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FRANK J. SEILER RESEARCH LABORATORY

FJSRL TECHNICAL REPORT-81-0004

APRIL 1981

CALIBRATION METHOD FOR SOLID STATE CHLORIDE ION ELECTRODES IN HYDROGEN PEROXIDE/STRONG BASE SOLUTION

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PROJECT 2303

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FJSRL-TR-81-0004

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CALIBRATION METHOD FOR SOLID STATE CHLORIDE ION ELECTRODES IN HYDROGEN PEROXIDE/STRONG BASE SOLUTION

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APRIL 1981

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A

PREFACE

This interim report documents work done under Work Unit 2303-F4-01, Chemiluminescent Gas Phase Reactions, between 1 March 1980 and 15 December 1980. 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.

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I. INTRODUCTION

Bubbling chlorine gas through a basic hydrogen peroxide solution produces $O_2(^1\Delta_g)$, an excited state of molecular oxygen. This $O_2(^1\Delta_g)$ can be used to excite atomic iodine for use in a chemical laser (1). Since larger quantities of $O_2(^1\Delta_g)$ relative to ground state oxygen result in greater amounts of energy available for transfer to the iodine, it is desirable to optimize the percentage of $O_2(^1\Delta_g)$ produced. To do this most effectively the reaction mechanism for $O_2(^1\Delta_g)$ generation should be understood. Recent research shows an unexplained trend in the chloride ion concentration during the generation of $O_2(^1\Delta_g)$ in a batch process (2). To explain this trend and to better understand the reaction mechanism, chloride ion concentration can be followed in-situ by use of an ion specific electrode. This requires a valid calibration procedure for the chloride probe.

We have used an Orion chloride ion probe (#941700) to measure the chloride ion concentration. This probe is a solid-state electrode with a $AgCl/AgS_2$ membrane (3). When the membrane is in contact with a chloride solution, silver ions dissolve from the membrane surface and a potential develops due to the Ag^+ ion concentration. This Ag^+ concentration depends on the Cl^- concentration in the test solution. At high or constant ionic strengths the activity of the chloride ion is directly proportional to its concentration. The relationship between the probe potential and the activity of the chloride ion is given by the Nernst equation

$$E = E^o - (\text{slope}) \log[Cl^-] \qquad (1)$$

where E is the measured potential, E^o is the standard potential, slope equals 2.303RT/F, and $[Cl^-]$ is the chloride ion activity. To relate equation 1 to the calibration line it is rewritten as

$$mV = Int - (\text{slope}) \log[Cl^-] \qquad (2)$$

where mV is the measured potential, and the intercept (Int) and slope are determined by calibration.

Our reaction medium presents two major obstacles to calibration. First, the temperature of the H_2O_2/KOH system ranges between -20°C and 5°C during the generation of $O_2(^1\Delta_g)$. The Orion probe is designed to operate in the temperature range of 0°C to 100°C. The effects of such reduced temperatures on the probe must be understood. Second, the H_2O_2/KOH solution is a very high ionic strength (3 molar) and very chemically active solution. No evidence was found in the literature to support the use of the probe in this chemical environment (4). The Orion probe was designed for low ionic strength samples (<1 molar). To maintain a constant ionic strength for all sample solutions, $NaNO_3$ is normally used as an ionic strength adjuster. Thus, calibration required characterization of the probe in the H_2O_2/KOH solution.

II. EXPERIMENTAL

Aqueous Characterization

To ensure proper operation of the probe, it was first characterized in aqueous solutions of KCl. Figure 1 shows the experimental set-up for this and subsequent studies. Aqueous KCl standard solutions varied in concentration from 2.5 M to 1.0×10^{-3} M. The probe was immersed for three minutes in the standard prior to recording the mV reading. The probe was then rinsed with deionized water and placed in the next standard. The internal reference of an Orion pH probe was used as the reference electrode for the chloride ion probe. Calibration data collected at room temperature are shown in Figure 2. These data give a linear correlation coefficient of 0.998 and were reproducible. Experimental conditions were then modified to determine the effects of 1) time, 2) temperature, 3) pH and 4) ionic strength. These conditions are important because they are directly applicable to the H_2O_2/KOH reaction mixture.

Time

The operating manual for the chloride probe suggests calibration every two hours, indicating the instability of the probe over a long period of time. In aqueous solutions reproducible data were collected over a 90 minute period of time. Operations of our $O_2(^1\Delta_g)$ generator is usually for one hour, so recalibration during a run may not be necessary.

Temperature

Experiments dealing with the aqueous standards reveal no change in the probe operation between 0°C to 20°C. However, during the generation of $O_2(^1\Delta_g)$, the temperature fluctuates between -20°C to 0°C. Further investigation of the H_2O_2/KOH solutions is required to understand this temperature effect on the chloride ion measurement.

pH

The recorded pH (using a glass electrode) of the chloride standards was varied between 5 and 10 by adding KOH to the solution. No change in the probe output was observed for a solution of constant chloride ion concentration over this pH range. This is important because the pH of the reaction mixture changes between 5 and 10, as measured by a glass pH electrode.

Ionic Strength

The importance of ionic strength was discussed in the Introduction to this paper. Two experiments were conducted to determine the effect of ionic strength on calibration. In one experiment, all standards had the same ionic strength and in the other experiment the ionic strength was varied in a standard of constant chloride ion concentration. In both experiments $NaNO_3$ was used to adjust the ionic strength. In the first experiment the adjustment of the ionic strength showed no effect on the calibration as compared to the standard calibration. The second experiment showed that a ten-fold change in the ionic strength is required to change the probe output by more than 2mV. These experiments indicate satisfactory operation of the chloride ion probe in H_2O_2/KOH solutions where the ionic strength is relatively constant over the range of chloride ion concentration.

The aqueous characterization confirmed a working probe and a justification for using the probe in the H_2O_2/KOH reaction mixture.

H_2O_2/KOH Calibration

The first calibration of the chloride ion probe in a H_2O_2/KOH standard was at 0°C (ice bath). Excessive bubbling of the H_2O_2 at the electrode surface caused erratic probe readings. To minimize the decomposition of the H_2O_2, future calibrations were performed at -3°C. The -3°C temperature was maintained using a salt-ice bath. Standards of KCl were prepared from equal volumes of 6 M KOH and 90% H_2O_2. The KCl concentration varied from 1 M to 0.02 M. During calibration the probe was placed in the standard for 1 to 2 minutes (depending on the experiment) before recording the probe reading. The probe was then rinsed with cold, deionized water and dried with a Kimwipe before it was inserted in the next standard. The order of measuring the chloride ion concentration in the standards was to alternate measurements in the high, then the low chloride ion concentration standards. Calibration data were collected for 60 - 90 minutes.

The initial calibration data collected at -3°C is plotted in Figure 3. The first trial does not define a linear calibration curve. Subsequent calibration data did yield linear calibration curves (linear correlation coefficients = 0.998). However, the data were not reproducible. This behavior was interpreted as a need to condition the probe prior to achieving linear, reproducible data. This conclusion is based on two observations. First, linear data were obtained after the first trial. Second, the change in the slope of the calibration curves appears to approach a limit, suggesting reproducible data can be obtained. Possible factors influeincing the need for conditioning could be the low solution temparature (below 0°C), the high ionic strengths of the standards (greater than 4 M), and possible uncontrolled reactions of the probe membrane with the solution.

Two conditioning methods were tried to improve the reproducibility of the calibration. In the first method the probe was placed in an H_2O_2/KOH solution with no chloride ion present for 50 minutes. In the second method the probe was placed in H_2O_2/KOH solutions of 1.0 M KCl and 0.025 M KCl, each for 20 minutes. Neither conditioning method was successful in achieving reproducible calibration data, although the second method did improve the linear correlation of the data for the first trial.

The aqueous characterization data show stable, reproducible operation of the probe in basic solution. So, the nonreproducibility of the data might be due to H_2O_2. As mentioned earlier, decomposition of H_2O_2 at 0°C caused erratic probe readings. Therefore, the chloride probe was placed in a solution of 90% H_2O_2 and the probe readings monitored. During a 50 minute period the reading continually dropped from an initial value of 1168 mV to 152 mV. Apparently, the H_2O_2 is reacting with the Ag_2S/AgCl membrane and causing a change in the potential.

III. RESULTS

The objective of this work is to establish a valid calibration procedure for a chloride ion probe. However, the nonreproducible data severely limits conventional calibration techniques. Therefore, a calibration procedure is necessary to account for what appears to be the reaction of the H_2O_2 on the electrode membrane surface. A closer look at Figure 3 shows a continuous change in slope of the calibration line as the experiment progressed, suggesting a "time dependent" relationship of the slope. A graph of slope versus time might provide some insight into this time dependent relationship. The time for a particular trial is simply the midpoint during data collection for that trial. For example, if trial one is accomplished between time zero and time = 12 minutes, then the time used in the slope versus time plot is 6 minutes. A plot of slope for each calibration versus time was constructed, Figure 4. The linear correlation of the data suggests a time dependent nature of the slope. Instead of the slope being a constant value, it now changes with time. Thus, equation2 must now be changed to account for the time dependent slope.

$$mV = Int + slope(t) \text{ Log } [Cl^-] \qquad (3)$$

where slope(t) is defined as

$$slope(t = A + B(time) \qquad (4)$$

where A is the intercept of the line from the slope versus time graph and B is the slope of that same line. Equation 3 can be rearranged to calculate the chloride ion concentration from the probe reading

$$[Cl^-] = 10^{\left[\frac{mV - Int}{slope(t)}\right]} \qquad (5)$$

The present work accounts for the time dependent slope, but does not resolve the questions of what value the intercept (Int) should be. Figure 5 shows that there is no obvious time, intercept relationship. However, the average intercept value can be used to obtain reasonable results, until further studies are completed.

The calculated values of the chloride ion concentration determined from an individual calibration line compared to the actual values of the standard have an average error of 5% (range 0% - 20%). However, calculating the concentrations using equation 5 and the average intercept value results in an average error of only 7% (range 0% - 25%). The second method could provide an acceptable means to calibrate the chloride ion probe in the reaction mixture. Table 1 shows a comparison of the calculated chloride ion concentrations using the two methods.

IV. CONCLUSIONS

The work accomplished on the calibration of the chloride ion probe has established a valid procedure for calibration of such probes in strong H_2O_2/KOH solutions. This work is significant because it is the first report of using a chloride ion probe in a high ionic strength environment at temperatures below 0°C.

However, work must continue in this area to refine the calibration procedure. Experiments need to be performed to understand the time dependence of the intercept of the calibration line. Further studies are required to determine the confidence levels of the results. Also, the temperature dependence of the probe reading must be understood over the range -20°C to 0°C to complete the characterization of the chloride ion probe in H_2O_2/KOH solutions. Finally, the above areas must be integrated into experiments that produce $O_2(^1\Delta_g)$.

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3. Operating Manual for Orion Probe #94-17A

4. Literature search and private phone converstation with Orion Company, Mass., August 1980.

FIGURE 1

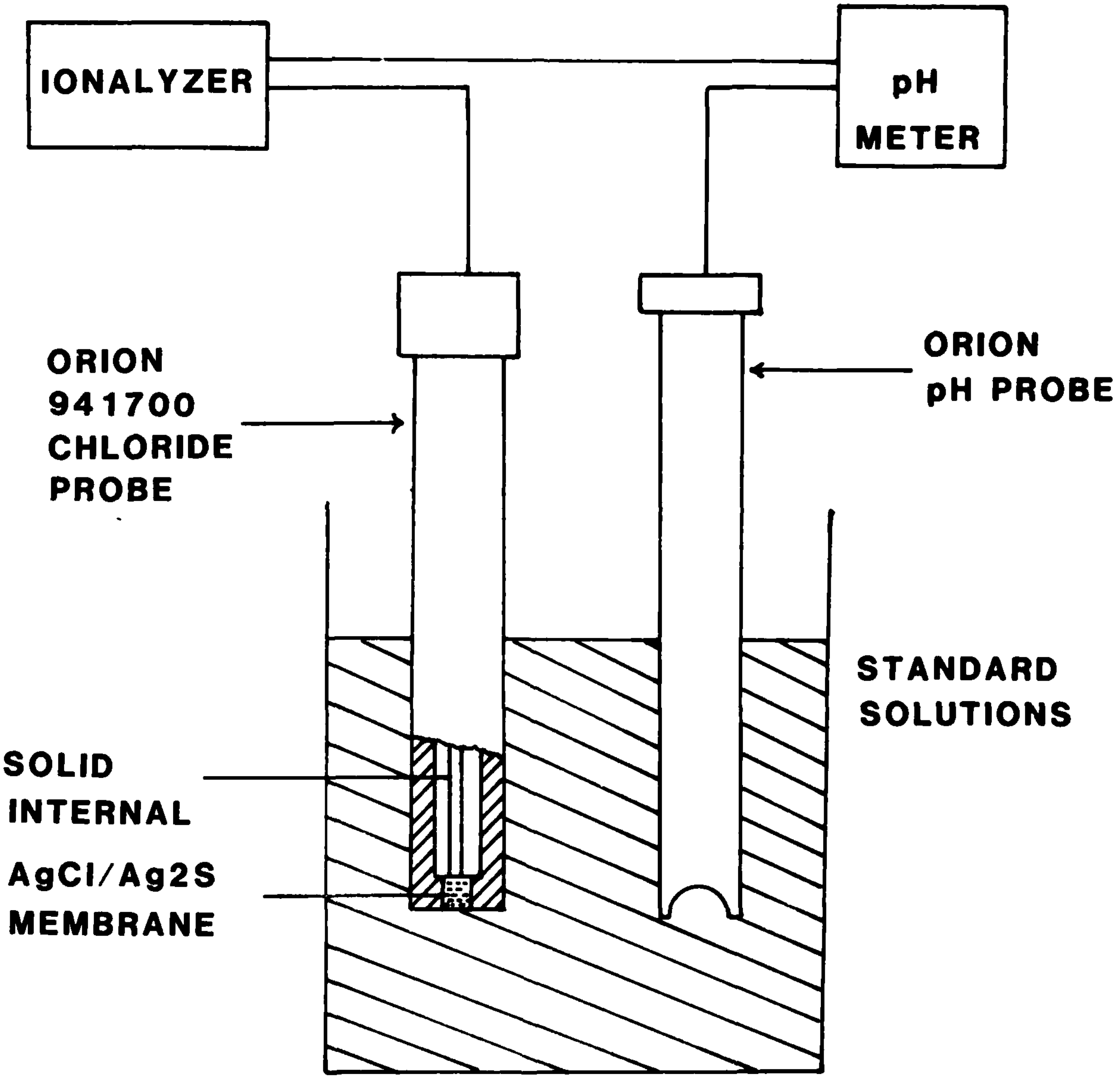
IONALYZER
pH
METER
ORION
941700
CHLORIDE
PROBE
ORION
pH PROBE
STANDARD
SOLUTIONS
SOLID
INTERNAL
AgCl/Ag2S
MEMBRANE

FIGURE 2

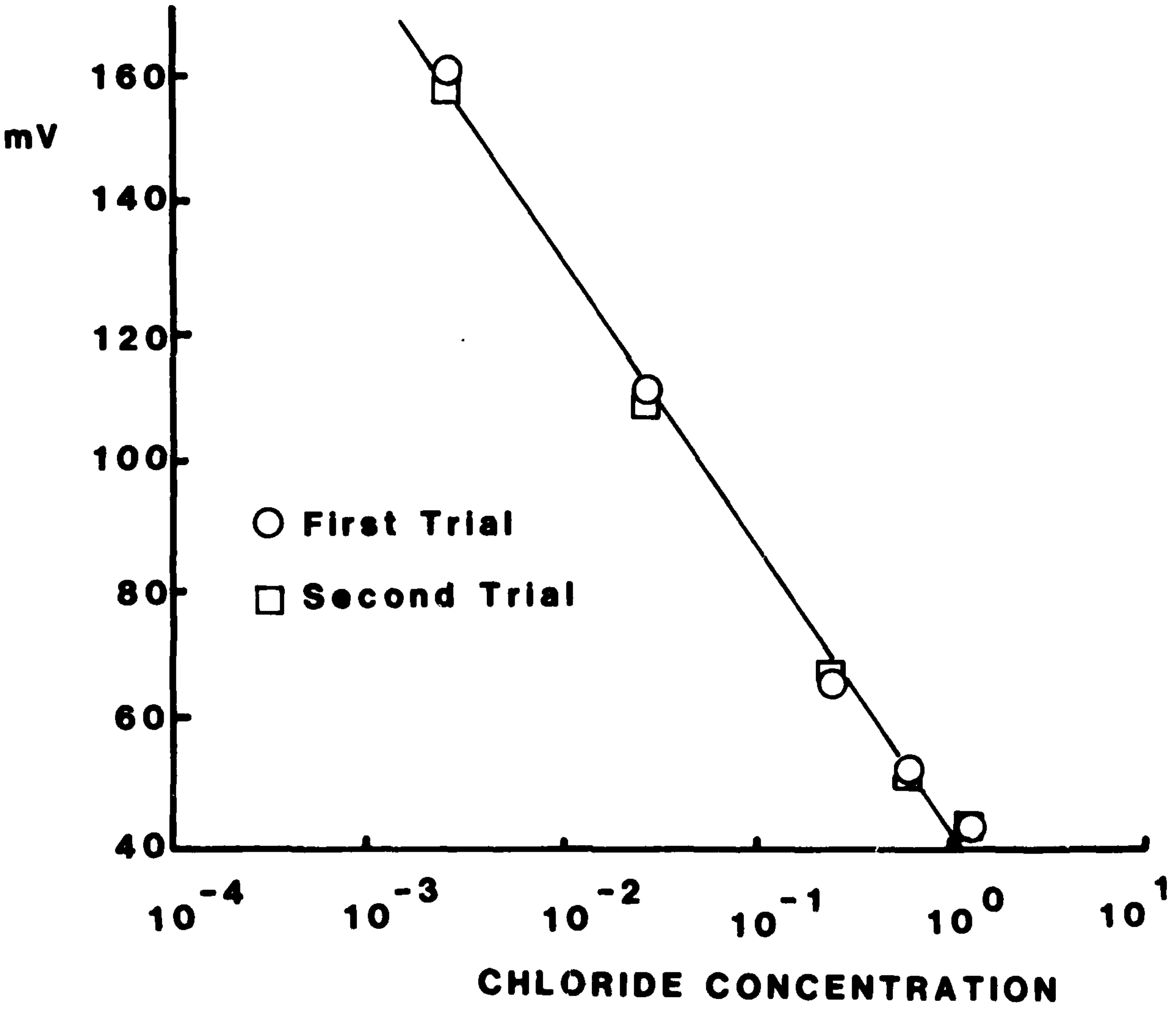
mV
160
140
120
100
80
60
40
○ First Trial
□ Second Trial
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
CHLORIDE CONCENTRATION

FIGURE 3

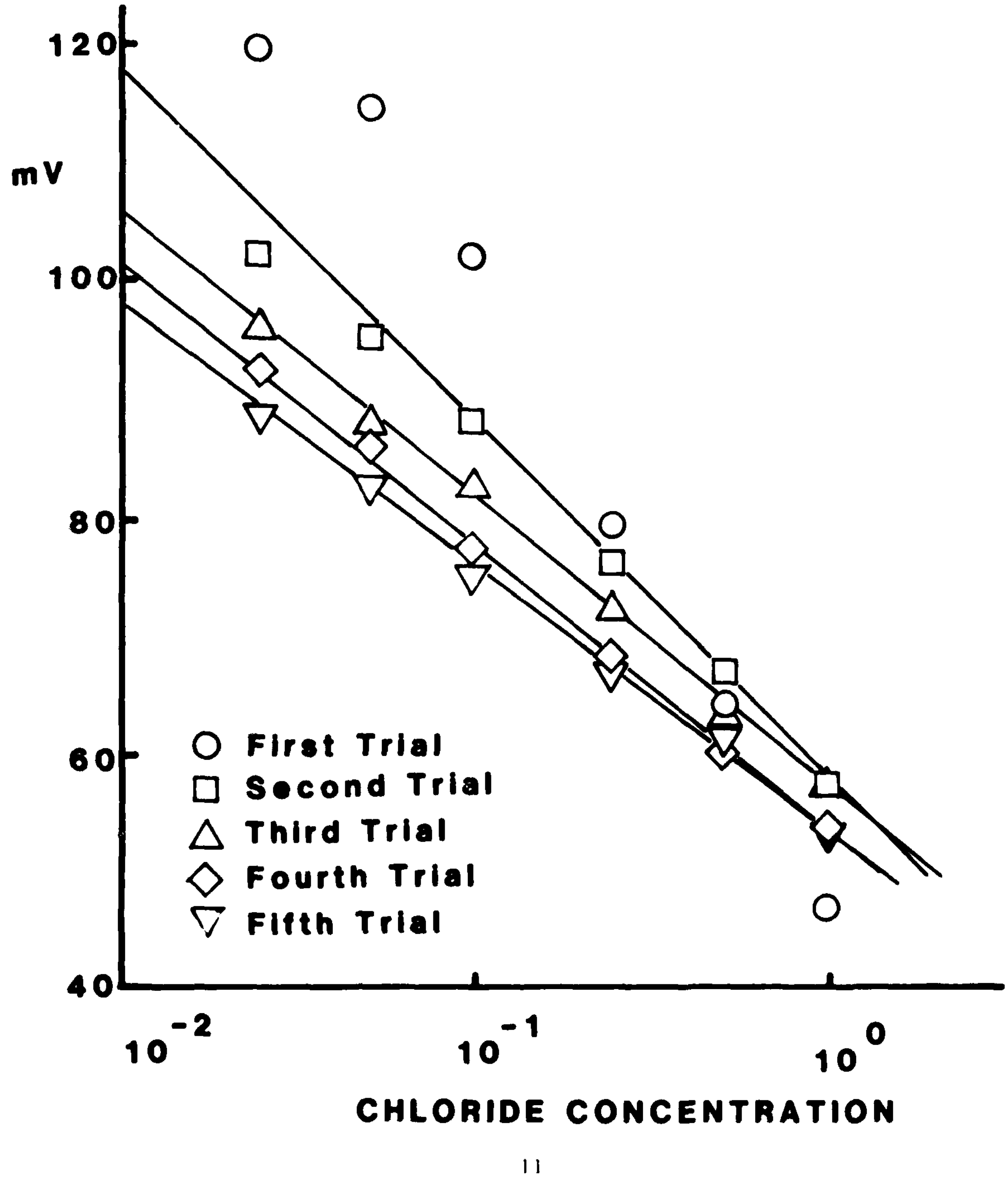
mV
120
100
80
60
40
○ First Trial
□ Second Trial
△ Third Trial
◇ Fourth Trial
▽ Fifth Trial
10^{-2}
10^{-1}
10^{0}
CHLORIDE CONCENTRATION

FIGURE 4

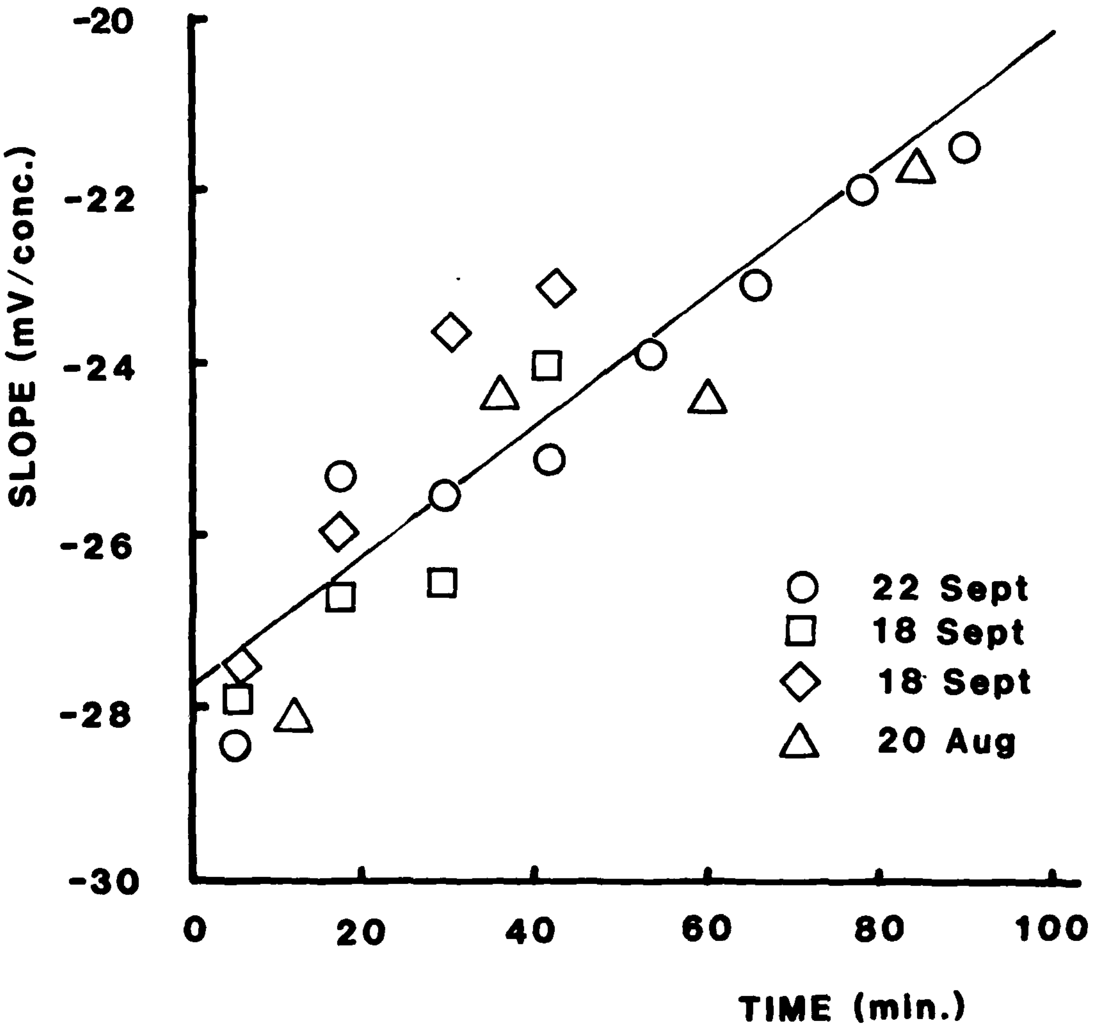
SLOPE (mV/conc.)
-20
-22
-24
-26
-28
-30
0
20
40
60
80
100
TIME (min.)
○ 22 Sept
□ 18 Sept
◇ 18 Sept
△ 20 Aug

FIGURE 5.

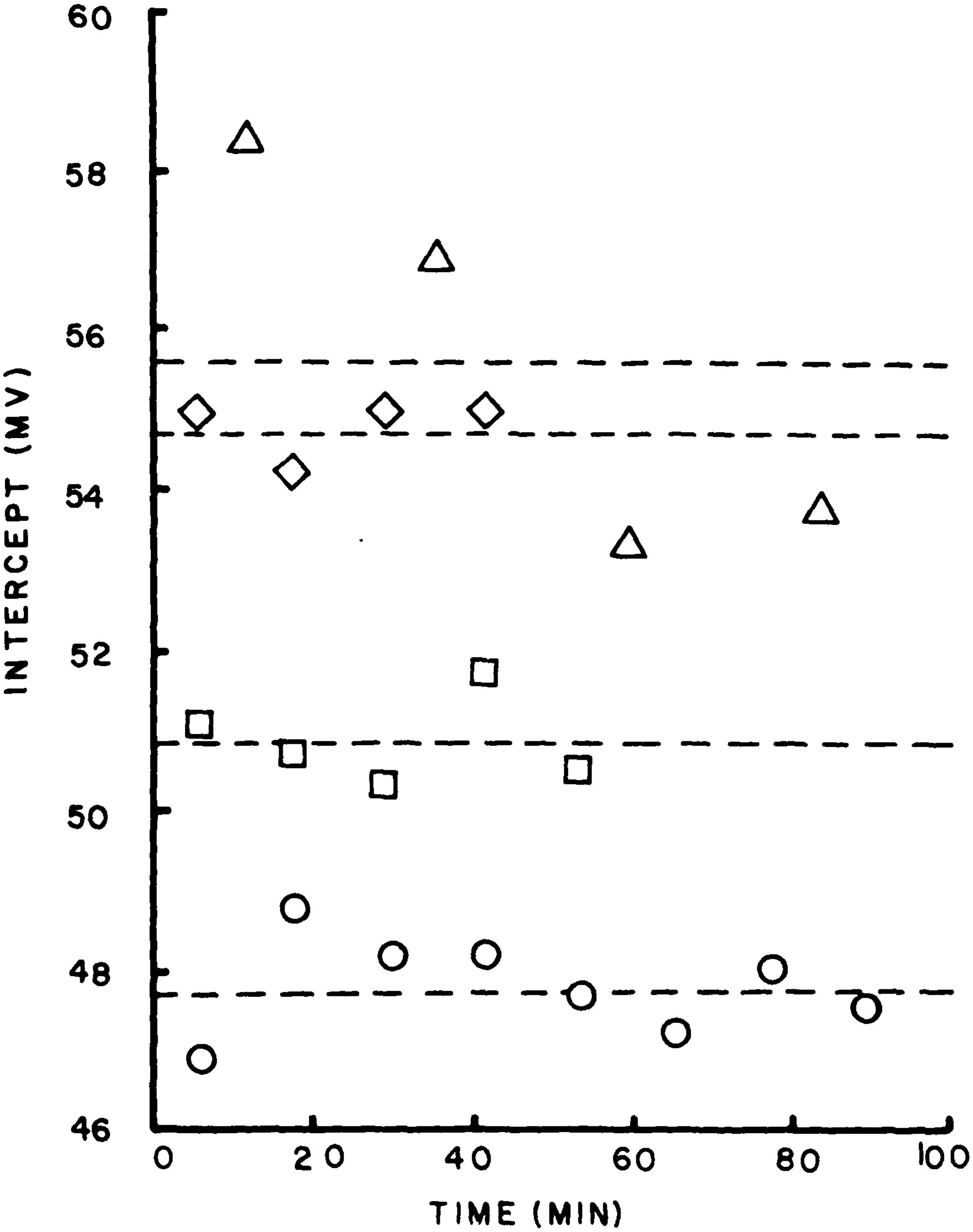

TABLE I

COMPARISON OF CALCULATED VALUES OF CHLORIDE CONCENTRATION BASED ON CALIBRATION DATA.[a]

Time (Min)	Actual $[Cl^-]$ (Molarity)	mV from Probe	Calculated $[Cl^-]$ (Molarity)		% Error	
14	1.00	49.0	.974[b]	.897[c]	2.1[d]	10.3[c]
16	.500	55.6	.535	.505	7.0	1.0
18	.250	64.3	.241	.235	3.5	5.8
20	.100	74.3	.0965	.0970	3.4	2.9
22	.0500	81.4	.0504	.0511	.9	2.2
24	.0250	88.9	.0253	.0258	1.5	3.2

a. Probe was conditioned in basic peroxide 1M and 0.25 M KCl solutions.

b. Calculated using equation 5 using the slope for that specific calibration line.

c. Calculated using equation 5 using average intercept of 47.74 mV.

d. % Error based on calculated chloride from b.

e. % Error based on calculated chloride from c.

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