Chemical Temperature Integration¹

RICHARD LEE²

Institute for Research on Land and Water Resources, The Pennsylvania State University, University Park

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ABSTRACT

The sugar-inversion method (Pallmann method) of deriving mean temperatures related the reaction velocity of sucrose hydrolysis to temperature by means of an Arrhenius-type equation. The method was tested for precision, accuracy and adaptability to climatological networks.

Twenty-milliliter glass ampoules filled with a clear sucrose solution were used as temperature sensors. The sensors were virtually unaffected by shortwave radiation. Precision of the method for half-month periods in forested terrain was $\pm 0.02^\circ\text{C}$. Absolute accuracy of the method was severely affected by the nonlinearity of sensor response; this was circumvented by use of empirical corrections based on the temperature mean and amplitude. At five standard climate stations, arithmetic mean temperatures for half-month periods (1967–1968) were predicted with an average error of 0.37 – 0.64°C in summer (over mean temperatures of 30 to 10°C) and 0.86 – 1.05°C in winter (over mean temperatures of 10 to -10°C).

The Pallmann method of temperature integration is simple and economical. With the addition of 150 gm liter^{-1} sodium chloride to the sucrose solution, the method is usable in all seasons.

1. Introduction

Mean temperature is a standard index of the thermal climates of air, soil and water media. It is employed universally as an independent variable relating average reaction rates of physical and biological processes to their environment. Mean temperatures usually are obtained in a two-step process of observation and numerical or graphical summation of periodic values. A direct chemical method of observation and integration has become feasible and incorporates several distinct advantages.

The velocity of a chemical reaction depends on temperature, in general according to the van't Hoff-Arrhenius law, i.e.,

$$\log k = c_1 - (c_2/T), \quad (1)$$

where the logarithm of the velocity coefficient k varies linearly with the reciprocal of absolute temperature T . The mean value of k for any time period t is

$$\bar{k} = [1/(t-t_0)] \int_{t_0}^t k dt. \quad (2)$$

If c_1 and c_2 are known and $\bar{k}$ can be determined experimentally, substitution in (1) yields an effective mean temperature T_e for the period.

Pallmann *et al.* (1940) introduced a temperature technique using sucrose hydrolysis as the sensing reac-

tion. Their method has been used or tested by Pallman and Frei (1943), Kundler (1954), Murdock (1956), Schmitz and Volkert (1959), Lützke (1963), and others. Brechtel (1967) applied the method as a totalizer of radiant energy. The research reported here is the basis for improvements in Pallmann-method technology. Companion studies are those reported by Sharpe (1968), Lee and Sharpe³, and Chang (1968).

2. The Pallmann method

The most readily available English references to the Pallmann method are translations of reports by Schmitz and Volkert (1959) and Schmitz (1964). These describe sucrose hydrolysis as an irreversible reaction of the type

in which the mean reaction velocity coefficient is

$$\bar{k} = (1/t) \log[A/(A-x)]. \quad (3)$$

Here A is the initial concentration of sucrose, of which an amount x inverts to glucose and fructose after time t . All of the sugars are optically active in solution; their effective concentrations can be determined polarimetrically and a rotation angle ratio substituted for the concentration ratio in (3). The reaction velocity is proportional to the hydrogen-ion concentration H^+ , and for t in days (3) becomes

$$\bar{k} = [1/(H^+t)] \log[(R_0 - R_\infty)/(R_t - R_\infty)], \quad (4)$$

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² Current affiliation: Division of Forestry, West Virginia University, Morgantown.

³ Lee, R., and W. E. Sharpe, 1968: Time-integrated thermal effects of forest irrigation. Paper presented at the 8th Natl. Conf. on Agricultural Meteorology, Ottawa.

where R_0 , R_t , and R_∞ are rotation angles observed at the times indicated by the subscripts. Since $\log(1/H^+) = \text{pH}$, substitution of (4) in (1) yields

$$T_e = \frac{-c_2}{\text{pH} - c_1 - \log t + \log[\log(R_0 - R_\infty) - \log(R_t - R_\infty)]} \quad (5)$$

For the Pallmann solution, in which equal volumes of a) 1500 gm sucrose in 1000 ml water, and b) 404 ml 0.2*m* sodium citrate and 596 ml 0.2*n* HCl are used, $c_1 = 20.1998$ and $c_2 = 5856.6$.

In practice, Pallmann temperature sensing elements usually are prepared by sealing small samples of the sucrose solution in clear glass ampoules (Fig. 1). These are exposed at measurement sites in soil, air or water bodies over the time period for which T_e is of interest. After recovery from the field, the ampoule contents are analyzed polarimetrically for values of the definitive parameter, R_t . For a given sensor set (sensors prepared from the same batch of solution), (5) reduces to an expression in T_e and R_t .

The number of sensing elements required to complete an observation series may be prepared at the outset. If the ampoules are frozen at once, hydrolysis is prevented, and the elements may be stored for future use or transported directly to the exposure site. They are transported to and from the field in cold cases.

The pH of the sensing solution is adjusted by adding HCl to insure that inversion occurs rapidly enough to

be measured accurately. The pH level must be chosen to coincide with the length of the measurement period and the expected mean temperature. A minimum practical pH level ranges from 1.2–1.6, which requires a minimum observation period in the middle latitudes of about 5–15 days in summer or 15–30 days in winter.

Detailed treatment of some technical measurement problems were elaborated by Schmitz (1964). Recent improvements in laboratory and field procedures were reported by Sharpe (1968). He developed a flow-through apparatus for the polarimeter which simplifies the read-out operation and greatly reduces its time requirement. The entire technique is easily reduced to a routine in which nonprofessional personnel can carry out a measurement program with limited professional supervision.

Application of the Pallmann method is most attractive where simultaneous measurements are required at many locations, and where measurement sites are unmanned and infrequently visited. The cost for materials is negligible by most standards—about 15 cents per sensor. Even with the extra costs of transportation and processing, the technique can be used to describe spatial variations of temperature economically. The major items of equipment are standard in physical chemistry laboratories.

In spite of its many advantages, the Pallmann method is relatively unused. Laboratory procedures are no longer tedious, and with the use of automatic photoelectric polarimetry even greater efficiency is possible. But several serious problems remain. The precision and accuracy of the method have been tested, but they have not been fully understood or explained. A fundamental weakness that has been responsible for much adverse criticism is the nonlinearity of sensor response to temperature, as shown in (5). Another problem is that the Pallmann solution freezes at about -5°C , introducing a spurious effect on the measurement. Research results and interpretation in each of these problem areas is reported in following sections.

3. Sensitivity and precision

The high sucrose content of the Pallmann solution causes a maximum change in optical rotation during hydrolysis of about 80° (measured in Hg light, 546.1 nm). In practice, it is desirable to utilize only about half the total range, and in general a difference in ambient temperature of 0.1°C corresponds to an optical rotation difference of about 0.4° . In terms of (5), if $R_0 = 60^\circ$, $R_t = 20^\circ$, and $R_\infty = -20^\circ$, $\Delta T_e / \Delta R_t \approx 0.25^\circ \text{ deg}^{-1}$. Based on polarimeter accuracy of $\pm 0.01^\circ$, therefore, read-out sensitivity is equivalent to $\pm 0.0025^\circ\text{C}$.

The precision of the Pallmann method is unusually high. Pallmann and Frei (1943), in spite of experimental handicaps, demonstrated that sensors exposed in a constant temperature chamber yield values of T_e that differ by less than 0.1°C . From their data it can be

FIG. 1. Sucrose temperature sensing elements, 25 ml capacity.

shown that the standard error of temperature means measured between 9 and 33C averaged about 0.04C. In their field studies, mean differences between paired sensors buried at 10 cm depths in the soil averaged 0.08C, which undoubtedly includes the effects of trivial exposure differences.

For a set of sensors prepared from the same batch of solution, pH, t , R_0 , and R_∞ are constant, and the precision with which R_t can be determined on a routine basis determines the practical precision of the method for that set. Polarimeter readability usually is to the nearest 0.01°, but to measure R_t with that precision requires strict temperature control in the laboratory, or the reduction of the readings to standard temperature (Schmitz, 1964). For example, in the usual range of R_t , say $10^\circ < R_t < 30^\circ$, a temperature difference of 1C (between two sensor solutions as they are analyzed in the polarimeter) introduces an error effect in R_t of from 0.10–0.20°, or in T_e of about 0.03–0.05C. Closer control than this is not difficult to achieve, but it may be impractical for most purposes.

During the summer half-year (from 22 March to 22 September), duplicate Pallmann sensors were exposed for half-month periods (from 13–18 days) in specially designed shelters (Fig. 2) at forest stations in central Pennsylvania. The primary purpose of the study, to observe thermal effects of topography and forest cover, insured that a range of sampling conditions was encountered. Excellent temperature control during laboratory analysis was obtained to reduce read-out errors to a minimum. Based on 320 observation pairs, the average field precision of the method was $\pm 0.02C$, a value which probably includes the effects of small exposure differences.

If observations from two or more sets of sensors are compared, pH, t , R_0 , and R_∞ are not constant and the precision of the method depends on the precision with which these factors can be measured. Modern pH meters give results repeatable to ± 0.002 pH with the same reference buffer and close temperature control. However, for routine measurements, variations up to ± 0.005 pH are more realistic. The exposure duration t usually can be recorded to the nearest 0.1 day without difficulty. The reliability of rotation angle readings of R_0 and R_∞ are the same as for R_t , but laboratory temperature controls are less important for R_0 and more important for R_∞ . It can be shown from (5) that repeatability in the estimates of T_e as affected by random errors of ± 0.005 pH, ± 0.05 day, and $\pm 0.1^\circ$ rotation angle will not exceed ± 0.08 , ± 0.02 and $\pm 0.05C$ in that order. The errors are not necessarily additive, so generally the precision level of $\pm 0.1C$ probably is valid.

In summary, the routine field precision of the Pallmann method for a given solution batch has been established through direct observation as $\pm 0.02C$. If the greatest possible precision is required in a measurement series, a set of sensing elements can be prepared

FIG. 2. Sucrose sensors in small shelters.

from a single solution batch and stored at low temperature until needed for individual observation periods within the series. If less precision is required, and a separate set of sensors is prepared for observation periods within a series, the probable precision of the method for the entire series is $\pm 0.1C$.

The precision of the Pallmann method is one of its principal advantages. In bioclimatological studies it often has been used to obtain indexes of thermal climates that affect organisms without regard to absolute temperature accuracy. However, when this is done, physical interpretations are hampered and it is impossible to relate the observations to an established climatological network.

4. Accuracy

The absolute accuracy of the Pallmann method is influenced by a series of minor laboratory and field measurement problems, and by a fundamental weakness in the technique itself. Schmitz (1964) evaluated laboratory measurement problems and associated errors related to the kinetics of the chemical reaction. An effect of a pH change during hydrolysis was discovered during the current study. In field studies, a small radiation effect is detectable if sensors are exposed to direct sunlight. But overshadowing all other sources of inaccuracy is that sucrose hydrolysis responds exponentially to temperature changes, so that T_e in (5) consistently overestimates the standard arithmetic mean temperature.

a. Laboratory measurement problems

Schmitz's (1964) evaluations of error sources concern the limitations of the assumptions that lead to (4) and (5), i.e., that 1) strict proportionality exists between optical rotation and sugar concentrations in the solution, 2) R_0 , R_t and R_∞ are obtained under specific standard conditions, and 3) hydrogen-ion concentrations and reaction velocities are strictly proportional.

Optical rotation and sucrose- or invert-sugar concentrations are not strictly proportional because the reaction is not entirely unimolecular, and because the concentration dependence of specific rotation differs among the sugars. Moreover, HCl and sodium citrate act as impurities in the solution, changing its specific rotation. In addition, a small quantity of formaldehyde or other poison usually is added to the solution to prevent the growth of microorganisms. While this is an additional impurity, the error effects are small. With precautions to keep $R_t > 0$ and R_0 near its maximum, resultant errors in T_e do not exceed $\pm 0.05^\circ\text{C}$.

The rotation of optically active substances changes with temperature. This dictates that rotation angles be measured at the standard temperature of 20°C , or that they be reduced to the standard based on an empirical relationship between temperature and optical rotation. In either case, the resulting accuracy depends on the closeness of the laboratory control. Other temperature-related errors arise if the measurements of optical rotation follow too quickly a major temperature change

in the solution. These mutarotation effects are eliminated by adherence to laboratory procedures given by Sharpe (1968). Residual errors in the measurements of R_0 , R_t and R_∞ affect the absolute accuracy of T_e by only about $\pm 0.05^\circ\text{C}$.

Schmitz (1964) reported that the reaction velocity of sucrose hydrolysis is proportional to hydrogen-ion concentrations above pH 1.84. He cited other studies in which deviations from strict proportionality were noted at pH 1.0, but Berthet (1960) found no deviations above pH 1.2. Apparently, no error is involved in the assumption of proportionality if very high hydrogen-ion concentrations are avoided.

Modern precision pH meters have expanded-scale readability to ± 0.002 pH, but usually their absolute accuracy is no greater than ± 0.01 pH. From (5), the rate of change of T_e per unit pH varies between 12.7 and 16.7°C for $0 < T_e < 40^\circ\text{C}$. It follows that routine errors in the measurement of pH will introduce errors in estimates of T_e from (5) of about $\pm 0.15^\circ\text{C}$.

b. Hydrogen-ion activity changes

Pallmann and Frei reported that their acidified-buffered sucrose solution (Pallmann solution) did not experience a pH change even after several months of field exposure. The precision of their pH measurements is not clear, but apparently it was ± 0.05 pH. During 25 years of recurring research with the Pallmann method, authors have openly or tacitly assumed that hydrogen-ion activity does not change as the reaction proceeds, and that pH may be entered in (5) as a dimensionless constant. The assumption is accurate only as a gross approximation.

In one phase of the current study, the pH of Pallmann sensors was measured before and after exposure in the field. Measurements were obtained with a Leeds and Northrup pH meter, precision model, readability ± 0.002 , absolute accuracy ± 0.01 . In every instance the pH was lower following exposure. In order to follow the trend of pH changes as the sucrose hydrolyzed, laboratory tests were conducted using a Hotpack constant temperature bath of $\pm 0.1^\circ\text{C}$. Pallmann sensors were prepared and immersed in the bath, and withdrawn one by one at more or less regular intervals of rotation angle between R_0 and R_∞ . Rotation angles were measured with Rudolph's precision polarimeter, Model 70, readability to 0.01° of arc. Characteristic results are illustrated in Fig. 3. In a series of 10 such tests at constant temperatures between 10 and 40°C , the mean pH change was -0.044 (range -0.030 to -0.058).

The decrease of pH with hydrolysis shows that the reaction velocity coefficient k is not strictly a single-valued function of temperature as assumed in (1). The constants c_1 and c_2 in (1) and (5) are based on mean values of k at constant temperature, as estimated by Pallmann *et al.* (1940) with (4) from rotation angle measurements between R_0 and $R_t \approx 0^\circ$. At constant

FIG. 3. Change in pH with optical rotation as sucrose inverts.

temperature $\Delta pH = \Delta \log k$, and from Fig. 3 and other measurements $\Delta pH/\Delta R_t$ is about 0.01 per 20° , or about 0.03 for the range of the calibration. It follows that pH changes introduce little error in the estimates of T_e from (5) if R_t is midway in the calibrating range, i.e., near 30° ; toward the extremes of the range, errors approach $\pm 0.25C$.

c. Radiation effects

The Pallmann solution is clear, and if clear glass is used in constructing the sensing elements (Fig. 1), they appear to be transparent to visible radiation. However, if a sensor is exposed to direct solar radiation its absorptivity may be great enough to induce a temperature rise in the solution that is not characteristic of the ambient air. Pallmann and Frei reported the effects of using colored glass sensors. W. Nägeli (personal communication), Swiss Forest Research Institute, Birmensdorf, found a "small" radiation error when radiation shields were not used.

A test of the radiation effect was conducted at University Park during a period of high solar radiation, August 1967. A row of nine sensors was suspended from a taut line at screen height over a grassy surface. The horizontal distance between sensors was about 4 ft. Odd-numbered sensors in the row were exposed to direct solar radiation. Even-numbered sensors were shaded by $50 \times 50 \times 1.3$ -cm Styrafoam shields.

The mean temperature indicated by the five unprotected sensors was $25.87C$, $\pm 0.02C$, and by the four controls $25.78C$, $\pm 0.02C$. Approximately the same difference, i.e., $0.09C$, was observed in other tests. It was concluded that the maximum effect of exposure to direct sunlight in central Pennsylvania is of the order of $0.1C$. The effect may be greater in microclimates where incoming and reflected radiation are greater, or where convective exchange is less efficient.

d. Nonlinearity of response

The inaccuracies of the Pallmann method examined in previous sections are small. Cumulative errors, even including possible radiation effects, probably do not exceed the errors inherent in standard climatological methods. However, the exponential response of sucrose hydrolysis to temperature changes entails inaccuracies of a higher order of magnitude, and these must not be ignored.

Pallmann and Frei attempted to obtain a quantitative measure of the differences between their chemically derived *exponential* or *effective* mean temperatures T_e and standard arithmetic means T_a . They exposed Pallmann sensors alternately for 14 days to each of two constant temperatures, and compared exponential and arithmetic temperature means based on the temperature range. For ranges of 0.0, 5.8, 10.0 and $30.5C$, the differences ($T_e - T_a$) were 0.0, 0.6, 1.6 and $10.5C$ in

TABLE 1. Theoretical mean temperature differences (exponential minus arithmetic, $^\circ C$) as a function of the temperature mean and range.

Temperature range ($^\circ C$)	Temperature mean		
	10C	20C	30C
0	0.0	0.0	0.0
5	0.3	0.3	0.2
10	1.0	0.9	0.8
15	2.1	1.9	1.7
20	3.5	3.3	3.0
25	5.1	4.8	4.5
30	6.8	6.5	6.1
35	8.6	8.3	7.8

that order. Lütze (1963) estimated that for temperature ranges of 24 and $36C$, the differences would be 5.1 and $10.2C$, respectively.

Theoretically, the differences between exponential and arithmetic means can be obtained by assuming that daily temperature varies with time according to the rule

$$T = T_a + (R_T/2) \sin(\pi t/12), \quad (6)$$

where t is the time in hours after the mean temperature is recorded, and R_T the temperature range. With this expression for T in (1), $\bar{k}$ is obtained from (2) by means of numerical integration (Simpson's rule) for any temperature mean T_a and amplitude $R_T/2$. Substitution of $\bar{k}$ in (1) yields an *effective* mean temperature T_e such that $T_e \geq T_a$. The differences ($T_e - T_a$) calculated in this manner for a range of temperatures are recorded in Table 1.

The theoretical temperature differences of Table 1 characterize the inaccuracy of the Pallmann method in estimating standard arithmetic mean temperatures. The errors increase rapidly with the temperature range. For $R_T < 5C$, exponential and arithmetic means are virtually the same. Hence, for temperature measurements in soil or water bodies, where R_T is low, the absolute accuracy of the Pallmann method is highly satisfactory. But at temperature ranges commonly observed in the air near the ground, the exponential mean probably is unsatisfactory as an estimate of the standard arithmetic mean.

5. Correction for nonlinearity

Possible methods of correcting for the exponential response of Pallmann sensors to temperature can be derived theoretically or empirically. The theory underlying Table 1 yields a first approximation of the quantitative relationship between T_a and T_e . Or, regression analysis with T_a as a function of T_e and R_T can be used to give estimates of the relationship with known limits of reliability. In either instance, in addition to the measurement of T_e , an estimate of R_T is required.

Tests of the two methods of correction were conducted with data from five climate stations of the Environmental Science Services Administration in

FIG. 4. The standard mean temperature T_a , estimated vs observed, during half-month periods in summer (solid dots) and winter (open circles).

central Pennsylvania. Pallmann sensors were exposed along with conventional instruments at the stations listed in Table 2. The measurements required for estimates of T_a , T_e and R_T were obtained during each of 12 half-month periods between 22 March and 22 September 1967. Arithmetic averages of each variable for the summer half-year, and estimates of T_a are given in Table 2.

Theoretical estimates of T_a from T_e and R_T , based on (1), (2) and (6), overcorrect for the nonlinear response. On the average, 60 estimates of T_a were 1.1°C lower than observed values. The maximum error for a half-month period was -3.6°C, and one error in five exceeded 2°C. It is obvious that (6) is not a valid representation of temperature variation during a series of days in which both the daily mean and amplitude vary. In particular, R_T for a half-month greatly exceeds the mean daily range, and from Table 1 it is clear that theoretical estimates of T_a can be very sensitive to differences in R_T .

Empirical estimates of T_a based on multiple regression analysis of 60 observations (5 stations, 12 periods)

TABLE 2. Averages of the temperature parameters T_e , R_T and T_a (°C) for 12 sampling periods during the summer half-year, 1967.

Station	Elevation (m)	T_e	R_T	T_a observed	T_a estimated from (7)	T_a estimated from (1), (2), and (6)
Lewistown	146	19.5	24.6	15.5	15.7	14.7
Huntingdon	207	20.8	24.4	16.7	17.0	16.1
Bellefonte	338	20.6	26.8	17.0	16.3	15.1
State College	358	19.6	23.1	15.9	16.2	15.3
Philipsburg	585	17.4	26.3	13.4	13.3	12.0
Mean		19.6	25.1	15.7	15.7	14.6

TABLE 3. Relative frequency (per cent) of errors in predicting T_a from T_e and R_T .

Error (°C)	Range of T_a (°C)			
	-10 to 0	0 to 10	10 to 20	20 to 30
≤ 0.5	33	46	51	71
≤ 1.0	61	65	81	94
≤ 1.5	78	87	95	100
≤ 2.0	83	100	100	
Absolute maximum error	2.80	1.96	1.66	1.07

are given by

$$T_a = 2.23326 + 0.9731T_e - 0.2264R_T. \quad (7)$$

In this the coefficient of determination is 0.982, and the standard error of estimate is 0.74°C. An error analysis is given in Table 3. Fig. 4 (solid dots) illustrates the "goodness of fit." It is important to note from (7) that the empirical prediction is relatively insensitive to differences in R_T . This is encouraging from the standpoint of practical applications; for example, in studies of terrain climatology, where it may be inconvenient to estimate or measure R_T with great accuracy.

If R_T is unknown, and estimates of T_a are based on a simple linear regression with T_e , the prediction equation is

$$T_a = -6.6262 + 1.1408T_e. \quad (8)$$

Here the coefficient of determination is 0.954, and the standard error of estimate is 1.14°C. A scatter diagram of T_a vs T_e , including the prediction line (8), are shown in Fig. 5.

FIG. 5. The standard mean temperature T_a as a function of the sucrose exponential mean T_e in summer.

All of the results are based on data obtained during the summer half-year in central Pennsylvania at elevations between 146 and 585 m. Observed arithmetic mean temperatures T_a for half-month periods varied between 5.8 and 23.4°C; temperature ranges R_T for the periods varied between 14.5 and 37.8°C. The corrections derived for nonlinearity of sensor response under these conditions may not apply universally, but probably they are valid for a large range of summer conditions in temperate climates of the middle latitudes.

6. Antifreeze solution

The Pallmann solution freezes at -4.7°C (Pallmann *et al.*, 1940). If a sensing element is exposed to lower temperatures, the solution solidifies and hydrolysis ceases. Moreover, a frozen sensor cannot respond to rising temperatures until complete melting occurs. It follows that the Pallmann sensors will not integrate temperatures below -4.7°C , and will not respond predictably when freezing and thawing occur during a measurement period. These limitations suggest the advisability of lowering the melting point of the Pallmann solution for cold weather temperature measurement.

During the winter half-year, from 23 September 1967 to 21 March 1968, a modified Pallmann solution was used in sensors exposed at climate stations. A reagent grade sodium chloride, 150 gm liter^{-1} , was added to the normal solution to serve as an antifreeze. This quantity of salt depresses the freezing point of water to -10.9°C , and the salt-sugar solution was thus expected to have a freezing point of about -16°C ($-4.7 - 10.9^\circ\text{C}$). In fact, however, the solution did not freeze either when stored indefinitely at -16 to -20°C , or at the Bellefonte climate station when the minimum temperature approached -25°C on 12 and 13 January 1968.

The addition of salt to the Pallmann solution affects the calibration constants, c_1 and c_2 , of (5) through its effect on the specific rotation of sucrose and invert sugar (Section 4a). Recalibration tests were conducted at constant temperatures of 10, 20, 30 and 40°C using a Hotpack bath ($\pm 0.1^\circ\text{C}$). The Arrhenius-type equation based on regression analysis of $\log k$ vs $T(^{\circ}\text{K})$ is

$$\log k = 19.5797 - (5656.3/T), \quad (9)$$

where the constants of (9) are those appropriate to use in (5) for the Pallmann solution modified by the addition of salt.

Empirical corrections for nonlinearity of response of the salt-sucrose solution were obtained statistically. Estimates of T_a based on 50 observations (5 stations, 10 periods: half-month periods from 23 September 1967 to 22 January 1968, month periods from 22 January to 21 March 1968) are given by

$$T_a = -1.3792 + 1.0373T_e - 0.1540R_T. \quad (10)$$

The coefficient of determination is 0.965, and the standard error of estimate is 1.18°C . An error analysis

is given in Table 3. The goodness of fit is illustrated in Fig. 4 (open circles) along with the summer data.

If R_T is unknown, and estimates of T_a are related statistically to T_e alone, the prediction equation is

$$T_a = -6.0344 + 1.1012T_e. \quad (11)$$

Here the coefficient of determination is 0.942, and the standard error of estimate is 1.50°C .

7. Discussion

The high sensitivity and precision of the Pallmann method recommend it as an environmental sensing mechanism. It was derived as an economical means of indexing the temperature climate in a way that might be useful in forestry, ecology and hydrology. The study reported here shows that the chemical method is also a reliable basis for estimating the standard mean temperature in climatology. This raises questions concerning the continued use of the index temperature T_e as opposed to chemically derived estimates of the standard mean T_a .

a. The index temperature T_e

Until now the Pallmann method has been used exclusively for purposes of deriving a biologically relevant temperature parameter—one that responds to temperature in the way plants or animals respond. For example, Schmitz and Volkert described the distribution of grayling in central European rivers in terms of T_e isotherms. Chang (1968) demonstrated a relationship between T_e and the growth, growing-season length, and seasonal development of forest trees by topographic positions. In studies of this type, if sucrose hydrolysis and biological phenomena are correlated, and no direct physical interpretations are required, T_e may have an advantage over T_a as an environmental indicator.

Biological reaction rates usually are not single-valued functions of temperature. But for restricted temperature ranges, a common method of expressing reaction rate changes with temperature is the ratio

$$k_2/k_1 = f(T+10)/f(T) = Q_{10},$$

where Q_{10} is a "temperature quotient" for the reaction. Pallmann and Frei listed temperature quotients for certain enzyme reactions, and Lee and Sharpe (*loc. cit.*) included values for reactions in microorganisms, insects and higher plants. For the range from 15 – 25°C , these vary generally between 2 and 6, compared to $Q_{10} = 4.8$ for sucrose hydrolysis. It is understandable, therefore, that T_e could correlate more closely than T_a with some biological processes.

But objections to the use of T_e , even in the study of life processes, are not trivial. The mere fact that both sucrose hydrolysis and many biological reaction rates are exponential, rather than linear temperature functions, does not assure a simple relationship between

them. In fact, as Lütke (1963) argues, $k=f(T_e)$ may be even more complicated than $k=f(T_a)$. And, even when reaction rates are simply defined in terms of T_e , there is the practical problem of relating the results to the climatological standard T_a .

b. Estimates of the standard mean T_a

In general, T_e cannot substitute for the arithmetic standard T_a , but estimates of the latter can be obtained from (7) and (10) as $f(T_e, R_T)$, or from (8) and (11) as $f(T_e)$. From comparison of (7) with (10), it appears that a single prediction equation may suffice for both summer and winter conditions (i.e., for both sucrose and salt-sucrose solutions). Combining the data for the year, from 22 March 1967 to 21 March 1968, yields

$$T_a = -1.2316 + 1.0645T_e - 0.1607R_T. \quad (12)$$

For this the coefficient of determination is 0.988, and the standard error of estimate is 1.00C. The errors of estimate are much smaller at the higher temperatures (see Table 3). By 10C intervals from -10 to 30C, the errors average 1.05, 0.86, 0.64 and 0.37C, respectively.

If R_T is unknown the combined data indicate, in lieu of (8) and (11), that

$$T_a = -6.1548 + 1.1174T_e. \quad (13)$$

Here the coefficient of determination is 0.980, and the standard error of estimate is 1.29C.

Either (12) or (13) will serve to reduce chemically derived temperature indexes from local climatological studies to the standard means of a regional climatological network. If the temperature range R_T varies significantly among local sites, the variation can be characterized through sampling, and related to continual observations at a control station. In (12), errors in T_a caused by errors in R_T are about $R_T/6$, so a relatively rough estimate of R_T is satisfactory for most purposes.

8. Summary and conclusions

The rate of sucrose hydrolysis is a known function of temperature, and its mean rate during a period of fluctuating temperature indicates an *effective* mean temperature T_e for the period. Through polarimetric analysis of small samples of an acidified-buffered sucrose solution (Pallmann solution) after exposure in the field, T_e is obtained with a routine precision of ± 0.02 C. The absolute accuracy of the method is virtually unaffected by calibration and read-out errors, and the sensing elements are not affected significantly by shortwave radiation. Addition of 150 gm liter⁻¹ of NaCl to the sucrose solution lowers its freezing point to below -20C.

Sucrose hydrolysis responds exponentially to temperature, so T_e does not correspond to the standard climatological mean temperature T_a . A theoretical correction for the nonlinear character of the sensing mechanism is valuable as a first approximation of T_a as a function of T_e and the temperature range R_T . Empirical corrections yield estimates of T_a with standard errors of 0.74C in summer and 1.18C in winter.

The Pallmann technique is an economical, highly precise method of sampling for mean temperatures in a climatological network. With the addition of an anti-freeze compound, it is usable in all seasons. The raw data can be reduced with acceptable accuracy to the standard arithmetic mean temperature as used in climatology.

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