

## Bioelectric Pyroelectricity

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### INTRODUCTION

The pyroelectric effect has been observed in mineral crystals such as tourmaline since antiquity, and in hundreds of natural and artificial crystals, ceramics, and polymers during the past century (1). However, its existence in biological materials was unknown until 1966 when Lang (2) first reported measurements of it in animal bone and tendon. Since then, its presence has been demonstrated in many animal and plant tissues. Most of the data are qualitative, but they are sufficient to establish the generality of the phenomenon in living tissues. The unique association of pyroelectricity with a vectorial electric polarization, and the high probability of the existence of the long-range ordering characteristics of ferroelectricity suggest that the presence of pyroelectricity may have a profound influence on the processes of life.

This chapter is written to introduce the reader to the fundamentals of the pyroelectric phenomenon, to describe the research that has been carried out on biomaterials, and to present an overview and some suggestions for future research.

### FUNDAMENTALS OF PYROELECTRICITY

The characteristics of pyroelectricity and related effects presented here are relevant to both nonbiological and biological materials. A more detailed treatment can be found elsewhere (1, 3, 4).

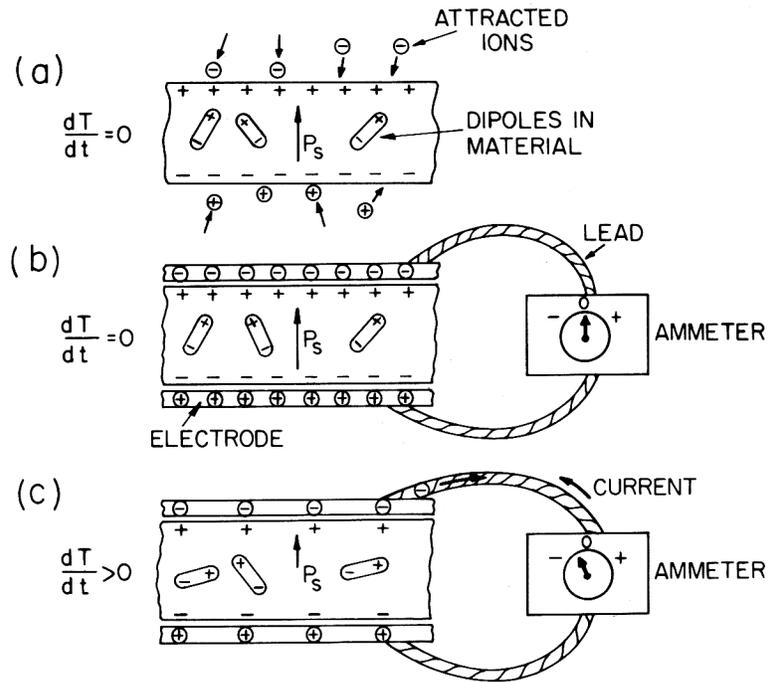
#### PYROELECTRICITY AND CONDITIONS FOR ITS EXISTENCE

Pyroelectricity is rigorously defined as the manifestation of the temperature dependence of the spontaneous polarization of certain anisotropic solids. The precise meaning of this definition will be clarified by means of a simple physical example which illustrates the character of the effect. Let us consider a thin parallel-sided sample of a pyroelectric material, such as a crystal of the mineral tourmaline or a disk of poled barium titanate ceramic, cut so that its crystallographic symmetry axis is perpendicular to the flat surfaces. The molecular subunits of the material have a dipole moment. The crystallographic symmetry of a pyroelectric material dictates that the unit dipoles pack in such a way that the components of these dipole moments in the direction normal to the

flat surfaces are additive rather than self-cancelling. The dipole moment per unit volume of the material is called the spontaneous polarization  $P_s$ . This quantity is always nonzero in a pyroelectric material, and it exists in the absence of an applied electric field. The spontaneous polarization is equivalent to a layer of bound charge on each flat surface of the sample. The amount of charge per unit area is given by

$$Q/A = |P_s| \quad (1)$$

If the sample is suspended in the atmosphere, free charges (electrons or ions) will be attracted and adhere to the material, as illustrated in Figure 1(a).



**Figure 1.** (a) Pyroelectric sample with spontaneous polarization and equivalent bound charges, and free charges attracted from its surroundings. (b) Sample with electrodes showing compensating free charges. (c) Charge distribution and current during increase in temperature.

Conductive electrodes may be applied to the flat surfaces and interconnected by an ammeter having zero internal resistance (Figure 1(b)). If the temperature of the sample is constant,  $P_s$  does not change and no current flows in the external circuit. A change in temperature will cause the spontaneous polarization to change. In most single crystals and ceramics, an increase in temperature causes the dipole moments and, consequently, the spontaneous polarization to decrease. (In pyroelectric polymeric materials such as polyvinylidene fluoride, an increase in temperature causes an increase in separation of centers of positive and negative charge, leading to an increase in the spontaneous polarization.) The quantity of bound charge then decreases, and the free charges are

redistributed to compensate for the change in bound charge resulting in a current flow in the external circuit (Figure 1(c)). The pyroelectric current  $I$  is given by

$$I = pA d\theta/dt \quad (2)$$

where  $d\theta/dt$  is the rate of change of temperature, and  $p$  is the pyroelectric coefficient. Rigorously, the pyroelectric coefficient is defined by

$$\bar{p} = (\partial \bar{P}_s / \partial \theta) \quad (3)$$

The partial derivative in Equation (3) is taken under the constraints of constant electric field and constant elastic stress. Both  $\bar{p}$  and  $\bar{P}_s$  have the mathematical character of vectors or first-rank tensors. However, only the components of the vectors that are normal to the electrode surfaces will be considered in this chapter, and the quantities will therefore be written as scalars. If the sample had been cooled instead of heated, the signs of both the temperature derivative and the current in Equation (2) would have been reversed. It is important to note that the pyroelectric effect is only observable during the period in which the temperature is changing, either increasing or decreasing.

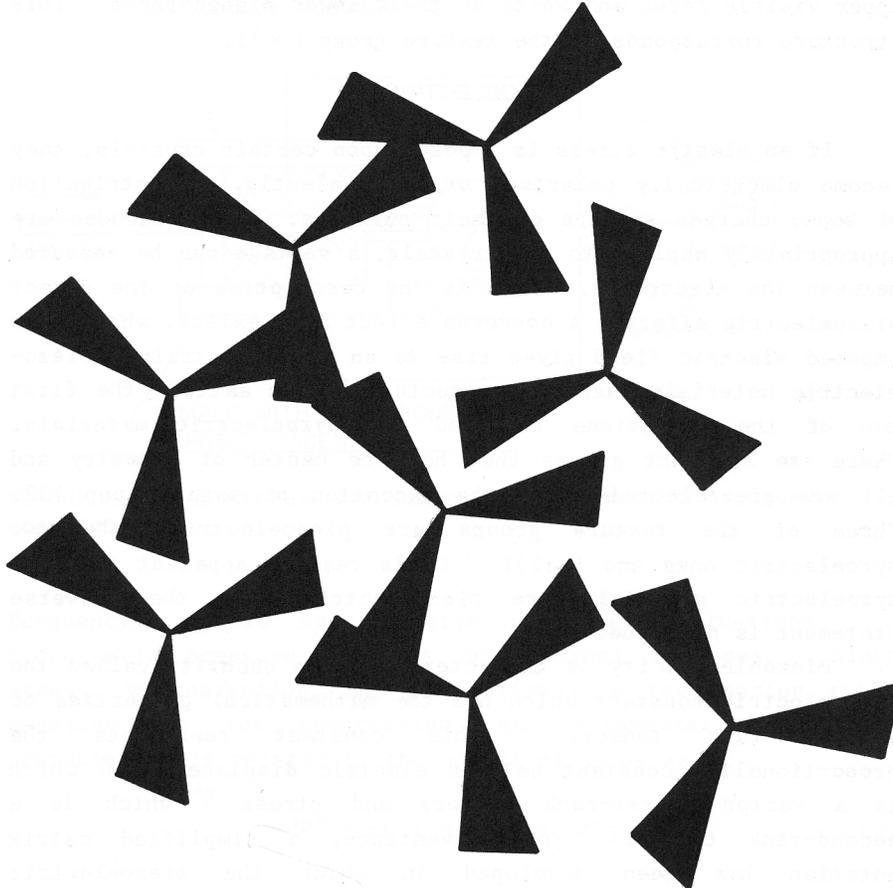
The existence of the pyroelectric effect in any solid material requires that three conditions must be satisfied: (a) the molecular structure must have a nonzero dipole moment; (b) pyroelectric substances must have no center of symmetry; and (c) pyroelectric substances must have either no axis of rotational symmetry, or have a single axis of rotational symmetry that is not included in an inversion axis.

Of the 32 crystal point-group symmetries (also called crystal classes), only ten permit the existence of pyroelectricity. These groups are: the triclinic group, 1; the monoclinic groups, 2 and  $m$ ; the orthorhombic group,  $mm2$ ; the tetragonal groups, 4 and  $4mm$ ; the trigonal groups, 3 and  $3m$ ; and the hexagonal groups, 6 and  $6mm$ .

The symmetry characteristics of biological pyroelectric materials can often be described in terms of texture point groups, as originally developed by Shubnikov et al. (5). The textures considered here consist of aggregates of crystallites randomly arrayed in a plane, but possessing elements of order in a direction normal to that plane. Of the seven texture groups described by Shubnikov, two groups  $(\infty)T$  and  $(\infty \cdot m)T$ , satisfy the symmetry requirements above, and thus may exhibit pyroelectricity. These groups possess, as elements of symmetry, an infinite-fold rotational axis and an infinite-fold rotational axis at the intersection of an infinity of mirror planes, respectively.

Bone is an example of a biological material describable by means of a texture group. The analysis is based on a consideration of both the molecular structures of the principal components and the histological character of osteons and interstitial lamellae. The major solid components of bone are the crystals of hydroxyapatite and the reinforcing collagen protein fibers. Hydroxyapatite has the centrosymmetric point group  $6/m$  (6) and is not

pyroelectric. Collagen has the point group 3 which has a threefold rotational axis as its single element of symmetry (7), and thus it is pyroelectric. The long collagen fibers are oriented with their rotational axes parallel to the bone axis but rotated in a random fashion in the bone transverse plane. This pattern is depicted schematically in Figure 2, in which it is assumed that the symbols are colored black on their upper visible faces and white on their lower hidden faces. This structure corresponds to the texture group  $(\infty)T$ .



**Figure 2.** Texture group  $(\infty)T$  consisting of subunits having point group 3 symmetry (8). The figures are assumed to be black on their visible surfaces and white on their hidden surfaces.

### PIEZOELECTRICITY

If an elastic stress is imposed upon certain crystals, they become electrically polarized or, equivalently, a distribution of bound charges appears on their surfaces. If electrodes are appropriately applied to the crystals, a voltage can be measured between the electrodes. This is the description of the direct piezoelectric effect. A converse effect also exists, whereby an imposed electric field gives rise to an elastic strain. Piezoelectric materials must have structures which satisfy the first two of the conditions required for pyroelectric materials. There are 21 point groups that have no center of symmetry and all

are piezoelectric with the exception of point group 432. Three of the texture groups are piezoelectric, the two pyroelectric ones and  $(\infty:2)T$ . It is readily apparent that all pyroelectric materials are piezoelectric, but the converse statement is not true.

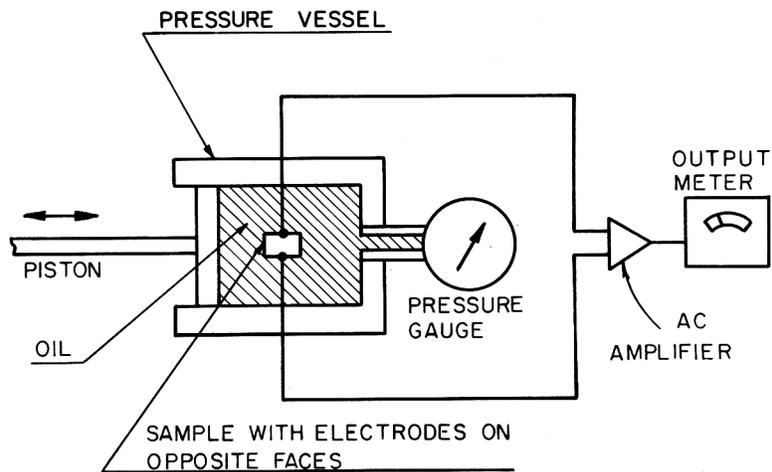
Piezoelectricity is characterized by a quantity called the piezoelectric constant which has the mathematical properties of a third-rank tensor. This constant represents the proportionality constant between electric displacement  $\vec{D}$  which is a vector (first-rank tensor) and stress  $\vec{T}$  which is a second-rank tensor. For convenience, a simplified matrix notation has been developed in which the piezoelectric coefficient  $d$  is given by a  $3 \times 6$  matrix and the stress by a  $1 \times 6$  vector, as follows:

$$dD_i = d_{ij}dT_j \quad (i = 1,2,3; j = 1,2,\dots,6) \quad (4)$$

The 1, 2, and 3 components of the stress are normal stresses parallel to the  $x_1$ ,  $x_2$ , and  $x_3$  crystallographic axes, and the 4, 5, and 6 components are shear stresses.

Piezoelectric effects in biological materials are beyond the scope of this chapter, with the exception of one special case. A hydrostatic piezoelectric response can be produced by placing a small electroded sample in an oil-filled cell which is closed by piston (Figure 3). The piston can be driven at a low frequency, say 20 Hz, to give pressure fluctuations. A hydrostatic pressure produces only normal stresses. Since stress, by convention, has a positive sign for tension and a negative one for compression, an incremental hydrostatic pressure  $dP^h$  is related to the normal stresses as

$$dP^h = -dT_1 = -dT_2 = -dT_3 \quad (5)$$



**Figure 3.** Apparatus for measuring hydrostatic piezoelectric coefficients.

Equation (4) can then be written in the form

$$\begin{aligned}
 dD_1 &= -(d_{11} + d_{12} + d_{13})dP^h = -d_1^h dP^h \\
 dD_2 &= -(d_{21} + d_{22} + d_{23})dP^h = -d_2^h dP^h \\
 dD_3 &= -(d_{31} + d_{32} + d_{33})dP^h = -d_3^h dP^h
 \end{aligned} \tag{6}$$

The quantities  $d_i^h$  are called the hydrostatic piezoelectric coefficients. It can be shown that they have the symmetry characteristics of a vector, just as do the pyroelectric coefficients. Thus a hydrostatic piezoelectric effect can only exist in a material having one of the ten polar point groups or two polar texture groups. A hydrostatic piezoelectric effect can be observed in tourmaline which is also pyroelectric, but not in quartz which is piezoelectric but not pyroelectric. The existence of a hydrostatic piezoelectric effect is proof that the material is pyroelectric.

### ELECTRETS

An electret is a dielectric material that produces an external electric field which results from an ordering of molecular dipoles, or uncompensated surface or space charges. The dipole ordering or the introduction of charges may produce either permanent or transient structural changes. However, if the changes are transient, they must decay at a rate which is slow relative to the duration of the measurements made on the dielectric. The presence of the dipoles or charges will often permit the existence of pyroelectricity and piezoelectricity, so that pyroelectrics and piezoelectrics might be considered as subgroups of electrets. Electrets have been produced by a number of different techniques: dipole ordering by means of imposed electric fields at elevated temperatures, excitation of space charge by photoeffects and rearrangement of the charge distribution with an applied electric field, and implantation of electric charge by electron irradiation or corona charging processes. Several authors have explained biological pyroelectric effects by means of an electret model, as discussed later in this chapter.

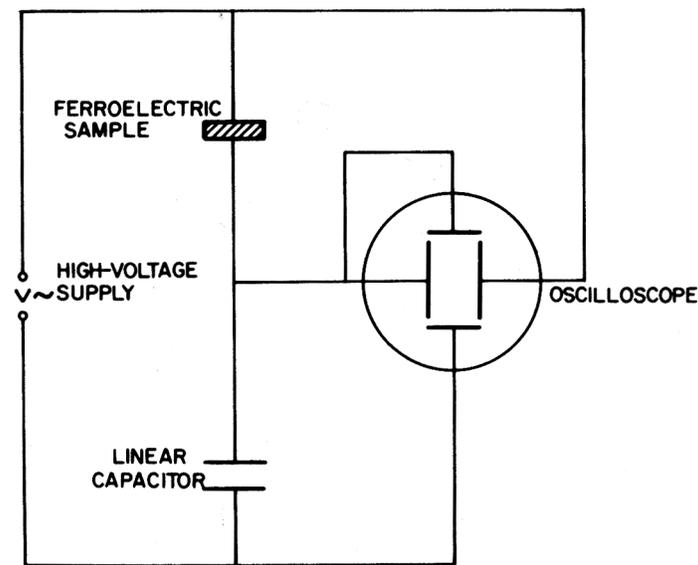
### FERROELECTRICITY

A polar material whose electric dipoles can be reversed in direction by means of an electric field is defined as ferroelectric. Ferroelectric materials form a subgroup of pyroelectric materials. Some evidence has been found for ferroelectricity in various biomaterials, as described later in this chapter.

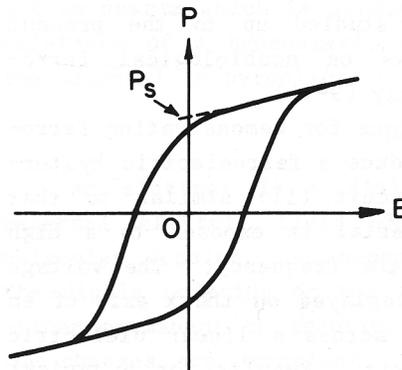
Ferroelectric materials usually, but not always, exist in a nonpolar (paraelectric) state above a temperature known as the Curie point. Their dielectric constants are usually anomalously large and highly temperature dependent, especially in the region of the Curie point. At one time, ferroelectricity was thought to be quite rare, but it is now considered to be one of the commonest cooperative phenomena in nature. More than 1000 ferroelectric materials have been studied up to the present time. Several

comprehensive books on nonbiological ferroelectrics have been published recently (9-11).

The most frequently used technique for demonstrating ferroelectricity in a material is to produce a ferroelectric hysteresis loop using a Sawyer-Tower circuit (9) similar to that shown in Figure 4. The test material is exposed to a high alternating voltage, typically at line frequency. The voltage drop across the test material is displayed on the x axis of an oscilloscope, and the voltage drop across a linear dielectric capacitor is displayed on the y axis. Results for a typical ferroelectric are illustrated in Figure 5. The spontaneous polarization is calculated by means of the construction shown. It is difficult, but possible, to determine  $p$  from the temperature dependence of  $P_s$  using Equation (3).



**Figure 4.** Sawyer-Tower hysteresis loop circuit.



**Figure 5.** Polarization versus applied electric field for a ferroelectric, showing the calculation of the spontaneous polarization.

Ferroelectric hysteresis loops have been determined on several very interesting biomaterials, as discussed later. However, unless precautions are taken, it is possible to get results similar to those of Figure 5 using nonlinear, nonferroelectric, conductive dielectrics. As a result, all claims of observed ferroelectricity in biomaterials are still quite controversial.

#### TECHNIQUES FOR MEASURING THE PYROELECTRIC EFFECT

A number of techniques have been used for quantitatively measuring the pyroelectric effect. The three described below have been used for testing biomaterials.

##### 1. Static Method

The static method was used in studies of biomaterials by Lang (2) and Liboff and Furst (12). It is based on a technique developed by Lang and Steckel (13). It is the only one of the methods capable of giving absolute values of the pyroelectric coefficient without a calibration or additional measurement.

$$p = V/AR(d\theta/dt) \quad (7)$$

where  $A$  is the area of an electrode and  $d\theta/dt$  is the time derivative of the temperature change. Alternately, if the current  $I$  is measured, the following equation is used:

$$p = I/A(d\theta/dt) \quad (8)$$

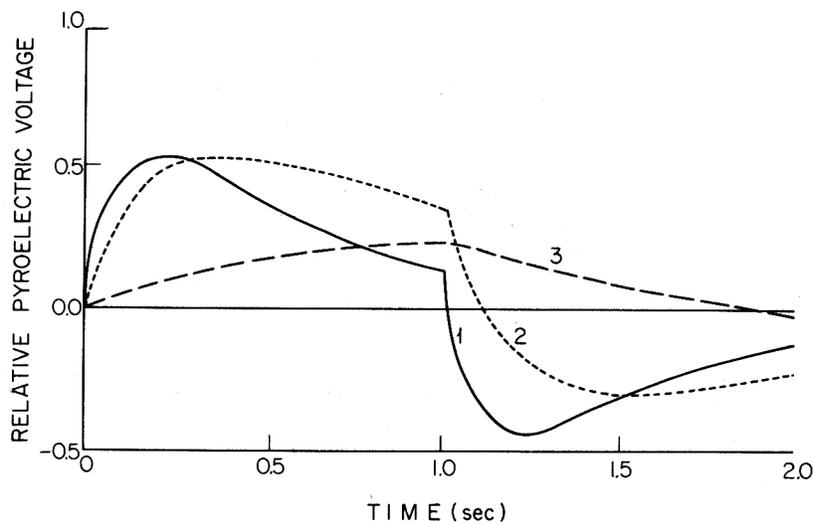
A third modification uses a charge amplifier as a measuring instrument. Then the charge  $Q$  produced during a change in temperature  $\Delta\theta$  is related to  $p$  by

$$p = Q/A\Delta\theta \quad (9)$$

The method is subject to two major sources of error: (1) steady or slowly varying voltages or currents are produced by many dielectrics, even when the temperature is held constant, and (2) voltages or currents can result from a varying nonuniform temperature distribution. The former error can be corrected by subtracting the voltage or current produced at constant temperature as measured either before or after a run. The latter error is known as the tertiary pyroelectric effect (1). It can be observed in any piezoelectric material, not only the pyroelectric ones. It can best be avoided by using thin samples, taking care in mounting them with respect to heating elements, and not using excessively large heating or cooling rates. The precautions of reversing the leads from the sample to the measuring instrument, making both heating and cooling runs, and trying several types of electrode materials are also advisable.

## 2. Rectangular Pulse Heating Method

The rectangular-pulse heating technique has been used extensively in recent years. It was first quantitatively analyzed by Shaulov and Simhony (14). In this method, samples cut in the form of thin plates are electroded and then connected to an electrometer or charge amplifier. A light beam from a xenon or argon lamp is focused on the sample, and the beam is broken into rectangular pulses by means of a photographic shutter or a light chopper. The output voltage of the amplifier may be displayed on an oscilloscope. Shutter speeds of 0.01–1 sec or chopping rates of 1–100 Hz are generally used. Rectangular pulse-heating of a pyroelectric material produces a characteristic pyroelectric signature, some examples of which are shown in Figure 6. The quasi-symmetric character of the heating and cooling curves should be noted.



**Figure 6.** Calculated responses of a typical pyroelectric material to rectangular heat pulses (according to Equation (10)). Heat pulse was initiated at 0 seconds for a duration of 1 second. The thermal and electrical time constants (in seconds), respectively, were (0.1, 0.1), (1.0, 0.2), (2.0, 1.0) for curves 1–3 respectively.

The analysis (14) shows that the voltages rise at an exponential rate determined by the electrical time constant of the system, and fall at a rate set by the thermal time constant. Mathematically, the voltage is given by

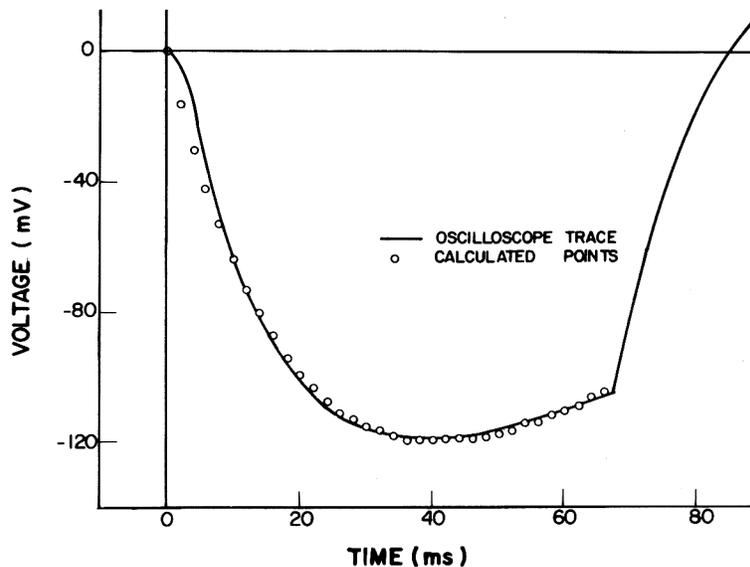
$$V = V_0 [\exp(-t/\tau_T) - \exp(-t/\tau_E)] \quad (10)$$

where

$$V_0 = PA^2 F_0 / CC_T [(1/\tau_E) - (1/\tau_T)] \quad (11)$$

The parameters in Equation 10 are:  $\tau_T$ , thermal time constant ( $= C_T/G_T$ );  $\tau_E$ , electrical time constant ( $= RC$ );  $F_0$ , thermal heat flux absorbed;  $C$ , capacitance of sample and

measuring circuit;  $C_T$ , thermal mass of sample;  $G_T$ , thermal conductance for heat loss of sample;  $R$ , electrical resistance of sample. The other parameters have been defined previously. The parameter of primary interest is the pyroelectric coefficient. The two time constants, although often measured, are not of fundamental importance. The electrical time constant is usually determined by the value of the amplifier shunt resistance, and the thermal time constant depends upon the mounting of the sample. It is often helpful to vary the electrical time constant with various shunt resistors, but only in order to verify that it is actually the pyroelectric effect that is being measured. The initial slope, maximum voltage, and the time to reach maximum voltage can be used to determine  $V_0$ ,  $\tau_E$ , and  $\tau_T$ . These three values can be determined even more accurately by using a nonlinear least-squares curve-fitting technique to match Equation (10) to the experimental data. This is illustrated in Figure 7 from Lang and Athenstaedt (15).



**Figure 7.** Oscilloscope trace of the response of a pyroelectric sample to a 1/15 second duration rectangular light pulse (15). The function which fits the data best in the sense of least squares was  $V = -0.777 [\exp(-t/0.0328) - \exp(-t/0.051)]$ .

This method yields only relative values of  $p$  unless the absorbed thermal flux is known. It can be calibrated by use of a test material whose properties have been previously measured such as tourmaline. However, corrections must be introduced for the differences in the thermal and electrical properties of the two materials.

### 3. Dielectric Heating Method

One of the difficulties in the two previous methods is that the temperature distribution in the sample may not be uniform. This can be largely overcome by a technique utilizing dielectric heating recently reported by Sussner et al. (16). He used a 500-kHz 20-msec pulse whose energy was uniformly absorbed in the sample, rapidly

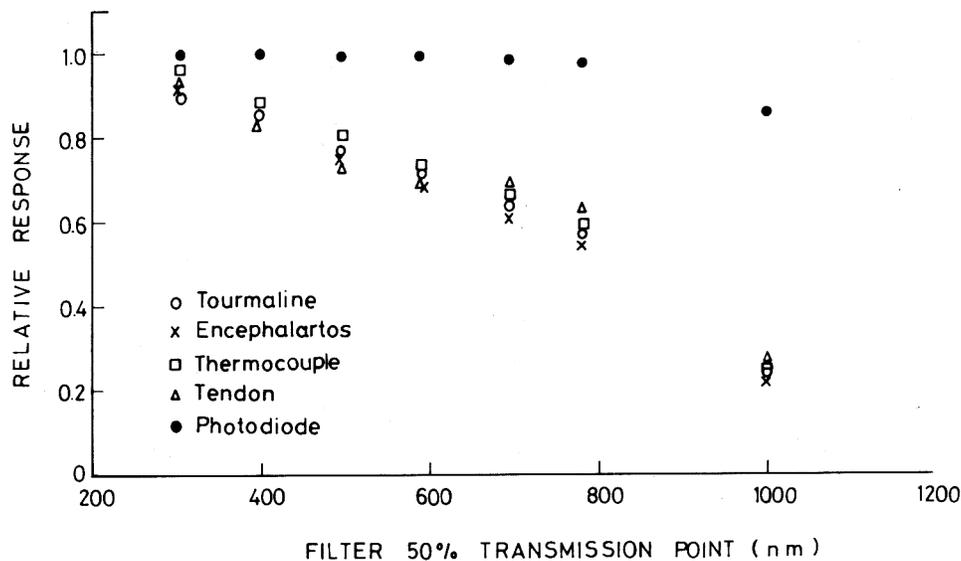
raising its temperature. The process is especially efficient in biological specimens because of their high electrical loss tangents.

If the loss tangent of the material is known independently as well as its density, heat capacity, and dielectric constant, it is possible to calculate the temperature increase. Thus, a quantitative value of the pyroelectric coefficient can be obtained without the need for temperature measurement. Furthermore, the rate of change of temperature is very great, yielding readily measureable voltages with small pyroelectric coefficients.

## STUDIES OF BIOLOGICAL MATERIALS

### PYROELECTRIC NATURE OF ELECTRICAL RESPONSES

A number of different artifacts may be confused with a true pyroelectric response, including dielectric absorption currents, thermally stimulated discharge currents, various electrochemical effects, and photocurrents. To prove that bovine tendon and the leaf of the *Encephalartos villosus* gave pyroelectric responses upon heating, Lang and Athenstaedt (15, 17) performed the following experiment. Samples of tendon and *Encephalartos*, a tourmaline crystal, a copper-constantan thermocouple, and a silicon photodiode, were in turn exposed to rectangular pulses of filtered light from a xenon lamp. The filters were a series with 50% transmission points ranging from 305 to 1000 nm. The light was absorbed on each sample by a layer of silver paint. The electric charges produced by the tendon, *Encephalartos*, and tourmaline, and the voltages from the thermocouple and photodiode were measured. The relative responses are graphed versus the 50% transmission points in Figure 8. According to Equation (9), the responses of the pyroelectric materials should be proportional to the change in temperature, which is also the case with regard to the response of the thermocouple. The relative responses of these four items clearly diminished with increased filter opacity, whereas the photodiode, which responds to red and near infrared radiation, had a nearly constant output. The correspondence of the behavior of pyroelectric materials to the phenomenological theory was thus demonstrated.



**Figure 8.** Effects on pyroelectric and photoelectric materials of optically absorbing the shorter wavelengths of light (15, 17).

#### ANIMAL TISSUES

The first report of an observation of the pyroelectric effect in a biomaterial was made by Lang (2) in 1966. He examined bovine femur and phalanx bones and hoof tendon. The bone samples were degreased, and disk-shaped specimens 6 mm in diameter and 3 mm in thickness were prepared and oven-dried at 50–150°C. The tendon specimens were dehydrated in absolute alcohol and then dried. After drying, all samples had resistances greater than  $10^{14} \Omega$ . Several phalanx disks were demineralized in 2%  $\text{HNO}_3$ , which dissolved about 75 wt-% of the samples. Either silver paint or colloidal graphite electrodes were used. No effects due to differences in the electrodes were observed. The static method of measurement was used, utilizing a platinum resistance thermometer for temperature sensing and a vibrating-reed electrometer shunted with a  $10^{10} \Omega$  resistor. The sample holder was heated or cooled at temperature rates as great as 14°K/min. The pyroelectric coefficients in samples cut with electrodes normal to the bone or tendon longitudinal axis are given in Table 1. No pyroelectric effect was observed in any sample cut with electrodes parallel to the axis. The pyroelectric coefficients were only slightly greater than the noise level of the system, accounting for the large standard deviations. The pyroelectric coefficient of the demineralized bone (based on the area of the sample before demineralization) had the same magnitude as those of the untreated specimens. The tendon, which is almost pure collagen, had a slightly larger pyroelectric effect. The results definitely indicate that pyroelectricity, like piezoelectricity, is due to the protein rather than the mineral component of bone.

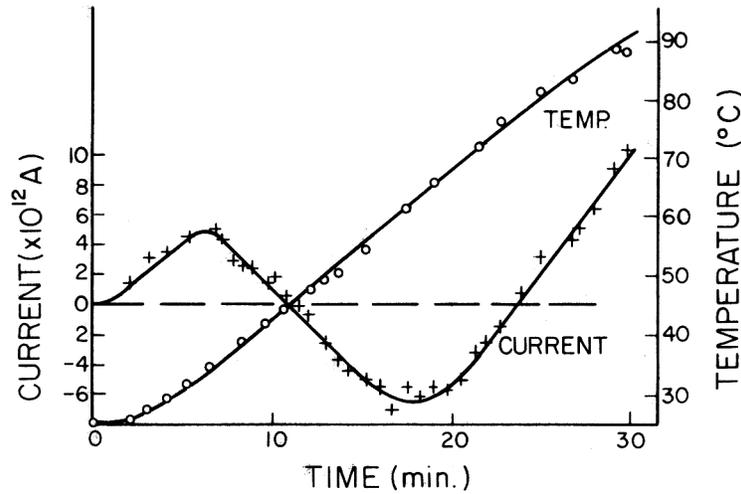
**Table 1.** Pyroelectric Coefficients (at constant stress) of Bovine Bone and Tendon (2)

<b>Materials</b>	<b>Temperature Range</b>	<b>Pyroelectric Coefficient and Standard Deviation (<math>\mu\text{Cm}^{-2}\text{K}^{-1}</math>)</b>
Phalanx	-35 to 55	$0.0025 \pm 0.0018$
Demineralized phalanx	-35 to 60	$0.0038 \pm 0.0018$
Femur	-25 to 60	$0.0036 \pm 0.0021$
Hoof tendon	-35 to 85	$0.0041 \pm 0.0024$

Liboff and Furst (12) conducted similar experiments with bovine femur. In some tests, they found that the logarithm of the pyroelectric current varied inversely with the reciprocal of the absolute temperature, with a change in slope at the 200°C denaturation point. If the current obeys an Arrhenius relation of the form

$$I = I_0 \exp(-\Delta\varepsilon/k\theta) \quad (11)$$

where  $k$  is the Boltzmann constant, then the activation energy  $\Delta\varepsilon$  was 0.6 eV below the denaturation point and 1 eV above it. Similar anomalous behavior was noted in the vicinity of the 160°C denaturation point of bovine Achilles tendon. In other experiments on bovine femur, pyroelectric currents that exhibited extremes and even reversals in sign were observed (Figure 9). No detailed explanations were given, although the possibility of electret behavior was suggested. A very brief description of a pulsed infrared CO<sub>2</sub> laser measurement technique was given. In a later abstract, Furst and Liboff (18) described successful application of the technique. Pulses of 250 nsec at a level of 0. J impinged upon samples of various collagenous materials. A rapid initial rise in electric signal due to the pyroelectric effect followed by an oscillatory ringing due to a piezoelectric effect was observed.



**Figure 9.** Reversal of sign of pyroelectric current (12).

The origin of the pyroelectricity in a material can often be better understood by decomposing the pyroelectric coefficient into two parts. As defined in Equation (3), the change in spontaneous polarization is measured under the constraint of constant stress. Instead of maintaining constant stress while the temperature is changed, the material, in principle, could be rigidly clamped so that expansion or contraction is not possible (constant strain). The change in electric displacement per unit temperature change at constant strain is called the primary pyroelectric coefficient. Then the material is released and allowed to deform. The new change in displacement per unit temperature change is the secondary pyroelectric coefficient. The conventionally measured total pyroelectric coefficient is the sum of the two. Mathematically, the pyroelectric coefficient is decomposed as follows:

$$P_i^T = P_i^S + d_{ijk}^\theta C_{jklm}^{E,\theta} \alpha_{lm}^E \quad (12)$$

Total                  Primary                  Secondary

Here the subscripts are the tensor indices and the superscripts indicate constraints of constant stress ( $T$ ), strain ( $S$ ), temperature ( $\theta$ ), and field ( $E$ ). Parameters not previously defined are the elastic stiffness coefficients ( $c$ ) and the thermal expansion coefficients ( $\alpha$ ). Readers unfamiliar with the notation should consult Nye (4) or Mason (3).

The only separation of the primary and secondary components for a biological material was carried out by Lang (19). Equation (12) was expanded using the symmetry characteristics of texture group  $(\infty)T$  to give

$$P_3^T = P_3^S + 2d_{31}(c_{11} + c_{12})\alpha_1 + 2d_{31}c_{13}\alpha_3 + 2d_{33}c_{13}\alpha_1 + d_{33}c_{33}\alpha_3 \quad (13)$$

The primary pyroelectric coefficient cannot be measured directly because rigid clamping is experimentally impossible. Instead it must be calculated from Equation (13). The experimental parameters used and the calculated results are listed in Table 2. The sign convention used was that the positive direction of the  $x_3$  axis was toward the proximal end of the bone. It is interesting to note that the primary and secondary components have opposite signs but that the contribution of the secondary effect is the dominant one.

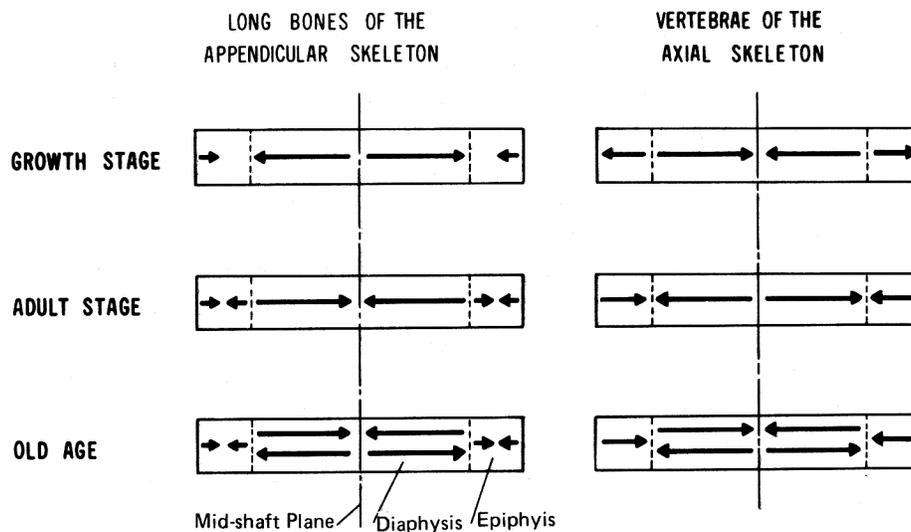
**Table 2.** Calculation of Primary and Secondary Pyroelectric Coefficients of Bovine Phalanx Bone

Parameter	Value	Reference
$p_3^T$	$0.0025 \mu\text{Cm}^{-2}\text{K}^{-1}$	(2)
$d_{31}$	$0.0033 \text{pCN}^{-1}$	(20)
$d_{33}$	$0.0033 \text{pCN}^{-1}$	(20)
1	$30 \times 10^{-6}\text{K}^{-1}$	(19)
3	$18 \times 10^{-6}\text{K}^{-1}$	(19)
$c_{11}$	$2.12 \times 10^{10}\text{Nm}^{-2}$	(21)
$c_{12}$	$0.95 \times 10^{10}\text{Nm}^{-2}$	(21)
$c_{13}$	$1.02 \times 10^{10}\text{Nm}^{-2}$	(21)
$c_{33}$	$3.74 \times 10^{10}\text{Nm}^{-2}$	(21)
$p_3^S$ (calculated primary)	$-0.0092 \mu\text{Cm}^{-2}\text{K}^{-1}$	(19)
$p_3^T - p_3^S$ (calculated secondary)	$0.0117 \mu\text{Cm}^{-2}\text{K}^{-1}$	(19)

A comprehensive program of polarization studies on animal tissues was carried out by Athenstaedt, resulting in a series of more than 10 papers published in 1967–1974 (22–33). Tissues from a large number of animal species were examined. The major objective was to study the direction of spontaneous polarization in the tissues as a function of species and age of the animal. The orientation of the spontaneous polarization is uniquely related to the orientation of the pyroelectric vector as shown by Equation (3). Thus the pyroelectric vector clearly relates the orientation of the spontaneous polarization to the histology. However, Athenstaedt attempted to characterize the orientation of the spontaneous polarization by means of the hydrostatic piezoelectric coefficient. These two do not necessarily have the same sign, and, therefore, the vectors may be either parallel or antiparallel. As a result, the existence of a hydrostatic piezoelectric effect confirms that the spontaneous polarization is nonzero, but is ambiguous concerning its orientation. Because the term “electric polarization” in these papers (22–33) is not the same as “spontaneous polarization,” we will refer to it in this chapter as “hydrostatic piezoelectric polarization” ( $d^h$  polarization).

Athenstaedt's results have some very interesting physiological implications. However, it is highly recommended that these data be verified by a more conventional measuring technique before further interpretation is made. The major results can be summarized as follows:

1. All the collagenous tissues tested exhibited a hydrostatic piezoelectric polarization in the axial direction and occasionally in a radial direction. Some chitin-and keratin-containing tissues also had a dh polarization.
2. The directions of dh polarization were different in the epiphyses (end sections) and the diaphyses (midshaft sections) of either the long bones of the appendicular skeleton (e.g., femur, tibia) or the vertebrae of the axial skeleton. The dh polarization directions were reversed during the processes of growth so that the directions differed between the growth stage and the adult stage. The polarization in the diaphyses in old age had an antiparallel character so that large specimens had a small or zero net dh polarization. These points are summarized in Figure 10, which shows typical results for higher mammals including humans.



**Figure 10.** Directions of  $d^h$  polarization in different types of bones at various stages in the human life span (8). The arrows point to the ends which become positive under hydrostatic compression.

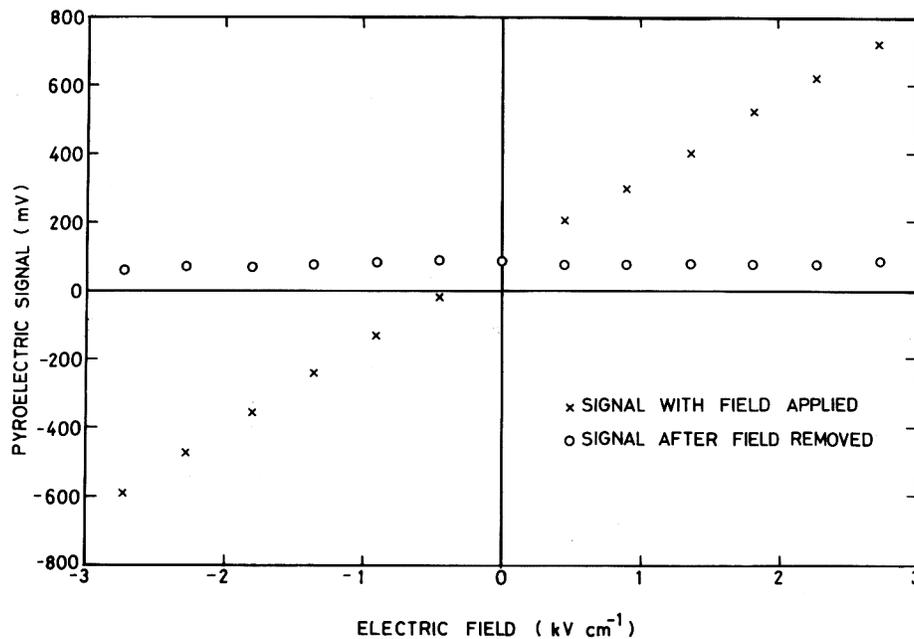
3. The reversal of polarization with biological maturity occurred in all mammals as well as in birds. The bones of crocodiles exhibited a similar behavior, but those of simpler reptiles and all amphibians showed no reversal. The relative directions of polarization in the axial and appendicular skeletons of amphibians and simpler reptiles were alike, but they were opposite in higher animals.
4. Cartilage in higher animals exhibited a  $d^h$  polarization in the thickness direction. The

polarization did not reverse after the cessation of growth, and it did not disappear in old age.

### PLANT TISSUES

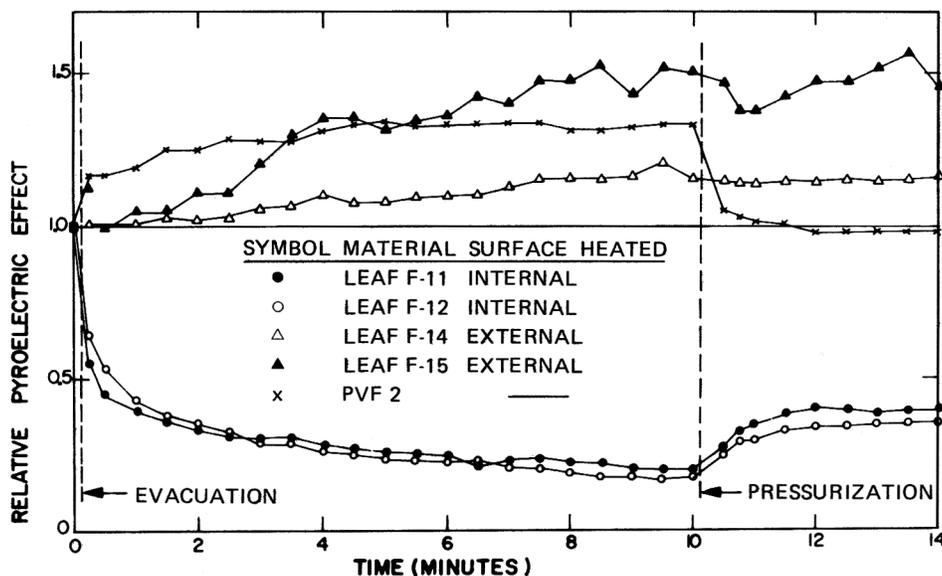
A large number of qualitative and a lesser number of quantitative studies on cells, tissues, and organs of plants were made by Athenstaedt (34). Many of the materials exhibited two directions of polarization, one parallel to a longitudinal axis and the second normal to the axis, usually in an inside–outside direction. This implies that the spontaneous polarization vector made an acute angle with the longitudinal axis. Athenstaedt also reported some interesting results on grains of wheat and rye (35). Some measurements were made on the shell of the grain and others on intact single grains. The rectangular-pulse heating method was used, and it was made quantitative by using a tourmaline crystal for calibration. Pyroelectric coefficients were measured as a function of temperature over the range  $-20^{\circ}\text{C}$  to  $40^{\circ}\text{C}$ . The surprising feature of the work was the striking difference between the temperature dependencies of the pyroelectric coefficient of the winter and spring species of the grain. The winter varieties showed a peak in  $p$ , at or below  $0^{\circ}\text{C}$ , whereas the pyroelectric coefficients of the spring varieties increased monotonically with temperature. Winter wheat forms ears only when exposed for a lengthy period of time after sowing to a temperature of about  $0^{\circ}\text{C}$  (up to a maximum of  $+3^{\circ}\text{C}$ ). For this reason, it is sown in autumn, before the beginning of winter with its low temperatures. If winter wheat is sown in spring, or if from the time of sowing in autumn the temperature remains constantly above  $5^{\circ}\text{C}$ , strong vegetation growth appears, but the reproductive phase does not follow. Spring wheat, however, shows a normal formation of ears when sown in spring. Athenstaedt emphasized the relationship between this physiological behavior and the differences in pyroelectric effect. He suggested that a pyroelectric test might serve as a simple means of distinguishing among the species.

Lang and Athenstaedt (15, 17) examined the pyroelectric behavior of the leaves of the palmlike plant *Encephalartos villosus*. Samples of leaves were scraped with a scalpel until their thickness was 0.06–0.12 mm. They were air-dried briefly and then tested using the rectangular pulse method with a tourmaline calibration. Differences were observed in both the pyroelectric activity and the thermal time constant dependent on whether the scraped or the original external surface was heated. They suggested that only a thin layer in the epidermis close to the surface was pyroelectrically active. A room-temperature pyroelectric coefficient of  $0.0129 \mu\text{Cm}^{-2}\text{K}^{-1}$  was determined. The polarity was such that the external surface acquired a positive charge upon heating. Direct-current (DC) bias voltages used to determine if the epidermis was ferroelectric produced unexpected results. An example is shown in Figure 11. Without bias, a pyroelectric signal of 85 mV was observed. Stepwise increase of the bias field to 2.7 kV/cm caused the pyroelectric response to increase linearly to 710 mV; a negative DC bias of 2.7 kV/cm caused the pyroelectric signal to decrease to -595 mV. In all cases, removal of the bias



**Figure 11.** Dependence of pyroelectric response of *Encephalartos villosus* epidermis on bias electric field (15, 17).

caused the pyroelectric signal to immediately return to its original value. On other samples, the same magnitude bias field caused the pyroelectric response to increase from 175 mV to 8.8 V, but the response was no longer linear with the bias field. Bias fields as large as 18.2 kV/cm were used in an attempt to reverse the polarization as an indication of ferroelectricity. No reversal could be achieved, suggesting that the material was not ferroelectric. These results were interpreted phenomenologically by considering that the pyroelectric coefficient could be expressed as a power series in electric field. A large term proportional to the electric field and a smaller one proportional to the cube of the field were present, but no effect proportional to the square of the field was observed. A nonlinear stress-induced effect due to changes in hydrostatic pressure was also observed. Figure 12 shows the relative pyroelectric effects of several samples as functions of time after evacuation of the sample chamber to 0.05 torr followed by repressurization to atmospheric pressure. The pyroeffects increased for samples whose external surfaces were heated but decreased when the internal surfaces were heated. A similar effect was also observed in a sample of polyvinylidene fluoride. An explanation of these results in terms of a stress-dependent pyroelectric coefficient is given elsewhere (15).



**Figure 12.** Relative pyroelectric coefficients of several *Encephalartos* and a polyvinylidene fluoride sample as functions of time after sample chamber evacuation and repressurization (12).

The origin of the pyroelectric effect in plant materials is uncertain. Wax and lipid deposits have been suggested (15, 17). Bazhenov (36), in his classic treatise on the piezoelectric properties of wood, found that the only nonzero piezoelectric coefficients of wood were  $d_{14}$ ,  $d_{25}$ , and  $d_{36}$  (with  $|d_{14}| > |d_{25}|$  and  $d_{36}$  extremely small. This suggests a texture group  $(\infty:2)T$  (which, however, requires that  $d_{14} = -d_{25}$  and  $d_{36} = 0$ ) or a point group 222 (in which  $d_{14}$ ,  $d_{25}$ , and  $d_{36}$  are all independent). In any event, neither group is pyroelectric. However, Preston (37) does not seem to rule out the possibility that cellulose may have a polar (pyroelectric) point group.

#### LIVING TISSUES

Recently, a series of papers by Athenstaedt and coworkers (38-41) appeared describing pyroelectric studies of living tissues. In order to make such measurements, a new technique was developed in which both electrodes were on the same surface of the sample. As described by Simhony and Athenstaedt (41), an adhesive tape strip containing two small holes was applied to the living specimen. Electrodes made from an aqueous suspension of graphite were painted through the holes onto the specimen. Contact to the electrodes was affected by means of aluminum foil leads attached to silver paste rings applied around the perimeters of the holes. In use, one of the holes was exposed to rectangular pulses of light from a xenon lamp and the other hole was shielded from the light source. The electrical responses showed the classical pyroelectric signature. A detailed theoretical analysis of a pyroelectric structure with such electrodes has not been published. The specimens studied were assumed to consist of a nonconductive thin

pyroelectric layer overlying a thick nonpyroelectric layer in which ion conduction occurred. Presumably the lines of electric flux passed from one electrode through the pyroelectric layer, then the conductive layer, and through the pyroelectric layer again to the second electrode. This type of structure, with curved flux lines and layers having vastly different conductive and dielectric properties is not likely to behave in the same way as a homogeneous pyroelectric crystal. Although a true pyroelectric effect was apparently measured in these experiments, the results cannot be quantitatively interpreted by means of any present theory.

In these studies, three types of specimens were used: living materials, nonliving materials which had been excised within the previous several hours, and aged nonliving materials. Two electrodes on a single surface as described above were applied to the living specimens and the measurements were generally conducted in a Faraday cage. The nonliving ones had conventional electrodes and both rectangular-pulse and dielectric heating methods were used. The materials studied were leaves of the *Rhododendron* and *Encephalartos*, the insect *Periplaneta americana* (41), thorax or abdomen segments of the insect *Blaberus giganteus* (38), human skin (40), and skin specimens from a series of birds, mammals, reptiles, amphibians, insects, and others (39). Table 3 contains some of the quantitative results (values cited for living specimens are subject to uncertainty because of the lack of a theoretical model for the geometry).

1. The pyroelectric properties are due to the polar structures of the materials and not to the presence of a living state.
2. The living samples exhibited larger effects than fresh nonliving samples and far larger ones than dried nonliving specimens.
3. Pyroelectric activity in skin samples was due to the epidermis layer and not to the underlying corium. The outside surface invariably acquired a negative charge when the sample was heated and the inner surface, a positive sign. Insect integuments exhibited similar polarity. The pyroelectric axis was normal to the outside surface.

#### SENSORY ORGANS

Several authors have suggested that the pyroelectric effect may be of fundamental physiological importance in various sensory organs. All the evidence appears to be indirect. It is generally based on the similarity between the pyroelectric response to a rectangular pulse, as shown in Figure 6, and the physiological reaction of a stimulated sensory organ. Because the pyroelectric current is proportional to the rate of change of temperature (Equation (2)), a physiological response that is also related to  $d\theta/dt$  would be expected to have a time dependence similar to that shown in Figure 6.

**Table 3.** Pyroelectric Coefficients of Living Tissues

<b>Material</b>	<b>Pyroelectric Coefficient (<math>\mu\text{Cm}^{-2}\text{K}^{-1}</math>)</b>	<b>Reference</b>
<i>Periplaneta americana</i>		
Abdomen rings (scraped)	0.2	(41)
Thorax ( <i>in vivo</i> )	3.5	(41)
<i>Encephalartos</i> leaves		
Upper epidermis (whole)	0.02	(41)
Upper epidermis (scraped layer)	0.005	(41)
Lower epidermis (whole)	0.06	(41)
Lower epidermis (scraped layer)	0.03	(41)
<i>Rhododendron</i> leaves		
Upper epidermis (whole)	0.03	(41)
Upper epidermis (scraped layer)	0.02	(41)
Lower epidermis (whole)	0.15	(41)
<i>Blaberus giganteus</i>		
<i>In vivo</i>	2.6—7.5	(38)
Dried	0.3—1.1	(38)
Human Skin		
<i>In vivo</i>	0.018—0.265	(40)
In vitro (fresh)	0.021—0.27	(40)

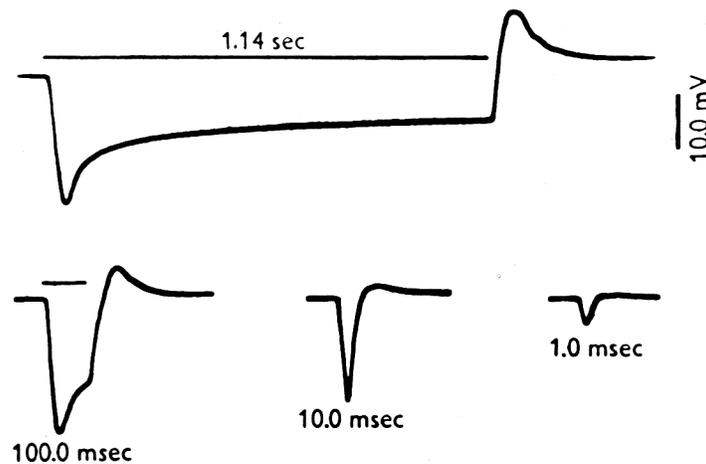
The major conclusions which were drawn from these studies were:

Cope (42, 43) examined data on the frequency of impulses in single nerve fibers from the thermoreceptors in the ampulla of Lorenzini of fishes when they were subjected to temperature transients. A graph of rate of change of impulse frequency with time versus  $d\theta/dt$  was linear, constituting preliminary quantitative evidence for pyroelectricity in this system.

Other examples have been given by Athenstaedt (44). He pointed out that the electrical responses of many thermoreceptors, photoreceptors, electroreceptors, chemoreceptors, and mechanoreceptors can be considered as pyroelectric or piezoelectric signals. The evidence is based on the known pyroelectric properties of many integument tissues and the observation that the physiological responses are proportional to  $d\theta/dt$ , as shown by the similarity of their behavior to that of known pyroelectrics.

A good example of the similarity between some receptor responses and those of pyroelectric materials is shown by the results of Grundfest (45) in Figure 13. The recordings represent the responses of a single photoreceptor cell of the retina of a cat to

light flashes of constant intensity but having durations which varied from 1.0 msec to 1.14 sec. It is possible to generate almost identical electrical responses by varying the electrical and thermal time constants of an inorganic pyroelectric material exposed to similar light flashes.



**Figure 13.** Responses of a single photoreceptor cell of the retina of a cat (45).

#### BIOLOGICAL FERROELECTRICITY

A very few experiments designed to determine if any biomaterials are ferroelectric have been carried out. Although somewhat outside of the scope of this chapter, the studies are nevertheless interesting from the point of view of pyroelectricity.

In 1960, Duchesne et al. (46) proposed that the sodium salt of deoxyribonucleic acid (NaDNA) was piezoelectric. In the same year, Polonsky et al. (47) and Douzou et al. (48) measured ferroelectric hysteresis loops on NaDNA using a Sawyer-Tower circuit similar to that described in an earlier section. A frequency of 50 Hz and a maximum electric field of 1000 V/cm were used. Based on the hysteresis data, the Curie temperature appeared to be in the range of 50–60°C. The dielectric constant increased rapidly with temperature to a maximum near 70°C, although the Curie-Weiss law was not obeyed above the Curie point [ $\epsilon \approx 1/(\theta - \theta_c)$ , where  $\theta_c$  is the Curie temperature (9-11)]. Stanford and Lorey (49) observed hysteresis loops and anomalous dielectric constant behavior in the sodium salt of ribonucleic acid (NaRNA). They suggested, “RNA is seen to have the attributes of a ferroelectric substance at life temperatures and possesses the capability of storing information by a physical process, hysteresis.”

However, O’Konski and Shirai (50) and Brot et al. (51) in experiments with NaDNA and Mascarenhas et al. (52) in studies of RNA disagreed with the ferroelectricity hypothesis. The latter groups all found evidence that the DNA and RNA behaved as

nonlinear conductors, and the hysteresis loops were merely artifacts. O'Konski and Shirai explained the observed effects by means of electrolytic processes, and Mascarenhas et al. proposed an electret theory.

## CONCLUSIONS AND SOME SPECULATIONS

We have two major objectives in this chapter: (1) to concisely summarize the physics of pyroelectricity and closely related effects and describe the techniques for measuring them; and (2) to present a brief discussion and some analysis of all the studies of biological pyroelectricity to date. Relatively little has been said of the physiological implications of the existence of pyroelectricity in biological tissues and biological systems. This is true largely because most of the research to date has been very exploratory in nature. It was first necessary to demonstrate that pyroelectricity and concomitant spontaneous polarization were fundamental and inherent properties of biomaterials. Although much of the data in the literature are qualitative and some require additional verification, it now seems certain that pyroelectricity is a widespread phenomenon in biomaterials.

The generality of materials in which pyroelectricity may exist is even further extended by studies such as the optical second harmonic generation measurements of Delfino (53) on 71  $\alpha$ -amino acids, 22 dipeptides, 6 tripeptides, 16 proteins, and 5 viruses. He found that all  $\alpha$ -amino acids with the exception of  $\alpha$ -glycine, all peptides containing at least one enantiomeric  $\alpha$ -amino acid residue, and all proteins and viruses were noncentrosymmetric, permitting the existence of piezoelectricity and possibly pyroelectricity as well.

Since possible physiological significance is the *raison d'être* for the study of pyroelectricity in biomaterials, it is appropriate to speculate on some areas wherein further research may be warranted. These speculations may not necessarily be valid and they certainly should not limit the scope of research; hopefully, they will be provocative (54).

1. What mechanism could produce a change in direction of polarization or a diminishing of polarization with biological growth and maturation (22-33)? Lang (55) has suggested that if this mechanism functions improperly, calcification might not occur where it should or might occur where it should not. For example, excessive calcium losses in bone and calcium deposits in cartilage are both pathological conditions. Is there a correlation between these conditions and behavior of polarization?
2. Why is there no polarization reversal in the simpler animals (28)? Is there some relationship to the ability of the simpler animals to spontaneously regenerate large organs?

3. Could some biomaterials be ferroelectric? The positive results on DNA and RNA have been challenged, but almost no other biomaterials have been tested for ferroelectricity. Matthias (56) has commented on the generality of the effect. Could ferroelectricity be the mechanism for the apparently easy reversal in the polarization of bone during the growth stages? The hysteresis phenomenon in ferroelectrics has been used as a reversible information storage device in electronic systems. Fong (57) has suggested a brain memory mechanism based on biological electricity. Could ferroelectricity be related to this and other biological memory processes? Ferroelectrics are characterized by long-range ordering effects, and biological systems depend upon long-range order for their existence, Is there a correlation?
4. Mascarenhas (58) has discussed electret characteristics such as thermally stimulated currents in biomaterials. Are there possible relationships between pyroelectricity and the proposed electret properties?
5. Many biological membranes consist of highly oriented proteins such as collagen. If the protein is pyroelectric, the membrane itself would be expected to be pyroelectric and to exhibit spontaneous polarization. Could the large internal electric fields due to the polarization influence the mass transport of ions through the membrane?
6. According to the wheat studies of Athenstaedt (35), a subtle physiological difference manifested itself in significant differences in the temperature dependence of the pyroelectric effect. Are there other physiological factors that could be conveniently studied by means of their pyroelectric behavior?
7. Small bias DC fields were shown by Lang and Athenstaedt (15, 17) to have a very large effect on the biological pyroelectricity of *Encephalartos* leaves. Pyroelectric effects in biomaterials are usually very small, perhaps too small to have biological significance. Very large DC fields exist naturally in biological systems, often due to the very small dimensions of relevant structures such as cells (59). Could these fields have a strong amplifying effect on the pyroelectricity?
8. Pyroelectricity may be responsible for various biological sensors and receptors. Lipinski (60) has suggested a relationship between an ancient Chinese therapeutic heating technique called moxibustion, which stimulates acupuncture loci, and the pyroelectric properties of tissues. Are there mechanisms whereby pyroelectric responses can affect or control the nervous system?

In conclusion, it is suggested that pyroelectricity is an essential and universal property of all biological systems and that polarization homeostasis may be an important new biomechanism of living matter.

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