



Chemical clocks on the basis of rotating waves. Measuring irrational numbers from period ratios

Oliver Steinbock¹, Petteri Kettunen²

West Virginia University, Department of Chemistry, Morgantown, WV 26506-6045, USA

Received 10 October 1995; in final form 24 January 1996

Abstract

An ink-jet printer is utilized to generate catalyst-loaded patterns such as circles, triangles, and squares on polysulphone membranes. These patterns define excitable domains for the Belousov–Zhabotinsky reaction in which rotating waves can be initiated. The resulting wave propagation is exploited for the implementation of chemical clocks with stable period ratios. Based on this approach the irrational numbers π , $\sqrt{2}$, and the golden mean are measured with a relative error of 0.1–0.2%.

1. Introduction

Chemical reaction systems far from equilibrium can exhibit a wide variety of complex temporal and spatio-temporal dynamics [1]. Some systems like the well-known Belousov–Zhabotinsky (BZ) reaction go through many oscillation cycles while approaching the thermodynamic equilibrium [1,2]. The intrinsic rhythm of these oscillations shows fascinating similarities to physiological rhythms frequently observed in biological systems [3]. This phenomenon has stimulated a lot of interest in these chemical clock reactions [4]. However, oscillations are not the only surprising feature of this class of chemical reactions.

The spatial coupling of their non-linear reaction mechanism by diffusion can give rise to propagating waves that organize in complex spatio-temporal structures like rotating spiral waves [1,4]. It is now well established that these dissipative wave structures are not limited to specific chemical reactions but are also found in numerous biological media [3–6].

Recently, we have shown that propagating chemical waves can be used to find minimum-length paths in complex labyrinths [7]. This general approach is based on the characteristic feature of chemical waves to propagate according to Huygen's principle, while not showing any reflection, amplitude damping or interference. The optimal pathways were experimentally determined by the collection of time-lapse position information on waves propagating through mazes made from cut vinyl–acrylic membranes saturated with BZ reaction mixture. In this Letter we utilize a more efficient technique [8,9] for the controlled preparation of specific excitable geometries and demonstrate the intriguing possibility of an alterna-

¹ Current address: Florida State University, Department of Chemistry, Tallahassee, FL 32306-3006, USA.

² Permanent address: University of Oulu, Department of Physical Sciences, Division of Biophysics, Linnanmaa, 90570 Oulu, Finland.

tive mechanism for the generation of rhythms in non-linear media.

2. Experimental

Our experimental technique is based on the loading of polysulphone membranes (Gelman Supor-450; pore size $0.45 \mu\text{m}$) with the BZ catalyst bathoferroin [8–11]. The underlying chemical procedure was developed by Lázár et al. [8] and demonstrated for several excitable geometries. More recently, their approach was refined by Steinbock et al. [9], who used an ink-jet printer for immobilizing catalyst solution with high spatial resolution on membranes.

The catalyst solution was prepared by dissolving 50.0 mg 4,7-diphenyl-1,10-phenanthroline and 31.4 mg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 10.0 ml glacial acetic acid. The immobilization process was performed with a standard ink-jet printer (Hewlett-Packard DeskJet 520) and with a standard printer cartridge (Hewlett-Packard 51626A) that was carefully washed and refilled with catalyst solution. The thin polysulphone membranes were taped on a regular paper and inserted into the paper tray. Geometrical objects used for the measurements were generated as black and white graphics with a commercial PC program and printed on a membrane. Ready-to-use membranes were then soaked in BZ solution (5–6 min), quickly placed in a plastic petri dish, and covered with silicone oil. The oil prevents concentration changes in the system which would otherwise arise from evaporation. It also minimizes undesired oxygen effects on the medium. The composition of the BZ solution was prepared so that no spontaneous wave initiation occurred; however, waves could be initiated by contacting a silver wire to the reagent-loaded membrane. The initial reactant concentrations (before bromination of malonic acid) were: $[\text{NaBrO}_3] = 0.25 \text{ M}$, $[\text{malonic acid}] = 0.18 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.35 \text{ M}$, $[\text{NaBr}] = 0.10 \text{ M}$. Stock solutions were prepared with doubly distilled water from reagent-grade chemicals. Temperature was maintained constant at $25 \pm 1^\circ\text{C}$. Oxidation waves were detected by monitoring the reflected light ($\lambda = 500 \text{ nm}$) from the medium with a CCD video camera. The video images were eventually processed through an image-acquisition board and analyzed on a personal computer.

3. Results and discussion

The accuracy of chemical length analysis strongly depends on the precise measurement of wave velocities. Since in most experimental systems the propagation velocity changes in the course of time, it is reasonable to compare pairs or sets of geometrical objects in one experiment. Results obtained by direct comparison are not influenced by velocity changes due to temperature or parameter variations (e.g. consumption of reactants). Of particular interest are objects consisting of closed excitable pathways, which can support rotating waves. We will see that these objects are indeed spatio-temporal clocks capable to maintain constant period ratios during many cycles.

Our approach is demonstrated for three examples in which the period ratios yield experimental values for irrational numbers. The measurements are based on the detection of wave propagation along the boundaries of simple geometrical objects. Fig. 1A shows a square and a circle of immobilized catalyst defining excitable race-tracks for the waves on the membrane. The diameter $d = 12.8 \text{ mm}$ of the circle equals the side length of the square. The ratio of the perimeters s is therefore:

$$s_{\text{circle}}/s_{\text{square}} = (\pi d)/(4d) = \pi/4. \quad (1)$$

Our goal is to measure this ratio – and thereby π – from the periods T_{circle} and T_{square} of wave rotation which are directly related to the lengths of the perimeters by the wave velocity $v = s/T$. In order to establish a single rotating wave in each object, one of the two wave segments generated by the silver wire had to be erased (otherwise clockwise and counter-clockwise rotating segments would annihilate after $T/2$). For this purpose, we utilized the inhibitory effect of an iron wire which is sufficient to suppress wave propagation locally when contacted to the membrane [9]. Under the given experimental conditions the resulting solitary waves rotate around the excitable perimeters for up to 2 h. Fig. 1A shows a 21-frame composite image of the waves propagating along the perimeters. The contrast of each digitized snapshot was enhanced by image subtraction ($\Delta t = 10 \text{ s}$). Average rotation periods were obtained during 75 min of experiment as $T_{\text{square}} = 1139.3 \pm 2.0 \text{ s}$, and $T_{\text{circle}} = 893.8 \pm 2.0 \text{ s}$, corresponding to four

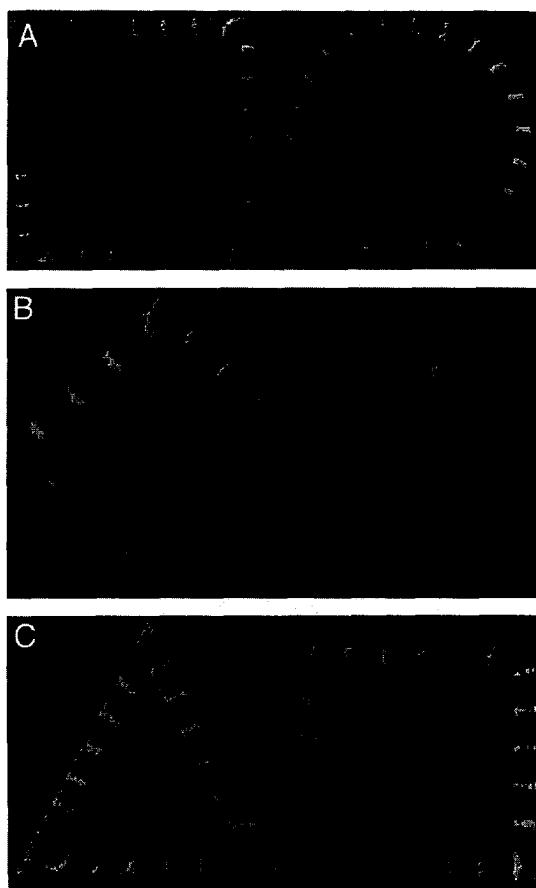


Fig. 1. Composite images of chemical waves spinning around catalyst-loaded tracks. White segments indicate the wave position at successive times (time between successive snapshots 40 s). The geometry of the tracks allows the measurement of (A) π , (B) $\sqrt{2}$, and (C) the golden mean from the characteristic rotation periods. Diameter of circle in (A) 12.8 mm; side length of the small right square in (B) 5.7 mm; side length of square in (C) 9.7 mm.

and five rotations, respectively. The wave velocity was found to decrease significantly during the experiments, but revealed at no time differences between the circle and the square. Hence, it is possible to consider the experimental value $4T_{\text{circle}}/T_{\text{square}} = 3.138 \pm 0.004$ as an estimate of π which is known to be approximately 3.14159. The relative and absolute errors of this measurement are 0.1% and 0.0034, respectively.

Note that deviations of the wave velocity due to curvature effects of the front [12,13] were not detected. Curvature effects caused by dispersion of the

propagator species (HBrO_2) have to decelerate the wave while turning around sharp corners. A simple explanation of this finding is provided by the fact that the portion of curved boundary segments is negligible compared to the overall perimeter. However, curvature effects along the inner boundary of the patterns are also influenced by the particular nature of the boundary itself: the boundary between catalyst-loaded and catalyst-free domains on the membrane allows the diffusion of HBrO_2 into unexcitable regions. This phenomenon could smooth the effective curvature of the boundary and thus weaken curvature-related changes in wave velocity.

Figs. 1B and C illustrate the chemical measurement of the numbers $\sqrt{2}$ and golden mean γ performed and analyzed following the procedures described above. In a right-angled isosceles triangle $\sqrt{2}$ is given on the basis of Pythagoras' theorem as the perimeter ratio of the hypotenuse square to the side square. Fig. 1B shows the two corresponding squares printed and ten superimposed snapshots of waves. Based on the data obtained during approximately 90 min, we measured the average rotation periods of the hypotenuse and the side square as 595.5 ± 2.0 s and 421.5 ± 2.0 s, respectively. Their ratio 1.413 ± 0.008 gives the experimental estimate of $\sqrt{2} = 1.4142\dots$ with relative and absolute errors 0.1% and 0.0014, respectively. The golden mean γ describes how to subdivide a piece of straight line so that the ratio of the shorter segment to the larger equals the ratio of the larger to the whole. This problem can be formulated as a quadratic equation yielding the positive solution $\gamma = (\sqrt{5} - 1)/2 = 0.618034\dots$ However, the value $2/(\gamma + 1)$ is also given by the perimeter ratio of a square to the largest enclosed isosceles triangle. Using this geometrical construction (Fig. 1C) we measured the rotation period for the triangle with 712.4 ± 2.0 s and for the square as 882.6 ± 2.0 s. The ratio of these periods multiplied by two yields the experimental value 1.614 ± 0.005 for $\gamma + 1$ (relative error 0.2%; absolute error 0.004). It is noteworthy that we obtained the experimental values of the numbers π , $\sqrt{2}$, and γ without using the actual values in neither the preparation of the membranes, the experiment nor the analysis. The described experiments therefore add a chemical technique to the existing spectrum of experimental procedures for the determination of irrational numbers [14]. The dura-

tion of wave propagation and therefore the precision of the presented measurements could be further increased by utilizing continuously fed unstirred reactors (CFUR) [8].

Our results show that excitation waves can be utilized for measuring relative distances with surprisingly high accuracy. Although it is not immediately obvious that technical applications can arise from the presented methodology, the measurements reveal a feature of excitable media that might be exploited by biological systems: excitation waves are indeed a non-electronic, non-mechanical yardstick offering organisms like the slime mold *Dictyostelium* [5] efficient strategies for their aggregation and could be involved in the biological realization of robust rhythms with stable period ratios. Further experiments are under way to utilize chemical length measurements and excitable circuits in the context of complex network analysis and percolation problems.

Acknowledgment

We thank K. Showalter for his hospitality and fruitful discussions. One of the authors (O.S.) thanks the Fonds der Chemischen Industrie for a Liebig Fellowship.

References

- [1] H.L. Swinney and V.I. Krinsky, eds., *Waves and patterns in chemical and biological media* (Elsevier, Amsterdam, 1991) [conference issue: *Physica D* 49 (1991)].
- [2] A.N. Zaikin and A.M. Zhabotinsky, *Nature* 255 (1970) 535.
- [3] M. Markus, S.C. Müller and G. Nicolis, eds., *From chemical to biological organization* (Springer, Berlin, 1988).
- [4] A.T. Winfree, *The geometry of biological time* (Springer, New York, 1980).
- [5] F. Siegert and C.J. Weijer, *J. Cell Sci.* 93 (1989) 325.
- [6] J.M. Davidenko, A.M. Pertsov, R. Salomonsz, W. Baxter and J. Jalife, *Nature* 355 (1992) 349.
- [7] O. Steinbock, Á. Tóth and K. Showalter, *Science* 267 (1995) 868.
- [8] A. Lázár, Z. Noszticzius, H.-D. Försterling and Z. Nagy-Ungvárai, *Physica D* 84 (1995) 112.
- [9] O. Steinbock, P. Kettunen and K. Showalter, *Science* 269 (1995) 1857.
- [10] A. Lázár, Z. Noszticzius, H. Farkas and H.-D. Försterling, *Chaos* 5 (1995) 443.
- [11] T. Yamaguchi, L. Kuhnert, Zs. Nagy-Ungvárai, S.C. Müller and B. Hess, *J. Phys. Chem.* 95 (1991) 5831.
- [12] P. Foerster, S.C. Müller and B. Hess, *Science* 241 (1988) 685.
- [13] K. Agladze, J.P. Keener, S.C. Müller and A. Panfilov, *Science* 264 (1994) 1746.
- [14] R.A.J. Matthews, *Nature* 374 (1995) 681.