

CONTENTS

PREFACE	ix
I. INTRODUCTION	1
1.1. Basic Principles	2
1.2. Types of Polarographic Limiting Currents	6
1.2.1. Diffusion currents	6
1.2.2. Kinetic currents	12
1.2.3. Catalytic currents	17
1.2.4. Adsorption currents	20
1.3. Characterization of the Different Types of the Electrode Processes	22
1.4. Other Types of Currents in Polarography	27
II. POLAROGRAPHIC INSTRUMENTATION	32
2.1. Dropping Electrode	32
2.2. Reference Electrode	34
2.3. Electrolysis Vessels	35
2.4. The Polarograph	41
2.5. Derivative and Subtractive Methods	45
2.6. Auxiliary Methods	48
2.6.1. Estimation of reversibility	48
2.6.2. Proof of the character of polarographic processes	50
2.6.3. Determination of the number of electrons transferred in the electrode reaction	52
2.6.4. Identification of the product of electrode processes	53
III. EXPERIMENTAL TECHNIQUES IN ORGANIC POLAROGRAPHY	61
3.1. Supporting Electrolyte	61
3.2. Removal of Oxygen	69
3.3. Recording of Polarographic Curves	70
3.4. The Measurement of the Limiting Current	70
3.5. Evaluation of the Wave-height: Calibration Curve and Standard Addition Methods	73
3.6. Sensitivity and Accuracy of the Method	77
3.7. Measurement of Half-Wave Potentials	79

IV. CLASSIFICATION OF POLAROGRAPHIC METHODS FOR THE ANALYSES OF ORGANIC SUBSTANCES	83
4.1. Polarographically Active Substances	83
4.2. Surface Active Substances	101
4.3. Direct and Indirect Methods of Analysis	102
4.4. Elemental Analysis	102
4.5. Functional Analysis	103
V. DIRECT METHODS OF POLAROGRAPHIC ANALYSIS	107
5.1. Examination of a Compound not previously Studied	108
5.2. Simultaneous Determination of Several Substances	110
VI. INDIRECT METHODS	112
6.1. Transformations into Electroactive Form	112
6.1.1. Nitration	112
6.1.2. Nitrosation	119
6.1.3. Condensations	120
6.1.4. Additions	129
6.1.5. Substitutions	132
6.1.6. Oxidations	132
6.1.7. Complex formation	135
6.1.8. Other reactions	140
6.2. Concentration Change of Polarographically Active Substances	141
6.2.1. Condensations	142
6.2.2. Additions	142
6.2.3. Oxidations	143
6.2.4. Complex formation	145
6.3. Polarometric (Amperometric) Titrations of Organic Compounds	145
6.3.1. Precipitation reactions	152
6.3.2. Oxidation-reduction reactions	159
6.3.3. Coupling reactions	162
6.3.4. Addition and substitution reactions	163
6.3.5. Soluble complex reactions	163
6.3.6. Condensations	165

VII. SEPARATION TECHNIQUES	172
7.1. Precipitation and Complex Formation	172
7.2. Extraction	173
7.3. Distillation and Steam Distillation	175
7.4. Dialysis	176
7.5. Electrolysis	177
7.6. Chromatography	177
VIII. PRACTICAL APPLICATIONS	185
8.1. Pharmacy	185
8.2. Medicine and Biochemistry	192
8.3. Agricultural and Food Chemistry	198
8.4. Purity of Technical Products	203
8.5. Petroleum and Fuels	206
8.6. Plastics	209
8.6.1. Monomers	210
8.6.2. Catalysts and other Substances present in Polymers	212
8.6.3. Polymers	213
8.6.4. Identification of polymers	214
8.7. Explosives	215
8.8. Textile Industry	220
8.8.1. Cellulosic fibres	220
8.8.2. Protein-based fibres	220
8.8.3. Dyeing process	222
8.8.4. Auxiliary materials	222
IX. POLAROGRAPHY IN ORGANIC SYNTHESSES AND ISOLATION OF NATURAL PRODUCTS	227
9.1. Preparative Electrochemistry	227
9.2. Applications in Organic Synthesis	229
9.3. Applications in the Isolation of Natural Products	230
X. POLAROGRAPHIC ANALYSIS IN THE STUDY OF REACTION RATES AND EQUILIBRIA	232
10.1. Equilibrium Constants	232
10.2. Homogeneous Reactions in Solutions	238
10.3. Fast Reactions Accompanying the Electrode Process and Rates of Electrode Process Proper	243

XI. EFFECTS OF STRUCTURE; POLAROGRAPHY AS A TOOL IN THE ANALYSIS OF STRUCTURES OF ORGANIC SUBSTANCES	245
11.1. Effects of Structure on Half-Wave Potentials	245
11.2. Structural Effects and Other Factors	248
11.3. Polarography as a Tool in the Analysis of the Structure of Organic Substances	248
11.4. Detection of Reactive Forms and Intermediates	250
11.4.1. Reactions in the bulk of solution	250
11.4.2. Chemical reactions accompanying the electrode process	251
11.4.3. Electrochemical reactions	251
LITERATURE CONCERNED WITH ORGANIC POLAROGRAPHIC ANALYSIS	254
AUTHOR INDEX	261
SUBJECT INDEX	269