Physica A 188 (1992) 47–54
North-Holland

PHYSICA A

# Autonomous pacemaker of chemical waves created by spiral annihilation

S.C. Müller, O. Steinbock and J. Schütze

*Max-Planck-Institut für Ernährungsphysiologie, Rheinlanddamm 201, W-4600 Dortmund 1, Germany*

A leading center of a target pattern in the Belousov–Zhabotinsky (BZ) reaction emerges after mutual annihilation of a pair of counterrotating spirals. The spiral waves propagate in an oscillatory medium which oscillates with a period much larger than that of spiral rotation. The annihilation process is induced by two methods: (1) in the light-sensitive ruthenium-catalyzed BZ reaction an inhibitory laser-spot erases the core structure of two adjacent spirals whereupon the spiral ends merge to form a continuous front; (2) in the ferroin-catalyzed BZ reaction an externally applied electric field forces the spirals to coalesce by a drift towards each other. In both cases, bulk oscillations of regular frequency follow inside the region enclosed by the newly emerging closed wave front. The phenomenon is observed and analyzed by computerized video techniques.

## 1. Introduction

Target patterns are a frequently observed example of spatio-temporal organization in two-dimensional active media. They consist of a number of concentric rings of expanding wave fronts emerging from a common center. One of the most thoroughly investigated systems generating target patterns is the Belousov–Zhabotinsky reaction [1–3], but other examples have been also reported [4]. Numerous experimental and theoretical studies have been performed on the dynamic properties of such travelling waves, for instance their propagation velocity and concentration profiles [5, 6], thus contributing to the mechanistic understanding of the underlying reaction–diffusion mechanism [7, 8].

However, a fundamental point, not yet settled, concerns the origin of the trigger waves forming these targets that often appear spontaneously in a thin layer of solution of an oscillatory or excitable chemical system. Quite frequently, there is a heterogenous center (a dust particle, an impurity, a gas bubble) from which these waves arise deterministically [2, 9]. On the other hand, experiments on carefully filtered solutions of the BZ reaction have shown that spontaneous formation of trigger waves can be suppressed in an excitable system, but not in an oscillatory system [5, 10]. Therefore, the question remains open whether these waves arise as a result of a symmetry-breaking fluctuation or are associated with the presence of an impurity. The issue is under discussion in the theoretical literature [11–13].

In recent years, the use of gel matrices and the design of suitable reactors has provided novel experimental tools for the study of spatial waves under open conditions and controlled external constraints [14, 15]. In this contribution we apply external fields (electric currents [16] and light [17, 18]) to counterrotating chemical spiral waves embedded in a shallow gel layer in order to force spiral collision. The subsequent annihilation process results in the formation of a closed wave front which travels into the surrounding active medium.

We find that in a medium which is initially oscillatory with a period significantly longer than that of spiral rotation there appear new trigger waves in a periodic sequence inside this closed wave front. In the following, we describe the preparation of the system and its handling in externally applied fields. A brief analysis of the dynamic features of this type of target patterns and their centers is given on the basis of video imaging techniques.

## 2. Experimental

All solutions were prepared from distilled water and reagent grade chemicals. In the light-controlled experiments we used the $\mathrm{Ru(bpy)}_3^{2+}$ complex as catalyst (concentration, 4 mM), immobilized in silica gel to avoid hydrodynamic convection.

A reactive mixture contained 0.18 M NaBr, 0.39 M $\mathrm{NaBrO_3}$, 0.33 M malonic acid, and 0.77 M $\mathrm{H_2SO_4}$ (disregarding bromination of malonic acid). After pouring an equal volume of this solution on top of the gel in a petri dish, the reactive species diffuse into the catalytic layer and initiate the formation of propagating waves. Experiments were carried out at room temperature (≈23°C) (for details see ref. [18]).

An argon laser (514 nm line; 0.8 W; attenuated by a neutral density filter OD 2.0) was used to influence locally the excitability of the system. The laser beam penetrated the gel layer in almost perpendicular direction. The diameter of the circular light spot (0.2–3.0 mm) was controlled by small diaphragms. Inside this illuminated region the system lost its excitability. The optical set-up was kept fixed, while the dish containing the gelled BZ-system was movable.

In the experiments controlled by an electric field, reaction solutions were prepared and mixed with liquid agar (0.4%), which after solidification prevents hydrodynamic effects during the experiment. The final composition of the solution was 0.05 M $NaBrO_3$, 0.05 M malonic acid, 0.2 M $H_2SO_4$, and $6.25 \times 10^{-4}$ M ferroin $[Fe(phen)_3SO_4]$. The mixture was placed in a flat, rectangular dish ($71.6 \times 21.0\,mm^2$) with a layer thickness of 3 mm. In order to account for the Ohmic heating, a cooling box controlled the temperature of the dish at $(25 \pm 1.0)°C$. The electrodes were placed parallel to the short edges of the dish as described elsewhere [16].

In both types of experiments, the 2D transmission through the layer of green light (490 nm) emitted from a spatially extended light source was detected by a CCD camera (Hamamatsu C3077) and stored on a time-lapse video recorder. Single pictures were selected, digitized by an image acquisition card and stored on a PC for further analysis [16, 18].

## 3. Results

Two similar approaches were used to create autonomous pacemakers of target patterns: one in the light-controlled and the other in the electric-field controlled wave experiments. In both cases one starts from a pair of adjacent spiral waves with different topological charge rotating in a previously oscillating medium. One then induces a continuous wave front by destroying the spiral structure.

The sequence of events in the light-sensitive ruthenium-catalyzed BZ reaction is depicted in fig. 1. The cores of a spiral pair are illuminated by a sufficiently large laser disk (image (a)) which forces the spiral tips to move along the boundary of the disk. Thus, the two open wave ends are bound to collide and, as a consequence, coalesce to form a continuous, closed wave front as soon as they leave the disk area during outward propagation. At this moment the laser illumination is switched off and an expanding trigger wave travels outward (image (b)). Further on, the oscillatory kinetics of the BZ medium produces a bulk transition to the oxidized state of the oscillation in a crescent-shaped region inside the area enclosed by this front (image (c)), reflecting the phase distribution of the oscillation in space. This leads, shortly later, to the new trigger wave front shown in image (d) with a characteristic cusp reminiscent of the process of coalescence. The same scenario follows now in a periodic sequence and results in an expanding target pattern with a period determined by the intrinsic dynamics of the initial chemical preparation. Due to phase diffusion [3], the characteristic cusp becomes less pronounced during later oscillatory cycles. At locations far outside the pacemaker region, the cusp is smoothed out as a consequence of the curvature–velocity relationship for

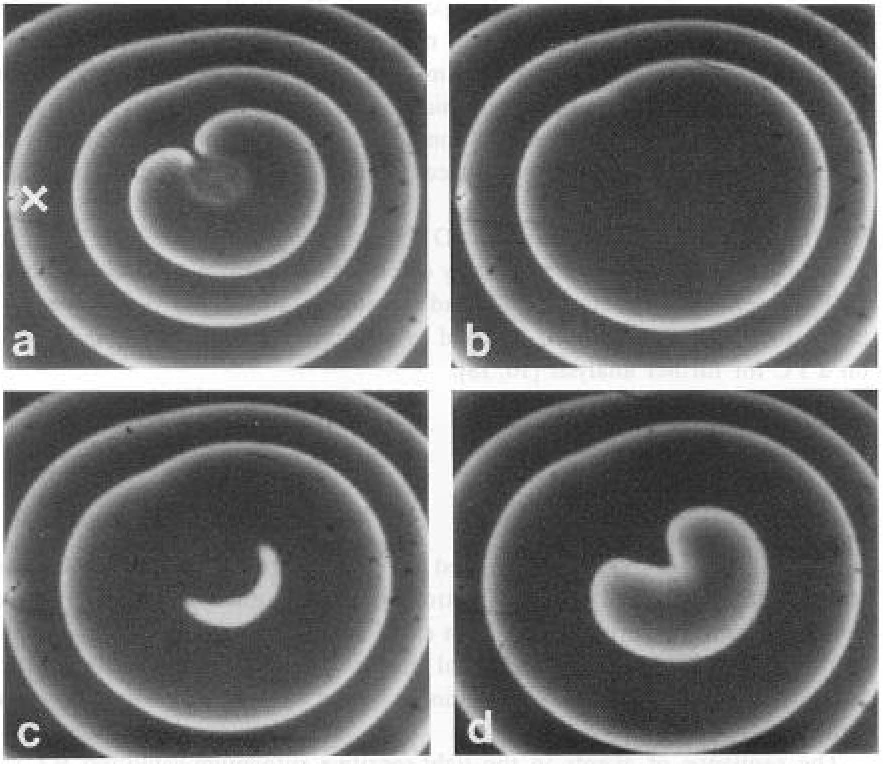

Fig. 1. Image sequence of light-induced generation of a pacemaker in the ruthenium-catalyzed BZ reaction. (a) Pair of counter-rotating spirals, guided along the boundary of an inhibitory laser disk, (b) closed wave front after spiral collision, (c) bulk oscillation in a crescent-shaped central region, (d) closed trigger front with a cusp. Time interval between (a) and (b), 25 s; (b) and (c), 4 s; (c) and (d), 10 s. Image area: 11.5 × 10.0 mm$^2$.

wave propagation [19, 20]. The transition from spiral rotation to target patterns induced by laser illumination is further shown in fig 2. A time trace of intensity variations was extracted at a specific location in the immediate neighbourhood of the externally induced pacemaker (marked by a cross in fig. 1a). The fast period of spiral rotation ($T = 23$ s) changes to the slower period characteristic for the expanding target ($T = 42$ s).

In the second experiment used for creating an autonomous pacemaker, a pair of counter-rotating spirals was created in the ferroin-catalyzed BZ reaction (fig. 3a) and subjected to an externally applied electric field of typically 5 V/cm. The spiral orientation was chosen such that the field induces a drift of

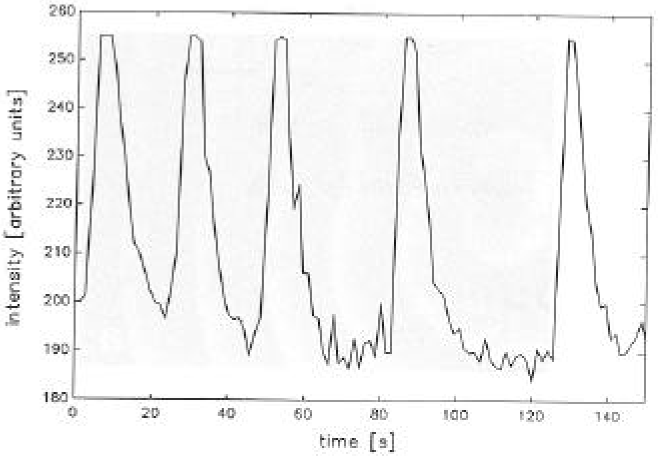

Fig. 2. Time trace of local intensity extracted from the experiment shown in fig. 1 at the location marked with a cross in fig. 1a. The change of period from 23 s to 42 s reflects the transition from a spiral to a target pattern.

the spiral cores towards each other. If the phases of spiral rotation are sufficiently symmetric with respect to the field direction, the drift finally results in a mutual annihilation of the spirals. A continuous wave front is produced which propagates outward as a closed trigger wave of roughly circular geometry. Subsequently, there occur bulk oscillations of the BZ medium in the area enclosed by this trigger wave in close analogy to the observation in the light experiment. These give rise to periodically emanating trigger fronts, i.e. a target pattern.

The temporal evolution of spiral annihilation in an electric field and associated target propagation is represented in the time–space plot of fig. 3b produced along the spatial cut indicated in the original spiral pattern (fig. 3a). The arrow on the right margin indicates the transition from spirals to targets. At this transition point the dislocation in the front propagation along the selected spatial cut vanishes.

The emanation of waves from an autonomous pacemaker in this experiment is further illustrated in the sequence of spatial intensity profiles assembled in fig. 4. These profiles were extracted along a spatial cut very close to that used for the time-space plot in fig. 3b. They cover a characteristic time period for one period of target emission. Starting from a bulk oscillation in a restricted spatial region (profiles (a)–(c)), the formation of a trigger front is completed (profile (d)) which then travels in outward direction (profiles (e), (f)).

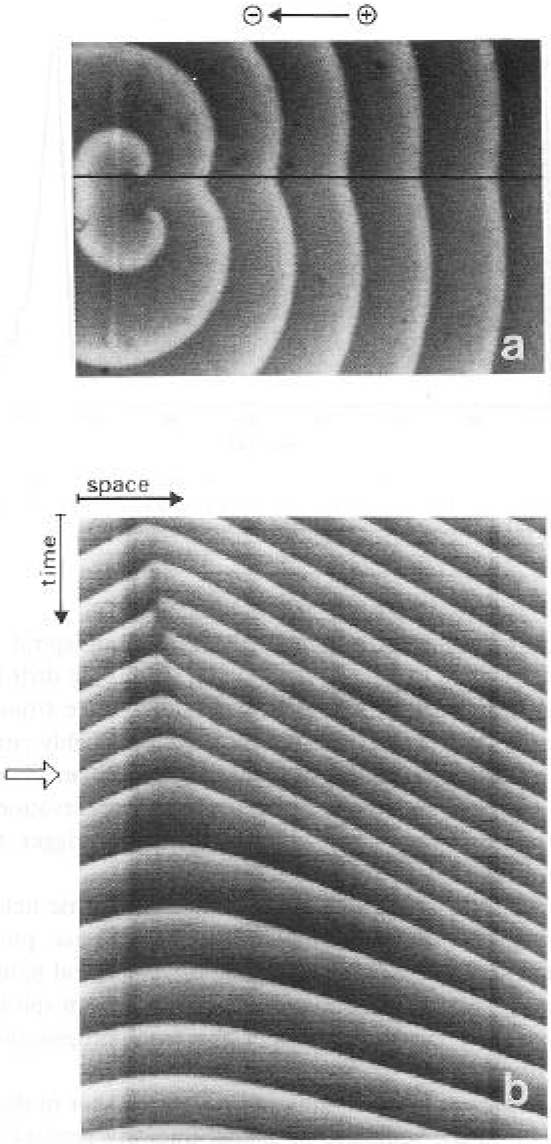

Fig. 3. (a) Snapshot of a pair of counter-rotating spirals drifting towards each other in an external electric field. Image area: $2.9 \times 2.0\,\mathrm{cm}^2$. The field direction is indicated. The straight line indicates the spatial cut used in (b). (b) Space–time plot of the pattern of (a) with evolution of intensity profiles along the spatial cut indicated in (a). Time interval: 42.6 min. The plot clearly shows the transition from spiral rotation to a target pattern with an autonomous frequency (open arrow).

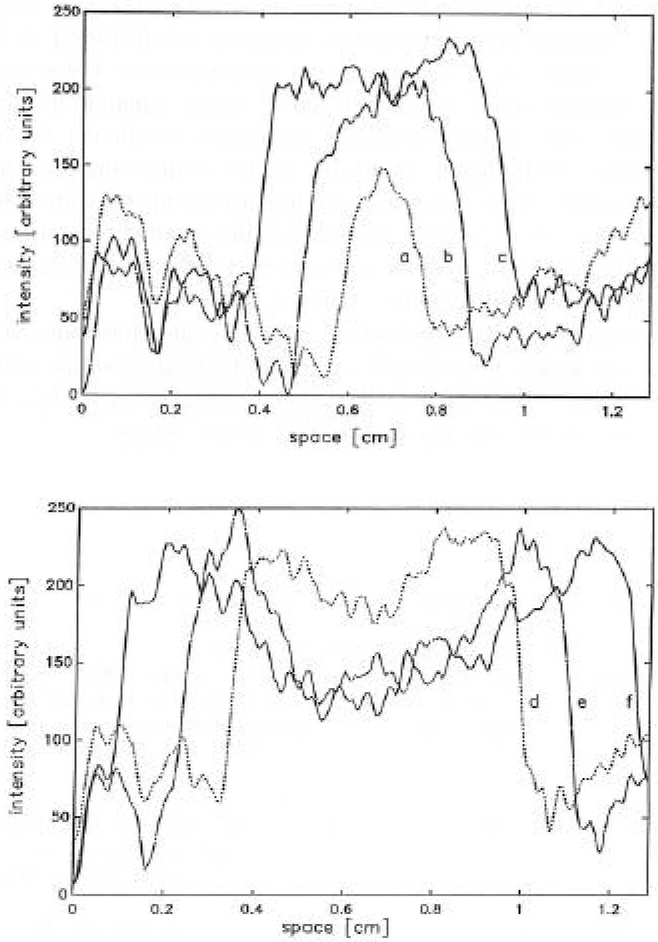

Fig. 4. Intensity profiles passing through the pacemaker region along a cut close to the one indicated in fig. 3a, at consecutive instants of time. Time intervals: (a, b) 20 s; (b, c) 20 s; (c, d) 10 s; (d, e) 30 s; (e, f) 40 s.

## 4. Conclusion

Experimental evidence was provided that an autonomous pacemaker for target patterns can be generated by newly developed techniques for external control of an active medium. In this study, a solution layer of the Belousov–Zhabotinsky reaction was prepared in an oscillatory state, then spiral waves were initiated which dominate the reaction territory by emitting trigger waves which suppress the slower oscillations arising from the dynamics of the preparation. External control by light and electric field was used to force spirals with opposite topological charge to mutual annihilation [16, 18]. Thus, a continuous trigger wave front was created which encloses a region around the previously existing spiral cores. This small region remains protected against excitation by a wave front. Therefore, the intrinsic oscillatory dynamics of the medium comes to life again, producing a bulk oscillation in a confined area with a geometric shape that reflects the actual phase distribution of the oscillation. This "phase wave" converts rapidly to an expanding trigger wave with its characteristic steep front and smooth relaxation tail. A more detailed study of this conversion remains a task for the future.

Further refinement of the presented method could contribute to clarify the conditions, for which the non-uniform phase distribution of an oscillation in a very small spatial volume of an active medium can give rise to the emanation of a trigger front or, by repeated action, to a target pattern.

## References

[1] A.N. Zaikin and A.M. Zhabotinsky, Nature (London) 225 (1970) 535.
[2] C. Vidal and P. Hanusse, Int. Rev. Phys. Chem. 6 (1986) 1.
[3] J. Ross, S.C. Müller and C. Vidal, Science 240 (1988) 365.
[4] P. De Kepper, I.R. Epstein, K. Kustin and M. Orban, J. Phys. Chem. 86 (1982) 170.
[5] P. Hanusse, C. Vidal and A. Pagola, in: From Chemical to Biological Organization, M. Markus, S.C. Müller and G. Nicolis, eds. (Springer, Berlin, Heidelberg, 1988) p. 99.
[6] Zs. Nagy-Ungvarai, S.C. Müller, J.J. Tyson and B. Hess, J. Phys. Chem. 93 (1989) 2760.
[7] J.J. Tyson and P.S. Fife, J. Chem. Phys. 73 (1980) 2224.
[8] J.P. Keener and J.J. Tyson, Physica D 21 (1986) 307.
[9] K.I. Agladze and V.I. Krinsky, in: Self-Organization. Autowaves and Structures far from Equilibrium, V.I. Krinsky, ed. (Springer, Berlin, Heidelberg, 1984) p. 147.
[10] C. Vidal, A. Pagola, J.M. Bodet, P. Hanusse and E. Bastardie, J. Phys. (Paris) 47 (1986) 1999.
[11] Y. Kuramato, Chemical Oscillations, Waves, and Turbulence (Springer, Berlin, Heidelberg, 1984).
[12] D. Walgraef, G. Dewel and P. Borckmans, J. Chem. Phys. 78 (1983) 3043.
[13] A.S. Mikhailov, Physica D 55 (1992) 99.
[14] G.S. Skinner and H.L. Swinney, Physica D 48 (1991) 1.
[15] T. Yamaguchi, L. Kuhnert, Zs. Nagy-Ungvarai, S.C. Müller and B. Hess, J. Phys. Chem. 95 (1991) 5831.
[16] J. Schütze, O. Steinbock and S.C. Müller, Nature 356 (1992) 45.
[17] L. Kuhnert, Naturwissenschaften 73 (1986) 96.
[18] O. Steinbock and S.C. Müller, Bifurcation and Chaos, submitted.
[19] V.S. Zykov and G.L. Morozova, Biofizika 23 (1979) 717.
[20] P. Foerster, S.C. Müller and B. Hess, Science 241 (1988) 685.