**PACIFIC NORTHWEST LABORATORY
ANNUAL REPORT FOR 1967
TO THE
USAEC DIVISION
OF
BIOLOGY AND MEDICINE
VOLUME II: PHYSICAL SCIENCES
PART 2. RADIOLOGICAL SCIENCES**

OCTOBER 1968

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ANNUAL REPORT FOR 1967
to the
USAEC Division of Biology and Medicine
VOLUME II: PHYSICAL SCIENCES
Part 2. Radiological Sciences

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RADIOLOGICAL CHEMISTRY

ELECTRODEPOSITION OF PLUTONIUM AND AMERICIUM
FROM ASHED BIOLOGICAL SPECIMENS

P. O. Jackson

An established electrodeposition procedure for the actinides has been modified to permit its use in the presence of iron from biological samples. The presence of 0.005M to 0.012M HF was found to greatly reduce the inhibiting effect of iron on electroplating yields. Essentially quantitative recoveries were demonstrated when up to 200 μ g of iron were present in the electrolyte.

The increased use of plutonium as a nuclear fuel leads to a greater potential for accidental exposure of personnel to airborne contamination. Plutonium always contains some ^{241}Am , the exact amount depending on the exposure history and subsequent aging period of the fuel or separated plutonium. Exposures to plutonium, therefore, are accompanied by an exposure to ^{241}Am . To evaluate the biological effects of such an exposure, it is essential to determine the relative translocation behavior of plutonium oxide and americium oxide and other chemical forms of these radionuclides, subsequent to their deposition in the lungs. One study currently in process is the measurement of the plutonium to americium ratios in the organs of beagle dogs which had been exposed to airborne mixtures of those oxides. For this

study, a very precise technique for measuring these ratios was required. To meet this need, a technique has been developed for the simultaneous electrodeposition of both actinides from a solution obtained from an ashed sample. This direct procedure has the advantage of simplicity and, thus, minimizes the risk of preferential loss of either one of the nuclides.

Methods^(1,2) have been developed for electroplating the actinides from an ammonium chloride electrolyte. They are useful for some bioassay samples, but are limited in application because traces of iron as small as 50 μ g significantly reduce the recovery.⁽³⁾ Because animal organs contain significant concentrations of iron, a technique which would be satisfactory in the presence of iron was required. One reported method⁽³⁾ for the simultaneous electrodeposition of

plutonium and americium involved electrodepositing with 500 V potential from an isopropanol matrix; however, this method was unsatisfactory for the samples of concern here.

Our laboratory studies have established a method for masking the effect of iron to permit electrodepositing of both ^{239}Pu and ^{241}Am with recoveries exceeding 98% from electrolytes containing up to 200 μg of iron. This procedure involves a modification of the method of Donnan and Dukes⁽¹⁾ by introducing a trace of hydrofluoric acid to the electrolyte and making a more precise pH adjustment prior to electrodepositing. Concentrations of 0.005M to 0.012M HF were found to allow essentially quantitative electrodepositing of ^{239}Pu and ^{241}Am in the presence of up to 200 μg of iron. Higher concentrations of HF inhibited the electroplating significantly. The additional improvement in this method involved the use of methyl violet as an indicator for obtaining the optimum pH. When adjusted to a yellow-green color of this indicator, the correct pH was obtained more reproducibly than by adding excess hydrochloric acid after adjusting to the methyl red end point. The electroplating cells employed were also of a modified design, having a 60 mil wire bent at a right angle as a stirring anode. The cathode was a platinum disc of 3 cm² plating area. Briefly, the modified procedure consists of the following steps:

1. After ashing the sample with nitric acid and hydrogen peroxide,

convert the salt to chloride by evaporating with concentrated HCl.

2. After evaporating to incipient dryness, transfer the samples to the electroplating cell using 4 ml of saturated ammonium chloride; 10 μl of 2.7M HF, 5 μg uranium carrier, and methyl violet indicator are added. The desired acidity is obtained by adding 2M HCl to the yellow-green end point.
3. Electroplate at 2 A for a total of 30 min adding additional 5 μg amounts of uranium carrier after 5 and 15 min.

Because thicker deposits are obtained when using this method in the presence of iron, care must then be taken to avoid blistering of the deposit when flaming the disc subsequent to the electrodeposition. Gradual heating of the platinum disc to a dull red was found to reduce the risk of blistering.

The effect of hydrofluoric acid on the deposition of ^{239}Pu in the presence of 200 μg of iron is presented in Table I. Recoveries apparently exceeding 100% are due to self-absorption effects in the directly evaporated comparison standards. Two additional tests were run, one using ^{241}Am tracer and the other a sample of ashed liver from a beagle dog which had been exposed to a Pu-Am source. In both tests, 10 μl of 2.7M HF were added to the electrolytes prior to plating. In each, recoveries for the sources plated in the presence of 200 μg of iron were compared with those obtained without

TABLE I. ^{239}Pu Electrodeposition in the Presence of 200 μg of Iron Plus Various Amounts of Hydrofluoric Acid

μl of 2.7M HF Added	^{239}Pu Deposited c/min	% Recovery
0	716	48
	877	59
	897	60
10	1446	98
	1580	105
25	1525	104
	1547	104
50	1351	91
	1350	91
	1211	86
100*	1110	75
250**	663	45

* 10 λ of 27M HF actually added

** 25 λ of 27M HF actually added

iron. The results are listed in Tables II and III. From Table I it is evident that the recovery was increased from the 40 to 60% level without added HF to essentially quantitative recovery with 10 and 25 λ (equivalent to about 0.005 to 0.012M) of 2.7M HF. Since iron concentration in the electrolyte was approximately $7 \times 10^{-4}\text{M}$, the 0.005M fluoride exceeds the stoichiometric amount required to form the FeF_6^{-3} complex. When the hydrofluoric acid concentration was increased to 0.024M and above, a reduction in recovery was noted, apparently caused by the fluoride. Tables II and III demonstrate that $5 \times 10^{-3}\text{M}$ hydrofluoric acid is effective for masking iron when electrodepositing both ^{241}Am and a mix-

TABLE II. Electrodeposition of ^{241}Am in the Presence of $5 \times 10^{-3}\text{M}$ HF

Iron Added, μg	^{241}Am on Cathode, c/min	^{241}Am Remaining in Electrolyte, c/min
0	1301	2
200*	1161	22
200	1312	3

* Deposit blistered during heating

TABLE III. Electrodeposition of ^{239}Pu and ^{241}Am in Ashed Beagle Liver in the Presence of $5 \times 10^{-3}\text{M}$ HF

Iron Added, μg	Activity of Cathode, c/min	Residual Activity of Electrolyte, c/min
0	664	1.0
200	640	1.0
200	616	2.9

ture of ^{239}Pu and ^{241}Am in the chemical states obtained from wet ashing flesh.

The deposits obtained in the presence of iron had a brownish-red color after heating. Because there is a need to analyze the alpha spectrum, the effect of the deposited iron on alpha resolution was determined. The resolution (F.W.H.M.) of several sources with and without added iron was compared using silicon surface barrier detectors and a multichannel analyzer. The F.W.H.M. for weightless sources was 88 keV, while that for sources plated in the presence of 200 μg of iron was between 100 keV

and 166 keV. This degradation of resolution did not prevent a fairly precise determination of the ^{241}Am to ^{239}Pu ratios, and these resolutions are considerably better than those frequently obtained by direct pipetting and evaporating aqueous samples on a platinum disc. The presence of 200 μg of iron represented the maximum amount expected from the biological sample sizes necessary to achieve sufficient sensitivity. It should also be pointed out that the ^{238}Pu to ^{239}Pu ratios in samples must be known for this determination since corrections are needed for the contribution of the alphas of ^{238}Pu which are not resolvable from those of ^{241}Am .

Additional tests are in progress to permit a statistical evaluation of the accuracy and precision of ^{239}Pu to ^{241}Am ratios derived from this technique.

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DETERMINATION OF INDIVIDUAL RARE EARTH RADIONUCLIDES FOLLOWING A RAPID GROUP SEPARATION BY HIGH RESOLUTION GAMMA SPECTROMETRY

P. O. Jackson

The feasibility of determining a large number of the rare earth radionuclides by direct spectrometric analysis of a chemically separated rare earth group is demonstrated. A technique is described for the rapid chemical separation of the rare earth group from the other radionuclides in reactor effluent water, and a concentration technique for separating the rare earths from a large volume of river water is discussed.

Rare earth radionuclides are formed both in fission and on neutron activation of many natural materials and are thus of major concern in almost every type of nuclear operation. Prior to the development of chromatographic ion exchange techniques for the separation of the individual rare earth elements, it was very difficult

and time consuming to separate them from one another. Therefore, the determination of the individual rare earth radionuclides in many complex mixtures was simply not practical, and early rare earth radionuclide measurements were typically reported as "total rare earths." Rare earth

radionuclide analyses were particularly difficult for freshly irradiated materials because of the abundance of the short-lived rare earths. The development of ion exchange techniques^(1,2) provided a practical means for the separation of the rare earth elements and thus provided a basis for the determination of the individuals. The ion exchange separation procedures provided several fractions, each of which might contain a few radioisotopes of one or two rare earths. These fractions required analysis by gamma-ray spectrometric techniques and/or by decay characteristics to finally determine the individual rare earth radionuclides. The time and expense of these chromatographic ion exchange separation techniques are considerable and have limited progress on many problems which involve studies of the behavior of both stable rare earths and the rare earth radionuclides.

Of particular interest at Hanford is the behavior of the very small amounts of the rare earth radionuclides which are produced by neutron activation of reactor cooling water. This water, which is pumped from the Columbia River, is returned to the river following a one-trip pass through a reactor. With the availability of high resolution Ge(Li) gamma-ray spectrometry, there seemed a very good possibility of performing a reasonably complete radiochemical analysis of the rare earth radionuclide group without resorting to separation of the individual rare earth elements.

The feasibility of measuring a large number of the rare earth radionuclides by direct spectrometric analysis of a chemically separated rare earth group is demonstrated. A technique is described for the rapid chemical separation of the rare earth group from the other radionuclides in reactor effluent water, and a concentration technique for separating the rare earths from a large volume of river water is discussed.

Because of the low concentrations of rare earth radionuclides in reactor effluent water, sources for the 20 cm³ Ge(Li) detector were prepared from a very large volume of sample. One-hundred milligrams of mixed rare earth carrier plus 100 mg of iron carrier for every 10 liters of sample were added to 50 ml of 2M HNO₃ in a large polyethylene container. After collecting effluent water in the container at the reactor, 2 liters of concentrated ammonium hydroxide were added to precipitate the rare earths and iron. The precipitate was collected by filtration on 0.3 μ membrane filters. After dissolution with concentrated nitric acid containing 0.05M HF, the group separation was performed.

The group separation follows typical rare earth gravimetric techniques. After the addition of hold back carriers including Mn⁺², an initial oxidation of the latter to MnO₂ is accomplished by boiling in the presence of potassium bromate. This precipitate scavenges the

majority of interfering radionuclides from solution. By the same reagent, ^{239}Np is oxidized to the +6 valence in which form it tends not to follow the rare earths. The filtrate from the MnO_2 scavenge is made 2.7M in HF and the rare earths fluoride is allowed to settle. After centrifuging and washing, the precipitate is dissolved in concentrated HCl and boric acid and the rare earths are precipitated as the oxalate with saturated ammonium oxalate and oxalic acid. After washing, the precipitate is transferred to a weighed counting dish, dried, ignited over a burner, and weighed to determine the chemical recovery of the separation. (After consistent chemical recovery is demonstrated by a particular operator, the ignition and weighing steps can be omitted.) The precipitate is fixed to the dish with clear lacquer. Because of the large water volumes being processed, 100 mg of rare earths carrier is required for each 10 liters sampled to limit losses in the initial precipitation steps. A mixed rare earth carrier consisting of equal parts of each of the stable rare earths was available and was used for this test. The effect of using a single carrier will be examined in the future.

RESULTS OF GAMMA COUNTING

Typical gamma spectra obtained with a 20 cm³ coaxial lithium drifted germanium diode at times of 9 hr, 32 hr, and 6 days after sampling

are shown in Figure 1, together with radionuclide identifications. Thirteen gamma emitting rare earth radionuclides (including those of yttrium) are definitely identified by a combination of gamma energies and half-lives. Six others are tentatively identified. Neptunium-239 is present, but sufficiently reduced in quantity by the group separation to present no difficulty in the measurement. The only other contaminants observed in the spectra were isotopes of strontium.

LARGE VOLUME SAMPLING

This group separation and measurement procedure for the rare earths has been developed by use of the relatively higher concentrations of rare earth radionuclides in reactor effluent water. However, the method would be applicable also to the analysis of Columbia River water if a concentration procedure were developed for the removal of the rare earths from about 200 gal of river water by flowing it at a reasonable rate and collection efficiency through a bed or column. A good separation from interfering radionuclides, while desirable, is not essential. Previous work in this laboratory with large volume water samplers^(3,4) included sorption beds prepared from a number of sorbants such as ion exchange resins, aluminum oxide, iron oxide, aluminum metal turnings and potassium hexacyanocobalt (II) ferrate. For this investigation, silver iodide, barium-potassium-sulfate, neodymium

FIGURE 1. Gamma Spectra Following Group Separations

oxalate (crystalline and gelatinous), neodymium oxide and aluminum oxide were tested as potential sorption bed materials for collecting rare earths. All were prepared at this laboratory except for the chromatographic grade aluminum oxide which was obtained commercially.*

Laboratory experiments run with ^{152}Eu and ^{154}Eu tracers in tap water demonstrated higher retention and better flow rate characteristics in the Al_2O_3 than in the other materials tested. In a scaled up experiment using a 1/4 in. thick by 4 1/2 in. diam Al_2O_3 bed, a retention of 98% of the tracer was obtained at a flow rate of ~ 2500 ml/min and a total sample volume of 10 liters. The Al_2O_3 filter bed was supported on a 0.3μ membrane filter, and it was necessary to carefully "fine" the Al_2O_3 by wet settling to prevent plugging of the filter. The bed was prepared by settling the Al_2O_3 onto the support through distilled water. A cloth filter was tightly fitted on top of the bed and care was taken to keep water over the bed during the filtration to prevent aeration. Batch contacting boiling concentrated hydrochloric acid plus 0.05M HF in the presence of rare earth carriers removed over 99% of the sorbed tracer. Later, 2M HNO_3 was found to be satisfactory for the leaching step. It was essential to prepare the laboratory filter

unit so as to prevent channeling and bed agitation which can drastically reduce recovery. On application of the procedure to reactor effluent water, the water was filtered prior to passage through the sorption bed since a significant fraction of the rare earths exists in particulate forms.^(5,6) The particulate material which is held on a membrane filter is easily dissolved for rare earth separation by boiling with concentrated nitric acid, 0.05M in hydrofluoric acid. The fractions may be analyzed separately or combined with the sorption bed leach for processing by the group separation scheme.

This technique appears to be satisfactory for the rapid sampling of rare earths from Columbia River water. Its use in measuring the rare earth group at several locations downstream will provide a sufficient number of isotope ratios, for isotopes of different half lives, to define the rates of the sorption-desorption processes occurring between the river water and bottom sediments.

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* Alumina Woelm Neutral, Alupharm Chemicals, New Orleans, Louisiana

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DIRECT DETERMINATION OF PLUTONIUM AND AMERICIUM CONTENT OF ASHED BIOLOGICAL SPECIMENS USING PHOTON SPECTROMETRY

P. O. Jackson and Y. M. Jones

The recent general availability of high resolution Si(Li) photon spectrometry⁽¹⁾ permits an alternative to alpha energy analysis for the determination of ^{239}Pu to ^{241}Am ratios in biological materials. This method offers the intrinsic advantage that no chemical separation of any kind is required for the determination. After the sample is ashed, it is mounted as a uniform thin source, and analyzed with the photon spectrometer to measure the 13, 17, and 20 keV, uranium L X-ray photons from ^{239}Pu decay and the 26 and 60 keV gamma rays of ^{241}Am . Calibration curves were prepared

which correct for the self-absorption of these photon energies for different source thicknesses. Since the photons from ^{239}Pu do not fall in the energy region of the ^{241}Am gamma rays, no corrections for ^{239}Pu content are required when determining ^{241}Am . X-rays emitted in the ^{241}Am decay do interfere with the determination of ^{239}Pu . Calibration curves have been prepared which correct for the ^{241}Am contribution to the observed ^{239}Pu photopeaks as a function of source thickness.

To determine the ^{239}Pu to ^{241}Am ratio, the 60 and 26 keV photopeaks

of ^{241}Am are summed and corrected for the counter efficiency corresponding to the source thickness, to yield the disintegration rate. The 13 and 17 keV ^{239}Pu photopeaks are each corrected for the ^{241}Am contribution and the results are summed. Application of the appropriate counter efficiency factor then yields the disintegration rate of ^{239}Pu .

When the isotopic composition of plutonium in the samples varies significantly from that used in calibration, correction for the effect of differences in X-ray fluorescence yields of the different Pu isotopes on the efficiency factor can be made.

Using this technique, a range of only 6% was observed in the determined ^{239}Pu to ^{241}Am ratios for five sources prepared from the same sample, but with salts added to yield sources ranging from 5 to 25 mg/cm² thick. The intrinsic errors for each of these calibration factors were determined and when statistically combined indicated a total standard deviation for $^{239}\text{Pu}/^{241}\text{Am}$ ratio measurements of $\pm 2.5\%$ (exclusive of the intrinsic counting statistics of the samples). Typical precisions of ± 5 to $\pm 10\%$ for samples having sufficiently high counting rates have been obtained.

This method requires samples of relatively high total activity since the efficiency of Si(Li) detectors is low and the decay of ^{239}Pu and ^{241}Am produces few photons

per disintegration. Efficiencies for both are in the range of 1×10^{-3} to 5×10^{-3} counts per disintegration, depending on sample thickness. For samples having a total activity too low to permit assay by this method, an alpha spectrometric technique may be used.

Although the precisions already achieved exceed the requirements of many radiochemical analyses of biological samples, it is desired to measure even smaller variations than can be presently detected by this method. To make a significant improvement, a method for reproducibly making even more uniform sources, is necessary.

The problems of source uniformity are similar to those encountered in precise low energy beta counting. Methods which may provide sufficiently uniform sources include the pressing of the ashed salts into precision built containers and the fusion of the salts with a low temperature melting point flux, such as potassium pyrosulfate, to form a uniform source. The goal of this work is to obtain intrinsic calibration errors of less than $\pm 2.5\%$.

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RADIONUCLIDE DISTRIBUTION IN SALMON

C. E. Jenkins

Nineteen gamma emitting radionuclides were determined in four different species of Pacific salmon. The concentrations of the radionuclides ^{54}Mn and ^{60}Co decreased from northwestern Alaska to southern Alaska and the Oregon-Washington coast by factors of 1.5 to 3 and 4.5 to 12, respectively, and the concentration of ^{137}Cs decreased by approximately 25% from northwest Alaska to the Oregon-Washington coast. Concentrations of ^{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 per day intake using ICRP recommendations of 1/30 MPC for the nonoccupationally exposed individual. Other radionuclides determined were ^7Be , ^{22}Na , ^{40}K , ^{46}Sc , ^{51}Cr , ^{57}Co , ^{59}Fe , ^{65}Zn , ^{88}Y , ^{110}Ag , ^{140}Ba , ^{152}Eu , ^{203}Hg , ^{208}Tl , and ^{214}Bi .

Fallout radionuclides which are deposited in the oceans show variations in concentration and location and depth. These variations are a function of the input rate from the atmosphere and of the horizontal and vertical mixing of the oceans. Because of our limited knowledge of the temporal and spatial variation of fallout radionuclide concentrations in the oceans, it is difficult to determine from radionuclide measurements in marine organisms, the extent to which they concentrate radionuclides. Concentration factors for marine organisms represent the ratio of a radionuclide concentration in the organism to that in sea water. To date, very little information on the capacity of marine organisms to assimilate radionuclides from their natural environment has been acquired. Some natural radionuclides such as ^{40}K and ^{226}Ra ^(1,2) have been extensively determined in sea water and for these reasonably accurate concentration factors can be calculated. Artificial radionuclide concentra-

tions in sea water must certainly reflect the past air concentrations and precipitation rates for a given location. There are several relatively long-lived radionuclides from the 1961-62 nuclear tests, as well as shorter-lived radionuclides from the more recent Chinese and French tests which can serve as tracers of the uptake by marine organisms if the ocean water concentrations are reasonably well known.

The elements zinc, iron, manganese, cobalt, phosphorus and copper are known to be essential for growth in plant and animal life. Previous investigations indicate that marine organisms during normal growth concentrate essential elements relative to their concentration in sea water by factors which may vary from less than unity to 10^6 .⁽³⁾ Manganese, zinc, iron and calcium have been found necessary for cell division in phytoplankton.^(4,5) Essential nutrients such as phosphorus and nitrogen control the rate of growth but can be tolerated over wide concentration ranges.

Recent measurements of ^{55}Fe concentrations⁽⁶⁾ in the marine environment indicated that salmon had concentrations of 100 to 200 times the levels which were present before the 1961-62 nuclear weapons test series. In addition, the specific activity of the ^{55}Fe ($^{55}\text{Fe}/\text{g}$ of stable iron) was estimated to be 10^4 times higher in the salmon than in sea water. Further knowledge of the enrichment processes and effects is essential to gain an understanding of the biological paths involved and of the uptake rates, turnover, and mechanisms of elemental transfer in the marine food chain. Because salmon form a major portion of the diet of many Eskimos and Indians on the west coast of Alaska, a study of Pacific salmon was initiated to determine the concentrations of the various radionuclides which they contain and the variations in concentration with location and species.

Recent developments in $\text{Ge}(\text{Li})$ and $\text{Si}(\text{Li})$ spectrometry in our laboratory and their application in conjunction with multidimensional gamma-ray spectrometry have made it possible to perform direct instrumental analysis of a large number of gamma and X-ray emitting radionuclides in samples which contain complex radionuclide mixtures. In the work reported here, all of the radionuclides except ^{210}Pb and ^{55}Fe (where ^{55}Fe is in exceptionally low concentrations) were determined without chemical separations. The $\text{Ge}(\text{Li})$ diode was used where possible to verify values obtained with the multidimensional spectrometer and

to determine some radionuclides which could not be resolved with the multidimensional analyzer.

Four different species of salmon were sampled at five different sites as follows: 1) Alakanuk (Yukon River), 2) Dillingham (Nushagak River), 3) Kenai (Cook Inlet), 4) Seward (Bear Creek) and 5) Ilwaco (Columbia River). All of the salmon samples were mature fish caught as they began their spawning run. The salmon flesh was generally subdivided into three parts as follows: 1) muscle tissue, 2) liver and 3) roe or gonads. In this initial work, the head of the salmon and viscera (small amount in spawning run) were discarded. Blood and bone samples were analyzed separately in one case to provide comparative data.

All samples were ashed at 450° in a muffle furnace. Thirty-five grams of this ash were pressed into a standard geometry $1/2$ in. high x 2 in. diameter polyvinylchloride ring and counted for 1000 min on a multidimensional analyzer,⁽⁷⁾ a $\text{Ge}(\text{Li})$ spectrometer⁽⁸⁾ and $\text{Si}(\text{Li})$ photon spectrometer, consecutively. Ashed samples of less than 35 g of total weight were mixed with NaCl to bring the weight to the standard 35 g size.

Nineteen different radionuclides were measured in the salmon, giving the concentrations listed in Table I. On comparing radionuclides in salmon caught in northwestern Alaska with those in salmon caught in southern Alaska and on the Oregon-Washington coast, concentrations of ^{54}Mn and ^{60}Co are 1.5 to 3 higher than those caught in southern Alaska and 4.5 to

TABLE I. Radionuclide Concentrations in Pacific Salmon, 1967 [dis/min/kg (wet weight)]

Location	Species and Tissue		⁷ Be	²² Na	⁴⁰ K	⁴⁶ Sc	⁵¹ Cr	⁵⁴ Mn	⁵⁷ Co	⁵⁹ Fe	⁶⁰ Co	⁶⁵ Zn	⁸⁸ Y	^{110m} Ag	¹³⁷ Cs	¹⁴⁰ Ba	¹⁵² Eu	²⁰³ Hg	²⁰⁸ Tl	²¹⁴ Bi	²²⁶ Ra
Alakanuk	King Muscle	F		0.15	3650	n		43.5		n	4.7	45			99		n	n	0.93		n
63N 165W	King Liver		209	0.42	5790			217			25	77	0.26	5.0	82	4					n
63N 165W	King Roe			0.10	3280			141	2.1	279	21	46		0.38	49			70	0.20		n
63N 165W	Dog Muscle	F		4.70	5010		387	105			6.7	56		0.37	57			38	2.9	5.1	76
63N 165W	Dog Muscle	M		1.40	5130			94			6.7	0	0.03	0.83	55				0.18		
63N 165W	Dog Muscle	F		2.45	5240			100			3.3	22	0.02	0.39	59	21			0.18	9.1	105
63N 165W	Dog Muscle	F		0.63	5270			66			3.9	0		0.85	66						66
63N 165W	Dog Livers	C		3.93	5570			82			16	140		105	41	4081				60	129
63N 165W	Dog Roe	C		1.20	4310			281			30	123		5.7	40	4					
Kenai	Sockeye Muscle	F	199		5760			23			1.6	56	0.08	0.37	64						n
60N 150W	Sockeye Muscle	F			5770		680	26			2.6	11			61						n
60N 150W	Dog Muscle	M			6020	2.2	1097	40			3.0	200	0.12	0.26	54						n
60N 150W	Salmon Livers	C	176		5790		3227	167			11	370	10.4	108	46						
60N 150W	Sockeye Roe	C			4090			132			14	270	0.11	5.7	45						
60N 150W	Salmon Bone	C			5170			233			5.5	102		1.4	63		36.9				
Seward	Silver Muscle	F		1.64	3700			189			3.2	105		0.28	209				0.56		5
60N 149W	Silver Muscle	M		1.96	3680			119			4.3	58			205				2.64		17
60N 149W	Silver Muscle	F		2.35	3850			94			2.8	153		0.26	69						24
60N 149W	Silver Muscle	M		1.31	3800			220			2.3	101			72						46
60N 149W	Silver Livers	C			5230			100			16.7	1014		13.0	24						
60N 149W	Silver Livers	C		2.30	5470			217			23.4	498		3.8	42						
60N 149W	Silver Roe	C		1.72	3400			317			18.4	440		3.7	96						
60N 149W	Silver Roe	C		0.97	3370			348			7.1	255			172						
Iliwaco	Silver Muscle	F	104		5650		512	52			1.6	837		0.27	64						
45N 125W	Silver Muscle	F			5060		66	34			1.2	386		0.51	53						
45N 125W	Silver Livers	C			6670			86			28	9705		7.1	44	2.5	8.3				
45N 125W	Silver Livers	C			6730			70			26	8104		6.8	36	7.2					

C = Combined
F = Female
M = Male
n = not measured

12 higher⁽⁹⁾ than those caught on the Oregon-Washington coast. The ^{137}Cs concentration increases by approximately 25% in going from the Oregon-Washington coast to northwestern Alaska; although in the case of two silver salmon samples from Seward, the relative concentration factors were similar to those observed for ^{54}Mn and ^{60}Co . Cesium-137 has a longer half-life, a relatively short biological half-life⁽¹⁰⁾ and the ^{137}Cs content should, therefore, represent a more nearly steady-state condition. The differences in concentration ratios between ^{137}Cs , ^{54}Mn and ^{60}Co are certainly significant and must be indicative of the relative availability to the marine organisms of the stable element counterpart or of an essential element of similar biochemistry. It is significant that the two silver salmon from Seward with the lowest ^{40}K had a fourfold higher ^{137}Cs concentration than other salmon.⁽¹¹⁾

The radionuclides ^{65}Zn , ^{51}Cr , ^{59}Fe and ^{203}Hg are some of the neutron-induced radionuclides which are normally present in atomic reactor effluent streams but are also produced by nuclear testing. Unusual concentrations of these radionuclides were observed in two Alakanuk salmon. The concentrations of ^{54}Mn , ^{60}Co and ^{137}Cs suggest a northerly migration pattern for these salmon. The unusually large concentrations of ^{51}Cr , ^{65}Zn , and ^{203}Hg are difficult to explain. Mercury-203 has not been observed in salmon samples from the mouth of the Columbia River. Present knowledge

about migratory habits and range of the salmon would eliminate the Columbia River as the source, unless the influence of the Columbia River extends much farther north than the presently defined limits.⁽¹²⁾ The half-life, locality, spectrum and radionuclide concentration indicate a source of neutron induced radionuclides other than the Columbia River.

Zinc-65 was observed in all samples. Chromium-51 and ^{65}Zn were observed in Kenai chum and sockeye salmon and in Ilwaco silver salmon. High ^{65}Zn , ^{51}Cr and ^{46}Sc concentrations suggests that part of the migratory path of the silver, sockeye and chum salmon includes a region under the influence of the Columbia River. Differences in the spectrum and concentration of radionuclides observed for a given salmon species from the same location and run suggest a different migratory pattern and/or feeding pattern.

The cosmic ray produced radionuclides ^7Be and ^{22}Na produced in the atmosphere are deposited over the earth.^(13,14) The ^{22}Na concentration and specific activities are extremely low in sea water, seemingly making it impossible for salmon to accumulate a significant amount of ^{22}Na from the ocean. The most likely explanation for the presence of ^{22}Na in salmon is that they concentrate it during their growth in fresh water prior to their migration to the sea. The presence of ^{22}Na in these salmon which have spent a year or more in the ocean

requires a considerably longer biological half-life than the 11 days⁽⁴⁾ reported for man.

Consistently higher levels of cosmic ray and artificially produced radionuclides are associated with salmon of northern origin. The reason for this is not clear since the fallout of all airborne radionuclides is normally less at higher latitudes than at mid-latitudes. Perhaps the combination of the long winter season in the Bering Sea region which reduces the supply of stable minerals to the sea from river inflow, and the smaller amount of sunlight for photosynthesis results in an increased available ratio of radionuclides to stable nuclides despite the lower fallout rates. It is also possible that in these colder northern waters the fallout radionuclides may remain in a chemical or physical form more biologically available for uptake by marine organisms for a longer period of time.

The natural radionuclides ^{208}Tl and ^{214}Bi are decay daughters of ^{228}Th and ^{226}Ra , respectively, and can be used in estimating the concentrations of the parent radionuclides. The concentrations of ^{226}Ra in salmon tissue were sufficiently high to warrant attention, especially when considered in association with the higher level of artificial radionuclides in northern salmon and the large quantities of salmon flesh consumed by Eskimos and Indians. From these preliminary measurements, it appears that the native fish-eating populations may

be receiving from 50% to greater than 100% of their maximum permissible concentrations (percent MPC calculated for a 300 to 600 g/day intake using ICRP recommendations of 1/30 MPC for nonoccupationally exposed individuals) of ^{226}Ra alone.

In the livers of the Alakanuk chum salmon, high concentrations of ^{140}Ba were observed. Since ^{140}Ba is a bomb-produced nuclide of short half-life, the activity probably comes from recent Chinese nuclear tests and points out that short-lived radionuclides can be concentrated rapidly by marine organisms. The radionuclide $^{110\text{m}}\text{Ag}$ was observed in flesh, roe, liver and bone tissue. The highest concentrations were in the liver, roe, bone and muscle tissues, in that order. The higher levels were observed in the Alakanuk chum salmon and these steadily declined in going further south. The radionuclide $^{110\text{m}}\text{Ag}$ has also been observed in Pacific squid by Folsom⁽¹⁵⁾ and stable silver by Robertson.⁽¹⁶⁾ Goldberg⁽¹⁷⁾ found high concentrations of stable silver (5 to 30 ppm) in liver of tuna and albacore. Rapoport and Luebering⁽¹⁸⁾ reported on an enzyme system that is activated by Hg^{++} and Ag^{+} ions, which suggests that Ag or Hg may be biologically active. Activation analysis of salmon muscle and liver tissue at our laboratory has shown Ag and Hg, with Ag usually associated with blood and liver and Hg with muscle tissue. The radionuclides ^{46}Sc and ^{152}Eu were observed in the Kenai chum salmon muscle tissue. These are neutron induced

radionuclides and are present in the Columbia River. The role of scandium in biological systems is unknown.

On comparing the radionuclide concentrations in salmon tissues, the liver with few exceptions shows substantially higher concentrations than muscle tissue. It could therefore serve as a monitor of the approximate radionuclide concentrations in the muscle. The roe samples studied here showed higher radionuclide concentration than muscle tissue and, in some instances, had higher levels of ^{54}Mn and ^{60}Co than liver. If this is generally true, it indicates a preferential deposition of the parent radionuclide content in the offspring. An adequate definition of the behavior of radionuclides in the marine environment as they affect radionuclide uptake by salmon will require further measurements on the temporal and spatial distribution of radionuclides in salmon, together with information on the chemical forms and concentrations of stable and radioelements in the ocean.

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^{55}Fe IN PACIFIC SALMON

C. E. Jenkins, J. C. Langford and H. E. Palmer*

Iron-55 concentrations in Pacific Salmon have been decreasing at a rate corresponding to or greater than the stratospheric fallout rate. The ^{55}Fe levels decrease from northern Alaska to the Washington-Oregon Coast by more than an order of magnitude. Iron-55 concentrations observed in coastal dwelling Eskimos average between one and two orders of magnitude higher than levels observed in Richland.

The presence of iron in the structural material of thermonuclear weapons produces upon detonation large amounts of ^{55}Fe (half life 2.4 yr) and ^{59}Fe (half life 45 days). Iron-55, a product of (n, γ) and (n, 2n) reactions on ^{54}Fe and ^{56}Fe , is now one of the most abundant radionuclides in the biosphere.⁽¹⁾ Iron-55 is also produced by thermal neutron capture of ^{54}Fe in nuclear

reactors and is released to the biosphere in the reactor coolant stream, but this contribution to the marine environment is extremely small and usually can be neglected.⁽²⁾

High yield Russian and American thermonuclear detonations in the 1952-58 and especially the 1961-62 tests resulted in large quantities of ^{55}Fe and ^{59}Fe being introduced into the atmosphere. The washout of the tropospheric fallout (an approximate residence half time of

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30 days)⁽³⁾ occurred within a matter of weeks. The Russian tropospheric fallout (testing sites at 75°N, 55°E, and 52°N, 78°W) generally occurred in a northern to mid-latitude pattern as the debris moved in a west to east direction. American tropospheric (test sites at 2°N, 157°W and 17°N, 169°W) short lived nuclear debris was not detected in significant quantities in high or mid-latitudes of the northern hemisphere.⁽⁴⁾ Stratospheric fallout occurs at a slower rate corresponding to a residence time of approximately 1 yr with high deposition rates in the mid-latitudes where breaks in the tropopause occur.⁽⁵⁾ Therefore, a relatively short time after the initial tropospheric fallout, the concentration of radionuclides in marine organisms might be expected to begin to reflect the stratospheric fallout rate.

Iron-55 has a longer half life than that of ⁵⁹Fe and will be present in large quantities for many years. The comparatively long half life, the abundance, and the biological importance of iron provide an excellent opportunity to trace the movement of this essential mineral through living organisms.

Iron-55 concentrations observed in marine organisms are considerably higher than measured in terrestrial organisms^(1,*) with the

highest levels being measured in salmon and tuna.⁽¹⁾ Little is known about the uptake rates, distribution or activity of ⁵⁵Fe in the marine environment. Although ⁵⁵Fe decays by electron capture, it emits a soft 5.9 keV X-ray that is potentially harmful to man because it does so in the red blood cell forming region of the body. Since marine organisms are extremely efficient in concentrating iron, particular attention must be given to their consumption by man and in particular to coastal groups of people whose diet is dependent upon salmon and other marine life forms.

Iron-55 concentrations in four different species of salmon were observed at 5 different sites as follows: 1) Alakanuk (63°N, 165°W); 2) Dillingham (59°N, 159°W); 3) Kenai (61°N, 151°W); 4) Seward (60°N, 149°W); and 5) Ilwaco (45°N, 125°W). All salmon were mature and were caught as they began their spawning run.

The general method for analysis of biological samples in our laboratories has been described in detail.** Briefly, salmon muscle tissue was ashed at 450 °C in a muffle furnace and 35 g of ash pressed into a 1/2 in. x 2 in. PVC ring. Samples were counted for 1000 min on a Si(Li) diode; were then wet ashed and the iron separated chemically and the stable iron content determined by colorimetric methods.

* H. E. Palmer, J. C. Langford, T. M. Beasley, C. E. Jenkins and J. M. Aase. "Levels of ⁵⁵Fe in Humans, Animals and Food 1964-1967," this report, pp. 142-147.

** C. E. Jenkins. "Radionuclide Distribution in Salmon," this report, pp. 11-17.

Table I indicates the results of individual analysis of salmon sampled in 1967. Table II lists the average of ^{55}Fe concentrations observed at similar latitudes since 1967. Increasingly higher levels of ^{55}Fe were observed the further north the origin of the salmon. The same general trend was found for other long lived fallout radionuclides,* but ^{55}Fe appears to be less species-dependent. Salmon sampled at Alakanuk showed average

factors of 2.4, 2.0, and 9 higher than the salmon measured at Dillingham, Kenai and Ilwaco,

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

Sampling Location	Average nCi ^{55}Fe /kg of Wet Muscle**		
	1965	1966	1967
Northeast Alaskan Coast	(2) 50	(44) 19	(10) 5.0
Southern Alaskan Coast	(4) 33	(14) 25	(17) 5.6
Washington State Coast	(2) 9.0	(6) 0.91	(10) 1.5

* C. E. Jenkins. "Radionuclide Distribution in Salmon," this report, pp. 11-17.

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

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TABLE I. ^{55}Fe in Pacific Salmon

No.	Salmon	Tissue	Location	^{55}Fe Activity, 10^5 dis/min/kg*	Stable Iron, mg/kg*	Specific Activity, dis/min/mg
10	Chum	Muscle	Alakanuk	22.6	25.4	890
1	Chum	Muscle	Alakanuk	24.7	24.6	1000
1	Chum	Muscle	Alakanuk	20.9	25.5	818
1	Chum	Muscle	Alakanuk	24.2	26.8	901
1	Chum	Muscle	Alakanuk	17.7	22.7	780
10	Chum	Muscle	Dillingham	9.1	17.4	521
10	Sockeye	Muscle	Kenai	11.3	12.9	872
1	Sockeye	Muscle	Kenai	12.4	10.4	1190
1	Sockeye	Muscle	Kenai	18.6	9.7	1920
1	Chum	Muscle	Kenai	13.8	16.8	820
1	Silver	Muscle	Seward	17.3	11.9	1450
1	Silver	Muscle	Seward	17.0	12.7	1340
1	Silver	Muscle	Seward	8.6	15.6	551
1	Silver	Muscle	Seward	18.8	10.8	1740
1	Silver	Muscle	Ilwaco	2.4	9.2	264
1	Silver	Muscle	Ilwaco	1.7	10.9	156
25	Silver	Livers	Ilwaco	8.7	88.1	99
25	Silver	Livers	Ilwaco	9.1	85.5	106

* kg on wet weight basis

respectively. A blood sample from an Alakanuk Chinook salmon contained 800×10^3 dis/min kg wet wt (360 nc/kg wet wt), a factor of 36 higher than the muscle tissue. Results indicate that salmon in the Bering Sea region are concentrating ^{55}Fe by a factor greater than an order of magnitude over levels observed in Washington-Oregon coastal fisheries.* Jennings reported an order of magnitude increase in ^{55}Fe specific activity (1964 samples) in Chinook salmon from Astoria, Oregon, to Eureka, California.⁽⁶⁾ Our studies do not show any definite difference in specific activity of ^{55}Fe for a salmon species. Low specific activities would be expected to occur in long lived salmon the first 2 or 3 yr after a test series because their rapid growth period took place prior to the tests.⁽⁶⁾

Iron-55 studies by this laboratory relative to the physical and chemical forms of iron in the ocean indicate that perhaps 90% or more of the iron is in particulate form in the upper 100 m of the North Pacific Ocean. Approximately 3000 ppm and 15 to 40 ppm stable iron concentrations have been observed in diatoms and salmon, respectively, a factor of 10^5 and 10^3 over the iron concentration observed in the upper layer of the ocean. Diatoms are among the primary producers in the

ocean utilizing inorganic and decomposed organic matter for growth and are at the beginning of the marine food web. Diatoms have been observed to reduce iron content in Puget Sound during a bloom⁽⁷⁾ and represent one pathway for fallout ^{55}Fe to enter into the marine food web.

Figure 1 shows a comparison of the relative decrease of ^{55}Fe in fallout since 1965. The slope of the line represents the relative rate of yearly change. The decrease in ^{55}Fe content in salmon is more pronounced than is fallout measured in air and rain samples. This is surprising and not readily explained. It does show that ^{55}Fe deposited on the ocean is turned over in the biosphere rapidly and becomes unavailable for further recycling in less time than a year. This rapid iron depletion limits the effect of weapon testing tropospheric fallout extending past a year, except to long lived organisms exposed to the initial fallout. Obviously, the ^{55}Fe levels observed in salmon and other marine organisms, with exceptions noted previously, reflect stratospheric fallout rates integrated over the life of the organism. Presently, it is unclear why the slope of the line for salmon in Figure 1 is greater than the fallout rate. Perhaps an aging process for iron is occurring in the stratosphere which is making the ^{55}Fe less biologically available. A large variance exists in the slope between Westwood, Barrow and Seattle. The slope difference here is

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FIGURE 1. A Comparison of the Relative Decrease of ^{55}Fe in Fallout, Salmon (Curves are not corrected for decay.)

probably a function of the precipitation rate and location. More data are needed to establish if, in reality, the rate of decrease in activity in salmon is more rapid than that of fallout.

Specific activities observed in salmon indicate that a wide variance can occur in a given salmon species from the same location and indicate a different migratory pattern and/or feeding pattern. Alakanuk Chum salmon have nearly twice the stable iron content of the other salmon. The reason for this large increase is not clear. Not enough samples

are available to determine if the iron is species, feeding level, run, or locality dependent. Salmon with low stable iron are observed to have correspondingly higher concentrations of ^{55}Fe . Lower specific activities in the liver tissue of Ilwaco Silver salmon than in the muscle tissue suggest that the iron has a shorter biological half life than the muscle tissue and is more nearly in equilibrium with its environment.

Table III contains results from a limited number of blood samples from male Eskimos. Compared with

TABLE III. ^{55}Fe in Alaskan Male Eskimos

July, 1967

No.	Total Body Burden,* nCi	Location
1	468	Kasiglook (61°N, 161°W)
1	318	Kasiglook (61°N, 161°W)
1	237	Nunapitchuk (61°N, 162.5°W)
1	199	Nunapitchuk (61°N, 162.5°W)
1	242	Nunapitchuk (61°N, 162.5°W)
1	192	Nunapitchuk (61°N, 162.5°W)
1	109	Dillingham (59°N, 158.5°W)
84**	17	Richland (46°N, 118°W)

* Based on 60% of Fe in blood and blood volume of 5 liters

** Total body burden in adult Richland males

previous ^{55}Fe measurements (1,*) these values indicate that the concentrations are decreasing at approximately the same rate as in salmon and that substantially higher body burdens of ^{55}Fe occur in the northern coastal Eskimos. Iron-55 levels observed in these Eskimo males are 6 to 30 times higher than observed in Richland males. Pre-

* H. E. Palmer, J. C. Langford, T. M. Beasley, C. E. Jenkins and J. M. Aase. "Levels of ^{55}Fe in Humans, Animals and Food 1964-1967," this report, pp.142-147.

vious studies have indicated that concentration levels in some instances may be a factor of 10^2 higher in Alaska Eskimos than in Richland residents.**

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THE DETERMINATION OF PARTICULATE ^{210}Po , ^{210}Pb , ^{55}Fe AND LEAD
AND IRON IN A NORTH PACIFIC OCEAN DEPTH PROFILE

J. C. Langford

A study of the ^{210}Po , ^{210}Pb -total Pb, and ^{55}Fe -total Fe depth profile in the Pacific ocean gives insight into the transport processes not only in the ocean but also in the atmosphere. Lead-210 and ^{210}Po in the ocean surface waters are believed to originate principally from the decay of the ^{222}Rn (emanation) from the earth's crust into the atmosphere.⁽¹⁾ Lead aerosols are injected into the atmosphere as exhausts of internal combustion engines and volatile wastes of the smelting industry.⁽²⁾ Iron-55 is a neutron activation product which has entered the atmosphere during past nuclear testing operations and is now present in all iron containing biological systems.⁽³⁾ Stable iron in ocean water is carried to the ocean by river and wind transport processes. Iron-55, ^{210}Po and ^{210}Pb are, of course, sources of radiation to the biological systems.⁽⁴⁾ Both ^{55}Fe and common lead are known to be concentrated by fish and other marine organisms.^(5,6)

Until about 1953, most studies of ocean water concerned estuary regions or surface water.⁽⁷⁾ Isolated measurements have been made of the iron concentration versus depth down to 1000 m.⁽⁸⁾ The concentration of lead has been measured only in isolated samples which does not permit its depth profile delineation.⁽⁸⁾ In June,

1967, a cruise was made to a point 350 mi off the coast of Oregon at 41° N latitude and 131° W longitude. Samples were taken at the 0.020, 0.3, 0.6, 0.91 and 1.52 km depths, each of which represented up to 4000 liters of ocean water filtered through 300 μ pore-size millipore filter paper.* Particulate matter was collected on the filter paper and this was subsequently analyzed for ^{55}Fe , ^{210}Pb and ^{210}Po by radiochemical techniques.

PROCEDURE

The filter papers were dried and weighed and ashed with concentrated nitric acid followed by a perchloric acid fuming. Silica was separated by filtration and the solution was diluted to a standard volume for the subsequent sequential analysis. Polonium-210 was removed first, then lead and finally stable and radioiron.

POLONIUM-210

Polonium was determined by spontaneous deposition on silver discs according to the procedure of S. C. Black.⁽⁹⁾ A ^{208}Po spike was

* D. E. Robertson, W. O. Forster, H. G. Rieck and J. C. Langford. "A Study of the Trace Element and Radionuclide Behavior in a Northeast Pacific Ocean Ecosystem 350 Miles Off Newport, Oregon," this report, pp. 92-108.

added to each sample to allow an alpha energy determination of the yield.

LEAD AND LEAD-210

A simplified procedure was devised using the extraction of the lead diethylammonium diethyldithiocarbamate in chloroform from 0.6N hydrochloric acid. After ashing, the lead iodide complex was extracted into hexone and total lead measured by atomic absorption at 282 mμ. Yield was determined using ^{212}Pb tracer. After decay of ^{212}Pb , ^{210}Pb was measured by evaporating an aliquot of the solution on a standard counting dish and beta counting the sample.

IRON AND IRON-55

Total iron and ^{55}Fe were extracted from 6N HCl using 20% alamine in Xylene. After back extraction with 1M HClO_4 , the

solution was diluted to volume. Total iron was determined using the standard orthophenanthroline method and then the remaining solution was electroplated using the procedure of Maletskos and Irvine.⁽¹⁰⁾ The electroplated discs were counted on an argon-methane gas-flow proportional counter with a thin (0.0038 mm) aluminized Mylar window.⁽⁵⁾

RESULTS

Table I presents the results of the chemical and radiochemical analyses of sea water at various depths. The data have a standard deviation of about $\pm 20\%$. Variations in the data other than analytical error, therefore, reflect actual variations in ocean concentration.

From Table I we can see that ^{210}Pb and ^{210}Po concentrations decrease generally with depth by the same order of magnitude. This might be expected since ^{210}Po is a

TABLE I. Results of the Chemical and Radiochemical Analyses of Sea Water at Various Depths

Depth, km	^{210}Po , pc/liter	^{210}Pb , pc/liter	Total Pb, μg/liter	$^{210}\text{Pb}/\text{total Pb}$, pc/μg	^{55}Fe , pc/liter	Total Fe, μg/liter	$^{55}\text{Fe}/\text{total Fe}$, pc/μg
0.020*	0.061	0.054	2.1	0.026	0.12	132	0.00091
0.020	0.022	0.022	0.23	0.096	0.0015	12.1	0.00012
0.3048	0.014	0.0044	0.069	0.064	0.0014	3.7	0.00037
0.6096	0.0061	0.013	0.10	0.13	--	11.6	----
0.9144	0.011	0.0053	0.060	0.088	0.0021	8.5	0.00025
1.524	0.0079	0.0042	0.036	0.12	0.0014	8.5	0.00016

* This sample was the first obtained and the volume collected is believed in error.

daughter of ^{210}Pb and would approach secular equilibrium with ^{210}Pb . Total lead also decreases with depth and shows a minimum at the lowest point at which observations were made, namely 1.5 km. This lowest value is approaching that reported by Tatsumoto and Patterson⁽¹¹⁾ who show a nearly constant lead concentration below 2 km of about 0.02 $\mu\text{g/liter}$.

Both lead and iron are present to a large extent in sea water as particulates.⁽⁶⁾ If we assume that the lead in sea water is mainly from the deposition of airborne aerosols from industrial consumption of petroleum which began its rapid increase in 1940,⁽¹²⁾ and if we also assume that the concentration of lead at 1.524 km was due to lead deposited at the surface in 1940,⁽¹³⁾ then the stable lead concentration between this depth and the surface show a very good correlation with the world crude oil production⁽¹²⁾ from 1940-67.

These data are shown in Figure 1. The equation of the curve is given from the least squares fit:

$$Y = 0.006745 + 0.01425 X$$

where

$Y = \mu\text{g of Pb/liter of sea water}$

$X = \text{billions of barrels of world crude oil production.}$

This model may over-simplify the actual situation and may even be somewhat misleading in implying that the surface input of lead during the past several years can now be found at discrete levels; however, the apparent relationship

FIGURE 1. Stable Lead Concentration in Sea Water Versus World Crude Oil Production from 1940-67

is excellent and provides a basis for further correlation of stable and radiolead.

In contrast to the large variation in lead concentration with depth, stable and radioiron concentrations change only slightly with depth. This is very surprising and suggests that while the stable iron probably is in an equilibrium condition, the ^{55}Fe is carried to great depths rather rapidly. This must be through biological processes which result in its incorporation in detrital material which settles rapidly. The one high surface value was in a plankton bloom and was far different in both stable and radioelement concentrations from other surface samples.

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AN ANALYTICAL PROCEDURE FOR ^{210}Pb AND TOTAL Pb
IN BIOLOGICAL SAMPLES

J. C. Langford

An improved procedure for ^{210}Pb and total Pb is presented. Fewer manipulations are required to separate the lead, thereby improving precision. The chemical yield is measured from added ^{212}Pb tracer. After sample dissolution, the procedure requires about 6 hr, including preparation of the ^{212}Pb tracer. The separated ^{210}Pb fractions are held 5 days before counting to allow decay of ^{212}Pb .

Because of the toxicity of lead to man and animals and the increased deposition of lead on the earth from air pollution sources, it is important to know present contamination levels in biological samples. The high concentrations of lead found in surface waters of the ocean and in snow from California, have been attributed to industrial pollution products, mainly lead tetraethyl aerosols.^(1,2) Recently, stable lead as well as ^{210}Pb ⁽³⁾ has been measured in rainwater. Current concepts of the "normal" concentrations of lead in human blood and urine are being questioned.⁽⁴⁾ By improving the sensitivity and accuracy of total lead measurements in biological materials, it may be possible to give biological significance to the specific activity of ^{210}Pb in its movement from the atmosphere through the biosphere.

Stable lead is usually determined in biological samples by diethylammonium diethyldithiocarbamate (DDTC) extraction and separation and then is followed by numerous dithizone washings in buffered solution to obtain sufficient purity for an accurate colorimetric measurement, using dilute dithizone to develop

the color.⁽⁵⁾ A variation of this method has been used to measure ^{210}Pb in biological materials.^(3,6) The largest losses of lead in this procedure are reported to be due to absorption on the glass walls when the solutions are made basic with ammonium hydroxide. A recent procedure for determining ^{210}Pb used methyl isopropyl ketone extractions of thiocyanate complexes of interfering ions from 0.6N HCl followed by a lead iodide complex extraction⁽⁷⁾ and a subsequent dithizone extraction to separate ^{210}Bi and ^{210}Po . Total lead has also been determined in the solvent, after lead iodide complex extraction into hexone, by atomic absorption,⁽⁸⁾ but the extraction was into 170 ml of hexone which diluted the total lead too much for detection on our atomic absorption equipment (J-A Model 82-362). These procedures were unsatisfactory for our work, either because of colorimetric instability with consequent lack of precision or because of insufficient overall sensitivity.

This present method which utilizes a diethylammonium diethyldithiocarbamate (DDTC) in chloroform extraction and, after wet ashing,

an extraction of lead iodide complex into hexone, has seven times greater sensitivity than other extraction procedures which are coupled with atomic absorption spectrometry. The chemical yield is determined with ^{212}Pb (10.6 hr) tracer. Total lead is measured by atomic absorption. The yield as determined from standards in water solutions was $98 \pm 3\%$. However, on fourteen difficult biological samples, a yield of $70.5 \pm 11\%$ was obtained. As little as 5 μg of lead can be measured at $\pm 20\%$ accuracy.

SAMPLE PREPARATION

The biological samples including animal tissue and bone are ashed at low temperature in a muffle (the temperature should never be above 500°C). Urine samples, with concentrated nitric acid added, are evaporated to dryness under a heat lamp. Final wet ashing is done with concentrated nitric acid and perchloric acid on a hot plate. Baking of salts is avoided.

PROCEDURE

Dissolve the sample or residue from the ashing with heating, in about 50 ml of 0.6N HCl in a 400 ml beaker. Add 100 μg of bismuth carrier and an appropriate amount of ^{212}Pb spike (see next section). After cooling, transfer to a 125 ml separatory funnel and add 20 ml of 1% diethylammonium diethyldithiocarbamate (DDTC) in chloroform. Extract both lead and bismuth by

shaking for 1 min, then transfer the organic layer to a clean, labeled 100 ml beaker. Repeat the extraction and combine the organic extracts obtained from the samples. To each beaker, add 1 ml of concentrated nitric acid and evaporate the organic under a heat lamp. Destroy any charred organic matter with concentrated nitric acid, 30% hydrogen peroxide, then 70% perchloric acid. Evaporate excess acid to less than 0.4 ml and cool. Add 5 ml of water, mix, and transfer the solutions to clean, labeled, 4 dram screwcap vials. Dilute the solution to 8 ml with distilled water. Add 2 ml of 9M NaI and mix well on a vortex mixer. Add 10 ml of hexone which has been freshly washed with 1N HCl and mix 1 min. Allow the phases to separate and transfer the organic layer to a colorless 4 dram vial. Repeat the extraction with 10 ml of hexone and combine the two extracts.

To determine yield, prepare a standard and dilute an aliquot of ^{212}Pb (the same amount as added to the samples) to the 20 ml volume in a 4 dram vial with water. Count the samples and the standard on a multichannel gamma-ray spectrometer for 10 min each.

Separate a 2 ml aliquot of the organic layer for analysis by the atomic absorption at 284 $\text{m}\mu$ for total lead. This solution should not be allowed to stand overnight as lead will be absorbed out of solution onto the walls of the vial.

Evaporate the 18 ml organic layer to dryness in a beaker under

a heat lamp. Add concentrated nitric acid several times to destroy organic residue, then transfer to a 1 1/2 in. s.s. planchet with concentrated nitric acid. Count the ^{210}Bi beta through a 6.42 mg/cm² aluminum absorber. Calculate ^{210}Pb and correct for yield, sample size and other factors characteristic of the equipment used.

PREPARATION OF THE ^{212}Pb TRACER

Dissolve 12 mg of thorium nitrate in 15 ml of 6N HCl. Transfer to a 125 ml separatory funnel. Add 70 ml of 0.3M di-2-ethylhexylphosphoric acid in normal paraffin hydrocarbon solvent and extract for 5 min. Discard the aqueous layer. Let sit overnight for ^{212}Pb buildup then back-extract ^{212}Pb with 10 ml of 6N HCl. Transfer the aqueous fraction to a prepared 4 mm ID x 2 in. Dowex-1 (100 to 200 mesh, X-8) resin column and save the eluant. Dilute the eluant a factor of 5 and transfer to a clean 125 ml separatory funnel. Extract with 20 ml of 1% DDTC in chloroform and transfer the organic layer to a 100 ml beaker. Evaporate to dryness under a heat lamp; add all 10 ml of concentrated nitric acid and evaporate to dryness on the hot plate. If charring occurs, add more nitric acid and a few drops of 30% hydrogen peroxide. Evaporate to a small volume (to reduce acidity), cool and dilute to 10 ml. This gives sufficient activity for spiking eight samples, plus a like aliquot to dilute to the final extraction

volume of the total lead procedure for counting when the yield is measured. The procedure can be run rapidly enough to permit analysis the same day as ^{212}Pb separation.

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ELECTRONIC DESIGN AND CONSTRUCTION OF A
NOBLE GAS ATMOSPHERIC TRACER SYSTEM

J. J. Lashock

An electronic system has been developed and built which combines much available commercial equipment with specially designed transistor and integrated circuit components to continuously collect and store data from at least 63 field located radiation detectors. Atmospheric beta activity introduced by means of a radioactive noble gas tracer, ^{85}Kr , is monitored by 63 Geiger counters. The resultant signals enter specially designed preamplifiers which facilitate transmission through a long cable of up to 1600 m, to a central data sorting and accumulation and readout center.

An atmospheric tracer program requiring the emission of continuous and puff releases of radioactive gases for investigating various parameters of wind transport and diffusion is underway at Battelle-Northwest.

To implement the tracer program and allow the variety of uses desired, a major effort was extended in the design and construction of complementary electronic equipment. Measurement of the tracer material was anticipated to be performed by field located radiation detectors. Several problems relating to information transmission from field locations to the central accumulation site required solution. Since it was desirable to measure short term wind fluctuations, particularly in the case of puff-type tracer releases, an automatic real-time electronic data collection system was necessary. To properly define the down wind behavior of a tracer with time, a large number of data points were required. This necessitated a rather large computer type memory storage system along with its associated programming. A more general description of the

system, including its application in a field study, is being published.⁽¹⁾ The communication covers a brief description of the design and construction of the critical electronic components. A description including all of the essential circuit designs and logic is also being prepared.

The overall tracer detection system consists of 63 field located detectors from which counting information is relayed to a central data collection center. This central data center is housed within a specially instrumented trailer. A block diagram of the system is shown in Figure 1. A photograph of the centrally located electronics components which are located in a trailer on the Meteorology Grid is shown in Figure 2.

The field package consists of a radiation detector and preamplifier sealed inside a weatherproof lead shield. The detectors are large-window halogen-quenched counters with a high sensitivity for beta particles. A special preamplifier was designed and assembled using solid state electronics to facilitate transmission of the Geiger

FIGURE 1. Block Diagram of the Complete Data Accumulation and Storage System

FIGURE 2. Complete Sorting and Storage System
a. Discriminators and High Voltage Filters
b. Programmer
c. High Voltage Supply
d. Magnetic Tape Transport
e. Computer Memory
f. Timer Memory Advance

signals over long cable distances to the central electronics. Incorporated in its design were field reliability, low current consumption and the ability to utilize power from the high voltage supply for operation.

Information relayed from the field packages was received at the central data collection center. Here the signals first enter a post type discriminator, the design of which allowed rejection of the small line-type noise pulses. The discriminator output pulses were normalized as to amplitude and duration before being sent to the encoding gates of the programmer. The two discriminator chassis were constructed so as to accommodate the input signals from a total of 64 field detector packages. Each chassis consisted of 16 printed circuit boards with two discriminators per board. A total of 32 detectors were handled by each chassis and each chassis contained its own power supply. Integrated into each discriminator circuit was a high voltage filter network which decoupled incoming signals from the high voltage supply. This was necessary since each high voltage supply operated several detectors.

Special modified high voltage power supplies were utilized for the Geiger counters (John Fluke model 412 A/B). These were provided with a monitor to measure the overall current drain created by the field detectors. To supply sufficient power for the 64 field

packages, four such high voltage supplies were necessary.

The discriminator output signals enter the programmer whose function is manifold. This critical instrument, with integrated circuit design, serves as the heart of the electronic transformation. Its fundamental function is to act as the interface between the 64 separate discriminators, as well as the timer memory advance for the computer memory. The 64 discriminator positions are uniquely encoded by the programmer so that their respective positions (field locations) are identified in the computer memory by a 6 bit binary code. The command from the timer memory advance unit is also transformed into a 6 bit code which serially shifts the position of storage in the computer memory in groups of 64. The count rate information from the 64 field detectors is thus encoded by the programmer, fed into specific memory groups of 64 channels and these groups are shifted at predetermined time intervals. The programmer will start a storage cycle in the memory after it has made a channel selection. This unit was constructed on one chassis and is shown in Figure 2 with its own power unit protruding from the left side.

Two purposes are served by the timer memory advance. This solid state unit utilizing printed circuit boards serves first as an electronic switch for the computer memory commanding the operations of accumulation and stopping. Subsequently,

it directs automatic magnetic tape readout. The second function is one of time interval programming which is directed through the programmer and was mentioned in the previous discussion. The time interval selector, which essentially determines the data integration time of the computer in each step, is operated from a crystal controlled oscillator. This unit has an 18 stage binary scaler, from which specific rigid time intervals were selected. This unit contains its own power supply.

The computer memory (Packard Instrument Co. Model 45 LaGrange, Ill.) is a 4096 address which accepts a 12 bit binary code con-

sisting of two 6 bit identifications from the programmer. A scope display incorporated in this instrument allows one to visually observe data accumulation entering from all of the field packages. When the 4096 address system has been filled, the accumulated data are automatically dumped to the magnetic tape deck.

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AUTOMATIC REAL-TIME AIR MONITORING OF ^{85}Kr UTILIZING THE
4096 MEMORY OF A MULTIPARAMETER ANALYZER*

J. D. Ludwick, J. J. Lashock,
R. E. Connally and P. W. Nickola**

A noble gas atmospheric monitoring field grid system in which ^{85}Kr is used as a tracer has been designed, assembled and used for studying atmospheric transport and diffusion. This system has demonstrated its usefulness in the quantitative measurement of the transport and diffusion of both continuous and true puff-type radioactive gas releases on a real-time basis. Small fluctuations in the air concentrations of the tracer are determined by using electronic instrumental data collection times as short as 1 sec. The system consists of a large group of field detectors which relay their information to a 4096 address memory. The memory is programmed to accept information from 64 detectors. Information is accumulated in groups of 64 time channels and these groups are automatically stepped by the programmer. A time interval selector allows automatic advance of the stepping process at a slow or fast rate allowing the desired differential data accumulation. The memory is read out on magnetic tape and the equipment is ready for the next field test 35 sec after completion of the first.

INTRODUCTION AND DISCUSSION

Experimental atmospheric diffusion research over considerable distances generally involves a major effort in manpower and equipment over a considerable time period in order to produce definitive results. Factors relating to uncertain meteorological conditions compound the problems associated with conducting a successful field test, and the expense of holding large crews until the onset of acceptable meteorological conditions can be considerable. As a consequence of this situation and other factors to be described, an automatic field monitoring system has

been developed for use in studying atmospheric diffusion processes.

Atmospheric diffusion research is concerned with fundamental processes which, when understood, allow the prediction through practical models of air concentrations of pollutants at various distances from a point of release. Such information is essential for estimating the downwind air concentrations which would result from accidental or controlled releases of radioactive or other physiologically harmful materials. Because of technical and financial limitations, certain critical diffusion experiments which could improve the models upon which predictions are based have never been satisfactorily accomplished or, in many cases, even attempted. The system described here is an improvement in

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several areas in which these difficulties have precluded extensive experimentation. These areas include: 1) the use of an inert gas tracer to precisely follow atmospheric motions; 2) the generation of an instantaneous puff of an atmospheric tracer; and 3) the simultaneous measurement in real time of downwind atmospheric tracer concentrations at many locations.

Our investigation over a period of several years with various particulate and gaseous air tracers^(1,2,3) led to the conclusion that if a rare gas radioisotope were used as a tracer, the essential experiments considered above could be rather easily conducted. Studies were conducted to select the most favorable combination of radionuclide and detector that would reliably function under normal field conditions. Consideration was given to the wide temperature and other environmental variation which were anticipated in the field. It was found that ^{85}Kr would provide the most acceptable atmospheric tracer for the desired studies. Detection of this isotope was satisfactorily accomplished by measurement of its moderate air range beta particle (0.69 MeV) with Geiger counters. Its long half-life (10.76 yr) allowed storage until meteorological conditions were proper for its release. This noble gas tracer could be easily handled, it is chemically inert, and it would be expected to follow exactly the atmospheric transport and diffusion processes. Adequate specific

activity sources of this isotope are available and sources of small physical size were readily prepared for release as true instantaneous puffs. Simple dilution techniques were easily performed to provide sources more satisfactory for continuous emission when desired.

Experimentation with various gaseous and scintillation detectors indicated that a large-face thin window halogen-quenched Geiger-Muller counter would be most satisfactory for the simple rugged field detector package desired.⁽⁴⁾ A preamplifier was designed and built into the field packages to drive a coaxial cable at its characteristic impedance of 50 Ω . This allows signals to traverse at least 2 mi of cable to the central data collection station. Here the signals were decoupled, shaped and encoded for storage in the memory of a 4096 channel analyzer. After the data had been collected in the memory, they were transferred to magnetic tape and were then available for subsequent processing and read-out. Some very important features of the final instrumental design include real-time tracer detection, rather long distance data relay, real-time information discrimination, accumulative field data display, and rapid instrumental recovery for consecutive atmospheric diffusion tests. In addition to these important features, a marked savings in time and crew size to conduct a successful field test was achieved.

In practice, a typical experimental field test proceeded as

follows. The ^{85}Kr tracer material was released either as a continuous source or as a puff. In the case of a continuous release, the analyzer memory was started prior to the tracer release using a 38.4 sec data accumulation interval. The variable time interval was selected to suit the experiment. This allowed 41 min of counting since there were 64 available intervals. For puff releases, a visual watch was made of the 4096 memory scope display. At the first indication of increasing activity, the 64 time interval cycle was initiated. The process of initiating the cycle when activity was first observed, conserves the memory of the computer for the pertinent differential data. At high wind speeds, one can select the 1.2 or 2.4 sec time intervals which give better differential data since the tracer activity quickly traverses the 800 m arc. At slow wind speeds, the 4.8 sec interval was used and even then the memory was often filled before the tracer had completely negotiated the downwind detector system. In these cases, the data were immediately dumped to the magnetic tape, the memory cleared, and the programmer restarted. Time losses of 35 to 40 sec resulted during this process; however, the more valuable feature of short-time interval, real-time differential data collection was maintained.

There are, of course, methods of relieving the technical problems associated with the finite size of

the computer memory. As a compromise between the number of detectors and time intervals available, the 4096 channels were originally divided into a 64 by 64 network. This gave the minimum of desired detectors, while leaving a reasonable number of time intervals for differential data collection. It is apparent from the observed tracer sensitivities that a field network of detectors extending to a 3200 m arc and having a capacity of over 200 would be very useful during favorable meteorological conditions. To accomodate such a large system with a similar or even reduced size memory, a much faster tape dump would be needed. Computer compatible tape decks are presently available which can dump 1600 channels in considerably less than 1 sec. In this way, the network can be divided to accomodate more detectors and the memory can be filled and then dumped in a much shorter time. An even more desirable arrangement, also quite feasible, would be one in which two smaller memories work alternately, storing and dumping to the tape deck, thus allowing continuous data collection.

The entire field operation including meteorological information collection, tracer release, and analytical data collection is only a two man operation. This is in marked contrast to the crew of 10 or more men which is often required for atmospheric diffusion tests in which a single sample is collected at each monitoring location for

subsequent analysis. In addition, only a very short preparation time is necessary to become operational (on the order of 10 min). This is very important since it allows advantage to be taken of meteorological situations which would not have persisted for longer preparation times.

After completion of a field test, the data contained on the magnetic tapes were transferred back into the 4096 memory. The memory was then read out by an Optikon unit (Nuclear Data Inc. Palatine, Ill., OPTIKON model ND 307) which provides a photographic reproduction of the counts accumulated in each channel. The entire 4096 channels were reproduced by a four quadrant readout, each with data from 16 of the 64 time intervals. The vertical position on the photographs identifies the field detector location with the exception of a live time count appearing in the first channel of each column. There is a total of 64 channels, 63 of which identify field detectors. The first 31 detector channels represent a sampling network located 200 m downwind, while the last 32 represent the 800 m sampling arc. As

one reads down the display, he is proceeding across the pertinent arc with respect to the ground level samplers. After 20 positions, the tower samplers of that arc are introduced. The same is true for both detector arcs. Figure 1 is a typical display of such data utilizing the 4.8 sec counting interval during a puff release. Those

channels which contain significant information above the normal background levels are evident. This display includes only 30 of the 64 time intervals and the rapid buildup and decline in count rate is a result of the rather high wind speed during this field test. One can readily distinguish the puff of activity abruptly approaching some of the 200 m detectors both on the ground and on towers. Then, after passing in this vicinity for 20 to 30 sec, the activity continues downwind, reaching the 800 m ground and tower locations. The very clear delineation of the tracer activity from the normal background activity of about 1 count/sec makes this technique very valuable in wind transport diffusion studies.

ACKNOWLEDGEMENT

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FIGURE 1. Data Display from ^{85}Kr Puff-Release

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POLAROGRAPHIC TECHNIQUES APPLIED TO PROSPECTIVE ATMOSPHERIC PARTICULATE TRACERS

J. D. Ludwick

Many problems associated with cloud nucleation, ice crystal formation and washout studies can be fruitfully investigated using particulate materials as tracers. In most cases, the size distribution of these materials affect their response to the atmospheric processes; consequently, one would desire to conduct this type experiment with multiple tracers, each of which would represent a known particle size range.

To measure a minimum of one single tracer particle in a rain drop or snow crystal, special low level analysis techniques are necessary. In many cases, this involves tedious chemical and physical processing, which emphasizes the need for simple analytical methods applicable to potential tracer materials. Polarographic methods, including pulse polarography and anodic stripping analysis, provide a high degree of sensitivity for the determination of certain chemicals. In addition, these

methods are highly specific and permit measurement of selected materials in the presence of large concentrations of other ions such as sodium, potassium and calcium. Among those elements that are easily measured by polarography are cadmium, zinc and antimony, all of which have insoluble compounds that are suitable for use as tracers. Natural background concentrations of 0.1, 30 and less than 1 ppb for Sb, Zn and Cd, respectively, measured in rain samples collected on the Washington coast, were sufficiently low to permit measurement of these materials at the concentrations to be expected in tracer studies.

EXPERIMENTAL

The most sensitive polarographic method is the anodic stripping technique, in which the material to be analyzed is first cathodically reduced and concentrated as an amalgam in a mercury surface or

drop. This process quantitatively removes the element from solution, provided the reduction is conducted for a sufficient time interval. To achieve the highest sensitivity, the cathodic concentration step requires at least 30 min. The material is then quickly (5 to 30 sec) stripped from the mercury by reversing the potential and the amount of material present is determined from the current produced.

Samples that are suspected to contain greater than 1.6×10^{-7} g of cadmium may be successfully analyzed using the much more rapid pulse polarographic method. Table I indicates the time required for the anodic stripping process and the concentration at which pulse polarography is applicable to the determination of cadmium. These measurements were made using rain water and standard amounts of trace material.

This sensitivity allows measurement of one particle of CdS having an average diameter of 10μ which

contains about 1.6×10^{-9} g Cd. However, as noted, more than 30 min is required for analysis of each sample.

In order for the tracer material to be useful in the field, an insoluble form must be utilized, thus necessitating dissolution before analysis. This reduced the sensitivity in the case of zinc, because its oxidation-reduction potential in an acid medium lies in a region where interference from a competing water reaction resulted. In the case of antimony, the tracer compound must be carefully selected since its amphoteric nature does not lend itself to simple dissolution techniques.

The potential for dual tracer analysis is illustrated in Figure 1. This polarogram was obtained from a solution $5 \times 10^{-7} M$ in both Cd and Sb. The wide divergence in their respective oxidation potentials makes resolution of these elements relatively easy.

TABLE I. Polarographic Technique Time Requirements and Sensitivities for Cadmium Determination

<u>Cadmium Content, g</u>	<u>Molarity</u>	<u>Analytical Method</u>
1.6×10^{-9}	5×10^{-9}	Anodic Stripping, 30 min
1.6×10^{-8}	5×10^{-8}	Anodic Stripping 5 min
1.6×10^{-7} (or greater)	5×10^{-7} (or greater)	Direct Pulse Polarograph

FIGURE 1. Stripping Analysis

TRACE ELEMENT VARIATIONS IN SILVER SALMON
AND KING SALMON MUSCLE TISSUE

L. A. Rancitelli, W. A. Haller and
J. A. Cooper

The trace element content of three types of muscle tissue in a Silver Salmon and one type of muscle tissue in an Alaskan King Salmon has been determined by neutron activation analysis. The elements determined include: Na, K, Rb, Cs, Br, Zn, Se, Fe, Co, Hg, Ag, and Sb. The sensitivity and precision of the method permits a study of the variations of several elements in the different tissues. A correlation between K, Rb, and Cs exists, as well as a correlation between Na, Br and Zn. A comparison of the abundances of Rb and Cs relative to K shows both ratios to be quite constant for the red, white and cheek muscle tissue of Silver Salmon. The Rb to K ratio in tissue compares favorably with the ratio found in sea water, while the Cs to K ratio differs from that in sea water by a factor of 10.

When one examines the available data concerning the trace element contents of muscle tissue,⁽¹⁾ it is evident that the values for many elements are either poorly known or nonexistent. This is in part due to the high sensitivity required for an accurate analysis of many trace elements. It is also apparent that a good portion of the reported analyses have been plagued by contamination problems, inherent when conventional wet chemical and instrumental methods are applied at the trace element level. However, the large variations observed in fish muscle cannot be solely attributed to experimental errors. It has been shown that the sodium and potassium contents of salmon muscle tissue are sensitive to several factors.⁽²⁾ Seasonal variations in the sodium and potassium levels occur, as well as changes attributed to the age of the fish and its local environment. Several workers have demonstrated that a

considerable variation exists in the sodium and potassium content of different species.^(3,4)

This work is concerned with measurements of the variations occurring in a single organism which previous work has demonstrated actually occur for the different organs.

Neutron activation analysis was employed to determine the trace element contents in the muscle tissue. This ensured the highest sensitivity for many of the elements of interest, as well as greater freedom from contamination errors. In addition, the high sensitivity of the method permitted the analysis of small samples, a prerequisite to a study of local variations in tissue. An added advantage was the fact that thirteen elements could be determined in a single tissue sample by the direct instrumental methods which were available thus permitting a study of the interdependence of several trace elements.

Two fish were sampled in this study, a mature female Silver Salmon from Ilwaco, Washington caught in August, 1967, and a mature Alaskan King Salmon from Alakanuk, Alaska caught in July, 1967. Six tissue samples were removed from the Silver Salmon under ultra clean conditions.* Two samples of red tissue were taken from the left side of the fish along the lateral line, the first under the leading edge and the second below the back edge of the dorsal fin. The white muscle tissue was removed approximately 5 cm above the lateral line directly above the regions previously sampled for red tissue. Two samples were also removed from the left cheek of this specimen. Two samples of red tissue were removed from the left side of the King Salmon along the lateral line and below the leading edge of the dorsal fin.

The general method employed in our laboratory for the analysis of biological material has been described in detail.* 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 to an integral 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, macerated, mixed with a hot 2% agar solution and poured into a 1/2 in. x 2 in. ring to achieve a standard counting geometry. The sample and standards were then counted for 10 min 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 essentially complete decay of ⁸²Br (35.3 hr half-life). 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 1000 min on an anticoincidence shielded gamma-gamma coincidence multiparameter analyzer to determine the activity of ⁴⁶Sc, ⁶⁰Co, ⁶⁵Zn, ^{110m}Ag, ¹²⁴Sb and ¹³⁴Cs. The observed activity of each isotope after applying a suitable decay correction was compared with the specific activity of a standard irradiated together with the sample to determine the quantity of each element present. Three elements, cobalt, cesium and zinc, were determined by both the gamma-gamma coincidence method of analysis and with the diode detector. The excellent agreement (10%) of results obtained by the two instrumental methods confirmed the reliability of the two direct methods of gamma ray analysis.

* L. A. Rancitelli, W. A. Haller and J. A. Cooper. "Instrumental Neutron Activation Analysis of Biological Tissue," this report, pp. 53-67.

The precision with which Na, Br, Cs, Ag, Zn, Fe, Sb and Co can be determined has been demonstrated to be very high* at concentrations far lower than those encountered in muscle tissue. An estimate of the error associated with the determination of each element is presented in Table I together with the results. These estimates are based upon counting statistics, self-shielding errors,** contamination, volatilization loss during processing, and side reactions leading to the same isotope. In all but one case, this latter effect was negligible. A fast neutron reaction on ^{46}Ti will also produce ^{46}Sc . Thus, the scandium contents reported in Table I should be considered upper limits to the actual values. Since all six Silver Salmon tissue samples were irradiated simultaneously and in a flat flux region, errors associated with variations in irradiation time and neutron flux are eliminated.

The results of the analyses of the three types of Silver Salmon muscle tissue are presented in Table I as micrograms of the element per gram of freeze dried tissue. The water content of these tissue samples which was removed by the freeze drying process varied from

77 to 81%. Results of a previous study involving the neutron activation analysis of three Silver Salmon livers[†] are included for comparison in Table I. An examination of Table I shows replicate samples to be in excellent agreement. A given type of muscle tissue proved to be quite homogeneous, although the variations between different types of tissue were striking. Several interesting features arise in these data, such as the correlation between potassium, cesium and rubidium as well as the correlation between sodium, zinc and bromine. The ratios of cesium and rubidium relative to potassium are presented in Table II for the various types of muscle tissue. The rubidium to potassium ratio is quite constant in the various tissues and compares favorably with the ratio in sea water. Although the cesium to potassium ratio is constant in the three types of muscle tissue, it differs by a factor of 10 from that of sea water.^(5,6) This would seem to indicate that rubidium occurs in sea water in concentrations which meet the demands of the organism or that no biological selection occurs between K and Rb at these levels, while a biological concentration of cesium is required.

Although the cheek muscle physically resembles white muscle tissue, several outstanding differences in

* L. A. Rancitelli, W. A. Haller and J. A. Cooper. "Instrumental Neutron Activation Analysis of Biological Tissue," this report, pp. 53-67.

** L. A. Rancitelli and W. A. Haller, "Neutron Activation Analysis of Biological Tissue I: Neutron Self-Shielding Errors," this report, pp. 68-72.

† L. A. Rancitelli, C. E. Jenkins and W. A. Haller. "Trace Element Content and Specific Activity of Several Nuclides in Silver Salmon Liver," this report, pp. 47-52.

TABLE I. Trace Element Concentrations and Their Variation in Silver Salmon Tissues

Element (10 ⁻⁶ g/g Dry Tissue)	Red Muscle			White Muscle			Cheek Muscle			Liver ⁽⁷⁾
	1	2	Ave.	1	2	Ave.	1	2	Ave.	Average
Na	1040	1100	1070 ±30	940	890	920 ±30	3080	3690	3380 ±300	3000 ±300
K	9900	9900	9900	16,900	16,700	16,800 ±100	10,300	9000	9600 ±700	18,000 ±3000
Rb	3.8	3.4	3.6 ±0.2	5.7	5.5	5.6 ±0.1	3.7	3.9	3.8 ±0.1	7.2 ±1.3
Cs	0.066	0.068	0.067 ±0.001	0.110	0.100	0.105 ±0.005	0.058	0.054	0.056 ±0.002	0.047 ±0.008
Br	34	30	32 ±2	27	24	26 ±2	72	88	80 ±8	66 ±5
Fe	34	46	40 ±6	7.0	8.3	7.6 ±0.6	29	32	30 ±2	270 ±40
Zn	19	22	20 ±2	12	12	12 ±1	49	53	50 ±2	95 ±8
Se	0.68	0.78	0.73 ±0.05	0.98	0.94	0.96 ±0.02	0.92	1.04	0.98 ±0.06	3.8 ±0.6
Hg	0.2	0.2	0.2 ±0.1	0.3	0.3	0.3 ±0.1	0.6	0.6	0.6 ±0.1	0.3 ±0.1
Co	0.021	0.030	0.025 ±0.005	0.005	0.006	0.006 ±0.001	0.014	0.015	0.014 ±0.001	0.17 ±0.09
Sc	0.00003	0.00004		0.00004	0.00002		0.00008	0.00009		0.00020
Ag	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	170 ± 130 x 10 ⁻³
Sb	0.0006	0.0002	0.0004	0.0001	0.0002	0.0002	0.0006	0.0003	0.0004	0.0008

TABLE II. Rubidium and Cesium Concentrations in Silver Salmon Tissue Relative to Potassium

	$\frac{\text{Rb}}{\text{K}}$	$\frac{\text{Cs}}{\text{K}}$
Red Muscle	3.6×10^{-4}	6.8×10^{-6}
White Muscle	3.3×10^{-4}	6.3×10^{-6}
Cheek Muscle	4.0×10^{-4}	5.8×10^{-6}
Liver	3.8×10^{-4}	2.5×10^{-6}
Sea Water	3.3×10^{-4}	7.9×10^{-7}

elemental composition appear. The sodium, bromine and iron content of the cheek muscle is three to four times as high as in white muscle. Bromine has been classified as an element which structurally replaces chlorine and then fails to act as a functional element.⁽¹⁾ Hence, it is not possible to draw any conclusions about an increased bromine content without information concerning the chlorine level.

Selenium is known to be a biologically important element as it replaces vitamin E⁽¹⁾ in mammals. The selenium content is constant in white muscle and cheek muscle, but is significantly lower in red muscle tissue. However, the selenium content of all salmon tissue is much lower than similar measurements of aquatic organisms from a certain series of samples.*

* L. A. Rancitelli, W. A. Haller and J. A. Cooper. Unpublished Data. Pacific Northwest Laboratory, 1968.

The results of the analysis of two samples of King Salmon red muscle tissue are presented in Table III. The concentrations of Na, K, Cs, Se and Hg are somewhat higher in King Salmon tissue than in Silver Salmon, while the other elements are approximately the same.

It is not possible to explain the physiological and metabolic processes responsible for the observed variations at this time. However, it appears that a significant contribution to a study of the life processes could be made by considering the intradependence of as many trace elements as possible within a tissue sample. This

TABLE III. Trace Element Content of Red Muscle Tissue of an Alaskan King Salmon ($\mu\text{g/g}$ Freeze Dried Tissue)

Element	Sample 1	Sample 2	Average
Na	1700	1600	1600 ± 100
K	13,000	13,000	$13,000 \pm 1000$
Rb	2.9	3.1	3.0 ± 0.1
Cs	0.11	0.12	0.12 ± 0.01
Br	25	23	24 ± 1
Fe	18	12	15 ± 3
Zn	25	18	22 ± 4
Se	1.7	1.5	1.6 ± 0.1
Hg	0.8	0.8	0.8 ± 0.1
Co	12	9.3	11 ± 2
Sc	0.00001	0.00002	0.00002
Ag	<0.001	<0.001	<0.001
Sb	0.0009	0.0009	0.0009

work demonstrates the feasibility of such a study and the unique applicability of neutron activation analysis to the problem. A natural extension of this analysis could be made to include other biologically important elements such as chlorine and manganese.

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TRACE ELEMENT CONTENT AND THE SPECIFIC ACTIVITY OF SEVERAL RADIONUCLIDES IN SILVER SALMON LIVER

L. A. Rancitelli, C. E. Jenkins
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Neutron activation analysis of liver tissue from silver salmon was employed to determine Na, K, Rb, Cs, Br, Zn, Fe, Co, Cr, Ag, Sb, Sc, Se and Hg by direct instrumental gamma-ray analysis. The radionuclide concentration of an average sample of silver salmon livers was determined by gamma-gamma coincidence techniques and the data combined with the trace elemental composition to obtain the specific activities of ^{40}K , ^{60}Co , ^{65}Zn , $^{110\text{m}}\text{Ag}$ and ^{137}Cs . The specific activity of ^{60}Co , ^{65}Zn and ^{137}Cs in silver salmon is compared with values found in sea water. The results indicate that the specific activity of ^{137}Cs is constant in both the organism and its environment, while that of ^{65}Zn and ^{60}Co are factors of 1000 and 80 times higher in the fish.

The detection and subsequent measurement of artificial radionuclides in the natural environment⁽¹⁾ have provided a basis for important

practical applications including the study of the transport of trace elements in the biosphere. The injection into the environment of

radioisotopes produced by nuclear weapons testing and nuclear reactor operation has significantly altered the radioactivity in the nutritional chain of several species, notably Alaskan Eskimos and caribou.⁽²⁾ Previous work has been concerned with the sources of radionuclides such as ^{55}Fe and ^{137}Cs in the food chain and the resultant accumulated body burdens.^(2,3) It is not known whether or not artificially produced long-lived radionuclides eventually become intimately mixed and then behave in a manner similar to the stable elements in the natural environment. The uptake of any nuclide by a biological system will depend on several factors, including its physical and chemical properties and the biological importance of the element. Also, under steady state conditions, its total accumulation will be controlled by the effective half life⁽⁴⁾ of the radionuclide.

To reach a better understanding of the physiological consequences of radionuclides in our environment, it is important to define the specific activity of a nuclide with reference to the trace element content of an organism. In this way one is able to determine the body burden of a radionuclide as well as study the effects of chemical composition upon the uptake of radionuclides. Since a biological system cannot significantly separate the isotopes of heavier elements,⁽⁵⁾ the specific activity of a radioisotope will be constant for the various tissue types within an

organism. Hence, the analysis of liver tissue with its high relative concentrations of trace elements should reflect the specific activity of the entire organism.

A determination of the specific activities of ^{40}K , ^{60}Co , ^{65}Zn , $^{110\text{m}}\text{Ag}$ and ^{137}Cs in silver salmon liver was made by a combination of neutron activation analysis and low-level counting. The livers were removed from mature silver salmon caught off the coast of Ilwaco, Washington in September, 1967.

Three livers were chosen randomly and samples of about 5 g wet weight were taken from each for neutron activation analysis. The samples were freeze dried, activated with an integrated thermal neutron flux of about 10^{17} n/cm^2 , and a gamma-ray analysis performed after an appropriate decay time with both a $20 \text{ cm}^3 \text{ Ge(Li)}$ detector and an anti-coincidence shielded gamma-gamma coincidence multichannel analyzer.* Counting statistics were less than 5% for all elements except Cr, Sb, Sc and Hg. The experimental error in the determination of all the elements, with the possible exception of Ag and Sb, is estimated to be less than 10%. This estimate based upon a consideration of counting statistics, neutron self-shielding in the sample, and possible contamination has been

* L. A. Rancitelli, W. A. Haller and J. A. Cooper, "Instrumental Neutron Activation Analysis of Biological Tissue," this report, pp. 53-67.

verified by replicate analysis of several types of biological tissue.* The elements determined by neutron activation analysis include Na, K, Rb, Cs, Br, Zn, Fe, Co, Cr, Ag, Sb, Se and Hg. The trace element content of these liver samples is presented in Table I as micrograms of the element per gram freeze dried tissue (ppm) together with the average of the three values and its standard deviation. The large variation of several elements such

as Ag and Co in the tissue is striking. Equally interesting is the small variation of other elements such as Br, Zn and the alkali metals in the livers of the three fish.

The determination of the natural and artificial activity in the salmon livers was accomplished by low level counting with an anti-coincidence shielded gamma-gamma coincidence multidimensional analyzer. The low activity level of the samples necessitated the use of several kilograms of material. Hence, the livers from about twelve fish were carefully removed, and after removing several samples for

* L. A. Rancitelli, W. A. Haller and J. A. Cooper, "Instrumental Neutron Activation Analysis of Biological Tissue," this report, pp. 53-67.

TABLE I. Trace Element Content of Silver Salmon Livers
($\mu\text{g/g}$ Freeze Dried Tissue)

Element	Sample 1	Sample 2	Sample 3	Avg $\pm$ σ
Na	3,200	2,700	3,100	3000 $\pm$ 300
K	15,000	20,000	21,000	18,000 $\pm$ 3000
Rb	5.4	8.6	5.9	6.6 $\pm$ 1.7
Cs	0.038	0.054	0.049	0.047 $\pm$ 0.008
Br	65	71	62	66 $\pm$ 5
Zn	100	86	100	95 $\pm$ 8
Fe	260	240	310	270 $\pm$ 40
Co	0.27	0.13	0.11	0.17 $\pm$ 0.09
Cr	<0.020	<0.020	<0.020	<0.020
Ag	0.210	0.020	0.270	0.170 $\pm$ 0.130
Sb	0.001	0.0006	0.001	0.001 $\pm$ 0.0003
Sc	<0.0002	<0.0002	<0.0002	<0.0002 $\pm$ 0.0001
Se	4.5	3.4	3.4	3.8 $\pm$ 0.5
Hg	0.3	0.2	0.4	0.3 $\pm$ 0.1

activation analyses, the livers were split into two fractions and subjected to a low temperature (500 °C) ashing process. The ashed samples were pressed into two 1/2 in. by 2 in. discs and finally counted for 1000 min with a multi-dimensional gamma-ray spectrometer.

The activities of ^{40}K , ^{54}Mn , ^{60}Co , ^{65}Zn , $^{110\text{m}}\text{Ag}$ and ^{137}Cs found in wet tissue of silver salmon livers are presented in Table II together with the standard deviation of these values based upon counting statistics. The activities of the two samples proved to be quite similar for all nuclides. The activities of the two ashed samples were averaged to obtain a mean value for all the fish samples.

The trace elemental composition of the three liver samples as obtained by neutron activation analysis was assumed to be a reasonable representation of the range of values one might expect. The average trace element content in Table I and the radionuclide con-

centrations presented in Table II were used to calculate the specific activities of ^{40}K , ^{60}Co , ^{65}Zn , $^{110\text{m}}\text{Ag}$ and ^{137}Cs . These specific activities together with their error based upon the variation of that trace element in the three livers sampled for activation are also presented in Table II. The specific activity of ^{40}K of 0.81 ± 0.14 nCi/gK is in good agreement with the accepted value of 0.81 nCi/gK, though the error was large (17%) because of the variation of stable potassium in the three samples (see Table I). The specific activities of the four artificially produced radionuclides ^{60}Co , ^{65}Zn , $^{110\text{m}}\text{Ag}$ and ^{137}Cs vary from 100 nCi/g to 1800 nCi/g. This is a rather small range of values when one considers that the radionuclide concentration (^{65}Zn to $^{110\text{m}}\text{Ag}$) varies by about three orders of magnitude.

A comparison of the specific activity of ^{60}Co , ^{65}Zn and ^{137}Cs in silver salmon liver with typical

September 1967 Ellwood, OJA.

TABLE II. Radionuclide Concentrations and Specific Activities in Silver Salmon Livers

Isotope	Half-Life	Activity, dpm/kg wet tissue			Specific Activity, nCi/g element	Specific Activity of Sea Water, nCi/g element*
		Sample A	Sample B	Average		
^{40}K	1.3×10^9 y	6600 ± 100	6700 ± 100	6600 ± 100	0.81 ± 0.14	0.81
^{60}Co	5.2 y	28 ± 1	26 ± 1	27 ± 1	360 ± 180	4.5
^{65}Zn	243 d	8900 ± 100	7800 ± 100	8300 ± 500	220 ± 30	<0.05
$^{110\text{m}}\text{Ag}$	260 d	7.0 ± 0.5	6.6 ± 0.5	6.8 ± 0.3	100 ± 60	---
^{137}Cs	30 y	40 ± 10	30 ± 10	35 ± 15	1800 ± 600	~1800

* D. E. Robertson, W. O. Forster and H. G. Rieck, and J. C. Langford, "A Study of the Trace Element and Radionuclide Behavior in a Northeast Pacific Ocean Ecosystem 350 Miles Off Newport, Oregon," this report, pp. 92-108.

values for sea water gives some insight into the biological uptake of these isotopes relative to the stable trace elements.

The specific activity of ^{137}Cs is essentially the same in the organism and its environment, indicating that ^{137}Cs is chemically well mixed with stable cesium. This is not an unreasonable result considering the chemical properties of the alkali metals. In an aqueous medium, cesium occurs as the hydrated ion and any radiocesium injected into the marine environment should immediately achieve the same chemical state as the stable cesium. The uniform absorption of all isotopes of cesium present from the ocean would then maintain a constant specific activity throughout the biosphere.

This does not appear to be true for ^{60}Co and ^{65}Zn . A comparison of the specific activity of ^{65}Zn in salmon with that in sea water demonstrates that it is higher in the organism by several orders of magnitude. Robertson* also reports the concentration of ^{65}Zn in several marine organisms to be 100 times higher than the specific activity found in sea water. The high specific activity of ^{65}Zn in the Columbia River, approximately 8900 nCi/g Zn^(1,6), may possibly be

responsible for this observed activity. If the 91 day biological half life of Zn in the human liver⁽⁴⁾ is a reasonable approximation to the half-life in the salmon liver, the activity we observe may reflect the response of the organism to its environment during its entire life span. Any ^{65}Zn accumulated during its first year in the Columbia River would be reduced to one thousandth through biological elimination and radioactive decay and to about one fifth through growth when the fish reaches maturity. However, the specific activity of ^{65}Zn in the Columbia River is five orders of magnitude greater than sea water and several orders of magnitude higher than the specific activity found in Alaskan salmon.** Thus, a significant portion of the ^{65}Zn in these salmon could be attributed to contact with the Columbia River or the estuary.

The ratio of the specific activity of ^{60}Co in the salmon to that in sea water is about 80. This is in reasonable agreement with data reported for 5 other marine organisms.* The specific activity of ^{60}Co in the Columbia River is about 10^5 nCi/g of cobalt. The ^{60}Co activity observed in the salmon could be attributed to its residence in or near the Columbia River estuary. However, we cannot rule out the possibility that ^{60}Co and

* D. E. Robertson. "A Study of the Trace Element and Radionuclide Behavior in a Northeast Pacific Ocean Ecosystem 350 Miles off Newport, Oregon," this report, pp. 92-108.

** C. E. Jenkins, "Radionuclide Distribution and Specific Activity in Salmon," this report, pp. 11-17.

^{65}Zn may occur in chemical forms which are more readily assimilated by the organism than is the stable element.

Although the data at present are sparse, several conclusions can be drawn. The uptake of a particular radionuclide by an aquatic organism cannot be accurately predicted solely from trace element considerations of the system. It appears that chemical species and stability play an important role in the transport of a radioisotope. Radioisotopes which exhibit a simple monovalent chemistry in aqueous solutions such as the Group I elements should mix quickly with the medium with resultant uniform uptake of radio-and-stable isotopes by a biological system. Radionuclides of other elements exhibiting an aqueous chemistry predominated by complexes, colloids and insoluble salts or having a high degree of adsorption on particulate matter will not necessarily follow the trace element paths in the biosphere. Generally, it will be necessary to examine the uptake of each nuclide by comparing the specific activity of the organism with its environment. Estimates of radionuclide uptake based on specific activity

measurements of ocean water may be in error by several orders of magnitude.

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INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF BIOLOGICAL TISSUE

L. A. Rancitelli, W. A. Haller
and J. A. Cooper

A method of instrumental neutron activation analysis capable of determining fourteen elements in biological tissue is described. Gamma-ray analysis of neutron irradiated muscle tissue is performed with a Ge(Li) detector and an anticoincidence-shielded multidimensional analyzer. The elements determined with a precision of better than 10% include: Br, Co, Cs, Fe, Hg, K, Na, Rb, Se and Zn. The elements Ag, Sc, Sb and Cr were determined at concentrations approaching the lower limit of detection (several parts per billion). Excellent agreement was achieved between the results obtained by gamma-ray analysis with a Ge(Li) detector and those determined by coincidence gamma-ray analysis. The contribution of sample contamination, secondary reactions, counting statistics and self-shielding to the error in the determination of each element are considered.

A vast amount of data concerning the trace element concentrations in muscle tissue have been accumulated over the years.⁽¹⁾ However, the role of most trace elements remains at best poorly understood. This situation can in part be attributed to the lack of a practical analytical method capable of high sensitivity, precision and versatility. Conventional instrumental methods are limited by sensitivity or errors introduced during the preparation of the sample. The same is true, to a great extent, for wet chemical methods. Ashing procedures risk the partial loss of volatile elements such as Hg, Br, Se, As and Sb while the contamination introduced by reagents is often far from negligible. The lack of sensitivity can be overcome somewhat by increasing the sample size. But in the case of many biological specimens, this requires averaging over many individual samples. Thus, information concerning variations within a population is lost.

The development of neutron activation analysis as a useful

tool has been one of the major accomplishments in the field of analytical chemistry. The virtues of this analytical tool, high sensitivity, precision and applicability, have been extensively documented.⁽²⁾ It is not unexpected, then, that a good deal of the data concerning trace elements in biological tissue have been revised using various methods of activation analysis. However, previous work has been concerned with the instrumental determination of several of the more abundant trace elements⁽³⁾ or vast multielement determinations involving extensive radiochemical separations prior to gamma-ray analysis.⁽⁴⁾ The former method lacks the flexibility necessary to simultaneously determine many of the essential trace elements, while the latter method can be rather involved and time consuming.

The question arises as to whether the determination of a large number of elements within a single sample is worthy of the effort. Studies have been made of the variation of major trace elements such as sodium

and potassium in salmon muscle tissue.⁽⁵⁾ The indications are that significant variations do occur. It is not unreasonable to expect the same to be true for other trace elements. Thus, the method of analysis should be capable of determining a large number of intrarelated trace elements in a small sample if variations in trace element concentrations are to be studied. This work demonstrates a method of instrumental neutron activation analysis that is capable of simultaneously determining a large number of the biologically important elements.

EXPERIMENTAL

Sample Preparation and Irradiation

Biological specimens were thoroughly washed with distilled water and placed in an Agnew-Higgins Laminar Flow Work Station which provided an environment where particles as small as 0.3μ had been removed. A rectangular incision was made through the skin with a clean Bard-Parker No. 11 surgical knife blade. After stripping the skin back with a pair of Teflon coated tweezers, a flesh sample was removed from the center of the divided area with a second blade. It has been demonstrated by cutting samples of fish with a neutron activated knife blade, that this sampling procedure results in a negligible amount of contamination (see Table I). The sample was washed briefly in distilled water

and placed in a preweighed No. 25 Nalgene polyethylene container. Washing irradiated tissue demonstrated the loss of ^{24}Na to be less than 3%. All of the polyethylene containers employed in the neutron activation analysis were leached in warm redistilled nitric acid for several days before use. The polyethylene container was placed inside a second No. 34 polyethylene container which had several 1 cm slits in the side. The doubly encapsulated sample was then placed in a Thermovac Industries Corporation freeze drier. The sample was considered "dry" when a weight loss of less than 1% in 24 hr occurred. Three to four days were generally required to dry a 5 g wet weight sample. Immediately after removal from the freezer drier, the sample was reweighed and the inner container was capped and sealed with Scotch Brand Plastic Tape. The sample container was then wrapped in 1 mil aluminum foil.

The trace element content of each sample was determined by comparing the neutron induced activity of a radionuclide in the sample with the specific activity produced in a known amount of the element irradiated with the sample. This was found to be superior to calculations involving the reactor flux since changes in the thermal to fast ratio in a production reactor can lead to an unnecessary error.

Each standard consisted of a dilute (10^{-6} to 10^{-8} g/ml) aqueous solution of the element of interest.

TABLE I. Trace Element Contamination of Fish Muscle Tissue Produced by Dissection with a Stainless Steel Surgical Knife Blade* (10^{-9} g Element/g Tissue)

Element	1	2	3	4	Concentration (ppb) Observed in the Fish Muscle**
Co	<0.05	0.1	0.1	0.1	2
Fe	20	50	40	50	4000
Zn	15	<10	15	<10	10,000
Rb	1.5	1.5	<1	1.5	3000
Cr	0.3	0.2	<0.1	0.2	<20
Se	0.8	1.5	0.7	0.4	600

* The knife blade had been neutron-activated so that its loss to the sample could be readily observed. (10^{17} n/cm²).

** L. A. Rancitelli, W. A. Haller, and J. A. Cooper. Unpublished Data. Pacific Northwest Laboratory, 1968.

Matty Specpure Material was dissolved in redistilled nitric acid and diluted with doubly distilled water. Quartz ampoules (3 mm ID) were cleaned by boiling in nitric acid for several days prior to use. One-hundred microliter aliquots of each standard were sealed in ampoules and placed in an aluminum irradiation can.

The samples and standards were simultaneously irradiated in the "quickie" facility of a Hanford K production reactor to an integrated thermal neutron exposure of about 7×10^{17} n/cm². The neutron flux gradient in the region of the reactor used for these irradiations varied only a few percent across seven adjacent positions. The flux was highly thermalized, having a cadmium ratio in excess of 100.

Postirradiation Handling

A two day decay interval was required before the samples could be handled safely without elaborate remote facilities. The protective aluminum foil was removed and the containers lacquered to prevent any transfer of contamination from the exterior portions of the capsule to the sample. The plastic tape was then removed from the polyethylene capsule and a second coating of lacquer applied. The sample was then transferred from the irradiation container to a plastic bag and crushed to a fine powder. Freeze drying and irradiation transformed most muscle tissue to a brittle or friable state. This powder was placed in a 1/2 in. by 2 in. PVC ring containing several

milliliters of hot water and was allowed to soak for several minutes. A hot 2% agar mixture was added to the ring and the particles of the sample were finely dispersed with a high speed mixer. The agar mixture was allowed to cool about 30 min before the ring was wrapped in plastic tape and two layers of Saran Wrap. The samples were then ready for gamma-ray analysis.

The standards were mounted in the same configuration as the sample to eliminate differences of source self-shielding and geometry. Each quartz ampoule containing a standard was washed in concentrated nitric acid and rinsed in distilled water before it was opened. Fifty microliters of the standard were placed in a 1/2 in. by 2 in. PVC ring containing a 2% agar solution and were thoroughly mixed to achieve a geometry identical to the sample.

Two detector systems were employed in the gamma-ray analysis of the samples and standards. The first consisted of a high resolution, five sided coaxial Ge(Li) detector (Nuclear Diodes, Inc.) with an active volume of 20 cm³. This detector was contained in a 4 in. thick Cd-Cu lined lead cave. In conjunction with this diode was a Tennelec TC-130 preamplifier, a TC-200 amplifier and a Nuclear Data Model 2200 pulse height analyzer.⁽⁶⁾ This detector system had a resolution (FWHM) of about 3.3 keV for the 1332 keV photon of ⁶⁰Co. The second detector system was an

anticoincidence-shielded, gamma-gamma coincidence multidimensional analyzer.⁽⁷⁾

The samples were placed on a source holder 12 cm above the Ge(Li) detector and counted for 10 min. The major activities two days after irradiation were ²⁴Na, ⁴²K and ⁸²Br. A typical spectrum is presented in Figure 1. The content of these three elements was obtained by comparing the area under the most prominent peak for each isotope with the specific activity of the standards. The purity of the ²⁴Na (1369 keV), ⁴²K (1525 keV) and ⁸²Br (777 keV) photopeaks, were confirmed by measuring the half-life of each photopeak.

Approximately one month after irradiation, the sample was again counted on the Ge(Li)/diode for 1000 min and the activities of interest were compared with standards to obtain the trace element contents. This decay interval was particularly important in ensuring the purity of the 1292 keV photopeak of ⁵⁹Fe. The ⁴⁷Ca (4.5 d) is permitted to decay thus eliminating its 1300 keV photon from the spectrum. An additional benefit of the decay interval is the partial removal of ³²P (14.8 d) and its accompanying beta-spectrum, resulting in a relative enhancement of the ⁵¹Cr, ⁷⁵Se and ²⁰³Hg photopeaks. The following isotopes can be readily identified from their characteristic photopeaks (see Figure 1): ⁵¹Cr (320 keV), ⁵⁹Fe (1292 keV), ⁶⁰Co (1332 keV), ⁶⁵Zn

Neg 0681141

FIGURE 1. Gamma Spectra of Neutron Activated Fish Muscle

(1115 keV), ^{75}Se (265 keV), ^{134}Cs (796 keV), ^{203}Hg (279 keV). In the case of radionuclides which emit several gamma rays, only the photon used for the actual activity measurement is listed. The optimum photopeak for each isotope was chosen by considering possible interfering photopeaks, the photon intensity and the peak to Compton ratio. Since ^{75}Se and ^{203}Hg emit gamma rays with nearly identical energies, it is necessary to strip the contribution of ^{75}Se from the 279 keV photopeak to obtain the ^{203}Hg activity. The relative intensities of the 265 keV and 279 keV photopeaks of the selenium standard and the 265 keV photopeaks of the sample are used to obtain the contribution of ^{75}Se to the 279 keV peak. The presence of ^{203}Hg can also be verified by counting the sample six months after irradiation. The nearly complete complete decay of ^{32}P (14.8 d) reveals the characteristic X-rays associated with the ^{203}Hg decay (72.9 keV and 82.6 keV). The stripping of the ^{75}Se component from the 279 keV photopeak, of course, greatly reduces the sensitivity of the mercury determination. The accuracy with which the ^{75}Se contribution could be stripped from the 279 keV photopeak was determined by preparing simulated sources containing constant amounts of ^{32}P and ^{75}Se and various known amounts of ^{203}Hg . Statistical considerations of the counting errors involved indicate a detection limit of 0.1 ppm Hg with a 25% error in the

presence of 1 ppm Se. Although ^{46}Sc and ^{65}Zn also have gamma rays of nearly identical energies, the fact that muscle tissue contains five orders of magnitude more zinc than scandium eliminates any significant contribution of ^{46}Sc to the 1115 keV photopeak of ^{65}Zn .

Table II contains a list of the elements identified from their neutron-induced radioisotopes with a Ge(Li) detector. Also included are the photon energies used for the analysis. Two additional columns included in Table II show other radioisotopes produced by (n, γ) reactions which emit photons with energies similar to the isotope of interest, and possible neutron reactions on other elements which could produce the observed radioisotope.

Approximately 45 days after irradiation, the specific activities of several isotopes in the samples and standards were finally determined with an anticoincidence-shielded multidimensional gamma-gamma coincidence analyzer by counting for 1000 min. In addition to detecting ^{60}Co , ^{65}Zn and ^{134}Cs , it was also possible to measure the ^{46}Sc , $^{110\text{m}}\text{Ag}$ and ^{124}Sb activities. Due to the very low concentrations of scandium, silver and antimony in biological tissue, gamma-gamma coincidence techniques offered the best possible method of analysis without recourse to radiochemical separations. A list of the isotopes identified by multidimensional analysis is presented in Table III. The determination of cobalt, cesium

*TABLE II. Elements Identified with a Ge(Li) Detector
in Neutron Activated Muscle Tissue*

Element	Isotope Produced by (n,γ) Reactions	Photon Measured keV ⁽⁸⁾	Possible Interfering* Isotopes Emitting Photon of Similar Energy	Possible Interfering Nuclear Reactions Producing the Isotope of Interest
Na	²⁴ Na(15 h)	1369	¹²⁴ Sb(60.2 d), ⁷⁷ Ge(11.3 h) ¹³⁴ Cs(2.1 yr)	²⁴ Mg(n,p) ²⁴ Na ²⁷ Al(n,α) ²⁴ Na
K	⁴² K(12.4 h)	1524		⁴³ Ca(n,p) ⁴² K ⁴⁵ Sc(n,α) ⁴² K
Cr	⁵¹ Cr(27.8 d)	320	¹⁴⁷ Nd(11 d) ¹⁹² Ir(74 d)	⁵⁴ Fe(n,α) ⁵¹ Cr
Fe	⁵⁹ Fe(45 d)	1292	⁴⁷ Ca(4.5 d)	⁵⁹ Co(n,p) ⁵⁹ Fe ⁶² Ni(n,α) ⁵⁹ Fe
Co	⁶⁰ Co(5.2 yr)	1332	¹²⁴ Sb(60.2 d)	⁶⁰ Ni(n,p) ⁶⁰ Co ⁶³ Cu(n,α) ⁶⁰ Co
Zn	⁶⁵ Zn(234 d)	1115	⁴⁶ Sc(83.9 d), ¹⁶⁰ Tb(73 d)	-----
Se	⁷⁵ Se(120 d)	265	^{113m} Cd(14 yr), ¹⁸² Ta(115 d)	⁷⁸ Kr(n,α) ⁷⁵ Se
Br	⁸² Br(35.3 h)	777	¹⁸⁷ W(24 h), ^{131m} Te(30 h)	⁸⁵ Rb(n,α) ⁸² Br
Rb	⁸⁶ Rb(18.7 d)	1078	¹²⁵ Sn(9.6 d), ^{123m} Sn(131 d)	⁸⁶ Sr(n,p) ⁸⁶ Rb ⁸⁹ Y(n,α) ⁸⁶ Rb
Cs	¹³⁴ Cs(2.1 yr)	796	-----	¹³⁴ Ba(n,p) ¹³⁴ Cs
Hg	²⁰³ Hg(46.6 d)	279	⁷⁵ Se(120 d), ^{166m} Ho(30 yr) ¹⁷⁵ Yb(101 h)	²⁰³ Tl(n,p) ²⁰³ Hg ²⁰⁶ Pb(n,α) ²⁰³ Hg

* Isotopes with half-lives similar to that of the isotope of interest

*TABLE III. Radioisotopes Identified in Neutron Activated
Muscle Tissue by Gamma-Gamma Coincidence Techniques*

Isotope	Half Life	Coincidence Gamma Rays, keV	Possible Interfering Reactions Producing the Isotope of Interest
⁴⁶ Sc	83 d	889, 1121	⁴⁶ Ti(n,p) ⁴⁶ Sc
⁶⁰ Co	5.2 yr	1173, 1332	(See Table II)
⁶⁵ Zn	243 d	511, 511(β ⁺)	-----
^{110m} Ag	260 d	658, 1384 + 884 658, 764 + 1505	¹¹⁰ Cd(n,p) ¹¹⁰ Mg ¹¹³ In(n,α) ¹¹⁰ Mg
¹²⁴ Sb	60 d	603, 1692	¹²⁴ Te(n,p) ¹²⁴ Sb ¹²⁷ I(n,α) ¹²⁴ Sb
¹³⁴ Cs	2.1 yr	605, 796	(See Table II)

and zinc with both the Ge(Li) detector and a multidimensional detector system serves as an internal check of the measurements.

Results and Discussion

Replicate samples of a high purity cellulose material, IPC filter, available from Knowlton Bros. Specialty Products, were analyzed to demonstrate the precision and sensitivity with which antimony, cesium, cobalt, iron, scandium, silver, sodium and zinc can be determined. Since the trace element concentrations of this material are very low, it was necessary to perform the gamma-ray analysis with a multidimensional analyzer system. The results obtained for this material together with the average for the five samples are presented in Table IV.

The standard deviation of the average has been calculated in the usual manner.⁽⁹⁾ The estimated error for each element is due almost entirely to counting statistics. This is a conservative estimate of the precision with which these elements can be determined in muscle tissue, since, with the possible exception of antimony and scandium, these elements have much lower concentrations in this material than in muscle tissue.

The results of the analysis of five sets of replicate samples of fish muscle are presented in Tables V and VI. The estimated errors are based upon consideration of counting statistics, self-shielding errors, source homogeneity, contamination errors and interfering nuclear reactions (see Table II). The large variations observed in biological tissue make

*TABLE IV. Trace Element Content of Cellulose Filter Material**

Element	Concentration, ppb**					Avg $\pm$ σ	Experimental Error
	1	2	3	4	5		
Na (ppm)	71	70	71	74	75	72 $\pm$ 2	5%
Zn (ppm)	0.64	0.64	0.65	0.60	0.66	0.64 $\pm$ 0.03	5%
Co	2.7	2.7	2.5	2.5	2.5	2.6 $\pm$ 0.1	10%
Sb	1.3	1.7	1.6	1.3	1.5	1.5 $\pm$ 0.2	10%
Sc	0.41	0.43	0.39	0.41	0.39	0.40 $\pm$ 0.01	5%
Cs	0.29	0.32	0.24	0.25	0.28	0.30 $\pm$ 0.04	25%
Fe (ppm)	5.8	5.8	5.7	5.8	5.5	5.7 $\pm$ 0.1	15%
Ag	<1	<1	<1	<1	<1	<1	15%

* IPC paper, Knowlton Bros. Specialty Products

** Except as noted

TABLE V. Trace Element Determinations of Salmon Muscle Tissue
(Concentration 10^{-6} g/g dry weight tissue)

Element	Analyzer* System	Red Muscle		White Muscle		Cheek Muscle		Estimated Error
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	
Na	D	1040	1100	940	890	3100	3700	5%
K	D	9900	9900	16900	16,700	10,000	9000	5%
Rb	D	3.8	3.4	5.7	5.5	3.7	3.9	5%
Cs	D	0.070	0.065	0.11	0.11	0.063	0.052	10%
Cs	M	0.066	0.068	0.10	0.098	0.058	0.054	5%
Br	D	34	30	27	24	72	88	5%
Fe	D	35	46	8.1	8.3	29	32	10%
Zn	D	18	21	12	12	47	54	5%
Zn	M	19	22	12	12	49	53	5%
Se	D	0.68	0.78	0.98	0.94	0.92	1.1	10%
Hg	D	0.16	0.21	0.25	0.21	0.56	0.62	15%
Co	D	0.021	0.031	0.0053	0.0060	0.016	0.018	15%
Co	M	0.021	0.030	0.0051	0.0057	0.014	0.015	5%
Sc	M	0.00003	0.00004	0.00004	0.00002	0.00008	0.00009	25% - 50%
Ag	M	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	10% - 20%
Sb	M	0.0006	0.0002	0.0001	0.0002	0.0006	0.0003	15% - 25%
Cr	D	0.020	0.030	<0.020	<0.020	0.32	0.30	25%
Weight of Sample (g dry tissue)		0.49	0.28	0.34	0.35	0.19	0.21	

* D - Ge(Li) Detector System

M - Multidimensional Analyzer System

it impracticable to compare these results directly with values in the open literature. They are within the range of concentrations previously reported.⁽¹⁾ Because of the variation of trace elements in different types of tissue from the same specimen, it is difficult to compare the precision of the analysis except for replicate tissue samples. It is also possible that the trace elements within a given type of tissue are not uniformly distributed. Hence, these data

should be considered as a most conservative estimate of the experimental precision.

The results presented in Table V indicate that the precision in the alkali metal analyses was better than 10%. The results of the Na analysis of cheek muscle varied 9% from the average of 3400 ppm, while the K and Rb varied about 5%. The cesium content varied from 1 to 7%. The results of the Cs determinations obtained by gamma-ray analysis with a Ge(Li) detector compared quite

TABLE VI. Trace Element Determination of Trout Muscle Tissue
(Concentration, 10^{-6} g/g dry tissue)

Element	Red Muscle		White Muscle		Estimated Error
	Sample 1	Sample 2	Sample 1	Sample 2	
Na	820	770	570	620	5%
K	7600	6300	18,000	20,000	5%
Rb	8.0	6.2	17	17	5%
Cs	0.052	0.036	0.11	0.11	5%
Br	18	16	11	10	5%
Fe	77	50	10	8.5	10%
Zn	24	26	12	11	5%
Se	0.49	0.37	0.70	0.64	10%
Co	0.052	0.034	0.011	0.011	5%

well with those obtained with a multidimensional analyzer system.

The results of the Br, Zn, Se and Hg analysis of duplicate samples of tissue varied by less than 10%. The results of the Zn analysis obtained with the two analyzer systems agreed within 5%. The Fe and Co analysis of duplicate samples of white muscle and cheek tissue indicated a high degree of precision. However, duplicate samples of red muscle varied by 12 and 25%, respectively. Variations of this magnitude have been observed in the Fe and Co content of the red muscle tissue of trout (see Table VI) indicating that the variation is characteristic of red muscle tissue. The Fe and Co analysis of cellulose (Table IV) does not indicate an experimental variation in the determination of these elements.

The apparent concentrations of Ag, Cr, Sb and Sc are very low in the muscle tissue of fish. With the exception of the Cr content in the cheek muscle, the values reported in Table V are near or below our detection limits. The precision of the Sb and Sc analyses of cellulose was 13 and 2%, respectively.

It was stated above that the estimated errors in the determination of each element were based upon considerations of counting statistics, self-shielding errors,* source homogeneity, sample contamination, and interfering nuclear reactions. The magnitude of these

* L. A. Rancitelli and W. A. Haller. "Neutron Activation Analysis of Biological Tissue Self-Shielding Errors," this report, pp. 68-72.

possible sources of error will be considered. Errors associated with counting statistics are based upon the activities resulting from the lowest concentration of each element we have observed in the muscle tissue of a series of fish samples* except when noted otherwise. The neutron capture products of the alkali metals and of Br, Co and Zn can be measured with a high degree of accuracy. The standard deviations for these elements were less than 5% with the possible exception of Co and Cs. Tissue samples containing less than 10 ppb cobalt or 20 ppb cesium had a standard error of about 10% for the measurement of ^{60}Co and ^{134}Cs with the Ge(Li) detector. Fortunately, the multi-dimensional detector system was capable of measuring these radio-nuclides with a high degree of accuracy (5%) at concentrations as low as several ppb. The counting error associated with the measurement of ^{59}Fe in tissue samples is about 5% at an iron concentration of 8 ppb and about 10% at a concentration of 3 ppb. The accuracy of detecting ^{75}Se and ^{203}Hg should be considered together. The standard deviation associated with measuring ^{75}Se in tissue samples containing as little as 0.5 ppb Se is less than 5% if sufficient time is allowed for the decay of the ^{32}P .

The accuracy of the measurement of ^{203}Hg in tissue samples depends not only on the ^{32}P and ^{203}Hg in the activated tissue, but also on the Se concentration. The measurement of 150 ppb mercury in the presence of 1 ppm selenium has a standard error of 25% and is considered to be our lower limit of detection. As mercury concentrations exceed 200 ppb, the counting statistics improve to a standard deviation of about 15%. This was demonstrated by making up a series of synthetic samples containing ^{32}P , ^{75}Se and ^{203}Hg . On mathematically stripping the ^{32}P and ^{75}Se components of the spectrum from the 279 keV photopeak, the remaining activity was within 10% of the ^{203}Hg component and decayed with a 46 day half-life. The counting error associated with the ^{51}Cr measurements from its 320 keV photopeak is about 30% for Cr concentrations of 20 ppb. This is considered to be the lower limit for its detection and the overall error at this concentration is about 50%. Chromium-51 can be detected with a standard deviation of about 25% in samples containing 50 ppb Cr, while the counting error for samples containing more than 100 ppb Cr is less than 10%. The very low concentrations of silver, scandium and antimony in muscle tissue results in generally poor counting statistics. An additional problem arises in the measurement of ^{46}Sc with a multidimensional analyzer in the presence of the large Compton background caused by ^{60}Co . Thus, the statistical errors

* L. A. Rancitelli, W. A. Haller, and J. A. Cooper. *Unpublished Data, Pacific Northwest Laboratory, 1968.*

in the determination of silver, scandium and antimony at the concentrations reported in Table V are about 25%. Silver concentrations in excess of 5 ppb and antimony concentrations of about 1 ppb can be determined with a standard deviation of 10%.

The possible loss of bromine by vaporization during freeze drying or irradiation was studied. The bromine content of three freeze dried samples corresponded to within 5% with the bromine content of three wet samples which were frozen in liquid nitrogen before being irradiated.

Errors attributed to source inhomogeneity and differences in the geometry of the sample and standard are estimated to be less than 3%. Problems of source inhomogeneity were eliminated by counting the sample from both sides of the 1/2 in. by 2 in. ring and using an average activity. The geometry and source density were constant to a few percent since both the sample and the standards were dispersed in an agar solution.

Possible contamination may occur during several steps in the preirradiation sample preparation. The first potential source of contamination occurs during the sampling of the specimen. As stated in the experimental portion of this report, a carbon steel surgical blade was used to remove muscle tissue samples. The contamination resulting from the knife blade was shown to be negligible. The results of cutting

several samples of fish muscle with a neutron-irradiated knife blade are presented in Table I. The total neutron exposure the knife blade received was about 10^{17} n/cm². A second source of contamination is the combined effect of accumulation of dust while the sample is being freeze dried and transfer of contamination from the irradiation container to the sample. An upper limit was placed upon the contamination introduced during freeze drying and irradiation by carrying several polyethylene irradiation containers through the same procedures employed for the biological sample. After being irradiated with an integrated neutron exposure of about 10^{17} n/cm², the containers were leached with hot HNO₃ and the solution was subsequently counted on an anticoincidence-shielded multidimensional analyzer for 1000 min. No discernible activity was detected indicating that any transferable contamination either from the surface of the irradiation container or the freeze drier is far below our limits of detection.

The possibility of side reactions, neutron induced nuclear reactions in other elements which also yield the isotope of interest, must be considered. Photon induced reactions are not considered important. The relatively low energy distribution of the gamma-ray spectrum of a reactor would indicate that these reactions will not be competitive with (n,p) and (n, α) reactions. Several factors can lead to an

appreciable error in neutron activation analysis from side or secondary reactions. If the irradiation facility has an appreciable epithermal and fast neutron flux, secondary reactions should be considered. Since at our selected irradiation position in the Hanford reactors the cadmium ratio is in excess of 100, the relative extent of fast neutron reactions is rather limited. However, even in a highly thermalized reactor, secondary reactions can be important when they occur with an isotope present in higher concentrations than the isotope responsible for the thermal capture (see Tables II and III), or when the reaction threshold lies below the epithermal region. These conditions exist for four elements of interest in this work; cobalt, chromium, antimony and scandium.

An upper limit can be placed on this source of error in the determination of each element by considering the lowest concentration observed in various materials as being produced entirely by secondary reactions. Copper occurs in concentrations about 1000 times greater than cobalt in muscle tissue.⁽¹⁾ Thus, the $^{63}\text{Cu} (n,\alpha) ^{60}\text{Co}$ reaction may produce a significant portion of the total ^{60}Co activity in neutron irradiated tissue. Recent trace element data of 99.999% copper wire indicates a cobalt content of 50 ppb.⁽¹⁰⁾ If all the observed cobalt occurs from a secondary reaction on the copper wire, this would place a negligible estimated error on the cobalt data in Table V.

Estimates can be made of the contribution of the $^{127}\text{I} (n,\alpha) ^{124}\text{Sb}$ reactions to the ^{124}Sb activity by considering the lowest observed concentration of antimony in biological tissue as resulting entirely from a secondary reaction. The lower limit of detection of chromium (<0.02 ppm) in the presence of 35 to 45 ppm iron may be considered the maximum contribution to the observed chromium concentrations. The fact that the secondary reactions discussed above have cross sections of the order of a millibarn and threshold energies in the thermal energy region⁽¹¹⁾ enhances their importance. The last case, the contribution of titanium to the observed scandium content, is not easily estimated. Because of the very low concentration of scandium in muscle tissue (several hundredths of a part per billion), the $^{46}\text{Ti} (n,p) ^{46}\text{Sc}$ reaction probably makes a significant contribution to the observed scandium content. We estimate from Table V that the maximum contribution of titanium to the observed scandium content is an apparent 0.04 ppb.

An additional source of error arises from other neutron induced radioisotopes which emit photons with an energy very similar to the radioisotope of interest. This problem does not occur for those radionuclides detected with a multidimensional analyzer, since the combination of coincidence gamma rays is unique. This possibility, though remote in light of the high resolution of a Ge(Li) detector,

does exist for a single detector. Radioisotopes which might interfere with the radionuclide under consideration are listed in Table III. With the exception of ^{60}Co and ^{134}Cs , the half-life of each photopeak was measured to confirm the quality of the spectrum. The contribution of ^{75}Se to the ^{203}Hg photopeak has been discussed above, as well as the elimination of the ^{47}Ca component of the ^{59}Fe photopeak with a suitable decay interval. In all cases except that of the ^{75}Se - ^{203}Hg photopeak, the contribution of other radioisotopes to the photopeak of interest is negligible. Our estimate of the total error in the determination of each element based upon the above consideration is presented in Table V.

We have attempted to describe a highly sensitive method of trace element analysis capable of simultaneously detecting a large number of the biologically important elements in a relatively small sample of tissue. The method is capable of determining 14 element concentrations in biological tissue without resorting to radiochemical separations. Although four elements (scandium, silver, antimony and chromium) were present in concentrations near or below our detection limits, recent work with other types of fish tissue indicates that this is the exception. Significant data concerning these elements in biological tissue are within the capability of this method.

We have the capability to extend this method of analysis to include at least 6 more elements. The half-life of the beta spectrum at 167 keV obtained with the Ge(Li) detector was followed to determine its origin. The fourteen day half-life confirmed the fact that it resulted from the decay of ^{32}P . This portion of the spectrum was used to calculate the phosphorus content of a dozen samples. The range of values of 0.7 to 0.9% was in reasonable agreement with the reported concentrations of phosphorus in biological muscle tissue. However, several variables must be studied before applying the analysis of this element routinely. Irradiations of 1 to 5 min in the "rabbit" facility of the PRTR reactor followed by direct counting are being conducted to determine the concentrations of chlorine, magnesium and manganese. The addition of an anticoincidence-shielded Ge(Li) detector to our counting facilities will extend our capability even further. The method of instrumental neutron activation analysis described in this work is the nucleus of a highly sensitive and versatile tool for the future study of trace element composition of biological materials.

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NEUTRON ACTIVATION ANALYSIS OF BIOLOGICAL TISSUE:
NEUTRON SELF-SHIELDING ERRORS

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and T. M. Tanner

An estimate is made of the self-shielding error arising in the determination of several elements in biological tissue by neutron activation analysis. The elements considered are Co, Cs, Sb, Sc, Zn, Fe, Ag, Cu, Br, and Na. The activities induced in standards wrapped in tissue are compared with the corresponding activities of unshielded standards. Two grams of tissue resulted in an error of less than 10% for all the elements under consideration. A comparison is made between the results of this work and those expected based upon the departure of a nuclide's cross section from a $1/v$ behavior.

INTRODUCTION

The insertion of a sample into an isotropic source of thermal neutrons will result in an attenuation of the neutron flux by neutron absorption in the outer portions of the sample. Thus, the center of the sample will experience a reduced thermal flux relative to the unperturbed neutron source. The magnitude of this flux depression will depend on both the sample size and the absorption cross section of its constituents. However, if the energy spectrum in the irradiation facility is not completely thermalized, the variation of the flux within the sample becomes much more complex. In addition to attenuation of thermal neutrons by absorption, epithermal neutrons can become thermalized by moderation within the sample or removed by resonance absorption. Thus, the production rate of a radionuclide by neutron capture could exhibit a strong dependence on sample size if resonance absorption represents a large portion of the neutron

capture or if the sample has a large thermal or resonance absorption cross section. This effect of neutron self-shielding within the sample or flux monitor can represent a major source of error in neutron activation analysis.

Several analytical attempts to determine the flux variation within a sample have been made in recent years.⁽¹⁻⁵⁾ The approach has been one of estimating the error when bare metal foils and wires of various geometries are irradiated. Bowen and Gibbons⁽⁶⁾ summarize the problem of self-shielding corrections by suggesting that self-shielding calculations should be made to estimate the magnitude of the effect and, if significant, subsequent steps should be taken to minimize it.

Neutron activation analysis of biological materials such as muscle or plant tissue presents a unique problem since they contain a complex mixture of elements with high absorption and scattering cross sections. Although the average neutron absorption cross section

of biological material based upon the major elements (N, C, H, O) is not large, the production of radioisotopes from isotopes with high resonance absorption cross sections could be affected by neutron thermalization within the sample. This, of course, is a very different process from that occurring in metal foils where resonance neutron attenuation occurs almost solely by absorption.

Rather than attempt to estimate the contribution of each effect to the total self-shielding, two experiments were performed which place an upper limit on the error in determining several elements in biological samples by neutron activation analysis. The magnitude of this error like that of the secondary production of isotopes by fast neutron reactions is determined by the given neutron flux spectrum and hence must be evaluated for each reactor irradiation position.

EXPERIMENTAL PROCEDURES

Two identical sets of standards were prepared by sealing 100 μ l of a solution containing about 10^{-8} g/ml of each element of interest in 5 mm diameter by 30 mm long clean quartz ampoules. The elements were chosen to cover a large variation in infinite dilution resonance integrals and included the elements cobalt, antimony, scandium, cesium, zinc, iron, silver, bromine, sodium, and uranium. One set of standards was wrapped in 1.75 g ($\sim$ 5 mm thick)

of dry Kleenex tissue, a plant tissue representative of biological tissue, and placed in an aluminum irradiation can, while the duplicate set was placed in a second irradiation can. Both sets of standards were simultaneously irradiated in a region of the Hanford KE Reactor where the cadmium ratio is in excess of 10^2 to an integrated flux of about 10^{17} n/cm². After opening both sets of standards and mounting 50 μ l of each sample on individual 1 in. stainless steel counting dishes, they were counted with an anticoincidence-shielded multidimensional gamma ray spectrometer.⁽⁷⁾ Counting statistics were better than $\pm 3\%$ standard deviation and pipetting errors were less than 0.3%.⁽⁸⁾ The flux variation between the two adjacent irradiation positions of the Hanford KE Reactor was less than 4%.⁽⁹⁾ The daughter radionuclides produced by the irradiation and measured by the gamma-gamma coincidence analysis were ²⁴Na, ⁴⁶Sc, ⁵⁹Fe, ⁶⁰Co, ⁸²Br, ^{110m}Ag, ¹²⁴Sb and ¹³⁴Cs. The specific activities of the two sets were decay-corrected to a standard counting time for comparison.

An additional direct experiment was performed on biological material by inserting sections of 5 mil copper wire in samples of freeze dried beef muscle of various sizes. These samples were irradiated as described above, the wire removed, cleaned with distilled water and the ⁶⁴Cu activity determined. The

specific activity of each wire was then compared to determine the effect of sample size on self-shielding.

Results and Discussion

A comparison of the activities obtained by the simultaneous irradiation of tissue-shielded and unshielded standards is presented in Table I together with the ratio of the activities, and the standard deviation of these ratios. The first five isotopes (^{46}Sc , ^{60}Co , ^{65}Zn , ^{124}Sb , ^{134}Cs) were contained in a single mixed standard thus providing a high degree of internal consistency for their comparison. It is evident from Table I that self shielding in biological samples weighing less than 2 g, irradiated in the Hanford KE Reactor, results in an error of less than 10% when

compared to an unshielded standard. The results presented in Table II for the irradiation of copper wire which was shielded with beef muscle shows a similar trend.

It is interesting to compare the ratio of induced activities of several isotopes in Table I with

TABLE II. Neutron Induced Specific Activity of Tissue-Shielded Copper Wire

<u>Wet Weight of Sample, g</u>	<u>Specific Activity of Cu Wire, counts/g</u>
0.10	10,200
0.50	10,300
0.10	10,100
1.00	9,900
10.0	10,000

TABLE I. Activities of Tissue-Shielded and Unshielded Standards

<u>Isotope</u>	<u>Activity, counts/10 min</u>		<u>Ratio of Activities</u>
	<u>With Tissue</u>	<u>Without Tissue</u>	
^{124}Sb	1330	1460	0.91 ± 0.03
^{60}Co	1710	1830	0.93 ± 0.03
^{46}Sc	2320	2450	0.95 ± 0.03
^{134}Cs	4340	4510	0.96 ± 0.02
^{65}Zn	2180	2340	0.93 ± 0.03
^{59}Fe	37,800	40,300	0.95 ± 0.01
$^{110\text{m}}\text{Ag}$	7460	8230	0.91 ± 0.01
^{82}Br	8570	9200	0.94 ± 0.01
^{24}Na	67,600	68,300	0.99 ± 0.01

their corresponding infinite dilution resonance absorption integrals (I_0).⁽¹⁰⁾ The ratio of the infinite dilution resonance absorption integral above the cadmium cutoff energy (0.4 eV) to the thermal absorption cross section (σ_t) is 0.5 for a 1/v absorber.⁽¹¹⁾ Thus, the magnitude of the deviation from this value of 0.5 should give a qualitative index of the contribution of resonance absorption to the total production of a particular isotope. The ratio of I_0 to σ_t is about 0.5⁽¹¹⁾ for ^{23}Na indicating that it should be close to a 1/v absorber, while the ratio of shielded to unshielded ^{24}Na activity is 0.99, also indicating a 1/v behavior. Antimony-123, on the other hand, has a value of 40 for I_0/σ_t and a ratio of induced activities of 0.91. Both are indicative of large departures from 1/v behavior for antimony. Cobalt-59 has a ratio of I_0/σ_t of about 1.3, indicating some departure from a 1/v cross section. Other ratios of I_0/σ_t include 0.47 for ^{45}Sc , 1.0 for ^{63}Cu and 130 for ^{109}Ag . All are consistent with the data of Table I.

Thus, the self-shielding error in the determination of those elements exhibiting a high resonance absorption can be reduced to less than 5% by limiting the sample size to 1 g. The small error associated with neutron self shielding in biological material can be attributed to several factors. The very high thermal to fast neutron ratio of the Hanford

reactors reduces the effect of resonance absorption. The low thermal absorption cross section (0.4 b) based upon the average composition of biological material results in a flux attenuation by thermal neutron capture of about 2%/cm of material. The self-shielding errors associated with determining other elements in biological tissue could be estimated by comparing their resonance integrals and thermal absorption cross sections with those nuclides considered in this work.

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NEUTRON ACTIVATION ANALYSIS OF HIGH ALTITUDE AIR FILTERS

L. A. Rancitelli

Air filters containing material collected at altitudes of 10,000 ft to 63,000 ft were analyzed by a method of instrumental neutron activation analysis. The precision of the method for determining Na, Br, Zn, Co, Sb, Sc, Cs, Ag and Fe in blank filter material is quite good. In actual practice, however, contamination problems arise during sample collection. The concentration of particulate matter at 10,000 ft was high enough in September and October, 1967, to permit the measurement of several elemental concentrations. The concentrations of Ag, Co, Cs, Sb and Zn at 10,000 ft appears to be rather constant. Estimates are made of the trace element concentrations above 20,000 ft.

Although it seems well established that the stratospheric aerosol is primarily composed of ammonium sulfate, its precise chemical nature and origin is not known. Several sources contribute to the trace element inventory of the atmosphere; among them are extra-terrestrial material, volcanic ash, terrestrial debris and the aerosol produced during wave action over the ocean marine atmosphere.⁽¹⁾ Since the chemical composition of materials from these sources is significantly different, a comprehensive knowledge of the trace element composition as a function of altitude in the atmosphere would

be a major step toward explaining the mechanisms of aerosol buildup and depletion from the atmosphere. The composition of condensation nuclei has been inferred from the chemical analysis of rain, snow and glacial ice. Such indirect measurements are certainly of value, but provide only some form of integrated composition between cloud height and ground level and do not provide information on composition as a function of altitude.

A recent attempt has been made to measure directly the composition of stratospheric aerosols by neutron activation analysis of high altitude filters.⁽²⁾ Unfortunately, random

contamination of the filters accounted for a inordinately large amount of material. This was not unexpected in the light of the extremely diffuse nature of particulate matter in the upper atmosphere. This work is aimed also at a direct measurement of the elemental composition of the atmospheric aerosols and includes altitudes between the lower stratosphere and troposphere. It is not only an attempt to refine previous measurements, but to extend the analysis to elements which have not previously been determined.

Aerosol collections were made by the U.S. Air Weather Service, 58th Weather Group under the technical direction of Battelle-Northwest staff members. A standard sampling apparatus employing IPC filter paper mounted in a specially designed sampling apparatus on a U.S. Air Force aircraft performed the missions over Spokane, Washington. The aircraft sampling system was meticulously cleaned with absolute alcohol and sealed with plastic covers until takeoff.

Extreme care to avoid contamination was exercised in the loading and removal of the filters in the aircraft. All surfaces of the filter assembly were cleaned with absolute alcohol before loading with filter paper. The filter medium consisted of IPC material as obtained from Knowlton Bros. Specialty Paper Products. This material is a high purity cellulose impregnated with Kronisol. Random samples from several rolls of IPC filter paper were analyzed by

neutron activation analysis. The trace element content of the material proved to be both uniform and of a low level. The loaded filter assembly was placed in the aircraft just prior to takeoff. At the conclusion of the mission, the filter assembly was placed in polyethylene bags for transport to our laboratory at Richland, Washington.

Samples of each filter were taken for neutron activation analysis. The filter was removed from the assembly with Teflon-covered forceps, placed on a polyethylene sheet in an Agnew-Higgins Laminar flow work station and a 3 in. diameter sample taken from the center. The samples were cut with a 3 in. ID quartz tube which had a honed edge. Prior to its use, the quartz cutter was boiled in nitric acid for several hours to ensure its freedom from surface contamination. Each sample was carefully folded with the exposed surfaces against each other to prevent transfer from the sample to the container and was placed in a number 24 Nalgene polyethylene capsule which had previously been leached in warm nitric acid for 24 hr. Previous work has demonstrated that a minimal amount of material is leached from this type container with a corrosive medium such as nitric or hydrochloric acid. After freeze-drying the sample, the capsule was sealed with plastic tape and wrapped in one mil aluminum foil to prevent any contamination of the outer surface of

the container during irradiation. The filter samples were irradiated to an integral thermal neutron exposure of 7×10^{17} n/cm² together with a set of neutron flux monitors. The region of the Hanford Reactor employed for these irradiations has a highly thermalized neutron flux. The flux standards consisted of dilute ($\sim 10^{-8}$ g/ml) aqueous solutions of each element of interest sealed in a 3 mm ID x 3 cm quartz ampoule. Prior to their use, the quartz ampoules were boiled in nitric acid for several days. Several experiments involving the irradiation of doubly-distilled water indicated a negligible transfer of activity from the quartz.

The irradiated samples were permitted to decay several days before preparing them for gamma ray analysis. The aluminum foil was removed and the polyethylene container heavily lacquered to prevent any transfer of contamination from its outer surface to the sample. After removing the plastic tape and applying a second coat of lacquer, the container was opened. The filter was opened up, the edges cut off as an additional precaution against contamination from the quartz cutter and the sample weighed. The filter at this point was in a friable condition from irradiation damage. This proved to be advantageous since it permitted the easy preparation of a homogeneous dispersion of the filter in a 2% hot agar solution. The dispersion was subsequently added to a 0.5 in. by 2 in. diameter plastic ring to

achieve a standard counting geometry. The quartz ampoules containing the irradiated standards were thoroughly washed with nitric acid, opened, and 50 μ l of each solution were removed and mixed with a 2% hot agar solution in a 0.5 in. by 2 in. ring.

Gamma ray analysis consisted of counting the samples with an anticoincidence-shielded multi-dimensional analyzer for 1000 min.⁽³⁾ This permitted the simultaneous detection of ⁴⁶Sc, ⁵¹Cr, ⁵⁹Fe, ⁶⁰Co, ⁶⁵Zn, ^{110m}Ag, ¹²⁴Sb, ¹³⁴Cs and ¹⁴⁰(Ba-La) from U-fission. The activities of the radionuclides in each sample were compared with the induced specific activity of the standards to obtain the trace element content.

The sensitivity and precision of this analysis proved to be quite high. This was determined by analyzing random samples from a roll of IPC filter. The results of the analysis of IPC filter material are presented in Table I. The average composition and the standard deviation of the average were computed in the usual manner.⁽⁴⁾ The trace element contents of filters from three missions are presented in Tables II through IV.

In addition to the exposed filters, several unexposed filters were analyzed to place an upper limit on the inherent contamination from the sampling system. These unexposed filters were those which had been mounted in the aircraft sample change rack during the flight but had never been exposed to the

*TABLE I. Trace Element Content of IPC Filter Paper
Treated with Kronisol (10^{-9} g/g of material)*

Element	1	2	3	4	5	6	Avg $\pm$ σ	Experimental Error, %
Na ($\times 10^{-3}$)	79	84	82	83	82	84	83 ± 2	5
Zn ($\times 10^{-3}$)	0.56	0.53	0.49	0.59	0.52	0.49	0.53 ± 0.04	5
Co	2.1	1.9	2.8	1.9	1.8	1.8	2.1 ± 0.4	10
Sb	3.0	3.0	2.8	3.4	2.8	2.8	3.0 ± 0.2	10
Sc	0.46	0.48	0.44	0.46	0.44	0.41	0.45 ± 0.02	5
Cs	0.08	0.02	0.08	0.04	0.06	0.05	0.06 ± 0.02	25
Cr ($\times 10^{-3}$)	0.24	0.21	0.15	0.13	0.12	0.14	0.16 ± 0.04	25
Fe ($\times 10^{-3}$)	4.1	3.5	3.3	3.4	4.6	3.3	3.7 ± 0.3	15
Ag	<1	<1	<1	<1	<1	<1	<1	15
U	<2	<1	<2	<2	<2	<2	<2	15

*TABLE II. Trace Element Content of High Altitude Filters
Collected on September 5, 1967 (10^{-9} g/g filter material)*

Altitude, ft	Volume of Air Sampled, sec/ft ³ (STP)/g filter	Sc	Zn($\times 10^3$)	Co	Ag	Sb	Cs
60,000-62,000	1.4×10^3	3.0	4.6	6.9	5.1	25	1.6
30,000	1.1×10^3	0.87	1.6	3.2	3.0	10	0.4
20,000	1.6×10^3	0.74	1.1	2.4	1.7	3.0	0.2
15,000	1.8×10^3	2.2	1.9	4.0	2.4	9.7	1.1
10,000	2.1×10^3	12.2	3.3	16.9	3.3	37	4.2
Unexposed		3.7	0.9	7.2	1.5	2.7	1.3
Unexposed		0.44	1.8	3.0	2.0	14	0.1
Blank IPC Filter $\pm$ σ		0.45 ± 0.02	0.53 ± 0.04	2.0 ± 0.04	<1	3.0 ± 0.2	0.06 ± 0.02
Experimental Error		5%	5%	10%	15%	10%	25%

*TABLE III. Trace Element Content of High Altitude Filters
Collected on October 23, 1967 (10^{-9} g/g filter material)*

Altitude, ft	Volume of Air Sampled, sec/ft ³ (STP)/g filter	Sc	Zn($\times 10^{-3}$)	Co	Fe($\times 10^{-3}$)	Cr	Ag	Sb	Cs
60,000-62,000	1.6×10^3	0.64	1.4	5.6	6.0	0.14	2.6	2.5	0.23
62,000-63,000	0.48×10^3	0.48	0.91	3.5	5.5	0.10	1.5	3.6	0.07
50,000	0.76×10^3	0.55	2.0	5.6	6.7	0.20	6.9	29	0.15
45,000	0.84×10^3	0.41	1.7	6.1	5.7	0.10	<1	4.1	0.06
40,000	0.98×10^3	0.50	7.7	36.0	10.0	<0.10	1.6	50	0.70
30,000	1.4×10^3	0.43	1.4	3.2	4.0	<0.10	38	2.7	0.70
20,000	1.8×10^3	0.63	2.0	4.5	7.8	<0.10	<1	5.6	0.34
15,000	1.7×10^3	0.43	0.72	2.4	6.2	<0.10	<1	3.2	0.21
10,000	2.0×10^3	11.0	2.3	14.0	53.0	0.10	1.8	18	3.1
Unexposed		0.34	0.67	1.6	4.7	0.10	1	2.6	0.12
Unexposed		0.37	2.0	9.4	7.8	0.10	1.8	4.1	0.16
Blank IPC Filter $\pm$ σ		0.45 ± 0.02	0.53 ± 0.04	2.0 ± 0.04	3.7 ± 0.3	0.16 ± 0.04	<1	3.0 ± 0.2	0.06 ± 0.02
Experimental Error		5%	5%	10%	15%	25%	15%	10%	25%

*TABLE IV. Trace Element Content of High Altitude Air Filters
Collected on November 20, 1967 (10^{-9} g/g filter material)*

Altitude, ft	Volume of Air Sampled, sec/ft ³ (STP)/g filter	Na($\times 10^{-3}$)	Sc	Zn($\times 10^{-3}$)	Co	Fe($\times 10^{-3}$)	Cr	Ag	Sb	Cs
50,000	1.4×10^3	80	0.53	1.1	4.1	9.3	0.6	2.9	3.6	0.36
45,000	0.48×10^3	85	0.49	1.7	6.9	10.2	0.6	<1	2.9	0.21
40,000	0.73×10^3	80	0.48	0.86	4.5	6.9	0.3	<1	3.6	0.11
30,000	0.88×10^3	85	0.48	0.80	3.3	6.5	0.2	<1	2.8	0.20
Unexposed		80	0.41	6.1	2.6	5.3	0.2	<1	5.1	<0.1
Unexposed		85	0.41	0.8	2.2	6.6	0.2	<1	2.3	<0.1
Blank IPC Filter $\pm \sigma$		83	0.45	0.53	2.0	3.7	0.2	<1	3.0	<0.1
		82	0.02	0.04	0.04	0.3	0.05		0.2	

air stream. These data are included in Tables II through IV together with the analysis of several samples of blank IPC filter (see Table I). An estimate of the error in determining the absolute amount of each element is also presented in these tables. These estimates are based upon counting statistics, self-shielding errors and contamination inherent in the analyses. It is evident from a comparison of exposed filters with unexposed filters that most material can be attributed to random contamination. Only in the case of samples collected below 15,000 ft is an appreciable quantity of material collected. Several of the higher altitude filters contain relatively high amounts of Co, Ag, Fe, Sb and Zn. It is tempting to attribute some significance to these values. However, the random nature of these high values leads one to believe that they may have occurred from structural material contamination. One source of contamination that has not been evaluated is the amount of structural material eroded from the surface of the sampling apparatus by the

air stream. The unexposed filters do not give a measure of the materials a filter might pick up from erosion of these structural materials by a high velocity air stream.

The 10,000 ft samples collected in September and October both contain a significant amount of material compared with the unexposed filters. From these values, the trace element concentrations at 10,000 ft are calculated. For these calculations, it was assumed that the average of two unexposed filters represents the background contamination. These results are presented in Table V together with an estimated error based upon the variation of the background contamination. The agreement between the two samples is rather good, though the errors involved are large.

An estimate of the elemental concentration above 20,000 ft is also presented in Table V. These values are obtained by considering the lowest concentration measured in an exposed filter as the upper limit which one might expect. The

TABLE V. Trace Element Concentrations at 10,000 ft

Element	Concentration, 10^{-16} g/cm ³ air STP		Estimated Concentrations Above 20,000 ft, 10^{-16} g/cm ³ air STP
	9/5/67	10/23/67	
Ag	0.3 $\pm$ 0.1	0.1 $\pm$ 0.1	0.1
Co	1.7 $\pm$ 0.3	1.5 $\pm$ 0.7	0.2
Cs	0.6 $\pm$ 0.1	0.5 $\pm$ 0.1	0.01
Fe	---	8200 $\pm$ 500	500 - 1000
Sb	5 $\pm$ 1	2.6 $\pm$ 0.2	0.1
Sc	1.7 $\pm$ 0.3	1.9 $\pm$ 0.1	0.01
Zn	320 $\pm$ 70	180 $\pm$ 140	150

background of the blank IPC filter is assumed to represent the background contamination level. Although this is an idealized situation, it indicates the levels one must be prepared to encounter. It is true, of course, that local concentrations probably vary considerably from these estimates, particularly at the lower altitudes.

The relative elemental content of the structural material of the air sampling inlet of the aircraft was also determined by neutron activation analysis. The air sampling system was first carefully washed with absolute alcohol and dried. The surface of the air intake system was then wiped with clean IPC filter. This filter was analyzed in the manner described above. The results are presented in Table VI as relative abundances of the elements of interest. This should represent the relative composition of any eroded structural material on a filter. One might

TABLE VI. Relative Elemental Abundances of Several Elements in the Structural Material of the High Altitude Sampling System

Element	Relative Abundance, g/g element		
	g/g Sc	g/g Zn	g/g Co
Sc	1.0	0.0004	0.05
Cr	90	0.03	5
Fe	12,000	5	600
Co	20	0.007	1.0
Zn	2000	1.0	140
Ag	470	0.2	25
Sb	9	0.003	0.5

expect a high zinc and iron content, but the large amount of silver present is rather surprising.

The low scandium content of the structural material lends more support to the validity of the 10,000 ft samples. These samples show an elemental abundance relative to scandium too low to have an origin associated with the structural material. Unfortunately, this is not true of the other samples;

they seem to be biased by surrounding material. This points up the major problem in sampling the atmosphere for trace elements. The background in the filter can be overcome by sampling larger volumes of air; however, the contamination caused by the sample holder must be reduced either by modifying existing equipment to eliminate material containing the elements of interest, or air velocities must be reduced to decrease any abrasion of the surface. These problems have not been resolved.

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THE ADSORPTION OF TRACE ELEMENTS IN SEA WATER ONTO VARIOUS CONTAINER SURFACES*

D. E. Robertson

The adsorption behavior of the trace elements Sc, Fe, Zn, Sr, Rb, Ag, In, Sb, Cs, and U in sea water, which had been stored in various containers, was studied as a function of time. Serious losses were observed for Sc, Fe and In and to a lesser extent for Co, Ag and U due to adsorption onto the container surfaces. The addition of hydrochloric acid to lower the pH of the sea water to about 1.5 prevented the adsorption of Fe, Co, Ag and In and retarded the adsorption of Sc, but had no effect on the adsorption of U. Optimum conditions for storing sea water for trace element analysis are suggested.

INTRODUCTION

The trace element analysis of sea water can be complicated by the fact that serious losses of trace elements can occur due to their adsorption onto the walls of the

containers used for storing the sea water samples. Murphy and Riley⁽¹⁾ observed that phosphate ions in sea water were strongly adsorbed onto polyethylene and polyvinyl chloride surfaces, while Hassenteufel et al.⁽²⁾ found that phosphate adsorption onto Pyrex glass surfaces was only slight. Hummel⁽³⁾ discovered that sea water stored in polyethylene bottles lost over 75%

* BNWL-SA-1703, Submitted for journal publication in *Analytica Chimica Acta*, 1968.

of its content of gold in three weeks and Koczy⁽⁴⁾ noted a similar decrease in the uranium content of sea water stored in glass bottles. Schutz and Turekian, using radioactive tracers, concluded that no significant adsorption of selenium, silver, cobalt, cesium, zinc, chromium and antimony occurred when sea water was stored in Pyrex glass bottles for periods of up to 6 months.⁽⁵⁾ Strickland and Parsons⁽⁶⁾ reported the slow deposition of iron onto both polyethylene and glass container surfaces. Riley⁽⁷⁾ has suggested several reasons for the adsorptive properties of glass and plastic surfaces. Since these materials are supercooled liquids, they possess high adsorption energies due to their distorted and broken bonds. This leads to the adsorption of ions from solution and to the formation of bonds between the surface and the adsorbed ions. Glass can act both as an anion and cation exchanger, while surfaces of plastics under the influence of oxygen, heat or light may become degraded with the formation of carboxyl or carbonyl groups which may show adsorptive properties. Also, catalysts, filters and plasticizers present in plastics may also present active sites for adsorption.

This study was to determine the optimum conditions for storing sea water and to describe the adsorption behavior of the eleven trace elements Sc, Fe, Zn, Co, Sr, Rb, Ag, In, Sb, Cs and U in sea water samples stored in polyethylene

bottles, in Pyrex glass bottles and in polyethylene bottles containing sufficient hydrochloric acid to lower the pH of the sea water to about 1.5.

EXPERIMENTAL

Radioactive tracers of the elements of interest were separately added to 3000 ml samples of unfiltered sea water. These tracers were contained in dilute HCl or HNO₃ and, when necessary, the pH of the spiked sea water was adjusted to its original pH of 8.0 by the addition of dilute NaOH. Two hundred milliliter aliquots were immediately poured into a series of 250 ml polyethylene bottles, Pyrex glass bottles, and polyethylene bottles containing 1 ml of concentrated hydrochloric acid to lower the pH of the spiked sea water to about 1.5. The polyethylene bottles were immediately counted in a 9 in. diameter by 9 in. thick NaI(Tl) well crystal to determine the initial counting rate of the radioactive tracers. After several predetermined periods of storage, the contents from one of each type of container were poured into new 250 ml polyethylene bottles which were then counted in a NaI(Tl) well crystal to determine the amount of tracer lost by adsorption onto the walls of the original containers.

This procedure was used with the radioactive tracers ⁴⁶Sc, ⁵⁹Fe, ⁶⁰Co, ⁶⁵Zn, ⁸⁵Sr, ⁸⁶Rb, ¹¹⁰Ag, ¹¹⁴In, ¹²⁴Sb and ¹³⁴Cs. The specific activities of these tracers were sufficiently high to insure

that the amount of stable element added with the tracers did not exceed the concentration of these elements already present in sea water. Thus, precipitations and other complications induced by exceeding the solubility products of these elements were minimized.

For the uranium adsorption studies, ^{235}U tracer was added to 600 ml of unfiltered sea water and the pH adjusted to 8.0 by adding dilute NaOH. The sea water was then divided into 200 ml aliquots which were placed in a 250 ml polyethylene bottle, a Pyrex glass bottle and a polyethylene bottle containing 1 ml of concentrated hydrochloric acid to lower the pH of the sea water sample to about 1.5. The uranium concentration was initially and then periodically measured after several storage periods by removing 5 ml aliquots from each container and determining the uranium by neutron activation analysis. The uranium concentration in the sea water was increased from about 3 to about 120 ppb by the addition of the ^{235}U tracer and this may have altered the uranium behavior.

RESULTS AND DISCUSSION

The behavior of these tracers in sea water stored in the various containers is presented in Figure 1. It is evident that serious losses of indium, scandium, iron, silver, uranium and cobalt can occur due to their adsorption onto container surfaces. Indium was lost most

rapidly, with greater than 90% adsorbed onto polyethylene surfaces after about 20 days of storage. However, when the pH of the sea water was lowered to about 1.5 with hydrochloric acid, the adsorption onto polyethylene was completely eliminated. Indium was slowly adsorbed from sea water onto Pyrex glass surfaces, with about a 20% loss after 75 days of storage. The behavior of iron was quite similar to that of indium. After 55 days, greater than 90% of the iron was adsorbed onto polyethylene surfaces. Again, however, the addition of the hydrochloric acid completely prevented this adsorption onto polyethylene. After 55 days nearly 70% of the iron was adsorbed onto Pyrex glass surfaces. The behavior of scandium was similar to that of indium and iron except that the addition of the hydrochloric acid was only partially effective, allowing about 35% of the scandium to become adsorbed after 60 days. After 50 days about 20% of the uranium was lost to Pyrex glass surfaces and about 10% to polyethylene surfaces even with the addition of hydrochloric acid to the sea water. The uranium adsorption studies are being continued beyond 50 days to determine its subsequent behavior. About 20% of the silver adsorbed onto the polyethylene surface after about 10 days and remained at that level throughout the experiment. Insignificant silver adsorption occurred on Pyrex glass surfaces and on polyethylene surfaces when

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FIGURE 1. The Adsorption of Trace Elements in Sea Water onto Various Container Surfaces

the sea water was acidified with hydrochloric acid. About 10 to 20% of the cobalt was lost on polyethylene after about 10 days. However, the adsorption onto polyethylene was prevented by the addition of the hydrochloric acid. About 5 to 10% of the cobalt was lost on the Pyrex glass surfaces after about 20 days and remained constant at that level throughout

the experiment. About 10% of the rubidium was lost on the Pyrex glass surfaces after about 10 days and remained constant at that level. However, no adsorption occurred for rubidium in sea water stored in polyethylene containers. Negligible adsorption of zinc, cesium, strontium and antimony on all container surfaces was observed for storage periods of up to 75 days.

All of the radioactive tracers were added to the sea water samples in a soluble form. The ^{110m}Ag was added as Ag^+ , while the forms reported to exist in sea water are AgCl_2^- and AgCl_3^{-2} .⁽⁸⁾ The ^{235}U tracer was added as UO_2^{+2} , while the uranium in sea water exists as the carbonate complex, $\text{UO}_2(\text{CO}_2)_3^{-4}$.⁽⁸⁾ Iron is reported to exist in sea water mainly as colloidal ferric hydroxide and ferric phosphate,^(7, p. 378) but the ^{59}Fe tracer was added as Fe^{+3} ion. The ^{124}Sb tracer was added as Sb^{+3} ; however, the chemical form of antimony in sea water is unknown, but might parallel the chemistry of arsenic which is reported to exist as HASO_4^{-2} , $\text{H}_2\text{AsO}_4^{-1}$, H_3AsO_4 and H_3AsO_3 .⁽⁸⁾ The Cs, Rb, Sr, Zn, Co, Sc and In were added as Cs^+ , Rb^+ , Sr^{+2} , Zn^{+2} , Co^{+2} and In^{+3} , respectively, and these are probably the principal forms in which these elements exist in sea water.

It appears that the optimum conditions for storing sea water consists of immediately acidifying the sea water to a pH of about 1.5 and storing the samples in polyethylene bottles. Most polyethylene is very pure except for traces of iron (~ 10 ppm), whereas Pyrex glass contains relatively high impurity levels of many elements and could present some contamination problems.⁽⁹⁾ It is recommended that the polyethylene bottles be well rinsed prior to use with purified hydrochloric or nitric acid

to remove traces of iron or other materials on the surface of the bottles.

Freezing the acidified sea water samples may retard the adsorption of scandium and uranium onto polyethylene surfaces. Freezing has been used effectively to preserve sea water samples for the determination of nitrate and nitrite,⁽¹⁰⁾ reactive phosphate⁽¹¹⁾ and probably silicate.⁽¹²⁾ However, the effect of this procedure on trace elements has not been determined.

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THE MEASUREMENT OF TRACE ELEMENTS IN DEEP SEA SEDIMENTS BY NEUTRON ACTIVATION ANALYSIS AND DIRECT COUNTING TECHNIQUES

D. E. Robertson

Twenty major and trace constituents in pelagic red clay sediments and in micromanganese nodules were measured by neutron activation and direct counting techniques using a 20 cm³ Ge(Li) diode detector. The application of this technique to the in situ activation analysis of marine sediments is discussed.

A knowledge of the chemical composition of the sediments of the ocean is essential for an understanding of the biogeochemical processes taking place on the ocean floor. Such a knowledge can lead to an understanding of the origin of the sediments, the mechanisms of their formation, their rates of accumulation and their ages, and their interactions in the marine environment. Also, the sediments contain potentially valuable mineral

deposits and these need to be located and analyzed.

Neutron activation analysis provides a very sensitive and selective method for determining many of the elements contained in ocean sediments. Recent developments in Ge(Li) gamma-ray spectrometry have permitted the resolution of complex mixtures of activation products, making it now possible to determine up to about

20 radionuclides in a single sample by direct counting techniques.

This work describes the application of this technique for the identification and determination of 20 major and trace constituents in pelagic red clay sediments and in micromanganese nodules found in such sediments.

Small samples (25 to 32 mg) of deep sea red clay sediments taken from the North Pacific Ocean were dried and encapsulated in small polyethylene vials. One sample was irradiated for 10 sec in the rabbit facility of the Plutonium Recycle Test Reactor which provides a thermal neutron flux of about 3×10^{12} n/cm²/sec. A second irradiation was performed in a Hanford production reactor to give a total exposure of about 6×10^{15} n/cm². The samples were counted after decay periods of 1 min, 2 hr and 5 days on a 20 cm³ Ge(Li) diode with a depletion depth of 11 mm. Also, a 10 mg sample of neutron irradiated micromanganese nodules, which was sieved from similar red clay sediments, was counted after a 23 day decay period.

The gamma-ray spectrum of deep sea red clay 1 min after neutron irradiation consisted mainly of ²⁸Al (2.3 min) and ⁵⁶Mn (2.58 hr) plus small photopeaks due to ⁵²V (3.8 min) and ²⁴Na (15 hr) (see Figure 1). After about 2 hr the ²⁸Al and ⁵²V had decayed and the gamma ray spectrum was composed almost entirely of ⁵⁶Mn and ²⁴Na, plus a small ⁴²K photopeak and, perhaps, a small ³⁸Cl photopeak. After 5.3 days decay, 14 radionu-

clides were observed. These included ²⁴Na, ⁴²K, ⁴⁶Sc, ⁵¹Cr, ⁵⁹Fe, ⁶⁰Co, ⁸²Br, ¹³¹Be, ¹³⁴Cs, ¹⁴⁰La, ¹⁴¹Ce, ¹⁵³Sm, ¹⁷⁵Yb and ¹⁷⁷Lu. The spectrum still contained a relatively large ²⁴Na component which contributed to a rather large Compton continuum. By waiting an additional 2 or 3 days, the ²⁴Na would be greatly reduced, allowing better resolution and counting statistics for the remaining radionuclides. Mero⁽¹⁾ has reported the average concentrations for many of these constituents of red clay sediments from the Pacific Ocean. Aluminum, manganese and sodium are present in these sediments at concentrations of about 8, 1 and 2%, respectively, and their daughters ²⁸Al, ⁵⁶Mn and ²⁴Na almost completely dominate the early gamma-ray spectra. After these short-lived radionuclides have decayed, the previously mentioned long-lived activation products can then be measured.

The gamma-ray spectrum of micromanganese nodules counted 23 days after neutron irradiation showed the eleven activation products ⁴⁶Sc, ⁵¹Cr, ⁵⁹Fe, ⁶⁰Co, ⁶⁵Zn, ¹²⁴Sb, ¹³¹Ba, ¹⁴¹Ce, ¹⁵²Eu, ¹⁵⁴Eu and ²³³Pa (see Figure 2). These micromanganese nodules were contained in a pelagic red clay sediment and were removed by sieving. Their trace element composition is quite similar to that of the large manganese nodules found extensively on the ocean floor.*

* D. E. Robertson, "Trace Elements in Micromanganese Nodules and Deep-Sea Sediments," this report, pp.108-110.

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FIGURE 1. Gamma-Ray Spectra of Neutron Irradiated Deep Sea Red Clay Sediment After 1 min, 2 hr and 5 Days Decay

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FIGURE 2. Gamma-Ray Spectrum of Neutron Irradiated Micromanganese Nodules

The manganese nodules taken from the Pacific Ocean contain about 24% manganese by weight and the early gamma-ray spectra (up to about 10 hr after neutron irradiation) are almost entirely due to ⁵⁶Mn. After the ⁵⁶Mn decays, other activation products with intermediate half-lives of about 0.5 to 5 days could be determined in addition to the longer-lived radionuclides listed above.

Thus, by counting deep sea red clays and micromanganese nodules immediately and then 5 to 6 days after neutron irradiation on a Ge(Li) diode, the elements Al, Mn, V, Na, K, Sc, Cr, Fe, Co, Br, Ba, Cs, La, Ce, Sm, Eu, Yb, Zn, Sb and Th can be determined from their respective activation products.

Presently, sediment samples must be taken by coring devices and the

chemical analyses conducted in land-based laboratories. A desirable method of measuring the constituents of ocean sediments would be a portable, sea-going detection system which could be lowered to the ocean floor to perform an in situ analysis of the sediments. Some thought has been given to the feasibility of using a portable neutron generator and a Ge(Li) diode detector which could be lowered to the ocean floor to perform in situ neutron activation analysis of the sediments. From the observations made in this study, this technique would seem to offer only limited applications. Since the gamma-ray spectra of the very short-lived activation products are composed almost entirely of ²⁸Al and ⁵⁶Mn, the presence of other short-lived activation products is completely masked. Also,

the spectra 2 to 5 hr after the neutron irradiation are due almost completely to ^{56}Mn and ^{24}Na , and a much longer decay period before counting would be necessary to detect other activation products. The wait aboard ship for these short-lived interfering radionuclides to decay would probably prove too inconvenient for practical purposes. However, this technique could prove useful in locating

manganese deposits on the ocean floor or other mineral deposits near shore or near river estuaries where the sediment composition is substantially different from that of the pelagic red clay sediments.

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TRACE ELEMENTS IN THE PACIFIC COASTAL WATERS OF CENTRAL AMERICA AND MEXICO

D. E. Robertson

The concentrations of the trace elements Sr, Rb, Cs, Zn, U, Sb, Co and Sc were measured in surface and deep waters in the North Pacific Ocean off the coast of Central America and Mexico. The surface and deep water distributions of Sr, Rb, U and Cs were quite homogeneous, while the concentrations of Zn, Sb, Co and Sc showed greater diversity. Very low concentrations were observed for Co and Sc in this area relative to other areas of the ocean.

The concentrations of many of the trace elements of the ocean do not bear the relatively constant relationship to chloridity which is found for the more abundant elements and very little is known concerning their distribution and behavior in the marine environment. Characterization of the behavior of these elements can lead to an understanding of the biogeochemical and hydrological processes in which they participate. However, the majority of these trace elements exist in sea water near or below the

parts-per-billion concentration range, and very sensitive methods are required for their detection and measurement. Neutron activation analysis, when used in conjunction with recently developed instrumental methods for radionuclide measurements,^(1,2) provides an extremely sensitive and selective method for the direct measurement of many of these trace constituents.

This present work includes measurements which were designed to determine the concentrations of the trace elements Sr, Rb, Cs, Zn, U,

Sb, Co and Sc in surface and deep waters off the coast of Central America and Mexico by employing neutron activation analysis and direct counting techniques.

Surface sea water samples were collected in a plastic bucket on the end of a polyethylene rope by Pacific Oceanographic Laboratory personnel aboard the R/V McArthur. Most of the deep sea water samples were taken in Nansen bottles which were partially lined with Teflon. However, one of the deep water samples was taken in an epoxy lined Bodman sampler and one other was taken in a modified, all plastic Van Dorn bottle. The sea water was stored in 500 ml polyethylene bottles which had been rinsed with doubly-distilled nitric acid and doubly-distilled water. Sufficient purified hydrochloric acid was added to lower the pH of the sea water to about 1.5. The low pH inhibited the adsorption of several trace elements onto the surface of the polyethylene containers.*

The samples were prepared for neutron activation by repeatedly pipetting 5.00 ml aliquots of sea water into cleaned, 7 ml plastic vials and evaporating these samples to dryness under a heat lamp until a 15 to 20 ml sample of sea water had been dried. The vials were then sealed with plastic tape and irradiated together with comparison

standards of the elements of interest in a very well moderated neutron flux to an integrated thermal neutron exposure of about 2×10^{18} n/cm². All of the sample preparation was performed in a laminar flow clean hood (Agnew-Higgins) to minimize airborne contamination.

The neutron irradiation produces high concentrations of the radionuclides ²⁴Na (15 hr), ⁴²K (12.8 hr) and ⁸²Br (36 hr), which prevent the direct measurement of other radionuclides. Therefore, the samples were allowed to decay for about 4 to 5 weeks to reduce these interferences to insignificant amounts. The salts were then transferred to 1 in. diameter stainless steel planchets and counted directly on a multidimensional gamma-ray spectrometer for 1000 min.* The planchets were sandwiched between a pair of thin Pb-Cd absorbers (0.7 mm Pb followed by 0.7 mm Cd) to attenuate the intense bremsstrahlung spectra resulting from the high concentrations of ³⁵S and ³²P, in the samples. The zinc content can be measured more precisely by counting its daughter product ⁶⁵Zn on a 20 cm³ Ge(Li) diode and this method was used for its determination.

The results of these analyses are presented in Table I. The precision with which these elements are determined by neutron activation and direct counting techniques was estimated by the analyses of six replicate samples and these data are presented in Table II.

* D. E. Robertson. "The Adsorption of Trace Elements in Sea Water onto Various Container Surfaces," this report, pp. 78-83.

TABLE I. Trace Elements in North Pacific Ocean Water Samples - Panama to San Diego

Sample	Lat. (N)	Long. (W)	Sample Depth, meters	Water Depth, meters	Date	Concentrations, $\mu\text{g/l}$							
						Sr	Rb	Zn	U	Sb	Cs	Co	Sc
1	08-10.0	84-57.0	0		6/15/67	6300	156		3.60	0.86*	0.21	0.018	0.0009
2	11-23.5	87-57.1	0		6/16/67	7000	149	4.5	3.68	0.16	0.22	0.018	0.0004
3	13-00.0	91-41.3	0		6/17/67	6500	168	1.1	3.12	0.15	0.24	0.009	0.0004
4	14-41.5	94-55.4	0		6/18/67	6900	159	13.1	3.68	0.28	0.24	0.180*	0.0008
5	16-22.7	99-24.7	0		6/19/67	8500	153	20*	3.60	0.18	0.25	0.017	0.0007
6	17-50.0	103-40.0	0		6/22/67	8500	168	5.0	3.68	0.25	0.27	0.616*	0.0012
7	20-24.6	107-40.5	0		6/23/67	6600	165		3.76	0.19	0.26	0.013	0.0011
8	22-52.4	112-10.5	0		6/24/67	7400	141		3.62	0.55*	0.25	0.019	0.0006
9	26-44.7	115-13.6	0		6/25/67	7600	158		3.32	0.19	0.26	0.017	0.0003
Average Surface Concentration						7400	157	5.9	3.56	0.20	0.24	0.016	0.0007
Coefficient of Variation, %						11	5.4	48	5.5	22	7.8	14	43
10	06-56	79-14	3260	3269	6/14/67	5800	117		4.68	6.43	0.36	0.099	--
11	06-55	82-54	2070	2283	6/15/67	--	149		4.00	1.17	0.34	0.084	--
12	07-20	83-53	946	950	6/15/67	6100	193	1.4	--	--	0.27	--	--
13	08-46	86-17	3120	3156	6/16/67	6800	--	170	4.40	0.32	0.33	0.087	0.0025
14	08-46	86-17	3122	3156	6/16/67	8800	143	10	3.32	2.04	0.23	0.025	0.0018
15	11-33	88-10	4915	4966	6/16/67	8800	129	4.5	3.70	0.36	0.27	0.067	0.0023
16	13-09	91-57	5560	5663	6/17/67	5900	134		3.26	1.02	0.21	0.021	0.0016
17	14-41	94-31	4475	4690	6/18/67	6500	121	9.6	3.44	0.78	0.26	0.017	0.0019
18	16-29	100-39	5365	5380	6/22/67	8200	--		3.56	3.78	0.24	0.027	0.0027
19	14-41	94-31	4475	4690	6/18/67	9400	--	11.9	3.42	1.19	0.25	0.035	0.0019
20	14-41	94-31	4475	4690	6/18/67	8900	--	47.4	3.14	0.48	0.24	0.030	0.0011

Note: Samples 1-9 were surface samples taken in a plastic bucket on the end of a polyethylene rope. Samples 10-17 (except 14) were taken in Nansen bottles partially lined with Teflon. Sample 14 was taken in an epoxy lined Bodman bottle and Samples 19 and 20 were taken in a modified all-plastic Van Dorn bottle.

* Excluded from surface average; major sample contamination suspected

TABLE II. Precision in Measuring Trace Elements in Sea Water from Six Replicate Analyses by Neutron Activation and Direct Counting Techniques

Sample	Concentration, ppb						
	Sr	Rb	U	Cs	Sb	Co	Sc
1	9000	108	3.20	0.22	0.13	0.0083	0.00046
2	9400	109	3.36	0.23	0.13	0.0098	0.00061
3	8200	102	3.40	0.22	0.13	0.0085	0.00046
4	8800	112	3.26	0.23	0.14	0.0089	0.00046
5	8500	111	3.49	0.23	0.13	0.0098	0.00050
6	8600	119	3.06	0.23	0.14	0.0084	0.00044
Average Concentration	8800	110	3.30	0.23	0.13	0.0089	0.00049
% Standard Deviation	4.4%	4.6%	4.3%	2.5%	4.4%	7.1%	11.5%
% Deviation at 95% Centerline	8.8%	9.2%	8.6%	5.0%	8.8%	14.2%	23%

The average surface concentrations of Sr, Rb, Zn, U, Sb and Cs were in fair agreement with previously published values⁽³⁾ for other areas of the ocean. However, the average surface concentrations of Co and Sc were about one quarter and one fifth, respectively, of our observed concentrations in the Northeast Pacific Ocean,* which were in turn one fifth to one twentieth of the published literature values.⁽³⁾ The lower concentrations of Co and Sc in the tropical waters relative to waters of higher latitude may be a function of biological productivity. Cobalt is a biologically active element and may, therefore, be much more concentrated in all areas which support relatively high produc-

tivity, such as the waters off the Oregon Coast, than in the relatively barren tropical waters.

The surface distribution of Sr, Rb, U, and Cs were quite homogeneous, with the observed variations in concentrations being about the same as the variations due to the analytical techniques and counting statistics. The concentrations of Zn, Sb, Co and Sc in the surface waters showed greater diversity. This may be due to the affinity of particulate or biological material in sea water for these elements. Several very high values of Zn, Co and Sb were observed and these were suspected to be due to contamination of the sea water during the sampling process.

Because of the wide variation in the concentrations of uranium in sea water reported by many investigators, there exists some question as to the amounts truly present in the oceans. However, it is believed to be present at about

* D. E. Robertson, W. O. Forster, H. G. Rieck and J. C. Langford. "A Study of the Trace Element and Radionuclide Behavior in a Northeast Pacific Ocean Ecosystem 350 Miles Off Newport, Oregon," this report, pp. 92-108.

3.3 $\mu\text{g}/\text{l}$ in well-mixed oceanic water.⁽⁴⁾ Our average surface concentration of 3.56 $\mu\text{g}/\text{l}$ is in good agreement with this value. We have, however, observed lower values of 1.5 to 2.3 $\mu\text{g}/\text{l}$ in surface sea water samples taken in the Bering Sea and between Kodiak and Hawaii⁽⁵⁾ and this indicates that rather large differences in the uranium concentrations exist in widely separated water masses.

The observed deep sea water sample concentrations reflect the great difficulty of obtaining uncontaminated water from the deep areas of the ocean. Sporadic contamination, particularly with Sb, appeared to be present in many of the samples and it was difficult to discern the actual concentrations of these elements in the deep waters bordering Central America and Mexico. The degree of contamination which occurred can be seen by comparing Samples 13 and 14. These samples were taken at the same location and depth, but Sample 13 was collected in a Teflon-lined Nansen bottle and Sample 14 was collected in an epoxy-lined Bodman bottle. The waters from these two samplers showed grossly different concentrations for most of the elements (see Table I). Also, Samples 17, 19 and 20 were taken at the same location and depth, but Sample 17 was taken in a Teflon-lined Nansen bottle and Samples 19 and 20 were taken in an all-plastic modified Van Dorn sampler. The water from these samplers also showed considerable variations in trace element concentrations.

These deep areas are believed to contain "trapped" sea water which is effectively isolated from the rest of the Pacific basin by the East Pacific Rise.⁽⁶⁾ However, the concentrations of Rb, U and Cs in deep samples which seem to be uncontaminated with these elements, appear to be representative of the mixed oceanic waters of the Pacific Ocean, suggesting that these deep waters become mixed by circulation processes. If these deep waters are relatively stagnant, it appears that no unusual biogeochemical processes have occurred to alter the concentrations of Rb, U and Cs in them.

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A STUDY OF THE TRACE ELEMENT AND RADIONUCLIDE BEHAVIOR IN A
NORTHEAST PACIFIC OCEAN ECOSYSTEM 350 MILES OFF NEWPORT, OREGON

D. E. Robertson, W. O. Forster,*
H. G. Rieck and J. C. Langford

A study of the trace element and radionuclide concentrations in the marine ecosystem was conducted in the Northeast Pacific Ocean at a station 350 miles off Newport, Oregon. The distribution and behavior of the trace radionuclides ^7Be , ^{137}Cs , ^{106}Ru , ^{60}Co , ^{226}Ra , ^{228}Th , ^{55}Fe , ^{210}Pb and ^{210}Po was determined in an oceanic depth profile to about 1500 m. A specially designed large volume, deep-sea water sampler was used in obtaining clean depth samples. Samples of surface, midwater and benthic marine organisms from various trophic levels were collected and analyzed for radionuclide content. Trace element concentrations in the sea water and in marine organisms were measured by neutron activation analyses and direct counting techniques. Specific activities of ^{65}Zn and ^{60}Co in marine organisms were shown to be several orders of magnitude greater than their specific activities in sea water. This indicates that either the ^{65}Zn and ^{60}Co are in a form more readily available for biological assimilation than their corresponding stable elements in sea water, or that the organisms concerned had spent some time in the Columbia River estuary where higher ^{65}Zn and ^{60}Co concentrations are present. Measurements of the cosmic-ray produced radionuclide, ^7Be , indicate that this radionuclide may be very useful in studies of mixing processes in the upper 200 to 300 m of the ocean.

The oceans contain in solution and suspension all of the stable elements of the earth's crust. Also present are the primordial naturally occurring radionuclides and the cosmic-ray produced radionuclides which are continuously supplied to the oceans from the atmosphere. With the arrival of the nuclear age,

artificial radionuclides have been introduced into the marine environment as fallout from nuclear weapons testing and to a much lesser degree from nuclear waste released to the sea. The characterization of these radionuclides and stable elements in the marine environment can lead to a better understanding of the biogeochemical and hydrological processes in which they participate. The very low concentrations of these constituents require very sensitive methods of analysis for their detection and measurement, and to date,

* This study was conducted in cooperation with scientists from Oregon State University headed by W. O. Forster and including: A. Carey, J. McCauley, W. Pearcey and C. Osterberg.

very little is known concerning their distribution and behavior in the marine environment. Recent advances in instrumental methods for radionuclide measurements^(1,2) have provided sensitive means for the precise identification and determination of complex radionuclide mixtures. These methods, when used in conjunction with neutron activation analysis, provide, by far, the most sensitive method for measuring many of the stable trace elements in sea water and in marine organisms and sediments.

These analytical techniques were utilized in conducting an environmental study of the trace elements and radionuclides in the marine ecosystem at a Northeast Pacific Ocean station about 350 miles off Newport, Oregon (see Figure 1). This area was selected because it was representative of the open ocean

and remained essentially free from the influence of the Columbia River which transports a moderate quantity of radioactive material from the cooling waters of the Hanford reactors to the Pacific Ocean. This study was conducted as a cooperative effort by Battelle-Northwest and Oregon State University and was performed aboard the R/V Yaquina. Measurements of trace radionuclides and trace elements in the water column and in various trophic levels of marine organisms were performed which help to describe the inventory and behavior of these constituents in a marine ecosystem of this Northeast Pacific Ocean area.

SAMPLING OF SEA WATER, MARINE ORGANISMS AND SEDIMENTS

Trace radionuclides were extracted from large volumes of sea

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FIGURE 1. Surface Sea Water Sampling Locations and Oceanographic Station for Environmental and Radioecological Study in the Northeast Pacific Ocean

water (360 to 7600 liters) by pumping the sea water through a specially designed filtration-sorption apparatus.⁽²⁾ This assembly contained a large filter area provided by eight 12 in. diameter membrane filters (0.3 μ) followed by Al_2O_3^* and KCF-1** [potassium hexacyanocobalt (II) ferrate (II)] sorption beds. Particulate material was removed on the filters, while a known fraction of the radionuclides in the filtered water was held on the sorption beds. The KCF-1 specifically removed ^{137}Cs from sea water, while the Al_2O_3 removed many trace radionuclides with various efficiencies. Deep sea water samples were taken by pumping sea water through a 1 in. diameter polyethylene hose extended to depths of about 20, 300, 600, 900 and 1600 m. The hose was lowered and retrieved from a large, motorized reel. Samples of sea water for trace element analysis were also taken by bleeding a small portion of the water through a PVC tap placed in the hose just upstream from the pump. Sea water samples for trace element analysis were also collected in modified Van Dorn bottles lowered to depths as great as 3500 m on a hydrowire, while surface water samples were collected in a plastic bucket on the end of a polyethylene rope. All sea water samples were stored in cleaned polyethylene bottles containing suffi-

cient hydrochloric acid to lower the pH of the sea water to about 1.5. This procedure prevented the adsorption of certain trace elements from sea water onto the container surfaces.[†]

Samples of surface, midwater and benthic marine organisms were collected by trawling at night. A small sample of mixed zooplankton was also collected by pumping sea water through a fine-meshed net. The identification of species was done by Oregon State University marine biologists. A relatively undisturbed sediment sample was also obtained for analysis using a Smith-McIntire sediment sampler.

RADIONUCLIDE COUNTING

The Al_2O_3 beds were dried and placed in 1/2 in. thick by 4 in. diameter plastic Petri dishes and their radionuclide content measured by counting them for 1000 min in a large multidimensional gamma-ray spectrometer. The membrane filters were dried and pressed into 1/2 in. thick by 2 in. diameter discs and counted in a similar manner. Samples of marine organisms, which were large enough for radionuclide analysis, were ashed and then compressed into 1/2 in. thick by 2 in. diameter discs for counting. The sediment sample was dried and an aliquot was placed in a 1 in. thick by 6 in. diameter plastic

* Al_2O_3 - Woelm, neutral - Alupharm Chemicals

** KCF-1 - Bio-Rad. Laboratories

[†] D. E. Robertson. "The Adsorption of Trace Elements in Sea Water onto Various Container Surfaces," this report, pp. 78-83.

dish for counting. These samples were counted on a very sensitive multidimensional gamma-ray spectrometer.

This system, which is described in detail elsewhere,⁽³⁾ consists of two 11 in. diameter by 6 in. thick Na(Tl) crystals between which the sample is located for simultaneous coincidence and normal counting. The high efficiency of the large NaI(Tl) crystals plus the low background and Compton response obtained by anticoincidence shielding permit an extremely sensitive and selective analysis of even minor constituents in complex radionuclide mixtures.

The KCF-1 containing the ^{137}Cs was dried, placed in 500 ml polyethylene bottles and counted directly in a 9 in. diameter by 9 in. thick anticoincidence-shielded NaI(Tl) well crystal.⁽⁴⁾

The particulate material contained on the membrane filters was subsequently analyzed for ^{55}Fe , ^{210}Pb , ^{210}Po , plus stable iron and lead following standard chemical and radiochemical separations. The ^{55}Fe and ^{210}Pb were determined by beta proportional counting and the ^{210}Po was determined by alpha scintillation counting. The stable iron was determined by spectrophotometric methods, while the stable lead was determined by atomic absorption spectrometry.

NEUTRON ACTIVATION ANALYSIS

The sea water samples were prepared for neutron activation by evaporating 15 to 20 ml aliquots in clean, small polyethylene vials

using a heat lamp. The vials were then sealed with plastic tape and irradiated, together with comparison standards of the elements of interest, in the well-thermalized region of a Hanford production reactor. After the neutron irradiation, the samples were stored for about 5 weeks to allow the initially high concentrations of ^{24}Na , ^{42}K and ^{82}Br to decay to insignificance. The samples were then counted for 1000 min on a multidimensional gamma-ray spectrometer. In this manner, the trace elements Sr, Rb, Cs, U, Sb, Co and Sc could be directly measured. In addition, Zn and Fe could also be measured by counting the samples for 1000 min on a 20 cm^3 Ge(Li) diode.

The small marine organisms were freeze-dried and placed in clean polyethylene vials for neutron irradiation. The larger organisms were dissected and individual organs freeze-dried and placed in clean vials for irradiation. These vials were sealed, irradiated, along with dilute cobalt flux monitors, then allowed to stand for several weeks while the short-lived radionuclides ^{24}Na , ^{42}K and ^{82}Br decayed to non-detectable amounts. The samples were then counted on a multidimensional gamma-ray spectrometer for 1000 min.

RESULTS AND DISCUSSION

Radionuclides in the Ocean

The concentrations of the soluble and particulate fractions of the radionuclides ^{137}Cs , ^{106}Ru , ^{60}Co ,

^{226}Ra , ^{228}Th and ^7Be in a 1600 m depth profile are presented in Table I. Only the particulate fractions of ^{55}Fe , ^{210}Pb and ^{210}Po were measured and are presented in Table II. The first 20 m sampling was conducted on June 25, 1967 in what appeared to be an area of high plankton growth, since the membrane filters became clogged after passing only 360 liters of sea water. Relatively high concentrations of ^{60}Co , ^{106}Ru , ^{226}Ra , ^{137}Cs , ^{55}Fe , ^{210}Po and ^{210}Pb were observed both on the

filters and in the sorption beds, indicating that these radionuclides had been concentrated in the water and in particulate material by biological processes. The radionuclide concentrations observed at 20 m on the following day (June 26, 1967) were more representative of other surface measurements.

Cesium-137 which exists almost totally in solution and is not taken up to a large extent by biological material, was present at 20 m at a concentration of about

TABLE I. Radionuclide Concentration in Depth Profile Taken in the Pacific Ocean 350 Miles Off Newport, Oregon, June, 1967

Radionuclide	Depth, m	Particulate d/min/1000 l	Soluble d/min/1000 l	% Particulate
^{137}Cs	20 (6-25-67)	0	2116	0
	20 (6-26-67)	0	1330	0
	328	0	94	0
	656	0	~4	0
	984	0	<4	--
	1639	0	<4	--
^{106}Ru	20 (6-25-67)	~11	262	4
	20 (6-26-67)	3.4	78	4
	328	0.3	2.6	10
	656	~0.6	~1.1	~35
	984	<0.6	<1	--
	1639	<0.6	<1	--
^{60}Co	20 (6-25-67)	1.4	5.4	21
	20 (6-26-67)	0.3	~0.2	~62
	328	0.2	~0.3	~32
	656	~0.03	~0.3	~3
	984	<0.03	<0.3	--
	1639	<0.03	<0.3	--
^{226}Ra	20 (6-25-67)	0	228	0
	20 (6-26-67)	0	110	0
	328	1.4	42	3
	656	~0.3	84	~0.4
	984	~0.6	116	~0.5
	1639	~0.7	132	~0.5
^{228}Th	20 (6-25-67)	--	--	--
	20 (6-26-67)	<0.5	~3	--
	328	0.9	3.5	20
	656	~0.5	<0.5	--
	984	<0.5	<0.5	--
	1639	~0.6	<0.5	--
^7Be	20 (6-25-67)	74	370	17
	20 (6-26-67)	10	412	2
	328	<10	~50	--
	656	<10	<50	--
	984	<10	<50	--
	1639	<10	<50	--

NOTE: The Al_2O_3 adsorption bed efficiencies for ^{106}Ru , ^{60}Co , ^{226}Ra , ^{228}Th and ^7Be were 43, 14, 5, 51, and 43%, respectively. The KCF-1 adsorption bed efficiency for ^{137}Cs was 49%.

The volumes of sea water sampled at each depth were 367 liters at 20 m on 6-25-67, 2615 liters at 20 m on 6-26-67, 7608 liters at 328 m, 3785 liters at 656 m, 4031 liters at 984 m and 3861 liters at 1639 m.

TABLE II. The Vertical Distribution of Particulate ^{210}Po , ^{210}Pb , ^{55}Fe and Stable Lead and Iron in the Northeast Pacific Ocean 350 Miles Off Newport, Oregon, June, 1967

Depth, m	Volume of Sea Water Sample, liters	^{210}Po d/min/1000 l	^{210}Pb d/min/1000 l	Stable Pb $\mu\text{g/l}$	^{55}Fe d/min/1000 l	Stable Fe $\mu\text{g/l}$
20 (6-25-67)	357	134.2	119.9	2.09	266.4	132
20 (6-26-67)	2615	48.8	48.8	0.231	3.3	12.1
328	7608	31.1	9.8	0.0693	3.1	3.7
656	3785	13.5	28.9	0.0999	---	11.6
984	4031	24.4	11.8	0.0603	4.7	8.5
1639	3861	17.5	9.3	0.0355	3.1	8.5

1330 d/min/1000 liters and could be traced to a depth of about 656 m where its concentration was about 4 d/min/1000 liters. Since this radionuclide is relatively unreactive in the marine environment, its vertical distribution provides an indication of the mixing rates in the upper layers of the ocean. The ^7Be concentrations at the surface and at 328 m were about 422 and 50 d/min/1000 liters, respectively. The measurements provide the first information on the depth profile of this radionuclide. Beryllium-7 is continuously being deposited in the oceans from the atmosphere where it is produced by cosmic-ray spallation of oxygen and nitrogen. Its half-life of 53 days makes it a potentially valuable tracer for studying the rates of mixing in the upper 200 to 300 m of the ocean.

Cobalt-60 was observed to a depth of 656 m and its concentration at this depth was comparable to its surface concentration of about 0.5 d/min/100 liters (except in the waters associated with the high produc-

tivity where its surface concentration was about 6.8 d/min/100 ml). Since its mixing rate is far greater than that of ^{137}Cs , it appears that ^{60}Co is mixed by biological transport or sedimentation of detrital material enriched in ^{60}Co .

Ruthenium-106 was present at the surface and at 656 m at concentrations of about 81 and 1.7 d/min/1000 liters, respectively. This radionuclide is associated to a lesser extent with particulate material than ^{60}Co , thus its concentration decreased rapidly with depth.

The observed radium-226 concentrations were in good agreement with those reported by Koczy in Pacific Ocean vertical profiles.⁽⁵⁾ The ^{226}Ra , which was measured by counting its daughter, ^{214}Bi , was present at the surface at about 110 d/min/1000 liters (except for the sample taken in the plankton bloom), and reached a minimum concentration of about 42 d/min/1000 liters at about 328 m. The concentration then gradually increased to about 132 d/min/1000 liters at

1639 m. Koczy has postulated that this type of profile is due to ^{226}Ra becoming dissolved from the sediments and diffusing through the lower layers of the ocean and that some of this deep water reaches the surface by up-welling processes. Thus, the high ^{226}Ra concentration at the surface and in deep waters and the minimum concentrations in the midwater regions of the profile suggests that some up-welling had taken place off the Oregon coast during the summer of 1967. However, other factors may also be important in producing this effect, and more profiles taken under a variety of conditions would be necessary to substantiate this observation.

Thorium-228 was measured by counting its daughter ^{208}Tl . Except for two high values at 20 and 328 m, the concentrations observed at 656 and 1639 m, of about 0.5 d/min/1000 liters, were in fair agreement with previous measurements.⁽⁶⁾ The ^{228}Th in deep waters appeared to be present mainly in the particulate form. This was not surprising since thorium is known to be rapidly precipitated from sea water by chemical processes.

Except for the high ^{55}Fe concentrations in the plankton bloom, particulate ^{55}Fe was observed at nearly the same concentration of about 3 d/min/1000 liters throughout the water column down to 1524 m. This rather uniform distribution with depth was quite unexpected and suggests that ^{55}Fe is transported to deep waters at a relatively rapid rate by biological transport or sedimentation of detrital material

containing iron, or by a combination of both processes. Menzel and Spaeth⁽⁷⁾ have reported the soluble and particulate ($>0.5 \mu$) concentrations of iron in depth profiles in the Sargasso Sea and concluded that these two forms were present in roughly a 1:1 ratio and that there was little variation in the concentrations of total iron as a function of depth. Lewis and Goldberg⁽⁸⁾ found a similar behavior for iron in Pacific Ocean waters and our data indicate roughly similar results. If the particulate ^{55}Fe concentrations measured in this work represent a definite fraction of the total ^{55}Fe from fallout, then the ocean inventory could be estimated.

Particulate ^{210}Po and ^{210}Pb were present at 20 m at about 49 d/min/1000 liters (except in the area of the plankton bloom) and their concentrations showed a variable decrease with depth. The higher surface values were presumably due to the introduction of ^{210}Pb from the atmosphere where it is produced by the decay of ^{222}Rn gas. Rama et al.⁽⁹⁾ and Goldberg⁽¹⁰⁾ reported about 100 d/min/1000 liters in surface waters of the Northeast Pacific Ocean and found the ^{210}Pb to be completely in solution. They found a higher concentration (280 d/min/1000 liters) at 2000 m and suggested a removal of ^{210}Pb from surface waters to deep waters by biological or inorganic processes, although they could detect no ^{210}Pb in biological material nor in particulate material collected on membrane filters. Our data indicate that

higher ^{210}Pb concentrations are present at the surface and that a significant fraction is associated with particulate material. The ^{210}Pb concentrations in surface waters observed in all of these studies is much lower than the amounts predicted from estimates of washout rates of ^{210}Pb from the atmosphere.⁽¹⁰⁾

Radionuclides in Marine Organisms

The concentrations of several fallout and natural radionuclides were measured in 14 surface, mid-water and benthic marine organisms (see Table III). All of the organisms contained ^{65}Zn and ^{60}Co . This was not surprising since it is well known that most marine organisms concentrate stable zinc and cobalt from sea water. However, it was surprising to observe such

high concentrations of ^{65}Zn and ^{60}Co in the benthic marine organisms taken from a depth of about 3800 m. This observation again confirms the speculation that radionuclides which are readily accumulated by marine organisms and detrital material are transferred to deep waters at a relatively rapid rate by biological transport or sedimentation processes. Manganese-54 was present in all surface and midwater organisms and in the benthic organisms, *Chalnara serrula* (rat-tail fish) and *Ophiuroidea*. The high concentrations of ^{226}Ra and ^{228}Th observed in most benthic organisms limited the sensitivity for measuring ^{54}Mn . The ^{226}Ra and ^{228}Th were evidently accumulated in the benthic organisms from the sediments, where they exist at concentrations of 23,700 and 3590 d/min/kg, respectively.

TABLE III. Radionuclide Concentrations in Marine Organisms
Taken 350 Miles Off Newport, Oregon June, 1967

Organism	Depth, m	Wet Weight, g	Wet Weight, d/min/kg						
			^{65}Zn	^{54}Mn	^{60}Co	^{106}Ru	^{137}Cs	^{226}Ra	^{228}Th
1. <i>Cololabis saira</i> (saury)	Surface	369	144	377	22	UD	65	UD	UD
2. Kelp Scrapings (mostly barnacles)	Surface	1010	64.9	312	21.3	195	UD	15.4	UD
3. <i>Tactostoma macropus</i>	Midwater	130	166	141	3.4	UD	UD	UD	UD
4. <i>Sergestes similis</i>	Midwater	135	275	129	8.1	UD	UD	UD	UD
5. <i>Diaphus theta</i>	Midwater	172.2	410	282	10.4	UD	34	5.8	UD
6. <i>Lampanyctus ritteri</i>	Midwater	189.0	174	129	3.1	UD	45	UD	UD
7. <i>Lampanyctus leucopsarus</i>	Midwater	56	354	108	1.0	UD	UD	UD	UD
8. Mixture of small organisms	Midwater	137.0	124	132	<2	UD	27	UD	UD
9. <i>Chalnara serrula</i> (rat-tail)	3750	204	80	6.9	9.9	UD	UD	12	UD
10. <i>Dytaster gilberti</i>	3750	170	~123	UD	3.9	UD	UD	221	12
11. <i>Paelopatides confundens</i>	3750	60	~100	<11	11	UD	UD	265	58
12. <i>Abyssicucumis albatrossi</i>	3750	517	~100	UD	21.4	~28	UD	860	240
13. <i>Ophiuroidea</i>	3750	119	355	~290	84.2	UD	UD	2810	304
14. <i>Scotoplanes theeli</i>	3750	237	82	UD	56.3	UD	UD	3350	766

UD = Undetectable

Ruthenium-106 was found in a surface sample of kelp which contained many barnacles. The barnacles were removed with part of the kelp and the sample was ashed and counted. Mauchline and Templeton⁽¹¹⁾ have reported that the edible seaweed, Porphyra umbilicalis, concentrates ¹⁰⁶Ru from fission products discharged into the Irish Sea at Windscale. It is likely that many species of seaweed concentrate ruthenium from sea water, and that ruthenium may possibly be an essential element for these species. Radium-226 was also found in this sample and was probably present in the shells of the barnacles. These shells are composed mainly of calcium carbonate and the ²²⁶Ra was probably co-deposited with calcium (since their chemical properties are similar) from sea water during the construction of the shells by the barnacles.

Trace Elements in the Ocean

The concentrations of Sr, Rb, Fe, Zn, U, Cs, Sb, Co and Sc were measured in 12 surface samples collected at locations between Newport, Oregon and the major sampling station 350 miles off Newport, Oregon. These elements were also measured on station in a depth profile (see Table IV). The precision with which these elements can be measured was determined by six replicate analyses of a sea water sample taken off the coast of Central America (see Table V). The

standard deviations range from 3% for Cs to 11.5% for Sc.

The concentrations of most of these elements were in reasonable agreement with presently accepted values,⁽¹²⁾ except for Co and Sc which were about 1/3 to 1/10. The strontium, cesium and antimony were about 10 to 30% lower than several recently reported values.⁽¹²⁾ The variations observed for Sr, Rb, U, Cs and most Sb concentrations were generally within the statistical and experimental deviations associated with their measurement. These elements, particularly U, Cs and Sb, may be very useful as tracers of the movement of water masses in which their concentrations show relatively large differences, but more precise methods will be needed to resolve very small differences in their concentrations. The Fe, Zn, Co and Sc concentrations were highly variable and this may be due to their association with biological and particulate material contained in sea water. The Sc measurements are believed to be the first measured in sea water since Wattenberg first estimated its concentration to be 0.04 ppb in 1943.⁽¹²⁾

Contamination of sea water during sampling procedures is a major problem in trace element analysis and these measurements provided a good opportunity to study the quality of sea water sampled through plastic hose and in Van Dorn and Nansen bottles. The sea water

TABLE IV. Trace Element Concentrations in the Northeast Pacific Ocean

Sample	Sampler	Depth, m	Date	Concentration, µg/liter									Salinity
				Sr	Rb	Fe	Zn	U	Cs	Sb	Co	Sc	
1	Plastic Bucket	Surface	6-23-67	6300	158			2.92	0.183	0.258	0.300	0.0105	----
2	Plastic Bucket	Surface	6-23-67	7000	138			2.96	0.207	0.174	0.032	0.0010	32.098
3	Plastic Bucket	Surface	6-24-67	6000	135			3.12	0.216	0.228	0.063	0.0024	29.561
4	Plastic Bucket	Surface	6-24-67	5400	162	190	16.4	2.92	0.199	0.215	0.403	0.0108	29.526
5	Plastic Bucket	Surface	6-24-67	5200	128	24	7.3	2.56	0.194	0.140	0.057	0.0023	30.962
6	Plastic Bucket	Surface	6-24-67	5700	157	80	5.7	2.70	0.209	0.159	0.087	0.0016	32.072
7	Plastic Bucket	Surface	6-24-67	6800	139			2.94	0.202	0.133	0.062	0.0027	32.126
8	Plastic Bucket	Surface	6-24-67	6300	137			2.80	0.204	0.130	0.060	0.0019	32.601
9	Plastic Bucket	Surface	6-24-67	6500	147	140	2.6	3.28	0.234	0.126	0.033	0.0014	32.677
10	Plastic Bucket	Surface	6-24-67	5900	151	97	13.6	2.98	0.214	0.101	0.118	0.0033	32.658
11	Plastic Bucket	Station Surface	6-25-67	6200	137			2.86	0.217	0.145	0.044	0.0014	32.670
12	Plastic Bucket	Station Surface	6-25-67	6600	145			3.00	0.215	0.166	0.091	0.0035	32.697
Average Surface Concentration				6100	145		9.1	2.92	0.208	0.165	0.065	0.0036	
ON STATION PUMP													
13	Plastic Hose	20	6-25-67	6400	134			2.98	0.237	0.156	0.021	0.0012	32.718
14	Plastic Hose	20	6-26-67	6500	137	13	1.5	3.16	0.217	0.137	0.042	0.0004	32.776
15	Plastic Hose	305	6-25-67	6900	101	21	2.1	2.94	0.238	0.143	0.039	0.0012	33.937
16	Plastic Hose	609	6-25-67	6900	163		8.7	3.28	0.212	0.136	0.017	0.0007	34.139
17	Plastic Hose	914	6-26-67	8600	159	41	6.5	3.02	0.220	0.149	0.103	0.0039	34.351
18	Plastic Hose	1524	6-27-67	7000	95.2		2.3	3.38	0.240	0.149	0.046	0.0016	34.527
ON STATION CAST													
19	OSU Van Dorn	25	6-26-67	6200	127			2.94	0.227	0.164	0.021	0.0005	32.744
20	BNW Van Dorn	200	6-26-67	5700	142			3.38	0.234	0.207	0.039	0.0005	32.877
21	BNW Van Dorn	500	6-26-67	7400	145			3.44	0.230	0.170	0.060	0.0006	34.060
22	BNW Van Dorn	1000	6-26-67	7500	159			3.60	0.255	0.193	0.023	0.0010	34.280
23	BNW Van Dorn	2500	6-26-67	6500	121			2.76	0.200	0.174	0.027	0.0006	34.565
24	BNW Van Dorn	3500	6-26-67	6500	164			3.82	0.269	0.215	0.041	0.0008	34.646
ON STATION CAST													
25	Nansen Bottle	940	6-27-67	8700	146		43.4	3.40	0.238	0.222	0.031	0.0005	----
26	BNW Van Dorn	960	6-27-67	7300	119	29	34.3	3.22	0.239	0.222	0.087	0.0011	----
27	OSU Van Dorn	980	6-27-67	7100	158			3.56	0.233	0.169	0.023	0.0006	----
28	BNW Van Dorn	1000	6-27-67	6800	136			3.16	0.227	0.164	0.026	0.0004	34.255

TABLE V. Precision for Measuring Trace Elements in Sea Water by Neutron Activation and Direct Counting Techniques - Six Replicate Analyses of a Sea Water Sample Taken Off the Central America Coast

Sample	Sr	Rb	U	Cs	Sb	Co	Sc
1	9050	108	3.20	0.218	0.129	0.0083	0.00046
2	9430	109	3.36	0.231	0.131	0.0098	0.00061
3	8180	102	3.40	0.215	0.131	0.0085	0.00046
4	8820	112	3.26	0.228	0.141	0.0089	0.00046
5	8460	111	3.49	0.230	0.131	0.0098	0.00050
6	8570	119	3.06	0.233	0.136	0.0084	0.00044
Average Concentration	8750	110	3.30	0.226	0.133	0.0089	0.00049
% Standard Deviation	4.7	4.6	4.3	3.0	3.1	7.1	11.5
% Standard Deviation at 95% Centerline	9.4	9.2	8.6	6.0	6.2	14.2	23.0

samples pumped through the polyethylene hose appear to be relatively free from contamination except for one high cobalt concentration which may or may not be due to contamination. Samples taken in Van Dorn bottles appeared to contain sporadic contamination from zinc and cobalt. The surgical rubber tubing used in the construction of these samplers contained about 0.3 to 4% zinc as an impurity and this is the probable source of the zinc contamination.⁽¹³⁾ Several Nylon components of the Battelle-Northwest samplers contained about 0.1% cobalt and this is a possible source of contamination.⁽¹³⁾ A sea water sample taken in a Nansen bottle appeared to be contaminated with strontium and zinc. The zinc contamination probably originated from zinc impurities in the metallic components of the Nansen bottle, but the high strontium value is presently inexplicable.

Trace Elements in Marine Organisms

The trace elements Zn, Co, Ag, Cs, Sb and Sc were determined in about 28 marine organisms (see Table VI). When the organisms were very small, only their whole-body content was determined. When the organisms were large enough, they were dissected and samples of flesh, internal organs, and, in some fish, the liver and gills were analyzed.

Most organisms contained relatively high concentrations of zinc and cobalt. These elements are essential in biological systems, zinc being an enzyme activator while cobalt is associated with vitamin B₁₂. Some samples, including the internal organs of several species of shrimp, squid and fishes, contained extremely high concentrations of silver, suggesting that silver is either an essential element or is trapped during metabolism and may therefore act as a poison to the organism.

TABLE VI. Trace Element Concentrations in Marine Organisms
Taken 350 Miles Off Newport, Oregon, June, 1967

Organism	Concentration, ppb wet weight					
	Zn	Co	Ag	Cs	Sb	Sc
1. Lepas anitifera	8,250	21.9	<8	~20	<10	<0.4
2. Gonatus fabricii	18,800	47.6	<5	~10	<9	<0.09
3. Mytilus californianus	5,280	92.6	<3	~8	<8	~0.04
4. Mixed zooplankton	56,600	78.5	<1	~9	18.4	5.46
5. Aeolidia foliolota (squid)(flesh)	19,800	10.8	2.4	~9	--	<0.1
6. Aeolidia foliolota (tentacles)	11,600	5.2	2.9	~9	<7	<0.2
7. Cololabis saira (saury)(flesh)	11,500	19	--	10.8	<0.1	<0.02
8. Cololabis saira (gills)	16,500	7.6	--	<9	4.6	0.27
9. Cololabis saira (liver)	26,200	37.3	2.3	16.6	<0.3	<0.1
10. Hierops crockeri (whole)	11,700	5.5	5	13.1	4.8	~0.07
11. Argyropelecus lychnus (whole)	27,200	17.5	1.5	9.1	6.1	~0.09
12. Large Gammarid Amphipod (whole)	13,800	14	11	3.6	3.5	0.05
13. Periphylla periphylla (whole)	3,710	4.3	5	~0.5	8.7	0.05
14. Melamphaes lugubris (gut)	7,840	20.1	2.7	9.5	2.5	0.17
15. Large shrimp (whole)	9,830	21.2	114	<6	<2	0.11
16. Large shrimp (tail)	5,190	9.9	7.3	11.2	2.5	~0.02
17. Large shrimp (gut)	5,480	18.1	258	<2	--	~0.06
18. Nansenia Sp. candida (?) (flesh)	8,950	9.9	--	13.6	0.9	0.095
19. Nansenia Sp. candida (gut)	21,600	25.2	1.0	11.6	0.7	0.13
20. Bathylagus ochotensis (flesh)	5,190	4.5	~0.6	12.9	1.4	0.33
21. Bathylagus ochotensis (gut)	12,800	27.1	2.2	17	1.3	0.09
22. Chauliodus macouni (flesh)	5,870	4.5	8.8	11.6	2.1	~0.03
23. Chauliodus macouni (gut)	13,700	8	184	9.5	4.7	0.17
24. Lampanyctus ritteri (flesh)	2,990	5.9	<4	21.9	3.8	0.29
25. Lampanyctus ritteri (gut)	74,500	11.5	521	14.6	23.4	0.73
26. Tarletonbeania crenularis (flesh)	18,800	9	--	24.2	1.3	~0.04
27. Tarletonbeania crenularis (gut)	22,500	18.8	200	24.7	7.9	~0.09
28. Lampanyctus leucopsarus (flesh)	7,360	3.3	<0.04	19.2	4.9	<0.01
29. Lampanyctus leucopsarus (gut)	38,400	8.8	101	15.9	21.3	<0.008
30. Sergestes similis (whole)	9,760	6.7	10	5.4	<2	~0.5
31. Sergestes similis (whole)	11,300	8.9	242	13.2	5.6	~0.08
32. Tactostoma macropus (flesh)	2,380	3.9	<9	11.3	4.2	~0.06
33. Tactostoma macropus (liver)	12,100	3.5	<9	6.3	5.2	~0.02
34. Tactostoma macropus (gut minus liver)	11,300	6.2	68	7	7.3	0.19
35. Hetropod (large free-living mollusk)(gut)	10,500	472	54.5	4.3	25.5	3.3
36. Chiroteuthis (squid)(body and gut)	16,200	13.1	250	6.4	<2	0.21
37. Chiroteuthis (tentacles and flesh)	16,200	4.7	46	9	3.3	0.11
38. Diaphus theta (whole)	11,900	23.8	74	<4	4.1	0.26
39. Diaphus theta (gut and gills)	18,300	24.1	25.3	8.3	9	~0.06
40. Chalnara serrula (rat-tail)(flesh)	2,710	6.4	--	18.1	22.6	0.16
41. Chalnara serrula (gills)	15,000	66.2	5.1	~8	12.1	8.47
42. Chalnara serrula (liver)	47,000	64	11.1	6.5	24.7	0.25
43. Unidentified medusa	18,700	12.2	2.8	1.3	~2	0.22
44. Nuda medusa	368	0.28	<0.05	~0.2	~0.4	~0.003
45. Microstomus pacificus (whole)	10,300	6.3	5.5	4.7	~3	0.08
46. Microstomus pacificus (flesh)	5,590	1.2	~0.5	3.7	<0.2	<0.005
47. Sponge spicule (hexactinellid)	1,670	15.1	131	~3.4	~5	1.6

Generally, much higher concentrations of zinc, cobalt and antimony were found in the internal organs and liver samples of marine organisms than in their flesh, whereas cesium was generally distributed rather evenly throughout

their bodies. High concentrations of scandium were most often found in samples of gills and internal organs.

It was impossible to perform a reasonable trace element analysis for most benthic organisms because

of the relatively high concentrations of sediments in their bodies. Attempts to clean these organisms to remove all of the associated sediments were unsuccessful.

Specific Activities of Sea Water and Marine Organisms

From the concentrations of the radionuclides and stable trace ele-

ments measured in the ocean and in marine organisms, it was possible to calculate the specific activities of ^{60}Co , ^{65}Zn and ^{137}Cs in sea water and in several marine organisms (see Table VII). In cases where the trace element concentrations were measured in both the flesh and internal organs of marine organisms, the trace element content of their whole bodies was estimated by taking

TABLE VII. Comparison of Specific Activities of ^{60}Co , ^{65}Zn and ^{137}Cs in Surface Sea Water and in Marine Organisms

<u>Sea Water</u>	<u>Specific Activity, d/min/g of element</u>	
^{60}Co - Co	1×10^4	
^{65}Zn - Zn	$<1 \times 10^2$	
^{137}Cs - Cs	4×10^6	
<u>Marine Organism</u>	<u>Specific Activity, d/min/g of element</u>	<u>Ratio: Specific Activity in Organisms Specific Activity in Sea Water</u>
1. <u>Cololabis saira</u> (saury)		
^{60}Co - Co	$\sim 1 \times 10^6$	~ 100
^{65}Zn - Zn	$\sim 1 \times 10^4$	>100
^{137}Cs - Cs	$\sim 6 \times 10^6$	~ 1.5
2. <u>Diaphus theta</u>		
^{60}Co - Co	4×10^5	40
^{65}Zn - Zn	3.4×10^4	>340
^{137}Cs - Cs	$\sim 4 \times 10^6$	~ 1
3. <u>Lampanyctus ritteri</u>		
^{60}Co - Co	$\sim 4 \times 10^5$	~ 40
^{65}Zn - Zn	$\sim 6 \times 10^3$	>60
^{137}Cs - Cs	2×10^{-6}	0.5
4. <u>Sergestes similis</u>		
^{60}Co - Co	1×10^6	100
^{65}Zn - Zn	3×10^4	>300
5. <u>Tactostoma macropus</u>		
^{60}Co - Co	$\sim 7 \times 10^5$	~ 70
^{65}Zn - Zn	$\sim 2 \times 10^3$	>20

weighted averages, assuming that the weight of the internal organs represented about 20% of the total weight of the organism.

A comparison of the specific activities in the marine organisms and in sea water showed that the specific activities of ^{60}Co and ^{65}Zn were generally several orders of magnitude greater in the marine organisms than in the sea water. However, the specific activities of ^{137}Cs in both sea water and marine organisms were essentially the same. This is an extremely important observation, since it suggests that the ^{60}Co and ^{65}Zn exist in the oceans in physical and/or chemical forms which are different from their corresponding stable elements contained in the oceans, and that these forms are more readily available for biological assimilation. It also means that predictions of the uptake of certain radionuclides in the ocean by marine organisms may be several orders of magnitude too low, when based on the concentrations of their corresponding stable elements. Conversely, predictions of the inventory of certain radionuclides in the oceans, based on radionuclide measurements in marine organisms may be several orders of magnitude too high. Palmer⁽¹⁴⁾ recently found that the specific activity of ^{55}Fe in salmon was about 10,000 times greater than the ^{55}Fe specific activity in Northeast Pacific Ocean water, which indicates that ^{55}Fe is also in a form which is different and more readily avail-

able for biological uptake than the stable iron in the ocean.

Although all of this sampling was conducted in an area of the ocean essentially free from the influence of the Columbia River, the possibility that some of these organisms had migrated from the estuary of the river should not be disregarded. If this had indeed happened, then they would be expected to contain higher specific activities of ^{65}Zn and ^{60}Co relative to open ocean water.

CONCLUSIONS

The following general conclusions may be drawn from the observations made during the environmental and radiological study which was conducted in June, 1967, 350 miles off Newport, Oregon:

1. Artificial radionuclides, such as ^{137}Cs , which are mainly in true solution and are not taken up to a large extent by the biota, have penetrated to about 650 m by hydrological mixing processes; however, greater than 95% of their total activity resides in the first 300 m. Radionuclides such as ^{55}Fe , ^{65}Zn , ^{60}Co and ^{54}Mn , which are readily assimilated by marine organisms, have reached great depths by biological transport or sedimentation processes. Iron-55 was present through a depth of 1524 m at concentrations comparable to the surface, while ^{65}Zn , ^{60}Co

- and ^{54}Mn were detected and determined in benthic marine organisms taken from a depth of about 3750 m.
2. Concentrations of all the radionuclides studied were much higher in both the water and in particulate material ($>0.3 \mu$) in localized areas of high biological productivity. The high concentrations in the water may be due to excretion from the organisms. Thus, surface waters may show highly variable concentrations for radionuclides and trace elements which are readily accumulated by marine biota.
 3. The specific activities of ^{65}Zn , ^{60}Co and ^{55}Fe were generally orders of magnitude greater in marine organisms than in Northeast Pacific Ocean water, indicating that these radionuclides exist in forms which are different and more readily available to marine organisms than their corresponding stable trace elements contained in the oceans. Thus, estimates of the uptake of these radionuclides in the oceans based on the specific activities of marine organisms may be several orders of magnitude too high. These observations were based on the assumption that the marine organisms had not migrated from the Columbia River estuary where they would be expected to contain high specific activities of ^{65}Zn and ^{60}Co .
 4. The cosmic-ray produced radionuclide ^7Be (53 d) was measured at the surface and at a depth of 328 m. This radionuclide appears to be an excellent tracer for studies of mixing rates in the upper layers of the oceans. However, its biogeochemical behavior in the ocean should be better characterized to take full advantage of it as a tracer of ocean processes.
 5. Vertical profiles of ^{226}Ra in the Northeast Pacific Ocean may be good indicators of coastal up-welling processes. High concentrations of ^{226}Ra in surface waters and in deep waters (where the ^{226}Ra content is increased by the dissolution of the sediments) and minimum concentrations in the midwater regions of the profile suggest that deep waters had reached the surface by coastal up-welling processes. However, more vertical profiles of ^{226}Ra taken during a variety of conditions would be necessary to characterize its distribution and behavior.
 6. Except for a few samples, the trace elements Sr, Rb, U, Cs and Sb appeared to be quite homogeneously distributed in surface and deep waters of the Northeast Pacific Ocean and their concentrations observed in this work were in fair agreement with recently reported values. The Fe, Zn, Co and Sc showed greater variability in the surface and deep water

samples and the Co and Sc concentrations averaged about 1/3 to 1/10 of previously accepted values. These elements are associated to a large extent with biological and particulate material which accounts for their heterogeneous distribution in the oceans. The Sc values are believed to be the first measurements in sea water since Wattenberg first estimated its concentration to be 0.04 ppb in 1943, and the new values are an order of magnitude lower.

7. Marine organisms accumulate relatively large amounts of zinc and cobalt in their bodies, particularly in the liver and internal organs. These elements are well known for their role in the biochemical functions. Several species, particularly shrimp, squid and some fishes, concentrate silver in their bodies, suggesting that this element may play an important role in certain biological systems. The antimony, cesium and scandium were concentrated less extensively in marine organisms. Their biochemical behavior is largely unknown and they have not been considered to be essential elements.

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TRACE ELEMENTS IN MICROMANGANESE NODULES

D. E. Robertson

During their formation, the ferromanganese minerals found on the ocean floor and in deep sea sediments in the form of nodular concretions (the so-called manganese nodules) co-deposit relatively high concentrations of several trace elements from sea water, including Co, Zn, Cu, Ni, Pb and the rare earths.⁽¹⁾ These guest metals all exist in sea water in a highly unsaturated condition and their assimilation by these minerals has been postulated to account at least in part for this situation.⁽¹⁾ The equilibria controlling the distribution and behavior of the trace elements of the ocean are therefore strongly affected by the biogeochemical processes which lead to sedimenta-

tion and mineral formation on the ocean floor.

This work describes the first measurements of the concentrations and depth distributions of Mn, Fe, Cu, Zn, Co, La, Sc and Sb in micromanganese nodules which were sieved from five sections of a deep sea red clay sediment core taken in the North Pacific Ocean. These samples were supplied through the courtesy of Mr. Fred Naugler of the Pacific Oceanographic Research Laboratory, Seattle, Washington.

The micromanganese nodules contained in five 100 cm long sections of core SU-UMP-3 were removed by sieving. The nodules ranged in diameter from less than 0.1 to about 0.5 mm with the smaller sizes being more common in the upper

section of the core. Several milligrams of the nodules, as well as a sample of deep sea red clay, were encapsulated in small polyethylene vials and irradiated together with dilute manganese and cobalt neutron flux monitors in a Hanford production reactor. The manganese concentrations were determined in the samples by directly counting the activation product, ^{56}Mn , several hours after the irradiation on a 5 in. diameter by 3 in. thick Na(Tl) crystal. The samples were allowed to decay for several days and were then counted on a multidimensional gamma-ray spectrometer. Using this direct counting technique, it was possible to determine Fe, Cu, Zn, Co, La, Sc and Sb.

The elemental concentrations of the micronodules and deep sea red clay are presented in Table I. Also included in Table I for comparison purposes are the maximum, minimum and average concentrations of these elements in larger manganese nodules from the Pacific Ocean as reported by Mero.⁽²⁾

There appeared to be no systematic variation in the trace element content of the micromanganese nodules as a function of depth in the core. The concentrations of Mn, Fe, Cu, Co and Sc were within the range reported by Mero for trace elements in larger manganese nodules. However, the zinc concentrations were somewhat higher and the lanthanum concentrations were significantly lower in

TABLE I. Comparison of Trace Element Concentrations in Micromanganese Nodules Taken from Various Depths in Core SU-UMP-3 with Those in Manganese Nodules from the Pacific Ocean

Sample (Depth in Core)	Mn, %	Concentration, ppm						
		Fe	Cu	Zn	Co	La	Sc	Sb
1. 100-108 cm	-----	45,600	9480	1870	672	47.9	13.8	26.3
2. 200-208 cm	25.0	35,800	5800	1100	483	25.2	6.0	20.5
3. 300-310 cm	25.8	50,000	5970	1170	865	33.4	10.7	50.9
4. 400-409 cm	25.4	37,200	6750	1340	614	32.3	9.2	27.2
5. 500-509 cm	22.6	64,900	5470	1290	727	54.9	25.3	15.8
6. Red clay from core PI-UMP-8	0.46	39,700	2960	201	59.5	22.0	11.5	5.4
A. Enrichment Factors from Red Clay*	54.0	1.2	2.3	6.7	11	1.8	1.1	5.2
B. Enrichment Factors from Sea Water*	1×10^8	5×10^6	2×10^6	3×10^5	1×10^7	1×10^5	3×10^6	1×10^5

Maximum, Minimum and Average Concentrations (ppm) of Trace Elements in Manganese Nodules from the Pacific Ocean⁽²⁾

Maximum	41.1	266,000	16,000	800	23,000	240	30	Not Reported
Minimum	8.2	24,000	280	400	140	90	10	Not Reported
Average	24.2	140,000	5,300	470	3,500	160	10	Not Reported

* Average concentration of elements in micromanganese nodules
Concentration of elements in a) deep sea red clay core PI-UMP-8 b) sea water

the micromanganese nodules relative to those reported by Mero in larger nodules. The micronodules were enriched with Mn, Co, Sb, Zn, Cu and La relative to their concentrations in the deep sea red clay in which they were embedded, while the Fe and Sc were present in about equal amounts (see Table I). All of these elements were highly enriched in both the micromanganese nodules and red clay relative to their concentrations in sea water.

These micromanganese nodules exhibited a physical appearance quite similar to the black cosmic spherules of extraterrestrial origin found in deep sea sediments by several investigators. (3-5) However, the high manganese and low iron content of the micromanganese nodules relative to meteoritic material, plus the fact that they were nonmagnetic clearly established the authigenic nature of these micronodules.

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BERYLLIUM-7 IN OCEAN WATER*

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The cosmic ray produced radioisotope ^7Be was determined in waters collected from both the Atlantic and Pacific Oceans. This short-lived isotope will fulfill a unique requirement as a tracer for air-sea interface reactions and for measurement of rapid mixing processes in the surface layer of the ocean.

Natural and artificial radioisotopes that have entered the oceans are useful tracers in studying circulation and diffusion processes. The long-lived artificial radioisotopes ^{90}Sr and ^{137}Cs have received particular attention because they tend to remain in true solution, and their movement then reflects that of the water masses with which they are associated. The vertical distribution of these isotopes, as well as of ^3H , ^{14}C and ^{226}Ra , have been used for calculation of the rate of water transport across the thermocline and in the deep ocean.⁽¹⁻⁴⁾ Owing to their long half-lives, these isotopes are useful in studying only relatively slow oceanic processes; thus, attempts to measure the rapid mixing that occurs in the surface layer require utilization of some shorter lived nuclide. This need is filled by ^7Be , a cosmic ray produced radioisotope, with a half-life of 53 days, which can be used to monitor processes over a time interval of perhaps

200 days. This spallation product is constantly produced in the atmosphere at a rate that is both altitude and latitude dependent.⁽⁵⁾ Following formation, it becomes attached to the atmospheric aerosols and deposits on the earth's surface after an average residence period in the troposphere of about 30 days.⁽⁶⁾ This flux thus furnishes a continuous input of ^7Be to the ocean surface.

The major limitation associated with the use of this isotope as a tracer of ocean processes is its very low concentration in sea water. An upper possible limit of ^7Be of 40 d/min/liter was given by Koczy,⁽⁷⁾ who based his value on the average concentrations in rain water reported by Peters⁽⁸⁾ and Schaeffer et al.⁽⁹⁾ Lal et al.⁽¹⁰⁾ reported concentrations of 0.01 to 0.07 d/min/liter of ^7Be in waters of the Indian Ocean from collections of the radioberyllium on ferric hydroxide impregnated jute which was towed through the sea water.

Through the combined use of a collector designed for sampling large volumes of sea water and ultra-sensitive counting techniques, we were able to measure the ^7Be

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in surface waters of the Atlantic Ocean between the Bahamas and the Ivory Coast, Africa and in a vertical profile from the Pacific Ocean taken about 350 miles off the Oregon coast. Our sampling equipment is similar to that used in earlier studies of the natural and artificial radioisotopes in the hydrosphere.⁽¹¹⁾ It consists of a suitable pump and a filtration assembly that contains a sorption bed in the top section. The filtration assembly contains eight 304 mm diameter membrane filters (0.3 micropore size) which are operated in parallel, providing a total filtration area of about 5000 cm². The outlet streams from the filters are directed through either a 20 cm diameter (200 g) or a 30 cm diameter (300 g) by 0.6 cm deep bed of aluminum oxide.* The sampling line is plastic and the filtration unit is constructed from polyvinyl chloride. Those portions of the pump to which the sea water was exposed are coated with plastic to avoid both sample contamination and adsorption of trace impurities.

We employed two different methods for sampling. The samples from the 1967 Atlantic cruise of the R/V Pillsbury were taken over an extended period of time while the ship was underway. These were collected at a flow rate of about 4 liters/min from a depth of 2 m. Pacific ocean samples were taken

while the R/V Yaquina was on station, at flow rates approximating 30 liters/min. In laboratory studies that simulated these two sampling conditions, it was determined that the aluminum oxide bed retained 84 and 72%, respectively, of the nonfilterable ⁷Be from spiked sea water. There are always some reservations when an efficiency thus determined is applied to a field study; however, considering the chemistry of beryllium in sea water,⁽¹²⁾ such a comparison should be valid. These retention efficiencies are therefore used until such time as they can be reevaluated under natural conditions.**

After 1000 to 5000 liters of sea water had been sampled, the filters were removed, dried and compressed into a 1.25 cm by 5 cm diameter polyvinyl chloride ring and the aluminum oxide dried and placed in a 1.25 cm by 10 cm diameter plastic Petri dish. These samples were then counted directly for 1000 min on an anticoincidence-shielded multidimensional gamma ray spectrometer to measure the contained radionuclides. This instrument, described in detail by Wogman et al.⁽¹³⁾ has two sodium iodide crystals 22.9 cm diameter by 20.3 cm thick, between which the samples were accurately positioned for counting. The ⁷Be was

* Alumina, Woelm Neutral, Alupharm Chemicals, New Orleans, Louisiana.

** Pacific Northwest Laboratory plans to concentrate the radio-beryllium from a large volume sea water sample by precipitation scavenging to compare with that removed by the sorption bed. 1968.

determined from the contribution of its 477 keV transition to the gamma ray spectrum and was measured with an efficiency of 4.3% (defined as counts per disintegration). The background counting rate in this energy interval was 58 counts/min and contributed most of the statistical error associated with the determination. The aluminum oxide is not specific for retention of ^7Be ; indeed, many natural and artificial radioisotopes are also concentrated to various degrees. The corrections necessary for cross interference of these isotopes generally contributed less than 10% of the reported error. The

concentration of ^7Be in ocean water samples, together with the standard deviations of the measurements are presented in Table I.

These data show that the major fraction of ^7Be is present as a soluble species, or more properly stated, in a form that is not removed by a $0.3\ \mu$ filter. Merrill et al.⁽¹⁴⁾ found that an average of one-third of the total concentration of inert beryllium in sea water obtained from a depth of 1000 m was present as a particulate that was removed by passage through a $0.45\ \mu$ filter. Beryllium-7 in rainfall exists as a soluble form,⁽¹⁵⁾ thus the current data

TABLE I. Beryllium-7 Concentrations in Ocean Water

Sample Location

<u>North Latitude</u>	<u>West Longitude</u>	<u>Collection Date</u>	<u>Sample Depth, m</u>	<u>Particulate d/min/1000 l</u>	<u>Soluble</u>
<u>Atlantic Ocean</u>					
25° 30'	74° 00'	7-24-67	Surface	30 ± 10	310 ± 36
25° 38'	72° 20'	7-25-67	Surface	ND*	360 ± 50
25° 10'	65° 55'	7-26-67	Surface	ND	290 ± 42
24° 28'	62° 18'	7-27-67	Surface	ND	240 ± 18
24° 48'	59° 20'	7-28-67	Surface	20 ± 47	310 ± 72
8° 50'	38° 28'	8-16-67	Surface	20 ± 27	250 ± 107
5° 48'	16° 35'	8-21-67	Surface	70 ± 33	400 ± 48
<u>Pacific Ocean</u>					
44° 40'	130° 49'	6-25-67	20	70 ± 35	220 ± 32
44° 40'	130° 49'	6-26-67	20	10 ± 20	260 ± 26
44° 40'	130° 49'	6-26-67	328	ND	30 ± 37
44° 40'	130° 49'	6-26-67	656	ND	ND
44° 40'	130° 49'	6-26-67	984	ND	ND
44° 40'	130° 49'	6-26-67	1640	ND	ND

* ^7Be not detected (ND) in these samples - less than 10 d/min/100 liters

suggest that either beryllium is present in a different physical form at the surface or that the radioisotope does not exchange rapidly with the inactive species present.

Although there was some variation between samples, the surface concentration of ^7Be was quite uniform across the Atlantic Ocean. An indication of the depth to which the radioberyllium will occur can be postulated by a simple model that requires rapid and complete mixing of surface water to a discrete depth. This will take the form of $D = R/C$; where D is the depth in cm, R the steady state input rate in d/min/cm², and C is the measured concentration in d/min/cm³. If we take the value 0.9 d/min/cm²⁽¹⁶⁾ for the average deposition at this approximate latitude, and 3.3×10^{-4} d/min/ml for the surface ^7Be concentration, the depth of total mixing is found to be about 30 m. The assumption of homogeneity in the surface layer is certainly valid when considering long time periods required for total ocean mixing, but is oversimplified in the actual situation. Wind stress and the resultant wave action will cause a more rapid mixing at the ocean surface, and vertical turbulence will decrease with depth until it is suppressed at the top of the thermocline. The magnitude of these changes is the subject for future studies, and development of a descriptive model awaits additional data. Inference that a more detailed model

is necessary is derived from the fact that the samples taken at a higher latitude in the Pacific Ocean from a depth of 20 m contained less ^7Be than the Atlantic surface water. As both the tropospheric production rate and stratospheric injection predict a greater concentration at the higher latitude, the inverse would be true if the mixing time is short compared with the beryllium half-life.

Our results show ^7Be concentrations an order of magnitude higher than the values reported by Lal et al.,⁽¹⁰⁾ a difference too great to be ascribed to latitudinal or temporal variations. We feel that much of this discrepancy can be related to differences in the two sampling methods used. Kharkar⁽¹⁶⁾ concluded that the towed adsorption bed method of collection was unsatisfactory for quantitative analyses, owing to loss of bed matrix during the tow, and difficulty in assessing the quantity of water to which the bed was exposed. Other factors could also contribute to these differences among which are the depth to the thermocline at the different locations and the variable seasonal deposition.

Although our data are limited, they do demonstrate the feasibility of determining ^7Be in sea water. This short-lived radionuclide fulfills a unique and much needed service as a tracer of interactions at the air-sea interface as well as of mixing rates to limited depths below the surface of the

ocean. To investigate these processes, vertical profiles must be established over significant areas of the ocean.

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AN ALL SODIUM IODIDE ANTICOINCIDENCE SHIELDED
MULTIDIMENSIONAL GAMMA RAY SPECTROMETER*

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Radionuclides enter the atmosphere and other areas of the environment from numerous sources including nuclear weapons testing, the operation of nuclear plants, emanation of radon and thoron from the soil, cosmic ray radionuclide production in the atmosphere, and accretion of meteoritic dust which contains cosmic ray activation products. In addition, many of the earth's natural radionuclides are continually redistributed through various natural processes. The measurement of many of these radionuclides in environmental samples is difficult because of their extremely low concentrations. A multidimensional detector system has been built which permits the measurement of minute amounts of radionuclides in the environment and provides a major improvement in the measurement of low-level complex radionuclide mixtures. This detector system consists of two 23 cm diameter by 20 cm thick sodium iodide crystals. Each of these is viewed through 7.6 cm thick pure sodium iodide light pipes by photomultiplier tubes and they are surrounded by 38 cm diameter by 28 cm thick sodium iodide anticoincidence shields. Each principal detector, along with its light pipe and anticoincidence annulus, is hermetically sealed in a single container. The annulus, and the principal detector with its light pipe, are optically separated only by a thin layer of MgO to minimize internal energy losses. This detector system very nearly approaches a total absorption spectrometer since a gamma ray from the sample must traverse a minimum distance of 20 cm to escape the principal detector without traversing the anticoincidence shield. The background response of this detector system has been measured both at ground level and at several hundred feet below ground level where the cosmic ray contribution is minimized. The two principal sodium iodide crystals have resolutions of 8.7 to 9.2% at the ^{137}Cs 0.662 MeV photopeak. The absolute efficiency for counting ^{137}Cs is about 60%, while the coincidence counting efficiency for the ^{60}Co gamma rays is about 14%. This detector system provides the most sensitive means available for the direct measurement of many radionuclides in environmental samples. The background contribution has been resolved to show the fraction due to natural radioactivity in the detector system, that from the surrounding shielding, and that from cosmic radiation. The general response of the detector system is discussed and compared with other detector systems of somewhat similar design. The application of this instrument to several environmental studies is discussed.

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THE DETERMINATION OF THE DEPTH AND AMOUNT OF ^{239}Pu
IN WOUNDS WITH $\text{Si}(\text{Li})$ DETECTORS*

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A method has been developed for defining the average depth of ^{239}Pu in wounds by X-ray spectrometry using a lithium drifted silicon detector. Lithium drifted silicon detectors are now available which, with appropriate electronics and when cooled to liquid nitrogen temperature, give a resolution of less than 1 keV for the full width at half maximum for X-rays with energies as low as about 3 keV. The three low energy X-rays, 13, 17 and 20 keV, associated with the decay of ^{239}Pu are well resolved with the $\text{Si}(\text{Li})$ detectors. The attenuation of the 13 keV X-ray in tissue is about 3 times greater than that of the 20 keV X-ray; therefore, the relative counting rates of these two photons define the depth of a point source or the average depth of a spread source in the wound. The ratio of these counting rates could also be modified by self-absorption of a ^{239}Pu particle which may be embedded in the wound. This modified ratio can be used to correct an observed counting rate to that of a point source which does not undergo any absorption and provides a more accurate estimate of the ^{239}Pu in the wound. Plutonium-239 always contains some ^{241}Am , which emits 60 and 26 keV photons. The relative attenuation of these high energy photons along with those of ^{239}Pu allows similar measurements at all depths within the human body. The use of this method on actual ^{239}Pu wound cases is described.

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** Radiological Physics Section

COSMIC RAY PRODUCED RADIONUCLIDES AS TRACERS
OF ATMOSPHERIC PRECIPITATION PROCESSES*

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R. J. Engelmann** and R. W. Perkins

Radionuclides are produced continuously in the atmosphere by cosmic rays. Their absolute production rates vary considerably with both altitude and latitude but remain relatively constant with time. Following formation, most of these radionuclides quickly become attached to the normal atmospheric aerosols and thus can serve as tracers of the subsequent behavior of these aerosols. Some of the radionuclides with half-lives of months to years have been used in studying atmospheric mixing processes, while the longer-lived radionuclides have served as tracers of geophysical processes and in dating biological and geological phenomena. Through recent developments in instrumental analysis, it is now possible to measure with good precision the rain water concentrations of five short-lived radionuclides, ^{34}mCl (32.4 min), ^{38}Cl (37.3 min), ^{39}Cl (55 min), ^{38}S (2.9 hr) and ^{24}Na (15.0 hr), which are produced by cosmic ray spallation of atmospheric argon. These measurements provide a basis for studying in-cloud nucleation times and aerosol scavenging efficiencies, and promise to provide information on short-term processes which occur in rain and snow formation. The concentrations of these radionuclides have been measured in several precipitation samples and tentative relationships have been established between the ratios of the radionuclide concentrations and the time spent by condensation nuclei in a rain cloud.

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THE APPLICATION OF SOLID STATE DETECTORS
TO ENVIRONMENTAL AND BIOLOGICAL PROBLEMS

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Investigations involving the behavior of complex mixtures 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 present. The applicability of the new high-resolution solid state detectors has been evaluated in the analysis of several complex radionuclide mixtures which are encountered in both natural and neutron activated 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.

Nuclear weapons testing plus the operation of nuclear reactors and associated chemical processing plants release trace amounts of several radionuclides to the environment and their distribution must be followed. The concentrations of these artificial radionuclides together with the natural radionuclides in the atmosphere are measured in air filters by radiochemical and instrumental analysis. The radionuclide mixture collected on air filters is extremely complex, containing nuclear bomb debris, radon and thoron daughters and cosmic ray produced radionuclides. The mixture becomes much more complex where fresh fallout debris is present. The gamma ray spectrum, recorded with a Ge(Li) detector, of an air filter sample collected shortly after the January, 1967, Chinese test is shown in

Figure 1. Eighteen radionuclides were identified and can be determined from the spectrum. With NaI(Tl) detector systems, it is difficult to analyze for airborne ^7Be (0.48 MeV) in the presence of ^{140}La (0.49 MeV), ^{103}Ru (0.50 MeV), ^{106}Ru (0.51 MeV) and ^{125}Sb (0.43 MeV), and to discern between ^{141}Ce (0.145 MeV) and ^{144}Ce (0.134 MeV). The Ge(Li) detector allows reasonably clear definition of the ^7Be , ^{140}La and ^{103}Ru peaks as shown in Figure 1. In all, 31 airborne radioisotopes have been measured on air filters with solid state detectors. These detectors have also been evaluated for the analysis of radionuclides in Columbia River water, nuclear process plant waste streams, and several types of environmental samples including vegetation and biota. In all cases, the Ge(Li) diode provided some advantages and they at least complement and, in many cases, provide superior

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FIGURE 1. Gamma Ray Spectrum of the Airborne Radionuclides Collected on an Air Filter at Richland, Washington

performance to even the most sophisticated NaI(Tl) detector systems.

Studies of trace element concentrations throughout the environment and their behavior in living organisms help determine the origin of trace elements, their biological function, effects and retention time in various organisms. A major deterrent to extensive trace element studies in environmental and biological samples has been the lack of a practicable method for the simultaneous measurement of several

trace elements in the ppm to ppb concentration range. By use of a large-volume high resolution Ge(Li) detector, the practicability of measuring several trace elements in various biological and environmental samples by neutron activation and direct counting has been demonstrated. The gamma ray spectrum of a neutron activated human lung tissue sample measured with a 20 cm³ Ge(Li) diode and with a NaI(Tl) crystal for comparison are presented in Figure 2. By using different irradiation

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FIGURE 2. A Comparison of the Gamma Ray Spectrum of a Neutron Activated Human Lung Tissue Sample as Measured with a 5 in. Diameter by 3 in. Thick NaI(Tl) Scintillator and a Ge(Li) diode

and cooling times, up to 25 elements can be determined without chemical separation in various environmental and biological samples.

The applicability of Si(Li) detectors to various environmental and biological problems has also been evaluated. Although their

applicability to high energy gamma ray spectroscopy is limited by their low photopeak efficiency, they have many unique applications in the X-ray region. The ability of the Si(Li) detector to completely resolve the 13, 17 and 20 keV L X-rays associated with the decay of ²³⁹Pu has provided a

method for estimating depth of deposition of ^{239}Pu tissue. Other important applications of the Si(Li) detector where unique or superior performance is realized

include the measurement of ^{55}Fe from its 5.9 keV X-rays and of ^{210}Pb from its L X-rays in air filters and various environmental samples.

TRACE ELEMENT ANALYSIS OF HUMAN LUNG TISSUE
BY NEUTRON ACTIVATION AND INSTRUMENTAL ANALYSIS*

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The measurement of trace elements in tissues in the ppm to ppb range requires very careful and specialized techniques both in the sample acquisition and in subsequent analysis. Many of the trace elements which are present in human tissues are at lower concentrations than those in super pure chemical reagents; also, an acid rinse of typical laboratory glassware may contain as much of some trace elements as the tissue sample being studied. An analytical technique based on neutron activation for the measurement of trace elements in tissues has been developed which requires a minimum of preirradiation handling followed by the direct measurement of the activation products on a multidimensional or a solid state gamma ray spectrometer. This technique has been applied to a study of trace elements in human lung tissue. Lung tissue contains not only the tissue bound elements but also those which have been deposited in the cells of the pulmonary alveoli through inhalation. The method permits the direct measurement of 15 trace elements. The analysis of lung tissues thus provides information on the integrated trace element deposition resulting during the life of an individual. The concentrations of several of these including Fe, Br, P, Se, Ag, Zn, Cs, Co, Sc, U and Sb have been measured in several autopsy and biopsy samples of both normal and diseased tissues from several subjects with known case histories. The variations in the observed trace element compositions are presented and considered in terms of the occupational and medical history of the subjects.

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THE INSTRUMENTAL DETERMINATION OF TRACE ELEMENTS
IN PLANT TISSUE BY NEUTRON ACTIVATION ANALYSIS
AND Ge(Li) GAMMA RAY SPECTROMETRY*

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and J. A. Cooper

By use of neutron activation and a large volume high resolution Ge(Li) detector, the practicability of determining the concentrations of 15 elements in various types of plant tissue was demonstrated. These elements include Mn, K, Cu, Na, As, Br, P, Rb, Cr, Fe, Hg, Se, Zn, Cs and Co. This instrumental method requires no chemical or ashing manipulation and eliminates many of the inherent errors associated with chemical determinations.

The samples are freeze dried prior to neutron activation. Following neutron activation to an integral neutron flux of about 7×10^{17} n/cm²/sec, a sample is allowed to decay for a few hours then counted for 10 min to measure the relatively short-lived radionuclides. After an additional decay period of 8 weeks, the samples are recounted to measure the longer-lived radionuclides. This method allows Se, Fe, Zn, Mn, Cu to be measured with a standard deviation of better than 10% and Co, Cs, Cr, Hg, Rb, Na, K, Br and P to be measured with a standard deviation of better than 25%. Replicate analyses have shown a relatively small variation in the elemental content of cereal grains from a given lot, but large variations of several fold between lots. These results coupled with crop yield data may help define the importance of trace elements in plant metabolism.

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THE INSTRUMENTAL DETERMINATION OF 17 ELEMENTS IN URANIUM MINERS
TISSUE BY NEUTRON ACTIVATION ANALYSIS AND Ge(Li) SPECTROMETRY*

W. A. Haller, R. W. Perkins and L. A. Rancitelli

Instrumental neutron activation analysis has been employed to determine 17 elements in lung tissue. In addition to the elements normally found in tissue such as P, Fe, Zn, Rb, Na, K, Br, Se, Co and Hg, several other elements were detected. Abnormally high concentrations of Ag, Au, Sc, Cr, W, U and Sb were observed. The uranium content can be determined from the ^{239}Np activation product or the $^{140}\text{(Ba-La)}$ fission product.

The relatively high incidence of lung cancer in uranium miners has been attributed to exposure to radon daughters in the mine atmosphere. However, it is recognized that dust and other lung irritants may contribute to the development of lung cancer. To obtain a better understanding of the materials which are retained in the lungs of individuals exposed to a uranium mine atmosphere, a study was started to measure the trace element concentrations of biopsy and autopsy lung tissue samples. These samples are being obtained as they become available from individuals in uranium mining occupations and also from some individuals with other than uranium mining occupations. A medical case history of miners as determined by Public Health medical authorities will be used in the final analysis of the data.

Two biopsy samples were made available for this study which had been taken for pathological examination during exploratory surgery

on uranium miners suffering from respiratory disorders. These initial biopsy samples were removed by normal surgical procedures with a stainless steel scalpel and stored in formalin solution for several weeks prior to analysis. It is recognized that storage in formalin may have added to or removed some trace elements from the samples. Arrangements have been made to store subsequent samples in specially cleaned polyethylene containers and to keep them in a frozen state prior to neutron activation analysis.

Upon receipt, the samples were transferred to 10 ml polyethylene containers and freeze-dried for 2 days. To avoid external contamination of the polyethylene containers, in the course of the neutron activation, they were wrapped in several layers of 0.001 in. thick aluminum foil. The containers were then irradiated to an integrated neutron exposure of about $5 \times 10^{17} \text{ n/cm}^2$ in a graphite moderated reactor. A set of standard solutions which contained known concentrations of all the elements of interest were irradiated simultaneously with the

* This study is being performed jointly with Dr. A.D. Renzetti, Jr., The University of Utah Medical Center, Salt Lake City, Utah.

samples. This method of simultaneous irradiation of sample and standard is particularly satisfactory where the neutron flux is relatively constant and the fission to thermal flux ratio is low as was the case in this study. A more complete description of sample handling, encapsulation, and irradiation parameters, is contained elsewhere.^(1,*)

After irradiation, the neutron induced radionuclides were allowed to decay for 4 days. The aluminum wrap was removed from the polyethylene container and its outer surfaces were heavily lacquered to insure that any surface contamination would not be transferred to the sample during its removal. The cap of the polyethylene container was removed and the irradiated sample was transferred to a 1 in. counting disk for gamma ray spectrometric analysis.

The gamma ray spectrometer system which was employed in this work used a 20 cm³ coaxial Ge(Li) diode detector with less than 10% uncompensated material. By operation with a 1408A Canberra pre-amplifier, a Tennelec TC 200 amplifier and a Nuclear Data 2200 multiparameter analyzer, a system resolution as measured at the ⁶⁰Co 1.33 MeV line of 3.4 keV was obtained. The peak to Compton ratio for the 1.33 MeV ⁶⁰Co gamma ray

was 12 to 1. A 30 min count on the Ge(Li) spectrometer was taken to measure the short-lived neutron activation products ²⁴Na, ⁴²K, ⁸²Br, ¹⁸⁷W, ¹⁹⁷Au, and ²³⁹Np.** The samples were allowed to decay for an additional 6 weeks to permit their short-lived activation products to decay and also to allow partial decay of ³²P (14.3 d) which contributes a great deal of interference in the form of bremsstrahlung radiation. The samples were next counted for 1000 min to measure the long-lived activation products ³²P, ⁴⁶Sc, ⁵¹Cr, ⁵⁹Fe, ⁶⁰Co, ⁶⁵Zn, ⁷⁵Se, ⁸⁶Rb, ^{110m}Ag, ¹²⁴Sb, ¹⁴⁰(Ba-La),[†] and ²⁰³Hg. The neutron activated standards were counted at appropriate times and compared directly with the sample counts to calculate the elemental composition.

Figure 1 shows the gamma spectra recorded at the two time periods after irradiation. Table I presents the elemental concentrations in the tissue samples which were determined from these spectra.

It is evident from these spectra that either the ¹⁴⁰(Ba-La) or the ²³⁹Np photopeaks could be used in determining the uranium content of the samples; however, ¹⁴⁰Ba does provide a more sensitive measurement and is normally used. Perhaps the factor of greatest significance in the study to date is the demonstration that such a large group

* L. A. Rancitelli and W. A. Haller. Neutron Activation Analyses of Biological Tissue: I Neutron Self-Shielding Errors, this report, pp. 68-72.

** ²³⁹Np is the daughter of the neutron capture isotope ²³⁹U.

† ¹⁴⁰(Ba-La) is a fission product of ²³⁵U.

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FIGURE 1. *Gamma-Ray Spectrum of Activated Lung Tissue*

TABLE I. Trace Element Concentrations in
Uranium Miners' Lung Tissue

Subject No.	nano g/g of Tissue									
	W	Co	Sc	Sb	Hg	Cr	Se	U	Rb	Ag
1	22	19	14	12	310	354	115	514	333	5.2
2	<4	23	21	23	474	604	192	19	445	3.8

	μg/g of Tissue						
	Zn	Fe	P	Br	Na	K	Au
1	22	370	740	2	480	138	1.12
2	9	119	820	4	409	104	0.01

of trace elements can be analyzed with reasonably good precision (the precision is better than $\pm 10\%$ standard deviation in almost all cases) by a completely instrumental technique. The application of the method, however, is also of immediate interest. The analysis of the two tissue samples in Table I shows large variations in U, W, and Au content. Upon comparing these trace element concentrations with those in lung tissue samples from nonuranium miners, other variations are evident.⁽¹⁾ A continuing study of the trace element composition of lung tissues will allow the unusual concentrations asso-

ciated with various occupations and, perhaps, geographical areas to be determined and will provide a basis for determining any relationships which may exist between respiratory disorders and the trace element deposition in the lungs.

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THE MEASUREMENT AND BEHAVIOR OF AIRBORNE RADIONUCLIDES SINCE 1962*

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

Airborne radionuclides which have resulted from both natural and artificial sources provide a means of studying atmospheric processes. Since initiation of the 1961-1962 nuclear test series, the airborne radionuclides have been measured continuously at Richland, Washington, and more recently at Point Barrow, Alaska and Rio de Janeiro, Brazil. Also, vertical profiles of radionuclide concentrations through 60,000 ft have been determined on a periodic basis. The instrumental and sampling techniques developed for the measurement of some 20 airborne radionuclides are presented and the implications of the observed concentrations considered. From the long term measurements at the ground level sites, it has been possible to determine the apparent stratospheric residence time of a large group of the longer lived radionuclides and to determine the amplitude and width variations of the spring radioactivity peaks. Differences in the apparent stratospheric residence time as measured at ground level are considered in terms of the chemistry and point of injection of the radionuclides. Time variations in the vertical radionuclide concentration gradient are discussed and the factors influencing the gradient are considered.

* BNWL-SA-1739DETERMINATION OF FISSION PRODUCTS USING A Ge(Li) DIODE
SPECTROMETER AND A RAPID CHEMICAL SEPARATION

C. W. Thomas

With the advance of gamma ray spectrometry to include multidimensional gamma ray spectrometry, the concentrations of many radionuclides in complex mixtures could be determined without radiochemistry. Certain radionuclide mixtures, however, produce such complicated spectra that even with these sophisticated NaI(Tl) systems, chemical separations were required before detailed measurements could be made. The recent availability of large-volume high resolution germanium diodes has further reduced the need for supporting radiochemistry. These detectors have modified the role of radiochemistry

from that of individual radioisotope separations to that of group separations. Thus, radiochemical methods are being developed to separate samples into two or more components to minimize the interferences in the gamma ray spectra of these mixtures and allow the high resolution of the instrumental technique to be used to its full advantage. One application has been in the analysis of fission product mixtures produced by a short irradiation of fissionable materials. This produces a mixture similar to that resulting from nuclear weapons testing.

Examination of a Ge(Li) diode gamma ray spectrum of fresh fission products showed that a preponderance of the gamma rays were due to the various short-lived radioisotopes of iodine. Several of the radioiodine photopeaks interfered directly with the measurement of other fission products and the high Compton continuum also reduces the accuracy for their measurement. The chemical separation of the iodine radioisotopes did not eliminate their interference, since some of these built back into the samples from their radiotellurium parents.

A procedure has been developed which removes both radioiodine and radiotellurium and permits a more detailed and precise measurement of fresh fission product mixtures. This method consisted of precipitating the radiotellurium from a 3.5M HCl solution by reducing it to metal with sulfur dioxide and then removing it by filtration through a 450 mm millipore filter. The iodine daughter products are then precipitated as insoluble palladous iodide and removed by filtering through a second 450 mm filter. The two filters are combined and counted for radiotellurium and iodine. The filtrate is

evaporated to a small volume and mounted for counting. From this measurement, the remaining fission products are determined. The separation is simple and fast, requiring less than 10 min.

A coaxial drifted Ge(Li) detector having a 20 cm³ sensitive volume and a resolution of 2.9 keV(FWHM) at the 1332 photopeak of ⁶⁰Co was used to measure the two fractions. Figure 1 shows the spectrum of the gross fission product mixture from a short neutron irradiation ²³⁹Pu and that of the tellurium-iodine fraction and the residue. The gamma rays are identified for each isotope and the normal interference of the tellurium-iodine fraction in the measurement of other radionuclides is evident. Since this was a very short irradiation (minutes) and the samples were measured 4 hr later, the majority of the gamma ray photopeaks were due to shorter lived fission products. Removal of the tellurium-iodine fraction provided two groups, each containing about the same number of photopeaks. From these spectra, 24 fission products, which ranged in half-life from a few hours to many days, could be accurately determined.

Neg 0673701

FIGURE 1. Fission Product Mixtures After Rapid Chemical Separation

LONG-LIVED RADIONUCLIDES FROM BINKINI ATOLL SEDIMENTS

C. W. Thomas

A recent sample of sediments from the Bravo Crater at Bikini Atoll was measured for gamma radioactivity using multidimensional analysis employing large NaI(Tl) crystals, high resolution Ge(Li) diodes, and low energy Si(Li) diode detectors. Results show the presence of radionuclides which range in half-life from 285 days to several thousand years and include radionuclides produced by neutron activation, by fission and natural processes. Concentration of fission-produced radionuclides ^{106}Ru , ^{125}Sb , ^{137}Cs , ^{144}Ce , ^{155}Eu , neutron activated radionuclides ^{54}Mn , ^{55}Fe , ^{60}Co , ^{101}Rh , ^{102}Rh , ^{207}Bi and the natural occurring isotopes of ^{210}Pb and ^{228}Th were determined in this sample.

In 1955, a large crater was produced by the Bravo detonation at the nuclear testing site in the South Pacific at Bikini Atoll. Since that time, several studies have been made using debris from the crater. One such study in 1956-57 was to evaluate the translocation of radionuclides into edible plants.⁽¹⁾ The radionuclide concentration of the soil was determined at that time which was 319 days after detonation (see Table I). Since then, techniques used in determining radionuclide concentrations have changed considerably and it was felt that a measure of those radionuclides that were still prominent would be of interest.

Three gamma ray detecting systems were used in measuring the sample

TABLE I. Radionuclide Concentration of Bravo Soil at 319 Days Postfission (Reference Date: January 13, 1955)*

Isotope	Concentration d/min/g
T β	1.6×10^5
RE	6.0×10^4
^{144}Pr	1.4×10^4
^{144}Ce	1.4×10^4
^{141}Ce	$<6.6 \times 10^2$
^{89}Sr	2.6×10^2
^{90}Sr	6.2×10^1
^{95}Zr	8.8×10^3
^{95}Nb	2.6×10^4
^{140}Ba	$<1.5 \times 10^2$
^{137}Cs	2.2×10^2
^{103}Ru	$<1.9 \times 10^2$
^{106}Ru	1.5×10^3

* Total beta activity is corrected by utilizing factors based on the isotopic distribution of the sample.

that consisted of 31 g of sediment packed in a 1.25 cm thick by 5 cm diameter holder. A large crystal multidimensional gamma ray spectrometer⁽²⁾ measured those radionuclides that had cascading gamma rays. Because of the high efficiency of this system for high energy gamma rays and the copious amounts of ^{207}Bi and ^{60}Co that were in the sample, the only other isotope that could be readily measured was ^{208}Tl from the ^{228}Th chain. A 20 cm³ Ge(Li) coaxial diode⁽³⁾ was used to measure other gamma emitting radionuclides. This detector had a resolution of

2.9 keV or better at the 1332 keV peak of ^{60}Co and from the gamma ray spectrum obtained from this instrument, the radionuclides of ^{54}Mn , ^{101}Rh , ^{102}Rh , ^{106}Ru , ^{125}Sb , ^{136}Cs , ^{144}Ce and ^{155}Eu were determined. A Si(Li) diode⁽³⁾ with a very thin window was used to detect low energy X-rays and gamma rays. Radionuclides ^{55}Fe and ^{210}Pb were readily detected by this system. The concentrations of the radionuclides determined by these instruments are presented in Table II. The presence of relatively short-lived radionuclides ^{54}Mn , ^{106}Ru and ^{144}Ce in the crater sediments indicate that a significant amount of post-1955 debris has intermixed with the older activity.

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Prof. E. E. Held, University of Washington who furnished the sample of sediments from the Bravo Crater.

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TABLE II. Concentration of Radionuclides in Bikini Sediments

Radionuclide	d/min/g (11-29-67)	d/min/g (1-13-55)
^{60}Co	1.2×10^2	6.7×10^2
^{101}Rh	1.5	2.3×10^1
^{102}Rh	1.7×10^1	1.6×10^2
^{106}Ru	3.2×10^1	2.5×10^5
^{125}Sb	2.6×10^2	7.4×10^3
^{137}Cs	3.0×10^1	4.1×10^1
^{144}Ce	4.2×10^1	5.3×10^6
^{155}Eu	2.2×10^1	3.3×10^6
^{207}Bi	2.0×10^2	2.7×10^2
^{208}Tl	5×10^{-1}	5×10^{-1}
^{54}Mn	3.3	--
$^{55}\text{Fe}^*$	--	--
$^{210}\text{Pb}^*$	--	--

* The Si(Li) diode was not calibrated for this source size or particular soil.

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AIRBORNE RADIONUCLIDES ASSOCIATED WITH NORMAL
AND ANOMALOUS REACTOR OPERATIONS*

C. W. Thomas and R. W. Perkins

Many radionuclides become airborne as a result of reactor operations both through normal and anomalous processes. These include both reactive and nonreactive gases, and aerosols of solid radionuclides. At the Hanford Reactors, near Richland, Washington, Columbia River water is used on a once-through basis as a reactor coolant, then is retained in cooling basins for a few hours prior to its release to the river. Air-sampling studies near these effluent water basins have shown that not only the gaseous radionuclides but also relatively large amounts of solid radionuclides from the effluent water basins become airborne. Solid radionuclides, including ^{56}Mn , ^{24}Na , ^{65}Zn , ^{64}Cu , ^{51}Cr , ^{140}La , ^{46}Sc and ^{60}Co , gaseous precursor radionuclides, including ^{137}Cs and ^{138}Cs , and the gaseous radionuclides, including ^{134}I , ^{135}I and ^{38}Cl , have been studied and their physical and chemical forms defined in air samples taken at distances between 50 to 1000 m from the basins. The relative concentrations of the solid radionuclides in the air compared to their water concentrations varied by about 1000 times. Physical and chemical form measurements along with the fractionation factors, water to air, have defined much of the natural behavior for these radionuclides in their movement from thermally hot effluent water into the atmosphere. During abnormal reactor operations where the cladding of a fuel element fails, the entire fission product spectrum, including both gaseous and solid fission products, can become airborne. A reactor incident at Hanford, in which a purposely defected fuel rod failed in an unexpected manner, provided the opportunity of studying the behavior of the resulting airborne fission products in the reactor containment vessel. The fuel rod rupture was accompanied by the formation of a hole in the surrounding process tube, and the subsequent flashing of the superheated process water released a fission product aerosol to the containment vessel atmosphere. About 50% of the noble gases, 1% of the radioiodine and a somewhat smaller fraction of the solid fission products entered the containment vessel atmosphere. The air concentration, movement, deposition behavior, and physical and chemical form of some 15 fission product radionuclides and Pu in the reactor containment vessel atmosphere were studied, and their overall behavior was well defined. The sampling and instrumental analytical technology essential to these studies is also briefly described.

* Published in the Proceedings of the IAEA International Symposium on "Assessment of Airborne Radioactivity," Vienna, Austria, July 3-7, 1967.

CONCENTRATIONS OF AIRBORNE RADIONUCLIDES BETWEEN GROUND LEVEL
AND THE MIDDLE STRATOSPHERE FROM 35° TO 47° N IN 1967*

J. A. Young

The atmosphere contains a large number of radionuclides from different sources, including nuclear bomb tests, radon emanation from the earth's surface, and spallation reactions of atmospheric gases caused by cosmic rays. The longer lived radionuclides can serve as tracers of large scale atmospheric processes, while radionuclides with half-lives of minutes to hours can be used to study small scale, short term processes such as vertical air movements and the precipitation scavenging of natural aerosols. Beginning in March 1967, air filter samples were collected from 10,000 to 63,000 ft from 35° to 47° N. The disintegration rates of the cosmic ray produced radionuclide ^{24}Na (15 hr) in these samples were determined. The disintegration rates did not vary with time. At 46° N, the disintegration rate for a given weight of air increased approximately exponentially with increasing altitude by a factor of about 2,000 between ground level and 63,000 ft. The measured disintegration rates should be approximately equal to the production rates. The concentrations of the longer lived cosmic ray produced radionuclides ^7Be (53 d) and ^{22}Na (2.6 yr) and several nuclear bomb produced radionuclides were also measured in the air filter samples. The time and altitude variation of the ^7Be and ^{22}Na concentrations were very similar to those of the bomb produced radionuclides. The concentrations increased by factors of 100 to 500 between ground level and 63,000 ft. The tropospheric concentrations were highest in the samples collected on June 5, 1967. The ^7Be and ^{22}Na disintegration rates were considerably lower than the calculated production rates except at ground level. At ground level, the ^7Be disintegration rates were significantly higher than the production rate.

* BNWL Forthcoming

LIQUID SCINTILLATION COUNTING*

J. D. Ludwick

Liquid scintillation counting techniques offer one of the most versatile tools for measurement of radioactivity. A host of materials can be directly added to the scintillating medium while still allowing light pulse emission for radionuclide detection. This rather unique ability lends itself to the measurement of inorganic as well as organic materials. Whereas liquids and solids are routinely added to the liquid scintillating system, there also appear to be important applications involving additions of gases to the scintillating solution. In some instances, this technique stands as an excellent method for the primary standardization of radioisotopes.

Instrumentation generally used for liquid scintillation counting was designed to effectively measure small light pulses in the presence of certain background and electronic noise. These very features can be useful for measurement of small light pulse from other phenomena such as fluorescence and phosphorescence emission.

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A PORTABLE LABORATORY

H. G. Rieck and N. A. Wogman

Concentrations of short half-life cosmic ray and naturally produced isotopes are being measured in atmospheric physics and fallout studies.⁽¹⁾ When these experiments are conducted at sites remote from the home laboratory, the time element prohibits return of the sample to the counting laboratory for a successful measurement. In other investigations, the samples must be reduced in volume or, as in studies of uranium ore inhalation,⁽²⁾ the subjects must be counted at their home site. A portable laboratory was fabricated to be taken to the experimental site where the sample would be collected and rapidly processed in the chemical section. Chemical processes might include separation, volume reduction, drying, sample mounting, etc. The concluding step would be the measurement of radioactivity in a low background gamma ray spectrometer system⁽³⁾ located in the adjoining counting room. A minimum time delay between sample collection and counting would allow determination of isotopes such as ^{38}Cl (37.3 min), ^{39}Cl (55 min), and ^{214}Bi (19.7 min). In addition, studies of these isotopes could be done in real time so as to follow any experimental condition. A used, 15 ton rated, tandem axle, semi-trailer was used as the laboratory shell. The basic trailer, 30 ft long by 8 ft wide by 12 3/4 ft high was equipped with a curbside door, a full opening rear door and 3 in. fiber-

glass insulation. A plywood partition containing 3 in. fiberglass insulation was installed near the curbside door to isolate the rear portion of the trailer as the counting room. The chemistry laboratory was located in the forward section. A floor plan of the laboratory is shown in Figure 1.

A stable ambient counting room temperature is provided by a 15,000 Btu commercial air conditioning unit equipped with 4000 W of resistive heating. This unit was installed in the right wall of the counting room as shown in the trailer side view, Figure 2. Resistive heat is supplied on demand from a thermostat located in the counting room. Room cooling is supplied by the air conditioner on demand from a thermostat located in the air conditioning unit. Counting room air is continuously circulated through the unit during counting operations and the room temperature can be maintained to $\pm 1^\circ\text{F}$.

Counting instrumentation is installed in shock-mounted racks near the rear of the trailer. During transit, lead bricks used in shield fabrication are stacked in several layers on the floor over the trailer axles. Caster equipped frames are used to move the heavy detector assemblies. During transit, the upper detectors of the three low-level multidimensional gamma ray spectrometers are stored in specially padded containers located in the

FIGURE 1. Portable Laboratory Floor Plan

FIGURE 2. Portable Laboratory Trailer

counting room. The lower NaI(Tl) crystals, which range in size from 6 in. diameter by 4 in. thick to 13 1/2 in. diameter by 6 in. thick are positioned in permanent lead caves and are shock mounted for travel.

For operation, the detectors are moved from the storage boxes into position above the rear axles and the top half of the lead shields is built up around them (see Figure 3).

Sample evaporation equipment, five propane hot plates and a 2 ft x 3 ft propane grill are located on the right wall of the forward or chemistry laboratory. A stainless steel fume hood attached to a 1/3 hp squirrel cage blower exhausts the vapors through the trailer wall. A standard 10 ft long by 20 in. wide laboratory bench with drawers is located on the left wall. Figure 4 shows the laboratory in complete remote operation in atmospheric studies of the short-lived cosmic-ray produced radionuclides. The mobility of the counting laboratory system has and will enable studies in atmospheric physics, biology, oceanography and other environmental sciences with the ultra low backgrounds and high sensitivities provided by gamma ray multidimensional analyses.

Electrical power for heating, cooling, lighting, and instrumentation is supplied by a 5 kW, 220 V, single phase, 60 cycle propane motor-generator located under the trailer. Provision is made by external plug and switching to use available commercial power. During transit, the motor generator is operated to maintain stable counting room temperatures. Propane for sample evaporation equipment and motor operation is stored in two 50 gallon tanks located under the trailer.

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*FIGURE 3. Mobile Multidimensional Gamma Ray Spectrometer
Counting Room*

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*FIGURE 4. Laboratory Preparation of Precipitation Samples
at Quillayute, Washington*

THE DETERMINATION OF PLUTONIUM TO AMERICIUM RATIOS
IN BIOLOGICAL SPECIMENS*

Y. M. Jones, P. O. Jackson and W. J. Bair**

To aid in the evaluation of biological translocation of plutonium and americium, two precise measurement techniques were developed to determine the plutonium to americium ratios in organs of animals which had inhaled a mixed plutonium-americium oxide. In one method, after wet ashing, the actinides in the sample were electroplated and alpha pulse height analysis was used to determine the ratio. In the other, the ashed sample was precisely mounted and photon spectrometry was used for the determination.

In the evaluation of the relative behavior of plutonium and americium in exposed animals, a very precise method of measurement is required. Two techniques were developed and are illustrated with spectra in Figure 1. In each, the plutonium and americium were not chemically separated from each other since this could result in preferential loss of one radioisotope, but direct counting techniques were employed which allowed their simultaneous measurement. In one case, following wet ashing, all salts were converted to chlorides and the plutonium and americium were electroplated from an ammonium chloride electrolyte in a method similar to that previously described.⁽¹⁾ This method had typical plating recoveries exceeding 99% when there were no interfering trivalent elements present in the dissolved sample. Following electroplating, alpha pulse height analysis was used to measure the ratio of

**SPECTRA OF MIXED ^{239}Pu + ^{241}Am
IN BIOLOGICAL SAMPLES**

**ALPHA ENERGY ANALYSIS
REQUIRES PRELIMINARY PURIFICATION
(ELECTRODEPOSITION) TO ACHIEVE
NECESSARY RESOLUTION**

**PHOTON SPECTROMETRY CAN BE
PERFORMED DIRECTLY ON THE
ASHED SAMPLE**

* Also reported in the Pacific Northwest Laboratory Annual Report for 1967, in Biological Sciences, BNWL-714.

** Biology Department

Neg 0673920

FIGURE 1. Plutonium-Americium Measurements in Biological Materials

5.15 MeV alphas to the 5.48 MeV alphas. The 5.15 MeV alphas are emitted by ^{239}Pu and ^{240}Pu , while the 5.48 MeV alphas are emitted by both ^{241}Am and ^{238}Pu . The additional peak at 4.18 is due to ^{238}U which is added as a carrier for electrodeposition. To use this method for plutonium-amerium analysis, it is necessary that the ratios of the plutonium isotopes be known.

Photon spectrometry, the second method (illustrated in Figure 1) is preferable where it is applicable. Here, the plutonium X-rays and the low energy americium gamma rays are measured with a recently developed lithium drifted silicon diode having approximately 1 keV resolution. The excellent resolution permits separation of the 13, 17, and 20 keV X-ray lines from plutonium decay, from the 26 and 60 keV gamma rays from ^{241}Am decay. The greater penetration of X-rays allows direct counting of wet ashed samples if corrections for self-absorption effects are made. These effects depend on the sample mounting technique and a very uniform mount must be used. Calibration

curves for the corrections are made by preparing standards of known Pu-Am content but with different weights of tissue ash.

The primary limitation of the X-ray spectrometry method is that present silicon diode detectors are small and the X-ray fluorescence yields for ^{239}Pu are low. Therefore, the overall counter efficiency is rather low. Where sufficiently high levels of exposure have occurred, however, the technique offers the advantage that no chemical separation is required for measuring both absolute amounts of plutonium and americium and their ratios. Samples which could be analyzed by both methods gave results which were in good agreement.

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LEVELS OF ^{55}Fe IN HUMANS, ANIMALS AND FOOD 1964 - 1967*

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T. M. Beasley,[†] C. E. Jenkins and J. M. Aase^{††}

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 ^{55}Fe in humans at Richland, Washington increased until about January, 1967 and then began to decrease. This peak level in humans occurred about 4 yr after the 1962 nuclear test series. This lag time of 4 yr is much longer than that for ^{137}Cs in humans, where peak levels occurred 1-1/2 yr after the nuclear tests stopped.

The relatively high abundance of ^{55}Fe in the 1961-1962 nuclear tests by the U.S.S.R. and the United States resulted in a deposition of this isotope on the earth's surface which at one time was comparable to or slightly higher than the ^{90}Sr and ^{137}Cs levels.⁽¹⁾ However, the relative amount of ^{55}Fe in the environment has decreased much more rapidly than the ^{90}Sr and ^{137}Cs due to its shorter half-life of 2.4 yr.

Because of the high uptake of the fallout ^{55}Fe in the various food chains leading to humans, it can be measured in all people of the world.⁽²⁻⁴⁾ Although the energy of the radiation emitted from the disintegration of an atom of ^{55}Fe is small,

it is of interest because most of the radiation dose is absorbed by the red blood cells of the body.^(5,6)

The two main routes from fallout to humans for ^{55}Fe are the terrestrial food chain of plant to animal to man and the marine food chain from sea water through the lower trophic levels to fish, then to man. The purpose of this paper is to discuss the levels of ^{55}Fe in the components of these food chains and the changes in these levels during the past few years, and to compare the rate of uptake of this isotope by man with that of ^{137}Cs .

 ^{55}Fe IN THE MARINE ENVIRONMENT

A preliminary survey of ^{55}Fe in the most common foods consumed by people showed that ocean fish contained a higher concentration of ^{55}Fe than most other foods.⁽³⁾ Salmon and tuna were among those fish having the highest concentrations.⁽⁷⁾ For both of these fish, the concentration increased in the more northern latitudes. The highest concentrations observed in salmon were in those

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caught at Kotzebue, Alaska. This change in concentration with latitude has been observed for the last 4 yr and Table I lists the levels in salmon at various locations.

The data in Table I are averages of several or more salmon of several species and include silver, sockeye, chinook, and chum salmon. Our studies do not yet show any definite difference in ^{55}Fe content between the various species. The decrease of ^{55}Fe in the salmon with time is about the same or slightly more rapid than the decrease of the fallout rate as measured from air and rain concentration both in the United States and Alaska. This suggests that the ^{55}Fe deposited in the ocean may be rapidly taken up by the biomass and becomes relatively unavailable for further recycling into the salmon.

Other recent studies⁽⁸⁾ confirm our results of yearly decreases in salmon levels since 1964 and the increased concentration at northern latitudes. The reason for the relative high ^{55}Fe levels in salmon is not entirely clear and the route of ^{55}Fe intake has not

been well established. Recent studies at our laboratory have shown that the ^{55}Fe specific activity in salmon (the μCi of ^{55}Fe per gram of stable iron) is 1000 to 10,000 times greater than in the particulate fraction of sea water. This sea water was filtered through a 0.3μ pore size membrane filter at a point 15 miles off the northern California coast away from any major river influence where the salinity and the stable iron content were normal. This suggests again that the ^{55}Fe from fallout is in a form which is more readily available for uptake in the marine food web than the stable iron in the ocean.

It has been shown that whole population groups including the Japanese, the Scandinavians and the Southeast Alaskan Eskimos, who eat large quantities of ocean fish, have far higher ^{55}Fe body burdens than the average for other people in the world.^(3,4) It has also been observed that females have higher burdens than the males and that the specific activity of ^{55}Fe remains constant on transfer from mother to fetus. The nature of this transfer of ^{55}Fe from mother to fetus was characterized in a study during 1967 to 50 mother-fetus pairs from an area surrounding Dillingham, Alaska. The results will be published elsewhere. The specific activity of the mother's blood was essentially the same as that in the baby's cord blood at birth except in 2 or 3 cases. The average specific activity for all the mothers and all the newborn babies was approximately 0.10 nCi/mg when decay corrected to January, 1967.

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

Sampling Location	Average nCi ^{55}Fe /kg of Wet Muscle		
	1965	1966	1967
Northeast Alaskan Coast	(2) 50	(44) 19	(10) 5.0
Southern Alaskan Coast	(4) 33	(14) 25	(17) 5.6
Washington State Coast	(2) 9.0	(6) 0.91	(10) 1.5

Note: Numbers in parentheses are the numbers of salmon included in the average.

Assuming a total iron content of 4000 mg, the average body burden was 400 nCi for the adult females in that area during January, 1967, as compared with an average body burden of 700 nCi measured in a similar group of fish-eating female natives from the Bethel Alaska area in early 1966.

^{55}Fe IN THE TERRESTRIAL ENVIRONMENT

The main source of ^{55}Fe in the diets of most of the people of the world is animal meats and grains. The decrease with time of ^{55}Fe resulting from the plant to animal to man food chain is shown in Table II where the levels of ^{55}Fe in the blood of cattle near Richland, Washington, are listed for the years 1964 to 1966. This decrease with time in the ^{55}Fe content of cattle is slightly less than the decrease in fallout rate. This relationship is probably because grass and other cattle feeds collect most of their ^{55}Fe directly from the atmosphere. The ^{55}Fe which reaches the soil undergoes tremendous dilution by stable iron in the soil, and only a small fraction is absorbed by

TABLE II. Total Body ^{55}Fe Content* in 1000 lb Steers Raised Near Richland, Washington, 1964-1966.

Sampling Date	Number of Steers	Average Body Burden, nCi
Nov. 1964	8	441
Nov. 1965	4	226
Dec. 1966	10	108

* Body Burden determined from blood samples by assuming that 60% of iron is in the blood.

the plants. An exception to this type of relationship is the food chain of lichen to caribou to man where the lichen does not die off each year but collects and holds a large fraction of the fallout for a period of years and provides a more concentrated source of ^{55}Fe to the caribou. For this reason, the caribou blood levels increased for a period of years and then decreased as the radioactive decay exceeded the deposition of ^{55}Fe on the lichen from fallout (see Table III).

The decrease in ^{55}Fe levels in common foods purchased at local grocery stores between December, 1964, and April, 1967, is shown in Table IV. This time interval is 2.4 yr which is the same as the half-life of ^{55}Fe and, therefore, the 1967 results can be multiplied by a factor of 2 to correct for the radioactive decay since 1964. If this is done, the average for the foods for 1967 would be about the same as the average in foods for 1964. This result

TABLE III. Total Body ^{55}Fe * in Caribou from Anaktuvuk Pass, Alaska 1964-1967.

Sampling Date	Number of Caribou	Average Body Burden, nCi
Nov. 1964	5	744
Feb. 1965	6	714
Oct. 1965	6	953
May 1966	6	654
Jan. 1967	10	670

* Body burden determined from blood concentration by assuming that 60% of iron is in the blood.

TABLE IV. Comparison of ^{55}Fe in Various Foods Purchased at Richland, Washington in 1964 and 1967.

Food	Content*					
	1964			1967		
	Stable Fe, mg	^{55}Fe , nCi	Specific Activity, nCi/mg	Stable Fe, mg	^{55}Fe , nCi	Specific Activity, nCi/mg
Beef, round steak	23	0.70	0.030	23	0.24	0.010
Beef, liver	70	1.1	0.016	100	1.45	0.015
Bologna	9.1	0.34	0.037	14	0.083	0.006
Wieners	12	0.21	0.018	25	0.33	0.013
Pork Chops	6.7	0.013	0.002	10	0.007	0.0007
Pork and Ham Loaf	16	0.060	0.004	9.7	0.047	0.005
Salmon, Washington Coast	5	3.42	0.68	11	1.5	0.13
Tuna, Pacific Ocean	4.6	5.8	1.26	8.6	3.7	0.43
Clams, Pacific Ocean	17.7	0.045	0.003	26	0.046	0.002
Oysters, Pacific Ocean	170	0.087	0.0005	68	0.075	0.001
Whole Wheat Flour	38	0.29	0.008	38	0.23	0.006
White Flour	31	0.044	0.001	40	0.006	0.0002
Wheat Flakes	56	0.25	0.004	54	0.12	0.002
Quaker Oats	41	0.15	0.004	52	0.093	0.002
Eggs	23	0.25	0.011	23	0.013	0.0006
Lettuce	4.5	0.011	0.002	8.5	0.0014	0.0002
Carrots	4.1	0.028	0.007	8.4	0.0006	0.00007

* Stable Fe and ^{55}Fe are expressed per kilogram of sample.

does not agree with those obtained in the cattle and salmon where the changes in concentration are significantly lower in 1967 even after a decay correction is made. One possible explanation for the grain products is that the samples were collected from stored grain which had been harvested prior to the 1962-1963 peak fallout levels and when compared to grain sampled in 1967, the results happened to be similar. Another possible explanation for the similarity is that the geographical source of the raw materials differed in 1964 from that of 1967.

The body burdens of ^{55}Fe in people in Richland, Washington, have been

determined for the past 4 yr by measuring the levels in blood samples taken at hospitals and Red Cross blood drawings. The blood left in the plastic tubing after the blood samples are taken in blood donations is sufficient for determining ^{55}Fe if it is collected and combined for at least 25 people. The body burdens in Richland adults at various times are listed in Table V. The four people in the first two samplings were the same people and it is obvious that their average body burdens of ^{55}Fe were lower than the average for 100 men obtained a few months later. The results do demonstrate an increasing body burden until the July

TABLE V. Total Body ^{55}Fe in Adults in Richland, Washington

Sampling Date	Male		Female	
	Number of Samples	Average Body Burden, nCi	Number of Samples	Average Body Burden, nCi
Nov. 1964	4	9	--	--
Oct. 1965	4	13	--	--
Jan. 1966	100	21	25	16
March 1966	--	--	25	18
Dec. 1966	100	24	25	22
July 1967	84	17	--	--

1967 sample which showed that the levels had started to decrease. The levels in the females are almost the same as those in the males and this is due to the fact that anemic women, who have the highest uptake of ^{55}Fe and, therefore, the highest body burden, are not accepted as blood donors. It is also possible that regular male blood donors do not represent the normal population since their regular loss of blood may cause them to have a higher ^{55}Fe body burden.

The body burdens in the male caribou-eating Eskimos of Anaktuvuk Pass, Alaska, showed increased levels during 1965; body burden of 61 nCi were observed in January and 81 nCi in November. Samples at later dates have not been obtained, but levels in the caribou which they eat and the long biological half-life in the body suggests that the levels in these Eskimos have continued to increase until recently.

Although the major nuclear testing by the United States and the U.S.S.R. was stopped in 1962, the levels in humans in Richland, Washington, did not reach peak values until the latter part of 1966 or early 1967. This 4 yr lag is probably caused by 1) the time for the fallout to reach

the earth's surface, and transfer through the food chain, and 2) the long biological half-life in humans which allows the levels in humans to continue to increase for a period of time after the levels in the food have begun to decrease. This lag time is about 2 1/2 yr longer than that for ^{137}Cs in humans in Richland, Washington, where the peak levels were reached during mid-1964. This is reasonable when the shorter biological half-life of ^{137}Cs in humans and in the various components of the food chain is considered. If the ^{55}Fe levels are corrected for radioactive decay, the lag time for the peak levels in humans after injection of ^{55}Fe into the atmosphere would be somewhat longer than that shown by the actual levels.

SUMMARY

Iron-55 levels in fallout and most foods have been decreasing since 1964. The relative decrease in some of these components of the human food chain and fallout is shown in Figure 1. The levels in humans have been increasing until recently when they showed a decreasing trend.

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FIGURE 1. A Comparison of the Relative Decrease of ^{55}Fe in Fallout, Salmon and Cattle (Curves are not corrected for decay)

IRON-55 LEVELS IN HUMANS LIVING IN RICHLAND, WASHINGTON (1964-1967)

H. E. Palmer* and J. C. Langford

Body burdens of ^{55}Fe in people of Richland, Washington were determined for the period 1964-1967 by measuring the levels in blood samples taken at hospitals and at Red Cross blood drawings. The small amount of blood (1 ml) left in the plastic tubing after the blood is withdrawn is sufficient for measuring ^{55}Fe if it is collected and combined for at least 25 people. Each day that these samples were collected at the blood bank, a combined sample from about 100 men and a separate sample from about 25 women was obtained for ^{55}Fe determination.

These blood bank samples are not truly representative of the average for the population since people with low iron content in the blood are not allowed to donate blood. For the male population, this will not cause a serious error but the results obtained from blood bank samples for females are a factor of 1.5 to 2 lower than the female population average. This is because women tend to be anemic and have a higher uptake and turnover of iron than men. This causes them to have a higher body burden of ^{55}Fe than men, but the women with the highest levels are likely to be those rejected for blood donation.

Figure 1 shows the levels of ^{55}Fe in Richland males from 1964 to 1967 and also shows the levels of ^{137}Cs in humans measured at Richland during the same period of time by the Environmental Health Department.⁽¹⁾ The ^{55}Fe data for 1964 and 1965 were from only four people but they were the same four people each year. These values were normalized to the data from 100 males by comparing measurements on samples from both groups taken at about the same time. The peak levels for ^{55}Fe appear to have occurred about January, 1967, whereas the peak levels for ^{137}Cs occur about September, 1964. The time interval between the stopping of nuclear tests by the U.S.S.R. and the United States and the peak levels of ^{55}Fe and ^{137}Cs in humans is 4 and 1 1/2 yr respectively. This difference is reasonable in view of the fact that the biological half-life of ^{137}Cs is much shorter than that of ^{55}Fe in humans and most components of the food chain.

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* Radiological Physics Section

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

RADIATION CHEMISTRYACCUMULATION OF RADIONUCLIDES IN BOTTOM SEDIMENTS
OF THE McNARY RESERVOIR IN THE COLUMBIA RIVER*

J. L. Nelson and W. L. Haushild**

Inventories of radionuclides in bottom sediments of the Columbia River between the Hanford reactors and McNary Dam have been determined by a comprehensive bottom-coring program. The spatial distribution of the nuclides in relation to geographical features of the river and sediment particle sizes has been examined. It was found that between 15,000 and 20,000 Ci of gamma-emitting radionuclides were resident in the reach during the fall of the year. Levels of radionuclides were only about 10% as great above Pasco as they were between Pasco and McNary Dam. This is principally due to the smaller particle size of sediments near the dam. Inventories found by bottom coring agree within about 15% with those calculated from water and suspended-sediment samples at the top and bottom of the reach.

* This paper has been submitted for publication in "Water Resources Research."

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BUFFERING EFFECTS OF COLUMBIA RIVER SEDIMENT ON CHANGES
IN LEVELS OF WATERBORNE RADIONUCLIDES*

J. L. Nelson and W. L. Haushild**

Calculations using data collected during a shutdown of all of the Hanford reactors show that the large inventory of radionuclides held in bottom sediments acts as a buffer to minimize changes in radionuclide concentrations of the river water. Although concentrations of radionuclides being added to the river decreased to about 10% of normal levels during the shutdown, concentrations in river water at McNary Dam were about 50% of those found in other years. Concentration levels at Vancouver, Washington, differed only slightly from those for the same season in normal years. Calculations indicate that only about 3 to 10% of the inventory of the various radionuclides held in bottom sediments of the river were released during the 45 days of the shutdown.

* This paper will be submitted for publication in "Limnology and Oceanography."

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

D. R. Kalkwarf

Electron spin resonance measurements on gamma-irradiated, neutral, aqueous solutions of either the indigo dye, FD&C Blue No. 2, or the phenothiazine dye, thionine, revealed the presence of organic radicals stable for days in the absence of molecular oxygen. Solutions containing $10^{-3}M$ concentrations of the dyes were irradiated in sealed bottles containing an argon atmosphere and samples were then transferred to a Varian aqueous sample cell with gas-tight end-plates. The ESR spectra shown in Figures 1 and 2 were obtained using a Varian V4500 spectrometer with 100 kHz field modulation.

While the spectrum of the radical formed during radiolysis of FD&C Blue No. 2 solutions consists of at least 17 lines, spectral resolution was not sufficient to suggest a chemical structure for the radical. Pronounced broadening of the lines also occurred when more concentrated solutions were irradiated, indicating a rapid electron exchange between the radical and the parent molecule. The ESR signal disappeared rapidly when molecular oxygen was admitted into the solution.

The ESR spectrum of the radical derived from irradiated solutions of thionine consists of only four lines and thus gives little struc-

tural information. Continued irradiation of the solution eventually eliminated both the ESR spectrum and the color of the dye, while careful admission of molecular oxygen restored both the color and the ESR spectrum. Clearly, the reversible behavior shows that the radical is the semiquinone derivative of the phenothiazine-ring structure, formed in all probability by reaction of the dye with hydrated electrons. Addition of ethanol to the irradiated solution increased the radical yield, indicating that the $CH_3\dot{C}HOH$ radical was also capable of reducing the dye to its semiquinone form.

Discovery that FD&C Blue No. 2 forms relatively stable free radicals in irradiated aqueous solution is of particular interest since it has been shown to significantly protect irradiated agarose jellies, i.e., extend by a factor of 15 the radiation dose which a jelly can tolerate before liquefying.⁽¹⁾ As such, it joins flavin mononucleotide and the triphenylmethane dye, FD&C Blue No. 1, which also show both of these properties. Although radicals derived from these compounds react rapidly with molecular oxygen, a ubiquitous component of living tissue, large concentrations of inorganic salts and organic

FIGURE 1. ESR Spectrum of Radical Formed in Irradiated Aqueous Solutions of FD&C Blue No. 2

FIGURE 2. ESR Spectrum of Radical Formed in Irradiated Aqueous Solutions of Thionine

solutes have been shown to inhibit this effect greatly.⁽²⁾ Long-lived radicals could protect other solutes both by slowing down particular steps in the damage-propagating process, allowing more time for repair, and by stopping this process through disproportionation or dimerization reactions. Continued study of their formation and properties thus offers a promising approach to the development of chemical agents to protect persons from radiation damage.

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ABSOLUTE RATE CONSTANTS FOR THE REACTIONS OF ORGANIC SOLUTES WITH HYDROXYL RADICALS IN AQUEOUS SOLUTION

D. R. Kalkwarf

Studies of the competition kinetics between various solutes and Erioglaurine (FD&C Blue No. 1) for the hydroxyl radicals formed in irradiated solutes have provided a large number of relative rate constants for the competing reactions.^(1,2) This dye-competition method is particularly convenient for evaluating the reactivity of hydroxyl radicals with both simple and complex biochemical structures because of the nontoxicity of the reference compound and the ease of making the required spectrophotometric measurements. While many predictions concerning the sensitivity of biochemical sites to hydroxyl-radical attack can be made with these values, more complex situations involving, for

example, reactions of both hydroxyl radicals and hydrated electrons at biochemical sites requires an evaluation of the relevant rate constants on an absolute basis. Evaluation of absolute rate constants for particular reactions of the hydroxyl radical by pulse radiolysis has recently provided results which can be used to transform the relative rate constants obtained by the dye-competition technique to absolute values. The present report considers these transformations and tabulates data for compounds examined during the past several years.

Rate constants obtained from pulse radiolysis of aqueous solutions usually depend upon formation

of a characteristic optical absorption spectrum in the solution during the pulse. If it can be shown that the spectrum is due solely to a species formed by direct hydroxyl-radical attack on the solute, the rate of increase in absorption intensity measures the rate of the reaction. The major problem is finding solutes which react in this ideal way. Adams, Boag, and Michael⁽³⁾ irradiated several inorganic ions, finding, for example, that the absorption buildup at 500 nm in thiocyanate solutions indicated that $k(\text{OH} + \text{SCN}^-) = 6.6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. More recently, Baxendale and Stott⁽⁴⁾ have shown evidence that the species absorbing in this latter system is formed by two successive reactions and that $k(\text{OH} + \text{SCN}^-) = 2 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. Thomas⁽⁵⁾ irradiated iodide ion and found that the absorption buildup at 400 nm indicated that $k(\text{OH} + \text{I}^-) = (1.0 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. Still more recently, Neta and Dorfman,⁽⁶⁾ extending and correcting previous work, have determined the rate constants for the reactions of hydroxyl radicals with a series of aromatic compounds in aqueous solutions. Many of these solutes have also been examined by the competition method with Erioglaucine and so the absolute rate constant $k(\text{OH} + \text{Erioglaucine})$ can be calculated in several ways and cross-checked. The values thus obtained are shown in Table I.

The agreement between the values shown in Table I is quite reasonable in view of the uncertainties surrounding the interpretation of the

measurements; and the average value of $1.5 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ for $k(\text{OH} + \text{Erioglaucine})$ serves below as a basis for calculating absolute value for the rate constants of other reactions between hydroxyl radicals and various organic compounds in aqueous solution at pH 7 (see Table II). These values, in turn, can now be used to predict and interpret the course of radiation-induced reactions in biochemical systems.

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TABLE I. Absolute Rate of OH + Erioglaucine Reaction

Reference Reactions and Rate, $\text{M}^{-1}\text{sec}^{-1}$	$\frac{k(\text{Reference Reaction})}{k(\text{OH} + \text{Erioglaucine})}$	$k(\text{OH} + \text{Erioglaucine}),$ Units, $10^{10}\text{M}^{-1}\text{sec}^{-1}$
$k(\text{OH} + \text{SCN}^-) = 6.6 \times 10^9$ (a)	0.89 ± 0.08	0.7
$k(\text{OH} + \text{SCN}^-) = 2 \times 10^{10}$ (b)	0.89 ± 0.08	2.2
$k(\text{OH} + \text{I}^-) = (1.0 \pm 0.1) \times 10^{10}$ (c)	1.02 ± 0.06	1.0
$k(\text{OH} + \text{C}_6\text{H}_5\text{NO}_2) = (2.9 \pm 0.4) \times 10^9$ (d)	0.34 ± 0.05	0.9
$k(\text{OH} + \text{C}_6\text{H}_5\text{COOH}) = (5.5 \pm 0.6) \times 10^9$ (d)	0.36 ± 0.03	1.5
$k(\text{OH} + \text{C}_6\text{H}_6) = (7.4 \pm 0.1) \times 10^9$ (d)	0.41 ± 0.06	1.8
$k(\text{OH} + \text{C}_6\text{H}_5\text{CH}_2\text{OH}) = (7.7 \pm 0.1) \times 10^9$ (d)	0.45 ± 0.02	1.7
$k(\text{OH} + \text{C}_6\text{H}_5\text{OH}) = (1.4 \pm 0.3) \times 10^{10}$ (d)	0.60 ± 0.05	2.3
$k(\text{OH} + \text{p-NO}_2\text{C}_6\text{H}_4\text{CO}_2^-) = (2.4 \pm 0.4) \times 10^9$ (d)	0.17 ± 0.02	1.4
$k(\text{OH} + \text{p-OHC}_6\text{H}_5\text{CO}_2^-) = (8 \pm 1) \times 10^9$ (d)	0.48 ± 0.04	<u>1.7</u>
	Average =	1.5

a. Reference 1

b. Reference 2

c. Reference 3

d. Reference 4

TABLE II. Rate Constants for the Reactions of Hydroxyl Radicals with Various Compounds, Units, $10^9 M^{-1} sec^{-1}$

Aliphatic Alcohols and Sugars

Methanol	1.0	2-Methyl-2-propanol	0.60
Ethanol	1.9	1-Pentanol	6.0
2-Aminoethanol	2.7	3-Pentanol	3.6
2-Bromoethanol	1.0	Cyclopentanol	6.0
1,2-Ethanediol	1.9	2,2-Dimethyl-1-propanol	3.1
2-Methoxyethanol	2.7	1,2-Dimethyl-1,3-propanediol	2.9
2,2,2-Trifluoroethanol	0.11	Pentaerythritol	3.1
1-Propanol	2.7	3-Methyl-1-butanol	6.1
2-Propanol	1.6	2-Methyl-2-butanol	1.8
2-Propen-1-ol	5.9	1-Heptanol	7.8
2-Propyn-1-ol	1.6	1-Nonanol	11.1
1,2-Propanediol	2.2	Ribose	2.4
2-Amino-1-propanol	2.1	i-Inositol	2.2
Glycollic acid	0.9	Glucose	2.2
1-Butanol	3.7	Fructose	1.7
2-Butanol	2.5	Galactose	2.0
2-Methyl-1-propanol	4.0	Sucrose	3.0
		Maltose	3.0

Amino Acids and Peptides

Glycine	0.012	Phenylalanine	6.9
Alanine	0.069	Tyrosine	7.8
Aspartic acid	0.045	Cystine	7.8
Proline	0.36	Methionine	8.5
Serine	0.37	Tryptophane	9.4
Threonine	0.51	Norleucine	3.1
Lysine	0.74	Norvaline	1.8
Glutamic acid	0.19	Leucylglycine	2.0
Arginine	1.8	Glycylglycine	2.7
Valine	1.7	Histidylhistidine	6.1
Leucine	2.7	Glutathione	2.4
Cysteine	3.1	Bovine serum albumin	84
Histidine	5.1	Bovine hemoglobin	90

Other Aliphatic Compounds

Taurine	0.037	Ornithine	0.22
Pyruvate	0.054	Citrate	0.22
Oxalate	0.074	Succinate	0.15
Urea	0.0042	Sodium butanesulfonate	5.1
Thiourea	15	Acetone	0.11
Diethylthiourea	8.7	Ascorbate	3.7
Sodium lauryl sulfate	7.5	Acrylamide	4.9
Sodium diethyldithiocarbamate	8.5	Dimethylsulfoxide	5.6
2-Aminoethylisothiuronium bromide	4.9	Cysteamine	3.4

Aromatic Compounds

Benzene	6.1	Pyrogallol	6.5
Toluene	3.1	2-Phenoxyethanol	7.5
Benzyl alcohol	6.7	o-Toluidine	10.0
Phenethyl alcohol	7.9	p-Toluidine	9.3
Sodium benzenesulfonate	5.1	Sodium 2-naphthalenesulfonate	13
Resorcinol	8.7	1-Phenyl-2-thiourea	11
Sulfanilic acid	9.3	2-Naphthol	13
p-Nitroaniline	11	Sodium 2-naphthol-3,6-disulfonate	8.4
Nitrobenzene	5.1	Sodium 4,4-biphenylsulfonate	4.7
Benzoic acid	5.4	Sodium diphenylbenzidine	7.5
o-Aminobenzoic acid	7.0	Sodium diphenylaminesulfonate	11
m-Aminobenzoic acid	5.7	Sodium anthraquinone-2-sulfonate	2.5
p-Aminobenzoic acid	8.5	Phenol	9.0
o-Nitrobenzoic acid	2.4		
m-Nitrobenzoic acid	2.7		
p-Nitrobenzoic acid	2.5		
p-Hydroxybenzoic acid	7.2		
p-Methoxybenzoic acid	6.9		

Heterocyclic Compounds

Flavin mononucleotide	5.5	Pyridine	2.7
Adenosine	3.9	Barbituric acid	0.57
Dihydropyran	4.2	Uric acid	6.4
Cytosine	5.5	Dioxane	2.4
Adenine	3.1	Hexamethylenetetramine	6.0
Thymine	5.9		

Inorganic Compounds

Potassium iodide	15	Sodium thiocyanate	13
Potassium bromide	0.99	Sodium nitrate	<0.0001
Sodium chloride	<0.0001	Sodium nitrite	8.1
Sodium sulfate	<0.0001	Sodium thiosulfate	12.0
Sodium dihydrogen phosphate	<0.0001		

THE RADIATION-INDUCED BLEACHING OF FD&C BLUE NO. 2
IN AQUEOUS SOLUTION AND ITS USE IN MEASURING
THE OXIDIZING ABILITIES OF AMINO-ACID FREE RADICALS

D. R. Kalkwarf

While water radiolysis is the predominant initial effect of ionizing radiation on wet biological systems, the development of tissue damage depends on a whole series of chemical reactions initiated by this step. Considerable progress has been made in determining the reactivities of the water-radiolysis products with biochemical substrates and quantitative comparisons of these reactions can now be made by means of their rate constants.^(1,*) Very little is known, however, concerning the damage-propagating abilities of the products from these reactions. Many of these substances will be organic free radicals since reactions of a biochemical substrate with the most potent water-radiolysis products, i.e., the OH, e_{aq}^- , and $H^\cdot$ radicals, create compounds with unpaired electrons. Because of rapid reactions with themselves or other substances, these radicals are difficult to detect directly; therefore, the following procedure was devised to determine indirectly the oxidation-reduction properties of an important group, the radicals produced during radiolysis of naturally occurring amino acids.

FD&C Blue No. 2, an indigo dye also known as Indigocarmine, was selected for the study because of its ease of oxidation which slowly occurs even by exposure to air. In neutral aqueous solutions, this dye has an intense absorption band with a maximum at 608 nm which was used for its spectrophotometric determination. During ^{60}Co -gamma irradiation of air-saturated solutions containing FD&C Blue No. 2, bleaching occurred irreversibly and with no postirradiation effect. The concentration of dye decreased exponentially with absorbed dose and the decomposition amounted to $G(-\text{Dye}) = 1.8$ molecules per 100 eV. Air-saturated solutions of the dye also irradiated at pH 3 in the presence of $5 \times 10^{-3} \text{M}$ 2,5-dichloro-hydroquinone which reportedly scavenges only hydroxyl radicals from irradiated aqueous solutions.⁽²⁾ Under these conditions, the decomposition yield of the dye decreased by 81%, indicating that bleaching was predominantly due to hydroxyl-radical attack.

The effects of the naturally occurring amino acids were then tested on air-saturated solutions of FD&C Blue No. 2 at pH 7 during irradiation. Earlier,⁽³⁾ all of these amino acids were found to protect the triphenylmethane dye,

* D. R. Kalkwarf. "Absolute Rate Constants for the Reactions of Aqueous Solutes with Hydroxyl Radicals," this report, pp. 154-157.

Erioglaucine (FD&C Blue No. 1) although the magnitudes of the protective effects were quite different. In solutions of FD&C Blue No. 2, however, some protected the dye, others sensitized the bleaching and still others produced no net effect, as shown in Table I.

Cysteine was also tested but was found to bleach the dye spontaneously to a form which could be converted back to the original colored structure by air-oxidation. These side reactions obscured the effect of cysteine in irradiated dye solutions.

In the third column of Table I are shown rate constants for reactions of the amino acids with hydroxyl radicals. On the basis of competition kinetics, each amino acid should have protected the dye to a significant extent at the concentrations used. That this did not always occur is a clear indication that radicals derived from the amino acids also reacted with the dye. The ease of oxidation of FD&C Blue No. 2 and the irreversibility of its bleaching under the above conditions suggests that these organic radicals act as oxidizing

agents. As such, they would be expected to attack other easily oxidized substances in living tissue. Radicals derived from amino acids near the end of Table I would be expected to be particularly effective in this regard since they must have initiated a chain of oxidation reactions to account for the overall sensitization.

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TABLE I. Decomposition of 4.00×10^{-4} M FD&C Blue No. 2 in the Presence of Various Amino Acids at pH 7

<u>Amino Acid</u>	<u>G(-Dye)</u>	<u>k(OH+Acid)* Units, $10^{-9}\text{M}^{-1}\text{sec}^{-1}$</u>
None	1.8	
10^{-2} M Tryptophan	0.8	9.4
10^{-2} M Methionine	1.3	8.5
10^{-2} M Glycine	1.6	0.012
10^{-2} M Threonine	1.7	0.51
10^{-2} M Serine	1.8	0.37
10^{-2} M Arginine	2.0	1.6
10^{-2} M Alanine	2.1	0.072
10^{-2} M Lysine	2.4	0.75
10^{-2} M Aspartate	3.0	0.045
10^{-2} M Glutamate	3.1	1.3
10^{-2} M Phenylalanine	3.3	6.9
10^{-2} M Proline	3.7	0.36
10^{-2} M Valine	4.1	1.6
10^{-2} M Isoleucine	4.1	--
10^{-2} M Leucine	4.2	2.0
10^{-2} M Histidine	4.3	4.9

* D. R. Kalkwarf. "Absolute Rate Constants for the Reactions of Aqueous Solutes with Hydroxyl Radicals," this report, pp. 154.

NITROBENZENE RADICAL IONS AS INDICATORS FOR REDUCING SPECIES
FORMED DURING RADIOLYSIS OF AMINO ACID SOLUTIONS

R. N. Diebel

A method is presented for detecting the formation of radicals derived from solutes such as amino acids during gamma irradiation of aqueous solutions. These radicals are expected to form as a result of hydroxyl-radical or hydrogen-atom attack on amino acids and other compounds. In our irradiator-ESR flow system,⁽¹⁾ they disappear too rapidly for direct observation and so we have resorted to an indirect method of detection. In this method, the short-lived amino-acid radicals reduce nitrobenzene to form the long-lived nitrobenzene radical ion.

In irradiated, oxygen-free alkaline solutions, nitrobenzene is converted to its radical anion which has a characteristic 54-line ESR spectrum with a lifetime of several seconds. This ESR spectrum can be eliminated by saturating the solution with nitrous oxide which results in removal of the hydrated electron through rapid reaction to form hydroxyl radicals. If other reducing species, in addition to the hydrated electron, are present and capable of reducing nitrobenzene, then we can expect an enhancement of the signal amplitude of the nitrobenzene-radical. If the ESR signal also persists after saturating the solution with nitrous oxide, this indicates that the new reducing species has been produced

by hydroxyl-radical attack on the solutes (i.e., amino acids) present with the nitrobenzene. Both methanol and formate ion have been shown to form such reducing species⁽²⁾ and now some of the naturally-occurring amino acids have also been tested in this manner.

The results obtained with serine, alanine, valine and methanol are presented in Figure 1. There we see that the hydroxyl-containing amino acid, serine, is in the same class as methanol and forms a radical capable of reducing nitrobenzene. Its structure is most likely $\text{HO}\dot{\text{C}}\text{HCH}(\text{NH}_2)\text{COO}^-$ in analogy with radicals formed from other simple alcohols.^(3,4) These alcohol radicals are thought to reduce nitrobenzene to its radical ion at essentially the same rate as does the hydrated electron.⁽⁵⁾ Much higher concentrations of alanine, the nonhydroxylated analog of serine, and valine are required to provide the same enhancement of the nitrobenzene-radical signal. When nitrous oxide is added, we see evidence for a reducing radical produced by hydroxyl-radical attack on alanine, but this is not seen with valine. Since the alanine concentration is 0.1M, this reducing species might be due to secondary products of radiolysis. The enhancement of the ESR signal produced by alanine and valine in the absence of nitrous oxide is probably due primarily to

FIGURE 1. Nitrobenzene Radical-Ion Concentration as a Function of Added Solutes With and Without Nitrous Oxide (N_2O). Initial conditions were nitrobenzene at $4.8 \times 10^{-3} M$; $pH = 11$ throughout. (Dose was about 2500 rads delivered at a rate of 35 rads/sec)

the removal of hydroxyl radical from competition with the reduction by the hydrated electron.

Other compounds present in living tissue may also be expected to form free radicals during radiolysis and these can attack easily reduced substances and thus extend radiation damage. We expect to extend our technique for detecting such radicals into the neutral pH range by using more stable nitroaromatic radicals such as nitrobenzoic radical-anion. There seems to be a wide variety of uses for nitroaromatic or other long lived, easily produced radicals as indirect probes of radiation-chemical damage in biochemical systems where the chemical constituents as well as conformational variation leave a great number of interactions to be explored.

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PULSE-RADIOLYSIS STUDIES OF FD&C BLUE NO. 1
USING 2 MeV SWEEPED-BEAM ELECTRONS

W. D. Felix

Triphenylmethane dyes have proved effective as protective agents against ionizing radiation in biological systems;^(1,2) however, the nature of the species formed by the interaction of ionizing radiation with these dyes has not been clearly established. Since an understanding of the mechanism involved should illuminate some of the basic aspects of the protection processes, an investigation of the kinetics of the short-lived free radical or transient species formed in irradiated solutions of FD&C Blue No. 1 has been initiated. For this approach, high-speed kinetic techniques are required, pulse radiolysis being the method of choice.

The 2 MeV Van de Graaff with beam sweeping modification⁽³⁾ was used to irradiate aerated, aqueous solutions of FD&C Blue No. 1 at pH 6. The beam pulse-length was about 1 msec at half-maximum intensity. Light from a xenon high-pressure lamp was passed through a 3 cm sample cell into two 0.25 m mono-

chromators. Signals from the 1P28 photomultiplier tubes were monitored on a dual-beam oscilloscope. The absorbed dose per pulse was about 1500 rads as determined by chemical dosimetry. Electrons from the accelerator passed through a 0.25 mm quartz cell face and through 3 mm of solution. With a beam energy of 2 MeV, energy deposition should have been uniform within the solution.

Transient formation in the FD&C Blue No. 1 solutions was too rapid to follow within the time resolution available; the initial bleaching observed duplicated the shape of the beam pulse. Transient species formed during the pulse had lifetimes greater than 10 msec. Figure 1 shows the spectrum constructed point by point from observations made immediately following each pulse. The largest absorption band peaks near 460 nm, while other bands peak near 500 and 600 nm.

Product spectra from the γ -radiolysis of FD&C Blue No. 1 were

FIGURE 1. Spectra Following Irradiation of FD&C Blue No. 1: Pulse Radiolysis Spectrum Taken Immediately at Pulse End; γ -Radiolysis Curve Obtained by Subtracting Postirradiation Spectrum from Preirradiation Spectrum; and Spectrum of FD&C Blue No. 1 Before Irradiation.

observed with a Beckman DK2 spectrophotometer. The second spectrum in Figure 1 was obtained by subtracting the product spectrum from that of the original dye solution. These corrections were computed by assuming that the unchanged FD&C Blue No. 1 was the sole species contributing to the absorbance at 631 nm. Absorption at other wavelengths, A'_i , was then given by

$$A'_i = A_{pi} - \sigma A_{oi}$$

where A_{pi} was the absorption of the irradiated solution at a given wavelength, i ; A_{oi} , was the absorbance of the solution before irradiation; and σ was the ratio of absorbances at 631 nm, $A_{p, 631}/A_{o, 631}$.

In the pulse-radiolysis technique, a change in optical transmission through the solution is measured with respect to the transmission before irradiation. If the transmission being observed is at a wavelength of high absorptivity, then the determination of the spectrum of the transient in that region is complicated by the corrections necessary to account for the change in transmission due to bleaching. For this reason, detailed kinetic studies of transient decay have been limited to the spectral windows of the dye solution.

Comparison of the spectrum before and after γ -irradiation suggests that the peaks at 460 and 500 nm decayed to a stable or long-lived species, which is either present at low concentration or which has a low absorptivity at 460 nm. It is also of interest to note that

the final product spectrum apparently shows a large peak at about 600 nm, near the 631 nm peak of FD&C Blue No. 1. If the assumption that absorption at 631 nm was due solely to FD&C Blue No. 1 were in error, then this could be an artifact of the method used in subtracting the two spectra; however, some indication of a peak in this region is also seen in the pulse-radiolysis spectrum.

In an air-saturated solution, it is usually safe to assume that the hydrated electrons have been scavenged by oxygen. Thus, the transients formed which absorbed at 460 nm were undoubtedly due to reaction of the dye with hydroxyl radicals resulting in either hydrogen abstraction or hydroxylation of a phenyl group. Subsequent dimerization, disproportionation or reaction with oxygen to form a peroxy derivative would be expected. This reaction scheme may be generally outlined:

where A is the original dye molecule.

Formation of the dye radical was too rapid to be observed; however, the decay of this radical may be expected to follow either first, or second-order kinetics as required by reaction (2) or (3). Taking the absorbance at 460 nm as proportional to the concentration, the logarithm and the reciprocal of absorbance are plotted against time in Figures 2 and 3 to test for first, and

FIGURE 2. First Order Test of Decay of Transient at 460 nm at Two Different Initial Concentrations. Absorbance not corrected for cell path length of 2 cm.

second-order dependence, respectively. Both the first, and second-order plots are linear; however, note that the slopes of the first-order curves are equivalent at the two concentrations which differed by a factor of 100. On the other hand, the second-order slopes change with original dye concentration. For a true second-order reaction, the slopes should remain the same or increase with increasing concentration. Thus, the major reaction responsible for the transient decay at 460 nm

is apparently first-order with a rate constant of 57 sec^{-1} . If this reaction corresponds to reaction (2), then this rate constant would correspond to a pseudo first-order reaction of dye radical with oxygen. Using the oxygen concentration for an air saturated solution, $2.5 \times 10^{-4} \text{ M}$, and factoring this out of the pseudo first-order rate constant, the second-order rate constant for reaction (2) is $2.3 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$. The second-order rate constant, $2k_3$, for reaction (3), taken at the higher

FIGURE 3. Second Order Test of Decay of Transient in Pulse-Irradiated FD&C Blue No. 1 at 460 nm and Two Different Initial Dye Concentrations.

initial concentration in Figure 3, is $1.8 \times 10^4 \text{ } \epsilon \text{ cm sec}^{-1}$. This number should only be taken as an upper limit. A further comparison of rates of reactions (2) and (3) is dependent upon a future determination of the molar absorptivity, ϵ , of the transient species at 460 nm, and on further tests of oxygen dependence.

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RADIATION CHEMISTRY OF AERATED, AQUEOUS SOLUTIONS OF p-AMINOBENZOIC ACID

W. D. Felix

Despite its rapid reaction with hydroxyl radicals, p-aminobenzoic acid (PABA) has not been found to be an effective radiation protective agent in several living organisms.^(1,2) The mechanisms in the radiation chemistry of this important biochemical have been the subject of recent investigations by at least two groups,⁽³⁻⁵⁾ and are still open to question, particularly the specific reaction pathways of the free radical intermediates formed from PABA.

A tentative mechanism for reactions of the hydroxyl-radical adduct of PABA may be formulated using the results from irradiation of the similar systems of benzene and benzoic acid.

The generally accepted mechanism for the reaction of hydroxyl radicals with aromatic compounds in aqueous solution is illustrated with benzoic acid in which a hydroxycyclohexadienyl radical is formed:

The recombination reactions of the cyclohexadienyl radical in its two protolytic forms have also been measured⁽⁶⁾

In the presence of oxygen, the cyclohexadienyl radical resulting from the reaction of hydroxyl radicals with benzene has been shown to react with oxygen⁽⁷⁾

The resulting radical apparently then undergoes further reaction to form peroxides, hydroperoxides and phenols. The phenolic compound, 3-hydroxy-4-aminobenzoic acid has been identified

by paper chromatography as the major product of γ -irradiation of oxygenated solutions of PABA.⁽⁴⁾

The techniques of pulse and static γ -radiolysis were used to investigate the mechanism of radical intermediate decay following reaction of hydroxyl radicals with PABA. PABA, recrystallized from doubly distilled water, was irradiated in aqueous solution containing N_2O and oxygen. For static irradiation, a Gammacell 200^(R) source was used.

The ultraviolet spectrum of γ -irradiated PABA generally agreed with that reported by Nakken.⁽⁴⁾ The spectrum of the final products of γ -irradiated PABA is compared with that of PABA immediately after a 1.7 μ sec burst of electrons in Figure 1. The transient formed has absorption peaks at 325 and 410 nm. By way of comparison, spectral maxima at 320 and 420 nm have been ascribed to the hydroxyl adducts of the benzoate and nitrobenzoate ions, respectively.⁽⁸⁾

Nakken,⁽⁴⁾ using paper chromatography, ascribed products of PABA irradiation to p-hydroxybenzoic acid, p-aminophenol, aniline and 3-hydroxy-4-aminobenzoic acid with the latter being predominant.

Products from the γ -irradiated solutions were separated on cellulose TLC plates, using a mixture of ammonium hydroxide, water, butanol, and methanol as the developing solvent. The components were detected with UV light and Ehrlich's reagent. At least nine components were distinguishable in irradiated PABA as seen

FIGURE 1. Comparison of Spectra of p-Aminobenzoic Acid After γ and Pulsed Electron Irradiation. PABA concentrations: $5 \times 10^{-4}M$, pH 9. Solutions were N_2O/O_2 saturated, (1/1, v/v).

in a typical separation in Figure 2. Possible products of PABA irradiation were also run on the same plate; and, of the products compared, only the one with the highest RF value could be tentatively assigned as m-hydroxybenzoic acid. No evidence was found for the assignment of the products to p-aminophenol, or aniline. P-hydroxybenzoic acid was not sufficiently separated from PABA to eliminate it from the list of possible products. The suspected major product, 3-hydroxy-4-aminobenzoic acid was not available for comparison.

Solutions of PABA were irradiated with the electrons from a Varian V-7715 pulsed accelerator, characteristics of which have been described elsewhere.⁽⁹⁾ The solutions were saturated with nitrous oxide and oxygen, nitrous oxide added to convert hydrated electrons to

FIGURE 2. Thin-Layer Chromatographic Separation on Cellulose of Products Present in Irradiated Solutions of PABA. Solvent: Butanol-methanol-ammonium hydroxide-water (5:1:1:1).

hydroxyl radicals. Detailed kinetic studies have been carried out at the 410 and 450 nm wavelength positions.

A typical oscilloscope trace is shown in Figure 3 for decay at 410 nm. The absorption at 410 did not decay back to the I_0 line, decay apparently resulting in a product which also absorbed in the same region. Assuming that the product absorption was increasing directly proportional to the transient absorption decrease, a corrected transient absorption was calculated.

On a long-time scale during which about 95% of the 410 nm transient decay occurred, first- and second-order rate tests were inconclusive. The second-order test gave linear plots; however, mixed order dependence was indicated since the slopes were functions of the initial concentrations.

On a shorter time scale, the oxygen-free system shows good first-order dependence for the period

FIGURE 3. Typical Oscilloscope Trace of Transient at 410 nm in Deaerated Solution, N_2O Saturated. Upper trace 2 μ sec/cm; lower 20 μ sec/cm.

corresponding to 60% decay of the original absorbing species (Figure 4). The rate constant, k_5 , for the first order reaction

is $(8.6 \pm 0.7) \times 10^4 \text{sec}^{-1}$.

The addition of oxygen introduces a pseudo first-order reaction,

which occurs simultaneously with reaction (5). First-order rate constants are additive for reactions with the same precursor:

$$\frac{dA}{dt} = -k_1A - k_2A = -(k_1 + k_2)A \quad (7)$$

Examples of the results at one particular oxygen concentration ($\text{N}_2\text{O}:\text{O}_2 = 56:25$) are plotted in Figure 5. The initial linear portions again correspond to a decay of at least 60% of the original transient. The oxygen concentration was calculated from Henry's law. Correcting the combined rate constant, k_7 , for the k_5 component, and multiplying the pseudo first order rate constant by the oxygen

FIGURE 4. First-Order Test of Decay of Transient at 410 nm, Deaerated Solution, N_2O Saturated, pH 9. PABA $3.2 \times 10^{-3}M$.

FIGURE 5. First-Order Test of the Decay of the Transient at 410 nm, Oxygenated Solution ($N_2O:O_2$, 56:25), pH 9, $3.2 \times 10^{-3}M$ PABA.

concentration, the rate constant for the reaction of the cyclohexadienyl radical of PABA with oxygen, k_6 , is $(5.4 \pm 1.5) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$. The result is nearly the same as that obtained for benzene solutions (reaction 4).⁽⁷⁾

By assuming Gaussian distributions around the spectral peaks, the total transient spectrum at a given time could be resolved into component peaks by using the duPont 310 Curve Resolver[®]. In this way, the complex reactions occurring were readily visualized as changes in individual peaks. The results at six different times after irradiation are shown in Figure 6. Initially, four peaks were present, P_1 , P_2 , P_3 , and P_4 . At 1.09 μsec , P_3 had decreased significantly. This rapid decrease of P_3 continued into the 2.18 μsec frame; the transition in time corresponds to that used to determine the first-order oxygen-dependent reaction. Note also that in the 2.18 μsec frame, a fifth peak, P_5 , appeared. By 10.9 μsec , P_3 and P_4 had decreased further while P_2 had started to increase. By 21.8 μsec , P_4 and P_5 had nearly disappeared while P_2 had increased significantly; at 65.4 μsec P_1 had decreased and P_2 had become the dominant transient peak. From this analysis, it is understandable that the kinetic results for the reactions occurring after reactions (5) and (6) appear complex. This analysis also indicates that the first-order results for the initial decay at 410 nm should be generally correct since

interfering reactions have not yet become dominant.

The possibility of slowing down a very fast reaction to a rate at which techniques requiring time resolution longer than that of optical spectroscopy prompted an investigation of viscosity effects on the PABA reaction. Since the reactions are in the diffusion-controlled range, increasing the viscosity of the aqueous solution should limit the collision frequency. Viscosity of the solution was increased by the addition of sodium sulfate. This solution was relatively inert as an irradiation matrix. Concentrated solutions of sodium sulfate, over the wavelength range from 220 to 700 nm gave no evidence of transient formation resulting from pulse irradiation.

Smoluchowski derived an equation for the rate of diffusion-controlled reactions by assuming the validity of Fick's law. In its general form, the equation predicts that the rate constant will be inversely proportional to the viscosity:

$$k_D = \frac{8RT}{3000\eta} \quad (8)$$

where η is the viscosity in poise.⁽¹⁰⁾

Rate constants were calculated for the decay of PABA in sulfate solutions at 410 nm and were plotted as a function of the reciprocal viscosity. The plot of the first-order reaction which occurs in the first few microseconds is shown in Figure 7. At infinite viscosity, the rate of pseudo first-order reactions, such as the reaction of oxygen with the hydroxy adduct of PABA, should be

FIGURE 6. Resolution of Transient Spectra into Gaussian Components. PABA $3.2 \times 10^{-4}M$, pH 7.6, N_2O/O_2 -1:1 (v/v). Time after pulse in microseconds: (a) 0; (b) 1.09; (c) 2.18; (d) 10.9; (e) 21.8; (f) 65.4.

FIGURE 7. Inverse Viscosity Dependence of First-Order Rate Constants for Initial Decay at 410 nm. Intercept is $7 \times 10^5 \text{sec}^{-1}$. ($\text{N}_2\text{O}/\text{O}_2$, 1/1), $3.2 \times 10^{-3} \text{M}$ PABA, pH 5.5.

zero. True first-order reactions would not be affected by the increase in viscosity. In the present case, the results indicate that at least two reactions have occurred, one being viscosity dependent, the other being a true first-order reaction with a rate constant of about $0.7 \times 10^5 \text{sec}^{-1}$, the intercept at infinite viscosity. This is in excellent agreement with the value of $0.9 \times 10^5 \text{sec}^{-1}$ calculated for reaction (5).

As an example of a possible application of these results, consider the oxygen reaction (6), which has a half-time of 2.5 μsec at an oxygen concentration of $6 \times 10^{-4} \text{M}$. A decrease in the rate constant of two orders of magnitude

would give a half-time of 0.25 msec which is within the time resolution of such powerful tools as electron paramagnetic resonance. To effect this decrease in rate, solutions having viscosities of 20 to 200 cp would be required. This is well above the saturation limit of sodium sulfate; however, other media having the required viscosity are available. The use of viscous solutions to bring the fast reactions within the range of physical techniques is then justified.

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ESTIMATION OF OZONIDE RADICAL RATE OF DECAY CONSTANTS USING
THE QUASILINEARIZATION METHOD

W. D. Felix

A quantitative description of the kinetics for reactions occurring in irradiated aqueous samples usually requires solutions to a system of nonlinear differential equations. In almost all cases, published computer techniques for achieving these solutions evaluate the most critical of the unknowns, the reaction-rate constants, indirectly by a process of iteration in which refined approximations to the constants are determined by comparison of the synthetic data with the experimental data. Iteration continues until the synthetic-experimental difference comes within acceptable bounds, or until it becomes obvious that the system is not convergent. Because of the tedious calculations involved when many rate constants are involved, the value of a technique is proportional to its efficiency of convergence and upon its range of acceptance of initial approximation.

A method has been recently developed which makes more efficient use of the data to obtain the rate constants directly; i.e., it is an inverse technique which utilizes the experimental data within each iteration step in calculating new approximations to the rate constants. This particular approach, the quasilinearization technique, is quadratically convergent; thus, if a good initial estimate for any given rate constant is available, the num-

ber of correct digits is doubled asymptotically with each additional step in the process beyond the third iteration.⁽¹⁾

A test of the particular data fitting method, the quasilinearization technique, as developed by Bellman and co-workers,⁽¹⁻³⁾ was applied to the rate equations proposed for the decay of the ozonide radical, O_3^- , formed during pulse radiolysis of an alkaline, oxygenated solution.⁽⁴⁾ The rate equations were:

$$\frac{d(O_3^-)}{dt} = -k_1 (O_3^-) - 2k_2 (O_3^-)^2 - k_3 (O_3^-)(HOO^-) \quad (1)$$

$$\frac{d(HOO^-)}{dt} = -k_3 (O_3^-)(HOO^-) \quad (2)$$

Experimental data used were from Reference 4, Figure 5, for which second-order rate constants had been calculated with the help of an analog computer. Values of $2k_2$ calculated in this manner for many sets of data ranged from 0.8 to $1.1 \times 10^6 M^{-1} \text{sec}^{-1}$. The first-order rate constant varied from 40 to 100 sec^{-1} at oxygen concentrations represented by these data. Initial approximations for $2k_2$ and k_1 in the quasilinearization calculations presented here were taken near these analog values.

The constant k_3 for the reaction of O_3^- with peroxide was independently determined.⁽⁴⁾ Peroxide concentrations

were calculated from the known rate constant and from the ozonide concentration as a function of time.

The quasilinearization technique as applied to Equations (1) and (2) gave the results shown in Table I. The entire calculation required less than 9 sec on an UNIVAC 1108 computer. In Figure 1, experimental data have been compared with synthetic data obtained from the final calculated values of the rate constants. The agreement is exceptionally good.

The technique is rather sensitive to the closeness of the initial approximations. For example, in the present case, initial approximations of $4.7 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ and 500 sec^{-1} for $2k_2$ and k , did not result in convergence. Nevertheless, it is clear that the quasilinearization method is an extremely powerful tool for the refinement of kinetic parameters, and for efficient use of kinetic data when rough approximations to the unknown constants are available by the usual methods.

TABLE I. Numerical Results by Iteration Level

Approximation	k_1, sec^{-1}	$2k_2, 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$
0	50	19
1	91.3	7.9
2	91.3	8.6
3	87.4	10.0
4	87.9	9.93
5	88.4	9.73

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FIGURE 1. Synthetic and Experimental Data⁽⁴⁾ for Ozonide Ion Decay at 430 nm.

RADIOLOGICAL PHYSICSHIT THEORY

W. C. Roesch

Last year I reported a new hit theory that is able to explain many of the phenomena observed in radiobiological experiments.⁽¹⁾ The new theory postulates two types of lethal events: a) those caused by the passage of a single charged particle through a biological entity; here there is a probability S_1 of surviving each individual hit; and b) those caused by interaction between the products of hits by two different charged particles; here there is a probability $s(t)$ of surviving interactions between any pair of hits, where t is the interval between the hits. In the present report, $s(t)$ is taken to equal $(1 - a e^{-bt})$, where a and b are constants. The present report describes calculations and current work based on the theory.

The formulas provided by the theory are complicated enough so that it is difficult to visualize what numerical results they will provide. Calculation is also difficult because of the occurrence of slowly converging infinite series and products. Computer programs were prepared that compute the basic quantities provided by the theory. Certain subprograms are the heart of these programs: SRVIVL calculates the surviving fraction given S_1 , a , $bc/(b+c)$ (where c is the hit rate), and m

(the average number of hits).

Subprogram DOSE calculates m given the surviving fraction and S_1 , a , and $bc/(b+c)$. EXNO has three options that are related to the asymptotic form of the survival curve:

$$S = A e^{-(1 - BS_1)m} \quad (1)$$

The first option calculates A , the extrapolation number, and B , given a and $bc/(b+c)$; the second calculates a and B , given A and $bc/(b+c)$; the third calculates $bc/(b+c)$ and B , given a and A .

The following figures show some of the results of using these computer programs. Figure 1 gives the inverse of the extrapolation number as a function of the probability, a , of a lethal interaction between two nearly simultaneous hits for different values of the normalized "rate", $x = bc/(b+c)$. The rate usually appears in the combination given in the parameter x , which means that an increase in hit rate c is equivalent, in effect, to an increase in the rate of disappearance of the products that might react. It is evident that the theory predicts that any value of the extrapolation number greater than or equal to 1.0 can be achieved. Increasing either the probability of lethal interaction or the normalized rate will increase the

extrapolation number. Very high extrapolation numbers result if both of these parameters are large. For these very high extrapolation numbers, experimental survival curves would probably not reach the asymptotic form given by Equation (1); they would instead give continually steepening curves of $\log S$ versus m in the range observable. Figure 2 gives similar curves for B . The parameter $(1 - BS_1)$ is inversely proportional to what is usually denoted D_0 in radiobiology. The shapes of the B curves are similar to those for A^{-1} , but they do not change as rapidly with either a or x . This helps to explain the fact that experiments show the extrapolation number to be much more sensitive to changes in experimental conditions than is D_0 .

The ratio of the doses (values of m) for a given survival at very low and very large dose rates ($c =$

0 and c very large; i.e., $x = 0$ and $x = 1$) depends only on the probabilities S_1 and a . Figure 3 shows this dose ratio for 10% survival. The portions of each curve for S_1 greater than $(1 - a)$ are dotted, because the chance of surviving a single hit, S_1 , ought to be less than the average chance of surviving interactions between two simultaneous hits, $(1 - a)$. Figure 3 shows, in agreement with experiment, that the increase in effectiveness of higher dose rates is a relatively modest factor and that the highest factors are obtained when the single-event survival probability, S_1 , is highest and the interaction survival probability, $(1 - a)$, is lowest.

In last year's report, I analyzed the effect of dividing a dose into two fractions delivered separately when both fractions were large enough to lie in the asymptotic region where Equation (1) holds.

FIGURE 1. Theoretical Inverse Extrapolation Number, A^{-1}

FIGURE 2. Theoretical Sensitivity Factor B

FIGURE 3. Ratio of Doses for the Same Survival at Zero and Infinite Dose Rates

An equation was written that holds for any doses given in two fractions and a program was prepared that computes the surviving fraction. Figure 4 shows a typical result. From $S = 1.0$ to 0.1 , the survival curve is that for a single dose; beyond $S = 0.1$, the curves give the effects of two doses—the first large enough to reduce the survival to 0.1 if given alone, the second large enough to bring the total m up to the value on the abscissa. The curves are for different waiting periods, bd (dimensionless), between the fractions. The curves show the general properties found by Elkind and Sutton,⁽²⁾ but they do not show the detailed structure that has been associated with variations in sensitivity of cells during their mutation cycle.⁽³⁾

FIGURE 4. The Effect of Fractionation.

FIGURE 5. Survival and Extrapolation-Number Data from Sinclair and Morton⁽⁴⁾ and the Quotient of the Survival and Extrapolation Number as a Function of Time During the Life Cycle.

To study the effects of variations in cell sensitivity, some data of Sinclair and Morton⁽⁴⁾ are being analyzed. The curve marked S in Figure 5 is the survival they found for Chinese hamster cells

after a 1000 rad dose at different times during their life cycle. The curve marked A is one that I fitted arbitrarily to five values of the extrapolation number that I deduced from other curves in their paper.

According to the theory, the extrapolation number depends only on a and x . Figure 6 shows a as deduced from the fit to A for different values of x . Although the numerical values depend strongly on the choice of x , the shapes of the curves are all quite similar and show peaks of high sensitivity to lethality by interactions in G_1 and in late S phase. Similarly, curves of the B corresponding to the fit for A can be deduced. The curve marked S/A in Figure 5 is the quotient of the survival and the extrapolation number from the other two curves. If we assume that 1000 rads is in the

dose region where Equation (1) holds, $\ln(A/S) = (1 - BS_1)$, and S_1 can be deduced from the "known" B if m is known. Figure 7 shows values of S_1 obtained by guessing at m ; they are of similar shape regardless of the value of m chosen. S_1 is a minimum at mitosis and increases steadily throughout the life cycle until it is time for mitosis again; stated an alternate way, the probability of lethality due to single hits is high at mitosis and then decreases approximately linearly with time until a sudden increase just before the next mitosis.

FIGURE 6. Lethal-Interaction Parameters for the Extrapolation Numbers in Figure 5

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FIGURE 7. Single-Hit Survival Probabilities Deduced from Data in Figures 5 & 6.

CALCULATION OF POISSON SERIES

W. C. Roesch

Functions $P(z, m)$ defined by the Poisson series

$$P(z, m) = \sum_{n=0}^{\infty} e^{-m} m^n (n!)^{-1} P_n(z) \quad (1)$$

where $P_0(z)$ is the Dirac delta function,

$$P_n(z) = \int_0^z P_{n-1}(x) P_1(z-x) dx \quad (2)$$

for n greater than 2, and $P_1(z)$ and m are given, occur in the theory of local energy density and of charged-particle energy straggling. In the latter, for example, $P_1(z) dz$ is the probability of production of a delta ray of energy in dz at z in a single interaction of a charged particle with the medium; $P_n(z) dz$ is the probability that the sum of the delta-ray energies produced in n interactions will be in dz at z ; $P(z, m) dz$ is the probability that the sum of the delta-ray energies produced in a layer in which the average number of interactions is m will be in dz at z . The calculation of $P(z, m)$ from Equations (1 and 2) is straightforward, but the amount of computation required becomes prohibitive for large m , say m greater than about 20. The present paper reports an alternative way of computing $P(z, m)$ that requires far less numerical work. A. M. Kellerer⁽¹⁾ has independently developed the same method of simplifying the calculation.

The alternative calculation makes use of the equation

$$P(z, m_1 + m_2) = \int_0^z P(x, m_1) P(z-x, m_2) dx \quad (3)$$

whose proof is as follows. Substitute infinite series from Equation (1) for the P 's on the right of Equation (3). Eliminate integrals of products of the P_n 's by the relation

$$P_{n+i}(z) = \int_0^z P_n(x) P_i(z-x) dx \quad (4)$$

which can be proved by repeated use of Equation (2). Then, change the order of summation and use the binomial expansion to produce an infinite series that can be identified by comparison with Equation (1) as giving the left side of Equation (3).

The physical interpretation of Equation (3) in the case of energy straggling is that the probability of energy loss z in a layer of material is the sum of the probabilities of the mutually exclusive events of losing x in part of the layer and $z-x$ in the rest of the layer.

The method of using Equation (3) to calculate $P(z, m)$ is as follows. First, choose an $m' = m/2^N$, where N is an integer chosen so that only a few terms, preferably just the first two, of Equation (1) are needed to calculate $P(z, m')$ to sufficient accuracy:

$$P(z, m') = e^{-m'} [\delta(z) + m' P_1(z) \dots] \quad (5)$$

For example, if m' is less than about 0.001, the error is $P(z, m')$ resulting from using only the first two terms would be only about 0.1%. Equation (4) is then used N times, with both m_1 and m_2 equal to m' on the right the first time. The first result is $P(z, 2m')$. Then m_1 and m_2 are taken equal to $2m'$ and so on. After N iterations, the final result will be $P(z, m)$.

The savings in numerical work comes about because use of Equations (1 and 2) requires about $2m$ integrations per value of z , while use of Equations (3 and 5) requires only about $10 \log m$. For m equal to 100, for example, about one tenth the work is required by the latter pair of equations.

The method of computing Poisson series presented here is being used in analyzing experimental data on the distribution of energy losses of protons in thin layers of tissue-equivalent gas. Figure 1 shows an example for 2.04 MeV protons in a $10 \mu\text{g}/\text{cm}^2$ layer. The solid curve is $P(z, m)$, where z is the energy loss and m is about 41. $P_1(z)$ was a simplified single-event spectrum: $z^2 P_1(z)$ was zero below $z = 10$ eV,

rose to a peak at 20 eV, was constant from 100 to 1000 eV, and was zero above 1000 eV (to simulate loss of delta rays from the experimental apparatus). The constant part of $P_1(z)$ at high energy, without the decrease to zero above 1000 eV, was adjusted to fit the known mechanics of heavy-particle free-electron collisions; the peak at 20 eV was then adjusted to give a stopping power in agreement with experiment. The points in Figure 1 are experimental values from Glass.* It is evident that this simple approximation to $P_1(z)$ gives good agreement with experiment except for large losses. The lack of agreement for large losses means that the approximation does not represent delta-ray losses adequately.

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FIGURE 1. Theoretical Curve and Experimental Points* for the Distribution of Energy Losses of 2.04 MeV Protons in $10 \mu\text{g}/\text{cm}^2$ of Tissue-equivalent Gas

DELTA RAYS OF HIGH-ENERGY HEAVY PARTICLES

W. C. Roesch

The fluence-dose equation used in radiation dosimetry⁽¹⁾ for the energy imparted to matter by charged particles is

$$D = \phi (S/\rho) \quad (1)$$

where D is the absorbed dose, ϕ is the fluence of the charged particles (assumed monoenergetic for the time being), and S/ρ is the mass stopping power of the medium for the particles. The left-hand side of this

equation is the energy absorbed per unit mass by the medium. The right-hand side is the energy lost by the charged particles per unit mass of medium. These two quantities are approximately equal in two circumstances as follows. In the first case, for low-energy charged particles, the delta rays have such short ranges that they can be considered absorbed where the charged particles produced them; then the energies on the two sides are the same. In the second case, for moderate energy electrons, the ranges of most delta rays are still very short compared to the ranges of their primary particles, hence, energy lost by delta-ray escape from one local region is usually compensated for by gain from delta rays entering from neighboring regions; such compensation fails when there is a very abrupt change in the radiation field or in the composition of the medium. The purpose of the present paper is to show that, as far as measurement of absorbed dose or irradiation of thin specimens is concerned, delta-ray compensation takes place for heavy charged particles of up to about 100 MeV/amu. For higher energies, satisfactory compensation occurs also, but for thicker layers.

For this study it proves convenient to divide the delta rays into two groups. The low-energy group comprises those with ranges short enough that compensation is sure to exist. The low-energy group was arbitrarily taken to include those with ranges less than

1 μm of tissue-like material; 1 μm is the range of an electron of approximately 6 keV. The thickness of most detectors or specimens will be at least ten times this cutoff range, i.e., 10 μm or 1 mg/cm^2 . A lack of delta-ray compensation over a distance of 1 μm is then not too serious. The choice of a 6 keV cutoff energy is quite different from the 100 eV often made for the purposes of LET analysis of biological phenomena. Electrons of 100 eV have a range of a few hundredths of a micrometer, an appropriate cutoff when studying radiation sensitive sites of about a tenth of a micrometer, sizes much smaller than of interest here. The high-energy delta-ray group, of course, comprises those with ranges greater than 1 μm . They are of energy high enough that their energy (E) spectrum is proportional to E^{-2} and their energy is related to their emission angle (θ) by $E = E_{\text{max}} \cos^2 \theta$. Different high-energy heavy particles of the same energy to mass ratio have the same delta-ray spectra.

It is necessary to determine, in some meaningful way, how far the delta rays in the high-energy group travel. This was done by finding the distance between a very short segment of the heavy-particle track and the position of the average of the absorbed dose distribution of the delta rays released along that segment of the track. This distance is called the longitudinal spread of the delta rays. The calculation method was that used earlier in a similar gamma-ray study⁽²⁾ and

employed electron-moment data reported last year.⁽³⁾ The results are given in Figure 1. The results show that the average forward motion of the high-energy delta rays, and hence their propensity for not providing delta-ray compensation, is fairly small. It is much less than might have been anticipated from the ranges of the maximum energy delta rays. For protons of less than a few tens of MeV, the longitudinal spread is hardly larger than that which was already neglected by choice of the 1 μm cutoff. Above a few hundred MeV, the longitudinal spread is comparable to the thickness of the thinnest layers of interest here. The longitudinal spread approaches a maximum of only about 25 μm in spite of the appearance of higher and higher energy delta rays in the spectrum as the heavy-particle energy increases. The number of these high-energy delta rays is just not sufficient to change very much the absorbed dose distribution of the delta rays from a track segment.

The proportion of the delta rays in the two groups was found by ordinary stopping power theory. For example, 10 MeV protons lose 88% of their energy to electrons of less than 1 μm range; 30 MeV protons lose 62%.

Figure 2 illustrates what happens at the boundary between two media crossed by a high-energy beam. Part (a) of the figure shows the absorbed dose distribution due to the low-energy group of delta rays. It was taken as equal to 75% (as an example) of $\Phi(S/\rho)$ on each side of the bound-

ary. Because of the short range of distances plotted, distances comparable to the longitudinal spread of the delta rays, $\Phi(S/\rho)$ is taken as constant on either side. The difference between the two values of $\Phi(S/\rho)$ is exaggerated, for clarity, by depressing the vertical scale. Similarly, part (b) shows the dose distribution for the high-energy group. At a distance great enough from the boundary, there is no effect from the boundary and the dose is 25% of $\Phi(S/\rho)$. Close to the boundary, delta-ray compensation fails, and the absorbed dose changes gradually between its limiting values in the two media. The present study does not calculate the shape of this curve, only the average distance over which the change takes place. Finally, part (c) shows the total absorbed dose distribution, the sum of the doses in parts (a) and (b).

Noncompensation of delta rays will also occur at the edge of a beam or at any sudden change in fluence over the cross section of the beam. For a study of this effect, the lateral spread of the delta rays, rather than their longitudinal spread, is required. Since most of the delta rays are ejected at nearly right angles to the track of the heavy particle, it was assumed that they all were, and the lateral spread was calculated as the distance between the point of ejection and the center of the absorbed dose distribution for the whole E^{-2} spectrum. Figure 1 shows the results. The largest lateral spread in the

figure is $100\text{ }\mu\text{m} = 0.1\text{ mm}$. Seldom will a layer this thick at the edge of a beam and not receiving the full dose calculated from Equation (1) be of any importance.

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FIGURE 1. Longitudinal and Lateral Spread of Proton Delta Rays

FIGURE 2. Absorbed Dose at the Boundary Between Two Media:
a) Contribution from Low-Energy Delta Rays, b) Contribution
from High-Energy Delta Rays, and c) Total Absorbed Dose

ELECTRON EJECTION FROM GASEOUS TARGETS BY PROTON IMPACT

L. A. Braby, L. H. Toburen and W. A. Glass

The energy and angular distributions of electrons ejected from target molecules are important parameters in the investigation of energy deposition by fast particles passing through matter. The published studies of these electron distributions have been confined primarily to electrons ejected by low-energy protons ($E_p \leq 150$ keV) and to the target molecules H_2 and He. The importance of secondary electrons in the determination of chemical and biological effects of irradiation has prompted our investigation of the feasibility of measuring the energy and angular distribution of electrons ejected from such molecules as N_2 , O_2 , and H_2O by fast heavy particles. During the past year, an experiment has been designed and a large part of the equipment fabricated for the measurement of these secondary electron distributions. This report is a description of the progress of that work.

The overall energy and angular distribution of electrons ejected from the target atom or molecule by proton impact is a combination of distributions of electrons originating from the following sources:

- Electrons ejected by direct interaction between the incident particle and atomic electrons.
- Auger electrons which arise from vacancies produced in the electron shells of the target atom.

- Electrons ejected from excited molecules (a molecular internal conversion process).
- Shake-off electrons produced as a consequence of target recoil.
- Electrons released by charge reactions between the particle and the target atoms or molecules.

The direct interaction between the incident beam and target electron is generally assumed to be the primary source of ejected electrons. The energy distribution of these electrons, neglecting the effects of binding, is expected to have a ϵ^{-2} dependence where ϵ is the energy transferred. The ϵ^{-2} energy dependence of the distribution would indicate that a large number of very-low-energy electrons will be released by this mechanism. Since low-energy electrons released in this manner are related to long distance or glancing interactions which transfer momentum to the electrons in a direction perpendicular to the primary beam, the electron distribution is expected to peak at near 90° with respect to the incident beam. Auger electrons and electrons ejected from excited molecules are further sources of low-energy electrons. Electrons from these sources should show the effects of atomic or molecular binding in their energy distribution and be ejected isotropically from the target. Because of the finite lifetimes of the excited atomic and molecular states from

which electrons may be ejected, these electrons may be delayed with respect to the prompt electrons ejected by direct interactions. The lifetimes for electron ejection from the excited states of some molecules may be as long as several nanoseconds. Electron ejection by recoil, another source of very-low-energy electrons, should be negligible due to the small momenta transferred to the molecule during collisions. The last source of electrons listed above can be neglected if incident particles completely stripped of electrons and target densities which allow only single collisions to occur are used.

The availability in our laboratory of a pulsed proton source and delayed coincidence electronics has provided the basic tools for our study of secondary electron distributions. A Van de Graaff generator provides a beam of protons in the energy range from 200 to 2,000 keV which is chopped into pulses of a few nanoseconds duration. A pulse of protons defines the time, $t=t_0$, at which the prompt electrons are ejected from the target and the ejected electron energy distribution is measured by means of the delayed coincidence technique from their time-of-flight to the detector. Electron energies from a few eV to a few keV can be measured in this way so long as the time necessary to eject an electron from the target is short compared to its drift time to the detector.

Since the time-of-flight technique requires sharply defined interaction time, less than approximately 1 nsec, an alternate method must be used if the lifetimes of the excited states are sufficient to smear out the interaction time. A 127° electrostatic analyzer has been designed and is in construction to be used when the time-of-flight technique is impracticable.

An estimation of the number of electrons ejected into a given solid angle by proton impact may be obtained from the expression⁽¹⁾

$$N_e = N_p \sigma(\epsilon, \theta) \tau n \ell \csc \theta \, d\Omega \, d\epsilon,$$

where N_e is the number of secondary electrons; N_p is the number of incident protons; $\sigma(\epsilon, \theta)$ is the cross section, per unit solid angle and unit energy range, for production of secondary electrons of energy ϵ at an angle θ from the incident beam ($\text{cm}^2/\text{eV}\cdot\text{sr}$); τ is the effective transmission of the detector, $d\Omega$ is the solid angle intercepted by the detector (sr); $d\epsilon$ is the effective electron energy range accepted by the detector (eV); n is the number of gas molecules per cm^3 ; and ℓ is the effective geometric length of the gas target when the detector slit system is set at $\theta = 90^\circ$ (cm). For the proposed experimental arrangement, the following parameters are assumed: a reasonable value of N_p is considered to be a nanoampere (6.25×10^9 P/sec) for the pulsed beam and it may be a factor of 10^3 larger if a dc beam is used; $\sigma(\epsilon, \theta)$, which must be estimated for a particular proton

energy, electron energy, and angle, is estimated from previous measured values for low energy protons⁽¹⁾ to be approximately $10^{-20} \text{ cm}^2/\text{eV}\cdot\text{sr}$ [σ (100 eV, 45°)] = 9×10^{-20} for $E = 100 \text{ keV}$ and is not expected to vary rapidly with proton energy; τ is approximately 0.95 for the electron multiplier system to be used; $d\Omega$ is calculated to be approximately $1.6 \times 10^{-3} \text{ sr}$; $d\epsilon$ is estimated to be 1 eV; n is calculated as 3.32×10^{13} molecules per cm^3 at 1 μ target gas pressure; and the path length through the target is constructed to be 1.4 cm. When Equation (1) is evaluated with the above quantities, N_e is found to be approximately 30 counts/sec for a target gas pressure of 1 μ . One micron is assumed because the target gas pressure will tend to scatter the low-energy ejected electrons, whereas a lower pressure will reduce the number of interactions which produce secondary electrons and limit the statistical validity of the results. The path length for an ejected electron to escape the target gas is designed to be as short as possible to reduce scattering within the target gas and a differentially pumped target cell enables the ejected electron to drift in a relatively high vacuum once it has escaped from the target region. The region in which the electron drifts during the time-of-flight measurements is surrounded by layers of mu-metal shielding to reduce the influence of external magnetic fields.

A schematic drawing of the apparatus constructed to measure the

ejected electron distributions is shown in Figure 1. The system consists basically of a collimator with apertures of 0.020 in. in diameter, the main vacuum chamber, a differentially pumped gas target cell which contains a slit aperture 0.025 in. wide cut approximately 195° around the target chamber, a detector assembly for the electrons capable of rotating 360° around the target cell, and a Faraday cup for monitoring the intensity of the incident beam.

The main vacuum chamber, beam collimator, and Faraday cup have been constructed and aligned with the beam. A vacuum of approximately 5×10^{-6} torr was obtained in the chamber by means of a mercury diffusion pump and a proton beam of a few nanoamperes was detected at the Faraday cup. A more accurate alignment of the beam optics is expected to greatly increase the beam intensity. To measure target pressures, independent of the nature of the gas under study, a capacitance manometer will be used. This is important especially for the condensable gases such as H_2O which will be studied.

Aside from the general interest in δ -ray distributions and in the radial extent of charged particle tracks, there is an immediate application of the experimental results to be obtained with this apparatus to our investigation of energy loss straggling in absorbers.* Computer

* W. A. Glass. "Progress Report on Energy Loss Straggling of Protons," this report, pp. 198

codes have recently been developed^(**,2) which can generate energy loss distributions for charged particles as they penetrate absorbers of arbitrarily chosen thickness. These codes require as input the energy loss distributions for individual proton collisions. Only meager information now exists concerning these distributions and this is for proton energies below 300 keV.

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FIGURE 1. Schematic Drawing of Scattering Chamber

INTERACTION OF LOW ENERGY PROTONS WITH
THIN LAYERS OF TISSUE-LIKE MATERIAL*

W. A. Glass

The ionization resulting from the passage of monoenergetic protons through thin layers of tissue-like gas was investigated. The ions produced by individual protons are collected from a well defined layer of low density gas and amplified in a proportional counter. The resulting distributions have been investigated for absorbers corresponding to layers of unit density material with thickness between 0.1 and 1.0 μ and for proton energies from a few keV to 2 MeV. The maximum value for the mean ionization loss per unit path length has been found to depend on the sample thickness, varying from a value of 101 keV/ μ for a 1 μ layer to about 108 keV/ μ for a 0.1 μ layer. The measured distributions were compared with distributions calculated by Seltzer and Berger using the energy loss straggling theory due to Vavilov. General agreement between theory and the experimental results was found with minor deviations caused by electron binding energies and escape of δ -rays from the absorbing layers.

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PROGRESS REPORT ON ENERGY LOSS STRAGGLING OF PROTONS

W. A. Glass

Previously, we compared the shape of measured proton energy loss distributions in thin tissue-like layers with those calculated by Seltzer and Berger from a theory due to Vavilov.⁽¹⁾ That work showed general agreement between the experimental results and the theory. More extensive measurements have been made and a computer program written which compares statistical parameters of the distributions. The program normalizes the mean

value of the distribution to a value taken from previous experimental work;⁽²⁾ the standard deviation, fractional standard deviation, and skewness of the distributions are then calculated and compared with the Vavilov theory. The results are summarized in Table I. This comparison points out certain systematic variations between experiment and theory. Figure 1, for example, shows that the fractional standard deviation - a

TABLE I. Parameters of Energy Loss Distributions

Shape Factor	Experimental Quantities			Statistical Parameters							
	E_p , keV	$\bar{\Delta}$, keV	Δx , μ	Vavilov Theory				Experimental			
				σ^2	σ	$\sigma/\bar{\Delta}$	S	σ^2	σ	$\sigma/\bar{\Delta}$	S
0.04	2040	1.6	0.1	0.74	0.86	0.54	2.2	0.48	0.69	0.43	1.5
0.07	1550	2.05	0.1	0.77	0.88	0.43	1.8	0.51	0.72	0.36	1.2
	1500	2.05	0.1					0.55	0.75	0.37	1.2
0.10	1280	2.35	0.1	0.81	0.90	0.39	1.6	0.56	0.75	0.32	1.0
	1280	2.35	0.1					0.54	0.73	0.31	1.0
	1825	3.50	0.2	1.6	1.3	0.38	1.6	0.86	0.93	0.26	1.0
0.40	646	3.85	0.1	0.77	0.88	0.23	0.83	0.71	0.85	0.22	0.72
	9.14	5.90	0.2	1.5	1.2	0.22	0.83	1.1	1.0	0.17	0.58
	1120	7.85	0.3	2.3	1.5	0.21	0.85	2.6	1.6	0.21	1.1
0.70	490	4.7	0.1	0.77	0.87	0.18	0.57	0.87	0.94	0.20	0.61
	690	7.3	0.2	1.6	1.2	0.17	0.59	1.2	1.1	0.15	0.76
	690	7.3	0.2					1.3	1.1	0.15	0.77
	847	9.3	0.3	2.3	1.5	0.17	0.58	2.6	1.6	0.18	1.2
1.0	408	5.3	0.1	0.78	0.88	0.16	0.49	0.80	0.89	0.17	0.55
	578	8.3	0.2	1.5	1.2	0.15	0.48	1.4	1.2	0.14	1.1
	708	10.8	0.3	2.3	1.5	0.15	0.48	3.0	1.7	0.16	1.3
4.0	210	9.0	0.1	0.75	0.86	0.095	0.20	1.3	1.1	0.12	0.17
	289	13.2	0.2	1.6	1.2	0.094	0.21	2.5	1.6	0.12	0.50
	354	17.4	0.3	2.3	1.5	0.093	0.21	6.3	2.5	0.13	1.5

measure of the relative width of the distribution - progressively becomes less than theory would predict for increasing proton energies. Also, it was noted that high energy-loss events occur less frequently than predicted.⁽¹⁾ Both facts suggest that an increasing amount of energy is being carried out of the absorbing layer by δ -rays as the proton energy is increased. The greater than expected standard deviations for

the distributions at low proton energies is consistent with the fact that the Vavilov theory assumes an energy transfer cross section for individual collisions with absorber electrons to be proportional to $1/\epsilon^2$ (where ϵ is the energy transferred). The upper and lower energy limit of ϵ is set by treating the stopping medium as a free electron gas. This is not a good approximation for small energy transfers as it neglects atomic binding energies.

FIGURE 1. Fractional Standard Deviation of Energy Loss Straggling Distributions as a Function of Proton Energy for Three Different Absorber Thicknesses

In the intermediate proton energy range, i.e., from about 400 to 800 keV and for absorbers of the order of a few tenths micron thickness, the two effects (binding energy and δ -rays) tend to compensate and the measured distributions appear to be very much like those predicted by Vavilov theory. For greater absorber thickness, this region of apparent agreement shifts to higher energy as can be seen by comparing the three curves in Figure 1. This is in agreement with the previous assumption regarding δ -ray effects.

It is apparent, however, that a more comprehensive theory is necessary to adequately explain the observed energy loss distributions in thin specimens resulting from the passage of low energy protons.

During the past year, two new theoretical treatments of the problem have been introduced. W. C. Roesch and A. M. Kellerer have independently developed theories based on successive convolutions of an arbitrarily chosen energy-transfer cross section for interactions between the incident proton and absorber electrons.*

Both theories permit the introduction of realistic estimates of the energy lost from the absorber by high energy δ -rays and also the introduction of the meager data existing for cross sections involving small energy transfer.

A. M. Kellerer of the University of Munich reported some results of his work at the Ispra Symposium on Micro-dosimetry.⁽³⁾ He assumed that the data of Rauth and Simpson⁽⁴⁾ for energy transfer cross sections could be applied to correct for the binding energy effects and made an approximate calculation for energy losses due to δ -rays. Figure 2 is reproduced from Kellerer's paper and shows the fit of our data with his theoretical results for protons of 1.58 MeV.

These new theories provide a connecting link between energy loss transfer experiments** and the energy loss distributions in absorbers of various thickness.

FIGURE 2. Comparison of Experimental Loss Distribution for 1.58 MeV Protons in a 0.1μ with Vavilov Theory and with Theory of A. M. Kellerer. Figures taken from Reference (2).

* W. C. Roesch, "Calculation of Poisson Series," this report, pp. 187-189.

** Braby, Toburen, and Glass. "Electron Ejection from Gaseous Targets by Proton Impact," this report, pp. 194-197.

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PRELIMINARY INVESTIGATION OF A WALL-LESS
COUNTER DESIGN FOR MICRODOSIMETRY

W. A. Glass

The ideal detector for microdosimetry measurements is one which represents a microscopic absorption site of specified shape, normally spherical, within a continuous medium. Detectors currently in use are cavities of a few centimeters diameter in solid plastic which are filled with a rarified atmosphere of gas having the same atomic composition as the wall. Such a cavity, with appropriate electrodes for collecting and amplifying the ionization produced in the gas, can be made to detect energy losses in absorption sites of a few tenths micron to several microns. It is assumed that the charged particle spectrum within the cavity is unaltered by the change in density at the boundary of the cavity. This assumption is based on a theoretical treatment by Fano⁽¹⁾

which shows that the average energy transfer to such a cavity is independent of the density change. However, when considering individual crossings of the cavity by charged particles, there can be subtle differences in the spectrum. These differences arise from δ -rays produced by heavy charged particles, from back scatter of electrons into the cavity from the wall which again produce essentially simultaneous tracks that probably would not have occurred in an actual microscopic site, and from other similar anomalies. The extent to which the wall effects distort a measured event-size spectrum has not yet been analyzed, but it will depend on the type and energy of the radiation and will probably be small except when low energy electrons or heavy charged

particles with sufficient energy to produce long range δ -rays are involved.

H. H. Rossi and B. Biavati⁽²⁾ have reported on a wall-less proportional counter utilizing the spherical electrical field produced between two shaped electrodes, the anode being a grid through which the collected electrons are accelerated and gas multiplication taking place on a hemispherical electrode held at high potential with respect to the grid.

A counter based on a principle described by Failla⁽³⁾ for spherical ionization chambers has been constructed and some preliminary tests made to show that such a proportional counter may be feasible. The counter utilizes the quasi-spherical field existing between two oppositely charged spherical electrodes. The electrodes are 0.030 cm diameter spheres supported on 75 μ rods. The anode is recessed into and concentric with a hemispherical guard electrode which prevents the collection of ionization except from the approximately spherical region defined by the unintercepted field lines. The guard electrode is operated at a potential adjusted to the equipotential around the anode at that location.

Figure 1 illustrates the electrode structure. The guard electrode is 0.18 cm in diameter and the separation of the cathode sphere and the anode structure is 2 cm. All electrodes are of glass and are made conductive by a gold layer.

FIGURE 1. *Electrode Construction of the Wall-less Proportional Counter. (Note: Spacing between cathode and anode structure is not to scale)*

Figure 2 shows a typical spectrum produced by aiming a collimated alpha particle beam across the center of the counter perpendicular to its axis. In this case, the counter was being operated at about 70 torr which would represent an absorption site of 2 μ of unit density absorber.

FIGURE 2. *Response of Wall-less Counter to Collimated Alpha Particles*

The 17% f.w.h.m. compares favorably with the 15% f.w.h.m. typical of a 4 in. spherical counter of conventional design when operated as a 2 μ site. However, this number is not indicative of overall counter performance. No attempt has yet been made to determine how nearly the counter represents a spherical site nor has there been any measurement of the uniformity of gas gain over the surface of the anode.

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MICRODOSIMETER DEVELOPMENT

L. A. Braby

The theory of microdosimetry with a spherical gas cavity is well developed, and typical measurements have been made. However, little has been done to correlate microdosimetric data with biological effects, partly because of the lack of a reliable rugged detector that can be used in biological experiments. The spherical counter most frequently used employs a helical grid about the anode wire to control gas gain. It is quite sensitive to vibration and rough handling, and easily loses its resolution.

A spherical counter volume is more amenable to theoretical evaluation than other shapes but, to produce quantitative results, the counter's output pulse must be proportional to the primary ionization, no matter where it occurs

in the sphere. Uniform gain is a problem since it is very difficult to set up a uniform electric field gradient in a spherical volume. Counters with wire anodes typically suffer from high gain at the ends of the anode.

A test facility was set up to critically measure the effect on gas gain of various counter geometries. The counter was mounted with its center on the axis of a vacuum chamber, with its anode horizontal, and with a horizontal slit in the wall from the center to one end of the counter. A collimated alpha source was mounted on an arm, aimed through the slits and across the center of the counter. The arm could be moved in an arc so that the α tracks would make any desired angle with respect to the counter anode.

Since the gas pressure was so low that an α particle lost only a fraction of its energy in crossing the counter, the primary ionization was uniform along any track, and since any track was a diameter, the total ionization was constant. Thus, any change in pulse height with angle of track was due to a variation in gain along the anode. With the α tracks at 90° to the anode, only the center of the anode is checked, but at 20° 94% of the length of the anode is used.

Benjamin et al.⁽¹⁾ developed a rugged spherical proportional counter for operation at high pressure as a neutron spectrometer and reported that it had fairly uniform gain over all but the last 7% of the anode length at each end. In this end region the gain dropped rapidly to zero.

We have tested their design and modifications of it at low pressures for use as a microdosimeter. Figure 1 shows the counter as they described it and its response to α tracks as a function of angle.

The 13% decrease in pulse height between 40 and 30° corresponds to a 13% increase in projection of the α track on the counter anode. This indicates that no gas gain is occurring along the last eighth of the anode at each end. This is not surprising since this is about the same distance as the diameter of the field shaping electrode and it can be shown that the electric field will be substantially reduced over a region approximately equal in size to the field shaping electrode. About 8% of the volume of a sphere is projected onto the last 1/8th of the anode at each end. The significance of low gain for this much of the spherical volume can be seen by comparing Y spectra obtained with this type and with a counter having standard grid; they appear to be substantially identical in shape.

The two modifications of the field shaping electrodes illustrated in Figures 2 and 3 were tried in an attempt to improve gain at the ends of the anode. Figure 2 shows that

FIGURE 1. Benjamin Type Proportional Counter with Gain Versus Track Angle When Used as Microdosimeter

FIGURE 2. Counter with Sloped Electrodes and Gain Versus Track Angle

sloping the electrode back slightly from the wire has very little effect. Figure 3 indicates that recessing the electrode does improve gain at the ends of the anode, but by sacrificing it in the center.

This type of counter can not be significantly miniaturized because in order for the field shaping electrodes to work properly, the sphere diameter must be 1.8×10^3 times the anode diameter. That is,

for a 0.001 in. anode (the minimum that can be handled conveniently) a 1.8 in. sphere is required.

A scheme that removes the restriction on the ratio of anode to sphere diameter, and hence that might be more easily miniaturized, involves dividing the sphere into segments with planes perpendicular to the anode. A counter of this type was constructed by scribing a conductive coating painted inside

FIGURE 3. Counter with Recessed Electrodes and Gain Versus Track Angle

an insulating sphere. Given the potential difference between the anode and one point on the sphere, the potential at any other point necessary to maintain the same field at the anode can be calculated by considering the sphere as a collection of very short cylinders with field fringing eliminated by the presence of the cylinder at each end. The response of this counter to alpha particles as a function of angle is presented in Figure 4. The counter works very well down to 25° ; the error at smaller angles can probably be improved still further by empiri-

cally adjusting the voltage on the appropriate segments. For this counter, the lower limit to size is set by the maximum tolerable deviation in field and by the thickness of the thinnest plastic segment which can be made; counters as small as $1/2$ cm in diameter may be possible.

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FIGURE 4. Spherical Counter with Concentric Rings for Field Shaping and Gain Versus Track Angle

MICRODOSIMETRY*

W. A. Glass

This paper outlines the present concept of microdosimetry, defines the most commonly used quantities of microdosimetry, and presents typical experimental results to illustrate these quantities for gamma-rays and intermediate energy neutrons.

* BNWL-SA-1003: Presented seminar series at University of Washington, Department of Radiology.

A METHOD OF EVALUATING NEUTRON DOSE
IN THE PRESENCE OF GAMMA-RAYS*

W. A. Glass and G. W. R. Endres**

The evaluation of absorbed dose due to the neutrons in a mixed neutron and gamma-ray radiation field is a long standing problem in dosimetry. It is a particularly difficult problem if the spectrum includes neutrons of intermediate energy and/or thermal neutrons as is common in the working environment around reactors. Devices which rely on selective thermalization and subsequent detection of the thermalized neutrons tend to over-respond to such neutrons. Correction of the measured dose requires some knowledge of the existing neutron spectrum. A more direct approach to measurement of absorbed dose can be made by integrating the pulse heights

resulting in a tissue-equivalent proportional counter. Assuming the average energy necessary to produce an ion pair to be constant, the method becomes an absolute determination of dose. As such, the measurements need no corrections by energy response functions. Such a method has been proposed by Hurst⁽¹⁾ for the measurement of fast neutron dose. Hurst's dosimeter is a polyethylene lined cylindrical proportional counter filled with a gas of equivalent atomic composition. Typical pulses from gamma-ray produced electrons are smaller than the pulses from neutron produced recoiling nuclei (primarily protons), hence a bias set above the smaller pulses discriminates against the gamma-ray response. The bias necessary in this counter also eliminates an appreciable fraction of the neutron dose.

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** Biophysical Sciences Section

The detector we propose is spherical, which nearly eliminates directional effects, and is composed of tissue-equivalent plastic, which makes the counter responsive to thermal neutrons as well as fast.⁽²⁾ The major advantage, however, is that the detector is operated at a gas density such that it simulates an absorption site of only 2 μ diameter in a unit density absorber. This accentuates the separation of pulse heights produced by the two types of radiation. Figure 1 shows the counter response to monoenergetic neutrons both with and without ^{60}Co gamma ray contamination. The quantity Y is the energy deposited per pulse divided by the equivalent diameter of the counter in microns of unit density absorber. The ordinate is the contribution of the dose per unit interval of Y. This figure shows the rather clear-cut distinction between the pulses contributing to the neutron dose and those due to gamma rays.

The absorbed dose is represented by the integral

$$D = \int_0^{Y_{\max}} D(Y) dY$$

For radiation protection purposes, it is conceivable to construct an instrument that performs this integration from zero to 10 keV/ μ and displays it as gamma ray dose or dose due to small events; and also, using the same detector, a second integration could be done for pulses greater than 10 keV/ μ and the result displayed as neutron dose. If a bias is set at 10 keV/ μ and the neutron dose represented by the integral with a lower limit of 10 keV/ μ , less than 4% of the neutron dose is lost as a result of the bias.

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FIGURE 1. Dose as a Function of Event Size for 1 MeV Neutrons, ^{60}Co Gamma Rays, and for a Mixed Field.

A TWIN CALORIMETER FOR THE MEASUREMENT OF ABSORBED DOSE*

D. M. Fleming

Absorbed dose measurements using the calorimeter were completed. Calorimetric measurements were compared with ion chamber measurements on the same ^{60}Co source. The calorimetric measurements yielded an absorbed dose rate of 32.0 ± 0.5 rad/hr compared to 31.6 ± 1.7 rad/hr for the ion chamber.

* BNWL-655.

MEASUREMENT OF ENDOTHERMIC PROCESSES IN MUSCLE
EQUIVALENT PLASTIC INDUCED BY PROTON IRRADIATION

D. M. Fleming and W. A. Glass

A limiting factor in the use of tissue equivalent plastic in absorbed dose calorimeters is the uncertainty existing in the corrections for endothermic chemical reactions induced in the plastic by radiation. Measurements have been conducted to determine this correction for tissue equivalent plastic irradiated with monoenergetic protons.

Muscle-equivalent plastic of the Shonka type (13.5% carbon, 51.1% polyethylene, 28.2% Nylon, 2.2% silica, and 4% calcium fluoride) was irradiated with 1.7 MeV protons. The difference between the energy delivered to the plastic by the proton beam and that which appeared in the form of heat was assessed by making the absorbing element of a calorimeter from the plastic. The plastic surface was uniformly irradiated by the proton beam at an average beam current of about

1 nanoampere/cm² (6×10^9 protons/cm²-sec). Since 1.7 MeV protons penetrate only about 70 μ (0.003 in.), and an average measurement required about 500 sec, the dose to the plastic was of the order of 10^7 rads per run. A Faraday cup (the absorber) was used to monitor and control the beam current.⁽¹⁾ The beam power was determined by the calorimeter which is constructed in such a way that by 180° rotation of the absorber either plastic or aluminum can be exposed to the beam.

The calorimeter used in the experiment is operated adiabatically. A cross section of the calorimeter is shown in Figure 1 and Figure 2 is an exploded and a cross sectional detail of the absorber. The manganin heating coil used for calibration purposes is cemented with epoxy into a 0.010 in. thick aluminum disk.

Epoxy is also used to cement a 0.010 in. thick aluminum disk over the front surface of the heating coil. The assembly is then pressed into a Lucite holder. A thin layer of silicone grease is used to attach the tissue equivalent plastic sample to the aluminum surface. The Lucite holder fits into holes drilled in the adiabatic jacket and may be rotated from outside the vacuum jacket by the shaft shown in Figure 1.

The temperature difference between the adiabatic jacket and the absorber is sensed by a two junction thermopile. The thermopile output is amplified and fed to a proportional control system which feeds power to

a heating coil surrounding the jacket. Temperature difference with the system can be easily maintained to less than 0.001 °C. The rate of temperature rise of the system is monitored by means of a thermistor embedded in the inside wall of the adiabatic jacket. The jacket is maintained at -300 V to return electrons which have been ejected from the absorber. The thermopile and absorber heating coil leads pass through a guard ring which is maintained at ground potential.

Thermal radiation transfer between the absorber and objects outside the adiabatic jacket is prevented by a 5×10^{-5} in. thick

FIGURE 1. Cross Section of Calorimeter

FIGURE 2. Exploded Detail of the Absorber

nickel foil across the beam path, and thermal baffles shielding the holes which allow evacuation of the adiabatic jacket. The nickel foil is at ground potential so that electrons ejected by the beam are not lost.

The isothermal jacket is held at a constant temperature by means of a feedback system using thermistors as the sensing element and manganin wire wrapped around the jacket as a heater. A Styrofoam cover completely encloses the calorimeter isolating it from minor fluctuations in room temperature. Thermal isolation from the accelerator is provided by the plastic coupling sleeve.

The results of the measurement are presented in Figure 3 which shows the thermal power in milliwatts measured by the plastic absorber as a function of accumulated dose. The input beam power, as determined by the aluminum absorber, was 1.7107 mW with a standard deviation of 0.05%. The maximum observed deviation from the above mean was 0.0013 mW. These errors are indicative of the combined uncertainties existing in the beam current regulator, the beam energy control, and the calorimeter measurements. Damage to the plastic appears to be linear at first and shows signs of saturation above about 5×10^7 rads. Extrapolation of the curve back to zero exposure gives a heat deficit of $4.45 \pm 0.07\%$. The error quoted is the standard deviation based on the statistical scattering of the

data. Systematic errors which may exist between electrical calibration and beam current operation are now being investigated. A second sample of the same plastic in a preliminary measurement gave a difference of $4.2 \pm 0.3\%$. These values are in rough agreement with the 1 to 3% estimated by Milvy, Genna, Barr and Laughlin⁽²⁾ for electrons.

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FIGURE 3. Observed Power in Tissue Equivalent Plastic for 1.7107 ± 0.0009 mW Beam Power

OPTICAL LIFETIME MEASUREMENTS USING A
POSITIVE ION VAN DE GRAAFF ACCELERATOR*

L. L. Nichols and W. E. Wilson

A system for direct observation of excited state optical lifetimes using the delayed coincidence counting technique is described. The system uses a pulsed proton beam for excitation, a high speed time-to-amplitude converter and an on-line digital computer for data reduction. Lifetimes longer than 1 nsec can be measured. Preliminary measurements on the 3^1P , 4^3S , and 4^1D levels of helium and several vibrational bands of N_2 are presented to illustrate the capabilities of the system.

* Published in Journal of Applied Optics, vol. 7, pp. 167-170. 1968.

GAS PRESSURE CONTROL FOR FLOW TYPE PROPORTIONAL COUNTERS

L. A. Braby

Control of gas pressure in proportional counters is critical because of the strong dependence of counter gain on gas density. Experiments in microdosimetry and energy loss in thin gas layers require careful control of pressure for the additional reason that quantitative measurements require knowing the absolute quantity of gas in a known volume. Cartesian diver manostats have been used to control pressure, but it has been our experience that in the pressure range of interest (5 to 50 torr) they are hard to use and drift badly. To improve gas control, we have employed an electronic servo system using a lab-built pressure transducer of our own design and a commercial motor-driven needle valve. The transducer is simply a thin nickel bellows with a reference

pressure held captive on one side and system pressure on the other. The end of a linear displacement sensor is in contact with the free end of the bellows. For this sensor, we use a differential transformer micro-inch meter.* If the pressure in the system drops below that on the reference side of the bellows, the bellows expands producing a negative voltage at the differential transformer output. A high pressure produces a positive output. This output is fed to the needle valve motor control amplified** in such a way that a positive signal causes the valve to open and increase gas flow out to the system. This system actually

* Daytronic Model 300 BH.

** Brown Electronik "Continuous Balance" Unit.

controls gas density (moles/cm³) if transducer temperature is proportional to the temperature of the main gas volume because pressure changes due to temperature will cancel out.

The system is arranged as shown in Figure 1. Valves are placed to bypass each function and for ease in set up.

Transducer sensitivity, calculated for a bellows with an effective area of 0.86 in.² and spring rate of 5.2 lb-in., and a differential transformer sensitive to 2×10^{-6} in. is 6×10^{-4} torr. The system actually controls a pressure between 1 and 50 torr with a flow rate of 2 standard cm³/min or greater to better than 0.04 torr which is the resolution of our gage. Drift is less than 0.1 torr in 24 hr.

Setting up the pressure is quite easy, the system is pumped to the desired pressure with the reference valve open. The differential transformer controls are adjusted for zero, the servo valve is activated, and the reference valve is closed. Pressure will oscillate for a few cycles as the servo valve settles down to the proper flow. Fine pressure adjustments can be made with the transformer zero control.

FIGURE 1. Pressure Control

THE FEASIBILITY OF IN VIVO NEUTRON ACTIVATORS ANALYSIS OF
TOTAL BODY CALCIUM AND OTHER ELEMENTS OF BODY COMPOSITION*

H. E. Palmer,** W. B. Nelp,[†] R. Murano,[†] C. Rich,[†] and K. G. Pailthorp**

Measurement of the gamma rays emitted from human cadavers and phantoms after exposure to relatively low levels of fast neutrons show that several elements of body composition can be determined by this procedure. These elements include calcium, sodium, chlorine, nitrogen, and phosphorus. The determination of total body calcium may be one of the most important applications of this method. The results of this study show that the calcium content in a human can probably be measured to an accuracy of $\pm 8\%$ and that a change of 3% or more in the calcium content in the same person over a period of time can be detected. These results can be obtained with neutrons produced at a cyclotron and with radiation doses to the subject of 0.1 rad or less. The uniformity of irradiation can be significantly improved by exposing both front and back sides of the cadaver during the neutron irradiation. A method to compensate for the decay of the ^{49}Ca during irradiation was developed. A sensitive whole body counter consisting of a circular array of 4 in. thick by 9 3/8 in. diameter NaI (Tl) detectors is used to measure the induced radioactivity.

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** *Radiological Sciences Section.*

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THE USE OF TOTAL BODY PHOSPHORUS AS A MEASURE OF BONE MASS

H. E. Palmer*

In a previous report,⁽¹⁾ the high sensitivity for measuring total body phosphorus after exposure of cadavers to low levels of fast neutrons was described. The determination of total body bone mass might be possible by determining the amount of phosphorus in bone. If the phosphorus not bound in the bone (about 10%) could be determined by an isotopic

dilution method and the total phosphorus determined by in vivo activation analysis, the bone content could be determined by the difference. The determination of total body phosphorus by the fast neutron (n, α) reaction can be made more accurately and with less radiation dose than total body calcium due to less interference from other induced isotopes and the use of fast neutrons which

* *Radiological Sciences Section*

allow a more uniform exposure. The remaining question is that of the relationship of phosphorus to bone mass, and it appears that a loss of bone mass is accompanied by a loss of phosphorus as well as calcium.

A specific application of phosphorus activation may be the determination of the relative bone mass of particular bone areas such as a single vertebra. Whereas, it is very difficult to collimate neutrons for thermal neutron reactions, the fast neutrons can be collimated by materials which merely reduce the energy of the desired reaction. Solid iron makes an excellent collimator of 14 MeV neutrons for the (n, α) reaction on phosphorus and Figure 1 shows the degree of this collimation. A single vertebra of the Remab phantom

was irradiated to a dose of 0.15 rad with this 1 in. diameter beam. An immediate count with a large NaI (Tl) crystal gave the spectrum shown in Figure 2. The number of counts in the 1.78 MeV gamma ray peak from ^{28}Al are sufficient for the relative amount to be compared to the relative amount in neighboring vertebrae. We are presently studying the usefulness and practicability of this technique.

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Neg. 0680456-1

FIGURE 1. The Effectiveness of Iron for Collimating Fast Neutrons for Fast Neutron Reactions

Neg. 0680456-3

FIGURE 2. Gamma-Ray Spectrum of a Single Human Vertebra
After Irradiation with 0.15 rad of Collimated 14 MeV Neutrons

THE UPTAKE, DISTRIBUTION AND EXCRETION OF PROMETHIUM IN HUMANS

H. E. Palmer,** G. H. Crook* and I. C. Nelson**

Large scale separation of ^{147}Pm fission product waste and preparation of the material for several applications constitutes a potential source of radiation exposure to workers in this field. To form a basis for radiation exposure limits and to determine the dose from

accidental exposure, the uptake, retention, distribution and excretion of promethium must be known.

An experiment using ^{143}Pm ⁽¹⁾ and human volunteer test subjects was performed to determine these metabolic parameters. Whole body counting techniques and urinary and fecal measurements were used to study the course of the promethium following both intravenous

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and oral administration of $^{143}\text{PmCl}_3$ to humans. When this experiment is completed, the results will provide correlation between body burden and urinary excretion of promethium which should be useful in evaluating cases of accidental exposure to ^{147}Pm .

Promethium-143 decays by electron capture and subsequent gamma ray emission. The gamma ray energy is 0.74 MeV and is excellent for whole body counting purposes. The ^{143}Pm used in this experiment was prepared by Oak Ridge National Laboratory using high energy proton irradiation of enriched $^{144}\text{Nd}_2\text{O}_3$ (94.4%). A small amount of ^{144}Pm was also formed. The ^{143}Pm was separated from the irradiated neodymium at Battelle-Northwest by an ion exchange method using Dowex 5-X4 fine mesh resin and eluting the ^{143}Pm essentially carrier free with 0.25 N α -hydroxybutyric acid at a pH of 4.6. The separated ^{143}Pm was sent to Abbott Radio-pharmaceutical Laboratories where it was sterilized, dissolved in isotonic saline solution, made acidic to pH 3, and pyrogen tested in rabbits.

Localization and distribution of the ^{143}Pm within the body was followed using a shadow shield whole body counter.⁽²⁾ A 2 in. wide slit system over the 9 3/8 in. diameter NaI(Tl) detector permitted differential scanning of the subject as he traveled under the crystal. Whole body counts were made periodically to determine the total ^{143}Pm remaining in the

body and these counts will continue for at least one year. Urine, feces, and blood samples were collected and analyzed for ^{143}Pm from each volunteer for periods up to 85 days after injection of the ^{143}Pm .

The $^{143}\text{PmCl}_3$ was administered to eight normal human volunteers by physicians of the Hanford Environmental Health Foundation. Six volunteers received approximately 0.1 μCi of ^{143}Pm intravenously and two volunteers received an oral dose of 10 μCi .

Figure 1 shows a typical distribution of ^{143}Pm in a human volunteer with time following intravenous administration. The uptake in the liver is very rapid with most of the liver fraction arriving there within 90 sec. A rough measure of the amount in the liver was made and found to be between 40 to 50% of the injected dose. Whole body scans after 24 hr show that the distribution in the body remains unchanged up to 85 days after injection with the exception that the peak over the bladder area disappears during the second day. The ^{143}Pm which does not go immediately to the liver appears to remain in the blood for a short time and gradually to deposit in the bone. Figure 2 shows the total estimated content of ^{143}Pm in the blood as a function of time obtained by analyzing periodic blood samples of a volunteer. The ^{143}Pm activity was not detectable in the blood at 24 hr.

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FIGURE 1. Differential Scan of ^{143}Pm in Test Subjects at Various Times After Injection

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FIGURE 2. Percent ^{143}Pm Remaining in Blood Following Intravenous Administration

The excretion of ^{143}Pm following intravenous injection is via both the urine and feces. During the first week, the amount excreted in the urine is 10 times that excreted in feces. The daily excretion in urine for 84 days following injection and in feces for 7 days following injection is shown in Figure 3. The rate of the ^{143}Pm in fecal excretion does not decrease so rapidly as the rate in urinary excretion. Results from a pig injected with the same ^{143}Pm solution by the Biology Department indicate that the ^{143}Pm in fecal

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FIGURE 3. Daily Urinary and Fecal Excretions of Intravenously Injected ^{143}Pm

excretion will exceed that in urinary excretion after a few weeks. Measurements of urinary excretion were not made after 3 months following injection because the content in the urine was near or below the detection limit of the counting method.

The retention of the ^{143}Pm as measured by the whole body counter agrees with the excretion results and is shown in Figure 4 as a function of time. An extrapolation of the retention curve between 20 and 84 days indicates that the biological half-life of ^{143}Pm in

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FIGURE 4. Retention* of ^{143}Pm with Time

the total body is greater than 1000 days. Whole body counts will be continued for at least 1 yr so that the half-life can be determined more accurately. Any redistribution of the ^{143}Pm between liver, bone or other organs has not been detected in comparing periodic counts over the legs, liver and head of the volunteers.

Two volunteers orally ingested 10 μCi of the $^{143}\text{PmCl}_3$ solution mixed with orange juice. Subsequent excretion analysis showed that essentially none of the material was absorbed by the body and all of it was excreted in the feces. No activity was detected in the urine samples. After

one week, regular whole body counts showed that there was no activity remaining in the body. However, a 1 hr count directly over the liver of one of the volunteers showed a liver content of about 0.0001 μCi . The ^{143}Pm content in the liver remained constant in subsequent counts up to a month later which confirmed that the activity was actually in the liver and not temporarily lodged in the G.I. tract. The uptake by this volunteer was estimated to be about 0.001% which agrees with the ICRP estimates of the uptake of Pm from ingestion. Promethium-143 activity was not detectable in the other

volunteers and the uptake was probably less than 0.0005%.

Although the results of this experiment are not complete, it appears that they agree with the results obtained in animal studies,⁽³⁾ but they disagree with the liver uptake parameters listed by the ICRP.⁽⁴⁾ The ICRP Handbook lists the fraction from the blood to liver as 0.06, whereas this experiment shows this fraction to be 0.4 to 0.5. Further experiments are planned to determine if the distribution in the body after inhalation of soluble $^{143}\text{PmCl}_3$ is the same as that obtained from this injection experiment.

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