

INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.
2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of "sectioning" the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.

**University
Microfilms
International**

300 N. Zeeb Road
Ann Arbor, MI 48106

8312337

Bratin, Peter

**IN-SITU COMPENSATION OF CAPACITIVE CHARGING CURRENT IN
INCREMENTAL DC POLAROGRAPHY**

City University of New York

PH.D. 1983

**University
Microfilms
International** 300 N. Zeeb Road, Ann Arbor, MI 48106

PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark ✓.

1. Glossy photographs or pages _____
2. Colored illustrations, paper or print _____
3. Photographs with dark background _____
4. Illustrations are poor copy _____
5. Pages with black marks, not original copy _____
6. Print shows through as there is text on both sides of page _____
7. Indistinct, broken or small print on several pages ✓
8. Print exceeds margin requirements _____
9. Tightly bound copy with print lost in spine _____
10. Computer printout pages with indistinct print _____
11. Page(s) _____ lacking when material received, and not available from school or author.
12. Page(s) _____ seem to be missing in numbering only as text follows.
13. Two pages numbered _____. Text follows.
14. Curling and wrinkled pages ✓
15. Other _____

**University
Microfilms
International**

In-Situ Compensation of Capacitive
Charging Current in Incremental
dc Polarography

by

Peter Bratin

A dissertation submitted to the
Graduate Faculty in Chemistry
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy,
The City University of New York

February 1983

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

Feb. 15, 1983
date

Joseph Geinster
Chairman of the Examining Committee

15 February 1983.
date

David C. Locke
Executive Officer

Harmon L. Finston

by Lee Finston

David C. Locke
Supervisory Committee

The City University of New York

Abstract

In-Situ Compensation of Capacitive Charging

Current in Incremental dc Polarography

by

Peter Bratin

Advisor: Professor Joseph Glickstein

A new method and computerized instrument for compensation of capacitive charging current in incremental dc polarography are introduced. The incremental charging current is directly proportional to the differential double layer capacitance, which can be measured in-situ, in the presence of faradaic current, by the phase-null technique. This technique eliminates interference of the faradaic current in the range where the compensation is most needed, namely at low concentrations.

The new method offers advantages over existing methods in respect to both, a rigorous theoretical basis and experimental capabilities of versatility and accuracy, including an improved approach to incremental measurements which was necessary to attain good precision in the sub-micromolar range. The performance of the instrument was tested with Zn(II), Cd(II) and Pb(II) solutions. with terms derived directly from experimental measurement. In all cases, for the concentration range between $2 \times 10^{-7} M$ and $1 \times 10^{-5} M$, the calibration curves were linear with a standard deviation of the slope better than +6%.

To Ariel

Acknowledgements

I would like to express my gratitude to Dr. Joseph Glickstein for his guidance and limitless patience, for his countless hours spent in lab aiding in troubleshooting and mostly for his moral support during the difficult moments.

I also would like to acknowledge Professors H.Finston, V. Fried, D.Locke and M.Tomkiewicz for their assistance and guidance.

I am indebted to Bill Knoop, Ottmar Safferling, Armand Gazes and classmates Tony Popowicz, Lucia Babcock, Sid Goldberg, Russell Seltzer, Sene Bauman, Allan Rychtman, Phil Band and others for their friendship and assistance during my years at Brooklyn College.

Special thanks to my parents for their consistent encouragements to continue my education, and to my brothers Milan and Karl for their assistance and advice.

Most importantly, I express my gratitude to my wife Viera for her support and patience during all these years.

TABLE OF CONTENTS

1	Introduction.....	1
2	Capacitive Charging Current and its Compensation....	8
2.1	Double Layer Theory.....	8
2.2	Charging Current.....	11
2.2.1	Electrical Capacitor.....	11
2.2.2	Electrical Double Layer.....	12
2.3	Charging Current Compensation.....	17
2.3.1	Current Sampled dc Polarography.....	17
2.3.2	Derivative and Incremental Polarography.	18
2.3.3	Differential Techniques.....	18
2.3.4	<u>In-Situ</u> Compensation Techniques.....	20
3	Incremental dc Polarography with <u>In-Situ</u> Charging Current Compensation.....	23
3.1	Statement of the Problem.....	23
3.2	Theory.....	24
3.2.1	The Equivalent Circuit.....	25
3.2.2	Faradaic Current.....	27
3.2.2.1	Curve Width.....	31

3.2.2.2	Irreversible Waves.....	33
3.2.3	Capacitive Charging Current.....	33
3.2.4	Differential Double Layer Capacitance Determination by Phase-Null Technique...	36
3.2.5	Conditions Under which the Faradaic Impedance May be Neglected.....	40
3.2.5.1	DC Potential.....	41
3.2.5.2	Concentration of Electroactive Species.....	42
3.2.5.3	Frequency.....	42
4	Experimental.....	44
4.1	Instrumentation.....	44
4.1.1	Description of Operations.....	45
4.1.2	Sequence of Operations.....	49
4.2	Equipment.....	55
4.2.1	Cell.....	55
4.2.2	Electrodes.....	57
4.2.2.1	Dropping Mercury Electrode.....	59
4.2.2.2	Auxiliary Electrode.....	59
4.2.2.3	Reference Electrode.....	60
4.2.3	Instrumental Assembly.....	60
4.3	Solutions and Chemicals.....	61
4.4	Procedures.....	62
4.4.1	Calibration of Electronics.....	62
4.4.2	Data Acquisition.....	65
4.4.3	Calculations.....	66
4.4.4	Determination of Flow Rate of Mercury...	68

5	Results and Discussion.....	70
5.1	Performance Checks with the Dummy Cell.....	70
5.1.1	Potentiostat and Input Potentials.....	71
5.1.2	DC Measuring Network.....	72
5.1.3	AC Measuring Network.....	72
5.1.4	Rectifier.....	73
5.2	Systems Tested and Objectives.....	76
5.2.1	Supporting Electrolyte.....	78
5.2.2	Zinc (II).....	101
5.2.3	Cadmium (II).....	113
5.2.4	Lead (II).....	156
5.2.5	Presence of Surfactants.....	169
5.3	Error Analysis.....	174
5.3.1	Precision.....	174
5.3.2	Accuracy.....	179
6	Conclusion.....	209
6.1	Summary.....	209
6.2	Applications.....	211
6.3	Possible Future Improvements.....	213
APPENDIX.A	Faradaic Current Derivations.....	214
A.1	Current - Potential Derivations.....	214
A.2	Potential at the Maximum.....	216
A.3	Incremental Current at its Maximum....	218
A.4	Average Incremental Current.....	221
APPENDIX.B	Charging Current Derivations.....	225

APPENDIX.C	Derivation of the Equation for the ac Gain of the Measuring Amplifier.....	232
APPENDIX.D	Derivation of Equation for the dc Output of the Multiplier.....	236
APPENDIX.E	Circuitry.....	239
	E.1 Potentiostat and Signal Inputs.....	240
	E.2 DC Measuring Network.....	248
	E.3 AC Measuring Network.....	251
	E.3.1 Amplification of the Signal and Phase-Shifting by 90°	253
	E.3.2 Phase-Shift Detection.....	263
	E.3.3 Servo System.....	265
	E.3.4 Rectifier.....	268
	E.4 Triggering Network.....	268
	E.5 Computer Interfacing and Programming..	272
	E.5.1 PDP - 11/20.....	273
	E.5.2 PDP - 11/45.....	278
	E.5.3 Calculations at UCC.....	279
APPENDIX.F	Specification of Components.....	281
	F.1 Resistors.....	281
	F.2 Capacitors.....	284
	F.3 RC Networks.....	286
	F.4 Amplifiers.....	287
	F.5 Other Modules.....	288
	F.6 Switches.....	288
	F.7 Transformers.....	289

F.8	Diodes.....	289
F.9	Power Supplies.....	289
APPENDIX.G	Program INCPOL.....	290
APPENDIX.H	Program POLWAVE.....	320
References.....		336

LIST OF TABLES

4.1.	Sequence of Operations.....	50
4.2.	Parameters Entered in Task 1.....	50
5.1.	Performance of the ac Measuring Network with the Dummy Cell.....	74
5.2	Regression Analysis Results of the ac Network Test.....	75
5.3.	Effect of Uncompensated Resistance.....	75
5.6.	Capacitance of 1.0M KCl - Comparison with Literature.....	90
5.7.	Capacitance of 0.1M KCl - Comparison with Literature.....	95
5.8.	Incremental Polarograms of Zn^{+2} in 0.1M KCl....	106
5.9.	Incremental Polarograms of Cd^{+2} in 0.1M KCl with 0.01M HCl.....	119
5.10.	Incremental Polarograms of Cd^{+2} in 0.1M KCl with 0.01M HCl, Offset Scans.....	129
5.11.	Incremental Polarograms of Cd^{+2} in 0.1M KCl with 0.01M HCl, Smaller Steps.....	132
5.12.	Incremental Polarograms of Cd^{+2} in 0.1M KCl....	137
5.13.	Incremental Polarograms of Cd^{+2} in 0.1M KCl, Offset Scans.....	146
5.14.	Incremental Polarograms of Cd^{+2} in 0.1M KCl, Offset Scans.....	154
5.15.	Summary of Experimental Parameters Obtained for Cd^{+2}	155

5.16.	Incremental Polarograms of Pb^{+2} in 0.1M KCl....	168
5.17.	Statistical Summary of the Data.....	178
5.18.	Maximum Concentrations of Ions for Determination of C_d^0 to within 2%.....	181
A.1.	Evaluation of Derivatives at $E=E_{1/2}$	219
A.2.	Significance of the Higher Terms in the Taylor Expansion.....	222
E.1.	Impedances, Gains and Phase-Shifts of A-10 at Different Frequencies.....	255
E.2.	Gains and Phase-Shifts of the Reference Signal.	257
E.3.	Impedances, Gains and Phase-Shifts of A-11 at Different Frequencies.....	259
E.4.	Gains and Phase-Shifts of the Measuring Signal.	261
E.5.	Impedances, Gains and Phase-Shifts of A-13 at Different Frequencies.....	264

LIST OF FIGURES

1.1.	Polarographic Wave.....	2
1.2.	Derivative Polarographic Curve.....	4
3.1.	Randle's Equivalent Network.....	26
3.2.	Simplified Cell Impedance.....	37
3.3.	Experimental Arrangement for Phase-Null Measurements Used by Schwartz.....	37
3.4.	Experimental Arrangements for Measurements Used in this Work.....	39
4.1.	Block Diagram of the Instrument.....	47
4.2.	Timing Sequence.....	52
4.3.	Schematic Diagram of Task 3.....	54
4.4.	Cell.....	56
4.5.	Dropping Mercury Electrode.....	58
4.6.	Dummy Cell Circuit.....	63
5.1.	Dummy Cell.....	70
5.2.	Capacitance and Polarographic Curves of 1.0M KCl.....	81
5.3.	Incremental Polarograms of 0.1M KCl.....	84
5.4.	Incremental Polarograms of 0.1M KCl with 0.01M HCl	86
5.5.	Incremental Polarograms of 0.1M KNO ₃	88

5.6.	Capacitance Curve of 1.0M KCl - Comparison with Literature.....	94
5.7.	Capacitance Curve of 0.1M KCl - Comparison with Literature.....	98
5.8.	Incremental Polarograms of 0.1M KCl with 0.01M HCl.....	100
5.9.	Incremental polarograms of 10^{-7} M Zn^{+2} in 0.1M KCl.....	103
5.10.	Incremental polarograms of 10^{-6} M Zn^{+2} in 0.1M KCl.....	105
5.11.	Calibration Curve for 10^{-7} M Zn^{+2} in 0.1M KCl...	109
5.12.	Calibration Curve for 10^{-6} M Zn^{+2} in 0.1M KCl...	111
5.13.	Incremental Polarograms of 0.1M KCl with Added Zn^{+2} Concentration of 0.28 μ moles/l.....	115
5.14.	Incremental Polarograms of 10^{-6} M Cd^{+2} in 0.1M KCl with 0.01M HCl.....	118
5.15.	Calibration Curve for 10^{-6} M Cd^{+2} in 0.1M KCl with 0.01M HCl.....	121
5.16.	Incremental polarograms of 10^{-6} M Cd^{+2} in 0.1M KCl with 0.01M HCl, Offset Scan.....	124
5.17.	Calibration Curve for 10^{-6} M Cd^{+2} in 0.1M KCl with 0.01M HCl, Offset Scan.....	126
5.18.	Incremental polarograms of 10^{-6} M Cd^{+2} in 0.1M KCl with 0.01M HCl, Smaller Steps.....	128
5.19.	Calibration Curve for 10^{-6} M Cd^{+2} in 0.1M KCl with 0.01M HCl, Smaller Steps.....	131
5.20.	Incremental polarograms of 10^{-7} M Cd^{+2} in 0.1M KCl.....	134
5.21.	Calibration Curve for 10^{-7} M Cd^{+2} in 0.1M KCl...	136
5.22.	Capacitance and Polarographic Curves of 1.0M KCl	139
5.23.	Incremental polarograms of 10^{-7} M Cd^{+2} in 0.1M KCl, Large Steps with Offset Scan.....	142
5.24.	Calibration Curve for 10^{-7} M Cd^{+2} in 0.1M KCl, Large Steps with Offset Scan.....	144

5.25.	Incremental polarograms of $10^{-7}M$ Cd^{+2} in $0.1M$ KCl	147
5.26.	Compensated Incremental Polarogram of $8.7 \times 10^{-7}M$ Cd^{+2} in $0.1M$ KCl	149
5.27.	Incremental Polarograms of $10^{-7}M$ Cd^{+2} in $0.1M$ KCl , Large Steps with Offset Scan.....	151
5.28.	Calibration Curve for $10^{-6}M$ Cd^{+2} in $0.1M$ KCl , Large Steps with Finer Offset Scan.....	153
5.29.	Capacitance Curves of $0.1M$ KCl in the Absence and Presence of Pb^{+2}	159
5.30.	Incremental Polarograms of $10^{-7}M$ Pb^{+2} in $0.1M$ KCl	161
5.31.	Incremental Polarograms of $10^{-6}M$ Pb^{+2} in $0.1M$ KCl , Offset Scans.....	163
5.32.	Calibration Curves for $10^{-7}M$ Pb^{+2} in $0.1M$ KCl , Offset Scans.....	165
5.33.	Calibration Curves for $10^{-6}M$ Pb^{+2} in $0.1M$ KCl Offset Scans.....	167
5.34.	Incremental Polarograms of $4 \times 10^{-7}M$ Pb^{+2} in $0.1M$ KCl	171
5.35.	Capacitance and Incremental Polarographic Curves of Mixture of Reducible Ions.....	173
5.36.	Capacitance and Incremental Polarographic Curves of $3.8 \times 10^{-6}M$ Cd^{+2} in $0.1M$ KCl with $0.01M$ HCl , Determined with $1kHz$ ac.....	183
5.37.	Capacitance and Incremental Polarographic Curves of $7.0 \times 10^{-6}M$ Cd^{+2} in $0.1M$ KCl with $0.01M$ HCl , Determined with $1kHz$ ac.....	185
5.38.	Capacitance and Incremental Polarographic Curves of $5.0 \times 10^{-5}M$ Cd^{+2} in $0.1M$ KCl with $0.01M$ HCl , Determined with $1kHz$ ac.....	187
5.39.	Capacitance and Incremental Polarographic Curves of $3.8 \times 10^{-6}M$ Cd^{+2} in $0.1M$ KCl with $0.01M$ HCl , Determined with $5kHz$ ac.....	190

5.40.	Capacitance and Incremental Polarographic Curves of $8.5 \times 10^{-6} \text{ M Cd}^{+2}$ in 0.1M KCl with 0.01M HCl, Determined with 5kHz ac.....	192
5.41.	Capacitance and Incremental Polarographic Curves of $5.0 \times 10^{-5} \text{ M Cd}^{+2}$ in 0.1M KCl with 0.01M HCl, Determined with 5kHz ac.....	194
5.42.	Capacitance and Incremental Polarographic Curves of $5.0 \times 10^{-5} \text{ M Cd}^{+2}$ in 0.1M KCl with 0.01M HCl, Determined with 10kHz ac.....	196
5.43.	Capacitance and Incremental Polarographic Curves of $1.1 \times 10^{-5} \text{ M Zn}^{+2}$ in 0.1M KCl	199
5.44.	Capacitance and Incremental Polarographic Curves of $6.3 \times 10^{-5} \text{ M Zn}^{+2}$ in 0.1M KCl	201
5.45.	Capacitance and Incremental Polarographic Curves of $1.1 \times 10^{-4} \text{ M Zn}^{+2}$ in 0.1M KCl	203
5.46.	Capacitance and Incremental Polarographic Curves of $7.8 \times 10^{-6} \text{ M Pb}^{+2}$ in 0.1M KCl	205
5.47.	Capacitance and Incremental Polarographic Curves of $4.9 \times 10^{-5} \text{ M Pb}^{+2}$ in 0.1M KCl	207
E.1.	Potentiostat.....	241
E.2.	AC Potential Inputs.....	243
E.3.	Driver for Trigger Voltage Control.....	243
E.4.	DC Potential Inputs.....	244
E.5.	Driver for Stepper Control.....	246
E.6.	DC Network.....	249
E.7.	AC Measuring Network.....	252
E.8.	Dummy Cell Circuit.....	260
E.9.	Servo Network.....	266
E.10.	Rectifier Network.....	269
E.11.	Trigger Network.....	271

Chapter 1

INTRODUCTION

More than fifty years have passed since Jaroslav Heyrovský's first experiments led to the discovery of polarography (1), and the emergence of the first automatic polarograph (2). The classical technique which used a dropping mercury electrode has been extended to other electrodes and now polarography is only one of the powerful group of electroanalytical techniques called voltammetry. Detailed discussion of polarography can be found in original papers (1,3,4), reviews (5,6,7,8) and authoritative monographs (9,10,11,12,13).

The classical polarographic technique involves measurement of current produced by the oxidation or reduction of electroactive species on the dropping mercury electrode (DME) as a function of the DME potential. The shape of the polarographic wave (polarogram) is shown in Figure 1.1. The current flowing through the cell at any potential on the plateau of the wave is the sum of the diffusion limited current, i_d and residual current, i_r , equation [1-1].

$$i = i_d + i_r \quad [1-1]$$

The value of the half-wave potential, $E_{1/2}$, is characteristic of the electroactive species undergoing the electrode reaction; the magnitude of the diffusion current is the measure of its concentration. This enables a simultaneous qualitative and quantitative determination of the active species.

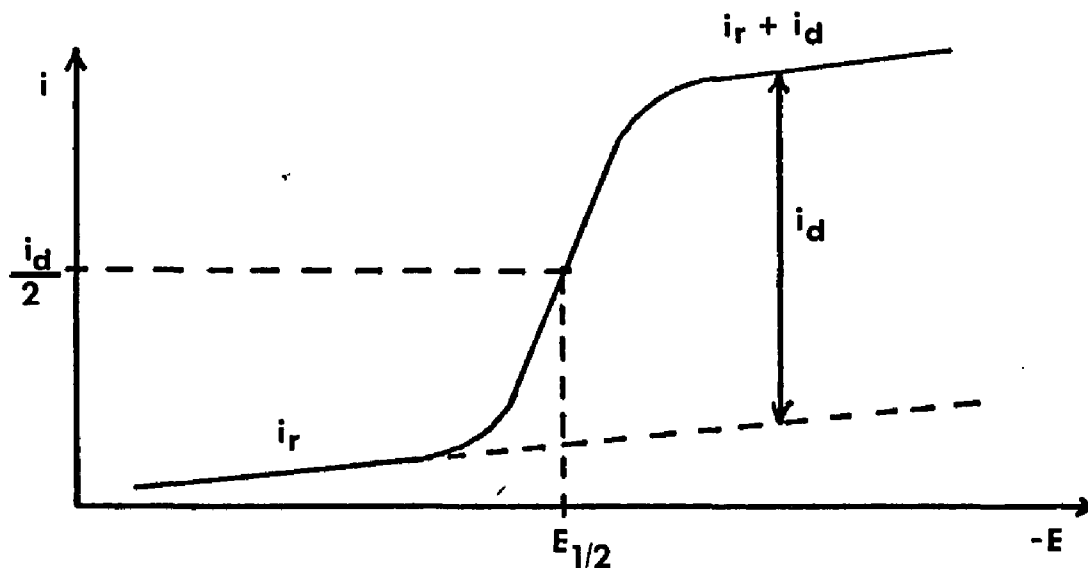


Figure 1.1 Polarographic Wave.

When more than one reducible species is present in the solution, a number of successive reductions occur, each producing its own polarographic wave. The current at each potential then includes contributions from each electrode reaction taking place at that potential. When two species are reduced at similar potentials, or if reduction of a major component closely precedes that of a minor component, it is difficult and sometimes even impossible to resolve a

polarogram. Soon after its discovery, these limitations of classical polarography became apparent to the inventors and other researchers (14); their efforts to overcome the drawbacks have resulted in methods with higher sensitivity, accuracy and resolution.

One approach, which does not involve changes in instrumentation and which is still used, is chemical pretreatment of the solution. The interfering species are complexed, which shifts their reduction to more negative potentials, or they are completely removed from the solution.

Semerano and Riccoboni in their differential technique (15) measured the difference in current flow through two cells, one containing the solution to be analyzed and the second containing only supporting electrolyte, to which interfering ions could be added. Thus, background and response due to the major interferences were eliminated if the cells were electrically and mechanically identical.

The "derivative" method introduced by Heyrovský (16) also measured the current difference. His technique used only one cell with two synchronized DMEs kept 10mV apart during the potential sweep. The polarograms produced were peaks (see Figure 1.2), rather than the waves obtained in classical polarography. This increased resolution of the overlapping waves and decreased relative response to the background current. Both, differential and derivative, techniques provide better resolution, thus increasing sensitivity and accuracy. However, both suffer from the diffi-

culty of synchronizing two dropping mercury electrodes. Recently this problem has been partially overcome by use of mechanical drop-knockers; the techniques, however, are not expected to see significant use (17).

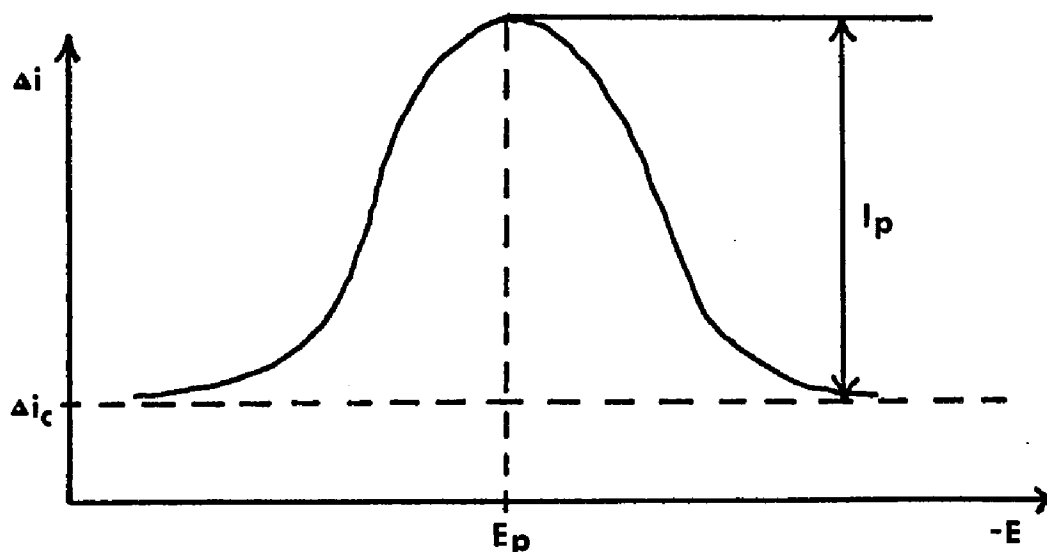


Figure 1.2 Derivative Polarographic Curve.

The peaked curve produced by Heyrovský's derivative technique made readout of data more convenient and accurate. It also led to further developments of derivative techniques, since the stepped waves of the classical polarography can be converted to peaked curves by differentiation (i.e. i vs E to di/dE vs E). The first method to measure derivative currents with but one electrode was introduced by Leveque and Roth (18) and independently by Vogel and Říha (19). Their circuit consisted of a conventional polarograph with an added high capacitance memory condenser in series with the measuring galvanometer. The current derivative was measured with respect to time, di/dt , and was made

proportional to the potential derivative, di/dE , by linearly scanning the voltage with time. The technique has been improved by the use of operational amplifiers introduced by Kelley, Fisher and associates (20,21,22), but the limitations imposed by the implicit time dependence remain.

Peak-shaped curves are also produced by a number of modern ac (23,24,25,26) and pulse (27,28) techniques, with resolution as good as the best derivative polarograms, and even better rejection of background current. Although these techniques cannot be classified as derivative, polarograms of this kind have peak-heights and peak-potentials related theoretically to di/dE , together with time dependent terms. These techniques have been reviewed by Schmidt and von Stackelberg (29), Bond (30), and Bard and Faulkner (31).

A technique producing peak-shaped polarograms without introducing any time dependence was introduced by Glickstein et al. (32,33,34). The technique measures the change in current, Δi , produced by a change of potential, ΔE , a principle introduced earlier by Heyrovský (16) using two synchronized DMEs. The problems of synchronization are avoided in our incremental method by sampling current at a specific time of one drop-life, and taking another current reading at the same time of the next drop, as in strobe (Tast) polarography (35). The potential is held constant during the life of each drop until the current reading has been stored; the potential is then increased by a constant value ΔE to give a new constant potential during the next drop life. The

difference in current, Δi , corresponding to this potential change, ΔE , is recorded as a function of DME potential.

The incremental ratio, $\Delta i/\Delta E$, is a good approximation to di/dE when ΔE is small, but its precision deteriorates as ΔE decreases. However, large ΔE values can be used for precise quantitative analysis, which only requires measurement of peak-heights, without the need for $\Delta i/\Delta E$ to represent di/dE over a wide range of potential, provided that peak-heights be proportional to concentrations. The feasibility of this approach has been demonstrated both theoretically (Chapter 3, Appendix A) and experimentally (Chapter 5).

A problem remains in locating the maximum Δi when ΔE is large, since a given incremental scan might not include it. The polarogram would then have a peak, smaller than the maximum Δi and located at a potential as much as $1/2 \Delta E$ away from it. This problem has been solved here by using "offset" scanning, where the origins of successive scans differ by known fractions of ΔE . The region of peak potential is located in the first scan; the second begins at a potential, near the peak, which is offset from the first by a fraction of ΔE , and the succeeding scans are offset by equal amounts. The Δi values will then have the small amplitude errors corresponding to the large ΔE , while the potential of the maximum can be located to within a small fraction of ΔE by choosing a sufficiently small offset.

The main goal of this work, to increase the sensitivity of incremental polarography, has been attained by in-situ

determination and compensation of the charging current contribution to Δi , as discussed in Chapters 2 and 3.

Chapter 2

CAPACITIVE CHARGING CURRENT AND ITS COMPENSATION

The interference of capacitive charging current in polarographic analysis has been recognized almost from the birth of the technique. This current is the primary factor limiting the sensitivity of polarographic determinations. The practical sensitivity limit of classical dc polarography for reversible, one-electron reduction was estimated by Laitinen (36) to be reached with about $10^{-5}M$ solution, assuming a 1:1 ratio of diffusion to charging current as the limit. Incremental and derivative polarography extends this limit to about $10^{-6}M$ concentrations of depolarizers. The origin of the capacitive charging current, its role in polarography and ways to compensate for it are considered in the following chapters.

2.1 DOUBLE LAYER THEORY

The metal-solution interface consists of arrays of charged particles and oriented dipoles, forming a region referred to as the electrical double layer. The mercury-

solution interface has served as a model, providing most of the present knowledge of the electrode-solution interface.

The modern theory of the electrical double layer separates the region into several layers (37). On the electrode side, most of the charge resides on the metal surface in a two dimensional sheet. The solution side of the interface is much more complicated, and can be divided into two sub-regions. The layer closest to the electrode, the inner layer (also called compact, rigid, Stern, or Helmholtz layer), contains solvent molecules and sometimes other species (ions or molecules stripped of their solvation sheaths), that are said to be specifically adsorbed. The locus of electrical centers of the specifically adsorbed ions is called the inner Helmholtz plane (IHP).

Solvated ions are attracted to the electrode only by long-range electrostatic forces and cannot approach as close as the specifically adsorbed ions. They are said to be non-specifically adsorbed, and the locus of these solvated ions nearest to the electrode is called the outer Helmholtz plane (OHP). Because of the thermal agitation in the solution, the nonspecifically adsorbed solvated ions are distributed in a three-dimensional region, called the diffuse layer, which extends from the OHP into the bulk of the solution.

This model of double layer was proposed by Grahame (38), who modified the earlier model of Stern (39). More detailed theory of the electrical double layer can be found in a series of articles by Grahame (40,41), textbooks

(37,42), and reviews (43,44,45).

Although the precise geometrical analogy between the electrical capacitor and the double layer, as presented in the parallel-plate condenser model of Helmholtz (46), has been invalidated, the concept is still valid. The double layer behaves as if there were two capacitances, one representing the compact layer, C_H , and the other the diffuse layer, C_G , connected in series:

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_G} \quad [2-1]$$

The measurement of this capacitance has provided much of the knowledge of the structure of the double layer (47,48). The capacitance of the double layer can be greatly affected if charged or neutral species become specifically adsorbed on the DME (49,50), especially if the species is a reactant or product of the electrode reaction. Thus in polarography, formation of the double layer on the DME-solution interface and its changes during the potential scan introduce complications which must be dealt with, if accurate results are to be attained.

One of the complications is the capacitance current required to charge the double layer in order to keep up with the changing area of the DME and changes in the applied potential. The charging current accounts for most of the background current in polarography, and it must be compensated for when low concentrations of the electroactive species are to be determined (29).

2.2 CHARGING CURRENT

2.2.1 ELECTRICAL CAPACITOR

Let us now consider the double layer interface as if it were an electrical capacitor in the equivalent circuit of the cell. The relationship between the double layer capacitance and the charging current can be developed by starting from the definition of the charge stored on a capacitor:

$$q = C.V \quad [2-2]$$

where C is the capacitance in farads, q is the charge in coulombs and V is the potential difference between the plates of the capacitor. The derivative of q with respect to time is:

$$\frac{dq}{dt} = V \frac{dC}{dt} + C \frac{dV}{dt} \quad [2-3]$$

Since instantaneous current in any electrical circuit is the first derivative of charge with respect to time, the charging current is:

$$i_c = \frac{dq}{dt} = V \frac{dC}{dt} + C \frac{dV}{dt} \quad [2-4]$$

One or both terms in equation [2-4] need to be evaluated, depending on the electroanalytical technique and electrode used.

In classical dc polarography, where a DME with continuously changing surface area is used, the $V(dC/dt)$ term is not zero, as long as potential V is non-zero. The second

term, $C(dV/dt)$ is zero for "staircase" potential scan and approaches zero when slow "ramp" scans are employed. For dc polarography, equation [2-4] then reduces to:

$$i_c = v \frac{dC}{dt} \quad [2-5]$$

However, the dV/dt term does not disappear when time-varying potentials such as sine-wave or square-wave are used. In ac polarography, therefore, the measured charging current is given by:

$$i_c^{\sim} = C \frac{dV}{dt} \quad [2-6]$$

2.2.2 ELECTRICAL DOUBLE LAYER

Two difficulties arise when the operational definition of the capacitor (equation [2-2]) is applied to the double layer capacitance. First, the absolute potential drop across the double layer capacitance is not an experimentally measurable quantity, and second the capacitance of the double layer is not constant, but depends on the potential difference across the interface. Neglecting the possibly complicated structure of the solution side of the double layer and considering the interface in terms of electrical capacitor behaviour, a specific integral capacitance of the double layer, C_1^0 , can be defined as:

$$C_1^0 = \frac{\sigma^M}{E} \quad [2-7]$$

To circumvent the inability to measure absolute potential difference across the interface, the potential E^* , is measured relative to the potential of zero charge, E_z , at which the surface charge density, σ^M , is zero. Thus,

$$E^* = E - E_z \quad [2-8]$$

The charging current is defined as the first derivative of charge with respect to time, and its value increases as the DME is made more cathodic:

$$i_c = - \frac{dq}{dt} \quad [2-9]$$

and

$$q^M = A \cdot \sigma^M \quad [2-10]$$

Combining equations [2-7],[2-9],[2-10] and differentiating yields the general equation for the current needed to charge the double layer interface:

$$-i_c = C_i^O E^* \cdot \frac{dA}{dt} + A E^* \cdot \frac{dC_i^O}{dt} + A C_i^O \cdot \frac{dE}{dt} \quad [2-11]$$

where $dE^* = dE$, since E_z is constant for a given electrode and solution.

Since the double layer capacitance is a function of potential, the second term in equation [2-11] can be rewritten as:

$$A E^* \cdot \frac{dC_i^O}{dt} = A E^* \cdot \frac{dC_i^O}{dE} \cdot \frac{dE}{dt} \quad [2-12]$$

Substituting equation [2-12] into [2-11] and rearranging we get:

$$-i_c = C_i^O E^* \cdot \frac{dA}{dt} + \left[\left(C_i^O + \frac{dC_i^O}{dE} \right) A \right] \frac{dE}{dt} \quad [2-13]$$

In dc polarography, during the life of any single mercury drop the variation of potential is so small that the potential may be considered to be constant, and dE/dt approaches zero. Thus dc charging current is given by equation [2-14](17):

$$i_c = - C_i^O E^* \cdot \frac{dA}{dt} = C_i^O (E_z - E) \frac{dA}{dt} \quad [2-14]$$

Potential, in an ac experiment, is a function of time; thus the charging current can be written as a sum of the dc and ac components. Since only current of the applied frequency is measured in ac polarography, the ac charging current is given by equation [2-15]:

$$|i_c| = \left[\left(C_i^O + \frac{dC_i^O}{dE} \right) A \right] \frac{dE}{dt} \quad [2-15]$$

Comparing equation [2-15] with [2-6], we see that the term in brackets in equation [2-15] plays the same role as does C in equation [2-6]. This is the differential double layer capacitance, C_d , whereas the term in parenthesis is the specific differential capacitance, C_d^O , which is defined by equation [2-16]:

$$C_d^O = \frac{d\sigma^M}{dE} \quad [2-16]$$

The equation for the ac charging current can then be rewritten as:

$$|i_c| = C_d^0 \cdot A \frac{dE}{dt} \quad [2-17]$$

Comparing equations [2-14] and [2-17] we see that ac charging current is directly proportional to the specific differential capacitance, C_d^0 , whereas dc charging current is directly proportional to the specific integral capacitance, C_i^0 . In order to calculate the charging current in classical dc polarography, and to compensate for it, it is necessary to know C_i^0 and of the potential of the zero charge, E_z . Since both depend on the nature of the solution and the electrodes, separate experiments for each solution would be required. In ac polarography it is necessary to determine only C_d for the charging current compensation (see equation [2-17]). A similar relationship, as is shown below, exists in derivative polarography.

In derivative polarography one records the potential derivative of current as a function of polarizing potential. The total current, whose derivative is recorded, is the sum of the faradaic and charging current contributions, and is given by:

$$\frac{di_T}{dE} = \frac{di_f}{dE} + \frac{di_c}{dE} \quad [2-18]$$

To obtain the derivative of charging current, we differentiate equation [2-14] with respect to potential and get:

$$\frac{di_c}{dE} = -\left(C_1^O + E^* \cdot \frac{dC_1^O}{dE}\right) \frac{dA}{dt} \quad [2-19]$$

The term in parentheses is the specific differential capacitance, C_d^O . Equation [2-19] can then be rewritten as:

$$\frac{di_c}{dE} = -C_d^O \cdot \frac{dA}{dt} \quad [2-20]$$

Since

$$C_d^O = \frac{C_d}{A} \quad [2-21]$$

and for the DME the surface area is given as (13):

$$A = kt^{2/3} \quad [2-22]$$

where t is the time in the life of the drop at which the measurement takes place, the equation [2-20] can be rewritten to give:

$$\frac{di_c}{dE} = - \frac{C_d}{kt^{2/3}} \cdot \frac{d(kt^{2/3})}{dt} \quad [2-23]$$

Differentiating and rearranging equation [2-23] we get:

$$\frac{di_c}{dE} = - \frac{2C_d}{3t} \quad [2-24]$$

Thus in derivative polarography, the charging current response, di_c/dE , is directly proportional to C_d , with known constants. It is therefore possible to use ac measurements of C_d to compensate for this response. That idea was originally proposed by Barker for dc polarography (51) and later by Schwartz for derivative polarography (52). In

the research described here, ac potential has been employed to measure C_d and to compensate for the charging current response in incremental polarography.

2.3 CHARGING CURRENT COMPENSATION

All improvements in sensitivity of polarographic determinations must stem from elimination or compensation of the capacitive charging current. Only when this has been achieved, do other factors limiting sensitivity acquire significance (29). Several techniques have been used to eliminate or compensate for the charging current.

In general, these techniques can be divided into four groups, based on the approach: (i) techniques based on the different time dependence of the charging and faradaic currents, (ii) derivative and incremental techniques, (iii) differential techniques, and (iv) in-situ compensation techniques. Only techniques pertaining to dc polarography will be discussed here.

2.3.1 CURRENT SAMPLED DC POLAROGRAPHY

The diffusion limited faradaic current, i_d , increases proportionally to $t^{1/6}$ where t is the age of the mercury electrode drop, whereas the capacitive charging current, i_c , is proportional to $t^{-1/3}$. The ratio i_d/i_c is thus smallest

at the beginning of the drop, and increases as a function of time. It is obvious, that current readings should be taken just before the end of the drop-life, rather than early on. Such instantaneous readouts or short-time averages give better rejection of charging current than do the readings averaged throughout the drop-life. An instrument for current-sampled applications (Tastpolarograph), introduced by Kronenberger (35) gave somewhat increased sensitivity over the classical dc readings. However a large portion of the charging current still remained.

2.3.2 DERIVATIVE AND INCREMENTAL POLAROGRAPHY

Derivative and incremental (also called "pseudoderivative"(53)) techniques increase the sensitivity of polarographic determinations by about factor of ten (17,29,33). The reason for this increase is a decrease of the charging current response in the derivative techniques, which leads to detection limits on the order of 10^{-6} M. Despite the improvement, charging current response, di_c/dE , remains the limiting factor as far as the sensitivity of these techniques is concerned.

2.3.3 DIFFERENTIAL TECHNIQUES

Differential techniques for charging current compensation are based on subtraction of the background current from

the total current. This background current can be obtained (i) by employing a linear compensation network (54,55), (ii) using a second cell containing only supporting electrolyte (15), and (iii) from a polarogram of supporting electrolyte only (17).

Linear charging current compensation is performed by subtracting from the measured current a fraction of the linearly increasing applied potential. The capacitive charging current, however, is not a linear function of the applied potential except for very limited regions. The linear form of compensation can produce significant distortions of the polarographic waves, if applied without discretion. This is most apparent for electrode reactions occurring near the electrocapillary maximum, near the solvent limits or in the presence of surface active species (17). The linear compensation circuits are thus useful only in the limited potential range where charging current is a linear function of potential, and even then only with great care.

The problem caused by the nonlinearity of the charging current can be circumvented by using a second cell filled only with the supporting electrolyte, and measuring the difference in current between the two cells. The resulting signal is proportional to the faradaic current only if no surface active species are present in the solution and if the cell geometries and characteristics of the two DMEs are matched. In practice, charging current compensation using two cells is seldom used due to the instrumental difficul-

ties.

The problem of matching cells and electrodes can be eliminated by recording residual current and total current in two successive runs using the same cell and DME. In the first run current is recorded only for the supporting electrolyte, while for the second run electroactive species is added. The faradaic current is the difference between the two runs. The difference can be obtained using a point-by-point subtraction of the recorded curves, or done automatically, with the use of curve follower (56) or computer-equipped polarograph (57,58,59). The above form of the charging current compensation is the most commonly used approach in practical dc polarography today.

2.3.4 IN-SITU COMPENSATION TECHNIQUES

All of these compensation techniques suffer from one basic fault: it is not always possible to ensure that the "blank" used to obtain the background current is the actual matrix of the unknown sample to be determined. The problem can be avoided only by compensating in-situ. Recently two such techniques have been introduced.

One technique, introduced by the Princeton Applied Research Corporation, makes use of so-called static drop mercury electrode, SDME (60). The SDME works like conventional DME for 50 to 200 milliseconds, at which time the drop stops growing. During this "static" period current

measurements are taken and the drop is then knocked off. The process is then repeated with a new drop. Since dc charging current is given by equation [2-14] as:

$$i_c = C_i^O E \frac{dA}{dt} \quad [2-14]$$

and the surface area of the SDME does not change during the "static" period, so that virtually all of the charging current is compensated for. Determinations of $10^{-7}M$ concentrations have been reported in the literature (17) using the SDME. However, the use of a stationary electrode also changes the behaviour of the faradaic current. For the DME i_f is proportional to $t^{1/6}$; for static electrodes i_f is proportional to $t^{-1/2}$, causing an increase in signal-to-noise ratio for longer sampling periods, in addition to mechanical difficulties.

An earlier approach, suggested by Barker (51) involves use of a small amplitude ac signal superimposed on the dc polarizing voltage. The resulting ac cell current is processed to obtain the differential double layer capacitance, C_d , from which the integral capacitance, C_i , required in calculation of dc charging current could be determined by integration (31):

$$C_i = \frac{\int_{E_z}^E C_d dE}{\int_{E_z}^E dE} \quad [2-25]$$

This approach has recently been analyzed by Rajagopalan

et al.(61,62), particularly regarding the problems of integration. They introduced various methods to compensate for charging current, all requiring empirical corrections needed to translate the ac current into dc charging current. Using a dc polarograph with this compensation circuitry, they were able to determine $3 \times 10^{-6} \text{M}$ solutions of Cd^{+2} , Zn^{+2} and Pb^{+2} in 0.1M KCl and 0.001% Triton X-100. However, the technique is only an approximation, since the ac current measured contains both, charging and faradaic components, whereas only the charging current is related to C_d .

The charging current compensation method presented in this work also employs the in-situ approach using a combination of ac and dc signals. The compensation here, however, is a true one, since experimental and instrumental conditions are used that allow a direct, in-situ, measurement of C_d . Since this compensation is applied to the dc incremental polarography where, as it will be shown in Chapter 3, the charging current increment, Δi_c , is directly proportional to C_d , the need for troublesome integration is avoided.

Chapter 3

INCREMENTAL DC POLAROGRAPHY WITH IN-SITU CHARGING CURRENT COMPENSATION

3.1 STATEMENT OF THE PROBLEM

The need for charging current compensation in accurate polarographic determinations was pointed out in Chapter 1, and some techniques presently used were discussed in Chapter 2. In this thesis new polarographic instrumentation, combining the technique of incremental dc polarography (32) with a novel approach to in-situ charging current compensation is introduced.

The new instrument offers increased sensitivity without the need for a blank allowing for increased precision in direct quantitative analysis of micromolar concentrations of electroactive species. Since this is a dc technique, irreversibly reduced ions can be determined with fewer complications than with most other modern polarographic techniques. Included in the following chapters are equations for faradaic and charging current, derived for experimental conditions used by the new instrument, and experimental results for a few species undergoing electrode reduction on

the DME in various potential regions.

3.2 THEORY

There are two pathways by which the polarographic current is carried across the solution - DME interface. One path is the electrochemical reaction, carrying current by virtue of oxidation or reduction of an electroactive species on the electrode surface. Because this process obeys Faraday's laws of electrolysis it is called the faradaic process, and the current derived from it is called the faradaic current, i_f . The second path does not involve electrode reactions and charged particles do not cross the solution - DME interface. This current is created by the charging and discharging of the double layer. Since this current does not obey Faraday's laws, it is called the non-faradaic current, i_{nf} . The total cell current, i_t , can be written as

$$i_t = i_f + i_{nf} \quad [3-1]$$

This a priori separability of the faradaic and nonfaradaic components of the cell current has been questioned in the past (63). However, after a thorough study the separability was supported in all but a few cases (64). The major reason for doubt of the separability arose from use of the charging current as measured in the potential region without the faradaic current. A method developed by Sluyters and

coworkers at Utrecht (65), which made it possible to measure the double layer charging current in the presence of faradaic process is responsible for the current acceptance of this separability (64).

In most theoretical work it is assumed that one deals only with the faradaic current, whereas polarographic instruments record the total cell current as a function of applied potential. Thus the non-faradaic contributions have to be either subtracted from the cell current, or better, eliminated instrumentally from the readout (66). In order to attempt separation of the faradaic and non-faradaic currents, it is necessary to consider the theory of both currents as applicable to given instrumentation.

3.2.1 THE EQUIVALENT CIRCUIT

It is a common practice in electrochemistry to describe the response of an electrolytic cell to electrical signals in terms of the "equivalent circuit" of the cell. This equivalent circuit is a network of passive electronic elements, which would give the same response to the electrical perturbation as the actual cell does. Since the total current is by definition a sum of the faradaic and nonfaradaic components, it is convenient to regard the interface as electrically equivalent to two impedances in parallel. The simplest and most commonly accepted equivalent circuit for response to the ac signals was described by Randles

(67)(Figure 3.1).

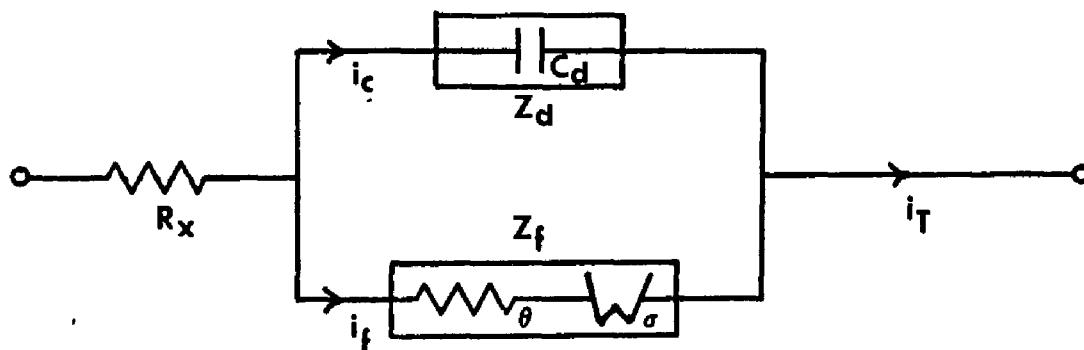


Figure 3.1 Randle's Equivalent Network.

The circuit consists of the sum of uncompensated resistances of the solution, circuit and DME, R_x , in series with the parallel combination of double layer impedance, Z_d , and faradaic impedance, Z_f . The impedance of the double layer can be represented simply as a capacitance, C_d (68). The faradaic impedance, Z_f , on the other hand cannot be represented in any simple fashion. In its simplest form (Figure 3.1) it consists of the activation polarization resistance, θ , and diffusion polarization (also called Warburg impedance), W_σ , (68):

$$Z_f = \theta + W_\sigma \quad [3-2]$$

Using the previously discussed assumption that the faradaic and nonfaradaic components of the cell current are separable*, we can derive expressions for these currents related to the experimentally used conditions.

3.2.2 Faradaic Current

For a reversible electrode reduction, the polarographic wave can be described by the Heyrovský-Ilkovič equation (30):

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_d - i}{i} \quad [3-3]$$

where E is the electrode potential, $E_{1/2}$ is the half-wave potential of the reducible species, R is the gas constant, T is the absolute temperature, n is the number of electrons involved in the electrode process, F is the Faraday constant, i is the faradaic current at potential E , and i_d , given by the Ilkovič equation [3-4] (13) is the diffusion limited faradaic current at time t in the electrode drop-life.

$$i_d = 0.732nFm^{2/3}D^{1/2}C_0t^{1/6} \quad [3-4]$$

If m is the flow rate of mercury in g/sec out of the DME, D is the diffusion coefficient of the electroactive species in cm^2/sec and C_0 is its bulk concentration in $\text{mole}/\text{cm}^{-3}$, the diffusion controlled current, i_d , is expressed in amperes.

Equation [3-3] can be rearranged (for derivation see Appendix A) to give:

$$i = \frac{i_d}{1 + e^{2u}} \quad [3-5]$$

* Separability does not hold for cases with strong specific adsorption, where coupling between faradaic and nonfaradaic current exists.

where

$$u = \frac{nF}{2RT}(E - E_{1/2}) \quad [3-6]$$

and the faradaic current is a function of the applied potential, $i(E)$. The incremental polarogram is a plot of the differences, Δi , between two consecutive current measurements as a function of potential. Since potential is applied discontinuously in equal steps, ΔE , the current is a discontinuous function as well. The potential at each point can be expressed as a value, E_j , j increments away from the potential E_A , at which the maximum of the incremental polarogram occurs:

$$E_j = E_A + j \Delta E \quad [3-7]$$

Since j can have integral values from 0 to $+\infty$, it defines a set of discrete points (E_j, i_j) but not a continuous function. The latter can be obtained by defining E_A as:

$$E_A = E_{1/2} + f \Delta E \quad [3-8]$$

where f defines a fraction with values:

$$0 \leq f < 1 \quad [3-9]$$

The potential:

$$E_a = E_{1/2} + a \Delta E \quad [3-10]$$

where

$$a = j + f \quad [3-11]$$

thus defines a continuous function: $i=f(E)$.

Current at any potential, E_a , can then be expressed in terms of Taylor series:

$$i_a = f(E_{1/2} + a \Delta E) = \sum_{n=0}^{\infty} i_{1/2}^{(n)} \cdot a^n \cdot \frac{\Delta E^n}{n!} \quad [3-12]$$

and the current increment, Δi_a as:

$$\Delta i_a = i_a - i_{a-1} = \sum_{n=1}^{\infty} i_{1/2}^{(n)} \cdot \frac{\Delta E^n}{n!} [a^n - (a-1)^n] \quad [3-13]$$

In both equations, [3-12] and [3-13], $i_{1/2}^{(n)}$ is the n-th potential derivative of current evaluated at $E_{1/2}$:

$$i_{1/2}^{(n)} = \frac{d^n i(E_{1/2})}{dE^n} \quad [3-14]$$

The maximum of the Δi vs E curve, Δi_A , appears at a potential, E_A :

$$E_A = E_{1/2} + \frac{1}{2} \Delta E \quad [3-15]$$

where

$$\frac{d(\Delta i)}{dE} = 0 \quad [3-16]$$

and

$$\frac{\Delta i_A}{\Delta E} = i'_{1/2} + i_{1/2}^{(3)} \cdot \frac{\Delta E^2}{24} + i_{1/2}^{(5)} \cdot \frac{\Delta E^4}{1920} + \dots \quad [3-17]$$

with all even derivatives equal to zero. Substituting for $i_{1/2}^{(n)}$ and rearranging we get:

$$\Delta i_A = -i_d \left[\frac{\Delta E}{4} \left(\frac{nF}{RT} \right) - \frac{\Delta E^3}{192} \left(\frac{nF}{RT} \right)^3 + \frac{\Delta E^5}{7680} \left(\frac{nF}{RT} \right)^5 \right] \quad [3-18]$$

The incremental polarograph presented here measures an average current, $\bar{i}$, obtained during the measuring period, $\Delta t = t_2 - t_1$, rather than the instantaneous current defined by equation [3-5]. This average current can be defined as:

$$\bar{i} = \frac{1}{\Delta t} \int_{t_1}^{t_2} i \, dt = \frac{1}{2} \bar{i}_d (1 - \tanh u) \quad [3-19]$$

where $\bar{i}_d$ is the average diffusion current (see Appendix A):

$$\bar{i}_d = 0.627 n F m^{2/3} D^{1/2} C_o \left(\frac{t_2^{7/6} - t_1^{7/6}}{\Delta t} \right) \quad [3-20]$$

Combining equations [3-18], [3-19] and [3-20] we get (12):

$$\Delta \bar{i}_A = k C_o \quad [3-21]$$

where

$$k = -0.627 n F m^{2/3} D^{1/2} \left(\frac{t_2^{7/6} - t_1^{7/6}}{t_2^{1/6} - t_1^{1/6}} \right). \quad [3-22]$$

$$\cdot \left[\frac{\Delta E}{4} \left(\frac{nF}{RT} \right) - \frac{\Delta E^3}{192} \left(\frac{nF}{RT} \right)^3 + \dots \right]$$

Thus in theory, $\Delta i / \Delta E$ can be made to approach di/dE by decreasing ΔE . The corresponding decrease in Δi , however, will result in an increase in the relative error of the measured Δi . Knowledge of di/dE is not required in analytical applications, and neither is the knowledge of the exact equations for Δi as a function of E as long as the maximum, Δi_A , is directly proportional to the bulk concentration of electroactive species.

Equations [3-21] and [3-22] show the peak of the incremental polarogram, occurring at potential $E_A = E_{1/2} + \frac{1}{2} \Delta E$, to be linearly dependent on bulk concentration of the reversibly reducible species, regardless of the size of the potential step. Thus it is possible to obtain accurate quantitative results at low concentrations of the electroactive species using larger ΔE , provided that the peak values of the incremental polarograms can be accurately determined. This can be accomplished without decreasing ΔE by running a series of offset scans limited to the vicinity of the peak and using large steps (20 - 50mV), with each scan starting at a slightly shifted potential (e.g. 2-10mV). Such a procedure, which takes only slightly longer gives the same resolution as if small steps were used, but providing larger Δi and thus improved signal-to-noise ratio.

3.2.2.1 Curve Width

The width of the curve, in addition to the peak height and half-wave potential, is another parameter characterizing the shape of the polarographic wave, as well as the performance of the instrument. The width of the curve at the half-height or the two-thirds-height is often used as a measure of the reversibility of the electrode process (17). The theoretical width of the derivative curve (di/dE vs E) can be calculated at any height relative to the peak from equation [3-23](17):

$$E = E_{1/2} + \frac{2RT}{nF} \ln \left[\left(\frac{I_p}{I} \right)^{1/2} \pm \left(\frac{I_p - I}{I} \right)^{1/2} \right] \quad [3-23]$$

where $I = di/dE$ and $I_p = \frac{i_d}{4}(nF/RT)$ is the peak value of the derivative polarogram.

Solving for $I = I_p/2$ and $I = 2I_p/3$ we get $\frac{90.6}{n}$ mV and $\frac{67.7}{n}$ mV for the half-width and two-thirds-width of the derivative polarogram respectively. The curve-width at two-thirds-height is a more reproducible value, since the derivative has the largest slope here. The two-thirds-height is also a very convenient point for comparison purposes, since here the incremental response $\Delta i/\Delta E$, is equal to the true derivative, di/dE (75) to a good approximation:

$$\frac{\Delta i_a / \Delta E_a}{di_a / dE} = \left[1 + \left(\frac{nF \Delta E}{4RT} \right)^2 \left(\frac{di_a/dE}{di_A/dE} - \frac{2}{3} \right) \right]^{-1} \quad [3-24]$$

In practice, however, it is not always possible to locate accurately the potential and current responses at either two-thirds-height or half-height and interpolation has to be performed. The width of the curve thus becomes dependent on the size of ΔE , as was already shown by Bond (53). Any technique which improves location of the current and potential values at half-height and two-thirds-height (e.g. offset scans) will produce derivative curves with curve shapes closer to the theoretical values. The experimental curve width will be evaluated in Section 5.2.

3.2.2.2 Irreversible Waves

It can be shown that the incremental peak, Δi_A , is proportional to concentration for irreversible waves as well as for reversible. Equation [3-19] can be rewritten for completely irreversible waves as (69)

$$\bar{i} = \frac{1}{2} \bar{i}_d [1 - \tanh \frac{\alpha n F}{2RT} (E - E_{1/2})] \quad [3-25]$$

where α is a potential dependent transfer coefficient. For a quasi-reversible reaction, the bracketed term in equation [3-25] is slightly more complicated (70). However, equation [3-20] is still valid and can be used for quantitative analysis in virtually all cases.

3.2.3 CAPACITIVE CHARGING CURRENT

In potential regions where no charge transfer process takes place, there is still current flowing through the cell; i.e. the current required for charging of the renewed surface of the DME to the applied potential. This is the capacitive charging current.

A general expression for charging current in dc polarography was derived leading to

$$i_c = - C_i^0 E^* \frac{dA}{dt} \quad [2-14]$$

where C_i^0 is specific integral capacitance and E^* is the electrode potential referred to the potential of zero

charge. In order to apply this equation to charging current compensation, the equation has to be modified to a form suitable for the experimental conditions used, namely measurement of average current during the sampling period, Δt .

The dc charging current increment, Δi_{c_a} , at any potential E_a , can be derived starting from the definition of dc charging current, equation [2-14] (for detailed derivation see Appendix B). The change in the charging current upon going from potential $E_{(a-1)}^*$ to E_a^* can be written as:

$$\Delta i_{c_a} = i_{c_a} - i_{c_{(a-1)}} = - \frac{dA}{dt} \left[\Delta E \cdot C_{i(a-1)}^0 + E_a^* \left(\frac{\Delta E}{1!} C_{i(a-1)}^{0'} + \frac{\Delta E^2}{2!} C_{i(a-1)}^{0(2)} + \frac{\Delta E^3}{3!} C_{i(a-1)}^{0(3)} + \dots \right) \right] \quad [3-26]$$

where $C_{i(a-1)}^{0'}$, $C_{i(a-1)}^{0(2)}$ and $C_{i(a-1)}^{0(3)}$ are first, second and third potential derivatives of the specific integral capacitance at potential $E_{(a-1)}^*$ and they originate from the use of Taylor expansion as shown in Appendix B.

Using the basic relationship between integral and differential capacitance (13):

$$C_d^0 = C_i^0 + E^* \frac{dC_i^0}{dE} \quad [3-27]$$

and some mathematical manipulation, Δi_{c_a} can be expressed as a function of specific differential capacitance, C_d^0 , in terms of the Taylor polynomial

$$\Delta i_{c_a} = -\frac{dA}{dt} \left[\frac{\Delta E}{1!} C_{d(a-1)}^o + \frac{\Delta E^2}{2!} C_{d(a-1)}^{o'} + \dots + \frac{\Delta E^n}{n!} C_{d(a-1)}^{o(n-1)} \right] \quad [3-28]$$

in order to derive an equation pertinent to the instrumentation. Since the instrument measures average current increments during the sampling period Δt , equation [3-28] needs to be integrated and converted to the absolute differential capacitance values. Equation [3-29] shows such an expression obtained by neglecting the higher order terms in equation [3-28]:

$$\Delta I_{c_a} = -\frac{\Delta E}{\Delta t} [C_{d(a-1),t_2} - C_{d(a-1),t_1}] \quad [3-29]$$

Here ΔI_{c_a} is the average charging current increment and $C_{d(a-1),t_2}$ with $C_{d(a-1),t_1}$ are experimental values of differential capacitance measured with DME at potential $E_{(a-1)}^*$ at the end and beginning of the sampling period respectively.

In the potential regions where the C_d vs E curve shows a large slope, higher order terms in equation [3-28] might be required. When this is the case, the potential derivative of C_d can be approximated by the incremental ratio, e.g.:

$$C_{d(a-1)}^{o'} \approx \frac{\Delta C_{d(a-1)}^o}{\Delta E} = \frac{C_{d(a-1)}^o - C_{d(a-2)}^o}{\Delta E} \quad [3-30]$$

In the work presented here, the first two terms in equation [3-28] were employed to calculate the charging current com-

pensation according to

$$\Delta \bar{I}_{c_a} = - \frac{\Delta E}{\Delta t} \left\{ \frac{3}{2} \left[c_{d(a-1),t_2} - c_{d(a-1),t_1} \right] - \right. \quad [3-31]$$

$$\left. - \frac{1}{2} \left[c_{d(a-2),t_2} - c_{d(a-2),t_1} \right] \right\}$$

Note that the average charging current compensation, $\Delta \bar{I}_c$ (equation [3-31]), is defined by terms in t_1 and t_2 , but does not depend explicitly on the electrode area. The usual assumption that the latter is a function of $t^{2/3}$ and the flow rate of mercury is not required here for measuring of $\Delta \bar{I}_c$. Subtracting $\Delta \bar{I}_c$ from the average cell current increment, $\Delta \bar{I}_t$, leaves only the pure faradaic component, $\Delta \bar{I}_f$, which is directly proportional to the concentration of the measured species (see equation [3-20]).

3.2.4 DIFFERENTIAL DOUBLE LAYER CAPACITANCE

DETERMINATION BY PHASE-NULI TECHNIQUE

The following section describes the phase-null method for determination of the differential double layer capacitance and its application to charging current compensation. As was shown in Section 2.2.2, the ac charging current, $i_c^{\sim}$, is given by

$$i_c^{\sim} = C_d^O A \frac{dE}{dt} \quad [2-17]$$

A judicious choice of experimental conditions gives a faradaic impedance much larger than the double layer

impedance, causing virtually all of the ac current to flow through the double layer. When this condition is fulfilled, the equivalent circuit shown in Figure 3.1 is reduced, in effect, to a simple series RC network (see Figure 3.2).

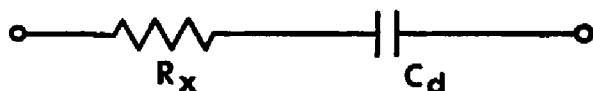


Figure 3.2 Simplified Cell Impedance.

When this approximation is valid, C_d can be determined by connecting the cell to the input of an operational amplifier, O.A., with a series RC network in its feedback loop (see Figure 3.3).

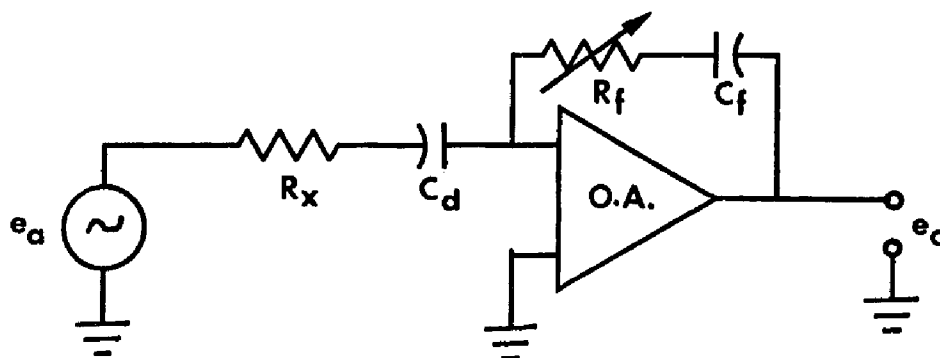


Figure 3.3 Experimental Arrangement for Phase-Null Measurements Used by Schwartz (52).

R_x - C_d is the cell impedance shown in Figure 3.2, C_f is feedback capacitor, R_f is an adjustable feedback resistor and e_a with e_o are input and output voltages, respectively. Nemec (71) used such arrangement for studies of capacitance in absence of faradaic current.

If R_f is adjusted so that the phase of e_o matches that of e_a , the phase angle of the feedback and cell impedance can be shown to be equal, and the gain of the operational amplifier, O.A., is given by (52)

$$G = \frac{e_o}{e_a} = \frac{C_d}{C_f} \quad [3-32]$$

Schwartz (52) used this arrangement to measure C_d of various systems in the absence and presence of faradaic process. He named this approach the phase-null method.

The necessity to provide separate paths for faradaic current and the ac current places limitations on this simple configuration. To avoid experimental difficulties, a shunt resistor is placed across the R_f - C_f feedback elements to provide a path for dc current. This modification changes the gain of the amplifier from equation [3-32] to (52):

$$|G| = \frac{C_d}{C_f} \left[1 + \frac{\sin \Delta \alpha}{\tan \alpha_f} - \frac{2 \cdot R_f}{R_s} \right] \quad [3-33]$$

where α_f is the phase angle of the feedback network, $\Delta \alpha$ is the phase shift between the output of O.A. and the applied signal ($\Delta \alpha < 0.3^\circ$), and R_s is the shunt resistor. The error created by the shunt resistor and the uncompensated phase-shift, $\delta \alpha$, was analyzed earlier by Schwartz (52).

To reduce the limitation imposed by the need for the faradaic path, a slightly different configuration was used in this work (see Figure 3.4). The input into the amplifier, O.A. is a potential drop created by the cell current,

i_{cell} , across the measuring resistor, R_m , in parallel with the transformer impedance. Assuming that the impedance of the blocking transformer is constant in the frequency range used, the output of O.A. can be written as (see Appendix C for derivation)

$$e_o = \frac{C_d}{C_f} \cdot \frac{R_m \cdot a}{R_i} e_a \quad [3-34]$$

where a is the signal gain in the transformer, R_i is an input resistor and the rest of the variables are as described in Figure 3.3.

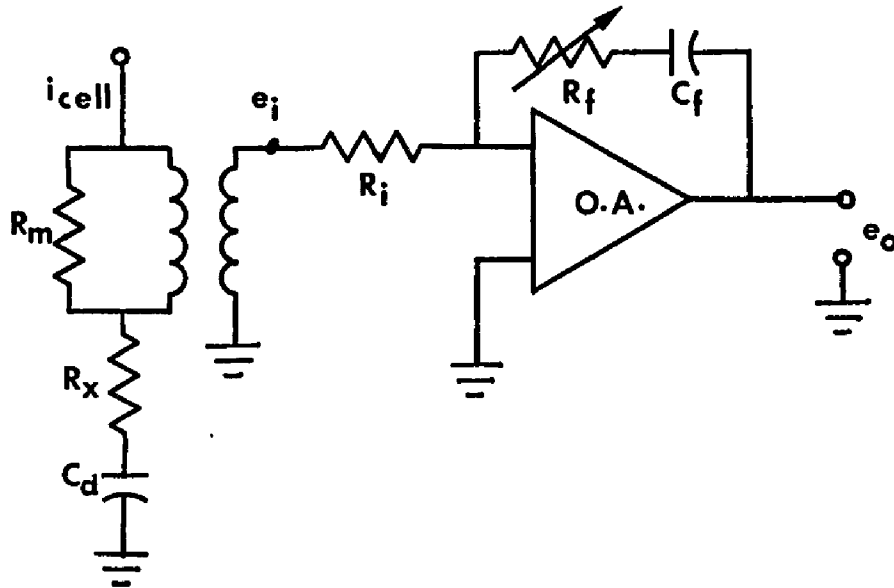


Figure 3.4 Experimental Arrangement for Measurement Used in this Work.

In practice, the output of the operational amplifier, O.A., and the applied ac signal are multiplied using a multiplier module whose output, E_o , is governed by (72)

$$E_o = \frac{1}{10} [A \sin(\omega t) \cdot B \cos(\omega t + \phi)] \quad [3-35]$$

where $A \sin(\omega t)$ is the applied ac signal and $B \cos(\omega t + \phi)$ is the output of O.A. phase-shifted by $(90 + \phi)$ degrees. As long as there exists a phase shift, ϕ , between these two signals, the output of the multiplier will contain a dc component proportional to ϕ by equation [3-36] (see Appendix D for derivation):

$$D_{\phi} = \frac{-AB}{2\theta} \sin \phi \quad [3-36]$$

The phase null can be maintained automatically by a negative feedback system in which, for example, R_f is a photoconductive cell whose resistance depends on the light output of the lamp shining on it, which in turn depends on D_{ϕ} . As long as there is considerable phase difference between the signals, the R_f will change to drive the system closer to the phase null (zero phase error). The actual arrangement of the circuits for measuring C_d and maintaining the phase null are described in Chapter 4.

3.2.5 CONDITIONS UNDER WHICH THE FARADAIC IMPEDANCE MAY BE NEGLECTED

When the double layer impedance acts as a pure capacitance it can be expressed as

$$Z_d = \frac{1}{2\pi f C_d} \quad [3-37]$$

where C_d is double layer capacitance and f is the ac frequency. The faradaic impedance, on the other hand, was

given by equation [3-2]:

$$Z_f = \Theta + W_{\sigma} \quad [3-2]$$

where the activation polarization, Θ , behaves as a pure resistance. It depends exponentially on dc polarization voltage and is inversely proportional to the rate constant of the electrochemical reaction, k_{SH} , and the concentration of the electroactive species. The Warburg impedance, W_{σ} , is due to the finite rate of mass transfer of the electroactive species to the electrode surface. W_{σ} is a complex quantity which behaves as resistive and capacitive components connected in series that remain of equal magnitude over the whole frequency range (73,74):

$$W_{\sigma} = \sigma(2\pi f)^{-1/2} - j\sigma(2\pi f)^{-1/2} \quad [3-38]$$

where σ is a quantity that is inversely proportional to the concentration of the electroactive species and it depends exponentially on the applied dc voltage and the diffusion coefficients.

3.2.5.1 DC Potential.

Both σ and Θ increase exponentially as a function of $|E - E_{1/2}|$, where E is the electrode potential and $E_{1/2}$ is the half-wave potential of the electroactive species. Thus for an electrode reduction of a given species, at electrode potentials sufficiently more positive than $E_{1/2}$, there will

be no electrode reaction and it will hold that $Z_f \gg Z_d$, which is the desired condition to simplify the equivalent circuit.

3.2.5.2 Concentration of Electroactive Species.

The value of the faradaic impedance, Z_f , is indirectly proportional to concentration of the electroactive species (74), thus the lower the concentration, the greater the Z_f will be and more valid the approximation that $Z_f \gg Z_d$. When no electroactive species is present in solution, as is the case in pure supporting electrolyte solutions, $Z_f \rightarrow \infty$ and the simplified equivalent circuit, Figure 3.2, is an exact representation of the electrode - solution interface.

3.2.5.3 Frequency.

As was shown in equation [3-37] double layer capacitance, Z_d , is indirectly proportional to the applied frequency. The faradaic impedance, on the other hand, is a sum of purely resistive activation polarization, θ (independent of frequency) and a Warburg impedance, W_ω , which according to equation [3-38] is inversely proportional to the square root of frequency. Thus as the frequency is increased, Z_d approaches zero, while Z_f approaches θ :

$$\lim_{f \rightarrow \infty} Z_d = 0 \quad [3-39]$$

and

$$\lim_{f \rightarrow \infty} z_f = \theta \quad [3-40]$$

Moreover, Z_f approaches its limit more slowly (as $\omega^{1/2}$) than does Z_d (as ω). Thus it is true for any electrode reaction that at sufficiently high frequency of the applied ac signal, $Z_f \gg Z_d$. In the case of a slow electrode reaction where the rate constant, k_{SH} , is small and thus causes θ to be large, Z_f reaches its limit at relatively low frequency. Since, both θ and Z_f are large, the condition that $Z_f \gg Z_d$ is valid even at relatively low frequencies. For fast reactions, where k_{SH} is large and thus θ is small, a measuring signal of much higher frequency will be necessary for the approximation to be valid.

Chapter 4

EXPERIMENTAL

4.1 INSTRUMENTATION

The instrument constructed and used for charging current compensation is based on a previously described incremental polarograph (75) and circuits developed by Schwartz for differential double layer capacitance measurements (52). The new instrument incorporates a digital mini-computer for timing, current averaging and subtraction functions, in addition to operational amplifiers for analog measurements. The computer interfacing also allows easier selection of experimental variables, statistical manipulation, calculation of charging current and its compensation, and plotting of the results. The experimental data and results can be stored, and if necessary, transferred to a larger computer for additional processing. The advantages of computer interfacing have already been pointed out by Bond and Grabaric (76), Smith (77) and Bond (30). Applications of operational amplifiers to electrochemistry have been reviewed by Smith (77), Reilley (78), Booman and Holbrook (79), Schwartz and Shain (80), Vassos and Ewing (81),

and recently Bard and Faulkner(31).

4.1.1 DESCRIPTION OF OPERATIONS

The functional characteristics of the instrument are shown in the block diagram, Figure 4.1, with detailed discussion of each functional block given in Appendix E.

The applied potential consists of sinusoidal ac signals for measuring of C_d and drop-fall trigger, superimposed on the dc polarizing "staircase" scan. The potential of the DME, with respect to the reference electrode, is maintained by potentiostatic control at a value defined by the ac and dc voltages.

The ac and dc components of the cell current are separated at the output of the potentiostat. The dc component is passed to the dc measuring network, consisting of a differential instrumentation amplifier and a low-pass filter. The instrumentation amplifier configuration allows a direct connection of DME to ground, instead of the virtual ground of a current-to-voltage converter (82). The dc response of the cell is sampled through an analog-to-digital converter (ADC) by the minicomputer, at intervals based on the drop-fall trigger.

The ac response of the cell is transferred from the potentiostat circuit into the ac measuring circuit through a transformer. The output of the ac measuring network is proportional to C_d , as was shown in equation [3-31], provided

Figure 4.1

Block diagram of the instrument.

Symbols used are:

A - Auxiliary electrode.

R - Reference electrode.

W - Working electrode.

C_d - Differential double layer capacitance.

E - DME potential.

i - Cell current.

t - Drop-fall pulse.

ADC - Analog-to-digital converter.

ST - Schmitt trigger input.

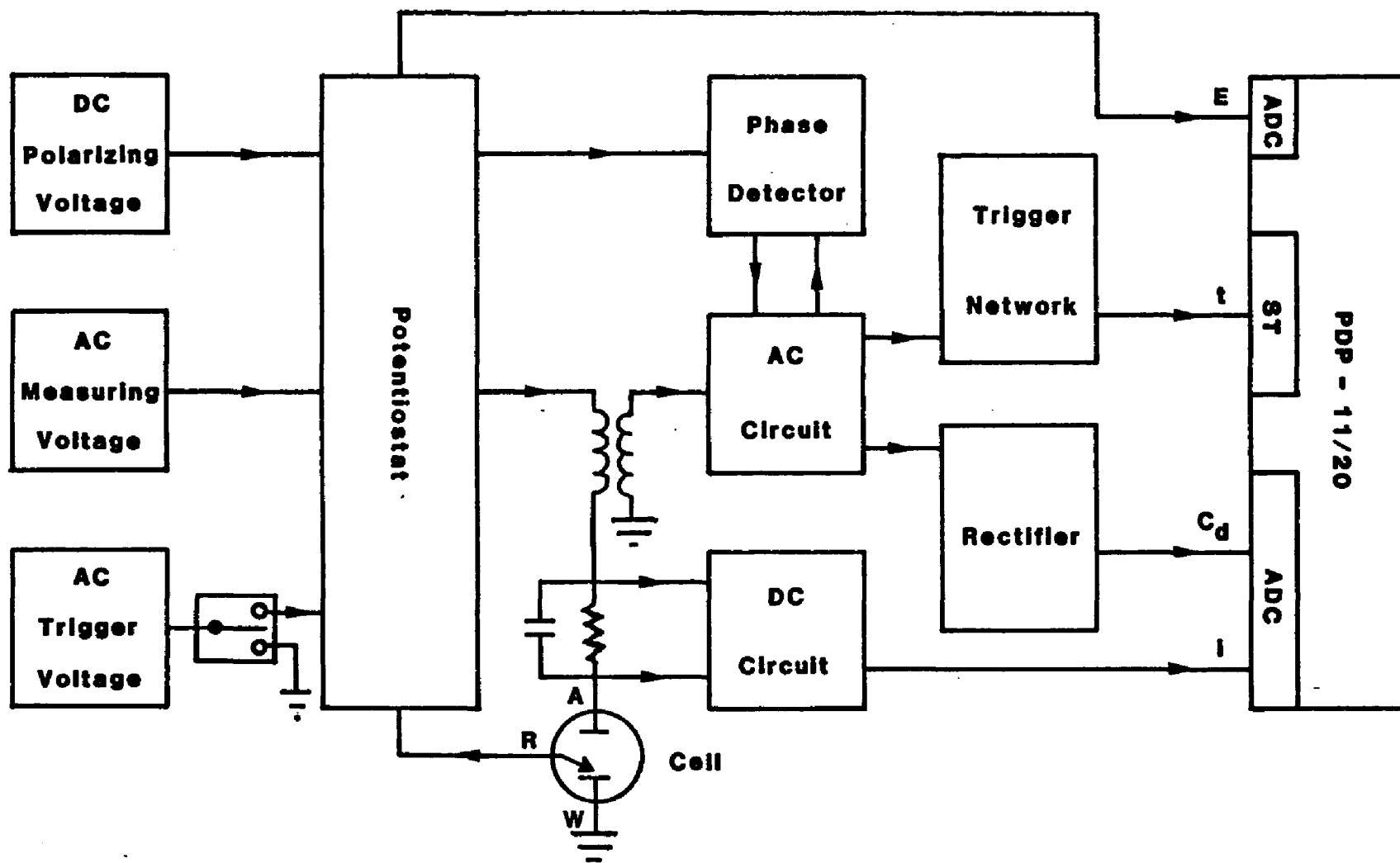


Figure 4.1 Block Diagram

that the phase-null condition prevails. It is the function of the ac measuring circuit in conjunction with the phase detector to enforce the phase-null condition, and thus facilitate correct measurement of C_d . The enforcement of the phase-null is accomplished through use of negative feedback on the ac measuring amplifier.

The phase detector compares the applied ac signal to the output of the ac measuring amplifier. If a phase-shift exists between the two signals, the resulting dc component of the detector output (see Appendix D for equations) drives the light emitting diode (LED), changing its brightness. This in turn affects the value of the photoresistor, R_f , of the feedback circuit ($R_f C_f$) and consequently the phase-shift and amplitude of the ac measuring signal. In order to satisfy equation [3-31], the phase-shift of the feedback network, $R_f C_f$, is kept to within 0.3 degrees. The rectified output of the ac measuring network, proportional to the C_d , is then sampled by the minicomputer through the ADC at preprogrammed intervals.

To increase the signal-to-noise ratio, the new instrument employs digital averaging of the measured signal. However, neither the dc current nor C_d are constant during the drop-life. They vary as a function of the electrode area (see equations [3-5] and [2-21]). Thus in order to provide meaningful results, the timing associated with the measurements must be reproducible from one drop to the next. This is accomplished by accurate detection of the drop-fall,

which is then used as a reference point in all timed measurements. This provides reproducibility in time and therefore in electrode area, since the latter is a function of time.

The drop-fall detector employed in this instrument is based on detection of the increase in electrode impedance at the drop-fall, using a high frequency ac signal (33). This change in the impedance is converted by the drop-fall trigger circuit to a pulse, which starts an accurately timed sequence of operations, described in detail in the next section.

The computer is equipped with a lab peripheral interface, and is used to sample and store the signals corresponding to the dc cell current (i), electrode potential (E), and differential double layer capacitance (C_d), by following a preprogrammed sequence described in the next section. All calculations and plotting for this work were done using IBM or AMDAHL mainframe computers at the City University Computer Facility.

4.1.2 SEQUENCE OF OPERATIONS

The programmed sequence of operations can be divided into five tasks (Table 4.1). The parameters entered by the operator in Task 1 are listed in Table 4.2, while Figure 4.2 shows the timing sequence for Tasks 2 and 3, data collection and potential control, during three consecutive cycles.

Table 4.1 Sequence of Operations.

- Task 1 - Operator enters the instructions and values of parameters for run and calibration, performs the calibration and leaves the computer ready to start the run.
- Task 2 - After receiving the drop-fall pulse, the computer starts the timing sequence and samples, averages and stores values of E, i and Cd.
- Task 3 - Computer controls the electrode potential, checks for the end of run and turns the triggering ac on and off.
- Task 4 - When the run is finished, the minicomputer checks its connection to the larger computer and transfers the data for storage and future use. If the connection cannot be established, the minicomputer stores the data using its own permanent paper tape storage device.
- Task 5 - The mainframe computer converts the input numbers into calibrated values of Cd, $\bar{I}$ and E, calculates $\Delta \bar{I}$, $\Delta \bar{I}_c$ and $\Delta \bar{I}_f$, and returns the results in the form of a printout, graph or both.

Table 4.2 Parameters Entered in Task 1.

date
sample identification
run number
assignment of ADC channels to i, E, and Cd
delay time
sampling time
potential limit
number of drops at one potential
filling-in option
value of instrumentation resistor, R_m
permanent storage destination
calibration values: E, R_{dummy} and C_{dummy}

Figure 4.2.

Timing sequence.

E_{DME} - Potential of the DME vs the SCE reference electrode.

I_{cell} - dc cell current.

I_{out} - Current measuring period.

E_{out} - Potential measuring period.

C_{out} - Capacitance measuring period.

ΔI - Current output of the auxiliary circuit for recording of approximate incremental polarograms.

t_{0i} - Drop fall of the i-th drop, beginning of the delay period.

t_{1i} - End of delay period, beginning of measuring period.

t_{2i} - End of measuring period.

t_{3i} - Time of potential increment.

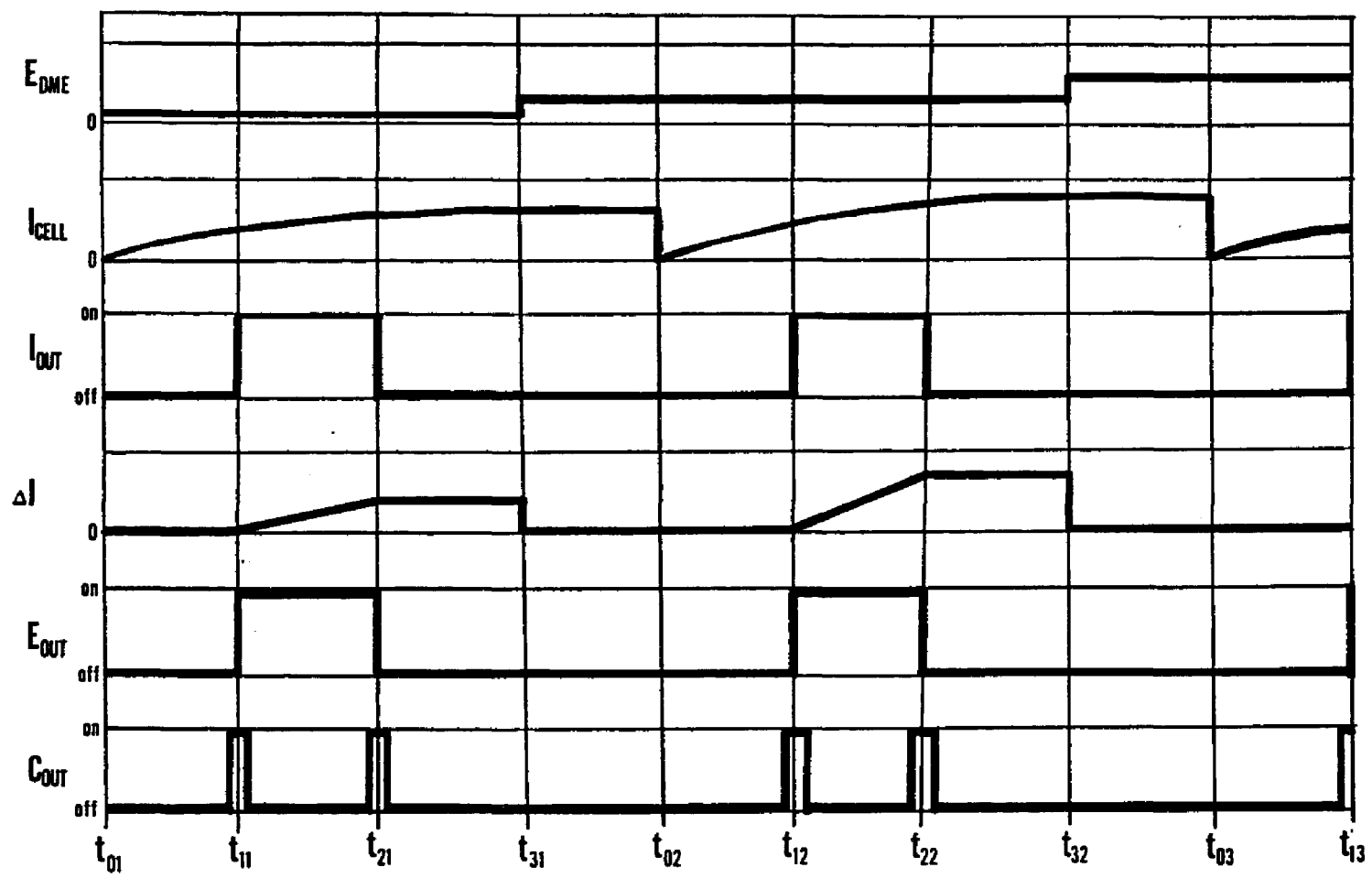


Figure 4.2 Timing Sequence

The sequence of operations is controlled by the computer's internal clock and initiated for each drop by the trigger pulse, generated at the drop-fall. At this time, t_0 , the delay period begins, and the high frequency trigger detection signal is turned off. The end of the delay period, time t_1 , initiates a series of pulses one millisecond apart, lasting until the end of the measuring period, t_2 . Each one of these pulses initiates analog-to-digital conversions of the DME potential, dc current and C_d in the following manner: (i) the first two and last two pulses initiate capacitance conversion only, (ii) the third, fourth and fifth pulse from the beginning and the end of the measuring period initiate conversion of all three variables, and (iii) all intermediate pulses initiate conversion of current, immediately followed by conversion of potential. All of the current and potential values are summed and at the end the result is divided by the number of points taken, producing average current and potential values. A similar procedure is used to obtain the two capacitance values; one at the beginning and one at the end of the measuring period.

When the measuring period is over, the computer starts Task 3, shown schematically in Figure 4.3. A 50 millisecond delay is initiated, during which the potential value is checked for the preprogrammed end of the run. If the end of the run is reached, the computer goes to the output mode (Task 4) and waits for the instruction to start data transfer to permanent storage. If the end of run is not

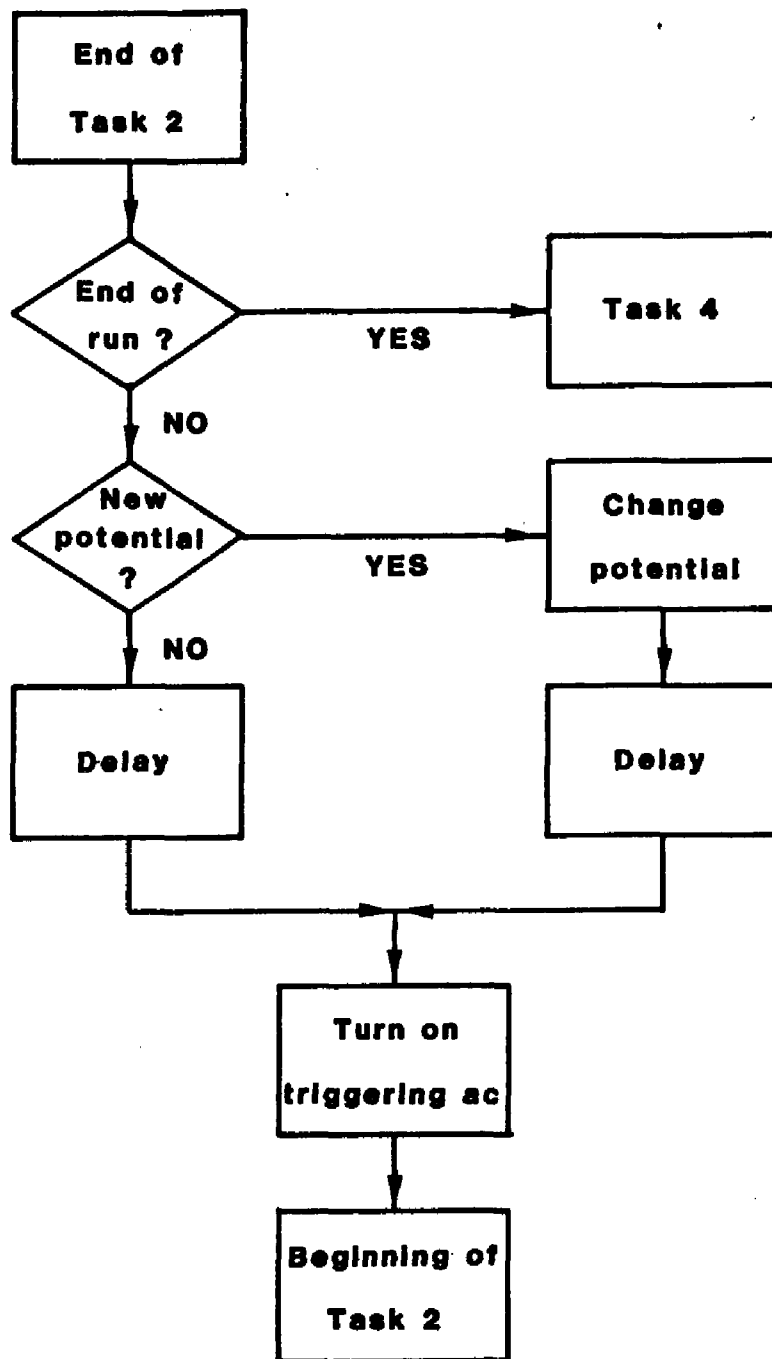


Figure 4.3 Schematic Diagram of Task 3

reached, the computer checks if the potential is to be increased for the next drop. If the answer is YES, the potential is increased by ΔE at time t_3 and the high frequency ac is turned back on at time t_4 . If the next drop is to stay at the same potential, a longer delay is initiated and the high frequency is turned on at the same time t_4 , 500 milliseconds after the end of sampling period. Once the triggering signal is back on, the computer starts Task 2 again, by returning to a waiting loop, set for the next trigger pulse. When the pulse is detected, the timing sequence is repeated.

4.2 EQUIPMENT

4.2.1 CELL

A diagram of the cell used in this work is shown in Figure 4.4. The cell was constructed from borosilicate glass with a teflon stopcock. Four ground joints were provided on the top of the cell for the three electrodes and an argon bubbler tube. The latter was a piece of 6mm glass tubing sealed on the bottom, with a few small holes in the bottom portion under solution. The fifth opening provided an inlet port for passing a stream of argon over the solution during the experiments. The cell was equipped with a water jacket sealed onto it. Water at $25.0 \pm 0.1^\circ\text{C}$ was pumped through the jacket. The water hoses were disconnected dur-

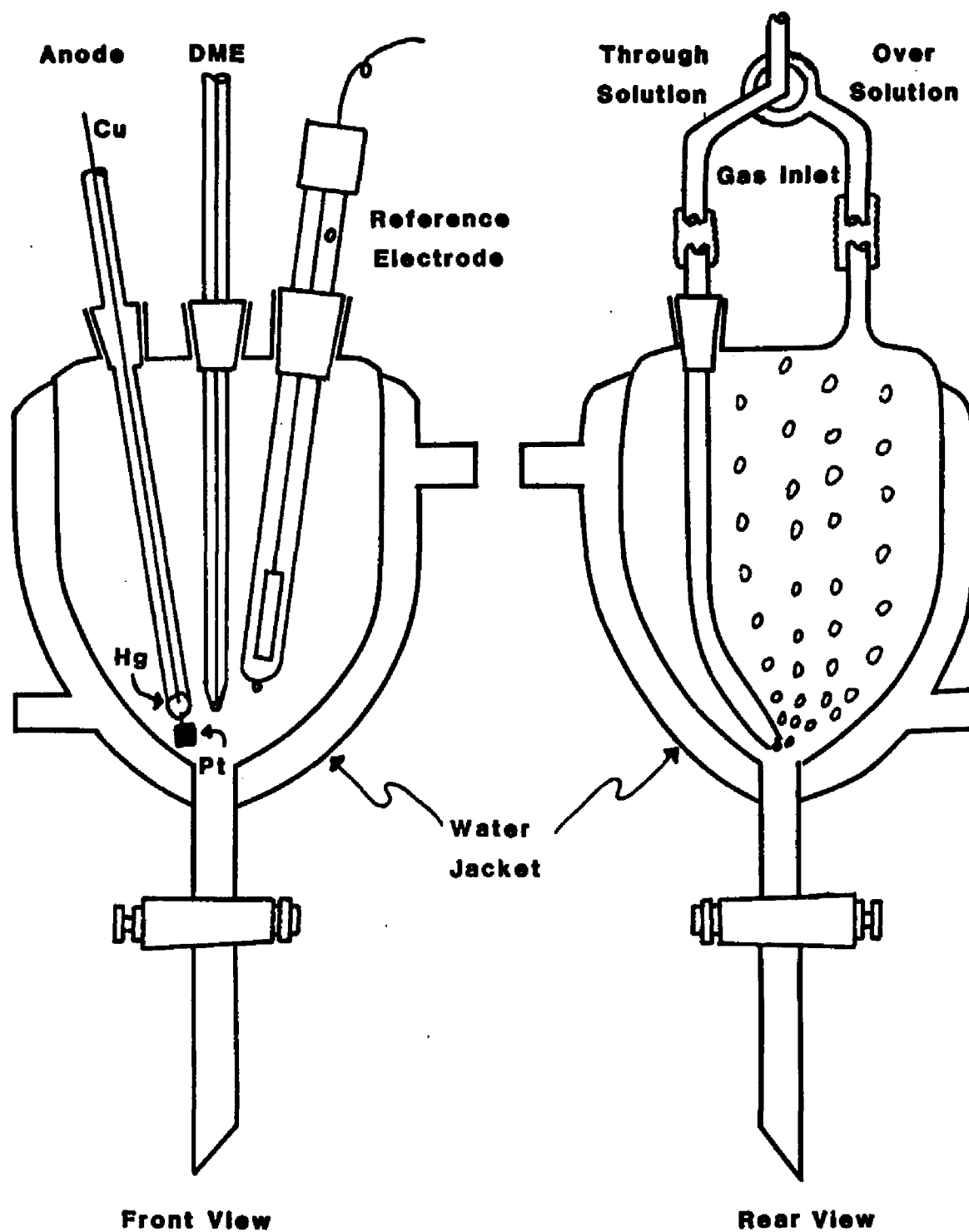


Figure 4.4 Cell

ing the run to avoid vibrations. A teflon stopcock at the bottom of the cell permitted periodic withdrawal of mercury for flow rate determinations, and easy cleaning of the cell. The active volume of the cell was approximately 100ml.

4.2.2 ELECTRODES

The electrodes used in all experiments were a pressurized DME, a platinum auxiliary electrode and a calomel reference electrode with 3.5M KCl salt bridge.

4.2.2.1 Dropping Mercury Electrode

The pressurized DME (Figure 4.5) was constructed from borosilicate glass, 316 stainless steel and teflon.

The capillaries used were constructed from "Common Spirit white back" thermometer tubing (Corning Glass Co.) with inner diameter of approximately 0.076mm and outer diameter of approximately 3.3mm.

The glass reservoir was partly filled with mercury and pressurized with argon. All capillaries used had drawn-down tips approximately 5mm long, with inner diameter at the tip of about 0.038mm. A teflon reducing union was used to attach the capillaries to the assembly, enabling easy exchange of the capillaries. A stainless steel tube with outer diameter of 0.25 inches was used to provide electrical contact to the DME. A Z-shaped piece of glass tubing connecting the

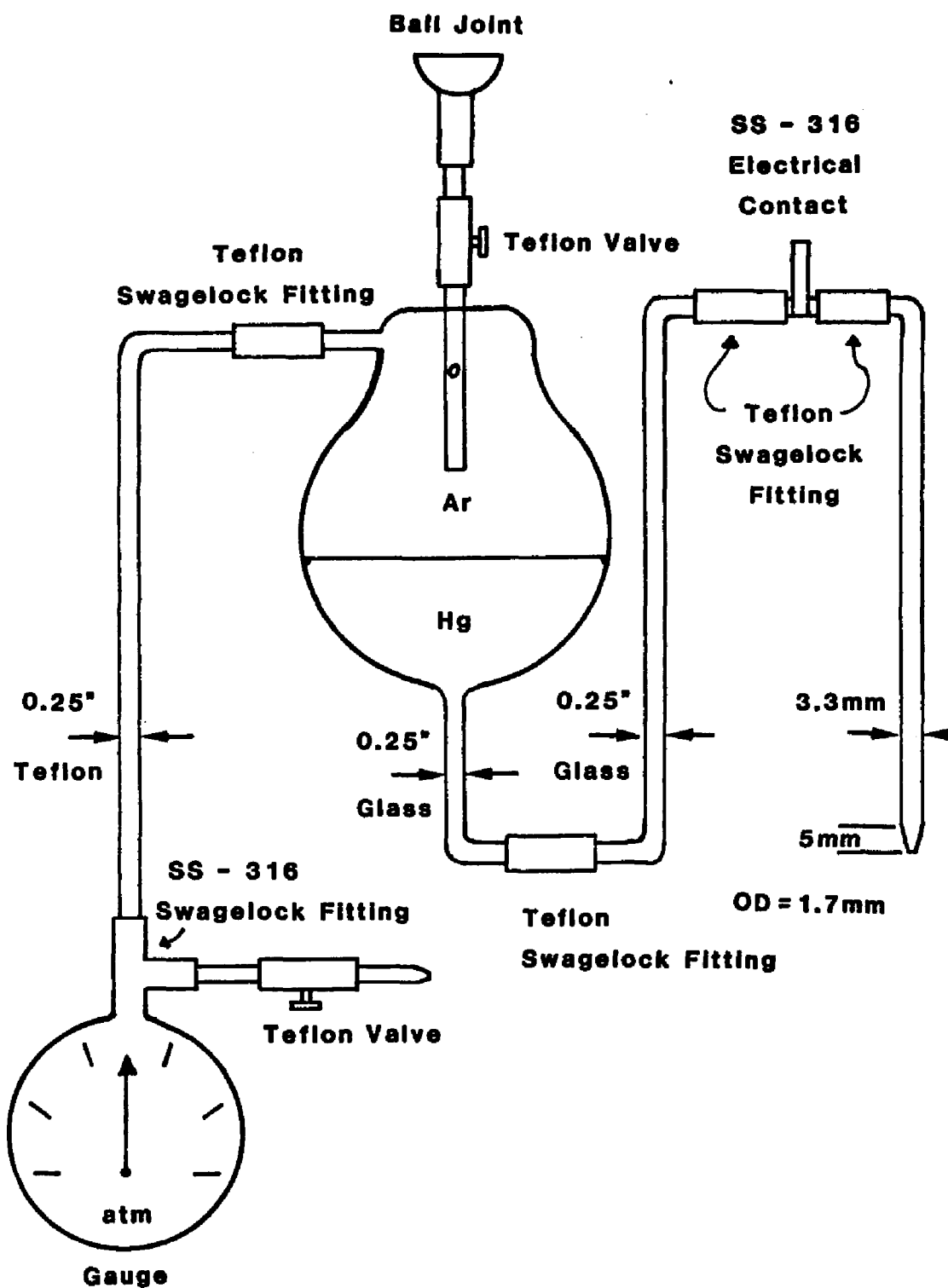


Figure 4.5 Dropping Mercury Electrode

capillary to the reservoir allowed the position of the DME to be easily adjusted.

The reservoir was flushed with argon, filled with mercury and pressurized through the top outlet, controlled by a teflon valve fitted with a glass tube ending in a ground ball-joint. The pressure of the argon above the mercury was read from a five-inch diameter, stainless steel gauge; it was adjusted by operating a teflon relief valve fitted with a capillary for better control. The pressure gauge was also used to monitor any pressure changes during the experiment.

The DME had a flow rate of about 1.0mg/sec and a drop-time in deaerated 1M KCl on open circuit of about 5.5 seconds at a pressure of 0.6 atm of argon, and with the mercury meniscus at the same level as the capillary tip. The resistance of the mercury column, measured from the tip to the stainless steel connector ranged from 50 to 100 ohms, with most capillaries used having a resistance of about 70 ohms.

4.2.2.2 Auxiliary Electrode

The auxiliary electrode was constructed by fusing a piece of platinum about 10mm x 7mm, into a piece of borosilicate glass tubing. The top of the tubing had a ground joint for insertion into the cell. Electrical contact to the auxiliary electrode was made by partly filling the glass tube with mercury and inserting into it a copper wire.

4.2.2.3 Reference Electrode

Reference electrodes used for all the experiments were "Dual-glass Junction" calomel electrodes (Leeds & Northrup Co. #117208) filled with 3.5M KCl. Three such electrodes were kept in a beaker filled with 3.5M KCl at 25°C. Before each set of runs these three electrodes were compared to each other, and periodically to a group of three saturated calomel electrodes of the same construction, kept under identical conditions. The electrodes filled with 3.5M KCl always agreed to better than 1mV, as did the SCEs. All experiments were performed using 3.5M calomel electrode, with results converted to values referred to SCE by adding to the potential reading the difference between SCEs and 3.5M calomel electrodes in 1M KCl.

4.2.3 INSTRUMENTAL ASSEMBLY

The cell with the electrodes and the stand was mounted on a vibration isolation table. The assembly consisted of a soap-stone plate loaded with a sand-filled stand and four lead bricks mounted on four spring mounts. The use of a vibration isolation table was necessary to eliminate building vibrations. In some cases vibrations were so pronounced, that drop vibrations were clearly visible to the naked eye and drops were sometimes detached prematurely. The assembly was designed to keep the center of gravity as low as possible, and to limit the transmission of vibrations through

wire connections and deaeration tubing.

4.3 SOLUTIONS AND CHEMICALS

The water used in preparation of all solutions was deionized through an ion exchange cartridge (Barnstead Co.) and then doubly distilled, with the second distillation from alkaline KMnO_4 , carried out in a quartz still. All chemicals were of ACS reagent grade (Baker or Fisher) and were used without further purification. The mercury used for the DME was triply-distilled, instrument grade (Bethlehem Apparatus Co.) with less than 0.1ppm residue on evaporation. The DME was filled by pouring mercury slowly through a pinholed filter paper. Argon of 99.995% purity (Linde Co.) was used for deaeration and pressurization of the DME. The gas line was constructed from teflon and glass tubing. The argon was presaturated with water vapor by passing it through a scrubbing tower filled with distilled water and immersed in water bath at 25.0°C . The gas was then directed via a three-way stopcock either through the solution or over it.

4.4 PROCEDURES

4.4.1 CALIBRATION OF ELECTRONICS

The calibration of the instrument can be divided into three independent procedures. One procedure, usually performed daily before the start of the experiments, involved checking and adjustment of the output offsets of the operational amplifiers. The second procedure was concerned with maintenance of the phase null, and setting of the operating point of the feedback system. This procedure was performed periodically every few runs, or whenever there was a change in the measuring frequency. The need for this procedure stemmed from the assumptions made in the process of deriving equation [3-31]. In the derivation, transformers used in the instrument were considered to have a constant impedance and the phase of the measuring signal at the multiplier input was considered to be shifted by exactly $90 + \phi$ degrees from the phase of the reference signal. In reality, however, not only the transformers, but also the amplifiers contain phase-shifts, so a variable phase-adjusting network was included in the feedback network of the ac measuring circuit (see Appendix E) to adjust the phase difference of the two signals to exactly $90 + \phi$ degrees. The actual calibration, described in greater detail in Appendix E, consists of several steps and makes use of a "dummy cell" (Figure 4.6).

The dummy cell circuit is shown within the dashed line of Figure 4.6. Resistor R_{DA} with a value of 250 ohms simu-

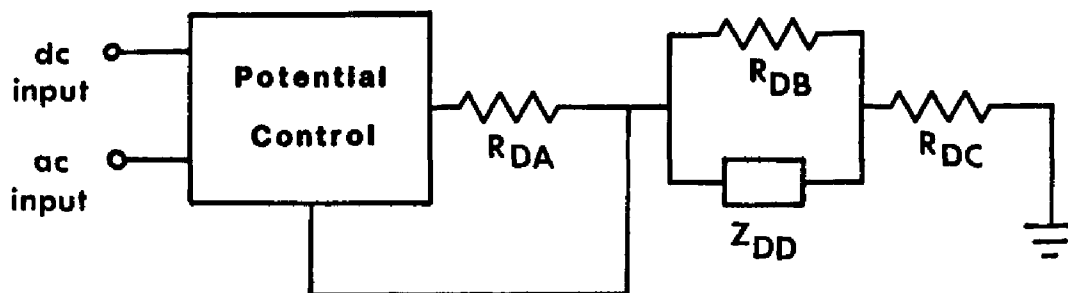


Figure 4.6 Dummy Cell Circuit.

lates the solution resistance. Resistor R_{DB} with a value of 1 Mohms simulates the faradaic dc path. Z_{DD} is a standard variable capacitor or a resistor of similar impedance, simulating the double layer capacitance. Resistor R_{DC} has a value of 50 to 200 ohms and is used to simulate the resistance which is uncompensated by the potentiostat; it is mainly due to the resistance of the mercury thread in the DME.

For calibration, impedance Z_{DD} , expressing the double layer capacitance is replaced by a pure resistor, thus creating a zero phase-shift in the dummy cell. The variable phase-shifting network is then adjusted until the dc component of the multiplier is reduced to zero. At that point the instrument is ready for experiment.

The third and last procedure is performed as an initial part of each run. For this calibration the instrument is set up in exactly the same way as during the run. The only difference is substitution of dummy cell for the polaro-

graphic cell. The calibration establishes the relationship between the instrumental response and the electrode potential, cell current and the differential double layer capacitance. In the calibration itself, an accurately known potential is applied to the dummy cell and the electrode potential, cell current and C_d are measured by the minicomputer, as they would be in a real run. All components of the dummy cell are accurately known, enabling the evaluation of measured parameters. A decade capacitor (General Radio Corp. type 980A) was used to simulate the double layer capacitance, Z_{DD} . The value of the capacitor could be varied from 0 to $1.0\mu\text{F}$ in $0.1\mu\text{F}$ steps. Each value of the capacitor was checked on a Wayne-Kerr Universal Bridge, model B221, and all were found to be within 3ppt of the nominal value. The resistor R_D was varied from 1 Mohm to 10 Mohms and R_{DC} from 50 ohms to 200 ohms. Their values (listed in Appendix F) were obtained using a PVB instrument. The dc current through the dummy cell was calculated as a ratio of the applied potential and the sum of resistors R_{DB} and R_{DC} .

The calibration consists of two to ten samplings of applied potential, cell current and C_d , all with the identical applied potential and resistor R_{DB} and R_{DC} , but each one taken with different capacitance value, Z_{DD} . The sampled values of applied potential and cell current are independent of capacitance. A statistical Q-test was then applied to eliminate improbable points, and the rest of the values were averaged by the computer and used to obtain conversion fac-

tors needed to translate the instrument readings into the potential and cell current in runs with a polarographic cell. The capacitance results obtained with the dummy cell were used to construct a calibration curve, which was then used to calculate the values of C_d . The timing sequence of the computer during the calibration was kept the same as during the run, with exception of the operations concerned with the trigger.

4.4.2 DATA ACQUISITION

Each run consisted of calibration and one or more potential scans, depending on whether the fill-in option was in effect. During the course of each run the computer measured electrode potential, cell current and C_d , stored the values, converted the instrument readings into the absolute values using the conversion factors, calculated current increments and capacitive charging current, performed the charging current compensation and stored the results for future plotting and printout. During the initial interchange between the operator and the computer, the following variables were set: delay time, measuring period, potential at the end of the scan, number of drops at the same potential, the fill-in option and assignment of ADC channels. Other instrumental parameters, such as gain setting, step size, initial potential, frequency, instrumentation resistor and phase-null capacitor were set manually before the calibra-

tion procedure.

4.4.3 CALCULATIONS

The calculations performed by the computer can be divided into eight tasks:

1. Determination of conversion factors from calibration data.
2. Conversion of instrument outputs into absolute values using conversion factors.
3. Performing the Q-test on the data to eliminate improbable points.
4. Calculation of first and second increments.
5. Calculation of charging current increments.
6. Charging current compensation.
7. Using polynomial smoothing routine for plotting.
8. Plotting and printing of the results.

The conversion factors for electrode potential and cell current were obtained from the following equations:

$$EFACT = \frac{CALVOL}{ECAL} \quad [4-1]$$

and

$$CFACT = \frac{CALVOL}{RDUMMY} \cdot CCAL \quad [4-2]$$

where EFACT and CFACT are the potential and current conversion factors respectively, CALVOL and RDUMMY are values of input potential and R_{DB} used in the dummy cell (see Figure 4.5), and ECAL and CCAL are averaged instrument outputs for potential and current ADC channels obtained during calibration and screened by Q-test. The capacitance conversion is obtained by plotting a calibration curve; the instrument output of the capacitance ADC channel as a function of the value of the capacitor in the dummy cell.

The data from each run are converted to absolute values using the following equations:

$$E = EIN.EFACT \quad [4-3]$$

$$CUR = CURIN.CFACT \quad [4-4]$$

$$CSUBD = BINT + ASLOPE.CDIN \quad [4-5]$$

where E, CUR, and CSUBD are absolute values of potential, current and capacitance; EIN, CURIN, and CDIN are readings of the potential, current and capacitance ADC channels; BINT and ASLOPE are the intercept and slope values respectively of the capacitance calibration curve.

If more than one drop is held at the same potential, the converted data is checked by a Q-test routine and averaged before further calculations. Current increments are then calculated by subtracting consecutive current readings and storing them in arrays. The charging current increments are calculated according to equation [3-31]:

$$\Delta \bar{I}_{c_a} = - \frac{\Delta E}{\Delta t} \left\{ \frac{3}{2} \left[C_{d(a-1),t_2} - C_{d(a-1),t_1} \right] - \frac{1}{2} \left[C_{d(a-2),t_2} - C_{d(a-2),t_1} \right] \right\} \quad [3-31]$$

where ΔE is the averaged potential increment, Δt is the measuring period ($t_2 - t_1$), $C_{d(a-1),t_2}$ and $C_{d(a-1),t_1}$ are averaged values of C_d at t_2 and t_1 respectively. The charging current increments are then subtracted from total current increments to give the compensated faradaic current.

The plotting is performed using the DISSPLA plotting package (86). The data is fitted to a smooth curve by a polynomial least squares fit subroutine, SMOOTH, of the DISSPLA package. However, the points shown in the plots, are the experimental values without any smoothing.

4.4.4 DETERMINATION OF FLOW RATE OF MERCURY IN THE DME

Although it is not required for compensation, C_d^0 values have been obtained for comparison with literature values. The measured C_d must be divided by the surface area of the drop at the time of measurement. The surface area was calculated using the assumption that the drops are spherical (13):

$$A = 0.8518(mt)^{2/3} \quad [4-6]$$

where A is the area in cm^2 , m is the flow-rate of mercury in mg/sec , and t is the time of measurement. To determine the flow-rate for the above calculations, mercury was collected

for a measured period of time, at a given potential. The mercury was then withdrawn from the cell, washed with distilled water and acetone, dried in a stream of N_2 and weighed. A minimum of 500mg of mercury was collected, corresponding to a collection period longer than 500 seconds, since the flow-rate was about 1mg/sec. Since the mercury was weighed to ± 0.1 mg and the time was measured to ± 0.1 seconds, the accuracy of these measurements was better than 1 part per thousand.

The flow-rate was determined at three or four different potentials and used to construct a calibration curve of flow-rate versus potential. This curve was then used to convert C_d to C_d^0 . The flow-rate changes by about 1% within the working potential range due to the variation in back pressure, which is a function of surface tension and thus a function of potential.

Chapter 5

RESULTS AND DISCUSSION

5.1 PERFORMANCE CHECKS WITH THE DUMMY CELL

Each functional network was tested independently using a dummy cell, an equivalent circuit with known values of passive electrical components (see Figure 5.1), before the instrument was used for recording of polarograms. These preliminary tests were followed by measuring the differential capacitance of the DME and comparing the results with literature values.

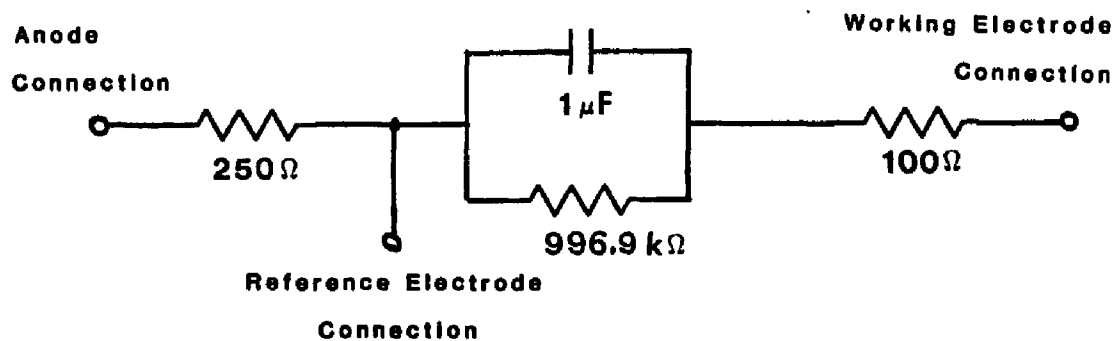


Figure 5.1 Dummy Cell. The 250 ohm resistor simulates the resistance of the electrolyte to be compensated by the potentiostat, the $1 \mu\text{F}$ capacitor simulates the double layer capacitance, the 1 Mohm resistor the faradaic impedance and the 100 ohm resistor the series resistance uncompensated by the potentiostat.

5.1.1 POTENTIOSTAT AND INPUT POTENTIALS

Two different tests were used to ascertain proper functioning of the potentiostat. In the first test, accurately known ac and dc potentials were applied to the potentiostat inputs. The potential at the input and output of the follower, A-2 (see Figure E-4), and at the output of the buffer amplifier, A-3, were then measured and compared to the applied potentials. The dc potentials agreed to better than 1 part in 10,000, while the ac potentials agreed to better than 1 part in 1000 over the frequency range tested (1kHz - 20kHz).

The second test was performed to determine the phase-shift within the potentiostat circuit. A phase meter was used to measure phase-shifts between the ac potential applied to the potentiostat and output of the follower, A-2. Phase shifts of 0.2° at 1kHz up to about 3° at 20kHz were found. This necessitated the use of the follower output voltage as a reference signal to the phase detector, in place of the applied ac voltage.

As described in Section E.1, the stepper circuit was used to create the "staircase" polarizing voltage. To test its performance, a series of potential steps was measured using different values of ΔE . The average values for steps of 10 and 20mV were $9.934 \pm 0.004\text{mV}$ and $19.864 \pm 0.004\text{mV}$ respectively. Since only the reproducibility of ΔE is important, no further adjustments were made to improve the absolute accuracy of the steps. Similar results were

obtained with other values of ΔE . No measurable drift was detected over a period of about one hour, a time span long enough for any experiment.

5.1.2 DC MEASURING NETWORK

The linearity of the dc measuring network was tested by passing current through the measuring resistor, R_m (see Figure E.13) and measuring the response of the dc measuring network. The value of this current was calculated by dividing the applied potential by the sum of the uncompensated resistance of the dummy cell (996.9 ± 0.1 kohms). Using measuring resistor of 100.4 kohms, the test produced a straight line with slope of $5.438\text{V}/\mu\text{A}$, intercept of 2.29mV and standard deviation of $0.6\text{mV}/\mu\text{A}$ (0.01%).

With an applied cell current of $1.5\mu\text{A}$ passing through a series of different measuring resistors, a plot of the response of the dc measuring network vs the value of the R_m gave a straight line with slope of $85.85\text{mV}/\text{kohm}$, intercept of -2.59mV and standard deviation of $0.047\text{mV}/\text{kohm}$ (0.06%).

5.1.3 AC MEASURING NETWORK

The proportionality of amplitude of the ac signal at phase null to the value of C_d is shown by equation [C-15] (see Appendix C for derivation):

$$e_o = kC_d \quad [C-15]$$

where e_o is the ac output of the measuring amplifier A-13 (see Figure E.9) and k is the proportionality constant that depends only on the values of circuit elements. The dummy cell (Figure 5.1) was used with an adjustable capacitor (variable in $0.1\mu F$ steps) and a $50\ \text{ohm}$ resistor representing uncompensated resistance. Table 5.1 lists data obtained at 1, 5, 10 and 20kHz; the linear regression analysis (Table 5.2) shows e_o proportional to C_d within a standard deviation of 0.1% up to 5kHz, and 0.6% up to 20kHz.

The final test of the ac measuring network with the dummy cell, was the performance of the instrument by simulating different uncompensated solution resistances. In this test the uncompensated resistance, represented by the $100\ \text{ohm}$ resistor in Figure 5.1 was varied from $40\ \text{ohms}$ to a $200\ \text{ohms}$. The results for 1kHz are shown in Table 5.3. As can be seen from Table 5.3, the change in the output signal is about 1% for the five-fold change in the uncompensated resistance. Tests with a 10kHz signal showed a change of about 5-10% for the same range of uncompensated resistance.

5.1.4 RECTIFIER

The performance of the rectifier network (Figure E.12) was checked by simultaneous measurements using an ac voltmeter. The linearity of the rectifier in the range from $0.5V$

Table 5.1 Performance of the ac Measuring Network with the Dummy Cell.

f [kHz]	C_D [μ F]	e_{13} [V]	e_M [mV]	ϕ [$^\circ$]
1.003	1.00	5.968	-2.05	0.030
1.003	0.90	5.377	-1.70	0.030
1.003	0.80	4.780	-1.24	0.025
1.003	0.70	4.181	-0.66	0.015
1.003	0.60	3.584	0.12	0.003
1.003	0.50	2.988	1.18	0.040
1.003	0.40	2.391	2.70	0.11
1.003	0.30	1.796	4.89	0.26
1.003	0.20	1.201	7.87	0.63
1.003	0.10	0.607	9.96	1.6
4.995	1.00	5.268	-1.85	0.040
4.995	0.90	4.741	-1.46	0.030
4.995	0.80	4.215	-0.93	0.020
4.995	0.70	3.689	-0.26	0.010
4.995	0.60	3.163	0.67	0.020
4.995	0.50	2.637	1.96	0.080
4.995	0.40	2.111	3.97	0.21
4.995	0.30	1.586	7.33	0.51
4.995	0.20	1.062	13.41	1.4
10.023	1.00	6.938	-1.96	0.040
10.023	0.90	6.299	-1.57	0.030
10.023	0.80	5.587	-1.06	0.020
10.023	0.70	4.874	-0.40	0.010
10.023	0.60	4.167	0.51	0.010
10.023	0.50	3.469	1.81	0.070
10.023	0.40	2.775	3.80	0.20
10.023	0.30	2.085	7.24	0.40
10.023	0.20	1.397	14.0	1.2
20.007	1.00	4.128	-1.87	0.040
20.007	0.90	3.699	-1.45	0.030
20.007	0.80	3.280	-0.91	0.020
20.007	0.70	2.871	-0.22	0.010
20.007	0.60	2.468	0.73	0.030
20.007	0.50	2.070	2.07	0.080
20.007	0.40	1.673	4.13	0.20
20.007	0.30	1.273	7.65	0.50
20.007	0.20	0.898	25.0	2.3

f is the measuring frequency, C_D is the value of the capacitor simulating the double layer capacitance, e_M is the dc output of the multiplier - error signal, e_{13} is the ac signal proportional to C_d at the phase null and ϕ is the error phase shift. At all frequencies, the feedback capacitor in amplifier A-13 was 0.005 μ F.

Table 5.2 Regression Analysis Results of the ac Measuring Network Test.

f [kHz]	slope [V/ μ F]	intercept [mV]	st.dev. [mV/ μ F]	rel.st.dev. [%]
1.003	5.962	8.4	2.27	0.04
4.995	5.258	8.7	1.21	0.01
10.023	6.973	-6.7	23.4	0.34
20.007	4.036	63.1	24.3	0.60

Table 5.3 Effect of Uncompensated Resistance.

R_D [ohms]	C_D [μ F]	C_f [μ F]	R_f [kohms]	e_M [mV]	V_{ac} [V]
190	0.40	0.005	15.2	0.16	2.06
100	0.40	0.005	8.1	-0.35	2.07
75	0.40	0.005	5.9	-0.74	2.07
50	0.40	0.005	3.9	-1.61	2.08
37	0.40	0.005	2.9	-2.71	2.08

to about 7V was better than 1% for all frequencies used.

5.2 SYSTEMS TESTED AND OBJECTIVES

To test the performance of the instrument with electrochemical cells, five different systems were employed, using well-behaved, polarographically reversibly reducible ions. The five systems were:

1. supporting electrolyte alone - KCl and KNO_3
2. Zn^{+2} in KCl supporting electrolyte
3. Cd^{+2} in KCl supporting electrolyte
4. Pb^{+2} in KCl supporting electrolyte
5. a mixture of Cd^{+2} , Pb^{+2} , Zn^{+2} in KCl supporting electrolyte.

The characteristics of each system are well-documented, and each system places different demands on the instrument.

The supporting electrolyte alone represents the closest approximation to the simplified equivalent circuit. It is the simplest and closest to ideal case to test.

Zinc (II) in 0.1M KCl has a rather slow charge transfer kinetics (small k_{SH} and large Θ), but is polarographically reversible system. The simple equivalent circuit should therefore apply even for relatively high concentrations of Zn^{+2} . Furthermore, Zn^{+2} in 0.1M KCl has a half-wave poten-

tial of $-0.995V$ (12) and is therefore reduced in the linear charging current region where C_d is low and the slope of the C_d vs E curve is small.

Cadmium (II) electroreduction in KCl , on the other hand, has one of the highest rate constants, and therefore relatively low Z_f even at low concentrations. Cd^{+2} is reduced in the region of moderately high capacitance and large slope near E_z , where the dc charging current curve changes its slope. Cd^{+2} is one of the worst cases for using linear methods of charging current compensation.

Lead (II) in KCl has a reasonably high rate constant and undergoes electroreduction in the region of high capacitance near the "hump" of the C_d vs E curve. In addition, Pb^{+2} is suspected to be specifically adsorbed on the DME (87,88), affecting the capacitance of the double layer, which does not interfere with in-situ compensation, but makes the background curve obtained with pure KCl unusable for charging current compensation.

The mixture of ions concluded the testing of the instrument's performance. Its purpose was to check the resolution of the new polarograph at sub-micromolar concentrations.

In the following sections a number of important experimental considerations are presented and compared with calculated and literature values. For the technique to be applicable to analytical determinations, it is important that the calibration curve be a linear function of concen-

tration. It was predicted from the theoretical developments, leading to equation [3-21], that the peak height of the incremental polarogram is a linear function of concentration of the electroactive species. To test this relationship, calibration curves for various concentration ranges were constructed and their linearity evaluated.

Other parameters characterizing the performance of the instrument are the shape of the curve and the location of the peak. The shape of the curve was determined in terms of its width at half-height and two-thirds height and the results are compared to the calculated values as discussed in Section 3.2.2.1.

The location of the peak occurs at $E_{1/2} + \Delta E$ as was shown by equation [3-15], thus allowing determination of half-wave potentials. $E_{1/2}$ values for all three ions at various concentrations were determined from the zero-crossing of the second increment curves, and are in very good agreement with the literature values.

5.2.1 SUPPORTING ELECTROLYTE

As was noted in the previous section, in the absence of impurities, the solution of the supporting electrolyte represents the closest approximation to the simplified equivalent network and thus offers the most favorable conditions to test the in-situ charging current compensation.

Four different supporting electrolytes were used:

- a. 1M KCl
- b. 0.1M KCl
- c. 0.1M KCl + 0.01M HCl
- d. 0.1M KNO₃

The compensated and uncompensated polarograms of 1M KCl, together with the differential capacitance curves recorded at the beginning and the end of the measuring period are shown in Figure 5.2. As can be seen from this figure, compensation to within few tenths of a nanoampere was maintained throughout most of the potential range, from the region of mercury oxidation on the positive end to the reduction of hydrogen ions on the negative end. The compensation itself was limited by DME and instrumental noise. The new baseline appears at Δi values of about 0.1-0.3nA, which represents as much as ten-fold improvement when compared to the 1.5-4nA level present in the uncompensated polarograms.

The shape of the uncompensated charging current curve closely resembles the shape of a capacitance curve (see Figure 5.2), as was predicted by equation [2-24]:

$$\frac{\Delta i_c}{\Delta E} \approx \frac{di_c}{dE} = - \frac{2}{3t} C_d \quad [2-24]$$

Most of the experiments performed, however, used 0.1M KCl, rather than 1M KCl; the major advantage of 0.1M KCl was the ten-fold decrease in impurities present in the support-

Figure 5.2

Capacitance and polarographic curves of
1.0M KCl.

- a. Capacitance at the beginning of the
measuring period.
- b. Capacitance at the end of the measur-
ing period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of
1.003kHz, 25°C, $\Delta E = 20\text{mV}$,
delay time of 2 seconds and
measuring period of 1 second.

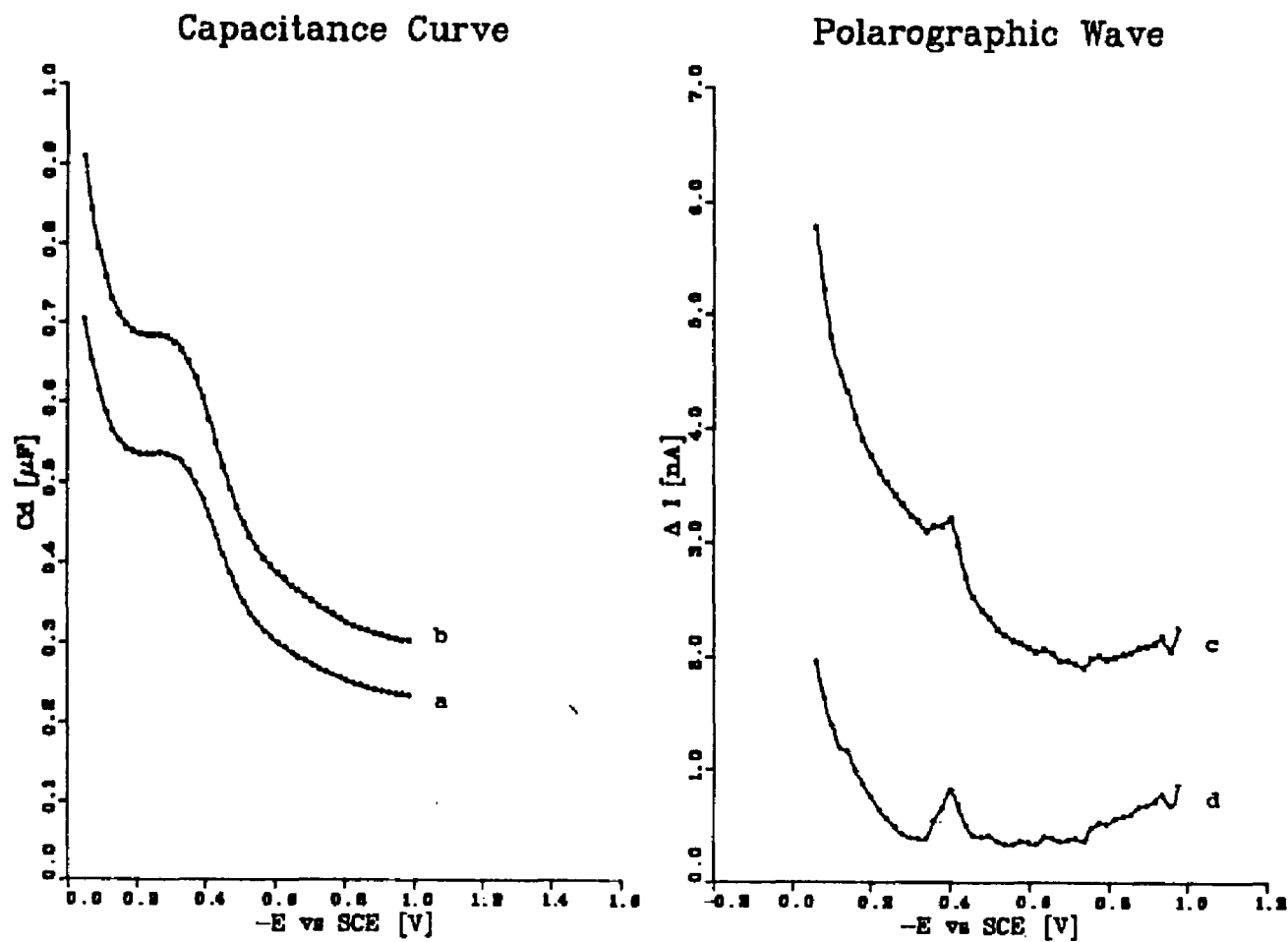


Figure 5.2

ing electrolyte. The slight increase in the resistance of the electrolyte posed no problem for the instrument, as was shown in the tests with the dummy cell. The compensated and uncompensated polarograms of 0.1M KCl are shown in Figure 5.3, displaying a close to perfect compensation within the potential region bordered by the mercury oxidation and hydrogen ion reduction.

To confirm the origin of the rapid Δi increases in the potential regions around -0.2V and -1.5V vs SCE, two additional experiments were performed. In the first experiment, HCl was added to the 0.1M KCl to make the supporting electrolyte 0.01M in HCl. This increased the hydrogen ion concentration and shifted the foot of the hydrogen ion reduction from about -1.5V vs SCE to about -1.0V (see Figure 5.4). In the second experiment, 0.1M KNO₃ was used instead of KCl (see Figure 5.5). Since KNO₃ does not form an insoluble compound with mercury as KCl does (Hg₂Cl₂), oxidation of mercury in KNO₃ occurs at much more positive potential, and accordingly the increase in Δi around -0.2V is missing in the KNO₃ polarogram. The peak at about -1V vs SCE appears to be due to a sub-micromolar concentration zinc impurity present in the 0.1M KNO₃.

Capacitance data obtained for 1M and 0.1M KCl were converted to the specific capacitance values, C_d^0 , for comparison with results reported in the literature. The C_d^0 values for 1M KCl, obtained in this experiment along with the literature values are listed in Table 5.6, and shown in

Figure 5.3

Incremental polarograms of 0.1M KCl.

- a. Uncompensated incremental polarogram.
- b. Compensated incremental polarogram.

Conditions: measuring frequency of
1.003kHz, 25°C, $\Delta E = 20\text{mV}$,
delay time of 2.3 seconds and
measuring period of 1 second.

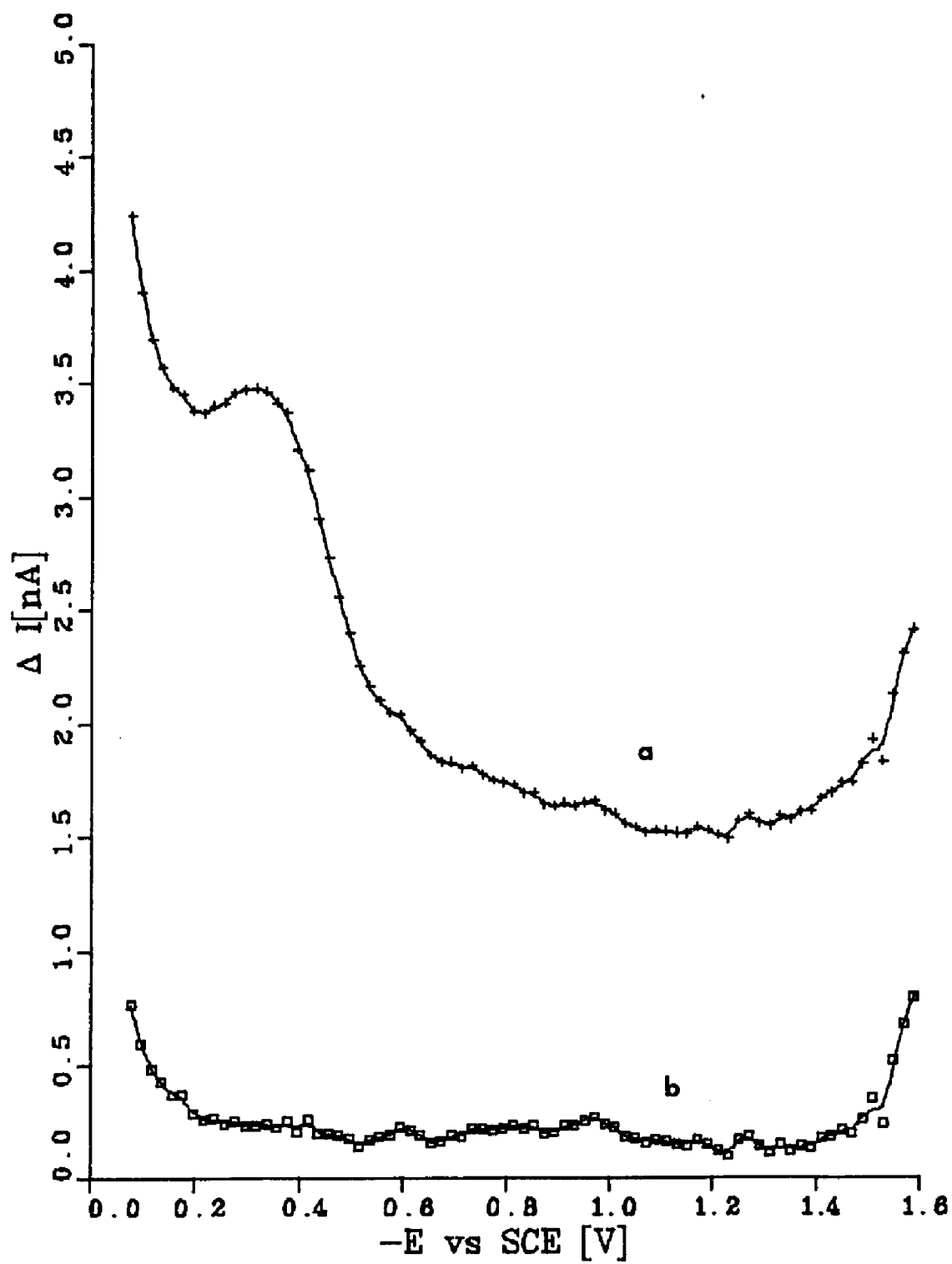


Figure 5.3

Figure 5.4

Incremental polarograms of 0.1M KCl with
0.01M HCl.

- a. Uncompensated incremental polarogram.
- b. Compensated incremental polarogram.

Conditions: measuring frequency of
1.001kHz, 25°C, $\Delta E = 20\text{mV}$,
delay time of 2.5 seconds and
measuring period of 1 second.

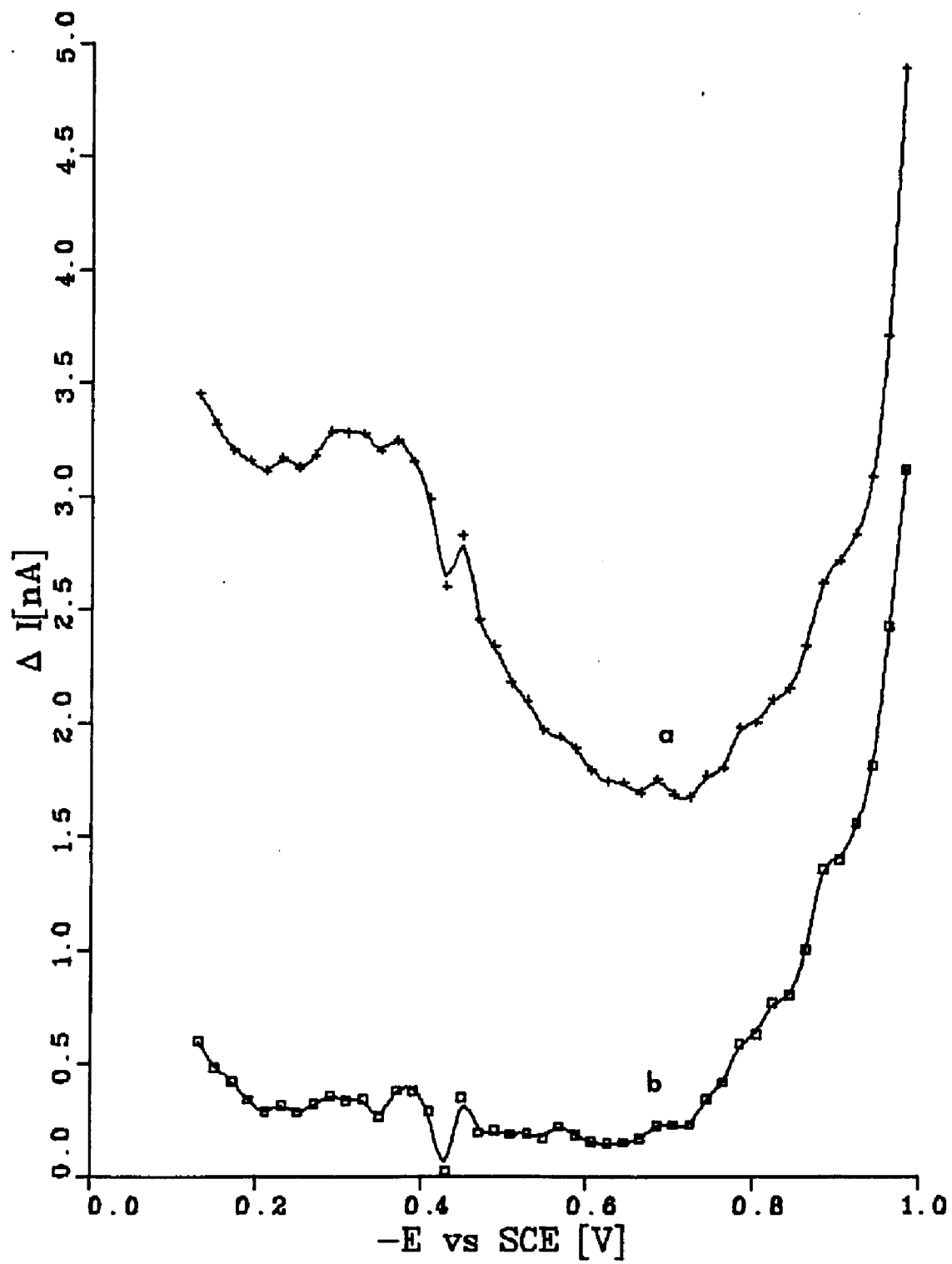


Figure 5.4

Figure 5.5

Incremental polarograms of 0.1M KNO_3 .

- a. Uncompensated incremental polarogram.
- b. Compensated incremental polarogram.

Conditions: measuring frequency of
1.003kHz, 25°C, $\Delta E = 20\text{mV}$,
delay time of 2.0 seconds and
measuring period of 0.5
seconds.

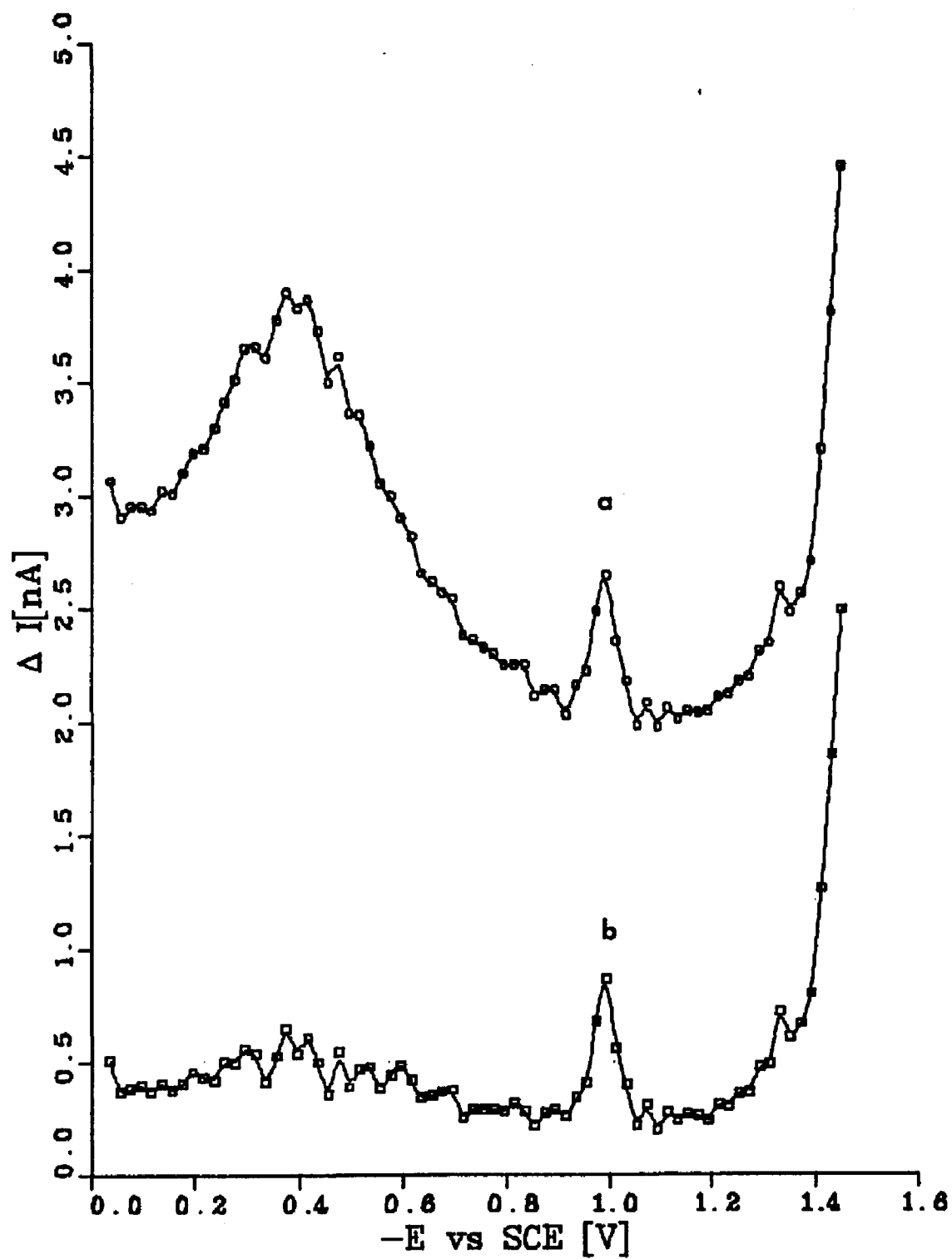


Figure 5.5

Figure 5.6 as a function of DME potential.

As can be seen from the curve in Figure 5.6, the 1kHz results obtained in this experiment for 1M KCl follow very closely the curves taken from previously reported data, obtained by a variety of techniques. At the "hump", which occurs at about -0.44V vs SCE, the absolute deviation from the literature value is less than $2\mu\text{F}/\text{cm}^2$, which corresponds to about 4% error. Similar relative errors were obtained in the vicinity of the two minima, at about -0.26V and -1.08V , with absolute deviations of less than $2\mu\text{F}/\text{cm}^2$ and $0.2\mu\text{F}/\text{cm}^2$ respectively.

The results obtained at 1kHz for 0.1M KCl are shown in Table 5.7 and Figure 5.7, and once again agreement with published values is very good. The "hump" occurs at about -0.32V vs SCE, with the minima around -0.18V and -1.10V vs SCE. In the high capacitance region near the hump and the minima, the absolute deviation is about $0.2\mu\text{F}/\text{cm}^2$, corresponding to about 2.5% relative error, while in the low capacitance region near the second minimum, the absolute deviation is about $0.2\mu\text{F}/\text{cm}^2$ or about 1.5%.

Some tests were also performed using 10kHz and 20kHz signals. The capacitance results obtained were considerably lower than those obtained with 1kHz signal, thus leading to incomplete compensation of the charging current, as can be seen in Figure 5.8 for 0.1M KCl + 0.01M HCl. These discrepancies were later attributed to instrumental problems stemming from the poor frequency response of the transform-

Table 5.6 Capacitance of 1.0M KCl - Comparison with Literature Values.

Potential [V]	Barker Faircloth	Sluyters Rehbach	Schwartz 1kHz	Holmquist	Holmquist lit.	This work 1kHz
-0.10	58.1	-	57.8	58.4	58.8	58.9
-0.12	-	-	-	-	-	51.1
-0.14	-	-	-	49.9	48.8	-
-0.15	-	-	-	-	-	47.0
-0.16	-	-	-	-	-	44.1
-0.18	-	-	-	42.7	42.7	41.8
-0.20	40.7	41.6	40.6	-	-	40.3
-0.22	-	-	-	-	-	39.2
-0.24	-	-	-	39.2	39.5	38.6
-0.26	-	-	-	-	-	38.4
-0.28	-	-	-	39.3	39.3	38.5
-0.30	38.7	39.1	39.1	-	-	38.9
-0.32	-	-	-	-	-	39.6
-0.33	-	-	-	41.3	40.5	-
-0.34	-	-	-	-	-	40.3
-0.36	-	-	-	-	-	41.0
-0.38	-	-	-	43.3	42.6	41.8
-0.40	41.8	42.0	42.8	-	-	42.5
-0.42	-	-	-	44.0	43.6	42.9
-0.44	-	-	-	-	-	43.0
-0.46	-	-	-	-	-	42.6
-0.47	-	-	-	43.0	42.9	-
-0.48	-	-	-	-	-	41.9
-0.50	39.9	41.1	40.7	-	-	40.8
-0.52	-	-	-	39.4	39.6	39.2
-0.53	-	-	-	-	-	37.5
-0.55	-	-	-	-	-	35.4
-0.57	-	-	-	-	34.0	33.5

Table 5.6 (continued)

Potential [V]	Barker Faircloth	Sluyters Rehbach	Schwartz 1kHz	Holmquist	Holmquist lit.	This work 1kHz
-0.58	-	-	-	33.6	-	-
-0.59	-	-	-	-	-	31.5
-0.60	31.2	31.0	31.5	-	-	-
-0.61	-	-	-	-	-	29.6
-0.63	-	-	-	-	27.8	27.8
-0.64	-	-	-	27.6	-	-
-0.65	-	-	-	-	-	26.3
-0.67	-	-	-	-	-	24.8
-0.69	-	-	-	-	-	23.6
-0.70	23.3	23.5	23.5	-	-	-
-0.71	-	-	-	-	-	22.4
-0.72	-	-	-	-	22.5	-
-0.73	-	-	-	22.1	-	21.5
-0.75	-	-	-	-	-	20.6
-0.77	-	-	-	-	-	19.9
-0.79	-	-	-	-	-	19.3
-0.80	19.2	19.1	19.2	-	-	-
-0.81	-	-	-	18.7	-	18.7
-0.83	-	-	-	-	19.0	18.3
-0.85	-	-	-	-	-	17.8
-0.87	-	-	-	-	-	17.6
-0.89	-	-	-	-	-	17.3
-0.90	17.4	17.3	17.2	-	-	-
-0.91	-	-	-	-	-	17.0
-0.92	-	-	-	-	17.0	-
-0.93	-	-	-	-	-	16.9
-0.94	-	-	-	17.1	-	-
-0.95	-	-	-	-	-	16.7
-0.97	-	-	-	-	-	16.5
-0.99	-	-	-	-	-	16.4
-1.00	16.5	16.6	16.4	-	16.4	-

Table 5.6 (continued)

Potential [V]	Barker Faircloth	Sluyters Rehbach	Schwartz 1kHz	Holmquist	Holmquist lit.	This work 1kHz
-1.01	-	-	-	16.4	-	16.3
-1.03	-	-	-	-	-	16.2
-1.05	-	-	-	-	-	16.3
-1.07	-	-	-	-	-	16.2
-1.09	-	-	-	-	-	16.2
-1.10	16.4	16.3	16.1	-	-	16.2
-1.12	-	-	-	-	-	16.3
-1.14	-	-	-	-	-	16.3
-1.16	-	-	-	-	-	16.4
-1.17	-	-	-	-	16.6	-
-1.18	-	-	-	16.6	-	16.3
-1.20	16.6	16.5	16.4	-	-	16.4
-1.22	-	-	-	-	-	16.5
-1.24	-	-	-	-	-	16.6
-1.26	-	-	-	-	-	16.7
-1.28	-	-	-	-	17.0	16.9
-1.30	17.2	17.0	16.8	17.5	-	17.1
-1.32	-	-	-	-	-	17.1
-1.34	-	-	-	-	-	17.3
-1.36	-	-	-	-	-	17.5
-1.38	-	-	-	-	-	17.6
-1.40	18.0	17.8	17.5	-	-	17.7
-1.41	-	-	-	18.2	-	-
-1.42	-	-	-	-	-	17.9
-1.44	-	-	-	-	-	18.1
-1.46	-	-	-	-	-	18.3
-1.50	18.9	-	18.3	-	19.0	-
-1.52	-	-	-	18.9	-	-
-1.60	20.2	-	19.5	-	-	-
-1.61	-	-	-	-	20.2	-
-1.62	-	-	-	20.1	-	-

Figure 5.6

Capacitance curve of 1.0M KCl - comparison
with literature values.

- a. This work.
- b. Barker and Faircloth (85).
- c. Sluyters and Rehbach (73).
- d. Holmquist (84).
- e. Holmquist, literature (84) -
 (Devanathan).
- f. Schwartz (52).

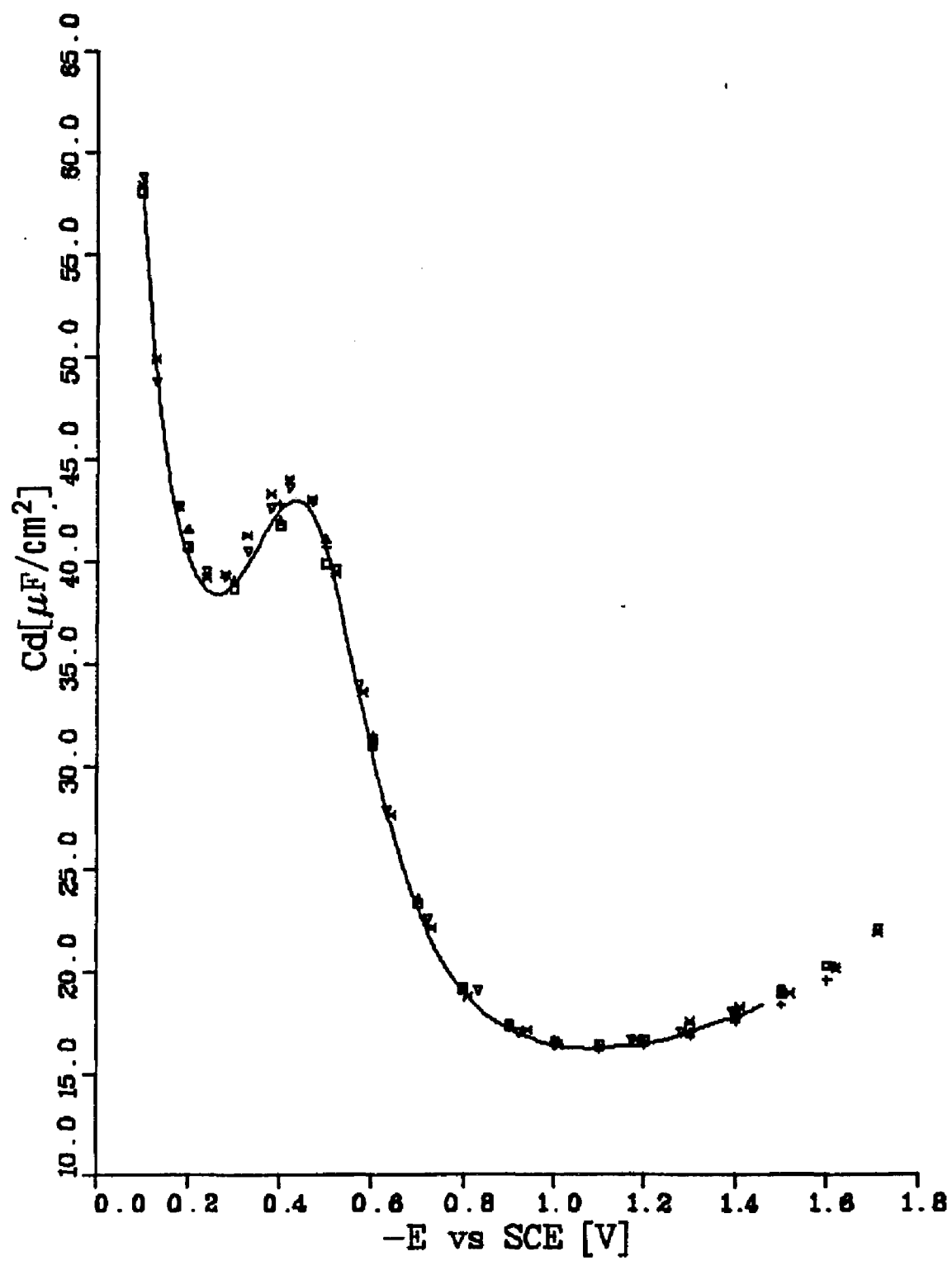


Figure 5.6

Table 5.7 Capacitance of 0.1M KCl - Comparison with Literature Values.

Potential [V]	Holmquist lit.	Holmquist exp.	This work 1kHz
-0.04	123	109	-
0.01	58.5	54.4	-
0.02	-	-	50.9
0.04	-	-	48.1
0.06	45.8	44.5	44.5
0.08	-	-	41.9
0.10	-	-	40.0
0.11	40.5	40.1	-
0.12	-	-	38.7
0.14	-	-	37.8
0.16	38.3	38.5	37.3
0.18	-	-	37.0
0.20	-	-	37.1
0.21	38.2	38.5	-
0.22	-	-	37.3
0.24	-	-	37.6
0.26	38.9	39.5	38.2
0.28	-	-	38.6
0.30	-	-	38.8
0.31	39.9	40.0	-
0.32	-	-	38.9
0.34	-	-	38.6
0.36	39.0	39.0	38.0
0.38	-	-	37.0
0.40	-	-	35.6
0.41	35.6	34.9	-
0.42	-	-	33.9
0.44	-	-	32.0
0.46	30.5	30.1	30.0
0.47	29.9	29.7	-
0.48	-	-	28.0
0.50	-	-	26.3
0.51	25.9	26.1	-
0.52	-	-	24.9
0.54	-	-	23.7
0.56	23.0	23.3	22.7
0.58	-	-	21.9
0.60	-	-	21.3
0.61	21.2	21.3	-
0.62	-	-	20.8
0.64	-	-	20.4
0.66	20.0	19.7	20.0
0.68	-	-	19.6
0.70	-	-	19.3
0.72	-	-	19.0
0.74	-	-	18.7

Table 5.7 (continued)

Potential [V]	Holmquist lit.	Holmquist exp.	This work kHz
0.76	18.4	17.8	18.4
0.78	-	-	18.1
0.80	-	-	17.9
0.82	-	-	17.6
0.84	-	-	17.4
0.86	17.2	16.8	17.2
0.88	-	-	17.0
0.90	-	-	16.8
0.92	-	-	16.7
0.93	-	-	16.5
0.95	-	-	16.4
0.96	16.4	16.2	-
0.97	-	-	16.3
0.99	-	-	16.2
1.01	-	-	16.2
1.03	-	-	16.1
1.05	-	-	16.1
1.06	16.1	16.0	-
1.07	-	-	16.0
1.09	-	-	16.0
1.11	16.0	16.1	16.0
1.13	-	-	16.0
1.15	-	-	16.1
1.16	16.1	16.2	-
1.17	-	-	16.1
1.19	-	-	16.2
1.21	-	-	16.2
1.23	-	-	16.3
1.25	-	-	16.4
1.26	16.4	16.5	-
1.27	-	-	16.5
1.29	-	-	16.6
1.31	-	-	16.8
1.33	-	-	16.9
1.35	-	-	17.0
1.36	17.0	17.0	-
1.37	-	-	17.2
1.39	-	-	17.3
1.41	-	-	17.5
1.45	-	-	17.9
1.46	17.8	17.7	-
1.47	-	-	18.1
1.49	-	-	18.2
1.51	-	-	18.5
1.56	18.3	18.7	-
1.66	20.1	19.8	-
1.76	21.8	21.7	-

Figure 5.7

Capacitance curve of 0.1M KCl - comparison
with literature values.

- a. This work.
- b. Holmquist (84).
- c. Holmquist, literature - Grahame
 (83).

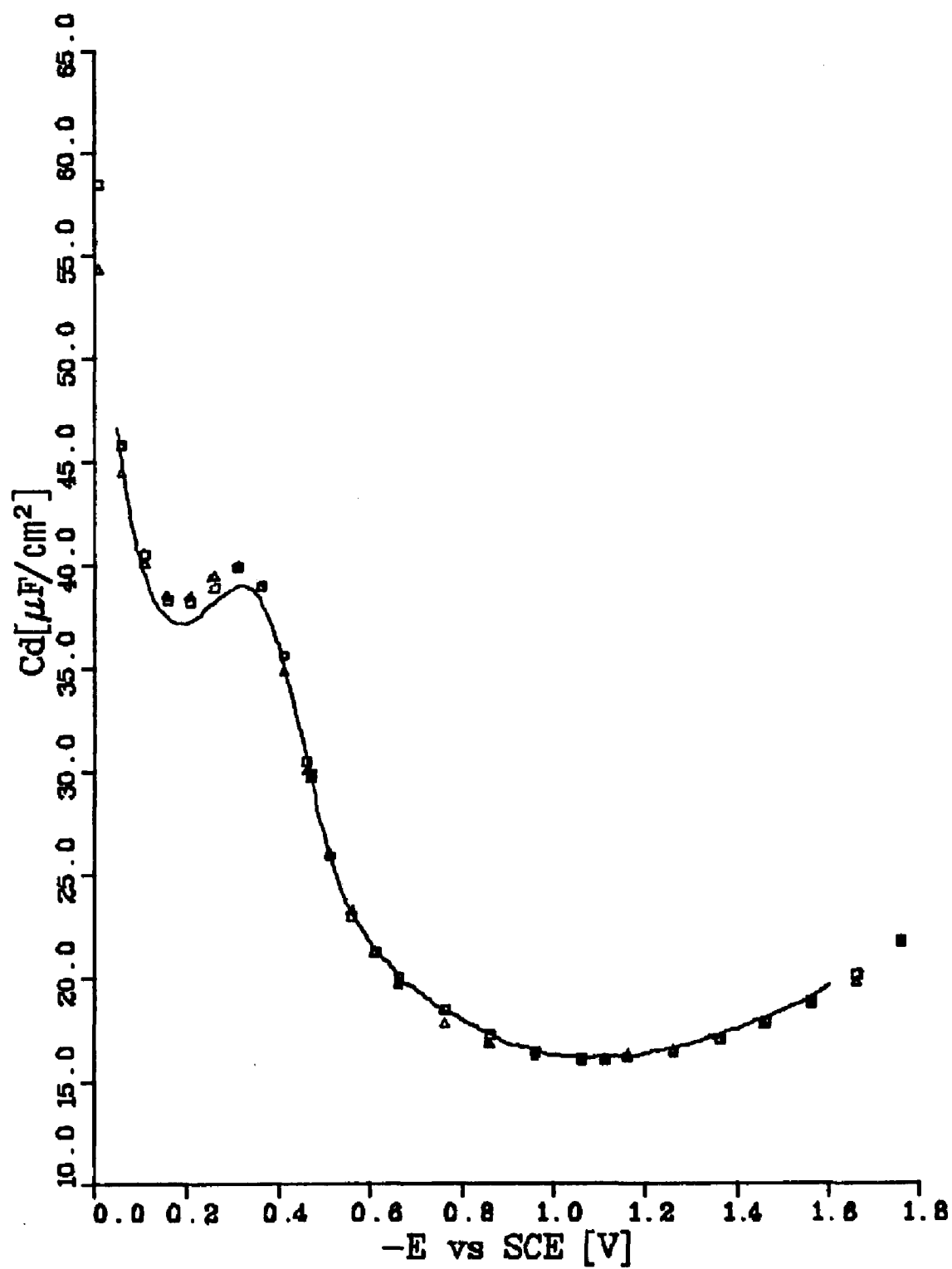


Figure 5.7

Figure 5.8

Incremental polarograms of 0.1M KCl with
0.01M HCl.

- a. Uncompensated incremental polarogram.
- b. Compensated incremental polarogram.

Conditions: measuring frequency of
10.02kHz, 25°C, $\Delta E = 20\text{mV}$,
delay time of 2.5 seconds and
measuring period of 1 second.

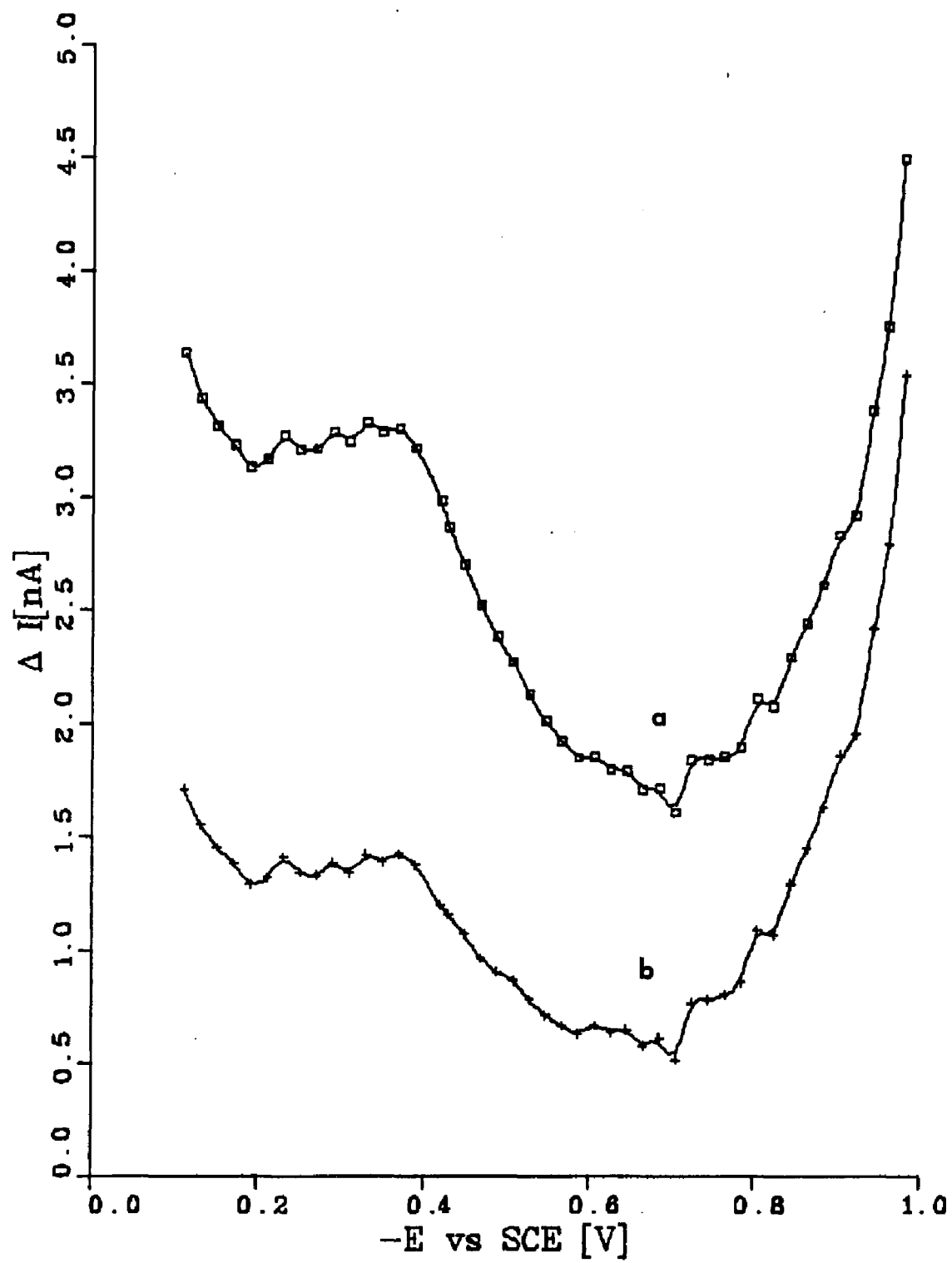


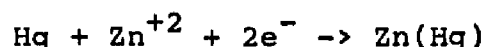
Figure 5.8

ers used. To avoid this problem, most of the experiments were performed using 1kHz measuring signal.

All curves included in this thesis show actual data points without any modification. Some of the curves drawn through these points were obtained by computer smoothing subroutines using a least squares fit with very low correction coefficients.

5.2.2 ZINC (II)

As was already mentioned in the introduction to Chapter 5, zinc (II) in KCl supporting electrolyte is reversibly reduced according to equation:



with half-wave potential, $E_{1/2} = -0.995 \pm 0.006\text{V}$ vs SCE (9), and heterogeneous rate constant of $4 \times 10^{-3} \text{ cm}^{-1}$ in 1M KCl (89), and $1.4 \times 10^{-2} \text{ cm}^{-1}$ in 0.3M KCl (90).

Figure 5.9 shows a series of incremental polarograms obtained in 0.1M KCl supporting electrolyte for standard additions of Zn(II) ranging from 0 to $1 \times 10^{-6}\text{M}$, and Figure 5.10 for Zn(II) concentration ranging from $1 \times 10^{-6}\text{M}$ to $1 \times 10^{-5}\text{M}$. Table 5.8 lists the data obtained from plots and computer printouts of the Zn(II) polarograms shown in Figures 5.9 and 5.10. Four different values for the peak height at each concentration are listed, in order to allow for better evaluation of the charging current compensation.

Figure 5.9

Incremental polarograms of 10^{-7} M Zn^{+2} in 0.1M KCl.

- a. Supporting electrolyte alone.
- b. Added Zn^{+2} concentration of 2.80×10^{-7} M.
- c. Added Zn^{+2} concentration of 5.39×10^{-7} M.
- d. Added Zn^{+2} concentration of 7.80×10^{-7} M.
- e. Added Zn^{+2} concentration of 10.03×10^{-7} M.

Conditions: measuring frequency of 1.003kHz,
25°C, $\Delta E = 20$ mV, delay time of
2 seconds, measuring period of
0.5 seconds, 3 drops at each
potential.

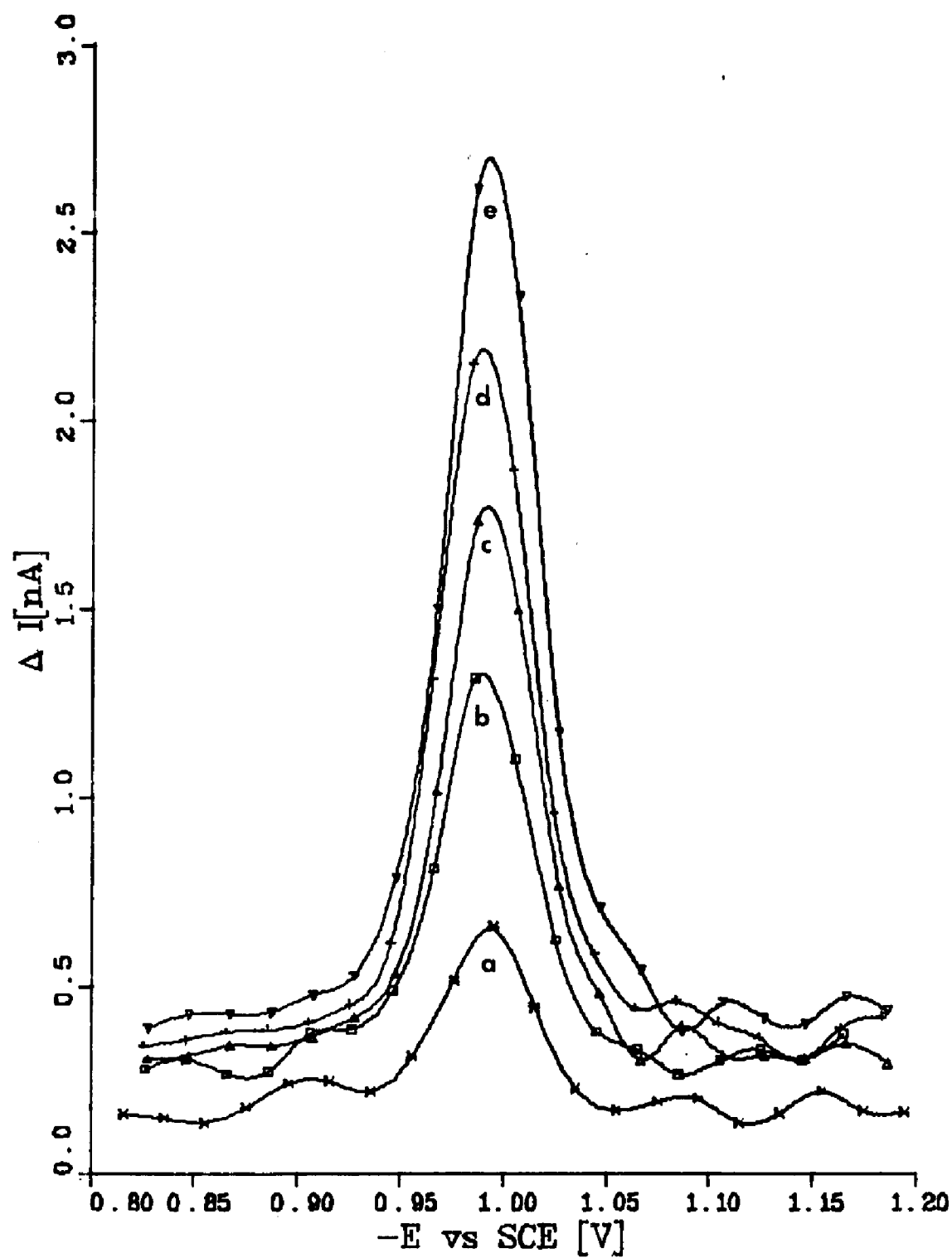


Figure 5.9

Figure 5.10

Incremental polarograms of 10^{-6}M Zn^{+2} in 0.1M KCl .

- a. Supporting electrolyte alone.
- b. Added Zn^{+2} concentration of $1.003 \times 10^{-6}\text{M}$.
- c. Added Zn^{+2} concentration of $3.52 \times 10^{-6}\text{M}$.
- d. Added Zn^{+2} concentration of $5.68 \times 10^{-6}\text{M}$.
- e. Added Zn^{+2} concentration of $7.72 \times 10^{-6}\text{M}$.
- f. Added Zn^{+2} concentration of $9.63 \times 10^{-6}\text{M}$.
- g. Added Zn^{+2} concentration of $11.40 \times 10^{-6}\text{M}$.

Conditions: measuring frequency of 1.003kHz ,
 25°C , $\Delta E = 20\text{mV}$, delay time of
2 seconds, measuring period of
 0.5 seconds, 3 drops at each
potential.

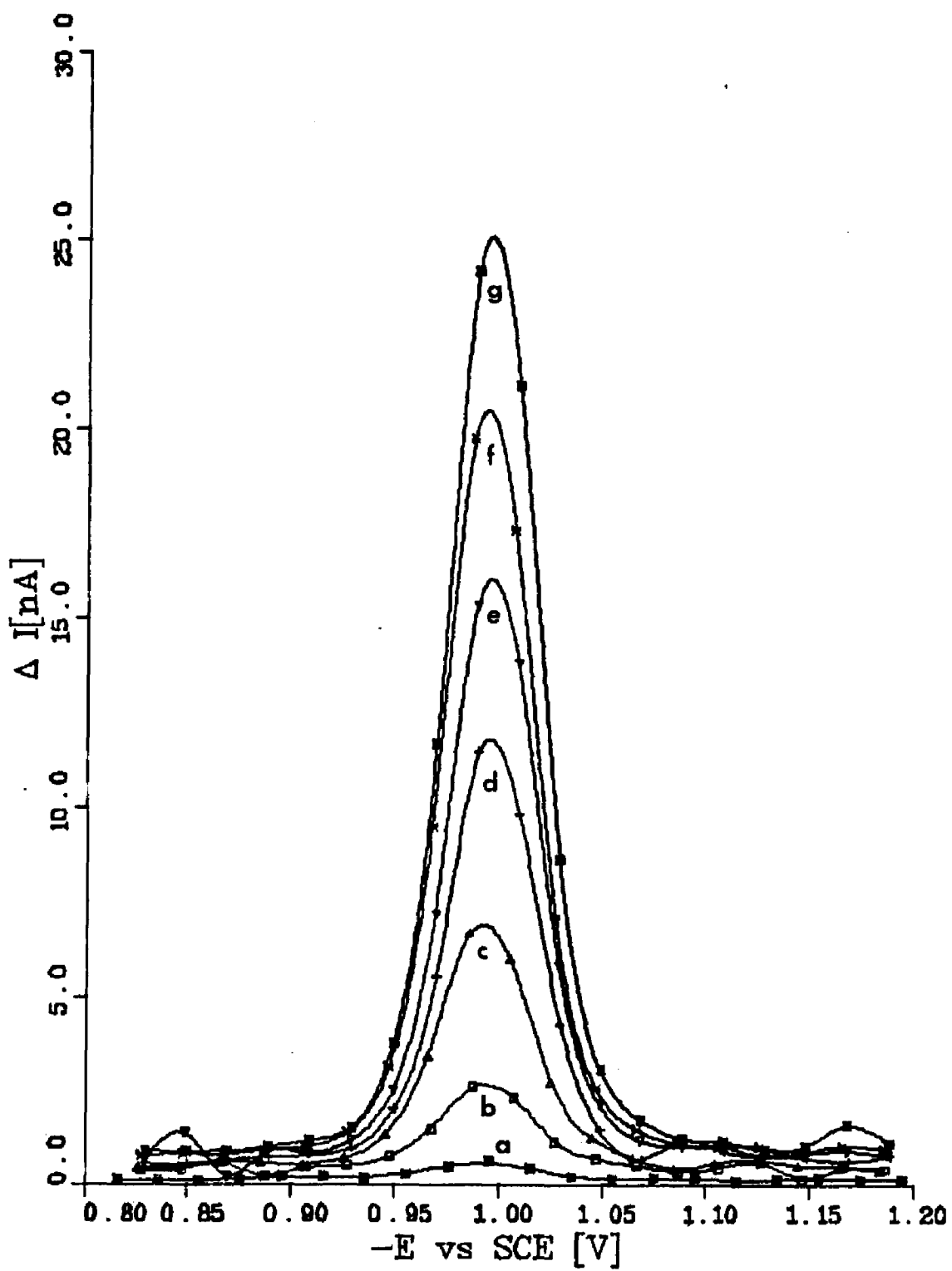


Figure 5.10

Table 5.8 Incremental Polarograms of Zn^{+2} in 0.1M KCl.

concentration	uncor. print.	cor. print.	cor. plot	d.cor. plot	$w_{1/2}$	$w_{2/3}$	$-E_{1/2}$
2.80×10^{-7}	2.94	1.32	1.33	1.03	51.3	39.2	0.994
5.39×10^{-7}	3.39	1.73	1.77	1.47	51.3	38.3	0.997
7.80×10^{-7}	3.81	2.15	2.19	1.88	53.4	40.8	0.994
10.03×10^{-7}	4.29	2.62	2.70	2.27	51.3	39.2	0.997
3.52×10^{-6}	8.40	6.68	6.90	6.38	52.2	40.8	0.996
5.68×10^{-6}	13.13	11.46	11.80	11.29	50.7	38.6	0.999
7.72×10^{-6}	17.03	15.32	16.10	15.53	50.7	38.6	0.999
9.63×10^{-6}	21.5	19.73	20.6	19.62	50.7	43.8	0.997
11.40×10^{-6}	25.9	24.2	25.2	24.2	50.7	38.3	0.999

Column 2 of Table 5.8 lists the peak value of the incremental polarograms obtained, from the computer printout, before the charging current correction was applied. The calibration curves corresponding to values in column 2 are shown in Figures 5.11a and 5.12a for 10^{-7} and 10^{-6} molar solutions respectively.

Column 3 of Table 5.8 shows the printout peak values after the charging current compensation, and the calibration curves are shown in Figures 5.11b and 5.12b. The difference between columns 2 and 3 is about 1.7nA, corresponding to the charging current calculated using the phase-null technique. The 1.7nA corresponds to a percentage of total incremental peak from about 0.7% for $1.1 \times 10^{-5} \text{M}$ solution to almost 60% for $3 \times 10^{-7} \text{M}$ standard addition of Zn(II).

Since $\Delta E = 20 \text{mV}$ is quite high, the values of the highest experimental points in most cases do not represent the actual maximum, which may occur between the two highest points, thus causing increased uncertainty in the linearity of the calibration curves. Values listed in column 4 of Table 5.8 are peak values obtained from the plot created by passing a curve within 0.25mm of each experimental point using a least squares interpolation technique. The calibration curves obtained by using data from column 4 are shown in Figures 5.11c and 5.12c. The difference between columns 3 and 4 is caused by the fact that the heighest experimental point is not necessarily the maximum of the polarogram, and thus may cause a low reading of about 1-3% for the given

Figure 5.11

Calibration curve for 10^{-7}M Zn^{+2} in 0.1M KCl .

These curves are constructed from the data shown in Figure 5.9 and Table 5.8.

- a. + Uncorrected results obtained from the printout:

$$\begin{aligned}\text{slope} &= 1.85 \text{ nA}/\mu\text{mole l}^{-1} \\ \text{intercept} &= 2.40 \text{ nA}\end{aligned}$$

- b. x Corrected results obtained from the printout:

$$\begin{aligned}\text{slope} &= 1.79 \text{ nA}/\mu\text{mole l}^{-1} \\ \text{intercept} &= 0.79 \text{ nA}\end{aligned}$$

- c. ⊙ Corrected results obtained from the plot:

$$\begin{aligned}\text{slope} &= 1.88 \text{ nA}/\mu\text{mole l}^{-1} \\ \text{intercept} &= 0.78 \text{ nA}\end{aligned}$$

- d. ● Doubly corrected results obtained from the plot:

$$\begin{aligned}\text{slope} &= 1.76 \text{ nA}/\mu\text{mole l}^{-1} \\ \text{intercept} &= 0.51 \text{ nA}\end{aligned}$$

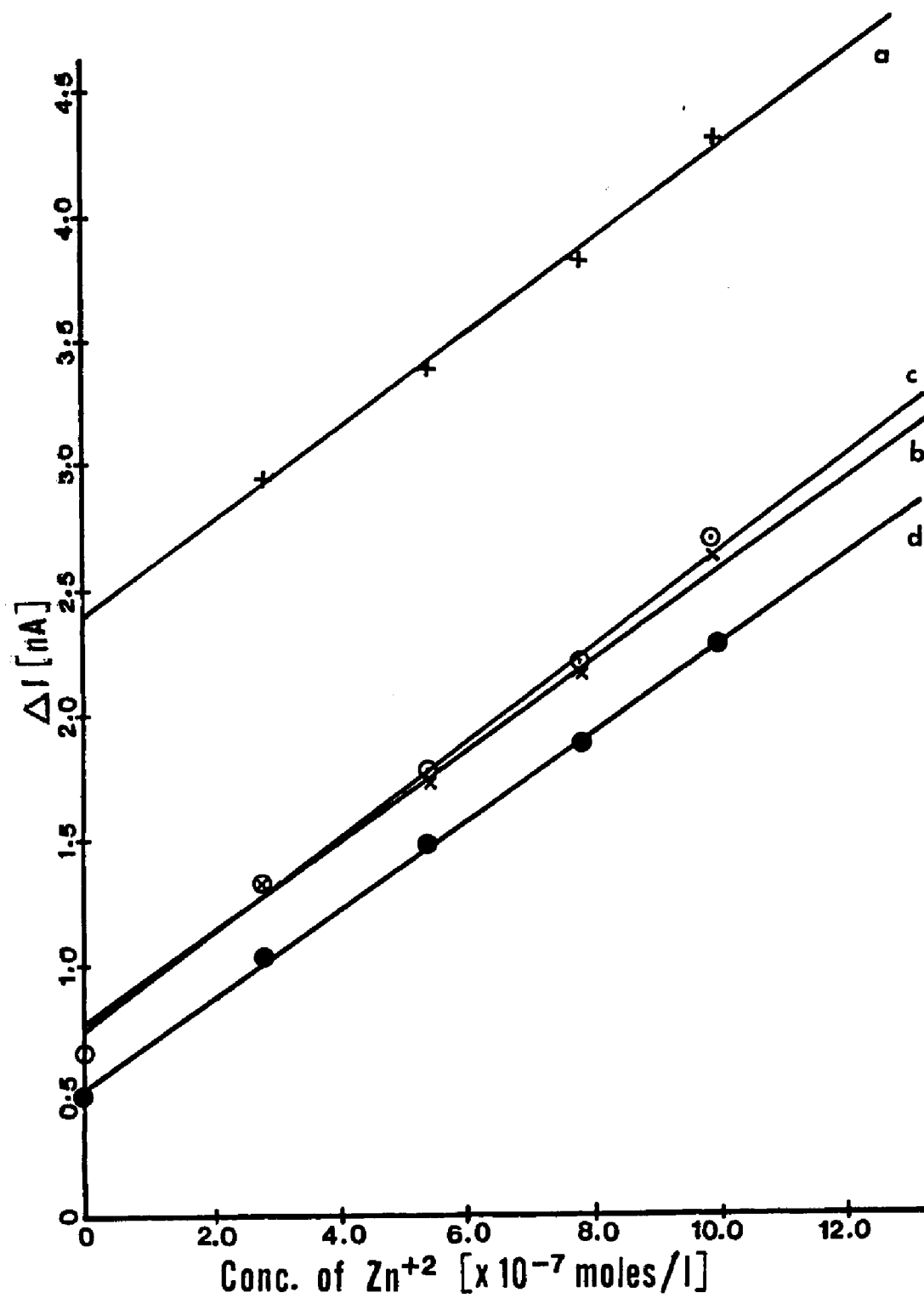


Figure 5.11

Figure 5.12

Calibration curve for 10^{-6}M Zn^{+2} in 0.1M KCl.

These curves are constructed from the data shown in Figure 5.10 and Table 5.8.

a. + Uncorrected results obtained from the printout:

$$\begin{aligned}\text{slope} &= 2.08 \text{ nA}/\mu\text{mole l}^{-1} \\ \text{intercept} &= 1.52 \text{ nA}\end{aligned}$$

b. x Corrected results obtained from the printout:

$$\begin{aligned}\text{slope} &= 2.03 \text{ nA}/\mu\text{mole l}^{-1} \\ \text{intercept} &= -0.15 \text{ nA}\end{aligned}$$

c. ⊙ Corrected results obtained from the plot:

$$\begin{aligned}\text{slope} &= 2.12 \text{ nA}/\mu\text{mole l}^{-1} \\ \text{intercept} &= -0.23 \text{ nA}\end{aligned}$$

d. ● Doubly corrected results obtained from the plot:

$$\begin{aligned}\text{slope} &= 2.07 \text{ nA}/\mu\text{mole l}^{-1} \\ \text{intercept} &= -0.09 \text{ nA}\end{aligned}$$

This curve was not plotted to preserve clarity of the graph.

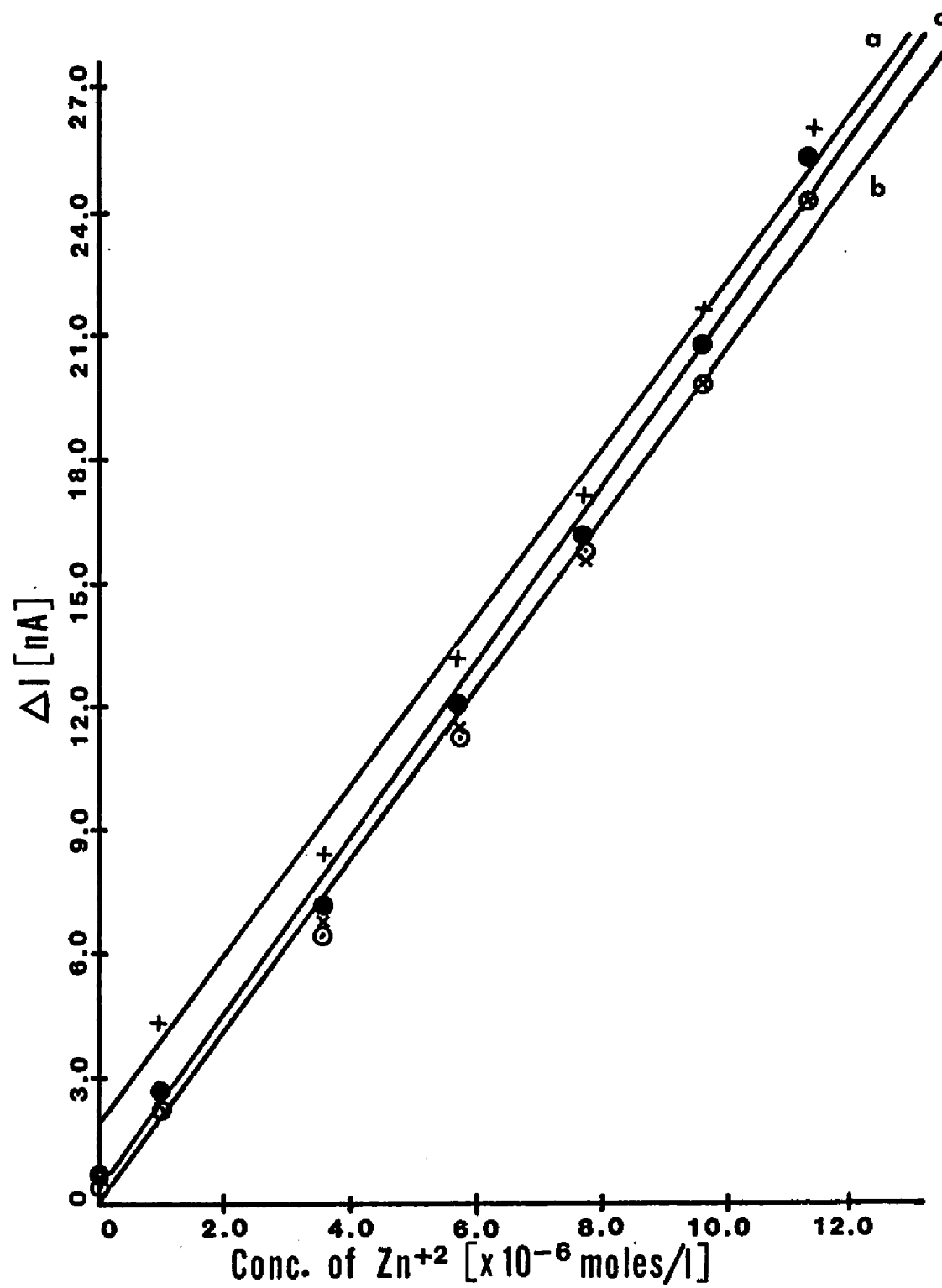


Figure 5.12

experimental conditions.

Column 5 of Table 5.8 also lists peak values determined using the plot, but the peak heights are measured from the interpolated baseline, rather than from the zero current as was the case in column 4. The calibration curves for column 5 data are shown in Figures 5.11d and 5.12d. The difference between values in columns 4 and 5 is due to uncompensated background current, which accounts for about 1% of the signal at $1 \times 10^{-5} \text{ M Zn}^{+2}$ level to about 10% of the uncorrected signal at $10^{-7} \text{ M Zn}^{+2}$ level.

The compensated calibration curves shown in Figures 5.11b and 5.11c have intercepts of about 0.74 nA. This relatively high intercept value indicates presence of impurity, clearly visible in Figure 5.9a in form of a peak, with $E_{1/2}$ equal to that of Zn^{+2} . If the impurity is Zn^{+2} , its concentration is about $3.8 \times 10^{-7} \text{ M}$. Despite the presence of this impurity, accurate analysis can be performed using a standard addition technique, even at these low concentrations.

Columns 6 and 7 of Table 5.8 list the peak widths at half-height and two-thirds-height respectively. The average peak width at half-height was 51 mV, as compared to the theoretical value of 45.3 mV calculated for the derivative (see Section 3.2.2.1). No deviation in the experimental peak width is visible even at the lowest concentration of Zn(II) . For the two-thirds-height, the experimentally obtained average curve width is 39 mV, as compared to the calculated value of 33.8 mV for the derivative.

Column 8 of Table 5.8 lists the half-wave potentials, $E_{1/2}$, determined from the corrected incremental polarograms by finding the zero crossing of the second incremental curve. The average $E_{1/2}$ determined from the runs at various concentrations was $-0.997 \pm 0.002V$ vs SCE, in excellent agreement with the published value of $-0.995 \pm 0.006V$ vs SCE (9).

Figure 5.13 shows the compensated and uncompensated incremental polarograms obtained for "added" Zn(II) concentration of 2.8×10^{-7} moles/l. As can be seen from this graph, baselines of both curves are parallel to the x axis as expected, since the Cd vs E curve shows a minimum with only a very slight slope in the potential region near $E_{1/2}$ of Zn^{+2} (see Figure 5.2). The amplitude of the compensated charging current is about 1.7nA, a value found throughout the set of zinc experiments.

5.2.3 CADMIUM (II)

Cd^{+2} in chloride media is reduced much more rapidly than Zn^{+2} with a heterogeneous rate constant, k_{SH} of $5.0cm^{-1}$ in 1M KCl for the reaction (91):



The half-wave potential of the Cd(II) in 0.1M KCl, $E_{1/2} = -0.599 \pm 0.005V$ vs SCE (9), is near the potential of the electrocapillary maximum and thus the region of high double

Figure 5.13

Incremental polarograms of 0.1M KCl with added Zn^{+2} concentration of 0.28 $\mu\text{moles/l}$.

- a. Uncompensated incremental polarogram.
- b. Compensated incremental polarogram.

Conditions: measuring frequency of 1.003kHz,
25°C, $\Delta E = 20\text{mV}$, delay time of
2.3 seconds and measuring period
of 1 second.

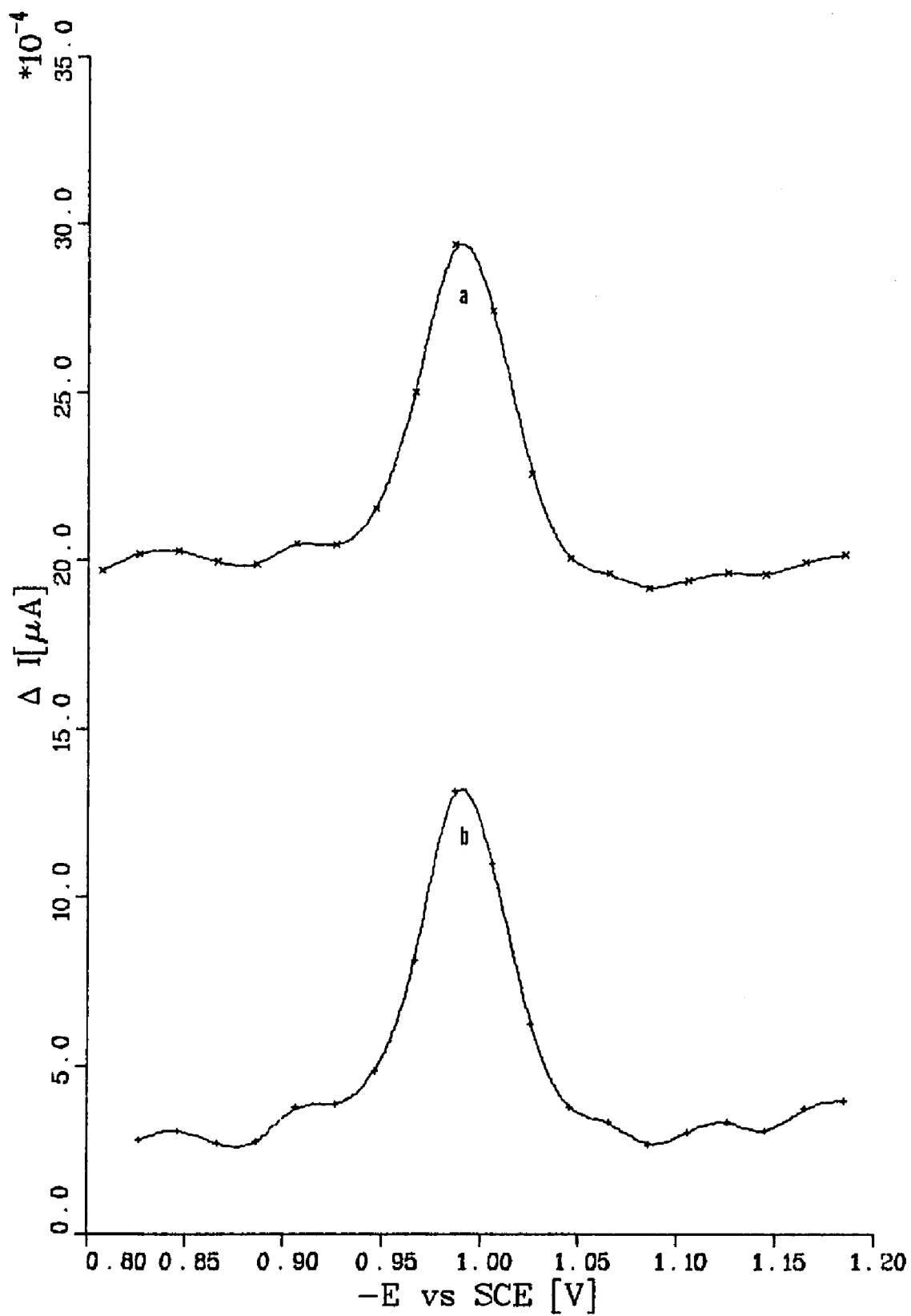


Figure 5.13

layer capacitance (for reference use Figure 5.2).

What is more important for the charging current compensation, however, is not only the absolute value of the double layer capacitance, but also the large slope of the C_d vs E curve in the potential region near $E_{1/2}$ of $Cd(II)$. This importance arises from equation [3-31], relating ΔI_c to C_d .

$$\Delta I_{c_a} = - \frac{\Delta E}{\Delta t} \left\{ \frac{3}{2} \left[C_{d(a-1),t_2} - C_{d(a-1),t_1} \right] - \right. \quad [3-31]$$

$$\left. - \frac{1}{2} \left[C_{d(a-2),t_2} - C_{d(a-2),t_1} \right] \right\}$$

In the region of low slope $C_{d(a-1)} \approx C_{d(a-2)}$ and the equation [3-31], above, reduces to equation [3-29]. In the region of high slope, as is the case near $E_{1/2}$ of cadmium, such approximation introduces unacceptable errors, thus necessitating the use of equation [3-31].

Figure 5.14 shows a series of incremental polarograms obtained with $\Delta E = 20mV$ for $Cd(II)$ in the concentration range from 1×10^{-6} to $1 \times 10^{-5}M$, with $0.1M$ $KCl + 0.01M$ HCl as supporting electrolyte. The peak values obtained from the computer printout and plot, curve widths, and half-wave potentials for the polarograms in Figure 5.14 are listed in Table 5.9, and the calibration curves in Figure 5.15.

The potential steps of $20mV$ correspond to a rather low resolution scan. As was described in Section 3.2.2 it is possible with the help of fill-in scans to increase the sensitivity of incremental polarography, while keeping the resolution at a high level.

Figure 5.14

Incremental polarograms of 10^{-6}M Cd^{+2} in 0.1M KCl with 0.01M HCl .

- a. Supporting electrolyte alone.
- b. Added Cd^{+2} concentration of $0.99 \times 10^{-6}\text{M}$.
- c. Added Cd^{+2} concentration of $1.95 \times 10^{-6}\text{M}$.
- d. Added Cd^{+2} concentration of $3.76 \times 10^{-6}\text{M}$.
- e. Added Cd^{+2} concentration of $5.44 \times 10^{-6}\text{M}$.
- f. Added Cd^{+2} concentration of $7.01 \times 10^{-6}\text{M}$.
- g. Added Cd^{+2} concentration of $8.47 \times 10^{-6}\text{M}$.

Conditions: measuring frequency of 1.001kHz ,
 25°C , $\Delta E = 20\text{mV}$, delay time of
2.5 seconds, measuring period of
1.0 second, 1 drop at each poten-
tial.

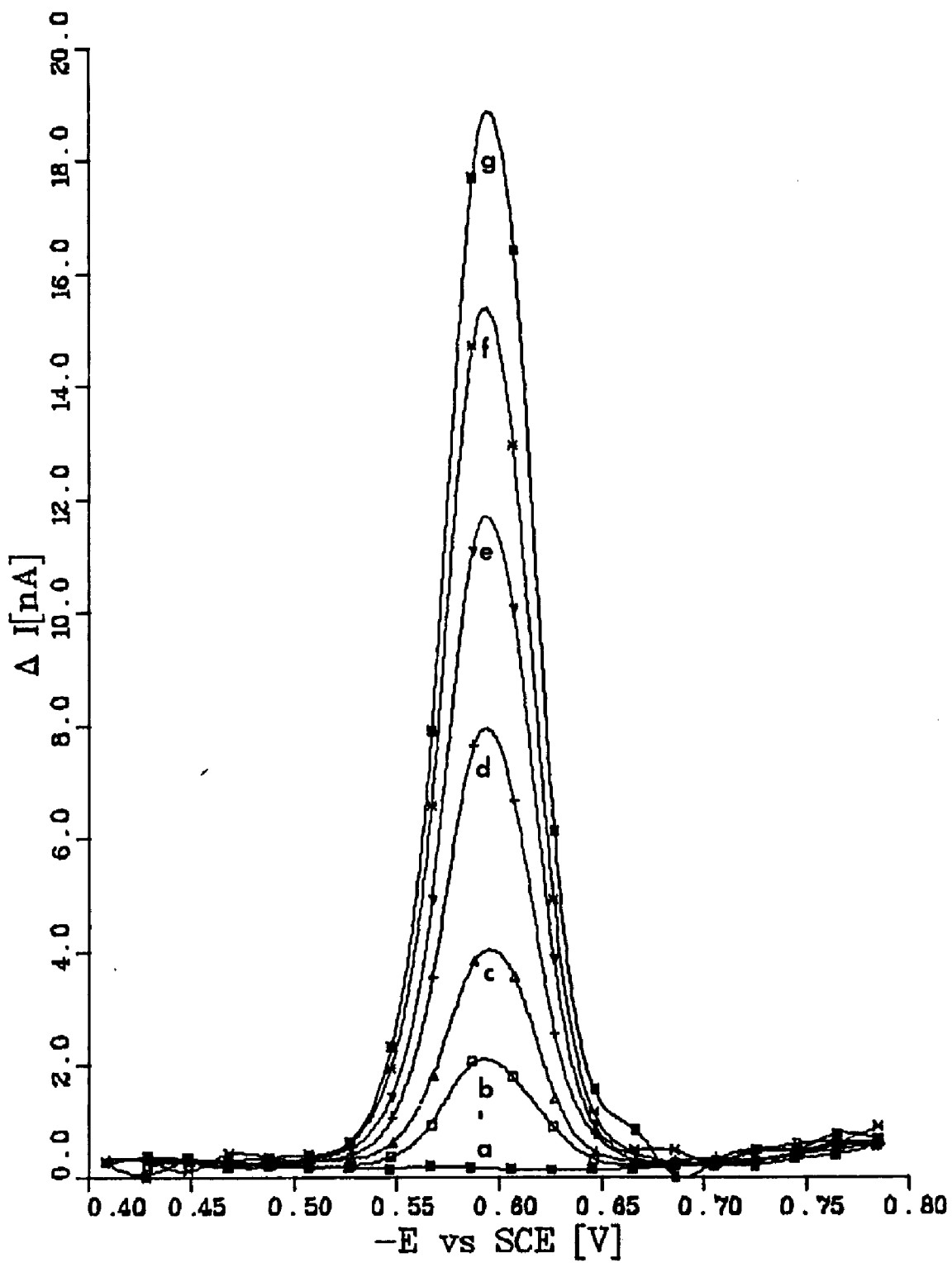


Figure 5.14

Table 5.9 Incremental Polarograms of Cd^{+2} in 0.1M KCl with 0.01M HCl.

concentration	uncor. print.	cor. print.	cor. plot	d.cor. plot	$w_{1/2}$	$w_{2/3}$	$-E_{1/2}$
0.99×10^{-6}	3.72	2.06	2.09	1.93	51.3	37.7	0.597
1.95×10^{-6}	5.61	3.84	4.03	3.87	50.4	39.8	0.599
3.76×10^{-6}	9.39	7.64	7.96	7.79	48.9	38.3	0.597
5.44×10^{-6}	12.88	11.06	11.73	11.55	48.9	39.2	0.598
7.01×10^{-6}	16.57	14.71	15.41	15.20	49.8	37.7	0.597
8.47×10^{-6}	19.64	17.69	18.85	18.75	49.8	39.2	0.599

Figure 5.15

Calibration curve for 10^{-6}M Cd^{+2} in 0.1M KCl with 0.01M HCl.

These curves are constructed from the data shown in Figure 5.14 and Table 5.9.

- a. + Uncorrected results obtained from the printout:

$$\text{slope} = 2.14 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = 1.45 \text{ nA}$$

- b. x Corrected results obtained from the printout:

$$\text{slope} = 2.11 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = -0.20 \text{ nA}$$

- c. O Corrected results obtained from the plot:

$$\text{slope} = 2.24 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = -0.33 \text{ nA}$$

- d. Doubly corrected results obtained from the plot:

$$\text{slope} = 2.25 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = -0.50 \text{ nA}$$

This curve was not plotted to preserve clarity of the graph.

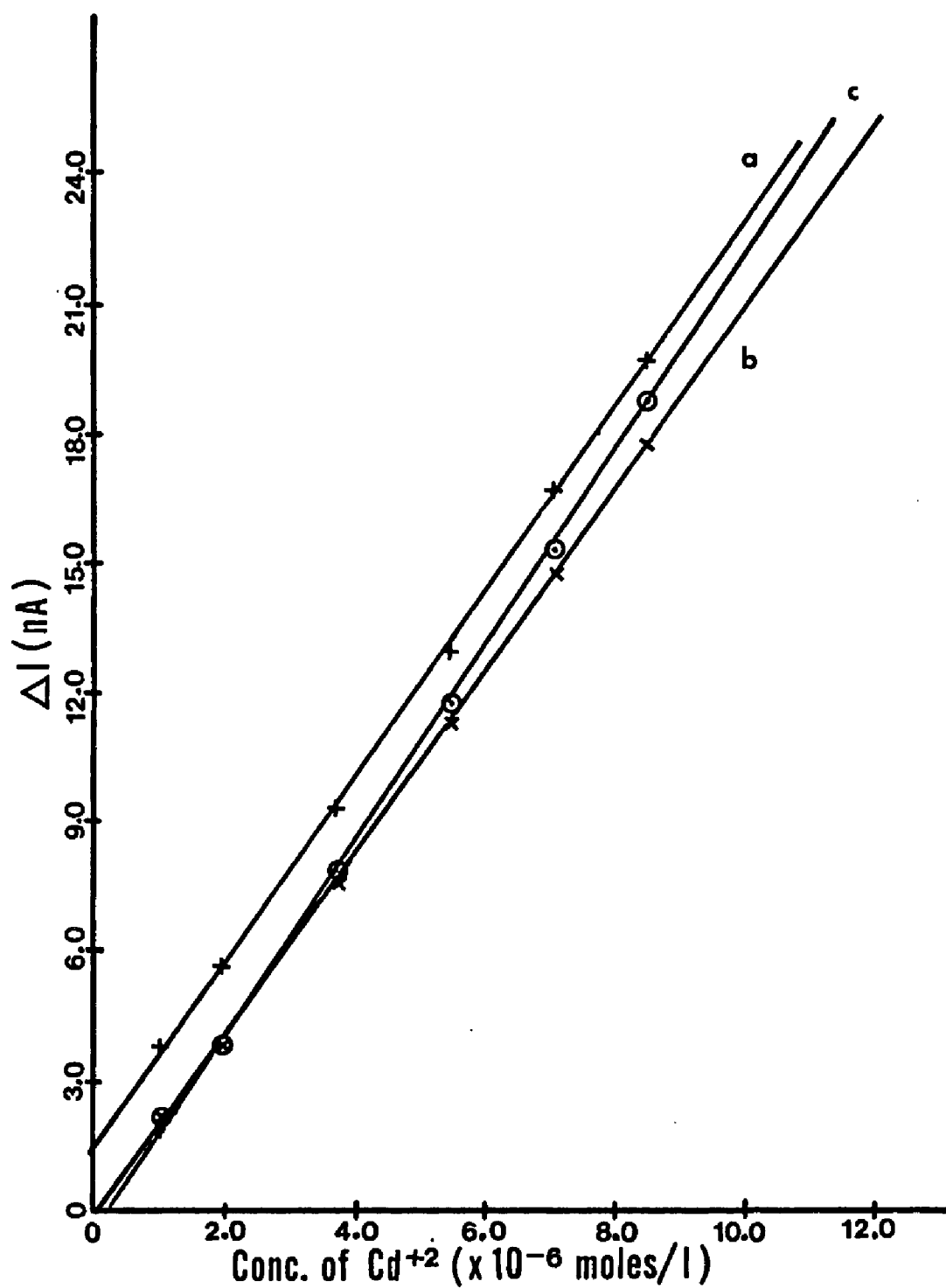


Figure 5.15

Figure 5.16 shows a set of such fill-in runs recorded for electroreduction of Cd(II) in 0.1M KCl + 0.01M HCl for the concentration range from $1 \times 10^{-6} \text{M}$ to $1 \times 10^{-5} \text{M}$, $\Delta E = 20 \text{mV}$ and fill-ins at 4mV intervals. The calibration curves for these runs are shown in Figure 5.17, with curve characteristics listed in Table 5.10.

For Cd^{+2} at concentration above $1 \times 10^{-6} \text{M}$, the signal-to-noise ratio is high enough to use smaller ΔE without need for the fill-ins, thus decreasing the time needed for each run. Figures 5.18 and 5.19, and Table 5.11 show results for runs with $\Delta E = 10 \text{mV}$, to allow comparison with results obtained with 20mV steps with and without fill-ins.

To test the charging current compensation more thoroughly, Cd(II) concentration was decreased by another factor of 10. Figure 5.20 shows the incremental polarograms of Cd^{+2} in the concentration range from $2 \times 10^{-7} \text{M}$ to $1 \times 10^{-6} \text{M}$ using 0.1M KCl as supporting electrolyte. The calibration curves for these polarograms are shown in Figure 5.21 and curve characteristics listed in Table 5.12. The intercept of Figure 5.21b of about 0.1nA is the uncompensated charging current and residual faradaic current from impurities, their sum corresponding to Cd^{+2} concentration of about $5 \times 10^{-8} \text{M}$. This can be seen in a slightly sloped baseline in Figure 5.22 and small peak in Figure 5.20a. This level of uncertainty represents a present limitation of the instrument; however, it represents only a fraction of the incremental charging current (see Figure 5.22) correction. The

Figure 5.16

Incremental polarograms of 10^{-6}M Cd^{+2} in 0.1M KCl with 0.01M HCl , offset scan.

- a. Supporting electrolyte alone.
- b. Added Cd^{+2} concentration of $0.99 \times 10^{-6}\text{M}$.
- c. Added Cd^{+2} concentration of $1.95 \times 10^{-6}\text{M}$.
- d. Added Cd^{+2} concentration of $3.76 \times 10^{-6}\text{M}$.
- e. Added Cd^{+2} concentration of $5.44 \times 10^{-6}\text{M}$.
- f. Added Cd^{+2} concentration of $7.01 \times 10^{-6}\text{M}$.
- g. Added Cd^{+2} concentration of $8.47 \times 10^{-6}\text{M}$.

Conditions: measuring frequency of 1.001kHz ,
 25°C , $\Delta E = 20\text{mV}$ with 4mV offset
scans, delay time of 2.5 seconds,
measuring period of 1.0 second,
1 drop at each potential.

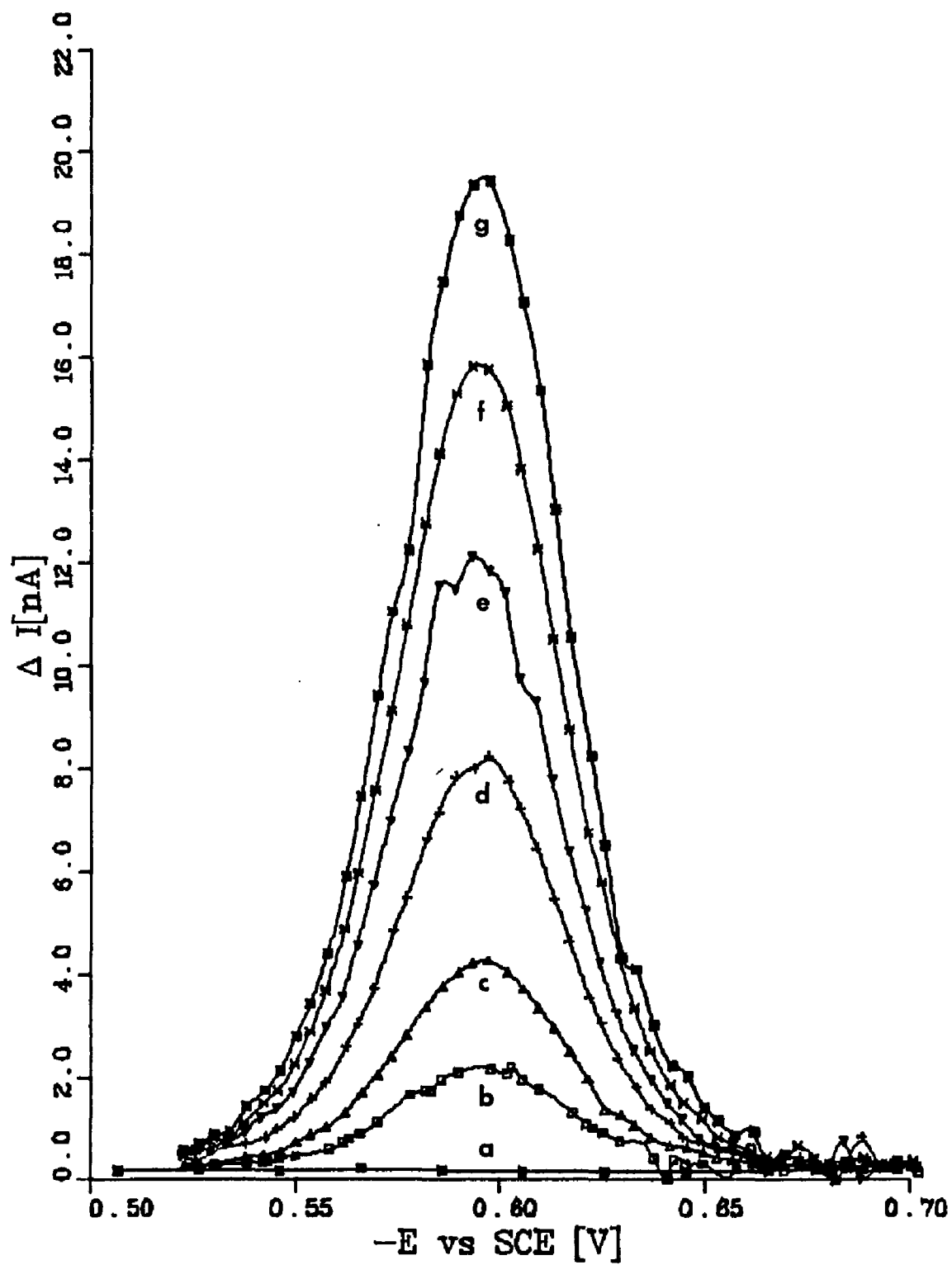


Figure 5.16

Figure 5.17

Calibration curve for 10^{-6}M Cd^{+2} in 0.1M KCl with 0.01M HCl , offset scans.

These curves are constructed from the data shown in Figure 5.16 and Table 5.10.

a. + Uncorrected results obtained from the printout:

$$\text{slope} = 2.33 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = 1.39 \text{ nA}$$

b. ● Corrected results obtained from the printout and plot, and doubly corrected results from the plot:

$$\text{slope} = 2.30 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = -0.28 \text{ nA}$$

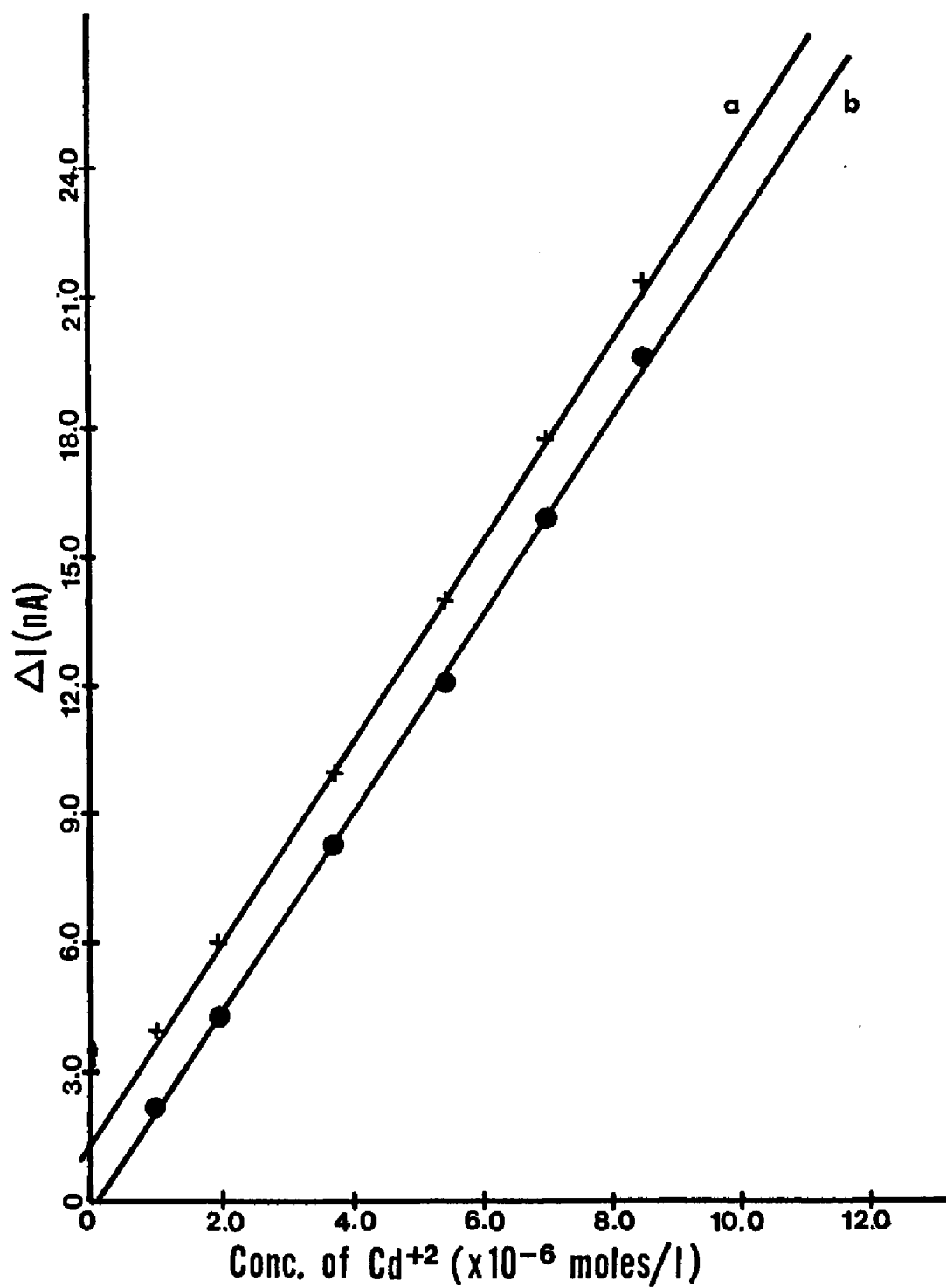


Figure 5.17

Figure 5.18

Incremental polarograms of 10^{-6}M Cd^{+2} in 0.1M KCl with 0.01M HCl , smaller steps.

- a. Supporting electrolyte alone.
- b. Added Cd^{+2} concentration of $0.99 \times 10^{-6}\text{M}$.
- c. Added Cd^{+2} concentration of $1.95 \times 10^{-6}\text{M}$.
- d. Added Cd^{+2} concentration of $3.76 \times 10^{-6}\text{M}$.
- e. Added Cd^{+2} concentration of $5.44 \times 10^{-6}\text{M}$.
- f. Added Cd^{+2} concentration of $7.01 \times 10^{-6}\text{M}$.
- g. Added Cd^{+2} concentration of $8.47 \times 10^{-6}\text{M}$.

Conditions: measuring frequency of 1.001kHz ,
 25°C , $\Delta E = 10\text{mV}$, delay time of
2.5 seconds, measuring period of
1.0 second, 1 drop at each poten-
tial.

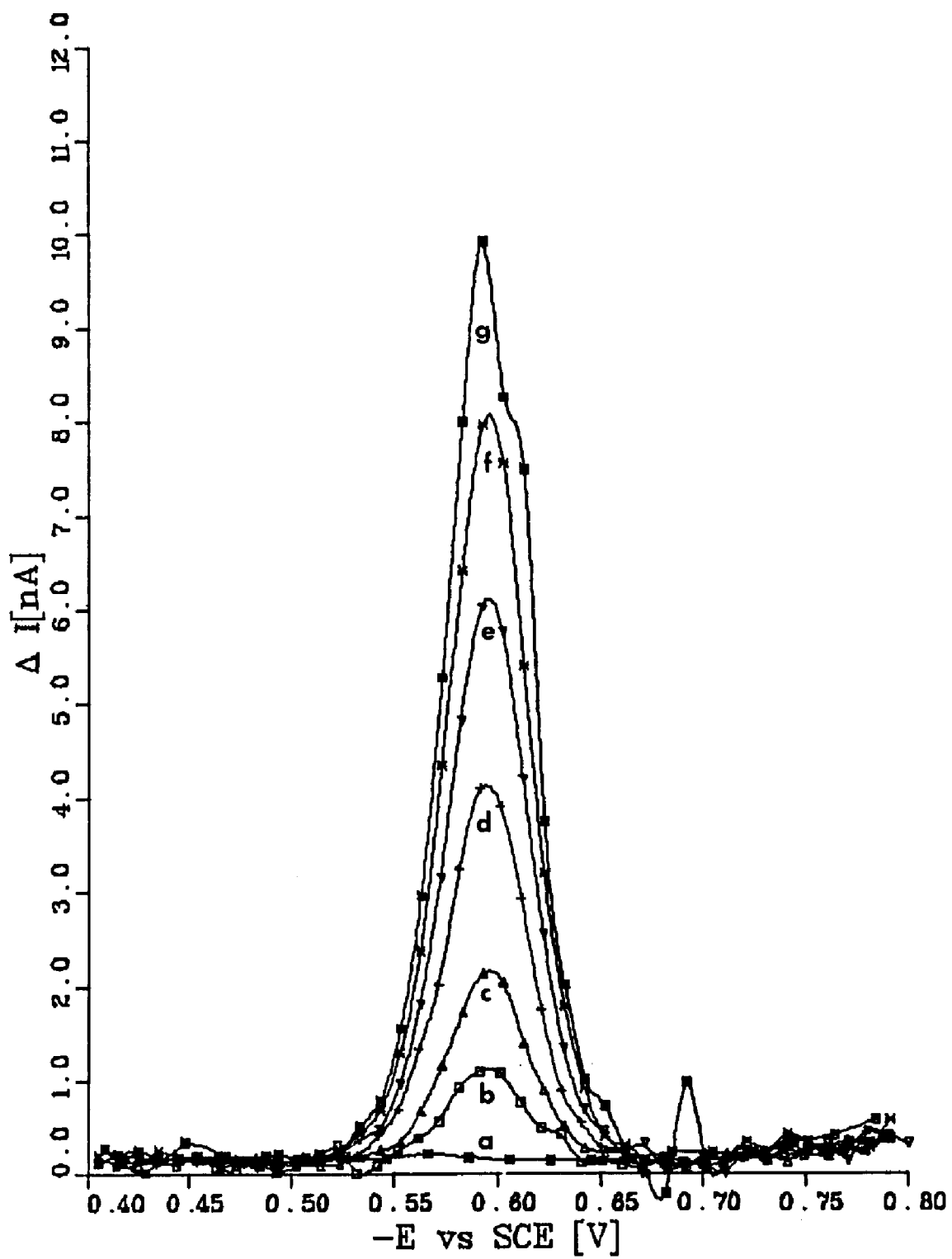


Figure 5.18

Table 5.10 Incremental Polarograms of Cd^{+2} in 0.1M KCl with 0.01M HCl, offset scan.

concentration	uncor. print.	cor. print.	cor. plot	d.cor. plot	$w_{1/2}$	$w_{2/3}$	$-E_{1/2}$
0.99×10^{-6}	3.87	2.16	2.22	2.06	49.1	38.5	0.600
1.95×10^{-6}	5.98	4.26	4.26	4.10	48.3	37.3	0.600
3.76×10^{-6}	9.94	8.21	8.21	8.05	49.1	37.7	0.599
5.44×10^{-6}	13.95	12.11	12.11	11.95	47.5	39.2	0.598
7.01×10^{-6}	17.65	15.81	15.89	15.73	47.5	39.2	0.599
8.47×10^{-6}	21.3	19.41	19.54	19.38	44.5	34.7	0.599

Figure 5.19

Calibration curve for 10^{-6}M Cd^{+2} in 0.1M KCl with 0.01M HCl, smaller steps.

These curves are constructed from the data shown in Figure 5.18 and Table 5.11.

a. + Uncorrected results obtained from the printout:

$$\text{slope} = 1.19 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = 0.64 \text{ nA}$$

b. * Corrected results obtained from the printout:

$$\text{slope} = 1.17 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = -0.19 \text{ nA}$$

c. Corrected results obtained from the plot:

$$\text{slope} = 1.17 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = -0.17 \text{ nA}$$

This curve was not plotted to preserve clarity of the graph.

d. ● Doubly corrected results obtained from the plot:

$$\text{slope} = 1.17 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = -0.33 \text{ nA}$$

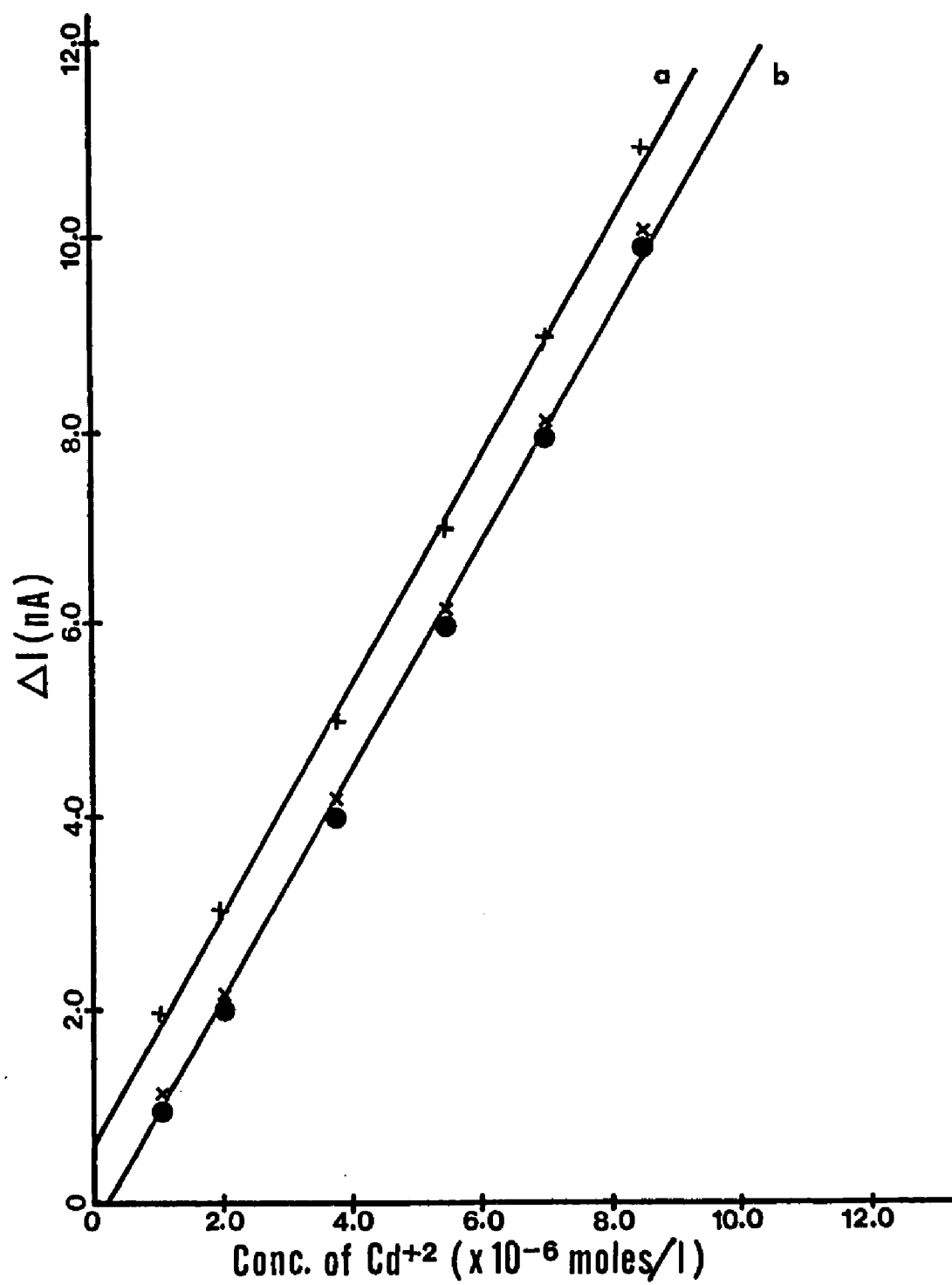


Figure 5.19

Table 5.11 Incremental Polarograms of Cd^{+2} in 0.1M KCl with 0.01M HCl, smaller steps.

concentration	uncor. print.	cor. print.	cor. plot	d.cor. plot	$w_{1/2}$	$w_{2/3}$	$-E_{1/2}$
0.99×10^{-6}	1.95	1.10	1.11	0.95	42.3	33.2	0.599
1.95×10^{-6}	2.99	2.14	2.16	2.00	44.1	33.2	0.601
3.76×10^{-6}	5.00	4.09	4.12	3.96	43.8	34.7	0.598
5.44×10^{-6}	6.94	6.02	6.11	5.95	46.8	34.7	0.599
7.01×10^{-6}	8.92	7.97	8.08	7.92	46.8	34.7	0.599
8.47×10^{-6}	10.89	9.91	9.94	9.78	46.8	36.2	0.597

Figure 5.20

Incremental polarograms of 10^{-7} M Cd^{+2} in 0.1M KCl.

- a. Supporting electrolyte alone.
- b. Added Cd^{+2} concentration of 2.01×10^{-7} M.
- c. Added Cd^{+2} concentration of 3.88×10^{-7} M.
- d. Added Cd^{+2} concentration of 5.59×10^{-7} M.
- e. Added Cd^{+2} concentration of 7.20×10^{-7} M.
- f. Added Cd^{+2} concentration of 8.70×10^{-7} M.
- g. Added Cd^{+2} concentration of 10.10×10^{-7} M.

Conditions: measuring frequency of 1.003kHz,
25°C, $\Delta E = 20\text{mV}$, delay time of
2.3 seconds, measuring period of
1.0 second, 3 drops at each
potential.

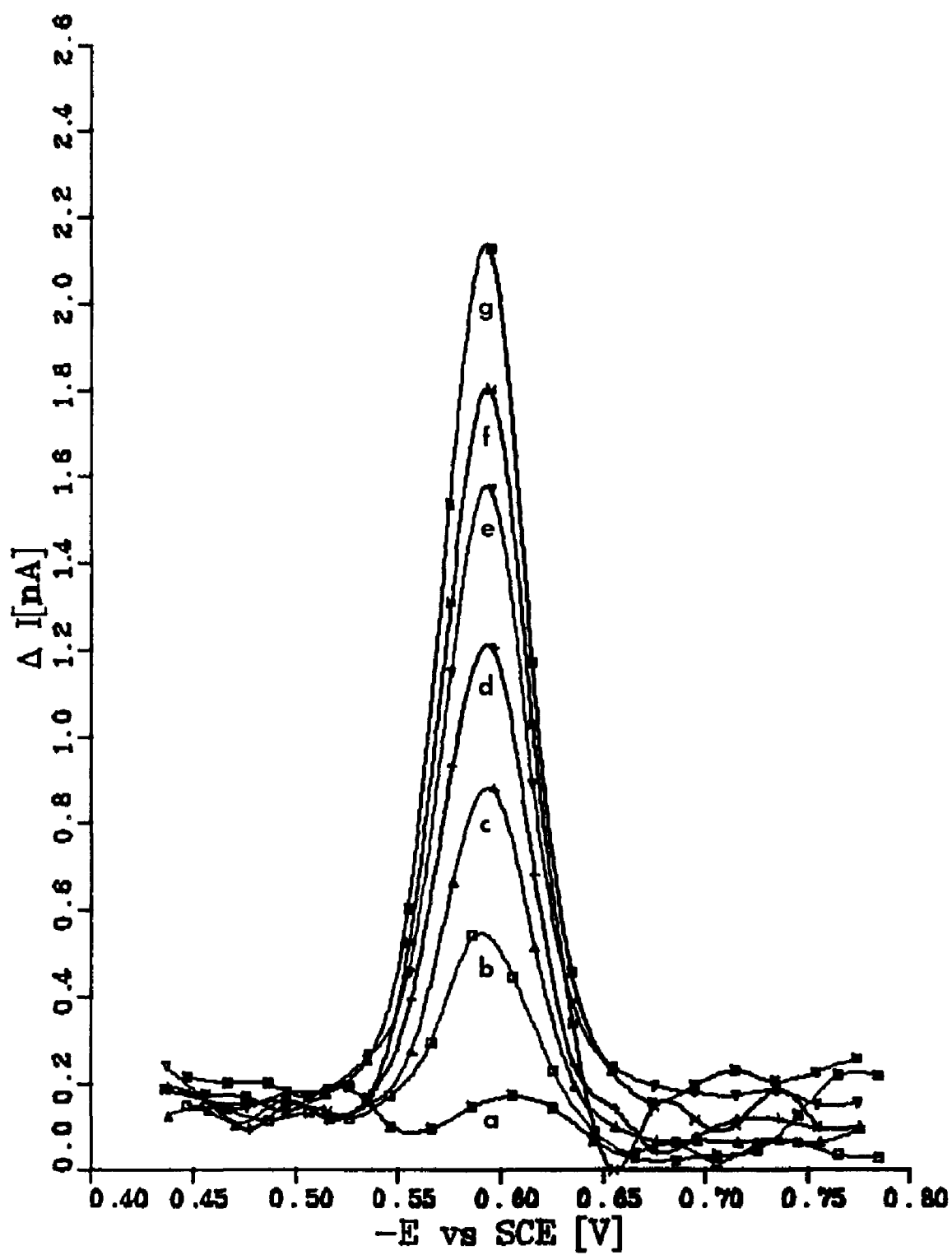


Figure 5.20

Figure 5.21

Calibration curve for 10^{-7}M Cd^{+2} in 0.1M KCl .

These curves are constructed from the data shown in Figure 5.20 and Table 5.12.

a. + Uncorrected results obtained from the printout:

$$\text{slope} = 1.87 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = 2.03 \text{ nA}$$

b. x Corrected results obtained from the printout and plot:

$$\text{slope} = 1.96 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = 0.13 \text{ nA}$$

c. ● Doubly corrected results obtained from the plot:

$$\text{slope} = 1.96 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = -0.01 \text{ nA}$$

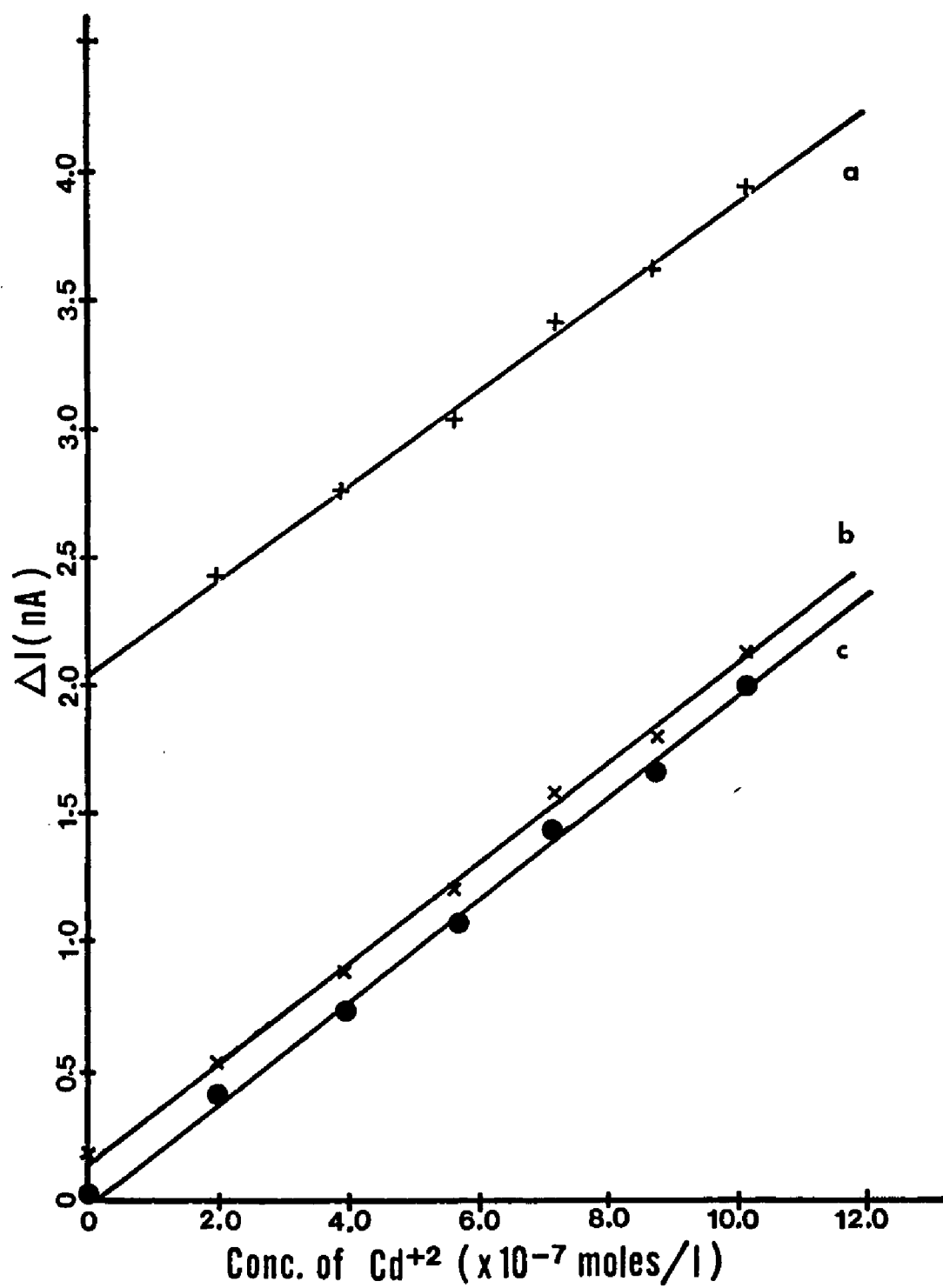


Figure 5.21

Table 5.12 Incremental Polarograms of Cd^{+2} in 0.1M KCl.

concentration	uncor. print.	cor. print.	cor. plot	d.cor. plot	$w_{1/2}$	$w_{2/3}$	$-E_{1/2}$
2.01×10^{-7}	2.42	0.540	0.553	0.407	45.3	34.7	0.594
3.88×10^{-7}	2.76	0.880	0.881	0.740	47.4	36.2	0.598
5.59×10^{-7}	3.04	1.20	1.21	1.07	49.2	36.8	0.597
7.20×10^{-7}	3.41	1.57	1.58	1.44	47.7	35.6	0.597
8.70×10^{-7}	3.61	1.80	1.81	1.66	48.3	37.1	0.597
10.10×10^{-7}	3.95	2.13	2.15	2.00	48.3	37.1	0.596

Figure 5.22

Capacitance and polarographic curves of 1.0M KCl.

- a. Capacitance at the beginning of the measuring period.
- b. Capacitance at the end of the measuring period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of 1.001kHz,
25°C, $\Delta E = 20\text{mV}$, delay time of
2.3 seconds, measuring period of
1 second, 3 drops at each poten-
tial.

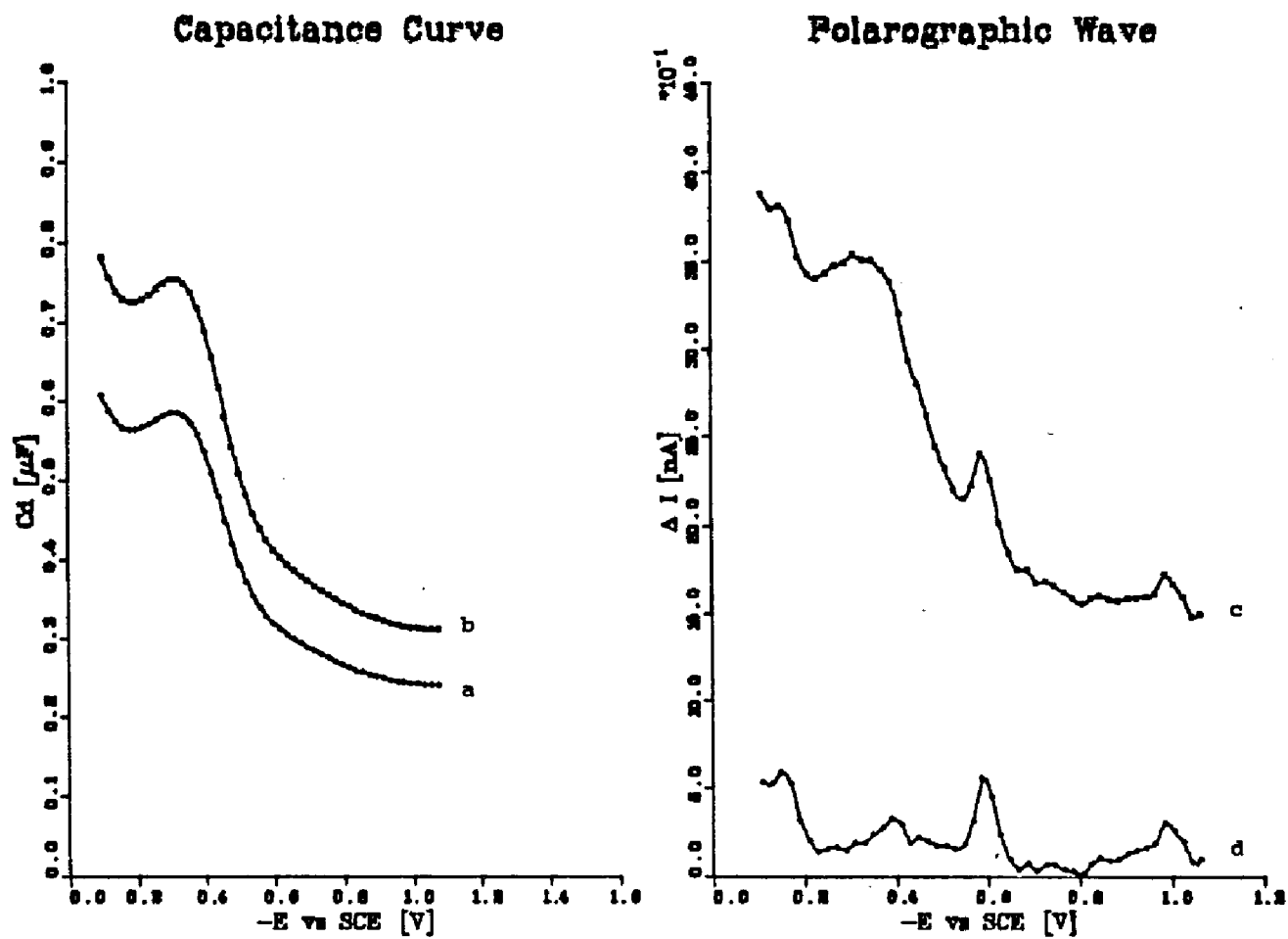


Figure 5.22

small peak in Figure 5.22 with $E_{1/2} = -0.40\text{V}$ is probably due to a sub-micromolar lead impurity.

To realize further signal-to-noise improvements and to test the performance of the instrument with large ΔE , the fill-in runs were recorded with 40mV steps spaced at 5mV intervals. The resulting polarograms are shown in Figure 5.23, with calibration curves in Figure 5.24 and data in Table 5.13.

As previously seen, here also we find a slight slope in the baseline, indicating an incomplete charging current compensation at these signal levels. However, the total error from the sloping baseline and noise corresponds to less than 5×10^{-8} moles/l of Cd^{+2} (see Figure 5.25).

Even with the 5mv fill-in, errors of about 1-2% in the peak height could occur due to improper location of the peak. As can be seen from Figure 5.26, the actual peak height should be higher than either of the two experimental points. To increase the accuracy of locating the peak, an offset scan procedure with, individual scans as close as 2mv apart, and covering only about 100mV around the $E_{1/2}$ can be used. One such experiment with $\Delta E = 40\text{mV}$ and 2mV fill-ins is shown in Figure 5.27, with calibration curves shown in Figure 5.28 and curve characteristics listed in Table 5.14.

The summary in Table 5.15 shows that the width of the incremental curves does depend on values of ΔE as was discussed in Section 3.2.2.1. The curve width decreases with decreasing ΔE , and for $\Delta E = 10\text{mV}$ the values of 45mV and

Figure 5.23

Incremental polarograms of 10^{-7}M Cd^{+2} in 0.1M KCl , large steps with offset scan.

- a. Supporting electrolyte alone.
- b. Added Cd^{+2} concentration of $2.01 \times 10^{-7}\text{M}$.
- c. Added Cd^{+2} concentration of $3.88 \times 10^{-7}\text{M}$.
- d. Added Cd^{+2} concentration of $5.59 \times 10^{-7}\text{M}$.
- e. Added Cd^{+2} concentration of $7.20 \times 10^{-7}\text{M}$.
- f. Added Cd^{+2} concentration of $8.70 \times 10^{-7}\text{M}$.
- g. Added Cd^{+2} concentration of $10.10 \times 10^{-7}\text{M}$.

Conditions: measuring frequency of 1.001kHz ,
 25°C , $\Delta E = 40\text{mV}$ with 5mV offset
scan, delay time of 2.3 seconds,
measuring period of 1.0 second,
 3 drops at each potential.

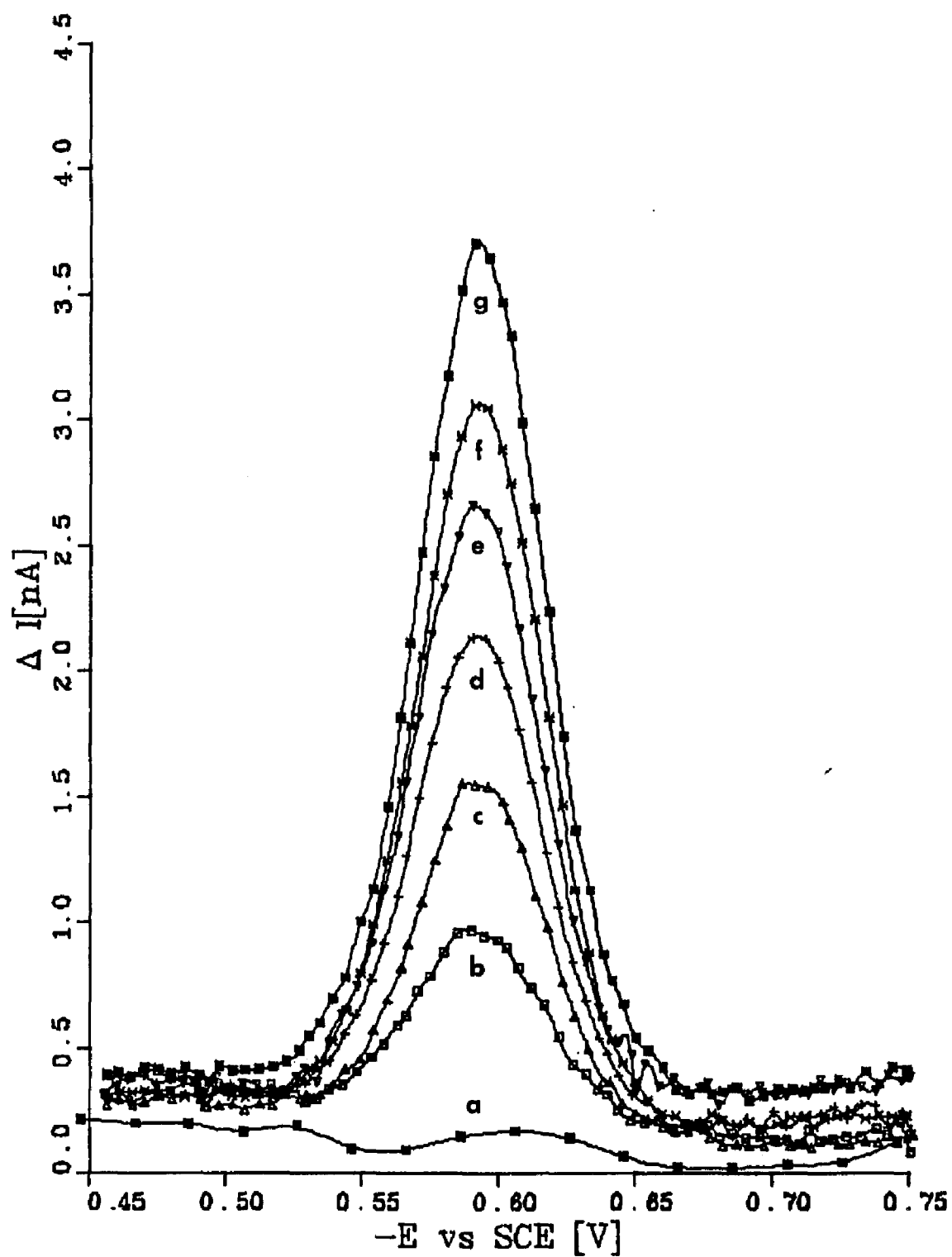


Figure 5.23

Figure 5.24

Calibration curve for $10^{-7}M$ Cd^{+2} in $0.1M$ KCl ,
offset scans.

These curves are constructed from the data
shown in Figure 5.23 and Table 5.13.

a. + Uncorrected results obtained from the
printout:

$$\text{slope} = 3.13 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = 3.79 \text{ nA}$$

b. × Corrected results obtained from the
printout and plot:

$$\text{slope} = 3.30 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = 0.28 \text{ nA}$$

c. ● Doubly corrected results obtained from
the plot:

$$\text{slope} = 3.31 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = -0.03 \text{ nA}$$

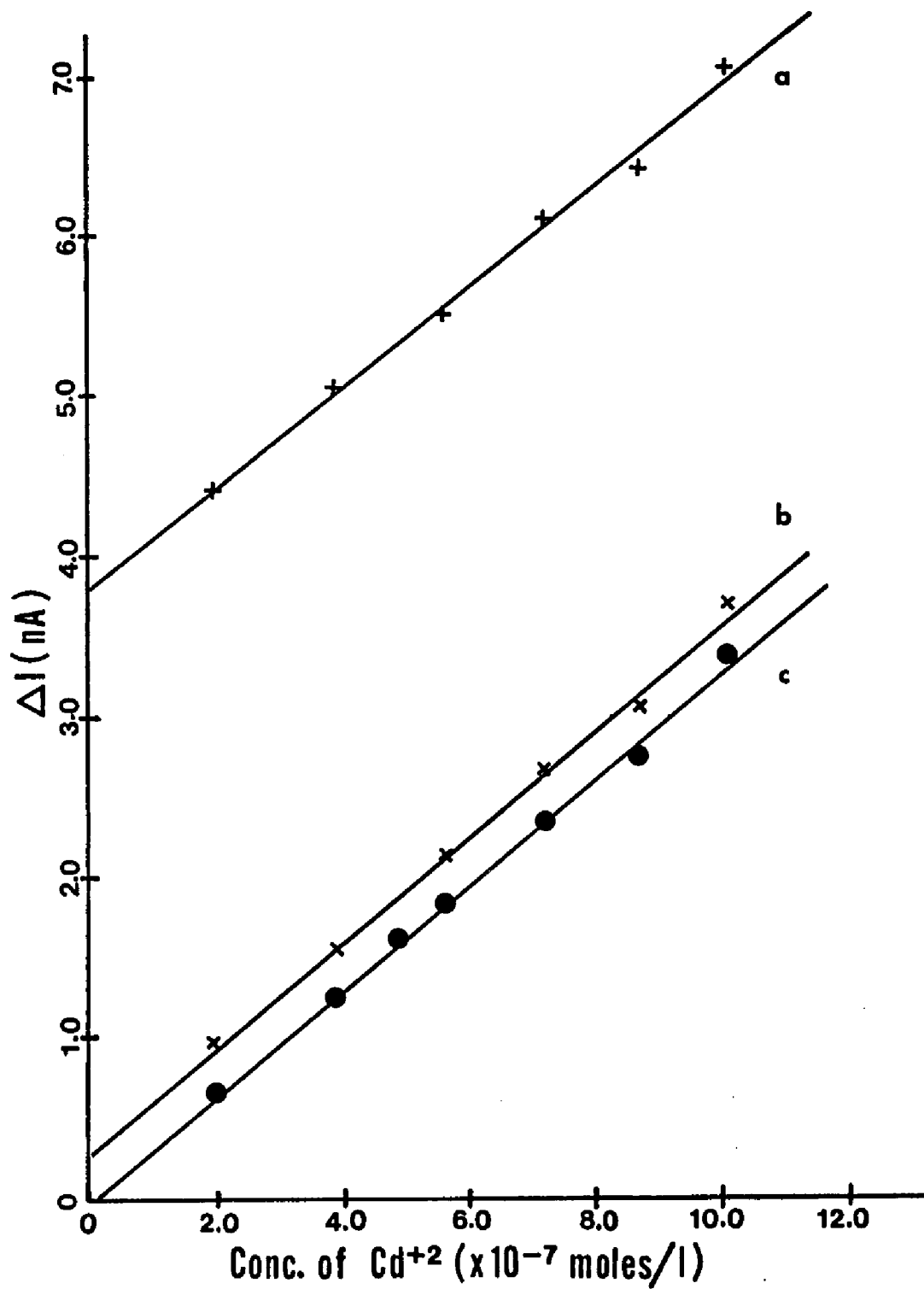


Figure 5.24

Table 5.13 Incremental Polarograms of Cd^{+2} in 0.1M KCl, offset scan.

concentration	uncor.	cor.	cor.	d.cor.	$w_{1/2}$	$w_{2/3}$	$-E_{1/2}$
<u> </u>	<u>print.</u>	<u>print.</u>	<u>plot</u>	<u>plot</u>	<u> </u>	<u> </u>	<u> </u>
2.01×10^{-7}	4.41	0.969	0.969	0.655	51.6	39.6	0.595
3.88×10^{-7}	5.04	1.55	1.56	1.24	52.0	39.6	0.598
5.59×10^{-7}	5.51	2.13	2.15	1.83	52.7	41.9	0.596
7.20×10^{-7}	6.08	2.66	2.66	2.34	53.2	41.7	0.596
8.70×10^{-7}	6.39	3.05	3.07	2.75	53.9	41.2	0.597
10.10×10^{-7}	7.03	3.70	3.70	3.40	54.8	41.4	0.598

Figure 5.25

Incremental polarograms of $2 \times 10^{-7} \text{M}$ Cd^{+2} in 0.1M KCl .

- a. Uncompensated incremental polarogram.
- b. Compensated incremental polarogram.

Conditions: measuring frequency of 1.001kHz ,
 25°C , $\Delta E = 40 \text{mV}$ with 5mV offset
scan, delay time of 2.3 seconds,
measuring period of 1 second,
 3 drops at each potential.

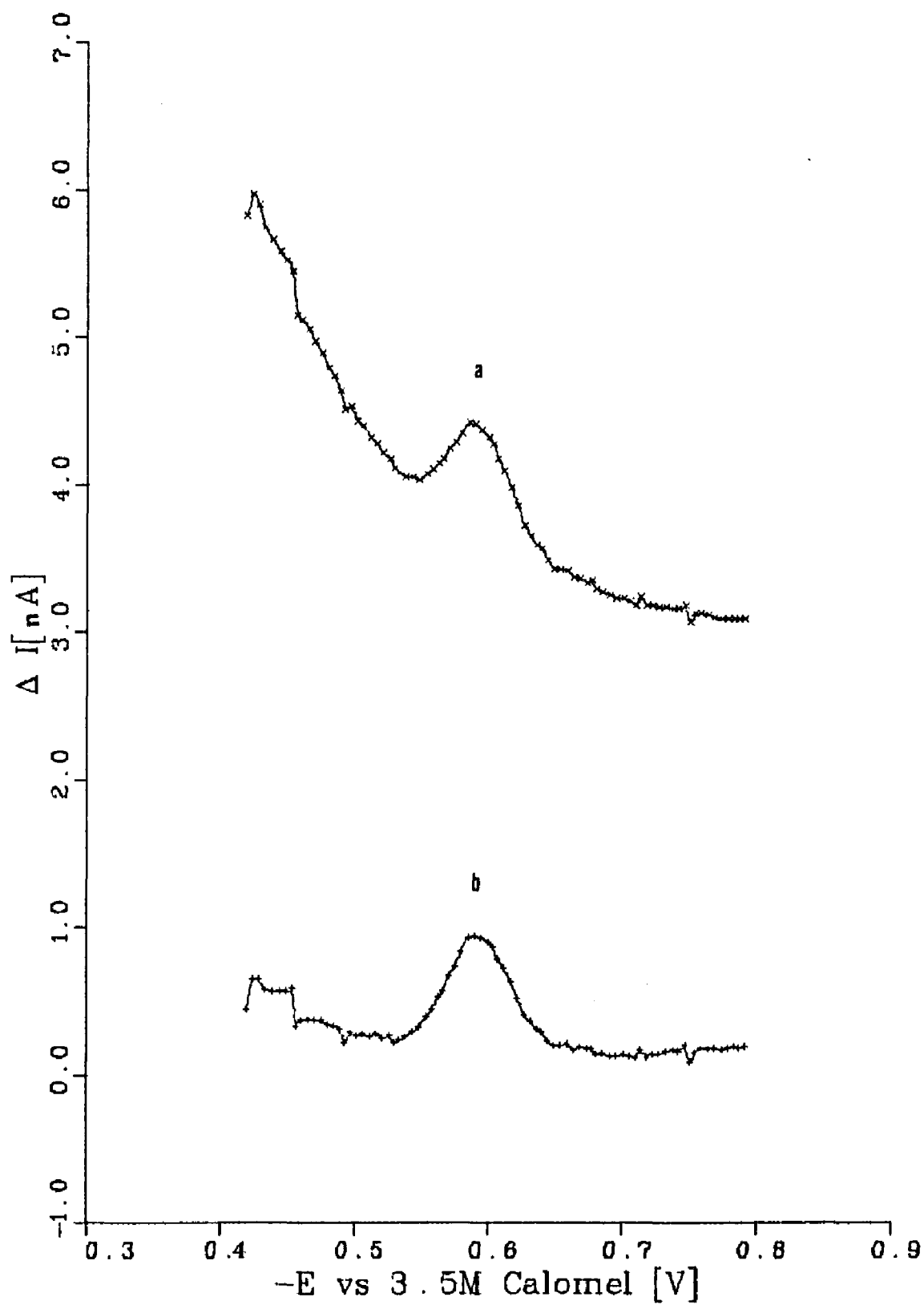


Figure 5.25

Figure 5.26

Compensated incremental polarogram of
 $8.7 \times 10^{-7} \text{M Cd}^{+2}$ in 0.1M KCl .

Conditions: measuring frequency of 1.001kHz ,
 25°C , $\Delta E = 40 \text{mV}$ with 5mV offset
scan, delay time of 2.3 seconds ,
measuring period of 1 second ,
 3 drops at each potential.

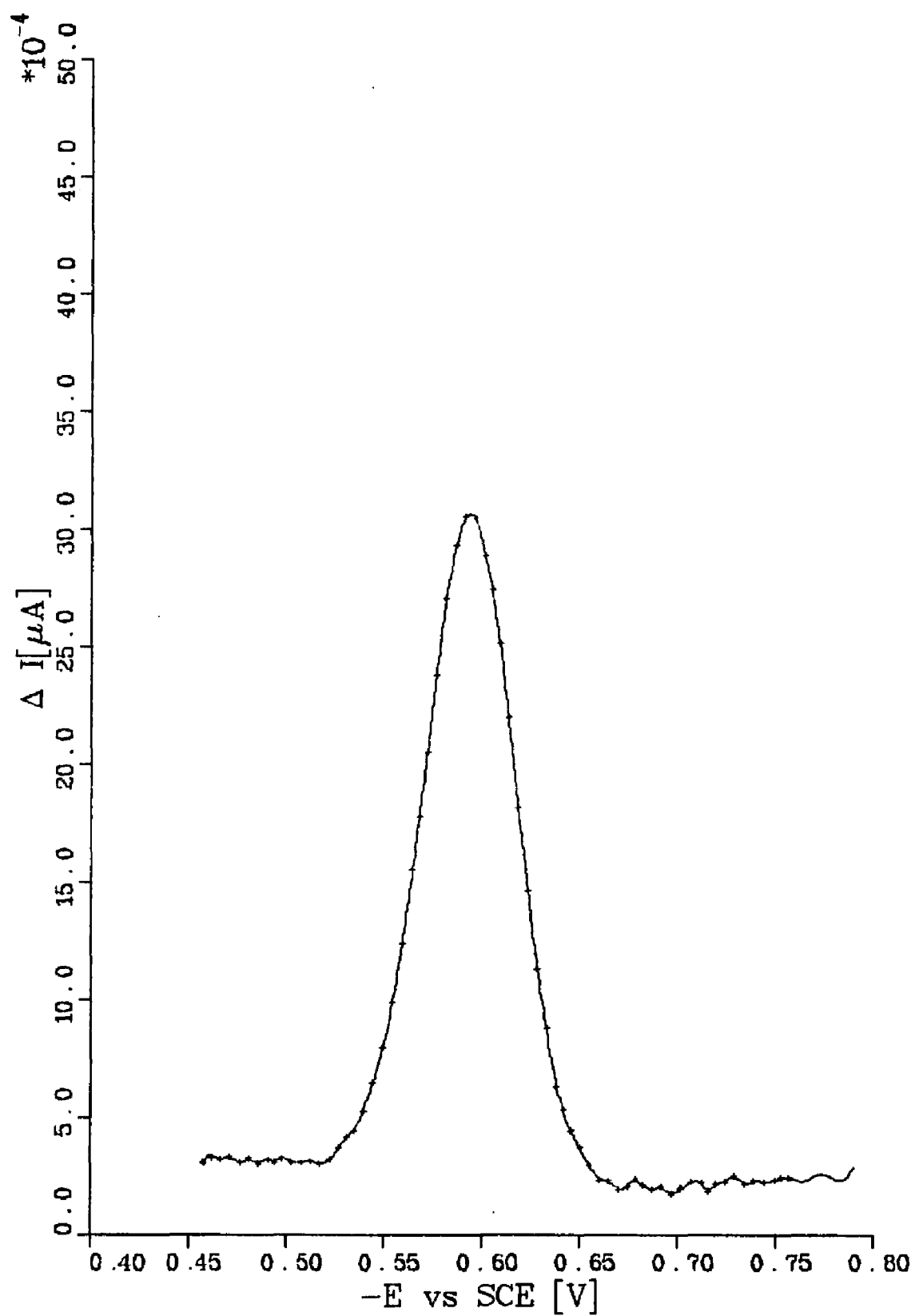


Figure 5.26

Figure 5.27

Incremental polarograms of 10^{-7}M Cd^{+2} in 0.1M KCl , large steps with offset scan.

- a. Supporting electrolyte alone.
- b. Added Cd^{+2} concentration of $2.01 \times 10^{-7}\text{M}$.
- c. Added Cd^{+2} concentration of $3.88 \times 10^{-7}\text{M}$.
- d. Added Cd^{+2} concentration of $5.59 \times 10^{-7}\text{M}$.
- e. Added Cd^{+2} concentration of $7.20 \times 10^{-7}\text{M}$.
- f. Added Cd^{+2} concentration of $8.70 \times 10^{-7}\text{M}$.
- g. Added Cd^{+2} concentration of $10.10 \times 10^{-7}\text{M}$.

Conditions: measuring frequency of 1.001kHz ,
 25°C , $\Delta E = 40\text{mV}$ with 2mV offset
scan, delay time of 2.3 seconds,
measuring period of 1.0 second,
 3 drops at each potential.

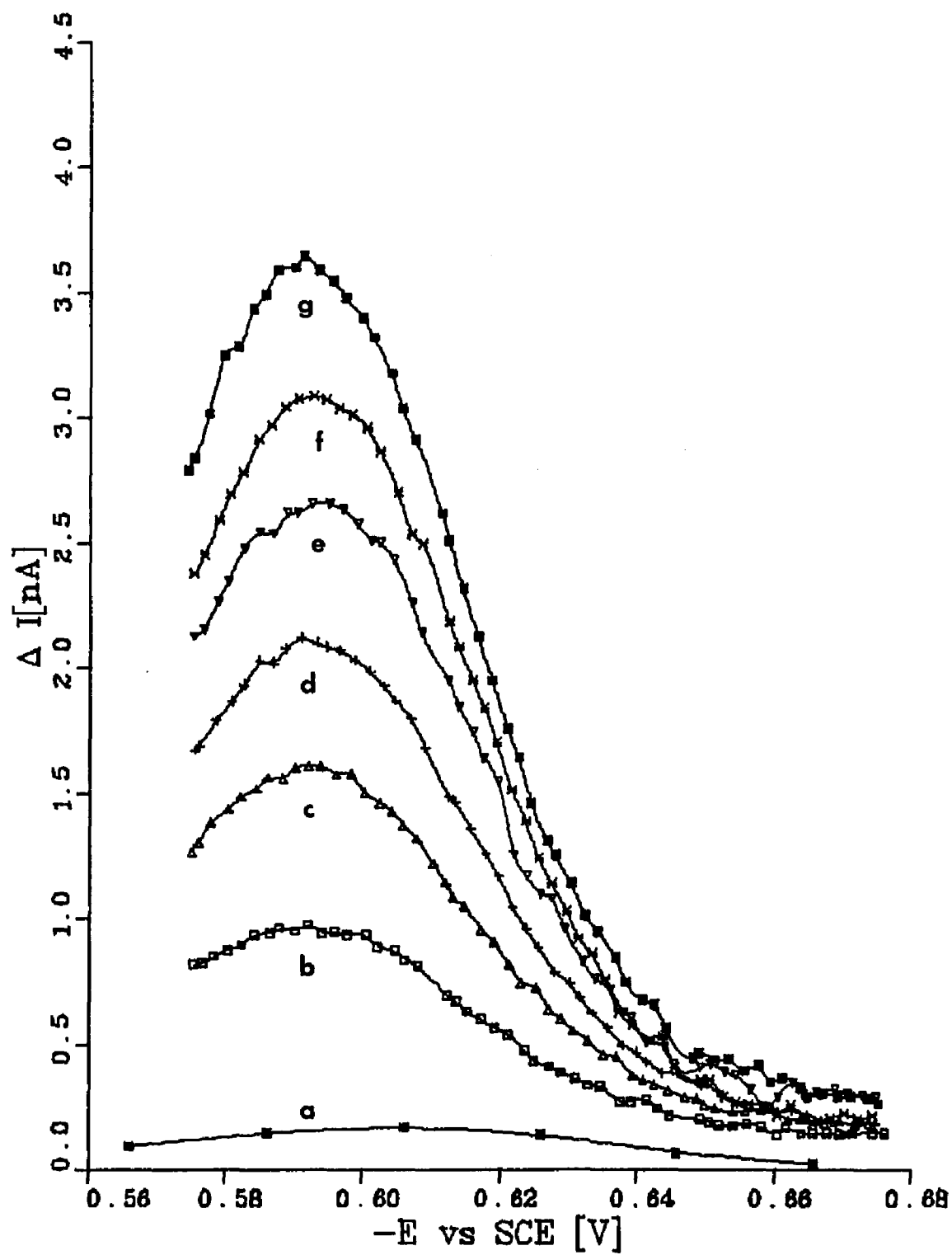


Figure 5.27

Figure 5.28

Calibration curve for 10^{-7}M Cd^{+2} in 0.1M KCl ,
finer offset scans.

These curves are constructed from the data
shown in Figure 5.27 and Table 5.14.

a. + Uncorrected results obtained from the
printout:

$$\begin{aligned}\text{slope} &= 3.12 \text{ nA}/\mu\text{mole l}^{-1} \\ \text{intercept} &= 3.80 \text{ nA}\end{aligned}$$

b. x Corrected results obtained from the
printout and plot:

$$\begin{aligned}\text{slope} &= 3.23 \text{ nA}/\mu\text{mole l}^{-1} \\ \text{intercept} &= 0.33 \text{ nA}\end{aligned}$$

c. ● Doubly corrected results obtained from
the plot:

$$\begin{aligned}\text{slope} &= 3.04 \text{ nA}/\mu\text{mole l}^{-1} \\ \text{intercept} &= 0.21 \text{ nA}\end{aligned}$$

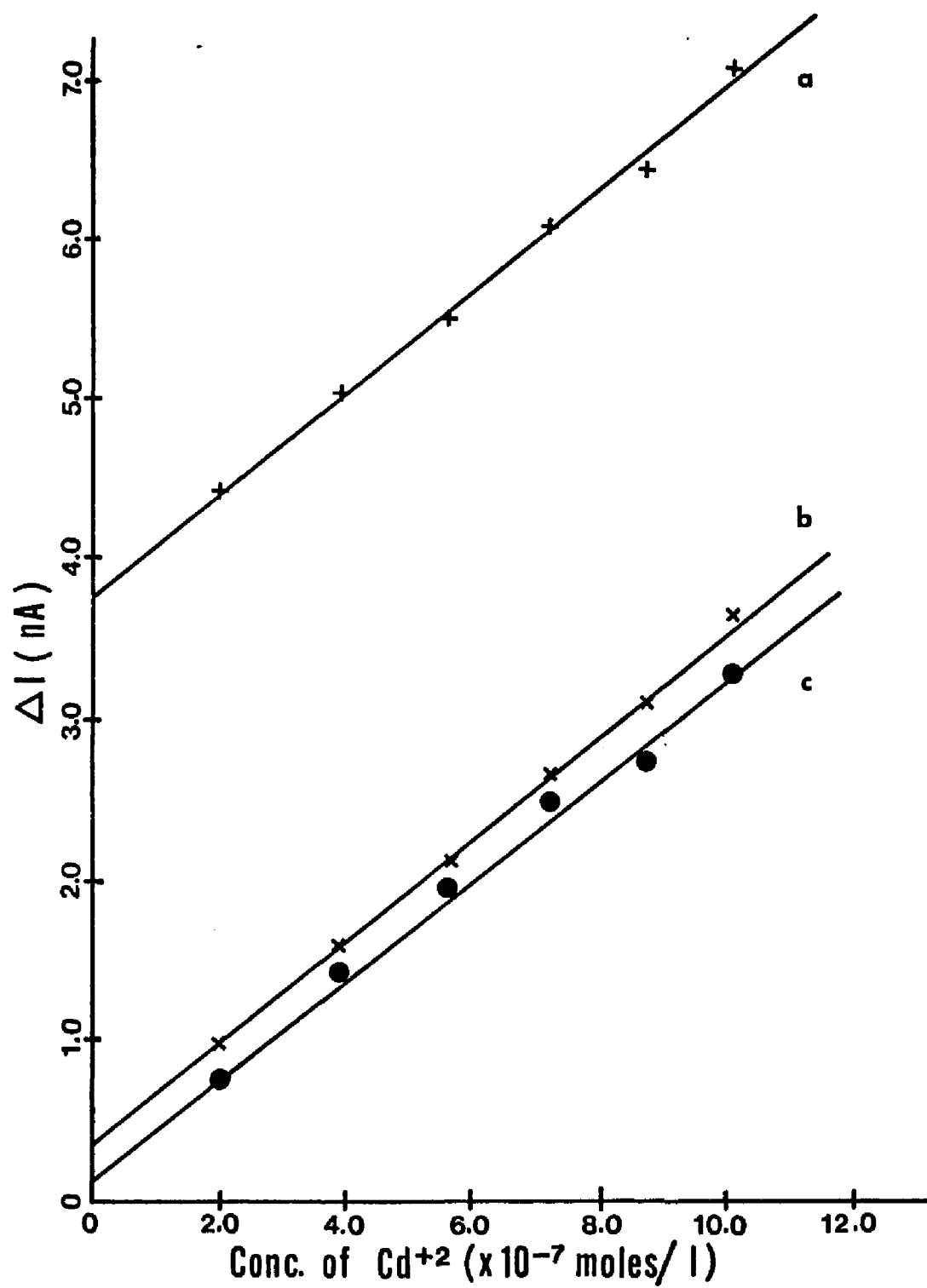


Figure 5.28

Table 5.14 Incremental Polarograms of Cd^{+2} in 0.1M KCl, offset scan.

concentration	uncor.	cor.	cor.	d.cor.	$-E_{1/2}$
<u> </u>	<u>print.</u>	<u>print.</u>	<u>plot</u>	<u>plot</u>	<u> </u>
2.01×10^{-7}	4.44	0.978	0.969	0.772	0.696
3.88×10^{-7}	5.05	1.61	1.61	1.42	0.596
5.59×10^{-7}	5.49	2.12	2.12	1.94	0.595
7.20×10^{-7}	6.08	2.66	2.66	2.47	0.597
8.70×10^{-7}	6.43	3.08	3.09	2.75	0.597
10.10×10^{-7}	7.03	3.64	3.64	3.30	0.595

Table.5.15 Summary of Experimental Parameters Obtained for Cd^{+2} .

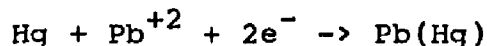
conc. [moles/l]	ΔE [mV]	$w_{1/2}$ [mV]	$w_{2/3}$ [mV]	$E_{1/2}$ [V]	slope	st.dev. [%]
$1 \times 10^{-6} - 1 \times 10^{-5}$	20	50	39	-0.598	2.11	1.2
$1 \times 10^{-6} - 1 \times 10^{-5}$	20 - fill	48	37	-0.599	2.30	1.1
$1 \times 10^{-6} - 1 \times 10^{-5}$	10	45	34.5	-0.599	1.17	2.0
$1 \times 10^{-7} - 1 \times 10^{-6}$	20	48	36	-0.597	1.96	2.2
$1 \times 10^{-7} - 1 \times 10^{-6}$	40 - fill	53	41	-0.597	3.30	3.1
$1 \times 10^{-7} - 1 \times 10^{-6}$	40-fine fill	-	-	-0.596	3.23	1.9
derivative	—	45.3	33.8	-0.599	—	—

34.5mV for half-height width and two-thirds-height width respectively are within experimental error of the theoretical values of 45.3mV and 33.8mV calculated for derivative curves (see Section 3.2.2.1). A slight improvement in curve shape is obtained when fill-ins are used due to better resolution.

The accuracy of $E_{1/2}$ was within the experimental error of the literature value of $-0.599 \pm 0.005V$ vs SCE (9), with experimental uncertainty of about $0.002V$. No significant deterioration in experimental $E_{1/2}$ values can be found even at $2 \times 10^{-7}M$ concentrations of Cd(II).

5.2.4 LEAD (II)

Electroreduction of Pb^{+2} in KCl according to the equation



is a reversible process with $k_{SH} = 0.2cm^{-1}$ in 1M KCl (92) and $E_{1/2} = -0.396 \pm 0.003V$ vs SCE (9). The reduction of Pb(II) occurs at potentials where the double layer capacitance is large and changes rapidly; at potentials near the "hump" in the C_d vs E curve. Also, Pb represents a case in which the polarogram of the supporting electrolyte alone is not suitable for background current subtraction, since it does not correspond to the charging current alone. It is suspected that Pb specifically adsorbs on the DME (87,88)

which would change the value of C_d . Figures 5.29a and 5.29b show the difference in the capacitance curves obtained with 0.1M KCl before and after addition of Pb^{+2} . As can be seen from these curves, the capacitance wave decreases by about 10% after addition of Pb^{+2} . This effect is almost constant in the $Pb(II)$ concentration range from $2 \times 10^{-7}M$ to $1 \times 10^{-6}M$. It will be shown that this specific adsorption of Pb^{+2} does not interfere with the in-situ compensation as presented here.

The incremental polarograms of Pb^{+2} in 0.1M KCl obtained over the concentration range from $2 \times 10^{-7}M$ to $1 \times 10^{-5}M$ are shown in Figures 5.30 and 5.31, for $\Delta E = 40mV$ with 5mV fill-ins. The calibration curves for these results are shown in Figures 5.32 and 5.33 respectively and curve characteristics are listed in Table 5.16. The incremental polarograms in Figures 5.30 and 5.31 show that the charging current compensation in this very difficult region is quite good, with virtually zero slope in the baseline, and only slight offset. The sharper rise in the slope starting at about -0.3V and increasing towards the less negative potentials is not a failure of the resulting charging current compensation, but rather shows the onset of the faradaic current from the oxidation of mercury in the chloride media. However, since it is a more difficult potential region to work in, the results are expected to show higher deviation from the theoretical values than obtained with $Cd(II)$ or $Zn(II)$ ions.

Figure 5.29

Capacitance curves in the absence and presence of Pb^{+2} in 1.0M KCl.

- a. Capacitance at the beginning of the measuring period - 0.1M KCl only.
- b. Capacitance at the end of the measuring period - 0.1M KCl only.
- c. Capacitance at the beginning of the measuring period - 0.1M KCl + $4 \times 10^{-7}\text{M}$ Pb^{+2} .
- d. Capacitance at the end of the measuring period - 0.1M KCl + $4 \times 10^{-7}\text{M}$ Pb^{+2} .

Conditions: measuring frequency of 1.003kHz, 25°C , $\Delta E = 20\text{mV}$, delay time of 2.3 seconds and measuring period of 1 second, 3 drops at each potential.

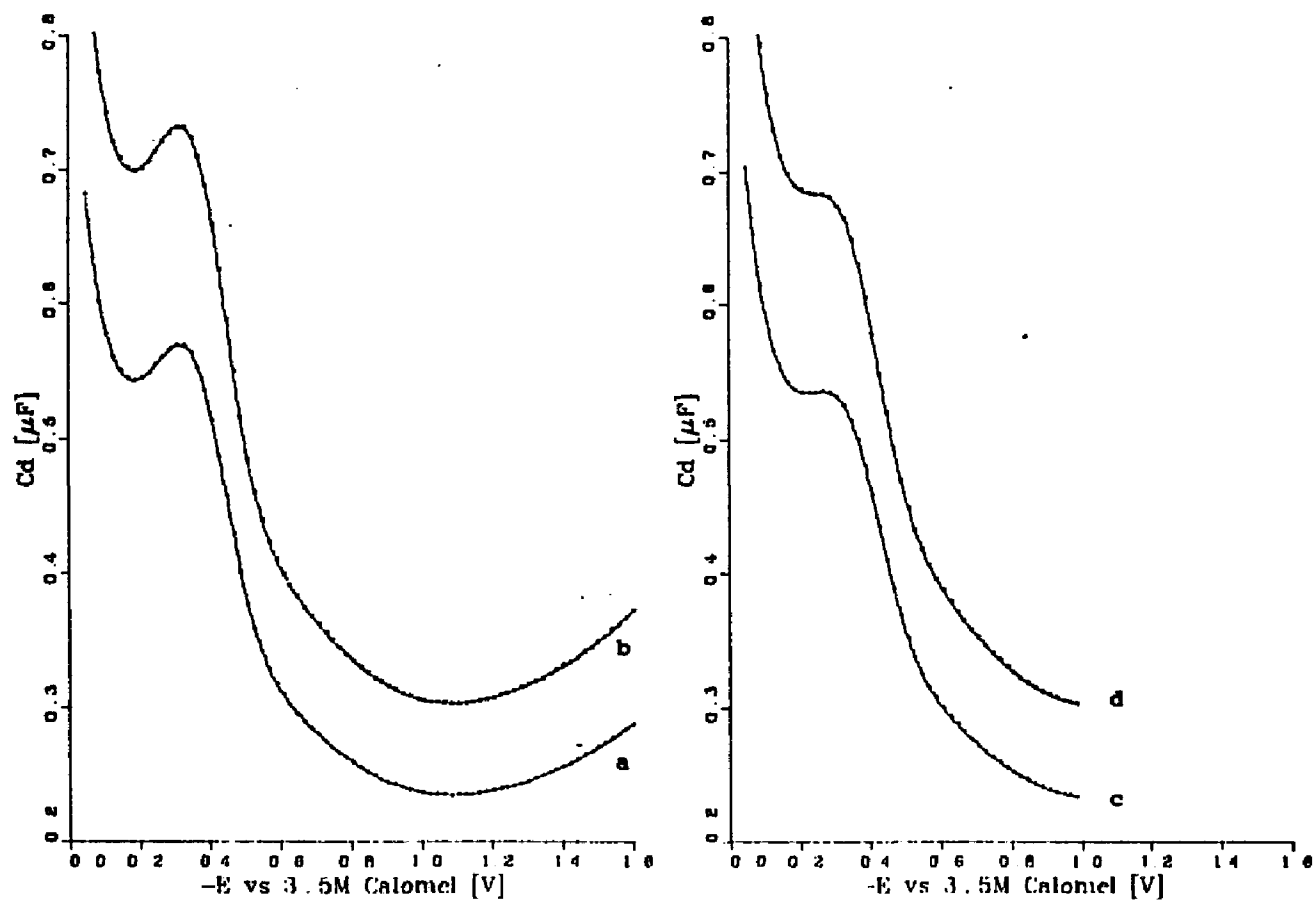


Figure 5.29

Figure 5.30

Incremental polarograms of 10^{-7}M Pb^{+2} in 0.1M KCl .

- a. Supporting electrolyte alone.
- b. Added Pb^{+2} concentration of $1.94 \times 10^{-7}\text{M}$.
- c. Added Pb^{+2} concentration of $3.73 \times 10^{-7}\text{M}$.
- d. Added Pb^{+2} concentration of $8.40 \times 10^{-7}\text{M}$.
- e. Added Pb^{+2} concentration of $10.40 \times 10^{-7}\text{M}$.

Conditions: measuring frequency of 1.003kHz ,
 25°C , $\Delta E = 40\text{mV}$ with 5mV offset
scan, delay time of 2.3 seconds,
measuring period of 1.0 second,
3 drops at each potential.

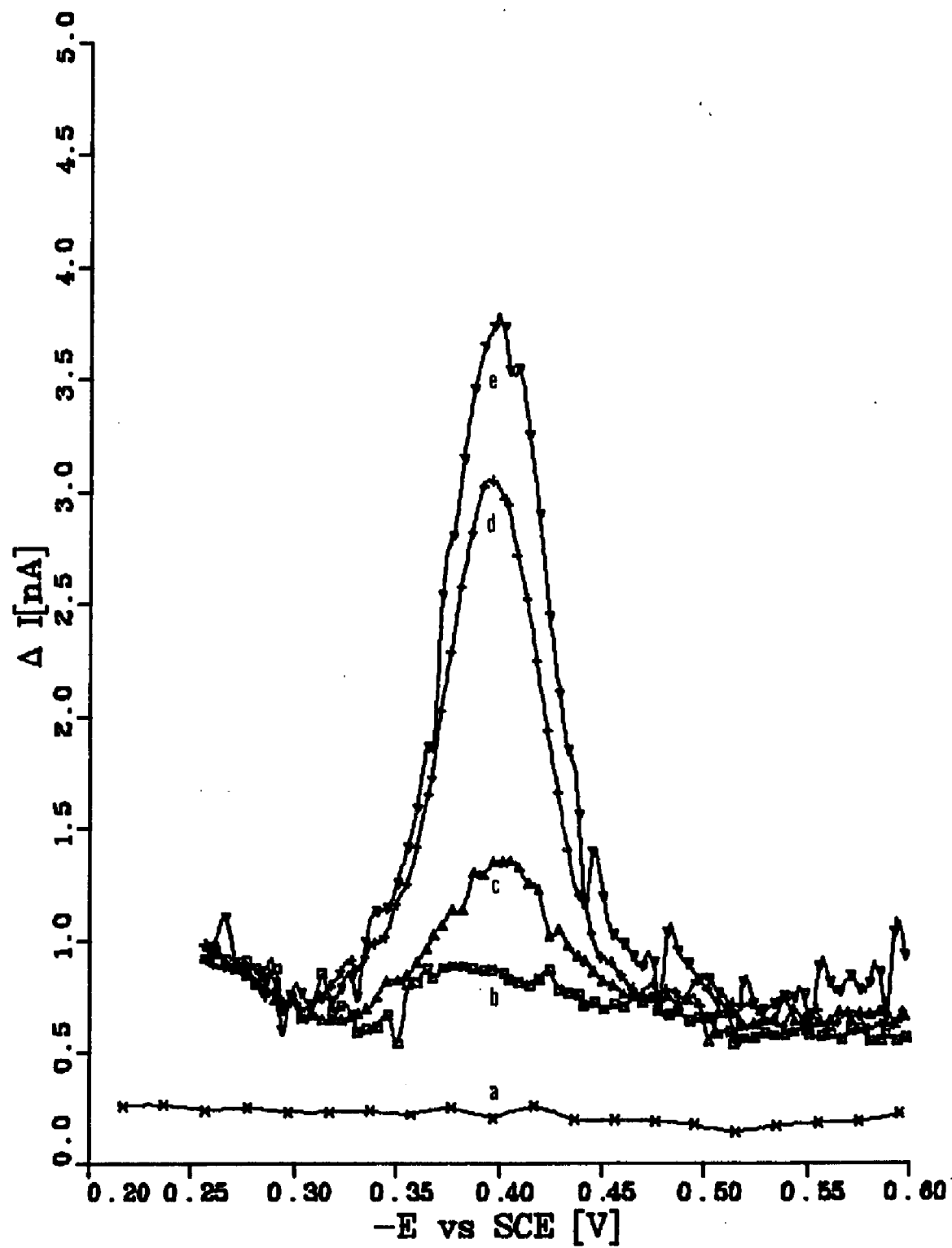


Figure 5.30

Figure 5.31

Incremental polarograms of 10^{-6}M Pb^{+2} in 0.1M KCl , offset scans.

- a. Supporting electrolyte alone.
- b. Added Pb^{+2} concentration of $1.04 \times 10^{-6}\text{M}$.
- c. Added Pb^{+2} concentration of $2.53 \times 10^{-6}\text{M}$.
- d. Added Pb^{+2} concentration of $3.99 \times 10^{-6}\text{M}$.
- e. Added Pb^{+2} concentration of $5.98 \times 10^{-6}\text{M}$.
- f. Added Pb^{+2} concentration of $7.80 \times 10^{-6}\text{M}$.
- g. Added Pb^{+2} concentration of $10.5 \times 10^{-6}\text{M}$.

Conditions: measuring frequency of 1.003kHz ,
 25°C , $\Delta E = 40\text{mV}$ with 5mV offset
scans, delay time of 2.3 seconds,
measuring period of 1.0 second,
3 drop at each potential.

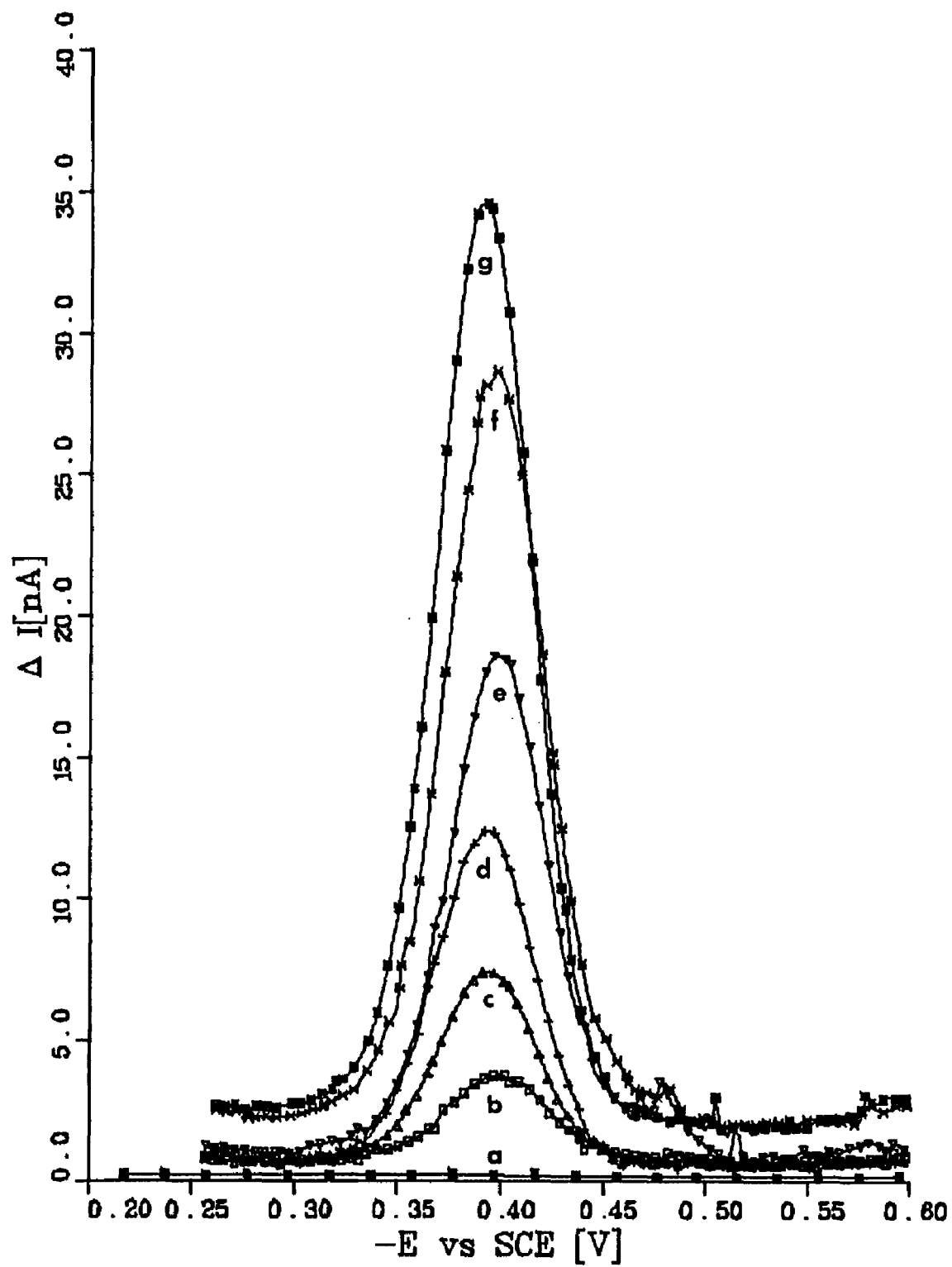


Figure 5.31

Figure 5.32

Calibration curve for 10^{-7}M Pb^{+2} in 0.1M KCl, offset scans.

These curves are constructed from the data shown in Figure 5.30 and Table 5.16.

a. + Uncorrected results obtained from the printout:

$$\text{slope} = 3.91 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = 4.53 \text{ nA}$$

b. x Corrected results obtained from the printout and plot:

$$\text{slope} = 3.42 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = 0.17 \text{ nA}$$

c. ● Doubly corrected results obtained from the plot:

$$\text{slope} = 3.34 \text{ nA}/\mu\text{mole l}^{-1}$$

$$\text{intercept} = -0.43 \text{ nA}$$

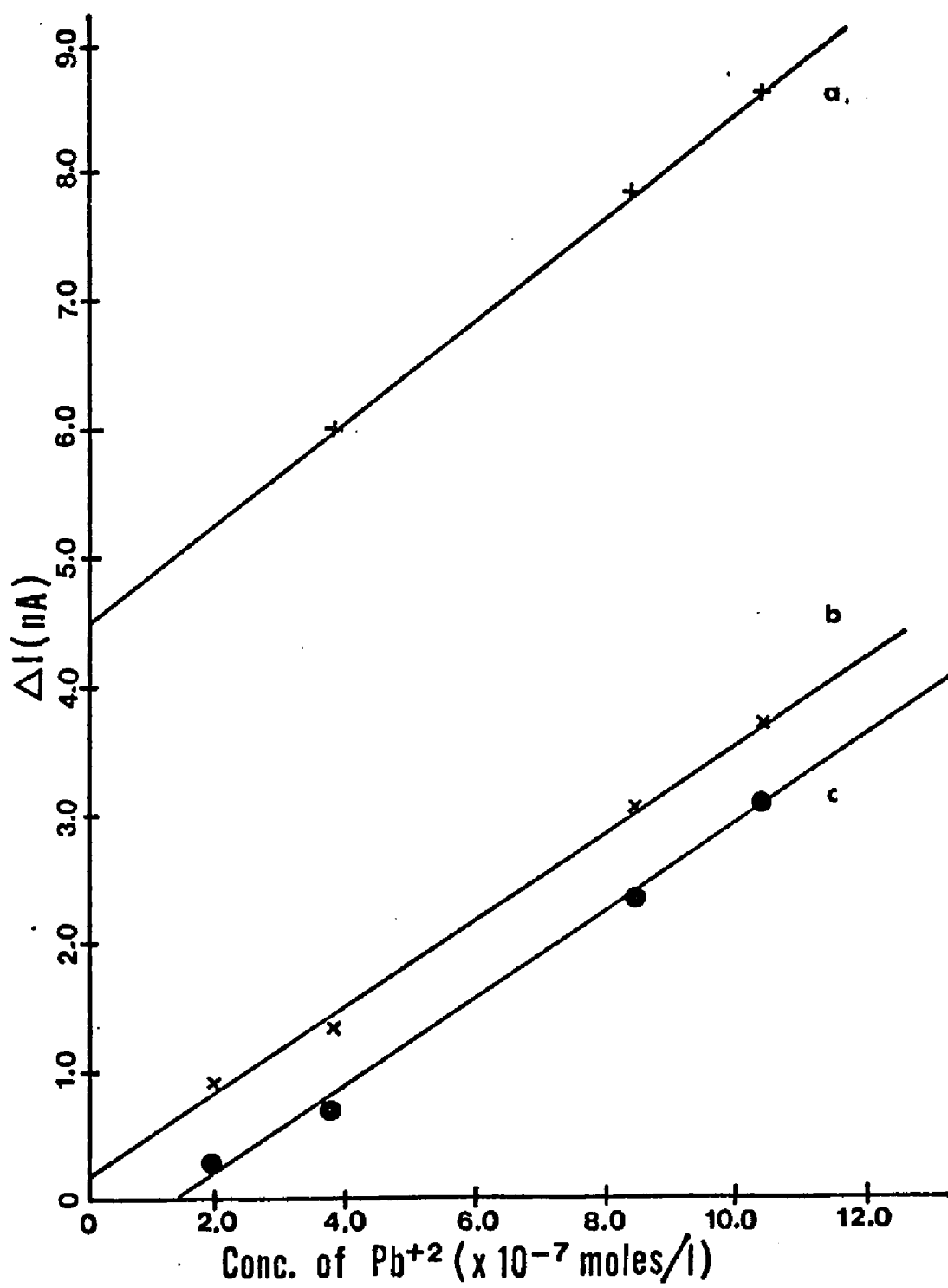


Figure 5.32

Figure 5.33

Calibration curve for 10^{-6}M Pb^{+2} in 0.1M KCl,
offset scans.

These curves are constructed from the data
shown in Figure 5.31 and Table 5.16.

a. + Uncorrected results obtained from the
printout:

$$\begin{aligned}\text{slope} &= 3.54 \text{ nA}/\mu\text{mole l}^{-1} \\ \text{intercept} &= 4.20 \text{ nA}\end{aligned}$$

b. x Corrected results obtained from the
printout and plot:

$$\begin{aligned}\text{slope} &= 3.44 \text{ nA}/\mu\text{mole l}^{-1} \\ \text{intercept} &= -0.74 \text{ nA}\end{aligned}$$

c. ● Doubly corrected results obtained from
the plot:

$$\begin{aligned}\text{slope} &= 3.26 \text{ nA}/\mu\text{mole l}^{-1} \\ \text{intercept} &= -0.94 \text{ nA}\end{aligned}$$

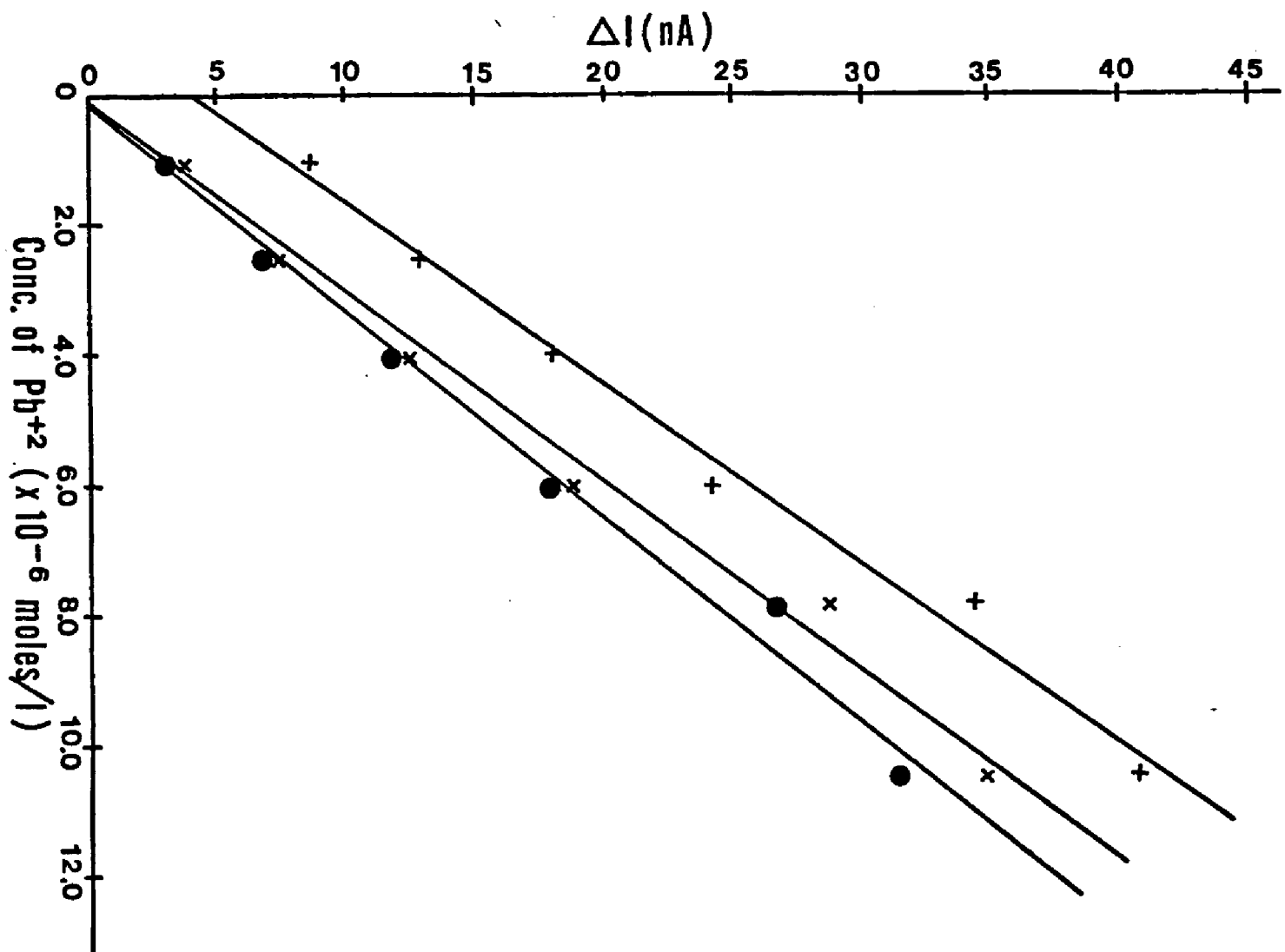


Figure 5.33

Table 5.16 Incremental Polarograms of Pb^{+2} in 0.1M KCl.

concentration	uncor. print.	cor. print.	cor. plot	d.cor. plot	$w_{1/2}$	$w_{2/3}$	$-E_{1/2}$
1.94×10^{-7}	--	0.89	0.89	0.30	--	--	0.391
3.73×10^{-7}	6.00	1.36	1.36	0.71	66.1	42.4	0.402
8.40×10^{-7}	7.79	3.05	3.06	2.36	55.5	42.1	0.400
1.04×10^{-6}	8.62	3.73	3.80	3.07	57.3	45.5	0.401
2.56×10^{-6}	12.7	7.38	7.38	6.72	55.5	43.0	0.395
3.99×10^{-6}	17.9	12.4	12.4	11.8	57.6	42.4	0.396
5.98×10^{-6}	24.1	18.6	18.6	17.7	55.8	42.7	0.401
7.80×10^{-6}	34.2	28.6	28.7	26.6	56.1	42.7	0.400
10.5×10^{-6}	40.6	34.6	34.7	32.5	53.9	41.5	0.395

This deterioration is visible in the form of curve broadening. The width at the half-height increased to an average value of 56mV, with two-thirds-height average value of about 43mV. The half-wave potential, however, was not affected, with an average value of $-0.398 \pm 0.004V$ vs SCE. A slight deviation from this value was observed only at the lowest Pb(II) concentration used ($2 \times 10^{-7}M$), where the sensitivity limit of the present instrument is reached. Figure 5.34, obtained for Pb^{+2} with $\Delta E = 40mV$ with 2mV fill-ins shows the reproducibility of the instrument under difficult conditions. The reproducibility shown is for 19 consecutive scans with Pb^{+2} concentration of $3.7 \times 10^{-7}M$.

5.2.5 PRESENCE OF SURFACTANTS

It is quite customary in polarography to add a small amount of surfactant to the analyzed solutions to suppress polarographic maxima. One of the most popular maximum suppressor is Triton X-100, a non-ionic surfactant. Figure 5.35 shows the polarogram of a mixture of $6.3 \times 10^{-7}M$ Cd^{+2} , $4.7 \times 10^{-7}M$ Pb^{+2} , $5.4 \times 10^{-7}M$ Zn^{+2} in 0.1M KCl solution and 0.0013% Triton X-100.

Triton suppresses the double layer capacitance in the region from -0.4V to -1.4V vs SCE, but causes no problem for the determination of the three ions even at these low concentrations.

Figure 5.34.

Incremental polarograms of $4 \times 10^{-7} \text{M Pb}^{+2}$ in
0.1M KCl.

- a. Uncompensated incremental polarogram.
- b. Compensated incremental polarogram.

Conditions: measuring frequency of 1.003kHz,
25°C, $\Delta E = 40\text{mV}$ with 2mV offset
scan, delay time of 2.3 seconds,
measuring period of 1 second,
3 drops at each potential.

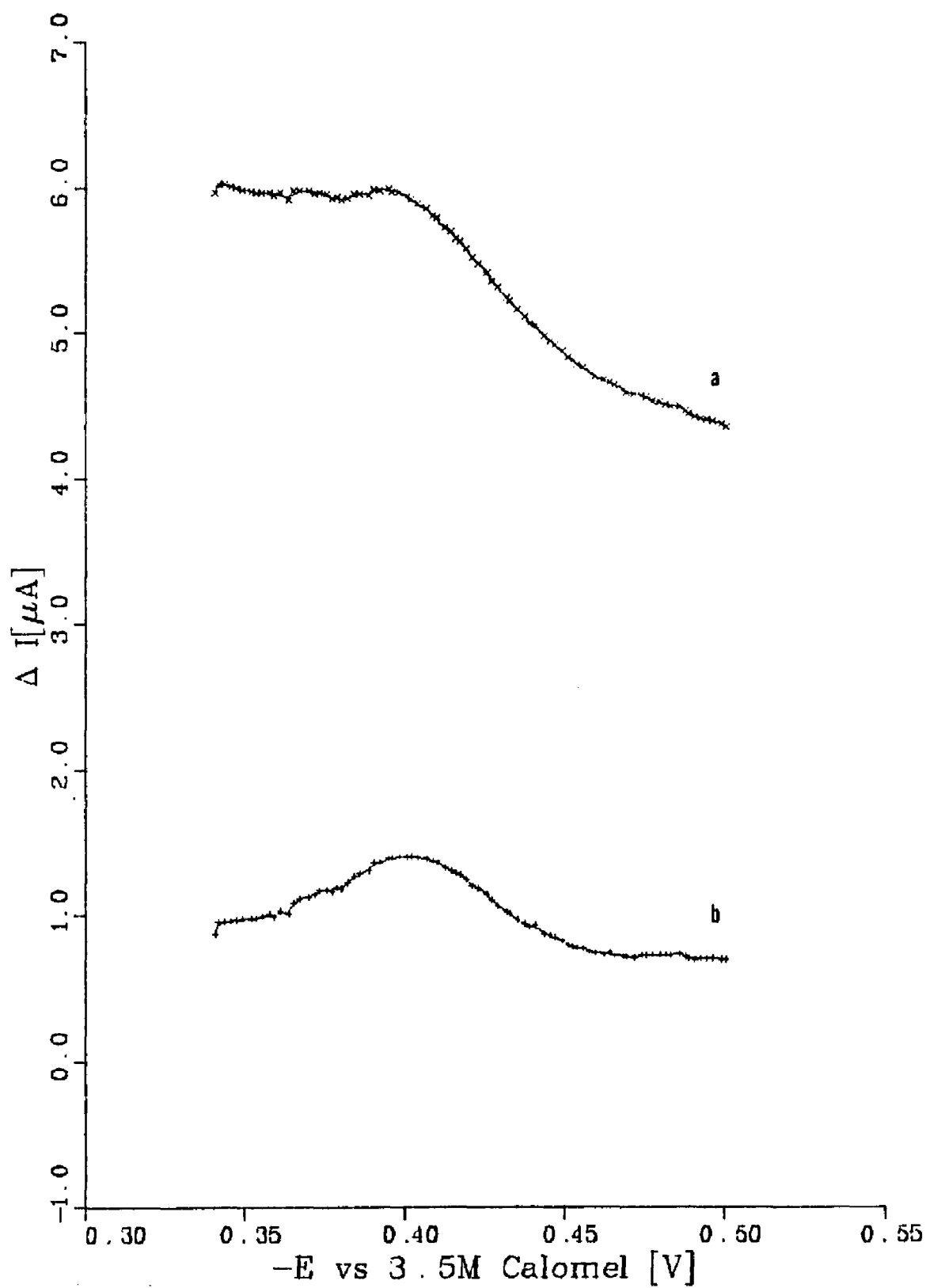


Figure 5.34

Figure 5.35

Capacitance and incremental polarographic curves of mixture of reducible ions.

Solution contains $6.3 \times 10^{-7} \text{M}$ Cd^{+2} , $4.7 \times 10^{-7} \text{M}$ Pb^{+2} , $5.4 \times 10^{-7} \text{M}$ Zn^{+2} and 0.013% Triton X-100 in 0.1M KCl.

- a. Capacitance at the beginning of the measuring period.
- b. Capacitance at the end of the measuring period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of 1.003kHz, 25°C ,
 $\Delta E = 20\text{mV}$, delay time of 2.0 seconds,
measuring period of 1.0 second, 1 drop
at each potential.

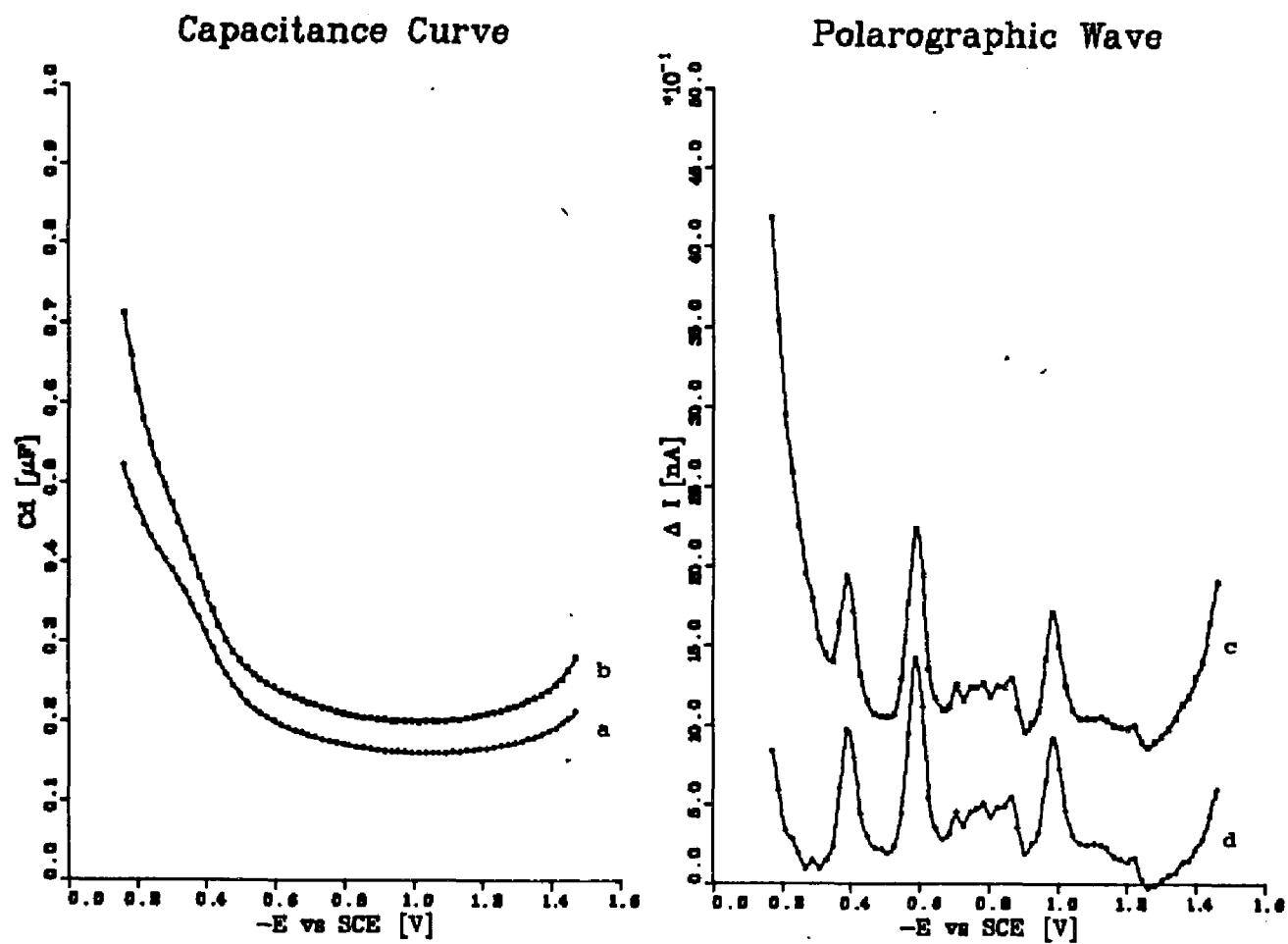


Figure 5.35

5.3 ERROR ANALYSIS

Errors occurring during any experiment can be estimated by evaluating the precision and accuracy of the experiment.

5.3.1 PRECISION

The precision of incremental polarography with charging current compensation depends on errors in the polarographic measurements and in the compensation procedure.

The precision in the determination of the double layer capacitance at a specific time in the drop life of the DME depends on the following factors:

1. ac input voltage
2. drop area
3. computer timing
4. computer ADC converter
5. potential of the DME
6. phase null

Schwartz (52) evaluated the precision of determination of C_d^0 in 1M KCl using the phase-null method. The precision is a function of DME potential and measuring frequency. The worst case error, occurring in the high-slope region of the C_d vs E curve when measured with 1kHz ac signal, was

estimated to be about 3%. In the low-slope region of the curve, the error decreased to about 1.2%.

The instrument developed here is designed for charging current compensation and thus has a number of modifications that can alter the estimated precision:

1. The ac potential was not monitored during the experiment, however, the potential was applied from a highly stable oscillator and calibration (see Section 5.1.1) preceded each run. No deterioration in the precision is expected from this modification.
2. The signal measurement was performed using a 12 bit analog-to-digital converter with resolution of 1 in 4096. Assuming signal levels above 1/10th of full scale, the measuring precision will be better than 0.2%.
3. Computer timing and drop-fall triggering are critical in repeating the measurements at the same surface area of the drop. The timing is derived from a crystal controlled oscillator with a stability better than 0.01%. The drop-fall detection is related to the frequency of the triggering ac signal and the length of the delay and measuring period. For a 250kHz trigger signal, and 0.2 to 2 seconds delay and measuring periods, the error is less than 0.01%.

The overall precision in C_d^O was about the same as estimated

by Schwartz.

The factors limiting the precision of the polarographic determination are:

1. drop area
2. computer timing
3. computer ADC converter
4. potential of the DME
5. temperature
6. mercury height

As was mentioned above, the computer ADC introduces errors of no more than 0.2% and the timing is better than 0.01%. The precision in the surface area of the drop as calculated from the weight of mercury flowing during a given period was better than 0.1%. The dc polarizing voltage, as shown in Section 5.1.1, was reproducible to better than 4 μ V (< 0.05% of ΔE). The relative errors in mercury pressure and temperature are, however, of the highest order. Changes in the mercury pressure were on the order of 0.5%, while temperature variations of about 0.2°C correspond to errors of about 0.5% (13). The worst case error in polarographic determination thus adds up to less than 2%.

For the 2×10^{-7} M concentration of the ions, the ratio of charging incremental response to the faradaic incremental response is between 2:1 (Zn^{+2}) and 9:1 (Pb^{+2}). The

precision of the incremental polarography with charging current compensation will thus be determined by the relative errors in determination of the faradaic and charging components.

The observed precision in the measurements was calculated from the deviations of the calibration curves. The relative standard deviations of the various calibration curves are listed in Table 5.17.

These relative standard deviations show that a precision of 1 to 6% can be obtained for these three ions down to the $10^{-7}M$ levels. Precision for determination of Cd^{+2} is extremely good. Deterioration of precision in the lead determination is expected, since $E_{1/2}$ for lead is in a very difficult potential region for this technique - a region with very high and fast changing C_d , near the hump of the capacitance curve. The precision of 3-6% is thus satisfactory. An improvement can be expected by using more than one drop at the same potential and averaging the current value as was the case with cadmium (3 drops at the same potential were used). The precision of the zinc determination was dissapointing, since the charging current correction is of much lower amplitude than for Cd^{+2} and Pb^{+2} ions. The region near the $E_{1/2}$ of Zn^{+2} , can often be affected by capillary effects (93) and the presence of small amounts of oxygen in the solution. More careful deaeration and use of multiple drops at the same potential can improve the precision of this determination.

Table 5.17 Statistical Summary of the Data.

ion	ΔE [mV]	conc.range [mole/l]	st.dev. [nA/ μ mole l ⁻¹]	rel.st.dev. [%]
Zn ⁺²	20	2×10^{-7} - 1×10^{-6}	0.083	4.6
Zn ⁺²	20	1×10^{-6} - 1×10^{-5}	0.071	3.4
Cd ⁺²	20	1×10^{-6} - 1×10^{-5}	0.024	1.2
Cd ⁺²	20 fill	1×10^{-6} - 1×10^{-5}	0.025	1.1
Cd ⁺²	10	1×10^{-6} - 1×10^{-5}	0.024	2.0
Cd ⁺²	20	2×10^{-7} - 1×10^{-6}	0.044	2.2
Cd ⁺²	40 fill	2×10^{-7} - 1×10^{-6}	0.101	3.1
Cd ⁺²	40 fill	2×10^{-7} - 1×10^{-6}	0.061	1.9
Pb ⁺²	40 fill	2×10^{-7} - 1×10^{-6}	0.106	3.1
Pb ⁺²	40 fill	1×10^{-6} - 1×10^{-5}	0.204	5.9
Pb ⁺²	20	2×10^{-7} - 1×10^{-6}	0.075	4.4

Worsening of the precision from the projected value can be caused partly by DME related problems, vibrations and capillary response, and partly by instrumental artifacts.

5.3.2 ACCURACY

The accuracy of the phase null method of determination of C_d in the presence and absence of the faradaic process was analyzed in detail by Schwartz (52). Initial performance tests included comparison of C_d^O vs E curves obtained with this instrument to those reported in literature. As can be seen in Section 5.2.1, agreement to better than 5% has been obtained with most of the published results.

A variety of factors affects accuracy of the polarographic results. Most of the analytical polarographic work, however, relies on calibration curves. Thus as long as the various parameters affecting the results are similar during the calibration and determination runs, the accuracy of the determination will be closely linked to the precision of the calibration runs.

The expected accuracy of the determination would be lowered, however, if some factors affecting linearity of the calibration curve would be present. One such factor, pseudocapacitance, is present to a certain degree in these determinations. However, it is expected to effect the results only at higher concentrations of the electroactive ions. In the vicinity of their half-wave potentials, reduc-

tion of these ions produces a faradaic ac impedance (faradaic pseudocapacitance) which then shunts the double layer capacitance causing an error in the determination of the charging current. The magnitude of this error increases with increasing concentration of the electroactive species, increasing k_{SH} and decreasing frequency of the measuring ac (see Section 3.2.5). Schwartz calculated maximum concentrations of the electroactive ions that would allow C_d measurements with errors of less than 2%. These values are reproduced in Table 5.18.

As was already pointed out in the Section 5.3.3, electroreduction of Cd^{+2} in the chloride media has a high heterogeneous rate constant, $k_{SH} \approx 1 \text{ cm/sec}$, and therefore a relatively high faradaic pseudocapacitance even at low concentration of Cd^{+2} . However, as can be seen from Figure 5.36, the pseudocapacitance effect on the measured differential double layer capacitance is small at micromolar concentrations of Cd^{+2} . An even smaller effect is observed in the charging current compensation, since ΔC_d is used here. With 1KHz measuring frequency, the deviation due to the faradaic pseudocapacitance starts appearing at concentrations of Cd^{+2} higher than $5 \times 10^{-6} \text{ M}$, as predicted from Table 5.18, and as can be seen from Figure 5.36. For the $8 \times 10^{-6} \text{ M}$ solutions the deviation is clearly visible, shown by Figure 5.37. At $5 \times 10^{-5} \text{ M}$ concentration the effect of pseudocapacitance is unquestionable, and an ac polarographic peak appears on the capacitance curves, as shown in Figure 5.38.

Table 5.18 Maximum Concentrations of Ions for Determination of C_d^0 to within 2%.

freq. [kHz]	conc. in moles/l x n^2					
	k_{SH} [cm/sec]					
	<u>∞</u>	<u>10</u>	<u>1.0</u>	<u>0.1</u>	<u>0.01</u>	<u>0.001</u>
1	0.012	0.012	0.012	0.04	0.8	8.0
10	0.04	0.04	0.08	0.8	8.0	-
100	0.12	0.12	0.4	8.0	-	-
1000	0.4	0.6	4.0	-	-	-

Figure 5.36

Capacitance and incremental polarographic curves of $3.8 \times 10^{-6} \text{M Cd}^{+2}$ in 0.1M KCl with 0.01M HCl , determined with 1kHz ac .

- a. Capacitance at the beginning of the measuring period.
- b. Capacitance at the end of the measuring period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of 1.001kHz , 25°C , $\Delta E = 10 \text{mV}$, delay time of 2.5 seconds, measuring period of 1 second, 1 drop at each potential.

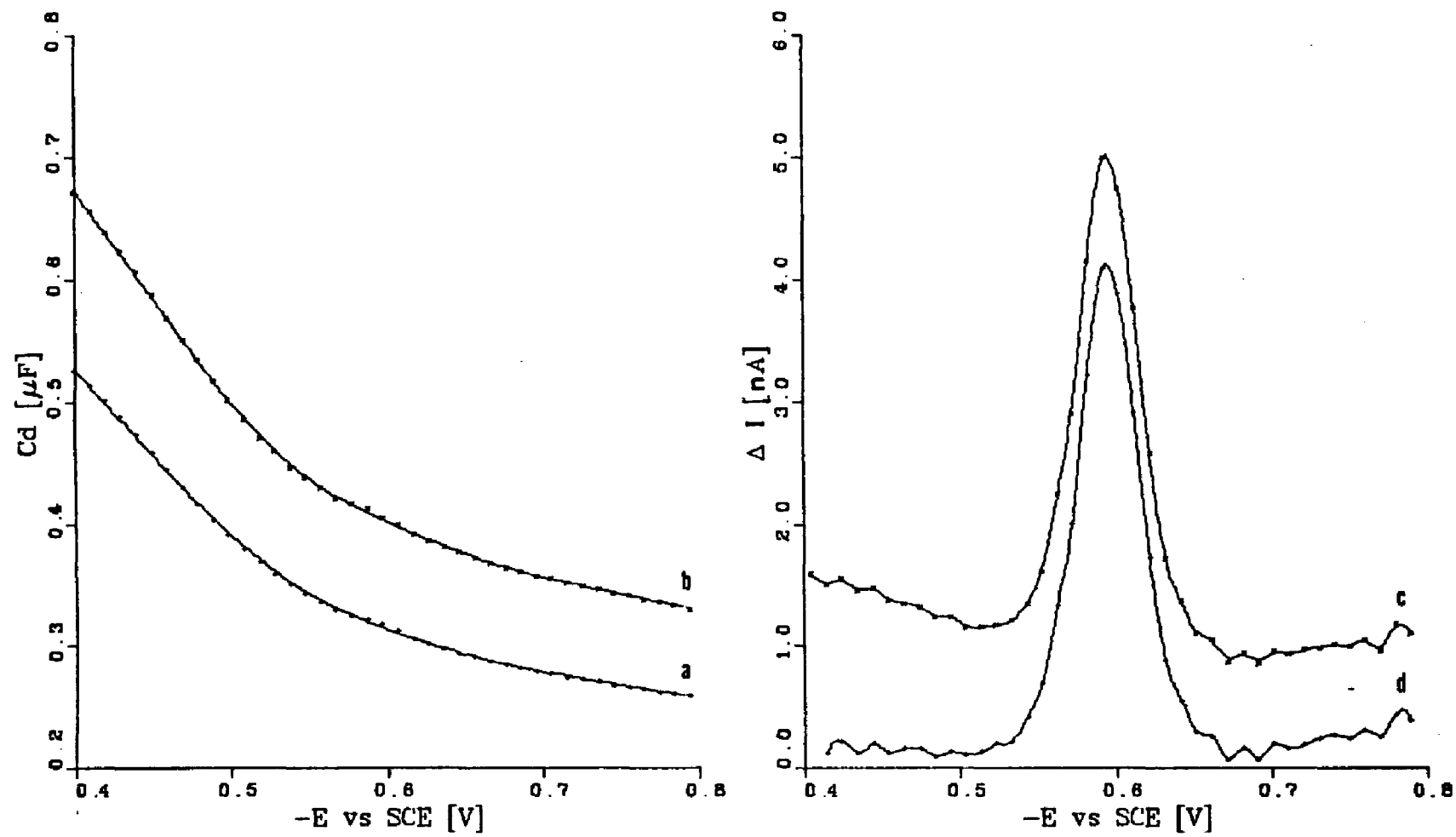


Figure 5.36

Figure 5.37

Capacitance and incremental polarographic curves of $7.0 \times 10^{-6} \text{M Cd}^{+2}$ in 0.1M KCl with 0.01M HCl , determined with 1kHz ac .

- a. Capacitance at the beginning of the measuring period.
- b. Capacitance at the end of the measuring period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of 1.001kHz , 25°C , $\Delta E = 10 \text{mV}$, delay time of 2.5 seconds, measuring period of 1 second, 1 drop at each potential.

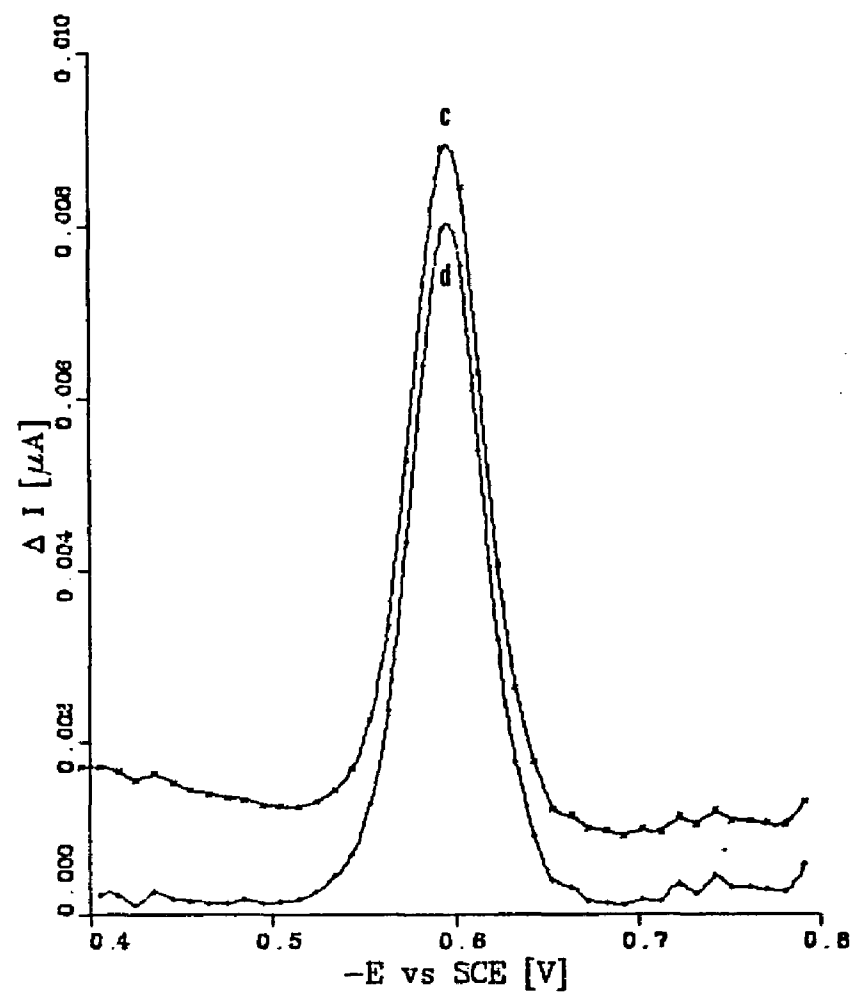
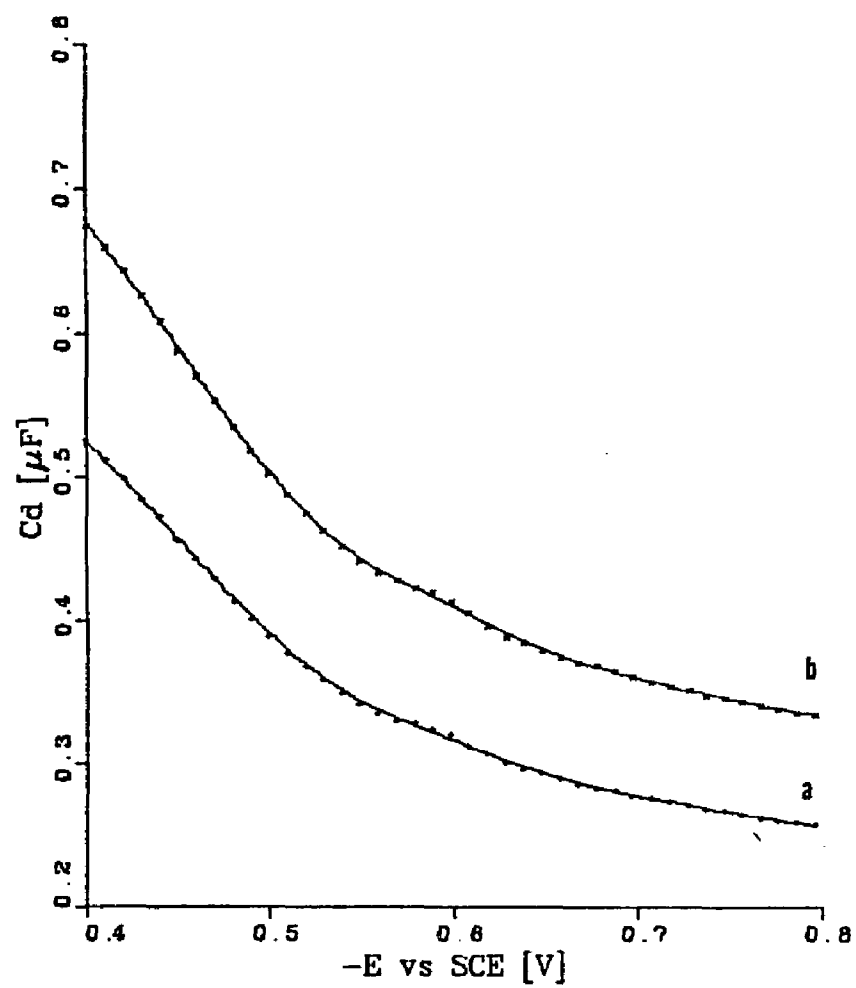


Figure 5.37

Figure 5.38

Capacitance and incremental polarographic curves of $5.0 \times 10^{-5} \text{M}$ Cd^{+2} in 0.1M KCl with 0.01M HCl , determined with 1kHz ac.

- a. Capacitance at the beginning of the measuring period.
- b. Capacitance at the end of the measuring period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of 1.001kHz , 25°C , $\Delta E = 10 \text{mV}$, delay time of 2.5 seconds, measuring period of 1 second, 1 drop at each potential.

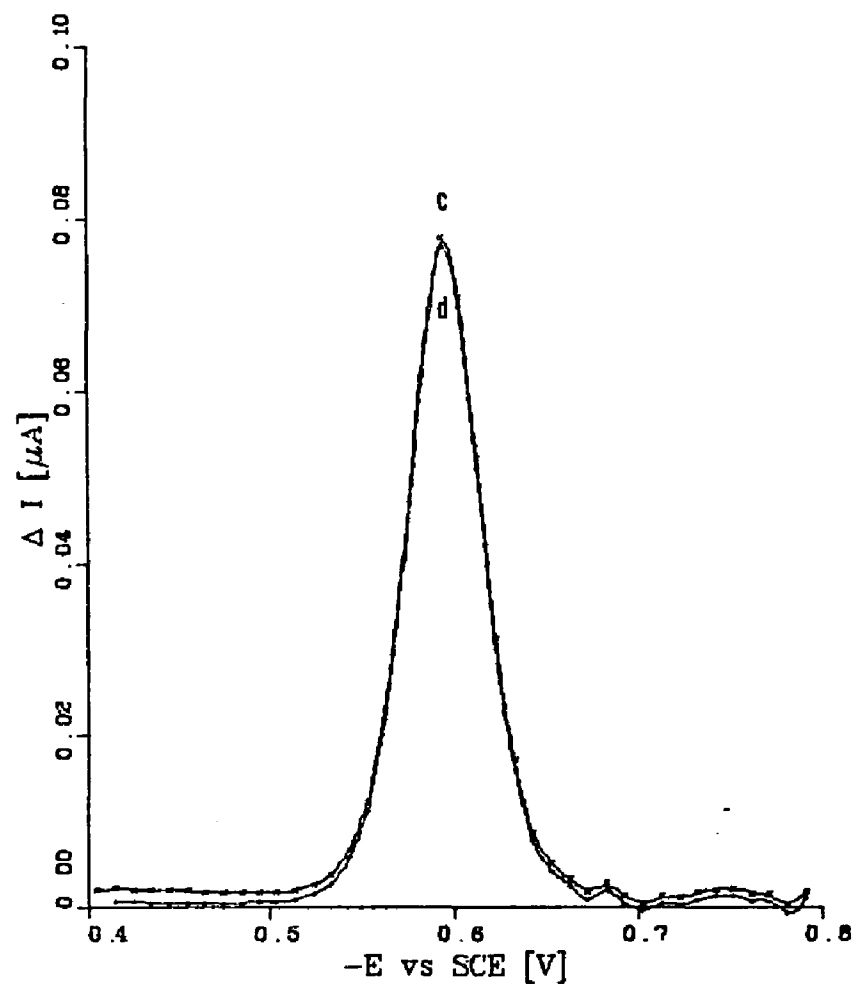
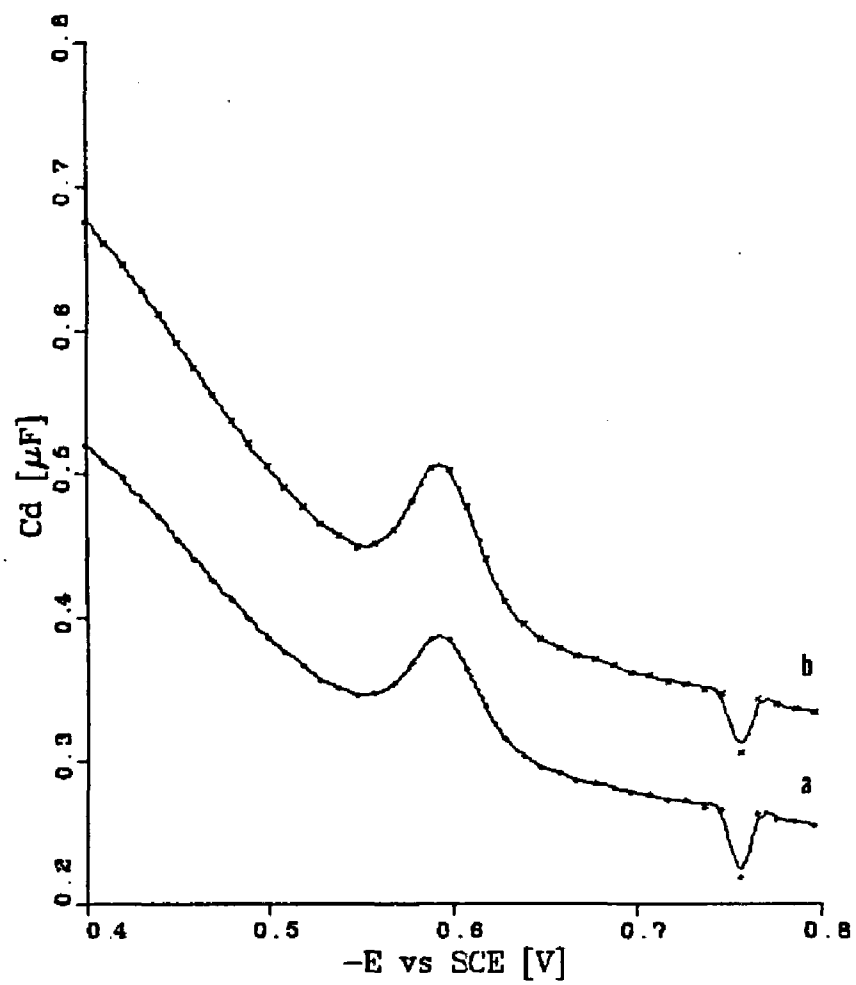


Figure 5.38

Contributions due to the faradaic pseudocapacitance can be reduced by increasing the measuring frequency to 5kHz, and as can be seen from Figures 5.39 and 5.40, no deviation is visible at concentrations below $1 \times 10^{-5} \text{M}$, where as at 1kHz there was a clear deviation. At $5 \times 10^{-5} \text{M}$ level the deviation is clearly visible even at 5kHz, but less than at 1kHz (see Figure 5.41). Increasing the measuring frequency even further to 10kHz greatly suppresses even the deviation at $5 \times 10^{-5} \text{M}$ Cd^{+2} concentration, as can be seen from Figure 5.42.

In general, however, the charging current correction as obtained by the phase null technique is applicable to the compensation of the incremental polarograms of Cd^{+2} only if the concentration is below about $5 \times 10^{-5} \text{M}$. Fortunately, at Cd^{+2} concentrations above $5 \times 10^{-5} \text{M}$ the charging current compensation becomes insignificant, since it accounts for less than 3% of the peak value.

On the other hand, electroreduction of Zn^{+2} in KCl, as was shown in Section 5.3.2, is a rather slow, but polarographically reversible process with $k_{\text{SH}} \approx 5 \times 10^{-2} \text{cm/sec}$ and thus high activation polarization, θ . Under such condition simplification of the equivalent network by neglecting faradaic pseudocapacitance does not introduce significant errors in the C_d values, even with Zn^{+2} concentrations as high as $5 \times 10^{-5} \text{M}$. As can be seen from Figure 5.43, there is no visible effect due to the faradaic pseudocapacitance at Zn^{+2} concentration of $1.1 \times 10^{-5} \text{M}$, and only a slight effect with $6 \times 10^{-5} \text{M}$ Zn^{+2} . This is shown by Figure 5.44 and is expected

Figure 5.39

Capacitance and incremental polarographic curves of $3.8 \times 10^{-6} \text{ M Cd}^{+2}$ in 0.1 M KCl with 0.01 M HCl , determined with 5 kHz ac .

- a. Capacitance at the beginning of the measuring period.
- b. Capacitance at the end of the measuring period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of 5.008 kHz , 25°C , $\Delta E = 10 \text{ mV}$, delay time of 2.5 seconds , measuring period of 1 second , 1 drop at each potential.

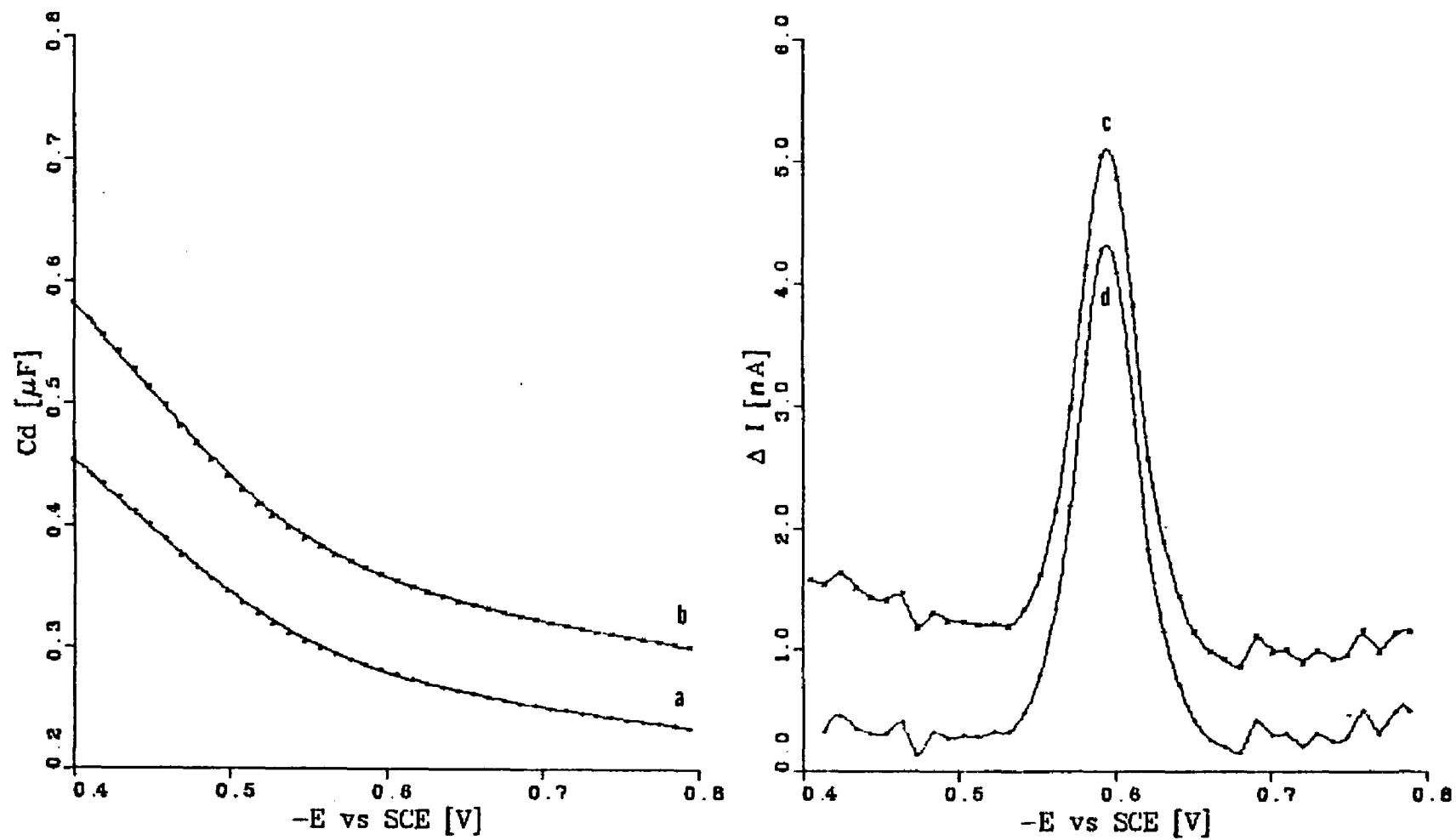


Figure 5.39

Figure 5.40

Capacitance and incremental polarographic curves of $8.5 \times 10^{-6} \text{M Cd}^{+2}$ in 0.1M KCl with 0.01M HCl , determined with 5kHz ac .

- a. Capacitance at the beginning of the measuring period.
- b. Capacitance at the end of the measuring period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of 5.008kHz , 25°C , $\Delta E = 10 \text{mV}$, delay time of 2.5 seconds , measuring period of 1 second , 1 drop at each potential.

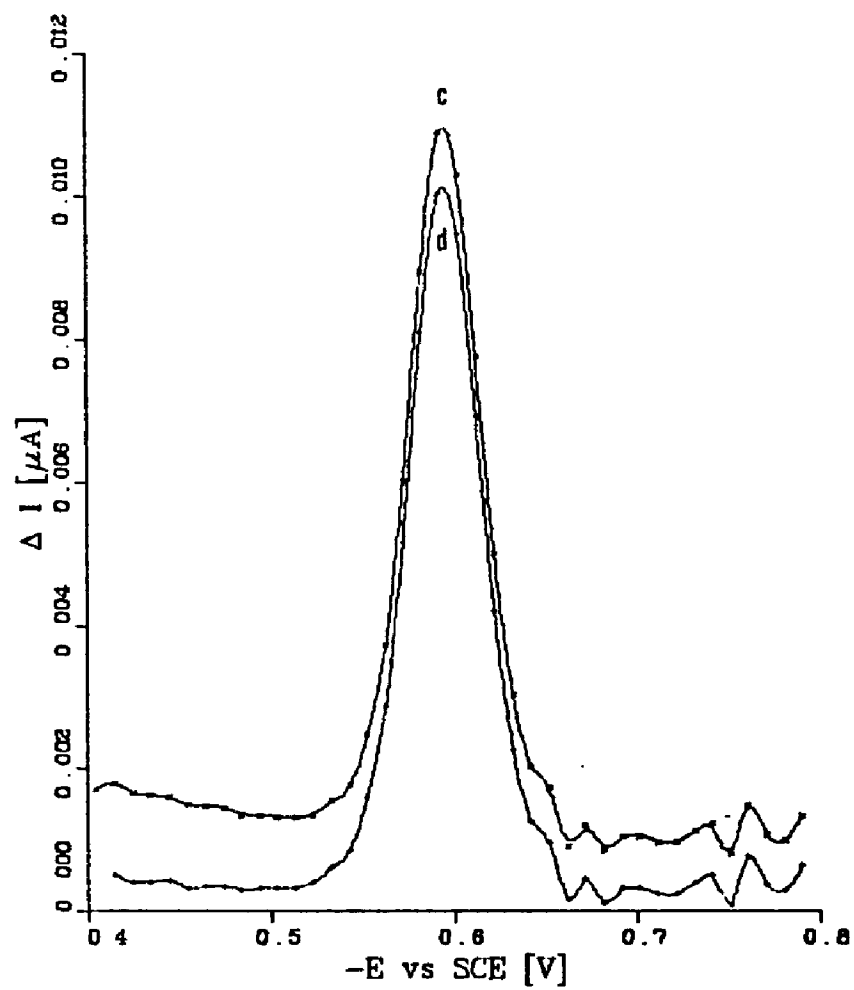
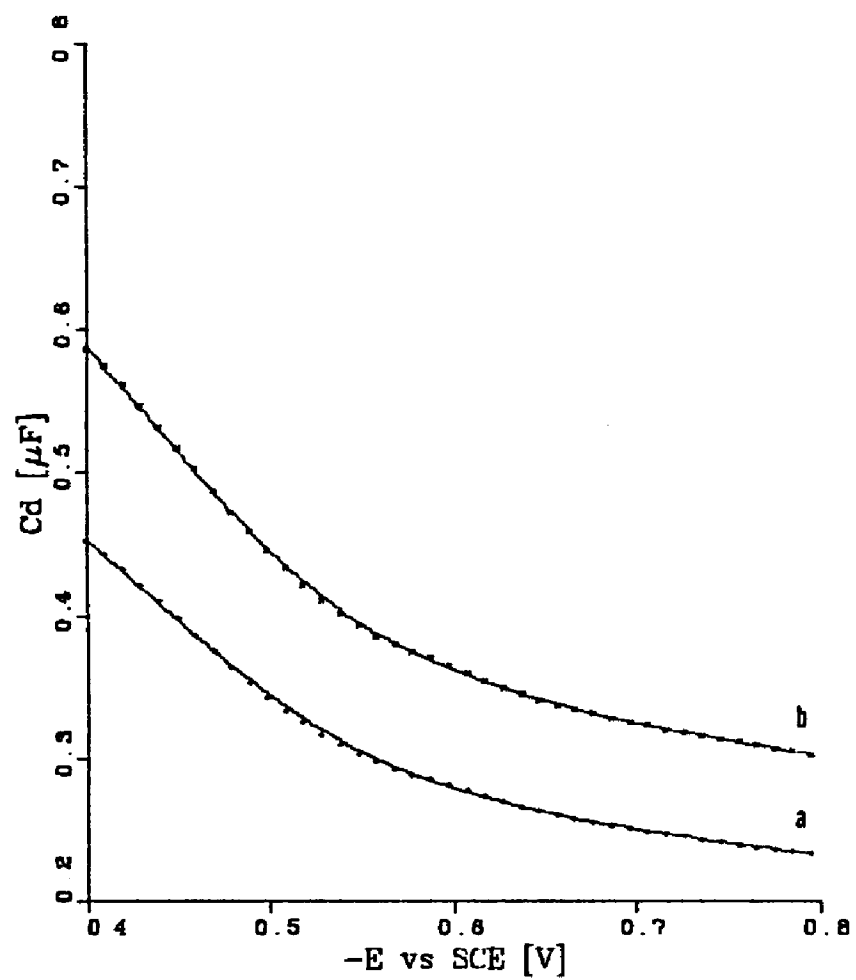


Figure 5.40

Figure 5.41

Capacitance and incremental polarographic curves of $5.0 \times 10^{-5} \text{M Cd}^{+2}$ in 0.1M KCl with 0.01M HCl , determined with 5kHz ac .

- a. Capacitance at the beginning of the measuring period.
- b. Capacitance at the end of the measuring period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of 5.008kHz , 25°C , $\Delta E = 10 \text{mV}$, delay time of 2.5 seconds, measuring period of 1 second, 1 drop at each potential.

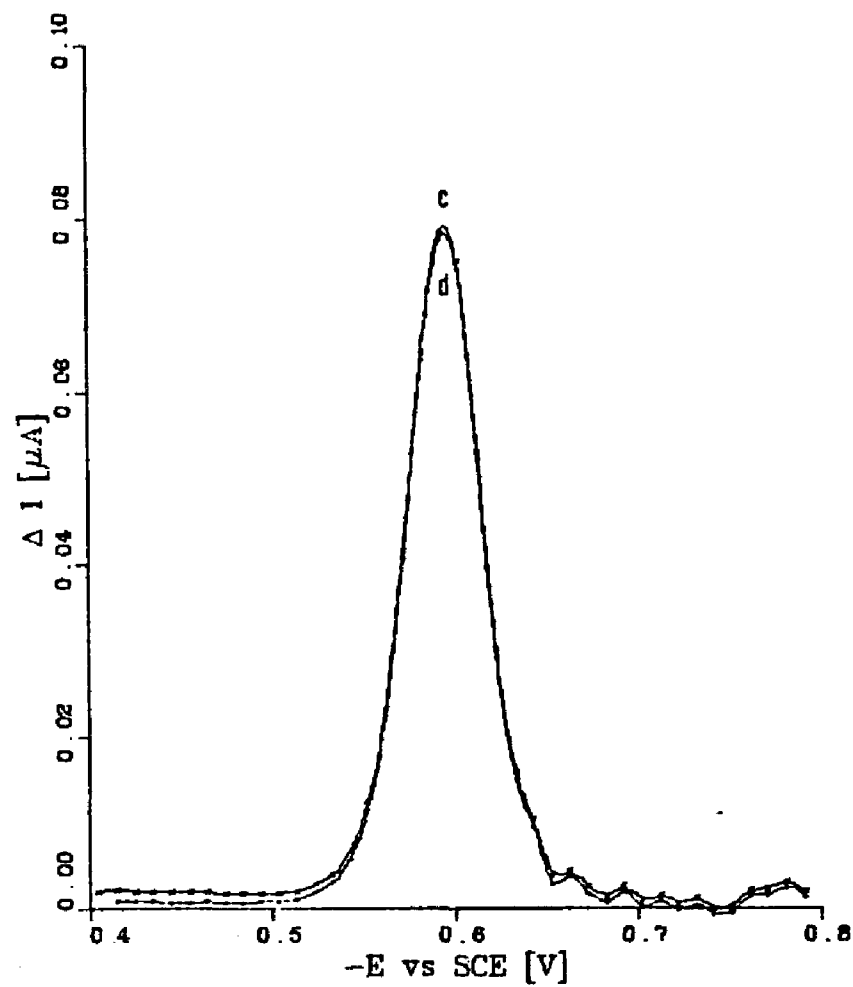
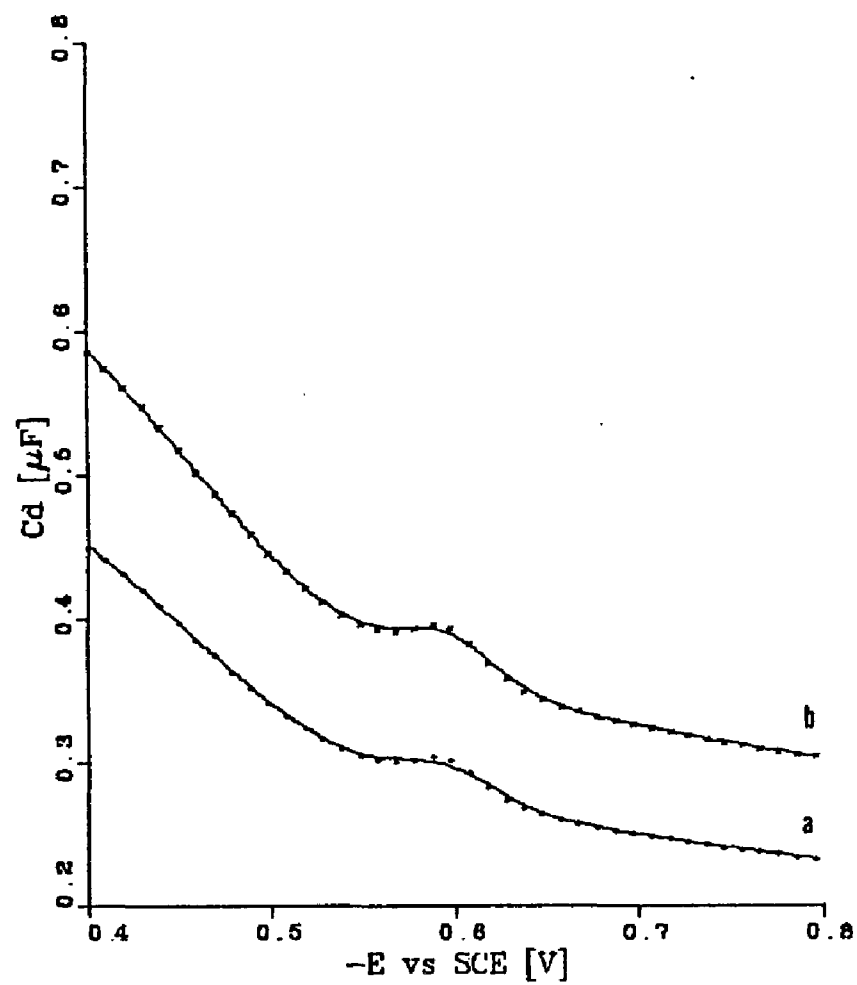


Figure 5.41

Figure 5.42

Capacitance and incremental polarographic curves of $5.0 \times 10^{-5} \text{M Cd}^{+2}$ in 0.1M KCl with 0.01M HCl , determined with 10kHz ac .

- a. Capacitance at the beginning of the measuring period.
- b. Capacitance at the end of the measuring period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of 10.023kHz , 25°C , $\Delta E = 10 \text{mV}$, delay time of 2.5 seconds, measuring period of 1 second, 1 drop at each potential.

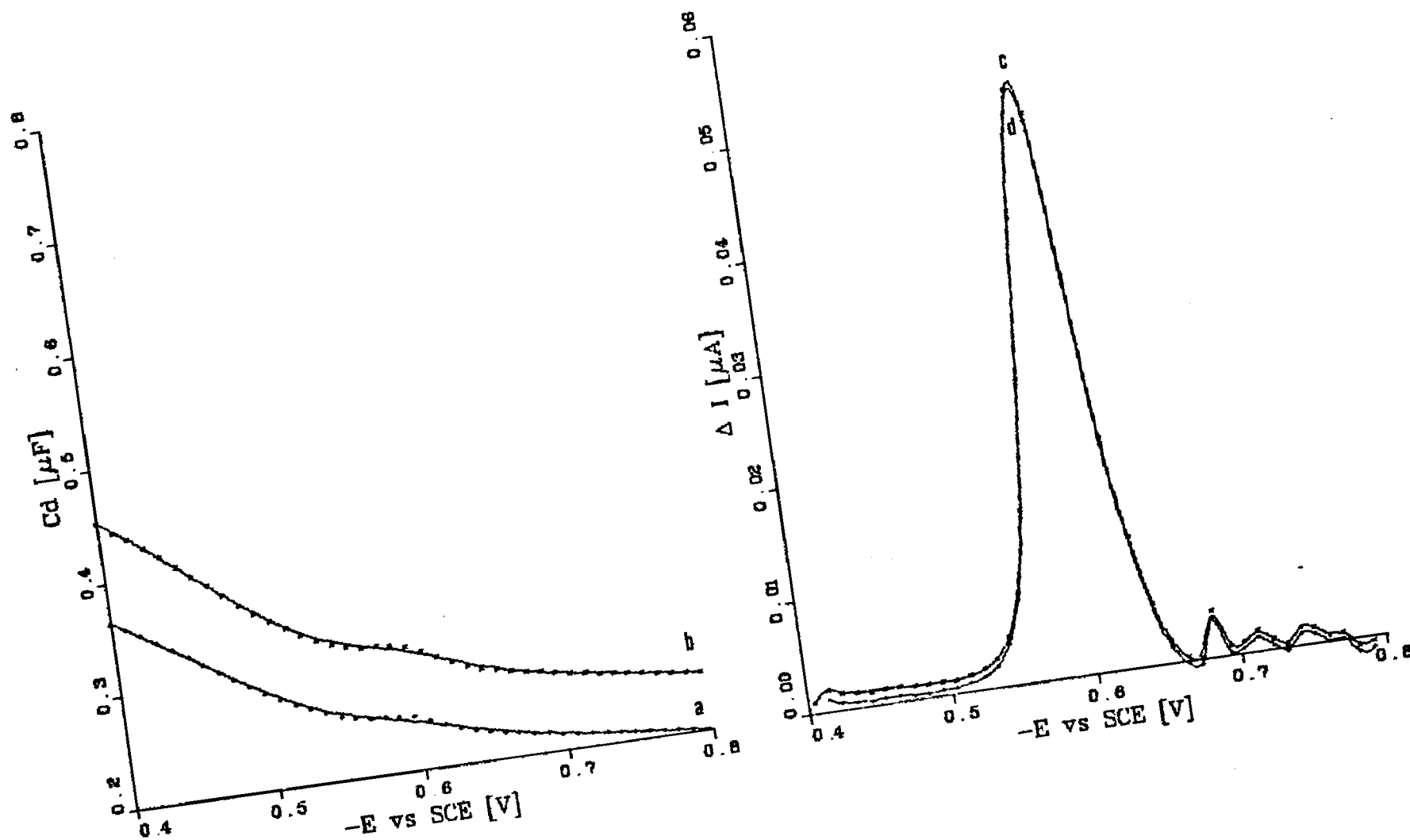


Figure 5.42

according to Table 5.18. At the $1 \times 10^{-4} \text{M}$ level, however, the effect is clearly visible (see Figure 5.45).

The error in the charging current compensation is negligible even at $1 \times 10^{-4} \text{M}$ Zn^{+2} concentration, since as can be seen from equation [3-28], it is ΔC_d that is proportional to Δi_c . Most of the effect due to the faradaic pseudocapacitance is thus cancelled, increasing the upper limit of applicability of this compensation technique.

Lead has a heterogeneous rate constant between cadmium and zinc, and thus it is expected to behave accordingly. Figures 5.46 and 5.47 show that to be the case, thus allowing charging current compensation to be performed with Pb^{+2} concentrations below $1 \times 10^{-5} \text{M}$.

As previously mentioned, Δi_c is proportional to ΔC_d , and thus C_d values with errors well above 2% are acceptable for the charging current compensation. The non-zero intercepts of the calibration curves and sharp decrease of C_d values at higher frequencies of measuring signal, point out that some instrumental, and possibly theoretical refinements, are still possible for future improvements of the technique.

Figure 5.43

Capacitance and incremental polarographic curves of $1.1 \times 10^{-5} \text{M Zn}^{+2}$ in 0.1M KCl .

- a. Capacitance at the beginning of the measuring period.
- b. Capacitance at the end of the measuring period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of 1.003kHz , 25°C , $\Delta E = 20 \text{mV}$, delay time of 2.0 seconds, measuring period of 0.5 second, 3 drops at each potential.

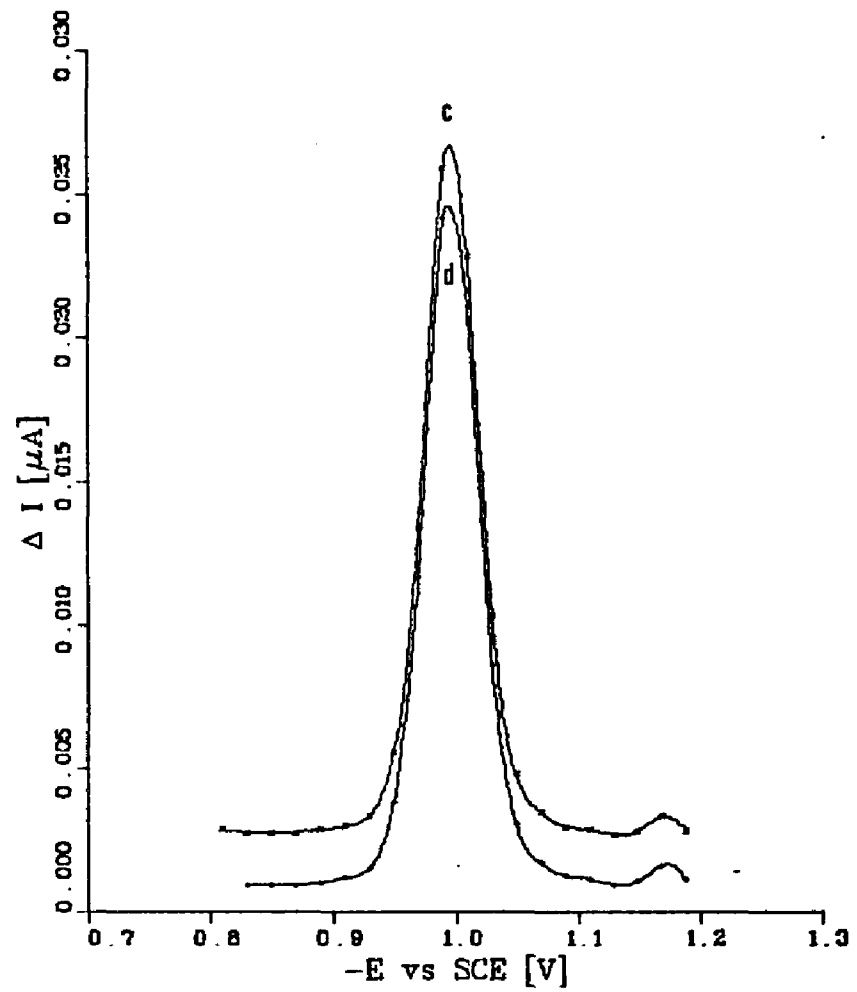
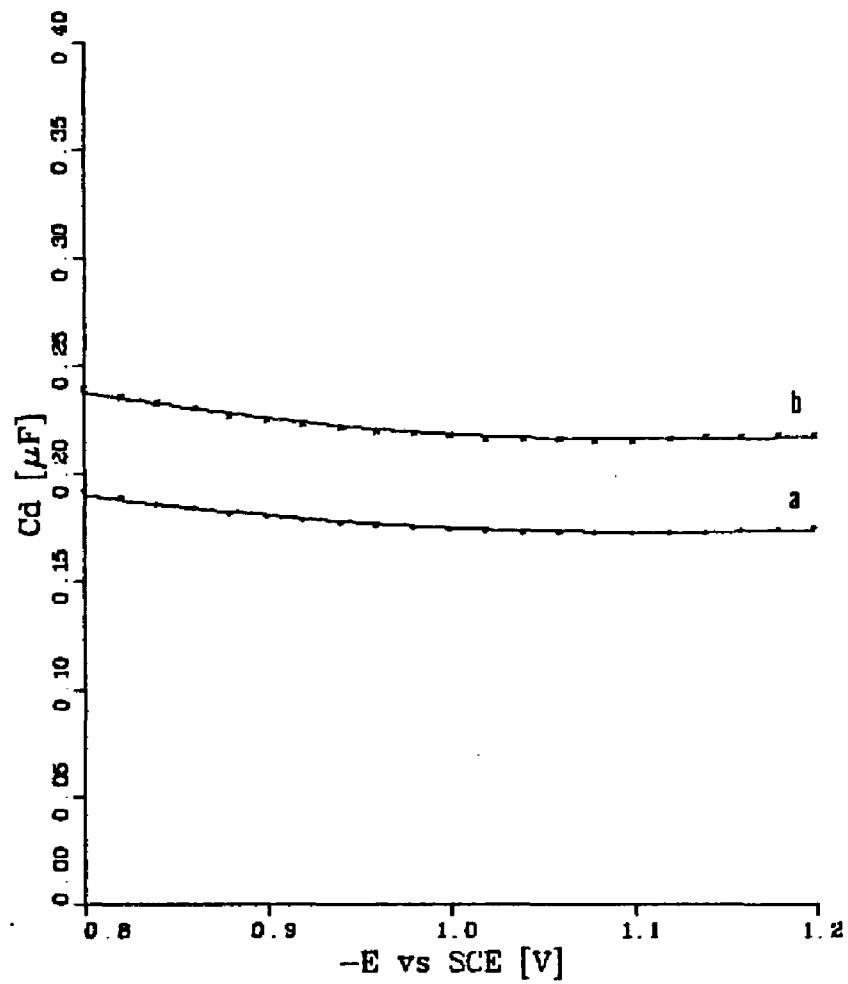


Figure 5.43

Figure 5.44

Capacitance and incremental polarographic curves of $6.3 \times 10^{-5} \text{M Zn}^{+2}$ in 0.1M KCl .

- a. Capacitance at the beginning of the measuring period.
- b. Capacitance at the end of the measuring period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of 1.003kHz , 25°C , $\Delta E = 20 \text{mV}$, delay time of 2.0 seconds, measuring period of 0.5 second, 3 drops at each potential.

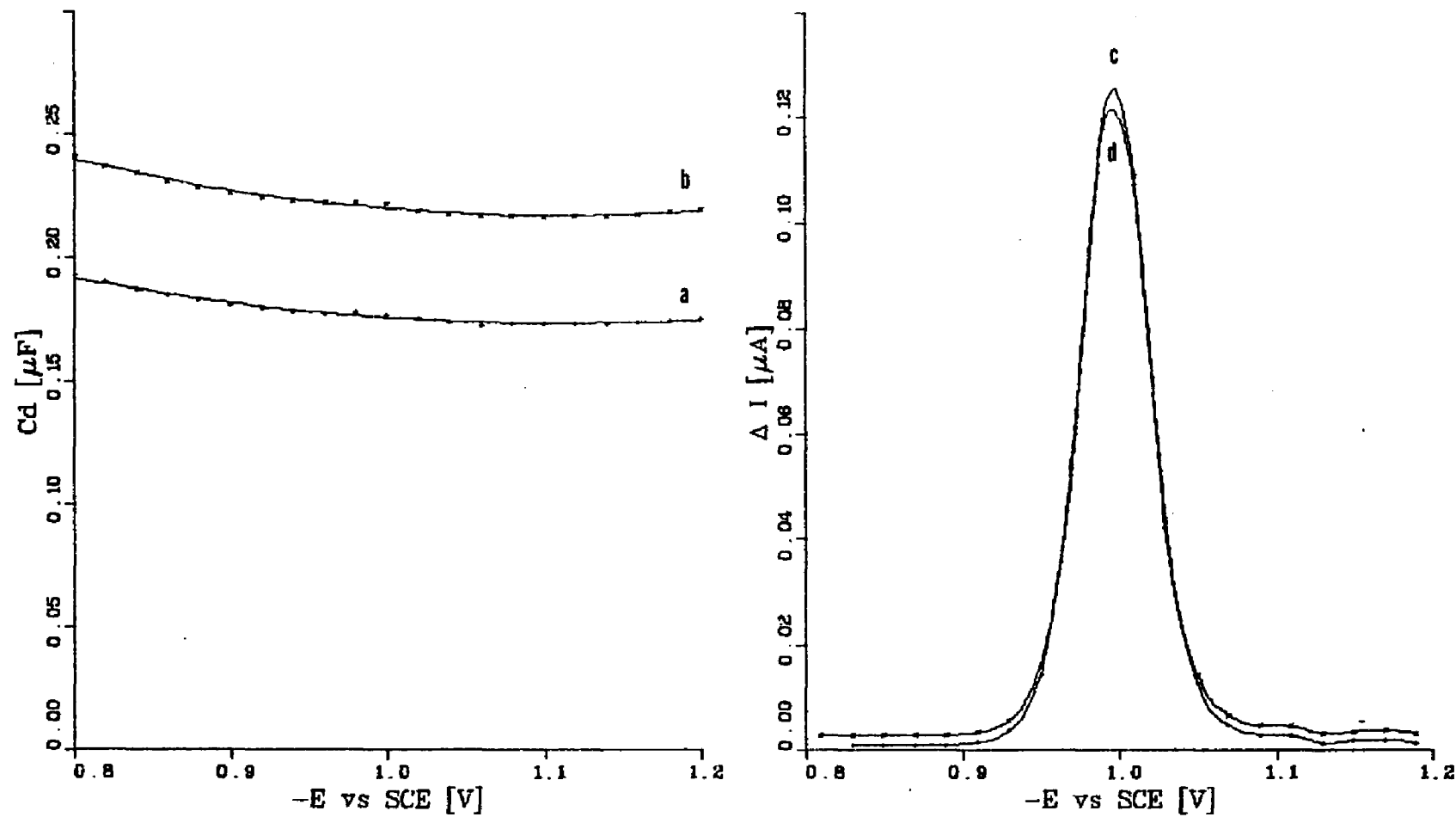


Figure 5.44

Figure 5.45

Capacitance and incremental polarographic curves of $1.1 \times 10^{-4} \text{ M Zn}^{+2}$ in 0.1 M KCl .

- a. Capacitance at the beginning of the measuring period.
- b. Capacitance at the end of the measuring period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of 1.003 kHz , 25°C , $\Delta E = 20 \text{ mV}$, delay time of 2.0 seconds, measuring period of 0.5 second, 3 drops at each potential.

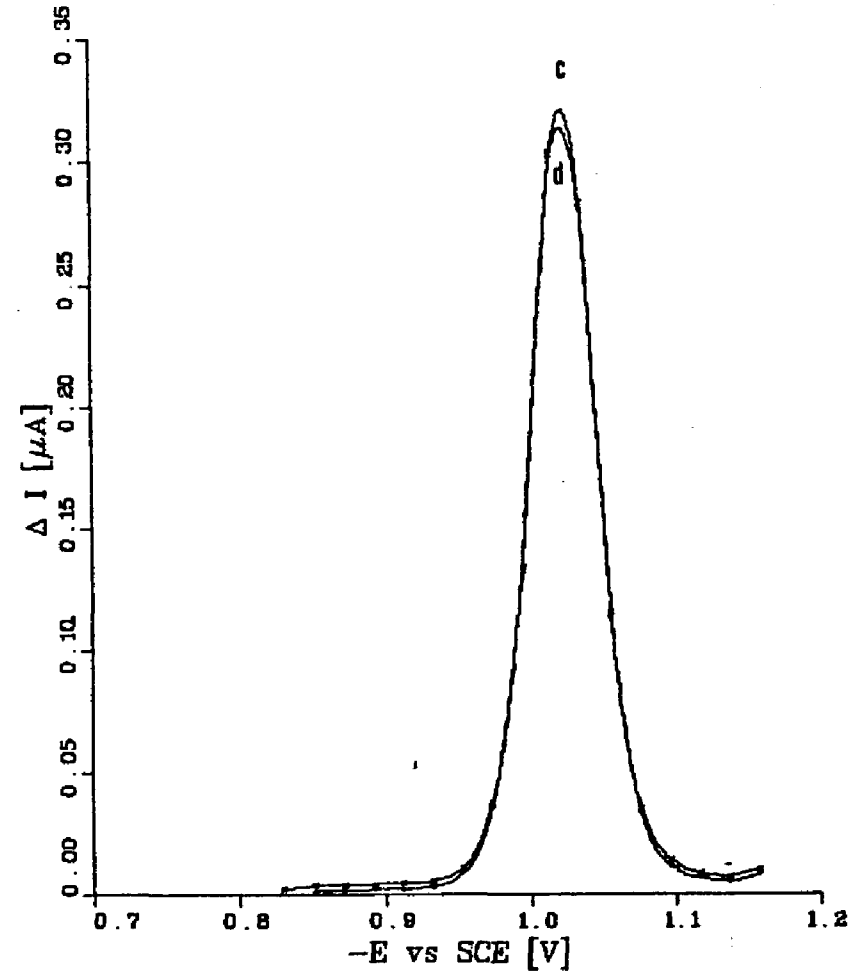
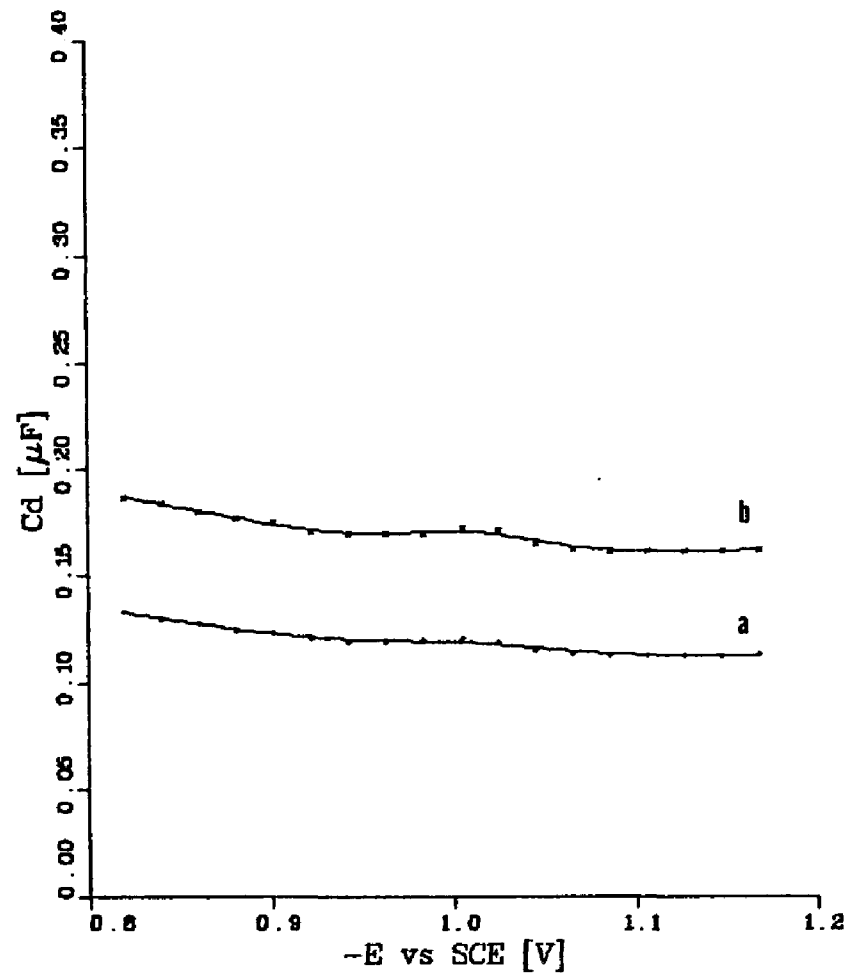


Figure 5.45

Figure 5.46

Capacitance and incremental polarographic curves of $7.8 \times 10^{-6} \text{M Pb}^{+2}$ in 0.1M KCl .

- a. Capacitance at the beginning of the measuring period.
- b. Capacitance at the end of the measuring period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of 1.003kHz , 25°C , $\Delta E = 20 \text{mV}$, delay time of 2.3 seconds, measuring period of 1.0 second, 3 drops at each potential.

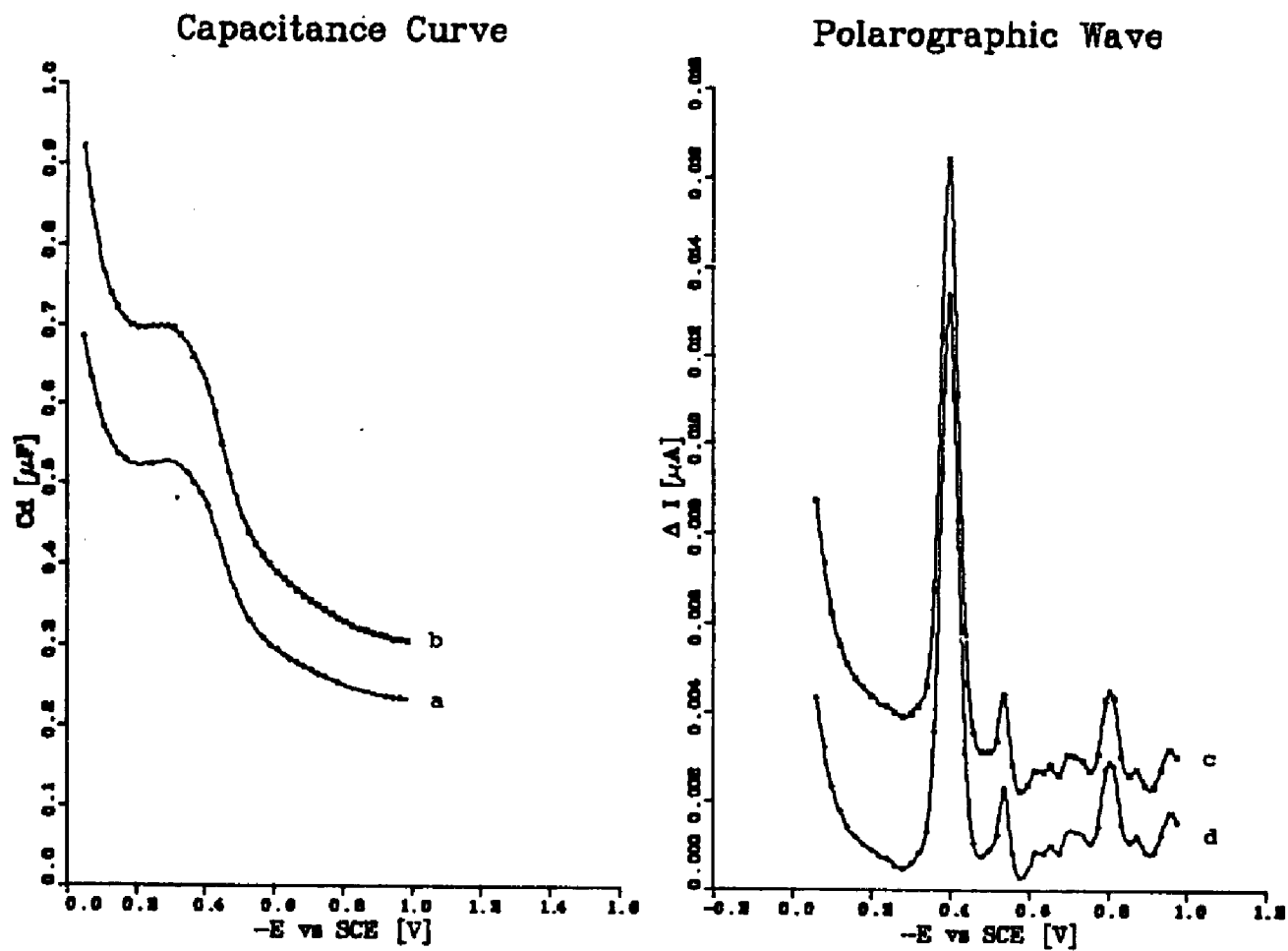


Figure 5.46

Figure 5.47

Capacitance and incremental polarographic curves of $4.9 \times 10^{-5} \text{M Pb}^{+2}$ in 0.1N KCl .

- a. Capacitance at the beginning of the measuring period.
- b. Capacitance at the end of the measuring period.
- c. Uncompensated incremental polarogram.
- d. Compensated incremental polarogram.

Conditions: measuring frequency of 1.003kHz , 25°C , $\Delta E = 20 \text{mV}$, delay time of 2.3 seconds, measuring period of 1.0 second, 3 drops at each potential.

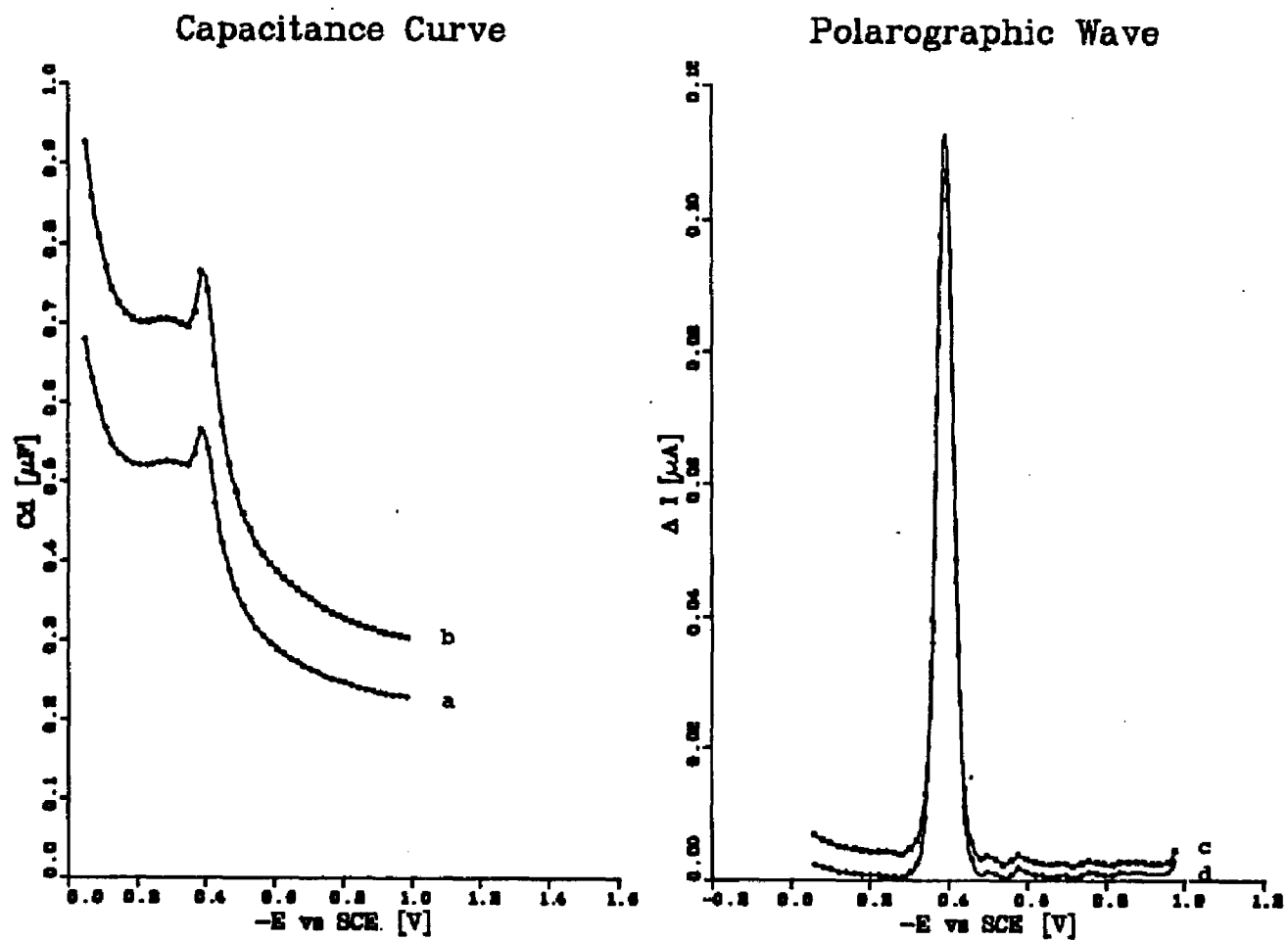


Figure 5.47

Chapter 6

CONCLUSION

6.1 SUMMARY

This thesis addressed a long standing polarographic problem - capacitive charging current. A novel approach to the compensation of the capacitive charging current in incremental polarography was described and a new instrument was constructed and tested.

The theory of the capacitive and faradaic components of the polarographic current as well as previous approaches to the charging current compensation were presented in Chapter 2. Various attempts of compensation were introduced and their advantages and disadvantages discussed.

Chapter 3 described the compensation based on the phase-null technique described by Schwartz (52). It showed that if proper choice of experimental conditions is made, the equivalent circuit of the cell is simplified to give a series RC network. Once the cell is connected to an amplifier circuit that contains a similar series RC network, and the phase-shift of the two networks is identical (phase-null), the output voltage of the circuit is directly proportional to the value of the double layer capacitance. This

value of C_d can then be used for in-situ compensation of the capacitive charging current in the incremental polarography.

Also in Chapter 3, exact equations were derived for the capacitive and faradaic components of the cell current, applicable to the particular configuration of the instrument introduced in this work.

Chapter 4 describes the new instrument, details of its functional and timing characteristics, and the programming details.

Tests of the various systems to evaluate the performance of the instrument, and comparison of the results with literature values were described in Chapter 5. The tests with the dummy cell concentrated on the individual networks of the instrument, while the tests with the supporting electrolyte allowed first, comparison with literature values, and with the results previously obtained by the phase-null instrument described by Schwartz. The later tests showed deviations of the order of 1.5 - 2.5 % over the entire potential range, for this system in absence of faradaic current. The tests have also uncovered some instrumental inadequacies leading to erroneous results at higher measuring frequencies.

The results obtained with systems containing reducible ions showed a definite improvement of the incremental polarograms with the introduction of this form of charging current compensation. The degree of improvement depends on the concentration and the heterogeneous rate constant of the

reducible ion, as well as the value of its half-wave potential. In $1 \times 10^{-7} \text{M}$ to $1 \times 10^{-5} \text{M}$ concentration range the compensation is absolutely necessary, and the results obtained had precision better than 6% and agreed very well with literature values for $E_{1/2}$ and peak width (see Chapter 5).

Faradaic interference from reduction of the ions in the vicinity of $E_{1/2}$ is also evaluated in Chapter 5. This faradaic pseudocapacitance effects cause errors in excess of 2% for $5 \times 10^{-6} \text{M}$ Cd^{+2} solutions, $5 \times 10^{-5} \text{M}$ Zn^{+2} solutions and $1 \times 10^{-5} \text{M}$ Pb^{+2} solutions, thus limiting this compensation technique to the low concentration regions. However, this is precisely the concentration region where the compensation of the capacitive current is essential, while there is no need for compensation at higher concentrations of the reducible ions.

6.2 APPLICATIONS

The new instrument incorporating the charging current compensation and allowing for direct measurement of the differential double layer capacitance and incremental polarographic response can be useful in a variety of applications.

The increase in sensitivity, allowing determination of 10^{-7}M concentrations of reducible ions, makes the instrument more competitive with other modern polarographic techniques, such as ac polarography and differential pulse polarography.

These techniques are slowly gaining popularity in the field of analytical chemistry. One of the advantages of this technique, for example, would be in polarography using short drop-times. Bond and O'Halloran (53) have pointed out some of the advantages of the short drop times and found that the charging current is a critical hurdle in the wider use of the technique. In-situ charging current compensation might just be the needed breakthrough for this technique.

Another good application for this instrument is in the field of HPLC, where it could be used as either an amperometric detector (94), or a capacitive detector (95), or a combination of both. Since the C_d is less sensitive to the presence of oxygen and to the flow-through of the solution, it might provide some advantages over presently used detectors.

Since the instrument is capable of measuring C_d values independently of the incremental current, it can be used for determination of surface active species, as well as for investigation of electrode kinetics. A recent paper by Rosen et al (96) describes an application of this instrument to determination of parts-per-million levels of surfactants in the solution.

Furthermore, the instrument could be used for investigation of the phenomena of polarographic maxima. A relation between the polarographic maximum and specific adsorption has been indicated in a recent paper (97). Since the instrument described here can measure polarographic current

and the double layer capacitance simultaneously, further insight into the origin of these phenomena can be sought.

6.3 POSSIBLE FUTURE IMPROVEMENTS

The tests performed with the pure supporting electrolyte at higher measuring frequencies showed some instrumental inadequacies, probably caused by phase-shifts in the transformers and the amplifier networks. A better design and layout of the critical circuits is essential for higher frequencies. Another possibility is to return to the current amplifier configuration used by Schwartz (52), but with some improvements. This would eliminate need for troublesome transformers and decrease the number of operational amplifiers. Such a circuit will be more amenable to theoretical analysis.

Other instrumental improvements might include use of (i) voltage-to-frequency converters in place of analog-to-digital converters, allowing for a simplified scaling procedure and simultaneously providing time averaging; (ii) a dedicated microcomputer to replace the three computers used in this work; (iii) a digital resistive ladder network in place of the photomodule, which would speed-up the feedback mechanism.

Appendices.

Appendix A

FARADAIC CURRENT DERIVATIONS

A.1 CURRENT - POTENTIAL RELATIONSHIP

The potential of the DME when using "staircase" scan can be expressed as a number of steps, j , away from the origin of the scan, or a potential at any other arbitrary reference point, E_0 :

$$E_j = E_0 + j\Delta E \quad [A-1]$$

where ΔE is the step-size and j is the step number which can have discrete values from zero to $+\infty$:

$$j = 0, \underline{+1}, \underline{+2}, \underline{+3}, \dots, \underline{+\infty} \quad [A-2]$$

A convenient reference point is the potential E_A at which the incremental polarogram has its maximum. Then

$$E_j = E_A + j\Delta E \quad [A-3]$$

The current at potential E_j can be abbreviated as i_j . A given value of E_A defines a set of discrete points E_j , i_j but not a continuous function. The latter can be obtained

by defining the peak potential for a single component as:

$$E_A = E_{1/2} + f\Delta E \quad [A-4]$$

where $E_{1/2}$ is the half-wave potential and f is a positive fraction with values from zero to one. Then

$$E_a = E_{1/2} + (j+f)\Delta E \quad [A-5]$$

defines a continuous range of potentials, allowing the current, i_j , and current increment, Δi_j , to be expressed in terms of the Taylor series. Let us define a variable a :

$$a = j + f \quad [A-6]$$

then

$$E_a = E_{1/2} + a\Delta E \quad [A-7]$$

and

$$E_{a-1} = E_{1/2} + (a-1)\Delta E \quad [A-8]$$

In the vicinity of $E_{1/2}$, the currents at potentials E_a and E_{a-1} can then be expanded in terms of Taylor's series:

$$i_a = i_{1/2} + i'_{1/2} a\Delta E + i_{1/2}^{(2)} \frac{a^2 \Delta E^2}{2} + \dots = \sum_{n=0}^{\infty} \frac{i_{1/2}^{(n)} a^n \Delta E^n}{n!} \quad [A-9]$$

and

$$i_{a-1} = i_{1/2} + i'_{1/2} (a-1)\Delta E + i_{1/2}^{(2)} \frac{(a-1)^2 \Delta E^2}{2} + \dots = \quad [A-10]$$

$$= \sum_{n=0}^{\infty} \frac{i_{1/2}^{(n)} (a-1)^n \Delta E^n}{n!}$$

where $i_{1/2}^{(n)}$ is the n -th potential derivative of current evaluated at $E=E_{1/2}$. The current increment for going from potential E_{a-1} to potential E_a can be defined as:

$$\Delta i_a = i_a - i_{a-1} \quad [A-11]$$

and is given by

$$\begin{aligned} \Delta i_a &= i_{1/2}' \Delta E[a-(a-1)] + i_{1/2}^{(2)} \frac{\Delta E^2}{2} [a^2-(a-1)^2] + \dots = [A-12] \\ &= \sum_{n=1}^{\infty} i_{1/2}^{(n)} \frac{\Delta E^n}{n!} [a^n-(a-1)^n] \end{aligned}$$

A.2 POTENTIAL AT THE MAXIMUM

The maximum of the incremental polarogram was defined to occur at potential E_A , where

$$E_A = E_{1/2} + f\Delta E \quad [A-4]$$

To locate the potential E_A , one must differentiate Δi with respect to potential and set it equal to zero. That is at E_A :

$$\frac{d\Delta i_a}{dE} = 0 \quad [A-13]$$

Since

$$E_a = E_{1/2} + a\Delta E \quad [A-7]$$

and

$$dE_a = da \quad [A-14]$$

equation [A-13] can be rewritten as:

$$\frac{d\Delta i_a}{da} = 0 \quad [A-15]$$

Substituting for Δi_a from equation [A-12] we get:

$$\frac{d\Delta i_a}{da} = \sum_{n=2}^{\infty} \frac{i_{1/2}^{(n)} \Delta E^n}{n!} [na^{n-1} - n(a-1)^{n-1}] = 0 \quad [A-16]$$

or

$$\sum_{n=2}^{\infty} \frac{i_{1/2}^{(n)} \Delta E^n}{(n-1)!} [a^{n-1} - (a-1)^{n-1}] = 0 \quad [A-17]$$

Writing out the first three terms of the series:

$$i_{1/2}^{(2)} \Delta E^2 + \frac{i_{1/2}^{(3)} \Delta E^3}{2} (2a-1) + \frac{i_{1/2}^{(4)} \Delta E^4}{6} (3a^2-3a+1) = 0 \quad [A-18]$$

Recalling equations [3-5] and [3-6]

$$i = \frac{i_d}{1+e^{2u}} \quad [3-5]$$

where

$$u = \frac{nF}{2RT} (E - E_{1/2}) \quad [3-6]$$

and using identity (99):

$$\frac{1}{1+e^{2u}} = \frac{1}{2} [1 - \tanh(u)] \quad [A-19]$$

equation [3-5] can be rewritten to give

$$i = \frac{1}{2} i_d [1 - \tanh \frac{nF}{2RT} (E - E_{1/2})] \quad [A-20]$$

In order to evaluate equation [A-18], equation [A-20] was differentiated to the n-th degree and solved for $E=E_{1/2}$. The results of the n-th derivatives are listed in Table A.1. Substituting from Table A.1 to equation [A-18] we get

$$\left(\frac{1}{8}i_d \cdot \frac{nF}{RT}\right) \frac{\Delta E^3}{2} (2a-1) = 0 \quad [A-21]$$

Since i_d , n , F , R , T or ΔE are not zero, the only solution for the equation [A-21] is

$$a = \frac{1}{2} \quad [A-22]$$

where

$$a = j + f \quad [A-23]$$

The potential of the maximum, E_A , was defined at a point where $j=0$, thus we can write:

$$f = \frac{1}{2} \quad [A-24]$$

and equation [A-4] then becomes:

$$E_A = E_{1/2} + \frac{1}{2}\Delta E \quad [A-25]$$

The maximum of the incremental polarogram for a reversible electrode reduction thus occurs $1/2\Delta E$ from the half-wave potential.

A.3 INCREMENTAL CURRENT AT ITS MAXIMUM

The general expression for current increment, Δi_a , was

Table A.1 Evaluation of Derivatives at $E = E_{1/2}$.

<u>n</u>	<u>exp</u>	<u>at $E=E_{1/2}$</u>
0	$(1/2)i_d(1-\tanh u)$	$(1/2)i_d$
1	$-(1/4)i_d P(1-\tanh^2 u)$	$-(1/4)i_d \left(\frac{nF}{RT}\right)$
2	$(1/4)i_d P^2 \tanh u(1-\tanh^2 u)$	0
3	$(1/8)i_d P^3(1-\tanh^2 u)(1-3\tanh^2 u)$	$(1/8)i_d \left(\frac{nF}{RT}\right)^3$
4	$-(1/4)i_d P^4 \tanh u(1-\tanh^2 u)(-2+3\tanh^2 u)$	0
5	$-(1/8)i_d P^5(1-\tanh^2 u)[(2-3\tanh^2 u)(1-7\tanh^2 u)+2\tanh^2 u]$	$-(1/4)i_d \left(\frac{nF}{RT}\right)^5$
6	$(1/8)i_d P^6 \tanh u(1-\tanh^2 u)[6(3-7\tanh^2 u)(1-\tanh^2 u)-1]$	0

where $P = \frac{nF}{RT}$

given in equation [A-12]:

$$\Delta i_a = \sum_{n=1}^{\infty} i_{1/2}^{(n)} \frac{\Delta E^n}{n!} [a^n - (a-1)^n] \quad [A-12]$$

Using the first five terms, equation [A-12] gives:

$$\begin{aligned} \Delta i_a = & i_{1/2}' \Delta E + i_{1/2}^{(2)} \frac{\Delta E^2}{2} (2a-1) + i_{1/2}^{(3)} \frac{\Delta E^3}{6} (3a^2-3a+1) + [A-26] \\ & + i_{1/2}^{(4)} \frac{\Delta E^4}{24} (4a^3-6a^2+4a-1) + i_{1/2}^{(5)} \frac{\Delta E^5}{120} (5a^4-10a^3+10a^2-5a+1) \end{aligned}$$

Substituting from equation [A-22] we get:

$$\Delta i_A = i_{1/2}' + i_{1/2}^{(3)} \frac{\Delta E^3}{24} + i_{1/2}^{(5)} \frac{\Delta E^5}{1920} \quad [A-27]$$

Dividing both sides by ΔE we have:

$$\frac{\Delta i_A}{\Delta E} = i_{1/2}' + i_{1/2}^{(3)} \frac{\Delta E^2}{24} + i_{1/2}^{(5)} \frac{\Delta E^4}{1920} \quad [A-28]$$

Thus $\Delta i/\Delta E$ can be made to approach di/dE by making the potential increment, ΔE , very small. This, however, is not practical nor required for analytical applications. By substituting for the derivatives from Table A.1 and rearranging we get:

$$\Delta i_A = - i_d \left[\frac{\Delta E}{4} \left(\frac{nF}{RT} \right) - \frac{\Delta E^3}{192} \left(\frac{nF}{RT} \right)^3 + \frac{\Delta E^5}{7680} \left(\frac{nF}{RT} \right)^5 \right] \quad [A-29]$$

where we can see that the peak of the incremental polarogram, Δi_A , is directly proportional to the diffusion current, i_d , and thus to the concentration of the electroactive species. All that is required for analytical application is the calibration curve.

At 25°C, $F/RT = 38.95n \text{ Volts}^{-1}$ and equation [A-29] reduces to:

$$\Delta i_A = -i_d [9.74n\Delta E - 307.8n^3\Delta E^3 + 11,672n^5\Delta E^5] \quad [A-30]$$

Table A.2 lists the contributions of each of the first three terms for various n and ΔE values.

A.4 AVERAGE INCREMENTAL CURRENT

This instrument measures an average current, $\bar{I}$, obtained during the measuring period, Δt , rather than the instantaneous current defined by equations [3-5] and [A-20]. This average current flowing between time t_1 and t_2 after the drop-fall can be expressed as:

$$\bar{I} = \frac{1}{\Delta t} \int_{t_1}^{t_2} i \, dt \quad [A-31]$$

where $\Delta t = t_2 - t_1$. Substituting for i from equation [A-20] we can write:

$$\bar{I} = \frac{1}{\Delta t} \int_{t_1}^{t_2} \frac{1}{2} i_d [1 - \tanh \frac{nF}{2RT} (E - E_{1/2})] dt \quad [A-32]$$

Removing constants from within the integral we get:

$$\bar{I} = \frac{1}{2\Delta t} [1 - \tanh \frac{nF}{2RT} (E - E_{1/2})] \int_{t_1}^{t_2} i_d \, dt \quad [A-33]$$

Which can be rewritten as:

Table A.2 Significance of the Higher Terms in the Taylor Expansion.

n	1				2				3			
ΔE [mV]	5	10	20	40	5	10	20	40	5	10	20	40
term 1 [%]	99.9	99.7	98.7	94.8	99.7	98.7	94.8	79.9	99.3	97.1	88.5	58.7
term 2 [%]	0.1	0.3	1.3	4.9	0.3	1.3	4.9	16.2	0.7	2.8	10.1	26.4
term 3 [%]	-	-	0.02	0.3	-	0.02	0.3	3.9	-	0.1	1.4	14.6

$$\bar{I} = \frac{1}{2} \bar{I}_d [1 - \tanh \frac{nF}{2RT} (E - E_{1/2})] \quad [A-34]$$

where

$$\bar{I}_d = \frac{1}{\Delta t} \int_{t_1}^{t_2} i_d dt \quad [A-35]$$

Substituting for i_d from the Ilkovic equation, [3-4], we can write:

$$\bar{I}_d = \frac{1}{\Delta t} \int_{t_1}^{t_2} 0.732 n F m^{2/3} D^{1/2} C_o t^{1/6} dt \quad [A-36]$$

Removing constants from the integral we get

$$\bar{I}_d = \frac{0.732 n F m^{2/3} D^{1/2} C_o}{\Delta t} \int_{t_1}^{t_2} t^{1/6} dt \quad [A-37]$$

Integrating and substituting for Δt :

$$\Delta t = t_2 - t_1 \quad [A-38]$$

we have

$$\bar{I}_d = 0.627 n F m^{2/3} D^{1/2} C_o \left(\frac{t_2^{1/6} - t_1^{1/6}}{t_2 - t_1} \right) \quad [A-39]$$

Noting that the only difference between the instantaneous current, i , given by equation [A-20] and the average current, $\bar{I}$, given by equation [A-34] is the value of the diffusion current, the peak of the average incremental current, $\Delta \bar{I}_A$, vs E curve can be written as:

$$\Delta \bar{I}_A = - \bar{I}_d \left[\frac{\Delta E}{4} \left(\frac{nF}{RT} \right) - \frac{\Delta E^3}{192} \left(\frac{nF}{RT} \right)^3 + \frac{\Delta E^5}{7680} \left(\frac{nF}{RT} \right)^5 \right] \quad [A-40]$$

Substituting for I_d from equation [A-39] and grouping all constants we have:

$$\Delta I_A = k C_O \quad [A-41]$$

where

$$k = -0.627 n F m^{2/3} D^{1/2} \left(\frac{t_2^{7/6} - t_1^{7/6}}{t_2 - t_1} \right). \quad [A-42]$$

$$\cdot \left[\frac{\Delta E}{4} \left(\frac{nF}{RT} \right) - \frac{\Delta E^3}{192} \left(\frac{nF}{RT} \right)^3 + \frac{\Delta E^5}{7680} \left(\frac{nF}{RT} \right)^5 \right]$$

Equations [A-41] and [A-42] show linear dependance of the peak height on the concentration of the electroactive species, thus allowing for simple quantitative determination of the species using a calibration curve.

Appendix B

CHARGING CURRENT DERIVATIONS

The change in the dc capacitive charging current, Δi_{c_a} , at any potential E_a can be derived starting from the definition of the dc charging current, equation [2-14], paying detailed attention to proper sign conventions:

$$i_{c_a} = - C_{i_a}^O E_a^* \frac{dA}{dt} \quad [B-1]$$

The negative sign in equation [B-1] stems from the definitions of polarography; for $E_a > E_z$ (potentials more positive than the potential of zero charge) charging current is anodic and therefore negative by convention. For $E_a < E_z$, i_c is cathodic and thus positive.

For two consecutive potentials, E_a and $E_{(a-1)}$, where

$$E_a = E_{(a-1)} + \Delta E \quad [B-2]$$

the difference in the charging current is:

$$\Delta i_{c_a} = i_{c_a} - i_{c_{(a-1)}} \quad [B-3]$$

From equations [B-1] through [B-3]:

$$\Delta i_{c_a} = - c_{i_a}^o E_a^* \frac{dA}{dt} + c_{i_{(a-1)}}^o (E_a^* - \Delta E) \frac{dA}{dt} \quad [B-4]$$

and

$$\Delta i_{c_a} = \frac{dA}{dt} \left[-E_a^* (c_{i_a}^o - c_{i_{(a-1)}}^o) - \Delta E c_{i_{(a-1)}}^o \right] \quad [B-5]$$

Defining $\Delta c_{i_a}^o$ as:

$$\Delta c_{i_a}^o = c_{i_a}^o - c_{i_{(a-1)}}^o \quad [B-6]$$

then

$$\Delta i_{c_a} = \frac{dA}{dt} \left[-E_a^* \Delta c_{i_a}^o - \Delta E c_{i_{(a-1)}}^o \right] \quad [B-7]$$

or

$$\Delta i_{c_a} = - \Delta E \frac{dA}{dt} \left[c_{i_{(a-1)}}^o + \frac{E_a^*}{\Delta E} \Delta c_{i_a}^o \right] \quad [B-8]$$

$c_{i_a}^o$ is an explicit function of E_a^* :

$$c_{i_a}^o = f(E_{(a-1)}^* + \Delta E) \quad [B-9]$$

and can be expressed by Taylor expansion around point $E_{(a-1)}^*$:

$$c_{i_a}^o = c_{i_{(a-1)}}^o + \frac{\Delta E}{1!} c_{i_{(a-1)}}^{o'} + \frac{\Delta E^2}{2!} c_{i_{(a-1)}}^{o(2)} + \frac{\Delta E^3}{3!} c_{i_{(a-1)}}^{o(3)} + \dots [B-10]$$

Then

$$\begin{aligned} c_{i_a}^o - c_{i_{(a-1)}}^o &= \Delta c_{i_a}^o = \\ &= \frac{\Delta E}{1!} c_{i_{(a-1)}}^{o'} + \frac{\Delta E^2}{2!} c_{i_{(a-1)}}^{o(2)} + \frac{\Delta E^3}{3!} c_{i_{(a-1)}}^{o(3)} + \dots \end{aligned} \quad [B-11]$$

where for the sake of simplicity we use:

$$C_{i(a-1)}^{O(n)} = \frac{d^n C_{i(a-1)}^O}{dE^n} \quad [B-12]$$

Substituting equation [B-11] into [B-8] we get:

$$\begin{aligned} \Delta i_{c_a} = -\Delta E \frac{dA}{dE} \left[C_{i(a-1)}^O + \frac{E_a^*}{\Delta E} \left(\frac{\Delta E}{1!} C_{i(a-1)}^{O'} + \right. \right. \\ \left. \left. + \frac{\Delta E^2}{2!} C_{i(a-1)}^{O(2)} + \frac{\Delta E^3}{3!} C_{i(a-1)}^{O(3)} + \dots \right) \right] \end{aligned} \quad [B-13]$$

To relate equation [B-13] to our work, Δi_c will now be developed in terms of the specific differential double layer capacitance, C_d^O , previously defined by equation [2-16]:

$$C_d^O = \frac{d\sigma}{dE} \quad [2-16]$$

Substituting for σ from equation [2-7] and differentiating:

$$C_d^O = C_i^O + E^* \frac{dC_i}{dE} \quad [B-14]$$

Rewriting equation [B-14] for potential $E_{(a-1)}^*$ gives:

$$C_{i(a-1)}^O = C_{d(a-1)}^O - E_{(a-1)}^* C_{i(a-1)}^{O'} \quad [B-15]$$

Substituting for $E_{(a-1)}^*$ from equation [B-2] and rearranging equation [B-15]:

$$C_{i(a-1)}^O = C_{d(a-1)}^O - E_a^* C_{i(a-1)}^{O'} + \Delta E C_{i(a-1)}^{O'} \quad [B-16]$$

Substituting for $C_{i(a-1)}^O$ in equation [B-13]:

$$\Delta i_{c_a} = -\Delta E \frac{dA}{dt} \left[c_{d(a-1)}^o + \Delta E c_{i(a-1)}^{o'} + \right. \quad [B-17]$$

$$\left. + \frac{E^*}{\Delta E} \left(\frac{\Delta E^2}{2!} c_{i(a-1)}^{o(2)} + \frac{\Delta E^3}{3!} c_{i(a-1)}^{o(3)} + \dots \right) \right]$$

Differentiation of equation [B-15] gives:

$$\frac{dc_{i(a-1)}^o}{dE} = c_{i(a-1)}^{o'} = c_{d(a-1)}^{o'} - E_{(a-1)}^* c_{i(a-1)}^{o(2)} - c_{i(a-1)}^{o'} \quad [B-18]$$

and

$$c_{i(a-1)}^{o'} = \frac{c_{d(a-1)}^{o'}}{2} - \frac{E_{(a-1)}^* c_{i(a-1)}^{o(2)}}{2} \quad [B-19]$$

Substituting equation [B-19] into [B-17]:

$$\Delta i_{c_a} = -\Delta E \frac{dA}{dt} \left[c_{d(a-1)}^o + \frac{\Delta E}{2} \left(c_{d(a-1)}^{o'} - \right. \quad [B-20]$$

$$\left. - E_{(a-1)}^* c_{i(a-1)}^{o(2)} \right) + \frac{E_a^*}{\Delta E} \left(\frac{\Delta E^2}{2!} c_{i(a-1)}^{o(2)} + \frac{\Delta E^3}{3!} c_{i(a-1)}^{o(3)} + \dots \right) \right]$$

Since

$$E_{(a-1)}^* c_{i(a-1)}^{o(2)} = E_a^* c_{i(a-1)}^{o(2)} - \Delta E c_{i(a-1)}^{o(2)} \quad [B-21]$$

equation [B-21] can be rewritten as :

$$\Delta i_{c_a} = -\Delta E \frac{dA}{dt} \left[c_{d(a-1)}^o + \frac{\Delta E}{2} c_{d(a-1)}^{o'} + \right. \quad [B-22]$$

$$\left. + \frac{\Delta E^2}{2} c_{i(a-1)}^{o(2)} + \frac{E_a^*}{\Delta E} \left(\frac{\Delta E^3}{3!} c_{i(a-1)}^{o(3)} + \dots \right) \right]$$

By repeating the steps from equation [B-18] to equation [B-22] with higher potential derivatives of $C_{i(a-1)}^o$, equation [B-22] can be shown to give:

$$\Delta i_{c_a} = - \frac{dA}{dt} \left[\frac{\Delta E}{1!} C_{d(a-1)}^o + \frac{\Delta E^2}{2!} C_{d(a-1)}^{o'} + \frac{\Delta E^3}{3!} C_{d(a-1)}^{o(2)} + \dots + \frac{\Delta E^n}{n!} C_{d(a-1)}^{o(n)} \right] \quad [B-23]$$

Taking only the first three terms of equation [B-23], the charging current increment, Δi_{c_a} , corresponding to the potential step from $E_{(a-1)}$ to E_a can be written as:

$$\Delta i_{c_a} = - \frac{dA}{dt} \left(\Delta E C_{d(a-1)}^o + \frac{\Delta E^2}{2} C_{d(a-1)}^{o'} + \frac{\Delta E^3}{6} C_{d(a-1)}^{o(2)} \right) \quad [B-24]$$

Since the instrument presented in this thesis measures average current, rather than instantaneous one, the above expression has to be modified to account for it. The average charging current during the measuring period, Δt , can be obtained by integrating the instantaneous charging current from t_1 to t_2 :

$$\Delta \bar{i}_{c_a} = - \frac{1}{\Delta t} \int_{t_1}^{t_2} \frac{dA}{dt} \left(\Delta E C_{d(a-1)}^o + \frac{\Delta E^2}{2} C_{d(a-1)}^{o'} + \frac{\Delta E^3}{6} C_{d(a-1)}^{o(2)} \right) dt \quad [B-25]$$

and

$$\Delta \bar{i}_{c_a} = - \frac{1}{\Delta t} \left(\Delta E C_{d(a-1)}^o + \frac{\Delta E^2}{2} C_{d(a-1)}^{o'} + \frac{\Delta E^3}{6} C_{d(a-1)}^{o(2)} \right) \int_{t_1}^{t_2} dA \quad [B-26]$$

Integrating:

$$\Delta I_{c_a} = - \frac{1}{\Delta t} \left(\Delta E C_{d(a-1)}^o + \frac{\Delta E^2}{2} C_{d(a-1)}^{o'} + \frac{\Delta E^3}{6} C_{d(a-1)}^{o(2)} \right) (A(t_2) - A(t_1)) \quad [B-27]$$

and

$$\Delta I_{c_a} = - \frac{1}{\Delta t} \left\{ \Delta E \left(C_{d(a-1)}^o A(t_2) - C_{d(a-1)}^o A(t_1) \right) + \frac{\Delta E^2}{2} \left(C_{d(a-1)}^{o'} A(t_2) - C_{d(a-1)}^{o'} A(t_1) \right) + \frac{\Delta E^3}{6} \left(C_{d(a-1)}^{o(2)} A(t_2) - C_{d(a-1)}^{o(2)} A(t_1) \right) \right\} \quad [B-28]$$

Since

$$C_d^o \cdot A = C_d \quad [B-29]$$

equation [B-28] can be rewritten as:

$$\Delta I_{c_a} = - \frac{1}{\Delta t} \left\{ \Delta E \left(C_{d(a-1),t_2} - C_{d(a-1),t_1} \right) + \frac{\Delta E^2}{2} \left(C_{d(a-1),t_2}' - C_{d(a-1),t_1}' \right) + \frac{\Delta E^3}{6} \left(C_{d(a-1),t_2}^{(2)} - C_{d(a-1),t_1}^{(2)} \right) \right\} \quad [B-30]$$

The average charging current increment can be approximated by the first term in equation [B-30]:

$$\Delta \bar{I}_{c_a} = - \frac{\Delta E}{\Delta t} \left(c_{d(a-1),t_2} - c_{d(a-1),t_1} \right) \quad [B-31]$$

In a potential region where large changes in the differential double layer capacitance occur, the second term in equation [B-30] might be required. Here the potential derivative of $c'_{d(a-1)}$ can be approximated by the incremental ratio:

$$c'_{d(a-1)} \approx \frac{\Delta c_{d(a-1)}}{\Delta E} = \frac{c_{d(a-1)} - c_{d(a-2)}}{\Delta E} \quad [B-32]$$

and

$$\begin{aligned} \Delta \bar{I}_{c_a} = & - \frac{\Delta E}{\Delta t} \left[c_{d(a-1),t_2} - c_{d(a-1),t_1} + \right. \\ & \left. + \frac{1}{2} \left(c_{d(a-1),t_2} - c_{d(a-1),t_1} \right) - \frac{1}{2} \left(c_{d(a-2),t_2} - c_{d(a-2),t_1} \right) \right] \end{aligned} \quad [B-33]$$

or

$$\begin{aligned} \Delta \bar{I}_{c_a} = & - \frac{\Delta E}{\Delta t} \left[\frac{3}{2} \left(c_{d(a-1),t_2} - c_{d(a-1),t_1} \right) - \right. \\ & \left. - \frac{1}{2} \left(c_{d(a-2),t_2} - c_{d(a-2),t_1} \right) \right] \end{aligned} \quad [B-34]$$

APPENDIX C

DERIVATION OF EQUATION FOR THE AC GAIN OF THE MEASURING AMPLIFIER

In Figure 3.5, the operational amplifier, O.A., is connected in the inverting configuration and its output is governed ideally by the equation:

$$e_o = \frac{Z_f}{Z_i} e_i \quad [C-1]$$

where e_o is the amplifier output voltage, e_i is the output of the transformer's secondary, and Z_f and Z_i are the feedback and input impedances respectively. From the ac circuit theory we can write for Z_f and Z_i :

$$Z_i = R_i \quad [C-2]$$

$$Z_f = R_f - \frac{j}{2\pi f C_f} \quad [C-3]$$

where $j = -1$, R_f and C_f are the feedback resistance and capacitance, and R_i is the input resistance. Substituting [C-2] and [C-3] into [C-1] we obtain:

$$e_o = \frac{R_f - j/2\pi f C_f}{R_i} e_i \quad [C-4]$$

and rearranging

$$e_o = \frac{1 + j2\pi f C_f R_f}{j2\pi f C_f R_i} e_i \quad [C-5]$$

The voltage e_i present at the secondary of the transformer is a measure of the potential drop across the measuring resistor, R_m , caused by the ac component of the cell current, i_{cell} :

$$e_i = i_{cell} R_m a \quad [C-6]$$

where a is the step-up ratio of the transformer, whose phase-shift will be considered to be constant within the range of measuring frequency used. Substituting equation [C-6] into [C-5] gives:

$$e_o = \frac{1 + j2\pi f C_f R_f}{j2\pi f C_f R_i} R_m a i_{cell} \quad [C-7]$$

Since instrument employs potentiostatic control (see Chapter 4 for details) all of the applied potential, e_a , appears across the cell, which can be represented by the simplified equivalent circuit, Figure 3.2. The cell current can then be written as :

$$i_{cell} = \frac{e_a}{Z_{cell}} \quad [C-8]$$

where

$$Z_{cell} = R_x - \frac{j}{2\pi f C_d} \quad [C-9]$$

Substituting equations [C-8] and [C-9] into [C-7] and rearranging we get:

$$e_o = \frac{C_d}{C_f} \frac{1 + j2\pi f C_f R_f}{1 + j2\pi f C_d R_x} \frac{R_m}{R_i} a e_a \quad [C-10]$$

At phase null the phase angle of the equivalent circuit, α_{cell} is equivalent to the phase angle of the feedback network, α_f . Since

$$\alpha_{cell} = \tan^{-1}[-2\pi f R_x C_d] \quad [C-11]$$

and

$$\alpha_f = \tan^{-1}[-2\pi f R_f C_f] \quad [C-12]$$

at phase null

$$R_x C_d = R_f C_f \quad [C-13]$$

Substituting equation [C-13] into [C-10] we can see that the output of the measuring amplifier, O.A. is:

$$e_o = \frac{C_d}{C_f} \cdot \frac{R_m}{R_i} a e_a \quad [C-14]$$

Since C_f, R_m, R_i and a are values of passive components whose values are constant, we can reduce equation [C-14] to:

$$e_o = k C_d \quad [C-15]$$

where

$$k = \frac{R_m a}{C_f R_i} \quad [C-16]$$

Equation [C-15] thus shows the ac output of O.A. to be

directly proportional to the differential double layer capacitance of the electrode-solution interface.

APPENDIX D

DERIVATION OF EQUATION FOR THE DC OUTPUT OF THE MULTIPLIER

If two sinusoidal signals, e_1 and e_2 , which are $90^\circ + \phi$ out of phase, are multiplied a new sinusoidal signal is obtained. Writing

$$e_1 = A \sin(2\pi ft) \quad [D-1]$$

and

$$e_2 = B \cos(2\pi ft + \phi) \quad [D-2]$$

where sine and cosine of the same function are 90° out of phase, and A and B are the amplitudes of the two signal of frequency f. Multiplying e_1 and e_2 we get:

$$e_1 \cdot e_2 = A \sin 2\pi ft \cdot B \cos(2\pi ft + \phi) \quad [D-3]$$

Using the identity:

$$\cos(x+y) = \cos x \cdot \cos y + \sin x \cdot \sin y \quad [D-4]$$

we have:

$$e_1 \cdot e_2 = AB[\sin(2\pi ft)\cos(2\pi ft)\cos\phi - \sin^2(2\pi ft)\sin\phi] \quad [D-5]$$

Using additional identities:

$$\sin x \cdot \cos x = \frac{1}{2} \sin 2x \quad [D-6]$$

and

$$\sin^2 x = \frac{1}{2}(1 - \cos 2x) \quad [D-7]$$

we can rewrite equation [D-5] as:

$$e_1 \cdot e_2 = AB \left[\frac{1}{2} \sin(4\pi ft) \cdot \cos \phi - \frac{1}{2} (1 - \cos 4\pi ft) \sin \phi \right] \quad [D-8]$$

and rearranging

$$e_1 \cdot e_2 = \frac{AB}{2} [\sin(4\pi ft) \cos \phi + \cos(4\pi ft) \sin \phi - \sin \phi] \quad [D-9]$$

where $\sin(4\pi ft) \cos \phi$ and $\cos(4\pi ft) \sin \phi$ are the periodic, or ac, terms and $\sin \phi$ is the non-periodic, or dc, term:

$$D_\phi = - \frac{AB}{2} \sin \phi \quad [D-10]$$

If $\phi=0$, which is the case of the phase-null, equation [D-9] reduces to

$$e_1 \cdot e_2 = \frac{AB}{2} \sin(2\pi ft) \quad [D-11]$$

Since the output of the commercial multiplier modules is given by equation:

$$E_o = \frac{e_1 \cdot e_2}{10} \quad [D-12]$$

the general equation of the multiplier module is:

$$E_o = \frac{AB}{20} [\sin(4\pi ft) \cos \phi + \cos(4\pi ft) \sin \phi - \sin \phi] \quad [D-13]$$

and the dc component of the output, E_{dc} , as:

$$E_{dc} = - \frac{AB}{2\theta} \sin\phi \quad [D-14]$$

In the phase-null method, where we work with phase-shifts of less than 0.5° ,

$$\sin\phi \approx \phi \quad [D-15]$$

and

$$E_{dc} \approx - \frac{AB}{2\theta} \phi \quad [D-16]$$

Thus for very small phase-shifts, the dc component of the multiplier module is directly proportional to the phase shift.

APPENDIX E

CIRCUITRY

The general introduction of the instrument in the form of a block diagram and timing sequence was made in chapter 4. This appendix will provide further details of the circuitry of the instrument. The description itself is divided into five parts:

- (i) potentiostat and signal inputs
- (ii) DC measuring network
- (iii) ac measuring network and phase-null detection
- (iv) trigger network
- (v) computer interfacing and processing

Each network is described in detail, pointing out its function as well as similarities and differences with published circuits. Specifications of each component are listed in Appendix F.

E.1 POTENTIOSTAT AND SIGNAL INPUTS

The principle of the potentiostat was introduced in 1942 by Hickling (98) and has seen wide acceptance, particularly since the development of operational amplifiers (op-amps). A comprehensive discussion of potentiostat circuits similar to one used in this instrument has been written by Schwartz and Shain (80). In their discussion they stated following requirements that any instrument used for potential control in connection with three-electrode cell must be able to fulfill:

"First the potential between the working and the reference electrodes must be compared with an arbitrarily-adjustable external potential. Then, the instrument must be able to react to the difference between these two potentials through a negative feedback circuit, containing the counter electrode, in such a way as to reduce the difference to zero. In addition, these operations must be performed without drawing significant current through the reference electrode."

The potentiostat circuit employed in this instrument (see Figure E.1) is the familiar two - amplifier network conforming to all of the above requirements. Both amplifiers used are high speed units with a bandwidth of 15MHz.

The signal that the potentiostat must deliver to the working electrode has three components:

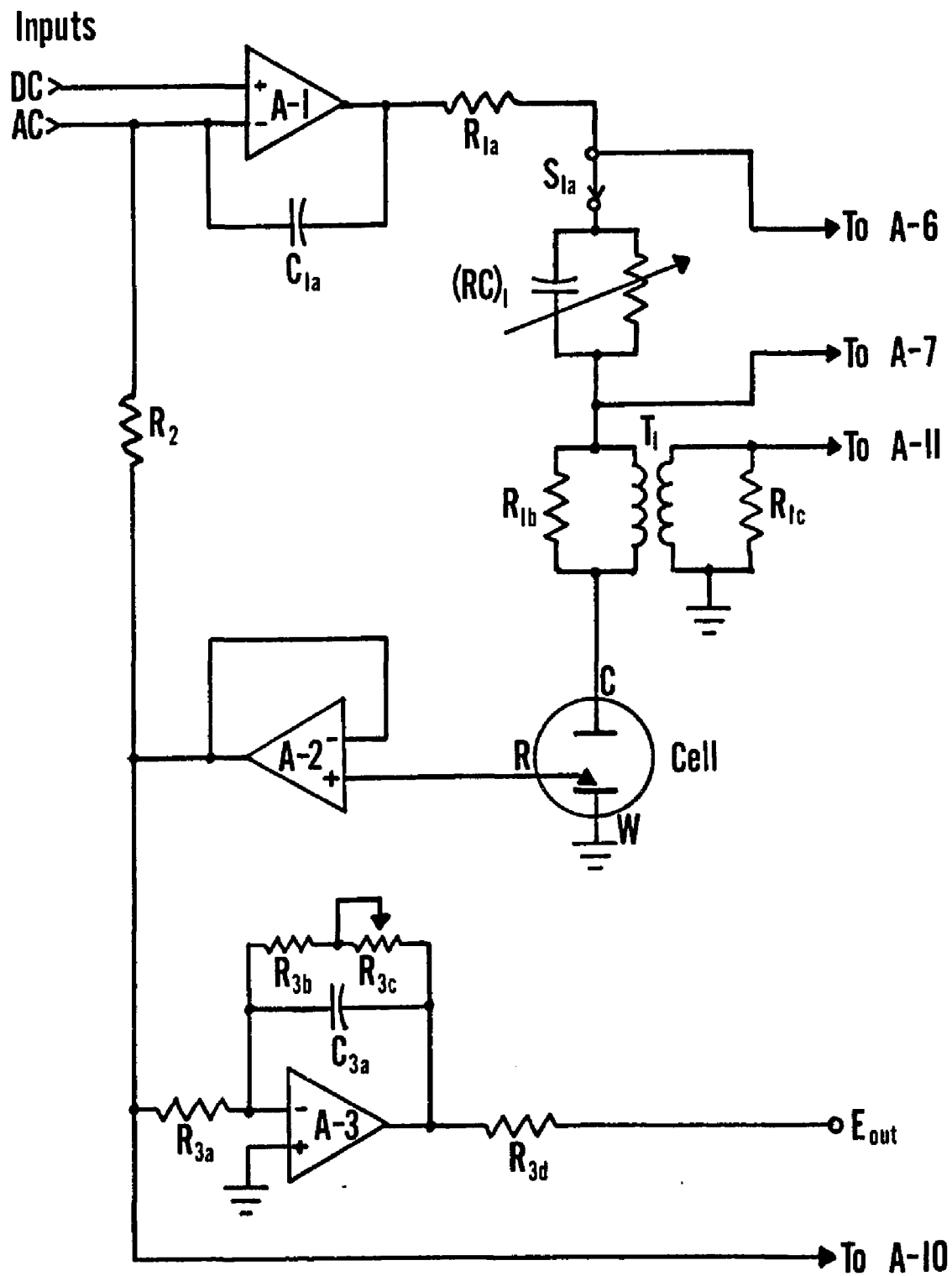


Figure E.1 Potentiostat

- (i) dc polarizing potential
- (ii) low frequency sine-wave measuring potential
- (iii) high frequency triggering potential

The dc potential is applied to the positive input of the amplifier A-1, while the ac signals are injected into the negative input.

The ac signals were supplied from two highly stable oscillators (Hewlett Packard Co.). The measuring signal of 1,5,10 and 20kHz with amplitude less than 10mV peak-to-peak, was supplied from model 204D, while the 200kHz trigger signal of 20mV peak-to-peak came from the model 4204A. Both signals were injected through a series RC network with a time constant of 0.1 seconds, in order to avoid large phase shifts and dc offsets (see Figure E.2). The low amplitude of the measuring signal was necessary to avoid distortions due to rectification effects as was pointed out by Grahame (48). To avoid interactions of triggering and measuring signals during the sampling period, the high frequency ac signal is turned off immediately after drop-fall by grounding capacitor C_{1b} , using a computer controlled relay S_{c1} (see Figure E.3). The signal is reapplied after sampling is completed. The dc polarizing voltage is applied in equal steps, rather than by the usual continuous sweep. The amplitude of the step, produced using a "charge pump" circuit (Figure E.4), could be varied from 0.1mV to 200mV in a 1,2,5 sequence. The charge-pump stepper circuit is based on

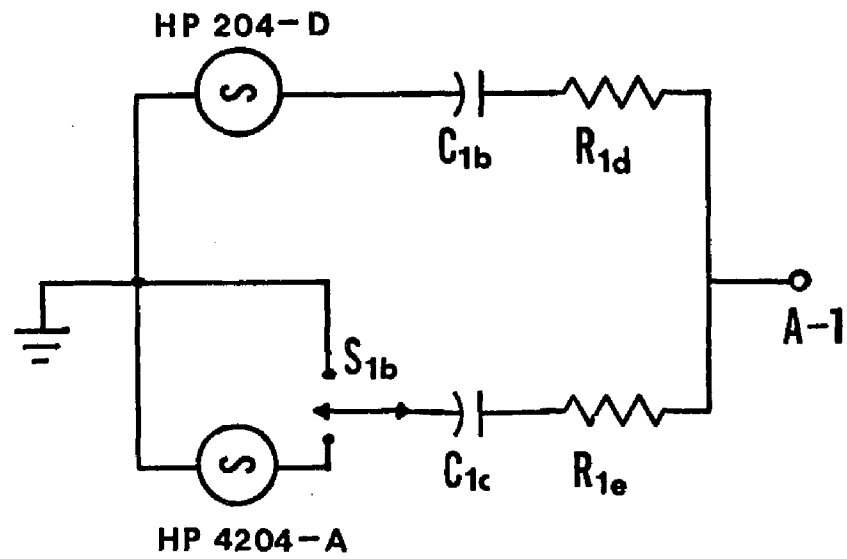


Figure E.2 AC Potential Inputs

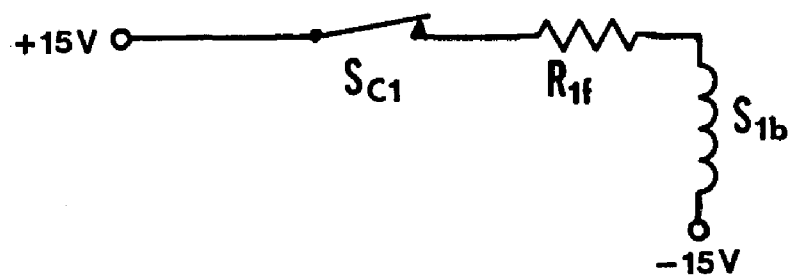


Figure E.3 Driver for Trigger Voltage Control

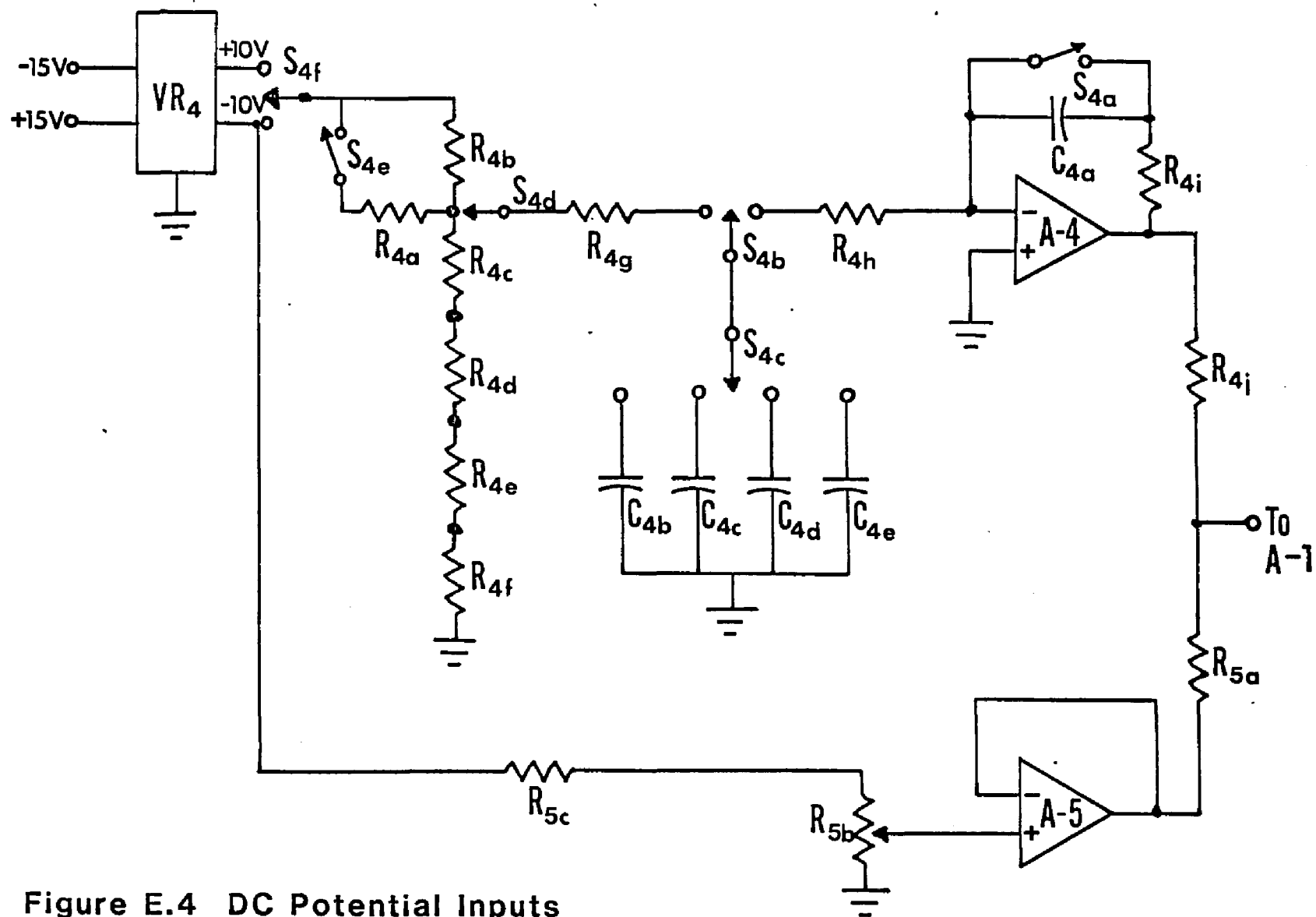


Figure E.4 DC Potential Inputs

charging the input capacitor ($C_{4b}-C_{4e}$) to a voltage between 0.5V and 10V, depending on the choice of the step-size resistor ($R_{4b}-R_{4f}$). The charge is then "pumped" to the integrating capacitor, C_{4a} , using switches S_{4b} and S_{4c} at time t_3 , causing the output of the amplifier A-4 to change by a value ΔE , given by equation [E-1]:

$$\Delta E = \pm 10V \frac{R_4}{10k\Omega} \cdot \frac{C_4}{C_{4a}} \cdot \frac{R_{5a}}{R_{5a} + R_{4j}} = \pm \frac{R_4 C_4}{50} \quad [E-1]$$

where R_4 expressed in kohms is the sum of the resistance values from the position of the switch to the ground (e.g. 10kohm for the top position); C_4 expressed in μF is the input scaling capacitor used and ΔE is the increase in the dc input to the potentiostat in volts. Thus, e.g., a maximum step with 0.1 μF scale capacitor is 20mV. Depending on the position of switch S_{4g} , the stepper can be operated manually by depressing momentary switch S_{4h} , or automatically by activating computer relay S_{4c} (Figure E.5). In either case a positive pulse is created, activating pulse relay S_{4b} and causing the charge to be transferred from the scaling capacitor to the integrating one. Releasing manual switch S_{4g} or deactivating computer relay S_{4c} produces a negative, pulse returning the contacts of pulse relay S_{4b} to their original "charging" position. To reset the output of amplifier A-4 back to zero, switch S_{4a} is provided, to discharge the integrating capacitor.

An initial offset potential, which is added to the staircase scan is delivered by amplifier A-5. The variable

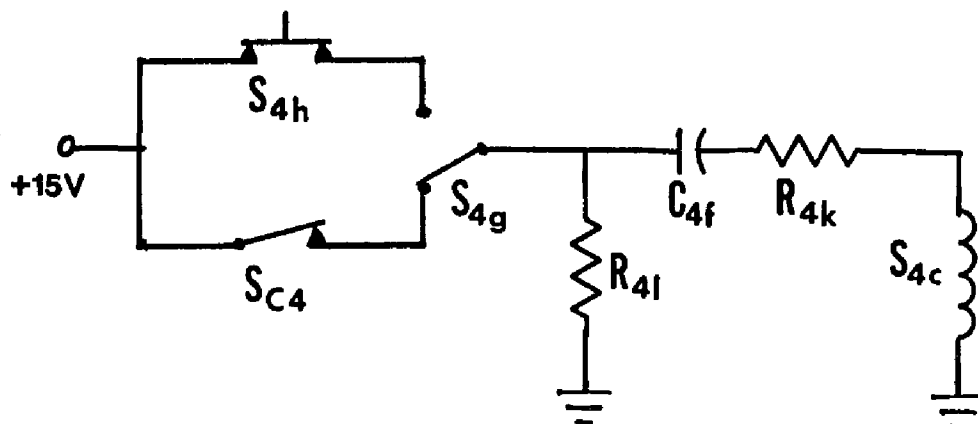


Figure E.5 Driver for Stepper Control.

0 to -1V offset is simply "dialed" by using a 10-turn potentiometer with calibrated dial. Both dc polarizing signals are derived from the precision voltage reference module, VR_4 , (Analog Devices Inc.), supplying $\pm 10.000V$ signal. The outputs of amplifiers A-4 and A-5 are reduced to one fifth and four fifths respectively, before being introduced to the potentiostat input. This decreases noise, while increasing the accuracy of ΔE .

The potentiostat amplifier will drive all the current necessary (up to the limits of the amplifier) to deliver the potentials applied at its inputs to the DME. Since no current is drawn through the reference electrode, the cell current containing both, ac and dc components also flows through the transformer T_1 and a parallel network $(RC)_1$. It is here that the separation of the ac and dc components of the cell current takes place. Transformer T_1 provides a

very low impedance for the dc component, thus causing its secondary coil to respond only to the ac signal. The capacitor in $(RC)_1$ network, on the other hand, provides low impedance for the ac component, causing most of the dc signal to appear across the $(RC)_1$. The ac component is thus transferred to the ac measuring network through the transformer T_1 , while the dc component is transferred to the dc measuring circuit through the $(RC)_1$ network. A different $(RC)_1$ network was used for each measuring frequency as a compromise, since high resistance was needed to measure the dc component of the cell current, while a large value of the capacitor was needed to avoid phase-shifts of the ac component. The compromise was made to limit the values of resistance and capacitance and thus keep the time lag reasonably low. The output of the follower, A-2, is the true value of the DME potential referred to the calomel electrode. It is the output of A-2 that is used as a reference signal in the phase detector in order to eliminate the non-ideality of the potentiostat at high frequencies. The follower output is also used as a measure of the polarizing voltage. The ac signal is filtered from the follower output in the buffer amplifier A-3. In the configuration used (see Figure E.1), A-3 has a dc gain of -1.00, while less than 2% of the ac above 1kHz is transmitted. In addition to its filtering action, A-3 acts as a buffer for the potential data transferred to the computer, since the input impedance of the computer's analog-to-digital converter (ADC) is only

25kohm. The resistors R_{1a} and R_2 , and capacitor C_{1a} are needed to stabilize the potentiostat and prevent oscillations.

E.2 DC MEASURING NETWORK

As was the case in the previous incremental polarograph (75), current to voltage conversion is performed using a measuring resistor in an instrumentation amplifier configuration. The major difference between this configuration and the more conventional current amplifier configuration (100) is the connection of the DME. With the current amplifier configuration the DME is connected to the summing point of the amplifier, a so called "virtual ground" point, while with the instrumentation amplifier configuration the DME is connected to a "hard" ground.

The actual circuit employed is shown in Figure E.6. The input to A-8 is taken across the $(RC)_1$ network and through a pair of high input impedance front-end amplifiers, A-6 and A-7, interconnected through a common-mode resistor, R_{6d} , in a manner similar to the instrumentation amplifier circuit described in the Burr-Brown Handbook of operational amplifiers (101). To eliminate ac from the dc measuring network, capacitors C_{6a} and C_{7a} have been placed in the feedbacks of A-6 and A-7 amplifiers. The dc and ac gains of the interconnected A-6 and A-7 amplifiers are given by equa-

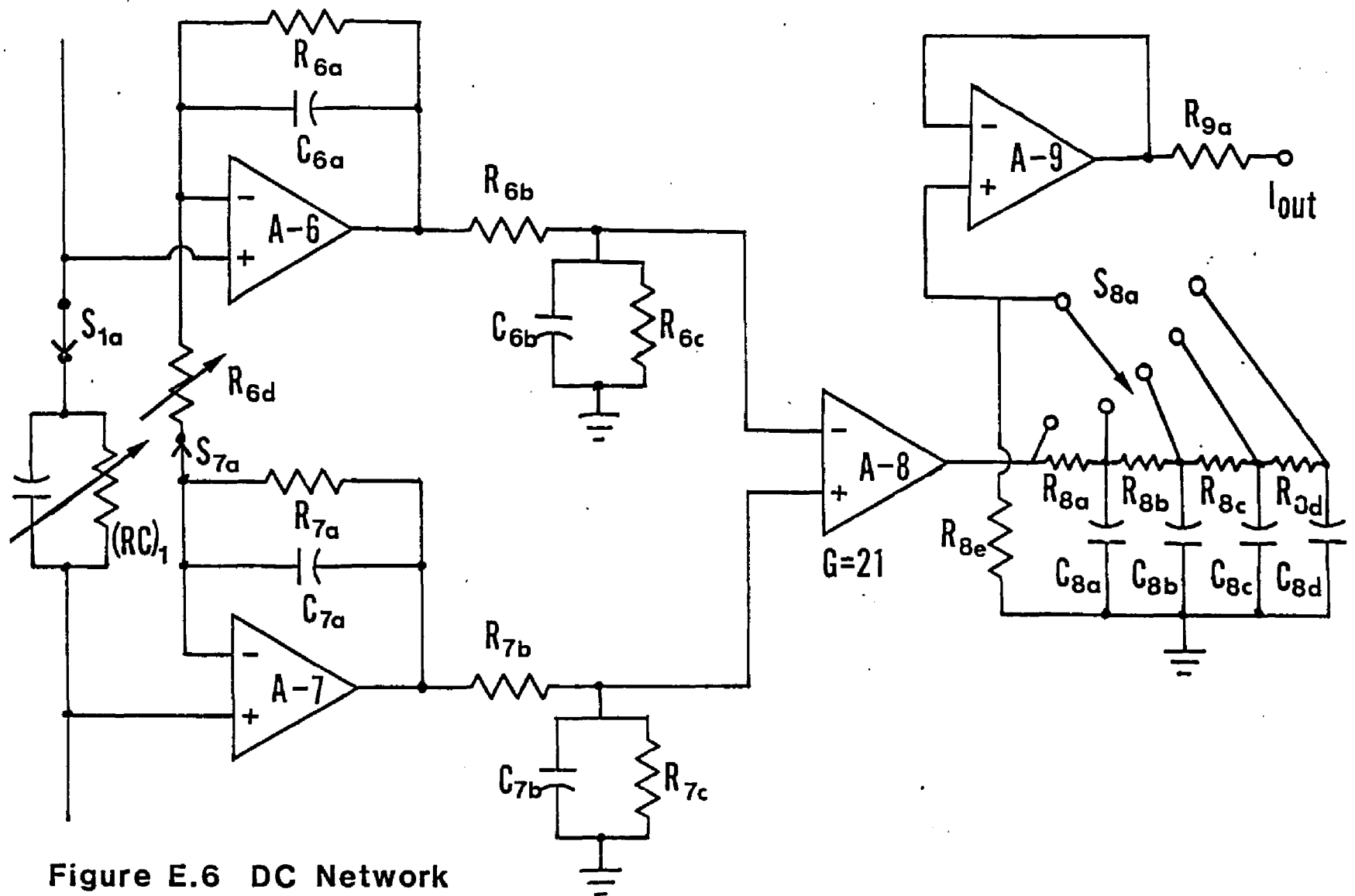


Figure E.6 DC Network

tions [E-2] and [E-3]:

$$G_{dc} = \frac{R_{6a} + R_{7a}}{R_{6d}} + 1 \quad [E-2]$$

and

$$G_{ac} = 1 + \frac{2R_{6a}}{R_{6d}(2\pi f C_{6a} R_{6a} + 1)} \quad [E-3]$$

Thus for $R_{7a} = R_{6a} = 1\text{Mohm}$, $C_{7a} = C_{6a} = 0.047\mu\text{F}$, $R_{6d} = 10\text{kohm}$ and $f = 1\text{kHz}$, the dc gain of the front end is 201, while the ac gain is 0.7. An additional decrease in the amplitude of the ac signal is accomplished by the low-pass RC filters placed on the output of the A-6 and A-7 amplifiers. The signal is then further amplified in the differential instrumentation amplifier A-8 wired for a gain of 21, using a single external resistor. A-8 is followed by a series of low-pass filters with a time constant of 5 milliseconds each.

All these filters, plus a shunt capacitor across the measuring resistor are necessary due to the large ac cell current, compared to the dc current. While the dc component is in the range from 1nA to $1\mu\text{A}$, the ac component is in the range from $10\mu\text{A}$ to 1mA peak-to-peak, or about a factor of 1000 higher. The output of the low pass filters is buffered using a voltage follower, A-9, in order to avoid loading of the filters by the low input impedance of the computer's ADC.

The overall gain of the dc measuring network can be

varied from $3.2\text{V}/\mu\text{A}$ to $0.3\text{V}/\text{pA}$ by varying the value of common mode resistor, R_{6d} and/or the measuring resistor in the $(RC)_1$ network. The latter is accomplished by switching a complete RC couple, in which the resistance and capacitance are matched to decrease the phase-shifts and time delays in the potentiostat, while allowing high dc gain of the network. The time constant of the RC networks used ranges from 40ms for high dc currents to 200ms for the low currents. In most of the experiments reported here a 50kohm or 100kohm resistor was used in parallel with a 1 μF capacitor.

E.3 AC MEASURING NETWORK

The output of the ac measuring amplifier, A-13 (see Figure E.7), is proportional to the differential double layer capacitance, C_d , at the phase-null, i.e. when there is no phase-shift between the ac potential applied to the DME and the output of A-13. The role of the ac measuring network in conjunction with the phase detector is to create the above mentioned condition. The phase-null condition is maintained by a negative feedback system or "servo", using a multiplier circuit, M_1 , as the phase difference detector. According to the mathematical theory of the multiplier, when two sine waves of the same frequency, phase-shifted by $90 \pm \phi$ degrees are multiplied, the multiplier output contains a dc component, D_ϕ , which is proportional to the phase differ-

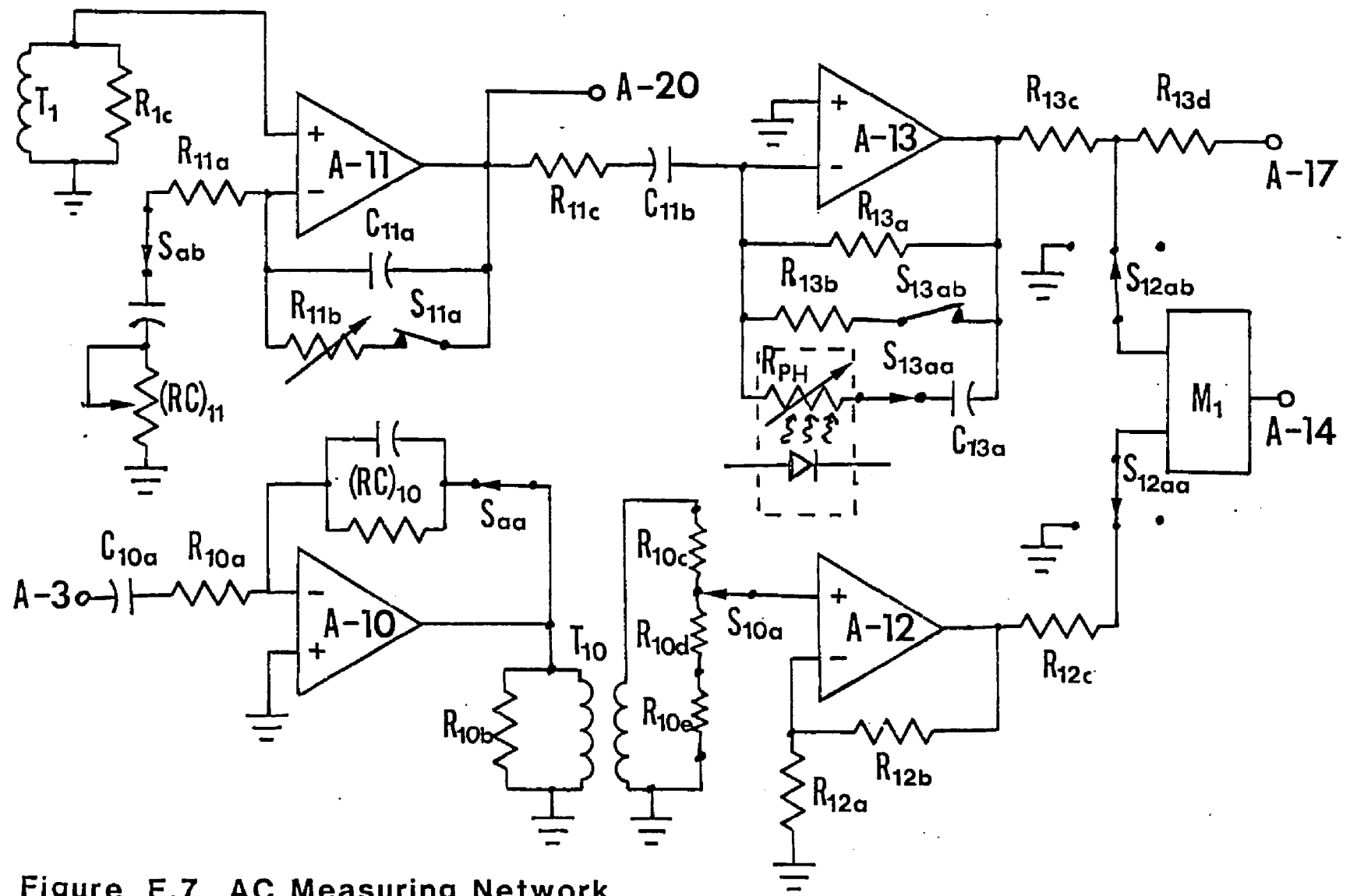


Figure E.7 AC Measuring Network

ence, ϕ , between these two signals (see Appendix D). The ac measuring network must perform the following functions:

- (i) amplification of the measuring and reference signals to the level required by the multiplier
- (ii) introduction of an accurate 90° phase-shift in addition to the ϕ° already present
- (iii) phase-error detection by the multiplier, by separation of the dc component of the multiplier output
- (iv) amplification of the phase-error signal to the proper level
- (v) operation of a servo system to accomplish the phase-shifting of the measuring signal to obtain the phase-null condition.

Let us now examine how the ac measuring circuit (shown in Figure E.7) performs these functions.

E.3.1 AMPLIFICATION OF THE SIGNAL AND PHASE-SHIFTING BY 90°

These two tasks are inseparable, because they are performed simultaneously by amplifiers A-10, A-11, A-12, and A-13 (see Figure E.7). The reference signal, taken from the output of the follower, A-2, is amplified and phase-shifted by amplifiers A-10 and A-12, while the measured signal is

conditioned using amplifiers A-11 and A-13. Using follower output as a reference signal in place of the applied potential corrects for some non-ideality in the potentiostat's performance at the high frequencies.

The first stage of amplification and phase-shifting of the reference signal is done by amplifier A-10, whose output is given by equation [E-4]:

$$e_o = -e_i \frac{Z_f}{Z_i} = \frac{Z_{(RC)_{10}}}{Z_{C_{10a}} + Z_{R_{10a}}} \quad [E-4]$$

where e_o and e_i are output and input potentials of the A-10, Z_f and Z_i are impedances in the feedback and input networks of A-10, $Z_{C_{10a}}$, $Z_{R_{10a}}$, and $Z_{(RC)_{10}}$ are vector impedances of capacitor C_{10a} , resistor R_{10a} and the parallel RC network respectively.

Since $Z_{(RC)_{10}}$ and $Z_{C_{10a}}$ depend on the frequency of the applied ac signal, a different RC combination in the $(RC)_{10}$ network is switched-in for each of the four frequencies used. This is done to keep the gain and the phase-shift of A-10 at more or less constant level. Impedances, gain and phase-shift of A-10 and its feedback and input networks are shown in Table E.1.

The output of the amplifier A-10 is fed into the transformer, T_{10} , which together with transformer T_1 in the signal path allows separation of the potentiostat and measuring ac network power supplies, to avoid "ground loops".

Table E.1 Impedances, Gains and Phase-shift of A-10 at Different Frequencies.

f	$(RC)_{10}$	$Z_{(RC)_{10}}$	R_{10a}	$Z_{C_{10a}}$	z_i	G	ϕ
[kHz]	[kohm pF]	[kohm °]	[kohm]	[ohm °]	[kohm °]		[°]
1	500 1500	104 -78	1	723 -90	1.23 -35.9	-85	-42
5	300 200	140 -62	1	144 -90	1.0 -8.2	-139	-54
10	200 100	124 -51	1	72.3 -90	1.0 -4.1	-124	-47
20	150 70	91 -53	1	36.2 -90	1.0 -2.1	-91	-51

In above table || signifies parallel connection, while nnn|dd is the vector notation for impedance of given component.

The voltage dividers on the T_{10} secondary coil decrease the level of the reference signal to 1/3 or 2/3 of original value. The gain of the amplifier A-12 is given by equation [E-5]:

$$G_{12} = \frac{e_o}{e_i} = 1 + \frac{R_{12b}}{R_{12a}} = 1 + \frac{50\text{kohm}}{2\text{kohm}} = 26 \quad [\text{E-5}]$$

where e_o and e_i are output and input signals of A-12, while R_{12b} and R_{12a} are feedback and input resistors respectively. There is no phase-shifting of the reference signal in the amplifier A-12. The total gain and phase-shift of the reference signal network, consisting of A-10, A-12 and transformer, T_{10} , with the voltage divider on its secondary is given as:

$$G_{\text{total}} = \frac{e_{12}}{e_2} = G_{10} \times G_T \times G_{12} \times \frac{R_{10}}{9\text{kohm}} \quad [\text{E-6}]$$

where G_{10} , G_{12} and G_T are gains of amplifiers A-10 and A-12, and transformer T_{10} respectively, while e_2 and e_{12} are output potentials of A-2 and A-12. R_{10} is the value of the resistance from the positive input of A-12 to ground. $R_{10}/9\text{kohm}$ can have values of 1/3, 2/3 or 1 only. Table E.2 shows gains and phase shifts of reference signal pathway at different frequencies.

Since ac input voltage was kept between 5 and 10mV peak-to-peak, the value of the reference signal on the multiplier input was between 5 and 20V peak-to-peak. For most runs, this value was kept at about 10V.

Table E.2 Gains and Phase-shifts of the Reference Signal.

	<u>1kHz</u>	<u>5kHz</u>	<u>10kHz</u>	<u>20kHz</u>
$G_{\min}$	$-737G_T$	$-1205G_T$	$-1075G_T$	$-789G_T$
$G_{\max}$	$-2210G_T$	$-3614G_T$	$-3224G_T$	$-2366G_T$
ϕ	-42°	-54°	-47°	-51°

The ac cell current is transferred from the potentiostat to the ac measuring network through the transformer T_1 . Here it is first amplified and phase-shifted in amplifier A-11 (see Figure E.7) using a capacitive and resistive feedback components. As was the case in amplifier A-10, a different $(RC)_{11}$ feedback network is employed for each measuring frequency. The output of the amplifier A-11 is given by equation [E-7]:

$$e_o = e_i \cdot 1 + \frac{z_f}{z_i} = e_i \cdot 1 + \frac{z_{C_{11a}} || z_{R_{11b}}}{z_{(RC)_{11}} + R_{11a}} \quad [E-7]$$

or rearranging:

$$e_o = e_i \cdot 1 + \frac{j2\pi f C_{11} R_{11b}}{[1 + j2\pi f C_{11a} R_{11b}][1 + j2\pi f C_{11} (R_{11} + R_{11a})]} \quad [E-8]$$

where e_o and e_i are output and input potentials of A-11, and values of all feedback components are given in Appendix F and Table E.3. The resistor R_{11b} can be varied from 10ohm to 500kohm and together with R_{11} in $(RC)_{11}$ is used to calibrate the 90° phase-shift between the reference and measuring signals (see Section 4.4.1 for procedure).

The signal is further amplified and phase-shifted in the measuring amplifier, A-13. With the servo system inactive and resistor R_{13b} substituted for the $R_{ph} - C_{13a}$ combination in the A-13 feedback network, the system is in the calibration stage, and its gain is given by equation [E-9]:

$$G_{13} = \frac{e_{13}}{e_{11}} = - \frac{z_f}{z_i} = - \frac{R_{13a}}{X_{C_{11b}} + R_{11c}} = - \frac{10kohm}{5kohm} = -2 \quad [E-9]$$

Table E.3 Impedances, Gains and Phase-shifts of A-11 at Different Frequencies.

	<u>1kHz</u>	<u>5kHz</u>	<u>10kHz</u>	<u>20kHz</u>
C_{11}	$0.15\mu\text{F}$	$35,000\text{pF}$	$15,000\text{pF}$	$4,700\text{pF}$
R_{11}	$1.3-1.8\text{kohm}$	$0.9-1.4\text{kohm}$	$0.3-1.3\text{kohm}$	$0.3-1.3\text{kohm}$
$X_{C_{11}}$	1.1kohm	909ohm	1.1kohm	1.7kohm
C_{11a}	12pF	12pF	12pF	12pF
$X_{C_{11a}}$	13Mohm	2.7Mohm	1.3Mohm	0.66Mohm
R_{11b}	$10-500\text{kohm}$	$10-500\text{kohm}$	$10-500\text{kohm}$	$10-500\text{kohm}$
$(Z_i)_{\min}$	$1.7\text{kohm} -39^\circ$	$1.3\text{kohm} -45^\circ$	$1.1\text{kohm} -74^\circ$	$1.7\text{kohm} -80^\circ$
$(Z_i)_{\max}$	$2.1\text{kohm} -31^\circ$	$1.7\text{kohm} -33^\circ$	$1.7\text{kohm} -39^\circ$	$2.1\text{kohm} -52^\circ$
$(Z_f)_{\min}$	$10\text{kohm} \theta.0^\circ$	$10\text{kohm} \theta.2^\circ$	$10\text{kohm} \theta.4^\circ$	$10\text{kohm} \theta.9^\circ$
$(Z_f)_{\max}$	$500\text{kohm} -2^\circ$	$490\text{kohm} -10.5^\circ$	$470\text{kohm} -21^\circ$	$400\text{kohm} -37^\circ$
G	$6-300$	$7-385$	$7-425$	$6-235$
ϕ	$28-39^\circ$	$23-45^\circ$	$19-74^\circ$	$15-79^\circ$

where e_{13} and e_{11} are output voltages of A-13 and A-11, and Z_f and Z_i are feedback and input impedances of A-13. The gain of A-13 is thus at constant -2, while its phase shift varies from 1.8° at 1kHz to 0.1° at 20kHz. The total amplification of the measuring signal in the calibration mode, G_{meas} , is then given as

$$G_{meas} = \frac{e_{13}}{i_{cell}} = G_T \times G_{11} \times G_{13} \times Z_{Tp} \quad [E-10]$$

where G_T , G_{11} and G_{13} are gains in transformer, A-11 and A-13 respectively, Z_{Tp} is ac impedance of the primary coil of the transformer T_1 and i_{cell} is the ac cell current. The actual gain and phase-shift at different frequencies are shown in Table E.4.

During the calibration procedure (see Section 4.4.1), the resistor R_{13b} is the feedback element of the measuring amplifier A-13, and the phase-shift between the measuring and reference signals is set to $90.0^\circ \pm 0.1^\circ$. When this is done, the output of the multiplier module, M_1 , has no dc component. To perform the calibration, a set of resistors (see Figure E.8) replaces the cell.

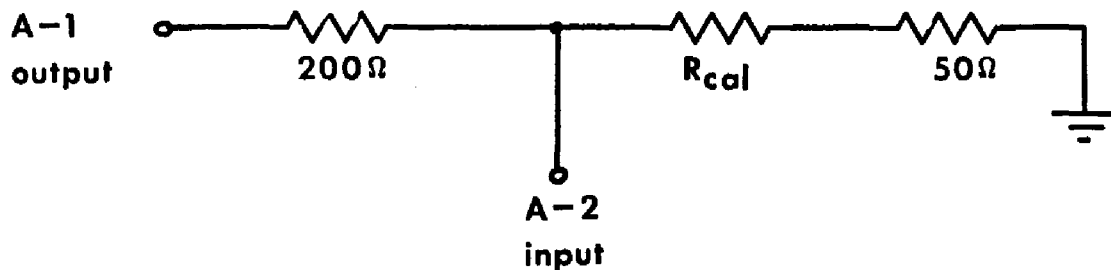


Figure E.8 Dummy Cell Circuit.

Table E.4 Gains and Phase-shifts of the Measuring Signal at Different Frequencies.

	<u>1kHz</u>	<u>5kHz</u>	<u>10kHz</u>	<u>20kHz</u>
$G_{\min}$	$-12G_T Z_{TP}$	$-14G_T Z_{TP}$	$-14G_T Z_{TP}$	$-12G_T Z_{TP}$
$G_{\max}$	$-600G_T Z_{TP}$	$-770G_T Z_{TP}$	$-850G_T Z_{TP}$	$-470G_T Z_{TP}$
ϕ	$28-39^\circ$	$23-45^\circ$	$19-74^\circ$	$15-79^\circ$

The resistor R_{cal} has a value of 500ohm at 1kHz, 100ohm at 5kHz, 50ohm at 10kHz and 30ohm at 20kHz, approximating the impedance of a double layer capacitance of about 0.3 μ F. With this arrangement there is no phase-shift in this dummy cell, and its impedance is similar to the expected cell value. Once the dummy cell is in place, the gains of reference and measuring pathways are set to give $90.0^{\circ} \pm 0.1^{\circ}$ by trimming the resistance in the $(RC)_{11}$ network. By performing this calibration, any phase-shift in transformers and amplifiers is compensated.

During the measurement itself, resistor R_{13b} is replaced by the photoresistor R_{ph} in series with a scale capacitor C_{13a} . The gain and phase-shift of the amplifier A-13 then change as required to balance the phase-shift in the cell.

The photoresistor, R_{ph} , must be set to operate in region where it has the greatest sensitivity and the smallest response time to changes in the light level. Since the photocell responds most rapidly at high light level and is most sensitive at low light level, a trade off was made in terms of response vs sensitivity, and the photoresistor was set to operate only over a five-fold range of resistance values from 2kohm to 10kohm.

In order to achieve phase null over the entire capacitance range, and at the same time maintain R_{ph} within the limited range, five different capacitors for C_{13a} are employed - 1000, 2000, 5000, 10 000 and 20 000pF. Each

capacitor was used over a certain range of C_d values, covering a range from about 20nF to 2μF, assuming a value of 100ohm for the uncompensated resistance. The gain and phase-shift ranges of the amplifier A-13 are listed in Table E.5.

In experiments reported here only three of the five scaling capacitors were used - 5000, 10 000 and 20 000pF - and they were sufficient to cover entire range of C_d values of the DME.

E.3.2 PHASE-SHIFT DETECTION

The amplifier and phase-shifted reference and measuring signals from amplifiers A-12 and A-13 respectively are introduced into the multiplier M_1 . As shown in Appendix D, when two signals:

$$f_1 = A \sin(\alpha t) \quad [E-11]$$

and

$$f_2 = B \cos(\alpha t + \phi) \quad [E-12]$$

are multiplied, the output of the multiplier module in addition to the ac signal also contains a dc component, D_ϕ :

$$D_\phi = \frac{AB}{2\theta} \sin\phi \quad [E-13]$$

A and B are the amplitudes of the measuring and reference signals and ϕ is the phase shift between the two signals. Equation [E-13] shows that the sensitivity of multiplier

Table E.5 Gains and Phase-shifts of A-13 at Different Frequencies.

	<u>1kHz</u>	<u>5kHz</u>	<u>10kHz</u>	<u>20kHz</u>
$G_{\min}$	-1.6	-0.5	-0.4	-0.4
$G_{\max}$	-32	-6.7	-3.8	-2.6
$\phi_{\min}[^{\circ}]$	-39	-9	-4.5	-2
$\phi_{\max}[^{\circ}]$	-89	-86	-80	-76

increases with signal amplitude. In practice the amplitudes of the signals were kept at about $5V_{pp}$, giving a sensitivity of about 20mV/deg of phase-shift.

E.3.3 SERVO SYSTEM

The servo network, shown in Figure E.9, links the multiplier with the measuring amplifier, A-13. The ac component of the multiplier output is filtered out in the instrumentation amplifier, A-14. One input of A-14 contains both, ac and dc, components, while the dc component is blocked by capacitor C_{14a} in the other input. The output is:

$$e_o = G(e_+ - e_-) \quad [E-14]$$

where e_+ and e_- are the positive and negative inputs respectively. Thus the ac component is cancelled, while the dc component is amplified by a gain G . In most of the experiments the gain was set to 50. The output of A-14 is in amplifier A-15, with a dc gain of 20 and ac gain of less than 1. Amplifier A-16 serves as a driver for the light emitting diode (LED). The total gain of the servo network is thus:

$$\begin{aligned} G_{\text{servo}} &= G_M \times G_{14} \times G_{15} \times G_{16} = \quad [E-15] \\ &= 20\text{mV/deg} \times 50 \times 20 \times 3 = 60\text{V/degree} \end{aligned}$$

Thus for a phase-shift of 1° between the measuring and

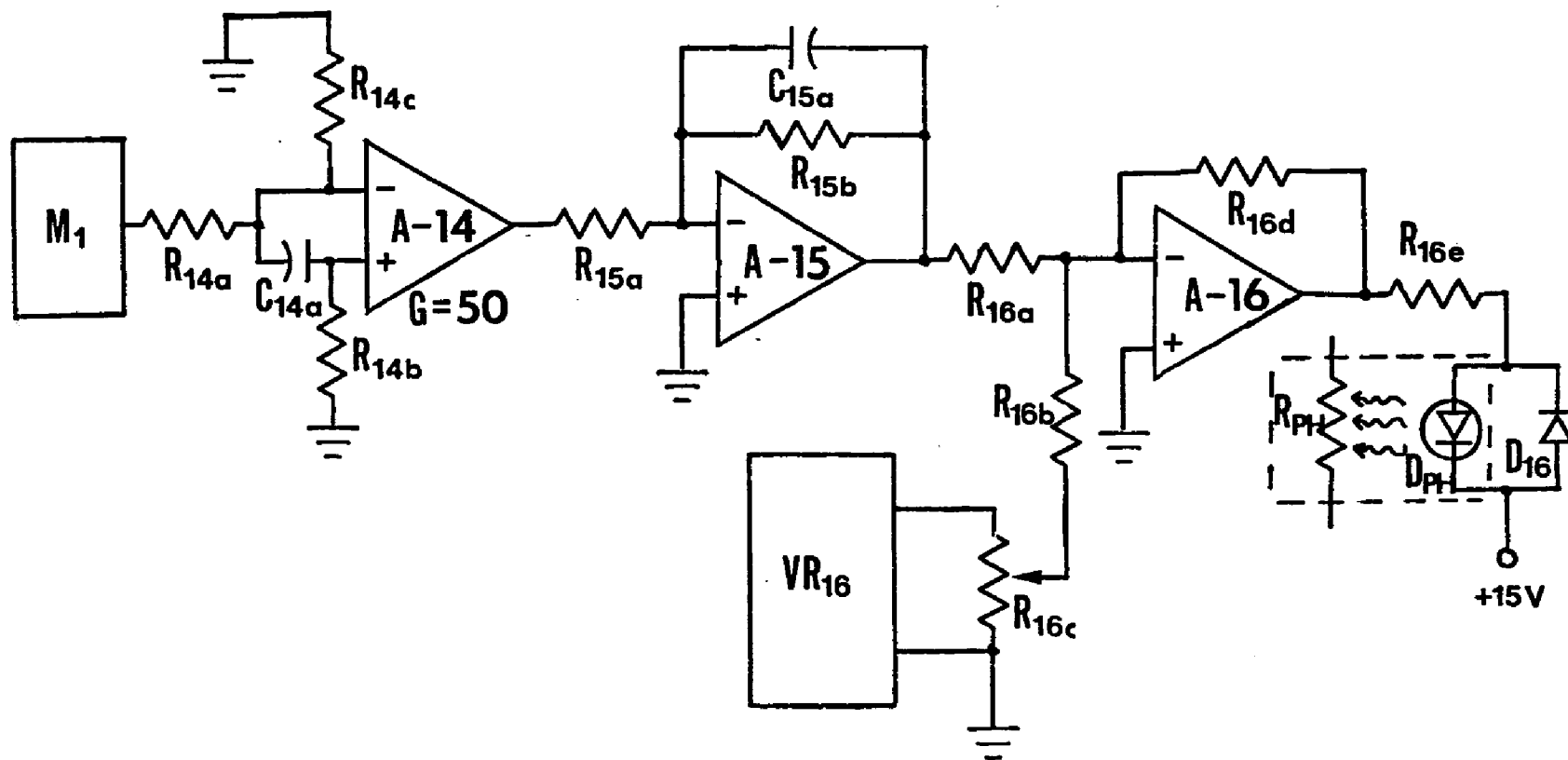


Figure E.9 Servo Network

reference signals, both having amplitude of 5V, output of the A-16 would be about $60V \pm 4.V_{\text{off}}$. Since V_{off} can be between 0 and 2.5V and amplifier output is limited to $\pm 12V$, 1° phase-shift produces saturation. The phase-shift will always be less than 0.3° .

The lamp driver, A-16, converts the voltage into a current, i_L , to drive the LED of the photomodule, D_{ph} . The magnitude of this current is:

$$i_L = \frac{e_{16} - (-15V)}{R_{16e} + R_{D_{\text{ph}}}} \quad [\text{E-16}]$$

Since A-16 is rated at 20mA, current no larger than about 25mA can be drawn from it. The operating point of the servo is set by adjusting V_{off} , using a trimmer, R_{16c} , to give a photoresistor value of about 5kohm at zero phase-shift. This allows the photoresistor to operate on either side of the phase-null.

In practice the operation of the phase-null servo may be illustrated as follows. If the phase of the output of A-13 lags the phase of reference signal, the phase-angle of the feedback loop of A-13 would be too negative and the resistance of R_{ph} must then be increased to retain the phase-null. The multiplier therefore produces a change in output to oppose the phase-error, namely a negative output. This decreases the current into the LED, causing an increase in the resistance of the R_{ph} , and decrease in the phase lag of the feedback network, and thus a return to the phase-null. A similar argument may be employed if the phase shift

were a lead instead of the lag.

E.3.4 RECTIFIER

At the phase-null, the ac amplitude at the output of amplifier A-13 is directly proportional to the value of the double layer capacitance, C_d . A precision half-wave rectifier, described in various sources (101,102) was used to convert the ac to dc (see Figure E.10). The rectifier, A-17, is followed by a two-stage low-pass filter to remove the ac ripple and a buffer amplifier, A-18, with a variable gain of 2,3 or 5. The output of A-18 is sampled periodically by the minicomputer.

E.4 TRIGGERING NETWORK

The triggering network is used to detect a drop-fall and to send a negative pulse to the computer. This pulse will then serve as a reference point for all the timing operations performed by the computer. The pulse is produced by the sharp increase in electrode impedance at drop-fall, caused by the separation of the mercury drop from the column inside the capillary. A 200KHz sinusoidal signal is applied from the oscillator to the potentiostat. The high frequency decreases the time lag in detecting the drop-fall. After amplification in A-11, (Figure E.9) the ac signal is

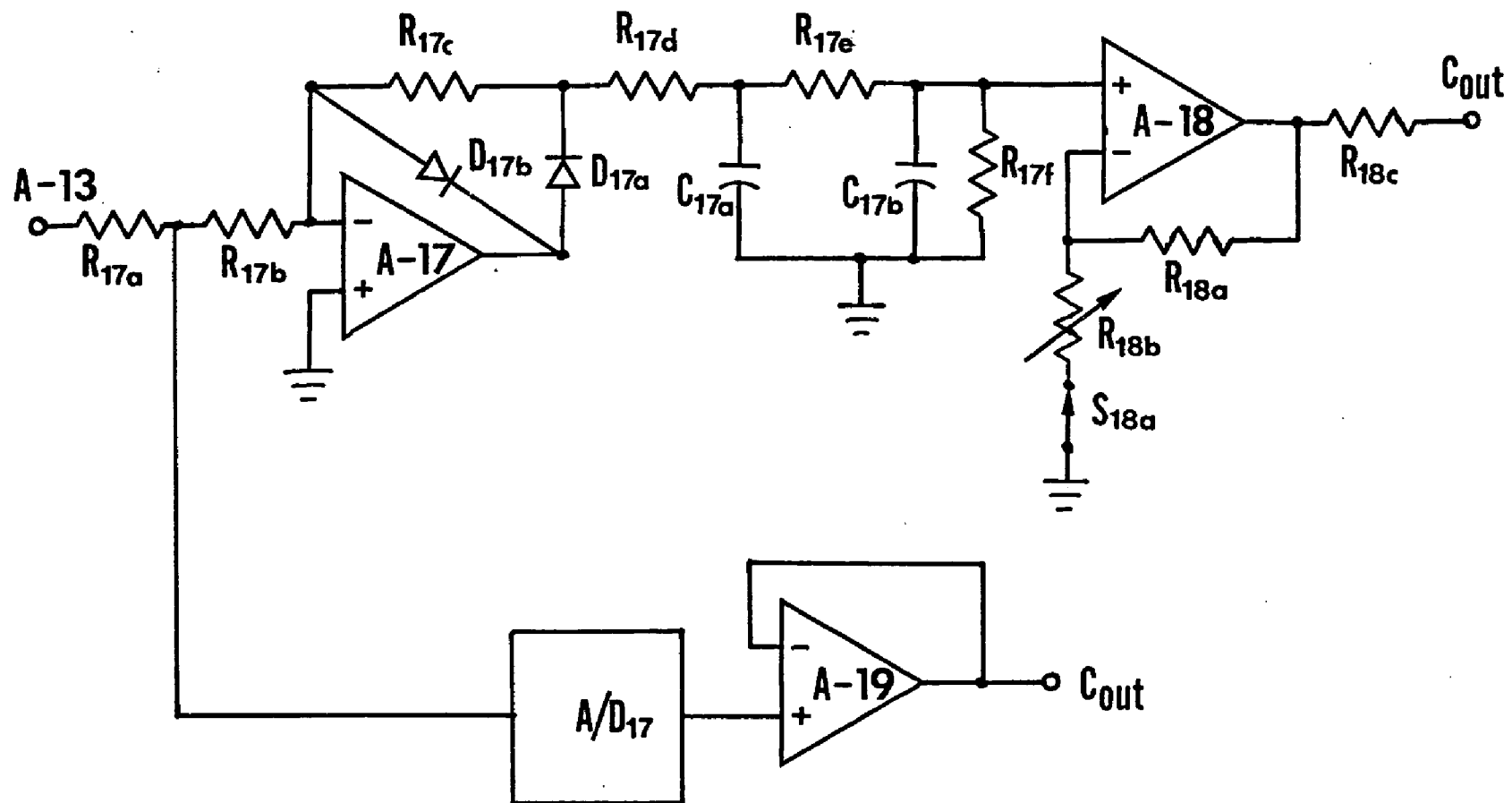


Figure E.10 Rectifier Network

transferred to the triggering circuit (Figure E.11), and further amplified by amplifier A-20. The 200kHz signal is selectively amplified and rectified by a full-wave bridge rectifier placed on the secondary coil of the transformer, T_{20} , and then filtered by a low-pass filter to remove remains of the ac signal. The resulting dc signal is amplified in A-21 to a level of about 10V and passed through an optical isolator, IO_{21} , before introduction to the computer.

At drop-fall output of A-21 drops from 10V to about 3V producing a negative pulse that is introduced into the computer.

To prevent errors in triggering three independent precautions have been taken:

- (i) The 200kHz signal is turned off immediately after the drop-fall (see Section 4.1.2) and reapplied only after all DME operations at the current drop have been completed.
- (ii) The threshold level of the Schmitt trigger in the minicomputer is set to about -4V, and it discriminates against the noise and false trigger signals.
- (iii) After detecting the trigger pulse, the computer does not check for the appearance of new pulses until measurements of the given drop cycle are completed.

These precautions are essential for correct performance of the trigger network which is critical to precision and

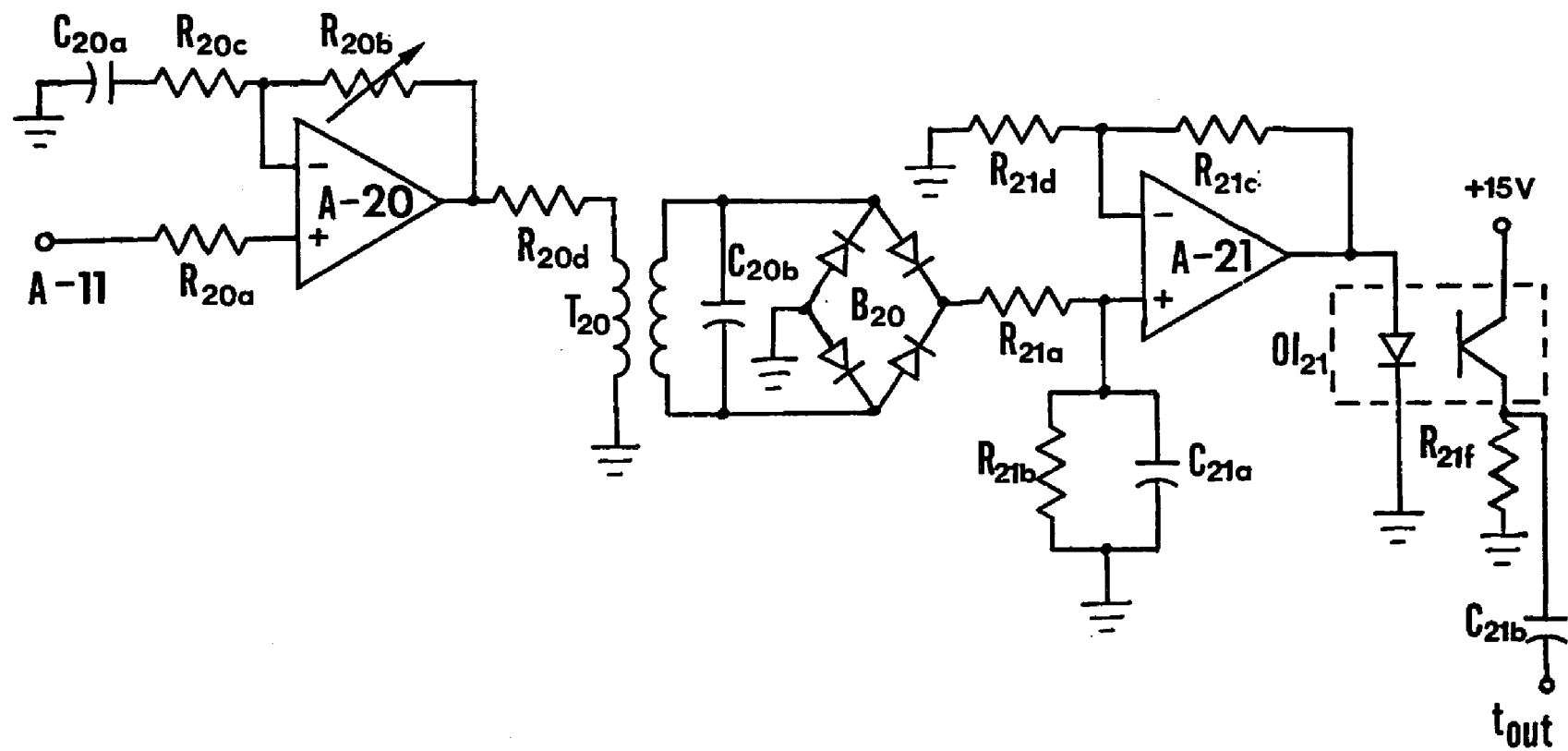


Figure E.11 Trigger Network

accuracy of the results.

E.5 COMPUTER INTERFACING AND PROGRAMMING

The use of computers to control polarographic and voltammetric instrumentation and to evaluate data is not new (58,59). The advantages of interfacing electroanalytical instruments to computers have been pointed out by various researchers(58,59,30) and need not be further emphasized here.

The work described in this thesis employed three different computers. A dedicated PDP-11/20 minicomputer controlled the data acquisition phase of the experiment. The data was then transferred to a mass storage disk which was attached to a PDP-11/45 minicomputer in the Brooklyn College Data Acquisition Facility. Here the data were combined with Fortran program for calculations and statistical manipulation, and transferred through a high-speed line to mainframe computers at City University Computer Center. The results were then returned to the Data Acquisition Facility in plot and printout form. The use of three computers is not essential, since a well equipped microcomputer could handle all the calculations. The decision to use three computers was based on what equipment was available.

E.5.1 PDP - 11/20

The PDP-11/20 minicomputer (Digital Equipment Corp.) was equipped with the following accessories: 24 kwords of core memory, an ASR-33 teletype with paper tape punch/reader, an LPS-11 lab peripheral system, a PC-11 high speed paper tape reader, and a DL-11W serial I/O board for communication with the PDP-11/45 or for storing of the data on a digital cassette recorder. The LPS-11 lab peripheral system consisted of following accessories:

LPSAD-12: 12-bit ADC with sample and hold, 8 channel multiplexer and 6 digit LED display

LPSAG: 4 independent amplifiers with $\pm 1V$ input

LPSAG-VG: 4 independently selectable multigain differential amplifiers with $\pm 1V$, 0 to 2V, $\pm 5V$ and 0 to 10V ranges

LPSKW: programmable real-time clock a two Schmitt triggers

LPSDR: 16-bit buffered digital I/O with drive capabilities and two programmable, N.O. relays.

The data acquisition and control program for the PDP-11/20 was written in macro-assembly language and consisted of the following sections:

IOX-11: a slightly modified DEC proprietary I/O executive program used to handle all I/O operations to the teletype and digital cassette recorder

FPP-11: DEC proprietary software for performing floating point calculations

TRANSFER: program for communication between PDP-11/20 and PDP-11/45

INCPOL: program controlling the data acquisition and storage.

The polarograph control program, INCPOL, was written in DEC macro-assembly language and was edited, assembled, linked and stored using the more powerful PDP-11/45 system. The program occupies about 10 kwords of the core memory, which includes the storage area for 15,000 points (5,000 each for current, potential and capacitance data), with a total of about 16 kwords needed to include the IOX, FPP and TRANSFER programs.

The functions performed by the PDP-11/20 and their sequence has been described in detail in Sections 4.1.1 and 4.1.2. This appendix will describe the data acquisition program, INCPOL, concentrating on the program itself, rather than the physical measurement. To aid in this analysis, the full listing of the program is presented in Appendix G.

Once the experimental setup is ready and the instrument has been manually calibrated (Section 4.4.1), the computer

memory is loaded with the binary code of the program from the paper tape. The computer then takes over, starting by initializing the input/output devices and floating point facility followed by a question-and-answer period during which various operational parameters are entered through the use of the teletype. Once the parameters are entered, they are converted from ASCII to integer form and used to set-up the experimental conditions, such as delay and measuring periods, ADC channels sampled, output destination, etc. The computer then clears various control flags, and enters the second stage of the question-and-answer section, this time receiving the experiment ID, potential limit and value of the measuring resistor. Information is again converted to the integer form and stored, followed by clearing of the data storage area. The computer then checks on the need for additional calibration. Depending on the answer received, the computer either skips the calibration or proceeds to input the calibration parameters (voltage and dummy-cell resistance), then it halts and waits for operator to set-up the calibration and return control of the experiment to the computer. Calibration is done by inputting the value of the dummy cell capacitance and sampling the ADC channels using a timing sequence identical to that used for recording of the polarographs. Each set of data is stored and calibration cycle is repeated as many times as requested by the operator. The number of calibration cycles is then stored, and the address of the data storage location picked

up. The operator replaces the dummy cell with the DME and returns control to the computer by depressing the "continue" switch. The computer initializes counters, sets-up the delay time, enables the drop-fall trigger detection and waits until the drop-fall pulse, which starts the delay period timer. During the delay period the high frequency ac is turned off to avoid interference with measuring signal. Once the delay period expires, the timer is reset to provide pulses 1 millisecond apart, each pulse triggering a measurement of current, followed by measurements of potential and capacitance. Each data point is stored before next ADC conversion is initiated until the measurement period ends. 200ms after measuring period the triggering ac is turned back on, the dc voltage is changed by ΔE and drop-fall detection is activated. These steps are repeated until pre-set potential limit is reached. If this run is one of the offset scans, whole run is repeated after the manual change in the starting potential. If the fill-in option was not exercised, or if it was the last run in the set, computer proceeds to output data to the chosen storage device.

If data is transferred directly to the PDP-11/45, the computer initializes the transfer program, establishes the communication with the 11/45 through the hard wired connection, checks if the connection and 11/45 are working properly and proceeds to output data.

The output heading consists of the date, run number, sample name, value of the measuring resistor, number of the

data points taken, ADC channel selection, values of the calibration parameters and number of calibration points taken. The heading is followed by calibration data and experimental values of i , E , and C_d . At the end of data, the computer stores the closing statement and rings a bell.

At this point the computer asks for next instruction. The choices are: start with new parameters, start with old parameters, establish communication with PDP-11/45, go to specific address or if there were output problems, go to emergency recovery of the data using the paper tape punch. The computer then starts execution at the requested location in the program. If any fatal error occurs, the computer goes to an error recovery routine to allow for smooth operation.

The following service routines are included in the program INCPOL (Appendix G):

- data conversion and display
- reinitialize IOX
- check mode
- error recovery
- paper tape output

The data conversion and display subroutine gets each potential value in the binary form, converts it to the decimal form and displays the value using the LED display. The reinitialize IOX routine is a housekeeping routine allowing for use of both, IOX and TRANSFER, programs which duplicate some instructions and facilities and cannot be used simultaneously. The routine determines which one of the two programs will be in effect by loading the trap vectors with the

address of the given program. The check mode routine makes sure that the TRANSFER program sets the proper operating mode for 11/20. The output subroutine eliminates the repetition by combining the frequently used sequence of output commands into one. The last subroutine - error recovery allows for continuity if operator error occurs. The routine calls the initialize IOX subroutine and then asks for the next instruction.

To allow for immediate visual inspection of the progress of the experiment in the absence of a digital-to-analog converter (DAC), the digital I/O output is used to control an analog circuit (75) which produces approximate incremental polarograms on an X-Y recorder. The instructions controlling this circuit are coded with label "ANALOG" throughout the program.

E.5.2 PDP - 11/45

The PDP-11/45 used belongs to the Brooklyn College Data Acquisition Facility. It runs under the UNIX operating system and has following peripherals: magnetic and DEC tapes, floppy discs, RK05 removable mass storage discs, dial-up modems and a variety of terminals. In addition, the PDP-11/45 is hardwired to a PDP-11/20 which acts as a remote job entry (RJE) station of the City University Computer Center (UCC); the latter controls a high speed card reader, printer and Calcomp digital plotter.

At the completion of each run, data were transferred from the PDP-11/20 to the 11/45 (see Section E.5.1), and stored on the RK05 disc, then combined with a Fortran program and transmitted using the RJE station to the UCC facility. Once the calculations were completed at the UCC, results were transferred to the Data Acquisition Facility for printing and plotting.

E.5.3 CALCULATIONS AT UCC

The Fortran program called POLWAVE with the data from individual experiments was compiled and executed at the City University Computer Center (CUCC). A more detailed description of this program is presented, with complete listing in Appendix H.

After setup procedures such as dimension statements and counter initializations, the program reads the run ID, run variables and option pointers, and prints out the input values. This I/O operation is followed by the input of calibration values for current, potential and capacitance.

A linear regression analysis of capacitance calibration values gives the slope and intercept. The current and potential values are checked in the subroutine TST for inconsistent data by a Q-test to reject invalid points. The remaining values are then averaged and transferred back to the main program, where the calibration factors for $\bar{I}$, E and C_d are calculated and printed out.

Once the calibration factors are calculated, the experimental data is read in point-by-point using subroutine INPUT, until the end-of-file (EOF) is reached. Each point is converted to $\bar{I}$, E and C_d using the conversion factors, printed out, and checked with subroutine TST2. The average values of i , E and ΔC_d are then returned to the main program.

Values of $\bar{I}$, E and ΔC_d are then passed to the main program to the subroutine DERIV for calculation of ΔE , Δi , Δi_c and E_h (E_h is the midpoint between two experimental potential values) and $\Delta \bar{I}_c$ is subtracted from $\Delta \bar{I}$ to give the compensated faradaic response.

Subroutine SDERIV is then used to calculate second increment values that are used in subroutine FMAXIM to locate peaks and the values of the absolute maxima of the $\Delta \bar{I}$. The compensated and uncompensated current values are then printed out and passed to the plotting portion of the main program.

The plotting is done using Calcomp plotter, with all of the set-up performed using the DISSPLA plotting package. For automatic scaling the plot limits are calculated from the data, followed by set-up of the plot area. The plotting of various curves is then performed using the DISSPLA subroutines.

Appendix F
SPECIFICATION OF COMPONENTS

F.1 RESISTORS

Unless otherwise stated all resistors used are Corning, 1/2 Watt, 1%; all values are in ohms with k = 1000, M = 1,000,000.

R _{1a}	-	50 ohm
R _{1b}	-	150 ohm
R _{1c}	-	30 kohm
R _{1d}	-	1.0 Mohm
R _{1e}	-	1.0 Mohm
R _{1f}	-	50 ohm, <u>+10%</u> , 1/4 Watt
R ₂	-	1.0 kohm
R _{3a}	-	100 kohm
R _{3b}	-	100 kohm
R _{3c}	-	1 kohm pot, Bourns #3069P
R _{3d}	-	200 ohm
R _{4a}	-	10 kohm
R _{4b}	-	5.0 kohm
R _{4c}	-	2.5 kohm
R _{4d}	-	1.5 kohm

R _{4e}	-	500 ohm
R _{4f}	-	500 ohm
R _{4g}	-	402 kohm
R _{4h}	-	100 kohm
R _{4i}	-	51 ohm $\pm 5\%$, 1/4 Watt
R _{4j}	-	2.0 kohm
R _{4k}	-	10 kohm
R _{4l}	-	5.0 kohm
R _{5a}	-	500 ohm
R _{5b}	-	10 kohm, Bourns 7241B, 3610S-1 pot
R _{5c}	-	70 kohm
R _{6a}	-	1.0 Mohm
R _{6b}	-	100 kohm
R _{6c}	-	1.0 Mohm
R _{6d}	-	500 ohm, 1 kohm, 2 kohm, 5 kohm, 10 kohm, 20 kohm, 50 kohm, 100 kohm, 200 kohm, 500 kohm, 1 Mohm
R _{7a}	-	1.0 Mohm
R _{7b}	-	100 kohm
R _{7c}	-	1.0 Mohm
R _{8a}	-	50 kohm
R _{8b}	-	50 kohm
R _{8c}	-	50 kohm
R _{8d}	-	50 kohm
R _{8e}	-	2.0 Mohm
R _{9a}	-	200 ohm
R _{10a}	-	1.0 kohm

R _{10b}	-	5.0 kohm
R _{10c}	-	3.0 kohm
R _{10d}	-	3.0 kohm
R _{10e}	-	3.0 kohm
R _{11a}	-	300 ohm
R _{11b}	-	10 kohm, 20 kohm, 30 kohm, 50 kohm, 100 kohm, 150 kohm, 200 kohm, 250 kohm, 300 kohm, 500 kohm
R _{11c}	-	5.0 kohm
R _{12a}	-	2.0 kohm
R _{12b}	-	50 kohm
R _{12c}	-	50 ohm
R _{13a}	-	20 Mohm $\pm 5\%$, 1/4 Watt
R _{13b}	-	10 kohm
R _{13c}	-	50 ohm
R _{13d}	-	2.2 kohm
R _{14a}	-	100 ohm
R _{14b}	-	50 kohm
R _{14c}	-	50 kohm
R _{15a}	-	5.0 kohm
R _{15b}	-	100 kohm
R _{16a}	-	35 kohm
R _{16b}	-	25 kohm
R _{16c}	-	10 kohm pot, Bourns # 3069P
R _{16d}	-	100 kohm
R _{16e}	-	2.0 kohm
R _{17a}	-	200 ohm

R _{17b}	-	2.0 kohm
R _{17c}	-	2.0 kohm
R _{17d}	-	70 kohm
R _{17e}	-	70 kohm
R _{17f}	-	2.0 Mohm
R _{18a}	-	20 kohm
R _{18b}	-	5.0 kohm, 10 kohm, 20 kohm
R _{18c}	-	150 ohm
R _{20a}	-	2.2 kohm $\pm 10\%$, 1/4 Watt
R _{20b}	-	1.0 kohm $\pm 10\%$, 1/4 Watt
R _{20c}	-	1.0 kohm $\pm 10\%$, 1/4 Watt
R _{20d}	-	2.2 kohm $\pm 10\%$, 1/4 Watt
R _{21a}	-	100 kohm $\pm 5\%$, 1/4 Watt
R _{21b}	-	1.0 Mohm $\pm 5\%$, 1/4 Watt
R _{21c}	-	100 kohm $\pm 10\%$, 1/4 Watt
R _{21d}	-	15 kohm $\pm 10\%$, 1/4 Watt
R _{21e}	-	470 ohm $\pm 5\%$, 1/4 Watt
R _{21f}	-	1.0 kohm $\pm 10\%$, 1/4 Watt
R _{ph}	-	Clairex CLM 8200 photomodule

F.2 CAPACITORS

All capacitors, unless specified, are polystyrene, rated at 200V dc, and specified in μ Farads. $p = 1 \times 10^{-12}$.

C _{1a}	-	18 pF mica
C _{1b}	-	0.1 μ F Sprague Vitamin-Q, 100VDC
C _{1c}	-	0.1 μ F Sprague Vitamin-Q, 100VDC

C _{3a}	-	0.1μF PC-AM2-104
C _{4a}	-	10μF Jensen KTTE
C _{4b}	-	0.01μF Jensen KTTE
C _{4c}	-	0.1μF Jensen KTTE
C _{4d}	-	0.2μF Jensen KTTE
C _{4e}	-	1.0μF Jensen KTTE
C _{6a}	-	0.047μF mica, 200VDC
C _{6b}	-	0.039μF polystyrene
C _{7a}	-	0.047μF mica, 200VDC
C _{7b}	-	0.039μF polystyrene
C _{8a}	-	0.1μF PC-AM2-104
C _{8b}	-	0.1μF PC-AM2-104
C _{8c}	-	0.1μF PC-AM2-104
C _{8d}	-	0.1μF PC-AM2-104
C _{10a}	-	0.22μF, 200VDC TWKP3C224K
C _{11a}	-	12pF mica
C _{11b}	-	1.0μF PC-AM2-105, 200VDC
C _{13a}	-	1000pF, 2000pF, 5000pF, 10 000pF, 20 000pF
C _{14a}	-	4.0μF Sprague Vitamin-Q
C _{15a}	-	0.047μF mica
C _{17a}	-	1.0μF PC-AM2-105, 200VDC
C _{17b}	-	0.1μF PC-AM2-104, 200VDC
C _{20a}	-	0.22μF PC-AM2-224, 200VDC
C _{20b}	-	220pF polystyrene
C _{21a}	-	20pF polystyrene
C _{21b}	-	0.01μF Sprague Vitamin-Q

F.3 RC NETWORKS

- (RC)₁ - a. 50 kohm $\pm 1\%$ || 1 μ F
b. 100 kohm $\pm 1\%$ || 1 μ F
c. 100 kohm $\pm 1\%$ || 0.4 μ F
d. 301 kohm $\pm 1\%$ || 0.4 μ F
e. 500 kohm $\pm 1\%$ || 0.2 μ F
f. 1.0 Mohm $\pm 1\%$ || 0.2 μ F
g. 4.0 Mohm $\pm 1\%$ || 0.05 μ F

All above capacitors are Jensen polystyrene type KTTE, 200 WVDC.

- (RC)₁₀ - a. for 1 kHz - 500 kohm, 1500 pF
b. for 5 kHz - 300 kohm, 200 pF
c. for 10 kHz - 200 kohm, 100 pF
d. for 20 kHz - 150 kohm, 70 pF

All capacitors above are polystyrene, 600VDC.

- (RC)₁₁ - a. for 1 kHz - 1 kohm + 500 ohm trimmer, 0.15 μ F
b. for 5 kHz - 600ohm + 500ohm trimmer, 35000pF
c. for 10 kHz - 1 Kohm trimmer, 15,000 pF
d. for 20 kHz - 1 kohm trimmer, 4,700 pF

All resistors above are 1% Corning, trimmers are Bourns 3069P type and capacitors are polystyrene, 600VDC.

F.4 AMPLIFIERS

All amplifiers are of modular design, powered by +15V power supplies.

A-1	Analog Devices	# 48J
A-2	Analog devices	# 48J
A-3	Teledyne-Philbrick	# 1425-01
A-4	Teledyne-Philbrick	# 1021
A-5	Teledyne-Philbrick	# 1021
A-6	Analog Devices	# 43K
A-7	Analog Devices	# 43K
A-8	Analog Devices	# AD522BD
A-9	Teledyne-Philbrick	# 1425-01
A-10	Analog Devices	# 48J
A-11	Analog Devices	# 48J
A-12	Analog Devices	# 48J
A-13	Analog Devices	# 48J
A-14	Analog Devices	# AD521KD
A-15	Analog Devices	# 180K
A-16	GPS	# 801C
A-17	Analog Devices	# 148A
A-18	Teledyne-Philbrick	# 1026
A-19	Analog Devices	# 40J
A-20	Teledyne-Philbrick	# 1322
A-21	Teledyne-Philbrick	# 1322

F.5 OTHER MODULES

VR ₄	Analog Devices	# AD2702L voltage reference
VR ₆	Analog Devices	# AD580JH voltage reference
M ₁	Teledyne-Philbrick	# 4456 multiplier
OI ₂₁	Texas Instruments	MCT2 optical isolator
A/D ₁₇	Hewlett-Packard	2410B AC-ohms /DC converter for 2401C integrating DVM

F.6 SWITCHES

S _{1a}	-	SP12T	Centralab
S _{1b}	-	SPDT	Magnecraft # W103-MX-4 relay
S _{4a}	-	DP6T	Centralab PA-2002
S _{4b}	-	SPDT	Sigma # 72A03Z
S _{4c}	-	DP5T	Centralab PA-6002
S _{4d}	-	DP6T	Centralab PA-2002
S _{4e}	-	SPST	Radio Shack
S _{4f}	-	SPDT	Radio Shack
S _{4g}	-	SPDT	Radio Shack
S _{4h}	-	Moment.	Radio Shack
S _{7a}	-	SP12T	Centralab
S _{8a}	-	SP6T	Radio Shack
S _{10a}	-	DP6T	Centralab
S _{11a}	-	SP12T	Centralab
S _{12a}	-	DP5T	Centralab
S _{13a}	-	DP6T	Centralab

S _{18a}	-	SP6T	Radio Shack
S _a	-	4P6T	Centralab
S _{c1}	-	PDP-11/20 LPS-11 LKWD,	relay # 2
S _{c4}	-	PDP-11/20 LPS-11 LKWD,	relay # 1

F.7 TRANSFORMERS

T ₁	-	Pico # X-15100
T ₁₀	-	Pico # F-5793
T ₂₀	-	Miller, 262kHz

F.8 DIODES

D _{16a}	-	unspecified germanium diode
D _{20a}	-	ITT # G331-752A
D _{20b}	-	ITT # G331-752A
D _{20c}	-	ITT # G331-752A
D _{20d}	-	ITT # G331-752A
D _{ph}	-	Clairex # CLM 8200 photomodule

F.9 POWER SUPPLIES

3	-	Semiconductor Circuits Inc. SPS5920 200mA, <u>+15V</u> supplies
2	-	Analog Devices Inc. #902 100mA, <u>+15V</u> supplies

APPENDIX G PROGRAM INCPOL

```

;
;
        .title capacitance compensation
incpol          dec.10.1979

r0      =%0          ;register initialization
dec0     =%0          ;LED digit #1 counter
r1      =%1
dec1     =%1          ;LED digit #2 counter
r2      =%2
dec2     =%2          ;LED digit #3 counter
r3      =%3
dec3     =%3          ;LED digit #4 counter
r4      =%4
r5      =%5
sp       =%6
pc       =%7
pusr     =177554      ;address assignment -punch status reg.
pubuf    =pusr+2      ;punch buffer register
ksr      =pubuf+2     ;keyboard status register
kbuf     =ksr+2       ;keyboard buffer register
prsr     =kbuf+2      ;printer status register
prbuf    =prsr+2      ;printer buffer register
switch   =prbuf+2     ;assembly switch register
adsr     =170400      ;a/d status register
adbuf    =adsr+2      ;a/d buffer register
led       =adbuf+2    ;led display buffer
clock    =adbuf+2     ;clock status register
countr   =clock+2     ;clock buffer register
relay    =countr+2    ;relay status register
analog    =relay+4    ;digital output controlling relays
tpins    =176500      ;tape input status register
tpinb    =tpins+2     ;tape input buber register
tpouts   =tpinb+2     ;tape output status register
tpoutb   =tpouts+2    ;tape output buffer register
ps       =177776      ;process status register
kslot    =0           ;slot assignment
prslot   =1
tinslot  =5
toutslot =6
init     =1           ;direct assignments
reset    =2
restrt   =3
waitr    =4
read     =11
write    =12
cr       =15
lf       =12

```

```

tab      =11
space    =40
mitoa    =emt+15      ;integer to ascii conversion call
mjtoa    =emt+16      ;double word integer to ascii call
matoi    =emt+22      ;ascii to integer conversion call
matoo    =emt+24      ;ascii to octal conversion call
.page
;*****
;
; .asect
; . =1000                ;starting point
;*****
;
;
;
;////////////////////////
; unix subroutines
;////////////////////////
;
;
;
; .nlist ttm             ;printout on 132 columns, not 72
; .nlist me              ;do not list macro-expansions
; .list com              ;list comments
; .sbt1 initializations
; .page
; *****
;
;
;
;////////////////////////
; reserve space for inputs
;////////////////////////
;
;
;
; .nlist meb
points: 0                ;# of points
point2: 0                ;# of points-2 - start of cap. measurement (cl)
point5: 0                ;# of points-4 - start of cap. measurement (ch)
delay: 0                 ;delay time
limit: 0                 ;potential limit
blank2: 0                ;blank space - dumping of unwanted data
chane: 0                 ;potential channel #
chani: 0                 ;current channel #
chanc: 0                 ;capacitance channel #
choice: 0                ;next run choice
pot: 0                   ;set pot. channel # with adsr command
cur: 0                   ;set cur. channel # with adsr command
cap: 0                   ;set cap. channel # with adsr command
kcur: 0                  ;set calib. cur. channel # with adsr command
kpote: 0                 ;set calib. potchannel # with adsr command
ptsout: 0                ;store # of data points collected
ptcount: 0               ;# of points to be output
wylbur: 0                ;is the tape for wylbur or unix
fcount: 0                ;number of filling runs done
e: 0                     ;potential data - double precision
; . =.+5000.
il: 0                    ;current data - double precision

```

```

        .=.+5000.
cd:      0          ;capacity data - single precision
        .=.+5000.
kal:     0          ;capacity calibration data
        .=.+170.
tincod:  11         ;iox assignments-tape input
toutcod: 0          ;tape output or UNIX
drops:   0          ;# of drops at the same potential
where2:  0          ;optional jump to address input
filin:   0          ;optional 5-run filling set
blank:   0          ;blank space - storage for analog delay count
ptscal:  0          ;# of calibration points
        .page
        .sbttl  users i/o output buffers
;
;////////////////////////////////////////
;output buffers
;////////////////////////////////////////
;
mbuf0:   0
        0
mes0:    end0-mes0-2
        .byte   cr,lf,cr,lf,cr,lf
end0:    .even
mbuf00:  0
        0
mes00:   end00-mes00-2
        .byte   cr,lf
        .ascii  /this is  program  incpol /
        .byte   cr,lf
        .ascii  /last updated on dec.10.1979 /
        .byte   cr,lf
        .ascii  /for instructions see printout of program /
        .byte   cr,lf
end00:   .even
mbuf0a:  0
        0
mes0a:   end0a-mes0a-2
        .ascii  /output on paper tape ? /
end0a:   .even
mbuf1:   0
        0
mes1:    end1-mes1-2
        .byte   cr,lf,cr,lf,cr,lf
        .ascii  /# of points:/
        .byte   tab,tab
end1:    .even
mbuf2:   0
        0
mes2:    end2-mes2-2
        .ascii  /delay time: /
        .byte   tab,tab
end2:    .even
mbuf3:   0

```

```
0
mes3:  end3-mes3-2
      .ascii  /potential at the end:  /
end3:  .even
mbuf4: 0
0
mes4:  end4-mes4-2
      .ascii  /potential channel #: /
      .byte   tab
end4:  .even
mbuf5: 0
0
mes5:  end5-mes5-2
      .ascii  /current channel #: /
      .byte   tab
end5:  .even
mbuf6: 0
0
mes6:  end6-mes6-2
      .ascii  /capacitance channel #: /
end6:  .even
mbuf7: 0
0
mes7:  end7-mes7-2
      .ascii  /    date: /
      .byte   tab,tab
end7:  .even
mbuf8: 0
0
mes8:  end8-mes8-2
      .ascii  /    run# /
      .byte   tab,tab
end8:  .even
mbuf9: 0
0
mes9:  end9-mes9-2
      .ascii  /    sample:  /
      .byte   tab,tab
end9:  .even
mbuf10: 0
0
mes10: end10-mes10-2
      .ascii  /    ir= /
      .byte   tab,tab
end10: .even
mbuf11: 0
0
mes11: end11-mes11-2
      .byte   cr,lf
      .ascii  /get ready for calibration,set potential /
      .byte   cr,lf
      .ascii  /hit continue when ready. /
      .byte   cr,lf
end11: .even
```



```
mbufa11:0
0
mes11a: end11a-mes11a-2
        .byte    cr,lf
        .ascii   /change to DME assembly, zero & enable voltage stepper /
        .byte    cr,lf
end11a: .even
mbuf12: 0
0
mes12:  end12-mes12-2
        .ascii   /when ready : hit continue /
        .byte    cr,lf
end12:  .even
mbuf13: 0
0
mes13:  end13-mes13-2
        .byte    cr,lf
        .ascii   /if you want to run... /
        .byte    cr,lf
        .ascii   /with new parameters type in - "0" /
        .byte    cr,lf
        .ascii   /with the same parameters type in - "1" /
        .byte    cr,lf
        .ascii   /if communication is not working save data /
        .byte    cr,lf
        .ascii   /on paper tape - type in - "2" /
        .byte    cr,lf
        .ascii   /if you want to logoff from unix type "3" /
        .byte    cr,lf
        .ascii   /to jump to any location to be input on tty type "4" /
        .byte    cr,lf
        .ascii   /where to ? /
        .byte    tab,tab
end13:  .even
mbuf14: 0
0
mes14:  end14-mes14-2
        .ascii   /when output finished turn punch off.../
        .byte    cr,lf
        .ascii   /(if on) and hit continue /
        .byte    cr,lf
end14:  .even
mbufb14:0
0
mes14a: end14a-mes14a-2
        .ascii   /ready to output data, hit continue when ready /
        .byte    cr,lf
end14a: .even
mbuf15: 0
0
mes15:  end15-mes15-2
        .byte    cr,lf
        .ascii   /put punch on /
        .byte    cr,lf
```

```
end15: .even
mbuf16: 0
0
mes16: end16-mes16-2
      .byte   cr,lf
      .ascii  /          e          i          ol          ch /
      .byte   cr,lf
      .ascii  /-----/
      .byte   cr,lf
end16: .even
mbuf17: 0
0
mes17: end17-mes17-2
      .byte   cr,lf
      .ascii  /input address of the next instruction /
      .byte   cr,lf
end17: .even
mbuf18: 0
0
mes18: end18-mes18-2
      .ascii  /calibration yes or no /
end18: .even
mbuf19: 0
0
mes19: end19-mes19-2
      .ascii  /is this tape for wylbur ? /
end19: .even
mbuf20: 0
      ;errors
0
mes20: end20-mes20-2
      .byte   cr,lf,cr,lf
      .ascii  / *****error.....error+++++error:::error,,,,,error--/
      .byte   cr,lf,cr,lf
end20: .even
mbuf21: 0
0
mes21: end21-mes21-2
      .ascii  /calibration voltage: /
      .byte   tab
end21: .even
mbuf22: 0
0
mes22: end22-mes22-2
      .ascii  /dummy cell resistor: /
      .byte   tab
end22: .even
mbuf23: 0
0
mes23: end23-mes23-2
      .ascii  /how many filling runs /
      .byte   tab
end23: .even
mbuf24: 0
0
```

```

mes24:  end24-mes24-2
        .byte    cr,lf
        .ascii   /set potential - hit continue when ready /
        .byte    cr,lf
end24:  .even
mbuf25: 0
        0
mes25:  end25-mes25-2
        .ascii   /drops at one potential :/
end25:  .even
mbuf26: 0
        0
mes26:  end26-mes26-2
        .ascii   /capacitance: /
        .byte    tab
end26:  .even
mbuf27: 0
        0
mes27:  end27-mes27-2
        .ascii   /there must be a minimum of 6 points ! ! ! /
        .byte    cr,lf
        .ascii   /# of points:/
        .byte    tab,tab
end27:  .even
        .page
        .sbttl   users i/o input buffers
;
;////////////////////////////////////////
;input buffers
;////////////////////////////////////////
;
devbuf: 2                ;UNIX, tape or paper-tape ?
        0
        0
dev1:   .=-.+2
ptbuf:  20                ;# of points
        0
ptcnt:  0
point1: .=-.+20
delbuf: 20                ;delay time
        0
        0
delay1: .=-.+20
limbuf: 20                ;potential limit
        0
        0
limit1: .=-.+20
chanebuf:10              ;potential channel
        0
        0
chane1: .=-.+10
chanibuf:10              ;current channel
        0
chicnt: 0

```

```

chan1: .=.+10
chanbuf: 10          ;capacitance channel
0
chcnt: 0
chanc1: .=.+10
datbuf: 20          ;date
0
datcnt: 20
date1: .=.+20
runbuf: 10          ;run #
0
runcnt: 10
run1: .=.+10
sambuf: 40          ;sample name
0
sament: 40
sample1: .=.+40
irbuf: 10           ;instrum. resistor value
0
ircnt: 10
ir1: .=.+10
outbuf: 100         ;output data storage
0
100
data: .=.+100
ptcnbf: 4           ;wylbur or unix tape option
0
0
ptcn1: .=.+4
endbuf: 10          ;end statement, -1 to show end of data
0
endcnt: 6
ends: 26440
20061
5015
chbuf: 10           ;next run choice
0
10
choic1: .=.+10
whereb: 10          ;optional input address
0
10
where1: .=.+10
calbuf: 6           ;calibration option
0
calcnt: 6
calib1: .=.+6
volcal: 20          ;calibration voltage
0
volcnt: 0
vcal: .=.+20
rdummy: 20          ;calibration resistor
0
dument: 0

```

```

dummy:  .=.+20
filbuf: 6                ;filling option
        0
filcnt: 6
filin1:  .=.+6
drpbuf: 4                ;# of points at the same potential
        0
drpcnt: 4
drop1:  .=.+4
capcal: 10               ;calibration capacitance
        0
capcnt: 0
cpcal:  .=.+10
kalbuf: 12               ;calibration curve for capacitance
        0
kalcnt: 12
kalib1:  .=.+12
        .page
        .sbttl  users subroutines
;
;////////////////////////////////////////
;data conversion and display subroutine
;////////////////////////////////////////
;
subconv:mov    r0,-(sp)    ;save registers on stack
        mov    r1,-(sp)
        mov    r2,-(sp)
        mov    r3,-(sp)
        mov    #1400,dec3  ;digit #4 (highest)
        mov    #1000,dec2  ;digit #3
        mov    #400,dec1   ;digit #2
        clr    dec0        ;digit #1 (lowest)
        asr    r4          ;divide potential count by 2
conv1:  cmp    r4,#1750     ;is potential over 1V ?
        bmi    conv2       ;if not go lower
        sub    #1750,r4     ;if yes subtract 1V and...
        inc    dec3        ;add 1 to digit #4
        br     conv1       ;see if potential is still over 1V
conv2:  cmp    r4,#144      ;is potential over 100mV ?
        bmi    conv3       ;if not go lower
        sub    #144,r4     ;if yes subtract 100mV and...
        inc    dec2        ;add 1 to digit #3
        br     conv2       ;see if it is still over 100mV
conv3:  cmp    r4,#12       ;is potential over 10mV
        bmi    conv4       ;if not go lower
        sub    #12,r4     ;if yes subtract 10mV and...
        inc    dec1        ;add 1 to digit #2
        br     conv3       ;see if it is still over 10mV
conv4:  cmp    r4,#1        ;is potential over 1mV?
        bmi    conv5       ;if not display values
        dec    r4          ;if yes subtract 1mV and ...
        inc    dec0        ;add 1 to digit #1
        br     conv4       ;see if it is still over 1mV
conv5:  mov    dec0,led     ;display digit #1

```

```

        mov     dec1,led      ;display digit #2
        mov     dec2,led      ;display digit #3
        mov     dec3,led      ;display digit #4
        mov     (sp)+,r3      ;restore registers from stack
        mov     (sp)+,r2
        mov     (sp)+,r1
        mov     (sp)+,r0
        rts      r5           ;return to main program
;
;/////////////////////////////////////////
;  reinitialize IOX subroutine
;/////////////////////////////////////////
;
recaliox:cmp     mode,#user    ;is system in user mode ?
        bne     jcalin        ;if not, go to jcalin to reinitialize
        mov     #I.KBDIR,60    ;reinitialize IOX after UNIX call
        mov     #200,62
        mov     #I.TTYIR,64
        mov     #200,66
        iot
        .word    0
        .byte    reset,0
        iot
        whereto
        .byte    restrt,0
        iot
        mbuf0
w0aa:     .byte    write,prslot
        iot
        w0aa
        .byte    waitr,prslot
        rts      r5           ;return
jcalin:  call    initialize    ;reinitialize
        br       recaliox     ;and try again
;
;/////////////////////////////////////////
;  check mode
;/////////////////////////////////////////
;
ckmode:  cmp     mode,#transfer ;check if mode is set for transfer
        beq     endck         ;if yes, return
        jmp     whereto       ;if not,go to "whereto" routine
endck:   rts      pc           ;return
;
;/////////////////////////////////////////
;  error recovery routine
;/////////////////////////////////////////
;
error:   jsr     r5,recaliox    ;rinitialize iox
        iot                ;write -"error..."
        mbuf20
        .byte    write,prslot
we:      iot
        we
```

```

        .byte   waitr,prslot
        jmp     whereto           ;go to input next address
;
;////////////////////////////////////
;  output subroutine
;////////////////////////////////////
;
outdata:iot
        outdata
        .byte   waitr,toutslot
        iot                                ;print out converted data
        outbuf
        .byte   write,toutslot
w25:    iot
        w25
        .byte   waitr,toutslot
        rts     r5                 ;return
;
        .page
        .sbt1   main program
;
;////////////////////////////////////
;  starting point of the program
;////////////////////////////////////
;
begin:  iot                                ;iox initialization
        .word   0
        .byte   reset,0
        iot
        whereto
        .byte   restrt,0
        iot
        mbuf0
        .byte   write,prslot
w0:     iot
        w0
        .byte   waitr,prslot
        iot                                ;write - "testpol, updated..."
        mbuf00
        .byte   write,prslot
w00:    iot
        w00
        .byte   waitr,prslot
        mov     #M.EMT,30           ;emt innitialization
        mov     #340,32
;
;////////////////////////////////////
;new data starting point
;////////////////////////////////////
;
gonew:  clr     r0
        mov     #137400,sp          ;stack address assignment
        clr     toutcod
        clr     filin

```

```

        iot                                ;write - "# of points"
        mbuf1
w1:      .byte    write,prslot
        iot
        w1
        .byte    waitr,prslot
        iot                                ;get - # of points
        ptbuf
w2:      .byte    read,kslot
        iot
        w2
        .byte    waitr,kslot
        matoi
        cmp      point1,points            ;
        cmp      points,#6                ;ascii to integer conversions-# of pts.
        bge      w14a                     ;is number larger than 6 ?
back:    iot                                ;if yes, continue
        mbuf27                             ;if not, write -
        .byte    write,prslot              ;"there must be minimum of 6 points"
w14b:    iot
        w14b
        .byte    waitr,prslot
        iot                                ;read in "new # of points"
        ptbuf
w14bb:   .byte    read,kslot
        iot
        w14bb
        .byte    waitr,kslot
        matoi                             ;ascii to integer conv -# of points
        cmp      point1,points
        cmp      points,#6                ;is number larger than 6 ?
        blt      back                     ;if yes, go back
w14a:    iot                                ;write -"drops at one potential"
        mbuf25
w2a:     .byte    write,prslot
        iot
        w2a
        .byte    waitr,prslot
        iot                                ;read in # of drops at one pot.
        drpbuf
w2b:     .byte    read,kslot
        iot
        w2b
        .byte    waitr,kslot
        iot                                ;write - "delay time"
        mbuf2
w3:      .byte    write,prslot
        iot
        w3
        .byte    waitr,prslot
        iot                                ;get - delay time
        delbuf
w4:      .byte    read,kslot
        iot

```



```
w4
.byte   waitr,kslot
iot      ;write - "paper tape output ?"
mbuf0a
w0a:
.byte   write,prslot
iot
w0a
.byte   waitr,prslot
iot      ;read in the choice of output
devbuf
w0b:
.byte   read,kslot
iot
w0b
.byte   waitr,kslot
iot      ;write - "potential channel"
mbuf4
w7:
.byte   write,prslot
iot
w7
.byte   waitr,prslot
iot      ;get - potential channel
chanobuf
w8:
.byte   read,kslot
iot
w8
.byte   waitr,kslot
iot      ;write - "current channel"
mbuf5
w9:
.byte   write,prslot
iot
w9
.byte   waitr,prslot
iot      ;get - current channel
chanibuf
w10:
.byte   read,kslot
iot
w10
.byte   waitr,kslot
iot      ;write - "capacity channel"
mbuf6
w9a:
.byte   write,prslot
iot
w9a
.byte   waitr,prslot
iot      ;read - capacity channel
chanobuf
w9b:
.byte   read,kslot
iot
w9b
.byte   waitr,kslot
iot      ;write - "date:"
mbuf7
w13:
.byte   write,prslot
iot
```

```

w13
.byte waitr,prslot
iot          ;read - date
datbuf
.byte read,kslot
w14: iot
w14
.byte waitr,kslot
goold: clr r1
matoi
cmp drop1,drops ;ascii to integer conversion -
matoi          ;# of drops at each potential.
cmp delay1,delay ;ascii to integer conv. - delay time
neg delay      ;make delay time negative
matoi          ;ascii to integer convs. - pot. chan.
cmp chane1,chane
matoi          ;ascii to integer conv. - current chan.
cmp chani1,chani
matoi          ;ascii to integer conv. - capacity chan.
cmp chanc1,chanc
mov #400,r0     ;move immediate adsr start to r0
add chane,r0   ;add channel # for potential
swab r0        ;swap bytes in r0
mov r0,pot     ;sample potential channel
mov #20000,r0  ;move - start adsr with clock to r0
add chani,r0   ;add channel # for current
swab r0        ;swap bytes in r0
mov r0,cur     ;sample current channel with clock
mov #400,r0    ;move immediate adsr start to r0
add chanc,r0   ;add channel # for capacity
swab r0        ;swap bytes in r0
mov r0,cap     ;sample capacity channel
mov #400,r0    ;move start adsr immediately to r0
add chani,r0   ;add current channel #
swab r0        ;swap bytes in r0
mov r0,kcur    ;sample current channel
mov #20000,r0  ;move - start adsr with clock to r0
add chane,r0   ;add potential channel #
swab r0        ;swap bytes in r0
mov r0,kpot    ;sample potential channel with clock
;
;////////////////////////////////////
;starting point with old parameters
;////////////////////////////////////
;
clr r2
clr r3
clr r4
clr r5
clr countr
clr adbuf
clr pubuf
clr prbuf
clr ptscal

```

```

mov    #177767,analog    ;close reset relays
clr    filin
bic    #177600,dev1      ;mask upper byte of device choice
cmp    dev1,#131         ;was tape chosen ?
bne    cont              ;if no, skip ahead
mov    #4,toutcod        ;if yes, set code for paper tape punch
iot    ;initialize tape input
.word   tincod
.byte   init,tinslot
iot    ;initialize data output device
.word   toutcod
.byte   init,toutslot
cont:  bic    #100000,runbuf+2    ;enable run # storage
      bic    #100000,sambuf+2    ;enable sample name storage
      bic    #100000,irbuf+2     ;enable instr. resistor storage
      iot    ;write - "run #"
      mbuf8
w15:   .byte   write,prslot
      iot
      w15
      .byte   waitr,prslot
      iot    ;get - run #
      runbuf
w16:   .byte   read,kslot
      iot
      w16
      .byte   waitr,kslot
      iot    ;write - "sample:"
      mbuf9
w17:   .byte   write,prslot
      iot
      w17
      .byte   waitr,prslot
      iot    ;read - sample name
      sambuf
w18:   .byte   read,kslot
      iot
      w18
      .byte   waitr,kslot
      iot    ;write - "ir="
      mbuf10
w19:   .byte   write,prslot
      iot
      w19
      .byte   waitr,prslot
      iot    ;get - ir
      irbuf
w20:   .byte   read,kslot
      iot
      w20
      .byte   waitr,kslot
      iot    ;write - "potential at the end"
      mbuf3
      .byte   write,prslot

```

```

w5:    iot
        w5
        .byte    waitr,prslot
        iot                ;get - potential limit
        limbuf
        .byte    read,kslot
w6:    iot
        w6
        .byte    waitr,kslot
        iot                ;write -"how many filling runs?"
        mbuf23
        .byte    write,prslot
w6a:   iot
        w6a
        .byte    waitr,prslot
        iot                ;read in filling option
        filbuf
        .byte    read,kslot
w6b:   iot
        w6b
        .byte    waitr,kslot
        matoi                ;ascii to int. conv. - # of fillings
        cmp      filin1,filin
        mov      filin,fcoun
        inc      fcoun
        iot                ;set counter for # of fillings
        mbuf18                ;true # of filling runs
        .byte    write,prslot
        matoi                ;calibration ?
        cmp      limit1,limit
        asl      limit        ;ascii to int. conv. - potential limit
        iot                ;multiply limit by 2
w20a:  iot
        w20a
        .byte    waitr,prslot
        iot                ;get answer on calibration option
        calbuf
        .byte    read,kslot
w20b:  iot
        w20b
        .byte    waitr,kslot
        mov      #e,r0
        mov      #tincod,r1
        set1:  clr      (r0)+
        cmp      r0,r1
        bne      set1
        cmp      calib1,#47516
        beq      nocall
        iot                ;clear area for data
        mbuf21                ;need calibration ?
        .byte    write,prslot
        iot                ;if no skip calibration
        w20e:  iot                ;calibration voltage
        w20e
        .byte    waitr,prslot
        iot                ;read in calibration voltage

```

```

        volcal
        .byte  read,kslot
w20f:   iot
        w20f
        .byte  waitr,kslot
        iot                    ;dummy resistor value
        mbuf22
        .byte  write,prslot
w20g:   iot
        w20g
        .byte  waitr,prslot
        iot                    ;read in dummy resistor value
        rdummy
        .byte  read,kslot
w20h:   iot
        w20h
        .byte  waitr,kslot
        iot                    ;write - "get ready for calibration..."
        mbuf11                  ;...set potential ...
        .byte  write,prslot      ;...hit continue when ready"
w21:    iot
        w21
        .byte  waitr,prslot
        halt
;
;////////////////////////////////////
;calibration section
;////////////////////////////////////
;
        mov     #kal,r2          ;address for calibration data storage
        clr     r3
loop1:   iot                    ;write -"capacitance:"
        mbuf26
        .byte  write,prslot
w20ff:   iot
        w20ff
        .byte  waitr,prslot
        iot                    ;read in calibration capacity
        cpcal
        .byte  read,kslot
w20fff:  iot
        w20fff
        .byte  waitr,kslot
        cmp     cpcal,#5015      ;end of calibration ?
        beq     endcal           ;if yes, go to "endcal"
        mov     points,r5        ;points counter
        mov     #-1000.,countr   ;clock counter
        mov     #403,clock       ;1ms time interval - repeated
loop2:   mov     kpot,adsr        ;measure current
done1:   tstb    adsr             ;check a/d - ready ?
        bpl     done1            ;if not wait
        add     adbuf,(r2)+       ;store current calibration data
        adc     (r2)+             ;store second word of curr.cal.data
        mov     kcur,adsr        ;measure potential

```

```

done2:  tstb    adsr                ;check a/d - ready ?
        bpl     done2              ;if not wait
        add     adbuf,(r2)+        ;store potential calibration data
        adc     (r2)+              ;store second word of pot.cal.data
        cmp     r5,#5              ;5 points to go ?
        bgt     cnt3              ;if no, skip capacity measurement
        mov     cap,adsr          ;measure capacity
done2a:  tstb    adsr                ;check a/d ready ?
        bpl     done2a            ;if not wait
        add     adbuf,(r2)        ;store capacity calibration data
cnt3:    cmp     -(r2),-(r2)        ;prepare for next calibration point
        cmp     -(r2),-(r2)        ;
        dec     r5                ;subtract 1 from # of pts. to be taken
        bne     loop2            ;enough points ? if not continue
        mov     #cpcal,r1        ;point to cal. value input on tty
        add     #12,r2            ;prepare for next data
        mov     (r1)+,(r2)+      ;move calibration value...
        mov     (r1)+,(r2)+      ;...fo capacity as input...
        mov     (r1)+,(r2)+      ;...on teletype.
        clr     clock            ;stop clock
        mov     #-10000.,count    ;set clock for 10ms
        mov     #3,clock         ;start clock at 1mhz
check1:  tstb    clock            ;delay finished ?
        bpl     check1           ;if not wait
        inc     r3               ;did you go 5 times ?
        br      loop1           ;if not go again
endcal:  mov     r3,ptscal        ;store # of calibration points
nocal:   mov     #e,r1           ;potential - data pointer
        mov     #i1,r2          ;current - data pointer
        mov     #cd,r0          ;capacity - data pointer
        clr     r3
        clr     r4
        mov     #1,ptsout        ;# of points taken - no calibration
        mov     #000001,relay    ;turn on 250khz
        iot                     ;write - "change to DME assembly..."
        mbufa11
w21a:    .byte   write,prslot
        iot
        w21a
        .byte   waitr,prslot
        iot                    ;write - "when ready hit continue "
        mbuf12
w22:     .byte   write,prslot
        iot
        w22
        .byte   waitr,prslot
        add     #4,points        ;add 4- cap. taken before & after e & i
        mov     points,point2    ;place to start cur. and pot. sample
        sub     #2,point2        ;
        mov     points,point5    ;place to start high cap. data taking
        sub     #4,point5        ;
        halt
;
;////////////////////////////////////

```

```

;collection of data
;////////////////////////////////////
;
start:  mov     drops,r3          ;sample x drops at the same potential
start2: mov     points,r5        ;# of points to be sampled
      clr      blank
      mov      #000001,relay    ;turn off potential step relay (#2)
                                   ;keep 250khz on.
      mov      delay,countr     ;set delay time to the input value
                                   ;(number should be + decimal integer)
      mov      #20006,clock     ;set clock sr for single mode at 10khz,
                                   ;triggered by st1
trig:   tst     clock           ;check if st1 fired
      bpl      trig            ;if not wait
      clr      relay           ;turn ac signal off (relay #1)
      bic      #10,analog      ;reset integrator
up:     inc     blank           ;count up to 177777
      bne      up              ;finished ? if no go back
      bis      #10,analog      ;open reset relay of integrator
check2: tstb    clock           ;check if delay time is over
      bpl      check2          ;if not wait
      mov      #-1000.,countr  ;sample every msecond
      mov      #403,clock      ;set clock to sample at 1 ms intervals
      bic      #1,analog       ;start analog sampling
loop:   mov     cur,adrsr       ;start a/d current convs. with clock
done3:  tstb    adrsr           ;check if a/d completed
      bpl      done3           ;if not done wait
      cmp      r5,point2       ;third data point ?
      bgt      skip1           ;if no,don't store this point
      cmp      r5,#3           ;two more points to go ?
      bmi      skip1           ;if no, don't store this point
      add      adbuf,(r2)+      ;store current data
      adc      (r2)             ;add carry to upper portion of 1
      tst      -(r2)           ;get ready for next current reading
      br       skip3
skip1:  mov     adbuf,blank2     ;discard this point
skip3:  mov     pot,adrsr       ;sample potential
done4:  tstb    adrsr           ;check a/d, completed ?
      bpl      done4           ;if not wait
      cmp      r5,point2       ;is this third point ?
      bgt      skip2           ;if no, don't store this point
      cmp      r5,#3           ;two more points to go ?
      bmi      skip2           ;if no, don't store this point
      mov      adbuf,r4        ;data to be tested for pot. limit
      add      r4,(r1)+        ;store potential data
      adc      (r1)            ;store carry to upper portion of e
      tst      -(r1)           ;get ready for next potential data
      br       skip4
skip2:  mov     adbuf,blank2     ;discard this point
skip4:  mov     cap,adrsr       ;sample capacity
done3a: tstb    adrsr           ;check if a/d completed
      bpl      done3a          ;if not wait
      cmp      r5,point5       ;one of first 5 points ?
      bge      cnt1            ;if yes store this point

```

```

        cmp     r5,#5           ;last 5 points ?
        bgt     cnt2           ;if yes store this point
        cmp     r5,#5           ;fifth point from end ?
        bne     cnt1           ;if no store the point
        tst     (r0)+          ;if yes, store it in next location
cnt1:    add     adbuf,(r0)      ;
        br      cnt4
jstrt2: jmp     start2         ;needed to extend reach of branch
cnt2:    mov     adbuf,blank2   ;discard this point
cnt4:    dec     r5            ;update counter
        bne     loop          ;check whether sampling complete
                                ;if not go again
                                ;end analog sampling
                                ;stop clock
        bis     #1,analog      ;after sampling delay of 5ms
        clr     clock          ;start 5ms delay
        mov     #-5000.,countr ;get ready for next current data
        mov     #3,clock       ;get ready for next potential data
        cmp     (r2)+,(r2)+    ;get ready for next capacity data
        cmp     (r1)+,(r1)+
        tst     (r0)+
check3:  tstb    clock          ;is delay over ?
        bpl     check3        ;if not wait
        bic     #2,analog      ;get incremental value
        mov     #-200.,countr  ;set counter for 200ms
        mov     #11,clock
                                ;
        inc     ptsout         ;# of points taken
ok1:    tstb    clock          ;is time up for analog increments ?
        bpl     ok1           ;if not, wait
        bis     #2,analog      ;if yes,open analog increments relay
        dec     r3             ;# of points to be taken at given pot.
        bne     jstrt2        ;if more needed,go get it
        cmp     r4,limit       ;check if limit is reached
        bpl     check7        ;if yes see where to go next
        mov     #000400,relay  ;turn on step potential
        mov     #-500.,countr  ;set delay time for
        mov     #7,clock       ;stepping voltage
        jsr     r5,subconv     ;dislpay potential on LED's
check4:  tstb    clock          ;is time over?
        bpl     check4        ;if not wait
        jmp     start          ;if yes go again
check7:  bit     #7,filin      ;is this a set of filling runs?
        beq     out            ;if not, start output
        dec     fcount         ;if yes, is this 5th. run ?
        beq     out            ;if yes, start output
        mov     #-1.,(r1)+    ;if not, mark end of run by "-1"
        iot                     ;write - "set potential,...
        mbuf24                  ;...hit continue when ready"
        .byte   write,prslot
w21b:    iot
        w21b
        .byte   waitr,prslot
        halt
        jmp     start          ;take next run
out:     iot                    ;write -"ready to output data,hit cont."
        mbufb14

```



```

        .byte    write,prslot
w22a:   iot
        w22a
        .byte    waitr,prslot
        cmp      #4,toutcod      ;is this output on paper tape ?
        beq      tape            ;if yes, skip next output
        iot      ;write -"when output finished..."
        mbuf14
        .byte    write,prslot
w22b:   iot
        w22b
        .byte    waitr,prslot
tape:   nop
        halt
        cmp      #4,toutcod      ;is this output on paper tape ?
        bne      out1            ;if not go to standard output
emer:   jmp      emc              ;if yes jump to paper tape output
junx1:  jmp      unx1             ;extension of branch reach
        .page
        .sbttl   users data output
;
;////////////////////////////////////
;output data
;////////////////////////////////////
;
out1:   mov      ptsout,ptcount    ;# of points to be output
        cmp      #4,toutcod      ;is this output on paper tape ?
        bne      junx1            ;if no, go to unix output routine
        iot      ;write date
        datbuf
        .byte    write,toutslot
w27:    iot
        w27
        .byte    waitr,toutslot
        iot      ;write run #
        runbuf
        .byte    write,toutslot
w28:    iot
        w28
        .byte    waitr,toutslot
        iot      ;write sample name
        sambuf
        .byte    write,toutslot
w29:    iot
        w29
        .byte    waitr,toutslot
        iot      ;write value for ir
        irbuf
        .byte    write,toutslot
w23:    iot
        w23
        .byte    waitr,toutslot
        iot      ;write # of points taken
        ptbuf

```

```

w23a:  .byte  write,toutslot
       iot
       w23a
       .byte  waitr,toutslot
       iot                                ;write value of current channel
       chanibuf
w24:    .byte  write,toutslot
       iot
       w24
       .byte  waitr,toutslot
       iot                                ;write value of calib. voltage
       volcal
w24a:   .byte  write,toutslot
       iot
       w24a
       .byte  waitr,toutslot
       iot                                ;write value of dummy resistor
       rdummy
w24b:   .byte  write,toutslot
       iot
       w24b
       .byte  waitr,toutslot
       iot                                ;write # of points at potential
       drpbuf
w24c:   .byte  write,toutslot
       iot
       w24c
       .byte  waitr,toutslot
       mov    #ptscal,r4                ;# of calibration points
       mov    #kalib1,r1                ;address of cap. data output buffer
       mov    #subconv,r2              ;address of subconv subroutine
set4:   clr    (r1)+                    ;clear area for # of cap. data points
       cmp    r1,r2                    ;finished ?
       bne    set4                    ;if not, continue
       mitoa
       cmp    (r4),kalib1              ;# of calib. data points
       bis    #20000,kalib1+6          ;" "
       bis    #5015,kalib1+10         ;"cr,lf"
       iot                                ;output # of calibration data points
       kalbuf
w24d:   .byte  write,toutslot
       iot
       w24d
       .byte  waitr,toutslot
outcal: mov    #kal,r3                  ;address of calib. data storage
       mov    ptscal,r4                ;# of calibration points
filcal: dec    r4                      ;was this the last point ?
       bmi    out10                    ;if yes, go to next step
       mov    #data,r1                 ;clear area for calibration data
       mov    #endbuf,r2
set3:   clr    (r1)+
       cmp    r1,r2
       bne    set3
       bis    #20040,data              ;" "

```

```

bis      #20040,data+16 ;" "
bis      #20040,data+34 ;" "
bis      #20040,data+36 ;" "
bis      #20040,data+40 ;" "
bis      #20040,data+42 ;" "
bis      #20040,data+52 ;" "
mjtoa    ;dw integer to ascii conversion
cmp      (r3),data+2    ;"calibration potential"
cmp      (r3)+,(r3)+    ;get ready for next point
mjtoa    ;dw integer to ascii conversion
cmp      (r3),data+20    ;"calibration current"
cmp      (r3)+,(r3)+    ;get ready for next point
mitoa    ;integer to ascii conversion
cmp      (r3),data+44    ;"calibration capacity"
tst      (r3)+          ;get ready for next point
bis      #20075,data+54  ;" ="
mov      (r3)+,data+56   ;capacity value input on tty
mov      (r3)+,data+60   ;
mov      (r3)+,data+62   ;
bis      #20000,data+62  ;" "
cmp      #4,toutcod      ;paper tape output ?
bne      junx3           ;if no, go to unix output
jsr      r5,outdata      ;if yes, go to paper-tape output
br       filcal          ;go again
junx3:   jmp      unx3    ;extension of branch instruction
out10:   mov      #e,r3    ;move adress of potential to r3
mov      #i1,r4          ;move adress of current to r4
mov      #cd,r5          ;move address of capacity to r0
output:  mov      #data,r1 ;
mov      #endbuf,r2      ;clear area for converted
set2:    clr      (r1)+    ;output data
cmp      r1,r2           ;
bne      set2           ;
cmp      (r3),#-1.       ;is this end of one run ?
bne      filnxt          ;if no, put data into output buffer
tst      (r3)+          ;if yes, skip this marker...
jmp      filend          ;...and go for data from next filling
filnxt:  bis      #20040,data ;output buffer loading - " "
bis      #20040,data+16 ;" "
bis      #20040,data+34 ;" "
bis      #20040,data+36 ;" "
bis      #20040,data+40 ;" "
bis      #20040,data+42 ;" "
bis      #20040,data+52 ;" "
bis      #20040,data+54 ;" "
bis      #20040,data+56 ;" "
bis      #20040,data+60 ;" "
bis      #20040,data+70 ;" "
bis      #5015,data+72 ;"cr,lf"
tst      wylbur          ;is this output for wylbur ?
beq      wjump           ;if no, skip this portion
bis      #11451,data+72 ;"cr,^s"
bis      #12,data+74      ;"lf"
wjump:   mjtoa          ;dw integer to ascii conv.

```

```

    cmp      (r3),data+2      ;"potential data"
    mjttoa   ;dw integer to ascii conv.
    cmp      (r4),data+20     ;"current data"
    mitoa    ;dw integer to ascii conv.
    cmp      (r5),data+44     ;"capacity data-low"
    tst      (r5)+            ;get ready for next capacity data
    mitoa    ;integer to ascii conversion
    cmp      (r5),data+62     ;"capacity data-high"
    cmp      (r3)+,(r3)+      ;get ready for next potential data
    cmp      (r4)+,(r4)+      ;get ready for next current data
    tst      (r5)+            ;get ready for next capacity data
    cmp      #4,toutcod       ;is this paper tape output ?
    bne      junx2            ;if no, go to unix output
    jsr      r5,outdata       ;if yes, go to paper tape output
    dec      ptcoun          ;points outputted counter
    cmp      ptcoun,#1        ;more points ?
    bne      output          ;if yes go again
    iot      ;write "-1" for end of data
    endbuf
w26:  .byte   write,toutslot
      iot
      w26
      .byte   waitr,toutslot
      iot      ;write calibration - "yes" or "no"
      calbuf
w22c: .byte   write,toutslot
      iot
      w22c
      .byte   waitr,toutslot
      cmp      #4,toutcod      ;is this for paper tape ?
      bne      end100          ;if not ring bell
      clr      r0
trail: mov      #0,prbuf        ;punch trailer
check5: tstb    prsr           ;printer ready for next character ?
      bpl      check5          ;if not, wait
      inc      r0              ;if yes update counter
      cmp      #50,r0          ;do we have 50 ?
      bpl      trail           ;if not go again
      clr      wylbur          ;back to unix mode
      clr      toutcod         ;clear tape mode
end100: mov      #207,prbuf     ;ring bell
      halt
junx2: jmp      unx2            ;extension of branch instruction
;
;////////////////////////////////////
;run finished - time to make decision for next run
;////////////////////////////////////
;
again: iot      ;write - "if you want to run ..."
      mbuf13
      .byte   write,prslot
w30:  iot
      w30
      .byte   waitr,prslot

```

```

        iot                ;read starting address for next pass
        chbuf
        .byte    read,kslot
w31:    iot
        w31
        .byte    waitr,kslot
        iot                ;write -"when ready - hit continue"
        mbuf12
        .byte    write,prslot
        matoi                ;convert ascii to integer
        cmp      choic1,choice
w31a:   iot
        w31a
        .byte    waitr,prslot
        halt
;
;////////////////////////////////////
;start next run
;////////////////////////////////////
;
        cmp      choice,#1    ;where next ?
        bmi      jgonew       ;new parameters ?
        beq      jgoold       ;old parameters ?
        cmp      choice,#3
        bmi      jemerg       ;paper tape output
        beq      jlogof       ;logoff from unix
        bpl      jwhere       ;any address
jgonew: jmp      gonew        ;start with new parameters
jgoold: jmp      goold        ;start with old parameters
jemerg: jmp      emerg        ;punch data on paper tape
jlogof: jmp      logof        ;extension of branch instruction
jwhere: jmp      whereto      ;extension of branch instruction
;
;
;////////////////////////////////////
;send data to unix
;////////////////////////////////////
;
;
unx1:   call      initialize    ;initialize for unix transfer
        call      callunix     ;establish connection with unix
        jsr      pc,ckmode     ;are we in user mode ?
        mov      #date1,r1     ;address of "date"
        mov      datcnt,r2     ;# of characters of "date"
        call      writetounix,<#date1,r2> ;send it to unix
        jsr      pc,ckmode     ;are we in user mode ?
        mov      #run1,r1     ;address of "run #"
        mov      runcnt,r2     ;# of characters of "run #"
        call      writetounix,<#run1,r2> ;send it to unix
        jsr      pc,ckmode     ;are we in user mode ?
        mov      #sample1,r1   ;address of "sample name"
        mov      samcnt,r2     ;# of char. in "sample name"
        call      writetounix,<#sample1,r2> ;send it to unix
        jsr      pc,ckmode     ;are we in user mode ?

```

```

mov      #ir1,r1          ;address of "ir value"
mov      irect,r2         ;# of characters in "ir value"
call     writetounix,<#ir1,r2> ;send it to unix
jsr      pc,ckmode        ;are we in user mode ?
mov      #point1,r1       ;address of "# of points"
mov      ptent,r2         ;# of characters in "# of points"
call     writetounix,<#point1,r2> ;send it to unix
jsr      pc,ckmode        ;are we in user mode ?
mov      #chani1,r1       ;address of "current chan."
mov      chiont,r2        ;# of char. "in cur. chan."
call     writetounix,<#chani1,r2> ;send it to unix
jsr      pc,ckmode        ;are we in user mode ?
mov      #vcal,r1         ;address of "calib. voltage"
mov      volent,r2        ;# of char. in "calib. voltage"
call     writetounix,<#vcal,r2> ;send it to unix
jsr      pc,ckmode        ;are we in user mode ?
mov      #dummy,r1        ;address of "dummy resistor"
mov      dument,r2        ;# of char. in "dummy resistor"
call     writetounix,<#dummy,r2> ;send it to unix
jsr      pc,ckmode        ;are we in user mode ?
mov      #drop1,r1        ;address of "# of drops"
mov      drpent,r2        ;# of char. in "# of drops"
call     writetounix,<#drop1,r2> ;send it to unix
jsr      pc,ckmode        ;are we in user mode ?
mov      #ptscal,r4       ;addr. of # of cal. points
mov      #kalib1,r1       ;addr. of # of cal.pts.- out.stor.
mov      #subconv,r2      ;address of subconv subroutine
set5:    clr      (r1)+    ;clear area for output of # of
        cmp      r1,r2    ;calibration points
        bne      set5     ;
        mitoa     ;integer to ascii conversion
        cmp      (r4),kalib1 ;# of calibration points
        bis      #20000,kalib1+6 ;" "
        bis      #5015,kalib1+10 ;"cr,lf"
        mov      #kalib1,r1 ;address of # of calib.points
        mov      kalent,r2  ;# of char. in "# of cal.pts."
        call     writetounix,<#kalib1,r2> ;send it to unix
        jsr      pc,ckmode  ;are we in user mode ?
        jmp      outcal    ;go output data
        . unx3: mov      #data,r1 ;address of "output data"
        mov      outbuf,r2  ;# of characters in output data
        call     writetounix,<#data,r2> ;send it to unix
        jsr      pc,ckmode  ;are we in user mode ?
        jmp      filcal    ;jump to fill in data
        unx2: mov      #data,r1 ;address of "output data"
        mov      outbuf,r2  ;# of char. of "output data"
        call     writetounix,<#data,r2> ;send it to unix
        jsr      pc,ckmode  ;are we in user mode ?
        dec      ptcoun     ;decrement output data counter
        cmp      ptcoun,#1  ;is all data output ?
        beq      clos      ;is yes go to closing statements
        jmp      output    ;if no, go again
        clos: mov      #ends,r1 ;address of "end buffer"
        mov      endent,r2  ;# of char. in "end buffer"

```

```

        call    writetounix,<#ends,r2>    ;send it to unix
        jsr     pc,ckmode                  ;are we in user mode ?
        mov     #calib1,r1                 ;address of "calib. choice"
        mov     calent,r2                  ;# of char. in "calib.choice"
        call    writetounix,<#calib1,r2>    ;send it to unix
        jsr     pc,ckmode                  ;are we in user mode ?
        mov     #207,prbuf                 ;end of output - ring bell
        clr     r1                         ;prepare closing command
        clr     r2
        call    writetounix,<#0,#0>         ;send closing command to unix
        cmp     mode,#user                 ;are we in user mode ?
        bne     jwto                       ;if not, go to whereto
        jsr     r5,recaliox                ;reinitialize iox
        jmp     again                      ;get ready for next run
jwto:    jmp     whereto
;
;////////////////////////////////////
; filling -.1 to mark end of run in a set of 5
;////////////////////////////////////
;
filend:  bis     #27055,data                ;load " -. "
        bis     #6461,data+2              ;load "1",cr
        bis     #12,data+4                ;load lf
        cmp     #4,toutcod                ;is this output on paper tape ?
        bne     unxfil                    ;if not go to unix output
        jsr     r5,outdata                 ;if yes, send data to punch
        jmp     output                    ;go for next point
unxfil:  mov     #data,r1                  ;put address of data to r1
        mov     #6,r2                     ;put # of point to r2
        call    writetounix,<#data,r2>     ;send the data to unix
        jsr     pc,ckmode                  ;chee the mode of tty
        jmp     output                    ;go for next point
;
;////////////////////////////////////
;logoff from unix
;////////////////////////////////////
;
logof:   call    initialize                ;initialize for unix transfer
        call    print,#msg1               ;print helpful message
        call    print,#msg2               ;another message
        call    callunix                  ;establish communic. with UNIX
        jmp     whereto
msg1:    .asciz  <cr><lf>/ when in UNIX type in control C to get out
msg2:    .asciz  <cr><lf>/hit return, then control d to get "login"/
        .even
;
;////////////////////////////////////
; where to go next ? input address
;////////////////////////////////////
;
whereto: jsr     r5,recaliox                ;reinitialize iox
        iot                                     ;write -"input addr. of next instr."
        mbuf17
        .byte   write,prslot

```

```

w35:  iot
      w35
      .byte  waitr,prslot
      iot          ;read in input addr. of the next instr.
      whereb
      .byte  read,kslot
w36:  iot
      w36
      .byte  waitr,kslot
      matoo        ;ascii to octal conversion - next address
      cmp     where1,where2
      mov     where2,-(sp)    ;store the address on stack
      cmp     where2,#1000    ;is it smaller than the first statement
      bmi     jerr           ;if yes, wrong address
      cmp     where2,#stop    ;is it larger than the last statement?
      bpl     jerr           ;if yes, wrong address
      bic     #177776,where2  ;is it odd ?
      bne     jerr           ;if yes, wrong address
      jmp     @(sp)          ;go to given address
jerr:  jmp     error         ;go to error routine
      halt
      .page
      .sbttl  user's emergency routine

```

```

;
;////////////////////////////////////
;emergency storing of data on paper tape
;////////////////////////////////////
;
emerg: jsr     r5,recaliox
      mov     #4,toutcod    ;reassign this spot to punch
      iot          ;re-initialize toutslot
      .word   toutcod
      .byte   init,toutslot
emc:   iot          ;write - "unix or wylbur ?"
      mbuf19
      .byte   write,prslot
w32a:  iot
      w32a
      .byte   waitr,prslot
      iot          ;read in decision
      ptenbf
      .byte   read,kslot
w32b:  iot
      w32b
      .byte   waitr,kslot
      iot          ;write - "put punch on..."
      mbuf15
      .byte   write,prslot
w32:   iot
      w32
      .byte   waitr,prslot
      iot          ;write - "when ready-hit continue"
      mbuf12

```



```
w33:    .byte    write,prslot
        iot
        w33
        .byte    waitr,prslot
        iot                ;write - "when output finished..."
        mbuf14
w33a:   .byte    write,prslot
        iot
        w33a
        .byte    waitr,prslot
        iot                ;write - " e i  ----"
        mbuf16
w34:   .byte    write,prslot
        iot
        w34
        .byte    waitr,prslot
        halt
        clr      r0          ;clear character counter
        cmp      pten1,#42531 ;is this wylbur tape ?
        bne      emcy        ;no it is for unix
        mov      #1,wylbur    ;yes it is for wylbur
emcy:   mov      #0,prbuf      ;send leader
check6: tstb     prsr         ;printer ready for next character ?
        bpl      check6      ;if not, wait
        inc      r0          ;if yes, update counter
        cmp      #250,r0      ;do we have 250 ?
        bpl      emcy        ;if not, go again
        jmp      out1        ;output data as if to UNIX
stop:   halt
        .end    begin        ;start at begin
```

APPENDIX H PROGRAM POLWAVE

```

c
c      for5beg
c
c  symbols used :
c
c  einp  =  uncorrected input potential -one value
c  curinp=  uncorrected input current -one value
c  capinp= uncorrected input capacity -one value
c  ein   =  uncorrected array of voltage at the same potential
c  curin =  uncorrected array of current at the same potential
c  capin =  uncorrected array of capacity at the same potential
c  e     =  corrected potential value
c  cur   =  corrected current value
c  csubd =  corrected capacitance value
c  einav =  average potential value, after q-test
c  curav =  average current value after q-test
c  capav =  average capacity value after q-test
c  eincal= potential value for calibration
c  cincal= current value for calibration
c  odincl= capacity value for calibration
c  einc  =  first potential increment
c  cinc  =  first current increment
c  esinc =  second potential increment
c  csinc =  second current increment
c  curent= value of current if more than one curve is taken
c  voltage= value of potential if more than one curve taken
c  curinc= value of first increment current if more than one curve
c  potinc= value of inc.potential if more than one curve taken
c  deltae= value of potential difference between two steps
c  eincm =  potential value of peaks
c  cincm =  current value of peaks
c  offset =  current second increment plus offset
c  zero   =  dotted zero line for second current increment
c  ebeg   =  starting point of potential x-axes in plot
c  eend   =  ending point of potential x-axes in plot
c  erange=  range of potential values
c  cbeg   =  starting point of regular current y-axes in plot
c  cend   =  endind point of regular current y-axes in plot
c  cinbeg=  starting point of first increment y-axes in plot
c  cinend=  ending point of first increment y-axes in plot
c  cinchi=  maximum value of incremental current
c  date   =  storage for date
c  sample=  storage for sample name
c  efact  =  potential conversion factor
c  cfact  =  current conversion factor
c  cdfact=  capacitance conversion factor

```

```
c ecal = averaged calibration potential
c ccal = averaged calibration current
c cdcal = averaged calibration capacity
c calvol= potential used for calibration
c calcap= capacitance used for calibration
c rdummy= value of dummy cell resistor for calibration
c ichan = # of A/D channel used for current
c ri     = instrumentation resistor used
c pts    = # of points averaged during the same drop
c where  = end of run indicator (if < 0)
c re     = potential range (e5-e1) used for q-test
c rc     = current range (i5-i1) used for q-test
c rp     = capacity range (r5-r1) used for q-test
c de1    = deviation between potentials 1 and 2 for q-test
c de2    = deviation between potentials 4 and 5 for q-test
c dc1    = deviation between currents 1 and 2 for q-test
c dc2    = deviation between currents 4 and 5 for q-test
c dp1    = deviation between capacities 1 and 2 for q-test
c dp2    = deviation between capacities 4 and 5 for q-test
c qc1    = q value for current point #1
c qc2    = q value for current point #5
c qe1    = q value for potential point #1
c qe2    = q value for potential point #5
c qp1    = q value for capacity point #1
c qp2    = q value for capacity point #5
c qt     = literature q value for 5 points
c temp   = temporary variable for current and potential used
c         in subroutine tst
c iplot  = plotting selector
c iprint= printing selector
c idrp   = 5, used for # of drops at one pot. in calibration
c idrops = # of drops taken at one pontial
c idrop  = idrops - 1, used in q-test calculations
c irun   = # of runs taken
c i      = counter - # of input points
c itotal= counter - total # of points input
c j      = counter - # of first increments
c jtotal= counter - total # of first increments
c k      = counter - # of second increments
c l      = counter - used for maxima location
c lq     = counter - used for maxima location
c max    = counter - # of peaks
c mm     = counter - date (input and output)
c mn     = counter - sample (input and output)
c it     = counter - temporary on do loops
c jt     = counter - temporary on do loops (subroutines)
c kt     = counter - temporary on do loops (subroutines)
c it1    = counter - temporary for do loops on prints
c
c reserve workspace for smoothing routine
c minimum workspace = 10*(# of points +2 )
c store smoothing factor (from 0.001 up) to first tenth of reserved sp.
c initialize variables
c input date, sample name, run #, value of instrumentation resistor,
```

```

c      # of points taken in each drop, choices for printout and plot.
c -----
c read in decision on type of output
c iprint = 1 ,print input data(ein,curin,capin,e,cur,osubd),
c           average values of potential, current and capacity,
c           first and second increments, maxima and cal. values.
c           2 ,print average values of potential, current and capac-
c           ity, first and second incs., maxima and cal. values.
c           3 ,print values of maxima only
c           4 ,print capacitance values and calibration data only
c           5 ,print capacitance values only
c           9 ,print run id only.
c iplot   = 1 ,do not plot
c           2 ,plot regular wave,first and second increment
c           3 ,plot regular wave and first increment
c           4 ,plot regular wave only
c           5 ,plot first increment only
c           6 ,plot first & second increments only
c           7 ,plot capacitance curve only
c           8 ,plot calibration curve
c -----
c input value of calib. voltage, dummy cell resistor and cur.chan.
c write out date, run # and sample name,output selections,
c instrum.resistor, # of points taken in drop and current chan.
c
c      common work(5000)
c      dimension e(5),date(5),cur(5),einc(300),cinc(300),curent(1550),
c      1 esinc(300),csinc(300),cincm(15),eincm(15),curin(5),ein(5),
c      2 sample(10),curav(300),eina(300),offset(300),voltage(1550),
c      3 zero(300),eincal(10),cincal(10),curinc(1500),potinc(1500),
c      4 deltae(300),capav(300),osubdh(5),capin(5),edinc(10),cal(10),
c      5 edinc(5),edinh(5),csubdh(5),chcur(300),cinc(300),
c      6 capav(300),capavh(300),edplot(10)
c      do 1 it=1,500
c      1 work(it)=0.005
c
c      irun=0
c      itotal=0
c      jtotal=0
c
c      read(5,201)iprint,iplot,(date(mm),mm=1,3),run,(sample(mn),
c      1 mn=1,7),ri,pts
c      201 format(12/12/3a4/a4/7a4/f9.6/f4.0)
c      read(5,203)ichan,calvol,rdummy,idrops,ical
c      203 format(11/f8.6/f9.6/i1/i6)
c
c
c      write(6,202)(date(mm),mm=1,3),(sample(mn),mn=1,7),run,iprint,
c      1 iplot,ri,pts,ichan
c      202 format(1h1,'date: ',3a4,5x,'sample: ',7a4,5x,'run #',
c      1 a4//5x,'iprint= ',i2,5x,'iplot= ',i2,5x,'instrum.resistor= ',
c      2 f6.3,5x,'# of points= ',f5.0,5x,'cur.channal=',i1)
c
c input value of current, potential and capacitance from calibration

```

```

c do q-test on calibration values and average them (if needed)
c (use subroutine TST)
c calculate calibration factors
c output calibration data
c
c
2 read(5,204)(eincal(it),cincal(it),cdincl(it),cal(it),it=1,ical)
204 format(f13.0,f14.0,f15.0,4x,f4.2)
c
c if(ical-1)100,103,3
3 sumx=0.0
sumy=0.0
sumxx=0.0
sumxy=0.0
do 240 it=1,ical
sumx=sumx + cdincl(it)
sumy=sumy + cal(it)
sumxx=sumxx + cdincl(it)**2.
sumxy=sumxy + cdincl(it) * cal(it)
240 continue
d = ical * sumxx - sumx **2.
aslope = (ical * sumxy - sumx * sumy)/d
bint = (sumxx * sumy - sumx * sumxy)/d
c
103 if (iprint.ge.5)go to 102
if (iprint.eq.3)go to 102
c
write(6,205)(eincal(it),cincal(it),cdincl(it),cal(it),
1 it=1,ical)
205 format(1h0,9x,'calibration data'/(3f14.0,' = ',f4.2))
write(6,206)aslope,bint
206 format(1h ,'intercept = ',e12.4,5x,'slope = ',e12.4)
102 call tst(cincal,eincal,ccal,ecal,ical)
continue
c
efact=calvol/ecal
calcur=calvol/rdummy
cfact=calcur/ccal
if(ichan.eq.1)cfact=calcur/(ccal-pts*2047)
if(ical.eq.1)cdfact=cal(1)/cdincl(1)
c
if (iprint.ge.5)go to 101
if (iprint.eq.3)go to 101
c
write(6,220)calvol,ecal,calcur,ccal,rdummy,ical,idrops
220 format(1h0,1x,f7.4,'V= ',f10.0,5x,e12.5,'mamps= ',f10.0,5x,
1 'rdummy= ',f8.4,'mohms',5x,i2,2x,'calibration capacity values',
2 /5x,i1,' drops at the same potential')
c
c input first "idrops" points (use subroutine input)
c convert input values to voltage, current and capacitance using
c calibration factors, check if input data is to be printed out, if yes,
c print them out
c do q-test on input points and average them-if needed

```

```
c      (use subroutine tst)
c      check if input completed, if yes start looking for maxima
c      if not, calculate first increments
c      calculate second increments
c      go back and read next five points.
c
101    max=0
       irun=irun+1
c
       call input(wher,cfact,efact,curav,einav,i,pts,iprint,
1       idrops,ichan,aslope,bint,ical,capav,cdfact,capavh)
       continue
c
       do 4 it=1,i
         itotal=itotal+1
         curent(ittotal)=curav(it)
         voltag(ittotal)=einav(it)
4       continue
         if (iplot.eq.7)go to 26
         call deriv(curav,einav,i,cinc,einc,deltae,cheur,
1         capav,crcinc)
         continue
         j=i-1
         do 5 it=1,j
           jtotal=jtotal+1
           curinc(jtotal)=cinc(it)
           potinc(jtotal)=einc(it)
5         continue
           call sderiv(cinc,einc,j,csinc,esinc)
           continue
           k=j-1
           call fmaxim(cinc,einc,csinc,esinc,i,cincmx,eincmx,
1           cincm,eincm,max)
           continue
c
c      *****      output follows      *****
c
       if(iprint-3)18,25,26
c
18     write(6,207)
207    format(///4x,'i',5x,'einav',5x,'delta e',6x,'curav',4x,
1      'capavh',6x,'einc',8x,'cinc',8x,'cheur',8x,
2      'crcinc',8x,'capav',8x,'csinc'/130(1h*))
c
       do 24 it=1,i
         if(it-1)100,20,19
19      if(it-i)21,20,100
20      write(6,208)it,einav(it),curav(it),capavh(it)
208     format(1x,i4,4x,f7.4,13x,e11.4,2x,f7.4)
         if(it-1)100,22,23
c
21     it1=it-1
c
       write(6,209)it,einav(it),curav(it),capavh(it),csinc(it1)
```

```
209  format(1x,14,4x,f7.4,13x,e11.4,2x,f7.4,68x,e11.4)
c
22  write(6,210)deltae(it),einc(it),cinc(it),chcur(it),
1  creinc(it),capav(it)
210  format(1x,20x,f5.1,27x,f7.4,3x,e11.4,3x,e11.4,3x,e11.4,
1  3x,f9.6)
23  continue
24  continue
c
      if(max.eq.0)go to 26
25  write(6,211)((it),eincm(it),cincm(it),it=1,max)
211  format(////(5x,'maximum # ',i2,'=',f7.4,'V,',e11.4,'mcamps'/))
c
      write(6,212)eincmx,cincmx
212  format(1h0,4x,'absolute maximum =',f7.4,'v,',e11.4,'microamps')
26  if (iprint.le.3)go to 34
      if (iprint.ge.6)go to 34
      write(6,213)
213  format(1h ,15x,'E(V)',6x,'cd(mcf)',/1x,40(1h*))
      write(6,214)(it,einav(it),capav(it),it=1,i)
214  format(///(5x,i2,5x,f7.4,5x,f7.4))
34  continue
c
c
c  ***** plotting routines follow *****
c
c  define end of x - axes
c  define end of y - axes (for regular wave)
c  define beginning of y - axws (regular wave)
c  define beginning of x - axes
c  define end of incremental x - axes
c  define beginning of incremental x - axes
c  make x -axes and offset second increment
c
      if (iplot.ge.7)go to 42
      if(irun.ne.1)go to 41
      erange=einav(i)-einav(1)
      eend=einav(i)+0.1*erange
      cend=1.1*curav(i)
      cbeg=-0.1*curav(i)
      ebeg=einav(1)-0.1*erange
      cinchi=cinc(1)
      do 35 it=2,j
      it1=it-1
      if(cinc(it).gt.cinchi)cinchi=cinc(it)
35  continue
      cinend=1.1*cinchi
      cinbeg=-0.1*cinchi
c
41  do 27 it=1,k
      ofset(it)=csinc(it)+0.3*cinchi
      zero(it)=0.3*cinchi
27  continue
      write(6,250)erange,ebeg,eend,cbeg,cend,cinchi,cinbeg,cinend
```

```

250  format(1h0,'erange=',f7.4,5x,'ebeg=',f7.4,5x,'eend=',f7.4,5x,
      1  'obeg=',e11.4,5x,'cend=',e11.4/1x,'cinchi=',e11.4,5x,
      2  'cinbeg=',e11.4,5x,'cinend=',e11.4)
c
c  see if and what plot type was choosen
c  if no plot chosen, skip plotting routines
c  if yes, start plot routines, set up origin, mixed alphabets,
c    title,axis,letter size,messages,etc.
c
42   if (iplot.eq.1)go to 31
      if(irun.ne.1)go to 40
c
      call bgnpl(1)
      call rjcalc
      call physor(1.90,1.69)
      call complx
      call basalf('stand')
      call mx2alf('1/cstd','+')
      call mx3alf('mathematic','<')
      call mx4alf('1/cgr','*')
      call mx5alf('greek','>')
c
      if(iplot.lt.5)call title('p+olarographic )w+ave)$',100,
      1  '-e +vs) 3.5m c+alomel) <0>v<1)$',100,'c+current )<0>*m)a<1)$',
      2  100,5.3,7.8)
      if (iplot.eq.7)go to 36
      if (iplot.ge.8)go to 43
c
      if(iplot.ge.5)call title('p+olarographic )w+ave)$',100,
      1  '-e +vs) 3.5m c+alomel) <0>v<1)$',100,'>d) i<0>*m)a<1)$',
      2  100,5.3,7.8)
c
36   if(iplot.eq.7)call title('c+apacitance )c+urve)$',100,
      1  '-e +vs) 3.5m c+alomel) <0>v<1)$',100,'c+d )<0>*m)f<1)$',
      2  100,5.3,7.8)
c
43   if(iplot.eq.8)call title('c+alibration )c+urve)$',100,
      1  'c+d) <0>*m)f<1)$',100,'instrument reading <0>v<1)$',
      2  100,5.3,7.8)
      call yaxang(0.)
      call height(0.10)
      dates=date(1)
      call messag(dates,4,0.6,7.8)
      dates=date(2)
      call messag(dates,4,'abut','abut')
      dates=date(3)
      call messag(dates,4,'abut','abut')
      call messag(' sample:$',100,0.6,7.6)
      do 28 it=1,7
      sam=sample(it)
      call messag(sam,4,'abut','abut')
28   continue
      call messag(' run #$',100,0.6,7.4)
      call messag(run,4,'abut','abut')

```



```

      call sclpic(0.5)
      call reset('yaxang')
      call reset('height')
      if(iplot.lt.5)call graf(ebeg,'scale',eend,ebeg,'scale',cend)
      if(iplot.eq.5)call graf(ebeg,'scale',eend,cinbeg,'scale',cinend)
      if(iplot.eq.6)call graf(ebeg,'scale',eend,cinbeg,'scale',cinend)
      if(iplot.eq.7)call graf(0.,'scale',2.0,0.,'scale',0.5)
      if(iplot.eq.8)call graf(0.,'scale',1.0,0.,'scale',2.0)
c
40  go to (31,29,29,29,30,30,37,38),iplot
29  call marker(3)
      call curve(einav,curav,i,-1)
c
      if(iplot.eq.4)go to 31
      call ygraxs(0.,'scale',cinend,7.8,'>d) i <0)*m)a<1)$',
1  -100,0.,0.)
30  call marker(4)
      call curve(einc,cinc,j,-1)
      call marker(1)
      call curve(einc,orcinc,j,1)
c
      go to (31,32,31,31,31,32),iplot
32  call dash
      call marker(2)
      call curve(esinc,offset,k,1)
      call dot
      call curve(esinc,zero,k,0)
c
31  if(where+5.)33,33,101
33  if(iplot.eq.1)go to 100
      call sort2(curinc,potinc,jtotal)
      continue
      call smooth
      call curve(potinc,curinc,jtotal,0)
      go to 99
c
37  call marker(3)
      call curve(einav,capav,i,-1)
      call smooth
      call curve(einav,capav,i,0)
      go to 99
38  do 39 it=1,ical
      cdplot(it)=(2.*cdincl(it))/(4095.*5.)
39  continue
      call curve(cal,cdplot,ical,1)
99  call endpl(0)
      call donepl
100 stop
      end
c
c
c
c *****
c ////////////// subroutines //////////////////////

```

```

c *****
c
c
c      subroutine input(where,cfact,efact,curav,einav,i,pts,
1      iprint,idrops,ichan,aslope,bint,ical,capav,cdfact,capavh)
c -----
c
c this subroutine reads current and potential values, stores them
c in arrays, corrects them by appropriate correction factors from
c calibration and returns them to main program for further use.
c
c      dimension curav(300),einav(300),e(5),cur(5),
1      curin(5),ein(5),cdinl(5),csubdl(5),capav(300),
2      cdinh(5),csubdh(5),capavl(300),
3      capavh(300)
c      where = 0
c      i=0
c      it=1
c
c      if (iprint.ne.1)go to 400
c      write(6,412)
412  format(///9x,'ein',10x,'curin',9x,'capinl',9x,'capinh',9x,
1      'e(v)',6x,'cur(mcamp)',6x,'capl(mcfads)',3x,'caph(mcfads)',
2      /1x,120(1h*))
c
c 400  if(idrops.eq.1)go to 409
c      do 404 it=1,idrops
c 409  read(5,401)einp,curinp,capinl,capinh
c 401  format(f13.0,f14.0,f15.0,f14.0)
c
c      if(einp)402,403,403
c 402  where = einp
c      go to 408
c
c 403  curin(it)=curinp
c      ein(it)=einp
c      cdinl(it)=capinl
c      cdinh(it)=capinh
c
c      e(it)=ein(it)*efact
c      cur(it)=curin(it)*cfact
c      if(ichan.eq.1)cur(it)=(curin(it)-pts*2047)*cfact
c      if(ical.eq.1)go to 405
c
c
c      csubdl(it)=bint + aslope * cdinl(it)
c      csubdh(it)=bint + aslope * cdinh(it)
c      go to 407
c 405  csubdl(it)=cdinl(it)*cdfact
c      csubdh(it)=cdinh(it)*cdfact
c 407  continue
c 404  continue
c
c      if(iprint.ne.1)go to 406

```

```
c      write(6,413)(ein(it),curin(it),odinl(it),cdinh(it),e(it),
1      cur(it),csubdl(it),csubdh(it),it=1,idrops)
413      format(1h ,4f14.0,f14.4,e18.4,2f15.4)
406      call tst2(cur,e,csubdl,csubdh,curav,einav,capav1,capavh,
1      capav,i,idrops,pts)
      continue
      go to 400
408      continue
      return
      end
```

c
c
c
c

```
      subroutine tst(cincal,eincal,ccal,ecal,ical)
```

c
c
c

c this subroutine arranges "idrops" input current,potential and
c capacitance values from largest to smallest, calculates range
c and deviations between the highest two(d1) and lowest two(d2)
c values, does q-test, rejects bad values and calculates average
c for current, potential and capacitance.

c

```
      dimension cincal(10),eincal(10)
      if(ical.eq.1)go to 606
      idrop=ical-1
      if(ical.le.2)go to 605
      if(ical.eq.3)qt=0.90
      if(ical.eq.4)qt=0.76
      if(ical.eq.5)qt=0.64
      if(ical.eq.6)qt=0.56
      if(ical.eq.7)qt=0.51
```

c

```
      do 600 it=1,idrop
      jt=it+1
      do 601 kt=jt,ical
      if(cincal(it)-cincal(kt))602,609,609
602      temp=cincal(it)
      cincal(it)=cincal(kt)
      cincal(kt)=temp
609      continue
601      continue
600      continue
```

c

```
      do 611 it=1,idrop
      jt=it+1
      do 612 kt=jt,ical
      if(eincal(it)-eincal(kt))613,619,619
613      temp=eincal(it)
      eincal(it)=eincal(kt)
      eincal(kt)=temp
619      continue
```

```
612 continue
611 continue
c
c
    rc=cincal(1)-cincal(ical)
    if(rc.eq.0)go to 605
    dc1=cincal(1)-cincal(2)
    qc1=dc1/ro
c
    if(qc1.ge.qt)go to 603
    dc2=cincal(idrop)-cincal(ical)
    qc2=dc2/ro
c
    if(qc2.ge.qt)go to 604
605    sum=0.
        do 618 it=1,ical
            sum=sum+cincal(it)
618    ccal=sum/ical
        go to 610
603    cincal(1)=0.
        go to 625
604    cincal(ical)=0.
625    sum=0.
        do 617 it=1,ical
            sum=sum+cincal(it)
617    ccal=sum/idrop
c
610    if(ical.le.2)go to 616
        re=eincal(1)-eincal(ical)
        if(re.eq.0)go to 616
        de1=eincal(1)-eincal(2)
        qe1=de1/re
c
        if(qe1.ge.qt)go to 615
        de2=eincal(idrop)-eincal(ical)
        qe2=de2/re
c
        if(qe2.ge.qt)go to 614
616    sum=0.
        do 621 it=1,ical
            sum=sum+eincal(it)
621    ecal=sum/ical
        go to 620
615    eincal(1)=0.
        go to 622
614    eincal(ical)=0.
622    sum=0.
        do 633 it=1,ical
            sum=sum+eincal(it)
633    ecal=sum/idrop
620    continue
        go to 699
606    ecal=eincal(1)
        ccal=cincal(1)
```

```
c
c
699  return
    end
c
c
    subroutine tst2(cur,e,csubdl,csubdh,curav,einav,capavl,
1   capavh,capav,i,idrops,pts)
c
c
c
c   this subroutine arranges "idrops" input current,potential and
c   capacitance values from largest to smallest, calculates range
c   and deviations between the highest two(d1) and lowest two(d2)
c   values, does q-test, rejects bad values and calculates average
c   for current, potential and capacitance.
c
    dimension cur(5),e(5),csubdl(5),csubdh(5),curav(300),einav(300),
1   capavl(300),capavh(300),capav(300)
    i=i+1
    if(idrops.eq.1)go to 544
    idrop=idrops-1
    if(idrops.le.2)go to 505
    if(idrops.eq.3)qt=0.90
    if(idrops.eq.4)qt=0.76
    if(idrops.eq.5)qt=0.64
    if(idrops.eq.6)qt=0.56
    if(idrops.eq.7)qt=0.51
c
    do 500 it=1,idrop
        jt=it+1
        do 501 kt=jt,idrops
            if(cur(it)-cur(kt))502,509,509
502    temp=cur(it)
        cur(it)=cur(kt)
        cur(kt)=temp
509    continue
501    continue
500    continue
c
    do 511 it=1,idrop
        jt=it+1
        do 512 kt=jt,idrops
            if(e(it)-e(kt))513,519,519
513    temp=e(it)
        e(it)=e(kt)
        e(kt)=temp
519    continue
512    continue
511    continue
c
    do 506 it=1,idrop
        jt=it+1
        do 507 kt=jt,idrops
```

```

    if(csubdl(it)-csubdl(kt))508,523,523
508    temp=csubdl(it)
    csubdl(it)=csubdl(kt)
    csubdl(kt)=temp
523    continue
507    continue
506    continue
c
    do 524 it=1,idrop
    jt=it+1
    do 536 kt=jt,idrops
    if(csubdh(it)-csubdh(kt))534,535,535
534    temp=csubdh(it)
    csubdh(it)=csubdh(kt)
    csubdh(kt)=temp
535    continue
536    continue
524    continue
c
    rc=cur(1)-cur(idrops)
    if(rc.eq.0)go to 505
    dc1=cur(1)-cur(2)
    qc1=dc1/rc
c
    if(qc1.ge.qt)go to 503
    dc2=cur(idrop)-cur(idrops)
    qc2=dc2/rc
c
    if(qc2.ge.qt)go to 504
505    sum=0.
    do 518 it=1,idrops
    sum=sum+cur(it)
518    curav(i)=sum/idrops
    go to 510
503    cur(1)=0.
    go to 525
504    cur(idrops)=0.
525    sum=0.
    do 517 it=1,idrops
    sum=sum+cur(it)
517    curav(i)=sum/idrop
c
510    if(idrops.le.2)go to 516
    re=e(1)-e(idrops)
    if(re.eq.0)go to 516
    de1=e(1)-e(2)
    qc1=de1/re
c
    if(qc1.ge.qt)go to 515
    de2=e(idrop)-e(idrops)
    qc2=de2/re
c
    if(qc2.ge.qt)go to 514
516    sum=0.
```

```
do 521 it=1,idrops
  sum=sum+e(it)
521  einav(i)=sum/idrops
  go to 520
515  e(1)=0.
  go to 522
514  e(idrops)=0.
522  sum=0.
  do 533 it=1,idrops
    sum=sum+e(it)
533  einav(i)=sum/idrop
520  continue

c
  if(idrops.le.2)go to 526
  rp=csubdl(1)-csubdl(idrops)
  if(rp.eq.0)go to 526
  dp1=csubdl(1)-csubdl(2)
  qp1=dp1/rp

c
  if(qp1.ge.qt)go to 527
  dp2=csubdl(idrop)-csubdl(idrops)
  qp2=dp2/rp

c
  if(qp2.ge.qt)go to 528
526  sum=0.
  do 529 it=1,idrops
    sum=sum+csubdl(it)
529  capav1(i)=sum/idrops
  go to 530
527  csubdl(1)=0.
  go to 531
528  csubdl(idrops)=0.
531  sum=0.
  do 532 it=1,idrops
    sum=sum+csubdl(it)
532  capav1(i)=sum/idrop
530  continue

c
  if(idrops.le.2)go to 537
  rp=csubdh(1)-csubdh(idrops)
  if(rp.eq.0)go to 537
  dp1=csubdh(1)-csubdh(2)
  qp1=dp1/rp

c
  if(qp1.ge.qt)go to 538
  dp2=csubdh(idrop)-csubdh(idrops)
  qp2=dp2/rp

c
  if(qp2.ge.qt)go to 539
537  sum=0.
  do 540 it=1,idrops
    sum=sum+csubdh(it)
540  capavh(i)=sum/idrops
  go to 541
```

```

538  csubdh(1)=0.
      go to 542
539  csubdh(idrops)=0.
542  sum=0.
      do 543 it=1,idrops
        sum=sum+csubdh(it)
543  capavh(i)=sum/idrop
541  continue
      go to 545
544  curav(i)=cur(1)
      einav(i)=e(1)
      capav1(i)=csubdl(1)
      capavh(i)=csubdh(1)
545  capav(i)=(1000.*(capavh(i)-capav1(i)))/pts
c
      return
      end
c
c
c
c
      subroutine deriv(curav,einav,i,cinc,einc,deltae,
1  chcur,capav,orcinc)
c
c
c  this subroutine calculates first increments
c
      dimension curav(300),einav(300),cinc(300),einc(300),
1  deltae(300),chcur(300),capav(300),orcinc(300)
c
      do 801 it=2,i
        jt=it-1
        cinc(jt)=curav(it)-curav(jt)
        einc(jt)=(einav(it)+einav(jt))/2.
        deltae(jt)=(einav(it)-einav(jt))*1000.
        chcur(jt)=(deltae(jt)*(capav(it)+capav(jt)))/(2.*1000.)
        orcinc(jt)=cinc(jt)-chcur(jt)
801  continue
      return
      end
c
c
c
c
      subroutine sderiv(cinc,einc,j,csinc,esinc)
c
c  this subroutine calculates second increments
c
      dimension cinc(300),einc(300),csinc(300),esinc(300)
c
      do 810 jt=2,j
        kt=jt-1
        csinc(kt)=cinc(jt)-cinc(kt)
        esinc(kt)=(einc(jt)+einc(kt))/2.

```



```
      810  continue
          return
          end
c
c
c
      subroutine sort1(curav,einav,i)
c
c  this subroutine arranges curren and potential values
c  from smallest to largest, based on potential
c
      dimension curav(300),einav(300)
      imax=i-1
      do 710 it=1,imax
          jt=it+1
          do 711 kt=jt,i
              if(einav(it)-einav(kt))719,719,712
712          temp1=einav(it)
              temp2=curav(it)
              einav(it)=einav(kt)
              curav(it)=curav(kt)
              curav(kt)=temp2
              einav(kt)=temp1
719          continue
711          continue
710          continue
c
          return
          end
c
      subroutine sort2(curinc,potinc,jtotal)
c  -----
c
c  this subroutine arranges current and potential increments
c  from smallest to largest
c
      dimension potinc(1500), curinc(1500)
      jmax=jtotal-1
      do 700 it=1,jmax
          jt=it+1
          do 701 kt=jt,jtotal
              if(potinc(it)-potinc(kt))709,709,702
702          temp1=potinc(it)
              temp2=curinc(it)
              potinc(it)=potinc(kt)
              curinc(it)=curinc(kt)
              potinc(kt)=temp1
              curinc(kt)=temp2
709          continue
701          continue
700          continue
          return
          end
c
```

```
o
o
o      subroutine fmaxim(cinc,einc,csinc,esinc,i,cincmx,
1      eincmx,cinom,eincm,max)
o
o  this subroutine finds maxima in the first increment curve
o
      dimension cinom(15),eincm(15),cinc(300),einc(300),csinc(300),
1      esinc(300)
      lq=1-4
      do 901 l=3,lq
        if(csinc(l))902,902,909
902      if(csinc(l-1))909,909,903
903      if(csinc(l-2))909,909,904
904      if(csinc(l+1))905,909,909
905      if(csinc(l+2))906,906,909
906      max=max+1
          cincm(max)=cinc(l)
          eincm(max)=einc(l)
o
          if (max-1)920,908,907
907      if (cincm(max)-cincmx)909,909,908
908      cincmx=cinom(max)
          eincmx=eincm(max)
909      continue
901      continue
920      continue
          return
          end
/*
//go.sysin dd *
1
3
```

REFERENCES

1. Heyrovský, J. Chemické Listy 1922, 16 ,256.
2. Heyrovský, J.; Shikata, M. Rec.Trav.Chim. 1925, 44 ,496.
3. Heyrovský, J. Philosophical Magazine 1923, 45 ,303.
4. Ilkovic, D. Coll.Czech.Chem.Communs. 1934, 6 ,498.
5. Brezina, M. in "Progress in Polarography", Zuman and Kolthoff, eds., V-2, Interscience, N.Y. (1962), p.667.
6. Cozzi, D. "Progress in Polarography", Zuman and Kolthoff, eds., V-2, Interscience, N.Y. (1962), p.703.
7. Spálenka, M. in "Progress in Polarography", Zuman and Kolthoff, eds., V-2, Interscience, N.Y. (1962), p.661.
8. Zuman, P., Brezina, M. in "Progress in Polarography", Zuman and Kolthoff, eds., V-2, Interscience, N.Y. (1962), p.687.
9. Kolthoff, I.M.; Lingane, J.J. "Polarography", 2nd. ed., Interscience, N.Y. (1952).
10. Muller, O.H. "The Polarographic Method of Analysis", 2nd. ed., Chem.Ed.Pub.Co., Easton Pa. (1956).
11. Milner, G.W.C. "The Principles and Applications of Polarography", Longmans, Green, and Co., London (1957).
12. Meites, L. "Polarographic Techniques", 2nd. ed., Wiley, N.Y. (1965).
13. Heyrovský, J.; Kuta, J. "Principles of Polarography", Acad.Press, N.Y. (1966).

14. Müller, O.H. J.Chem.Ed. 1941, 18 ,320.
15. Semerano, G.; Riccoboni, L. Gaz. Chim. Ital. 1942, 72 ,297.
16. Heyrovský, J. Analyst 1947, 72 ,229.
17. Bond, A.M. "Modern Polarographic Methods in Analytical Chemistry", Dekker, N.Y. (1980), pp.147,158.
18. Leveque, M.P.; Roth, F. J.Chim.Phys. 1949 46 ,680.
19. Vogel, J.; Riha, J. J.Chim.Phys. 1950, 47
20. Kelley, M.T.; Fisher, D.J. Anal.Chem. 1956, 28 ,1130.
21. Kelley, M.T.; Fisher, D.J.; Cooke, W.D.; Jones, H.C. in "Advances in Polarography", Pergamon Press, London (1960), p.158.
22. Jones, C.H.; Belew, W.L.; Stelzner, R.W.; Mueller, T.R.; Fisher, D.J. Anal. Chem. 1969, 41(6) ,772.
23. Breyer, B.; Gutman, F.; Hacopian, S. Austr.J.Sci.Research 1950, A3 ,559.
24. Barker, G.C.; Jenkins, I.L. Analyst 1952, 77 ,685.
25. Barker, G.C.; Anal.Chim.Acta 1958, 18 ,118.
26. Takahashi, T.; Niki, E. Talanta 1958, 1 ,245.
27. Barker, G.C.; Gardner, A.W. Z.Anal.Chem. 1960, 173 ,79.
28. Kalousek, M. Coll.Czech.Chem.Comm. 1948, 13 ,105.
29. Schmidt, H.; von Stackelberg, M. "Modern Polarographic Methods", Acad. Press N.Y. (1963).
30. Bond, A.M. "Modern Polarographic Methods in Analytical Chemistry", Dekker, N.Y. (1980).
31. Bard, A.J.; Faulkner, L.R. "Electrochemical Methods: Fundamentals and Applications", Wiley, N.Y. (1980).
32. Glickstein, J.; Rankowitz, S.; Auerbach, C.; Finston, H.L. in "Advances in Polarography" Pergamon Press, London (1960), p.144.
33. Auerbach, C.; Finston, H.L.; Kissel, G.; Glickstein, J. Anal. Chem. 1961, 33 ,1480.

34. Rankowitz, S.; Higinbotham, W.A.; Glickstein, J. IRE Intern. Convention Record - Part 9, 1961, p.87.
35. Kronenberger, K.; Nichols, W. Z. Anal. Chem. 1962, 186, 79.
36. Laitinen, H.A. in "Trace Characterizations", Meinike, W.W. and Scribner, B.F., eds., NBS Monograph 1967, 100, 78.
37. Bockris, J. O'M.; Reddy, A.K.N. "Modern Electrochemistry", V-2, Plenum, N.Y. (1970).
38. Whitney, R.B.; Grahame, D.C. J. Chem. Phys. 1941, 9, 827.
39. Stern, O. Z. Elektrochem. 1924, 30, 508.
40. Grahame, D.C. Chem. Rev. 1947, 41, 441.
41. Grahame, D.C. Ann. Rev. Phys. Chem. 1955, 6, 337.
42. Delahay, P. "Double Layer and Electrode Kinetics", Wiley, N.Y. (1965).
43. Parsons, R. in "Advances in Electrochemistry and Electrochemical Engineering", Delahay, P. ed., V-1, Wiley, N.Y. (1961).
44. Parsons, R. in "Modern Aspects of Electrochemistry", Bockris, J.O'M. ed., V-1, Butterworth, London (1954), Chapter 3.
45. Frumkin, A.N.; Damaskin, B.B. in "Modern Aspects of Electrochemistry" Bockris, J.O'M. ed., V-3, Butterworth, London (1965), Chapter 3.
46. Helmholtz, H.L. Ann. Physik. 1853, 89, 211.
47. Mohilner, D.M. in "Electroanalytical Chemistry", Bard, A.J. ed., V-1, Dekker, N.Y. (1966), Chapter 4.
48. Grahame, D.C. J. Am. Chem. Soc. 1941, 63, 1207.
49. Grahame, D.C.; Soderberg, B.A. J. Chem. Phys. 1954, 22, 449.
50. Breyer, B.; Bauer, H.H. "Alternating Current Polarography and Tensammetry" in "Chemical Analysis", Elving, P.J. and Kolthoff, I.M. eds., V-13, Wiley, N.Y. (1963).
51. Barker, G.C. "Proc. Congress Modern Anal. Chem. in Ind., St. Andrews", Heffer, Cambridge (1957), p.215.

52. Schwartz, R.S. Ph.D. Dissitation, CUNY (1974).
53. Bond, A.M.; O'Halloran, R.J. J. Electroanal. Chem. 1967, 68, 257.
54. Ilkovic, D.; Semerano, G. Coll. Czech. Chem. Comm. 1932, 4, 176.
55. Enke, C.G.; Baxter, R.A. J. Chem. Ed. 1964, 41, 202.
56. Kelley, M.T.; Miller, H.H. Anal. Chem. 1952, 24, 1895.
57. EG&G Princeton Applied Research Corp., Application Notes and Advertising literature for Model 374 Polarographic Analyzer.
58. Clem, R.G.; Goldsworthy, W.W. Anal. Chem. 1971, 43(7), 918.
59. Bos, M. Anal. Chim. Acta 1976, 81, 21.
60. EG&G Princeton Applied Research Corp., Application Note ANT2.
61. Poojary, A.; Rajagopalan, S.R. J. Electroanal. Chem. 1975, 62, 51.
62. Rajagopalan, S.R.; Poojary, A.; Rangarajan, S.K. J. Electroanal. Chem. 1977, 75, 135.
63. Delahay, P. J. Phys. Chem. 1966, 70, 2373 and J. Electrochem. Soc. 1966, 113, 967, and discussion following.
64. Smith, D.E. CRC Critical Reviews in Analytical Chemistry, Sept. 1971, p. 247.
65. Sluyters-Rehbach, M.; Sluyters, J.H. in "Electroanalytical Chemistry", Bard, A.J. ed., V-4, Dekker, N.Y. (1970).
66. Bond, A.M. "Modern Polarographic Methods in Analytical Chemistry", Dekker, N.Y. (1980), p. 72.
67. Randles, J.E.B. Disc. Faraday Soc. 1947, 1, 11.
68. Grahame, D.C. J. Electrochem. Soc. 1952, 99, 370C.
69. Bond, A.M. "Modern Polarographic Methods in Analytical Chemistry", Dekker, N.Y. (1980) p. 99, also

- Bard, A.; Faulkner, L.R. "Electrochemical Methods: Fundamentals and Applications", Wiley, N.Y. (1980) p.169.
70. Ruzic, I. J. Electroanal. Chem. and Interfacial Electrochem. 1974, 49, 407.
71. Nemec, L. Coll. Czech. Chem. Comm. 1966, 31, 1162.
72. Teledyne-Philbrick Spec Sheet and Application Notes for Multiplier Module 4456.
73. Sluyters-Rehbach, M. Ph.D. dissertation, Utrecht State University (1963).
74. Sluyters-Rehbach, M.; Kooijman, D.J.; Sluyters, J.H. "Polarography 1964", Hills, G.J. ed., McMillan, London (1966).
75. Bratin, P. Master Thesis, Brooklyn College of CUNY (1974).
76. Bond, A.M.; Grabaric, B.S. Anal. Chim. Acta. 1978, 101, 309.
77. Smith, D.E. "AC Polarography and Related Techniques: Theory and Practice" in "Electroanalytical Chemistry", Bard, A.J. ed., V-1, Dekker, N.Y. (1966).
78. Reilley, C.N. J. Chem. Ed. 1962, 39, A853 and A933.
79. Booman, G.L.; Holbrook, W.B. Anal. Chem. 1963, 35, 1793.
80. Schwartz, W.M.; Shain, I. Anal. Chem. 1963, 35, 1770.
81. Vassos, B.H.; Eving, G.W. "Analog and Digital Electronics for Scientists", Wiley, N.Y. (1972).
82. Malmstadt, H.V.; Enke, C.G.; Toren, E.C. "Electronics for Scientists", Benjamin, N.Y. (1963) p.346.
83. Grahame, D.C. J. Am. Chem. Soc. 1949, 71, 2975.
84. Holmquist, P. J. Electroanal. Chem. 1976, 68, 31.
85. Barker, G.C.; Faircloth, R.L. in "Advances in Polarography", Longmuir, I.S. ed., V-1, Pergamon Press, London (1960) p.313.
86. Disspla User's Manual, Integrated Software Systems Corp (1970).
87. Murray, R.W.; Gross, D.J. Anal. Chem. 1966, 38, 392.

88. Barker, G.C. "Faradaic Rectification" in "Trans. of the Symposium on Electrode Processes", Yeager, E. ed., Wiley, N.Y. (1961) p.325.
89. McCord, T.G.; Smith, D.E. Anal.Chem. 1970, 42, 126.
90. Kambara, T.; Ishi, T. Rev. Polarography 1961, 9, 30.
91. Kooijman, D.J.; Sluyters, J.H. Electrochim.Acta 1967, 12, 693, 1579.
92. Heyrovský, J.; Kuta, J. "Principles of Polarography", Acad.Press, N.Y. (1966) p.216.
93. Meites, L. "Polarographic Techniques", 2nd.ed., Wiley, N.Y. (1965) p.75.
94. Bratin, K.; Felice, L.J.; Kissinger, P.T.; Miner, D.J.; Preddy, C.R.; Shoup, R.E. "Introduction to Detectors for Liquid Chromatography", Kissinger, P.T. ed., BAS Press, W.Lafayette (1981)
95. Bratin, P. Research Proposal to the National Research Council, Dec.1977.
96. Rosen, M.J.; Hua, X.; Bratin, P.; Cohen, A.W. Anal.Chem. 1981, 53, 232.
97. Vishvanath, S.R.; Sathyanarayana, S.; Rangarajan, S.K. J.Electroanal.Chem. 1976, 68, 377.
98. Hickling, A. Trans.Faraday Soc. 1942, 38, 27.
99. Abramowitz, M.; Stegun, I.A. eds., "Handbook of Mathematical Functions", National Bureau of Standards Applied Mathematic Series 55 (1965).
100. Bard, A.J.; Faulkner, L.R. "Electrochemical Methods: Fundamentals and Applications", Wiley, N.Y. (1980) p.566.
101. Handbook of Operational Amplifiers, Burr-Brown Research Co. (1969).
102. Application Manual for Operational Amplifiers, Philbrick/Nexus Research, a Teledyne Co. (1968).