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Argonne National Laboratory

RADIOLOGICAL PHYSICS DIVISION

SUMMARY REPORT

July 1962 through June 1963

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ERRATA for ANL-6769

RADIOLOGICAL PHYSICS DIVISION SUMMARY REPORT,
July 1962 through June 1963

Moments of the Oscillator Strength Distribution
and Some Associated Quantities for the Hydrogen Atom

by

Mitio Inokuti

Please make the following changes as indicated:

Page 10 Eq. (17) should read $P(-1) = \langle \vec{r}^2 \rangle / (3a_0^2)$.

Page 12 Lines 6 and 18 should read "where the wavelength λ is measured in cm. ..."

Page 13 Eq. (33) should read

$$\begin{aligned} m_j &= 2^{-j} \sum_n \frac{f_n}{E_n} \left(1 - \frac{1}{E_n} \right)^j \\ &= 2^{-j} \sum_{p=0}^j \binom{j}{p} (-1)^p P(-p-2). \end{aligned}$$

Page 14 The sentence at the bottom should read "For excitation to discrete level n , including all states with different angular momenta, of the hydrogen atom, ..."

Page 18 Eq. (54) should read $M_n^2 \ln(4c_n) \rightarrow Dn^{-3}$.

ANL-6769
Biology and Medicine
(TID-4500, 26th Ed.)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
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RADIOLOGICAL PHYSICS DIVISION
SUMMARY REPORT

July 1962 through June 1963

J. E. Rose, Division Director
L. D. Marinelli, Associate Division Director

December 1963

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FLUORESCENCE DECAY-TIME MEASUREMENTS

I. B. Berlman and O. J. Steingraber

Measurements have been made of the fluorescence decay time of several organic scintillators in the nanosecond range. The technique of making these measurements has been described previously.⁽¹⁾ Basically, it consists of directly exciting a solute in a scintillation solution with pulsed monochromatic uv radiation and accurately recording and analyzing the fluorescence pulse contour.

Progress in three phases of this work is reported herewith:

- 1) The apparatus for measuring fluorescence decay times has been improved, and its capability of making decay time measurements in the subnanosecond region has been investigated.
- 2) The fluorescence decay times of several deuteriated compounds have been measured and compared with those of similar but hydrogen-containing compounds.
- 3) The apparatus has been modified to measure longer decay times (e.g., in the microsecond and possibly in the millisecond regions).

I. Fluorescence Decay-Time Measurements

The apparatus has been improved by replacing several component parts, among them the RIDL 100-channel analyzer by an RIDL model 512B 400-channel analyzer and the Tektronix N unit by a Lumitron model 120 pulse-sampling oscilloscope.

The modified equipment has been shown to be functional in the subnanosecond region in the following manner. Analytical determinations⁽¹⁾ have been made of the expected pulse shapes when the solute decay times are smaller as well as greater than a nanosecond. A limited search has been made to find solutes with very short decay times. By comparing the measured pulse contours to the analytical curves, the operational capability of the apparatus in the subnanosecond region has been confirmed.

The solutes and their respective experimental decay times are listed in Table 1. An uncertainty of $\pm 10\%$ is placed on the measurements. Each solute was dissolved in a common solvent, cyclohexane, at a concentration of 0.1 g/l. The solutions were bubbled with nitrogen to obviate quenching by oxygen. Each solute was directly excited with pulsed

monochromatic uv radiation, and the fluorescence pulse contour was detected and recorded. As demonstrated by the values for p-quaterphenyl and BBD the apparatus is functional in the subnanosecond region.

Table 1

Solute	T(nsec)	
	Ordinary	Deuteriated
Biphenyl	15.5	-
p-terphenyl	1.2	1.1
p-quaterphenyl	0.9	-
Naphthalene	89.0	92.0
Anthracene	6.3	6.2
Diphenyloxadiazole (PPD)	1.2	-
Phenylbiphenyloxadiazole (PBD)	1.2	-
2,5 Di-(4-biphenyl)-1,3,4-oxadiazole (BBD)	0.9	-

II. The Decay Time of Deuteriated Compounds

The fluorescence decay time of each of a series of completely deuteriated compounds was measured as explained above. These compounds are also listed in Table 1. Within the accuracy of the experiment, the deuteriated and normal compounds have equal decay time values.

Equal fluorescence decay times for deuteriated and ordinary compounds is a surprising result and in definite contrast to the published⁽²⁾ phosphorescence decay time of 16.9 sec for deuteriated naphthalene and 2.1 sec for naphthalene-H₈. The phosphorescence state as reported in Reference 2 was also excited by uv radiation.

III. The Measurement of Longer Decay Times

The pulse sampling technique described by us elsewhere⁽¹⁾ suffers from the lack of signal strength when the decay times are long. When the signal becomes small, it is soon lost in the dark current of 56 UVP photomultiplier tube normally used in the apparatus. Therefore, when measurements are made on solutes with long decay times, one of the techniques of reducing the background noise has been to use an EMI 6256S photomultiplier tube, a tube with a low noise background.

An alternate method of reducing the effect of the dark current has also been tried and found successful. A second photomultiplier tube which

looks directly at the flash tube in the pulse uv apparatus is used to provide a large stable trigger pulse which previously was taken from the anode of the first tube. By a proper setting of a discriminator bias level the dark current pulses in the second tube are eliminated and only pulses in coincidence between the two photomultiplier tubes are recorded. More work is in progress along each of these three phases of the research.

References

1. O. J. Steingraber and I. B. Berlman. A versatile technique for measuring fluorescence decay times in the nanosecond region. Rev. Sci. Instr. 34, 524 (1963).
2. C. A. Hutchinson, Jr. and B. W. Mangum. Effect of deuterium substitution on the lifetime of the phosphorescent triplet state of naphthalene. J. Chem. Phys. 32, 1261-1262 (1960).

EXCITED STATES OF A LINEAR MOLECULAR CHAIN CONTAINING AN IMPURITY*

Kanji Katsuura** and Mitio Inokuti

Abstract

A one-dimensional model of coupled molecules containing an impurity is proposed, and properties of its excited states are examined for the purpose of understanding excitation energy localization and delocalization in radiation chemistry. The model consists of a linear array of equally-spaced identical molecules and an impurity molecule and is characterized by Coulomb and resonance integrals, viz., matrix elements of the Hamiltonian of the total system between the wave functions corresponding to localized excitation. The eigen energies of the excited states of this model are shown to form a band with a particular level separated downward from the bottom and/or another one upwards from the top of the band. Another model containing a displaced molecule in a chain of otherwise equally-spaced identical molecules is also studied and shown to possess the same type of level scheme. The separation of the bottom or the top level from the band edge is calculated for particular cases where the coupling between the wave functions corresponding to localized excitation is of dipole-dipole or quadrupole-quadrupole type. Implications of the results for radiation chemistry are discussed.

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MOMENTS OF THE OSCILLATOR STRENGTH DISTRIBUTION AND SOME ASSOCIATED QUANTITIES FOR THE HYDROGEN ATOM

Mitio Inokuti

Introduction

Numerous properties of an atomic or molecular system can be expressed in terms of the oscillator strength distribution characteristic of the system. The average excitation energy in the Bethe stopping power formula^(1,2) is an example. At the present time, the hydrogen atom is the only system whose oscillator strength distribution is rigorously known. In this respect we present a systematic tabulation of moments of the oscillator strength distribution and some associated quantities for this case of the simplest atomic system.

The cross section for excitation and ionization of an atomic or molecular system by impact of a fast charged particle has a close connection with the corresponding oscillator strength. In fact, the Bethe asymptotic expression for the cross section at high incident energies^(1,2) involves the oscillator strength and another constant associated with the final state of the system. We also present a tabulation of the latter constants for the hydrogen atom.

It is hoped that the present calculation will be helpful, not only for a detailed application of the Bethe collision theory, but also as an orientation in the study of the oscillator strength distributions of more complicated atomic and molecular systems.

The Oscillator Strength for the Hydrogen Atom

The dipole oscillator strength f_n associated with the transition from the ground state 0 to an excited state n is defined by

$$f_n = E_n M_n^2 \quad , \quad (1)$$

where E_n is the excitation energy of the state n measured in units of the rydberg energy R ($R = 13.60488 \pm 0.00022$ eV).⁽³⁾ M_n^2 is the square of the dimensionless dipole matrix element between the states 0 and n :

$$M_n^2 = \frac{1}{3a_0^2} \left| \int \psi_n^* \vec{r} \psi_0 d\vec{r} \right|^2 \quad , \quad (2)$$

where a_0 is the Bohr radius, $\vec{r}$ the electronic coordinate, and ψ the wave function of the state 0 or n . For the discrete excited (nP) states, the only ones connected by dipole transition with the ground state, of the hydrogen atom, we have^(1,2,4)

$$E_n = 1 - n^{-2} \quad , \quad (3)$$

$$M_n^2 = \frac{f_n}{E_n} = \frac{2^8}{3} \cdot \frac{n^7 (n-1)^{2n-5}}{(n+1)^{2n+5}} \quad , \quad (4)$$

for $n = 2, 3, 4, \dots$. For the continuum (ionized) state ψ_k where the electron asymptotically has the wave number k measured in units of $1/a_0$ at infinity, we may use the differential oscillator strength df/dk , which is defined by

$$df/dk = E_k dM^2/dk \quad , \quad (5)$$

where dM^2/dk is given by the right-hand side of (2) with ψ_n replaced by ψ_k . It is further understood that ψ_k has been normalized with respect to k . In the case of the hydrogen atom, explicit expressions read^(1,2,4)

$$E_k = 1 + k^2 \quad , \quad (6)$$

$$\frac{1}{E_k} \frac{df}{dk} = \frac{2^8}{3} \frac{k}{(1+k^2)^5} \cdot \frac{\exp(-4k^{-1} \arctan k)}{1 - \exp(-2\pi k^{-1})} \quad . \quad (7)$$

Equations (3) through (7) give the distribution of the oscillator strength over the allowed excitation energies. We define the partial moments $P_d(s)$ and $P_c(s)$ over discrete excited states and the continuum, respectively:

$$P_d(s) = \sum_{n=2}^{\infty} f_n E_n^s \quad , \quad (8)$$

$$P_c(s) = \int_0^{\infty} dk \frac{df}{dk} E_k^s \quad , \quad (9)$$

and the total moment

$$P(s) = P_d(s) + P_c(s) \quad . \quad (10)$$

We define analogous quantities $Q_d(s)$, $Q_c(s)$, and $Q(s)$:*

$$Q_d(s) = \sum_{n=2}^{\infty} f_n E_n^s \ln E_n \quad , \quad (11)$$

$$Q_c(s) = \int_0^{\infty} dk \frac{df}{dk} E_k^s \ln E_k \quad , \quad (12)$$

$$Q(s) = Q_d(s) + Q_c(s) \quad . \quad (13)$$

Numerical evaluation of the above quantities was done on a computer. In evaluating sums $P_d(s)$ and $Q_d(s)$, the following asymptotic expression for f_n was helpful:

$$f_n \rightarrow Cn^{-3} \text{ for } n \rightarrow \infty \quad ,$$

$$C = 2^8 e^{-4} / 3 = 1.5629345 \quad . \quad (14)$$

Taking sufficiently large m , we can write

$$\begin{aligned} P_d(s) &= \sum_{n=2}^m f_n E_n^s + \sum_{n=m+1}^{\infty} Cn^{-3} + \text{correction term} \\ &= \sum_{n=2}^m f_n E_n^s + C \left[\zeta(3) - 1 - \sum_{n=2}^m n^{-3} \right] + \text{correction term} \quad , \end{aligned} \quad (15)$$

where $\zeta(3)$ is the value of the Riemann zeta function for argument 3 and equals 1.20205690.⁽⁵⁾ In actual calculation the value of m is chosen large enough so that the correction term in (15) contributes only a negligible amount. Desired accuracy (of six or seven figures) was obtained by setting $m=60$. A similar method was used in evaluation of $Q_d(s)$.

The $P_c(s)$ and $Q_c(s)$ were evaluated by using a numerical integration subroutine which allows the programmer to prescribe the limit of

*It may be noted that Q 's are derivatives of P 's with respect to s :

$$Q(s) = dP(s)/ds, \quad Q_d(s) = dP_d(s)/ds, \quad Q_c(s) = dP_c(s)/ds.$$

error. Because of errors arising from truncation, accuracy of five to six figures was the best we could attain.*

Results are given in Tables 2 and 3. The values of $P(s)$ for $s = -2, -1, 0, 1,$ and 2 agree perfectly with the known exact values:^{(4)**}

Table 2

Calculated values of $P_c(s)$, $P_d(s)$, and $P(s)$

s	$P_c(s)$	$P_d(s)$	$P(s)$
-10	0.066854	7.755574	7.822428
-9	0.073093	5.874513	5.947606
-8	0.080613	4.458806	4.539419
-7	0.089852	3.392602	3.482454
-6	0.101473	2.588966	2.690439
-5	0.116527	1.982648	2.099175
-4	0.136788	1.524670	1.661458
-3	0.165487	1.178263	1.343750
-2	0.209186	0.915814	1.125000
-1	0.283413	0.716587	1.000000
0	0.43500	0.56500	1.00000
1	0.88397	0.44936	1.33333
2	4.97249	0.36084	5.33333

Table 3

Calculated values of $Q_c(s)$, $Q_d(s)$, and $Q(s)$

s	$Q_c(s)$	$Q_d(s)$	$Q(s)$
-10	0.005708	-2.161407	-2.155699
-9	0.006820	-1.626232	-1.619412
-8	0.008292	-1.224333	-1.216041
-7	0.010295	-0.922444	-0.912149
-6	0.013118	-0.695613	-0.682495
-5	0.017276	-0.525119	-0.507843
-4	0.023758	-0.396915	-0.373157
-3	0.034660	-0.300465	-0.265805
-2	0.055062	-0.227860	-0.172798
-1	0.099914	-0.173168	-0.073254
0	0.228916	-0.131934	0.096982
1	0.86198	-0.100817	0.76116
2	15.9930	-0.077306	15.9157

$$P(-2) = \alpha/4 = 9/8 \quad , \quad (16)$$

$$P(-1) = \langle \vec{r}^2 \rangle / a_0^2 = 1 \quad , \quad (17)$$

$$P(0) = 1 \quad , \quad (18)$$

$$P(1) = 4/3 \cdot \langle K \rangle / R = 4/3 \quad , \quad (19)$$

$$P(2) = 16\pi/3 \cdot \langle \delta^3(\vec{r}) \rangle \cdot a_0^3 = 16/3 \quad (20)$$

In Equation (16), α is the polarizability in units of a_0^3 of the hydrogen atom and equals $9/2$.⁽⁴⁾ In Equations (17), (19), and (20), the symbol $\langle \rangle$ denotes expectation value over the ground state wave function, $\vec{r}^2$ the square of the electronic Cartesian coordinate, K the kinetic energy operator, and $\delta^3(\vec{r})$ the three-dimensional delta function of the electronic coordinate. Equation (18) is the celebrated Thomas-Kuhn sum rule.

*In fact, this accuracy is good enough for the purpose of physical consideration, because the very concept of the oscillator strength is based on the dipole approximation in the treatment of interaction of radiation with atomic or molecular systems.

**After the completion of the work the author found a paper by Dalgarno and Kingston [Proc. Roy. Soc. (London) A259, 424 (1960)], which gave analytical evaluation of $P(s)$ for $s = -3$ through -6 . Their results $P(-3) = 129/96$, $P(-4) = 319/192$, $P(-5) = 9673/4608$, $P(-6) = 297541/110592$ are in perfect agreement with our values in Table 2.

Some of the entries in Tables 2 and 3 can be compared with corresponding values found in literature. Harriman⁽⁶⁾ calculated $P_d(0)$, $P_c(0)$, $P_d(2)$, $P_c(2)$, $Q_d(2)$, and $Q_c(2)$.^{*} Our values for the first five are in perfect agreement with his up to the least significant figure, our accuracy being essentially the same as his. However, he gave a perhaps more accurate value $Q_c(2) = 15.99277 \pm 0.00002$. For the average excitation energy K_0 for the Lamb shift defined by⁽⁴⁾

$$\ln(K_0/R) = Q(2)/P(2) \quad , \quad (21)$$

our values for $Q(2)$ and $P(2)$ lead to $K_0/R = 19.770$, whereas Harriman gave $K_0/R = 19.76967 \pm 0.00006$.

The average excitation energy I appearing in the Bethe stopping power formula^(1,2) is defined by

$$\ln(I/R) = Q(0) \quad . \quad (22)$$

Thus our value of $Q(0) = 0.096982$ leads to $I = 1.10184 R = 14.990$ eV. It is hoped that this value is more accurate than that previously given, 15.0 eV.⁽⁷⁾ [Bethe originally gave $I = 1.105 R$ ⁽¹⁾ and later $I = 1.103 R$.⁽²⁾]

Another type of average excitation energy I_1 , defined by

$$\ln(I_1/R) = Q(1)/P(1) \quad , \quad (23)$$

appears in the theory of statistical fluctuation of energy loss of particles in matter.⁽⁸⁾ Using the values in Tables 2 and 3, we obtain $\ln(I_1/R) = 0.57087$ or $I_1 = 1.76981 R = 24.078$ eV, for the hydrogen atom. This quantity does not seem to have been calculated before.

Some of the moments $P(s)$ are connected with optical properties of atomic hydrogen. The refractive index n at 0°C, 1 atm, is given by

$$n - 1 = 8\pi (N_L a_0^3) \sum_n \frac{f_n}{E_n^2 - h^2 \nu^2 / R^2} \quad (24)$$

where N_L is the Loschmidt number, ν the frequency, and the sum is taken over all the excited states, discrete as well as continuum. The right-hand side can be expressed in a series

^{*}Actually Harriman gives $P_d(2)$, $P_c(2)$, $Q_d(2)$, and $Q_c(2)$ multiplied by 3/16 in his Table I.

$$\begin{aligned}
n - 1 = & 1.00076 \times 10^{-4} [P(-2) \\
& + 8.30408 \times 10^{-11} \lambda^{-2} P(-4) \\
& + 6.89577 \times 10^{-21} \lambda^{-4} P(-6) \\
& + 5.72630 \times 10^{-31} \lambda^{-6} P(-8) \\
& + 4.75516 \times 10^{-41} \lambda^{-8} P(-10) + \dots] \quad , \quad (25)
\end{aligned}$$

where the wave length λ is measured in A. Inserting our values of $P(s)$, we obtain

$$\begin{aligned}
n - 1 = & 1.12586 \times 10^{-4} \\
& + 1.38074 \times 10^{-14} \lambda^{-2} + 1.85668 \times 10^{-24} \lambda^{-4} \\
& + 2.60138 \times 10^{-34} \lambda^{-6} + 3.72252 \times 10^{-44} \lambda^{-8} \\
& + \dots] \quad . \quad (26)
\end{aligned}$$

The Verdet constant V for a gas of atoms in an S state at 0°C , 1 atm, is given by⁽⁹⁾

$$V = 64 \pi^3 (e/R)(a_0/\lambda)^2 (N_L a_0^3) \sum_n \frac{f_n}{(E_n^2 - h^2 \nu^2/R^2)^2} \quad , \quad (27)$$

or

$$\begin{aligned}
\lambda^2 V = & 1.67615 \times 10^{-14} [P(-4) + 1.66082 \times 10^{-10} \lambda^{-2} P(-6) \\
& + 2.06873 \times 10^{-20} \lambda^{-4} P(-8) + \dots] \quad , \quad (28)
\end{aligned}$$

where the wavelength λ is measured in A, and V in minutes/oersted cm. Our $P(s)$ values lead to

$$\begin{aligned}
\lambda^2 V = & 2.78485 \times 10^{-14} + 7.48960 \times 10^{-24} \lambda^{-2} \\
& + 1.57404 \times 10^{-33} \lambda^{-4} + \dots \quad (29)
\end{aligned}$$

The dipole-dipole interaction energy U between two atoms at a separation of d is expressed by the celebrated London formula^(10,11)

$$\frac{U}{2R} = -12S \left(\frac{a_0}{d} \right)^6 \quad , \quad (30)$$

where

$$S = \sum_n \sum_{n'} \frac{f_n f_{n'}}{E_n E_{n'} (E_n + E_{n'})} \quad (31)$$

The double sum in (31) is taken over all the excited states, discrete as well as continuum. A convenient method of evaluating the sum S is to express it in terms of the moments $P(s)$,* though direct evaluation is also possible. Using an expansion

$$\begin{aligned} \frac{E_n E_{n'}}{E_n + E_{n'}} &= \frac{1}{E_n^{-1} + E_{n'}^{-1}} = [1 - 1/2 (1 - E_n^{-1}) - 1/2 (1 - E_{n'}^{-1})]^{-1} \\ &= \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \frac{(j+k)!}{j! k!} 2^{-j} (1 - E_n^{-1})^j 2^{-k} (1 - E_{n'}^{-1})^k, \end{aligned}$$

which converges for all E_n because $E_n \geq E_2 = 3/4$, we can rewrite S as

$$S = \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \frac{(j+k)!}{j! k!} m_j m_k, \quad (32)$$

where m_j is defined by

$$\begin{aligned} m_j &= 2^{-j} \sum_n \frac{f_n}{E_n^2} \left[1 - \left(\frac{1}{E_n} \right)^j \right] \\ &= 2^{-j} \sum_{p=0}^j \binom{j}{p} (-1)^p P(-p-2). \end{aligned} \quad (33)$$

Putting the values of $P(s)$ into the right-hand side of (33), we find that m_j decreases rapidly with increase of j so that the series (32) is rapidly convergent. Thus simple numerical evaluation of the sum (32) gives $S = 0.541557 \pm 0.00004$. Our value $12S = 6.49864 \pm 0.0005$ can be compared with Eisenschitz and London's result $6.47^{(13)}$ evaluated by direct numerical summation (31), and with Pauling and Beach's $6.49903 \pm 0.00001^{(14)}$ obtained by a variational calculation of interatomic interaction. The agreement of our result with Pauling and Beach's within the limit of error confirms their calculation.

*This method is due to Platzman.⁽¹²⁾

In the case of one-electron atomic ions such as He^+ , Li^{++} , etc. with nuclear charge Z , the quantities $P(s, Z)$ and $Q(s, Z)$ defined by the same expressions as Equations (8) through (13) can be expressed in terms of Z and the hydrogenic quantities $P(s)$ and $Q(s)$:

$$\begin{aligned} P(s, Z) &= Z^{2s} P(s) \quad , \\ Q(s, Z) &= Z^{2s} [Q(s) + 2P(s) \ln Z] \quad . \end{aligned}$$

These relations enable one readily to evaluate $P(s, Z)$ and $Q(s, Z)$ with the aid of Tables 2 and 3.

The Bethe Asymptotic Cross Section for Inelastic Impacts of Charged Particles

The total cross section for excitation to the state n of an atom by impact of a fast electron is expressed by^(1,15)

$$Q_n = \frac{4\pi a_0^2}{T/R} \cdot M_n^2 \ln \frac{4Tc_n}{R} \quad , \quad (34)$$

where T denotes the kinetic energy of the incident electron. For other charged particles the above formula applies with the following modification. Namely, the right-hand side of (34) contains an additional factor z^2 , and T should be replaced by $mv^2/2$, where ze is the charge on the particle, v the incident velocity, and m the electron mass. The constant c_n is defined by⁽¹⁵⁾

$$\begin{aligned} \ln c_n &= -2 \ln E_n + \int_0^\infty \frac{f_n(K)}{f_n} d \ln Q \\ &\quad - \int_{-\infty}^0 [1 - f_n(K)/f_n] d \ln Q \quad , \end{aligned} \quad (35)$$

where $Q = a_0^2 K^2$ and $f_n(K)$ is the generalized oscillator strength^(1,15)

$$f_n(K) = \frac{E_n}{a_0^2 K^2} \left| \int \psi_n^* \exp(i \vec{K} \cdot \vec{r}) \psi_0 d\vec{r} \right|^2 \quad . \quad (36)$$

For excitation to discrete nP states of the hydrogen atom, explicit evaluation of (35) gives⁽¹⁾

$$\ln c_n = 2 \ln \frac{n}{n-1} - \sum_{t=1}^{n+2} \frac{c_{nt}}{t} \quad , \quad (37)$$

where

$$c_{nt} = 1 - \left(\frac{n+1}{n-1} \right)^{2n-6} \left[\sum_{k=0}^{t-6} \binom{n-3}{k} \nu^k + 3 \frac{n+1}{n-1} \binom{n-3}{1-5} \nu^{t-5} \right], \quad (38)$$

$$\nu = -4n/(n+1)^2$$

It should be noted that the first and the second term in the square bracket in the right-hand side of (38) are replaced by zero for $1 \leq t \leq 5$ and for $1 \leq t \leq 4$, respectively.

Table 4 is a tabulation of $\ln c_n$, c_n and the square of the dipole matrix element $M_n^2 = f_n/E_n$ for $n = 2$ through $n = 30$. In Figure 1 the value of $-\ln(c_n E_n)$ is plotted against E_n . Surprisingly, the points lie very closely on a straight line. The reason for this behavior remains obscure.

Table 4

Calculated values of c_n and M_n^2

n	$\ln c_n$	c_n	M_n^2
2	-6.970389×10^{-1}	0.4980579	5.549289×10^{-1}
3	-2.724031×10^{-1}	0.7615472	8.898926×10^{-2}
4	-1.153766×10^{-1}	0.8910305	3.092376×10^{-2}
5	-4.121289×10^{-2}	0.9596248	1.451911×10^{-2}
6	-5.323850×10^{-4}	0.9994678	8.022334×10^{-3}
7	2.413091×10^{-2}	1.024424	4.914241×10^{-3}
8	4.019261×10^{-2}	1.041011	3.233958×10^{-3}
9	5.122916×10^{-2}	1.052564	2.243810×10^{-3}
10	5.913456×10^{-2}	1.060918	1.621583×10^{-3}
11	6.499043×10^{-2}	1.067149	1.210525×10^{-3}
12	6.944946×10^{-2}	1.071918	9.278785×10^{-4}
13	7.292114×10^{-2}	1.075646	7.270413×10^{-4}
14	7.567721×10^{-2}	1.078614	5.803639×10^{-4}
15	7.790112×10^{-2}	1.081016	4.707160×10^{-4}
16	7.972316×10^{-2}	1.082987	3.870904×10^{-4}
17	8.123376×10^{-2}	1.084624	3.221906×10^{-4}
18	8.249616×10^{-2}	1.085994	2.710473×10^{-4}
19	8.356648×10^{-2}	1.087157	2.301954×10^{-4}
20	8.448558×10^{-2}	1.088157	1.971680×10^{-4}
21	8.527110×10^{-2}	1.089012	1.701757×10^{-4}
22	8.595301×10^{-2}	1.089755	1.478992×10^{-4}
23	8.654703×10^{-2}	1.090403	1.293511×10^{-4}
24	8.706917×10^{-2}	1.090972	1.137820×10^{-4}
25	8.753315×10^{-2}	1.091478	1.006168×10^{-4}
26	8.794082×10^{-2}	1.091923	8.940830×10^{-5}
27	8.830330×10^{-2}	1.092319	7.980591×10^{-5}
28	8.863024×10^{-2}	1.092677	7.153173×10^{-5}
29	8.891868×10^{-2}	1.092992	6.436372×10^{-5}
30	8.918676×10^{-2}	1.093285	5.812286×10^{-5}

Figure 1

Equations (34) and (35) hold for excitation to the continuum when f_n and $f_n(K)$ are replaced by df/dk and $df(K)/dk$, respectively, the latter being defined by (36) with ψ_n and E_n replaced by ψ_k and E_k . Thus summation over all the discrete excited states and integration over the entire continuum give the total excitation cross section Q_{ex} and the total ionization cross section Q_{ion} , respectively:

$$Q_{ex} = \frac{4\pi a_0^2}{T/R} M_{ex}^2 \ln \frac{4Tc_{ex}}{R} \quad , \quad (39)$$

$$Q_{ion} = \frac{4\pi a_0^2}{T/R} M_{ion}^2 \ln \frac{4Tc_{ion}}{R} \quad , \quad (40)$$

where

$$M_{ex}^2 = \sum_{ex} M_n^2 = P_d(-1) \quad , \quad (41)$$

$$M_{ex}^2 \ln c_{ex} = \sum_{ex} M_n^2 \ln c_n \quad , \quad (42)$$

$$M_{ion}^2 = \int_{ion} M_n^2 = P_c(-1) \quad , \quad (43)$$

$$M_{ion}^2 \ln c_{ion} = \int_{ion} M_n^2 \ln c_n \quad . \quad (44)$$

Here $\sum_{ex}$ denotes the summation over all the discrete excited states, and $\int_{ion}$ integration over the entire continuum. The total inelastic cross

section Q_{in} can be written as

$$Q_{in} = Q_{ex} + Q_{ion} = \frac{4\pi a_0^2}{T/R} M_{tot}^2 \ln \frac{4Tc_{tot}}{R} \quad , \quad (45)$$

where

$$M_{tot}^2 = M_{ex}^2 + M_{ion}^2 = P(-1) \quad , \quad (46)$$

$$M_{tot}^2 \ln c_{tot} = M_{ex}^2 \ln c_{ex} + M_{ion}^2 \ln c_{ion} \quad . \quad (47)$$

In the case of the hydrogen atom M_{tot}^2 is equal to unity, and the following sum rule for $\ln c_n$ can be derived:*

$$\sum_n M_n^2 \ln (c_n E_n^2) = I_1 - I_2 \quad , \quad (48)$$

where

$$I_1 = \int_1^\infty \frac{dQ}{Q^2} [1 - |u_0(K)|^2] \quad , \quad (49)$$

$$I_2 = \int_0^1 \frac{dQ}{Q} \left\{ 1 - \frac{1}{Q} [1 - |u_0(K)|^2] \right\} \quad , \quad (50)$$

$$u_0(K) = \int |\psi_0|^2 \exp(i \vec{K} \cdot \vec{r}) d\vec{r} \quad . \quad (51)$$

In Equation (48), $\sum_n$ means the sum over all the excited states, discrete as well as continuum. Using explicit form of the ground state wave function in (49) - (51), we obtain

$$I_1 - I_2 = \ln 4 - 13/12 \quad . \quad (52)$$

Then Equations (47), (48), and (52) enable us to give

$$\ln c_{tot} = \ln 4 - 13/12 - 2Q(-1) \quad . \quad (53)$$

*The content of this sum rule was implicitly used by Bethe^(1,2). The above explicit form and its generalization to many-electron atoms, however, are due to Platzman.⁽¹²⁾

Thus, once $\ln c_{ex}$ is calculated by performing the sum in (42), $\ln c_{ion}$ is readily obtained by the use of (47) and (53). On evaluating the sum in (42), the contribution from terms with $n \leq 30$ was calculated from Table 4, while the contribution from $n > 30$ was estimated by using the asymptotic value

$$M_n^2 \ln c_n \rightarrow D n^{-3} \quad \text{for } n \rightarrow \infty, \quad (54)$$

$$D = 2.31197$$

of Brown.⁽¹⁶⁾ Equation (54) implies

$$\lim_{n \rightarrow \infty} \ln c_n = 0.092955.$$

$$n \rightarrow \infty$$

This value is consistent with the limiting behavior of our c_n given in Table 4 and Figure 1, and has been confirmed by Platzman's independent calculation based on the zero-energy continuum wave function.⁽¹²⁾

Following are our calculated values of constants in the cross section formulas (39), (40), and (45):

$$M_{ex}^2 = 0.7165875$$

$$M_{ion}^2 = 0.2834125$$

$$\ln c_{ex} = -0.578017$$

$$c_{ex} = 0.561010 = 1/1.782499 \text{ (1/1.79)}$$

$$\ln c_{ion} = 3.047390$$

$$c_{ion} = 21.0603 = 1/0.0474827 \text{ (1/0.048)}$$

$$\ln c_{tot} = 0.449469$$

$$c_{tot} = 1.56748 = 1/0.637967 \text{ (1/0.638)}$$

Values in parentheses are those originally calculated by Bethe.⁽¹⁾

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A MUSCLE-EQUIVALENT ENVIRONMENTAL RADIATION METER OF EXTREME SENSITIVITY*

Jacob Kastner, John E. Rose, and F. R. Shonka**

Abstract

A 16.5-liter spherical ion chamber was constructed of conduction muscle-equivalent plastic and filled to 760 mm Hg with a muscle-equivalent gas. The use of the chamber for measurements of natural environmental backgrounds was made quite feasible with the aid of the recently developed Shonka vibrating quartz fiber electrometer. This instrument is routinely operable at the extremely high sensitivity of better than 5000 divisions per volt. This system, therefore, has made possible reproducible measurements of absorbed dose rates of fractions of the micro-rad per hour without any need for the usual corrections for wall effect, stopping power, and so forth.

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DIFFUSION AND ABSORPTION OF GASES IN PLASTIC-WALLED IONIZATION CHAMBERS*

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with the Technical Assistance of T. Prevender

Abstract

In the design of stable, tissue-equivalent ionization chambers, important factors are the solubility and permeability of the wall materials to the contained gases. Diffusion measurements for N_2 , O_2 , He, CO_2 , CH_4 , C_2H_6 , C_2H_4 and Ne have been carried out on thin discs of a variety of tissue-simulating plastics.

The data are used for the determination of the equilibrium times and pressure changes to be expected for typical large, thick-walled, ion chambers.

Introduction

A matter of some concern in the design of tissue-equivalent⁽¹⁾ ionization chambers is a knowledge of the solubility and permeability of the wall materials to the enclosed gases. Direct measurement on full-scale chambers is difficult because changes in gas pressure may be small except over periods of months. In order to reduce the measurement time and magnify the effects, diffusion and solubility measurements have been made on thin discs of several plastics. The results have been applied to typical ionization chamber designs.

If at $t = 0$ a gas is admitted to one side of a plane slab of plastic initially free of that gas, there will be a delay before the gas reaches a steady rate of diffusion through the slab (see Figure 2). This delay, L , is

Figure 2

Diffusion of gas through a slab as a function of time. The ordinate is proportional to the number of molecules of gas which has penetrated the slab. The abscissa is the length of time that the gas has been exposed to one side. Time L is obtained by extrapolating the straight line portion back to the abscissa.

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directly related to the diffusion coefficient, D , and to the thickness of the slab, w :(2)

$$L = \frac{w^2}{6D} \quad (1)$$

After a time $t = 2L$, there will be a constant rate of flow through the slab (assuming that the concentration difference $C_1 - C_0$ is held constant) which is given by:

$$F = AD \frac{\alpha(C_1 - C_0)}{w} \quad t > 2L \quad (2)$$

where

- $\alpha D = \bar{P}$ = permeability coefficient (cm^2/sec)
- D = diffusion coefficient (cm^2/sec)
- A = area of slab (cm^2)
- F = flow of gas through slab (molecules/sec)
- C_1 = concentration of gas on high pressure side (molecules/ cm^3)
- C_0 = concentration of gas on low pressure side (molecules/ cm^3)
- w = thickness of slab (cm)
- α = solubility of gas in slab material (dimensionless)

The solubility α is here defined as the ratio, at equilibrium, of the number of molecules of a particular gas dissolved in unit volume of solid to the number of molecules per unit volume of that gas in contact with it (see Figure 3). This

definition of solubility enables one to use the same units (cm^2/sec) for both the diffusion coefficient, D , and the permeability coefficient, αD .

Figure 3

Steady state concentrations of gas within and outside a slab which show the effect of the solubility, α .

Measurement of the time delay, L , for a slab of known thickness yields D , and measurement of the subsequent permeation rate, F , yields αD . Therefore, measurement of the penetration of gas through a slab as a function of time provides values of both the diffusion coefficient, D , and the solubility, α , from which the behavior of the gas filling in an ionization chamber of that material may be calculated.

Procedure

Figure 4 shows a diagram of the cell* used in these measurements. The upper and lower chambers of this cell were separated by a thin disc of the plastic to be tested. Each disc was 2 inches in diameter, from 0.015 to 0.03 inch thick, and was supported by a stainless steel grid. A tight seal was provided by a knife edge and by neoprene O-rings both above and below the plastic disc. The region at the periphery of the disc was evacuated. The area of the disc used in Expression (2) was that inside the knife edge, 8.89 cm^2 . Replacing the supporting steel grid with a fine glass frit produced no change in permeation rate; so any reduction of the effective disc area by the grid was assumed to be negligible. With the disc sealed in place, the upper and lower chambers were evacuated for a time comparable to $3L$. The lower and upper valves were closed, and the small pressure rise due to outgassing was measured as a function of time. The lower chamber was again evacuated, and at time zero, the test gas was admitted to the upper chamber at a pressure between 100 and 800 mm of mercury. The subsequent pressure rise in the lower chamber, corrected for outgassing, yielded data like that in Figure 2. The gas concentration C_0 in the collecting volume during a run was always negligible compared to C_1 .

Figure 4
Diffusion cell.

*Modified version of design proposed by G. Failla, Radiological Research Laboratory, Columbia University, New York, N. Y.

The chamber was evacuated by a mechanical pump, oil diffusion pump, and liquid nitrogen trap. Pressure in the lower chamber was measured continuously by a thermocouple gauge and Brown recorder. The gauge was calibrated for each gas at each temperature using a McLeod gauge. Additional collecting volume was connected to the lower chamber when necessary to keep the vacuum gauge in a convenient range. Several recent runs (collecting volume 384.2 cm³ in Table 5) used an Alphatron 530 vacuum gauge (NRC Equipment Corporation), the linearity of which, over a wide range in pressure, proved to be convenient.

Table 5
Experimental results The membrane area A was 8.89 cm² for all measurements except those with the 0.0254-cm membrane for which A was 13.2 cm²

Material	Gas	Temperature, deg C	Pressure mm Hg	Thickness (w) cm	Collecting volume cc	Rate of steady state pressure rise microns/min	Time intercept (L) min	Solubility (a)	Diffusion coefficient (D) cm ² /sec	Permeability coefficient (P) cm ² /sec
A-153	N ₂	70	734	0.0296	1013.4	3.33	12.6	1.3	1.9×10^{-7}	2.6×10^{-7}
	N ₂	50	302	0.0296	406.0	2.28	28.9	2.0	8.4×10^{-8}	1.7×10^{-7}
	N ₂	30	400	0.0296	1013.4	0.803	78.9	3.7	3.1×10^{-8}	1.1×10^{-7}
	CO	70	760	0.0296	1013.4	2.96	18.3	1.6	1.3×10^{-7}	2.2×10^{-7}
	CO	50	550	0.0296	1013.4	1.54	46.0	3.0	5.3×10^{-8}	1.6×10^{-7}
	CO	30	254	0.0296	1013.4	0.436	122.6	4.9	2.0×10^{-8}	9.6×10^{-8}
	CH ₄	70	360	0.0296	1013.4	1.27	47.7	3.9	5.1×10^{-8}	2.0×10^{-7}
	CH ₄	30	276	0.0296	1013.4	0.335	416.3	11.7	5.8×10^{-9}	6.8×10^{-8}
B-100	N ₂	70	761	0.0146	11.4	9.16	5.5	0.035	1.1×10^{-7}	3.8×10^{-9}
	N ₂	30	760	0.0146	11.4	1.37	43.7	0.041	1.4×10^{-8}	5.6×10^{-10}
	CO	70	760	0.0146	11.4	12.0	4.5	0.037	1.3×10^{-7}	5.0×10^{-9}
	CO	50	760	0.0146	11.4	5.82	13.7	0.055	4.3×10^{-8}	2.4×10^{-9}
	CH ₄	70	535	0.0146	11.4	13.4	3.6	0.048	1.6×10^{-7}	7.8×10^{-9}
	CH ₄	50	760	0.0146	28.8	4.10	12.2	0.088	4.8×10^{-8}	4.2×10^{-9}
	O ₂	70	639	0.0146	11.4	20.5	2.7	0.046	2.2×10^{-7}	1.0×10^{-8}
	O ₂	50	760	0.0146	28.8	5.28	7.2	0.066	8.2×10^{-8}	5.5×10^{-9}
A-150	N ₂	70	351	0.0185	11.4	3.86	11.8	0.054	8.1×10^{-8}	4.4×10^{-9}
	N ₂	30	600	0.0185	28.8	0.421	116.0	0.085	8.2×10^{-9}	7.0×10^{-10}
	CO	70	370	0.0185	11.4	6.54	10.8	0.079	8.8×10^{-8}	7.0×10^{-9}
	CO	30	500	0.0185	28.8	0.542	116.8	0.13	8.1×10^{-9}	1.1×10^{-9}
	CH ₄	70	350	0.0185	11.4	7.73	8.6	0.079	1.1×10^{-7}	8.7×10^{-9}
	CH ₄	30	750	0.0185	28.8	0.755	76.0	0.080	1.2×10^{-8}	1.0×10^{-9}
	O ₂	70	357	0.0185	11.4	11.1	6.2	0.080	1.5×10^{-7}	1.2×10^{-8}
	O ₂	30	370	0.0185	28.8	0.977	43.7	0.12	2.2×10^{-8}	2.6×10^{-9}
	CO ₂	70	407	0.0185	105.6	9.72	12.1	1.1	7.9×10^{-8}	8.8×10^{-8}
	CO ₂	30	750	0.0185	1013.4	0.205	93.9	1.0	1.0×10^{-8}	9.6×10^{-9}
	C ₂ H ₄	29	301	0.0185	384.2	0.0192	158.5	0.14	6.0×10^{-9}	8.5×10^{-10}
	C ₂ H ₆	27	395	0.0160	384.2	0.037	102.8	0.15	6.9×10^{-9}	1.0×10^{-9}
	Ne	50	341	0.0185	384.2	0.188	0.8	0.006	1.2×10^{-6}	7.4×10^{-9}
	Ne	30	348	0.0185	384.2	0.054	2.9	0.006	3.2×10^{-7}	2.1×10^{-9}
P-1	N ₂	70	777	0.0243	89.0	3.15	0.9	0.009	1.8×10^{-6}	1.6×10^{-8}
	N ₂	28	760	0.0254	60.0	0.76	13.1	0.014	1.4×10^{-7}	1.9×10^{-9}
	CO	70	747	0.0243	105.6	3.97	1.2	0.019	1.4×10^{-6}	2.6×10^{-8}
	CO	27	760	0.0254	82.0	0.74	16.2	0.023	1.1×10^{-7}	2.5×10^{-9}
	CH ₄	70	747	0.0243	105.6	7.34	2.1	0.06	7.8×10^{-7}	4.7×10^{-8}
	CH ₄	28	760	0.0254	178.0	0.81	14.2	0.05	1.3×10^{-7}	5.6×10^{-9}

Results

Diffusion and solubility measurements for three tissue-equivalent plastics and for polyethylene are listed in Table 5. Representative measurements are plotted in Figure 5, together with some values reported earlier.⁽³⁾ The composition by weight of these plastics is as follows (see Shonka et al.⁽¹⁾ for discussion of their radiation equivalence).

A-150 Tissue equivalent-muscle (for photons and neutrons):

Nylon-Zytel	35.22%	Compression molded at 160°C.
Carbon	16.06%	
Polyethylene	45.14%	
Calcium fluoride	3.58%	

A-149 Same as A-150 but prepared at an earlier time with the addition of 0.1% stearic acid.A-153 Tissue equivalent-muscle (insensitive to neutrons):

Teflon	56.75%	Sintered in air at 380°C.
Carbon	43.25%	

B-100 Tissue equivalent-bone (for photons and neutrons):

Nylon-Zytel	21.6%	Compression molded at 160°C.
Carbon	14.0%	
Polyethylene	30.0%	
Calcium fluoride	34.4%	

P-1 Polyethylene (Marlex 50 supplied by Phillips Chemical Company). Compression molded at 160°C.

Figure 5

Plot of experimental results for permeability coefficient P and diffusion coefficient D for several gases in four materials at about 30°C. Note that $P = \alpha D$, so that solubility α can also be determined from this plot.

In Figure 5, a number of relationships in the data are clear. A-153 shows much higher permeability than the other materials due primarily to the high solubility of the gases within it. The permeability even for this material is due to solution diffusion,⁽²⁾ as is partially verified in Figure 6 by the strict linearity between rate of flow F and upper chamber pressure C_1 . For each of the four similar materials, A-150, A-149, B-100, and P-1, the relative positions of the different gases in a plot such as Figure 5 are similar, carbon dioxide having several times the permeability of the other gases. Data for B-100 would fall between that for A-150 and A-149. The rare gases plot well to the right of the others, which indicates that they penetrate a membrane more quickly, but that the amount of gas which penetrates per unit of time

Figure 6

Steady state flow F versus gas pressure C_1 . The linearity of the plot shows that the permeability coefficient, αD , is independent of pressure.

is not correspondingly large because the concentration gradient within the membrane is limited by the low solubility.

Measurement of the permeability and diffusion coefficients at the several temperatures shown in Table 5 can be used to estimate the temperature dependence of these coefficients. It is shown by Barrer⁽²⁾ that the permeability, $\bar{P}$, and diffusion, D , coefficients of polymer-gas systems conform to equations of the type

$$\bar{P} = \bar{P}_0 e^{-E/RT} \quad (3)$$

where E is an activation energy, R is the universal gas constant, and T is absolute temperature. Thus a semilogarithmic plot of $\bar{P}$ versus the reciprocal of the absolute temperature yields straight lines (Figure 7). Similar lines can be drawn for the diffusion coefficients and solubilities, except that solubility is much less dependent on temperature. Several instances of a slight increase

of solubility with temperature in Table 5 should be interpreted as no significant change in α with T .

Application

Assuming that the solubilities and permeability coefficients we have measured apply to thick walls of these plastics, we can calculate the equilibrium times and the pressure changes to be expected for actual ionization chambers. Notice that the time necessary to reach equilibrium permeation, about $2L$, increases as the square of the wall thickness and may be days or months for chamber walls. This is important in evaluating the pressure stability of chamber fillings because at times much less than L after a chamber has been filled with gas, the rate of flow into the chamber wall will be much larger than the final permeation rate. This flow rate is given by

$$F = \frac{A D \alpha C_1}{\sqrt{\pi D t}} \quad t < L \quad (4)$$

where the symbols have the same meanings as above. This expression follows from differentiation of Barrer's expression(4) for the concentrations of gas near the surface of a semi-infinite solid initially free of gas. The

Figure 7

Temperature dependence of the permeability coefficient for representative gases in A-153 (upper two) and A-150 (lower six).

10 days after the admission of the gas, the rate of pressure drop would still be about four times that due to steady permeation. One day after filling, the rate would be over 12 times the steady rate. If the chamber had been filled and sealed immediately at $t = 0$, the total drop in pressure by $t = 2L$ would have been $4L$ times the steady state rate of pressure drop. (This follows either from integration of Expression (4) or from calculating the gas content of the wall at equilibrium).

rate of flow as given by this expression would equal the final steady state flow given by Expression (2) for $C_0 = 0$ when $t = w^2/\pi D$, or $t = 2L$. For simplicity, the expressions for plane slabs have been used to estimate the behavior of chambers. Barrer(4) gives exact solutions for different geometries. Expression (1) for L , however, holds both for plane slabs and for spherical shells.

Suppose that a plastic chamber has not recently been exposed to a particular gas. The chamber is evacuated, and at time $t = 0$ the gas is admitted. The gas pressure is maintained constant for a time t , and then the chamber is sealed off. If the time t is less than $2L$, then it is clear from the above that the rate of flow of gas into the wall at that time will be about $\sqrt{2L/t}$ times the steady rate. The value of L for a chamber made of A-150 plastic with a wall one-quarter inch thick would typically be about 11 weeks ($D = 10^{-8} \text{ cm}^2/\text{sec}$, $w = 0.635 \text{ cm}$). Thus, even

The rate of pressure drop dp/dt due to steady permeation from a chamber with gas volume V is given by:

$$-\frac{1}{p} \frac{dp}{dt} \approx \frac{A\alpha D}{Vw} = \frac{A\bar{P}}{Vw} \quad t > 2L \quad (5)$$

where p is the partial pressure of the particular gas in the chamber, w is the thickness of the chamber wall, A is the area of the wall, and $\bar{P}$ is the permeability coefficient, αD . If the chamber is a spherical shell, this area would be exactly $4\pi ab$ where a and b are its inner and outer radii. Expression (5) follows from Expression (2), provided that the outside concentration C_0 for the gas is negligible and that the pressure drop is small enough that C_1 may be assumed constant. A typical value of $\bar{P}$ for tissue equivalent-muscle (A-150) would be $2 \times 10^{-9} \text{ cm}^2/\text{sec}$. In a spherical chamber 12 inches in diameter with a wall thickness of one-quarter inch, this value of $\bar{P}$ would yield a pressure drop of 2.0%/year. Apparently permeation will only be a serious problem with this material for very small chambers since pressure drop in Expression (5) is inversely proportional to both wall thickness and chamber diameter.

A 12-inch diameter, quarter-inch thick spherical chamber, if made of A-153, would show, however, a 2%/week pressure drop ($\bar{P} = 10^{-7} \text{ cm}^2/\text{sec}$). Enclosing such a chamber in a relatively impermeable sheath would not help much because half the gas filling would be absorbed by the walls before equilibrium was reached ($\alpha = 5$ to 10).

Whenever the wall volume times the solubility is not small compared to the gas volume (as for A-153 above, or for a small chamber of A-150), considerable reduction in pressure drop could be obtained by holding constant the pressure of the filling gas for a time $2L$ before sealing the chamber. If the chamber were immersed in filling gas for a time $L/2$ so that both sides of the wall came to equilibrium, there would be practically no change in the filling gas for a time L after sealing. If such equilibration were impractical due to the time involved, L could be shortened by a factor of 10 by equilibrating at 70°C , rather than at 30°C , at a somewhat higher pressure to correct for the reduced solubility.

Summary

Permeability measurements have been carried out for various gases through thin discs of typical ionization chamber plastics. The diffusion and solubility data obtained can be used for the evaluation of pressure changes to be expected for large and small, thick-walled, ion chambers filled with the usual variety of tissue-equivalent gases.

We wish to thank Dr. F. R. Shonka of St. Procopius College for providing us with molded discs of his plastic material.

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A NEW ELECTROMETER OF HIGH SENSITIVITY*

Francis R. Shonka,** G. Failla[†] and John E. RoseAbstract

This electrometer consists of a movable quartz fiber element which, at zero potential, is in stationary equilibrium in a strong ac electric field. A dc signal on the fiber causes it to oscillate. The motion of the fiber is viewed in a microscope. Designed as a detector to establish a null between the dc signal and a bucking voltage, the electrometer operates readily at sensitivities in excess of 5000 divisions per volt or nearly 10^{16} divisions per coulomb. Other features not common to existing electrometers include extreme ruggedness and stability, low inherent capacity, negligible geotropism, wide voltage range, portability, small size and ability to measure its own contact potential. It is extremely non-linear and cannot be damaged or paralyzed by excessively large signals. The present model has the disadvantage of viewing through a microscope.

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PORTABLE POWER SUPPLY FOR THE SHONKA ELECTROMETER

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Field measurements with a muscle equivalent radiation meter⁽¹⁾ necessitated the development of a compact battery-powered control unit for the Shonka Electrometer.^(2,3)

The requirements for the unit were that it do essentially the same as the mains-operated Shonka Electrometer control described in Figure 2 of Reference 2. We also decided to incorporate the collection, compensation and illumination potentials necessary for the operation of the radiation meter.

A system with reasonable battery life and temperature independence was developed to meet the specifications and is described below.

Figure 8 is a schematic diagram of the circuit. The ac power supply consists of a stable Wein Bridge oscillator with both positive and negative voltage feedback. Negative current feedback is used to improve the temperature stability. Appropriate amplifying and impedance matching stages drive a medium power complementary pair terminating in a step-up transformer which supplied the required alternating voltage. The network beyond the transformer was designed to reduce power consumption. With a Mallory 27-volt Mercury Battery #302580, the life of this section is 150 hours. For stability 1% deposited carbon resistors were used in this network, in the compensation potential network, and in the oscillator stage. All other resistors, except where noted, are $\frac{1}{2}$ -watt carbon.

The complete unit has been tested in the laboratory and in the field and proven useable in ambient temperatures ranging from freezing to those of a Texas summer.⁽⁴⁾

Thermal insulation of the collecting-potential source (two 42-volt Mallory Mercury Batteries #RM-415) is essential for operating stability over this temperature range. Thermal insulation proved unnecessary for the calibration and compensation-potential sources (1.35-volt Mallory Mercury Batteries #302651), which vary by less than 2 millivolts per hour owing to temperature changes in this range.

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MEASUREMENT OF THE COSMIC-RAY NEUTRON BACKGROUND

Jacob Kastner, B. G. Oltman and L. D. Marinelli

The natural environmental fast neutron dose being received by man may be an important fraction of the total. Studies at Argonne of the fast neutron background centered around the "twin" scintillators fast neutron spectrometer first described by Berlman and Marinelli⁽¹⁾ and later improved by Berlman et al.⁽²⁾

The maximum response of this type of fast neutron detector is obtained, as pointed out by Marinelli,⁽³⁾ when one of the solutions has a relatively low proton-electron ratio and the other has a high concentration of electrons. The combination now employed by us is xylene and hexafluorobenzene (C_6F_6). The latter is a rare compound which only recently became available as a special product of 97% purity from the Imperial Smelting Company in England. The pulse height of the material as received relative to xylene is 25%,⁽⁴⁾ which is quite good enough.

Figure 9 shows the electronic system for pulse height analysis of the two cells. Each of the solutions is viewed by a pair of photomultipliers operated in coincidence. The outputs from a pair are summed, amplified and then fed to the input of a 400 channel pulse height analyzer (P.H.A.). The spectrum from each of the two solutions is recorded in the opposing halves of the analyzer memory, thus permitting simultaneous recording of the data from both, neglecting coincidences between cells. The gamma-ray induced distribution in C_6F_6 must be corrected for its higher electron density before subtracting it from that of the xylene to get the net proton recoil distribution.

Figure 9

Block diagram of one half of twin scintillator

The twin system proved to be an excellent system for fast neutron spectroscopy when the ratio of neutrons to gammas is not too small ($>1\%$).

Figure 10

Comparison of response of "twin" liquid scintillators, C_8H_{10} and C_6F_6 to 14-MeV neutrons

Figure 10 shows the difference in the response of the twin scintillators to an essentially monoenergetic neutron flux. The system proved to be disappointing, however, as a tool for background studies simply because of the relatively large errors produced by internal radioactive contamination of the system. Numbers which made sense could only be developed after many subsidiary operations and manipulation of the data.⁽⁵⁾

On the other hand, pulse shape discrimination circuits have been reported⁽⁶⁻¹²⁾ and even become commercially available. These have proved to be superior to the "twins" for the unequivocal determination of the small but significant numbers of fast neutrons with which we are continuously being bombarded.

Our hope in developing these techniques is based on the use of large, hydrogen-rich organic scintillators, to provide the necessary high efficiency and tissue-like characteristics. Furthermore we want reasonable portability for field studies.

We have tested two different electronic circuits designed to discriminate between neutron and gamma-ray produced scintillations (see Figure 11). Both circuits utilize an RCA type 6810A 14-stage PM tube. Stilbene has been employed with the circuit of Broek and Anderson⁽⁸⁾ wherein the discrimination pulses which gate the pulse height analyzer to admit neutron events are taken from the last dynode of the photomultiplier. The latter is operated with only a small accelerating potential between the dynode and the anode so that space charge limitation of the anode current occurs with large pulses. Under the proper conditions of operation proton-recoil scintillations will produce positive pulses at the dynode which will gate the TMC pulse height analyzer. However, electron scintillations, in which the high intensity, fast component of decay is of considerably greater importance, will produce at the last dynode only negative pulses due to space charge repulsion and will thus be eliminated.

Figure 11

Block diagram showing circuit functions
in pulse shape discrimination probe

The second circuit is the W. Daebnick and R. Sherr⁽⁹⁾ type commercially available.* The discrimination pulses which gate the P.H.A. for analysis of neutron events are formed by adding negative pulses from the PM anode to the corresponding positive pulses from the 13th dynode. In operation, the relative amplitudes of the two which are to be combined are adjusted so that after the addition and subsequent charge integration the resultant pulses for electrons are as small as possible. These pulses, then, will not gate the P.H.A. However, since proton-recoil scintillations contain a relatively larger proportion of slow components than those due to electrons, they will produce positive resultant pulses which will gate the P.H.A. The pulses to be analyzed are taken directly from a third element of the phototube.

Calibration of pulse height vs. electron energy was carried out using Co^{60} , Cs^{137} , and Zn^{65} gamma rays for their Compton interaction.⁽¹³⁾ Figure 12 is an example of the spectrum obtained with Co^{60} . Subsequent calibration of pulse height vs. proton recoil energy was carried out using essentially monoenergetic neutrons from D-D and D-T reactions produced with 250-KeV Cockcroft-Walton linear accelerator; also used were neutrons from a p,n on Li reaction produced with a 3.5 MeV Van de Graaff accelerator and operated with the kind cooperation of the Reactor Engineering

*Nuclear Enterprise Ltd., 1750 Pembina Highway, Winnipeg, Manitoba, Canada. NE 5571 PSD Probe and NE 213 liquid scintillator.

Division. The resultant calibration curve for the NE 213 liquid scintillator is given in Figure 13. The proton calibration curve for stilbene although well known and reported elsewhere^(14,20) has been confirmed in our laboratory using the same technique.

Figure 12
Cobalt-60 calibration of liquid scintillator NE 213

Figure 13
Response of liquid scintillator
NE 213

Using 20 cc of stilbene and 100 cc of NE 213 we obtained data over a period of a month in Room B-110, Bldg. 3-203. The proton-recoil spectra were analyzed for the incident fast neutron flux and spectral distribution in the usual way.^(14,19-21) Preliminary results are given in Table 6 and compared with data presented by Patterson and Hess.⁽¹⁵⁻¹⁷⁾

Because our detectors were small, our results are based on poor statistics and, therefore, lack precision. We are in the process of improving the situation by going to much larger detector volumes.

Table 6

Fast neutron environmental background

Energy MeV	Neutrons/cm ² /sec/MeV		
	UCRL-8268	ANL (Stilbene) 2.5 x 10 ⁶ sec	ANL (NE 213) 7.6 x 10 ⁵ sec
1.00	0.0075	0.0094	0.02
1.25	0.0051	0.0054	0.01
1.50	0.0039	0.0039	0.005
1.75	0.0031	0.0021	0.003
2.00	0.0025	0.0018	0.002

The small range of energies covered also points up the need for further work in the adjustment of the discrimination electronics to give uniform efficiency over a broader energy range.⁽¹⁸⁾

Although the agreement with the UCRL results⁽¹⁵⁻¹⁷⁾ seems to verify the existence of a fairly high natural neutron background, we feel that neutrons artificially produced in the vicinity by accelerators, etc. might well be responsible for a significant portion of the detected flux. More recent monitoring with a Hanson and McKibben-type long counter and also a paraffin-moderated LiI(Eu) scintillator showed that, indeed, the counting rate increased at least by a factor of ten when the accelerators were running. Grismore⁽¹⁸⁾ found this to be the case in his earlier work with the twin scintillators. Our final neutron flux measurements will be made at an off-site location.

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A METHOD OF COMPENSATION FOR INSTRUMENTAL INSTABILITY IN A MULTICHANNEL GAMMA-RAY SPECTROMETER

Robert M. Parr

Introduction

The pulse height data recorded by multichannel gamma-ray spectrometers are generally of little direct value, other than for brief qualitative examination. More or less elaborate methods of data processing and computation must usually be applied before useful quantitative results can be obtained. Unfortunately, the complexity of the data-handling problem is in many cases so great, especially for analyzers having several hundred or more channels, that many types of hand computation are not feasible, and the use of some form of electronic digital computer is called for.

Several computer programs for analyzing gamma spectra have recently been reported. All of these require the spectrometer to be accurately calibrated in some way, either in terms of a mathematically defined response function,⁽¹⁻³⁾ or in the form of a library of reference spectra of known gamma emitters.⁽³⁻⁷⁾ The validity of these methods of computation, however, is in many cases seriously undermined by instrumental instability. Due both to drifts in gain and in the zero-energy channel-intercept, the response characteristics of the spectrometer constantly change, and may at times deviate considerably from the initial calibration. One, therefore, needs either a physical device which will correct for these changes as they occur, or a procedure by which allowance may be made for them in the computer analysis.

The first approach - that of correcting for the changes as they occur - has been followed by several workers.⁽⁸⁻¹¹⁾ Most commonly a known gamma or alpha emitter, in conjunction with a suitable scintillator, is employed to generate reference pulses, which by means of negative feedback are used to stabilize the calibration of the spectrometer. Devices of this type, making use of high and low energy reference pulses for stabilizing both gain and zero-intercept, have recently been described by Fite et al.⁽¹⁰⁾ and Dudley et al.⁽¹¹⁾

The second approach - that of transforming the data by computation - depends on the assumption that only "long-term" drifts need be considered. Thus, changes in response characteristics which occur during the time that a spectrum is being accumulated are assumed to be negligible, and only those changes occurring on a day-to-day or week-to-week basis, between the counting of one sample and another, are taken into account. This approach appears to be valid, provided that the source activity is neither so high that it causes a gain shift of the type described by Guinn and Lasch,⁽¹²⁾ nor so low that very long counting times are required.

Salmon⁽⁶⁾ has briefly described a procedure of this kind which can be used when the spectrum possesses a peak sufficiently prominent to allow precise measurement of its location. The center position of the peak is found by using the method of least squares to fit a Gaussian function to its peak channels, and on the basis of the change in position from that expected, a new spectrum is then computed channel by channel. As used by Salmon, this procedure corrects only for changes in gain. A similar method briefly reported by Heath⁽³⁾ also makes use of recognizable detail in the experimental spectrum, but corrects both for zero drifts and gain drifts.

The principal disadvantage of these procedures is that they depend on the existence of recognizable photopeaks in the spectra. They may also be subject to small systematic errors due to other features of the spectra since the apparent position of a photopeak is changed if its "baseline" is other than a horizontal straight line.

Method Employing a Separate Reference Source

The method of compensation for instrumental drifts described in this report also makes use of recognizable detail in a spectrum for calculating changes in instrumental parameters. A special reference source is employed, which is counted either just before or just after the experimental source whose spectrum is to be analyzed. This reference spectrum is then compared with one accumulated during the initial calibration of the spectrometer, and by an iterative process, the net changes in gain and zero-energy intercept since that time are calculated. The data which constitute the experimental spectrum are then transformed by a computer program which "shifts" and "stretches" the experimental spectrum so as to compensate for the instrumental changes.

This method differs from those of Salmon⁽⁶⁾ and Heath⁽³⁾ in that the calculation of instrumental drifts is based on the use of a separate reference source of constant and unique spectral form. It, therefore, does not suffer from the disadvantages of their procedures outlined above. It is based, however, on the assumption that the short-term instrumental stability is sufficient for there to be no sensible difference in energy calibration between the spectrum of the experimental source and that of the reference source counted either immediately before or afterwards.

In this report, the iterative method which has been used for computing the changes in zero-intercept and gain is described and evaluated, and the equations for transforming spectra so as to compensate for these instrumental variations are developed. As an example of the applications of this procedure, results of a preliminary investigation of the long term stability of our spectrometer are presented.

Theoretical Considerations

Principle of Method for Calculating Changes in Peak Locations

If a photopeak approximating the shape shown in Figure 14a is moved laterally by a small amount Δn , and its ordinates in the one position subtracted from those in the other, a "difference curve" is generated which has the form shown in Figure 14b. Evidently the following relationships hold

$$\text{Areas } X - Y = A + B \quad \text{approximately*} \quad (1)$$

$$A = \Delta n(h_2 - h_1) \quad \text{approximately} \quad (2)$$

$$B = \Delta n(h_2 - h_3) \quad \text{approximately} \quad (3)$$

Thus the relative displacement of the two peaks may be evaluated from the equation

$$\Delta n = \frac{X - Y}{2h_2 - h_1 - h_3} \quad \text{approximately} \quad (4)$$

and the direction of the displacement may be deduced from the sign of Δn .

An important property of the "difference curve" (Figure 14b) is that for relative displacements of the peaks, Δn , less than about one F.W.H.M. unit, the separation of its maximum and minimum is almost independent of Δn .** For this reason, the areas X and Y may be approximately evaluated by integration over a fixed range of pulse heights, and in practice, the range of about one F.W.H.M. unit on either side of the zero ordinate point has been found to be adequate for the purposes reported here.

In order to use this method for following changes in the position of a photopeak, both spectra used for generating the "difference curve" must necessarily be of the same reference source, counted in the same position relative to the detector, and normalized to the same counting time and total radioactivity.

The Calculation of Shift and Stretch

In the following discussion "shift" is taken to mean a change in the zero-energy channel-intercept, and is denoted by "z"-channels. "Stretch" is a fractional change in gain, and is denoted by "g." The calculation of shift and stretch requires measurements of the changes in positions of two peaks in the spectrum of the reference source. Ideally, one of these should be at a low energy where any drift in channel position is principally due to shift, and the other should be at a high energy where drift is mainly due to stretch.

* Areas below the zero-ordinate line are negative.

**If the photopeaks were accurately Gaussian in shape, the separation of the maximum and minimum of the difference curve would be approximately 2σ units or 0.85 F.W.H.M. units of the peak.

Figure 14

- a. Photopeak showing change in position due to instrumental drift (diagrammatic)
- b. "Difference" curve

Suppose that the energy calibration of the spectrometer is initially defined by a "primary reference spectrum" of the reference source. All estimates of shift and stretch are determined by comparison with this particular spectrum. Any other reference spectrum of the same source, whose shift and stretch relative to the primary reference are to be computed, is known as a "secondary reference spectrum."

In the primary spectrum let n_2 and n_5 be the peak-channel numbers of the two peaks whose changes in position are used to provide estimates of shift and stretch. Let n_1 , n_3 , n_4 , and n_6 be channel numbers which are of the order of one F.W.H.M. unit on either side of these peaks as in Figure 15, and let n_0 be the zero-energy channel intercept.

Figure 15

Gamma spectrum of reference source used in shift and stretch calculations (diagrammatic)

If A_j denotes the counting rate in channel j in the primary reference spectrum, and a_j that in the secondary reference spectrum, the areas corresponding to X and Y of Figure 14b are, for the lower peak

$$X = \sum_{n_1}^{n_2} (A_j - a_j) \quad \text{approximately} \quad (5)$$

and

$$Y = \sum_{n_2}^{n_3} (A_j - a_j) \quad \text{approximately} \quad (6)$$

Hence, from Equation (4), $\Delta n'$, the drift in position of the lower peak is given by

$$\Delta n' = \frac{\sum_{n_1}^{n_2} (A_j - a_j) - \sum_{n_2}^{n_3} (A_j - a_j)}{2A_{(n_2)} - A_{(n_1)} - A_{(n_3)}} \quad \text{channels approximately} \quad (7)$$

Similarly $\Delta n''$, the drift in position of the upper peak is given by

$$\Delta n'' = \frac{\sum_{n_4}^{n_5} (A_j - a_j) - \sum_{n_5}^{n_6} (A_j - a_j)}{2A_{(n_5)} - A_{(n_4)} - A_{(n_6)}} \quad \text{channels approximately} \quad (8)$$

Channel number is very nearly linearly related to pulse height: thus

$$\Delta n' = z + g(n_2 - n_0) \quad (9)$$

$$\Delta n'' = z + g(n_5 - n_0) \quad (10)$$

Hence

$$z = \frac{\Delta n'(n_5 - n_0) - \Delta n''(n_2 - n_0)}{n_5 - n_2} \quad \text{channels approximately} \quad (11)$$

and

$$g = \frac{\Delta n'' - \Delta n'}{n_5 - n_2} \quad \text{approximately} \quad (12)$$

Precise values of z and g are computed by a rapidly convergent method of successive approximations. In each iteration of this procedure, the secondary reference spectrum is transformed (vide infra) according to the current estimates of z and g obtained by the application of Equations (7) to (12). This provides a new secondary reference spectrum which may be used again to calculate values of z and g . When, after several iterations a good "fit" is obtained, the net values of z and g are calculated by summing all the individual estimates.

Compensation for Instrumental Drifts by Transformation of the Data

Given a spectrum having an energy calibration which differs by z in zero-intercept and g in gain from the standard settings of the spectrometer, a method is required for transforming the data by computation so as to compensate for these changes. Such a procedure has two functions. First, as already described, it is needed for shifting and stretching the secondary reference spectrum as part of the iterative procedure used for calculating accurate estimates of z and g . Second, it is needed for transforming the experimental spectrum in a way appropriate to these estimates.

There is a problem in making this transformation due to the fact that a pulse-height spectrum is in reality a histogram (Figure 16). In general, fractions of a channel are involved in the computation, and thus a method is required for apportioning the counts among the various fractional parts. The procedure adopted has been to divide the total counts in the channel in direct proportion to the width of the fractional part. This has no significant effect on spectral shape, provided that the channel width is much less than the F.W.H.M. of any of the peaks.

Figure 16

Gamma spectrum drawn as a histogram to illustrate method for applying shift and stretch.

In addition to the discrete channel number variable j , ($j = 1, 2, 3, \dots, k, (k+1), \dots$ etc.), let a continuous channel number variable n be defined, so that channel j is equivalent to the range $n = j$ to $n = j+1$. When a zero-shift z and a fractional change in gain g occur, the pulse height corresponding to the lower boundary of channel j in the primary reference spectrum no longer falls on the n -axis at $n = j$. The new channel position will be $n = N_1$, where

$$N_1 = j + z + g(j - n_0) \quad (13)$$

Similarly the pulse height corresponding to the upper boundary of channel j in the primary reference spectrum falls at $n = N_2$, where

$$N_2 = j + 1 + z + g(j + 1 - n_0) \quad (14)$$

Thus if α_j denotes the counting rate in channel j of the experimental spectrum before computed shift and stretch are applied, the "true" counting rate $\hat{\alpha}_j$, after shift and stretch, is given by

$$\hat{\alpha}_j = (1 - F_1) \alpha_{(I_1)} + \phi + F_2 \alpha_{(I_2)} \quad (15)$$

In this equation, F_1 and F_2 denote respectively the fractional parts of N_1 and N_2 , and I_1 and I_2 their integral parts. The term ϕ represents channels between $j = I_1$, and $j = I_2$, i.e.,

$$\phi = 0 \quad \text{when } I_2 - I_1 \leq 1$$

$$\phi = \sum_{I_1+1}^{I_2-1} \alpha_j \quad \text{when } I_2 - I_1 > 1 \quad (16)$$

The new spectrum computed by the use of Equations (15) and (16) differs in at least three ways from that which would be obtained if no change in instrumental parameters had occurred.

First, an end effect occurs when the values of either I_1 or I_2 called for by Equation (15) are outside the range of channel numbers appropriate to the spectrometer. This effect, when present, is apparent as a distortion of the spectrum in the lowermost or uppermost few channels.

Second, the spectrum is smoothed by the shift and stretch routine. Consider, for example, the simple case of a spectrum accumulated over unit time, and with no subtraction of background. Since Poisson statistics apply, the variance of the number of counts in each channel is equal to that number, i.e.,

$$\text{Var } (\alpha_j) = \alpha_j$$

But for the transformed spectrum

$$\text{Var } (\hat{\alpha}_j) = (1 - F_1)^2 \text{Var } (\alpha_{(I_1)}) + \text{Var } (\phi) + F_2^2 \text{Var } (\alpha_{(I_2)}) \quad \text{or}$$

$$\text{Var } (\hat{\alpha}_j) = (1 - F_1)^2 \alpha_{(I_1)} + \phi + F_2^2 \alpha_{(I_2)}$$

Comparison with Equation (15) demonstrates the smoothing effect since evidently $\text{Var } (\hat{\alpha}_j)$ is less than $\hat{\alpha}_j$.

Third, a degree of correlation is introduced since the computed counting rates in adjacent channels are no longer statistically independent. This may affect the statistical treatment of the data in subsequent computations, as for example analysis by the method of least squares.

Practical Considerations

Experimental Evaluation of the Shift and Stretch Calculations

The shift and stretch calculations were tested using spectra obtained by a Nuclear Data 512 channel analyzer from a 4x4-inch sodium iodide crystal coupled to a 5-inch EMI photomultiplier tube. The data were collected on punched paper tape and were processed by an IBM 704 computer programmed in Fortran II.

The radioactive source used as a reference was a sample of thorium more (equilibrium) which gave a counting rate of about 70,000 cpm. This material has a gamma spectrum which possesses several peaks suitable for the shift and stretch calculations; the 0.24-MeV peak of the daughter nuclide, Pb^{212} , was used as a low energy reference, and the 3.20-MeV peak of Tl^{208} was used as a high energy reference. There was, of course,

no need to apply any correction for radioactive decay over the time that the source was in use as a reference for the shift and stretch calculations.

Accuracy and Precision of the Experimental Results. From the known spectrum of the reference source and the equations used for estimating z and g , the theoretical accuracy of the shift and stretch calculations was deduced. For a ten-minute counting time the standard deviations of the computed values of z and g are 0.045 channels and 0.0012 respectively. Since these figures are determined by the Poisson statistics of the counting rate, longer counting times improve the accuracy in proportion to the half-power of the time.

Invariably the precision of the results is much greater than their accuracy. For example, in Table 7 are shown computed values of z and g determined in a case in which the amplifier and analyzer controls had been adjusted in such a way as to introduce artificially a known shift and stretch. In this case, the zero-energy channel intercept had been changed by 1.50 channels, and a 1.43% decrease in gain had been introduced (i.e., expected value of $z = 1.50$; expected value of $g = -0.0143$).

Table 7

Computed values of z and g in test case for
shift and stretch program

Number of iterations	z	g
1	0.1425×10^1	-0.1392×10^{-1}
2	0.6352×10^{-1}	0.8754×10^{-4}
3	0.3315×10^{-2}	-0.1752×10^{-4}
4	0.3296×10^{-4}	0.6675×10^{-6}
5	0.6929×10^{-6}	-0.2868×10^{-7}
Over-all estimate	1.492	-0.0138
Theoretical S.D.	0.045	0.0012
Expected value	1.50	-0.0143

The rate of convergence of the calculations is obviously very rapid, and after the first one or two iterations, it is apparent that the successive increments in z and g become much less than their expected standard deviations. In relation to this theoretical accuracy the final estimates of z and g obviously agree well with their expected values.

In order to evaluate the effect of making small errors in the choice of the channel-number input-parameters, $n_0, n_1, \dots, n_6$, the data used for the calculation of the results in Table 7 were reprocessed. In

this case (Table 8) an error of 2 channels was made in the specification of n_0 , the zero-energy channel-intercept; the lower peak channel-number, n_2 , was incorrectly specified as a channel which contained only 57% of the true peak counts; and the upper-peak channel-number, n_5 , was specified as one which contained only 84% of its true peak counts. From Table 8 it is apparent that the principal effect of such errors is merely a reduction in the rate of convergence; the final estimates obtained are still in good agreement with their expected values. Thus the accuracy of the shift and stretch calculations does not appear to be critically dependent on the precise choice of channel-number input-parameters.

Table 8

Computed values of z and g after changes in input parameters
(same test case as for Table 7)

Number of iterations	z	g
1	0.1353×10^1	-0.1514×10^{-1}
2	0.1483×10^0	-0.9264×10^{-4}
3	0.1318×10^{-1}	-0.1053×10^{-3}
4	-0.3748×10^{-2}	0.4136×10^{-4}
5	0.1142×10^{-2}	-0.1669×10^{-4}
Over-all estimate	1.511	-0.0153
Theoretical S.D.	0.045	0.0012
Expected value	1.50	-0.0143

Test of Shift and Stretch Calculations with Known z and g . A series of two-minute counts of the reference source was made in which the zero-energy channel-intercept was varied by adjustment of the energy zero control of the analyzer. In this series of runs the gain was held constant. From Figure 17 it may be seen that good agreement is obtained between the actual values of shift and stretch and those computed.

In a second series of runs, each of ten minutes' duration, the zero-energy channel-intercept was held constant, and the gain was varied by adjustment of the fine gain control of the amplifier by amounts between plus and minus 2.67%. Quite good agreement between the actual and computed values of shift and stretch was again obtained (Figure 18) although the measurements of g in this case appear to have a small systematic error of about -0.0028. This is of the order of magnitude of the long-term drift of the spectrometer. The single estimate which did not fall close to the expected line is the result of an end effect error. The gain in this instance was so high that only part of the upper reference peak was recorded.

Figure 17

Test of shift and stretch calculations - variable zero intercept, constant gain

Figure 18

Test of shift and stretch calculations - variable gain, constant zero intercept

Measurement of Spectrometer Stability

The stability of all components of our gamma-counting system as a whole was investigated using the shift and stretch routine for calculating the changes in the instrumental parameters. The thorium ore reference source was counted in the "auto-repeat" mode of operation of the analyzer, and data were accumulated for every 100 minutes of "live" time (about 105 minutes of real time) over a total period of about three days. The changes in the instrumental parameters during this time are shown in Figure 19, together with a record of the ambient temperature in the laboratory. In each case the temperature plotted was the mean ambient temperature over the counting time.

Figure 19

Spectrometer stability over a period
of about three days

It may be seen that the zero-energy channel intercept, z , changed very little with time, and was not correlated with the temperature (correlation coefficient = 0.08). The changes in gain, on the other hand, were strongly dependent on temperature (Figure 20) and gave a correlation coefficient of -0.87. A least squares linear fit of these data gave the following relationship between g and the temperature, $t^{\circ}\text{F}$

$$g = (0.227 \pm 0.021) - (0.00292 \pm 0.00026) t$$

Thus at channel 500, a 1°F increase in temperature produced a spectral drift of about -1.5 channels.

Figure 20

Correlation between observed change
in gain and ambient temperature

Evidently the scatter of the points in Figure 20 about the line of best fit is in general greater than their expected errors, and thus the measured temperature changes do not fully account for the variations in gain observed. A better fit to the data could be obtained by the use of two straight lines, as shown by the dashed lines of Figure 20. One is appropriate to the first 40 hours of data collection during which g was positive, and the other to the remaining time during which g was negative. Whether this points to the existence of a long-term instrumental drift independent of temperature, or to g being determined by a more complex function of temperature than the linear relationships assumed here has not yet been determined. It would appear, however, that the order of instrumental stability attainable by very precise control of the ambient temperature should be about 0.2% in gain, and 0.03 channels in zero intercept.

Discussion

The procedure described for computing changes in gain and zero-energy intercept appears to be very accurate, but inevitably when spectra are transformed according to these estimates, small distortions and other effects are introduced which would not be present if perfect instrumental stability had been maintained. However, from a limited experience of its use as part of a computer program for analyzing gamma spectra by the method of least squares, prior adjustment of the data by this procedure appears to be very successful, and the distortions and other effects introduced do not seem to be very important. It is perhaps worth noting that instrumental methods for maintaining stability also introduce small distortions.⁽¹¹⁾

The stability of our spectrometer is fortunately very good. With adequate control of the ambient temperature it appears to be not greatly inferior to the elegant system of Dudley and Scarpatetti,⁽¹¹⁾ which can maintain the stability of peak channel number to about 0.1%.

The cause of the observed correlation between ambient temperature and change in gain in our spectrometer has not been fully investigated. The photomultiplier tube, preamplifier, amplifier, high voltage supply and analyzer are all temperature dependent; however, the most critical component has not as yet been identified. It should also be possible to evaluate the effect of counting rate on gain by this procedure although the experience of Guinn and Lasch⁽¹²⁾ suggests that this particular effect should not be important under our usual operating conditions of low photomultiplier voltage and low or moderate source activity.

Many of the ideas which are incorporated in the procedure described in this report are those of Henry F. Lucas, Jr., whom I would like to thank sincerely for his valuable advice and criticism. The computer programming was undertaken by William J. Snow, Applied Mathematics Division, to whom I would also like to express my thanks.

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SCINTILLATIONS IN ARGON AND NITROGEN

Harvey A. Schultz

Introduction

It has been known for many years that high-speed particles may produce scintillations in gases as well as in condensed matter. A portion of the energy lost by a decelerating particle is eventually released as light. In the gaseous state, energy of excitation cannot be transferred from one molecule to another as freely as in a liquid or solid. Direct transfer is possible only during a molecular impact. Indirect transfer may, of course, take place through the emission and reabsorption of photons.

An investigation of gaseous scintillations has been undertaken to obtain a more complete understanding of the energy transfer processes in pure gases and mixtures when bombarded by various types of particles. This report covers some observations made upon argon and nitrogen, alone and in mixtures, excited by alpha particles.

Description of Apparatus

The cavity of the gas cell was a truncated cone with aluminized walls, designed to reduce the effect of multiple reflections (Figure 21). The quartz window was sealed to the cavity by a lead ring. No solid

Figure 21

Cross section of cell. The cavity, in the form of a truncated cone, has a diameter of 3.97 cm at the lower base and is 1.43 cm deep. The half angle of the apex is 30 degrees. The retaining and clamping rings are each secured by six machine screws (not shown).

wavelength shifter or organic material of any kind was used within the cell since it has been reported that organic materials, such as O-rings, tend to quench the scintillations.⁽¹⁾ The alpha source consisted of Cm^{244} (5.8 MeV alpha) deposited upon a 0.32-cm diameter stainless steel surface extending 0.16 cm into the cavity. The counting rate was 2.8×10^4 counts per minute.

The scintillations were detected by an RCA 6903 photomultiplier tube, a ten-stage tube with a 3.8-cm diameter photocathode having an S-13 response (Figure 22), operated at 770 volts with the photocathode at ground potential. Glycerin, which transmits ultraviolet radiation at wavelengths greater than 2300 Å (vs. the quartz limit of 1900 Å), was used as an optical coupling fluid. A transistorized preamplifier and an RCL model 20609 256-channel pulse height analyzer were used. The noise level did not interfere with the signal except when the cell contained 100% nitrogen.

Figure 22

Spectral sensitivity of a 6903 photomultiplier tube (S-13 response)

Charles Egger of the Physics Division kindly contributed the gas-handling system and some of the gases remaining from the investigations of Egger and Huddleston;⁽²⁾ to this apparatus was added a second liquid nitrogen trap on the high vacuum side of the mercury vapor pump to reduce the effect of diffusion into the system, as noted by L. Koch.⁽³⁾ Argon believed to be 99.99% pure and nitrogen specified as 99.995% pure was used.

Experimental Results

The greatest pulse heights were obtained with argon alone. This was unexpected, in view of published results.⁽²⁻⁴⁾

At pressures above 4 atmospheres the pulse height decreased with increasing pressure without distortion of the shape of the pulse height spectrum. Below 4 atmospheres the pulse height spectra were distorted because of impacts of alpha particles with the walls.

The variation of pulse height with the composition of the gas, at constant alpha-track length, is summarized in Figure 23. The pressures, adjusted to correspond to 0°C temperature, range from 5.36 atmospheres for argon to 5.14 for nitrogen, and the calculated track length is 0.82 cm.^(5,6) Figure 23 shows a pulse height minimum near 1% and a maximum near 10% N₂ concentration.

Figure 23

Effect upon pulse height of volume percent nitrogen in argon-nitrogen mixtures with the pressure adjusted to produce 0.82-cm track lengths (from 5.34 atmospheres for 100% argon to 5.14 for 100% nitrogen)

Eggler and Huddleston,⁽²⁾ Koch,⁽³⁾ and Bergheim and Skarsvag⁽⁴⁾ all found that with argon-nitrogen mixtures the pulse height-concentration relation showed a pulse height maximum, at 10% nitrogen or less, but they reported no minimum. Their experimental arrangements differed somewhat from each other and from the one described below. Northrup, Gorsky, and Johnsrud⁽⁷⁾ have published a curve of pulse height vs. concentration of He in Xe which shows both a maximum and a minimum.

In our experiments the decrease of pulse height with increasing pressure above 4 atmospheres is consistent with theoretical expectations whenever collisions cause de-excitation of molecules, but it may also depend upon variation of light collection efficiency with track length.

The observed effect of nitrogen concentration upon pulse height is consistent with the following hypotheses: 1) Both argon and nitrogen in the pure state produce detectable light. 2) The detectable emission process of argon is quenched by nitrogen. 3) Argon is excited by alpha particles also to levels which do not produce detectable light emission. 4) The energy of these argon levels, however, can be transferred to nitrogen, which then produces detectable light.

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THE Pb^{210} (RaD) CONCENTRATIONS OF SOME BIOLOGICAL MATERIALS FROM ARCTIC REGIONS

Richard B. Holtzman

Studies of the radiation dose to the human skeleton have shown Pb^{210} (RaD) to be important because its radiations contribute an average of 20% or more to the total natural radiation dose.⁽¹⁾ In turn, natural radiation usually contributes 90% or more of the total radiation dose, exclusive of that received from x-ray machines.⁽²⁾ However, in arctic regions the dose levels people receive from radioactive fallout from nuclear weapons tests have been found to be 20 to 30 times those of people outside these areas. Liden et al.⁽³⁾ reported high concentrations of Cs^{137} in Laplanders and more recently, Miettinen et al.⁽⁴⁾ correlated these concentrations with the diet of Finnish Laplanders. Palmer et al.⁽⁵⁾ found similar concentrations in Alaskan Eskimos and Schulert⁽⁶⁾ observed analogous concentrations of Sr^{90} in biological samples from Alaska.

Because the fallout rates in these areas are not appreciably different from those in the rest of the northern hemisphere, the excessive uptake of these activities has been attributed to continual accumulation on the long-lived, slow-growing arctic lichens and sedges.^(4,7) These plants constitute important sources of forage for reindeer (Europe) and caribou (Alaska), which, in turn, constitute a substantial portion of the diets of Laplanders and Eskimos.

Because Pb^{210} , formed in the atmosphere from Rn^{222} emanating from the soil, is a natural fallout product with a relative geographical distribution in the atmosphere similar to fallout (Sr^{90}) in the northern hemisphere,⁽⁸⁾ its relative distribution in the leaves of plants might be analogous to that of artificial fallout. Therefore, quantities large relative to those found in non-arctic regions should be observed in lichens, and consequently in reindeer and people of the area. Evidence of this exists in a measurement of Hill⁽⁹⁾ on a rib bone from an Eskimo (otherwise unidentified), in which he observed a Pb^{210} concentration of 2.3 pC/g ash, a value more than ten times his other values and those of the U. S. population.⁽¹⁾

Further data are presented here on the Pb^{210} content of some biological specimens from the arctic, namely, lichens from Finland and Alaska, the stomach contents (rumen, mostly lichens) of some caribou, a Finnish water plant used for fodder (*Equisetum flaviatile*), antler, meat and bone from reindeer and caribou and bones from an Icelandic lamb. For comparison some measurements of grass from Chicago are also shown. The origin and characterizations of the specimens are given in Table 9.

Table 9

Data on samples

Sample	Region	Characteristics
<u>Plants</u>		
Lichens	Inari, Finland	Species: <u>Cladonia alpestris</u>
Lichens I	Chariot Site, Cape Thompson, Alaska	Species: predominantly <u>Cladonia sylvatica</u>
Lichens II	Chariot Site, Cape Thompson, Alaska	Species: predominantly <u>Cornicularia divergens</u> . Ach., <u>Alectoria nigricans</u> Ach. Myl., <u>Alectoria ochroleuca</u> (Ehrh.) and small amounts of other species
Lichens III	Chariot Site, Cape Thompson, Alaska	
Grass	Chicago, Ill., USA	Species: Kentucky blue grass
<u>Animals</u>		
Reindeer	Finland	2- to 4-yr-old animal, female composite of 10 animals Meat: powder, from shoulder Bone: marrow-free tibia
Caribou I	Denali Highway, Alaska (Lat. 63° 30' Long. 148° 30')	2-yr-old, male Meat: hind quarter Bone: Femur shaft Rumen and Antler
Caribou II	Denali Highway, Alaska (Lat. 63° 30' Long. 148° 30')	3- to 7-yr-old, male Meat: hind quarter Bone: Femur shaft Rumen and Antler
Lamb	Iceland	Commercial lamb obtained in Chicago

The Pb^{210} was determined by first wet ashing the samples (except the Alaskan lichens which had been previously dry ashed at 400°C) in nitric and perchloric acids. The nitrates were then removed by repeated fumings with hydrochloric acid. The pH was adjusted to 0.3, and the Pb^{210} decay product Po^{210} was plated onto a silver disk which was then alpha counted.⁽¹⁾ The Ra^{226} was determined by the emanation method of Lucas.⁽¹⁰⁾

The results are presented in Table 10. Concentrations are given in terms of dry weight of the material dried at 110°C, except for bone and antler which are given in terms of ash weight.

A large fraction of the forage of the reindeer and caribou is supplied by lichens which, as shown in Table 10, appear to have high and

variable concentrations of Pb^{210} . However, if the unusually high value of Lichens II from Alaska is excluded, the variations are slightly more than a factor of two. The Finnish cattle fodder, E. flaviatile, is appreciably lower in Pb^{210} content and similar in content to Chicago grass.

Table 10

Pb^{210} and Ra^{226} in animal and plant materials

Sample	Region	$\text{Pb}^{210}(\text{pC/g})^*$	$\text{Ra}^{226}(\text{pC/g})^*$
<u>Plant material</u>			
		(dry weight)	
Lichens	Finland	8.29 ± 0.047	0.0035 ± 0.0010
Lichens I	Alaska	10.5 ± 0.1	0.101 ± 0.006
Lichens II	Alaska	61.2 ± 0.3	0.415 ± 0.017
Lichens III	Alaska	19.4 ± 0.7	0.156 ± 0.004
Rumen I	Alaska	10.3 ± 0.084	
Rumen II	Alaska	9.87 ± 0.11	
<u>Equisetum flaviatile</u>	Finland	0.516 ± 0.011	0.042 ± 0.005
<u>Grass, soil</u>			
Top of grass	Chicago	0.128 ± 0.010	
Center	Chicago	0.230 ± 0.010	
Lower	Chicago	0.717 ± 0.020	
Roots	Chicago	0.819 ± 0.050	
Soil I (from grass)	Chicago	1.86 ± 0.016	
Soil II (from Monee, Ill.)	Chicago	1.23 ± 0.03	
<u>Reindeer and caribou</u>			
Meat	Finland	0.174 ± 0.006	0.0013 ± 0.009
Meat I	Alaska	0.366 ± 0.007	
Meat II	Alaska	0.272 ± 0.007	
		(ash weight)	
Bone	Finland	5.00 ± 0.04	1.84 ± 0.022
Femur I	Alaska	13.8 ± 0.08	
Femur II	Alaska	11.2 ± 0.10	
Antler I	Alaska	7.20 ± 0.08	
Antler II	Alaska	6.68 ± 0.12	
<u>Lamb</u>			
Rib	Iceland	0.314 ± 0.019	0.043 ± 0.007
Rib	Iceland	0.353 ± 0.012	0.104 ± 0.007
Femur	Iceland	0.337 ± 0.013	0.041 ± 0.005
Iliac crest	Iceland	0.269 ± 0.013	0.099 ± 0.005

*Plant material and meat given in units of pC Pb^{210} /g dry material.

Bone given in units of pC Pb^{210} /g ash.

Errors: 90% confidence limit of counting statistics.

The Pb^{210} concentrations in lichens appear to be comparable to the Po^{210} (Pb^{210} decay product) concentrations in grass observed by Hill⁽¹¹⁾ which range from 1 to about 23 pC/g dry grass. The relatively high Pb^{210} concentrations in reindeer as compared to those found in cattle by Di Ferrante⁽¹²⁾ and by Hill and Jaworowski⁽¹³⁾ may be due to several causes: 1) the ash content of the Finnish lichens is appreciably lower than that of grass, 1% as compared to 5% (although the Alaskan lichens are about 5-7% ash), so that animals, in order to obtain sufficient minerals, consume much larger amounts of lichens; 2) the mean annual rainfall of more than 100 cm in the areas Hill studied may not be typical of the regions from which the cattle come; and 3) the Po^{210} content of the grass measured by Hill may not be typical of that consumed over the year, i.e., this grass was collected in early December at which time it may be growing slowly or even dormant so that the Pb^{210} concentration could increase if its precipitation rate is constant over the year. On the other hand, during the growing season, the mass of the grass would increase more rapidly, thereby preventing a buildup of large Pb^{210} concentrations. This phenomenon is shown in Chicago grass collected in the spring in which the average concentration is only 0.3 pC/g of dry grass in spite of a fair amount of precipitation (25 cm) in the 40 days prior to collection. Also demonstrated in Chicago grass is the large variation in concentration from root to stem, in this case a factor of six, which may be due to the stagnation of Rn^{222} near and under the ground.⁽¹⁴⁾

The source of Pb^{210} in the plant material is apparently fallout from decay of the Rn^{222} naturally present in the atmosphere since there is little Ra^{226} precursor present in the samples themselves as shown in Table 10.

Bone from animals, though not a direct source of Pb^{210} for the human, is also of interest since, by integrating the intake, it can be considered an indicator of the average Pb^{210} content of the meat. The Pb^{210} concentration in meat represents the intake immediately prior to slaughter (a week or two) and thus may not be representative of the meat from the region at all times. The Pb^{210} and its daughters produce a radiation dose to the bone of these animals which is from 10 to 50 times that from the Pb^{210} decay series in humans and may, therefore, be useful in the study of the effects of low-level radiation. The skeletal radiation dose rate from natural internal radioactivity is nearly double that estimated from Di Ferrante's data on cattle,⁽¹²⁾ if the relative rad dose is taken as $1/2(\text{Pb}^{210}) = 3(\text{Th}^{228}) = (\text{Ra}^{226})$ where the parentheses represent the concentration of the enclosed nuclide in units of pC/g ash. The dose rate to the Alaskan animals is still higher by another factor of two.

The differences in Pb^{210} concentration in the Finnish and Alaskan animals are possibly metabolic, but it seems more likely (because they are very closely related) to be due to dietary intake since the former are domesticated and may, therefore, have received supplementary feed, of grass or E. flaviatile, which has lower Pb^{210} content. An analogous

explanation may also account for the differences in the Pb^{210} concentrations between antler and femur of the same animal, i.e., the antler is formed over a short period of time (3 months)⁽¹⁴⁾ in the spring, when, owing to the presence of other vegetation, lichens may constitute a smaller fraction of the diet than that averaged over the entire year. Comparisons of Pb^{210} concentrations in Femurs I and II and Antlers I and II indicates that these concentrations do not vary much from animal to animal from a given region and that the concentration of Pb^{210} in the antler is roughly 1.8 times that in the femur. Thus, it is possible a few animals may be representative of all, and antlers alone may be useful in survey measurements.

Not all sources of food from arctic regions are likely to be high in Pb^{210} , as shown in the results measured in bones taken from an Icelandic lamb. In this animal Pb^{210} and Ra^{226} concentrations are comparable to those in the bovine bones⁽¹²⁾, suggesting that the Pb^{210} content in the diets of these animals is more like that of the United States cattle.⁽¹⁵⁾

As shown in Table 10, the concentrations of Pb^{210} in reindeer and caribou meat range from 0.174 to 0.366 pC/g dry or 0.06 to 0.09 pC/g wet, values more than 10 times the 0.007 pC/g wet U. S. midwestern steer meat.⁽¹⁾ The low Ra^{226} concentrations show that this nuclide is not a source of the Pb^{210} in meat or bone.

Miettinen et al.⁽⁴⁾ report that male Finnish Laplander reindeer breeders consume about 12.4 kg/month or 400 g/day of reindeer meat which, if we take the data of the Finnish reindeer meat, implies that these people ingest about 17 pC Pb^{210} /day. This is a rate about 10 times the United States rate of about 1.8 pC/day.⁽¹⁾ Since American dietary intake represents about one-half the total intake, the other half being from inhalation⁽¹⁾ the Pb^{210} content of arctic people living on reindeer meat, but who probably inhale the same absolute amount as Americans, could be about 5 times that of Americans.

Other Lapps listed by Miettinen et al.⁽⁴⁾ consume from 1.2 to 12.0 kg/month which represents 2.4 to 16 pC/day from meat alone. If the other food consumed has about the same Pb^{210} concentrations as United States food, even these other Lapps would ingest an amount at least twice that of the United States residents. Similar dietary information is not available for Alaskans, but it is estimated, based on a report on the nutritional status of the Eskimo,⁽¹⁶⁾ that their consumption of caribou is roughly comparable to the reindeer meat consumption of the Lapps, and, therefore, their Pb^{210} levels should also be comparable. The results given here tend to substantiate the reasonableness of Hill's value on Eskimo bone and indicate that certain groups of arctic residents should possess relatively high Pb^{210} concentrations.

These findings imply also that skeletal radiation dose rates are several times those of temperate zone residents. The total skeletal dose

rates to United States residents is about 100 mrad/year, based on the estimates of Dudley⁽²⁾ and an assumed Pb^{210} concentration of 0.146 pC/g ash.⁽¹⁾ On the other hand, if we assume all other factors to be the same, Hill's Eskimo bone experiences a total dose rate of about 200 mrad/year (half from the Pb^{210} alone), which is about twice the United States average.

Since preliminary studies indicate apparently high dose rates to these people, further studies along these lines seem desirable to study further the sources of the radiation and to determine accurately the total radiation dose experienced by these people. The sources of radiation may be determined by measurement of the concentrations in the atmosphere of the Pb^{210} and its precursors, Rn^{222} and its daughters, and by further Pb^{210} measurements of the food chain. Whole body content of Pb^{210} can be determined most accurately by analysis of body tissues; however, because of difficulties in obtaining such specimens from arctic residents, an alternative, if less accurate method, is the study of Pb^{210} excretion rates. These rates, along with the proper application of the metabolic parameters of Pb^{210} , may then permit a reasonable estimate of total body content.

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THE CONCENTRATION OF Ra^{226} , Ra^{228} , Pb^{210} , LEAD AND FLUORIDE IN HUMAN BONE FROM INDIVIDUALS WITH AN OSTEOGENIC SARCOMA

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Introduction

As part of a program to determine the toxicity to humans of internally deposited radioelements, we have studied the uptake and retention of Ra^{226} , Ra^{228} , Th^{228} , and Pb^{210} arising from the environment.⁽¹⁻³⁾ Since large amounts of Ra^{226} or other bone-seeking radioelements have been shown to produce a high incidence of osteogenic sarcoma,⁽⁴⁾ it is conceivable that the normal natural environmental radiation may have a direct effect on the spontaneous incidence of this disease.

Natural levels of radium, however, are more than a factor of 10^4 lower than the levels known to be toxic and the range of the variations in dose is small. In addition, exposure is lifelong, and the dose is distributed more uniformly throughout the skeleton than that at the known toxic levels. In spite of these differences in deposition and dose, it has been presumed that the variation in natural radiation dose will result in a corresponding variation in the incidence of osteogenic sarcoma.

Naturally occurring radioisotopes which contribute significant radiation doses to bone include K^{40} , Ra^{226} , Ra^{228} , and Pb^{210} . The metabolism of K^{40} is such that there is little individual variation within a given age group.⁽⁵⁾ We have, therefore, compared the Ra^{226} , Ra^{228} , and Pb^{210} content of the bone from normal individuals with that in proven cases of osteogenic sarcoma. In addition, we have determined the concentrations of two stable bone-seeking elements, lead and fluorine.

The concentrations of these nuclides depend on the environmental concentrations. Ra^{226} is acquired through both food and water, but since most of the world's population consumes water with no significant concentration of radium, food is the primary source. In these individuals the Ra^{226} concentration is low, and the values span a relatively small range. In some areas, however, the drinking water comes from wells which have a high Ra^{226} concentration, and individuals consuming this water may have body burdens 10 or more times higher than those whose only source of radium is food.⁽¹⁾ The Ra^{228} content of the body is similarly controlled, but because of the short half-life of the Ra^{228} (5.8 yr)^(6,7) a variation with age of its concentration in the body exists. Thorium-228, a decay product

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of Ra^{228} is not appreciably absorbed from either food or water, and hence its presence in bone is due to the decay of its parent, Ra^{228} . Fluoride, like radium, enters the body primarily through food and drinking water, whereas Pb^{210} and lead are acquired from both food and air.

Experimental Method

For this study uninvolved bone was obtained from the area adjacent to the tumor. Although some samples had been stored in formalin, no contamination or leaching was found. When received, the samples were cleaned of soft tissue and bone marrow, dried at 110°C and stored in sealed polyethylene bags at a temperature of -27°C until analyzed.

Samples selected for analysis were given a preliminary treatment to remove blood residues by boiling three times in 50- to 100-ml portions of freshly distilled ethylene diamine, and three times in distilled water. A portion of each sample (approximately a one-third cross section) was then dried at 100°C , weighed, placed in a small (50 ml) platinum crucible and ashed at 600°C overnight in an electric muffle furnace lined with Crystalon* to reduce the possibility of contamination by the fire brick. The weighed ash was then transferred to a 50-ml centrifuge cone, dissolved with 1.85 ml concentrated nitric acid per gram ash, and diluted with distilled water to give 0.20 g ash/ml. No insoluble residue was observed.

The thorium was extracted into dibutyl phosphate, and the Th^{228} was determined using the procedure of Stehney et al.^(8,9) Ra^{228} was determined from the grow-in of Th^{228} over a one- to two-year period. Since in most samples at the time of death the Th^{228} -to- Ra^{228} ratio was not significantly different from 1.0,⁽²⁾ corrections (5% or less) were made for growth and decay between death and assay. Ra^{226} was determined by the emanation method previously described.⁽¹⁾ All computations necessary for the analysis of Ra^{226} and Ra^{228} were made on an IBM-704 computer. The estimate of the 90% confidence interval included the effect of the decay scheme on the counting statistics.⁽¹⁰⁾

Pb^{210} (RaD) was determined by wet ashing a dry, but otherwise untreated, portion of bone in concentrated nitric and perchloric acids. After repeated fuming with hydrochloric acid, the solution was converted to 0.5N HCl, from which the Pb^{210} daughter, Po^{210} , was plated onto a clean silver disk which was then counted for alpha particles. A repeat assay after 4 to 20 months was used to determine the Pb^{210} content at the time of death.

Stable lead was determined on a separate portion of bone which was ashed overnight at 600°C and dissolved in nitric acid. The lead was

*Cat. 204MC Lindberg Eng. Co. E. H. Sargent and Co., 4647 W. Foster Avenue, Chicago, Illinois.

extracted at pH 0.5 with diethyldithiocarbamide, back extracted with 6 N HCl, evaporated to dryness, and then determined spectrophotometrically with dithizone.⁽¹¹⁾

Fluoride was determined in separate portions of bone ash by the diffusion method of Singer and Armstrong.⁽¹²⁾ Comparison of these measurements with those of normal bone analyzed here and by others is discussed elsewhere.⁽¹³⁾

Results and Discussion

The samples chosen to represent bone from subjects with osteogenic sarcomas were specimens of bone removed in the treatment of this disease at the Mayo Clinic over a period of about a year. These subjects, with one exception, had been exposed only to natural environmental radium. The one exception had received the equivalent of an I.V. injection of about 400 μ g radium and is discussed elsewhere.⁽¹⁴⁾

An osteogenic sarcoma is defined as a malignant tumor, the malignant cells of which produce osteoid tissue even if in only small foci. These sarcomas may be classified as osteoblastic, chondroblastic or fibroblastic depending on whether there is a predominance of osteoid, chondroid or fibromatoid differentiation. Osteogenic sarcomas may be graded from 1 to 4, the value corresponding to the degree of cellular dedifferentiation. As shown in Table 11, the distribution of the grades of malignancy in this series of 32 cases is similar to that in a larger series of 430 cases.⁽¹⁵⁾ There is a corresponding similarity in the classification by histologic types as shown in Table 12. The sex ratio of 19 males and 13 females, and the anatomical distribution of skeletal involvement shown in Table 13, are also typical for any group of osteogenic sarcoma cases. The group of subjects selected for this study, therefore, appears to be a representative sample.

Table 11

Grade of malignancy

Grade	This series		430 Cases in overall series, Percent
	Number	Percent	
1	0	0	1.6
2	7	22	17.2
3	14	44	54.4
4	11	34	26.7

Table 12

Histologic types of osteogenic sarcoma

Type	This series		430 Cases in overall series, Percent
	Number	Percent	
Osteoblastic	20	63	50
Chondroblastic	4	12	27
Fibroblastic	8	25	23

Table 13

Skeletal localization of tumors

Location	Number of cases	Location	Number of cases
Fibula	1	Femur	21
Rib	1	Tibia	4
Humerus	5		

The measurements of the Ra^{226} , Ra^{228} , Pb^{210} , stable Pb and F in bone from these individuals having verified osteogenic sarcomas are summarized in Table 14. The mean Ra^{226} and Ra^{228} concentrations of

Table 14

Concentrations of Ra^{226} , Ra^{228} , Pb^{210} , Pb and F in bone ash of individuals with an osteogenic sarcoma

Sample No	Age	Sex*	Bone	Ra^{226} pC/g ash	Ra^{228} pC/g ash	Pb^{210} pC/g ash	Pb μ g/g ash	F μ g/g ash
524	20	M	Femur	0.008 $\pm$ 0.002	0.0030 $\pm$ 0.0014			199
407	17	M	Femur	0.011 $\pm$ 0.002	0.0036 $\pm$ 0.0021	0.109 $\pm$ 0.009		191
342	12	F	Femur	0.011 $\pm$ 0.003	0.005 $\pm$ 0.003	0.076 $\pm$ 0.006	9.5	244
411	15	F	Fibula	0.012 $\pm$ 0.002	0.0058 $\pm$ 0.0042		16.4	247
280	9	M	Femur	0.012 $\pm$ 0.003	0.007 $\pm$ 0.003	0.075 $\pm$ 0.003	4.2	140
370	23	M	Femur	0.013 $\pm$ 0.0014	0.004 $\pm$ 0.001	0.061 $\pm$ 0.007	17.7	190
384	11	F	Femur	0.013 $\pm$ 0.002	0.0057 $\pm$ 0.0014	0.077 $\pm$ 0.007	9.9	192
282	50	F	Femur	0.013 $\pm$ 0.001	0.002 $\pm$ 0.001	0.054 $\pm$ 0.006	22.0	620
378	15	F	Femur	0.016 $\pm$ 0.002	0.006 $\pm$ 0.002	0.043 $\pm$ 0.003		123
522	14	M	Tibia	0.016 $\pm$ 0.003	0.0048 $\pm$ 0.0017			83
376	23	M	Femur	0.017 $\pm$ 0.002	0.0032 $\pm$ 0.0012	0.054 $\pm$ 0.006	24.0	110
554	13	M	Humerus	0.018 $\pm$ 0.014	0.0056 $\pm$ 0.0032			
412	44	M	Femur	0.020 $\pm$ 0.001	0.0037 $\pm$ 0.0023	0.097 $\pm$ 0.008	13.8	390
283	12	M	Femur	0.020 $\pm$ 0.003	0.006 $\pm$ 0.002	0.042 $\pm$ 0.005	7.0	83
539	17	M	Humerus	0.022 $\pm$ 0.003	0.0054 $\pm$ 0.0019		10.8	930
368	67	M	Femur	0.023 $\pm$ 0.003	0.005 $\pm$ 0.002	0.105 $\pm$ 0.006	15	456
483	27	M	Femur	0.024 $\pm$ 0.003	0.0071 $\pm$ 0.0021		6.5	1110
369	16	M	Humerus	0.027 $\pm$ 0.002	0.007 $\pm$ 0.001	0.054 $\pm$ 0.008	7.6	465
408	32	M	Femur	0.031 $\pm$ 0.003	0.0072 $\pm$ 0.0028	0.099 $\pm$ 0.008		1190
379	14	F	Femur	0.033 $\pm$ 0.002	0.0098 $\pm$ 0.0018	0.064 $\pm$ 0.008		81
386	12	F	Humerus	0.033 $\pm$ 0.006	0.0090 $\pm$ 0.0088			210
523	47	F	Tibia	0.033 $\pm$ 0.006	0.0033 $\pm$ 0.0019			533
375	30	F	Femur	0.035 $\pm$ 0.006	0.008 $\pm$ 0.001	0.092 $\pm$ 0.011	20.6	251
387	13	M	Femur	0.037 $\pm$ 0.003	0.0133 $\pm$ 0.0058			134
377	15	F	Femur	0.038 $\pm$ 0.002	0.0085 $\pm$ 0.0017	0.088 $\pm$ 0.011	24.7	135
409	47	M	Femur	0.038 $\pm$ 0.003	0.0032 $\pm$ 0.0019	0.072 $\pm$ 0.007	24.5	944
373	46	F	Humerus	0.042 $\pm$ 0.002	0.004 $\pm$ 0.002	0.110 $\pm$ 0.009	25.9	998
367	48	M	Rib	0.044 $\pm$ 0.004	0.016 $\pm$ 0.003		25.8	608
374	62	F	Tibia	0.048 $\pm$ 0.003	0.018 $\pm$ 0.002		26.2	1080
278	59	M	Tibia	0.050 $\pm$ 0.002	0.010 $\pm$ 0.001	0.182 $\pm$ 0.010		1150
383	13	M	Femur	0.058 $\pm$ 0.003	0.0130 $\pm$ 0.0043	0.066 $\pm$ 0.007		386
372	7	F	Femur	0.075 $\pm$ 0.003	0.019 $\pm$ 0.002	0.063 $\pm$ 0.008	22.6	223
Mean $\pm$ Std Dev				0.028 $\pm$ 0.016	0.007 $\pm$ 0.004	0.080 ⁽²¹⁾ $\pm$ 0.031	16.7 ⁽²⁰⁾ $\pm$ 7.6	411 $\pm$ 371

*M male F female

0.028 ± 0.016 and 0.007 ± 0.004 pC/g ash, respectively, are significantly higher ($P < 0.001$) than the 0.0124 ± 0.005 pC Ra^{226} /g ash and 0.003 ± 0.002 pC Ra^{228} /g ash found in individuals consuming water of low radium content.^(1,2) In contrast, the Pb^{210} , stable lead, and fluoride concentrations of 0.080 pC/g ash, 17 $\mu\text{g/g}$ ash, and 411 $\mu\text{g/g}$ ash, respectively, are not significantly different from those in individuals not having osteogenic sarcomas.^(3,1,13)

The somewhat high value of the mean Ra^{226} concentration found in this survey may be shown to correlate very well with the probable Ra^{226}

Table 15

Comparison of the observed and calculated concentrations of Ra^{226} from osteogenic sarcoma cases

Observed	Calculated
0.052	0.075
0.046	0.060
0.042	0.065
0.033	0.020
0.033	0.025
0.030	0.015
0.030	0.043
0.027	0.017
0.023	0.069
0.022	0.015
0.021	0.015
0.020	0.050
0.018	0.015
0.016	0.022
0.013	0.023
0.013	0.017
0.012	0.025
0.012	0.018
0.011	0.015
Mean 0.025 ± 0.016	0.032 ± 0.021

intake of these subjects and, thus, is not due to metabolic differences. In nineteen of the osteogenic sarcoma cases, the residential history was sufficiently stable and water samples were available so that comparison could be made with the uptake previously observed for other individuals. The expected concentration of Ra^{226} in bone ash, R, was computed from the following equation:⁽¹⁾

$$R = 0.0124 + 0.002 C_w \quad (1)$$

where R is in units of pC Ra^{226} /g ash and C_w is the concentration of Ra^{226} in drinking water in units of pC Ra^{226} /liter. When extrapolated to the 2600 g of ash in a Standard Man, this corresponds to a body content equal to that from food plus that contained in 52 liters of drinking water. The observed and calculated concentrations are shown in Table 15. The means of these concentrations, 0.025 pC/g ash and 0.032 pC/g ash respectively, are not statistically different

($P < 0.01$). Thus, the overall metabolism of radium in patients with an osteogenic sarcoma does not appear to be significantly different from that in other individuals.

Evaluation of the total radiation dose requires information about type of housing and medical X-ray exposure history which is not now available. If, however, we compare only the internal radiation dose in these patients with that of the average person, an indication of the significance of internal emitters may be inferred. The absorbed dose ratios for equal concentrations (pC/g ash) of Ra^{226} , Ra^{228} , and Pb^{210} are 3:6:1; i.e. 3 pC/g Ra^{226} gives the same dose rate in rads per unit time as 6 pC/g Pb^{210} or 1 pC/g Ra^{228} . As shown in Table 16, the Ra^{226} and Ra^{228} concentrations are higher in bone of osteogenic sarcoma patients than in bone from the average person. However, the lower Pb^{210} concentrations compensate to reduce the difference in dose to insignificance particularly in view of the larger K^{40} contribution. The increase in the radium dose rate is only 2 mrad/yr which is only about 10% of the total dose from the internal emitters. If one also includes the average radiation dose rate to the skeleton from cosmic and terrestrial sources of about 80 mrad/yr,⁽¹⁶⁾ then the 2 mrad/yr difference in radium dose rate amounts to only about 2% of the total. The relative biological effectiveness (RBE) of the various radiations, however, has not been considered.

Table 16

Comparison of absorbed dose to the skeleton from internal emitters in average individuals and in those with an osteogenic sarcoma

Emitter	Average individual		Osteogenic sarcoma patient	
	pC/g ash	mrad/yr	pC/g ash	mrad/yr
Ra^{226}	0.012	1	0.027	2
Ra^{228}	0.003	0.4	0.007	1
Pb^{210*}	0.105	4	0.080	3
K^{40}	-	10	-	10
Total		15.4		16

*Values in cortical bone

Unfortunately, good values for the relative biological effectiveness of the radiations involved in the continuous, low-level human exposure are not available, and the dose equivalent,* (RBE dose), cannot be estimated with any degree of certainty. Since the RBE for alpha-particle irradiation appears to be greater than one, the effect of the irradiation from Ra^{226} ,

*As defined in Reference 17.

Ra^{228} and Pb^{210} may be greater than that from the other internal emitters. However, the same RBE factor must be used for the normal individual as for the one having an osteogenic sarcoma so that the difference in dose is still relatively small.

In addition, no great significance can be attached to the slightly higher dose rates calculated for the osteogenic sarcoma cases because the hospital from which the osteogenic sarcoma samples were obtained is located within the geographical area having high concentrations of radium in municipal waters. Consequently, one expects a higher skeletal concentration of Ra^{226} and Ra^{228} in these individuals than in those from other areas.

In conclusion, this study has demonstrated that for an individual with an osteogenic sarcoma, the internal dose rate, radium metabolism, and possibly the metabolism of Pb^{210} , stable lead and fluoride, do not differ significantly from those of the average human being. Thus, in future studies, the metabolism of these substances by individuals with osteogenic sarcomas may be assumed to be identical to those of the unaffected population, so that measurements on the former group are unnecessary.

While it is conceivable that the variation in environmental radiation may have a direct effect on the spontaneous incidence of osteogenic sarcoma in man, this study is not suitable for this purpose. Estimation of the osteogenic sarcoma incidence requires knowledge of the population at risk for each of the dose levels. Although these data are available for a limited geographical area, they are not available for the region in which these individuals lived. This estimate must await completion of an epidemiological study such as is in progress in the Midwest.

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THE LEVEL OF RADIUM IN HUMAN BLOOD FORTY YEARS AFTER INGESTION

H. F. Lucas, Jr., J. H. Marshall, and L. A. Barrer*

Considerable information about radium metabolism has been obtained from measurements of radium retained at long times after exposure and from autoradiographic and microradiographic studies of the deposits in the bone.^(1,2) From theoretical considerations of the possible physical-chemical and biological process involved⁽³⁻⁵⁾ the importance of blood radium concentrations was apparent. While measurements at relatively short times after injection of Ra^{226} have been reported by Aub et al.⁽⁶⁾ and by Mays et al.,⁽⁷⁾ no measurements are available of the Ra^{226} in human blood at long times after exposure. It has been suggested by Rowland⁽⁸⁾ that the value by Aub et al.⁽⁶⁾ may be high owing to the medication given which had increased the daily rate of elimination by a factor of 3 to 6.

Samples of whole blood, cell-free serum, and cells containing some serum were obtained from four former New Jersey dial painters. The blood samples were obtained with a blood-letting needle under gravity flow to minimize cell fracture. Serum was obtained by placing about 30 ml whole blood in a clean 50-ml centrifuge tube, allowed to stand at room temperature for 20-30 min and then centrifuged for 10 min. The serum and cells were decanted into small bottles, frozen with solid carbon dioxide (-80°C), and sent to the Argonne National Laboratory for assay. No hemolysis was visible, and the serum is believed to be cell free.

Urine and fecal samples were obtained for three-day periods at about monthly intervals. Complete collection of urine was obtained for a total of 12 days, except for Case No. 5215 which was for 3 days. While complete collection of feces (12 days) was obtained for Case Nos. 5284 and 5025, only 7 and 3 day samples were obtained for Cases 5281 and 5215, respectively. For these last two cases, daily samples were not obtained, and further samples are required accurately to establish the fecal excretion rate.

The whole-body Ra^{226} content of these patients was determined by C. E. Miller using the tilting chair and multicrystal counting arrangements previously described.⁽⁹⁾ The Ra^{228} burden was low in all cases and could be disregarded. Breath radon samples were taken using the standard helmet and alpha scintillation radon counter system.^(10,11) For each subject, five samples of breath, each of ten minutes' duration, were taken. The helmet was worn for 90 to 115 minutes with each subject lying on a bed. Calculation of the emanating Ra^{226} was made from the time duration of breath collection.⁽¹⁰⁾

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The results of the gamma-ray and breath-radon measurements are summarized in Table 17. Subjects 5215 and 5281 were very apprehensive and uncomfortable in the helmet, as evidenced by a high respiratory rate of 20 to 24 exhalations per minute. The 20% variation between successive 10-min samples in subject 5215 is typical for apprehensive individuals. The much larger variation for subject 5281 has not been previously observed. In contrast, the nearly constant radon exhalation by subject 5284 is typical of patients who are completely relaxed or asleep. The Rn/Ra ratio ranged from 0.63 to 0.71; the average of 0.68 is not significantly different from the 0.69 found in other radium cases.⁽¹⁾

Table 17

Summary of breath radon and gamma ray measurements of four New Jersey cases

Subject	Emanating radium, μg						Gamma-ray Ra^{226} , μg	Rn/Ra	Total Ra^{226} , μg
	First	Second	Third	Fourth	Fifth	Mean			
5215	0.99*	1.00	0.98	0.86	0.78	0.92	0.43	0.68	1.35
5281	0.55	0.52	0.40	0.39	0.32	0.44	0.18	0.71	0.62
5284	0.167	0.150	0.147	0.149	0.156	0.154	0.09	0.63	0.24
5025	0.123	0.069	0.067	0.078	0.087	0.084	0.040	0.68	0.12

*May be low by 5% or less due to analytical error.

Measurements of the Ra^{226} in blood, feces, urine and body of the four subjects are summarized in Table 18. As has been found previously,⁽¹⁾ the radium excreted in the urine is a small fraction of the total ranging from 0.7 to 2.6% with an average of 1.7%. The average daily Ra^{226} excretion divided by the body burden gives a coefficient of elimination ranging from 0.5 to $1.2 \times 10^{-4} \text{ day}^{-1}$ with an average of $0.80 \times 10^{-4} \text{ day}^{-1}$. The

Table 18

Summary of Ra^{226} measurements in blood, feces, urine, and body of four New Jersey cases

Case number	5281	5215	5284	5025
Age	64	76	63	69
Years carried	39	45	45	45
Body Ra^{226} , μc	0.62	1.35	0.24	0.12
Feces, pc/day	30.9(7)	118(3)	28.2(12)	7.5(12)
Urine, pc/day	0.40 ± 0.03	0.86 ± 0.05	0.70 ± 0.03	0.18 ± 0.03
Urine/feces, %	1.3	0.7	2.5	2.4
Serum, pc/kg	0.34 ± 0.15	0.50 ± 0.24	0.54 ± 0.15	-
Cells, pc/kg	0.03 ± 0.10	0.21 ± 0.18	0.34 ± 0.13	-
Whole blood, pc/kg	0.18 ± 0.04	0.50 ± 0.05	0.25 ± 0.05	0.12 ± 0.04
Blood clearance, liters/day				
Urine	2.2 ± 0.6	1.7 ± 0.1	2.8 ± 0.3	1.4 ± 0.3
Feces	170	240	115	60

range and average values are not significantly different from the average of ten cases for which Norris et al.⁽¹⁾ found $0.80 \times 10^{-4} \text{ day}^{-1}$ about 20 years after injection. The similarity in the coefficient of elimination in these four cases, 40 years after ingestion, with that at 20 years suggests that the power law may break down at these long times. In any case, these findings are important enough to require confirmation.

Measurements of the Ra^{226} in the serum, cells and whole blood for these four cases is also summarized in Table 18. Since the calcium content of these samples has not yet been determined, a detailed and complete interpretation of the significance of these measurements will not be made at this time. However, if the accepted average calcium content in the serum and the whole blood in humans is assumed, then the calculated radium/calcium ratio in these tissues is less than 1% of the average for the skeleton. From the radium content of the whole blood and the excreta, clearance of radium by the kidney and the G. I. tract are found to range from 1.4 to 2.8 and 60 to 240 liter/day, respectively. These values are to be compared with a plasma clearance of 0.5 liter/day for the kidney and 69 liter/day for the G. I. tract which was found by Mays et al.⁽⁷⁾ a few days after a single I. V. injection.

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NORMAL FLUORIDE CONCENTRATION IN HUMAN BONE

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Introduction

Because of both the toxic and beneficial effects of fluoride on man and animals, great interest has been shown in the absorption and distribution within the body as well as in the excretion from the body following ingestion or inhalation. The toxic effects, bone changes and dental fluorosis have been observed with high levels of fluoride intake either from occupational exposure or from natural potable water. The cariostatic effect of approximately 1 ppm fluoride in drinking water has been well established in the epidemiological studies of H. T. Dean.^(1,2) A collection of Public Health Service publications in this field has been issued recently.⁽³⁾ Although experiments have been conducted to prove the physiological necessity of fluoride in the skeleton, the principal tissue in which fluoride accumulates, nothing conclusive has been demonstrated.^(4,5)

Studies at high or supplemented fluoride⁽⁶⁻⁹⁾ levels in man have yielded considerable information about the relative absorption by the lung and gastrointestinal tract of most of the compounds encountered. In continuous feeding experiments, an evaluation of human uptake has been obtained by differential measurement of intake and excretion. Direct measurement of long-term metabolism in living humans is not possible, since no long-lived radioactive isotope is available.

Measurements have been made of the intake and excretion of fluoride at low or natural levels.⁽⁹⁻¹²⁾ A normal human on an unselected diet and consuming water of low fluoride content over a 20-week period was found to excrete 0.4 to 0.6 mg fluoride per day.⁽¹¹⁾ Over 80% of the fluoride in the food was absorbed and then excreted in the urine. Since the maximum deviation between intake and excretion was 10%, it is estimated that less than 10% of the fluoride intake was accumulated by the body.

An early evaluation of the uptake of fluoride by the human was made by Zipkin et al.⁽¹³⁾ and more recently by Smith et al.^(14,15) In these studies, the fluoride content of the skeleton was estimated from the analysis of bone from individuals who had consumed water of known fluoride content for 10 or more years. Over the range of 0.1 to 4.0 ppm fluoride, a linear relationship was found between the fluoride content of the bone and that of the drinking water.⁽¹³⁾ In a study in which all of the subjects had consumed water of low fluoride content, Smith et al.⁽¹⁵⁾ stated that "a straight line relationship is apparent between fluoride concentration (in bone) and log age." Unfortunately, no comparison was made with an alternate hypothesis, such as linearity with age.

The average intake of a normal unselected diet provides 0.4 to 0.6 mg fluoride per day.⁽¹¹⁾ Adding either tea or fish (from the ocean) to the diet would approximately double the daily intake of fluoride. Drinking water with 1 ppm fluoride would also greatly increase the daily intake. Since waters having as high as 2.5 ppm fluoride are still being consumed, an average daily intake of fluoride of 0.5 to 5 mg/day is common. The effect of the recently introduced fluoride-containing toothpaste remains to be evaluated.

In this study, we have made additional measurements of the concentration of fluoride in normal human bone in order to correlate them with 1) the age of the subject, 2) natural radioelements Ra^{226} and Th^{228} in the bone, and 3) the fluoride concentration in individuals having a verified osteogenic sarcoma. Some data are also presented on placental transfer of fluoride.

Experimental Method

For this study, 109 bone samples obtained at surgery, autopsy, or amputation were analyzed for fluoride. These samples consisted of 48 cortical, 40 rib and 21 vertebral bone of which 32 cortical and one rib bone were from subjects having osteogenic sarcoma.

The analysis of fluoride was by the diffusion method of Singer and Armstrong⁽¹⁶⁾ and titration with thorium nitrate as employed by Ma and Gwirtsman.⁽¹⁷⁾ In this procedure, one to two grams of bone were ashed in platinum at 600°C for 15-16 hr and then ground in a mortar to a fine powder. About 50 mg were placed in the 2-oz diffusion bottle, covered with 0.5 ml water, frozen with dry ice (-80°C), and 2 ml cold perchloric acid added. A Teflon receiver strip having 2 mg dry sodium hydroxide uniformly distributed over approximately 2 cm² of striated area on one side was inserted. The bottle was tightly sealed and placed in an oven at 50°C for at least 20 hrs. The receiver strip was then removed from the bottle, and the NaOH(NaF) was dissolved and washed from the strip with 5 to 10 ml of distilled water. Aliquots were taken, and the fluoride analysis was made by back-titrating with thorium nitrate and a standard sodium fluoride solution in the presence of sodium alizarin sulfonate indicator. In agreement with Singer and Armstrong,⁽¹⁶⁾ nearly quantitative collection of fluoride on the receiver strip was observed. In an approximately 30-ml volume, recovery of standard samples was 97% and 90% when titrating 24 $\mu\text{g F}$ and 6 $\mu\text{g F}$, respectively. The blank with 50 mg of tribasic calcium phosphate was less than 0.5 $\mu\text{g F}^-$. The standard error for a single measurement obtained on a series of duplicate samples was 2.7%.

Discussion

Variation of Fluoride with Age of the Subject

The fluoride concentration in bone samples from 109 persons (61 male, 48 female) is presented in Table 19 in three groups according to bone type; a) cortical (tibia, femur or humerus), b) rib and c) vertebra. Ages range from 0-85 years with a mean of 39.0 years. Fluoride concentrations in the bone ash range from 46 to 3290 ppm with a mean of 815 ± 66 ppm. A linear plot of fluoride concentration versus age,

Table 19
Fluoride in human bone ash

Cortical				Rib				Vertebra			
Sample	Age	Sex	ppm F	Sample	Age	Sex	ppm F	Sample	Age	Sex	ppm F
372B*	7	F	223	477B	0	M	81	416B	0	F	46
485B	8	M	243	526B	3	M	410	418B	0	F	184
280B*	9	M	140	513B	8	F	83	291B	0 5	M	147
384B*	11	F	192	520B	8	M	932	230B	9	F	413
283B*	12	M	83	445B	18	F	771	258B	28	M	715
342B*	12	F	224	635B	22	M	1350	495B	28	M	1660
386B*	12	F	210	638B	23	M	984	648B	30	F	641
383B*	13	M	386	390B	25	F	183	206B	34	F	554
387B*	13	M	134	475B	27	M	1730	650B	42	M	978
540B	13	F	100	262B	30	M	328	601B	43	F	475
379B*	14	F	81	427B	32	F	406	651B	44	M	1130
377B*	15	F	135	528B	32	F	464	494B	46	F	1470
378B*	15	F	123	555B	32	M	335	470B	53	M	3290
411B*	15	F	247	525B	34	F	390	321B	55	F	771
369B*	16	M	455	575B	35	F	679	552B	57	M	989
407B*	17	M	191	336B	36	M	417	496B	59	M	1340
539B*	17	M	930	199B	37	M	494	489B	65	F	1070
486B	19	M	285	301B	37	M	906	535B	65	F	1210
370B*	23	M	190	420B	37	M	421	493B	71	M	1550
376B*	23	F	110	450B	37	F	399	446B	85	F	1240
483B*	27	M	1110	643B	37	F	3140	452B	85	F	1040
375B*	30	F	251	303B	38	M	720				
408B*	32	M	1190	334B	38	M	519				
343B	42	M	310	351B	38	F	1525				
412B*	44	M	390	518B	40	F	408				
373B*	46	F	998	335B	41	F	1190				
409B*	47	M	944	506B	41	M	1290				
523B*	47	F	533	264B	42	M	976				
276B	48	M	938	514B	42	F	387				
487B	49	M	504	458B	43	F	156				
282B*	50	F	620	443B	44	M	2290				
366B	53	M	981	426B	46	F	1950				
549B	56	M	1270	367B*	48	M	608				
385B*	58	M	462	556B	49	F	1880				
278B*	59	M	1150	329B	59	M	2690				
340B	59	M	796	423B	65	F	661				
286B	61	M	2400	394B	68	F	1020				
287B	61	F	605	480B	68	M	1150				
374B*	62	F	1080	396B	74	M	1470				
371B*	63	M	1210	587B	80	F	667				
484B*	64	M	389								
281B	65	M	2390								
277B	66	M	2300								
368B*	67	M	456								
413B*	68	M	1000								
285B	72	F	836								
406B	72	M	655								
341B	85	M	943								
Mean	38.3		654	Mean	37.9		912	Mean	42.8		997
σ Mean			84	σ Mean			113	σ Mean			153

*Samples from patients having osteogenic sarcoma

Figure 24, shows a variation in concentration as much as a factor of eight within the various age groups. However, there is still a very definite increase in fluoride content with age. While the water fluoride exposure histories are only 40% complete, it has been assumed that no individual consumed amounts greater than that naturally found in food and drinking water.

Figure 24

Correlation of the fluoride concentration in human bone ash with age.
 △ Reference 13; × Reference 15; □ Reference 14; ● This study.

Support for this assumption is derived from the data of Zipkin et al.⁽¹³⁾ and Smith et al.^(14,15) in that, on an ash basis, these results are within the limits for people consuming water with 1 ppm fluoride. The data of Smith et al.⁽¹⁵⁾ on rib and vertebra and of Smith et al.⁽¹⁴⁾ on whole body ash from a different set of subjects are not significantly different from the results of Zipkin et al.⁽¹³⁾ and those reported here.

In order to demonstrate a correlation of fluoride content of bone with age, the results obtained here, those of Smith et al.^(14,15) and those of Zipkin et al.⁽¹³⁾ which were obtained from areas of low fluoride water, all were plotted as a function of age in Figure 24. Although the data of

Smith et al.⁽¹⁵⁾ were obtained from 83 individuals, only the mean for each decade of life was reported. Neither the age distribution nor the variation from the mean fluoride content was given. Nevertheless, these measurements have been treated in this paper as 19 individual (10 male, 9 female) samples. When measurements on both rib and vertebra have been reported,^(13,15) the average value has been used.

Further proof of this increase with age is obtained by fitting a straight line to the data by a least squares analysis. A straight line of the form $y = a + bT$ was chosen as the simplest curve since none other is apparent either from the data or theory. Each point was weighted equally. The 71 values from the other investigators⁽¹³⁻¹⁵⁾ and the 109 values obtained here were fitted to a linear curve separately and combined by the method of least squares analysis. The three equations were as follows:

$$\text{Other data (71): } F = (278 \pm 158) + (11.7 \pm 2.6)t \quad (1)$$

$$\text{This study (109): } F = (250 \pm 116) + (14.5 \pm 2.6)t \quad (2)$$

$$\text{Combined (180): } F = (288 \pm 83) + (12.9 \pm 1.7)t \quad (3)$$

where F = ppm fluoride (on ash basis) and t = age (yrs).

These lines are shown as a broken, dashed and solid line, respectively in Figure 24. Considering the scatter in the data, neither the zero intercepts nor the slopes of the three curves are significantly different.

The fraction of the fluoride intake which is permanently bound in the skeleton can be estimated from the slope of the least squares line. The increase in fluoride concentration of 12.9 ppm/yr corresponds to a 0.1 mg/day increase in the skeleton of the 2600-g ash Standard Man. Since the normal daily intake of fluoride is from 0.5 to 1.0 mg/d, uptake and retention by the skeleton corresponds to 10% to 20% of the daily intake.

Powder x-rays studies have shown that fluoride directly substitutes in the hydroxyl position in the bone (human) apatite structure.⁽¹⁸⁾ Complete substitution, i.e., complete conversion to fluoro apatite, will give a fluoride concentration of 3.8×10^4 ppm. From Figure 24 and Equation (3), the average fluoride concentration at age 65 is 1200 ppm. This means that 3.2% of the bone crystals in the average skeleton may have been converted to fluoro apatite. Since fluoride concentrations in bone as high as 8700 ppm (23% of maximum) have been found,⁽¹⁸⁾ fluoride cannot be considered a trace element and may have a considerable effect on bone kinetics.

High Fluoride

The possibility of including samples from individuals with a high fluoride exposure was of concern since fluoride exposure histories were

not known in all cases. Thus, those having values in excess of twice the average were studied in greater detail. The constants in the least-squares line were doubled and the fifteen samples above this value are summarized in Table 20. All available information of the residence histories and sources of fluoride from water are included. Four samples were from areas where the fluoride content of drinking water ranged from 1 to 2.5 ppm. This would more than double the daily intake of fluoride, and these high values may be attributed to the increased exposure. The possibility of exposure to high fluoride waters could not be evaluated for nine of the samples. It is, however, significant that eleven of the fifteen samples were male, and industrial exposure may have been an important factor.

Table 20

Samples with fluoride concentration more than twice average

Sample no.	Age and sex*	Bone type	Fluoride in ash, ppm	Fluoride in water, ppm	Residence, years	Source
27	40F	Vertebra-rib	1700	0.1-0.4	10	Zipkin ⁽³⁰⁾
1255	57M	Whole body	2360	-	-	Smith ⁽²⁴⁾
277B	66M	Cortical	2300	-	-	This study
281B	65M	Cortical	2390	-	-	This study
286B	61M	Cortical	2400	-	-	This study
329B	59M	Rib	2690	0.8-1.2	55	This study
426B	46F	Rib	1950	0.3-1.0	32	This study
443B	44M	Rib	2290	-	-	This study
470B	53M	Vertebra	3290	1.2	53	This study
475B	27M	Rib	1730	-	-	This study
495B	28M	Vertebra	1660	-	-	This study
520B	8M	Rib	932	2.5	8	This study
556B	49F	Rib	1880	Well; creek	49	This study
635B	22M	Rib	1350	River	-	This study
643B	37F	Rib	3140	River	-	This study

*F = female, M = male.

The highest concentration of fluoride observed in this study was 3290 ppm in the vertebra of a 53-yr-old man (470B) with a lifetime consumption of 1.2 ppm F in his drinking water. This value is approximately one-third that found by Wolff and Kerr⁽¹⁹⁾ in the analysis of a similar specimen of human bone in a case believed to be chronic fluoride poisoning. However, it should be noted that McClure and his associates⁽²⁰⁾ found a woman with a fluoride level in the bone comparable to that of Wolff and Kerr's subject but with no apparent skeletal pathology. This indicates that the differences in toxic levels of fluoride in bone tissue may depend on several factors, such as individual tolerance and the method of acquisition of the toxic agent.

Placental Transfer

In order to determine the effect of placental transfer, bone ash from three human fetuses were analyzed. Concentrations of 46, 184, and 81 ppm fluoride were found. The first two subjects were from an area in which the water had a low fluoride concentration, 0.1 ppm, whereas the third was presumed to have been from such an area. These data demonstrate first, that there is a definite transfer of fluoride across the placenta and, second, that there is apparently some discrimination against fluoride in that these concentrations are significantly different ($P = 0.03$) from the 288 ± 83 ppm found by a least squares analysis of the data as a whole [Equation (3)].

Fluoride and Osteogenic Sarcoma

Samples of the uninvolved cortical bone were obtained from 32 subjects with verified osteogenic sarcoma.* For comparison, samples of cortical bone were obtained from 16 subjects having a similarly debilitating nonmalignant bone disease. Direct comparison of the fluoride concentration in these two groups of subjects was not possible because of the wide difference in mean age of 31.5 and 51.8 years, respectively. However, an approximately equal mean age is obtained if only those samples from individuals 40 years or older are considered. As shown in Table 21 for these selected samples the osteogenic sarcoma group has a mean age of 56.3 years and a mean fluoride concentration of 769 ± 93 ppm, while the control group has a mean age of 60.7 years and a mean fluoride concentration of 1148 ± 203 ppm. The ratio of the concentration of the osteogenic sarcoma group to the control group is 0.67 ± 0.13 . As shown in Figure 24, the mean fluoride concentration at an age of 60 years is approximately

Table 21

Fluoride concentration in selected osteogenic sarcoma and control bone

Sample no	Age	Sex	Fluoride in ash ppm	Pathology	Sample no	Age	Sex	Fluoride in ash ppm	Pathology
412B	44	M	390	Osteogenic sarcoma	343B	42	M	310	Atherosclerotic gangrene
373B	46	F	998	Osteogenic sarcoma	276B	48	M	938	Atherosclerotic gangrene
409B	47	M	944	Osteogenic sarcoma	487B	49	M	504	Fibrosarcoma
523B	47	F	533	Osteogenic sarcoma	366B	53	M	981	Fibrosarcoma
282B	50	F	620	Osteogenic sarcoma	549B	56	M	1270	Chondrosarcoma
385B	58	M	462	Osteogenic sarcoma	340B	59	M	796	Atherosclerotic gangrene
278B	59	M	1150	Osteogenic sarcoma	286B	61	M	2400	Melanoma
374B	62	F	1080	Osteogenic sarcoma	287B	61	F	605	Gangrene
371B	63	M	1210	Osteogenic sarcoma	281B	65	M	2390	Atherosclerotic
484B	64	M	389	Osteogenic sarcoma	277B	66	M	2300	Gangrene
368B	67	M	456	Osteogenic sarcoma	285B	72	F	836	Atherosclerotic gangrene
413B	68	M	1000	Osteogenic sarcoma	406B	72	M	655	Chondrosarcoma
					341B	85	M	943	Atherosclerotic gangrene
Mean	56.3		769		Mean	60.7		1143	
σMean			93		σMean			203	

*We are indebted to Dr. D. C. Dahlin, Pathologist, Mayo Clinic, for these samples of bone.

1100 ppm. This value is derived from a group of predominantly trabecular bone samples which have been shown to have a higher fluoride content than cortical bone.⁽¹³⁾ Consequently, the low ratio appears to result from the high values in the control group. It is concluded that uptake and retention of fluoride by individuals having an osteogenic sarcoma is not very different from that for any other person.

Fluoride and Natural Radioisotopes

No correlation was found to exist between fluoride and naturally occurring radioisotopes in human bone ash. The Ra^{226} concentration in 68 and Th^{228} concentration in 49 of the samples ranged from 0.007 to 0.229 and 0.002 to 0.026 pc/g ash, respectively. Although a correlation was found to exist between the Ra^{226} and the fluoride content of certain well waters in Illinois,⁽²¹⁾ no correlation existed for areas in which the subjects of this study resided. Therefore, considering the low level of fluoride in the water consumed by the majority of the individuals from which samples were obtained, no correlation was to be expected.

Variation of Fluoride Concentration with Bone Type

The fluoride concentration of different bones from the same individual has been found by Zipkin et al.⁽¹³⁾ and in this study to vary by more than a factor of two. Zipkin et al.⁽¹³⁾ found that, for a group of 33 individuals with a mean age of 55.5 yrs, the mean concentration of fluoride in ash of the vertebra (1120 ± 100 ppm) was similar to that of the sternum (1340 ± 230 ppm). However, the fluoride concentration in the vertebra was significantly higher than that in the ash of the iliac crest (720 ± 60 ppm, $P < 0.01$) or of the rib (860 ± 80 ppm, $P < 0.05$).⁽¹³⁾

Our measurements of the fluoride concentration in these same bone types from three individuals with ages of 30, 42 and 44 do not differ significantly from this larger study. Measurements of the fluoride concentration in these same bone types but from different individuals are summarized in Table 19. The mean fluoride concentration in the vertebra was extrapolated to that for the same age as found for the other bone types (38.0 yr) by the previously-determined relationship [Equation (3)] of 12.9 ppm F/yr. This reduced the mean concentration of the vertebra to 935 ppm. As had been found by Zipkin et al.⁽¹³⁾ the mean concentration of fluoride in ash of the vertebra (935 ± 153 ppm) was significantly higher than that in cortical bone (654 ± 84 ppm, $P < 0.05$). In contrast, the fluoride concentration in the vertebra (935 ± 153 ppm) was not significantly different from that in the rib (912 ± 112 ppm). However, these samples were not all obtained from the same geographical region, and no great importance is attributed to the difference between these measurements and those of Zipkin.⁽¹³⁾

Summary

Measurements have been made of the fluoride concentration in portions of femur, rib and vertebra from 109 individuals. Although residential, and hence fluoride exposure, histories were not complete, it has been found by comparison of these measurements with those of other investigators⁽¹³⁻¹⁵⁾ that no individual consumed amounts greater than those normally found in food and local drinking water.

An increase of fluoride concentration with age has been noted in this and other studies.^(3,15,22) The data from all investigators (180 individuals) was combined in a single figure, and a linear increase with age was chosen since no other is apparent from the data or required by theory.

A linear least squares fit by an equation of the form $F = a + bt$ was used, where a and b are constants, t was the age in years, and F is the ppm fluoride in the bone ash. The least squares fit of the data of other investigators and of this study gave nearly identical results. The equation $F = (288 \pm 83) + (12.9 \pm 1.7)t$ was obtained from the combined data. From the slope of this equation and from the average daily fluoride intake of 0.5 to 1.0 mg, it is estimated that uptake and retention by the skeleton is 10% to 20% of the intake. In addition, the average fluoride concentration at age 65 of 1200 ppm and the maximum reported in humans of 8700 ppm correspond to 3.2% and 23% of the maximum attainable. Consequently fluoride, even at these low levels of intake, cannot be considered a trace element and may, in fact, have a significant influence on bone kinetics.

Fluoride was found in the bone from three human fetuses. The mean concentration of 103 ppm demonstrates that transfer across the placenta occurs and that apparently some discrimination occurs since this value ($P < 0.03$) is significantly different than the 288 ± 83 ppm found by a least square analysis of the data as a whole.

Samples of femur or tibia were obtained from 32 individuals having a verified osteogenic sarcoma and from 16 individuals having a similarly debilitating bone disease. These two groups were not well correlated in age, and direct comparison even for age-matched samples is not significant. It was apparent, however, that uptake and retention of fluoride by individuals having an osteogenic sarcoma is not significantly different from that for any other person.

Although a correlation between the Ra^{226} and the fluoride concentration has been found for certain well waters in Illinois, few of the individuals in this study consumed water from these sources. In addition the only source of fluoride for many of the subjects was that in their food so that no correlation was to be expected and none was found.

Variations by as much as a factor of two in the fluoride concentration of different bones from the same individual were found in this as well as in the previous study of Zipkin et al.⁽¹³⁾ Significantly higher fluoride concentrations were found in vertebra than were found in either iliac crest or rib. In this study, in contrast with the study by Zipkin et al.,⁽¹³⁾ the concentration in the vertebra was not different from that in the rib. However, not all of these samples were from the same geographical region, and no significance is attributed to the difference.

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THE KINETICS OF ALKALINE EARTH METABOLISM IN ANIMALS. I. BASIC PRINCIPLES

Richard B. Holtzman

Introduction

Although calcium, one of the vital elements in the body, has been intensively studied for many years, quantitative aspects of its metabolism are poorly understood. Moreover, the role and metabolic properties of the calcium-like elements, i.e., strontium, barium, radium, and some of the heavy metals, have not been quantitatively related to calcium metabolism.⁽¹⁾ A method that has been used extensively in these studies is the measurement of the kinetics of retention. However, because of the metabolic intricacies involved, a mathematical description of the results may be quite complex.

When a tracer is used to follow a reaction, compartmental analysis is often used to interpret the results. In a single steady-state compartment the property measured decreases exponentially with time,^(2,3) while in a multicompartment system of N compartments, N exponentials are needed which require $2N$ adjustable parameters. With more than 2 exponential terms the mathematical manipulation becomes unwieldy and the meaning of the terms and identification of the compartments may become obscure. This latter point is particularly important since the basic purpose of a quantitative description is to provide an understanding of the mechanisms involved and to allow predictions of further phenomena.

It has been noted, however, that an empirical description of the retention of the alkaline earths and some other elements in man and animals⁽⁴⁾ is provided by a power function of the form

$$R = At^{-b} \quad (1)$$

where R is the fraction of the original dose (fractional retention) remaining at time t , A is a constant (usually the fractional retention at 1 day), and b is another constant where $0 < b < 1$. Since this function becomes infinite at $t = 0$, it has been more or less arbitrarily modified to

$$R = \frac{(t+\gamma)^{-b}}{\gamma^{-b}} \quad (2)$$

where γ is a constant. This function is more satisfactory than Equation (1) and appears to describe the retention of calcium and calcium-like elements.⁽⁴⁾ Cohn et al.⁽⁵⁾ and Marshall⁽¹⁾ have discussed this recently in great detail. There are, however, several objections to the use of the

power function. First of all, except for the simple mathematical derivation of Marshall and Rowland,⁽⁶⁾ and of Anderson et al.,⁽⁷⁾ there has been no quantitative theoretical justification of this function,⁽⁸⁾ and, secondly, there are objections to the qualitative interpretations of this function.⁽⁸⁾

Norris et al.⁽⁴⁾ have also applied this function to the case of the continuous uptake of a tracer. The time integral of Equation (2) over the interval 0 to t gives

$$R_t = \frac{(t+\gamma)^{-b+1}}{(-b+1)\gamma^{-b}} \quad (3)$$

where R_t is the total uptake of the tracer. While this equation describes the few available data fairly well, it is objectionable because the retention, R_t , approaches infinity as t becomes very large ($R_t \rightarrow \infty$ as $t \rightarrow \infty$). This concept is biologically unreasonable since no element which is excreted to any extent concentrates indefinitely in tissue. This is shown by the experimental evidence of Lucas⁽⁹⁾ and of Finkel et al.⁽¹⁰⁾ The former data indicate that the total body content of Ra^{226} in persons consuming water containing a large amount of Ra^{226} is independent of age. Similarly, the latter data indicate that mice on Sr^{90} diets approach a constant total content of tracer.

It is suggested here, however, that the power function can be derived from some relatively simple principles of chemical kinetics, application of which will alleviate many of the difficulties involved in the acceptance of this function. Thus, it is possible to derive functions which meet the above objections, at least qualitatively describe the data, explain several fairly complicated phenomena, and suggest a mechanism which is reasonable in terms of physical chemistry. This mechanism is the continual recrystallization of the mineral.⁽¹¹⁾

Derivation of the Power Function

In order to derive the power function several assumptions will be made: 1) The system described is a pure chemical system of constant mass. 2) The effects of biological activity will be neglected, i.e., the system is assumed to be pure "inorganic bone mineral," hydroxyapatite or octacalcium phosphate, bathed in a solution in which the calcium in solution is in chemical equilibrium with that of the bone. Only ionic effects are considered, with organic material acting only as pH buffers; chemical complexing effects are neglected. 3) The blood serum and interstitial fluid in contact with the bone mineral are considered to be a single compartment in the steady state with respect to calcium metabolism, i.e., the calcium is perfectly mixed in the fluid, and the amount entering the

compartment is equal to that leaving at any instant. 4) The system is analogous to the in vitro system of Newman,⁽¹²⁾ i.e., hydroxyapatite is in a proper blood serum-like solution in a flask. However, the ratio of the mass of the solid to the volume of the solution may not be identical in the two systems. 5) Finally, radioactive decay of the tracer is neglected.

Only two situations will be discussed: first, the "single-injection" case describing the retention in the solid phase (bone) in a solid-liquid mixture of a tracer initially incorporated into the solid, and, second, the "continuous-uptake" case describing the change in concentration of a tracer which is continuously incorporated into the solid phase of the system. Two other applications will be discussed in a second paper,⁽¹³⁾ i.e., the "single-injection" case involving the retention of the tracer in the liquid phase after initial injection of this tracer into the liquid, and a more general extension of the single-injection cases in which an additional mechanism is also operative.

Single Injection, Retention in Solid

The first case to be considered because of its relative simplicity is that in which the tracer is initially incorporated into the solid (bone) phase. A certain fraction of the labelled calcium is deposited in the bone, and the remainder excreted. Further deposition from liquid to solid phase is then neglected. The retention of the deposited calcium and tracer is then followed, the label (Ca^{45} , Sr^{90} , Ra^{226} , etc.) being assumed to depict calcium retention to a greater or lesser extent.

Before going into the actual derivation, it should be noted that the power function in Equation (2) may be expressed as an exponential:

$$R = \frac{(t + \gamma)^{-b}}{\gamma^{-b}} = \frac{1}{\gamma^{-b}} \exp [-b \log (t + \gamma)] \quad . \quad (4)$$

The power function, thus, is an exponential in $\log (t + \gamma)$ space instead of t -space. This time-space may be called "growth time-space."*

The essential point of this paper, however, is that the power and exponential functions, in addition to being mathematically related, have in many cases a common origin in the theory of reaction kinetics. An exponential is derived from the differential equation describing first-order kinetics^(16,17)

$$\frac{dc}{dt} = -kc \quad (5)$$

*Examples of this time-space are animal growth, individual cell growth and learning response, which increase more or less logarithmically with time. Other logarithmic functions are also known, such as sensitivity to sound and light in which response is a logarithmic function of intensity.^(14,15)

where c is the concentration of the material at time t and k is a rate constant. The fractional retention is then

$$R = \frac{c}{c_0} = e^{-k t} \quad (6)$$

where c_0 is the initial concentration of the material at $t = 0$.

First-order kinetics implies a process in which only one atom or molecule is required to complete each reaction, as in radioactive decay. In the context of interest, a calcium atom (or a molecule containing a calcium atom) leaves the bone crystal and enters the blood (solution):

This process may be generalized to one of n^{th} order requiring the simultaneous** interaction of $n\text{Ca}$ atoms and to one requiring the simultaneous interaction of other atoms and molecules, such as the alkaline earths, phosphate, and carbonate, i.e.,

The generalized kinetic equation for the change of Ca in the bone is then

$$\frac{d(\text{Ca})}{dt} = -k(\text{Ca})^n (\text{M})^m (\text{P})^p \dots \quad (9)$$

where the parentheses represent the concentration of the enclosed species in the bone. Where only calcium and a tracer, T, are observed (all other constituents being constant), the process becomes

Only one unit of tracer, T, is shown per reacting unit because of the very low concentration of the tracer relative to that of the calcium. (Inclusion of more than one unit of T does not essentially alter the following argument.)⁽³⁾ The rate equation for the tracer then becomes

$$\frac{dc^*}{dt} = -k c^n c^* \quad (11)$$

where c is the concentration of the calcium deposited with the tracer [g Ca deposited per g Ca in the system (bone)], and c^* is the tracer

**Simultaneous: the lifetimes of any intermediate reactions are short relative to that of the measured one, e.g., the collision of 4 molecules "simultaneously" may actually be the collision of 2 short-lived dimers.

concentration (per g of deposited bone calcium). If the specific activity of the traced (deposited) calcium is constant (see discussion at the end of this section), i.e., $c^* = Sc$, where S is a constant, then

$$\frac{dSc}{dt} = -k c^n Sc = -k Sc^{n+1} \quad (12)$$

or

$$\frac{dc}{dt} = -k c^{n+1} \quad (13)$$

Separating variables and integrating c between c_0 (the concentration at $t = 0$) and c (the concentration at time t) and integrating t between 0 and t , we obtain

$$c^{-n} - c_0^{-n} = n k t \quad (14)$$

The fractional retention [Equation (6)] is then

$$R^{-n} = \left(\frac{c}{c_0} \right)^{-n} = \frac{n k t}{c_0^{-n}} + 1 \quad (15)$$

or

$$R = \frac{\left[t + \frac{c_0^{-n}}{n k} \right]^{-1/n}}{c_0 \left[\frac{1}{n k} \right]^{-1/n}} \quad (15')$$

Since $c^* = Sc$ and $c_0^* = Sc_0$, this equation applies to any tracer for which $n > 0$ in Equation (11). However, both n and k of Equation (11) are dependent upon the nature of the tracer. This same derivation also applies to stable calcium if T in Equation (10) is replaced by Ca .

Finally, if we set $b = \frac{1}{n}$ and $\frac{1}{n k} = \frac{b}{k} = \beta$, we obtain:

$$R = \frac{\left(t + c_0 \frac{-1}{b} \beta \right)^{-b}}{c_0 \beta^{-b}} \quad (16)$$

which is analogous to Equation (2)

$$R = \frac{(t + \gamma)^{-b}}{\gamma^{-b}} \quad (2)$$

if

$$\gamma = c_0^{\frac{-1}{b}} \beta$$

The form of the Norris' equation, therefore, can be obtained by a basic chemical kinetic derivation which demonstrates the relation between this equation and calcium and tracer metabolism. The constant γ is thus

Figure 25

Fractional retention as a function of time. This diagram shows how the fractional retention varies as the initial concentration c_0 varies. ($c_{02} > c_{01}$).

tion to be other than one. This also applies in a well-mixed compartment in a steady state,* regardless of the order of the reaction which the gross material undergoes.⁽³⁾ However, in calcium metabolism in bone, the bone is not in a well-mixed state, the tracer remains with the calcium with which it is deposited ($c^* = S_c$), and, therefore, the kinetics observed are, more or less, those of the calcium itself. In actuality, since only the tracer is followed, the kinetics observed are precisely those of the calcium-tracer

shown to be an essential part of the derivation and to be separable into three components, c_0 , b and k , each of which, in principle, is separately measurable. An example of the variation of R with c_0 may be seen in Figure 25 [Equation (16)]. If c_{02} is greater than c_{01} the slopes will be the same at $t \gg \gamma$, but the γ -term will be smaller so that R of c_{02} will be below, but parallel to that of the R of c_{01} . The quantity of calcium deposited at the time of tracer uptake, c_0 , would be proportional to the calcium content of the medium in contact with the bone crystals, i.e., interstitial fluid or serum in bone.

An objection to the application of a function of the form of Equation (16) to tracer studies is that usually the tracer concentration is too low for the order of the reac-

*"Steady state" is defined as the state in which the concentration of the material of interest (not the tracer) is constant, and the amount entering the compartment is equal to that leaving.

reaction ($n\text{Ca} + \text{T}$) of Equation (10). The description presented here, however, does not imply a change in total calcium content, in that deposition and dissolution may occur simultaneously, but at different locations. In the case discussed only retention and not deposition has been considered, and thus only the dissolution component is observed. The deposition case is to be treated in a second paper.

Continuous Uptake

The continuous uptake or continuous feeding case is derived by modification of Equation (11). If the amount of the tracer deposited in the bone per unit time, q^* , is assumed to be constant

$$\frac{dc^*}{dt} = q^* - k c^n c^* \quad . \quad (17)$$

If, as in the single injection case, we assume the specific activity of the calcium to be constant, $c^* = S c$ and $q^* = S q$, and we observe c^* rather than c , then

$$\frac{dc^*}{dt} = q^* - S^{-n} k c^{*n+1} \quad . \quad (18)$$

Separating variables, setting $n + 1 = m$, and integrating, we obtain

$$\int \frac{dc^*}{q^* - S^{-n} k c^{*m}} = t \quad . \quad (19)$$

The left-hand term is not generally integrable in analytic form, except when m is an integer. Some of these integrals are given in Appendix I, and are seen to be of the form,

$$\log F(q^*, c^*) + \tan^{-1} f(q^*, c^*) = t \quad . \quad (20)$$

Thus, solving for c^* one obtains $c^* = g(t)$ which is finite when $t > 0$. Also, since the integrand is continuous for all c^* and $m > 0$, the integral will be continuous for all positive values of m . The same reasoning may also be applied to c since the specific activity of the calcium is assumed to be constant.

A more exact proof that c^* approaches an asymptotic limit for all $m > 0$ is shown by solving Equation (18) for c^* ,

$$c^* = \left[\frac{S^n q^*}{k} - \frac{S^n}{k} \frac{dc^*}{dt} \right]^{1/m} \quad (21)$$

in which all the parameters are positive. Thus, at the maximum value of c^* , the slope of the function $dc^*/dt = 0$ and $c^* = \sqrt[n]{(q^* S^n)/k}$ or $c = \sqrt[n]{q/k}$, which is finite and independent of time.

Discussion

Theory

The theory as presented appears to describe the data quite well, at least in a qualitative fashion. The power function in one form or another has been shown by Norris et al.,⁽⁴⁾ Cohn et al.,⁽⁵⁾ and most recently by Marshall⁽¹⁾ to apply reasonably well to the bone-seeking tracers. Evidence tending to support the particular derivation presented here is more meager and less obvious.

One of the merits of the kinetic derivation is self-consistency. Thus, a power function similar to that of Norris et al.⁽⁴⁾ has been derived, and by a logical modification for the continuous uptake case, a function representing a limited uptake of tracer has also been presented. Functions describing other cases involving the effect of serum and soft-tissue retention in which different mechanisms apply may also be derived by logical extensions of the method. The whole-body retention, therefore, may also be estimated. Another merit of this method is that, in principle, many of the situations can be set up as differential equations to which meaningful, if only approximate solutions, may be found.

A major objection is that the orders of the reactions involved are extremely high. In general, textbooks on chemical kinetics state that orders greater than three are not meaningful,^(16,17) but the reactions discussed are usually molecular rather than ionic. [Benson⁽¹⁷⁾ does, however, mention precipitation reactions.] In a following paper, however, Edgington has demonstrated that this restriction on reaction order does not apply to the kinetics of crystal growth and recrystallization in which orders as high as 8 or 9 have been reported.⁽¹¹⁾

A second objection to this method is that one might expect a form of the equation for the continuous uptake case to be at least similar to that of Norris et al.⁽⁴⁾ Compared to Norris' results [Equation (3)], the kinetic derivation indicates a limited accretion of calcium and, as discussed previously, of a calcium tracer, which is a concept more in accord with theory and experiment.^(9,10) However, it should be noted that the solution no longer embodies the power function. The discrepancy between the direct integration of the power function and the derivation of this paper is the result of the implied statement in the former that when a quantity of tracer, Adt , is deposited at time, t , in the past, the amount remaining at the time

of measurement will be $At^{-b}dt$. This implies that tracer deposited at one time is independent of that deposited at any other time, which is an apparently reasonable assumption since the power function $R = At^{-b}$ is assumed to describe tracer retention and tracer concentration is negligible. However, as has been shown here, the observed retention is essentially that of calcium and not of the tracer itself. Therefore, the tracer (or calcium) deposited in the bone at one time is dependent on that deposited at other times. In the previous treatment there is a contradiction in that the method of integration employed implies that each injection is independent of any other injection, i.e., it follows a first order reaction. However, the power function implies a high order kinetic reaction. Thus, this discussion illustrates some of the problems in the use of an empirical equation to derive further equations. For example,

$$R = \frac{(t + \gamma)^{-b}}{\gamma^{-b}} \quad (2)$$

refers to both tracer and gross material (calcium) metabolism, but as shown in the derivation of this paper, no difference can be observed except for some changes in the constant. Consequently, direct integration of Equation (2) (which implies independence of successive depositions) leads to theoretically unreasonable results.

A third objection is that the derivation proposed in this paper is not the only possible one. One previously proposed is a first-order reaction [Equation (5)] in which the rate factor is time dependent:

$$k = k(t) = K/t \text{ or } K/t + \gamma \quad (22)$$

This is essentially the treatment used by Marshall and Rowland⁽⁶⁾ and by Anderson et al.⁽⁷⁾ A description and extension of the derivation is given in Appendix II. A second derivation is that of Reynolds⁽¹⁸⁾ taken from ion exchange theory in which the reaction is first order, but it is diffusion controlled.⁽¹⁹⁾ However, neither of these methods appears suitable. In the first place each results in an equation which gives a fractional retention independent of the initial concentrations of the calcium. Experimental evidence indicates that this is not so. Secondly, in continuous feeding neither method results in a limited accretion of tracer at long times. Thirdly, diffusion theory always appears to lead to a value of $b = 0.5$, or an integral multiple thereof, regardless of the initial conditions, as shown by Reynolds⁽¹⁸⁾ and Marshall.⁽²⁰⁾ The actual values of b may be appreciably different, e.g., 0.1. Finally, as shown in Appendix II in the time-dependent-rate-factor derivation, Equation (22), the γ -term is not inherent in the derivation, but must be added arbitrarily.

A third alternative description of alkaline earth metabolism, the sum of exponentials, which is self-consistent, is generally undesirable because each exponential requires two adjustable constants. Moreover, if the metabolism is controlled by a set of steady-state compartments, it appears very improbable that in the many apparently different situations studied, the parameters of the compartments are always such as to lead to a sum of exponentials which so closely approximates the simpler power function.

Mechanism

The method of derivation of the power function and the results suggest a mechanism. The apparent molecularity of the reaction, $n + 1$, is quite high in that for $b = 0.14$ (Ca^{45} in rats), $n + 1 = 8$. Thus, 7 stable Ca atoms must simultaneously leave the bone matrix with each Ca^{45} atom (and subsequently be excreted). In addition 8 to 10 is the number of calcium atoms in a unit cell of some types of crystals thought to exist in bone (calcium octaphosphate or hydroxyapatite). While the order of this reaction appears to be quite high, Edgington has shown that reactions of this order do occur in at least two processes, namely, crystal growth and the closely related one of recrystallization.⁽¹¹⁾ The former process is a type of reaction which has been shown to involve reaction orders of 8 or 9 in the crystal growth of CaF_2 , where the reaction order is the number of CaF_2 units in a crystalline unit cell. The power function, therefore, in these systems, may be explained on the basis of an inorganic crystalline system. For example, synthetic hydroxyapatite crystals in vitro take up tracers at a rate described remarkably well by a power function.⁽¹¹⁾

In the case of other nuclides, such as Sr^{90} where $b = 0.2$ and $n + 1 = 6$, a somewhat different unit cell may exist where only 6 cations (5 Ca atoms + 1 Sr^{90} atom) must be removed simultaneously to dissolve the unit cell. One piece of evidence often cited as necessary to the establishment of the recrystallization mechanism is an observed increase of crystal size, a phenomenon so far unobserved in bone.⁽²¹⁾ This phenomenon is actually unnecessary to the argument, however, in that chemical or crystal-solution equilibria are dynamic phenomena in which both forward and backward processes occur. Equilibrium implies only that the forward process occurs at the same rate as the backward one.

While the mechanism proposed here is not original,^(12,21) in contrast to previous treatments it is quantitative and quite analogous to the well-established concepts of crystal growth.⁽¹¹⁾ Moreover, it is suggested that in bone this mechanism is the main one operating, even at short times in that all the parameters of the power function [Equation (16)] appear to be quantitatively explainable in terms of this mechanism. Modifications will be described in Part II of this study.

Correlation of Experimental Data

The power function as derived here may also be shown to be consistent with much of the experimental data. It appears that the fractional retention, R , is independent of the amount of tracer injected, but dependent on the initial calcium deposition, c_0 . The work of Van Dilla et al.⁽²²⁾ showed the radium retention in dogs to be independent of the amount of radium injected even though this amount ranged over several orders of magnitude. Comparison of the results of Bishop et al.⁽²³⁾ with those of Cohn et al.⁽⁵⁾ in which different quantities of Sr^{85} were injected into human subjects indicates no dependence on dose since both workers observed about the same constants for initial retention and for b .

That fractional retention is dependent on calcium intake is demonstrated by the rat data of Thompson and Palmer⁽²⁴⁾ in which the one-day retention of injected Sr^{90} varied by a factor of two or more when the calcium content of the diet varied from 0.03% to 2%. Thus, in general terms, in agreement with the work of Van Dilla et al.,⁽²²⁾ R is independent of the tracer and its concentration, except for differences in b . It is also dependent on the value of c_0 , the quantity of calcium deposited in the system with the tracer. The work of Cohn et al.⁽²⁵⁾ shows that for rats on high strontium diets, Sr^{85} retention is decreased 76%. However, the strontium is no longer a tracer, but a gross element. Even in this case, while the gross element is increased many orders of magnitude over that of the tracer alone, only a relatively small decrease of Sr^{85} retention was noted.

An objection to the application of the power function is that in the derivation of this function the value of the exponent, b , is dependent only on the reaction mechanism, so that variations in b are expected only under drastic conditions. The results of Thompson and Palmer⁽²⁴⁾ as shown in Table 22 (taken from Table 4 of their paper), however, appear to contradict this conclusion in that after a single injection of Ca^{45} into rats the exponent did vary as a function of dietary calcium.* To complicate the situation further the value of b describing Sr^{90} retention did not vary. However, it will be shown that these results are, nevertheless, compatible with the proposed mechanism, even with the simplifying assumptions that b is constant and that the interaction of the soft tissue is not significant, i.e., the system is a purely chemical one. Moreover, regardless of the correctness of the above contention, this treatment does illustrate the importance of taking into account the γ -term in the analysis of retention data.

*In these experiments rats were divided into groups, and each group was fed a controlled diet containing either 0.03, 0.1, 0.5 or 2% calcium. Each animal was then injected with 15 μC Ca^{45} and 10 μC Sr^{90} . Blood and femur were analyzed for the nuclides and for stable calcium.

Table 22

Retention of Ca^{45} and Sr^{90} as a function of total calcium
in the diets of rats*

Dietary calcium level, % of diet	Skeletal retention of Ca^{45} , %	Skeletal retention of Sr^{90} , %	$A_{\text{Ca}}/A_{\text{Sr}}$
0.03	$61 t^{-0.007}$	$52 t^{-0.20}$	1.17
0.1	$63 t^{-0.056}$	$51 t^{-0.22}$	1.24
0.5	$49 t^{-0.083}$	$38 t^{0.21}$	1.28
2.0	$32 t^{-0.14}$	$24 t^{-0.19}$	1.33

*Taken from Table 4 of Reference 24.

Of the three mechanisms controlling the loss of a nuclide after a single injection, excretion, bone uptake and bone retention, the first two are the most significant. Loss from bone one day after injection is negligible, as shown in the data of Norris and Kisielewski,⁽²⁶⁾ and consequently, the 1-day retention factor, A , represents the excretion and uptake rates, only. Table 22 shows the A 's for both Ca^{45} and Sr^{90} to be strongly dependent on the dietary calcium levels. For example, the initial Ca^{45} retention varied from 32% on the 2% calcium diet to 61% on the 0.03% diet, while the comparable 1-day Sr^{90} retentions varied from 24 to 52%. However, on all diets the Ca^{45} -to- Sr^{90} retention ratio was 1.27 ± 0.06 at 1 day. This constant ratio indicates the slight influence of calcium intake on the excretory and bone-uptake discrimination between calcium and strontium. Since these mechanisms are initially invariant in their discrimination, they might be expected to remain so (except for aging effects). There is, however, a long-term diet-dependent discrimination as shown by the fact that the apparent value of b in the power function describing Ca^{45} retention varies directly with the calcium content of the diet, while the b describing Sr^{90} retention is unaffected by diet. This diet-dependent discrimination factor, therefore, must be due to the third mechanism, bone retention, since excretion and bone uptake discrimination do not exhibit this dependence. The rate-controlling factors should, therefore, be found in the power function

$$R = \frac{(t + \gamma)^{-b}}{\gamma^{-b}} \quad (2)$$

Because the mechanism implies the b is likely to be a constant, the discrepancy between the behavior of Ca^{45} and that of Sr^{90} may be explained by variations in the $(t + \gamma)$ term rather than by variations in b .

Thus, $\gamma = (c_0^{-1/b})b/k$ where b/k is approximately a constant. In the Ca^{45} case $b = 0.14$ (the maximum observed b) and $1/b = 7$, so that $\gamma \propto c_0^{-7}$. If we assume that c_0 is approximately proportional to the amount of calcium deposited, Thompson and Palmer's data for the cumulative deposition of total calcium after 100 days on the diet show the c_0 for animals on the 0.03% calcium diet to be about $1/3$ the c_0 for animals on the 2% calcium diet. Thus the ratio of the γ 's is $\gamma_{0.03}/\gamma_2 = (1/3)^{-7} \approx 2.2 \times 10^3$. On the other hand, for Sr^{90} , $b = 0.2$ so that using the same c_0 's as for calcium $\gamma_{0.03}/\gamma_2 = (1/3)^{-5} \approx 240$. If, arbitrarily, $\gamma = 1$ hour for calcium and strontium in the rats on the high calcium diet, then for those on the low calcium diet γ is about 100 days for Ca^{45} and only 10 days for Sr^{90} . The apparently small value of the exponent of the retention function then could be caused by the large value of γ because in this case only the flat part of the retention curve is observed. The inaccuracies in the data are such that this could be the case in addition to the relatively short observation period of 200 days. Moreover, the ratio of c_0 's used is the maximum and the consequent ratio of the γ_{Ca} to γ_{Sr} is the minimum obtainable from the data. If the ratio of cumulative calcium retention after 3, instead of 100 days, is taken, this ratio of c_0 's is $1/13$ instead of $1/3$. The γ_{Ca} -to- γ_{Sr} ratio is then about 200 instead of 9.

The data of Finkel et al.⁽¹⁰⁾ on the continuous feeding of Sr^{90} to mice demonstrate that some animals apparently reach an asymptotic total-body content at a rate which depends on the age of the animals at the beginning of the feeding of the tracer. While the curves follow the $[(t + \gamma)^{-(b+1)}/\gamma^{-b}]$ curve initially [Equation (3)] on a log-log plot they do tend to bend over to the asymptotic value (except for the oldest group which appears to reach this value much more slowly than do the others). The theoretical curves, Equations (19) and (20), were not fitted because of the difficulty in analysis, particularly as far as the uncertainties in determining q^* were concerned. Interestingly enough, the retention curves, after the radioactive diet was stopped, appeared to follow retention curve Equation (21) with apparent values of γ ranging from less than 10 days for the oldest animals to more than 70 days for some of the others. The youngest animals (feeding started at 20 days prior to birth and at 14 days after birth) appeared to have values of γ of the order of 100 to more than 200 days, respectively, and, therefore, they appear to be analogous to Thompson and Palmer's rats on low calcium diets.⁽²⁴⁾

Estimation of the Constants of the Power Function

The data of Bishop et al.⁽²³⁾ and of Cohn et al.⁽⁵⁾ on the whole-body counting of Sr^{85} in humans were examined in order to estimate the constants, γ , k , b and c_0 in the power function. It was concluded that the constant b was the only one amenable to analysis, it being the slope of the log-log curve at long times and given by both groups as about equal to 0.2. The constant γ derived here is a factor related to the short-term bone

retention, and to bone retention only. This γ should produce a flattening of the fractional retention curve at short times such that the $[(t+\gamma)^{-b}]/\gamma^{-b}$ curve lies below the straight line portion of the curve (t^{-b}) (on log-log coordinates) extrapolated to short times. However, in both sets of data the actual whole-body retention lies above the t^{-b} curve until $t = 20$ or 30 days, apparently because of the soft tissue and plasma retention, as demonstrated by Schulert et al.⁽²⁷⁾ They showed the soft tissue retention of Sr^{90} and Ca^{45} to be appreciable even after 18 days. Anderson et al.⁽⁷⁾ indicate that the normal human blood level of Ca^{47} at 100 hours is more than 10% of the originally injected dose (at 3 min), thus tending to confirm the above conclusions. One should be able to estimate γ by extrapolation of the linear portion of the curve on a log-log plot to the point at which $R = 1$. The time at this point is equal to γ . However, R , as seen in bone, is not the injected dose since a large fraction leaves the body through excretion without entering the bone. Thus, the value of γ can only be determined from the break in the plotted curve or from the other constants which make it up. The value of γ , however, appears to be necessary in the determination of these other constants, k and c_0 .

In animals, on the other hand, plasma (soft tissue) levels appear to drop more rapidly. Glad et al.⁽²⁸⁾ estimate the plasma levels in beagles to be 1-2% of the initial dose at 2 days so that only about 5% of the whole body level is due to soft tissue retention. The data of Thompson and Palmer⁽²⁴⁾ show the blood levels in rats to be still lower, 0.2 to 1% at 1 day, and thus the soft tissues account for only a few per cent of the total body count. These workers also measured the Sr^{90} in rat femurs, but their data, because of large scatter, do not allow estimation of γ .

The data of Richmond et al.^(29,30) on the retention of Ba^{133} in mice and rats, as determined by whole-body counting and by excretion studies, indicate a γ of about 8 days. Both of these sets were measured over a period of 300 days. These same workers⁽³¹⁾ observed for the retention of Ru^{106} in dogs over a period of 270 days a value of γ of about 9 days and a value of b of 0.402. It also should be noted that it took four exponential terms to describe these same results.⁽³⁰⁾ The excretion data indicate a large initial drop in retention for four days, a leveling off and then the power function with a b of about 0.6. The γ in this case is about 7 days, a result which tends to confirm the value of γ derived from the whole-body retention data.

Conclusions

The results presented here have shown that the mathematical description of calcium and calcium tracer metabolism is analogous to a relatively simple chemical system. Nevertheless, although biological

systems are basically chemical systems, the description and proposed mechanism do not preclude modification by biological factors to give different mechanisms which follow very similar laws.

The initial calcium concentration, c_{02} , has been shown to be quite sensitive to biological conditions, and the various rate constants probably vary also. Since b , however, depends on the reaction mechanism, causes of variations in b are not obvious. Possibilities are that factors in the blood could vary the mechanism, parts of the organic matrix could substitute for calcium atoms, or hormone mechanisms and cellular activity could change the apparent value of n (and thus of b).

The power function does describe the retention of the alkaline earth and similar elements, but great care must be exercised in its application. It refers only to organs which are not in a steady state and not well mixed with respect to the element under study. For example, Na,⁽³²⁾ Cs⁽³³⁾ and Zn⁽³⁴⁾ are apparently in steady states and are well mixed in the body and, thus, over long periods of time, the fractional retention follows an exponential, or possibly two exponentials in the single-injection case.

The advantage of this theory over those previously proposed^(1,6,7) is that no extra constants are introduced. An additional advantage of the kinetic treatment is that the effects of other reactants, such as magnesium, phosphate, and carbonate, may be quantitatively taken into account as shown by Equation (9).

These conclusions, it is hoped, will lead to new and improved experimental tests of this theory, to determination of the factors involved and to more comprehensive models of mineral metabolism.

APPENDIX I: INTEGRALS USED IN THE SOLUTION OF THE CONTINUOUS UPTAKE CASE⁽³⁵⁾

Integrals

$$\int \frac{dx}{a-x} = -\log(a-x) \quad (1)$$

$$\int \frac{dx}{a^2-x^2} = \frac{1}{2a} \log \frac{a+x}{a-x} \quad (2)$$

$$\int \frac{dx}{a^3-x^3} = \frac{1}{6a^2} \log \frac{a^2+ax+x^2}{(a-x)^2} + \frac{1}{a^2\sqrt{3}} \tan^{-1} \frac{2x+a}{a\sqrt{3}} \quad (3)$$

$$\int \frac{dx}{a^4-x^4} = \frac{1}{4a^3} \log \left| \frac{a+x}{a-x} \right| + \frac{1}{2a^3} \tan^{-1} \frac{x}{a} \quad (4)$$

Examples

The solution for $x = f(t)$, $n = 4$, $b = 0.33$ is

$$\frac{1}{4a^3} \log \left| \frac{a+x}{a-x} \right| + \frac{1}{2a^3} \tan^{-1} \frac{x}{a} = t \quad (5)$$

and

$$\frac{x}{a} = \frac{\exp \left[4a^3 \left(t - \frac{1}{2a^3} \tan^{-1} \frac{x}{a} \right) \right] - 1}{\exp \left[4a^3 \left(t - \frac{1}{2a^3} \tan^{-1} \frac{x}{a} \right) \right] + 1} \quad (6)$$

To demonstrate that x/a does not approach infinity as t becomes large, approximations will be made to eliminate the $\tan^{-1} x/a$ term so that the mathematics may be handled easily.

Case 1)

$$x \ll a, \tan^{-1} \frac{x}{a} = 0 \quad ; \quad (7)$$

$$\frac{x}{a} = \frac{\exp[4a^3t] - 1}{\exp[4a^3t] + 1} \quad (8)$$

Case 2)

$$x = a, \quad \tan^{-1} \frac{x}{a} = \tan^{-1} 1 = \frac{\pi}{4} \quad ; \quad (9)$$

$$\frac{x}{a} = \frac{\exp[4a^3 t - \pi] - 1}{\exp[4a^3 t - \pi] + 1} \quad (10)$$

(In any case $\tan^{-1}$ is a limited function varying between 0 and $\pi/2$.)

Thus at $t \rightarrow \infty$, $x/a \rightarrow 1$. Other cases are similar as may be seen from the nature of the integrals.

APPENDIX II: DERIVATION OF POWER FUNCTION FROM TIME-DEPENDENT RATE FACTOR

Single Injection

The power function may be derived from the first order kinetic equation if the rate factor, $K = k/(t + \gamma)$, i.e.,

$$\frac{dc}{dt} = -Kc = -\frac{k}{t + \gamma} c \quad (1)$$

$$\int_{c_0}^c \frac{dc}{c} = \int_0^t -\frac{k}{t + \gamma} dt \quad (2)$$

$$\log c/c_0 = -k \log \frac{t + \gamma}{\gamma} \quad (3)$$

$$c/c_0 = R = \left(\frac{t + \gamma}{\gamma} \right)^{-k} \quad (4)$$

Continuous Intake

In the continuous intake case

$$\frac{dc}{dt} = A - \frac{k}{t + \gamma} c \quad (5)$$

Substitute $c = (t + \gamma)x$ and $dc/dt = (t + \gamma) dx/dt + x$ so that

$$\frac{dc}{dt} = (t + \gamma) \frac{dx}{dt} + x = A - kx \quad (6)$$

Separating variables and integrating we get

$$\int_{x_0}^x \frac{dx}{A - x(k + 1)} = \int_0^t \frac{dt}{t + \gamma} \quad (7)$$

or

$$-\frac{1}{k + 1} \log \frac{A - (k + 1)x}{A - (k + 1)x_0} = \log \frac{t + \gamma}{\gamma} \quad (8)$$

or

$$\frac{A - (k+1)x}{A - (k+1)x_0} = \left(\frac{t + \gamma}{\gamma} \right)^{-(k+1)} \quad (9)$$

If at $t = 0$, $x_0 = 0$ ($c = 0$ at $t = 0$), substitution of c gives

$$c = R_t = \frac{A}{k+1} t \left[1 - \left(\frac{t + \gamma}{\gamma} \right)^{-(k+1)} \right] \quad (10)$$

The amount of tracer deposited, c , is therefore directly proportional to t , so that c approaches infinity as t becomes large ($c \rightarrow \infty$ as $t \rightarrow \infty$). This result, like that of Norris et al.,⁽⁴⁾ also gives an undesirable value at large t , and, in addition, the γ -term exists only because it is arbitrarily added into K .

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THE KINETICS OF ALKALINE EARTH METABOLISM IN ANIMALS II. EXTENSION OF CONCEPTS

Richard B. Holtzman

Introduction

In the case of calcium tracers incorporated into bone after a single injection, the principles of chemical kinetics and of tracer theory were shown in Part I of this paper⁽¹⁾ to lead to a derivation of the power function as a mathematical description of calcium and calcium tracer retention. In the case of continuous uptake of tracer these principles were shown to lead to a function which predicts only a limited uptake of the tracer. However, further analysis is necessary to extend and establish more firmly the application of these principles.

First, in order to correlate the in vitro experiments of Neuman et al.⁽²⁾ with the biological aspects of retention, a function will be derived (again a power function) which describes the retention in solution of a tracer injected into the liquid phase of a heterogeneous liquid-solid system. This is necessary in order to correlate these data with the recrystallization mechanism proposed by Edgington.⁽³⁾ Second, the kinetic description will be somewhat generalized to include a system in which the rate-controlling reaction not only follows n^{th} order kinetics, but is also influenced by a reaction which follows first order kinetics. This generalization lends itself to relatively simple mathematical treatment while still illustrating three important points - namely, that an apparently simple change in the mechanism may have a distinct effect on the mathematical form of the retention; that, as in continuous uptake (Part I), because of the interactions of the various processes, care must be taken in integrating the functions; and finally, that other functions, at present experimentally indistinguishable from the power function, may be useful in describing some biological systems.

Derivations

Single Injection, Retention in Solution

In the in vitro experiments of Neuman,⁽²⁾ a solid phase (synthetic hydroxyapatite or bone) is placed in a solution in a flask, and the mixture is stirred. The tracer is then injected into the system, and the liquid phase is analyzed periodically for tracer.

In a closed system, the change of tracer in the solution with time is

$$\frac{dc_{\ell}^*}{dt} = -k_{\ell}c_{\ell}^nc_{\ell}^* + k_sc_s^nc_s^* \quad (1)$$

where c is the concentration of the calcium, c^* the concentration of the tracer (See Part I), the subscripts ℓ and s refer to the solution (liquid) and solid, respectively, and k and n are the rate constant and reaction order, respectively. If initially there is little tracer in the solid,

$$k_{\ell}c_{\ell}^nc_{\ell}^* \gg k_sc_s^nc_s^* \quad (2)$$

so that

$$\frac{dc_{\ell}^*}{dt} = -k_{\ell}c_{\ell}^nc_{\ell}^*. \quad (3)$$

If the liquid phase is in a steady state, that is, if the amount of calcium entering the solid phase is equal to that dissolving from it and if particular calcium atoms in solution are not labelled with tracer, then c_{ℓ}^* is independent of c and the fractional retention is

$$R = \frac{c^*}{c_0^*} = \exp(-kc_{\ell}^nt) \quad (4)$$

However, Edgington⁽³⁾ has shown that in Neuman's in vitro experiments R does follow a power function. This function may be obtained from Equation (3) if we assume $c_{\ell}^* = Sc_{\ell}$ and $c_0^* = Sc_0$ (Part I),

$$R = \frac{\left(t + \frac{c_0_{\ell}^{-n}}{nk_{\ell}}\right)^{-1/n}}{c_0_{\ell}/(nk_{\ell})^{-1/n}} = \frac{(t + \gamma_{\ell})^{-b}}{\gamma_{\ell}^{-b}}. \quad (5)$$

The assumptions associated with this derivation imply a non-steady-state condition even in the solution phase. This condition might result if the tracer labels only particular calcium atoms, either because of a strong association phenomenon in the solution or because of some artifact, such as an initial or continued precipitation of the calcium from solution. This case, therefore, is analogous to that of retention in the solid described in Part I and can be analyzed in a similar fashion.

Retention Function with Competing Reactions (First and Nth Order Reactions)

While the retention functions of Part I, derived under the assumption that retention is controlled by a single reaction of the n^{th} order, appear to

describe the data well,^(1,4) the fit is not always perfect. One possible reason for this may be the existence of a second competing reaction which follows first-order kinetics. Other reactions are possible, but this one has been chosen as one of the simplest to illustrate the effects of modifications of the kinetics upon the retention function.

Inclusion of a first-order reaction with rate constant K in Equation 11, Part I gives

$$\frac{dc^*}{dt} = Kc^* - kc^n c^* \quad . \quad (6)$$

If, as before, $c^* = Sc$ with S a constant,

$$\frac{dc}{dt} = -Kc - kc^{n+1} \quad . \quad (7)$$

Separating variables and integrating c between c_0 (the concentration at $t = 0$) and c and t between 0 and t , we find

$$c = \left[\frac{-K \exp(-Knt)}{k \exp(-Knt) - \frac{K + kc_0^n}{c_0^n}} \right]^{1/n} \quad (8)$$

which has the form of a power function if $n = 1/b$ and $R = c/c_0$:

$$R = \frac{\left[\exp\left(\frac{Kt}{b}\right) - \frac{kc_0^{1/b}}{K + kc_0^{1/b}} \right]^{-b}}{\left[\frac{K}{K + kc_0^{1/b}} \right]^{-b}} \quad . \quad (9)$$

Here the exponential replaces the term t , and two constant terms containing c_0 , k and K are analogous to γ of Part I. (The constant terms are also not identical to each other.)

The self-consistency of these equations is apparent in that if K is small ($K \ll k$) Equation 9 approximates a power function because the Kc term in Equation 7 is negligible. If Kt/b is small (less than about 0.2), Equation 9 also approximates a power function upon expansion of the exponential as a polynomial.

Discussion

The power function description of the in vitro retention studies of Neuman et al.,⁽²⁾ as analyzed by Edgington,⁽³⁾ demonstrates the strong associative effects of the calcium ions in these solutions. If we neglect the possibility of experimental artifacts, such as precipitation of the calcium or tracer, the tracer appears to be associated with particular calcium atoms at the moment of injection and to remain so throughout the time of measurement. On the other hand, without this association, the tracer would be removed from the solution by a first-order reaction. This effect appears to be important in solution chemistry and should be studied further.

The consequence of the addition of a first-order mechanism to that of the n^{th} order is that eventually the first-order reaction will control the mathematical form of the function. One must exercise care, therefore, in the use of power functions to describe tracer retention since the 1st and n^{th} order reactions are not independent. For example, the power function, modified to take care of the first order reaction of radioactive decay, depicted by equation

$$R = e^{-\lambda t} \frac{(t + \gamma)^{-b}}{\gamma^{-b}} \quad (10)$$

is, strictly speaking, not correct in terms of the above derivation although it may be a good approximation.

An example to which Equation 9 should apply and which may serve to distinguish between Equations 9 and 10 is the case of the retention of a radioactive tracer with a half-life that is short relative to the observation time (K large, $K > k$). Under these conditions, if the retention data are corrected for radioactive decay by multiplication by $e^{\lambda t}$, they should be more closely fitted by an exponential function similar to that of Equation 9 than by a power function derived from Equation 10. However, the accuracy of measurement necessary to demonstrate this difference may be difficult to achieve.

Another operative process which may be of 1st order is that of bone resorption (by cellular activity). Consequently, even if resorption is only 1 to 2% per year (half-life of 35 to 70 years), this process could be significant in 30 to 40 years and could thus explain the apparently exponential behavior of Ra^{226} retention in dial painters 30 to 40 years after ingestion.⁽⁴⁾

Similarly, rapid bone resorption may also account for the results of Decker et al. described by Marshall⁽⁴⁾ in which the retention of a tracer injected into very young puppies is initially higher and then later lower than that of the tracer injected into more mature dogs. The difference may

be a result of the more rapid resorption in the younger dogs so that K is larger, thereby causing the exponential term to predominate. This problem is, however, complicated by the rapid skeletal accretion rate of these animals.

Finally, it appears that, while Equation 7 is by no means general, it may, nevertheless, provide a good description of some biological systems in the absence of feedback. As indicated in other discussions,^(1,3) a process with a high reaction order, n , is apparently specific to a crystalline system and dependent upon the lack of mixing within the system. Consequently, it appears that only one reaction mechanism of this type would exist in a given system. The tracer kinetics are likely to be governed by the very specialized reaction of a high order, $n \gg 1$, (recrystallization which involves a high degree of association), or a simpler one with $n = 1$. No intermediate values appear likely since thermodynamically only one crystalline form is stable under a given set of conditions.

In conclusion, it should be emphasized that functions derived from the principles of chemical kinetics, and not the functions themselves, e.g., power functions provide the basic description of calcium tracer metabolism. The power function is descriptive of only a particular case. However, because it fits the data well and is derivable from the above principles, it does provide a link between experiment and theory.

The proposed derivations and principles on which these functions are based are only approximations to real systems. Both in setting up the basic differential equations and in their solutions many points have not been considered: The effect of other associated ions, $\text{PO}_4^{=}$, OH^- , etc., on the kinetics of calcium and its tracers; the problems of feedback, i.e., tracer reactions have been assumed to proceed in only one direction, either from solid to liquid or from liquid to solid; and, finally, some very important facts remain uninterpreted, such as the apparent variation of the value of b among species, particularly that of Ra^{226} , which in most animals studied is about 0.2 to 0.3, whereas in man it is 0.5.

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A RAPID SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF LEAD IN BONE ASH

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Introduction

Lead is one of the most toxic of the trace elements. It is found in all fluids and tissues of the human body, and has been extensively investigated in past years.⁽¹⁾ A rapid and precise procedure was sought for metabolic studies of stable lead in bone specimens in conjunction with the study of Pb^{210} in human tissue by Holtzman.⁽²⁾

Previous procedures for the determination of lead in bone employed spectrographic,⁽³⁾ polarographic,⁽⁴⁾ and colorimetric dithizone methods. Of these, the most precise has been the latter, a modification of which was used by Krause.⁽⁵⁾

Bone ash requires a high acid concentration to maintain complete solution. Because of this, the procedure used by Krause involved an initial extraction of lead from the bone solution with diethyl dithiocarbamate, followed by a conventional extraction and colorimetric determination with dithizone. The method was rather long and contained numerous steps where contamination from reagents and reaction vessels was possible.

Merritt et al.⁽⁶⁾ suggested a method for the spectrophotometric determination of lead and other heavy elements through the ultraviolet absorption of their chloro complexes. Evaluations were made of some possible interferences, and this procedure was found applicable to pure acid solutions containing only lead, bismuth and thallium.

On the basis of their work, we present a simple, rapid and accurate procedure for the analysis of microgram amounts of lead in concentrated calcium phosphate or bone ash solutions (up to about 0.2 g/ml) and an effective means of eliminating possible interferences.

Reagents and Apparatus

Spectrophotometers. The measurements were made on a Perkin-Elmer, Model 350, recording spectrophotometer and a Beckman DU spectrophotometer with 1.0-cm silica cells.

Standard Solutions. A 1000-ppm lead solution prepared by dissolving 1.3422 g of lead chloride in a liter of water was used for all calibration curves and recovery studies. The stock 1000-ppm solutions for the interference studies were prepared by dissolving ferric chloride in water,

molybdenum trioxide in 0.1 N NaOH, and titanous, cupric, mercuric and stannic chlorides, bismuth trioxide, cadmium and thallous nitrates, and tellurium and zinc metals in 9 M HCl. The amount of nitrate introduced in the thallium and cadmium studies was assumed to be insignificant.

Diethylammonium Salt of Diethyldithiocarbamate (DDC). 1% w/v DDC was dissolved in chloroform.

Triisooctylamine (TIA). TIA (20% by volume) was dissolved in chloroform and washed twice with equal volumes of 9 M HCl.

Chloroform. All chloroform was washed twice with equal volumes of 9 M HCl.

Reference Solution. 100 ml 9 M HCl was extracted three times with 5 ml TIA and washed three times with 5 ml chloroform.

Calibration Solution. (0.20 g Pb-free synthetic bone salts per ml 9 M HCl). Lead-free synthetic bone solution was prepared by extraction with 1% DDC.⁽⁵⁾ It was then evaporated to dryness and ashed at 620°C overnight in a Vycor beaker to remove any residual organic material. The ash was dissolved in 9 M HCl. Any residual carbonaceous material was removed by filtering with a previously washed glass fiber filter paper. The solution was brought to a volume calculated to give a concentration of 0.20 g Ca₃(PO₄)₂ per ml of 9 M HCl. This solution (100 ml) was then extracted three times with 5 ml 20% TIA and three times with 5 ml of chloroform. The absorption spectrum of the solution showed quantitative removal of lead and ferric ion.

Glassware. All glassware (Pyrex) was cleaned with hot, dilute nitric acid (1:1) and rinsed with distilled water.

Procedure

Bone specimens obtained at autopsy or surgery were oven dried at 100°C, scraped clean of excess flesh, and ashed at 620°C overnight. The ash was dissolved in 9 M HCl and brought to volume not to exceed an ash concentration of 0.20 g per ml. The solution was extracted three times with 20% TIA and washed three times with chloroform. The size of the sample vessel, the amount of extractant and wash used, and the technique of mixing the two phases were dependent upon the concentration and sample size. For volumes of 10 ml or less, 15-ml graduated centrifuge tubes were used with 0.5-ml portions of extractant and wash. Two-minute extractions and one-minute washes were used. A 6- to 8-ml transfer pipette and a 5-cc syringe were used to pump the solution in and out of the test tube which mixed the organic and aqueous phases and gave good contact. Larger samples were dissolved and brought to volume in 50-ml graduated centrifuge tubes. They

were extracted with 3- to 5-ml of extractant and washed with similar volumes of chloroform. A mechanical stirrer was used to agitate and mix the organic and aqueous phases. Samples were centrifuged and the organic portion removed with a transfer pipette. After removal of the last wash, the samples were again centrifuged and aliquots taken with a clean pipette for absorbance measurements at 271 m μ .

Discussion and Results

Interferences

Merritt et al.⁽⁶⁾ observed both the absorbance maximum and the wavelength of the lead peak to increase with acid concentration. In 6 M HCl the maximum was at 271 m μ . The change in the wavelengths of the absorbance maxima was caused by the change in the chloride concentration. Of the interfering cations, ferric and cupric appeared to be most significant. The former, but not the latter, interference was satisfactorily eliminated by reduction with titanous chloride.

Based on the results of Merritt's paper and on the trace elements in bone,⁽¹⁾ an evaluation was made of the spectra of several additional elements for possible interference in this procedure. In all tests and samples, the reference solution had the same hydrochloric acid molarity as that of the solvent in order to maintain the same chloride concentration in each. The spectra were studied for 9 M HCl solutions containing either 5 ppm of iron or 10 ppm of copper, molybdenum, titanium, mercury, tin, bismuth, cadmium, thallium, tellurium, or zinc. Except for zinc, all showed some degree of absorbance in the ultraviolet region of the spectrum (220 - 400 m μ). Because of the high sensitivity and its prevalence in bone, ferric ion was the most likely interference. While an average copper concentration of 0.6 ppm in fresh bone (1.3 ppm ash) has been reported,⁽¹⁾ no interference from copper was noted in 17 cortical and 2 rib bones.

Ferric ion was quantitatively removed by the triisooctylamine extraction method of Ebersole et al.,⁽⁷⁾ without apparent removal of lead. Because of the solubility of chloroform in the solution, it was necessary to treat the reference solution with the same extractants as the sample.

Because iron, copper, bismuth, thallium and titanium are considered the elements most likely to interfere with the lead analysis, their absorption spectra in 9 M HCl are presented in Figure 26; however, extraction with TIA, in addition to removing ferric ion, removes Mo, Hg, Sn, Cd, Tl, and Te. In the standard procedure, approximately 50% Cu removal was achieved even with use of a minimum extractant-to-sample volume ratio of 1:20. Bismuth and titanium, however, were not extracted even when a 1:1 ratio of extractant-to-sample was used.

Figure 26

Absorption spectra of elements likely to interfere in 9 M HCl.

If copper is present, increasing the extractant-to-sample volume ratio to 1:2 and extending the extraction time to 10 min will remove approximately 87% of the Cu in 3 and 97% in 5 extractions. Less than 1 ppm of Cu in the presence of Pb may be detected from the absorption peak at about 385 mμ with the use of a scale expansion of about 5 in transmittance on the recording spectrophotometer or by the differential spectrophotometric techniques suggested by Reilly and Crawford⁽⁸⁾ on a single-beam instrument.

While interference by titanium could not be eliminated, it was not considered a serious problem for this study. Less than 2 ppm titanium has been found in human bone,⁽¹⁾ and this level would increase the lead concentrations which normally range from 13 to 80 ppm by only an apparent 0.2 ppm.

As an over-all test of the procedure, a synthetic bone solution containing 0.10 g Ca₃(PO₄)₂ per ml, 10 μg Tl, Bi, Cu, and Pb, and 50 μg Fe per ml 9 M HCl was prepared and extracted four times with an extractant-to-sample volume ratio of 1:1. The determination of the added Pb was 1.1% high, but within the precision of the procedure. Thus, the extraction with TIA eliminates all interfering elements present in normal bone.

Calibration

The absorbance was found to vary with both the concentration of the acid and the bone ash $[\text{Ca}_3(\text{PO}_4)_2]$. The absorbance for solutions with 0.00 g, 0.10 g and 0.20 g lead-free calcium phosphate are shown in Figures 27-29 for 4 M, 6 M, and 9 M hydrochloric acid concentrations, respectively. Beer's law was followed under all of these conditions. Maximum absorbance was at 271 $\text{m}\mu$, except for 0.00 g and 0.10 g $\text{Ca}_3(\text{PO}_4)_2$ in 4 M HCl which peaked at 268 and 270 $\text{m}\mu$, respectively. The 9 M HCl solutions are preferred since the slope of the absorbance curve changes with sample concentration for both the 4 M and 6 M HCl solutions. In addition, a lower absorbance by the bone ash or calcium phosphate and a higher sensitivity to lead are found in the 9 M HCl solutions.

Figure 27

Calibration curves of various concentrations of synthetic Pb-free bone in 4 M HCl (at the absorption peak).

Figure 28

Calibration curves of various concentrations of synthetic Pb-free bone in 6 M HCl at 271 $\text{m}\mu$. (Least squares plot of optimum range values).

Figure 29

Calibration curves of various concentrations of synthetic Pb-free bone in 9 M HCl at 271 $m\mu$. (Least squares plot of optimum range values).

The most favorable concentration range was determined from the plot of Figure 30 as suggested by Delahay.⁽⁹⁾ In this figure $1-T$ (where T is transmittance) is plotted against log concentration for both a 0.10 g/ml and a 0.20 g/ml synthetic bone in 9 M HCl. The optimum range is 4-12 $\mu\text{g Pb}$ per ml. The curves in Figures 28 and 29 were constructed from values within this range by the method of least squares analysis.

Accuracy and Precision

The accuracy of the method was determined by adding known amounts of lead to calcium phosphate with and without iron present. Known quantities of lead and iron were added to 1.00 g of $\text{Ca}_3(\text{PO}_4)_2$ in a 15 ml graduated centrifuge tube. The sample was dried under a heat lamp, brought to 5.0 ml with 9 M HCl and the iron was extracted with TIA. Lead contained in the calcium phosphate was determined by taking the plot of absorbance measurements of all

Figure 30

$1 - T$ vs. log concentration plot of 9 M HCl calibration data.

samples to which iron was not added and extrapolating to zero absorbance. The difference of this absorbance from that of the Pb-free $\text{Ca}_3(\text{PO}_4)_2$ was taken as the value due to the lead in the salts used. The standard error of all results in Table 23 was 2.0%, of those samples with added iron 2.0% and of those without added iron 2.2%. Thus, the presence of iron in the samples and its subsequent extraction did not affect the precision of the lead determination.

Table 23

Lead recovery from solutions containing 0.20 g/ml $\text{Ca}_3(\text{PO}_4)_2$ and iron

Pb present $\mu\text{g/ml}$	Pb added, $\mu\text{g/ml}$	Total Pb, $\mu\text{g/ml}$	Fe added, $\mu\text{g/ml}$	Pb found, $\mu\text{g/ml}$	Error, %
0.75	4	4.75	0	4.90	+3.2
"	"	"	0	4.84	+1.9
"	"	"	10	4.82	+1.5
"	"	"	100	4.70	-1.1
0.75	5	5.75	0	5.90	+2.6
"	"	"	0	5.89	+2.4
"	"	"	10	5.75	0.0
"	"	"	100	5.92	+3.0
0.75	7	7.75	0	7.97	+2.8
"	"	"	0	7.73	-0.3
"	"	"	10	7.70	-0.6
"	"	"	100	7.87	+1.5
0.75	10	10.75	0	10.93	+1.7
"	"	"	0	10.83	+0.7
"	"	"	10	10.50	-2.3
"	"	"	100	10.72	-0.3
0.75	12	12.75	0	12.80	+0.4
"	"	"	0	12.42	-2.6
"	"	"	10	12.39	-2.8
"	"	"	100	12.43	-2.5
Standard error					2.0

To determine the precision of the procedure for bone, two bone samples were ashed, ground to a fine powder, thoroughly mixed, and five equal portions from each weighed for analysis. Both samples were rib containing large quantities of iron. As shown in Table 24, the standard deviations of the results of samples 389B and 775B were ± 0.12 and $\pm 0.11 \mu\text{g Pb/ml}$, respectively. These standard deviations also indicate the relative sensitivity of the method.

Table 24

Precision of lead determination in bone solutions (9 M HCl)

Sample	Bone No. 775B		Bone No. 389B	
	g ash/ml	$\mu\text{g Pb/ml}$	g ash/ml	$\mu\text{g Pb/ml}$
1	0.20	1.78	0.10	4.35
2	0.20	1.95	0.10	4.55
3	0.20	1.87	0.10	4.47
4	0.20	1.85	0.10	4.68
5	0.20	1.65	0.10	4.46
Mean		1.82		4.50
Standard deviation		± 0.11		± 0.12

Bone specimens were available which had been previously sampled and analyzed for lead by DDC-Dithizone method of Krause.⁽⁵⁾ The Pb concentrations are summarized in Table 25. Concentrations ranged from

Table 25

Comparison of lead in bone ash by DDC-dithizone and HCl methods

Sample	Type	DDC-Dithizone method		HCl method	
		Sample size, g ash	Pb*, ppm	Sample size, g ash	Pb*, ppm
286B	Tibia	1.122	29.6	0.711	31.5
340B	Tibia	0.834	80.2	0.686	79.3
341B	Femur	1.002	59.0	0.689	40.5
343B	Femur	1.169	32.0	0.751	38.9
366B	Femur	1.136	33.4	0.920	34.5
368B	Femur	0.580	15.1	0.726	28.2
374B	Tibia	0.537	26.2	0.488	40.0
375B	Femur	0.680	20.6	0.609	19.6
385B	Femur	0.747	50.8	0.728	50.0
406B	Humerus	0.875	37.4	0.702	43.3
409B	Femur	0.772	24.5	0.756	31.8
412B	Femur	1.048	13.8	0.857	17.3
413B	Femur	1.031	29.0	1.123	33.4
483B	Femur	0.840	6.3	0.755	13.7
484B	Humerus	0.616	30.0	0.543	33.9
539B	Humerus	0.844	10.8	0.690	13.0
549B	Femur	0.720	35.0	0.839	43.5

*Standard deviation 4.0 ppm

6.3 to 80.2 ppm and differ by as much as a factor of two from those of Krause. Unfortunately, these samples are not suitable for comparison of the two techniques since lead, as represented by Pb^{210} may not be uniformly distributed throughout bone.⁽¹⁰⁾ The standard deviation of the present procedure from the mean of both procedures is 4.0 ppm Pb, with a relative standard deviation of 13%.

Stability of Bone Solutions

The absorbance of the chloro complex of lead in bone solutions was found to be within the precision of the method in all samples and test cases in which the extractions and measurements were completed in the same day. Contrary to observations in many samples, calibration solutions were found to be stable for as long as four days. Stability of the absorbance spectrum of bone ash samples is probably due to the presence of ferrous ion, which is not extracted by TIA, and which is slowly converted to the ferric state. Re-extraction of old solutions with TIA has been found to give results identical to those at early times. Five samples of bone (389B), initially put into solution with hydrochloric acid and evaporated to dryness overnight on a steam bath, showed absorbance spectra which were stable for twenty-four hours.

Over a period of several weeks, samples 343B and 368B were extracted three times and 374B four times and measured following each extraction. Reproducible results were obtained. After two months, the three samples were again measured without prior treatment. The results from samples 343B and 368B were in agreement with previous measurements, while sample 374B was found to be approximately 13% high. Re-extraction produced a result within 0.3% of the initial value.

Interference from ferric ion can be established from the absorbance at 245 and 305 $m\mu$. The readings at these wavelengths are unaffected by the lead content (as shown in Figure 30) but are very sensitive to ferric ion. In general, an absorbance of 0.02 to 0.06 at 245 $m\mu$ and 0.01 to 0.03 at 305 $m\mu$ were obtained in iron-free solutions. The absorbance at 245 and 305 $m\mu$ were not affected by lead concentrations as high as 10 $\mu\text{g}/\text{ml}$.

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CRYSTAL GROWTH - A NEW PHYSICAL APPROACH TO THE DEPOSITION OF RADIOACTIVE ISOTOPES IN BONE

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Introduction

In recent years a considerable number of papers have been published describing the uptake and retention of radioactive isotopes in the body as a whole and in bone in particular.⁽¹⁾ Studies have been made with bone that has been treated with ethylenediamine to remove the organic material and with inorganic materials corresponding to bone mineral in composition.^(2,3) Retention and uptake (in the case of in vivo and in vitro studies, respectively) of radioactive isotopes have been represented mathematically by a series of exponentials, and it has been possible to propose a stepwise mechanism to explain their behavior. This stepwise mechanism can be shown to apply only over an interval of time, short compared to the lifetime of the isotope in the system.⁽⁴⁻⁶⁾ Norris et al., however, have shown that the retention in vivo can be described conveniently by a simple power function relationship for very long periods of time.⁽⁷⁾

In this paper it will be shown that the representation of the in vitro results by a power function can be rationalized in terms of well-established physical-chemical principles.

Experimental Observations

In Vivo

It has been shown that certain isotopes (e.g., Ca, Sr, Ba) can be incorporated into the bone mineral by purely cellular activity. The radioactivity in this case is concentrated at the sites of the osteoblasts, where new organic matrix becomes available for crystallization.⁽⁸⁾ Secondly, each ionic grouping (e.g., Ca^{2+} , PO_4^{3-}) in the crystal of the bone mineral (hydroxy apatite) appears to have the ability to undergo an ion-exchange reaction. This process is believed to give rise to the so-called "diffuse activity," and if this is the reaction involved, then the kinetics of the reaction should be in agreement with the already well-established laws of such systems.⁽⁹⁾ Both of these processes lead to the idea that the skeleton is a dynamic system with continual accretion and resorption of mineral taking place.*

*On the other hand, isotopes like plutonium, which form colloids under physiological conditions, are readily absorbed on the surfaces of the bone and are retained over very long periods of time.

It was first suggested by Norris et al.⁽⁷⁾ that the results obtained for the retention and uptake of radioactive isotopes in mammals could be represented by a power function $R = [(t+\gamma)/\gamma]^{-b}$. Marshall has extended this idea and has shown that the power function describes the data over many orders of magnitude for both R , the retention, and t , the time after administration; b and γ are constants.⁽¹⁰⁾ He has also given operational descriptions of b and γ , making no assumptions of the basic mechanisms involved, whether they be physical or biological.

In Vitro

There has been a great deal of effort expended in attempting to understand the basic physical processes involved in the uptake and retention of diffuse activity by studying both bone and hydroxy apatite in vitro. These results have been summarized in reviews by Neuman⁽²⁾ and Dalle-magne.⁽³⁾ They believe that the physical processes involved are ion exchange and recrystallization and present their evidence in such a way as to support these mechanisms.

Weikel and Neuman have carried out uptake experiments over fairly long periods of time using Ca^{45} and hydroxy apatite.^(6,11) These exper-

Figure 31

Results of uptake experiments of Weikel and Neuman.^(6,11) Curve A represents the uptake over the first forty hours. Curve B is the long-term uptake.

iments are assumed to give the same results as retention studies. They find that for a period of up to one hundred hours, their experimental results can be analyzed into three distinct stages and that for periods of time greater than this another process takes place, which they call recrystallization. In order to explain the three-stage process they proposed the following model. The crystals of hydroxy apatite, in an aqueous solution, are surrounded by a hydration layer of polarized calcium and phosphate ions such that charge asymmetry at the surface of the crystal is minimized. Beyond the hydration shell there is a weakly-held orientated boundary. Their results are shown in Figure 31. Curve A represents the uptake over the first forty hours and is divided into three parts, I-III, corresponding to the three-stage process. Curve B represents the long-term uptake. Stage I of their kinetic results represents the exchange of the radioactive ions between the bulk solution

and the chemisorbed double layer or hydration shell. Stage II is the exchange of ions between the hydration shell and the surface of the crystal, and stage III is the exchange between the non-hydrated surface and the interior of the crystal. They found that stages I and II were highly dependent on the ionic strength of the bulk solution, whereas stage III did not show any such dependence and took this to demonstrate that the latter stage represented reaction in the solid phase. If the experiments are continued for longer periods of time, as they were with Ca^{45} , the exponential relationship for stage III ceases to hold, and another stage takes over. They describe this stage as recrystallization and make no attempt to handle it mathematically. They fail to note that their results to 1,000 hours could be handled by postulating another two compartments and hence another two exponentials.

The results for experiments using radioactive labelled phosphate ions can be analyzed similarly into three distinct stages, but there are no data available beyond 40 hours.⁽⁶⁾

The mathematical handling of a series of exponentials is simple, but what physical justification is there for all of these compartments? From physical-chemical principles it would be expected that an ion-exchange reaction would exhibit first-order kinetics, i.e., an exponential relationship between concentration and time. The proposed mechanism of separate ion-exchange processes for each of the first three stages (I-III) is justified. However, a new exponential has to be added to the series for each order of magnitude in the time scale. Neither anatomical nor chemical identification of these compartments has been proposed; moreover, it is impossible to envisage other first-order mechanisms once the ion has entered the crystal lattice. Diffusion-controlled reactions would give rise to 0.5th order equations.⁽¹²⁾

Physico-Chemical Derivations of the Power Function.

Although it can be shown that a sum of exponentials will approximate a power function, it seems fruitful to inquire whether there is any direct physical interpretation for the power function itself.

It will be shown that there are two physical descriptions of the power function, which are in good agreement with the observed experimental facts.

Interpretation Based on Chemical Kinetics. Holtzman⁽¹³⁾ has shown that the power function may be derived from the kinetic equation for an n^{th} order reaction,

$$dx/dt = -k'x^n \quad (1)$$

where x is the concentration of any reactant at time, t , and k' is the rate constant. If this equation is integrated between limits $t = 0$ and $t = t$ and $x = x_0$ and x , and then solved for x , one obtains

$$x = \left\{ (n-1) k' t + x_0^{1-n} \right\}^{1/(1-n)} \quad (2)$$

dividing by x_0 , the concentration of x at $t = 0$, and rearranging, one gets

$$R = \frac{x}{x_0} = \left(\frac{t + \gamma}{\gamma} \right)^{-b} \quad (3)$$

where $\gamma = x_0^{1-n}/k'(n-1)$ and $b = 1/(n-1)$ (the slope), which is the same as the power function observed for a large number of the biological radio-isotope retention studies. The significance of γ will be discussed later.

If Neuman's results for Ca^{45} , (6,11) Sr^{89} , (14) Ra^{226} (15) and Y^{90} (16) in vitro are plotted on log-log graph paper, it is found that these, too, can be described by a power function. A typical power function relationship is shown in Figure 32. For calcium, strontium, and radium $b = 0.11$ and for yttrium $b = 0.4$ and $\gamma = 0.21$ hours. Thus, from Equation (3) the alkaline earth elements exhibit a 10th order reaction over a range of 1,000 hours. Yttrium exhibits a 3.5th order reaction over a similar time scale. This unexpected result then would tend to eliminate ion exchange (which requires first order reaction kinetics) as a possible mechanism and would, in addition, rule out diffusion (as the dependence of rate on time would be 0.5 or an integral multiple thereof). A third-order reaction is not often encountered in conventional kinetic studies of simple molecules. However, for ionic reactions in solution, which are too rapid to be measured by conventional experimental methods, orders of three and higher must be quite common.

Interpretation Based on Crystal Growth Theory. It has been known for some years that the rate of nucleation and growth of crystals from supersaturated solutions is dependent on the q th power of the concentration, where q can vary from 2-9, depending on the precipitate being studied. (17)

A new crystal nucleus is formed when there is a discontinuous change from a metastable or unstable system into the initial fragments of a more stable phase. (18) The nucleation process can be initiated by either local changes in density (or other property) in the unstable phase or by the introduction of some foreign material. The single ions or molecules form clusters which grow by a stepwise addition of additional ions or molecules. When these clusters have grown to a critical size (composition or structure), which depends on the degree of supersaturation of the unstable phase, they are capable of further spontaneous growth with a net decrease in free energy and can initiate the formation of the new phase. These changes are shown in Figure 33. These clusters of critical size are nuclei. The mathematical description of this process was developed by Volmer and Weber (19) and Becker and Döring. (20)

Figure 32

Results of Neuman for Ca^{45} , Sr^{89} , Ra^{226} and Y^{90} in vitro plotted on a log-log scale. (6,11,14-16)

Figure 33

Nucleation and growth of crystals from supersaturated solutions. In the graph free energy is plotted against ion or molecule cluster size. (See Reference 18.)

Once the nuclei have been formed, they continue to grow and form crystallites. The size and number of crystallites formed is determined by the relative rate of nucleation and the rate of growth. The rate of growth of the crystal will depend on the diffusion rate, the surface and the presence of surface defects. Furthermore, recrystallization (the growth of large crystals at the expense of smaller ones) will also be important. Growth at the surface can take place in three different ways. First, there is the addition of ions or ion-pairs randomly on the crystal surface. This is not very likely because of the small free-energy change and the concomitant low stability of the added ions. Then there is the hypothesis of "two-dimensional growth nuclei" proposed by Becker and Döring,⁽²⁰⁾ in which two-dimensional nuclei grow in the third dimension by successive repetitions of two-dimensional nucleations followed by spreading reactions. Last, growth can take place along imperfections or dislocations in the lattice of the developing crystallite. Dislocations in the form of molecular terraces serve to stabilize growth units, and these can perpetuate themselves

throughout the development of the crystallite, thus permitting growth without the high energy required for the formation of two-dimensional nuclei. The addition to dislocations is expected to take place in the smallest neutral units.

It will now be shown how these basic ideas of crystal nucleation and growth can be expressed in terms of a power function, be applied to retention and uptake studies in vitro, and may be extended to describe in vivo results as well.

The kinetics of crystal growth from supersaturated solutions have been studied by several workers using two different mathematical approaches which, however, give the same answer. In a recent paper O'Rourke and Johnson⁽²¹⁾ have reviewed the concepts involved for slightly soluble ionic precipitates. Nucleation takes place at a regular rate throughout an induction period, τ . The number of particles being formed for the reaction of p monomers X , $pX \rightarrow X_p$ (the nucleus), is given by

$$\frac{dv}{dt} = Kc^p \quad (4)$$

where dv/dt is the rate of formation of nuclei X_p , c is the concentration of the monomer X , and K is a constant. The rapid depletion of supersaturation after the induction period sharply curtails nucleation. Thereafter precipitation occurs by growth alone.

The rate of crystal growth is dependent both on the surface available for growth and the concentration of the precipitating solute; hence,

$$dc/dt = -k \cdot f(s) \cdot f(c) \quad (5)$$

where $f(c)$ is a function of the concentration of the precipitating solute and $f(s)$ is a function of the available surface. If growth were a diffusion-controlled reaction, the concentration function would be first order.

It has been shown that for very small particles a surface-controlled reaction is more probable. The equation as used by O'Rourke and Johnson for the growth of nuclei has the form

$$\frac{da}{dt} = -k(c_0 - c)^\sigma a^q \quad (6)$$

where a is the mean ionic activity of the reacting ions at time, t , c_0 and c are the molar concentrations of the solute available for precipitation at t_0 and t , respectively, and k , q , and σ are constants. The term in parentheses is in molar concentration units since it relates mass to surface. The rate constant, k , includes a shape factor, and σ represents a complicated set of surface functions in the nucleation process. For the growth of barium

sulphate crystals it was found by a numerical method of integration that $\sigma = 2/3$ and $q = 4$. The fractional value of σ arises from a consideration of where on the crystal surface growth nucleation is taking place.⁽²²⁾

In order to integrate Equation (6) it is necessary to make some assumptions. If the term $(c_0 - c)^\sigma$ is assumed to be constant in time, the remainder of the expression can be integrated easily. The validity of this assumption can be justified in two ways: first, in the case of crystal growth, the contribution of the $(c_0 - c)^\sigma$ term is important only in considering the short-term results during and immediately after the nucleation process since the rate of change of activity over a long period of time depends only on the a^q term, [$a^q > (c_0 - c)^\sigma$]; second, in the case of the deposition or retention of activity in the bone, the solid present is in equilibrium with the solute, hence $(c_0 - c)^\sigma$ remains constant, and the rate of formation of nuclei is also constant. Integrating Equation (6), we obtain the following equation which is of the same form as Equation (3): (substituting $a = x$, $a_0 = x_0$).

$$R = \frac{a}{a_0} = \left(\frac{t + \gamma}{\gamma} \right)^{-b} \quad (7)$$

$$\text{where } \gamma = \frac{a_0^{(1-q)}}{(q-1) k(c_0 - c)^\sigma} \quad \text{and } b = \frac{1}{(q-1)}.$$

This expression, then, gives a description of b and γ in physical terms. It can be seen that γ is proportional to $a_0^{(1-q)}$ and inversely proportional to $(c_0 - c)^\sigma$. Therefore, it can be concluded that the value of γ depends on the surface function of the crystal and the rate of nucleation.

O'Rourke and Johnson have shown how it is possible to estimate theoretically a value for σ which is in agreement with their observed value for BaSO_4 . They assume there is an induction period, τ , and a short time afterwards, during which nucleation takes place, where the value of a^q is nearly constant. The value of τ is assumed to be the time at which the first change in concentration may be detected, and for their system this was a one per cent change. During this period, any change in activity will be due to the rate of nucleation and growth due to the surface effect only. If it is assumed that $c \approx a$ and $c_0 \approx a_0$, then the change in activity due to the growth of a single crystal from the end of the induction period to a time, t , is

$$\int_{a_0}^a (a_0 - a)^\sigma da = -ka^q \int_{\tau}^t dt \quad \text{or}$$

$$(a_0 - a) = [(1 - \sigma) ka^q(t - \tau)]^{1/(1 - \sigma)} \quad (8)$$

Nuclei are forming at all times after mixing, the rate being given by Equation 4. The term a^q is constant during the induction period, τ , and we assume

this to hold for a short time afterwards; then the rate of formation of particles is constant, and in a time interval $\tau \leq t \leq (t + d\tau)$ the number of nuclei formed is

$$d\nu = Ka^p d\tau .$$

The total change in activity caused by growth due to the surface function on these crystals is given by

$$(a_0 - a) = \int_0^t (1 - \sigma) ka^q (1 - \sigma)^{1/(1-\sigma)} Ka^p (t - \tau)^{1/(1-\sigma)} dt , \quad (9)$$

$$\text{or } (a_0 - a) = K't^{(2-\sigma)/(1-\sigma)}$$

where

$$K' = \left[kK^{(1-\sigma)} (1 - \sigma)^{(2-\sigma)} a^{[q+p(1-\sigma)]} \right]^{1/(1-\sigma)} .$$

So for a short time after the induction period,

$$(a_0 - a) = K't^y \text{ where } y = (2 - \sigma)/(1 - \sigma) \quad (10)$$

and a plot of $\log (a_0 - a)$ vs. $\log t$ should have a limiting slope of y .

In this derivation we have assumed that a^q and $(c_0 - c)$ are constant throughout the induction period. However, in the case of the hydroxy apatite system in vitro in which we are interested, the gross system is always in a state of dynamic equilibrium. When the radioactive isotope is injected into the system, the system at this time behaves in exactly the same way as the kinetic system of barium sulphate precipitation because all the ions in the system must go through the same mechanism of reaction, i.e., nucleation, growth due to surface function and the final changeover into the main growth factor, which is proportional to a^q . Because of this, both types of systems are wholly comparable. However, if the solid phase has not been allowed to come to equilibrium with the solution phase before the radioactive isotope is added, the uptake of radioactivity will follow an irregular course with time.⁽²³⁾

The formation of nuclei can only proceed to a certain extent. As crystals grow larger, their specific surface area gets smaller, and they grow at the expense of the newer nuclei which have a larger specific surface and tend to lose ions back into solution more readily. Therefore, the importance of the initial term decreases and the second growth term a^q becomes more important.

Comparison with Results for In Vitro Systems

O'Rourke and Johnson's data for barium sulphate⁽²¹⁾ have been plotted in Figure 34 as a power function. It is found from Equation (7)

Figure 34

Data for barium sulphate from O'Rourke and Johnson's paper on crystal growth in supersaturated solutions⁽²¹⁾ plotted as a power function

that the slope $b = 0.33$ (or $q = 4$) and the intercept $\gamma = 4.6$ mins. Similarly, the results for the initial part of the experiment are plotted according to Equation (10) (Figure 35); it is found that the limiting slope of 4 passes through the point with coordinates $(c_0 - c) = 1\%$, $t = 4.6$. In the derivation of Equation (10) it was assumed that the induction period, τ , was over when $(c_0 - c) = 1\%$ of the total reaction.

We can now see that the value of τ is equal to the value of γ from the power function. The value of γ , then, is a measure of the length of the induction period for nucleation. When the time of observation is greater than γ , the growth of the nuclei already formed becomes more important than the formation of new ones.

We are now in a position to interpret, in terms of this theory, the data for the in vitro retention or uptake of radioactive isotopes in hydroxy apatite. The results of some typical data have been shown in Figure 32. The data are taken from various papers of Neuman. Unfortunately, for the simplest case to discuss, that of Ca^{45} , accurate results have not been obtained for times of an hour or less. The most comprehensive data, so far, have been obtained using yttrium. Here $b = 0.4$ and $\gamma = 12$ min. In Figure 32 we show the plot of $\log(c_0 - c)$ vs. $\log t$ for yttrium. The limiting slope is 3, so $\sigma = 1/2$. For yttrium then,

$$\frac{dc}{dt} = -k(c_0 - c)^{1/2} a^{3.5}$$

Figure 35

O'Rourke and Johnson's data⁽²¹⁾ plotted according to Equation (10)

the data for the in vitro retention or uptake of radioactive isotopes in hydroxy apatite. The results of some typical data have been shown in Figure 32. The data are taken from various papers of Neuman. Unfortunately, for the simplest case to discuss, that of Ca^{45} , accurate results have not been obtained for times of an hour or less. The most comprehensive data, so far, have been obtained using yttrium. Here $b = 0.4$ and $\gamma = 12$ min. In Figure 32 we show the plot of $\log(c_0 - c)$ vs. $\log t$ for yttrium. The limiting slope is 3, so $\sigma = 1/2$. For yttrium then,

General Discussion

In this paper it has been shown how the long-term retention or uptake of radioactive isotopes in the skeleton can be explained in terms of the power function in place of a series of exponentials and how the power function can be rationalized in terms of known physical processes. Previously in the analysis of these systems a multicompartment process has had to be postulated for which it was possible to assign two or three different physical processes to explain the presence of the initial compartments, but there was no obvious reason for the presence of the later compartments. On the other hand, the power function provides a single expression to describe the results over many orders of magnitude, and would appear to give an explanation of the mechanism for the deposition or retention of activity in terms of the growth of crystals, which is acceptable both mathematically and, more important, chemically.

There are, however, several questions which still remain to be answered. In showing how the results for both crystal growth and the uptake of radioisotopes can be explained by the power function we have tacitly avoided a precise definition of some of the terms (a_0 , a , c) that we were using. In the crystal growth experiments, the conductivities obtained were a direct measure of the total number of ions present in the solution. Therefore, the terms a_0 and a , c_0 and c , refer to the total ionic activity or concentration. In the radioisotope in vitro uptake experiments there are two situations: 1) Ca^{45} and other calcium-like nuclides, which act as tracers for the total calcium in the system; and 2) all other radioactive isotopes that obey the power function* although they trace their own path independently of the total calcium concentration. Therefore, in the latter case, a_0 and a refer to the concentration of the given radioactive isotope. There is also the view that all radioactive nuclides follow the calcium mechanism, and the variations of the value of q can be explained by their ability to be a good tracer or not as the case may be. If all radioactive isotopes introduced into the system (in vitro) were acting as tracers for calcium, the value of the exponent b should be the same in each case and the retention should depend on the total calcium concentration and not on the concentration of the tracer. If the radioactive nuclide is tracing itself then the retention should be dependent on its initial concentration [from Equation (7) $R \propto 1/a_0$].

Christiansen and Nielsen⁽²⁴⁾ have suggested for crystal growth that the value of the exponent b depends on the number of ions in the unit of material that forms the nucleus and precipitates. It is noteworthy that as the crystal structure of the precipitated substances becomes more complicated, e.g., AgBr , BaSO_4 , CaF_2 , the value of $q = 1 + (1/b)$ increases from 2 to 9. In the case of the growth of hydroxy apatite crystals in the presence of foreign (to calcium) radioactive ions, the value of q observed

*Alkali metal ions and hydrogen ions follow an exponential expression.

may reflect the limiting solid-solution range of that particular ion in the hydroxy apatite structure. It is well known, for example, that there are definite ranges of solid solubility for strontium in hydroxy apatite,^(25,26) and other divalent ions behave similarly. There is no experimental evidence yet concerning trivalent ions. In order to test this hypothesis it would be interesting to perform studies with hydroxy apatite using mixtures of Ca^{45} with other nuclides and observe what values of q would be obtained in these circumstances for each of the isotopes. It would also be instructive to see what effect varying the total calcium concentration would have on the value of q for radionuclides other than Ca^{45} over a long period of time, as the initial nucleation must depend on the degree of supersaturation. It is known, for example, for yttrium, that the initial uptake increases with increasing supersaturation.⁽¹⁶⁾

Extension of the Theory to In Vivo Systems

So far in this paper we have been concerned with in vitro studies, either with pure hydroxy apatite or bone which has had its organic components removed by chemical treatment. The problem that remains to be considered is how well these ideas can be applied to in vivo systems.

In the in vitro experiments we were dealing with a closed system, which was uninfluenced by any external factors. However, for in vivo systems, the system is no longer closed, and there are several external factors which would be quite important. In particular, we should consider the possible effect of cellular activity, excretion and other competing reactions (e.g., with complexing agents) on the two constants, γ and b , in the power function [Equation (7)]. These factors, acting together, would modify the values of γ and b in a way that is not easy to predict. However, we can make some predictions if they are considered separately.

First, there is the question of cellular activity. Nucleation in new bone has been shown to take place on the collagen matrix and to be influenced by the presence of certain enzymes and foreign ions (i.e., citrate ion). The turnover of bone at sites of osteoblasts involves the removal of a comparatively large volume of bone matrix at any one time. Both of these factors would affect the value of a_0 and, hence, the value of γ , ($\gamma \propto b a_0^{-1/b}$). However, the turnover of a large volume of bone mineral at any one time at an osteoblast or osteocyte center could have an apparent effect on the reaction kinetics by increasing the value of b (and lowering the value of q). In young animals, where the formation of new bone is most prevalent, higher values of b would be expected than for older animals (or older bone), where remodelling is more important. It might be suggested that once nucleation has taken place by some biochemical reaction, the loss or gain of activity would continue in the same manner as for the in vitro system. As there is no change in the over-all reaction mechanism, only the value of γ , the termination time of the nucleation growth period, would be affected. The value of b would be the same for in vivo and in vitro cases.

Next, we should consider what effect excretion has on the parameters of the power function. In the case of the retention of a radioactive nuclide by the bone, there is a net passage of activity from the bone to the blood, and a net loss by excretion via the gut or the kidney. If the rate-determining step for these processes were the rate of loss of activity from the bone to the blood, the value of γ should remain unaltered. However, if the rate determining step is the rate of excretion (i.e., it is less than the rate of loss of activity from the bone to the blood) the value of γ will be increased as the rate of excretion decreased. Because the mechanism for excretion is independent of the kinetic processes in the bone, there should be no effect on the value of b in either of the two cases above.

Finally there is the possibility of competing reactions. These can affect the values of both b and γ . For example, a complexing agent can alter the effective concentration of the nuclide in the blood and thus reduce the value of a_0 and, in turn, the value of γ . It could also affect the actual reaction mechanism in some way, altering the order of reaction and thus the value of b .

The situation as a whole is very complex, and it requires a great deal of thought to devise the most useful experiments to test these hypotheses. Until such time as conclusive experimental data are made available, the discussion of this application of the power function to the in vivo case remains open to conjecture.

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A RAPID SOLVENT EXTRACTION METHOD FOR THE
DETERMINATION OF STRONTIUM-90 - YTTRIUM-90
USING DI-(2-ETHYLHEXYL) PHOSPHORIC ACID*

David N. Edgington

Abstract

The dialkyl phosphoric acids have been shown to be excellent reagents for the solvent extraction of many cationic species from dilute mineral acid solution. By careful control of the acidity of the aqueous phase many useful group separations can be effected.

In particular, di-(2-ethylhexyl) phosphoric acid has been widely used as an extracting agent and proven to be quite versatile. Tracer-level yttrium-90 may be quantitatively separated from its parent strontium-90 in dilute acid solution by a single extraction with a 5 per cent solution of the reagent in toluene. (Recently it has been used to separate large amounts of strontium-90 and cesium-137 from other fission products.) When the sample solution is adjusted to a pH of 2, the distribution coefficient for yttrium is greater than 10,000 and for strontium is less than 0.001, giving a separation factor of greater than 10^7 . As the values of the distribution coefficients are unaffected by the presence of calcium phosphate, this method is particularly useful for the determination of strontium-90 in bone samples. In contrast the extraction of yttrium-90 into TBP from strong nitric acid solution, which has also been employed for the rapid determination of strontium-90, is very dependent on the concentration of calcium ions in solution.

This method has been used to determine strontium-90 in the bones, antler, meat and rumen of Alaskan caribou. It has been modified somewhat to allow a separation of yttrium-90 and cerium-144. Large amounts of heavy metals, e.g., iron in rumen, are removed by passing the sample, dissolved in 11M hydrochloric acid, down a column of Dowex-1 or 2. Certain elements which occur in fallout and have been found in some of the samples by gamma-spectrometry (i.e., Zr^{95} , Ru^{106}) are also held on the column and can be eluted later for determination.

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PERIODICITY OF MITOSIS. S^{35} -SULFATE AND C^{14} -
GLYCINE UPTAKE IN RAT BONE

David J. Simmons

Studies using the colchicine method to achieve metaphase arrest⁽¹⁾ and tritiated thymidine⁽²⁾ as a marker for DNA synthesis have shown that events related to cell division in epiphyseal cartilage are subject to diurnal variations. Okada⁽³⁾ has studied the 24-hour periodicity of bone and dentin with respect to the mineralization of these tissues. This paper describes experiments designed to detect daily changes in the functional activity of cartilage and bone cells by the use of S^{35} -sulfate as an index of chondroitin sulfate synthesis, and of C^{14} -glycine to show collagen synthesis. In view of definitive evidence^(4,5) that a) chondrocytes are the loci in which chondroitin sulfate is synthesized and subsequently elaborated from the cells as a constituent of the ground substance of cartilage matrix and b) that it is principally the osteoblast that incorporates glycine immediately after administration,^(6,7) the possibility existed that differences in the amount of these radioisotopes concentrated in the tissues might occur over a 24-hour period.

Materials and Method

Albino rats (Sprague-Dawley Strain), 45 to 50 g, were singly housed and maintained for two weeks under a photoperiod of 12 hours (09:00-21:00) alternating with 12 hours of darkness (21:00-09:00) and at a temperature of 73-75°F. Food and water were supplied ad libitum. The animals were weighed 24 hours prior to experimentation, and groups were established according to their weight-gain performance during the two-week conditioning period.

Two experiments were performed: In the first, nineteen rats (175-200 g) were injected with 30 μ c S^{35} -sulfate/100 g, body weight in 0.1 ml distilled water via the tail vein between 09:00-11:00 (Day Group); a second series (Night Group) was injected between 21:00-22:30. Subgroups of 4-5 rats were sacrificed by decapitation at 2-3, 4, 8, and 12 hours after receiving the tracer dose. The left femora obtained at autopsy were fixed in 95% alcohol,⁽⁸⁾ embedded undecalcified in methyl methacrylate, and sectioned at 100 microns on a high-speed rotary saw. The sections were exposed for three weeks in a freezer on Kodak Type A autoradiographic plates. The darkening of the developed images on the film was measured at 5 sites on the distal epiphyseal and articular cartilages and epiphyseal marrow space by scanning these areas parallel to the long axis of the femur with a microscope-densitometer (30-micron aperture) - Brown recorder combination. Transverse scans across the metaphysis and mid-shaft cortex and marrow were also performed. The values were corrected for background.

In the second experiment, 3-4 rats (150-170 g) were injected intravenously with 35 μ c glycine-2-C¹⁴ (specific activity, 14 mc/mM; Volk Radiochemical Corp.) in 0.2 ml distilled water at six, four-hour intervals during a 24-hour period to gain a more detailed picture of cellular activity. The animals were sacrificed an hour after radiotracer administration by asphyxiation, and the bones of the left hind limb were removed at autopsy. The femora were split longitudinally and fixed in 10% neutral formalin. The pieces were decalcified in 10% EDTA (pH 7.4)⁽⁹⁾ and divided into distal epiphyseal-metaphyseal and shaft segments. One hemiepiphysis-metaphysis was embedded in paraffin, sectioned longitudinally at 7 μ , and the sections were stained with iron hematoxylin and phloxin to visualize mitotic figures. The per cent of chondrocytes in the proliferating zones (Zone 1-3)⁽¹⁰⁾ of the epiphyseal cartilage of the femur undergoing mitosis was calculated by direct counts (at least 1000 cells) under an oil-immersion lens at a magnification of 970X. A rough approximation of osteoclastic activity in the metaphyses was obtained by scanning a few sections from each bone at high power under an ocular reticule and by calculating the percentage of the grid intersections covered by osteoclasts. Gross autoradiographs of each epiphyseal-metaphyseal segment were also prepared to localize the deposition of the tracer by placing the histologic sections in contact with Kodak Type A autoradiographic plates for a period of 4 weeks in a freezer. The corresponding hemiepiphysis-metaphysis and the total shaft segments were dried overnight, weighed, dissolved in ethylene diamine (0.5 ml/mg tissue), and aliquots were pipetted and evaporated on planchets for C¹⁴-glycine assay. These were measured by a thin end-window beta geiger tube against a known standard. Each determination was carried out in triplicate. The tibias were divided into proximal epiphyseal-metaphyseal and shaft segments and similarly assayed but were not examined histologically.

Results

S³⁵-Sulfate Incorporation in the Femur

The data (Figure 36) reveal that differences in the pattern of S³⁵ incorporation occur only in the distal growth cartilage. The uptake of the tracer is very uniform over the first four hours after injection in both groups, but the cartilages of the day rats clearly retain (ca. 20%) more S³⁵ after 8-12 hours. The retention of S³⁵ in articular cartilages is very constant. The curves of the metaphysis, diaphyseal shaft and marrow are nearly identical, and the intensity of the autoradiographic image remains relatively constant after an initial small decrease from 2-3 hours.

C¹⁴-Glycine Incorporation

Gross localization of the tracer an hour after injection can be seen in an autoradiograph of the distal end of the femur (Figure 37). The

Figure 36

The microdensitometric pattern of S^{35} incorporation into various areas of the rat femur during two continuous 12-hr periods within a single 24-hr day.

Figure 37

An autoradiograph of the distal end of the femur from a rat 1 hr after an injection of glycine- $2-C^{14}$. a, articular cartilage; b, proliferating zones and c, zone of hypertrophic cells of the epiphyseal growth cartilage; d, metaphysis; e, periosteum; f, endosteum.

articular and epiphyseal cartilage (zones of proliferation and cell enlargement) appear rather uniformly labeled except for the more intense reaction over the lateral edges of the epiphyseal cartilage where the width of the plate is increased as the bone grows larger. The image over the zone of cellular hypertrophy is markedly less reactive. There is, in addition, a narrow subarticular zone of small hotspots indicating foci of intense tracer uptake, but the hotspot activity is greatest in the metaphysis and along the endosteum and marrow spaces of the compact bone of the shaft.

The retention of radioglycine in the femur and tibia at different intervals within a single 24-hour period has been recorded in Figures 38 and 39. A statistically significant diurnal pattern is very evident in

Figure 38
The 24-hour changes in C^{14} -glycine incorporation into rat femora
A Distal epiphyseal-metaphyseal segments B Shafts

Figure 39
The 24-hour changes in C^{14} -glycine incorporation into rat tibiae
A Proximal epiphyseal-metaphyseal segments B. Shafts.

epiphyseal-metaphyseal segments of the femur (Figure 38A). Maximum retention occurred at 13:00, while minimum incorporation was seen from 01:00-05:00. No clear periodicity was recorded in the femoral shaft (Figure 38B) or in either segment of the tibia (Figure 39).

Mitotic and Osteoclastic Periodicity

Maximum mitotic activity in the distal epiphyseal cartilage of the femur (Figure 40) was noted at 18:00. The values at other times during the day were relatively constant, but the differences between the peak and minimum mitotic index were nearly twofold and statistically significant. A diurnal periodic change of about 40% was also observed for the area occupied by osteoclasts in the metaphysis of the distal femur, but whether this is related to an increase in the numbers of these cells or simply to changes in their configuration is not clear. The period of maximum osteoclastic "area" (Figure 41), however, corresponded to peak glycine incorporation at 14:00-18:00, but the values at other intervals during the day remained rather constant.

Figure 40

The daily changes in the per cent of the chondrocytes of the proliferating zones in the distal femoral epiphyseal cartilage plate undergoing mitoses.

Figure 41

The daily changes in the per cent of distal femoral metaphyseal area occupied by osteoclasts.

Discussion

Exchange phenomena between tissue chondroitin sulphuric acid and blood within the first 4 hours after S^{35} administration probably account for the early apparent absence of day-night differences in the tracer content of epiphyseal cartilage, shaft and marrow.⁽¹¹⁾ Since high-resolution autoradiography of mineralized and demineralized preparations have shown intense labeling of newly-synthesized chondroitin sulfate in bone and in the cells of cartilage for at least 24 hours^(11,12) despite a rapid depletion of S^{35} in serum dialysates,⁽¹³⁾ the labeling after 4 hours in epiphyseal cartilage, at least, suggests a true variability in cellular activity. The uniform label over articular cartilage in both time series suggests relative cellular inactivity, and this is consistent with the fact that this area contains largely hypertrophic senescent cells. Similarly, one would not expect to find differences in the elaboration of the ground substance of bone tissue at the level of the mid-shaft since the periosteal and endosteal cells are generally inactive and spindle shaped elements. The intensity of the S^{35} autoradiographs in this area was nearly identical in both time series, but since some radiosulfur is apparently associated with the mineral phase in undecalcified preparations,⁽¹¹⁾ this data may not be conclusive proof of an absence of periodic events.

Since work in bone from several other laboratories^(6,7) has indicated that it is predominately the osteoblast which takes up radioglycine within an hour after administration, and that it is secreted as a part of newly-formed collagen in approximately four hours, it is unlikely that these experiments have measured fluctuations in the size of the glycine pool. In these studies, which were limited to the first hour after tracer administration, a diurnal pattern of radioglycine uptake was seen in the distal end of the femur. The tissue, however, did contain some cartilage from the epiphyseal plate which incorporates the tracer.⁽¹⁴⁾ While the relative participation of bone and cartilage tissue to the emergent pattern must await further work, the coincidence between the maxima of glycine incorporation and the osteoclast frequency index strongly suggests that the data must, in part, reflect processes basic to the remodeling of bone, i.e., new matrix synthesis by osteoblasts preparatory to repair of tissue destroyed by osteoclastic action. One might also speculate upon the possibility of a daily periodism in a) the intensity of cellular modulation in bone from undifferentiated reticular and preosteoblast cells to the more highly specialized osteoblasts and osteoclasts, and b) the amount of parathyroid hormone released from the gland since parathyroid extract can increase the osteoclast census.⁽¹⁵⁾ Synchronization of RNA synthesis might occur throughout skeletal tissue. Chondrocytes would acquire glycine more avidly at these times since some collagenous fibers are present in cartilage matrix.

The maxima of all mitotic and metabolic functions studied so far occur during the light period. However, there is an inverse temporal

relationship between the curves of the two processes, which has also been seen in liver⁽¹⁶⁾ and other tissues.⁽¹⁷⁾ Metabolic functions are proceeding at a decreasing rate when mitotic activity is highest. Although it was previously shown in mice⁽²⁾ that peak DNA synthesis in epiphyseal cartilage cells occurred at 10:00, the present finding that peak mitotic activity occurred at 18:00 - an interval of 8 hours - compares well to the difference of 8 hours for liver.⁽¹⁶⁾ Maximum DNA synthesis in mouse cartilage and peak RNA synthesis in rat epiphyseal-metaphyseal segments, however, are nearly coincident; a phase difference of 6-8 hours has been detected in liver,⁽¹⁶⁾ but the bone experiments may not be quite comparable since the skeletal tissues were not uniform. Since it was previously shown that a mitotic period existed for chondrocytes in the proximal cartilage of the tibia,⁽¹⁾ it is of interest that diurnal patterns of RNA synthesis could only be demonstrated for the femoral epiphysis-metaphysis. That variations in the intensity of a response in the different bones of the same animal to a given stimulus occur is well known. It was surprising to find peak mitotic activity in these studies at 18:00, in view of our preliminary estimate that it should occur earlier in the day (02:00-10:00).⁽¹⁾ It must be realized, however, that the colchicine method initially used is in itself subject to question since the relative sensitivity of animals to the agent administered at different times of the day is not known.

Present studies have marshalled additional evidence that the processes of bone and cartilage formation operate against a background of diurnal periodic changes. It is becoming extremely important to recognize periodic phenomena where they exist since their presence may mask or accentuate experimental data. What may appear to be a significant change in a morphologic or metabolic parameter may merely reflect normal patterns. In the present studies, moreover, it has been shown that different bones may or may not show diurnal change in one or both of these parameters.

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THE POSTNATAL DEVELOPMENT OF BONE OF JAPANESE QUAIL, I. THE CORTEX*

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Most of our knowledge about the differences in the bone structure of avian species derives from broad surveys or compendia which show that degrees of complexity exist at the histologic level which are, in part, correlated to body size and to particular bones.⁽¹⁻⁶⁾ The first systematic investigation of the histodifferentiation of cartilage and bone from mesenchymal tissue was reported by Fell⁽⁷⁾ in the chick from the 52nd hour of incubation to the first day after hatching. Subsequently, Jackson⁽⁸⁾ described the changes in the fibrous structure of the embryonic cortex in chickens, while Policard⁽⁹⁾ published a short paper which dealt with the development of the neonatal cortex from hatching through the first three months of age. The studies were extended by Pratt⁽¹⁰⁾ in a very complete age series from embryonic life to one year postnatally. In view of the differences between avian species, it is the purpose of this paper to describe the skeletal development of a small bird, the Japanese quail (Coturnix coturnix japonica) at various posthatching periods.

Materials and Method

Twenty-seven male and female Coturnix, 1-3 months of age, obtained from the Department of Poultry Husbandry, Auburn University, Auburn, Alabama were singly housed in 11 by 10 by 6-inch rat cages and maintained at a temperature of 75-80°F and at a photoperiod of 14 hours.⁽¹¹⁾ Under these conditions, the females obtained at 30 days of age began to lay when they were 60-70 days old. The egg production of a second series of females was followed for a period of three months. While we did not correlate the bone changes with the egg-laying history of the birds, the 3- to 12-month-old females examined were actively laying animals. Several young quail were hatched in the laboratory and provided information relative to the new-born animal.

The birds examined were largely females 2-4 hours, 30, 35, 40, 60, 67, 90 and 270-365 days old. Five, 74- to 365-day-old male quail were included for comparison. Estradiol valerate[†] was administered to both males

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and females in a second study to determine the effect of the hormone upon bone maturation, and the results will be reported separately.⁽¹²⁾ Only the tibiae were taken from the youngest birds at autopsy. In all others, the femur, tibia, tibiotarsus, adrenals, oviducts and ovaries or testes were preserved. The bones were fixed in neutral formalin, decalcified in EDTA and embedded in either paraffin or celloidin. Longitudinal and cross sections of the tibiae and cross sections of the femora from the distal metaphysis and mid-shaft were cut at 6-10 microns and stained with hematoxylin, eosin and azure II.

The bones of the left limb, the adrenals and reproductive structures were X-rayed on the same plate to obtain a permanent record of their dimensions. The femora and tibiae were embedded undecalcified in methyl methacrylate, cut on a high speed rotary saw at 75-100 microns, and the sections were microradiographed for comparison with the histologic material. The distal half of a femur from each age group was serially sectioned to provide known reference points since considerable histologic variation along the shaft is known to occur. Microradiographs were also prepared from mid-shaft and metaphyseal sections of tibiotarsi obtained from 3- to 12-month-old birds.

Microradiography.

While the findings reported are based upon intercomparisons of histologic sections and microradiographs, the latter were largely used as illustrative material since they presented a clearer picture of the progressive changes during cortical maturation. Stained histologic preparations were not as useful because the stain did not clearly differentiate between areas of new and old bone where remodeling had not occurred. Despite the fact that microradiography of undecalcified sections reveals only differences in mineral density and cannot show the nature of the cells and other soft tissue structures associated with bony surfaces, the character of the surfaces revealed by X-rays can be directly related in most instances to cellular function. Sites of new bone formation where surfaces are lined by osteoblasts are smooth and not as densely mineralized as older regions of bone, and these appear darker since they are not as resistant to the passage of X-rays. Foci of osteoclastic resorption, on the other hand, are marked by irregular borders and rather abrupt changes in mineral density consistent with the concept that matrix and mineral removal occur concurrently or nearly so. The interpretation of microradiographs is facilitated once these relationships are realized.

Results

2-Hour to 4-Day Coturnix

Cross sections from the tibiae of serially sacrificed birds show a progressive consolidation of the cortex. The shaft of the new bone is thin

and consists of woven non-lamellar bone trabeculae (1-2 cells thick) surrounding irregular vascular spaces lined with osteoblasts and an occasional osteoclast (Figure 42). The vascular spaces narrow by the fourth day after hatching (Figure 43). Epiphyseal differentiation is progressing rapidly in the tibiae and the cartilage appears honeycombed in microradiographs owing to the broad discontinuous front of hypertrophied cells.

30- to 35-Day Coturnix

The bone of the femoral mid-shaft cortex is thicker (2-6 cells) and encloses a reticular network of large vascular spaces which open at the periosteum (Figure 44). There are no limiting lamellae. While periosteal osteogenesis continues, most of the canals deeper in the cortex are of smaller caliber, lose their osteogenic layer of cells, and are limited by single lamellae of low mineral density; the endosteum contains a few mature primary osteons. Several radial vessels pass completely through the cortex at points of muscle attachment and send off a few incomplete circumferential canals. Highly calcified bands of cartilage and cement lines limit larger replacement osteons in the distal metaphyseal cortex (Figure 45). Mid-shaft sections of tibiae (Figure 46) reveal larger numbers of small primary osteons than occur in the femora.

60- to 67-Day Coturnix

The structure of the mature bone is well established in the diaphysis. In the femora, the subperiosteal lamellae contain a few primary canals, while the deeper portions of the cortex contain proportionately more primary osteons than in the month-old groups (Figure 47). Microradiographs reveal the distribution of vessels more clearly than the thinner histologic sections; the pattern is somewhat intermediate between a reticular and radial type, and short segments of lamellae may be organized into laminae by incomplete circumferential canals.

The growth cartilage of the proximal tibia has been replaced by marrow and endochondral trabeculae. Unresorbed spicules of cartilage incorporated during longitudinal growth persist in the proximal and distal thirds of the cortex. Intramedullary bone formation is beginning, but it does not extend into the distal metaphyseal and epiphyseal areas of the tibiae. Consistent with the month-old animals, the proportion of primary osteons to primitive vascular canals in the tibial shaft bone (Figure 48) is greater than in corresponding areas of the femur (Figure 47).

90 - to 365-Day Coturnix

These histologic and microradiographic preparations are more uniform in this age group than in younger animals. Primary osteons are the predominate histologic feature while the radial pattern of non-haversian vessels is reduced still further (Figure 49). A narrow relatively avascular band of periosteal lamellae overlies the thicker zone of haversian bone, and

Figure 42

Microradiograph of a transverse section through the diaphysis of a tibia from a 2-hour old quail showing the vascular spaces in the bone.

Figure 43

Microradiograph of a transverse section through the diaphysis of a tibia from a 4-day-old quail showing the early contraction of the vascular spaces. (Compare with Figure 42.)

Figure 44

Microradiograph of a transverse section through the diaphysis of the femur from a 30- to 35-day-old female quail showing the reticular network of vascular channels. Trabeculae of bone are forming subperiosteally, and there are a few primary vascular canals deeper in the cortex.

Figure 45

Microradiograph of a transverse section through the distal metaphysis of the femur from a 30- to 35-day-old female quail showing periosteal osteogenesis and endosteal primary osteons which have formed by remodeling of trabeculae incorporated during longitudinal growth.

Figure 46

Microradiograph of a transverse section through the diaphysis of the tibia from a 30- to 35-day-old female quail showing periosteal osteogenesis and numerous primary osteons.

Figure 47

Microradiograph of a transverse section through the diaphysis of a femur from a 60- to 67-day-old female quail showing the laminar arrangement of lamellae between incomplete circumferential canals. There are a few primary osteons.

Figure 48

Microradiograph of a transverse section through the diaphysis of a tibia from a 60- to 67-day-old female quail showing numerous primary osteons and a radial organization of blood vessels. Note the fusion of irregular osteocyte lacunae in the interstitial substance (arrow) between primary osteons.

Figure 49

Microradiograph of a transverse section through the diaphysis of a femur from a year-old male quail showing primary osteons. The larger osteon was probably formed by lamellar deposition about a large vascular space; note the enlarged lacunae (arrow) in the peripheral lamellae of the osteon and in the interstitial substance.

intramedullary bone formation has largely obliterated the femoral marrow cavity; in the metaphysis of the female quail, new bone is deposited about the edges of endosteal marrow spaces which open into the medullary cavity and within the larger primary vascular canals (Figure 50), but this never occurs in normal males (Figure 51).

Longitudinal sections of the tibiae of laying females resemble the bone of 60-day-old birds. Large marrow spaces replete with endosteal bone occur in the proximal third of the shaft. Cross sections demonstrate numerous primary osteons (Figure 52).

The mid-shaft of the tibiotarsus contains many small primary osteons (Figure 53); these systems become larger and less numerous in the proximal epiphysis, and the innermost lamella about the central canals may be hypercalcified indicating arrested growth (Figure 54).

The cortical bone of male quail was identical in structure to that of the laying females.

Resorption of Cortical Bone

An unusual picture of resorption in the densely mineralized interstitial substance between primary osteons and in the outer periosteal lamellae was observed in microradiographs of bones from quail of all ages. Some lacunae were quite enlarged, had ragged borders and often united to form narrow clefts in the tissue; the perilacunar bone appeared in some instances to be demineralized (Figure 55). Whereas soft X-rays did not reveal contained soft tissue, comparative histologic preparations showed contiguous groups of large osteocytes with little intervening matrix which appeared to be abnormal (Figure 56). These erosion cavities were followed as much as a millimeter in length by serial microradiographs. A similar microradiographic picture appeared in trabeculae of epiphyseal bone (Figure 57).

An exaggerated, but misleading picture of perilacunar resorption occurs at sites of muscle attachment, particularly in the metaphyses owing to the inclusion of fibrocartilage during transverse periosteal growth and subsequent remodeling (Figures 58 and 59). The relative sizes of the cells involved in these microradiographic lesions is a general clue to the type of involvement, but in most instances it is necessary to refer to comparable histologic material for the proper diagnosis.

Discussion

The findings confirm what has generally been observed for avian cortical bone, but some new information is presented which contributes to a more complete description of this development. First, this study emphasizes the consistent histologic appearance of the neonatal skeleton of different

Figure 50

Photomicrograph of a transverse section through the distal metaphysis (C) of a femur from a 90-day-old female quail showing endosteal bone formation (IM) about cortical vascular spaces and trabeculae of intramedullary bone. Hematoxylin, eosin and azure stain.

Figure 51

Photomicrograph of a transverse section through the distal metaphysis of a femur from a 90-day-old male quail. Hematoxylin, eosin and azure stain.

Figure 52

Microradiograph of a transverse section through the diaphysis of a tibia from a year-old female quail showing many small primary osteons and intramedullary bone.

Figure 53

Microradiograph of a transverse section through the diaphysis of a tibiotarsus from a 90-day-old female quail showing many primary osteons.

Figure 54

Microradiograph of a transverse section through the metaphysis of a tibiotarsus from a 90-day-old female quail showing large endosteal primary and secondary osteons. Note the extensive areas of lacunar enlargement and fusion (arrows) in the interstitial substance.

Figure 55

Microradiograph of a transverse section through the metaphysis of a tibiotarsus from a year-old female quail showing extensive voids (arrow) of the interstitial substance between the zones of periosteal and endosteal ossification produced by lacunar enlargement.

Figure 56

Photomicrograph of a transverse section through the metaphysis of tibiotarsus from a year-old female quail showing areas (arrows) of lacunar enlargement and faulty matrix. Hematoxylin, eosin, azure II stain.

Figure 57

Microradiograph of a transverse section through the distal epiphysis of a femur from a 30- to 35-day-old female quail showing extensive destruction of trabeculae by lacunar resorption and fusion.

Figure 58

Microradiograph of a transverse section through the diaphysis of a tibiotarsus from a year-old female quail showing extensive areas of apparent destruction (arrows) of the interstitial substance by lacunar resorption and fusion. This is an area of fibrocartilage. (Compare with Figure 59.)

Figure 59

Photomicrograph of a transverse section through the metaphysis (C) of a tibiotarsus from a year-old female quail showing fibrocartilage cells (FC) in a zone of muscle attachment and embedded in the osseous matrix. Hematoxylin, eosin and azure II stain.

vertebrates, for the cortex is uniformly composed of embryonic woven bone and includes large vascular spaces which are sites of intense osteogenesis. In studies of mammalian bone growth, Ca^{45} and Sr^{90} autoradiographs have shown that the sites of growth at the level of the diaphysis become confined to the periosteum as the size of the spaces deeper in the shaft are reduced subsequently.⁽¹³⁻¹⁵⁾ The situation in the month-old quail is entirely comparable, and one might expect results identical to those obtained in dogs and rabbits using radiotracers. Beyond this stage, however, species variability complicates internal patterning, and the bones of smaller vertebrates seldom exhibit secondary structures which are built within irregular cavities formed in exsistant osteons by osteoclastic resorption, for example, as in man and dogs throughout the first months of life. The cortical bone of quail, rather, becomes consolidated by the deposition of bone about large vascular spaces, effectively reducing the number of anastomotic vessels, narrowing their caliber, and establishing a vascular supply oriented parallel to the long axis of the bone within primary osteons. In the hen, at least, consolidation of the cortex is effected by the deposition of two types of bone: one consisting of longitudinally-running and densely-packed fiber bundles,^(5, 10) and the other of a rather peculiar tissue devoid of fibers and confined to static surfaces and to older parts of the bone.⁽¹⁰⁾ The latter type, apparent only in sections stained by silver-impregnation techniques, was termed "hyaline matrix" (2-7 μ thick) and contained lacunae occupied by elongated cells. Longitudinal sections of the quail tibiae indicated that the vessels follow a diagonal course proximo-distally from the periosteum to the endosteum described for other species.⁽¹⁶⁻¹⁹⁾

There is little evidence of resorption along the walls of vessels at the level of the mid-shaft; osteoclasts are seldom seen, and there are very few microradiographically identifiable areas of resorption, i.e., ragged edges or highly mineralized borders,⁽²⁰⁾ even on the periosteum of bone from the youngest quail. Although most periosteal surfaces abut on regions of high mineral density, the picture suggests rather rapidly forming and mineralizing new bone. That the vascular spaces deeper in the cortex lack an osteogenic layer by one month of age is typical of the picture of rapid transverse growth described by Lacroix.⁽²¹⁾ Since mid-shaft osteons in the quail lacked delimiting cement lines characteristic of systems which arise to replace sites of erosion, the osteons are more properly called "addition" osteons, which form periosteally. Resorption probably accounts in large part for the lateral migration of existing vessels; however, the lamellar systems of the majority of primary osteons are concentrically disposed about the central canals, and skewed patterns suggestive of resorption and subsequent osteogenesis are very rare (Figure 49). Gross turnover of cortical bone material mediated by osteoclasts has been reported in ducks and waders⁽²²⁾ and in chickens during the molt,⁽²³⁾ and in hens maintained on a low calcium regimen;⁽²⁴⁾ unstressed, actively-laying hens, however, normally derive their mineral needed for calcium homeostasis and egg laying from dietary sources and from deposits of labile intramedullary bone.⁽²⁵⁾ In view of the apparent absence of secondary replacement systems

in the diaphyseal bone of quail, the role of the sometimes spotty but extensive lacunar enlargement in the interstitial lamellae, which may appear demineralized in microradiographs, is not clear. Enlarged lacunae and rather bizarre resorption cavities have been reported in normal bone^(26,27) and in instances of radiation damage,⁽²⁸⁾ where the latter occurs within osteons and is often accompanied by cellular death and filling of the lacunae and haversian canals with dense mineral deposits as a consequence of primary vascular damage. The process in normal bone has been termed osteolysis as opposed to osteoclasts, i.e., resorption occurring from osteoclastic activity.^(26,27) Since the lacunae in osteolytic areas of quail cortical bone are apparently occupied by viable osteocytes, and since soft-shelled eggs indicative of a deficient mineral nutrition were not produced, the nature of the microradiographic defects is not clear, but this type of bone destruction might play a role in mineral homeostasis. The corresponding picture of local matrix degradation in areas of enlarged lacunae seen histologically in this study is surprisingly like that occurring in the osteoporotic condition described by Little et al.⁽²⁹⁾ in which osteocytes and their associated collagen are affected in patches. Autoradiographic studies using tritiated thymidine as a marker⁽³⁰⁻³²⁾ have provided direct evidence that bone cells are capable of morphologic and biochemical modulations enabling them to function as osteoblasts, osteocytes, and osteoclasts. Although the fate of the osteocyte is known in part - that it may be liberated by osteoclastic resorption and incorporated into that cell - it is not known if osteocytes in situ may modulate and operate as osteoclasts; uninucleate osteoclasts are not unknown.⁽³³⁾ Experiments by Fell⁽³⁴⁾ demonstrate that bone cells can release proteolytic enzymes to degrade collagen after treatment with excess Vitamin A, and in vitro studies suggest also that they produce acids which might cause a local demineralization;⁽³⁵⁾ this concept of mineral solubilization by local pH changes deep within the cortex has been challenged, however, by McLean and Urist⁽³⁶⁾ and others.⁽³⁷⁾ Finally, it is of interest that Urist and Deutsch⁽³⁸⁾ have reported non-osteoclastic resorption at the endosteal side of the cortex in hens bred for laying, and these cavities were not repaired.

The presence of replacement systems, if not their significance, in avian bone has been described many times.^(1,2,4,5,39) Secondary osteons, identified by their investing cement lines, were common in the metaphyseal bone at the endosteum and then most probably formed by remodeling of incorporated endochondral bone since cartilage is present. Mid-shaft primary osteons were observed in greater numbers and earlier in the tibiae and tibiotarsi than in the femora. Amprino and Godina⁽¹⁾ observed that where there are many osteons in avian species, they tend to be of small size and that they were generally more common in the metatarsals and other foot bones than elsewhere. The pelvis and wing bones may also contain osteons. Marked structural differences from area to area along the shaft occur in quail bone as in other species,^(13,16,40,41) and these as well as other interspecies variations have been ascribed to differential rates of growth involving factors of "the life span of the form, and the size, specific shape and the proportions of individual bones considered."⁽⁴²⁾

Summary

The development of the long bones of Japanese quail was studied histologically and microradiographically at different post-hatching periods from birth to one year of age. At the level of the mid-shaft, the woven bone of the neonatal animal becomes thicker by rapid periosteal growth and becomes consolidated by the deposition of bone within large vascular spaces throughout the first month of life. Continued periosteal growth and formation of osteons is most rapid during the second and third month, and the mature architecture of the cortex - primary haversian bone - is established at the end of this period. Osteon formation is more progressive in the tibiotarsus and tibia than in the femur. Replacement osteons are established by remodeling endochondral bone incorporated into the metaphyses near the endosteum, but these deposits delimited by cement lines do not seem to be remodeled to any significant degree. Bizarre resorption cavities were frequently observed in highly mineralized interstitial lamellae.

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THE POSTNATAL DEVELOPMENT OF BONE OF JAPANESE QUAIL.

II. THE EFFECT OF ESTROGEN*

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The skeleton of sexually mature female birds is altered during the reproductive cycle by new bone deposition within the medullary cavities of the long bones, and this response can be induced in male birds treated with estrogen. This endocrine-bone relationship has been intensively investigated in several avian species. The anatomy and formation of intramedullary bone has been studied in the pigeon,^(1,2) chicken⁽³⁾ and duck.^(4,5) The purpose of this report is to describe the bone changes coincident with the onset of reproductive maturity in a small avian species, the Japanese quail (*Coturnix coturnix japonica*) and the effects of estrogen administered to both females and males at different posthatching intervals. The development of the cortical bone of this species contrasted with that of larger birds has been considered in a previous report.⁽⁶⁾

Materials and Method

Twenty-eight quail (19 females, 9 males) were used in this experiment,[†] and the animals ranged in age from 30-365 days. Eighteen served as controls and were the same individuals previously studied.⁽⁶⁾ Groups of 3-4 birds were sacrificed when they were 30-35, 60-67, 74, 81, 90 and 270-365 days old. Three, 30- to 35- and three, 60- to 67-day-old females each received intramuscular injections of 1 mg estradiol valerate (Delestrogen^{††}) and were sacrificed after 7 days. Four males each received 1-3 mg of the hormone by the same route at 74-90 days of age and were killed 1-3 weeks after injection to study the prolonged effect of the dosages. At autopsy, the femora, tibiae and tibiotarsi, adrenals, ovaries and oviducts or testes were dissected out, measured and weighed. The bones of the right side were fixed in formalin, decalcified in EDTA, embedded in

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[†]The birds were obtained at 1-3 months of age from the Department of Poultry Husbandry, Auburn University, Auburn, Alabama.

^{††}Delestrogen was generously supplied by Edward C. Reifenstein, Jr., M.D., Squibb Institute, New Brunswick, New Jersey.

either paraffin or celloidin; and transverse sections of the femoral diaphyses and longitudinal sections of the tibiae were cut at 6-10 μ and stained with hematoxylin, eosin and azure II. The left bones were X-rayed on the same plate with the soft tissues, embedded in methyl methacrylate and sectioned undecalcified by a high-speed rotary saw for comparison with the histologic material. Cross sections of tibial shafts were also obtained by this latter method, and, in a few instances, the femoral diaphyses were hand-sectioned with a carborundum disc prior to embedding to obtain a few thick cross sections which were X-rayed with the remaining intact proximal and distal segments. Care and maintenance of the quail has been outlined in the previous report.⁽⁶⁾

Results

Cortical Bone

The previous study demonstrated that the mature structure of the femoral diaphyseal cortex is achieved at 3 months of age by the deposition of lamellae within large vascular spaces of the young postnatal woven bone matrix, and by continuing periosteal osteon formation. Concomitantly, the anastomotic vascular pattern and caliber of the vessels was progressively reduced until the blood supply to the bone became predominantly established within longitudinal primary haversian canals.

The normal cortex of 30- to 35-day-old *Coturnix* consists of woven lamellar bone enclosing a reticular network of large vascular spaces which open at the periosteum and endosteum, and there may be a few endosteal primary longitudinal canals (Figure 60). This anastomotic vascular non-haversian pattern is somewhat reduced in the femora of birds receiving estrogen (Figure 61), but large vessels persist at sites of muscle attachment. The lamellar structure of bone appeared, moreover, better defined and the osteocyte lacunae were more regularly distributed. There were no apparent structural changes in the tibial cortex owing to estrogen treatment, and this is probably related to the earlier establishment of lamellar bone and a mature primary haversian pattern in this bone compared to the femur. While the hormone did not affect the structure of cortical bone when administered to animals 60-67 days of age or older, the onset of normal age changes in the medullary cavity of female quail described below were dependent upon the time at which hormone treatment was begun.

The Endosteal Reaction and Intramedullary Bone Formation

The medullary cavity of the long bones of female quail somewhat younger than 3 months old and in males throughout their first year of life at least is normally filled with fatty marrow. Females at 3 months of age showed a different organization of intramedullary tissue. When freshly

obtained femora were hand-sectioned into thick segments, a core of tissue was often dislodged from the medullary cavity. Radiographs of intact cortical-medullary segments revealed an inner halo of tissue less dense than and separated from the cortical bone by a narrow radiolucent zone. Microscopically, the core consisted of trabeculae which were rarely continuous with the endosteum at the mid-shaft, but contact was better in the metaphysis (Figures 62 and 63). The core was thin and separated from the endosteum except at two or three points (Figure 64). Marrow and osteogenic cells filled the radiolucent zone. This new bone had largely replaced the marrow elements except at the center of the cavity occupied by large veins, and had extended into the endosteal spaces at the metaphyses which open into the medullary cavity and into the larger primary vascular canals. In older, laying female quail, the intramedullary trabeculae become very robust, and deposits may be remodelled and form nodules (Figures 65 and 66). Bone nodules were first seen at three months of age in the distal

Figure 60

Microradiograph of a transverse section through the diaphysis of the femur from a 30- to 35-day-old female quail showing the reticular network of blood vessels. Trabeculae of bone are forming subperiosteally, and there are a few primary vascular canals deeper in the cortex.

Figure 61

Microradiograph of a transverse section through the diaphysis of a femur from a 30- to 35-day-old female estrogen-treated quail showing the formation of subperiosteal trabeculae and numerous primary vascular canals. The reticular network of blood vessels (compare with Figure 60) has been reduced. Note the periosteal resorption cavity at the lower left of the section.

Figure 62

Photomicrograph of a longitudinal section through the proximal third of a tibia from a 60- to 67-day-old female quail showing extensive intramedullary bone formation in the marrow cavity and cortical vascular spaces (C, cortex). Spicules of unresorbed cartilage persist in the cortex. Hematoxylin, eosin and azure stain.

Figure 63

Photomicrograph of a longitudinal section through the diaphysis of a tibia from a 60- to 67-day-old female quail. There is little continuity between the intramedullary bone and the endosteum of the shaft. Hematoxylin, eosin and azure stain, C, cortex.

0.1 mm

Figure 64

Microradiograph of a transverse section through the diaphysis of a femur from a 60- to 67-day-old estrogen-treated female quail. The cortex has a reticular pattern of blood vessels. Note the poor contact between the intramedullary trabeculae and the endosteum of the cortex. C, cortex; IM, intramedullary bone.

Figure 65

Microradiograph of a transverse section through the diaphysis of a femur from a 90-day-old female quail showing extensive intramedullary bone formation. Note the robust trabeculae in the center of the marrow cavity. C, cortex, IM, intramedullary bone.

Figure 66

Photomicrograph of a transverse section through the distal metaphysis of a femur from a 90-day-old female quail showing the compaction and remodeling of intramedullary trabeculae in the center of the medullary cavity. Hematoxylin, eosin and azure II stain.

metaphysis of the femur (Figure 66), but thereafter, irregular masses were found in the proximal and distal thirds of the tibiae as well (Figure 67). Intramedullary ossification in tibiotarsi was observed only in 9- to 12-month females, where it was quite minimal in extent.

— 0.1 mm

Figure 67

Microradiograph of a longitudinal section through the proximal third of a year old female quail showing nodules of robust intramedullary trabeculae. Mt, metaphyseal cortex; IM, intramedullary bone nodules.

Estrogen treatment initiated an endosteal reaction (new bone proliferation) and intramedullary bone formation in the femora of only one 30- to 35-day-old female quail and in all 60- to 67-day-old females (Figure 64); the deposits were approximately as thick as the cortical bone. The hormone also stimulated an over-growth of intramedullary bone in the tibial shaft of 60- to 67-day-old quail, and the trabeculae extended into the distal metaphyses and epiphyses, where they are normally not present. Bone nodules owing to remodelling of trabeculae were not seen in these immature age groups. Intramedullary bone formation was stimulated in male quail by estrogen, and the amount of bone formed was roughly proportional to the dose and to the duration of time after treatment.

Intramedullary bone spicules were surrounded in each case by a variety of cell types - osteoblasts, osteoclasts, or undifferentiated osteogenic cells, alone or in combinations. Estimations of the degree of trabecular resorption by osteoclasts were made from complete cross sections of femora from a few specimens of different ages to determine the degree of bone removal as a reflection of the metabolic utility of the deposits which

are, as will be discussed later, temporary mineral depots. A rough approximation of osteoclastic activity was obtained by scanning a few sections from each bone at high power under an ocular reticule and by comparing the frequency with which osteoclasts fell under the intersection of the orthogonal lines of the reticule to the possible number of "hits." The values (Table 26) suggest that osteoclasts become more evident from 2-3 months of age and that peak frequency is timed to occur with the establishment of egg laying. The interpretation of these findings should be taken with a degree of caution owing to the well-documented cell cycles in avian bone; the bone changes were not precisely correlated to the particular stage in the egg-laying cycle, and the considerable variability shown is expected since the reproductive cycles of the different birds are not synchronous. The effect of estrogen in the 60- to 67-day-old quail is somewhat indeterminate. Findings relative to estrogen-treated males were included for comparison with those of laying females, and osteoclast formation seemed to be restricted in male birds - a reflection of the more physiologic role of the tissue in the female.

Table 26

Percent area of the medullary cavity
occupied by osteoclasts in quail

Group	Age, days	Sex	Intramedullary* osteoclast index, %	
			Metaphysis	Diaphysis
Control	60-67	Female	0.1 ± 0.002 (3)**	0.3 ± 0.05 (3)
Estrogen treated	60-67	Female	0.2 (2)	1.3 (2)
Control	90	Female	3.9 ± 0.01 (5)	4.5 ± 1.2 (5)
Estrogen treated	90	Male	1.3 ± 0.01 (3)	1.5 ± 1.0 (3)

*Mean $\pm$ S.D.

**Numbers in parentheses are numbers of animals

Bone Weight

The weight of the femora (Table 27) in normal females is not significantly different after 60 days of age. The bones of laying females are heavier than those of untreated males, and the differences can be explained by the presence or absence of intramedullary bone. The tibial weights do not mirror these changes owing perhaps to the more restricted formation of intramedullary bone.

Table 27

Bone and organ weights of *Coturnix coturnix japonica**

Group	Age days	Sex	Body weight g	Right limb bones			Adrenal** mg	Ovary † mg	Oviduct mg	Testes** mg
				Femur mg	Tibia, mg	Tibiotarsus mg				
Control	30-35	Female	50 0 ± 2 7 (5) ^{††}	294 0 ± 14 1 (5)	374 0 ± 18 1 (5)	-	9 0 ± 1 1 (3)	33 0 ± 3 5 (4)	17 0 (2)	-
Estrogen treated	30-35	Female	56 3 ± 4 2 (3)	368 0 ± 17 1 (3)	402 0 ± 10 0 (3)	-	18 0 ± 2 4 (3)	26 0 ± 0 6 (3)	371 0 ± 37 1 (3)	-
Control	60-67	Female	106 3 ± 4 6 (4)	407 0 ± 9 5 (4)	452 0 ± 18 0 (4)	-	7 0 ± 1 2 (3)	430 0 ± 1 2 (3)	2175 0 ± 8 0 (4)	-
Estrogen treated	60-67	Female	101 0 ± 2 2 (3)	400 0 ± 34 1 (3)	456 0 ± 45 9 (3)	-	7 0 ± 1 0 (3)	790 0 ± 32 4 (3)	2690 0 ± 46 5 (3)	-
Control	90	Female	93 6 ± 4 4 (5)	363 0 ± 22 3 (5)	390 0 ± 21 8 (5)	-	37 0 ± 8 6 (5)	3036 0 ± 36 4 (5)	5938 0 ± 15 5 (5)	-
Control	90	Male	99 0 ± 6 1 (3)	347 0 ± 10 0 (3)	420 0 ± 4 5 (3)	-	18 0 ± 7 1 (3)	-	-	484 0 ± 29 4 (3)
Estrogen treated [§]	74	Male	93 0 (1)	476 0 (1)	401 0 (1)	-	10 0 (1)	-	-	110 0 (1)
Estrogen treated ^{§§}	90	Male	75 0 (1)	402 0 (1)	422 0 (1)	-	13 0 (1)	-	-	497 0 (1)
Estrogen treated [¶]	81	Male	108 0 (1)	397 0 (1)	464 0 (1)	-	3 0 (1)	-	-	731 0 (1)
Estrogen treated ^{¶¶}	90	Male	115 0 (1)	411 0 (1)	499 0 (1)	-	18 0 (1)	-	-	1640 0 (1)
Control	270-365	Female	117 8 ± 9 7 (4)	440 0 ± 30 2 (4)	487 5 ± 10 6 (4)	227 5 ± 9 6 (4)	13 3 ± 2 8 (4)	6576 6 ± 1111 1 (4)	14200 0 ± 2111 0 (4)	-
Control	270-365	Male	117 0 (2)	315 0 (2)	385 0 (2)	205 0 (2)	8 0 (2)	-	-	5400 0 (2)

*Data expressed as the mean ± S E

**Combined weights

†Yolk weight included

††Numbers in parentheses represent number of animals

[§]1 mg Estradiol administered 1 week prior to sacrifice^{§§}1.25 mg Estradiol administered 1 week prior to sacrifice[¶]2.0 mg Estradiol administered 2 weeks prior to sacrifice^{¶¶}3.0 mg Estradiol administered 3 weeks prior to sacrificeOrgan Weights (Table 27)

Adrenal. Only the adrenals of 30- to 40-day quail treated with estrogen are significantly heavier than their controls. Although the adrenals of estrogen-treated chickens are normally larger in the males, considerable variability exists in these birds.⁽⁷⁾ In drakes, although glands may be enlarged, there are no histologic changes owing to hormone therapy.⁽⁸⁾ Atrophied adrenals accompanied by an osteoporotic condition occur in hens bred for egg-laying.^(7,9) It has been suggested that the adrenals of quail may be comparatively non-reactive since they are unresponsive to stress provided by ACTH and cortisol treatment.⁽¹⁰⁾

Ovary. Except for the month-old group, the data relative to ovarian weight are inconclusive owing to variable amounts of yolk contained in the ripening follicles. The follicles are small in 30- to 40-day birds (1-2 mm) and somewhat larger in 60-day quail (7-9 mm) whose marrow cavities were

unossified. In a single 67-day animal showing medullary ossification and in actively laying quail, follicles were 11-19 mm in diameter. Follicular development was suppressed in quail treated with estrogen, and maturation was comparable to that of normal 30-day-old birds. The weight of the ovaries from immature birds 30-40 days old which show no yolk formation, and the ages at which these birds begin to lay under a 14-hour photoperiod agree well with published data.⁽¹¹⁾ Reduction of ovarian weight gain by exogenous hormone is ascribed to the suppression of pituitary gonadotropin production⁽¹²⁾ which governs the ovulability of ovaries.⁽¹³⁾ Egg production records show that quail lay about 16 days per month with an average hiatus of 14 days. It was not unusual for birds to lay continuously for 1-3 days, and in one instance, egg laying continued for as long as 9 days. The mean egg weight was 7.1 grams, or nearly 8% of body weight.

Oviduct. The oviducts of estrogen-treated quail are heavier than those of the untreated control animals. Eggs were detected in the upper tracts of two 90-day females and in the uteri of the oldest birds, where the shells were calcifying. While the weights of the oviducts in this experiment only agree with data published for 30-day quail (they are heavier in subsequent age groups than reported heretofore), considerable variability is known to exist.⁽¹¹⁾ With age and maturity the oviducts normally increase in weight owing to ovarian hormone production.⁽¹⁴⁾

Testes. The testes are markedly reduced in size (-50%) in mature male quail treated with estrogen and are approximately 80% lighter than the controls. Suppression of the testes has been observed in estrogenized ducks.⁽⁸⁾ Testicular maturation in wild birds, such as the sparrow⁽¹⁵⁾ and ducks, is related to the lengthening photoperiod (February-March), low temperature, and the normal fluctuations in thyroid and serum calcium values.⁽¹⁶⁾

Discussion

The morphologic findings reported in this paper do not essentially modify any existing concepts of avian physiology. As previously reported in other species by the investigators cited below, intramedullary bone formed in the long bones of laying female Japanese quail, and in males treated with estrogen. This phenomenon was first observed in the pigeon and was correlated with ovarian follicle development. In this original study, Kyes and Potter⁽¹⁷⁾ noted incipient marrow ossification when follicles were 2.8 - 4.0 mm in diameter and complete ossification when follicles were 9.0 - 10.0 mm. Reported increases in the weight of the oviducts of laying ducks indicated that the new bone formation was stimulated by endogenous estrogens,⁽¹⁸⁾ and this condition was subsequently reproduced in males, in which the marrow cavities are normally never ossified, by the administration of estrogens. The present coincidence with the Japanese quail data relative to the increase in ovarian follicle dimensions and

oviduct weight prior to the onset of medullary osteogenesis has been reported for a variety of avian species,^(1,3,19) including the bob white quail.^(20,21) It is of interest that marrow ossification in these studies could be precipitated by the administration of the hormone as early as 30-35 days; although the incipient changes were observed in only one bird, this time may represent the earliest maturational period at which the response can be elicited. It is known that the somewhat similar response to estrogen in the bones of mice cannot be observed if hormone is administered prior to 10 days after birth.⁽²²⁾ The early accelerated maturation of cortical bone in estrogen-treated, 1- to 2-month-old quail in these studies is of particular interest since, with the exception of the rabbit where cortices were thinner, the diaphyseal bone of other experimental animals is unaffected.⁽²³⁾

Laying birds were earlier found to exhibit a marked hypercalcemia which was related to the preovulatory phase of egg laying, and this could be produced in species treated with estrogens. The hypercalcemia was later identified with the non diffusible fraction of serum, and the response is proportional to the dose.⁽²⁴⁻²⁶⁾ Although the true significance of the elevated serum calcium values - phosphoprotein bound for yolk formation - has only been appreciated recently,^(27,28) many investigators had understandably been led to relate the temporal coincidence between a) estrogen secretion, egg maturation and intramedullary osteogenesis and b) hypercalcemia, shell calcification and destruction of the medullary deposits.^(1,3,26) This evidence suggested that birds accommodate to the severe demands upon their mineral metabolism during the egg-laying cycle by first providing a structural tissue competent to store a readily mobilizable source of calcium.^(1,29) The studies of Comar and Driggers⁽³⁰⁾ show that hens derive their mineral needs for calcium homeostasis from dietary sources as well as from these deposits of labile intramedullary bone. The rapidity with which the resorptive phase follows egg laying is most dramatic in seasonal layers, such as the sparrow, where removal of the tissue occurs within 1-2 weeks.^(31,32) In continuous layers, such as hens and the quail used in this experiment, the phases of bone deposition and resorption overlap somewhat.^(1,3) These changes are readily explained by the morphologic and functional modulations of osteoblasts, osteoclasts and their precursor cell types in the medullary cavity outlined in experiments utilizing tritiated thymidine as a "permanent" nuclear label.^(31,33-37) The cells surrounding the intramedullary trabeculae in quail bone were quite variable and in some instances were entirely reticular in nature. That there was little continuity between the intramedullary deposits and endosteum in laying quail may be explained in part by the fact that animals were sacrificed at a time immediately after laying and prior to the completed development of the next ovum. This time would correspond to a period of high endosteal osteoclastic activity in bone and a somewhat low serum estrogen titer. A similar observation was made by Bloom et al.⁽¹⁾ and by Riddle et al.⁽¹⁴⁾ in the pigeon, where there was a partial resorption of bone between successive cycles of egg laying and a return to bone formation within a few hours after laying

the first egg of a series. In these studies, the osteoclast index increased along the medullary trabeculae in the bones of female quail from 2-3 months of age, coincident with the onset of the egg-laying cycle at these times; the lower index recorded in estrogen-treated males most probably reflects the low physiological demand for the stored mineral, but one should consider that unphysiologic doses of the hormone tend to inhibit osteoclast formation in analogous studies with mice.⁽²²⁾ With respect to the numerous instances of intramedullary osteogenesis and subsequent remodelling of the tissue to form secondary bone in the form of nodules in control female quail, a rather similar effect has been recorded in the duck treated continuously with estrogen for several months.⁽⁴⁾ The mineral content of intramedullary bone is apparently normal in hens,⁽³⁸⁾ but it may be hypermineralized in pigeons⁽³⁹⁾ and in hens treated with parathyroid extract.⁽⁴⁰⁾ Marrow ossification could account for the increased retention of calcium in the bones of fowl.^(41,42) Folliculine bone fibers and their apatite crystals are poorly oriented, and the fiber density is quite variable.^(41,43-47)

The changes which occur in the bones of estrogenized male birds and normal laying females do not affect the skeleton uniformly, and species differences have been noted in ducks.⁽⁸⁾ Most of the literature indicates a gradient of activity, i.e., indices of medullary bone formation beginning with the femur and terminating with the metatarsals^(1,5,48) and the latter elements fail to form post-fracture endosteal callus to any great degree.⁽⁴⁹⁾ The bone response to estrogen has been attributed to an altered vascular supply,⁽⁴⁾ but Brookes and Lloyd⁽⁵⁰⁾ were unable to confirm this idea in mice which show a similar bone reaction to the hormone. An alternative mechanism of local vasodilation and augmented capillary permeability has been suggested by the local estrogen-mimetic bone reaction following intraosseous injection of histamine, yohimibine and acetylcholine;^(44,45) however, the results are not precisely parallel since the fibrillar pattern of the medullary deposits is atypical and these are hypocalcemic agents when introduced systematically. Nevertheless, histamine-containing mast cells are normal constituents of bone marrow, and estrogen can stimulate histamine release, at least in uterine tissue.⁽⁵¹⁾

There is some evidence for the supporting role of other hormones than estrogen in avian intramedullary bone formation. Extreme atrophy of the oviduct of pigeons, for example, is not accompanied by complete resorption of marrow bone.⁽¹⁴⁾

Testes. Apparently, the testes must be functional in pigeons to produce folliculine bone during the nonbreeding seasons although an endosteal reaction is not inhibited.⁽¹⁾ In the male quail, intramedullary bone formed in the absence of fully developed testes, but it was not established histologically whether the atrophied glands retained any ability to produce sperm.

Adrenals. Adrenalectomy does not alter the development of medullary bone in estrogen-treated male birds.⁽⁵²⁾ ACTH administered to hens tended to preserve intramedullary deposits and to reduce the thickness of the cortex slightly.⁽⁹⁾

Parathyroids. The parathyroids are probably not involved in the formation of intramedullary bone although the concept was stressed earlier by Benoit and his coworkers.⁽¹⁸⁾ Parathyroid hormone is apparently only requisite to maintain an adequate concentration of calcium ions in blood since intramedullary osteogenesis can proceed in parathyroidectomized animals.^(14,26)

Thyroid. Thyroid hormone promotes ovarian maturity and bone matrix deposition in ducks.^(52,53) While it does not contribute to the hypercalcemic role of estrogen in the sparrow,⁽⁵⁾ thyroidectomy will diminish the serum calcium and bone responses in ducks.⁽⁵³⁾

Pituitary. The role of the pituitary in the formation of avian intramedullary bone is poorly understood since there are wide species differences. Hens hypophysectomized⁽⁵⁴⁾ or treated with anterior pituitary preparations containing gonadotropins⁽¹²⁾ lose their ability to ovulate, while estrogen hypercalcemia is significantly reduced in hypophysectomized ducks.⁽⁵⁵⁾ The ovaries of juvenile female sparrows were unresponsive to a gonadotropic substance in pregnant mare's serum in nonlaying seasons, and no new bone was produced.⁽¹⁹⁾ However, in the pigeon, estrogen serum calcium values were not affected by hypophysectomy and intramedullary bone formation was unimpeded.⁽¹⁴⁾

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METEOROLOGICAL MODEL EXPERIMENTS*

Paul Frenzen

A brief summary of the current revival of interest in meteorological model experiments (which began at The University of Chicago in 1946) was presented and illustrated in terms of three models of large scale atmospheric circulations:

1) The obstacle experiment in which a homogeneous fluid is caused to flow past a barrier in a rotating, hemispherical shell; the resulting formation of long waves in relative westerly flow is considered analogous to circulations found in the earth's atmosphere downstream of large-scale mountain barriers.

2) The two-liquid experiment in which relative cyclonic velocity shear is produced across a domed interface between two fluids of slightly different density in a rotating, cylindrical container; a model analogue of a train of wave cyclones results, each member of which undergoes realistic development as it proceeds along the "polar front," that region in the model where the sloping outer edge of the dense, lower dome of liquid intersects the bottom of the container.

3) The "dishpan experiment" in which a continuous radial density gradient is maintained across a fluid in a rotating cylindrical container by means of a heat source around the outer edge and a heat sink centered on the axis of rotation; with suitable combinations of rotation rate and radial temperature difference, complex circulation patterns closely resembling those found in the middle and lower levels of the earth's atmosphere are produced; other conditions remaining in the appropriate range, a low rotation rate will result in a symmetrical circulation closely resembling the trade-wind cells of the equatorial and subtropical atmosphere, while higher rotations produce surprisingly realistic model jet streams, long waves, and cut-off systems, very similar to those which characterize the circulation of the earth's atmosphere in middle latitudes.

By their very simplicity, models such as these frequently clarify the understanding of the dynamics of complicated meteorological systems, for they reduce such problems to their bare essentials.

*Abstract of a talk given before the Meteorological Colloquium, Melbourne, Australia on 13 June 1963 during an extended visit by the author to the Division of Meteorological Physics, Commonwealth Scientific & Industrial Research Organization. Complete summary to appear in a forthcoming issue of The Australian Meteorological Magazine.

Talk accompanied by motion pictures kindly loaned by Professor Dave Fultz, Dept. of Geophysical Sciences, The University of Chicago, Consultant to the Meteorology Group, Radiological Physics Division, Argonne National Laboratory.

A NOTE ON ELLIPSOIDAL WIND DISTRIBUTIONS

Harold L. Crutcher* and Harry Moses

Abstract

The present paper extends the concept of wind distributions from two to three dimensions.

Homogeneous random wind observations may be described by the trivariate normal distribution. A multivariate normal distribution is distributed as chi square with degrees of freedom equal to the number of variates. The probability density function of the trivariate normal distribution can be written as

$$f(x_1, x_2, x) = C \exp -(1/2) x \sigma^{ij} x^i$$

where σ^{ij} is the inverse of the positive definite covariance matrix, σ_{ij} , x^i is the transpose of the x matrix, and $C = |\sigma_{ij}|^{1/2} (2\pi)^{-3/2}$. In the isotropic case, the distribution will be spherical. In all other cases, except the limiting straight-line form, the distribution will be ellipsoidal with magnitude and direction of the semi-axes determined respectively from the eigenvalues and eigenvectors of the covariance matrix. Tests for sphericity or isotropy are shown and application to diffusion problems indicated.

Introduction

Atmospheric motion affects man's activities. In spite of all the observations available on atmospheric motion of winds, there are not many data available in three dimensions, for most of the observations provide only information on the horizontal motion of the air.

In dynamic processes vertical motions in the upper air are just as important as those near the surface of the earth. Recent rocket experiments and observation of meteor trails are beginning to add a little more information on the three-dimensional characteristics of atmospheric motion. At lower levels, the constant-height balloon observations, and lower still, the tethered balloon observations as reported by Angell and Pack⁽¹⁾ are adding to our store of data

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In the surface layers, diffusion of waste material of all types directly affects the health and progress of all communities. Therefore, increased knowledge and application of beneficial or of remedial procedures are required.

Atmospheric motions (winds) are of greatest importance in the problems of diffusion. Exhaustive studies of winds have been made with respect to diffusion. In some cases, only the wind directions in the horizontal have been studied. In the search for better instrumentation to permit more detailed study, the bivane, hot-wire, and sonic anemometers have been developed. These instruments are used to measure the three-dimensional motion of the atmosphere.

Statistical Distributions

The normal distribution law in one dimension due to De Moivre⁽²⁾ is usually associated with the names of Gauss and Laplace. More than a century later, Bravais⁽³⁾ developed and published his study of normal frequency distributions in two and more variables. Outstanding contributions to this problem were also made by Bertrand,⁽⁴⁾ Czuber,⁽⁵⁾ Kluver,⁽⁶⁾ and Student.⁽⁷⁾ Pearson⁽⁸⁾ in his studies on multivariate normal distributions showed that these are chi-square distributions with k degrees of freedom, where k is the number of variables or dimensions. The three-dimensional distributions are sometimes called Rayleigh⁽⁹⁾ or Maxwellian⁽¹⁰⁾ distributions.

The multivariate (k -variate) normal distribution may be written as:

$$f(x_1, x_2, \dots, x_k) = C \exp -(1/2) \psi \quad (1)$$

where C is a constant and ψ is a positive definite matrix of the quadratic form.

Here,

$$C = |\sigma^{ij}|^{1/2} (2\pi)^{-k/2} \quad (2)$$

and

$$\psi = (x - \mu) \sigma^{ij} (x - \mu)' \quad (3)$$

where the σ^{ij} matrix is the inverse or reciprocal of the dispersion or covariance matrix of the variables, σ_{ij} , and $|\sigma^{ij}|$ is the determinant. $(x - \mu)'$ is the transpose of $(x - \mu)$.^(11,12) If the variables are measured from the origin $\mu = (\mu_1, \dots, \mu_k)$, then the above reduces to

$$\psi = x \sigma^{ij} x' \quad (4)$$

Wind Roses

In the twentieth century, numerous investigations have dealt with the mathematical representation of wind variations. Robitzsch,⁽¹³⁾ in his study on surface wind speeds, stated that wind distributions might follow the probability law proposed by Maxwell.⁽¹⁰⁾ Hesselberg and Bjorkdal⁽¹⁴⁾ followed this same line of reasoning. In 1946, Brooks et al.⁽¹⁵⁾ proposed and used a limiting form of the elliptical distribution, the circular normal distribution, for winds in the horizontal plane, and Crutcher⁽¹⁶⁾ used the elliptical bivariate normal distribution form for wind roses. Court⁽¹⁷⁾ has proposed the equal area type of wind rose.

Instrumentation

The study of three-dimensional wind distributions, of course, depends upon instruments which can be used to measure wind variation in three dimensions adequately. Several types of bivanes and hot-wire and sonic anemometers have been developed to measure the vertical variation of the wind. These are described by Taylor,⁽¹⁸⁾ Scrase,⁽¹⁹⁾ Best,⁽²⁰⁾ Hewson,⁽²¹⁾ Swinbank,⁽²²⁾ Pasquill,⁽²³⁾ Mazzarella,⁽²⁴⁾ Gill,⁽²⁵⁾ and Suomi and Businger.⁽²⁶⁾ Gill⁽²⁵⁾ briefly discusses the history of hot-wire anemometry. Installations of bivanes have been made at a few locations in the United States, and a few data sets have become available.

Data

The data used for this paper have been obtained from the Project Prairie Grass Reports edited by Barad⁽²⁷⁾ and Haugen⁽²⁸⁾ and from a paper by Angell and Pack.⁽¹⁾ The Project Prairie Grass data were collected by the U.S. Air Force and the Massachusetts Institute of Technology at O'Neill, Nebraska in the summer of 1956. The data used by Angell and Pack were obtained from observations made at Wallop's Island, Virginia during January 1960. The instrumentation and observational errors are discussed to some extent by those engaged in both programs. Although these errors are a part of the computed variability of the winds, no effort will be made here to assess or to remove the errors.

A complete summary of the Project Prairie Grass including details of the bivanes, data reduction, and computational procedures has been published.⁽²⁷⁻²⁹⁾ Stewart et al.⁽³⁰⁾ at Iowa State University made the necessary computations.

In the Prairie Grass investigation, there were five fast-response bivane anemometers oriented along or perpendicular to the prevailing horizontal winds. The instruments were placed two meters above the ground at selected distances apart. The observation time was generally about 20 minutes.

The data ensembles have already been processed and statistical parameters computed, tabulated, and published in the above report. The parameters computed are those for which normality of distribution is known or assumed. The results of this paper are based upon the assumption of normality, i.e., the distribution is Gaussian. Any deviation from normality in data would, of course, vitiate the results; however, these data are used to illustrate the procedures which, in themselves, are valid.

Data Processing and Tabulation

Computations of the Project Prairie Grass bivariate data⁽²⁸⁾ were made with reference to the east-west, north-south, and vertical axes, x , y and z , respectively. Electronic computers were used to provide the mean azimuth angle in degrees from north and the mean elevation angle of the wind where a minus value of the elevation angle indicates a mean downward flow of air past the bivariate.

Haugen (Reference 28, Table 17.2, pp. 140-144) gives the run number, the anemometer number, the elevation angle, the azimuth angle, and estimates of standard deviations of the components along the mean vector wind, s_u ; at right angles to the vector mean wind and parallel to the ground, s_v ; and perpendicular to both the axes, s_w . Table 17.3, pp. 145-150, of the same report, provides the necessary covariance estimates of the u , v , and w components. The variance estimates of the u , v , and w components are obtained by squaring the standard deviations given in Table 17.2. Two hundred sets of velocity data in units of meters per second (mps) are provided by Haugen.⁽²⁸⁾ One hundred and eighty of these have been processed for this study. Angell and Pack,⁽¹⁾ using Wallop's Island tetron data, provide seven sets of measurements in knots (kt), but these have been converted to mps to conform to Haugen's data.

In the Wallop's Island data there is no actual direction given because of the procedures of observation. The radial axis (V_r) is oriented approximately downstream, the transverse axis (V_0) is oriented at right angles to the (V_r) axis and the vertical w -axis is oriented at right angles to the (V_r) and (V_0) axes.

One hundred and eighty sets of data are too many to show in this paper. Therefore, only five sets of Haugen's data and four sets of Angell and Pack's data, which appeared to exhibit ellipsoidal characteristics are shown. These are illustrated in Tables 28 and 29, respectively.

Table 28

Project Prairie Grass bivane wind data extracted from Project Prairie Grass Vol. III edited by Haugen⁽²⁸⁾ and used with permission of the Air Force Geophysical Research Directorate. The units are degrees and m/sec. E is the elevation angle, A is the azimuth angle in degrees from north, $\bar{u}$ is the three-dimensional vector mean wind and the s_u , s_v and s_w are the estimates of the standard deviations of the wind components along the u, v and w orthogonal axes, with the v axis parallel to the earth's surface.

Run No.	E	A	$\bar{u}$	s_u	s_v	s_w
5.3	-6.5	169.9	5.557	1.17	1.23	0.433
10.1	-0.9	205.6	5.962	2.18	1.76	0.556
23.1	-11.6	122.9	6.270	1.15	0.745	0.519
56.1	-6.2	156.4	4.673	0.735	0.694	0.400
58.1	-7.3	177.4	2.330	0.234	0.207	0.133

Table 29

Wallop's Island tetron wind data obtained from Table 5 of Angell and Pack's report⁽¹⁾ and used by permission of the U.S. Weather Bureau. $\bar{H}$ is height in meters; $\bar{V}_r$ is radial velocity; $\bar{V}_\theta$ is transversal velocity; and $\bar{w}$ is vertical velocity, statistics. The overbar indicates a mean. The s is the estimate of the standard deviation. Velocity is m/sec.

Run No.	$\bar{H}$	$\bar{V}_r$	$\bar{V}_\theta$	$\bar{w}$	s_r	s	s_w
1*	1323	16.68	1.70	0.10	1.85	4.68	1.49
1**	991	16.58	1.24	0.00	0.93	4.32	0.93
3	914	8.80	0.67	0.00	0.21	0.26	0.57
8	856	0.98	1.13	0.00	0.88	0.51	0.10

*Data obtained by 584 Mod II radar

**Data obtained by FPS 16 radar

Equation (4) requires that the data be centered on the mean of the distribution, and this is exactly what is provided by Haugen⁽²⁸⁾ and by Angell and Pack.⁽¹⁾ The above data now form the required input for the IBM 704 computer programs at the Argonne National Laboratory to obtain the required three-dimensional parameters. Although all sets have been

processed, the eigenvalues and eigenvectors for only the runs shown in Tables 28 and 29 will be shown.

The covariance matrix, σ_{ij} , the inverse of which is shown in Equation (4) may be transformed into an eigenvalue matrix. The eigenvalue estimates may be obtained by solving the following determinant of the covariance matrix estimates

$$\begin{vmatrix} s_{11} - k & s_{12} & s_{13} \\ s_{21} & s_{22} - k & s_{23} \\ s_{31} & s_{32} & s_{33} - k \end{vmatrix} \equiv 0 \quad (5)$$

where s_{ij} are estimates of the variances if $i = j$ and covariances if $i \neq j$. The roots of the resulting cubic equation are the eigenvalues and represent the variances along the major and two minor axes of the ellipsoid. These are sometimes called latent roots or characteristic roots. The center of the ellipsoid is displaced from the origin and is located at the head of the mean wind vector. The eigenvectors then provide the necessary information for the location of the major and minor axes. Reference may be made to Lanczos⁽³¹⁾ for matrix solution techniques. In the solution of Equation (5), the roots, k_1 , k_2 and k_3 are real and positive; hence, $k_1 \geq k_2 \geq k_3 \geq 0$.

Table 30 gives the estimates of the covariance matrices, the eigenvalues, their square roots and the eigenvectors corresponding to the eigenvalues and original axes of the Prairie Grass and Wallop's Island data.

The three computed eigenvectors provide the direction numbers or direction cosines of the major and two minor axes of the ellipsoid ordinarily referred to as a , b and c . The center of each ellipsoid is located at the head of the respective vector mean wind which is given in Table 28. The eigenvectors, therefore, show the orientation of the ellipsoidal axes rotating on the distribution centroid and the eigenvalues are a measure of the variance of the wind components along these axes. The correlations among the wind components along these axes are zero.

The sum of the diagonal elements of a matrix is called the trace. In the covariance matrix representing the wind components the trace represents the vector variance, i.e.,

$$s_{11} + s_{22} + s_{33} = s_x^2 + s_y^2 + s_z^2 = s_u^2 + s_v^2 + s_z^2$$

In a transformation representing a rotation of the coordinate axes, the trace remains invariant.

Table 30

Covariances, eigenvalues (e), square roots of eigenvalues ($e^{1/2}$), and eigenvector matrices for selected runs of winds at O'Neill, Nebraska, and Wallop's Island, Virginia.

Run No.	Covariance matrix			Eigenvalue		Eigenvectors		
				e	$e^{1/2}$			
5.3	1.3689	0.3990	-0.1380	1.851	1.366	0.6457	0.7618	-0.0532
		1.5129	0.0014	1.049	1.024	0.7528	-0.6467	-0.1231
			0.1874	0.1796	0.424	0.1282	-0.0394	0.9910
10.1	4.7524	-0.374	-0.174	4.834	2.200	0.9768	-0.2105	-0.0391
		3.0976	0.0349	3.017	1.737	0.2106	0.9776	-0.0009
			0.3091	0.302	0.550	0.0385	-0.0073	0.9992
23.1	1.3225	-0.0213	-0.2210	1.3676	1.1694	0.9800	-0.0267	-0.1973
		0.5550	0.0043	0.5544	0.7446	0.0262	0.9996	-0.0053
			0.2694	0.2249	0.4742	0.1974	0.0001	0.9803
56.1	0.54025	-0.0726	-0.0349	0.5933	0.7703	0.8249	-0.5569	-0.0971
		0.4816	0.0239	0.4326	0.6576	0.5596	+0.8289	0.0010
			0.1600	0.1559	0.3948	0.0799	-0.0552	0.9953
58.1	0.0548	-0.0037	-0.0122	0.0590	0.2430	0.9423	-0.1948	-0.2728
		0.0428	-0.0011	0.0424	0.2058	0.1653	0.9783	-0.1257
			0.0177	0.0139	0.1178	0.2912	0.0733	0.9538
1*	3.4346	-1.3675	-0.0451	22.0505	4.6958	0.0732	-0.9972	0.0140
		21.9462	-0.2809	3.3380	1.8270	0.9956	0.0723	-0.0588
			2.288	2.2211	1.4903	0.0576	0.0182	0.9982
1**	0.8587	-0.9726	-0.1908	18.7547	4.3307	0.0541	-0.9985	0.0108
		18.6997	-0.2041	1.0344	1.0171	0.6609	0.0277	-0.7499
			0.8587	0.6280	0.7925	0.7485	0.0476	0.6614
3	0.0424	-0.0132	-0.0212	0.3227	0.5680	-0.0736	-0.0374	0.9966
		0.0663	-0.0106	0.0722	0.2686	-0.4080	0.9130	0.0041
			0.3207	0.0346	0.186	-0.9100	-0.4063	-0.0825
8	0.7659	-0.1299	0.0000	0.7976	0.8931	0.9715	-0.2370	0.0000
		0.2650	0.0000	0.2331	0.4830	0.2370	0.9715	0.0000
			0.0106	0.0106	0.1030	0.0000	0.0000	1.0000

*Data obtained by 584 Mod II radar.

**Data obtained by FPS 16 radar.

Figure 68 is a schematic three-dimensional wind distribution where the variances are equal and the covariances are zero. This would be an illustration of an isotropic distribution in the main wind stream for the period under examination. Figure 69 is a schematic illustration of the axisymmetric case where the covariances are equal to zero. Here one of the ellipsoidal axes is collinear with the vector mean wind. The association of symmetry and axisymmetry is discussed by Batchelor⁽³²⁾ in his excellent treatise on homogeneous turbulence.

Figure 68

Spherical vector standard deviation wind rose in three dimensions. The centroid of the distribution is at the head of the vector mean wind, V . The distribution is isotropic.

Figure 69

Vector standard deviation wind rose in three dimensions. This illustrates the axisymmetric case where one of the principal axes is oriented along the vector mean wind.

Construction of Wind Roses (Ellipsoids)

Bravais,⁽³⁾ as indicated by Czuber,⁽⁵⁾ gave the equation for the construction of specified probability ellipsoids. As indicated previously, the chi-square tables with three degrees of freedom may be used for three-dimensional probability distributions.

Table 31 has been abridged from Tables of the Fractiles of the chi-square distribution of Hald.(33) The chi-square value for the 0.90 probability ellipsoid with three degrees of freedom is 6.25. The chi value is 2.50. The standard deviation of the components along each axis multiplied by the value 2.5 provide the lengths of the semi-axes of the 0.90 probability ellipsoid, i.e., the ellipsoid which contains 90% of the observations. If the semi-axes are taken equal to the respective standard deviations, that is, with chi and chi-square values equal to one, the 0.20 probability ellipsoid is obtained. If the semi-axes are equal $\sqrt{3}$ times the standard deviations, the ellipsoid will be the 0.608 probability ellipsoid. The vector radius of the ellipsoid which is the square root of the trace of the eigenvalue matrix may be called the vector standard deviation. The term standard vector deviation for the two-dimensional case is due to Brooks⁽¹⁵⁾ and was modified to the vector standard deviation by Crutcher.^(34,35)

Table 31

Fractiles of the χ^2 distribution*

Degrees of freedom	Probability in per cent								
	1	5	10	20	50	70	90	95	99
1	0.000157	0.00393	0.0158	0.0642	0.459	1.07	2.71	3.84	6.63
2	0.0201	0.103	0.211	0.446	1.39	2.41	4.61	5.99	9.21
3	0.115	0.352	0.584	1.00	2.37	3.67	6.25	7.81	11.3

*Abridged from Hald⁽³³⁾ with the permission of the publishers.

Construction of ellipsoids may proceed as follows, where the data of run 5.3, Table 30, are used for illustration:

1) Begin at the end point of the vector mean (the centroid) positioned by E, A and $\bar{u}$, respectively, -6.5° , 169.9° and 5.557 mps. The eigenvector values are now used. From the centroid proceed along the u-axis an arbitrarily chosen scale distance of 0.6457, then parallel to the v-axis, 0.7618 and then downward parallel to the w-axis, 0.0532. This will locate the major axis of the ellipsoid. The next eigenvector will locate the next largest axis of the ellipsoid, the third eigenvector will locate the smallest of the ellipsoidal axes.

2) From Table 31 let us choose, for example, to construct the 20 per cent ellipsoid, that is, the ellipsoid which will contain 20 per cent of the end points of the three-dimensional wind vectors. In the chi-square table, Table 31, under the 20 per cent probability with three degrees of freedom, the value of 1.00 is taken. Therefore, an ellipsoid with axes equal to the square roots of the eigenvalues (standard deviations) along the respective axes constructed as in the above paragraph will contain 20 per cent of the wind vectors. Figure 70 is an example of a trivariate distribution of the wind vector positions.

Figure 70

Vector standard deviation wind rose in three dimensions

Mauchly⁽³⁹⁾ using Neyman and Pearson's⁽⁴⁰⁾ likelihood ratio criterion arrives at a significance test which may be applied to a trivariate normal distribution. Mauchly's expression for a sphericity criterion, L , may be written as

$$P = (1/2) (L)^{N-4} [(N-2) - (N-4) (L)^2] \quad (6)$$

where P is the probability of obtaining a value less than L and N is the number of observations.

$$L = |s_{ij}|^{1/2} / s_0^{3/2} \quad (7)$$

where $|s_{ij}|$ is the determinant of the covariance matrix, s_{ij} , and s_0 is defined as the trace of the covariance matrix divided by 3 in the three-dimensional case.

The range of the probability is from one to zero with one for a sphere and zero for complete lack of sphericity. As the computed probability departs from a value of one, the less the sphericity the greater the ellipsoidality. The test is made on the hypothesis that the distribution is

For many problems, probability spheres centered on the distribution mean are required. Hotelling⁽³⁶⁾ discusses this problem. Solomon⁽³⁷⁾ and Owens⁽³⁸⁾ provide tables whereby spheres may be constructed which will contain specified probabilities of the ellipsoidal distributions. The problem of determining the probability content of an offset sphere or ellipsoid is beyond the scope of this present paper.

Tests for Sphericity

The question arises as to whether sampling error may have produced an apparent ellipsoidal distribution when the population from which the sample was taken was in reality spherical. Wilks⁽¹²⁾ provides a discussion of the tests of sphericity and symmetry.

spherical. The test may be made at the 0.05 level. If a computed probability is greater than 0.05, the hypothesis will not be rejected. If the computed probability is equal to or less than 0.05, say 0.03, the hypothesis will be rejected, and the distribution will be termed ellipsoidal.

A test is now made of data given in Table 30. For this test, the number of observations is needed. Reference to Haugen⁽²⁸⁾ indicates that about 1130 observations were available for each run of the Project Prairie Grass data. The trace of s_0 in run 5.3 is $1.851 + 1.049 + 0.1796$ or 3.0796 . This quantity, when divided by 3 and raised to the $3/2$ power becomes 1.0400. The determinant is $(1.851)(1.049)(0.1769)$ or 0.348729 and its square root is 0.5905. L of Equation 6 then equals $0.5905/1.0400$ or 0.568. Solution of Equation 6 with L equal to 0.568 leads to an infinitesimal probability that a distribution more ellipsoidal than the sample used would occur. The hypothesis of sphericity is therefore rejected. That this was an expected conclusion is noted when comparison of the square roots of three eigenvalues, 1.366, 1.024, and 0.429 is made. The distribution is distinctly disc shaped, for the eigenvalues are in the ratio of 3:2.5:1.

Since the question of serial correlation may be raised, it is assumed that the effective number of observations is a function of the lag (auto) correlation published by Haugen (Reference 28, Table 17.5 p. 156). It is noted that the correlation of the u components does not fall to zero in 60 observations. It is also noted that for a nearby anemometer, #4, the autocorrelation goes to zero at the 46th lag. Arbitrarily, $N = 65$ is taken for the determination of a representative divisor to obtain an effective number of random observations. Such a procedure has been suggested by Wilson⁽⁴¹⁾ and parallels that suggested by Brooks et al. (Reference 42, p. 234). The division of the total number 1130 by 65 gives an effective number for N of about 18. The value obtained for the probability in Equation 6 obtained by using $N = 18$ is then about 2×10^{-3} . This still is such a small probability that it is not likely to be exceeded many times by chance.

Table 32 gives, for each of the runs in Table 30, the probabilities of a distribution being more ellipsoidal than the ones shown.

Table 32
Probabilities of a distribution occurring which is more ellipsoidal than the sample used

Run No	$ S_{ij} $	$ S_{ij} ^{1/2}$	Trace/3	$S_0^{3/2}$	L	N	Eff $N^{\dagger}$	P
5.3	0.3487	0.5905	1.0265	1.0400	0.568	1130	18	2×10^{-3}
10.1	4.4045	2.0984	2.7177	4.4810	0.468	1130	18	2×10^{-4}
23.1	0.1705	0.4129	0.7156	0.6053	0.6821	1130	43	4×10^{-6}
56.1	0.0400	0.2000	0.3973	0.2550	0.7843	1130	18	12×10^{-2}
58.1	0.000035	0.0059	0.0384	0.0077	0.7662	1130	18	9×10^{-2}
1	163.4831	12.786	9.2032	27.9200	0.4580	150	≈ 30	10^{-7}
1**	12.1831	3.490	6.8057	17.7540	0.1966	150	≈ 30	10^{-10}
3	0.00081	0.0283	0.1432	0.0542	0.5221	600	≈ 150	10^{-10}
8	0.00197	0.0444	0.3471	0.2045	0.2171	170	≈ 34	10^{-10}

* Data obtained by 584 Mod II radar.

Data obtained by FPS 16 radar.

[†] Effective N is the N divided by the lag of the autocorrelation where the autocorrelation goes to zero. This was obtained by scanning autocorrelation tables given by Haugen (28). In the case of runs 1, 1*, 3 and 8 from Angell and Pack's data (Reference 1, Table 2, p. 23), the predominant periods of approximate vector oscillations were used as divisors.

It was expected that the results of the sphericity tests would indicate the rejection of the hypothesis that the data were spherically distributed. One might claim that usually this is the case. However, it is desired here to set forth the procedures by which the hypothesis is tested. One hundred and eighty cases were computed of which 9 were selected for the test. These were selected after an examination of the eigenvalues and eigenvectors indicated a possibly large rotation of axes. Examination of others might not indicate the rejection of the hypothesis. In examining Table 32, a first look may be made at the sphericity statistic, L .

A low value of this statistic is an indication of an ellipsoid. Only if the statistic is near one is there a chance that with large N the hypothesis will not be rejected. The probability values have been computed. Some are very small. If they were smaller than 10^{-10} , the value of 10^{-10} was entered in column 9 of Table 32.

Further examination of Table 32 indicates that the data of runs 56.1 and 58.1 offer some indication of isotropy. The Mauchly sphericity test for these data using an effective number of observations rather than the total number of observations provides a probability value of 12×10^{-2} and 9×10^{-2} , respectively. This means that there is about one chance in 10 that a more ellipsoidal distribution would have been obtained. At the 95 per cent level of significance, the hypothesis of sphericity would not be rejected for the data are significant at the 0.88 and 0.91 probability level. It will be noted here that the eigenvalues (variances) are approximately in the ratio of 4:3:1, while the standard deviations are in approximate ratios of 2:2:1. If the above hypothesis is not rejected, then a sphere could be drawn which would represent the distributions.

A quick check for the sphericity of a three-dimensional distribution may be made from a graph based on Equation 6 as shown in Figure 71.

Figure 71

Test of trivariate sphericity of Project Prairie Grass wind data (Probability level, 0.95)

On this chart, the abscissa represents the ratio of the largest to the smallest and the ordinate represents the ratio of the intermediate to the smallest eigenvalues. Assuming a probability level of significance of 0.95, curves for $N = 10, 20$ and 100 were drawn, separating the plane into areas where the hypothesis of sphericity may or may not be rejected. If $N = 20$, then points to the left of the $N = 20$ curve represent runs where the distributions may be considered spherical.

To illustrate the use of this chart on a specific example, let us examine Run 56.1 of Table 30, where the eigenvalues are in the ratios of 3.8:2.8:1, and the effective N is taken as 18. The plot of this run is designated by a heavy black dot in Figure 71. Although the $N = 18$ curve was not drawn, it is readily seen that this point would fall to the left of the curve and would thus represent a wind distribution which could not be considered ellipsoidal at the 0.95 probability level of significance.

The eigenvalue ratios for the 180 sets of data used in this study are plotted in Figure 71. The effective number of observations has not been computed for each set. However, an effective number of 20 or more is expected to fit most sets owing to the time correlations in the data presented by Haugen.⁽²⁸⁾ Examination of Figure 71 reveals that about 9 per cent of the sets indicate the nonrejection of the hypothesis of spherical distribution.

Summary

The development and application of three-dimensional (trivariate normal) statistics to the problem of three-dimensional wind data have been discussed. As indicated previously, the trivariate normal distribution is a chi-square distribution with three degrees of freedom. When the covariance matrix associated with the trivariate normal distribution is transformed to the eigenvalue and eigenvector matrices, eigenvectors may be used to determine the axes of the wind distribution centered on the vector mean wind and the eigenvalues, with appropriate multipliers obtained from chi-square tables, may be used to construct any desired probability ellipsoid centered on this mean wind vector. Application to diffusion problems are indicated.

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AN EVALUATION OF WIND PROFILE LAWS BY LEAST SQUARES TECHNIQUES

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Introduction

Physical interpretation and mathematical representation of wind profiles, in the atmosphere's frictional boundary layer near the surface of the earth, are complex problems which have long challenged meteorologists. Although it is generally accepted that the logarithmic law adequately describes the wind profile near the ground under near neutral conditions, no one has formulated a law which satisfactorily describes the wind profile under nonadiabatic or diabatic conditions. Much research has been performed and several profile laws have been proposed and studied; however, only a few have achieved widespread recognition and usage.

The problem of the present investigation is to take the most generally accepted laws and study their application using a control set of data for comparison. The roles played by atmospheric stability and wind speed in shaping these wind profiles will also be investigated. A carefully conducted series of observations taken at the Argonne National Laboratory in conjunction with an atmospheric radon study, conducted in the summer of 1960, is used as the control data.

Wind Profile Laws

Four wind profile laws are included in this investigation. Three of these laws may be loosely considered as classical laws because they are presented and discussed in recognized standard meteorological textbooks of several years' standing. This group of profile laws includes the power law, logarithmic law and Deacon's law. The fourth profile law selected, the log plus linear law, was proposed in 1954 by the Russian meteorologists, Monin and Obukhov⁽¹⁾ and earlier by Halstead.⁽²⁾ This particular presentation has been widely considered in subsequent profile investigations and deserves attention in the current investigation.

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For convenience, each of the four profile laws to be studied is listed here in sequence using consistent notation:

$$\text{Power Law: } \bar{u} = cz^p \quad (1)$$

$$\text{Logarithmic Law: } \bar{u} = \frac{u_*}{k} \ln \left(\frac{z}{z_0} \right) \quad (2)$$

$$\text{Deacon's Law: } \bar{u} = \frac{u_*}{k(1-\beta)} \left[\left(\frac{z}{z_0} \right)^{1-\beta} - 1 \right] \quad (3)$$

$$\text{Log plus Linear Law: } \bar{u} = \frac{u_*}{k} \left[\ln \left(\frac{z}{z_0} \right) + \alpha \left(\frac{z}{L} \right) \right] \quad (4)$$

In the equations, $\bar{u}$ is the average wind speed at the level, z , to be investigated; u_* is the friction or dynamic velocity and equal to $\sqrt{\tau/\rho}$ where τ is the shearing stress and ρ the density; z_0 is the roughness parameter; k is the von Karman constant; p is the power law parameter; β is Deacon's parameter; α is Monin and Obukhov's "constant" (originally referred to as β in their 1954 paper); and L is a length characteristic of the atmospheric ground layer and is called the height of the substrate of dynamic turbulence.

Argonne Measurements

Wind profile data were taken during the summer of 1960 between 8 June and 5 August. Observations of wind, temperature and radon were measured using a specially-prepared, portable 16.5-meter tower with sensing devices located at 0.5, 1, 2, 4, 8 and 16 meters above ground. The terrain around the tower is gently rolling with open terrain in the immediate vicinity of the tower. Measurements of wind speed were made using sensitive, individually calibrated cup anemometers manufactured by the C. F. Casella and Company, Ltd., of London. Temperature differences between the significant levels were measured by using copper-constantan thermopile pairs. Each thermopile consisted of six thermocouple junctions imbedded in paraffin filling the last two centimeters of the enclosing Pyrex tube, 8 mm in diameter and 5 cm long. Ambient temperature was measured by a mercury-in-glass thermometer. Twenty-minute averages of temperatures and wind were used for this investigation. A detailed description of the site, instrumentation, and its calibration has been reported by Pearson and Moses.⁽³⁾

Nine series of profile runs were taken with 13 to 18 runs at 90-minute intervals in each series. The profiles were taken under a variety of summer meteorological conditions. Calculations of the profile

parameters were made using Argonne's IBM 704 computer. Wind and temperature data used in this study are presented in Table 33 (a-i).*

Table 33a

Wind speed (U) and temperature (T) measurements, Series 100, June 8-9, 1960

Run No.	Height	0.5 m		1.0 m		2.0 m		4.0 m		8.0 m		16.0 m	
	Time, CST	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C
101	1130	3.08	23.35	3.57	22.78	3.98	22.30	4.36	21.87	4.76	21.63	5.18	21.39
102	1300	3.54	23.35	4.16	22.78	4.70	22.30	5.18	21.88	5.62	21.68	5.96	21.47
103	1430	3.38	23.00	3.98	22.50	4.47	22.09	4.94	21.67	5.42	21.45	5.94	21.19
104	1600	3.29	21.91	3.87	21.67	4.30	21.52	4.73	21.29	5.23	21.13	5.80	20.94
105	1730	2.63	20.38	3.12	20.39	3.52	20.44	3.91	20.42	4.38	20.40	4.93	20.34
106	1900	1.49	10.72	1.82	11.22	2.12	11.75	2.47	12.13	2.83	12.35	3.40	12.48
107	2030	1.10	7.98	1.53	8.89	1.93	10.06	2.41	11.00	2.88	11.56	3.46	11.90
108	2200	1.49	7.45	1.87	7.94	2.26	8.55	2.80	9.23	3.37	9.80	3.93	10.19
109	2330	1.37	7.31	1.69	7.72	2.07	8.27	2.62	8.94	3.26	9.57	3.81	10.02
110	0100	0.97	7.25	1.21	7.94	1.37	8.62	1.68	9.14	2.10	9.55	2.87	9.98
111	0230	1.20	10.12	1.68	11.00	2.18	12.47	2.47	13.03	2.81	13.41	3.41	13.96
112	0400	0.91	7.36	1.25	8.50	1.51	9.97	1.92	11.21	2.32	12.32	2.87	13.63
113	0530	0.98	12.55	1.22	12.67	1.45	12.95	1.80	13.26	2.12	13.64	2.53	14.34
114	0700	1.92	18.61	2.20	18.44	2.44	18.29	2.69	18.10	2.89	17.89	3.02	17.70
115	0830	3.07	20.63	3.49	20.33	3.91	20.02	4.39	19.71	4.90	19.40	5.22	19.15
116	1000	2.91	15.48	3.32	15.00	3.73	14.52	4.17	14.09	4.55	13.77	4.86	13.52
117	1130	2.50	14.66	2.88	14.00	3.22	13.44	3.53	12.92	3.86	12.58	4.16	12.31

Table 33b

Wind speed (U) and temperature (T) measurements, Series 200, June 15-16, 1960

Run No.	Height	0.5 m		1.0 m		2.0 m		4.0 m		8.0 m		16.0 m	
	Time, CST	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C
201	1100	4.16	25.30	4.93	25.00	5.67	24.77	6.42	24.48	-	24.34	7.68	24.15
202	1230	-	24.60	5.24	24.44	6.06	24.33	6.88	24.16	7.46	24.08	8.27	23.96
203	1400	4.64	26.04	5.46	25.83	6.33	25.68	7.24	25.47	7.90	25.37	8.93	25.19
204	1530	4.35	27.23	5.14	27.11	5.97	27.05	6.76	26.90	7.43	26.84	8.28	26.74
205	1700	2.35	23.31	2.80	23.44	3.26	23.77	3.77	24.04	4.25	24.25	4.93	24.38
206	1830	2.27	22.70	2.70	22.89	3.10	23.09	3.53	23.25	3.94	23.40	4.55	23.53
207	2000	1.13	22.37	1.39	22.72	1.65	23.09	2.15	23.49	2.62	23.88	3.30	24.17
208	2130	1.18	20.79	1.45	21.17	1.73	21.60	2.24	22.02	2.71	22.43	3.33	22.72
209	2300	1.51	19.79	1.85	20.11	2.17	20.43	2.58	20.71	3.02	20.98	3.60	21.20
210	0030	1.19	17.70	1.40	18.06	1.69	18.39	2.06	18.67	2.39	18.90	2.89	19.04
211	0200	1.83	17.66	2.17	17.89	2.48	18.10	2.88	18.28	3.22	18.43	3.80	18.56
212	0330	2.00	18.17	2.33	18.33	2.65	18.47	3.01	18.58	3.40	18.68	4.02	18.74
213	0500	3.16	18.20	3.71	18.33	4.36	18.45	4.92	18.54	5.48	18.60	6.22	18.61
214	0630	3.69	20.11	4.26	20.17	4.83	20.22	5.59	20.25	6.18	20.26	6.88	20.24
215	0800	3.78	18.63	4.39	18.89	5.07	19.31	5.84	19.23	6.48	19.04	7.20	19.04
216	0930	3.51	20.49	4.13	20.39	4.74	20.66	5.36	20.52	5.84	20.54	6.50	20.26
217	1100	3.40	22.78	3.97	22.67	4.53	22.56	5.16	22.42	5.66	22.30	6.29	22.16

*Profiles 201, 202, 302, 303, 412, 508, 604, 608, 609, 805, 806, 809, 901, and 902 are partially or entirely omitted in the study because of missing or incorrect data or errors in the machine calculations.

Table 33c

Wind speed (U) and temperature (T) measurements, Series 300, June 23-24, 1960

Run No.	Height	0.5 m		1.0 m		2.0 m		4.0 m		8.0 m		16.0 m	
	Time, CST	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C
301	0900	5.84	21.22	6.80	21.22	7.96	21.22	8.70	21.18	9.54	21.12	10.89	21.04
302	1030	2.05	23.36	2.84	22.78	3.57	22.30	4.18	21.78	4.67	21.60	-	21.36
303	1200	6.40	22.17	7.54	22.11	8.71	22.04	9.76	21.96	10.84	21.87	11.97	21.75
304	1330	5.53	25.39	6.50	25.11	7.46	24.85	8.33	24.57	9.08	24.42	9.92	24.19
305	1500	4.88	25.06	5.76	25.00	6.63	24.96	7.48	24.88	8.11	24.82	9.06	24.72
306	1630	3.97	23.99	4.71	24.06	5.38	24.12	6.04	24.15	6.57	24.17	7.39	24.16
307	1800	4.76	23.87	5.67	23.94	6.51	24.02	7.30	24.07	7.92	24.10	8.73	24.09
308	1930	2.93	22.93	3.54	23.06	4.07	23.17	4.79	23.28	5.16	23.36	5.92	23.42
309	2100	2.88	19.06	3.50	19.33	4.11	19.59	4.67	19.85	5.20	20.05	5.96	20.24
310	2230	2.19	16.41	2.67	16.72	3.08	17.03	3.50	17.32	4.05	17.57	4.83	17.84
311	0000	2.46	15.28	3.00	15.56	3.52	15.81	3.99	16.05	4.52	16.27	5.48	16.51
312	0130	2.22	14.64	2.70	14.89	3.15	15.13	3.61	15.36	4.15	15.54	4.99	15.72
313	0300	2.97	14.34	3.65	14.56	4.23	14.76	4.78	14.97	5.41	15.14	6.14	15.27
314	0430	2.57	13.70	3.16	13.89	3.67	14.05	4.14	14.20	4.64	14.32	5.19	14.38
315	0600	3.17	14.86	3.84	14.89	4.46	14.86	5.00	14.83	5.48	14.81	5.94	14.77
316	0730	3.47	17.05	4.18	16.94	4.83	16.70	5.46	16.44	6.00	16.20	6.56	15.95
317	0900	3.80	18.73	4.54	18.50	5.25	18.14	5.86	17.77	6.42	17.46	7.01	17.15

Table 33d

Wind speed (U) and temperature (T) measurements, Series 400, June 30-July 1, 1960

Run No.	Height	0.5 m		1.0 m		2.0 m		4.0 m		8.0 m		16.0 m	
	Time, CST	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C
401	1530	1.98	19.67	2.46	19.72	2.85	19.78	3.22	19.80	3.67	19.81	4.11	19.80
402	1700	2.18	17.84	2.70	17.89	3.08	17.92	3.44	17.92	3.84	17.91	4.14	17.87
403	1830	2.00	17.78	2.51	17.89	2.90	17.99	3.27	18.04	3.63	18.09	3.90	18.10
404	2000	1.96	16.03	2.43	16.00	2.78	15.98	3.19	15.95	3.68	15.94	4.25	15.90
405	2130	2.53	15.03	3.16	15.11	3.67	15.18	4.19	15.26	4.87	15.34	5.39	15.37
406	2300	1.99	14.77	2.46	14.83	2.82	14.87	3.17	14.91	3.56	14.94	3.89	14.94
407	0030	1.62	14.94	2.03	15.00	2.31	15.04	2.64	15.08	3.07	15.12	3.44	15.13
408	0200	1.40	14.49	1.73	14.56	1.96	14.58	2.28	14.62	2.70	14.66	3.15	14.69
409	0330	1.71	14.10	2.16	14.17	2.50	14.22	2.88	14.25	3.31	14.29	3.70	14.30
410	0500	1.14	14.24	1.44	14.33	1.63	14.41	1.98	14.48	2.59	14.56	2.82	14.63
411	0630	1.84	14.99	2.25	15.00	2.55	15.00	2.87	14.98	3.34	14.95	3.83	14.90
412	0800	2.70	18.61	3.47	18.33	3.81	18.04	-	17.76	4.65	17.43	5.07	17.12
413	0930	2.86	21.53	3.74	21.22	4.05	20.86	4.51	20.49	5.29	20.07	5.48	19.73
414	1100	2.16	22.69	2.71	22.22	3.03	21.80	3.32	21.40	3.63	21.11	3.84	20.87
415	1230	1.66	23.44	2.02	22.89	2.24	22.52	2.43	22.14	2.68	21.95	2.83	21.80

Table 33e

Wind speed (U) and temperature (T) measurements, Series 500, July 7-8, 1960

Run No.	Height	0.5 m		1.0 m		2.0 m		4.0 m		8.0 m		16.0 m	
	Time, CST	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C
501	0930	1.72	23.24	1.90	23.06	2.05	22.75	2.27	22.37	2.40	22.01	2.54	21.69
502	1100	1.73	26.20	1.91	25.83	2.04	25.45	2.30	24.96	2.56	24.74	2.75	24.50
503	1230	1.43	26.30	1.58	26.00	1.69	25.68	1.88	25.31	2.08	25.13	2.19	25.00
504	1400	1.99	27.23	2.23	26.83	2.42	26.46	2.70	25.97	3.00	25.74	3.27	25.53
505	1530	1.30	27.80	1.43	27.50	1.52	27.26	1.72	26.82	1.87	26.62	1.95	26.41
506	1700	1.32	26.34	1.50	26.28	1.61	26.20	1.88	25.98	2.13	25.88	2.36	25.74
507	1830	0.34	22.86	0.75	23.39	0.41	23.87	0.41	24.18	0.49	24.32	0.67	24.57
508	2000	0.39	-	0.53	-	0.27	-	0.38	-	0.88	-	1.21	-
509	2130	0.42	15.31	0.62	17.00	0.40	17.99	0.90	18.90	1.61	19.97	2.38	20.63
510	2300	0.80	15.97	1.05	16.72	1.34	17.50	1.92	18.44	2.56	19.39	3.29	19.99
511	0030	1.39	15.95	1.70	16.61	2.10	17.47	2.61	18.25	3.08	18.80	3.56	19.10
512	0200	0.96	13.93	1.24	14.56	1.61	15.33	2.25	16.13	2.90	16.85	3.79	17.45
513	0330	0.74	13.22	1.05	14.06	1.38	15.04	1.97	15.95	2.61	16.71	3.74	17.55
514	0500	1.13	15.70	1.31	16.11	1.70	16.64	2.20	17.20	2.81	17.75	3.76	18.21
515	0630	1.78	18.93	2.00	18.89	2.22	18.83	2.47	18.72	2.63	18.55	2.77	18.37
516	0800	2.04	23.70	2.29	23.50	2.51	23.31	2.72	23.09	2.90	22.85	3.03	22.59
517	0930	2.37	25.33	2.66	25.00	2.95	24.71	3.24	24.37	3.47	24.09	3.62	23.81

Table 33f

Wind speed (U) and temperature (T) measurements Series 600 July 14-15 1960

Run No	Height	0.5 m		1.0 m		2.0 m		4.0 m		8.0 m		16.0 m	
	Time CST	U m/sec	T °C	U m/sec	T °C	U m/sec	T °C	U m/sec	T °C	U m/sec	T °C	U m/sec	T °C
601	1630	1.64	22.22	1.95	21.94	2.12	21.73	2.32	21.47	2.59	21.23	2.79	21.01
602	1800	1.36	20.67	1.65	20.72	1.82	20.75	2.07	20.73	2.31	20.67	2.55	20.59
603	1930	0.84	15.30	1.14	16.61	1.27	17.09	1.50	17.39	1.79	17.60	2.24	17.77
604	2100	0.35	13.37	-	14.50	1.29	15.08	2.07	15.52	2.32	15.88	2.74	16.18
605	2230	0.69	11.45	0.97	12.83	1.17	13.43	1.47	13.81	1.82	14.08	2.47	14.43
606	0000	0.77	12.19	1.09	13.43	1.25	13.83	1.60	14.24	2.04	14.59	2.63	14.89
607	0130	0.43	10.58	0.58	11.94	0.52	12.96	0.82	13.93	1.17	14.70	1.83	15.17
608	0300	-	-	-	-	-	-	-	-	-	-	9.30	-
609	0430	-	-	-	-	-	-	-	-	-	-	-	-
610	0600	1.04	13.92	1.23	14.00	1.39	13.87	1.60	13.67	1.71	13.51	1.96	13.35
611	0730	0.93	17.05	1.08	17.11	1.14	17.16	1.30	17.17	1.34	17.20	1.40	17.22
612	0900	1.28	21.91	1.45	21.56	1.56	21.28	1.73	20.98	1.81	20.73	1.89	20.48
613	1030	2.19	24.33	2.56	23.89	2.86	23.50	3.09	23.07	3.26	22.87	3.47	22.64

Table 33g

Wind speed (U) and temperature (T) measurements Series 700 July 20-21 1960

Run No.	Height	0.5 m		1.0 m		2.0 m		4.0 m		8.0 m		16.0 m	
	Time CST	U m/sec	T °C	U m/sec	T °C	U m/sec	T °C	U m/sec	T °C	U m/sec	T °C	U m/sec	T °C
701	1000	2.41	26.34	2.74	25.83	3.02	25.39	3.29	25.02	3.57	24.74	3.75	24.44
702	1130	2.31	25.63	2.55	25.00	2.76	24.54	3.18	24.16	3.17	24.00	3.24	23.78
703	1300	2.14	26.56	2.41	26.00	2.65	25.57	2.89	25.14	3.06	24.93	3.26	24.70
704	1430	2.68	25.49	3.05	25.00	3.37	24.61	3.65	24.27	3.94	24.03	4.16	23.77
705	1600	2.51	24.73	2.80	24.33	2.98	24.03	3.45	23.72	3.55	23.47	3.84	23.20
706	1730	1.82	22.87	2.09	22.89	2.33	22.93	2.64	22.92	2.96	22.89	3.24	22.80
707	1900	1.13	18.90	1.37	19.28	1.60	19.68	1.96	19.95	2.35	20.13	2.83	20.22
708	2030	1.40	16.97	1.70	17.33	1.98	17.73	2.35	18.05	2.82	18.30	3.33	18.45
709	2200	1.09	15.93	1.35	16.28	1.59	16.67	1.98	17.06	2.44	17.35	3.02	17.56
710	2330	0.72	14.48	0.99	15.06	1.17	15.65	1.50	16.04	1.91	16.31	2.55	16.57
711	0100	0.69	14.79	1.03	15.44	1.01	15.82	1.19	16.06	1.53	16.29	1.87	16.62
712	0230	1.13	15.16	1.35	15.44	1.57	15.78	1.98	16.12	2.39	16.45	2.94	16.75
713	0400	0.74	14.13	0.98	14.72	1.15	15.29	1.51	15.74	1.83	16.01	2.49	16.27
714	0530	1.00	17.36	1.16	17.50	1.31	17.69	1.67	17.88	2.13	18.13	2.82	18.41
715	0700	2.17	21.34	2.41	21.22	2.61	21.12	2.86	20.95	3.07	20.72	3.27	20.49
716	0830	2.87	26.74	3.19	26.39	3.45	26.07	3.71	25.75	3.95	25.42	4.26	25.11
717	1000	3.14	29.53	3.49	29.06	3.81	28.65	4.16	28.21	4.47	27.89	4.78	27.61
718	1130	3.73	32.91	4.14	32.22	4.53	31.72	4.92	31.14	5.34	30.84	5.86	30.53

Table 33h

Wind speed (U) and temperature (T) measurements Series 800 July 28-29 1960

Run No	Height	0.5 m		1.0 m		2.0 m		4.0 m		8.0 m		16.0 m	
	Time CST	U m/sec	T °C	U m/sec	T °C	U m/sec	T °C	U m/sec	T °C	U m/sec	T °C	U m/sec	T °C
801	0900	3.08	27.36	3.49	26.94	3.86	26.58	4.18	26.16	4.48	25.84	4.78	25.48
802	1000	3.38	29.17	3.83	28.67	4.27	28.28	4.63	27.72	5.00	27.40	5.44	27.05
803	1130	3.85	30.63	4.39	30.00	4.92	29.50	5.38	28.91	5.74	28.65	6.29	28.38
804	1300	4.03	31.88	4.62	31.39	5.18	30.99	5.67	30.48	6.16	30.24	6.88	30.00
805	1430	4.49	-	5.13	-	5.76	-	6.35	-	6.90	-	7.59	-
806	1600	2.87	-	3.28	-	3.69	-	4.02	-	4.30	-	4.70	-
807	1730	1.55	23.97	1.80	24.06	2.02	24.09	2.31	24.10	2.54	24.12	2.89	24.11
808	1900	1.08	21.14	1.44	21.83	1.73	22.44	2.08	22.83	2.46	23.13	3.05	23.32
809	2030	0.78	20.21	1.46	20.67	-	21.25	3.03	21.89	2.37	22.50	3.07	22.91
810	2200	0.96	19.66	1.25	20.22	1.51	20.85	1.87	21.43	2.22	21.91	2.88	22.34
811	2330	0.44	17.37	0.74	18.33	0.73	18.88	1.10	19.50	1.48	20.05	2.24	20.53
812	0100	0.36	17.08	0.61	17.78	0.48	18.12	0.84	18.59	1.57	19.45	2.64	20.77
813	0230	0.36	17.09	0.60	18.28	0.32	18.60	0.46	18.89	0.76	19.33	1.88	20.67
814	0400	0.37	15.82	0.53	17.28	0.29	17.68	0.71	18.10	1.18	18.70	1.97	19.47
815	0530	0.70	18.28	0.88	18.44	1.02	18.54	1.35	18.67	1.84	19.06	2.60	19.70
816	0700	1.52	23.24	1.69	23.11	1.77	22.99	1.81	22.82	1.88	22.61	2.03	22.39
817	0830	1.90	27.69	2.15	27.44	2.39	27.14	2.51	26.77	2.60	26.46	2.74	26.12
818	1000	1.83	28.57	2.04	28.11	2.17	27.77	2.35	27.31	2.44	27.02	2.65	26.74

Table 33i

Wind speed (U) and temperature (T) measurements, Series 900, August 4-5, 1960

Run No.	Height	0.5 m		1.0 m		2.0 m		4.0 m		8.0 m		16.0 m	
	Time, CST	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C	U, m/sec	T, °C
901	0900	2.00	-	2.28	24.67	2.43	-	2.56	-	2.73	-	2.97	-
902	1130	1.40	22.66	1.64	22.61	1.81	22.55	2.00	22.47	2.16	22.40	2.40	22.35
903	1300	2.52	20.84	2.90	20.83	3.23	20.49	3.60	20.37	4.06	20.23	4.50	19.95
904	1430	2.41	20.30	2.78	20.28	3.13	20.15	3.49	19.97	3.88	19.94	4.31	19.74
905	1600	2.66	20.59	3.05	20.56	3.38	20.52	3.77	20.47	4.19	20.43	4.51	20.35
906	1730	2.03	21.08	2.39	21.11	2.67	21.14	2.99	21.14	3.37	21.13	3.84	21.10
907	1900	1.53	18.62	1.85	18.78	2.18	19.00	2.58	19.24	3.13	19.49	3.75	19.69
908	2030	1.37	17.17	1.69	17.33	2.01	17.54	2.45	17.81	2.95	18.07	3.54	18.26
909	2200	1.09	15.87	1.35	16.00	1.56	16.12	1.83	16.26	2.38	16.48	3.28	16.76
910	2330	0.64	15.51	0.91	15.72	1.09	15.90	1.34	16.11	1.88	16.35	2.81	16.65
911	0100	1.08	15.33	1.37	15.50	1.65	15.71	1.94	15.98	2.27	16.28	3.05	16.70
912	0230	1.18	15.43	1.47	15.56	1.71	15.70	2.01	15.89	2.38	16.09	3.11	16.34
913	0400	1.64	15.19	1.92	15.28	2.16	15.34	2.43	15.40	2.84	15.47	3.74	15.60
914	0530	1.22	16.37	1.46	16.39	1.67	16.39	1.88	16.36	2.11	16.34	2.77	16.35
915	0700	2.22	19.09	2.58	19.00	2.88	18.90	3.19	18.74	3.41	18.54	3.63	18.35
916	0830	2.09	22.57	2.39	22.39	2.60	22.24	2.83	22.07	3.03	21.91	3.34	21.72
917	1000	2.56	26.45	2.92	26.11	3.18	25.80	3.44	25.50	3.72	25.28	3.97	25.01

Classical Profile Laws

Power Law

One of the oldest and most studied of the profile laws is the power law which was presented above as Equation 1.

Frost^(4,5) in summarizing the work of earlier investigators using the power law, cited several studies where the parameter, p , had been evaluated using multiple anemometer levels under specified conditions. The values of p cited were remarkably consistent in magnitude and generally showed p to be an increasing function of stability. Frost showed that the value of p was a function of stability in the layer from 5 to 400 ft. His value of p for the isothermal lapse rate was 0.29, and for near adiabatic conditions 0.15, which are in close agreement with the values of p reported by earlier investigations. Frost's values of p varied from 0.10, for a strong lapse rate, to 0.80, for extreme stability. The value of p was described as decreasing with increasing height and increasing with increasing surface roughness, for a given wind speed and lapse rate.

For the present investigations, the value of p was computed from a regression equation written to represent the power law and the value of p determined using the method of least squares. The power law regression equation used in this analysis was

$$\ln \bar{u} = \ln c + p \ln z \quad (5)$$

where c is considered a constant.

In the profile calculations, p was computed using anemometers at 2, 4, 8 and 16 meters; 1, 2, 4 and 8 meters; 0.5, 1, 2 and 4 meters; and all six levels.

From the Argonne computations using all levels, the parameter p for the lapse rates averaging approximately adiabatic was 0.17. This value is consistent with the value given by Frost and others. Table 34 (a-1) summarizes the Argonne computations for the four profile laws. Column 6 shows the values of p computed from all six levels of wind for the various profile series. The values of wind shear are represented in column 4 by the difference in wind speed between 16 and 0.5 meter observations expressed in meters/sec. Figure 72a is a scatter diagram of grouped values of p versus stability and wind speed. The lowest values are found at high wind speeds and instability. Highest values of p are associated with low speeds and stability. The parameter, p , is apparently a non-linear function of lapse rate and wind speed in the layer studied.

Table 34a

Summary of profile calculations Series 100 June 7 8 1960

Run No	Time CST	u_4 m/sec	$\Delta u_{16-0.5}$ m/sec	$\Delta T_{16-0.5}$ °C	p	β	α	u_* cm/sec			Z_0 cm		L_{MO} meters	RMSD values cm/sec			
								LL	DL	LPLL	LL	LPLL		PL	LL	DL	LPLL
101	1130	4.36	2.10	1.96	0.15	1.04	0.13	24	29	25	0.26	0.42	16.56	7	3	5	2
102	1300	5.18	2.42	1.88	0.15	1.18	0.89	28	55	34	0.27	0.70	21.95	15	8	36	2
103	1430	4.94	2.56	1.81	0.16	1.04	0.17	29	33	30	0.44	0.51	23.75	9	3	11	3
104	1600	4.73	2.51	0.97	0.16	0.95	0.70	28	23	27	0.45	0.34	53.01	7	4	13	4
105	1730	3.91	2.30	0.04	0.18	0.92	5.66	26	17	23	0.85	0.53	224.83	5	4	11	3
106	1900	2.47	1.91	+1.76	0.23	0.82	0.34	21	7	16	3.41	1.25	4.47	3	7	9	2
107	2030	2.41	2.36	+3.92	0.32	0.89	0.05	27	10	23	10.48	7.78	1.51	9	5	26	1
108	2200	2.80	2.44	+2.74	0.28	0.80	0.20	28	7	24	7.09	4.39	4.28	6	8	3	1
109	2330	2.62	2.44	+2.71	0.30	0.73	0.26	29	5	23	9.14	5.11	4.05	6	10	11	6
110	0100	1.68	1.90	+2.73	0.30	0.43	0.66	21	1	8	10.38	0.41	1.72	10	18	87	2
111	0230	2.47	2.21	+3.84	0.28	1.09	0.02	24	23	23	6.49	5.71	1.60	13	7	43	7
112	0400	1.92	1.96	+6.27	0.32	0.76	0.06	22	4	17	10.99	5.83	0.82	4	8	5	2
113	0530	1.80	1.55	+1.79	0.27	0.79	0.33	18	5	14	6.45	3.28	5.16	2	6	2	2
114	0700	2.69	1.10	0.91	0.13	1.19	0.91	13	29	16	0.11	0.79	19.77	7	4	15	1
115	0830	4.39	2.15	1.48	0.16	0.97	0.28	25	22	27	0.41	0.51	26.97	8	4	9	4
116	1000	4.17	1.95	1.96	0.15	1.07	0.33	23	31	25	0.30	0.50	15.10	8	3	13	1
117	1130	3.53	1.66	2.35	0.14	1.05	0.13	19	25	20	0.24	0.35	8.96	6	2	6	1

u_4 4 meter wind speed $\Delta u_{16-0.5}$ wind shear between 16 and 0.5 wind speed $\Delta T_{16-0.5}$ 16 meter temperature minus 0.5 meter temperature PL Power Law
 LL Log Law DL Deacon's Law MO Monin and Obukhov's Law LPLL Log Plus Linear Law (other symbols are explained in the text) Unless otherwise specified
 all computed values shown in Table 34 (a) are based on six levels of data Values of Z_0 used in the Deacon computations are as follows

100 series	0.4 cm	200 series	1.0 cm	300 series	1.0 cm
400 series	1.4 cm	500 series	0.3 cm	600 series	0.7 cm
700 series	0.3 cm	800 series	0.3 cm	900 series	0.9 cm

Table 34b

Summary of profile calculations Series 200 June 15 16 1960

Run No	Time CST	u_4 m/sec	$\Delta u_{16-0.5}$ m/sec	$\Delta T_{16-0.5}$ °C	p	β	α	u_* cm/sec			Z_0 cm		L_{MO} meters	RMSD values cm/sec			
								LL	DL	LPLL	LL	LPLL		PL	LL	DL	LPLL
201	1100	6.42	3.52	1.15													
202	1230	6.88		0.64													
203	1400	7.24	4.29	0.85	0.19	1.05	1.07	49	57	48	1.14	1.01	165.76	14	6	22	6
204	1530	6.76	3.93	0.49	0.18	1.06	1.03	45	56	46	1.03	1.10	293.16	15	4	23	4
205	1700	3.77	2.58	+1.07	0.21	0.90	1.43	29	18	25	2.19	1.18	34.59	5	6	11	2
206	1830	3.53	2.28	+0.83	0.20	0.92	1.47	26	18	22	1.52	0.81	37.80	5	5	13	2
207	2000	2.15	2.17	+1.80	0.31	0.64	0.82	25	4	16	10.53	3.16	5.75	3	13	32	4
208	2130	2.24	2.15	+1.93	0.30	0.69	0.59	25	5	17	9.46	3.63	5.43	3	11	23	4
209	2300	2.58	2.09	+1.41	0.25	0.79	0.81	24	8	18	4.48	1.85	10.94	2	8	20	1
210	0030	2.06	1.70	+1.34	0.26	0.80	0.49	20	7	14	5.35	2.06	5.81	2	7	10	2
211	0200	2.88	1.97	+0.90	0.21	0.86	1.40	22	12	17	2.02	0.75	21.61	3	7	20	2
212	0330	3.01	2.02	+0.57	0.20	0.80	3.32	23	9	16	1.64	0.39	37.11	4	9	40	2
213	0500	4.92	3.06	+0.41	0.19	1.00	1.86	35	33	33	1.38	1.04	108.17	8	4	7	3
214	0630	5.59	3.19	+0.13	0.18	0.95	4.43	37	31	35	0.99	0.77	325.44	8	5	17	4
215	0800	5.84	3.42	+0.41	0.19	0.99	0.31	40	38	39	1.17	1.06	55.39	10	3	3	3
216	0930	5.36	2.99	0.23	0.17	1.07	0.82	34	45	35	0.79	0.86	195.90	11	4	15	3
217	1100	5.16	2.89	0.62	0.18	1.02	0.31	33	37	33	0.84	0.80	141.49	9	2	3	2

Table 34c

Summary of profile calculations, Series 300, June 23-24, 1960

Run No.	Time, CST	u_a , m/sec	$\Delta u_{16-0.5}$, m/sec	$\Delta T_{16-0.5}$, °C	ρ	β	α	u_a , cm/sec			Z_0 , cm		L_{MO} meters	RMSD values, cm/sec			
								LL	DL	LPLL	LL	LPLL		PL	LL	DL	LPLL
301	0900	8.70	5.05	-0.18	0.17	1.05		56	70		0.79	0.55		17	13	20	
302	1030	4.18		-2.00													
303	1200	9.76	5.57	-0.42	0.18	1.03		64	73		0.90	0.95		20	3	13	
304	1330	8.33	4.39	-1.20	0.17	1.11	2.90	50	80	55	0.58	0.85	-153.66	20	7	32	4
305	1500	7.48	4.18	-0.34	0.17	1.09	3.57	47	67	49	0.79	0.87	-657.16	17	6	29	6
306	1630	6.04	3.42	+0.17	0.17	1.05	1.02	38	49	38	0.77	0.73	338.78	12	6	13	6
307	1800	7.30	3.97	+0.22	0.17	1.13	-7.48	45	73	49	0.68	0.96	419.56	19	7	35	6
308	1930	4.79	2.99	+0.49	0.20	1.05	0.71	34	39	33	1.56	1.39	103.56	12	7	23	7
309	2100	4.67	3.08	+1.18	0.20	1.01	0.68	35	33	33	1.81	1.43	45.50	10	5	14	4
310	2230	3.50	2.64	+1.43	0.22	0.79	1.94	29	11	22	2.77	0.87	23.36	5	11	38	3
311	0000	3.99	3.02	+1.23	0.22	0.86	2.75	33	17	25	2.80	0.92	34.31	8	13	20	6
312	0130	3.61	2.77	+1.08	0.23	0.81	2.48	31	13	23	3.11	1.02	30.03	5	11	29	3
313	0300	4.78	3.17	+0.93	0.20	0.96	0.96	36	28	34	1.78	1.39	61.45	10	5	4	3
314	0430	4.14	2.62	+0.68	0.20	1.02	-0.10	30	30	30	1.49	1.54	54.53	10	3	12	3
315	0600	5.00	2.77	-0.09	0.18	1.16		32	55	37	0.82	1.50		16	7	34	3
316	0730	5.46	3.09	-1.10	0.18	1.11	2.08	36	52	39	0.92	1.38	-95.15	15	5	28	2
317	0900	5.86	3.21	-1.58	0.17	1.13	1.54	37	59	41	0.73	1.14	-66.89	16	6	30	3

Table 34d

Summary of profile calculations, Series 400, June 30-July 1, 1960

Run No.	Time, CST	u_a , m/sec	$\Delta u_{16-0.5}$, m/sec	$\Delta T_{16-0.5}$, °C	ρ	β	α	u_a , cm/sec			Z_0 , cm		L_{MO} meters	RMSD values, cm/sec			
								LL	DL	LPLL	LL	LPLL		PL	LL	DL	LPLL
401	1530	3.22	2.13	+0.13	0.21	0.97	0.63	24	21	24	1.82	1.68	125.40	8	3	4	2
402	1700	3.44	1.96	+0.03	0.18	1.08	-5.77	22	31	25	0.88	1.50	202.12	11	5	9	3
403	1830	3.27	1.90	+0.32	0.19	1.14	-2.49	22	35	26	1.08	2.11	66.15	13	6	19	2
404	2000	3.19	2.29	-0.13	0.22	0.84	-11.58	26	13	22	2.48	1.34	-271.73	5	6	26	2
405	2130	4.19	2.86	+0.34	0.21	0.93	0.47	33	23	32	2.27	2.17	149.18	11	4	10	4
406	2300	3.17	1.90	+0.17	0.19	1.04	-2.23	22	25	23	1.15	1.55	133.82	9	3	5	2
407	0030	2.64	1.82	+0.19	0.21	0.87	1.68	21	12	19	2.17	1.66	93.14	6	4	18	3
408	0200	2.28	1.75	+0.20	0.23	0.73	5.57	20	6	15	3.26	1.26	77.38	3	7	40	2
409	0330	2.88	1.99	+0.20	0.22	0.94	0.32	23	17	22	2.40	2.27	86.87	8	2	3	2
410	0500	1.98	1.68	+0.39	0.27	0.60	1.29	20	3	17	6.05	3.70	27.96	8	10	60	9
411	0630	2.87	1.99	-0.09	0.20	0.80	59.30	22	10	18	1.94	0.89	1166.17	4	6	39	3
412	0800																
413	0930	4.51	2.62	-1.80	0.18	0.91	1.63	30	23	35	0.89	1.71	-46.64	20	15	38	13
414	1100	3.32	1.68	-1.82	0.16	1.20	0.92	19	41	24	0.38	1.17	-18.31	13	8	17	5
415	1230	2.43	1.17	-1.64	0.15	1.12	0.40	13	24	16	0.26	0.68	-9.93	8	5	4	3

Table 34e

Summary of profile calculations, Series 500, July 7-8, 1960

Run No.	Time, CST	u_a , m/sec	$\Delta u_{16-0.5}$, m/sec	$\Delta T_{16-0.5}$, °C	ρ	β	α	u_a , cm/sec			Z_0 , cm		L_{MO} meters	RMSD values, cm/sec			
								LL	DL	LPLL	LL	LPLL		PL	LL	DL	LPLL
501	0930	2.27	0.82	-1.55	0.11	1.09	0.21	10	17	11	0.04	0.08	-8.98	3	2	2	1
502	1100	2.30	1.02	-1.70	0.14	0.76	-0.20	12	4	11	0.18	0.08	-6.23	3	4	48	3
503	1230	1.88	0.76	-1.30	0.13	0.84	-0.02	9	5	9	0.10	0.08	-5.06	2	2	27	2
504	1400	2.70	1.28	-1.70	0.14	0.82	-0.26	15	6	13	0.25	0.12	-8.30	2	3	37	2
505	1530	1.72	0.65	-1.39	0.12	0.91	0.06	8	6	8	0.07	0.10	-4.72	3	3	16	3
506	1700	1.88	1.04	-0.60	0.17	0.71	-1.17	12	2	10	0.75	0.26	-20.97	3	4	42	3
507	1830	0.41	0.33	+1.71	0.09			1			<0.01			14	14		
508	2000	0.38	0.82		0.31			9			16.97			19	21		
509	2130	0.90	1.96	+5.32	0.51			22			41.11			21	31		
510	2300	1.92	2.49	+4.02	0.42	0.56	0.15	29	1	18	22.67	9.99	0.97	4	17	14	7
511	0030	2.61	2.17	+3.15	0.28	0.87	0.08	26	9	23	6.54	4.69	2.36	7	6	16	4
512	0200	2.25	2.83	+3.52	0.40	0.62	0.23	33	2	20	20.85	8.67	1.47	3	19	5	6
513	0330	1.97	3.00	+4.33	0.46	0.53	0.23	33	1	16	28.59	9.14	0.86	4	25	9	3
514	0500	2.20	2.63	+2.51	0.35	0.56	0.73	30	2	14	15.94	2.68	2.87	7	21	33	3
515	0630	2.47	0.99	-0.56	0.13	1.18	1.84	12	25	14	0.10	0.30	-47.52	5	3	14	1
516	0800	2.72	0.99	-1.11	0.11	1.18	0.69	12	28	14	0.04	0.14	-16.18	5	3	11	0
517	0930	3.24	1.25	-1.52	0.12	1.18	0.60	15	33	18	0.07	0.26	-13.79	7	5	17	1

Table 34f

Summary of profile calculations Series 600 July 14 15 1960

Run No	Time CST	u_4 m/sec	$\Delta u_{16-0.5}$ m/sec	$\Delta T_{16-0.5}$ °C	ρ	β	α	u_{∞} cm/sec			Z_0 cm		L_{MO} meters	RMSD values cm/sec			
								LL	DL	LPLL	LL	LPLL		PL	LL	DL	LPLL
601	1630	2.32	1.15	-1.21	0.15	0.93	0.06	13	11	13	0.29	0.32	-13.11	5	3	17	3
602	1800	2.07	1.19	-0.08	0.18	0.93	0.25	13	10	13	0.85	0.78	57.60	4	2	8	2
603	1930	1.50	1.40	+2.47	0.26	0.66	0.16	15	2	10	5.92	1.54	1.30	5	8	27	3
604	2100																
605	2230	1.47	1.78	+2.98	0.35	0.62	0.17	19	2	11	14.72	3.77	0.87	5	12	15	3
606	0000	1.60	1.86	+2.70	0.34	0.56	0.21	21	2	12	13.61	4.13	1.31	4	12	33	3
607	0130	0.82	1.40	+4.59	0.40			15			26.05			13	20		
608	0300																
609	0430																
610	0600	1.60	0.92	0.57	0.18	1.04	-0.75	10	12	10	0.88	0.66	50.39	3	2	5	2
611	0730	1.30	0.47	+0.17	0.12	1.26	-0.98	5	17	7	0.04	0.25	16.96	4	3	6	2
612	0900	1.73	0.61	1.43	0.11	1.22	0.27	7	21	9	0.03	0.16	5.45	4	3	6	1
613	1030	3.09	1.28	1.69	0.13	1.31	0.64	14	47	18	0.09	0.36	13.01	9	6	22	3

Table 34g

Summary of profile calculations Series 700 July 20 21 1960

Run No.	Time CST	u_4 m/sec	$\Delta u_{16-0.5}$ m/sec	$\Delta T_{16-0.5}$ °C	ρ	β	α	u_{∞} cm/sec			Z_0 cm		L_{MO} meters	RMSD values cm/sec			
								LL	DL	LPLL	LL	LPLL		PL	LL	DL	LPLL
701	1000	3.29	1.34	1.90	0.13	1.10	0.32	16	26	18	0.09	0.23	-9.66	7	4	8	1
702	1130	3.18	0.93	1.85	0.10	1.60	0.58	11	78	17	0.01	0.26	-6.98	12	10	31	6
703	1300	2.89	1.12	1.86	0.12	1.17	0.22	13	29	15	0.06	0.14	-7.19	5	3	13	1
704	1430	3.65	1.48	-1.72	0.13	1.13	0.42	17	32	20	0.08	0.21	12.88	7	4	13	1
705	1600	3.45	1.33	1.53	0.12	1.11	0.24	15	28	17	0.07	0.12	-13.78	8	6	11	6
706	1730	2.64	1.42	-0.07	0.17	0.89	1.37	17	9	16	0.64	0.48	91.29	3	2	13	2
707	1900	1.96	1.70	+1.32	0.26	0.69	0.32	19	3	14	6.01	2.01	3.16	1	8	22	2
708	2030	2.35	1.93	+1.48	0.25	0.72	0.42	22	4	16	4.67	1.72	4.91	1	8	26	2
709	2200	1.98	1.93	+1.63	0.29	0.63	0.45	22	2	14	8.68	2.49	3.27	2	11	31	2
710	2330	1.50	1.83	+2.09	0.35	0.55	0.24	20	1	11	15.25	3.64	1.16	4	13	27	2
711	0100	1.19	1.18	+1.83	0.26	0.34	0.24	12	<1	7	5.70	0.84	1.40	8	10	107	7
712	0230	1.98	1.81	+1.59	0.28	0.63	0.54	21	2	13	7.34	1.89	3.90	3	11	33	3
713	0400	1.51	1.75	+2.14	0.34	0.59	0.25	19	1	10	13.85	2.78	1.15	5	13	21	3
714	0530	1.67	1.82	+1.05	0.30	0.37	2.38	20	<1	8	10.45	0.41	6.18	9	18	113	3
715	0700	2.86	1.10	-0.85	0.12	1.02	0.34	13	16	13	0.05	0.07	-32.31	3	1	7	1
716	0830	3.71	1.39	-1.63	0.11	1.03	0.01	16	23	16	0.03	0.03	19.05	4	2	9	2
717	1000	4.16	1.64	1.92	0.12	1.03	0.17	19	26	20	0.06	0.08	-17.40	5	1	6	1
718	1130	4.92	2.13	2.38	0.13	0.92	0.52	24	20	22	0.11	0.05	18.81	3	4	35	1

Table 34h

Summary of profile calculations Series 800 July 28 29 1960

Run No	Time CST	u_4 m/sec	$\Delta u_{16-0.5}$ m/sec	$\Delta T_{16-0.5}$ °C	ρ	β	α	u_{∞} cm/sec			Z_0 cm		L_{MO} meters	RMSD values cm/sec			
								LL	DL	LPLL	LL	LPLL		PL	LL	DL	LPLL
801	0900	4.18	1.70	-1.88	0.12	1.13	0.51	19	38	22	0.08	0.17	-19.25	7	4	15	2
802	1000	4.63	2.06	-2.12	0.13	1.07	0.12	23	33	24	0.14	0.17	-19.65	7	3	9	3
803	1130	5.38	2.44	-2.25	0.14	1.13	0.23	28	48	29	0.17	0.23	-21.49	9	5	26	4
804	1300	5.67	2.85	-1.88	0.15	1.00	-0.53	32	33	30	0.32	0.21	-30.99	7	5	6	4
805	1430	6.35	3.10		0.15	1.03		35	41		0.30			9	3	12	
806	1600	4.02	1.83		0.14	1.14		21	37		0.18			7	4	21	
807	1730	2.31	1.34	+0.14	0.18	0.92	1.20	15	9	13	0.90	0.47	34.47	2	3	5	2
808	1900	2.08	1.97	+2.18	0.29	0.80	0.17	22	5	16	7.65	3.50	2.08	4	8	6	2
809	2030																
810	2200	1.87	1.92	+2.68	0.31	0.72	0.24	21	3	14	9.84	2.98	1.77	4	11	6	2
811	2330	1.10	1.80	+3.16	0.44	0.23	0.32	19	<1	6	27.03	2.33	0.59	10	19	85	6
812	0100	0.84	2.28	+3.69	0.55			24			46.98			22	36		
813	0230	0.46	1.52	+3.58	0.38			14			32.80			33	35		
814	0400	0.71	1.60	+3.65	0.48			17			39.48			22	29		
815	0530	1.35	1.90	+1.42	0.37	0.31	2.38	21	<1	7	19.61	1.07	4.75	9	20	94	2
816	0700	1.81	0.51	0.85	0.07	1.08	0.14	5	13	5	0.00	0.00	-14.28	3	3	9	3
817	0830	2.51	0.84	1.57	0.10	1.47	0.62	9	53	13	0.01	0.10	-10.10	7	6	22	4
818	1000	2.35	0.82	1.83	0.10	1.09	0.02	9	18	9	0.01	0.02	6.55	3	3	3	3

Table 34i

Summary of profile calculations Series 900 August 4-5 1960

Run No	Time CST	$u_{0.5}$ m/sec	$\Delta u_{16-0.5}$ m/sec	$\Delta T_{16-0.5}$ °C	p	β	α	u_* cm/sec			Z_0 cm		L_{MO} meters	RMSD values cm/sec			
								LL	DL	LPLL	LL	LPLL		PL	LL	DL	LPLL
901	0900	2.56	0.97		0.11	1.00		10	30		0.02			4	4	31	4
902	1130	2.00	1.00	-0.31	0.15	1.02	-0.25	11	14	11	0.30	0.27	-46.24	3	2	5	2
903	1300	3.60	1.98	-0.89	0.17	0.85	-1.47	23	13	20	0.62	0.33	-45.93	3	4	43	2
904	1430	3.49	1.90	-0.56	0.17	0.93	-1.91	22	18	20	0.61	0.41	-97.55	4	2	20	1
905	1600	3.77	1.85	-0.24	0.15	0.95	0.58	22	20	22	0.36	0.38	-248.32	5	2	24	2
906	1730	2.99	1.81	+0.02	0.18	0.84	9.13	20	11	17	0.97	0.49	184.18	3	5	34	2
907	1900	2.58	2.22	+1.07	0.26	0.69	1.86	25	5	18	5.40	1.68	17.85	2	11	42	2
908	2030	2.45	2.17	+1.09	0.27	0.73	1.30	25	6	18	6.59	2.71	15.06	1	9	22	2
909	2200	1.83	2.19	+0.89	0.30	0.37	8.02	24	1	8	11.00	0.22	16.79	13	22	129	3
910	2330	1.34	2.17	+1.14	0.40	0.32	3.04	23	<1	7	23.17	1.08	5.07	12	23	84	4
911	0100	1.94	1.97	+1.37	0.28	0.70	2.09	21	4	11	7.91	1.11	10.20	8	14	22	5
912	0230	2.01	1.93	+0.91	0.27	0.65	3.33	21	3	11	6.60	0.78	16.09	7	14	39	3
913	0400	2.43	2.10	+0.41	0.22	0.52	20.32	22	2	9	3.47	0.03	54.44	13	19	117	4
914	0530	1.88	1.55	0.02	0.22	0.69	55.52	16	4	8	3.04	0.11	224.95	9	12	40	5
915	0700	3.19	1.41	-0.74	0.14	1.19	2.49	16	37	19	0.18	0.49	-63.50	8	5	14	2
916	0830	2.83	1.25	-0.85	0.13	1.01	-0.33	14	18	13	0.11	0.09	-32.81	4	3	15	3
917	1000	3.44	1.41	1.44	0.12	1.05	0.43	16	25	17	0.07	0.12	-24.72	5	3	13	2

Figure 72a

Power law p values as related to wind speed and stability

Argonne's wind profiles, taken over a gently rolling surface, show p to be generally a decreasing function of height, as suggested by Best⁽⁶⁾ and also by Frost,⁽⁴⁾ but with occasional reversals during periods of strong stability and light winds, as indicated in Table 35 (a-i). Marked reversals in the normal changes of p with height are observed when a low-level microjet appears in the profiles. This microjet is characterized by a greater wind speed at the 1-meter level than at the 0.5 and

2.0 meter levels and occurs during periods of light winds and strong stability. It is believed to be a katabatic effect. Profiles 507, 508, 509, 607, 711, 811, 812, 813 and 814 show the microjet. When the microjet was present, the Deacon and log plus linear law calculations gave unreasonable results. These results have been omitted in Table 34.

Table 35a

Values of p for layers indicated,
Series 100, June 8-9, 1960

Run No	Time	P _{0 5-4}	P ₁₋₈	P ₂₋₁₆	P _{0 5-16}
101	1130	0 17	0 14	0 13	0 15
102	1300	0 18	0 14	0 11	0 15
103	1430	0 18	0 15	0 14	0 16
104	1600	0 17	0 14	0 14	0 16
105	1730	0 19	0 16	0 16	0 18
106	1900	0 24	0 21	0 22	0 23
107	2030	0 37	0 31	0 28	0 32
108	2200	0 30	0 29	0 27	0 28
109	2330	0 31	0 32	0 30	0 30
110	0100	0 26	0 27	0 35	0 30
111	0230	0 35	0 24	0 21	0 28
112	0400	0 35	0 30	0 31	0 32
113	0530	0 29	0 27	0 26	0 27
114	0700	0 16	0 13	0 10	0 13
115	0830	0 17	0 16	0 14	0 16
116	1000	0 17	0 15	0 13	0 15
117	1130	0 17	0 14	0 12	0 14

Table 35b

Values of p for layers indicated,
Series 200, June 15-16, 1960

Run No	Time	P _{0 5-4}	P ₁₋₈	P ₂₋₁₆	P _{0 5-16}
201	1100	0 21	-	-	-
202	1230	-	0 17	0 15	-
203	1400	0 21	0 18	0 16	0 19
204	1530	0 21	0 18	0 16	0 18
205	1700	0 23	0 20	0 20	0 21
206	1830	0 21	0 18	0 18	0 20
207	2000	0 30	0 31	0 33	0 31
208	2130	0 30	0 31	0 31	0 30
209	2300	0 25	0 24	0 24	0 25
210	0030	0 26	0 26	0 25	0 26
211	0200	0 22	0 19	0 20	0 21
212	0330	0 20	0 18	0 20	0 20
213	0500	0 21	0 19	0 17	0 19
214	0630	0 20	0 18	0 17	0 18
215	0800	0 21	0 19	0 17	0 19
216	0930	0 20	0 17	0 15	0 17
217	1100	0 20	0 17	0 16	0 18

Table 35c

Values of p for layers indicated,
Series 300, June 23-24, 1960

Run No.	Time	P _{0 5-4}	P ₁₋₈	P ₂₋₁₆	P _{0 5-16}
301	0900	0.20	0.16	0 15	0 17
302	1030	0.34	0.24	-	-
303	1200	0 20	0.17	0 15	0.18
304	1330	0.20	0.16	0 14	0.17
305	1500	0.21	0 17	0.15	0 17
306	1630	0.20	0 16	0.15	0.17
307	1800	0.21	0.16	0.14	0.17
308	1930	0.23	0 19	0 17	0 20
309	2100	0.23	0.19	0.18	0.20
310	2230	0.22	0 20	0 22	0 22
311	0000	0.23	0.20	0.21	0 22
312	0130	0.23	0.21	0 22	0 23
313	0300	0.23	0 19	0 18	0 20
314	0430	0 23	0.18	0.17	0 20
315	0600	0 22	0.17	0 14	0 18
316	0730	0 22	0.17	0 15	0 18
317	0900	0 21	0 17	0 14	0 17

Levels used in computations of p

P_{0 5-4} 0 5, 1, 2 and 4 meters
P₁₋₈ 1 2, 4 and 8 meters
P₂₋₁₆ 2 4 8 and 16 meters
P_{0 5-16} 0 5, 1, 2, 4, 8 and 16 meters
(all levels)

Table 35d

Values of p for layers indicated,
Series 400, June 30-July 1, 1960

Run No.	Time	P _{0.5-4}	P ₁₋₈	P ₂₋₁₆	P _{0.5-16}
401	1530	0.23	0.19	0.18	0.21
402	1700	0.22	0.17	0.14	0.18
403	1830	0.23	0.18	0.14	0.19
404	2000	0.23	0.20	0.20	0.22
405	2130	0.24	0.21	0.19	0.21
406	2300	0.22	0.18	0.16	0.19
407	0030	0.23	0.20	0.19	0.21
408	0200	0.23	0.21	0.23	0.23
409	0330	0.25	0.21	0.19	0.22
410	0500	0.26	0.28	0.28	0.27
411	0630	0.21	0.19	0.20	0.20
412	0800	-	-	-	-
413	0930	0.21	0.17	0.15	0.18
414	1100	0.20	0.14	0.12	0.16
415	1230	0.18	0.13	0.12	0.15

Table 35e

Values of p for layers indicated,
Series 500, July 7-8, 1960

Run No.	Time	P _{0.5-4}	P ₁₋₈	P ₂₋₁₆	P _{0.5-16}
501	0930	0.13	0.12	0.10	0.11
502	1100	0.13	0.14	0.14	0.14
503	1230	0.13	0.13	0.13	0.13
504	1400	0.14	0.14	0.15	0.14
505	1530	0.13	0.13	0.12	0.12
506	1700	0.16	0.17	0.18	0.17
507	1830	-0.01	-0.18	0.24	0.09
508	2000	-0.11	0.27	0.77	0.31
509	2130	0.27	0.53	0.86	0.51
510	2300	0.41	0.44	0.43	0.42
511	0030	0.30	0.29	0.25	0.28
512	0200	0.41	0.42	0.41	0.40
513	0330	0.46	0.45	0.47	0.46
514	0500	0.33	0.37	0.38	0.35
515	0630	0.16	0.13	0.10	0.13
516	0800	0.14	0.11	0.09	0.11
517	0930	0.15	0.13	0.10	0.12

Table 35f

Values of p for layers indicated,
Series 600, July 14-15, 1960

Run No.	Time	P _{0.5-4}	P ₁₋₈	P ₂₋₁₆	P _{0.5-16}
601	1630	0.16	0.14	0.13	0.15
602	1800	0.20	0.16	0.16	0.18
603	1930	0.27	0.22	0.27	0.26
604	2100	-	-	0.34	-
605	2230	0.35	0.31	0.35	0.35
606	0000	0.34	0.31	0.36	0.34
607	0130	0.26	0.37	0.60	0.40
608	0300	-	-	-	-
609	0430	-	-	-	-
610	0600	0.20	0.16	0.16	0.18
611	0730	0.15	0.11	0.09	0.12
612	0900	0.14	0.11	0.09	0.11
613	1030	0.16	0.12	0.09	0.13

Table 35g

Values of p for layers indicated,
Series 700, July 20-21, 1960

Run No.	Time	P _{0.5-4}	P ₁₋₈	P ₂₋₁₆	P _{0.5-16}
701	1000	0.15	0.13	0.11	0.13
702	1130	0.15	0.11	0.07	0.10
703	1300	0.14	0.12	0.10	0.12
704	1430	0.15	0.12	0.10	0.13
705	1600	0.15	0.12	0.11	0.12
706	1730	0.18	0.17	0.16	0.17
707	1900	0.26	0.26	0.27	0.26
708	2030	0.25	0.24	0.25	0.25
709	2200	0.28	0.29	0.31	0.29
710	2330	0.34	0.32	0.37	0.35
711	0100	0.23	0.19	0.30	0.26
712	0230	0.26	0.28	0.30	0.28
713	0400	0.33	0.31	0.36	0.34
714	0530	0.24	0.30	0.37	0.30
715	0700	0.13	0.12	0.11	0.12
716	0830	0.12	0.10	0.10	0.11
717	1000	0.13	0.12	0.11	0.12
718	1130	0.13	0.12	0.12	0.13

Table 35h

Values of p for layers indicated,
Series 800, July 28-29, 1960

Run No.	Time	P _{0.5-4}	P ₁₋₈	P ₂₋₁₆	P _{0.5-16}
801	1000	0.15	0.12	0.10	0.12
802	1130	0.15	0.13	0.12	0.13
803	1300	0.16	0.13	0.12	0.14
804	1430	0.16	0.14	0.13	0.15
805	1600	0.17	0.14	0.13	0.15
806	1730	0.16	0.13	0.11	0.14
807	1900	0.19	0.17	0.17	0.18
808	2030	0.31	0.26	0.27	0.29
809	2200	-	-	-	-
810	2330	0.32	0.28	0.30	0.31
811	0100	0.39	0.36	0.53	0.44
812	0230	0.33	0.49	0.83	0.55
813	0400	0.02	0.15	0.84	0.38
814	0530	0.20	0.48	0.90	0.48
815	0700	0.31	0.36	0.45	0.37
816	0830	0.08	0.05	0.06	0.07
817	1000	0.14	0.09	0.06	0.10
818	1130	0.12	0.09	0.09	0.10

Table 35i

Values of p for layers indicated,
Series 900, August 4-5, 1960

Run No.	Time	P _{0.5-4}	P ₁₋₈	P ₂₋₁₆	P _{0.5-16}
901	0900	0.12	0.09	0.10	0.11
902	1130	-	-	-	-
903	1300	0.17	0.13	0.13	0.15
904	1430	0.17	0.16	0.16	0.17
905	1600	0.18	0.16	0.15	0.17
906	1730	0.17	0.15	0.14	0.15
907	1900	0.18	0.17	0.17	0.18
908	2030	0.25	0.25	0.26	0.26
909	2200	0.28	0.27	0.27	0.27
910	2330	0.25	0.27	0.36	0.30
911	0100	0.35	0.34	0.46	0.40
912	0230	0.28	0.24	0.29	0.28
913	0400	0.25	0.24	0.28	0.27
914	0530	0.19	0.19	0.26	0.22
915	0700	0.21	0.18	0.24	0.22
916	0830	0.17	0.14	0.11	0.14
917	1000	0.14	0.11	0.12	0.13
918	1130	0.14	0.12	0.11	0.12

Root mean square deviations (RMSD), i.e., the root mean square of the deviations between the observed and calculated wind speeds, for the power law are plotted as a function of stability and wind speed in Figure 72b. The RMSD values were generally largest for the profiles

Figure 72b

Relation of wind speed and stability
to root mean square deviation of
observed from calculated values
according to the power law

with the strongest and weakest winds and were usually at a minimum when average wind at 4 meters was in the vicinity of 2 mps. For the lower wind speeds, the RMSD values were considerably more variable than for the intermediate or strong wind cases.

Argonne's profile study shows the power law to give a reasonable representation of the wind profile in the lowest 16 meters of the atmosphere with the average RMSD for the profile generally less than 0.2 of a meter/sec. A discussion of how the power law results compare with the other profile laws will be presented later.

Logarithmic Law

It has long been accepted by meteorologists and aerodynamicists that the logarithmic law should hold at times of neutral stratification. Deacon⁽⁷⁾ and Monin and Obukhov,⁽¹⁾ who proposed more complex laws, accepted the logarithmic law as holding during periods of neutral stability, but felt that a stability correction was required for the diabatic case

For the purpose of the Argonne profile study, a regression equation of the form

$$\bar{u} = A + B \ln z \quad (6)$$

was written to represent the logarithmic law and the constants A and B evaluated for each profile. The regression equation constant A is equal to $-(u_*/k) \ln z_0$ and B is equal to u_*/k . Since k is the von Karman constant and taken to be 0.4, u_* is easily evaluated. With the aid of the computed u_* , the value of z_0 is readily determined from the relationship for A. In the logarithmic law, z_0 is the nominal height at which $\bar{u}$ would equal zero in the profile.

Figure 73 is a scatter diagram of the grouped RMSD values for the logarithmic law versus stability and wind speed. These values are generally small when the lapse rate is unstable and the winds are strong. They become larger in stable conditions and particularly with light winds.

The computed values of z_0 for the logarithmic law are a function of both wind speed and wind shear. When the wind is strong, z_0 is generally very small, and when it is light, z_0 is generally large. Corrections for displacement of the surface at which the wind speed reduces to zero due to grass height were neglected in this study since the grass height was relatively small.

Figure 73

Relation of wind speed and stability to root mean square deviation of observed from calculated values according to the logarithmic law

Deacon's Law

In 1949, Deacon proposed a profile law of the form

$$du/dz = az^{-\beta} \quad (7)$$

which becomes Equation 3 after integration. By writing the equation in this form, Deacon was able to adjust for increasing or decreasing shear in the profile by varying β . Deacon proposes β , which is a function of the Richardson number, as a stability parameter. If β is less than one, as in inversion conditions, a plot of the profile on a $\ln z$ versus u diagram ($\ln z$ as ordinate and u as abscissa) will be concave downward (increasing shear with height); if β is greater than one, lapse conditions, the profile curve would curve upward with height (decreasing shear); and if β is equal to one, this law would revert to the logarithmic form. Profiles of this type are observed throughout the plotted Argonne data.

The computations of β were made using an extension of a method first proposed by Langley.⁽⁸⁾ The computational formula is

$$\beta = 1 - \frac{\ln \left\{ \frac{\bar{u}_{16} + \bar{u}_8 - \bar{u}_4 - \bar{u}_2}{\bar{u}_4 + \bar{u}_2 - \bar{u}_1 - \bar{u}_{0.5}} \right\}}{2 \ln 2} \quad (8)$$

The subscripts represent the height above ground, in meters, of the velocities $\bar{u}$.

Values of u_* for the Deacon computations as shown in Column 10 Table 34 (a-i) were then determined using the relationship

$$u_{*16} = \frac{0.4 \bar{u}_{16} (1-\beta)}{\left[\left(\frac{z_{16}}{z_0} \right)^{1-\beta} - 1 \right]} \quad (9)$$

For the profile calculations, the relationship

$$u = \frac{\bar{u}_*}{0.4(1-\beta)} \left[\left(\frac{z}{z_0} \right)^{1-\beta} - 1 \right] \quad (10)$$

was to obtain computed winds at the remaining levels.

The values of β and u_* were computed from Equations 8 and 9. There is good agreement between stability and the magnitude of β as illustrated in Figure 74a. In order to use Equation 10, an assumption of z_0 has to be made in advance. The value of z_0 in Table 34a was determined for periods of near adiabatic lapse rate from a plot of $\ln z$ versus wind speed, from the intersection of the line of best fit with the $u = 0$ axis, i.e., the height at which the wind speed is reduced to zero.

The final computations made for Deacon's law were to determine the RMSD and maximum deviation (MD) of the computed winds from the observed winds.

The results based on Deacon's law are not quite comparable with those of the power and logarithmic laws, since a least squares fit was not obtained for this law. The large magnitudes of the RMSD and their erratic behavior from profile to profile indicates that the method of calculating β is apparently not adequate. If parameters, z_0 , u_* and β were computed using a least squares technique and the RMSD calculated as before, a more satisfactory correspondence between the observed and calculated values probably would have been obtained. Table 34 (a-i) gives the computed values of β and RMSD based on six levels of measurement.

Figure 74a is a plot of Deacon's β versus stability and wind speed. The plot shows good agreement between stability and β . At low wind speeds and strong stability, the values of β become erratic. Figure 74b is a plot of

Figure 74a

Deacon's β values as related to wind speed and stability

Figure 74b

Relation of wind speed and stability to root mean square deviation of observed from calculated values according to Deacon's law

the RMSD versus stability and wind speed. The method of computation breaks down when the wind decreases with height. In general, the RMSD values for the Deacon computations are larger than for the other two laws. It is obvious that Deacon's law is difficult to apply in routine operations as pointed out by Deacon himself⁽⁹⁾.

Log Plus Linear Law

In 1954, the Russian meteorologists, Monin and Obukhov, proposed the profile law listed above as Equation 4. This law includes the familiar logarithmic law plus a linear term which reduces to zero for the adiabatic case. The parameter, α , was claimed to be a universal constant and L is a length characteristic of the atmospheric ground layer and is called the height of the substrate of dynamic turbulence. With stable stratification ($L > 0$), the wind increase with height is more rapid than for neutral stratification.

For the Argonne computations, the log plus linear law regression equation was used in the form

$$u = A(\gamma + \log z) + Cz \quad (11)$$

and the values of A , γ and C determined by the method of least squares. From the coefficients, the values of u_* and z_0 were computed from the expressions:

$$u_* = \frac{0.4 A}{\ln 10} \text{ and } z_0 = 10^{-\gamma} .$$

$$C = \frac{u_*}{k} \frac{\alpha}{L} = \frac{A}{\ln 10} \frac{\alpha}{L} .$$

The calculation of α and L require involved algebraic manipulation. The reader is referred to Monin and Obukhov's paper for the method used.

RMSD values and the MD were computed from the observations and the least squares fit to the log plus linear form of the regression equations. The RMSD values computed for the log plus linear form are reproduced in Table 34 (a-i). Figure 75 is a plot of grouped RMSD values for the log plus linear law as a function of lapse rate and wind speed. These values are generally small with a slight tendency for higher values when the wind speed is very light during stable conditions. When the RMSD values for all the profile laws studied are compared (Figure 76), the log plus linear law values prove smallest of the four. Figure 77 shows the distribution of the maximum deviations for the four sets of computations. The distribution of both the RMSD and MD values indicate that the log plus linear law gives the best fit. The logarithmic and power laws are

Figure 75

Relation of wind speed and stability to root mean square deviation of observed from calculated values according to log plus linear law

Figure 76a

"Less than" ogive for root mean square deviation values during the day (0700-1800 CST)

Figure 76b

"Less than" ogive for root mean square deviation values during the night (1830-0630 CST)

Summary and Conclusions

Of the three types of regression equations used to study the Argonne data, the log plus linear regression equation gave the best general fit. The power law and the logarithmic law both proved reasonably accurate, with the power law giving better fit at night and the logarithmic law during the day. Deacon's law, when applied by computing β from the profile data instead of the solution of a regression equation, did not compare favorably with the other three laws studied.

Each of the three profile laws studied by the use of a regression equation gave good correspondence between observed and computed values. Even the power law used during the day and the logarithmic law applied at night, i.e., the least favorable periods for their application, give reasonable results for the lowest sixteen meters of the atmosphere at Argonne.

The six anemometers used together and in combinations of top four, middle four, and bottom four showed the profile parameters to be reasonably consistent with height except during periods of very weak winds and strong stability. These results may have useful consequences for routine industrial applications. For the lowest sixteen meters of the atmosphere, two anemometers properly spaced should be adequate for most routine needs; however, a third might prove useful at night. If the log plus linear or Deacon's laws are to be applied, a minimum of three anemometers are required to determine the profile parameters.

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MAN-MADE IONIZED COLUMNS IN THE ATMOSPHERE - A NEW TOOL FOR METEOROLOGICAL RESEARCH

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Abstract

The use of a high-energy proton or electron beam, directed vertically to act as a probe for the study of atmospheric processes is proposed. An outstanding feature of such an atmospheric probe is its capability to ionize a column of air repeatedly in a few microseconds and in approximately the same place. Characteristics of a vertical proton beam which may be generated by the Zero Gradient Synchrotron at the Argonne National Laboratory are discussed, and calculations are presented to provide an estimate of the ion concentration as a function of height in the atmosphere.

The potential uses of an atmospheric ionized column for meteorological research are discussed. Such investigations include the artificial initiation of lightning, the production of atmospheric ozone resulting from lightning, and the line spectra associated with the lightning channel. Also presented is a method whereby a combination of the high-energy particle beam and infrared techniques may be used to determine the air circulation within a thunderstorm. Brief mention is made of the possible uses of a high-energy particle beam for aerospace sciences, such as the study of whistlers and electromagnetic radiation phenomena associated with the aurora and air glow.

Introduction

Beams of high energy protons or electrons, the products of modern particle accelerators may be sent vertically into the atmosphere to act as probes for studying atmospheric processes. In a sense, they may be considered as intense beams of "cosmic rays in reverse." Such beams may be useful for atmospheric research since 1) they can ionize a column of air to great heights in a matter of microseconds; 2) they can be generated repeatedly, that is every few seconds; and 3) they may be generated in the same place in space. Never before has man had a tool with this capability!

Although either a proton or electron beam can be used for these investigations, the following discussion is devoted to the proton beam produced by the Zero Gradient Synchrotron (ZGS) at the Argonne National Laboratory.

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Characteristics of the ZGS

The Argonne ZGS is designed to produce 10^{13} protons per pulse of 10-microsecond duration, once every four seconds, with energies ranging to 12.5 BeV. At the exit, the beam has a cross-sectional area of about 50 cm^2 . With suitable bending magnets, it is feasible to turn the beam upward and to aim it in a predetermined direction.

The Effect of a High-Energy Proton Beam in the Atmosphere

According to Aron, Hoffman, and Williams,⁽¹⁾ a beam of 3-BeV protons would lose roughly 2 MeV/g/cm^2 of dry air. Assuming normal temperature and pressure conditions (NTP) the beam will pass through about 8 meters of atmosphere before losing 2 MeV of energy. This assumes that no nuclear interactions are involved. Since a homogeneous atmosphere at common ambient temperatures has a height of about 8 kilometers a proton beam having energy greater than 3 BeV would pass through most of the vertical extent of the atmosphere and gyrate along the geomagnetic lines of force toward the conjugate point on earth.

The flux of particles, F , may be represented as

$$F = \frac{N_0}{AT} \quad (1)$$

where N_0 = the number of particles per pulse emitted at the exit,

T = the pulse time in seconds, and

A = the cross-sectional area of the beam in cm^2 .

At the exit, the flux is, therefore, 2×10^{16} particles/ cm^2/sec . Since the energy necessary to form an ion pair in air is about 35 electron volts, the beam will generate 57,000 ion pairs per particle for every gram of air per cm^2 (8 meters) traversed, that is about 71 ion pairs are formed per cm^3 per particle at NTP.

At any instant, the number of ion pairs present per cm^3 can be determined by the equation

$$\frac{dn}{dt} = q - \alpha n^2 \quad (2)$$

where n = the number of ion pairs per cm^3

q = the ion pair production rate per second per cm^3

α = the recombination coefficient in cm^3 per ion pair per second and taken as equal to 1.6×10^{-6}

t = time in seconds.

Even without considering secondary ionizations resulting from nuclear interactions, the computation of the ionization as a function of height in the atmosphere is quite involved. Nevertheless, a crude semi-quantitative calculation is presented to indicate the order of magnitude of ion concentration produced by a high energy proton beam.

The beam, as it exits from the accelerator, is divergent with an angle of about 0.4 milliradians and disperses further owing to multiple scattering. It also becomes attenuated because of nuclear interactions. Thus, the ionization produced per unit volume decreases with increasing heights. The rate of ionization production, q , at a height corresponding to an air density, ρ , may be expressed by the equation

$$q = \frac{N_0 \exp \left\{ -\frac{1}{L} \int_0^Z \rho dZ \right\}}{\theta^2 (Z+k)^2 T} \times 71 \times \frac{\rho}{\rho_0}$$

$$= \frac{N_0 \exp \left\{ -\frac{1}{gL} \times (p_0 - p) \right\}}{\theta^2 (Z+k)^2 T} \times 71 \times \frac{\rho}{\rho_0} \quad (3)$$

where

- ρ_0 air density at NTP which equals 1.293×10^{-3} grams/ cm^3
- ρ air density in grams/ cm^3
- Z height above ground in centimeters
- k distance from beam exit to a virtual point source
- θ angular spread of the beam upon exit and equal to 0.4 milliradians
- 71 ion pair production per centimeter per particle as described above
- L absorption thickness, taken as 120 grams/ cm^2 (Reference 2, p. 490)
- p_0 atmospheric pressure at the surface in dynes/ cm^2
- p atmospheric pressure at height Z in dynes/ cm^2
- g acceleration of gravity taken as 980 cm/sec^2

Integrating Equation 2 yields

$$n_p = \frac{\sqrt{q/\alpha} [(\exp 2 t \sqrt{\alpha q}) - 1]}{(\exp 2 t \sqrt{\alpha q}) + 1} \quad (4)$$

where n_p represents the number of ions due to electronic collision just after the tail of the proton beam has passed. Equation 4 applies for a given height during the time the beam passes. After the beam has left, the ionization production falls to zero and the number of ions may be expressed by the equation

$$n = \frac{n_p}{1 + \alpha n_p t} \quad (5)$$

In Figure 79 are shown the vertical profiles of ionization concentration based on Equations 2, 4 and 5. The NACA standard atmosphere was

Figure 79

a) Ion concentration as a function of height 10, 20, and 30 microseconds after exit of proton beam's leading edge. b) Ion concentration as a function of height 30, 40, and 80 microseconds after exit of proton beam's leading edge.

assumed. Ionization due to meson production and other spallation reactions may yield total ionizations several orders of magnitude greater than indicated. However, because of the divergence of the nuclear interaction products, this will contribute negligibly to the specific ionization density of the main column at higher altitudes. Multiple scattering of the primary proton beam in the atmosphere will reduce the ionization concentrations shown in Figure 79, but the effect is not large for protons of high energy. In spite of the uncertainties, it appears reasonable that the proton beam would produce a highly ionized column from the surface to heights well above the tropopause.

Potential Uses of Atmospheric Ionized Columns for Meteorological Research

The ability to produce an ionized column in the atmosphere extending from the ground to levels well beyond the tropopause presents intriguing possibilities for studying processes associated with thunderstorms. Some of these are:

The Triggering of Lightning

An air-ionizing proton beam with a flux of 2×10^{16} protons/cm²/sec traveling at a speed of 0.98 times the velocity of light directed at a negative charge center of a mature thunderstorm cell, as defined by Byers and Braham,⁽³⁾ would result in an appreciable deformation of the electric field. Under certain conditions this would increase the potential gradient to values exceeding the dielectric strength of air and may well initiate a lightning stroke. The use of a vertically-directed proton beam for triggering lightning was first suggested by Ronald L. Martin.

In experiments involving the triggering of lightning, protection to the accelerator from a leader or return lightning stroke may be obtained by enclosing it in a Faraday cage which may take the form of an aluminum enclosure. The high-energy protons would pass through the aluminum with negligible loss, but the ions of substantially lower energy in a lightning stroke would be unable to penetrate the aluminum enclosure and would pass to the ground.

In recent literature^(4,5) are reported cases where lightning was apparently triggered by the rapid introduction of a conducting path between a thundercloud and ground. Newman⁽⁴⁾ reports that lightning strokes were induced by rapidly injecting a wire propelled by a rocket into a thundercloud. Brook et al.⁽⁵⁾ discuss the work of G. A. Young in triggering a lightning stroke by a plume of water particles, which were undoubtedly charged, extending from the sea surface to about 70 meters. The water plume was generated by a depth charge tested by the U.S. Navy.

Brook et al.⁽⁵⁾ describe a laboratory experiment where an arc discharge was created in a strong electric field between a sphere and a plane by rapidly introducing a conducting path, in this case a wire, to ground. This evidence and theoretical considerations, suggest that a proton beam with the characteristics described above may trigger a cloud-to-ground lightning stroke.

To carry out meaningful experiments involving lightning charges with a proton beam, it is necessary to determine the location in space and the magnitude of the electric charge centers in the thunderstorm cell. A network of potential gradient recorders of the field mill type, such as described by Fitzgerald,^(6,7) and suitable data processing equipment are therefore essential. The field-mill data may be transmitted to a data-processing center where a computer would determine continuously the location and magnitude of the charge centers. This information may then be used in controlling and directing the proton beam from the accelerator exit point.

Also necessary for these experiments is a suitable radar for determining the position in space of the individual thunderstorm cells which may be selected for treatment by the proton beam. The data provided by the radar may be used for studying the cloud changes in time and space resulting from the proton injection.

Appropriate photographic equipment capable of resolving individual lightning strokes is also essential.

Types of Investigations with a Triggered Lightning Stroke

If one assumed that a thunderstorm cell has a radius of one to two kilometers, then natural cloud-to-ground lightning would occur anywhere in an area of about 10 square kilometers. The advantages for meteorological research that would result from lightning occurring repeatedly in the same place instead of randomly distributed over a sizeable area would be substantial. For example, information could be obtained on both the areal and temporal distribution of rainfall with respect to the location of the lightning stroke.

Moore, Vonnegut, Machado and Survilas⁽⁸⁾ have observed increased radar echo development followed by heavy rainfall within a few minutes after a lightning flash occurred within a given region. These authors state that the lightning flash probably contributes to the formation of the "rain gush," by greatly enhancing the rate of coalescence of rain droplets. This, in turn, modifies the circulation within the storm cell. If the Moore-Vonnegut hypothesis is correct and if a proton beam can indeed induce a lightning stroke, then one would expect to find a maximum in the isohyetal (rainfall) pattern some distance downwind from the proton accelerator. A

sufficient number of such experiments could establish, with an acceptable level of statistical significance, whether the Moore-Vonnegut hypothesis is valid. If it were valid, then one would be tempted to argue that a proton beam can indeed modify the distribution of rainfall on the ground. To establish the magnitude of this effect would require careful consideration, but the economic value may be substantial.

The availability of repetitive lightning strokes at a known location would facilitate the placement of the fixed instrumentation necessary to obtain the simultaneous photographic, electrical, magnetic, spectroscopic, and meteorological data needed in the formulation of a good physical model of lightning. The location of spectrographic equipment close to the lightning flash would aid materially, not only in obtaining data on the line spectra, but also in obtaining data on the continuous radiation from lightning at 3000 Angstroms and below where the intensity levels are ordinarily low. Information of this latter type would aid in determining quantitatively the ozone production associated with a lightning flash. Further, it would be feasible to locate ozone-detection equipment on the ground for this purpose.

As pointed out by Prueitt⁽⁹⁾ and Salanave,⁽¹⁰⁾ the temperature in a lightning flash is of the order of tens of thousands of degrees above ambient. It should, therefore, be possible to follow this heated column by means of infrared detecting equipment. Two infrared detectors located on a suitable base line tracking the heated column would provide measurements on the position in space of points on the heated column over a given time interval. These data may be translated into wind speeds and directions as a function of height. Valuable information on the circulation within a thunderstorm cell would thus be provided.

Atlas,⁽¹¹⁾ among others, has observed lightning strokes by means of radar from the top of thunderclouds extending into the upper portion of the atmosphere. With a proton beam having sufficient energy to reach into the high atmosphere, it is not unreasonable to expect lightning strokes similar to those observed by Atlas. Clarence⁽¹²⁾ discusses the generation of whistlers by an upward jet of electrons, originating from runaway electrons in the thundercloud, i.e., electrons which have been accelerated to several hundred MeV. If the ionization produced by the proton beam in combination with the electric field above the thundercloud gives rise to such an electron jet, then it may be possible, if other atmospheric conditions are suitable, to generate and study the whistler phenomenon.

Clouds in the Thunderstorm Building Stage

A proton beam of suitable energy and an appropriate number of particles may serve to decrease lightning frequency if injected into a thunderstorm cell in the building stage. In this stage, when the magnitude of the charge center is small, a proton beam of relatively fewer particles

to produce a weakly-ionized path may serve to dissipate the charges in the cloud without an accompanying flash, and, thereby, prevent the development of well-defined charge centers. The effect on the life cycle of the storm which would result from suppressing the development of well-defined charge centers is problematical since we do not know enough about the role played by electric fields in the raindrop coalescence process.⁽¹³⁾

Fair Weather Cumulus and Stratus Clouds

Interesting studies in cloud physics could be carried out by injecting a proton beam of suitable characteristics into stratus or fair-weather cumulus clouds, thus bringing about a rapid redistribution of the charges within them. Although such clouds are formed primarily by thermodynamic and hydrodynamic processes, the occurrence of a measurable effect on the cloud circulation pattern, such as a change in the growth or dissipation rate, would provide valuable information on cloud dynamics.

Conclusions

It has been pointed out that a high-energy proton beam, or similarly, a high-energy electron beam, injected into the atmosphere would create an ionized path from the ground to high levels. The artificial creation of an ionized path would assist materially in the investigation of a number of atmospheric processes, such as the physics of the lightning strokes, the relation between raindrop coalescence and electric fields, the determination of wind profiles to high levels in the vicinity of a thunderstorm, and possibly other high atmospheric phenomenon, such as whistlers, air glow, and aurorae.

A lightning stroke triggered by a beam of high-energy particles would have many advantages in studying atmospheric phenomenon, since it could be produced repeatedly at a known position in space. This would allow simultaneous photographic, electrical, magnetic, spectroscopic, meteorological, and chemical measurements to aid in the formulation of a physical model of the lightning processes.

Only a few of the possible studies which can be carried out with a tool of this type have been enumerated. Others will, no doubt, think of many other areas of investigation by this means. It appears that the use of energetic particles injected into the atmosphere may open up a new profitable area for meteorological research.

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EXPANSION OF ARGONNE'S SOIL CLIMATOLOGY PROGRAM

James E. Carson and Frank C. Kulhanek

Introduction

Three additional soil thermal parameters (moisture, density and heat flux) have recently been added to Argonne's climatological observing program. The temperature of the soil at seven depths below the surface has been continuously measured since November 1952. This long, continuous record of hourly soil temperatures at multiple depths is unique in this country and probably also in the world.

A parameter of considerable interest to meteorologists is the flux of energy between the air and the soil below. The amount of energy passing through a unit area of soil surface in a given time interval can be calculated if the temperature distribution within the soil at the beginning and end of the interval and the heat capacity of soil as functions of depth are known; this technique is known as the temperature-integral method.^(1,2) The heat capacity, as well as the thermal conductivity and thermal diffusivity, of the soil depend on its dry density and water content; the latter can and does vary considerably with depth and time. All of the important thermal properties of soil are strongly controlled by its water content. Hence, the heat storage capacity and surface heat flux cannot be measured with accuracy by this procedure unless the density and moisture profiles are also known.

Until the advent of the atomic era, rapid and accurate procedures for measuring soil moisture and density in situ were lacking. Gravimetric techniques, in which a soil sample of known volume is removed, weighed, dried and reweighed, are laborious and not very accurate, and are destructive in nature. The soil in the hole from which the sample is taken cannot be replaced exactly; this hole permanently modifies the distribution of water and temperature in the nearby soil. This procedure does not permit repeated measurements at a given location. The lack of horizontal homogeneity in the soil could introduce serious errors in studies in which changes of moisture and/or heat content are important since space variation from one sample to the next would be confused with time variations.

Recently, emissions from radioisotopes have been used to measure soil moisture and density in situ without the need for destructive sampling procedures. In order to measure soil moisture, a source of fast neutrons is placed at the desired depth below the surface. These fast neutrons are moderated by the hydrogen molecules in the surrounding soil; some of the thermal (slow) neutrons are scattered back to a detector near the source. The number of counts per unit time from a given source is related to the hydrogen content in a sphere near the source. Most of the hydrogen in the soil (except in the root zone) is in the form of water.

Radioactive techniques are also being used to measure soil density. A source of gamma rays is placed in the soil; a detector which senses only those photons emitted into the soil and reflected back by the orbital electrons in the soil is used to count the returning gamma rays. The count rate is inversely proportional to the moist density of the surrounding medium. The dry density can then be computed with the aid of the soil moisture data.

Soil Moisture Measuring Program

A program to measure soil moisture continuously at three depths by means of radioactive probes was begun in the fall of 1962 and is continuing. In addition, several vertical profiles of soil moisture and density have been made. The depths at which soil moisture is being monitored are one, two and four feet.

The moisture probe selected for use is the P-19 Depth Moisture Gauge made by Nuclear-Chicago Corporation, Des Plaines, Illinois. By means of a stepping switch, a programmer, and a rate meter, all supplied by Nuclear-Chicago, the output of the three probes is recorded on one strip-chart recorder. Each unit contains a 4- to 5-millicurie fast-neutron source of radium-226 and finely ground beryllium in a probe 15 in. long and $1\frac{1}{2}$ in. in diameter. The probe also contains a boron trifluoride gas detector tube and a preamplifier. Each unit is supplied with a lead and paraffin carrying shield for use when the probe is outside the shield. The shield is also used for standardizing measurements. The combined weight of the probe and shield is 46 lbs.

A large number of papers describing this equipment and the results of field operations in construction and agricultural activities has appeared in the literature. A rather complete summary of all techniques for measuring soil moisture, including the neutron method, has appeared recently.⁽³⁾ This report also contains an extensive bibliography. Johnson states that most investigators have reported an accuracy of one to two per cent by volume.

Argonne's soil moisture program is unique in that it is the only installation for the continuous measurement of soil moisture at multiple depths by radioactive techniques.

Soil Density Measuring Program

The soil density sensor selected is a Nuclear-Chicago P-20 Depth Density Gauge which is used with the same rate meter, programmer, access tubes, and recorder as the soil moisture system. The probe is stainless steel, $17\frac{1}{4}$ in. long and $1\frac{1}{2}$ in. in diameter, containing a nominal 13-millicurie cesium-137 source and three Geiger-Muller gamma ray counters. This unit, with its protective lead shield, weighs 50 lbs.

This unit is used only to measure the density profile when desired and is not being used for continuous observation although it is capable of being used in this manner.

The size of the "sphere of influence," the volume of soil measured by the probe, varies inversely with the amount of water (mass for the density probe) near the source. The manufacturer claims that a sphere of 6-in. radius is measured at very high moisture or density and a sphere of about 12-in. at low values. In other words, the method produces an average moisture or density value for a spherical region of variable radius. This characteristic of the probe makes it unsatisfactory for measuring soil conditions above one foot where the largest and most interesting changes occur. Special radioactive probes for surface measurements are available but are not suitable for continuous operation at one location since they cover the soil at the site measured.

Installation of Moisture and Density Probes

In order to raise and lower the probes and to protect them from mechanical damage, an access tube must be placed in the soil. The calibration curves furnished by the manufacturer assume that the tube is 1.625-in. O.D. steel tubing with 0.035-in. walls although other materials may be used with proper calibration.

The access tubes for the Laboratory's soil moisture program were made of cold-drawn seamless steel tubing with the above dimensions. Sharp steel tips were welded to one end and the pipes driven into the ground with an air hammer. It was originally planned to drive one tube to 15 ft, the others to 4 and 6 ft; heavy soil and/or rocks prevented penetration below the 10-ft level in three trials. The access tubes were installed in August 1962 and are located about 250 ft ESE of the Meteorology Building. The tubes are placed in a triangular pattern about 10 ft apart and are near (20 to 30 ft) the soil temperature measuring site. The cable connecting the probes and programmer with the recorder in the Meteorology Building was placed in underground conduit. After considerable testing and some modification of the system, routine observation of soil moisture at three levels was begun on November 15, 1962.

The results of the first eight months of operation will be discussed later. The first impression obtained from use of the equipment is that soil moisture can be measured within the accuracy claimed and that the equipment can be successfully used for continuous operation. The system is not sufficiently accurate to permit calculation of hour-to-hour water uses and for other uses requiring great accuracy. Experience has revealed several inherent difficulties. The first is the need for an access tube, which will, of course, modify the soil density and moisture profile no matter how carefully installed. Two methods for driving the access pipe into the ground are

suggested - with or without first drilling out a hole slightly smaller than the tube. If the pipe is driven without providing at least a partial opening, the soil near the probe will be compacted and will resist penetration. A pre-drilled hole will, in most cases, result in voids near the pipe, which will soon fill with water. Driving a tube of the type recommended with its relatively thin and weak walls into the undisturbed ground leads to practical difficulties.

Another problem is the lack of horizontal homogeneity in the soil. This is quite serious in soils like the glacial till at Argonne. Considerable differences in soil moisture at a given depth are found at the three access tubes, even though they are located only 10 ft apart. These differences are real and are not due to instrumental error, but rather to differences in soil structure, such as stones near the tubes. A third difficulty is the accumulation of water in the access tubes. Even though the tubes are welded closed at the bottom and the tops are sealed with water-proof plastic, sufficient water has accumulated in the probes to influence the readings and necessitate removal of the moisture. Part of the water in the tube is the result of leaks at the upper end around the seal; the rest is due to condensation of moist air on the cold inner surface of the steel. In addition, the counting rate in the detector tube is quite sensitive to the high voltage supplied to it by the rate meter. There are drifts in this circuit, and no provision has been made to check and adjust the high voltage supply and the calibration and zero check circuits in the system automatically. The final intrinsic difficulty is the variable nature of the signal. Despite a 20-sec time constant built into the rate meter, the neutron counting rate varies by as much as ± 5 per cent in the sampling interval of $7\frac{1}{2}$ min. These fluctuations are caused partially by irregularities in the flux of neutrons from the source, random scattering, etc. It is, therefore, necessary to average the counting rate for a period of many minutes to arrive at a representative value.

Preliminary Results with the Moisture Probes

Figure 80 shows the soil moisture content at midnight of the day indicated since observations were begun. Some smoothing of the data was done by eye to eliminate small fluctuations. The large gap in April-May was due to instrument failure and recorder modification. The 24-hr rainfall total for the day is also shown on the chart. The day-to-day changes of soil moisture in the winter are very small. This pattern was present both when the soil was frozen and briefly unfrozen. The 1-ft value increased sharply in mid-March after the frost left the soil permanently. At the two deeper levels, smaller fluctuations were found.

In the summer months, the moisture content at one foot responds most markedly to rainfall amounts larger than 0.50 in., such as on July 13 and 16, 1963. Smaller amounts, such as the 0.27-in. total on June 19, 1963

Figure 80

Soil moisture and precipitation at the Argonne National Laboratory November 1962 - July 1963

and the 0.28 in. on June 27, 1963, do not change the moisture content at the 1-ft level. The curves do show the drought period in June and July and the recharge of the soil moisture after the heavy rains of mid-July.

The moisture content at a given depth in a given hole as measured by each of the three probes are in reasonable, but not exact, agreement. However, it was found that large differences in moisture are found at the different locations at one depth. Table 36 shows results of four such sets of measurements. This table indicates the instruments require careful calibration and further testing. The table also indicates that the differences between holes are real; the suggested cause is lack of homogeneity in the soil. This lack of uniformity complicates the analysis problem.

Table 36

Soil moisture in per cent as measured at a given depth
in each access tube by each of the three probes

Probe	Access tube			Date and depth
	A	B	C	
1	30.5	23.5	27.5	Aug. 30, 1962 3 feet
2	30.5	23.5	27.0	
3	30.0	23.0	28.0	
1	29.0	21.5	26.0	Sept. 10, 1962 1 foot
2	29.0	21.5	28.0	
3	30.0	22.5	26.5	
1	28.5	28.0	28.0	July 24, 1963 1 foot
2	30.0	30.0	29.5	
3	31.5	31.5	28.5	
1	31.0	30.0	30.5	July 25, 1963 2 feet
2	31.0	32.0	32.5	
3	33.0	33.5	33.0	

Figure 81 shows the vertical profile of soil moisture on two separate occasions. Both profiles were made in the same tube with the same probe. On August 15, 1962, the surface soil was very dry, while the July 23, 1963 situation shows the soil profile after the heavy rains of mid-July. These profiles show that the water capacity of the soil varies with depth, being larger in the 2- to 3-ft layer than above or below.

A typical soil density profile is shown in Figure 82. This figure shows that the wet density increases rapidly with depth to about $3\frac{1}{2}$ ft, then remains essentially constant with depth.

Figure 81

Soil moisture profiles

Figure 82

Soil density profile, October 2, 1962

Soil-Heat Flux Program

The simplest, most direct and probably most accurate method of measuring heat flux in the soil is by means of a heat-flux transducer. This sensor consists of a thermopile imbedded in a thin plastic plate which is placed horizontally in the soil at the depth of measurement. The thermopile measures the temperature difference across the plate. Since the thickness and conductivity of the plate are known, the heat conducted through the plate can be easily computed and is assumed to be equal to that in the surrounding soil.

Five heat-flux plates have been installed at Argonne near the soil-temperature thermometers. The sensor selected is the Beckman & Whitley heat-flow transducer designed specifically for the soil, Model ST 201-1. This element is $3 \frac{3}{8}$ in. $\times$ $1 \frac{1}{8}$ in. $\times$ $\frac{3}{64}$ in. thick and is composed of 400 silver-constantan thermocouples in a phenolic resin plate. The element also contains a thermocouple to measure the temperature of the plate itself as the output of the plate varies with temperature. A complete description of the element, as well as other techniques for measuring soil heat flow, has been given by Lettau and Davidson.⁽⁴⁾ The first of the major difficulties in using these plates is installing the plate in the soil with a minimum disturbance of the surrounding soil and with good thermal contact between the plate and soil. The other is providing perfect electrical insulation in the element itself.

In order to install the measuring elements, it was necessary to dig a pit about the size of a 3-ft cube near the soil-temperature sensors. A soil scientist from the University of Illinois took several soil samples from this pit on April 11, 1963, just before the probes were inserted. The results of the analyses of these samples have not been received, as yet; but they will add to the usefulness of our soil thermal and moisture data. The 1-cm level probe was installed by removing a section of grass, leveling the soil, laying the element and then recovering the area with grass. The other four levels (10, 20, 50 and 100cm) were installed in a different manner. A sharp steel plate, the width and thickness of the sensor, was driven horizontally into the relatively undisturbed soil at the edge of the pit at the desired depths. The soil in the pit was carefully replaced, with lead-in wires kept at the depth of observation for several feet. The signal wires were brought to a recorder in the Meteorology Building by means of underground conduit. This method of installation places the measuring elements in the soil with the least possible change of soil structure, compaction, and density and allows a good thermal contact between the soil and transducer. This method is, of course, not completely satisfactory since the moisture, density, and thermal patterns are altered by the refilled pit.

Routine observations of soil heat flux were begun in April 1962. Beginning some time in August 1963, the output of the sensors will be processed automatically and punched on paper tape, once each hour at each of the five depths by means of the equipment listed below. The output at one level only was recorded without automatic processing between the time of installation and July 26, 1963. This interval allowed the soil at the measuring site to settle and tend to revert to a state more nearly that of the undisturbed soil.

Figures 83 and 84 show the flux of heat energy at two depths on different days. The first of the two shows the heat flux at 1 cm on June 2, 1963,

Figure 83
1-cm Heat flux,
June 2, 1962

Figure 84

20-cm Heat flux, June 15, 1963

a mostly sunny, warm day with daytime fair-weather cumulus. The maximum temperature on the 2nd was 87°F. The second diagram shows the heat flow at 20 cm on June 15, 1963. The skies were mostly clear during the early morning hours with cumulus clouds covering more than half of the sky for the remainder of the day. The highest temperature was 71°F. A study of the heat-flux charts shows that the flux at 1 cm follows changes in net radiation quite rapidly. These fluctuations are less pronounced at 10 cm and are not present at 20 cm. No daily pattern is detectable at the 50- and 100-cm depths.

Modification of the Soil Climatology Program

Before the new equipment listed above was received, the Automatic Meteorological Data Processing System⁽⁵⁾ was used to list the temperature of the soil at seven depths below the surface (1, 10, 20, 50, 100, 305 and 884 cm) on punched paper tape every hour. The signals from the soil heat flux and moisture sensors are being incorporated into this system. The equipment to process automatically these new data is being installed at the time of writing.

It was also decided to expand the soil temperature program to include four new values, which will also be included in the data-processing system - air temperature 5.5 ft above the ground and the temperature of the soil at 1 cm below the ground surface under three different types of cover (bare black soil, bare white sand, and Kentucky blue grass). These new values will be measured with the same type of sensor as in the original soil temperature system, 100-ohm copper resistance bulbs called Thermohms and manufactured by Leeds & Northrup. Measurements at 1 cm below pasture grass have been made for over 10 years; the new soil probes are to illustrate the effect of variable soil colors and covers. The air temperature will be useful for comparing air and soil conditions.

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