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A STUDY OF COMPLEX CHEMICAL OSCILLATIONS IN THE PSEUDO-CLOSED SYSTEM OF BELOUSOV-ZHABOTINSKY REACTION

METHASIT PORNPROMPANYA

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
(PHYSICAL CHEMISTRY)

With compliments
of
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IN
FACULTY OF GRADUATE STUDIES
MAHIDOL UNIVERSITY
1997

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Thesis
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Methasit Pornprompanya
Candidate

Prapin Wilairat, Ph. D.
Advisor

Orapin Rangsiman, Dr. rer. nat.
Co-advisor

Preedeeporn Limcharoen, Ph. D.
Co-advisor

Waret Veerasai, Dr. rer. nat.
Co- advisor

Adulya Viriyavejakul,
M. D., LL. B., F. R. C. P.
Dean
Faculty of Graduate Studies

Prapin Wilairat, Ph. D.
Chairman
Master of Science Program in
Physical Chemisty
Faculty of Science

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was submitted to the Faculty of Graduate Studies, Mahidol University
for the degree of Master of Science (Physical Chemistry)
on
April 22, 1997

Methasit Pornprompanya
Candidate

Prapin Wilairat, Ph. D.
Chairman

Orapin Rangsiman, Dr. rer. nat.
Member

Preedeeporn Limcharoen, Ph. D.
Member

Waret Veerasai, Dr. rer. nat.
Member

Adulya Viriyavejakul,
M. D., LL. B., F. R. C. P.
Dean
Faculty of Graduate Studies

Pornchai Matangkasombut,
M. D., Ph. D.
Dean
Faculty of Science

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BIOGRAPHY

NAME: Mr. Methasit Pornprompanya

DATE OF BIRTH: February 4, 1972

PLACE OF BIRTH: Bangkok, Thailand

INSTITUTIONS ATTENDED:

Kasetsart University
Bachelor of Science (Chemistry), 1991-1994
Mahidol University
Master of Science (Physical Chemistry), 1995-1997

RESEARCH GRANT: Institutional Strengthening Program supported by National Science and Technology Development Agency (NSTDA) and Faculty of Science, Mahidol University, 1995-1997

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ACKNOWLEDGMENT

Firstly, I would especially like to thank my thesis advisor, Dr. Prapin Wilairat, for his numerous advice, assistance in the experimental set up and discussion of all parts of this work.

Secondly, I am very grateful to Prof. Dr. Stefan C. Müller, Max-Planck-Institüt für Molekulare Physiologie, Dortmund, Germany and Prof. Dr. Orapin Rangsiman, for their valuable suggestions. I also acknowledge Dr. Preedeeporn Limcharoen, and Dr. Waret Veerasai for their helpful consultations for completion of this thesis and my friend, Mr. Yuthana Tantiroungrotechai, for his useful recommendations of the literature.

In addition, I would like to sincerely thank NSTDA for financial assistance, and the Department of Chemistry for providing instruments and laboratory facilities for the experiments.

Finally, I wish to dedicate this thesis to the memory of my parents. I hope my father and mother spirits somewhere in heaven, will learn of this dedication.

Methasit Pornprompanya

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ชื่อวิทยานิพนธ์ การศึกษาการกวัดแกว่งอย่างซับซ้อนเชิงเคมีในระบบปิดไม่แท้ของปฏิกริยาเบลูซอฟ-ชาโบทินสกี้

ผู้วิจัย เมธาสิทธิ์ พรพรหมปัญญา

ปริญญา วิทยาศาสตรมหาบัณฑิต (ฟิสิคัลเคมี)

คณะกรรมการควบคุมวิทยานิพนธ์

ประพิณ วิไลรัตน์ Ph. D.

อรพินท์ รังสิมันต์ Dr. rer. nat.

ปรีดีพร ลิ้มเจริญ Ph. D.

วเรศ วีระสัย Dr. rer. nat.

วันที่สำเร็จการศึกษา 22 เมษายน พ.ศ. 2540

บทคัดย่อ

ในการศึกษาการกวัดแกว่งอย่างซับซ้อนของสารมัธยันต์โบรไมด์และซีเรียมไอออนโดยวิธีการวัดศักย์ไฟฟ้าในระบบปิดไม่แท้ของปฏิกริยาเบลูซอฟ-ชาโบทินสกี้โดยมีซีเรียม(IV)เป็นคะตะลิสต์ที่อุณหภูมิ30.0±0.1องศาเซลเซียส,ความเข้มข้นของกรดมาโลนิกและซีเรียม(IV)เท่ากับ0.44และ0.00133โมลาร์ตามลำดับและความเข้มข้นของโบรเมตถูกทำให้เพิ่มขึ้น:0.093,0.105,0.118โมลาร์ใน1.00โมลาร์กรดซัลฟูริกได้พบปรากฏการณ์ชั่วคราว(transient phenomena)อันได้แก่การกวัดแกว่งแบบmixed-mode(MM)และintermittency(I)ในระหว่าง2ชุดของการกวัดแกว่งอย่างธรรมดา,เมื่อความเข้มข้นของกรดซัลฟูริกถูกทำให้ลดลงจาก1.00โมลาร์เป็น0.500โมลาร์การกวัดแกว่งชั่วคราวอย่างซับซ้อนไม่ตรวจพบอีกต่อไปมีเพียงแต่การกวัดแกว่งอย่างธรรมดาแบบdampedพร้อมกับการกวัดแกว่งแบบperiod-doubled 1-3รอบ

ช่วงเวลาการชักนำ(induction period)ไม่ขึ้นกับความเข้มข้นของโบรเมตสำหรับการศึกษาอันนี้แต่มันลดลงอย่างมีนัยสำคัญเมื่อความเข้มข้นของกรดซัลฟูริกถูกทำให้ลดลงจาก1.00โมลาร์เป็น0.500โมลาร์

การกวัดแกว่งอย่างซับซ้อนสามารถทำซ้ำได้เพียงเชิงคุณภาพเท่านั้นดังเห็นได้จากความไวมากต่อความเข้มข้นของสารตั้งต้นหลักในปฏิกริยา

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Thesis Title A Study of Complex Chemical Oscillations in the Pseudo-closed System of Belousov-Zhabotinsky Reaction

Name Methasit Pornprompanya

Degree Master of Science (Physical Chemistry)

Thesis Supervisory Committee

Prapin Wilairat	Ph. D.
Orapin Rangsiman	Dr. rer. nat.
Preedeeporn Limcharoen	Ph. D.
Waret Veerasai	Dr. rer. nat.

Date of Graduation 22 April B. E. 2540 (A. D. 1997)

ABSTRACT

In the investigation of the complex oscillations of intermediates bromide and cerium ions by potentiometric method in a pseudo-closed system of cerium(IV)-catalyzed Belousov-Zhabotinsky reaction at a constant temperature of 30.0±0.1°C, malonic acid and cerium(IV) concentrations were 0.44 and 0.00133 M, respectively, and bromate concentration was increased: 0.093, 0.105 and 0.118 M in 1.00 M sulfuric acid. A number of transient phenomena including mixed-mode (MM) and intermittency(I) oscillations were observed in between two series of simple oscillations. When the sulfuric acid concentration was reduced from 1.00 to 0.500 M, the complex transient oscillations were no longer observed. There were only damped simple oscillations with 1-3 cycles of period-doubled oscillations.

The induction period was independent of the bromate concentration employed in this study, but it decreased significantly when the sulfuric acid concentration was reduced from 1.00 to 0.500 M.

The complex oscillations could only be reproduced in a qualitative manner as they have shown to be very sensitive to the concentrations of the major reactants in the reaction.

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List of Abbreviations

(used in the experiments)

MA = Malonic Acid

E_{Br} = Bromide ion-potential

E_{Ce} = Cerium ion-potential

MM = Mixed-Mode oscillation

I = Intermittency oscillation

P = Periodic behavior

AP = Aperiodic behavior

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"Everything that happens in our world resembles a vast game of nothing determined in advance."

Manfred Eigen

Nobel Prize Winner in Chemistry

1967

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CHAPTER I

INTRODUCTION

The study of oscillating chemical dynamics is an exciting, active area of research that has been the subject of numerous papers.

For a long period of time, many chemists suspected that a chemical reaction in a homogeneous solution might proceed in an oscillatory manner, that is, showing periodic changes of concentration of some chemical species with respect to time. But these observations of chemical oscillations have been ascribed to artifacts of heterogeneous phenomena, such as bubble formation[1], or the influence of dust particles[2]. Some argued that oscillating chemical reaction violated the second law of thermodynamics[3,4]. These ideas began to change, at least, on the theoretical side, with the work of Prigogine and Nicolis[5] on nonlinear thermodynamics that began in the 1940s.

Generally, for a spontaneous chemical reaction occurring at constant temperature and pressure, the concentrations of individual chemical species usually approach equilibrium monotonically corresponding to a decrease in the Gibbs Free Energy of the system, as a consequence of the Second Law of thermodynamics. The occurrence of intermediates in the system still leads to the concentrations of the reactants decreasing and the products increasing with time, with the concentrations of the intermediates rising to a maximum and then decreasing to zero. For the chemical oscillating reaction, the

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concentrations of intermediates can increase and decrease with time (non-monotonic behavior) while the free energy monotonically decreases as the system approaches equilibrium, as shown in Figure 1.1.

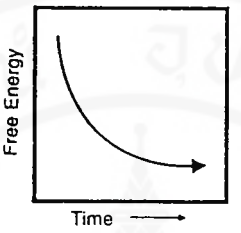

Figure 1.1 The allowed temporal evolution of Gibbs Free Energy in a closed system [6]

The first clear experimental evidence of a chemical oscillating reaction came in the 1960s from a redox reaction in aqueous solution, known as the Belousov-Zhabotinsky(BZ) reaction. The classical BZ-reaction is the metal ion-catalyzed simultaneous bromination and oxidation of an aliphatic polycarboxylic acid by acidic bromate reagent. This reaction is one of the most widely studied and best understood chemical oscillators because it is a prime example of nonlinear behavior in chemistry and affords an accessible and easily reproducible system. The ever increasing number of literature on the BZ-reaction in the past three decades provided much progress in mechanistic elucidation of the chemistry, the discovery of complex oscillations, chaos, and mathematical modeling. A recent review is reference [7].

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1.1 Historical survey of BZ-reaction and mechanistic studies

In the early 1950s, Boris Belousov, a Soviet biophysicist, was seeking an inorganic analogue of the biochemical Krebs cycle when he noticed that the color of a mixture consisting of bromate and cerium ions with citric acid in dilute sulfuric acid solution oscillated back and forth, with a period of about one minute, between colorless and pale yellow. Belousov carefully characterized the phenomenon and submitted his results, with recipes included, to a number of journals, all of which rejected them on the grounds that such a phenomenon could not occur. He eventually settled, before leaving the field, for a single short abstract in the unrefereed proceedings of a conference on radiation medicine[8]. Belousov 's recipes circulated among Moscow laboratories, and a young graduate student, Anatol Zhabotinsky, began to study and refine the reaction. Zhabotinsky modified the reagents and discovered that malonic acid could replace citric acid and that the redox indicator ferroin gave a more dramatic color change than the cerous-ceric couple[7]. From this discovery, B. P. Belousov was posthumously awarded the Lenin Prize, together with A. M. Zhabotinsky in 1980.

A crucial advance in the detailed chemical mechanism for the BZ-reaction was the developmental work by Field, Körös, and Noyes (FKN) [9] confirming that chemical oscillations could be explained by the same set of chemical kinetic principles that apply to normal reactions. Field and Noyes[10,11] were able to abstract from the FKN-mechanism a three-variable model, the Oregonator, that contains the essence of the

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chemistry while allowing for detailed numerical and analytical investigation. However, the mechanism of the BZ-reaction is very complicated, and a recent model contains 80 elementary steps and 26 variable species concentrations[12]. But the early mechanism (FKN) is still adequate to explain the course of the BZ-reaction and how oscillations occur. A very good description of the FKN-mechanism is the article by Field and Schneider[13] and the book by Scott and Gray[14].

1.2 Kinetics and mechanisms of oscillatory BZ-reaction

A chemical system at, or close to equilibrium will not oscillate since it is a stable state. Therefore, one necessary requirement for oscillation is the system to be far from equilibrium which can be met by having the reaction proceeds under open conditions, i.e., continuously supplying the reaction vessel with fresh reactants and allowing reacted material to leave so as to maintain a constant volume[15]. The second condition is that some product of a step in the reaction scheme must exert influence on its own rate of formation. This mechanism is called autocatalysis.

In 1920 Lotka presented a mechanism[16] in which two coupled autocatalytic reactions gave rise to oscillations,

$$\text{step 1: } A + X \rightarrow 2X \quad , \text{rate} = k_1[A][X] \qquad (1.2.1)$$

$$\text{step 2: } X + Y \rightarrow 2Y \quad , \text{rate} = k_2[X][Y] \qquad (1.2.2)$$

$$\text{step 3: } Y \rightarrow Q \quad , \text{rate} = k_3[Y] \qquad (1.2.3).$$

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The overall reaction is $A \rightarrow Q$, X and Y are intermediates, and k_1, k_2, k_3 are rate constants of each respective step. Both step 1 and step 2 are autocatalytic processes.

In order to illustrate how sustained oscillations in the concentrations of X and Y arise, let us consider an open system or a flow reactor in which the concentration of species A is maintained at a constant value A_0 at all times and Q is drawn off continuously with intermediates X and Y remaining at a steady state concentration. Then the kinetic equations for these intermediates are

$$d[X]/dt = k_1A_0[X] - k_2[X][Y] = 0 \qquad (1.2.4)$$

$$d[Y]/dt = k_2[X][Y] - k_3[Y] = 0 \qquad (1.2.5)$$

and the steady state solutions,

$$k_2[X]_{ss} = k_3 \qquad (1.2.6)$$

$$k_2[Y]_{ss} = k_1A_0 \qquad (1.2.7).$$

When the concentrations are temporarily displaced a small extent from their steady state values, we get

$$[X] = [X]_t + [X]_{ss} \qquad (1.2.8)$$

$$[Y] = [Y]_t + [Y]_{ss} \qquad (1.2.9).$$

By substituting equations 1.2.7, 1.2.8, 1.2.9 into equation 1.2.4 and equations 1.2.6, 1.2.8, 1.2.9 into equation 1.2.5, and solving these differential equations, we obtain a general form of the solution as

$$[X]_t \text{ or } [Y]_t = \cos[(k_1k_3A_0)^{1/2}t] \qquad (1.2.10).$$

The functional form of equation 1.2.10 is an oscillation with a period of $1/(k_1k_3A_0)^{1/2}$.

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Although the Lotka mechanism has not proved to be a model for any actual chemical reaction, it drew the attention of many chemists to the importance of autocatalysis in oscillatory processes.

The first thoroughly studied and by far the best characterized of BZ-systems is bromate ions, sulfuric acid, cerium ions and malonic acid (MA). In a closed, well-stirred system, the reaction typically exhibits a short induction period, followed by temporal oscillatory phase. The color alternates between the yellow color of ceric ion (Ce^{4+}) and the colourless of cerous ion (Ce^{3+}). The periodic change of color is made more visible by adding iron(II)-phenanthroline complex (ferroin) into the reaction mixture. The colour changes between the blue ferriin ($Fe(phen)_3^{3+}$) and the red ferroin ($Fe(phen)_3^{2+}$), correspond to the redox reaction,

$$Ce^{4+} + Fe(phen)_3^{2+} \leftrightarrow Ce^{3+} + Fe(phen)_3^{3+} \qquad (1.2.11).$$

The understanding of the BZ-reaction mechanism has been developed primarily in terms of the Field-Körös-Noyes(FKN) mechanism. The FKN-scheme contains three essential processes.

The first process, process A, is the bromate oxidation of bromide to produce HOBr and Br_2, which subsequently brominate malonic acid. The important steps are

$$R1: BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr \qquad (1.2.12)$$

$$R2: HBrO_2 + Br^- + H^+ \rightarrow 2HOBr \qquad (1.2.13)$$

$$R3: HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \qquad (1.2.14)$$

$$R4: Br_2 + CH_2(COOH)_2 \rightarrow BrCH(COOH)_2 + Br^- + H^+ \qquad (1.2.15).$$

The net reaction of process A is R1 + R2 + 3(R3 + R4):

$$BrO_3^- + 2Br^- + 3CH_2(COOH)_2 + 3H^+ \rightarrow 3BrCH(COOH)_2 + 3H_2O \qquad (1.2.16).$$

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The net effect of process A is the removal of bromide ion from the system. The next process, process B, is the autocatalytic generation of $HBrO_2$ with the concurrent oxidation of the cerium ion catalyst. This process is the heart of the mechanism,

$$R5: BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2^{\cdot} + H_2O \quad (1.2.17)$$

$$R6: BrO_2^{\cdot} + Ce^{3+} + H^+ \rightarrow HBrO_2 + Ce^{4+} \quad (1.2.18)$$

$$R7: 2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+ \quad (1.2.19)$$

followed by R3 and R4, to give the net reaction of process B as

2(R5+2R6) + R7 + R3 + R4:

$$BrO_3^- + 4Ce^{3+} + CH_2(COOH)_2 + 5H^+ \rightarrow 4Ce^{4+} + BrCH(COOH)_2 + 3H_2O \quad (1.2.20).$$

The consumption of each mole of $HBrO_2$ leads to the production of two more. However, R7, the disproportionation of $HBrO_2$, limits the amount of this compound.

A third net process, or process C, is the reduction of cerium(IV) to cerium(III), mainly by malonic acid, to regenerate Br^-. The overall change is often represented in the form,

$$2Ce^{4+} + BrCH(COOH)_2 + CH_2(COOH)_2 \rightarrow fBr^- + 2Ce^{3+} + Org. \quad (1.2.21),$$

Org. = other organic oxidation products (e.g. HCOOH, CO_2 etc.).

The stoichiometric factor " f " is an adjustable parameter. It represents the number of bromide ions produced when two cerium(IV) ions are reduced and varies with the instantaneous concentrations of MA and BrMA. A chain mechanism involving malonyl radicals $^{\cdot}CH(COOH)_2$ and bromine atom radicals $Br^{\cdot}$ has been proposed to account for stoichiometric factors greater than 2 [12,14]. Furthermore, the ambiguity

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associated with process C has allowed further scope particularly for modeling the more complex phenomena.

The three processes take place successively to constitute one oscillation. As the bromide ion concentration decreases to a critical concentration in process A, bromate starts to compete for $HBrO_2$ in R5 in process B, and the rates of R2 and R5 become equal to each other.That is

$$k_2[HBrO_2][Br^-][H^+] = k_5[BrO_3^-][HBrO_2][H^+] \quad (1.2.22)$$

leading to the following equation,

$$[Br^-]_{critical} = (k_5/k_2)[BrO_3^-] \quad (1.2.23).$$

The Br^- regeneration in process C returns the system to process A and the cycle begins again.

The revised rate constants of each major elementary step in FKN-mechanism, as reported by Field and Försterling[17], are given in Table 1.1.

Reaction	Rate constant
R1	$k_1 = 2\ M^{-3}sec^{-1}$
R2	$k_2 = 3x10^6\ M^{-2}sec^{-1}$
R3	$k_3 = 8x10^9\ M^{-2}sec^{-1}$
R5	$k_5 = 42\ M^{-2}sec^{-1}$
R6	$k_6 = 8x10^4\ M^{-2}sec^{-1}$
R7	$k_7 = 3x10^3\ M^{-1}sec^{-1}$

Table 1.1 Revised experimental rate constants of the main steps in FKN-mechanism

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The driving force for the BZ-reaction is oxidation and bromination of malonic acid by bromate to carbon dioxide and bromomalonic (BrMA) as the major products. The overall stoichiometry with an excess MA and trace amount of Ce(III) or Ce(IV) ion as a catalyst, can be approximated by the following reaction:

$$2BrO_3^- + 3MA + 2H^+ \rightarrow 2BrMA + 3CO_2 + 4H_2O \qquad (1.2.24)$$

The reaction is highly exothermic, and the heat of reaction is 650 $\pm$10 kiloJoules per mole of bromate[18].

1.3 Experimental observation and modeling of oscillating behaviors in closed BZ-system

In closed systems, there are no exchange of mass with surrounding. The simplest example of a closed system in BZ-reaction is the batch reactor consisting of a beaker containing the BZ-reagent, stirrer, detector, and recorder.

Various intermediates of cerium ion-catalyzed BZ-reaction, such as bromide and cerium ions, exhibit temporal concentration oscillations that can be easily monitored, either potentiometrically or spectrophotometrically.

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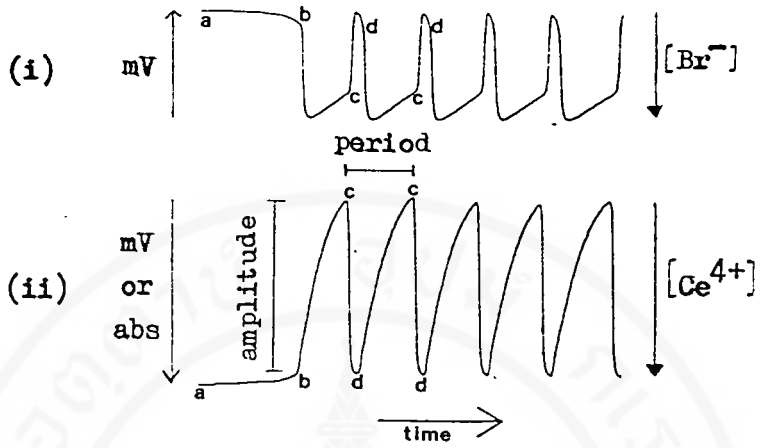

Figure 1.2 Typical experimental records of the temporal oscillations in a closed BZ-system [19]

(i) Bromide ion selective electrode potential

(ii) Platinum electrode potential or absorbance of Ce(IV)

Figure 1.2 shows the tracings of simple oscillations in the potential (mV) of each type of electrode or the absorbance (abs) of ceric ion at 340 nm. Both electrodes employ calomel electrode as the reference electrode, and for the platinum electrode, its potential is mainly the function of the redox couple Ce(IV)/Ce(III) concentrations ratio.

A period is the time for the reaction to complete one oscillatory cycle, an amplitude is the difference between a maximum value and a minimum value of the potential or the absorbance. These parameters depend on the temperature and initial concentrations of the reactants [9,20,21].

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During the induction period (the time before the oscillations commence), accumulation of BrMA to a critical value take places between points a and b (see Figure 1.2). Between points b and c, Ce(IV) reduction occurs as [Br^-] sharply increases. As [Ce(IV)] decreases, less bromide ion is produced and bromide consuming reactions in process A are significant. At point c, [Br^-] has decreased to a critical value, which permits oxidation of Ce(III) and removal of bromide ions. This gives rise to a relaxation waveform. As Ce(IV) accumulates between points c and d in process B, there is sufficient BrMA present so that [Br^-] eventually drifts upward to point d. This second critical value of [Br^-] permits reduction of Ce(IV) and sudden increase in [Br^-] by process C which is analogous to that seen at point b.

The chemical oscillations may only last for several hours, i.e., they can only be transient phenomena. They must decay and ultimately die out. The system drifts slowly and monotonically towards its chemical equilibrium state or homogeneous steady state in which the net rate of production of all chemical species is zero simultaneously.

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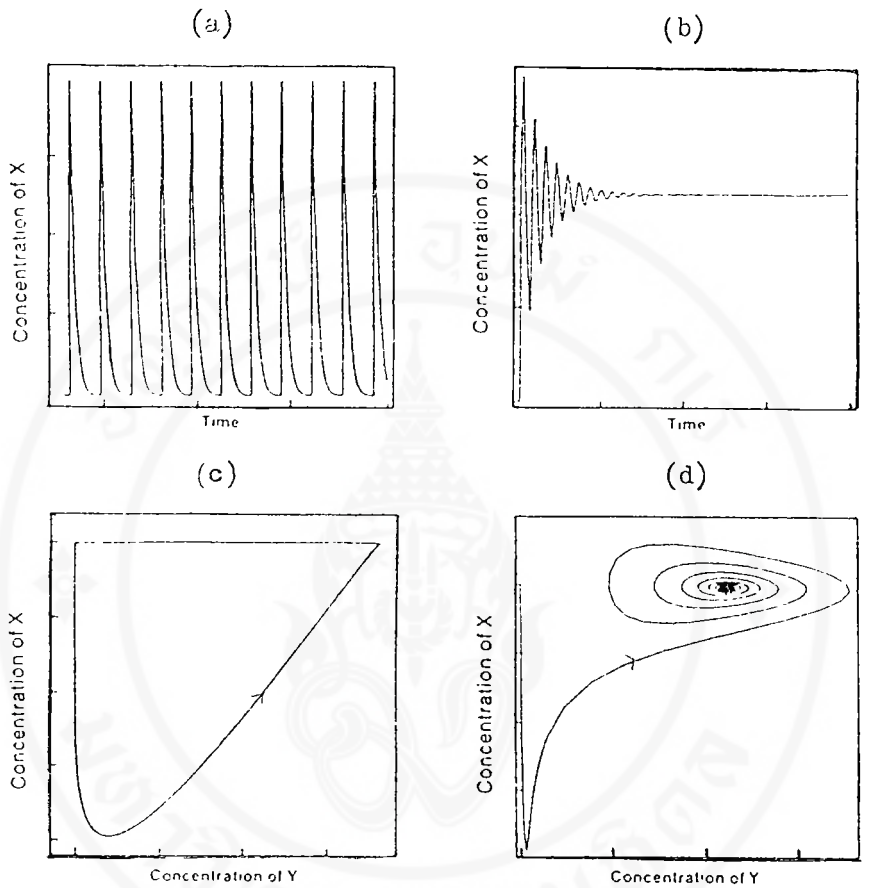

Figure1.3 Plots of concentration vs time and corresponding concentration phase space of the recycling intermediates in the closed system [22]

(a) Simple periodic oscillation (b) Damped oscillation to a steady state

(c) A limit cycle (d) A sink of limit cycle to a stationary point

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Figure1.3a,b show temporal behaviors of the recycling intermediate (X) concentration in a batch system. These changes can be illustrated in another way, that is, as phase portraits (Figure1.3c,d) in which the trajectory of the system is plotted in two axes of the intermediate concentration variables (X and Y), for example, bromide and cerium ions in BZ-reaction.

The reacting BZ-systems are sensitive to the addition of certain reagents in low concentrations. For example, chloride ion[23] inhibits the reaction, iodide ion[24] opens new recycling routes and silver ion[25,26] induces very short period oscillation by binding the control intermediate, bromide ion. Heterogeneities and stirring effect that affect on the period of the oscillation have also been observed[27].

In order to describe and to understand the individual experimental observations, and to predict the experimental conditions under which oscillations might be observed, it is convenient to use a simple model, the Oregonator Model, derived from the FKN-scheme[10,11]. This is frequently written in the form,

$$A + Y \rightarrow X + P \quad , \text{rate} = k_1[A][Y] \qquad (1.3.1)$$

$$X + Y \rightarrow 2P \quad , \text{rate} = k_2[X][Y] \qquad (1.3.2)$$

$$A + X \rightarrow 2X + Z \quad , \text{rate} = k_5[A][X] \qquad (1.3.3)$$

$$2X \rightarrow A + P \quad , \text{rate} = k_7[X]^2 \qquad (1.3.4)$$

$$Z \rightarrow fY \quad , \text{rate} = k_C[Z] \qquad (1.3.5).$$

The chemical species corresponding to the letters is given in Table 1.2. k_C is the rate constant of process C, in general, it is approximated as $1M^{-1}sec^{-1}$ in the model.

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Letter	Chemical species
A	BrO_3^-
P	HOBr
X	$HBrO_2$
Y	Br^-
Z	Ce^{4+}

Table 1.2 Identification of symbols for the Oregonator model

The concentrations of A and P are treated as constants and $[H^+]$ is combined into the rate constants.

The reaction rate equations for the intermediates X,Y and Z (three-variable model) are

$$d[X]/dt = k_1[A][Y]-k_2[X][Y]+k_5[A][X]-2k_7[X]^2 \quad (1.3.6)$$

$$d[Y]/dt = fk_C[Z]-k_2[X][Y]-k_1[A][Y] \quad (1.3.7)$$

$$d[Z]/dt = k_5[A][X]-k_C[Z] \quad (1.3.8).$$

For a suitable set of rate constants, the dynamical behavior has been investigated by numerical integration of the set of dimensionless equations obtained by substituting [X],[Y],[Z],t by dimensionless variables α,β,γ,τ, respectively, in the kinetic equations 1.3.6-1.3.8. Thus, these become

$$\sigma(d\alpha/d\tau) = \rho\beta-\alpha\beta+\alpha-\alpha^2 \quad (1.3.9)$$

$$\delta(d\beta/d\tau) = -\rho\beta-\alpha\beta+f\gamma \quad (1.3.10)$$

$$d\gamma/d\tau = \alpha-\gamma \quad (1.3.11),$$

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$$\alpha = 2k_7[X]/k_5[A] \quad (1.3.12)$$

$$\beta = k_2[Y]/k_5[A] \quad (1.3.13)$$

$$\gamma = k_C k_7[Z]/(k_5[A])^2 \quad (1.3.14)$$

$$\tau = k_C t \quad (1.3.15),$$

and dimensionless parameters σ,δ,ρ, depending only on initial reactant concentration, $[BrO_3^-]$, and rate constants,

$$\sigma = k_C/k_5[A] \quad (1.3.16)$$

$$\delta = 2k_C k_7/k_2 k_5[A] \quad (1.3.17)$$

$$\rho = 2k_1 k_7/k_2 k_5 \quad (1.3.18).$$

This model, consisting of five irreversible steps and three chemical intermediates is used extensively for numerical calculations and modeling of the BZ-reaction. Although it can not be solved analytically, it is very useful in simulating and predicting the qualitative features of the various types of dynamical behavior of BZ-systems.

1.4 Complex oscillations in batch BZ-reaction

In addition to simple periodic oscillations (period-1), the closed BZ- system can exhibit complex oscillations with many peaks per cycle, both periodic and non-periodic.

Complex periodic oscillations or multipeaked oscillations, the concentration vs time waveform consists of combinations of distinct large and small amplitude oscillations per cycle. In characterizing these oscillations, the periodic repetition of a basic pattern is represented with

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the number L of large amplitude oscillations followed by the number s of small amplitude oscillations. Thus, the notation for a complete period or repeating unit is L^s [28]. For example, a period-doubling (period-2) consisting of one large amplitude and one small amplitude per cycle, is represented as 1^1-oscillation. Period-3 or 1^2-oscillation consists of one large amplitude and two small amplitudes per oscillation, etc. .

Complex aperiodic oscillations or chemical chaos is a regime having a random-looking mix of small and large amplitude oscillations. The concentrations of the intermediates show unpredictable amplitudes and periods.

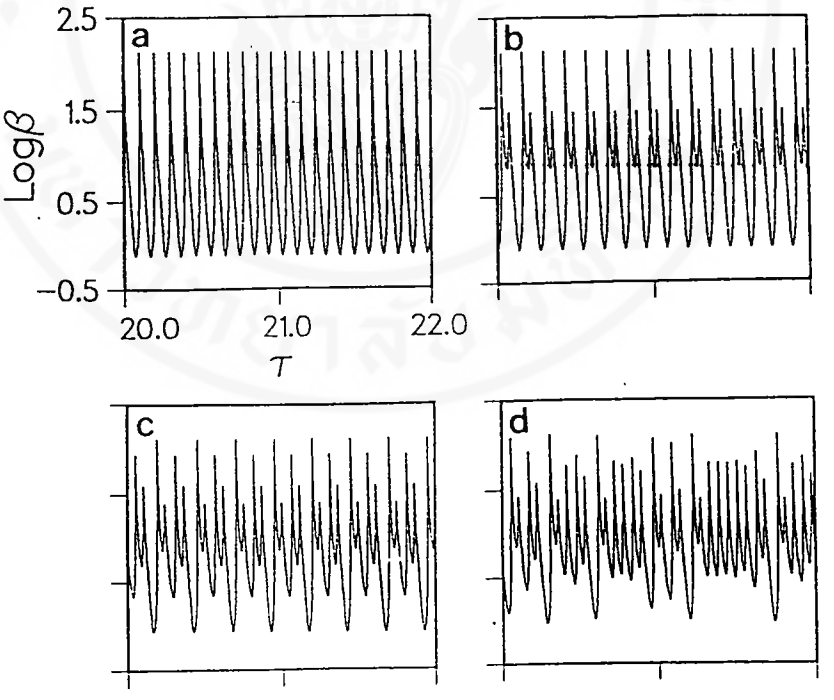

Figure 1.4 Computer simulations of some complex oscillatory behaviors based on a three-variable autocatalator model [29]

(a) Period-1 (1^0 - oscillation) (b) Period-2 (1^1 - oscillation)

(c) Period-4 (1^3 - oscillation) (d) Chaotic oscillation

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Figure 1.4 shows some types of complex periodic oscillations and aperiodic oscillations. Note that β,τ represent the concentration of reaction intermediate and dimensionless time, respectively.

Chaotic solutions for certain sets of well-defined, simple nonlinear (second-order) differential equations of the rate laws are called deterministic chaos. Although fully determined by the structure of the equations, it is not possible to predict the composition of the system from the initial composition. In other words, it is extremely sensitive to the initial condition. Thus, the results are not quite repeatable in quantitative details.

Chemical chaos can be reached in a variety of different ways depending on the values of the constraints, e.g. the initial concentration of reactants. The most common route, period-doubling cascades[28,30], is a successive sequence of periodic transition from period-2 to period-4 to period-8 etc. (twice of the predecessor period). Other routes, for example, is the transition through mixed-mode oscillations[28,31] or intermittency[28].

In period-doubling cascades route, where the period-doubling occurs, the phase portraits of the system must circulate twice round the circle before an initial pair of concentration is restored. Then, after a further modification of the constraints, the period doubles again, and the limit cycle circulates four times before repeating itself, as shown in Figure 1.5.

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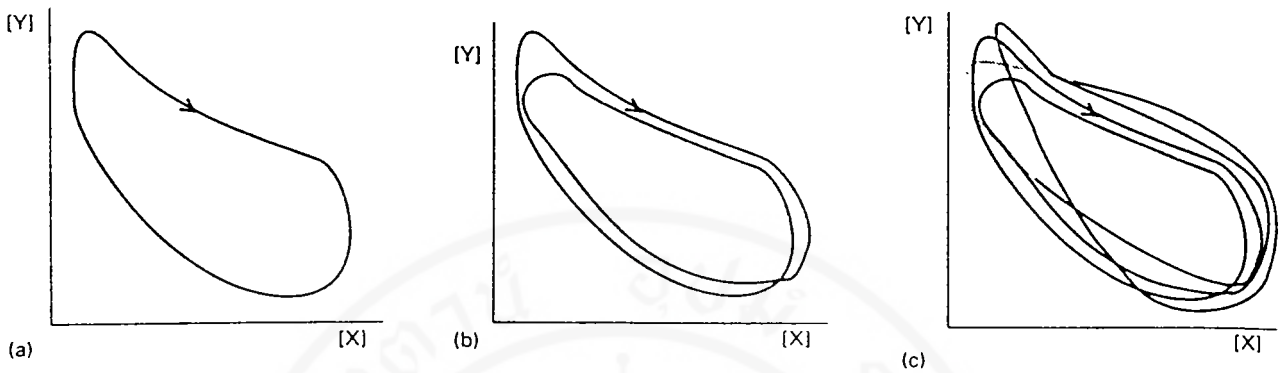

Figure 1.5 Successive trajectories of period-doubling in concentration spaces [32]

(a) Before period-doubling

(b) After one period-doubling step

(c) After several period-doubling steps

As each period doubles, the periodicity of the motion becomes less apparent, and finally appears like random fluctuations(the period has doubled ad infinitum). The trajectory of the composition of the system is now highly complex, and may take a path that never retraces its path or crosses itself. Such a path is called a strange attractor. Thus, the phase portrait is necessarily from a higher dimensional space (at least three dimensions), as shown in Figure 1.6.

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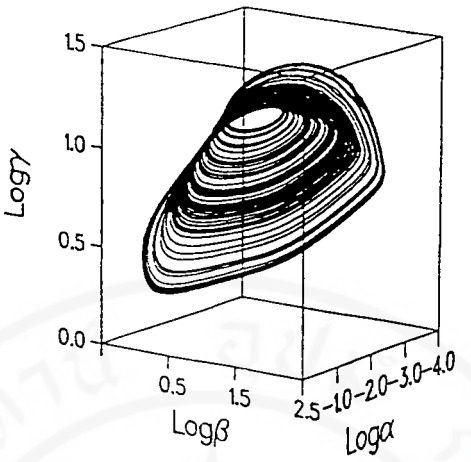

Figure 1.6 A three-dimensional representation of the phase portrait of a strange attractor for a system showing chemical chaos [29] (α,β,γ represent the concentration of reaction intermediates)

For a route to chaos by mixed-mode oscillations (see Figure 1.7), the waveform typically has a repeating unit consisting of a number of both large and small amplitude excursions. Different periodicities are formed by combining different numbers of small and large peaks. Aperiodicity is also possible.

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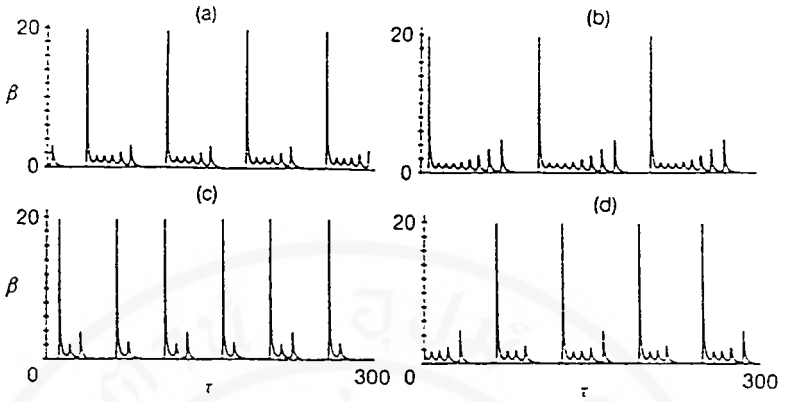

Figure 1.7 Numerical simulations of some mixed-mode oscillations based on a three-variable autocatalator model [28]

(a) 1^5 - oscillation (b) 1^8 - oscillation

(c) $1^1 1^2$ - oscillation (d) $1^3 1^4$ - oscillation

For intermittency route to chaos or bursting pattern, its waveform has short trains of perhaps four large excursions separated by periods of non-oscillatory or at least much smaller amplitude evolutions. As shown in Figure 1.8.

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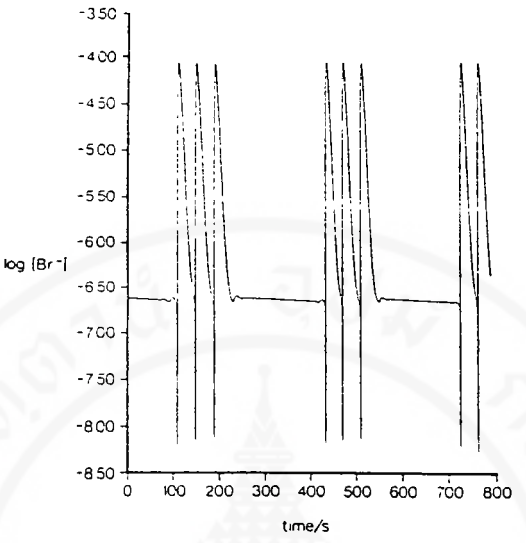

Figure 1.8 A simulation of bursting oscillations from a modified Oregonator model [33]

In closed chemical systems, only transients exist, but the oscillations may be sustained a very long time. The concepts of the exotic behaviors, such as period-doubling and its associated cascades, chaos do not apply, strictly speaking[5,28]. Irregularities and fluctuations have been seen[34,35] but deterministic chaos has not applied in a closed system[36]. However, often it is possible to view transients as composed of motions of widely different characteristic, finite interval of duration times[37]. Such transients may be understood as dynamical structures slowly changing in time while the composition of the system is changed as reactants are consumed.

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Recently, the first convincing and spectacular experimental evidence of transient phenomena, including successive period-doublings,

intermittency, mixed-mode oscillations, as well as combinations of these modes (see Figure 1.9), and genuine transient chaos in a closed, stirred BZ-system under anaerobic(oxygen free) condition were reported by Wang et al.[38,39]. They also showed that the reproducibility of even quite complex, nonchaotic oscillations was virtually independent of the stirring rate. The simulations of some of the transient complex behaviors were carried out using a modified Oregonator model[39,40], and the construction of the phase portraits were from the experimental data in a pseudo-closed stirred BZ-system under aerobic condition[41]. Complex periodic transient oscillations in closed BZ-reaction using ferroin as a catalyst under atmospheric oxygen has been also reported[42].

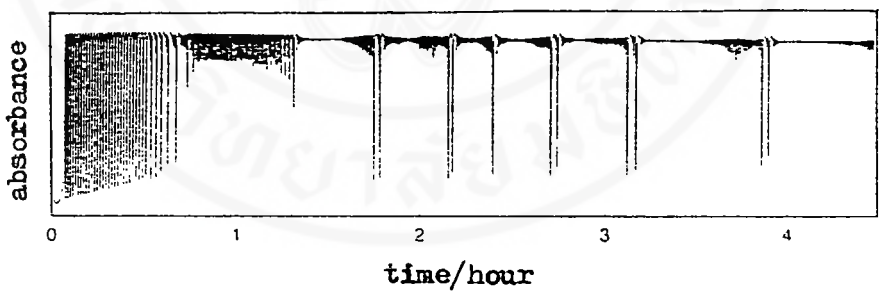

Figure 1.9 Time evolution showing the complex combinations of transient chaotic intermittency and transient mixed-mode oscillations in a closed BZ-system [39]

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Figure1.10a,b demonstrates transient double-peaked oscillations, occurring at excess initial concenrtration of malonic acid over bromate. The phase portrait of Figure 1.10c reconstructed by plotting the time series of potentials of the bromide sensitive electrode (a measure of (log[Br^-]) against that of the platinum electrode (a measure of (log{[Ce^{4+}]/[Ce^{3+}]}) shows the alternation of small and large amplitude oscillations.

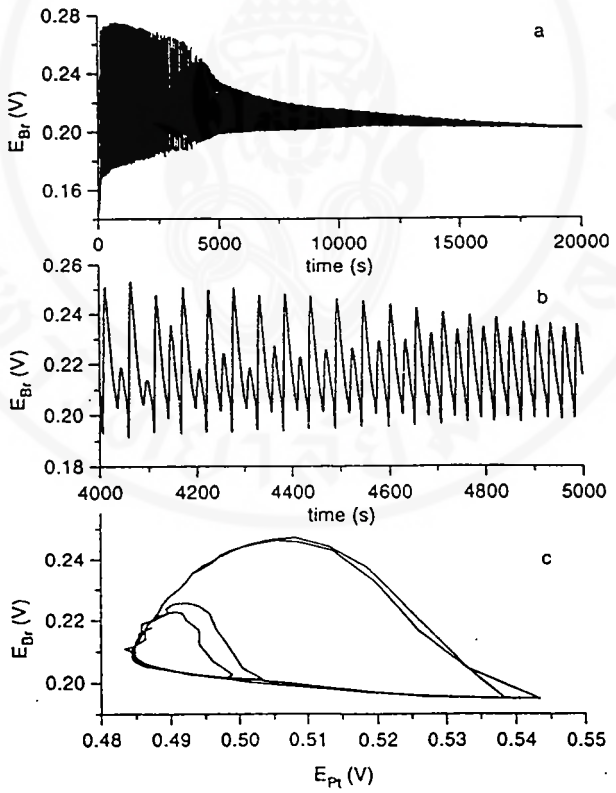

Figure 1.10 Time series and corresponding phase portrait of transient period-doubling phenomenon in a pseudo-closed BZ-system [41]

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The transition between different types of behavior in closed systems is similar to open systems, carried out in a Continuous-flow Stirred Tank Reactor(CSTR)[28,43,44]. Moreover, the existence of complex oscillations in closed chemical systems offers an unique opportunity to test the origin of the complexity, because there is no problem of incomplete mixing of reactants from feed streams, insufficient stirring causing spatial inhomogeneities or the problem of small local differences of reaction rates as in a CSTR[45].

1.5 Scope of this thesis

In previous works[46,47], using bromide ions for initiating the oscillations, the influence of the initial concentrations of reactants on the temporal behavior, including period and amplitude, and the temperature oscillations as the consequence of the exothermicity of the reaction, were studied. The purpose of this work is to demonstrate and describe a wide variety of complex oscillations in the pseudo-closed, cerium-catalyzed BZ- system under atmospheric oxygen, to determine how the behavior of the complexity changes with bromate and sulfuric acid concentrations, and to check the reproducibility of such a system.

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CHAPTER II

APPARATUS, MATERIALS AND EXPERIMENTAL METHODS

2.1 Instruments

The apparatus used in this work are listed below.

- Platinum Inlay Electrode
  Cat. No. 476060
  Corning Glass Works, U. S. A.

- Bromide Sensitive Electrode
  Model 94-35
  Orion Research Inc., U. S. A.

- Double Junction Calomel Electrode
  Model 4092-H10
  Arthur H. Thomas Company, U. S. A.

- Digital Ionalyzer Meter
  Model 601A
  Orion Research Inc., U. S. A.

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- Potentiometric Recorder

  SERVOSCRIBE 1S Model RE 541.20

  Smith Industries Ltd., England

- Thermometer

  Measured temperature range: -5.0±0.1°C to 50.0±0.1°C

  Cat. No. TJ-070-2

  Gallenkamp Scientific Ltd., England

- Digital Bath Thermostatic Controller

  Controlled temperature range: 0.0±0.1°C to 100.0±0.1°C

  EYELA Model UNIACE UA-100

  Tokyo Rikakikai Co. Ltd., Japan

- Thermostated Glass Vessel

  Cat. No. 6.1418.220

  Methrohm Ioneanalytik AG, Switzerland

- Magnetic Stirrer

  Model 542A-2

  Zinsser Analytic Inc., U. S. A.

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2.2 Chemicals

All chemicals used in the experiments are listed below.

Name/Formula	Molecular weight	Grade/Purity	Supplier
Malonic acid $CH_2(COOH)_2$	104.06	synthesis > 99 %	E.Merck, Germany
Sodium bromide NaBr	102.90	extra pure > 99.9 %	E.Merck, Germany
Potassium bromate $KBrO_3$	167.00	analyzed 101.2 %	J. T. Baker, U.S.A.
Potassium nitrate KNO_3	101.11	pro analysi > 99 %	E.Merck, Germany
Potassium chloride KCl (saturated solution)	74.56	-	TOA Electronics, Japan
Ceric sulfate tetrahydrate $Ce(SO_4)_2.4H_2O$	404.30	pro analysi > 99%	E.Merck, Germany
Sulfuric acid H_2SO_4(solution for 0.5M in 1L)	98.08	titrisol	E.Merck, Germany

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2.3 Experimental method

The BZ-reaction comprised a solution of malonic acid and potassium bromate with cerium(IV) sulfate as a catalyst in aqueous sulfuric acid. All the reactions were carried out in a thermostated glass container at 30.0±0.1°C. The solution was stirred with a magnetic bar at a constant rate (fixed setting of the magnetic stirrer) with the solution surface exposed to air.

2.3.1 Preparation of the reaction mixture

The reaction solution had a total volume of 50.0 ml, and deionized water was used for preparation of all solutions.

Initial concentration of the reactants studied are given below with initial concentrations of the reactants similar to those of Wang et al. [38] denoted by *.

Initial condition	$[MA]_0$ (M)	$[KBrO_3]_0$ (M)	$[Ce(SO_4)_2]_0$ (M)	$[H_2SO_4]_0$ (M)	$KBrO_3$ (g) (±0.0001g)
* 1A	0.44	0.093	0.00133	1.00	0.9708
1B	0.44	0.105	0.00133	1.00	1.1011
* 1C	0.44	0.118	0.00133	1.00	1.2317
2A	0.44	0.093	0.00133	0.500	0.9708
2B	0.44	0.105	0.00133	0.500	1.1011
2C	0.44	0.118	0.00133	0.500	1.2317

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Malonic acid (2.8617±0.0001g) and potassium bromate were dissolved in 50.0 ml aqueous sulfuric acid (using volumetric pipette). 40.0 ml of this solution mixture was transferred into the reactor vessel, and stirred at a constant rate. When the temperature of the solution attained 30.0±0.1°C, the reaction was initiated by adding 10.0 ml solution (also at 30°C) of 0.0405±0.0001g ceric sulfate tetrahydrate dissolved in 15.0 ml aqueous sulfuric acid.

2.3.2 Potentiometric measurement of temporal oscillations in BZ-reaction

The electrical potential of the reaction mixture was measured with a pair of electrodes, a platinum electrode or a bromide ion selective electrode as the working electrode and a double junction calomel electrode as the reference electrode in both systems. The reference electrode was filled with saturated KCl and 1M KNO_3, with the nitrate solution making contact with the reaction mixture.

The arrangement of the instruments in the reactor is shown in Figure 2.1.

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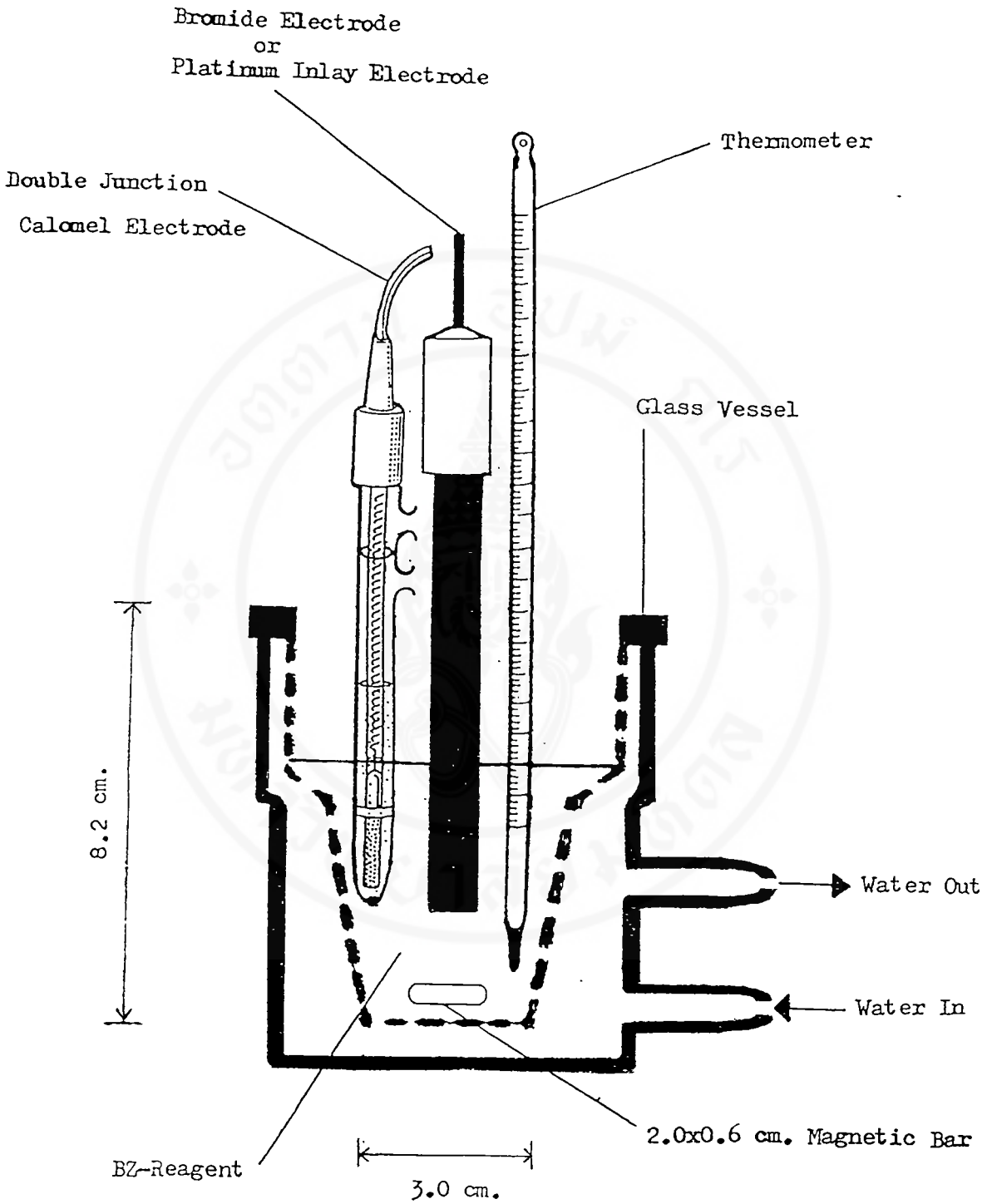

Figure 2.1 A diagram of the potential measurement apparatus

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The output from the potentiometer was fed to single-channel strip chart recorder, with the signal from platinum electrode or bromide electrode attached to the negative terminal and from calomel electrode attached to the positive terminal. The chart speed used was 0.5 cm/min and the voltage scale was set at 20 mV (full scale). Because the observed potential of cerium ions was much greater than that of bromide ions[14], the signal was offset -300 % , to bring the signal within range.

The experiment was repeated four times for each initial condition. Whenever it was noticed that the potential reading of bromide electrode showed poor reproducibility, the surface of the sensing element was gently polished with the sand paper (provided with the electrode). The electrode was then rinsed and soaked in 1M NaBr for 30 minutes before reuse.

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CHAPTER III

RESULTS

3.1 Complex oscillations of bromide and platinum electrode potentials

The potentiometric traces with respect to time and their maximum amplitudes of bromide (E_{Br}) and cerium (E_{Ce}) ions for each initial condition are shown in Figures 3.1.1-3.1.3.

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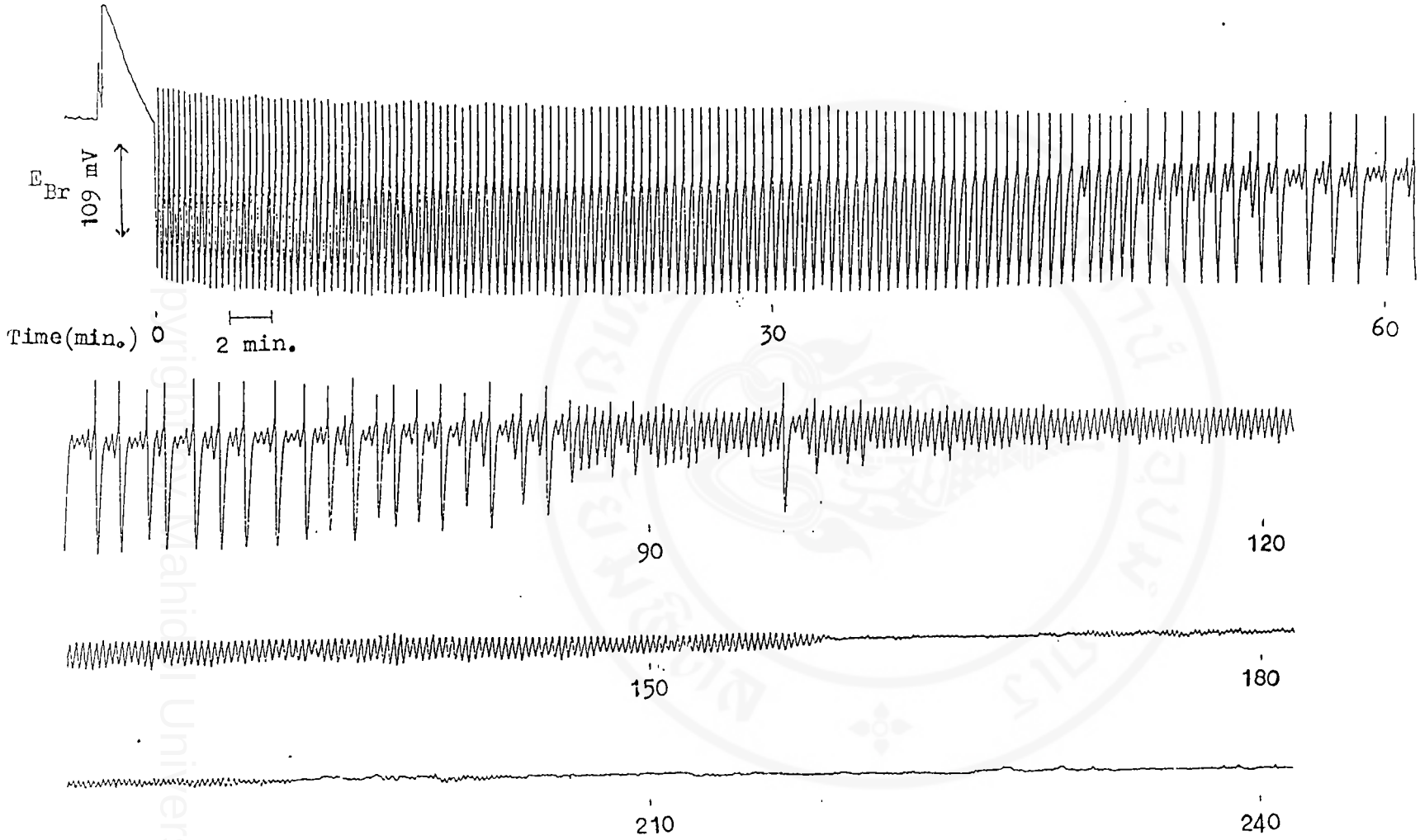

Figure 3.1.1 Potentiometric traces of bromide and cerium ions with respect to time for initial condition 1A

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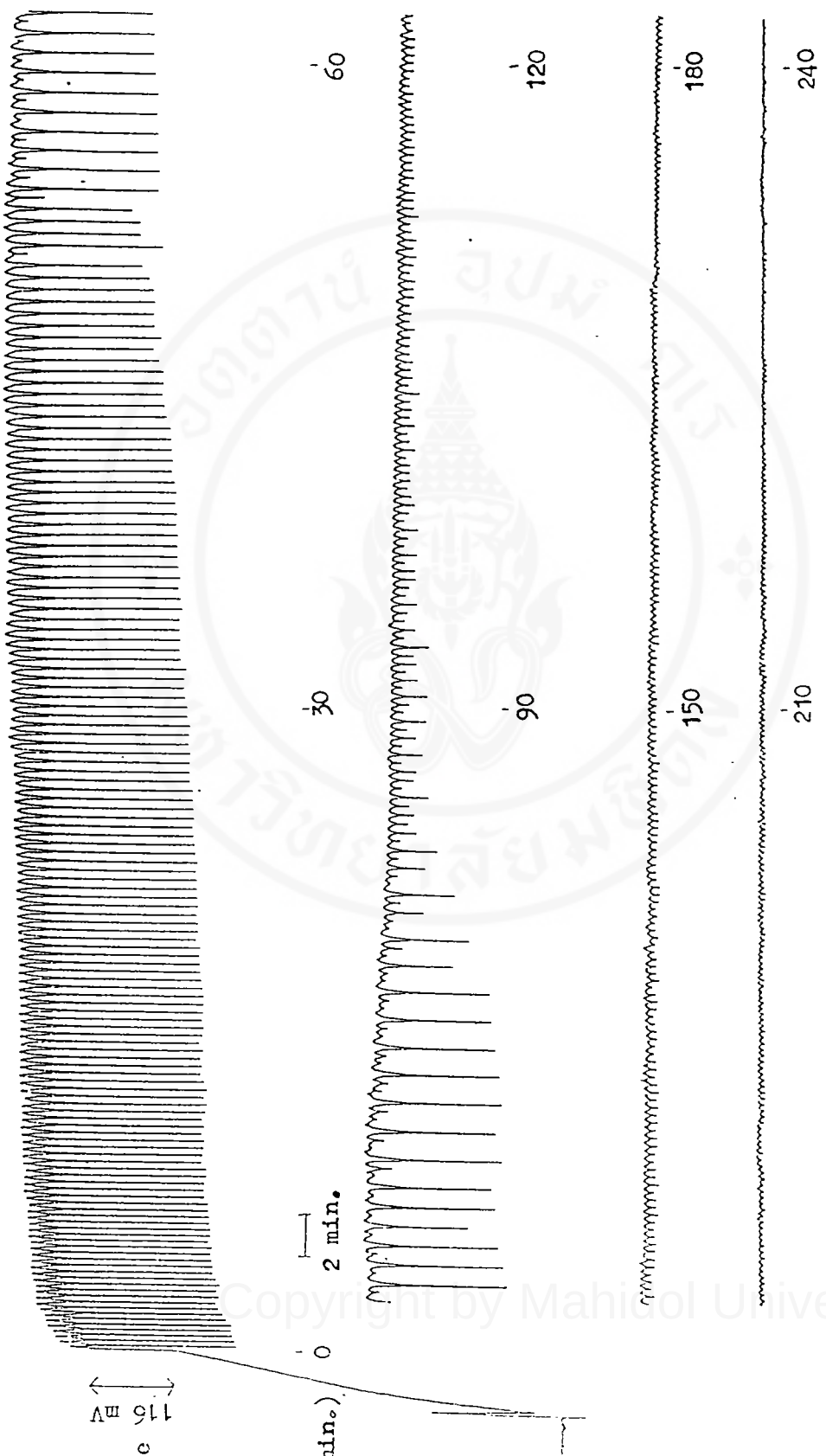

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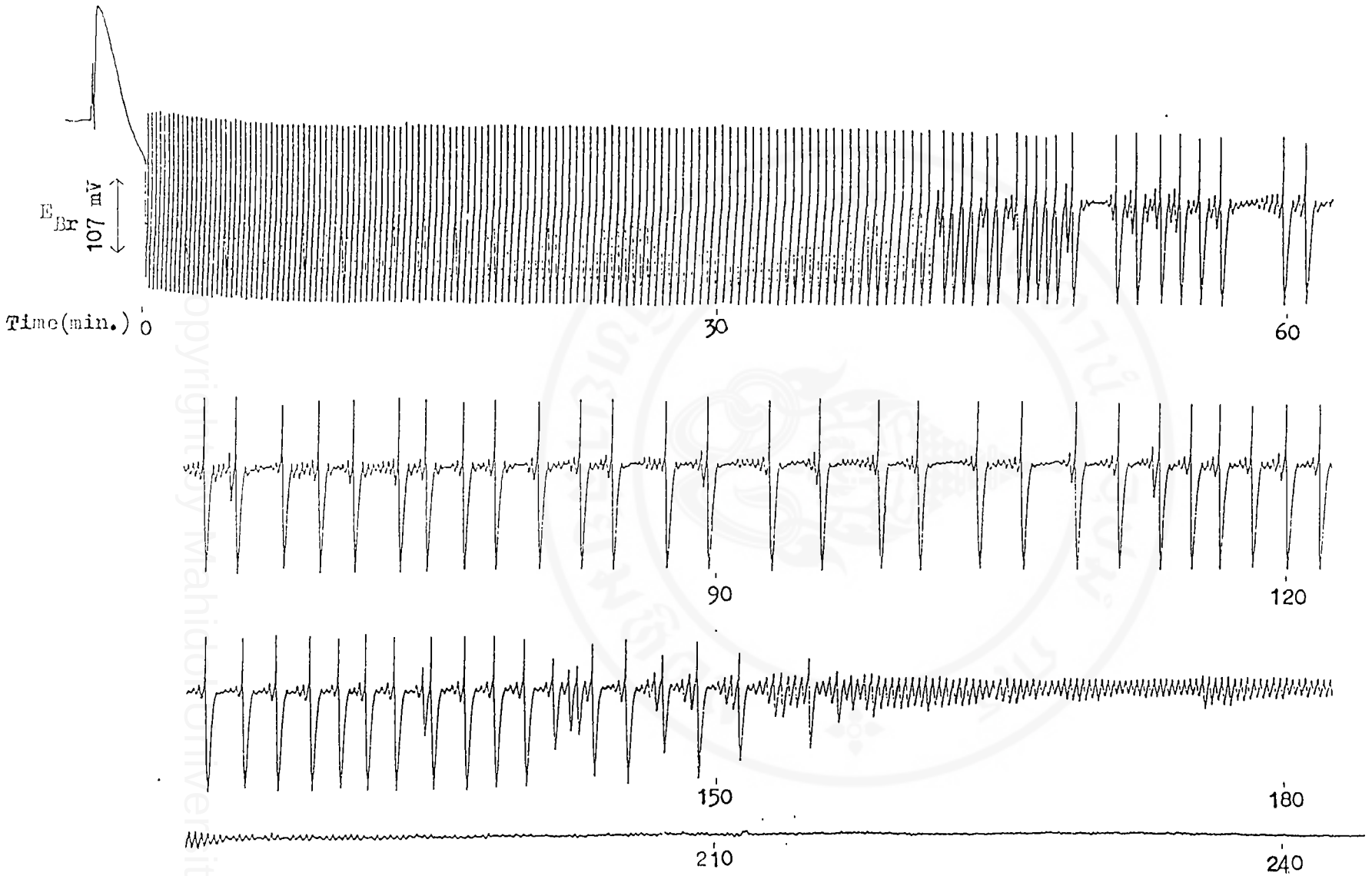
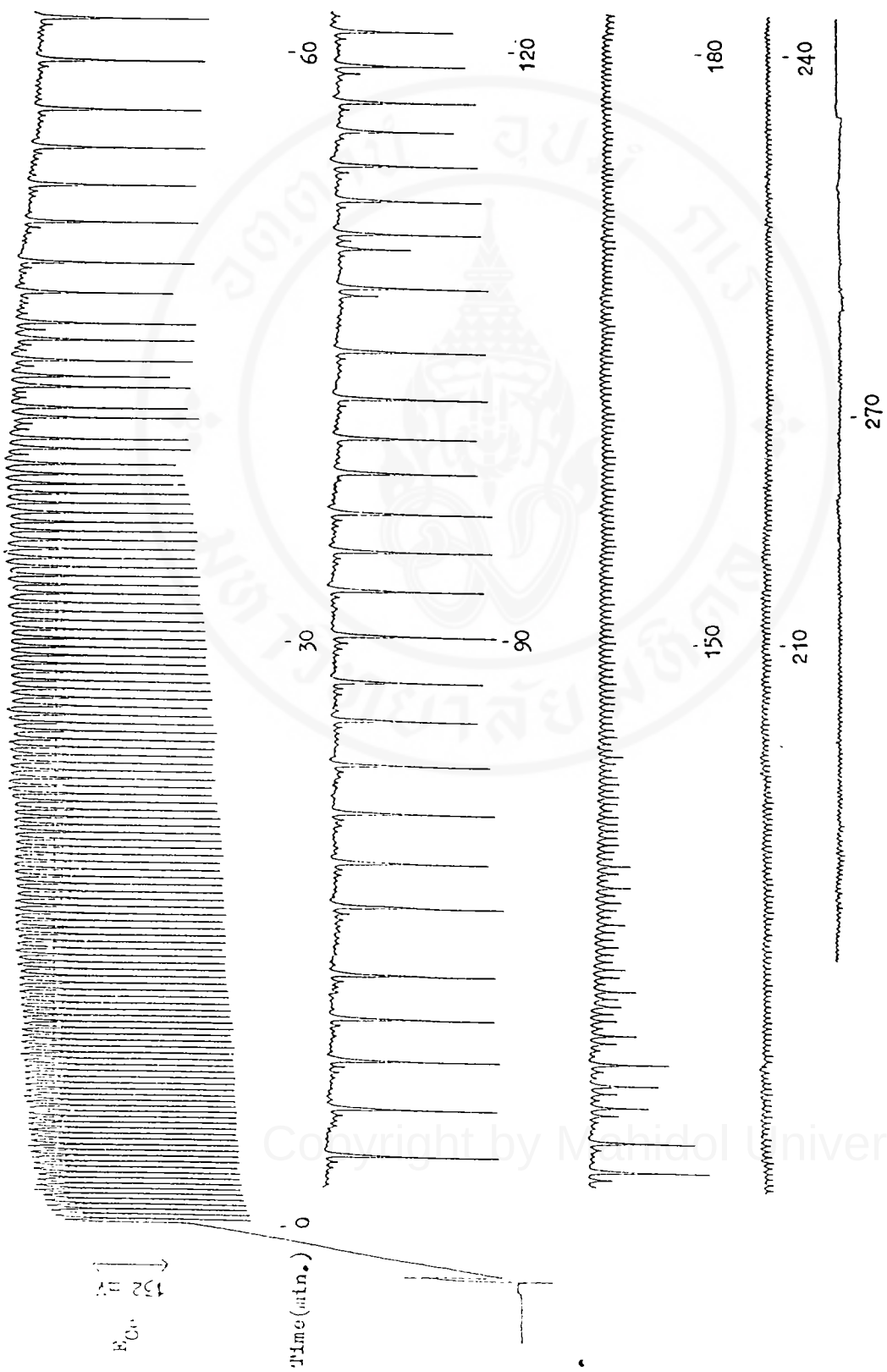


Figure 3.1.2 Potentiometric traces of bromide and cerium ions with respect to time for initial condition 1B



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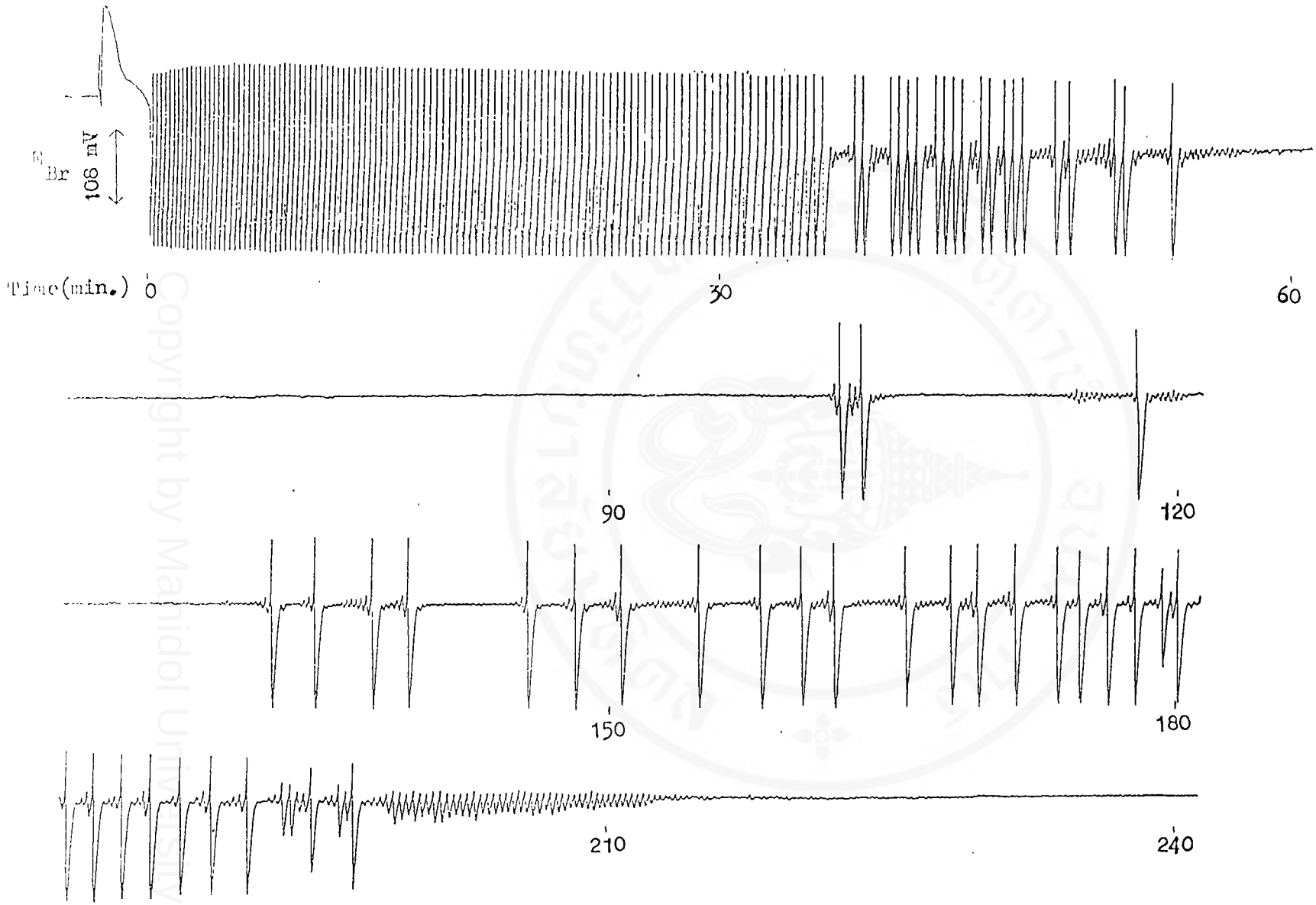

Figure 3.1.3 Potentiometric traces of bromide and cerium ions with respect to time for initial condition 1C

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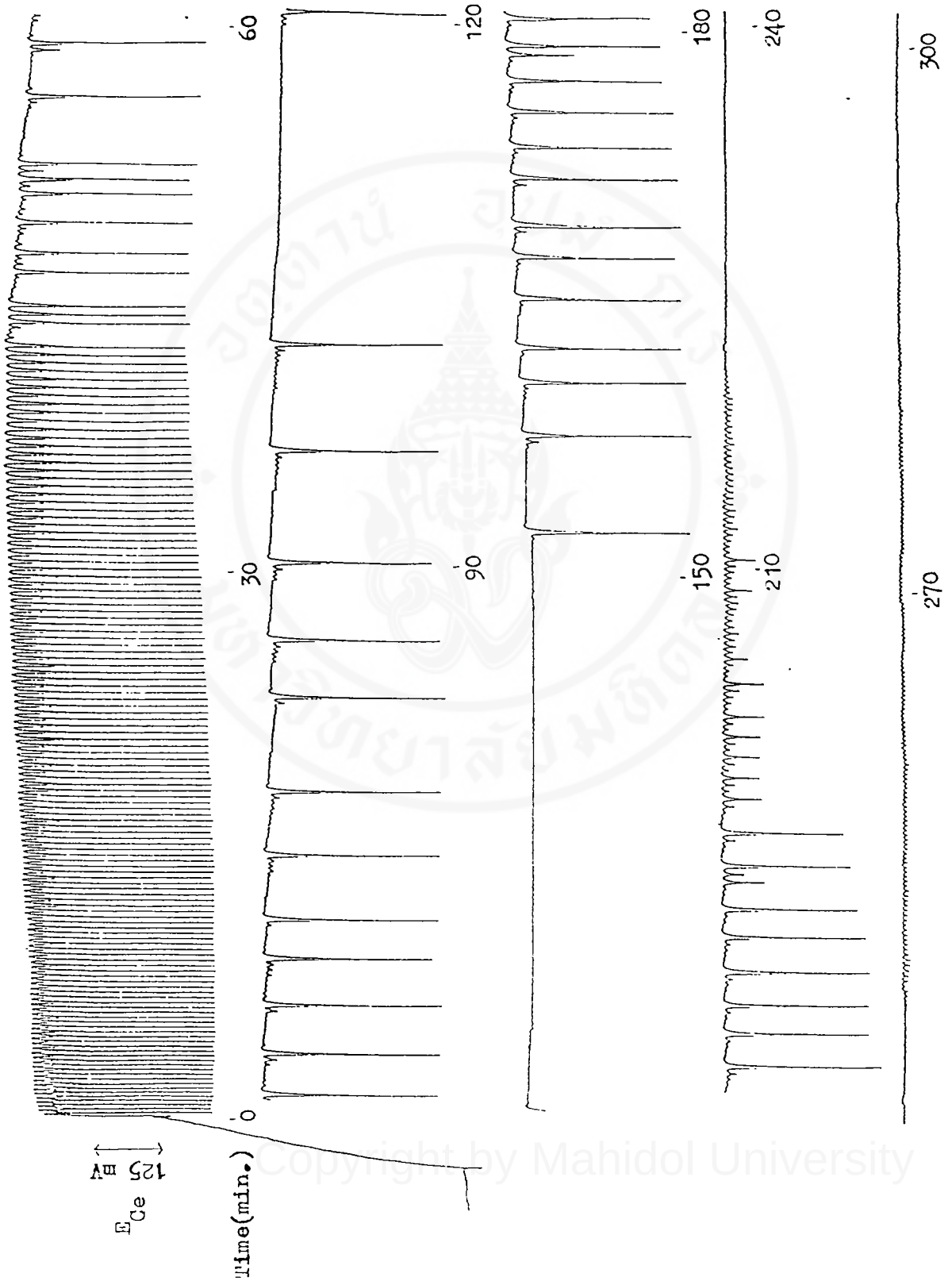

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From Figures 3.1.1-3.1.3, the complex transient oscillations for all the initial conditions, are always preceded by a number of periodic simple oscillations with large amplitude, and are followed by a number of simple damped oscillations with small amplitude. The final equilibrium state was a colorless solution. It should be noted that the first jump of the potential before the sudden birth of the oscillations was caused by the addition of the acidic ceric sulfate solution to the solution mixture.

The total temporal features in Figures 3.1.1-3.1.3 could only be reproduced qualitatively.

The average induction period, and general qualitative features of transient complex oscillations mainly observed for each initial condition, are given in Table 3.1.1.

Initial condition	$[H_2SO_4]$ (M)	$[KBrO_3]$ (M)	Average induction period (sec.)	Transient complex oscillations
1A	1.00	0.093	150 ± 7	MM: $P1^s$(s = 1,2)
1B	1.00	0.105	153 ± 4	MM: $AP1^s$(s = 2-8)
1C	1.00	0.118	156 ± 5	I: AP

Table 3.1.1 Average induction periods and major types of transient complex oscillations observed for initial condition 1A, 1B and 1C (MM = Mixed-Mode, I = Intermittency, P = Periodic, and AP = Aperiodic)

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It can be seen from Table 3.1.1 that the average induction period gradually increased as the bromate concentration was increased.

The duration time of the various types of transient complex oscillations or the time interval between the two series of simple oscillations was not constant. However, on the average, it was found that the duration period was increased from initial condition 1A to 1C, as shown in Table 3.1.2.

Initial condition	Average duration time (min.)
1A	22-74
1B	70-134
1C	70-168

Table 3.1.2 Average duration times of all complex transient oscillations for initial condition 1A , 1B and 1C

For the early simple oscillations, there was an increase of period with time (see Table 3.1.3).

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Initial condition	Average oscillatory period (±1sec.)					Average amplitude E_{Br} / E_{Ce} (mV)
	6min.	12min.	18min.	24min.	30min.	
1A	18	21	23	25	26	89-95 / 82-108
1B	16	19	21	23	24	89-99 / 85-111
1C	16	18	20	22	23	91-101 / 85-117

Table 3.1.3 Average oscillatory periods of large amplitude simple oscillations in the time interval(0-30minutes) as measured every 6 minutes, and their average constant amplitudes for initial condition1A, 1B and 1C

From the data in Table 3.1.3, it can be seen that the oscillatory period decreased with increasing bromate concentration. However, the amplitude did not increase significantly when the bromate concentration was increased.

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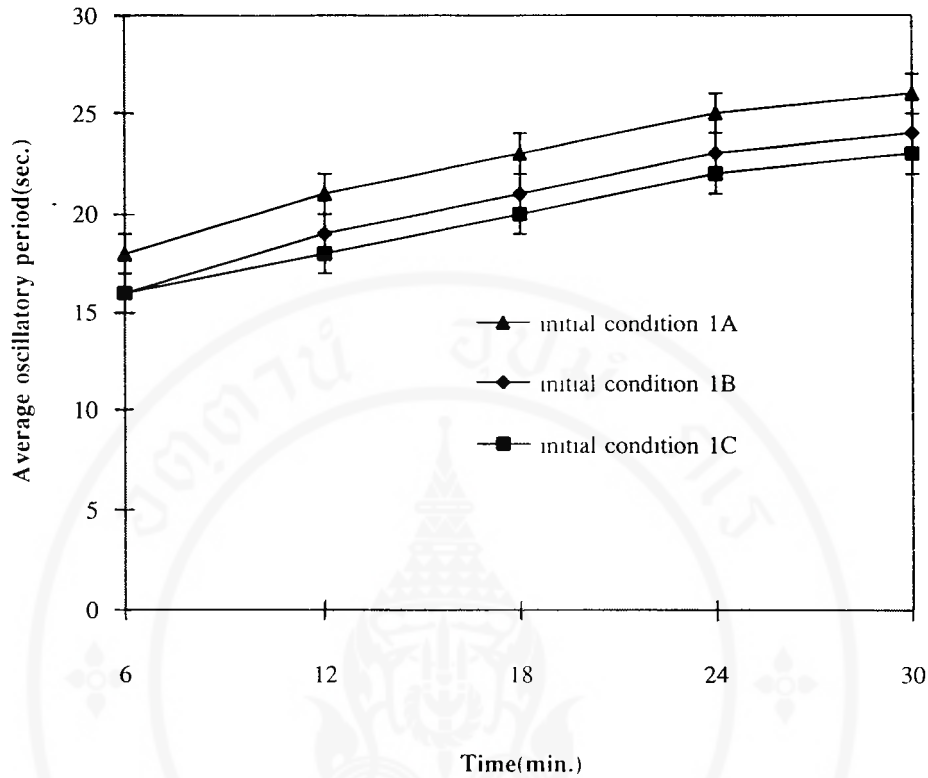

Figure 3.1.4 Graphs of plotting average oscillatory periods of the large amplitude simple oscillations with time from the data in Table 3.1.3 for initial condition 1A, 1B and 1C

3.2 Simple oscillations of bromide and platinum electrode potentials

The potentiometric traces with time of bromide and cerium ions for the initial conditions 1A, 1B and 1C when the sulfuric acid concentration was reduced from 1.00M to 0.500M (initial condition 2A, 2B and 2C), are shown in Figures 3.2.1-3.2.3.

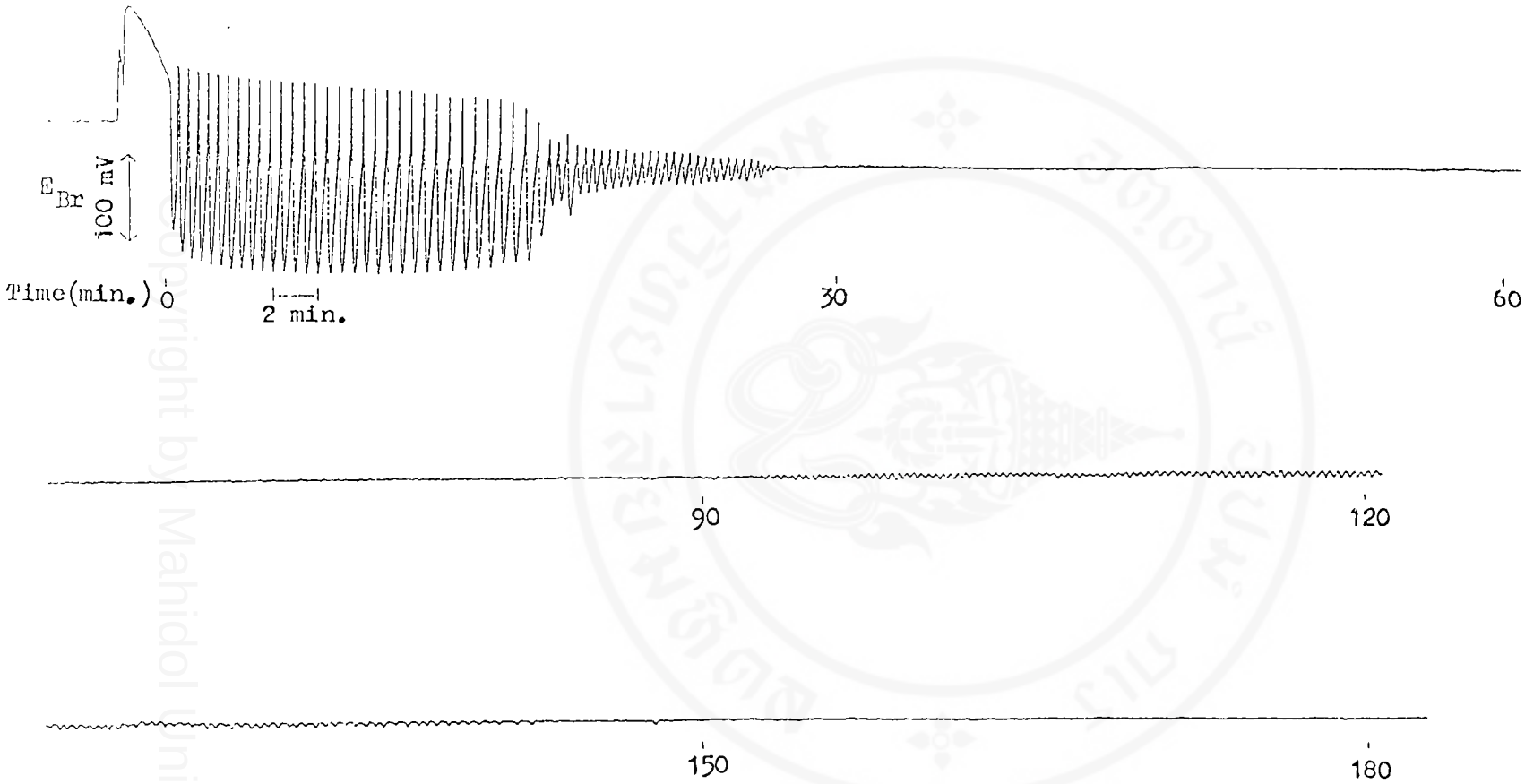

Figure 3.2.1 Potentiometric traces of bromide and cerium ions with respect to time for initial condition 2A

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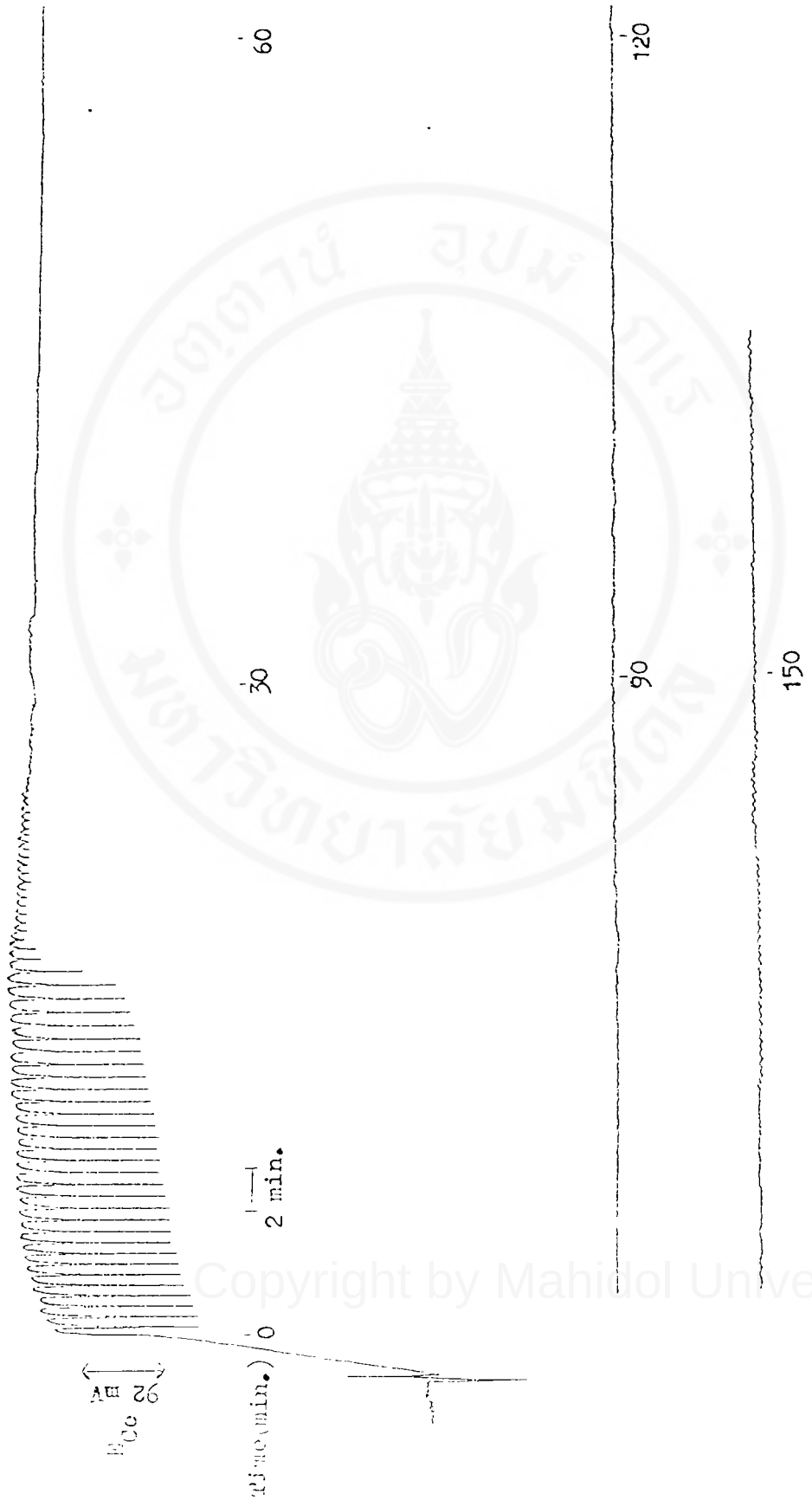

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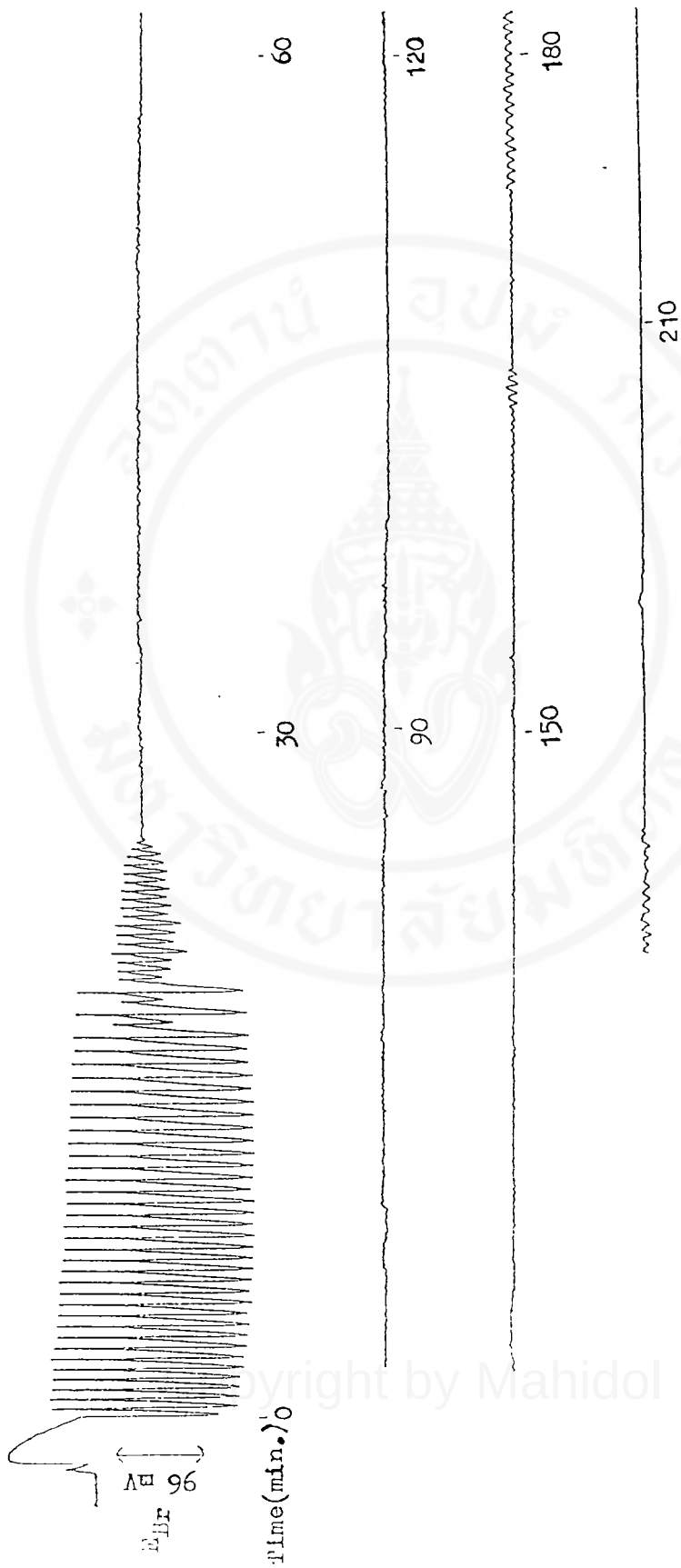

Figure 3.2.2 Potentiometric traces of bromide and cerium ions with respect to time for initial condition 2B

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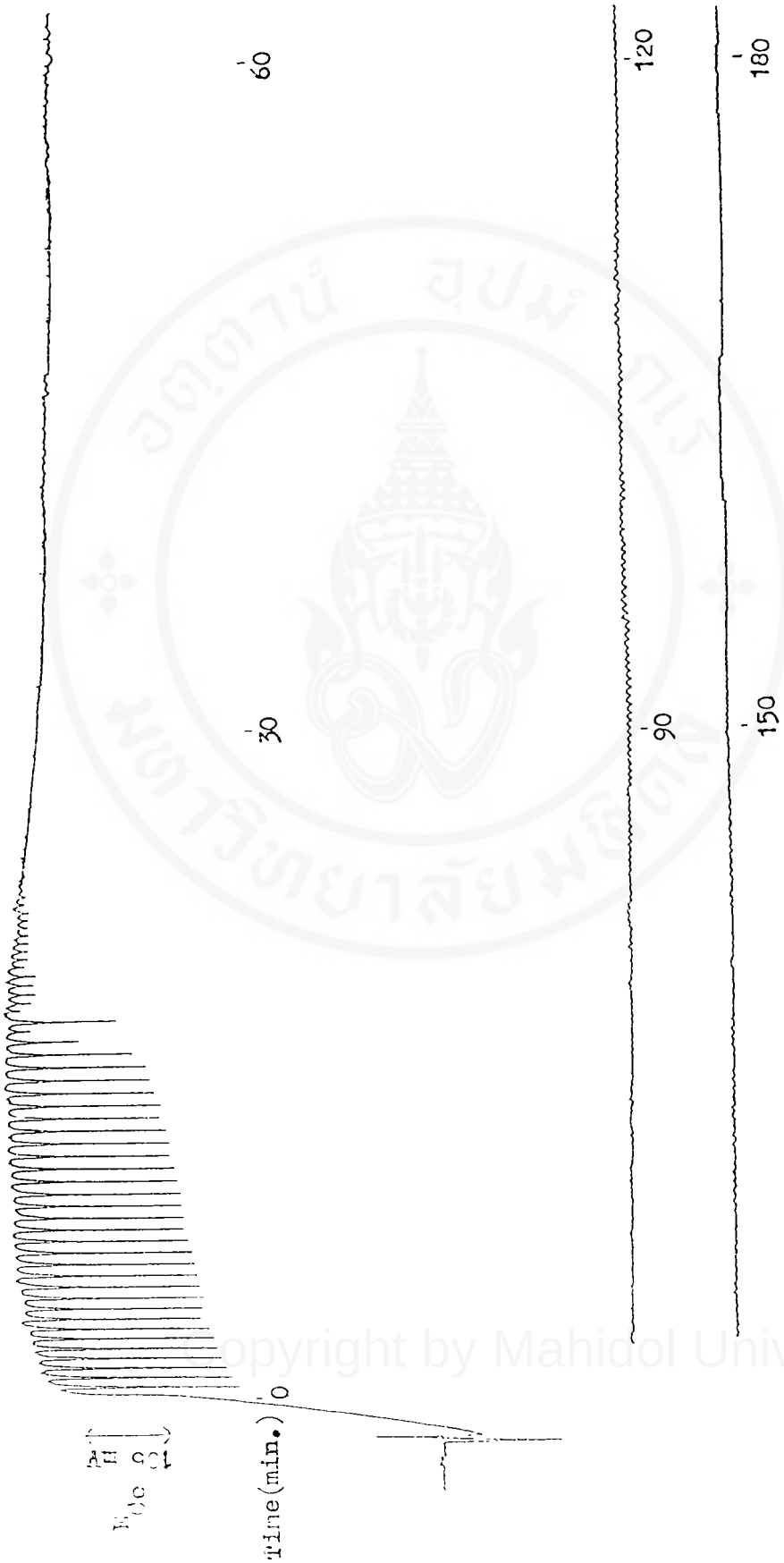

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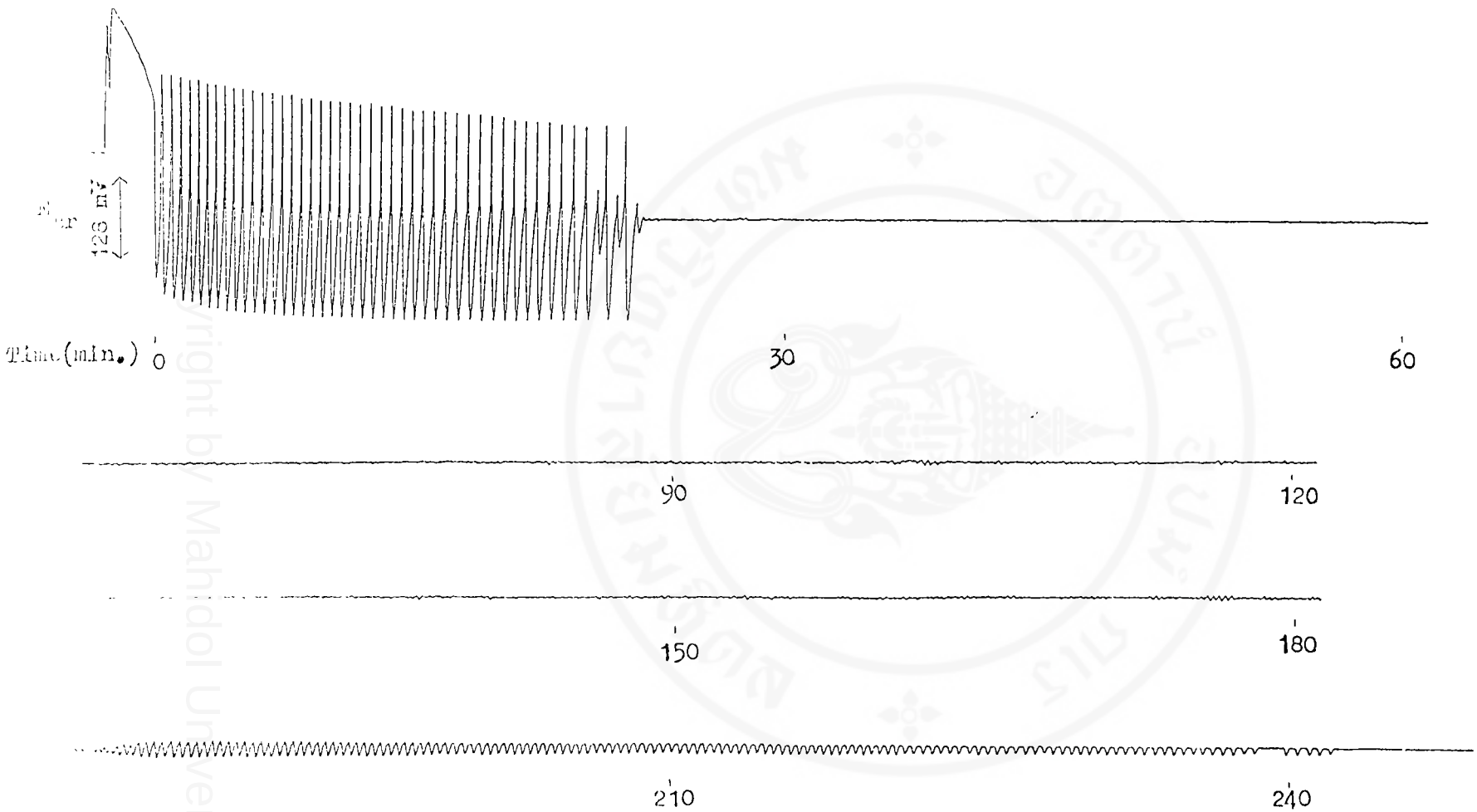

Figure 3.2.3 Potentiometric traces of bromide and cerium ions with respect to time for initial condition 2C

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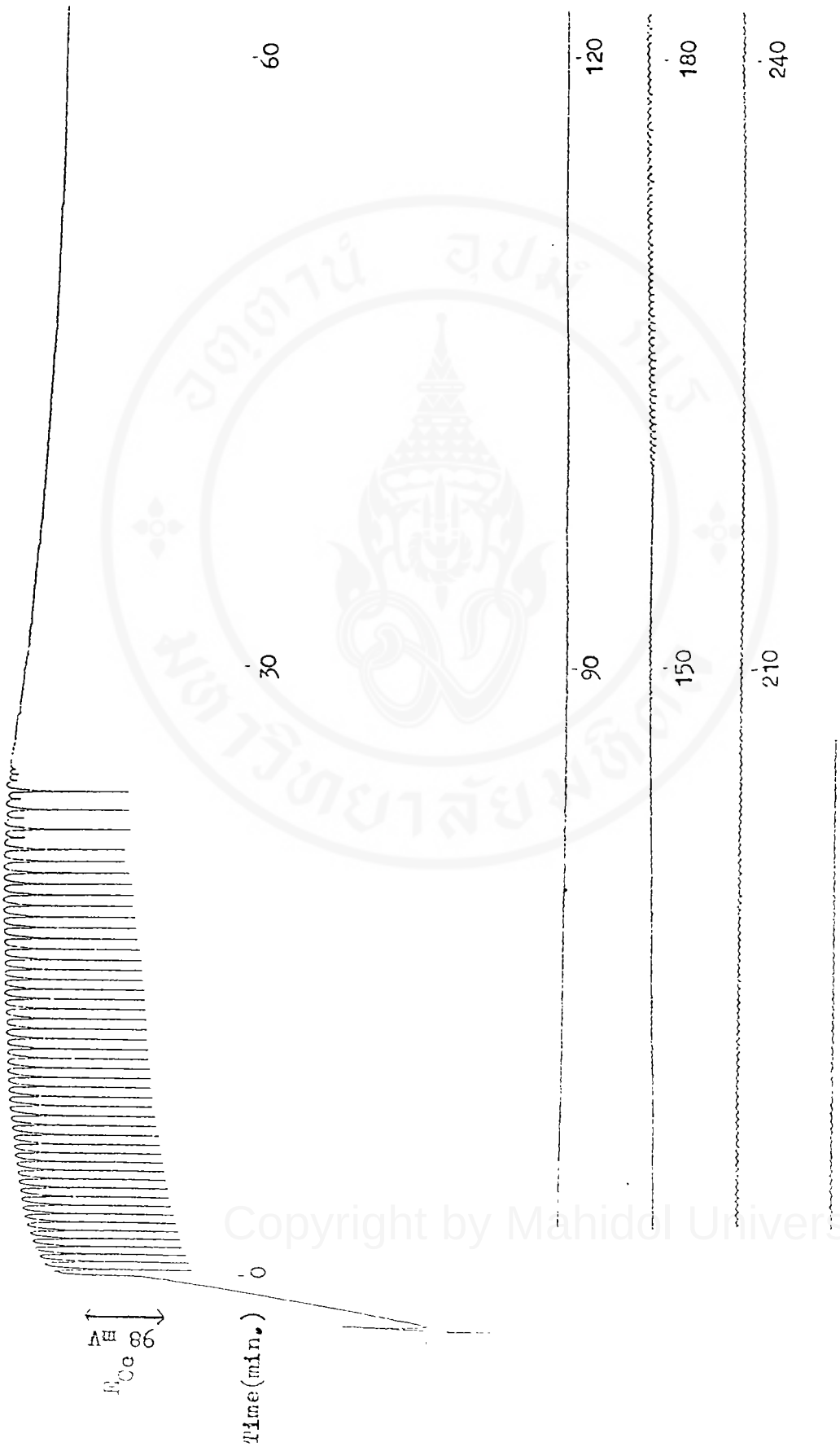

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From Figures 3.2.1-3.2.3, when the sulfuric acid concentration was decreased, the transient complex oscillations were no longer observed. The initial simple oscillations with large amplitude were followed by damped oscillations to give a final colorless solution. Finally, a number of simple oscillations of very small amplitude with increasing period and decreasing amplitude was observed before the final homogeneous steady state.

The cessation of these large amplitude simple oscillations was always abrupt.

For initial condition 2B and 2C, few period-2 oscillations (1-3 cycles) were often seen before the simple oscillations with large amplitude ended.

The average induction period decreased significantly, as given in Table 3.2.1.

Initial condition	$[H_2SO_4]$ (M)	$[KBrO_3]$ (M)	Average induction period (sec.)
2A	0.500	0.093	114 ± 9
2B	0.500	0.105	117 ± 4
2C	0.500	0.118	123 ± 7

Table3.2.1 Average induction periods for initial condition 2A,2B and 2C

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The change in the periods and amplitudes with time for the initial simple oscillations are given in Table 3.2.2 and Table 3.2.3. It can be seen that the period gradually increased and the amplitude slowly decreased with time.

Initial condition	Average oscillatory period (± 1 sec.)					
	2min.	4min.	6min.	8min.	10min.	12min.
2A	27	28	30	31	32	34
2B	24	26	28	29	30	31
2C	23	24	25	26	28	29

Table 3.2.2 Average oscillatory periods of large amplitude simple oscillations in the time interval (0-12minutes) as measured every 2 minutes for initial condition 2A, 2B and 2C

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Time (min.)	Average amplitude E_{Br} / E_{Ce} (mV)		
	2A	2B	2C
2	77±12/79±7	88±18/87±9	90±19/91±7
4	77±12/78±7	88±17/86±10	89±17/90±7
6	76±11/76±7	88±16/86±9	89±17/89±6
8	76±10/74±7	87±15/83±9	88±16/86±7
10	74±10/72±7	86±15/82±9	87±16/84±6
12	72±10/69±8	86±14/81±9	86±15/81±9

Table 3.2.3 Average amplitudes of large amplitude simple oscillations in the time interval(0-12minutes) as measured every 2 minutes for initial condition 2A, 2B and 2C

The data in Table 3.2.2 also showed that the oscillatory periods decreased with increasing bromate concentration as was observed for initial condition 1A, 1B and 1C.

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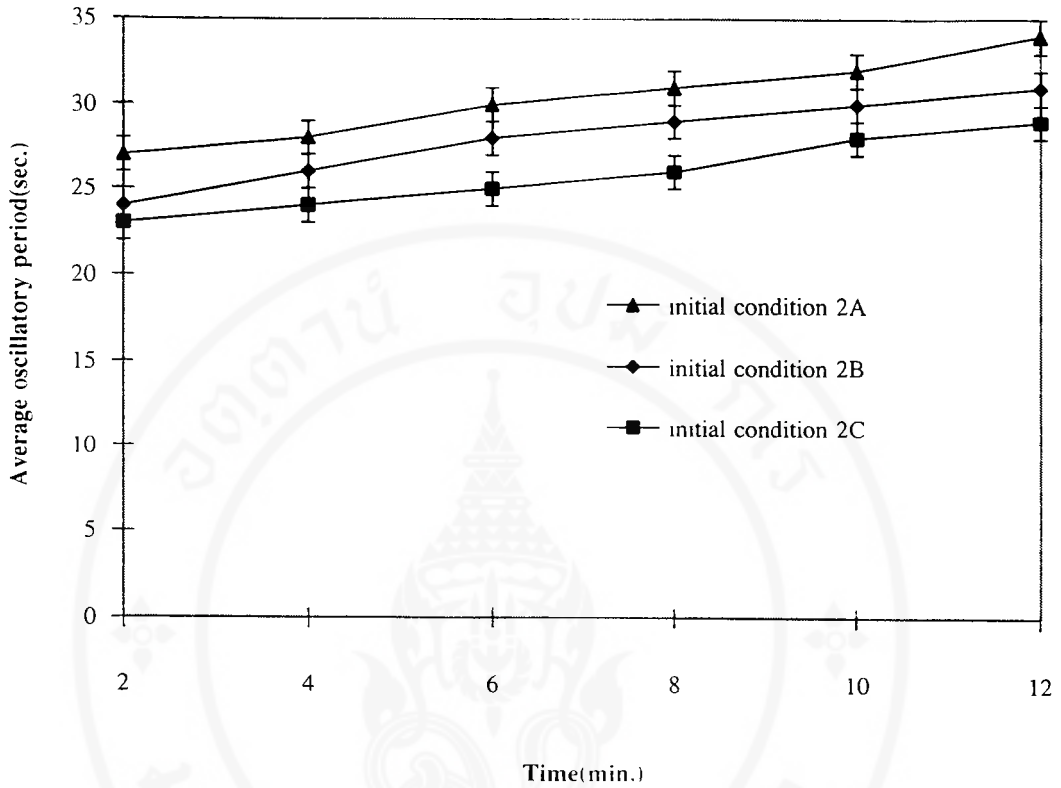

Figure 3.2.4 Graphs of plotting average oscillatory periods of the large amplitude simple oscillations with time from the data in Table 3.2.2 for initial condition 2A, 2B and 2C

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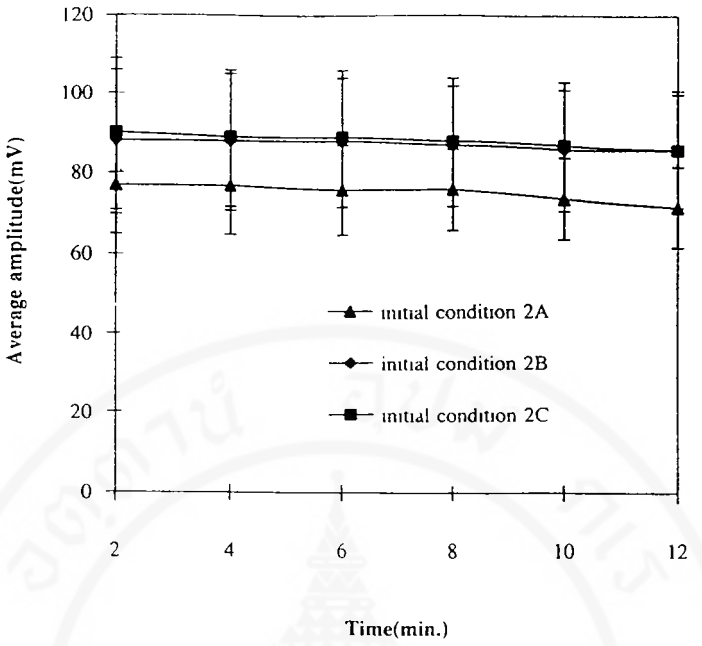

Figure 3.2.5 Graphs of plotting average amplitudes (E_{Br}) of the large amplitude simple oscillations with time from the data in Table 3.2.3 for initial condition 2A, 2B and 2C

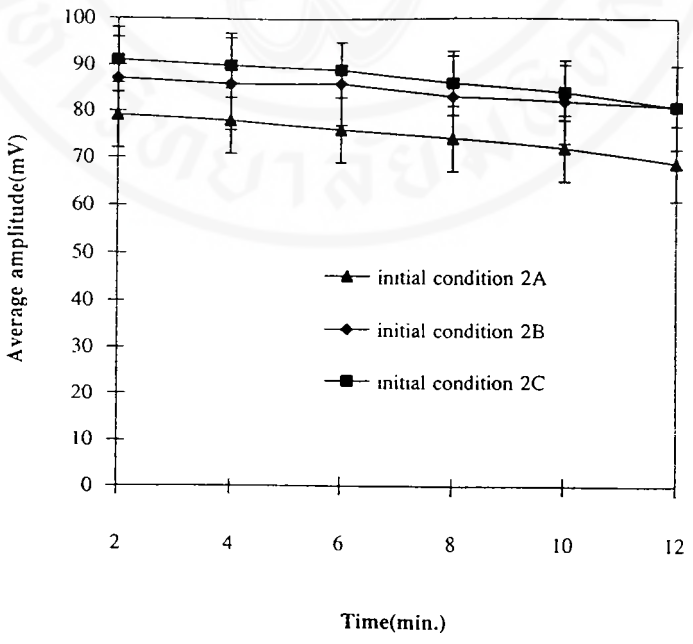

Figure 3.2.6 Graphs of plotting average amplitudes (E_{Ce}) of the large amplitude simple oscillations with time from the data in Table 3.2.3 for initial condition 2A, 2B and 2C

3.3 Relation between sulfuric acid and bromate concentrations and induction period

The graph showing the relation between the induction period and the sulfuric acid and bromate concentrations is shown in Figure 3.3.1.

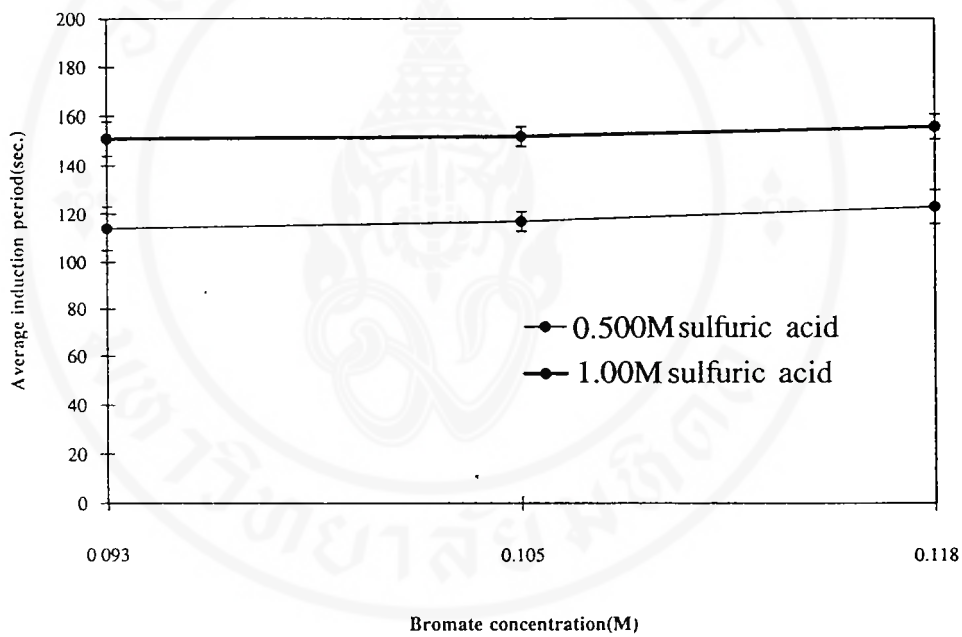

Figure 3.3.1 Graphs showing the change of average induction period with the concentration of sulfuric acid and bromate

The graph shows that the average induction period before commencement of the oscillations was independent of the concentration of bromate ion but there was significant decrease when the concentration of sulfuric acid was reduced from 1.00M to 0.500M.

CHAPTER IV

DISCUSSION AND CONCLUSION

4.1 The effect of bromate and sulfuric acid on the induction period and large amplitude simple oscillations

During the course of the reaction at all initial conditions, for the large amplitude simple oscillations, the oscillatory periods increased and the amplitude decreased with time (Figure 3.1.4, 3.2.4, 3.2.5, 3.2.6). These are the results of the slow continuous consumption of reactants from their initial concentrations which corresponds to the computational and experimental results of limit cycle behavior reported by Field and Noyes [10,11]. However, the amplitude of large amplitude simple oscillations for initial condition 1A, 1B and 1C was constant with time (Table 3.1.3) in agreement with the results reported by Wang et al.[38].

During the time of each oscillation, small but nonzero amounts of the reactants are consumed, so providing the overall driving force for the reaction. Eventually, the reactant consumption will become sufficiently great so as to take the solution out of the composition range in which simple oscillations occur, and the system may settle to different regimes of complex oscillations (Figure 3.1.1-3.1.3) or to the unstable steady state (Figure 3.2.1-3.2.3) as described later, depending on the initial conditions,

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before its final approach to the stable steady state (or the homogeneous steady state).

From the experiments, increasing the initial bromate and sulfuric acid concentrations increases the induction period, as seen in Figure 3.3.1. This result agree with the trend reported by Field, Körös and Noyes[9].

In the case of large amplitude simple oscillations, oscillatory period becomes increasing longer when bromate concentration gradually decreased and also when sulfuric acid concentration was reduced from 1.00M to 0.500M, as shown in Table 3.1.3, 3.2.2. These results agree with the trends reported in references [6] and [9]. For the amplitude, it was found to decrease as bromate concentration was reduced, as shown in Table 3.1.3, 3.2.3.

4.2 The effect of bromate and sulfuric acid on the complexity of the system

The existence of complex transient oscillations in pseudo-closed system for initial condition 1A, 1B and 1C (Figure 3.1.1-3.1.3) was found to be dependent on the initial concentration of bromate and the complexity of the patterns increases with increasing concentration of bromate. This result agrees with the trend reported in references [38] and [39], as seen from major types (Table 3.1.1) and the duration time of the complex transient oscillations (Table 3.1.2). There is a reason to believe that this result may be associated with increasing BrMA in process C. Wang et al.

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[39] carried out experiments with various added initial concentrations of BrMA. They found that the reference experiment ([MA] = 0.44M, $[BrO_3^-]$ = 0.0622M, $[Ce^{3+}]$ = 0.00133M, $[H_2SO_4]$ = 1.0M and $[BrMA]_{added}$ = 0) showed only simple oscillations, and the complexity and duration of the intervening complex oscillations increased with increasing of the initial concentration of BrMA (0.03M, 0.072M and 0.11M).

The complex oscillation disappeared when the concentration of sulfuric acid was reduced from 1.00M to 0.500M, as seen in initial condition 2A, 2B and 2C (Figure 3.2.1-3.2.3). The remained oscillation is damped simple oscillations with 1-3 cycles of period-doubled oscillations. The observed abrupt disappearance of these oscillations to the unstable steady state followed by very small amplitude simple oscillations was also observed in the work of Strizhak and Menzinger[41] when the malonic acid concentration was reduced from 0.44M to 0.3M. Thus, the hydrogen ion concentration is an important parameter in the production of the complex behavior, corresponding to the result reported in reference [39].

It may be concluded that the initial concentrations of bromate and sulfuric acid are critical in giving rise to the complexity of the oscillations [38,39].

4.3 Reproducibility of the complex oscillation

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All of the complex oscillations observed in the experiments including mixed-mode (MM) and intermittency (I) oscillations are genuine

results of the chemical dynamics because they exist as transient phenomena[38-41]. The complex oscillations appearing in the central period of the reaction are always preceded and followed with regular simple oscillations. This general feature corresponds to the simulation of complex oscillations in closed system[39,40]. Further, they may be the possible precursors of transient chaos[38,39,41].

The degree of quantitative reproducibility for the complex transient oscillations decreases from initial condition 1A to 1C because of the increase in complexity of the pattern[38,39], however, the qualitative picture is preserved[41]. There are reasons to believe that the more complex patterns (1^s, s>2 and I), are more susceptible to external perturbations[39,41], for example, in the present aerobic experiment, from the exchange of reactive gases O_2, Br_2 between the solution surface and the atmosphere[41], and the effect of atmospheric oxygen[41] on scavenging of radicals that are found in the course of the oxidative degradation of BrMA in process C. The aperiodic behaviors, are reproduced only qualitatively because of this sensitivity to the initial condition[28,40,41]. The more simpler complex patterns, especially the period-doubled oscillations, are reproducible in main qualitative features [38,39,41].

It should be noted that the total temporal oscillatory patterns observed by bromide and cerium ions traces are not exactly the same for identical initial conditions. This may be because the platinum electrode measures a mixed potential affected by concentrations of bromate as well as of Ce(IV) [9].

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APPENDIX

Temporal patterns observed in other experiments for initial condition 1A, 1B and 1C are shown in Figure A1, A2 and A3, respectively.

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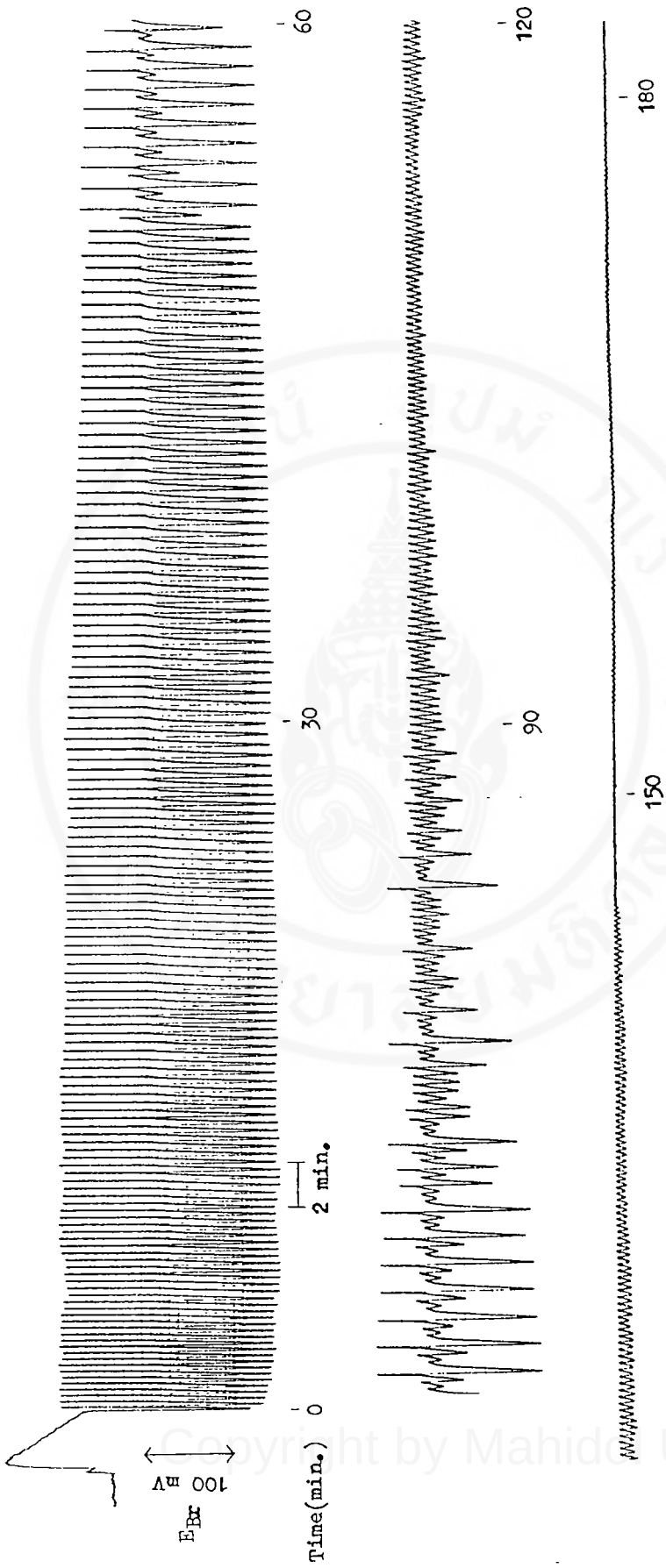

FIGURE A1

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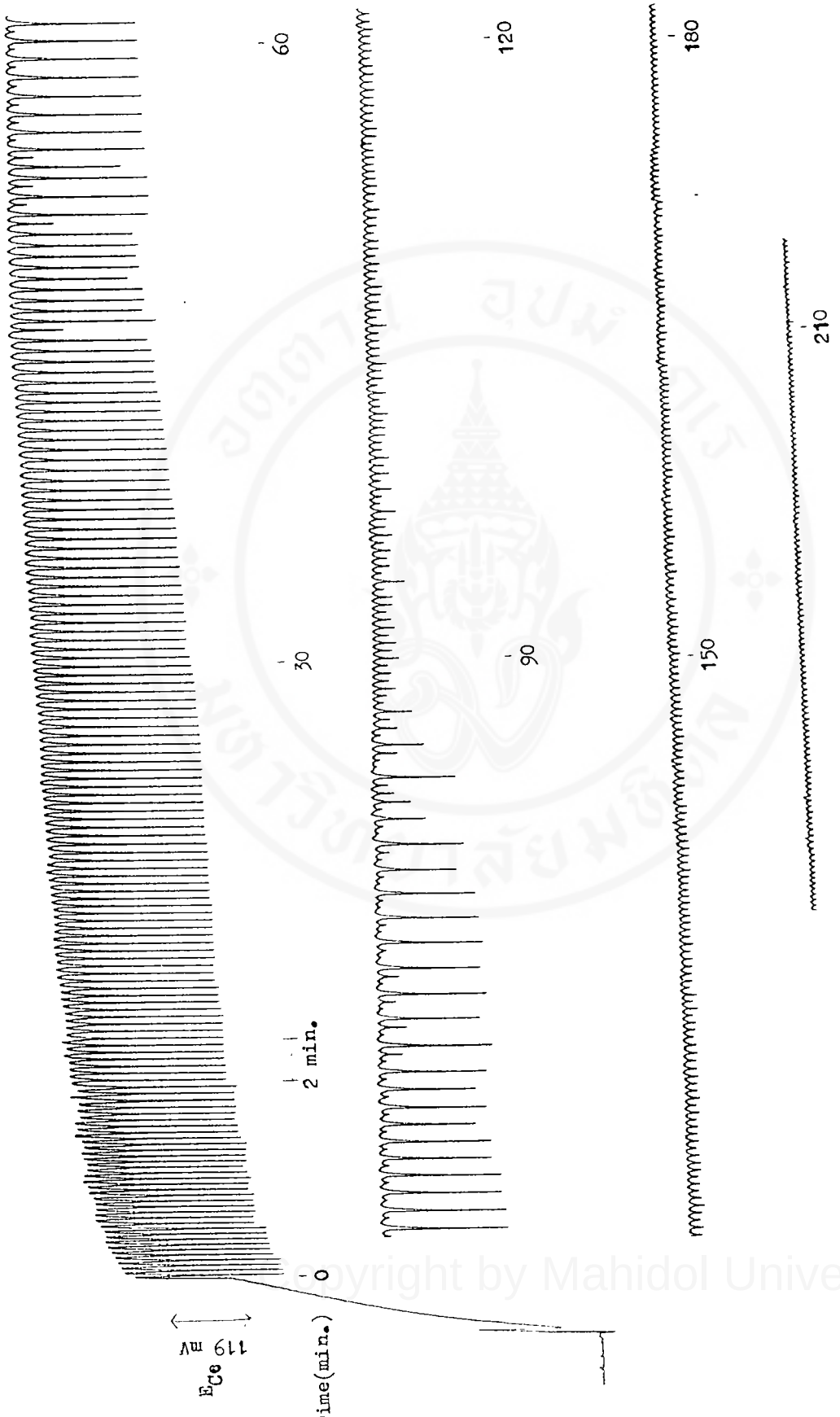

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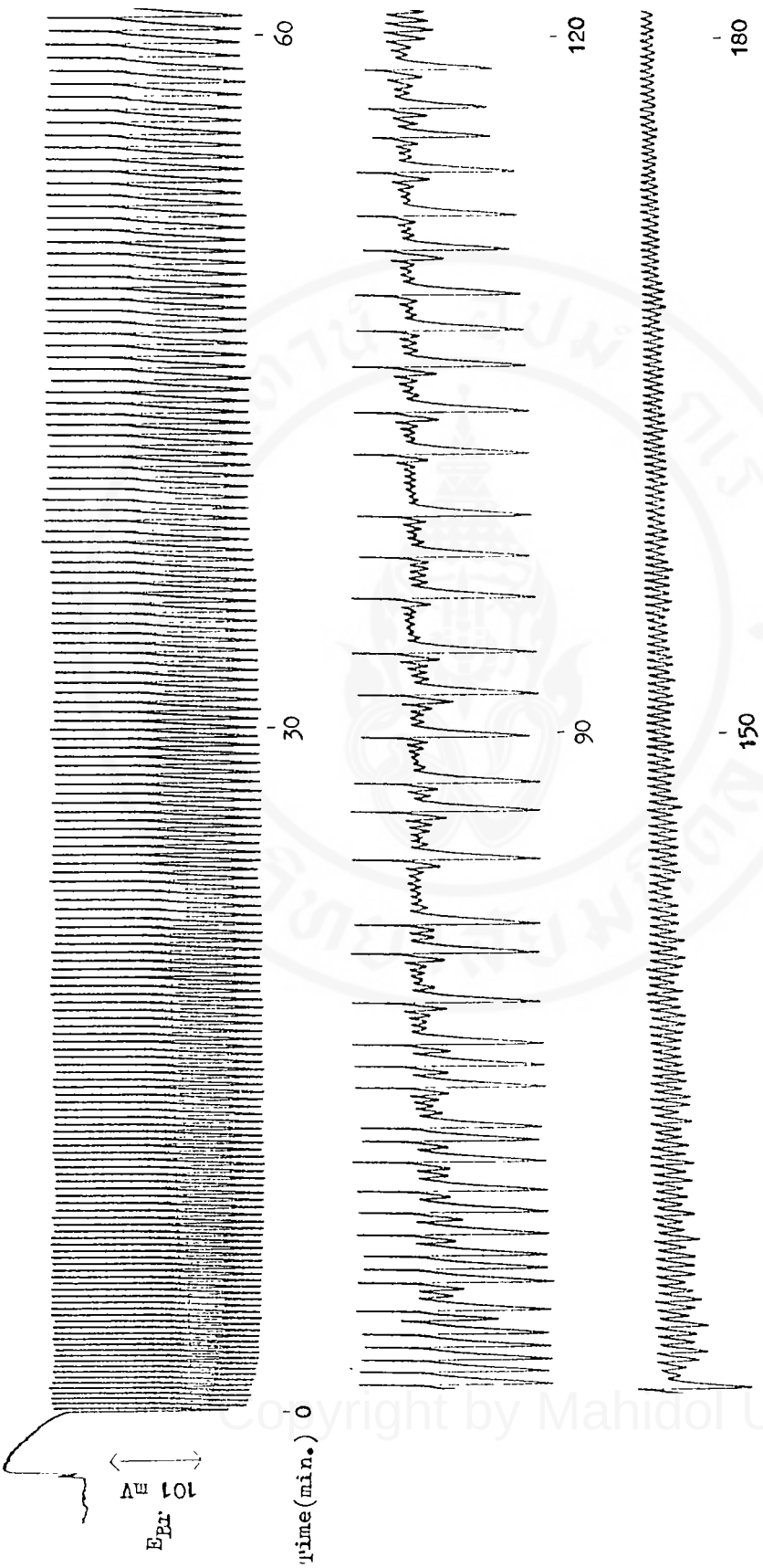

FIGURE A2

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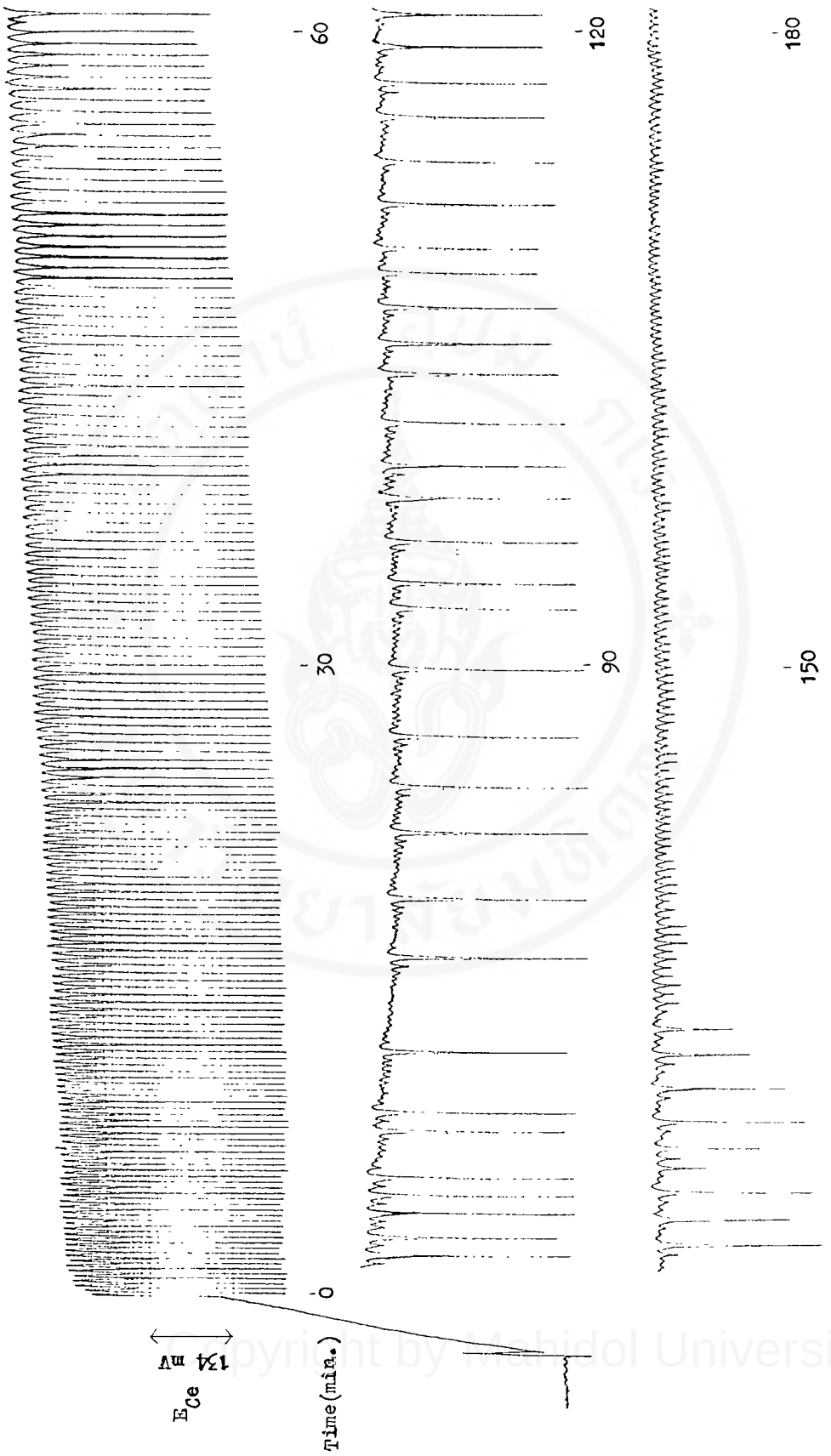

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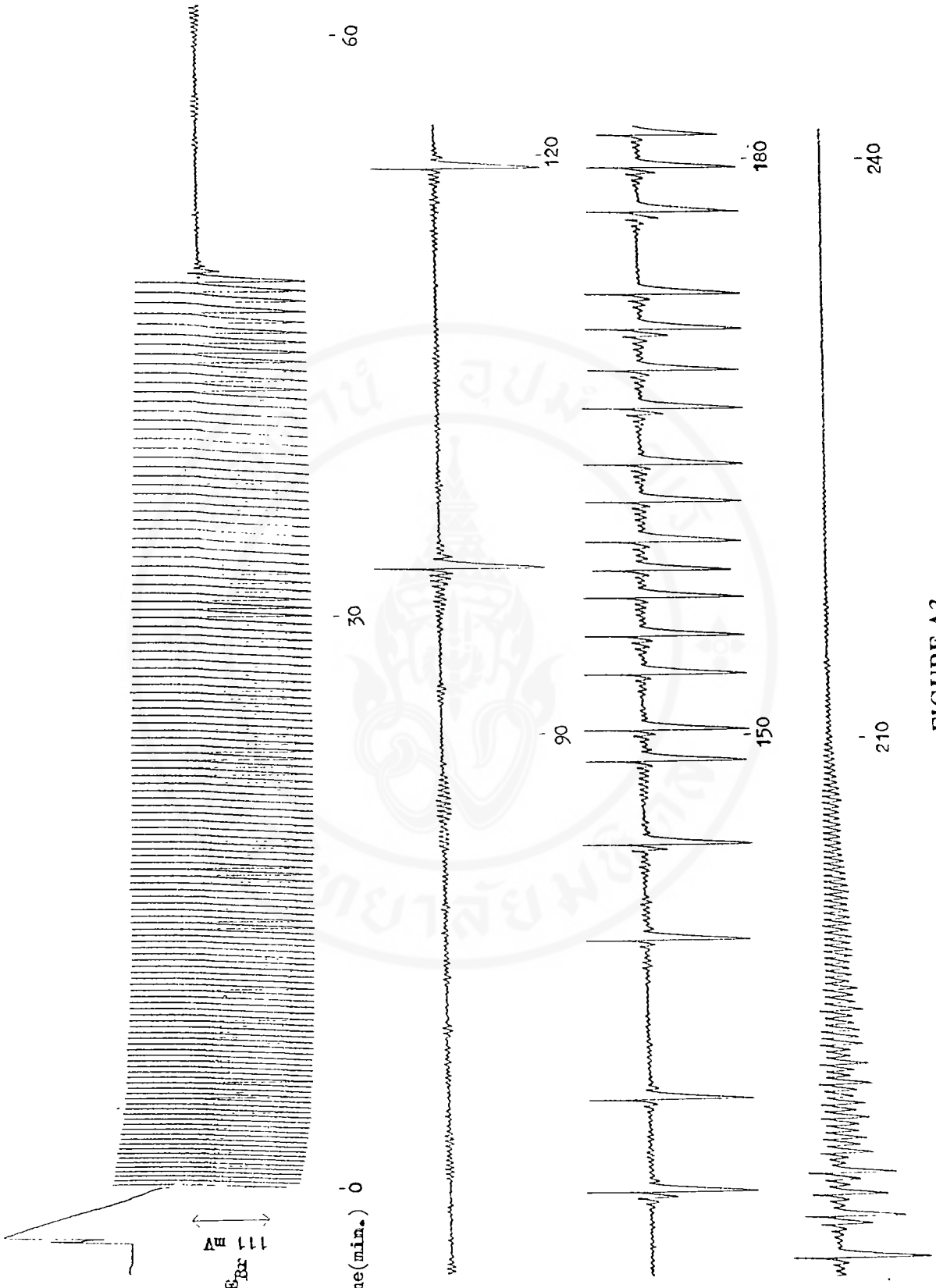

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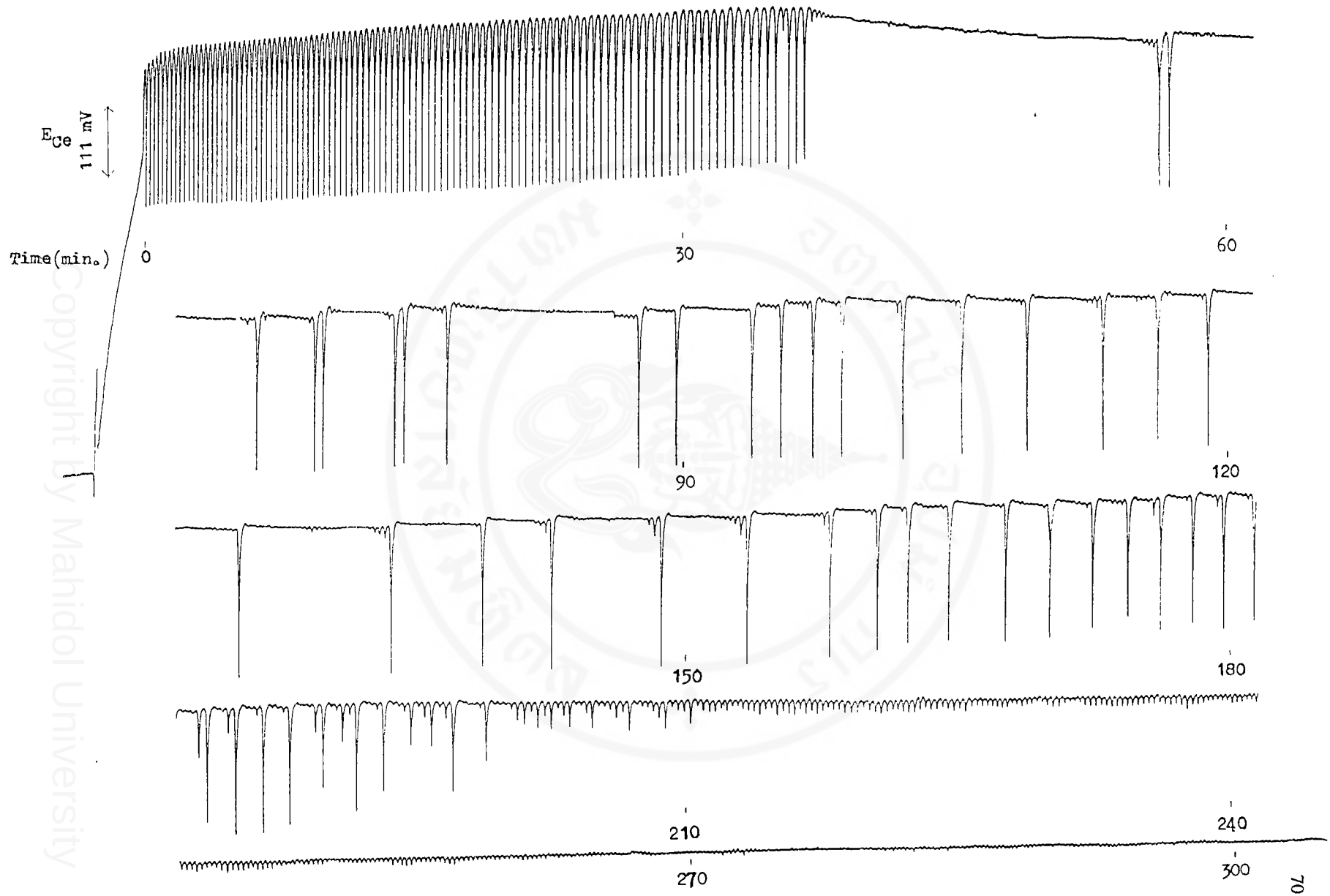

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