# A BZ ASSEMBLAGE WORKING FOR A DAY

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## ABSTRACT

Our work is focused on the experimental observation of Bielousov-Zhabotinsky reaction oscillations in ferroin loaded Dowex 50w beads in a batch reactor open to the atmosphere. We investigated the conditions for the maximum oscillation lifetime and the change of wave regimes as the answer to the applied potential. The catalyst-free solution in the batch reactor is a mixture of concentrated sulphuric acid, NaBrO3, and different ratios of malonic acid and 1,4 cyclohexanedione. We are using three types of cation Dowex 50w beads, namely type x2, x8, which differ by their level of crosslinking and cation exchange capacity. Their mesh size is 16-50 and 50-100. We investigate the influence of such parameters as the distance between a bead and the electrode and the value of electrode potential on the oscillations. Moreover, we study the character of oscillations in the function of the number of adjacent beads and the layout of the beads.The reduction of formation of CO2 bubbles has been achieved by choice of Dowex beads type, solution composition, and usage of acetone.We report oscillations with stable amplitude and varying period and lifetime over 19 hours and oscillations with decreasing amplitude with a lifetime of 10 hours. The investigated media and beads type seem to be promising candidates for experimental realization of chemical computers based on interacting oscillators.

## INTRODUCTION

Ever since we record ideas, we can find stories about the creation of something artificial, which can perform tasks like humans. One example is a clay creature build to fulfil given duties described in an old Egyptian story [1], a being made of soil though not liquid or purely organic in its nature. The need for thinking, automatic machines able to perform repetitive tasks on assembly lines, and control such processes appeared at the end of the 19th century. One of the first “liquid computers” was the hydraulic algebraic machine, followed by hydraulic integrators, mappers, and up to fluid logic in 1960, later followed by Belousov-Zhabotisky computers (1985), other types of reaction-diffusion computers. These developed through liquid brain robots and maze solvers into current techniques of liquid marbles, vesicles, and droplet logic systems [2]. There was a parallel development of non-liquid computers, which eventually proven themselves in WWII due to Alan Turing’s computer breaking Enigma code [3]. Our current focus is to deepen techniques proposed by Kuze et al. [4] using electric potential and incorporating groups of connected beads to assess their dynamic behavior in reaction to electric potential as a first step towards creating marble logic assemblages [5] with an electric interface.

## EXPERIMENTAL

Used chemicals: Deionized water. Sulphuric acid 95% from Chempur Poland, malonic acid 99% from Sigma-Aldrich (Japan), 1,4 cyclohexanedione 98% from Sigma-Aldrich (Germany), NaBrO3 99% from Fluka (Netherlands). Ferroin solution 0.025M from Sigma-Aldrich (Switzerland). Acetone 99.5% from Avantor Performance Materials Poland S.A. Dowex 50w-x2/x8 hydrogen form (50-100) mesh/(16-50) mesh from Sigma-Aldrich (USA).

Beads are loaded prior to the experiment, 50w-x2 are loaded with $4.66*10^{-9}$ mol/bead in average, 50w-x8 are loaded with $1.89*10^{-7}$ mol/bead in average. Ambient temperature is maintained at 23°C. The experimental setup is shown in Fig. 1. The glass reactor, which is, prior to its usage thoroughly washed with acetone to remove/inhibit remaining Br ions [5], is filled with catalyst free reaction solution of volume 5ml. Ferroin loaded beads are placed inside reactor with BZ solution near the electrode, using different spatial arrangements. Colour change of beads duel to BZ reaction occurrence is recorded on CCD camera using lenses with 110x magnification. Resulting videos are cut and decomposed into frames by Ffmpeg program. Frames are put into stack using ImageJ program, resliced and put into montages of reslices. Each montage is divided into three colour channels, red, green, blue, where green channel is equivalent to brightness channel with values of brightness 0-255. The brightness channel of each montages is analyzed for oscillation periods per each bead.

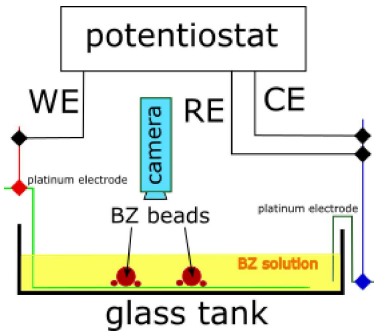



**Figure 1.** Schematic diagram of experimental setup. WE – working electrode, RE- reference electrode, CE – counter electrode.

## RESULTS AND DISCUSSION

Electric potential creates activator species for BZ reaction, $HBrO_2$, according to reaction: $BrO_3^- + 2e^- + 3H^+ \rightarrow HBrO_2 + H_2O$. The negative potential on working electrode attracts activator molecules, while positive potential is attracting $Br^-$ [4]. According to our observations, after application of positive potential, bubbles occur near electrode and on beads much more frequently. Using different than glass reactor lead into change of colour and structural integrity of whole reactor body, due to sorption of bromide ions. These inhibitor ions were later diffusing into new solutions inhibiting the BZ reaction completely. This effect could be avoided by washing the reactor with acetone for period of 7+ days before the reactor body became unusable, and on some occasions, damaged by mere $CO_2$ bubbles. Each experiment consists of several electric potential changes, while keeping the original batch solution. Therefore, each presented part of experiment shows initial concentration of species in negative time values in subscript. The first experiment shows 2nd change of potential in the row (potential change from 0V to -1.5V) with two beads not touching the electrode and a ring of seven coupled beads touching the working electrode by bead number 3, see Fig. 2A).

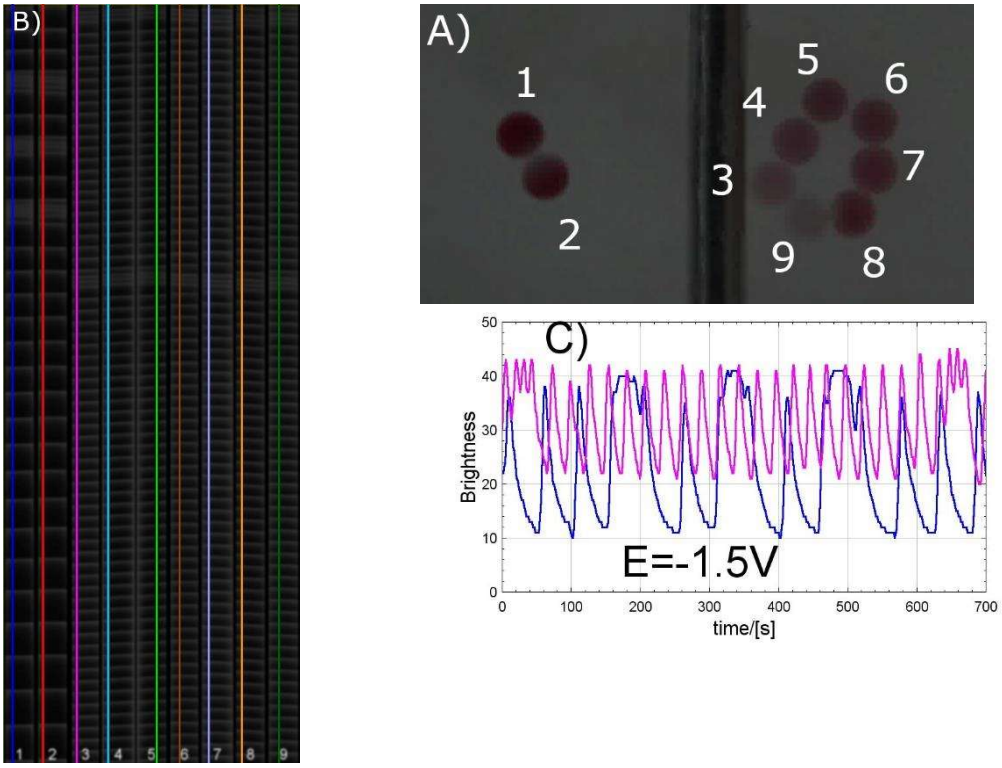



**Figure 2.** The first experiment showing 2nd change of potential, from 0V to -1.5V, time length 1799 seconds, A) layout of beads Dowex 50w- x2 (50-100) mesh and beads numbering, B) space-time plot of brightness intensity in each bead, C) oscillation in beads number 1(blue) and 3(magenta), colour respective to B), zoomed time. $[NaBrO_3]_{(-1800s)}$=0.45M, [malonic acid]$_{(-1800s)}$=0.4M, $[H_2SO_4]_{(-1800s)}$=0.9M. Diameter of the electrode is 0.43mm.

Interesting part of this particular experimental set is observation of bursts in both groups of beads, see Fig 2B). Beads number 1 and 2 oscillate with much slower pace, 60 seconds at the beginning and slowing down to 80 seconds in the end of this experiment, bursts occur as 6, 5 and 6 peaks with 150 second period between beginning of each burst. For seven coupled beads, general oscillation period is holding at 28±2seconds whole experimental set, which burst go with period 600 seconds and three peaks, see Fig. 2C).

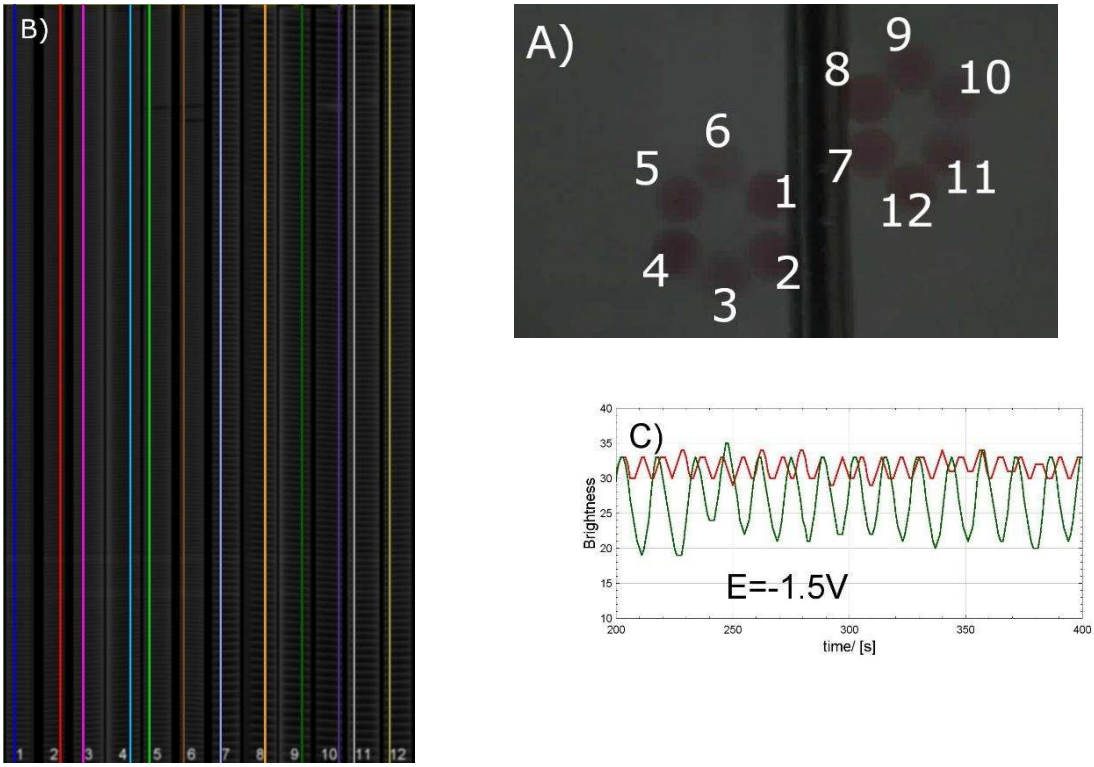



**Figure 3.** The second experiment showing 2nd change of potential, from 0V to -1.5V, time length 1794 seconds. A) layout of beads Dowex 50w-x2 (50-100) mesh and beads numbering B) space-time plot of brightness intensity in each bead, C) oscillation in beads number 2(red) and 9(green), colour respective to B), zoomed time. $[NaBrO_3]_{(-1900s)}$=0.45M, [malonic acid]$_{(-1900s)}$=0.4M, $[H_2SO_4]_{(-1900s)}$=0.9M. Diameter of the electrode is 0.43mm

The second experiment shows two equivalent group of 6 beads, se Fig. 3B). While the left group starts the experimental cascade without applied potential with period 30 seconds and slowing down to 50 seconds, right group goes into spiral waves oscillating with period 19±2 seconds. After negative potential is applied, left group goes into superspiral waves with period 8±2 slowing down eventually to 13±2 seconds, right group is uninfluenced in its period and spiral wave behaviour, see Fig. 3B). With shorter period, amplitude of oscillations is smaller, see Fig. 3C).

The third experiment shows combination of two Dowex types, type x2 (16-50)mesh and type x8 (50-100) mesh, while it is also possible to see diminishing amplitude of brightness by naked eye, see Fig. 4A). While both groups operate with same period 17±2 seconds, see Fig. 4B), C), both their current group behaviour and their evolution behaviour differs. The left group operates as quadruple spiral wave with center in bead 1, while it started as a wave coming from bead number 5, went through changing of origin of the wave and into a triple spiral wave with center in bead 1. Positive electric potential had no effect on this group. The right group has origin of waves simultaneously in bead 6 and 10, while it changes to bead 6 and 11 after application of positive potential. The central beads operate over 19 hours, while the small bead up 10 hours, while their brightness amplitude is continuously decreasing.

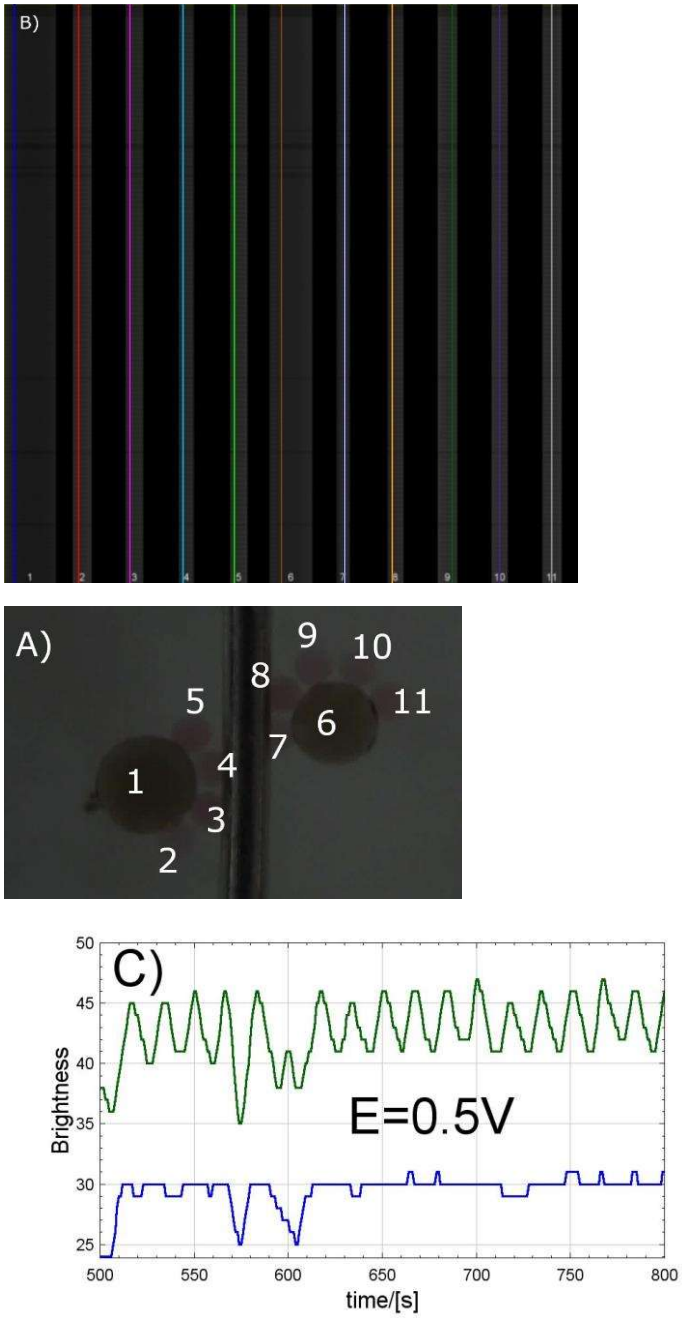
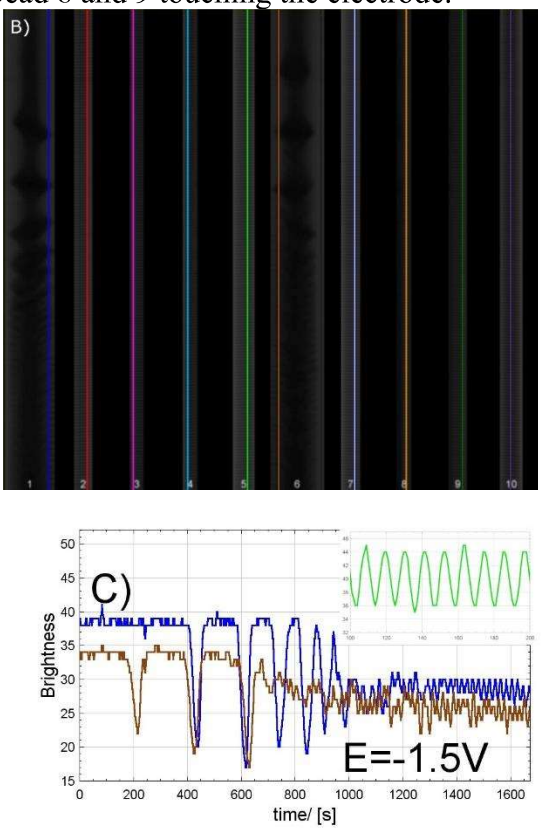



**Figure 4.** The third experiment showing 8th change of potential, from 0V to 0.5V, time length 2035 seconds. A) layout of beads Dowex 50w -x8 (12-50)mesh(bigger ones)/ -x2 (50-100)mesh and beads numbering, B)montage of eighth set in the row with applied potential 0.5V, B) space-time plot of brightness intensity in each bead, C) oscillation in bead numbers 1(blue) and 9 (dark green), colour respective to B).[NaBrO3](-13000s)=0.45M, [malonic acid](-13000s)=0.4M, [H2SO4](-13000s)=0.9M. Diameter of the electrode is 0.43mm.

The fourth experiment deals again with combination of different type of beads, but also uses equimolar solution of malonic acid and 1,4 cyclohexanedione, see Fig. 5A). The small beads oscillate with period 10±1 seconds while the big beads start around 200 second period and shorten the period to 20±2 seconds by the end of the experimental set, see Fig. 5B), C). The long period appears as blinking eye and ands up as wave patterns looking like a blossomed rose. The wave in left group of beads starts with separate oscillations of beads 3 and 4 and changes into a travelling wave from bead 5 without applied potential, after application of negative potential, the origin of waves go to beads 3,4 touching the electrode. The right group is more dynamic, starting separate oscillations of beads 8 and 9 while forming the origin of travelling waves in beads 7 and 11 without applied potential. After the application of negative potential, the travelling wave originates from beads 7 and 10, then transforms into spiral wave with center in bead 6, and then traveling waves occur and originate from bead 8 and 9 touching the electrode.



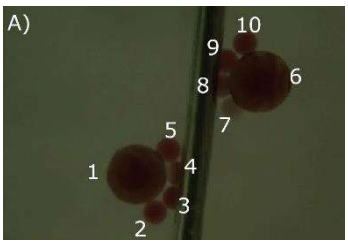







**Figure 5.** The fourth experiment showing 2nd change of potential, from 0V to -1.5V, time length 1674 seconds. A) layout of beads Dowex 50w -x8 (12-50)mesh (bigger ones)/ -x2 (50-100)mesh and beads numbering, B) space-time plot of brightness intensity in each bead, C) oscillation in bead numbers 1 (blue), 6(brown) and 5(green-zoomed), colour respective to B).$[NaBrO_3]_{(-1900s)}$=0.45M, [malonic acid]$_{(-1900s)}$=0.2M, [1,4-cyclohexanedione]$_{(-1900s)}$=0.2M, $[H_2SO_4]_{(-1900s)}$=0.9M. Diameter of the electrode is 0.43mm.

## CONCLUSION

Experimental sets with various layouts have been performed while electric potential has been applied. We have observed bursts, travelling waves, and group behaviour like spiral waves inside BZ bead assemblage. Most importantly, the electrode can be the origin of wave signal, as shown in the work by Kuze et al. [4]. The repeatability of such process seems to be currently limited, influenced by layout of BZ assemblage and type of BZ solution. Ion exchange resins with smaller mesh value,

having more ferroin loaded, seem to be able to operate more than 19 hours without creation of $CO_2$ bubbles compared to resins with high mesh value and less ferroin loaded, which can oscillate up to 10 hours.

We will focus further into new layouts and higher concentration of ferroin loaded into beads to increase its oscillation/operation lifetime to get closer to liquid marble logic technique [5] operating more than a day.

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