

parameters of the spin probe are similar in each environment so that resolution is not achieved, which leads to pitfalls in the interpretation of the ESR spectra and incorrect numerical assignments.

These complications have been found to be important for other spin probes such as 2,2,6,6-tetra methyl piperidine-1-oxyl and its derivatives in micellar solutions and they can also exist in mesomorphic phase systems. The complexity of the ESR spectrum depends on the solubility of the spin probe in the aqueous phase and the position which the solubilized molecule takes up in the micelle or membrane.

The presence of two superimposed ESR spectra can be demonstrated by the following. (1) Asymmetry in the recorded spectrum (Fig. 1a) and careful examination of line-shapes at surfactant concentrations above the CMC. (2) Broadening of the spectrum of the spin probe in the micellar phase (Fig. 1b) when two or more spin probes occupy the same micelle. Spin-spin broadening facilitates partial resolution of the high field line of the recorded spectrum. The other hyperfine components of the two spectra are less resolved because of the higher  $g$ -value of the spectrum of the solubilized spin probe. (3) Doping the solution with paramagnetic ions, such as  $Mn^{2+}$  or  $Cu^{2+}$ , which preferentially bind to the micellar surface.

As the last experiment can also be used to measure the affinity of ions for colloidal surfaces, it is described in more detail. The line-broadening of the peaks of the ESR spectrum of (I) in  $Mn^{2+}$  doped SDS solutions as a function of cation concentration can be described by an equation of the form<sup>7,8</sup>

$$\left(\frac{1}{NT_2}\right) = \frac{4}{60} S(S+1) P \left(\frac{g^2 \beta^2 \gamma^2 e}{r^6}\right) \left[7\tau_c + \frac{13\tau_c}{1 + \omega_s^2 \tau_c^2}\right] + \frac{1}{3} S(S+1) P \left(\frac{A^2}{\hbar^2}\right) \left[\tau_c + \frac{\tau_c}{1 + \omega_s^2 \tau_c^2}\right]$$

in which the first term represents the dipole-dipole interaction and the second the spin exchange contribution to the relaxation rate. Because the spin exchange term is negligible in this system, the equation predicts that line broadening should be proportional to the cationic concentration,  $N$ , and the average distance,  $r$ , between  $Mn^{2+}$  and (I).  $P$  represents the fraction of (I) interacting with the cation, which is constant in dilute solutions, and similarly  $\tau_c$  which consists of contributions

$$\frac{1}{\tau_c} = \frac{1}{\tau_s} + \frac{1}{\tau_h} + \frac{1}{\tau_r}$$

in which the first two terms have their usual significance<sup>7,8</sup> but  $\tau_r$  here represents the correlation time for random Brownian motion of the  $Mn^{2+}$  ion relative to that of (I).

Consequently, the two spectra of (I) in micellar solutions will be discriminately broadened as the  $Mn^{2+}$  ion concentration is increased, because  $Mn^{2+}$  tends to be absorbed preferentially into the Stern layer of the micelle in SDS solutions<sup>9</sup>, which results in greater proximity of  $Mn^{2+}$  and (I) solubilized in the micelle. Experimentally, a spectrum resembling that in Fig. 2 is observed in 0.5% SDS solution containing  $10^{-4}$  M  $Mn^{2+}$  and at  $10^{-3}$  M  $Mn^{2+}$  there is considerable reduction in signal amplitude and the spectrum of (I) in water remains. This is because the spectrum of solubilized (I) has been broadened beyond detection as a result of spin-spin interactions with  $Mn^{2+}$  ions absorbed in the Stern layer of the micelle. Finally, at  $10^{-2}$  M  $Mn^{2+}$  the aqueous spectrum becomes severely broadened, indicating the existence of "free"  $Mn^{2+}$  ions in the aqueous phase.

In conclusion, I emphasize that care must be taken in the interpretation of the ESR spectra of spin probes in micellar and related systems, as the recorded spectrum consists of a superposition of two spectra which is not obvious. I have demonstrated how doping with  $Mn^{2+}$  helps to resolve this difficulty.

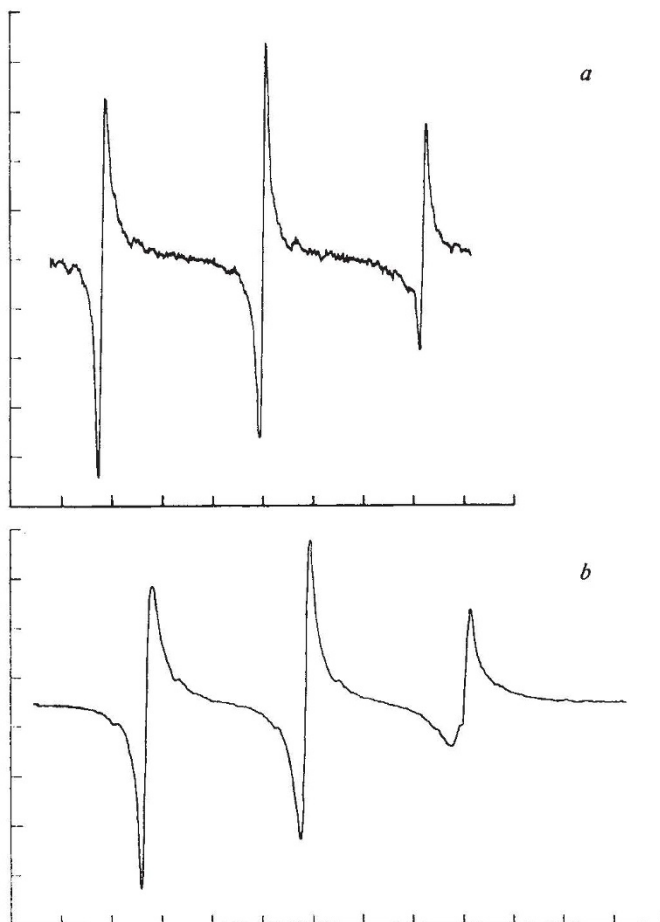


Fig. 1 a, Electron spin resonance spectrum of  $10^{-5}$  M (I) in 0.3% SDS solutions. b, Electron spin resonance spectrum of  $1.3 \times 10^{-4}$  (I) in 0.5% SDS solutions. The solutions were saturated with spin probe and the average number of molecules of (I) per micelle was  $\sim 2$ .

I thank Mr M. Barratt for a gift of (I), Mr M. C. Cafe for experimental assistance, my colleagues for helpful discussions and Dr Eastmond of Liverpool University for the use of the Varian E-3.

J. OAKES

Unilever Research Port Sunlight Laboratory,  
Port Sunlight,  
Wirral, Cheshire

Received November 27, 1970; revised March 18, 1971.

- Waggoner, A. S., Griffith, O. H., and Christensen, C. R., *Proc. US Nat. Acad. Sci.*, **57**, 1198 (1967).
- Waggoner, A. S., Keith, A. D., and Griffith, O. H., *J. Phys. Chem.*, **72**, 4129 (1968).
- Griffith, O. H., and Waggoner, A. S., *Accounts. Chem. Res.*, **2**, 17 (1969).
- Rabold, G. P., *J. Polymer Sci.*, A-1, **7**, 1187 (1969).
- Stone, T. J., Buckman, T., Nordio, P. L., and McConnell, H. M., *Proc. US Nat. Acad. Sci.*, **54**, 1010 (1965).
- Ohnishi, S., Cyr, T. J. R., and Fukushima, H., *Bull. Chem. Soc. Japan*, **43**, 673 (1970).
- Solomon, I., *Phys. Rev.*, **99**, 559 (1955).
- Bloembergen, N., *J. Chem. Phys.*, **27**, 572, 595 (1957).
- Pearson, J. T., and Lawrence, A. S. C., *Trans. Faraday Soc.*, **63**, 488 (1967).

## A Cappadocian Speculation

IN 1925, F. Hrozny discovered the source of the "Cappadocian" tablets near the village of Kültepe ( $38^{\circ} 44' N$ ,  $35^{\circ} 34' E$ ). These cuneiform tablets provide a foundation for study of the

pre-Hittite (*circa* 1940 BC to 1740 BC) network of Assyrian merchant colonies in Bronze Age Anatolia<sup>1</sup>. Bilgic<sup>2</sup> has published the names of 119 towns active in this exchange, as evidenced by their citation on a tablet. The exact location of most of these sites is not known, and historical and archaeological investigations would be greatly facilitated if they could be found. We have used Bilgic's compilation to estimate the geographical position of several of the towns, in the sense of Bunge<sup>3</sup>, which is conditional on several assumptions. We invoke assumptions to enhance the analysis by applying the leverage obtained from geographical theory. We assume, for example, that mathematical models based on contemporary (largely western) data have a temporally and geographically invariant structure and can be applied to the Cappadocian situation. Our approach differs from several previous attempts<sup>1,2,4</sup>, to which it should be considered complementary rather than competitive. For example, we do not require the existence of itineraries; the mere mention of two town names on the same tablet is taken to define a relation between these towns. We recognize that one of the simplest geographical relations is distance and attempt to convert the tabular data into geographical distances. If this is possible then it is an almost routine matter to convert these distances into relative positions. Thus it may be possible to specify the actual locations of the towns; that is, to predict their latitude and longitude. The simplest model asserts that places which are mentioned together frequently are probably closer together than are places which are not mentioned together frequently. This spatial decay is similar to the temporal decay of linguistic relations postulated in glottochronology<sup>5</sup>, or of isotopic changes used in radiocarbon dating<sup>6</sup>. Our procedure attempts to estimate spatial, rather than temporal, origins and can be considered the geographical equivalent to these methods. It also has comparable limitations. We know of no previous use of the procedure presented here.

On a purely random basis, one would expect the names of large towns to occur more frequently than the names of small towns. The total expectation is thus that the interaction between places depends on the size of the places and the separation between the places. This rather obvious result has been verified in a large number of societies and for many phenomena<sup>7</sup>. Specifically, we expect the interaction to increase as the places get bigger, and to decrease as they are farther apart. Many functions satisfy such a requirement. For social interaction the most common formulation is the so-called gravity model<sup>8</sup>

$$I_{ij} = k P_i P_j / d_{ij}^2$$

where  $I_{ij}$  is the interaction between places  $i$  and  $j$ ;  $k$  is a constant, depending on the phenomena;  $P_i$  is the population of  $i$ ;  $P_j$  is the population of  $j$ ; and  $d_{ij}$  is the distance between places  $i$  and  $j$ .

Distance may be in hours, dollars, or kilometres; populations may be in income, numbers of people, numbers of telephones and so on; and the interaction may be in numbers of letters exchanged, number of marriages, similarity of artefacts or cultural traits and so on. The evidence that it "works" has been assembled for more than 20 yr; why such an equation should work is sometimes interpreted as a metaphysical question and continues to be debated<sup>9</sup>. Here, we assume that this model might hold for the number of joint occurrences of place names in merchants' letters. We know of no specific data on this topic, although a modern empirical test seems feasible. The gravity model can of course be inverted to solve for the distance  $d_{ij}$ , as can several alternate interaction models<sup>10</sup>. For our purpose this is essential. The step from distances to coordinates can be solved by iterative least squares trilateration techniques<sup>11</sup>. These have recently been generalized in psychology under the heading of multidimensional scaling<sup>12</sup>. For the computation we have used a non-metric computer program made available by Lingoes<sup>13</sup>. This procedure attempts to preserve only the rank order of the distances, not their absolute

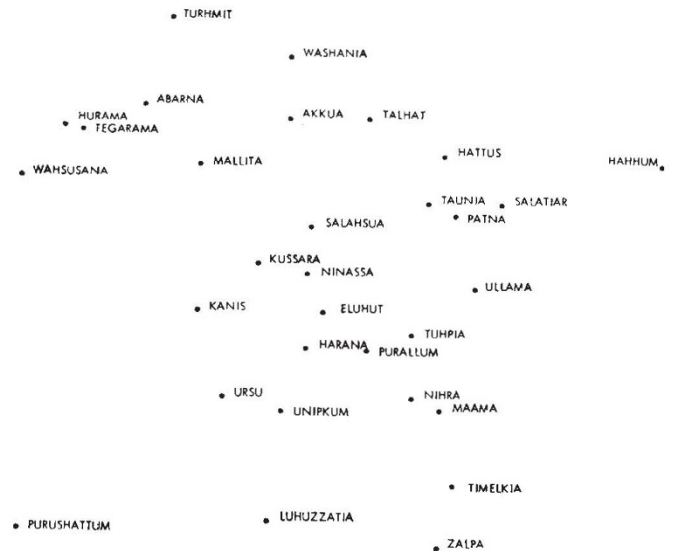


Fig. 1 Predicted location of the more important of the pre-Hittite towns. Based on interaction among sixty-two towns as evidenced by citation on cuneiform tablets. See text for details.

ratios, and thus partitions spatial interaction models into monotonic equivalence classes. Shepard<sup>14</sup> has emphasized the value of the weaker ordinal assumptions and that the form of the model can be determined after the analysis. This is because the geometric constraints override inconsistencies in the data and minor distinctions between alternate models. The specific equation used for interaction is thus of no great significance.

Bilgic's table gives, for each of 119 towns, the tablets on which the name of that town occurs (a total of 819 tablets is thus referenced). We have taken the number of occurrences of a town name to be proportional to the population of that town. The table can be inverted to list place names by tablet and this is quickly converted to a frequency count. Sixty-five tablets are eliminated from the ensuing analysis since they lead to dead ends, in the sense that they contain the sole reference to a particular town. There remain sixty-two towns occurring on at least two of 754 tablets. These results are most conveniently arrayed in a table of sixty-two rows (one for each town), and sixty-two columns, with the entry at the intersection of any row and column made equal to the number of times that the names of the particular towns occur together on a tablet. This table of joint-mention frequencies is symmetrical so that only the lower half need be completed. The site near Kültepe has been identified as the Assyrian karum Kanis and most of the tablets can thus be considered to bear the implicit imprimatur "found at Kanis". Thirteen of the tablets (OIP XXVII 1-53) were excavated at Alishar (35° 35' N, 35° 15' E), commonly identified as Akkua<sup>15</sup>, a small number of Cappadocian tablets have also been uncovered at Bogazköy (40° 02' N, 34° 37' E), now known to have been the Hittite capital Hattus. Out of the possible  $n(n-1)/2 = 1,891$  connexions, only 187 actually occur if we ignore the implicit imprimatur (which would add forty-four new connexions) and the Alishar tablets (adding nine more connexions if Akkua is assumed to be implicit on these tablets). This is approximately 10% of all possible connexions, and averages three connexions per town. The actual numbers of connexions ranges from a low of two to a high of twenty-three. The frequency ranges from a low of one joint mention to a high of twelve joint mentions. Some towns are mentioned only once, Purushattum 101 times (seventy-two times in isolation and on twenty-nine tablets with at least one other place name). Our entire analysis is based on Bilgic's work, which is the only currently published complete tabulation. Obvious minor typographical errors have been corrected but Bilgic may have confused regional

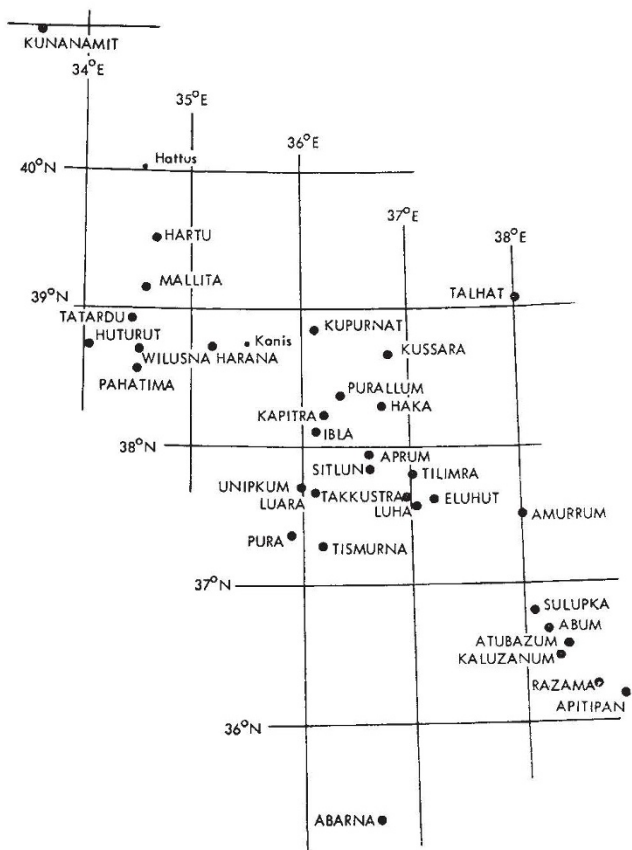


Fig. 2 Predicted location of thirty-three pre-Hittite towns, contingent on the assumption that the towns shown on Orlin's map are correctly located. See text for details.

names with town names, or mistranslated a personal name as a town name, or confused the names of two similar towns, and so on. The most obvious improvement to our analysis would be to use a more extensive collection of data, such as a tabulation prepared from all of the 17,000 Cappadocian tablets excavated so far. Such compilations are in preparation<sup>16</sup> but were not available to us.

Our experiment resulted in the configuration shown in Fig. 1, which is based on all the joint mentions and the estimated populations, without constraints to fix the positions of any locations. The fit of this figure to the available data is high (>80%) as is usual for the gravity model, but this is mostly a measure of the internal consistency of the data. The more critical test is to compare our results with known sites. Any solution results in relative coordinates and at least two points must be known in absolute coordinates to determine the scale, and a third point to determine the absolute orientation. For statistical stability many positions should be known in advance. In this case there are sixty-two points to be located and only Kanis and Hattus (perhaps also Akkua) can be considered known, although reasonable speculations are available concerning the locations of several other sites. In a formal sense our results would allow calculation of a latitude and longitude coordinate for each town, but such precision does not seem warranted until further data become available for analysis.

We can of course compare our results with other published estimates, most of which are based on a few itineraries. In many cases the interpretations differ and the authors do not agree with each other. Locations are rarely precise, often indicating only the general area. Geographical maps require a more precise specification and we have been able to compare our results with the map given by Orlin<sup>17</sup>. Twenty-nine towns are common to the two studies; the correlation coefficient comparing the twenty-nine locations as given by these

two studies is essentially zero. This is disappointing. Both are speculations, of course, one based on a few specific details, the other on 754 tablets indicating general interaction. Our statistical procedure would be more convincing if an extensive network of sites were known exactly and only one or two additional locations were to be found. Orlin's data allow such an estimate to be made, for if it is assumed that his map is correct then this can be incorporated as a weighted constraint in the computer program. On this basis thirty-three locations have been computed from the interaction data and the twenty-nine fixed positions (Fig. 2). We thus obtain coordinates with a precision which is contingent on empirical data, on geographical location theory, and on previous Assyrian scholarship. Five typical results are:

Harana	38° 44' N ± 22'	35° 04' E ± 32'
Huturut	38° 46' N ± 11'	34° 03' E ± 31'
Kussara	38° 40' N ± 21'	36° 49' E ± 35'
Pahatima	38° 33' N ± 04'	34° 31' E ± 10'
Tilimra	37° 49' N ± 70'	37° 01' E ± 49'

The probable errors are obtained as an automatic byproduct of our procedure and can be interpreted in the usual manner. The average of roughly 50 km may seem too large for the field archaeologist, especially in an area as rich in mounds as central Turkey, but this does not invalidate the technique. As a tool for investigation it has specific data requirements and thus provides a focus for investigation. As in the dating of sites a convergence of evidence is more convincing than a single indicator. Particular sites may deviate from the model but this is then an important method of drawing attention to anomalous situations worthy of more detailed investigation.

W. TOBLER  
S. WINEBURG

Department of Geography,  
University of Michigan,  
Ann Arbor, Michigan 48104

Received October 8, 1970; revised April 13, 1971.

- <sup>1</sup> Garelli, P., *Les Assyriens en Cappadoce* (Maisonneuve, Paris, 1963).
- <sup>2</sup> Bilgic, E., *Arch. Orientforsch.*, **50**, 1 (1951).
- <sup>3</sup> Bunge, W., *Theoret. Geog.* (Gleerup, Lund, 1966).
- <sup>4</sup> Garstang, J., and Gurney, O., *The Geography of the Hittite Empire* (British Institute of Archaeology, Ankara, 1959).
- <sup>5</sup> Gudschinsky, S., *Word*, **12**, 175 (1956).
- <sup>6</sup> Libby, W., *Science*, **159**, 621 (1961).
- <sup>7</sup> Olsson, G., *Distance and Human Interaction* (Regional Science Association, Philadelphia, 1965).
- <sup>8</sup> Isard, W., et al., *Methods of Regional Analysis* (Wiley, New York, 1960).
- <sup>9</sup> Niedercorn, J., and Bechdolt, B., *J. Reg. Sci. Assoc.*, **9**, 273 (1969).
- <sup>10</sup> Tobler, W., Detwyler, T., and Mielke, H., *Bioscience*, **20**, 537 (1970).
- <sup>11</sup> Wolf, P., *Surveying and Mapping*, **29**, 635 (1969).
- <sup>12</sup> Guttman, L., *Psychometrika*, **33**, 469 (1968).
- <sup>13</sup> Lingoes, J., and Roskam, E., *Multivariate Behavioral Research*, **5**, 183 (1970).
- <sup>14</sup> Shepard, R., *J. Math. Psychol.*, **2**, 287 (1966).
- <sup>15</sup> Gelb, I., *Oriental Institute Publications*, 27 (University of Chicago Press, 1935).
- <sup>16</sup> Gardin, J., in *The Use of Computers in Anthropology* (edit. by Hymes, D.) (Moulton, The Hague, 1965).
- <sup>17</sup> Orlin, L., *Assyrian Colonies in Cappadocia* (Moulton, The Hague, 1970).

## Surface Wave Momentum and Energy Velocities

REYNOLDS<sup>1</sup> defined the energy velocity associated with a simple periodic wave train on the surface of deep water as the phase velocity multiplied by the ratio of the energy transmitted across a fixed vertical plane during one wave period to the energy of the waves per wavelength. In other words,