

Convenient Chemical Method for Measuring Mean Temperature at Sites of Degradation Studies in the Field

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Accurate measurement of the effect of temperature on degradation of herbicides and pesticides in field soil is hampered by the work, expense and risk involved in installing properly calibrated temperature-recording equipment at each site. Often, data from meteorological stations are used for rough estimation of temperatures at sites some distance away. We describe below a chemical method of measuring mean temperature at field sites, over periods of up to a month or more, which offers a simple and economical way out of these difficulties.

Methods of determining mean temperature by means of chemical reactions have been described previously (Jones 1972; Workman 1980) but these require sophisticated equipment. A method which employs the hydrolysis of potassium ethyl xanthate requires only a milligram balance; a previous version (Ashworth 1980) is inconvenient because the user is restricted to a weekly schedule of site visits. We have modified the method to allow the user to visit sites at intervals of any convenient duration up to 10 days at 25° C, 1 month at 15° C or 3 months at 5° C.

In the modified procedure, a glass vial containing potassium ethyl xanthate in a neutral buffer solution is left at the site of the degradation experiment. After a suitable interval of time (usually several weeks, which can correspond with a sampling visit to the degradation experiment) the hydrolysis reaction is stopped by precipitating the remaining xanthate as its insoluble nickel salt. The mixture is filtered in the laboratory and the mean temperature for the interval is determined from the dry weight of material filtered off. Results of field tests compared well with average soil temperatures recorded hourly.

MATERIALS AND METHODS

All the work reported here was done using pure potassium ethyl xanthate (KETX) made as follows. A slight excess of carbon disulphide (14 mL) is added to a freshly prepared, magnetically stirred solution of KOH pellets (11 g) in ethanol (400 mL) in a beaker at room temperature, inside a fume hood. The ethanol must be methanol-free. The reaction is rapid and quantitative. The contents of the beaker are poured into a large wide-neck screw-top bottle containing diethyl ether (400 mL) chilled in ice-water. The bottle is then closed and left until the contents have attained 5° C (note: there is a risk of fire if ether-containing solutions are left in an electric refrigerator). The precipitated KETX is filtered off, spread out to dry (1 h) in the current of air entering a fume hood, then stored in a screw-top glass jar. The yield is 18 g (about 70%; the rest of the product stays in solution). The product keeps for long periods at room temperature.

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Commercially available grades of KEtX are generally not pure enough for the present purpose. The Fluka Chemical Corp. can supply a purified grade which performs adequately.

Buffer solution of pH approximately 7.05 is prepared by dissolving potassium dihydrogen phosphate (KH_2PO_4 , 80.0 g analytical grade) in deionized water (about 600 mL), adding *exactly* 200 mL of *exactly* 2 M NaOH (volumetric standard solution) and making up to 1 L in a volumetric flask. Potassium dihydrogen phosphate is virtually anhydrous and need not be oven-dried. Care must be taken not to use the di-potassium salt by mistake. Keep the solution in a capped bottle, preferably refrigerated. The precipitating solution is 25 g of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ made up to 1L in 1 M acetic acid solution, which prevents precipitation of nickel phosphate when the two solutions are mixed.

Suitable glass vials are those that hold roughly 35 mL and have a tight-fitting plastic cap. The vials should be cleaned, preferably by immersion (24 h) in chromic acid (60 g of sodium dichromate per liter of concentrated sulphuric acid) then washed thoroughly with tap-water, rinsed in distilled water and dried. Clean glass is essential because the nickel xanthate precipitate adheres to plastic and to grease. Vials containing 0.250 g of KEtX are taken to the field site where the temperature-monitoring reaction is started (taking note of the time and date) by adding 25 mL of buffer solution. This can be dispensed by manual or automatic pipet; in the field we found it convenient and accurate to use plastic syringes (60 mL size).

For monitoring soil temperature (usually at 20 cm depth), we used appropriate lengths of plastic plumbing pipe buried vertically. Vials made a close sliding fit and were installed and retrieved using a rod with a rubber suction-tip. The air space above the vial was taken up with a nylon stocking filled with polystyrene packing nuggets. The exposed end of the pipe was capped with a close-fitting plastic lid to keep out rain.

At the end of the period of exposure the reaction was stopped by adding a slight excess (10-12 mL) of the nickel sulphate solution described above and the nickel xanthate precipitate separated by filtering under gravity, using glass funnels. Folded filter papers (Whatman no. 41, 7 cm diameter) numbered in pencil were left for several hours in the balance room, to equilibrate with the ambient relative humidity, before weighing. We used one paper for each vial to be filtered, plus two blanks. (The precipitate should be allowed to flocculate for at least an hour before filtering but it is advisable to filter it off the same day or, if this is not possible, to chill the vials until filtering is done, because of continuing, slow hydrolysis of the nickel xanthate).

After filtering, the precipitate was washed thoroughly with distilled water; blank papers received only water. Each moist filter paper was then placed upright in the rim of a plastic vial. The vials were left in the current of air entering a fume hood (for at least 5 h) then taken to the balance room for re-equilibration. A small correction for the mean change in weight of the blank filter papers (usually 2 or 3 mg) was applied to the gain in weight of the papers with precipitate. A slow weight loss (less than 1 mg per day), due to evaporation of the precipitate after drying, was an insignificant source of error in weighing.

The effective mean temperature T_m in degrees Celsius for a reaction period of t days is calculated from the dry weight y of the precipitate using equation (1), which was derived as described in the Appendix.

$$T_m = \frac{3983}{\{ c + \log_{10} t + f(y) \}} - 273.1 \quad (1)$$

In equation (1) the value of the constant, c , may be set at 12.250 or for greater accuracy can be slightly modified on the basis of a calibration run with an individual batch of buffer solution (see Appendix). The value of the function $f(y)$ depends on y and can either be calculated from equation (2) or obtained by interpolation from a plot of the data in Table 1.

$$f(y) = - \log_{10} \{ \log_e (y_0/y) \} \quad (2)$$

In equation (2), y_0 is the maximum possible (zero-time) dry weight of the precipitate. The value determined experimentally was 0.233 g which is >99% of the theoretical yield from 0.250 g of KEtX (the formula weights of $C_2H_5OCS_2K$ and $(C_2H_5OCS_2)_2Ni$ are 160.3 and 301.0).

Table 1. Corresponding values of $f(y)$ and y , for graphical interpolation.

Value of y (grams)	Corresponding value of $f(y)$
0.10	0.073
0.11	0.125
0.12	0.178
0.13	0.234
0.14	0.293
0.15	0.356
0.16	0.425
0.17	0.501
0.18	0.588
0.19	0.690
0.20	0.816
0.21	0.987
0.22	1.242

RESULTS AND DISCUSSION

The method was verified by comparing its results with data from meteorological installations at Ellerslie experimental farm near Edmonton. Mean soil temperature measurements (20 cm under fallow) at Ellerslie (Table 2) are well within 2° C of arithmetic means obtained from daily records.

The integrating chemical reaction is exponentially dependent on temperature and therefore weights the warm part of the diurnal cycle, giving results generally slightly higher than the arithmetic mean. The significance of this "exponential" mean temperature has been discussed by Jones (1972).

Table 2. Results of Measuring Soil Temperature (20 cm below fallow) at Ellerslie Experimental Farm (Edmonton) in Spring and Fall 1987.

Date of installing vials	Date of removing vials	Mean wt. filtered off (g)	f(y)	$\log_{10} t$	$T_m^{(a)}$	Recorded mean ^(b)
Apr. 26	May 13	0.178	0.570	1.226	11.1	n.a.
May 6	May 27	0.168	0.485	1.324	10.8	(11.0)
May 13	June 4	0.163	0.447	1.344	11.2	12.1
May 28	June 17	0.136	0.269	1.302	15.7	16.0
Sept. 29	Oct. 20	0.169	0.493	1.326	10.6	9.1
Oct. 9	Oct. 30	0.185	0.637	1.319	7.9	6.3
Oct. 20	Nov. 16	0.186	0.647	1.431	5.5	(4.3)
Oct. 30	Dec. 9	0.181	0.598	1.602	3.1	(2.4)

(a) Calculated from equation (1) putting $c = 12.220$ for the buffer solutions used at Ellerslie. The mean std. dev. in T_m was $\pm 0.3^\circ \text{C}$.

(b) Arithmetic mean of meteorological max/min record for thermistor buried nearby at 20 cm depth. n.a. = not available, due to recorder malfunction for entire period of measurement. Values in parentheses are estimates, because of recorder malfunction for part of the period of measurement.

The method is of course not confined to investigations of degradation. The need for a relatively frequent sampling schedule when mean temperatures are 20°C or more should not be a disadvantage; rapid ecological activity and marked temperature differences between sites in warm weather will necessitate intensive measurements and should also coincide with a time of easy access to remote areas. The method is more vandal-proof and far more robust than recording equipment, which can break down between visits to the site (see footnote (b) to Table 2).

APPENDIX

The acid hydrolysis of potassium ethyl xanthate (KETX) to carbon disulphide and ethanol (King and Dublon 1932) is pseudo first-order in a buffer solution of constant pH, so that

$$\log_e (x_0/x) = kt \quad (3)$$

where x_0 is the amount of KETX at zero time, x is that remaining after time t and k is the pseudo first-order rate coefficient, which is related to the absolute temperature T according to

$$k = A e^{-E/RT} \quad (4)$$

the constants A , R and E being respectively the Arrhenius pre-exponential factor, the universal gas constant and the activation energy for the reaction.

Combining (3) and (4)

$$\log_e (x_0/x) = A t e^{-E/RT} \quad (5)$$

The hydrolysis reaction can be stopped as described above under Materials and Methods; the amount of unreacted KEtX is proportional to the dry weight of precipitate. If we replace x_0/x by y_0/y , where y_0 is the weight that would be obtained at zero time, and y the weight obtained after time t , and take logarithms, we get

$$\log_{10} \{ \log_e (y_0/y) \} = \log_{10} A + \log_{10} t - E/(2.303RT) \quad (6)$$

Equation (6) can be re-arranged to give

$$f(y) + \log_{10} t = -\log_{10} A + (E/2.303R) (1/T) \quad (7)$$

in which $f(y)$ is as given in equation (2). Equation (7) has the form

$$Y = a + bX \quad (8)$$

where $Y = f(y) + \log_{10} t$, and $X = 1/T$. The constants a and b are respectively $-\log_{10} A$ and $E/2.303R$.

The values of X and Y obtained from eighteen separate laboratory runs for known periods at known, near-constant temperature (Table 3) were used to solve equation (8) by a standard least-squares procedure in which Y was the dependent and X the independent variable. The estimates of the constants a and b thus obtained were -12.251 and 3983.4 respectively and the regression coefficient r^2 was 0.994.

Substituting these values into equation (7) and re-arranging gives

$$T \text{ (Kelvin)} = 3983.4 / \{ 12.251 + \log_{10} t + f(y) \} \quad (9)$$

from which equation (1) follows directly (for practical purposes no more than four significant figures for the values of the constants are justified). Re-inserting the observed values of $f(y)$ and t into equation (9) gave calculated temperatures T_c in good agreement with thermometer readings T_{obs} showing that the measurements were self-consistent (Table 3).

Slight variability in composition from one batch of buffer solution to another affects the accuracy of the method. For best results, therefore, it is advisable to calibrate each new batch at one convenient, known temperature. The value of the constant b in equation (8) depends only on the activation energy of the reaction and can be expected to be insensitive to small changes in buffer solution pH from batch to batch. However, these changes affect the value of the constant a , whose value for an individual batch can be calculated from the mean value of $f(y)$ obtained in the calibrating run, the mean absolute temperature of the run (mean degrees Celsius plus 273.1) and the duration of the run, using equation (8).

An example of calibrating an individual buffer solution is given below Table 3.

Table 3. Data from laboratory experiments used to calculate the constants a and b in equation (8).

Dry weight (y) of precipitate (grams) f(y)		Duration (t) of reaction (days) Y		Measured temperature T_{obs} (° C) 1000 X		Calculated temperature from eqn. (9) T_c (° C)
0.2129	1.044	1.013	1.050	26.3	3.339	26.3
0.1968	0.772	1.903	1.052	26.3	3.339	26.3
0.1810	0.598	3.000	1.075	26.2	3.341	25.8
0.1821	0.608	3.000	1.085	26.1	3.342	25.5
0.1607	0.430	4.070	1.040	26.0	3.343	26.6
0.1351	0.264	6.000	1.042	26.1	3.342	26.5
0.1245	0.203	7.000	1.048	26.3	3.339	26.4
0.1919	0.712	7.000	1.557	14.9	3.472	15.3
0.1589	0.417	14.000	1.563	14.9	3.472	15.2
0.1318	0.245	21.000	1.567	14.9	3.472	15.1
0.1154	0.153	28.000	1.600	14.9	3.472	14.4
0.2087	0.959	7.000	1.804	9.5	3.538	10.3
0.1920	0.713	14.000	1.859	9.5	3.538	9.2
0.1763	0.555	21.030	1.878	9.5	3.538	8.8
0.1557	0.395	28.000	1.842	9.4	3.539	9.5
0.1560	0.397	28.000	1.844	9.5	3.538	9.5
0.1339	0.256	40.200	1.860	9.4	3.539	9.1
0.1223	0.191	45.000	1.844	9.5	3.538	9.5

Values of y are the mean of 2 dry weights differing by 0.0017 g on the average.

Slight variations in T_{obs} are due to temperature drift during run.

The thermometer used was calibrated against a thermometer certified by the National Physical Standards Laboratory (Teddington, U. K.).

In calibrating the batch of buffer solution used at Ellerslie in the fall of 1987 (see Table 2), a mean precipitate dry weight of 0.173 g was obtained after 7.813 days in the laboratory at a controlled temperature of 19.0° C ($T = 292.1$ K). In this run, $X (= 1/T) = 0.003423$; $f(y)$ was 0.526 (from equation 2), $\log_{10} t$ was 0.893 and so $Y (= f(y) + \log_{10} t) = 1.419$. Putting these values of X and Y into equation (8) and assuming $b = 3983$ gives a value of $a (= Y - bX)$ of - 12.216. Although the fifth significant figure in the value of the constant a does affect the calculated temperature very slightly, including it is for practical purposes not justified; hence the value of $c (= -a)$ used in equation (1) was set at 12.220 for this batch.

If indeed pseudo first-order kinetics apply to the hydrolysis reaction, equation (3) holds and a plot of $-\log x$ or $-\log y$ against time (Figure 1) should be linear.

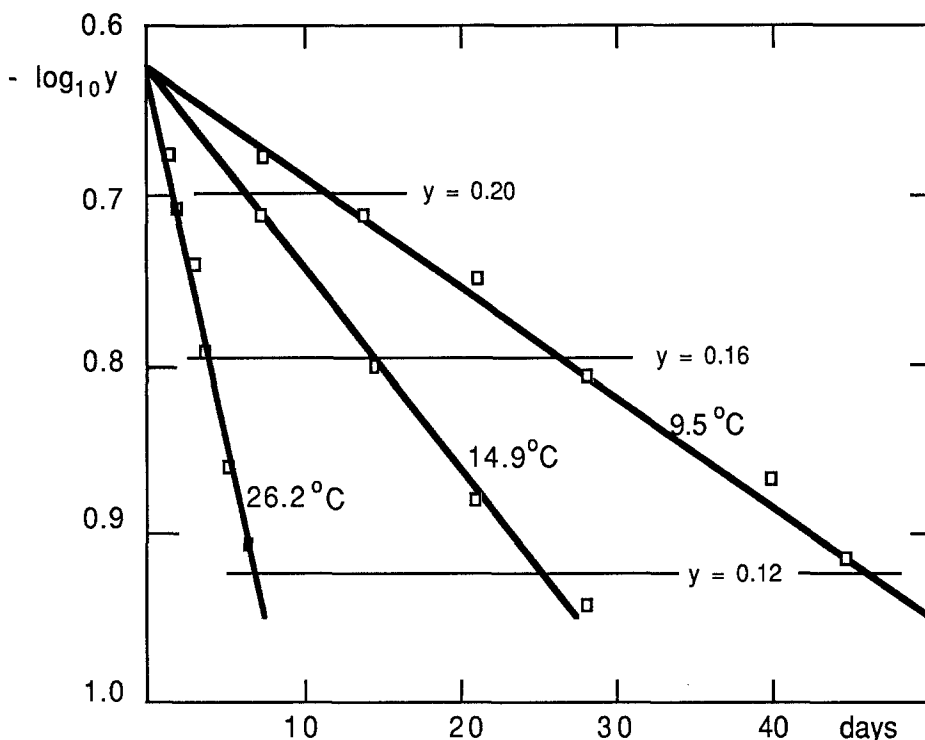


Figure 1. A plot of data in Table 3 (squares) and the result predicted by equation (9) for three temperatures (bold lines).

Factors that would be expected to cause non-linearity include the gradual increase in pH due to consumption of hydrogen ion, and the side-reaction which accompanies the main hydrolysis and produces ethyl dixanthogen. The absence of any consistent departure from linearity in Figure 1 is fortuitous, but indicates that the method is valid at least over the range $0.11 < y < 0.22$ grams. The side-reaction and the variable appearance of the precipitate have been discussed previously (Ashworth 1980). They do not invalidate the procedure.

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