LIGNIN KINETICS AND ITS IMPLICATIONS FOR THE SHROUD

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During chemical tests on samples from the Shroud of Turin, we noticed that the lignin at the linen's growth nodes did not give the common test for vanillin. This test is the most popular method for the identification of lignin. This poses a problem.

Stan Kosiewicz of Los Alamos, an analytical chemist, aged samples that contained lignin at 40, 70, and 100°C for up to 24 months. Just as we suspected, he found that lignin loses its vanillin with heating and/or time.

Chemical rates depend very strongly on temperature. Rates of all kinds of reactions are modeled with an exponential equation called the Arrhenius expression:

$$\frac{d\alpha}{dt} = kf(\alpha)Ze^{-E/RT}$$

Rates can be predicted from amounts of reactants (α is the fraction reacted at any time t) and known, measured chemical kinetics constants (k, the rate constant in units of s^{-1}; Z, the Arrhenius frequency factor; E, the Arrhenius activation energy; R, the gas constant; and T, the absolute temperature in degrees Kelvin). The $f(\alpha)$ is called the "depletion factor," and it depends on the physical state of the reactant, the type of reaction, and/or the number of molecules involved in the reaction. Any chemical process involved in Shroud aging or image formation will have properties in accordance with this equation.

The rates of lignin degradation were so slow that we could not make accurate determinations of the rate constants in the amount of time we could spare, but we could make estimates. We used the time until phloroglucinol/HCl failed to detect lignin (vanillin) as the criterion, not a very rigorous method; however, it gave the following Arrhenius predictive model.

$$k = 3.7x10^{11}e^{-\frac{29,600}{1.987T}}$$

After the rate constant has been determined at a specific temperature, the amount of time required for vanillin to be depleted from lignin by a first-order reaction at that specific temperature can be calculated from the following equation:

$$-\ln(1 - \alpha) = kt$$

Because the rate law is exponential, the maximum diurnal temperature is much more important than is the lowest storage temperature; however, if the Shroud had been stored at a constant 25°C, it would have taken about 1,319 years to lose 95% of its vanillin. At 23°C, it would have taken about 1,845 years. At 20°C, it would take about 3,095 years.

If the Shroud had been produced between AD 1260 and 1390, as indicated by the radiocarbon analyses, its lignin should be easy to detect. A linen produced in AD 1260 should have retained 37% of its vanillin in 1978. All of the medieval linens we have tested gave a good test for vanillin.

The disappearance of all traces of vanillin from the lignin in the Shroud indicates a much older age than did the radiocarbon analysis.

The fire of 1532 could not have greatly affected the vanillin content of lignin in all parts of the shroud equally. The thermal conductivity of linen is very low, 2.1×10^{-4} cal cm^{-1} s^{-1} $°C^{-1}$; therefore, the unscorched parts of the folded cloth could not have become very hot. The temperature gradient through the cloth in the reliquary should have been very steep, and the cloth's center would not have heated at all in the time available. The rapid change in color at scorch margins from black to white illustrates this fact.

Any heating at the time of the fire would decrease the amount of vanillin in the lignin as a function of the temperature and time heated; however, different amounts would have decomposed in different areas. No samples from any location on the Shroud gave the vanillin test. Since the shroud and other very old linens do not give the vanillin test (e.g., linen from the Dead Sea scrolls), the cloth must be quite old.

With enough work, we could get much more accurate and confirmed kinetics numbers. It would be a good dissertation project for some chemistry student who is interested in the Shroud. However, under any assumptions we may make, chemistry would suggest that the cloth is older than the published radiocarbon date.