenylalanine were reagent grade and used without further purification. All water was doubly distilled.

RESULTS AND DISCUSSION

Photolysis of an aqueous solution of hydrogen peroxide results in the formation of hydroxyl radicals by a mechanism not completely understood which is represented here by

In neutral solution, the hydroperoxy ion, O_2^- , has an optical absorption peak at 240 nm with an absorptivity of $1060\text{M}^{-1}\text{cm}^{-1}$.⁽²⁾ Flash photolysis of hydrogen peroxide resulted in a species having similar characteristics and which is therefore ascribed to the hydroperoxy ion. This ion exhibited a rate of decay that appeared to be partly dependent on hydrogen peroxide concentration. A possible mechanism for the hydrogen peroxide system following the flash is

$$k_2 = 2.3 \times 10^7 \text{ (3)}$$

$$k_5 = 1.7 \times 10^7 \text{ (3)}$$

To test this mechanism, the experimental decay curves at 250 nm and 260 nm were compared with curves synthesized by a digital-analog simulation computer program, MIMIC.^(4,5) Values of k_4 were modified until a fit compatible with the experimental data was obtained. The best fit, as shown in Figure 1, gave $k_4 = 5.2 \times 10^6$. Since the absorptivity of hydrogen peroxide at 250 nm is only about $20 \text{ M}^{-1} \text{ cm}^{-1}$,⁽⁶⁾ the apparent change in O_2^- absorption at 250 nm due to a decrease in the hydrogen peroxide concentration was ignored.

The introduction of phenylalanine into the hydrogen peroxide system resulted in a new transient species. Phenylalanine is known to react with hydroxyl radicals, a reaction rate constant having been reported, $K_6 = (9.5 \pm 1.5) \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ in deaerated water.⁽⁷⁾

FIGURE 1. Experimental Decay Curve for O_2^- - Compared with Synthesized Decay, Using $k_{\text{O}_2^- + \text{O}_2^-} = 1.7 \times 10^7$ and $k_{\text{O}_2^- + \text{HOOH}} = 5.2 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$.

In a solution of phenylalanine at $1 \times 10^{-4} \text{ M}$ and HOOH at $1 \times 10^{-3} \text{ M}$, the ratio of reaction rates, k_6 (phenylalanine) / k_2 (HOOH) is 42. Under these conditions, Reaction (6) should predominate.

Photolysis of phenylalanine in the presence of hydrogen peroxide, resulted in the formation of a transient for which absorption spectra are presented in Figure 2. Tailing from the flash lamp precluded observations at times shorter than about 200 μsec . The negative absorption at 350 nm is presently unexplained. Since phenylalanine shows negligible absorption in this region, the negative absorption could not be caused by a decrease in the phenylalanine concentration.

In oxygenated solution, aromatic rings are known to react with hydroxyl radicals to form hydroxycyclohexadienyl radicals, which,

FIGURE 2. Absorption Spectra of Transient Species in Flash Photolysed Aqueous, Aerated Solution of Phenylalanine ($1 \times 10^{-3} \text{ M}$).

in turn, react with oxygen to form the hydroxycyclohexadienyl peroxy radical.⁽⁸⁾ A probable mechanism for the reactions of the

phenylalanine-hydrogen peroxide aqueous system would include the Reactions (1) through (5) plus the aromatic ring reactions

Similar reactions of benzene indicate that Reactions (7) and (8) would be very rapid and would be completed within the 200 μsec time limit imposed by the lamp flash. Thus, the transient observed in the ultraviolet in aerated solutions of flash irradiated phenylalanine is probably the hydroxycyclohexadienyl peroxy radical. The hydroxycyclohexadienyl peroxy radical of benzene showed decay characteristics of a second order reaction with a relatively long half-life of tenths of milliseconds. Its absorption peak was at 275 to 285 nm.⁽⁸⁾

Decay of the hydroxycyclohexadienyl peroxy radical of phenylalanine at 270 nm cannot be readily ascribed to either a first or second order reaction. Kinetic plots are given in Figures 3 and 4. Both the first and second order tests are apparently satisfied over the initial decay range. Analysis of the kinetics is complicated by the presence of a long-lived species having an

FIGURE 3. First-Order Kinetic Test of Decay of Transient at 270 nm.

absorption band in the same region. As shown in Figure 2, decay to the 1.2 msec level is rapid, but further changes in absorption are slow. This would indicate either a long-lived transient present concurrently with the hydroxycyclohexadienyl peroxy radical or that the peroxy radical decays to the long-lived transient.

FIGURE 4. Second-Order Kinetic Test of Decay of Transient at 270 nm.

The nondefinitive results of the kinetic order tests leaves open the possibility of mixed dependence. A plausible mechanism would be the reaction of the peroxy radical with itself to form a peroxide

and self-decomposition to a phenol and the hydroperoxy radical

Further reasonable speculation on the nature and kinetics of the species present cannot be made until more quantitative information on the product concentrations is known.

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RADIOLOGICAL PHYSICSINTRODUCTION TO RADIATION DOSIMETRY

W. C. Roesch and W. A. Glass

We are preparing an introductory textbook on radiation dosimetry to be entitled "Introduction to Radiation Dosimetry." The book grew out of a lecture course in radiation dosimetry given in the Department of Radiology of the University of Washington since 1953. G. N. Whyte's "Principles of Radiation Dosimetry"⁽¹⁾ served as the textbook for this course, after its publication in 1959. Its usefulness was impaired, however, when in 1962 the International Commission on Radiological Units and Measurements (ICRU) issued recommendations for new quantities and for new definitions of old quantities used in radiation dosimetry. These changes required so much lecture time to explain and to integrate with the older material that a next text was indicated. Doctor Whyte's untimely death prevented him from revising his book.

The ICRU was much influenced in preparing its new recommendations by a mathematical model of the radiation field and its relation to the quantities used in dosimetry.⁽²⁾ The model showed that one could understand the absorption of radiation energy in matter by studying the flow of energy in the radiation field and its transformation from one form of radiation to another. We have used the ideas of the model in the present book. The power of

this approach becomes apparent when applied, for example, to cavity theory. It substitutes a single analysis for all cavity sizes in place of the cluster of ad hoc assumptions that have usually been used in the past. Measurement of X and gamma rays, neutrons, radionuclides and charged-particle beams are now all treated in nearly the same way. The same formulas as before result, of course, but they are now evident as easily picturable limiting cases of a single coherent theory. It is also possible to discuss more easily such things as the delta-ray effect, cavity perturbation, absorption of primary radiation in the cavity, etc.

The first chapter reviews the physics of ionizing radiation and its interaction with matter, emphasizing those aspects directly applicable to dosimetry. The next chapter introduces and develops the concept of the radiation field. The discussion of dosimetry begins in the third chapter with the definition of absorbed dose and derivations of the relations between dose and the radiation field quantities. Special attention is given to the behavior of the dose and kerma at interfaces between media. Cavity theory is developed in a general way, with the Bragg-Gray principle treated as a limiting case of the general theory.

The next chapter describes practical instrumentation. The emphasis in this book is on the initial transfer of energy from the radiation field to the sensitive part of the instrument. How the energy is employed to produce instrument readings is considered only in an elementary way. The next four chapters deal with the dosimetry of photons, radioactive materials, neutrons and charged-particle beams. The next chapter concerns dosimetry such as required at high-energy accelerators or for space radiation. The ninth chapter goes a step beyond "classical" dosimetry and discusses concepts and quantities other than absorbed dose that may be useful in studying the effects of radiation on matter. That dose alone is not enough is evident from the observation that equal doses of different radiations often produce unequal or different effects. Because research in these extensions of dosimetry is very active now, it is not possible to write a definitive chapter about it. Nevertheless, we have tried to

attack the subject in such a fundamental way that our treatment will be compatible with future research results. The last chapter is a brief survey of some of the applications of dosimetry.

There is a set of problems at the end of each chapter. These problems serve both to illustrate the material in the text and to present many of the typical applications. We present quite a mixture of units in the problems to accustom the student to the profusion encountered in practice. The three special units of dosimetry, the rad, the roentgen and the curie are used frequently; however, we often use their equivalents in other units also.

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HIT THEORY AND MICRODOSIMETRY*

W. C. Roesch

The statistics of randomly occurring events play an important role in the biophysical analysis of radiation effects because most radiation absorption events are so potent that only a few are required for observable effects, and these small numbers are subject to large statistical fluctuations. To deduce survival curves similar to those found experimentally, classical hit theory assumed that a certain number of hits in a certain number of targets were necessary and sufficient to cause death of an entity. Recently (Roesch, Radiation Research Society meeting, 1967) a hit theory based on lethality from either single hits or pairs of hits was shown to predict correctly survival curves and also dose-rate and fractionation effects. The theory contains parameters characteristic of the probabilities of the single-hit and paired-hit lethal events. The present paper is concerned with the connection of these probabilities to the LET, event size, or local energy density produced in the irradiated medium and the resulting relations among survival curves, dose-rate and fractionation effects, etc.

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FOLDING OF DISTRIBUTIONS

W. C. Roesch

A rapid and efficient method was developed for performing the folding process for the summing of Poisson series.

Last year, I reported a method for summing the Poisson series that appear in the theories of local energy density and of charged-particle energy straggling.⁽¹⁾ The method employs the well known folding operation

$$F(Y) = \int_0^Y G(Y-X) H(X) dx \quad (1)$$

which produces a new function, F,

from two known ones, G and H; all functions are restricted to positive arguments. In summing a Poisson series, a certain function is folded with itself; the result folded with itself; etc. This process is called repeated folding. The present report is of an efficient means of performing the folding process, particularly for repeated folding.

The function resulting from folding has a greater range and shows less detail than either of the starting functions. By the "range" of a function we mean the distance along the abscissa from the origin to the last non-zero value of the function. The range of the function resulting from folding equals the sum of the ranges of the component functions. The example of folding given in Figure 1 illustrates the increase in range. Also, the H-function in the figure has a sharp projection on it, while no such sharp detail appears in the resulting F-function.

In performing folding, the continuous functions are replaced by histograms. The method of folding that was developed employs a non-linear series of steps along the abscissa for the histogram. The series starts with twenty 1-unit steps. Then there are one 2-unit steps, ten 4-unit, ten 8-unit, etc. The series ends with ten 2^{19} -unit steps. If each unit is 1 eV, the last steps are 0.524 MeV wide, and the range covered is 0 to 9.96 MeV.

FIGURE 1. An Example of the Folding of Distributions

The steps are 50 to 10% of the value of the abscissa at the position of the step. The loss of detail and increase in range with folding justify the use of the progressively larger steps. Also, since fewer steps are required for a given range, less computer time is required than for equal size steps. Kellerer⁽²⁾ described use of logarithmic and square root scales; the piece-wise linear scale described here was chosen in preference to these other non-linear scales, because it appeared to require less computer time.

The mean of the F-function equals the sum of the means of the G and H-functions; similarly, the variance of F equals the sum of the variances. On the other hand the area under F equals the products of the areas under G and H. Usually, in repeated foldings, the functions are all probabilities; the areas of G and H are unity and hence that of F is unity. However, due to round-off error for example, an area may not be exactly unity. Then the area of the resulting function may rapidly diverge from unity in the course of repeated folding. For example, if an area is less than 1.0 by only 1 ppm, after 20 repeat foldings the resulting area will be 0.35 instead of 1.0. Continued checking and adjusting of the normalization of the curves is required during repeated folding.

Computer subroutines were prepared for:

- Folding any two curves
- Folding a curve with itself [slightly faster than using (a) for the purpose]

- Tabulating
- Plotting (linear or log scale)
- Calculating the mean and variance of the result.

Another subroutine was developed for summing Poisson series by the method described last year. The new subroutines replaced ones that used uniform histogram steps along the abscissa. The time for folding a curve with itself was reduced from about 2 sec to about 0.05 sec. The time for summing a series was reduced from about 30 sec to less than 1 sec. The reduction in the computer time required made feasible some of the

studies described elsewhere in this report.

Figure 2 shows the results of a typical test used to show that the programs were working properly. The tests employ the Poisson functions, $P(X,N)$. Defined by

$$P(X,N) = \frac{X^{(N-1)}}{(N-1)!} e^{-X} \quad (2)$$

It is easily shown that folding Poisson functions of order N and M together gives the Poisson function of order $N+M$, i.e.,

$$P(Y,N+M) = \int_0^Y P(Y-X,N) P(X,M) dx \quad (3)$$

FIGURE 2. A Test of the Folding Program.

The ○ in Figure 2 gives the result of four repetitions of folding $P(X,1)$. The result should be $P(X,16)$. The ● in the figure give $P(X,16)$ calculated from Equation (2). The agreement is satisfactory and is typical of the agreement found in such tests.

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ENERGY ABSORPTION STRAGGLING

W. C. Roesch and W. A. Glass

The theory of multiple energy losses of charged particles is studied and then applied to experimental data on the energy loss distributions of protons in thin layers. A discussion of delta-ray losses from thin layers is given.

The folding procedures and computer routines that we have developed^(1,2) are for use in analyzing charged-particle stopping and energy straggling experiments and, ultimately, for use in radiobiological investigations. This paper reports some studies made of the data of Glass and Samsky.⁽³⁾ These authors reported distributions of ionization (reported as equivalent energy loss) produced by protons in thin, plane layers of tissue equivalent gas.

Glass and Samsky measured pulse heights in a proportional counter. A chain of events takes place between the passage of a charged particle and the appearance of a pulse in the counter, and each event in the chain is subject to random fluctu-

ations.^(4,5) Events in the chain are:

1. Energy is lost by the proton; the number and magnitudes of the losses are random.
2. Energy is absorbed in the sensitive volume; for short range secondary particles, all of the energy lost by the proton is absorbed in the sensitive volume, but losses of some delta rays through the surface of the volume are random.
3. Some of the absorbed energy appears as ionization; the number of ions produced by a given absorbed energy is random.
4. The number of ions is increased by the action of the proportional

counter; the number of ions resulting from a given initial number is random.

There may be other random influences, e.g. noise in the electronic system, but the above appear to be the principal ones for the present work.

Kellerer⁽⁵⁾ made an analysis-of-variance study of the various random influences and concluded that the major one for the distribution of ionization in thin layers is the first above, fluctuations in the number and magnitudes of the proton energy losses. Kellerer had no way of estimating the effects of delta-ray loss. The aim of the present work was to study the effects of energy loss fluctuations and, to a lesser extent, the effects of delta-ray loss; it was assumed that there were no fluctuations in ionization or multiplication (3 and 4 above).

As reported last year,⁽¹⁾ the distribution $N(T, m)$ of proton energy losses, T , in a thin layer where the average number of losses is m , is found from the distribution of losses in individual collisions, $N_0(T)$. First, the distribution $N(T, m/2^i)$ is found, where i is chosen large enough that $m/2^i$ is very small; then to good accuracy

$$N(T, m/2^i) = e^{-(m/2^i)} [\delta(T) + (m/2^i) N_0(T)] \quad (1)$$

Then $N(T, m/2^i)$ is folded with itself; the result is $N(T, m/2^{i-1})$. The latter is folded with itself to give $N(T, m/2^{i-2})$. After i repetitions of this process, one obtains $N(T, m)$.

Stopping-power theory and experiment give the product of the mean energy loss in individual losses and the mean number of losses per unit path length; the former is the mean of the N_0 distribution, the latter is the quotient of m by the thickness of the layer. Consequently, knowledge of N_0 and of the stopping power suffice for the calculation of N . Also, the inverse proportion between m and the mean of N_0 required by the stopping power means that any uncertainties in N_0 are to a considerable extent offset because they affect the choice of m . This is fortunate, because N_0 is not known very well. Stopping power theory indicates that for losses above a few hundred eV and up to the kinematic maximum energy loss, N_0 is inversely proportional to T^2 . At lower energies N_0 rises, with decreasing energy, to a peak(s) and then falls to zero; little is known about N_0 in the peak region.

For this study, we approximated the peak region of N_0 by

$$N_0^{(1)}(T) = (n/T_p) (nT/T_p)^n e^{-(nT/T_p)} / n! \quad (2)$$

This curve has a peak at T_p . The parameter n , which we gave integral values, controls the width of the curve; the width decreases with increasing n . At high energies, up to the kinematic maximum loss, we took

$$N_0^{(2)}(T) = k/T^2 \quad (3)$$

We chose k so that $N_0^{(1)} = N_0^{(2)}$ at the energy dividing the two regions.

This energy and k were chosen so that the mean of N_0 , T_m , was a value we could choose.

Figures 1 through 3 show the effects of changes in the parameters in our approximation to N_0 . In each case the figure(a) gives N_0 for 2-MeV protons, and the figure(b) gives N for a 0.1μ layer (unit density equivalent). In Figure 1, $n = 3$ and $T_m = 60$ eV; the energy of the peak, T_p , is changed from 22 to 33 eV. Increasing the peak energy of N_0 shifts N to higher energies. In Figure 2, $T_p = 22$ eV and $T_m = 60$ eV; $n = 1, 3$, and 5 to change the width of N_0 . Increasing the width of N_0 (decreasing n) shifts the peak of N to higher energies. In Figure 3, $T_p = 22$ eV and $n = 3$; the mean energy, T_m , equals 40, 60, and 80 eV. Increasing the average energy shifts N to lower energies.

Another qualitative generalization about Figures 1 through 3 is that the variations in the event distributions, N , are substantially less than those in the proton energy loss distributions, N_0 , from which they were generated. To a large extent this reduced variation is due to the inverse relation between the mean number of losses, m , and the mean of N_0 noted above.

Figure 4 shows an important aspect of the delta-ray loss phenomenon. The solid line is the event distribution, N , without an allowance for delta-ray loss. The dashed line shows the alteration produced by a change in N_0 for large energy losses. The energy losses under the N_0 curve and between the kinematic maximum

loss and the energy of an electron whose range equals the thickness of the layer were removed and placed as a delta function at a loss equal to the latter energy. The folding for the dashed curve was performed for the same average number of losses, m , as for the solid curve, even though the change of N_0 just described changes the mean of N_0 and hence changes m . The figure shows that the changes in N produced by alterations in the high-energy part of N_0 such as might be due to delta-ray loss are mostly changes on the high-energy side of the peak. Roughly, one expects that the effect of delta rays on N will be a shift, [Figure 3(b)], due to a change in the mean energy loss plus a change in the shape of the high-energy side of the curve.

Figure 5 shows a typical example of the current status of our work in trying to fit the data of Glass and Samsky. The solid line is their experimental curve. The dotted line is a spectrum calculated as described above without allowance for delta-ray loss. The peak of the N_0 curve is at 22 eV and the mean energy loss is 60 eV. These energies give as good a fit as any we have tried, and they agree with the values found by Rauth and Simpson⁽⁶⁾ for low-energy electrons. The dashed curve includes an allowance for delta-ray loss on the N_0 spectrum used for the dotted line. The area under N_0 at energies greater than that of the electron whose range equals the thickness of the layer was redistributed over the spectrum below that energy.

FIGURE 1.a. Effect of Displacing the Peak of the Distribution of Individual Energy Losses, T_p .

FIGURE 1.b. Effect of Displacing the Peak of the Distribution of Individual Energy Losses, T_p . The Distribution of Energy Losses in a 0.1μ Layer. ($n = 3$, $T_m = 60$ eV)

FIGURE 2.a. Effect of Changing the Width of the Peak in the Distribution of Individual Energy Losses (changing n). ($T_p = 22$ eV, $T_m = 60$ eV, 2 MeV protons)

FIGURE 2.b. Effect of Changing the Width of the Peak in the Distribution of Individual Energy Losses (changing n). The Distribution of Energy Losses in a 0.1μ Layer. ($T_p = 22$ eV, $T_m = 60$ eV, 2 MeV protons)

FIGURE 3.a. Effect of Changing the Mean Energy of the Distribution of Individual Energy Losses, T_m . ($n = 3$, $T_p = 22$ eV, 2 MeV protons)

FIGURE 3.b. Effect of Changing the Mean Energy of the Distribution of Individual Energy Losses, T_m . The Distribution of Energy Losses in a 0.1μ Layer. ($n = 3$, $T_p = 22$ eV, 2 MeV protons)

FIGURE 4. Effect of Changes in the High-Energy Side of the Distribution of Individual Energy Losses.

FIGURE 5. Comparison of Theory and Experiment for an Individual Energy Loss Distribution. (1.55 MeV protons in a 0.1 μ layer) ($n = 1$, $T_p = 22$ eV, $T_m = 60$ eV)

This time (in contrast to Figure 4) the folding was performed for the average number of losses determined from the altered N_0 ; hence, the shift in N to higher energies. While there are evidently further corrections needed to get a more perfect fit to the experimental data, we feel that all the principal features of the data are explained by our calculations.

In place of fitting individual distributions, another approach to studying the data is to fit statistical parameters of the distributions as a function of proton energy. The points in Figure 6 show the relative

FIGURE 6. Comparison of Theory and Experiment for the Relative Standard Deviation of Proton Energy Loss Distributions in 0.1μ Layers. ($n = 1$, $T_p = 22$ eV, $T_m = 60$ eV)

standard deviations obtained experimentally for protons in a 0.1μ layer. The curve was calculated from N_0 curves modified for delta-ray loss as just described. Again, the principal features of the data are explained by the calculations.

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ENERGY ABSORPTION SPECTRA IN A UNIFORM MEDIUM

L. A. Braby, W. C. Roesch, and W. A. Glass

Gas proportional counters are commonly used to measure energy absorption spectra for small sites in an irradiated medium.⁽¹⁾ Rossi⁽¹⁾ pointed out that the difference in density between the wall and the gas of the counter would distort some of the events in the counter. For example, a strongly scattered charged particle could re-enter the counter, while in the small site simulated by the counter re-entry would not occur. Fano⁽²⁾ showed the absorbed dose is unchanged by density changes; hence, the absorbed dose for the counter, the quotient of the mean of the energy absorption spectrum, and the mass of gas in the counter, would be the same in the counter and in the site it simulated. Therefore, when re-entry does not occur in the actual site, there must be another event(s) at some other time(s) that deposits as much energy as the re-entrant particle deposits in the counter. The time resolution of proportional counters is far too poor to distinguish between the first traversal and the re-entry of a single particle. Hence, the counter would produce a single large event for the two, while the site simulated would have undergone more than one, smaller events. Consequently, the event spectrum obtained from the counter is shifted to higher event sizes than the true spectrum in the site. (Other phenomena can produce similar effects, for example: delta rays, other secondary charged particles, shower phenomena,

etc.) Rossi was unable to estimate the magnitude of the resulting spectral shift.

The present experiment was done to obtain some idea of the magnitude of the spectral shift resulting from the density difference between the walls and the gas of the counter. The experiment consisted in comparing the spectrum produced in a solid-wall counter with the spectrum produced in a similar counter in which there was no difference in density between the gas and the wall (a gas-wall counter).

To make the absorbed dose the same in the two counters, the sensitive volumes of the two counters must be surrounded by material of the same composition out to the greatest distance from which a charged particle can penetrate to the sensitive volume, and the same number and energy spectra of charged particles must be emitted per unit mass in the materials of both counters. The wall of our solid-wall counter was Lucite; the gas was 37.3% carbon dioxide and 62.7% ethylene. The compositions of the two materials are not identical, but their mass straggling powers for electrons between 10 and 150 keV differ by less than 0.5%. We chose ^{14}C beta rays for the radiation in both cases. The ^{14}C was incorporated in the Lucite and in the ethylene. The maximum range of any ^{14}C beta ray is 51 cm at 20 °C and 310 torr in the gas used. The sensitive volume of the gas-wall counter was surrounded by this much gas by suspending it in

the center of a 122 cm diameter spherical tank filled with the gas. The activity per unit mass in the ethylene equaled that in the Lucite, so the data needed no correction. This is not quite right in principle, because it treats incorrectly the contribution of beta rays emitted by the gas inside the detector in the case of the solid-wall counter; however, we estimate that only about one in a million of the events are due to beta rays emitted in the gas in this case, a negligible amount.

The experiment was performed with a grid-walled cylindrical proportional counter⁽³⁾ 1 cm in diameter with field tubes that limited its effective length to 1 cm. When mounted in the center of the spherical tank mentioned above, this counter constituted the gas-wall counter. To form the solid-wall counter, a cylindrical Lucite sleeve was slipped along guide wires until it surrounded the grid-wall system. The inner wall of Lucite was about 1 1/2 grid spacings from the grid structure. The Lucite tube was about 5 cm long; it extended two counter lengths beyond each end of the sensitive volume. Hence, it did not completely cover the ends with solid material. Thus our experiment can only indicate how the spectrum is altered and give a lower limit to the magnitude of the change; it cannot be used to correct results obtained with a completely solid-wall counter. The gain of the counter was determined with and without the Lucite wall by measuring the pulse heights for a beam of alpha particles passed

through the center of the counter. The gain proved to be unchanged by the presence of the wall, which we consider shows that the walls do not produce any change in the proportional counting action that could affect the results.

The results are given in Figure 1. The ordinate is the product of the energy absorbed and the number of events per energy interval; the abscissa is the logarithm of the energy absorbed. For data plotted this way, equal areas anywhere under the curves represent equal number of events. The curves extend from about 350 eV (the smallest energy we could measure) to about 30 keV, the maximum energy an electron can lose in the detector. The results show that the solid-wall does indeed distort the spectrum by shifting events to larger energies. In addition to the obvious change in shape, there are 10% more events above 350 eV under

FIGURE 1. The Effect of a Solid Wall on Energy Absorption Spectra

the solid-wall-counter curve. We feel that in general the effects of the solid walls are too large to neglect. Measurements of radiation consisting mostly of low energy electrons will have to be made with counters that somehow approximate the conditions of the gas-wall counter; we are investigating such counters.

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ENERGY ABSORPTION DISTRIBUTIONS IN A CYLINDER OF UNIT ELONGATION FOR MONOENERGETIC PROTONS

W. A. Glass and L. A. Braby

We have previously reported results for energy absorption distributions in thin layers of absorbers^(1,2) and have discussed the importance of differentiating between the energy lost by the proton and that absorbed by the thin absorber. The difference between these two quantities is principally due to energy carried into and out of the absorber by δ -rays. Since the energy and angular distribution of these δ -rays is as yet unknown, and since information on the range and multiple scattering of low energy electrons is very meager, we have experimentally determined energy absorption spectra for a geometry not greatly different from the spherical shape normally used in microdosimetry. This was an effort to answer the question of just how much the interplay

of geometry and the finite radial extent of the proton track would influence calculated distributions based on zero radial extent of the proton track. In calculation of local energy deposition spectra, such as proposed by Caswell⁽³⁾ and Turner,⁽⁴⁾ the proton track is treated as though the deposited energy is locally concentrated along the track. We have demonstrated that this is not a valid picture of the energy deposited by protons. Both the mean energy deposited along various chord lengths and the straggling distributions show rather dramatic effects that can be explained only on the basis of rather large amounts of energy being deposited by δ -rays. Results of this experiment indicate that measurable amounts of energy are

deposited as far as $1200 \text{ \AA}$ from the path of a 1.7 MeV proton.

The experiment consists of measuring the energy deposition spectrum of 1.7 MeV protons in a cylindrical absorber of unit elongation and 0.25μ diameter. The protons were collimated to a microbeam with a lateral uncertainty of only $15 \text{ \AA}$. The absorption site was a grid-walled ($\sim 95\%$ transmission for electrons) proportional counter mounted on a micrometer screw so that it could be traversed across the proton beam. Energy absorption spectra were measured as the beam traversed various chords of the cylinder. Figure 1 shows some representative spectra with an indication of the proton path through the absorber. The most obvious observation is that the mean energy deposited by tracks near the edge of the absorber is considerably greater than that predicted on the basis of stopping power and the known path length. For example, if the protons traverse the counter along a chord equal to $1/4$ the diameter, the absorbed energy is 54% greater than the product of path length and stopping power. Such a discrepancy can be accounted for only by assuming that energy is carried into the absorber by δ -rays created outside the absorbing site. An explanation of the fact that more energy is carried into the absorber by δ -rays than is lost from the absorber by the same mechanism is not at first obvious. However, if one treats the proton track as a cylinder in which energy is being deposited and then considers the intersection of such a "cylinder

of energy" with the absorber, you find that the gain in energy due to δ -rays is greater than the loss.

Figure 2 shows the systematic increase of measured mean energy losses over that expected on the basis of completely localized energy deposition along the proton path. Since proportional counters are relative instruments we had to assume that there were no δ -ray effects for tracks crossing the diameter of the counter--not a completely valid assumption. Thus, the data plotted in Figure 2 were normalized to $x \cdot S$ at the value of 4.4 keV mean absorbed energy.

In the theory of energy loss straggling⁽⁵⁾ there are certain relationships which exist between the moments of the straggling distribution and the moments of the distribution, $P(\epsilon)$, the energies transferred to the absorber by individual electrons ejected in primary interactions between proton and atoms of the absorber. This distribution will have a mean value, $\bar{\epsilon}$, and a second moment $\bar{\epsilon}^2$; etc. The straggling distribution of absorbed energies, Δ , (each made up of a random combination of ϵ 's) may also be characterized by a normalized distribution, $P(\Delta)$, with a mean absorbed energy, $\bar{\Delta}$, and a standard deviation, σ . If the mean absorbed energy, $\bar{\Delta}$, is the result of an average number, $\bar{n}$, of primary collisions then the following properties of the distributions result:

$$\bar{\Delta} = \bar{n} \bar{\epsilon}$$

$$\text{and } \sigma^2 = \bar{n} \bar{\epsilon}^2.$$

FIGURE 1. Energy Absorption Spectra for Various Paths of 1.7 Mev Protons Through a 0.25 μ Cylindrical Absorber.

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FIGURE 2. Observed Mean Absorbed Energies in a 0.25μ Cylinder due to the Passage of 1.7 MeV Protons Versus the Product of Chord Length and Stopping Power.

Thus, $\frac{\sigma^2}{\bar{\Delta}} = \frac{\overline{\epsilon^2}}{\bar{\epsilon}}$; i.e., the ratio of

the mean absorbed energy to its variance is equal to the ratio of the first and second moments of the distributions of energies transferred by individual primary collisions and by the resulting δ -ray. Therefore, so long as the contribution to the absorbed energy, Δ , from individual primary interactions remains constant [i.e., so long as $P(\epsilon)$ does not change], the ratio of $\sigma^2/\bar{\Delta}$ will remain constant. However, as geometrical factors become more important the distribution of ϵ is altered and hence its moments will change. This change will be reflected in the experimental quantity $\sigma^2/\bar{\Delta}$. Note that $P(\epsilon)$ is not as yet a measured quantity. We have experiments now in progress* which attack this problem;

but, at this time we can determine (through $\sigma^2/\bar{\Delta}$) only the ratio of the first and second moments of the distribution.

Figure 3 shows that the ratio $\sigma^2/\bar{\Delta}$ for the absorbed energy distributions remains nearly constant up to a point where the mean energy loss is equal to about one-half the maximum, i.e., for chord length greater than the radius of the cylindrical absorber (0.125μ). This implies that $\overline{\epsilon^2}/\bar{\epsilon}$ does not change in this region of chord lengths which is fair evidence that geometry is not a critical factor until the proton path length becomes about equal to the radius of the absorber. For shorter chords, or for proton tracks nearer the edge of the absorber, the measured ratio $\sigma^2/\bar{\Delta}$ increases with decreasing chord length. This implies that the distribution of energies absorbed from individual interactions, $P(\epsilon)$, is changing in such a way that $\overline{\epsilon^2}/\bar{\epsilon}$ is increasing. That is,

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FIGURE 3. Experimental Values of $\sigma^2/\bar{\Delta}$ for 1.7 MeV Protons Along Various Chords of a 0.25μ Cylindrical Absorber

* L. H. Toburen, et al. "Electron Ejection from Gaseous Targets by High-Energy Proton Impact," pp. 200 et seq.

the distribution is becoming relatively broader, which is not surprising since $P(\epsilon)$ represents a combination of the energies involved in the primary proton interactions with the geometry of the absorption site and this geometry is changing rapidly near the edge of the absorber.

It must be kept in mind that this experiment has thus far been done only for one absorber size and for one proton energy. It is not possible at this time to predict whether this type of experiment will be of great benefit in understanding the deposition of energy by δ -rays. However, we do see that δ -rays present a serious problem that must be dealt with in any realistic calculation of energy deposition spectrum.

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PRELIMINARY INVESTIGATION
OF THE RADIAL EXTENT OF PROTON TRACKS
W. A. Glass, L. A. Braby, and W. C. Roesch

Elsewhere in this report⁽¹⁾ we discussed the effect that delta rays have on the energy deposition in a 0.25μ (unit density) cylindrical absorber. That experiment indicated significant amounts of energy were deposited at distances of hundreds of angstroms from the proton track. We have begun a second experiment with the same equipment in which the proton beam passes outside the absorber. As in the previous experiment the 1.7 MeV proton beam was collimated so that the uncertainty in its lateral position is equivalent to about 15 Å. Distributions of the energy deposited in the absorber by delta rays was determined for several different distances of the beam from the boundary of the absorber. These distributions are shown in Figure 1 along with a scale drawing that shows the location of the proton beam relative to the cylindrical grid-walled proportional counter that simulated the very small absorption site.

Many of the counter pulses were very small. The smallest pulses measured were equivalent to about 30 eV (the system gain was 22 eV per analyzer channel) deposited in the counter. Electronic noise did not interfere significantly with the measurement of these small pulses, because the gas gain of the proportional counter was between 5×10^3 and 10^4 while the FET preamplifier had an rms noise equivalent to about 300 electrons. With the proton beam off, only

a few counts per minute were accumulated in the first analyzer channel. The low noise level was achieved by installing the preamplifier inside the apparatus, close to the proportional counter. Although there was little interference in observing the low energy pulses, these pulses were distorted by the proportional counter multiplication statistics and have yet to be corrected.

The proton microbeam was stopped in a surface barrier detector after passing the proportional counter. Only those counter pulses were analyzed that were gated by signals from this detector. Particularly for protons at large distances from the counter, there were many gating pulses that were not accompanied by counter pulses. In these cases either no delta rays entered the counter or so little energy was deposited in the counter that no ionization resulted. Each curve in Figure 1 is for the same number of gating pulses, i.e., the same number of protons. The area under the curves, corresponding to the number of analyzable energy depositions in the counter, is therefore not normalized to unity but to the quotient of the number of counter pulses by the number of protons. The area decreases with increasing distance of the protons from the counter.

The mean energy deposited in the counter per proton is plotted in Figure 2 versus the distance of the proton beam from the counter. The

FIGURE 1. Energy Absorption Distributions for Various Paths of 1.7 MeV Protons Outside a 0.25μ Absorber

extrapolation of the curve in Figure 2 to zero distance gives a mean energy equal to the extrapolation to zero chord length of the mean energy losses within the counter.⁽¹⁾ All the mean energies in Figure 2 are larger than the mean energy of individual delta rays, which is about 60 eV. Consequently, on the average, the pulses due to protons close to the counter are still due to many delta rays. For protons at greater

distances, the delta rays that reach the counter must be of higher average energy, and fewer of them will be required.

Even for the 0.25μ site simulated in this experiment, the contribution of the delta rays from the tracks outside the site to the energy deposited within the site is substantial. For much smaller sites, it is clear that most of the energy deposited will come from tracks that

FIGURE 2. Mean Energy Deposited per Proton in a 0.25μ Absorber by 1.7 MeV Protons Passing at Various Distances from the Absorber Edge

do not cross the site. An apparatus for measurement of energy absorption spectra for small sites must measure

the delta ray contribution from external tracks accurately.

The quotient of the mean energy absorbed by the mass of material in the site gives the absorbed dose per proton. In a uniform field of 1.7 MeV protons, our data indicate that 3.7% of the dose is produced by proton tracks that do not enter the site. We are exploring other "classical" dosimetry conclusions that can be reached from our data.

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WALL-LESS DETECTOR FOR MEASURING ENERGY DEPOSITION SPECTRA

W. A. Glass and L. A. Braby

Last year we described an electrode design for a spherical wall-less proportional counter. Experiments completed during the past year^(1,2) indicate a definite need for such a detector, so we have continued investigation of the device.

For a detecting device to be useful in measuring energy deposition spectra, it should have the following characteristics:

- the volume from which ionization is collected should be well defined without the use of solid walls, i.e., there should be no density change at the boundary of the detector;
- the sensitive volume should be nominally spherical;
- the gas multiplication occurring near the surface of the anode must be independent of where the primary ionization occurred within the sensitive volume;
- the gas multiplication factor (gas gain) should be in excess of 10^3 so low energy events can be accurately recorded.

Minor modification of the previously reported proportional counter has resulted in a detector which we believe will meet these criteria; we have already shown that most are satisfied.

The shape of the sensitive volume was determined in a straightforward way by using a well collimated beam of alpha particles as a probe. The detector was operated under gas flow

conditions at a pressure so that it simulated an absorber of 10^{-4} g/cm² diameter. The spherical shape was demonstrated by passing the alpha particle beam across the counter along representative chords of the wall-less sensitive volume. Relative mean pulse heights were then plotted for the various chord lengths as shown in Figure 1. In this figure the pulse heights have been normalized so that if the counter is spherical in shape the means of the pulse height distributions will fall on the arc of a circle when plotted as a function of alpha particle beam distance from the detector center. The agreement of the measured mean energy

FIGURE 1. Comparison of Mean Energy Loss of Alpha Particles Along Various Chord Lengths with that Expected for a Spherical Collecting Volume

losses with those expected for a spherical volume is within the uncertainty in location of the alpha particle beam.

The detector anode and cathode are gold plated glass spheres of $150\ \mu$ radius supported on $25\ \mu$ rods. The electrodes are separated by 1.4 cm, therefore the solid parts are insignificant compared to the size of the collecting volume. Details of the electrode structure have been described previously.⁽³⁾ With this geometry a gas gain of $\sim 10^4$ has been measured with an anode voltage of only 900 V.

The detector has been used to measure the energy deposition spectrum of a broad beam of 5.4 MeV alpha

particles. Figure 2 shows the chord length distribution for a uniformly irradiated spherical volume (the dashed triangle) and the theoretical response of a $1.0\ \mu$ absorber (calculated by W. C. Roesch) to alpha particles assuming the energy deposition, Δ , to be localized along the alpha particle track (solid line). Good agreement is shown between the data and the predicted response except for small energy losses; i.e., those occurring near the edge of the detector or for short chord lengths. This rise in the frequency of small events is attributed to δ -rays entering the detector from alpha particles which pass outside the sensitive region. Such an interpretation

FIGURE 2. Energy Deposition Spectrum for a Broad Beam of Alpha Particles in a $1\ \mu$ Absorber Compared with that Calculated on the Basis of Zero Radial Extent of the Alpha Track

is supported by independent experiments done with protons. Results of the proton experiments appear elsewhere in this report.⁽¹⁾

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PULSE READ ION CHAMBER SYSTEM*

L. A. Braby

A method of reading capacitor ion chambers using fast pulse electronics has been developed. This system can read commercial pencil chambers to 10 mV over a range of 0-2 V. A tissue equivalent ion chamber 3.6 cm long and 1.2 cm in diameter has been designed and found to operate reliably when used in conjunction with this reader. The combination will measure neutron and gamma doses of less than 1.5 rad to $\pm 15\%$ with a minimum sensitivity of 0.05 rad. The dosimeter system has been successfully used for inphantom neutron dose distribution measurements.

* Published in Health Physics, vol. 15, pp. 351-356. 1968.

BEAM CURRENT REGULATOR*

E. M. Sheen,** W. A. Glass, and C. A. Ratcliffe**

To improve the average current stability of the positive ion beam from a Van de Graaff type accelerator, a feedback regulator is described that stabilizes the beam current by controlling the portion of the beam removed by a linear-sweep deflection system. The deflection system is linear on both axes to provide a uniform current density over the face of the target. The error signal for the feedback system is derived from a measurement of the target current. Beam currents as small as 1 nA can be regulated to $\pm 0.1\%$ of a preset value.

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FAST PULSE SIGNAL AVERAGING*

W. E. Wilson

This report describes a system which couples a sampling oscilloscope with a small digital computer. This combination makes it possible to digitally record very high frequency (up to 1 GHz) and low-level (down to mV) electronic waveforms. By having the data in digital form in a computer, it is possible to do elementary calculations on individual waveforms or process many repetitions of a waveform (signal average). Some familiarity with sampling techniques and digital computers is assumed.

* BNWL-868, August 1968.

ENDOTHERMIC PROCESSES IN TISSUE-EQUIVALENT PLASTIC*

D. M. Fleming and W. A. Glass

The use of tissue-equivalent plastic as the absorbing element for absolute calorimetric measurement of dose is limited by uncertainties existing in the heat lost by endothermic processes induced in the plastic by the absorbed radiation. Measurements have been conducted to determine experimentally the difference between the absorbed energy and the resulting thermal energy, a thermal defect, for Shonka type tissue-equivalent plastic when irradiated by monoenergetic protons. Results of this work indicate that the thermal defect varies with total absorbed dose and is nearly twice as great as has been predicted for a similar plastic on the basis of independently determined G values. An extrapolated zero-dose value for the thermal defect was found to be $4.17 \pm 0.2\%$. The thermal defect decreases with accumulated absorbed dose and appears to reach a saturation value of 3.67% for doses above 10^8 rads.

* To be published in Radiation Res., 1969.

PROGRESS IN ENDOTHERMIC MEASUREMENTS

D. M. Fleming and W. A. Glass

Preliminary results on the energy loss to endothermic processes in tissue-equivalent plastic were presented in last year's Annual Report (BNWL-715 Part 2, pp. 211-214). These results were refined and have been accepted for publication in Radiation Research. In response to a suggestion by Dr. N. I. Barr and Dr. D. V. Cermock in behalf of an I.C.R.U. Task Group on Absorbed Dose Standards, of which they are members, we are extending measurements of endothermic processes to other materials. These materials will include polystyrene, polyethylene, and polymethyl methacrylate. Also various mixtures of these plastics with graphite (the graphite mixture is

used to make the plastic conducting) will be examined.

The calorimeter used in the tissue-equivalent plastic studies was not designed for nonconducting samples. Furthermore, our experience with that particular instrument indicated a new calorimeter design could decrease the time required for the measurements by eliminating repeated electrical calibration.

The improved calorimeter has been developed. The new design is based on the calorimeter previously described. The principal improvement in the calorimeter is the design of the source holder shown in Figure 1. The sample is clamped inside the plastic support by the two aluminum

FIGURE 1. Exploded Diagram of Redesigned Source Holder

clamp rings. This system eliminates errors resulting from a temperature drop across the silicon grease used to mount around the sample in the old system. Temperature readout is by thermistor embedded in the aluminum clamps.

To prevent the surface condition of the sample from influencing the sensitivity of the calorimeter a thin ($\sim 25 \times 10^{-6}$ in. thick) nickel foil is mounted over each face of the clamp ring. Since the sample is now totally enclosed in the sample holder measure-

ments may be made on different types of samples without recalibration of the calorimeter.

Samples to be used on this calorimeter consist of disks 0.750 in. diameter by 0.030 in. thick to which a 0.003 in. thick disk of metal has been bonded. The endothermic loss is determined by the difference between the thermal power observed when the plastic side is irradiated and that measured when the metal side is irradiated.

ELECTRON EJECTION FROM GASEOUS TARGETS
BY HIGH-ENERGY PROTON IMPACT

L. H. Toburen, W. A. Glass, and L. A. Braby

There is very little information available concerning the energy and angular distributions of electrons ejected from gaseous targets by fast protons. Those distributions which have been measured are for the target gases H_2 , He, and Ne and for proton energies less than 300 keV. The measurements for low-energy impact have shown that the electron energy distributions peak at near zero energy and that the relative number of electrons ejected with higher energies increases as the incident proton energy increases.⁽¹⁾ A knowledge of the shape of ejected electron (delta-ray) energy distributions as well as the angular dependence of these distributions is necessary if one is to calculate the energy loss distributions or energy deposition spectra⁽²⁾ for the passage of charged particles through absorbers of arbitrarily chosen thickness. For proton energies greater than approximately 500 keV, it becomes energetically possible to eject electrons from the inner electron shells of target atoms. As a result of these inner shell vacancies, one may expect to see energetic electrons being ejected due to Auger processes. These Auger electron spectra will influence the second and higher moments⁽²⁾ in the calculations of energy loss straggling distributions. In the present experiment protons with energies

from 500 to 2,000 keV will be used to study electron ejection from gaseous targets.

Figure 1 is a schematic drawing of the apparatus used for secondary electron energy and angular distribution measurements. This system differs from the apparatus described previously⁽³⁾ in that an electrostatic energy analyzer is being used in place of the time-of-flight system. The time-of-flight technique will be used to compliment the present work when the necessary fast electronics are available. In the present system, the proton beam from a Van de Graaff accelerator enters the scattering chamber and is collimated by two apertures 0.033 cm in diameter. Following the second aperture are two large apertures, 0.076 and 0.152 cm in diameter respectively, the first of which is positively biased and serves to suppress electrons ejected from the collimator walls by proton-wall collisions. The target cell is approximately 1.3 cm in diameter, has walls 0.025 cm thick and a slit 0.076 cm wide cut approximately 200° around the diameter. The proton beam passes through the slit along a diameter of the cell and is then collected in a Faraday cup. The electrons ejected at a given angle (θ) enter the electrostatic analyzer after they have passed through the slit into the high vacuum region.

FIGURE 1. Schematic Drawing of the Apparatus.

At the present time a pressure differential of 100 can be obtained between the interior of the gas target and the surrounding volume.

The 127° electrostatic analyzer has cylindrical walls with radii of 5.08 and 6.35 cm. The relationship between the voltage applied to the analyzer plates (V_p) and the energy (E) of a transmitted electron is calculated to be $V_p = 0.446 E$. The best resolution obtained thus far has been approximately 3% FWHM; however, in order to increase the transmission of the analyzer to obtain reliable statistics the size of the apertures was increased and presently a resolution

of approximately 15% is used. The electrons are counted after they pass through the electrostatic analyzer by an electron multiplier. A 500 V acceleration is applied to the electrons immediately preceding the first dynode of the multiplier in order to improve the detection efficiency. The electron detection efficiency is assumed constant over the electron energy range, 0-500 eV, presently under study. The absolute counting efficiency of the detector has not yet been measured.

In order to reduce the interference of external magnetic fields, a

box fabricated of Co-Netic AA magnetic shielding material surrounds the interaction region. A second smaller shielding box is used to enclose the electrostatic analyzer. This box serves not only to reduce the magnetic field in the vicinity of the analyzer-detector system but also to shield the interaction region from the electrical potentials applied to the energy analyzer. The magnetic shielding reduces the residual magnetic field to less than 3 mG in the region of the analyzer. Since the magnetic shielding boxes limit the usable space within the vacuum chamber as well as reduce the pumping speed needed for differential pumping, a three pair set of helmholtz coils has been constructed and will be used when power supplies are available.

Preliminary data have been obtained for the energy spectra of electrons ejected from N_2 and He by 1.7 MeV protons. Electrons were detected at 45° with respect to the forward direction of the proton beam and the electron energy distribution was scanned from 0 to 400 eV. With the proton beam intensity available, approximately 20 mA, it was necessary to use large apertures in the electrostatic analyzer to obtain reliable statistics for the number of electrons counted. By increasing the size of the apertures used in collimating the proton beam, additional proton intensity can be obtained and analyzer resolution can be improved. The data shown in Figures 2 and 3 were obtained with an energy resolution of approximately 15% FWHM.

FIGURE 2. Electron Energy Distribution for 1.7 MeV Protons on Nitrogen. Preliminary raw data - not corrected for detector efficiency, analyzer transmission, etc.

FIGURE 3. Electron Energy Distribution for 1.7 MeV Protons on Helium. Preliminary raw data - not corrected for detector efficiency, analyzer transmission, etc.

These data have not been corrected for the transmission characteristics of the electrostatic analyzer, detection efficiency of the electron multiplier, possible attenuation of electrons in the residual gas of the vacuum chamber, or the effects of the small residual magnetic field. The rather broad peak in Figure 2 has been tentatively attributed to K-Auger electrons. Calculations indicated that the KLL and KL-LLL Auger transitions will result in electrons with energies from approximately 320 to 360 eV and the maximum energy of electrons from KLLL transitions is near 310 eV. It must be emphasized that these data in Figures 2 and 3 are preliminary, and no definite conclusions regarding intensities and energies can be

drawn until further investigation is completed.

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LUMINESCENCE KINETICS FOLLOWING PULSED PROTON IRRADIATION

M. L. West and L. L. Nichols

Luminescence kinetics following pulsed proton irradiation provides a convenient method for studying energy transfer processes in organic molecules. Optical emission spectra and formation and decay kinetics are analyzed as a function of intensity, wavelength, and time. Previous studies have dealt primarily with luminescence decay; the details of early processes as reflected in the pulse rise time characteristics have been obscured by inadequate time resolution. Primary effort this year has been directed toward a better understanding of the capabilities and limitations of this time analysis.

The experimental apparatus has been previously described.⁽¹⁾ Protons from a 2 MeV Van de Graaff accelerator pass through a high voltage chopper (3 MHz) into the liquid sample cell. Emitted light enters a spectrometer and is focused onto a photomultiplier tube. A high speed time-to-amplitude converter and an on-line digital computer are used for data acquisition and reduction.

Ideally, we desire an instantaneous excitation of the liquid followed by an exact representation of the light output. In practice, however, the time curves represent the combined effect of instrumental response and the buildup and decay of the luminescence. The most important effects contributing to the instrumental response are (1) proton pulse width and rise time, (2) phototube

transit time spread, and (3) time jitter in the associated electronics. The proton pulse width and rise time (chopped beam profile) make the major contribution to the observed resolution function of 2.05 nsec FWHM with a 0.35 nsec rise time as shown in Figure 1 (10 MHz) has been designed and is being built to improve the beam profile.

Preliminary pulse studies have been made on benzene, toluene, and solutions of p-terphenyl in cyclohexane, toluene, and xylene. The luminescence curves of benzene, toluene, and p-terphenyl in cyclohexane exhibit rise times that are limited only by the system resolution, while those of p-terphenyl in toluene and

FIGURE 1. Instrumental Response Curve

xylene are noticeably longer and depend on solute concentration. Typical spectra are shown in Figure 2. The observed rise time reveals the transfer time of electronic energy between molecules and its dependence on molecular concentration. A computer program for unfolding the system response function is being developed so that the true luminescence response functions may be studied in detail.

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FIGURE 2. Luminescence Response Curves
(A) 0.1 g/l p-terphenyl in cyclohexane
(B) 0.1 g/l p-terphenyl in toluene

A METHOD TO ELIMINATE THE REDUCED COUNTING EFFICIENCIES AT THE ENDS OF TRAVEL FOR SCANNING TYPE WHOLE BODY COUNTERS

H. E. Palmer and J. C. Langford

In whole body counters where the detector scans from one end of the body to the other, the total count is not completely independent of the linear position of the radioactivity unless the detector travels well beyond the end of the person.

Any counting that is not done over the person significantly decreases the sensitivity since essentially only background is being counted; therefore, most scanning type counters stop the detectors near the end of the person. If this is done, the detectors do not spend as much time over the head and feet as they do at the center of the body.

To eliminate this problem, a travel distance of 6 ft 6 in. was selected as the maximum height of people that would be counted. A count rate profile was then constructed by placing a uniformly distributed source of ^{137}Cs along this distance and counting it with the detector at 1 in. intervals from one end to the other. At each end position, the center of the detector was directly over the end of the distributed source. From this count rate profile, a speed profile was then calculated for the detector which would compensate for this end effect. The speed profile is shown in Figure 1 and a

FIGURE 1. The Count Rate of the Six-Crystal Counter Along a Uniformly Distributed Source

6 ft 6 in. long cam of the profile was constructed alongside the counter. A linear variable potentiometer was installed to ride along the cam at the same linear position as the detector. The voltage across the potentiometer controls the speed of the

stepping motor which moves the detector and changes the speed at the ends so that for every linear section of the body the product of efficiency times the counting time is the same.

This method was applied to the sensitive rotational method whole body counter previously described.⁽¹⁾ A point source placed anywhere within the volume the body normally occupies gave the same total count as this detector system traveled from one end of the 6 ft 6 in. distance to the other. The count rate, neglecting gamma ray absorption in the body, is constant for any person of any size except those over 6 ft 6 in. in height.

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A TWO-DIMENSIONAL SCANNING WHOLE BODY COUNTER

J. C. Langford, B. I. Griffin,* and H. E. Palmer**

The investigation of the properties of a whole body counter in which the detector oscillates laterally simultaneously with the longitudinal transport of the body has led to the discovery of a mechanical function generation. The motion, as above, generates a function which eliminates the effect of geometry (converts $1/r^2$ to a constant) and converts the exponential absorption relation to a linear function for isotopic, symmetric media. This will allow simplified computer methods of data treatment to be used in data analysis where this motion is used to accurately integrate the data and also to locate the X-Y-Z positions of a radionuclide within absorbing media.

Despite the large amount of research in whole body counting during the past ten years, good precision and accuracy in determining the total body content of an isotope is limited to only a few isotopes, such as ^{24}Na , ^{40}K , and ^{137}Cs , which are rather uniformly distributed throughout the body. The error in measuring an isotope which is redistributing with time in the body limits the usefulness of whole body counting for many applications in the field of medicine and precise health physics studies.

In an attempt to overcome this problem, the Hanford shadow shield counter⁽¹⁾ was modified so that the detector is oscillated laterally while the person is scanned lengthwise as he moves through the counter. The detector was also collimated on all four sides so that in both the lengthwise and lateral directions the subject being counted could be

out of view of the detector at the ends of the travel for the detector and the bed.

Although a reduction of sensitivity of the counter resulted from these changes, it was found that a radionuclide gave approximately the same counting rate regardless of its position within an air volume normally occupied by the body. The reason for the count rate being independent of the position with lengthwise and lateral scanning is that the decrease in the solid angle geometry for increasing distance is exactly compensated for by the source being viewed by the crystal for a longer period of time. This independence of distance holds true only if the lengthwise and lateral movement of the subject and crystal, respectively, occurs simultaneously. If either movement is used alone, the count rate assumes a $1/r^2$ dependence on the source distance. The two main problems that limit the accuracy of whole body counting are: (1) the effect on the counting efficiency due to geometrical considerations where the radioactivity is at different positions in the

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body and (2) the self-absorption of the radiation on penetrating the body. With this counter the first problem has been completely eliminated; the problem of self-absorption remains but has been considerably simplified.

The design of this X-Y scanning whole body counter was based on the shadow shield whole body counter, except that provision was made to oscillate the detector laterally 60 in. between end limit switches. The detector was shielded with a 10 in. square lead brick collimator which extended 5 in. below the bottom of the crystal. A lead shield

was built over the oscillating mechanism to reduce the natural background radiation. The detector was located 4 in. higher than in the regular shadow shield counter to permit greater collimation. An eddy current motor with a screw mechanism was used to oscillate the detector at constant speed. A 400-channel pulse height analyzer with a normal paper strip readout was used to handle data acquisition. Figure 1 shows an oblique projection of the modified shadow shield whole body counter with its 18 in. wide and 73 in. long bed.

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*FIGURE 1. Shadow Shield Whole Body Counter
(absolute calibration model)*

Figure 2 (a,b,c) shows the relative counting efficiency rate for a ^{137}Cs point source as a function of lateral distance from the bed centerline and of height above the bed for three collimator lengths. An important observation is that for a 5 in. collimator and 60 in. oscillation the counting rate is almost independent of source geometry.

However, because the counting efficiency for this arrangement is about one-fifth of that for the regular shadow shield counter, its usefulness is restricted to situations where relatively larger amounts of radioactivity are present in the body, such as in medical diagnosis and radioisotope treatment.

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FIGURE 2. Effects of Varying Collimator Length and Oscillation Distance

To study more efficient counting geometries, modifications were made in collimator length by decreasing to 3 in. and 1 in. The changes in relative counting efficiencies as shown in Figure 2 (a) and (b), respectively, are due to the crystal being lower in the collimator and the source being in the "field of vision" of the detector at the ends of the oscillation distances. The counting efficiency increased a factor of 2 by decreasing the collimator length from 5 in. to 1 in. below the surface of the detector.

Figure 2 (d) and (e) show the counting efficiency measurements using the same ^{137}Cs point source as before for the X-Y scanning whole body counter, except that the oscillation distance has been decreased as noted and the 1 in. collimator has been used. Although the counting efficiency has increased by a factor of greater than 3 as shown in Figure 2 (c) versus (d), the counting efficiency has become more dependent on the position of the source. This dependence on position is largely compensated for by absorption in the body, making the 1 in. collimator a satisfactory geometry as indicated below.

Absorption corrections in whole body counting are generally difficult to make and depend on the particular counting geometry being examined. The near geometry-free systems of 5 in. collimator and 1 in. collimator with 60 in. oscillation were examined first. Figure 3 shows the absorption as a function of water depth in a simulated torso of

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FIGURE 3. Collimator Size Versus Absorption in Water

polyethylene filled with water. The absorption was approximately a linear function of depth for a point source. In Figure 4 it is shown mathematically that $1/r^2$ is a constant and that for a symmetrically distributed source having a linear absorption coefficient, the activity can be considered to lie on the centerline.

At present, there is no convenient method of measuring body depth continuously such that correction could be made for absorption. Also, many of the radionuclides do not deposit uniformly, and a detection method which is reasonably independent of position in the body is needed.

From data collected by X-Y scanning of the water-filled polyethylene torso, which had a point source of ^{137}Cs at various positions within the torso, approximate plots of counting efficiency were prepared

$$A_1 = \pi r_1^2 = \pi h_1^2 \tan^2 \theta$$

$$A_2 = \pi r_2^2 = \pi h_2^2 \tan^2 \theta$$

$$\frac{A_1}{A_2} = \frac{h_1^2}{h_2^2}$$

The detector is collimated and oscillates laterally sufficiently to pass out of view of source 2 which represents the radioactivity at the greatest distance designed into the system. The sources are moved past the detector at constant speed longitudinally. Hence, the time taken for the detector to scan the areas in question is a ratio of the size of the areas. Since the ratio of areas is proportional to the ratio of the heights squared, the dependence on $1/h^2$ or $1/r^2$ is cancelled.

$$C = C_0 (1 - my)$$

ACo = Count Rate with Sources
at Center of Sphere

$$dv = \pi x^2 dy = \pi (a^2 - y^2) dy$$

$$S = \frac{A}{V} = \frac{3}{4} \left(\frac{A}{\pi a^3} \right)$$

$$S = \text{Specific Activity} = \frac{\text{Activity}}{\text{Volume}}$$

$$dC = SCdv = SC\pi(a^2 - y^2)(1 - my)dy$$

$$C = SC\pi \left[\int_{-a}^{+a} (a^2 - y^2) dy - m \int_{-a}^{+a} y(a^2 - y^2) dy \right]$$

$$= ACo$$

$$dV = 2 \times b \, dy = 2b \sqrt{a^2 - y^2} dy$$

S = Specific Activity

$$C = C_0 (1 - my) = \text{Count Rate}$$

ACo = Count Rate all Activity at y = 0

$$dC = Scdv$$

$$c = Sc \int_{-a}^{+a} 2b \sqrt{a^2 - y^2} (1 - my) dy$$

$$= 2Scb \left[\int_{-a}^{+a} \sqrt{a^2 - y^2} dy - m \int_{-a}^{+a} y \sqrt{a^2 - y^2} dy \right]$$

$$= 2SCo b a^2 \pi = Co A$$

for the various collimator and oscillation distances. The data were calculated from ten minute counts of a point source in the torso by the formula:

$$\frac{(C \text{ upright} + C \text{ inverted})}{2 C \text{ centered}}$$

Figure 5 (a) shows the graphs of these data. Since the configuration of 1 in. collimation and 51 in. oscillation gave the most uniform response with nearly the highest counting rate, it was chosen to be investigated further. While it is true that the outer 1 in. of the torso represents one half of the volume, few vital organs would be present to selectively concentrate activity in that section.

The relationships of counting rate versus location for different radioisotopes for the torso are shown in Figure 5 (b). Except at high energies and at positions near the edge of the torso, the total count obtained in the upright plus the inverted position are independent of source location.

The advantages of this whole body

counter over others are: (1) the elimination of changes in counting efficiency due to geometrical consideration where the radioactivity is at different positions in the body and (2) the self-absorption problem is considerably simplified.

Potentially, the principle for elimination of geometrical dependence applies to any radiation field having the $1/r^2$ relationship. This includes light, sound, and other electromagnetic radiation. Using a computer, one could obtain an accurate measure of the whole body radiation burden by making absorption corrections and integrating the counts. Also, by data analysis of the count rate as it was being accumulated, one could determine the location of the radioactivity in three dimensions.

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FIGURE 5a. Torso Absorption Versus Counter Configuration Isocount Lines for 1/4 of Torso Geometry

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FIGURE 5b. Torso Absorption Versus Energy

PRECISION WHOLE BODY COUNTING OF ^{59}Fe IN HUMANS

H. E. Palmer, J. Cook,* and K. G. Pailthorp

During the last decade ^{59}Fe has been extensively used in iron absorption and kinetic studies in humans. The use of ^{59}Fe requires a method that will accurately determine the total body content such as a measurement with a whole body counter,^(3,4) subtraction of the excreted ^{59}Fe ,⁽²⁾ or a "double isotope" method⁽¹⁾ in which ^{59}Fe is administered by mouth and ^{55}Fe is bound to the patients plasma protein and injected intravenously after which the ^{59}Fe uptake is then determined by the ratio of ^{59}Fe to ^{55}Fe . Of these methods, whole body counting is the simplest and most convenient for both the physician and patient if such a counter is available. However, erroneous iron absorption results as large as $\pm 50\%$ ^(5,6,7) have been obtained from whole body counters due to changes in distribution as the ^{59}Fe changes from a localized source in the stomach to a diffuse source throughout the entire body. these errors can be significantly reduced by appropriate correction methods which involve a prior injection of ^{59}Fe to establish the counting efficiency for absorbed iron in each patient. This paper describes a method in which the total content of ^{59}Fe in the body can be determined with an accuracy of $\pm 2\%$ regardless of whether it is

in a 10 lb newborn infant or a 220 lb adult and regardless of whether the isotope is localized in the stomach, bone marrow, blood, or in any combination of these distributions.

PRINCIPLE OF METHOD

Whole body counters produce the best results when the isotope in the body rapidly reaches a fixed distribution as do ^{40}K , ^{137}Cs and ^{24}Na . The main problem affecting the accuracy of whole body counters is caused by the absorption of gamma rays within the body and this absorption changing with changing distribution of the isotope. For instance, several counter arrangements have been developed which give very constant count rates from a point source in air when placed in any position normally occupied by the body, but when the source is placed in various positions within a water-filled phantom, count rates may vary by as much as a factor of 2. However, studies with such a counter⁽⁸⁾ show that if the Compton scatter region of the gamma ray spectrum is used rather than the photopeak region which is normally used, the count rate is quite independent of the position of the source. Table 1 shows a comparison of counts in the Compton scatter region versus the photopeak region for a ^{137}Cs

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TABLE 1. Comparison of Count Rate in Compton Scatter Region with That in Photopeak Region for a Point Source of ^{137}Cs in Cylindrical Water Phantom

Source Position	Compton Scatter Region, counts/min	Photopeak Counts
Center of Phantom	67,662	30,919
1 in. from Center	68,170	31,843
2 in. from Center	68,357	34,343
3 in. from Center	69,231	38,207
4 in. from Center	69,453	44,572
5 in. from Center (outside)	67,216	56,508
Average	68,348	39,398
Range =	+1.6% -1.6%	+43% -22%

source (gamma ray energy = 0.663 MeV) placed in various positions from the center to the outside of a 10 in. diameter phantom. All the counts in the Compton scatter region were within $\pm 1.6\%$ whereas the outside position counted 83% higher than the center position when photopeak counts were used. Similar results have been obtained by other investigators,^(7,9,10) and it has been suggested⁽¹⁰⁾ that probably the majority of gamma rays emitted in the body with energies exceeding 0.1 MeV ultimately emerge from the body although their energy may be reduced and their angular distribution altered by Compton collisions. However, results in Table 1 show that when both photopeak and Compton scatter counts are used, the count rate is not nearly as constant with changing source position as it is with just the Compton scatter counts.

Since the body is not cylindrical in shape but more nearly ellipsoidal, a water phantom of such a shape was constructed from Styrofoam

plastic to provide phantom walls of low mass. The phantom was 9 in. thick, 15 1/2 in. wide and 12 in. high and filled with water. Four 6 in. diameter by 4 in. thick NaI(Tl) detectors were placed around the phantom as shown in Figure 1 and their position was empirically determined such that a point source of ^{59}Fe placed anywhere in the phantom on a plane parallel to the center of all four detectors gave exactly the same count rate in the Compton scatter region. The optimum arrangement of the detectors for ^{59}Fe gamma rays is 17 in. between the faces of the two sets of opposing detectors and 15 in. between the sides of the detectors in the two sets.

The detectors in the arrangement described above were placed in a shadow shield type⁽¹¹⁾ whole body counter shown in Figure 2. This counter was designed so that a minimum amount of lead brick shielding would be required and, therefore would be easily transported to various locations. The subject travels completely through the counter and beyond the major viewing space of the detectors. All people can essentially be made the same size with respect to absorption and Compton scatter effects by adding small pellets of a heavy plastic called "Delrin"* over the person until level with the top of the aluminum carrier. The subject's face

* Manufactured by du Pont Chemical Company.

*FIGURE 1. Water Phantom Used to Determine Optimum
Capital Position*

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FIGURE 2. ^{59}Fe Counter Using Delrin Plastic Around Subject to Produce Uniform Thickness.

is not covered. The Delrin plastic has a density of 1.40 but the bulk density of the small 1/8 in. plastic pellets is about 1.0 or about the same as the human body. The aluminum carrier is made from 1/8 in. thick aluminum.

When a point source of ^{59}Fe was placed anywhere in the Delrin filled carrier, the total count rate obtained by allowing the carrier to pass through the counter was within $\pm 4\%$ for any position for a Delrin thickness of 8 1/2 in. Figure 3 shows the relative count rate throughout a vertical cross section

of the Delrin pellets. As the thickness of Delrin is increased, the average count rate goes down

FIGURE 3. The Relative Count Rate of a Point Source of ^{59}Fe in a Vertical Cross-Section of Delrin Plastic Pellets

slightly and the deviation of the count rates at the various positions increases.

Since ^{59}Fe in the body will not concentrate into point sources and move to such extremely different locations as those in Figure 3, the variation of the count rate of the ^{59}Fe in the body should be much less than that observed with a point source if the body is covered with the Delrin to form a medium of tissue and tissue equivalent material of constant thickness and width. In addition, a tracer dose of ^{59}Fe placed in the center of the Delrin and counted will give the same count rate in the person after he has ingested or has been injected with the dose. Therefore, a standard ^{59}Fe dose can be counted in Delrin of the same thickness as that of the subject and it will represent a 100% uptake or retention by the body. If the subject is counted immediately before or after the standard dose is counted, the uptake or retention in the body can be directly calculated from the two count rates and the result is independent of instrumental changes or radioactive decay of the ^{59}Fe . If a standard method is to be developed for all sizes of people, a Delrin thickness of 11 in. would be as thick as the thickest part of essentially any person when in a supine position. However, the 9 1/2 in. thick Delrin would be sufficient for most people.

COUNTER RESULTS WITH HUMAN SUBJECTS

^{59}Fe was administered to normal human volunteer subjects by both in-

gestion and injection to test the counter described in the previous section and shown in Figure 2. The ingestion studies provided a test of variability of the counting rate with changing geometry as the ^{59}Fe travels through the gastrointestinal tract. The injection studies provide a test of the variability of count rate as it goes from blood to bone marrow and back to the blood and also provides a comparison with the count rate obtained after ingestion.

Table 2 shows the ratio of the counts of ^{59}Fe in the body to that in Delrin of the same thickness as the thickest part of the body. Ratios are shown both with the body surrounded with Delrin to a constant thickness and also with the body unpacked. The three volunteers ingested 1 μCi of ^{59}Fe and three counts were made on each of them during the next 7 hr. The volunteers were then injected with an additional 1 μCi of ^{59}Fe and then counted immediately while the injected material was all in the blood. These data show that the variation in the count rate during the movement of ^{59}Fe through the

TABLE 2. Ratio of Counting Rate of ^{59}Fe Dose in the Body After Ingestion to That in Delrin of Same Thickness

Elapsed Time After Ingestion of 1 μCi ^{59}Fe , hr	Counts in Body/Counts in Delrin		
	Subject 1	Subject 2	Subject 3
0.1	0.980 (0.999) ^(a)	0.996 (0.018)	1.018 (1.017)
3	0.989 (1.001)	0.978 (1.022)	0.988 (1.003)
7	0.990 (1.003)	0.990 (1.003)	1.013 (1.003)
8.5 (b)	0.987 (0.992)	1.000 (1.017)	0.995 (0.996)

a. Ratios in parameters are for counts with the subjects not covered with Delrin

b. Subject injected intravenously with an additional 1 μCi ^{59}Fe at 8.4 hr.

stomach and small intestine and for that contained only in the blood was within $\pm 2\%$ of that obtained from the same dose of ^{59}Fe counted in the Delrin. Therefore, very reliable iron uptake studies should be possible since there is essentially no difference in the counting efficiency for absorbed and unabsorbed iron in the body. These data also indicate that packing with Delrin to make all parts of the body the same thickness may not be necessary in average sized people. The unpacked values were as good as the packed. This is probably due to the fact that a major portion of the iron in both the ingestion and injection cases is in the torso of the body which requires very little packing. With very large or very thin people this effect may not hold true and further experiments are planned to study this.

In another experiment three volunteers were injected with ^{59}Fe and then counted at intervals during the next 10 days. In this case essentially none of the ^{59}Fe leaves the body but it does transfer from the blood to bone marrow within 10 hr and then gradually about 80% of it returns to the blood within the next 4 to 10 days. Whole body counts were done on these subjects at the time of injection and at daily intervals for the next 10 days. The results of these counts are plotted in Figure 4 and show that all the whole body counts are within $\pm 2\%$ of the count obtained from the same ^{59}Fe dose counted in Delrin of the same thickness as the subjects. There is no apparent effect on the count rate due

FIGURE 4. Whole Body Counts on Subjects After Injection of ^{59}Fe

to differences in geometry from the iron being all in the blood or all in the bone marrow.

SUMMARY

These whole body counting results and those from the water phantom experiments show that the total body content of ^{59}Fe can be determined in a person of any size within an error of $\pm 2\%$. Small people and the smaller sections of the body are brought to a constant size by adding Delrin plastic pellets. This constant thickness of scattering material seems to provide constant Compton scatter count that is quite independent of the distribution. For average size people, packing

with the plastic pellets appears to be unnecessary; however, in a standardized procedure that would include people of all sizes packing would be necessary.

Since all counts can be compared to a standard ^{59}Fe dose in the Delrin plastic which is counted just before or after the count on the subject, a single channel analyzer and scaler will adequately perform the counting.

The accuracy of this counter for total body ^{59}Fe measurement has made possible many studies which were previously impractical to do. Several immediate studies are planned at the University of Washington Medical School which will use this type of counter. These include studies of ^{59}Fe uptake and retention in infants during the period of a few weeks to 1 year, iron uptake in humans from various foods tagged with ^{59}Fe , and uptake of iron in humans at high mountain altitudes.

The application of Compton scatter counting to gamma ray energies that are different from those of ^{59}Fe has not been investigated. The data shown in Table 1 indicate that the method will work with gamma ray energies as low as 0.66 MeV, but a slightly different detector arrangement may be required for different energies.

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AN INHALATION APPARATUS FOR HUMAN METABOLISM STUDIES

D. McConnon

Studies of the uptake, distribution, retention and excretion of radioactive materials in humans are necessary to provide adequate bases for calculating maximum permissible limits and to establish realistic models for assessing the dose following accidental intake. Studies following inhalation and deposition in the lungs are of prime importance because it is by this intake route that most atomic energy workers have the greatest potential for accidental exposure to radioactive material.

To conduct these studies, a mechanism is needed with which the amount of test material can be quantitatively controlled. A prototype of an aerosol generator and inhalation apparatus which may be suitable for human studies has been built and tested. The equipment arrangement is shown schematically in Figure 1. The aerosol generator which operates as a conventional aspirator is a modified Lauterbach-type generator.⁽¹⁾ Air jets, formed by seven radial holes each 0.007 in. in diameter near the closed end of a stainless steel tube, are positioned such that they skim the surface of the solution to be aspirated. Since the closed end of the tube is

submerged, surface tension of the solution pulls liquid up the sides of the tubes and around the jet openings. The high velocity air columns pick up this liquid to form a dense mist, a portion of which escapes from the container as an aerosol.

The aerosol is directed into a 20 liter mixing chamber where diluting air is introduced to adjust the air concentration of the radioactive material. The mixing chamber is fitted with outlets for exhausting the air through an absolute filter, for sampling the contained atmosphere, and for directing the aerosol to an exposure mask worn by the test subject. A mouth tube may be substituted for the mask when mouth breathing only is required. The exposure mask or mouth tube is designed such that the air exhausted from either one can be sampled. Butterfly valves control airflow such that inhaled air comes from the mixing chamber and exhaled air goes through a sampler. A vacuum pump maintains the aerosol in the mixing chamber at a slightly negative pressure with respect to the atmosphere.

It was found through a series of tests that as the air pressure at the

FIGURE 1. Diagram of Aerosol Generator and Inhalation Equipment

jets is increased, the air flow through the jets increases. Above a jet pressure of about 6 psig, this relationship is linear as shown in Figure 2. At a jet pressure of 24 psig, the maximum possible jet pressure, 7.5 μ l of solution are aerosolized per liter of jet air. Inclusion of a pressure relief valve is planned for the system so that, in the unlikely event of a sudden increase in system pressure, the aerosol will be routed through the valve rather than to the breathing device.

Particle size measurements from aspirated material using this generator were made with an SAI model CI-S-8 cascade impactor* and a Na_2CO_3

FIGURE 2. Variation of Air Flow with Pressure Drop Across Jets 0.007 in. Jets

solution containing ^{24}Na . These tests indicated that the generator forms an aerosol from this solution that has a mass median diameter (MMD) of 0.3 to 0.4 μ with a standard deviation of 1.3 to 2.0. There was no definite

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correlation observed between the measured mass median diameter and sodium concentration. Aerosols with MMD of 0.3 to 0.4 μ are well suited for metabolism studies in which lung deposition and subsequent translocation are of primary interest.

Figure 3, taken from the report of the ICRP Task Group on Lung Dynamics,⁽²⁾ shows that pulmonary deposition of particles of this size is a factor of 4 greater than the deposition in the nasopharynx and tracheobronchial compartments. Aerosols of lower MMD afford greater pulmonary deposition, however, problems of a practical nature involving aerosol generation and particle sizing are encountered. As the particle size increases, pulmo-

nary deposition decreases because of the filtering action of the upper respiratory tract and increased particle settling velocity. Aerosols of other particle sizes may be produced, should it become necessary, by changing the diameter of the jets.

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FIGURE 3. Mass Deposition Probabilities with Different Aerosol Distributions

THE USE OF ^{235}Np FOR HUMAN METABOLISM STUDIES

D. McConnon

Neptunium-239 is formed in an intermediate step during the production of ^{239}Pu and large quantities of ^{237}Np , a by-product of nuclear power generation, are being separated in this country as target material for the production of ^{238}Pu .⁽¹⁾ The human metabolism of neptunium is therefore of interest in order to assess workers' dose from accidental exposures.

Neptunium-237 and ^{239}Np are not suitable for human metabolism studies or in vivo measurements because the half life of the former is so long (2.2×10^6 yr) that chemically toxic quantities would be necessary for measurable radiation, and so short in the latter case (2.33 d) that studies of adequate duration are not possible. In addition, the radiation dose to volunteers from quantities suitable for metabolic studies would be excessive.

Neptunium-235, however, has a half life of 410 days, decays primarily by electron capture to ^{235}U , and may be useful in determining metabolic parameters of neptunium in human volunteer test subjects. In only 0.0016% of its disintegrations, ^{235}Np decays by emission of a 5.02 MeV alpha particle to ^{231}Pa .⁽²⁾ Both daughter radionuclides are extremely long-lived and contribute little to the dose following intake of ^{235}Np . Neptunium-235 is produced by the (d,2n) reaction in a cyclotron bombardment of high-purity ^{235}U (99.9+%) with 18 MeV deuterons.⁽³⁾

Measurements were made on an experimental quantity of ^{235}Np consisting of about 1.5 μCi obtained from the Lawrence Radiation Laboratory at Livermore to ascertain the purity of product and to determine the energies and yields of the K and L X-rays of ^{235}Np . An X-ray spectrum of the sample was obtained with a 9 3/8 in. $\times$ 4 in. NaI(Tl) detector and it was determined that a K X-ray of about 100 keV is emitted in approximately 2% of the disintegrations of ^{235}Np . The K X-rays of 100 keV energy are well suited for external measurements and differential scanning by whole body counting techniques.

Further measurements with a high resolution lithium-drifted germanium detector indicate that the K X-ray spectrum, as shown in Figure 1, is complex with energies ranging from 94.63 keV ($\text{U}_{\text{K}\alpha_2}$) to 114.55 keV ($\text{U}_{\text{K}\beta_2}$). Calculations indicate that L X-rays are emitted in approximately 35% of the disintegrations of ^{235}Np . The L X-rays are identical to those associated with the decay of ^{239}Pu and therefore, ^{235}Np may also prove to be a convenient substitute, of lower radiotoxicity, for plutonium measurement studies. There was no evidence of a gamma-emitting contaminant in the sample.

Based on the above measurements, the doses to selected critical organs of a standard man from intravenous injection and from ingestion of ^{235}Np were calculated using ICRP parameters.⁽⁴⁾ It is anticipated that in

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FIGURE 1. L and K X-Ray Spectrum of ^{235}Np

an experiment involving human volunteer test subjects approximately 2 μCi of ^{235}Np would be necessary for intravenous injection in order to permit external measurements of body distribution by whole body counting. This quantity would result in a maximum total dose of 50 mrem to the critical organ, the kidneys. Similarly, in an ingestion experiment, the required quantity of ^{235}Np would be 20 μCi resulting in a maximum total dose to the lower large intestine of 18 mrem. These doses are

less than 1% of the maximum permissible annual limits for occupational exposure as specified by the ICRP.

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THE EFFECT OF DTPA ON EXCRETION OF PROMETHIUM IN HUMANS

H. E. Palmer, G. H. Crook,* and I. C. Nelson

Studies of the uptake, distribution and excretion of promethium in humans after administration of ^{143}Pm have been described previously.⁽¹⁾ The effect of the calcium-trisodium salt of diethylenetriaminepentaacetic acid (DTPA) on these parameters of ^{143}Pm in humans was studied as a function of the time interval between the injection of ^{143}Pm and administration of DTPA. DTPA was given at different times to eight subjects from 5 min before to 86 days after injection of ^{143}Pm . Figure 1 shows the retention of ^{143}Pm with time up to 6 days after injection for six subjects who were given DTPA according to the schedule shown in Table 1. Figure 1 also shows the average retention of ^{143}Pm in six subjects not given DTPA.

The excretion of the injected ^{143}Pm varied from 100% of dose for the case where DTPA was injected 5 min before the ^{143}Pm injection to only 20% of dose when DTPA was administered 24 hr after the ^{143}Pm injection.

FIGURE 1. The Effect of DTPA on ^{143}Pm Retention in Humans

These results indicate that DTPA is very effective in significantly reducing the body content of promethium when administered within about an hour after the internal disposition. If the DTPA is given five or more hours later, the body burden will decrease by only 50% or less.

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TABLE 1. Schedule of DTPA Administration

<u>Subject</u>	<u>Time of Administration of 1 g DTPA Relative to Time of Injection of ^{143}Pm</u>
1	5 min before
2	30 min after
3	1 hr, 5 hr, and 24 hr after
4	1 hr, 24 hr, 48 hr, and 72 hr after
5	5 hr after
6	24 hr after

To study the effect of DTPA on long term internal depositions of promethium, DTPA was given to two subjects 80 days after a previous injection of ^{143}Pm . Urinary excretion measurements indicated that only about 5% of the body content of ^{143}Pm was excreted during the following week.

In following the excretion of ^{143}Pm from the body after DTPA administration, it was found that the whole body counting results always indicated a greater loss than did the excretion results. Since the ^{143}Pm in the liver is counted with a greater efficiency than that in the bones, these results indicate that much more of the ^{143}Pm extracted by DTPA comes from the liver than from the bone. Further studies are needed to more accurately determine the relative excretion rates from liver and bone.

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