Potentiometric scanning electrochemical microscopic mapping of the distributed Belousov-Zhabotinsky oscillating reaction

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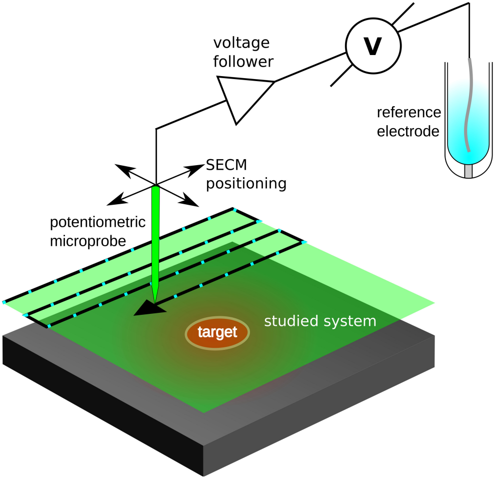
Scanning Electrochemical Microscope



Belousov-Zhabotinsky reaction

Zaikin, A. N., and A. M. Zhabotinsky. "Concentration wave propagation in two-dimensional liquid-phase self-oscillating system." *Nature* 225, no. 5232 (1970): 535.

Optical method

Noyes, Richard M., Richard Field, and Endre Kőrös. "Oscillations in chemical systems. I. Detailed mechanism in a system showing temporal oscillations." *Journal of the American Chemical Society* 94, no. 4 (1972): 1394-1395.

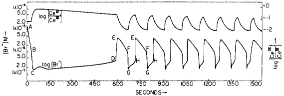
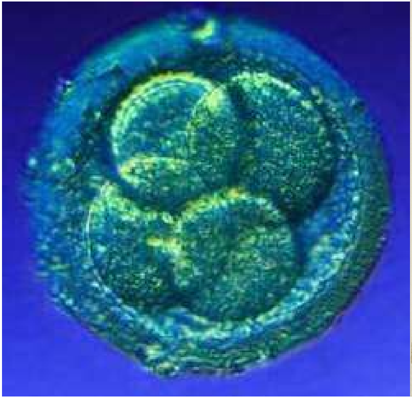


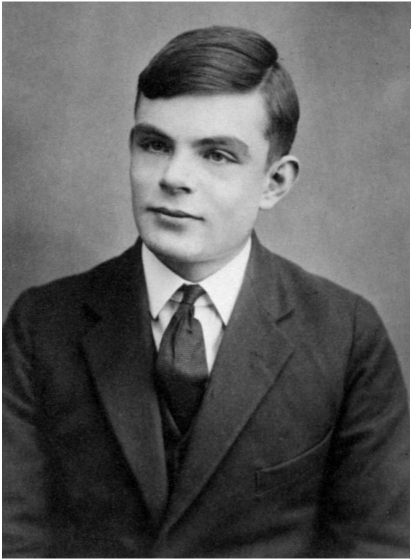
Figure 1. Potentiometric traces at room temperature of log [Br^-] and of log [Ce(IV)]/[Ce(III)] for a stirred solution in which the initial concentrations were [$CH_2(COOH)_2$] = 0.032 *M*, [$KBrO_3$] = 0.063 *M*, [KBr] = 1.5 × 10^{-5} *M*, [$Ce(NH_4)_2(NO_3)_5$] = 0.001 *M*, and [H_2SO_4] = 0.8 *M*.

Electrochemical method

The BZ-reaction as a model for pattern formation



„The chemical basis of morphogenesis"



THE CHEMICAL BASIS OF MORPHOGENESIS

By A. M. TURING, F.R.S. *University of Manchester*

(*Received* 9 *November* 1951—*Revised* 15 *March* 1952)

It is suggested that a system of chemical substances, called morphogens, reacting together and diffusing through a tissue, is adequate to account for the main phenomena of morphogenesis. Such a system, although it may originally be quite homogeneous, may later develop a pattern or structure due to an instability of the homogeneous equilibrium, which is triggered off by random disturbances. Such reaction-diffusion systems are considered in some detail in the case of an isolated ring of cells, a mathematically convenient, though biologically unusual system. The investigation is chiefly concerned with the onset of instability. It is found that there are six essentially different forms which this may take. In the most interesting form stationary waves appear on the ring. It is suggested that this might account, for instance, for the tentacle patterns on *Hydra* and for whorled leaves. A system of reactions and diffusion on a sphere is also considered. Such a system appears to account for gastrulation. Another reaction system in two dimensions gives rise to patterns reminiscent of dappling. It is also suggested that stationary waves in two dimensions could account for the phenomena of phyllotaxis.

The purpose of this paper is to discuss a possible mechanism by which the genes of a zygote may determine the anatomical structure of the resulting organism. The theory does not make any new hypotheses; it merely suggests that certain well-known physical laws are sufficient to account for many of the facts. The full understanding of the paper requires a good knowledge of mathematics, some biology, and some elementary chemistry. Since readers cannot be expected to be experts in all of these subjects, a number of elementary facts are explained, which can be found in text-books, but whose omission would make the paper difficult reading.

1. A model of the embryo. Morphogens

In this section a mathematical model of the growing embryo will be described. This model will be a simplification and an idealization, and consequently a falsification. It is to be hoped that the features retained for discussion are those of greatest importance in the present state of knowledge.

The model takes two slightly different forms. In one of them the cell theory is recognized but the cells are idealized into geometrical points. In the other the matter of the organism is imagined as continuously distributed. The cells are not, however, completely ignored, for various physical and physico-chemical characteristics of the matter as a whole are assumed to have values appropriate to the cellular matter.

With either of the models one proceeds as with a physical theory and defines an entity called 'the state of the system'. One then describes how that state is to be determined from the state at a moment very shortly before. With either model the description of the state consists of two parts, the mechanical and the chemical. The mechanical part of the state describes the positions, masses, velocities and elastic properties of the cells, and the forces between them. In the continuous form of the theory essentially the same information is given in the form of the stress, velocity, density and elasticity of the matter. The chemical part of the state is given (in the cell form of theory) as the chemical composition of each separate cell; the diffusibility of each substance between each two adjacent cells must also

,,Only the future can say whether such reactions will become more than a laboratory curiosity."

Endre Kőrös – 1972 (Oscillating in Chemical Systems. II.)

Chemical waves in *Xenopus* embryo

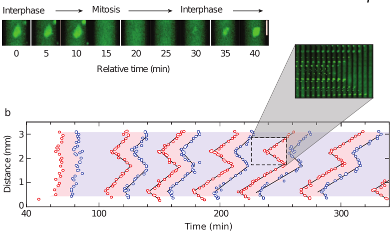
LETTER

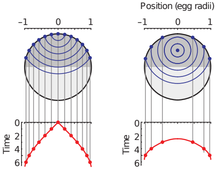
doi:10.1038/nature12321

Mitotic trigger waves and the spatial coordination of the *Xenopus* cell cycle

Jeremy B. Chang[1] & James E. Ferrell Jr[1,2]

"green fluorescent protein (GFP)-nuclear localization signal (NLS) protein were added to the extracts as reporters of mitotic entry"





Stationary measurement

Method

Stationary measurement

The measured parameters

oxidized

$[Fe(o\text{-}phen)_3]^{3+}$

$\updownarrow$

reduced

$[Fe(o\text{-}phen)_3]^{2+}$

Ferroin redox–indicator

$$E = E^{\theta} + \frac{RT}{z_i F} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

Nernst–equation

Oscillation of the $[Fe^{2+}]/[Fe^{3+}]$ ratio

Explained by the FKN–mechanism

$$BrO_3^- + Br^- + CH_2(COOH)_2 + 3H^+ \longrightarrow 3BrCH(COOH)_2 + 3H_2O \tag{1}$$

$$BrO_3^- + Fe^{2+} + CH_2(COOH)_2 + 5H^+ \longrightarrow BrCH(COOH)_2 + 4Fe^{3+} + 3H_2O \tag{2}$$

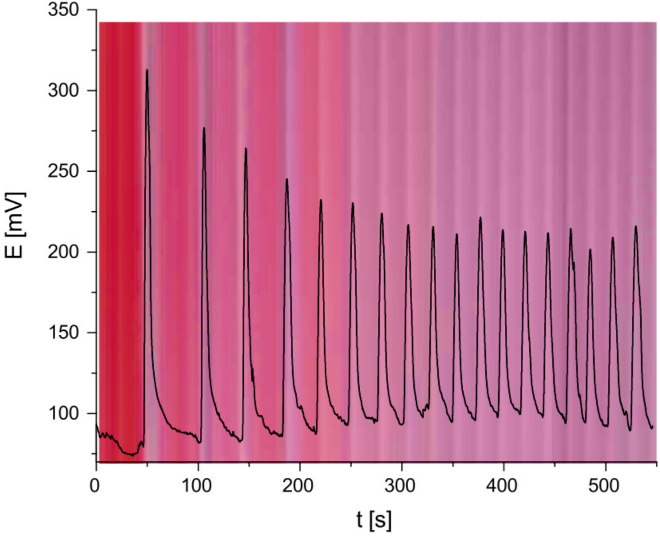
$$4Fe^{3+} + BrCH(COOH)_2 + 2H_2O \longrightarrow Br^- + 4Fe^{2+} + HCOOH + 2CO_2 + 5H^+ \tag{3}$$

$$CH_2(COOH)_2 + 6Fe^{3+} + 2H_2O \longrightarrow 6Fe^{2+} + HCOOH + 2CO_2 + 6H^+ \tag{4}$$

$$3BrO_3^- + 5CH_2(COOH)_2 + 3H^+ \longrightarrow 3BrCH(COOH)_2 + 2HCOOH + 4CO_2 + 5H_2O \tag{5}$$

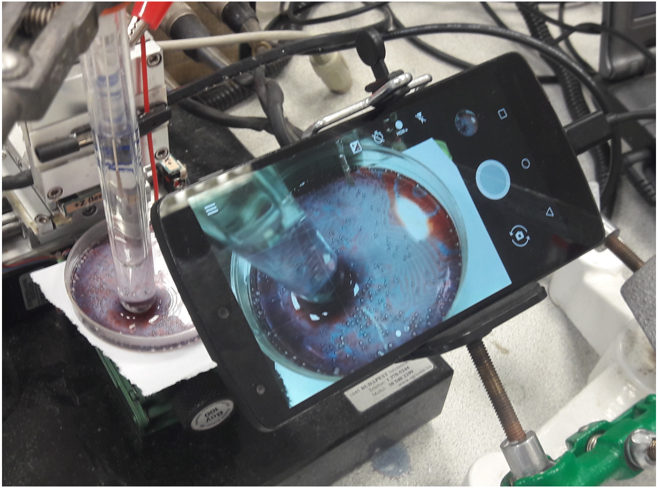
Stationary measurement

Result



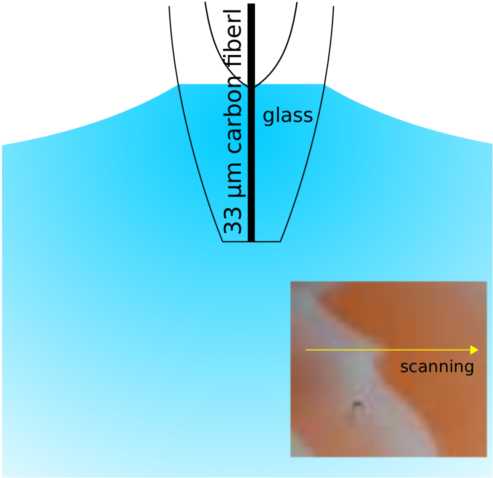
SECM scanning

Measurement setup



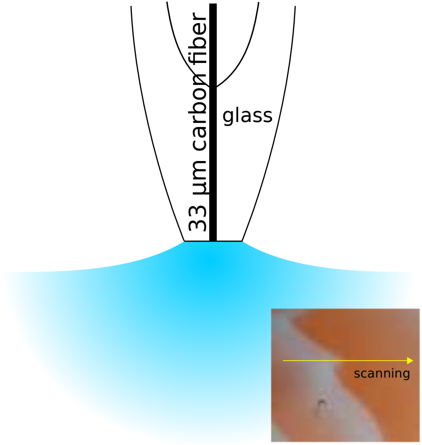
Convective disturbance

Conventional carbon microelectrode in the reaction mixture



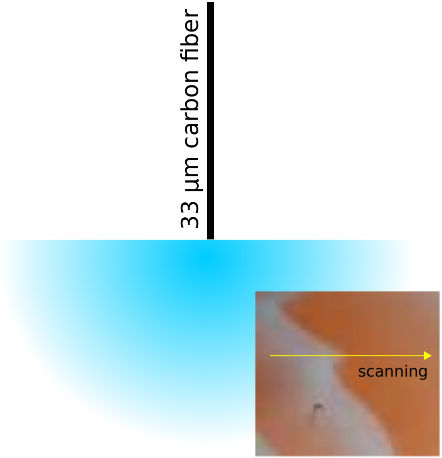
Convective disturbance

Conventional carbon microelectrode on the surface of the reaction mixture



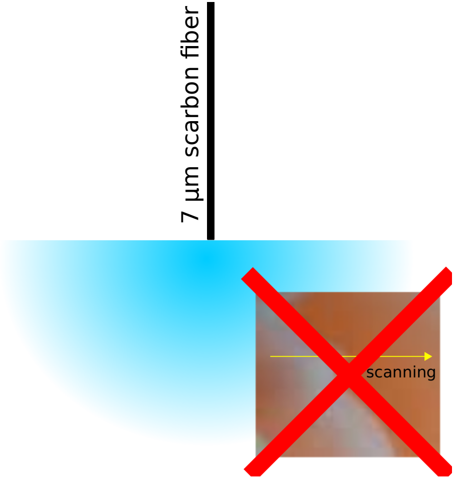
Convective disturbance

Uninsulated carbon fiber on the surface of the reaction mixture (d = 33 μm)



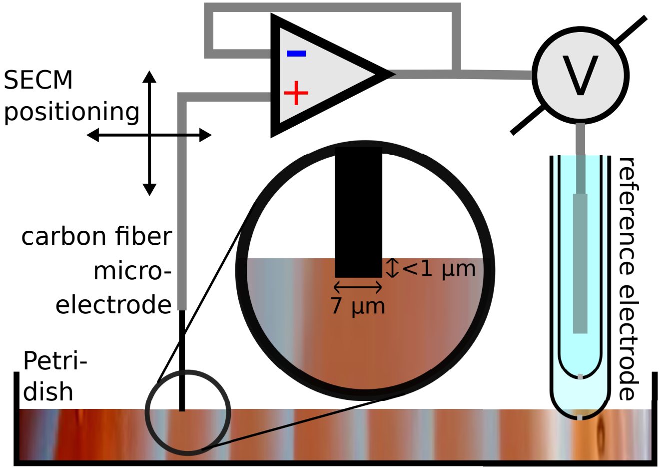
Convective disturbance

Uninsulated carbon fiber on the surface of the reaction mixture (d = 7 μm)



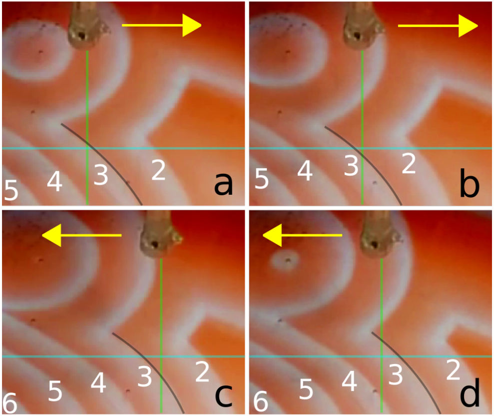
SECM scanning

Measurement setup



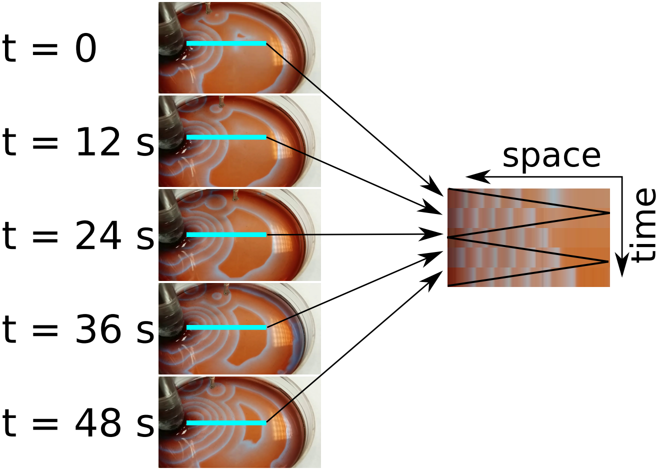
SECM scanning

Convective disturbance



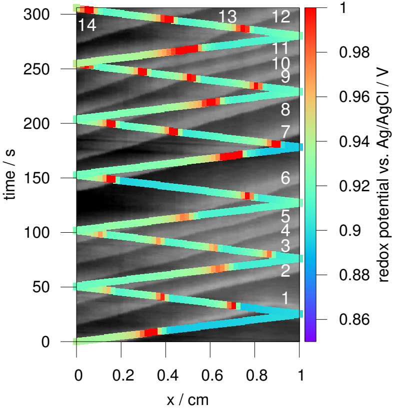
SECM scanning

Evaluating the result



SECM scanning

Result



SECM scanning

Result

Wave #	t, s	E, mV	x, mm	v, μm/s
	47	957	1.4	
3	67	978	6.4	218.8
	80	977	8.6	
	99	968	1	
6	114	975	4.8	191.3
	133.5	1027	7.6	
	148.5	1052	1.6	
7	171	1127	7.2	218.18
	181.5	1059	8.8	
	200	1016	1.4	
9	219.5	1074	6.2	191.3
	234.5	1016	8	
	253.5	1060	0.4	
12	268	1120	5.2	208.96
	287	1053	7.4	

Conclusion

- A small enough scanning probe will not disturb the BZ–reaction.
- Using the SECM, the advantages of the optical and electrochemical methods can be combined, and spatially resolved chemical images can be obtained about the distributed BZ–reaction.
- Replacing the carbon fiber with an ion-selective microelectrode, bromide-ion activity and pH could be mapped.
- The surface scanning could be used in other cases, where minimal disturbance is required.

Acknowledgements

Most of the experiments were performed by my first supervised student, **Szilárd Szili** (Chemistry BSc.).

Thank you for your attention.