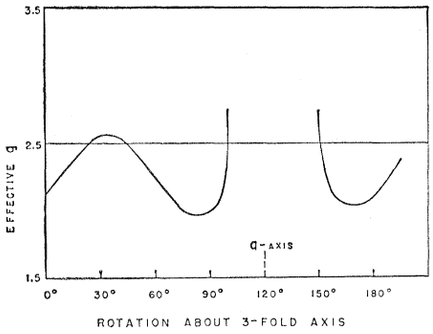

Fig. 1. Electron paramagnetic resonance line of amethyst color center measured at 9.28 Gc/sec.

545 mμ, to compute the oscillator strength f.

$$Nf = 1.29 \times 10^{17} \frac{n}{(n^2+2)^2} \alpha_M \omega \text{ cm}^{-2}$$

With α_M (5.97 cm^{-1}) the maximum absorption coefficient, ω (0.64 ev) the half-width of the transition, and n the refractive index (1.55), the resultant value of f is 2×10^{-2}.

This oscillator strength is much larger than values typical of crystal-field absorption spectra, which may be as low as 10^{-8}. It is of the same order of magnitude as f for the most intense absorptions in MnO_4^{1-}, which have been explained as transitions of the charge-transfer type (*6*, *7*). We therefore suggest that the amethyst color is due to a charge-transfer transition, which may be written (*8*):

$$O^{2-} + Fe^{4+} \rightleftharpoons O^{1-} + Fe^{3+}$$

The large anisotropy of the effective g value and the intensity of the EPR line indicate that the quadrivalent iron rather than the hole on oxide ion (which should be delocalized) is the ground state of the center. The close relation between axes of pleochroism in amethyst and magnetic axes of the S_1 precursor center also support this assignment (*1*).

An Fe^{3+} ion in a constricted substitutional site should be more readily oxidized. The only other known compounds of quadrivalent iron, however, are the ferrates (*9*) and the complex ion (*10*)

$$\left[Fe^{IV}[o\text{-}C_6H_4(As(CH_3)_2)_2]_2Cl_2\right]^{2+}$$

The complex is green in very dilute solutions, dark red in moderate concentrations, and black in solid salts.

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Lead-210 and Polonium-210 in Biological Samples from Alaska

Abstract. *The naturally occurring concentrations of lead-210 and polonium-210 in certain biological samples from Alaska are unusually high. The concentration processes are similar to those observed for artificially produced radioactive fallout. Concentrations of these nuclides are greater in Alaskan natives than they are in other United States residents.*

In the past two decades research workers in the radiological sciences have increased their efforts to identify and measure the natural radiation levels to which man is subject. These investigations have been prompted in large measure by the introduction of radioactive material into the environment by nuclear weapons and by the high natural radiation levels in various parts of the world (*1*).

More recently, the concentrating of fallout radionuclides in some ecosystems, such as that observed in the arctic regions for ^{137}Cs (*2*) and ^{55}Fe (*3*), has prompted research in the area of "natural fallout," notably the concentrations in the environment of the naturally occurring radioisotopes ^{210}Pb (half-life, 22 years) and ^{210}Po (half-life, 138 days). We now consider the levels of these two isotopes in certain biological samples from Alaska.

The most extensive investigation of natural ^{210}Pb concentrations in man is that of Holtzman (*4*), who also found relatively high concentrations of this isotope in arctic lichens, caribou bone, and antler. This ^{210}Pb undoubtedly derives from the decay of ^{222}Rn in the atmosphere. The high levels of ^{210}Pb in caribou result from concentration by lichens; the process is similar to one observed for ^{137}Cs. We have extended these measurements to include a variety of biological samples from the Alaska region and have analyzed not only ^{210}Pb content, but also ^{210}Po content.

To determine ^{210}Po, samples were first wet-ashed in concentrated nitric and perchloric acids and 30 percent hydrogen peroxide; chemical electrodeposition of the polonium from a dilute hydrochloric acid solution, by the method of Black (*5*), followed. Polonium-208 was used to measure radiochemical yield through the dissolution and plating procedure, the polonium finally being determined by alpha energy analysis with a silicon diode detector and a 400-channel pulse-height analyzer. Since lead is not lost in this procedure, ^{210}Pb was determined in the residue from the polonium plating by the procedure of Sill and Willis (*6*). Lead-212 was used to measure radiochemical yield, and the ^{210}Pb activity was determined by low background beta counting through aluminum absorbers following decay of the ^{212}Pb and the attainment of partial equilibrium between ^{210}Pb and its daughter, ^{210}Bi.

The identification and origin of the caribou samples which were analyzed and the levels of ^{210}Pb and ^{210}Po observed are shown in Table 1. The values listed for caribou are the concentrations existing at time of slaughter and show the relative concentrations in the various organs. Since isotopic tracers were used as determinants of yield, the probable errors in the determinations are due almost exclusively to counting statistics. Care was taken to insure that probable errors from this source were less than 10 percent for the measurements of both isotopes at the 90-percent confidence level.

Table 2 contains the results of the ^{210}Po analysis of a composite lichen sample and certain foodstuffs used by Eskimos living on the western coast of Alaska. Analyses of ^{210}Pb are not included in these particular samples since they are used here only as an indication of the relative levels of ^{210}Po to which these particular in-

Table 1. Concentrations of ^{210}Pb and ^{210}Po in caribou slaughtered in November 1965. Animals collected at Anaktuvuk Pass.

Tissue	Concentration (nanocurie/kg wet wt.)		$^{210}Po/^{210}Pb$
	^{210}Po	^{210}Pb	
Caribou No. 1, 6-year-old female			
Meat	0.41	0.03	13.7
Liver	4.13	.81	5.1
Kidney	3.51	.56	6.3
Spleen	0.82	.04	20.5
Bone	3.12	3.35*	0.93
Caribou No. 2, 7-year-old male			
Meat	0.35	0.03	11.7
Liver	5.47	2.45	2.2
Kidney	4.36	0.42	10.4
Spleen	0.68	.15	4.5
Bone	5.08	5.22*	0.97
Caribou No. 3, 8-year-old male			
Meat	0.26	0.03	8.7
Liver	4.28	.60	7.1
Kidney	3.92	.55	7.1
Spleen	0.74	.11	6.7
Bone	3.15	4.50*	0.70

* These values, in picocuries per gram of ash, are 8.42, 13.1, and 11.3, respectively, and are nearly identical with those reported by Holtzman (*4*).

dividuals might be exposed. However, in samples such as seal meat and seal liver, one might expect the activity to be supported in part by ^{210}Pb.

Several common foodstuffs (such as meats, grain products, and eggs) from local foodmarkets have been analyzed in this laboratory (*7*). Generally the levels of ^{210}Po in these foods are some 1/10 to 1/100 as high as they are in caribou flesh, seal meat, and salmon (Tables 1 and 2).

Although more samples must be analyzed to obtain a clear picture of the concentrations of both nuclides in the Alaskan ecosystem, certain conclusions can be drawn from the data of Tables 1 and 2. First, caribou have been subjected to higher than "natural" levels of internal radiation; presumably this condition has existed for centuries. If the concentrations of ^{210}Po in the various organs of the caribou are constant at the levels listed in Table 1, the dose rates to these various organs would be those shown in Table 3. Since this dose is due to alpha particles it is probably more effective than an equal dose of x-rays, because of a higher relative biological effect (RBE) and because of a lack of a protraction effect.

Table 2. Concentrations of ^{210}Po in other selected samples.

Sample	^{210}Po (nanocurie/kg wet wt.)
Lichens*	4.70
Salmon†	0.026
Butterfish	.007
Whitefish	.007
Seal meat	.220
Seal liver	.880
Polar bear meat	.008

* Composite sample taken from Anaktuvuk Pass. The type of lichen present is not known. The concentration reported corresponds to a value of 14.9 nanocurie/kg of dry lichen, which is in general agreement with that reported by Holtzman (*4*).
† Average of four salmon.

Since certain of the Alaskan natives depend upon caribou meat for a large portion of their diet, they will also be subjected to a higher radiation dose than other United States residents. The problem can be put in better perspective by comparing the problem of ^{210}Pb and ^{210}Po with that of ^{137}Cs arising from fallout. In making this comparison we have assumed that the maximum permissible concentrations (MPC) for ^{137}Cs, ^{210}Po, and ^{210}Pb are the same in meat as they are in water. These values are listed in the report of the International Commission for Radiological Protection (*8*) as 2.4×10^{-4}, 7×10^{-6}, and 1×10^{-6} microcurie/cm^3, respectively. The ratio of MPC ^{210}Po/MPC ^{137}Cs is 1/30. Thus, the ^{210}Po if present in the same concentration as ^{137}Cs would provide 30 times the radiation dose. Similarly, the MPC ^{210}Pb/MPC ^{137}Cs is 1/200. Since the average ^{137}Cs content of caribou flesh is approximately 20 nanocurie/kg (*9*) and the ^{210}Po and ^{210}Pb concentrations have tentatively been determined as 0.3 and 0.03 nc/kg, respectively, the relative hazard to the Eskimo can be computed in the case of ^{210}Po as $(0.3/20) \times 30 = 0.45$, and, in the case of ^{210}Pb, as $(0.03/20) \times 200 = 0.30$.

Thus, if an Eskimo should consume enough caribou flesh containing the concentrations of ^{137}Cs, ^{210}Po, and ^{210}Pb listed above, and should reach a maximum permissible body burden of ^{137}Cs as a result, he would also be technically overexposed by some 45 percent due to ^{210}Po and by some 30 percent due to ^{210}Pb. The maximum permissible body burden, sustained, which has been recommended by the International Commission for Radiological Protection for general populations not exposed to ^{137}Cs in the course of their work is 3 microcuries. Some Alaskan natives already have ^{137}Cs body burdens approaching 3 μc (*10*). These high body burdens are known to vary according to the seasonal changes that occur in the ^{137}Cs content of the caribou themselves and consequently in the Alaskan natives. It is possible, however, that even with the seasonal variations that occur in the ^{137}Cs body burdens, the permissible exposure of these individuals might be exceeded for periods of time due to the presence of ^{210}Pb and ^{210}Po in their diet.

Table 3. Approximate dose rates to caribou organs from ^{210}Po.

Tissue	Av. ^{210}Po content (nanocurie/kg wet wt.)	Dose (rad/yr)
Liver	4.62	0.45
Kidney	4.05	.39
Spleen	0.74	.07
Bone	3.78	.37

There is direct evidence that Eskimos indeed contain much higher concentrations of ^{210}Pb and ^{210}Po than other United States residents. Hill (*11*) has measured the ^{210}Pb content of a rib bone obtained from a Canadian Eskimo and has observed a concentration of 2.3 picocurie/g of ash, which is some 15 times greater than the average ^{210}Pb bone content observed by Holtzman (*4*) in surgery and autopsy specimens obtained from individuals residing in Illinois. Secondly, measurements of ^{210}Po in urine specimens obtained from natives living at Anaktuvuk Pass, Alaska, showed average concentrations of 3.2 pc/1.4 liter, a concentration some 230 times that observed by Sultzer and Hursh (*12*) for normal individuals who were exposed only to normal environmental levels of ^{210}Pb and ^{210}Po. If we use the data of Fink (*13*) for animals, which imply that 0.1 percent of the ^{210}Po body content is excreted per day in the urine, and if we assume the natives are at equilibrium with their intake, the calculated average ^{210}Po body burden of the people measured would be 3500 pc, or approximately 10 percent of a maximum permissible body burden of ^{210}Po under the definition given above for ^{137}Cs.

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Enzyme Action: Comparison on Soluble and Insoluble Substrate

Abstract. *The action of trypsin on gelatin solution is compared with its action on swollen gel microspheres in suspension. Both the solution gelatin and gel spheres, which are readily permeable to the enzyme, follow Michaelis-Menten kinetics. The apparent rate constants for dissociation of the enzyme-substrate complexes to hydrolysis products are essentially the same for both solution gelatin and spheres, an indication that gel structure in this system has a negligible influence on reaction rate once the enzyme forms a complex with the substrate. In contrast, the Michaelis constant for the gel system is greater than that for solutions below the melting point of the gel; this difference disappears as the melting point of the gel is approached.*

Despite the observed ubiquity of enzyme action on insoluble substrates in nature (*1*), most kinetic studies have concerned only the action of enzymes on soluble substrates. A rigorous comparison of enzyme action on both soluble and insoluble forms of the same substrate is complicated by the fact that one cannot, in general, find two distinct equilibrium states (soluble and insoluble) or phases of a single substrate under the same physical conditions, except at phase transitions, where both forms coexist. Thus, the elaboration of the kinetics of enzyme action on each of two separate forms or phases of the same substrate requires that at least one of these forms be a nonequilibrium configuration under the prevailing conditions.

The most satisfactory situation is one in which both soluble and insoluble forms arise naturally as a consequence of hysteresis of the substrate with respect to variation of one or more thermodynamic variables. In this event substrate molecules of identical chemical composition and molecular weight comprise both forms. In the comparison, reported by Mazia and Hayashi (*2*), of the action of pepsin in pepsin-ovalbumin fibers and on free heat-denatured ovalbumin it is probable that the substrate molecules do not have the same chemical composition and molecular weight in both soluble and insoluble forms. Attempts to disperse fibers of ovalbumin in familiar protein solvents, including the potent combination of high *p*H, 8*M* urea, and excess mercaptoethanol (which completely disperses irreversibly aggregated heat-denatured ovalbumin), were uniformly unsuccessful. Thus, it must be presumed that covalent intermolecular bonds are present in the fibers.

Ordinary gelatin is a suitable substrate because, upon cooling sufficiently concentrated solutions, it readily forms gels which are essentially stable against dispersion into excess solvent, and which may be redissolved by mild heating. However, in studying the kinetics of enzymatic digestion of a gel it is desirable to employ volumes of gel sufficiently small so that the enzyme

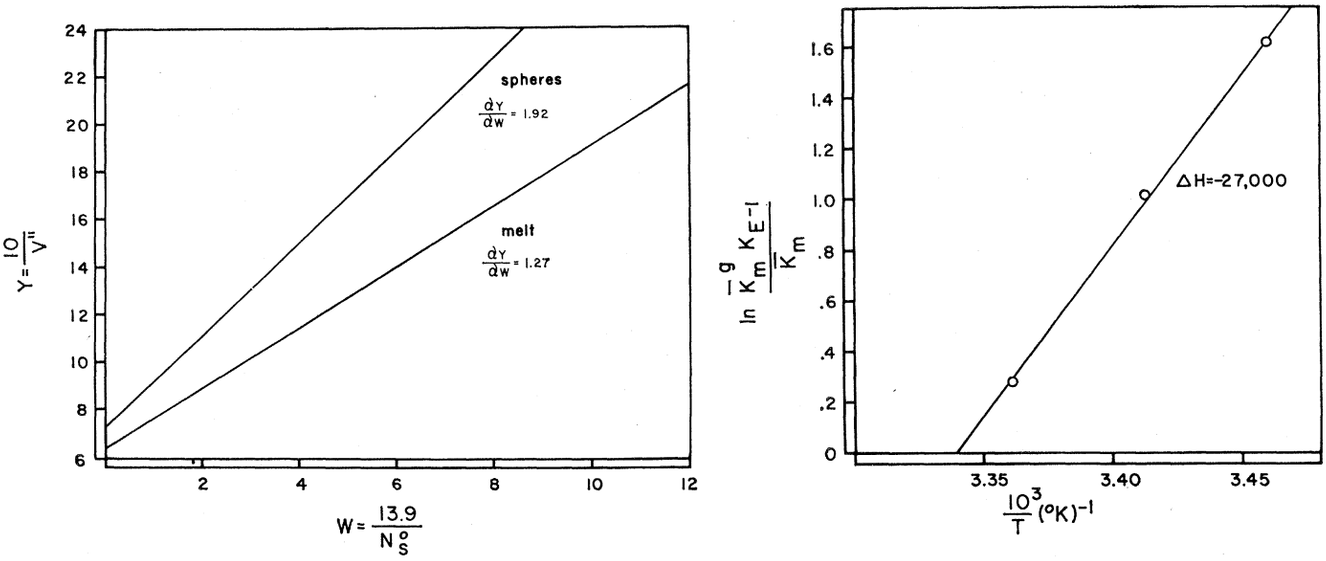

Fig. 1 (left). For both spheres and free-solution gelatin, $10/V''$ is plotted against W which is equal to $13.9/N_S^0$. Here V'' is the observed initial rate in units of syringe volume (percent) delivered per minute, and the value for W is a reciprocal factor for the dilution of a stock suspension (13.9 mg/ml) to N_S^0. The trypsin concentration is $7.5 \times 10^{-11}M$ in both situations. The syringe contained 0.01*N* NaOH, and the solution was 0.15*M* KCl in both cases; *T* 24.5°C; *p*H, 8.90. Fig. 2 (right). The unusual temperature dependence of $\bar{K}_m^g K_E^{-1}$ is completely exposed after factoring out the temperature dependence of the ordinary free solution constant K_m. The ordinate represents ln $\bar{K}_m^g K_E^{-1}/\bar{K}_m$ and the abscissa represents $10^3/T$, where T is the absolute temperature.