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FRANK J. SEILER RESEARCH LABORATORY

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CHEMICAL GENERATION OF $O_2(^1\Delta_G)$ II.

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Production of singlet delta oxygen has been measured with electron spin resonance spectroscopy. A chemical reaction between chlorine and basic hydrogen peroxide was used to produce the excited oxygen. Several chemical and physical parameter variations were studied and analyzed on the basis of the fraction of singlet delta oxygen in the total oxygen product gas.

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CHEMICAL GENERATION OF $O_2(^1\Delta_g)$ II.

By

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AUGUST 1980

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PREFACE

This interim report documents work done under Work Unit 2303-F4-01, Chemiluminescent Gas Phase Reactions, between 18 December 1978 and 30 March 1979. Work is continuing and will be documented in future interim reports and/or a final report as events warrant. The authors wish to thank B. J. Darcy for typing the manuscript and F. C. Kibler, Jr. for his assistance and skill in preparing and maintaining the glass generator vessel.

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I. INTRODUCTION

Since the initial illustration of the feasibility of an $O_2(^1\Delta_g)/I$ lasing system[1], the efficient production of gaseous $O_2(^1\Delta_g)$ has become a topic of considerable interest. The major role of $O_2(^1\Delta_g)$ in this lasing system is that of an energy pump for atomic iodine. As higher concentrations of $O_2(^1\Delta_g)$ imply a greater pumping capacity, optimization of $O_2(^1\Delta_g)$ production is crucial to overall laser efficiency.

The most frequently used scheme for producing $O_2(^1\Delta_g)$ is the reaction between $Cl_2(g)$ and a basic hydrogen peroxide solution. This reaction yields high concentrations of $O_2(^1\Delta_g)$ in the gaseous phase, which can then be used in a lasing device. Results from reactors based upon this chemical reaction have been previously discussed in the literature[2,3,4].

The effects of chemical and physical parameters are important to $O_2(^1\Delta_g)$ yield optimization. General results for several parameters have been previously reported by this group[5]. The present paper presents results from two qualitative screening-type studies and two detailed quantitative studies. The qualitative investigations involved the use of $ClF(g)$ instead of $Cl_2(g)$ as a reactant and the addition of surfactants to the liquid reagents. The specific parameters varied for the quantitative studies were the reactant volume and concentration. Quantities routinely monitored during the reaction include pressure, flow rate, temperature (5), pH, and chloride ion concentration, $[Cl^-]$, in the liquid reagents.

II. EXPERIMENTAL

A. Qualitative Screening

A simplified small volume test reactor, Fig. 1, was used to qualitatively test the use of surfactants and $ClF(g)$. This configuration proved to be very useful for consecutive short runs. As both experiments could potentially destroy the reaction vessel, this system was also time and cost effective. Production of $O_2(^1\Delta_g)$ was monitored on the basis of visible dimol emission for operating pressures of several torr.

1. Surfactants

The two surfactants tested were DuPont "Zonyl" FSP and FSB fluorosurfactants. The isopropanol solvent was evaporated and the condensed surfactants were tested for safety with concentrated H_2O_2 before use in a reactor vessel. "Zonyl" FSP is a stable, anionic, low-foaming fluorosurfactant whereas "Zonyl" FSB is amphoteric and high-foaming. Prior to the addition of surfactant, the reactor was run to observe the dimol emission. Once the dimol emission was well established, several drops of surfactant were added and the effects upon the reaction system and dimol emission were observed.

2. ClF

ICN Pharmaceuticals' ClF was bubbled through the reaction mixture in lieu of Cl_2. A small amount of "Zonyl" FSB surfactant was also tested for this reaction system.

B. Quantitative

1. General Description

A schematic diagram of the overall experimental apparatus is given in Fig. 2 and a more detailed illustration of the chemical generator is given in Fig. 3. The general experimental set-up, apparatus, and run procedure have been previously discussed in detail[5].

A Matheson mass flowmeter and mass flow controller was utilized to gauge and monitor the $Cl_2(g)$ flow into the reactor for the concentration studies. The same apparatus was used to control the O_2 flow through the reactor system for ESR calibration.

The reaction mixture pH was monitored by an Orion 91-25 combination pH electrode. Free chloride ion concentration was followed by an Orion 94-17A chloride Selectrode. Both electrodes used the same reference electrode and results were displayed on Orion Digital Ionalyzer/501s.

Five temperatures were continuously monitored on a 5-channel Doric Trendicator 412A. These included 1) the reaction vessel ice bath temperature, 2) post trap gas temperature, 3) Cl_2 nozzle temperature, 4) dry ice and ethanol trap temperature, and 5) the reaction solution temperature.

2. Chloride Ion Analysis

Chloride ion concentrations in the reaction mixture were continuously monitored by an Orion 94-17A Chloride Selectrode. Calibration of the probe was done using solutions similar to the actual reaction mixture. In addtion, the final reaction mixture was analyzed for free chloride ion and the presence of chloride ion in any precipitate which was formed. This chloride ion analysis was done by gravimetric analysis after acidification of the reactants. Results indicate that the chloride ion probe gives reliable results for free chloride ion in the reactant fluid under the conditions present during reactor operation.

III. RESULTS

A. Qualitative Screening

1. Surfactants

a. "Zonyl" FSB. Reactor pressures greater than 2 torr were necessary for the observance of dimol emission prior to surfactant addition. At these pressures a distinct red glow appeared at the Cl_2 nozzle and persisted for several centimeters downstream from the fluid surface. After the addition of surfactant, higher system pressures (~6 torr) were required to produce comparable dimol intensities to the pre-surfactant system. The emission was considerably more diffuse due to extensive foaming above the reactant solution. The surfactant appeared to be stable in the reaction mixture and the actual effect upon the level of dimol emission after surfactant addition was ambiguous.

b. "Zonyl" FSP. The results for this surfactant were similar to those for "Zonyl" FSB. One exception was the appearance of two distinct bright zones of dimol emission, one at the gas nozzle and the other at the top of the foam column.

2. ClF. Dimol emission was visible for reactor pressures of approximately 5 torr when ClF was used in lieu of Cl_2. The emission appeared to be slightly weaker than for comparable Cl_2 tests. The addition of "Zonyl" FSB surfactant had no significant effect upon the reactant system.

B. Quantitative Studies

1. Volume Variations

The volume of reactants for the four conditions used in this study are tabulated in Table 1. The Cl_2 flow-rate was maintained between 30 and 32 STDCC/min. of Cl_2. The reactor temperature showed a slow increase over the reaction, from an initial value of ~-6.°C to a final temperature of ~3.°C. Figs. 4a, b, and c compare some of the results from these experiments.

Figure 4a illustrates the pH of the reactants as a function of time. Each run has an initial pH of approximately 8.5 (uncorrected)[6] which slowly decreases to a sudden drop. The production of $O_2(^1\Delta_g)$ ceases soon after this pH endpoint, as can be seen in Figs. 4b and c. It is noteworthy that the conclusions of Hurst, et. al.[7], suggests a cessation of $O_2(^1\Delta_g)$ production in dilute H_2O_2 solutions at an uncorrected pH[6] of approximately 3. This value is in good agreement with the results shown in Fig. 4a.

This suggests that the reaction mechanism in concentrated H_2O_2 could be the same as the alkaline mechanism supported by Hurst, et.al., in dilute H_2O_2.

Increased reactant volume produces extended reaction times as shown clearly in Figs. 4b and c. It is interesting to note the slight increase in % $O_2(^1\Delta_g)$ just before reaction completion. We believe that this reproducible but transient increase in % $O_2(^1\Delta_g)$ is due to a decrease in gas phase $O_2(^1\Delta_g)$ deactivation as the overall gas pressure begins to decrease. A possible cause is a decrease in % $O_2(^1\Delta_g)$ deactivation due to changes in deactivating gas species concentrations, e.g., H_2O, or $O_2(^1\Delta_g)$.

2. Concentration Variations

The results of the concentration variation will be given in three sections. First, the results for a run made with a "standard" set of concentrations. These conditions were chosen for experimental convenience and economy. The second and third studies will be for lower and higher NaOH concentrations than the standard run. A tabulation of the concentrations used for this study is given in Table 2.

a. Standard Conditions.

The standard run concentrations are tabulated in Table 2. The chlorine flow-rate for the reported run was approximately 30. STDCC/min. and showed a slow decrease over the run time. Percent O_2 total and $O_2(^1\Delta_g)$ are given in Fig. 5a as a function of time. There is a characteristic increase in % $O_2(^1\Delta_g)$ just prior to reaction completion due to the total pressure decrease at the end of the run.

The reaction solution pH and chloride ion concentration are given in Fig. 5b. There is a continuous, slow increase in chloride ion concentration up to the reaction completion at which point a sizeable concentration increase occurs. This final increase is not always present for the standard conditions. The theoretical final chloride ion concentration, assuming all Cl_2 is converted to free chloride ion, is approximately 3.6$\underline{M}$ Cl^-, whereas the probe indicates a free chloride ion concentration of 1$\underline{M}$. This discrepancy between the theoretical maximum and the probe recorded free chloride ion concentration is possibly due to the formation of chlorine-containing precipitates.

b. Low NaOH to H_2O_2 Concentrations Compared to the Standard Run.

Concentrations for the low NaOH relative concentration run are given in Table 2 and results for the run at these concentrations are presented in Figs. 6a and b. Figure 6a shows the pH and chloride ion concentration as a function of time, which is very similar to the standard run results. The percent O_2 total and $O_2(^1\Delta_g)$ are given in Fig. 6b and also resemble closely the standard run results.

c. High NaOH to H_2O_2 Concentrations Compared to the Standard Run.

Concentrations for two high NaOH relative concentration runs are given in Table 2 and results for the second of these starting concentrations are presented in Figs. 7a and b. Figure 7a presents the pH and chloride ion concentrations as a function of time and Fig. 7b gives the percent O_2 total in the product gas and the percent of $O_2(^1\Delta_g)$ in the oxygen product. For higher NaOH concentrations than that illustrated, solidification of reactants occurs, which results in a very inefficient reaction in terms of the percent of Cl_2 which reacts. Fig. 7b shows a very low total O_2 product percentage for the first half of the reaction. This is due to the thick slurry-like consistency of the reactants at this concentration. During the same period the percent $O_2(^1\Delta_g)$ is high due to the overall decrease in gas pressure which results in decreased $O_2(^1\Delta_g)$ deactivation. At slightly less than 60 minutes the consistency of the reactants became more liquid and a sizeable increase in total O_2 percentage occurs. Simultaneously, the percent $O_2(^1\Delta_g)$ drops slightly. At approximately 90 minutes a sharp temporary decrease occurs in the percent total O_2. This drop is reproducible and occurs at a characteristic time after the chloride ion bump which will be discussed below. The cause of this effect is unknown at present.

Fig. 7a shows the pH and chloride ion concentrations as functions of time. Although the decrease in pH is not as sharp as in the standard run it still resembles earlier results qualitatively. This is not true of the chloride ion concentration which develops a "bump" during the middle of the reaction. This bump is reproducible and gravimetric analysis of reaction mixtures indicate it is not probe-related. It is probably a result of the complex competing processes involved in the chemical reaction mixture. Additional work needs to be done to understand this interesting phase of the reaction.

IV. CONCLUSIONS

1. Both surfactants screened were stable in the reaction mixture. It was not clear whether there were significant changes in the $O_2(^1\Delta_g)$ production when the surfactants were added. Although foaming appears to be a potential problem for the standard apparatus, quantitative work should be done on this system.

2. Although the use of ClF in lieu of Cl_2 as the reactant gas appears to give lower $O_2(^1\Delta_g)$ levels, quantitative studies should be carried out.

3. The volume studies showed consistency with pH results reported by Hurst, et.al.[7]. This suggests a similar reaction mechanism to that reported for dilute H_2O_2 systems[7]. Evidence for pressure deactivation of $O_2(^1\Delta_g)$ is observable at the end of the reactions. Increased volume gives longer run times.

4. Very high NaOH concentrations (see Table 2) result in extreme thickening of the liquid reactants and very poor $O_2(^1\Delta_g)$ production efficiency. Additional studies should be performed to understand the chloride ion "bump" which is observed for high NaOH concentrations.

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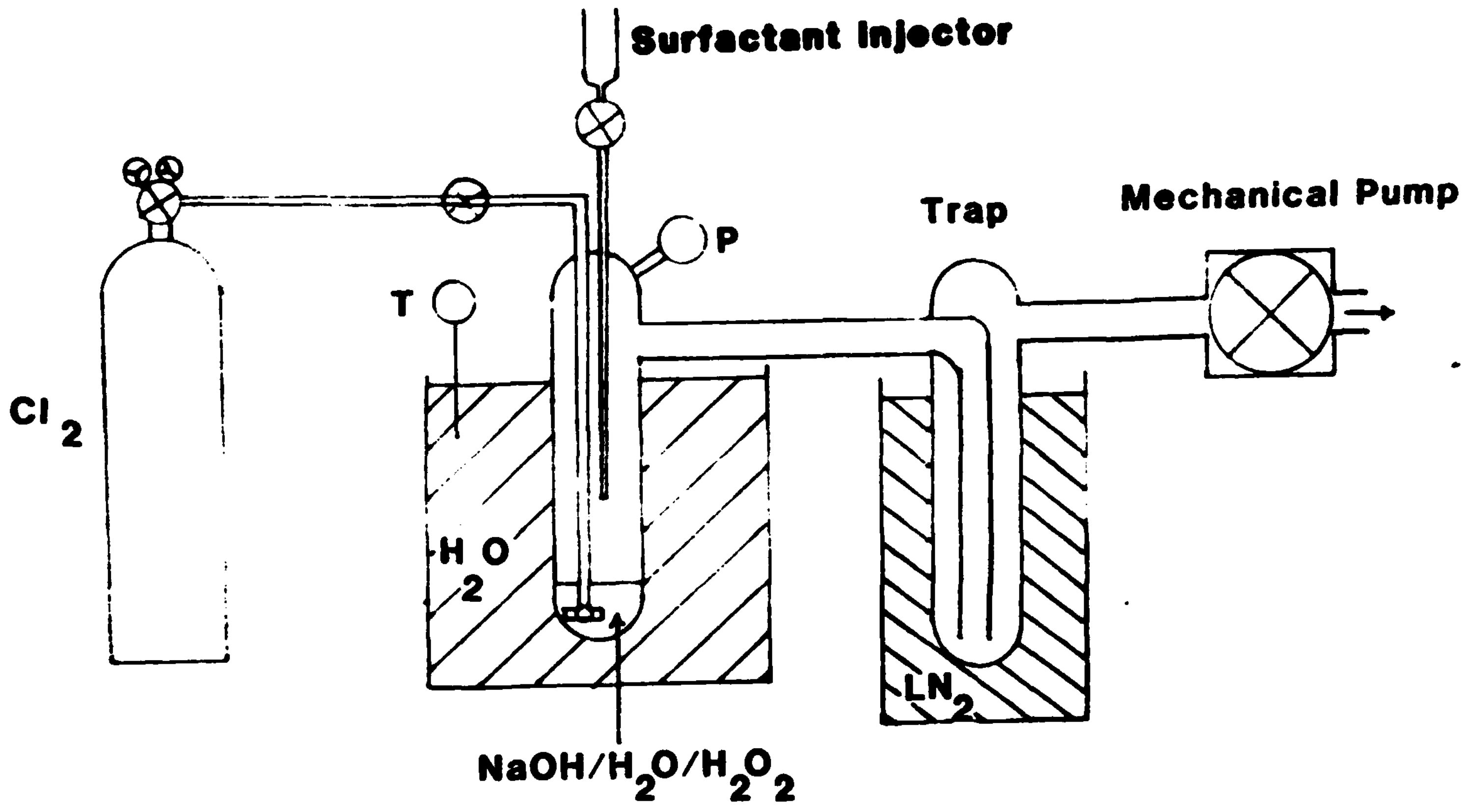
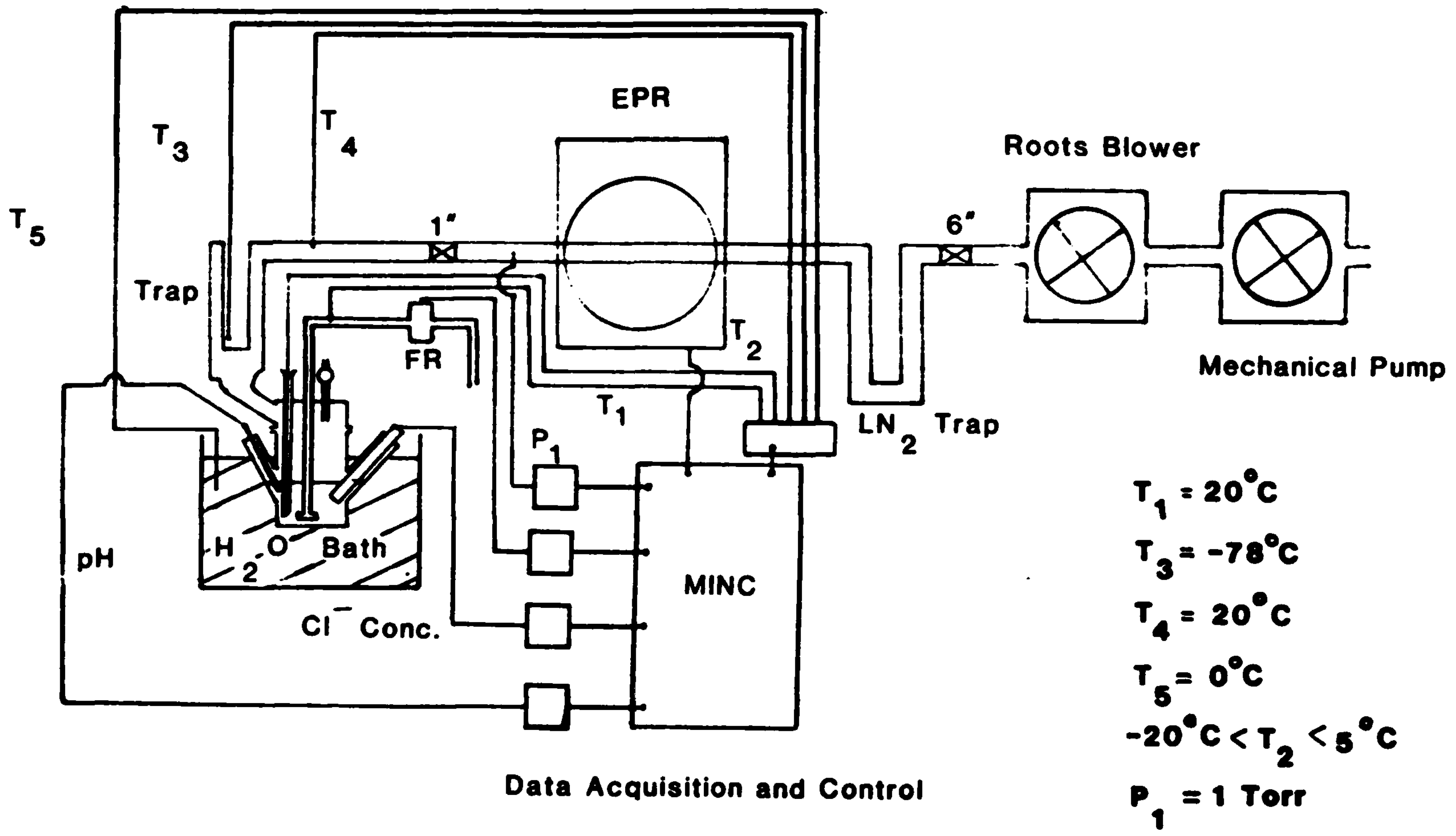
FIGURE 1



QUALITATIVE TEST REACTOR

FIGURE 2

OVERALL EXPERIMENTAL SET-UP



$T_1 = 20^\circ C$

$T_3 = -78^\circ C$

$T_4 = 20^\circ C$

$T_5 = 0^\circ C$

$-20^\circ C < T_2 < 5^\circ C$

$P_1 = 1$ Torr

FIGURE 3

CHEMICAL GENERATOR

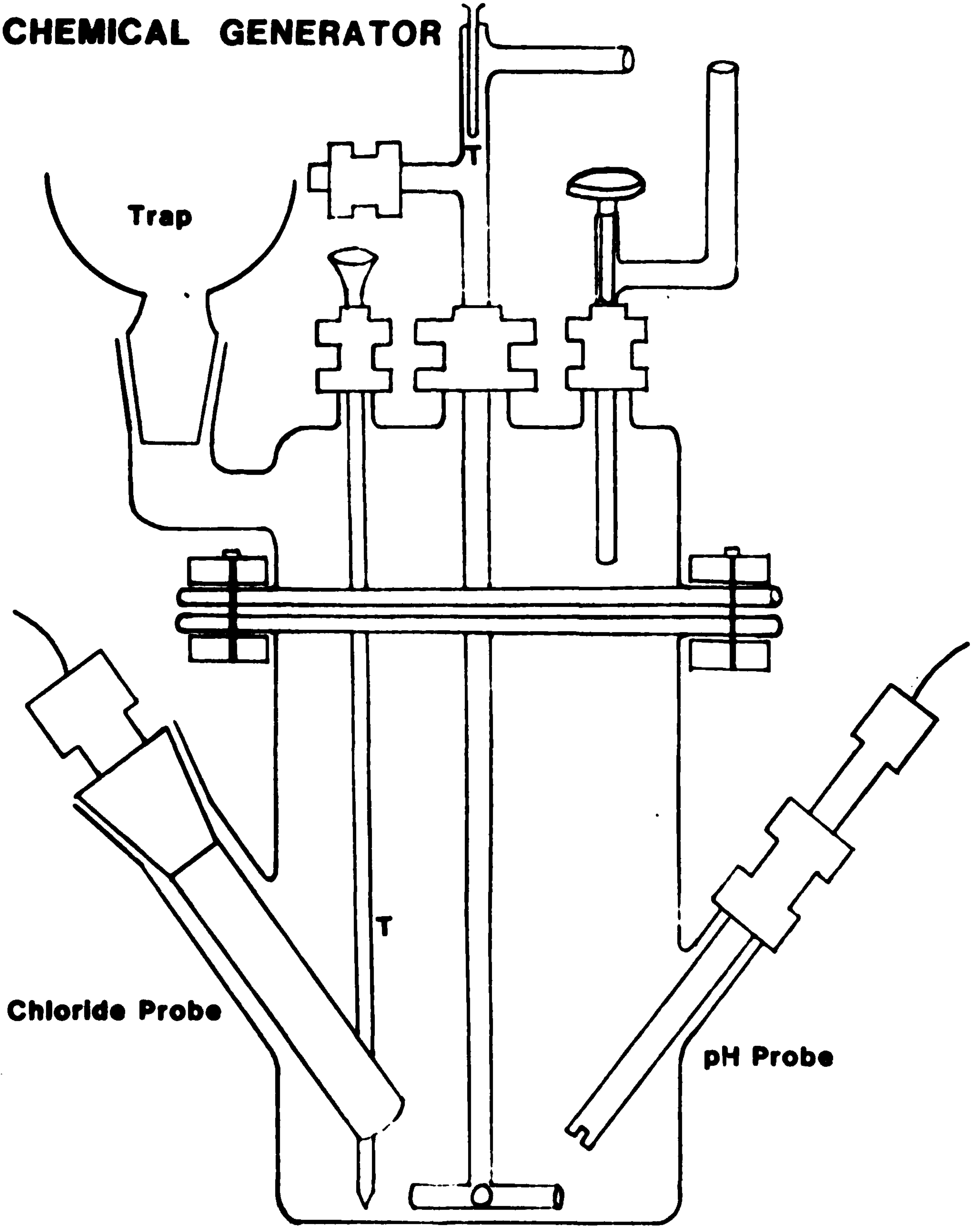


FIGURE 4A

Volume Variations

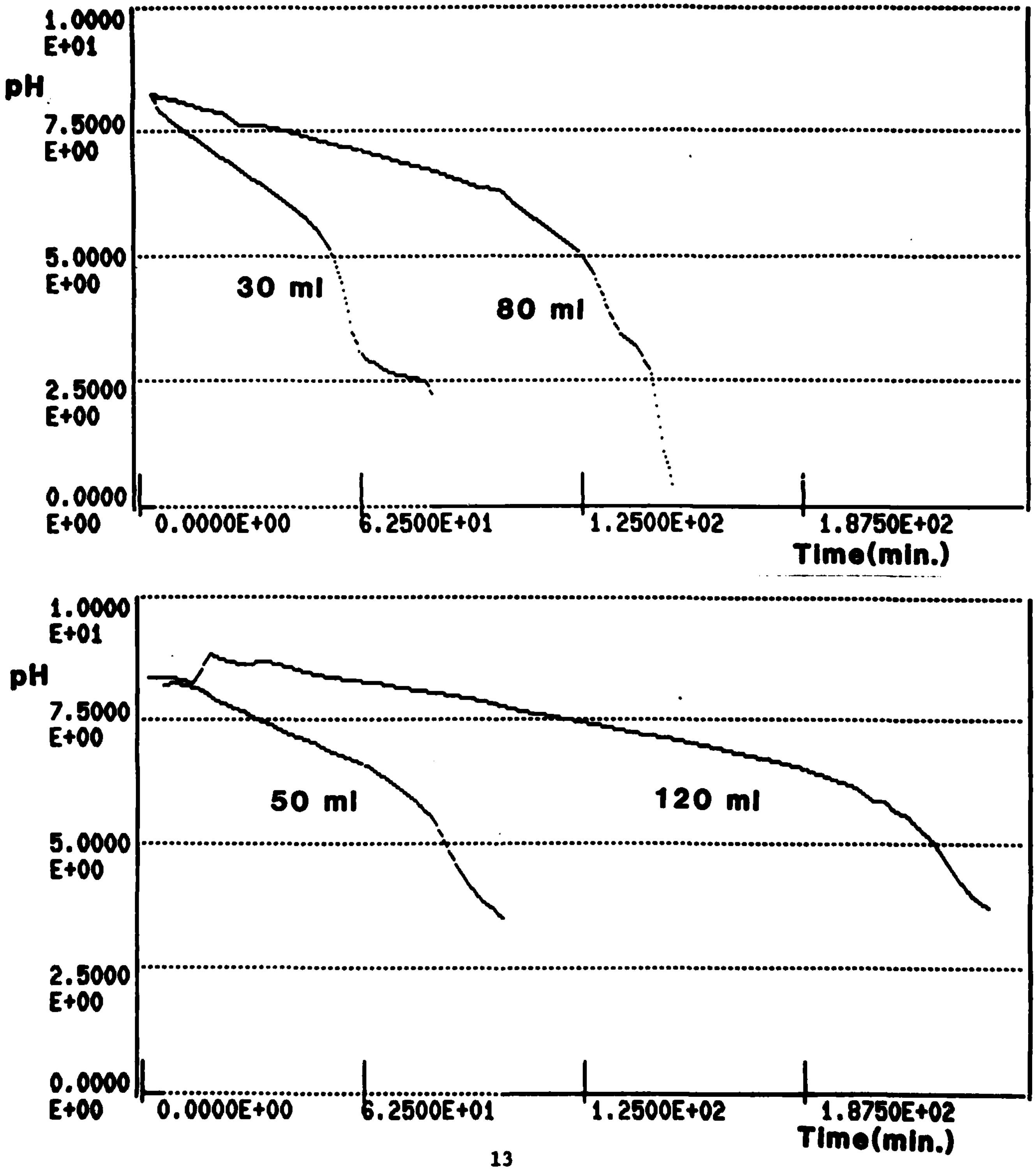


FIGURE 4B

Volume Variations

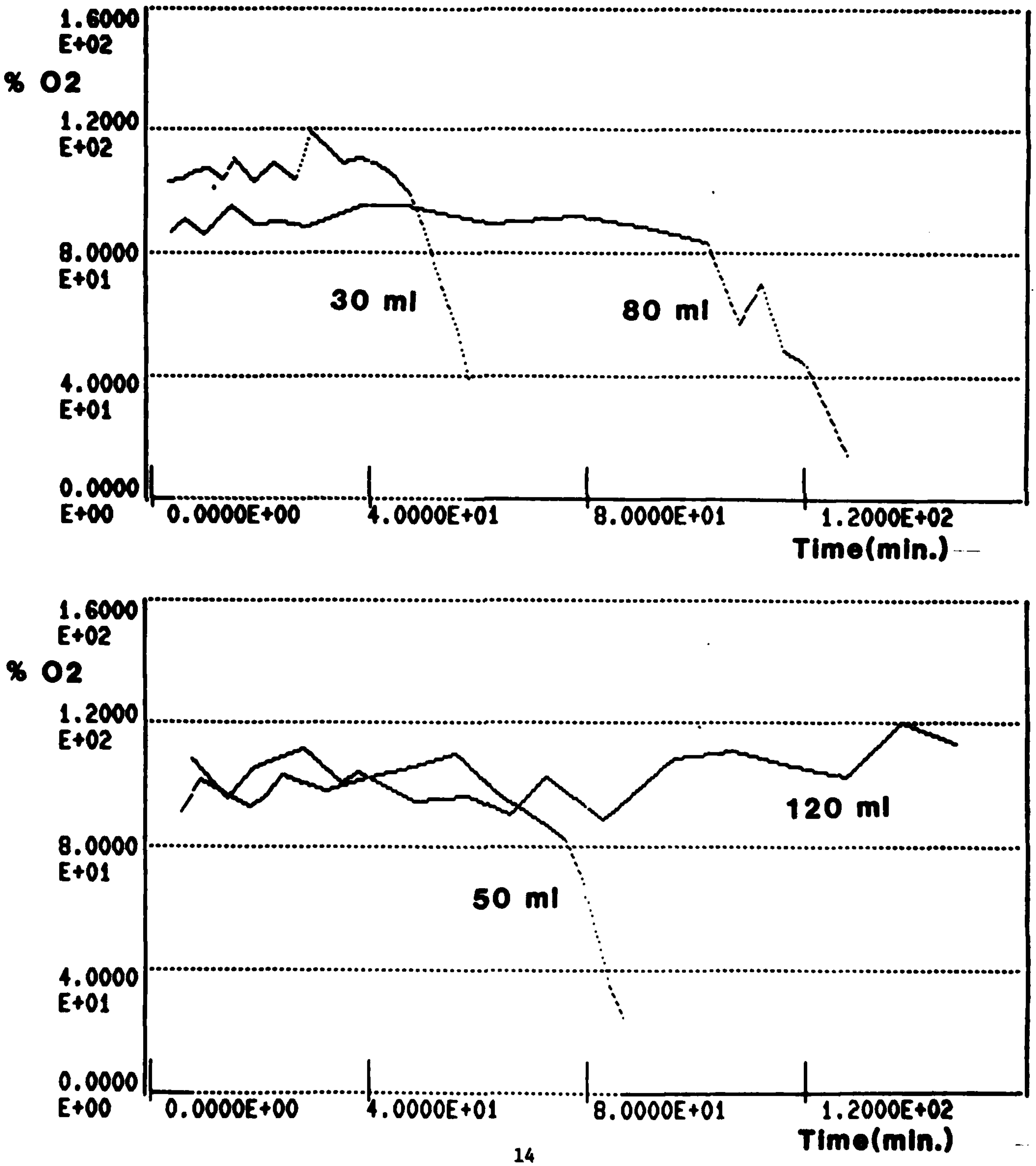
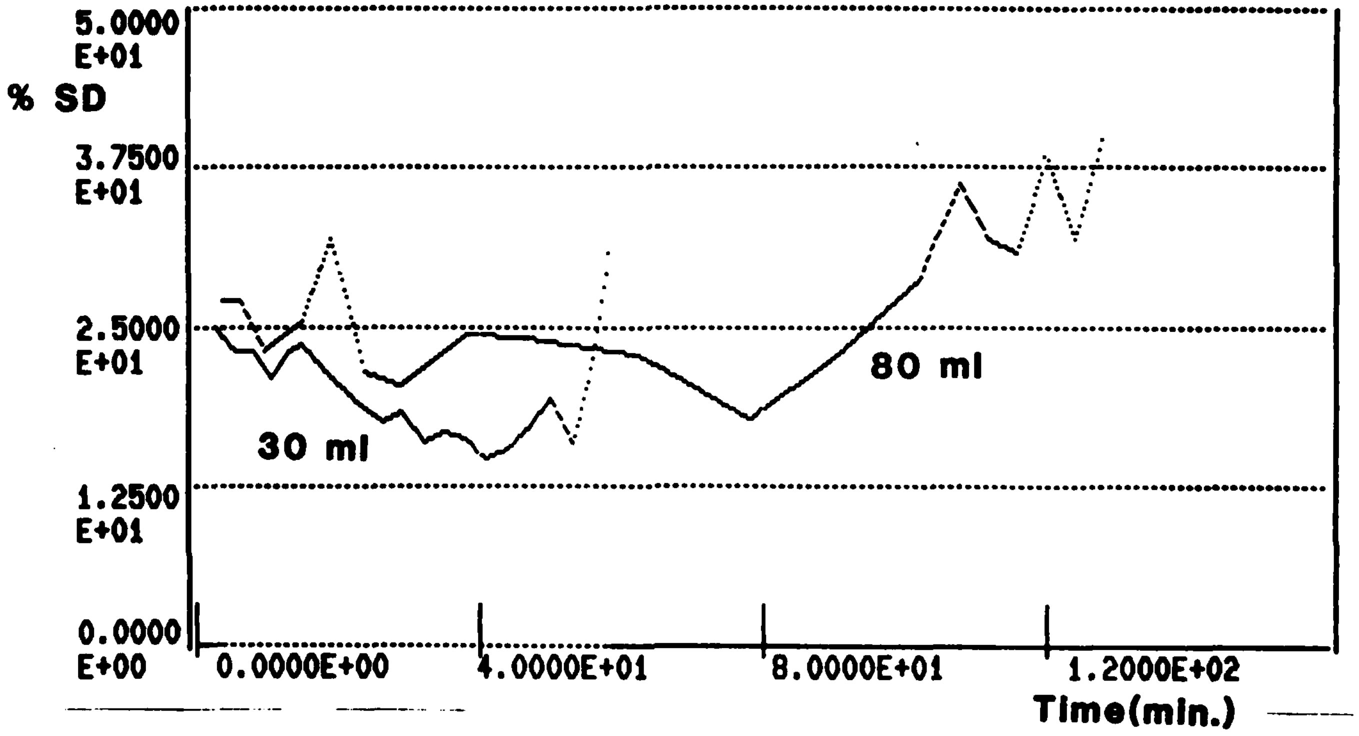


FIGURE 4C

Volume Variations



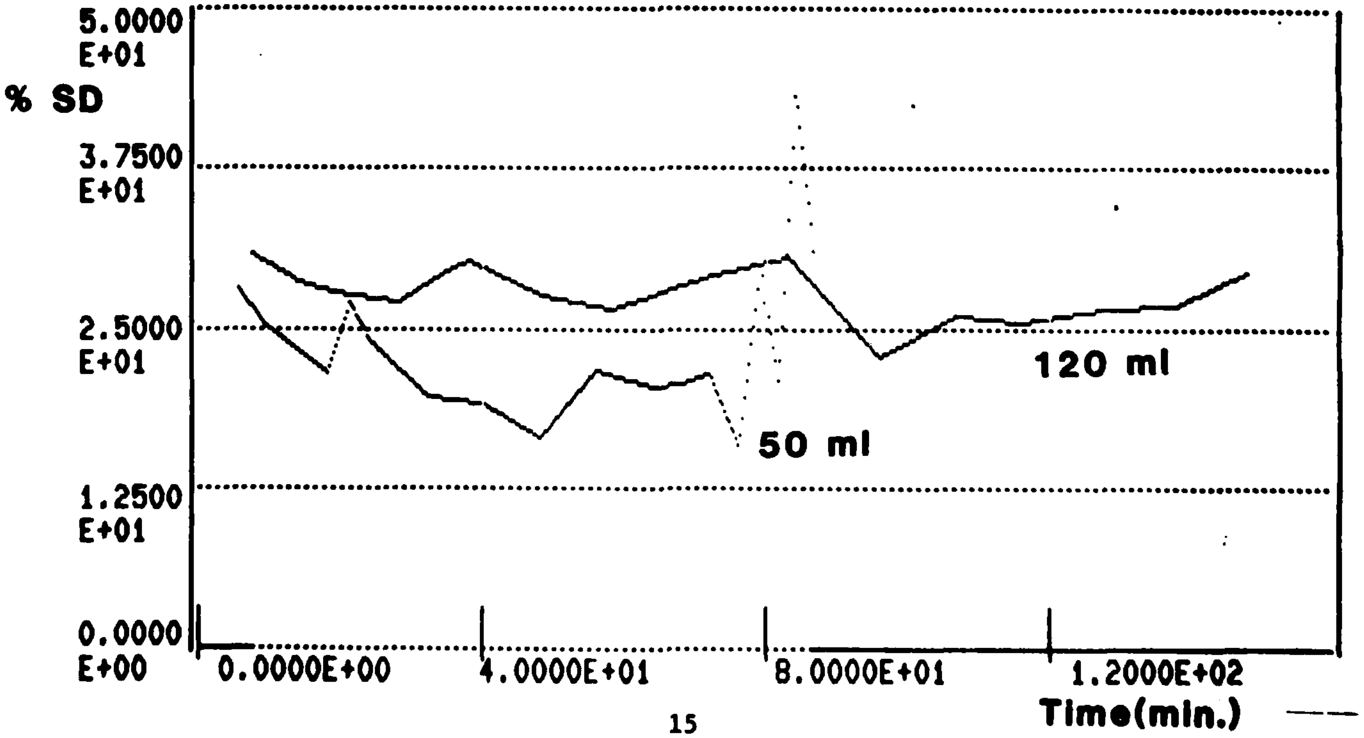


FIGURE 5

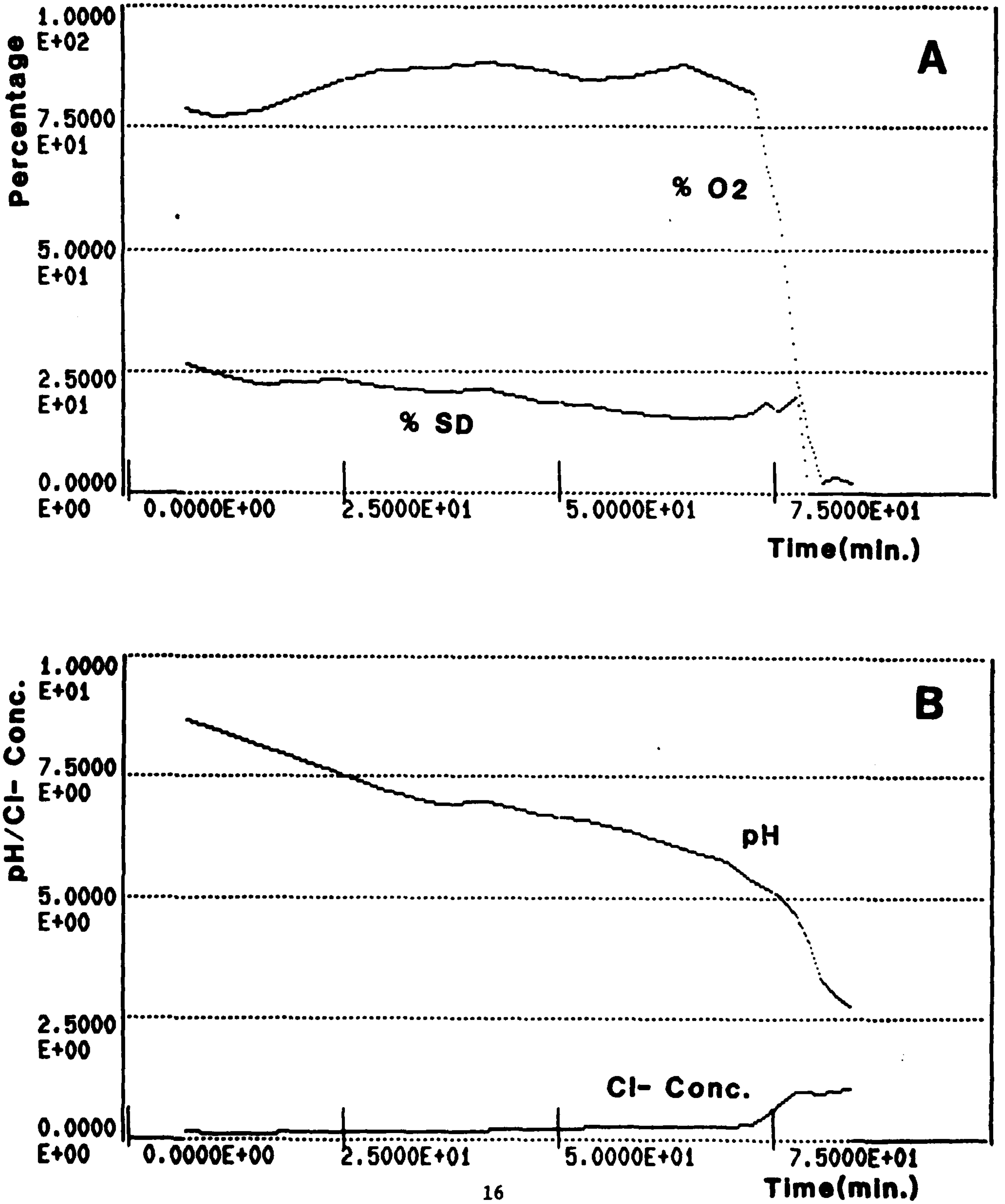
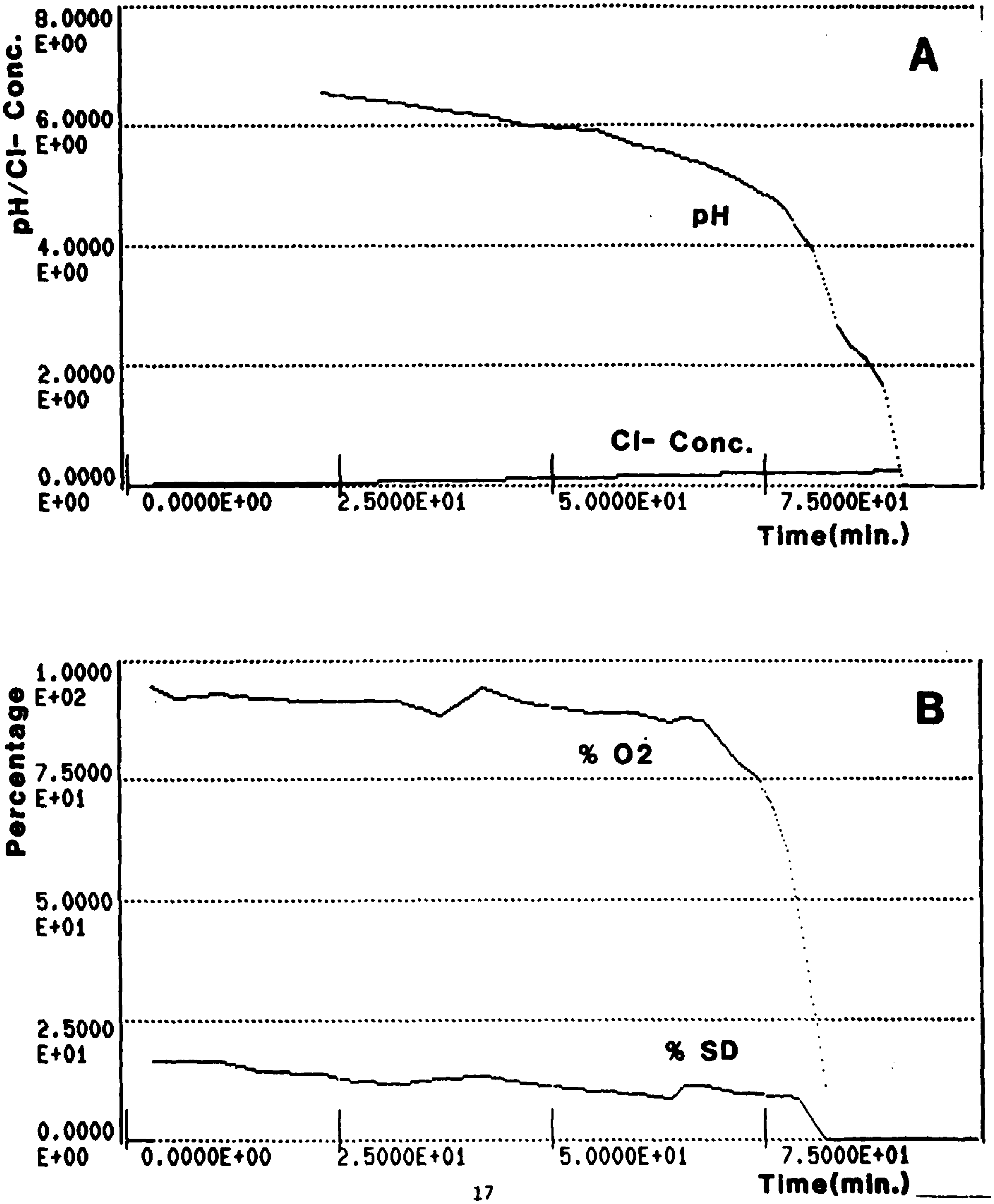

A
Percentage
1.0000 E+02
7.5000 E+01
5.0000 E+01
2.5000 E+01
0.0000 E+00
% O2
% SD
0.0000E+00
2.5000E+01
5.0000E+01
7.5000E+01
Time(min.)
B
pH/Cl- Conc.
1.0000 E+01
7.5000 E+00
5.0000 E+00
2.5000 E+00
0.0000 E+00
pH
Cl- Conc.
0.0000E+00
2.5000E+01
5.0000E+01
7.5000E+01
Time(min.)

FIGURE 6


A
pH/Cl- Conc.
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6.0000 E+00
4.0000 E+00
2.0000 E+00
0.0000 E+00
pH
Cl- Conc.
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2.5000E+01
5.0000E+01
7.5000E+01
Time(min.)
B
Percentage
1.0000 E+02
7.5000 E+01
5.0000 E+01
2.5000 E+01
0.0000 E+00
% O2
% SD
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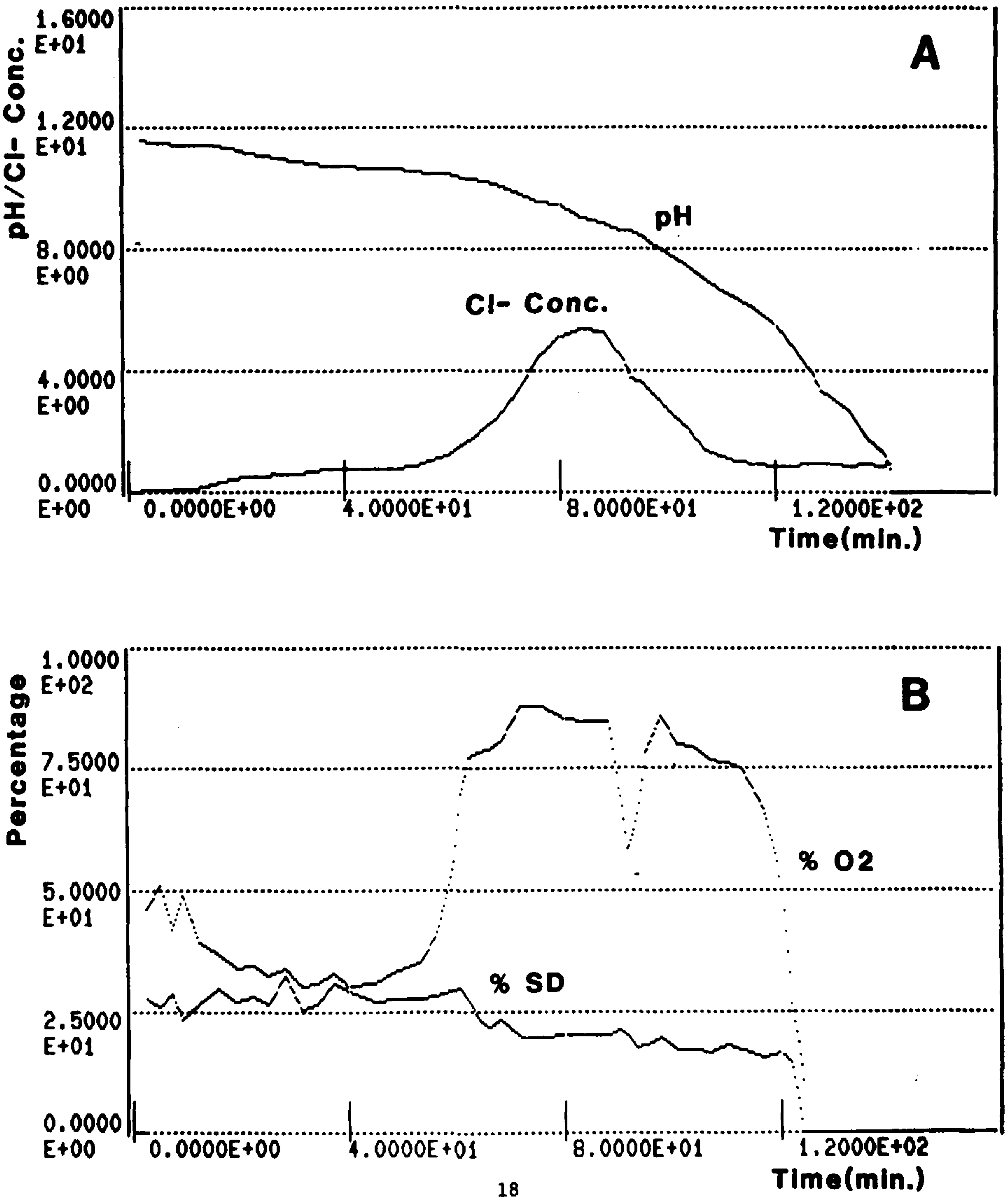
7.5000E+01
Time(min.)

FIGURE 7


A
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4.0000 E+00
0.0000 E+00
pH
Cl- Conc.
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4.0000E+01
8.0000E+01
1.2000E+02
Time(min.)
B
Percentage
1.0000 E+02
7.5000 E+01
5.0000 E+01
2.5000 E+01
0.0000 E+00
% O2
% SD
0.0000E+00
4.0000E+01
8.0000E+01
1.2000E+02
Time(min.)

TABLE 1

REACTANT VOLUMES USED FOR VOLUME VARIATION STUDY

EXPERIMENT #	VOLUME (6M NaOH)	VOLUME (90% H_2O_2)
1	30. ml.	30. ml.
2	50. ml.	50. ml.
3	80. ml.	81. ml
4	120. ml.	120. ml